Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO₂ Capture

(DOE/NETL Agreement No. DE-FE0004360)

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Pittsburgh, PA  •  July 8-11, 2013
Prime Contractor

- Illinois State Geological Survey (ISGS)
  - One of five scientific surveys at Prairie Research Institute, University of Illinois
  - 200 scientists and technical support staff
  - Lead organization of Midwest Geological Sequestration Consortium (MGSC) Partnership
  - ISGS’s Applied Research Laboratory conducts carbon capture and other energy & environmental technology researches
Project Overview
Project Team

Illinois State Geological Survey-University of Illinois

- Bench- and lab-scale experimental studies
- Nick Devries, Yongqi Lu (PI), David Ruther, Manoranjan Sahu, Qing Ye, Xinhuaie Ye, Shihan Zhang

Carbon Capture Scientific, LLC

- Risk analysis and techno-economic studies
- Scott Chen, Zhiwei Li, Kevin O’Brien (Sub-PI)

DOE/NETL (Funder)

- Project manager - Andrew Jones

Illinois Clean Coal Institute (Co-Funder)

- Project manager – Joseph Hirschi
## Project Performance Dates and Budget

- **Project duration:** 39 months
  - **BP1:** 1/1/11 - 12/31/11
  - **BP2:** 1/1/12 - 3/31/13
  - **BP3:** 4/1/13 - 3/31/14

- **Budget**

<table>
<thead>
<tr>
<th></th>
<th>Budget, $</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE/NETL</td>
<td>1,291,638</td>
</tr>
<tr>
<td>ICCI (cash)</td>
<td>201,000</td>
</tr>
<tr>
<td>UIUC (in kind)</td>
<td>134,357</td>
</tr>
<tr>
<td>CCS, LLC (in kind)</td>
<td>47,713</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1,674,708</strong></td>
</tr>
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(Cost share: ~23%)
Project Objectives

- Perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the proposed CO$_2$ capture process to a pilot-scale demonstration level upon completion of the project

  - ISGS/UIUC team: Lab- and bench-scale tests to generate thermodynamics and reaction engineering data for major unit operations
  
  - CCS, LLC team: Technical risk mitigation analysis and techno-economic studies
Technology Fundamentals/Background
Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP)

- Absorption into 30-40wt% potassium carbonate (PC) solution at 60–80°C
- Working capacity of PC: 15/20% to 40/50% carbonate-to-bicarbonate (CTB) conv.
- Crystallization at near room temperature (~30°C)
- Stripping of bicarbonate slurry at ≥10 atm
**Major Reactions**

**CO₂ absorption at 60−80°C:**

\[
CO_2 + H_2O + K_2CO_3 = 2KHCO_3
\]

**CO₂ desorption at ≥130°C:**

\[
KHCO_3 = CO_2(g) \uparrow + H_2O + K_2CO_3
\]

**Crystallization at 30°C:**

\[
KHCO_3 = KHCO_3(s) \downarrow
\]
Advantages of Hot-CAP over Conventional MEA

<table>
<thead>
<tr>
<th>Items</th>
<th>MEA</th>
<th>Hot-CAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>30wt% MEA</td>
<td>30-40wt% K$_2$CO$_3$</td>
</tr>
<tr>
<td>Solvent degradation</td>
<td>Y</td>
<td>N</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Y</td>
<td>Less significant</td>
</tr>
<tr>
<td>Absorption temperature</td>
<td>40-50°C</td>
<td>60-80°C</td>
</tr>
<tr>
<td>Stripping temperature</td>
<td>120°C</td>
<td>130-200°C</td>
</tr>
<tr>
<td>Stripping pressure</td>
<td>1.5-2 atm</td>
<td>≥10 atm</td>
</tr>
<tr>
<td>Phase change bw absorb. and stripping</td>
<td>N</td>
<td>Crystallization</td>
</tr>
<tr>
<td>FGD required</td>
<td>Y</td>
<td>N</td>
</tr>
</tbody>
</table>

- **High stripping pressure**
  - low compression work
  - low stripping heat (high CO$_2$/H$_2$O ratio)

- **Low sensible heat**
  - Comparable stripping working capacity to MEA
  - Lower Cp (60% of MEA)

- **Low heat of absorption**
  - 18 kcal/mol CO$_2$ (crystallization heat included) vs. 21 kcal/mol for MEA
Technical Risks/Challenges to Be Addressed

