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CO_2 uptake by carbonation in lime and dolime products

Calculation methods for national greenhouse gas inventories

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Preface

This report presents the results of a project to develop methods for quantifying carbon dioxide (CO_2) uptake in lime-containing products through carbonation. The study was carried out by IVL Swedish Environmental Research Institute during 2025–2026.

Lime production releases CO_2 from the calcination of limestone and from fuel combustion in lime kilns. These emissions are included in national greenhouse gas inventories, whereas existing IPCC inventory methods for lime production do not provide a method for quantifying the subsequent uptake of CO_2 through carbonation. Depending on their chemical composition, application, and exposure conditions, lime and dolime products can take up CO_2 during their service life, at end-of-life, and during secondary use. Transparent and consistent methods for quantifying this uptake are therefore needed to improve the completeness and accuracy of greenhouse gas inventories.

The project established a scientific and methodological basis for calculating annual CO_2 uptake in lime-containing products and developed practical calculation methods that could support future implementation in national greenhouse gas inventories. The work included a review of carbonation mechanisms in lime-containing products, identification and categorization of relevant product applications, evaluation of carbonation throughout the product life cycle, and development of calculation methods with different levels of complexity and data requirements. The resulting methodology framework comprises Tier 1, Tier 2, and Tier 3 methods designed for different national circumstances and levels of data availability.

The project was commissioned and funded by the European Lime Association (EuLA AISBL). The work has benefited from consultations with industry experts coordinated through EuLA, who provided valuable technical input and comments during the study. The author gratefully acknowledges these contributions.

The analyses, conclusions, and recommendations presented in this report are those of the author and do not necessarily reflect the views of EuLA or the lime industry.

The study and report were prepared by Håkan Stripple (hakan.stripple@ivl.se) at IVL Swedish Environmental Research Institute.

Gothenburg, September 2026

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Summary

Lime production releases carbon dioxide (CO_2) from the calcination of limestone and from fuel combustion in lime kilns. National greenhouse gas inventories account for these emissions under the current IPCC Guidelines, but they do not include a corresponding method for the CO_2 subsequently taken up when lime-containing products carbonate. Inventories therefore report the emissions from lime production without systematically accounting for removals that occur during product use, end-of-life management, and secondary use. This report develops a scientific and practical basis for estimating those removals at national level.

The study reviews the chemistry and kinetics of carbonation, the historical production and use of lime, the treatment of lime emissions and removals in the IPCC framework, and the behaviour of major lime applications throughout their life cycles. It then develops calculation methods with different data requirements and provides a worked national example. The methods are intended as input to future greenhouse gas inventory guidance and can also support country-specific method development.

Carbonation reverses the principal calcination reaction. Calcium oxide (CaO), normally after hydration to calcium hydroxide ($Ca(OH)_2$), reacts with CO_2 to form calcium carbonate ($CaCO_3$). Reactive magnesium phases in dolomitic lime can also form carbonates, but magnesium carbonation is generally slower, more complex, and less complete under ambient conditions. Calcium and magnesium components should therefore be calculated separately. The maximum uptake is fixed by stoichiometry, while the uptake achieved in practice depends on the reactive mineral content, chemical conversion into other compounds, porosity, moisture, particle size, geometry, surface treatment, and access to atmospheric or dissolved CO_2.

The review covers six broad product and application groups: construction and building materials; soil, agricultural, and land applications; environmental and water treatment; industrial process uses; dolomitic and magnesium-based products; and end-of-life and secondary materials. Their carbonation behaviour varies widely. Mortars, renders, limewash, finely divided lime, and exposed residues may carbonate rapidly, whereas encapsulated materials or lime converted into sulfates, chlorides, nitrates, phosphates, silicates, or other non-carbonatable products may have little or no eligible uptake. Many lime products carbonate more rapidly than concrete because they contain accessible reactive hydroxides and often have open pore structures or large exposed surface areas. Substantial carbonation commonly occurs within years or decades, although the applicable period must be determined for each product group and exposure condition.

All three proposed methods use the same accounting principles. Uptake is reported in the territory and year in which carbonation physically occurs and is reported separately from calcination and fuel-combustion emissions. Imported lime that carbonates domestically is included, while exported lime that carbonates abroad is excluded. Each material flow must be assigned to one mutually exclusive category, and each unit of reactive lime may be credited only once. Uptake is limited to chemically eligible and physically accessible material and may not exceed the stoichiometric capacity of the reactive calcium and magnesium phases. End-of-life or secondary-use uptake is included only for the residual fraction that has not already carbonated. The source and inventory treatment of deliberately supplied industrial CO_2 must be documented separately to prevent double counting.

For each application group, the ultimate eligible uptake is calculated from the amount of reactive lime, the appropriate stoichiometric conversion factor, an ultimate carbonation factor (F_{carb}), and a separate exposure factor (F_{exp}). F_{carb} represents the chemically achievable fraction, whereas F_{exp} represents the physically accessible fraction; the same limitation must not be included in both factors. In dynamic calculations, the ultimate uptake of each annual lime-use cohort is distributed over time with a cumulative carbonation function. Annual uptake is calculated from the increment between two consecutive year boundaries, ensuring that the annual fractions sum to the ultimate eligible uptake and that uptake occurring in previous years is not credited again. Linear, square-root, or documented country-specific progression functions may be used.

The *recommended Tier 1* method is a simplified steady-state calculation. It uses current apparent national lime use, converted to a consistent reactive-oxide basis, together with national average stoichiometric, carbonation, and exposure factors. Apparent use is derived from production, imports, exports, stock changes, and other documented balance adjustments. Because many lime products carbonate over a relatively short period, annual uptake from several active historical cohorts can be approximated by the ultimate eligible uptake associated with current annual use when the market and application mix are reasonably stable. The characteristic carbonation period supports this assumption; it is not used to divide the steady-state result. Tier 1 is suitable for preliminary estimates, countries with limited data, and categories that are not key categories, but it is less reliable where lime use is changing rapidly or non-carbonating applications represent a large share.

The *recommended Tier 2* method applies the same steady-state principle but divides national lime use among major application categories. Each category receives its own chemical basis, carbonation factor, and exposure factor. This improves the treatment of national use patterns and distinguishes applications with high carbonation potential from chemically ineligible or poorly exposed uses. Tier 2 is the preferred practical method where reliable sectoral consumption data are available. Historical cohorts and temporal progression functions are introduced only in the recommended Tier 3 method.

The *recommended Tier 3* method explicitly follows annual consumption cohorts. For every reporting year, it sums the uptake from the current cohort and all earlier cohorts that remain within their carbonation periods. It therefore represents changes in national lime use, application shares, and carbonation timing that the steady-state methods cannot capture. Historical consumption data for approximately 10 to 30 years will cover most applications described in the report, although the required period depends on the slowest relevant category. The report also describes a full dynamic stock-and-flow model as an alternative advanced method for countries with sufficiently detailed information on stocks, service lives, end-of-life treatment, and secondary use.

The comparison of methods shows that uncertainty often concerns the timing of uptake more than the ultimate quantity. Stoichiometry and the achievable carbonation fraction constrain cumulative uptake, but the selected carbonation period and progression function determine the reporting years in which it is credited. Tier 1 and Tier 2 can therefore provide useful national estimates under stable conditions, while Tier 3 is preferable for key categories, rapidly changing markets, changing application patterns, or countries with suitable historical and country-specific data. Regardless of tier, inventories should document data sources, chemical-basis conversions, eligibility decisions, exposure and carbonation factors, time functions, exclusions, uncertainty, and quality-control checks, and should apply the method consistently across the time series.

Appendix A demonstrates the three recommended methods for a hypothetical country using the same 2025 apparent lime use and chemical basis. The illustrative Tier 1, Tier 2, and Tier 3 results are

70.7, 70.7, and 65.5 kt CO_2, respectively. Tier 3 is lower than Tier 2 because lime consumption increased during the active cohort period, making current use larger than the earlier cohorts contributing to 2025 uptake. These values demonstrate the effects of disaggregation and timing and are not proposed defaults. The report concludes that lime carbonation is a measurable anthropogenic CO_2 removal that can be incorporated into national inventories using tiered methods consistent with IPCC good practice. The framework provides a basis for testing, refinement, and possible inclusion in future international inventory guidance.

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 lime:	A lime-containing product in which calcium hydroxide has reacted with atmospheric CO_2 to form calcium carbonate.
Carbonated zone:	The portion of a lime-containing product in which carbonation has occurred. Typically used for mortar, render, plaster, and stucco.
Carbonation depth:	The distance from the exposed surface to the carbonation front, determined using an appropriate analytical method (e.g. phenolphthalein indicator where applicable). Depending on the material and test method, carbonation may extend beyond the visually identified carbonation front. Typically used for mortar, render, plaster and stucco.
Carbonation rate:	The rate at which carbonation progresses into a lime-containing product. It depends on factors including CO_2 concentration, moisture, temperature, porosity, permeability, and the chemical composition of the material. For practical purposes, carbonation rate is often expressed as the increase in carbonation depth with time.
Carbonation:	The chemical process by which atmospheric CO_2 diffuses into a lime-containing product and reacts primarily with calcium hydroxide, forming calcium carbonate. In hydraulic lime and lime-cement products, carbonation may also involve other calcium-bearing phases. In this report, only post-production carbonation is considered; process-related CO_2 uptake during lime production is excluded.
CO_2 uptake area:	Is the area in lime and dolime containing products where CO_2 can be absorbed through carbonation.
C:	Calcium oxide, CaO
S:	Silicon dioxide (silica), SiO_2
A:	Aluminium oxide, Al_2O_3
H:	Water
C-S-H:	Calcium silicate hydrate
C-A-H:	Calcium aluminate hydrates
DOC:	Degree of carbonation.
Degree of carbonation:	The extent to which the carbonation potential of a lime-containing product has been realized, expressed as the fraction of the maximum theoretical CO_2 uptake that has occurred at a given point in time. The degree of carbonation may be determined locally within a carbonated zone or for the entire product.
Local degree of carbonation:	The extent of carbonation within the carbonated zone or at a specific location in the material.

Overall degree of carbonation:	The cumulative CO_2 uptake of the entire product relative to its maximum theoretical carbonation potential.
GGBS:	Ground granulated blast furnace slag.
Gt C:	Gigatonne carbon.
IPCC:	Intergovernmental Panel on Climate Change.
Mortar:	A general term for masonry and pointing materials. Historically often lime mortar; today commonly cement-lime mortar or cement mortar.
Render:	An exterior wall coating. Traditional renders were often lime-based; modern renders are frequently lime-cement or cement-based.
Plaster:	An interior wall or ceiling finish. Traditional plasters were commonly lime plasters; modern plasters may be lime, gypsum, cement, or combinations thereof.
Stucco:	Usually refers to an exterior decorative render. Traditional stucco is lime-based; modern stucco is often Portland cement with hydrated lime.
NIR:	National Inventory Report
tonne or t:	metric tonne = 1000 kg
UNFCCC:	United Nations Framework Convention on Climate Change.

1 Background and introduction

1.1 Background

Emissions of greenhouse gases (GHGs) have a major impact on global and national development. To monitor and control these emissions, countries compile and report their GHG inventories to the United Nations Framework Convention on Climate Change (UNFCCC), following guidelines developed by the Intergovernmental Panel on Climate Change (IPCC). These guidelines, most recently presented in 2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, provide standardized methodologies for estimating emissions and removals across sectors.

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

$CaCO_3 \rightarrow CaO + CO_2$

The production of lime in a lime kiln requires high temperature (900-1000 °C) and is therefore energy intensive. The calcination temperature for $CaCO_3$ (limestone) at 1 atm is about 900 °C. The net climate effect of anthropogenic activities can be complex, as some processes act both as sources and sinks of carbon dioxide (CO_2). This applies particularly to the production and use of lime products such as quicklime (CaO) and hydrated lime ($Ca(OH)_2$). During lime production, CO_2 is released from the decomposition of limestone ($CaCO_3$) in the lime kiln through calcination. Later, during the use phase, end-of-life, and secondary use, CO_2 can be reabsorbed through carbonation—a well-established and scientifically recognized process in which lime reacts with atmospheric CO_2 to form calcium carbonate once again. 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 lime kilns.

Despite the well-documented nature of this reversible reaction, the current IPCC guidelines account only for CO_2 emissions from calcination and fuel combustion, while neglecting the subsequent CO_2 uptake through carbonation. This omission results in an overestimation of net emissions from the lime sector and reduces the accuracy of national inventories. It is therefore important to establish standardized and transparent methods for quantifying the CO_2 uptake in lime products throughout their lifetimes.

The production of lime in kilns requires high temperatures, typically achieved through combustion of fossil fuels such as coal, oil, natural gas, or petroleum coke, although alternative fuels derived from residues (e.g., waste oils, plastics, solvents, and scrap tires) are increasingly used. These fuels contribute to fossil CO_2 emissions, while other GHGs such as CH_4 and N_2O are emitted only in minor amounts. Overall, the global CO_2 emissions from lime production represent approximately 1 % of the total global CO_2 emissions, while around 60 % - 75 % of the CO_2 emissions from lime production originate from the raw material itself (calcination) and thus have a potential to be reabsorbed through carbonation during product use, secondary use, and at end-of-life. The remaining part of

the CO_2 emissions, 25 % - 40 %, originates from the fuel combustion in the lime kilns. Thus, approximately 0.6 % – 0.75 % of the global CO_2 emissions come from the calcination (process), while approximately 0.25 % – 0.4 % of the global CO_2 emissions come from fuel combustion in lime kilns [1]. In addition to fossil fuels, biofuels can also be used in lime kilns, such as biomass powders, tall oil pitch, gasified biomass, or other liquid biofuels such as biobased oils and Hydrotreated Vegetable Oil (HVO).

Carbonation can occur in a wide range of lime-containing products, including products, by-products and secondary mineral streams containing reactive lime phases capable of carbonation. Carbonation occurs in key lime applications, including iron and steel production, environmental protection, construction materials, civil engineering, and other industrial applications. As examples, steel slag carbonate during storage, flue gas cleaning residues carbonate rapidly and fix CO_2 in alkaline residues, lime-treated soils for stabilization and civil engineering carbonate over exposure time. The rate and extent of carbonation depend on factors such as exposure to air, CO_2 concentration, humidity, product geometry, and surface area. For example, crushed or porous materials carbonate much faster than dense structures. Since carbonation continues over long timeframes, often well beyond the product's service life, it is essential to consider the entire lifecycle of lime products to assess their net CO_2 balance accurately.

Recognizing the importance of carbonation as a carbon sink, the IPCC's Sixth Assessment Report (AR6, Working Group I, 2021) [55] identified carbonation of lime and cement-based materials as a significant anthropogenic CO_2 removal process. This scientific recognition underlines the need to incorporate such uptake mechanisms into national GHG inventories to improve their accuracy and completeness.

To address this methodological gap, this project aims to develop calculation methods for CO_2 uptake in lime products that can be applied within the framework of national GHG reporting under the UNFCCC. The methods will be harmonized with the IPCC Tier system—ranging from simple default approaches (Tier 1) to detailed, data-intensive models (Tier 3)—and will serve as a foundation for future inclusion in updated IPCC guidelines. The resulting methodologies will also be applicable for assessing CO_2 uptake in a product perspective, supporting life cycle assessments and climate impact evaluations.

1.2 Introduction

The scientific understanding of CO_2 uptake through carbonation in mineral products has advanced significantly in recent years, especially in the context of cement and concrete. Standards such as EN 16757 and various national research projects have already established models and parameters for estimating carbonation rates in concrete. This knowledge provides a valuable foundation for developing analogous models for lime products, with appropriate adaptation of the carbonation kinetics, product categories, and exposure conditions specific to lime.

The ongoing development of IPCC methodologies provides a timely opportunity for such advancement. The IPCC Task Force on National Greenhouse Gas Inventories (TFI) held a Scoping Meeting for the Methodology Report on Carbon Dioxide Removal Technologies and Carbon Capture, Utilization and Storage (CDR & CCUS) in Copenhagen, October 2024. This meeting initiated the drafting of a methodology report to supplement the 2006 IPCC Guidelines [55,56], with

a focus on refining methods for estimating CO_2 removals and storage. Both carbonation in lime products and in cement/concrete were discussed and preliminarily included for consideration in the update. However, at the Sixty-second Session of the IPCC (Hangzhou, February 2025), consensus could not be reached due to unresolved issues related to CO_2 removals from water bodies, and the final decision was postponed to the Sixty-third Session (Lima, October 2025).

At the 63rd Plenary Session of the IPCC (Lima, October 2025), the Panel agreed on the outline and scope of the forthcoming Methodology Report on Carbon Dioxide Removal (CDR) Technologies, including Carbon Capture, Utilization and Storage (CCUS). In particular, the scope now explicitly includes mineral carbonation processes (for example in lime-containing materials, in cement, and in concrete), which represents a critical step toward formally recognizing CO_2 uptake by such materials in national inventory reporting. While the workplan for the Seventh Assessment Report (AR7) remains unresolved, the decision to include CDR and carbonation pathways strengthens the case for including the uptake of CO_2 in lime products (via carbonation) in future versions of the IPCC Guidelines for National Greenhouse Gas Inventories.

Previous work by IVL Swedish Environmental Research Institute has developed methods for quantifying CO_2 uptake in concrete products, presented in an IVL report [57] and communicated to the IPCC and UNFCCC through national inventory reporting. A corresponding methodological development for lime products is now needed to ensure consistent and comprehensive treatment of carbonation across both material systems.

In the present 2006 IPCC Guidelines, the lime production sector includes CO_2 emissions from both fossil fuel combustion and raw material calcination, but no method for calculating CO_2 carbonation uptake. Consequently, national GHG inventories currently report only gross emissions, not net emissions after carbonation. This project therefore seeks to fill that methodological gap by providing science-based, practical models for estimating annual CO_2 uptake in lime products, both during use and at end-of-life.

Developing accurate CO_2 uptake models for lime products is complex, as these products vary widely in composition, application, geometry, and service life across countries. Reliable methods must therefore consider historical production data, product lifetimes, carbonation rates, and secondary uses of lime-containing materials. The goal is to develop a Tier 3 calculation model—data-rich, dynamic, and computer-based—capable of quantifying national annual CO_2 uptake. Simplified Tier 2 and Tier 1 methods can then be derived for countries with more limited data availability.

This study provides the scientific and methodological foundation for integrating carbonation of lime products into national GHG inventories and, ultimately, into future updates of the IPCC Guidelines. The outcomes will enhance the accuracy of global CO_2 reporting, support the recognition of carbonation as a legitimate carbon sink, and promote more complete climate accounting for lime and related products.

Currently, greenhouse gas emissions are reported by individual nations to support various climate strategies. These reports are submitted to national authorities and internationally to the United Nations Framework Convention on Climate Change (UNFCCC). Guidelines for emission calculations are developed and updated by the Intergovernmental Panel on Climate Change (IPCC).

While the current version, the *2006 IPCC Guidelines for National Greenhouse Gas Inventories*[1], covers emissions from lime production, it accounts only for fossil fuel combustion and raw material calcination. Carbonation of lime products is notably excluded. As an initial step toward integrating this process into national CO_2 reporting, carbonation in cement/concrete and lime products will be included in the upcoming update to the IPCC Guidelines. Because carbonation is a critical factor in climate modeling, refining these calculations to better reflect real-world conditions is essential. This study proposes improved methods and models for quantifying CO_2 sequestration across various lime-containing products.

1.3 Purpose and goal

The primary objective of the study is to provide input to the national and international greenhouse gas inventories by developing novel models for calculating annual uptake of CO_2 within the lime industry sector. This research aims to quantify the uptake of CO_2 by carbonation in lime-based products across their entire lifecycle including service life, end-of-life and secondary use, while ensuring uptake is allocated to the appropriate year. As robust data is fundamental to informed decision-making, particularly regarding climate policy, this study builds upon established scientific frameworks while proposing new methodologies for calculating CO_2 uptake.

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. According to the IPCC guidelines, emission/removal estimates should neither be over- nor underestimated and uncertainties reduced as far as practicable. An IPCC Tier 1 method generally is less resource-demanding due to its simplification and should be possible for any country to develop, but in turn associated with the highest uncertainty. It may serve as a good starting point for making a rough estimate. More accurate results can be derived using Tier 2 or Tier 3 methods; however, more knowledge and resources are usually required. The exact definition of the levels can vary between this study and the IPCC guidelines. The method that a country will use depends on the country's ability to access statistics on lime production and its use in different products.

According to the IPCC guidelines, the methods used should also depend on if a source of annual emissions or annual uptake in a carbon sink, 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. For such key categories, the IPCC guideline states that Tier 2 or Tier 3 methods should be used. For insignificant categories (i.e. non-key categories), Tier 1 methods can be used.

The uptake of CO_2 in lime-based products, both during the use phase and at end-of-life and secondary use, generally occurs at a higher rate than in cement-based concrete products, owing to the higher reactivity of calcium hydroxide and the typically more open pore structure of lime materials. Carbonation is nevertheless governed by exposure to atmospheric CO_2 and moisture. The atmospheric CO_2 concentration is currently about 427 ppm and is increasing by approximately 1–3 ppm per year. Most lime-based products that are exposed to air take up CO_2 progressively over time

[1] In 2019, IPCC published the *2019 Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories*. However, no refinement or amendment was made in relation to cement or lime carbonation.

through carbonation, with rates that depend on material composition, porosity, exposure conditions, and age, and that are often sufficiently rapid for substantial carbonation to occur over years to decades rather than centuries.

In contrast, annual CO_2 emissions from lime production are closely linked to current production volumes, as a significant share of emissions arises from the calcination of limestone. The annual net CO_2 contribution of lime as a material within a country therefore depends both on present lime production and on the accumulated stock of lime-containing products in use and at end-of-life that continue to carbonate. Calculation approaches typically focus on cumulative CO_2 uptake over time. However, since these approaches are time-generic, they can also be used to derive time series and annual estimates of CO_2 uptake.

CO_2 uptake by lime-based products can offset a meaningful share of the process emissions associated with lime production and therefore has a material influence on national CO_2 balances. This issue primarily concerns the lime industry but also affects downstream sectors such as construction, environmental applications, and infrastructure. For all relevant sectors, it is essential that material flows, service lives, and exposure conditions are described accurately, so that both emissions and CO_2 uptake associated with lime use are assessed in a transparent and consistent manner.

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

2 Theoretical background to CO_2 uptake in lime-containing products

2.1 General description

Lime products are based on calcium oxide (CaO), commonly referred to as quicklime, which is primarily produced by the thermal decomposition of limestone ($CaCO_3$) in a lime kiln. This process, called *calcination*, releases carbon dioxide (CO_2) and produces reactive CaO. Lime products are subsequently used in various applications such as construction materials, soil stabilization, steel and paper production, water treatment, and environmental control processes. Many of these lime-containing products are chemically active toward CO_2 and can, over time, reabsorb CO_2 from the atmosphere or other CO_2-containing gases through *carbonation*.

The overall CO_2 balance of lime products therefore involves both the CO_2 released during calcination and the CO_2 reabsorbed during the service life or post-use phase through carbonation. The understanding of the underlying chemical and physical processes is essential to quantify this uptake and assess the net climate performance of lime-based products.

Calcination of limestone
The principal reaction in lime production is the endothermic decomposition of calcium carbonate (calcination):

$$CaCO_3(s) + \text{heat} \rightleftharpoons CaO(s) + CO_2(g)$$

This reaction is an equilibrium reaction, and the calcination reaction typically takes place in the temperature range of ~850–1100 °C, depending on the partial pressure of CO_2 and the characteristics of the limestone. If this equilibrium reaction is driven to the right, it is called calcination and if it is driven to the left, it is called carbonation. The equilibrium conditions for this reaction can be studied by its thermodynamic properties and especially Gibbs free energy (G), which gives an estimation of how spontaneous this reaction is at different temperatures. The changes in Gibbs free energy can be calculated as:

$$\Delta_r G°(T) = \Delta_r H°(T) - T\Delta_r S°(T)$$

where $\Delta_r G°$, $\Delta_r H°$ and $\Delta_r S°$ are the standard reaction Gibbs energy, enthalpy and entropy, respectively, each defined as Σ(products) - Σ(reactants) at temperature T.

- When $\Delta_r G°(T) = 0$, the system is at equilibrium.
- If $\Delta_r G°(T) < 0$, the decomposition reaction is spontaneous in the forward direction (calcination) under the specified standard-state convention.
- If $\Delta_r G°(T) > 0$, the reverse direction (carbonation) is thermodynamically favoured under the specified conditions.

This equation can connect thermodynamics to the equilibrium CO_2 pressure during calcination.

The equilibrium between $CaCO_3$, CaO, and CO_2 can be described thermodynamically by:

$$K_p = \frac{f_{CO_2}}{f°} \approx \frac{p_{CO_2,eq}}{p°} = \exp\left[-\frac{\Delta_r G°(T)}{RT}\right]$$

where K_p is dimensionless, f_{CO_2} is the CO_2 fugacity, $f°$ is the standard-state fugacity, $p_{CO_2,eq.}$ is the equilibrium CO_2 partial pressure, and p° is the standard pressure. The pressure-ratio approximation is appropriate when the gas behaves ideally.

At about 900 °C, the equilibrium CO_2 pressure is around 1 atm; at lower pressures, decomposition can occur at slightly lower temperatures. During calcination, CO_2 is released both from the chemical reaction and from combustion of the kiln fuel (fossil or biogenic).

Carbonation Pathways of Lime (CaO)
Carbonation of lime can proceed through two principal chemical pathways: (1) a direct reaction between calcium oxide (CaO) and carbon dioxide (CO_2), and (2) an indirect route in which CaO first reacts with water to form calcium hydroxide ($Ca(OH)_2$), which subsequently carbonates. Although both pathways are thermodynamically feasible at ambient conditions, their practical significance and reaction rates differ substantially. The following section provides a description of these routes and explains which mechanism dominates in real lime carbonation.

Direct Carbonation of CaO
The direct carbonation reaction can be written as:

$$CaO\ (s) + CO_2\ (g) \longrightarrow CaCO_3\ (s)$$

This reaction is thermodynamically favorable at ambient temperatures; however, the kinetics are very slow under typical environmental conditions. The reaction occurs at the interface between the solid CaO and the CO_2 gas, forming a thin $CaCO_3$ layer on the CaO surface. This newly formed carbonate layer is dense and has low permeability, which significantly inhibits further diffusion of CO_2 into the interior of the CaO particle. As a result, the carbonation front does not progress deeply into the material. Only a very small fraction of the available CaO becomes carbonated directly in air at room temperature. High temperatures (> 400–500°C), very high porosity, or specific engineered microstructures are needed for direct carbonation to proceed at significant rates. Under normal storage, use, or environmental exposure, direct CaO carbonation is therefore negligible.

Carbonation via hydration to $Ca(OH)_2$

In practical applications, the carbonation of lime is dominated by an indirect pathway. Calcium oxide is highly reactive with water and rapidly hydrates even at moderate relative humidity. The hydration reaction is:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

This step is fast and strongly exothermic. It produces calcium hydroxide with a high surface area, high porosity, and significantly higher solubility in water than CaO. These material properties strongly favor carbonation. Once $Ca(OH)_2$ is formed, it reacts readily with CO_2 according to:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The carbonation of $Ca(OH)_2$ takes place in the aqueous phase within the pore system. CO_2 dissolves in the pore water, forming carbonic acid and subsequently carbonate ions, which then react with dissolved calcium ions from $Ca(OH)_2$ to precipitate $CaCO_3$. Because both reactants are mobile as dissolved ions, and because $Ca(OH)_2$ is highly accessible within the pore structure, this pathway exhibits much faster kinetics than the direct carbonation of CaO. In addition, the precipitation of $CaCO_3$ occurs throughout the accessible pore network, not only at the external surface. This allows the carbonation front to progress deeper into the material before diffusion becomes limiting.

Carbonation chemistry of lime

The carbonation chemistry can be described as follows. When lime or hydrated lime (slaked lime, $Ca(OH)_2$) is exposed to air containing CO_2 and moisture, carbonation occurs, leading to the formation of calcium carbonate ($CaCO_3$). The carbonation can be expressed by the following overall reactions:

For quicklime (direct):

$$CaO + CO_2 \longrightarrow CaCO_3 \text{ (slow)}$$

Via hydrated lime:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

The reactions proceed through several elementary steps involving gas dissolution, diffusion, and ion reactions in the aqueous phase as shown below:

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$$

$$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3(s)$$

Thus, in the presence of water, CaO first hydrates to $Ca(OH)_2$, which then reacts with dissolved CO_2 according to the reaction of hydrated lime shown above. Therefore, moisture is an essential component for carbonation to proceed, while excessive water saturation limits CO_2 diffusion and slows the process. [9]

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 425 - 430 ppm today. The rate of concentration increase in the atmosphere is today about 2-3 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.

Which pathway dominates?
Under real environmental and material conditions, carbonation via hydration to $Ca(OH)_2$ is overwhelmingly dominant. Several factors explain this:

1. CaO hydrates rapidly in the presence of moisture, even at moderate relative humidity levels. In practical applications, unhydrated CaO is rarely present for long periods unless kept in extremely dry conditions.
2. The carbonation of $Ca(OH)_2$ is much faster than that of CaO due to its:
    - higher solubility
    - larger surface area
    - higher porosity
    - ability to participate in solution-based reactions
3. Direct CaO carbonation is effectively self-limiting, because the $CaCO_3$ product layer prevents CO_2 from reaching unreacted CaO.

Experimental studies consistently show that hydration followed by carbonation can be one to two orders of magnitude faster than direct carbonation under comparable conditions.

Full and partial carbonation
Full carbonation refers to the theoretical condition in which all calcium hydroxide originating from calcined limestone has reacted with atmospheric CO_2 and has been converted to calcium carbonate. In this case, the amount of CO_2 taken up equals, on a molar basis, the amount of CO_2 released during calcination of the corresponding calcium carbonate, subject to material losses and impurities.
In practice, full carbonation is only approached in certain lime-based products and exposure conditions. Thin, highly porous air lime mortars and plasters that are continuously exposed to air and moisture may reach near-complete carbonation within years or decades. Even in such cases, complete conversion is rarely uniform throughout the material volume and may remain incomplete in sheltered or moisture-limited zones.

Partial carbonation is the more common condition for lime-based products. Carbonation typically proceeds from exposed surfaces inward and may be limited by:

- Diffusion of CO_2 through already carbonated layers.
- Availability of moisture.
- Material thickness and pore structure.
- Encapsulation of calcium in less reactive phases (e.g. calcium silicate hydrates).

As a result, a fraction of the calcium may remain uncarbonated over the service life, particularly in thicker elements, protected assemblies, or materials where calcium is partly bound in hydraulic or hydrothermal phases.

The *degree of carbonation (DoC)* is a quantitative measure of the extent to which a lime-based product has carbonated relative to its theoretical maximum. It is commonly defined as:

$$\text{Degree of carbonation (DoC)} = \frac{CO_2\ taken\ up\ by\ carbonation}{CO_2\ released\ during\ calcination\ of\ the\ corresponding\ CaCO_3}$$

The degree of carbonation can be expressed:

- as a **fraction** (0–1), or
- as a **percentage** (0–100 %).

A degree of carbonation of:

- **0 %** indicates no carbonation,
- **100 %** indicates full carbonation of the carbonatable calcium,
- Intermediate values represent partial carbonation.

In practical assessments, the degree of carbonation is often estimated based on carbonation depth, material geometry, and exposure conditions, or derived from analytical measurements such as thermogravimetric analysis or phase quantification.

Clarifying the definition of the Degree of Carbonation (DoC)

In the context of lime-based products, the term "degree of carbonation" can be interpreted through two distinct lenses, both of which are critical for accurate sequestration modeling:

- **Macro-level Spatial Carbonation (the carbonated zone):** This refers to the physical volume or depth of the material that has been reached by the carbonation front. In concrete and bulky lime products, this is often measured as the "carbonation depth." It describes **where** carbonation is occurring within the total volume of the product.
- **Micro-level Chemical Conversion (the Degree of Carbonation, DoC):** Within the zone that has already been reached by CO_2, the material may not be 100% converted. This aspect defines **how much** of the reactive lime (CaO or $Ca(OH)_2$) has actually reacted to form calcium carbonate ($CaCO_3$) relative to its theoretical maximum (the original calcination level). Even if a product is fully "reached" by CO_2, the DoC may only be 60–80% due to pore clogging or thermodynamic limitations.

The spatial extent is typically detected using a phenolphthalein indicator, where a color-change from pink to colorless (pH~9.0) identifies the carbonated zone reached by CO_2 ingress. While this test effectively maps the boundary of the carbonation front, it does not account for the chemical conversion efficiency within that zone. Specifically, DoC represents the fraction of the theoretical maximum CO_2 uptake, equivalent to the original calcination potential, that has been realized in the area where the indicator has already turned colorless. Accounting for both the visually detected carbonation depth and the actual chemical degree prevents the overestimation of carbon sequestration that occurs when assuming total conversion within the neutralized volume.

2.2 Chemical kinetics and rate-determining processes for carbonation of lime products

The carbonation of lime products is a heterogeneous gas–solid (or gas–liquid–solid) reaction sequence involving multiple coupled steps such as:

1. *Gas-phase transport of CO_2* from the surrounding atmosphere to the lime surface.
2. *Diffusion of CO_2* through any boundary layers or product films ($CaCO_3$ layer, moisture film).
3. *Dissolution of CO_2* in the adsorbed or pore water film and formation of carbonate species.
4. *Diffusion of Ca^{2+} and CO_3^{2-} ions* through the water film to the reaction interface.
5. *Chemical precipitation of $CaCO_3$* at or near the reaction front.

Experimental and modeling studies show that the overall carbonation rate is controlled by a combination of *chemical reaction kinetics* and *mass transport limitations*, depending on material structure, humidity, temperature, and reaction stage. Below, a number of important factors influencing carbonation of lime products are presented and analysed.

Early-stage kinetics
At the beginning, when the lime surface is exposed and unreacted, the *chemical reaction at the surface* is typically *rate-determining*. The reaction proceeds rapidly until a thin layer of $CaCO_3$ forms on the surface.

Diffusion-controlled stage
As carbonation progresses, the growing $CaCO_3$ layer reduces porosity and increases diffusion resistance for CO_2 and water molecules. The rate gradually becomes *diffusion-controlled*, governed by transport through the $CaCO_3$ product layer and through moisture-filled pores. This regime is often described by a *shrinking-core model* or a *parabolic rate law* [58,59], where the carbonation depth (x) is proportional to the square root of time t ($x \propto \sqrt{t}$). During carbonation under such conditions, the process is governed by several factors that are critical to its progress (kinetics). The most significant of these factors are presented and analyzed below.

Rate-determining factors

Key parameters influencing the overall rate include:

- *Relative humidity (RH):* optimum around 50–70 % RH; too dry → limited CO_2 dissolution; too wet → blocked pores and slow diffusion.
- *Temperature:* affects both reaction kinetics and moisture equilibrium; moderate temperatures (20–40 °C) typically maximize rate.
- *Porosity and specific surface area:* high porosity and small particle size enhance carbonation.
- *CO_2 concentration and partial pressure:* higher levels accelerate carbonation, particularly under industrial or controlled CO_2 curing.
- *Crystalline morphology of $CaO/Ca(OH)_2$:* fine-grained, porous lime carbonates faster than dense, sintered lime. Sintering refers to the process where fine solid particles partially fuse together at high temperature, below their melting point, forming a denser, less porous solid. In lime production, this occurs when limestone ($CaCO_3$) is calcined at the upper end or above the optimal temperature range for decomposition, typically >1100 °C. As a result, the lime becomes "dead-burned" or "over-burned", a dense, less reactive form of calcium oxide.

Carbonation under various exposure conditions

- *Atmospheric carbonation* proceeds slowly, with reaction depths typically a few millimeters over months to years, depending on humidity and exposure.
- *Accelerated carbonation* (increased CO_2 concentration, controlled humidity) can achieve full conversion within hours to days and is applied in some product curing processes.
- *Water-mediated carbonation* (e.g., in aqueous suspensions or slurries) can proceed rapidly since CO_2 dissolution and ion transport are enhanced, but product quality and morphology differ.

The *maximum theoretical CO_2 uptake* corresponds stoichiometrically to the CO_2 released in calcination, i.e. one mole CO_2 per mole CaO. However, the actual uptake depends on several factors such as the degree of exposure to CO_2, product geometry and porosity, environmental conditions, and potential encapsulation or surface treatments. For practical quantification, the *degree of carbonation (DOC)* is defined as the fraction of CaO or $Ca(OH)_2$ that has been converted to $CaCO_3$.

Understanding these mechanisms is essential for accurate assessment of CO_2 uptake in lime-based materials, for both inventory reporting and life cycle analyses. Furthermore, knowledge of rate-determining processes supports the design of optimized exposure, curing, or reuse conditions to maximize carbonation and hence enhance the climate performance of lime products.

Kinetic regimes — basic models and rate expressions

Carbonation of lime materials is commonly modelled using either *empirical laws* (e.g. parabolic law for depth vs time) or *mechanistic heterogeneous-reaction models* such as the Shrinking Core Model (SCM) or *product-layer diffusion models*. Below are the most commonly applied expressions.

Parabolic ($\sqrt{t}$) empirical law (depth-of-carbonation)

For many porous mineral materials, the carbonation front depth x follows an empirical square-root of time behaviour:

$$x(t) = k_c \sqrt{t}$$

where k_c is the empirical carbonation-depth coefficient (for example, in mm/$\sqrt{year}$). This behaviour arises when transport through a growing product layer or diffusion in pores controls the advance of the reaction front (diffusion limitation leads to $x \propto \sqrt{t}$). The parabolic model is widely used as a simple engineering descriptor for long-term penetration in building materials. [5]

To compare the CO_2 uptake in concrete with that in lime products, it is useful to recognise that both materials follow similar transport-limited carbonation behaviour. Although the chemical pathways differ—carbonation of portlandite and C–S–H phases in concrete versus carbonation of CaO or $Ca(OH)_2$ in lime products—the progression of the carbonation front in both cases is commonly controlled by diffusion of CO_2 through a porous matrix or through the layer of reaction products formed at the surface. This results in a characteristic square-root of time dependence, often expressed through the parabolic model:

$$x(t) = k_c \sqrt{t}$$

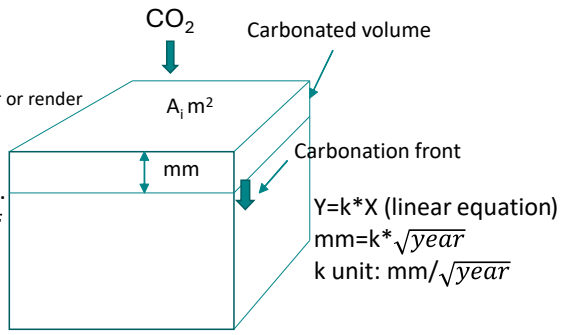
where $x(t)$ is carbonation depth, t is exposure time, and k_c is the empirical carbonation-depth coefficient reflecting material properties and environmental conditions. Thus, the same conceptual model that describes long-term CO_2 uptake at exposed concrete surfaces can also be applied to lime products with defined geometries.

Figure 1 illustrates this connection by showing how CO_2 exposure leads to a progressively advancing carbonation front for both concrete and lime-based materials. The model represented is equally valid for end-of-life conditions and for secondary uses where materials appear in more fragmented or particle-like forms, as the underlying controlling mechanism—diffusion-limited carbonation—remains the same.

Carbonation calculation for lime-containing solid products

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.)

CO_2 cum. uptake = $(\Sigma(k_i \times DOC_i \times A_i))(\sqrt{t}/1000) \times U_{tcc} \times C_L$
Units: mm/$\sqrt{year}$ × m² × $\sqrt{year}$ × kg CO_2/kg lime × kg lime/m³ mortar or render



Where
CO_2 cum. uptake is the total cumulative 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/$\sqrt{year}$
DOC_i is the local degree of carbonation for surface/volume i.
A_i is the CO_2 uptake surface area i in m².
t is the number of years from start of carbonation.
U_{tcc} is the maximum theoretical uptake in kg CO_2/kg lime (CaO). The value is ≈ 0.785 for CaO → $CaCO_3$
C_L is the lime content in kg lime/m³ of mortar or render.

Figure 1 Carbonation calculation with CO_2 in air exposed to a lime product surface with a distinct geometric form. This type of CO_2 uptake calculation is in principle also valid for uptake in end-of-life and in secondary use with more particle formed products.

Selection of carbonation-depth coefficient (k_c) for lime-containing products

The parabolic carbonation model presented in Figure 1 is identical in mathematical form to the model adopted in EN 16757, Annex BB, for concrete products. The model assumes that carbonation is controlled primarily by diffusion of atmospheric CO_2 through the already carbonated layer, resulting in a carbonation depth proportional to the square root of time:

$$x(t) = k_c\sqrt{t}$$

where k_c is the carbonation-depth coefficient (mm/$\sqrt{year}$).

Although the mathematical formulation is equally applicable to lime-containing materials, the carbonation-depth coefficient should not automatically be assumed to be identical to that used for concrete. The value of k_c depends on physical properties of the material, such as pore structure, moisture content, permeability, lime content, and exposure conditions. Pure air-lime mortars, renders and plasters generally have higher porosity and more readily available calcium hydroxide than concrete; consequently, carbonation usually proceeds substantially faster than in ordinary Portland cement concrete.

