





Use of a Novel Process for Revolutionizing CO₂ Capture

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Project team

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 - Co-PI: Professor Randy Lee vander Wal
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Collaboration Leader: Dr. Janice A. Steckel





Statement of Problems

 Low CO₂ sorption and desorption kinetics
 -NH₂ + CO₂ + H₂O <sup>k_{R1}, k_{-R1} (-NH₃⁺)(HCO₃⁻) R1 and -R1 where k_{R1} and k_{-R1} are determined by their corresponding activation energies (E_{R1} and E_{-R1}) are the apparent rate constants of the CO₂ sorption and desorption steps, respectively
</sup>

• $CO_2 + OH^- \xleftarrow{k_{R2}, k_{-R2}} HCO_3^-$ R2 and -R2 where k_{R2} and k_{-R2} determined by their corresponding activation energies (E_{R2} and E_{-R2}) are the apparent rate constants of CO_2 sorption and desorption steps, respectively.

High energy consumption

Hypothesis

<u>How can we accelerate both CO₂ sorption and desorption?</u> Firstly, let us how catalysis can help CO₂ desorption. Based on the reported E_a of CO₂ desorption in amine sorption system, 114.25 kJ/mol, the increase ratios of the reaction rate constant (*k*) in Arrhenius equation of CO₂ desorption at 80 °C due to the use of a catalyst is estimated according to:

$$\frac{k_{with-catalyst}}{k_{without-catalyst}} = \frac{A}{A} e^{-\frac{E_{with-catalyst}-E_{without-catalyst}}{RT}} = e^{\frac{m^*E_{without-catalyst}}{RT}}$$
(E1)

where *m* is the activation energy reduction percentage due to the use of a catalyst and presented below.

	1.00	Activation energy decrease %				
CO ₂ desorption rate	Assumed CO ₂					
constant increase ratio	desorption	1%	5%	10%	15%	20%
due to use of catalyst	temperature					
$k_{\text{with-cat}}/k_{\text{without-cat}}$	T = 393 K	2	6	33	188	1,080

Hypothesis (continued)

Obviously, <u>the catalytic potential for CO_2 desorption is significant</u>. Also, reducing the activation energy of the CO_2 desorption reaction can lead to a decrease in the <u>activation energy of the CO_2 sorption according to the relation</u>

$$\Delta H = E_{a,desorption} - E_{sorption}$$
(E2)

where ΔH is the heat of reaction, $E_{a, desorption}$ is the activation energy of the CO₂ desorption, and $E_{a,-adsorption}$ is the activation energy of CO₂ adsorption because ΔH is constant for a given temperature according to thermodynamic theories, a reduction in $E_{a, desorption}$ due to use of the catalyst means that $E_{a,-adsorption}$ is also decreased. Thus, a catalyst can accelerate both CO₂ sorption and desorption.

Potential significance of the results of the work

- Economic significance Overcoming the challenges
 - Lower CO₂ capture cost and make CO₂ capture acceptable in more industries
 - Generate high-quality CO₂ via relatively low temperature CO₂ capture via avoidance of amine oxidation
 - Increase employments through the commercialization of both CO₂ capture and utilization technologies
 - Reduce the cost of CO₂ utilization and thus improve CO₂ utilization-based economy

Potential significance of the results of the work

- Environmental benefits:
 - Capturing CO₂ is beneficial to environment. The additional benefits of this technology include
 - Lowering CO₂ emission resulting from CO₂ capture itself due to the lower energy demand of the new CO₂ capture technology
 ¤ lower energy consumption means lower CO₂ emission
 - Liquid waste discharge is reduced due to a higher CO_2 capture efficiency of the new technology (or higher amine utilization efficiency) and thus less demands for the solvent and water for capturing the same amount of CO_2
 - Secondary air pollution is reduced because
 - Any amines used for CO₂ captures could generate secondary pollution, resulting from the oxidation of amines
 - A higher CO₂ capture efficiency means less demand for amine

Relevancy to fossil energy

► The new CO₂ capture technology can help DOE

- Meet its mission ensuring America's access to and use of safe, secure, reliable, and affordable fossil energy resources and strategic reserves
- Realize its vision improving the living standards of the American people with clean, efficient, and reliable energy
- Achieve its goal
 - Develop secure and affordable fossil energy technologies
 - Enhance U.S. economic and energy security
 - Develop and maintain world-class organizational excellence

