Direct Air Capture of CO_2 via Reactive Crystallization

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ABSTRACT

Atmospheric CO_2 removal using engineered chemical processes, aka direct air capture (DAC), has become an essential component of our available portfolio for mitigating climate change. Here we describe a promising approach to DAC based on reactive crystallization of atmospheric CO_2 (RC-DAC) with aqueous guanidine and amino acid. Compared to the previously studied phase-changing DAC processes involving initial CO_2 absorption by an aqueous alkaline solvent followed by carbonate crystallization in a second step, RC-DAC combines the CO_2 absorption and carbonate crystallization into a single step. Thus, as the insoluble carbonate salts are removed from solution by crystallization, more CO_2 is pulled from the air into solution, further driving the DAC process. The RC-DAC was performed in a household humidifier as the air-liquid contactor, which can handle solid-liquid slurries effectively. The crystallization was monitored in situ by pH measurements, real-time imaging with a microscope probe, and by Raman spectroscopy, and ex situ by NMR spectroscopy, powder X-ray diffraction, and total inorganic carbonate analysis. The investigation provided a detailed mechanistic picture of the RC-DAC process, involving formation of carbamate and carbonate anions in solution, followed by sequential crystallization of different guanidinium carbonate phases.

INTRODUCTION

Direct air capture (DAC) is a carbon dioxide separation approach based on engineered chemical processes that targets the removal of CO_2 from the atmosphere to mitigate climate change.[1-7] To be economically viable, DAC technologies need to be energy-efficient, cost-effective, and sustainable. A general challenge for all DAC processes is the very low concentration of carbon dioxide in the atmosphere (422 ppm as of February 2024), thereby requiring strong binding of CO_2 to achieve an efficient separation. One way of realizing this is by employing aqueous alkaline solvents (e.g., NaOH, KOH), which absorb atmospheric CO_2 and convert it into bicarbonate/carbonate anions that are subsequently removed from solution by crystallization into insoluble salts (e.g., $MgCO_3$, $CaCO_3$), as demonstrated with the solvent-based DAC technology developed by Carbon Engineering.[8] We have recently demonstrated an analogous organic DAC process based on aqueous guanidine bases, i.e., bis-iminoguanidines,[9] or BIGs, that react with atmospheric CO_2 and convert it into bicarbonate/carbonate anions, which then crystallize as $BIGH_2(CO_3)(H_2O)_n$ salts of extremely low aqueous solubilities (on par with $CaCO_3$).[10, 11] Simple amino acid salts, such as potassium glycinate or sarcosinate, were found to significantly enhance this phase-changing DAC process, when employed in the initial CO_2 absorption step, leading to faster buildup of the bicarbonate/carbonate anions in solution, which can then be effectively crystallized with BIGs in a subsequent step.[12, 13]

The BIG DAC process described above can be considered an example of reactive crystallization of CO_2. Reactive crystallization[14] is defined as a process in which supersaturation is achieved via a chemical reaction producing molecular or ionic species that crystallize out of solution. In the specific case of DAC with aqueous BIGs, atmospheric CO_2 reacts with the alkaline BIG solution (pH 10-11) and generates CO_3^{2-} anions that crystallize with $BIGH_2^{2+}$ cations into

$BIGH_2(CO_3)(H_2O)_n$ salts. As the insoluble BIG carbonate salts are removed from solution by crystallization, more CO_2 from air is pulled into solution, further driving the DAC process. While thermodynamically favorable and driven by the very low aqueous solubility of the BIG carbonate salt, the overall DAC process is very slow, restricted by the diffusion of the CO_2 from air into the solution, and the limited alkalinity of the BIG solution.

Preliminary studies led us to identify a promising reactive crystallization DAC system (RC-DAC) based on aqueous methylglyoxal-bis(iminoguanidine) (MGBIG) and sarcosine (SAR) (Figure 1).[15] When left open to air for two weeks, an aqueous solution (10 mL) of MGBIG crystallizes into one of two crystalline carbonate phases, depending primarily on the initial MGBIG concentration. Phase 1 (P1), with the molecular formula $(MGBIGH^+)_2(CO_3^{2-})(H_2O)_2$, typically forms from more concentrated solutions (>0.75 M), while phase 3 (P3), with the molecular formula $(MGBIGH_2^{2+})(CO_3^{2-})(H_2O)_2$, tends to crystallize from more dilute solutions (<0.3 M).[16] Variable mixtures of the two phases are usually formed from solutions of intermediate concentrations. The main difference between the two phases is the degree of MGBIG protonation – mono-protonated in P1 and di-protonated in P3, as determined by single-crystal neutron diffraction.[16] From an atom economy perspective, P3 is preferred over P1, as only one equivalent of MGBIG is needed for the former, compared to two equivalents of MGBIG for the latter, for each equivalent of CO_2 captured. In both phases, the carbonate anions are stabilized by bidentate guanidinium hydrogen bonds, while in P3 the carbonate is also hydrogen-bonded by the water molecules included in the crystal. At a constant initial concentration of MGBIG (0.5 M), addition of a small amount of SAR – as little as 0.05 M – led to a 3-fold increase in the crystallization yield and preferential formation of P3.