The values for k_c presented in EN 16757, Annex BB, for lime mortars and renders (approximately 0.3–2 mm/$\sqrt{year}$ depending on product type) are intended primarily for environmental product declarations (EPDs) and life-cycle assessment calculations. These values are conservative default parameters for standardized environmental reporting and should not necessarily be interpreted as representative physical carbonation coefficients for natural lime materials under typical exposure conditions.

Experimental investigations reported in the scientific literature generally indicate considerably higher carbonation rates for pure air-lime products. Measurements of carbonation depth under natural exposure conditions commonly correspond to carbonation coefficients in the range shown in Table 1.

Table 1 Representative carbonation coefficients reported for lime-containing products under natural exposure conditions.

Material	Estimated k_C (mm/$\sqrt{year}$)	Basis	Confidence	Principal references
Air-lime mortar	19	Experimental	High	[19],[36],[51]
Air-lime render	18	Engineering estimate based on mortar	Medium	[19],[36]
Air-lime plaster	18	Engineering estimate based on mortar	Medium	[19],[36]
Lime–cement mortar/render	5	Experimental/ Literature synthesis	Medium	[19],[36]
Natural Hydraulic Lime (NHL) mortar	3–6	Limited experimental evidence	Low	[2],[69]
Lime–pozzolan mortar	2–5	Limited experimental evidence	Low	[62]

NHL = Natural Hydraulic Lime.

These values should be regarded as indicative ranges rather than universal constants. The carbonation coefficient depends strongly on several factors, including binder composition, water-to-binder ratio, aggregate grading, pore structure, relative humidity, CO_2 concentration, curing conditions, and exposure environment. Mixed cement–lime mortars generally carbonate more slowly than pure air-lime mortars because the hydration products formed by Portland cement reduce pore connectivity and decrease the effective diffusion coefficient for CO_2.

A simple comparison illustrates the importance of selecting realistic carbonation coefficients. For example, a 20 mm thick lime render that carbonates completely within approximately four years corresponds to a carbonation coefficient of approximately

$$k_c = \frac{20}{\sqrt{4}} = 10 \text{ mm}/\sqrt{year}$$

which lies well within the experimentally reported range for air-lime products but is substantially higher than the conservative default values reported in EN 16757 Annex BB. Similarly, carbonation depths of 8–15 mm after one year, commonly reported for exposed lime plasters, correspond to carbonation coefficients of approximately 8–15 mm/$\sqrt{year}$.

For the purposes of the present methodology, the parabolic carbonation model is therefore retained because it provides a robust and well-established description of diffusion-controlled carbonation. However, product-specific carbonation coefficients should preferably be selected from experimental studies on lime-based materials.

Shrinking core model (SCM) or product-layer models (grain scale)

At the grain/particle scale, the reaction of a spherical (or cylindrical) particle with a gas can be described by the SCM with alternative rate laws depending on the controlling sub-process:

Chemical reaction control (surface reaction rate limiting):

$1-(1-X)^{1/3} = k_{chem}\, t$

Diffusion through product layer control (product layer resistance):

$1-3(1-X)^{2/3} + 2(1-X) = k_{diff}\, t$

Gas film control: linear dependence of conversion X on time i.e. $X = k_{gas}\, t$.

Here X is the fractional conversion (0–1) of the initial reactive core and k are apparent rate constants (dependent on temperature via Arrhenius relationships). The SCM has been successfully fitted to many $CaO/Ca(OH)_2$ carbonation datasets (including both dry and wet carbonation experiments), although porous reactants often show mixed control and require combined (multi-term) rate laws. [11]

At the particle scale, carbonation of lime may be described using the Shrinking Core Model (SCM), which has been widely applied to gas-solid reactions involving calcium oxide and calcium hydroxide. Initially, carbonation is controlled primarily by the chemical reaction occurring at the particle surface. As carbonation proceeds, a layer of calcium carbonate develops around the unreacted core, progressively restricting transport of carbon dioxide to the reaction interface. The overall carbonation rate therefore changes from reaction-controlled to diffusion-controlled behaviour.

For finely divided lime products, industrial residues, APCR, crushed materials and other particulate systems, SCM provides a useful mechanistic description of carbonation. For monolithic lime products such as mortars, renders and plasters, however, carbonation is more conveniently represented using macroscopic carbonation-front models based on diffusion through the material, as described later in this report.

The SCM therefore provides the theoretical basis for understanding carbonation kinetics but is not directly applied in the Tier 1 or Tier 2 inventory methodologies developed in this report. Instead, simplified carbonation coefficients and application-specific uptake factors are used for practical inventory calculations.

Diffusion-reaction coupling and effective diffusivity

When a $CaCO_3$ layer forms and reduces porosity/permeability, the effective diffusivity D_{eff} (e.g. in m^2/s) of CO_2 (or CO_2 in pore water as molecular or ionic species) becomes central. For diffusion-limited stages, the overall rate (e.g. in mol/m^2s) can often be written as:

$$\text{rate} \sim \frac{D_{eff}\Delta C}{\delta}$$

where ΔC (e.g. in mol/m^3) is driving concentration difference and δ (e.g. in m) the effective diffusion path length (growing with time). D_{eff} in porous solids is much lower than the gas diffusion coefficient in free air and depends on porosity, tortuosity, and water saturation. Typical gas diffusion in free air

is $D_{CO2,air} \approx 1.6\times10^{-5}$ m^2/s (20 °C). Effective diffusivities in pore networks for long-term reaction often range many orders of magnitude lower, e.g. 10^{-8} to 10^{-12} m^2/s depending on saturation and tortuosity, values that must be empirically determined or estimated from microstructures. [5]

Arrhenius temperature dependence

The Arrhenius equation describes how the rate of a chemical reaction increases with temperature. The rate constants, k(T), are typically modelled with Arrhenius expressions:

$$k(T) = k_0\, e^{(-E_a/(RT))}$$

where k_0 is the Arrhenius constant, E_a is the activation energy (J/mol), R the gas constant (8.314 J/mol K), and T the absolute temperature in Kelvin. A higher k(T) results in a faster reaction. Reported apparent activation energies for carbonation vary substantially with the specific mechanism, temperature range and material:

- *$Ca(OH)_2$ carbonation at low/ambient temperatures*: reports of relatively low activation energies or complex multi-step apparent energies (e.g. Shih et al. reported E_a-values on the order of 10–20 kJ/mol for some rate constants). [6]
- *Surface CaO carbonation / high-T behaviour*: many studies report higher apparent E_a values around ~60–80 kJ/mol (typical cited value ≈ 72 kJ/mol) for isothermal carbonation of CaO or for effective sorbent reaction rates in the 400–700 °C regime used in CO_2 looping literature. [10,13]
- *Very low E_a reported in some dynamic non-isothermal gas-solid experiments*: e.g. 6–12 kJ/mol under certain experimental (non-isothermal or micro-particle) conditions; values depend strongly on experimental method and particle size. [9]

Because E_a values vary with microstructure and regime (dehydration, gas diffusion, precipitation morphology), it is important to use activation energies appropriate to the targeted temperature- and humidity-range for Tier-3 models. [3]

Typical numerical parameter ranges and example values (from literature)

These values are frequently reported ranges — use them as starting points for Tier-2/3 parameterization and calibrate to country- or plant-specific data where possible.

- **Gas diffusion coefficient in still air (CO_2):** $D_{CO2,air} \approx 1.6\times10^{-5}$ m^2/s at 20 °C. (useful reference for deriving effective diffusivity). [5]
- **Effective diffusion coefficient in porous lime materials:** typically Deff ≈ 10^{-8} to 10^{-12} m^2/s depending on porosity, RH and tortuosity; crushed powders approach the upper range, dense mortars the lower range. (empirical). [12]
- **Apparent activation energies:**
  - CaO isothermal carbonation (high-T sorbents literature): **~60–80 kJ·mol^{-1}** (many authors converge near ~72 kJ·mol^{-1}). [10,13]
  - $Ca(OH)_2$ at ambient/low-T: multi-step apparent values vary; reported values include **~17 kJ/mol** for certain rate constants, while other experimental setups report larger apparent E_a when dehydration or sintering steps are relevant. [6]
- **Parabolic coefficient k_p** (depth mm/$\sqrt{year}$): material and exposure specific; for concretes, k_p values often range from ~1 to >10 mm/$\sqrt{year}$ depending on quality and exposure, while lime mortars or powdered lime carbonates much faster — precise k_p should be derived from experiments for each product class. [5]

Rate-determining steps — chemical kinetics vs transport processes

A consistent conclusion across experimental and modelling studies is that elementary chemical reaction steps themselves are usually fast relative to the time-scales of interest for bulk material carbonation, particularly for hydrated lime under favourable moisture. This implies that transport processes (gas and liquid diffusion, product-layer permeability reduction, and access of CO_2 to reactive surfaces) commonly limit long-term uptake in bulk (dense) materials. However, there are important nuances:

A. Early stage — surface reaction control

Fine particles, fresh surfaces, or high CO_2 partial pressure: Initial carbonation can be chemically controlled because fresh $CaO/Ca(OH)_2$ surfaces react quickly with dissolved CO_2. Laboratory kinetic studies of powdered $Ca(OH)_2$ show very rapid early uptake. [3]

B. Transition to diffusion/product-layer control

As $CaCO_3$ precipitates, the porosity and permeability near the reaction front decrease; a dense product layer slows further transport of CO_2 and H_2O. This shifts control to diffusion through the product layer or through remaining pore water. The net result is a deceleration of rate often captured empirically as $x \propto \sqrt{t}$ or via SCM diffusion equations. Many studies fitting SCM to $CaO/Ca(OH)_2$ carbonation find excellent agreement with diffusion-limited behaviour in later stages. [11]

C. Effect of moisture

Moisture is double-edged: capillary-held pore water enables aqueous CO_2 speciation and rapid ionic reaction (favouring faster chemical steps), but excess water fill pores and reduces gas diffusivity (slowing CO_2 transport). Experiments identify an optimal relative humidity (often cited in cement studies ~50–80% RH; for lime materials the exact optimum may shift) where carbonation is fastest. Thus, RH strongly affects whether chemistry or transport limits the rate. [1]

D. Particle-size and surface area effects

Powders and crushed materials possess a large specific surface area, which accelerates carbonation and may prolong the period during which the reaction remains under chemical-rate control. Crushed demolition materials also carbonate significantly faster due to the exposure of fresh reactive surfaces. This behaviour is particularly important during end-of-life (EoL) and secondary-use stages, where fragmentation of lime-containing materials can substantially increase the rate and extent of CO_2 uptake. [12]

E. Temperature and pressure

Higher temperatures increase reaction rates (Arrhenius) but can also change water vapor pressure and dehydration behaviour ($Ca(OH)_2 \leftrightarrow CaO + H_2O$), complicating the controlling regime. High CO_2 partial pressures (accelerated carbonation) can push the process into chemical control at higher conversions. [3]

F. Practical recommendations for modelling uptake (Tier-3 readiness)

1. **Use multi-regime models:** implement coupled reaction-diffusion formulations (SCM or porous-media PDE models) that allow the simulation to switch between chemical control and diffusion control as porosity evolves. Several recent validated models for $CaO/Ca(OH)_2$ (both gas-solid and wet carbonation) exist and can be adapted. [12]
2. **Calibrate parameters per product class:** obtain or use literature values for activation energies and diffusion coefficients relevant to the product type (powder, mortar, dense block, slag mixture). Use lab tests (small scale accelerated carbonation and porosity measurement) to derive k_{chem}, D_{eff}, and k_p. [10]
3. **Explicitly represent moisture and CO_2 concentration:** include RH-dependent effective diffusion and kinetics (e.g., incorporate a function $D_{eff}(RH)$ and a kinetic term $k(T,RH,p_{CO2})$. Moisture and exposure regimes are often the largest uncertainty in national estimates. [1]
4. **Account for secondary use and EoL crushing:** include scenarios where products are crushed/recycled (greatly accelerated carbonation) because EoL processes can substantially increase lifetime uptake. Empirical EoL factors can be used if mechanistic modelling is infeasible. [12]
5. **Sensitivity analyses:** report how national uptake changes if D_{eff}, k_p, or particle-size distributions vary within realistic ranges (e.g., D_{eff} spanning 10^{-8}–10^{-12} m^2/s and E_a between 10–80 kJ/mol). This highlights data needs and uncertainty for Tier-2 vs Tier-3 reporting.

Short conclusions

- The **elementary chemical reactions** for lime carbonation are rapid once CO_2 and water reach reactive sites; mass transport (diffusion of CO_2 in gas or liquid phases, and through growing $CaCO_3$ product layers) commonly becomes the rate-limiting factor in dense products and at longer times. [2]
- **Kinetic modelling** should combine Arrhenius-type chemical rate laws with diffusion terms (SCM or porous media diffusion–reaction PDEs). Typical activation energies reported cluster around ~60–80 kJ/mol for many CaO carbonation experiments, while ambient $Ca(OH)_2$ kinetics show lower apparent Ea in some studies — parameter ranges must be chosen per product and regime. [10]
- For national inventory Tier-3 models, parameterization must include **product geometry, porosity evolution, moisture and CO_2 exposure**, and explicit treatment of end-of-life crushing and secondary uses which can greatly accelerate uptake. Empirical parabolic laws ($x \propto \sqrt{t}$) are useful for simpler Tier-2/Tier-1 approaches but should be derived from representative measurements. [10]

Table 2 Summary of representative parameter defaults.

Parameter	Default values (estimated)	Comments
E_a (chemical, ambient $Ca(OH)_2$):	~20 kJ/mol	Use range 10-30 kJ/mol
E_a (diffusion/product-layer, CaO literature)	~72 kJ/mol	Use range 60-80 kJ/mol
D_{eff} (porous lime)	1×10^{-12} – 1×10^{-8} m²/s	representative default: 1×10^{-10} m²/s
k_p (parabolic coefficient)	0.5-10 mm/$\sqrt{year}$	representative default: 3 mm/$\sqrt{year}$
$D_{CO2,air}$	≈ 1.6×10^{-5} m²/s	

Illustration of carbonation kinetics and controlling mechanisms

The carbonation process in lime-containing products is governed by a transition from initially rapid chemical reactions to progressively stronger transport and diffusion limitations. While the detailed mathematical descriptions presented above provide the theoretical basis for carbonation modelling, the overall behaviour can be illustrated conceptually using Figure 2–Figure 4.

Figure 2 illustrates how the controlling mechanism changes during carbonation. At early stages, the reaction between carbon dioxide and the reactive lime phases is rapid and the carbonation rate is primarily governed by chemical reaction kinetics. As carbonation proceeds, the formation of calcium carbonate reduces pore accessibility and increases transport resistance, causing diffusion processes to become increasingly important. The carbonation rate therefore decreases with time.

Figure 3 shows the resulting development of the degree of carbonation. Carbonation progresses rapidly initially but gradually slows as the remaining uncarbonated material becomes less accessible. This behaviour explains why many lime products achieve a large fraction of their total CO_2 uptake during the first years after application, while the remaining uptake occurs more slowly over time.

Figure 4 illustrates the parabolic carbonation model, where carbonation depth is proportional to the square root of time. This relationship is commonly observed in both lime-containing products and concrete and reflects the increasing influence of diffusion-controlled transport as carbonation progresses. Due to the generally higher porosity and reactivity of lime products, carbonation rates are typically considerably higher than those observed in concrete.

Together, these figures demonstrate that carbonation of lime products is generally characterised by rapid initial CO_2 uptake followed by a progressively slower carbonation phase. This behaviour provides the scientific basis for the carbonation models developed later in this report and explains why many lime products can achieve a high degree of carbonation within years or decades rather than over the much longer timescales often associated with concrete.

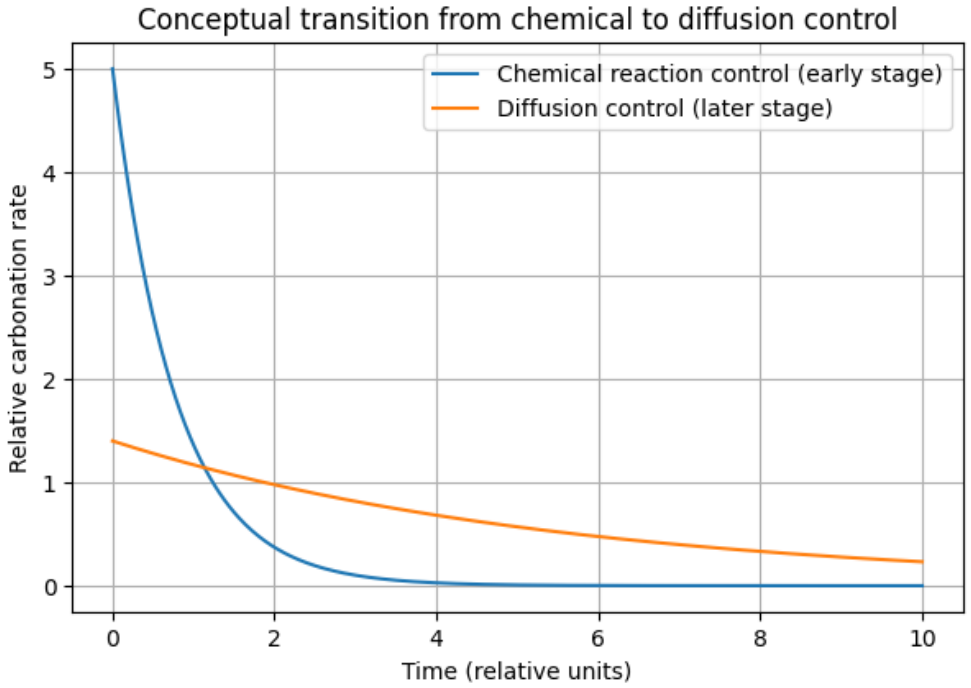


Figure 2 Rate-determining processes during carbonation of lime products.

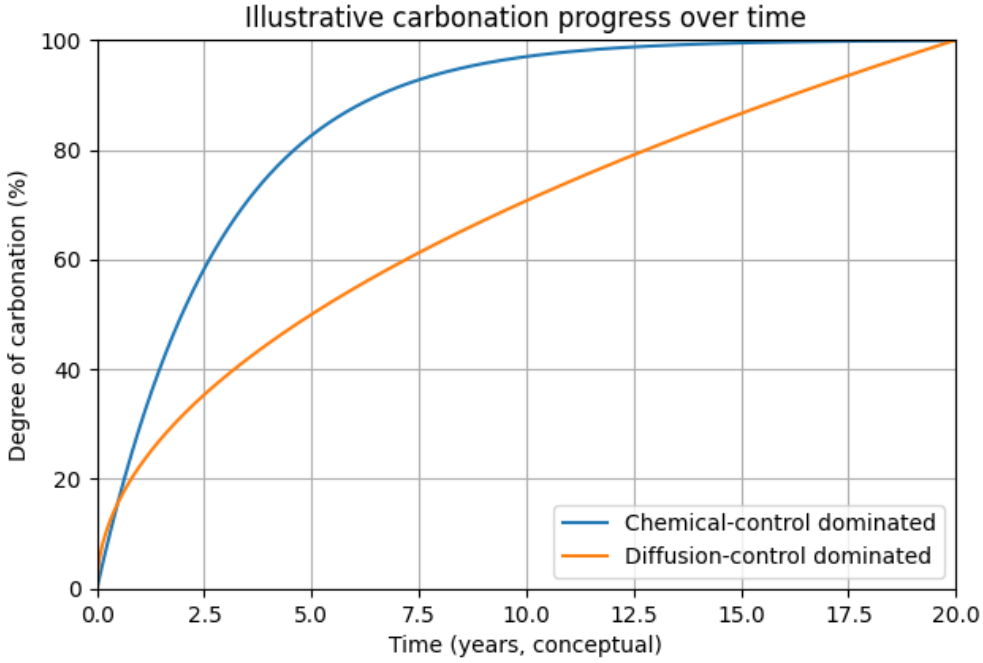


Figure 3 Illustrative development of carbonation degree with time.

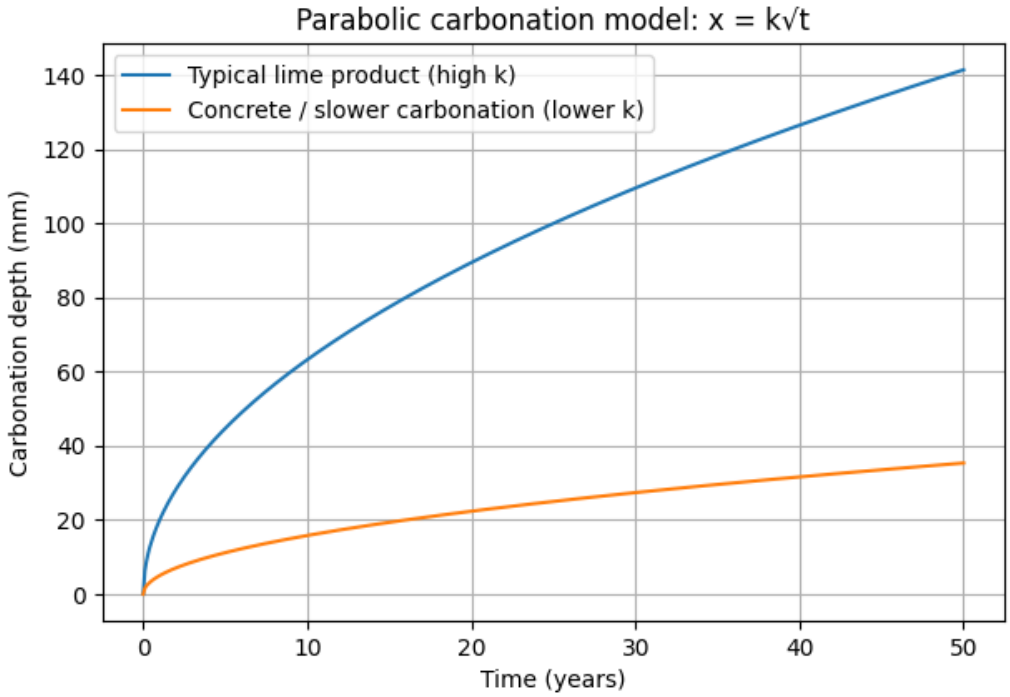


Figure 4 Parabolic carbonation behaviour ($x(t) = k_c\sqrt{t}$) for lime products and concrete.

Implications for CO_2 uptake modelling of lime products

The kinetic behaviour described in this chapter demonstrates that carbonation of lime products cannot be represented by a single universal reaction rate. Instead, carbonation is governed by a combination of chemical reactivity, mass transport processes, material properties, and environmental exposure conditions. The relative importance of these controlling mechanisms changes over time. During the initial stages, carbonation is often controlled by the intrinsic reaction rate between CO_2 and the reactive lime phases, whereas at later stages diffusion through the growing carbonate layer or through the pore structure becomes increasingly important.

For practical CO_2 uptake calculations, however, it is neither necessary nor desirable to represent all underlying physicochemical processes in full detail for every application. National greenhouse gas inventories require methodologies that are transparent, reproducible, and applicable across a wide range of product types and national circumstances. The challenge is therefore to translate the fundamental carbonation mechanisms into calculation approaches that balance scientific accuracy with practical applicability.

A key observation is that most lime-containing products exhibit substantially faster carbonation than cement-based concrete products. This is primarily due to the higher reactivity of calcium hydroxide, the generally higher porosity of lime-based materials, and the greater accessibility of reactive phases to atmospheric CO_2. Consequently, many lime products can achieve a high degree of carbonation within years or decades rather than over the much longer timescales typically associated with concrete carbonation.

The kinetics described in this chapter nevertheless show that carbonation behaviour varies considerably among product categories. Thin and highly porous products such as limewash, lime plasters, and air-lime mortars may approach complete carbonation within relatively short periods. In contrast, industrial lime applications, soil stabilization products, dolomitic materials, and certain

end-of-life materials may carbonate more slowly or only partially under ambient conditions. Product geometry, particle size, moisture availability, and exposure to atmospheric CO_2 are therefore critical factors that must be considered when developing CO_2 uptake methodologies.

These observations form the scientific basis for the methodology framework proposed later in this report. The simplified Tier 1 and Tier 2 methods use representative carbonation factors and uptake periods derived from the general behaviour described in this chapter, while the Tier 3 methodology allows more explicit representation of carbonation kinetics, product-specific behaviour, historical material stocks, and end-of-life processes. In all cases, the objective is to ensure that annual CO_2 uptake estimates remain consistent with the underlying carbonation mechanisms while remaining sufficiently practical for implementation in national greenhouse gas inventories.

The following chapter expands this discussion by considering carbonation behaviour in dolomitic and magnesium-based lime products. These materials introduce additional carbonation pathways associated with magnesium oxides and hydroxides, which differ substantially from calcium-based carbonation in both reaction mechanisms and timescales and therefore require separate methodological consideration.

2.3 Use of Dolime and carbonation of Magnesium-based lime products

2.3.1 Definition and production of Dolime

Dolime—also referred to as dolomitic quicklime—is produced by the calcination of natural dolomite ($CaMg(CO_3)_2$). When heated to temperatures typically above 900–1000 °C, dolomite undergoes sequential decomposition:

Decomposition of the magnesium carbonate fraction:
$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$

Decomposition of the calcium carbonate fraction:
$CaCO_3 \rightarrow CaO + CO_2$

The final product is a reactive mixture of calcium oxide (CaO) and magnesium oxide (MgO). Depending on the degree of calcination and process control, dolime may contain varying proportions of free CaO, free MgO, and residual carbonates. When hydrated, dolime forms calcium hydroxide ($Ca(OH)_2$) and magnesium hydroxide ($Mg(OH)_2$).

2.3.2 Applications of Dolime

Dolime is used where both calcium and magnesium oxides provide functional benefits. It is also used in locations where dolomite is the main resource e.g. hydrated dolime for mortar in North America and Europe. Major application areas include:

Metallurgical industry
Dolime is widely used as a flux and slag conditioner in ferrous and non-ferrous metallurgical processes, particularly:

- Steelmaking (e.g., in basic oxygen furnaces and electric arc furnaces)
- Production of ferroalloys
- Non-ferrous smelting

MgO contributes to slag viscosity, lining protection, and sulfur removal.

Refractories
Because MgO improves high-temperature stability, dolime is used in:

- Refractory brick and castable formulations
- Slag-resistant linings
- Protective coatings for steelmaking vessels

Environmental and chemical uses
Dolime is employed for:

- Water treatment (softening and pH adjustment)
- Flue-gas desulphurization
- Neutralization of acidic industrial effluents
- Precipitation and stabilization of heavy metals

Construction and civil engineering
Although less common than high-calcium lime, dolime can be used in:

- Soil stabilization
- Asphalt and bituminous mixtures (as filler or anti-stripping agent)
- Certain binder formulations
- Masonry units in regions where dolomitic materials dominate mineral resources

Agriculture
Dolomitic products are used as liming agents, especially when magnesium supplementation to soils is required.

2.3.3 Carbonation behaviour of Dolime

The carbonation of dolime differs from that of high-calcium lime due to the distinct reactivity of $MgO/Mg(OH)_2$ relative to $CaO/Ca(OH)_2$.

Carbonation of calcium components
The CaO or $Ca(OH)_2$ fraction carbonates through well-known pathways:

$CaO + CO_2 \longrightarrow CaCO_3$

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

These reactions occur relatively rapidly under typical ambient exposures and follow diffusion-controlled kinetics similar to other calcium-based lime products.

Carbonation of magnesium components
The carbonation of MgO and $Mg(OH)_2$ proceeds more slowly and under more restrictive conditions:

$MgO + H_2O \longrightarrow Mg(OH)_2$

$Mg(OH)_2 + CO_2 \longrightarrow MgCO_3 + H_2O$ (or basic magnesium carbonates such as hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$) or dypingite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$))

The magnesium component exhibits:

Lower carbonation kinetics
$Mg(OH)_2$ carbonates only slowly at ambient temperature and pressure. Carbonation is favoured under conditions of elevated CO_2 concentration and moderate moisture. In many applications, natural carbonation of the magnesium fraction is limited unless the material is finely divided, exposed over long time horizons, or undergoes post-use processing. Several factors contribute to this such as lower solubility of $Mg(OH)_2$ compared to $Ca(OH)_2$, formation of hydrated carbonate building nucleation and cristallisation barriers that can prevent further carbonation.

Formation of metastable or hydrated carbonate phases
Instead of forming pure $MgCO_3$, $Mg(OH)_2$ often carbonates to hydrated magnesium carbonates (e.g., nesquehonite ($MgCO_3{\cdot}3H_2O$), hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$)). These phases have lower CO_2 uptake per unit magnesium than theoretical magnesite formation.

Potential for deeper carbonation in crushed end-of-life fractions
After service life, fragmented or powdered dolomitic materials may carbonate more extensively due to increased surface area.

Theoretical CO_2 uptake potential
The maximum uptake, assuming full carbonation to $CaCO_3$ and $MgCO_3$, is:

$CaO + CO_2 \longrightarrow CaCO_3$: 0.785 tonne CO_2 per tonne CaO

$MgO + CO_2 \longrightarrow MgCO_3$: 1.09 tonne CO_2 per tonne MgO

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$: 0.594 tonne CO_2 per tonne $Ca(OH)_2$

$Mg(OH)_2 + CO_2 \longrightarrow MgCO_3 + H_2O$: 0.7546 tonne CO_2 per tonne $Mg(OH)_2$

However, full conversion of the magnesium component is rarely achieved under natural ambient conditions. Therefore, practical uptake values for dolime products tend to be significantly lower than theoretical maxima unless accelerated carbonation or controlled industrial processes are used.

2.3.4 Implications for CO_2 uptake method development

Dolime requires methodological treatment aligned with, but distinct from, high-calcium lime:

Dual reactive oxide system
The presence of MgO introduces a second, slower-reacting carbonation pathway and complicates the determination of overall uptake rates.

Importance of product-specific conditions
Applications involving high-temperature exposure (e.g., refractories, steelmaking) may destroy reactive oxides prior to carbonation; others (e.g., environmental uses, agriculture, construction fillers) allow partial carbonation over time.

Need for differentiated modelling of Ca- and Mg-based carbonation
For CO_2 accounting, separate stoichiometric factors and reaction-rate models may be required.

Potential need for end-of-life modelling
Many dolomitic products carbonate significantly only after disposal, reuse, or crushing, necessitating explicit treatment of the end-of-life phase.

3 IPCC documentation of CO_2 emissions and uptake for lime-containing products

Annual national greenhouse gas emissions and removals are reported by countries to international databases under the UNFCCC through their national Greenhouse Gas Inventory systems. The UNFCCC formulates its role 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 inventories form the basis for assessing global climate developments and for designing climate strategies at national, regional, and global scales. For this reason, it is essential that the uptake of CO_2 through carbonation of lime products is included in international emissions reporting so that the net atmospheric contribution associated with lime production, use, and end-of-life handling is correctly quantified.

National GHG inventory reporting is typically carried out by a Ministry or a designated national agency, often operating under the Ministry of Environment or the National Environmental Protection Agency (EPA). Due to the technical and data-intensive nature of carbonation modelling, it is recommended that national CO_2 uptake calculations for lime products be performed through cooperation between the national inventory organisation, lime and building-material industries, downstream product users, and relevant national statistics agencies.

Guidance on how emissions and removals should be calculated is specified in the IPCC control documents, primarily the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and the amendments introduced in the 2019 Refinement and the subsequent 2023 updates addressing carbonation and potential sinks in product use as well as future updates of these documents. These documents are available via the IPCC website:
https://www.ipcc-nggip.iges.or.jp/public/2006gl/

The 2006 Guidelines consist of five volumes:

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

For lime production, emission calculations are currently divided between energy-related emissions and industrial process emissions. As in cement production, the CO_2 released during calcination of limestone in lime kilns is classified as process emissions and regulated under Volume 3 – Industrial Processes and Product Use, specifically Chapter 2: Mineral Industry Emissions and Removals.

The subsequent CO_2 uptake occurring when lime (CaO) or hydrated lime ($Ca(OH)_2$) carbonates during use, storage, or at end-of-life is chemically linked to these process emissions. It is therefore appropriate that future updates of the IPCC guidelines also treat the CO_2 uptake from lime products within the same volume and chapter as the lime-related process emissions.

In the 2023 updates and in the direction indicated by ongoing methodological discussions, the IPCC recognizes that carbonation of mineral products during use may constitute a quantifiable CO_2 removal when supported by robust methods and activity data. Lime products fall clearly into this category, as carbonation can occur during application in for example building materials, soil stabilization, water treatment residues, industrial by-products, and later during end-of-life phases when materials are exposed to atmospheric CO_2.

Because several mineral industry product systems can exhibit carbonation (cement, lime, concrete, slags, ashes, and other calcium-bearing materials), it is important to prepare an integrated methodology that can be consistently applied across the mineral industry where relevant.

A revised structure of Volume 3, Chapter 2, in direct analogy with the proposal for concrete, may therefore include an expanded CO_2 removals section, with additions shown 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
  - **2.6.2 CO_2 uptake in lime products**

The proposed section 2.6.2 would include the methodology for calculating CO_2 uptake in lime products, including carbonation during product use, storage, service life, end-of-life, and secondary applications. Approaches may include empirical models (e.g., parabolic $\sqrt{t}$ carbonation), mass-balance approaches based on CaO/$Ca(OH)_2$ availability, or product-specific coefficients aligned with the methods used for Tier 1 in the cement and concrete sector.

This study can therefore serve as an input to future revisions of the IPCC Guidelines for National Greenhouse Gas Inventories, as well as a technical reference for national inventory compilers. It may also contribute to future entries in the IPCC Emission Factor Database (EFDB), supporting harmonized and transparent reporting of CO_2 uptake in lime products. Applying annual national CO_2 uptake calculation for lime products will also gain valuable knowledge and experience for future development of the CO_2 uptake calculation.

4 General description of CO_2 uptake models for lime-containing products and applications

4.1 General principles

As shown in Chapter 3, the CO_2 emission model for the raw materials used in a lime kiln is presented in the document *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. The calculated CO_2 emissions are based on the amount of lime (CaO) or dolime (CaO·MgO) produced by a lime kiln. This amount of CO_2 driven off from the raw material (limestone, $CaCO_3$ or Dolomite, $CaMg(CO_3)_2$) can normally be considered as the maximum theoretical uptake of CO_2 due to carbonation of lime or dolime containing products.

The CO_2 uptake model will thus calculate the CO_2 uptake in different lime and dolime containing products during their service life as well as in the end-of-life processes and when used as secondary products, such as crushed mortar or render, or as soil amendment and stabilization. The emission and uptake models are illustrated in Figure 5 below.

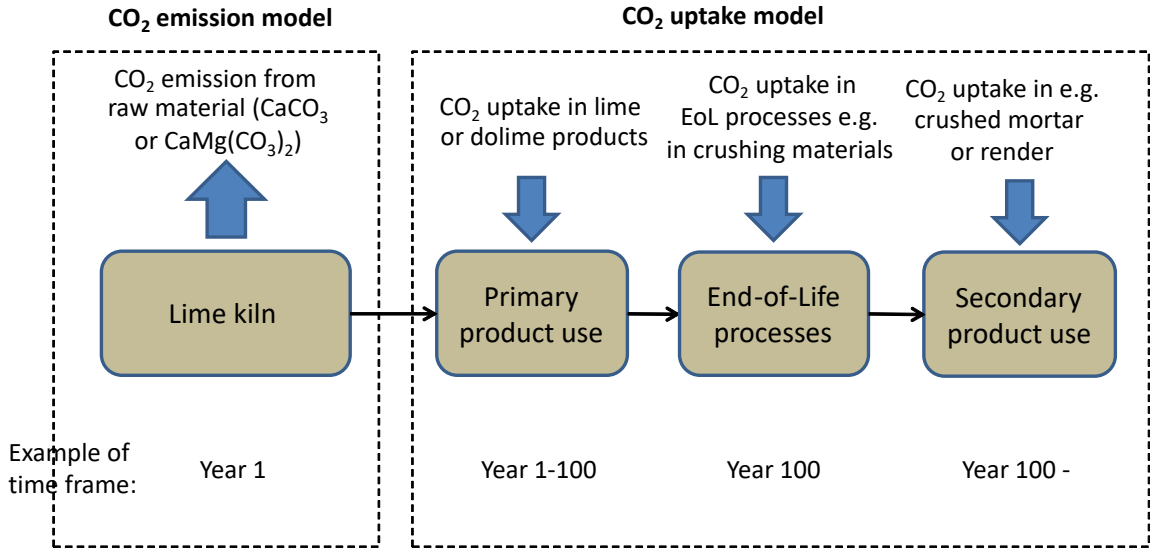


Figure 5 Schematic figure showing the CO_2 balance in lime and dolime containing products over a certain period of time.

The CO_2 uptake in lime and dolime products is a relatively slow process that typically occurs over several months or years. However, this carbonation process is generally faster than that of concrete. The initial phase involves uptake within structures such as mortar, render or plaster, or within smaller particles. Carbonation proceeds from the surface of the lime product, provided it exists in a solid phase rather than as a bulk aqueous solution.

When atmospheric CO_2 diffuses into the porous lime, it reacts with $Ca(OH)_2$ (typically dissolved within micropores) to form $CaCO_3$, according to the reactions described in Chapter 2. Consequently, the area and the area/volume ratio are critical factors for a CO_2 uptake model. By identifying the total annual use of lime in mortar, render, and plaster, as well as the physical dimension (area and thickness) of the products, the CO_2 uptake surfaces can be estimated. For these applications, a mixture of lime and cement can also be used, which ratio also must be known for accurate calculations.

From these estimated surface areas, the annual CO_2 uptake over time can be determined. Additional factors influencing this process include moisture content and environmental exposure; whether surfaces are located indoors or outdoors, or exposed to rain, can significantly affect both the carbonation rate and the ultimate degree of carbonation.

Beyond the carbonation of solid structures, CO_2 uptake also occurs directly in systems where calcium hydroxide is fully dissolved in an excess of water, such as in aqueous solutions or lime milk. In these cases, the mechanism is driven by the absorption of gaseous CO_2 into the liquid phase. Once the CO_2 is dissolved, it undergoes hydration to form carbonic acid and subsequent carbonate ions, which then react instantaneously with the already dissolved Ca^{2+} and OH^- ions. This results in the direct precipitation of calcium carbonate ($CaCO_3$) particles within the bulk liquid. Unlike the slow diffusion through solid pores, this process is generally limited only by the gas-liquid mass transfer rate and the availability of dissolved CO_2, making it a highly efficient pathway for carbon capture in liquid-based industrial applications.

Following the service life of structures containing lime, such as masonry or stabilized soils, the material is often demolished and crushed for secondary use. Similar to concrete, this crushing process significantly increases the specific surface area, thereby accelerating the carbonation rate (if not already fully carbonated). When lime-based materials are reduced to finer fractions, the potential for total carbonation throughout the volume is enhanced, provided that the secondary application allows for sufficient exposure to atmospheric CO_2.

To maximize this CO_2 uptake, active planning of end-of-life and secondary use processes is essential. For instance, using crushed lime-treated materials as loose aggregates in road foundations or as pH-adjusting soil amendments ensures the material remains accessible to air and moisture. However, because lime is often used in smaller volumes or thinner layers (such as renders and plasters) compared to structural concrete, tracking these materials through the waste stream can be challenging. Consequently, knowledge regarding the specific end-of-life and secondary use practices for lime products varies by region, leading to greater uncertainties in existing CO_2 uptake models. Despite these uncertainties, the CO_2 uptake potential during the secondary use phase remains substantial, offering a significant opportunity for carbon sequestration within the lifecycle of the material.

In a CO_2 uptake model, various levels of detail can be incorporated to improve model performance. However, there is a parallel need for simplified calculations based on limited input data. A practical method to achieve this is to approximate the inventory of lime-containing materials within a society by utilizing historical records of lime and dolime production (specifically the volume of decarbonated CaO and MgO units). The theoretical maximum CO_2 uptake of the produced lime can be adjusted using specific factors to account for the actual carbonation achieved during the primary application phase, the end-of-life phase, and any subsequent secondary use. Similar to the

approaches used for concrete, the IVL Tier 1–3 methods for lime include varying degrees of simplification, ranging from broad production-based estimates to more detailed, application-specific calculations, which are discussed in further detail in Chapter 5.

4.2 Territorial attribution and relationship between process emissions and CO_2 uptake

For greenhouse gas inventory purposes, a distinction shall be made between:

1. carbonation involving direct uptake of CO_2 from the atmosphere; and
2. carbonation involving CO_2 deliberately supplied from an industrial process, captured gas stream or carbon capture and utilisation system.

Carbonation occurring through exposure of lime-containing products to ambient air represents a physical transfer of CO_2 from the atmosphere into the product. This uptake shall be attributed to the territory and reporting year in which the carbonation occurs.

Consequently, lime imported into a country and subsequently carbonated within that country shall be included in the national uptake estimate. Lime exported before carbonation occurs shall be excluded from the exporting country's uptake estimate. Atmospheric carbonation is not conditional on the corresponding calcination emissions having previously been reported in the same national greenhouse gas inventory, because the calcination and carbonation may occur in different countries and different reporting years.

