

# **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. George Hirasaki**

A J. Hartsook Chair Professor in Chemical Engineering, Rice University

NETL CO<sub>2</sub> Capture Technology Meeting

**July 9<sup>th</sup>, 2012**

- About Rice University
- Project Team
- Project Overview
- Combined Pressure and Temperature Contrast and Surface-enhanced Separation of Carbon-dioxide
- Supporting experimental and simulation results
- Merits of proposed technology
- Project Objectives
- Project Budget

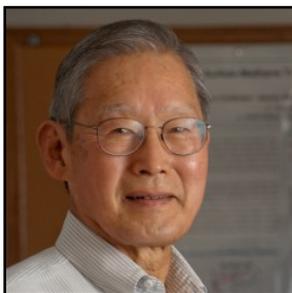
# Rice University



- Located in Houston, TX
- 295-acre, heavily wooded campus
- Ranked 17<sup>th</sup> 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

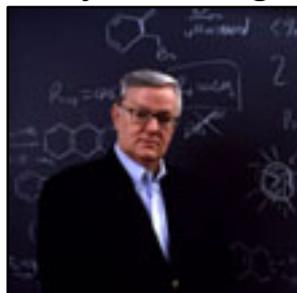
## Project Director



**George Hirasaki**

A. J. Hartsook Professor in Chemical & Biomolecular Engineering

## Co-Project Investigator



**Edward Billups**

Professor in Chemistry

## Co-Project Investigator



**Michael Wong**

Professor in Chemical & Biomolecular Engineering & Chemistry

## Co-Project Investigator



**Kenneth Cox**

Professor-in-practice in Chemical and Biomolecular Engineering

## Graduate Student



**Sumedh Warudkar**

PhD Candidate

## Postdoctoral Associate



**Jerimiah Forsythe**

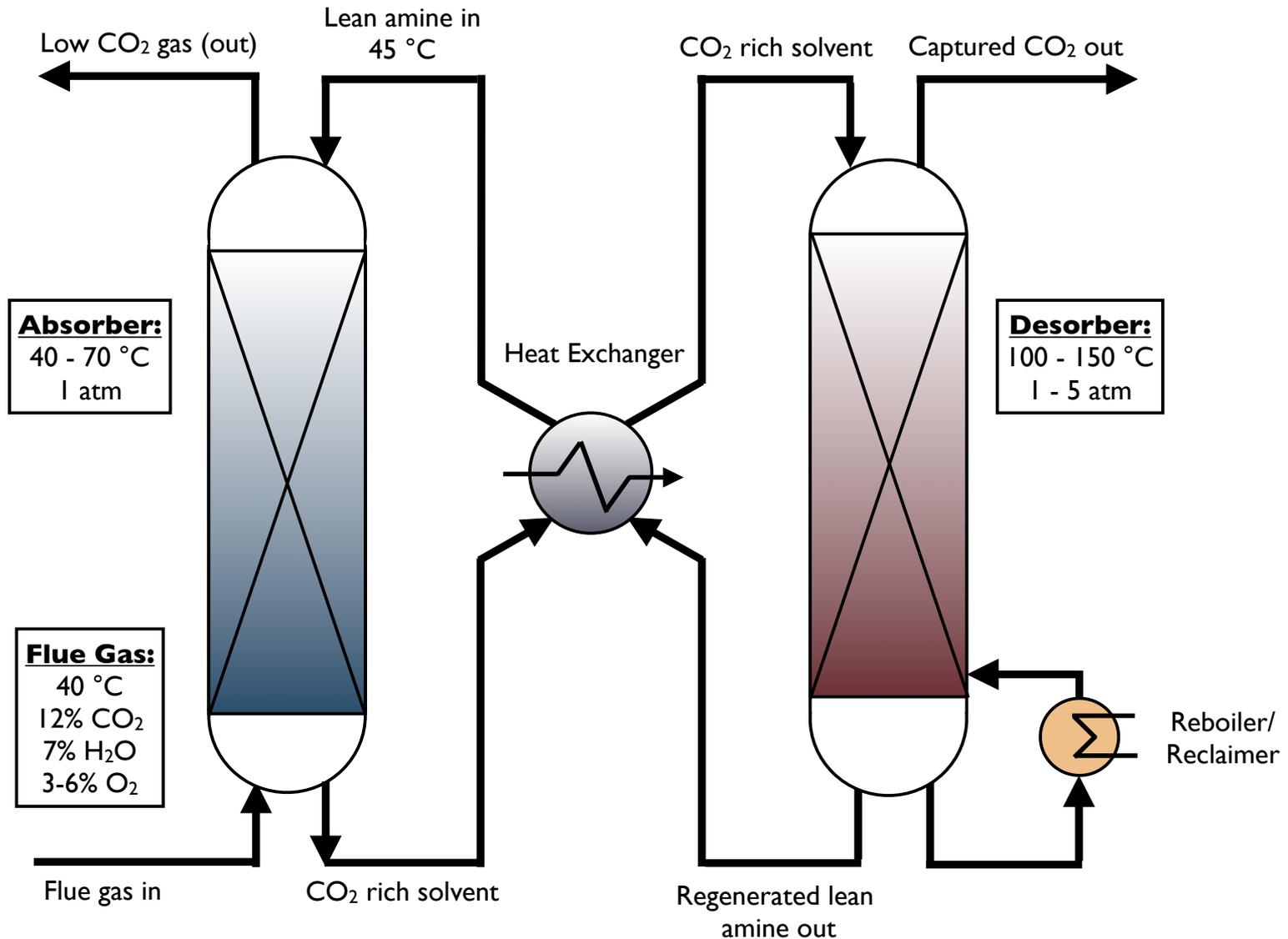
PhD, Chemistry (LSU, 2011)

# Project Overview

---

- Project funding under DOE agreement – DE-FE0007531
- Total project cost - \$960,811 over three years with 20% cost-share agreement
- Contract awarded executed October 2011
- 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<sub>2</sub> for post-combustion carbon capture to meet DOE's goal of at least 90% CO<sub>2</sub> removal at no more than 35% increase in the cost of electricity”*

# Conventional Amine Absorption Adapted for Carbon Capture



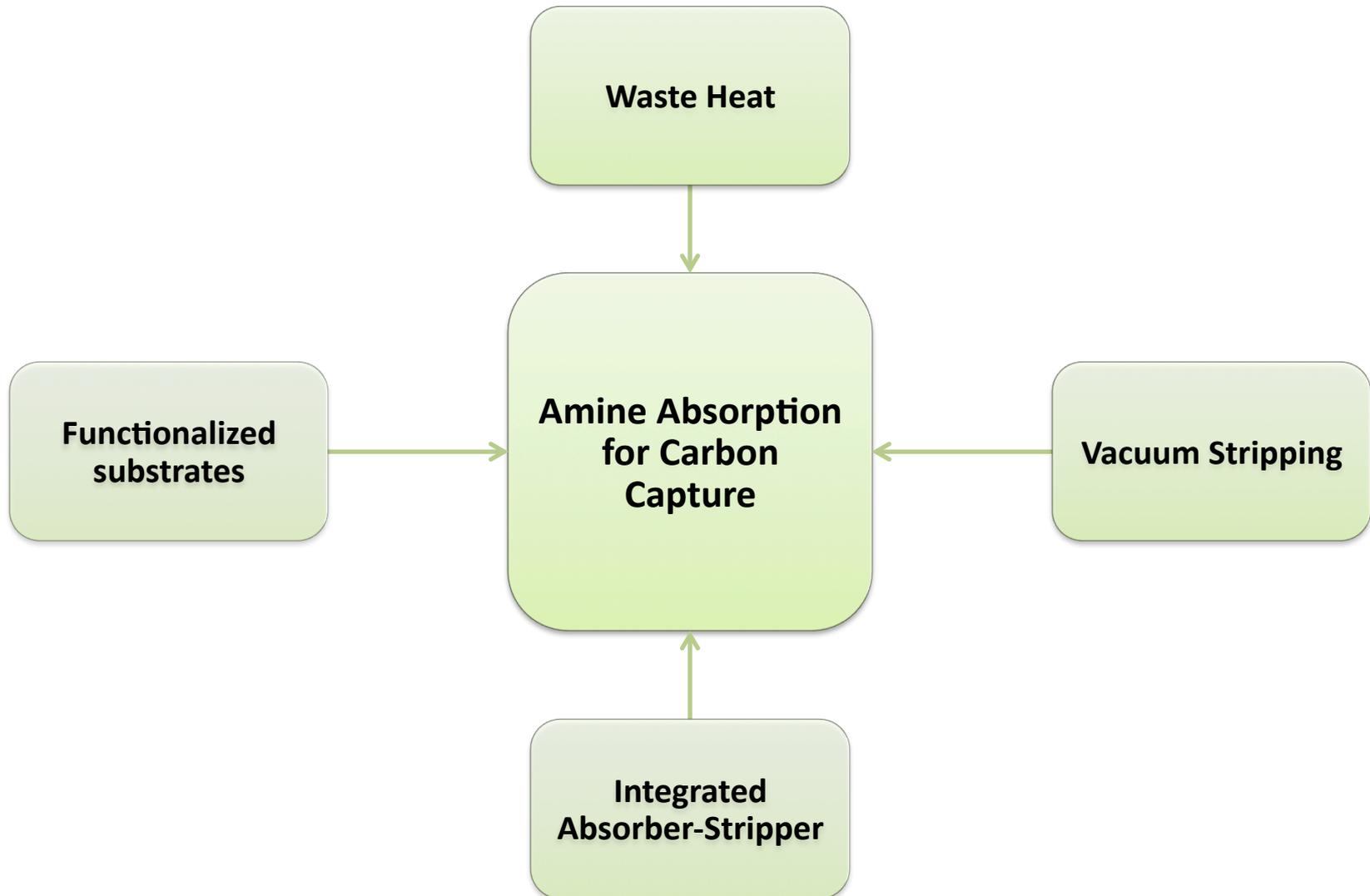
# Drawbacks of Conventional Amine Absorption

