

Direct Air Capture via Counter-Current NaOH Absorption System: Evolution of pH for Subsequent Plasma-Enhanced CO₂ Utilization

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DOI: 10.1002/cite.202400145

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Direct air capture (DAC) technologies offer a promising approach to mitigate anthropogenic climate change by enabling net negative emissions. CO₂ absorption using NaOH represents an efficient solution within the proposed BlueFire carbon cycle, which integrates DAC with plasma technology for syngas production. Optimizing a DAC plant control relies on understanding the pH profile as a key parameter. A bubble column absorption model with pure CO₂ was experimentally adapted for a counter-current flow setup with ambient air, reproducing a staged pH decrease. An optimal absorption endpoint was determined by identifying the maximum slope of the pH decline, indicating high reaction progress. X-ray diffraction analysis of the absorption products validated the theoretical model of carbonate formation.

Keywords: CCU, Counter-current absorption column, Direct air capture, pH evolution, Plasma technology

Received: November 04, 2024; *revised:* December 20, 2024; *accepted:* January 08, 2025

1 Introduction

“Climate change is not a far-in-the-future scenario,” states the latest 2024 Lancet Countdown on health and climate change by van Daalen et al. [1]. Besides economic risks due to extreme weather events, increasing heat-related deaths in Europe, and a spread of climate-sensitive viruses further north in Europe, greenhouse gas (GHG) emissions continue to rise [1]. The goal of limiting global warming to 1.5 °C is no longer achievable [2]. Therefore, a complex mix of measures is needed, including GHG reductions through efficiency improvements, electrification of processes, and the provision of renewable energies, as well as incorporating the circular economy through carbon capture and storage/utilization (CCS/CCU) as a crucial pillar of countermeasures.

To minimize the human-induced climate impact, we must extract atmospheric CO₂ and reuse carbon in cycles. The BlueFire research project, funded by the Vector Foundation, focuses on a feasibility study for a CO₂ loop based on carbon capture combined with a novel plasma technology for the production of sustainable synthetic fuels or CO₂-neutral cement. A techno-economic assessment by Kaufmann et al. [3] demonstrates the potential of the proposed approach. The presented CO₂ loop consists of direct air capture (DAC) based on alkaline CO₂ absorption, combined with an innovative plasma process to produce synthesis gas (syngas) while burning lime. This approach offers the potential to

facilitate the defossilization of two sectors: firstly, the mobility sector through the production of synthetic fuels, and secondly, the construction sector through the option of emission-free cement synthesis. While these sectors are responsible for about one-third of global CO₂ emissions (25 % transport sector [4] and 8 % concrete production [5]), the impact of GHG savings could be significant.

The present study focuses on the aspect of CO₂ capture from the atmosphere through the application of a DAC process based on sodium hydroxide in a counter-current absorption system. The captured CO₂ serves as a feedstock for subsequent CO₂ splitting in a plasma reactor within the BlueFire project. Due to its potential application in atmospheric CO₂ reduction, DAC technology is currently widely researched [6–8].

