

Controls on CO₂ Mineralization Using Natural and Industrial Alkaline Solids under Ambient Conditions

Erika Callagon La Plante,* Iman Mehdipour, Ian Shortt, Kai Yang, Dante Simonetti, Mathieu Bauchy, and Gaurav N. Sant*



Cite This: ACS Sustainable Chem. Eng. 2021, 9, 10727–10739



Read Online

ACCESS |



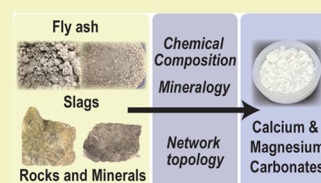
Metrics & More



Article Recommendations

ABSTRACT: The extent to which carbon dioxide (CO₂) mineralization (“carbonation”) using alkaline solids can reduce atmospheric CO₂ concentrations is dictated by the rate of divalent alkaline metal release from such solids. These solids have distinct reactivities, that is, bulk dissolution rates, which dictate their rates of carbonation. To assess the feasibility of utilizing alkaline solids to mitigate CO₂ emissions at scale, assessments of practical carbonation potentials under ambient conditions, which are often distinct from their stoichiometric carbonation potential as described by their bulk chemical composition, are needed. Therefore, the carbonation (or “CO₂ mineralization”) potentials of 16 naturally occurring (mafic and ultramafic) rocks and industrial alkaline solids (fly ashes and slags) were quantified. In general, the extent of carbonation for the pulverized and as-received solids which is achievable under ambient conditions [25 °C, 1 bar]—in the presence of excess CO₂ and water—that is, the *carbonation potential*, is correlated with the CaO and MgO content and varies inversely with the SiO₂ content. Particularly, the carbonation efficiency (i.e., the ratio of the measured to the stoichiometric carbonation potential) is controlled by the atomic topology (network connectivity) of the solid reactant—suggesting that network rupture is the rate-controlling step of dissolution and, hence, carbonation. Based on our data, we offer estimates of CO₂ removal that can be achieved under ambient exposure conditions to assess the controls and capacity of ambient CO₂ mineralization as a carbon dioxide removal strategy.

KEYWORDS: alkaline solids, mineral carbonation, silicate dissolution, CO₂ mitigation, reactivity



INTRODUCTION

The *in situ* and *ex situ* mineralization of carbon dioxide (CO₂) (“carbonation”) to form sparingly soluble carbonates has been suggested as an approach to mitigate climate change.^{1,2} This approach consumes atmospheric or flue gas-borne CO₂ by immobilizing it via a classical acid–base reaction (“mineralization”) within calcium and magnesium carbonates [e.g., calcite (CaCO₃), magnesite (MgCO₃), and variants thereof].^{3–5} Expectedly, herein, CO₂ (acid) is reacted with an alkaline solid (base). Because CO₂ mineralization (carbonation) is a dissolution–precipitation promoted reaction, it requires an aqueous environment or a humid atmosphere.⁶ The availability of water into which gas-phase CO₂ and the alkaline solid dissolve, remarkably affects carbonation reaction rates.⁷ The alkaline solid provides metal cations, for example, Ca²⁺ and Mg²⁺ (and occasionally Fe²⁺) that react with bicarbonate (HCO₃[−]) or carbonate (CO₃^{2−}) anions that speciate from the dissolved CO₂ to form carbonate minerals. The net reaction is thermodynamically favorable⁸ and produces stable products as evident from the abundance and persistence of large-scale carbonate deposits in nature.

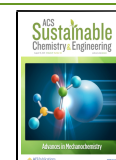
Carbonate mineral formation by *in situ* mineralization in basaltic formations injected with CO₂-saturated water has been suggested to occur within 2 years.⁹ This rate is consistent with experimental data and reactive transport modeling, which

indicate an induction time for calcite precipitation at depth on the order of 1.5 years.¹⁰ However, on the Earth’s surface, the conversion of silicates to carbonates (“weathering”) typically requires geological time scales. As a synthetic (“engineering”) intervention, *ex situ* carbonation relies overwhelmingly on accelerating silicate dissolution–carbonate precipitation reactions with the following: (i) using CO₂-rich streams (e.g., flue gas from power plants), (ii) imposing high pressures and temperatures wherein the dissolution of silicates, both natural (e.g., mafic and ultramafic igneous rocks) and those derived from industrial processes (e.g., coal combustion ash, metal processing slag, cement kiln dust, etc.), is enhanced, and (iii) using finely divided solids that present large surface areas.^{11–18} In these cases, carbonation is accomplished in a *direct process* in which CO₂ is reacted with an alkaline solid to form carbonate minerals^{19,20} or by a sequential process which involves alkaline solid dissolution, followed by carbonate precipitation.^{21,22} In

Received: February 5, 2021

Revised: July 20, 2021

Published: August 4, 2021



each case, the extent of achievable carbonation is limited by the amount of extractable divalent metal cations.

Practically, the viability of *ex situ* CO₂ mineralization to serve as a carbon management solution requires the fulfillment of rapid carbonation reaction rates. To enhance carbonation rates, because natural alkaline solids are inherently (far) less reactive than their industrial-waste counterparts, carbonation often requires high processing temperatures ($T > 100$ °C) and CO₂ partial pressures (>40 atm) and/or the use of finely divided solids that present large surface areas.^{23,24} The imposition of such conditions enhances Ca and Mg release, but resulting in a consequential energy cost. Often however, estimates of carbonation potentials are based on the mass abundance of the solids and their bulk chemical composition. For instance, basaltic lava flows, peridotites, and mid-ocean ridge basalts represent a CO₂ uptake potential of up to 60,000,000 Gt CO₂, 10,000–100,000,000 Gt CO₂, and 100,000–250,000 Gt CO₂,^{25–27} respectively, whereas industrial alkaline wastes present a carbon uptake potential of 100–1250 Mt CO₂ per year globally.^{2,8} However, such estimates are sensitive to assumptions of carbonation efficiency, that is, the extent of CO₂ uptake that is achieved relative to the stoichiometric uptake capacity.^{28–32} For example, carbonation efficiencies ranging from <10 to >90% have been reported for alkaline wastes.^{4,6,32,33} Efficiencies for rocks are much lower,³⁴ for example, on the order of <1% at ambient conditions at short time scales although a reactive silicate such as olivine ((Mg,Fe)₂SiO₄) features a reaction efficiency of ~50% after 1 year at room temperature.³⁵ In mafic and ultramafic mine tailings, brucite (Mg(OH)₂) is the primary phase that carbonates at ambient conditions over short reaction times.^{17,36,37}

Clearly, the carbonation potential (or efficiency) is significantly affected by the process conditions, for example, solution pH, temperature, CO₂ partial pressure, reaction duration, and so forth.³⁸ However, there have been few direct comparisons of carbonation potentials of different solids spanning both natural and synthetic compositions by a consistent method, with an abundance of primary reactants (CO₂, water) and a specific emphasis on revealing solute controls on CO₂ mineralization.² Also, polyphasic rocks, fly ash, and slags are heterogeneous solids consisting of multiple phases that present distinct reactivities, which may be uniquely influenced by each process variable.²⁸ Therefore, herein, the carbonation potentials of 16 natural and industrial alkaline silicates are quantified at near-ambient temperature and pressure conditions in a consistent way. We clarify the chemical and mineralogical linkages between silicate reactivity, dissolution kinetics, and carbonation potentials through batch experiments wherein dissolution and precipitation occur simultaneously. Based on such data, we present estimates of the carbonation potential of alkaline solids to determine the extent to which CO₂ mineralization of alkaline feedstocks could serve as a negative emissions technology to address the ongoing carbon crisis.

MATERIALS AND METHODS

Sample Preparation and Characterization. The alkaline solids examined included calcium hydroxide or hydrated lime (Ca(OH)₂): a reference solid, coal combustion fly ash, crystalline slags from iron and steel production (amorphous slags are not considered due to their desirability as a cement replacement material),^{39–41} and natural Ca- and Mg-rich rocks and minerals. Five different types of fly ash,

including Class C (CaO-rich), Class F (CaO-poor), trona (Na₃(CO₃)(HCO₃)·2H₂O)-rich, and reclaimed Ca-rich fly ash were supplied by Boral Resources LLC. Five crystalline slags, electric arc furnace (EAF), basic oxygen furnace (BOF), air-cooled blast furnace (ac-BF), stainless steel (SS), and ladle slag (LS), were supplied by TMS International. The natural rock and mineral samples including flood basalt, serpentinite, peridotite, anorthosite, and olivine (forsterite: Mg₂SiO₄) were sourced from Ward's Science.

The bulk chemical compositions of the samples in mass % of the simple oxides are shown in Figure 1. The mineralogical assemblage in

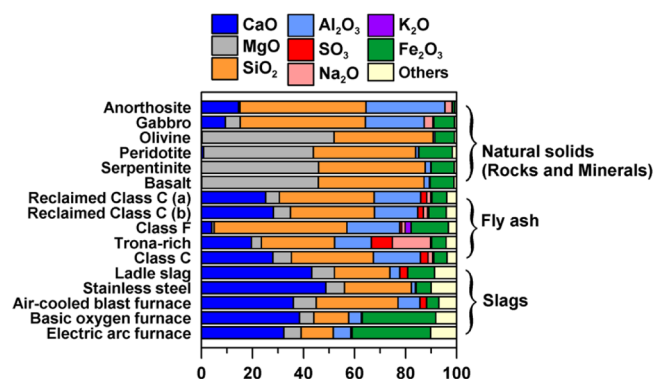


Figure 1. Chemical composition of the alkaline solids shown in terms of their simple oxide constituents (in mass %).

a subset of the solids was evaluated using X-ray diffraction (XRD). The major phases revealed by powder XRD carried out on finely divided homogenized powders are antigorite ((Mg,Fe)₃Si₂O₅(OH)₄), magnesite (MgCO₃), bytownite ((Ca_{0.7–0.9}Na_{0.3–0.1})Al(Al,Si)Si₂O₈), forsterite, periclase (MgO), and magnetite (Fe₃O₄) in the rocks, and larnite (β-Ca₂SiO₄ and γ-Ca₂SiO₄), brownmillerite (Ca₂(Al,Fe)₂O₅), magnetite, wüstite (FeO), kirschsteinite (CaFeSiO₄), melilite ((Ca,Na)₂SiO₇), cuspidine (Ca₄Si₂O₇(F,OH)₂), brucite (Mg(OH)₂), bredigite (Ca₂MgSi₄O₁₆), and calcite in the slags.

In general, the air-dried slags and rock samples were ground using a ball mill for 40 min, and a particle size fraction between 38 and 53 μm (corresponding to a grinding energy of ~40 kWh per ton using the Bond Work Index equation) was obtained via sieving. In the case of fly ash and hydrated lime, they were both used as received, wherein they present a median particle diameter, *d*₅₀, of ~2–5 μm. The particle size distributions of all solids were measured using a LS13-320 Beckman Coulter static light scattering analyzer on powder samples suspended in isopropanol following ultrasonication. Class C (high-Ca fly ash) was noted to have a *d*₅₀ ~ 1.5 μm, that is, smaller than the other fly ash samples, as observed elsewhere.⁴²

Assessing Carbonation Kinetics Using ICP-OES and TGA.