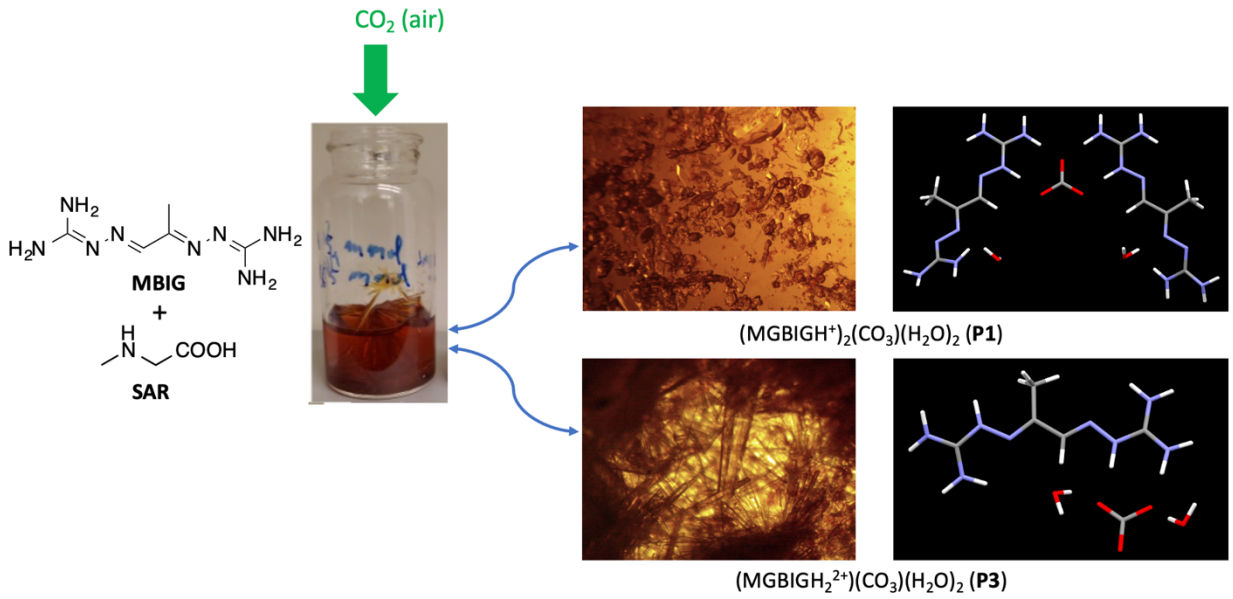


Figure 1. RC-DAC based on aqueous MGBIG (0.5 M) and SAR (0-0.5 M). As CO_2 is absorbed from air over the course of 2 weeks, carbonate phases P1 or P3 crystallize from solution depending on the solution composition. The crystal structures of P1 and P3, determined by single-crystal neutron diffraction, are shown on the right.

Building on these preliminary results, the primary goal of this study is to better understand the RC-DAC system based on MGBIG/SAR toward developing a predictable, larger scale, intensified DAC process. Outstanding questions addressed in this study are: 1) What is the reaction path from atmospheric CO_2 to the final MGBIG-CO_3 crystallized from solution and to what extent it determines the efficacy of the RC-DAC process? 2) What factors and reaction conditions favor the crystallization of P3 vs P1 and maximize the amount of CO_2 removed from the air? 3) What role does the sarcosine amino acid play in the RC-DAC process?

EXPERIMENTAL SECTION

Materials and Methods

Common reagents were purchased from commercial suppliers and used without further purification. MGBIG was synthesized using a previously published procedure.[15] All water used was deionized (≥18 MΩ/cm). Powder X-ray diffraction (PXRD) analysis was performed using a PANalytical Empyrean Powder X-ray Diffractometer. Each sample was scanned from 4° to 90°, with a step size of 0.02626°, and a time per step of 90.535 s.