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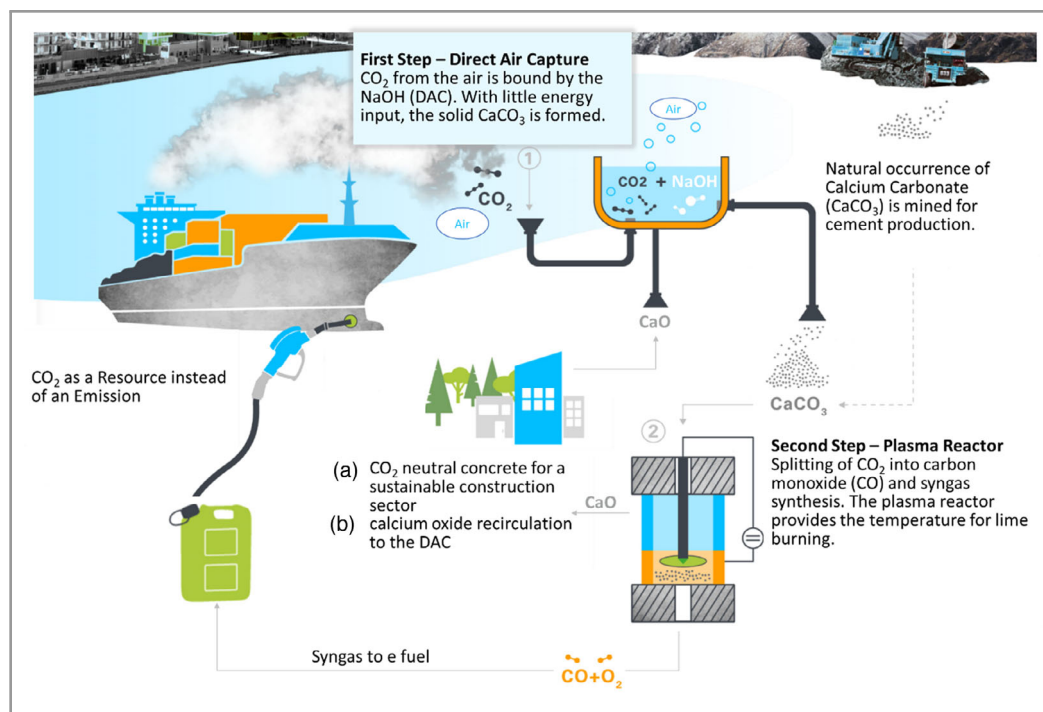


Figure 1. Schematic illustration of the BlueFire CO₂ loop.

For the application of atmospheric CO₂ capture, given its low atmospheric concentration (421 ppm [9]), continuous and semi-continuous absorption systems in counter-current setups with random packing can be considered a viable option, featuring a high specific surface area and low pressure drops.

In 1996 a stage model was presented by Fleischer et al. [10] for CO₂ absorption using NaOH in a bubble column with pure CO₂ and it can serve as a predictor of the absorption performance of the DAC system and has been experimentally validated by Yoo et al. [11]. Understanding the practical attainment of the stage by examining the pH development in the process is significant, as it is directly related to the CO₂ absorption performance of the system. This study experimentally applies the stage model of a bubble column with pure CO₂ to the operation of a counter-current absorption system using air with its atmospheric CO₂, thereby aiming to develop a crucial parameter for a DAC system control.

1.1 Fundamentals

Driven by rising carbon credit prices, various commercial DAC approaches have emerged. Among these, Carbon Engineering employs a liquid absorption system using potassium hydroxide (KOH), a cross-flow pattern in structured packings, followed by calcium carbonate precipitation and regeneration [12]. A critical factor influencing the energy

consumption in such systems is the demand for regeneration of the carbonate, which accounts for over 90 % of the overall energy demand and significantly impacts the efficiency [3, 13]. Additionally, the DAC process notably contributes to the total energy input, particularly due to its dependence on the gas flow rate [13]. Kaufmann et al. [3] estimated a specific energy input of approximately 6 MJ kg⁻¹ of CO₂ for the calcination while the ventilation of the DAC process amount to less than 1 % [3].

The proposed BlueFire approach explores an alternative pathway by replacing thermal regeneration with a gliding arc plasma, transforming the CCS process into a CCU process and utilizing electrical power instead of thermal energy. Additionally, control and integration efforts focus on the absorption with a sodium hydroxide (NaOH) counter-current column filled with a random packing.

1.2 Creating a CO₂ Loop Using DAC and Plasma Technology for e-Fuel Production

The proposed BlueFire CO₂ loop consists of two core steps, with a necessary process coupling in between. The first part involves the capture of atmospheric CO₂ using a DAC process based on the absorption of CO₂ into a sodium hydroxide solution (Fig. 1; first step). In the subsequent coupling step, the absorbed CO₂, in the form of dissolved Na₂CO₃, can be precipitated as CaCO₃ through the addition of CaO (Fig. 1; coupling first and second step). In the second