The solid particulates were suspended in excess ultrapure deionized (DI) water (>18 MΩ·cm) that was continuously bubbled with 100% CO₂ at an atmospheric pressure at 60 °C. A double-walled borosilicate reactor (Wilma-LabGlass)—that was used to contain the suspensions—was connected to a water bath for thermal regulation within ±0.1 °C. The suspensions were stirred using either a magnetic stir bar or an impeller-type mixer while ensuring matching of the Reynolds number (*Re*, unitless) in solution. Both pH and temperature were monitored as a function of time. After 24 and 72 h of aqueous carbonation, the reacted solids including any secondary precipitates were separated by vacuum filtration using a Buchner funnel lined with filter paper (3–5 μm). Thereafter, the filtrate was dried in an oven at 75 °C and then homogenized prior to taking a small sample for thermogravimetric analysis (TGA).

The extent of carbonation was measured using a Perkin Elmer STA6000, which quantified the temperature-dependent mass change of the residual solids (filtrate) as they were heated from 35 to 975 °C. Around 30 mg of the filtrate was placed in pure aluminum oxide crucibles and heated under an ultra-high purity N₂ gas purge at a flow rate of 20 mL/min and a heating rate of 10 °C/min. The total

carbonate content was quantified by considering the mass loss over the temperature range of 500–900 °C, corresponding to the decomposition of calcium and magnesium carbonates and subtracting the carbonate content of the initial unreacted (“pristine”) solid. For slags which have two distinct decomposition peaks, the peak at 500–650 °C is assigned to magnesium carbonates and amorphous calcium carbonate (ACC) and that at 650–900 °C to crystalline calcium carbonate.^{43–45} Based on previous measurements, the estimated uncertainty in the CO₂ uptake is approximately 5%.

Characterization of Carbonated Products. A selection of samples was further characterized using XRD (Siemens D500) and a field emission–scanning electron microscope (SEM) (Hitachi S4800). Particularly, non-carbonated and carbonated slag particulates were dried in air at ~45 °C prior to analysis. The samples were placed in a lucite holder for XRD measurements using Cu K α radiation (λ = 1.5406 Å) for a scattering angle range of 5–70° with a 0.02° step size. For SEM analyses, a small amount of the powdered sample was affixed onto a piece of carbon tape and then coated with Au. An accelerating voltage of 10.0 kV and a beam current of 10 μ A were used for a working distance of 7.6 mm.

Dissolution Rate. 1 g of slag was reacted with 100 mL of solution in “batch mode” to produce a solid to liquid (S/L) mass ratio of 1:100. The reaction solutions used were prepared by adding analytical reagent-grade chemicals, as needed, to ultrapure DI water. The experiments were conducted at 25 $\pm$ 0.2, 45 $\pm$ 0.2, and 90 $\pm$ 3 °C using temperature-controlled environmental chambers and under static conditions or at ambient temperature (~23 °C) under stirred conditions using a magnetic stir bar. After 0, 1, 3, 6, 24, 72, and 168 h of reaction, the reacted solution was sampled (~3 mL) for analysis of total dissolved Ca, Mg, Si, Fe, Al, Mn, and Na concentrations. The samples were filtered immediately using a syringe through 0.20 μ m nylon filters prior to acidification and dilution by a factor of 10 in 5 vol % HNO₃ (70%). Analysis of elemental concentrations was carried out using a Perkin Elmer Avio 200 inductively coupled plasma-optical emission spectrometer using calibration standards prepared from concentrated (1000 ppm) standards from Inorganic Ventures. In general, replicate experiments carried out using DI water at 90 °C indicate an uncertainty (i.e., relative standard deviation) of 3% in typical Ca-concentrations.

Network Topology Analysis. To decode the relationship between atomic structure, mineral dissolution, and subsequently carbonation kinetics, the atomic connectivity of the solids was assessed using the topological constraint theory (TCT).^{46–48} TCT reduces atomic networks into truss architectures wherein some nodes (the atoms) are interconnected via constraints (the chemical bonds). Atomic networks comprise both radial bond-stretching (BS) and angular bond-bending (BB) constraints, which maintain the interatomic distances and angles fixed around their average values. Atomic networks are described as flexible, stressed-rigid, or isostatic if the total number of constraints per atom (n_c) is lower than, larger than, or equal to the number of degrees of freedom per atom (i.e., 3). For each solid, the number of constraints per atom is calculated as follows. First, for crystalline phases, the number of constraints created by each element is estimated from their crystallographic structure, that is, based on the coordination number of each element. Fly ash and slags (except ac-BF) represent a significant fraction of poorly ordered solids and, here, for simplicity, are assumed to be fully glassy. For such disordered systems, we first calculate the number of bridging oxygen (BO) and non-bridging oxygen (NBO) atoms acting in their atomic networks—wherein BO and NBO atoms are connected to 1 and 2 network-forming atoms (Si, Al, or Fe), respectively. This is achieved as follows. Starting from pure SiO₂ (where all O atoms are BO), each alkaline-earth network (Ca or Mg) consumes 2 BOs whereas each Al or Fe atom creates 1 BO—for reasons of local charge-compensation.⁴⁹ As a conservative assumption, it is assumed that no free oxygen (connected to only network-modifying elements) or tricluster oxygen (connected to three network formers) exists in these solids. The number of NBOs is then calculated as the number of O atoms that are not BO. The number of constraints created by each element is then calculated based on their average coordination

number. In detail, each Si, Al, and Fe atom creates four BS constraints (with their four oxygen neighbors) and five BB constraints (which is the minimum number of independent angular constraints that are needed to fix the tetrahedral environment of the network-forming elements).⁴⁸ Based on previous studies, alkaline-earth atoms (Ca and Mg) form two BS constraints with their nearest NBO neighbors.^{50,51} However, due to the ionic, non-directional nature of the bond they form, alkaline-earth atoms do not create any BB constraints. For simplicity, all BS constraints are fully attributed to the cations—since each BS constraint is necessarily shared by a cation and an oxygen atom. Finally, each BO atom creates one BB constraint to fix the angle it forms with its two network-forming neighbors. The analytical calculation of the number of constraints per atom (n_c) in (CaO)_a(Al₂O₃)_b(SiO₂)_c(MgO)_d(Fe₂O₃)_e systems (where letter subscripts indicate the mole fraction of the respective oxide) can be summarized as follows. In the constraints enumeration, we distinguish disordered (slags and fly ash) from crystalline (rocks) systems. In disordered systems, n_c depends on whether or not there exist NBO atoms in the network. If there exist NBOs in the system (if $-a + b - d + e \leq 0$), n_c can be expressed as

$$n_c = \frac{a + 23b + 11c + d + 23e}{2a + 5b + 3c + 2d + 5e}$$

Otherwise, if all oxygen atoms act as BO atoms, n_c is given by

$$n_c = \frac{3a + 21b + 11c + 3d + 21e}{2a + 5b + 3c + 2d + 5e}$$

On the other hand, for crystalline systems featuring NBO atoms (i.e., if $-a + b - d + e \leq 0$), n_c can be expressed as follows:

$$n_c = \frac{5a + 23b + 11c + 5d + 23e}{2a + 5b + 3c + 2d + 5e}$$

Otherwise, for crystalline systems that do not present NBO atoms, n_c is given by

$$n_c = \frac{7a + 21b + 11c + 7d + 21e}{2a + 5b + 3c + 2d + 5e}$$

RESULTS AND DISCUSSION

How Should Carbonation Potential Be Assessed? CO₂ mineralization using silicate solids is a multi-step process involving the following: (i) the dissolution of CO₂ in water and its speciation to HCO₃[−] and CO₃^{2−} ions, (ii) the dissolution of the silicate solute that yields dissolved Ca²⁺ and Mg²⁺ in solution, and (iii) the nucleation and growth of insoluble metal carbonates (e.g., CaCO₃, MgCO₃, and their hydroxy-variants) as the solution exceeds a critical supersaturation with respect to these phases. The thermodynamic driving force for precipitation is given by the saturation ratio, Ω = IAP/ K_{sp} , where IAP is the ion activity product and K_{sp} is the solubility product. For calcite, these are the products of the activities of Ca²⁺ and CO₃^{2−} in solution and at equilibrium for a given thermodynamic temperature. The saturation index (SI) is the logarithm (log₁₀) of Ω .

The Gibbs free energy difference is a function of the saturation ratio according to ΔG = $RT \ln \Omega$, where R is the gas constant and T is the (isothermal) reaction temperature. Thus, the thermodynamic driving force for precipitation increases with an increasing extent of silicate dissolution, which releases metal cations (i.e., Ca²⁺ and Mg²⁺) into the solution while increasing the solution pH and the carbonate ion activity. As such, in systems involving relatively unreactive Ca- and Mg-silicates (e.g., the dissolution rate of olivine shows values of around 10^{−10} mol/m²/s at 25 °C),⁵² at near-neutral pH, the dissolution of the solid is most often the reaction-limiting step^{19,27,38} since both the dissolution of CO₂ and carbonate

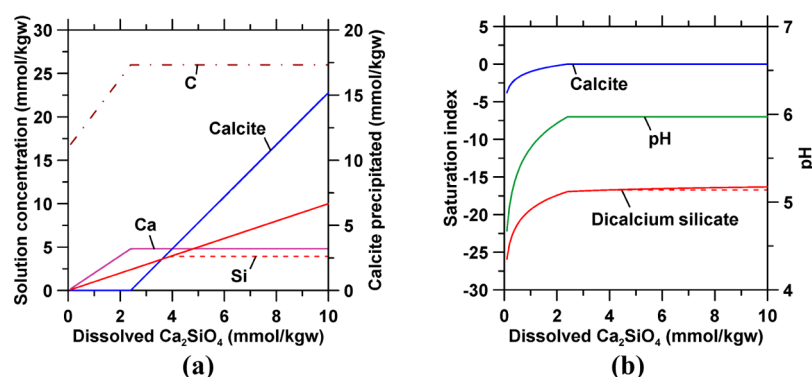


Figure 2. Illustrative geochemical simulations of the dissolution of dicalcium silicate (larnite: Ca_2SiO_4)—an exemplar silicate—showing: (a) concentrations of dissolved Ca, Si, and C and solid calcite (CaCO_3) and (b) saturation indices with respect to calcite and Ca_2SiO_4 and pH as a function of dissolved Ca_2SiO_4 in an ideal system wherein Ca_2SiO_4 dissolves in CO_2 -saturated water. The red curves in (a,b) indicate the evolution of [Si] and SI with respect to Ca_2SiO_4 assuming (solid red) supersaturation or (dashed red) equilibrium with respect to amorphous silica. Expectedly, an analogous system composed of forsterite (Mg_2SiO_4) instead of Ca_2SiO_4 results in the thermodynamic stability of magnesite (MgCO_3) instead of calcite. Here, dissolution–carbonation reactions occurred at ambient (“atmospheric”) pressure, and $T = 60^\circ\text{C}$ in excess water in equilibrium with pure CO_2 , that is, $\text{pH} \sim 4$.

mineral precipitation are relatively far more rapid.⁵³ Specifically, aqueous equilibrium with respect to $\text{CO}_{2(\text{g})}$ and Ca^{2+} is reached in 5.0×10^{-11} and 10^3 s, respectively.

