

Bench-Scale Development and Testing of Rapid PSA for CO₂ Capture

James A. Ritter & The Team



U N I V E R S I T Y O F
SOUTH CAROLINA



catacel™

Driving Reaction Technology

Battelle

The Business of Innovation

GRACE

Davison

2014 NETL CO₂ Capture Technology Meeting

Pittsburgh, PA, July 29, 2014

Overall Project Objectives

- ❖ design, develop and demonstrate a bench-scale process for the efficient and cost effective separation of CO₂ 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 CO₂ 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
(Hofer &
Jachimowicz)

USC
(Ritter &
Ebner)

materials
characterization,
and process
modeling and
experimentation

specification

Catacel
(Cirjak)

technology
development and
process integration

Battelle
(Saunders &
Swickrath)

validation

Budget

| Project Team Member | Budget Period 1 | | Budget Period 2 | | Budget Period 3 | | Total |
|---------------------|-----------------|------------|-----------------|------------|-----------------|------------|---------|
| | Gov. Share | Cost Share | Gov. Share | Cost Share | Gov. Share | Cost Share | |
| | Grace | 139441 | 34860 | 75084 | 18772 | 145089 | |
| USC | 670000 | 167500 | 490000 | 122500 | 490000 | 122500 | 2062500 |
| Battelle | 239115 | 59978 | 191791 | 47930 | 159744 | 39998 | 738556 |
| Catacel | 125592 | 31398 | 172187 | 43047 | 100662 | 25166 | 498052 |
| TOTAL | 1174148 | 293736 | 929062 | 232249 | 895495 | 223936 | 3748626 |

Breakdown in % of Total Budget

USC 55.0%

Battelle 19.7%

Catacel 13.3%

Grace 12.0%

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

A photograph of an industrial facility, possibly a power plant or refinery, with several tall smokestacks emitting thick white plumes of smoke. In the foreground, a train with several empty freight cars is visible on tracks. The sky is blue with scattered white clouds. The text "Where are we going?" is overlaid in the center in a bright cyan, bold, serif font.

Where are we going?

Scale of PSA System for CO₂ Capture from 550 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 CO₂ capture, the extent of size reduction achievable is, at the moment, unknown