An Envion air humidifier was employed as the air-liquid contactor, operated at low air flow, humidifier only (no heating) setting. A ThermoFisher Scientific FH 4-400 RPM Reversible Peristaltic Pump, model 77724-02, was used to continuously replenish the water in the humidifier as it evaporated during the DAC experiments. NMR spectra were collected using a Bruker Avance III 400 MHz NMR Spectrometer, using $DMSO_2$ (0.5 M in D_2O) as an internal standard for quantitative measurements. To prepare the NMR samples, to 100 μL solution retrieved from the humidifier were added 100 μL of internal standard and 400 μL of D_2O. The evolution of the solution pH during the CO_2 absorption was monitored with an Orion Dual Star pH/ISE Meter equipped with an Orion 8115BNUWP Ross Ultra Semi-Micro pH probe.

The total amount of CO_2 absorbed into solution was determined with a Total Inorganic Carbon (TIC) Analyzer containing an Acidification Module CM5300 and a Coulometer CM5017, using air as carrier gas (100 mL/min). Typical TIC procedure: 200 μL of liquid samples were transferred to a 15 mL sample flask using a single-channel pipette. Pre-fined solid samples (40-60 mg) were weighed out into small Teflon cups and the entire cup was transferred into a 15 mL sample flask. 5 mL of 2 M HCl acid was dispensed to acidify each sample. Liquid samples were

analyzed in triplicate. Solid samples were analyzed in duplicate. 1 M Na_2CO_3 solution was used as a standard.

RC-DAC Setup

The DAC experiments, combining atmospheric CO_2 capture and MGBIG carbonate crystallization were done with an Envion air humidifier serving as the air-liquid contactor (Figure 2).

Figure 2. RC-DAC setup

DAC experiments were performed using 1 L aqueous solutions containing different concentrations of MGBIG and sarcosine. To make the DAC solvent, MGBIG was placed in a 1 L volumetric flask and dissolved in 0.5 L of water by placing the flask in a sonicator water bath to facilitate dissolution. Solid sarcosine was subsequently added to the solution, allowed to dissolve, then the solution was topped off with water up to the 1 L mark. The pH of the solution was then measured, and 1 mL of the solution was withdrawn for TIC and quantitative ^{1}H NMR analyses. The weight of the clean, dry humidifier wick was then measured and recorded. The MGBIG/SAR solution was subsequently transferred to the humidifier reservoir and the initial liquid level was marked with tape. The DAC experiment was initiated by turning on the humidifier. The tubing from the

peristaltic pump was placed inside the humidifier's reservoir and attached to the wall, and the rpm speed of the pump was adjusted to compensate for the water evaporation during the experiment. Liquid samples were withdrawn with a pipette as the DAC experiment progressed to monitor the solution composition by TIC and ^{1}H NMR spectroscopy. After the crystallization of MGBIG carbonate phases had started, H-PTFE syringe filters with 0.2 μm pore size were used to filter off the solid crystalline particles. To determine the composition of the crystals by TIC and PXRD, the slurry was sampled at different times by passing through a 0.45 μm pore size PTFE membrane syringeless filter device. The solid was washed with 1 mL of water and left to dry in the air for 24 h before the analysis. After 24 h, the humidifier and the peristaltic pump were stopped, and the final slurry deposited in the reservoir was vacuum-filtered and the resulting solid was washed with 40 mL of water. The solid was subsequently transferred to a crystallization dish, breaking the larger chunks of solid into smaller pieces or a powder, and left to dry in the air for 48 h. The humidifier wick was left to dry in the air overnight. Subsequently, the final weight of the dry wick was measured to determine the amount of accumulated solids. The compositions of the crystalline solids collected from the humidifier reservoir were determined by a combination of TIC, elemental analysis, and PXRD.

Monitoring the crystallization with EasyViewer

An EasyViewer 100 probe (Mettler Toledo) was used to monitor *in situ* the crystallization of MGBIG carbonate inside the humidifier reservoir. The probe was placed in the humidifier container filled with the MGBIG and sarcosine solution, parallel to the humidifier wick, and at a 45° angle to the solution surface, 1.5 cm deep and 1.5 cm away from the wick. The time interval between the images was set to 1 min. The total time of the experiment was set to 24 h.

Monitoring the CO_2 absorption with ReactRaman

Raman spectra were collected in situ every 5 min during the DAC process using a Mettler Toledo ReactRaman 785 spectrometer (300 mW, 15 sec exposure time, 3 scans), with the probe head submerged in the MGBIG/SAR solution in the humidifier reservoir. Spectra were baseline corrected. The observed peaks at 1015 cm^{-1}, 1065 cm^{-1} and 1163 cm^{-1} were assigned to bicarbonate, carbonate, and carbamate species, respectively, based on literature data.[17, 18] There was significant overlap between these peaks and those corresponding to MGBIG and SAR, which prevented their accurate integration and quantification of the corresponding species (Figure S11, Supporting Information).

