Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture

James A. Ritter & The Team

University of South Carolina

catacel™
Driving Reaction Technology

Battelle
The Business of Innovation

GRACE
Davison

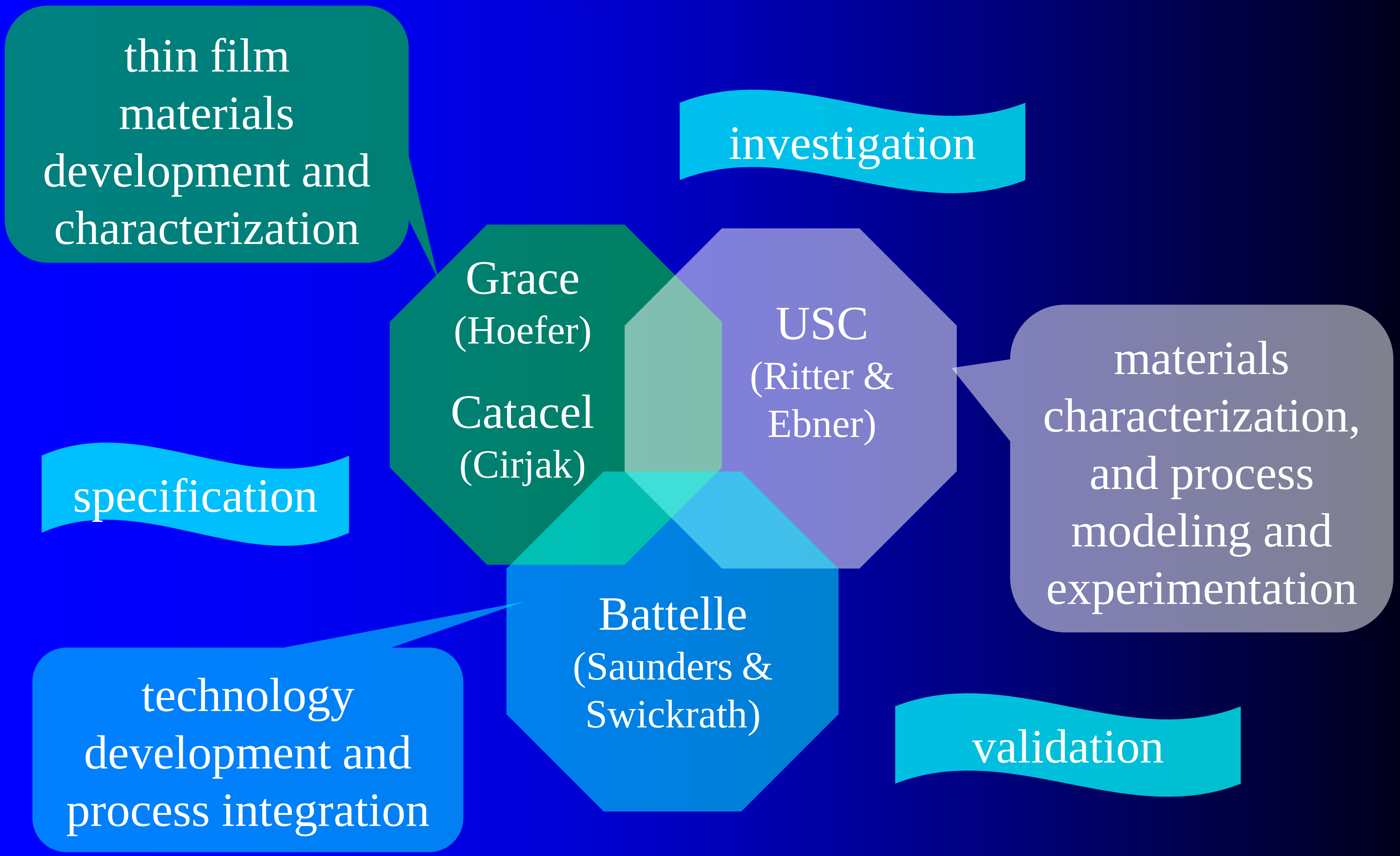
2013 NETL CO2 Capture Technology Meeting
Pittsburgh, PA, July 8, 2013

Overall Project Objectives

- design, develop and demonstrate a bench-scale process for the efficient and cost effective separation of CO_2 from flue gas using Pressure Swing Adsorption (PSA)
- goal to reduce energy consumption, capital costs, and environmental burdens with novel PSA cycle/flow sheet designs
- applicable to both large (500-1000 MW) and small (5-50 MW) capacity power plants, and industries with 10 to 100 times less CO_2 production

Process simulations and experiments; structured adsorbent material development, CFDs and experiments; and complete flow sheet analyses being used for demonstrating and validating the concepts.

The Team


thin film materials development and characterization
investigation
Grace (Hoefer)
Catacel (Cirjak)
USC (Ritter & Ebner)
materials characterization, and process modeling and experimentation
specification
Battelle (Saunders & Swickrath)
technology development and process integration
validation

PSA Technology Advantages

- established, very large scale technology for other applications
- needs no steam or water; only electricity
- tolerant to trace contaminants; possibly with use of guard or layered beds
- zeolite adsorbent commercial and widely available
- increase in COE lower than other capture technologies
- beds can be installed under a parking lot

PSA Technology Challenges

- energy intensive, but better than today's amines; possibly overcome by novel designs
- today, very large beds required → implies large pressure drop → more power; possibly overcome by structured adsorbents and faster cycling
- large footprint; possibly overcome by underground installation and faster cycling → smaller beds
- high capitol cost; possibly overcome by faster cycling → smaller beds

Key PSA Technology Project Challenge

- although a commercial tri-sieve zeolite could be used today in an efficient PSA cycle, it would only minimize to some extent the pressure drop issues, but not the adsorbent attrition and mass transfer issues
- key challenge is to develop a structured adsorbent around an efficient PSA cycle that exhibits a high enough packing density to allow the fastest possible cycling rate (→ smallest possible beds), while improving pressure drop and mass transfer issues and eliminating attrition issues


Where are we going?

Scale of PSA System for CO_2 Capture from 500 MW Power Plant

Is it possible to achieve a 1/10th volume reduction?

- increase working capacity 10 fold (herculean)
- operate at 1/10th cycle time (achievable)
- known as rapid PSA

although rapid PSA offers potential for a low-cost solution for CO_2 capture, the extent of size reduction achievable is, at the moment, unknown

QuestAir H-6200 Rapid PSA-Installed at ExxonMobil Facility

H_2 Production Rapid PSA
~ 12,000 Nm^3/h/module

H_2 Production
Conventional PSA
~ 20,000 Nm^3/h

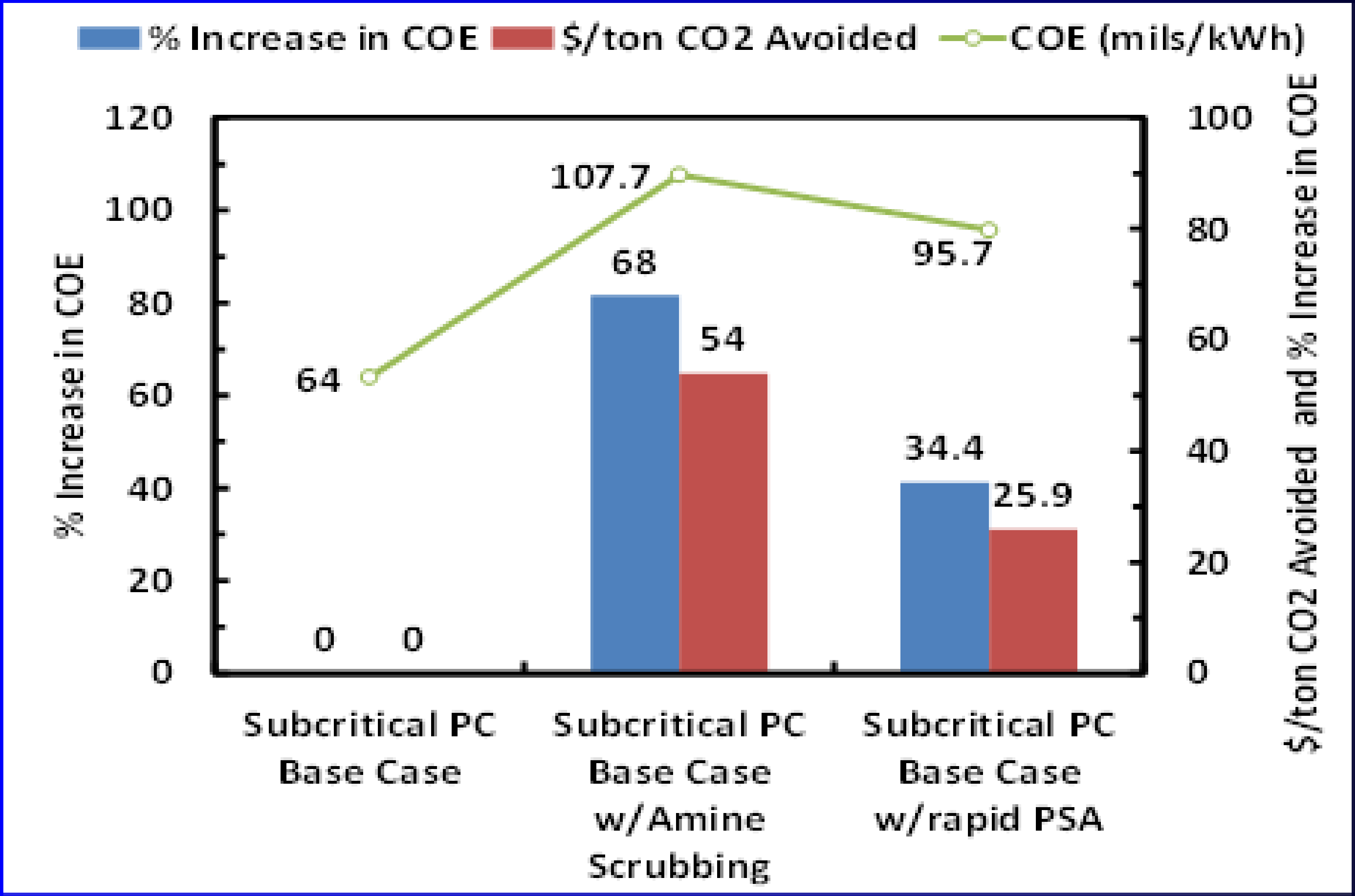
A 500 MW plant produces ~ 33,000 Nm^3/h at > 30 times lower pressure!

Two of Questair's modules do 20% better than this 6-bed PSA system and are much smaller.

Where are we now after completing first year?