QuestAir H-6200 Rapid PSA-Installed at ExxonMobil Facility



H₂ Production Rapid PSA
~ 12,000 Nm³/h/module

H₂ Production
Conventional PSA
~ 20,000 Nm³/h



**A 550 MW plant
produces ~ 33,000
Nm³/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 Budget Period (BP) 1?**

Significant Outcomes from BP 1

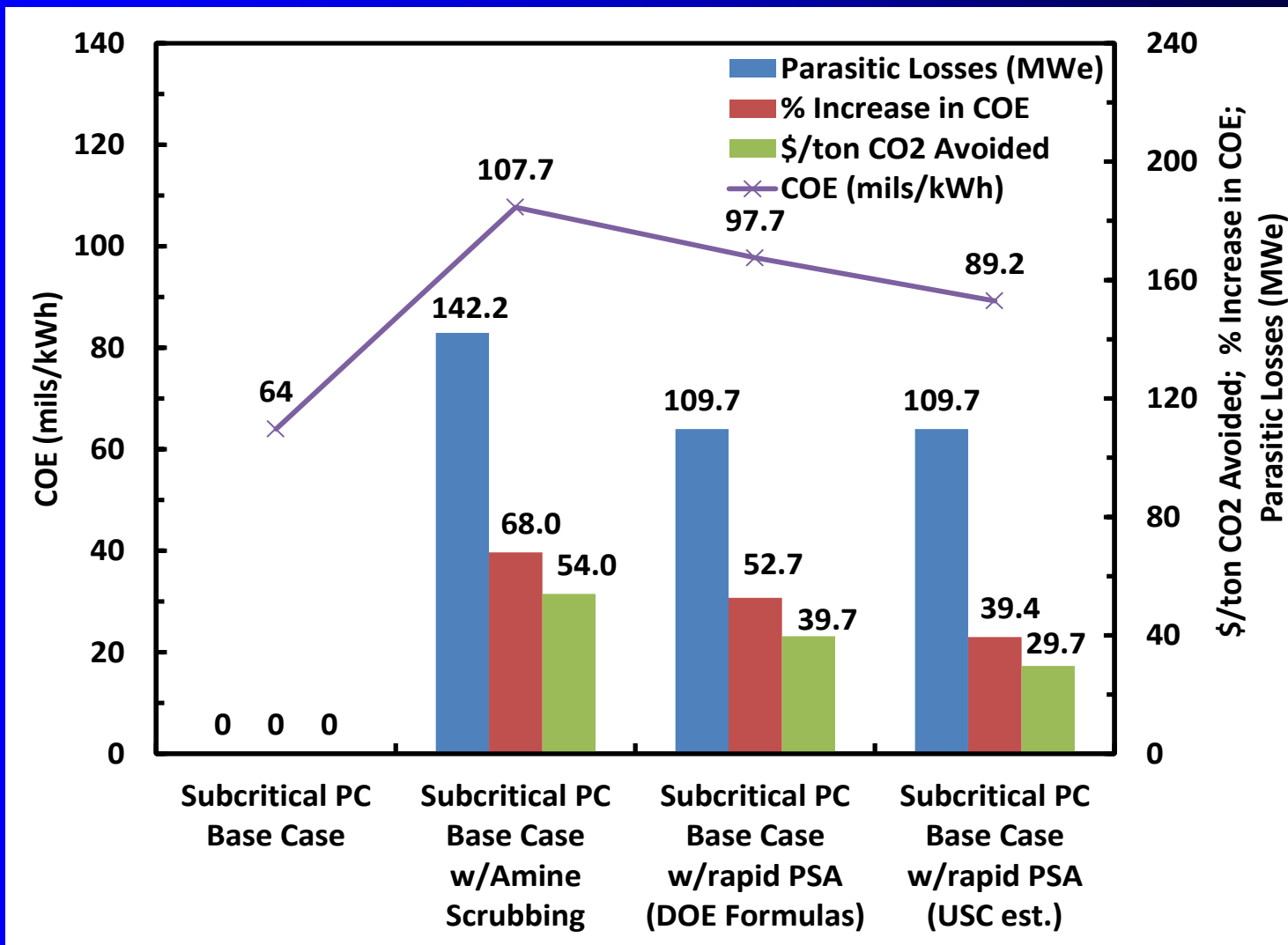
- developed PSA cycle and process flow sheet with less than 40% LCOE increase; *based on completed preliminary technical and economic feasibility study*
- demonstrated zeolite crystals can be coated onto basic metal structure with at least 50 μm thick coating; *suggests it may be possible to achieve even 100 to 150 μm coatings, if needed*
- demonstrated Catacel core structures can be made with up to 400 cells per square inch (cps); *makes goal of achieving 600 cps, possibly even 800 cps, within reach*
- demonstrated needed limit of < 20 kPa/m pressure drop through 400 cps core at very high velocities up to 25 m/s; *pressure drop limit utilized in preliminary technical and economic feasibility study*
- designed and sized concentration swing, rotary wheel driers via rigorous simulation to dry flue gas prior to PSA unit; *made economics viable*
- recently demonstrated via simulation, pressure drop limit not exceeded even for 100 μm zeolite coated Catacel core