With these considerations in mind, carbonation potentials were assessed in aqueous suspensions of the alkaline solid that were continuously bubbled with a gas stream of $\sim 100\%$ CO_2 at ambient pressure. For reference, point sources of CO_2 including natural gas- and coal-fired power plants, iron and steel mills, cement plants, and chemical plants feature concentrations ranging from 3 to >90 vol %.⁵⁴ The approach that we chose to apply seeks to induce carbonate precipitation by ongoing (simultaneous) dissolution–precipitation reactions wherein dissolution is promoted via the acidification induced by CO_2 dissolution in water ($\text{pH} \sim 4.0$ at 60°C).²³ For example, the slightly acidic conditions greatly promote the release of Mg from silicates, which dissolve appreciably only at low pH.^{55,56} Furthermore, the influences of relative humidity are eliminated,⁷ allowing for evaluation of the effects of the intrinsic reactivity of the solid on carbonation kinetics. A slightly super-ambient temperature of 60°C promotes the rate and extent of carbonation and seeks to model the exhaust (stack) temperature of many flue gas streams⁵⁷ and of formation waters during carbonation by geological CO_2 .^{9,58}

As an example of this method of assessing the carbonation potential, Figure 2 shows the dissolution and carbonation of Ca_2SiO_4 using equilibrium calculations. Because carbonation is rapid relative to dissolution, equilibrium calculations provide insights into the effects of CO_2 concentration and liquid-phase Ca-concentrations on carbonate yield. The idealized conversion of Ca_2SiO_4 (and analogously Mg_2SiO_4), common phases in slags and rocks, to CaCO_3 (and MgCO_3) is shown in Figure 2. Under these conditions, the evolution of [Ca], pH, and calcite yield were calculated using PHREEQC⁵⁹ with the minteq.v4 database. In general, a solution that is in equilibrium with 100% CO_2 at 1 atm will feature a total inorganic carbon concentration (i.e., $[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) that is dependent on pH, i.e., at a higher pH, the solution can host higher concentrations of carbon because its speciation to HCO_3^- and CO_3^{2-} lowers the concentration of H_2CO_3^* , allowing for additional dissolution of CO_2 . Herein, a decrease in the Si concentration (see dashed red curves in Figure 2a,b) results from the precipitation of amorphous silica. It is notable

that upon the initiation of calcite precipitation and the persistence of solid calcite, the solution pH remains constant at 6, consistent with separate experimental measurements (not shown). This pH reflects the equilibrium between the dissolved CO_2 and solid calcite at the relevant reaction conditions. pH measurements are useful for evaluating both thermodynamic and kinetic influences; specifically, the consistency between the measured and calculated pH implies that carbonate precipitation is rapid, and equilibrium represents the stabilization and persistence of solid calcite. However, pH measurements are limited in their ability to inform carbonation processes because they are simultaneously influenced by calcite precipitation, alkaline solid dissolution, and the partial pressure of CO_2 .

Effects of Chemical and Mineralogical Composition on Carbonation Efficiency. The stoichiometric (“maximum”) carbonation potential of a solid can be simply calculated from its simple oxide composition (e.g., as assessed by X-ray fluorescence spectroscopy)⁶⁰

$$\begin{aligned} \text{CO}_2 \text{ (mass \%)} &= (0.785(X_{\text{CaO}} - 0.700X_{\text{SO}_3}) + 1.091X_{\text{MgO}} \\ &+ 0.71X_{\text{Na}_2\text{O}} + 0.468X_{\text{K}_2\text{O}}) - \text{CO}_{2,\text{initial}} \\ &(\%) \end{aligned} \quad (1)$$

where X_i is the mass % of oxide i and $\text{CO}_{2,\text{initial}}$ is the mass % of CO_2 in the solid reactant prior to carbonation. In general, the carbonation potential is dictated by a solid’s CaO and MgO contents. The maximum carbonation extent of the solids considered herein ranges from 5.8 to 55% CO_2 (mass basis). To compare the actual versus stoichiometric carbonation potential, that is, the carbonation efficiency, the extent of carbonation was evaluated after 24 and 72 h using the procedure described above while accounting for the initial carbonate content of the solids. A CO_2 uptake of less than 0.5 mass % was noted to lie within the experimental uncertainty and hence taken as zero. The measured carbonation efficiencies after 24 and 72 h are given in Table 1 and the measured carbonation uptakes are given in Figure 3a. It is noticed that slags carbonated to the greatest extent, albeit with a considerably reduced rate after 24 h, showing strongly diminishing reactivity to CO_2 over time (Figure 3a). On the

Table 1. Carbonation Efficiencies (the Ratio between the Actual and Maximum CO₂ Uptake Multiplied by 100%) for Diverse Natural and Industrial Alkaline Solids in 100% CO₂ at Atmospheric Pressure at 60 °C after 24 and 72 h of Processing

type	alkaline solid	24 h (%)	72 h (%)	maximum CO ₂ uptake (%)
geologically derived rocks and minerals	anorthosite	0.0	0.0	13.9
	gabbro	0.0	0.0	16.1
	olivine	3.9	2.2	54.9
	peridotite	0.0	2.0	36.7
	serpentine	0.0	3.1	36.4
	basalt	1.7	1.9	36.9
coal combustion fly ash	reclaimed Class C (a)	0.0	20.9	24.5
	reclaimed Class C (b)	12.7	19.5	27.4
	Class F	0.0	0.0	5.8
	trona-rich	0.0	5.8	20.6
	Class C	17.4	32.7	28.6
iron and steel slags	ladle	46.5	46.8	39.1
	SS	49.9	50.6	44.0
	ac-BF	4.4	9.0	34.3
	BOF	34.2	34.6	32.1
	EAF	32.9	34.7	30.9
portlandite	Ca(OH) ₂	95.8	100	59.0

other hand, fly ash exhibited near-constant carbonation rates over the duration of the experiments. Natural silicates carbonated to a minimal extent, with only basalt, serpentine, olivine, and peridotite showing measurable carbonation. On account of the near-ambient (p , T) conditions used herein, the carbonation efficiency observed for rocks are much lower than in previous reports, which reached up to >90% at 150 bar CO₂ pressure, at elevated temperature, and following pretreatment (e.g., see ref 38).

Interestingly, as shown in Figure 3b, the actual and stoichiometric carbonation potentials are linearly proportionate (and, in fact, parallel) to each other, although the former lies inferior to the latter. Only portlandite (Ca(OH)₂) achieves its stoichiometric CO₂ uptake after 72 h of

carbonation.⁶¹ Using previously measured experimental carbonation efficiencies of 77, 75, and 82% for cement kiln dust, SS slag, and fly ash,^{16,19,20} the practical carbonation capacity for these three solids has been determined to be 7.6 Mt CO₂/year.²⁸ These carbonation efficiencies are considerably higher than those obtained in this study for fly ash and slag (see Table 1), as expected from the use of pressurized CO₂ (19 bar¹⁹ or 10–40 bar²⁰) and the higher reaction temperatures employed in other studies.

Although it may be suggested that at long reaction times, the actual and stoichiometric CO₂ uptake may coincide, the period of time required for this to occur is difficult to estimate. This is because numerous alkaline solids, synthetic and otherwise, for example, Class F fly ash, ac-BF slag, and the natural rocks and minerals, present a high degree of crystallinity, large grain size (e.g., polarized light microscopy revealed that the air-cooled BF slag is composed of well-crystallized melilite grains that are a few millimeters across), and, often, a rather low chemical reactivity. As such, it remains unclear if the stoichiometric carbonation potential is indeed accessible at all over sufficiently short periods of time (i.e., hours rather than years). It should be noted that a significant fraction of the precipitated solids from slags are composed of magnesium carbonates and amorphous calcium carbonate (ACC); for example, up to 37% of the total carbonates for the SS slag (Figure 4a) may have originated from brucite (Mg(OH)₂: SS) and bredigite (Ca₇Mg(SiO₄)₄: SS, LS), which represent the primary Mg-containing phases in the slags. This observation is also consistent with the stabilizing effect of Mg on ACC, which has been demonstrated previously in alkali-activated slags.⁶² The presence of both calcium and magnesium carbonates may be significant for producing cemented carbonates, wherein ACC, magnesium-, and calcium carbonate and their hydrated forms (e.g., nesquehonite, MgCO₃·3H₂O) can produce a binding action but also volume change by molar volume expansion, which acts to “fill in” and densify the pore spaces. For reference, the molar volumes of calcite, ACC, magnesite, and nesquehonite are 36.9, 54.1, 28.1, and 75.4 cm³/mol.⁶³ An SEM micrograph and an XRD diffractogram of carbonated SS slag stored for 1 year are shown in Figure 4b,c. These data reveal the dominance of calcite in the sample, implying the

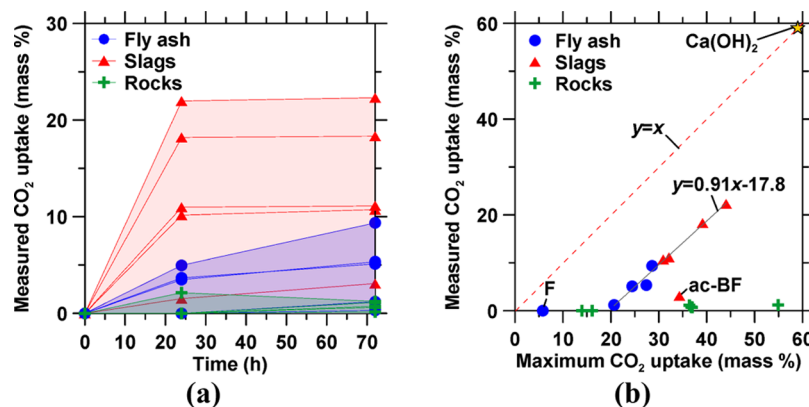


Figure 3. (a) CO₂ uptake of alkaline solids after 24 and 72 h of reaction. Slags exhibited the fastest initial carbonation and featured the highest carbonation extents, although the rates of carbonation plateaued at later times (i.e., between 24 and 72 h). (b) Relationship between actual and maximum (stoichiometric) CO₂ uptake after 72 h. The linear fit indicates proportionality, with a constant offset inferior to the line of equality. Herein, dissolution–carbonation reactions occurred at ambient (“atmospheric”) pressure and $T = 25$ °C in excess water in equilibrium with pure CO₂, that is, corresponding to pH $\sim$ 4.

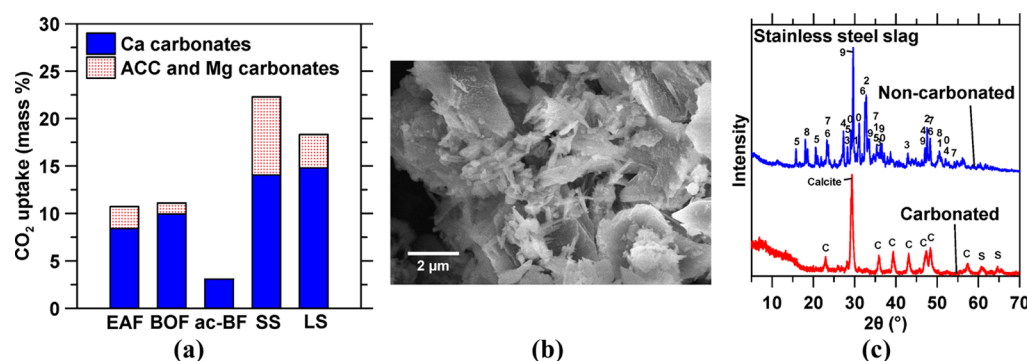


Figure 4. (a) Distribution of CO₂ uptake among crystalline and amorphous calcium- and magnesium-carbonates for the different types of slags: EAF, BOF, ac-BF, SS, and LS. (b) Micrograph of the carbonated SS slag showing prismatic crystals characteristic of calcium carbonate produced from solutions containing impurities.^{65,66} (c) XRD patterns for the non-carbonated (blue) and carbonated (red) SS slag. The phases are marked as follows: 0—melilite ((Ca,Na)₂SiO₇), 1—monticellite (CaMgSiO₄), 2—perovskite (CaTiO₃), 3—enstatite (MgSiO₃), 4—strontiwhitlockite (Sr₉Mg(PO₄)₆(PO₃OH)), 5—carboborite (Ca₂Mg(CO₃)₂B₂(OH)₈·4(H₂O)), 6—ilmenite (FeTiO₃), 7—bernalite (Fe(OH)₃), 8—brucite (Mg(OH)₂), and 9—mayenite (Ca₁₂Al₁₄O₃₃). The carbonated slag is composed of calcite (C) with minor peaks that suggest the presence of hydrated calcium silicates including plombierite (Ca₅H₂Si₆O₁₈·6H₂O) and xonotlite (Ca₆Si₆O₁₇(OH)₂).

