Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture

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RTI's Center for Energy Technology

RTI's Johnson Science and Engineering Building
Home of 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

CO_2 Capture & Utilization

- Post-combustion CO_2 capture
- Pre-combustion CO_2 capture
- CO_2 utilization

Biomass & Biofuels

- Biomass gasification
- Pyrolysis to biocrude and conventional fuels

Advanced Gasification

- Syngas cleanup/conditioning
- Substitute natural gas production

Fuels & Chemicals

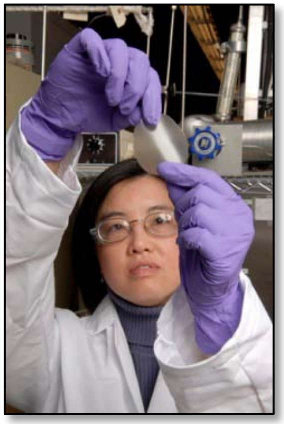
- Syngas conversion
- Hydrocarbon desulfurization
- ANG sorbents

Shale Gas

- Gas separation & processing
- Process water treatment

Water & Energy

- Industrial water reuse
- Energy and waste heat recovery



Project Overview

Overall objective: Address the technical hurdles to developing a solid sorbent-based CO_2 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

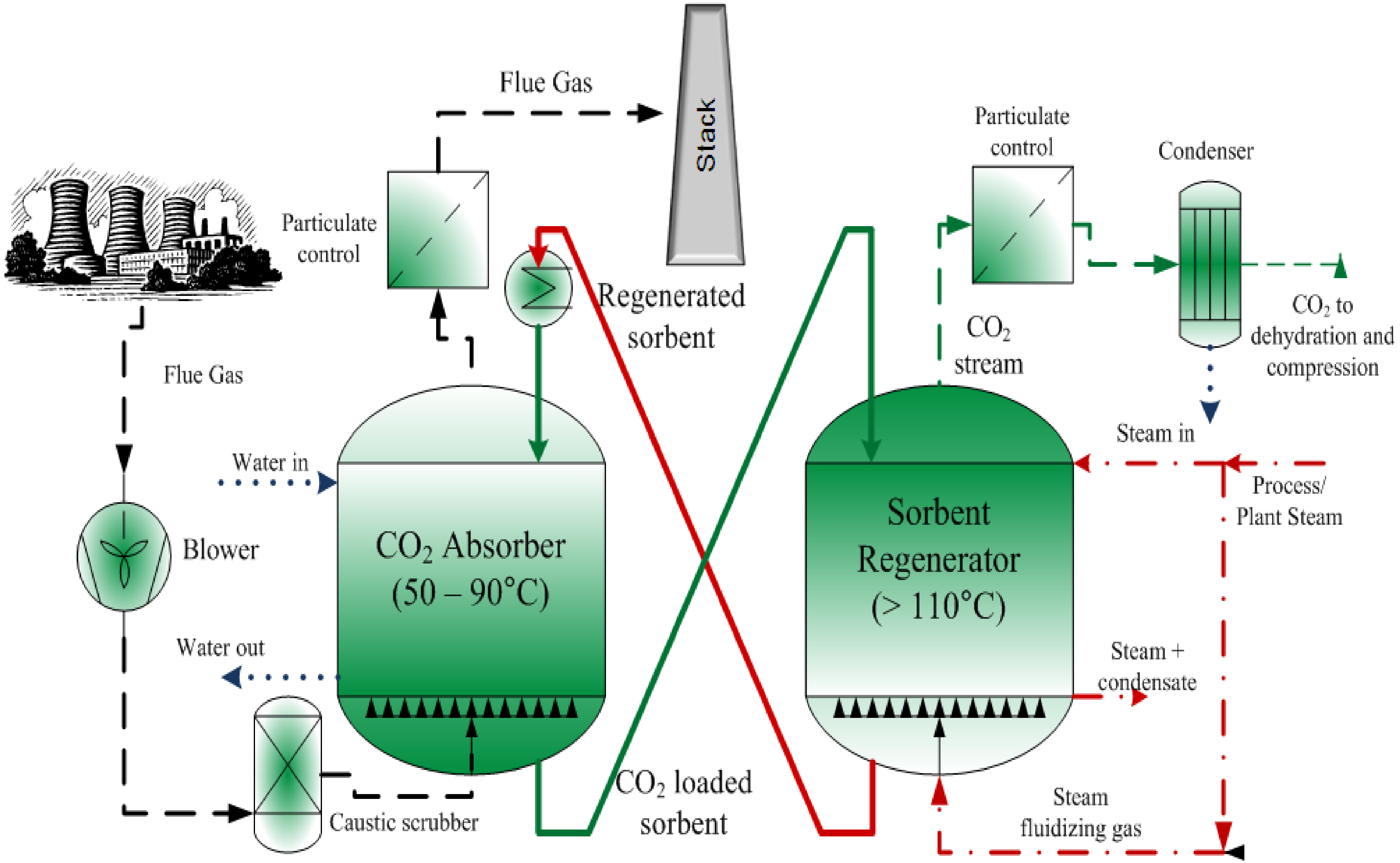
