RICE

Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide for Post-combustion Carbon Capture

DOE Project # DE0007531

Project Manager: Ms. Elaine Everitt

Dr. Michael S. Wong

Professor in Chemical and Biomolecular Engineering, Chemistry and Environmental Engineering

Rice University

NETL CO_2 Capture Technology Meeting

July 10th, 2013

Outline

- About Rice University
- Project Overview
- Project Team
- Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide
- Selection of materials
- Integrated absorber and stripper – A proof-of-concept demonstration
- Substrate functionalization
- Project Budget

Rice University

- Located in Houston, TX
- 295-acre, heavily wooded campus
- Ranked 17th in the US and in the top 100 in the world
- 650 full-time faculty, 3500 undergraduates and 2300 graduate students
- Chemical and Biomolecular Engineering program, 13 faculty members, 70 graduate students
- Chemistry program, 38 faculty members, 130 graduate students

Project Team

Project Director

George Hirasaki
A J. Hartsook Professor in Chemical & Biomolecular Engineering

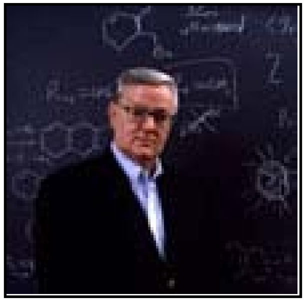
Co-Project Investigator

Michael Wong
Professor in Chemical & Biomolecular Engineering & Chemistry

Co-Project Investigator

Kenneth Cox
Professor-in-practice in Chemical and Biomolecular Engineering

Co-Project Investigator



Edward Billups
Professor in Chemistry

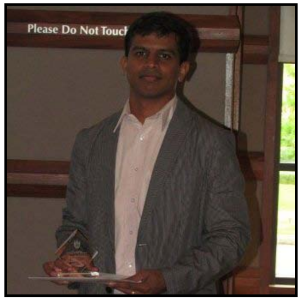
Postdoctoral Associate

Jerimiah Forsythe
PhD, Chemistry (LSU, 2011)

Undergrad Researcher

Colin Shaw
Chemical & Biomolecular Engineering

Past member



Sumedh Warudkar
PhD (April 2013)

Project Overview

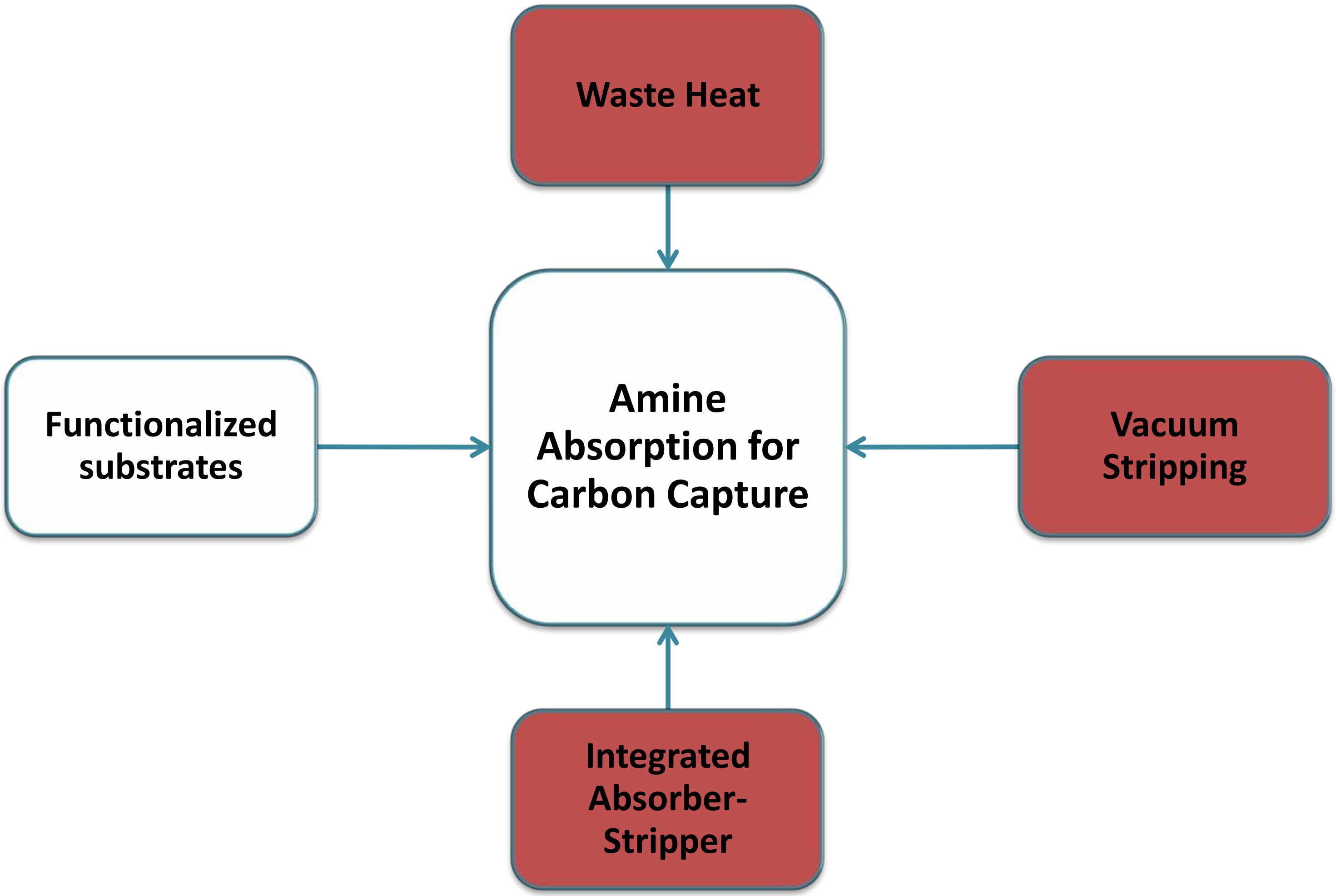
- Project funding under DOE agreement – DE-FE0007531
- Total project cost - $960,811 over three years. Federal share: $768, 647 | Non-federal share: $192,164
- Contract awarded executed October 2011
- Project duration: 10/2011 – 9/2014
- Project objective - Performance of bench-scale R&D to demonstrate and develop Rice University's "*combined pressure and temperature contrast and surface-enhanced separation of* CO_2 *for post-combustion carbon capture to meet DOE's goal of at least 90%* CO_2 *removal at no more than 35% increase in the cost of electricity*"

Reference Carbon Capture Scenario

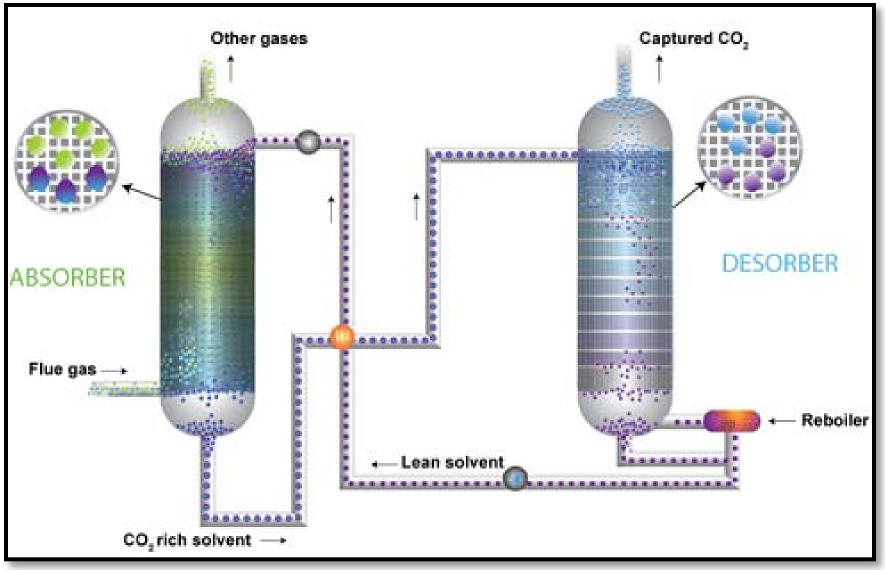
- Goals set by the DOE:
- Using 2nd generation technologies in post-combustion capture:
  - Demonstrate 90% CO_2 capture
  - Less than 35% increase in COE
  - Less than $40/tonne with carbon capture utilization and storage
- Estimates based off of Case 10: post-capture subcritical unit
  - 550 MW coal-fired power plant with a net plant efficiency of 26.2%