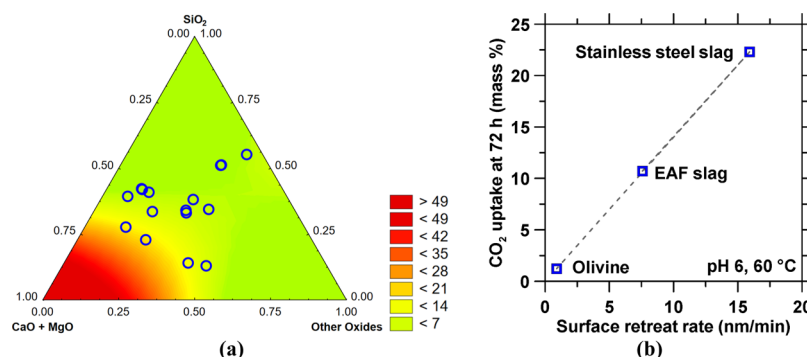


Figure 5. (a) Ternary contour plot representing the 72 h carbonation potentials of alkaline solids including slags, fly ash, mafic and ultramafic rocks and minerals, and portlandite (Ca(OH)₂). The oxide compositions are expressed in mass %. (b) Relationship between CO₂ uptake and surface retreat (i.e., mineral dissolution) rate under equivalent conditions (pH 6, 60 °C, far-from-saturation) measured using VSI. The division of the surface retreat rate by the homogeneous or heterogeneous (i.e., of a composite material) molar volume (V_m , cm³/mol) yields the surface-area-averaged mineral dissolution rate.

expected conversion of ACC to calcite under ambient conditions.⁶⁴

The effect of solid composition on CO₂ uptake is shown in Figure 5a. A strong correlation between CO₂ uptake and total CaO and MgO content is evidenced, in agreement with eq 1. In addition, a significant influence of the SiO₂ content that is indicative of the solid's reactivity (e.g., see refs 50 and 67–73) was also observed. The link between the solid's reactivity (i.e., mineral dissolution rate) and CO₂ uptake is explicitly elaborated in Figure 5b, which shows the surface retreat (dissolution) rate at pH 6 and 60 °C as measured using vertical scanning interferometry (VSI).^{66,74,75} Interestingly, the CO₂ uptake (rate and extent) is strongly correlated with the mineral dissolution rate, suggesting that predominantly, the rupture of the silicate framework is a prerequisite to releasing alkaline cations into solution. In silicates, the fraction of network-modifying elements controls the connectivity between the Si- and Al-centered polytopes—since network modifiers tend to result in the formation of terminating NBO atoms that are connected to only one Si or Al atom.⁴⁹ As such, silicate/aluminate tetrahedra (i.e., which form the rigid skeleton of aluminosilicate phases) may be isolated, as in nesosilicates, having a Si/O molar ratio of 1:4, form pairs as in sorosilicates (Si/O = 2:7), are connected in chains as in inosilicates (Si/O =

1:3 or 4:11), arranged in sheets as in phyllosilicates (Si/O = 2:5), or form a framework, as in tectosilicates (Si/O = 1:2). Because the breakage of Si–O and Al–O bonds is often rate-limiting in dissolution, lower dissolution rates are observed for solids with a greater numbers of these bonds.⁷⁶ This is also reflected in mean electrostatic O site potential, $V = \sum q_i/r_i$, where q_i and r_i are the charge of and the distance between each atom i , which increases with the increased sharing of oxygen atoms by Si-species.^{77,78}

Network Topology Governs the Carbonation Efficiency. To further explore the relationship between the atomic structure of the solids and their carbonation efficiency, their number of constraints per atom (n_c) was calculated (see the Materials and Methods section). This exploration is motivated by the fact that, in crystalline and glassy silicates, n_c has been shown to be an efficient reduced-dimensionality metric that is strongly correlated to their dissolution kinetics.^{50,67–72,79,80} The number of constraints per atom associated with each solid is given in Table 2. Crystalline solids are found to be systematically stressed-rigid (overconstrained, $n_c > 3$), whereas disordered phases are mostly flexible (underconstrained, $n_c < 3$)—which reiterates why disordered phases are often more reactive than their crystalline counterparts.⁸¹ In line with previous findings, Class F fly ash exhibits

Table 2. Number of BS, BB, and Total Number of Constraints per Atom (n_c) Associated with Each Solid

type	alkaline solid	BS	BB	n_c
geologically derived rocks and minerals	anorthosite	1.623	2.204	3.828
	gabbro	1.649	2.144	3.793
	olivine	2.245	0.846	3.091
	peridotite	2.138	1.078	3.216
	serpentinite	2.154	1.030	3.184
coal combustion fly ash	basalt	2.154	1.032	3.186
	reclaimed Class C (a)	1.309	1.703	3.012
	reclaimed Class C (b)	1.292	1.567	2.859
	Class F	1.411	2.344	3.754
	trona-rich	1.314	1.730	3.044
iron and steel slags	Class C	1.292	1.556	2.848
	LS	1.188	0.864	2.051
	SS	1.161	0.760	1.921
	ac-BF	1.225	1.174	2.399
	BOF	1.263	1.211	2.475
	EAF	1.290	1.356	2.647

higher n_c values than Class C fly ash—which is in agreement with the fact that Class F fly ash tends to exhibit a lower reactivity than Class C fly ash.^{67,82}

An inverse linear correlation between carbonation efficiency and number of constraints per atom is observed (Figure 6), suggesting, by extrapolation, that a fully depolymerized fictitious solid (with $n_c = 0$) would feature a full (~100%) carbonation efficiency—since such a solid would not feature any kinetic resistance to carbonation due to the absence of any interatomic connectivity. In turn, the addition of each new unit constraint tends to reduce the carbonation efficiency. Eventually, the carbonation efficiency plateaus toward 0 in highly stressed-rigid solids ($n_c > 3.2$). Within this overall trend, the ac-BF slag sample is noted to be an outlier, which suggests that its number of constraints therein may be underestimated. This could be explained by the high degree of crystallinity of this slag—unlike what is assumed herein when calculating n_c . Overall, the inverse correlation between carbonation efficiency and number of constraints per atom suggests that, for the solids considered herein, the carbonation kinetics are governed by the topology of the atomic network. This suggests that the depolymerization of the solids (i.e., the

rupture of their skeleton silicate network; dissolution) is the rate-controlling step of carbonation.

Herein, we offer carbonation potential assessments normalized to the geometric specific surface area (SSA) because we fractionated particles via mechanical sieving—a geometric size (i.e., a “circumscribed aperture”)-based separation. The geometric surface area (i.e., assessed based on the smallest sieve opening or based on light scattering measurements) is a reasonable basis of assessment because (i) it does not consider internal surface area (i.e., within voids) and (b) although numerically different from an adsorption-based “BET” surface area, both surface area assessments are a reasonable means to “calibrate” carbonation rates since they both only consider the exposed area that is accessible on a particle’s surface and disregard the surface area that presents itself within internal void spaces. It should be noted that 11 out of the 16 samples, which include the rocks and slags, have nominally similar particle sizes, that is, the 38–53 μm size fraction. In contrast, the fly ash and $\text{Ca}(\text{OH})_2$ were used as received, resulting in particle sizes that are much smaller than the other samples. As such, although an overall greater extent of carbonation might be expected for the fly ash because of its higher geometric SSA, an offset in the trendlines was not observed. Instead, the data points for all solids lie on the same trendline. This suggests that the fly ash is intrinsically less reactive than the other solids for an equivalent surface area. We offer a possible explanation for this observation, that is, that ball-milling of the slags and rocks increased its reactivity by increasing the reactive surface area, for example, by the formation of defects and fine fractures. Importantly, even when the trends for the solids of the same surface areas are separately considered, that is, fly ash only, slags and rocks only, our observations remain the same: (1) that there is a linear relationship between the measured and the maximum CO_2 uptake (Figure 3b), (2) that CO_2 uptake is influenced not only by the total CaO and MgO content but also by the SiO_2 content (Figure 5a), and (3) that the CO_2 uptake correlates with the number of constraints, n_c , a proxy for the solid’s reactivity that is independent of surface area and only dependent on the solid’s atomic topology (Figure 6).

CO_2 mineralization is a complex process that involves several steps (dissolution, change in speciation, reactivity between dissolved species, nucleation, crystal growth, etc.). Nevertheless, Figure 5b clearly establishes that when CO_2 is abundant, the rate of CO_2 uptake is controlled primarily by the dissolution of the silicate. Silicate dissolution can be limited by

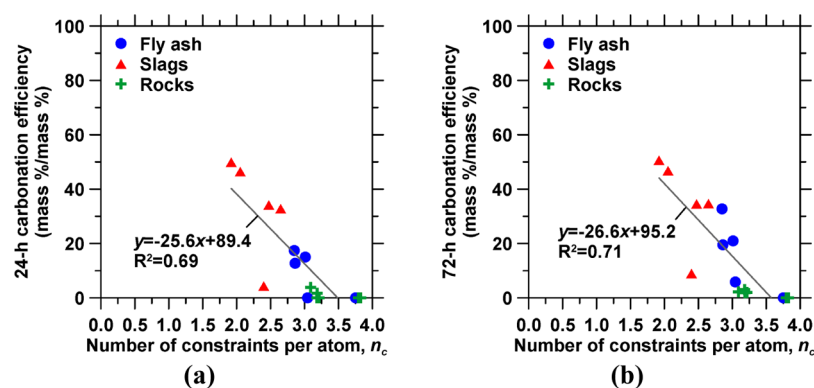


Figure 6. Carbonation efficiency after (a) 24 and (b) 72 h of reaction as a function of the number of constraints per atom (n_c). Herein, dissolution–carbonation reactions occurred at ambient (“atmospheric”) pressure and $T = 60^\circ\text{C}$ in excess water in equilibrium with pure CO_2 , i.e., corresponding to $\text{pH} \sim 4$.

