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# Tuning Reactive Crystallization Pathways for Integrated $CO_2$ Capture, Conversion, and Storage via Mineralization

*Published as part of the Accounts of Chemical Research special issue "Opportunities and Challenges of Nanomaterials in Sustainability: Pursuing Carbon Neutrality".*

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**Cite This:** https://doi.org/10.1021/acs.accounts.3c00482

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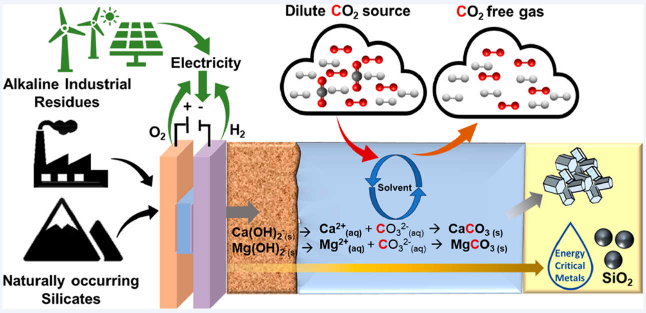

**CONSPECTUS:** Achieving carbon neutrality requires realizing scalable advances in energy- and material-efficient pathways to capture, convert, store, and remove anthropogenic $CO_2$ emission in air and flue gas while cogenerating multiple high-value products. To this end, earth-abundant Ca- and Mg-bearing alkaline resources can be harnessed to cogenerate Ca- and Mg-hydroxide, silica, $H_2$, $O_2$, and a leachate bearing high-value metals in an electrochemical approach with the *in situ* generation of a pH gradient, which is a significant departure from existing pH-swing-based approaches. To accelerate $CO_2$ capture and mineralization, $CO_2$ in dilute sources is captured using solvents to produce $CO_2$-loaded solvents. $CO_2$-loaded solvents are reacted Ca- and Mg-bearing hydroxides to produce Ca- and Mg-carbonates while regenerating the solvents. These carbonates can be used as a temporary or permanent store of $CO_2$ emissions. When carbonates are used as a temporary store of $CO_2$ emissions, electrochemical sorbent regeneration pathways can be harnessed to produce high-purity $CO_2$ while regenerating Ca- and Mg-hydroxide and coproducing $H_2$ and $O_2$. Figure 1 is a schematic representation of this integrated approach.

Tuning the molecular-scale and nanoscale interactions underlying these reactive crystallization mechanisms for carbon transformations is crucial for achieving kinetic, chemical, and morphological controls over these pathways. To this end, the feasibility of (i) crystallizing Ca- and Mg-hydroxide during the electrochemical desilication of earth-abundant alkaline industrial residues, (ii) accelerating the conversion of Ca- and Mg-carbonates for temporary or permanent carbon storage by harnessing regenerable solvents, and (iii) regenerating Ca- and Mg-hydroxide while coproducing high-purity $CO_2$, $O_2$, and $H_2$ electrochemically is established.

Evidence of the fractionation of heterogeneous slag to coproduce silica, Ca- and Mg-hydroxide, and a leachate bearing metals during electrochemical desilication provides the basis for further tuning the physicochemical parameters to improve the energy and material efficiency of these pathways. To address the slow kinetics of $CO_2$ capture and mineralization starting from ultradilute emissions, reactive capture pathways that harness solvents such as Na-glycinate are shown to be effective. The extents of carbon mineralization of $Ca(OH)_2$ and $Mg(OH)_2$ are 97% and 78% using $CO_2$-loaded Na-glycinate upon reacting for 3 h at 90 °C. During the regeneration of Ca- and Mg-hydroxide and high-purity $CO_2$ from carbonate sources, charge efficiencies of as high as 95% were observed for the dissolution of $MgCO_3$ and $CaCO_3$ while stirring at 100 rpm. Higher yields of $Mg(OH)_2$ are observed compared to that for $Ca(OH)_2$ during sorbent regeneration due to the lower solubility of $Mg(OH)_2$. These findings provide the scientific basis for further tuning these reactive crystallization pathways for closing material and carbon cycles to advance a sustainable climate, energy, and environmental future.

## KEY REFERENCES

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**Received:** August 13, 2023
**Revised:** December 5, 2023
**Accepted:** December 6, 2023

ACS Publications

https://doi.org/10.1021/acs.accounts.3c00482
*Acc. Chem. Res.* XXXX, XXX, XXX−XXX

*(gas–liquid–solid and liquid–solid) involved with $CO_2$ mineralization were drawn from this article.*

- Gadikota, G. Carbon Mineralization Pathways for Carbon Capture, Storage and Utilization. *Commun. Chem.* **2021**, *4*, 23.[2] *We highlighted the importance of scale in the design of $CO_2$ capture pathways. In particular, the abundance of Ca- and Mg-bearing resources in the form of naturally occurring silicates, tailings, and slags, coupled with their adaptability for large-scale $CO_2$ removal.*
- Liu, M.; Hohenshil, A.; Gadikota, G. Integrated $CO_2$ Capture and Removal via Carbon Mineralization with Inherent Regeneration of Aqueous Solvents. *Energy Fuels* **2021**, *35*, 8051–8068.[3] *We compared the reactivities of model alkalinity components present in alkaline residues such as Ca-oxides, Ca-silicates, and Mg-oxides for single-step $CO_2$ mineralization with various amine-based regenerable solvents such as the configuration used in this article.*
- Liu, M.; Gadikota, G. Single-Step, Low Temperature and Integrated $CO_2$ Capture and Conversion Using Sodium Glycinate to Produce Calcium Carbonate. *Fuel* **2020**, *275*, 117887.[4] *We investigated the influence of key $CO_2$ mineralization parameters such as time, temperature, and solvent concentration on the kinetics, reactivity, and chemical specificity of carbonate products from calcium oxides and silicates.*