A. Is overall rate of CO₂ absorption into PC comparable to 5M MEA?
B. Can CO₂ stripping operate at high pressure (e.g. ≥10 bar)?
C. Can fouling risk due to bicarbonate precipitation on surfaces of heat exchangers and crystallizer coolers be prevented?
D. Is crystallization rate fast enough (e.g., residence time of <1 hr)?
E. Can the stripper be designed to handle slurry while operating at high pressure?
F. Can SO₂ removal be combined in Hot-CAP?
Progress and Current Status of Project
### Project Major Tasks, Progress and Milestones Achieved

<table>
<thead>
<tr>
<th>Project Tasks</th>
<th>Progress to date</th>
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</thead>
<tbody>
<tr>
<td><strong>Task 0. Project planning &amp; management</strong></td>
<td>In progress</td>
</tr>
<tr>
<td><strong>Task 1. Kinetics of CO₂ absorption</strong></td>
<td>Completed (Supplementary tests (with Na₂CO₃) in progress)</td>
</tr>
<tr>
<td>• Absorption with and w/o promoters</td>
<td></td>
</tr>
<tr>
<td>• Absorption column tests</td>
<td></td>
</tr>
<tr>
<td><strong>Task 2. Crystallization kinetics &amp; solubility of bicarbonate</strong></td>
<td>Completed</td>
</tr>
<tr>
<td>• KHCO₃ crystallization tests</td>
<td></td>
</tr>
<tr>
<td>• NaHCO₃ crystallization tests</td>
<td></td>
</tr>
<tr>
<td><strong>Task 3. Phase equilibrium &amp; kinetics of high pressure CO₂ stripping</strong></td>
<td>VLE completed; Column tests in progress</td>
</tr>
<tr>
<td>• VLE measurements</td>
<td></td>
</tr>
<tr>
<td>• Stripping column tests</td>
<td></td>
</tr>
<tr>
<td><strong>Task 4. Reclamation of sulfate from SO₂ removal</strong></td>
<td>Proof-of-concept tests completed; Tests on process improvement in progress</td>
</tr>
<tr>
<td>• Semi-continuous reclamation tests</td>
<td></td>
</tr>
<tr>
<td>• Process modification/improvement</td>
<td></td>
</tr>
<tr>
<td><strong>Task 5. Techno-economic evaluation</strong></td>
<td>Risk analysis completed; Economic evaluation in progress</td>
</tr>
<tr>
<td>• Risk mitigation analysis</td>
<td></td>
</tr>
<tr>
<td>• Process simulation</td>
<td></td>
</tr>
<tr>
<td>• Economic evaluation</td>
<td></td>
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- Currently in 1st quarter of BP3
- 17 milestones in BP1 and BP2
  - 16 milestones completed on schedule
  - 1 milestone extended for 3 months
(1) Studies of CO\textsubscript{2} Absorption: Promoter Screening Tests Using a Stirred Tank Reactor (STR)

Screening tests using STR:
- 3 inorganic and 8 organic promoters
- 3 promoters selected for packed bed column testing

Instant rate of CO\textsubscript{2} absorption:

$$J_{CO2} = \frac{dP_{CO2}}{dt} \frac{V_g}{RTA_{GL}}$$
**CO₂ Absorption Column Tests: Experimental Setup**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column height, m</td>
<td>10 ft</td>
</tr>
<tr>
<td>Packed bed height</td>
<td>7 ft</td>
</tr>
<tr>
<td>Absorber diameter, cm</td>
<td>4 in</td>
</tr>
<tr>
<td>Height of packing element</td>
<td>4 in</td>
</tr>
<tr>
<td>Diameter of packing element</td>
<td>4 in</td>
</tr>
<tr>
<td>Specific surface area</td>
<td>800 m²/m³</td>
</tr>
<tr>
<td>Void fraction (ε)</td>
<td>0.66</td>
</tr>
</tbody>
</table>

**Diagram:**
- CO₂ analyzer
- Dryer
- Humidity meter
- Steam generator
- Air compressor
- CO₂ cylinder
- Solution discharge
- Peristaltic pump
- Column
- Stock Solution
- Heater
- TC: Thermal couple
- Pr: Pressure measure
- FM: Flow meter
- TCtr: Temperature controller
- TCtr: Temperature controller
Column Tests Revealed More Favorable Rate of CO₂ Absorption into 40wt% PC + Promoter than 5M MEA

(70°C absorption in 40wt% PC and 50°C in 5M MEA; inlet CO₂ = 14 vol%, L/G = 4.7 lb/lb)
(30% CO₂ removal efficiency equivalent to ~11% increase in CTB thru the column)

