Advanced Solid Sorbents and Process Designs for Post-Combustion CO$_2$ Capture (DE-FE0007707)

RTI International
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Project Overview

Objective
Address the technical hurdles to developing a solid sorbent-based CO₂ capture process by transitioning a promising sorbent chemistry to a low-cost sorbent suitable for use in a fluidized-bed process.

This project combined previous technology development efforts: RTI (process) and PSU (sorbent).

Period of Performance:
- 10/1/2011 to 12/31/2015

Cost Share in $1,000s

- DOE Share
- Cost Share

$850

$2,997

- Project management
- Process design
- Fluidized-bed sorbent

- PSU’s EMS Energy Inst.
- PEI and sorbent improvement

- Masdar New Ventures
- Masdar Institute
- TEA of NGCC application
Solid Sorbent CO₂ Capture

Advantages

• Potential for reduced energy loads and lower capital and operating costs
• High CO₂ loading capacity; higher utilization of CO₂ capture sites
• Relatively low heat of absorption; no heat of vaporization penalty
• Avoidance of evaporative emissions
• Superior reactor design for optimized and efficient CO₂ capture performance

Challenges

• Heat management / temperature control
• Solids handling / solids circulation control
• Physically strong / attrition-resistant
• Stability of sorbent performance

Technology Features

• Sorbent: supported polyethyleneimine
• Process: fluidized, moving-bed

Sorbent Chemistry (PEI)

Primary: \[ \text{CO}_2 + 2\text{RNH}_2 \rightleftharpoons \text{NH}_4^+ + \text{R}_2\text{NCOO}^- \]
Secondary: \[ \text{CO}_2 + 2\text{R}_2\text{NH} \rightleftharpoons \text{R}_2\text{NH}_2^+ + \text{R}_2\text{NCOO}^- \]
Tertiary: \[ \text{CO}_2 + \text{H}_2\text{O} + \text{R}_3\text{N} \rightleftharpoons \text{R}_3\text{NH}^+ + \text{HCO}_3^- \]
**Technical Approach & Scope**

<table>
<thead>
<tr>
<th>Previous Work</th>
<th>RTI's Project</th>
<th>Future Development</th>
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</thead>
</table>

**Proof-of-Concept / Feasibility**

**Laboratory Validation (2011 – 2013)**

**Economic analysis**
- Milestone: Favorable technology feasibility study

**Sorbent development**
- Milestone: Successful scale-up of fluidized-bed sorbent

**Process development**
- Milestone: Working multi-physics, CFD model of FMBR
- Milestone: Fabrication-ready design and schedule for single-stage contactor

**Prototype Testing (2015)**

**Prototype Testing**
- Milestone: Operational prototype capable of 90% CO₂ capture
- Milestone: Completion of extensive parametric and long-term testing campaigns

**Updated Economics**
- Milestone: Favorable technical, economic, environmental study (i.e. meets DOE targets)


**Process development**
- Milestone: Fully operational bench-scale FMBR unit capable of absorption / desorption operation
- Milestone: Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype

**Sorbent development**
- Milestone: Successful scale-up of sorbent material with confirmation of maintained properties and performance

**Technology Readiness Level**

1 2 3 4 5 6 7 8 9
Packed-bed Reactor

- Fully-automated operation and data analysis; multi-cycle absorption-regeneration
- Rapid sorbent screening experiments
- Measure dynamic CO$_2$ loading & rate
- Test long-term effect of contaminants

“visual” Fluidized-bed Reactor

- Verify (visually) the fluidizability of PEI-supported CO$_2$ capture sorbents
- Operate with realistic process conditions
- Measure $\Delta P$ and temperature gradients
- Test optimal fluidization conditions
**Objective**

Improve the thermal and performance stability and production cost of PEI-based sorbents while transitioning fixed-bed MBS materials into a fluidizable form.

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**PEI-impregnated Silica (“Gen1”)**

- Stability improvements through addition of moisture and PEI/support modifications.
- Suitable low-cost, commercial supports identified (1000x cost reduction).
- Converted sorbent to a fluidizable form.
- Optimized Gen1 sorbent through: solvent selection; drying procedure; PEI loading%; regeneration method; support selection; etc.