## ■ MOTIVATION AND BACKGROUND

Realizing our climate targets while meeting the growing needs for energy and resources requires transformative, scalable, and realizable carbon management solutions.[5−7] To address this challenge, transformative solutions are needed to remove $CO_2$ from air and ocean resources and decarbonize various industrial sectors including but not limited to iron and steel, cement, primary and secondary aluminum manufacturing, mining, and chemicals. This challenge calls for developing novel chemical pathways that can be widely applied for capturing, converting, storing, and removing $CO_2$ emissions from ultradilute sources (e.g., air) and concentrated sources (e.g., flue gas streams) by harnessing abundant alkaline resources (e.g., naturally occurring ores and industrial residues such as mine tailings and slags generated during iron and steel making). These alkaline resources contain sufficient alkalinity in the form of Ca- and Mg-bearing content to facilitate reactive $CO_2$ capture and conversion via solid carbonate formation, which is a pathway also known as carbon mineralization.[8,9]

While carbon mineralization was conventionally considered to be a reliable pathway to store $CO_2$ given the exothermic nature of carbonate transformations and the stable nature of the carbonates formed,[8,9] this approach has been less explored for $CO_2$ capture and use. Key challenges in harnessing carbon mineralization as a reliable and scalable pathway for $CO_2$ capture and use include challenges associated with the slow kinetics of crystallization and inadequate tunable controls for the carbonate phases formed. Resolving these scientific challenges is crucial for harnessing this highly promising thermodynamically downhill pathway for $CO_2$ capture and conversion as an alternative to conventional thermally intensive $CO_2$ capture routes. To provide more context, one of the well-established modes to produce high-purity $CO_2$ is by harnessing solvents, sorbents, and membrane-based separation pathways that capture $CO_2$ from emissions, and ultradilute sources including air are generated via a thermal- or pressure-based swing to produce high-purity $CO_2$.[10] To provide additional context, these $CO_2$ capture technologies are being developed to scale. The resulting high-purity $CO_2$ is compressed and transported for conversion to products or geologic carbon storage. Significant research advances are being made to address challenges associated with conventional modes of $CO_2$ capture and geologic storage including (1) multiple unit operations, (2) associated high capital expenditures, (3) heat for regenerating the $CO_2$ capture media, (4) scale to be economically viable, (5) potential degradation of materials, and (6) lower cycling efficiencies, selectivity, and stability primarily due to moisture content in $CO_2$ capture media ranging from aqueous and water-lean solvents to novel sorbents including metal–organic frameworks or hybrid materials.[11−17] Building a robust ecosystem for effective carbon management requires successful coupling of these $CO_2$ capture technologies with technologies for $CO_2$ conversion and geologic carbon storage. Ultimately, the safest and most permanent modality of storing $CO_2$ emissions is via carbonate formation or pressure dissipation via solvation in subsurface environments, which requires extensive monitoring. While this approach is relevant in regions that have abundant availability of geologic carbon storage, places that lack these resources and have an abundance of alkaline residues (e.g., mine tailings, slags) are better suited for innovative $CO_2$ capture and mineralization pathways that do not require extensive infrastructure for transportation, use, or storage. Alkaline residues can provide alkalinity sources that have the potential to remove about 200–300 Mt of $CO_2$ via *ex situ* mineralization as calcium or magnesium carbonates annually.[2] Moreover, inorganic carbonate products from *ex situ* mineralization can be used in various industries including cement making, thus reducing the carbon footprint associated with mining and processing limestone.

Carbon mineralization involves the conversion of Ca- and Mg-bearing minerals such as earth-abundant silicate minerals and ores or alkaline industrial residues to solid carbonates, as represented in reaction 1,[18,19] where Me represents a divalent metal cation (typically magnesium ($Mg^{2+}$) or calcium ($Ca^{2+}$)).

$$MeO(SiO_2)_{(s)} + CO_{2(g)} \rightleftharpoons MeCO_{3(s)} + SiO_{2(s)} \tag{1}$$

While this approach is analogous to calcium looping technologies for $CO_2$ capture which involve carbonate formation followed by calcination to release high-purity $CO_2$,[20] carbon mineralization pathways can be tuned to occur at temperatures below 100 °C, which is significantly lower than calcium looping which can reach temperatures of up to 800 °C. As an alternate to direct gas–solid carbon mineralization which occurs above 100 °C and $CO_2$ partial pressure greater than 20 bar,[19,21] gas–liquid–solid reactions can be tuned to occur below 100 °C with ultradilute $CO_2$ resources. In this context, sequential pH swing approaches which involve the use of acids and bases for the dissolution and formation of Ca- and Mg-bearing hydroxides for enhanced $CO_2$ mineralization from silicates have also been investigated as shown in reactions 2 and 3.[22,23]

$$MeO(SiO_2)_{(s)} + H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons Me(OH)_{2(s)} + SiO_{2(s)} \tag{2}$$

$$Me(OH)_{2(s)} + CO_{2(g)} \rightleftharpoons MeCO_{3(s)} + H_2O_{(l)} \tag{3}$$

