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

RTI International

Luke Coleman, Atish Kataria, Marty Lail, Thomas Nelson, Jian-Ping Shen

Pennsylvania State University

Eric Fillerup, Chunshan Song, Dongxiang Wang, Xiaoxing Wang

July 09, 2012

Project Overview

Overall objective: to develop an advanced solid sorbent CO_2 capture technology based on novel, amine-based (PEI) sorbent and demonstrate a potential to achieve DOE's CO_2 capture targets of >90% CO_2 capture with <35% increase in cost of electricity

Project Details

- Combination of two previously funded DOE projects
- Project Cost: $3,847,161
  - DOE Share: $2,997,038
  - Cost Share: $850,123
- Period of performance: 10/1/2011 to 9/30/2014
- Prime Recipient: RTI International

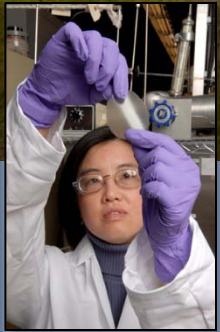
Project Objectives

- Improve stability and performance of novel amine-based (PEI) **"Molecular Basket Sorbent"** and make sorbents applicable for RTI's **fluidized, moving-bed reactor design** (FMBR)
- Improve reactor design; optimize operability & heat integration
- Conduct prototype testing and prove that the technology reduces parasitic energy load and capital and operating costs associated with CO_2 capture (economic study)

RTI International	Penn State	Masdar (A Mubadala Company)	Foster Wheeler	Süd-Chemie
▪ 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

RTI's Center for Energy Technology (CET)

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



- **RTI International** 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 some of the world's great energy challenges

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

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

CO_2 Capture & Conversion
- Post-combustion CO_2 capture
- Pre-combustion CO_2 capture
- CO_2 conversion

Fuels & Chemicals
- Syngas conversion
- Hydrocarbon desulfurization

Water & Energy
- Industrial water reuse
- Energy and waste heat recovery

Shale Gas
- Gas separation & processing
- Process water treatment

RTI INTERNATIONAL

Masdar

Masdar
A MUBADALA COMPANY

Project Roles

- Project co-funding partner
- Providing engineering expertise to evaluate technology feasibility and potential application to natural gas-fired plants
- R&D efforts focused on parallel development of technology for natural gas application

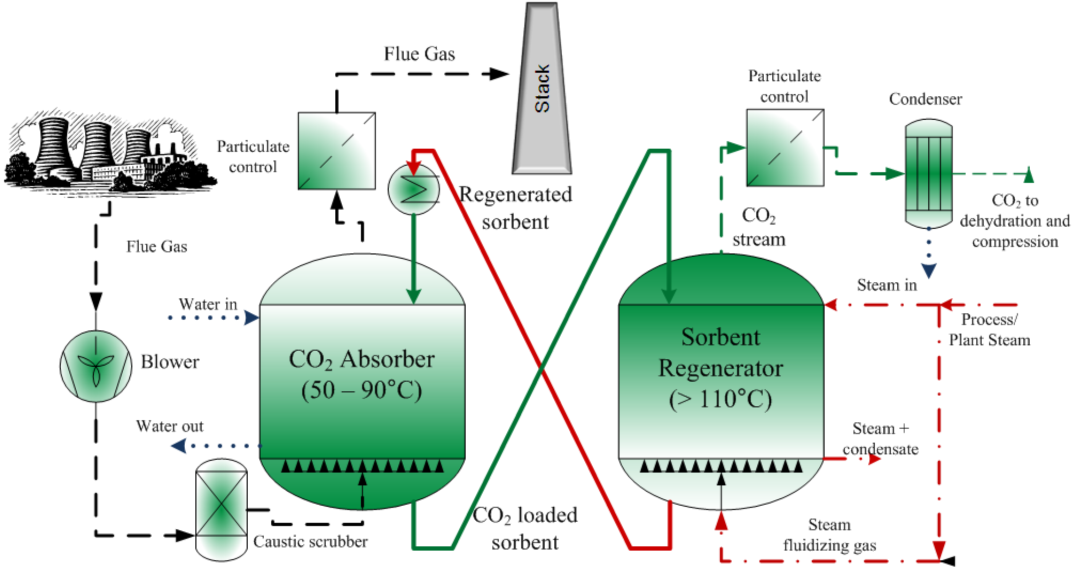
Memorandum of Understanding

- DOE & Masdar signed MoU in 2010 to promote collaboration on clean/sustainable energy technologies
- Cooperation in three key areas: Carbon Capture & Sequestration; Water & Biofuels; Building Technology