Significant Outcomes from BP 1

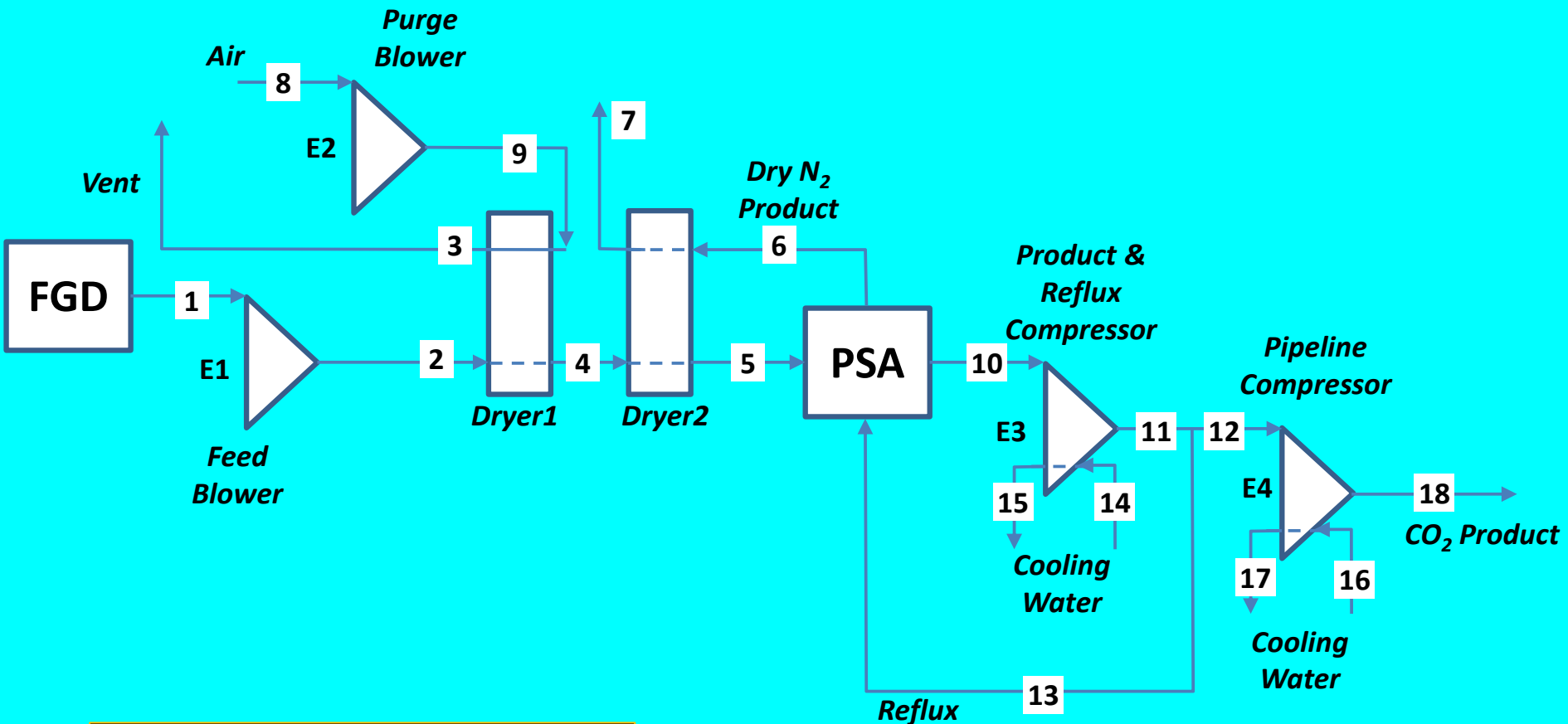
- predicted pressure drop through Catacel core nearly quantitatively using CFD model with no adjustable parameters; paves way to fabricate even more optimum core structures using computational tools
- demonstrated, via PSA process simulation, possibly lowest energy, highest feed throughput PSA cycle for CO₂ capture; amazing when considering bulk density reduced from 710 kg/m³ (typical for packed bed of zeolite beads) to 400 kg/m³ (entirely feasible with Catacel core)
- PSA cycle boasts feed throughput of around 3,000 L(STP)/hr/kg and separations energy < 18 kJ/mol CO₂ captured
- two, 1-bed PSA systems recently readied for pellet and core testing
- 2-D parallel channel open cell structure adsorption model recently revealed plug flow concentration behavior → corrugated structure not subject to premature breakthrough and can be simulated with packed bed model