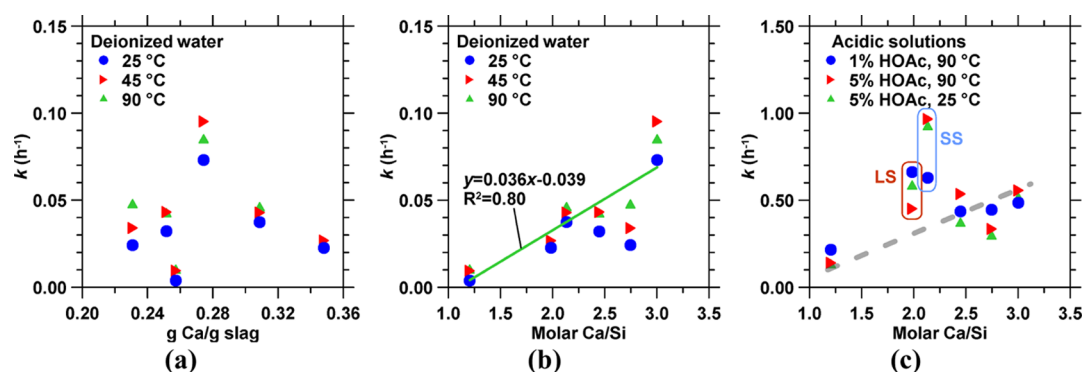


Figure 7. Apparent dissolution rate constant, k , as a function of (a) mass of Ca per unit mass of slag and (b), (c) molar Ca/Si ratio of the slag, in (b) DI water (i.e., under alkaline conditions) and (c) under acidic conditions (using acetic acid). The green line in (b) shows the best-fit line for the data obtained at 90 °C, whereas the dashed gray line in (c) is drawn to guide the eye to show the relationship between k and molar Ca/Si while excluding the data points corresponding to SS and LS. The fraction of Ca reacted, X_{Ca} , follows a power law dependence as a function of time, given by $X_{Ca} = m_{Ca,t}/m_{Ca,t_0} = kt^\alpha$, where k is the apparent rate constant and α is the apparent reaction order whereas $m_{Ca,t}$ and m_{Ca,t_0} (mg) are the total masses of Ca released in solution at time t (h) and initially present in the solid, respectively.

the formation of a passivation layer or the precipitation of secondary metastable phases; these mechanisms are primarily at play upon extended dissolution time (i.e., Stage II)⁸³ when the solution approaches a Si-saturated state.^{84–86} Far from saturation, the dissolution rate of silicate minerals is expected to be controlled by network hydrolysis or ion-exchange—which, in turn, are both controlled by the connectivity/topology of the silicate network.⁶⁹ The systematic relationship between carbonation efficiency and network topology indicates that under our experimental conditions, network hydrolysis/ion-exchange, and not surface passivation, controls the overall CO₂ mineralization rates. For further context, recently, Oey et al. highlighted circumstances such that far-from-saturation, n_c is indeed a robust indicator of dissolution rates, but on the other hand, close-to-saturation, n_c may be an insufficient basis for assessing dissolution, and in turn, carbonation behavior.^{67,80}

Role of Silicate Dissolution Kinetics. Generally speaking, alkaline species are often hosted within silicate/aluminosilicate frameworks. Therefore, to better understand the effects of atomic structure on dissolution rates, the dissolution behavior of a subset of the solids was examined to elucidate the linkages between dissolution and carbonation rates, and solid composition and structure. First, slags are composed of Ca-, Mg-, and Fe-silicates and oxides. While there are data on the bulk dissolution rates of slags, data on the dissolution rates of individual slag-forming minerals are sparse. Nonetheless, their relative reactivities can be inferred from observations of analogous rock-forming minerals. For example, the Ca-containing phases in slags can be separated into three types: Ca(OH)₂, Ca-(Fe)-silicates, and Ca-Fe-O¹⁹ such that the calcium and iron oxides are generally more reactive than their silicate counterparts. The crystalline phases in slags are primarily nesosilicates, where during dissolution the structure is decomposed (i.e., dissolved) by the breaking of Ca–O or Mg–O bonds. These bonds have energies lower than Si–O bonds,⁸⁷ resulting in faster dissolution. Forsterite (Mg₂SiO₄), a mineral often found in ultramafic rocks such as peridotite, dissolves via a similar mechanism. However, the water exchange rate around solvated Mg is lower than Ca, leading to slower dissolution compared to its calcium-rich counterpart, larnite (Ca₂SiO₄).⁸⁸ For chain silicates, in acidic conditions, ion exchange of H⁺ to Mg²⁺ occurs, resulting in the partial

liberation of Si and the breaking of Si–O bonds.⁸⁹ This implies that the release of Mg in silicates leads to accelerated dissolution. A similar mechanism has been proposed in talc (Mg₃Si₄O₁₀(OH)₂), a sheet silicate, which may undergo extensive ion exchange, leading to its exfoliation and increased surface area,⁹⁰ further enhancing dissolution. Analogous to the carbonation results presented above, this may also explain why the rate constants for Ca-release correlate with the Ca/Si ratio but show a more complex relationship with bulk Ca content (Figure 7a,b). The dissolution rate of silicates, including slags, generally increases with decreasing pH,^{91–93} but the relative increases are phase-dependent. For instance, Mg-containing silicates dissolve appreciably only at low pH. As a result, SS and LS, both of which are rich in Ca–Mg-, and Ca–F-silicates and contain the highest bulk Ca, dissolved more favorably than BOF slag in acidic conditions (Figure 7c). Under alkaline conditions, BOF slag, which is composed primarily of Ca-aluminates and Ca-silicates, exhibited the highest rates of Ca release. This is because the dissolution of Ca–Al-silicate, Ca–F-silicate, and Ca–Mg-silicate is more significantly enhanced in acidic conditions relative to Ca₂SiO₄.^{91,94} In addition, the dissolution rates of the isochemical phases β -Ca₂SiO₄ and γ -Ca₂SiO₄ have been shown to not depend strongly on pH over the range of 4–10,⁹³ whereas the dissolution rate of calcite, abundant in SS and LS but not in BOF slags, increases significantly with decreasing pH.⁹⁴ Hence, under acidic conditions, the phase composition of the slag, in addition to the molar Ca/Si, becomes a significant determinant of Ca extractability (Figure 7c). These results suggest that for solids having similar Ca contents, the fraction of Ca that is present in reactive (less polymerized, e.g., CaO) phases controls the relative differences in the rates of Ca solubilization. This is consistent with the observation made earlier that carbonation is inversely controlled by the Si content of the solid. These results imply, unsurprisingly, that solids with higher reactive Ca and Mg contents are more reactive and feature a higher CO₂ uptake capacity.

Estimating CO₂ Removal Based on Measured Carbonation Potentials. In order to limit global temperature rise to 1.5 °C and the effects of climate change, about 10–20 gigatons (Gt) of CO₂ need to be removed from the atmosphere, annually, over the next 100 years.² This translates to the production of at least 20 Gt of carbonate solids per year by

CO₂ mineralization. Ultramafic rocks present an abundance on the order of 50 km³ in the eastern United States.⁹⁵ Although ultramafic rocks are rich in Mg, for example, 36–48 mass % MgO, they dissolve rapidly only under highly acidic conditions, for example, >5 N HCl (energy intensity of: 0.88 MWh of energy per t of HCl produced).^{95,96} For the modest solvents considered herein, natural alkaline solids feature no measurable carbonation potential for practical time scales on the order of hours to days. While mechanical (e.g., ultra-fine grinding; energy intensity of 0.05 MWh of energy per t of solute to produce a median particle size (d_{50}) on the order of 50 μ m; also see ref 97), thermal (e.g., exposure to temperatures > 600 °C: energy intensity of 0.2 MWh of energy per t of solute), and/or pressure impositions (e.g., 15 MPa, energy intensity of 0.22 MWh of energy per t CO₂) processing and/or aggressive solvents^{98–102} do indeed enhance carbonation reaction rates—these can result in considerable expense (i.e., equipment and process complexity, energy, and carbon intensity) which may impede widespread adoption. However, processing costs may be offset by the production of valuable industrial solids (e.g., colloidal silica, magnesite) and recoverable thermal energy.¹⁰³ Moreover, recent advances in regenerable sorbents for CO₂ mineralization as well as the decreasing costs of renewable energy may render these processes feasible.^{104–107} Renewable generation capacity, globally, is fast expanding. Recent forecasts show that renewable energy will account for 60% of cumulative capacity additions from 2020 to 2050 and that generation is increasing faster than electricity demand such that renewable energy will account for 42% of total electricity generation in the United States.¹⁰⁵ However, the rate of expansion and the installed base of renewable energy generation at this time remain less than needed to achieve necessary levels of CO₂ removal.¹⁰⁸

Our results are applicable for passive CO₂ mineralization strategies. In such applications, an unlimited source of CO₂ (i.e., atmosphere) is present and the rate and extent of CO₂ mineralization is limited simply by the reactivity of the solid reactants (and the availability of sufficient moisture).^{109–111} The objective of using pure CO₂ in our experiments is not to highlight a specific application but rather to ensure sufficient dissolved carbon such that mineral dissolution is rate-limiting. Thus, our conditions are selected to accelerate passive carbonation by supplying sufficient amounts of reactants while maintaining ambient temperature and pressure to not alter the mechanisms of CO₂ mineralization reactions. In any event, mineralization effected via forced/enhanced (i.e., as opposed to passive) alkaline solid weathering would need to focus strictly on the utilization of renewable energy as existing fossil fuel sources result in far too high a carbon footprint to offer a negative emissions strategy (N.B.: 1 MWh of coal-based electricity and natural-gas-based electricity generation are associated with ~0.95 and ~0.45 t, respectively, of CO₂ emissions).² Lastly, while rocks do present volumetric abundance, unless a particular effort is made to utilize mine tailings and existing industrial byproducts, the mining of these resources results in its own environmental footprint. Nonetheless, strategies involving ambient/passive carbonation of surface rocks in coastal environments that induce natural grinding processes may result in net negative CO₂ emissions.^{112,113} Although unquestionably industrial alkaline wastes are substantially more reactive than their natural counterparts, they are far less abundant. For example, global annual productions of fly ash and slag are on the order of 440

and 530 Mt annually, respectively.¹¹⁴ The net carbonation potential (i.e., after accounting for the process and/or reagent CO₂ footprint) of this diversity of materials, that is, both geological-derived and industrial wastes, can be more accurately estimated by considering their reactivity. Our experimental carbonation conversions (Table 1, Figures 3b and 5a) suggest a carbonation potential on the order of ~600 Mt CO₂/year, which, given the applicable levels of uncertainty, is similar to the estimates of Renforth et al.⁸ (700–1200 Mt CO₂/year), contributing about 5% to required CO₂ removal rates. Accelerating this rate by decreasing the grain size entails significant grinding energy that is a function of the mineral's hardness and the required dissolution rate.⁹⁷ Based on experimental data on olivine dissolution in a soil column, a minimum energy requirement for dissolution of 0.42 MWh per ton of rock is estimated.¹¹⁵ Given the dissolution-limited nature of carbonation reactions, a specific opportunity may lie in utilizing pre-solubilized Ca and Mg, for example, from produced water, saline groundwater, and desalination brines for CO₂ mineralization. Based on current production rates, these waters can provide nearly 1 Gt of Mg and Ca in total per year.^{116–120} Moreover, seawater is a massive reservoir of divalent cations, with global inventories amounting to 520,000 Gt Ca and 1,272,000 Gt Mg.¹²¹ So long as the ocean's chemistry is not detrimentally affected, there may be additional opportunities in using ocean-derived Ca and Mg for CO₂ mineralization.¹²²

SUMMARY AND CONCLUSIONS

In this study, we systematically analyzed and compared the carbonation potentials of a collection of natural and industrial alkaline solids having wide-ranging chemical compositions and phase constituents. Special focus is placed on revealing the influences of the intrinsic reactivity of the solids by examining carbonation under aqueous conditions and in systems saturated with CO₂. The approach presented herein can be applied to assess the carbonation capacity (potential and efficiency) of heterogeneous solids that feature a complex distribution of distinct mineral species. In agreement with prior findings, our results show that natural alkaline solids are much less reactive than their industrial counterparts. Furthermore, we show that carbonation potentials and the rate of calcium release depend not only on the total Ca (and Mg) contents but also on the Si content, which is indicative of the silicate network's atomic topology and thus the reactivity of the solid. The dependence of carbonation on mineral dissolution indicates that enhancing dissolution, for example, using additives, or thermal, mechanical, electrical, or acoustic methods, at the lowest possible energy expenditure is a critical need to achieve sufficiently fast dissolution (i.e., generally greater than 10^{−9} mol/m²/s) and therefore carbonation rates. Taken together, this work presents an approach to ascertain the propensity for carbonation/carbon sequestration capacity using the bulk chemical composition of the solid at near-ambient conditions. Quantitative data of this nature are foundational to accurately estimate/constrain the ability of alkaline solid-based enhanced weathering to serve as a time- and scale-relevant carbon management strategy.