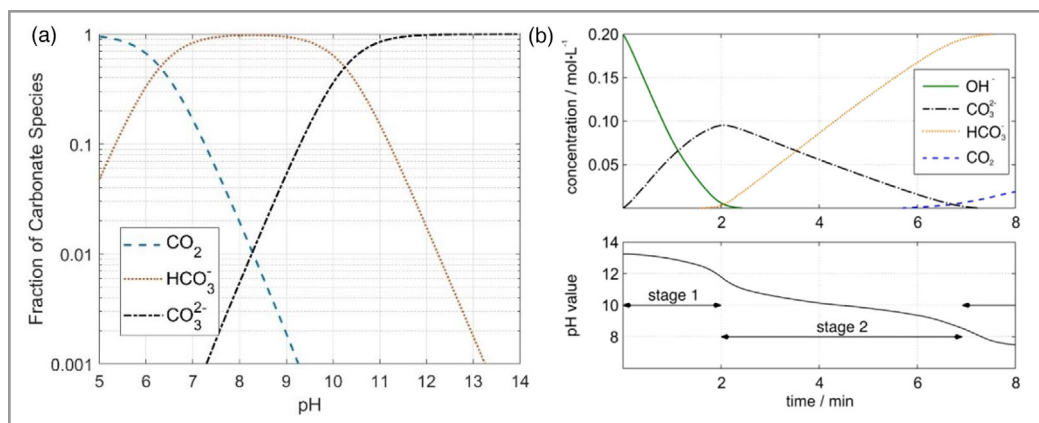


Figure 2. (a) Hägg diagram showing the fraction of the carbonate species as a function of the pH. Figure adapted from [10] with $pK_{s1} = 6.3$, $pK_{s2} = 10.25$, at 298.15 K. (b) Simulation results from [10] with pure CO₂ absorption in NaOH = 0.2 mol L⁻¹, $y_{CO_2} = 1$, $w_G = 2.8 \text{ cm s}^{-1}$ in an ideal mixed liquid phase. (Top) Evolution of species concentration over time, (bottom) pH evolution over time with characteristic stepwise pH decline.

step of the CO₂ loop, the resulting solid can be fed into the plasma reactor (Fig. 1; second step). Here, the regeneration of the absorbent occurs, converting CaCO₃ back into CaO. During this process, the released CO₂ can be split into CO and O₂ in the plasma, producing a precursor for syngas, which can then be used to produce e-fuel, thus closing the CO₂ loop. The techno-economic potential of the proposed loop was investigated by Kaufmann et al. [3]. In the study, the influence on the economic efficiency of plasma-based CO₂ splitting was analyzed in several scenarios. Once the process coupling can be realized in practice, the production costs of synthetic fuels can be reduced by up to 30 % using the BlueFire approach.

1.3 Chemical Fundamentals

The absorption of CO₂ using alkaline solutions has been well investigated (e.g. [10, 11, 14]). Experiments and models with pure CO₂ have identified a characteristic absorption process of CO₂ in bubble columns [10, 11]. The stepwise absorption process is marked by a characteristic decrease in pH, forming two distinct stages dominated by specific chemical reactions. The research shows a direct relationship between the CO₂ absorption capacity and rate, and their corresponding absorption stage. It was also demonstrated that the absorption capacity of stage 1 is nearly equal to that of stage 2, while stage 1 occurs significantly faster [11].

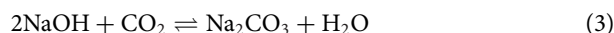
Initially, gaseous CO₂ is physically absorbed in the liquid phase, resulting in the formation of CO₂(aq). In solution, this subsequently reacts in two equilibrium reactions to form the carbonate ion CO₃²⁻ (Eqs. (1) and (2)).



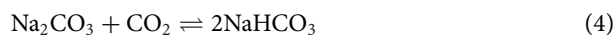
Due to the dependence of the equilibrium of the different species on the pH value (Fig. 2a), there is a preferential fast formation of carbonate, with a high enhancement factor at the onset of absorption at high pH values [10], such as those encountered in DAC applications using NaOH concentrations greater than 1 mol L⁻¹. Due to the rapid formation of carbonate, the physical CO₂ absorption becomes the rate-limiting factor, and the provision of a high specific surface area plays a crucial role.