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**Co-Precip Amine/Silica (“Gen2”)**

- Extremely stable sorbent, high CO₂ loadings (10 - 14 wt%).
- **Key benefits**: stability in liquid water, high CO₂ loadings, tailoring potential, diverse applications
- **Challenges**: density, physical strength, cost
- Mixed results with most promise identified in the use of blended amines and templates
Sorbent Scale-up

Initial Scale-up (150 kg)
- 30 wt% PEI on commercially-available silica
- Scaled-up sorbent matches performance and properties of lab sorbent

<table>
<thead>
<tr>
<th></th>
<th>Amount</th>
<th>PEI Loading</th>
<th>CO₂ Capacity</th>
<th>FBR Test</th>
<th>PSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab Sorbent</td>
<td>100+ g</td>
<td>30 %</td>
<td>8.5 wt%</td>
<td>Pass</td>
<td>75 – 250 um</td>
</tr>
<tr>
<td>Scaled-up Sorbent</td>
<td>150 kg</td>
<td>30 %</td>
<td>8.9 wt%</td>
<td>Pass</td>
<td>80 – 250 um</td>
</tr>
</tbody>
</table>

Sorbent Make-up Batch (100 kg) – following Oxidative Degradation
- Improved silica selection, optimized PEI loadings
- 6 months of bench-scale testing exhibited little to no degradation

Scale-up Batch (100 kg) – made for RTI’s project with Norcem (cement application)
- Improved commercial preparation
- Sorbent exhibits improved CO₂ capture performance
RTI’s Bench-scale Prototype System

Specifications

- **Flue gas throughput**: 300 and 900 SLPM
- **Solids circulation rate**: 75 to 450 kg/h
- **Sorbent inventory**: ~75 kg of sorbent
- **Adsorber temperature range**: 40 - 90°C
- **Regenerator temperature range**: 100 - 130°C
- **Heat exchange fluids**: CW in Adsorber; Steam in Regenerator
- **Footprint / Height**: 15’ x 5’ / 35’ H
- Pneumatic conveying of sorbent (Regen → Adsorber)
- Sorbent circulation rate controlled and monitored by measurement of the riser pressure drop

<table>
<thead>
<tr>
<th>FG Composition</th>
<th>CO₂</th>
<th>H₂O</th>
<th>N₂</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>15 vol%</td>
<td>3 vol%</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Operational improvements

- Optimized loop seal aeration to maximize solids circulation
- Eliminated static electricity build-up which caused agglomeration
- Added pneumatic vibrators to downcomers, improving circulation
- Modified gas entrance arrangement to primary cyclone and added secondary cyclone to improve sorbent recovery
- Added larger downcomers for additional circulation reliability
- Full system reconfiguration:
  - Original configuration: 4-stage Ads, 1-stage Regen
  - Reconfiguration to 2-stage Ads, 2-stage Regen
**CO₂ Capture Efficiency**

- Stage-1
- Stage-2
- Stage-3
- Stage-4

**CO₂ Mass Balance**

- Good correlation between calculated and experimentally measured heating and cooling duties (within +/- 10%)
Scaled-up sorbent was observed to have a steady decline in the sorbent’s CO₂ capacity over several hundred hours of testing. CO₂ sorption capacity was impacted while fluidizability and other key physical parameters remained unaffected.

### Potential Degradation Pathways

- PEI-leaching
- Dry flue gas
- Dry stripping gas
- Exposure to oxygen
- Combination of the conditions listed above.

### A Design of Experiments (DoE) study was implemented and a half factorial test campaign for five parameters

### Conclusions

- Two most important factors: O₂ concentration (i.e. exposure to O₂) and the temperature at which O₂ exposure occurs
- 3rd factor (absence of H₂O in stripping gas), important but is reversible
- Sorbent O₂ exposure at < 70°C is acceptable
- Sorbent cooler is recommended when conveying with air
• Reactor staging required to maximize performance; well-mixed single-stage reactors limit achievable rich and lean loadings
• Adsorber: equilibrium loading calcs and experimental observations suggest 2 stages are sufficient
• Regenerator: 2 stages, minimum required

Bench system reconfiguration
• Removed bottom two adsorber stages which do not participate in CO₂ capture but act as dead/inert volume
• 2-stage Adsorber, 2-stage Regenerator
Highlights of prototype testing

- Cumulative testing: 1,000+ circulation hours; 420+ CO$_2$ capture hours.
- The sorbent is capable of rapid removal of CO$_2$ from the simulated flue gas.
- Sustained 90% capture of the CO$_2$ in simulated flue gas stream is easily achieved.
- Collected a wealth of performance data, identified how system performance varies due to process variables, and proved the reliable nature of bench-scale testing.
Highlights of prototype testing

Heat Management
- Complicated by large heat losses to environment
- Able to demonstrate superior CO₂ capture performance with heat management

Operating Parameters
- Able to quantify system response and performance due to changing parameters
- Able to identify optimal conditions, balancing performance with other economic factors:
  - 70°C Absorber temperature
  - 120°C Regen temperature
  - > 1 ft/s FG velocity
  - Higher S/G ratios better, but energy and footprint impacts taken into account
  - Performance at a range of FG CO₂ concentrations was quantified