RESULTS

Screening RC-DAC tests were first done to determine the optimal concentrations of MGBIG and SAR that maximize the yield of crystallization, the proportion of P3, and the amount of CO_2 removed from air. All DAC measurements were run for 24 h with 1 L solution of variable MGBIG and SAR concentrations using the humidifier as the air-liquid contactor (Figure 2). The extents of the DAC reactions were monitored *in situ* by pH measurements, and *ex situ* by periodically withdrawing samples and measuring the total amount of CO_2 absorbed by TIC, and the amount of MGBIG crystallized out of solution by quantitative ^1H NMR spectroscopy. The results are summarized in Table 1, and typical evolutions of the pH and the [MGBIG] and [SAR] concentrations as a function of time are shown in Figure 3.

Sarcosine was found to have a dramatic influence over the yield of crystallization and the identity and phase composition of the crystals formed. Without any SAR present, the crystallization yield from a 0.5 M MGBIG solution was very low (14%), and little or no carbonate

crystals formed after 24 h of DAC, based on TIC and elemental analyses of the isolated solid (Supporting Information). Adding even a small amount of SAR (0.1 mol/L) dramatically increased the yield of MGBIG crystallization (77%), as an almost equimolar mixture of P1 and P3. Increasing the concentration of SAR to 0.2 mol/L maintained a high crystallization yield (64%), and P3 became the dominant phase formed after 24 h (up to 74 mol%). The proportion of P3 grew further to 83 mol% when the concentration of SAR was increased to 0.3 mol/L, while the yield of crystallization remained relatively high at 59%. Maintaining the concentration of SAR to 0.3 mol/L and gradually decreasing the initial concentration of MGBIG from 0.5 to 0.3 mol/L led to a similar crystallization yield (50-59%), and the phase formed was almost exclusively P3. Keeping the SAR concentration at 0.3 M and gradually increasing the concentrations of MGBIG from 0.5 to 0.7 led to a decrease in both the crystallization yield and proportion of P3. On the other hand, keeping the MGBIG concentration at 0.5 M and increasing the SAR concentration from 0.3 to 0.4 M did not lead to any improvements in the crystallization yield and proportion of P3. Finally, increasing the concentrations of both MGBIG and SAR to 0.7 mol/L and 0.4 mol/L, respectively, maintained a high crystallization yield, though the major phase became P1.

Table 1. Screening RC-DAC experiments with various initial MGBIG and SAR concentrations.

[MGBIG] mol/L	**[SAR]** mol/L	**pH initial**	**pH final**	**MGBIG cryst. yield**[a] %	**P1**[b] mol%	**P3**[b] mol%
0.5	0	12.12	11.24	14	NA	NA
0.5	0.1	10.30	9.67	77	54-67	46-33
0.5	0.2	10.50	10.09	64	26-37	74-63
0.5	0.3	10.20	9.91	59 ± 8[c]	17 ± 16[c]	83 ± 16[c]
0.5	0.4	10.11	9.62	52[d]	22	78
0.4	0.3	10.11	9.87	50	3	97
0.3	0.3	10.17	9.81	59	1	99
0.6	0.3	10.43	10.06	48	26	74
0.7	0.3	10.46	10.00	44	25	75
0.7	0.4	10.5	10.08	61	65	35

[a]From the concentration of MGBIG left in solution determined by quantitative NMR, unless otherwise noted; [b]From a combination of elemental analysis and TIC (Supporting Information); [c]Average values from 4 separate experiments; [d]Crystallization yield determined from the amount of isolated MGBIG-CO_3 solid.

Thus, from these screening experiments, the optimal concentrations of MGBIG and SAR that maximize the crystallization yield and the proportion of P3 appear to be 0.3-0.5 M and 0.3-0.4 M, respectively. Under these conditions, the solution pH dropped significantly for the first 8 h, then it plateaued around 9.9, while the concentration of MGBIG decreased monotonously throughout the DAC experiment (Figure 3). On the other hand, based on the quantitative NMR measurements, virtually no SAR was removed from solution.