- CO₂ removal by PC40+1M DEA or 0.5M PZ at 70°C > 5M MEA at 50°C
- W/o promoter, CO₂ removal efficiency by 40wt% PC was insignificant
(2) Studies of Bicarbonate Crystallization

A process configuration developed to address fouling risk and heat recovery:

- Conventional single-crystallizer design requires a large $\Delta T$ between inflow and outflow, undesirable for heat recovery

- Multiple crystallization tanks/modules developed with a vendor to reduce $\Delta T = \sim 5^\circ\text{C}$
Crystallization Tests in a Continuous Mixed Suspension-Mixed Product Removal (MSMPR) Reactor

- **CO₂-rich feed solution:**
  - Temperature: 70°C
  - Composition: K₂CO₃/KHCO₃ (PC40-40)

- Test conditions selected to simulate multiple-CSTR process
  - 70-55°C
  - 55-45°C
  - 45-35°C

- Crystallization rate constants (nucleation and growth) determined

1-liter calorimetric CSTR (Syrris Atlas);
Crystal size distribution analysis (Horiba LA-950)
Morphology and Composition of Crystal Particles

- High-purity kalicinite (KHCO₃) prevailed in crystal phase
- Prism-shaped (hexagonal) morphology
- Yield of KHCO₃ crystals consistent to its solubility at crystallization T

XRD pattern of a typical kalicinite (KHCO₃) sample

SEM image of KHCO₃ crystal (end T=45 °C)
Parametric Tests Indicated Fast Crystallization of KHCO$_3$

- Crystal growth and nucleation rates measured at different agitation rates, mean residence times (MRT, 15, 30, 45 min) and T-dependent super-saturation levels (TSL, T=35, 45, 55°C)

- Mean particle size of KHCO$_3$ crystals under test conditions: 233-455 µm
  - Crystal size large enough for ~100% liquid-solid separation in conventional hydrocyclone
  - Crystallization time ≤ 45 min is sufficient
(3) Studies of CO₂ Stripping: VLE measurement for K₂CO₃/KHCO₃ Slurry

- Gas analysis using GC and liquid analysis using a back-titration method
- 40-70wt% KHCO₃/K₂CO₃ slurry at 120-200°C
VLE Results Indicated that High Stripping Pressure is Thermodynamically Feasible in Hot-CAP

- High $P_{\text{total}}$ and low $P_{\text{H}_2\text{O}}/P_{\text{CO}_2}$ ratio attained
- Higher $P_{\text{total}}$ and lower $P_{\text{H}_2\text{O}}/P_{\text{CO}_2}$ ratio at higher temperature, CTB conversion, or PC concentration
- Stripping column: 7 ft high x 1 in ID; 3 kW electrically heated reboiler
- Slurry supply tank: 10 gallon vol., 5 kW electrical heater
- Control panel and monitoring (T, P, rpm, flow rate, etc.)
- System rated at 200 °C and 500 psia
Initial results indicated good performance of CO₂ stripping even with less concentrated feed slurry.

- Initial results with relatively low concentration slurry (30-50 wt%) confirmed that high $P_{total}$ and low $P_{H₂O/P_{CO₂}}$ were possible.
- Increasing feed CTB% conversion and reboiler temperature favored performance of CO₂ stripping.
- Parametric tests in progress to investigate:
  - Effects of CTB% in feed, slurry concentration, stripping T, slurry flow rate, etc.

<table>
<thead>
<tr>
<th>Temperature in reboiler (°C)</th>
<th>Rich solution*</th>
<th>Lean solution</th>
<th>Feed flow rate (LPM)</th>
<th>CO₂ flow rate (ml/min)</th>
<th>$P_{total}$ in column (psia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>PC40-40</td>
<td>PC40-33</td>
<td>0.1</td>
<td>660</td>
<td>39</td>
</tr>
<tr>
<td>160</td>
<td>PC40-40</td>
<td>PC40-20</td>
<td>0.1</td>
<td>2,022</td>
<td>81</td>
</tr>
<tr>
<td>160</td>
<td>PC30-60</td>
<td>PC30-54</td>
<td>0.1</td>
<td>270</td>
<td>89</td>
</tr>
<tr>
<td>140</td>
<td>PC32-80</td>
<td>PC32-55</td>
<td>0.1</td>
<td>1,900</td>
<td>69</td>
</tr>
<tr>
<td>170</td>
<td>PC32-80</td>
<td>PC32-48</td>
<td>0.1</td>
<td>2,435</td>
<td>97</td>
</tr>
<tr>
<td>180</td>
<td>PC50-60</td>
<td>PC50-48</td>
<td>0.1</td>
<td>1,700</td>
<td>108</td>
</tr>
</tbody>
</table>