AUTHOR INFORMATION

Corresponding Authors

Erika Callagon La Plante – Department of Materials Science and Engineering, University of Texas at Arlington, Arlington,

Texas 76019, United States; Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States; Institute for Carbon Management, University of California, Los Angeles, Los Angeles, California 90095, United States; orcid.org/0000-0002-5273-9523; Email: erika.laplane@uta.edu

Gaurav N. Sant – Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States; Institute for Carbon Management, Department of Materials Science and Engineering, and California Nanosystems Institute, University of California, Los Angeles, Los Angeles, California 90095, United States; orcid.org/0000-0002-1124-5498; Email: gsant@ucla.edu

Authors

Iman Mehdipour – Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States; orcid.org/0000-0002-6841-3907

Ian Shortt – Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, Texas 76019, United States

Kai Yang – Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States

Dante Simonetti – Institute for Carbon Management and Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States; orcid.org/0000-0002-5708-460X

Mathieu Bauchy – Department of Civil and Environmental Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States; Institute for Carbon Management, University of California, Los Angeles, Los Angeles, California 90095, United States; orcid.org/0000-0003-4600-0631

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acssuschemeng.1c00838>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial support for this research from the Department of Energy, Office of Fossil Energy via the National Energy Technology Laboratory (NETL; DE-FE0029825), the National Science Foundation (DMREF: 1922167), the U.S. Department of Transportation through the Federal Highway Administration (693JJ31950021), and the University of Texas at Arlington. This research was conducted in the Laboratory for the Chemistry of Construction Materials (LC²) at the University of California, Los Angeles (UCLA) and the Characterization Center for Materials and Biology at the University of Texas, Arlington (UTA). As such, the authors gratefully acknowledge the support that has made these laboratories and their operations possible. The contents of this paper reflect the views and opinions of the authors, who are responsible for the accuracy of the data sets presented herein and do not reflect the views and/or policies of the funders, nor do the contents constitute a specification, standard or regulation.

REFERENCES

- (1) Masson-Delmotte, V.; Zhai, P.; Pörtner, H.-O.; Roberts, D.; Skea, J.; Shukla, P. R.; Pirani, A.; Moufouma-Okia, W.; Péan, C.; Pidcock, R.; Connors, S.; Matthews, J. B. R.; Chen, Y.; Zhou, X.; Gomis, M. L.; Lonnoy, E.; Maycock, T.; Tignor, M.; Waterfield, T. IPCC, 2018: Global Warming of 1.5°C. An IPCC Special Report on the Impacts of Global Warming of 1.5 °C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change, Sustainable Development, and Efforts to Eradicate Poverty, 2018; In Press.
- (2) National Academies of Sciences, Engineering, and Medicine. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*; The National Academies Press, 2019.
- (3) Huijgen, W. J. J.; Comans, R. N. J. *Carbon Dioxide Sequestration by Mineral Carbonation. Literature Review*; ECN-C-03-016; Energy research Centre of the Netherlands ECN, 2003.
- (4) 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.
- (5) Romanov, V.; Soong, Y.; Carney, C.; Rush, G. E.; Nielsen, B.; O'Connor, W. Mineralization of Carbon Dioxide: A Literature Review. *ChemBioEng Rev.* **2015**, *2*, 231–256.
- (6) Pan, S.-Y.; Chang, E. E.; Chiang, P.-C. CO₂ Capture by Accelerated Carbonation of Alkaline Wastes. *A Review on Its Principles and Applications* **2012**, *12*, 770.
- (7) Mehdipour, I.; Falzone, G.; La Plante, E. C.; Simonetti, D.; Neithalath, N.; Sant, G. How Microstructure and Pore Moisture Affect Strength Gain in Portlandite-Enriched Composites That Mineralize CO₂. *ACS Sustainable Chem. Eng.* **2019**, *7*, 13053–13061.
- (8) Renforth, P.; Washbourne, C.-L.; Taylder, J.; Manning, D. A. C. Silicate Production and Availability for Mineral Carbonation. *Environ. Sci. Technol.* **2011**, *45*, 2035–2041.
- (9) Matter, J. M.; Stute, M.; Snaebjornsdottir, S. O.; Oelkers, E. H.; Gislason, S. R.; Aradottir, E. S.; Sigfusson, B.; Gunnarsson, I.; Sigurdardottir, H.; Gunnlaugsson, E.; Axelsson, G.; Alfredsson, H. A.; Wolff-Boenisch, D.; Mesfin, K.; Taya, D. F. d. l. R.; Hall, J.; Dideriksen, K.; Broecker, W. S. Rapid Carbon Mineralization for Permanent Disposal of Anthropogenic Carbon Dioxide Emissions. *Science* **2016**, *352*, 1312–1314.
- (10) McGrail, B. P.; Schaef, H. T.; Ho, A. M.; Chien, Y.-J.; Dooley, J. J.; Davidson, C. L. Potential for Carbon Dioxide Sequestration in Flood Basalts. *J. Geophys. Res.: Solid Earth* **2006**, *111*, B12201.
- (11) Jo, H. Y.; Kim, J. H.; Lee, Y. J.; Lee, M.; Choh, S.-J. Evaluation of Factors Affecting Mineral Carbonation of CO₂ Using Coal Fly Ash in Aqueous Solutions under Ambient Conditions. *Chem. Eng. J.* **2012**, *183*, 77–87.
- (12) Bonenfant, D.; Kharoune, L.; Sauvé, S.; Hausler, R.; Niquette, P.; Mimeault, M.; Kharoune, M. CO₂ Sequestration by Aqueous Red Mud Carbonation at Ambient Pressure and Temperature. *Ind. Eng. Chem. Res.* **2008**, *47*, 7617–7622.
- (13) Pan, S.-Y.; Chen, Y.-H.; Chen, C.-D.; Shen, A.-L.; Lin, M.; Chiang, P.-C. High-Gravity Carbonation Process for Enhancing CO₂ Fixation and Utilization Exemplified by the Steelmaking Industry. *Environ. Sci. Technol.* **2015**, *49*, 12380–12387.
- (14) Pan, S.-Y.; Shah, K. J.; Chen, Y.-H.; Wang, M.-H.; Chiang, P.-C. Deployment of Accelerated Carbonation Using Alkaline Solid Wastes for Carbon Mineralization and Utilization Toward a Circular Economy. *ACS Sustainable Chem. Eng.* **2017**, *5*, 6429–6437.
- (15) Pérez-López, R.; Montes-Hernandez, G.; Nieto, J. M.; Renard, F.; Charlet, L. Carbonation of Alkaline Paper Mill Waste to Reduce CO₂ Greenhouse Gas Emissions into the Atmosphere. *Appl. Geochem.* **2008**, *23*, 2292–2300.
- (16) Huntzinger, D. N.; Gierke, J. S.; Kawatra, S. K.; Eisele, T. C.; Sutter, L. L. Carbon Dioxide Sequestration in Cement Kiln Dust through Mineral Carbonation. *Environ. Sci. Technol.* **2009**, *43*, 1986–1992.
- (17) Entezari Zarendi, A.; Larachi, F.; Beaudoin, G.; Plante, B.; Sciortino, M. Ambient Mineral Carbonation of Different Lithologies

of Mafic to Ultramafic Mining Wastes/Tailings—A Comparative Study. *Int. J. Greenhouse Gas Control* **2017**, *63*, 392–400.

(18) Santos, R. M.; Van Bouwel, J.; Vandeveld, E.; Mertens, G.; Elsen, J.; Van Gerven, T. Accelerated Mineral Carbonation of Stainless Steel Slags for CO₂ Storage and Waste Valorization: Effect of Process Parameters on Geochemical Properties. *Int. J. Greenhouse Gas Control* **2013**, *17*, 32–45.

(19) Huijgen, W. J. J.; Comans, R. N. J. Mineral CO₂ Sequestration by Steel Slag Carbonation. *Environ. Sci. Technol.* **2005**, *39*, 9676–9682.

(20) Montes-Hernandez, G.; Pérez-López, R.; Renard, F.; Nieto, J. M.; Charlet, L. Mineral Sequestration of CO₂ by Aqueous Carbonation of Coal Combustion Fly-Ash. *J. Hazard. Mater.* **2009**, *161*, 1347–1354.

(21) Chang, E.-E.; Chiu, A.-C.; Pan, S.-Y.; Chen, Y.-H.; Tan, C.-S.; Chiang, P.-C. Carbonation of Basic Oxygen Furnace Slag with Metalworking Wastewater in a Slurry Reactor. *Int. J. Greenhouse Gas Control* **2013**, *12*, 382–389.

(22) Hosseini, T.; Selomulya, C.; Haque, N.; Zhang, L. Indirect Carbonation of Victorian Brown Coal Fly Ash for CO₂ Sequestration: Multiple-Cycle Leaching-Carbonation and Magnesium Leaching Kinetic Modeling. *Energy Fuels* **2014**, *28*, 6481–6493.

(23) 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.

(24) Penner, L.; O'Connor, W.; Dahlin, D.; Gerdemann, S.; Rush, G. Mineral Carbonation: Energy Costs of Pretreatment Options and Insights Gained from Flow Loop Reaction Studies (DOE/ARC-2004-042), 2004.

(25) Kelemen, P.; Benson, S. M.; Pilorgé, H.; Psarras, P.; Wilcox, J. An Overview of the Status and Challenges of CO₂ Storage in Minerals and Geological Formations. *Front. Clim.* **2019**, *1*. DOI: DOI: 10.3389/fclim.2019.00009.

(26) Snæbjörnsdóttir, S. Ó.; Wiese, F.; Fridriksson, T.; Ármannsson, H.; Einarsson, G. M.; Gislason, S. R. CO₂ Storage Potential of Basaltic Rocks in Iceland and the Oceanic Ridges. *Energy Procedia* **2014**, *63*, 4585–4600.

(27) 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.

(28) Kirchofer, A.; Brandt, A.; Krevor, S.; Prigione, V.; Becker, A.; Wilcox, J. Assessing the Potential of Mineral Carbonation with Industrial Alkalinity Sources in the U.S. *Energy Procedia* **2013**, *37*, 5858–5869.

(29) Kirchofer, A.; Becker, A.; Brandt, A.; Wilcox, J. CO₂ Mitigation Potential of Mineral Carbonation with Industrial Alkalinity Sources in the United States. *Environ. Sci. Technol.* **2013**, *47*, 7548–7554.

(30) Li, J.; Hitch, M.; Power, I.; Pan, Y. Integrated Mineral Carbonation of Ultramafic Mine Deposits—A Review. *Minerals* **2018**, *8*, 147.

(31) Zingaretti, D.; Costa, G.; Baciocchi, R. Assessment of Accelerated Carbonation Processes for CO₂ Storage Using Alkaline Industrial Residues. *Ind. Eng. Chem. Res.* **2014**, *53*, 9311–9324.

(32) Renforth, P. The Negative Emission Potential of Alkaline Materials. *Nat. Commun.* **2019**, *10*, 1401.

(33) Chang, E.-E.; Pan, S.-Y.; Yang, L.; Chen, Y.-H.; Kim, H.; Chiang, P.-C. Accelerated Carbonation Using Municipal Solid Waste Incinerator Bottom Ash and Cold-Rolling Wastewater: Performance Evaluation and Reaction Kinetics. *Waste Manage.* **2015**, *43*, 283–292.