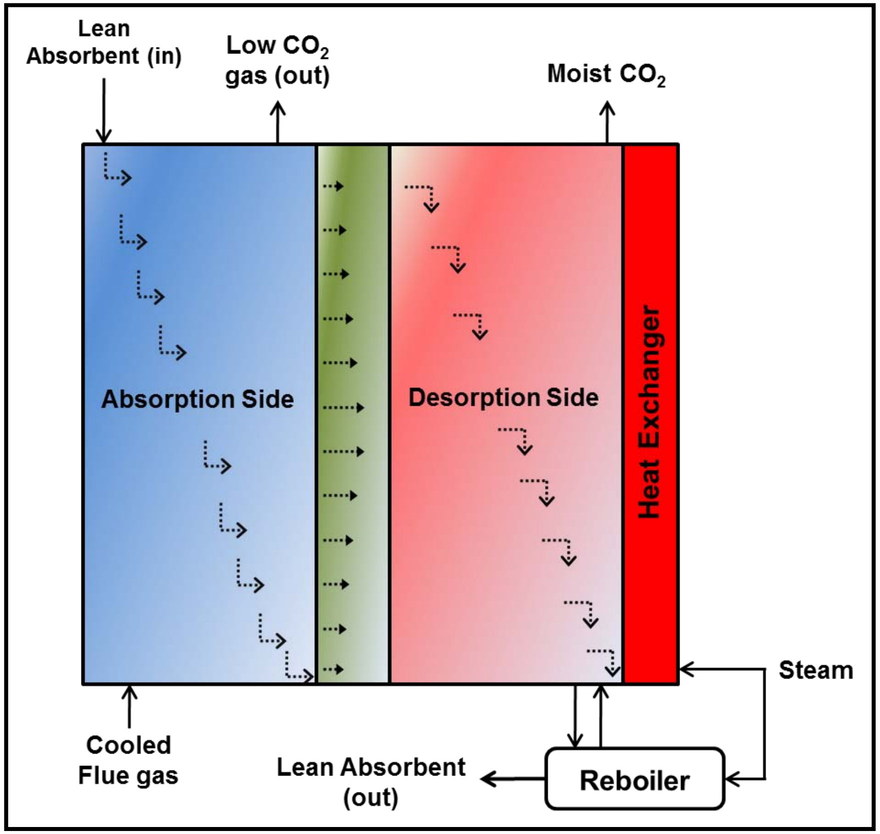
Our Approach

COMBINED PRESSURE, TEMPERATURE CONTRAST, AND SURFACE-ENHANCED SEPARATION OF CO_2



Combining the Absorber and Desorber Units

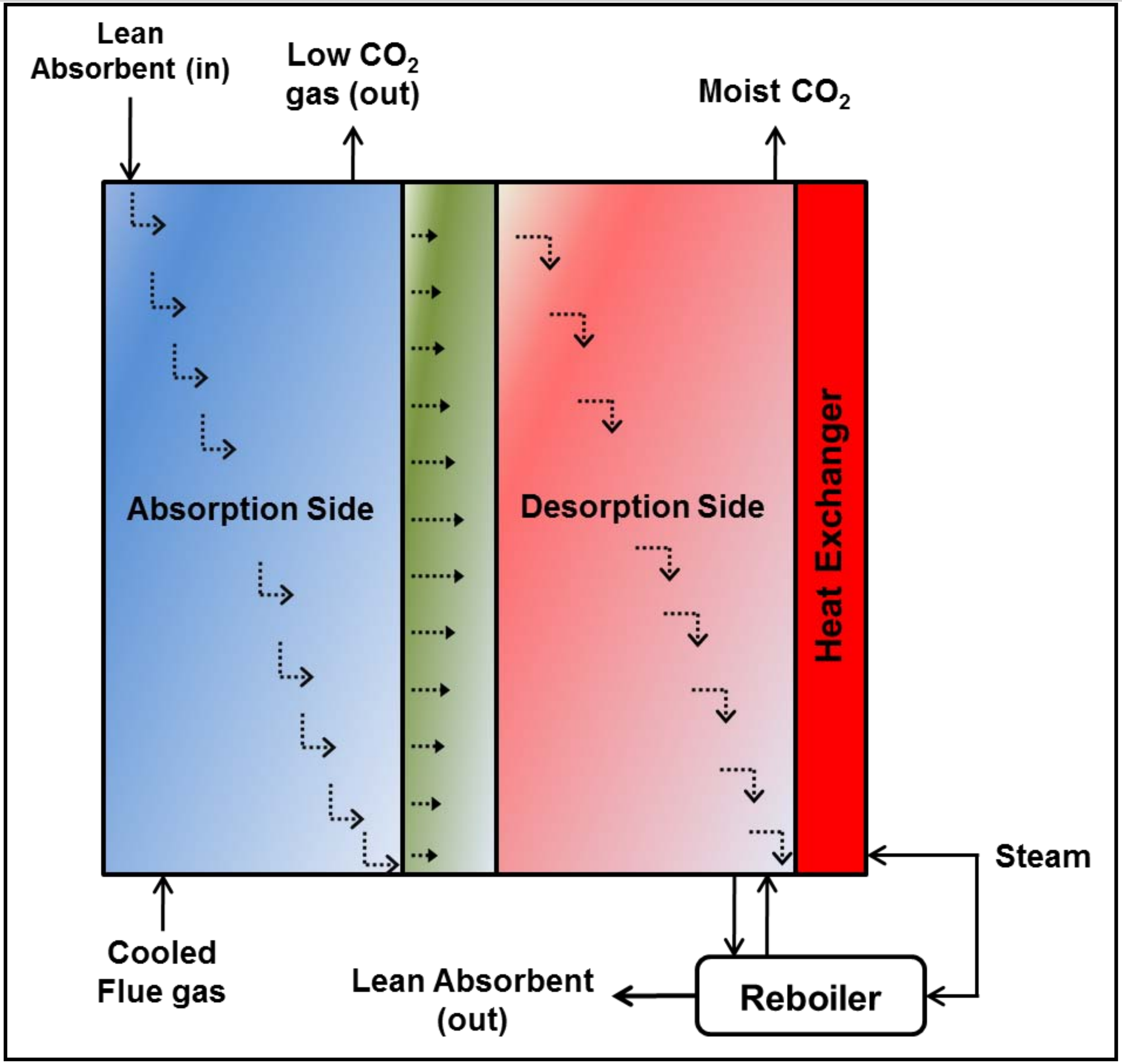




A comparison of the conventional amine system with the proposed 'combined' process

Ref: http://www.co2crc.com.au/aboutccs/cap_absorption.html

Process Schematic
Integrated Absorber-Stripper



Selection of Foam Material

Ceramic Foam

- Low bulk density
- Very high macro-porosity (80%-90%)
- Very high geometric surface area
- Regulated pore-size
- Low pressure drop
- High structural uniformity
- Ease of reproducibility of structure

Structure	S (m^2/m^3)	Porosity (ε)
5 mm packing spheres	600	0.392
Raschig ceramic rings, 25 mm	200[1]	0.646
Corrugated metal structured packing (AceChemPack) – 500 x/y	500[3]	0.93
30-PPI -Al_2O_3 foam, no washcoat	3360[2]	0.83

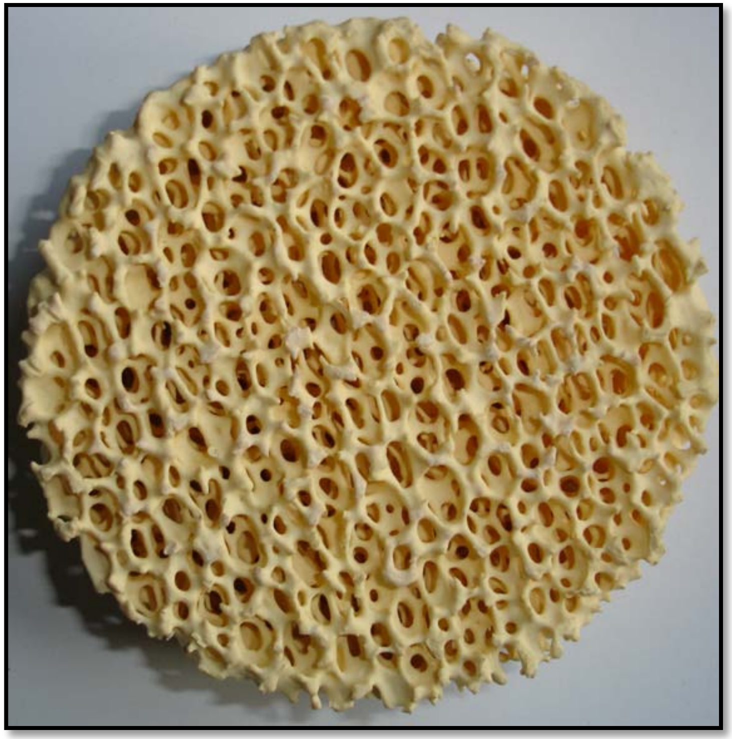


Figure: Commercial Sample of Ceramic foam

1: DOI: 10.1021/ie00027a023, **2:** DOI:10.1205/026387602753501906; **3:** http://www.tower-packing.com

