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

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NETL CO_2 Capture Technology Meeting

July 31, 2014

Outline

- Project Overview
- Project Budget
- Project objectives and technical approach
- Progress on process model to simulate gas/liquid flow and reaction in integrated CO_2 absorber/desorber
- Screening of metal oxide for CO_2 desorption/amine regeneration
- Summary and Conclusions

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 – 3/2015
- **Primary project goal :** 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*"

Project Team

Project Director

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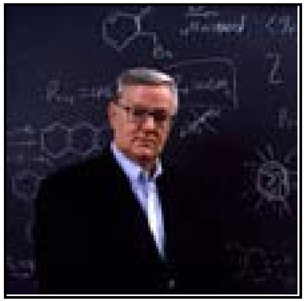

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PhD, Chemistry (LSU, 2011)

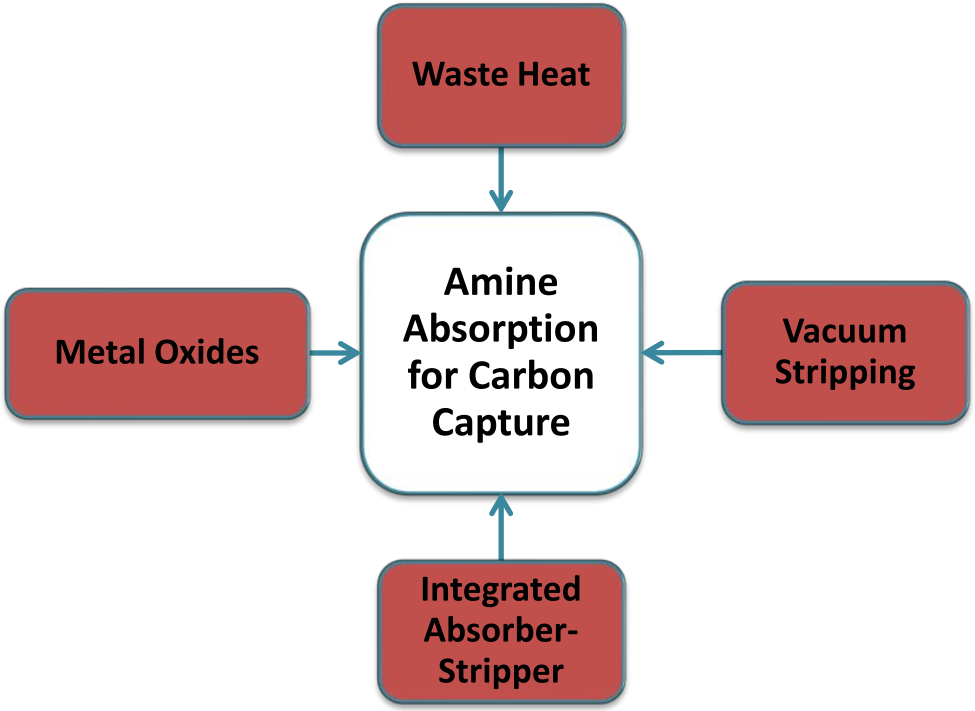
Project Budget

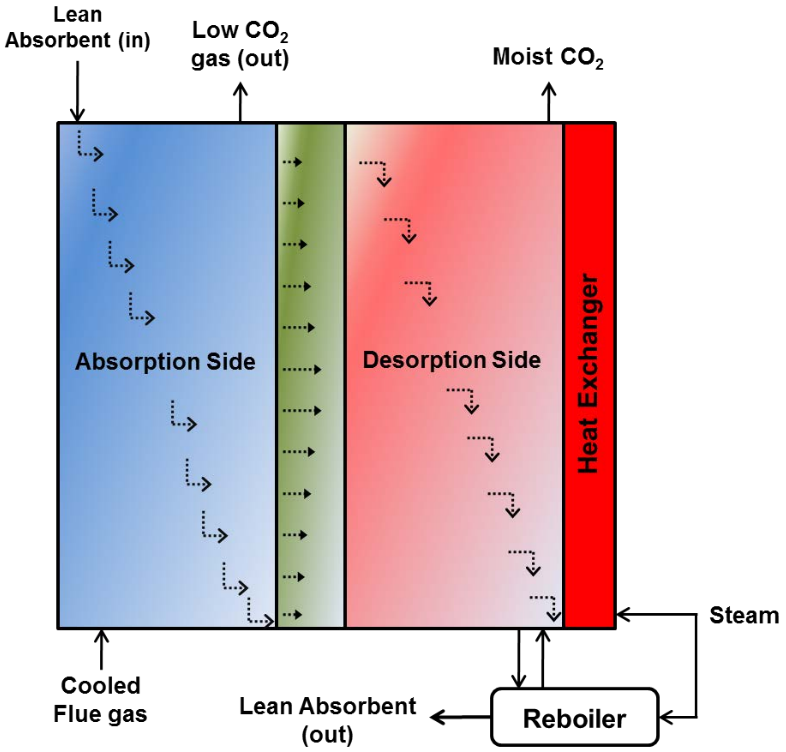
Budget Period Object Class Category	Budget Period 1 (10.01.11 – 09.30.12)	Budget Period 2 (10.01.12 – 12.31.13)	Budget Period 3 (01.01.14 – 03.31.15)	Total
Personnel	$134,079	$180,738	$113,637	$428,454
Fringe Benefits	$28, 586	$40,953	$29,811	$99,350
Travel	$4,700	$4,700	$4100	$13,500
Equipment	$27,035	$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

Objectives

- Develop a CO_2 capture process that uses a single integrated unit that combines both the absorber and desorber columns
- Use waste heat for absorbent regeneration instead of low-pressure steam by operating the desorber section of the integrated unit under vacuum
- Develop a 2-D model to simulate the CO_2 absorption process, to test different configurations, and to optimize the material properties (i.e., pore-size distribution, aspect ratio, etc.)
- Reduce energy requirement by lowering the desorption temperature with the addition of a metal oxide

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





Advantages

- Reduction of space requirement and capital cost due to integration of absorber and desorber sections into a single unit

- Favorable characteristics for mass transfer because ceramic gas-liquid contactors have large geometric surface areas

- Cost saving and less energy requirement due to low desorption temperature:
  - Metal oxide catalyzes the desorption of CO_2
  - Moderate vacuum helps desorption to be carried out at reduced temperatures

Key milestones

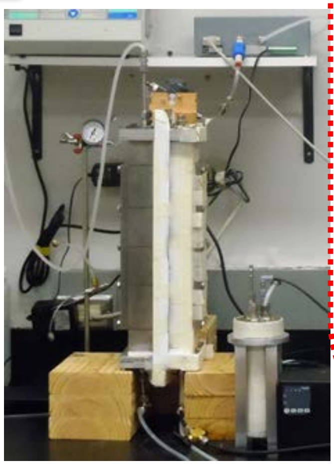
Completed

In progress

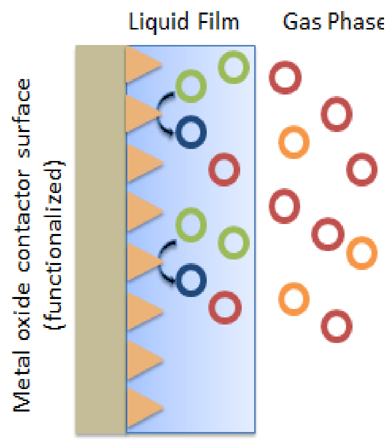
Not started

Preliminary Technical and Economic Feasibility Study

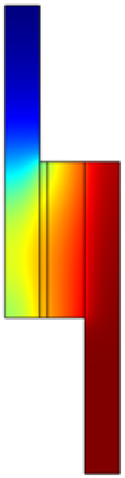
Bench-scale Prototype Design and Test



Addition of metal oxide in desorption zone



Process modeling and simulation (1D and 2D model)



