

Review

Laboratory Synthesis of Limestone for CO₂ Capture and Removal: A Review of Ca-Based Mineral Carbonation

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Abstract

Mineral carbonation offers a thermodynamically stable, permanent route for immobilizing CO₂ as solid carbonate minerals. Whether it constitutes genuine carbon dioxide removal (CDR) depends on the carbon source: net atmospheric removal requires CO₂ captured from air (e.g., by direct air capture) or biogenic sources and then durably stored, whereas mineralization of fossil-derived industrial CO₂ is better classed as carbon capture and storage or utilization (CCS/CCU). Calcium-bearing silicates and Ca-rich industrial residues are attractive feedstocks because their reaction with CO₂ yields calcium carbonate (CaCO₃), the mineral of natural limestone. In nature, Ca-silicate weathering and CaCO₃ precipitation buffer Earth's climate over millennia; engineered Ca-based carbonation seeks to reproduce this limestone-forming cycle in reactors orders of magnitude faster, enabling permanent storage on practical timescales. This review consolidates recent advances in ex situ Ca-based mineral carbonation under a unified framework in which the synthesis of “engineered limestone” is the central objective. It outlines the geochemical basis and its engineering translation, compares Ca-silicates and Ca-rich residues as feedstocks, and surveys direct and indirect routes, emphasizing conversion, energy demand, and control of CaCO₃ polymorph and morphology. Techno-economic and environmental assessments, demonstrations, and challenges to gigatonne-scale deployment are summarized, offering a reference for next-generation Ca-based CDR research.

Keywords: mineral carbonation; carbon dioxide removal (CDR); calcium carbonate; synthetic limestone; ex situ carbonation; carbon capture and storage (CCS)

1. Introduction

Atmospheric CO₂ has risen from a pre-industrial level of ~280 ppm to monthly mean values exceeding 420 ppm, and in 2025 the seasonal peak recorded at NOAA's Mauna Loa Observatory, Hilo, HI, USA surpassed 430 ppm for the first time—an increase of roughly 50% over the pre-industrial baseline [1]. Stabilizing global mean temperature below the thresholds identified in the Paris Agreement is understood to require two distinct strategies: deep reductions in anthropogenic greenhouse gas emissions, and active removal of CO₂ already present in the atmosphere [2]. Emission reduction includes avoiding emissions and capturing point-source CO₂ for permanent storage or utilization (carbon capture and storage or utilization, CCS/CCU), whereas the net drawdown of atmospheric CO₂ is what is properly termed carbon dioxide removal (CDR); only the latter is counted as CDR. Integrated assessment pathways consistent with 1.5–2 °C targets consistently include substantial volumes of CDR, rising from the current megatonne scale to the multi-gigatonne scale by mid-century [3,4]. This projected demand has driven rapid development of a broad



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CDR portfolio, including afforestation and reforestation, bioenergy with carbon capture and storage (BECCS), direct air capture with storage (DACs), ocean-based approaches, and enhanced rock weathering [4,5].

Engineered Ca-based mineral carbonation, the subject of this review, joins this portfolio as a CDR option when supplied with atmospheric or biogenic CO₂, and it is distinguished from the other approaches by the thermodynamic stability of its storage product. CO₂ is bound within solid carbonate phases whose Gibbs free energy is several tens of kilojoules per mole lower than that of gaseous CO₂, so the stored carbon is not expected to be re-released over geological timescales in the absence of strong acids or high temperatures sufficient to cause thermal decomposition (calcination, above roughly 800 °C) [6–8]. This contrast concerns the durability of the storage pool: whereas carbonate-bound CO₂ is retained over geological timescales, the carbon captured by forest-based approaches (such as afforestation and reforestation) and by some ocean-based approaches is held in biomass or seawater reservoirs that can reverse on decadal to centennial timescales.

Engineered Ca-based mineral carbonation is pursued along two routes, distinguished by where the carbonation reaction is carried out: in situ mineralization, in which CO₂ reacts with rock in the subsurface reservoir into which it is injected, and ex situ carbonation, in which mined or waste solids are reacted with a concentrated CO₂ stream in engineered surface reactors. The in situ route has recently been demonstrated at field scale in projects such as CarbFix in Iceland and the Oman ophiolite; there, the injected CO₂ was observed to convert to solid carbonate within months to a few years—a measure of the mineralization reaction rate rather than of storage permanence [9,10]. Parallel to these in situ efforts, ex situ mineral carbonation aims to carry out analogous reactions in engineered reactors fed with solid feedstocks and a concentrated CO₂ stream. When the feedstock contains calcium as its dominant reactive cation, the resulting carbonate is CaCO₃—the principal component of natural limestone. Ex situ routes relinquish some of the simplicity of subsurface injection, but they offer precise control of reaction conditions and, critically, direct access to the solid carbonate product, which can be tailored as a valuable material rather than merely disposed of underground [8,11–13]. A third, intermediate approach—enhanced rock weathering (ERW)—accelerates natural silicate weathering by applying finely milled Ca- and Mg-silicate rock (e.g., basalt or wollastonite) to soils and coastal settings, where ambient water and biologically elevated CO₂ drive dissolution and downstream (bi)carbonate formation [13]. ERW operates at lower intensity but over far larger areas than reactor-based ex situ carbonation, yet shares the same underlying dissolution–precipitation chemistry; it is therefore best viewed as a complementary member of the Ca-/Mg-silicate carbonation family treated in this review.

This general distinction applies directly to engineered Ca-based mineral carbonation, whose climate function is therefore determined not by the mineralization step itself but by the origin of the CO₂ that is mineralized. When the carbon is sourced from the air—through direct air capture (DAC) or coupling with biogenic CO₂—and durably stored as carbonate, the operation constitutes genuine CDR; when the CO₂ is instead captured from fossil or other industrial point sources, mineralization permanently stores or utilizes that carbon (CCS/CCU) and reduces or avoids emissions but does not draw down atmospheric CO₂, and therefore does not constitute CDR. Throughout this review, “removal” is used in this strict CDR sense, and the carbon-source dependence of the climate benefit is made explicit where relevant.

This carbon-source dependence has a direct accounting consequence: only the atmospheric- or biogenic-fed configuration may be credited as net removal, whereas mineralization of fossil-derived point-source CO₂ should be reported as avoided or durably stored emissions (CCS/CCU) under established CDR-accounting and monitoring, report-

ing, and verification (MRV) frameworks [3–5]. A practically important intermediate case is the unavoidable process of CO₂ released during cement-clinker calcination: mineralizing this stream is a “hard-to-abate” CCS/CCU pathway that is central to decarbonizing the construction sector but does not, by itself, draw down atmospheric carbon. Because the same engineered reactor can operate either as a CDR process (when fed atmospheric or biogenic CO₂) or as a CCS/CCU process (when fed fossil or industrial CO₂), depending solely on its CO₂ feed, a single Ca-based carbonation facility is best described as ‘CDR-ready’ rather than intrinsically a removal technology, and its climate function must always be reported together with its carbon source. Within this framework, the demand for CDR is itself staged over time. As illustrated in Figure 1, mitigation pathways consistent with the Paris Agreement envisage three successive phases—a pre-net-zero phase dominated by gross-emission reductions, a net-zero phase in which residual emissions are balanced by removals, and a net-negative phase in which removals exceed remaining emissions—each placing distinct demands on the scale, durability, and cost of CDR technologies.

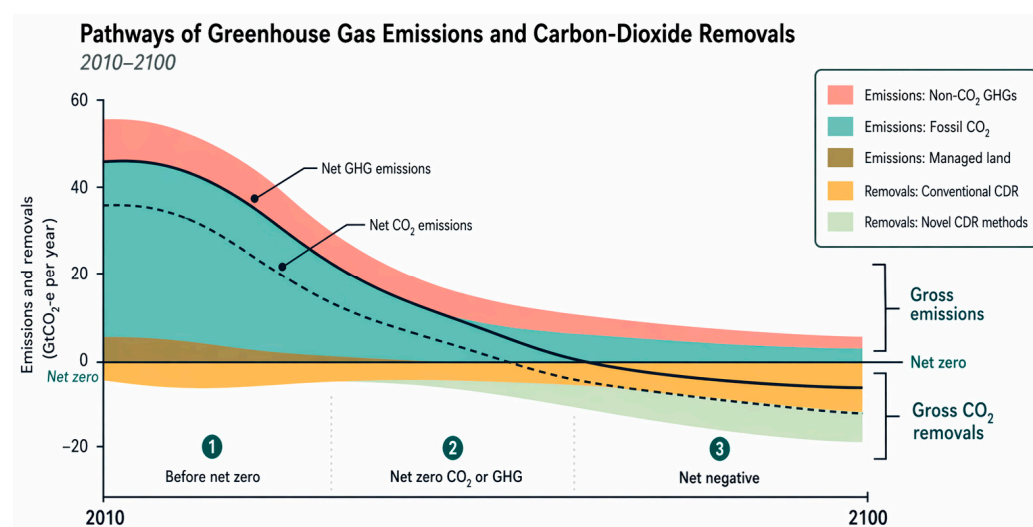


Figure 1. Conceptual mitigation pathway showing the changing balance between greenhouse gas (GHG) emissions and carbon dioxide removal (CDR) from 2010 to 2100 under an ambitious mitigation scenario; redrawn and relabeled by the author, originally based on IPCC AR6 WGIII [6]. Gross positive contributions comprise fossil CO₂, non-CO₂ GHGs, and managed-land emissions; gross negative contributions comprise conventional and novel CDR. The solid and dashed curves denote net GHG and net CO₂ emissions, respectively. As gross emissions decline and removals scale up, the system progresses through three successive phases: (1) before net zero, (2) net-zero CO₂ or GHG, and (3) net negative.

