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**Sustainability Spotlight.** Decarbonizing point-source CO<sub>2</sub> capture demands low-energy routes that avoid amine regeneration and degradation. We demonstrate an ambient-temperature capture-to-conversion scheme in which alkali-activated, H<sub>2</sub>O<sub>2</sub>-derived ROS transiently promote carbonate CO<sub>2</sub> absorption at 30°C and then self-dissipate, yielding bicarbonate liquors free from persistent promoter residues that precipitate phase-pure calcite with CaCl<sub>2</sub>; multi-reactor staging maintains high removal while preserving carbonate utilization. The chemistry uses commodity inputs (Na<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CaCl<sub>2</sub>), eliminates thermal stripping, and yields a utilizable CaCO<sub>3</sub> product and an O<sub>2</sub>-free CO<sub>2</sub> stream, highlighting a simple path to lower thermal energy demand and clearer pathways for future cost reduction through improved utilization, regeneration, and waste-derived reagents. This advance supports SDG 13 (Climate Action), SDG 9 (Industry, Innovation and Infrastructure), and SDG 12 (Responsible Consumption and Production).

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# Ambient, Two-Step CO<sub>2</sub>-to-CaCO<sub>3</sub> Conversion: Alkali-Activated H<sub>2</sub>O<sub>2</sub>-Promoted Carbonate CO<sub>2</sub> Capture and Direct Calcite Mineralization

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## Abstract

We demonstrate an ambient-temperature two-step CO<sub>2</sub>-to-CaCO<sub>3</sub> conversion in which alkali-activated H<sub>2</sub>O<sub>2</sub> accelerates carbonate CO<sub>2</sub> capture, followed by calcite mineralization upon CaCl<sub>2</sub> addition, without thermal stripping of the capture liquor. Alkali activation generates transient reactive oxygen species (ROS) that promote rapid CO<sub>2</sub> absorption at 30°C into aqueous Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> without persistent promoters, yielding bicarbonate-rich liquors that are directly mineralized to phase-pure calcite and release a CO<sub>2</sub> stream free of O<sub>2</sub>. Single-reactor screening identified concentration windows that maximize capacity while maintaining homogeneity, with Na<sub>2</sub>CO<sub>3</sub> optimal near 7-10 wt% and K<sub>2</sub>CO<sub>3</sub> near 20-25 wt%. Multi-reactor staging prolonged cycle duration and moderated the trade-off between outlet CO<sub>2</sub>-removal specification and first-stage carbonate-to-bicarbonate conversion, with K<sub>2</sub>CO<sub>3</sub> formulations showing the smallest penalty at stricter cutoffs. The CaCO<sub>3</sub> products were identified as calcite by XRD and ATR-FTIR, with SEM/EDS results consistent with rhombohedral CaCO<sub>3</sub> and no detectable secondary elements. A consumables-only techno-economic analysis using four geography-specific reagent price decks shows that LCOC is reagent-dominated, with carbonate utilization emerging as the principal cost lever through its effect on stoichiometric make-up demand. Overall, the results establish an ambient-temperature capture-to-mineralization route in which alkali-activated H<sub>2</sub>O<sub>2</sub>-derived ROS accelerate carbonate capture and direct mineralization avoids thermal regeneration.

## 1. Introduction

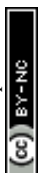
The increasing atmospheric concentration of CO<sub>2</sub> is a major driver of global climate change, requiring action to reduce emissions and achieve net-zero targets by mid-century.<sup>1-3</sup> Carbon capture, utilization, and storage (CCUS) technologies are widely regarded as a central pillar of decarbonization, enabling substantial reductions in emissions from point sources and, potentially, from the atmosphere itself.<sup>4,5</sup> Within the portfolio of existing CO<sub>2</sub> capture methods, amine-based absorption, particularly with monoethanolamine (MEA), is the most mature and

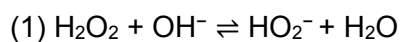


widely applied industrial method.<sup>6-8</sup> However, amine-based absorption systems suffer from well-documented disadvantages, including high energy requirements for thermal regeneration (typically 3.6-4.0 GJ t<sup>-1</sup> CO<sub>2</sub>), as well as thermal and oxidative degradation, corrosivity, volatility, and aerosol emissions.<sup>4,9</sup> These challenges impose both economic and environmental costs, limiting large-scale deployment.<sup>4,10</sup> Consequently, there is considerable interest in developing CO<sub>2</sub> capture strategies that reduce energy penalties, minimize environmental impacts, and enable direct integration with carbon utilization pathways to produce valuable products.<sup>11,12</sup>

Alkaline carbonate solutions, such as potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), are promising alternatives to amines due to their low cost, low volatility, negligible toxicity, and high chemical stability.<sup>13-15</sup> K<sub>2</sub>CO<sub>3</sub>-based processes, such as the Benfield process (also known as the hot potassium carbonate process), have already been implemented for CO<sub>2</sub> and H<sub>2</sub>S removal in more than 600 plants, demonstrating their industrial maturity.<sup>16,17</sup> Furthermore, carbonate-based systems have lower regeneration energy requirements than amines and avoid the degradation products associated with the latter.<sup>14,18</sup> Nevertheless, their main limitation is the relatively slow CO<sub>2</sub> absorption kinetics, particularly under ambient conditions.<sup>14,19</sup> Industrial processes such as the hot potassium carbonate process address this limitation by operating at elevated absorption temperatures (~100–120°C) and employing rate promoters, such as piperazine and amino acids, to accelerate the bicarbonate formation step.<sup>20-22</sup> These promoters are commonly classified into three groups: organic, inorganic, and enzymatic.<sup>14,23</sup> While effective for CCS, the persistence of organic promoters (such as amines or amino acids) leaves chemical residues in the resulting bicarbonate liquor. Integrating these promoted solutions directly into CCU processes can therefore complicate downstream conversion or necessitate additional separation steps to recover the capture agents.<sup>24-26</sup>

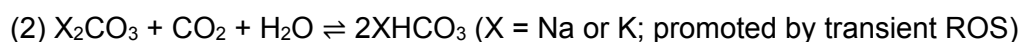
Recently, we presented a novel kinetic promotion method for K<sub>2</sub>CO<sub>3</sub> solutions that utilizes hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)-derived reactive oxygen species (ROS) as promoters for CO<sub>2</sub> absorption by K<sub>2</sub>CO<sub>3</sub>.<sup>26</sup> Mechanistically, we treat ROS as transient, in-situ promoters that accelerate the otherwise slow bicarbonate-forming chemistry in carbonate capture under near-ambient conditions, while decomposing to benign products and therefore not persisting into downstream mineralization. This approach achieved CO<sub>2</sub> uptake rates at room temperature comparable to those of piperazine-promoted systems, while leaving a promoter-free bicarbonate-rich solution after ROS decomposition. In strongly alkaline media, where H<sub>2</sub>O<sub>2</sub> is partially deprotonated as HO<sub>2</sub><sup>-</sup> (pK<sub>a</sub> ≈ 11.6 at 25-30°C), small additions of H<sub>2</sub>O<sub>2</sub> generate transient ROS under ambient conditions, including superoxide (O<sub>2</sub><sup>-</sup>), hydroxyl radicals (•OH), and singlet oxygen (<sup>1</sup>O<sub>2</sub>).<sup>27-30</sup>





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In related systems, oxygen-centered radical species have been reported to react rapidly with  $\text{CO}_2$  to give transient oxygenated intermediates; such chemistry offers a plausible kinetic basis for enhanced bicarbonate formation under strongly basic conditions.



For clarity, eqn (1) and (2) summarize the chemistry at the process level: alkaline peroxide activation generates transient promoter species, and the overall promoted capture step converts carbonate to bicarbonate; however, the present study does not seek to distinguish among the possible underlying elementary ROS-mediated pathways.

