# Integrated Process for Direct Air Capture through Reactive Crystallization and Electrochemical Conversion to Ethanol

TCF-20-20118

Radu Custelcean
Oak Ridge National Laboratory

2023 Carbon Management Research Project Review Meeting
August 28 – September 1, 2023

# Project Overview

## **ORNL Team** (DAC)

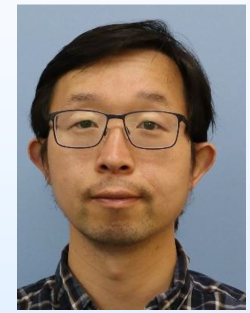
**Radu Custelcean**
Lead PI
Organic chemist

**Costas Tsouris**
Co-PI
Chemical engineer

**Kashif Nawaz**
Co-PI
Mechanical engineer

**Gyoung Jang**
R&D associate
Chemical engineer

**Diana Stamberga**
Technical associate
Organic chemist



**Kai Li**
R&D associate
Materials/manufacturing

**Abishek Kasturi**
Grad student
Georgia Tech

## **ReactWell** ($CO_2$ conversion)

**Brandon Iglesias**
Chemical engineer

**Project Timeline**
Jan 1, 2021 – Jan 1, 2024

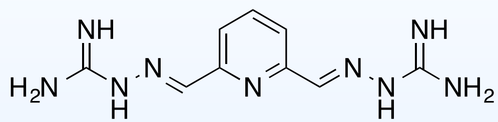
**Project budget**
$1.5 mil/3 years (DOE: OTT/FECM)
$1.5 mil in-kind match-up (ReactWell)

# Project Objectives

- Develop an energy-efficient, cost-effective, net-zero emission technology that closes the carbon cycle by combining DAC with electrochemical conversion of $CO_2$ into ethanol
- DAC: reactive crystallization of aq. amino acid + guanidines - ORNL
- Electrochemical conversion of captured $CO_2$ into ethanol using copper nanoparticles/carbon nanospike electrode - Reactwell
- Commercialize the ethanol as hand sanitizer, spirits, fuel - Reactwell
- Long-term goal: mature and scale up a standalone DAC technology for deployment at the much larger scale of $MtCO_2$/year + geological storage towards NET status (with Holocene)

# Technology Background

## Fundamental science (BES)

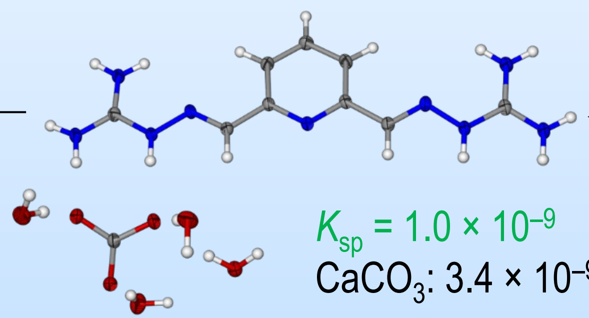



PyBIG$_{(aq)}$

**release**

**TGA**
80-120 °C
– $CO_2$
– 5 $H_2O$

**DSC**
$\Delta H$ = 223 kJ/mol
($H_2O$: 148 kJ/mol)

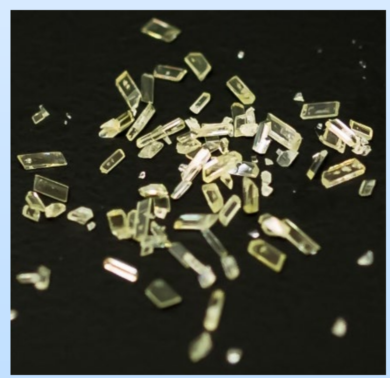


$K_{sp} = 1.0 \times 10^{-9}$
$CaCO_3$: $3.4 \times 10^{-9}$

**absorption**

$CO_2$ (air)

$K = 10^5$ atm$^{-1}$
$\Delta H$ = – 71 kJ/mol



**Benchmark**
$CaCO_3$ requires 900 °C for $CO_2$ release

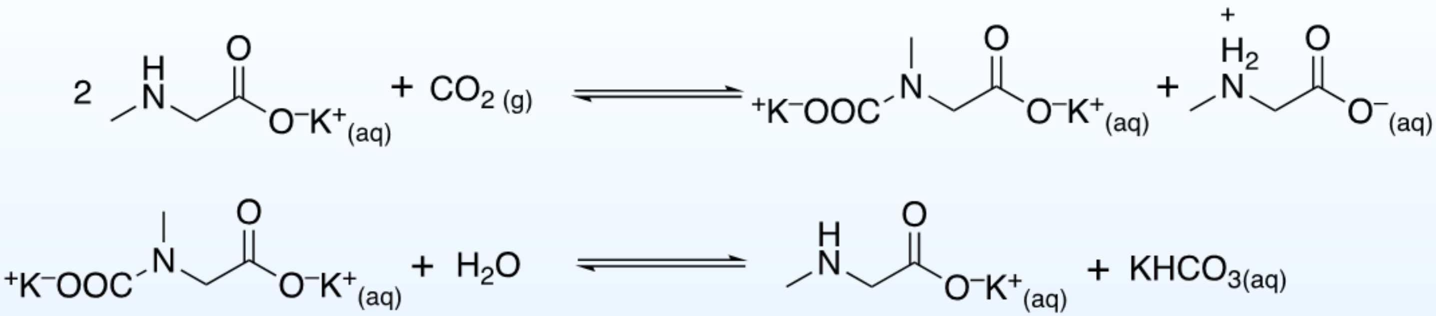
## Advantages
- Reactive crystallization and low solubility of BIG-$CO_3$ drive $CO_2$ removal from air
- Low regeneration T
- Low grade heat

## Challenges
- Slow kinetics of $CO_2$ abs
- Low BIG solubility/alkalinity
- Small air-liquid contact area

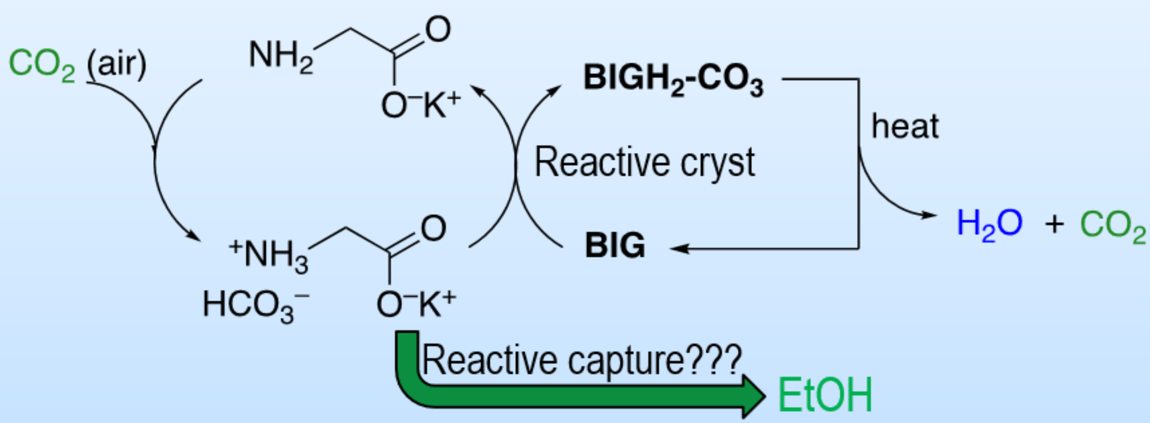
*Angew. Chem. Int. Ed.* **2017**, *56*, 1042
*ChemSusChem* **2020**, *13*, 6381
*Chem. Sci.* **2021**, *12*, 12518