The conceptual foundation of Ca-based mineral carbonation is rooted in geology. Over geological time, CO₂ is removed from the atmosphere by the weathering of Ca- and Mg-silicates on continents; the dissolved products are delivered by rivers to the ocean, where they precipitate as carbonate sediments that are ultimately buried and lithified into limestone [14–16]. This carbonate–silicate cycle stabilizes atmospheric CO₂ on multimillion-year timescales, and the vast quantity of carbon stored within the sedimentary limestone reservoir attests to its effectiveness as a long-term sink. The engineering question, then, is how to reproduce this natural limestone-forming process in a reactor and at a rate that is useful for climate mitigation—essentially, how to synthesize limestone in the laboratory as a CDR technology.

Accelerating natural weathering by many orders of magnitude requires strategies that address its known rate-limiting steps: the slow dissolution of Ca-silicates at ambient conditions and the kinetics of CaCO₃ nucleation and growth. Ex situ processes manip-

ulate temperature, partial pressure of CO₂, pH, particle size, and chemical additives to bring reactions that would otherwise take millennia down to minutes or hours [11,17–21]. An equally important degree of freedom is the choice of feedstock. Natural Ca-silicates such as wollastonite and anorthite possess well-defined stoichiometry and comparatively rapid dissolution kinetics relative to Mg-silicates [22,23], while Ca-rich industrial residues such as steel slag, cement kiln dust, fly ash, and construction and demolition waste contain highly reactive Ca phases that can often carbonate near ambient conditions without further activation [12,13,18,24–32].

Several earlier reviews have surveyed mineral carbonation, but each differs from the present work in scope, focus, or framing. Bobicki et al. [17] examined CO₂ storage using alkaline industrial wastes spanning both Ca- and Mg-bearing systems, whereas Sanna et al. [16] provided a broad technology-oriented survey covering Ca- and Mg-silicates and wastes across both in situ and ex situ routes. Snæbjörnsdóttir et al. [8] reviewed carbon mineralization with an emphasis on storage permanence and field-scale in situ injection in basaltic and ultramafic rocks. More recent reviews have narrowed to specific feedstocks or analytical lenses: Rashid et al. critically assessed the aqueous carbonation of peridotites for utilization [33], surveyed developments across natural and waste feedstocks for sequestration [34], and quantified publication trends in slag-based cementitious carbonation through a bibliometric analysis [35]. Collectively, these works treat Ca and Mg systems together, weigh in situ and ex situ routes jointly, and, being storage- or trend-oriented, give limited attention to the specification of the solid carbonate product or to the carbon-source dependence of the climate benefit.

The present review is deliberately narrower and is organized differently. First, it restricts attention to Ca-based feedstocks—natural Ca-silicates and Ca-rich industrial residues—and to ex situ processing (with enhanced rock weathering treated as a land-based analog), so that the underlying chemistry, the process routes, and the CaCO₃ product specifications can be developed as a single coherent thread rather than interleaved with Mg- and in situ systems. Second, it adopts the “laboratory synthesis of limestone” perspective as an explicit organizing principle—natural limestone formation as the geochemical analogue and engineered CaCO₃ as the target—which ties together the thermodynamic basis (Section 2), feedstock selection (Section 3), process design and product control (Section 4), and techno-economic and environmental assessment (Section 5). Third, in contrast to the storage-centric framing of earlier reviews, it makes the distinction between genuine CDR and CCS/CCU explicit and carbon-source-dependent throughout, and elevates control of CaCO₃ polymorph and morphology to a central theme. The result is a dual value proposition that remains largely implicit in previous reviews: a single operation delivers permanent CO₂ storage—and, when supplied with atmospheric or biogenic CO₂, genuine removal—while yielding a carbonate product that can substitute for mined limestone in construction and industrial applications [36,37], with the accompanying techno-economic, market-size, and MRV constraints being assessed in an integrated manner (Section 5).

This article is a critical, framework-oriented review organized around the concept of engineered Ca-based limestone synthesis, rather than a formal systematic review; the emphasis is accordingly on synthesizing mechanistic understanding and representative results. To support transparency and reproducibility, the literature was identified as follows. Peer-reviewed articles, authoritative technical reports, and conference proceedings were retrieved from Web of Science, Scopus, and Google Scholar, supplemented by backward and forward citation tracking of key reviews. The principal search terms—used individually and in combination—included “mineral carbonation,” “CO₂ mineralization,” “ex situ carbonation,” “calcium carbonate precipitation,” “wollastonite” and “anorthite carbonation,” “steel slag,” “cement kiln dust,” and “fly ash carbonation,” “pH-swing process,”

“precipitated calcium carbonate (PCC),” and “CO₂ curing of concrete.” Priority was given to studies published between 1990 and 2025, with particular weight on advances of the past decade, while retaining seminal earlier work that established the field. Studies were included when they (i) addressed Ca-dominated feedstocks, (ii) concerned ex situ (reactor-based) carbonation or its closely related land-based analog, enhanced rock weathering, and (iii) reported mechanistic, kinetic, techno-economic, or product-control findings relevant to CaCO₃ formation. Work focused exclusively on Mg-only systems, purely in situ subsurface mineralization, or non-carbonate CO₂ utilization was consulted only for context and otherwise excluded. Where multiple studies reported convergent findings, representative and widely cited examples were selected to keep the synthesis focused.

This narrative, framework-oriented synthesis is intended to complement rather than replace existing systematic and bibliometric treatments of the field: whereas those works quantify publication trends and aim at exhaustive cataloging, the present review prioritizes mechanistic coherence and the explicit “limestone-synthesis” organizing principle, selecting representative studies that best illustrate each conceptual step from feedstock dissolution to controlled CaCO₃ precipitation. As with any narrative review, this representative selection entails a degree of subjectivity and does not guarantee exhaustive coverage; this limitation was mitigated by anchoring the search in three major databases, applying the explicit inclusion/exclusion criteria stated above, and cross-checking key quantitative claims against the most highly cited primary sources and the most recent systematic reviews.

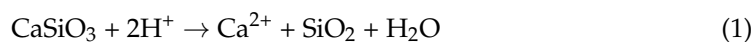
The remainder of this paper is organized as follows. Section 2 develops the scientific basis of Ca-based mineral carbonation, starting from the natural limestone cycle and deriving the thermodynamic and kinetic framework that governs engineered analogs, including the polymorphs of CaCO₃. Section 3 surveys Ca-bearing feedstocks, comparing natural silicates and industrial residues in terms of theoretical CO₂ uptake, reactivity, and availability. Section 4 reviews ex situ process routes—direct gas–solid and aqueous systems as well as indirect multi-step configurations such as pH-swing—together with intensification strategies and CaCO₃ product control. Section 5 assembles recent techno-economic and life-cycle assessments, summarizes demonstration projects, and identifies outstanding challenges. The review closes with a concise statement of conclusions and research priorities.

2. Fundamentals: From Natural Limestone Formation to Engineered Carbonation

2.1. The Natural Limestone-Forming Cycle as a Geochemical Analog

Limestone is the most abundant sedimentary carbonate rock on Earth, and the majority of surface-accessible inorganic carbon resides in limestone and related carbonate formations [14,15]. The formation of limestone is the terminal step of the long-term carbonate–silicate cycle, in which atmospheric CO₂ dissolves in rainwater to form carbonic acid, attacks Ca- and Mg-silicate minerals on land, and releases dissolved Ca²⁺, Mg²⁺, and HCO₃[−] that are transported to the ocean, where carbonate minerals eventually precipitate [11,12,15,16]. Over the Phanerozoic, this cycle has been the principal long-term sink of volcanic CO₂ and has played a central role in stabilizing Earth’s climate [14].

For the purposes of engineered Ca-based mineral carbonation, the natural cycle can be reduced to two coupled half-reactions. The dissolution of a Ca-silicate (using wollastonite as a simple stoichiometric example) proceeds as:



and the precipitation of CaCO_3 from the released cation is:



The sum of the two corresponds to the overall carbonation:



Reaction (3) is exothermic and exergonic under ambient conditions; in other words, nature spontaneously converts Ca-silicates and CO_2 to limestone and silica. Nevertheless, the process is extremely slow in the natural setting because dissolution of the parent silicate (Reaction (1)) is kinetically limited, and because dilute CO_2 concentrations and low reactive surface areas in the environment keep the overall rate low [14–17].

Reaction (3) illustrates a general feature of Ca-silicate and Ca-oxide carbonation: the reaction is accompanied by a substantial decrease in Gibbs free energy at 25 °C and 1 atm, typically in the range of -40 to -90 kJ per mole of CO_2 , depending on the parent phase [17]. This thermodynamic driving force underpins the permanence of storage, because once formed, CaCO_3 has a very low risk of CO_2 re-release under neutral to alkaline near-surface conditions, although dissolution can occur under acidic or undersaturated conditions. From a reactor engineering perspective, the negative ΔG also indicates that ambient or modestly elevated conditions can, in principle, drive the reaction, provided that kinetic barriers are overcome. This combination of net atmospheric drawdown and geological-timescale immobilization places engineered Ca-based mineral carbonation among the carbon-management pathways that satisfy all the operational principles required of genuine CDR (Figure 2)—but only when it is fed with CO_2 of atmospheric or biogenic origin. In that configuration (Figure 2A), atmospheric CO_2 is removed, the captured carbon is stored permanently, and the storage medium—crystalline CaCO_3 —is among the most durable carbon reservoirs known on Earth's surface. When the same process is instead supplied with fossil-derived industrial CO_2 , it maps onto Figure 2C: the carbon is durably stored or utilized, reducing or avoiding emissions, but atmospheric CO_2 is not drawn down, so the operation is CCS/CCU rather than CDR. By contrast, pathways such as DAC-to-fuel re-emit captured carbon, and short-lived biomass storage offers only decadal durability.