Preliminary Technical and Economic Feasibility Study

Overall Outcome



USC Rapid PSA Process Flow Sheet*



* USC Provisional Patent Filed

Summary of Power Demands and LCOE for Major Components in the Flow Sheet

| | Generated | Blower 1 | Blower 2 | Dryer1 | Dryer2 | PSA | Vacuum | Comp. | Sequest. | Total | |
|------------------------------|-----------|-----------|------------|------------|------------|------------|------------|------------|------------|-------|-----------------------|
| Power | 550 | (14.5) | (2.2) | | | | (53.5) | (39.6) | | | 440 MW |
| Capital | | \$ (6.84) | \$ (10.71) | \$ (17.92) | \$ (14.58) | \$ (31.63) | \$ (9.26) | \$ (49.99) | | \$ | (140.93) MM |
| Levelized Costs: | | | | | | | | | | | |
| Depreciation | | \$ (1.20) | \$ (1.87) | \$ (3.14) | \$ (2.55) | \$ (5.54) | \$ (1.62) | \$ (8.75) | | \$ | (24.66) MM/yr |
| Maintenance | | \$ (0.14) | \$ (0.21) | \$ (0.36) | \$ (0.29) | \$ (0.63) | \$ (0.19) | \$ (1.00) | | \$ | (2.82) MM/yr |
| Power | | (6.89) | (1.02) | | | | (25.51) | \$ (18.85) | | \$ | (52.27) MM/yr |
| SubTotal | | (8.22) | (3.11) | (3.49) | (2.84) | (6.17) | (27.31) | (28.60) | - | | (79.75) MM/yr |
| Cooling Water | | | | | | | \$ (0.75) | \$ (0.75) | | \$ | (1.51) MM/yr |
| Adsorbent bed | | | | | | \$ (3.64) | | | | \$ | (3.64) MM/yr |
| Sequestration | | | | | | | | | \$ (14.72) | \$ | (14.72) MM/yr |
| Recyclables | | | | | | \$ 0.11 | | | | \$ | 0.11 MM/yr |
| Labor | | | | | | \$ (0.31) | | | | \$ | (0.31) MM/yr |
| TOTAL Levelized costs | | \$ (8.22) | \$ (3.11) | \$ (3.49) | \$ (2.84) | \$ (10.01) | \$ (28.06) | \$ (29.35) | \$ (14.72) | \$ | (99.82) MM/yr |
| Flow | | 3,478,189 | 3,478,189 | 3,478,189 | 3,478,189 | 3,478,189 | 3,478,189 | 3,478,189 | 3,478,189 | | 3,478,188.74 ton/yr |
| Subtotalcost | | \$2.36 | \$0.90 | \$1.00 | \$0.82 | \$1.77 | \$7.85 | \$8.22 | \$0.00 | \$ | 22.93 /ton-CO2 |
| Total Cost | | \$2.36 | \$0.90 | \$1.00 | \$0.82 | \$2.88 | \$8.07 | \$8.44 | \$4.23 | \$ | 28.70 /ton-CO2 |
| Total Cost | | \$ 0.002 | \$ 0.001 | \$ 0.001 | \$ 0.001 | \$ 0.002 | \$ 0.007 | \$ 0.007 | \$ 0.004 | \$ | 0.024 /kWh |
| Separation energy | | 5.40 | 0.80 | | | | 20.00 | 14.78 | | | kJ/mol CO2 |
| | | 3.1% | 1.2% | 1.3% | 1.1% | 3.8% | 10.7% | 11.2% | 5.6% | | 38.1% |

* USC Provisional Patent Filed

Number and Sizes of the Adsorbent Rotary Wheel Gas Dryers*

Gas Dryer 1

10 wheels

$L = 1.00 \text{ m}$

$D = 9.79 \text{ m}$

$\Theta = 10,076.0 \text{ L(STP)/hr/kg}$

$t_c = 40 \text{ s}$

$t_F = 20 \text{ s}$

$t_P = 20 \text{ s}$

$\rho_b = 300 \text{ kg/m}^3$

Gas Dryer 2

10 wheels

$L = 1.00 \text{ m}$

$D = 8.83 \text{ m}$

$\Theta = 10,451.9 \text{ L(STP)/hr/kg}$

$t_c = 40 \text{ s}$

$t_F = 20 \text{ s}$

$t_P = 20 \text{ s}$

$\rho_b = 300 \text{ kg/m}^3$

PSA Process Conditions for DAPS*

Feed Composition (Dry)