Preliminary Technical and Economic Feasibility Study

Overall Outcome



Significant Outcomes from Year 1

- developed PSA cycle and process flow sheet with less than 35% LCOE increase; based on completed *preliminary technical and economic feasibility study*

- demonstrated zeolite crystals can be coated onto basic metal structure with at least 50 mm thick coating; suggests it may be possible to achieve even 100 to 150 mm coatings, if needed

- demonstrated Catacel core structures can be made with up to 400 cells per square inch (cpsi); makes goal of achieving 600 cpsi, possibly even 800 cpsi, within reach

- demonstrated needed limit of < 20 kPa/m pressure drop through 400 cpsi core at very high velocities up to 25 m/s; pressure drop limit utilized in *preliminary technical and economic feasibility study*

Significant Outcomes from Year 1

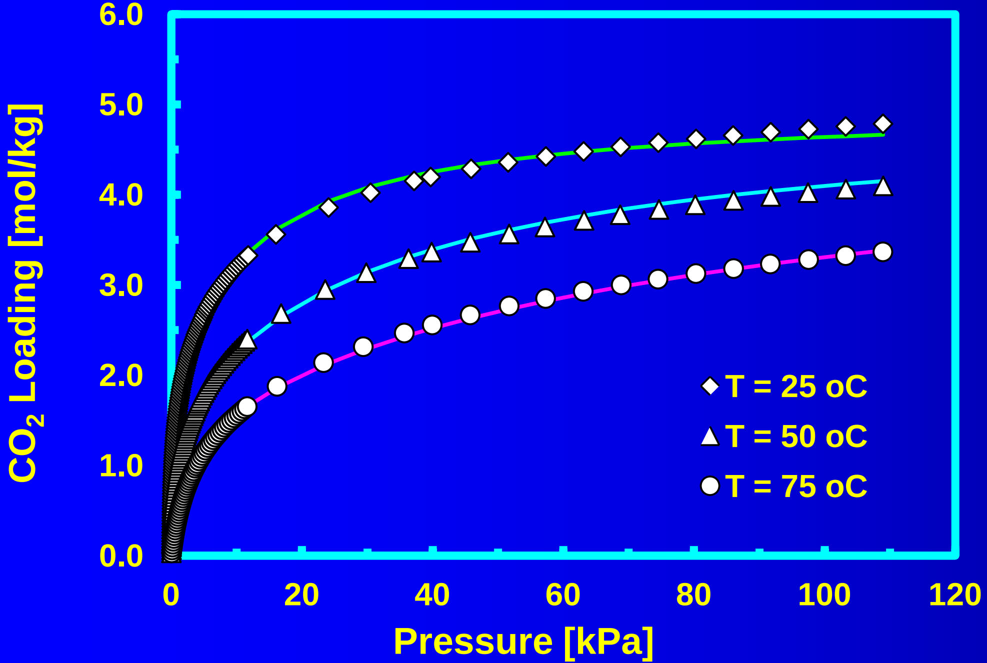
- Predicted pressure drop through Catacel core nearly quantitatively using CFD model with no adjustable parameters; paves way to fabricate even more optimum core structures using computational tools

- Demonstrated, via PSA process simulation, possibly lowest energy, highest feed throughput PSA cycle for CO_2 capture; amazing when considering bulk density reduced from 710 kg/m^3 (typical for packed bed of zeolite beads) to 400 kg/m^3 (entirely feasible with Catacel core)

- PSA cycle boasts feed throughput of around 3,000 L(STP)/hr/kg and separations energy < 18 kJ/mol CO_2 captured

How did we get to this point?

CO_2 Isotherm on Adsorbent and Dual Process Langmuir Fit

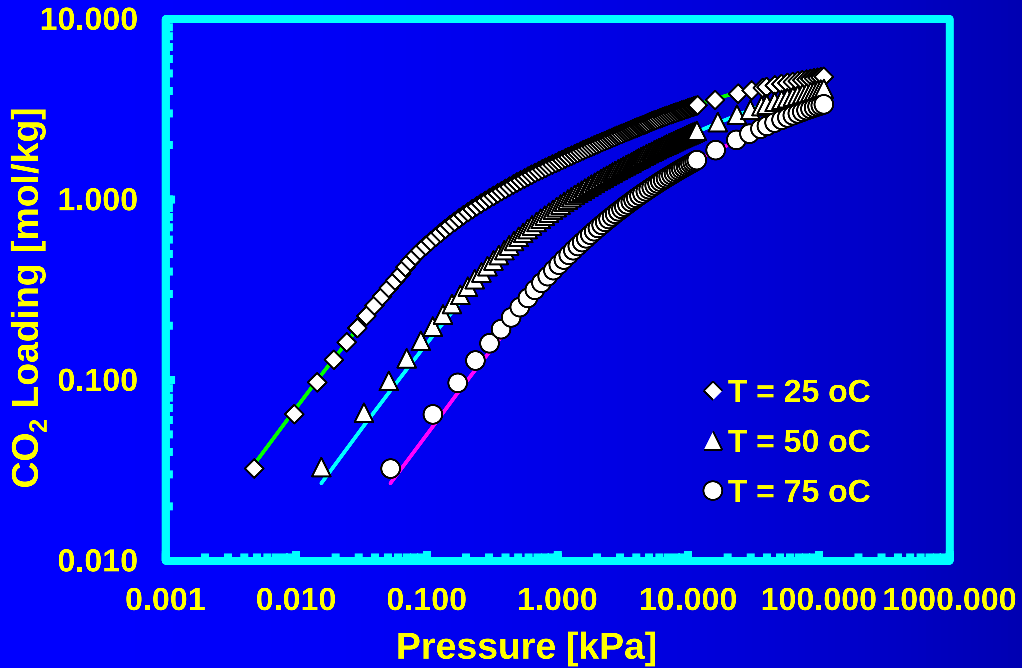


Dual Process Langmuir (DPL) Isotherm

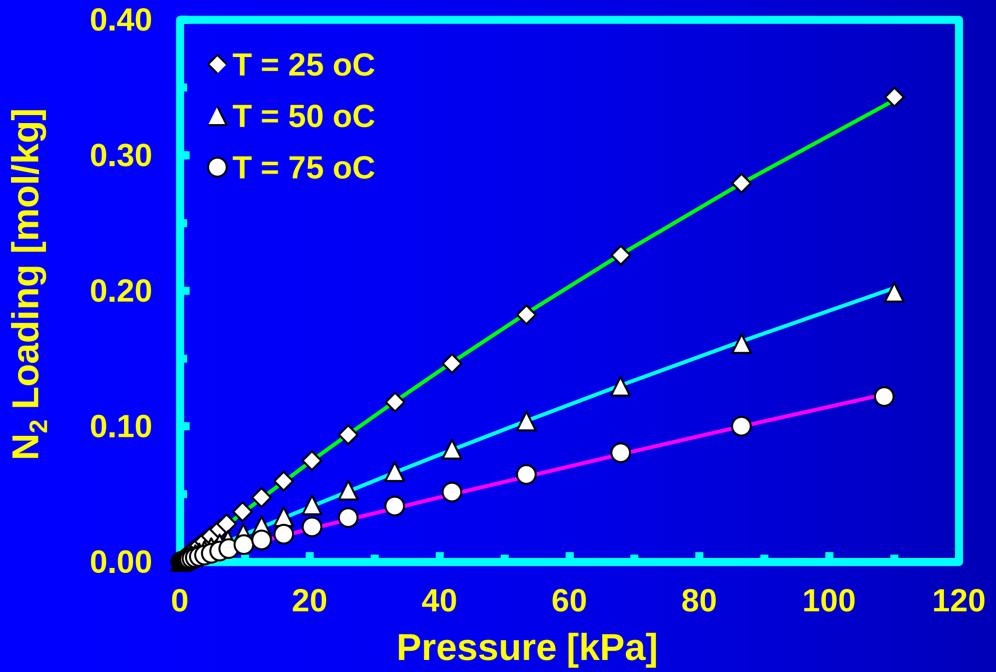
$$n_i = \left(\frac{n^s_{1,i} P y_i b_{1,i}}{1 + P y_i b_{1,i}} \right)_{site-1} + \left(\frac{n^s_{2,i} P y_i b_{2,i}}{1 + P y_i b_{2,i}} \right)_{site-2}$$

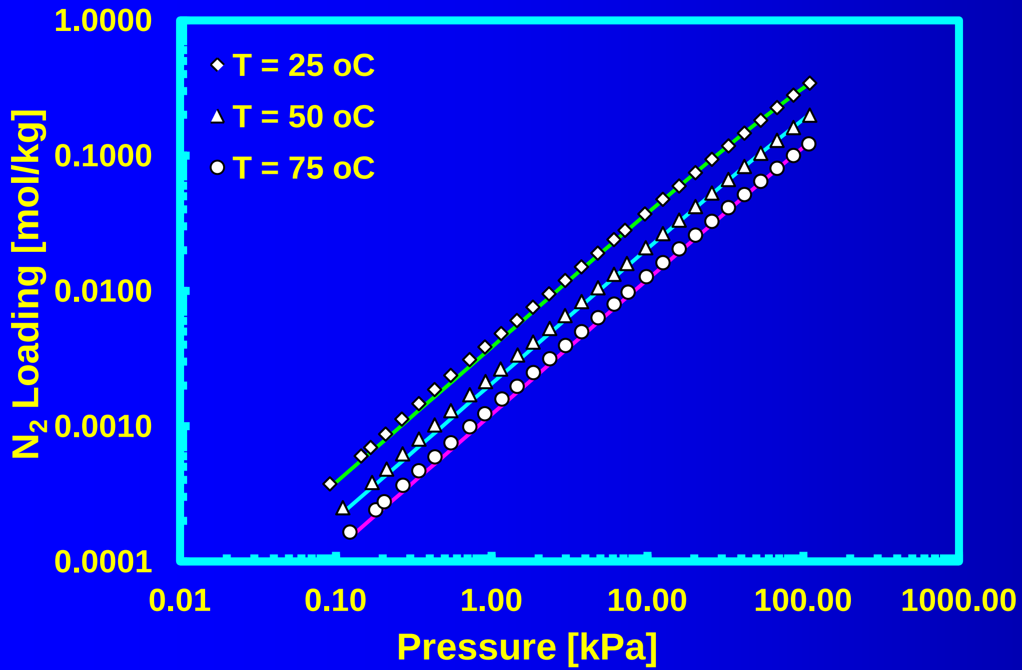
$$n^s_{j,i} = n^{s0}_{j,i} + n^{st}_{j,i} T$$