A fundamental principle for calculating CO_2 uptake is that uptake should only be reported for CO_2 that has previously been reported as an emission within the greenhouse gas inventory. Carbonation represents the partial or complete reabsorption of process CO_2 released during calcination of carbonate minerals. Consequently, the reported uptake must correspond to previously reported process emissions in order to maintain mass balance and to avoid double counting.

In many applications, the emission and the subsequent uptake occur in different parts of the product life cycle. For example, process-CO_2 is released during lime production, whereas carbonation occurs years or decades later during the use phase or after end-of-life. In such cases, the relationship between emission and uptake is straightforward, since the original calcination emissions are reported separately from the later uptake.

In other applications, however, the emission source and the carbonation process may occur within the same industrial system or may involve CO_2 originating from another industrial process. In these situations, particular care is required to ensure that the reported uptake corresponds to CO_2 that is included within the inventory and that no double counting occurs.

Examples include:

- **Precipitated calcium carbonate (PCC) production**, where calcination, CO_2 capture and recarbonation may occur within an integrated industrial process. If the process CO_2 released during lime production is directly recaptured to produce PCC before leaving the plant, only the net process emissions should be reported. Additional carbonation credits should not be assigned unless corresponding process emissions have first been reported.
- **Accelerated carbonation of air pollution control residues (APCR)**, where CO_2 used for carbonation may originate from flue gases of another industrial installation. If this CO_2 has already been reported as an emission from the originating installation, the subsequent mineralisation may be reported as CO_2 uptake provided that double counting is avoided. Conversely, if the CO_2 has not yet entered the inventory as an emission, no additional uptake credit should be assigned.
- **Integrated carbon capture and utilisation (CCU) systems**, where CO_2 is transferred directly between industrial processes. In such cases, consistent accounting requires clear identification of where emissions are reported and where subsequent uptake is credited.

Accordingly, the methodology presented in this report follows the general principle that reported CO_2 uptake shall always be linked to previously reported process CO_2 emissions. Where this relationship cannot be demonstrated, conservative assumptions should be applied, and no uptake should be credited until the corresponding emissions are included within the inventory.

5 Proposed CO_2 uptake models for lime-containing products

5.1 Overview description and strategies

This chapter documents the scientific and methodological investigation undertaken to develop the national inventory methods presented in Chapter 6. It reviews activity-data options, product and application groupings, carbonation mechanisms, temporal allocation functions, and alternative levels of model complexity. Some approaches examined in this chapter were retained and refined, while others were not selected for the final methodology. Chapter 6 therefore provides the operative Tier 1, Tier 2 and Tier 3 calculation methods; the material in Chapter 5 explains their technical basis and the choices made during method development.

The methodological development in this report builds upon the general principles established for carbonation in cement and concrete products, while adapting the approach to the specific chemical behaviour, use patterns, and carbonation characteristics of lime-based materials. Compared with concrete, carbonation in lime products is generally more rapid and more complete due to the higher reactivity of calcium hydroxide and the typically higher porosity and exposure conditions of lime-containing materials. At the same time, lime products are considerably more heterogeneous in terms of applications, material forms, and exposure environments, which requires a broader methodological framework.

The proposed strategy is based on the recognition that carbonation of lime products constitutes a scientifically well-established anthropogenic CO_2 removal mechanism. During lime production, CO_2 is released through calcination of carbonate minerals, primarily according to:

$$CaCO_3 \longrightarrow CaO + CO_2$$

Following production and use, the calcined lime products may subsequently reabsorb CO_2 through carbonation reactions such as:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

This reverse process can occur during the service life of products, during end-of-life handling, and during secondary use stages. Consequently, the net climate impact of lime products depends not only on emissions from calcination and fuel combustion, but also on the magnitude and timing of subsequent CO_2 uptake.

The methodological challenge is therefore to quantify annual CO_2 uptake in a manner that is scientifically robust, transparent, reproducible, and compatible with IPCC inventory principles. The methods proposed in this report are designed to fulfil the general IPCC requirements that emission and removal estimates should neither systematically overestimate nor underestimate actual values and that uncertainties should be reduced as far as practicable.

The investigation was structured around a tiered methodology corresponding conceptually to the IPCC Tier 1-3 system. Countries differ in their statistical information, technical resources, and access to data on lime production, trade, use, and carbonation. The final framework therefore provides methods with increasing data requirements and temporal detail.

The strategy proposed in this report consists of three methodological levels:

Tier 1 - an aggregate steady-state method using current apparent national lime use, a consistent reactive-oxide basis, and national average carbonation and exposure factors.

Tier 2 - an application-disaggregated steady-state method using current apparent national lime use allocated among mutually exclusive application categories with category-specific parameters.

Tier 3 - an application-specific annual consumption-cohort method using historical lime use and cumulative carbonation progression functions. A full dynamic stock-and-flow model, including service lives and explicit end-of-life flows, is retained in Chapter 6.5.2 as an alternative advanced method rather than as a defining requirement of the recommended Tier 3 method.

The proposed methodology framework is also based on the principle that carbonation must be evaluated over the full lifecycle of lime-containing products. Uptake can occur during:

- the primary use stage
- demolition and end-of-life handling
- crushing and stockpiling processes
- recycling and secondary use applications
- land application and environmental uses

This lifecycle perspective is particularly important for lime products because carbonation rates may vary substantially between applications. Thin and porous products such as lime mortars and renders may carbonate rapidly during service life, while industrial process lime or lime encapsulated in hydraulic systems may carbonate only partially or slowly. Crushed lime-containing materials at end-of-life may subsequently carbonate at much higher rates due to increased surface area exposure.

Another important strategic consideration concerns the classification of lime products. Unlike cement and concrete systems, lime is used across a very broad range of sectors including:

- construction materials
- soil stabilization and agriculture
- environmental and water treatment
- industrial process applications
- metallurgical processes
- flue gas cleaning
- secondary mineral products

The proposed methodology therefore introduces a structured product taxonomy that groups lime products according to carbonation behaviour, exposure conditions, and expected CO_2 uptake mechanisms. This grouping enables both simplified and advanced methods to be developed consistently across sectors.

A further strategic aspect is the need to distinguish between theoretical maximum carbonation potential and actual realized carbonation. Although the calcination reaction is, in principle, reversible, full recarbonation is rarely achieved under practical conditions. Actual uptake depends on several controlling factors including:

- exposure to atmospheric CO_2
- relative humidity and moisture conditions
- porosity and material structure
- product geometry and thickness
- carbonation kinetics
- service life duration
- end-of-life processing

Accordingly, the methodologies proposed in this report are based on estimation of realistic carbonation degrees and uptake rates rather than assuming complete carbonation.

The investigation also considered the effect of lime placed in use in earlier years. The recommended Tier 3 method represents this effect through annual consumption cohorts and their carbonation progression functions. Explicit modelling of physical stocks, service lives, demolition, and end-of-life flows is required only for the alternative full stock-and-flow method described in Chapter 6.5.2.

An important strategic objective of this work is compatibility with existing and future IPCC methodologies. The methodology structure, terminology, and reporting logic have therefore been developed to align as closely as possible with the principles used in the 2006 IPCC Guidelines for National Greenhouse Gas Inventories and the ongoing IPCC work concerning Carbon Dioxide Removal (CDR) methodologies and mineral carbonation processes.

The methodology framework presented in this chapter is intended to provide:

- a scientifically credible basis for quantifying CO_2 uptake in lime products
- practical methodologies applicable under different national conditions
- compatibility with future IPCC reporting structures
- transparency and reproducibility in inventory calculations
- a foundation for future methodological refinement and international harmonization

The following sections examine historical production and use patterns, candidate calculation structures, product-specific behaviour, and the implications of these findings for the final methods specified in Chapter 6.

5.2 Historical carbonation and future potential

Recent global assessments indicate that atmospheric CO_2 uptake by lime-containing products has increased substantially over the last century, reflecting the growth in worldwide lime production and use. Estimated annual CO_2 uptake increased from approximately 33.6 Mt CO_2 yr^{-1} in 1930 to 127.9 Mt CO_2 yr^{-1} in 2020, with a cumulative uptake of approximately 5.3 Gt CO_2 during 1930–2020. This cumulative uptake corresponds to approximately 39% of the cumulative process CO_2 emissions

released during limestone calcination over the same period. It should be noted that this comparison excludes CO_2 emissions from fuel combustion in lime kilns, since carbonation can only reabsorb CO_2 originating from the calcination of carbonate minerals. [51]

Beyond conventional lime products, mineral carbonation of lime together with other alkaline materials has been identified as a potentially important anthropogenic CO_2 removal pathway. Global assessments suggest that the combined annual CO_2 uptake potential of lime and other similarly behaving alkaline materials could reach approximately 2.9–8.5 Gt CO_2 yr^{-1} by 2100, depending on future material production, utilisation patterns, and deployment of carbonation technologies. [48,49,51]

5.3 Historical use and production of lime and lime products

5.3.1 An overview introduction

Lime (the processed forms of calcium carbonate—principally quicklime, CaO, and hydrated lime, $Ca(OH)_2$) has been used as a manufactured (industrial) material for millennia. Its applications have historically encompassed construction (mortars, plasters, renders), agriculture (soil amendment, pH control), metallurgy (fluxing and slag conditioning in iron and steel production), chemical manufacture, water and wastewater treatment, flue-gas desulfurisation, and numerous industrial processes (paper, sugar, alumina, and chemical synthesis). The long service life and repeated re-use of many lime-containing products mean that the lime lifecycle (production → use → end-of-life) is central to assessments of both CO_2 emissions from calcination and subsequent CO_2 uptake by carbonation. [51]

5.3.2 Historical development of production volumes — overview and data sources

Reliable, harmonised global time-series for lime production have been scarce historically, but recent syntheses have reconstructed production and use from 1930 to 2020 by combining national statistics, industrial reports, and gap-filling for regions with limited records. One recent peer-reviewed synthesis provides an analytical reconstruction of global lime production and estimates of CO_2 process emissions and subsequent uptake for the period 1930–2020; the authors supply regional time series and supplementary material containing the annual production estimates that underpin their analysis. Their results show a marked rise in lime production and the associated process emissions in the post-2000 period, driven predominantly by rapid industrial expansion in China. The study reports regional and global CO_2 process-emission trajectories and quantified the CO_2 uptake by lime products over the period 1930–2020; these data and their supplementary tables are the most comprehensive public dataset currently available for long-term global lime production and use. [51]

National statistical sources and commodity reports supply more recent (annual) production figures for individual countries. For example, United States Geological Survey (USGS) Mineral Commodity Summaries and associated country sheets provide reliable annual data for quicklime and hydrated

lime production in the United States; similar national or regional publications (industry associations, statistical yearbooks) are the principal sources for country-level data elsewhere. European production and technical information are summarised by the European Lime Association (EuLA), which also publishes production and plant-type information for Europe. [52]

Key points from the published data:

- Global lime production and the associated process CO_2 emissions were relatively moderate and slowly increasing through much of the 20th century but accelerated after ~2000, with substantial contribution from rapid growth in China's industrial sectors. [51]
- Country-level production varies widely; for example, US domestic production of quicklime and hydrated lime in recent years has been on the order of 15–17 million tonnes per year (latest USGS assessments). Comparable national totals for China and other large producers are reported in the regional datasets and are the principal drivers of the global trend. [52]

Data availability and uncertainty

Global totals and historical time series are available in the referenced synthesis (supplementary information) and in national compilations. Users should note that the global dataset contains uncertainties arising from incomplete national reporting (notably early-period data for some regions), differences in product classification (quicklime vs hydrated lime vs lime used internally by captive industries), and changes in industrial reporting practices over time. The ESSD synthesis provides uncertainty bounds and a documented gap-filling approach that is appropriate for national inventory method development. [51]

5.3.3 Classification of lime products (product types)

Industrial lime products are conventionally grouped according to chemical composition, reactivity and physical form. Principal categories used in inventories and industry reporting are:

- **Quicklime (calcium oxide, CaO)** — produced by direct calcination (thermal decomposition) of limestone or dolomite; sold as lumps, coarse material or sized fines for direct industrial use or for further processing into hydrated lime. [53], [https://mpalime.org]
- **Hydrated lime / slaked lime (calcium hydroxide, $Ca(OH)_2$)** — produced by controlled addition of water to quicklime (slaking); available as dry powder (dry-hydrated lime), as lime putty (wet slaked lime, historically used in traditional mortars), or as milk-of-lime suspensions. Hydrated lime is widely used in construction, water treatment, and chemical processes. [https://mpalime.org]
- **Hydraulic vs non-hydraulic lime** — a functional classification relevant to construction: hydraulic limes set by combined hydration and carbonation reactions (contain reactive silica/alumina), whereas non-hydraulic limes set primarily by carbonation. This distinction matters for uptake assessments because non-hydraulic lime carbonates readily during service and curing. [https://mpalime.org]
- **Dead-burned dolomitic lime / refractory lime** — produced under specific kiln conditions for refractoriness and lower reactivity; used in metallurgical and refractory applications. [https://mpalime.org]
- **Dolime:** or dolomitic quicklime is a reactive mixture of calcium oxide (CaO) and magnesium oxide (MgO) in various proportions. When hydrated, dolime forms calcium hydroxide ($Ca(OH)_2$) and magnesium hydroxide ($Mg(OH)_2$).

Inventory reporting and method development for CO_2 uptake must be explicit about which product categories are included, because the available reactive $CaO/Ca(OH)_2$ or $MgO/ Mg(OH)_2$ mass (and its exposure to atmospheric CO_2 over time) determines the theoretical maximum uptake and the kinetics of carbonation in service and at end-of-life.

5.3.4 Principal production routes and kiln technologies

Industrial lime production converts calcium carbonate ($CaCO_3$) feedstock into reactive lime by thermal decomposition (calcination). The principal production routes and kiln types in contemporary practice are:

- **Rotary kilns.** Continuous rotary kilns are widely used for high-volume production and permit good control of residence time and product reactivity; they are common in larger, modern lime plants. [54]
- **Shaft (vertical) kilns.** Historically widespread and still used in many regions for medium- and small-scale production; shaft kilns may be less energy efficient but are suitable for certain feedstock sizes and product grades. They tend to produce quicklime of medium reactivity. [EuLA web-page]
- **Gas suspension and flash kilns.** Employed in modern installations to achieve high throughput and more uniform product properties; these technologies can offer improved thermal efficiency and reduced specific CO_2 emissions per tonne of lime produced. [54]
- **Travelling grate / multiple hearth furnaces (for slaking and specific products).** These and similar unit operations may be used for slaking or for specialty lime grades. [54]

Fuel type and kiln energy integration (solid, liquid, gas fuels; use of waste fuels; heat recovery) influence the fuel-related CO_2 emissions and operational energy intensity; kiln design in turn affects product reactivity, which influences carbonation rates during subsequent use. Industry guidance documents and engineering texts describe the detailed thermochemical and material-handling arrangements used across these kiln types. [54]

5.3.5 Principal historical uses by sector

Historically and presently, the major end-use sectors for lime products include:

- **Construction and building materials:** mortars, plasters, renders, limecrete, stabilized soils, aerated concrete products and masonry additives. Non-hydraulic lime products used for traditional restoration works remain an important niche. [www.mpalime.org]
- **Metallurgy and steelmaking:** fluxing and slag conditioning agents in iron and steel production and in non-ferrous metallurgy. Lime supply to the steel sector constitutes a major industrial demand segment, especially in large steel-producing countries. [51]
- **Environmental applications:** water and wastewater treatment, flue-gas desulfurisation, gas scrubbing, and neutralisation processes. Lime's role in environmental control has expanded with regulatory drivers for emissions and effluent quality. [53]
- **Chemical industry and mineral processing:** pulp and paper, alumina production, sugar refining, ceramics, and various chemical synthesis routes. [54]
- **Agriculture and soil amendment:** liming of soils to correct acidity and supply calcium/magnesium. [53]

Because service-life exposure and the nature of the lime application (e.g., exposed mortar vs confined hydraulic binder) govern the rate and extent of carbonation, sectoral use profiles are essential input to any method that quantifies CO_2 uptake over time.

5.3.6 Recent production magnitudes and regional patterns

- **Regional production trends.** Synthesised global time series indicate that China has been the dominant producer of lime throughout the early 21st century and accounts for the largest share of cumulative production and cumulative carbon uptake in the 1930–2020 period. The rise in Chinese lime production after approximately 2000 is the principal driver of the accelerated global production and process-emission trend reported in the literature. [51]
- **Country examples and recent annual data.** United States domestic production of quicklime and hydrated lime has been reported at roughly 15–17 million tonnes per year in recent annual USGS assessments; country-level figures for China, India, Mexico and other major producers are available in national statistics and in the global synthesis dataset. These country figures should be used where available when constructing national-level CO_2 uptake estimates. [52]

Note on global totals. Published estimates of global lime production and the segmentation by product type vary among sources because of differing inclusion rules (e.g., exclusion of captive internal use, treatment of slaked lime producers, and incompletely reported national data). For historical reconstructions, the ESSD 1930–2020 dataset provides harmonized annual series and is recommended as a primary source for national-level method development; for the most recent single-year national and regional figures, consult the latest national statistics and USGS/industry association publications. [51]

5.3.7 Implications for a national CO_2-uptake methodology for lime products

Historical use patterns, product diversity, and application conditions determine both the mass of reactive lime available for carbonation and the timing of uptake. The method-development assessment therefore identified the following requirements:

1. Use current apparent national lime use for steady-state calculations and harmonized historical consumption or apparent-use time series for cohort calculations. Production series, including the ESSD 1930-2020 reconstruction where appropriate, may be used when adjusted for imports, exports, stock changes, and other relevant balance terms. [51]
2. Where the selected tier requires disaggregation, allocate lime use to mutually exclusive product or application categories because chemical eligibility, exposure, and carbonation timing differ between uses. [53]
3. Incorporate sectoral end-use profiles (construction, steel, environmental, chemical, agriculture) to estimate exposure and carbonation kinetics; where possible, use measured or literature-based carbonation rates for representative products and service conditions. [51]
4. Account for imports, exports, stock changes, captive internal use, and other documented balance adjustments so that activity data represent lime placed in use within the reporting territory and avoid double counting or omissions. National customs and industry data are typically required for this step. [53]
5. Propagate uncertainty in production data, product allocation and carbonation kinetics, and provide sensitivity analyses as part of the national reporting package. The ESSD study provides an example of a Monte-Carlo uncertainty approach applied to historical uptake estimates. [51]

5.3.8 References and primary data sources

The methodology developed in this study is based on a combination of scientific literature, industry information, technical reports, national and international statistics, and expert judgement. Since no comprehensive database currently exists for carbonation of lime-containing products comparable to those available for some concrete applications, information has been collected and synthesized from multiple sources covering lime production, product applications, carbonation mechanisms, carbonation rates, service lives, end-of-life treatment, and secondary use.

The theoretical basis for carbonation chemistry, reaction kinetics, and controlling mechanisms has primarily been derived from peer-reviewed scientific literature concerning carbonation of calcium oxide, hydrated lime, dolomitic lime, lime mortars, lime plasters, soil stabilization materials, and other lime-containing products. Additional information has been obtained from studies addressing mineral carbonation, carbon dioxide removal (CDR), and carbonation processes in related mineral systems.

Information regarding production volumes, application sectors, and use patterns for lime and dolomitic lime products has been collected from industry publications, national statistics, technical reports, and information provided by the European Lime Association (EuLA) and participating companies. These data have been used to identify major application categories and to estimate the distribution of lime products between different end uses relevant to carbonation calculations.

For several product categories, publicly available quantitative data on carbonation rates, service lives, and end-of-life management are limited. In such cases, estimates have been developed using a combination of published literature, engineering judgement, analogy with similar material systems, and information provided by technical experts within the lime industry. Where uncertainty is high, conservative assumptions have generally been applied in order to avoid overestimation of CO_2 uptake.

The development of the carbonation models has also benefited from previous methodological work performed by IVL Swedish Environmental Research Institute on carbonation of cement-based materials and concrete products. Although the carbonation behaviour of lime products differs from that of concrete, many of the fundamental concepts regarding carbonation kinetics, material stocks, service-life modelling, end-of-life treatment, and annual uptake calculations are similar and have provided valuable methodological guidance for the present work.

Particular importance has been placed on data sources suitable for national greenhouse gas inventories. Preference has therefore been given to information that inventory compilers can reasonably obtain, including production and trade statistics, industrial activity data, product-specific market information, current apparent national use, and historical consumption records. These sources support the final Tier 1, Tier 2, and Tier 3 methods described in Chapter 6.

The primary data sources used in this study can be grouped into the following categories:

- Peer-reviewed scientific literature on carbonation of lime, hydrated lime, dolomitic lime, mortars, plasters, soil stabilization products, and related mineral materials.
- Scientific literature on carbonation kinetics, diffusion processes, mineral carbonation, carbon dioxide removal (CDR), and carbon capture, utilization and storage (CCUS).
- Existing IPCC Guidelines for National Greenhouse Gas Inventories and related methodological documents.
- Technical reports and publications from the lime industry, including information from EuLA and national lime associations.
- National and international statistics on lime production, trade, and consumption.
- Information on product applications, service lives, material flows, demolition practices, recycling processes, and secondary-use pathways.
- Expert input from members of the project reference group and other industry specialists with knowledge of lime production, product applications, and carbonation behaviour.

As scientific understanding develops, the methods can incorporate improved activity data, carbonation parameters, exposure factors, and country-specific progression functions. Tier 2 and Tier 3 are particularly suited to such refinement because they distinguish application categories and, in Tier 3, the timing of uptake.

5.4 General framework for CO_2 uptake by carbonation in lime-containing products

5.4.1 Background

Carbonation of lime-containing materials, including dolomitic lime products, is a thermodynamically favourable process in which atmospheric carbon dioxide reacts primarily with calcium hydroxide ($Ca(OH)_2$) or calcium oxide (CaO) to form chemically stable calcium carbonate ($CaCO_3$) and also magnesium carbonate ($MgCO_3$). These reactions commonly result in a partial uptake of the CO_2 originally released during calcination in lime production. Quantifying this uptake is essential for establishing more complete greenhouse gas inventories and for ensuring consistency between accounting of emissions and removals across product life cycles.

Lime-based products are applied across a wide range of sectors, including construction, environmental remediation, agriculture, metallurgy, pulp and paper, and chemicals. This diversity presents methodological challenges: carbonation rates, exposure conditions, product geometries, and service lives vary significantly between applications. Nevertheless, carbonation follows well-defined physicochemical principles described above, and these principles provide the foundation for a systematic and generalizable framework for calculating CO_2 uptake.

Both carbonation via CaO and $Ca(OH)_2$ converge to the same end-product ($CaCO_3$) and the same theoretical uptake potential i.e. 1 mole can take up 1 mole of CO_2 thus 1 tonne CaO can bind up to approximately 0.785 tonnes of CO_2 if fully carbonated. For $Ca(OH)_2$, the corresponding value is approximately 0.590 tonnes CO_2 per tonne of hydroxide. The extent to which carbonation occurs depends on the product's formulation, microstructure, exposure to CO_2, moisture availability, surface accessibility, and time, which also has been covered earlier in this report.

5.4.2 Candidate approaches considered during method development

For lime-based products, several methodological pathways exist for developing robust CO_2 uptake estimation models. These include:

Material-specific models
These models are tailored to individual product categories with unique physical or chemical behaviours. For lime products, examples include:

- Building limes (e.g., lime mortar, lime plaster, limewash)
- Stabilized soils and geotechnical binders
- Industrial alkali residues with high CaO/$Ca(OH)_2$ content
- Metallurgical flux residues
- Water treatment sludges
- Agricultural liming materials applied to soil

Each category exhibits different exposure patterns, moisture regimes, and surface configurations, which may justify dedicated modelling approaches.

Generalized carbonation frameworks
A more unified methodology can be developed if carbonation across lime applications is expressed through general parameters that govern all carbonation reactions. This approach requires:

- A standardized representation of lime composition and reactivity.
- A generic diffusion-based or empirically derived carbonation model.
- Adjustable coefficients for moisture, CO_2 exposure, and material accessibility.
- Defined rules for primary use, end-of-life, and secondary use carbonation.

Such a generalized framework can enable harmonization across product categories where full granularity is not required or where data availability is limited.

Hybrid systems
In many cases, a hierarchical structure is appropriate. A general default model may be applied to the majority of applications, while specific sub-models are developed for categories where carbonation behaviour deviates significantly or where higher precision is warranted.

All these alternatives can also be modified if the applications include dolime, which can affect the carbonation rate and the degree of carbonation.

5.4.3 Evaluation of an annual-conversion-factor approach

5.4.3.1 Purpose of the evaluated approach

An early candidate for a simplified national method estimated annual uptake from annual lime production using an availability factor and an annual conversion factor. The approach is documented here because its evaluation informed the final Tier 1 method. It is not the recommended Tier 1 method; the operative method is specified in Chapter 6.3.1. The candidate was intended:

- to be transparent and easy to implement using annual production statistics and a small set of coefficients;
- to test whether an annual conversion factor could provide a first approximation where uptake was otherwise omitted; and
- to examine the uncertainty associated with aggregated calcium and magnesium parameters.

The evaluation identified three important limitations. Production alone does not represent lime placed in use within the territory; a single availability factor can combine chemical and physical restrictions; and applying an annual conversion factor only to current-year production does not consistently represent uptake from active historical cohorts. These findings led to the apparent-use, F_{carb}, F_{exp}, steady-state, and cohort structures adopted in Chapter 6.

5.4.3.2 Model concept and main assumptions

1. **Mass-basis approach examined.** Annual uptake was estimated from reactive lime produced in the reporting year, expressed as CaO, $Ca(OH)_2$, or MgO equivalents. The candidate did not consistently track uptake from earlier cohorts and therefore differed from both the steady-state approximation and the cohort accounting adopted in Chapter 6.
2. **Stoichiometric maximum uptake.** The model uses stoichiometric CO_2 uptake per unit mass of reactive oxide/hydroxide:
   - $CaO \longrightarrow CaCO_3$: 0.7848 t CO_2/t CaO (exact: 44.009/56.077).
   - $Ca(OH)_2 \longrightarrow CaCO_3$: 0.5942 t CO_2/t $Ca(OH)_2$ (44.009/74.092).
   - $MgO \longrightarrow MgCO_3$ (theoretical): 1.0919 t CO_2/t MgO (44.009/40.304).
   - $Mg(OH)_2 \longrightarrow$ hydrated carbonate (theoretical magnesite equivalent): 0.7546 t CO_2/t $Mg(OH)_2$ (44.009/58.319).

   (Use CaO-equivalent or $Ca(OH)_2$ data conversions as appropriate in national statistics.)
3. **Fraction of reactive oxide available for carbonation.** Not all produced lime is equally available for atmospheric carbonation during service life (e.g., some is consumed in closed industrial processes or permanently bound). The model therefore applies a product-availability factor α (fraction of produced reactive oxide that is exposed/opportunistic for atmospheric carbonation over the model year or life-time window).
4. **Annual conversion fraction.** The candidate used an annual conversion fraction β for the share of available reactive oxide carbonating in one year. This parameter was useful for sensitivity analysis but was not retained in the final Tier 1 method because, without cohort tracking, it does not ensure that uptake over time equals the ultimate eligible carbonation potential.
5. **Separate treatment of Ca and Mg.** Dolomitic (Mg-bearing) lime is handled separately because Mg carbonation is typically much slower and less complete under ambient conditions (see earlier sections). The model uses distinct α and β values for Ca and Mg fractions.
6. **End-of-life uplift examined.** A separate one-off correction was considered for demolition, crushing, or disposal. This was not retained as a generic Tier 1 addition because end-of-life uptake must be limited to residual uncarbonated material and must not duplicate uptake already represented by F_{carb} and F_{exp}. Explicit end-of-life flows belong in a documented Tier 3 category or the alternative stock-and-flow method.
7. **Reporting boundary.** The candidate estimated the uptake side only. The final methods retain this separation: carbonation uptake is reported as a removal and is not netted internally against calcination or fuel-combustion emissions.

5.4.3.3 Mathematical formulation evaluated

Let in a given year y:

- P_CaO_y = production (or production-equivalent) of lime expressed as tonnes CaO equivalent in year y. (If production data are in tonnes $Ca(OH)_2$ or other form, convert to CaO-equivalent using molecular weights)
- P_MgO_y = production (or production-equivalent) of dolomitic lime expressed as tonnes MgO equivalent in year y.
- α_Ca = fraction of produced Ca-equivalent lime available for carbonation (dimensionless, 0–1).
- β_Ca = annual conversion fraction for the available Ca fraction (dimensionless, fraction per year).
- α_Mg and β_Mg = corresponding parameters for Mg fraction.
- SF_CaO = stoichiometric factor for CO_2 per tonne CaO = 0.7848 t CO_2/t CaO.
- SF_MgO = stoichiometric factor for CO_2 per tonne MgO = 1.0919 t CO_2/t MgO.

The annual CO_2 uptake in the evaluated annual-conversion-factor formulation was:

$$U_y = P_{CaO,y} * \alpha_{Ca} * \beta_{Ca} * SF_{CaO} + P_{MgO,y} * \alpha_{Mg} * \beta_{Mg} * SF_{MgO}$$

If production is reported in $Ca(OH)_2$ or $Mg(OH)_2$, use the corresponding stoichiometric factors.

If an **end-of-life one-off** addition is to be applied in year y for lime produced in earlier years (or for the stock demolished in y), add:

$$U_y^{EoL} = \sum_v P_{demo,v\to y} * \alpha^{EoL} * \mathrm{SF}$$

where P_demo,v→y is the mass of lime from vintage v reaching demolition in year y, α^{EOL} is the fraction of remaining uncarbonated reactive mass carbonating after demolition or crushing, and SF is the corresponding stoichiometric factor. This expression illustrates the additional data needed for explicit end-of-life accounting; it is not part of the final Tier 1 method.

5.4.3.4 Illustrative parameter values examined

The following values and ranges were examined during method development. They are retained to document the sensitivity analysis and shall not be used as defaults for the final methods in Chapter 6.

Central values examined in the candidate approach

- **α_Ca (fraction available for carbonation):** 0.70 (70%)
  Rationale: substantial share of lime is used in exposed applications (construction, environmental uses), but some fraction is consumed in closed industrial processes or chemically sequestered where atmospheric carbonation is minimal.
- **β_Ca (annual conversion fraction for Ca fraction):** 0.03 (3% per year)
  Rationale: represents average ambient carbonation in mixed applications (exposed mortars, plasters, soils) across an assumed distribution of product exposure and particle size. Over decades this produces substantial cumulative uptake while remaining conservative for single-year accounting.
- **α_Mg (fraction available for Mg carbonation):** 0.60 (60%)
  Rationale: similar availability but somewhat more conservative because Mg fraction often occurs in industrial uses with lower exposure.
- **β_Mg (annual conversion fraction for Mg fraction):** 0.005 (0.5% per year)
  Rationale: Mg-based carbonation is typically an order(s) of magnitude slower than Ca; this default captures slow ambient kinetics.
- **Optional end-of-life additional uptake (country-level one-off):** EoL_add = 0.10 (10% of remaining uncarbonated available mass converted at demolition/processing) — applied in the year of demolition/crushing. (Alternative: apportioned over 1–5 years.)

Uncertainty ranges (for sensitivity / Monte Carlo)

- **α_Ca:** 0.4 – 0.9
- **β_Ca:** 0.01 – 0.07 per year
- **α_Mg:** 0.3 – 0.9
- **β_Mg:** 0.001 – 0.02 per year
- **EOL_add:** 0.0 – 0.30 (0–30% one-off)

These ranges demonstrate the large structural uncertainty of the candidate approach and helped motivate the separate treatment of chemical completeness, physical exposure, and timing in the final methods.

5.4.3.5 Worked example of the evaluated candidate approach

Assume in year y a country reports:

- P_CaO_y = 100 000 t (tonnes CaO-equivalent produced)
- P_MgO_y = 10 000 t (tonnes MgO-equivalent produced)

Apply the illustrative candidate values: α_Ca = 0.70, β_Ca = 0.03; α_Mg = 0.60, β_Mg = 0.005.

Compute Ca uptake component:

- SF_CaO = 0.7848 t CO_2/t CaO.
- Ca available mass = 100 000 × 0.70 = 70 000 t CaO.
- Annual fraction carbonated = 70 000 × 0.03 = 2100 t CaO carbonated per year.
- CO_2 uptake from Ca = 2100 × 0.7848 = 1649.55 t CO_2.

Compute Mg uptake component:

- SF_MgO = 1.0919 t CO_2/t MgO.
- Mg available mass = 10 000 × 0.60 = 6000 t MgO.
- Annual fraction carbonated = 6000 × 0.005 = 30 t MgO carbonated per year.
- CO_2 uptake from Mg = 30 × 1.0919 = 32.757 t CO_2.

Total annual uptake U_y ≈ 1649.6 + 32.8 ≈ 1682.4 t CO_2 per year.

If an end-of-life one-off EOL_add = 0.10 is applied to a demolition flux of 50 000 t CaO equivalent in that year, then additional uptake = 50 000×0.10×0.7848 = 3927.5 t CO_2 (apportionable to the demolition year or averaged over a short period).

The example demonstrates the arithmetic of the candidate formulation only. It is not comparable with the worked examples of the final Tier 1, Tier 2, and Tier 3 methods in Appendix A because it uses production rather than apparent use and applies annual conversion factors rather than the final steady-state or cohort structures.

5.4.3.6 Lessons for the final method design

The evaluation identified the following data and modelling needs for the final tiered framework:

1. **Inventory product distribution.** Disaggregate national production into major product categories (quicklime for steel, quicklime for chemical use, hydrated lime for construction, agricultural lime, etc.). Use industry statistics, customs data, and associations.
2. **Separate chemical eligibility from physical exposure.** Product or application data should support distinct F_{carb} and F_{exp} values so that the same limitation is not represented twice.
3. **Represent timing independently from ultimate uptake**. Literature, measurements, or engineering judgement may be used to define carbonation periods and cumulative progression functions for Tier 3 without changing the ultimate eligible uptake determined by F_{carb} and F_{exp}.
4. **Model end-of-life flows** explicitly only where data support a mutually exclusive residual flow. Building-stock and demolition models may be used in the alternative full stock-and-flow method, but a generic end-of-life uplift should not be added to Tier 1 or Tier 2 results.
5. **Use field or laboratory measurements**, where available, to derive or validate F_{carb}, F_{exp}, carbonation periods, and progression functions for representative national products.
6. **Uncertainty quantification.** Run Monte Carlo or scenario sensitivity using parameter ranges to generate confidence intervals for national uptake estimates.
7. **Documentation and transparency.** Provide clear documentation of data sources, assumptions, default values, and uncertainty ranges per IPCC principles.

5.4.3.7 Data-conversion issues identified during evaluation

- **Production units.** If national data are reported as tonnes of $Ca(OH)_2$ or hydrated lime, convert to CaO-equivalent using molecular masses: 1 t $Ca(OH)_2$ corresponds to (molar mass CaO / molar mass $Ca(OH)_2$) = 56.077/74.092 = 0.7567 t CaO-equivalent. Conversely, 1 t CaO corresponds to 1/0.7567 = 1.322 t $Ca(OH)_2$. (Use the stoichiometric factors to compute CO_2 uptake directly if using $Ca(OH)_2$ units.)
- **Dolime reporting.** Dolomitic lime should be separated into reactive CaO and MgO components using documented composition data. The base Tier 1 calculation in Chapter 6.3.1 includes only the reactive CaO component. MgO uptake may be calculated separately with the same Tier 1 structure, but it requires an MgO-specific stoichiometric factor and justified MgO-specific carbonation and exposure factors. The CaO defaults shall not be applied automatically to MgO.
- **Imports, exports, stock changes, and captive use.** Territorial activity data should represent lime placed in domestic use. Apparent use is therefore calculated from production, imports, exports, stock changes, and other documented balance adjustments. Captive internal use should be included or excluded according to its actual territorial placement and chemical eligibility, not solely according to whether it enters the market.

5.4.3.8 Documentation requirements identified

- The evaluation showed that **inventory documentation** must state the activity-data balance and units, chemical basis, stoichiometric factors, F_{carb} and F_{exp} values, temporal assumptions where applicable, exclusions, and uncertainty ranges. If the candidate α and β formulation is used for research comparison, it must be labelled clearly as non-recommended.
- **Present results**: annual uptake in t CO_2, fraction of theoretical maximum uptake achieved that year, and sensitivity analysis across the parameter uncertainty ranges.
- **Tier classification** shall follow Chapter 6. The annual-conversion-factor formulation documented in this section is not assigned to a final tier.

5.4.3.9 Assessment of the candidate approach

Advantages

- Simple to implement for exploratory calculations using production data.
- Transparent and auditable.
- Improves on current omission of uptake in many inventories.
- Explicit uncertainty ranges encourage conservative interpretation.

Limitations

- Large structural uncertainty due to averaging across widely different product types and exposure conditions.
- Does not represent dynamic accumulation and older vintage stocks other than via simplified EoL corrections.
- Mg carbonation uncertainties are particularly large and may be under- or over-estimated for countries with high dolime use.

Suitability

- Not retained as the recommended Tier 1 method because it does not consistently represent territorial apparent use, ultimate eligible uptake, and the contribution of historical cohorts.
- Useful only as a documented sensitivity or research formulation when comparing alternative method structures.

5.4.3.10 Implications for the final methods

1. Use apparent national lime use rather than production alone as the activity-data basis for territorial inventory estimates.
2. Use application disaggregation to improve national representativeness where reliable sectoral consumption data are available.
3. Use measurements and literature to improve F_{carb}, F_{exp}, carbonation periods, and progression functions rather than a single combined availability factor.
4. Use steady-state calculations for Tier 1 and Tier 2 under sufficiently stable conditions, and use annual consumption cohorts in Tier 3 when changes in activity or timing must be represented.
5. Count end-of-life or secondary-use uptake only for documented residual carbonation potential and prevent double counting with primary-use uptake.

5.4.3.11 Conclusion from the evaluation

The annual-conversion-factor approach provided a useful intermediate step in method development but was not selected as the final Tier 1 method. The final method uses apparent national lime use and separates ultimate chemical completeness (F_{carb}) from physical accessibility (F_{exp}). Under stable conditions, the annual steady-state uptake is approximated by the ultimate eligible uptake associated with current use. Where timing and changes in activity must be represented, the Tier 3 method follows annual consumption cohorts. The illustrative α and β values above are therefore not report defaults.

5.4.4 Data requirements identified during method development

The required inputs depend on the selected method:

- Tier 1 requires current apparent national lime use on a documented reactive CaO basis and national average F_{carb} and F_{exp} values.
- Tier 2 additionally requires allocation of apparent use to mutually exclusive applications and application-specific chemical bases, F_{carb} values, and F_{exp} values.
- Tier 3 additionally requires historical annual lime use, year-specific application allocation where relevant, carbonation periods, and cumulative progression functions.
- All tiers require a documented treatment of chemically ineligible uses, physical accessibility, imports and exports, and potential double counting.
- Product stocks, service lives, demolition, and explicit end-of-life flows are required only when applying the alternative full stock-and-flow method or when a specific residual end-of-life category is modelled.
- Measurements of composition, carbonation, exposure, porosity, particle size, and related properties may be used to derive or validate country-specific parameters.

Where detailed data are unavailable, the applicable defaults in Chapter 6 may be used, with transparent documentation and uncertainty assessment.

5.4.5 Considerations for an IPCC-Compatible Methodology

An uptake methodology intended for national greenhouse gas inventories must meet requirements for transparency, consistency, comparability, completeness, and accuracy. This implies:

- Clear definitions of system boundaries (in-use uptake vs end-of-life uptake).
- Avoidance of double counting between lime production and downstream product categories.
- Use of the Tier 1 method where data are limited, Tier 2 where application-specific consumption data are available, and Tier 3 where historical cohort data and timing functions can be supported.
- Alignment with existing methodological structure used for cement-based carbonation calculations.
- Documentation of uncertainties and country-specific circumstances.

5.5 Product-specific assessment supporting method development

5.5.1 Principles and scope of the product-specific assessment

The product-specific assessment examines atmospheric CO_2 uptake throughout use, end-of-life, and secondary use to identify the chemical, exposure, and timing parameters needed in national greenhouse gas inventories. The assessment was used to develop the application categories and parameters applied in Chapter 6 and therefore had to:

- Be mass-balanced and stoichiometrically consistent with reported lime production and process emissions.
- Cover most globally relevant lime and dolime products.
- Allow aggregation at national level while retaining product-specific kinetics.
- Support the aggregate Tier 1 method, the application-disaggregated Tier 2 method, and the annual consumption-cohort Tier 3 method without changing the common accounting principles.

Unlike cement-based products, many lime products:

- Are chemically simpler ($CaO/Ca(OH)_2$ and $MgO/Mg(OH)_2$),
- Are more porous and reactive, and
- Can carbonate rapidly, often reaching near-complete carbonation within years rather than decades.

This enables simplifications relative to concrete carbonation models.