Project Objectives

- 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 CO_2 capture (through prototype testing and economic analyses)

RTI International	PennState	Masdar (A Mubadala Company)	Foster Wheeler	Clariant
▪ Project management ▪ Process design ▪ Fluidized-bed sorbent	▪ PSU's EMS Energy Inst ▪ PEI and sorbent improvement	▪ Masdar Carbon ▪ Masdar Institute ▪ NGCC application	▪ Techno-economic evaluation ▪ Process design support	▪ Sorbent scale-up ▪ Commercial manufacture evaluation

Formerly Süd-Chemie, Inc.

Solid Sorbent CO_2 Capture



Solid Sorbent CO_2 Capture

Advantages

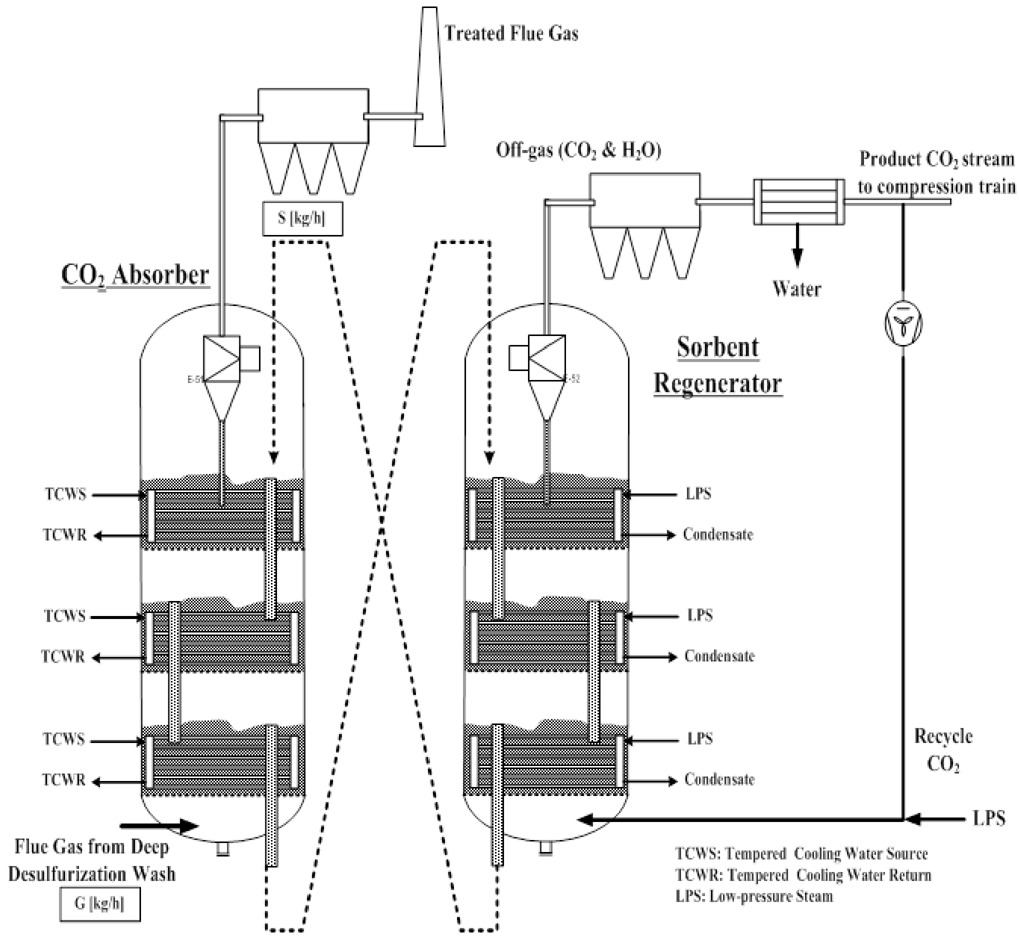
- Potential for reduced energy consumption compared to SOTA solvent processes
  - High CO_2 working capacity compared to solvents (higher active species concentration and utilization)
  - Reduced sensible heat load due to lower heat capacities
  - Steam stripping can be minimized
  - Avoids evaporative 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