Our previous work demonstrated that ROS, including superoxide, can facilitate the carbonate-to-bicarbonate conversion.<sup>26</sup> Earlier work by our group demonstrated in-situ superoxide generation upon introducing  $\text{H}_2\text{O}_2$  to  $\text{NaOH}$  and  $\text{KOH}$  solutions.<sup>31,32</sup> In this study, our approach omits the addition of excess caustic, relying instead on the hydroxide inherently present at the alkaline pH of  $\text{K}_2\text{CO}_3$  (or  $\text{Na}_2\text{CO}_3$ ) solutions to enable peroxide activation. The self-dissipating nature of ROS offers a unique advantage: the resulting bicarbonate-rich liquor can be directly repurposed for downstream utilization without additional purification. Economically, commodity  $\text{H}_2\text{O}_2$  can be competitive with organic promoters and avoids amine-derived degradation products. To circumvent the substantial energy penalty associated with conventional CCUS technologies, carbonate mineralization has been explored as a low-energy chemical conversion route.<sup>33,34</sup> Within the literature, carbonate mineralization approaches are broadly divided into direct gas-solid mineralization at elevated temperatures and pressures, and indirect aqueous mineralization at ambient conditions.<sup>13,34</sup> For positioning the present work within the broader aqueous alkaline  $\text{CO}_2$ -capture literature, two process archetypes are especially relevant: (i) chemical regeneration (looping) approaches, in which the alkaline capture capacity is restored while  $\text{CaCO}_3$  precipitates (e.g., causticization/looping schemes);<sup>35,36</sup> and (ii) single-pass capture-and-conversion routes. In the latter, the bicarbonate liquor is consumed stoichiometrically to form  $\text{CaCO}_3$  (and a corresponding brine), a step that can be coupled with the release of a concentrated  $\text{CO}_2$  stream without thermal stripping.<sup>13</sup>

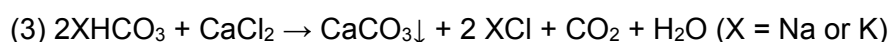
Barzagli et al. reported a similar two-step process in which  $\text{CO}_2$  is first absorbed into an aqueous  $\text{Na}_2\text{CO}_3$  solution, and the resulting bicarbonate-rich liquor is then reacted with  $\text{CaCl}_2$  at room temperature to yield  $\text{CaCO}_3$  and high-purity  $\text{CO}_2$ .<sup>13</sup> This method eliminates the need for thermal stripping by chemically transforming  $\text{NaHCO}_3$  into  $\text{CaCO}_3$ . However, its reliance on dilute  $\text{Na}_2\text{CO}_3$  solutions, limited  $\text{CO}_2$  removal thresholds (~80%), and the intrinsically slow



kinetics of unpromoted carbonate absorption present challenges for scale-up. Improving the kinetics and enabling the use of more concentrated solutions could enhance the practicality of such ambient-temperature capture-conversion schemes.

In this work, we present an improved two-step CO<sub>2</sub> capture and utilization process that combines ROS-promoted carbonate absorption with subsequent CaCO<sub>3</sub> precipitation. In the first step, CO<sub>2</sub> is absorbed into aqueous alkali carbonate solution containing a small concentration of H<sub>2</sub>O<sub>2</sub> (typically one-tenth of the carbonate concentration), enabling rapid CO<sub>2</sub> uptake at 30°C and high bicarbonate conversion while preventing precipitation. A transient O<sub>2</sub> signal occurs only in promoted runs during CO<sub>2</sub> absorption, typically peaking early but not confined to the onset, and is used solely as a diagnostic of promoter activity.

The promotion is self-terminating as CO<sub>2</sub> loading reduces alkalinity toward the HO<sub>2</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> boundary, yielding a bicarbonate-rich liquor without persistent promoter residues. Both K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were investigated to assess how carbonate solubility and cation identity influence ROS-promoted uptake and downstream precipitation, and to quantify the associated cost-performance trade-offs. In the second step, the bicarbonate-rich solution, free from persistent promoters, is treated with CaCl<sub>2</sub> to precipitate pure calcite CaCO<sub>3</sub> and release CO<sub>2</sub>, as summarized in eqn (3).



This single-pass design simplifies operation, avoids thermal regeneration, and yields phase-pure calcite and a CO<sub>2</sub> stream with O<sub>2</sub> below the detection limit. In our bench configuration this gas is N<sub>2</sub>-balanced due to the inert sweep; the headspace composition thus reflects the sweep rather than the chemistry. To sustain CO<sub>2</sub>-removal efficiency setpoints of 80%, 90%, and 100%, cycles were terminated at the corresponding CO<sub>2</sub> outlet threshold. Through single- and multi-reactor configurations, we evaluate the kinetics, bicarbonate conversion, and product quality, demonstrating the potential of this approach as a sustainable, low-energy CCU pathway.

## 2. Experimental

### 2.1 CO<sub>2</sub> absorption and conversion setup

Single-reactor CO<sub>2</sub> absorption experiments were conducted using the system described in our previous work.<sup>27</sup> A stirred reactor containing an aqueous carbonate/H<sub>2</sub>O<sub>2</sub> solution was supplied with a CO<sub>2</sub>/N<sub>2</sub> gas mixture (15 vol% CO<sub>2</sub> in N<sub>2</sub>) at a constant flow rate of 0.2 L/min, controlled by a mass flow controller (Aalborg DPC 17). The gas was introduced through a



sintered glass diffuser to ensure efficient dispersion. The reactor was immersed in a thermostated bath at  $30\pm 1^\circ\text{C}$ .

Outlet  $\text{CO}_2$  and  $\text{O}_2$  concentrations were logged every 20 s using an NDIR  $\text{CO}_2$  sensor (Senseair K33 BLG) and a fluorescence-based  $\text{O}_2$  sensor (LuminOx UV Flux). The first 2 min of recorded data correspond to an effective deadtime arising from gas transport lag in the sampling line. Baseline tests at 15 vol%  $\text{CO}_2/\text{N}_2$  gave standard deviations of  $\pm 0.047$ - $0.158$  vol% after deadtime, well below the manufacturer accuracy ( $\pm 0.5$  vol% + 3% of reading). Instrument specifications are therefore taken as error bounds. The  $\text{CO}_2$  removal efficiency (E) was calculated according to Equation 4:

$$(4) E = \frac{C_i - C_o}{C_i} \cdot 100$$

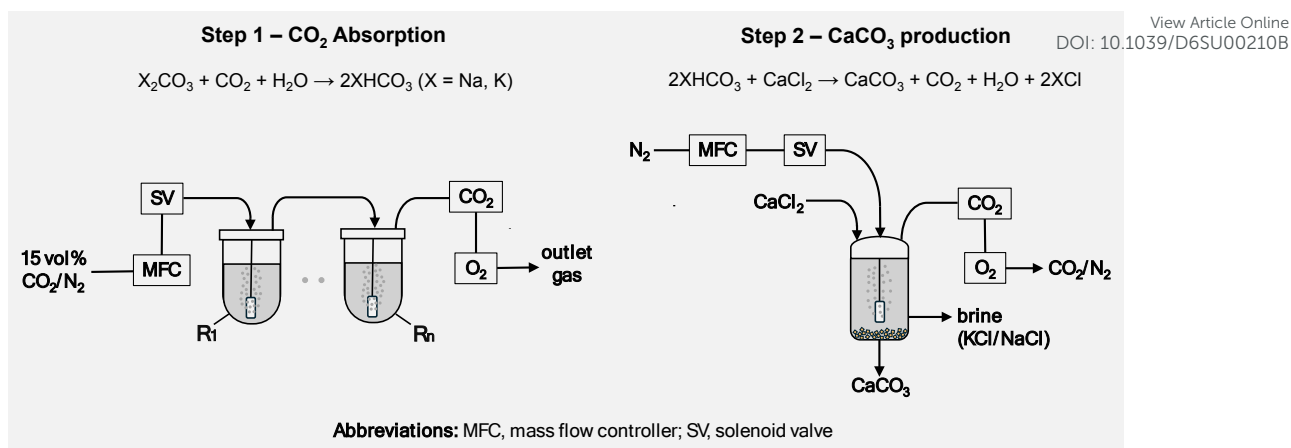
where  $C_i$  and  $C_o$  denote the inlet and outlet  $\text{CO}_2$  concentrations, respectively.

To provide non-ambient controls, we performed a single-reactor temperature series (25, 30, 50, and  $70^\circ\text{C}$ ;  $\pm 1^\circ\text{C}$ ) for 30 wt%  $\text{K}_2\text{CO}_3$  + 3 wt%  $\text{H}_2\text{O}_2$  (15 g) under the same feed conditions as above (15 vol%  $\text{CO}_2/\text{N}_2$ , 0.2 L/min).  $\text{CO}_2$  capacity (mmol  $\text{CO}_2$   $\text{g}^{-1}$  solution) was obtained by integrating the inlet-outlet  $\text{CO}_2$  difference ( $C_i - C_o$ ), over time.

For multi-reactor tests, two or three identical reactors were connected in series. The feed gas flow rate was adjusted to 0.35 L/min (two reactors) or 0.5 L/min (three reactors). The lead reactor was maintained at  $30\pm 1^\circ\text{C}$ , while downstream reactors were operated at room temperature. Runs were continued until the train-averaged  $\text{CO}_2$  removal efficiency fell below predefined thresholds (80%, 90%, or 100%). Each condition was tested over three consecutive cycles. Between cycles, the lead reactor was removed for  $\text{CaCl}_2$  treatment, the train was advanced by one position, and the tail stage was replenished with fresh absorbent.

The  $\text{CO}_2$  absorption-conversion configuration is illustrated in Figure 1, which schematically shows the staged multi-reactor absorption setup (Step 1) and the subsequent  $\text{CaCO}_3$  precipitation stage (Step 2). In Step 2, the bicarbonate-rich solution was reacted with a stoichiometric  $\text{CaCl}_2$  solution at ambient temperature, while  $\text{N}_2$  was supplied at 0.2 L/min. This process yielded solid  $\text{CaCO}_3$ , an  $\text{O}_2$ -free  $\text{CO}_2$  stream carried by the  $\text{N}_2$  sweep, and a brine ( $\text{NaCl}$  or  $\text{KCl}$ , depending on the starting carbonate). The  $\text{CaCO}_3$  precipitate was collected by filtration, washed with deionized water, and dried at  $60^\circ\text{C}$  prior to characterization.