$$y_{\text{CO}_2} = 0.1592$$

$$y_{\text{N}_2} = 0.8029$$

$$y_{\text{O}_2} = 0.0379$$

Mass Transfer Coefficients

$$k_{\text{CO}_2} = 10.0 \text{ s}^{-1}$$

$$k_{\text{N}_2} = 1.0 \text{ s}^{-1}$$

$$k_{\text{O}_2} = 1.0 \text{ s}^{-1}$$

Process Conditions

$$P_{\text{H}} = 120 \text{ kPa}$$

$$P_{\text{L}} = 5 \text{ kPa}$$

$$T_{\text{F}} = 75^\circ\text{C}$$

$$h = 0.0 \text{ W/m}^2 \text{ K (adiabatic)}$$

$$t_{\text{c}} = 120 \text{ s}$$

$$\theta = 2,600 - 3,100 \text{ L(STP)/kg/hr}$$

Structured Bed Properties

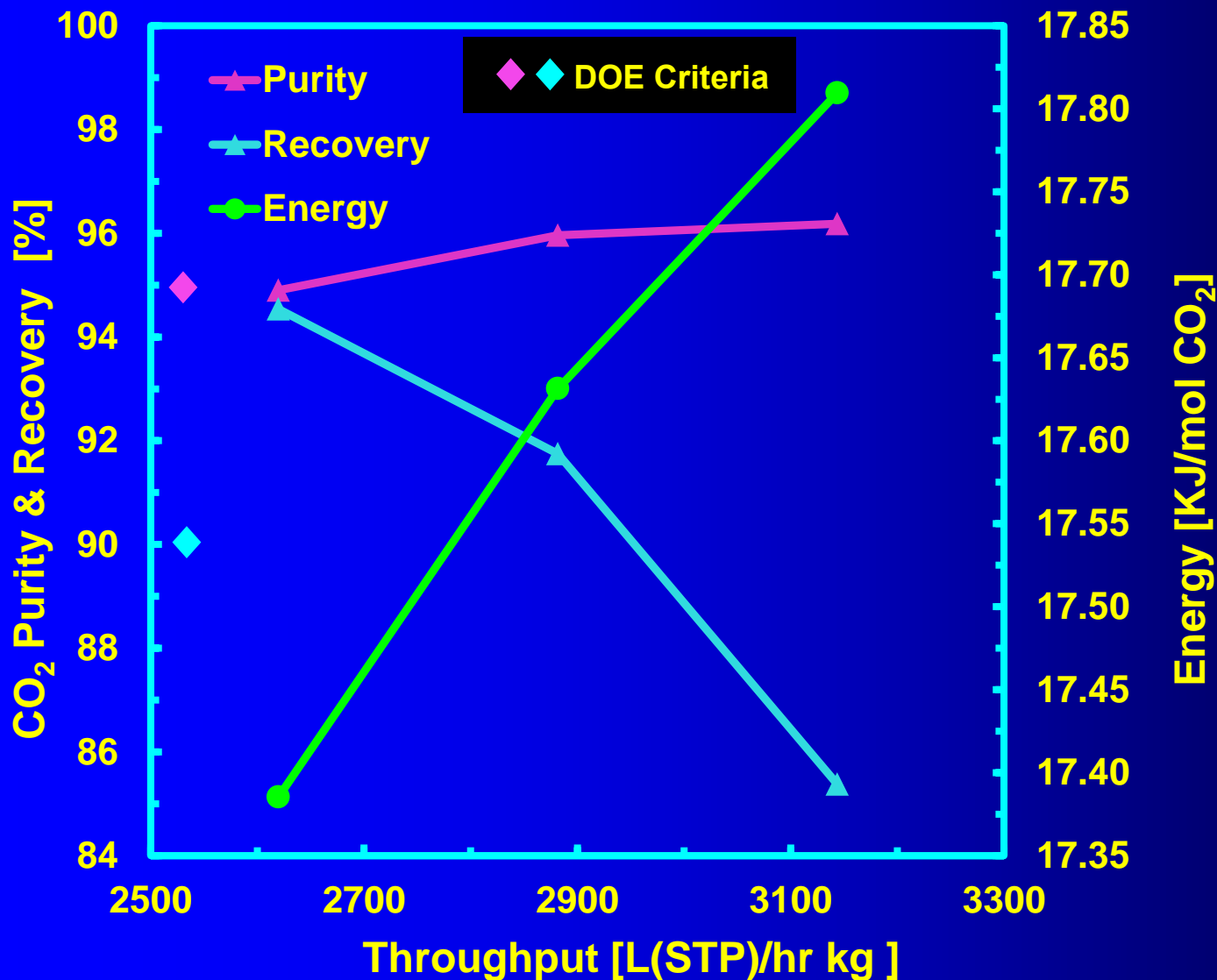
$$L_{\text{b}} = 0.125 \text{ m}$$

$$d_{\text{b}} = 0.09848 \text{ m}$$

$$\rho_{\text{b}} = 400 \text{ kg/m}^3$$

$$\varepsilon_{\text{b}} = 0.64$$

DAPS Results of Bench Scale PSA Process



this is a low energy, high feed throughput PSA cycle for CO₂ capture that meets the DOE criteria, especially when considering the bed density is only 400 kg/m³

Number PSA Units and Bed Size*

PSA Units

3 beds/train

20 trains = 60 beds

$L = 2.68 \text{ m}$

$D = 3.15 \text{ m}$

$\Theta = 3,000 \text{ L(STP)/hr/kg}$

$\rho_b = 400 \text{ kg/m}^3$

* USC Provisional
Patent Filed

This PSA design is achieving a working capacity of $\sim 0.028 \text{ lb CO}_2/\text{lb sorbent}$.