Fluidized-bed Process Arrangement

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 CO_2 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

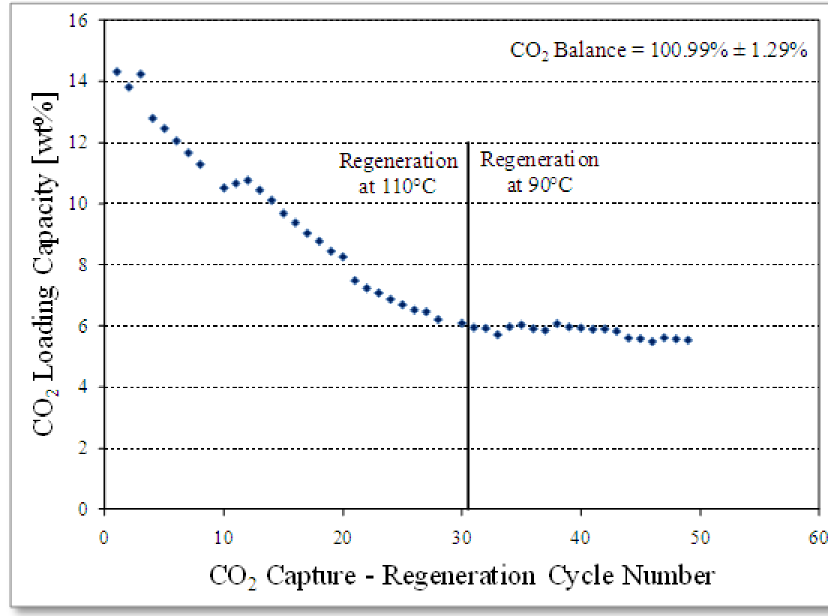
- Detailed fluidized bed reactor modeling
- Bench-scale evaluation of reactors designs
- Demonstration of process concept

Suitable CO_2 absorbent must:

- be a fluidizable and attrition-resistant material
- achieve dynamic CO_2 loadings in excess of 8 wt%
- exhibit a heat of CO_2 absorption <80 kJ/mol of CO_2
- be inexpensive (target < $10/kg)

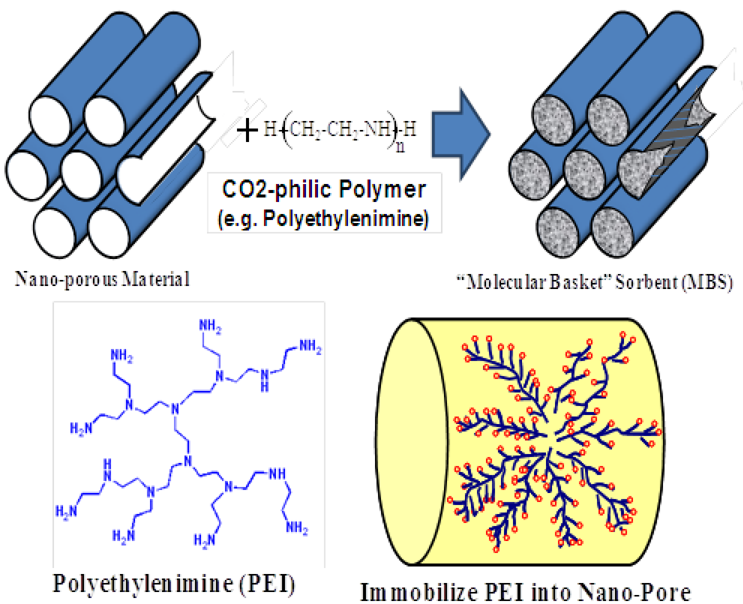
Polymeric Amine Sorbents

Dr. Chunshan Song's group (PSU) has contributed 10+ years of R&D and published data in field of polymeric amine CO_2 capture



PSU's Molecular Basket Sorbent (MBS) material offers very promising CO_2 absorption chemistry