Technical and Economic Feasibility Study; Technology EH&S Risk Assessment

10/2011-6/2012

6/2012-4/2013

9/2012-12/2014

4/2014-10/2014

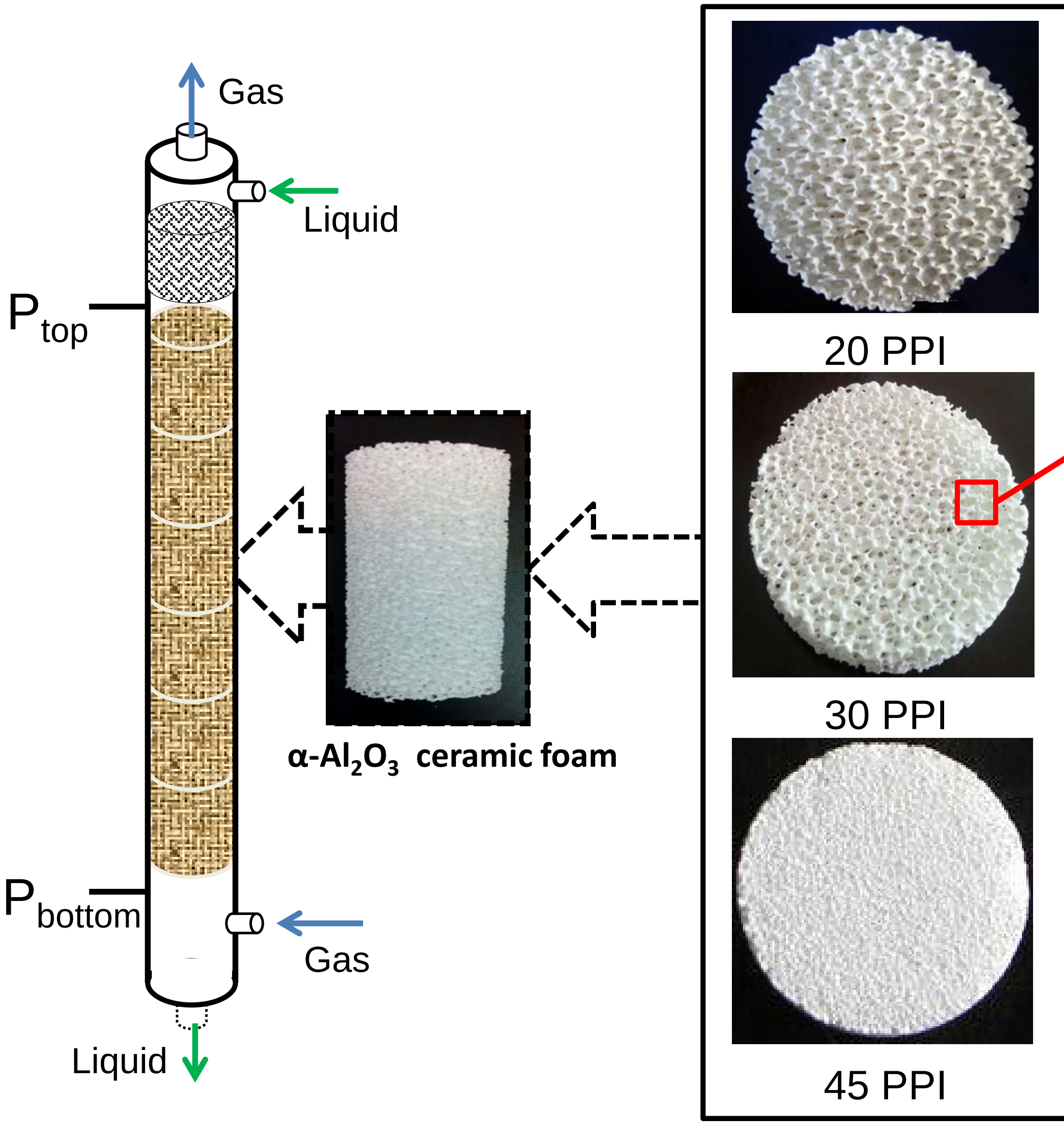
10/2014-3/2015

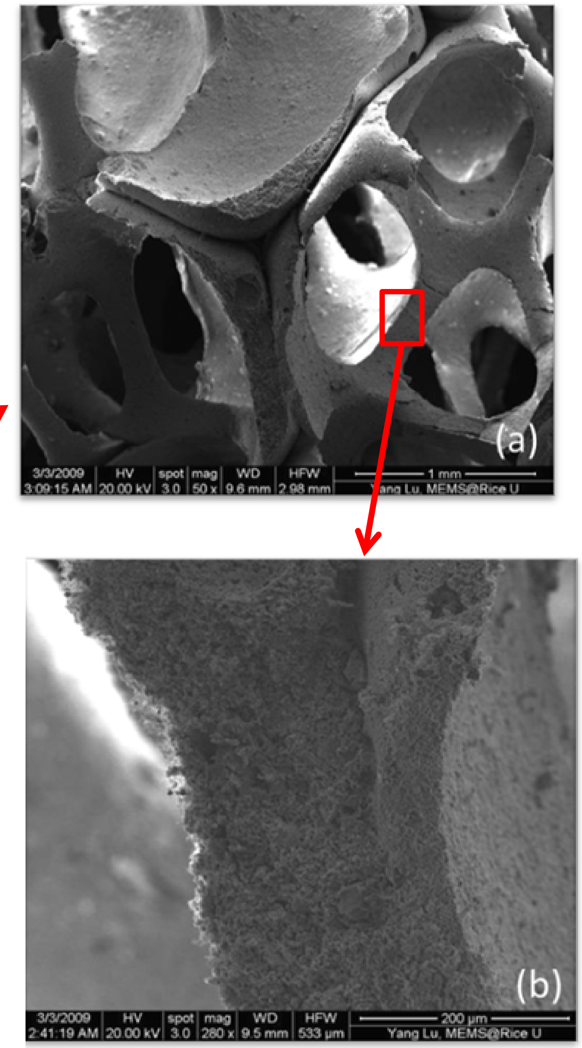
Content of Today's Talk

- Progress on process model to simulate gas/liquid flow and reaction in integrated CO_2 absorber/desorber unit (COMSOL)
  - Pressure drop, flooding prediction in 1D model
  - CO_2 absorption performance prediction in 1D model
  - Gas/liquid flow simulation in 2D model

- Screening of metal oxides that can enhance CO_2 desorption from amine solution at lower stripping temperature

Experimental Setup for Pressure Drop in 1D Column





Scanning Electron Micrographs of Ceramic Foam : (a) 50x (b) 280x

Material Properties

Advantages of ceramic foam:

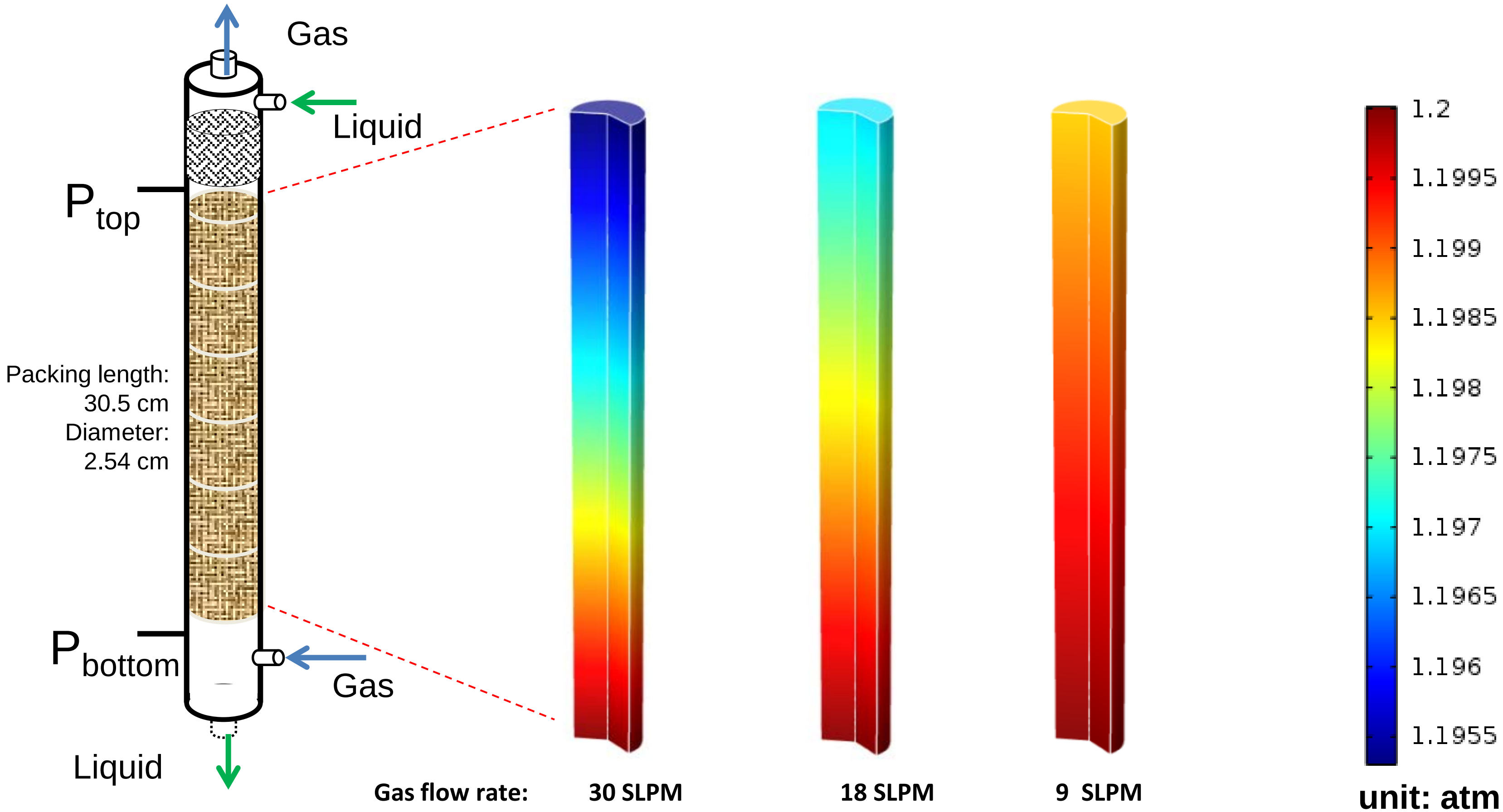
1) Low bulk density and pressure drop
2) Very high geometric surface area and macro-porosity (80%-90%)
3) Regulated pore-size and ease of reproducibility of structure
4) Low pressure drop 5)High structural uniformity

Packing Type	Structure	Porosity (%)	S (m^2/m^3)	Bulk density (g/cm^3)	Equivalent Pore diameter (mm)	Permeability[e] (m^2)
α-Al_2O_3 Ceramic Foam	20-PPI[a]	85	700[b]	0.60[d]	1.28	$8.0x10^{-9}$
	30-PPI	85	900[b]	0.65[d]	1.00	$7.3x10^{-9}$
	45-PPI	84	1400[b]	0.71[d]	0.60	$6.2x10^{-9}$
Random Packing[c]	Raschig Ring	62.6	239	0.58[e]	1.50	$3.87x10^{-8}$
	Pall Ring	94.2	232	0.48[e]	2.50	$3.53x10^{-7}$

(a) PPI: Number of pores per linear inch length; (b) C.P.Stemmet,IChemE, 2006 (c) Jerzy Maćkowiak, IChemE, 2011 (d) www.**ask-chemicals**.com

(e) http://www.tower-packing.com (f) permeability of packing was calculated by $k = \frac{3\phi d_e^2}{50}$

Predicted Pressure drops under Different Gas Velocities



Gas flow rate:	**30 SLPM**	**18 SLPM**	**9 SLPM**
Liquid flow rate:	**15 mL/min**	**15 mL/min**	**15 mL/min**

- Continuity equation (Steady-state)

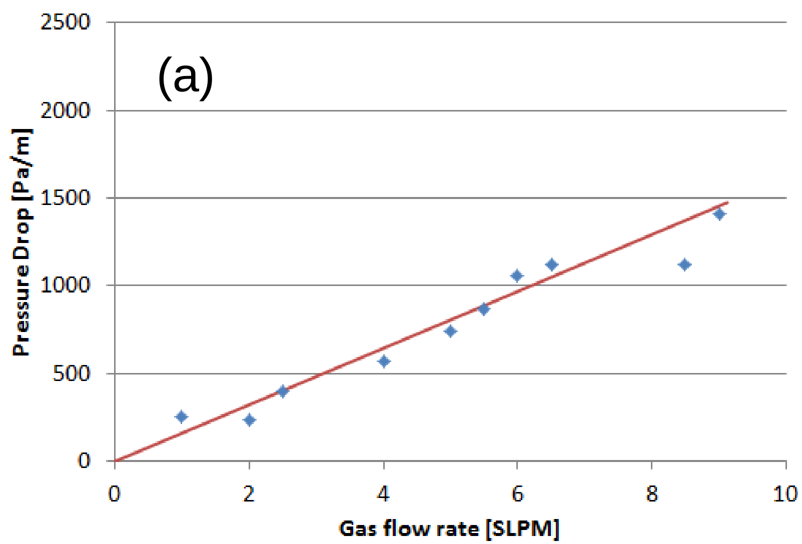
$$\rho_i \nabla \cdot U_i = 0$$

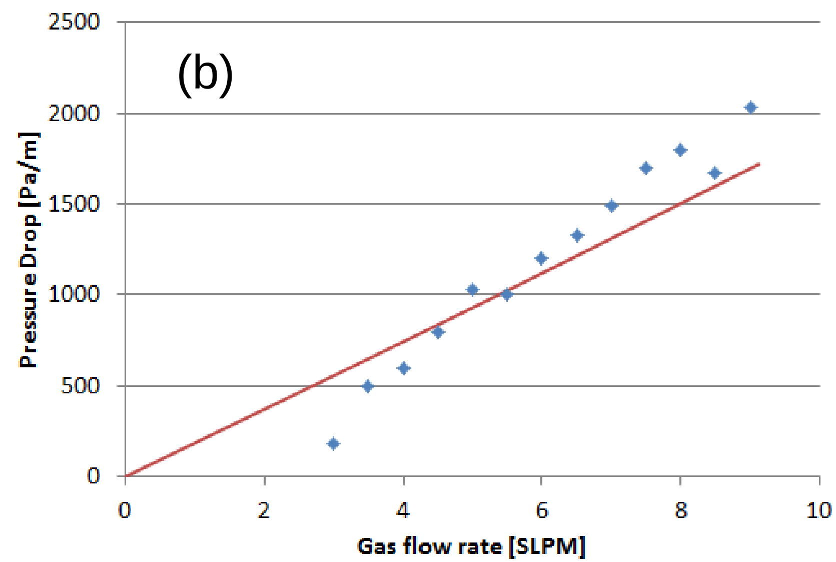
- Momentum Balance Equation (Steady-state)

