Advanced Solid Sorbents and Process Designs for Post-Combustion CO$_2$ Capture

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RTI’s Johnson Science and Engineering Building
Home of RTI’s Center for Energy Technology

**RTI’s Center for Energy Technology**

- **RTI** was established in 1958 in RTP, North Carolina
- One of the world’s *leading research institutes*
- **Mission**: To improve the human condition by turning knowledge into practice
- CET develops **advanced energy technologies** to address the world’s energy challenges

## CO₂ Capture & Utilization
- Post-combustion CO₂ capture
- Pre-combustion CO₂ capture
- CO₂ utilization

## Biomass & Biofuels
- Biomass gasification
- Pyrolysis to biocrude and conventional fuels

## Advanced Gasification
- Syngas cleanup/conditioning
- Substitute natural gas production

## Fuels & Chemicals
- Syngas conversion
- Hydrocarbon desulfurization
- ANG sorbents

## Shale Gas
- Gas separation & processing
- Process water treatment

## Water & Energy
- Industrial water reuse
- Energy and waste heat recovery
Overall 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.

Project Details
- Combines previous technology development efforts – RTI (process) and PSU (sorbent)
- Project Cost: $3,847,161
  - DOE Share: $2,997,038
  - Cost Share: $850,123
- Period of performance: 10/1/2011 to 6/30/2015

Project Objectives
- Improve stability, performance, and fluidizability of novel amine-based (PEI) “Molecular Basket Sorbents”
- Improve design of fluidized, moving-bed reactor; optimize operability and heat integration
- Prove that the technology reduces parasitic energy load and capital and operating costs associated with CO₂ capture (through prototype testing and economic analyses)
Solid Sorbent CO\textsubscript{2} Capture

Flue Gas → Stack

Particulate control

Regenerated sorbent

CO\textsubscript{2} Absorber (50 – 90°C)

Water in → Water out

Blower

Caustic scrubber

CO\textsubscript{2} loaded sorbent

CO\textsubscript{2} stream

Particulate control

Sorbent Regenerator (> 110°C)

CO\textsubscript{2} to dehydration and compression

Condenser

Steam in → Steam out

Process/Plant Steam

Steam + condensate

Steam fluidizing gas
Solid Sorbent CO₂ Capture

Advantages

- Potential for reduced energy consumption compared to SOTA solvent processes
  - High CO₂ working capacity compared to solvents (higher active species concentration and utilization)
  - Reduced sensible heat load due to lower heat capacities
  - Steam stripping can be minimized
  - Avoids evaporative emissions
- Potential for reduced capital costs through simplified process designs and inexpensive materials of construction

Challenges

- Developing a low-cost sorbent with high and stable working capacity suitable for fluidized-bed processes
- Effective heat management in absorption / regeneration
- Counter-current flow of gas and solids to achieve desired process operating window
- Pressure drop across sorbent bed
Conceptual Process Arrangement:
Circulating, Staged, Fluidized-bed Reactor with Internal Heat Management

Benefits
- Mimics conventional gas-liquid absorption processes
- Counter current gas-solids flow maximizes CO₂ driving force throughout reactor length
- Bed staging effectively enables counter-current flow
- Superior gas-solid heat and mass transfer characteristics and heat management strategy minimize thermal regeneration energy
- Reduced pressure drop in fluidized state

Development Needs
- Optimize reactor design and process arrangement

Development Approach
- Detailed fluidized bed reactor modeling
- Bench-scale evaluation of reactors designs
- Demonstration of process concept

Suitable CO₂ absorbent must:
- be a fluidizable and attrition-resistant material
- achieve dynamic CO₂ loadings in excess of 8 wt%
- exhibit a heat of CO₂ absorption <80 kJ/mol of CO₂
- be inexpensive (target <$10/kg)
Polymeric Amine Sorbents

Dr. Chunshan Song’s group (PSU) has contributed 10+ years of R&D and published data in field of polymeric amine CO₂ capture.

PSU’s Molecular Basket Sorbent (MBS) material offers very promising CO₂ absorption chemistry:

- CO₂philic polymer, polyethyleneimine (PEI), supported on high surface area materials (MCM-41, SBA-15, carbon)
- High CO₂ loadings (>14 wt% CO₂)
- Reasonable heat of absorption (66 kJ/mol)

![CO₂ Balance Graph](image)

**Development Needs**

- Improve stability at high temperatures is needed for optimal process performance
  - higher regeneration temperature → increased working capacity and CO₂ pressure in product gas
  - PEI-based sorbents deactivate by several mechanisms which are exacerbated with increasing temperature
- Convert sorbent powder to low-cost, fluidizable, attrition-resistant particle suitable for use in a fluidized-bed process
Project Schedule and Milestones

### Previous Work
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#### Proof-of-Concept Feasibility Studies

#### Laboratory Validation (2011 – 2013)
- **Economic analysis**
- **Milestone**: Favorable technology feasibility study
- **Sorbent development**
- **Milestone**: Successful scale-up of fluidized-bed MBS material
- **Process development**
- **Milestone**: Working multi-physics, CFD model of FMBR design
- **Milestone**: Fabrication-ready design and schedule for single-stage contactor

#### Relevant Environment Validation (2013 – 2014)
- **Process Development**
  - **Milestone**: Fully operational bench-scale FMBR unit capable of absorption/desorption operation
- **Sorbent Development**
  - **Milestone**: Successful scale-up of MBS material with confirmation of maintained properties and performance