Masdar Overview

- Established in 2006, based in Abu Dhabi, United Arab Emirates
- Commercially-driven enterprise that aims to reach the broad boundaries of the renewable energy and sustainable technology industry and help drive the development of clean fossil fuel energy technologies
- Operates through five integrated units:
  - Masdar Carbon • Masdar Institute • Masdar Capital • Masdar Power • Masdar City
- **Masdar Carbon's** flagship initiative involves the development of a large-scale CCUS network in Abu Dhabi
- **Masdar Institute** is an independent, research-driven graduate university, partnered with MIT

Engineering a Sorbent-based CO_2 Capture Process



Challenges

- Heat management is still critical; need for heat integration
- Water management is critical to avoid condensation
- Pressure drop needs to be controlled
- Process design has not been evaluated experimentally

Notes from engineering study / experience in field

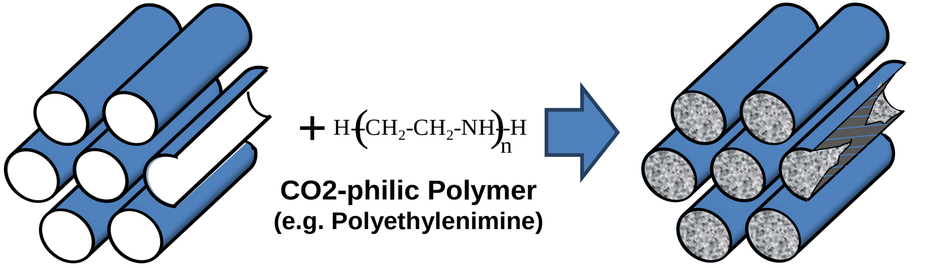
- Sorbent working capacity must be sufficient (8+ wt% CO_2) to control sorbent transport demands and scale of process
- Heat generated during capture leads to large temperature excursions in Absorber and reduced capture efficiency
- Sorbents have low C_p unlike aq. amine solvents, this internal heat management systems are necessary
- Commercial-scale fixed-bed processes have inadequate heat removal rates

RTI's Fluidized, Moving-bed Reactor process concept:

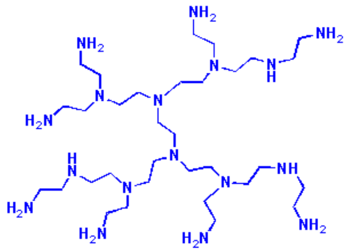
- Minimizes # of process vessels and sorbent load
- Superior gas-solid heat and mass transfer characteristics
- Minimizes thermal regeneration energy
- Reduced pressure drop once bed is fluidized
- Counter current gas-solids flow maximizes CO_2 driving force
- Minimizes sorbent attrition by avoiding entrained-bed mode
- Commercial embodiments of equipment

RTI INTERNATIONAL

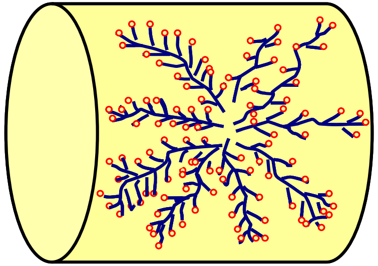
PSU's MBS CO_2 Absorbing Material



Nano-porous Material — **"Molecular Basket" Sorbent (MBS)**



Polyethylenimine (PEI)



Immobilize PEI into Nano-Pore

Challenges

- Poor performance stability above 90°C
- Currently in powdered or fixed-bed form
- Too costly (uses mesoporous silica supports)

Polymeric amines have high density of CO_2 absorbing sites. Sorbent carbamate chemistry:

Primary:	$CO_2 + 2RNH_2 \rightleftarrows NH_4^+ + R_2NCOO^-$
Secondary:	$CO_2 + 2R_2NH \rightleftarrows R_2NH_2^+ + R_2NCOO^-$
Tertiary:	$CO_2 + 2R_3N \rightleftarrows R_4N^+ + R_2NCOO^-$