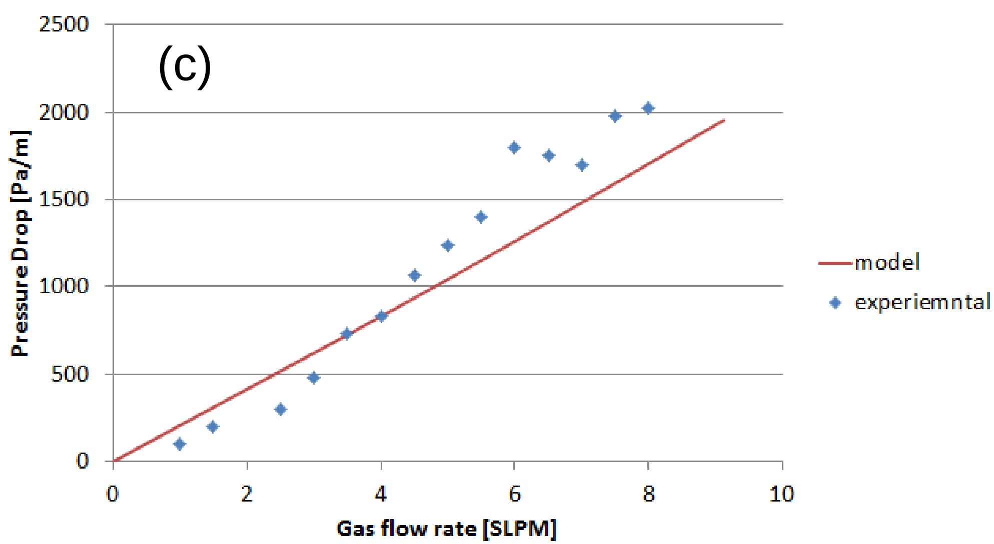
$$-\nabla \cdot p_L - \frac{\mu_L}{f_L K} U_L + \rho_L g \nabla D = 0$$ Darcy's Law

$$-\nabla \cdot p_G - \frac{\mu_G}{f_G K} U_G + \rho_G g \nabla D = 0 \qquad \nabla \cdot p_G = \nabla \cdot p_L$$

Predicted and Experimental Pressure Drops in 20ppi Ceramic Foam



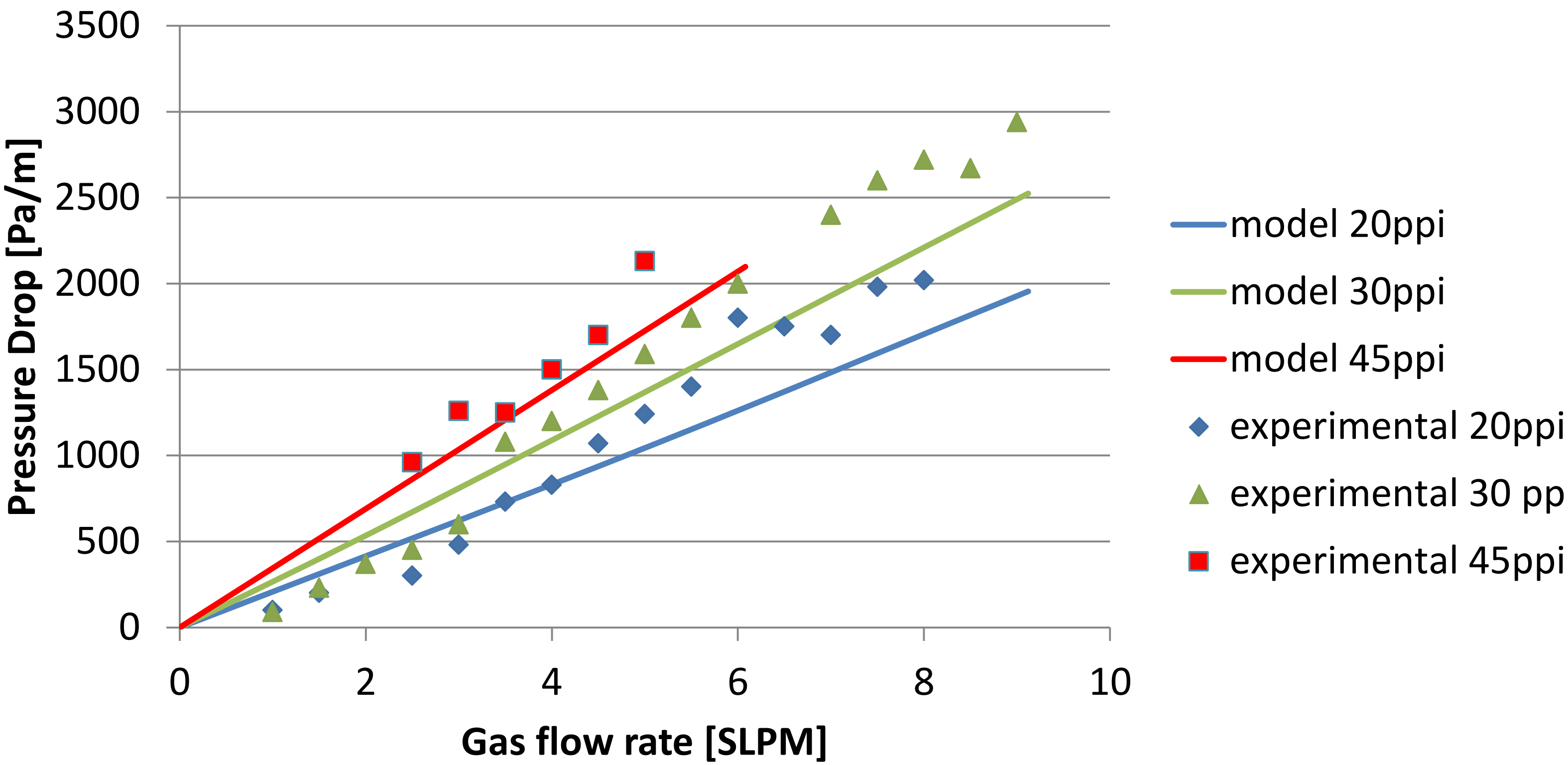




Packing Height: 30.5 cm
Liquid phase: water @25 ^{o}C
Gas Phase: air

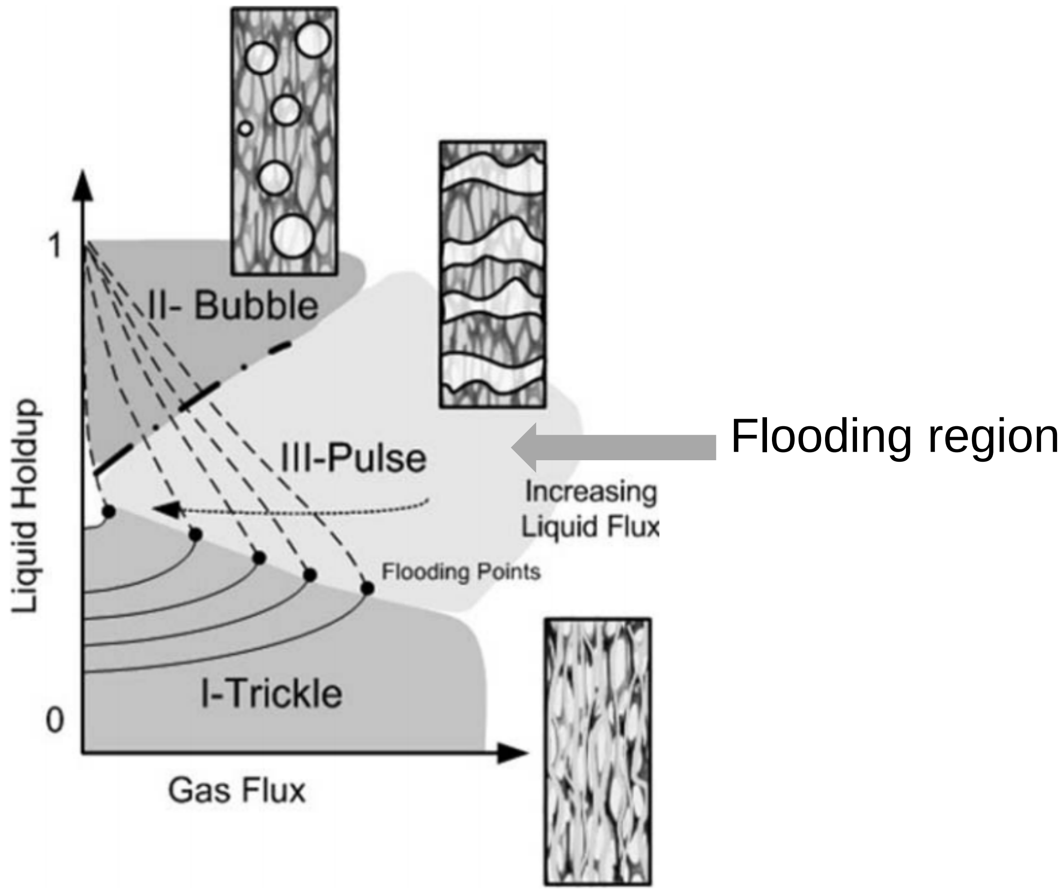
(a) Liquid flow rate 10 mL/min
(b) Liquid flow rate 30 mL/min
(c) Liquid flow rate 50 mL/min

Predicted and Experimental Drops in Ceramic foams



Packing Height: 30.5 cm
Liquid phase: water @25 ^{o}C
Gas Phase: air
Liquid flow rate 50 mL/min