- **Field Testing of Prototype Unit**
- **Milestone**: Operational FMBR prototype capable of 90% CO₂ capture
- **Milestone**: Completion of 1,000 hours of parametric and long-term testing
- **Updated Economics**
- **Milestone**: Favorable technical, economic, environmental study (meets DOE targets)

#### Future Development
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- **Pilot Validation**
  - 1 - 5 MW (eq)
- **Demo**
  - ~50 MW
- **Commercial**
**Approach**

**Stability improvements through process modification**
- Addition of moisture to the regeneration gas dramatically improves the multi-cycle performance stability.
- Improvement most likely related to reducing the formation of thermally-stable urea under regeneration condition:
  \[ 2RNH_2 + CO_2 \leftrightarrow RNH-CO-NHR + H_2O \]

**Stability improvements through sorbent chemistry modifications**
- Evaluation of various PEI types shows that linear PEIs exhibit better performance stability, but are too expensive.
- Novel amine cross-linking / copolymerization / complexation pathways have good potential for stabilizing sorbent capacity.
  - Cross-linking changes the physical properties of the polymer with respect to melting/glass transition temperature and water solubility.

**Progress**
- Improved stability of PEI-based sorbent with >6.6 wt% CO₂ loading with regeneration temperature of 100°C for > 25 cycles.
Sorbent cost improvement

- **Approach**: Replace expensive mesoporous silicas with low-cost support materials and retain sorbent performance
- 25+ support materials screened. Suitable silica-based (low-cost, commercially-available) supports identified
- 1000x cost reduction over mesoporous silicas
- Additional cost reduction expected when raw materials produced at commercial scale
- Superior performance
- Cost Target <$5/kg

Conversion to fluidizable form

- Commercially-relevant strategies employed
- Converted support powders and PEI to fluidizable, attrition-resistant particles
- Prepared PEI-based sorbents with water replacement of methanol
- Spray drying with binders exhibited desired particle size distribution and densities
- Two spray dried materials have targeted attrition indices
**Fluidized-bed modeling**

- Developed a fluidized bed reactor model to simulate the performance of conceptual fluidized-bed reactor configurations
- **Characteristics:** Gas-solid hydrodynamics; sorbent physical properties; heat transfer, temperature, pressure, concentration profile
- **Use:** Understand the effect of key process and sorbent parameters on the performance of the proposed FMBR designs
- **Use:** Optimize design of CO₂ Absorber and Sorbent Regenerator including heat transfer internals and bed-staging

**Bench-scale process unit development**

- Developed a detailed engineering design package of a bench-scale contactor evaluation unit
- Designed to evaluate the effectiveness of two proposed reactor designs for CO₂ removal from flue gas

- **Specifications:**
  - Flue gas throughput: 300 and 500 SLPM
  - Solids circulation rate: 75 to 450 kg/h
  - Sorbent inventory: ~100 kg of sorbent
- **Adequately sized to avoid issues related to bed slugging**
**Basis:** DOE/NETL’s *Cost and Performance Baseline for Fossil Energy Plants Volume 1*

**Approach:** Thorough T&E assessment using process modeling & cost estimation software
- Aspen Plus; Process Economic Analyzer; ProMax (caustic scrubbing simulation)

**Summary**
- Total cost of CO₂ captured estimated to be **$39.7 T-CO₂** (SOTA Amine Process ~$68 T-CO₂)
- Total capture plant capital cost significantly lower compared to SOTA MEA process
- Further reductions in cost would come through reductions in both power consumption and capital cost

**Breakdown of the Main Contributors to the Cost of CO₂ Captured, $/T-CO₂**
- **Capital Cost:** 14.8 (37.3%)
- **Steam:** 9.9 (25.1%)
- **Electricity:** 5.3 (13.5%)
- **Variable Operating:** 5.5 (13.7%)
- **Fixed Operating:** 4.1 (10.2%)
- **CO₂ TS&M Cost:** 0.1 (0.1%)

**Total CO₂ Capture Cost - $39.7 T-CO₂**

**R&D Directions**
- Kinetic/equilibrium studies
- Long-term contaminant studies
- Study effects of particle size
- Detailed design study of FMBR

RTI technology exhibits favorable technical feasibility and process economics
Bench-scale contactor and prototype system testing
- Evaluate two proposed reactor designs for CO₂ removal from flue gas
- Demonstrate long-term stability of the sorbent and process equipment
- Demonstrate continuous operation of process under high-fidelity flue gas conditions
- Testing at RTI’s Energy Technology Development Facility
- Parametric and long-term testing (1,000+ hours)
- Collect critical process data to perform detailed T&E assessment

Sorbent optimization and scale-up
- Integrate advancements in tethering PEI and physical property improvement
- Produce sorbent for bench-scale and prototype testing (500 kg scale)

Detailed technical and economic assessment
- Update economic analyses using bench- and prototype testing data
- Continue to show ability to achieve DOE/NETL programmatic goals

Application to other industrial sources of CO₂
- Demonstrating technology at cement plant in Norway – Norcem (part of HeidelbergCement)
- Continue evaluating economic factors of NGCC application - Masdar
Energy Technology Development Facility

- Facility dedicated to hosting bench- and pilot-scale systems
- 60 ft x 50 ft x 45 ft tall enclosed structure
- Adjacent to RTI’s existing research labs
- Equipped with:
  - flue gas generation system using a LPG-fired furnace
  - closed-circuit chilled water loop
  - steam generator
  - air compressor
  - adequate electrical supply for multiple systems
- Excellent facility for bench-scale testing of solid sorbent technology development
The R&D work presented herein was made possible through funding by:

- The U.S. DOE/National Energy Technology Laboratory
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- Masdar

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