The theoretical CO_2 uptake of a given feedstock can be estimated in two equivalent ways. For a pure mineral of known formula, it follows directly from the molar masses as $M(\text{CO}_2)/M(\text{mineral})$; for wollastonite (CaSiO_3), this gives $\approx 0.38 \text{ g CO}_2 \text{ g}^{-1}$, and for the simple Ca phases $\text{Ca}(\text{OH})_2$ and CaO , it rises to ≈ 0.59 and $\approx 0.79 \text{ g CO}_2 \text{ g}^{-1}$, respectively [7,17]. Equivalently, the uptake can be obtained from the CaO-equivalent content as $(\text{wt \% CaO}/100) \times M(\text{CO}_2)/M(\text{CaO})$, where $M(\text{CO}_2)/M(\text{CaO}) \approx 0.79 \text{ g CO}_2 \text{ per g CaO}$; this CaO-equivalent route is the practical choice for chemically heterogeneous feedstocks such as slags and fly ash, which are characterized by bulk oxide analyses rather than by a single mineral formula, and it underlies the values reported in Table 1. For a phase containing a single Ca cation—anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), for example—the two routes are algebraically identical and necessarily yield the same value ($\approx 0.16 \text{ g CO}_2 \text{ g}^{-1}$), because the CaO content is itself fixed by the mineral stoichiometry; the agreement is thus an identity, not an independent check. These figures bound the maximum carbon-capture performance of any Ca-based feedstock; real feedstocks contain non-reactive phases that reduce the effective uptake below the theoretical value.

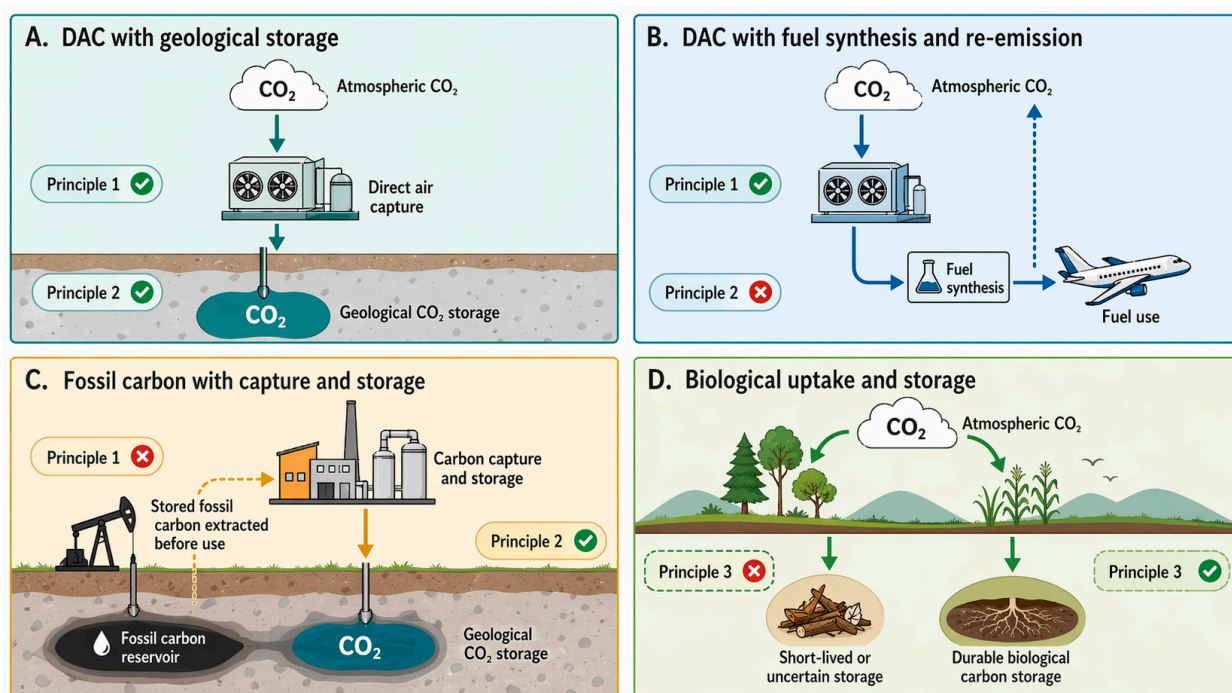


Figure 2. Three operational principles distinguishing genuine carbon dioxide removal (CDR) from related carbon-management pathways: Principle 1, net removal of atmospheric CO_2 ; Principle 2, permanent (geological-timescale) storage; Principle 3, durability of biological storage; redrawn and restructured by the author, adapted from [5]. (A) Direct air capture (DAC) with geological storage satisfies Principles 1 and 2. (B) DAC coupled with synthetic-fuel production re-emits captured CO_2 during use, failing Principle 2. (C) Fossil-fuel use with carbon capture and storage (CCS) stores carbon durably but does not draw down atmospheric CO_2 , failing Principle 1. (D) Biological uptake qualifies as CDR only when stored in long-lived pools (Principle 3). Engineered Ca-based mineral carbonation, the focus of this review, corresponds to category (A) when supplied with atmospheric or biogenic CO_2 , but to category (C) when supplied with fossil-derived industrial CO_2 .

Table 1. Representative Ca-bearing feedstocks for mineral carbonation. Theoretical CO_2 uptake is estimated from the CaO-equivalent content as $(\text{wt } \% \text{ CaO}/100) \times 0.79 \text{ g } \text{CO}_2 \text{ g}^{-1}$, assuming complete conversion to CaCO_3 ; for single-Ca minerals, this is identical to the direct mineral-stoichiometry value. Ranges reflect literature-reported variability across sources and operating conditions [2,14–19].

Feedstock	Typical Ca Phase(s)	CaO (wt%)	Theo. CO_2 Uptake (g/g)	Reactivity	Availability
Wollastonite	CaSiO_3	~48	~0.38	Moderate–high	Limited
Anorthite/Ca-plagioclase	$\text{CaAl}_2\text{Si}_2\text{O}_8$	~20	~0.16	Low–moderate	Very large
Ca-pyroxene(diopside)	$\text{CaMgSi}_2\text{O}_6$	~26	~0.21	Low–moderate	Large
Basalt (Ca-bearing)	Plag. + pyroxene + glass	~10–12	~0.08–0.10	Low (ambient)	Very large
BOF/EAF steel slag	Free CaO, $\text{C}_2\text{S}/\text{C}_3\text{S}$, portlandite	~30–50	~0.20–0.40	High	Large (>400 Mt/yr)
Cement kiln dust (CKD)	CaO, $\text{Ca}(\text{OH})_2$, clinker phases	~35–55	~0.25–0.45	Very high	Moderate
Class C fly ash	CaO, Ca-aluminosilicates	~10–30	~0.10–0.25	Moderate	Very large
Construction and demolition waste	Hydrated cement, $\text{Ca}(\text{OH})_2$	~20–35	~0.15–0.25	Moderate–high	Very large

2.2. Kinetics and Rate-Limiting Steps

While thermodynamics favors carbonation, the overall rate is controlled by kinetics. For natural Ca-silicates, dissolution of the parent phase (Reaction (1)) is widely recognized as the rate-limiting step at moderate temperatures [17,19–23]. The rate depends on the type of mineral, pH, temperature, dissolved CO₂, and the availability of reactive surface area. Wollastonite dissolves considerably faster than most Mg-silicates such as olivine and serpentine, and this kinetic advantage is one of the reasons why Ca-based feedstocks are often preferred when direct ambient-condition carbonation is desired [22].

A further kinetic complication arises from the formation of product layers on dissolving particles. As Ca²⁺ is leached, a silica-rich layer may form at the particle surface, and if CaCO₃ nucleates directly on the reacting grain, a passivating carbonate rim can impede further reaction [17,21,38]. This phenomenon, often referred to as passivation, is particularly important in gas–solid and concentrated slurry processes, and it has motivated the development of indirect (multi-step) processes in which dissolution and precipitation are decoupled [21].

The mechanism by which these product layers retard reaction remains debated, and the two principal interpretations carry different implications for process design. In the shrinking-core (product-layer diffusion) interpretation, a coherent, low-porosity rim of amorphous silica and/or carbonate envelops an unreacted core, so that the rate becomes limited by diffusion of reactants and products through the thickening layer; conversion then follows characteristically parabolic ($\sqrt{t}$) kinetics and slows progressively as the layer grows [17,37]. In the alternative interface- (surface-reaction)-controlled interpretation, the silica layer is porous and non-protective, fluid retains access to the mineral surface, and the apparent rate decline arises not from a diffusion barrier but from a loss of reactive surface area and from carbonate “armoring” of dissolution sites; in this regime dissolution kinetics remain close to linear and are governed by interfacial detachment, often through interface-coupled dissolution–precipitation [21,23,38]. Experimental support exists for both pictures, and the apparent disagreement is at least partly one of regime: diffusion control is favored at high conversion, elevated temperature and pCO₂, and in gas–solid or concentrated-slurry systems where dense, continuous layers form, whereas interface control dominates at low conversion, in dilute or vigorously agitated aqueous systems, and where additives or attrition continually expose fresh surface [17,21,23,37,38]. What remains unresolved is the quantitative criterion—expressed in terms of temperature, pCO₂, ionic strength, and layer microstructure—that marks the transition between the two regimes, and the extent to which the silica layer is intrinsically passivating rather than merely reducing reactive surface area. This question is not merely academic: it dictates whether intensification should target transport limitations (e.g., thin-film or attrition reactors) or interfacial chemistry (e.g., ligand-promoted dissolution), and resolving it will likely require in situ, particle-scale characterization that links evolving layer microstructure directly to measured kinetics rather than inferring mechanism from bulk conversion curves alone.