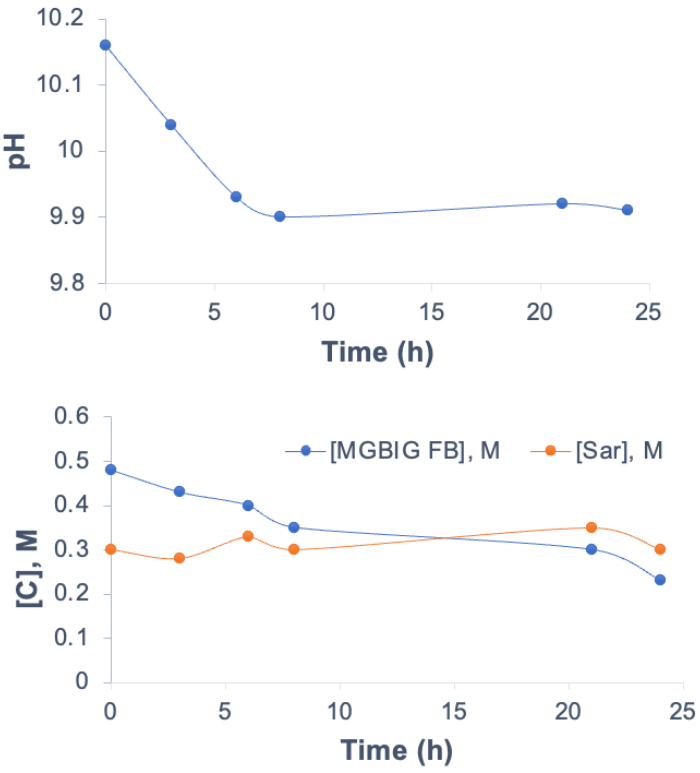


Figure 3. Monitoring the evolutions of pH (top), and of the concentrations of MGBIG free base (FB) and SAR as a function of time, as determined by quantitative ^{1}H NMR spectroscopy. Initial concentrations: [MGBIG] = 0.5 M; [SAR] = 0.3 M.

To gain insight into the crystallization of MGBIG-CO_3 and the evolution of the different crystalline phases involved during the RC-DAC, we monitored *in situ* the crystallization inside the humidifier reservoir with an EasyViewer 100 microscope probe (Figure 4), from a solution with initial MGBIG and SAR concentrations of 0.5 and 0.3 M, respectively. The total amount of CO_2 absorbed in the solution was monitored by periodically withdrawing samples using syringe filters and analyzing the filtrate by TIC. As shown in Figure 5, the concentration of CO_2 increases in the first 6 hours, up to a maximum value of 0.09 mol CO_2/L, after which it starts declining as MGBIG-CO_3 crystallizes out of solution, reaching a final value of 0.03 mol CO_2/L after 24 hours.

3D-shaped crystals characteristic to P1 were first observed after about 3 hours (Figure 4a). Samples of the crystals accumulated after 4 hours (Figure 4b) were collected and analyzed by TIC (Supporting Information), indicating they contained primarily P1 (74%) mixed with P3 (26%). The TIC analyses of the crystalline solids collected after 6 and 8 hours were also consistent with a mixture of P1 (major) and P3 (minor) phases (Table 2). PXRD analyses of these samples also confirmed that P1 was the dominant phase initially crystallized from solution (Figure S9, Supporting Information). The formation of needles characteristic to P3 became apparent from the EasyViewer images recorded after 6 hours. The proportion of the P3 needles continued to increase (Figure 4d), and the needles became the dominant phase at the end of the DAC experiment at 18 h and onwards (Figure 4e and 4f). Multiple samples withdrawn at 24 h and analyzed by TIC confirmed that P3 became the major phase (69-100%), mixed with smaller amounts of P1 (0-31%). The final crystalline solid was collected by vacuum filtration and analyzed by TIC (Supporting Information) and PXRD (Figure S10, Supporting Information), which confirmed the presence of preponderantly P3 (97-100%) in the isolated MGBIG-CO_3 product.