$$b_{j,i} = b^0_{j,i} \exp\left(\frac{B_{j,i}}{T} \right)$$



N_2 Isotherm on Adsorbent and Dual Process Langmuir Fit





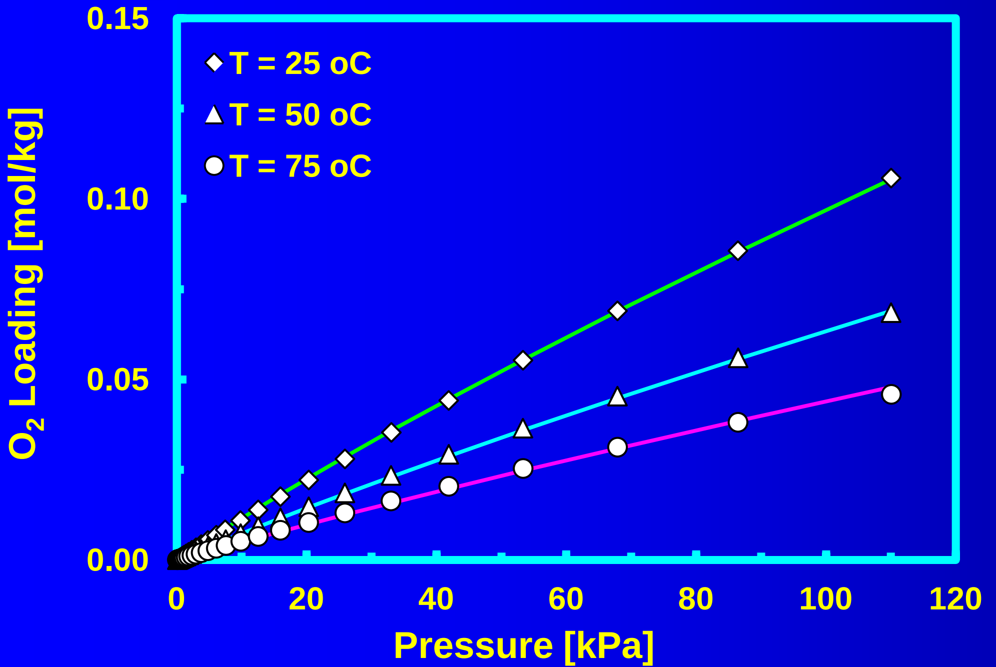
Dual Process Langmuir (DPL) Isotherm

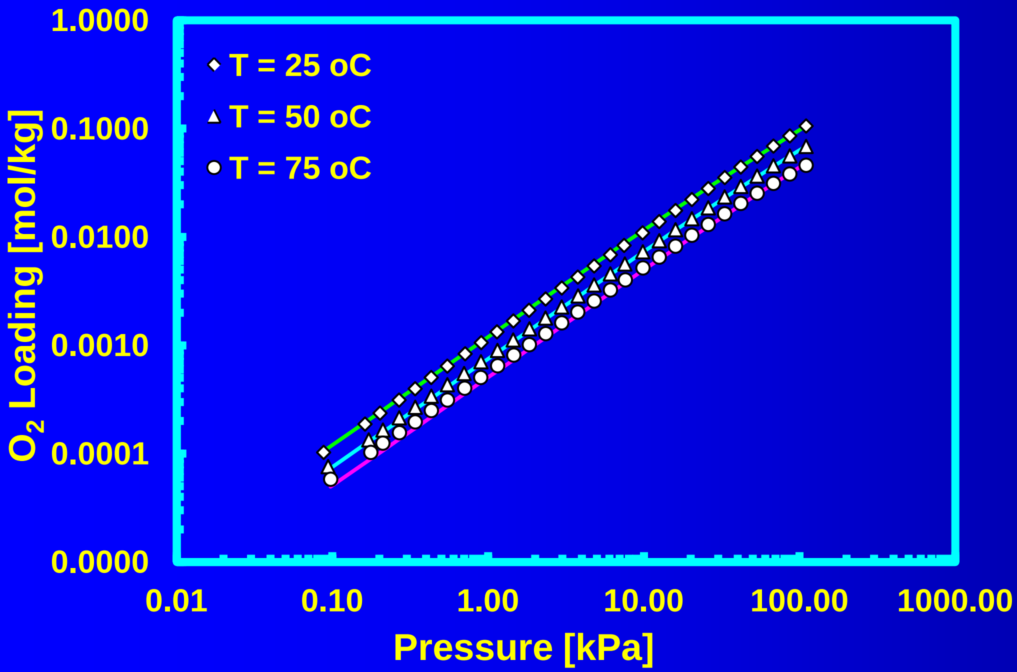
$$n_i = \left(\frac{n_{1,i}^s P y_i b_{1,i}}{1 + P y_i b_{1,i}} \right)_{site-1} + \left(\frac{n_{2,i}^s P y_i b_{2,i}}{1 + P y_i b_{2,i}} \right)_{site-2}$$

$$n_{j,i}^s = n_{j,i}^{s0} + n_{j,i}^{st} T$$

$$b_{j,i} = b_{j,i}^0 \exp\left(\frac{B_{j,i}}{T} \right)$$

O_2 Isotherm on Adsorbent and Dual Process Langmuir Fit





Dual Process Langmuir (DPL) Isotherm

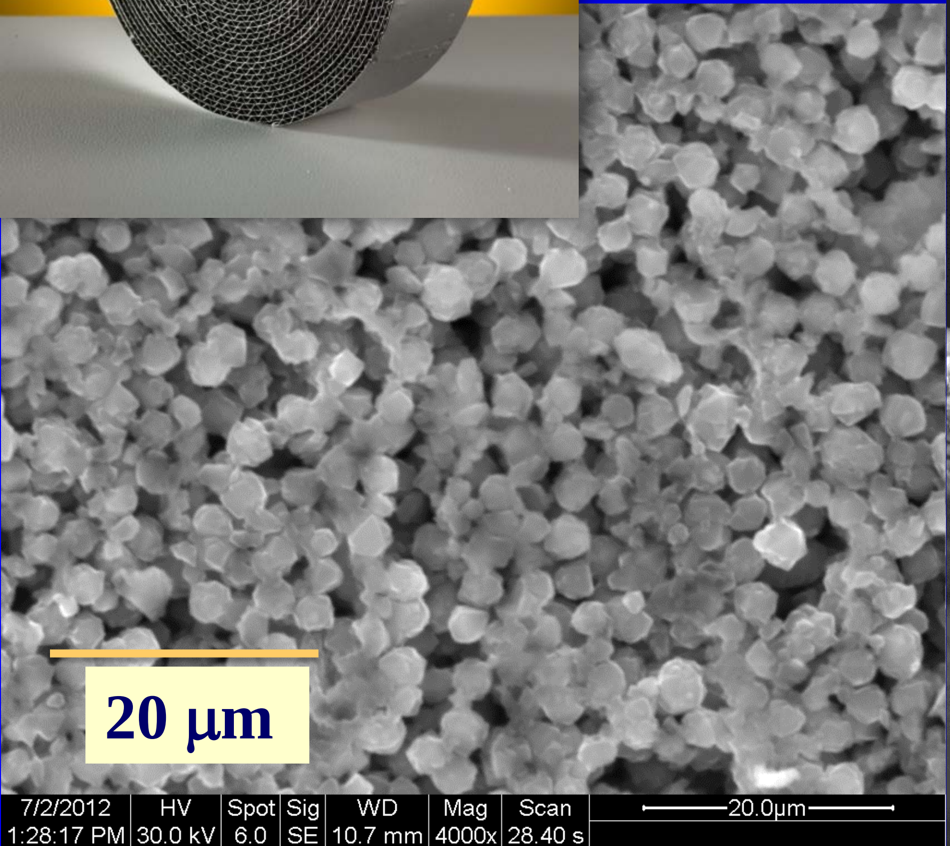
$$n_i = \left(\frac{n^s_{1,i} P y_i b_{1,i}}{1 + P y_i b_{1,i}} \right)_{site-1} + \left(\frac{n^s_{2,i} P y_i b_{2,i}}{1 + P y_i b_{2,i}} \right)_{site-2}$$

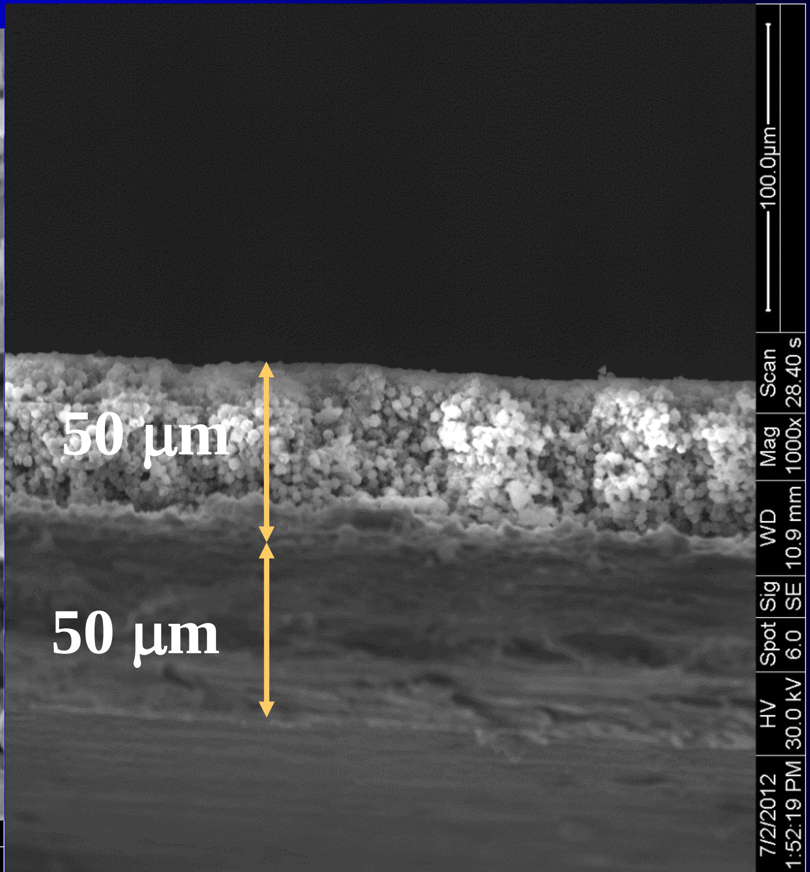
$$n^s_{j,i} = n^{s0}_{j,i} + n^{st}_{j,i} T$$

$$b_{j,i} = b^0_{j,i} \exp\left(\frac{B_{j,i}}{T} \right)$$

Zeolite Coated Metal Foil

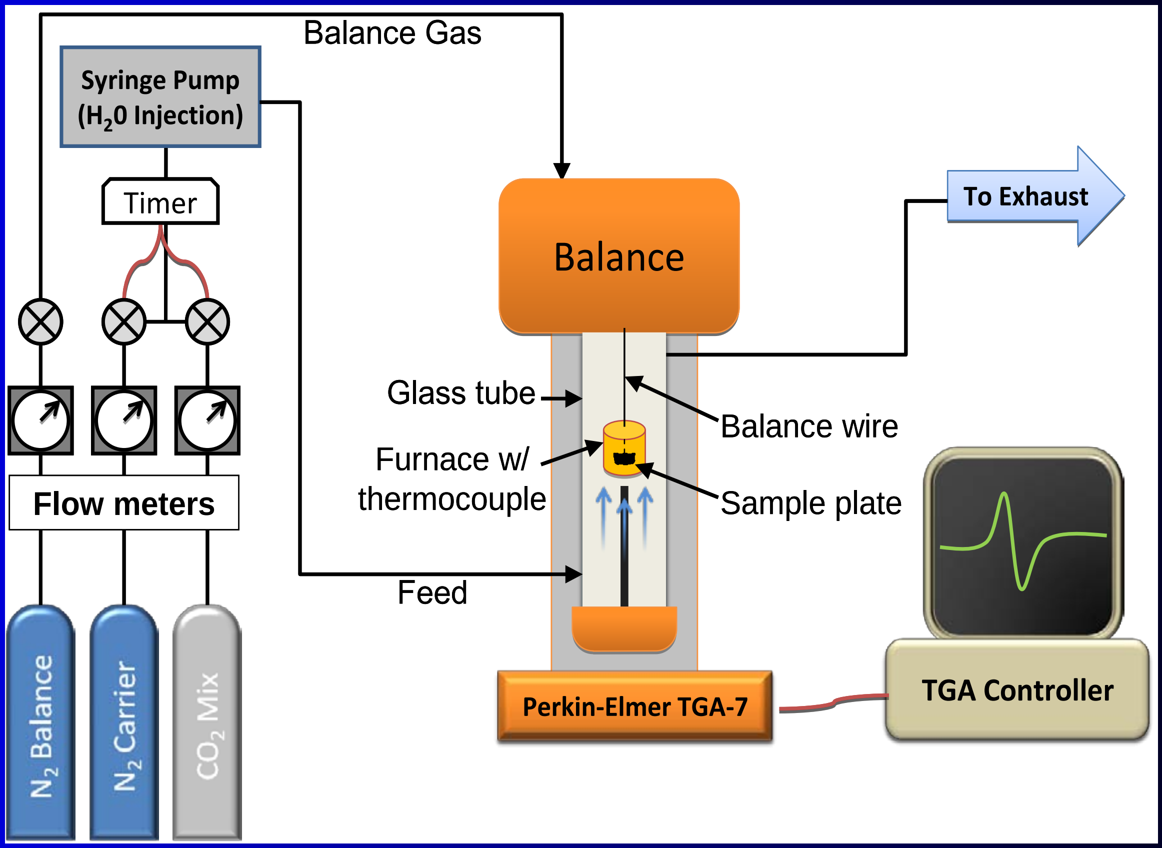
- **preliminary fabrication**
- **coated on flat foil coupon at 30 mg/in^2**
- **coating passed Catacel adhesion test**
- **goal: to make coating 100 – 150 µm thick**