5.5.2 Grouping and breakdown of lime products (global taxonomy)

5.5.2.1 Relationship to previous application reviews and development of the present classification

A comprehensive review of the applications of lime and lime-containing products has previously been carried out by Politecnico di Milano on behalf of the European Lime Association (EuLA) (Grosso M. et al., 2020) [36]. That report provides an extensive description of the major applications of lime, the associated industrial processes, the available scientific literature on carbonation, and the current state of knowledge regarding carbonation potential in individual applications. It therefore constitutes an important scientific reference for understanding the use of lime products and their carbonation behaviour.

The objective of the present report differs from that of the Politecnico review. Rather than assessing carbonation separately for each individual application, the purpose here is to develop a calculation methodology that can be implemented in national greenhouse gas inventories and, ultimately, within the framework of the IPCC Guidelines for National Greenhouse Gas Inventories. Such a

methodology requires calculation approaches that are sufficiently generic to be applicable across a broad range of products while still reflecting the governing carbonation mechanisms.

For this reason, the numerous individual applications described in the Politecnico report have been reorganised into a limited number of product groups. The grouping is not based primarily on industrial market sectors or end uses, but on similarities in carbonation chemistry, reaction mechanisms, exposure conditions, material form, and the controlling parameters governing CO_2 uptake. Products that exhibit similar carbonation behaviour can therefore be described using common calculation principles and, where appropriate, common default parameters.

The classification adopted in this report has also been developed with practical implementation in mind. It provides a structure that supports the development of consistent Tier 1, Tier 2 and Tier 3 methodologies, facilitates the use of common calculation models across similar applications, and reduces unnecessary methodological complexity while maintaining scientific consistency. The product groups should therefore be regarded as methodological groupings developed for greenhouse gas inventory purposes rather than as classifications of industrial products or market sectors.

The detailed descriptions and literature review presented by Grosso et al. (2020) have served as an important background source during the development of this methodology. However, the grouping and calculation approaches presented in this report have been developed independently to meet the specific requirements of national greenhouse gas inventory reporting.

Based on these principles, the following sections describe the proposed product groups and the scientific rationale for their classification, together with the principal carbonation mechanisms and calculation approaches applicable to each group.

5.5.2.2 Group A – Construction and building materials

These products are typically highly exposed to air and show rapid carbonation.

- Air lime mortars (masonry mortars)
- Lime plasters and renders
- Limewash and lime paints
- Lime-based restoration mortars (heritage use)
- Lime putty products
- Aerated Autoclaved Concrete (AAC)
- Calcium Silicate Masonry Units (Sand–Lime Bricks)

5.5.2.3 Group B – Soil, agriculture, and land applications

These products are dispersed, often finely divided, and in contact with air, moisture, and soil CO_2.

- Agricultural lime (ground quicklime or hydrated lime)
- Soil stabilisation lime
- Road base and embankment lime
- Land reclamation lime
- Sludge and sediment stabilisation lime

5.5.2.4 Group C – Environmental and water treatment

These products are often used in aqueous or semi-closed systems, with partial carbonation.

- Drinking water treatment
- Wastewater treatment
- Acid neutralisation of industrial effluents
- Flue gas cleaning and scrubber systems (dry/semi-dry)
- Sludge stabilisation and conditioning
- Treatment of contaminated soils and sediments
- Neutralisation of acid mine drainage

5.5.2.5 Group D – Industrial process uses (partly closed systems)

Carbonation varies widely depending on process configuration.

- Iron and steel production
- Non-ferrous metallurgy lime
- Pulp and paper industry lime
- Precipitated calcium carbonate (PCC) production
- Sugar refining lime
- Glass industry lime
- Calcium carbide and acetylene production
- Titanium dioxide production
- Aluminium industry
- Chemical and other industry applications (pH control, precipitation, stabilisation etc.)

5.5.2.6 Group E – Dolomitic and magnesium-based lime products

Carbonation is slower and forms hydrated magnesium carbonates.

- Dolomitic quicklime
- Dolomitic hydrated lime
- Magnesium hydroxide products
- Magnesia-based sorbents

5.5.2.7 Group F – End-of-life and secondary lime-containing materials

These represent delayed or enhanced carbonation.

- Demolition debris containing lime binders
- Recycled lime-stabilised soils
- Crushed lime mortars and plasters
- Carbonated residues reused as aggregates or fillers

5.5.3 Product group descriptions and carbonation chemistry

5.5.3.1 General description of carbonation chemistry and methodology for lime products

While the parabolic carbonation model is appropriate for solid lime products exposed to air, it is not applicable to CaO or $Ca(OH)_2$ used in wet or slurry-like conditions. In such systems, carbonation proceeds predominantly through solution-phase reactions controlled by CO_2 mass transfer into water, rather than by diffusion through a solid carbonation front. CO_2 uptake should therefore be calculated using stoichiometric or time-bounded approaches rather than depth-based models.

When CaO is exposed to water, it reacts rapidly and exothermically into $Ca(OH)_2$. This reaction occurs within minutes to hours, even at low moisture contents. As a result, CaO rarely carbonates directly in real applications so the dominant carbonation precursor is $Ca(OH)_2$. Direct carbonation of CaO is only relevant under dry or gas-solid conditions, which are uncommon outside laboratory or niche industrial settings. Calcium hydroxide is sparingly soluble in water with a solubility at 20 °C of ~1.5–1.7 g/L (≈ 0.02 mol/L) resulting in a limewater solution with pH ≈ 12.4. Thus, in most applications, solid $Ca(OH)_2$ particles coexist with an alkaline aqueous phase. The system is a solid–liquid equilibrium, not a fully dissolved solution. Thus, there are particles present unless the lime dosage is extremely low. The carbonation mechanism in wet $Ca(OH)_2$ systems proceeds via the water phase reaction of dissolved CO_2 and $Ca(OH)_2$, even when solid particles are present. In such cases, the parabolic carbonation model is not applicable.

The parabolic model assumes:

- A solid material
- A carbonation front
- Diffusion through a growing product layer

This applies well to:

- Concrete
- Lime mortars
- Plasters and renders (Group A)

It does **not** apply when:

- The material is fully wetted
- CO_2 reacts in solution
- No stable carbonation front exists

In wet systems:

- Carbonation does not proceed as a planar front
- Reaction occurs wherever Ca^{2+} and CO_3^{2-} meet
- $CaCO_3$ may precipitate away from the original particle
- Diffusion occurs primarily in water, not through solid $CaCO_3$ layers

Thus, there is **no meaningful carbonation depth** to model.

Carbonation of dispersed particles and finely divided lime materials
An intermediate carbonation behaviour exists between large solid lime products and fully aqueous systems. This occurs when lime is present as small particles dispersed in soils, sludges, aggregates, industrial residues, demolition materials, or other granular media.

In such materials, carbonation does not normally proceed as a well-defined macroscopic carbonation front advancing through the entire material volume. Instead, carbonation occurs simultaneously around a very large number of individual particles. Each particle may develop its own local carbonation front, but this front exists only at the particle scale, typically ranging from micrometres to millimetres. As a consequence, the concept of a single carbonation depth for the entire material becomes less meaningful.

For an individual particle, carbonation may still be described by diffusion-controlled mechanisms similar to those observed in larger solid products. Carbon dioxide diffuses from the particle surface towards the centre while calcium hydroxide is progressively converted to calcium carbonate. The characteristic carbonation time depends strongly on particle diameter. Because diffusion distances are short, complete carbonation can often be achieved within months or a few years, particularly for fine particles.

At the bulk material level, carbonation is therefore better described by the evolution of the degree of carbonation of the particle population rather than by a single carbonation depth. The overall uptake rate is controlled primarily by particle size distribution, exposed surface area, moisture conditions, and CO_2 availability.

This behaviour is particularly relevant for:

- agricultural lime and soil applications,
- lime-stabilized soils,
- environmental treatment residues,
- crushed mortars and renders,
- demolition materials,
- lime kiln dust and other fine industrial residues,
- secondary-use applications involving granular lime-containing materials.

For inventory modelling purposes, particle-based carbonation can often be represented using simplified kinetic functions or time-dependent carbonation fractions rather than geometrical carbonation-depth models. The high specific surface area of these materials generally results in substantially faster carbonation than in monolithic lime products and frequently allows a high degree of carbonation to be reached within relatively short periods of time.

Appropriate CO_2 uptake models for $CaO/Ca(OH)_2$ in wet conditions [63,64,65]

Case 1: Slurries, suspensions, soils, wastewater, flue-gas scrubbing
Rate-limiting step: CO_2 mass transfer into water
Carbonation rate is controlled by:

- CO_2 partial pressure
- Gas–liquid interfacial area
- Mixing and renewal of boundary layers
- pH buffering capacity

Recommended model type: Stoichiometric uptake potential, possibly time-bounded.

The CO_2 uptake limit calculation should be expressed on a consistent molar basis such as:
CO_2 uptake = min ($Ca(OH)_2$ available, CO_2 exposed)

For IPCC inventories, this often justifies:
- Assumption of full carbonation within 1 year
- Annual uptake equal to theoretical maximum

Case 2: Moist but unsaturated materials (e.g. soils, road base)
Mixed control:
- Partial water films
- Gas-phase diffusion still relevant
- No sharp carbonation front

Possible approaches:
- First-order kinetic model
- Fixed fractional annual uptake
- Empirical saturation time (e.g. 1–5 years)

Proposed CO_2 uptake calculation in such cases for IPCC applications

For $CaO/Ca(OH)_2$ used in wet or slurry-like applications:

1. Determine CaO or $Ca(OH)_2$ mass applied.
2. Convert to theoretical CO_2 uptake.
3. Apply a completion factor:
   - 1.0 for well-mixed aqueous systems
   - < 1.0 for limited exposure cases
4. Allocate uptake:
   - Entirely within the year of application, or
   - Over a short fixed period (e.g. 1–3 years)

Table 3 Proposed carbonation methodology for various carbonation conditions.

Lime use condition	Proposed carbonation model
Dry, solid product (plaster, mortar)	Parabolic $\sqrt{t}$ model
Wet slurry / suspension	Stoichiometric uptake
Soil application	Fractional or time-bounded uptake
Water treatment	Instantaneous uptake
End-of-life crushed lime	Usually already carbonated

Evaluation of temporal distribution functions for rapidly carbonating lime products
When CO_2 uptake by carbonation in lime products is expected to reach near-completion within a short and finite period (typically 3–5 years), the methodological question is how to allocate the total uptake across reporting years in a transparent and reproducible manner.
The choice of temporal allocation should reflect the dominant reaction kinetics while remaining practical for national greenhouse gas inventory implementation.

The following principles were used to evaluate candidate temporal allocation functions:

1. **Conservation of mass**
   The sum of annual uptake over the carbonation period must equal the total theoretical CO_2 uptake potential of the lime product.
2. **Simplicity and transparency**
   The approach should minimise data requirements and be easy to apply consistently across years and countries.
3. **Physical plausibility**
   Early uptake rates are typically higher due to fresh reactive surfaces and high alkalinity, with declining rates as carbonation progresses.
4. **Relation to the final tier structure.** Temporal allocation functions are required for the Tier 3 cohort method. The recommended Tier 1 and Tier 2 methods use steady-state calculations and do not distribute the result over a carbonation period.

Candidate approaches evaluated for annual cohort allocation

Option 1: Uniform linear allocation over the carbonation period
Description:
Total CO_2 uptake is distributed evenly over a fixed carbonation period (e.g. 3 or 5 years).

$$U(a) = \frac{U_{total}}{T} \quad (a=0, \ldots, T-1)$$

where:

- $U(a)$ = uptake allocated to the one-year interval from cohort age a to a + 1
- U_{total} = total CO_2 uptake potential,
- T = assumed carbonation period (years).

Example:
If full carbonation occurs over 5 years, 20 % of the total uptake is allocated to each year.

Advantages:
- Very simple to implement
- Requires no kinetic parameters
- Appropriate when annual timing uncertainty exceeds intra-period variability

Limitations:
- Does not reflect faster initial carbonation
- May slightly delay early uptake compared with reality

Outcome of evaluation: Retained as the linear cumulative progression option for the Tier 3 cohort method in Chapter 6.5.1.

Option 2: Front-loaded linear allocation examined during development
Description:
A higher fraction of uptake is allocated to early years, reflecting faster initial carbonation, with linearly decreasing uptake in later years.

Table 4 Example of a front-loaded five-year distribution examined during method development.

Year	Share of total uptake
1	30 %
2	25 %
3	20 %
4	15 %
5	10 %

Advantages:

- More physically realistic.
- Still simple and deterministic.

Limitations:

- Requires selection of a default distribution curve.
- Slightly higher methodological complexity.

Outcome of evaluation: This distribution illustrates an intermediate front-loaded profile but was not adopted as a default in the final Tier 1 or Tier 2 methods. A documented country-specific function may be used in Tier 3 where justified.

Option 3: Square-root cumulative uptake distribution
Description:
Even when full carbonation occurs within a few years, uptake may be distributed according to the cumulative form of the parabolic carbonation model:

$$\mathrm{F(a)} = \min\left(\frac{\sqrt{a}}{\sqrt{T}}, 1\right)$$

Uptake during the one-year cohort-age interval from a to a + 1 is:

$$\mathrm{U(a)} = U_{total}\left(\frac{\sqrt{a+1} - \sqrt{a}}{\sqrt{T}}\right)$$

where:

F(a) = cumulative fraction of ultimate CO_2 uptake achieved at exact annual boundary age a.

T = total carbonation time (years).

U(a) = CO_2 uptake allocated to the interval from cohort age a to a + 1.

U_{total} = Total CO_2 uptake over the years considered.

Table 5 Example of the square-root cumulative distribution over five years.

Year	Annual uptake share
1	44.7 %
2	18.5 %
3	14.2 %
4	11.9 %
5	10.7 %

Advantages:

- Directly linked to carbonation kinetics.
- Consistent with depth-based models.

Limitations:

- Strongly front-loaded.
- Requires explicit assumption of full carbonation time.

Outcome of evaluation: Retained as the square-root cumulative progression option for the Tier 3 cohort method in Chapter 6.5.1.

Outcome of the temporal-allocation assessment

The assessment led to the following treatment in the final methods:

- **Tier 1:** No annual allocation profile is applied. The characteristic carbonation period is used only to assess the validity of the aggregate steady-state assumption.
- **Tier 2:** No annual allocation profile is applied in the recommended application-disaggregated steady-state method.
- **Tier 3:** Annual consumption cohorts are distributed using the linear or square-root cumulative progression functions, or another documented country-specific function.

For Group A products, the steady-state Tier 1 or Tier 2 methods may be sufficient where lime use and the application mix are reasonably stable. Tier 3 should be used where historical changes or the timing of uptake materially affect the annual estimate.

Below, each product group is described with focus on technical function, exposure, and carbonation chemistry.

5.5.3.2 Group A – Construction and building lime products

Technical function

Air-lime construction products comprise a family of binders and surface treatments whose hardening and long-term performance depend primarily on the carbonation of calcium hydroxide. These products are characterized by high porosity, low hydraulicity, and a strong dependence on exposure to air and moisture. They have been used historically for masonry, plastering, and surface finishing and remain essential in conservation, restoration, and certain modern construction applications. In Table 6, the technical function and composition of the various products are described in more detail.

Table 6 Technical function and composition of construction and building lime products.

Construction lime products	Technical function	Composition
Air lime mortars	Air lime mortars are used as masonry mortars for brick, stone, and blockwork. Their primary functions are to bond masonry units, accommodate movement through flexibility, and facilitate moisture transport through capillary action. Compared with cement-based mortars, air lime mortars exhibit lower strength but greater deformability and vapour permeability.	Air lime mortars consist of hydrated lime (calcium hydroxide, $Ca(OH)_2$) as the binder, combined with aggregates such as sand or crushed stone and water. No significant hydraulic components are present. The binder-to-aggregate ratio varies depending on application and desired properties, typically ranging from 1:2 to 1:3 by volume.
Lime plasters and renders	Lime plasters (interior applications) and lime renders (exterior applications) serve as protective and decorative surface layers on masonry substrates. They regulate moisture by allowing vapour diffusion while shedding liquid water, thereby reducing moisture-related damage to underlying structures. Lime renders also provide weather protection and aesthetic finish.	These products are composed of hydrated lime, graded aggregates, and water. Multiple layers (e.g. base coat, floating coat, finishing coat) are often applied, with decreasing aggregate size toward the surface. In some formulations, small amounts of pozzolanic materials may be included to modify setting behaviour; however, in pure air lime plasters and renders, hardening is dominated by carbonation.
Limewash	Limewash is a traditional surface coating used for aesthetic, protective, and hygienic purposes. It provides a breathable, alkaline coating that inhibits biological growth and allows underlying materials to dry.	Limewash consists of a dilute suspension of calcium hydroxide in water, sometimes with natural pigments or additives to improve adhesion and durability. The solids content is low compared with mortars or plasters, resulting in very thin applied layers.
Lime paints	Lime paints serve similar functions to limewash but are typically formulated for improved durability, colour consistency, and adhesion. They are used on mineral substrates where vapour permeability is required.	Lime paints are based on finely dispersed calcium hydroxide, water, and mineral pigments. Some formulations may include small amounts of organic binders or stabilisers, but carbonation of calcium hydroxide remains the primary hardening mechanism.
Lime-based restoration mortars	Lime-based restoration mortars are designed for repair and conservation of historic masonry and plasterwork. Their function is to be mechanically and chemically compatible with original lime-based materials, avoiding damage caused by overly stiff or impermeable repair mortars.	These mortars are typically formulated with hydrated lime or lime putty as the binder, carefully selected aggregates, and, in some cases, low levels of pozzolanic additions to tailor strength and setting characteristics. The formulations are designed to closely match the porosity, strength, and moisture behaviour of historic materials.

Lime putty products	Lime putty is used both as a binder in mortars and plasters and as a standalone material in fine finishing and decorative applications. It provides high workability, cohesion, and plasticity.	Lime putty consists of calcium hydroxide produced by slaking quicklime with an excess of water and subsequently matured (aged) for extended periods, ranging from weeks to years. The aging process improves particle dispersion and rheological properties but does not involve carbonation until the putty is applied and exposed to air.
Aerated Autoclaved Concrete (AAC)	AAC is a lightweight, precast masonry material produced from a finely ground mix of siliceous material (quartz sand, fly ash), quicklime (CaO) and/or hydrated lime, Portland cement (minor fraction), water, and aluminium powder (gas-forming agent).	In the process, aluminium reacts with calcium hydroxide in the alkaline pore solution according to the following reaction $2Al+3Ca(OH)_2+6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O+3H_2$ The hydrogen gas forms the pore structure in the material. In the following autoclaving process at 180–200 °C and ~10–12 bar saturated steam, calcium hydroxide reacts with silica to form crystalline calcium silicate hydrates, mainly 1.1 nm tobermorite: $Ca(OH)_2+SiO_2+H_2O \rightarrow C–S–H$ (tobermorite) Carbonation is not needed for hardening.
Calcium Silicate Masonry Units (Sand–Lime Bricks)	Calcium silicate masonry units (often called sand–lime bricks) are produced from 90–95 % quartz sand, 5–10 % quicklime, and water. CaO is hydrated to $Ca(OH)_2$ in the material and compacted under high pressure. The following autoclaving at 180–200 °C in saturated steam, calcium silicate hydrates are formed such as Tobermorite and poorly crystalline C–S–H phases. Strength development is almost entirely due to hydrothermal Ca–Si reactions, not to carbonation.	Carbonation can occur at exposed surfaces: $Ca(OH)_2+CO_2 \rightarrow CaCO_3$ Also partial carbonation of C–S–H: $C–S–H+CO_2 \rightarrow CaCO_3+SiO_2 \cdot nH_2O$ The role of carbonation can be: Surface densification Long-term dimensional stability Not responsible for primary strength Balance emission and CO_2 uptake for the product and enhance further uptake.

Carbonation chemistry

The dominant carbonation reaction in these products is:

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

The carbonation is generally characterized by:

- High porosity
- Thin sections
- Continuous exposure to air
- Moisture present but not saturated

Carbonation behaviour

The carbonation process is typically fast and near-complete. Full carbonation is often achieved within 1–10 years, depending on the thickness of the product. Unlike concrete, carbonation is intended and required for strength development. As these products' carbonation behaviour varies significantly in time, a specific carbonation description is given in Table 7. The times refer to typical practical conditions (temperate climate, intermittent wetting/drying, exposure to air) and are intended for methodological use in CO_2 uptake modelling, not as prescriptive construction guidance. Importantly, "full carbonation" here means ≥90–95 % conversion of $Ca(OH)_2$ to $CaCO_3$ in the exposed lime phase, recognising that some residual hydroxide may persist in sheltered micro-pores.

Table 7 Carbonation (hardening) time for various construction lime products.

Construction lime products	Carbonation behaviour	Typical carbonation time
Air lime mortars	Carbonation initiates at exposed joint surfaces and progresses inward. Mortar joints typically have thicknesses of 10–20 mm, with carbonation rates governed by CO_2 diffusion through the pore network. In well-ventilated masonry, outer zones carbonate within 1–3 years, while deeper zones may require decades, especially in sheltered or damp conditions. For national inventories, the majority of CO_2 uptake can be assumed to occur within 10–20 years after application.	5–20 years, depending on joint thickness and exposure
Lime plasters and renders	Lime plasters and renders are applied in thin layers (typically 5–15 mm per layer) with high surface exposure. Their open pore structure facilitates rapid CO_2 ingress and moisture exchange, accelerating carbonation relative to masonry mortars. For IPCC, a near-complete carbonation can reasonably be assumed within a few years, enabling simplified annual uptake modelling.	1–5 years (interior plasters often faster)
Limewash	Limewash layers are extremely thin (tens to hundreds of micrometres). Carbonation proceeds rapidly upon drying, often reaching completion within days under favourable conditions. For IPCC, CO_2 uptake may be treated as instantaneous on an annual reporting basis.	Days to weeks
Lime paints	Compared with limewash, lime paints contain higher solids content and may include stabilisers that slightly retard carbonation. Nevertheless, thin application thickness ensures rapid hardening. For IPCC, full carbonation can be assumed within the year of application.	Weeks to a few months
Lime-based restoration mortars	Restoration mortars are often thicker than plasters but more permeable than modern cement mortars. Carbonation progresses steadily, though design choices prioritising compatibility over strength can slow complete conversion. For IPCC, most uptake occurs within the first decade, with diminishing uptake thereafter.	5–15 years
Lime putty products	Lime putty itself does not carbonate during storage. Carbonation begins only after application and exposure to air. Due to excellent particle dispersion, lime putty-based products often carbonate slightly faster than dry hydrated-	Same as corresponding product form

	lime formulations of equivalent thickness. For IPCC, no separate carbonation category is required. Uptake is attributed to the final product form.	(e.g. plaster, mortar, or finish layer)
Aerated Autoclaved Concrete (AAC)	AAC contains very little free $Ca(OH)_2$ and calcium is largely bound in tobermorite-type C–S–H. The carbonation reactions are mainly limited to residual portlandite and partial decalcification of C–S–H. Representative reactions can be: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ $C–S–H + CO_2 \rightarrow CaCO_3 + SiO_2 \cdot nH_2O$ Carbonation is diffusion-limited, slow and usually partial. Only a small fraction of the total CaO content is carbonatable during service life. In national inventories, AAC is typically assigned with a low use-phase uptake factor, often < 10–20 % of theoretical CaO carbonation potential. Carbonation in end-of-life and secondary use increases as demolition and crushing expose uncarbonated phases and, in this way, carbonation depth increases significantly in the products.	Typical wall thickness exposed from one side: 100 mm. Carbonation from both sides. Effective carbonation depth needed: ≈ 50 mm k_C=1.0 mm/$\sqrt{year}$ Before crushing in end-of-life. $t=(x/k_C)^2 = (50/1.0)^2$ =2500 years. No full carbonation during the assumed service period.
Calcium Silicate Masonry Units (Sand–Lime Bricks)	Carbonation during production is intentionally avoided. Carbonation after manufacturing can occur at exposed surfaces as: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3$ But also as partial carbonation of C–S–H such as: $C–S–H + CO_2 \rightarrow CaCO_3 + SiO_2 \cdot nH_2O$ Similar hydrothermal Ca–Si matrix as AAC but with typically higher density and slightly more residual $Ca(OH)_2$ than AAC. Thus, carbonation reactions are mainly surface carbonation of residual portlandite and slow decalcification of C–S–H near exposed surfaces. Carbonation in end-of-life and secondary use increases as demolition and crushing expose uncarbonated phases and, in this way, carbonation depth increases significantly in the products.	Typical brick thickness: 100 mm Carbonation from both faces. Effective depth: ≈50 mm k_C = 2.0 mm/$\sqrt{year}$ Before crushing in end-of-life. $t=(x/k_C)^2$ = $(50/2.0)^2$=625 years. No full carbonation during the assumed service period.

Degree of carbonation and completeness:
While many lime-rich products (such as limewash and thin plasters) can be assumed to reach near-complete carbonation under typical exposure conditions, this assumption is not universally valid. In particular, mixed cement–lime mortars, thicker sections, or materials with limited exposure (e.g., indoor or coated surfaces) may exhibit partial carbonation even after long service periods.

For national inventory purposes, it is therefore recommended that:

- Near-complete carbonation (90–100%) is assumed only for thin, lime-rich and well-exposed materials.
- Intermediate carbonation degrees (e.g. 70–90%) may be more appropriate for mixed mortars and renders.
- Lower values should be considered where exposure is limited or surface treatments are present.

This approach ensures conservative and realistic estimation of CO_2 uptake.

Carbonation modelling

The carbonation behaviour of Group A lime products (air lime mortars, plasters, renders, limewash, lime paints, lime-based restoration mortars, and lime putty–based products) exhibits several conceptual similarities to the carbonation of cement-containing products as described in IVL Report B2499 *"CO_2 uptake in cement-containing products – Background and calculation models for implementation in national greenhouse gas emission inventories"* [57]. In both cases, CO_2 uptake occurs through the diffusion of atmospheric CO_2 into a porous, calcium-based material, resulting in the formation of calcium carbonate. The methodology for lime products can therefore be developed using the same general framework, while introducing material-specific parameter values and simplifying assumptions.

Important note on mixed cement–lime mortars:
In many real-world applications, mortars, renders, and plasters are composed of mixtures of lime and cement rather than pure air lime systems. Technical data from European practice indicate that cement–lime mortars are common across a wide range of applications, with composition varying depending on strength class, exposure conditions, and construction standards. In such mixtures, the carbonation behaviour deviates from that of pure lime systems. Increasing cement content typically leads to lower porosity and a denser microstructure, which reduces the effective carbonation rate and may also limit the ultimate degree of carbonation. Consequently, the use of carbonation coefficients (k_C-values) corresponding to pure lime mortars may lead to overestimation of CO_2 uptake in mixed systems unless correction factors are applied. Application-specific Tier 2 assessments should reflect binder composition when selecting F_{carb} and F_{exp}. Tier 3 assessments may additionally adjust carbonation periods or progression functions, or model the lime and cement fractions separately where the necessary data are available.

Conceptual similarity to concrete carbonation

As with concrete products, Group A lime products have:

- A defined exposed surface area during their primary use phase.
- A progressive carbonation front advancing inward from exposed surfaces.
- A carbonation rate that can be described using a parabolic ($\sqrt{t}$) model, where carbonation depth is proportional to the square root of time.
- Potential exposure to carbonation both during use and, in principle, after demolition.

Accordingly, the carbonation depth *x(t)* may be expressed as:

$$x(t) = k_c\sqrt{t}$$

where x(t) is the carbonation depth (mm), t is time (years), and k_C is an empirical carbonation-depth coefficient expressed in mm/$\sqrt{year}$.

Empirical literature on carbonation in air-lime mortars indicates that carbonation depth follows a square-root-of-time behaviour consistent with diffusion-controlled processes. From literature and experimental data for natural carbonation, a carbonation coefficient $k_C \approx 1$ mm/$\sqrt{day}$ (1*$\sqrt{365}$ = 19 mm/$\sqrt{year}$) has been reported for air-lime mortars under natural conditions.

This suggests that, on average, an air-lime mortar layer may carbonate such that its carbonation depth increases by approximately **19 mm per $\sqrt{year}$** under ambient exposure conditions [19]. This value reflects high reactivity and porosity of pure lime mortars relative to dense concrete. It also aligns with experimental observations that air-lime mortars up to ~190 mm thick can achieve ~80–90 % carbonation over very long durations (centuries) if all else is equal [19].

Comparable experimental assessments for lime-rich plasters and renders also support high k_C-values. One investigated range reported k_C values for lime-based plasters (with sand or bioclastic aggregate) under unforced carbonation at typical building conditions to $k_C \approx 0.8$–1.2 mm/$\sqrt{day}$, again implying annual-scale coefficients on the order of **15–23 mm/$\sqrt{year}$** for lime-rich plaster systems at ~20 °C and moderate relative humidity [20]. **Note:** when combined with mineral additives (e.g., cement), rates may decrease due to reduced porosity; however, pure air-lime systems consistently exhibit high k_C values relative to concrete.

To support method development and possible country-specific kinetic calculations, the following default carbonation coefficients (k_C) can be considered for Group A lime products. These are expressed in units of mm/$\sqrt{year}$ for use directly in the parabolic model $x(t) = k_C\sqrt{t}$. The proposed k_C factors are shown in Table 8 below. [60,61,62]

Table 8 Indicative k_C factor ranges considered for parabolic diffusion model x(year)=$k_C \cdot \sqrt{year}$.

Lime product type	Indicative k_C ranges (mm/$\sqrt{year}$)	Basis and notes
Air-lime mortar (pure)	~18–22	Derived from 1 mm/$\sqrt{day}$ literature value (~19 mm/$\sqrt{year}$). [19]
Lime plaster/render	~15–20	Similar levels reported for lime-based plasters in natural conditions. [20]
Limewash/Lime paint	~20–30	Very thin coatings carbonate rapidly; near-surface diffusion dominates, so a higher effective k_C may be suitable (scaled from mortar data).
Restoration mortars / thicker applications	~15–18	Intermediate between plaster and mortar due to thickness and textural effects.
Lime putty products (applied form)	~16–22	Similar to mortars/plasters when applied; no carbonation in storage.
Aerated Autoclaved Concrete (AAC)	~0.5–2.0	Rarely exceeds approximately 2.5 mm/$\sqrt{year}$. Illustrative central value for evaluation: k_C = 1.0 mm/$\sqrt{year}$
Calcium Silicate Masonry Units (Sand–Lime Bricks)	~1.0–3.0	Higher than AAC due to higher density of Ca phases and less extreme pore structure. Illustrative central value for evaluation: k_C = 2.0 mm/$\sqrt{year}$

Note: These indicative k_C ranges are higher by approximately an order of magnitude than typical concrete carbonation-depth coefficients (often <10 mm/$\sqrt{year}$) because lime products are generally more permeable and chemically accessible. They should be validated before use in a country-specific Tier 3 calculation.

Adjustment of carbonation coefficients for mix composition and porosity:
The k_C values presented above represent typical ranges for lime-rich and relatively porous materials under favourable exposure conditions. Experimental studies show that carbonation rate is strongly influenced by material microstructure, including porosity, capillary absorption, binder-to-aggregate ratio, and aggregate grading. Mortars with higher porosity and finer aggregates tend to carbonate faster, while denser mixes with lower water/binder ratios carbonate more slowly.
In addition, the presence of cement reduces carbonation rates due to the formation of denser hydration products and lower permeability. As a guiding principle:

Pure or lime-rich mortars: the values in Table 8 may be used as starting points for country-specific evaluation.
Mixed cement–lime mortars: apply reduced k_C values or introduce a composition-dependent correction factor.
Dense or low-porosity systems: consider lower-end values or below-range estimates

For Tier 3 modelling, the carbonation-depth coefficient k_C should ideally be calibrated using representative national or product-specific data.

From the parabolic carbonation law, the time to full carbonation can be estimated for a product application as:

$$x = k_C\sqrt{t} \quad \Rightarrow \quad t = \left(\frac{x}{k_c}\right)^2$$

where:

x = carbonation depth (mm)

k_C = carbonation-depth coefficient (mm/$\sqrt{year}$)

t = time (years)

Key differences between lime products and concrete

Despite these similarities, several fundamental differences distinguish Group A lime products from cement-based materials and justify a simplified carbonation methodology:

1. *Reactive phase*
   In lime products, the dominant reactive phase is calcium hydroxide ($Ca(OH)_2$), which carbonates directly to calcium carbonate ($CaCO_3$). In contrast, concrete carbonation involves multiple phases, including portlandite and calcium–silicate–hydrate (C–S–H), with different reaction kinetics.
2. *Carbonation-depth coefficient (k_C)*
   The carbonation-depth coefficient for lime products is substantially higher than for concrete. This reflects:
   - Higher porosity and permeability;
   - Simpler reaction chemistry;
   - Absence of dense hydration products that impede CO_2 diffusion.

   Consequently, the value of k_C for lime products must be material-specific and cannot be adopted from concrete carbonation models.
3. *Time to full carbonation*
   For Group A lime products, near-complete carbonation (≥90–95 %) typically occurs within months to a maximum of approximately 20 years, depending on product thickness and exposure conditions. This time scale is short compared with concrete, where carbonation may continue for many decades or centuries.
4. *Carbonation during end-of-life (EoL)*
   Because Group A lime products are assumed to be fully carbonated during their primary service life, no significant additional CO_2 uptake is assumed to occur during end-of-life or secondary use phases. This is a key simplification relative to concrete, where crushed material may carbonate further after demolition.

Methodological implications for CO_2 uptake calculation

Based on these characteristics, the CO_2 uptake methodology for Group A lime products can be defined as follows:

- Carbonation is calculated only for the primary product phase, using exposed surface area and product thickness as governing parameters.
- The parabolic carbonation model is retained, but with lime-specific carbonation-depth coefficients (k_C).
- Carbonation is assumed to proceed until the entire lime-containing layer is carbonated, after which no further uptake occurs.
- For national inventory purposes, the full theoretical CO_2 uptake potential of the lime binder can be allocated over a short, finite carbonation period, typically not exceeding 20 years.
- End-of-life carbonation is set to zero for Group A products, avoiding double counting and simplifying inventory implementation.

5.5.3.3 Group B – Soil, agricultural, and land applications

Technical function

Lime in Group B is used to:

- Neutralise acidity.
- Improve soil structure.
- Stabilise fine-grained soils.

Carbonation chemistry

When lime or dolomitic lime is applied to soil or ground, carbonation occurs predominantly through reactions between calcium and magnesium hydroxides and carbon dioxide present in the soil atmosphere and soil pore water. Unlike dense construction materials, soils represent a highly heterogeneous and generally well-ventilated porous medium in which gaseous diffusion, aqueous transport, and biological CO_2 production jointly control the carbonation process. For dolomitic lime, magnesium hydroxide undergoes analogous but slower carbonation reactions leading to hydrated magnesium carbonates. These reactions occur primarily at particle surfaces and within thin water films surrounding lime particles.

Carbonation behaviour

The carbonation is characterised by:

- Large exposed surface area.
- Often finely divided material.
- Contact with soil CO_2 and atmospheric CO_2.

Carbonation is typically rapid, often reaching high degrees of conversion within months to a few years. However, the availability and transport of CO_2 in the soil is an important aspect to consider. Carbon dioxide is abundantly present in soil systems and is not limited to atmospheric CO_2 diffusing from the surface. In addition to atmospheric sources, CO_2 is continuously generated within the soil by biological respiration of plant roots, microorganisms, and soil fauna, as well as by the decomposition of organic matter. As a result, CO_2 partial pressures in soil air are commonly significantly higher than in the atmosphere, often ranging from two to ten times atmospheric levels, depending on soil type, moisture content, and biological activity.

Transport of CO_2 to reactive lime surfaces occurs through a combination of:

- Diffusion of CO_2 in the soil gas phase,
- Dissolution of CO_2 into soil pore water as dissolved CO_2 and bicarbonate species, and
- Advective gas movement driven by pressure and moisture gradients.

Under most agricultural and land application conditions, CO_2 availability is therefore not the primary rate-limiting factor for carbonation of calcium-based lime. Instead, the rate of carbonation is more commonly controlled by:

- Hydration state of the lime,
- Moisture availability (presence of liquid water or water films),
- Particle size and specific surface area of the applied lime,
- Formation of a carbonate product layer on particle surfaces, which may locally slow further reaction.

For magnesium-based lime components, carbonation is generally slower and more sensitive to moisture conditions and reaction product layers; however, CO_2 availability in soil is still rarely the dominant limitation.

The depth of CO_2 penetration and carbonation in soil is also important to consider. Carbon dioxide readily penetrates into the soil profile through interconnected pore spaces. In well-aerated soils, significant CO_2 concentrations are typically observed from the surface down to depths of at least 0.5–1 m, and in some cases, several meters, depending on soil structure, permeability, moisture content, and biological activity. However, for the purposes of lime carbonation, the relevant depth is governed less by CO_2 penetration and more by the depth of lime application and mixing.

Agricultural lime is generally incorporated into the upper soil layers (commonly the top 10–30 cm), where CO_2 concentrations are high and gas exchange with the atmosphere is effective. In these zones, carbonation of calcium hydroxide proceeds efficiently, and a high degree of conversion to calcium carbonate is typically achieved within relatively short timeframes (months to a few years).

In deeper ground applications such as soil stabilization for road bases or embankments, carbonation can still proceed provided that:

- The soil or fill remains unsaturated for part of the time, allowing gas diffusion, and
- Pore connectivity is maintained.

In fully water-saturated or compacted layers with very low gas permeability, carbonation may be slower; however, even in such cases, dissolved inorganic carbon transported by pore water can contribute to carbonation over longer timescales.

However, in addition to the above-mentioned soil stabilization methods, there is one that differs significantly and that is deep stabilization using *lime and cement–lime soil stabilization columns*. In ground improvement and soil stabilization, lime and cement–lime columns (often referred to as lime pillars, lime–cement columns, or deep soil mixing columns) are widely used to increase the strength, stiffness, and bearing capacity of soft or organic soils such as clays, silts, and peat. The technique involves mechanical mixing of quicklime, hydrated lime, cement, or blended binders directly into

the soil in situ using augers or mixing tools, forming vertical columns that typically extend from the ground surface to depths ranging from a few meters to more than 20 m, depending on geotechnical requirements.

Technical function and binder reactions

The primary stabilization mechanisms are chemical and physicochemical reactions between the binder and the soil. For lime-based systems, the dominant initial reactions include hydration of quicklime and cation exchange, followed by pozzolanic reactions between calcium hydroxide and reactive silica and alumina present in the soil, forming calcium silicate hydrates (C–S–H) and calcium aluminate hydrates (C–A–H). In cement–lime columns, cement hydration contributes to additional C–S–H formation.

These reactions occur relatively rapidly after installation and are largely responsible for the early and long-term mechanical performance of the columns. As a result, a significant fraction of the calcium in lime or cement–lime columns becomes incorporated into hydrated reaction products that are less readily carbonated than free calcium hydroxide.

Carbonation potential and controlling factors

Carbonation of lime or cement–lime columns can occur when carbon dioxide reaches reactive calcium-bearing phases within the column. The primary carbonation reaction is:

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

and, to a lesser extent, carbonation of calcium-bearing hydration products may occur over longer timescales. However, the carbonation behaviour of lime or cement–lime columns differs markedly from that of surface-applied lime or shallow soil stabilization.

The principal factors controlling carbonation in lime columns are:

- *Depth and gas transport limitations:*
  At typical column depths, access of atmospheric CO_2 is limited. Gas diffusion through overlying soil layers is slow, particularly in fine-grained, water-saturated, or compacted soils. Consequently, carbonation from the ground surface is generally restricted to the upper part of the column.
- *Soil moisture and saturation:*
  Lime columns are often installed in soils with high water content. While moisture is necessary for carbonation reactions, fully water-saturated conditions significantly reduce gas-phase CO_2 transport, limiting carbonation rates. In deeper zones, carbonation may occur only through dissolved inorganic carbon transported by pore water, which is a slow process.
- *Consumption of reactive lime in pozzolanic reactions:*
  A substantial fraction of the initially added lime reacts with soil minerals to form C–S–H and C–A–H phases. These reaction products are less reactive towards carbonation than free calcium hydroxide, reducing the fraction of lime that remains available for atmospheric CO_2 uptake.
- *Column geometry and surface area:*
  Compared with dispersed lime applications, lime columns have a relatively low specific surface area per unit mass of binder, further limiting carbonation rates.

Expected carbonation extent

In practice, carbonation of lime or cement–lime columns is typically:

- Limited to near-surface sections of the column (e.g. the upper decimetres to metres), where gas exchange with the atmosphere is possible.
- Incomplete over the full column length, especially for deep installations.
- Secondary in importance relative to hydration and pozzolanic reactions from a geotechnical perspective.

Over long timescales (decades), some additional carbonation may occur if soil conditions change, such as due to drainage, excavation, or exposure during maintenance or redevelopment. At end-of-life, excavation or demolition of stabilised soil and subsequent crushing or reuse can substantially increase exposure to air and thereby enhance carbonation of remaining reactive phases.