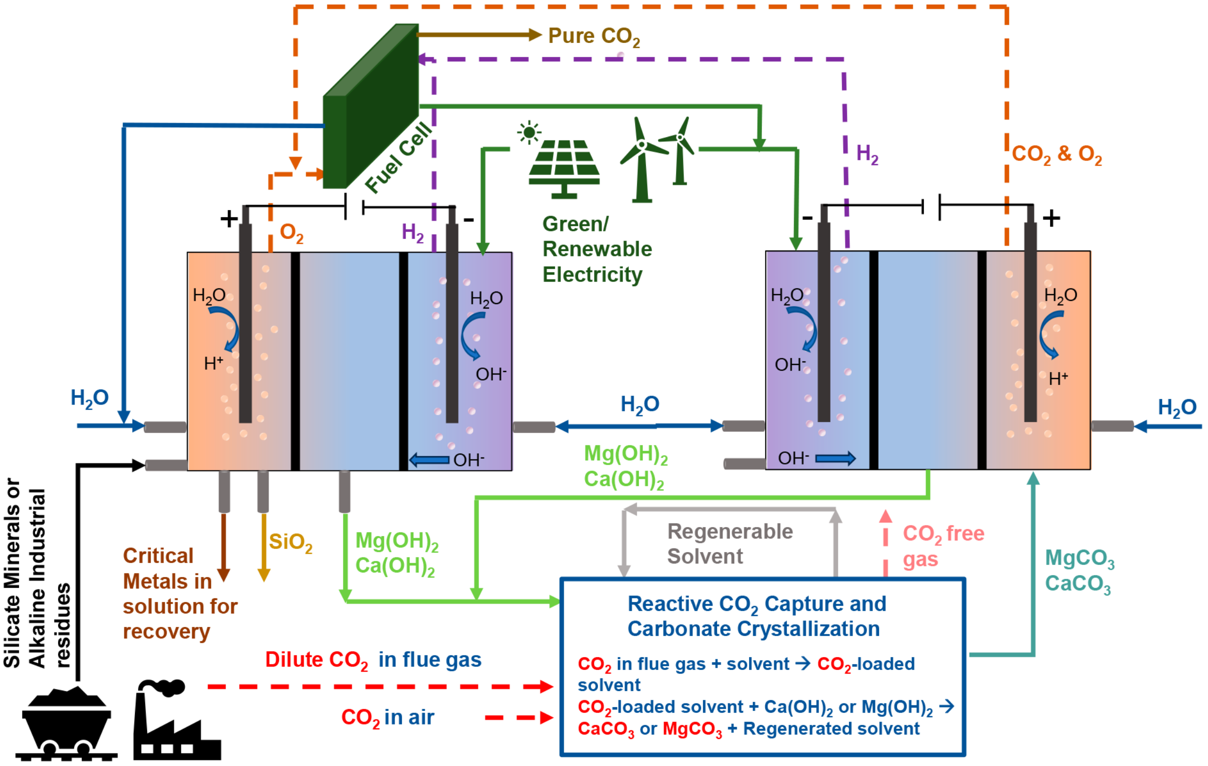

**Figure 1.** Schematic representation of the integrated approach for closing the carbon and material cycles while cogenerating high-value products. Electrochemical desilication fractionates alkaline resources to coproduce silica, $O_2$, $H_2$, leachate bearing metals, and Ca- and Mg-hydroxide. Reactive $CO_2$ capture and crystallization pathways are harnessed to capture $CO_2$ from dilute sources using solvents. $CO_2$-loaded solvents are reacted with $Ca(OH)_2$ and $Mg(OH)_2$ to produce the respective carbonates while regenerating the solvents. The carbonates can be used as a permanent or temporary store of $CO_2$. For applications that require high-purity $CO_2$, Ca- and Mg-carbonates are electrochemically converted to Ca- and Mg-hydroxide while coproducing $H_2$ and $O_2$.

By utilizing hydroxides for $CO_2$ mineralization, high selectivity, faster kinetics, and higher-purity carbonates can be obtained. However, the overall process of generating hydroxides from siliceous materials requires the use of stoichiometric levels of acid and base, which represents a significant economic and environmental challenge. Furthermore, tuning the molecular-scale and nanoscale interactions is crucial to achieving chemical and morphological control of the crystallized products for energy- and material-efficient carbon transformations.

