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# Looping-accelerated CO<sub>2</sub> mineralization for cost-competitive cementitious materials and hydrogen

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Advancing a net-negative carbon economy requires efficient and cost-effective CO<sub>2</sub> capture and utilization methods. Here, we introduce a novel sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) looping process that accelerates CO<sub>2</sub> capture and mineralization by silicate feedstocks such as steel slags, producing a carbonate-rich product and amorphous silica as cementitious materials. Unlike conventional direct or acid-assisted mineralization, our chemical looping approach first carbonates the silicate using a Na<sub>2</sub>CO<sub>3</sub> solution. The resulting solution then reactively captures CO<sub>2</sub> and precipitates high-purity, (sub)micron-sized amorphous silica, while simultaneously regenerating Na<sub>2</sub>CO<sub>3</sub>. Demonstrated on steel slags, the process achieved 59% and 35% capture for point-source and air CO<sub>2</sub>, respectively, mineralizing up to 2.79 mmol-C g<sup>-1</sup> slag. Compared to traditional slag-water CO<sub>2</sub> mineralization, Na<sub>2</sub>CO<sub>3</sub> looping captured and mineralized 4 to 9 times more CO<sub>2</sub>. Mechanistically, Na<sub>2</sub>CO<sub>3</sub> looping accelerates mineralization by rapidly removing Ca *via* carbonate precipitation, thereby sustaining a strong thermodynamic driving force for continued Ca–silicate dissolution, which governs the overall carbonation rate. The process offers several key advantages and novelties: (1) no net chemical consumption due to complete Na<sub>2</sub>CO<sub>3</sub> regeneration; (2) CO<sub>2</sub> capture and mineralization occur at room temperature and 1 atm; (3) the CO<sub>2</sub> source can be either a point source or ambient air; (4) both the carbonation and reactive capture steps are exothermic, lowering system energy demand and eliminating external heat input; and (5) two cementitious products—carbonate-rich solids and amorphous silica—are generated separately, enabling flexible blending in downstream applications. Additionally, utilization of slag waste heat enables its reaction with steam to produce up to 1.01 mmol-H<sub>2</sub> g<sup>-1</sup> slag. Without product revenues, levelized costs are only \$252 and \$50 per ton of CO<sub>2</sub> for air and point-source capture, respectively; considering product revenues, the payback periods are only 1.9 and 0.8 years for air and point-source CO<sub>2</sub>.

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## Broader context

Achieving climate stabilization will require scalable technologies capable of permanently removing carbon dioxide (CO<sub>2</sub>) from both industrial emissions and the atmosphere. Although direct air capture (DAC) is increasingly recognized as essential for addressing legacy and residual emissions, existing DAC approaches are often energy-intensive and producing concentrated CO<sub>2</sub> streams that require further handling and storage. Mineralization offers a fundamentally different pathway by converting CO<sub>2</sub> directly into stable solids, but most mineral carbonation routes remain limited by slow kinetics, high-temperature activation, or net chemical consumption. This study demonstrates a sodium carbonate looping process that couples CO<sub>2</sub> capture and accelerated mineralization in a fully regenerative cycle using steel slag, an abundant industrial waste. By regenerating the sodium carbonate under mild conditions and without chemical loss, the process enables permanent CO<sub>2</sub> storage while operating at substantially lower energy demand than conventional capture–storage systems. Importantly, the looping chemistry is compatible with both point-source CO<sub>2</sub> and atmospheric CO<sub>2</sub>, providing a pathway for mineralization-enabled DAC. Beyond carbon removal, the process valorizes steel slag into supplementary cementitious materials, linking negative emissions with decarbonization of the cement and steel sectors. This integrated approach illustrates how chemical looping mineralization can support climate-relevant, circular solutions for large-scale carbon management.

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## Introduction

To reverse global warming, advancements to drive a net-negative carbon economy are essential;<sup>1</sup> current approaches to capture and store CO<sub>2</sub> from industrial flue gas and the



atmosphere are relatively expensive and have significant energy requirements. Traditional CO<sub>2</sub> capture processes, such as amine capture<sup>2</sup> and calcium looping,<sup>3</sup> usually require significant amount of heat or work to regenerate capture media. Additionally, these processes produce pure CO<sub>2</sub> gas requiring further treatment for permanent storage.

One pathway for permanent CO<sub>2</sub> storage is mineralization, which utilizes alkaline minerals and wastes to convert CO<sub>2</sub> into stable carbonates (stable up to 500 °C).<sup>4</sup> Commonly used alkaline minerals for mineralization include wollastonite,<sup>5</sup> serpentine,<sup>6</sup> and olivine.<sup>7</sup> Additionally, industrial wastes such as mine tailings,<sup>8</sup> fly ash,<sup>9</sup> recycled concrete,<sup>10</sup> and steel slags<sup>11</sup>—the focus of this research—are also used.

Relevant literature has established iron and steel slags as promising, plentiful, and cost-effective feedstocks for CO<sub>2</sub> capture and mineralization.<sup>12</sup> While blast furnace slag (iron slag) is commercially used as a supplementary cementitious material (SCM) to partially replace Portland cement,<sup>13</sup> basic oxygen furnace (BOF) and electric arc furnace (EAF) slags (two types of steel slags, with 260 million tons disposed annually<sup>14,15</sup>) have almost no use in concrete due to their free CaO and MgO contents, which cause expansive reactions,<sup>16</sup> and because their low pozzolanic reactivity limits their ability to contribute to cement hydration.<sup>17</sup> However, CO<sub>2</sub> mineralization can carbonate CaO and MgO producing a carbonate-rich product and silica that can be used as SCMs.<sup>18</sup> A recently published high temperature process produces calcium silicates and MgO for reactive CO<sub>2</sub> capture,<sup>19</sup> which are already abundant in steel slags.

Mineralization of steel slags is a promising solution for the permanent storage of CO<sub>2</sub>.<sup>20</sup> However, direct mineralization methods are limited by slow reaction kinetics. For example, direct gas–solid and direct aqueous mineralization<sup>21,22</sup> can occur at low temperature and pressure, but reaction rates are slow—often taking hours to days—due to kinetic limitations.<sup>16</sup> To accelerate the process, temperature and CO<sub>2</sub> partial pressure are usually increased but with an energy penalty.<sup>23</sup> Another pathway to enhance mineralization rates is the indirect aqueous process, which uses inorganic acids or bases to dissolve magnesium or calcium silicates in alkaline solids, releasing ions that react with CO<sub>2</sub>.<sup>24</sup> Although effective, this approach incurs additional material and processing costs due to chemical consumption.

Our work aims to leverage the enhanced mineralization rates of the indirect aqueous process, while avoiding chemical consumption through chemical looping. We propose a novel sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) looping process, in which silicate minerals such as steel slags are first carbonated with aqueous Na<sub>2</sub>CO<sub>3</sub> to form a carbonate-rich product. The basic solution is then regenerated by capturing CO<sub>2</sub>, simultaneously producing high purity precipitated amorphous silica. Compared to traditional mineralization routes, this process stands out in that the employed Na<sub>2</sub>CO<sub>3</sub> gets fully regenerated and thus no chemical is consumed. Additionally, the separately precipitated amorphous silica introduces a highly pozzolanic and reactive phase that overcomes the inherently low pozzolanic reactivity of BOF steel slag.

Previous studies have explored coupling CO<sub>2</sub> capture and mineralization through chemical looping, but most rely on amine solvents such as monoethanolamine (MEA) or sodium glycinate. For example, Liu *et al.* demonstrated CO<sub>2</sub> absorption in amines followed by mineralization with Ca- or Mg-based oxides,<sup>25</sup> while Li *et al.* coupled MEA capture with lime kiln dust carbonation.<sup>26</sup> Although effective under controlled conditions, these methods relied on pure or concentrated CO<sub>2</sub> streams, depend on costly solvents less available than common alkalis, and do not generate a separable silica product. In addition, amine degradation and solvent loss remain major barriers to scale.

A closer parallel is the work of Li *et al.*, who investigated CO<sub>2</sub> capture with KOH to form potassium carbonate that then carbonated cement mortar waste.<sup>27</sup> While following an alkali looping process, their approach required 10% CO<sub>2</sub> feeds, suffered from significant KOH losses during cycling, and did not yield purified silica. A related study by Wu *et al.* examined the carbonation of ladle furnace slag using sodium bicarbonate, but their work was limited to a single batch cycle under pure CO<sub>2</sub> and focused on alumina extraction rather than isolating amorphous silica – which plays a dominant role, relative to alumina, in forming the primary cement hydration products.<sup>28</sup>

In contrast, our Na<sub>2</sub>CO<sub>3</sub> looping process avoids many of the limitations observed in prior carbonation systems reported in the literature. In addition to beginning with Na<sub>2</sub>CO<sub>3</sub>, a weak, inexpensive, and widely available base, the process introduces several key advantages: it consumes no net chemicals due to full Na<sub>2</sub>CO<sub>3</sub> regeneration; operates at room temperature and 1 atm; accommodates CO<sub>2</sub> from either point sources or air; and is driven by exothermic carbonation and capture steps that minimize external energy demand. It also produces two separate cementitious products—carbonate-rich solids and amorphous silica—enabling flexible blending in downstream applications.

Within the broader carbon capture, utilization, and storage (CCUS) landscape, mineralization-based utilization pathways differ from capture-and-storage approaches in that CO<sub>2</sub> is converted directly into stable solid products, avoiding the need for compression, transport, and geological storage. For alkaline solids, however, prior mineral carbonation strategies have generally required high-temperature silicate activation<sup>29</sup> or net chemical consumption<sup>24</sup> to achieve practical reaction rates. These tradeoffs motivate the development of chemical looping mineralization pathways that combine permanent CO<sub>2</sub> storage with accelerated kinetics under mild conditions and low energy and material inputs.

In addition to their CO<sub>2</sub> mineralization capacity, steel slags contain reduced iron species at +2 oxidation state that can be used for thermochemical hydrogen (H<sub>2</sub>) production. H<sub>2</sub> can be produced from an exothermic reaction between steam and solid steel slag at 250–1000 °C<sup>30</sup> or molten steel slag at 1500–1600 °C.<sup>31,32</sup> The BOF process occurs at 1650 °C, thus the BOF slag temperature is sufficient for the thermochemical H<sub>2</sub> production.<sup>33</sup> Optionally, steel slag may be reacted with steam prior to mineralization to generate H<sub>2</sub>, creating an additional pathway for integration with clean energy systems.



In this study, we implement a fully closed  $\text{Na}_2\text{CO}_3$  looping cycle on steel slag and demonstrate stable, multi-cycle operation with significantly accelerated  $\text{CO}_2$  mineralization under both point-source and air conditions, relative to conventional direct aqueous mineralization, and under mild operating conditions (24–45 °C, 1 atm). We quantitatively compare looping-based mineralization to direct aqueous carbonation and couple these experimental results with a techno-economic analysis evaluating the co-production of SCMs and  $\text{H}_2$ , demonstrating progress toward a cost target of \$100 per ton- $\text{CO}_2$  captured from air.<sup>34</sup> Finally, we perform a mechanistic investigation to distinguish the reaction pathways unique to  $\text{Na}_2\text{CO}_3$  looping from those governing direct aqueous mineralization.