SEM Micrographs of a Commercial Ceramic Foam Sample

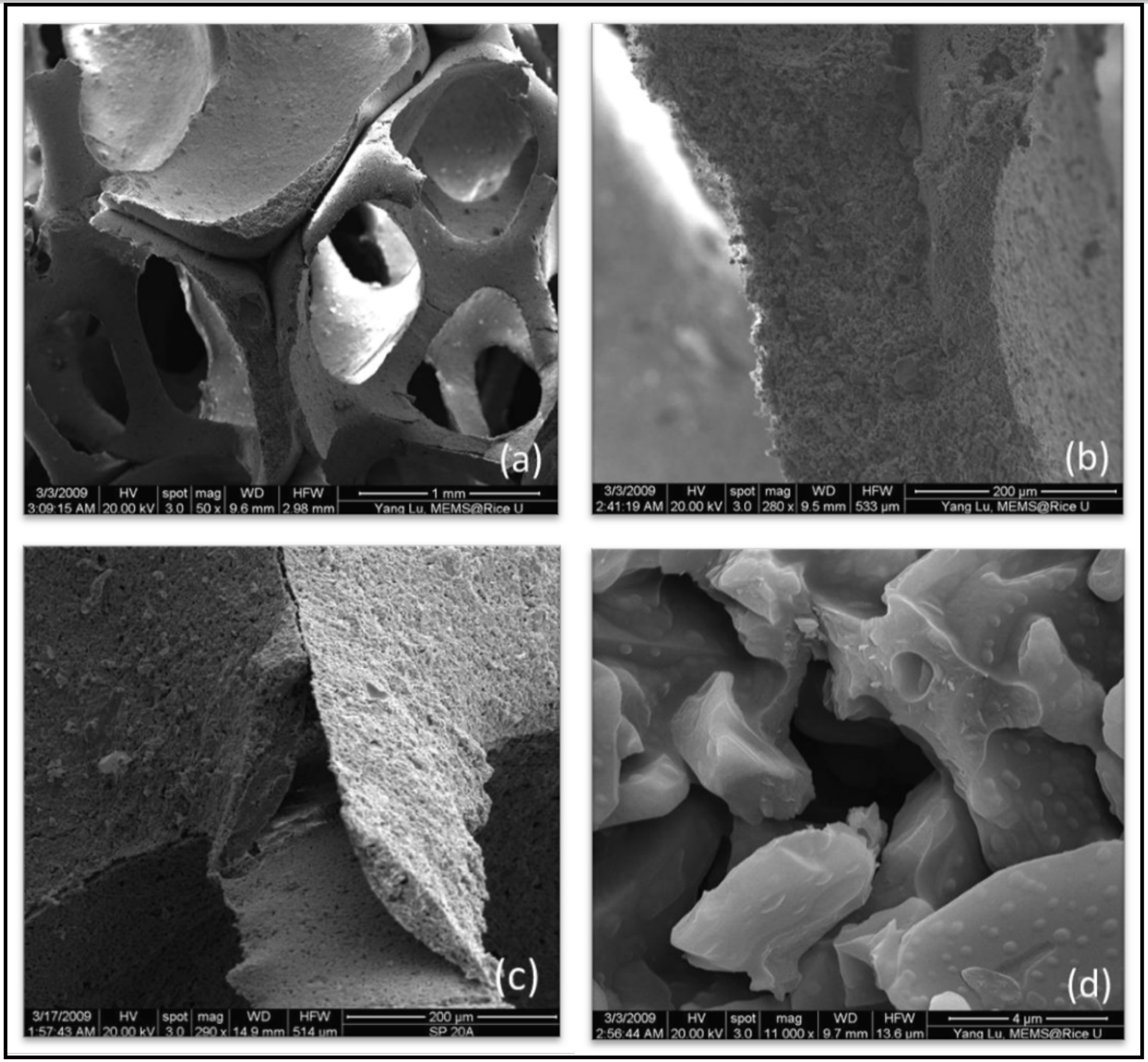
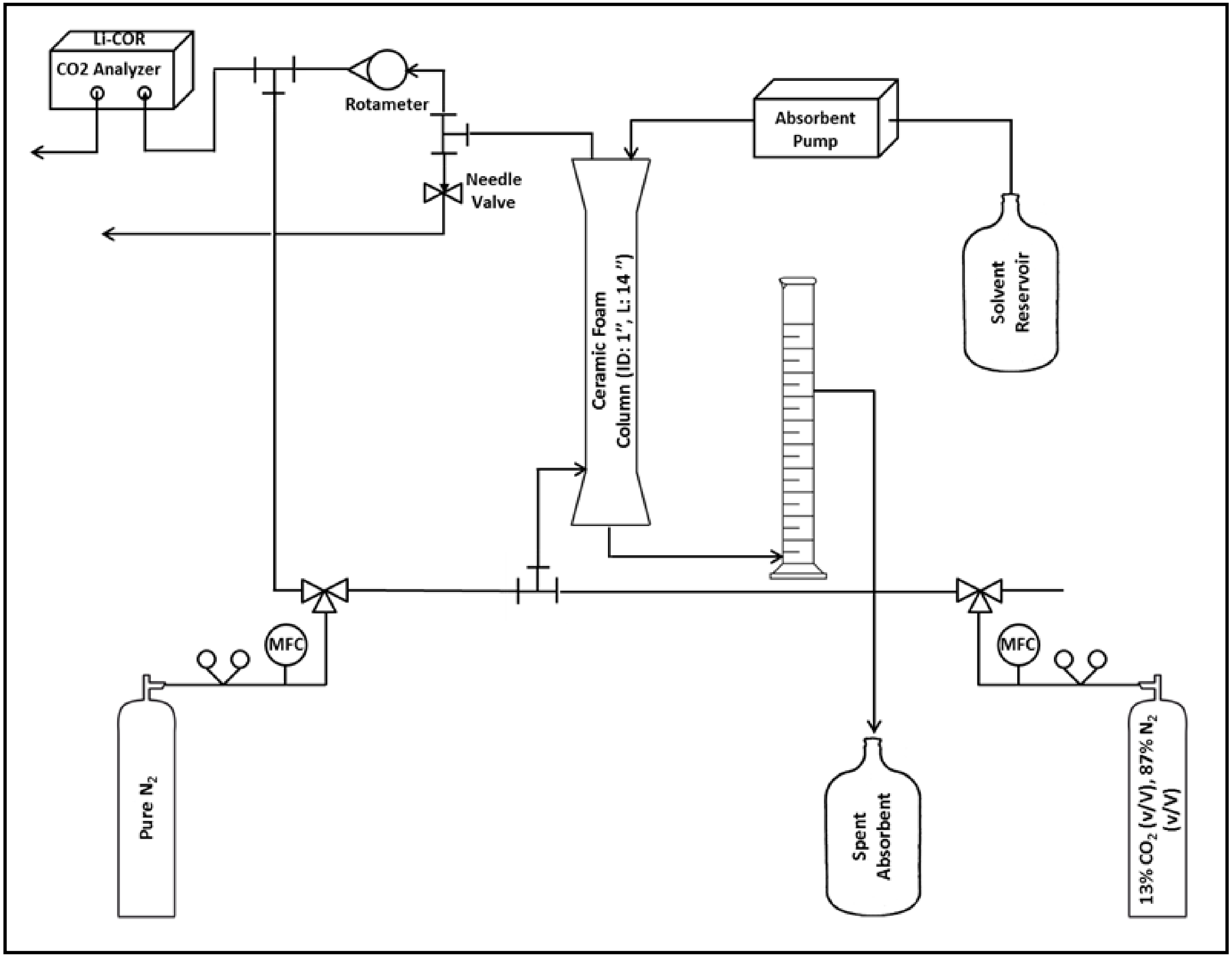


Figure: Scanning Electron Micrographs of 40-ppi Ceramic Foam (a) 50x (b) 280x (c) 290x (d) 11,000x

Material Properties

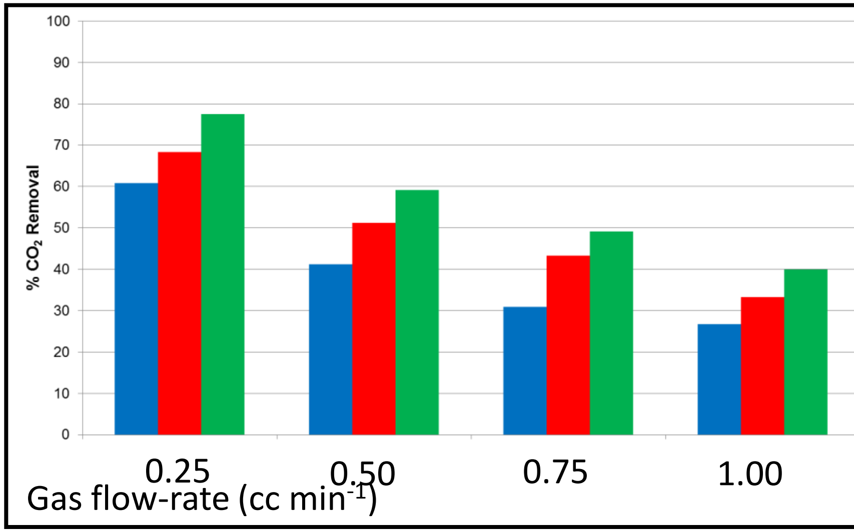
Ceramic Foam	
Property	Value
Material	99.5 % (α-Al_2O_3)
Supplier	ASK-Chemicals, USA
Dimensions	For absorption studies: L = 2’’, ϕ = 1’’
	For stainless steel prototype: 8’’ x 4’’ x 1’’
Porous Ceramic Membrane	
Material	99.5 % (α-Al_2O_3)
Supplier	Refractron Inc., USA
Dimensions	12’’ x 6 ‘’ x 1’’
Permeability & Gas Entry Pressure	5.37 Darcy | 0.8 psi (with water)
Gas-Liquid Separator Polymer Membrane	
Material	Polyethersulfone (Hydrophilic)
Supplier	Pall LifeSciences Corporation, USA
Dimensions	8’’ x 8’’
Permeability & Gas Entry Pressure	0.32–1.52 Darcy | 15-31 psi (with water)