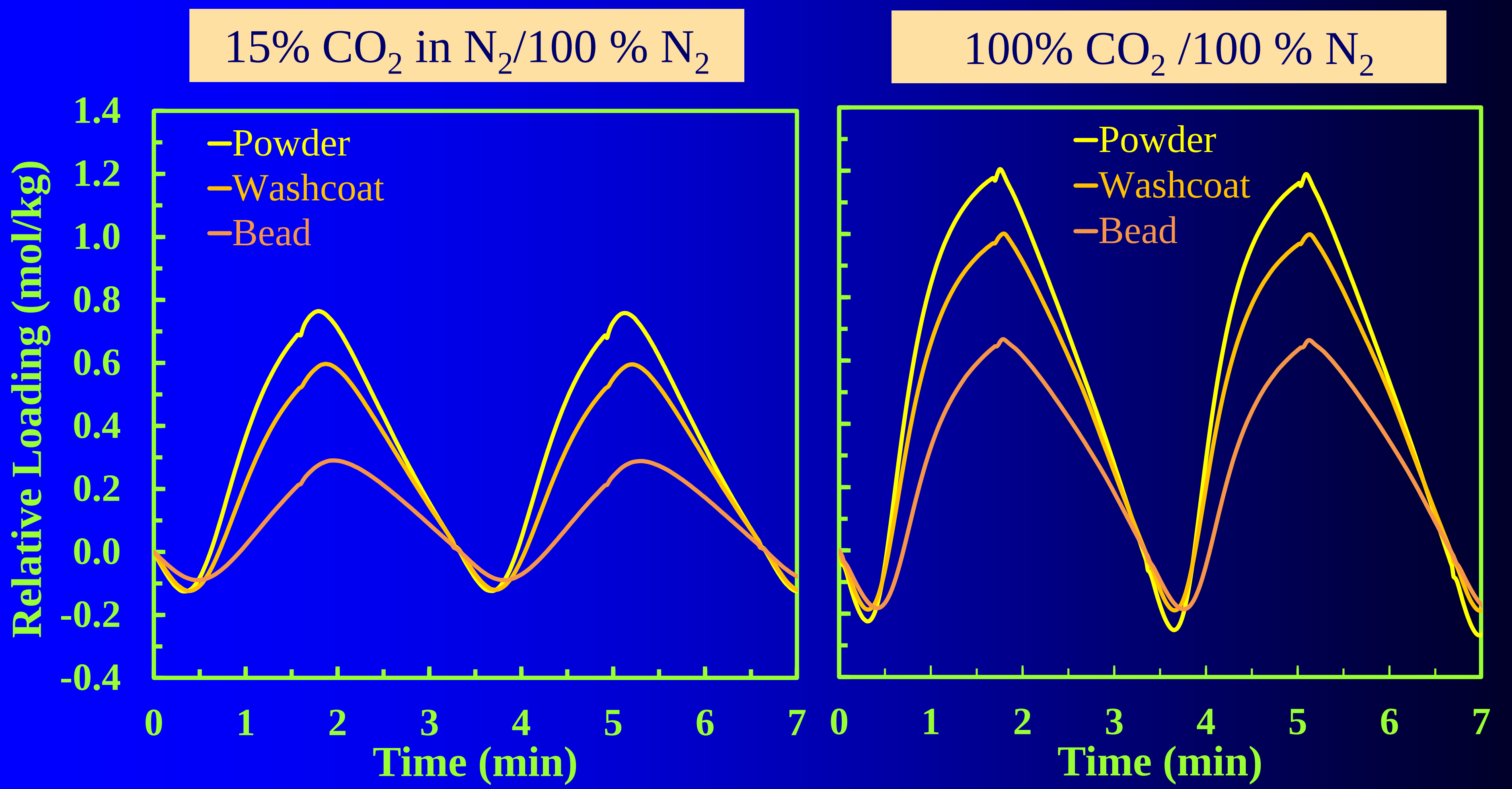
Rapid Adsorbent Characterization

- commercial zeolites
  - activation at 350 °C overnight in N_2
  - cycling at 90 °C
    - 2 min adsorption in 15% CO_2-N_2
    - 2 min desorption in 100% N_2
  - P_T = 1 atm



TGA Runs at 70 °C

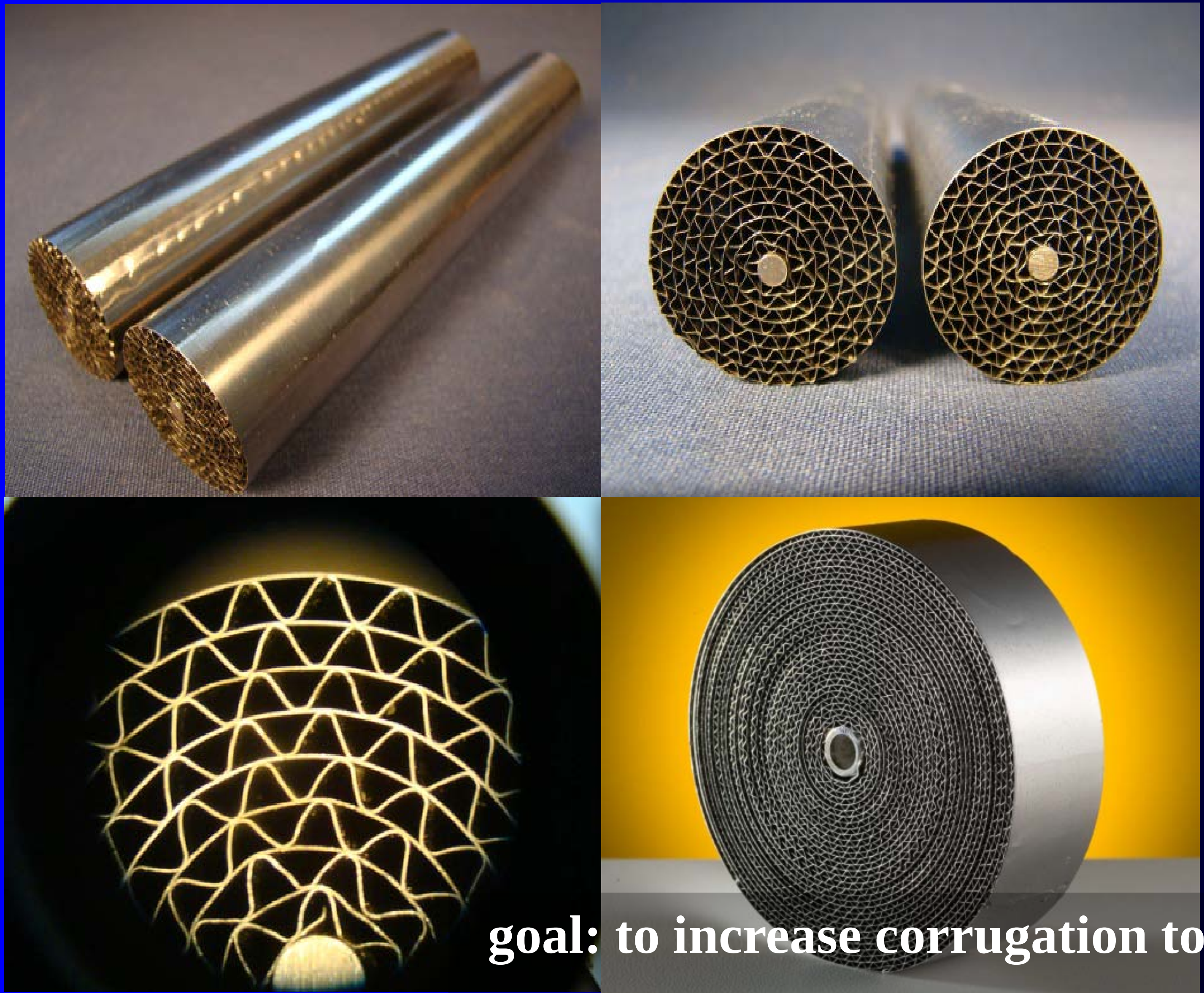
Cycle: 100 s Stream with CO_2 /100 s Pure N_2



Working Capacities of washcoat between 50 and 100% higher than commercial beads!

Corrugated Catacel Cores

1” x 6” x 400 cells/in^2



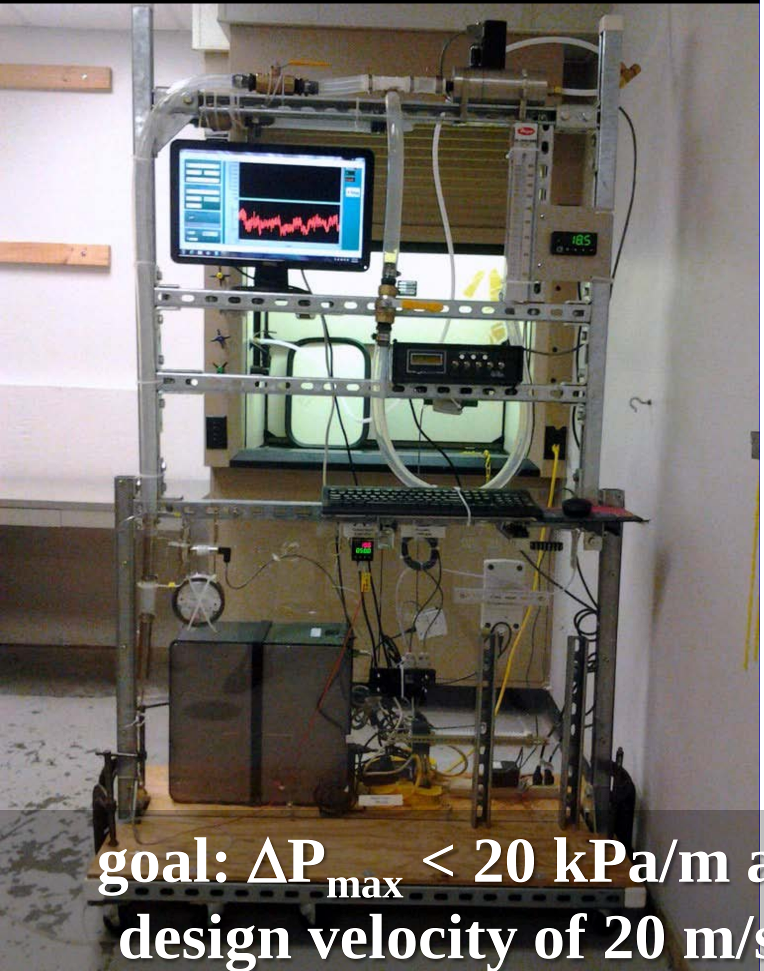
goal: to increase corrugation to 800 cpsi