## CARBON TRANSFORMATIONS WITH THE COGENERATION OF HIGH-VALUE PRODUCTS

As an alternative to the external pH-swing-based approach, electrochemical desilication approaches by harnessing the *in situ* generation of acids and bases can result in the cogeneration of Ca- and Mg-hydroxide, $H_2$, $O_2$, silica, and a leachate bearing other metals present in silicates. The resulting Ca- and Mg-hydroxide are then converted to their respective carbonates by harnessing regenerable solvents. $CO_2$ from dilute sources including flue gas streams and air is captured using solvents. These $CO_2$-loaded solvents then react with Ca- or Mg-hydroxide to produce Ca- or Mg-carbonate while regenerating the solvents for reuse over multiple cycles. The generated Ca- or Mg-carbonate can be directly used in various applications, including fillers and construction materials, or can be stored to realize carbon removal benefits. Alternatively, these materials can be harnessed as a temporary store of $CO_2$ and for on-demand generation of high-purity $CO_2$ while regenerating Ca- or Mg-hydroxide. The regeneration of $Me(OH)_2$ usually involves an energy-intensive thermally aided calcination step. The significant drop in the cost of electricity from renewable sources in the past decade[24] now enables the use of these resources for electrochemical regeneration of the sorbent and high-purity $CO_2$ generation with the coevolution of $H_2$ and $O_2$. This integrated approach is shown in Figure 1.

Electrolysis induced an inherent pH gradient across a three-chamber electrochemical cell to facilitate dissolution of the silicate-bearing minerals in the anode chamber to cogenerate $O_2$ and high-purity silica and leach energy-critical metals into the aqueous phase. The simultaneous precipitation of $Ca(OH)_2$ or $Mg(OH)_2$ and the generation of $H_2$ occur following Ca or Mg migration and reaction with excess hydroxide ions produced in the cathode chamber. The chemical reactions involved in electrochemical desilication are represented by reactions 4−8.

$$2H_2O_{(aq)} + 4e^- \rightleftharpoons 4OH^-_{(aq)} + 2H_{2(g)} \tag{4}$$

$$2H_2O_{(aq)} \rightleftharpoons 4H^+_{(aq)} + O_{2(g)} + 4e^- \tag{5}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(aq)} \tag{6}$$

$$MeO(SiO_2)_{(s)} + 2H^+_{(aq)} \rightleftharpoons Me^{2+}_{(aq)} + SiO_{2(s)} + H_2O_{(l)} \tag{7}$$

$$Me_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons Me(OH)_{2(s)} \tag{8}$$

https://doi.org/10.1021/acs.accounts.3c00482
*Acc. Chem. Res.* XXXX, XXX, XXX−XXX

First, water splitting via the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) results in the formation of protons, hydroxyl ions, $O_2$, and $H_2$ as shown in reactions 4 and 5. The continuous generation of $H^+$ and $OH^-$ ions via HER and OER leads to a local pH gradient across the cell. At steady state, protons recombine with hydroxyl ions to produce $H_2O$ as shown in reaction 6. Successful electrochemical desilication pathways harness protons to facilitate the dissolution of silicate minerals as shown in reaction 7 while limiting water formation as shown in reaction 6. The dissolved $Ca^{2+}$ and $Mg^{2+}$ ions migrate toward the cathode chamber (pH > 13) where stronger interactions with $OH^-$ ions lead to the precipitation of Ca- or Mg-hydroxide as shown in reaction 8. Ca- and Mg-silicates abundant in mafic and ultramafic rocks (e.g., olivine and serpentine) and alkaline residues (e.g., slags and mine tailings) are compatible with electrochemical desilication.

To demonstrate the feasibility of electrochemical desilication, ladle slag generated by Nucor was used as the alkaline resource. The composition of ladle slag is shown in Table 1.

**Table 1. Chemical Composition of Nucor Ladle Slag Using X-ray Fluorescence (XRF) Analyses**

| Elements | Nucor Ladle Slag Composition (%) |
|---|---|
| $SiO_2$ | 9.66 |
| $Al_2O_3$ | 11.2 |
| $Fe_2O_3$ | 5.35 |
| MgO | 31.3 |
| CaO | 33.4 |
| $Na_2O$ | 0.08 |
| $K_2O$ | 0.1 |
| $TiO_2$ | 0.51 |
| $P_2O_5$ | 0.09 |
| MnO | 0.92 |
| $Cr_2O_3$ | 0.11 |
| $V_2O_5$ | 0.02 |
| LOI | 6.4 |
| C (t) | 0.34 |
| Pb | 24.8 |

Experiments were conducted with 1 M $NaNO_3$ solution under an applied voltage of 6 V for 20 h with a ladle slag comprising 10 wt % of the solution. The formation of Ca- and Mg-hydroxide and silica is evident on the cathode and anode sides of the electrochemical cell based on X-ray diffraction (XRD) analyses (Figure 2(a)). In contrast, the starting ladle slag material is heterogeneous and comprises oxide, hydroxide, and silicate phases bearing calcium and magnesium. Metal leaching is evident from the solutions in the anodic chamber (Figure 2(b)). The concentrations of Mn, Ti, and Fe in the anolyte are promising and well-suited for the subsequent separation of metals. Except for Si and Al, significant concentrations (>1 ppm) of other elements are not observed in the catholyte. These findings unlock new possibilities for the co-recovery of multiple energy-critical metals, silica, and Ca- and Mg-hydroxide via electrochemical desilication.