For Ca-rich industrial residues, the controlling step can differ from that of natural silicates. Steel slag and cement-based residues contain highly reactive phases such as free CaO, Ca(OH)₂, and Ca-silicate hydrates, which dissolve rapidly and can carbonate at ambient or mildly elevated conditions [13,25–29,31]. In such systems, the rate is often limited by mass transport of CO₂ into the aqueous phase and by CaCO₃ nucleation, rather than by silicate dissolution. These differences have important implications for reactor design and are returned to in Section 4.

2.3. Polymorphs of CaCO_3 and Their Control

Calcium carbonate crystallizes in three anhydrous polymorphs—calcite, aragonite, and vaterite—together with hydrated phases (monohydrocalcite, ikaite) and an amorphous precursor (amorphous calcium carbonate, ACC) [29,35]. Calcite is the thermodynamically stable polymorph at ambient conditions and dominates natural limestone; aragonite is metastable but is preferred in warm, high-Mg environments, while vaterite is strongly metastable and is rarely encountered in geological settings [29].

For engineered synthesis, the polymorph is determined by the interplay of supersaturation, temperature, pH, ionic composition, and organic or inorganic additives [29,35]. High supersaturation and low temperature favor ACC, which can subsequently transform to vaterite or aragonite before eventually converting to calcite. The presence of Mg^{2+} suppresses calcite nucleation and stabilizes aragonite, while additives such as phosphate, sulfate, or dissolved organics can modulate nucleation rates and crystal habit [29]. These sensitivities mean that engineered limestone synthesis is not only a CDR technology but also a platform for producing tailored carbonate products with defined particle size, morphology, and polymorph content, which in turn determine the industrial value of the material.

Despite this rich phenomenology, the ability to predict—rather than merely rationalize after the fact—which polymorph and morphology will form under given process conditions remains limited. Equilibrium thermodynamic and speciation models reliably identify calcite as the stable phase and quantify saturation states, but they are silent on which metastable phase nucleates first and how long it persists, because polymorph selection is kinetically rather than thermodynamically governed. Classical nucleation theory, combined with Ostwald's rule of stages, provides a qualitative framework for the ACC → vaterite/aragonite → calcite sequence, yet its quantitative predictions are undermined by poorly constrained interfacial energies and by growing evidence that early-stage carbonate formation proceeds through prenucleation clusters and amorphous precursors that lie outside the classical picture. Phenomenological “polymorph maps” that correlate the product with temperature, supersaturation, Mg/Ca ratio, and additive dose are useful but largely interpolative and system-specific; they transfer poorly between additive chemistries and, critically, to the impurity-laden solutions generated from real Ca-bearing feedstocks, where Mg, Si, Fe, and trace metals co-released during dissolution can redirect polymorph selection in ways not captured by pure-system experiments. Molecular-scale simulation has begun to illuminate additive binding and step-growth kinetics, but is not yet predictive at the process scale. The central unresolved questions are therefore how to construct transferable, mechanistically grounded models that map process variables onto product polymorph and habit under industrially relevant high supersaturation, fast-precipitation conditions, and how to account quantitatively for the coupling between feedstock-derived impurities and precipitation pathways. Until these gaps are closed, polymorph and morphology control in engineered limestone synthesis will remain largely empirical, requiring case-by-case tuning rather than a priori design.

The engineering objective of Ca-based mineral carbonation can now be stated precisely: to reproduce Reactions (1) and (2), or their equivalents for Ca-oxide and Ca-hydroxide feedstocks, at rates that are compatible with industrial throughput. Several strategies are used together to achieve this acceleration. Feedstock comminution increases reactive surface area by one to three orders of magnitude relative to natural weathering conditions [17–19]. Elevated temperature (typically 50–200 °C) and elevated pCO_2 (1–150 bar) increase both intrinsic rate constants and the solubility of CO_2 in the aqueous phase, respectively [19,20,38]. Chemical additives such as NaCl, NaHCO_3 , organic acids, and ammonium salts enhance dissolution of the parent phase or buffer the precipitation pH [19–21,23,27,39,40]. Finally, multistep (indirect) process configurations, which are discussed in detail in Section 4, sepa-

rate dissolution and precipitation so that each step can be individually optimized. Figure 3 summarizes this conceptual mapping, juxtaposing the five canonical stages of the natural carbonate–silicate cycle (atmospheric dissolution → Ca-silicate weathering → riverine transport → marine precipitation → sedimentary lithification) with the five corresponding stages of engineered ex situ Ca-based carbonation (concentrated CO₂ delivery → activated Ca feedstock → controlled dissolution → controlled precipitation → engineered limestone product). Each engineered stage replicates the chemistry of its natural counterpart but compresses the characteristic timescale by six to nine orders of magnitude.

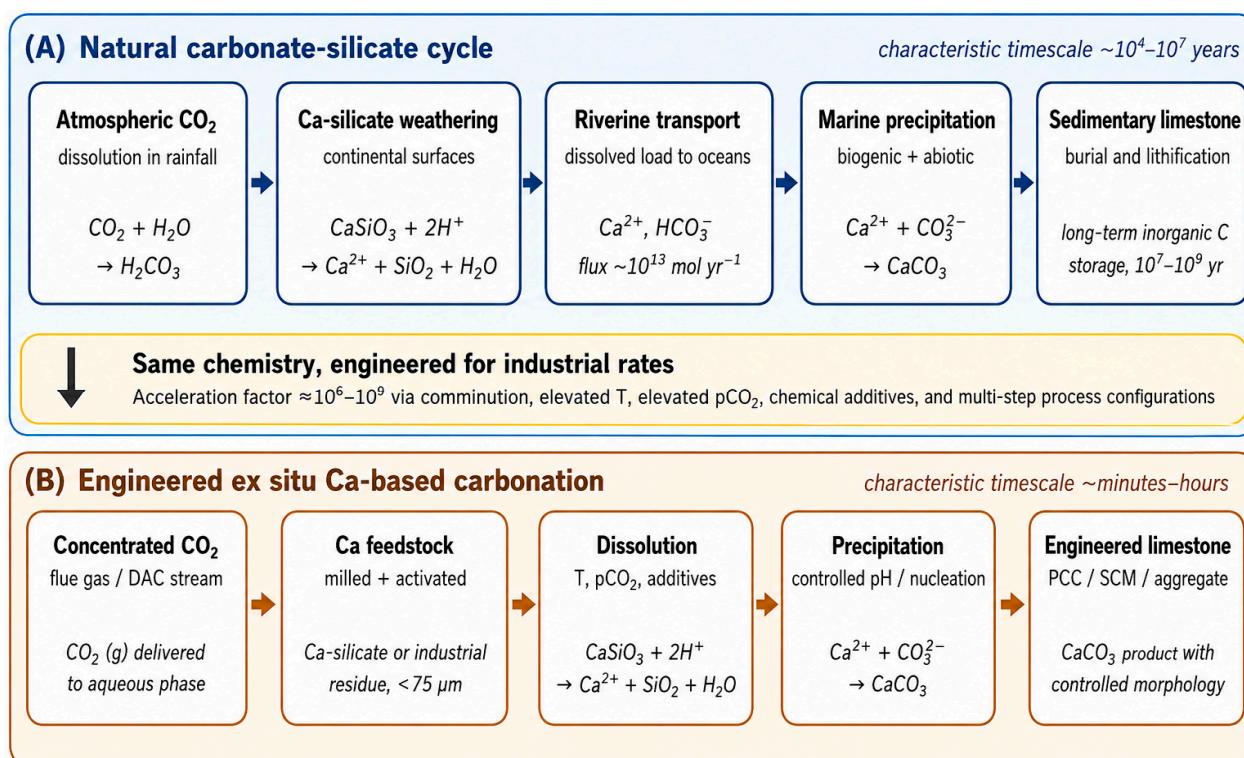


Figure 3. Comparison between the natural carbonate–silicate cycle and engineered ex situ Ca-based carbonation for limestone formation. The natural pathway converts atmospheric CO₂ into carbonate minerals through rainfall dissolution, Ca-silicate weathering, riverine transport, marine precipitation, and long-term sedimentary limestone storage over geological timescales ranging from decades for shallow-marine carbonate precipitation to 10⁶ years or more for deep burial and lithification. The engineered analog accelerates the same fundamental chemistry by using concentrated CO₂ streams, milled and activated Ca-bearing feedstocks, enhanced dissolution, and controlled carbonate precipitation to produce engineered limestone products such as precipitated calcium carbonate, supplementary cementitious materials, or aggregates within minutes to hours.

In combination, these strategies can accelerate the natural carbonate–silicate cycle by factors of 10⁶ or more, transforming a geological process into an industrial one. The remainder of this review examines how this acceleration is achieved in practice, starting from the choice of Ca-bearing feedstock.

3. Ca-Based Feedstocks for Engineered Limestone Formation

Ca-based feedstocks for mineral carbonation fall into two broad categories: natural Ca-silicate minerals, derived by mining or quarrying, and Ca-rich industrial residues, derived as by-products of metallurgical, cement, and thermal power operations [7,11–13,17]. The choice between these categories has far-reaching consequences for feedstock cost, transport, reactivity, product purity, and the environmental attributes of the overall process.

3.1. Natural Ca-Bearing Silicate Feedstocks

Among natural silicates, wollastonite (CaSiO_3) is the archetypal Ca-based feedstock for mineral carbonation. Its reactivity has been studied in detail under a wide range of conditions [17,22,23,38]. Wollastonite dissolves relatively rapidly at moderate pH and exhibits a theoretical CO_2 uptake of approximately $0.38 \text{ g CO}_2 \text{ g}^{-1}$ mineral, and its reaction with CO_2 -bearing aqueous solutions yields calcite with limited passivation compared with Mg-silicate systems [22]. However, economically significant wollastonite deposits are geographically concentrated in a few countries (notably China, Finland, India, Mexico, and the United States) [41]; pure wollastonite is therefore unlikely to support gigatonne-scale CDR by itself, and its cost is significantly higher than that of common rocks [12,17].