Methodological implications for CO_2 uptake calculation

From a CO_2 uptake modelling perspective, one can conclude that the generally high availability of CO_2 in soils, combined with large reactive surface areas and favourable moisture conditions, supports the assumption that lime applied in soil and land applications undergoes rapid and often near-complete carbonation over short periods relative to construction materials such as concrete. For national inventory purposes, it is therefore reasonable to model carbonation of calcium-based lime in soil applications as occurring predominantly within a few years of application, with CO_2 transport in soil rarely constituting the dominant rate-limiting step. As the lime product is available in particle form, a model using the carbonation depth in lime particles like the end-of-life approach in the IVL CO_2 uptake report [57] can be applicable. Magnesium-based carbonation should be treated separately with slower kinetics and capped conversion fractions. However, lime and cement–lime columns should be treated separately from surface-applied or shallow soil lime. A conservative and technically justified approach is to assume:

- Only a limited fraction of the calcium added in columns is available for carbonation during service life.
- Carbonation during use is slow and depth-limited, with low annual uptake rates.
- End-of-life exposure (excavation, reuse as fill, or crushing) may represent the dominant opportunity for additional CO_2 uptake if EoL is applicable for the installation.

Accordingly, product-specific CO_2 uptake models for lime columns should apply reduced availability factors and longer carbonation timescales compared with other soil and land lime applications.

Particle-based carbonation modelling for soil and dispersed applications:

In soil, agricultural, and land applications, lime is typically applied in finely divided form, resulting in a high specific surface area and short diffusion distances. In such systems, carbonation can be described using particle-based approaches analogous to those applied for crushed materials in end-of-life modelling.

For individual particles, carbonation progresses from the surface inward, and the extent of reaction can be approximated using a square-root-of-time relationship similar to bulk materials:

$$x(t) = k_C \cdot \sqrt{t}$$

where x(t) represents the carbonation depth within the particle. However, due to the small particle size (typically µm–mm scale), full carbonation may occur within a short period once the carbonation front reaches the particle centre. Consequently, particle size becomes a key controlling parameter, with smaller particles carbonating more rapidly and completely.
For inventory purposes, it is therefore reasonable to assume:

- Rapid and near-complete carbonation for finely divided lime (months to a few years).
- Time-bounded or fractional uptake for coarser or partially mixed materials.

This approach is consistent with end-of-life carbonation modelling for cementitious materials, where increased surface area and reduced particle size significantly accelerate CO_2 uptake.

5.5.3.4 Group C – Environmental and water treatment lime

Technical function
Lime products are widely used in environmental protection and water treatment applications due to their strong alkalinity, high reactivity, and ability to control chemical equilibria in aqueous systems. In this group, lime is applied primarily as quicklime (CaO) or hydrated lime ($Ca(OH)_2$), and more rarely as dolomitic lime, to modify pH, precipitate contaminants such as metals, neutralize acidic streams, stabilize residues, and gas scrubbing. A list of main applications for Group C is shown below in Table 9. In all these applications, the primary technical function of lime is achieved before or concurrently with carbonation, which may be considered a secondary but environmentally relevant reaction.

Table 9 Main lime applications for environmental and water treatment.

Group C main applications
Drinking water treatment
Wastewater treatment
Acid neutralisation of industrial effluents
Flue gas cleaning and scrubber systems
Sludge stabilisation and conditioning
Treatment of contaminated soils and sediments
Neutralisation of acid mine drainage

Unlike construction lime products (Group A), lime used in environmental and water treatment is typically applied in wet, slurry, or suspension form, or is rapidly exposed to water after application. As a result, carbonation does not proceed through a solid-state carbonation front, but instead occurs via solution-phase reactions, with CO_2 uptake governed by aqueous chemistry and gas–liquid mass transfer.

Lime applications in Group C with limited or no carbonation potential
While many environmental and water treatment applications of lime lead to partial or full carbonation, there are important cases within Group C where carbonation is prevented, strongly limited, or chemically impossible. These cases must be explicitly identified to avoid systematic overestimation of CO_2 uptake in greenhouse gas inventories.

Accounting implications for CO_2 uptake methodology can be as follows:

For Group C lime products, it is essential to distinguish between:

- Carbonating uses, where $Ca(OH)_2$ is converted to $CaCO_3$ via interaction with CO_2, and
- Non-carbonating uses, where calcium is bound into sulphates, chlorides, nitrates, phosphates, or other stable compounds.

For inventory purposes:

- Lime quantities used in non-carbonating applications should be assigned a CO_2 uptake factor of zero.
- Where mixed uses occur, application-specific allocation should be applied based on process chemistry.
- Conservative assumptions are recommended where use patterns are uncertain.

Examples of such processes are shown below.

Sulphur removal in flue gas treatment (FGD)

In flue gas desulphurisation (FGD) systems, limestone (wet FGD) or lime (dry and semi-dry FGD) is used to remove sulphur dioxide (SO_2) from combustion gases.

Wet flue gas desulphurisation using limestone

Wet flue gas desulphurisation (FGD) systems commonly use finely ground limestone ($CaCO_3$) as the sorbent for sulphur dioxide removal. Although these systems are outside the scope of the present report, since they do not use lime or hydrated lime as the primary sorbent, it is useful to clarify their behaviour with respect to CO_2 uptake.

In wet limestone FGD, sulphur dioxide is removed by dissolution of limestone followed by precipitation of calcium sulphate (gypsum). The overall reaction can be simplified as:

$$CaCO_3 + SO_2 + ½O_2 + 2H_2O \rightarrow CaSO_4{\cdot}2H_2O + CO_2$$

The process releases CO_2 from the limestone during sulphation but does not produce reactive lime phases such as calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$). Consequently, no subsequent carbonation of the sorbent can occur.

Wet FGD systems normally operate with a slight excess of limestone to ensure complete removal of sulphur dioxide. However, this excess remains as unreacted calcium carbonate, which is already in its fully carbonated state and therefore has no additional CO_2 uptake potential. Since neither CaO nor $Ca(OH)_2$ is formed during the process, wet limestone FGD does not contribute to carbonation-based CO_2 uptake and is therefore excluded from the calculation methodology presented in this report.

Dry and semi-dry flue gas cleaning using hydrated lime

In contrast, dry and semi-dry flue gas cleaning systems use hydrated lime as the principal sorbent. In these systems, a fraction of the supplied lime may remain as residual unreacted $Ca(OH)_2$ in the air pollution control residues (APCR), providing a limited but potentially significant opportunity for subsequent CO_2 uptake through carbonation.

When lime-based sorbents are applied, the dominant reactions are:

Hydration (if CaO is used):

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Sulphation:

$$Ca(OH)_2 + SO_2 + \frac{1}{2}O_2 \longrightarrow CaSO_4 + H_2O$$

or, in simplified form:

$$CaO + SO_2 + \frac{1}{2}O_2 \longrightarrow CaSO_4$$

Calcium sulphate ($CaSO_4$, including gypsum $CaSO_4 \cdot 2H_2O$) is a thermodynamically stable end product under environmental conditions and does not undergo carbonation. Once calcium is bound as sulphate:

- It is no longer available for reaction with. CO_2.
- Any potential CO_2 uptake capacity of the original lime that is sulphated is permanently eliminated.
- Subsequent exposure to atmospheric or aqueous CO_2 does not result in $CaCO_3$ formation.

However, during flue gas desulphurisation (FGD), hydrated lime is primarily used for neutralisation of sulphur dioxide and other acid gases. The dominant reactions are the formation of calcium sulphite and calcium sulphate, which are thermodynamically stable products and therefore do not undergo subsequent carbonation.

The reaction between $Ca(OH)_2$ and SO_2 proceeds considerably faster than the competing carbonation reaction with CO_2. Consequently, sulphation is the preferred reaction pathway whenever sulphur dioxide is present. Furthermore, any calcium carbonate formed during the process may itself react with SO_2 and subsequently be converted into calcium sulphate, releasing the previously absorbed CO_2. Carbonation occurring within the flue gas treatment reactor should therefore not automatically be regarded as permanent CO_2 uptake.

In dry and semi-dry flue gas cleaning systems, hydrated lime is intentionally supplied in excess of the stoichiometric requirement to ensure high removal efficiencies of acid gases. The amount of excess lime depends on process design, sorbent utilisation efficiency, reactor configuration, gas composition, residence time, humidity, and the required emission limits. As a result, the generated air pollution control residues (APCR) normally contain varying amounts of residual unreacted $Ca(OH)_2$ together with calcium sulphate, calcium sulphite, chlorides, fly ash, and already carbonated material.

Only this residual free $Ca(OH)_2$ remains available for subsequent carbonation during storage, landfilling, or dedicated accelerated carbonation treatment of the APCR. Accordingly, the potential CO_2 uptake should be calculated from the amount of residual reactive $Ca(OH)_2$ remaining after completion of the acid-gas neutralisation process, rather than from the total amount of lime supplied to the flue gas cleaning system. Calcium already converted into sulphates or other stable reaction products should be assigned a carbonation potential of zero.

For inventory applications, estimation of the residual carbonation potential therefore requires information on the degree of sorbent utilisation, or equivalently the amount of excess hydrated lime

remaining in the APCR after flue gas treatment. Where such information is available, it should be used directly. Otherwise, conservative default values should be applied to avoid overestimation of CO_2 uptake.

The amount of residual free $Ca(OH)_2$ remaining in APCR depends primarily on the degree of sorbent utilisation in the flue gas cleaning system. Typical dry and semi-dry desulphurisation systems intentionally operate with excess lime to ensure high removal efficiencies of SO_2 and other acid gases. Depending on process design and operating conditions, the residual reactive $Ca(OH)_2$ in the APCR may typically range from approximately 10% to 30% of the original lime input, while values up to 40–50% may occur under conditions of high excess dosing or lower sorbent utilisation. In the absence of plant-specific information, 10% residual free $Ca(OH)_2$ may be used as a conservative product-level screening assumption. It is not a national Tier 1 default and should be applied only within a documented application-specific assessment.

Residual carbonation potential in chemical treatment processes

In many environmental and water treatment applications, hydrated lime is used to promote chemical reactions other than carbonation. These include acid neutralization, precipitation of dissolved metals, phosphate removal, fluoride removal and other treatment processes in which calcium becomes incorporated into chemically stable compounds. The calcium that has reacted to form sulphates, chlorides, nitrates, phosphates or other stable salts is no longer available for carbonation and should therefore not be included in CO_2 uptake calculations.

In practical operation, however, lime is frequently added in excess of the theoretical stoichiometric requirement to ensure complete treatment, maintain the desired pH, and accommodate variations in process conditions and influent composition. Consequently, depending on the specific process and operating practice, a fraction of the added hydrated lime may remain unreacted in the generated sludge or other solid residues.

This residual free $Ca(OH)_2$ remains chemically available for subsequent carbonation if the residue is exposed to atmospheric CO_2 during storage, landfilling or beneficial reuse. Accordingly, the carbonation potential of these applications should not be determined from the total amount of lime added, but only from the residual reactive $Ca(OH)_2$ remaining after completion of the intended treatment reactions.

The amount of residual free $Ca(OH)_2$ is highly process-specific and depends on factors such as the degree of excess lime dosing, pH control strategy, residence time, mixing conditions and the composition of the treated stream. In the absence of process-specific information, no generic carbonation factor is recommended for these applications, and conservative assumptions should be applied to avoid overestimation of CO_2 uptake.

Acid neutralisation producing non-carbonate salts

Lime is frequently used to neutralise acidic industrial effluents containing strong acids such as hydrochloric acid (HCl), nitric acid (HNO_3), or sulphuric acid (H_2SO_4). Typical reactions include:

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$
$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$
$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$

The resulting calcium salts (e.g. $CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$):

- Are highly soluble or form stable crystalline phases.
- Do not revert to $Ca(OH)_2$ under environmental conditions.
- Do not carbonate upon exposure to CO_2.

As a result, lime consumed in such neutralisation reactions has zero carbonation potential, and its use should be excluded from CO_2 uptake estimates.

Precipitation of metals and phosphates

In wastewater treatment, lime is used to precipitate heavy metals and phosphates through the formation of insoluble calcium compounds. Typical target metals include iron (Fe), aluminium (Al), manganese (Mn), zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), and lead (Pb) with the following reactions:

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

Phosphates: $Ca^{2+} + PO_4^{3-} \longrightarrow Ca_3(PO_4)_2$

Iron: $Fe^{3+} + 3OH^- \longrightarrow Fe(OH)_3$

Aluminium: $Al^{3+} + 3OH^- \longrightarrow Al(OH)_3$

Zinc: $Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$

Copper: $Cu^{2+} + 2OH^- \longrightarrow Cu(OH)_2$

In some systems, lime treatment leads to the formation of mixed or secondary solids, such as metal carbonates (e.g. $ZnCO_3$, $PbCO_3$) under CO_2-rich conditions, mixed calcium–metal hydroxides or sorption of metals onto $CaCO_3$ surfaces. The role of lime is to supply alkalinity, not to form $CaCO_3$. Any carbonate formation typically involves metal carbonates, not calcium carbonate. Calcium is either discharged as dissolved Ca^{2+} or bound in non-carbonate solids. Thus, CO_2 uptake attributable to calcium carbonation remains negligible.

The implications for carbonation calculations can be summarised as follows:
Calcium bound in phosphates or mixed metal hydroxide/oxide phases:

- Is not available for carbonate formation.
- Remains chemically stable over long timeframes.
- Does not participate in secondary carbonation reactions.

Lime used primarily for metal precipitation should be assigned zero or near-zero CO_2 uptake. Any incidental carbonate formation should be conservatively neglected in inventory calculations.

High-purity process control and closed systems

In certain water treatment or industrial applications, lime is used in:

- Closed reactors.
- Systems with controlled gas composition.
- Environments with negligible CO_2 partial pressure.

In such cases, carbonation is intentionally avoided to maintain alkalinity or process efficiency. Even if $Ca(OH)_2$ remains present, the absence of CO_2 prevents carbonation from occurring to any significant extent. However, in such cases, further processes, after e.g. a closed reactor, always need to be considered. An overview of the carbonation potential is shown in Table 10.

Table 10 Carbonation relevance overview of selected Group C applications.

Application	Dominant reaction products	Carbonation potential	Inventory recommendation
Drinking water treatment	$CaCO_3$	High	Count full carbonation where CO_2 is supplied or atmospheric carbonation occurs.
Wastewater treatment	$CaCO_3$ + residual $Ca(OH)_2$	Moderate–High	Count carbonation of $CaCO_3$ formation and residual free $Ca(OH)_2$ where applicable.
Acid mine drainage	$CaCO_3$, metal hydroxides	Moderate	Count carbonation only of residual reactive $Ca(OH)_2$.
Wet limestone FGD	$CaSO_4 \cdot 2H_2O$	None	Exclude from methodology (limestone process).
Dry/semi-dry FGD	$CaSO_4$ + residual $Ca(OH)_2$ in APCR	Low–Moderate	Count only carbonation of residual free $Ca(OH)_2$ remaining in APCR.
Industrial acid neutralisation	$CaSO_4$, $CaCl_2$, $Ca(NO_3)_2$	Very low	Count only residual free $Ca(OH)_2$ if demonstrated.
Metal and phosphate precipitation	Metal hydroxides, Ca phosphates	Very low	Count only residual free $Ca(OH)_2$ if demonstrated.
Closed pH control systems	$Ca(OH)_2$ or dissolved Ca^{2+}	Negligible	Normally no carbonation unless subsequent exposure occurs.

Carbonation chemistry

Carbonation in environmental and water treatment applications differs fundamentally from that in construction materials. In most Group C applications, hydrated lime is used primarily as a chemical reagent rather than as a construction material. Consequently, carbonation is often a secondary process that occurs only after the intended chemical treatment has been completed.

Depending on the application, calcium may follow several different reaction pathways. Where calcium hydroxide reacts directly with dissolved or atmospheric carbon dioxide, stable calcium carbonate is formed, and the corresponding CO_2 uptake may be credited. However, in many applications, calcium instead reacts with sulphur compounds, chlorides, nitrates, phosphates, dissolved metals or silicates to form chemically stable non-carbonate products. These reaction products no longer possess carbonation potential and should therefore be excluded from CO_2 uptake calculations.

Many environmental treatment processes deliberately operate with excess lime in order to ensure complete neutralization, maintain pH control and accommodate process variability. Consequently, a fraction of the hydrated lime may remain unreacted after completion of the primary treatment process. This residual free $Ca(OH)_2$ represents the only significant carbonation potential in many applications, including flue gas cleaning residues, neutralization sludges and certain wastewater treatment residues. The carbonation potential should therefore be related to the residual reactive lime rather than to the total amount of lime added.

Carbonation behaviour

Unlike construction lime products, Group C applications cannot generally be described using a single carbonation model. Carbonation behaviour depends primarily on the chemical fate of the calcium after the intended treatment process has been completed.

Applications such as drinking water softening intentionally produce calcium carbonate as part of the treatment process and therefore exhibit immediate or nearly complete carbonation. In contrast, applications involving acid neutralization, precipitation of metals or phosphates, and flue gas desulphurization convert most of the lime into stable non-carbonate compounds with little or no subsequent carbonation potential.

Where excess hydrated lime remains after completion of the treatment process, subsequent carbonation may occur during sludge storage, landfilling, beneficial reuse or dedicated accelerated carbonation treatment. The magnitude of this uptake depends primarily on the amount of residual free $Ca(OH)_2$, exposure to atmospheric CO_2, moisture conditions and the residence time before final disposal or reuse.

For inventory purposes, carbonation in Group C should therefore be determined according to the actual reaction pathway followed by the lime. Carbonation should be credited only for calcium that remains chemically available for reaction with CO_2 after completion of the primary treatment process. Calcium incorporated into sulphates, chlorides, nitrates, phosphates, silicates or other stable compounds should be assigned zero carbonation potential.

Accordingly, the principal parameter governing CO_2 uptake in many Group C applications is not the total amount of lime consumed, but the fraction of residual reactive $Ca(OH)_2$ remaining after completion of the intended chemical treatment. Where this fraction can be quantified, either from plant-specific measurements or conservative default values, it provides the preferred basis for CO_2 uptake calculations.

5.5.3.5 Group D – Industrial use of process lime

Technical function

Industrial process lime comprises a broad range of applications in which lime functions primarily as a reactive chemical reagent rather than as a construction material or environmental treatment agent. Unlike the products described in Groups A–C, industrial process lime is generally consumed within integrated industrial processes where its principal role is to promote chemical reactions, remove impurities, regulate alkalinity, or modify the physical properties of process streams. Carbonation is therefore rarely the primary objective of the process and, in many cases, occurs only as a secondary reaction or after the industrial process has been completed.

The industrial use of lime encompasses a wide range of sectors, including iron and steel production, non-ferrous metallurgy, pulp and paper manufacture, precipitated calcium carbonate (PCC) production, sugar refining, glass manufacture, calcium carbide production, titanium dioxide manufacture, chemical processing, and numerous other mineral and chemical industries. These applications account for a substantial proportion of global lime consumption and therefore represent an important component of any methodology for estimating CO_2 uptake in lime-containing products.

Although the individual industrial processes differ considerably, they can generally be divided into four principal categories according to the ultimate chemical fate of the calcium introduced with the lime:

- **Closed calcium cycles**, where calcium carbonate is repeatedly calcined and regenerated within the industrial process (e.g. pulp and paper, precipitated calcium carbonate production, and, in many cases, sugar manufacture).
- **Permanent incorporation into products or process phases**, where calcium becomes chemically bound in stable silicates, aluminates, sulphates, phosphates or glass phases with little or no subsequent carbonation potential (e.g. glass manufacture and parts of the metallurgical industry).
- **Formation of industrial residues containing residual reactive lime**, where only the remaining free CaO or $Ca(OH)_2$ is available for subsequent carbonation (e.g. steel slags and certain process residues).
- **Formation of secondary lime products**, where hydrated lime or other reactive calcium compounds leave the industrial process and are subsequently used in other applications where carbonation may occur (e.g. carbide lime).

This classification is important because the carbonation potential is governed primarily by the chemical fate of the calcium after completion of the industrial process rather than by the amount of lime consumed. In many industrial applications, most of the calcium is converted into chemically stable compounds that no longer participate in carbonation. In others, significant quantities of reactive calcium remain available for carbonation during storage, secondary use or end-of-life. Consequently, CO_2 uptake should be determined from the fraction of calcium that remains chemically available for carbonation rather than from the total lime input to the industrial process.

Accordingly, the following sections describe the principal industrial applications of lime, the dominant chemical transformations occurring in each process, and the implications for estimating CO_2 uptake in national greenhouse gas inventories.

General carbonation principles for industrial lime

Unlike construction materials and many environmental applications, industrial process lime is generally consumed as a reactive chemical reagent within integrated manufacturing processes. Consequently, the carbonation potential is determined primarily by the chemical transformations occurring during the industrial process rather than by the amount of lime supplied.

During industrial use, calcium originating from quicklime or hydrated lime may follow several different chemical pathways. In some processes, calcium remains available as free calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$), allowing subsequent carbonation during storage, secondary use or end-of-life. In other processes, calcium becomes incorporated into chemically stable compounds such as silicates, aluminates, sulphates, phosphates or glass phases that no longer possess carbonation potential. In still other applications, calcium is continuously recycled within a closed industrial process where calcium carbonate is repeatedly calcined and regenerated without representing a net atmospheric CO_2 uptake.

From a carbonation perspective, industrial lime applications can therefore be divided into four principal categories:

Closed calcium cycles

Calcium is continuously recycled within the industrial process, for example through repeated calcination and recarbonation. Although calcium carbonate may be formed during the process, it is subsequently decomposed again in an integrated lime kiln. These systems therefore do not normally constitute a net atmospheric CO_2 sink.

Permanent incorporation into products or process phases

Calcium becomes chemically incorporated into stable reaction products such as silicates, aluminates, sulphates, phosphates or glass matrices. Once incorporated into these phases, the calcium is no longer available for carbonation and should therefore be assigned zero carbonation potential.

Industrial residues containing residual reactive lime

Part of the lime reacts within the industrial process, while another fraction remains as residual free CaO or $Ca(OH)_2$ in slags, ashes, dusts or other process residues. Only this residual reactive fraction remains available for subsequent carbonation and should therefore form the basis for CO_2 uptake calculations.

Secondary lime products

Some industrial processes generate calcium hydroxide or other reactive lime products as by-products. When these materials leave the primary industrial process and are subsequently used in applications where carbonation may occur, the corresponding CO_2 uptake should be attributed to the downstream application rather than to the originating industrial process, thereby avoiding double counting.

Accordingly, the fundamental accounting principle for industrial process lime is that CO_2 uptake should be related to the chemical fate of calcium after completion of the primary industrial process rather than to the total amount of lime consumed. Only calcium that remains chemically available for carbonation, either directly or in subsequent applications, should be included in CO_2 uptake calculations. Based on this principle, the major industrial applications of lime can be classified into four methodological categories according to the ultimate fate of the calcium and the corresponding implications for CO_2 uptake calculations, as summarized in Table 11.

Table 11 General classification of industrial lime applications according to the chemical fate of calcium and their implications for CO_2 uptake.

Category	Chemical fate of calcium	Typical industrial applications	Carbonation potential	Inventory implication
1. Closed calcium cycles	Calcium is repeatedly calcined and recarbonated within an integrated industrial process.	Pulp and paper, PCC production, sugar production (where lime is regenerated)	No net atmospheric uptake within the primary process	Report only uptake occurring outside the closed loop; avoid double counting.
2. Permanent incorporation into products or process phases	Calcium becomes chemically bound in stable silicates, aluminates, sulphates, phosphates, glass phases or similar compounds.	Glass manufacture, ceramics, parts of metallurgy, some chemical processes	None or negligible	Assign zero carbonation unless residual reactive lime is demonstrated.
3. Industrial residues containing residual reactive lime	Only part of the lime reacts; residual free CaO or $Ca(OH)_2$ remains in slags, ashes or other residues.	Steel slags, metallurgical residues, lime kiln dust, some process residues	Variable	Calculate uptake only from the residual reactive lime fraction.
4. Secondary lime products	Reactive lime leaves the industrial process as a by-product and is subsequently used in another application.	Carbide lime, some recycled process limes, selected industrial by-products	Potentially high, depending on subsequent use	Attribute CO_2 uptake to the downstream application where carbonation actually occurs.

The following sections describe the principal industrial applications of lime in more detail, together with the dominant chemical transformations occurring in each process and their implications for estimating CO_2 uptake in national greenhouse gas inventories.

Industrial process categories

The industrial applications of lime reviewed in the Politecnico report (Grosso et al., 2020, [36]) cover a wide range of manufacturing sectors with very different process conditions and end uses. From the perspective of greenhouse gas inventory methodology, however, the industrial sector can be simplified by considering the chemical fate of the calcium after completion of the primary industrial process rather than the industrial sector itself. This approach makes it possible to develop common calculation principles for applications that exhibit similar carbonation behaviour, despite belonging to different industrial sectors.

Based on the classification presented in Table 11, the industrial applications considered in this report can be grouped into four principal categories.

The first category comprises *closed calcium cycles*, where calcium carbonate is repeatedly calcined and regenerated within the industrial process. Typical examples include the pulp and paper industry, precipitated calcium carbonate (PCC) production, and, in many cases, sugar manufacture. Although carbonation reactions occur within these systems, they normally do not constitute a net atmospheric CO_2 uptake because the calcium carbonate is subsequently recalcined as part of the integrated process.

The second category comprises applications in which calcium becomes *permanently incorporated into chemically stable products or process phases*. Examples include glass manufacture, ceramics, and several metallurgical and chemical processes where calcium is bound in silicates, aluminates, phosphates or other stable compounds. Once incorporated into these phases, the calcium no longer remains available for carbonation.

The third category includes industrial processes that generate *residues containing residual reactive lime*. In these applications, only part of the added lime reacts during the primary process, while the remaining free CaO or $Ca(OH)_2$ remains in slags, ashes, dusts or other process residues. Steelmaking slags constitute the most important example. The carbonation potential of these applications is therefore governed by the amount of residual reactive lime rather than by the total lime consumption.

The fourth category comprises *secondary lime products*, where reactive calcium compounds leave the primary industrial process and subsequently enter other applications. Carbide lime is the most important example of this category. In such cases, carbonation should be accounted for in the downstream application where carbonation physically occurs, rather than in the primary industrial process that generated the by-product.

The following sections describe the principal industrial sectors in more detail. For each application, the dominant chemical reactions, the fate of the calcium, the expected carbonation behaviour, and the implications for CO_2 uptake calculations are discussed. Although the industrial applications differ considerably in their technical function, they can all be evaluated consistently using the general accounting principles presented above.

The principal industrial applications considered in this report, together with their primary technical function, methodological classification, and principal implications for CO_2 uptake calculations, are summarised in Table 12. The table also provides the structure for the more detailed discussions presented in the following sections.

Table 12 Industrial process applications considered in Group D and their principal methodological category.

Industrial application	Principal use of lime	Category according to Table 11	Main carbonation issue
Iron and steel production	Flux and slag formation	Residual reactive lime	Carbonation of free lime in slags
Non-ferrous metallurgy	Flux and impurity removal	Permanent incorporation / Residual lime	Limited carbonation of residues
Pulp and paper	Causticising and recausticising	Closed calcium cycle	Internal recycling of $CaCO_3$
Precipitated calcium carbonate (PCC)	Carbonation process	Closed calcium cycle	Accounting boundary and double counting
Sugar industry	Juice purification	Closed calcium cycle	Internal lime regeneration
Glass and ceramics	Network modifier	Permanent incorporation	No carbonation
Calcium carbide / acetylene	Carbide production	Secondary lime product	Carbonation of carbide lime after reuse
Titanium dioxide production	Neutralisation and residue treatment	Permanent incorporation / Residual lime	Process-dependent carbonation of residues
Aluminium industry	Slag conditioning and residue treatment	Permanent incorporation / Residual lime	Carbonation of residual lime in process residues
Other industrial applications	Various chemical uses	Process dependent	Case-specific assessment

Specific industrial process applications

Iron and steel production

Technical function

The iron and steel industry is the largest industrial consumer of lime worldwide and accounts for a substantial share of total lime production. Lime is used throughout ironmaking and steelmaking as a highly reactive flux and refining agent. Its principal functions are to remove impurities from molten iron and steel, control slag chemistry, protect refractory linings, improve process efficiency, and produce steel with the required chemical composition and quality. The use of lime is essential for efficient removal of silica, phosphorus, sulphur and other impurities and therefore forms an integral part of modern iron and steel production.

From the perspective of CO_2 uptake, the iron and steel industry differs fundamentally from most construction and environmental applications because the primary purpose of lime is not carbonation but chemical transformation within high-temperature metallurgical processes. The carbonation potential therefore depends on the fate of the calcium after completion of the metallurgical reactions rather than on the amount of lime consumed.

Principal production routes

Lime is used in several different iron and steel production routes, each generating different calcium-bearing products and residues with different carbonation potentials.

Blast furnace – Basic Oxygen Furnace (BF–BOF)

The integrated BF–BOF route is the dominant production route for primary steel worldwide. Iron ore is first reduced to hot metal in the blast furnace, after which the hot metal is refined into steel in the basic oxygen furnace. Lime is added in both stages but particularly in the BOF converter, where it reacts with silica, phosphorus, sulphur and other impurities to form a highly basic slag. BOF slag therefore represents the largest single calcium-bearing residue from the steel industry.

Electric Arc Furnace (EAF)

Electric Arc Furnaces primarily produce steel from recycled scrap. Lime is added to control slag basicity, remove impurities and protect refractory linings. Although total lime consumption is generally lower than in the BF–BOF route, significant quantities of EAF slag containing calcium-bearing phases are produced.

Secondary metallurgy

Additional lime may be used during ladle metallurgy and secondary refining processes, including Ladle Furnace (LF), Argon Oxygen Decarburisation (AOD), Vacuum Oxygen Decarburisation (VOD), and other specialised refining operations. These processes generally consume smaller quantities of lime but may generate additional slags and dusts containing reactive calcium phases.

Chemical fate of lime

During steelmaking, lime undergoes several competing reactions. A large proportion reacts with silica, alumina, iron oxides, phosphorus and sulphur to form complex calcium silicates, calcium aluminates, calcium ferrites and calcium phosphates that become incorporated into the metallurgical slag. These phases are generally stable under environmental conditions and exhibit little or no carbonation potential.

However, industrial slags are rarely chemically homogeneous. Depending on process conditions, slag chemistry, cooling rate and lime addition practice, part of the added lime remains as free calcium oxide (free CaO) or hydrates subsequently to calcium hydroxide ($Ca(OH)_2$). These residual reactive calcium phases remain capable of reacting with atmospheric CO_2 after the slag leaves the steel plant.

The proportion of residual free lime depends on several factors, including:

- lime addition practice and slag basicity
- steelmaking process (BF–BOF or EAF)
- slag composition
- cooling conditions
- particle size after crushing, and
- subsequent handling and storage

Consequently, the carbonation potential of steel slags varies considerably between plants and production routes.

Carbonation behaviour

Carbonation does not normally occur to any significant extent during ironmaking or steelmaking because the processes operate at temperatures well above the stability range of calcium carbonate. Carbonation begins only after the slag has cooled and becomes exposed to atmospheric CO_2.

The dominant carbonation reactions involve residual free calcium oxide and calcium hydroxide:

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

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

Carbonation occurs primarily during:

- temporary slag storage
- weathering
- crushing and processing
- stockpiling
- use as construction aggregate
- road construction
- embankments
- and other secondary applications

Fresh steel slags generally carbonate slowly because only external surfaces are initially exposed. Crushing and processing substantially increase the exposed surface area and therefore accelerate carbonation. Carbonation may continue for years or decades depending on storage conditions, particle size and subsequent use.

Most calcium incorporated into calcium silicates, calcium aluminates and related slag minerals remains unavailable for carbonation under normal environmental conditions. Consequently, the overall carbonation potential of steel slags is governed primarily by the amount of residual free CaO and $Ca(OH)_2$ rather than by the total calcium content of the slag.

Implications for CO_2 uptake calculations

From an inventory perspective, iron and steel production represents a typical example of *Category 3 – Industrial residues containing residual reactive lime.*

The principal metallurgical reactions consume most of the added lime by incorporating calcium into stable slag minerals. Only the residual reactive lime remaining in the slag after completion of the steelmaking process should therefore be considered available for subsequent carbonation.

Accordingly, CO_2 uptake should not be calculated from the total lime consumption of the steel plant but from the quantity of residual free CaO and $Ca(OH)_2$ present in the generated slags and other calcium-bearing residues. Where plant-specific measurements of free lime are available, these should be used directly. Otherwise, conservative default values should be applied to avoid overestimation of CO_2 uptake.

Subsequent carbonation should be allocated to the life-cycle stage where it physically occurs, typically during slag storage, weathering, secondary use or end-of-life management. This approach

is consistent with the general accounting principles presented in Chapter 4 and avoids double counting between industrial process emissions and downstream CO_2 uptake.

Non-ferrous metallurgy

Technical function

Lime is widely used in non-ferrous metallurgical industries as a reactive process material for the production and refining of metals such as aluminium, copper, lead, zinc, nickel, titanium, and precious metals. Similar to iron and steel production, the principal functions of lime are to control slag chemistry, remove impurities, regulate alkalinity, neutralise acidic process streams, and improve separation between metal and slag phases. In several processes, lime is also used for treatment of process water, neutralisation of acidic liquors, and stabilisation of process residues. Although the total lime consumption is considerably smaller than in the iron and steel industry, non-ferrous metallurgy represents an important industrial application because the chemical fate of the calcium differs between processes and directly influences the potential for subsequent carbonation.

Principal industrial applications

Lime is used in a wide range of non-ferrous metallurgical processes, including:

- aluminium production
- copper smelting and refining
- lead and zinc production
- nickel production
- titanium dioxide manufacture
- precious metal extraction
- and other hydrometallurgical processes

The specific function varies between industries, but generally includes slag conditioning, neutralisation of acidic process streams, precipitation of dissolved metals, pH control, and stabilisation of process residues.

Chemical fate of lime

The chemical transformations of lime depend on the individual industrial process.

In pyrometallurgical operations, calcium typically reacts with silica, alumina, iron oxides and other mineral components to form calcium silicates, calcium aluminates and other complex slag minerals. These compounds become incorporated into the slag and generally exhibit little or no subsequent carbonation potential.

In hydrometallurgical processes, hydrated lime is frequently used for neutralisation and precipitation of dissolved metals. Calcium may then become incorporated into gypsum, hydroxides, sulphates, or other stable mineral phases. Similar to the environmental applications discussed in Group C, these reaction products normally possess little carbonation potential because the calcium has been chemically consumed during the treatment process.

However, depending on process efficiency and operating practice, part of the added lime may remain as residual free CaO or $Ca(OH)_2$ in process residues or filter cakes. This residual reactive lime may subsequently carbonate during storage, landfilling or beneficial reuse.

Carbonation behaviour

Carbonation is generally negligible during the primary metallurgical process because the reactions occur either at high temperatures or under controlled chemical conditions where carbonation is thermodynamically or kinetically unfavourable.

Subsequent carbonation may occur only after the residues have left the industrial process and become exposed to atmospheric carbon dioxide. The carbonation behaviour therefore depends primarily on:

- the amount of residual free CaO or $Ca(OH)_2$
- particle size and exposed surface area
- moisture conditions
- storage conditions
- and the subsequent management of the residues

In most applications, the majority of the calcium is chemically incorporated into stable mineral phases before the residues leave the process. Consequently, the overall carbonation potential is generally limited compared with construction materials or many environmental applications.

Implications for CO_2 uptake calculations

From an inventory perspective, non-ferrous metallurgy primarily represents *Category 2 – Permanent incorporation into products or process phases, although some applications also fall within Category 3 – Industrial residues containing residual reactive lime.*

For most pyrometallurgical processes, calcium becomes chemically incorporated into stable slag minerals and should therefore be assigned zero carbonation potential.

Where hydrated lime is used for neutralization or precipitation in hydrometallurgical processes, only the residual reactive $Ca(OH)_2$ remaining after completion of the intended treatment reactions should be considered available for subsequent carbonation. Calcium incorporated into sulphates, silicates, hydroxides or other stable compounds should be excluded from CO_2 uptake calculations.

Where plant-specific information is available regarding residual free lime in process residues, this information should be used directly. Otherwise, conservative assumptions should be applied to avoid overestimation of CO_2 uptake.

Pulp and paper industry

Technical function

The pulp and paper industry is one of the major industrial consumers of lime and operates one of the largest integrated lime recycling systems in industry. Lime is used primarily in the kraft pulping process, where it regenerates sodium hydroxide (NaOH) from sodium carbonate (Na_2CO_3) in the recausticising process. The regenerated sodium hydroxide is subsequently reused for chemical pulping, while the resulting calcium carbonate is recycled internally through calcination in the lime kiln. Lime is also used in selected bleaching processes, wastewater treatment, pH control, and in the production of precipitated calcium carbonate (PCC) used as a paper filler and coating pigment.

Unlike most other industrial applications, the principal function of lime is therefore not to produce a final calcium-containing product but to maintain an internal chemical cycle in which calcium repeatedly alternates between calcium oxide, calcium hydroxide and calcium carbonate.

Principal process chemistry

Following slaking of quicklime,

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

the hydrated lime reacts with sodium carbonate in the recausticizing process according to

$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$

The precipitated calcium carbonate (lime mud or mesa) is subsequently separated from the white liquor and returned to the lime kiln, where it is recalcined:

$CaCO_3 \rightarrow CaO + CO_2$

The regenerated calcium oxide is then reused in the recausticizing process, thereby completing the internal lime cycle.

This closed regeneration loop is a defining characteristic of the kraft process and distinguishes it from most other industrial lime applications.

Chemical fate of lime

Within the recausticising process, calcium repeatedly cycles between CaO, $Ca(OH)_2$ and $CaCO_3$. Although calcium carbonate is continuously formed, it is normally an intermediate process product rather than a final product. Since the calcium carbonate is subsequently calcined in the lime kiln, no permanent storage of atmospheric CO_2 occurs within the closed chemical loop.

Only relatively small fractions of calcium leave the process as purge streams, process losses, dust, or sludge. Depending on the mill configuration and residue management, these materials may contain residual calcium hydroxide or calcium carbonate and may subsequently carbonate further during storage or disposal.

Some pulp and paper mills also manufacture precipitated calcium carbonate (PCC) for paper filling and coating. Because this represents a distinct industrial process with different accounting implications, it is treated separately in the following section.

Carbonation behaviour

The formation of calcium carbonate during recausticizing should not be interpreted as permanent CO_2 uptake. In the normal kraft process, the calcium carbonate is intentionally regenerated through calcination in the lime kiln, releasing essentially the same amount of process CO_2 that was previously incorporated into the carbonate.

Consequently, carbonation occurring within the recausticizing cycle represents an internal process reaction rather than a net atmospheric CO_2 removal.

Only calcium-containing residues that permanently leave the closed lime cycle and remain exposed to atmospheric CO_2 after disposal or beneficial reuse possess any additional carbonation potential. Where such residues contain residual free CaO or $Ca(OH)_2$, limited additional carbonation may

occur during storage, landfilling or secondary use. However, the quantities involved are generally small compared with the total lime throughput of the mill.

Implications for CO_2 uptake calculations

From an inventory perspective, the pulp and paper industry represents a typical example of *Category 1 – Closed calcium cycles*.

The internal formation of calcium carbonate during the recausticizing process shall not be credited as atmospheric CO_2 uptake because the calcium carbonate is subsequently recalcined within the integrated lime cycle. The corresponding process CO_2 emissions are already accounted for in the lime kiln, and additional carbonation credits would therefore result in double counting.

Accordingly, CO_2 uptake should normally not be assigned to the primary pulp and paper process itself.

Only calcium-containing residues that permanently leave the closed lime cycle and remain chemically available for carbonation after disposal or secondary use should be considered in CO_2 uptake calculations. Where such residual reactive lime can be demonstrated through plant-specific information, carbonation may be estimated using the methodology applicable to the subsequent use or disposal pathway. Otherwise, a conservative assumption of zero additional uptake should be applied.

A special application closely related to the pulp and paper industry is the manufacture of precipitated calcium carbonate (PCC). Unlike the internal recausticizing cycle, PCC production intentionally produces calcium carbonate as a commercial product and therefore introduces additional considerations concerning process boundaries, carbon accounting and the avoidance of double counting. This application is discussed separately below.

Biogenic carbon considerations

In modern kraft pulp mills, the energy required for calcination of the lime mud is commonly supplied by biomass-derived fuels, while the recovery boiler is fired primarily with black liquor containing dissolved lignin from the wood. Consequently, the carbon circulating within the recausticising cycle is largely of biogenic origin. The corresponding CO_2 emissions are therefore generally reported as biogenic rather than fossil emissions in greenhouse gas inventories.

This distinction does not alter the carbonation methodology proposed in the present report. The formation and subsequent calcination of calcium carbonate occur within a closed industrial lime cycle and therefore do not constitute a net atmospheric CO_2 uptake. Regardless of whether the carbon is of fossil or biogenic origin, carbonation within the recausticizing loop should not be credited separately, since the corresponding carbon dioxide is released again during recalcination unless the calcium carbonate permanently leaves the industrial system.