### Process description

The process includes steam to  $\text{H}_2$  conversion and  $\text{Na}_2\text{CO}_3$  looping for  $\text{CO}_2$  mineralization (Fig. 1). Here, “mineralization” refers to  $\text{CO}_2$  converted into stable carbonate phases (e.g.,  $\text{CaCO}_3$ ) that remain locked below 500 °C, while “capture” also includes less stable forms such as bicarbonate.

BOF slag contains mainly calcium silicates, calcium oxide, and magnesium iron(II) oxide. Four different BOF slags were obtained from Cleveland-Cliffs – Cleveland Works: quenched, aggregate non-metallic, fines, and aged fines. Slag descriptions are provided in the Methods section and Fig. S1. The quenched BOF slag elemental composition was experimentally determined through inductively coupled plasma optical emission spectroscopy (ICP-OES) (Table S1).

In Step 1 ( $\text{H}_2$  production), water vapor exothermically reacts with  $\text{Fe}^{2+}$  in steel slag to produce  $\text{H}_2$  (eqn (1)). Additionally, the steam can make the slag brittle, so that milling becomes less energy intensive.<sup>35</sup> The  $\text{H}_2$  production reaction is optional for  $\text{Na}_2\text{CO}_3$  looping afterwards. The  $\text{H}_2$  production results (Fig. S2 and S3) and discussion are available in the SI.



Step 2 (carbonation) is a set of exothermic reactions that carbonate the slag components, calcium silicates and calcium oxide, by  $\text{Na}_2\text{CO}_3$  solution at 20–70 °C and 1 atm, producing sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and sodium hydroxide ( $\text{NaOH}$ ) solution and  $\text{CaCO}_3$  precipitate to permanently store  $\text{CO}_2$  (eqn (2)–(4)). The  $\text{Na}_2\text{SiO}_3$  and  $\text{NaOH}$  solution is then filtered from the  $\text{CaCO}_3$  and unreactive slag components (a mixture described as carbonate-rich product).



Step 3 ( $\text{CO}_2$  capture) is a set of exothermic reactions (eqn (5) and (6)) that use the alkaline  $\text{Na}_2\text{SiO}_3$  and  $\text{NaOH}$  solution from



Fig. 1 (a) Basic oxygen furnace (BOF) steel slag generation process. (b) Hydrogen ( $\text{H}_2$ ) production and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) looping for  $\text{CO}_2$  capture and mineralization by BOF steel slag or other silicate feedstock.



Step 2 to absorb CO<sub>2</sub> and form silicic acid (H<sub>2</sub>SiO<sub>3</sub>) precipitate; meanwhile, the Na<sub>2</sub>CO<sub>3</sub> as well as part of H<sub>2</sub>O consumed in Step 2 are regenerated.



The H<sub>2</sub>SiO<sub>3</sub> precipitate is then filtered for Step 4 to decompose it into silica (SiO<sub>2</sub>) and water vapor (eqn (7)). This regenerates the remaining water consumed in Step 2. < ~100 °C heat is sufficient for the decomposition and can be supplied through the waste heat of slag. The decomposition is not required for Na<sub>2</sub>CO<sub>3</sub> looping, but it generates valuable amorphous silica.



Now, additional steel slag can be added, and the cycle can continue. Eqn (8) presents the overall Na<sub>2</sub>CO<sub>3</sub> looping reaction (excluding H<sub>2</sub> production), which converts silicate feedstock and CO<sub>2</sub> into a stable carbonate and amorphous silica.



## Results and discussion

### Na<sub>2</sub>CO<sub>3</sub> looping performance

To evaluate Na<sub>2</sub>CO<sub>3</sub> looping on steel slag mineralization (Step 2 and Step 3), we compared the Na<sub>2</sub>CO<sub>3</sub> looping case to a direct aqueous baseline for both point-source and air CO<sub>2</sub> scenarios. These are referred to as “looping” and “baseline” in the following sections.

**Point-source CO<sub>2</sub>.** The looping experiment consisted of four cycles, each including a carbonation (Step 2) and a CO<sub>2</sub> capture step (Step 3). In the looping case, 1 g of post-hydrogen-production quenched slag was reacted in an aqueous solution with a Na<sub>2</sub>CO<sub>3</sub>-to-slag mass ratio of 2.5 : 1 and a water-to-slag ratio of 50 : 1. The carbonation was carried out at 45 °C with a stirring rate of 400 rpm for 30 min.

After carbonation, the mixture was centrifuged to separate the carbonate-rich product from the solution. The solution was then used in the CO<sub>2</sub> capture step, where a 4% CO<sub>2</sub>/Ar gas was flowed through the solution at 90 standard cubic centimeters per minute (sccm) for 30 min, followed by an Ar flush to help the exhaust gas analysis quantify the remaining CO<sub>2</sub> in the reactor. The capture duration was optimized to regenerate the Na<sub>2</sub>CO<sub>3</sub> consumed during carbonation without further converting it into NaHCO<sub>3</sub>. After each capture step, 1 g of fresh slag was added to the regenerated solution, and the cycle was repeated for a total of four times. Detailed experimental steps are provided in the methods sections.

The baseline experiment followed the same procedure but without Na<sub>2</sub>CO<sub>3</sub> addition. In this case, the aqueous reaction served as a hydration step, releasing Ca(OH)<sub>2</sub> into solution, which then reacted with CO<sub>2</sub> during the capture step to form CaCO<sub>3</sub>. The looping and baseline cases are visualized in Fig. S4a.

The 4% CO<sub>2</sub> concentration was selected to represent post-combustion flue gas from a natural-gas combined cycle power plant.<sup>36</sup> Other major flue gas components, such as N<sub>2</sub> and O<sub>2</sub>, do not participate in reactions in the looping process under the conditions studied and primarily act as diluents; their effects are therefore expected to be equivalent to those of Ar in this system. Additionally, minor flue-gas contaminants (SO<sub>x</sub> and NO<sub>x</sub>) are typically reduced to low-ppm levels by upstream gas-conditioning processes and are therefore not expected to influence the chemistry studied here, as discussed further in the energy and technoeconomic analyses section.<sup>37</sup>

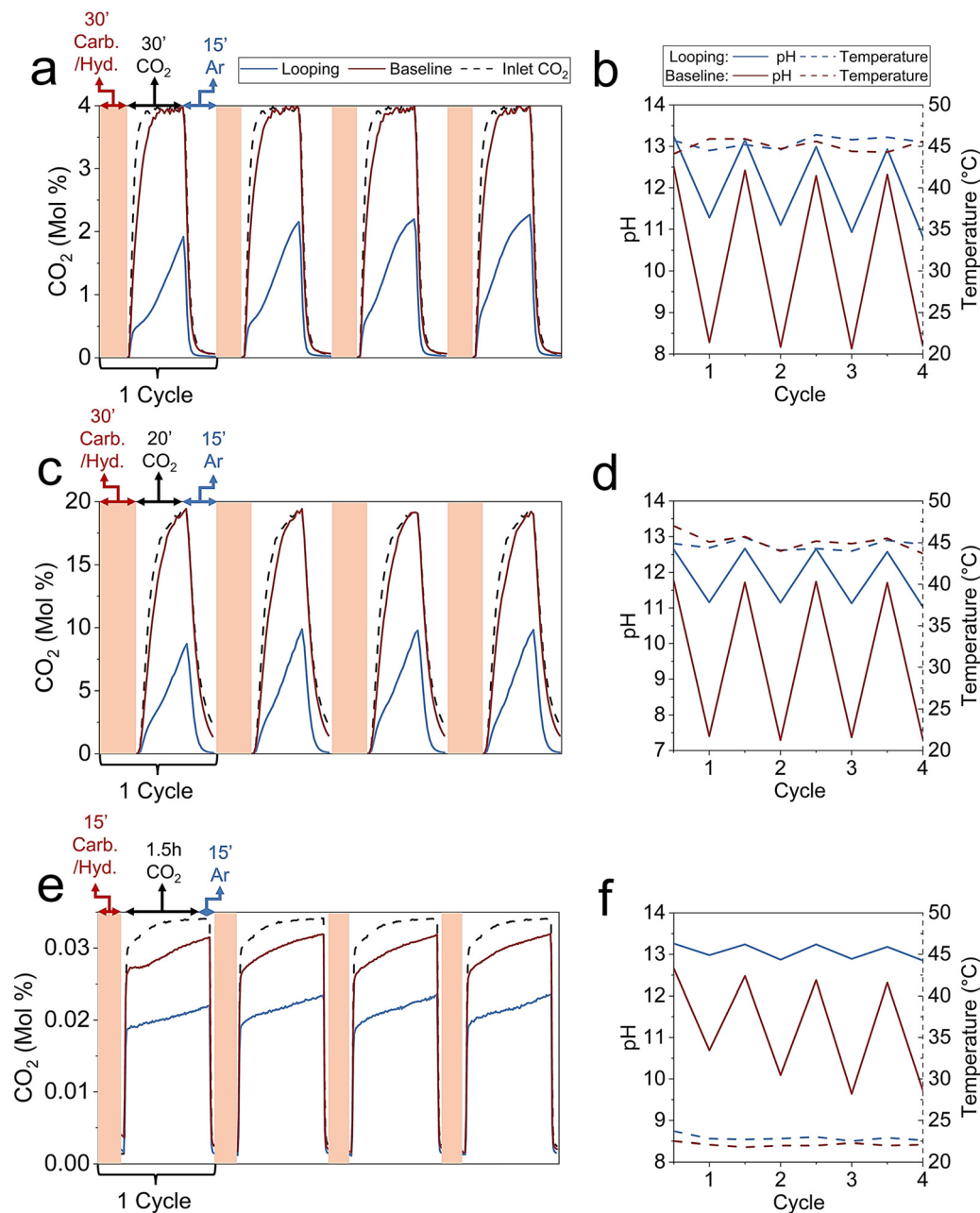
The cyclic performance of the looping and baseline cases is shown in Fig. 2a, along with a blank run (water only) representing the inlet CO<sub>2</sub>. After four cycles, the CO<sub>2</sub> capture ratio of the looping system reached 59%, compared to only 7% for the baseline.

Thermogravimetric analysis (TGA) was conducted on the carbonate-rich product after the fourth looping cycle (Fig. S5a). The amount of mineralized CO<sub>2</sub> determined from TGA (3.17 mmol-C g<sup>-1</sup> slag) was consistent with the CO<sub>2</sub> captured from the gas analysis (2.79 mmol-C g<sup>-1</sup> slag), within a reasonable 15% deviation.

For the baseline, TGA indicated 0.29 mmol C g<sup>-1</sup> slag (Fig. S5b), closely matching the 0.34 mmol-C g<sup>-1</sup> slag measured from the gas capture side. These values are expected to be equivalent since CaCO<sub>3</sub> is the sole carbonation product formed during the capture step.