- CO_2-philic polymer, polyethyleneimine (PEI), supported on high surface area materials (MCM-41, SBA-15, carbon)
- High CO_2 loadings (>14 wt% CO_2)
- Reasonable heat of absorption (*66 kJ/mol*)



Impregnation of PEI in the pore structure of a high surface area support

Development Needs

- Improve stability at high temperatures is needed for optimal process performance
  - higher regeneration temperature → increased working capacity and CO_2 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

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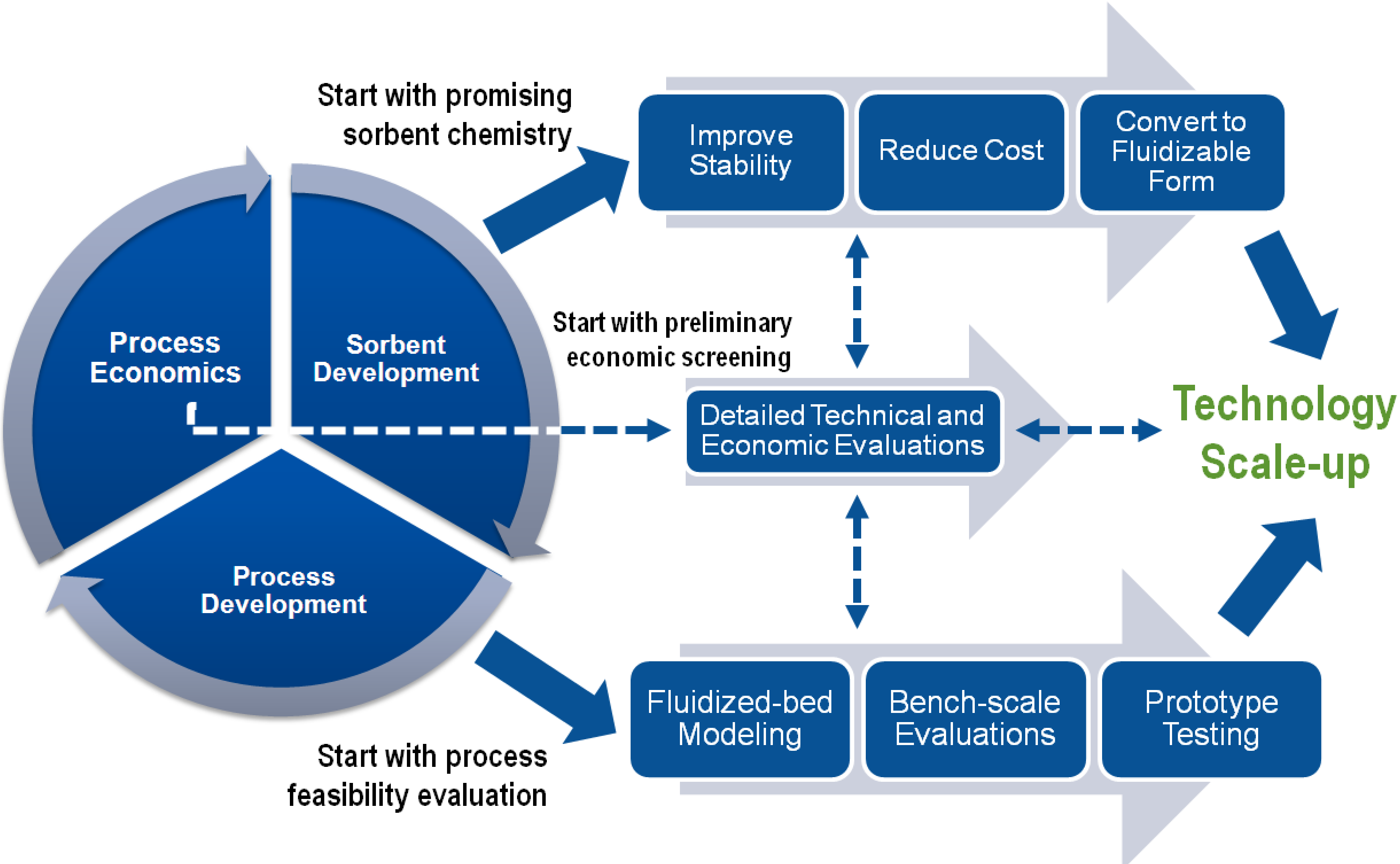
Technology Development Strategy