Experimental Setup
CO_2 Absorption Experiments

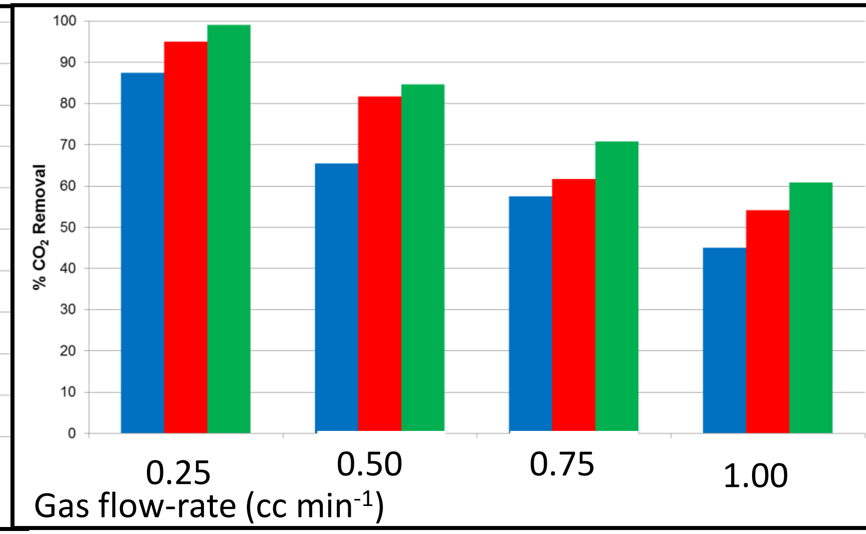


Degree of CO_2 Removal
Dependence on the Height of Ceramic Foam Packing

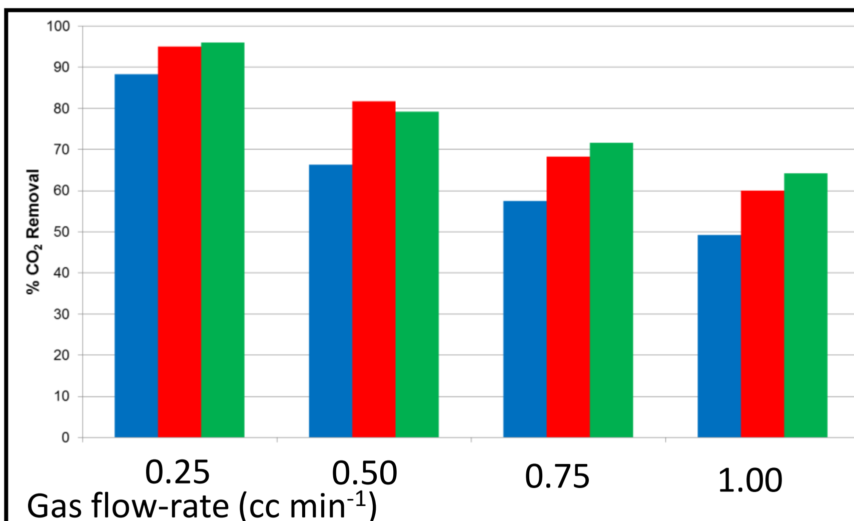
Height of ceramic foam packing: 10.1 cm



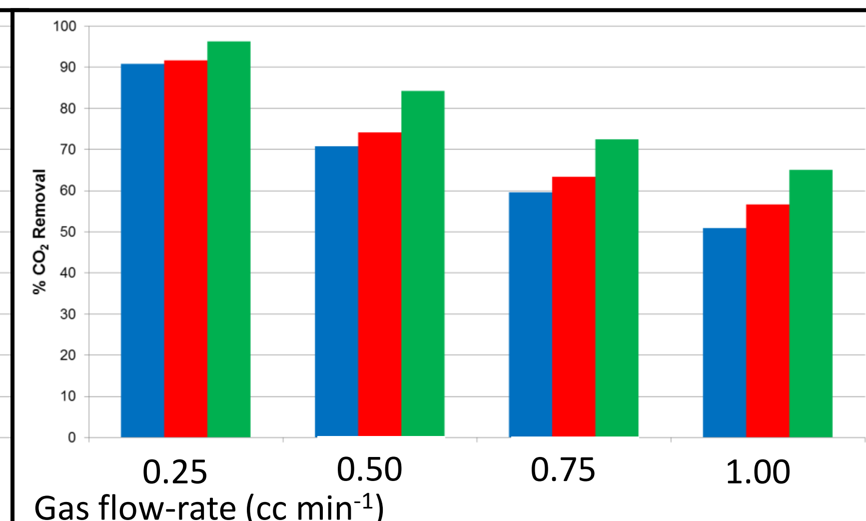
Height of ceramic foam packing: 15.2 cm



Height of ceramic foam packing: 20.3 cm



Height of ceramic foam packing: 25.4 cm



Liquid Flow:

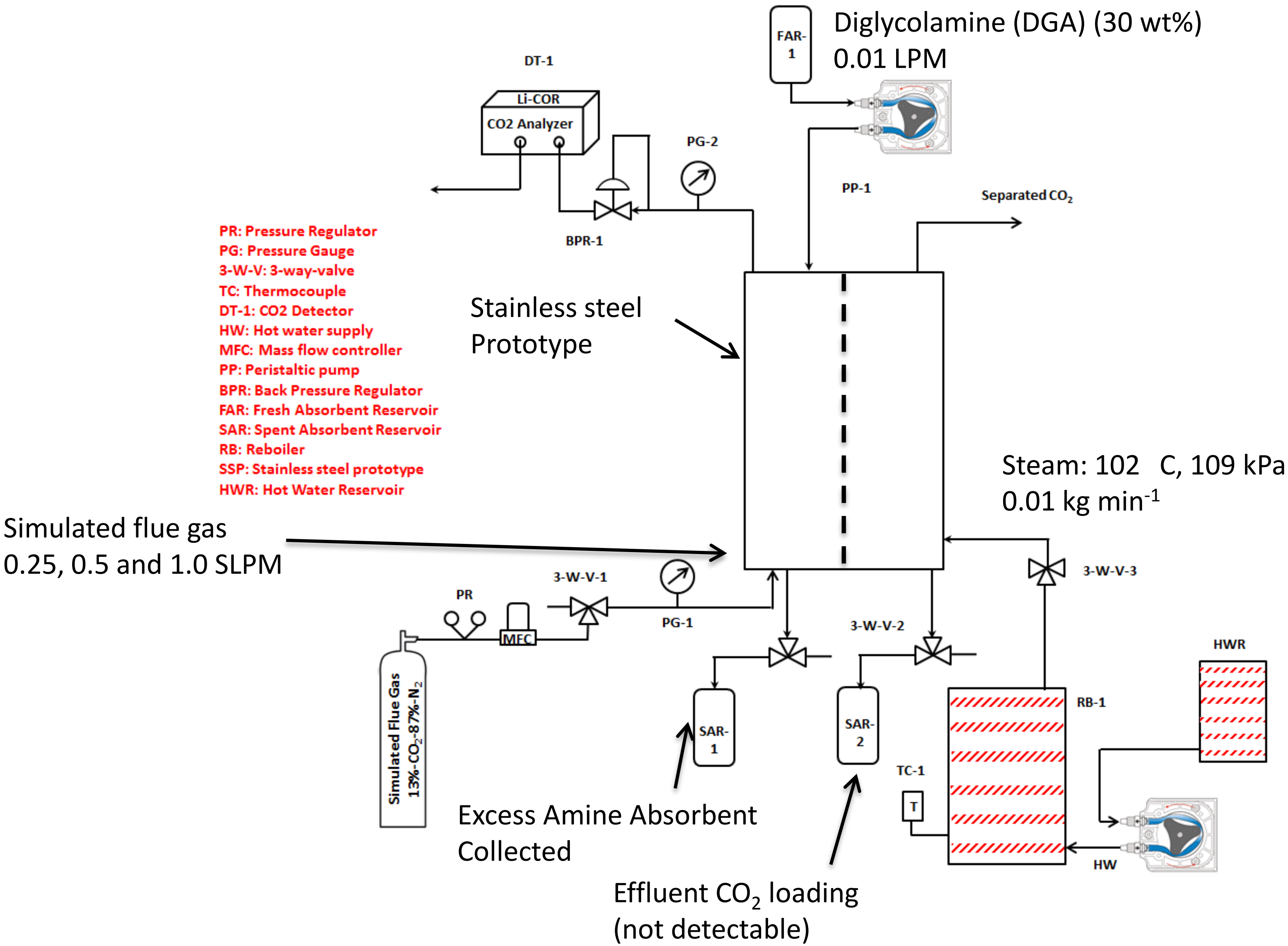
10 (cc/min)

20 (cc/min)

30 (cc/min)