Electrochemically generated Ca- and Mg-hydroxide are harnessed for $CO_2$ capture and mineralization. While Ca- and Mg-hydroxide are well known to react with $CO_2$ to produce Ca- and Mg-carbonates, the time scales of mineralization are slow with ultradilute sources of $CO_2$. To address this challenge, regenerable $CO_2$ capture solvents are being investigated for integrated $CO_2$ capture and mineralization.[1−4,25−27] In this approach, $CO_2$ is captured using solvents. These $CO_2$-captured solvents are reacted with Ca- and Mg-hydroxide to produce the respective carbonates with inherent solvent regeneration. The coupling of endothermic $CO_2$ capture pathways with exothermic carbon mineralization approaches aids the overall energy efficiency, and the regeneration of the solvents facilitates material efficiency.

$CO_2$ capture using less corrosive regenerable solvents such as Na-glycinate (Na-gly) has been reported to be very effective, achieving $CO_2$ absorption capacities of ∼0.18 ton of $CO_2$ captured/ton of 30 wt % Na-gly, which is higher than ∼0.11 ton of $CO_2$ captured/ton of 30 wt % MEA.[28,29] Postcapture, $CO_2$-loaded Na-gly is in contact with Ca/Mg-bearing alkaline sources for $CO_2$ mineralization to produce solid carbonates. By coupling both capture and mineralization in a single step, significant cost savings on capital expenditures can be realized. One of the key unresolved scientific knowledge gaps is a comparison of the reactivity of $Ca(OH)_2$ and $Mg(OH)_2$. To address this challenge, experiments were conducted to determine the extents of carbon mineralization and quantity of $CO_2$ stored in $Ca(OH)_2$ and $Mg(OH)_2$ sorbents at 90 °C for 3 h with a solid:liquid weight ratio of 3:17 using 2.5 M Na-glycinate. $CO_2$ capture is not the rate-limiting step, and the solvents were fully loaded with $CO_2$ for carbon mineralization. Under these conditions, the extents of carbon mineralization of $Ca(OH)_2$ and $Mg(OH)_2$ are 96.5 (±2.3)% and 78 (±0.6)%, respectively. In $Mg(OH)_2$ and $Ca(OH)_2$, the quantity of $CO_2$ stored is 12.1 (±1.3) and 13 (±0.8) mmol per gram of the sorbent. The lower molecular weight of Mg compared to Ca contributes to overlapping levels of $CO_2$ stored in $Mg(OH)_2$ compared to $Ca(OH)_2$ even though the extents of carbon mineralization are lower (Figure 3a). Prior studies have shown that lower temperatures of 50−75 °C are also effective in aiding $CO_2$ capture and mineralization in the presence of 2.5 M Na-glycinate. While $CO_2$ absorption is aided at 25−30 °C, carbonate formation is favored at higher temperatures due to the faster kinetics and lower solubility of Ca- and Mg-carbonate at higher temperatures. However, $CO_2$ ex-solution occurs more rapidly above 90 °C. Therefore, temperatures in the range of 50−90 °C favor integrated $CO_2$ capture, mineralization, and solvent regeneration. Metastable phases such as aragonite (spiky/orthorhombic) and stable phases of calcite (rhombohedral) are present in the product obtained after the mineralization of $Ca(OH)_2$, in which calcite (93%) was the dominant phase. The mineralization of $Mg(OH)_2$ resulted in the production of metastable hydromagnesite (needle-like crystals) phases and the unreacted brucite phase with a narrower but larger size distribution as shown in (Figure 3(b−d)). Once the carbonates are produced, they can serve as a permanent or temporary store of $CO_2$ emissions or can be used in construction and as filler materials.

When carbonate materials are used as temporary storage media of $CO_2$, approaches to recover $CO_2$ and regenerate the hydroxide materials need to be developed. While the thermal calcination of carbonate materials to produce high-purity $CO_2$ followed by hydration to produce $Ca(OH)_2$ has been well established,[30] analogous electrochemical pathways contrasting the recovery of $Ca(OH)_2$ and $Mg(OH)_2$ remain less developed. The electrochemical sorbent generation approach is proposed to address the challenges of sorbent sintering and the need for elevated temperatures (e.g., $CaCO_3$ calcination occurs at 800−900 °C). This electrochemical mode is