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Project Schedule and Milestones

	Previous Work			Current Project		Future Development			
Yr	< 2011			2011-15		2015 - 17		2018-22	> 2022
TRL	1	2	3	4	5	6	7	8	9
	Proof-of-Concept Feasibility Studies					Pilot Validation ▪ 1 - 5 MW (eq)		Demo ▪ ~ 50 MW	Commercial

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
- *Milestone:* Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype
- **Sorbent Development**
- *Milestone:* Successful scale-up of MBS material with confirmation of maintained properties and performance

Prototype Testing (2014 – 2015)

- **Field Testing of Prototype Unit**
- *Milestone:* Operational FMBR prototype capable of 90% CO_2 capture
- *Milestone:* Completion of 1,000 hours of parametric and long-term testing
- **Updated Economics**
- *Milestone:* Favorable technical, economic, environmental study (meets DOE targets)

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Sorbent Stability

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

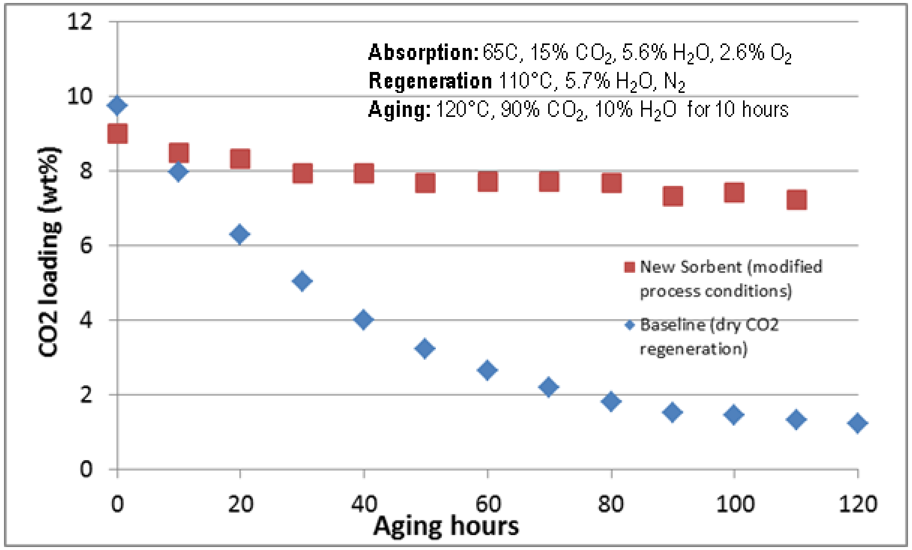
$$2RNH_2 + CO_2 \leftrightarrow RNH\text{-}CO\text{-}NHR + H_2O$$

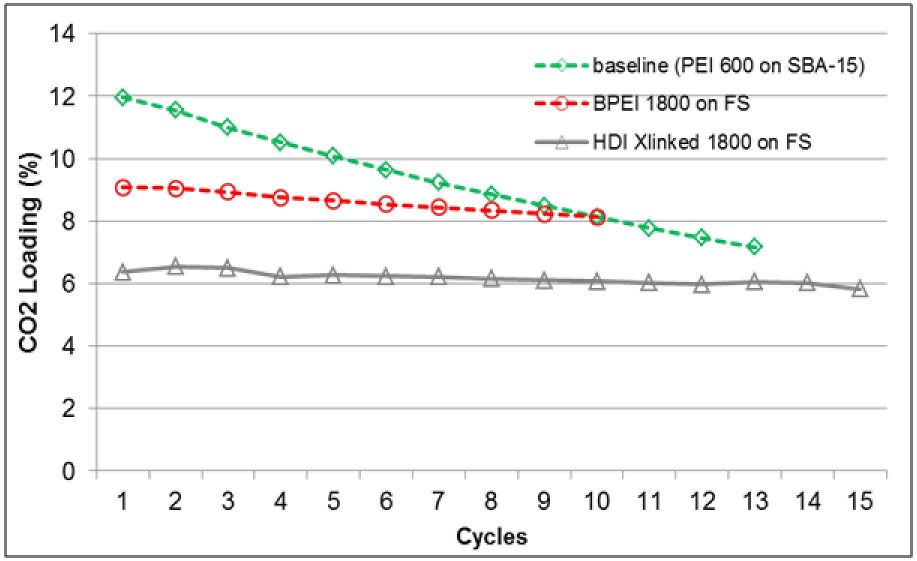
Stability improvements through sorbent chemistry modifications