Precipitated calcium carbonate (PCC) production:

Technical function

Precipitated calcium carbonate (PCC) is a high-purity synthetic calcium carbonate manufactured by reacting calcium hydroxide with carbon dioxide under controlled process conditions. PCC is widely used as a filler and coating pigment in the pulp and paper industry and is also employed in plastics, paints, sealants, pharmaceuticals, food products and numerous speciality chemical applications.

Compared with ground calcium carbonate (GCC), PCC offers improved control of particle size, morphology and purity, allowing the material to be tailored for specific industrial applications.

PCC production differs fundamentally from most other industrial lime applications because carbonation is intentionally used as the manufacturing process itself. Consequently, PCC represents one of the most important examples of industrial mineral carbonation.

Principal process chemistry

PCC production normally begins with quicklime produced by calcination of limestone:

$$CaCO_3 \rightarrow CaO + CO_2$$

The quicklime is subsequently hydrated:

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

The hydrated lime is then carbonated under carefully controlled conditions:

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

The resulting calcium carbonate is recovered as the commercial PCC product.

Depending on plant configuration, the carbon dioxide used for carbonation may originate from:

- the lime kiln itself
- other industrial flue gases
- purified captured CO_2
- or external commercial CO_2 supplies

The origin of the carbon dioxide is therefore an essential consideration for greenhouse gas accounting.

Chemical fate of lime

Unlike most industrial applications, the calcium introduced into the process is intentionally converted back into calcium carbonate. From a purely chemical perspective, the carbonation reaction is essentially complete and therefore corresponds to almost the full theoretical carbonation potential of the hydrated lime.

However, the inventory treatment depends not on the chemistry alone but on the origin of the carbon dioxide and the system boundary within which the process is operated.

Where quicklime production, hydration and PCC manufacture are integrated within the same industrial installation, the calcination emissions and the subsequent carbonation occur within a common industrial system. In this situation, the formation of PCC primarily represents internal recycling of process carbon rather than an independent atmospheric CO_2 removal.

Conversely, where externally supplied CO_2 is used, or where the calcination emissions have already been reported elsewhere in the inventory, the carbonation process must be evaluated according to the general accounting principles presented in Chapter 4.

Carbonation behaviour

From a process perspective, carbonation during PCC manufacture is rapid and essentially complete. The reaction occurs in aqueous suspension under carefully controlled operating conditions, and nearly all calcium hydroxide is converted into calcium carbonate before product recovery.

Unlike atmospheric carbonation of construction materials, the reaction is controlled by reactor conditions rather than by long-term diffusion of atmospheric CO_2. Consequently, carbonation during PCC production is effectively completed within minutes or hours.

After manufacture, the PCC product is already fully carbonated and therefore possesses no additional carbonation potential during its subsequent service life. The product should therefore be regarded as chemically stable calcium carbonate.

Implications for CO_2 uptake calculations

From an inventory perspective, PCC production represents a typical example of *Category 1 – Closed calcium cycles, although the accounting depends critically on the origin of the carbon dioxide and the system boundary adopted.*

Where the carbon dioxide used for PCC manufacture originates directly from the associated lime kiln and both processes are treated as an integrated industrial system, carbonation should not be reported as an additional atmospheric CO_2 uptake. Instead, only the net process emissions leaving the integrated system should be included in the greenhouse gas inventory. Crediting carbonation separately in such cases would result in double counting because the corresponding calcination emissions have not yet entered the atmosphere.

Where the carbonation process uses carbon dioxide originating from another industrial installation, or from captured CO_2 that has already been reported as an emission elsewhere in the inventory, carbonation may be reported as CO_2 uptake provided that the corresponding emissions have previously been accounted for and that double counting is avoided. Thus, the accounting shall identify whether the CO_2 has been deducted from the emissions of the originating installation or reported as stored in the receiving process. The same quantity of CO_2 shall not be both deducted at the source and credited again as a separate uptake. This treatment is fully consistent with the general accounting principles presented in Chapter 4.

Accordingly, the carbonation reaction itself should not automatically be interpreted as atmospheric CO_2 uptake. Instead, the reported uptake depends on the relationship between the carbonation process and the inventory boundary within which the associated process emissions are reported.

For greenhouse gas inventory purposes, PCC production therefore requires explicit documentation of the origin of the carbon dioxide and the system boundary adopted for emission reporting. Only where the relationship between reported process emissions and subsequent carbonation can be demonstrated should CO_2 uptake be credited.

Inventory note: PCC production demonstrates that chemical carbonation and reportable atmospheric CO_2 uptake are not necessarily equivalent. Although nearly complete carbonation occurs chemically, greenhouse gas inventories should only report CO_2 uptake where the corresponding process CO_2 emissions have previously been reported within the inventory system. Consequently, PCC production is one of the clearest examples of the importance of defining system boundaries and avoiding double counting.

Sugar industry

Technical function

The sugar industry uses lime as an essential process reagent during the purification of sugar juice obtained from sugar beet or sugar cane. The primary purpose of lime is to neutralize organic acids, coagulate suspended and colloidal impurities, precipitate phosphates and other dissolved compounds, and improve clarification prior to evaporation and crystallization. Lime is therefore used primarily as a process chemical rather than as a permanent constituent of the final sugar product. Carbon dioxide is subsequently introduced as part of the purification process to convert dissolved calcium hydroxide into calcium carbonate, which adsorbs impurities and is removed by filtration. This combination of liming and carbonation has been used in the sugar industry for more than a century and remains one of the principal clarification methods in modern sugar manufacture.

Unlike most industrial applications discussed in this chapter, carbonation is intentionally promoted as an integral part of the manufacturing process rather than occurring as a secondary reaction during storage or use.

Principal process chemistry

The purification process generally consists of two consecutive stages.

Following hydration of quicklime,

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

milk of lime is added to the raw sugar juice, increasing the pH and promoting precipitation and coagulation of impurities.

Carbon dioxide is subsequently introduced to convert the dissolved calcium hydroxide into finely divided calcium carbonate according to

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

The precipitated calcium carbonate forms a highly porous floc that adsorbs suspended solids, colouring substances and other impurities. The resulting filter cake is separated from the purified juice prior to further processing.

Chemical fate of lime

During sugar manufacture, essentially all reactive calcium is converted into calcium carbonate during the carbonation stage. The resulting calcium carbonate is removed from the process together with the adsorbed impurities as filter cake or carbonation sludge.

The subsequent fate of this calcium carbonate depends on the individual sugar factory. In many plants, the filter cake is removed from the process and used as an agricultural soil conditioner or

disposed of without further thermal treatment. In other installations, parts of the calcium-containing residues may be recycled or otherwise managed within integrated process systems.

Consequently, the calcium may either leave the industrial process as a permanently carbonated product or remain within an internal industrial loop, depending on the specific process configuration.

Carbonation behaviour

The carbonation reaction itself is rapid and proceeds essentially to completion under the controlled conditions used in sugar manufacture. Carbonation therefore occurs during the industrial process rather than during subsequent product use or storage.

From a purely chemical perspective, the process represents almost complete conversion of calcium hydroxide into calcium carbonate. However, this should not automatically be interpreted as atmospheric CO_2 uptake because the inventory treatment depends on the origin of the carbon dioxide and the subsequent fate of the calcium carbonate.

Where carbon dioxide is supplied directly from an associated lime kiln or another combustion process within the sugar factory, carbonation primarily represents an internal process reaction. Conversely, if the resulting calcium carbonate permanently leaves the industrial process and is not subsequently recalcined, the carbon remains stored within the filter cake or its subsequent application.

Implications for CO_2 uptake calculations

From an inventory perspective, the sugar industry normally represents *Category 1 – Closed or partially closed calcium cycles.*

The carbonation reaction occurring during sugar manufacture should not automatically be reported as atmospheric CO_2 uptake. The accounting depends on whether the carbon dioxide used during carbonation has already been reported as a process emission and whether the resulting calcium carbonate remains permanently outside the industrial process.

Where carbonation uses carbon dioxide originating directly from an associated lime kiln or another integrated process, only the net emissions leaving the industrial system should be reported. Separate carbonation credits should not be assigned because this would lead to double counting of the corresponding process emissions.

Where the carbonated filter cake permanently leaves the process and is used, for example, as an agricultural soil amendment or is otherwise permanently stored without subsequent recalcination, the resulting carbon storage may be considered in accordance with the general accounting principles presented in Chapter 4. Any additional carbonation occurring after the filter cake leaves the sugar factory should be attributed to the downstream application rather than to the sugar manufacturing process itself.

Accordingly, the sugar industry illustrates the importance of distinguishing between chemical carbonation and reportable atmospheric CO_2 uptake. Although carbonation is an essential process step and the conversion of calcium hydroxide to calcium carbonate is nearly complete, CO_2 uptake should only be credited where the corresponding process emissions have previously been reported

and where permanent storage of the carbon can be demonstrated, and double counting has been excluded.

Glass industry

Technical function

The glass industry uses lime as an essential raw material in the manufacture of most commercial glasses, particularly soda–lime–silica glass, which accounts for the majority of global flat glass and container glass production. Together with silica (SiO_2) and alkali oxides (primarily Na_2O), calcium oxide functions as a network modifier and stabilizing component that improves the chemical durability, mechanical strength, and weather resistance of the final glass product. Lime is therefore consumed as a raw material that becomes permanently incorporated into the glass structure rather than as a temporary chemical reagent.

Lime may be introduced either directly as quicklime (CaO) or, more commonly, through limestone ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) contained in the glass batch. Regardless of the raw material used, the calcium ultimately becomes incorporated into the silicate glass network during melting.

Principal process chemistry

During glass manufacture, carbonate-containing raw materials decompose at elevated temperatures, releasing carbon dioxide and forming calcium oxide:

$$CaCO_3 \rightarrow CaO + CO_2$$

The calcium oxide subsequently reacts with silica and other network-forming oxides during melting to form a homogeneous amorphous glass structure containing calcium silicate units. A simplified representation of this reaction is:

$$CaO + SiO_2 \rightarrow CaSiO_3$$

In practice, the calcium becomes distributed throughout a complex silicate network rather than forming discrete crystalline calcium silicate phases.

Chemical fate of lime

Unlike many other industrial applications, the calcium introduced into the glass batch does not remain as free CaO or $Ca(OH)_2$ after manufacture. Instead, it becomes chemically and structurally incorporated into the amorphous silicate network of the glass.

This incorporation fundamentally changes the chemical behaviour of the calcium. Once integrated into the glass structure, the calcium is no longer present as a reactive alkaline phase capable of reacting with atmospheric carbon dioxide. Consequently, the calcium cannot subsequently undergo carbonation under normal environmental conditions.

Carbonation behaviour

Carbonation does not occur during glass manufacture because the process operates at temperatures far above the stability range of calcium carbonate.

Following cooling, the glass consists of a dense, non-porous and chemically stable amorphous material with extremely limited permeability to gases and moisture. Unlike construction materials

containing calcium hydroxide, the glass contains no reactive calcium phases that are accessible for carbonation.

Consequently, neither the service life nor the end-of-life management of glass creates additional carbonation potential. Crushing, recycling or landfilling of glass may increase the exposed surface area, but it does not generate reactive calcium phases because the calcium remains chemically bound within the glass network. Therefore, no additional CO_2 uptake occurs after manufacture.

Implications for CO_2 uptake calculations

From an inventory perspective, the glass industry represents a typical example of *Category 2 – Permanent incorporation into products or process phases.*

Although process CO_2 is released during decomposition of carbonate raw materials, the resulting calcium oxide becomes permanently incorporated into the glass structure and is no longer available for subsequent carbonation. Accordingly, glass manufacture should be assigned zero carbonation potential in national greenhouse gas inventories.

No CO_2 uptake should be attributed during the service life, recycling, secondary use or end-of-life management of glass products unless exceptional process-specific evidence demonstrates the presence of residual reactive lime, which is generally not the case in commercial glass production.

Calcium carbide and acetylene production

Technical function

Calcium carbide is produced industrially by reacting quicklime (CaO) with carbon (typically metallurgical coke) in an electric arc furnace at temperatures of approximately 2000–2200 °C. The principal purpose of lime in this process is to provide the reactive calcium necessary for the formation of calcium carbide (CaC_2), which is subsequently hydrolysed to produce acetylene (C_2H_2), an important feedstock for the chemical industry.

Unlike most other industrial applications discussed in this chapter, the calcium does not remain in slags or process products but is regenerated as calcium hydroxide during acetylene production. Consequently, calcium carbide manufacture represents a unique industrial application in which the primary process itself has essentially no carbonation potential, whereas the resulting by-product possesses a very high potential for subsequent carbonation.

Principal process chemistry

Calcium carbide is produced according to the high-temperature reaction:

$$CaO + 3C \rightarrow CaC_2 + CO$$

During subsequent acetylene production, calcium carbide reacts rapidly with water:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

The resulting calcium hydroxide, commonly referred to as carbide lime or acetylene lime, is generated as a by-product in large quantities. Global production of carbide lime sludge is estimated to be approximately 25 million tonnes (dry basis) per year, of which more than 95% is generated in

China. The dry material typically contains more than 90% $Ca(OH)_2$, with only minor quantities of calcium carbonate and other impurities.

Chemical fate of lime

The calcium follows an unusual pathway compared with most industrial lime applications.

Initially, reactive calcium oxide is converted into calcium carbide during the furnace process. Following hydrolysis, however, the calcium reappears almost entirely as freshly formed calcium hydroxide.

Unlike calcium incorporated into slags or glass, this calcium hydroxide remains highly reactive and chemically available for carbonation. The carbide process therefore produces a secondary lime product rather than a permanently stabilized calcium phase.

Carbide lime is generally recovered as an aqueous suspension or filter cake. Depending on plant configuration, two principal by-product streams are commonly produced:

- a pumpable lime slurry containing approximately 25–30% solids, primarily used for water treatment, pH control and similar applications.
- a more concentrated slurry or filter cake containing approximately 50% solids, which is typically used in larger industrial applications or mechanically dewatered before transport.

Because these materials consist predominantly of freshly precipitated calcium hydroxide with high purity, fine particle size and large specific surface area, they are considerably more reactive than many commercial hydrated lime products.

Carbonation behaviour

The primary calcium carbide and acetylene production processes themselves do not involve carbonation. Carbonation begins only after the carbide lime leaves the industrial process and becomes exposed to atmospheric carbon dioxide.

The dominant carbonation reaction is identical to that of conventional hydrated lime:

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

The physical characteristics of carbide lime favour rapid carbonation. The material typically consists of very fine calcium hydroxide particles with high purity, large specific surface area and high alkalinity (pH > 12). These characteristics provide excellent conditions for rapid reaction with atmospheric CO_2.

Depending on handling and subsequent use, carbonation may occur during:

- storage of dewatered filter cake
- stockpiling
- landfilling
- agricultural use
- soil stabilization
- water treatment
- flue gas cleaning (unreacted excess of $Ca(OH)_2$)
- construction applications
- or other secondary industrial uses

Under favourable exposure conditions, a high degree of carbonation may be achieved within months or a few years.

The carbonation behaviour therefore depends primarily on the subsequent application rather than on the carbide production process itself.

Secondary use of carbide lime

Carbide lime is widely reused as a substitute for commercial hydrated lime in several applications, including:

- water and wastewater treatment
- pH adjustment
- soil stabilization
- flue gas cleaning
- construction-related applications
- and agriculture

In these applications, the carbonation behaviour is essentially identical to that of primary hydrated lime and should therefore be evaluated using the methodology developed for the corresponding product group rather than by assigning a specific carbonation factor to carbide production.

Implications for CO_2 uptake calculations

From an inventory perspective, calcium carbide manufacture represents a typical example of *Category 4 – Secondary lime products*.

The calcium carbide production process itself should be assigned zero CO_2 uptake, since no carbonation occurs during production and the calcium is not exposed to atmospheric CO_2.

The carbonation potential arises only after the calcium hydroxide by-product leaves the industrial process and enters a subsequent application where carbonation can occur.

Accordingly, CO_2 uptake should not be attributed to the carbide or acetylene production process itself but to the downstream application in which carbonation physically occurs. This follows the general accounting principle established in Chapter 4 that CO_2 uptake shall be reported only where the corresponding carbonation occurs and where the associated process emissions have already entered the greenhouse gas inventory.

For inventory purposes, the following principles therefore apply:

- Primary carbide production: zero CO_2 uptake.
- Generation of carbide lime: secondary lime product available for carbonation.
- Secondary use of carbide lime: apply the carbonation methodology corresponding to the actual downstream application (e.g. environmental treatment, soil application or construction).
- Recalcination of carbide lime: no net CO_2 uptake should be credited if the material re-enters a closed industrial lime cycle.

This approach ensures that carbonation is attributed only once throughout the complete life cycle of the calcium and prevents double counting between industrial production and subsequent use.

Titanium dioxide production

Technical function

Lime is used in the manufacture of titanium dioxide (TiO_2) primarily for neutralization, pH adjustment and purification of acidic process streams generated during the production process. Titanium dioxide is produced industrially by either the sulphate process or the chloride process. Lime consumption is almost entirely associated with the sulphate process, in which ilmenite or titanium slag is digested using concentrated sulphuric acid. During subsequent purification and waste treatment, hydrated lime is used to neutralize acidic liquors, precipitate dissolved metals and stabilize process residues. Consequently, lime functions primarily as a chemical treatment reagent rather than as a constituent of the final titanium dioxide product.

Principal process chemistry

The sulphate process generates large quantities of strongly acidic process liquors containing dissolved iron, titanium, aluminium and other metal ions together with excess sulphuric acid. Hydrated lime is added during the neutralization stage to increase pH and precipitate dissolved metals according to reactions such as:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

while dissolved metal ions are precipitated as hydroxides:

$$Me^{n+} + nOH^- \rightarrow Me(OH)_n$$

where Me represents dissolved metal ions such as iron, aluminium or titanium.

Depending on process conditions, calcium may also become incorporated into mixed sulphate phases or other mineral residues.

Chemical fate of lime

Most of the calcium introduced into the process is consumed by neutralization reactions and converted into calcium sulphate (gypsum) or incorporated into mixed mineral residues generated during purification. These compounds are chemically stable under normal environmental conditions and therefore possess little or no subsequent carbonation potential.

However, industrial neutralization processes are normally operated with excess lime to ensure complete neutralization and maintain process stability. Consequently, depending on process design and operating practice, a fraction of the hydrated lime may remain unreacted in the generated filter cakes or other solid residues.

Only this residual reactive $Ca(OH)_2$ remains available for subsequent carbonation after the residues leave the industrial process.

Carbonation behaviour

Carbonation is not an intended part of titanium dioxide production and generally does not occur to any significant extent during the primary industrial process. Carbonation may occur only after the neutralization residues have been dewatered and become exposed to atmospheric carbon dioxide during storage, landfilling or beneficial reuse.

The dominant carbonation reaction is

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

while calcium already converted into gypsum or other stable mineral phases should be regarded as permanently unavailable for carbonation.

The carbonation potential therefore depends primarily on:

- the amount of residual free $Ca(OH)_2$ remaining after neutralization
- residue composition
- particle size
- moisture conditions
- storage conditions
- and the subsequent management of the residues

Implications for CO_2 uptake calculations

From an inventory perspective, titanium dioxide production primarily represents Category 3 – Industrial residues containing residual reactive lime.

The majority of the lime is chemically consumed during neutralization and should therefore not be included in carbonation calculations. Only the residual reactive $Ca(OH)_2$ remaining in the generated residues should be considered available for subsequent carbonation.

Where plant-specific information on residue composition or residual free lime is available, this information should be used directly. Otherwise, conservative assumptions should be applied and only limited carbonation should be credited.

Accordingly, CO_2 uptake should be related to the residual reactive lime remaining after completion of the primary neutralization reactions rather than to the total amount of lime consumed during titanium dioxide production.

From a carbonation perspective, titanium dioxide production follows the same methodological principles as other industrial neutralization processes discussed in Group C. The carbonation potential is determined exclusively by the residual reactive $Ca(OH)_2$ remaining after completion of the intended chemical treatment reactions.

Aluminium industry

Technical function

The aluminium industry uses lime primarily during the production of alumina from bauxite in the Bayer process. Lime is added to improve digestion efficiency, control process chemistry, regenerate caustic liquor, reduce the concentration of impurities, and stabilize process residues. Smaller quantities of lime are also used during primary aluminium production, wastewater treatment, and residue management.

Unlike construction applications, lime functions almost exclusively as a process reagent and is consumed through chemical reactions during alumina production rather than remaining as a reactive constituent of the final product. Consequently, the carbonation potential depends primarily on the chemical fate of the calcium after completion of the Bayer process and the subsequent management of the generated residues.

Principal process chemistry

In the Bayer process, bauxite is digested in concentrated sodium hydroxide at elevated temperature and pressure to dissolve aluminium-bearing minerals. Lime is added for several purposes, including:

- removal of reactive silica
- control of liquor chemistry
- regeneration of sodium hydroxide
- precipitation of impurities
- stabilization of process residues

Calcium reacts with dissolved silica and alumina to form stable calcium aluminosilicate phases and other insoluble compounds. Depending on process conditions, lime may also react with carbonate species and other dissolved constituents.

The generated bauxite residue (red mud) therefore contains a complex mixture of iron oxides, aluminium oxides, titanium oxides, silica, calcium-bearing minerals and residual alkali.

Chemical fate of lime

Most of the calcium introduced into the Bayer process becomes chemically incorporated into stable mineral phases, particularly calcium silicates, calcium aluminosilicates and other complex reaction products. These compounds remain chemically stable under normal environmental conditions and exhibit little or no carbonation potential.

However, depending on process efficiency, lime dosage and residue treatment, part of the added lime may remain as residual free calcium oxide or calcium hydroxide in the bauxite residue. In addition, some calcium may occur as calcium carbonate formed within the process or during subsequent residue ageing.

Only the residual reactive CaO and $Ca(OH)_2$ remain available for subsequent carbonation.

Carbonation behaviour

Carbonation is not an intended part of alumina production and generally plays only a minor role during the primary industrial process. Following disposal or storage of bauxite residue, however, atmospheric carbon dioxide may react with residual alkaline phases present in the residue.

The principal carbonation reaction is

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

while calcium already incorporated into stable calcium silicates and aluminosilicates is not available for carbonation.

The extent of carbonation depends primarily on:

- residual free CaO and $Ca(OH)_2$
- residue composition
- particle size
- moisture conditions
- exposure to atmospheric CO_2
- storage conditions
- and any subsequent residue management or beneficial reuse

Fresh bauxite residue often exhibits high alkalinity. Progressive carbonation during long-term storage can reduce pH and improve environmental stability, and accelerated carbonation has therefore been investigated as a residue treatment method in several studies.

Implications for CO_2 uptake calculations

From an inventory perspective, the aluminium industry primarily represents Category 3 – Industrial residues containing residual reactive lime, although part of the calcium also belongs to Category 2 – Permanent incorporation into stable process phases.

Most of the lime consumed during alumina production becomes chemically incorporated into stable mineral phases and should therefore be assigned zero carbonation potential.

Only the residual reactive CaO and $Ca(OH)_2$ remaining in bauxite residue should be considered available for subsequent carbonation. Consequently, CO_2 uptake should be determined from the amount of residual reactive lime rather than from the total lime consumption of the Bayer process.

Where plant-specific information on residue composition or residual free lime is available, this information should be used directly. Otherwise, conservative assumptions should be applied to avoid overestimation of CO_2 uptake.

Where accelerated carbonation of bauxite residue is deliberately applied, any resulting CO_2 uptake should be reported according to the general accounting principles presented in Chapter 4, ensuring that the corresponding process emissions have previously entered the greenhouse gas inventory and that double counting is avoided.

Other industrial applications

Technical function

In addition to the major industrial sectors described above, lime is used in a wide range of other manufacturing and chemical processes where it functions primarily as a reactive process chemical. These applications include, among others, the production of chemicals, ceramics, mineral wool, refractories, foundry products, mining and mineral processing, petroleum refining, waste treatment,

and various speciality chemical processes. Although the quantities of lime consumed in these sectors are generally smaller than in iron and steel production, pulp and paper manufacture or alumina production, they collectively represent a significant share of industrial lime consumption. A comprehensive review of these applications is provided by Grosso et al. (2020) [36].

The technical function of lime in these industries is generally one or more of the following:

- neutralization of acidic process streams
- pH adjustment
- impurity removal
- slag or melt conditioning
- chemical synthesis
- stabilization of residues
- or control of process chemistry

Chemical fate of lime

Although the industrial processes differ considerably, the chemical behaviour of the calcium generally follows one of the four methodological categories introduced earlier in this chapter.

In many applications, calcium becomes chemically incorporated into stable mineral phases or reaction products such as silicates, aluminates, sulphates or phosphates. These compounds exhibit little or no subsequent carbonation potential.

In other applications, lime is consumed by neutralization or precipitation reactions similar to those described in Group C. Depending on process conditions, small quantities of residual free CaO or $Ca(OH)_2$ may remain in the generated residues.

Some industrial processes also generate secondary lime-containing materials that subsequently leave the industrial process and enter applications where carbonation may occur.

Consequently, the carbonation potential is determined primarily by the chemical fate of the calcium rather than by the industrial sector itself.

Carbonation behaviour

For most of these applications, carbonation during the primary industrial process is negligible because the calcium is either chemically consumed or incorporated into stable products before exposure to atmospheric carbon dioxide.

Where residual reactive lime remains in process residues, limited carbonation may occur during storage, landfilling, stockpiling or beneficial reuse. The magnitude of this uptake depends on the amount of residual free CaO or $Ca(OH)_2$, particle size, moisture conditions and exposure to atmospheric CO_2, in the same manner as described for other industrial residues in this chapter.

Because the industrial processes represented in this section are highly diverse, no single carbonation factor can adequately represent all applications.

Implications for CO_2 uptake calculations

From an inventory perspective, the industrial applications included in this section should be evaluated according to the general methodological framework established for Group D rather than by assigning a common default carbonation factor.

The following general principles should therefore be applied:

- Closed calcium cycles: report only net emissions leaving the integrated process.
- Permanent incorporation into stable products: assign zero carbonation potential.
- Industrial residues containing residual reactive lime: estimate carbonation only from the residual free CaO or $Ca(OH)_2$.
- Secondary lime products: attribute carbonation to the downstream application in which carbonation physically occurs.

Where plant-specific information on residue composition or residual reactive lime is available, this information should be used directly. In the absence of such information, conservative assumptions should be applied to avoid overestimation of CO_2 uptake.

Accordingly, no separate default carbonation methodology is proposed for the miscellaneous industrial applications included in this section. Instead, each application should be assigned to the appropriate methodological category according to the chemical fate of the calcium after completion of the industrial process.

5.5.3.6 Group E – Dolomitic and magnesium-based lime products

Technical function

Dolomitic and magnesium-based lime products are derived from dolomite ($CaMg(CO_3)_2$) or magnesite ($MgCO_3$) and are used where the presence of magnesium provides specific chemical, physical, or metallurgical advantages. These products are commonly referred to as dolime, magnesium lime, or magnesia-based materials, depending on composition and production route.

Typical product forms include:

- Dolomitic quicklime ($CaO{\cdot}MgO$)
- Dolomitic hydrated lime ($Ca(OH)_2{\cdot}Mg(OH)_2$)
- Reactive magnesium oxide (MgO)
- Light-burned magnesia
- Hydrated magnesium hydroxide ($Mg(OH)_2$)

Key industrial and environmental applications include:

- Steelmaking and non-ferrous metallurgy (fluxes, slag conditioning)
- Refractory production
- Environmental applications (soil stabilisation, water treatment, flue gas treatment)
- Construction materials (specialty mortars and renders)
- Chemical processing and pH control
- Carbon capture and mineral carbonation research applications

In many of these uses, the magnesium component dominates the long-term chemical behaviour, particularly with respect to carbonation kinetics and stability.

Carbonation chemistry

Dolomitic quicklime consists of a physical mixture of CaO and MgO formed during calcination:

$CaMg(CO_3)_2 \longrightarrow CaO + MgO + 2CO_2$

Upon hydration:

$CaO + H_2O \longrightarrow Ca(OH)_2$

$MgO + H_2O \longrightarrow Mg(OH)_2$

Carbonation then proceeds through two chemically and kinetically distinct pathways:

Calcium component:

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

Magnesium component:

$Mg(OH)_2 + CO_2 \longrightarrow MgCO_3 + H_2O$

However, unlike calcium carbonate, magnesium carbonate rarely forms as simple anhydrous $MgCO_3$ under ambient conditions.

Formation of hydrated magnesium carbonates

In natural and industrial environments, magnesium carbonation typically produces hydrated magnesium carbonates, such as:

$Mg(OH)_2 + CO_2 + 2H_2O \longrightarrow MgCO_3 \cdot 3H_2O$

Nesquehonite ($MgCO_3 \cdot 3H_2O$)

Hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$)

Dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$)

These phases are thermodynamically stable at low temperatures but require specific moisture and CO_2 conditions to form. Generally, these reactions are slower than Ca-based lime, strongly moisture-dependent and often incomplete under ambient conditions. Nesquehonite can often undergo transformation to hydromagnesite over time.

Carbonation behaviour

Kinetic differences relative to calcium-based lime

A key distinction between calcium- and magnesium-based lime is the rate-limiting step in carbonation:

- Calcium hydroxide is moderately soluble, allowing carbonation to proceed relatively quickly under ambient conditions.
- Magnesium hydroxide has very low solubility, which significantly restricts ion transport and slows carbonation.

As a result:

- Calcium components in dolime typically carbonate within months to a few years.
- Magnesium components may carbonate over years to decades or remain partially uncarbonated indefinitely under dry conditions.

Influence of moisture and CO_2 availability

Magnesium carbonation is strongly dependent on:

- High relative humidity or liquid water
- Elevated CO_2 partial pressure
- Fine particle size and high surface area
- Low temperatures (< 60 °C)

In dry atmospheric exposure, $Mg(OH)_2$ often forms a passivating surface layer, limiting further carbonation.

Carbonation behaviour in use and end-of-life

For most Group E products:

- Calcium fractions carbonate relatively quickly.
- Magnesium fractions carbonate incompletely under ambient exposure.
- End-of-life fragmentation can increase magnesium carbonation, but rates remain slow.

Unlike calcium carbonate, hydrated magnesium carbonates may:

- Dehydrate or transform over time
- Re-release water but not CO_2
- Remain stable once formed

An overview of carbonation for different dolomitic products is shown in Table 13 below.

Table 13 Dolomitic product form and carbonation behaviour.

Product form	Dominant carbonation behaviour	Inventory implication
Dense refractories	Negligible carbonation	Zero CO_2 uptake
Metallurgical slags	Partial carbonation of residual Ca phases; Mg carbonation limited	Count only residual reactive phases
Fine powders and slurries	Potentially high carbonation under favourable exposure	Application-specific assessment
Soil and environmental applications	Rapid carbonation of Ca fraction; slower carbonation of Mg fraction	Separate Ca and Mg where possible
Construction mortars and renders	Ca fraction carbonates readily; Mg fraction only partially	Apply separate carbonation factors for Ca and Mg

Implications for CO_2 uptake calculation

From an IPCC inventory perspective:

- Calcium fraction: Can be treated similarly to calcium-based lime products.
- Magnesium fraction: Requires conservative assumptions due to slow and uncertain carbonation.

Implications for the final methods:

- **Tier 1**: Include the reactive CaO component of dolime in the base calculation. MgO uptake may be calculated separately using MgO-specific data and justified factors.
- **Tier 2:** Calculate CaO and MgO components separately and apply application-specific chemical and exposure factors to each component.
- **Tier 3:** Use separate CaO and MgO cohort parameters and progression functions, with site- or country-specific information where available.

Magnesium carbonation should never be assumed complete within the product lifetime unless justified by specific application conditions.

5.5.3.7 Group F – End-of-life and secondary use

Technical function

Group F covers lime-based materials that enter a secondary phase of use or disposal after the end of their primary service life. Unlike Groups A–E, Group F does not represent a distinct product category but a life-cycle stage in which materials are fragmented, redistributed, or repurposed, thereby altering their exposure conditions and potential for carbonation.

Typical end-of-life and secondary use pathways include:

- Demolition of lime-based construction materials (mortars, plasters, renders)
- Crushing and recycling of lime-containing residues
- Landfilling of lime-rich wastes and by-products
- Use of lime-containing materials such as:
    - Fill material
    - Road sub-base
    - Construction backfill
    - Landscaping and soil amendment
- Storage or stockpiling of fine lime residues (e.g. kiln dust)

The technical function at this stage is no longer related to binding or chemical processing, but rather to structural support, volume filling, or waste management. Importantly, fragmentation and redistribution typically increase exposed surface area, which can enhance carbonation relative to the primary use phase. However, it is important to consider that many lime products fully carbonate already in the primary use phase. In such cases, no carbonation is taking place during end-of-life or secondary use phase.

Carbonation chemistry and behaviour

The carbonation reactions in Group F are fundamentally the same as in earlier groups but occur under different physical and environmental conditions. No new chemical pathways are introduced at end-of-life; rather, previously uncarbonated fractions are given renewed opportunity to react with atmospheric or soil-derived CO_2. Residual $Ca(OH)_2$ and CaO become exposed, crushing accelerates diffusion and carbonation may approach completion. This group is essential for closing the carbon balance. Several factors also influence the carbonation rate such as CO_2 availability (atmospheric vs soil CO_2), moisture content (optimal at intermediate humidity), particle size distribution, burial depth and compaction, and drainage and oxygen availability.

Despite increased surface area, carbonation may still be limited by, for example, burial under low-permeability layers, water saturation limiting CO_2 diffusion, encapsulation in cementitious or silicate matrices, prior full carbonation during primary use.

A critical methodological issue for Group F is double counting avoidance. Carbonation occurring at end-of-life must be limited to:

- Lime fractions not already carbonated during primary use.
- Calcium or magnesium phases, which remained chemically available.

For many lime-based construction products (Group A):

- Carbonation is effectively complete within the primary service life.
- End-of-life carbonation is therefore negligible.

For other uses (Groups C–E):

- Significant uncarbonated fractions may remain.
- Group F carbonation may represent the dominant uptake phase, but a detailed CO_2 uptake description can verify the case.

For dolomitic and magnesium-rich residues:

- Calcium carbonation may proceed similarly to pure lime
- Magnesium carbonation remains slow and incomplete
- Long-term uptake may occur over decades but with high uncertainty

Inventory methodologies should therefore:

- Separate Ca-based and Mg-based fractions
- Apply conservative caps to magnesium carbonation
- Avoid assuming full conversion to Mg carbonates

Implications for CO_2 uptake calculation in national inventories

From an IPCC inventory perspective, Group F requires careful structuring:

- Uptake should be attributed to material flows, not products
- Only residual carbonation potential should be counted
- Time-dependent uptake should be allocated across years following disposal

Recommended methodological principles:

- Tier 1 and Tier 2: Represent end-of-life effects only insofar as they are included consistently in non-overlapping F_{carb} and F_{exp} values; do not add a generic end-of-life uplift.
- Tier 3 cohort method: Include a separate end-of-life or secondary-use category only where the material flow is mutually exclusive and its residual carbonation potential is documented.
- Alternative full stock-and-flow method: Use explicit recycling, landfilling, reuse, particle-size, and exposure data where sufficient national information is available.

Group F uptake should be reported in a way that is transparent, conservative, and consistent with mass balance constraints.

5.5.4 Carbonation kinetics and lifetime behaviour (lime vs concrete)

The kinetics and extent of carbonation differ fundamentally between lime-based products and cement-based concrete, reflecting differences in material composition, microstructure, and intended technical function. While both material classes rely on calcium-bearing phases that are thermodynamically capable of binding atmospheric CO_2, the physical accessibility of these phases and the timescales over which carbonation occurs vary by orders of magnitude.

Concrete is a dense, composite material in which carbonation is an unintended, diffusion-controlled process affecting both portlandite and calcium–silicate–hydrate (C–S–H) phases. As a result, carbonation progresses slowly from exposed surfaces and typically remains incomplete over the service life of the structure. In contrast, many lime products are intentionally designed to carbonate as part of their hardening or stabilization mechanism. These materials are generally more porous, contain a higher fraction of readily available calcium hydroxide, and are exposed to atmospheric CO_2 over large surface areas.

Consequently, carbonation in lime products typically proceeds on timescales of months to years rather than decades to centuries, and the calcium fraction often approaches full conversion to carbonate within the primary product lifetime. This fundamental difference has important implications for national greenhouse gas inventories. In particular, it enables the use of simpler, lifetime-integrated CO_2 uptake models for lime products, whereas concrete carbonation often requires depth-controlled, diffusion-based approaches to avoid systematic under- or overestimation.

The key contrasts between lime and concrete carbonation behaviour are summarized in Table 14.

Table 14 Key contrasts between lime and concrete carbonation behaviour.

Aspect	Lime products	Concrete products
Dominant reactive phase	$Ca(OH)_2$	$Ca(OH)_2$ + C–S–H[2]
Porosity	High	Moderate–low
Intended carbonation	Yes (many products)	No
Carbonation time scale	Months–years	Decades–centuries
Model complexity	Moderate	High
Typical final conversion	Often near 100% (Ca)	Partial

[2] Calcium silicate hydrate

5.5.5 Product-specific CO_2 uptake calculation methodologies

5.5.5.1 Cohort notation developed for the recommended Tier 3 method

Throughout this report, the following harmonized notation is used for cohort-based calculations:

i = index identifying a mutually exclusive lime-product/application category included in the inventory. Each lime flow shall be assigned to exactly one category i. Where product form and application result in materially different carbonation parameters, i shall represent the corresponding product–application combination.

y = reporting calendar year.
n = cohort placement year, under the convention that the cohort enters use at the beginning of year n.
a = y-n: completed cohort age, in years, at the beginning of reporting year y. In annual inventory calculations, a is a non-negative integer.
j = a+1 = y−n+1: ordinal age-year label. The symbol j labels the annual interval from age a to age a+1; it is not an elapsed-time variable and is not used as the argument of the carbonation function in the equations below.

t = continuous elapsed physical time since placement, used in kinetic relations such as

$$x(t) = k_C\sqrt{t}$$

where x(t) is carbonation depth and k_C is the carbonation-depth coefficient. When t is expressed in years, the annual inventory boundaries correspond to t = a and t = a+1.

$F_i(a)$ = normalized cumulative carbonation progression function for category i, evaluated at the exact boundary age a. The function describes the timing of carbonation, with

$$F_i(0) = 0 \qquad 0 \le F_i(a) \le 1 \qquad F_i(a+1) \ge F_i(a)$$

The annual increment in the carbonation function is

$$\Delta F_i(a) = F_i(a+1) - F_i(a)$$

where $\Delta F_i(a)$ is the fraction of the ultimate eligible uptake occurring during reporting year y for cohort n, with a = y - n.

For each category i, cohort n, and reporting year y, the annual CO_2 uptake is calculated as

$$U_{i,n,y} = L_{i,n}\ CF_i\ F_{carb,i}\ F_{exp,i}\ [F_i(a+1)-F_i(a)] \text{ and } a=y-n$$

where:
$U_{i,n,y}$ = CO_2 uptake in reporting year y attributable to application category i and cohort n (tonne CO_2/year).
$L_{i,n}$ = mass of reactive lime, on a documented CaO- or MgO-equivalent basis, entering application category i in cohort year n.
CF_i = stoichiometric CO_2 uptake factor for category i, expressed as tonnes of CO_2 per tonne of reactive oxide equivalent.
$F_{carb,i}$ = ultimate chemically achievable carbonation fraction for category i (dimensionless, 0–1).
$F_{exp,i}$ = physically accessible fraction available for carbonation by atmospheric or dissolved CO_2 (dimensionless, 0–1).

$F_{carb,i}$ and $F_{exp,i}$ shall represent independent limitations and shall not account for the same restriction twice. Because $F_{carb,i}$ represents ultimate carbonation completeness, $F_i(a)$ shall describe the temporal progression only.

The total national annual uptake in reporting year y is:

$$U_y = \sum_i \sum_n U_{i,n,y}$$

where the summation over i includes all eligible, mutually exclusive product/application categories and the summation over n includes all cohorts contributing to uptake during reporting year y.

5.5.5.2 Product-specific modelling approaches

A. Construction lime products

- Assume complete carbonation over a defined carbonation time T_i
- Example: linear, square-root, or documented country-specific progression to the ultimate eligible uptake over 5-10 years.
- End-of-life adds little additional uptake (already carbonated).

B. Agricultural and soil lime

- Assume rapid carbonation.
- Often reasonable to assume near-complete carbonation within 1–3 years.
- Annual uptake can be approximated as full uptake within a short time window.

C. Water and environmental lime

- Split into:
  - Carbonated during use.
  - Residual entering sludge.
- Sludge carbonation modelled separately with exposure assumptions.

D. Industrial lime

- Partition lime into:
  - Chemically consumed fraction (no carbonation).
  - Residual $CaO/Ca(OH)_2$ in slags/residues.
- Apply delayed carbonation model to residues.

E. Dolomitic lime

- Separate Ca and Mg fractions.
- Ca fraction treated as above.
- Mg fraction uses slower, capped carbonation (e.g. 10–40% over decades).