Sorbent Stability
- CO₂ capacity stable between 8.5 – 9.0 wt% CO₂ loading after 6 months of testing
- Thermal and oxidative degradation avoided
Long-term Performance Testing

**Long-term testing**
- 100+ hr continuous testing, maintaining the performance target of 90% CO₂ capture while varying sorbent circulation rate
- Sorbent maintained CO₂ working capacity between 4 and 7 wt.%
- Desired set points for all process conditions and reactor settings were tightly controlled
- Robust nature of system proven

**Other Observations / Lessons**
- Attrition-resistance of sorbent is evident from similar PSD for used sorbent, fines collection rate and no sorbent make-up
- Sorbent maintains excellent hydrodynamic / fluidization properties
- Good approach-to-equilibrium achieved in all reactor stages
- Quality data collected allowing for revision of economic analysis assumptions
Summary

- **Basis**: DOE/NETL's Cost and Performance Baseline for Fossil Energy Plants – updated with lab and bench-scale test data
- Total cost of CO₂ captured ~ **45.0 $/T-CO₂**
- 43.3 $/T-CO₂ achievable through use of unproven spent sorbent scrubbing strategy
- Still represents > **25% reduction** in cost of CO₂ capture, significant energy and capital savings compared to SOTA aqueous amine solvents

Main Factors impacting TEA
- Sorbent Cost
- CO₂ content in Regenerator
- Sorbent working capacity
- Regeneration temperature

Pathway to Cost Reductions
- Adsorber/Regenerator Design
- Heat recovery and integration
- Sorbent stability and cost
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• Sorbent stability and cost
Bridge to Pilot Testing

Knowledge Gained:
- Lessons learned from bench-scale testing
- Optimal process design and operating conditions
- Sorbent scale-up and optimization

Additional Work:
- More extensive performance testing
- Testing in flue gas
- Application to multiple CO₂ sources
- Sorbent cost reduction

Concept

Commercial / Demo

Objective

Demonstrate the technical and economic feasibility of RTI’s advanced, solid sorbent CO₂ capture process in an operating cement plant

Period of Performance:
• 5/1/2013 to 12/31/2016

Two Phases

Phase I – Feasibility Review – Complete
• Sorbent exposure to actual cement plant flue gas
• Economic evaluation
• Commercial design for cement application

Phase II – Demonstration – In Progress
• Design, build, and test a prototype of RTI’s solid sorbent CO₂ capture technology
• Evaluate CO₂ capture performance
• Update economics with pilot test data
Progress and Lessons Learned

**Economics**
- Economic indicators of 38 – 46 €/t-CO2 avoided show RTI’s technology is economically competitive in CO2 capture field
- RTI’s technology is a good candidate for waste heat utilization

**Testing**
- Evaluated sorbent performance with actual cement flue gas
- No critical failure in performance over 300+ cycles. Achieved desired capacities

**Pilot Design**
- Design and engineering leveraged lessons learned on DOE-funded project
- Process Hazard Analysis
- Install complete
RTI Prototype

- **Completed:** Design, Engineering, Construction, Shipment, Installation, Commissioning, and Training
- Baseline and Parametric testing currently **underway** at Norcem’s cement plant
- Parametric and long-term performance testing planned **through Nov 2016**
Project Outcomes

Addressing Technology Challenges

- **Heat management**: Proved critical need for FMBR design through engineering analysis, lab-, and bench-scale testing
- Heat management technique in Bench system mimics commercial design
- **Solids handling**: improved sorbent working capacities, fluidizable material, and staged design reduce solids handling requirements
- Bench testing provided correlations to flow control, pressure balancing
- **Physical strength**: Bench testing proved excellent physical strength of fluidizable sorbent – very little attrition losses
- **Performance stability**: Excellent stability exhibited in bench testing
- Sorbent now has thermal-, chemical, and leaching-stability

Bridge to Pilot Testing

- Bench testing, lab screening, and modeling collected critical process design data for pilot design and detailed TEAs
- Economics are attractive with pathway to meet DOE goals
- Sorbent manufacturing has been optimized – “Gen1” sorbent is viable path forward; Gen2 sorbents exhibit great potential
- Expanding potential market application through cement plant testing and NGCC evaluations
- Detailed economic assessments highlight areas for improvement:
  - Expanded data collection, novel heat integration, sorbent cost, sorbent working capacity, further staging studies

Technology Challenges

- Heat management / temperature control
- Solids handling / solids circulation control
- Physically strong / attrition-resistant
- Stability of sorbent performance
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