- 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% CO_2 loading with regeneration temperature of 100 ^{o}C for > 25 cycles

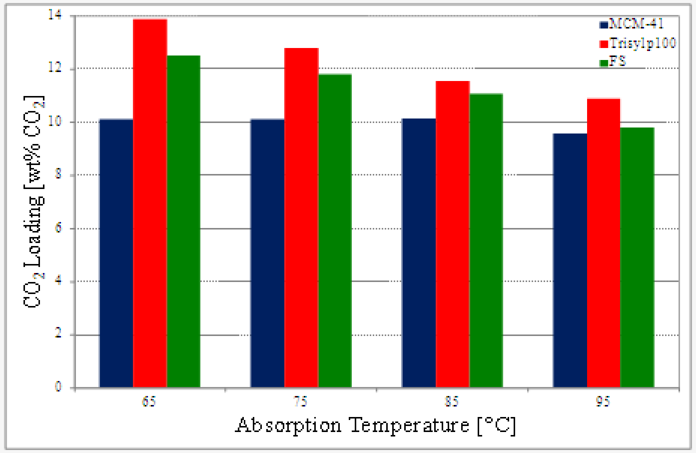




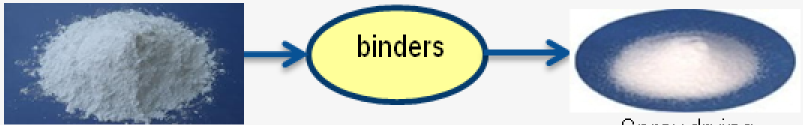
Sorbent Cost and Form

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

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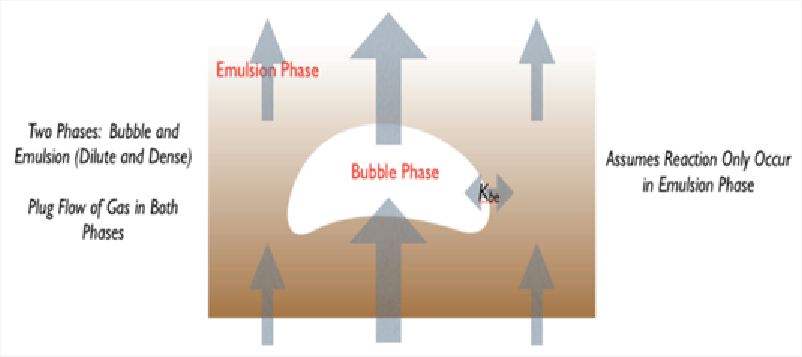
Process Development Progress

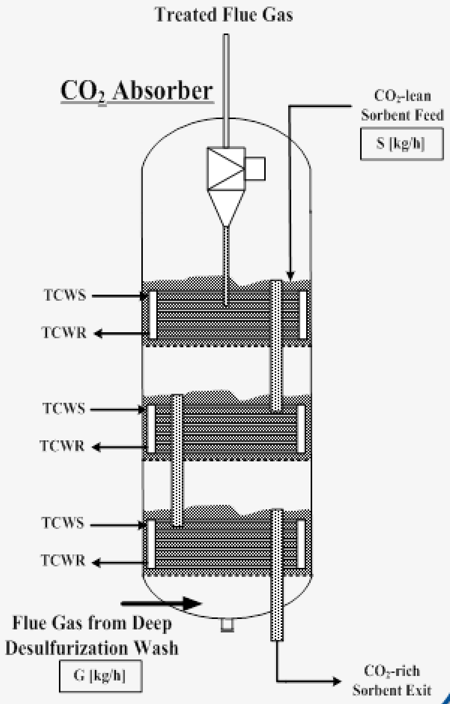
Fluidized-bed modeling

- 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 CO_2 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 CO_2 removal from flue gas
- Specifications:
  - Flue gas throughput: 300 and 900 SLPM
  - Solids circulation rate: 75 to 450 kg/h
  - Sorbent inventory: ~100 kg of sorbent
- Adequately sized to avoid issues related to bed slugging