**What are we going to do during
Budget Period (BP) 2?**

Key Tasks Planned for BP 2

- study adsorbent (zeolite crystals and silica gel) stability in the presence of trace levels of NO_x and SO_x
- coat Catacel cores with 50 to 100 μm thick layers of zeolite crystals
- optimize Catacel core structure via CFD modeling
- measure pressure drop through zeolite coated Catacel cores
- test breakthrough and cycling behavior of zeolite pellets and coated Catacel cores in 1-bed bench scale PSA apparatuses
- complete construction of multi-bed bench scale PSA apparatus
- characterize thermodynamic and mass transfer properties of zeolite coatings
- refine PSA cycle schedule via modeling with new thermodynamic and mass transfer information

Acknowledgements

Funding provided by

DOE/NETL and

SAGE is greatly appreciated!

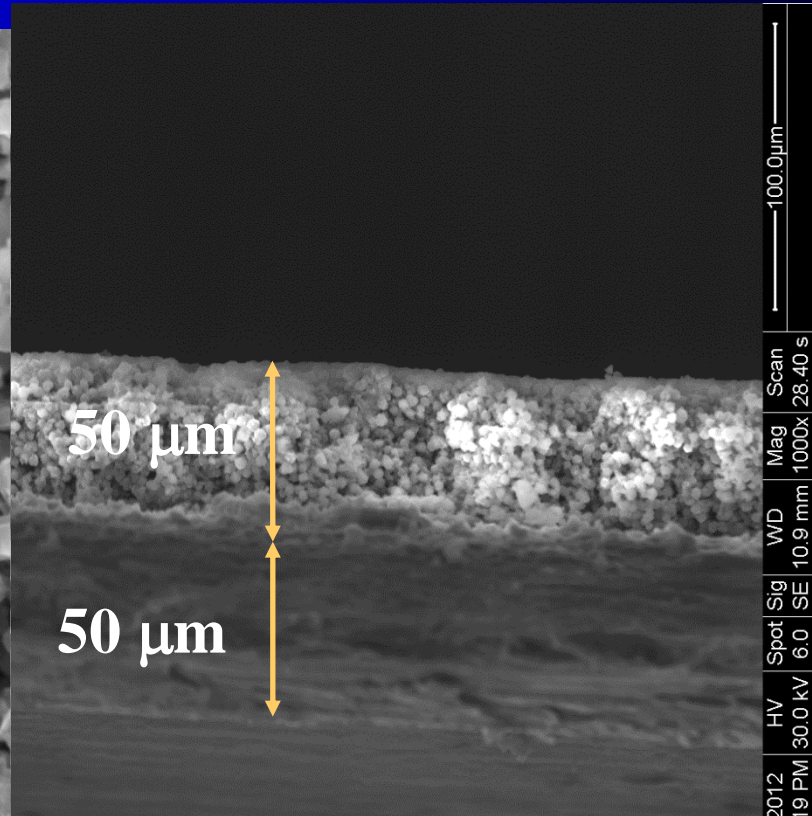
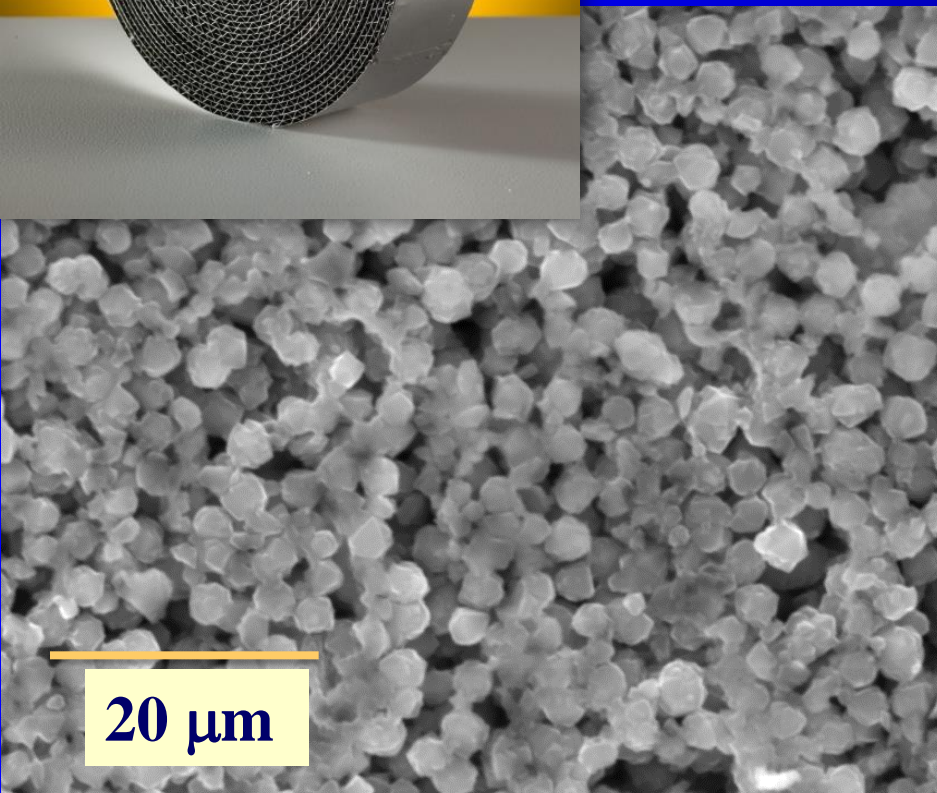