Plagioclase feldspars, especially Ca-rich varieties such as anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), are far more abundant and are important constituents of mafic igneous rocks, including basalt [8,17]. Their carbonation, however, is kinetically slower than that of wollastonite, partly because of the more complex stoichiometry and the formation of aluminosilicate product layers [17]. Ca-bearing pyroxenes, such as diopside ($\text{CaMgSi}_2\text{O}_6$) and augite, likewise combine significant Ca content with a more complex reaction chemistry [17,32].

Basalt itself, considered as a polymineralic feedstock, is of particular interest because of its very large global abundance, its reactivity relative to more evolved rocks, and its mixture of Ca- and Mg-bearing phases [8–10]. Although basalt has attracted the most attention in situ applications such as CarbFix [9], ex situ use of basaltic rock or its fines as a Ca- and Mg-source for CaCO_3 production is an emerging direction, especially in the context of enhanced rock weathering and by-product valorization [11,16,41].

3.2. Ca-Rich Industrial Residues

Industrial residues offer several advantages over natural silicates. Their Ca content is often present in highly reactive phases, they are generated close to point-source CO_2 emitters, and their reuse as mineral carbonation feedstock can offset waste-management costs, so that the net cost of CO_2 abatement is reduced [12,13,24,33,34].

Steelmaking slags—basic oxygen furnace (BOF), electric arc furnace (EAF), and ladle furnace (LF) slags—are among the most studied Ca-rich residues [13,25–28,42,43]. Typical slags contain 30–50 wt% CaO in the form of free lime, portlandite, and Ca-silicates such as C_2S and C_3S , giving theoretical CO_2 uptakes in the range $0.2\text{--}0.4 \text{ g CO}_2 \text{ g}^{-1}$ slag [25,26]. Annual global slag production exceeds 400 Mt, which corresponds to a non-trivial CO_2 abatement potential if fully utilized [13,33,37].

Cement-related residues include cement kiln dust (CKD), cement bypass dust, and end-of-life cement-based construction and demolition waste [24,29,31,36]. These materials are characterized by their fine particle size and high content of Ca(OH)_2 , CaO, or unreacted clinker phases, which carbonate readily at ambient conditions [29,36]. Fly ash, particularly the Class C (Ca-rich) variety from lignite and sub-bituminous combustion, is another globally abundant residue, with typical CaO contents of 10–30 wt% [24,31]. Red mud (bauxite residue) and mine tailings from certain ore bodies may also contribute reactive Ca phases in specific regional contexts [13,32].

A synoptic comparison of representative Ca-bearing feedstocks is given in Table 1. The table summarizes the typical CaO content, the theoretical CO_2 uptake, the broad reactivity behavior, and the global availability. Natural Ca-silicates tend to provide relatively homogeneous composition and high product purity but require activation and more severe conditions. Industrial residues provide rapid reaction kinetics and a waste-valorization co-benefit but introduce chemical heterogeneity, the possibility of trace-element leaching (e.g., Cr, V, Mo), and product-quality constraints [13,30,31,37]. The choice between categories is therefore driven by the specific objectives of the process—whether the priority is

to maximize CO₂ uptake per tonne of feedstock, to minimize cost, to co-manage a specific waste stream, or to produce a particular grade of CaCO₃ for downstream use.

Regardless of feedstock class, pretreatment is almost always required to achieve industrial reaction rates. Mechanical comminution to particle sizes below ~75 µm is standard practice [18,19,21]. Thermal activation, such as calcination of serpentine or controlled dehydroxylation of hydrated phases, can increase reactivity further but at substantial energy cost [18,19]. Chemical pretreatment, including acid leaching to selectively extract Ca, is central to indirect (pH-swing) processes and is discussed in Section 4.2.

In summary, Ca-based feedstocks span a wide compositional and reactivity spectrum, and the selection of an appropriate feedstock is a primary lever for process design. The next section examines how these feedstocks are transformed into engineered limestone under ex situ conditions.

4. Ex Situ Carbonation Process Routes and CaCO₃ Product Control

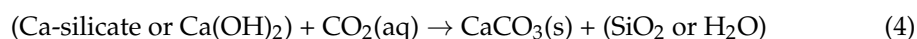
4.1. Direct Routes

In direct gas–solid carbonation, a CO₂-bearing gas stream contacts the solid feedstock, typically with a small amount of moisture to enable surface hydration [17,29,31]. The process is conceptually simple and avoids the need for liquid handling, but its rate is generally slow for natural silicates because of limited ion mobility in the near-dry environment. For highly reactive industrial residues such as CKD or APC (air pollution control) residues, however, direct gas–solid carbonation under mild conditions—typically 25–60 °C, 1–10 bar CO₂, 10%–40% relative humidity, and particle sizes below ~100 µm—can reach 30%–70% of theoretical CO₂ uptake within minutes to hours [29,31]. These mild conditions correspond to the highly reactive end of the broader gas–solid range summarized in Table 2, whose wider temperature and pressure span reflects the inclusion of less reactive feedstocks such as slag. This fact underlies the commercial deployment of accelerated carbonation technology for treatment of alkaline wastes [13,24,31].

Table 2. Comparison of representative ex situ Ca-based mineral carbonation routes. Values are indicative ranges compiled from the cited experimental and pilot-scale studies [20–22,24,26–37,44].

Route	Typical T (°C)	Typical pCO ₂ (bar)	Representative Feedstock	Conversion (%)	Key Features/Limitations
Direct gas–solid (dry)	25–300	1–40	APC residues, CKD, slag	30–80	Simple; low liquid inventory; slow for silicates; surface passivation
Direct aqueous (single-stage)	25–200	1–150	Wollastonite; steel slag	40–90	Faster than dry; severe conditions for natural silicates; passivation
Indirect pH-swing (organic acid)	25–100	1–40	Wollastonite; slag	50–95	High-purity PCC product; solvent regeneration demanding
Indirect pH-swing (ammonium salt)	25–100	1–10	Slag; CKD	60–95	Thermally regenerable solvent; NH ₃ slip must be managed
Thin-film/rotating bed	25–80	1–10	Slag; C&DW	50–90	Enhanced mass transfer; mitigates passivation; reactor complexity

Direct aqueous carbonation, by contrast, contacts the feedstock with a CO₂-charged aqueous solution, which accelerates both dissolution and precipitation relative to the dry case. The reference studies of O'Connor and co-workers established that direct aqueous carbonation of activated olivine and other silicates can achieve high conversion in a single stage at 155–185 °C and 100–150 bar CO₂ in the presence of NaCl/NaHCO₃ additives [19,20]. Analogous conditions applied to wollastonite yield near-quantitative carbonation at somewhat milder temperatures [17,22,23]. For industrial residues, direct aqueous carbonation is often effective at 25–100 °C and 1–40 bar CO₂ [13,25–28,31,43]. A typical reaction scheme is:



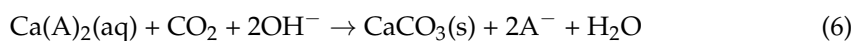
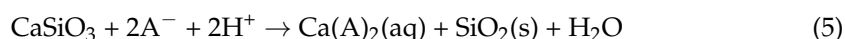
The main advantages of direct routes are process simplicity and low chemical inventory; the drawbacks are the relatively severe conditions needed for natural silicates and the tendency for CaCO₃ to nucleate on the dissolving particle, leading to passivation and incomplete conversion [21,38,40].

4.2. Indirect Routes and pH-Swing Processes

Indirect processes decouple dissolution and precipitation into separate reactors and typically involve three stages: (i) dissolution of the feedstock in an extraction solvent to release Ca²⁺ into solution, (ii) gas absorption and speciation control (often a pH increase) that drives CaCO₃ nucleation, and (iii) regeneration of the solvent to minimize net chemical consumption [14,16,22,24,28,33,44]. The pH-swing concept—in which dissolution proceeds under acidic conditions while precipitation occurs under mildly alkaline conditions—was pioneered for serpentine and has since been widely applied to both natural and waste Ca-silicates [22,33,44].

Acetic acid is a frequently used extractant because it is effective at dissolving Ca-silicates and can, in principle, be regenerated [24,28]. For wollastonite, Kakizawa et al. proposed a two-step scheme based on acetic acid extraction followed by CaCO₃ precipitation upon CO₂ uptake, with the acid regenerated during the precipitation step [24]. Teir and co-workers demonstrated the feasibility of the analogous scheme for steel slag, achieving high Ca extraction and the formation of high-purity precipitated calcium carbonate (PCC) [28,34]. Ammonium salts (NH₄Cl, NH₄NO₃, CH₃COONH₄) have also been used as lixiviants, with the advantage of near-total solvent recovery via thermal regeneration [35].

The overall pH-swing strategy can be summarized as:



where A[−] is the conjugate base of the extractant. Reaction (6) regenerates A[−], which is recycled to Reaction (5). In practice, the energy and chemical losses associated with solvent regeneration are the principal barriers to commercial deployment of pH-swing processes; these are addressed primarily through improved solvent selection, more efficient gas–liquid contactors, and heat integration [22,33,44].

Figure 4 contrasts these two process families side by side: the direct route (panel A) carries out dissolution and precipitation in a single reactor, yielding a mixed CaCO₃ + SiO₂ solid under relatively severe conditions, whereas the indirect pH-swing route (panel B) decouples the two steps and recycles the extractant, producing high-purity precipitated calcium carbonate (PCC) at milder conditions but at the cost of solvent-regeneration energy.