**Figure 1.** Schematic representation of the experimental two-step CO<sub>2</sub> capture-to-CaCO<sub>3</sub> process. In the absorption step, a 15 vol% CO<sub>2</sub>/N<sub>2</sub> stream is delivered via a mass flow controller and solenoid valve to stirred reactors connected in series, generating a bicarbonate-rich solution. R<sub>1</sub> denotes the first reactor in the series, whereas R<sub>n</sub> denotes the final reactor, with n = 2 or 3 depending on the number of reactors employed. In the CaCO<sub>3</sub> production step, the bicarbonate-rich solution is reacted with CaCl<sub>2</sub> under N<sub>2</sub> flow to yield CaCO<sub>3</sub> and the corresponding salt brine.

For representative multi-reactor runs, pH was measured to track alkalinity changes during CO<sub>2</sub> loading and subsequent mineralization. Measurements were performed for 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub> and 25 wt% K<sub>2</sub>CO<sub>3</sub> + 2.5 wt% H<sub>2</sub>O<sub>2</sub> at the 90% train-averaged CO<sub>2</sub>-removal threshold. pH in reactor 1 was monitored at four stages: in the fresh starting solution before cycle 1, in the CO<sub>2</sub>-loaded liquor at the end of cycle 1 immediately before CaCl<sub>2</sub> addition, in the corresponding liquor at the end of cycle 2, and in the recovered brine after CaCO<sub>3</sub> precipitation.

## 2.2 <sup>13</sup>C NMR analysis of carbonate/bicarbonate speciation

Post-absorption solution samples were analyzed by <sup>13</sup>C NMR spectroscopy using a Bruker Avance NEO 500 MHz spectrometer. Bicarbonate conversion was quantified from a linear regression of carbonate/bicarbonate chemical shifts ( $\delta$ , ppm) against their molar fraction ( $\chi$ ), following an established method ( $R^2 = 0.9996$ , RMSE = 0.008).<sup>26,37</sup> The bicarbonate conversion was quantified with reference to the carbonate/bicarbonate equilibrium corresponding to eqn (2).



Analytical uncertainty was taken as the calibration residual ( $\pm 0.8\%$  conversion) since the propagated peak-fit error ( $< 0.1\%$ ) was negligible. Error bars in Figures 4 and 6 reflect this uncertainty.

### 2.3 Characterization of CaCO<sub>3</sub> precipitates

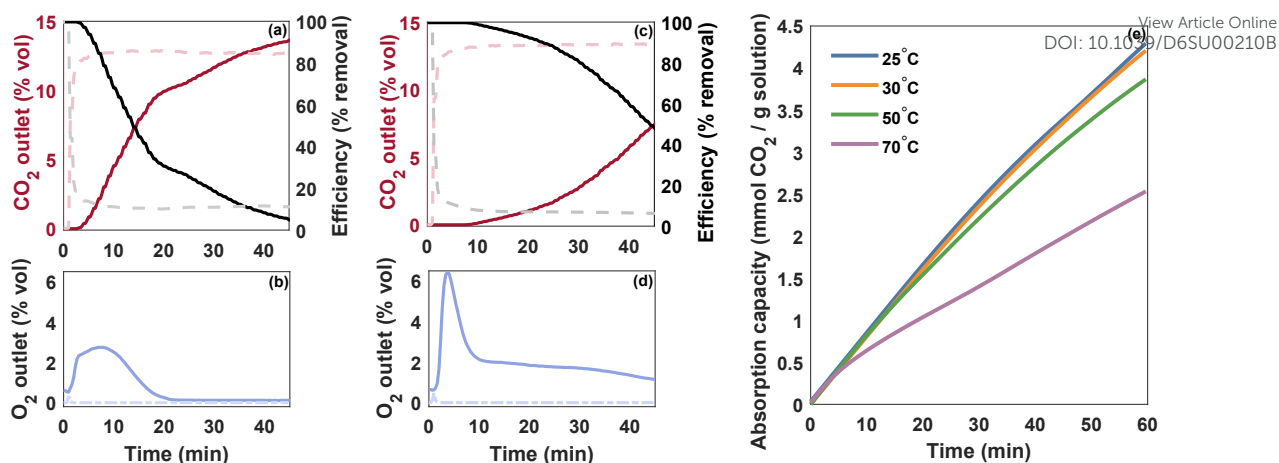
The solid CaCO<sub>3</sub> obtained after absorption-conversion cycles was characterized by X-ray diffraction (XRD, Bruker D8 Advance), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS, Thermo Fisher Scientific Apreo 2), and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Shimadzu IRAffinity-1S).

## 3. Results and Discussion

### 3.1 Single-reactor screening of carbonate/H<sub>2</sub>O<sub>2</sub> systems

Screening experiments were first conducted in a single stirred reactor to obtain CO<sub>2</sub> uptake curves and capacity, track O<sub>2</sub> evolution as a promoter diagnostic, and establish precipitation limits at 30°C. Figure 2 depicts the CO<sub>2</sub> absorption performance of two representative solutions from this single-reactor screening: 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub> and 20 wt% K<sub>2</sub>CO<sub>3</sub> + 2 wt% H<sub>2</sub>O<sub>2</sub>, operated at a flow rate of 0.2 L/min of a 15 vol% CO<sub>2</sub>/N<sub>2</sub> mixture, contacting 15 g of solution. Panels (a,c) show the outlet CO<sub>2</sub> concentration and the corresponding removal efficiency, and panels (b,d) show the simultaneously measured O<sub>2</sub>. Dashed curves in panels (a-d) represent the corresponding unpromoted (neat) Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> solutions of equivalent carbonate concentration, included for comparison. The promoted systems show distinctly higher CO<sub>2</sub> removal efficiency and measurable O<sub>2</sub> evolution, in clear contrast to the unpromoted baselines, which exhibit minimal O<sub>2</sub> and a rapid breakthrough. Both systems begin at ~100% removal (outlet CO<sub>2</sub>  $\approx$  0%). The Na-based liquor shows an early CO<sub>2</sub> breakthrough ( $\approx$  3 min) and a modest, broad O<sub>2</sub> peak ( $\approx$  2.5 vol%) that decays to a zero baseline within the first half of the run. The K-based liquor maintains quantitative removal for  $\sim$  9 min, exhibits a taller and narrower O<sub>2</sub> burst (peak  $\approx$  6.5 vol%) coincident with that period, followed by a slowly decaying non-zero O<sub>2</sub> baseline while CO<sub>2</sub> removal efficiency declines gradually over the remainder of the 45 min run.





**Figure 2.** Single-reactor CO<sub>2</sub> absorption behavior and temperature control experiments. Panels (a,b): 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub>; panels (c,d): 20 wt% K<sub>2</sub>CO<sub>3</sub> + 2 wt% H<sub>2</sub>O<sub>2</sub>, each at 30°C using 15 vol% CO<sub>2</sub>/N<sub>2</sub> (0.2 L/min) and 15 g solution. (a,c) CO<sub>2</sub> outlet concentration (red) and removal efficiency (black); (b,d) O<sub>2</sub> outlet signal. Dashed curves represent the corresponding unpromoted solutions. (e) CO<sub>2</sub> absorption capacity versus time for 30 wt% K<sub>2</sub>CO<sub>3</sub> + 3 wt% H<sub>2</sub>O<sub>2</sub> at 25, 30, 50, and 70°C (same gas feed and solution mass).

For Na<sub>2</sub>CO<sub>3</sub>, the profiles are readily divided into three regions: (i) an initial interval of quantitative capture with a rising O<sub>2</sub> signal, indicating abundant HO<sub>2</sub><sup>-</sup>/ROS at very high alkalinity, (ii) a transition where both the O<sub>2</sub> level and the removal efficiency decline as CO<sub>2</sub> loading lowers alkalinity, and (iii) a bicarbonate-rich interval in which O<sub>2</sub> is at baseline, below the analyzer's detection limit, and the CO<sub>2</sub> removal efficiency declines to low levels. This behavior is consistent with the promoter being effectively "off" as the solution nears the HO<sub>2</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> acid-base boundary (pK<sub>a</sub> ≈ 11.6 at 25–30°C), where the HO<sub>2</sub><sup>-</sup> fraction and the ROS-driven O<sub>2</sub> release become negligible.

For K<sub>2</sub>CO<sub>3</sub>, the mechanism is essentially the same, albeit persisting longer due to higher solubility and higher carbonate/H<sub>2</sub>O<sub>2</sub> loadings, which sustain promoter activity in the homogeneous regime. The O<sub>2</sub> peak falls within the 100%-removal window and is followed by a slowly decaying O<sub>2</sub> baseline starting at ~2 vol%, consistent with the slower decline in CO<sub>2</sub> removal efficiency.