(34) Zhang, S.; DePaolo, D. J. Rates of CO₂ Mineralization in Geological Carbon Storage. *Acc. Chem. Res.* **2017**, *50*, 2075–2084.

(35) Geerlings, H.; Zevenhoven, R. CO₂ Mineralization-Bridge between Storage and Utilization of CO₂. *Annu. Rev. Chem. Biomol. Eng.* **2013**, *4*, 103–117.

(36) Entezari Zarendi, A.; Larachi, F.; Beaudoin, G.; Plante, B.; Sciortino, M. Nesquehonite as a Carbon Sink in Ambient Mineral Carbonation of Ultramafic Mining Wastes. *Chem. Eng. J.* **2017**, *314*, 160–168.

(37) Harrison, A. L.; Power, I. M.; Dipple, G. M. Accelerated Carbonation of Brucite in Mine Tailings for Carbon Sequestration. *Environ. Sci. Technol.* **2013**, *47*, 126–134.

(38) 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.

(39) Escalante, J. I.; Gómez, L. Y.; Johal, K. K.; Mendoza, G.; Mancha, H.; Méndez, J. Reactivity of Blast-Furnace Slag in Portland Cement Blends Hydrated under Different Conditions. *Cem. Concr. Res.* **2001**, *31*, 1403–1409.

(40) Ramezani-pour, A. A. *Cement Replacement Materials*; Springer Geochemistry/Mineralogy; Springer, 2014; Vol. 10, pp 978–983.

(41) Shi, C.; Meyer, C.; Behnood, A. Utilization of Copper Slag in Cement and Concrete. *Resour., Conserv. Recycl.* **2008**, *52*, 1115–1120.

(42) Mehta, P. K. Testing and Correlation of Fly Ash Properties with Respect to Pozzolanic Behavior *Final Report*; EPRI-CS-3314; Department of Civil Engineering, California University: Berkeley (USA), 1984.

(43) Mo, L.; Panesar, D. K. Effects of Accelerated Carbonation on the Microstructure of Portland Cement Pastes Containing Reactive MgO. *Cem. Concr. Res.* **2012**, *42*, 769–777.

(44) Dung, N. T.; Unluer, C. Development of MgO Concrete with Enhanced Hydration and Carbonation Mechanisms. *Cem. Concr. Res.* **2018**, *103*, 160–169.

(45) Przepiórski, J.; Karolczyk, J.; Takeda, K.; Tsumura, T.; Toyoda, M.; Morawski, A. W. Porous Carbon Obtained by Carbonization of PET Mixed with Basic Magnesium Carbonate: Pore Structure and Pore Creation Mechanism. *Ind. Eng. Chem. Res.* **2009**, *48*, 7110–7116.

(46) Phillips, J. C. Topology of Covalent Non-Crystalline Solids .1. Short-Range Order in Chalcogenide Alloys. *J. Non-Cryst. Solids* **1979**, *34*, 153–181.

(47) Mauro, J. C. Topological Constraint Theory of Glass. *Am. Ceram. Soc. Bull.* **2011**, *90*, 31–37.

(48) Bauchy, M. Topological Constraint Theory and Rigidity of Glasses. 2019 <https://www.taylorfrancis.com/> (accessed Feb 11, 2020).

(49) Varshneya, A. K. *Fundamentals of Inorganic Glasses*; Academic Press Inc., 1993.

(50) Gin, S.; Wang, M.; Bisbrouck, N.; Taron, M.; Lu, X.; Deng, L.; Angeli, F.; Charpentier, T.; Delaye, J.-M.; Du, J.; Bauchy, M. Can a Simple Topological-Constraints-Based Model Predict the Initial Dissolution Rate of Borosilicate and Aluminosilicate Glasses? *npj Mater. Degrad.* **2020**, *4*, 1–10.

(51) Laurent, O.; Mantsi, B.; Micoulaut, M. Structure and Topology of Soda-Lime Silicate Glasses: Implications for Window Glass. *J. Phys. Chem. B* **2014**, *118*, 12750–12762.

(52) Oelkers, E. H.; Declercq, J.; Saldi, G. D.; Gislason, S. R.; Schott, J. Olivine Dissolution Rates: A Critical Review. *Chem. Geol.* **2018**, *500*, 1–19.

(53) Mitchell, M. J.; Jensen, O. E.; Cliffe, K. A.; Maroto-Valer, M. M. A Model of Carbon Dioxide Dissolution and Mineral Carbonation Kinetics. *Proc. R. Soc. A* **2010**, *466*, 1265–1290.

(54) 2.2 Characteristics of Large North American CO₂ Point Sources, Global CCS Institute <https://hub.globalccsinstitute.com/publications/building-cost-curves-co2-storage-north-america/22-characteristics-large-north-american> (accessed Apr 10, 2019).

(55) Golubev, S. V.; Bauer, A.; Pokrovsky, O. S. Effect of pH and Organic Ligands on the Kinetics of Smectite Dissolution at 25 °C. *Geochim. Cosmochim. Acta* **2006**, *70*, 4436–4451.

(56) Oelkers, E. H.; Schott, J. An Experimental Study of Enstatite Dissolution Rates as a Function of pH, Temperature, and Aqueous Mg and Si Concentration, and the Mechanism of Pyroxene/Pyroxenoid Dissolution. *Geochim. Cosmochim. Acta* **2001**, *65*, 1219–1231.

(57) Reddy, K. J.; John, S.; Weber, H.; Argyle, M. D.; Bhattacharyya, P.; Taylor, D. T.; Christensen, M.; Foulke, T.; Fahlsing, P. Simultaneous Capture and Mineralization of Coal Combustion Flue Gas Carbon Dioxide (CO₂). *Energy Procedia* **2011**, *4*, 1574–1583.

- (58) Snæbjörnsdóttir, S. Ó.; Oelkers, E. H.; Mesfin, K.; Aradóttir, E. S.; Dideriksen, K.; Gunnarsson, I.; Gunnlaugsson, E.; Matter, J. M.; Stute, M.; Gislason, S. R. The Chemistry and Saturation States of Subsurface Fluids during the in situ Mineralisation of CO₂ and H₂S at the CarbFix Site in SW-Iceland. *Int. J. Greenhouse Gas Control* **2017**, *58*, 87–102.
- (59) Parkhurst, D. L.; Appelo, C. A. J. *Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*; U.S. Geological Survey Techniques and Methods, 2013.
- (60) Steinour, H. H. Some Effects of Carbon Dioxide on Mortars and Concrete-Discussion. *J. Am. Concr. Inst.* **1959**, *30*, 905–907.
- (61) Falzone, G.; Mehdiipour, I.; Neithalath, N.; Bauchy, M.; Simonetti, D.; Sant, G. New Insights into the Mechanisms of Carbon Dioxide Mineralization by Portlandite. *AIChE J.* **2021**, *67*, No. e17160.
- (62) Morandeau, A. E.; White, C. E. Role of Magnesium-Stabilized Amorphous Calcium Carbonate in Mitigating the Extent of Carbonation in Alkali-Activated Slag. *Chem. Mater.* **2015**, *27*, 6625–6634.
- (63) Fernandez-Martinez, A.; Kalkan, B.; Clark, S. M.; Waychunas, G. A. Pressure-Induced Polyamorphism and Formation of “Aragonitic” Amorphous Calcium Carbonate. *Angew. Chem.* **2013**, *125*, 8512–8515.
- (64) Rodriguez-Navarro, C.; Kudłacz, K.; Cizer, Ö.; Ruiz-Agudo, E. Formation of Amorphous Calcium Carbonate and Its Transformation into Mesosstructured Calcite. *CrystEngComm* **2014**, *17*, 58–72.
- (65) Cheng, H.; Zhang, X.; Song, H. Morphological Investigation of Calcium Carbonate during Ammonification-Carbonization Process of Low Concentration Calcium Solution. *J. Nanomater.* **2014**, *2014* 03696, <https://www.hindawi.com/journals/jnm/2014/503696/>. DOI: DOI: 10.1155/2014/503696.
- (66) Wei, Z.; Wang, B.; Falzone, G.; La Plante, E. C.; Okoronkwo, M. U.; She, Z.; Oey, T.; Balonis, M.; Neithalath, N.; Pilon, L.; Sant, G. Clinkering-Free Cementation by Fly Ash Carbonation. *J. CO₂ Util.* **2018**, *23*, 117–127.
- (67) Oey, T.; Kumar, A.; Pignatelli, I.; Yu, Y.; Neithalath, N.; Bullard, J. W.; Bauchy, M.; Sant, G. Topological Controls on the Dissolution Kinetics of Glassy Aluminosilicates. *J. Am. Ceram. Soc.* **2017**, *100*, 5521–5527.
- (68) Oey, T.; Hsiao, Y.-H.; Callagon, E.; Wang, B.; Pignatelli, I.; Bauchy, M.; Sant, G. N. Rate Controls on Silicate Dissolution in Cementitious Environments. *RILEM Tech. Lett.* **2017**, *2*, 67–73.
- (69) Pignatelli, I.; Kumar, A.; Bauchy, M.; Sant, G. Topological Control on Silicates’ Dissolution Kinetics. *Langmuir* **2016**, *32*, 4434–4439.
- (70) Liu, H.; Zhang, T.; Anoop Krishnan, N. M.; Smedskjaer, M. M.; Ryan, J. V.; Gin, S.; Bauchy, M. Predicting the Dissolution Kinetics of Silicate Glasses by Topology-Informed Machine Learning. *npj Mater. Degrad.* **2019**, *3*, 1–12.
- (71) Mascaraque, N.; Bauchy, M.; Smedskjaer, M. M. Correlating the Network Topology of Oxide Glasses with Their Chemical Durability. *J. Phys. Chem. B* **2017**, *121*, 1139–1147.
- (72) Mascaraque, N.; Bauchy, M.; Fierro, J. L. G.; Rzoska, S. J.; Bockowski, M.; Smedskjaer, M. M. Dissolution Kinetics of Hot Compressed Oxide Glasses. *J. Phys. Chem. B* **2017**, *121*, 9063–9072.
- (73) Hsiao, Y.-H.; La Plante, E. C.; Krishnan, N. M. A.; Le Pape, Y.; Neithalath, N.; Bauchy, M.; Sant, G. Effects of Irradiation on Albite’s Chemical Durability. *J. Phys. Chem. A* **2017**, *121*, 7835–7845.
- (74) Hsiao, Y.-H.; La Plante, E. C.; Krishnan, N. M. A.; Dobbs, H. A.; Le Pape, Y.; Neithalath, N.; Bauchy, M.; Israelachvili, J.; Sant, G. Role of Electrochemical Surface Potential and Irradiation on Garnet-Type Almandine’s Dissolution Kinetics. *J. Phys. Chem. C* **2018**, *122*, 17268–17277.
- (75) Hsiao, Y.-H.; Wang, B.; La Plante, E. C.; Pignatelli, I.; Krishnan, N. M. A.; Le Pape, Y.; Neithalath, N.; Bauchy, M.; Sant, G. The Effect of Irradiation on the Atomic Structure and Chemical Durability of Calcite and Dolomite. *npj Mater. Degrad.* **2019**, *3*, 1–9.
- (76) Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*; John Wiley & Sons, 2012; Vol. 126.
- (77) Smyth, J. R. Electrostatic Characterization of Oxygen Sites in Minerals. *Geochim. Cosmochim. Acta* **1989**, *53*, 1101–1110.
- (78) Brady, P. V.; Walther, J. V. Controls on Silicate Dissolution Rates in Neutral and Basic PH Solutions at 25 °C. *Geochim. Cosmochim. Acta* **1989**, *53*, 2823–2830.
- (79) Oey, T.; Frederiksen, K. F.; Mascaraque, N.; Youngman, R.; Balonis, M.; Smedskjaer, M. M.; Bauchy, M.; Sant, G. The Role of the Network-Modifier’s Field-Strength in the Chemical Durability of Aluminoborate Glasses. *J. Non-Cryst. Solids* **2019**, *505*, 279–285.
- (80) Oey, T.; La Plante, E. C.; Falzone, G.; Yang, K.; Wada, A.; Bauchy, M.; Bullard, J. W.; Sant, G. Topological Controls on Aluminosilicate Glass Dissolution: Complexities Induced in Hyper-alkaline Aqueous Environments. *J. Am. Ceram. Soc.* **2020**, *103*, 6198–6207.
- (81) Hamilton, J. P.; Pantano, C. G.; Brantley, S. L. Dissolution of Albite Glass and Crystal. *Geochim. Cosmochim. Acta* **2000**, *64*, 2603–2615.
- (82) Oey, T.; Timmons, J.; Stutzman, P.; Bullard, J. W.; Balonis, M.; Bauchy, M.; Sant, G. An Improved Basis for Characterizing the Suitability of Fly Ash as a Cement Replacement Agent. *J. Am. Ceram. Soc.* **2017**, *100*, 4785–4800.
- (83) Vienna, J. D.; Ryan, J. V.; Gin, S.; Inagaki, Y. Current Understanding and Remaining Challenges in Modeling Long-Term Degradation of Borosilicate Nuclear Waste Glasses. *Int. J. Appl. Glass Sci.* **2013**, *4*, 283–294.
- (84) Cailleteau, C.; Angeli, F.; Devreux, F.; Gin, S.; Jestin, J.; Jollivet, P.; Spalla, O. Insight into Silicate-Glass Corrosion Mechanisms. *Nat. Mater.* **2008**, *7*, 978–983.
- (85) Gin, S. Open Scientific Questions about Nuclear Glass Corrosion. *Procedia Mater. Sci.* **2014**, *7*, 163–171.
- (86) Gin, S.; Jollivet, P.; Fournier, M.; Berthon, C.; Wang, Z.; Mitroshkov, A.; Zhu, Z.; Ryan, J. V. The Fate of Silicon during Glass Corrosion under Alkaline Conditions: A Mechanistic and Kinetic Study with the International Simple Glass. *Geochim. Cosmochim. Acta* **2015**, *151*, 68–85.
- (87) Bond Energies. *Encyclopedia of Inorganic Chemistry*; John Wiley & Sons, Ltd., 2006.
- (88) Brantley, S. L. Kinetics of Mineral Dissolution. In *Kinetics of Water-Rock Interaction*; Brantley, S. L., Kubicki, J. D., White, A. F., Eds.; Springer: New York, NY, 2008; pp 151–210.
- (89) Schott, J.; Berner, R. A.; Sjöberg, E. L. Mechanism of Pyroxene and Amphibole Weathering—I. Experimental Studies of Iron-Free Minerals. *Geochim. Cosmochim. Acta* **1981**, *45*, 2123–2135.
- (90) Saldi, G. D.; Köhler, S. J.; Marty, N.; Oelkers, E. H. Dissolution Rates of Talc as a Function of Solution Composition, pH and Temperature. *Geochim. Cosmochim. Acta* **2007**, *71*, 3446–3457.
- (91) Engström, F.; Adolfsson, D.; Samuelsson, C.; Sandström, Å.; Björkman, B. A Study of the Solubility of Pure Slag Minerals. *Miner. Eng.* **2013**, *41*, 46–52.
- (92) Hall, C.; Large, D. J.; Adderley, B.; West, H. M. Calcium Leaching from Waste Steelmaking Slag: Significance of Leachate Chemistry and Effects on Slag Grain Mineralogy. *Miner. Eng.* **2014**, *65*, 156–162.
- (93) Strandkvist, I.; Björkman, B.; Engström, F. Synthesis and Dissolution of Slag Minerals - a Study of β -Dicalcium Silicate, Pseudowollastonite and Monticellite. *Can. Metall. Q.* **2015**, *54*, 446–454.
- (94) Inoue, R.; Suito, H. Fluorine-Containing Mineral Phases in Ironmaking and Steelmaking Slags and Their Solubilities in Aqueous Solution. *ISIJ Int.* **2002**, *42*, 785–793.
- (95) Goff, F.; Guthrie, G.; Bruce, L.; Fite, M.; Chipera, S.; Dale, C.; Kluk, E.; Zioc, H. *Evaluation of Ultramafic Deposits in the Eastern United States and Puerto Rico as Sources of Magnesium for Carbon Dioxide Sequestration*; LA-13694-MS; 2000.
- (96) Worrell, E.; Phylipsen, D.; Einstein, D.; Martin, N. *Energy Use and Energy Intensity of the U.S. Chemical Industry*; LBNL-44314;