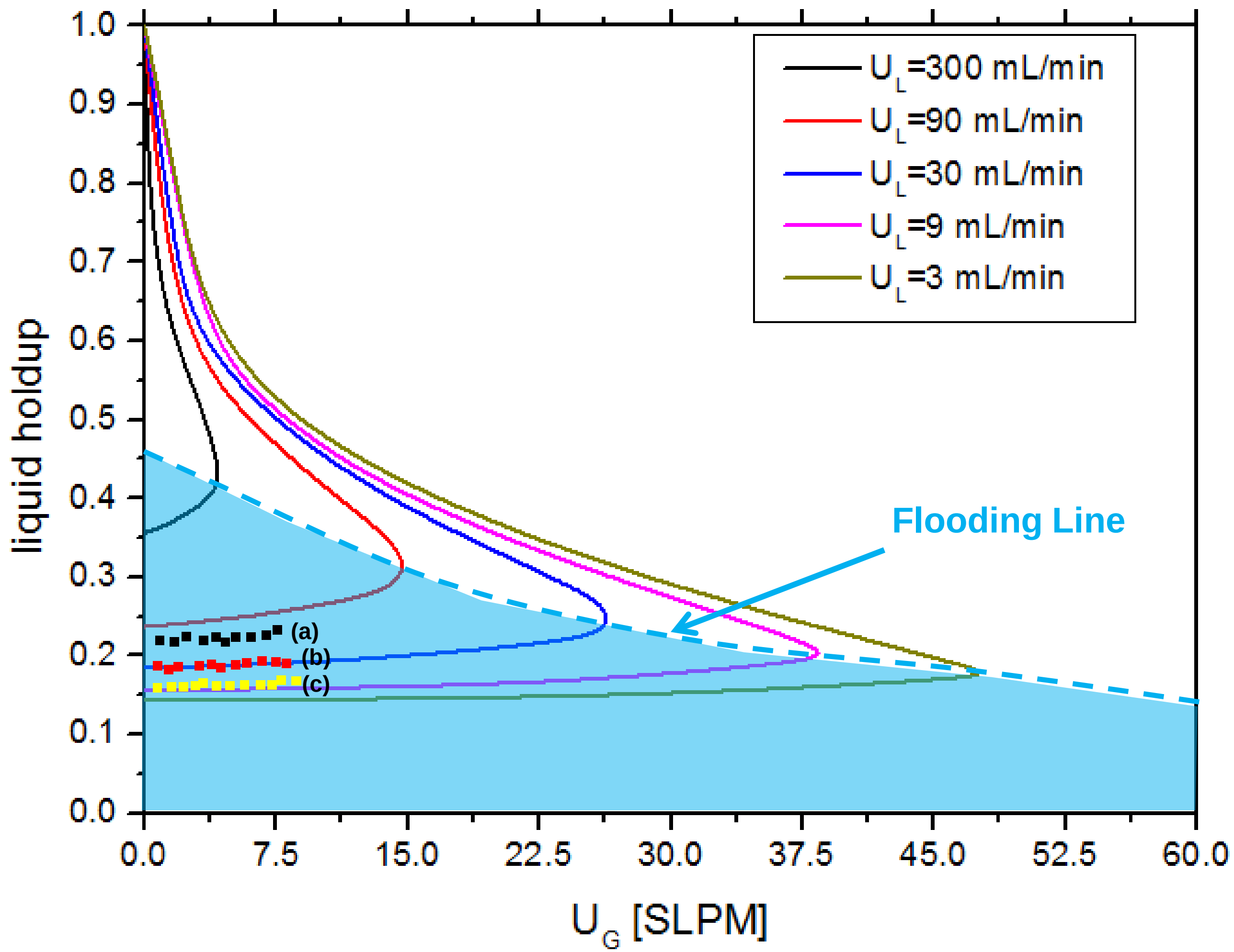
Flooding Point Prediction



$$\textit{Liquid holdup} = \frac{Volume\ of\ liquid\ in\ porous\ media}{void\ volume}$$

Typical liquid holdup for different gas and liquid Reynolds numbers. (Stemmet et al. 2005)

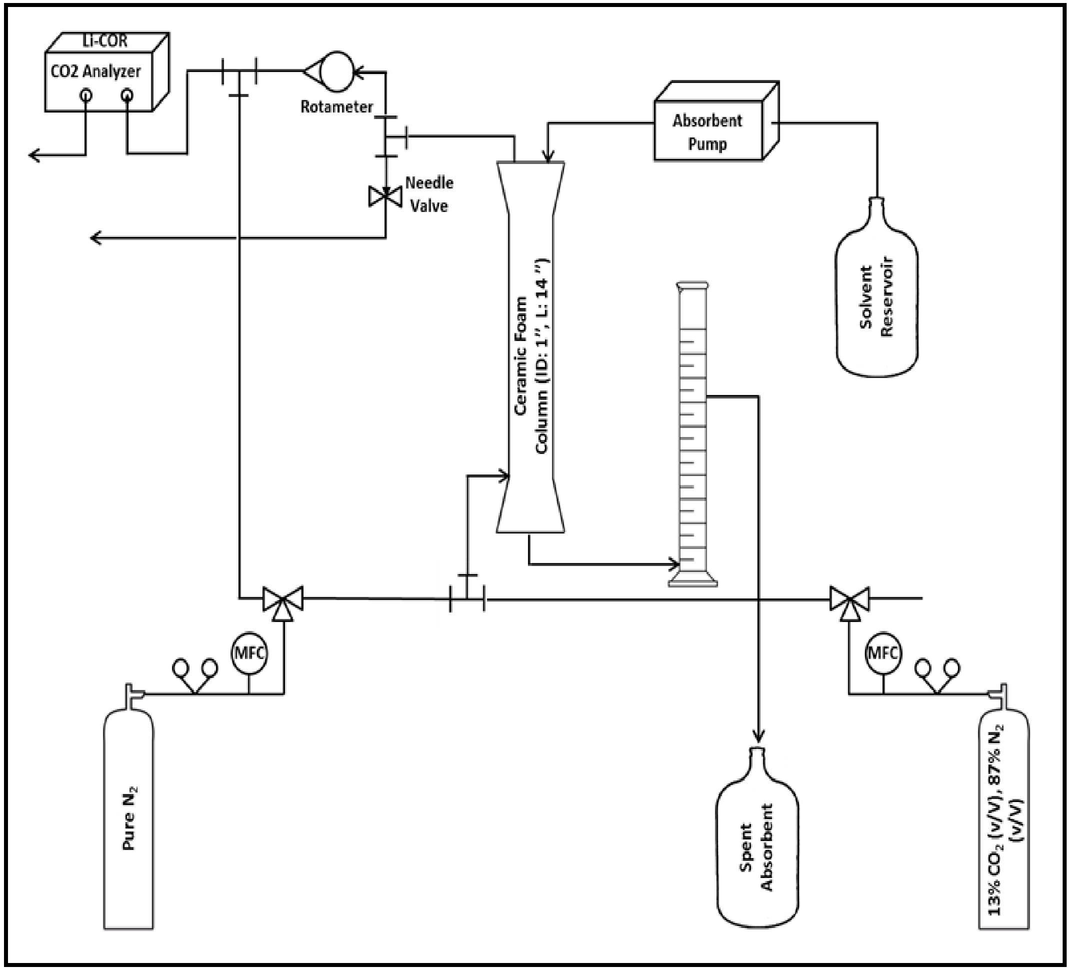
Operating Zone in 20-PPI Ceramic Foam



Figures: Modelling results of the liquid holdup versus gas flow rate:

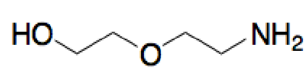
20-PPI ceramic foam; Packing Height: 30.5 cm; Liquid phase: water @25C; Gas Phase: air

CO_2 Absorption Experimental Setup-1D



Absorbent:
Aqueous Diglycolamine
(DGA) 30 wt%

Structure:



Operating conditions:
Inlet CO_2 concentration: 13 v/v%
Absorption temperature: 25 °C
Ceramic foam: 20-PPI

Model Equations and Major Reactions

- **Mass Balance of Species i**

$$\nabla \cdot (-D_i \nabla c_i + c_i U) = S_i$$

- **Source Terms for Gas Phase**

$$S_i = -K_{ov} a_{eff} [\frac{C_{Gi}}{H_i} - C_{Li}]$$

- **Source Terms for Liquid Phase**

$$S_i = K_{ov} a_{eff} [\frac{C_{Gi}}{H_i} - C_{Li}] - R_{ij}$$

$$S_j = -2R_{ij}$$

Main Kinetic Reactions

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$HCO_3^- \rightarrow CO_2 + OH^-$$

$$DGA + CO_2 + H_2O \rightarrow DGACOO^- + H_3O^+$$

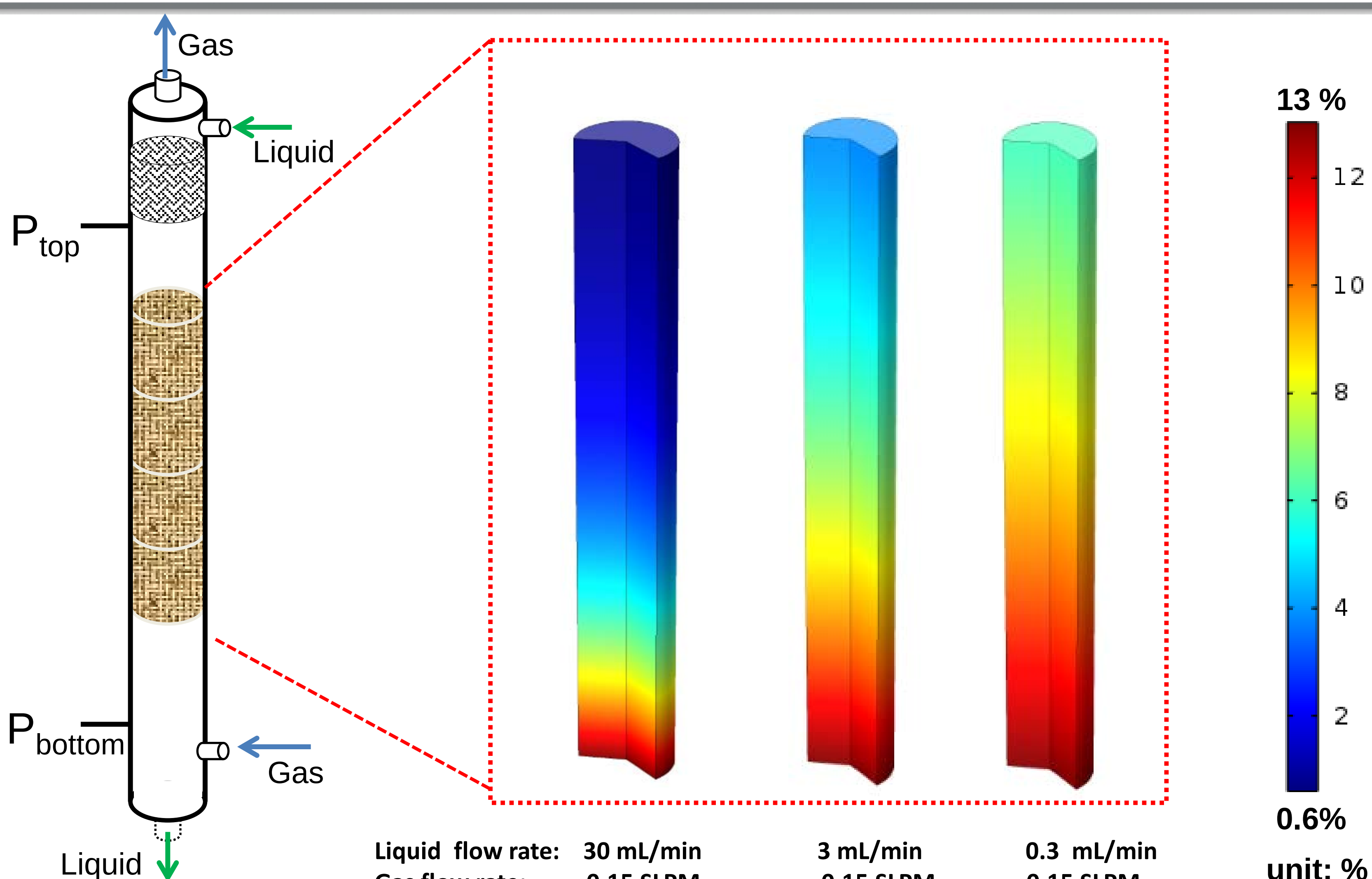
$$DGACOO^- + H_3O^+ \rightarrow DGA + H_2O + CO_2$$