To benchmark the 30°C operating condition against lower and elevated temperatures, an additional single-reactor temperature series (25, 30, 50, and 70°C) was performed for 30 wt% K<sub>2</sub>CO<sub>3</sub> + 3 wt% H<sub>2</sub>O<sub>2</sub>, and the resulting CO<sub>2</sub> absorption capacity profiles (mmol CO<sub>2</sub> g<sup>-1</sup> solution) versus time are shown in Figure 2e. This formulation was selected as a high-loading,



high-signal case to isolate temperature effects under otherwise identical conditions and is used here as a control comparison rather than as a proposed optimum composition. The 25 and 30°C traces are similar, with 25°C showing only a marginally higher capacity, whereas capacity decreases at 50°C and declines further at 70°C. This monotonic reduction with temperature is consistent with faster H<sub>2</sub>O<sub>2</sub> decomposition and increased self-quenching of ROS at elevated temperature, which shortens the effective promotion window for carbonate-to-bicarbonate conversion. Temperatures below 25°C were not pursued further because they increased the tendency toward premature precipitation and would require active cooling, introducing an additional energy penalty.

Table 1 summarizes the single-reactor screening, listing the concentration-time windows tested and the onset of precipitation during operation at 30°C and upon post-run cooling to room temperature. The performance outcomes across the homogeneous window, reported in Table 1, informed the selection of multi-reactor conditions (Section 3.2).

**Table 1.** Screening space and phase behavior at 30°C.

System	Conc. (wt%)	Homogeneous during run at 30°C (max time observed)	Precipitation during operation (first observed)	Cooling-induced precipitation after run
Na <sub>2</sub> CO <sub>3</sub>	5	60 min	none	none
Na <sub>2</sub> CO <sub>3</sub>	7	60 min	none	none
Na <sub>2</sub> CO <sub>3</sub>	10	55 min	None during ≤55 min	appears after ≥35 min runs
Na <sub>2</sub> CO <sub>3</sub>	15	≤30 min	by ~30 min	appears after ≥20 min runs
Na <sub>2</sub> CO <sub>3</sub>	20*	n/a	by ~20 min	n/a
Na <sub>2</sub> CO <sub>3</sub>	30*	n/a	<10 min	n/a
K <sub>2</sub> CO <sub>3</sub>	10	60 min	none	none
K <sub>2</sub> CO <sub>3</sub>	20	60 min	none	none
K <sub>2</sub> CO <sub>3</sub>	25	50 min	by 60 min	appears after ≥50 min runs

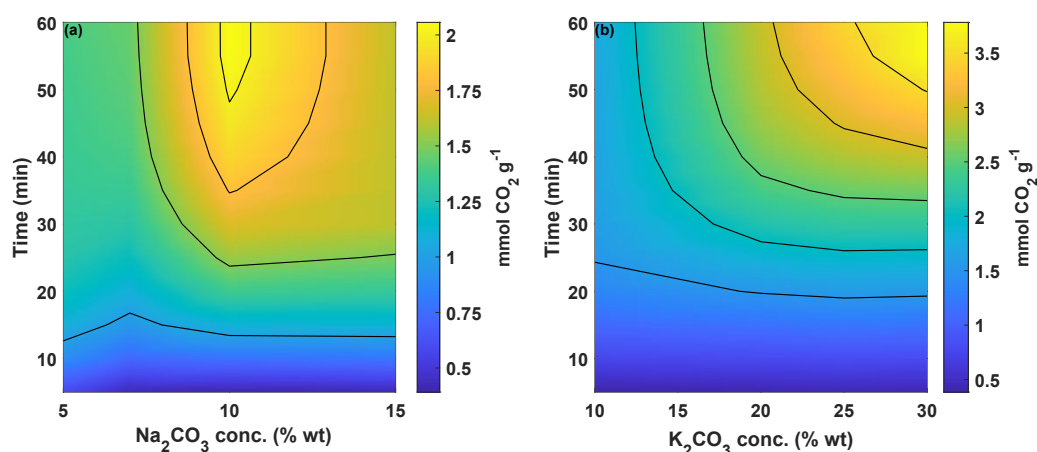


$K_2CO_3$	30	40 min	by ~45 min	appears after $\geq 40$ min runs
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\*Outside Figure 3 but observed in screening; included here for completeness.

Figure 3 maps the specific  $CO_2$  capacity ( $mmol CO_2 g^{-1}$  solution) versus run time (0-60 min) and concentration for (a)  $Na_2CO_3$  (5-15 wt%) and (b)  $K_2CO_3$  (10-30 wt%) at  $30^\circ C$ , across the concentration-time windows summarized in Table 1.  $Na_2CO_3$  loadings above 15 wt% (20-30 wt%) were excluded, as these solutions precipitated prematurely in operation or on cooling, which placed them outside the homogeneous operating window. Surfaces smoothed from discrete runs indicate apparent capacities of  $\sim 0.4$ - $2.1 mmol g^{-1}$  for Na and  $\sim 0.5$ - $3.8 mmol g^{-1}$  for K (from the color scales).



**Figure 3.** Specific  $CO_2$  capacity ( $mmol CO_2 g^{-1}$  solution) as a function of run time and carbonate concentration at  $30^\circ C$  for (a)  $Na_2CO_3$  (5-15 wt%) and (b)  $K_2CO_3$  (10-30 wt%).

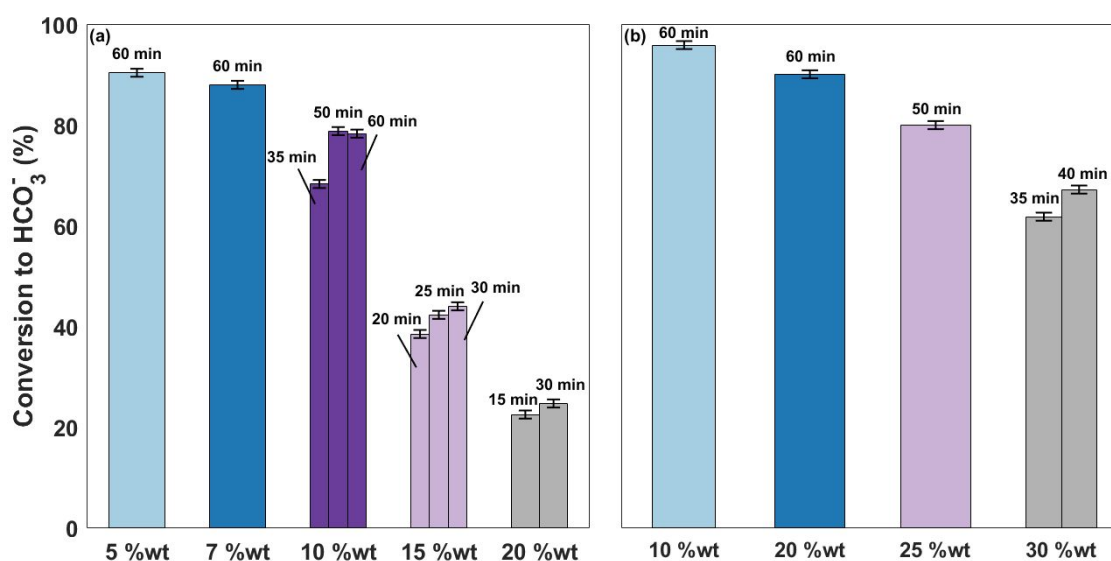
For  $Na_2CO_3$ , capacity rises steeply during the first 15-20 min across all concentrations, reaching  $\sim 1.0 mmol g^{-1}$ . At lower loadings (5-7 wt%), the increase slows thereafter and plateaus near  $\sim 1.4 mmol g^{-1}$  after  $\sim 30$  min, reflecting the intrinsic limit of these dilute solutions. At higher loadings, capacity continues to grow with time, reaching a maximum near 10 wt% where it peaks at  $\sim 2.1 mmol g^{-1}$  at 55-60 min. Beyond this mid-range, more concentrated solutions level off earlier due to precipitation, reinforcing 9-11 wt% as the region of highest attainable capacity. By contrast,  $K_2CO_3$  increases more monotonically with concentration and time; at 30 wt% the run is truncated by in-run precipitation beginning at  $\sim 45$  min, at which point the capacity is  $\sim 3.1$ - $3.3 mmol g^{-1}$ . Thus, the observed ceiling at 30 wt% is set by time-to-solids,



not by an intrinsic capacity limit. Within the homogeneous window, higher  $K_2CO_3$  concentrations and longer times consistently deliver greater capacities.

Several compositions remain homogeneous at 30°C but precipitate on cooling to room temperature ( $Na_2CO_3$ : 10-15 wt%;  $K_2CO_3$ : 25-30 wt%), distinguishing the in-run operating window from the post-run window and informing the process sequence. To avoid unintended solids, the absorber liquors should be kept at 30°C through  $CaCl_2$  addition, especially near the upper concentration/time edges, so that the only intentional precipitation is  $CaCO_3$  during the second step of the 2-step process.