---

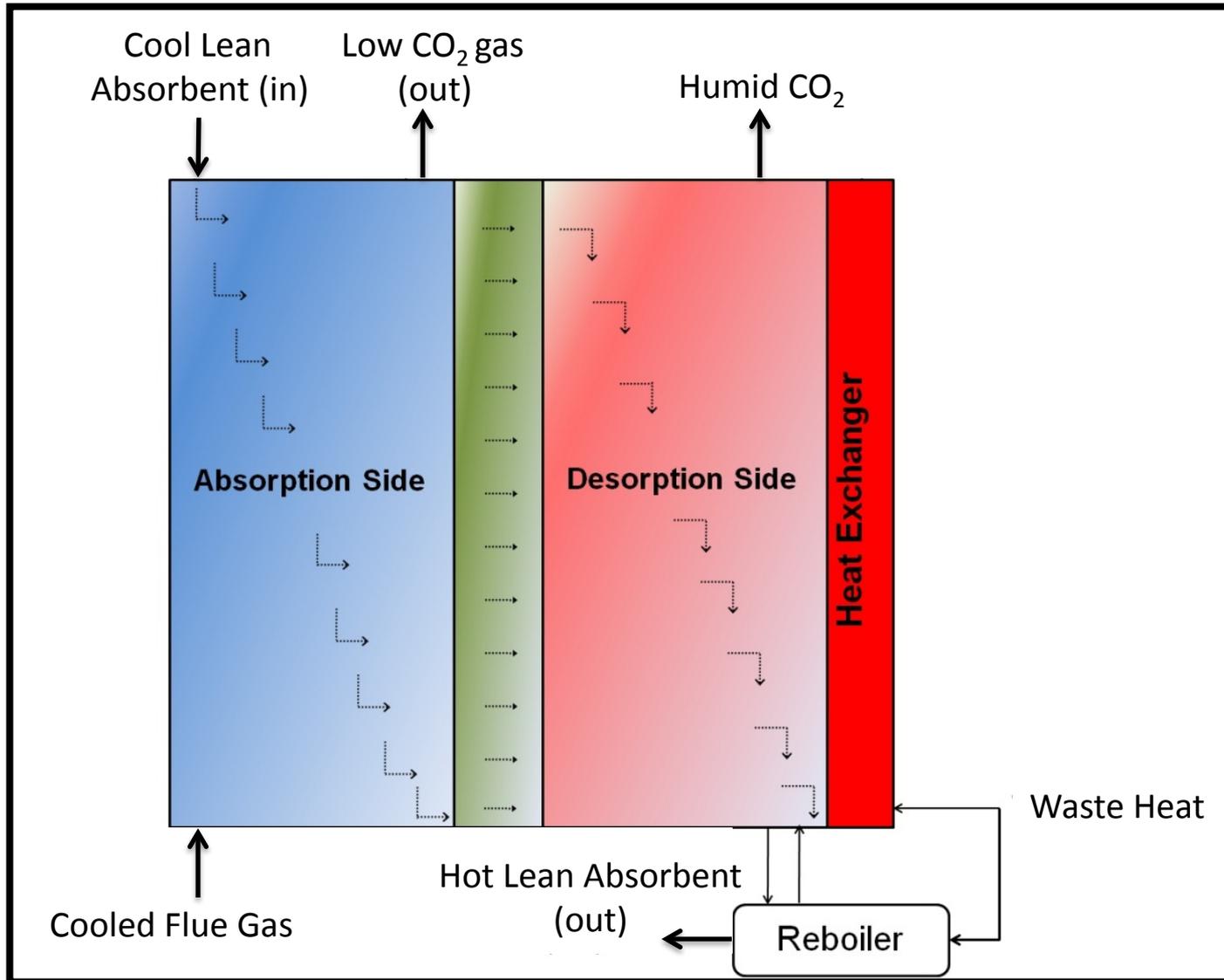
- Amine absorption was developed and optimized for Natural gas sweetening not Carbon Capture
- Absorbent regeneration is very energy intensive and requires diverting low pressure steam from the LP steam turbine at coal-fired utilities
- Parasitic load due to Carbon capture can be in excess of 50% of rated capacity of power plant
- Commonly used amines like MEA and DEA are very corrosive at high CO<sub>2</sub> loadings
- Corrosion problems are worse at higher operating temperatures which correspond to higher stripper pressure
- Requires space for a separate absorber and desorber column which can be a problem while retrofitting existing coal-fired utilities