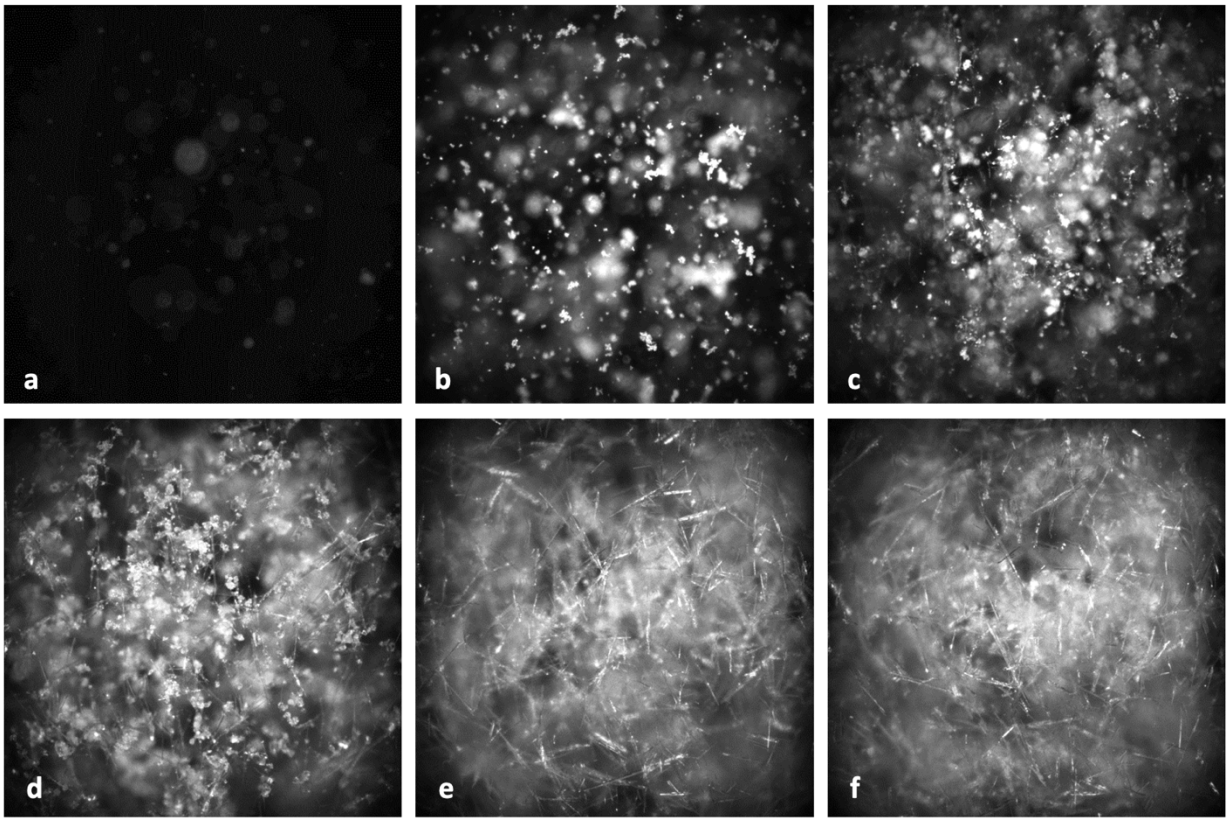


Figure 4. High-resolution images of MGBIG-CO_3 crystallization captured *in situ* using the EasyViewer 100 probe at different times during the DAC process: a) 3 h; b) 4 h; c) 6 h; d) 8 h; e) 18 h; f) 24 h. The side of each image is 1 mm long.

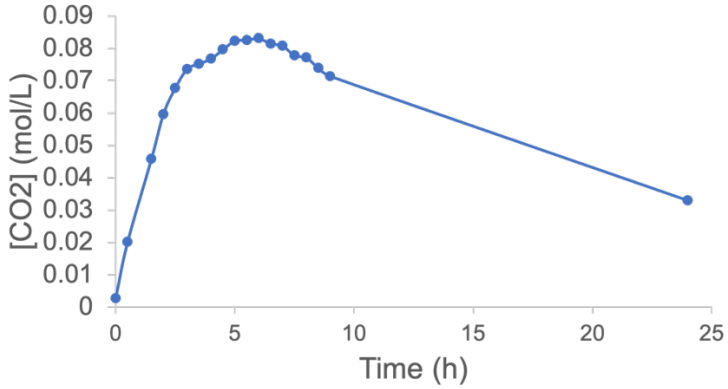


Figure 5. Evolution of CO_2 concentration in solution with time during DAC with humidifier, measured by TIC. Initial solution concentrations: [MGBIG] = 0.5 M; [SAR] = 0.3 M.

Table 2. Evolution of CO_2 concentration in solution and of crystallized MGBIG-CO_3 phase composition with time during DAC with humidifier. Initial solution concentrations: [MGBIG] = 0.5 M; [SAR] = 0.3 M.

Time h	**[CO_2]** mol/L	**P1** mol%	**P3** mol%
0	0	0	0
4	0.08	74	26
6	0.09	85	15
8	0.08	75	25
24	0.03	31-0[a]	69-100[a]

[a]Average values from 4 separate TIC measurements.

The RC-DAC process was also monitored *in situ* via Raman spectroscopy, which revealed peaks corresponding to HCO_3^-, CO_3^{2-} and carbamate species at 1015 cm^{-1}, 1065 cm^{-1} and 1163 cm^{-1}, respectively (Figure S11, Supporting Information). These peaks were first observed after about 10-11 min from the beginning of the RC-DAC experiment, and grew monotonously in time, up to about 3 hours, when the onset of the MGBIG-CO_3 crystallization started interfering with the Raman signals, thereby making further monitoring difficult. Furthermore, significant overlap of these peaks with those corresponding to MGBIG and SAR prevented quantitative determination of the corresponding concentrations and of their evolution in time.

DISCUSSION

Based on the cumulative evidence gathered from the *in-situ* Raman spectroscopy, EasyViewer microscopy, and pH measurements, as well as *ex-situ* TIC, PXRD, and NMR spectroscopy, we may propose a plausible reaction mechanism for the RC-DAC process (Scheme 1).