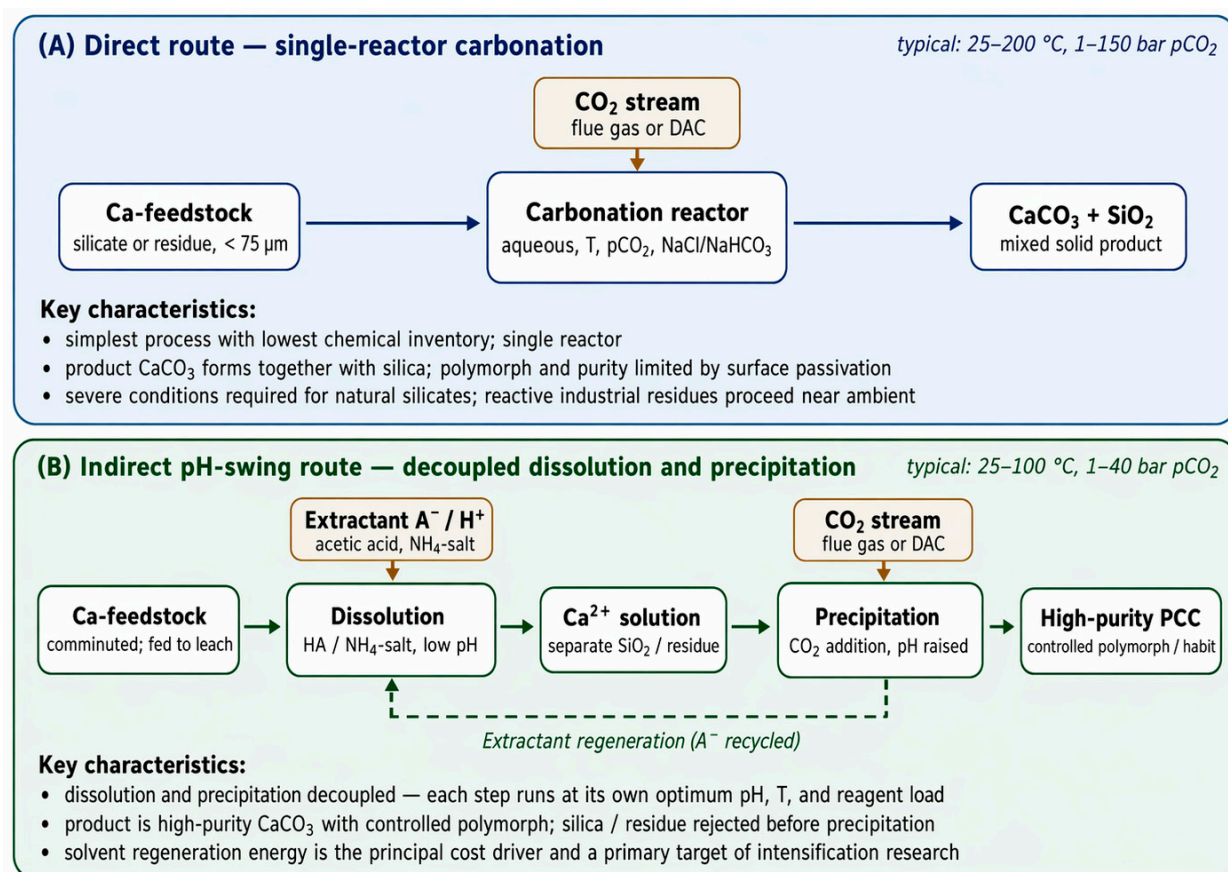


Figure 4. Schematic comparison of direct and indirect ex situ Ca-based mineral carbonation process architectures. **(A)** In the direct route, Ca-bearing feedstock and CO₂ are reacted in a single carbonation reactor to produce mixed CaCO₃–SiO₂ solid products, offering a simple process configuration but with limited control over product purity and polymorph formation. **(B)** In the indirect pH-swing route, dissolution and precipitation are decoupled: Ca is first extracted under acidic or ligand-assisted conditions, residual silica is separated, and high-purity CaCO₃ is subsequently precipitated under controlled pH and CO₂ conditions. Although the indirect route enables improved product control, solvent regeneration and reagent recycling remain key energetic and process-intensification challenges.

4.3. Process Intensification and CaCO₃ Product Control

A number of process-intensification strategies have been developed to narrow the gap between experimentally achievable rates and the natural limestone cycle. Mechanical activation by fine grinding reduces particle size and introduces lattice defects, both of which increase dissolution rates [18,19]. Thermal activation of hydrated phases (e.g., serpentine dehydroxylation) produces metastable structures with enhanced reactivity, although the energy cost is substantial [18]. Chemical additives—including NaCl and NaHCO₃ in O'Connor's classic recipe, organic acids in pH-swing processes, and catalytic additions such as carbonic anhydrase mimics—can accelerate either dissolution or CO₂ speciation [19–21,23,38,39]. Reactor design innovations include spray reactors, rotating packed beds, and thin-film reactors that enhance mass transfer [30,43,45]. Integration with CO₂ capture—so that the feedstock is contacted with a concentrated CO₂ stream from DAC or post-combustion capture rather than dilute flue gas—further improves rates and can also improve the economics of the combined capture-plus-mineralization chain [5,11,46].

A unique feature of Ca-based ex situ carbonation, and a principal rationale for its pursuit as a CDR technology, is that the solid product is a marketable form of limestone. Control of the CaCO₃ product, therefore, has substantial influence on the net economics and net CO₂ balance of the process [42].

Polymorph control is critical for high-value applications. Precipitated calcium carbonate (PCC) in the calcite and aragonite forms is used as a filler and coating in the paper, plastics, paint, and pharmaceuticals industries, and commands prices in the range of several hundred to more than a thousand USD per tonne depending on purity and particle size [35,42]. Vaterite, although metastable, has attracted interest for specialty biomedical uses [29,35]. For use as a supplementary cementitious material (SCM), aggregate, or direct CO₂-cured concrete ingredient, fine calcite with controlled particle morphology is generally preferred [35–37]. The PCC market route has been demonstrated experimentally for steel-slag-derived Ca [42,44], while CO₂ curing of fresh concrete and carbonation of recycled concrete fines have been commercialized [35,36].

Morphology control is achieved by tuning supersaturation, temperature, additives, and residence time during the precipitation step [29,35]. Because indirect processes separate precipitation from dissolution, they allow independent optimization of these variables and are therefore well suited to producing engineered-grade CaCO₃ that can substitute for mined limestone or mined-and-processed PCC [40,42,44]. This dual function—permanent CO₂ storage together with the supply of a product that would otherwise require quarrying of natural limestone—is one of the principal sources of the co-benefits and the favorable economics of Ca-based mineral carbonation in some applications [33–35,37].

A synthesis of representative ex situ Ca-based process configurations, including operating conditions and reported conversions, is provided in Table 2.

5. Techno-Economic Assessment, Challenges, and Future Perspectives

Translating laboratory demonstrations of Ca-based mineral carbonation into gigatonne-scale CDR requires assessment not only of technical feasibility but also of energy use, cost, life-cycle environmental impact, and policy alignment. Recent techno-economic and life-cycle studies have converged on a more nuanced picture than earlier assessments and have clarified where Ca-based routes are likely to compete.

5.1. Life-Cycle CO₂ Balance

Published techno-economic (TEA) and life-cycle (LCA) studies of Ca-based mineral carbonation adopt markedly different system boundaries, CO₂ sources, electricity carbon intensities, transport distances, product-credit assumptions, reagent-recovery treatments, and energy-accounting conventions; consequently, their headline cost and net-balance figures are not directly comparable. The net climate benefit, or net CO₂ removal when atmospheric/biogenic CO₂ is used, is the gross CO₂ bound in CaCO₃ minus the CO₂ emitted by the energy and chemicals used in the process [12,33,34]. For direct aqueous carbonation of natural silicates under O'Connor-type conditions, the electrical and thermal inputs associated with grinding, heating, and pressurization can offset a substantial fraction of the gross capture, particularly if the electricity is carbon-intensive [19,20]. More recent life-cycle analyses of Ca-based pathways using industrial residues and low-carbon electricity have reported net removal efficiencies in the range of 50%–90%, depending on process configuration and transport distances [40,41]. Utilization of the CaCO₃ product as SCM or PCC further improves the net balance by displacing emissions associated with clinker production or quarrying [36].

5.2. Cost

Reported costs for Ca-based mineral carbonation span a wide range, and much of this spread reflects differences in the cost metric and system boundary rather than in the process itself. Published figures should therefore be distinguished as levelized costs of CO₂ storage or avoidance, marginal abatement costs, or point estimates for a specific plant

configuration, and read together with the assumed CO₂ source, electricity carbon intensity, transport distance, and product credit. Direct carbonation of industrial residues at or near the emissions source can be economical even at modest carbon prices, because the feedstock is essentially free and the process may substitute for existing waste-management costs [13,24,33]; integrated techno-economic modeling of cement-sector mineralization indicates that such routes can even become net-profitable—by up to ~€32 per tonne of cement—when the carbonate product is used as a supplementary cementitious material and the stored CO₂ is eligible for carbon credits [40]. For natural Ca-silicates, levelized costs are higher because the feedstock must be mined, transported, and reacted under more severe conditions, with early process assessments reporting values of the order of tens to over a hundred USD per tonne of CO₂ [20,21]. Taken together, reported point estimates for integrated capture-plus-mineralization configurations span from approximately break-even, or even net-profitable when the product is credited, to roughly 150 USD tCO₂^{−1}, with the valuation of the CaCO₃ product as PCC or SCM playing a decisive role [20,21,40]. With these caveats, Ca-based mineral carbonation lies within the competitive range of other scalable CDR technologies, although further cost reduction and more standardized cost reporting are required for mass deployment [3,5].