The pH and temperature measured after each step for the looping and baseline cases are shown in Fig. 2b. Taken together, the carbon balance and cyclic pH behavior provide strong evidence for closed-loop regeneration of Na<sub>2</sub>CO<sub>3</sub> under the conditions studied. The carbon balance shown above demonstrates that the amount of CO<sub>2</sub> captured equals the amount carbonated in the fourth cycle, confirming mass closure across the looping sequence. In parallel, the stable cyclic pH observed in the looping system demonstrates that NaOH and Na<sub>2</sub>SiO<sub>3</sub> formed during carbonation are fully consumed during CO<sub>2</sub> capture, returning the solution to its initial state each cycle and preventing accumulation of unused capture capacity. As shown in Fig. 2b, both the maximum pH after carbonation and the minimum pH after CO<sub>2</sub> capture return to essentially the same values on every cycle. If sodium or alkalinity were being lost from solution through irreversible NaHCO<sub>3</sub> formation or incorporation of Na into solid phases, the post-carbonation pH would be expected to decrease over successive cycles. Conversely, accumulation of unused alkaline capacity would lead to an upward drift in the post-capture pH. The absence of either trend indicates that the alkalinity generated during slag carbonation is fully consumed during CO<sub>2</sub> capture and subsequently regenerated in the following cycle.





**Fig. 2** (a) Four Na<sub>2</sub>CO<sub>3</sub> looping cycles of 4% CO<sub>2</sub> with quenched BOF slag compared to the baseline; the conditions were 1 g slag per cycle, 45 °C, and 90 sccm 4% CO<sub>2</sub>/Ar. (b) pH and temperature after each step in 4% CO<sub>2</sub> looping and baseline. Half cycles are after carbonation and full cycles are after CO<sub>2</sub> capture. (c) Four Na<sub>2</sub>CO<sub>3</sub> looping cycles of 20% CO<sub>2</sub> with aged fines BOF slag compared to the baseline; the conditions were 10 g slag per cycle, 45 °C, and 90 sccm 20% CO<sub>2</sub>/Ar. (d) pH and temperature after each step in 20% CO<sub>2</sub> looping and baseline. (e) Four Na<sub>2</sub>CO<sub>3</sub> looping cycles of air CO<sub>2</sub> with quenched BOF slag compared to the baseline; the conditions were 0.05 g slag per cycle, 24 °C, and 90 sccm 343 ppm CO<sub>2</sub>. (f) pH and temperature after each step in air CO<sub>2</sub> looping and baseline.

In addition, the solution pH remains above ~11 throughout the looping experiments, a regime in which carbonate speciation is dominated by CO<sub>3</sub><sup>2-</sup> rather than HCO<sub>3</sub><sup>-</sup>. Under these conditions, any transient bicarbonate formed during CO<sub>2</sub> absorption is reconverted to carbonate during carbonation and does not accumulate.

The addition of Na<sub>2</sub>CO<sub>3</sub> significantly enhanced both the CO<sub>2</sub> capture ratio and the extent of mineralization. Specifically, the

looping system showed approximately nine times greater CO<sub>2</sub> capture ratio and CO<sub>2</sub> mineralization compared to the baseline. These results demonstrate the accelerated reaction kinetics and improved carbonation extent achieved through Na<sub>2</sub>CO<sub>3</sub> looping.

Building on the 4% CO<sub>2</sub> experiments, a scaled-up test was conducted using 10 g of aged fines per cycle, a water-to-slag ratio of 20:1, and a 20% CO<sub>2</sub> gas stream to evaluate looping



performance at higher dosages. Aged fines were selected because they represent an accumulation of slag from multiple production batches and have undergone environmental weathering, resulting in greater compositional variability. The 20% CO<sub>2</sub> was chosen to approximate the concentration of CO<sub>2</sub> in the flue gas of the BOF steel plant at Cleveland-Cliffs.

The cyclic performance of the 20% CO<sub>2</sub> looping and baseline is shown in Fig. 2c. After four cycles, the looping system achieved a CO<sub>2</sub> capture ratio of 69%, corresponding to 1.00 mmol-C g<sup>-1</sup> slag, whereas the baseline case reached only 11% capture (0.15 mmol-C g<sup>-1</sup> slag). Measurements of solution pH and temperature after each process step are shown in Fig. 2d.

Despite the increased slag mass, and the compositional variability of aged fines, the looping experiments retain the same kinetic advantage observed in the 1 g quenched slag tests. This result confirms that the Na<sub>2</sub>CO<sub>3</sub> looping mechanism remains effective at higher dosages and for more heterogeneous slag feedstocks.

**Air CO<sub>2</sub>.** For these experiments, the same Na<sub>2</sub>CO<sub>3</sub> looping procedure was applied with adjusted reaction conditions. In the looping case, 0.05 g of post-hydrogen-production quenched slag was reacted in an aqueous solution with a Na<sub>2</sub>CO<sub>3</sub>-to-slag ratio of 1:1 and a water-to-slag ratio of 100:1. The carbonation step was conducted at room temperature (24 °C) with a stirring rate of 400 rpm for 15 min.

Following carbonation and separation, the solution was exposed to 343 ppm CO<sub>2</sub> (from a compressed air cylinder) at 90 scfm for 1.5 h, followed by an Ar flush. After each capture step, 0.05 g of fresh slag was added to the regenerated solution, and the cycle was repeated four times. A corresponding baseline experiment without Na<sub>2</sub>CO<sub>3</sub> addition was performed for comparison.

The cyclic performance of the air CO<sub>2</sub> looping and baseline cases is shown in Fig. 2e. After four cycles, the looping system achieved 35% CO<sub>2</sub> capture, compared to 9% for the baseline. The pH and temperature for the processes are shown in Fig. 2f, demonstrating cyclic behavior under looping conditions similar to the point-source cases.

TGA of the carbonate-rich product after the fourth looping cycle (Fig. S5c) indicated 0.93 mmol-C g<sup>-1</sup> slag mineralized, consistent with 0.83 mmol-C g<sup>-1</sup> slag measured from gas analysis. For the baseline, insufficient CaCO<sub>3</sub> was recovered for TGA due to the small slag amount, but 0.23 mmol-C g<sup>-1</sup> slag was quantified from the gas capture data.

The Na<sub>2</sub>CO<sub>3</sub> looping system demonstrated a substantial enhancement in air CO<sub>2</sub> performance, achieving a four times higher CO<sub>2</sub> capture ratio and CO<sub>2</sub> mineralization than the baseline. Although the overall capture efficiency was lower than in the point-source case (as expected due to the dilute CO<sub>2</sub> concentration), the looping process maintained stable regeneration and carbonation across cycles, confirming its feasibility for continuous operation with air CO<sub>2</sub>.

**Silica production.** Because only small quantities of slag were processed during the looping experiments, the amount of precipitated silica was insufficient to isolate after each cycle. Therefore, a single large-scale carbonation experiment with an

extended CO<sub>2</sub> capture step under pure CO<sub>2</sub> was conducted to generate enough material for characterization (details in Fig. S6). The resulting high purity amorphous silica was confirmed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS), as shown in Fig. S6. SEM images also revealed (sub)-micron-sized silica particles. Complementary ICP-OES analysis (Table S2) further indicated minimal contamination from other elements.

### Energy and technoeconomic analyses

Energy and technoeconomic analyses were conducted for H<sub>2</sub> production and CO<sub>2</sub> mineralization. Four scenarios were analyzed: point-source capture and mineralization by Na<sub>2</sub>CO<sub>3</sub> looping and baseline as well as air CO<sub>2</sub> by Na<sub>2</sub>CO<sub>3</sub> looping and baseline. The Na<sub>2</sub>CO<sub>3</sub> looping scenarios followed the reactions detailed in the Process description section. In contrast, the baseline scenarios employed modified Steps 2 and 3 to first hydrate the slag, thereby releasing Ca(OH)<sub>2</sub> into solution, which subsequently reacted with CO<sub>2</sub> to form CaCO<sub>3</sub>. Detailed technoeconomic analysis methods are available in the SI.

The analysis is based on our experimental results using quenched slag as described in the Na<sub>2</sub>CO<sub>3</sub> Looping Performance section. CO<sub>2</sub> mineralization capacities were 2.79, 0.32, 0.83, and 0.23 mmol-C g<sup>-1</sup> slag for point-source looping, point-source baseline, air CO<sub>2</sub> looping, and air CO<sub>2</sub> baseline, respectively. FeO content was estimated from experimental H<sub>2</sub> production (0.76 mmol-H<sub>2</sub> g<sup>-1</sup> slag). TGA data was combined with XRD refinement (Table S3) to determine the mols of actively reacted components, namely calcium silicates and CaO (Table S4). Annually 100 000 tons of CO<sub>2</sub> captured and mineralized are used for the mass balance in each scenario (Table S5).

Reaction temperatures were optimized to reduce external cooling and heating. All reactions were exothermic except silicic acid decomposition, which was driven by waste heat from slag. Secondary processes require electricity for conveying, milling, filtering, stirring, pumping, and fan-driven gas flow. Four electricity sources were evaluated for each scenario: (1) external solar grid, (2) internal solar photovoltaic (PV) system with integrated 16-hour battery storage, (3) internal wind turbines with integrated 16-hour battery storage, and (4) internal steam power plant using slag waste heat (Table S6).

The capital cost of the system was estimated using engineering design books.<sup>38,39</sup> The gas/air contactor system was designed based on Carbon Engineering's air-contactor configuration, incorporating a slab contactor with packing for efficient gas-liquid contact, as well as fans for gas/air movement and pumps for circulating the absorption solution.<sup>40</sup> The plant was assumed to have a lifetime of 50 years, and the lifespan of the equipment was estimated to determine a replacement schedule (Table S7).

**Point-source CO<sub>2</sub>.** Fig. 3a presents the preliminary plant design for point-source Na<sub>2</sub>CO<sub>3</sub> looping, while Fig. 3b compares the process costs and revenue per ton-CO<sub>2</sub> to the baseline with a plant design shown in Fig. S7a. Cost components are detailed in Table S8. Na<sub>2</sub>CO<sub>3</sub> looping is more cost-effective than





**Fig. 3** (a) Proposed plant design for hydrogen (H<sub>2</sub>) production and point-source CO<sub>2</sub> mineralization through Na<sub>2</sub>CO<sub>3</sub> looping using BOF steel slag. (b) Technoeconomic analysis (TEA) comparing Na<sub>2</sub>CO<sub>3</sub> looping to the baseline process for 4% CO<sub>2</sub>. The process cost was evaluated for different energy (purely electricity) supply methods, including solar grid, internal solar PV with 16-hour battery storage, internal wind turbine with 16-hour battery storage, and an internal steam power plant using waste heat from the slag. The levelized costs of electricity are noted in Table S17. The revenue streams from 45Q tax credit, precipitated silica (SiO<sub>2</sub>), carbonate-rich product, and H<sub>2</sub> are presented on the right axis.

the baseline, primarily due to reduced slag usage, enabling smaller reactors and lower electricity consumption. Installed equipment costs are provided in Tables S9–S12 for both scenarios, and Fig. S8 shows capital and operating cost breakdowns for Na<sub>2</sub>CO<sub>3</sub> looping, with the major contributors being the carbonation reactor, vacuum filters for solid-liquid separation, the mill for slag crushing, the cooling tower and heat exchanger for thermal management, and electricity. Depending on the electricity source, process costs range from \$44 to \$70 per ton-CO<sub>2</sub> (excluding revenues) for the Na<sub>2</sub>CO<sub>3</sub> looping system, while energy demands are 211 and 2215 kWh<sub>e</sub> per ton-CO<sub>2</sub> for Na<sub>2</sub>CO<sub>3</sub> looping and baseline, respectively.