PSU has been working in field for ~10 years (Dr. Chunshan Song's research group)

PSU's Molecular Basket Sorbent (MBS) material is one of the most promising impregnated amine sorbents:

- High CO_2 loadings (>14 wt% CO_2)
- High CO_2/N_2 selectivity (> 1000)
- Reasonable heat of absorption (*66 kJ/mol*)
- Utilizes CO_2-philic polymer, polyethyleneimine (PEI)

RTI INTERNATIONAL

Project Schedule, Work Plan, Milestones

Sorbent Stability

- Explore cross-linking agents
- Different PEIs and strengthening PEI-support bond
- Support surface modification

Sorbent Form

- Convert existing MBS platform to a fluidizable and attrition-resistant material
- Explore impregnation, spray drying, and binders

Sorbent Cost

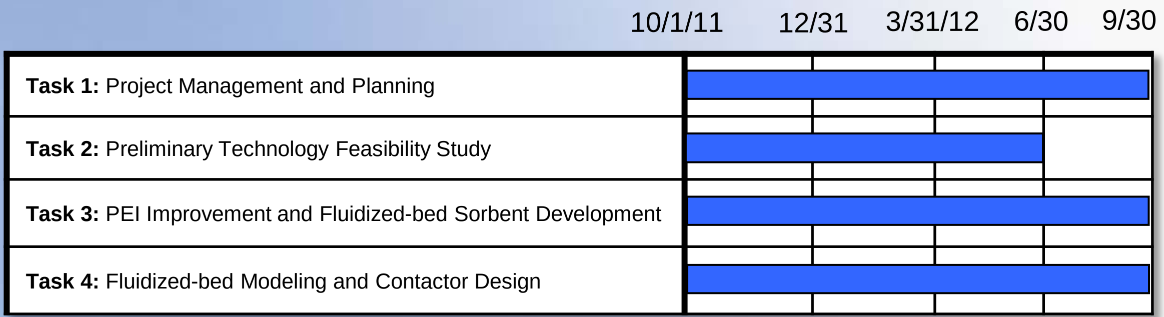
- Utilize low-cost, commercially-available supports
- Work with Süd-Chemie to devise low-cost commercial manufacturing techniques

Design Effectiveness

- Explore commercial embodiments of equipment
- Kinetic and equilibrium testing for detailed design
- Detailed CFD modeling

Economics

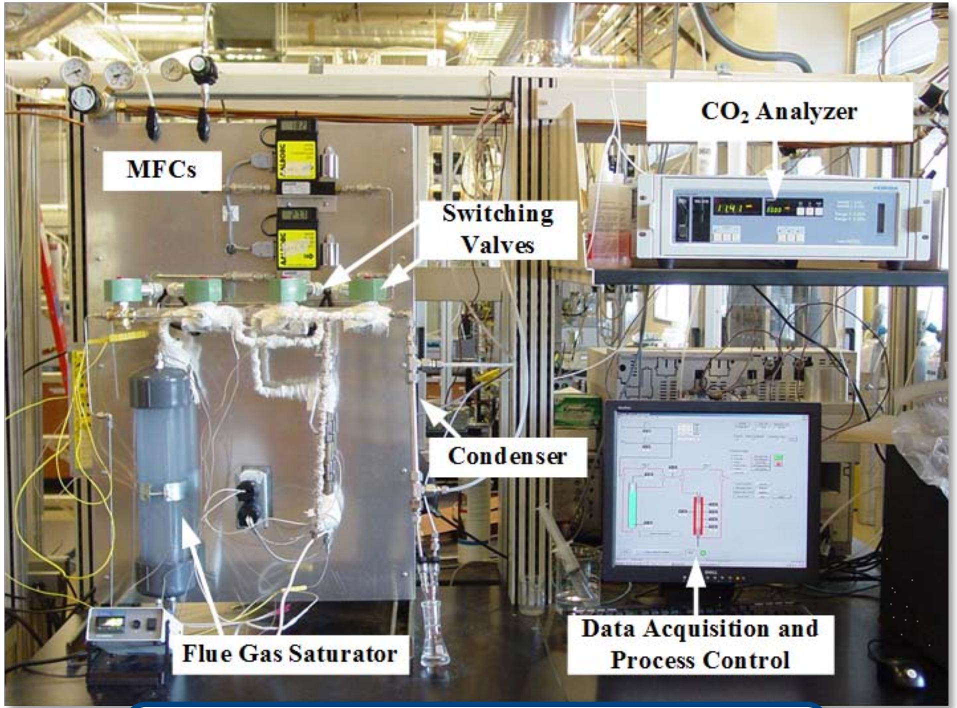
- True economic potential of combined (MBS + FMBR design) has not yet been studied
- Conduct rigorous techno-economic evaluation