Structured and Beaded Media Pressure Drop

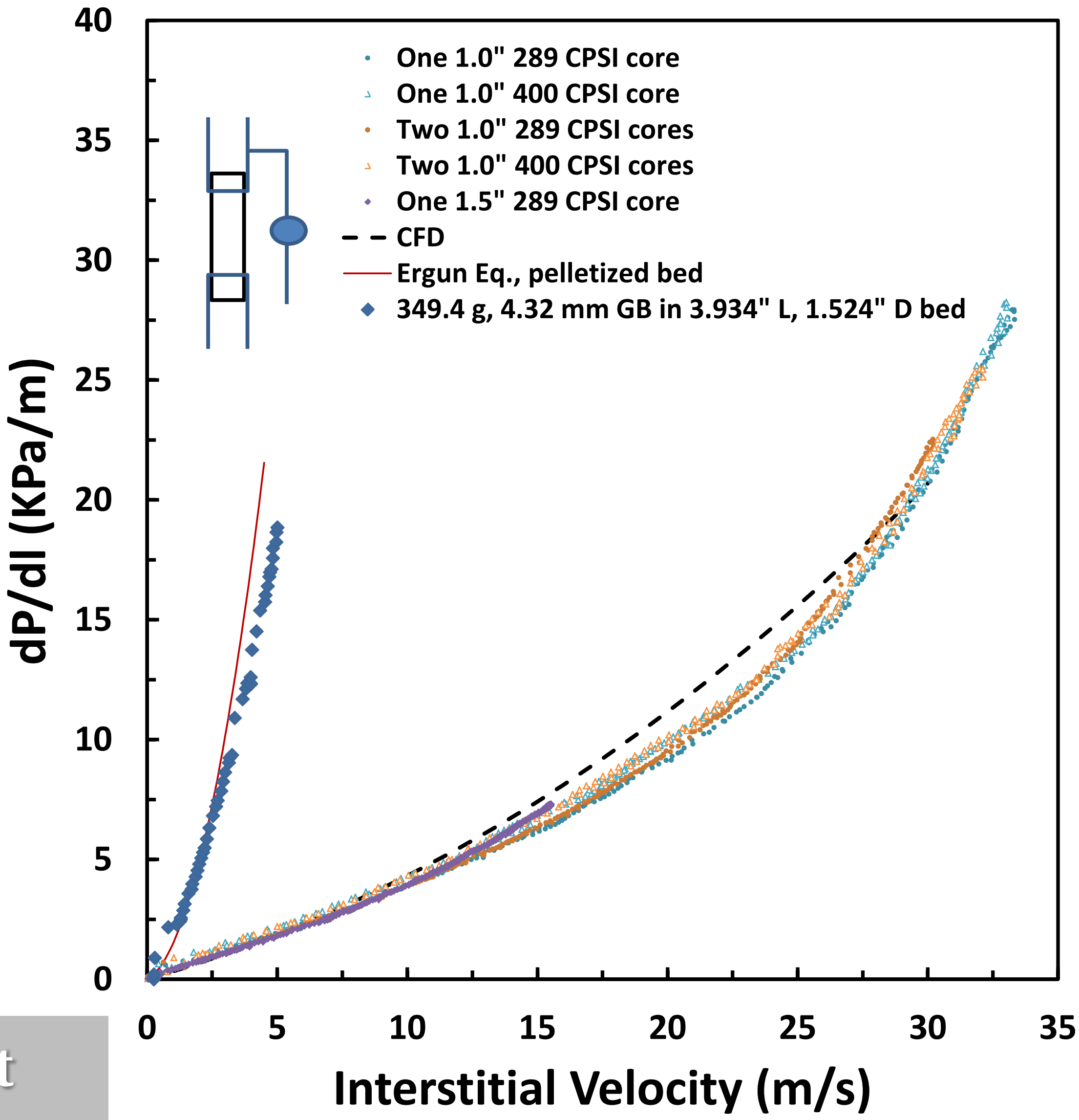
Pressure Drop Apparatus

Q_{max} = 1000 SLPM

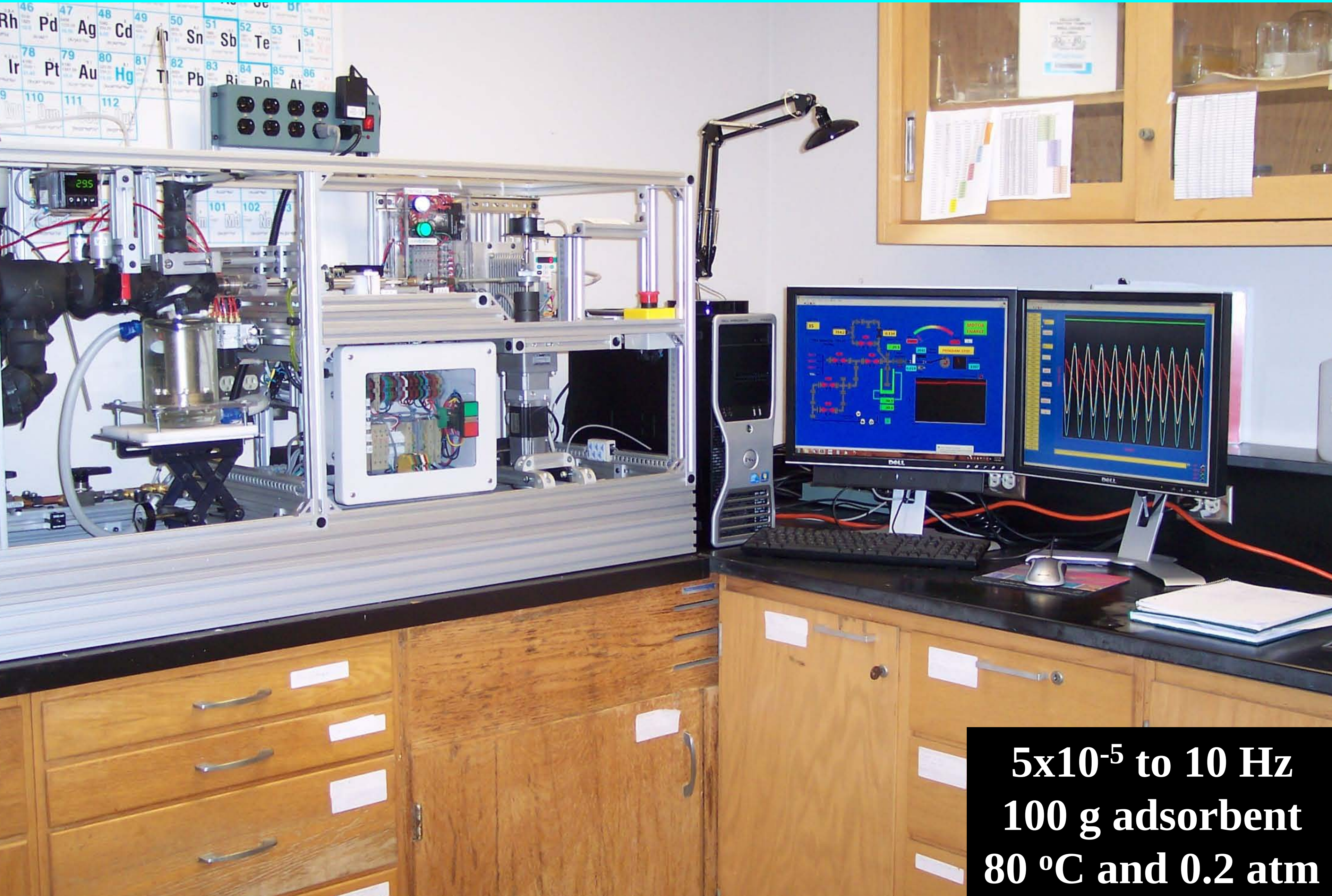
ΔP_{max} = 30, 70 or 140 in H_20



goal: ΔP_{max} < 20 kPa/m at design velocity of 20 m/s

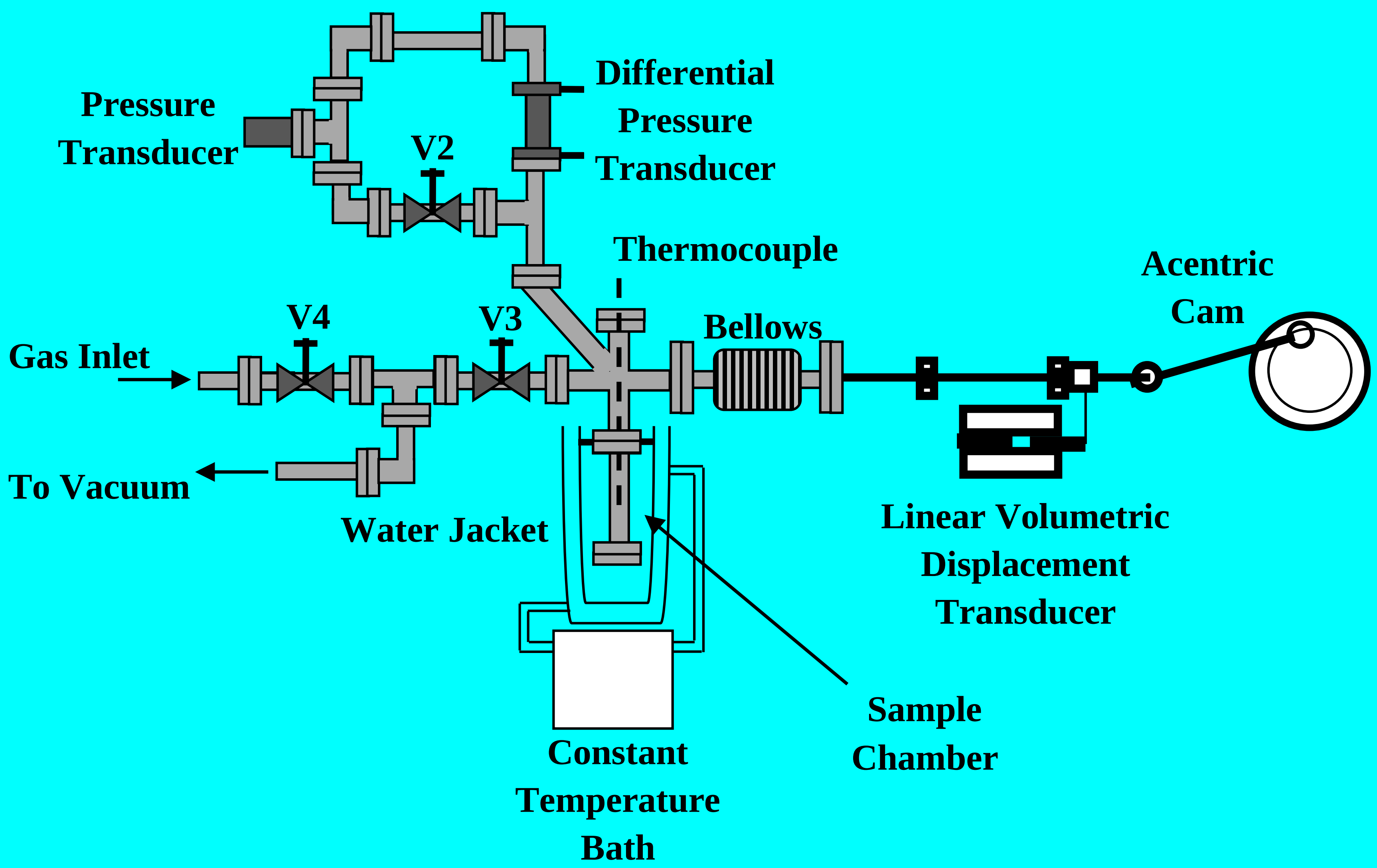


Volumetric Frequency Response Apparatus

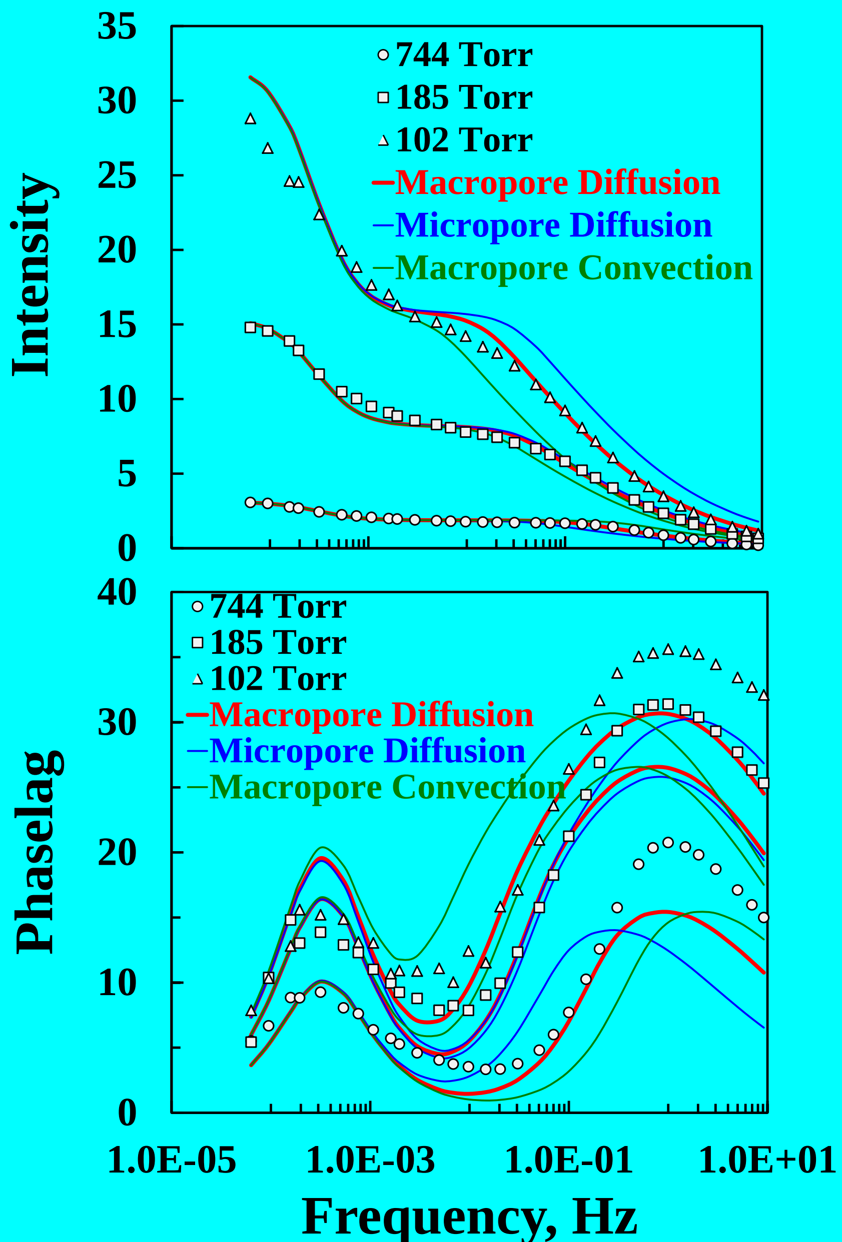


$5x10^{-5}$ to 10 Hz
100 g adsorbent
80 ºC and 0.2 atm

Volumetric Frequency Response Schematic