Statement of project objectives (SOPO)

Objectives

- Develop an innovative catalytic CO₂ capture technology (never reported in literature)
 - Dramatically increasing CO₂ sorption and desorption rates at <100 °C (especially CO₂ desorption rate)
 - So that the waste heat in industry can be well used
 - Avoiding the need for state-of-the-art spent solvent regeneration at >100 °C
 - ▶ Lowing CO₂ capture cost to <\$30/tonne-CO₂
 - ► Generating >95%-purity CO₂

Statement of project objectives (SOPO)

Scope of work

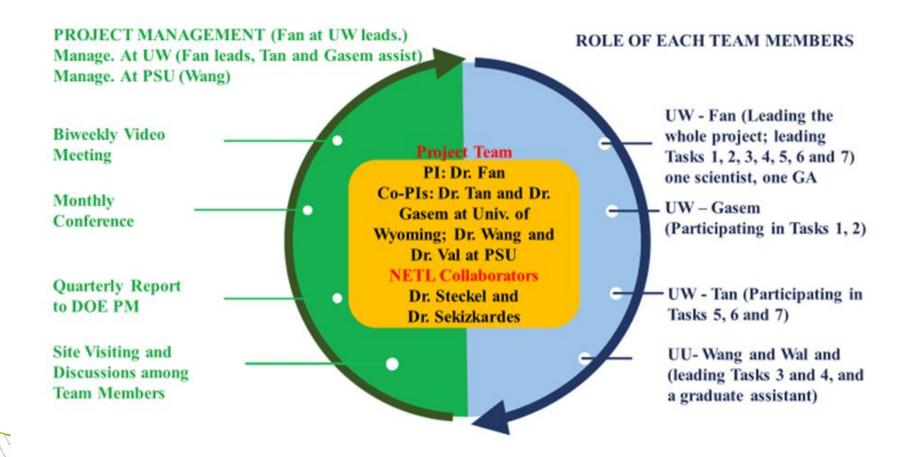
- Preparation and characterization of catalyst
 - ChCl-C₃H₃AlO₆ (choline chloride-aluminum formate) or CCAF
- Evaluation of the CO₂ capture performance of the catalytic solvent
- Study on the thermodynamics, reaction kinetics, mass and heat transfer, reaction mechanism
- Techno-economic analysis

Collaborative work with NETL

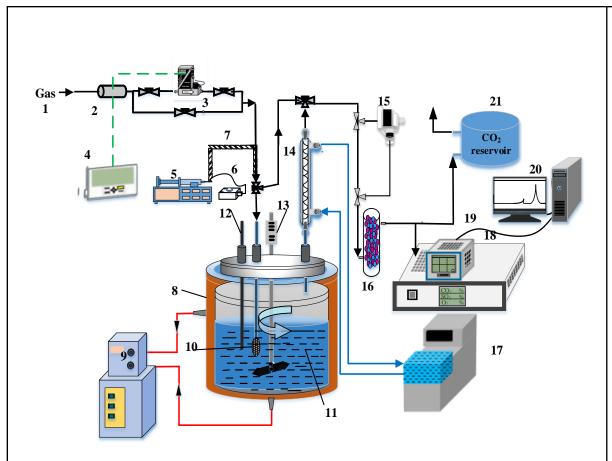
- Work with NETL's Materials Engineering & Manufacturing Directorate (MEM) on
 - Task 1 Catalyst preparation and characterization
 - Task 2 Evaluation of the new CO₂ capture technology
 - Task 3 Study on thermodynamics and reaction kinetics
 - Task 5 Investigation of mass and heat transfer
 - Task 7 Techno-economic analysis
- Work with System Engineering and Analysis (SEA) to quantify the potential advantages associated with the proposed novel CO capture technology via the performance of Task 7

Other relevant aspects of the project management plan (PMP)

- Project organization and structure



► CO₂ capture setup



1, Air; 2: filter; 3: mass flow controller; 4: mass flow controller control module; 5: syringe pump 5: temperature controller for heating tap; 7: heating tap; 8: furnace; 9: thermostatic water bath; 10: catalytic sorbent or CCAF-P; 11: muffler for inlet gas; 12: thermocouple; 13: mechanical stirrer; 14: condenser; 15: vacuum pump; 16: moisture remover; 17: cooling unit; 18: gas analyzer; 19: data recorder; 20: computer; 21: CO_2 reservoir.