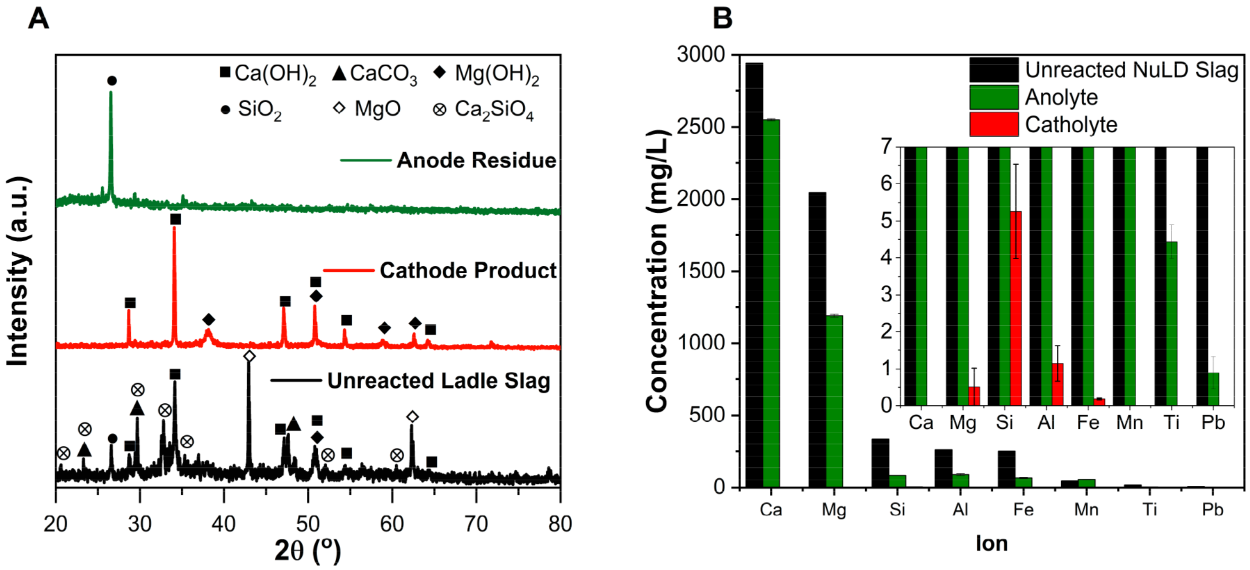

**Figure 2.** Electrochemical desilication of ladle slag results in fractionation to produce silica and Ca- and Mg-hydroxide as shown in the X-ray diffraction (XRD) data in (A). The concentrations of metal-bearing leachates are shown in (B). Slag used for this study had an average particle size of 30 $\mu$m, and the experiments were performed at 6 V for 20 h.

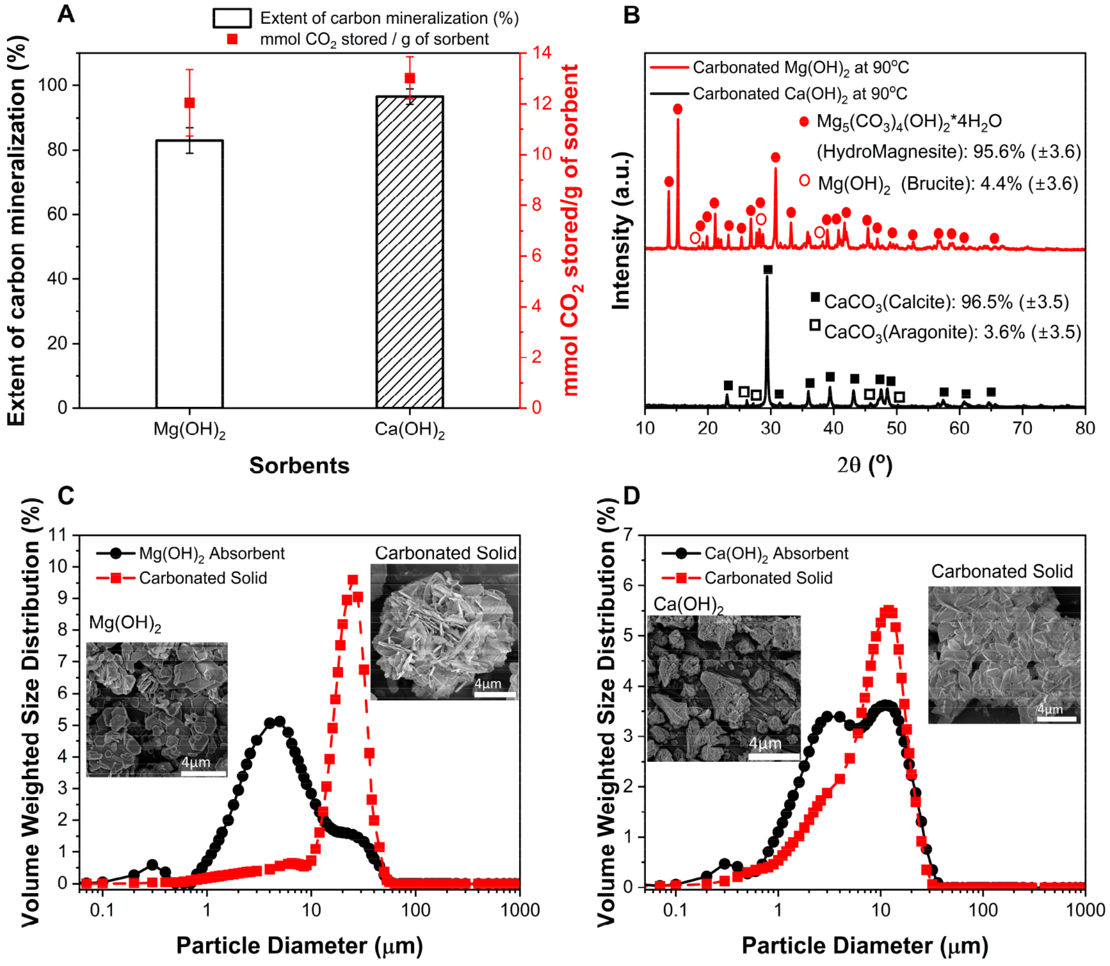

**Figure 3.** Extent of carbon mineralization and mmol of $CO_2$ stored/g of sorbent for $Mg(OH)_2$ and $Ca(OH)_2$ shown in (A). XRD patterns of carbonated solids with marked peaks of hydromagnesite, brucite, calcite, and aragonite shown in (B). Particle size distributions and scanning electron microscope images of $Ca(OH)_2$ sorbent before and after mineralization in (C) and $Mg(OH)_2$ sorbent before and after mineralization in (D). Experiments were performed using $CO_2$-loaded Na-glycinate with an initial solvent concentration of 2.5 M at 90 °C for 3 h and a solid to liquid weight ratio of 3:17.