The analysis incorporates revenue from several sources: H<sub>2</sub> sold at \$2 per kg,<sup>41</sup> precipitated silica at \$600 per ton,<sup>42</sup> and the 45Q tax credit providing \$85 per ton-CO<sub>2</sub> for CO<sub>2</sub> conversion into useful products.<sup>43</sup> The precipitated silica is assumed to be comparable to silica fume, an amorphous silica byproduct widely used as a SCM, for which reported market prices typically range from approximately \$150–800 per ton; the

assumed value of \$600 per ton therefore represents a mid-range benchmark for a high-purity SCM product.<sup>44</sup> The selling price of the point-source Na<sub>2</sub>CO<sub>3</sub> looping carbonate-rich product was assumed to be \$26 per ton.<sup>45</sup> This value was intentionally selected to be conservative relative to established SCMs such as ground granulated blast furnace slag (GGBFS), which typically sells for approximately \$36–38 per ton due to its well-established performance and market acceptance.<sup>46</sup> The baseline carbonate-rich product was assumed to be a mixture of the precipitated CaCO<sub>3</sub> and hydrated steel slag outputs to be comparable to the looping case. The selling price of the baseline carbonate-rich product was proportionally scaled to have equal yearly revenue for the carbonate-rich product in the looping case, considering the larger amount and lower quality (due to the lower carbonation extent) of the product in the baseline case compared to looping. With these revenue streams, the point-source Na<sub>2</sub>CO<sub>3</sub> looping achieves a breakeven time of 0.8 years.

**Air CO<sub>2</sub>.** Fig. 4a shows the preliminary plant design for Na<sub>2</sub>CO<sub>3</sub> looping for air CO<sub>2</sub>, while Fig. 4b compares the process costs and





Fig. 4 (a) Proposed plant design for hydrogen (H<sub>2</sub>) production and air CO<sub>2</sub> mineralization through Na<sub>2</sub>CO<sub>3</sub> looping with BOF steel slag. (b) Technoeconomic analysis (TEA) comparing Na<sub>2</sub>CO<sub>3</sub> looping to the baseline process for 343 ppm CO<sub>2</sub>. The process cost was evaluated for different energy (purely electricity) supply methods, including solar grid, internal solar PV with 16-hour battery storage, internal wind turbine with 16-hour battery storage, and an internal steam power plant using waste heat from the slag. The levelized costs of electricity are noted in Table S17. The revenue streams from H<sub>2</sub>, precipitated silica (SiO<sub>2</sub>), carbonate-rich product, and the 45Q tax credit are presented on the right axis.

revenue per ton-CO<sub>2</sub> to the baseline with a plant design shown in Fig. S7b. The looping scenario outperforms the baseline. For the air CO<sub>2</sub> system there is no need for the heat exchanger and cooling tower in the solar grid, solar PV with battery, or wind turbine with battery scenarios, as the 25 °C air flow removes reaction heat.

However, the steam power plant still requires it for the condenser. The process equipment costs are detailed in Tables S13–S16, and Fig. S9 shows capital and operating cost breakdowns for Na<sub>2</sub>CO<sub>3</sub> looping. The major cost contributors for air CO<sub>2</sub> include the air contactor system, vacuum filters, mill, carbonation reactor, and electricity. The air CO<sub>2</sub> Na<sub>2</sub>CO<sub>3</sub> looping process costs between \$175 to \$388 per ton-CO<sub>2</sub> (excluding revenues), aiming towards the Department of Energy's \$100 per ton of air CO<sub>2</sub> goal by 2032.<sup>34</sup> Energy demand is 1646 kWh<sub>e</sub> per ton-CO<sub>2</sub> for Na<sub>2</sub>CO<sub>3</sub> looping and 7412 kWh<sub>e</sub> per ton-CO<sub>2</sub> for the baseline. Including revenue, the breakeven time for air CO<sub>2</sub> Na<sub>2</sub>CO<sub>3</sub> looping is 1.9 years, with a 45Q tax credit providing \$180 per ton-CO<sub>2</sub> for converting CO<sub>2</sub> from air into useful products.<sup>43</sup> The assumed levelized cost of electricity (LCOE) for each scenario is reported in Table S17.

The technoeconomic analysis presented here is informed by gram-scale experiments and is intended to assess the system-level feasibility and relative performance of Na<sub>2</sub>CO<sub>3</sub> looping compared to baseline mineralization pathways. While kilogram-scale or larger systems are ultimately required to fully capture reactor-level heat and mass transfer, solids handling, and feedstock conditioning effects, these considerations do not alter the underlying material and energy balances evaluated here. Rather, they motivate subsequent larger-scale studies focused on energy requirements, slag type variability, and thermal management.

**Implications for scale-up.** Although the looping reactions are exothermic, the overall process requires 211–1646 kWh<sub>e</sub> per ton-CO<sub>2</sub> for secondary unit operations, making electricity a major operating cost driver. To clarify the origin of this demand, the electrical energy contributions from individual unit operations are broken down in Fig. S10. These results show that solid–liquid separation is a dominant contributor to both capital and operating expenses (Fig. S8–S10).

It is important to note that the vacuum filtration costs include both the filtration equipment and the associated



vacuum pumps, and the reported electrical demand reflects the combined power requirements of these components. Similarly, the gas–liquid contactor capital and operating expenses include both fans for gas flow and pumping for solution circulation. In the laboratory-scale experiments, centrifugation was used to minimize material losses; however, the scale-up analysis assumes vacuum filtration rather than centrifuges, reflecting substantially lower capital and operating costs at industrial scale.

At scale, filtration throughput directly determines equipment sizing and power consumption, making it a key engineering design variable. Fouling and filter-cake buildup are anticipated risks and will depend strongly on particle size distribution and slurry viscosity. Effective management of cake formation and fouling will be essential to avoid downtime associated with filter cleaning or replacement.

Because filtration costs scale with solution volume, the water-to-slag ratio is a key variable for cost optimization. The high ratios used in our laboratory experiments (20–100:1) were selected for small-scale validation; future optimization at scale to hopefully reduce liquid volume would directly affect pumping requirements, filtration duty, and equipment sizing. As an alternative, gravity clarification basins could partially or fully replace mechanical filtration, significantly lowering electrical power demand at the expense of a larger plant footprint. These tradeoffs highlight solid–liquid separation as a critical focus area for future process optimization and pilot-scale development.

Even with water recycling, industrial systems must manage hydraulic circulation, evaporation losses, and pumping energy. In the present analysis, water input is considered for the H<sub>2</sub> production step in both the baseline and Na<sub>2</sub>CO<sub>3</sub> looping cases. In the baseline process, additional makeup water is required to account for water retained in hydrated calcium silicate phases. In contrast, the Na<sub>2</sub>CO<sub>3</sub> looping case does not require makeup water for hydration or carbonation; water is fully conserved within the internal looping process, with a separate, steady water throughput associated with the silica washing step. Although water is temporarily consumed during slag carbonation, it is released during subsequent CO<sub>2</sub> capture and silicic acid drying steps, resulting in no net depletion of process water.

Evaporation losses within the process are expected to be modest, and the resulting makeup water requirement contributes negligibly to operating cost, consistent with assumptions made in prior analyses of aqueous CO<sub>2</sub> capture systems.<sup>40</sup> Pumping power and pressure drop are explicitly included in the present analysis across four stages: post-carbonation filtration, gas–liquid contactor circulation, post-contactor filtration, and silica washing and filtration.

Feedstock heterogeneity and process control are also critical considerations for scale-up. BOF slags are inherently heterogeneous, with batch-to-batch variations in free CaO content and calcium silicate phase distributions that can influence CO<sub>2</sub> mineralization capacity. As evaluated in the four-slag comparison presented later in this study (Mechanism study section), these compositional differences result in only minor variations in mineralization performance at the laboratory scale. At the industrial scale, greater feedstock variability is expected; however,

product consistency can be maintained through appropriate process monitoring and control.

Because the Na<sub>2</sub>CO<sub>3</sub> looping process both generates and consumes alkalinity within each cycle, the primary control objective is the consistent return of the solution to the same pH at the end of each CO<sub>2</sub> capture–carbonation sequence. Achieving a consistent cyclic pH confirms that alkalinity generation during carbonation is balanced by alkalinity consumption during CO<sub>2</sub> capture, independent of moderate variations in slag composition. Continuous pH monitoring therefore provides a practical feedback control strategy to accommodate feedstock heterogeneity while maintaining stable looping performance and a reproducible carbonate-rich SCM product.

Flue gas composition variability is another important consideration for industrial deployment. The point-source CO<sub>2</sub> experiments in this study employed a 4% CO<sub>2</sub>/Ar mixture rather than flue gas. In industrial practice, however, flue gas is typically conditioned upstream using established air-pollution control technologies that reduce SO<sub>x</sub> and NO<sub>x</sub> concentrations to the low-ppm range for natural-gas combustion sources.<sup>37</sup> At these levels, SO<sub>x</sub> and NO<sub>x</sub> are more than three orders of magnitude lower than CO<sub>2</sub> concentrations and are therefore not expected to significantly compete with carbonate chemistry in the alkaline Na<sub>2</sub>CO<sub>3</sub>/NaOH system. Additionally, the presence of N<sub>2</sub> and O<sub>2</sub> in the flue gas is not expected to participate in the looping chemistry.

Particulate matter is likewise removed upstream by standard particulate control equipment, resulting in low contamination to downstream capture systems. As a result, implementation of the Na<sub>2</sub>CO<sub>3</sub> looping process downstream of conventional flue gas cleanup is expected to face minimal additional risk from flue gas impurities. Nevertheless, integration with upstream gas conditioning and validation under representative flue gas compositions will be important considerations for future pilot-scale demonstrations.

Sensitivity to the CO<sub>2</sub> capture ratio was also evaluated as part of the scale-up analysis. Process costs were assessed for a ±20% variation around the experimentally observed capture ratios for both the point-source and air cases using a solar-grid electricity scenario (Fig. S11). For the point-source case, varying capture efficiency from 59% to 47% or 71% results in changes in the cost per ton of CO<sub>2</sub> of only approximately ±0.3%. This weak dependence reflects the dominance of solids handling and filtration costs and the relatively small gas-handling requirements at elevated CO<sub>2</sub> concentration.

In contrast, the air case exhibits a stronger dependence on capture ratio due to the much larger gas-handling equipment required at low CO<sub>2</sub> concentration. Varying capture efficiency from 35% to 28% and 42% results in cost changes of +8.6% and –5.8%, respectively. Even in this case, the overall cost variation remains within approximately +9/–6% for a ±20% change in capture ratio, indicating that the technoeconomic conclusions are robust to realistic variations in capture performance.

The deployment scale of the Na<sub>2</sub>CO<sub>3</sub> looping process will be constrained by slag availability and transportation. To minimize handling and transport of intermediates, the looping



system is envisioned to be co-located with steel plants, where fresh BOF slag and CO<sub>2</sub> streams are readily accessible. This configuration eliminates the need to ship raw slag to a separate processing site and enables air or direct point-source capture from steelmaking exhaust. Shipment of the carbonate-rich product and amorphous silica products aligns with existing logistics, as GGBFS is routinely transported from steel mills to cement plants. Because cementitious materials are bulk commodities, their economic transport radius is generally regional, with analyses indicating that most cement is distributed and consumed within ~200 miles of the production facility.<sup>47</sup>

Using slag generation data from a representative U.S. steel mill (Cleveland-Cliffs Burns Harbor; 4–5 million tons-steel per year)<sup>48</sup> and an estimated 126 kg BOF slag per ton of steel,<sup>15</sup> a large BOF plant produces ~2000 tons of slag per day. In the point-source case, a 100 000 ton-CO<sub>2</sub> per year facility requires approximately 2230 tons slag per day, which is within the same order of magnitude as the slag output of a single BOF plant. In practice, looping capacity would be matched to local slag availability rather than fixed at a nominal capture rate; because the slag requirements are comparable, the per-ton CO<sub>2</sub> cost estimates remain valid for point-source deployment.