# Technology Background

## Faster DAC with aq. Amino Acids




## DAC with aq. Amino Acid + BIG




Not compatible with solvent regeneration

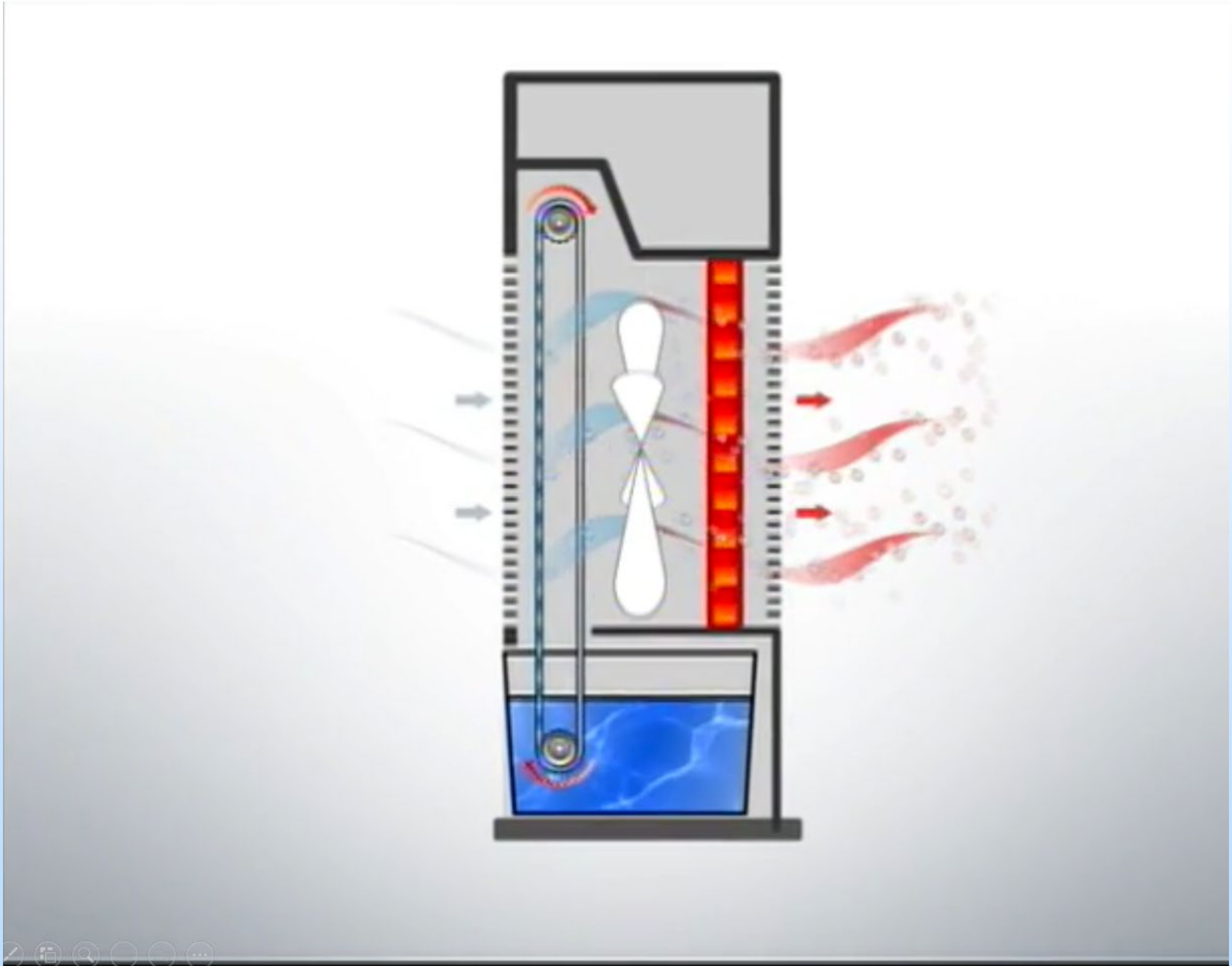
**Advantages**

- fast $CO_2$ absorption rates
54 μmol/m²/s for SAR 1 M, 25 °C vs 30 μmol/m²/s for NaOH
- negligible volatility & toxicity

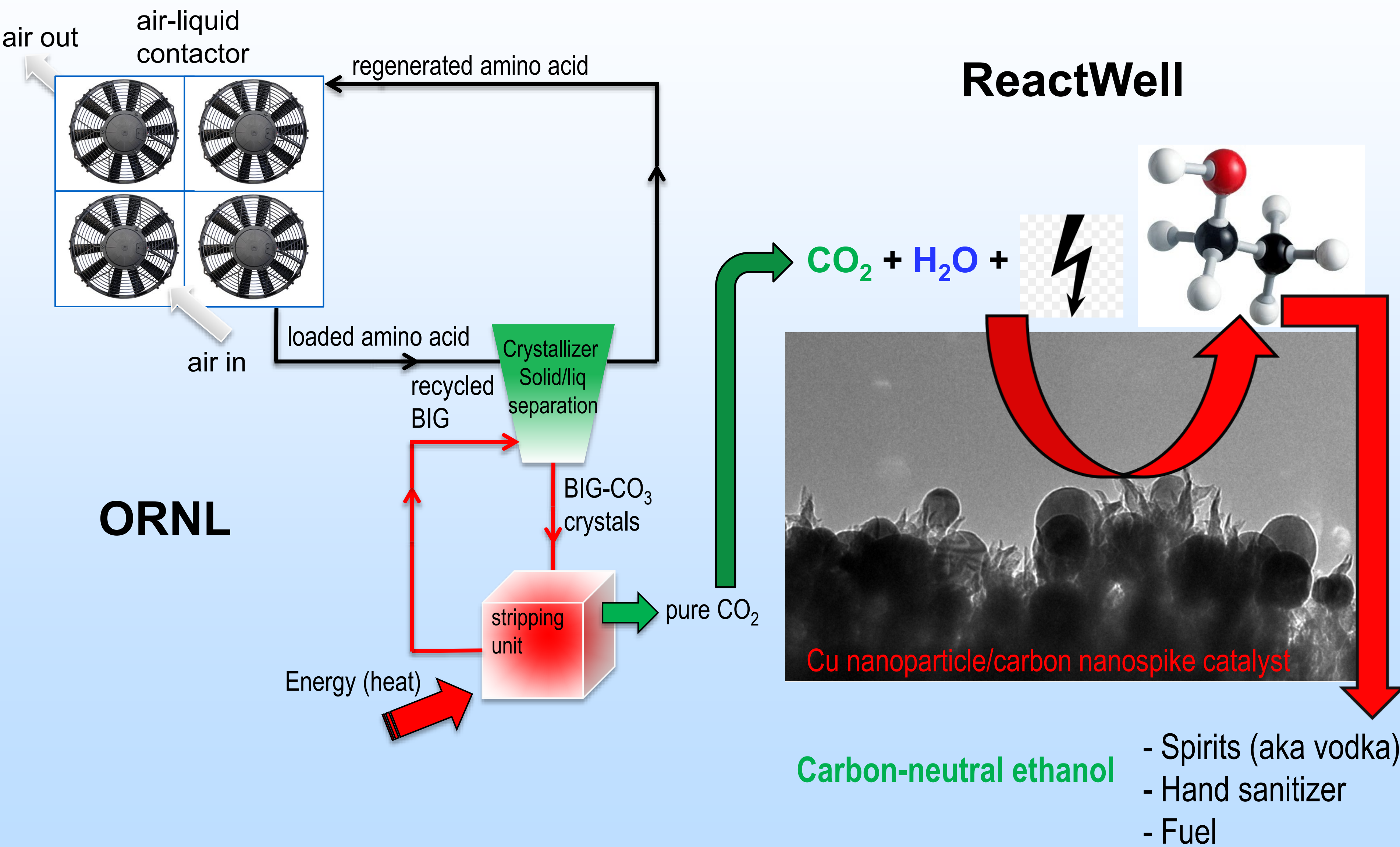
**Outstanding challenges**

- minimize regeneration energy
- minimize degradation
- improve $CO_2$ mass transfer (higher air/liquid contact area)

*Nature Energy* **2018**, 3, 553
*Ind. Eng. Chem. Res.* **2019**, 58, 23338



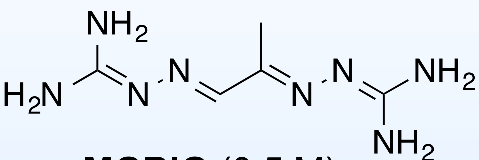
# Technical Approach/Project Scope



# Technical Approach/Project Scope

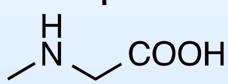
- **Optimization of DAC chemistry:** identify optimal amino acid/BIG
- **Design, build & test air-liquid contactor:** compatible with solids
- **Optimize BIG sorbent regeneration:** minimize time and energy
- **Process engineering & intensification:** combine $CO_2$ absorption and BIG-$CO_3$ crystallization into a single three-phase process
- **TEA and LCA:** evaluate the cost, energy & water consumption, carbon footprint (carbon neutral? carbon negative?)