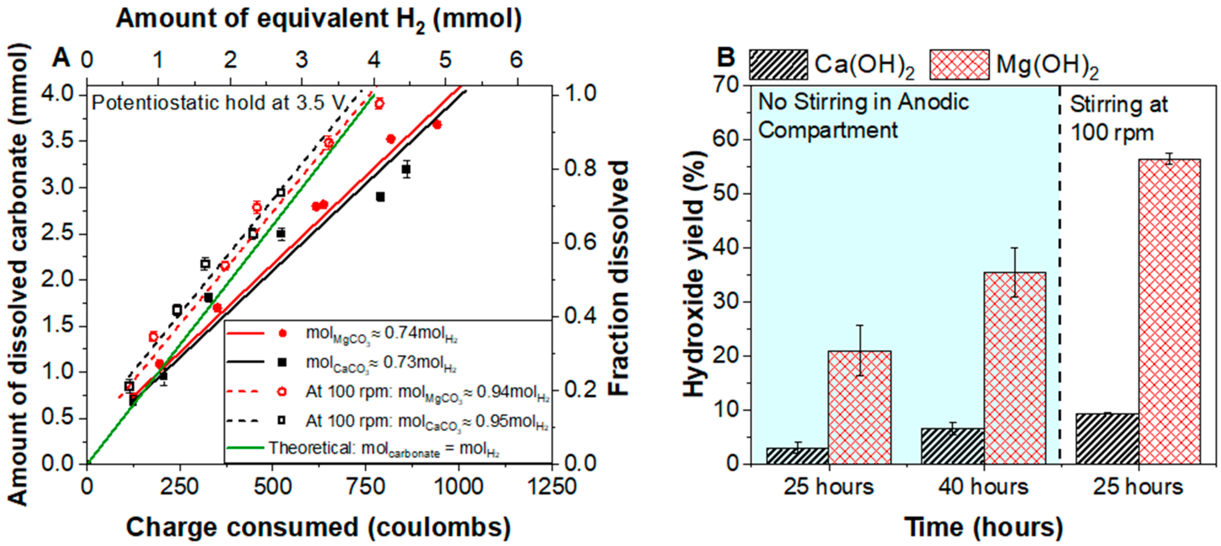

**Figure 4.** Electrochemical sorbent regeneration is represented using the Coulombic efficiency plot in (A) which shows the amount of carbonate species dissolved as a function of charge supplied to the electrochemical system and the equivalent amount of $H_2$ produced at the cathode. This process produces $O_2$, and $CO_2$ is released from the anode due to carbonate dissolution. Calcium and magnesium hydroxide yields obtained in the cathodic compartment as a function of reaction time in unstirred and stirred environments are shown in (B). Electrochemical reactions are carried out at 3.5 V.

analogous to the desilication mode described earlier in that proton generation is essential for dissolving the alkaline reactants. One of the crucial considerations is the overall energy efficiency of this pathway. To this end, a series of experiments were conducted to determine the Coulombic efficiencies as shown in Figure 4. The dissolution is observed to be complete when carbonate feedstock completely dissolves to produce $Ca^{2+}$ and $Mg^{2+}$ ions in solution as shown in reaction 9. The pH of the solution in the anodic chamber is less than 2, which facilitates a thermodynamic shift and facilitates the evolution of gaseous $CO_2$ based on $CO_2$−$H_2O$ equilibrium in a closed system.

$$MeCO_{3(s)} + 2H^{+}_{(aq)} \rightleftharpoons 2Me^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \qquad (9)$$

Charge efficiencies associated with dissolution as high as 73−74% were achieved in environments without stirring Ca- and Mg-carbonate reactants to favor dissolution. A calcium carbonate dissolution Coulombic efficiency of 85% was recently reported by Ellis and co-workers using a similar cell configuration.[31] However, lower overall concentrations of calcium carbonate were used in their study. We hypothesize that high concentrations of carbonate feedstock will lead to lower efficiencies due to the combined effects of limited proton−particle contact and longer time scales required for carbonate deconstruction, which implies a higher loss of protons due to recombination to produce water, as shown in reaction 6. However, by incorporating a stirring component in the anodic chamber, the exposed surface area of the solid particles is increased, and proton−particle interactions are enhanced, facilitating more efficient dissolution behavior. Charge efficiencies of as high as 95% were observed for the dissolution of $MgCO_3$ and $CaCO_3$ while stirring at 100 rpm.