F. End-of-life

- Apply surface-area-enhanced carbonation
- Model only the residual uncarbonated fraction, using a separate cohort category or the alternative full stock-and-flow method where justified.

5.5.6 Suitability of the product grouping for inventory method development

- Product-based grouping aligns with industrial statistics
- Stoichiometry ensures consistency with process emissions
- Carbonation timescales reflect physical reality
- Allows:
  - **Tier 1:** national average F_{carb} and F_{exp} factors applied under a steady-state assumption.
  - **Tier 2:** application-specific F_{carb} and F_{exp} factors applied under a steady-state assumption.
  - **Tier 3:** application-specific annual consumption cohorts with explicit carbonation progression functions.

Table 15 Lime product groups and representative products.

Product group	Representative products	Primary technical function	Typical exposure to air
A. Construction lime products	Air lime mortars, lime plasters, lime renders, limewash, lime putty	Binder and surface finishing	High
B. Soil, agricultural, and land lime	Agricultural lime, soil stabilisation lime, road base lime, embankment lime	pH control, soil improvement, stabilisation	High
C. Environmental and water treatment lime	Drinking water lime, wastewater lime, FGD lime, sludge conditioning lime	pH adjustment, precipitation, gas scrubbing	Medium
D. Industrial process lime	Steelmaking lime, non-ferrous metallurgy lime, chemical process lime, sugar lime	Flux, reagent, impurity removal	Low–medium
E. Dolomitic / Mg-based lime	Dolomitic quicklime, dolomitic hydrated lime, $Mg(OH)_2$ products	Chemical reactivity (Ca + Mg)	Medium
F. End-of-life and secondary materials	Crushed lime mortars, demolition debris, reused lime-stabilised soils	Secondary exposure and reuse	High

Table 16 Indicative carbonation timeframes and kinetic assumptions considered during method development.

Product group	Dominant carbonation control	Typical carbonation timeframe	Indicative representation considered
A. Construction lime	Diffusion through porous binder	1–10 years	Linear or square-root progression
B. Soil & agricultural lime	High surface area, moisture-enhanced	Months–3 years	Rapid progression or short-time full uptake
C. Environmental lime	Process chemistry + sludge exposure	1–20 years	Application-specific progression; separate residual flow where justified.
D. Industrial lime	Residue exposure (slag, waste)	10–50 years	Application-specific delayed progression.
E. Dolomitic (Ca fraction)	As Ca-based lime	1–10 years	Same as Ca-based
E. Dolomitic (Mg fraction)	Hydrated Mg-carbonate formation	10–100+ years	Slow, capped progression.
F. End-of-life materials	Increased surface area	1–5 years	Residual-only progression or stock-and-flow modelling.

Note: For many lime products, assuming full or near-full carbonation within a defined timeframe is technically justified and greatly simplifies modelling compared to concrete.

Table 17 Indicative exposure and ultimate carbonation ranges considered during method development.

Product group	Indicative physically accessible fraction (F_{exp})	Indicative chemically achievable carbonation fraction (F_{carb})
A. Construction lime	0.85–1.00	0.95–1.00
B. Soil & agricultural lime	0.90–1.00	0.90–1.00
C. Environmental lime	0.50–0.80	0.50–0.90
D. Industrial lime	0.20–0.50	0.20–0.60
E. Dolomitic (Ca fraction)	0.70–0.90	0.80–1.00
E. Dolomitic (Mg fraction)	0.50–0.80	0.10–0.40
F. End-of-life materials	0.80–1.00	Residual fraction to completion

Interpretation:

- For consistency with Chapter 6, the first factor in Table 17 is interpreted as F_{exp}, representing physical accessibility to atmospheric or dissolved CO_2.
- The second factor is interpreted as F_{carb}, representing the chemically achievable fraction of the stoichiometric maximum. Chemical conversion to non-carbonatable phases, such as $CaSO_4$ formation in flue-gas cleaning, belongs in F_{carb} and shall not also be represented in F_{exp}.

Table 18 Stoichiometric CO_2 uptake factors and modelling notes.

Reactive phase	Carbonation product (typical)	Stoichiometric CO_2 uptake factor
CaO	$CaCO_3$	0.785 t CO_2/t CaO
$Ca(OH)_2$	$CaCO_3$	0.594 t CO_2/t $Ca(OH)_2$
MgO	Hydrated Mg carbonates	≤ 1.09 t CO_2/t MgO (theoretical)
$Mg(OH)_2$	Nesquehonite / hydromagnesite	0.75–0.85 t CO_2/t $Mg(OH)_2$ (effective)

Important modelling note for Mg:
Although theoretical uptake for MgO to $MgCO_3$ is high, ambient carbonation commonly forms hydrated magnesium carbonates and full conversion is rarely achieved. MgO should therefore be calculated separately using justified MgO-specific F_{carb}, F_{exp}, and timing parameters.

Cross-cutting observation on carbonation variability:
Across all lime product groups, carbonation depends on chemical composition, physical structure, and exposure. Binder composition, porosity, particle size, and surface accessibility affect both the ultimate eligible uptake and its timing. The final Tier 1 method represents this variability through national average F_{carb} and F_{exp} factors; Tier 2 uses application-specific factors; and Tier 3 additionally represents annual cohorts and carbonation progression.

5.6 Synthesis and link to the final methodologies

5.6.1 General observations

The preceding sections have demonstrated that carbonation of lime-containing products is governed by well-established chemical and physical processes but that the rate and extent of carbonation vary considerably among different applications. The variability reflects differences in product composition, geometry, exposure conditions, moisture availability, particle size, and service life. Consequently, no single carbonation model can accurately represent all lime products.

The product-specific assessment presented in this chapter nevertheless reveals several important common characteristics. Most lime products carbonate substantially faster than cement-based concrete because calcium hydroxide is considerably more reactive than the hydration products present in concrete and because lime-containing materials are generally more porous and more readily exposed to atmospheric carbon dioxide. Furthermore, carbonation occurs throughout the life cycle of lime products, including during primary use, end-of-life management, and, for some applications, secondary use.

Although individual products exhibit different carbonation behaviour, the underlying carbonation mechanisms remain the same. Carbonation is governed primarily by the availability of reactive calcium or magnesium phases, exposure to carbon dioxide, moisture conditions, and the accessibility of the material to the surrounding environment.

5.6.2 From product-specific behaviour to sector-level representation

One of the principal findings of the present study is that the large variability observed at product level does not necessarily translate into equally large variability at sector level.

Some applications, such as drinking water treatment, limewash, and certain environmental processes, carbonate almost completely and often within a relatively short period. Other applications, particularly some industrial process uses, exhibit only limited carbonation because reactive lime is chemically transformed into non-carbonatable compounds or remains inaccessible to atmospheric carbon dioxide. Between these extremes lies a broad range of construction, agricultural, and environmental applications in which carbonation proceeds progressively over periods ranging from months to decades.

When these applications are considered collectively, their combined behaviour becomes considerably more stable than that of any individual product category. At national level, annual carbonation therefore reflects the combined contribution of numerous applications with different carbonation characteristics, rather than the behaviour of a single product.

This observation provides an important methodological basis for greenhouse gas inventories. While detailed product-specific models remain scientifically preferable where sufficient data are available,

the aggregated behaviour of the lime sector can be represented using simplified methodologies without introducing unacceptable uncertainty.

5.6.3 Implications for methodological development

The analyses presented in this chapter demonstrate that different methodological approaches are appropriate depending on the level of available information.

Where historical national lime-use data and application-specific parameters are available, the recommended Tier 3 method can represent carbonation through annual consumption cohorts and cumulative progression functions. Countries with sufficiently detailed information on physical stocks, service lives, end-of-life processes, and secondary material flows may instead apply the alternative full stock-and-flow model described in Chapter 6.5.2.

Many countries do not possess the historical and application-specific information required for cohort modelling. Under reasonably stable conditions, the investigation indicates that steady-state methods based on representative F_{carb} and F_{exp} factors can provide useful estimates of annual uptake. Tier 1 applies national average factors, while Tier 2 represents the application mix explicitly.

The progression from detailed product-specific descriptions towards simplified calculation approaches therefore represents a logical consequence of the scientific understanding developed in this chapter rather than a simplification lacking scientific justification.

5.6.4 Link to the proposed methodologies

The detailed carbonation assessment presented throughout Chapter 5 provides the scientific foundation for the methodologies proposed in Chapter 6.

The product-specific analyses identify the controlling carbonation mechanisms, plausible carbonation periods, chemical limitations, exposure conditions, and principal sources of uncertainty. These findings support the national average parameters used in Tier 1, the application-specific parameters used in Tier 2, and the progression functions used with annual consumption cohorts in Tier 3.

Chapter 5 therefore provides the scientific and methodological basis for the final methods but does not itself prescribe inventory calculations. The operative equations, defaults, applicability conditions, and reporting requirements are those specified in Chapter 6.

Thus, the assessment presented in Chapter 5 demonstrates that carbonation behaviour varies substantially among individual lime applications but follows common physicochemical principles. Although product-specific models provide the highest level of scientific detail, aggregation across the major application groups provides a sufficiently stable sector-level representation to support simplified inventory methodologies.

The following chapter builds directly upon these findings by presenting practical Tier 1, Tier 2, and Tier 3 methodologies for estimating annual CO_2 uptake in lime-containing products within national greenhouse gas inventories.

6 Proposed methodology for CO_2 uptake in lime products

6.1 General background

Lime products play a significant role in a wide range of industrial, construction, environmental, and agricultural applications. In many of these uses, lime is intentionally exposed to air, water, or soil environments in which calcium- and magnesium-based phases can react with atmospheric or dissolved carbon dioxide (CO_2) to form stable carbonate minerals. This process, commonly referred to as carbonation, represents a removal of CO_2 from the atmosphere and therefore constitutes a relevant component of national greenhouse gas inventories.

The extent, rate, and permanence of CO_2 uptake by lime products depend strongly on the chemical form of the lime, the physical characteristics of the product, and the conditions of use and exposure. Carbonation may occur through solid-state reactions at exposed surfaces, through pore systems within porous materials, or via aqueous-phase reactions where lime is partially dissolved in water as $Ca(OH)_2$. In many applications, carbonation is an intended and functional part of the product's performance, whereas in others it occurs only as a secondary process or is intentionally prevented.

Given this diversity, a single mechanistic model is not suitable for all lime products. Instead, a tiered methodological framework is required, allowing CO_2 uptake to be estimated using approaches of varying complexity and data demand, while maintaining consistency, transparency, and conservativeness in national inventories. The methodology must also clearly distinguish between applications that lead to carbonation and those in which carbonation is chemically or physically inhibited, in order to avoid overestimation of CO_2 uptake.

The purpose of this chapter is to present a harmonized set of calculation approaches for estimating CO_2 uptake by carbonation in lime products over their use phase and, where relevant, their end-of-life and secondary use. These approaches are designed to be compatible with national greenhouse gas inventory reporting, to support implementation at different Tier levels, and to provide a technically robust basis for future updates of international inventory guidelines.

6.1.1 Interpretation of the Tier 1, Tier 2 and Tier 3 levels

The Tier structure used in this report represents progressively increasing methodological detail, national specificity and data requirements. It is conceptually aligned with the Tier approach used in the IPCC Guidelines [55,56]. Because CO_2 uptake by carbonation of lime products is not yet covered by an adopted IPCC calculation method, the Tier designations used here describe a proposed methodological hierarchy rather than an existing formal IPCC classification.

Tier 1 is an aggregate default method. It uses total national apparent lime use, expressed on a consistent reactive-oxide basis, together with default parameters representing the average national share that is chemically eligible, physically accessible and ultimately carbonated. It does not require

allocation of lime use to individual product or application groups. Tier 1 is intended to be applicable where only national production and trade statistics are available.

Tier 2 is an application-disaggregated national method. It divides national lime use into a limited number of mutually exclusive application categories and applies category-specific parameters. Country-specific information should be used for the distribution of lime use and, where available, for chemical composition, carbonation completeness and exposure. The recommended Tier 2 method retains a steady-state treatment and does not require explicit tracking of historical consumption cohorts.

Tier 3 is a dynamic, country-specific method. It explicitly follows lime placed in use in different historical years and calculates the uptake occurring from each active cohort during the reporting year. Tier 3 uses application-specific activity data and carbonation progression functions and may additionally represent product geometry, material properties, service life, end-of-life treatment and secondary use. The method should be supported by country-specific data, measurements, validated models or other documented evidence.

The appropriate Tier should be selected according to data availability, national circumstances, the significance of the category and the results of key-category analysis. Different Tier levels may be applied to different application categories, provided that the results can be aggregated without omissions or double counting and that methodological consistency is maintained throughout the inventory time series.

6.2 General accounting principles (common to all methods and tiers)

The accounting of CO_2 uptake by lime products in national greenhouse gas inventories shall be based on a clear definition of system boundaries, chemically sound stoichiometry, and relevant assumptions regarding carbonation behaviour. The following general principles apply to all calculation approaches and Tier levels.

System boundary and attribution

CO_2 uptake shall be attributed exclusively to the life-cycle stage in which carbonation physically occurs. No CO_2 uptake shall be attributed to lime production, calcination, or other high-temperature industrial processes. Where lime or lime-derived materials are generated as by-products in industrial processes (e.g. carbide lime), any subsequent CO_2 uptake shall be attributed to the secondary use of the material, not to the primary process from which it originates. Each unit of lime shall be credited with CO_2 uptake only once over its entire life cycle, in order to avoid double counting across sectors or inventory categories.

Chemical eligibility for carbonation

Only lime products containing reactive calcium or magnesium oxides or hydroxides that are capable of forming stable carbonate minerals shall be considered eligible for CO_2 uptake. Applications in which lime is chemically transformed into non-carbonatable products (e.g. sulfates, nitrates, chlorides, phosphates, or silicates) shall be assigned zero CO_2 uptake, unless evidence demonstrates subsequent carbonation (e.g. uptake in excess/surplus/unreacted CaO). The maximum CO_2 uptake potential shall be determined from stoichiometric limits based on the molar conversion of CaO to

$CaCO_3$ and, where applicable, MgO to $MgCO_3$ or hydrated magnesium carbonates. So called dead-burned lime will still react with water to form calcium hydroxide and will also carbonate but with a significantly slower rate compared to soft-burned lime.

Physical access to CO_2

CO_2 uptake shall only be accounted for where physical access to atmospheric or dissolved CO_2 is plausible over the relevant time period.

Carbonation may be inhibited or negligible in applications where:

- lime is placed at significant depth in soil or ground.
- gas-phase diffusion is severely restricted.
- materials are permanently submerged or encapsulated.
- carbonation is limited to a shallow surface zone with negligible mass contribution.

In such cases, CO_2 uptake shall be conservatively assumed to be zero, unless country-specific evidence can support an alternative assumption.

Influence of surface treatments:

Surface treatments such as paints, coatings, renders, sealants, or wallpapers can significantly reduce or prevent CO_2 ingress into lime-based materials. In such cases, carbonation rates may be substantially reduced or effectively halted. Where such treatments are widespread or persistent, national inventory methodologies should account for their impact by applying reduced carbonation rates or lower effective carbonation degrees. In the absence of detailed data, a conservative approach should be adopted.

Time dependency and uptake distribution

CO_2 uptake by lime products is inherently time-dependent and shall be allocated to inventory years according to an appropriate uptake distribution.

Depending on product form and exposure conditions, uptake may be represented by:

- diffusion-controlled $\sqrt{t}$ behaviour.
- simplified lifetime-integrated uptake functions.
- or uniform annual uptake over a defined carbonation period.

The chosen uptake distribution shall:

- ensure that cumulative uptake does not exceed the stoichiometric maximum.
- reflect the expected physical and chemical behaviour of the product.
- be applied consistently across inventory years.

Where full carbonation is expected to occur within a defined period, total uptake shall be distributed only over that period, with no additional uptake assumed thereafter.

Product lifetime and end-of-life treatment

For many lime products, carbonation is expected to occur primarily or entirely during the use phase, often reaching completion within a few years to decades. Where full carbonation is achieved within the product lifetime, no additional CO_2 uptake shall be assigned at end-of-life. Where carbonation is incomplete at the end of the use phase and the material is subsequently reused, crushed, or otherwise exposed to CO_2, additional uptake may be accounted for in the secondary use phase, provided that carbonation is physically plausible, and that uptake is not already accounted for elsewhere in the inventory.

Tier consistency and conservativeness

All three Tiers shall apply the same system boundary, chemical basis, stoichiometric limits and rules for avoiding double counting. Increasing the Tier level shall improve the representation of national circumstances; it shall not change the fundamental definition of the removal.

- Tier 1 shall use aggregate national activity data and adopted default parameters.
- Tier 2 shall introduce nationally representative application distributions and category-specific parameters while retaining a simplified steady-state calculation.
- Tier 3 shall explicitly represent historical cohorts and the temporal development of carbonation and may use detailed kinetic, stock-and-flow or physically based models.

A method shall not be classified as Tier 2 or Tier 3 solely because it contains a more complex equation. The classification shall reflect the specificity and quality of the activity data, parameters and model used. Where default values are substituted for country-specific information, the resulting method should be described transparently as a hybrid application of the relevant Tiers.

Avoidance of double counting

CO_2 uptake by lime products shall not be double counted:

- across industrial sectors
- between primary and secondary uses
- or between use phase and end-of-life

Clear allocation rules shall be applied where lime products are used across sectoral boundaries or in multiple applications over time.

Reporting and transparency

National inventories shall document:

- which lime product categories are included.
- which applications are excluded or assumed to have zero uptake.
- the calculation methods and parameters used.
- and the Tier level applied for each product group.

Default values and assumptions shall be clearly distinguished from country-specific data.

Conservativeness of national totals

At the national level, CO_2 uptake estimates for lime products shall be capped by:

- total lime consumption.
- stoichiometric maximum uptake.
- and physically plausible carbonation behaviour.

Overestimation of uptake shall be avoided, particularly in Tier 1 applications, to ensure credibility and robustness of reported national greenhouse gas balances.

6.3 Tier 1: Simplified methodology

6.3.1 Aggregate steady-state Tier 1 method

This section defines the recommended Tier 1 method. It is the only Tier 1 method proposed in this report. The method uses aggregate national reactive-oxide use and default parameters and does not require allocation to product or application groups or explicit modelling of historical consumption cohorts.

Background and rationale

The carbonation behaviour of lime products differs fundamentally from that of cement-based concrete. In concrete, carbonation is generally slow and may continue for many decades or even centuries due to limited diffusion of carbon dioxide (CO_2) through relatively dense microstructures. For lime-containing products, carbonation generally proceeds considerably faster because carbonation predominantly occurs through calcium hydroxide ($Ca(OH)_2$), which has higher chemical reactivity, higher porosity, and greater accessibility to atmospheric CO_2.

Many lime products such as lime mortars, renders, plasters, soil stabilization layers, environmental treatment products, and exposed lime residues therefore carbonate substantially within years to decades rather than centuries. For several major applications, most carbonation occurs during an initial period after use, often within approximately one decade, although the exact rate depends on exposure conditions, geometry, humidity, material composition, and product type.

This faster carbonation behaviour makes it possible to use a substantially simplified methodology for national annual CO_2 uptake calculations compared with concrete carbonation methods. Instead of requiring detailed modelling of historical stocks and long-term carbonation kinetics, annual uptake can be estimated from current annual lime consumption combined with simplified assumptions regarding carbonation over time.

The simplified Tier 1 method is intended for:

- Countries with limited statistical data availability.
- First-order national estimates of CO_2 uptake.
- Non-key inventory categories where lower methodological complexity is acceptable.
- Countries initiating reporting of carbonation uptake from lime products.

The method is designed to be transparent, simple to implement, and consistent with IPCC principles that removals should neither be systematically overestimated nor underestimated.

Fundamental methodological principle

The simplified Tier 1 method is based on the observation that most carbonation in lime products occurs within a relatively short period of time after use/application. Unlike concrete, where carbonation often continues over many decades, lime carbonation generally takes place much faster and is often largely completed within approximately 10 years for many exposed applications.

If carbonation occurs approximately uniformly over a characteristic carbonation period, annual uptake can be estimated without explicitly tracking historical lime consumption for each previous year.

As an illustrative example, assume that full carbonation occurs over 10 years. In this case, approximately one tenth of the carbonation potential of each year's lime use is realized annually. The annual uptake in a given year can then be approximated by summing the uptake contributions from lime used during the previous 10 years.

However, under stable market conditions where national lime use does not change substantially over time, the sum of uptake contributions from historical years becomes approximately equal to the uptake potential associated with the present year's national lime use. This means that annual CO_2 uptake can be approximated directly from present national lime consumption without explicit historical modelling.

This steady-state assumption significantly simplifies the methodology while maintaining reasonable accuracy for national inventory purposes.

Activity data
The Tier 1 approach is based on national annual lime consumption, expressed in terms of lime product mass or CaO-equivalent mass. If the different lime products are reported separately (e.g. quicklime, hydrated lime, dolomitic lime), they may be aggregated using documented conversion factors. The national lime balance shall be calculated as:

National lime use = National lime production + Import - Export

Activity data may be obtained from:
- national statistics offices
- industry associations
- trade statistics

Tier 1 calculation method
The annual CO_2 uptake in year y is estimated according to the equation below:

$$U_y = L_{use,y} \times CF_{CaO} \times F_{carb} \times F_{exp}$$

where:
U_y = annual national CO_2 uptake in reporting year y (tonnes CO_2/year).
$L_{use,y}$ = total national apparent use of reactive CaO-eq. in year y, including the reactive CaO fraction of dolomitic lime, expressed as tonnes CaO-eq./year.
CF_{CaO} = stoichiometric carbonation factor for CaO equal to 44.01/56.08 = 0.785 tonnes CO_2 per tonne reactive CaO-eq.
F_{carb} = ultimate chemically achievable carbonation fraction (dimensionless, 0–1).
F_{exp} = physically accessible fraction exposed to atmospheric or dissolved CO_2 (dimensionless, 0–1); it shall not duplicate a limitation already included in F_{carb}.

Treatment of dolime and MgO
The base Tier 1 calculation includes only the reactive CaO content of the lime products. For dolomitic lime, the CaO component may therefore be included after conversion to its reactive CaO mass, whereas the MgO component is excluded from the base calculation.

As an option, CO_2 uptake by reactive MgO may be estimated separately using the same Tier 1 steady-state approach. In that case, MgO-specific activity data, a MgO-specific stoichiometric factor and appropriate MgO-specific carbonation and exposure factors shall be used. The stoichiometric factor, CF_{MgO}, for complete conversion of MgO to $MgCO_3$ is 44.01/40.30 = 1.092 tonnes CO_2 per tonne MgO. Because MgO carbonation is generally slower and may be less complete than CaO carbonation under ambient conditions, the CaO default values shall not be applied automatically to MgO. The MgO parameters and the applicability of the steady-state assumption shall be documented and justified. The separately calculated CaO and MgO uptake estimates may then be added to obtain the total Tier 1 CO_2 uptake.

The national apparent lime use may be estimated according to the equation below:

$$L_{use,y} = L_{production,y} + L_{import,y} - L_{export,y} + \Delta L_{stock,y} + L_{adjust,y}$$

where:
$L_{production,y}$ = domestic lime production in year y, converted to the common chemical basis.
$L_{import,y}$ = lime imported in year y and placed in domestic use, on the common chemical basis.
$L_{export,y}$ = lime exported in year y, on the common chemical basis.
$\Delta L_{stock,y}$ and $L_{adjust,y}$ = stock change and other documented balance adjustments; use a consistent sign convention and set these terms to zero only when demonstrably immaterial.

National production and trade data should preferably be obtained from national statistics, industrial associations, or official reporting systems.

Default assumptions for Tier 1 calculations
For a simplified Tier 1 estimate, the following default assumptions are proposed:

- Characteristic carbonation period: 10 years.
- Indicative applicability range (no used in Tier 1 calculations): 8–12 years.
- Carbonation completeness factor (F_{carb}): 0.80.
- Exposure factor F_{exp} = 0.90 ; this default may be replaced where national data justify another value.[3]

The default carbonation period of 10 years reflects the substantially faster carbonation of lime products compared with concrete and is considered representative for a broad mixture of exposed lime applications at national level. Although some products may carbonate within months or only a few years while others require longer periods, the use of a characteristic average carbonation period provides a sufficiently robust approximation for Tier 1 inventory calculations.

[3] Fcarb = 0.80 combined with Fexp = 0.90 credits 72% of the stoichiometric maximum for all apparent national lime use.

The carbonation factor F_{carb} represents chemical or mineralogical limitations on ultimate carbonate formation, including conversion of reactive lime into non-carbonatable phases. The exposure factor F_{exp} separately represents physical accessibility to atmospheric or dissolved CO_2, including encapsulation, burial and restricted contact with air or water. The same limitation shall not be represented in both factors.

Since complete stoichiometric carbonation is seldom achieved in all lime applications, a default factor of $F_{carb} = 0.80$ is proposed as a conservative estimate. An estimation of the exposure factor, F_{exp}, in general can be difficult as the local application can vary significantly. A value of 0.9 for F_{exp} has been used in this study.

Justification for the simplified Tier 1 method
The simplified methodology is justified by four main considerations.

1. Faster carbonation kinetics in lime products
Lime carbonation occurs considerably faster than carbonation in concrete because carbonation mainly proceeds through calcium hydroxide ($Ca(OH)_2$), which has higher reactivity and porosity. As a result, substantial carbonation often occurs within years rather than decades or centuries.

2. Limited influence of historical stocks
Because carbonation generally occurs over relatively short timescales, the influence of historical lime stocks becomes substantially less important than for concrete carbonation. Under relatively stable national lime consumption, annual uptake approaches equilibrium with annual lime use.

3. Availability of national statistics
Most countries already possess annual statistics on lime production, imports, and exports. The method can therefore be implemented without requiring detailed information on product categories, geometry, exposure conditions, or historical use patterns.

4. Conservative handling of uncertainty
The method incorporates conservative assumptions regarding carbonation completeness and exposure to avoid systematic overestimation of CO_2 uptake. This makes the method suitable as a Tier 1 methodology and as a first approximation for countries with limited available data.

Limitations of the method
The simplified Tier 1 method may be less accurate in countries with:

- Rapidly increasing or decreasing lime consumption.
- Unusually high shares of slowly carbonating applications.
- Large fractions of lime used in closed industrial systems without carbonation potential.
- Strongly deviating climatic or exposure conditions.

In such cases, Tier 2 or Tier 3 approaches should preferably be applied.

Reporting recommendations

Countries applying the Tier 1 method should transparently document:

- National lime production, import, and export statistics.
- Assumed carbonation period.
- Carbonation completeness assumptions.
- National adjustments to default factors.
- Treatment of lime applications assumed to have negligible carbonation.

The method is intended as a first-order estimate and a starting point for future development toward more country-specific Tier 2 and Tier 3 methodologies.

Summary of Tier 1 characteristics

Aspect	Tier 1 approach
Data requirement	Low
Complexity	Low
Uptake mechanism	Stoichiometric + default fractions
Temporal treatment	Annual steady-state estimate; characteristic period used only to assess applicability
Conservativeness	High
IPCC compatibility	High

6.4 Tier 2: Improved methodology

6.4.1 Application-disaggregated steady-state Tier 2 method

Background and rationale

The Tier 1 method described in Chapter 6.3 provides a simplified estimate of annual CO_2 uptake based on present national lime use and average carbonation assumptions. While suitable for countries with limited data availability, significant uncertainties may arise because carbonation behaviour differs substantially between various lime applications.

Tier 2 represents the intermediate methodological level between the aggregate Tier 1 method and the dynamic Tier 3 method. Its defining improvement is the use of national information to allocate current lime use among major, mutually exclusive application categories and to apply category-specific parameters. It retains the steady-state approximation and therefore does not require the historical cohort matrix used at Tier 3.

Lime products are used in a wide range of applications with different exposure conditions, geometries, moisture conditions, and service lives. Consequently, the carbonation rate and the ultimate degree of carbonation may vary considerably between application categories. For example, exposed lime mortars and plasters may carbonate almost completely within a few years, whereas carbonation of lime used in soil stabilization or in some industrial applications may proceed more slowly and may remain incomplete.

The objective of the Tier 2 method is therefore to improve the accuracy of annual CO_2 uptake calculations by dividing national lime use into major application categories and applying category-specific carbonation parameters. Unlike Tier 3 methods, no detailed modelling of historical lime consumption is required. The method instead relies on the observation that carbonation of most lime products occurs over relatively short timescales and that annual uptake can therefore be approximated using present national lime consumption.

The Tier 2 method is recommended for countries where information is available regarding the distribution of lime use between major application sectors.

Fundamental methodological principle

The Tier 2 method is based on the same steady-state principle as the Tier 1 method. Under relatively stable market conditions, the annual carbonation uptake from the accumulated stock of previously used lime products is approximately balanced by the carbonation potential represented by current annual lime use.

However, instead of treating all lime products as a single category, the Tier 2 method divides annual lime use into separate application groups. Each application group is assigned a specific carbonation completeness factor and exposure factor that better reflects its actual carbonation behaviour.

The annual CO_2 uptake is therefore estimated as the sum of the uptake from all application categories.

Tier 2 calculation method
The annual CO_2 uptake in year y is estimated according to the equation below:

$$U_y = \sum_i L_{i,y} CF_i F_{carb,i} F_{exp,i}$$

where:

U_y = annual national CO_2 uptake in reporting year y (tonne CO_2/year).

$L_{i,y}$ = apparent lime use in application category i in year y, on the stated chemical basis (e.g. tonne lime/year).

CF_i = stoichiometric CO_2 uptake factor for the chemical basis of category i (e.g. tonne CO_2/tonne lime).

$F_{carb,i}$ = ultimate chemically achievable carbonation fraction for application category i.

$F_{exp,i}$ = physically accessible fraction for category i; it shall not overlap with $F_{carb,i}$.

The total national lime use shall satisfy:

$$L_{use,y} = \sum_i L_{i,y}$$

where $L_{use,y}$ is the total national apparent lime use.

Recommended application categories
Countries should divide national lime consumption into major application categories where statistical information is available. The following categories are recommended:

- Lime mortars and masonry mortars.
- Lime renders and plasters.
- Soil stabilization and ground improvement.
- Environmental applications (water treatment, flue gas treatment, sludge treatment, etc.).
- Industrial applications with carbonation potential.
- Secondary products and residues.

Countries may further subdivide categories if more detailed national information is available.

Category-specific carbonation assumptions
Application-specific carbonation factors should reflect the expected degree of carbonation achieved during service life, end-of-life management, and possible secondary use.

Representative default values may be developed from available literature and national experience. Typical carbonation periods for many lime applications are substantially shorter than for concrete and commonly fall within the range of approximately 5–20 years.

Applications with direct atmospheric exposure generally exhibit higher carbonation completeness than applications where lime becomes physically encapsulated or where CO_2 access is restricted.

Tier 2 should use country-specific information for the distribution of lime use among application categories and for the most influential category parameters. Default category parameters may be used where country-specific values are unavailable, but their use shall be identified. A calculation based entirely on default application shares and default category factors should be described as a Tier 1/Tier 2 hybrid rather than as a fully country-specific Tier 2 method.

Steady-state approximation
The Tier 2 method assumes that annual uptake from historical lime use can be approximated by present annual lime use within each application category.

This assumption is justified because:

- Carbonation of lime products generally occurs within years to decades.
- The effective carbonation residence time is considerably shorter than for concrete.
- Most national lime markets exhibit relatively stable long-term consumption patterns.
- The resulting annual uptake estimate approximates the uptake that would be obtained from explicit modelling of recent historical cohorts.

Countries experiencing rapid growth or decline in lime consumption should evaluate whether the Tier 2 assumptions remain valid or whether a Tier 3 methodology should be applied.

Advantages of the Tier 2 method
Compared with Tier 1, the Tier 2 method provides improved accuracy by:

- Accounting for differences between major lime applications.
- Allowing national adaptation of carbonation factors.
- Reflecting differences in exposure conditions and carbonation completeness.
- Maintaining a relatively simple calculation procedure.

The method can be implemented using national statistics on lime production, imports, exports, and sectoral use without requiring advanced dynamic stock modelling.

Limitations

The method does not explicitly model historical lime stocks or annual carbonation progress of individual product cohorts. Consequently, some inaccuracies may occur in countries with rapidly changing lime consumption patterns or highly unusual application distributions.

For countries where carbonation uptake represents a key category, or where detailed national data are available, the Tier 3 methodology described in Chapter 6.5 should be preferred.

Reporting recommendations

Countries applying the Tier 2 method should document:

- National lime production, imports, and exports.
- Distribution of lime use between application categories.
- Carbonation completeness factors used.
- Exposure factors used.
- National deviations from default values.
- Sources of statistical data and expert judgement.

The Tier 2 method is intended to provide a transparent and practical balance between simplicity and accuracy and is recommended as the preferred methodology where sector-specific lime use statistics are available.

Summary of Tier 2 characteristics

Aspect	Tier 2 approach
Data requirement	Medium
Product resolution	Application-specific steady state
Temporal treatment	Annual steady-state estimate
Cohort modelling	Not required
End-of-life treatment	Included through non-overlapping category parameters or a mutually exclusive secondary-use category Linear/$\sqrt{t}$ model
Conservativeness	Medium–high
IPCC compatibility	High

6.5 Tier 3: Advanced methodology

6.5.1 Application-specific national consumption-cohort method

Background and rationale

The Tier 1 and Tier 2 methodologies described in Chapters 6.3.1 and 6.4.1 estimate annual CO_2 uptake using present annual lime use and the assumption that carbonation of lime products occurs over relatively short time periods. These methods are appropriate where limited information is available and where simplification is justified.

For key categories and countries with more detailed data availability, a more advanced methodology can be applied. The Tier 3 methodology explicitly represents the accumulated stock of lime-containing products originating from historical annual lime consumption and quantifies the annual CO_2 uptake from each individual consumption cohort.

The method recognizes that carbonation uptake occurring in a given year originates not only from lime used during the current year but also from lime products placed on the market during previous years that continue to carbonate.

Compared with concrete products, carbonation of lime products generally occurs much faster due to the high reactivity of calcium hydroxide and the typically more open pore structure of lime materials. Consequently, a dynamic stock model covering a limited number of previous years is often sufficient to describe the majority of national carbonation uptake.

The methodology is intended for countries where carbonation uptake constitutes a key category or where sufficient historical data exist regarding national lime consumption and application-specific use patterns.

The defining feature of this Tier 3 method is the explicit allocation of uptake from individual historical lime-use cohorts to the reporting year in which carbonation occurs. Tier 3 therefore removes the steady-state assumption used at Tier 1 and Tier 2. Application-specific activity data, chemical composition, eligibility, ultimate carbonation and temporal progression are represented separately.

A cohort calculation using only generalized default parameters may improve temporal representation but does not, by itself, provide full Tier 3 national specificity. Tier 3 implementation should therefore use country-specific or otherwise nationally representative activity data and parameters for the categories that materially affect the result.

Fundamental methodological principle

The Tier 3 methodology is based on annual consumption cohorts.

The method uses the convention that lime belonging to consumption cohort (n) enters use at the beginning of year (n). Its age at the beginning of the reporting year (y) is therefore:

$a = y–n$

where:
a = age of the cohort at the beginning of reporting year (y), in years. The corresponding ordinal interval label is j = a + 1 = y − n + 1.
y = reporting year.
n = year in which the lime enters use (normally the year of consumption/production).

Consequently, a cohort entering use during the reporting year has (a=0).

Examples for reporting year 2025 are shown below:

Consumption cohort n	Age at start of 2025, a=2025−n
2025	0
2024	1
2023	2
2022	3
2021	4
2020	5

Each year's lime use is treated as an individual cohort that continues to carbonate over a defined carbonation period. The annual uptake in a given reporting year is calculated as the sum of uptake contributions from all historical cohorts that remain active.

The method therefore explicitly represents the time lag between lime consumption and CO_2 uptake.

Annual uptake is calculated from:

- Historical lime consumption.
- Distribution of lime use among application categories.
- Application-specific carbonation functions.
- Application-specific carbonation completion factors.
- Application-specific exposure factors.

The annual national uptake is calculated as the sum of uptake from all application categories and all historical cohorts.

Purpose and scope
The recommended Tier 3 methodology provides country-specific annual estimates by combining historical lime-use cohorts with application-specific ultimate uptake parameters and cumulative carbonation progression functions. It is intended for countries that can compile historical activity data, allocate lime use to mutually exclusive product or application categories, and justify category-specific carbonation periods or progression functions. Detailed product properties and mechanistic kinetic models may be used to derive or validate these parameters where appropriate, but they are not required for every Tier 3 cohort calculation. Explicit physical-stock, service-life and end-of-life modelling belongs principally to the alternative advanced method described in Section 6.5.2.

Activity data and material characterisation
Tier 3 requires annual historical activity data by product or application category on a documented reactive-oxide basis, including:

Lime production and consumption by:

- product type (quicklime, hydrated lime, dolomitic lime, magnesium-based lime)
- application and sector
- primary and secondary use

Depending on the method used to derive or validate category parameters, supporting material properties may include:

- CaO and MgO content
- mineralogical composition
- porosity and pore size distribution
- particle size or layer thickness
- moisture content

Where by-product lime streams are used, their chemical composition and physical form shall be characterised separately.

Identification of eligible and non-eligible applications
At Tier 3, lime consumption shall be divided into two broad categories:

I. Carbonating applications
Applications in which lime is expected to undergo partial or full carbonation under typical conditions of use, such as:

- construction and building products
- soil and agricultural applications
- environmental and water treatment uses with CO_2 exposure
- secondary uses of lime-containing by-products

II. Non-carbonating applications
Applications shall be assigned zero CO_2 uptake where:

- lime is chemically converted to non-carbonatable compounds (e.g. sulfates, nitrates, chlorides, phosphates). In case of excess use of lime, such as in SO_2 removal in coal power plants, the surplus lime can still carbonate even if the main part of the lime is prevented from carbonation.
- lime is placed at depth or encapsulated such that CO_2 access is negligible.
- carbonation is confined to a shallow surface zone with negligible mass contribution.

In the absence of national data, verified specific or default fractions may be used to estimate the share of lime used in carbonating applications.

Maximum CO_2 uptake potential

For lime used in carbonating applications, the maximum CO_2 uptake potential shall be calculated based on stoichiometry.

For calcium-based lime:

$CaO + CO_2 \longrightarrow CaCO_3$

The theoretical maximum CO_2 uptake is:

$$U_{max\ CO2} = M_{CaO}\ CF_{CaO} = M_{CaO} \times \frac{44.01}{56.08}$$

For magnesium-based lime:

$MgO + CO_2 \longrightarrow MgCO_3$

The theoretical maximum CO_2 uptake is:

$$U_{max\ CO2} = M_{MgO}\ CF_{MgO} = M_{MgO} \times \frac{44.01}{40.30}$$

where:

$U_{max\ CO2}$ = total mass of carbonated CO_2 (kg).

M_{CaO} = total mass of reactive CaO for carbonation (kg).

M_{MgO} = total mass of reactive MgO for carbonation (kg).

Carbonation fraction

In Tier 3, the category-specific carbonation factor $F_{carb,i}$ represents the chemically achievable fraction of the stoichiometric maximum. It accounts for reactive mineral content, incomplete chemical conversion and transformation of reactive lime into non-carbonatable phases. Physical restrictions on contact with atmospheric or dissolved CO_2 shall be represented separately by $F_{exp,i}$. The same limitation shall not be included in both factors. Material losses should normally be corrected in the activity data or assigned to another documented material-flow category rather than included in $F_{carb,i}$.

Dependence on binder composition:

For each Tier 3 category, $F_{carb,i}$ should reflect the chemical and mineralogical characteristics of that category rather than an average across unrelated applications. In mixed cement–lime binders, incorporation of calcium in less reactive phases may reduce the chemically achievable carbonation fraction, while reduced porosity may also affect the carbonation period or progression function. These chemical and physical effects should be represented separately and documented.

Time distribution of CO_2 uptake

Tier 3 represents carbonation over a documented, category-specific carbonation period reflecting the behaviour of each lime-product or application category.

Two simple default time-distribution options are presented below: linear progression (I) and square-root progression (II). A different documented country-specific progression function may be used where supported by appropriate evidence.

First, national lime use is divided into mutually exclusive product or application groups with similar carbonation behaviour. For each group i, the ultimate eligible CO_2 uptake of lime used in year n $U_{i,n}^{ult}$ is calculated as:

$$U_{i,n}^{ult} = L_{i,n} CF_i F_{carb,i} F_{exp,i}$$

where $L_{i,n}$ is the quantity of lime used, CF_i is the stoichiometric CO_2 uptake factor, $F_{carb,i}$ is the ultimately achievable carbonation fraction, and $F_{exp,i}$ is the physically accessible fraction.

Each group is then assigned a carbonation period T_i and a carbonation progression function, using linear option I, square-root option II, or another documented country-specific function.

I. Linear uptake distribution (default)

Total uptake is distributed evenly over the documented category-specific carbonation period, T_i as follows:

$$F_i(a) = min(\frac{a}{T_i}, 1) \quad \text{linear progression}$$

When a reaches T_i, $F_i(a)=1$), meaning that 100% of the available lime has carbonated. The function remains equal to 1 thereafter, since uptake cannot exceed the available carbonation capacity.