For the air case, the slag requirement for a 100 000 ton-CO<sub>2</sub> per year facility (~7500 tons slag per day) exceeds the output of a single U.S. steel plant; however, this requirement is comparable to the upper end of slag production from large integrated steel facilities worldwide, which can produce up to ~14 million tons of steel per year, corresponding to ~5000 tons slag per day.<sup>49</sup> Accordingly, the air case is treated as a normalized benchmark scenario. In practice, deployment would likely involve smaller looping units scaled to individual plants, integration of legacy slag and multiple alkaline feedstocks (cement kiln dust, fly ash, mine tailings, *etc.*), or aggregation of slag from multiple steel mills within a region. Re-evaluating the air-case with solar grid at a slag BOF throughput consistent with the point-source case (~30 000 ton-CO<sub>2</sub> per year) yields a cost of \$271 per ton-CO<sub>2</sub>, compared to \$252 per ton-CO<sub>2</sub> for the 100 000 ton-CO<sub>2</sub> per year. This corresponds to an increase of only ~7%, indicating that the economics remain favorable when scaled to realistic slag availability.

In addition to slag throughput, air capture imposes higher gas–liquid contacting requirements than point-source operation due to the dilute CO<sub>2</sub> concentration giving limited mass transport. As a result, achieving cyclic stability under air conditions requires either increased CO<sub>2</sub> supply by supplying more air and/or limiting the extent of slag carbonation per cycle, thereby reducing the amount of NaOH and Na<sub>2</sub>SiO<sub>3</sub> that must be consumed during capture. From an economic perspective, it may be advantageous to accept lower per-cycle slag conversion while maintaining shorter cycle times and lower equipment capital cost, provided that overall throughput and material utilization remain favorable.

Silica precipitation behavior is another important consideration for scale-up and product quality. Under the strongly alkaline conditions maintained in the looping system (pH ≥ 11), silica is observed to remain as a dispersed colloidal

suspension rather than forming a bulk gel. This results in a free-flowing slurry that can be circulated through the gas–liquid contactor and filtered downstream without excessive buildup, consistent with prior reports showing increased silica solubility at high pH.<sup>50</sup> If maximizing silica recovery is desired, pH provides an effective control variable: controlled CO<sub>2</sub> addition can be used to lower pH and induce precipitation to a targeted extent while preserving flowability.

Regarding silica impurities, aluminum released during carbonation is expected to precipitate as amorphous aluminosilicate, which can beneficially participate in calcium aluminosilicate hydrate (C–A–S–H) formation during cement hydration. Iron incorporation is expected to be low and comparable to that reported for commercial silica fume (<1 wt%), where Fe-bearing phases act primarily as benign fillers rather than strength-limiting components.<sup>52</sup> Finally, silica particle size represents a tunable design parameter. Prior studies show that gas–liquid contactor conditions, such as superficial gas velocity, influence silica nucleation and growth, providing a pathway to tailor particle size distribution.<sup>53</sup> Because finer amorphous silica exhibits higher pozzolanic reactivity and greater market value in cementitious applications, particle size control represents an additional opportunity to optimize both performance and revenue at scale.<sup>54</sup>

### Literature benchmarking

To contextualize the performance of the Na<sub>2</sub>CO<sub>3</sub> looping process, a quantitative comparison with mineralization and looping-based systems from the literature is provided in Table 1. Relative to prior alkali-looping mineralization routes, the point-source Na<sub>2</sub>CO<sub>3</sub> looping process demonstrated here achieves CO<sub>2</sub> capacities on steel slag that are comparable to those reported for other alkaline wastes, while operating at substantially shorter cycle times. Notably, the present process operates at the lowest CO<sub>2</sub> concentration (4% and air CO<sub>2</sub>) and among the mildest temperatures reported for looping-based mineralization systems, while also demonstrating stable looping performance under air CO<sub>2</sub> conditions that have not been quantitatively evaluated in previous studies.

Unlike most prior research, which discusses energy requirements qualitatively, this study provides a quantified energy analysis for the complete looping process. While similar looping configurations may ultimately exhibit comparable energy demands, such analyses have not previously been reported. When compared to high-temperature silicate activation routes, which require substantial thermal input for mineral activation, the point-source Na<sub>2</sub>CO<sub>3</sub> looping process operates at lower energy demand under mild conditions. In the air Na<sub>2</sub>CO<sub>3</sub> looping case, operation with atmospheric CO<sub>2</sub> results in reduced CO<sub>2</sub> capacity and higher energy intensity on a per-ton-CO<sub>2</sub> basis; however, this tradeoff enables rapid cycling under ambient conditions and serves as a benchmark for demonstrating the feasibility of closed-loop mineralization directly from air.

Finally, the Na<sub>2</sub>CO<sub>3</sub> looping process uniquely demonstrates closed-loop regeneration of the carbonate carrier without observable loss. This behavior is demonstrated in the Na<sub>2</sub>CO<sub>3</sub> Looping Performance section and is supported by stable cyclic pH



Table 1 Benchmarking of CO<sub>2</sub> mineralization and looping-based systems

Route	Feedstock	CO <sub>2</sub> Capacity (g <sub>CO<sub>2</sub></sub> kg <sub>solid</sub> <sup>-1</sup> )	Kinetics	Operating conditions	Energy demand	Chemical consumption/loss
Monoethanolamine (MEA) (Liu <i>et al.</i> 2021) <sup>25</sup>	Pure CaO, CaSiO <sub>3</sub> , MgO	CaO: 776 CaSiO <sub>3</sub> : 136 MgO: 727	3 h batch carbonation and capture	75 °C; 1 atm CO <sub>2</sub>	Thermal heating with pure CO <sub>2</sub> ; no quantified analysis	Regeneration of MEA demonstrated qualitatively; solvent losses not quantified
MEA looping (Li <i>et al.</i> 2024) <sup>26</sup>	Lime Kiln dust	236	4–7 h carbonation	60 °C; 10% CO <sub>2</sub>	External heat could be supplied from exothermic reactions and hot flue gas; no quantified analysis	CO <sub>2</sub> absorption capacity recovery ~90% after four mineralization cycles; MEA mass recovery not quantified; solid washing required and post-wash MEA concentration remains challenging
KOH looping (Li <i>et al.</i> 2024) <sup>27</sup>	Mortar waste	112	7 h capture and carbonation	Ambient temperature; 10% CO <sub>2</sub>	Ambient conditions; no quantified analysis	KOH loss to solid–liquid separation and dilution; CO <sub>2</sub> absorption capacity decreases ~47% after 10 cycles
NaHCO <sub>3</sub> looping (Wu <i>et al.</i> 2023) <sup>58</sup>	Ladle furnace slag	244	4 h capture and carbonation	25–60 °C; pure CO <sub>2</sub>	Ambient conditions with pure CO <sub>2</sub> ; no quantified analysis	pH recovery shown from CO <sub>2</sub> flow; no mass balance or multi cycle stability
High-temperature silicate activation (Gerdemann <i>et al.</i> 2007) <sup>51</sup>	Serpentine, wollastonite, olivine	Olivine: 450 Wollastonite: 293 Serpentine: 438	≤2 h heat treatment; 1–12 h carbonation	630 °C heat treatment; 40–150 atm CO <sub>2</sub> , 100–185 °C carbonation	429–2431 kWh per ton <sub>CO<sub>2</sub></sub> (thermal and electric)	Buffered NaHCO <sub>3</sub> solution used as CO <sub>2</sub> carrier; no chemical looping or regeneration demonstrated
Thermochemical activation of Mg-rich silicates (Chen and Kanan 2025) <sup>19</sup>	Olivine, serpentine, augite (Mg-rich silicates) + CaCO <sub>3</sub> or CaSO <sub>4</sub> (CaO source)	CaCO <sub>3</sub> + Mg <sub>2</sub> SiO <sub>4</sub> : 519	1–4 h thermochemical activation; 2–7-week carbonation under air or <2 h under 1 atm CO <sub>2</sub>	1100–1200 °C thermochemical activation; ambient temperature carbonation with air or 1 atm CO <sub>2</sub>	510–1300 kWh per ton <sub>CO<sub>2</sub></sub> (thermal and electric)	Consumes CaCO <sub>3</sub> or CaSO <sub>4</sub> as CaO source; requires sequestration of process CO <sub>2</sub> ; no demonstrated Ca looping
Point-source Na <sub>2</sub> CO <sub>3</sub> looping (this study)	BOF steel slag	123	1 h capture and carbonation	45 °C; 4% CO <sub>2</sub>	211 kWh per ton <sub>CO<sub>2</sub></sub> (electric)	Closed-loop Na <sub>2</sub> CO <sub>3</sub> regeneration demonstrated <i>via</i> carbon mass balance and stable cyclic pH
Air Na <sub>2</sub> CO <sub>3</sub> looping (this study)	BOF steel slag	37	1.75 h capture and carbonation	Ambient temperature; air	1646 kWh per ton <sub>CO<sub>2</sub></sub> (electric)	

behavior and a carbon mass balance indicating equivalent CO<sub>2</sub> capture and subsequent carbonation within a single cycle, in contrast to the solvent dilution, degradation, or loss commonly reported for amine- and hydroxide-based systems.

### Mechanism study

The previous Na<sub>2</sub>CO<sub>3</sub> Looping performance section used experimental conditions designed to test more realistic process operation (relatively lower water-to-slag ratio and separation of slag and solution between cycles) and provide input data for the techno-economic analysis. In this section, we adopt an alternative procedure to distinguish the mechanistic differences between Na<sub>2</sub>CO<sub>3</sub> looping and direct aqueous carbonation. This approach decouples the effects of slag and Na<sub>2</sub>CO<sub>3</sub> by physically separating them into two reactors connected in series, enabling isolation of individual reaction pathways and verification of whether a new mineralization mechanism emerges under looping conditions.

The mechanism study included four experimental cases: a Na<sub>2</sub>CO<sub>3</sub> looping case, two control cases, and one blank run (Fig. S4b). In the Na<sub>2</sub>CO<sub>3</sub> looping case, steel slag was first carbonated with a Na<sub>2</sub>CO<sub>3</sub> solution (Step 2), after which CO<sub>2</sub>

at certain concentration was flowed through the reactor (Step 3). The control cases used two separate mixtures: a slag–water mixture and a Na<sub>2</sub>CO<sub>3</sub> solution. In these control cases, Step 2 involved hydration of the steel slag, followed by CO<sub>2</sub> capture in Step 3. In the first control, CO<sub>2</sub> was first exposed to the Na<sub>2</sub>CO<sub>3</sub> solution, then to the slag–water mixture; in the second, this order was reversed. The blank run measures the supplied CO<sub>2</sub> concentration profile.

A major procedural difference from the Na<sub>2</sub>CO<sub>3</sub> looping performance tests is that the slag and solution were not separated after each cycle in the mechanism study cycles.