Main Equilibrium Reactions

$$DGAH^+ + H_2O \leftrightarrow DGA + H_3O^+$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{-2}$$

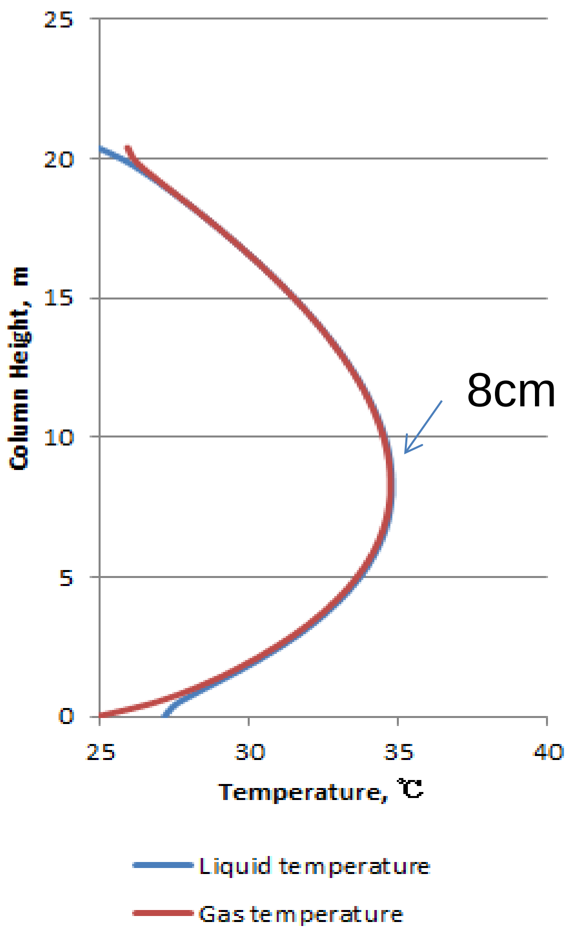
CO_2 Concentration Profile along Column under Different Liquid Velocities



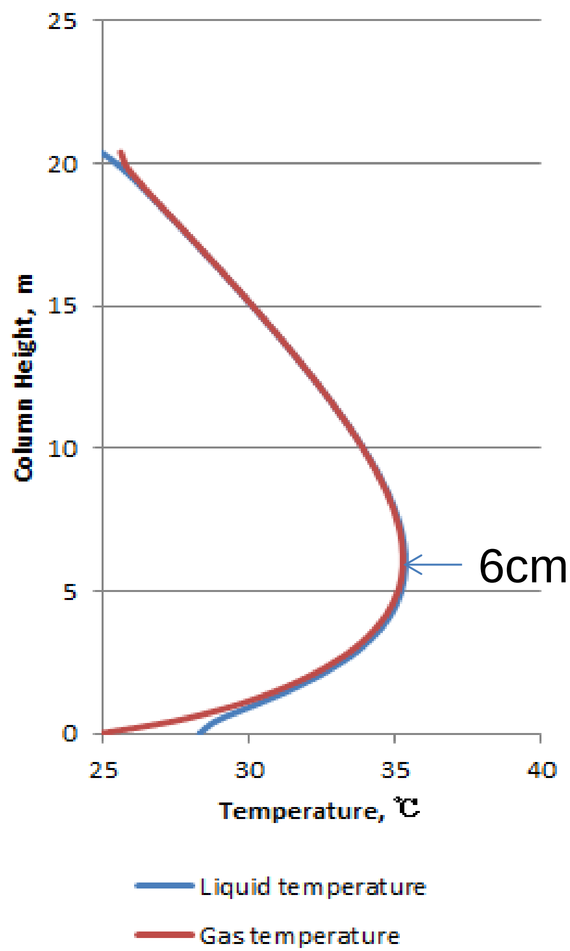
Liquid flow rate:	**30 mL/min**	**3 mL/min**	**0.3 mL/min**
Gas flow rate:	**0.15 SLPM**	**0.15 SLPM**	**0.15 SLPM**

Packing length: 20.4 cm
Diameter:2.54 cm
Liquid: 30 wt% DGA, 25C
Gas: 13% CO_2/87% N_2

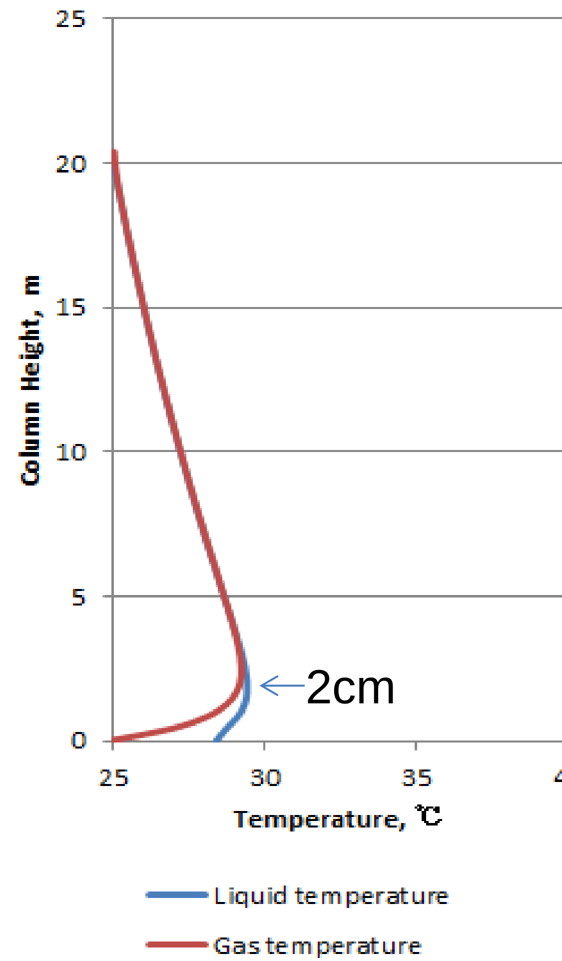
Temperature Profiles with Changing Liquid Velocities



Liquid flow rate: 0.076 mL/min



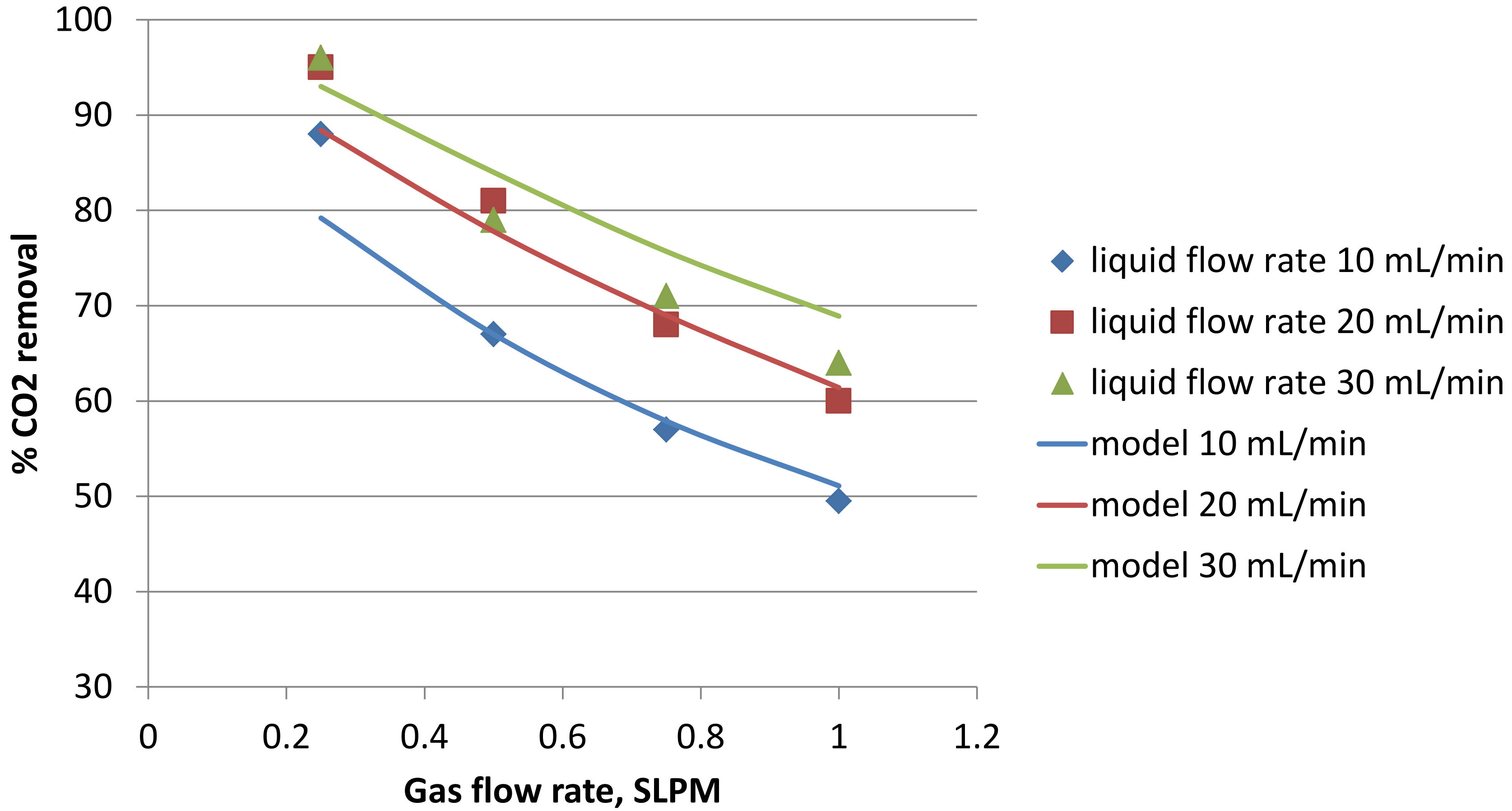
Liquid flow rate : 0.76 mL/min



Liquid flow rate : 7.6 mL/min

(constant gas flow rate 0.6 SLPM)