	Milestone / Criteria	Status
1	▪ Complete preliminary technolohy feasibility study ▪ Results improve upon SOTA and show potential to meet DOE targets	Complete
2	▪ Successful scale-up of fluidized-bed MBS material ▪ 15 kg of sorbent produced having same properties as lab-scale	Delayed, but in-progress
3	▪ Working multi-physics, CFD model of FMBR design ▪ Elicit effects of process elements on CO_2 capture, heat/mass transfer	In-progress
4	▪ Fabrication-ready design package for single-stage FMBR unit ▪ Complete engineering drawings, cost estimate, and schedule	On schedule

RTI INTERNATIONAL

Testing Equipment



RTI's Fully Automated, Packed-Bed Reactor System for Multi-cycle CO_2 Capture-Regeneration Testing

Objective: Improve the thermal and chemical stability of base PEI reactant while transitioning fixed-bed MBS material into a fluidizable form

RTI's automated packed-bed reactor systems

Capabilities

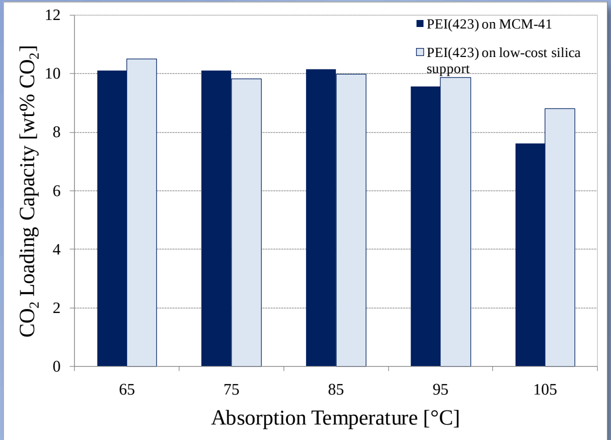
- Fully-automated operation, data analysis
- Multi-cycle, absorption-regeneration experiments
- Rapid sorbent screening experiments
- Comprehensive parametric evaluation
- Long-term effect of contaminants

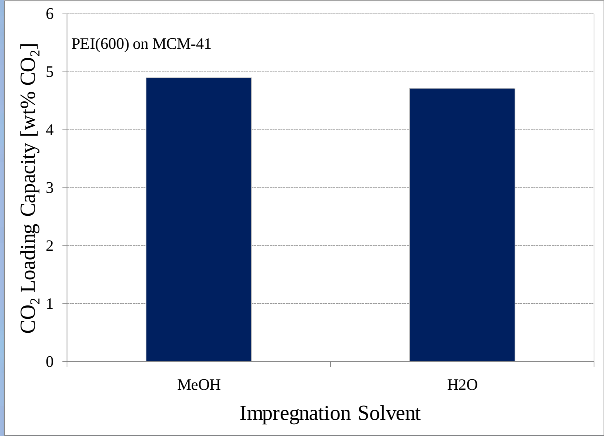
Measureables

- Dynamic CO_2 loading capacity
- Rate of CO_2 loading on sorbent (wt%/min)
- Thermal waves due to absorption or desorption
- Pressure drop across packed bed
- PBR #1 – sorbent screening
- PBR #2 – multi-cycle stability testing

RTI INTERNATIONAL

Towards producing a low-cost, attrition-resistant sorbent





RTI's lab-scale spray dryer

RTI's Davison Cup Attrition Tester

Motivation

- Need new support that is low-cost, fluidizable & attrition-resistant
- Need preparation method that is feasible for commercial scale-up

Methodology

- Screened 20+ commercially-available, low-cost support materials, Tested with automated, packed-bed absorption system
- Modified preparation procedure