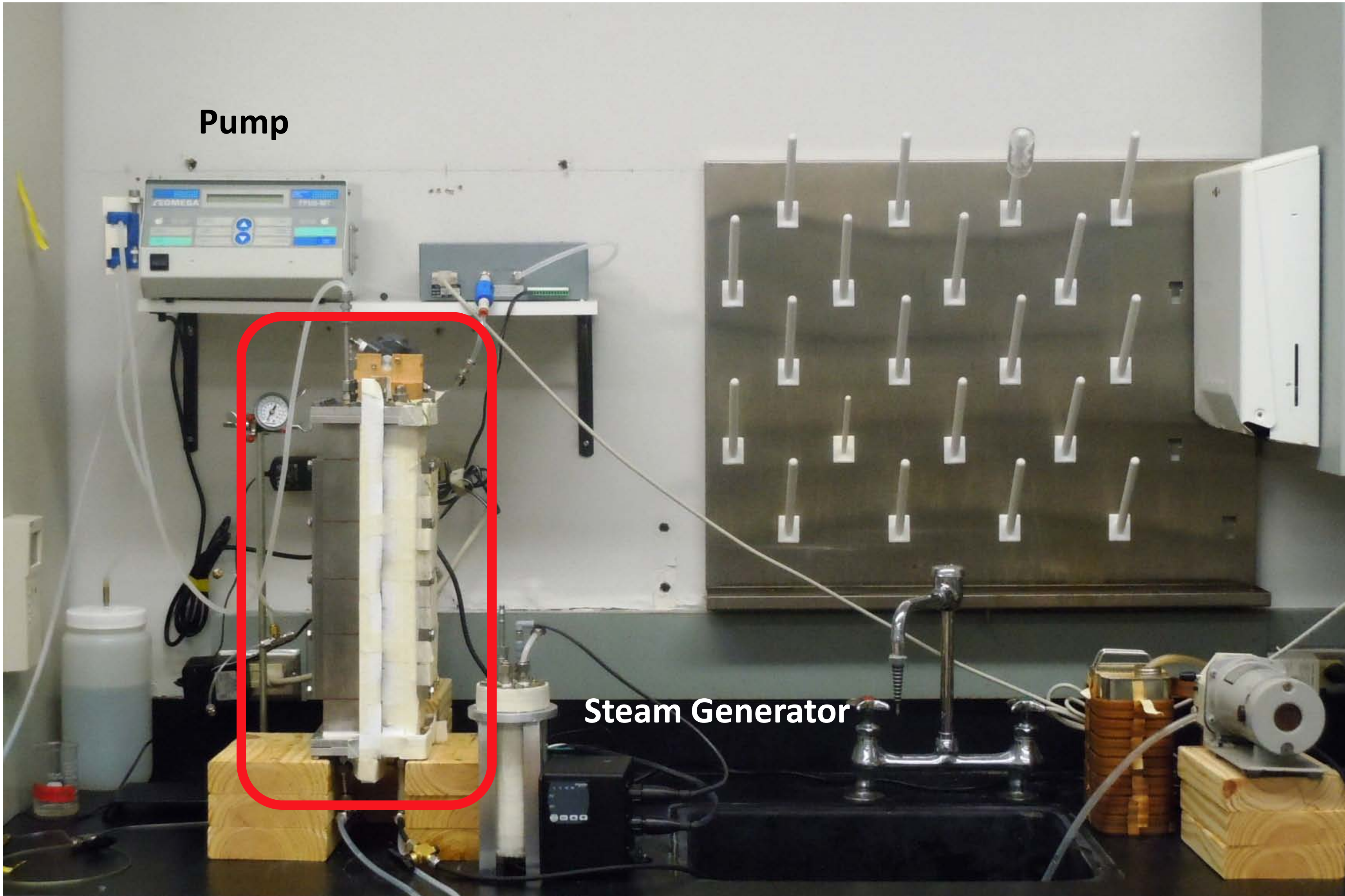
Combined Absorber and Stripper System

Experimental Setup for Proof-of-Concept Demonstration

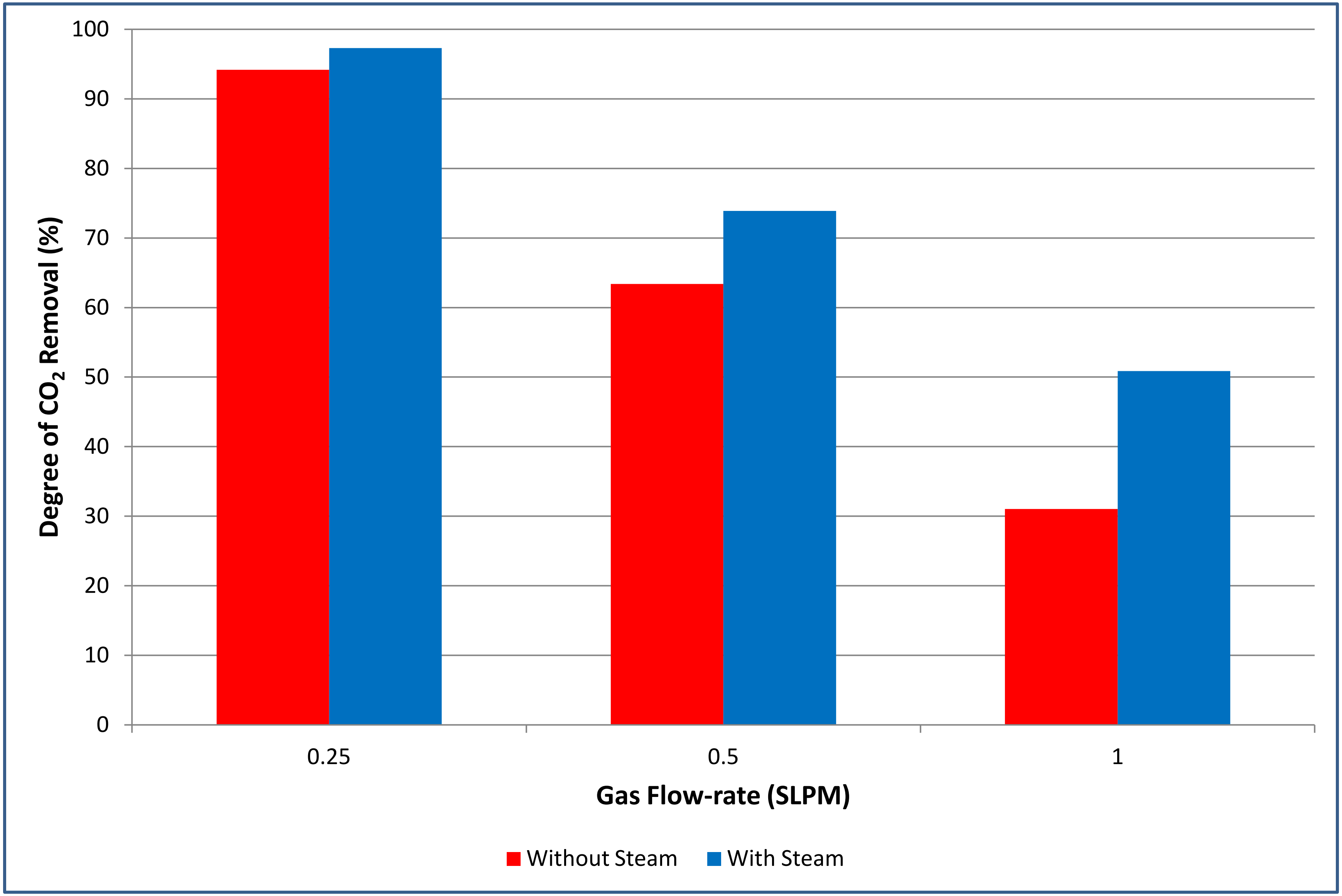


Combined Absorber and Stripper System

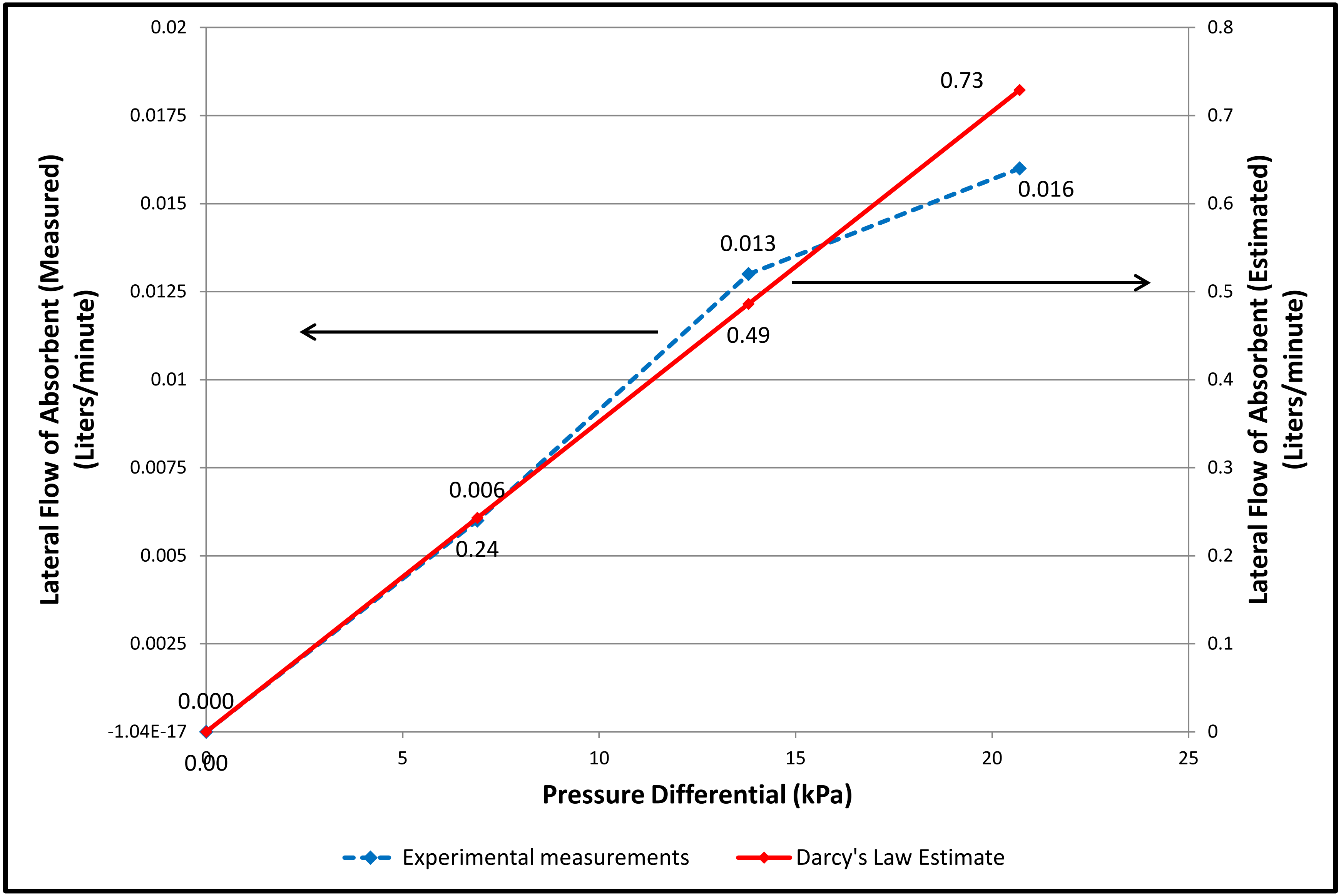
Experimental Setup



Combined Absorber and Stripper System
Degree of CO_2 Removal

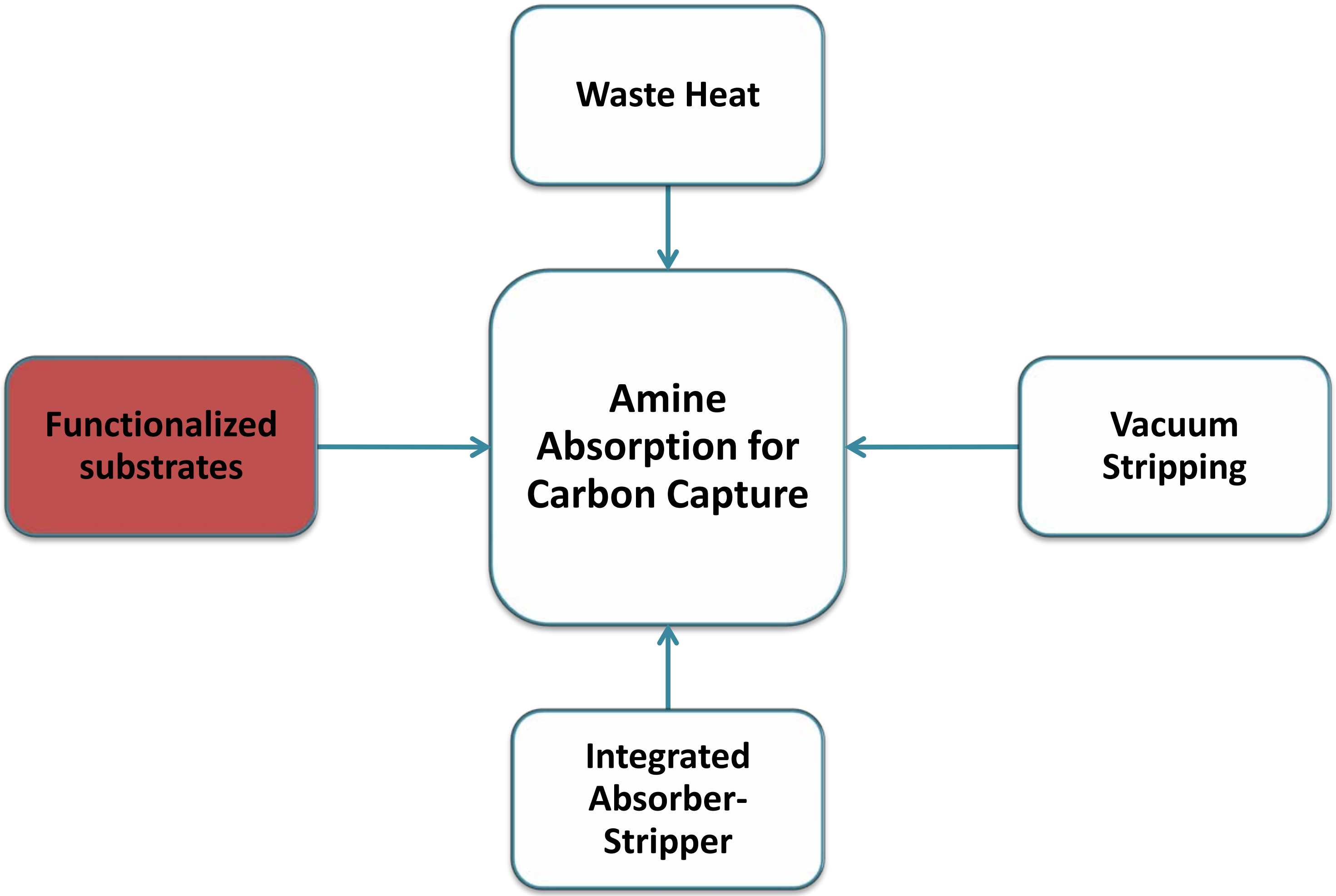


Combined Absorber and Stripper System
Lateral Flow of Absorbent

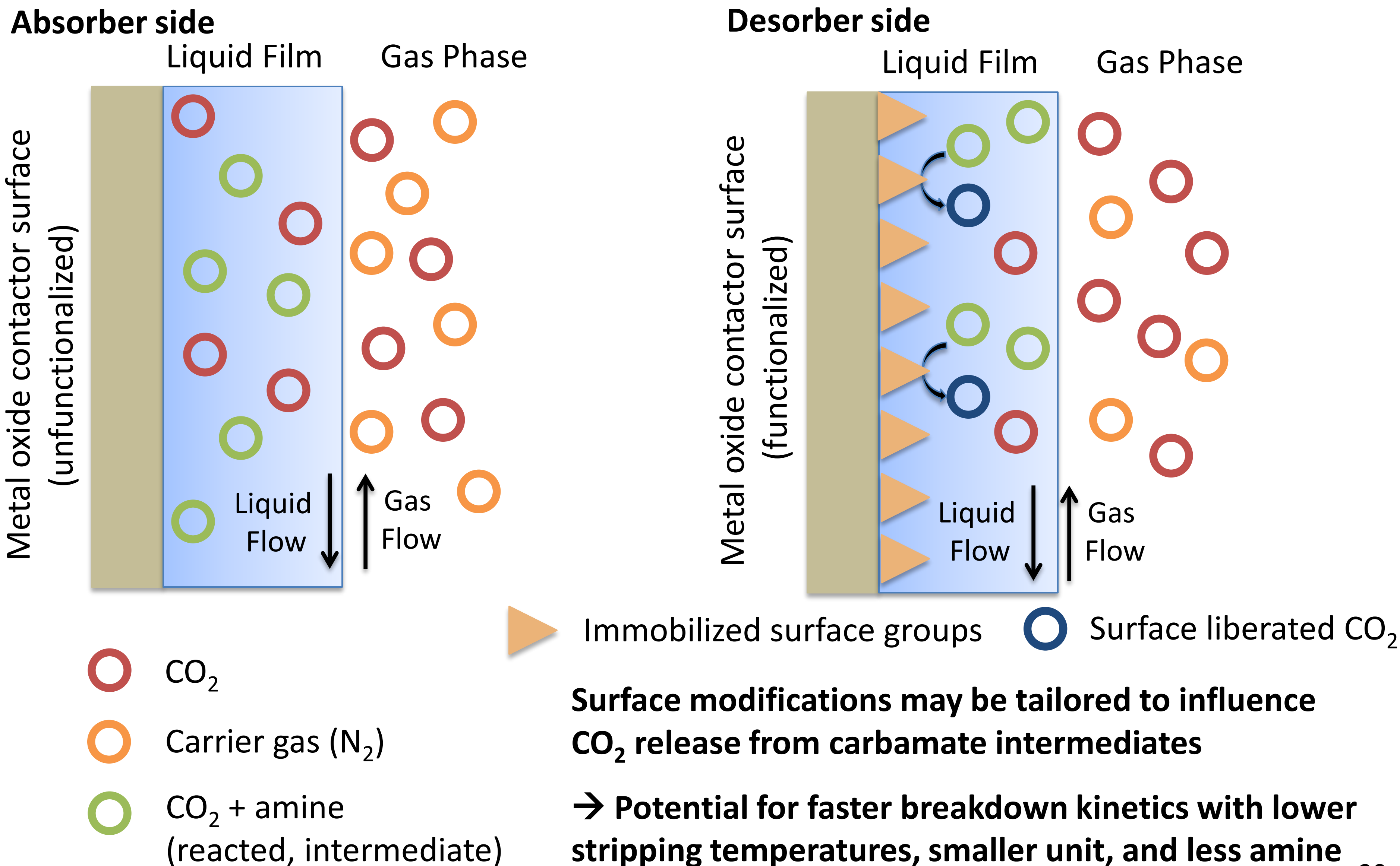


Our Approach:
Substrate functionalization

COMBINED PRESSURE, TEMPERATURE CONTRAST, AND SURFACE-ENHANCED SEPARATION OF CO_2



Ceramic Foam Surface Functionalization

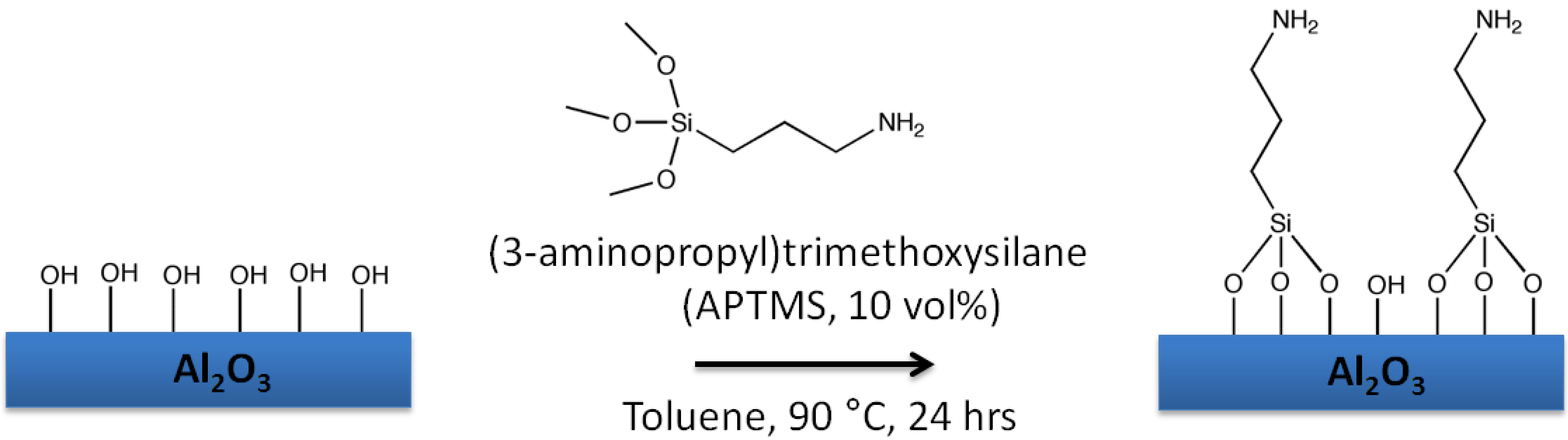


Surface modifications may be tailored to influence CO_2 release from carbamate intermediates