Volumetric Frequency Response Results



Correlation of Mass Transfer Models with Experimental Data

System and Conditions

CO_2-commercial zeolite beads

T = 25 ^{o}C

P = 102, 185, or 744 torr

f = 5x10^{-5} to 10 Hz

Mass Transfer Models

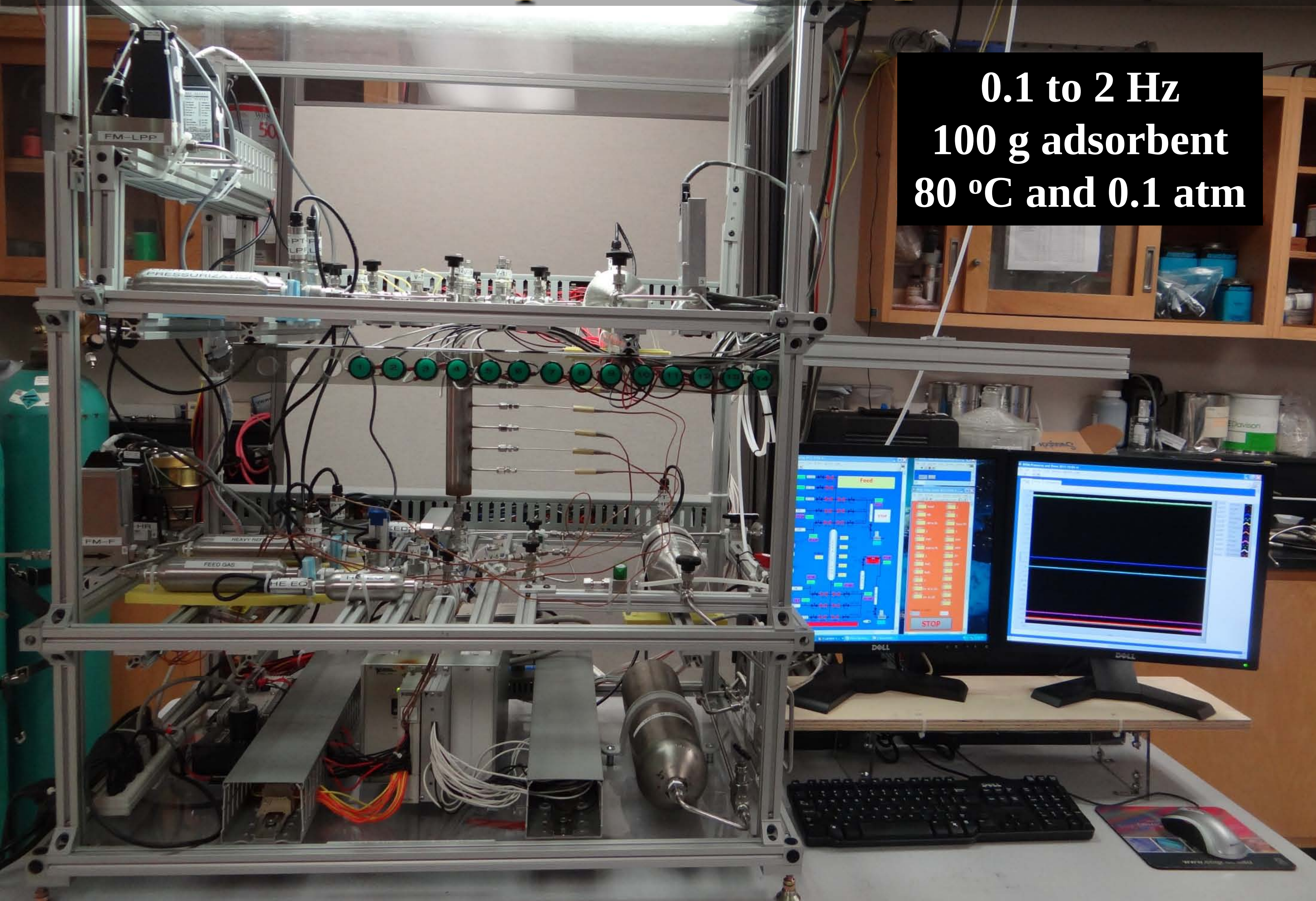
Macropore Diffusion

Macropore Convection

Micropore Diffusion

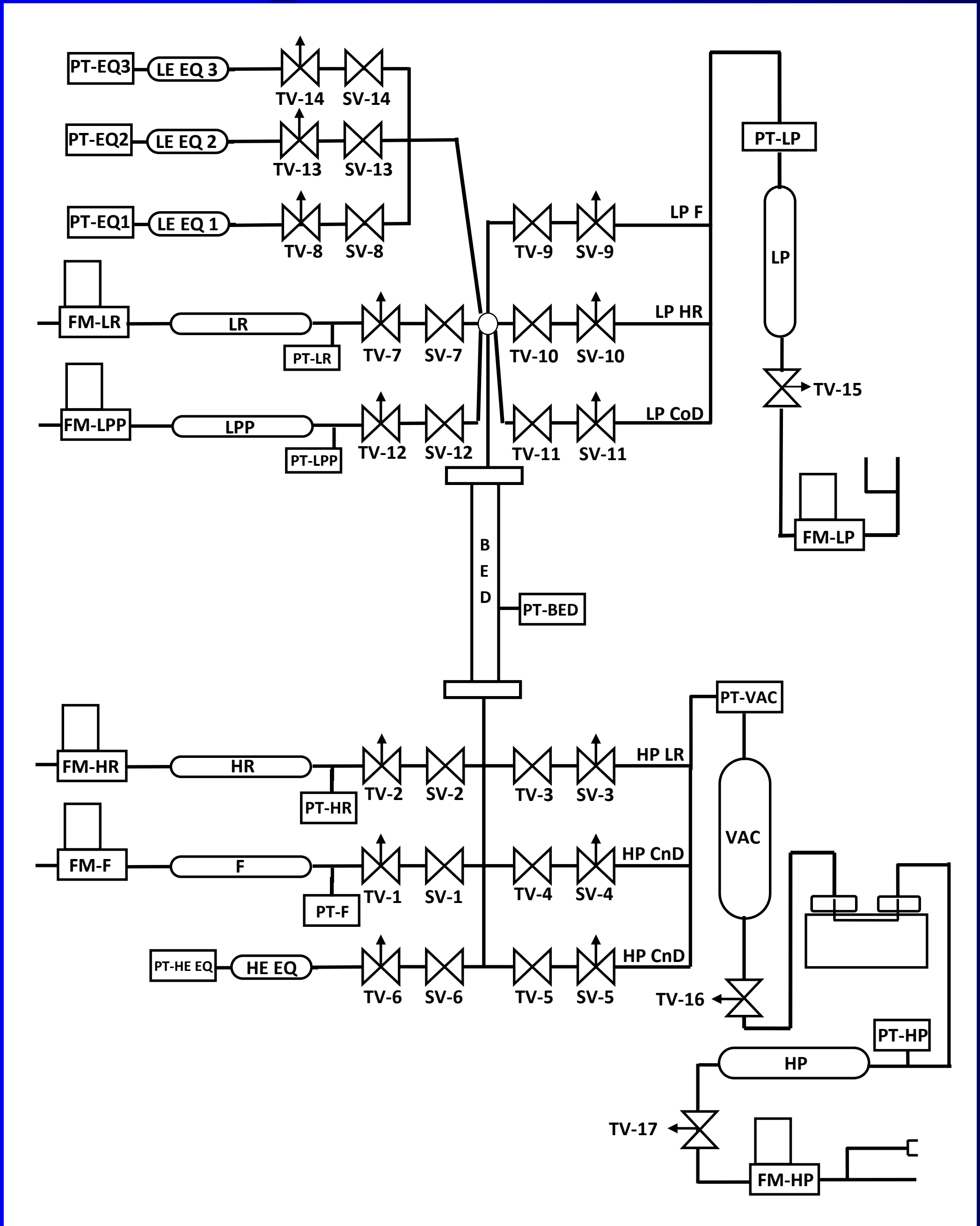
only macropore diffusion model unequivocally fits the data over the pressure range investigated