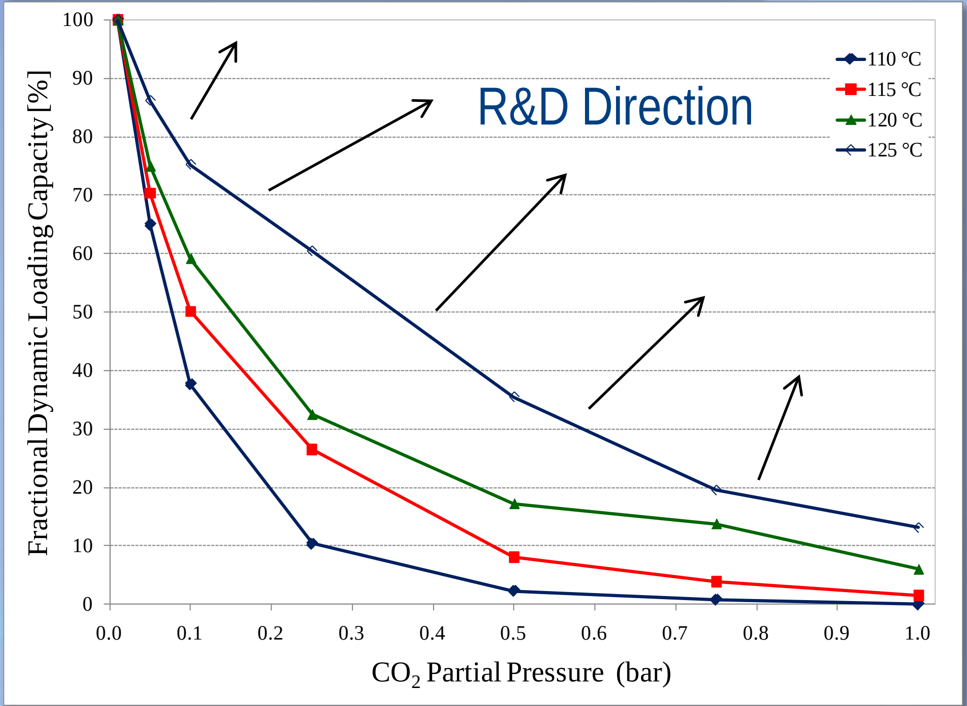
Results

- Identified a low-cost support material yielding a sorbent with comparable performance to expensive, mesoporous silica
  - *Cost of MCM-41: on the order of $1,000/kg*
  - *Cost of low-cost alternative: < $5/kg*
- Low-cost support is also more amenable to forming a strong, attrition-resistant, fluidizable particle
- Demonstrated that water can replace methanol (or any alcohol) as the PEI impregnation solvent

RTI INTERNATIONAL

Regeneration Under Realistic Conditions

Conditions	Absorption	Regeneration
Temperature [C]	65	110-125
Gas Composition [vol%]	13.3% CO_2, 5% H_2O, 2.35% O_2, bal. N_2	0-100% CO_2,0-5% H_2O, bal. N_2
GHSV [h^{-1}]	3,000	3,000
Fresh sorbent for each regeneration temperature		



Evaluated effect of regeneration temperature and CO_2 partial pressure on dynamic loading capacity

Motivation

- Need to avoid, to the greatest extent possible, high concentration steam sweep or vacuum regeneration