Starting from a pH value of about 13.5, a characteristic declining pH profile was observed (Fig. 2b). This decline is attributed to the initially rapid decrease in OH⁻ concentration, the subsequent formation of carbonate, and, with further decreasing pH, the increasing proportion of bicarbonate (Fig. 2a). In the range of pK_{s2} , the present system exhibits a pronounced buffer capacity [15] between carbonate and bicarbonate, which slows down the pH decrease at a pH of about 10.25. Consequently, the CO₂ absorption process in the DAC application with NaOH can be considered as a consecutive two-stage process (Fig. 2b) and was shown for bubble columns [10, 11]. In the aspect of chemistry, there is no boundary between the processes of each stage, whereas reactions occur partly in parallel.

The dominant reaction of the first stage can be considered in relation to the utilized DAC system, as described by Eq. (3).



As absorption progresses and, consequently, the OH⁻ concentrations and pH value decrease, the formation shifts towards bicarbonate, resulting in a higher proportion of this species. This step can be regarded as the second stage, in which additional CO₂ can be absorbed according to Eq. (4).



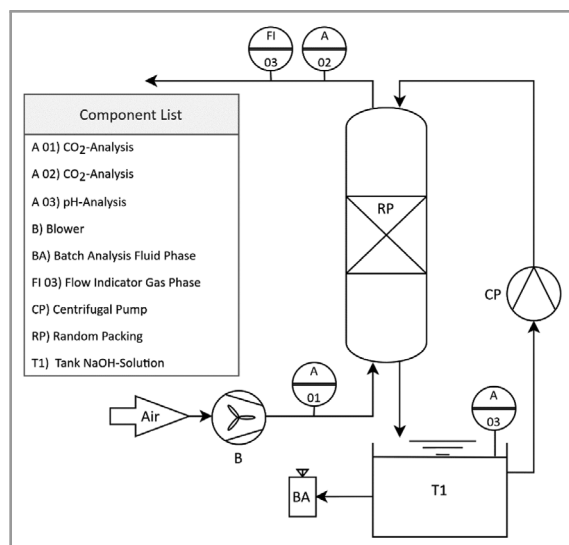


Figure 3. Schematic depiction of the DAC experimental setup, including the associated peripheral components, also listed in the “Component List”.

2 Materials and Methods

2.1 Materials

For the present experiments, commercially available chemicals were used. The sodium hydroxide solution was prepared from NaOH powder of technical grade. Fully deionized water provided by the University of Stuttgart was used as the solvent. Ambient air from the atmosphere was used as the gas phase. To provide and maximize the contact surface between the gas and liquid phases, a random packing of Hiflow®-Rings type 15-7 made of polypropylene (PP) from RVT Process Equipment was used. These used Hiflow®-Rings have a specific surface area of $313 \text{ m}^2 \text{ m}^{-3}$ and a void fraction of 91 % [16].

2.2 Experimental DAC Setup

To investigate the DAC process for the CO_2 absorption from ambient air using a liquid sodium hydroxide solution, a counter-current absorption system was employed (Fig. 3). The column features a transparent polymethyl methacrylate (PMMA) design and has an internal diameter of 144 mm. The gas phase, air, enters at the bottom of the column and flows upward through the system, exiting into the atmosphere at the top of the column after passing through a droplet separator. The airflow is provided by the EM 150 EC 02 blower (Ruck Ventilatoren GmbH) with a nominal volumetric flow rate of $\dot{V} = 415 \text{ m}^3 \text{ h}^{-1}$. The actual volumetric flow rate due to system pressure losses is $105 \text{ m}^3 \text{ h}^{-1}$, with a power input of 44 W. Of NaOH solution with an initial concentration of 1 mol L^{-1} , 6 L was prepared in the tank and applied to the top of the column via a centrifugal

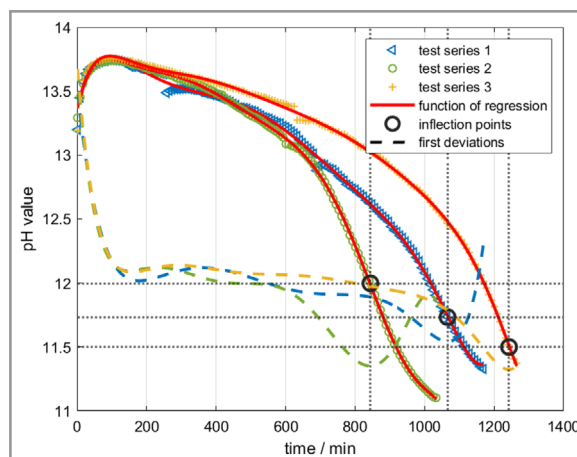


Figure 4. Evolution of the pH value over the time in the counter-current absorption column for three different test series with the same test setup. The first deviation of each regression curve and the inflection point of its mathematical minimum are displayed.