# Progress and Current Status
# DAC Chemistry Optimization



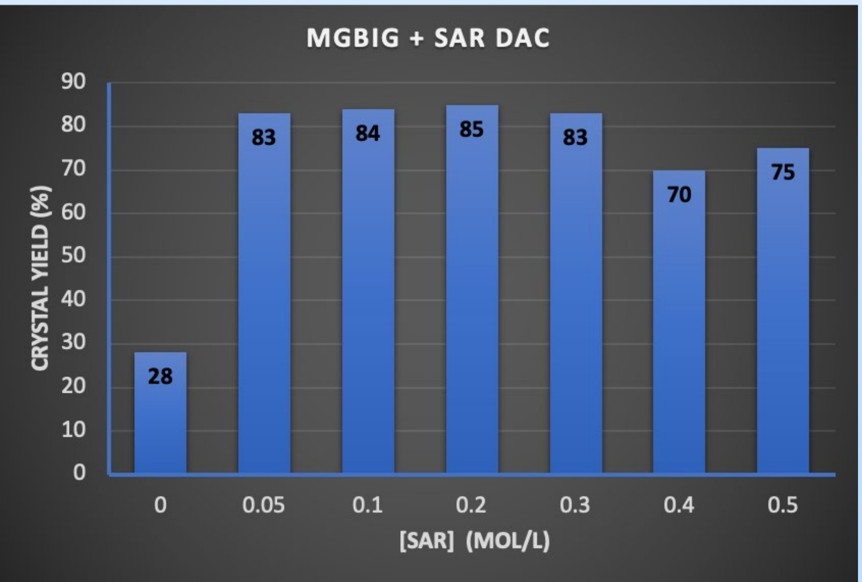
**MGBIG** (0.5 M)

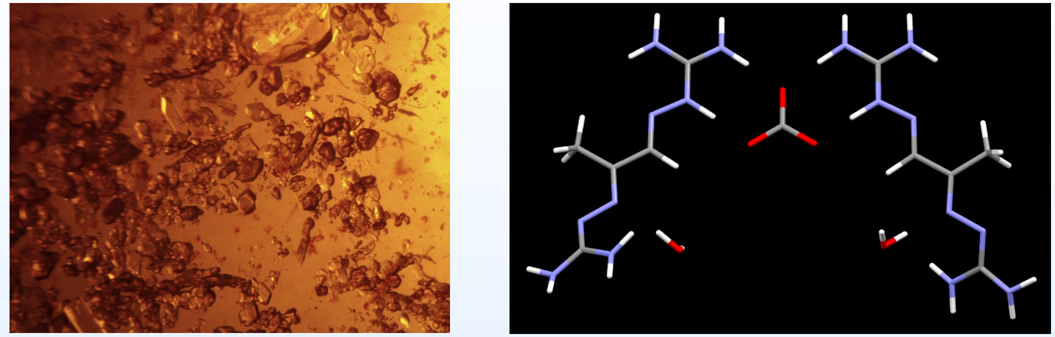
+



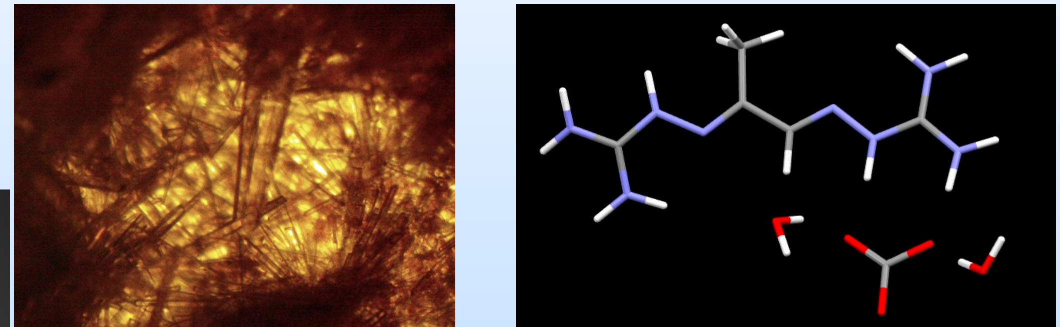
**SAR**

$CO_2$ (air)



$(MGBIGH^+)_2(CO_3)(H_2O)_2$ (**P1**) favored at [MGBIG] > 0.75 M



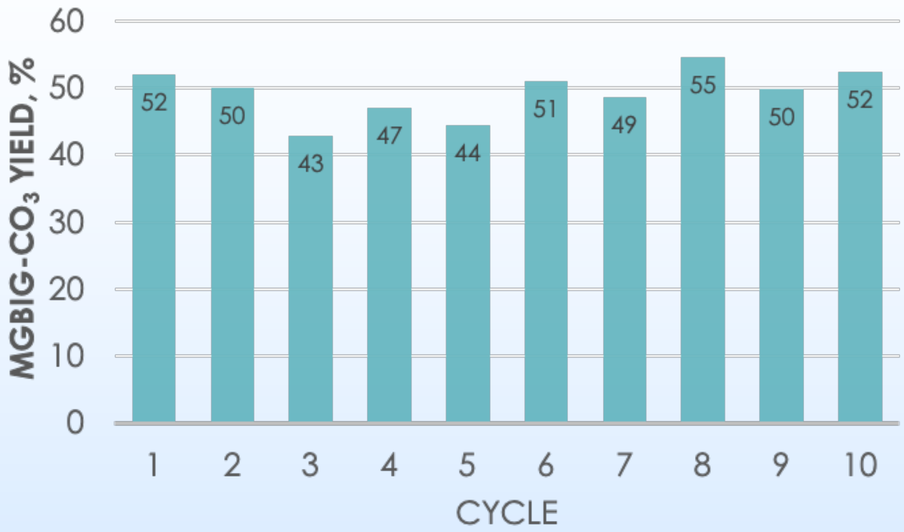
$(MGBIGH_2^{2+})(CO_3)(H_2O)_2$ (**P3**) favored at [MGBIG] < 0.3 M

**Amino acid advantages**:
- No additional base (KOH) needed
- Addition of SAR favors P3 over P1

**Intensified DAC process**:
- Combine $CO_2$ capture + MGBIG-$CO_3$ crystallization
- Need an air-liquid contactor that tolerates solids
- Scale up 100X to 1 L and beyond

# Intensified DAC with MGBIG/SAR


1 L scale, MGBIG (0.5 M) + SAR (0.3 M)
Run for 24 h




**Average results for 10 cycles**

Crystallization yield: 51% ± 10%

Phase 3 (mol%): 91 ± 13

Cyclic capacity (mol $CO_2$/L): 0.23 ± 0.02

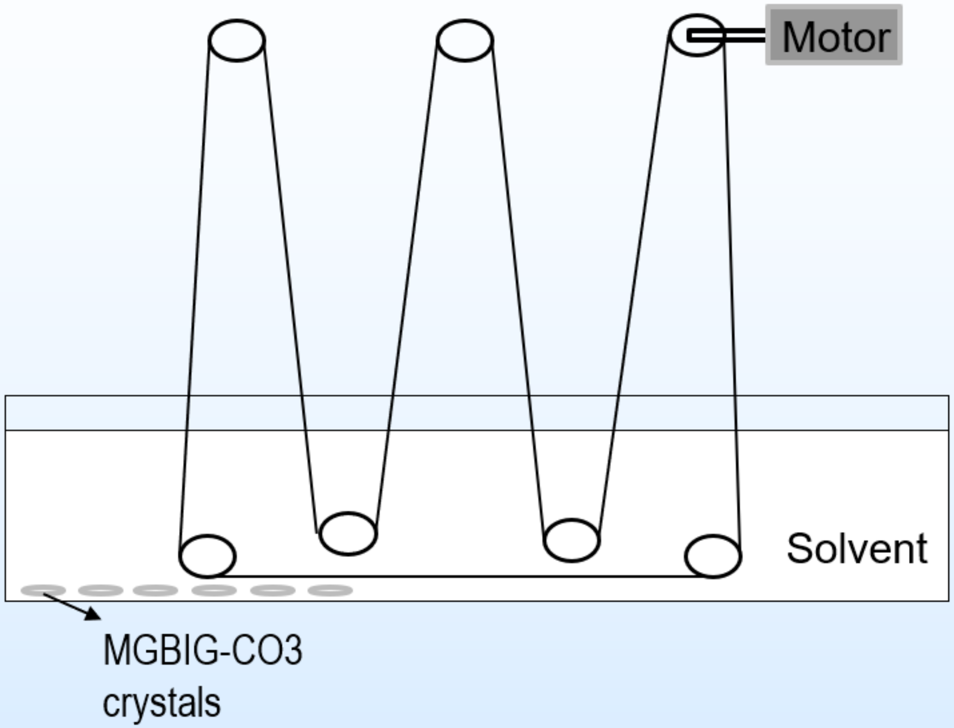
$CO_2$ removed from air (g $CO_2$/day): 10 ± 1