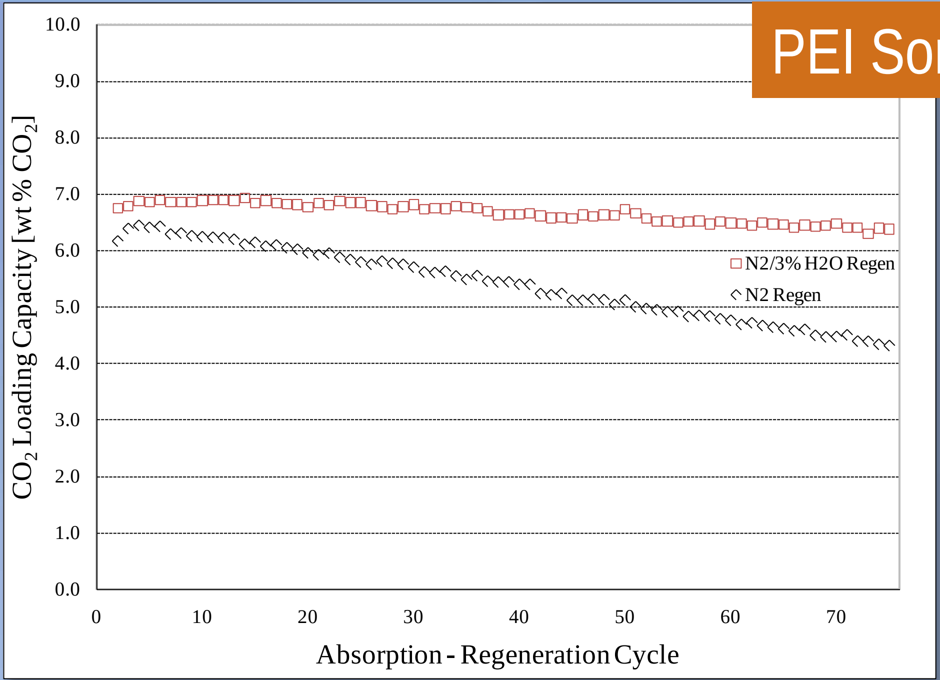
Methodology

- Automated, packed-bed absorption system
- Sorbent cycled between abs. and regen. conditions with increasing CO_2 content in the regen. gas
- Fresh sorbent sample used for each regen. Temperature

Results

- Increasing P_{CO2} has a significant detrimental effect on the dynamic loading capacity of the sorbent
- Increasing the regen. temperature drastically improves the dynamic loading capacity

PEI Sorbent Stability – Water



Conditions	Absorption	Regeneration
Temperature [C]	75	105
Gas Composition [vol%]	13.3% CO_2, 5% H_2O, 2.35% O_2, bal. N_2	a. 3% H_2O, bal N_2 b. 100% N_2
GHSV [h^{-1}]	3,000	3,000
Fresh sorbent was used for each experiment		

Determine the effect of moisture in regeneration gas on long-term performance stability

Motivation

- Explore operating conditions to improve sorbent stability

Methodology

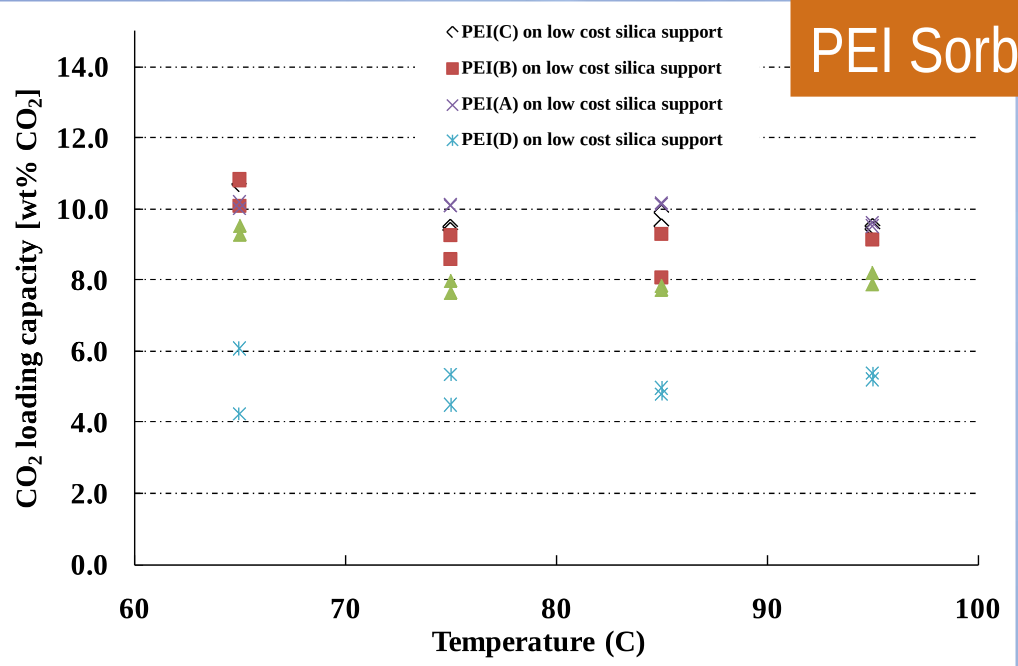
- Automated, packed-bed absorption system
- 75 abs. and regen. cycles at prescribed conditions