# Our Approach

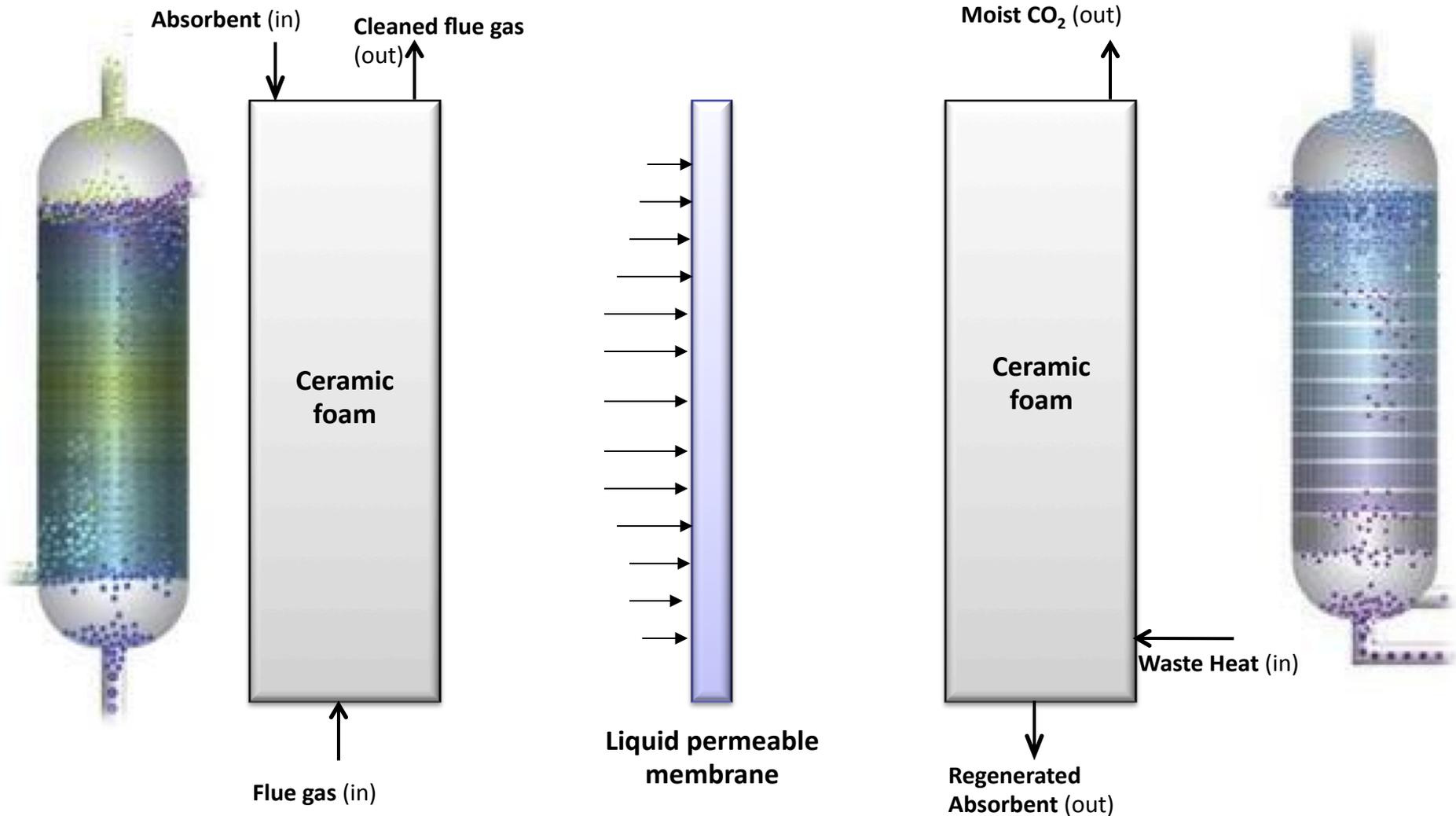
COMBINED PRESSURE AND TEMPERATURE CONTRAST AND SURFACE-ENHANCED SEPARATION OF CO<sub>2</sub>



# Process Schematic Integrated Absorber-Stripper



# Process Description

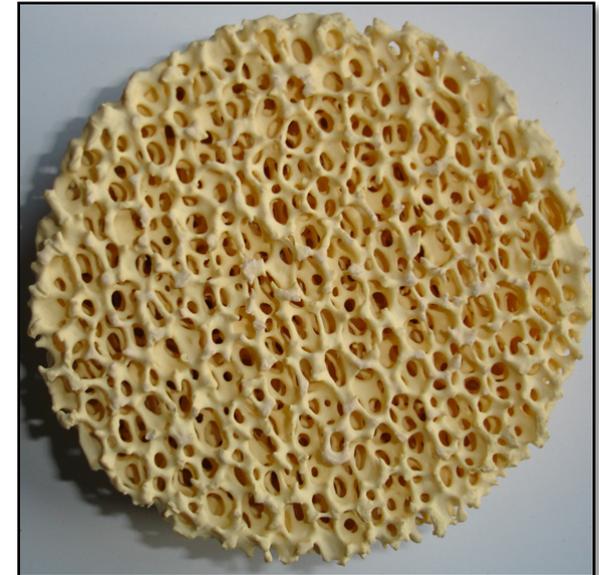


# Gas-liquid contactor – Ceramic Foam

## Ceramic Foam

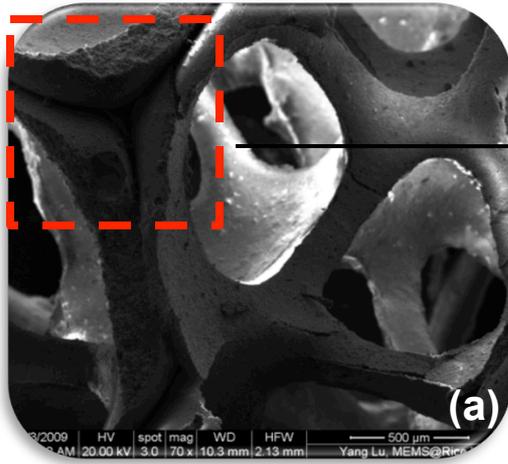
- Low bulk density
- Very high macro-porosity (80%-90%)
- Very high geometric surface area (upto 4756 m<sup>2</sup>/m<sup>3</sup> (solid))
- Regulated pore-size
- Low pressure drop
- High structural uniformity
- Ease of reproducibility of structure