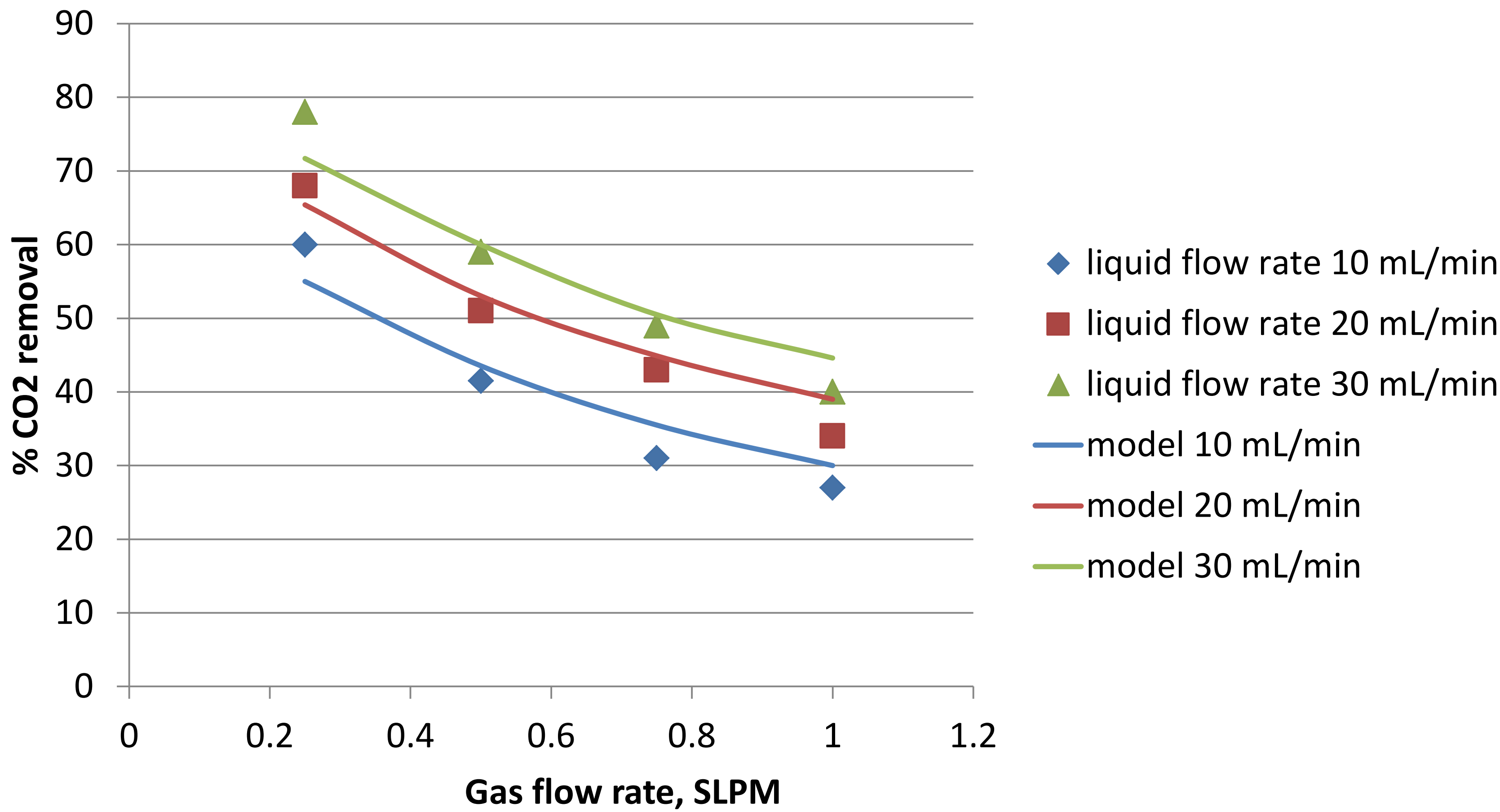
Experimental and Simulated CO_2 Removal Ratio
(ceramic foam column= 20.4 cm)



(experimental vs modelling)
ceramic foam column= 20.4 cm

Liquid phase: 30% DGA, Gas phase: 13% CO_2/87% N_2; Temperature: 25 ℃

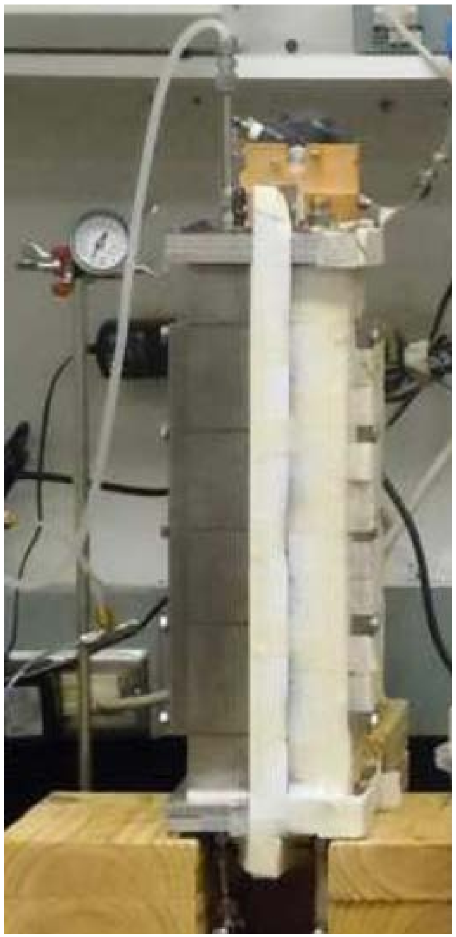
Experimental and Simulated CO_2 Removal Ratio
(ceramic foam column= 10.2 cm)



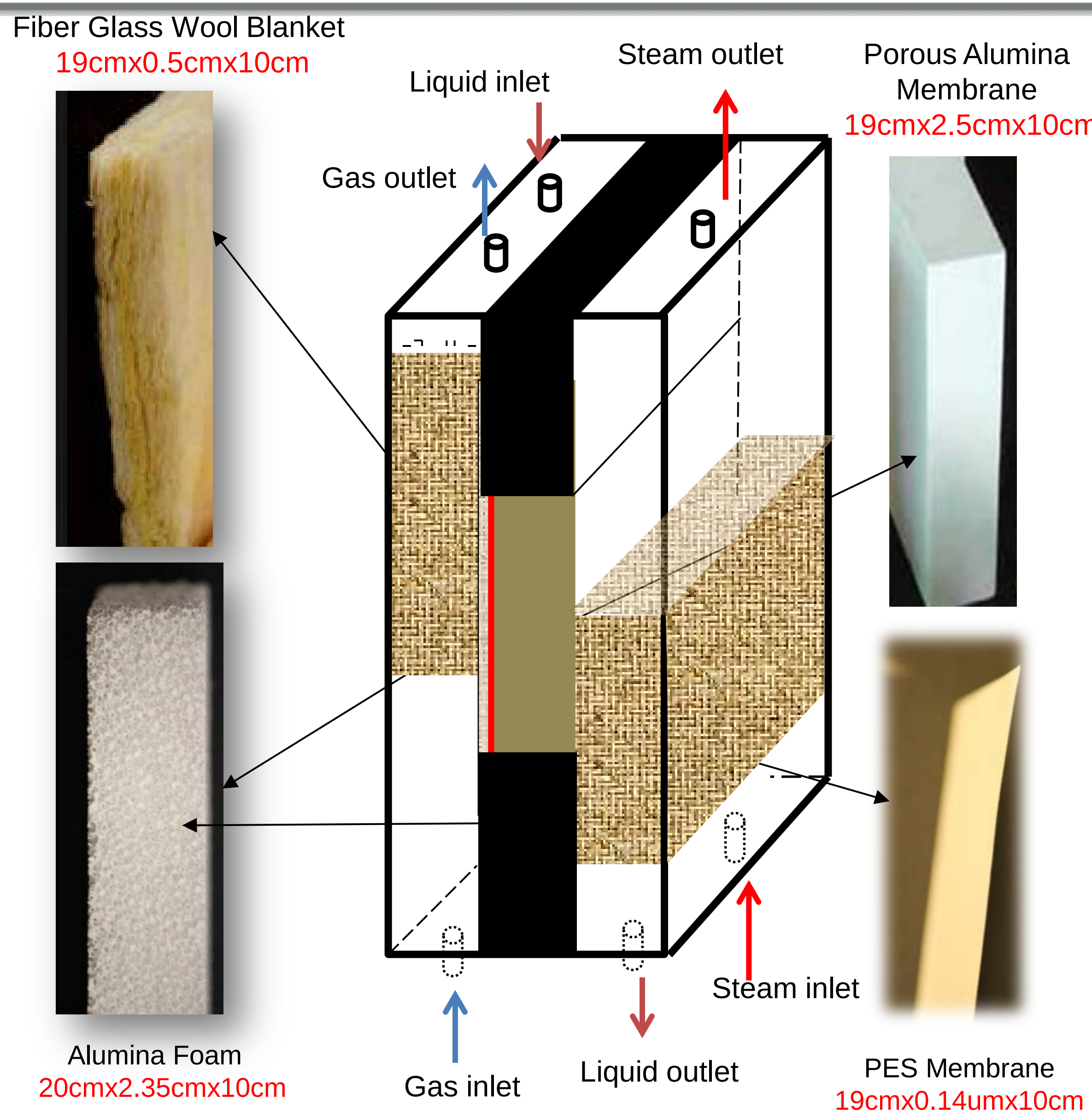
(experimental vs modelling)
ceramic foam column= 10.2 cm