5.3. Demonstration-Scale Activity

A number of demonstration and commercial operations now apply Ca-based carbonation in practice. CarbonCure Technologies has deployed CO₂-curing technology in hundreds of ready-mixed concrete plants worldwide, binding CO₂ in fresh concrete via reaction with hydrating cement phases [35,36]. Carbon8 Systems operates waste-carbonation facilities that treat APC residues and manufacture carbonated aggregates [24,29,31]. Calera, Blue Planet, and similar ventures have developed integrated capture-plus-mineralization concepts that yield synthetic carbonate aggregates from flue-gas CO₂ [35]. On the natural-silicate side, pilot-scale investigation of wollastonite and basalt carbonation has progressed in both Europe and North America [8,11,38,41]. Selected representative demonstrations are summarized in Table 3.

Table 3. Selected demonstration and commercial projects applying Ca-based mineral carbonation or closely related pathways [8,24–29,31–38,41,42].

Project/Operator	Feedstock and Configuration	Product	Status/Scale
CarbonCure Technologies	Hydrating cement phases; CO ₂ injection in ready-mix	CO ₂ -cured concrete	Commercial; hundreds of plants globally
Carbon8 Systems	APC residues; accelerated carbonation	Carbonated aggregates	Commercial; multiple facilities
Calera/Blue Planet	Flue-gas CO ₂ + alkaline brines or fines	Synthetic carbonate aggregates	Demonstration/early commercial
Åbo Akademi (ÅA) route	Steel slag; ammonium-salt pH-swing	High-purity PCC	Pilot/demonstration
Wollastonite field trials	Wollastonite fines on croplands	Soil-stored inorganic C	Field pilot

5.4. Outstanding Technical Challenges

Several technical issues remain unresolved. Passivation of reacting particles by silica-rich or carbonate-rich product layers continues to limit single-pass conversion in direct processes, and strategies to mitigate it (attrition, surfactant additives, thin-film reactors) add complexity and cost [30,38]. The regeneration of extractants in indirect processes is energy-intensive and remains a principal target of research [21,40]. For industrial-residue feedstocks, trace-element leaching (e.g., Cr, V, Mo from steel slag) during carbonation and during service of the resulting product must be controlled to avoid secondary environmen-

tal burdens [13,30,37]. Finally, water use and the management of aqueous effluents are non-trivial at an industrial scale, particularly in water-stressed regions [12,13].

5.5. Future Perspectives

Product markets also differ in absorptive capacity by orders of magnitude. The high-value PCC market is attractive per tonne but globally small—on the order of tens of megatonnes per year—and can accommodate only the early output of demonstration facilities, not gigatonne-scale removal. SCM and aggregate markets are far larger (hundreds of megatonnes to tens of gigatonnes per year), but aggregate applications command prices that rarely cover process costs, and SCM use is bounded by cement standards and product-quality requirements. Matching product grade to a market that is simultaneously large enough and valuable enough remains a central scale-up constraint.

Commercial deployment of mineral carbonation for CDR requires robust monitoring, reporting, and verification (MRV) to quantify the net quantity of CO₂ durably stored, including any emissions from process inputs and from the end-use of the CaCO₃ product [3–5]. Cement- and construction-sector use cases benefit from established standards for SCMs and aggregates, which reduce market-entry barriers [36,37]. High-value PCC markets are smaller but attractive on a per-tonne basis and can absorb the early output of demonstration-scale facilities [35,42]. Integration with carbon-pricing instruments, construction-sector decarbonization mandates, and procurement policies for low-carbon cement and concrete is likely to determine the pace of scale-up over the next decade [33,37].

Several directions emerge as priorities for the field. First, the development of intensified reactors that mitigate passivation and sustain high conversion over multiple cycles would make direct processes more competitive [30,38,43,45]. Second, systematic studies that couple feedstock characterization with CaCO₃ product specification—“feedstock-to-product” studies—are needed to connect laboratory results with market requirements [35,37,42]. Third, hybrid pathways that combine DAC-derived CO₂ with Ca-based feedstocks may become economically viable if DAC costs continue to decline [5,46]. Fourth, enhanced rock weathering of Ca-silicates—introduced in Section 1 as a lower-intensity, land-based analog of the reactor-based ex situ routes reviewed here—may provide a complementary, large-area CO₂-removal option, and coupling its agronomic co-benefits with carbonate/bicarbonate accounting is an active frontier [13,16,41].

Across these directions, the unifying question remains the one posed in the Introduction: how to accelerate the natural limestone-forming cycle sufficiently to deliver gigatonne-scale, permanent, and cost-effective CO₂ removal. The scientific and engineering toolkit to answer this question has grown substantially over the past decade, and the coming decade is likely to establish which of the available Ca-based pathways achieve sustained industrial deployment.

6. Conclusions

Whether a given implementation of mineral carbonation qualifies as carbon dioxide removal depends on the origin of the feed CO₂: only atmospheric or biogenic carbon, durably stored as CaCO₃, yields net removal, whereas mineralization of fossil-derived industrial CO₂ constitutes CCS or CCU [47,48]. Ca-based ex situ mineral carbonation constitutes a scientifically mature and operationally promising route for permanent CO₂ storage. The central logic is to reproduce the natural formation of limestone—nature’s long-term CO₂ sink—in engineered reactors, at rates that are orders of magnitude faster than those prevailing in the geological cycle. Several conclusions emerge. First, Ca-based feedstocks—both natural silicates such as wollastonite and Ca-rich industrial residues such as steel slag, cement kiln dust, and fly ash—offer complementary strengths, with

natural silicates providing compositional consistency and industrial residues providing rapid kinetics and waste-valorization co-benefits. Second, ex situ process routes span a wide design space, from simple direct gas–solid systems suitable for highly reactive wastes to multistep pH-swing configurations that enable independent optimization of dissolution and precipitation and allow for the production of high-purity, polymorph-controlled CaCO_3 . Third, the simultaneous generation of a valuable solid product gives Ca-based mineral carbonation a dual value proposition that is largely absent from other CDR pathways and that substantially improves its economics in construction- and filler-related applications. Fourth, although net CO_2 balances are now favorable under many realistic configurations, technical challenges around passivation, solvent regeneration, and trace-element management remain active research areas. Looking ahead, the field faces a twofold task: accelerating the fundamental carbonate-forming reactions even further, and integrating them into industrial value chains in which the CaCO_3 product is not a by-product but a deliberately engineered material. Coordinated progress on both fronts would allow laboratory-synthesized limestone to assume a durable role among the technologies enabling long-term climate stabilization.

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References

1. Lan, X.; Tans, P.; Thoning, K.W. *Trends in Globally-Averaged CO_2 Determined from NOAA Global Monitoring Laboratory Measurements, Version 2026-06*; NOAA Global Monitoring Laboratory: Boulder, CO, USA, 2026. [CrossRef]
2. Lackner, K.S.; Wendt, C.H.; Butt, D.P.; Joyce, E.L.; Sharp, D.H. Carbon dioxide disposal in carbonate minerals. *Energy* **1995**, *20*, 1153–1170. [CrossRef]
3. IPCC. *Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*; IPCC: Geneva, Switzerland, 2023.
4. National Academies of Sciences, Engineering, and Medicine. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*; The National Academies Press: Washington, DC, USA, 2019.
5. Smith, S.M.; Geden, O.; Nemet, G.F.; Gidden, M.J.; Lamb, W.F.; Powis, C.; Bellamy, R.; Callaghan, M.; Cowie, A.; Cox, E.; et al. *The State of Carbon Dioxide Removal*, 1st ed.; The State of CDR: Oxford, UK, 2023.
6. Babiker, M.; Berndes, G.; Blok, K.; Cohen, B.; Cowie, A.; Geden, O.; Ginzburg, V.; Leip, A.; Smith, P.; Sugiyama, M.; et al. Cross-sectoral Perspectives. In *Climate Change 2022: Mitigation of Climate Change*; Contribution of Working Group III to the Sixth Assessment Report of the IPCC., IPCC AR6 WGIII, Chapter 12; Shukla, P.R., Skea, J., Reisinger, A., Slade, R., Fradera, R., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2022.
7. McQueen, N.; Kelemen, P.; Dipple, G.; Renforth, P.; Wilcox, J. Ambient weathering of magnesium oxide for CO_2 removal from air. *Nat. Commun.* **2020**, *11*, 3299. [CrossRef] [PubMed]
8. Snæbjörnsdóttir, S.Ó.; Sigfússon, B.; Marieni, C.; Goldberg, D.; Gislason, S.R.; Oelkers, E.H. Carbon dioxide storage through mineral carbonation. *Nat. Rev. Earth Environ.* **2020**, *1*, 90–102. [CrossRef]