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

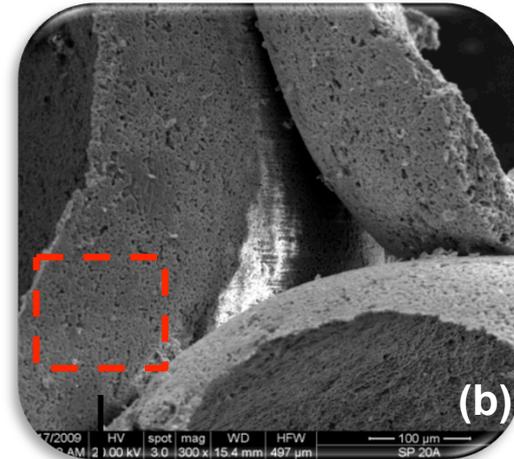


Commercial Sample of Ceramic foam

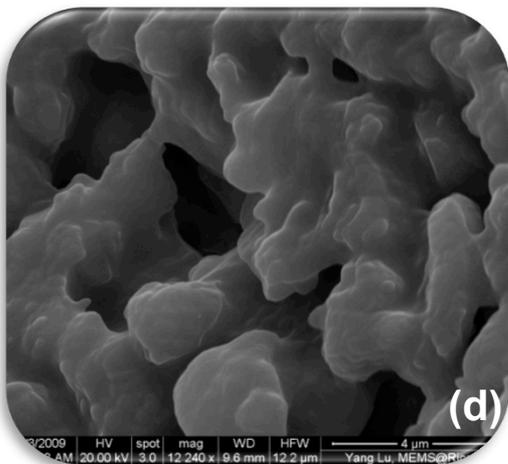
# Ceramic Foam – SEM Micrographs



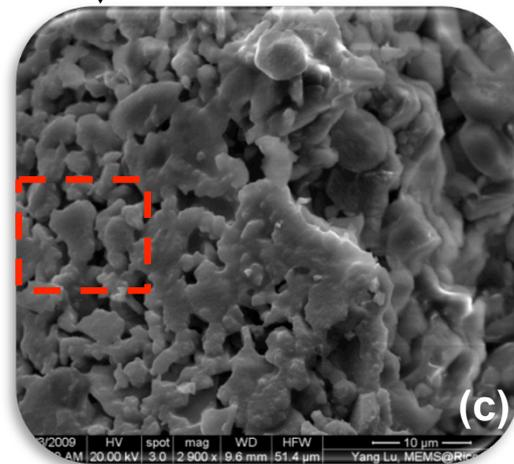
70x



300x

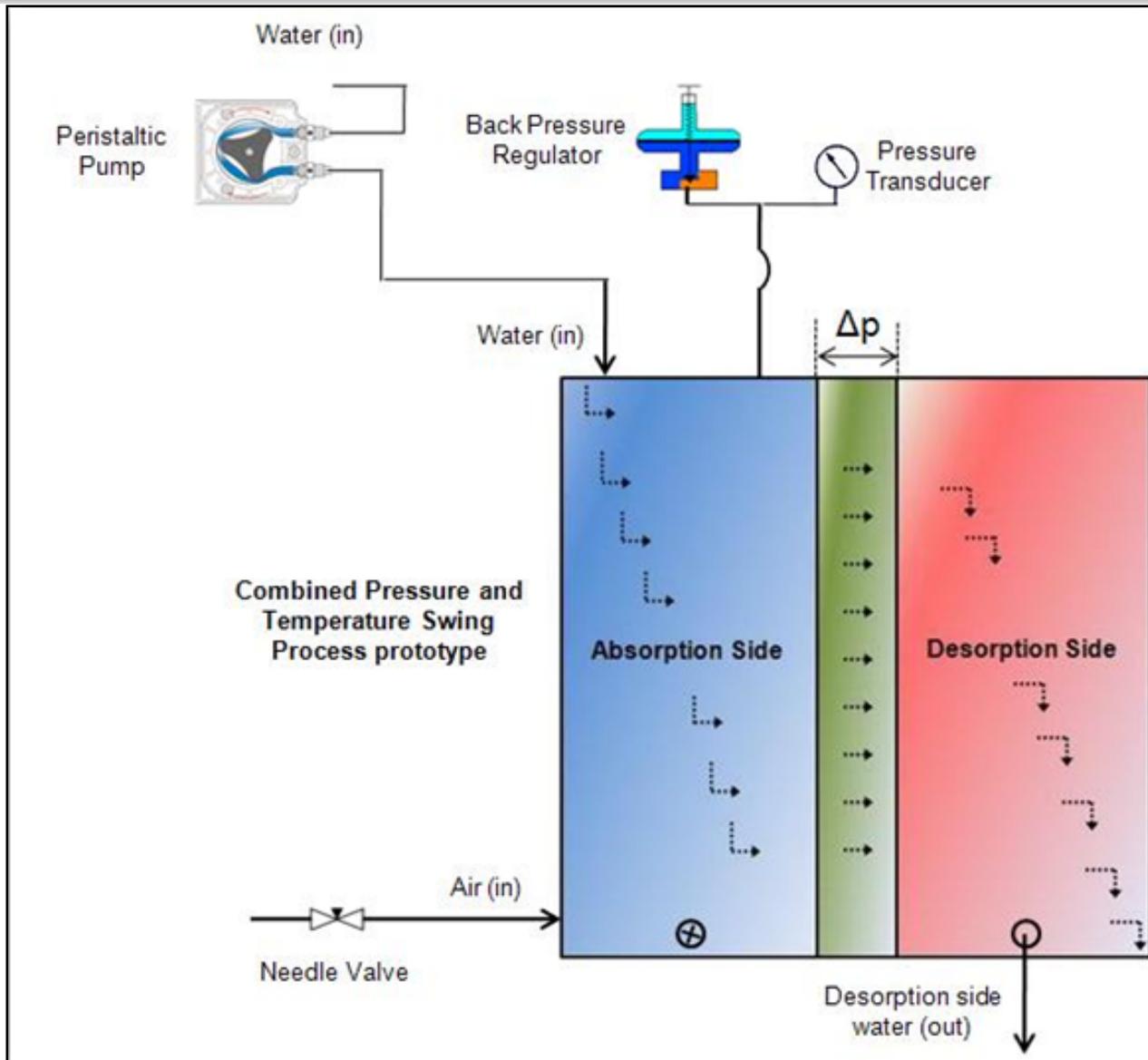


12400x

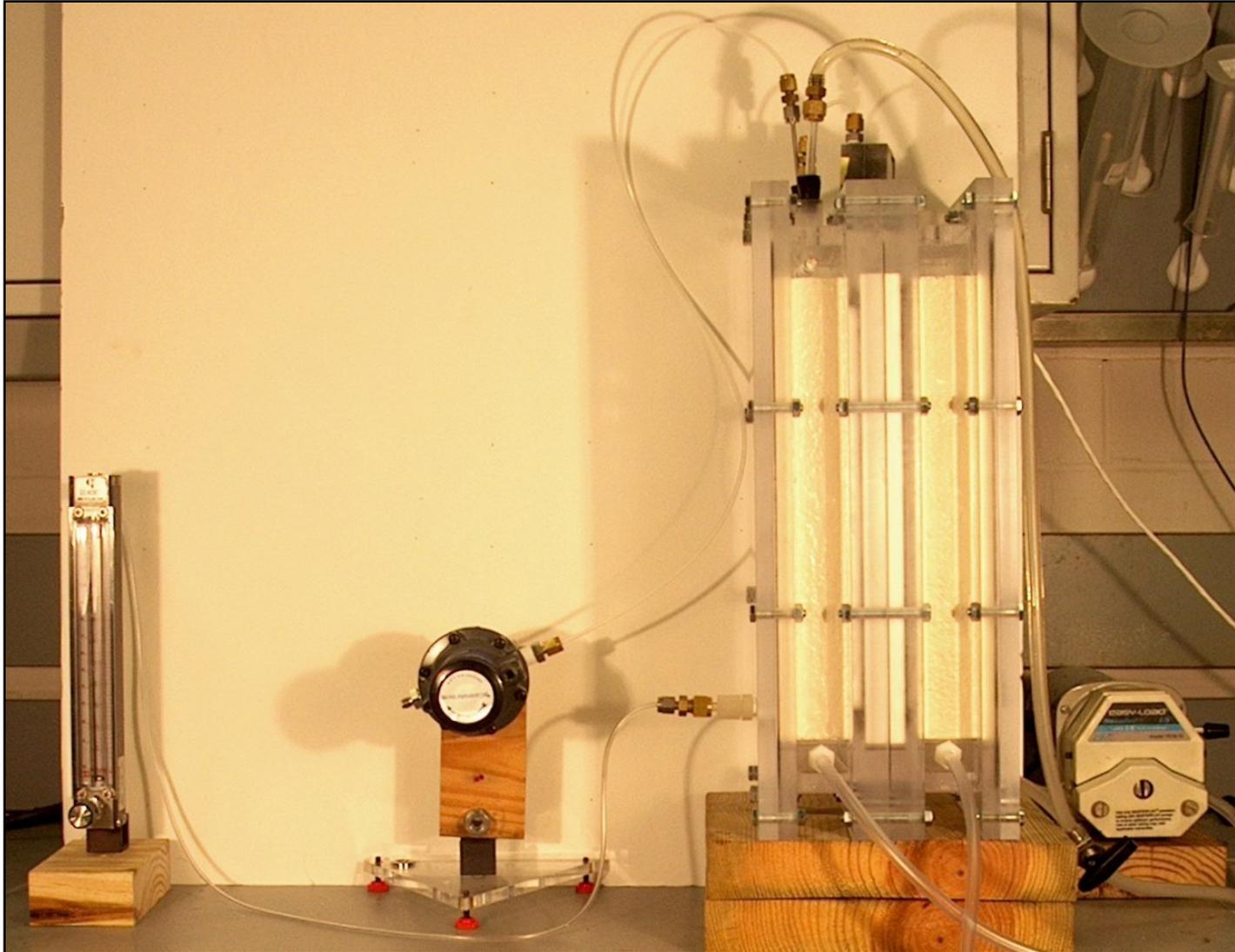