1-Bed Rapid PSA Apparatus

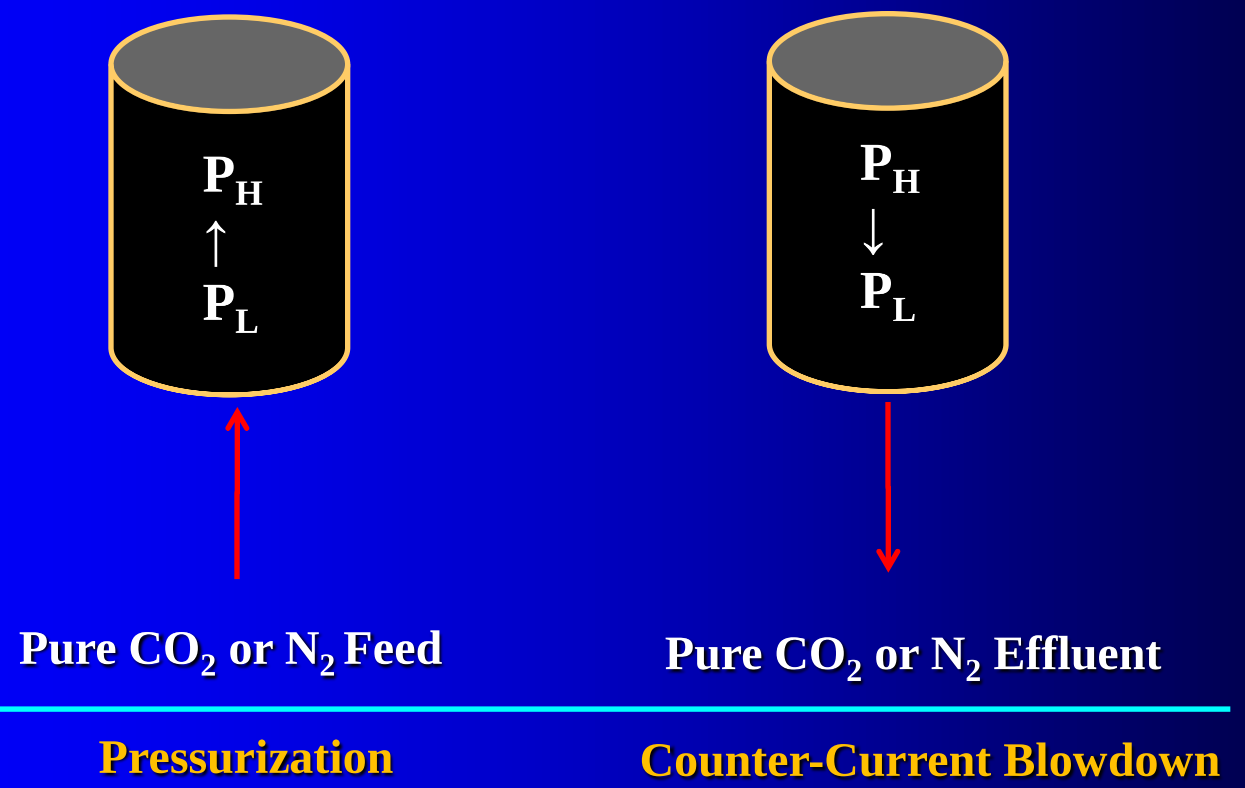


0.1 to 2 Hz
100 g adsorbent
80 ^oC and 0.1 atm

1-Bed Rapid PSA Schematic



Two-Step CO_2 and N_2 Cycling Experiments



Information Obtained

a) Determination of Valve C_v

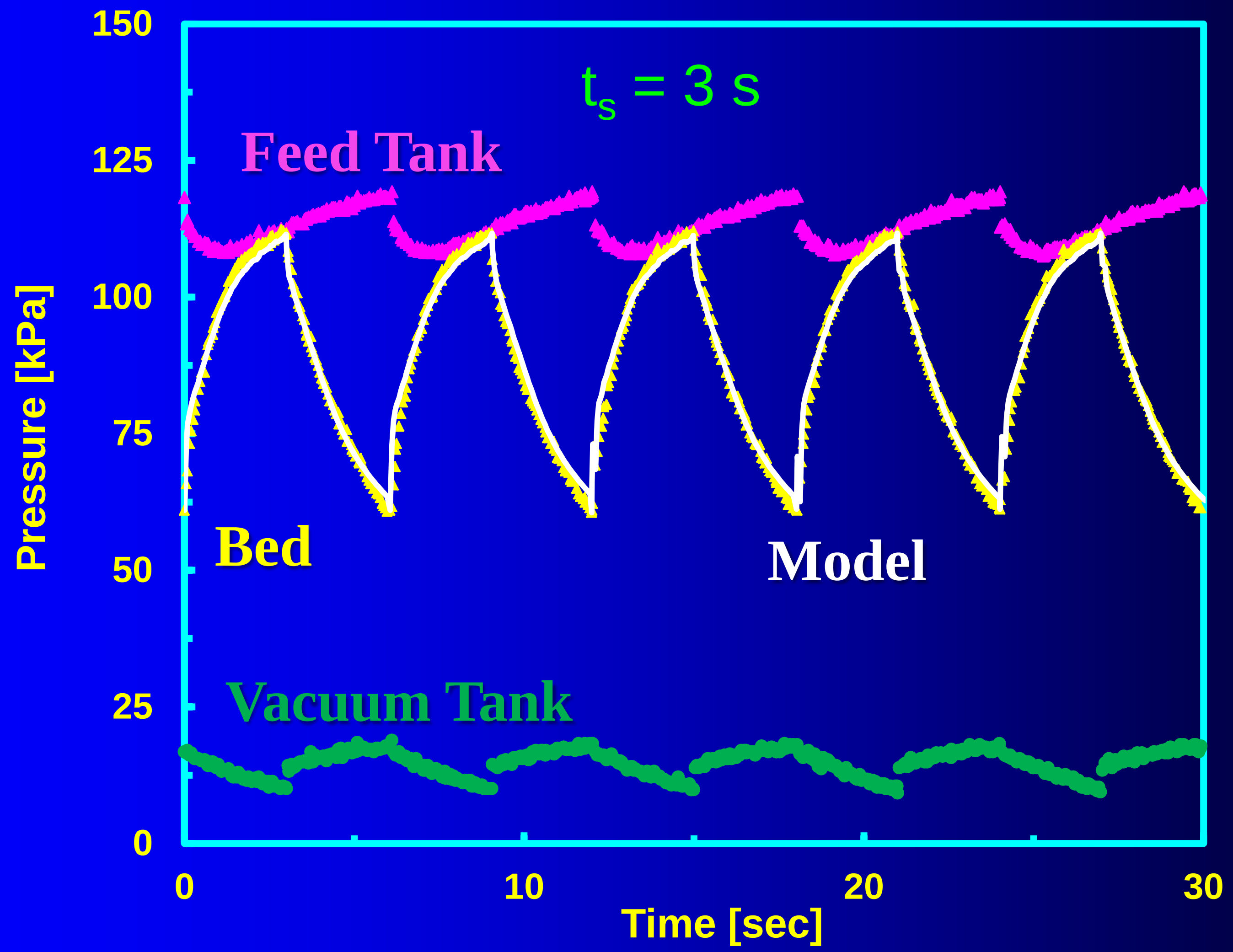
b) Determination of excluded volume

c) Validation of Single Component Isotherms

d) Validation Adsorption/Desorption Mass Transfer Coefficients

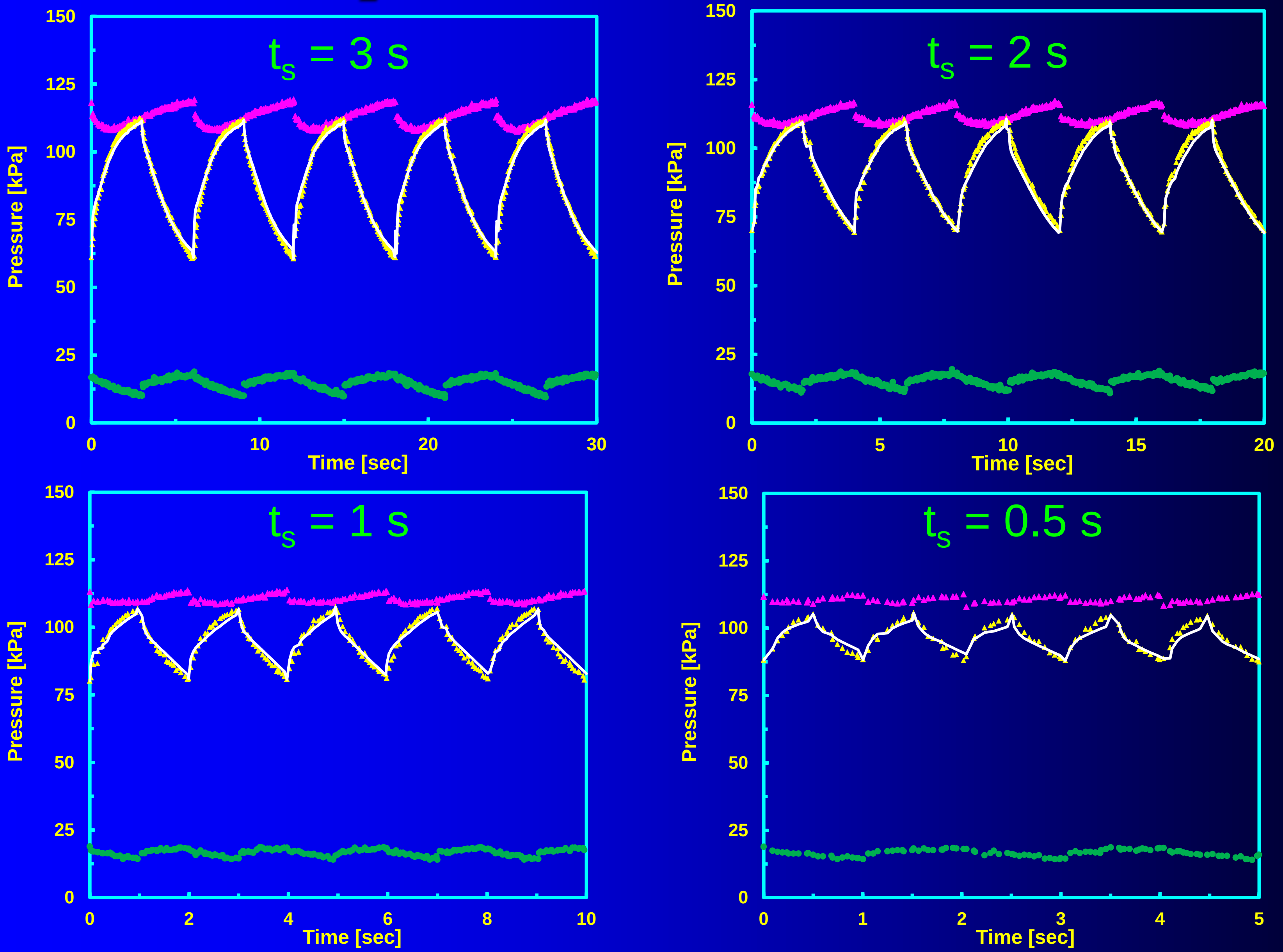
Pure Gas Cycling in 1-Bed Rapid PSA System

CO_2 on Beaded Zeolite at 22 ^oC



Pure Gas Cycling in 1-Bed Rapid PSA System

CO_2 on Beaded Zeolite at 22 °C



Comparison of Mass Transfer Coefficients

CO_2 on Beaded Zeolite

Volumetric Frequency Response Apparatus (25 ^oC)

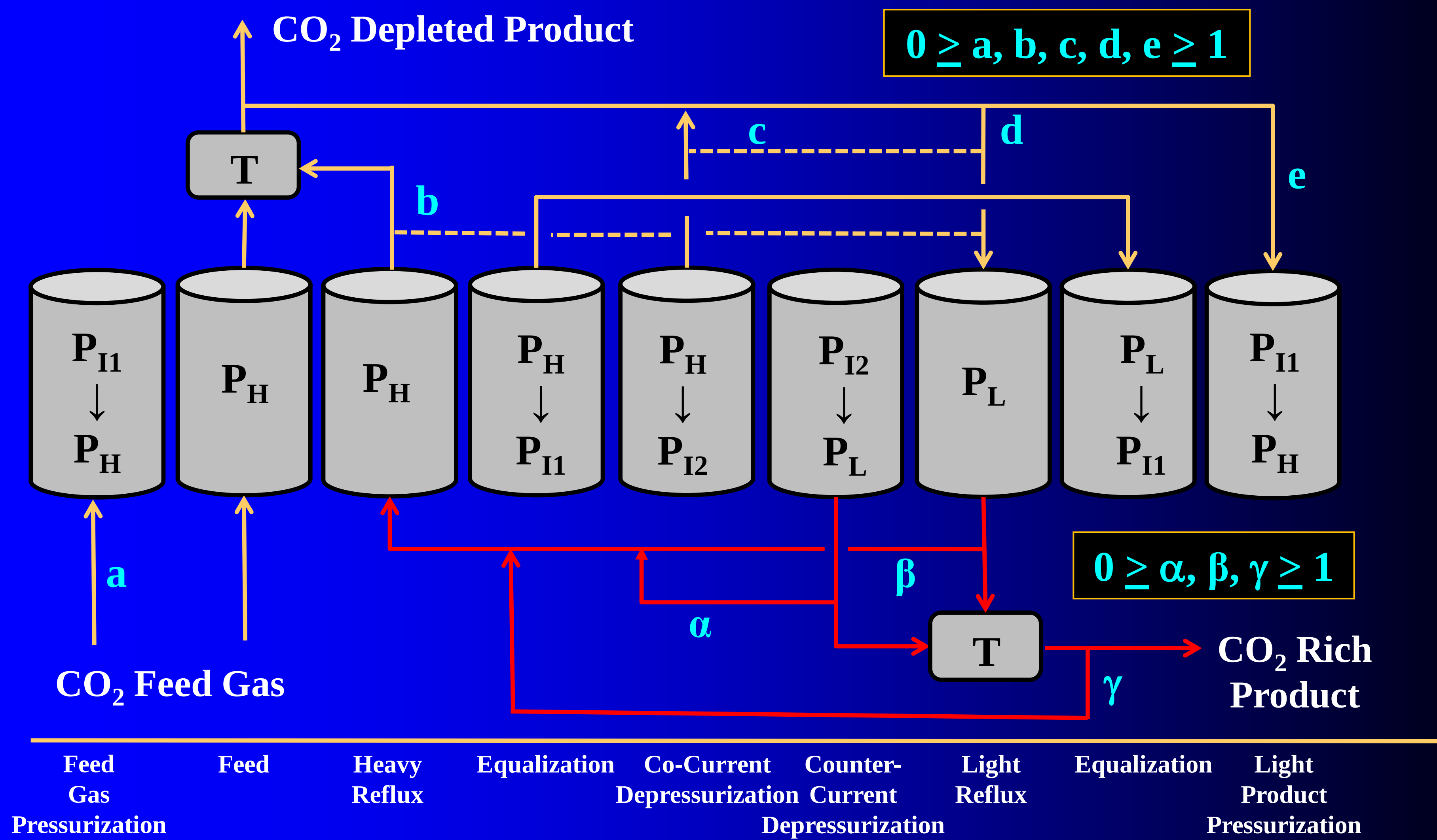
P **(Torr)**	***hA*** **(kJ/K/s)**	D_p/R_p^2 **(s^{-1})**	k_{LDF} **(s^{-1})**
744	**$1.7e^{-4}$**	**3.32**	**1.94**
185	**$1.7e^{-4}$**	**3.32**	**0.38**
102	**$1.7e^{-4}$**	**3.32**	**0.18**