MGBIG loss: 0%/cycle

SAR loss: 1.5%/cycle

# Air-Liquid DAC Contactor Design

### Rotating Air Contactor (RAC) Design



# Air-Liquid DAC Contactor Design

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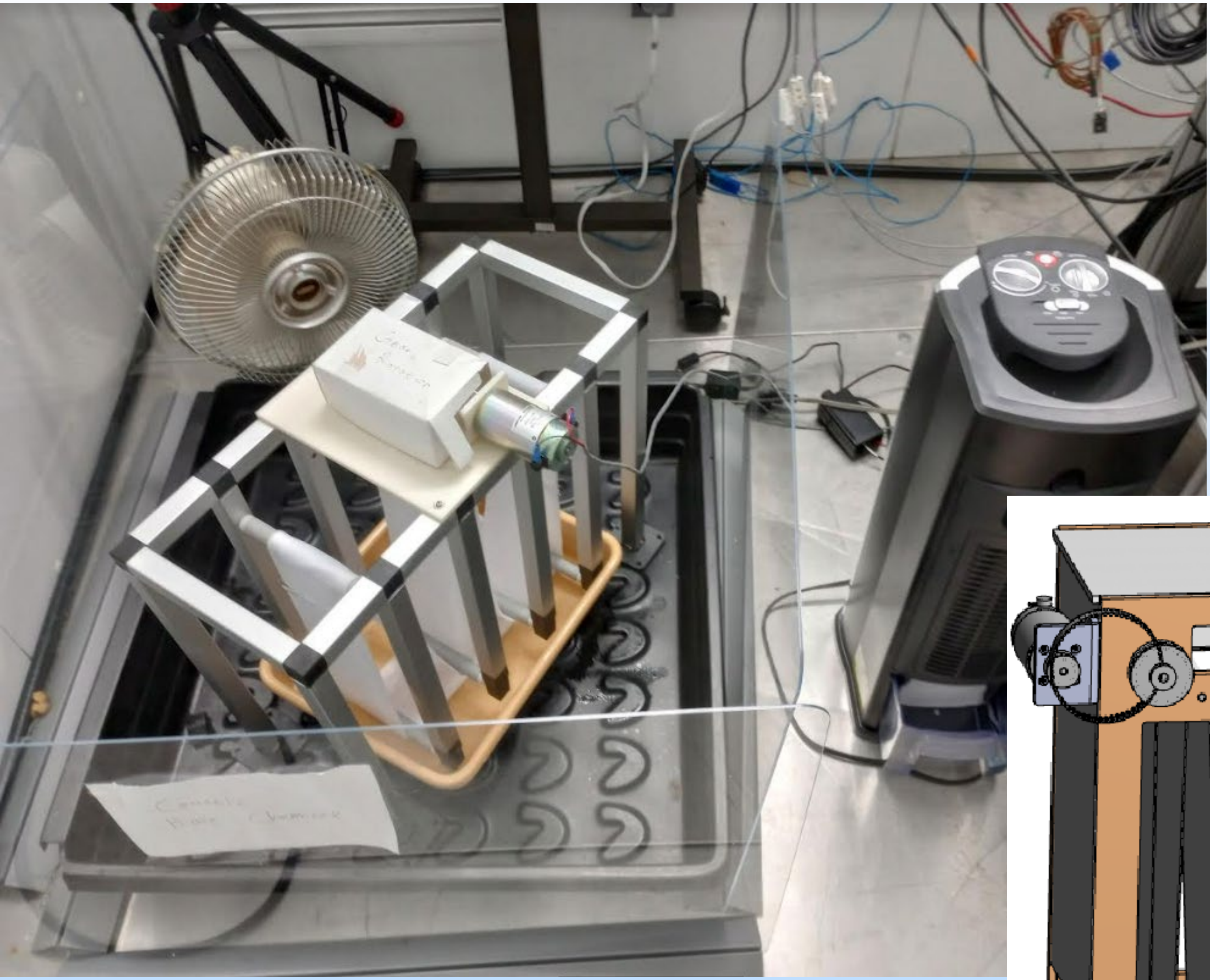
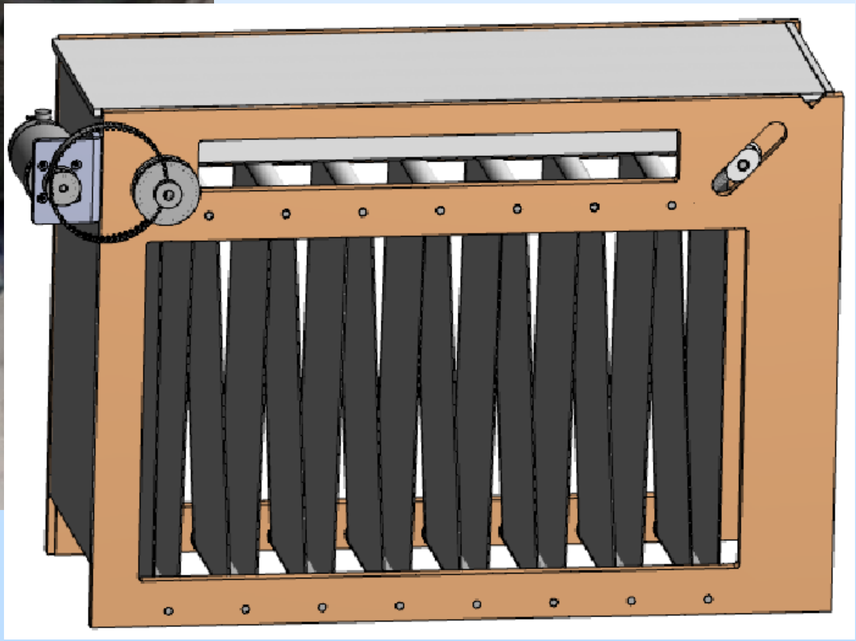