Figure 4 links capacity to base utilization by reporting the extent of carbonate-to-bicarbonate conversion at the end of each single-reactor run at 30°C, determined from  $^{13}C$  NMR speciation of endpoint aliquots. Run times are shown above the bars. Panel (a) covers  $Na_2CO_3$  (5-20 wt%) and panel (b)  $K_2CO_3$  (10-30 wt%). For dilute-to-intermediate compositions, these runs fall within the homogeneous operating window, whereas the highest-loadings illustrate endpoint behavior near or beyond the precipitation boundary identified in Table 1.



**Figure 4.** Extent of carbonate-to-bicarbonate conversion (%) at 30°C, determined by  $^{13}C$  NMR of endpoint aliquots for single-reactor runs. Run times (shown above bars) correspond to the endpoint aliquots used for NMR analysis. At higher carbonate loadings, these runs approach or exceed the precipitation limits summarized in Table 1.

For  $Na_2CO_3$ , the most dilute liquors (5 and 7 wt%) reach ~90%  $HCO_3^-$  after 60 min, indicating that nearly all of the initially charged carbonate is utilized. At 10 wt% the conversion is ~80% after a 50 min run, and it declines at higher loadings: 15 wt% levels off near 45% by 30 min,



whereas 20 wt% reaches only ~25% over the same period. These results, together with the capacity maximum near 9-11 wt% in Figure 3 and the earlier onset of in-run precipitation at higher Na<sub>2</sub>CO<sub>3</sub> loadings, indicate that approximately 10 wt% Na<sub>2</sub>CO<sub>3</sub> offers the best balance between attainable capacity and carbonate utilization.

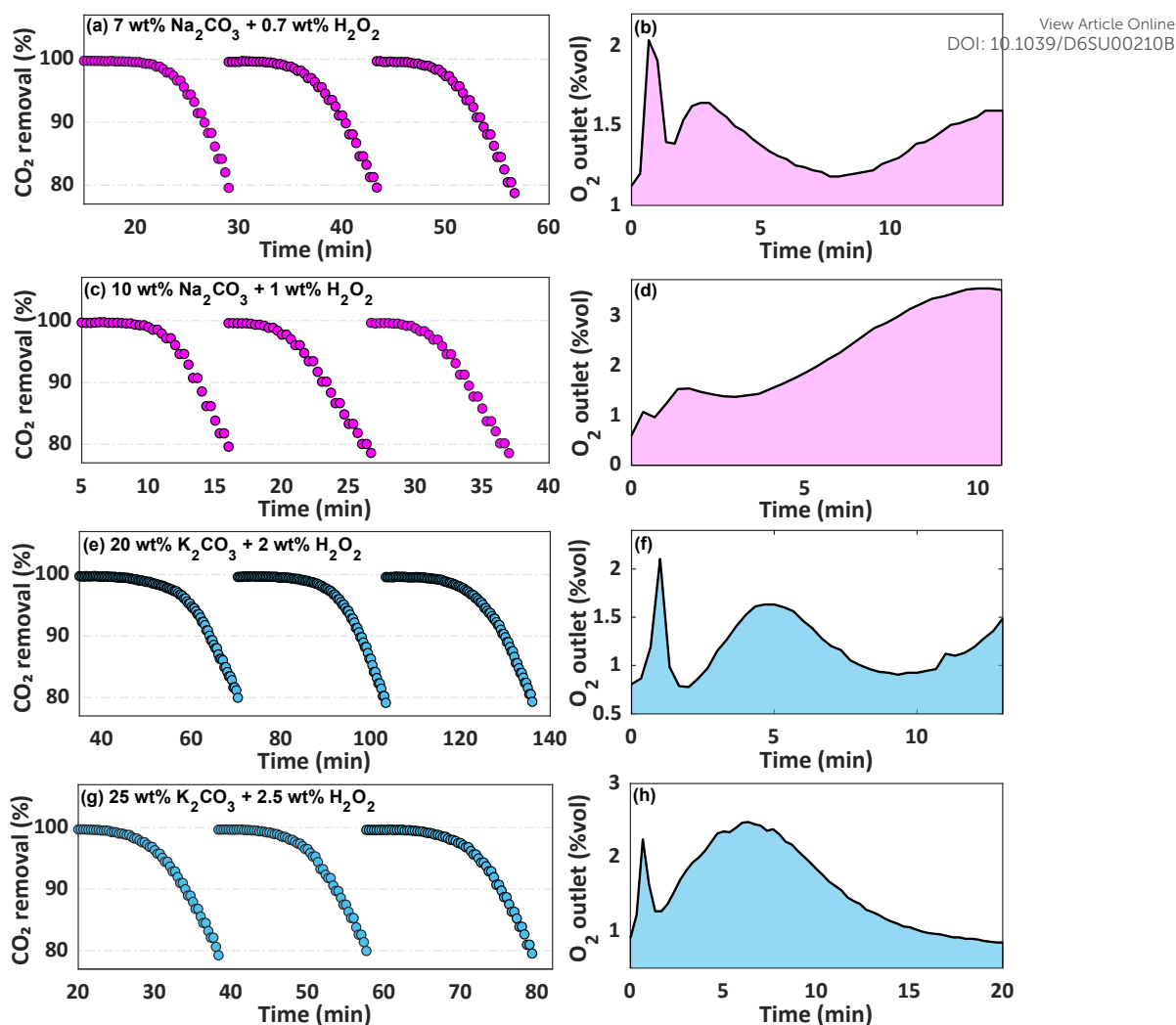
Over comparable run durations, K<sub>2</sub>CO<sub>3</sub> shows a markedly smaller fraction of residual carbonate. At 10 wt% the conversion is ≥95% at 60 min; at 20 wt% it is ~90% at 60 min. Even at 25 wt% conversion is ~80% by 50 min, whereas at 30 wt% it remains ~60–70% by 35-40 min. This pattern echoes the monotonic capacity rise and delayed precipitation mapped in Figure 3 and Table 1.

Overall, the single-reactor screening results (Table 1 and Figures 3-4) define the operating windows used in the multi-reactor experiments discussed next. Na<sub>2</sub>CO<sub>3</sub> should be maintained near 7-10 wt% to ensure both high base utilization and a homogeneous liquor at 30°C, whereas K<sub>2</sub>CO<sub>3</sub> can be increased to 20-25 wt% without significantly reducing conversion and carbonate residuals or triggering premature solids.

### 3.2 Multi-reactor operation of carbonate/H<sub>2</sub>O<sub>2</sub> systems

We implemented cyclic absorption in two- and three-reactor trains to improve CO<sub>2</sub>-removal efficiency while keeping the first reactor under the conditions established in the single-reactor screening. The aim of staging is not to increase total throughput, but to maintain high carbonate-to-bicarbonate conversion in the lead reactor while holding a tight outlet CO<sub>2</sub> specification throughout the run. Figure 5 presents three successive cycles at 30°C for four carbonate/H<sub>2</sub>O<sub>2</sub> formulations: 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub>, 10 wt% Na<sub>2</sub>CO<sub>3</sub> + 1 wt% H<sub>2</sub>O<sub>2</sub>, 20 wt% K<sub>2</sub>CO<sub>3</sub> + 2 wt% H<sub>2</sub>O<sub>2</sub>, and 25 wt% K<sub>2</sub>CO<sub>3</sub> + 2.5 wt% H<sub>2</sub>O<sub>2</sub>. Panels (a, c, e, g) show the train-averaged CO<sub>2</sub> removal efficiency for the three cycles, and panels (b, d, f, h) show the corresponding O<sub>2</sub> outlet traces for cycle 2, time-aligned with the CO<sub>2</sub> data. The 7 wt% Na and 20 wt% K cases ran as three-reactor trains at 0.5 L/min; the 10 wt% Na and 25 wt% K cases ran as two-reactor trains at 0.35 L/min to avoid early precipitation observed when adding a third stage at those concentrations. Each cycle was terminated when the train-averaged CO<sub>2</sub> removal efficiency reached a set threshold of 80%; the panels display these cut-off runs. After each cycle, the lead reactor was removed for CaCl<sub>2</sub> treatment, the train advanced one position, and a fresh solution was loaded at the tail.





**Figure 5.** Cyclic CO<sub>2</sub> absorption in two- and three-reactor trains at 30°C for four carbonate/H<sub>2</sub>O<sub>2</sub> formulations: (a,b) 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub>, (c,d) 10 wt% Na<sub>2</sub>CO<sub>3</sub> + 1 wt% H<sub>2</sub>O<sub>2</sub>, (e,f) 20 wt% K<sub>2</sub>CO<sub>3</sub> + 2 wt% H<sub>2</sub>O<sub>2</sub>, and (g,h) 25 wt% K<sub>2</sub>CO<sub>3</sub> + 2.5 wt% H<sub>2</sub>O<sub>2</sub>. Panels (a,c,e,g) show train-averaged CO<sub>2</sub> removal efficiency over three cycles; panels (b,d,f,h) show corresponding O<sub>2</sub> outlet traces for cycle 2. Each cycle was terminated at 80% CO<sub>2</sub> removal. Three-reactor trains (a,b,e,f) operated at 0.5 L/min; two-reactor trains (c,d,g,h) at 0.35 L/min.