2900x

# Schematic of Plexiglas Setup

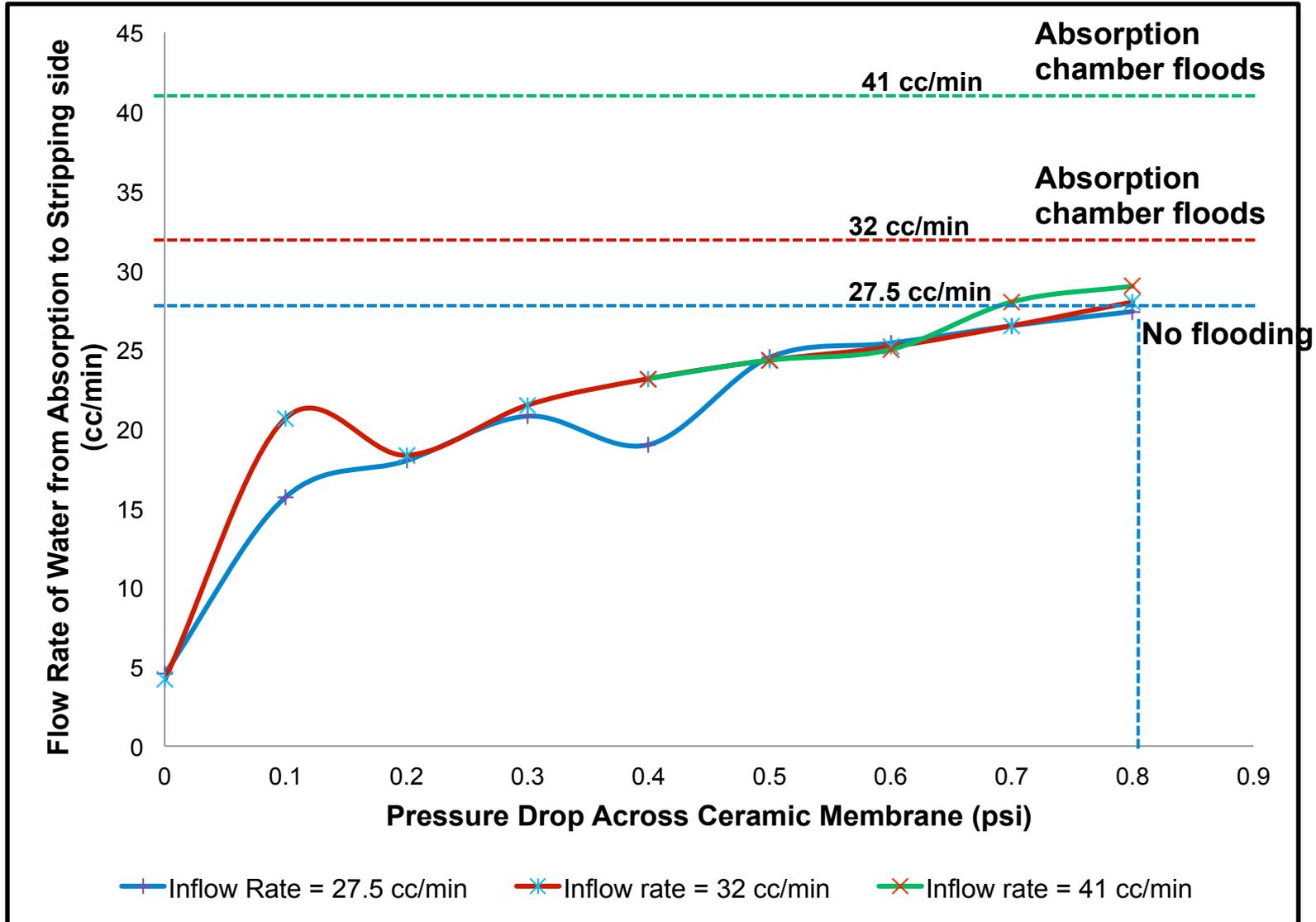


# Plexiglas Experimental Prototype

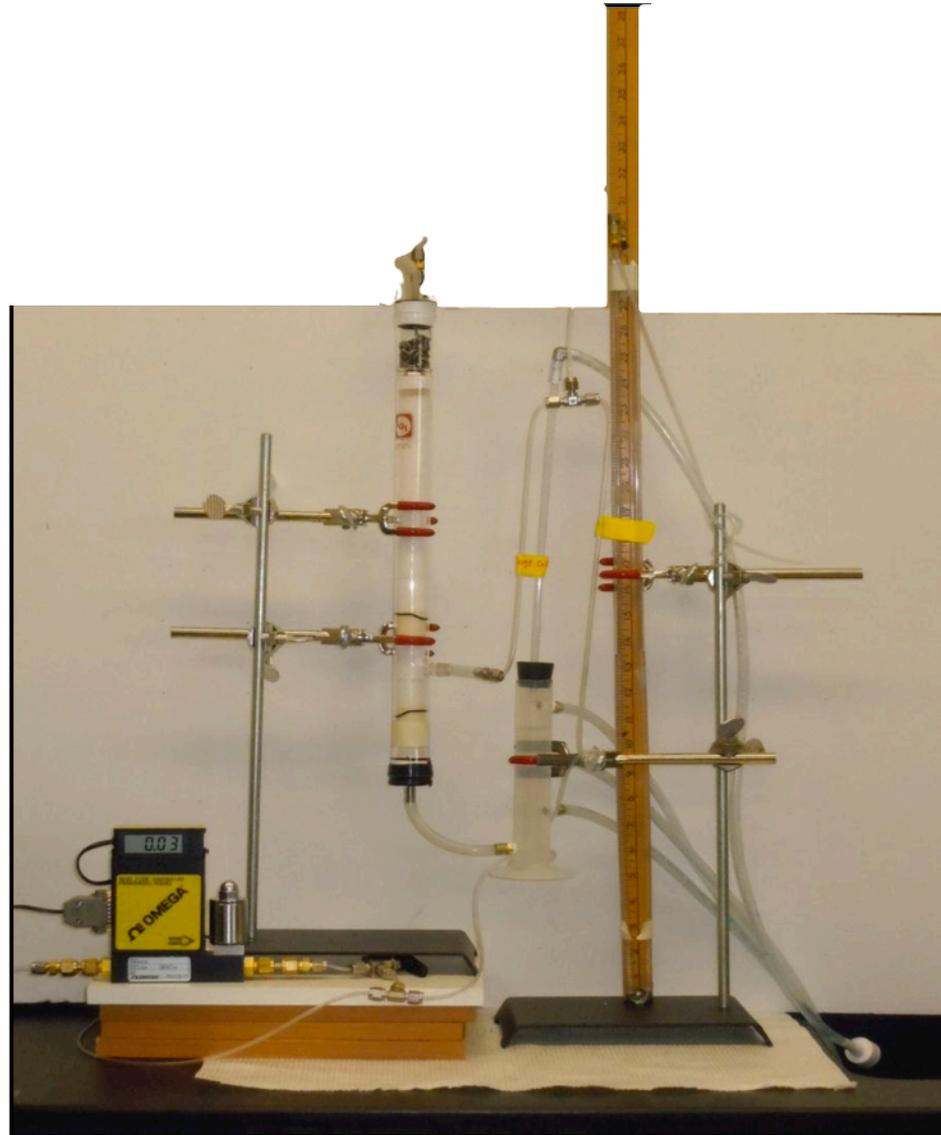


# Result of Flow Experiments

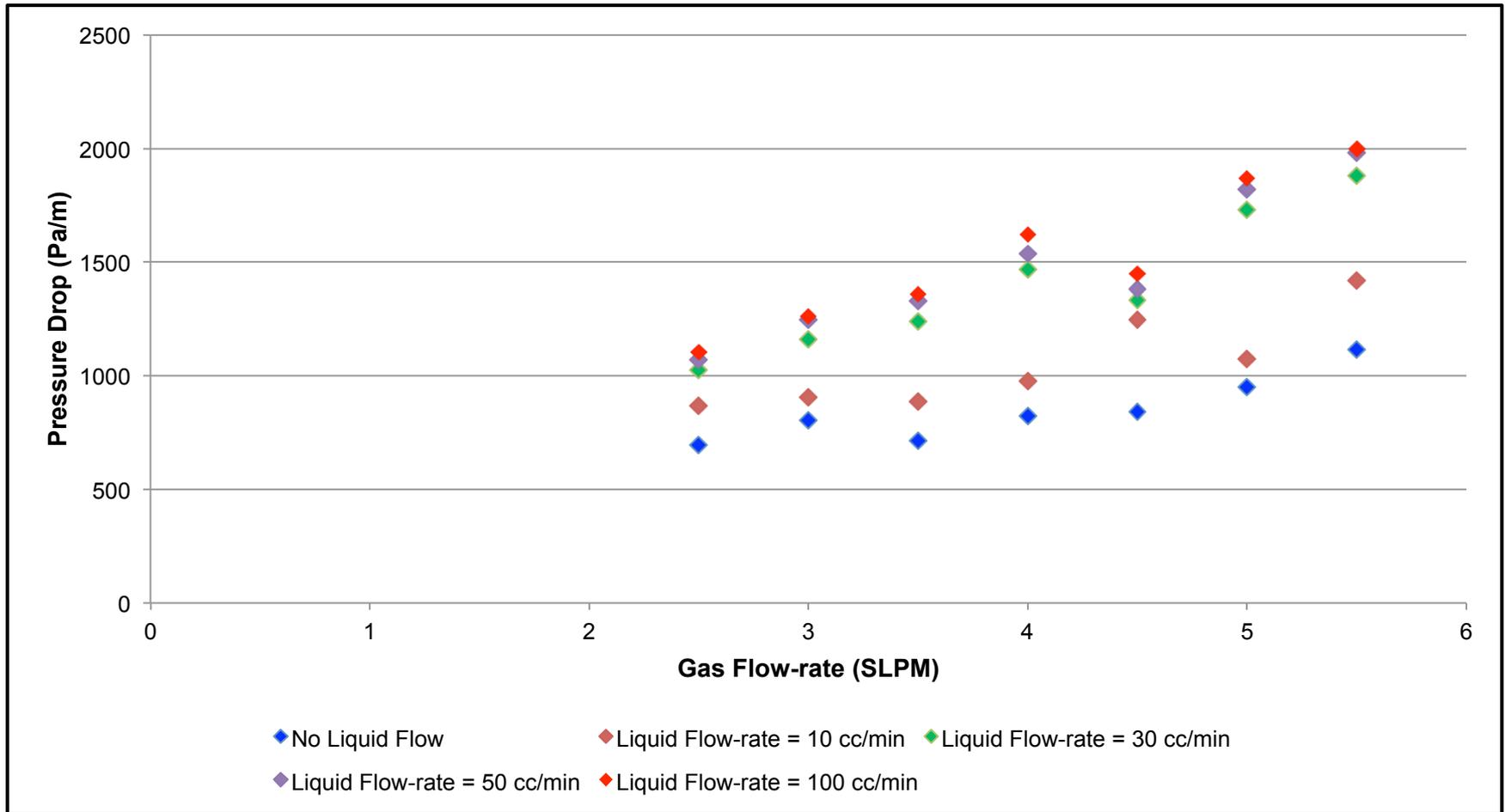
## A Proof-of-concept



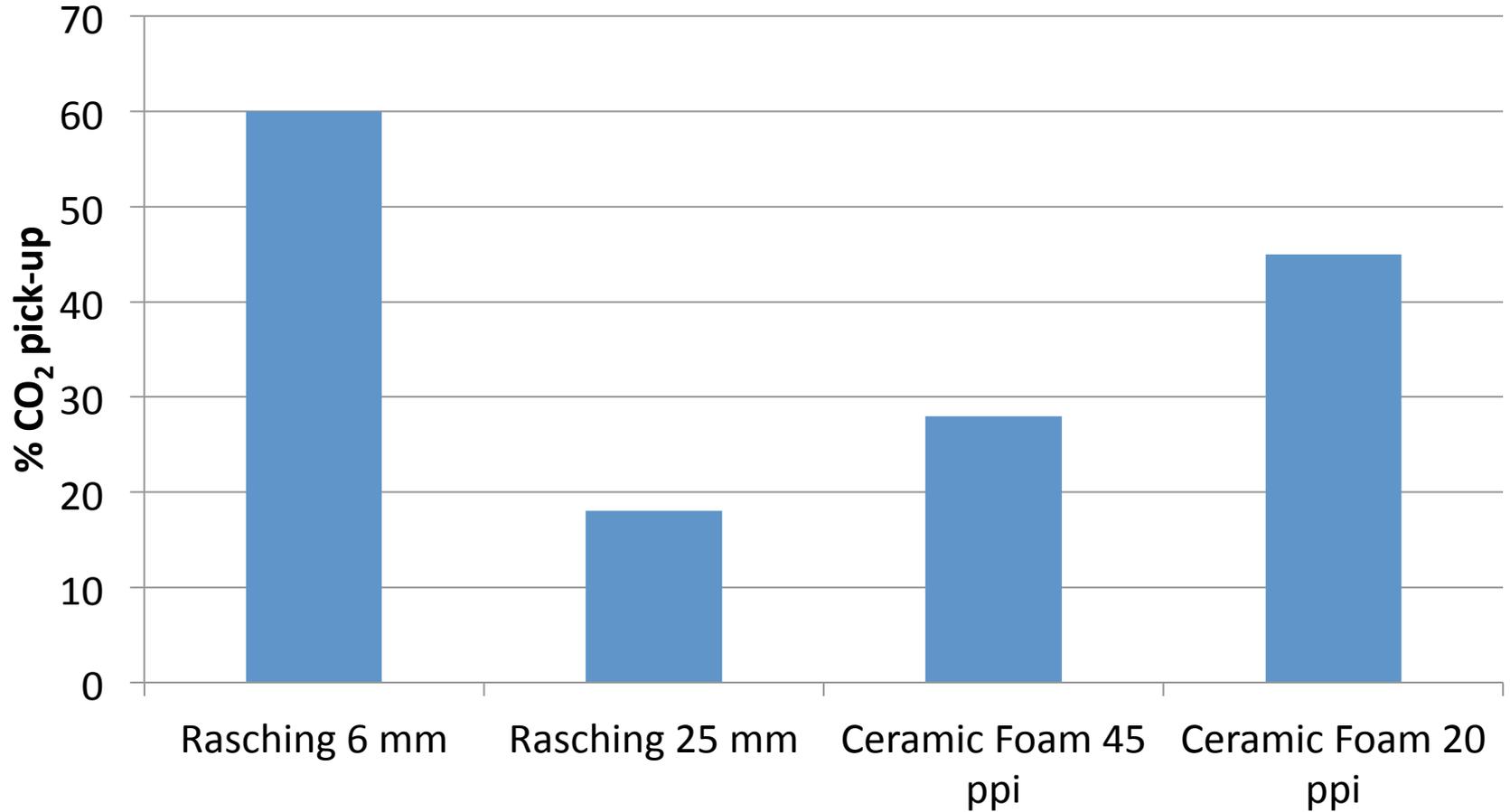