Each cycle was conducted at 45 °C and lasted 80 minutes: 45 minutes for carbonation or hydration, 15 minutes of 4% or 343 ppm CO<sub>2</sub> flow, and a 20-minute pure Ar flow to flush the remaining CO<sub>2</sub> for gas quantification. The slag samples were first reacted with steam for H<sub>2</sub> production before Step 2 and 3, unless stated otherwise.

**Point-source CO<sub>2</sub>.** For point-source capture, 0.5 g of steel slag was processed each cycle with 90 sccm of 4% CO<sub>2</sub>/Ar. The CO<sub>2</sub> capture performance for quenched slag over 10 Na<sub>2</sub>CO<sub>3</sub> looping cycles is depicted in Fig. 5a, compared to the controls and blank run. The 10 cycles showed stability with an average of





**Fig. 5** (a) Ten  $\text{Na}_2\text{CO}_3$  looping and control cycles of point-source  $\text{CO}_2$  capture with quenched BOF slag. 0.5 g of steel slag per cycle with 90 sccm 4%  $\text{CO}_2/\text{Ar}$ . (b) Thermogravimetric analysis (TGA) and  $\text{CO}_2$  evolution of carbonate-rich product after 10 cycles from a control method (Fig. S4b Case 3) with steel slag and water mixture capturing 4%  $\text{CO}_2$ . (c) TGA and  $\text{CO}_2$  evolution of carbonate-rich product after 10 cycles from  $\text{Na}_2\text{CO}_3$  looping capturing 4%  $\text{CO}_2$ , showing 1.9 times higher  $\text{CO}_2$  mineralization than the control in (b). (d) Ten  $\text{Na}_2\text{CO}_3$  looping and control cycles of air  $\text{CO}_2$  capture with quenched BOF slag. 0.05 g of steel slag per cycle with 90 sccm of 343 ppm  $\text{CO}_2/\text{Air}$ . (e) TGA and  $\text{CO}_2$  evolution of carbonate-rich product after 10 cycles from a control method with steel slag and water mixture capturing 343 ppm  $\text{CO}_2$ . (f) TGA and  $\text{CO}_2$  evolution of carbonate-rich product after 10 cycles from air  $\text{CO}_2$   $\text{Na}_2\text{CO}_3$  looping, showing 4.3 times higher  $\text{CO}_2$  mineralization than the control (e). (g) Comparison of  $\text{CO}_2$  capture capacity and  $\text{CO}_2$  conversion by quenched slag over 5 cycles for 20%  $\text{CO}_2$ , 4%  $\text{CO}_2$ , and 343 ppm  $\text{CO}_2$  (air) at 45 °C and room temperature (24 °C). (h)  $\text{CO}_2$  capture capacity of different BOF slags over 5 cycles for 4%  $\text{CO}_2$ . Quenched – No  $\text{H}_2$  is quenched slag that did not react with steam for  $\text{H}_2$  production prior to  $\text{Na}_2\text{CO}_3$  looping. All cycles were conducted at 45 °C, unless noted otherwise.

79%  $\text{CO}_2$  conversion. Fig. S12 illustrates carbon mass balance and the effect of increasing  $\text{CO}_2$  reaction time, showing how the amount of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  formed during the  $\text{CO}_2$

capture step can be tuned. With 20%  $\text{CO}_2$  concentration and 60-minute reaction time, the capture capacity reaches 14.02 mmol-C  $\text{g}^{-1}$  slag.



Thermogravimetric analysis (TGA) and CO<sub>2</sub> evolution evaluated the amount of CO<sub>2</sub> mineralized in the carbonate-rich product. Fig. 5b shows the TGA and CO<sub>2</sub> evolution from the control (Case 3 in Fig. S4b) experiment. The mass drop and CO<sub>2</sub> evolution around 800 °C are due to the decomposition of CaCO<sub>3</sub> within the carbonate-rich product into CO<sub>2</sub> and CaO. In comparison, Fig. 5c shows the mineralized CO<sub>2</sub> from the Na<sub>2</sub>CO<sub>3</sub> looping cycles. For comparison to both controls as well as pH and temperature data see Fig. S13.

The looping mineralizes 1.9 times more CO<sub>2</sub> than the controls. This difference arises because the looping mineralizes CO<sub>2</sub> *via* the reaction between Na<sub>2</sub>CO<sub>3</sub> and slag, while the control uses CO<sub>2</sub> and slag in water. The 50 times greater solubility of Na<sub>2</sub>CO<sub>3</sub> than CO<sub>2</sub> in water contributes to faster kinetics. Furthermore, in the control case, part of the CO<sub>2</sub> is converted to NaHCO<sub>3</sub> by the Na<sub>2</sub>CO<sub>3</sub> reactor, which does not interact with the slag.

**Air CO<sub>2</sub>.** To capture and mineralize air CO<sub>2</sub>, 0.05 g of steel slag was processed in each cycle with 90 sccm of 343 ppm CO<sub>2</sub> (from a compressed air cylinder). The performance of quenched slag over 10 Na<sub>2</sub>CO<sub>3</sub> looping cycles is depicted in Fig. 5d, compared to the controls and blank run. Over 10 cycles, the CO<sub>2</sub> capture performance increases due to the capture capacity of the slag from previous cycle(s) not being fully utilized, leading to a CO<sub>2</sub> conversion of 90%. TGA and CO<sub>2</sub> evolution results (Fig. 5e and f) show 4.3 times higher CO<sub>2</sub> mineralization by Na<sub>2</sub>CO<sub>3</sub> looping compared to the control (Case 3 in Fig. S4b). For comparison to both controls as well as pH and temperature data see Fig. S14.

**Effects of reaction conditions and slag types.** The CO<sub>2</sub> capture performance for quenched slag was compared over 5 cycles among 20%, 4%, and 343 ppm CO<sub>2</sub> (from compressed air cylinder) at 45 °C and room temperature (24 °C) (Fig. 5g and Fig. S15–S17).

Under the fixed cycle time, slag mass, and reaction conditions used in these experiments, the inverse trends observed between CO<sub>2</sub> capacity and conversion efficiency arise from the transition between CO<sub>2</sub> supply-limited and reaction kinetics limited scenarios. At low inlet CO<sub>2</sub> concentrations, nearly all the supplied CO<sub>2</sub> is consumed within each cycle, resulting in high conversion efficiency but lower absolute CO<sub>2</sub> uptake due to limited CO<sub>2</sub> availability. As the inlet CO<sub>2</sub> concentration increases, the amount of CO<sub>2</sub> delivered exceeds the amount that can be captured within the fixed reaction time, and the system becomes reaction kinetics limited. Consequently, the total CO<sub>2</sub> captured per cycle increases, while the conversion efficiency decreases.

Additionally, the difference in CO<sub>2</sub> capacity between 45 °C and 24 °C is only about 20% for both air and point-source, highlighting the high kinetics even at room temperature.

The CO<sub>2</sub> capture performance of the four BOF slags were then compared for 4% CO<sub>2</sub> at 45 °C over 5 cycles (Fig. 5h and Fig. S18–S21). “Quenched – No H<sub>2</sub>” refers to quenched slag that did not undergo H<sub>2</sub> production before Na<sub>2</sub>CO<sub>3</sub> looping.

Unlike in H<sub>2</sub> production, handling and aging of the slag did not significantly affect CO<sub>2</sub> capture, which primarily depends

on the calcium silicate and CaO components. Quenched slag captured more CO<sub>2</sub> than others because the main form, Ca<sub>3</sub>SiO<sub>5</sub>, is more reactive than Ca<sub>2</sub>SiO<sub>4</sub> and CaSiO<sub>3</sub>.<sup>55</sup> We infer Quenched – No H<sub>2</sub> captured more CO<sub>2</sub> due to two factors: first, CaO reacts with steam at high temperature to form calcium hydroxide, which may capture CO<sub>2</sub> between experiments without being measured. Second, when slag reacts with steam, iron oxide gains oxygen, increasing the total slag mass and reducing relative calcium silicate/CaO content.

**Material characterization for mechanism verification.** XRD was used to compare unreacted quenched slag with slags after 10 control cycles and after 10 Na<sub>2</sub>CO<sub>3</sub> looping cycles capturing 4% CO<sub>2</sub> at 45 °C (Fig. 6a). (Mg<sub>0.8</sub>Fe<sub>0.2</sub>)O was oxidized to Mg<sub>0.64</sub>Fe<sub>2.36</sub>O<sub>4</sub> by reacting with steam, leaving Mg<sub>0.9</sub>Fe<sub>0.1</sub>O. Na<sub>2</sub>CO<sub>3</sub> looping showed higher conversions of Ca<sub>2</sub>SiO<sub>4</sub>, Ca<sub>3</sub>SiO<sub>5</sub>, and CaO to CaCO<sub>3</sub> than the control, qualitatively confirming the mineralization capacity found by TGA and CO<sub>2</sub> evolution. Here, we observe that the Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> phase is largely unreactive. ICP-OES indicates the presence of a small amount of aluminum (Table S1), suggesting that this phase could exist as a calcium aluminoferrite; however, the low aluminum content makes it difficult to distinguish *via* XRD analysis. Fig. S22 shows the results of XRD analysis for the other BOF slags.

Solution-phase Ca and Si concentrations were measured by ICP-OES and UV-vis, respectively (Fig. 6b). Quenched slag was first hydrated in water for 150 min, during which Ca was rapidly released and approached near-saturation within 10 min. This fast initial increase is attributed to the fast reaction of free CaO with water and the formation of Ca(OH)<sub>2</sub>, which is known to dissolve rapidly in aqueous systems. After this initial period, the concentrations of dissolved Ca remained approximately constant, indicating depletion of the readily soluble Ca phases. Meanwhile, the amount of dissolved Si remains minimal, indicating that calcium silicate has very limited dissolution.

Upon the addition of Na<sub>2</sub>CO<sub>3</sub>, the dissolved Ca was immediately removed from the solution *via* CaCO<sub>3</sub> precipitation, leading to a sharp drop in Ca concentration. This rapid Ca removal was followed by a gradual increase in dissolved Si concentration. Because Ca is continuously taken from solution by carbonate precipitation, thermodynamic equilibrium is driving continuous dissolution of Ca from calcium silicate phases, with Si released as the counter-ion. The key observation is that CaCO<sub>3</sub> precipitation occurs almost instantaneously relative to the much slower replenishment of Ca *via* silicate dissolution.

The sharp decay in dissolved Ca combined with the slow rise in Si indicates that carbonate precipitation is not rate limiting under these conditions. Instead, the overall mineralization rate is governed by the kinetics of Ca release from Ca-silicate phases. This interpretation is further supported by the convergence of dissolved Si concentrations toward values analyzed from XRD-refined Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>3</sub>SiO<sub>5</sub> contents (~228 mg L<sup>-1</sup> by XRD analysis *versus* 207–276 mg L<sup>-1</sup> measured), consistent with near-complete conversion of calcium silicates 100 min after Na<sub>2</sub>CO<sub>3</sub> was introduced.