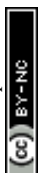
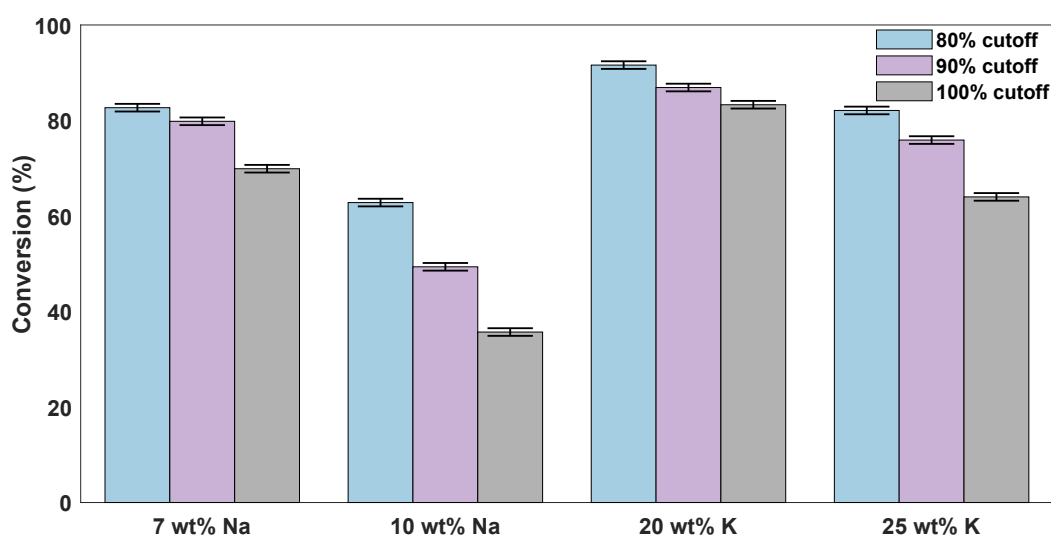
In panels (a, c, e, g), each cycle starts with a plateau at complete CO<sub>2</sub> removal, followed by a decline until the 80% threshold is reached. Cycle 1 is longest, whereas cycles 2 and 3 are shorter and nearly equal in duration, as they start with two partially spent stages and only one fresh stage, demonstrating replicability.

The O<sub>2</sub> outlet profiles (panels b, d, f, h) indicate the sequential operation of stages. Each O<sub>2</sub> peak marks the point at which a downstream stage first receives appreciable CO<sub>2</sub> slip while still at high pH (HO<sub>2</sub><sup>-</sup>-rich). As absorption drives the local pH toward the HO<sub>2</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> boundary,



promoter activity in that stage subsides and its O<sub>2</sub> signal declines until the next stage enters operation. Once the final stage crosses this boundary, residual capacity collapses and the train-averaged removal falls, resulting in the end of the cycle. In (panels b and f), three well-resolved peaks are observed, consistent with three-reactor trains operating at high pH. For two-reactor trains, the 25 wt% K<sub>2</sub>CO<sub>3</sub> + 2.5 wt% H<sub>2</sub>O<sub>2</sub> case (panel h) similarly exhibits two distinct peaks. By contrast, in the 10 wt% Na<sub>2</sub>CO<sub>3</sub> + 1 wt% H<sub>2</sub>O<sub>2</sub> case (panel d), the lower sweep flow (0.35 L/min), together with the greater O<sub>2</sub> peak intensity from Na<sub>2</sub>CO<sub>3</sub>-treated H<sub>2</sub>O<sub>2</sub> (relative to K<sub>2</sub>CO<sub>3</sub> at equal mass), causes the two stage contributions to merge into a broad, slightly delayed hump rather than two distinct peaks.

Figure 6 shows how first-stage conversion in multistage systems changes as a function of efficiency threshold. The bars report the carbonate-to-bicarbonate conversion from <sup>13</sup>C NMR measured at the end of cycle 2 for 7 and 10 wt% Na<sub>2</sub>CO<sub>3</sub> and 20 and 25 wt% K<sub>2</sub>CO<sub>3</sub>, each run at three thresholds: 80% (cyan), 90% (purple), and 100% (grey). Tightening the outlet specification shortens the cycle and therefore reduces conversion, but the magnitude of that penalty depends strongly on formulation. 20 wt% K<sub>2</sub>CO<sub>3</sub> remains highly converted across thresholds (about 95% at 80%, ~90% at 90%, ~85% at 100%). 25 wt% K<sub>2</sub>CO<sub>3</sub> shows a moderate decline (~80%, ~70%, ~60–65%). 7 wt% Na<sub>2</sub>CO<sub>3</sub> stays high at 80 and 90% (about 85–90%) but drops at 100% (~70%). 10 wt% Na<sub>2</sub>CO<sub>3</sub> is the most sensitive, falling from about 75–80% at 80% to ~50–55% at 90% and ~35–40% at 100%. These results show that K-based liquors tolerate stricter outlet specifications because they remain homogeneous and promoter-active at higher concentration, whereas Na-based liquors suffer a larger conversion penalty when the threshold is tightened.



**Figure 6.** First-stage carbonate-to-bicarbonate conversion at the end of cycle 2 for 7 and 10 wt% Na<sub>2</sub>CO<sub>3</sub> solutions and 20 and 25 wt% K<sub>2</sub>CO<sub>3</sub> solutions, each promoted with H<sub>2</sub>O<sub>2</sub>, as a function of efficiency cutoff (80%, 90%, and 100%).

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The pH evolution of representative reactor-1 liquors at the 90% cutoff supports the proposed self-terminating promotion mechanism (Table 2). The fresh 7 wt% Na<sub>2</sub>CO<sub>3</sub> + 0.7 wt% H<sub>2</sub>O<sub>2</sub> and 25 wt% K<sub>2</sub>CO<sub>3</sub> + 2.5 wt% H<sub>2</sub>O<sub>2</sub> liquors start at pH 10.80 and 11.40, respectively, consistent with sufficiently alkaline conditions for peroxide activation. By the cycle-termination point, the pH decreases to 9.00 (cycle 1) and 9.20 (cycle 2) for the Na-based liquor and to 9.47 (cycle 1) and 9.28 (cycle 2) for the K-based liquor. These values are well below the HO<sub>2</sub><sup>-</sup>/H<sub>2</sub>O<sub>2</sub> acid-base boundary discussed above, consistent with attenuation of the O<sub>2</sub> signal and loss of promoter activity as CO<sub>2</sub> loading proceeds. After CaCl<sub>2</sub> addition, the recovered brines show still lower pH values, 8.10 for the Na system and 6.25 for the K system, confirming that mineralization is carried out on CO<sub>2</sub>-loaded liquors that are no longer strongly alkaline. The close agreement between the cycle-1 and cycle-2 cutoff pH values also supports the reproducibility of the stage-swap protocol at the 90% threshold.

**Table 2.** pH at key process stages for reactor 1 in representative multi-reactor runs operated at the 90% CO<sub>2</sub>-removal threshold.

Process stage	7 wt% Na <sub>2</sub> CO <sub>3</sub> + 0.7 wt% H <sub>2</sub> O <sub>2</sub>	25 wt% K <sub>2</sub> CO <sub>3</sub> + 2.5 wt% H <sub>2</sub> O <sub>2</sub>
Fresh starting solution before cycle 1	10.80	11.40
End of cycle 1, before CaCl <sub>2</sub> addition	9.00	9.47
End of cycle 2, before CaCl <sub>2</sub> addition	9.20	9.28
Post-mineralization brine	8.10	6.25

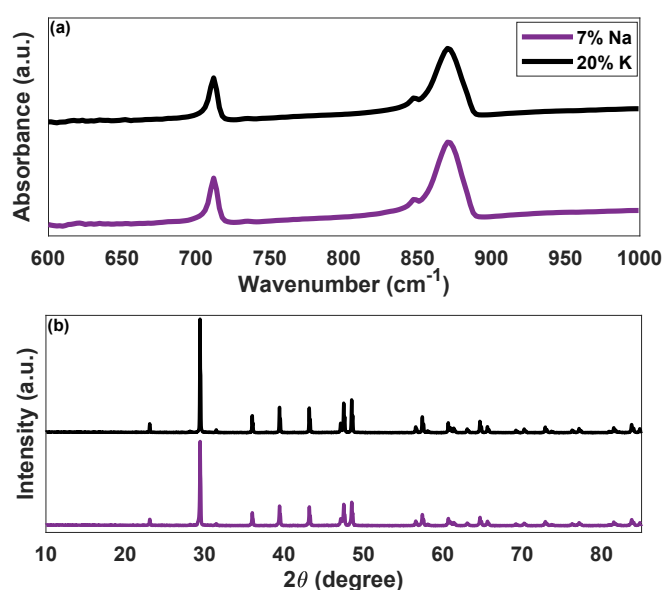
### 3.3 Product characterization: CaCO<sub>3</sub> phase and morphology

Calcium carbonate was precipitated by adding CaCl<sub>2</sub> to the bicarbonate-rich liquors at 30°C; the temperature was maintained during dosing to prevent cooling-induced precipitation of the absorber prior to conversion.