Here, a=y-n is the age of the lime-use cohort at the beginning of reporting year y. The fraction carbonating during that year is:

$\Delta F_i(a) = F_i(a+1) – F_i(a)$

and

$$U_y = \sum_i \sum_n U_{i,n}^{ult} \Delta F_i(y - n)$$

For the linear model, the annual fraction is $1/T_i$ in each year until carbonation is complete, thus,

$$U(a) = \frac{U_{total}}{T} \quad (a=0, \ldots, T-1)$$

where:

$U(a)$ = CO_2 uptake allocated to the one-year interval from cohort age a to a + 1.

U_{total} = total CO_2 uptake over the carbonation period.

T = total number of years in the carbonation period.

This approach is simple and transparent.

II. $\sqrt{t}$ uptake distribution

Where national practice allows, uptake may be distributed according to a $\sqrt{time}$ function such as:

$$F_i(a) = \min\left(\sqrt{\frac{a}{T_i}},\ 1\right) \quad \text{square-root progression}$$

When a reaches T_i, ($F_i(a)=1$), meaning that 100% of the available lime has carbonated. The function remains equal to 1 thereafter, since the uptake cannot exceed the available carbonation capacity.

and

$$\Delta F_i(a) = F_i(a+1) - F_i(a) = \frac{\sqrt{a+1} - \sqrt{a}}{\sqrt{T_i}} \quad (0 \le a < T_i) \quad \text{square-root progression}$$

Finally, uptake in reporting year y is obtained by summing the contributions from all application groups and all active historical cohorts:

$$U_y = \sum_i \sum_n U_{i,n}^{ult}\, \Delta F_i(a)$$

where:

$F_i(a)$ = cumulative fraction of ultimate uptake achieved at the exact annual boundary age a.

$\Delta F_i(a) = F_i(a+1) - F_i(a)$, the fraction of ultimate uptake occurring during the interval from age a to a + 1.

U_y = annual national CO_2 uptake in reporting year y.

T_i = total number of years in the carbonation period for category i.

a = completed cohort age at the start of reporting year y; a = y – n.

This distribution better reflects early rapid carbonation but remains simple to implement.

Annual CO_2 uptake calculation

Annual national CO_2 uptake is calculated as:

$$U_y = \sum_i \sum_n L_{i,n}\ CF_i\ F_{carb,i}\ F_{exp,i}\ [F_i(a+1)-F_i(a)], \quad a=y-n$$

where:

U_y = annual national CO_2 uptake in reporting year y.

$L_{i,n}$ = mass of reactive oxide in application category i entering use in cohort n.

$F_{carb,i}$ = ultimate chemically achievable carbonation fraction for oxide in application category i.

$F_{exp,i}$ = physically accessible fraction for oxide in application category i.

$F_i(a + 1) - F_i(a)$ = fraction of ultimate uptake allocated to reporting year y from cohort n, with a = y – n.

Thus, each year's lime use is distributed over its future carbonation years, while the uptake reported in any particular year is the sum of the relevant fractions from all lime-use cohorts still undergoing carbonation.

Treatment of by-products and secondary uses

Lime by-products (e.g. carbide lime) shall not be assigned CO_2 uptake in the primary industrial process. If such materials are reused in carbonating applications, they shall be included in the lime consumption of the corresponding use category, and uptake shall be calculated in the same manner as for primary lime products in the corresponding secondary application.

General calculation method

The annual CO_2 uptake in reporting year y is calculated as:

$$U_y = \Sigma_i \Sigma_n U_{i,n,y}$$

where:

U_y = annual national CO_2 uptake in reporting year y (tonne CO_2/year).

$U_{i,n,y}$ = uptake contribution during year y from application category i and consumption cohort n.

i = application category.

n = year of lime consumption.

For each application category, annual uptake is calculated as:

$$U_{i,n,y} = L_{i,n}\ CF_i\ F_{carb,i}\ F_{exp,i}\ \Delta F_i(a)$$

where:

$L_{i,n}$ = lime consumption in application category i during year n.

CF_i = stoichiometric carbonation factor.

$F_{carb,i}$ = ultimate carbonation completeness factor.

$F_{exp,i}$ = exposure factor.

$F_i(a)$ = cumulative carbonation progression function.

$\Delta F_i(a)$ = the annual increment carbonation function.

$\Delta F_i(a) = F_i(a+1) – F_i(a)$, the annual increment of the cumulative carbonation function assigned to reporting year y.

$a = y–n$

if an ordinal age-year is shown, j = a + 1

The complete uptake equation can therefore also be written as:

$$U_{i,n,y} = L_{i,n}\ CF_i\ F_{carb,i}\ F_{exp,i}\ [F_i(y\text{-}n+1) - F_i(y\text{-}n)]$$

$F_i(a)$ describes the normalized cumulative carbonation progression at the exact annual boundary age a. The symbol t is reserved for continuous elapsed physical time in kinetic relations such as $x(t) = k_C\sqrt{t}$.

Carbonation progression functions
The carbonation progression function may be represented by country-specific data or by default functions.

A simple linear cumulative progression function at annual boundary age a can be used:

$F_i(t) = t/T_i$ for $t \leq T_i$

$F_i(t) = 1$ for $t > T_i$

or

$F_i(a)=\min(a/T_i, 1)$

where:
T_i = characteristic carbonation period for application category i.

Alternatively, countries may apply more advanced functions representing observed carbonation behaviour.

Examples include:

- Parabolic carbonation functions based on diffusion-controlled carbonation, where carbonation progress is proportional to the square root of time.
- Exponential functions.
- Logarithmic functions.
- Sigmoidal functions.
- Functions derived from field measurements.

The use of country-specific carbonation functions is encouraged where sufficient information is available.

Recommended application categories
The same application categories as described for Tier 2 should be used where possible:

- Lime mortars and masonry mortars.
- Lime renders and plasters.
- Soil stabilization and ground improvement.
- Environmental applications.
- Industrial applications with carbonation potential.
- Secondary products and residues.

Countries may introduce additional categories where national statistics permit further subdivision.

Historical data requirements
When the methodology is first implemented, historical activity data are required for a period sufficient to cover all earlier lime-use cohorts that may still contribute to uptake in the first reporting year. Once the time series and cohort database have been established, annual updating is considerably simpler. For each new reporting year, only the activity data and relevant parameters for the new lime-use cohort normally need to be added. The calculation model retains the previously recorded cohorts and automatically calculates their remaining contributions, together with the contribution from the new cohort, to the CO_2 uptake in the current reporting year. Historical data should be revised only where improved information, corrected statistics or methodological changes require recalculation of the time series.

Thus, the methodology requires annual lime consumption data for previous years at start of the CO_2 uptake reporting. As carbonation of lime products generally proceeds considerably faster than carbonation of concrete, complete historical datasets extending many decades into the past are normally unnecessary. For most national inventories, historical consumption data covering approximately 10–30 years will capture the majority of annual carbonation uptake. The required historical period depends on the carbonation characteristics of the applications included. Applications with rapid carbonation may require only a limited historical dataset, whereas slower-carbonating applications may justify longer time series.

Advantages of the Tier 3 methodology
Compared with Tier 2, the Tier 3 methodology:

- Explicitly represents the time lag between lime consumption and carbonation uptake.
- Accounts for changing national lime consumption over time.
- Accounts for changes in application patterns.
- Allows use of measured carbonation functions.
- Provides a more detailed representation of annual time series.
- Better reflects national circumstances.

The methodology is particularly advantageous in countries experiencing significant changes in lime consumption or application patterns.

Limitations
The methodology requires:

- Historical national lime consumption data.
- Information on application-specific lime use.
- Additional modelling resources.
- Periodic updating of carbonation parameters.

The method is therefore more resource-intensive than Tier 1 and Tier 2 approaches.

Reporting recommendations
Countries applying the Tier 3 methodology should document:

- Historical lime consumption datasets.
- Application-specific allocation procedures.
- Carbonation functions applied.
- Carbonation completion assumptions.
- Exposure assumptions.
- Data sources and quality-control procedures.

Where country-specific carbonation functions are applied, supporting documentation should be provided describing the experimental data, field observations, or scientific basis used to derive the functions.

The Tier 3 methodology is recommended for key categories and provides the most detailed representation of annual CO_2 uptake at national level. Country-specific Tier 3 data and experience can also be used to improve national Tier 1 and Tier 2 parameters over time.

6.5.2 Full dynamic stock-and-flow model (alternative advanced method)

Product-specific carbonation mechanisms
For each lime or dolime product category, the dominant carbonation mechanism shall be identified and modelled explicitly. The following mechanisms may be applied individually or in combination:

- Surface-controlled carbonation with a moving reaction front,
- Bulk or particle carbonation for fine or porous materials,
- Aqueous-phase carbonation for dissolved or slurry systems,
- Magnesium-based carbonation forming hydrated magnesium carbonates.

The choice of mechanism shall be justified based on material properties and use conditions.

Kinetic modelling approaches
Tier 3 allows the use of explicit kinetic models tailored to the carbonation mechanism.

I. Diffusion-controlled carbonation (parabolic model)
For products with a defined exposed surface and carbonation front:

$$x(t) = k_C\sqrt{t}$$

where:
x(t) = carbonation depth as a function of time
k_C = product-specific carbonation-depth coefficient (length/$\sqrt{time}$)
t = time

Carbonated volume and CO_2 uptake are calculated from the evolving carbonation depth and product geometry. This model is mainly used for, for example, air lime mortar, lime render or lime plaster. Note that gypsum plaster ($CaSO_4$ ½H_2O, plaster of Paris) does not carbonate through the lime-carbonation reaction.

II. Particle-scale or bulk carbonation models

For fine or granular lime products, carbonation may be modelled using:

- shrinking-core models
- surface-area-controlled reaction rates
- particle size distribution–weighted uptake

III. Aqueous-phase carbonation models

For lime slurries and aqueous systems:

- CO_2 mass transfer
- dissolution equilibria
- residence time distributions

shall be used to determine the extent of carbonation. Where kinetic data are unavailable, conservative uptake bounds shall be applied.

Stoichiometric and thermodynamic constraints

For all models:

- CO_2 uptake shall not exceed the stoichiometric maximum determined by reactive CaO and MgO content.
- Thermodynamic feasibility of carbonate formation shall be verified for relevant environmental conditions.

Time-resolved uptake allocation

Tier 3 explicitly allocates CO_2 uptake to individual inventory years using the time-dependent results of the kinetic models. For products that fully carbonate within their service life, uptake is limited to the defined carbonation period. For partially carbonating products, residual uptake may be carried forward into secondary use or end-of-life stages.

End-of-life and secondary use modelling

Tier 3 explicitly tracks lime products through:

- demolition
- reuse
- crushing
- landfill application

Additional carbonation due to increased surface area or exposure shall be modelled using updated kinetic parameters and material states. The same type of carbonation models as mentioned above can also be applied for end-of-life and secondary use carbonation.

Treatment of non-carbonating pathways

Where lime reacts to form non-carbonatable compounds:

- these pathways shall be explicitly modelled or excluded
- competing reactions shall be quantified where possible

Normally, such pathways shall be set to zero CO_2 uptake.

Uncertainty analysis and model validation
Tier 3 methodologies shall include:

- parameter uncertainty ranges
- sensitivity analysis
- comparison with measured carbonation data where available

Model assumptions shall be documented and periodically reviewed.

Aggregation to national totals
National CO_2 uptake is calculated as the sum of time-resolved uptake across all product categories, applications, and life-cycle stages.

Consistency with Tier 1 and Tier 2 totals shall be checked to ensure no omissions or double counting.

Reporting and transparency
Tier 3 reporting shall include:

- detailed methodological descriptions
- data sources and parameter values
- justification for model choices
- documentation of uncertainties

Summary of Tier 3 characteristics

Aspect	Tier 3 approach
Data requirement	High
Product resolution	Product- and application-specific
Kinetic modelling	Explicit and mechanism specific
Time resolution	Annual or finer
Stock and end-of-life modelling	Explicit where relevant
Accuracy	Potentially high; dependent on data quality and validation
IPCC compatibility	High when consistent with the general accounting principles

Role of Tier 3 in national inventories
Tier 3 is recommended for:

- countries with significant lime consumption
- key lime-using sectors
- development of emission factors and methodological refinement

Tier 3 results may also be used to derive default parameters for Tier 2 and Tier 1 methodologies and to support future IPCC guideline development.

6.6 Comparison of Tier 1, Tier 2 and Tier 3 methodologies

The methodologies presented in Chapters 6.3, 6.4, and 6.5 represent increasing levels of complexity and national specificity for estimating annual CO_2 uptake in lime-containing products. The three tiers are based on the same fundamental carbonation principles but differ in their treatment of lime consumption data, application categories, carbonation progression, and historical stock development.

The choice of methodology should reflect the importance of carbonation uptake within the national greenhouse gas inventory, the availability of national data, and the resources available for inventory development and maintenance.

6.6.1 Methodological comparison

The Tier 1 methodology provides a simplified estimate of annual CO_2 uptake based on current national lime consumption and average carbonation assumptions. The method assumes that carbonation occurs over a relatively short period and that annual uptake can be approximated from present lime use under steady-state conditions.

The Tier 2 methodology improves upon Tier 1 by dividing national lime consumption into major application categories and assigning application-specific carbonation factors. This allows differences in carbonation behaviour between applications to be considered while maintaining a relatively simple calculation framework.

The Tier 3 methodology introduces explicit modelling of historical lime consumption cohorts and application-specific carbonation progression functions. Annual CO_2 uptake is calculated as the sum of contributions from historical lime use that continues to carbonate during the reporting year. The method therefore provides the most detailed representation of the timing of carbonation uptake and allows country-specific carbonation functions to be incorporated.

Although the methodologies differ in complexity, they are all based on the same ultimate carbonation potential of the lime products included in the calculation.

6.6.2 Data requirements

The three tiers require different levels of data availability.

Tier 1 requires only national statistics for lime production, imports and exports together with default carbonation assumptions. This methodology can therefore be implemented by most countries using existing national statistical information.

Tier 2 requires, in addition to national lime consumption data, information regarding the distribution of lime use among major application categories. Application-specific carbonation factors are then applied to improve the accuracy of the estimate.

Tier 3 requires historical lime consumption data, allocation of consumption to application categories, and carbonation progression functions describing the development of carbonation over time. Additional data may include country-specific measurements, field observations, service-life information, and end-of-life management practices.

Consequently, the data requirements, resource demands, and computational complexity increase from Tier 1 to Tier 3.

6.6.3 Uncertainty associated with carbonation timing

An important characteristic of lime carbonation is that most carbonation typically occurs over relatively short periods compared with many other mineral materials. Depending on application type, exposure conditions, and material characteristics, substantial carbonation often occurs within approximately 5–20 years.

The primary uncertainty in carbonation modelling is therefore frequently associated with the timing of uptake rather than the ultimate quantity of CO_2 uptake. The total carbonation potential is largely constrained by stoichiometry and by the achievable degree of carbonation, whereas the exact annual distribution of uptake depends on the carbonation function applied.

As a result, different methodologies may allocate uptake differently between individual years while still producing similar cumulative uptake over the full carbonation period. For example, a carbonation period assumed to be 8 years instead of 10 years will influence the annual uptake estimates during the active carbonation period, but the cumulative uptake after complete carbonation will generally be similar.

This characteristic differs from concrete carbonation, where uptake may continue over many decades or even centuries and where assumptions regarding long-term carbonation behaviour can have a larger influence on annual inventory estimates.

Because carbonation of lime products generally occurs over relatively short time periods, uncertainties associated with carbonation timing tend to diminish as carbonation approaches completion. Consequently, cumulative uptake over the full carbonation period can usually be estimated with higher confidence than annual uptake in any individual year.

This observation also explains why the simplified Tier 1 and Tier 2 methodologies can often provide robust national estimates despite their simplified treatment of carbonation kinetics. Although annual uptake estimates may differ somewhat from those obtained using a Tier 3 methodology, long-term cumulative uptake estimates will generally converge toward similar values provided that the same carbonation potential and carbonation completeness assumptions are applied.

6.6.4 Recommended application of the different tiers

Tier 1 is recommended for countries with limited data availability, for preliminary assessments, and for inventory categories where carbonation uptake is not considered a key category.

Tier 2 is recommended where national information is available regarding the distribution of lime consumption among major application categories. For many countries, Tier 2 may provide an appropriate balance between simplicity, transparency, and accuracy.

Tier 3 is recommended where carbonation uptake constitutes a key category, where detailed historical consumption data are available, or where country-specific carbonation functions can be developed. Tier 3 provides the highest level of national specificity and the most accurate representation of annual carbonation uptake.

In practice, the differences between the three methodologies are often smaller for cumulative uptake than for annual uptake because of the relatively rapid carbonation behaviour of many lime products. The selection of methodology should therefore be guided primarily by inventory objectives, data availability, and reporting requirements rather than by expectations of large differences in long-term total uptake.

6.7 Worked calculation example

Appendix A provides a complete, internally consistent example of a national annual CO_2 uptake calculation for one hypothetical reporting year using Tier 1 method from Chapter 6.3.1, Tier 2 method from Chapter 6.4.1, and Tier 3 method from Chapter 6.5.1. The same activity data and chemical basis are used at all three tiers so that the effects of disaggregation and cohort modelling can be compared directly. The example also demonstrates the annual-increment form of the Tier 3 carbonation progression function, uncertainty screening, quality control, and reporting conventions.

The numerical values in Appendix A are illustrative and do not constitute new IPCC defaults. Inventory compilers shall replace them with applicable defaults adopted in the guideline or with documented country-specific data.

7 Discussion and conclusions

A central outcome of this study is the development of three recommended methodologies for annual CO_2 uptake calculations in lime-containing products, corresponding to increasing levels of aggregation, national specificity, data requirements and temporal resolution. The operative methods are defined in Sections 6.3.1, 6.4.1 and 6.5.1 and constitute the principal methodological contribution of the report.

Chapter 5 documents the scientific and methodological investigation undertaken to develop these methods, including the evaluation of alternative activity-data structures, product groupings, carbonation parameters and temporal allocation functions. Chapter 6 defines the operative calculation methods. The product-specific assessment shows substantial variation among individual applications but also demonstrates that aggregation across the national application mix can support simplified steady-state methods where lime consumption and application shares remain reasonably stable.

The proposed Tier 1 methodology is an aggregate steady-state method intended for implementation where detailed national data are limited. It estimates annual CO_2 uptake from current apparent national lime use, expressed on a consistent reactive-oxide basis, together with national average stoichiometric, carbonation and exposure factors. Apparent national use is derived from production, imports, exports, stock changes and other documented balance adjustments. The method does not explicitly track historical lime-use cohorts. Instead, it assumes that, under reasonably stable market conditions, uptake from active historical cohorts can be approximated by the ultimate eligible uptake associated with current annual lime use. The characteristic carbonation period supports assessment of this steady-state assumption but is not used to divide the calculated uptake.

The proposed Tier 2 methodology is an application-disaggregated steady-state method. It divides apparent national lime use among mutually exclusive product or application categories and applies category-specific chemical bases, stoichiometric factors, carbonation factors and exposure factors. This improves the representation of the national application mix and distinguishes uses with high carbonation potential from uses with limited chemical eligibility or physical exposure. The recommended Tier 2 method does not require explicit modelling of service lives, historical consumption cohorts, product stocks or end-of-life flows. It is particularly suitable where reliable sectoral consumption data are available but the historical data needed for a Tier 3 cohort calculation are incomplete.

The recommended Tier 3 methodology is an application-specific national consumption-cohort method. It follows annual cohorts of lime entering use and allocates their eligible uptake to the reporting years in which carbonation occurs. For each reporting year, uptake is calculated by summing the annual increments from the current cohort and all earlier cohorts that remain within their carbonation periods. The method therefore represents changes in national lime consumption, application shares and carbonation timing that cannot be captured by the Tier 1 and Tier 2 steady-state methods. It requires historical consumption data, allocation to application categories, category-specific carbonation parameters and documented carbonation progression functions.

A full dynamic stock-and-flow model is described separately in Chapter 6.5.2 as an alternative advanced method. Such a model may explicitly represent product stocks, service lives, end-of-life processing and secondary use where sufficiently detailed national data are available. These elements

are not defining requirements of the recommended Tier 3 consumption-cohort method described in Chapter 6.5.1.

Together, the three recommended methodologies form a coherent hierarchy based on data availability and the required treatment of application differences and carbonation timing. Tier 1 applies national average factors under a steady-state assumption. Tier 2 retains the steady-state assumption but applies application-specific data and parameters. Tier 3 replaces the steady-state assumption with explicit annual consumption-cohort calculations. Countries may progress from one tier to another as more detailed national data become available. Where sufficiently detailed information on material stocks, service lives and end-of-life flows exists, the alternative full stock-and-flow model described in Chapter 6.5.2 may be applied instead of the recommended Tier 3 cohort method.

The principal limitations concern the availability and quality of national application data, the empirical basis for carbonation and exposure factors, and the annual distribution of uptake. Uncertainty frequently concerns the timing of uptake more than the cumulative stoichiometric potential. The proposed default parameters should therefore be regarded as provisional until they have been tested against national data, field measurements and independent inventory applications. Particular attention is required for magnesium-containing lime, for which the CaO and MgO components should be calculated separately.

The proposed framework links product-specific scientific understanding of lime carbonation with practical calculation methods for national greenhouse gas inventories. It allows carbonation removals to be estimated transparently and reported separately from lime-production emissions. Its reliability depends on consistent chemical bases, mutually exclusive material flows, independent treatment of chemical eligibility and physical exposure, documented temporal functions and effective controls against double counting. Subject to further validation and refinement of application-specific parameters, the framework provides a practical basis for national implementation and future international methodological development.

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Appendix A. Complete worked example of national annual CO_2 uptake calculations

A.1 Purpose, scope and interpretation

This appendix illustrates how a national inventory team can calculate CO_2 uptake by carbonation of lime-containing products for reporting year 2025 using the three methods from Chapters 6.3.1, 6.4.1, and 6.5.1. A hypothetical country (Exampleland) is used. The calculation follows the common accounting principles in Chapter 6.2 and is expressed as an annual territorial removal occurring within Exampleland.

The three calculations are deliberately based on the same apparent lime use, the same reactive-oxide basis, and the same stoichiometric factor. Tier 1 applies national average factors; Tier 2 applies application-specific factors under a steady-state assumption; and Tier 3 allocates uptake from historical consumption cohorts to the year in which carbonation occurs.

Important status of the data: all activity data, application shares, carbonation factors, exposure factors, progression functions, parameter ranges and results below are illustrative. They demonstrate the calculation procedure, not recommended default values for real inventories.

A.2 Inventory boundary and common input data

A.2.1 Reporting convention

- Reporting year: 2025.
- Geographical boundary: carbonation that physically occurs within Exampleland.
- Activity basis: tonnes of reactive CaO-equivalent lime entering eligible national uses.
- Gas and unit: tonnes CO_2 per year; results are also shown as kt CO_2 per year.
- Sign: uptake is calculated as a positive quantity in the worksheet. If the inventory table uses negative values for removals, the final reported value is entered with a minus sign.
- Calcination emissions and carbonation removals are reported separately. The uptake is not subtracted within the calculation worksheet unless the applicable reporting table explicitly requires a net value.

A.2.2 Apparent national lime use

The 2025 national lime balance, after conversion of all flows to the same reactive CaO-equivalent basis, is:

$$L_use,2025 = L_production,2025 + L_import,2025 - L_export,2025$$

Flow	Symbol	2025 value	Unit
Domestic production	L_production,2025	120 000	t CaO-eq.
Imports	L_import,2025	15 000	t CaO-eq.
Exports	L_export,2025	10 000	t CaO-eq.
Apparent national use	L_use,2025	125 000	t CaO-eq.

$$L_use,2025 = 120\,000 + 15\,000 - 10\,000 = 125\,000 \text{ tonne CaO-eq.}$$

Stocks, bunker sales, statistical discrepancies, and cross-border movements should be included where material. If apparent use is a poor proxy for territorial placement, direct national consumption data should be used instead.

A.2.3 Chemical basis and stoichiometric factor

For calcium-based lime expressed as reactive CaO-equivalent, the maximum reaction is:

$$CaO + CO_2 \rightarrow CaCO_3$$

$$CF_{CaO} = \frac{M_{CO2}}{M_{CaO}} = \frac{44.01}{56.08} = 0.785\ tonne\ CO_2\ per\ tonne\ CaO - eq.$$

Example of basis conversion: if 10 000 t of hydrated lime contains 90% reactive $Ca(OH)_2$, its reactive CaO-equivalent mass is 10 000 × 0.90 × (56.08/74.09) = 6813 t CaO-eq. The same mass would have a maximum uptake of 6813 × 0.785 = 5348 t CO_2. A country shall not combine product mass and oxide-equivalent mass in one calculation without conversion.

Dolomitic or magnesium-based lime shall be split into reactive CaO and MgO (or hydroxide) components and calculated with separate stoichiometric factors and carbonation parameters. MgO is not included in this numerical example so that the comparison of the three tier methods remains transparent.

A.3 Tier 1 calculation (Chapter 6.3)

A.3.1 Input parameters

The simplified steady-state Tier 1 equation is:

$$U_{CO2\ 2025} = L_{use,2025}\ CF_{CaO}\ F_{carb}\ F_{exp}$$

Parameter	Symbol	Value	Unit	Basis
Apparent lime use	$L_{use,2025}$	125 000	t CaO-eq.	National balance
Stoichiometric factor	CF_{CaO}	0.785	t CO_2/t CaO-eq.	CaO stoichiometry
Carbonation completeness	F_{carb}	0.80	dimensionless	Chapter 6.3.1 default
Exposure factor	F_{exp}	0.90	dimensionless	Chapter 6.3.1 default
Characteristic period	T	10	years	Supports steady-state assumption; not multiplied into the annual equation

A.3.2 Calculation and result

$$U_{CO2\ 2025} = 125\ 000 \times 0.785 \times 0.80 \times 0.90 = 70\ 650\ \text{t}\ CO_2$$

Tier 1 result: 70.65 kt CO_2 uptake in 2025 (reported as -70.65 kt CO_2 if removals are entered as negative values).

The 10-year period is not used as a divisor in this recommended steady-state calculation. It is the rationale for approximating the annual contribution from active historical cohorts by the ultimate carbonation potential associated with current annual use. Dividing the result by 10 would incorrectly count only one cohort while omitting the nine preceding active cohorts.

A.3.3 Applicability check

- The national market should be reasonably stable over approximately the characteristic carbonation period.
- The national use mix should not be dominated by chemically non-carbonating or physically inaccessible applications.
- The result shall remain below the stoichiometric cap: 125 000 × 0.785 = 98 125 t CO_2/year. The calculated 70 650 t is 72% of this cap.
- If these conditions are not met, Tier 2 or Tier 3 should be used.

A.4 Tier 2 calculation (Chapter 6.4)

A.4.1 Allocation to application categories

Exampleland has sectoral statistics that allocate the same 125 000 t CaO-eq. to six mutually exclusive application categories. F_{carb} represents the chemically achievable ultimate carbonation fraction within the category, while F_{exp} represents the physically accessible share. The two factors shall not describe the same limitation twice.

Application category i	$L_{i,2025}$ (t CaO-eq.)	$F_{carb,i}$	$F_{exp,i}$	U_{CO2} Uptake (t CO_2)
Lime mortars and masonry mortars	30 000	0.95	0.98	21 925
Lime renders and plasters	20 000	0.98	1.00	15 386
Soil stabilization and ground improvement	25 000	0.90	0.95	16 779
Environmental applications	20 000	0.65	0.80	8164
Industrial applications with carbonation potential	20 000	0.35	0.50	2748
Secondary uses/residues not counted elsewhere	10 000	0.80	0.90	5652
Total	125 000	-	-	70 654

Mass-balance check: 30 000 + 20 000 + 25 000 + 20 000 + 20 000 + 10 000 = 125 000 t CaO-eq. No category is omitted or counted twice.

A.4.2 Calculation and result

$$U_{CO2\ 2025}\ CO_2\ \text{uptake_2025} = \sum_i L_{i,2025}\ CF_i\ F_{carb,i}\ F_{exp,i} = 70\ 654\ \text{tonne}\ CO_2$$

Example for lime mortars: 30 000 × 0.785 × 0.95 × 0.98 = 21 925 t CO_2.

$$U_{CO2,2025} = 70\ 654\ \text{t}\ CO_2 = 70.7\ \text{kt}\ CO_2$$

Tier 2 result: 70.7 kt CO_2 uptake in 2025 (or -70.7 kt CO_2 under a negative-removal sign convention).

A.4.3 Steady-state applicability check

Exampleland's apparent lime use increased from 90 000 t CaO-eq. in 2016 to 125 000 t in 2025. This growth means that current use is higher than the older cohorts producing part of the 2025 uptake. The Tier 2 steady-state result may therefore overestimate the annual 2025 removal. A Tier 3 cohort calculation is appropriate to quantify the timing effect.

A.5 Tier 3 calculation (Chapter 6.5.1)

A.5.1 Annual-increment cohort equation

Tier 3 treats lime entering use in calendar year n as a separate cohort. For reporting year y, define a = y − n as the cohort age in completed years at the start of year y. $F_i(a)$ is the normalised cumulative carbonation fraction at that exact annual boundary. The uptake occurring during reporting year y is therefore $\Delta F_i(a) = F_i(a + 1) - F_i(a)$. If an ordinal label is useful in a table, define j = a + 1 = y − n + 1; j labels the interval [a, a + 1] and is not the argument used in the cohort equation.

$$\Delta F_i(a) = F_i(a + 1) - F_i(a), \qquad a = y - n$$

$$U_{i,n,y} = L_{i,n}\, CF_i\, F_{carb,i}\, F_{exp,i}\, \Delta F_i(a)$$

$$U_y = \sum_i \sum_n U_{i,n,y}$$

Using cumulative $F_i(a)$ directly as an annual multiplier would repeatedly credit uptake that occurred in previous years. The incremental form ensures that the annual fractions sum to 1.0 over the complete timing horizon and that no cohort exceeds its ultimate eligible uptake.

A.5.2 Historical activity data

Consumption cohort n	Apparent use (t CaO-eq.)	Index (2016 = 1.000)
2016	90 000	1.000
2017	94 000	1.044
2018	98 000	1.089
2019	102 000	1.133
2020	106 000	1.178
2021	110 000	1.222
2022	115 000	1.278
2023	120 000	1.333
2024	123 000	1.367
2025	125 000	1.389

For transparency, the example holds application shares constant at the Tier 2 shares (24%, 16%, 20%, 16%, 16% and 8%). A real Tier 3 inventory should use year-specific application shares where available. Because the longest central carbonation period is 10 years, cohorts before 2016 have ΔF_i = 0 in 2025 and do not contribute.

A.5.3 Carbonation progression functions

Category	Share	F_{carb}	F_{exp}	Cumulative $F_i(a)$	T_i (years)
Lime mortars	24%	0.95	0.98	$\sqrt{\frac{a_i}{T_i}}$	10
Renders and plasters	16%	0.98	1.00	Linear, $\frac{a_i}{T_i}$	5
Soil stabilization	20%	0.90	0.95	$\sqrt{\frac{a_i}{T_i}}$	10
Environmental	16%	0.65	0.80	Linear, $\frac{a_i}{T_i}$	5
Industrial	16%	0.35	0.50	Linear, $\frac{a_i}{T_i}$	10
Secondary uses/residues	8%	0.80	0.90	Linear, $\frac{a_i}{T_i}$	5

For the linear function, $F_i(a) = \min(a/T_i, 1)$ and $\Delta F_i(a) = 1/T_i$ for $a = 0,\ldots,T_i - 1$.

For the square-root timing function, $F_i(a) = \min(\sqrt{\frac{a}{T_i}}, 1)$ and

$\Delta F_i(a) = F_i(a+1) - F_i(a) = [\sqrt{(a+1)} - \sqrt{a}]/\sqrt{T_i}$ for $a=0,\ldots,T_i-1$.

A.5.4 Worked cohort calculations

Example 1 — 2025 mortar cohort: a = 2025 − 2025 = 0 at the start of 2025; ordinal age-year j = 1.

$$\Delta F_{mortar}(0) = F_{mortar}(1) - F_{mortar}(0) = \frac{\sqrt{1} - \sqrt{0}}{\sqrt{10}} = 0.31623$$

$$U_mortar,2025,2025 = (125\,000 \times 0.24) \times 0.785 \times 0.95 \times 0.98 \times 0.31623 = 6933 \text{ t } CO_2$$

Example 2 — 2024 mortar cohort: a = 2025 − 2024 = 1 at the start of 2025; ordinal age-year j = 2.

$$\Delta F_{mortar}(1) = F_{mortar}(2) - F_{mortar}(1) = \frac{\sqrt{2} - \sqrt{1}}{\sqrt{10}} = 0.13099$$

$$U_mortar,2024,2025 = (123\,000 \times 0.24) \times 0.785 \times 0.95 \times 0.98 \times 0.13099 = 2826 \text{ t } CO_2$$

Example 3 — 2023 environmental cohort: a = 2025 − 2023 = 2 at the start of 2025; ordinal age-year j = 3 (linear $T_i = 5$ years).

$$\Delta F_{environmental}(2) = F_{environmental}(3) - F_{environmental}(2) = \frac{1}{5} = 0.20$$

$$U_environmental,2023,2025 = (120\,000 \times 0.16) \times 0.785 \times 0.65 \times 0.80 \times (1/5) = 1567 \text{ t } CO_2$$

A.5.4.1 Aggregated 2025 results

Applying the same equation to every active category-cohort pair gives the following 2025 contributions by cohort:

Consumption cohort n	Age-year j=a+1 in 2025	Contribution to 2025 uptake (t CO_2)
2025	1	18 355
2024	2	11 006
2023	3	9605
2022	4	8643
2021	5	7924
2020	6	2448
2019	7	2184
2018	8	1968
2017	9	1786
2016	10	1628
Total	-	65 547

Application category	2025 uptake (t CO_2)	2025 uptake (kt CO_2)
Lime mortars	20 087	20.1
Renders and plasters	14 598	14.6
Soil stabilization	15 373	15.4
Environmental	7746	7.7
Industrial	2380	2.4
Secondary uses/residues	5363	5.4
Total	65 547	65.5

Tier 3 result: 65.5 kt CO_2 uptake in 2025 (or -65.5 kt CO_2 under a negative-removal sign convention).

A.5.5 Cohort-level stoichiometric check

For every category i and cohort n, the cumulative stoichiometric check is:

$$\sum_y U_{i,n,y} \leq \mathrm{L_{i,n}}\,\mathrm{CF_i}\,\mathrm{F_{carb,i}}\,\mathrm{F_{exp,i}}.$$

For the 2025 mortar cohort, the ultimate eligible uptake is 30 000 × 0.785 × 0.95 × 0.98 = 21 925 t CO_2. The first-year credit of 6933 t is 31.623% of that ultimate amount. The remaining 68.377% may be credited only in later reporting years according to $\Delta F_{mortar}(a) = F_{mortar}(a + 1) - F_{mortar}(a)$.

A.6 Comparison and interpretation of the three tiers

Method	Temporal treatment	2025 uptake (kt CO_2)	Main reason for result
Tier 1	National average steady state	70.7	Uses default F_{carb} and national-average exposure
Tier 2	Application-specific steady state	70.7	Reflects lower-uptake environmental and industrial uses
Tier 3	Application-specific historical cohorts	65.5	Reflects both use mix and the growing historical market

The Tier 3 value is 7.2% lower than Tier 2 because current 2025 use is larger than the historical cohorts still carbonating in 2025. If national use and application shares had been constant for at least the longest carbonation period, the Tier 3 cohort sum would approach the Tier 2 steady-state result. The Tier 3 value is 7.2% lower than Tier 1 because Tier 3 also replaces the national average factors with application-specific factors.

These differences do not imply that one tier changes the amount of CO_2 that a given cohort can ultimately bind. They mainly change (i) which uses are eligible and exposed and (ii) the reporting year in which uptake is credited.

A.7 Illustrative uncertainty and sensitivity screening

A complete national inventory should quantify uncertainty using the IPCC uncertainty guidance. The simplified ranges below are scenario bounds used only to demonstrate screening. They are not statistical 95% confidence intervals and are not proposed defaults.

Method	Illustrative sensitivity case	Low (kt)	Central (kt)	High (kt)
Tier 1	Low: F_{carb} 0.75, F_{exp} 0.85; central: 0.80 and 0.90; high: 0.85 and 0.95	62.6	70.7	79.2
Tier 2	Category-specific low/central/high F_{carb} and F_{exp} combinations	57.7	70.7	82.3
Tier 3	Tier 2 factor bounds plus longer/central/shorter category carbonation periods	52.1	65.5	77.9

For a formal uncertainty analysis, assign probability distributions to activity data, chemical composition, F_{carb}, F_{exp}, application shares and carbonation periods/functions; preserve correlations; run Monte Carlo propagation; and report the selected confidence interval. Trend

uncertainty shall also be evaluated, particularly when historical activity data or allocation methods change.

A.8 Quality assurance, double-counting controls and recalculation

- Activity reconciliation: production + imports - exports +/- stock changes and statistical adjustments shall reconcile with national use on one chemical basis.
- Chemical-basis control: product mass, CaO-equivalent, $Ca(OH)_2$-equivalent and MgO-equivalent data shall not be mixed without documented conversion.
- Eligibility control: uses forming sulfates, chlorides, nitrates, phosphates, silicates or other non-carbonatable products shall receive zero uptake unless subsequent carbonation is demonstrated.
- Territorial attribution: uptake is reported where carbonation occurs. Imported lime carbonating domestically is included; exported lime carbonating abroad is excluded.
- Carbon-source control: Atmospheric carbonation is reported as uptake in the territory and year in which it physically occurs and is not conditional on the associated calcination emissions having been reported in the same national inventory. Where CO_2 is deliberately supplied from an industrial process or capture system, its origin, inventory treatment, retention and permanence shall be documented, and double counting between the source and receiving processes shall be excluded.
- Mutually exclusive categories: each mass flow is assigned once. Secondary use or end-of-life uptake is limited to residual uncarbonated material and is not credited again as new lime input.
- Independent factors: F_{carb} and F_{exp} shall represent distinct chemical and physical limitations. Overlapping limitations shall not be multiplied twice.
- Incremental timing: Tier 3 shall use $\Delta F_i(a) = F_i(a + 1) - F_i(a)$ for each reporting year, not cumulative $F_i(a)$. For every cohort, $\Sigma a\ \Delta F_i(a) = 1$ over the defined timing horizon. The symbol j may appear only as the equivalent ordinal interval label $j = a + 1$.
- Stoichiometric cap: cumulative uptake for every cohort and the national total shall remain below the reactive CaO/MgO stoichiometric maximum after eligibility and exposure constraints.
- Time-series consistency: apply the same method to all years. When improved data or methods are introduced, recalculate the historical time series in accordance with IPCC good practice.
- Independent review: retain data sources, conversion factors, equations, version-controlled calculation files and checks sufficient for replication by a reviewer.

A.9 Example inventory reporting text and data table

Example narrative for the National Inventory Document: Exampleland estimated CO_2 uptake from carbonation of lime-containing products for 2025 using the Tier 3 annual cohort method described in Chapter 6.5.1. Apparent national lime use was derived from production and trade statistics and converted to reactive CaO-equivalent. Consumption was allocated to six application categories. Annual uptake was calculated from 2016-2025 consumption cohorts using application-specific ultimate carbonation and exposure factors and linear or square-root cumulative progression functions. Total 2025 uptake was 65.5 kt CO_2 and was reported as a removal. Tier 1 and Tier 2 cross-checks gave 70.7 and 70.7 kt CO_2, respectively. The Tier 1 and Tier 2 results are nearly identical in this illustrative example. This occurs because the application-weighted product of the Tier 2 carbonation and exposure factors is almost equal to the combined Tier 1 default factor of 0.80 × 0.90 = 0.72. This near equality is specific to the illustrative dataset and should not be interpreted as a general relationship between the two tiers. The lower Tier 3 result was mainly attributable to growth in lime consumption over the active cohort period and to category-specific treatment of lower-carbonating industrial and environmental uses.

Reporting item	Exampleland entry
Reporting year	2025
Method	Tier 3 annual consumption-cohort method (Chapter 6.5.1)
Activity data	Production 120 000; imports 15 000; exports 10 000; apparent use 125 000 t CaO-eq.
Historical period	2016-2025 (10 active cohort years for central case)
Applications	Six mutually exclusive application categories
Stoichiometric factor	0.785 t CO_2/t reactive CaO-eq.
Calculated uptake	65 547 t CO_2 = 65.5 kt CO_2
Inventory sign	-65.5 kt CO_2 where removals are entered as negative
Sensitivity screen	52.1-77.9 kt CO_2 (illustrative scenario range, not a confidence interval)
Cross-checks	Tier 1: 70.7 kt; Tier 2: 70.7 kt CO_2

Inventory compilers should accompany this table with citations to national statistics, industry surveys, chemical composition data, parameter studies, uncertainty calculations and QA/QC records. All deviations from adopted IPCC defaults shall be justified and applied consistently across the time series.

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