→ Potential for faster breakdown kinetics with lower stripping temperatures, smaller unit, and less amine

Silane Modification of Al_2O_3

Using established silane-based modifications of metal oxide (MO_x) surfaces



Calcinated α-alumina powder (74 – 44 μm, with surface area = 360 m^2 g^{-1})

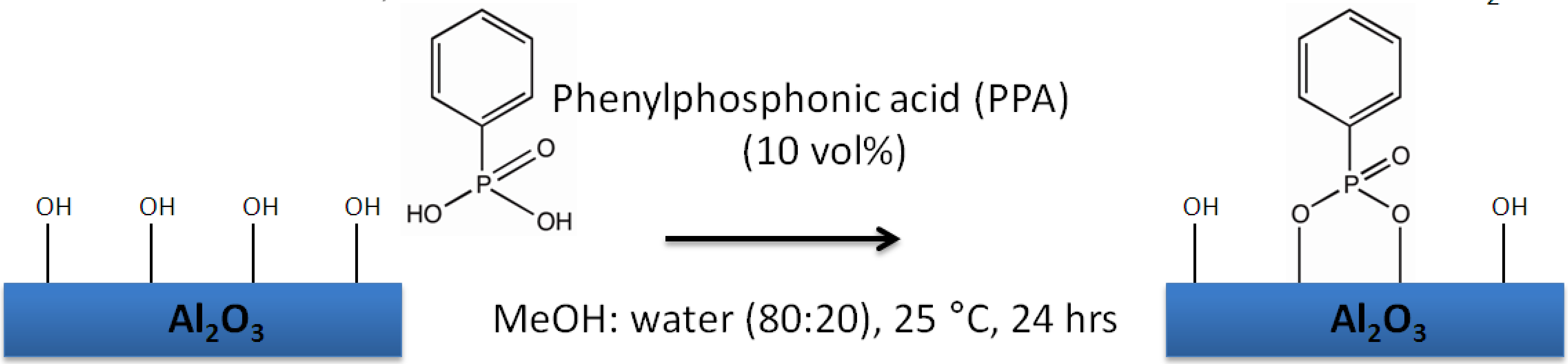
Stability studies: exposure to 3 M MEA with 0.3 mol CO_2, pH 10.30

TGA: weight loss from 200 to 600 °C under air at 10 °C min^{-1}

APTMS Al_2O_3	Weight Loss (%)	Grafting Density (molecules nm^{-2})	Loss from exposure (%)
As prepared	0.08	7.4×10^{-4}	N/A
1 hr exposure	0.05	6.6×10^{-4}	0.03
24 hr exposure	0.03	6.2×10^{-4}	0.02

Phosphonate Modification of Al_2O_3

Alternative to silanes, used for corrosion inhibition on steel and anti-biofilm on TiO_2