M510 Brushless Micropump from RS-PRO with a flow rate of $\dot{V} = 4.5 \text{ L min}^{-1}$. The liquid is distributed using a 3D-printed liquid distributor with about 3600 droplet points per square meter. The contact area for the phases is provided by a 1-m-high random packing of Hiflow®-Rings. The liquid phase is collected at the column sump and recirculated.

2.3 Methods and Analysis of Intermediates and Products

For reproducibility purposes, the presented experiments were conducted three times. For each experiment, 6 L of NaOH solution was prepared by dissolving NaOH powder in fully deionized water, with the mass of powder measured using a Satorius Extend analytical balance. To ensure optimal wetting of the packing material, the column was pre-wetted at the maximum pump speed before the start of each trial. The pH of the solution was continuously monitored in T1 using the Lab Grade Gen 3 pH sensor from Atlas Scientific (A03). After each experiment, samples were taken from T1 and subsequently dried, ensuring that the drying temperature did not exceed 60°C to analyze the product. The solid formation in the DAC process was analyzed using X-ray diffraction (XRD) measurements (Malvern Panalytical – Empyrean).

3 Results and Discussion

3.1 pH Evolution in a Counter-Current NaOH Absorption Process

The application of NaOH- CO_2 absorption in a counter-current column with ambient air demonstrates a characteristic and reproducible pH reduction pattern (Fig. 4).

Table 1. Times to reach the turning point (tp) and the respective pH value at tp for the three test series.

	Test series 1	Test series 2	Test series 3	Average
pH _{tp}	11.73	12.00	11.50	11.74
t _{tp} [min]	1066	844	1243	1051

An initial rise in the pH value is observed, which can be attributed to the measurement technique and the startup process. This is followed by a gradual pH decrease, which, in the present case, becomes steeper after approximately 600 min. A characteristic feature is the inflection point, mathematically defined by a minimum in the first derivative, where the slope of the derivative equals zero. After reaching the inflection point, a continuous slowing of the pH decline is observed.

The observed inflection points occur within a pH range of 11.5 and 12. It was noted that a higher inflection point correlates with a shorter time to reach that point (Tab. 1). The pH values of the inflection points fall within the expected range above pK_{s2} . The subsequent slowing of the pH decrease can be attributed to the increasing buffer capacity between the forming of the species CO_3^{2-} and HCO_3^- . According to the model by Fleischer et al. [10], the inflection point can be considered as the endpoint of stage 1, where the available NaOH has nearly fully reacted, and CO_3^{2-} formation reaches its peak as described (Eq. (3), Eq. (4), and Fig. 2).

3.2 Species Analysis by XRD Measurement of the DAC Products

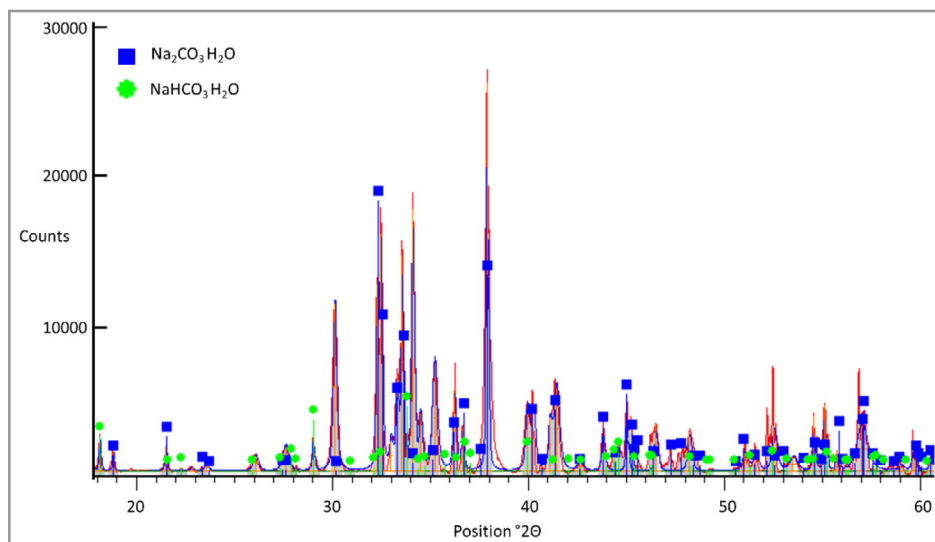
To analyze the species formed after the inflection point, a sample was taken and measured using XRD. The spectrum shows characteristic peaks of the monohydrate $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ as well as NaHCO_3 (Fig. 5). No reformation of NaOH was