1-Bed Rapid PSA System (22 ^oC)

$$k_{LDF} = 1.87 \ s^{-1}$$

Typical Cycle Steps for PSA Operation

Snapshot of Multi-Bed PSA System



PSA Process Conditions for DAPS*

Feed Composition (Dry)

y_{CO2} = 0.1592

y_{N2} = 0.8029

y_{O2} = 0.0379

Mass Transfer Coefficients

k_{CO2} = 10.0 s^{-1}

k_{N2} = 1.0 s^{-1}

k_{O2} = 1.0 s^{-1}

Process Conditions

P_H = 120 kPa

P_L = 5 kPa

T_F = 75 °C

h = 0.0 W/m^2 K (adiabatic)

t_c = 120 s

θ = 2,600 – 3,100 L(STP)/kg/hr

Structured Bed Properties

L_b = 0.125 m

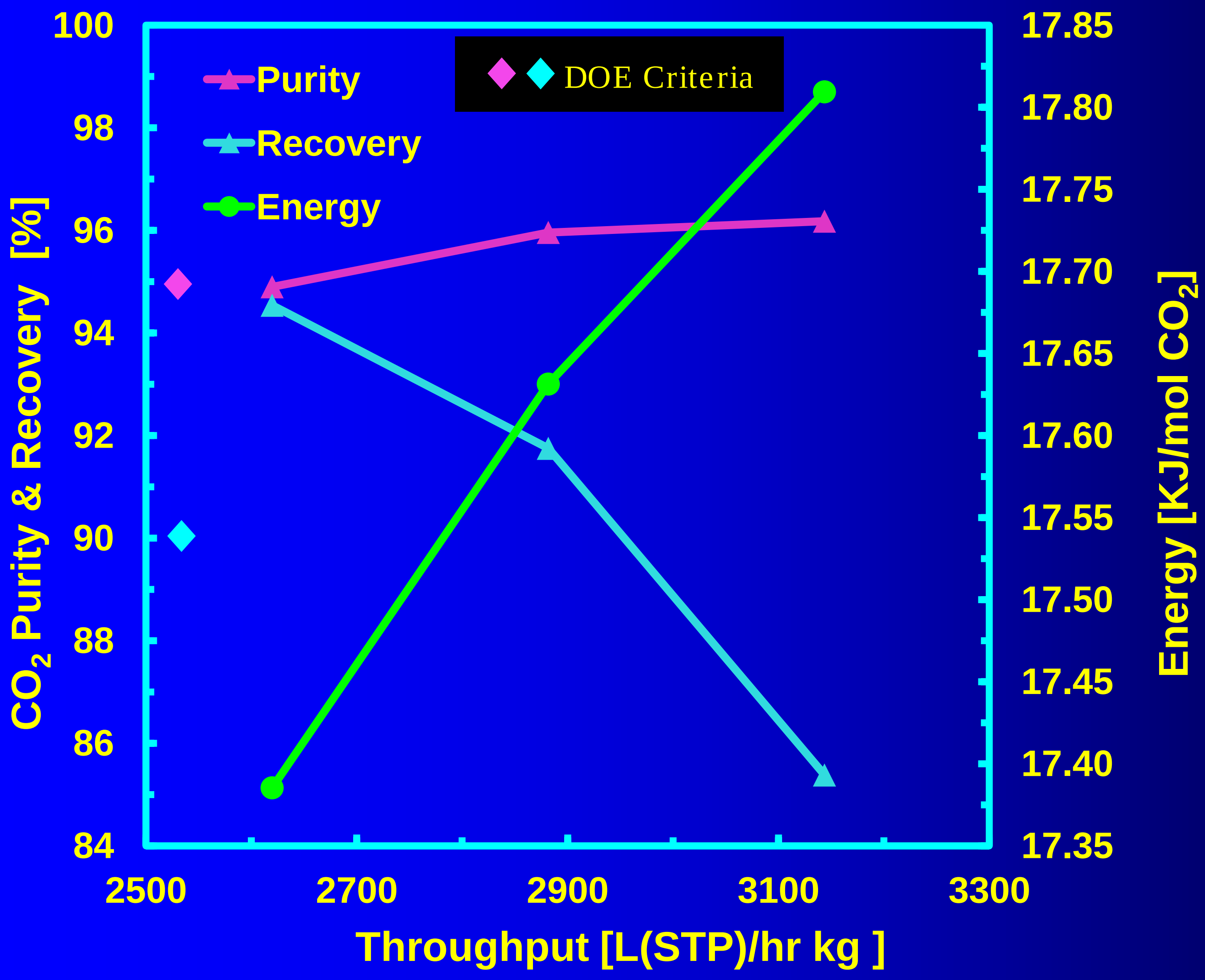
d_b = 0.09848 m

ρ_b = 400 kg/m^3

ε_b = 0.64

* DAPS: dynamic adsorption process simulator

DAPS Results of Bench Scale PSA Process



this is a low energy, high feed throughput PSA cycle for CO_2 capture that meets the DOE criteria, especially when considering the bed density is only 400 kg/m^3

Motivation to Compare Solid Amine to Zeolite

- sorbents for post-combustion CO_2 capture
  - zeolites
    - have sufficient working capacity for CO_2
    - not H_2O tolerant: *must be removed prior to PSA unit!*
  - solid amine sorbents
    - commercial amines grafted or immobilized within large pores of a high surface area support like silica gel
    - have sufficient working capacity for CO_2
    - H_2O tolerant: *will it pass through the PSA unit with N_2?*

solid amine sorbents have **NOT** been studied extensively for CO_2 capture from flue gas by PSA

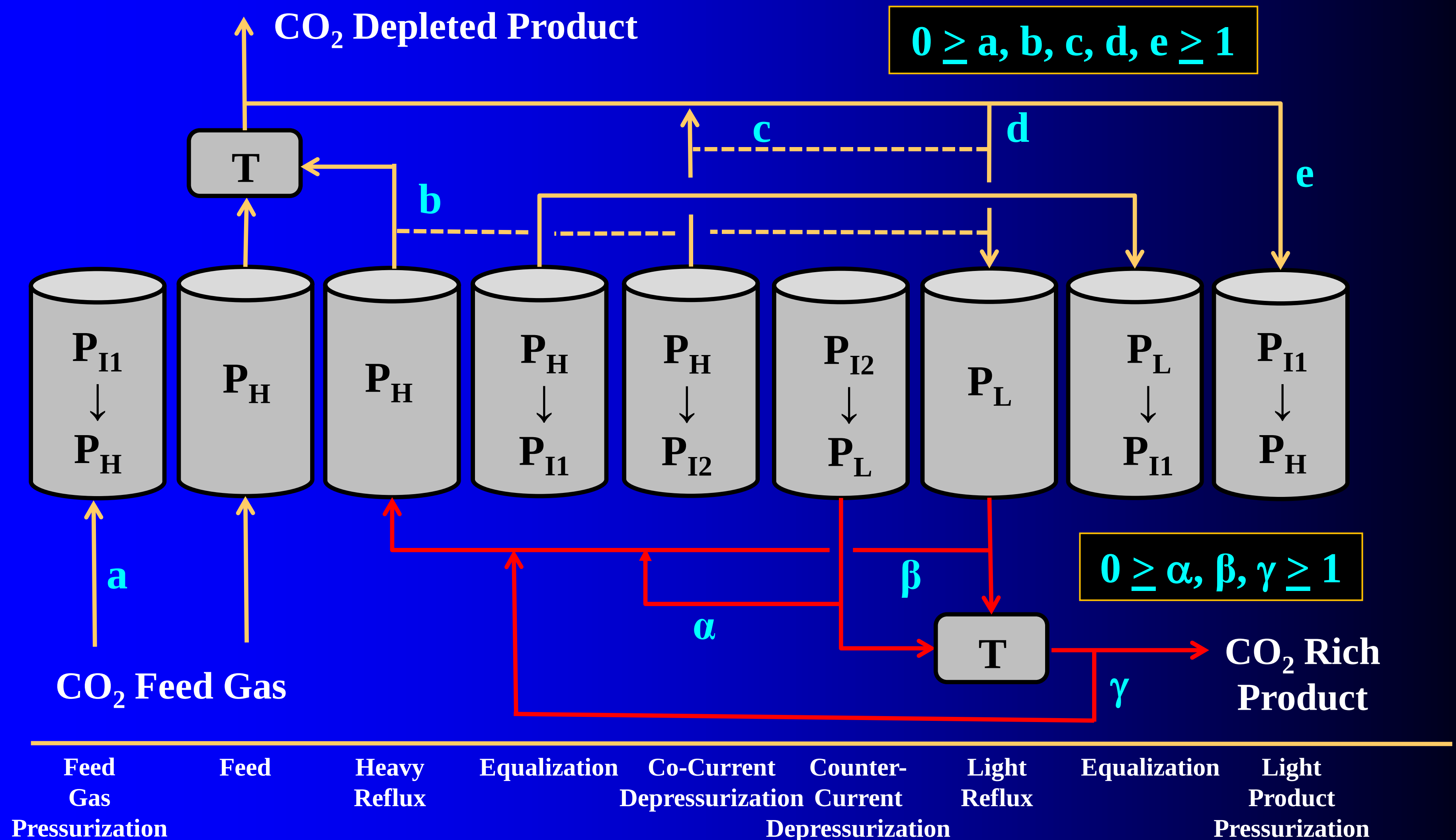
CARiACT G10 Solid Amine Sorbent*

- substrate: CARiACT G10 silicon dioxide (Fuji Silysia)
  - surface area: 300 m^2/g
  - pore volume: 1.3 ml/g
  - particle size: 75-150 µm
- polyethylenimine (PEI) (MN 423 Aldrich)
- 40 wt% PEI physically adsorbed (immobilized) onto G10

Gray et al., Energy Fuels, 23 (2009) 4840.

Typical Cycle Steps for PSA Operation

Snapshot of Multi-Bed PSA System



Comparison of PSA Process Performance

PEI vs Zeolite

	PEI	Zeolite
t_{cyc} (s)	300	120
Feed Throughput (L(STP)/kg/hr)	224	2870
CO_2 Recovery (%)	91.0	91.8
CO_2 Purity (%)	95.2	95.8
Energy (kJ/mol CO_2 Recovered)	34.2	17.6

for the same process performance and conditions (much different PSA cycle), zeolite beds are 10X smaller than PEI beds with PEI consuming 2X the energy => need amine with faster desorption kinetics

Conclusions

- metal foil coated with commercial zeolite and corresponding low pressure drop corrugated structure showing much promise for CO_2 capture from flue gas
- frequency response and 1-bed rapid cycling experiments both show very fast mass transfer rates of CO_2 in beaded zeolite
- very low energy, very high feed throughput PSA cycle configuration developed using validated DAPS
- novel hybrid adsorption process flow sheet resulted in < 35% COE increase
- shorter PSA cycle times showing potential to significantly reduce column size and thus plant footprint
- PEI solid amine sorbent showing potential in PSA process; it may allow H_2O to pass through bed with N_2; need better kinetics to make PSA process performance more like zeolites

Acknowledgements

Funding provided by

DOE/NETL and

SAGE is greatly appreciated!

Thank You!

?