**Fig. 6** (a) X-ray diffraction (XRD) comparing unreacted quenched BOF slag with slags after the control process and after the Na<sub>2</sub>CO<sub>3</sub> looping process, each process including 10 cycles with 4% CO<sub>2</sub> at 45 °C. (b) Calcium (Ca) and silicon (Si) concentration evolution in aqueous solution during hydration of quenched slag in water, followed by the addition of Na<sub>2</sub>CO<sub>3</sub>. (c) Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) maps to compare the distribution of Ca, Si, and carbon (C) in unreacted quenched BOF slag with slags after the control process and after the Na<sub>2</sub>CO<sub>3</sub> looping process, with each process including 10 cycles with 4% CO<sub>2</sub> at 45 °C. XRD and elemental mapping show a higher degree of CO<sub>2</sub> mineralization by Na<sub>2</sub>CO<sub>3</sub> looping than the control process.

Temperature-dependent measurements further support this assignment of the rate-limiting step. Increasing the solution temperature from 25 to 65 °C has only a minor effect on the rapid Ca dissolution and CaCO<sub>3</sub> precipitation steps but significantly accelerates the rate of Si release (Fig. 6b). Because the stirring rate, water-to-slag ratio, and solution chemistry were held constant, this temperature dependence is most consistent

with chemical reaction controlled Ca–silicate dissolution rather than diffusion-limited precipitation processes.<sup>56</sup> Taken together, these results indicate that Na<sub>2</sub>CO<sub>3</sub> looping accelerates mineralization primarily by rapidly removing Ca *via* carbonate precipitation, thereby sustaining a strong thermodynamic driving force for continued Ca–silicate dissolution, which ultimately governs the overall carbonation rate.



SEM and EDS maps were used to show carbonation products from quenched slag (Fig. 6c). Carbon (C) and Si maps reveal greater CO<sub>2</sub> mineralization by Na<sub>2</sub>CO<sub>3</sub> looping than the control. The replacement of Si by C is also apparent in the SEM images where rhombohedral CaCO<sub>3</sub> (calcite) crystals are growing.

## Conclusions

This study introduces a novel Na<sub>2</sub>CO<sub>3</sub> looping process that integrates CO<sub>2</sub> capture and mineralization using steel slags, producing a carbonate-rich product and high-value amorphous silica as supplementary cementitious materials. This process was demonstrated on BOF steel slags and achieved high capture rates of 59% and 35% for 4% and 343 ppm CO<sub>2</sub>, respectively. Compared to a slag and water mixture baseline case, the looping scenarios mineralized 4–9 times more CO<sub>2</sub>. Mechanistic analysis indicates that the enhanced mineralization rates from Na<sub>2</sub>CO<sub>3</sub> arise from rapid Ca removal *via* carbonate precipitation, which maintains a strong thermodynamic driving force for continued Ca–silicate dissolution and ultimately controls the overall carbonation kinetics. Additionally, reacting the slag with steam can produce up to 1.01 mmol-H<sub>2</sub> per g-slag. Overall, the looping process is exothermic, and there is no chemical consumed. Technoeconomic analysis shows Na<sub>2</sub>CO<sub>3</sub> looping costs of \$252 and \$50 per ton-CO<sub>2</sub> (not including revenues) from air and point-source resulting in only 15–30% of the cost of the baseline. If including revenues, the payback periods are only 1.9 and 0.8 years for air and point-source CO<sub>2</sub>.

## Methods

### Steel slag preparation

The BOF steel slag samples were collected from Cleveland-Cliffs – Cleveland Works. Four different types of slag were obtained: quenched, aggregate non-metallic, fines, and aged fines. The quenched slag was scooped directly from the BOF before slagging off. The aggregate non-metallic slag is typically reused in the blast furnace. The slag fines consisted of unrecyclable slag waste generated in the BOF, while the aged fines were similar but had been exposed to outdoor conditions for an unspecified period. The Cleveland-Cliffs – Cleveland Works BOF steel slag processing flow chart, with endpoints for the four types of slag analyzed, is shown in Fig. S1.

To prepare the slag for testing, large chunks were first crushed to approximately 0.5 cm using a sledgehammer. Then, 70 g of slag was loaded into a 75 mL alumina jar with a stainless-steel jacket under an argon atmosphere to prevent unwanted reactions with air during milling. The slag was milled for 30 minutes in an across international desktop high energy vibratory ball mill, rested for 20 minutes, and milled for another 30 minutes. The resulting powder was scraped out using a metal spatula and sifted through a 60-mesh (250-micron) sieve. Material that did not pass through was first processed with a 2 mm sieve, and any remaining oversized particles were reloaded into the alumina jar for additional

milling, with fresh slag supplemented to reach 70 g. The final steel slag powder was stored in a glovebox under argon before experiments.

### Hydrogen production performance testing

Hydrogen (H<sub>2</sub>) production experiments were conducted in a custom quartz tube with an outer diameter of 25 mm, a length of 609.6 mm, and a 3 mm thick G0 (160–250 micron) quartz frit positioned 15 mm off-center. A 6 g sample of steel slag was packed between layers of quartz wool, which rested on the frit at the center of the tube. The tube was then loaded into a vertically oriented 1100 °C split-tube furnace (Thermcraft Protégé XST). A gas mixture of 100 sccm containing 2% water vapor diluted in argon (created by a Cellkraft P-2 Humidifier) flowed through the packed sample bed. The furnace was heated to a certain temperature within 500 to 1000 °C at a ramp rate of 10 °C min<sup>-1</sup> and held at this temperature for 8 hours for the steam to H<sub>2</sub> conversion.

H<sub>2</sub> production was monitored using a gas chromatograph (Inficon Micro GC Fusion), with indicating Drierite used to remove any unreacted water vapor before analysis to protect the GC. To ensure consistent data collection, the gas chromatograph was started when the furnace setpoint reached 100 °C. After the experiment, the processed steel slag was returned to the argon glove box for storage.

### Na<sub>2</sub>CO<sub>3</sub> looping performance testing

**Point-source CO<sub>2</sub>.** In the 4% CO<sub>2</sub> looping case, 1 g of post-hydrogen-production quenched slag was reacted in an aqueous solution containing 2.5 g Na<sub>2</sub>CO<sub>3</sub> (Sigma-Aldrich) and 50 mL deionized (DI) water in a 50 mL centrifuge tube. The reaction was carried out at 45 °C and 400 rpm for 30 min by suspending the centrifuge tube in a 500 mL beaker filled with 450 mL water, maintained on a hotplate set to 108 °C.

After carbonation, the mixture was centrifuged at 1200 rpm for 10 min to separate the carbonate-rich product from the solution. The solution was then divided equally between two 100 mL gas washing bottles to enhance gas–liquid contact time. The bottles were insulated with 0.5-inch ceramic fiber insulation and heated on hotplates to maintain a reaction temperature of 45 °C (corresponding to a hotplate setpoint of 60 °C).

Prior to CO<sub>2</sub> exposure, the bottles were purged with argon (90 sccm) for 5 min. The CO<sub>2</sub> concentration during this flush averaged below 0.01%, and its cumulative amount was negligible compared to the captured CO<sub>2</sub> measured afterward. For the CO<sub>2</sub> capture step, a 4% CO<sub>2</sub>/Ar gas mixture was flowed at 90 sccm for 30 min, followed by a 15 min argon purge. This purge gradually decreased CO<sub>2</sub> concentration due to the empty space in the wash bottles. The outlet gas composition was quantified using the GC equipped with indicating Drierite to remove residual water vapor. The GC was started 1 min before CO<sub>2</sub> introduction to ensure synchronized data collection.

After each capture step, 1 g of post-hydrogen-production quenched slag was added to the regenerated solution, and the cycle was repeated for a total of four times. Additionally, after each carbonation and CO<sub>2</sub> capture step, pH and temperature



were measured using an Ohaus Starter 2200 pH Bench Meter (ST322 electrode) and a K-type thermocouple, respectively.

A corresponding baseline experiment was conducted under identical conditions but without  $\text{Na}_2\text{CO}_3$  addition. Fig. S4a visualizes the looping and baseline cases.

In the 20%  $\text{CO}_2$  looping case, 10 g of aged fines were reacted in an aqueous solution containing 25 g  $\text{Na}_2\text{CO}_3$  and 200 mL DI water in a 250 mL gas washing bottle. The reaction was carried out at 45 °C and 400 rpm for 30 min, maintained on a hotplate set to 74 °C with 0.5-inch ceramic fiber insulation around the bottle.

After carbonation, the mixture was vacuum filtered to separate the carbonate-rich product from the solution. The solution was then divided equally between two 250 mL gas washing bottles to enhance gas-liquid contact time. The bottles were insulated with 0.5-inch ceramic fiber insulation and heated on hotplates to maintain a reaction temperature of 45 °C (corresponding to a hotplate setpoint of 70 °C).

Prior to  $\text{CO}_2$  exposure, the bottles were purged with argon (90 sccm) for 5 min. For the  $\text{CO}_2$  capture step, a 20%  $\text{CO}_2/\text{Ar}$  gas mixture was flowed at 90 sccm for 20 min, followed by a 15 min argon purge. The outlet gas composition was quantified using the GC equipped with indicating Drierite to remove residual water vapor. The GC was started 1 min before  $\text{CO}_2$  introduction to ensure synchronized data collection.

After each capture step, 10 g of aged fines were added to the regenerated solution, and the cycle was repeated for a total of four times. Additionally, after each carbonation and  $\text{CO}_2$  capture step, pH and temperature were measured.

A corresponding baseline experiment was conducted under identical conditions but without  $\text{Na}_2\text{CO}_3$  addition.

**Air  $\text{CO}_2$ .** For air, the same  $\text{Na}_2\text{CO}_3$  looping procedure was applied with modified reaction conditions. In the looping case, 0.05 g of post-hydrogen-production quenched slag was reacted in an aqueous solution containing 0.05 g  $\text{Na}_2\text{CO}_3$  and 5 mL deionized (DI) water in a 50 mL centrifuge tube. The reaction was carried out at room temperature (24 °C) and 400 rpm stirring rate for 15 min.

After carbonation, the mixture was centrifuged at 1200 rpm for 10 min to separate the carbonate-rich product from the solution. Due to the small volume, the solution was then divided equally between two 50 mL centrifuge tubes. Each centrifuge tube was installed into a 100 mL gas washing bottle to get connected with gas delivery and exhaust lines.

Before  $\text{CO}_2$  exposure, the bottles were purged with argon (90 sccm) for 5 min. The  $\text{CO}_2$  concentration during this flush averaged below 0.002%, and its cumulative amount was negligible relative to the captured  $\text{CO}_2$  measured afterward. For the  $\text{CO}_2$  capture step, air containing 343 ppm  $\text{CO}_2$  (from a compressed air cylinder) was flowed at 90 sccm for 1.5 h, followed by a 15 min argon purge to displace the remaining gas for  $\text{CO}_2$  quantification purposes. The outlet gas composition was quantified using the GC equipped with indicating Drierite to remove residual water vapor. The GC was started 1 min before  $\text{CO}_2$  introduction to ensure synchronized data collection.

After each capture step, 0.05 g of post-hydrogen-production quenched slag was added to the regenerated solution, and the

cycle was repeated for a total of four times. To compensate for minor evaporative losses (<0.25 mL), DI water was added as needed to maintain a constant 5 mL solution volume between cycles. After carbonation and  $\text{CO}_2$  capture, pH and temperature were measured using an Ohaus Starter 2200 pH Bench Meter (ST322 electrode) and a K-type thermocouple, respectively.

A corresponding baseline experiment was performed under identical conditions but without  $\text{Na}_2\text{CO}_3$  addition.