MGBIG is an organic guanidine base with significant aqueous solubility (≈ 1 M).[16] An aqueous solution of MGBIG (0.5 M) is moderately alkaline (pH ≈ 12) and therefore can react with atmospheric CO_2 and convert it into carbonate anions (Eq. 1-3). However, the reaction is relatively slow, limited by the low concentration of OH^-. Thus, after 24 h of contacting the MGBIG solution

with air using the humidifier, the total concentration of bicarbonate and carbonate, measured by TIC, was only about 15 mM. In the same time, the solution pH dropped to about 11.2. As the pK_as of MGBIG are 8.94 and 7.55, at pH 11.2 most of the MGBIG is expected to be present as the free base. Under these conditions, although the aqueous solubility of MGBIG-CO_3 is quite low (K_{sp} = 1.63×10^{-7}),[15] the concentrations of CO_3^{2-} and $MGBIGH_2^{2+}$ are not sufficient to achieve supersaturation and induce the crystallization of $MGBIGH_2(CO_3)$ (Eq. 4).

Adding SAR to the initial solution changes the speciation and thereby the DAC mechanism significantly. Like amines, amino acids are known to have fast reaction rates with CO_2.[19] However, unlike amines, under neutral conditions amino acids are typically present in zwitterionic forms in aqueous solutions, and therefore not active for CO_2 capture. To become active for DAC, amino acids need to be deprotonated with one equivalent of base, which converts them into their active, anionic forms. In the present case, the guanidine groups of MGBIG act as bases that deprotonate the amine group of SAR, thereby activating it for DAC (Eq.5). Critically, the secondary amine group of SAR is not able to react with MGBIG (apart from the proton transfer mentioned above), unlike other amino acids with primary amine groups that were found to react with MGBIG and precipitate it out of solution.

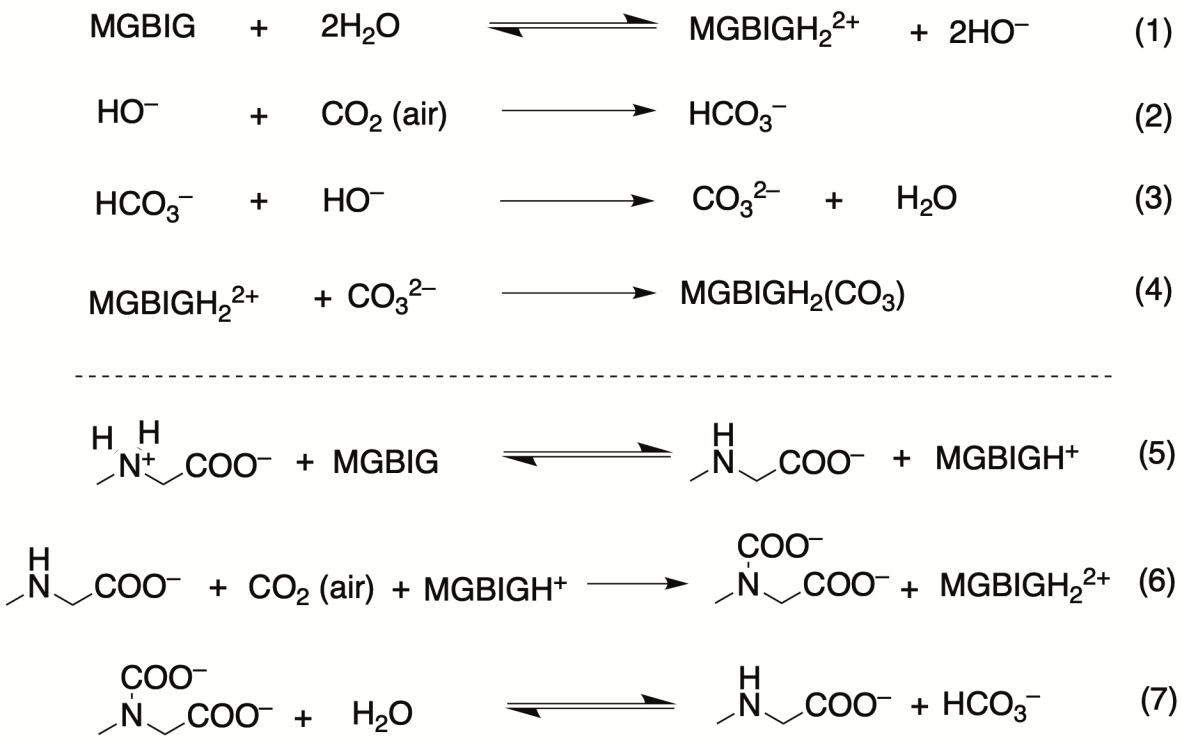
Following deprotonation by MGBIG, SAR reacts with atmospheric CO_2 and converts it to carbamate anions (Eq. 6), which are subsequently hydrolyzed to bicarbonate anions (Eq. 7).[17] Although the carbamate anion is an important intermediate in the overall DAC process, whose presence was confirmed by in situ Raman spectroscopy, it does not appear to accumulate in significant concentrations under these conditions, as indicated by NMR spectroscopy (Figures S6-8, Supporting Information). These observations stand in direct contrast with the DAC reaction involving potassium sarcosinate (K-SAR), in which the carbamate anion is initially the dominant