Humidifier
SA = 0.2 $m^2$

1st gen RAC
SA = 0.5 $m^2$

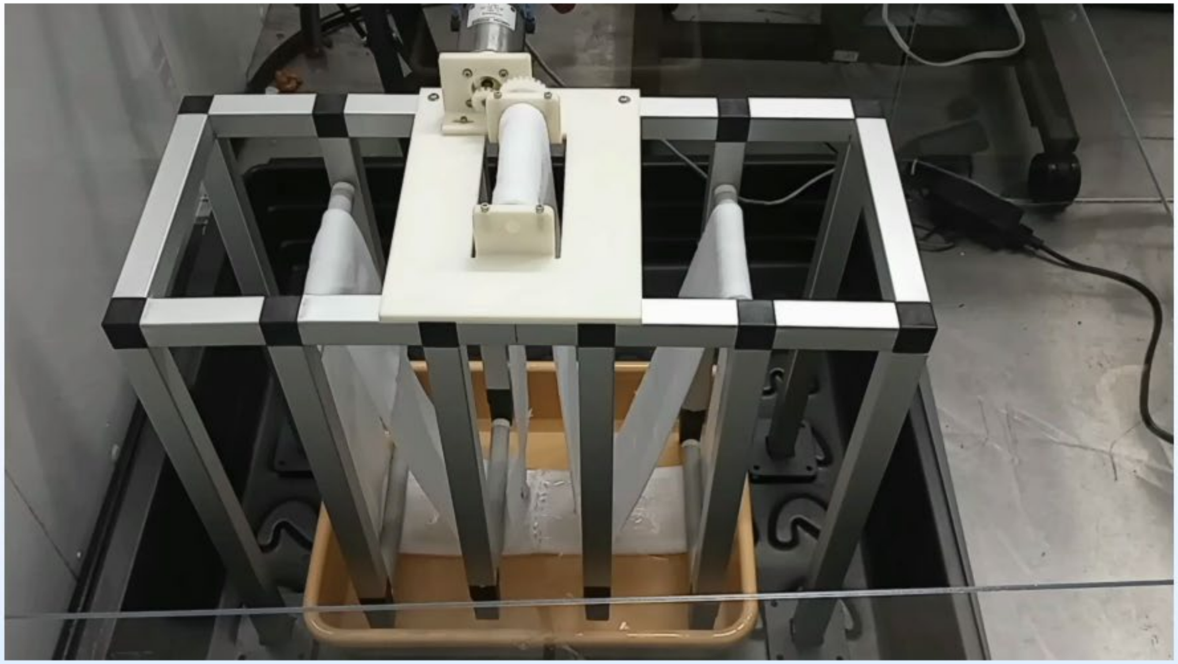
2nd gen RAC
SA = 2 $m^2$



Patent application no. 63/535,383; Patent ID 81948020

# Air-Liquid DAC Contactor Testing

**1st gen RAC** tested with 2 L of 1 M K-SAR with air at 35 & 65 °C, 80% RH



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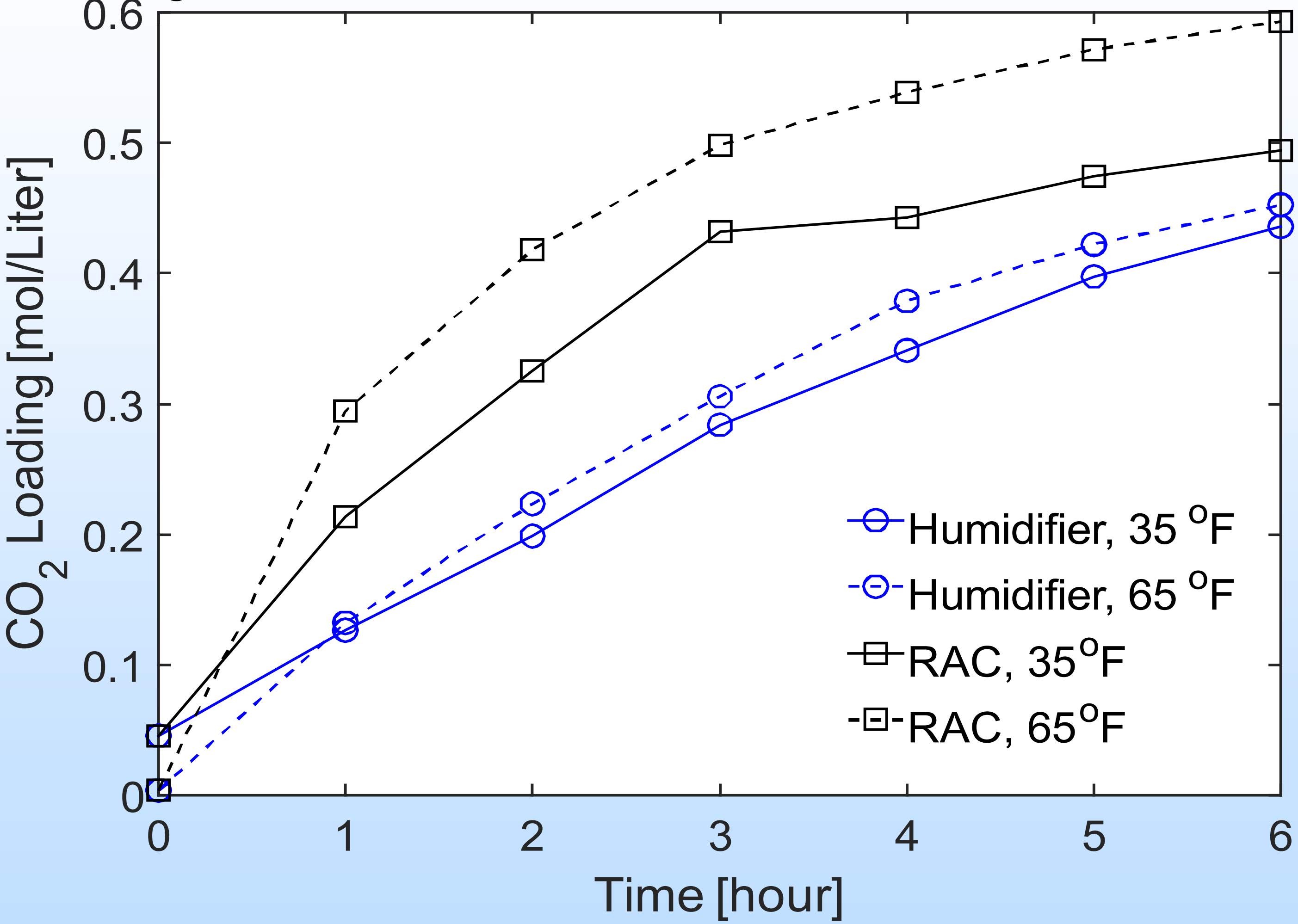
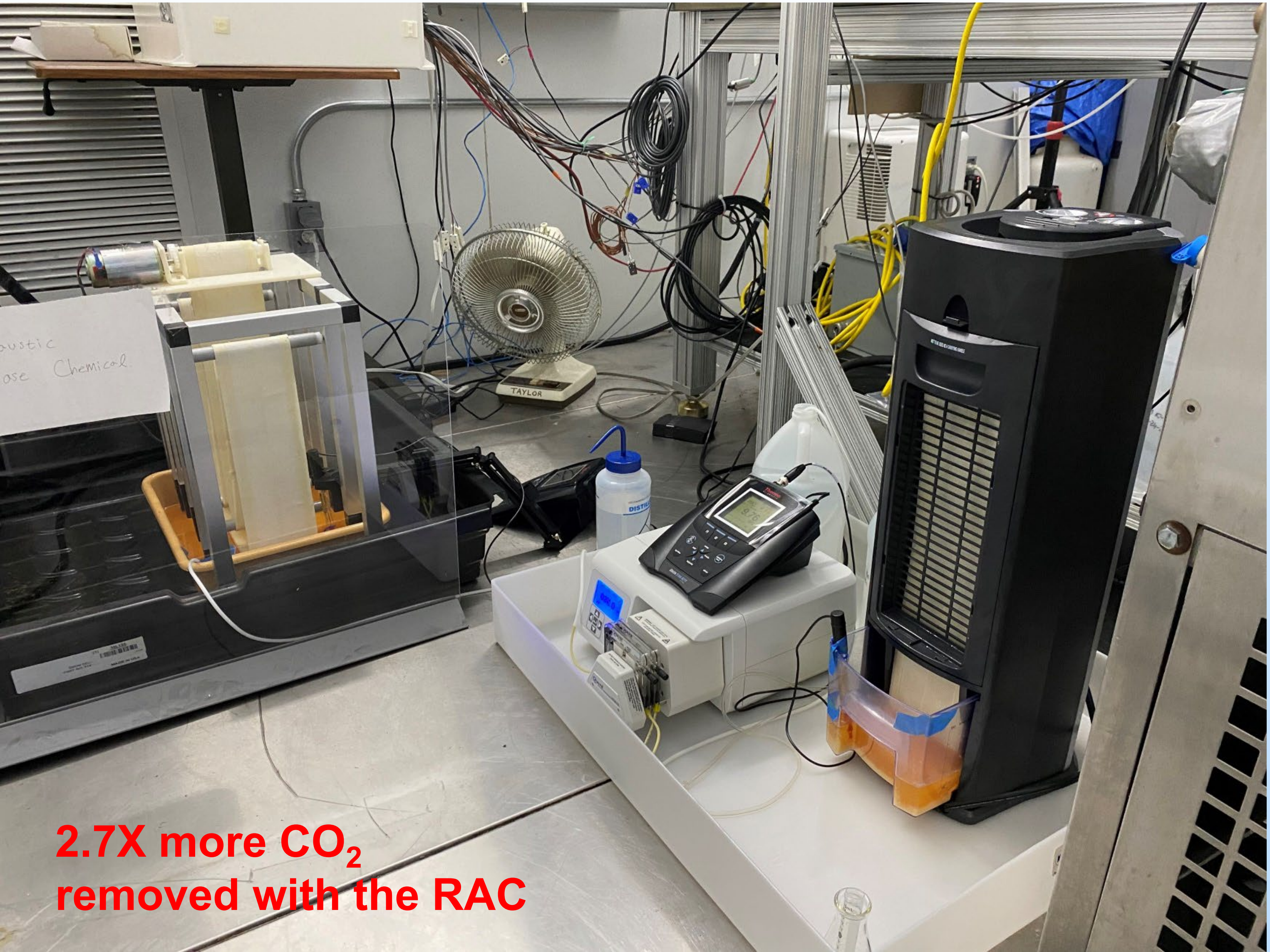


# Air-Liquid DAC Contactor Testing

**1st gen RAC** tested with 2 L SAR (0.3 M) + MGBIG (0.5 M) with air at 25 $^{o}C$, 70% RH, 24 h




**2.7X more $CO_2$ removed with the RAC**

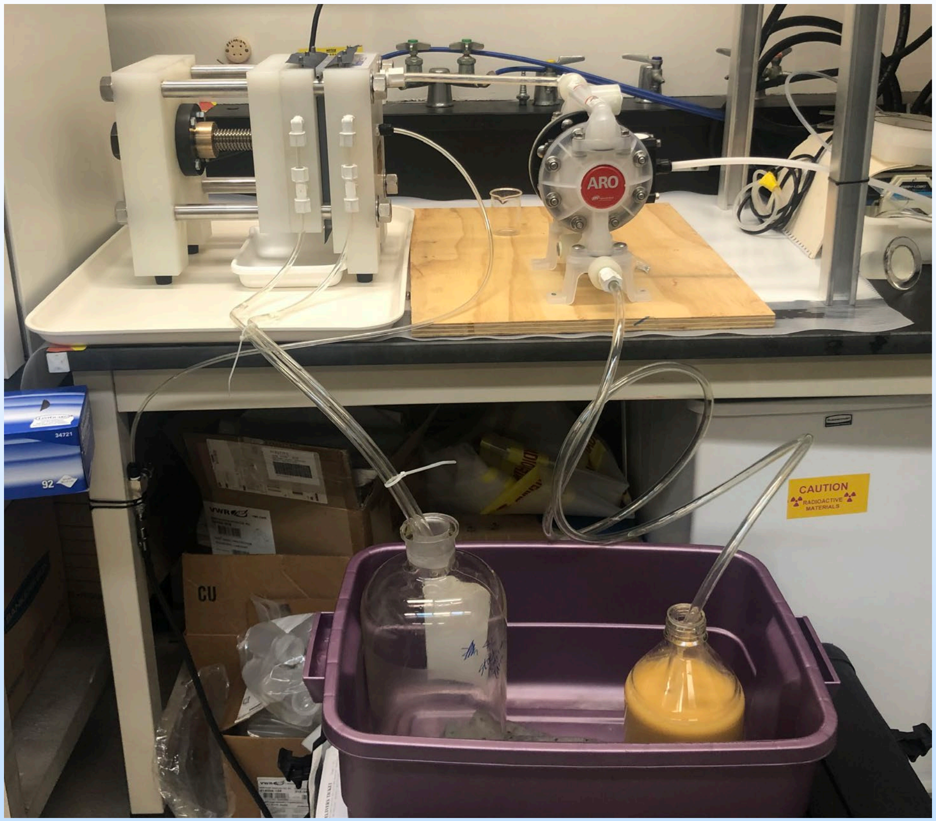
**RAC**
- 2 L solvent
- SA 0.5 $m^2$
- Cryst. yield: 62%
- Isolated MGBIG-$CO_3$: 120.6 g (89%)
- P3: 99.5%
- $CO_2$ removed: 22 g