### $\text{Na}_2\text{CO}_3$ looping mechanism testing

$\text{CO}_2$  capture and mineralization experiments were conducted using a series of two 250 mL gas washing bottles, each placed on a separate hotplate with a stir bar and wrapped in insulation. Unless otherwise noted, experiments were performed on steam reacted steel slag for both point-source and air.

**Point-source  $\text{CO}_2$ .** Four experimental cases were tested:  $\text{Na}_2\text{CO}_3$  looping, two controls, and a blank run (see Cases 1 through 4 in Fig. S4b). Each gas washing bottle was filled with 60 mL of deionized (DI) water. For  $\text{Na}_2\text{CO}_3$  looping experiments (Case 1 in Fig. S4b), 0.625 g of  $\text{Na}_2\text{CO}_3$  and 0.25 g of steel slag were added to each bottle. The bottle caps were secured, and dip tubes were placed halfway into the solution. Gas lines were connected using a two-way valve at the inlet of the first bottle and the outlet of the second. The system was flushed with argon before sealing. The bottles were insulated with 0.5-inch ceramic fiber insulation and heated on hot plates to the reaction temperature (24 °C or 45 °C) at 80 rpm for 45 minutes – this step is referred to as the carbonation reaction. To reach a mixture temperature of 45 °C measured by a thermocouple, the hotplates needed to be set to 60 °C.

After carbonation, pH and temperature were recorded using an Ohaus Starter 2200 pH Bench Meter (ST322 electrode) and a K-type thermocouple. The bottles were then flushed with 90 sccm argon for 5 minutes before initiating the  $\text{CO}_2$  capture step. The  $\text{CO}_2$  concentration was monitored during the flush to be on average less than 0.01%, whose cumulative amount is negligible compared to the  $\text{CO}_2$  captured afterwards. The  $\text{CO}_2$  capture step is where 90 sccm of either 4% or 20%  $\text{CO}_2/\text{Ar}$  was bubbled through the solution for 15 minutes, followed by 20 minutes of pure argon flow that gradually decreases  $\text{CO}_2$  concentration due to the empty space in the wash bottle.  $\text{CO}_2$  concentration in the outlet gas was quantified using the gas chromatograph, with indicating Drierite used to remove any residual water vapor. To ensure consistent data collection timing, the gas chromatograph was started 1 minute before the  $\text{CO}_2$  flow began.

One cycle consisted of both the carbonation and  $\text{CO}_2$  capture steps. After each cycle, 0.25 g of steel slag was added to each bottle, and the process was repeated for 5 or 10 cycles.

The control experiments followed the same procedure but with different initial reactant distributions so that the slag-water mixture did not interact with  $\text{Na}_2\text{CO}_3$ . Case 2 had 1.25 g of  $\text{Na}_2\text{CO}_3$  in the first bottle and 0.5 g of steel slag in the second. Case 3 had 0.5 g of steel slag in the first bottle and 1.25 g of  $\text{Na}_2\text{CO}_3$  in the second. Each wash bottle in the control cases also included 60 mL DI water.



CO<sub>2</sub> capture efficiency in looping and control experiments was calculated relative to a blank run, where CO<sub>2</sub> was bubbled through only water to characterize the supply gas CO<sub>2</sub> profile (Case 4).

**Air CO<sub>2</sub>.** These experiments followed the same procedure, with each gas washing bottle containing 30 mL of DI water. Case 1 used 0.0625 g of Na<sub>2</sub>CO<sub>3</sub> and 0.025 g of steel slag per bottle, while the control (Case 2 and 3) contained 0.125 g of Na<sub>2</sub>CO<sub>3</sub> in one bottle and 0.05 g of steel slag in the other. The blank run (Case 4) contained only DI water. 90 sccm of air (from a compressed cylinder containing 343 ppm CO<sub>2</sub>) was flowed for 15 minutes, followed by 20 minutes of argon flow. For the 5-minute flush after carbonation, the CO<sub>2</sub> concentration was monitored to be on average less than 0.002%, whose cumulative amount is negligible compared to captured CO<sub>2</sub>.

### Material characterization using XANES

X-ray absorption near edge structure (XANES) was conducted by easyXAFS300+ to measure the oxidation state of iron (Fe) in steel slag before and after the reaction with steam. The X-ray source was set at 36 kV and 20 mA to acquire energy absorption spectra ranging from 7000 eV to 7600 eV for Fe K edge. Steel slag and standard materials (FeO, Fe<sub>3</sub>O<sub>4</sub>, and CoFe<sub>2</sub>O<sub>4</sub>) were protected against air oxidation using Kapton tape. XANES data was analyzed by *Athena* software to give normalized absorption ( $\mu$ ) vs. absorption energy.

### Material characterization using TGA

Experiments were conducted using a Themys thermogravimetric analyzer (TGA). For quantifying the CO<sub>2</sub> release from the carbonate-rich product and from Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solution, 0.1 g of solid or 1 mL of solution was placed in a 1300 mm<sup>3</sup> alumina crucible. Argon (50 sccm) flowed over the sample, and the product gas was analyzed using a gas chromatograph, with indicating Drierite used to remove any residual water vapor. For 4% CO<sub>2</sub> capture slag and solution, the temperature profile consisted of 35 minutes at 20 °C, 120 minutes at 95 °C, and 60 minutes at 800 °C. For air CO<sub>2</sub> slag, the same temperature profile was used, except the dwell time at 95 °C was reduced to 30 minutes. The ramp heating and cooling rates were 5 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup>, respectively.

### Material characterization using XRD

X-ray diffraction (XRD) was performed using a Rigaku SmartLab X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 40 kV and 44 mA under ambient pressure and temperature. The Bragg–Brentano focusing method was used, and a diffracted beam monochromator was employed to reduce iron fluorescence. Steel slag data were collected over a  $2\theta$  range of 20° to 70° with a step size of 0.02° and a scan speed of 2.3° min<sup>-1</sup>. SiO<sub>2</sub> data was collected using the same procedure with a  $2\theta$  range of 10° to 70°. The samples were finely ground in a mortar and pestle and mounted on a glass holder. Phase identification and refinement were performed using *PDFXL* software with the *PDF2 2023* database.

### Material characterization using UV-vis and ICP-OES

Ca and Si concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) and Ultra-violet-visible spectroscopy (UV-vis), respectively. Ca concentrations were determined using a PerkinElmer Optima 3000DV ICP-OES system, while Si concentrations were measured using a SpectraMax Plus 384 spectrophotometer with the silicon-molybdenum yellow spectrophotometric method.

For sample preparation, 120 mL of DI H<sub>2</sub>O was added to a 250 mL gas washing bottle, which was then placed on a hotplate to maintain a constant solution temperature of 25 °C, 45 °C, or 65 °C with stirring at 80 rpm. The hotplate setpoints were 30 °C, 65 °C, and 100 °C, respectively. After reaching the set temperature, 0.5 g of slag was added to the water, and samples were collected at regular time intervals of 1, 2, 5, 10, 20, 40, 60, 100, and 150 minutes. After 150 minutes, 1.25 g of Na<sub>2</sub>CO<sub>3</sub> was introduced, and sampling continued at similar intervals. 100 sccm argon was continuously flown through the gas washing bottle to prevent unwanted reactions with air.

Amorphous SiO<sub>2</sub> purity was assessed using the PerkinElmer Optima 3000DV ICP-OES system. Sample preparation was done with 19 g of quenched BOF slag carbonated in an aqueous solution containing 47 g of Na<sub>2</sub>CO<sub>3</sub> in 900 mL DI H<sub>2</sub>O for 12 hours at 60 °C and 80 rpm. The mixture was then filtered, and the solution was subject to 48 hours of 90 sccm pure CO<sub>2</sub> to precipitate silicic acid which was filtered and dried to produce SiO<sub>2</sub>. To remove impurities, the SiO<sub>2</sub> was washed with DI H<sub>2</sub>O and ultrasonicated for 30 minutes. Finally, the washed SiO<sub>2</sub> was dissolved in 0.1 M NaOH for ICP-OES analysis.

### Material characterization using SEM/EDS

Scanning electron microscopy (SEM) was performed using a thermo Fisher scientific Apreo scanning electron microscope. Imaging was conducted in secondary electron (SE) mode with an Everhart–Thornley detector (ETD) at 5 kV and 0.8 nA. Energy-dispersive X-ray spectroscopy (EDS) was performed using the same microscope at 10 kV and 6.4 nA, equipped with an EDAX Octane Elect 30 mm<sup>2</sup> silicon drift detector (SDD).

The samples were dispersed in DI water and sonicated at 25 °C for 5 minutes. 10  $\mu$ L of the dispersion was pipetted onto an SEM stub and dried on a hotplate at 80 °C for 5 hours. Steel slag samples were directly dropped on aluminum SEM stubs, while a layer of carbon tape was used for precipitated SiO<sub>2</sub> samples.

### Measurement uncertainty

Measurement uncertainties were quantified for pH and temperature monitoring, TGA, GC, ICP-OES, and UV-vis. Instrument specifications give uncertainties of  $\pm 0.01$  pH units and  $\pm 2.2$  °C for solution measurements.

Uncertainty in TGA-based carbon quantification was evaluated using duplicate blank runs with a dwell at 800 °C. Signal noise was determined from the standard deviation over a 10-min dwell period, and long-term drift was obtained from



linear regression of the mass signal over the full dwell. These contributions were propagated through the mass-loss calculation to obtain the uncertainty in mmol-C g<sup>-1</sup> slag, resulting in a relative uncertainty of <0.03%.

GC uncertainties for 4% CO<sub>2</sub>, 20% CO<sub>2</sub>, and H<sub>2</sub> were determined from multi-point calibration curves using the standard error of the linear regression, reported as relative uncertainty. For ppm-level CO<sub>2</sub>, the certified cylinder specification ( $\pm 2\%$  relative) was applied. These uncertainties were propagated through integrated gas volumes to yield representative relative uncertainties in the calculated capacities (mmol-C g<sup>-1</sup> slag) of 3% (4% CO<sub>2</sub>), 1.5% (20% CO<sub>2</sub>), 7% (air CO<sub>2</sub>), and 0.6% (H<sub>2</sub>).

Uncertainties were also estimated for ICP-OES and UV-vis measurements. ICP-OES measurements were performed in quadruplicate. Relative standard deviations were typically 1–2%, corresponding to 95% confidence intervals of approximately  $\pm 1.6$ –3.2% on the reported concentrations. UV-vis calibration uncertainty was estimated from the standard error of regression and converted to concentration, yielding  $\pm 9.6$  mg L<sup>-1</sup>.

## Author contributions

S.Z. and K.S. conceived the project. K.S. conducted experimental work, data analysis, energy and technoeconomic analysis, and manuscript preparation. H.X. and Y.X. contributed to experimental H<sub>2</sub> production and CO<sub>2</sub> capture performance testing. A.K. contributed to XANES experiments and analysis, and energy and technoeconomic analysis. J.Q. contributed to ICP-OES and UV-vis experiments and analysis. S.Z. supervised this study and revised the manuscript.

## Conflicts of interest

The authors declare a non-provisional patent application has been filed by The Ohio State University covering aspects of the technology described in this manuscript.

## Data availability

The datasets used in this work are available from the corresponding author upon reasonable request.

Supplementary figures and tables, hydrogen production results, and details of technoeconomic analysis are included in supplementary information. See DOI: <https://doi.org/10.1039/d5ee07347b>.

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