Lawrence Berkeley National Laboratory (LBNL): Berkeley, CA, United States, 2000.

(97) Kelemen, P. B.; McQueen, N.; Wilcox, J.; Renforth, P.; Dipple, G.; Vankeuren, A. P. Engineered Carbon Mineralization in Ultramafic Rocks for CO₂ Removal from Air: Review and New Insights. *Chem. Geol.* **2020**, *550*, 119628.

(98) Kelemen, P. B.; Matter, J.; Streit, E. E.; Rudge, J. F.; Curry, W. B.; Blusztajn, J. Rates and Mechanisms of Mineral Carbonation in Peridotite: Natural Processes and Recipes for Enhanced, in situ CO₂ Capture and Storage. *Annu. Rev. Earth Planet. Sci.* **2011**, *39*, 545–576.

(99) Li, W.; Li, W.; Li, B.; Bai, Z. Electrolysis and Heat Pretreatment Methods to Promote CO₂ Sequestration by Mineral Carbonation. *Chem. Eng. Res. Des.* **2009**, *87*, 210–215.

(100) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An Overview of CO₂ Capture Technologies. *Energy Environ. Sci.* **2010**, *3*, 1645–1669.

(101) Eloneva, S.; Teir, S.; Revitzer, H.; Salminen, J.; Said, A.; Fogelholm, C.-J.; Zevenhoven, R. Reduction of CO₂ Emissions from Steel Plants by Using Steelmaking Slags for Production of Marketable Calcium Carbonate. *Steel Res. Int.* **2009**, *80*, 415–421.

(102) Rim, G.; Wang, D.; Rayson, M.; Brent, G.; Park, A.-H. A. Investigation on Abrasion versus Fragmentation of the Si-Rich Passivation Layer for Enhanced Carbon Mineralization via CO₂ Partial Pressure Swing. *Ind. Eng. Chem. Res.* **2020**, *59*, 6517–6531.

(103) Santos, R. M.; Knops, P. C. M.; Rijnsburger, K. L.; Chiang, Y. W. CO₂ Energy Reactor – Integrated Mineral Carbonation: Perspectives on Lab-Scale Investigation and Products Valorization. *Front. Energy Res.* **2016**, *4*, 5.

(104) Liu, M.; Hohenshil, A.; Gadikota, G. Integrated CO₂ Capture and Removal via Carbon Mineralization with Inherent Regeneration of Aqueous Solvents. *Energy Fuels* **2021**, *35*, 8051–8068.

(105) U.S. Energy Information Administration. *Annual Energy Outlook 2021 Narrative with Projections to 2050*: Washington, DC, 2021.

(106) Deutz, S.; Bardow, A. Life-Cycle Assessment of an Industrial Direct Air Capture Process Based on Temperature–Vacuum Swing Adsorption. *Nat. Energy* **2021**, *6*, 203–213.

(107) Ji, L.; Yu, H.; Yu, B.; Jiang, K.; Grigore, M.; Wang, X.; Zhao, S.; Li, K. Integrated Absorption–Mineralisation for Energy-Efficient CO₂ Sequestration: Reaction Mechanism and Feasibility of Using Fly Ash as a Feedstock. *Chem. Eng. J.* **2018**, *352*, 151–162.

(108) Realmonte, G.; Drouet, L.; Gambhir, A.; Glynn, J.; Hawkes, A.; Köberle, A. C.; Tavoni, M. An Inter-Model Assessment of the Role of Direct Air Capture in Deep Mitigation Pathways. *Nat. Commun.* **2019**, *10*, 3277.

(109) McQueen, N.; Kelemen, P.; Dipple, G.; Renforth, P.; Wilcox, J. Ambient Weathering of Magnesium Oxide for CO₂ Removal from Air. *Nat. Commun.* **2020**, *11*, 3299.

(110) Nowamooz, A.; Dupuis, J. C.; Beaudoin, G.; Molson, J.; Lemieux, J.-M.; Horswill, M.; Fortier, R.; Larachi, F.; Maldague, X.; Constantin, M.; Duchesne, J.; Therrien, R. Atmospheric Carbon Mineralization in an Industrial-Scale Chrysotile Mining Waste Pile. *Environ. Sci. Technol.* **2018**, *52*, 8050–8057.

(111) Khalidy, R.; Santos, R. M. The Fate of Atmospheric Carbon Sequestered through Weathering in Mine Tailings. *Miner. Eng.* **2021**, *163*, 106767.

(112) Myers, C.; Nakagaki, T. Direct Mineralization of Atmospheric CO₂ Using Natural Rocks in Japan. *Environ. Res. Lett.* **2020**, *15*, 124018.

(113) Meysman, F. J. R.; Montserrat, F. Negative CO₂ Emissions via Enhanced Silicate Weathering in Coastal Environments. *Biol. Lett.* **2017**, *13*, 20160905.

(114) 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.

(115) Renforth, P.; Pogge von Strandmann, P. A. E.; Henderson, G. M. The Dissolution of Olivine Added to Soil: Implications for Enhanced Weathering. *Appl. Geochem.* **2015**, *61*, 109–118.

(116) Dieter, C. A.; Maupin, M. A.; Caldwell, R. R.; Harris, M. A.; Ivahnenko, T. I.; Lovelace, J. K.; Barber, N. L.; Linsey, K. S. *Estimated Use of Water in the United States in 2015; Circular; USGS Numbered Series 1441*; U.S. Geological Survey: Reston, VA, 2018; p 76.

(117) Qi, S. L.; Harris, A. C. *Geochemical Database for the Brackish Groundwater Assessment of the United States*; U.S. Geological Survey Data Release, 2017.

(118) Jones, E.; Qadir, M.; van Vliet, M. T. H.; Smakhtin, V.; Kang, S.-m. The State of Desalination and Brine Production: A Global Outlook. *Sci. Total Environ.* **2019**, *657*, 1343–1356.

(119) Produced Waters - Homepage, USGS: Energy Resources Program. <https://energy.usgs.gov/EnvironmentalAspects/EnvironmentalAspectsOfEnergyProductionandUse/ProducedWaters.aspx#3822110-overview> (accessed Apr 4, 2018).

(120) Blondes, M.; Gans, K.; Engle, M.; Kharaka, Y.; Reidy, M.; Saraswathula, V.; Thordsen, J.; Rowan, E.; Morrissey, E. U.S. Geological Survey National Produced Waters Geochemical Database v2.3, 2018.

(121) McDuff, R. E.; Morel, F. M. M. The Geochemical Control of Seawater (Sillen Revisited). *Environ. Sci. Technol.* **1980**, *14*, 1182–1186.

(122) La Plante, E. C.; Simonetti, D. A.; Wang, J.; Al-Turki, A.; Chen, X.; Jassby, D.; Sant, G. N. Saline Water-Based Mineralization Pathway for Gigatonne-Scale CO₂ Management. *ACS Sustainable Chem. Eng.* **2021**, *9*, 1073–1089.