* PC X-Y stands for X wt% $K₂CO₃$-equivalent concentration and Y% carbonate-to-bicarbonate (CTB) conversion.
(4) Reclamation of Sulfate for SO$_2$ Removal in Hot-CAP: Process Proof-of-Concept Tests

SO$_2$ absorption into PC: $K_2CO_3 + SO_2 + 1/2O_2 = K_2SO_4 + CO_2$

K$_2$SO$_4$ reclamation process:

- Reaction with lime: $K_2SO_4 + CaO + 2H_2O + CO_2 = K_2CO_3 + CaSO_4 \cdot 2H_2O(\downarrow)$
- Competitive reaction: $Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3(\downarrow)$

Inhibition by high-P CO$_2$: $CaCO_3(s) + CO_2 + H_2O = Ca(HCO_3)_2(aq)$

Semi-continuous experimental results:

- Precipitates: gypsum (0-58wt%), syngenite (0-91%), vaterite/calcite (0-100%)
- Precipitates from most tests contained >30% vaterite/calcite
- Precipitation of CaSO$_4$ favored over CaCO$_3$ at lower T or lower PC concentration

Example: XRD of precipitates from three PC-0.4M K$_2$SO$_4$-0.4M CaCl$_2$ systems.
A Modified Process Option for K$_2$SO$_4$ Reclamation

- Major reactions:
  - Absorption: $2\text{K}_2\text{CO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_3 + \text{H}_2\text{CO}_3$;
  - $2\text{KHCO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_3 + 2\text{H}_2\text{CO}_3$
  - Oxidation: $\text{K}_2\text{SO}_3 + \frac{1}{2} \text{O}_2 \rightarrow \text{K}_2\text{SO}_4$ (s)$\downarrow$
  - Reclamation: $\text{K}_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow 2\text{KOH} + \text{K}_2\text{SO}_4$ (s)$\downarrow$

- Solubility:
  - $\text{K}_2\text{SO}_3, \text{K}_2\text{CO}_3, \text{KHCO}_3 \gg \text{K}_2\text{SO}_4$

- Tests of $\text{K}_2\text{SO}_3$ oxidation and $\text{K}_2\text{SO}_4$ precipitation in progress.
773 MWe power plant (gross w/o CO₂ capture) equipped with Hot-CAP
Preliminary Results of Process Simulation and Sizing

Column sizing:
- 2 absorbers, each of 14.7-m ID x 25-m height
- 1 stripper, 7.3-m ID x 10-m height
- Packed with Mellapak M250.Y

Energy performance:

<p>| | |</p>
<table>
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<tr>
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<tbody>
<tr>
<td>CO₂ Stripping (kWh/ kg CO₂)</td>
<td>0.155</td>
</tr>
<tr>
<td>Compression work (kWh/ kg CO₂)</td>
<td>0.075</td>
</tr>
<tr>
<td>Other loads (kWh/ kg CO₂)</td>
<td>0.04</td>
</tr>
<tr>
<td>Total electricity use (kWh/kg CO₂)</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Current simulation based on a low stripping P (2 bar) due to lack of data at T>140°C in ProTreat software

- Higher stripping P and better energy performance expected at T>140°C due to high adsorption + crystallization heat (~18 kcal/mol)
- High stripping-P scenarios (>>2 bar) will be simulated by incorporating measured VLE data into software
Plans for future testing/ development/ commercialization
Work Plan in BP3

- High pressure CO$_2$ stripping tests
  - Stripping performance tests
  - Stripping process optimization

- Proof-of-concept testing of a modified process option for combined SO$_2$ removal and CO$_2$ capture

- Techno-economic studies
  - Process optimization study
  - Equipment sizing and cost analysis
Technology Scale-up Development

- Process optimization and improvement to reduce technical risks and enhance performance
- Detailed techno-economic analysis
- If technically and economically viable,
  - Seek federal, state, and industrial support for a pilot-scale test (0.5-3 MWe)
  - Identify industrial partners (design, manufacturing and field testing) for pilot-scale demonstration
Acknowledgements

- U.S. Department of Energy/ National Energy Technology Laboratory under Agreement No. DE-FE0004360

- Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute under Project No. 11/US-6