Results

- Addition of a small amount of moisture to the regen. gas dramatically improves the multi-cycle performance stability
- Similar findings to the Sayari (UofO) and Jones (GIT) groups
- Improvement most likely related to reducing the formation of thermally-stable urea under regeneration condition
  - $2RNH_2 + CO_2 \leftrightarrow RNH\text{-}CO\text{-}NHR + H_2O$
- Observed reduction in carbonyl peak for sample regenerated in H_2O/N_2 using DRIFTS

RTI INTERNATIONAL

PEI Sorbent Performance – PEI Type



Conditions	Absorption	Regeneration
Temperature [C]	Varied	110
Gas Composition [vol%]	14.8% CO_2, 5.7% H_2O, 2.61% O_2, bal. N_2	2.5% H_2O, bal N_2
GHSV [h^{-1}]	3,000	3,000

Determine the effect of different PEI types on sorbent CO_2 capture performance

Motivation

- Baseline PEI(423) may not be suitable for commercial use

Methodology

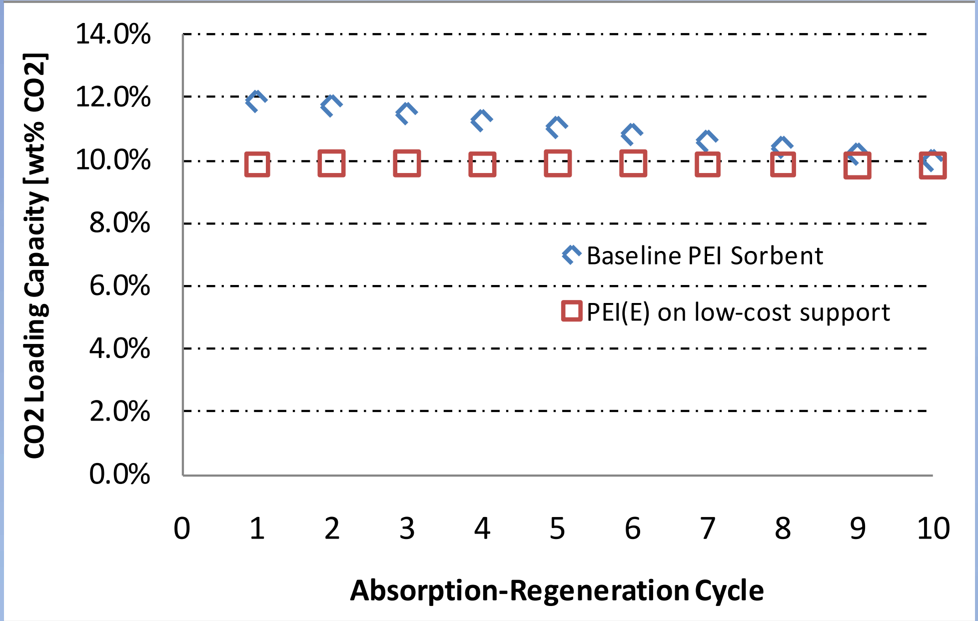
- Automated, packed-bed absorption system
- Single abs. and regen. cycle at different temperatures

Results

- Sorbent CO_2 capture performance can vary widely as a result of using different PEI types
- Identified most promising PEI types for further screening

RTI INTERNATIONAL

PEI Sorbent Stability – PEI Type



Conditions	Absorption	Regeneration
Temperature [C]	90	120
Gas Composition [vol%]	100% CO_2	100% N_2

Evaluate a promising new PEI type for improved sorbent thermal stability

Motivation

- Alternative PEIs and preparation procedure must lead to improved sorbent stability

Methodology

- Abssorption and regeneration cycling using thermogravimetric analyzer (TGA)
- Prepared new sorbent sample using PEI type – PEI(E) on low-cost silica support

Results

- Significant thermal stability improvement over 10 cycles at 120°C regeneration compared to baseline sorbent
- Slightly lower starting CO_2 capacity

Preliminary Technology Feasibility Study[1]