9. Matter, J.M.; Stute, M.; Snæbjörnsdóttir, S.Ó.; Oelkers, E.H.; Gislason, S.R.; Aradottir, E.S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardottir, H.; Gunnlaugsson, E.; et al. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* **2016**, *352*, 1312–1314. [[CrossRef](#)] [[PubMed](#)]
10. Kelemen, P.B.; Matter, J. In situ carbonation of peridotite for CO₂ storage. *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 17295–17300. [[CrossRef](#)]
11. Berner, R.A. The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* **2003**, *426*, 323–326. [[CrossRef](#)] [[PubMed](#)]
12. Berner, R.A.; Lasaga, A.C.; Garrels, R.M. The carbonate–silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. *Am. J. Sci.* **1983**, *283*, 641–683. [[CrossRef](#)]
13. Hartmann, J.; West, A.J.; Renforth, P.; Köhler, P.; De La Rocha, C.L.; Wolf-Gladrow, D.A.; Dürr, H.H.; Scheffran, J. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. *Rev. Geophys.* **2013**, *51*, 113–149. [[CrossRef](#)]
14. Oelkers, E.H.; Gislason, S.R.; Matter, J. Mineral carbonation of CO₂. *Elements* **2008**, *4*, 333–337. [[CrossRef](#)]
15. Gadikota, G. Carbon mineralization pathways for carbon capture, storage and utilization. *Commun. Chem.* **2021**, *4*, 23. [[CrossRef](#)] [[PubMed](#)]
16. Sanna, A.; Uibu, M.; Caramanna, G.; Kuusik, R.; Maroto-Valer, M.M. A review of mineral carbonation technologies to sequester CO₂. *Chem. Soc. Rev.* **2014**, *43*, 8049–8080. [[CrossRef](#)] [[PubMed](#)]
17. Bobicki, E.R.; Liu, Q.; Xu, Z.; Zeng, H. Carbon capture and storage using alkaline industrial wastes. *Prog. Energy Combust. Sci.* **2012**, *38*, 302–320. [[CrossRef](#)]
18. Pan, S.-Y.; Chang, E.E.; Chiang, P.-C. CO₂ capture by accelerated carbonation of alkaline wastes: A review on its principles and applications. *Aerosol Air Qual. Res.* **2012**, *12*, 770–791. [[CrossRef](#)]
19. Huijgen, W.J.J.; Comans, R.N.J. *Carbon Dioxide Sequestration by Mineral Carbonation: Literature Review Update 2003–2004*; Report ECN-C-05-022; Energy Research Centre of the Netherlands: Petten, The Netherlands, 2005.
20. O'Connor, W.K.; Dahlin, D.C.; Rush, G.E.; Gerdemann, S.J.; Penner, L.R.; Nilsen, D.N. *Aqueous Mineral Carbonation: Mineral Availability, Pretreatment, Reaction Parametrics, and Process Studies*; Report DOE/ARC-TR-04-002; Albany Research Center: Albany, OR, USA, 2005.
21. Gerdemann, S.J.; O'Connor, W.K.; Dahlin, D.C.; Penner, L.R.; Rush, H. Ex situ aqueous mineral carbonation. *Environ. Sci. Technol.* **2007**, *41*, 2587–2593. [[CrossRef](#)] [[PubMed](#)]
22. Park, A.-H.A.; Fan, L.-S. CO₂ mineral sequestration: Physically activated dissolution of serpentine and pH swing process. *Chem. Eng. Sci.* **2004**, *59*, 5241–5247. [[CrossRef](#)]
23. Daval, D.; Martinez, I.; Corvisier, J.; Findling, N.; Goffé, B.; Guyot, F. Carbonation of Ca-bearing silicates, the case of wollastonite: Experimental investigations and kinetic modeling. *Chem. Geol.* **2009**, *265*, 63–78. [[CrossRef](#)]
24. Kakizawa, M.; Yamasaki, A.; Yanagisawa, Y. A new CO₂ disposal process via artificial weathering of calcium silicate accelerated by acetic acid. *Energy* **2001**, *26*, 341–354. [[CrossRef](#)]
25. Lee, S.; Rhee, C.W.; Yoo, G. Cost-Effective Carbon Dioxide Removal via CaO/Ca(OH)₂-Based Mineralization with Concurrent Recovery of Value-Added Calcite Nanoparticles. *Sustainability* **2025**, *17*, 8875. [[CrossRef](#)]
26. Huijgen, W.J.J.; Witkamp, G.-J.; Comans, R.N.J. Mineral CO₂ sequestration by steel slag carbonation. *Environ. Sci. Technol.* **2005**, *39*, 9676–9682. [[CrossRef](#)] [[PubMed](#)]
27. Eloneva, S.; Teir, S.; Salminen, J.; Fogelholm, C.-J.; Zevenhoven, R. Fixation of CO₂ by carbonating calcium derived from blast furnace slag. *Energy* **2008**, *33*, 1461–1467. [[CrossRef](#)]
28. Teir, S.; Eloneva, S.; Fogelholm, C.-J.; Zevenhoven, R. Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production. *Energy* **2007**, *32*, 528–539. [[CrossRef](#)]
29. Bonenfant, D.; Kharoune, L.; Sauvé, S.; Hausler, R.; Niquette, P.; Mimeault, M.; Kharoune, M. CO₂ sequestration potential of steel slags at ambient pressure and temperature. *Ind. Eng. Chem. Res.* **2008**, *47*, 7610–7616. [[CrossRef](#)]
30. Fernández Bertos, M.; Simons, S.J.R.; Hills, C.D.; Carey, P.J. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂. *J. Hazard. Mater.* **2004**, *112*, 193–205. [[CrossRef](#)] [[PubMed](#)]
31. Baciocchi, R.; Costa, G.; Poletti, A.; Pomi, R. Effects of thin-film accelerated carbonation on steel slag leaching. *J. Hazard. Mater.* **2015**, *286*, 369–378. [[CrossRef](#)] [[PubMed](#)]
32. Fang, Y.; Lee, S.; Xu, H.; Farfan, G.A. Organic Controls over Biomineral Ca–Mg Carbonate Compositions and Morphologies. *Cryst. Growth Des.* **2023**, *23*, 4872–4882. [[CrossRef](#)] [[PubMed](#)]
33. Rashid, M.I.; Benhelal, E.; Anderberg, L.; Farhang, F.; Oliver, T.K.; Rayson, M.S.; Stockenhuber, M. Aqueous carbonation of peridotites for carbon utilisation: A critical review. *Environ. Sci. Pollut. Res.* **2022**, *29*, 75161–75183. [[CrossRef](#)]
34. Rashid, M.I.; Yaqoob, Z.; Mujtaba, M.A.; Fayaz, H.; Saleel, C.A. Developments in mineral carbonation for carbon sequestration. *Heliyon* **2023**, *9*, e21796. [[CrossRef](#)] [[PubMed](#)]
35. Rashid, M.I.; Nawaz, M.; Athar, M.; Aadil, M.A.; Umer, A.; Abbas, M.M.; Bashir, M.N.; Ali, M.M. Research trends in cementitious materials via slags aqueous mineral carbonation: A bibliometric analysis. *Results Chem.* **2025**, *15*, 102223. [[CrossRef](#)]

36. Morales-Flórez, V.; Santos, A.; Lemus, A.; Esquivias, L. Artificial weathering pools of calcium-rich industrial waste for CO₂ sequestration. *Chem. Eng. J.* **2011**, *166*, 132–137. [[CrossRef](#)]
37. Chang, E.-E.; Pan, S.-Y.; Chen, Y.-H.; Chu, H.-W.; Wang, C.-F.; Chiang, P.-C. CO₂ sequestration by carbonation of steelmaking slags in an autoclave reactor. *J. Hazard. Mater.* **2011**, *195*, 107–114. [[CrossRef](#)] [[PubMed](#)]
38. Power, I.M.; Harrison, A.L.; Dipple, G.M.; Wilson, S.A.; Kelemen, P.B.; Hitch, M.; Southam, G. Carbon mineralization: From natural analogues to engineered systems. *Rev. Mineral. Geochem.* **2013**, *77*, 305–360. [[CrossRef](#)]
39. Beuttler, C.; Charles, L.; Wurzbacher, J. The role of direct air capture in mitigation of anthropogenic greenhouse gas emissions. *Front. Clim.* **2019**, *1*, 10. [[CrossRef](#)]
40. Strunge, T.; Renforth, P.; Van der Spek, M. Towards a business case for CO₂ mineralisation in the cement industry. *Commun. Earth Environ.* **2022**, *3*, 59. [[CrossRef](#)]
41. Ostovari, H.; Sternberg, A.; Bardow, A. Rock ‘n’ use of CO₂: Carbon footprint of carbon capture and utilization by mineralization. *Sustain. Energy Fuels* **2020**, *4*, 4482–4496. [[CrossRef](#)]
42. Woodall, C.M.; McQueen, N.; Pilorgé, H.; Wilcox, J. Utilization of mineral carbonation products: Current state and potential. *Greenh. Gases Sci. Technol.* **2019**, *9*, 1096–1113. [[CrossRef](#)]
43. Monkman, S.; MacDonald, M. On carbon dioxide utilization as a means to improve the sustainability of ready-mixed concrete. *J. Clean. Prod.* **2017**, *167*, 365–375. [[CrossRef](#)]
44. Azdarpour, A.; Asadullah, M.; Mohammadian, E.; Hamidi, H.; Junin, R.; Karaei, M.A. A review on carbon dioxide mineral carbonation through pH-swing process. *Chem. Eng. J.* **2015**, *279*, 615–630. [[CrossRef](#)]
45. Pan, S.-Y.; Chen, Y.-H.; Fan, L.-S.; Kim, H.; Gao, X.; Ling, T.-C.; Chiang, P.-C.; Pei, S.-L.; Gu, G. CO₂ mineralization and utilization by alkaline solid wastes for potential carbon reduction. *Nat. Sustain.* **2020**, *3*, 399–405. [[CrossRef](#)]
46. Renforth, P. The negative emission potential of alkaline materials. *Nat. Commun.* **2019**, *10*, 1401. [[CrossRef](#)] [[PubMed](#)]
47. Lee, S. Facet-selective anisotropic growth of 1D calcite nanowhiskers via Mg/Zn/SO₄ additive-assisted carbonation. *Sci. Rep.* **2026**, *in press*. [[CrossRef](#)] [[PubMed](#)]
48. U.S. Geological Survey. Wollastonite. In *Mineral Commodity Summaries 2025*; U.S. Geological Survey: Reston, VA, USA, 2025. [[CrossRef](#)]

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