# 1-D Column for Mass Transfer Evaluation



# Pressure drop in 30-ppi ceramic foam at varying gas and liquid flow-rates

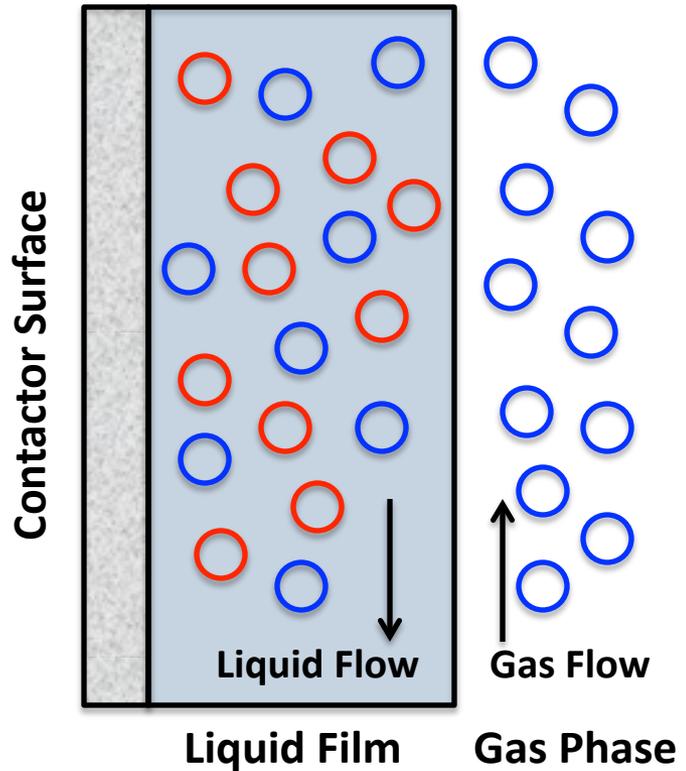


# Mass transfer characteristics of various tower packing materials

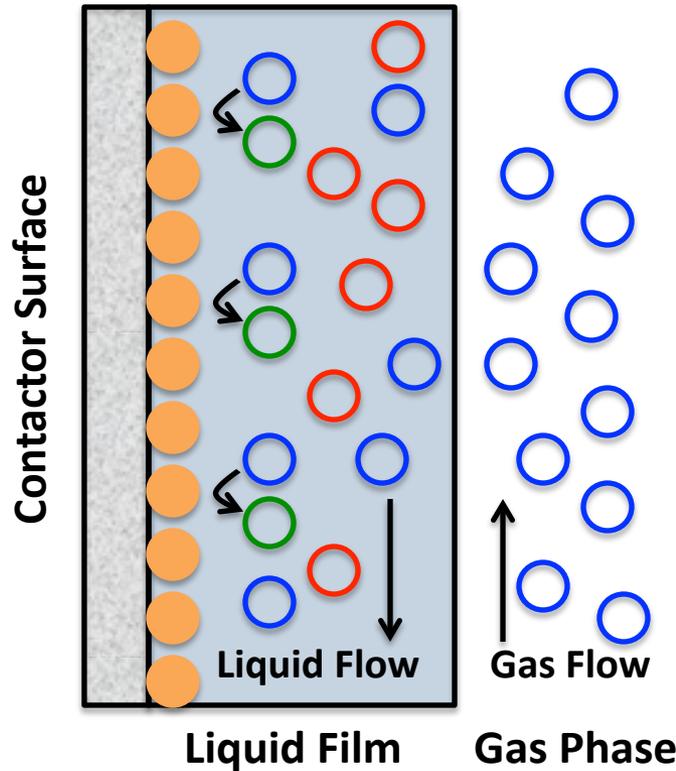


# Substrate Functionalization

Unfunctionalized Surface



Functionalized Surface



○ CO<sub>2</sub> (unreacted)