**vs**

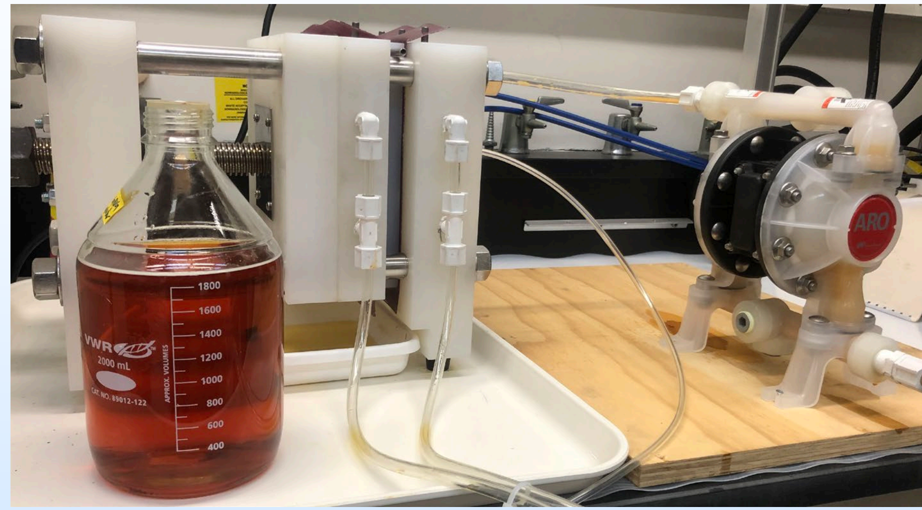
**Humidifier**
- 1 L solvent
- SA 0.2 $m^2$
- Cryst. yield: 60%
- Isolated MGBIG-$CO_3$: 43.1 g (95%)
- P3: 99.1%
- $CO_2$ removed: 8.3 g

# Solid ($MGBIG-CO_3$)/Liquid (SAR) Separation

**Filter press setup**



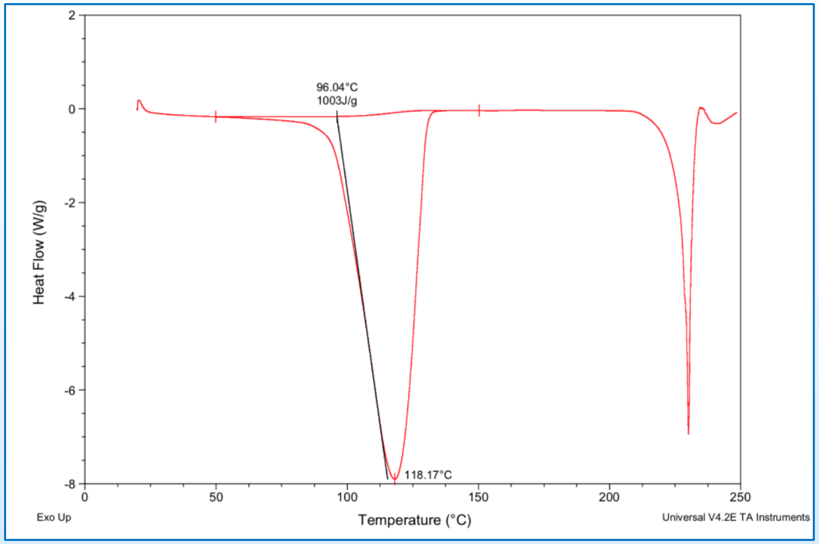

**Recovered solvent at the end of separation**



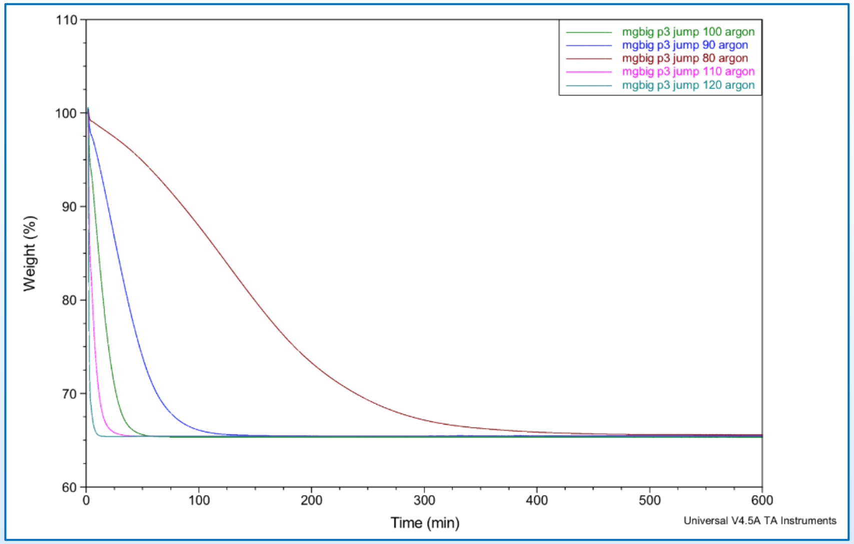

**Recovered $BIG-CO_3$ cake**

# $CO_2$ Release – Thermodynamics & Kinetics

$(MGBIGH_2^{2+})(CO_3)(H_2O)_2$ (**P3**)




**DSC**




**Isothermal TGA** (80, 90, 100, 110, 120 °C)

| E (kJ/mol $CO_2$) | MGBIG P1 | MGBIG P3 |
|---|---|---|
| Reaction enthalpy | 288 | 284 |
| Sensible heat | 70 | 39 |
| Regeneration energy | 358 | 323 |

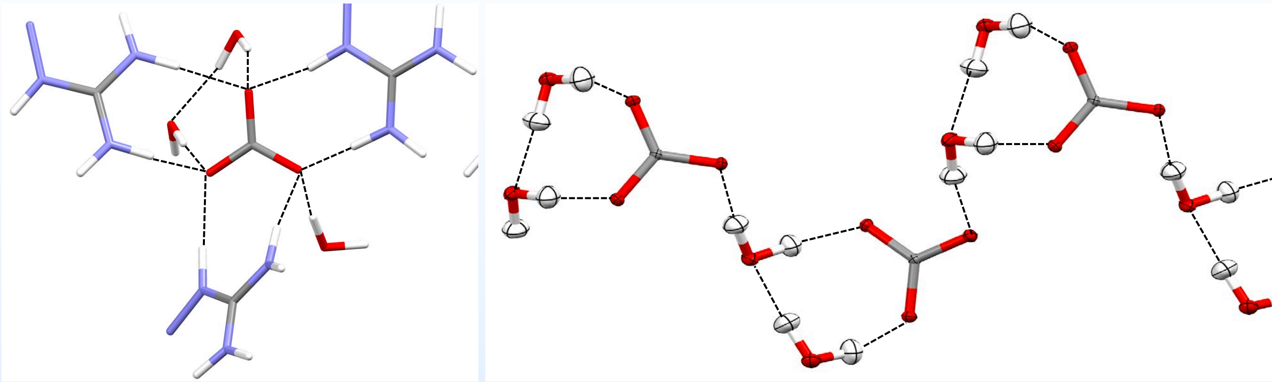
Crystal dehydration costs a lot of energy

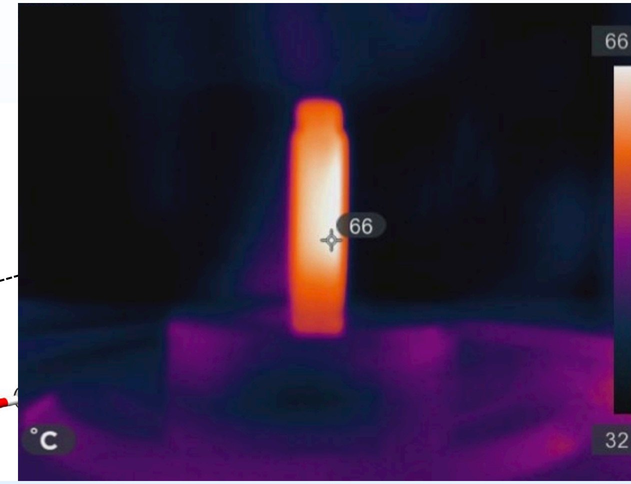
Acknowledgment: Michelle Kidder for TGA and DSC measurements