While the charge efficiencies associated with the dissolution of Mg- and Ca-carbonate are similar, the yields of solid Ca- and Mg-hydroxide are quite different. Higher hydroxide yields were observed with magnesium (∼40%) relative to calcium (<10%) after 40 h of operation with a potentiostatic hold of 3.5 V. This observation is attributed to the significantly lower solubility constant ($K_{sp}$) of $Mg(OH)_2$ of $5.61 \times 10^{-12}$ relative to $Ca(OH)_2$, which is $5.02 \times 10^{-6}$ at ambient temperature.[32,32] From a thermodynamic standpoint, the driving force for precipitation is the degree of supersaturation which is dependent on $K_{sp}$. In this context, a lower $K_{sp}$ leads to a higher degree of localized supersaturation, resulting in faster precipitation.[33] Some approaches to improve hydroxide precipitation from the aqueous phase include the addition of promoters or using crystal seeding approaches.[34,35] It is also important to note that Ca- or Mg-hydroxide formation could be potentially limited by ion transfer. Furthermore, the competing migration of cations [e.g., $Na^+$ ions] could limit $Mg^{2+}/Ca^{2+}$ interactions with hydroxyl ions to produce hydroxides.

## ■ RESEARCH DIRECTIONS AND OPPORTUNITIES

While reactive crystallization is a highly versatile pathway for capturing, converting, storing, and removing $CO_2$ emissions to scale, several scientific advances are ongoing to improve the overall energy efficiency and material efficiency of these pathways. In this context, scalable, highly efficient, stable, environmentally friendly, and cost-effective electrocatalysts for electrochemical desilication and sorbent regeneration are essential. Noble metal catalysts such as Pt, Ir, and Ru are commonly used due to their unique stability and structure that allow for rapid reduction−oxidation reactions.[36,37] However, the scarcity and high cost of these metals are key drivers motivating the development of other efficient, economical, and earth-abundant nickel, copper, or cobalt-bearing catalysts.[38] To challenge the issue of mass transfer, enhanced ion transfer can be tuned by investigating the influence of membranes. The addition of mass transfer promoters and approaches to adapt flow cell configurations can lead to improved cell designs.[39,40]

With respect to broader impacts, the electrochemical desilication and sorbent regeneration pathways would theoretically require ∼5.2 and 6.6 GJ of electrical energy per ton of $Ca(OH)_2$ and $Mg(OH)_2$ produced, operating at 2 V (0.77 V overpotential). While these estimated energy needs are in a similar range to those needed for external pH swings or calcination (4.92 and 5.54 GJ per ton of CaO and MgO, respectively), the overall carbon footprint can be addressed by directly utilizing electricity from renewable sources (e.g., wind and solar energy) and by harnessing the produced Ca- or Mg-hydroxide for capturing, converting, storing, or removing $CO_2$ emissions. Other considerations also include carbon emissions associated with preprocessing alkaline residues including sorting and grinding to achieve smaller particle sizes (<100 μm). Furthermore, integrated pathways to selectively recover energy-critical metals and post-treatment of the anolyte solution are needed to facilitate regeneration of the electrolyte solution and maximize the value of this approach.

Another advantage is tuning the coproduction of high-value resources, which is unique to this integrated approach. For example, $H_2$ and $O_2$ produced during electrolysis can be harnessed as feedstocks during iron and steel and cement making or can be used to generate green electricity by harnessing fuel cells as illustrated in Figure 1. Advanced metal recovery pathways compatible with this carbon management approach are essential to maximizing the cobenefits of this integrated approach. These transformative advances will enable the integration of cogenerated products and the coutilization of on-site alkaline residues and $CO_2$ emissions to close the materials and carbon cycles while decarbonizing crucial industrial sectors including the iron and steel, cement, mining, and aluminum industries for a sustainable energy and resource recovery future.

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### Author Contributions

CRediT: **Prince Ochonma** conceptualization, data curation, formal analysis, investigation, methodology, resources, software, supervision, validation, visualization, writing-original draft, writing-review & editing; **Xun Gao** conceptualization, investigation, validation; **Greeshma Gadikota** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, visualization, writing-original draft, writing-review & editing.

### Notes

The authors declare no competing financial interest.

### Biographies

**Prince Ochonma** is a Ph.D. candidate in the Smith School of Chemical and Biomolecular Engineering at Cornell University. His research is focused on advancing energy- and material-efficient reaction pathways for closing materials cycles and enabling negative emissions technologies. His B.S. and M.S. degrees in chemical engineering are from University of Lagos and Cornell University, respectively.

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## ACKNOWLEDGMENTS

The authors acknowledge the use of the shared facilities at the Cornell Center for Materials Research (CCMR), which are supported through the National Science Foundation Materials Research Science and Engineering Centers (NSF MRSEC) program (DMR-1719875). G.G. and X.G.'s contributions are supported by the DOE CAREER Award through the Office of Science: DE-SC0020263. G.G. gratefully acknowledges the support of ARPA-E through the MINER and OPEN 2021 Programs: DE-AR-0001608. P.O.'s efforts are supported by the Cornell Atkinson Small Grant Program through the Reducing Climate Risk Initiative funded by the Cornell Atkinson Center for Sustainability, Cornell University, and the Link Foundation Energy Fellowship. We gratefully acknowledge the support of Cord Heine, the environmental supervisor at Nucor Steel of Auburn (Auburn, NY) for providing the slag materials used in this study.

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