Liquid phase: 30% DGA, Gas phase: 13% CO_2/87% N_2; Temperature: 25 ℃

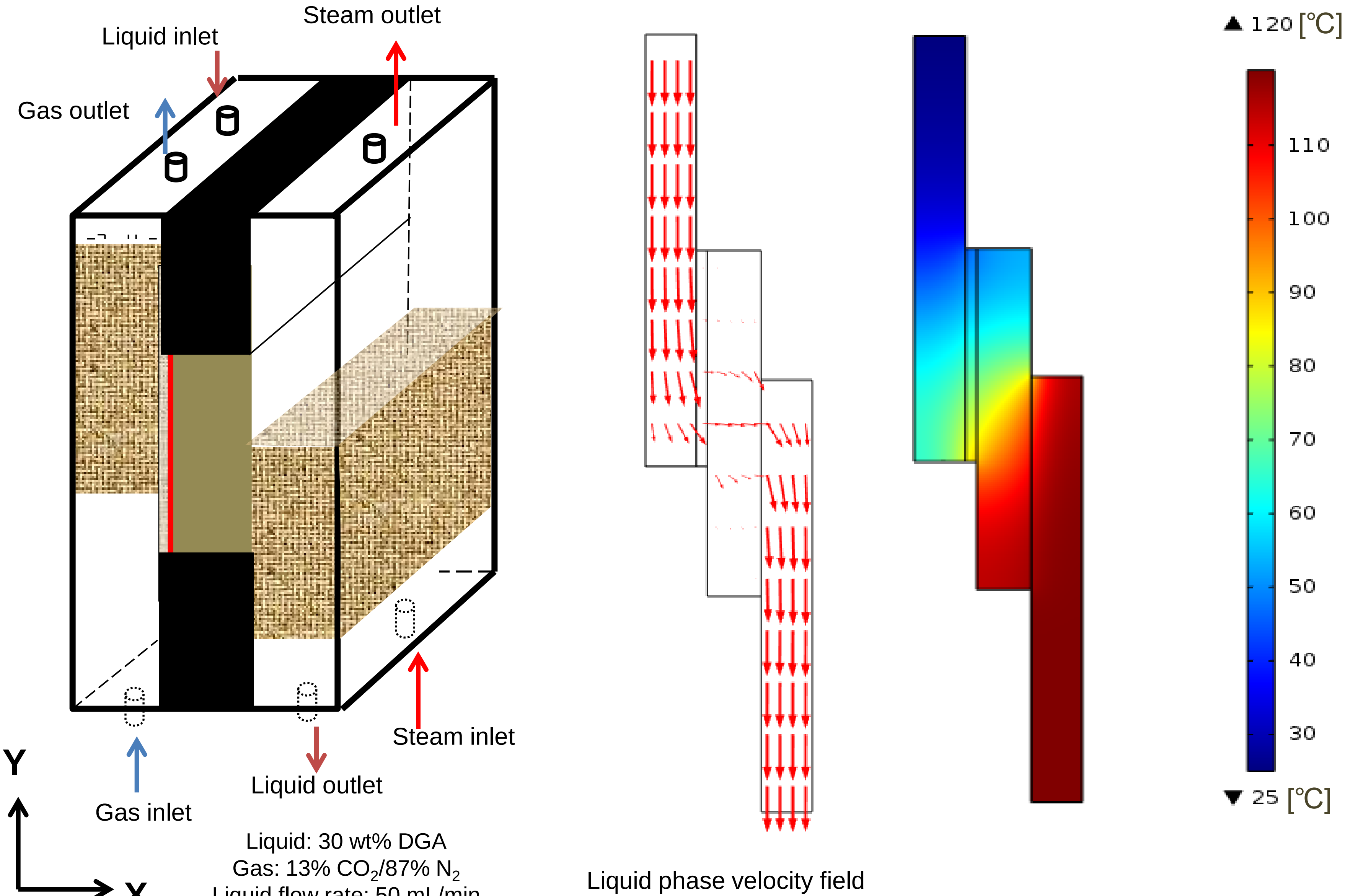
Prototype of Integrated CO_2 Absorber and Desorber Unit



Photograph of the experimental setup developed for the proof-of-concept demonstration



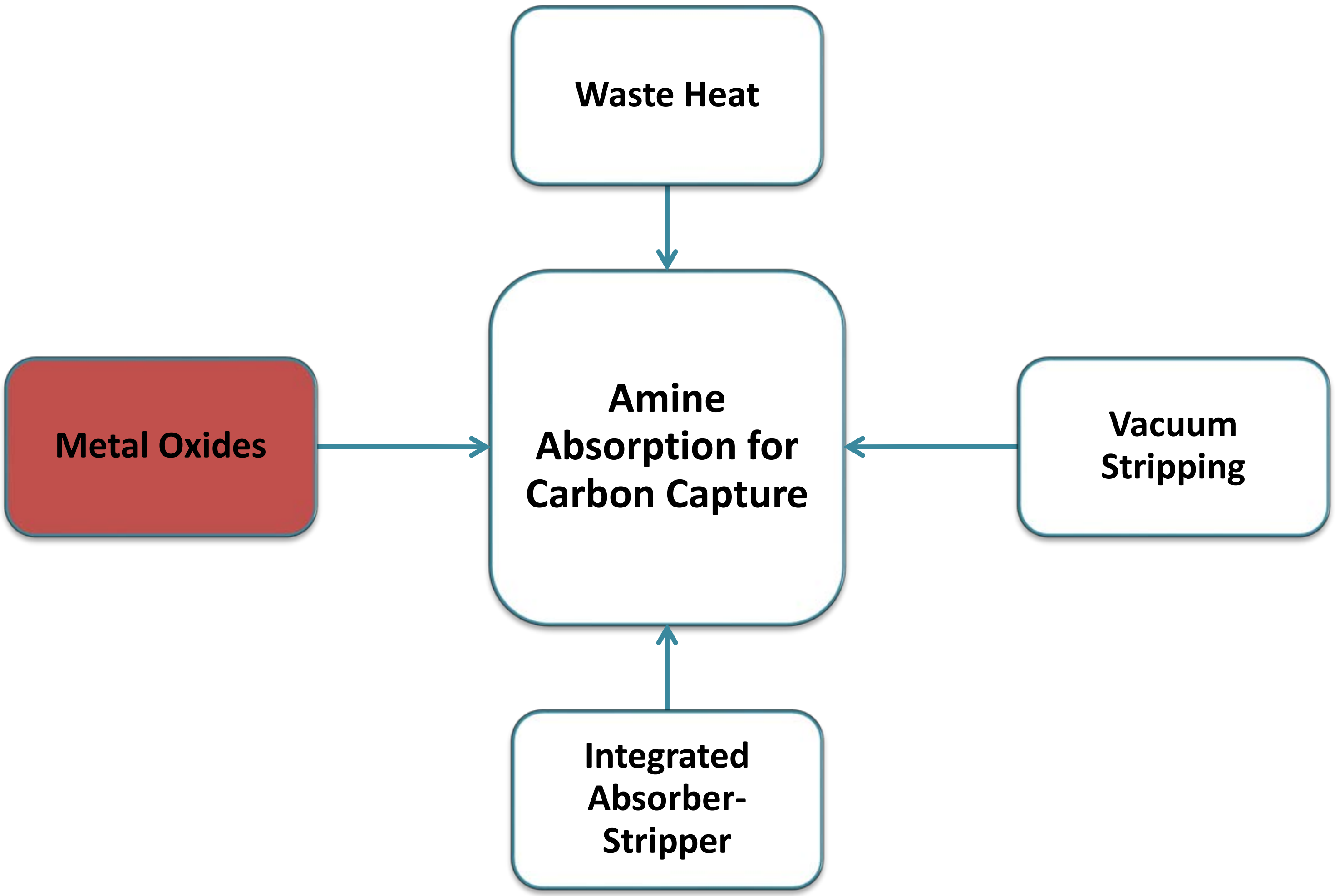
Representative of Liquid Phase Velocity and Temperature Profiles



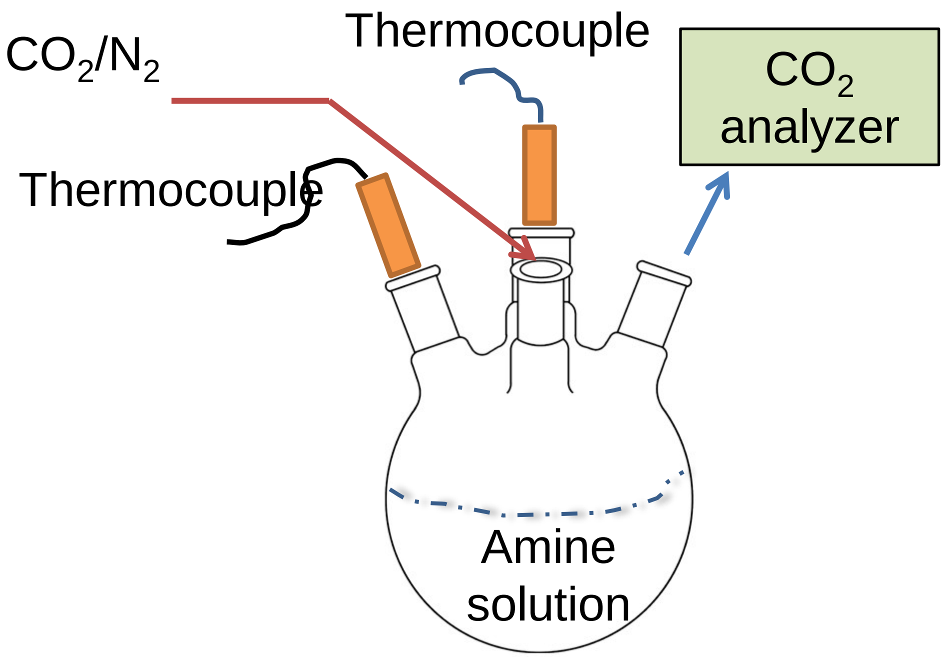
Liquid: 30 wt% DGA
Gas: 13% CO_2/87% N_2
Liquid flow rate: 50 mL/min
Gas flow rate: 4 SLPM