*ChemSusChem* **2020**, *13*, 6381

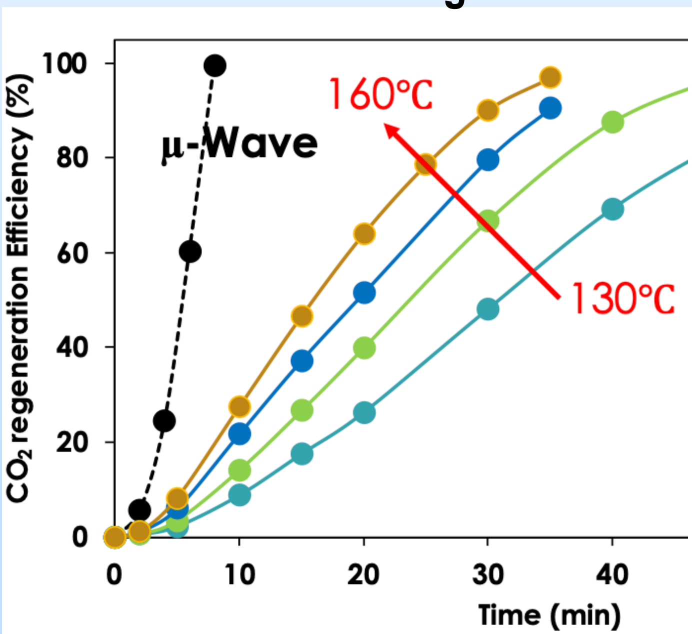
# MGBIG Regeneration – Microwaves

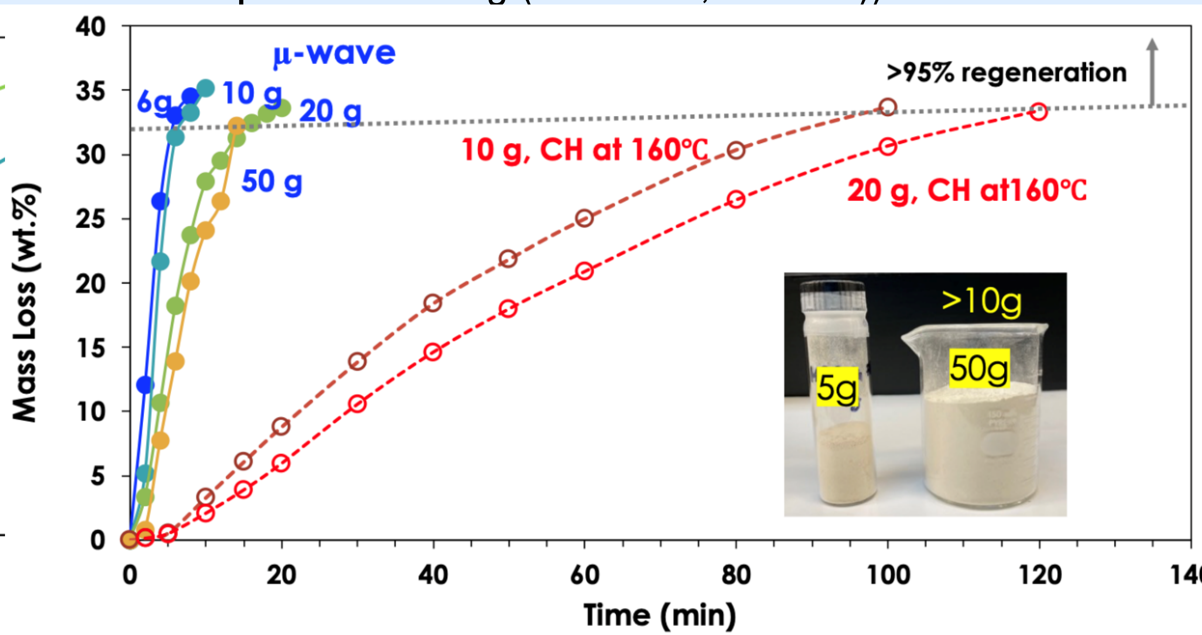
$(MGBIGH_2^{2+})(CO_3)(H_2O)_2$ (**P3**) crystal structure:
Water bound to carbonate





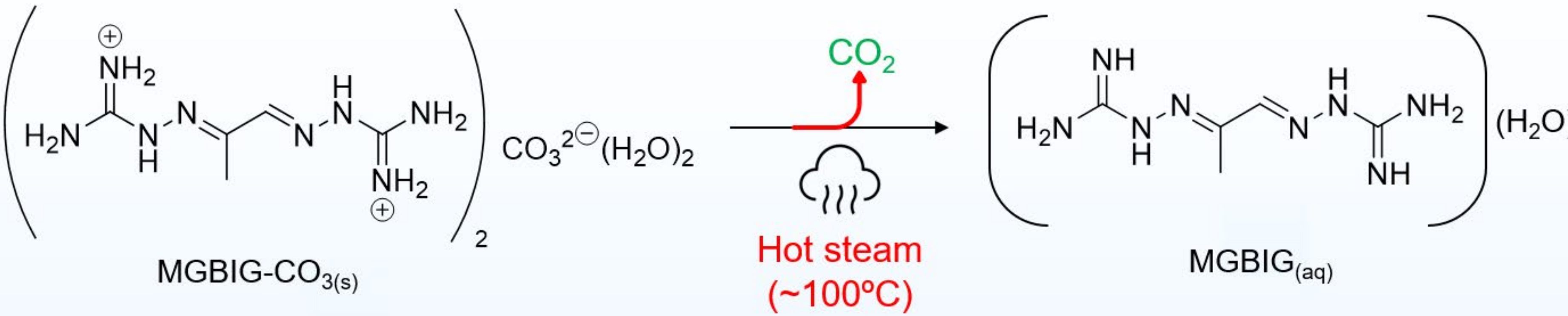

**Kinetics of MGBIG regeneration:** convection vs μ-wave heating (2.54 GHz, 1250 W))




*Sep. Pur. Tech*. **2023**, *309* 123053; Patent app. no. 18/235,081; Patent ID 81944506