observed, indicating that at the time of sampling, the consecutive reaction of Eq. (4) in stage 2 was already occurring, with the reaction of NaOH in stage 1 apparently complete. The XRD measurement results are therefore in good agreement with the predicted model. According to Yoo et al. [11], more than 50 % of the CO_2 capture capacity was reached after stage 1, while the reaction in stage 2 proceeds at a lower rate compared to stage 1.

4 Conclusion

The stepwise model for NaOH- CO_2 absorption processes with pure CO_2 in bubble columns was experimentally adapted and verified for a counter-current absorption system using ambient air. The experimental results exhibit the characteristic pH profile along the absorption process. The pH values at the inflection points ($\text{pH}_{\text{tp,avg}} = 11.51$) show strong agreement with theoretical models and experimental findings of Fleischer et al. [10] and Yoo et al. [11]. Compared to experiments with pure CO_2 , the time required to reach the inflection points was one order of magnitude higher ($t_{\text{tp,avg}} = 1051$ min), due to the lower CO_2 concentration in ambient air compared to typical CO_2 concentrations used in absorption processes. XRD measurements confirmed CO_2 absorption from the atmosphere in a counter-current absorption column, with the detected species aligning with the reaction progress as predicted by the stepwise model.

A highly reproducible and a characteristic pH profile was demonstrated with ambient air with a CO_2 concentration at only 420 ppm. With the capability to determine the pH inflection point reliably in situ through the first and second derivatives, this approach offers the potential to use the pH profile as a control parameter for an optimized DAC process. The end of stage 1 is associated with a beginning decrease of the reaction rate, which, in terms of the energy demand and the efficacy of CO_2 capture, signifies a lower

**Figure 5.** XRD pattern of a dried sample after finishing test series 1, with the expected peaks for $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ and $\text{NaHCO}_3 \cdot \text{H}_2\text{O}$.

efficiency in stage 2. Notably, approximately half of the theoretical and practical CO₂ absorption capacity is reached within stage 1 [11]. Thus, observing the inflection in situ can serve as the transition point for initiating the precipitation step in the BlueFire CCU process and supply the plasma reactor with carbonate.

Acknowledgment

The experimental work was conducted at the Institute for Photovoltaics, within the Electrical Energy Storage research group, at the University of Stuttgart. We would like to thank the start-up Cyclize for their support. The Hiflow®-Rings were provided by RVT Process Equipment. This project was financially funded by the Vector Foundation.

Open access funding enabled and organized by Projekt DEAL.

Abbreviations

avg.	average
DAC	direct air capture
GHG	greenhouse gas
tp	turning point
XRD	X-ray diffraction

Author Contributions – CRediT

Valentin Benedikt Seithümmer Conceptualization and Writing – Original Draft, Data Curation, Supervision, Visualization; **Christoph Dubiel** Data Curation, Validation, Visualization; **Samuel Jaro Kaufmann** Data verification, Writing – Review & Editing; **Haripriya Chinnaraj** Validation, Visualization; **Paul Rößner** Conceptualization, Methodology, Supervision, Writing – Review & Editing; **Kai Peter Birke** Resources, Writing – Review & Editing, Supervision, Funding acquisition. Note: During the preparation of this work, the authors used AI in order to facilitate coding for data visualization and linguistic optimization. After using this tool, the authors reviewed and edited the content as needed and take full responsibility.

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