Technology Feasibility Study

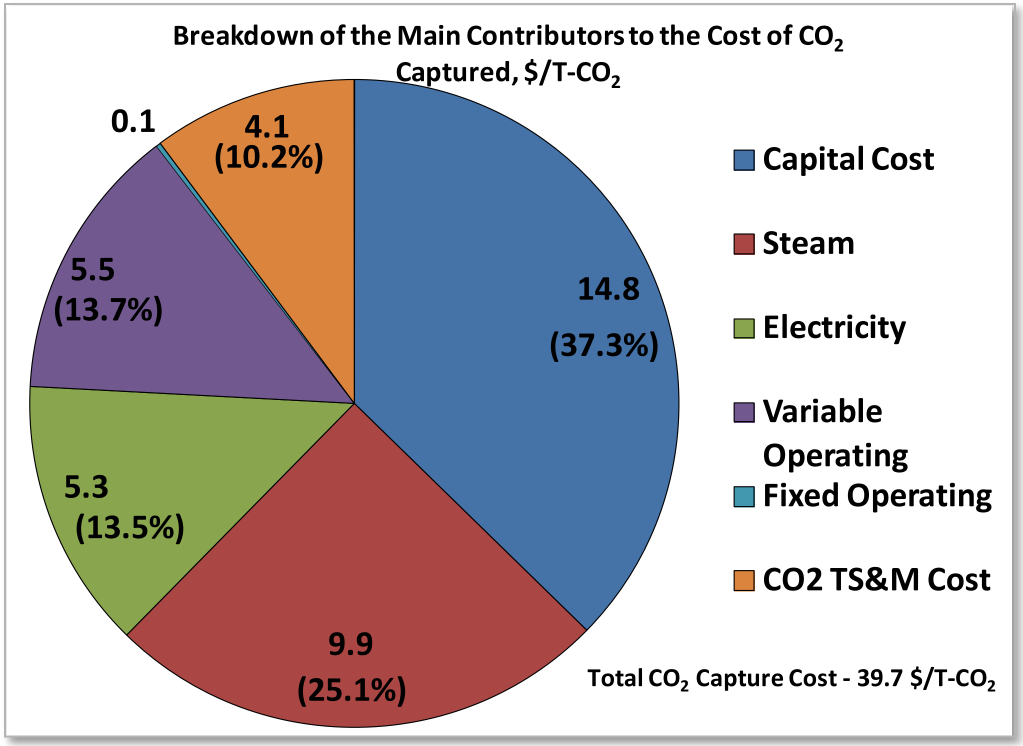
Basis: DOE/NETL's *Cost and Performance Baseline for Fossil Energy Plants Volume 1*

Approach: Thorough T&E assessment using process modeling & cost estimation software

- Aspen Plus; Process Economic Analyzer; ProMax (caustic scrubbing simulation)

Summary

- Total cost of CO_2 captured estimated to be 39.7 \$/T-CO_2 (SOTA Amine Process ~68\$/T-CO_2)
- 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



R&D Directions

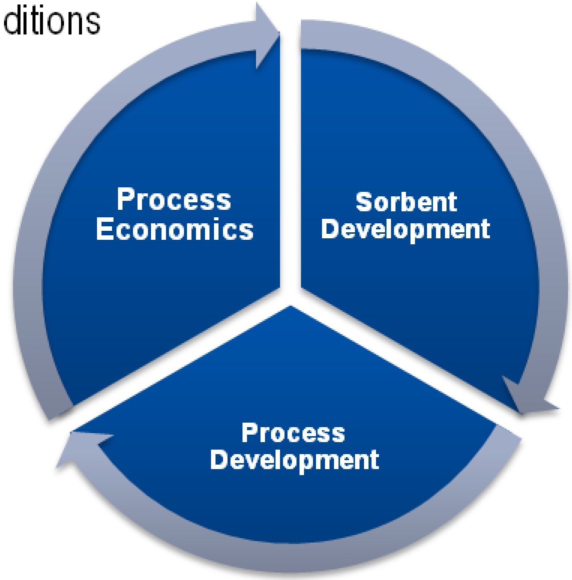
- Kinetic/equilibrium studies
- Long-term contaminant studies
- Study effects of particle size
- Detailed design study of FMBR

RTI technology exhibits favorable technical feasibility and process economics

Ongoing Work

Bench-scale contactor and prototype system testing

- Evaluate two proposed reactor designs for CO_2 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 CO_2

- Demonstrating technology at cement plant in Norway – Norcem (part of HeidelbergCement)
- Continue evaluating economic factors of NGCC application - Masdar

RTI's ETDF

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

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