To quantify the efficiency of the  $\text{CaCl}_2$ -induced precipitation, the isolated  $\text{CaCO}_3$  yield was determined gravimetrically. After addition of stoichiometric  $\text{CaCl}_2$  to the post-absorption liquor at  $30^\circ\text{C}$ , the precipitated  $\text{CaCO}_3$  was collected by filtration, washed with deionized water, and dried at  $60^\circ\text{C}$  to constant mass. The isolated yield was calculated as the ratio of recovered dry  $\text{CaCO}_3$  mass to the theoretical  $\text{CaCO}_3$  mass corresponding to the  $\text{CaCl}_2$  charge (1 mol  $\text{Ca}^{2+} \rightarrow$  1 mol  $\text{CaCO}_3$ ). On this basis, the isolated  $\text{CaCO}_3$  yields were 97.9% for the 7 wt%  $\text{Na}_2\text{CO}_3$  + 0.7 wt%  $\text{H}_2\text{O}_2$  case and 98.7% for the 25 wt%  $\text{K}_2\text{CO}_3$  + 2.5 wt%  $\text{H}_2\text{O}_2$  case.

Figure 7 presents ATR-FTIR spectra and XRD patterns of the solids, and Figure 8 presents SEM micrographs, for the two cases carried through the study: 7 wt%  $\text{Na}_2\text{CO}_3$  + 0.7 wt%  $\text{H}_2\text{O}_2$  and 25 wt%  $\text{K}_2\text{CO}_3$  + 2.5 wt%  $\text{H}_2\text{O}_2$ .

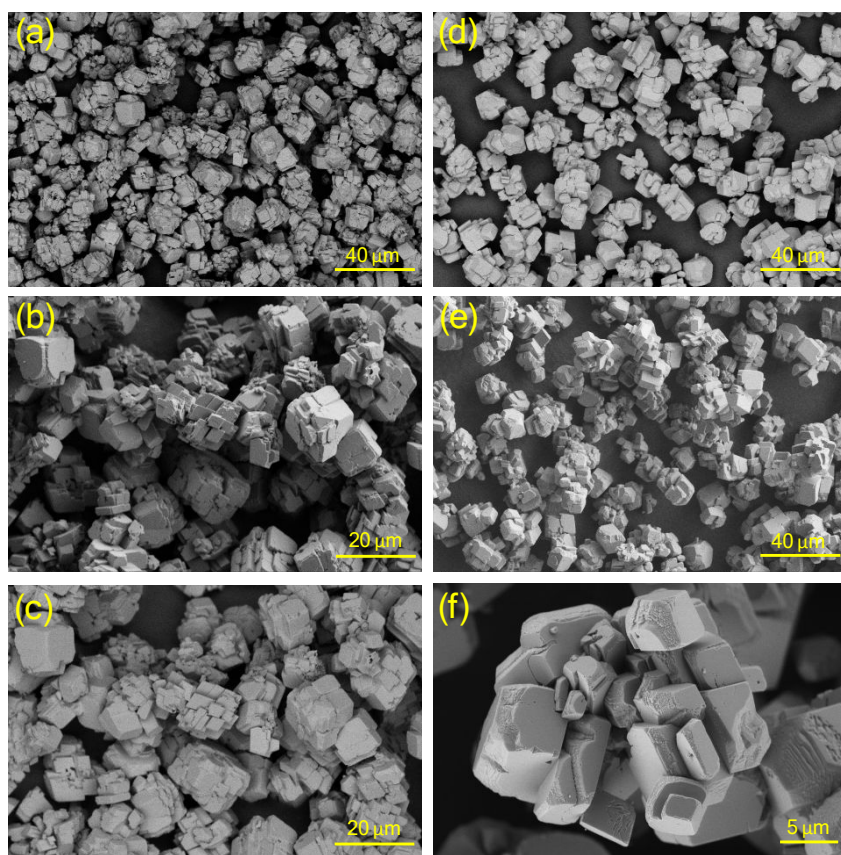


**Figure 7.** (a) ATR-FTIR spectra and (b) XRD patterns of  $\text{CaCO}_3$  precipitates obtained from 7 wt%  $\text{Na}_2\text{CO}_3$  + 0.7 wt%  $\text{H}_2\text{O}_2$  and 25 wt%  $\text{K}_2\text{CO}_3$  + 2.5 wt%  $\text{H}_2\text{O}_2$  solutions at  $30^\circ\text{C}$ .

The ATR-FTIR spectra in Figure 7a are consistent with calcite within the plotted range. Both samples exhibit characteristic bands near  $870\text{--}875\text{ cm}^{-1}$  and  $712\text{--}714\text{ cm}^{-1}$ , assigned to the out-of-plane and in-plane bending modes of carbonate, respectively. Bands characteristic of vaterite or aragonite are not evident within the plotted ranges. The XRD patterns are consistent with rhombohedral calcite, showing the expected diffraction peaks and no additional peaks attributable to other  $\text{CaCO}_3$  polymorphs or crystalline impurities. Within the detection limits of FTIR and XRD, the products from the Na-derived and K-derived liquors are indistinguishable and correspond to phase-pure calcite.



Morphology is consistent with this assignment. The SEM micrographs in Figure 8 show aggregates of well-faceted rhombohedral crystallites for both liquors. At lower magnification the solids appear as dense, grape-like agglomerates. Higher-magnification views reveal individual crystals bounded by flat faces and stepped edges typical of calcite. Needle-like forms associated with aragonite and spherical cauliflower morphologies associated with vaterite are not observed. Qualitatively, both products comprise micron-scale crystallites with moderate polydispersity; the K-derived material tends to show slightly sharper faceting, while the Na-derived sample appears somewhat more aggregated, yet the dominant habit in both cases remains rhombohedral calcite. Elemental compositions determined by EDS (Tables S1-S2) further support this assignment, showing only Ca, O, and C, with no detectable secondary elements, consistent with  $\text{CaCO}_3$ . Additional SEM/EDS outputs supporting Figure 8 and the calcite assignment are provided in the ESI (Figures S1-S6). Representative SEM micrographs for the Na- and K-derived products (Figures S1 and S4) confirm the same rhombohedral calcite habit observed in Figure 8. Corresponding EDS spectra (Figures S2 and S5) show only Ca, C, and O signals, while elemental maps (Figures S3 and S6) confirm spatially uniform Ca/O/C distributions.



**Figure 8.** SEM micrographs of  $\text{CaCO}_3$  precipitates from (a–c) 7 wt%  $\text{Na}_2\text{CO}_3$  + 0.7 wt%  $\text{H}_2\text{O}_2$  and (d–f) 25 wt%  $\text{K}_2\text{CO}_3$  + 2.5 wt%  $\text{H}_2\text{O}_2$  solutions at 30°C.

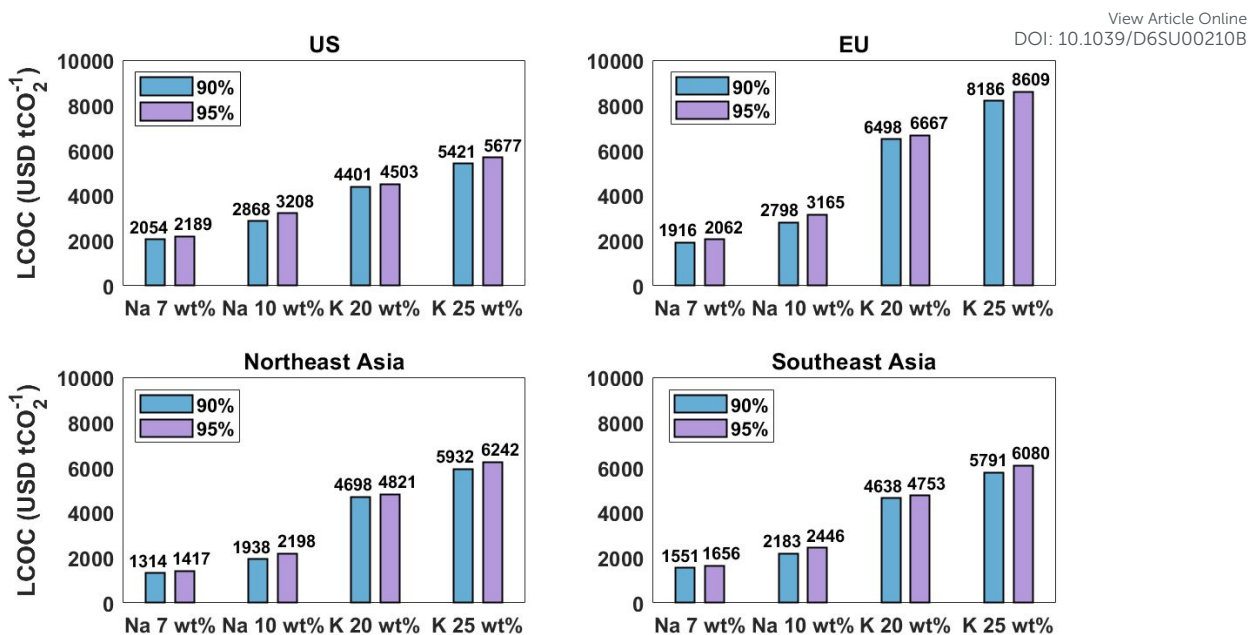
Collectively, ATR-FTIR, XRD, and SEM show that step-2 precipitation at 30°C yields phase-pure calcite, with no detectable metastable polymorphs, for both  $\text{Na}_2\text{CO}_3$ - and  $\text{K}_2\text{CO}_3$ -derived liquors. This consistency shows that differences in alkali, concentration, and reactor staging during the absorption stage do not lead to mixed-phase  $\text{CaCO}_3$  during precipitation at 30°C, simplifying product handling and underscoring the robustness of the capture-to-conversion sequence.