# MGBIG Regeneration – Steam



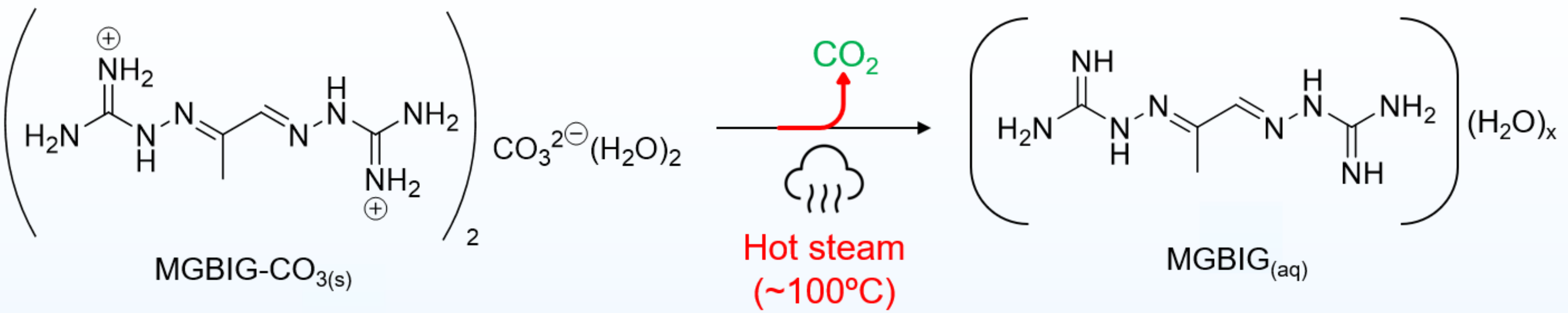


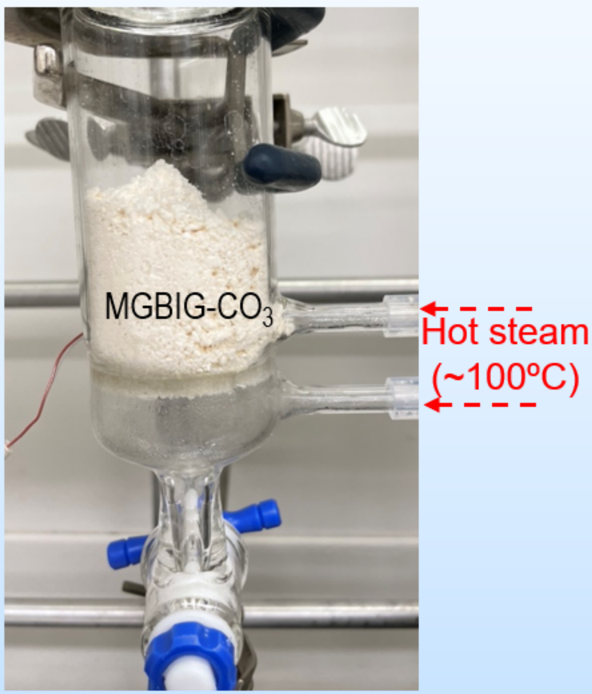


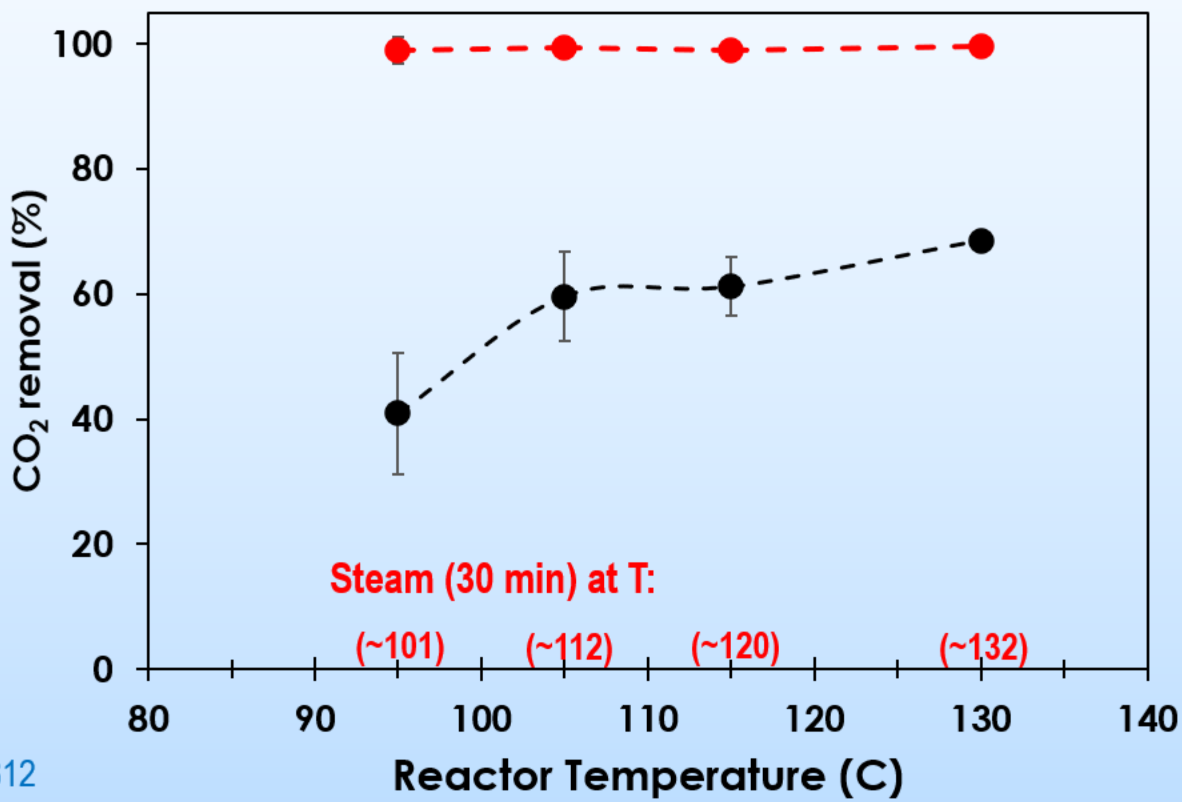


Patent app. no. 63/534,893; Patent ID 81947812

# MGBIG Regeneration – Steam

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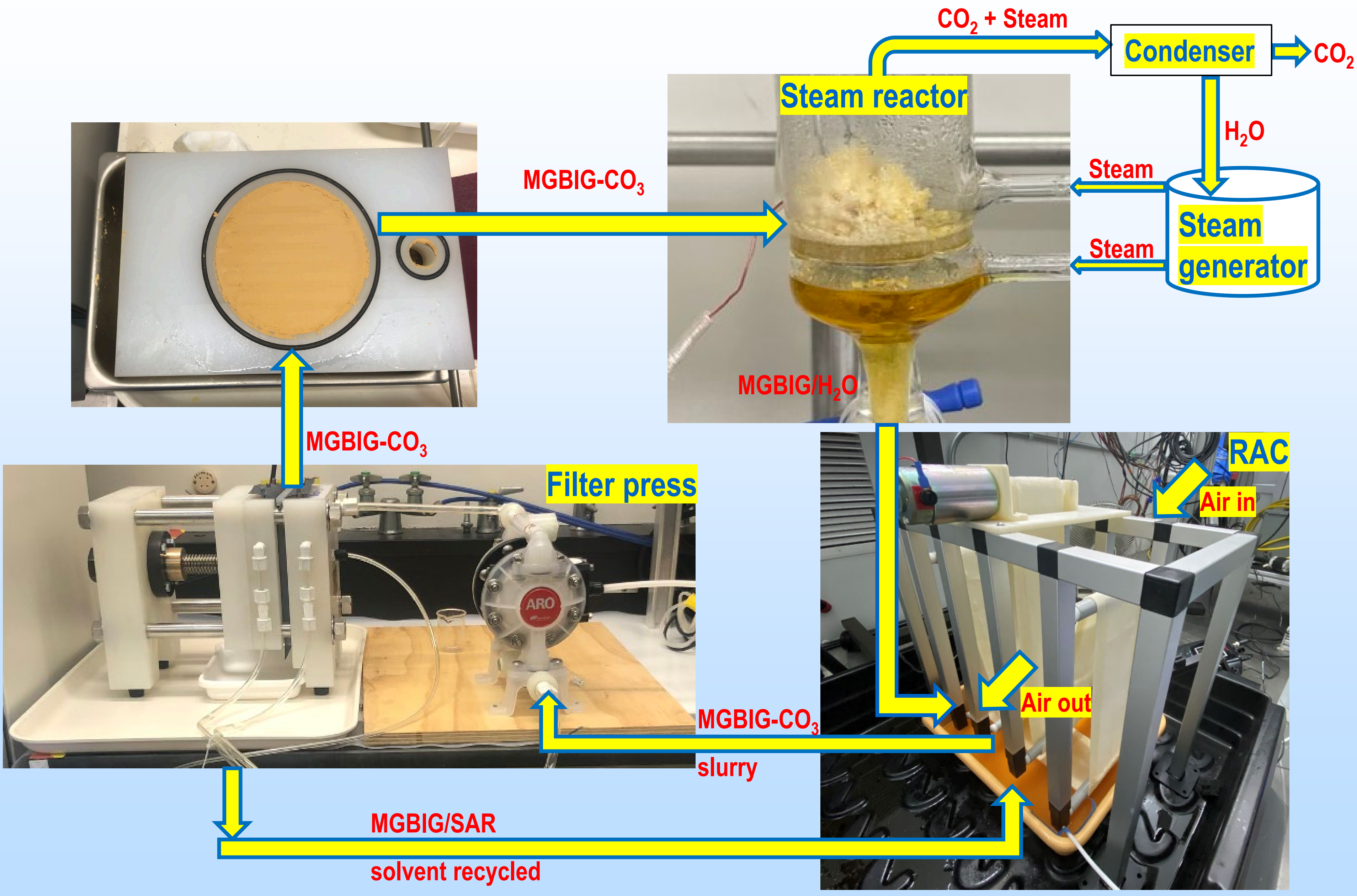
# Summary: DAC Process



# Lessons learned

- Reactive capture only makes sense if the conditions for $CO_2$ conversion are compatible with those for solvent regeneration

- Standalone DAC process may have some advantages over a continuous, integrated (capture + conversion) process:

1) Potential for NET
2) Scaleup of DAC independent of conversion
3) $CO_2$ stored temporarily as BIG-$CO_3$, transported and released on demand for conversion

# Plans for future testing/development/ commercialization

## In this project

- Complete bench-scale DAC process and demonstrate multiple cycles at 100 g $CO_2$/day
- TEA and LCA
- Send MGBIG-$CO_3$ batches to Reactwell for on-demand $CO_2$ release & conversion to EtOH for commercialization

## After this project

- Collaborate with Holocene on further developing a scalable, commercial DAC technology for $CO_2$ removal and storage

# Project Output

## Publications

**1.** Kasturi, A. et al., Determination of the Regeneration Energy of Direct Air Capture Solvents/Sorbents Using Calorimetric Methods, *Separation and Purification Technology* **2023**, *310*, 123154.

**2.** Jang, G. G. et al., Ultra-fast Microwave Regeneration of $CO_2$ Solid Sorbents for Energy-Efficient Direct Air Capture, *Separation and Purification Technology* **2023**, *309*, 123053.

## Patent applications

1. Gyoung Jang et al., *Microwave Regeneration of Carbon Dioxide Sorbents* **2023**, Application no. 18/235,081; Patent ID 81944506.
2. Gyoung Jang et al., *Methods of Energy Efficient Sorbent Regeneration Used for Direct Air Capture* **2023**, Application no. 63/534,893; Patent ID 81947812.
3. Keju An et al., *Direct Air Capture of $CO_2$ using RAC (Rotating Air Contactor*) **2023**, Application no. 63/535,383; Patent ID 81948020.

## Awards

2021 R&D100 Award for BIG NET: ORNL + Holocene + Reactwell