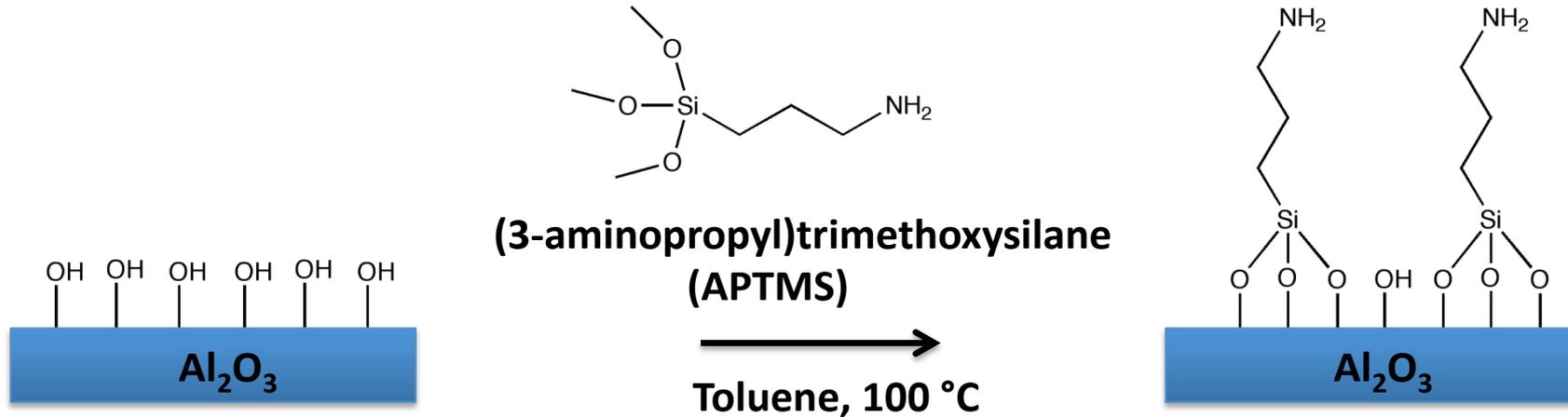
○ CO<sub>2</sub> + amine intermediate (in solution)

○ Surface generated CO<sub>2</sub> + amine (reacted, intermediate)

● Immobilized basic groups on surface

# Substrate Functionalization

## Silanization Chemistry Approach



Surface Modifier	Grafting Density ( $\rho$ , molecules $\text{nm}^{-2}$ ) $S(\text{BET}) = 250 \text{ m}^2 \text{ g}^{-1}$	Grafting Density ( $\rho$ , molecules $\text{nm}^{-2}$ ) $S(\text{BET}) = 155 \text{ m}^2 \text{ g}^{-1}$
APTMS	1.00	1.60
APTMS (Post-Bubbler #1)	0.90	1.50
APTMS (Post-Bubbler #2)	0.80	1.35

100 to 325 mesh  $\alpha$ -alumina substrate

Grafting density determined by thermogravimetric analysis (TGA)

10 wt% diglycolamine (DGA)/water with 1 hour contact time

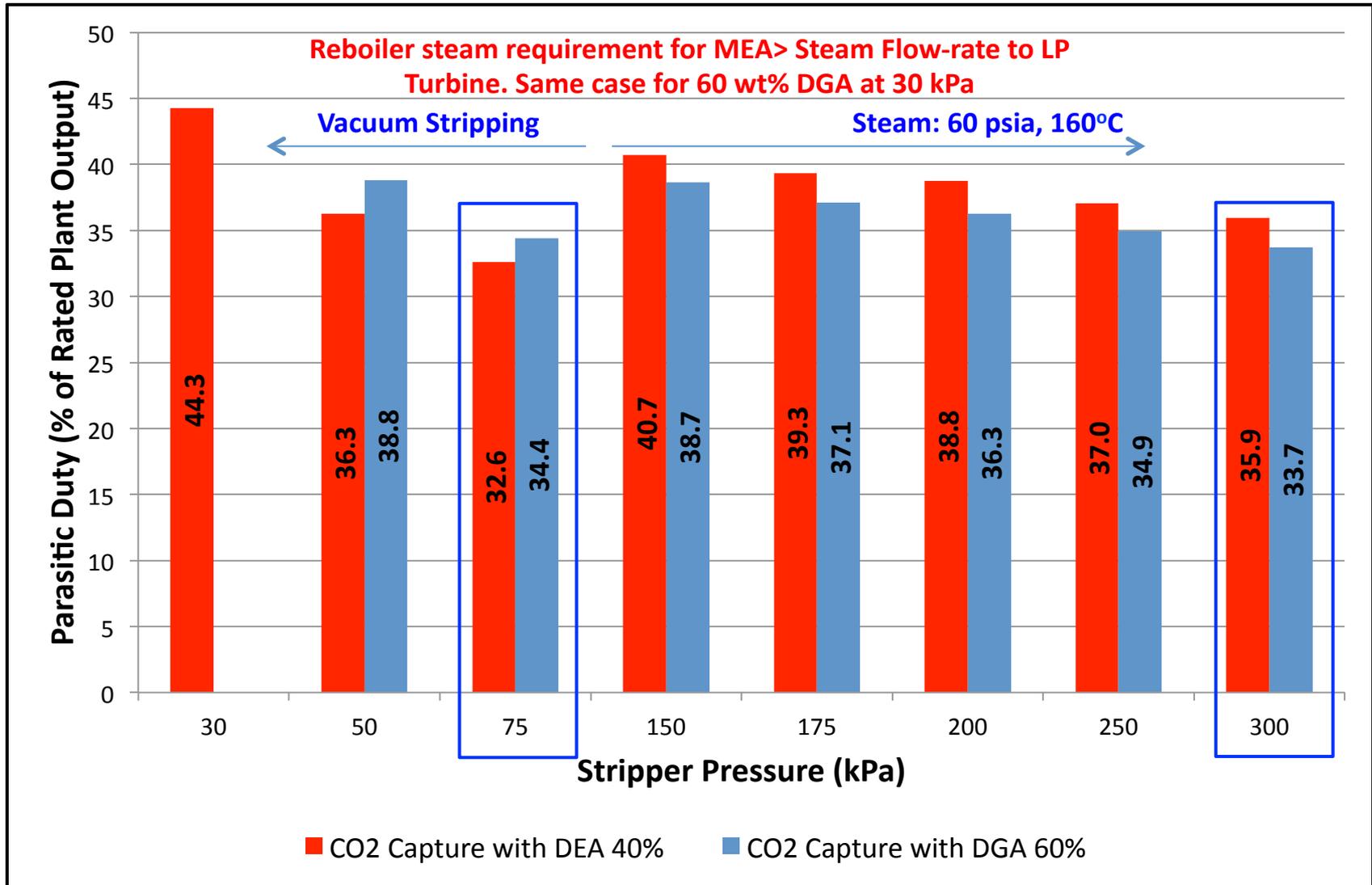
Silane functionalization not stable in amine solutions

Other directions:

- Phosphonates
- Other organic linkages (e.g. carboxyl)
- Protecting polymer layer
- Other surface coating to increase bond strength