Methodology

- Detailed PFDs of combined CO_2 capture and compression systems and major process components
- AspenPlus® to develop simulations and complete stream tables (assumptions and experimental data used)
- Detailed process equipment lists, consumables, and sizing using Aspen Process Economic Analyzer (PEA)
- Equipment cost estimates, operating costs, parasitic power load, levelized COE using Aspen PEA and quotes

Highlights

- Developed detailed estimates for a) parasitic power loss, b) levelized cost of power and steam, c) itemized installed equipment costs, d) cost of CO_2 capture, e) percent decrease in plant efficiency
- Estimated **increase in cost of electricity ~ 50%** with potential to reduce further through a) reactor refinements, b) sorbent cost reduction, c) improve sorbent strength, d) heat integration strategies, e) alternative SO_2
- Compared to SOTA MEA process, a) ~ **40% less steam consumption**, b) ~**5 point improvement** in decreased plant efficiency, c) ~**45% improvement in cost of CO_2 capture**

Sensitivity Analyses

- Sorbent loss rate, price, capacity
- Alternative SO_x removal processes
- Stripping steam demand
- Reactor design based on equilibrium-limited kinetic model

R&D Directions

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

[1]Basis: Attachment 3 – "Basis for Technology Feasibility Study" of the Funding Opportunity Announcement, DE-FOA-0000403

Plans for Future Development

	Previous Work			Current Project			Future Development		
Yr	< 2011		2011-14						
TRL	1	2	3	4	5	6	7	8	9

Laboratory Validation

- Improve stability by increasing PEI-support interaction
- Improve stability through novel cross-linking methods
- Continue developing method to convert support powders to fluidizable particles
- Detailed reactor design/CFD simulations
- Design bench-scale FMBR and internal heat management system
- Parametric studies of economic/process variables

Relevant Environment Validation

- Sorbent scale-up to 300 lbs
- Bench-scale testing of single-stage contactor
- Demonstrate that heat transfer internals and sufficient fluidization are essential for achieving optimal performance
- Detailed design and engineering of high-fidelity, bench-scale prototype

Prototype Testing

- Sorbent scale-up to 1,000+ lbs
- Prototype system shakedown testing at RTI natural gas-fired facility
- Prototype system long-term testing at coal-fired UNC power plant (~ 1 ton/day CO_2 capture)
- Sorbent optimization to near-commercial embodiment
- Detailed techno-economic study showing high confidence level that technology can meet ICOE target of < 35%

RTI INTERNATIONAL

Prototype Testing and Beyond

RTI's Central Utility Plant (CUP)

- ~ 5 MW_t boiler – Natural Gas-fired
- 13,800 lbs/hr steam production
- CO_2 produced: ~ 25 TPD

UNC–Chapel Hill Co-Generation Power Plant

- Generates steam and electricity
- Coal Feed: ~ 50,000 lbs/hr
- CO_2 Produced: 1500 TPD

Future Development

2014 - 16		2016-19	2020+
TRL-6	7	8	9

Pilot Validation (2014 – 2016)

- 5 MW (eq) pilot-scale testing at coal-fired utility
- > 100 ton/day CO_2 capture

Demonstration (2016 – 2019)

- 50 -100 MW (eq) pre-commercial scale testing

Commercial (2020+)

Prototype testing objectives

- Demonstrate long-term stability and performance of MBS-based sorbent and FMBR process with actual coal-fired flue gas
- Shakedown and troubleshoot at RTI
- Parametric and long-term testing (1,000 hrs) at UNC's power plant. Sorbent scale-up

RTI INTERNATIONAL

Acknowledgements

- The R&D work presented herein was made possible through funding by:
  - The U.S. DOE/National Energy Technology Laboratory (Project # DE-FE0007707)
  - Masdar (Abu Dhabi Future Energy Company)
- We would like to thank our various team members for their valuable contributions to the project

RTI	PSU	Masdar Carbon	Masdar Institute	DOE/NETL
▪ Laura Douglas ▪ Joshua Herr ▪ Jak Tanthana ▪ Matthew Von Holle	▪Wenying Quan	▪ Paul Crooks ▪ Mayuram Balasubramanian ▪ Maitha Al Mansoori	▪ Mohammad Abu Zahra ▪ Adel Seif El Nasr	▪ Bruce Lani

RTI INTERNATIONAL