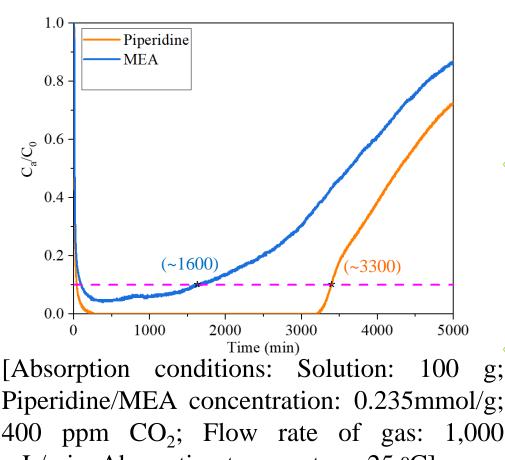
Pitures of CO₂ capture setup



CO₂ capture experiment

- **Absorption**: Piperidine solutions are prepared by mixing piperidine with deionized water. Predetermined amount of catalysts (ChCl-C₃H₃AlO₆) are added into the reactor. The mass flow controller is used to control flow rate of the simulated flue gas. H₂O is introduced into the inlet gas stream by a syringe pump The simulated flue gas is bubbled into piperidine solution via a corrosion-resistant muffler (<100 microns). The CO₂ concentration of the outlet gas of the reactor is measured with an inline gas analyzer, and the measured concentration-time profile is recorded by a data recording unit.
- **Desorption**: CO_2 desorption is realized by heating the spent sorbent obtained from CO_2 sorption step to a desired desorption temperature. A vacuum pump can be added to promoted the desorption. The desorbed CO_2 goes through a check valve and mixed with carrier gas (N_2) with a flow rate of 500 mL/min. The CO_2 concentration of the gas mixture is measured by an in-line gas analyzer. The quantity of CO_2 desorbed can be calculated by integrating the recorded CO_2 sorption profiles.

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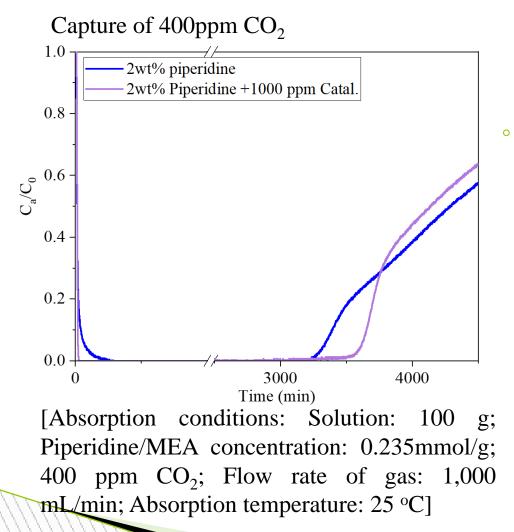


mL/min; Absorption temperature: 25 °C]

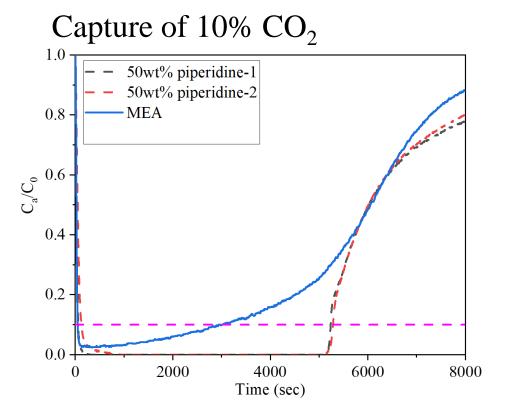
- Piperidine-based sorbent showed better CO_2 absorption performance than MEA-based sorbent, especially, the effective time for achieving 90% or 100% CO_2 absorption efficiency.
- Piperidine-based sorbent can keep achieving 100% CO₂ for 3200 min under tested conditions. MEA-based sorbent can not achieve 100% time.

Piperidine-based sorbent can achieve >90% CO_2 absorption for 3300 min under tested conditions. MEA-based sorbent can achieve >90% CO_2 absorption 1600 min.

Capture of 400 ppm CO₂



 1000 ppm is the optimal catalyst loading for 2 wt% piperidine-based sorbent.