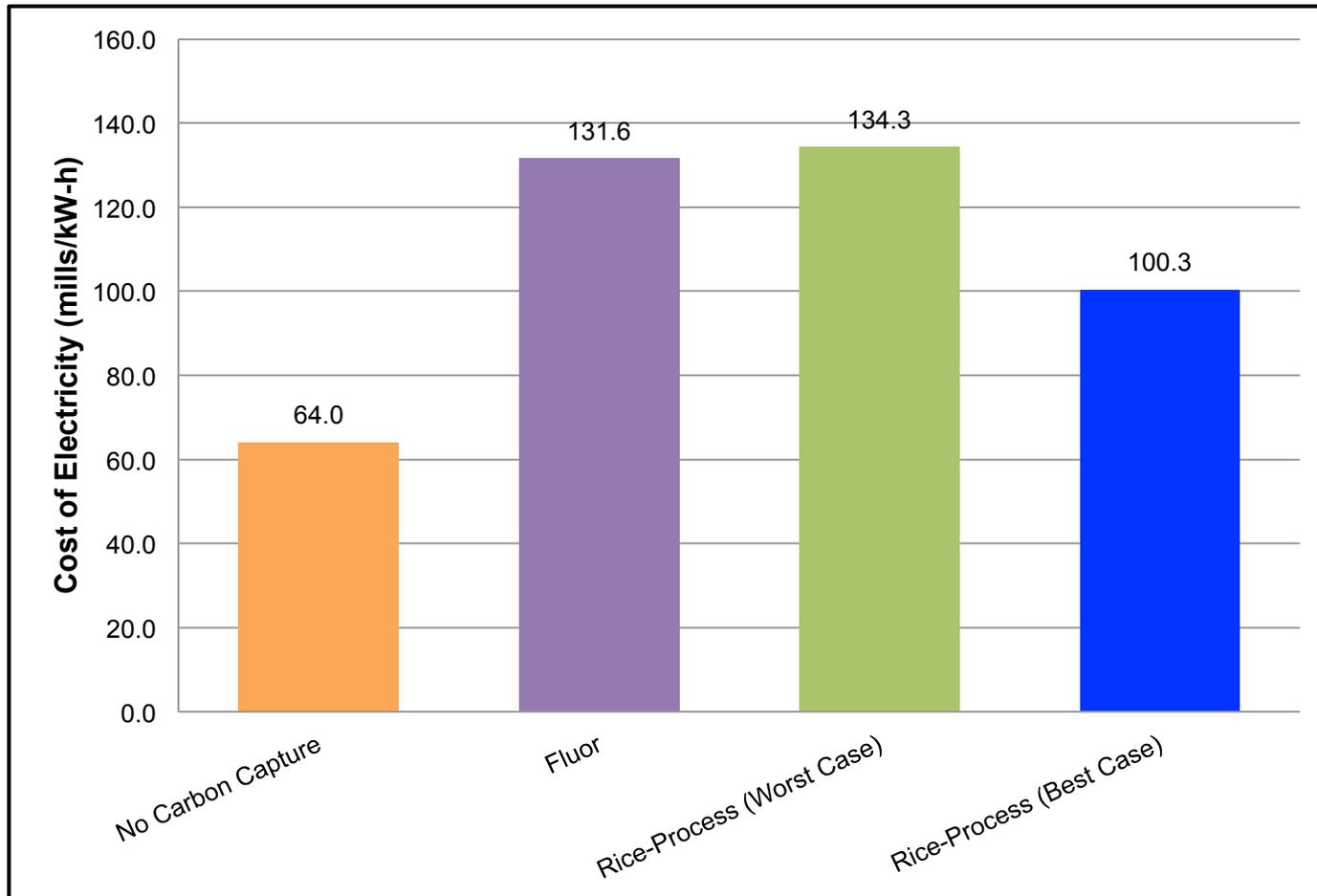
# Parasitic Power Losses

## Vacuum vs. Conventional stripping



# Technical & Economic Feasibility

## Comparison of cost of electricity for various processes



# Merits of Proposed Technology

---

- Ceramic foam has a geometric surface area up to 10x that of conventional packing (e.g. Raschig rings).
- Functionalized packing can increase the rate of CO<sub>2</sub> absorption into absorbent solution thus making it attractive to use slow reacting amines which also have low heat of regeneration.
- High geometric surface area packing, along with surface enhancement by functionalization can reduce the height of tower packing.
- Integrated absorber – desorber arrangement reduces space requirements. This will be an important factor when retrofitting existing coal-fired power plant with CO<sub>2</sub> capture technology.
- Waste heat usage for absorbent regeneration significantly reduces parasitic duty for power plant and thus, limit the increase in cost of electricity.
- Operating the desorber at lower temperatures decreases amine losses and equipment corrosion problems.

# Project Objectives

## 1. Project Initiation – Technical and Economic Feasibility Study

- At project initiation, a technical and economic feasibility study will be performed on this project to determine the possibilities of scaling up this process to pilot scale and beyond.
- As a part of the feasibility study, an environmental risk assessment will also be performed to evaluate the potential environmental impacts of the proposed technology.



## 2. Hydrodynamics and Mass Transfer Studies

- We will conduct studies to measure the hydrodynamic properties of the ceramic foam.
- We will conduct studies to measure the mass transfer properties for ceramic foam as compared to a standard tower packing material like ceramic Raschig rings.



## 3. Design of stainless steel prototype

- A stainless steel prototype will be designed and fabricated for demonstrating absorption and stripping of CO<sub>2</sub> in the combined absorber/desorber arrangement. In addition, absorbent regeneration will be carried out under vacuum.

## 4. Demonstrate absorption and stripping using stainless steel prototype

- Once the stainless steel prototype is designed and fabricated, the complete CO<sub>2</sub> capture process will be implemented and demonstrated
- Various factors affect CO<sub>2</sub> absorption and desorption. Some of these are (i) Absorbent and gas flow-rate (ii) Macro-pore sizing in ceramic foam (iii) Vacuum on stripping side

# Project Objectives (Contd..)

---

## 5. Substrate functionalization

- Amine and polycarboxylate functionalization on absorption and desorption side substrate
- Basic and acidic functionalities influence local pH conditions and increase forward and reverse reactions between amine and CO<sub>2</sub> respectively
- Effectiveness of substrate functionalization will be evaluated by measuring changes in the heat and mass transfer coefficients.

## 6. Process modeling

- Both horizontal and vertical mass and heat transport are significant.
- Develop a 2-D model to capture the influence of reaction kinetics, gas-liquid mass and heat transfer properties, operating pressure and temperature.

## 7. Sensitivity analysis and process optimization

- Large number of degrees of freedom like properties of ceramic foam and porous slab, operating pressure and temperature, gas and liquid flow rate, choice of absorbent
- Overall process optimization to reduce the energy requirement and costs

## 8. Project Completion – Feasibility and Economics Analysis

- The Feasibility and Economics analysis performed at project initiation will be updated based on information generated as a part of this project.
- This feasibility and economic analysis will indicate the possibility of scaling up the project to a pilot demonstration.

# Requested Personnel

Budget Period Personnel	Role	Budget Period 1 (10.01.11 – 09.30.12)	Budget Period 2 (10.01.12 – 09.30.13)	Budget Period 3 (10.01.12 – 09.30.13)
<i>Prof. George Hirasaki</i>	Project Director, Lead Investigator	✓ 1 month summer salary	✓ 1 month summer salary	✓ 1 month summer salary
<i>Prof. Michael Wong</i>	Co-Project Investigator	✓ 1 month summer salary	✓ 1 month summer salary	✓ 1 month summer salary
<i>Prof. Kenneth Cox</i>	Co-Project Investigator	✓ 1 month summer salary	✓ 1 month summer salary	✓ 1 month summer salary
<i>Prof. Ed Billups</i>	Co-Project Investigator	✓	✓	✓
<i>Mr. Sumedh Warudkar</i>	Graduate Student	✓ Graduate Student Salary	✓ Graduate Student Salary	
<i>Dr. Jerimiah Forsythe</i>	Postdoc (Substrate functionalization)	✓ Postdoctoral Salary	✓ Postdoctoral Salary	
<i>TBD</i>	Postdoc (Modeling)		✓ Postdoctoral Salary	✓ Postdoctoral Salary
<i>TBD</i>	Undergraduate researcher(s)	✓	✓	✓

# Project Budget

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

## Funding Support

- Energy and Environmental Systems Institute (EESI) at Rice University
- Rice Consortium on Processes in Porous Media
- Schlumberger
- US DOE DE0007531



---

# Questions