PPA1 = single PPA deposition, PPA2 = double PPA deposition

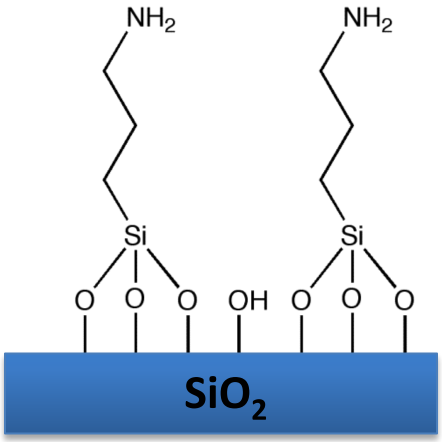
Stability studies: exposure to 3 M MEA with 0.3 mol CO_2, pH 10.30

TGA: weight loss from 200 to 600 °C under air at 10 °C min^{-1}

PPA Al_2O_3	Weight Loss (%)	Grafting Density (molecules nm^{-2})	Loss from exposure (%)
PPA1	3.64	0.04	N/A
PPA1 + 1 hr	0.00	0.00	3.64
PPA2	5.72	0.1	N/A
PPA2 + 1 hr	0.01	0.00	5.72

APTMS Modification of SiO_2

Due to the instability of silane and phosphonate bonds on Al_2O_3, other substrates explored



SiO_2: Evonik Areoperl colloidal silica 30 μm particles, 300 $m^2\ g^{-1}$

APTMS (10 vol%) deposition in toluene at 90 °C, 24 hours on SiO_2

Stability studies: exposure to 3 M MEA with 0.3 mol CO_2, pH 10.30
2 x wash with water, 2 x wash with EtOH, dry at 100 °C for 24 hours

APTMS SiO_2	Weight Loss (%)	Grafting Density (molecules nm^{-2})	Loss from exposure (%)
As prepared	6.64	5.0×10^{-2}	N/A
1 hr exposure	5.86	2.9×10^{-2}	0.8
24 hr exposure	5.30	2.0×10^{-2}	0.5

Typical Coverages: 2-4 molecules nm^{-2}

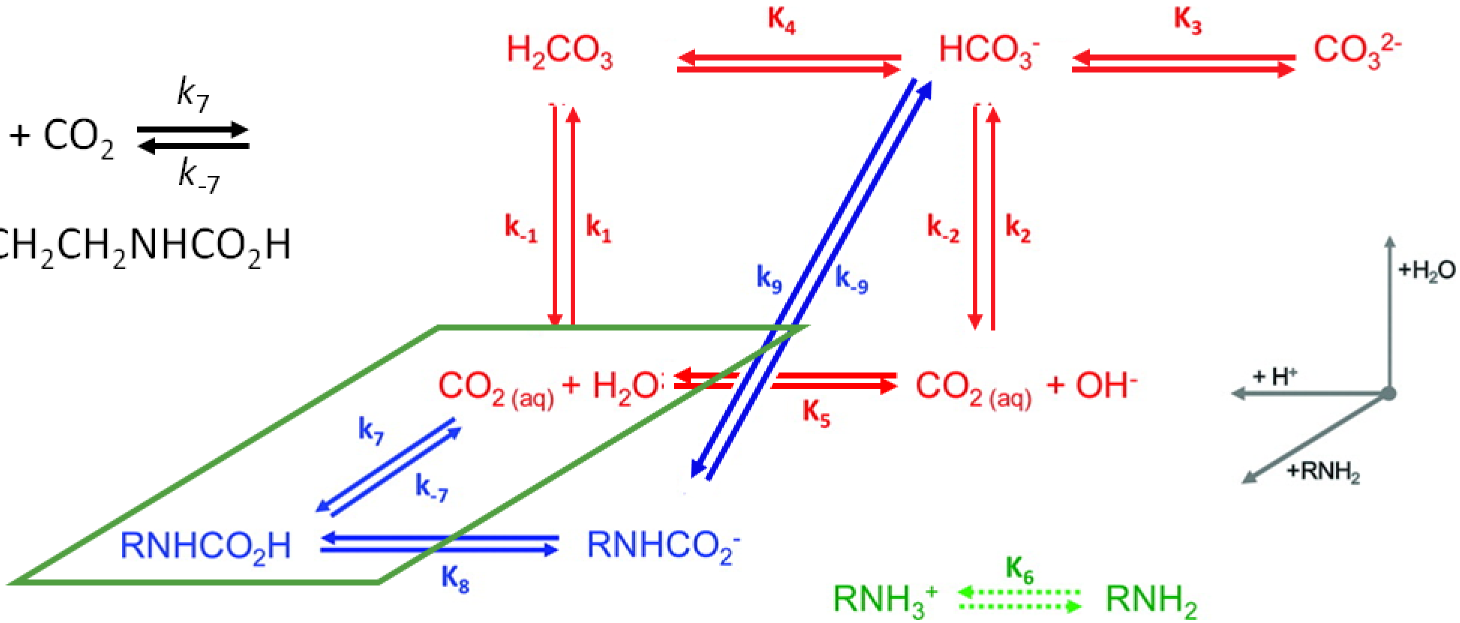
SiO_2 demonstrates a higher grafting density and slower loss of APTMS

Optimization should yield a stable functionalized surface under desorber conditions

Reactions between amine, CO_2, and bicarbonate

For MEA:

$$HOCH_2CH_2NH_2 + CO_2 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} HOCH_2CH_2NHCO_2H$$



		$k_7 = 5.8 \times 10^{10}\ e^{(-4872/T)}\ (M^{-1}\ s^{-1})$	$k_{-7} = 1.0 \times 10^{13}\ e^{(-7583/T)}\ (s^{-1})$	Calculated Equilibrium K_7
Absorber	30 °C	6.0×10^3	136	44
	70 °C	$\sim 3.9 \times 10^4$	$\sim 2.5 \times 10^3$	~16
Desorber	100 °C	$\sim 1.2 \times 10^5$	$\sim 1.5 \times 10^4$	~8
	150 °C	$\sim 5.8 \times 10^5$	$\sim 1.6 \times 10^5$	~3

Conway, W. et al. *J. Phys. Chem. A* **2011**, *115*, 14340.

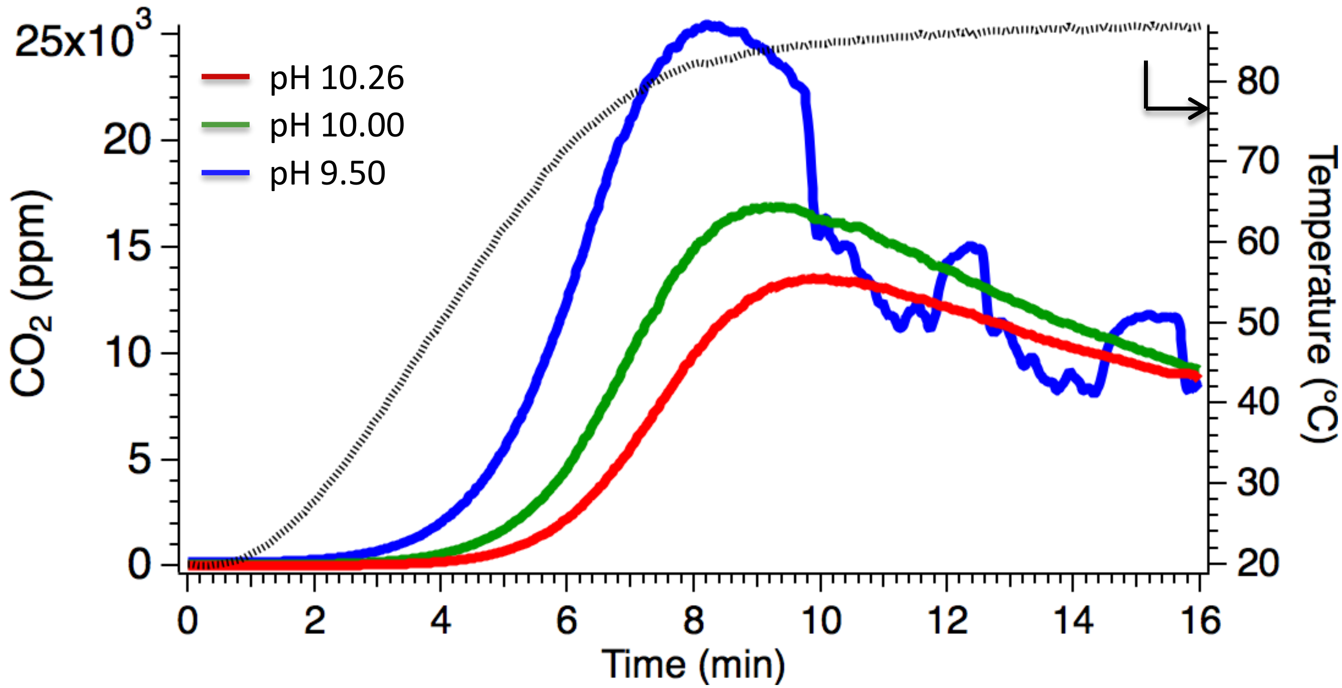
pH Effects on CO_2 Desorption with Temperature

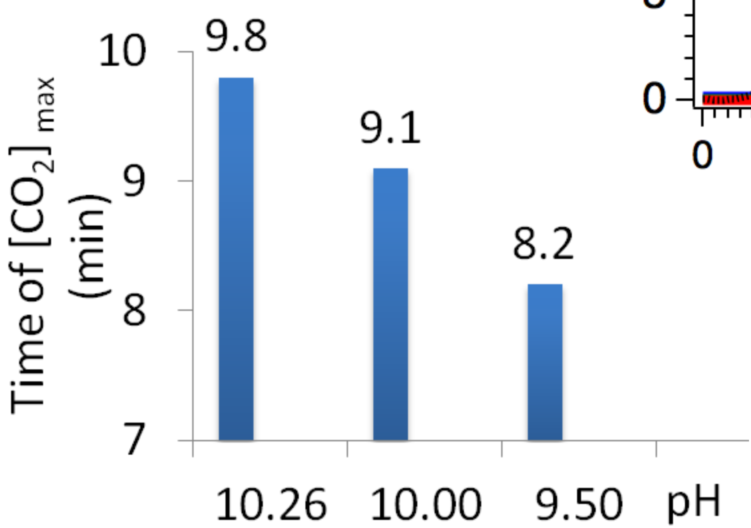
15 mL of 3 M MEA (~ 30 wt%) loaded with 0.3 mol CO_2