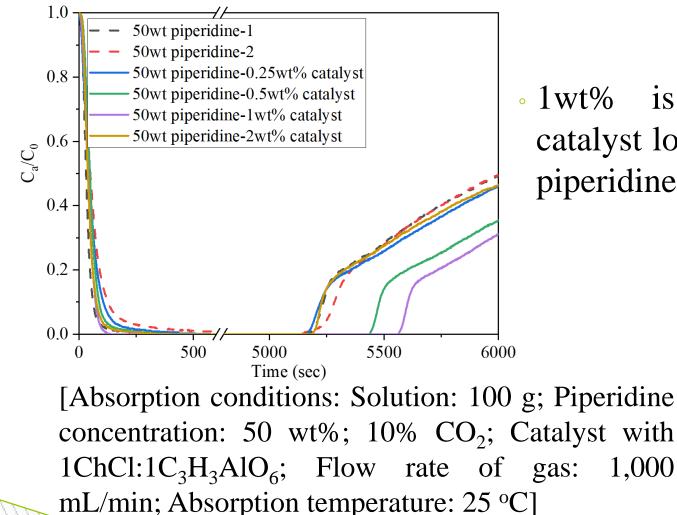


[Absorption conditions: Solution: 100 g; Piperidine/MEA concentration: 5.87mmol/g; 10% CO₂; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]

- Piperidine-based sorbent showed better CO_2 absorption performance than MEA-based sorbent, especially, the effective time for achieving 90% or 100% CO_2 absorption efficiency.
- Piperidine-based sorbent can keep achieving 100% CO₂ for 5150 sec under tested conditions. MEA-based sorbent can not achieve 100% time.

• Piperidine-based sorbent can achieve >90% CO_2 absorption for 5200 sec under tested conditions. MEA-based sorbent can achieve >90% CO_2 absorption 3000 sec.

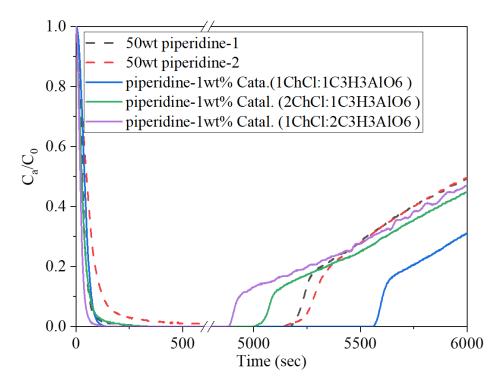
Capture of 10% CO₂



 1wt% is the optimized catalyst loading for 50 wt% piperidine-based sorbent.

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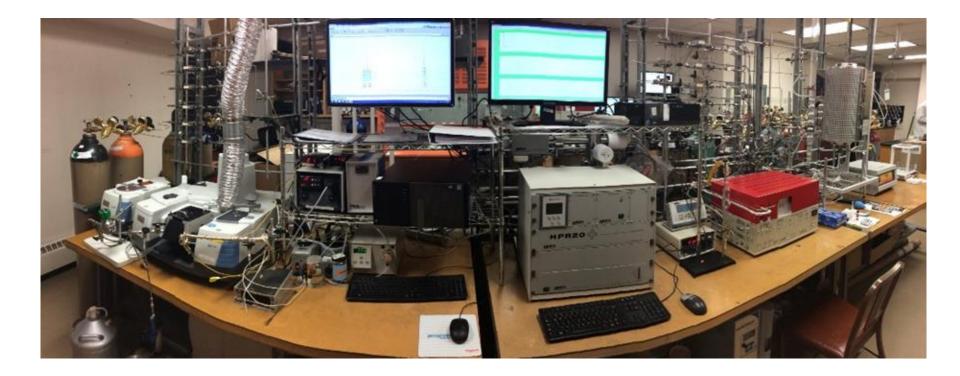
Capture of 10% CO₂



• 1ChCl:1C₃H₃AlO₆ is the best ratio for Piperidine-based sorbent.

[Absorption conditions: Solution: 100 g; Piperidine concentration: 50 wt%; 10% CO₂; Flow rate of gas: 1,000 mL/min; Absorption temperature: 25 °C]

FTIR based reaction mechanim study setup is ready



> Other frequently used instruments for the project are ready



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- Dr. Janice A. Steckel at all the people at NETL
- for their guidance!

Questions? Please.