### 3.4 Techno-economic implications of the multireactor operation

#### Scope.

Figure 9 reports the consumables-only levelized cost of capture (LCOC; USD  $\text{tCO}_2^{-1}$ ), excluding capital and energy contributions, for four geography-specific reagent price decks (US, EU, Northeast Asia, and Southeast Asia; all from 2025 Q3). Because the present scheme is a non-regenerative, capture-to-mineral route, this consumables-only LCOC should be interpreted as a conservative upper bound based on stoichiometric reagent purchase. We report this boundary-transparent metric to isolate how measured carbonate utilization and staging translate into reagent consumption, while allowing absolute LCOC to reflect regional reagent-price differences rather than site-specific CAPEX and energy assumptions or uncertain coproduct and policy values. This approach follows TEA best-practice emphasis on explicit system boundaries and intended use for early stage/screening comparisons.<sup>38</sup> Four representative liquors were considered,  $\text{Na}_2\text{CO}_3$  (7 and 10 wt%) and  $\text{K}_2\text{CO}_3$  (20 and 25 wt%), at train-averaged outlet specifications of 90% and 95%  $\text{CO}_2$  removal. The 95% values were obtained by linear interpolation between the measured carbonate utilizations at 90% and 100% removal (see §3.2). Detailed geography-specific price inputs are provided in Table S3, utilization factors in Table S4, and the underlying calculation assumptions are summarized in the ESI.





**Figure 9.** Consumables-only (upper-bound) levelized cost of capture (LCOC, USD tCO<sub>2</sub><sup>-1</sup>) for representative Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> liquors at 90% and 95% CO<sub>2</sub> removal, evaluated using four geography-specific reagent price decks (US, EU, Northeast Asia, and Southeast Asia; 2025 Q3). Values are derived from measured carbonate utilization at 90% and 100% CO<sub>2</sub> removal and linear interpolation to 95% (§3.2); supporting price inputs, utilization factors, and calculation assumptions are provided in the ESI (Tables S3-S4).

### Definition.

The consumables LCOC is defined as:

$$(5) \text{ LCOC} = \underbrace{\text{Price}(\text{CaCl}_2) \cdot 2.522}_{\text{CaCl}_2} + \underbrace{\text{Price}(\text{carbonate}) \cdot \frac{\text{stoich}_{\text{carb}}}{u(\text{spec})}}_{\text{carbonate}} + \underbrace{\text{Price}(\text{H}_2\text{O}_2) \cdot \frac{0.10 \cdot \text{stoich}_{\text{carb}}}{u(\text{spec})}}_{\text{H}_2\text{O}_2},$$

where  $u(\text{spec})$  is the measured carbonate utilization at the selected outlet specification, and the reagent-price terms correspond to the selected geography-specific price deck. The CaCl<sub>2</sub> term is fixed at 2.522 t tCO<sub>2</sub><sup>-1</sup> (1 mol mol<sup>-1</sup> basis). The carbonate requirements are 2.408 t Na<sub>2</sub>CO<sub>3</sub> or 3.140 t K<sub>2</sub>CO<sub>3</sub> per tCO<sub>2</sub>, each scaled by  $1/u$ . The H<sub>2</sub>O<sub>2</sub> term is modelled as 10 wt% of the carbonate dose (normalized to 100% H<sub>2</sub>O<sub>2</sub>), and scaling with  $1/u$ . No coproduct credits are applied for the CO<sub>2</sub> product stream, the CaCO<sub>3</sub> product, or brine handling/avoidance; accordingly, the values in Figure 9 represent a conservative reagent-purchase upper bound rather than a net commercial cost.

### Results.



Across all four geography-specific price decks, tightening the outlet specification from 90% to 95% increases the consumables-only LCOC for every formulation. This increase directly reflects the reduction in first-stage utilization measured in §3.2, whereas the absolute LCOC level varies by geography because the underlying reagent prices differ among the regional decks. Across all four decks, sodium formulations consistently show lower absolute costs owing to their lower stoichiometric mass and lower unit price, whereas potassium formulations are consistently more costly. Notwithstanding this higher absolute cost, the 20 wt%  $K_2CO_3$  case shows a smaller relative penalty upon tightening the outlet specification from 90% to 95%.

Because both the carbonate and promoter terms scale as  $1/u$ , maintaining high first-stage utilization through reactor staging and appropriate stage-swap timing is the primary lever for controlling consumables cost at tighter outlet specifications. Accordingly, despite variation in absolute LCOC across geography-specific reagent price decks, stoichiometric make-up demand emerges as the dominant cost lever within this consumables-only framework. Future TEAs should therefore prioritize strategies that reduce stoichiometric make-up demand, including (i) improving first-stage utilization at tight specifications, (ii) substituting purchased  $CaCl_2$ /alkali with low-cost waste brines or by-product alkalinity,<sup>34</sup> and (iii) evaluating reagent regeneration/looping<sup>35,36</sup> and explicit credit scenarios for  $CaCO_3$  and brine management.<sup>34</sup>

## Conclusions

This work demonstrates an ambient-temperature aqueous  $CO_2$  capture-to-conversion route in which ROS-promoted carbonate absorption is coupled to direct chemical precipitation of  $CaCO_3$ , without heat-driven regeneration. Transient ROS formed in-situ from  $H_2O_2$ -activated alkali carbonates substantially enhance  $CO_2$  uptake at 30°C, enabling rapid conversion of carbonate to bicarbonate without the need for persistent promoters. The promoter activity diminishes as the alkalinity approaches the  $HO_2^-/H_2O_2$  equilibrium boundary, marking a self-terminating mechanism that leaves a clean bicarbonate solution suitable for downstream mineralization.

Single-reactor screening defined the concentration and time windows that maximize capacity while avoiding premature precipitation, identifying optimal conditions near 7-10 wt%  $Na_2CO_3$  and 20-25 wt%  $K_2CO_3$ . Multi-reactor staging was shown to sustain high  $CO_2$ -removal efficiencies while preserving carbonate utilization, thereby reducing the trade-off between outlet specification and conversion.  $K_2CO_3$  systems exhibited greater operational stability and



higher conversion than their Na-based counterparts, consistent with their higher solubility and broader homogeneous operating window.

Reaction of the bicarbonate-rich liquors with  $\text{CaCl}_2$  yielded phase-pure rhombohedral calcite, confirmed by XRD, ATR-FTIR, SEM, and EDS analyses, regardless of alkali type or reactor configuration. The process consistently produced dense, well-faceted crystallites with no detectable vaterite or aragonite, underscoring the robustness of the capture-to-conversion sequence.

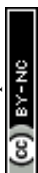
A consumables-only techno-economic analysis across four geography-specific reagent price decks revealed that the levelized cost of capture (LCO<sub>C</sub>) is strongly governed by carbonate utilization, with higher first-stage conversion and optimized staging providing the most effective means to minimize cost penalties at tighter CO<sub>2</sub> specifications. The present economics are therefore reagent-dominated, with the main cost-reduction levers being improved carbonate utilization and access to low-cost calcium/alkalinity sources and/or reagent looping. These constitute clear priorities for future scale-up studies, alongside scenario-based inclusion of coproduct and policy crediting. Overall, this study establishes a simple, ambient-temperature pathway that integrates accelerated CO<sub>2</sub> absorption with mineralization, eliminates the need for thermal regeneration, and yields a pure solid carbonate product suitable for utilization or storage.

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## Data Availability Statement

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All data supporting the findings of this study are available within the article and its Electronic Supplementary Information (ESI). Additional underlying datasets, including raw and processed CO<sub>2</sub>/O<sub>2</sub> outlet time-series for single- and multi-reactor experiments, original <sup>13</sup>C NMR, XRD and ATR-FTIR files, SEM micrographs and EDS outputs, and the consumables-only LCOC calculation workbook, are available from the corresponding author upon reasonable request.