N_2 bubbling through solution at 800 mL min^{-1}, temperature from 25 ^oC to 86 ^oC at 12 ^oC min^{-1}

Initial pH values:
3 M MEA (no CO_2): 12.30
+ 0.3 mol CO_2: 10.26

pH of solution reduced with 12 M HCl
(no CO_2 release observed until heat applied)





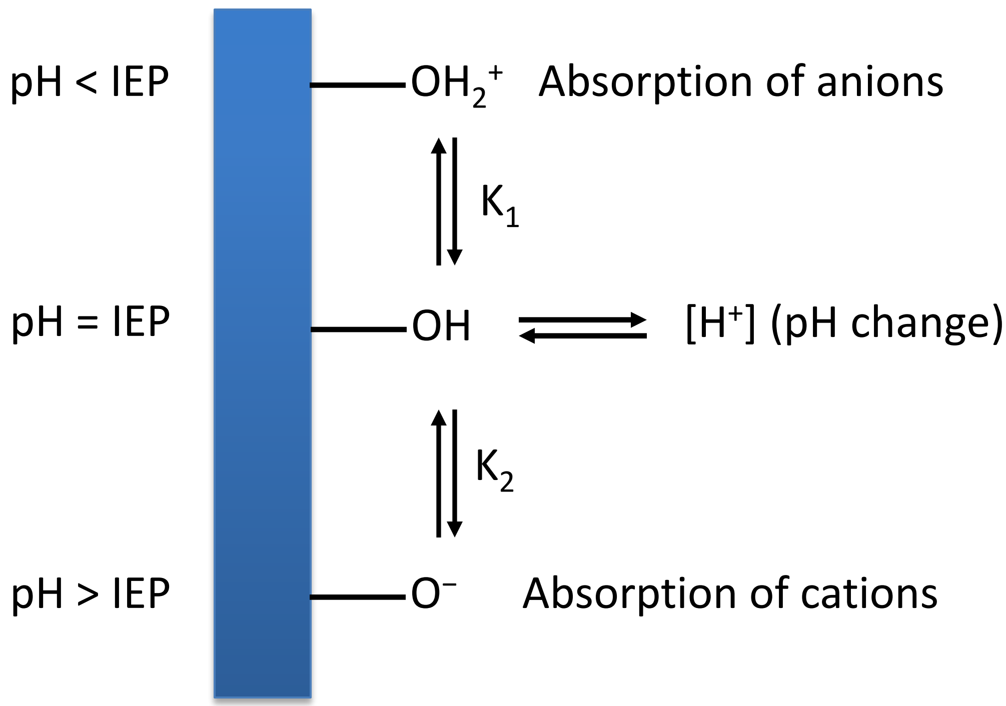
Others have demonstrated aqueous acid release of CO_2 from carbamates before. Do solid acids have a similar effect on CO_2 release?

Consider Acidity of Substrate Surface on CO_2 Desorption

Others have demonstrated ability of acids to liberate CO_2 from carbamates

It is not very practical to add aqueous acid to the desorber (separation issues)

However, metal oxide surfaces can function as an acid/base from the view of isoelectric points (IEP) (aka Brønsted acids/bases):



Metal Oxide:	$pH_{25\ C}$ of IEP at 25 ^{o}C
WO_3	0.2 – 0.5
SiO_2	1.7 – 3.5
γ-Al_2O_3	7 - 8
α-Al_2O_3	8 - 9
ZnO	9.5
NiO	10 – 11

Kosmulski, M. "Chemical Properties of Material Surfaces", Marcel Dekker, 2001.

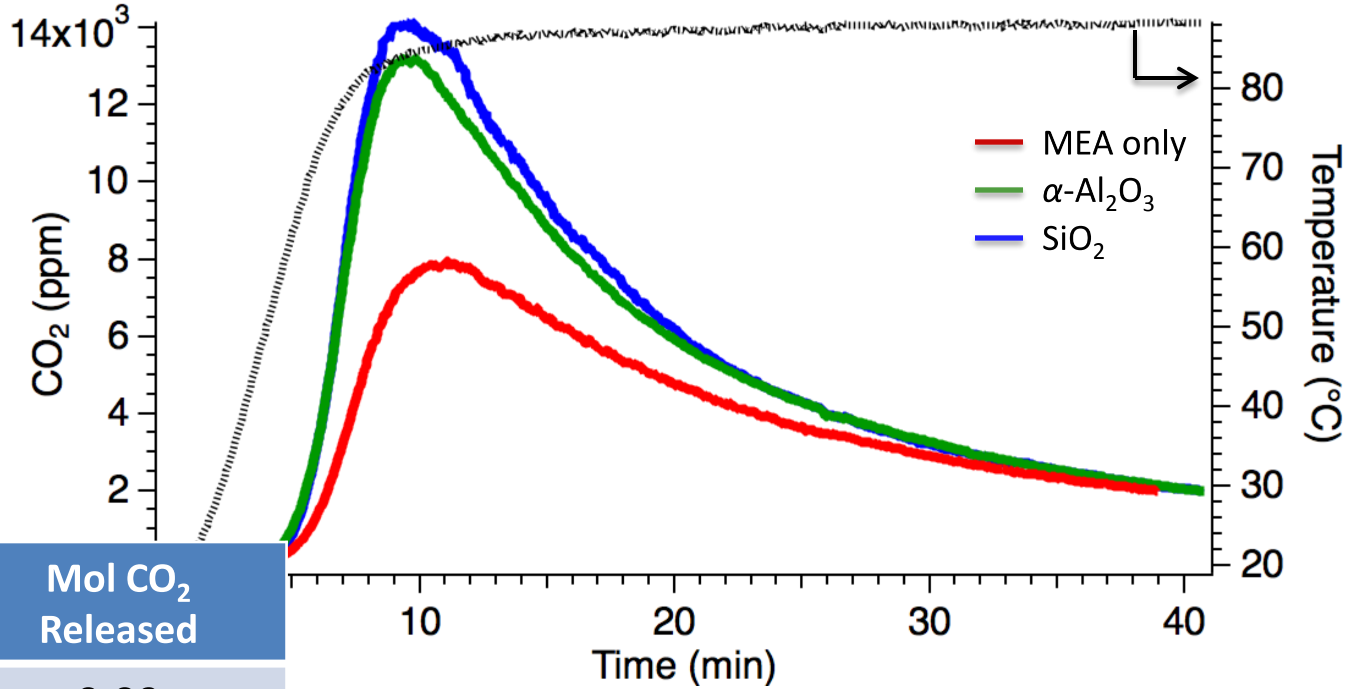
Preliminary Results: CO_2 Desorption in Presence of Metal Oxide

15 mL of 3 M MEA (~ 30 wt%) pre-loaded with 0.3 mol CO_2

To each solution, 1.5 g of MO_x powder added, 15 min equilibration

N_2 bubbling through solution at 800 mL min^{-1}, temperature from 25 ^oC to 86 ^oC at 12 ^oC min^{-1}

Initial pH values:
3 M MEA: 10.26
+ α-Al_2O_3: 10.32
+ SiO_2: 10.22



	Time (min)	Temp (C)	Mol CO_2 Released
MEA	9.8	84	0.09
Al_2O_3	8.8	83	0.13 (+ 44%)
SiO_2	8.6	82	0.14 (+ 56%)

→ The presence of metal oxide substrates has an effect on the extent of CO_2 desorption

Summary and Conclusions

- **Combined absorber/desorber for CO_2 removal**
  - We have identified commercially available materials – ceramic foams that can be used to combine the absorber and desorber
  - 1-D CO_2 absorption studies were conducted to select conditions suitable for achieving 90% CO_2 removal in a bench-scale system
  - Feasibility of the combined absorber/desorber system was demonstrated in a bench-scale, stainless steel prototype (90% CO_2 removal could be achieved for simulated flue gas containing 13% CO_2 with 30 wt% diglycolamine (DGA) as the absorbent)
- **Substrate functionalization and metal oxide effects**
  - α-Al_2O_3 is a poor substrate for silane and phosphonate functionalization due to low surface coverage and instability at high pH
  - Surface functionalization chemistry can be optimized to improve grafting density and stability at high pH
  - Presence of metal oxides increases CO_2 desorption amount, suggesting a simple approach to improve stripper performance

Research Tasks for 2013-14

- **Modeling combined absorber/desorber CO_2 separation process**
  - A commercial fluid flow simulation software such as COMSOL Multiphysics will be used to develop a flow model
  - A simpler, 1-D model is the first step, followed by models with greater complexity

- **Completion of surface functionalization**
  - Increase coverage and stability of APTMS on SiO_2 substrates
  - Test the hypothesis that metal oxides 'catalyze' carbamate decomposition
  - Demonstrate functionalized vs. non-functionalized substrates in absorption/desorption process

Project Budget

Budget Period Object Class Category	Budget Period 1 (10.01.11 – 09.30.12)	Budget Period 2 (10.01.12 – 09.30.13)	Budget Period 3 (10.01.13 – 09.30.14)	Total
Personnel	$134,079	$180,738	$113,637	$428,454
Fringe Benefits	$28, 586	$40,953	$29,811	$99,350
Travel	$4,700	$4,700	$4100	$13,500
Equipment	$27,035	$0	$0	$27,035
Supplies	$25,000	$15,000	$15,000	$55,000
Contractual	$0	$0	$0	$0
Construction	$0	$0	$0	$0
Other	$11,600	$10,480	$600	$22,680
Total Direct Charges	$231,000	$251,871	$163,148	$646,019
Indirect Charges	$102,094	$127,045	$85,653	$314,792
Federal Share	$243,621	$327,568	$197,458	$768,647
Non-Federal Share	$89,473	$51,348	$51,343	$192,164
Total	$333,094	$378,916	$248,801	$960,811

Acknowledgements

Personnel

•Dr. Joe Powell, Chief Scientist at Shell Oil Company

•Dr. TS Ramakrishnan, Scientific Advisor at Schlumberger-Doll Research Center

•Hirasaki Group & Wong Group members at Rice University

Additional Funding Support

•Energy and Environmental Systems Institute (EESI) at Rice University

•Rice Consortium on Processes in Porous Media

•Schlumberger