Our Approach:
Using Metal Oxides during Desorption

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

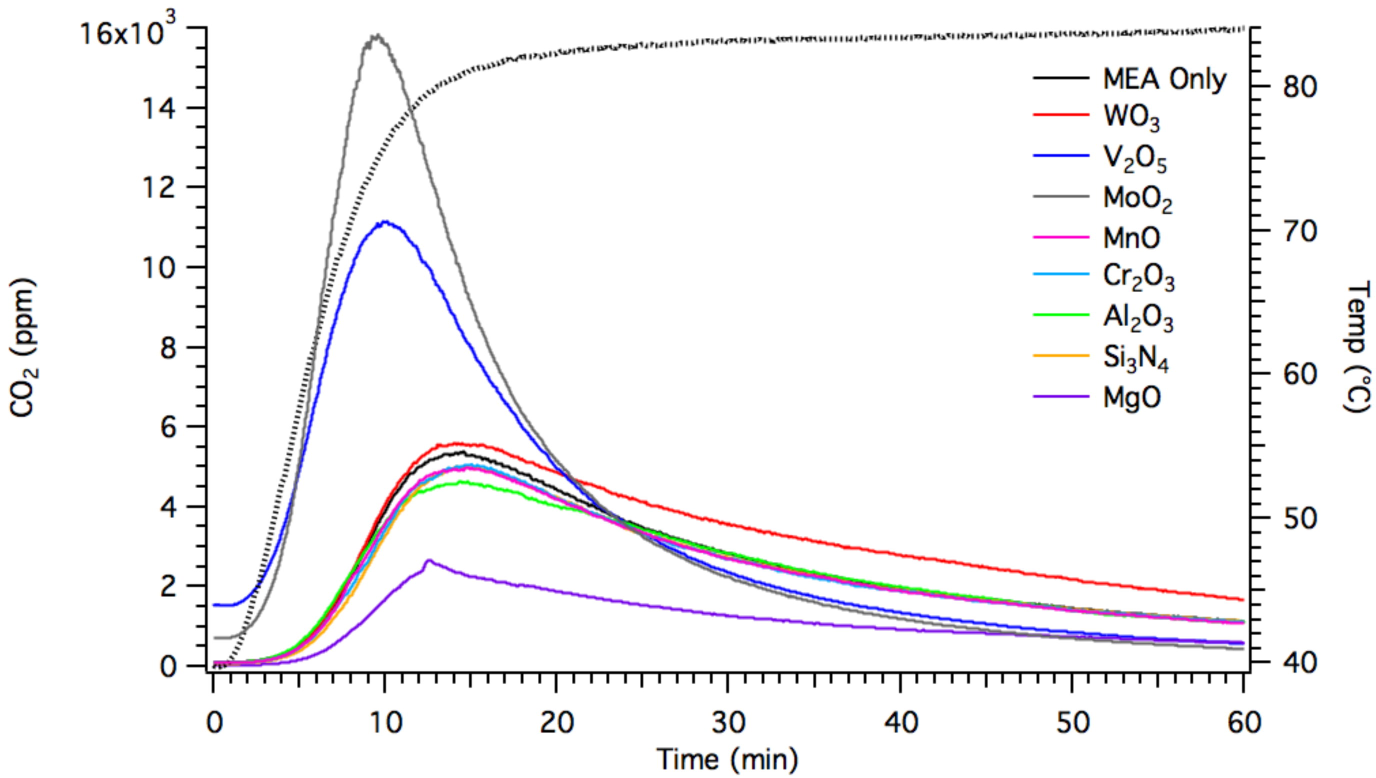


Experimental Setup



- 15 mL of an amine solution 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 °C to 86 °C at 10 °C min^{-1}

Screening of Metal Oxides for CO_2 Desorption (MEA)



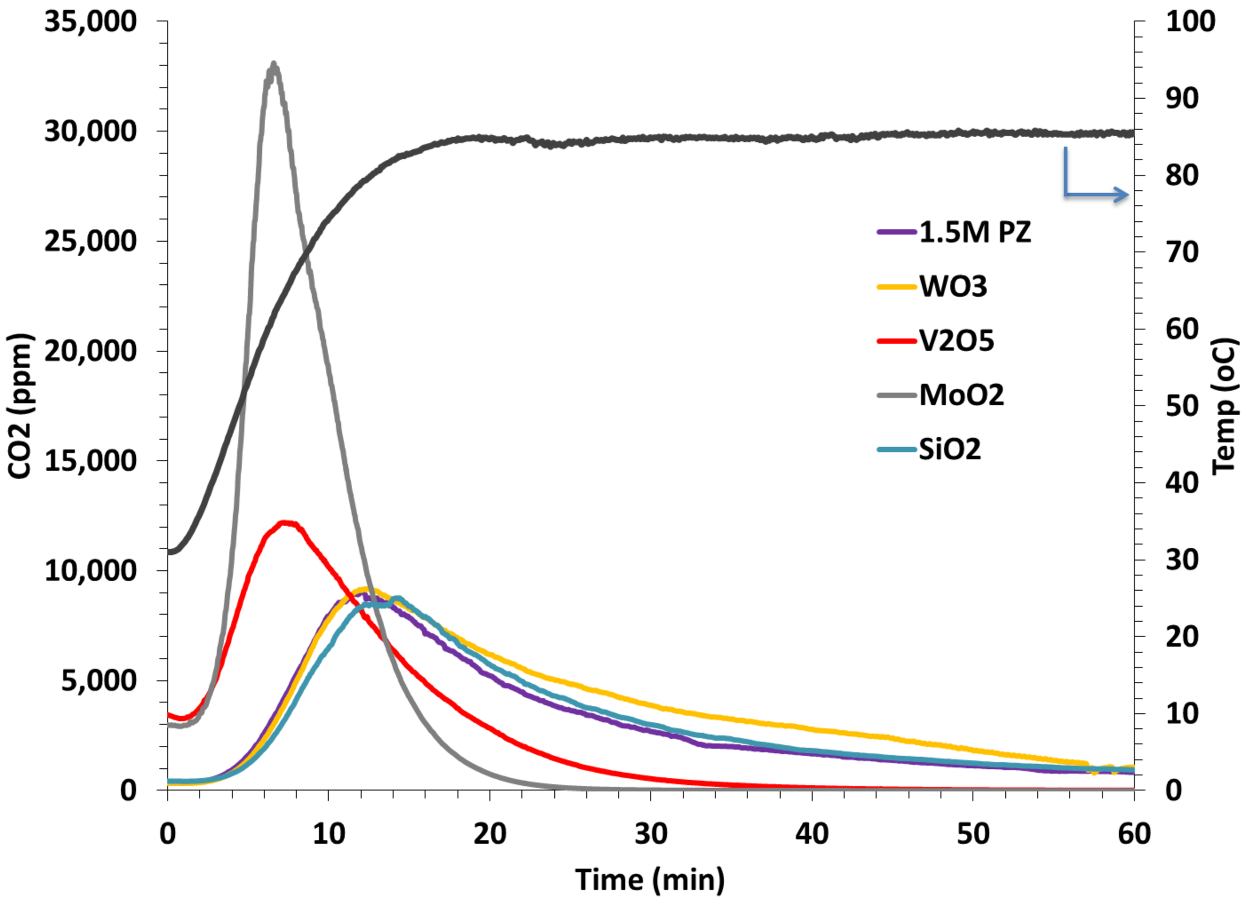
- WO_3, V_2O_5, and MoO_2 increased the release of CO_2 from MEA
- V_2O_5 and MoO_2 started desorbing CO_2 at 40 ° C during the initial 15-minute equilibrium step
- WO_3 caused more CO_2 release than MEA only after 76 ° C

Screening of Metal Oxides for CO_2 Desorption

MO_x (1.5 g)	Cumulative $\%CO_2$ released by 30 min at 86 °C	Cumulative $\%CO_2$ released by 60 min at 86 °C	Time (min), temperature (°C) of max CO_2 release peak	IEP
MEA only	31.6	49.2	14, 84	N/A
WO_3	34.7	60.0	13, 73	0.2 – 0.5
V_2O_5	45.8	69.0	10.5, 76	1 – 2
MoO_2	65.8	76.2	10, 82	2.5
MnO_2	29.8	46.8	15, 84	4 – 5
Cr_2O_3	29.7	46.8	15, 84	7
α-Al_2O_3	29.4	47.0	14, 84	8 – 9
Si_3N_4	29.3	46.5	15, 84	9
MgO	13.7	22.3	13, 80	12 – 13

- No correlation between IEP and CO_2 desorption
- WO_3 , V_2O_5, and MoO_2 caused CO_2 to desorb at lower temperatures than CO_2-loaded MEA solution
- WO_3 did not dissolve, which implies that ceramic foams made using WO_3 may be suitable in a stripper unit

Screening of Metal Oxides for CO_2 Desorption (Piperazine)



MOx	% CO2 released	IEP (est., 25° C)
PZ only	58.1	N/A
WO3	69.2	0.2-0.5
V2O5	81.1	1-2
MoO2	79.1	2.5
SiO2	58.9	3-3.5

- No correlation between IEP and CO_2 desorption
- WO_3,V_2O_5, and MoO_2 caused more CO_2 release than piperazine (PZ) only solution
- Similar to MEA, WO_3 did not dissolve in PZ.

Summary and Conclusions

- **Developed a process model to simulate gas/liquid flow and reaction in integrated CO_2 absorber/desorber unit**
  - Complete development of a 1D process model.
  - Successful to predict pressure drop, flooding and CO_2 absorption in 1D ceramic foam column.
  - Predicted fluid flow and temperature profiles of integrated absorber/desorber unit in 2D model
- **Screened various metal oxides for CO_2 desorption**
  - Metal oxides represent a new approach to reduce the desorption temperature
  - Our process can potentially reduce the cost of existing amine-based CO_2 capture technology by addressing the major challenges due to high desorption temperatures. These challenges are- high energy requirement, degradation and evaporation of amine solutions

Research Tasks for 2014-15

- **Model combined absorber/desorber CO_2 separation process**
  - Continue the development of a 2-D model to simulate gas and liquid flow in the capture process and compare simulation results with experimental measurements
  - Perform a sensitivity analysis and process optimization
- **Develop low temperature desorption zone**
  - Develop highly active and stable catalysts that can further lower the desorption temperature.
  - Perform appropriate tests to examine the amine solutions after experiments to check for any degradation products.
  - Design foams containing metal oxides
  - Reduce the cost of existing amine-based CO_2 capture technology by addressing major challenges due to high desorption temperatures.
- **Complete an exergy (available energy) and techno-economic analysis and perform an EH&S assessment of the process**

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

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

•Rice Consortium on Processes in Porous Media

•Schlumberger

Material Properties of alumina membrane and polymer (PES) membrane

Porous Alumina Membrane	
Material	99.5 % (α-Al_2O_3)
Supplier	Refractron Inc., USA
Dimensions	12’’ x 6 ‘’ x 1’’
Mean pore-size	19.3 um
Permeability & Gas Entry Pressure	5.37 x 10^{-12} m^2| 0.8 psi (with water)
Gas-Liquid Separator Polymer Membrane	
Material	Polyethersulfone (Hydrophilic)
Supplier	Pall LifeSciences Corporation, USA
Dimensions	8’’ x 8’’
Mean pore-size	0.8 um
Permeability & Gas Entry Pressure	0.32–1.52 10^{-12} m^2 | 15-31 psi (with water)