reaction product and accumulates in solution before it is slowly hydrolyzed to bicarbonate.[12] The observed difference could be explained by the *in situ* precipitation of MGBIG-CO_3, which continuously removes carbonate anions from solution, thereby shifting the carbamate to bicarbonate equilibrium reaction (Eq. 7) to the right. The lower pH of the MGBIG-SAR solution (≈10) compared to that of K-SAR (≈13) is another likely factor speeding up the carbamate hydrolysis reaction.[19]

As the CO_2 is absorbed into solution, the pH drops and the bicarbonate/carbonate concentrations increase until supersaturation with respect to MGBIG carbonate is achieved, thereby triggering its nucleation and crystallization (Eq. 4). P1 is formed initially, presumably because at the higher pH present earlier in the DAC process the $MGBIGH^+$ monocation is found in higher concentration in solution. However, as more CO_2 is absorbed from air the pH continues to drop until the concentration of the $MGBIGH_2^{2+}$ dication is sufficient to induce crystallization of P3. The two phases coexist for a period until P3 takes over and becomes almost the exclusive phase after 24 h.

The RC-DAC system provides a definitive example of reactive crystallization. Both the carbonate anions and the $MGBIGH^+$/$MGBIGH_2^{2+}$ cations are generated in situ from chemical reactions involving CO_2, H_2O and MGBIG. On the other hand, the sarcosine amino acid can be considered as a catalyst, although present in stoichiometric amount, as it does not get consumed in the reaction. Apparently, the role of SAR is simply to speed up the atmospheric CO_2 absorption via conversion into carbamate, which is immediately hydrolyzed to bicarbonate/carbonate, thereby regenerating the amino acid. Once the carbonate anions accumulate in the solution sufficiently to achieve supersaturation, and the solution pH becomes low enough to induce the protonation of

MGBIG, CO_3^{2-} crystallizes with the $MGBIGH^+/MGBIGH_2^{2+}$ cations into P1 followed by P3, respectively.



Scheme 1. Reactions scheme for the proposed RC-DAC mechanism.

CONCLUSIONS

Reactive crystallization offers a promising approach to DAC. Compared to the previously studied phase-changing DAC processes involving initial CO_2 absorption by an aqueous solvent (e.g., KOH, K-SAR) followed by carbonate crystallization in a second step, RC-DAC combines the CO_2 absorption and carbonate precipitation into a single step. Thus, as the insoluble carbonate salts are removed from solution by crystallization, more CO_2 from the air is pulled into solution, further driving the DAC process. Furthermore, the overall RC-DAC process is intensified by combining two operations, CO_2 absorption and MGBIG-CO_3 crystallization, into a single stage, which can lead to significant technology cost reductions. Furthermore, the amino acid is continuously

regenerated – no separate solvent regeneration stage is necessary – thereby facilitating the development of a continuous DAC process. However, the precipitation of solid carbonate phases inside the air-liquid contactor introduces additional complications with respect to contactor design, which needs to be able to tolerate and effectively handle solid-liquid slurries.

SUPPORTING INFORMATION. Additional experimental details, TIC and PXRD analyses, ^{1}H NMR and Raman spectra.

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Direct Air Capture of CO_2 via Reactive Crystallization

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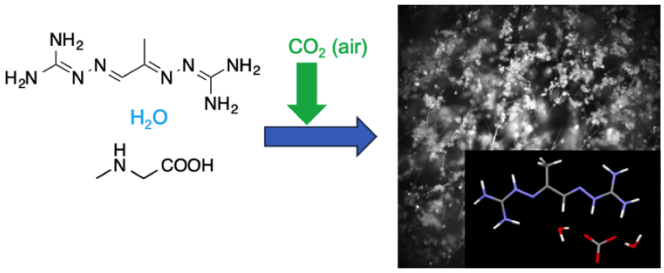
TOC Graphic



Synopsis

Atmospheric CO_2 removal using engineered chemical processes, aka direct air capture (DAC), has become an essential component of our available portfolio for mitigating climate change. The paper describes a promising approach to DAC based on reactive crystallization of atmospheric CO_2 (RC-DAC) with an aqueous guanidine and amino acid.