Thank You!



Zeolite Coated Metal Foil

- preliminary fabrication
- coated on flat foil coupon at 30 mg/in²
- coating passed Catacel adhesion test
- goal: to make coating 100 – 150 μm thick



| | | | | | | |
|------------|---------|------|-----|---------|-------|---------|
| 7/2/2012 | HV | Spot | Sig | WD | Mag | Scan |
| 1:28:17 PM | 30.0 kV | 6.0 | SE | 10.7 mm | 4000x | 28.40 s |

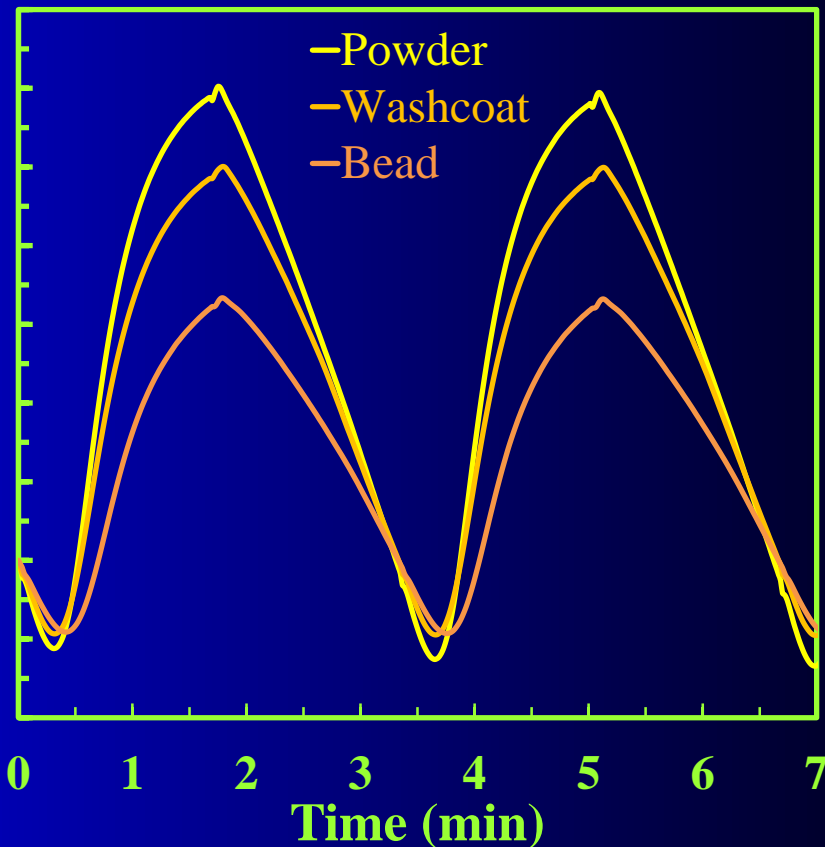
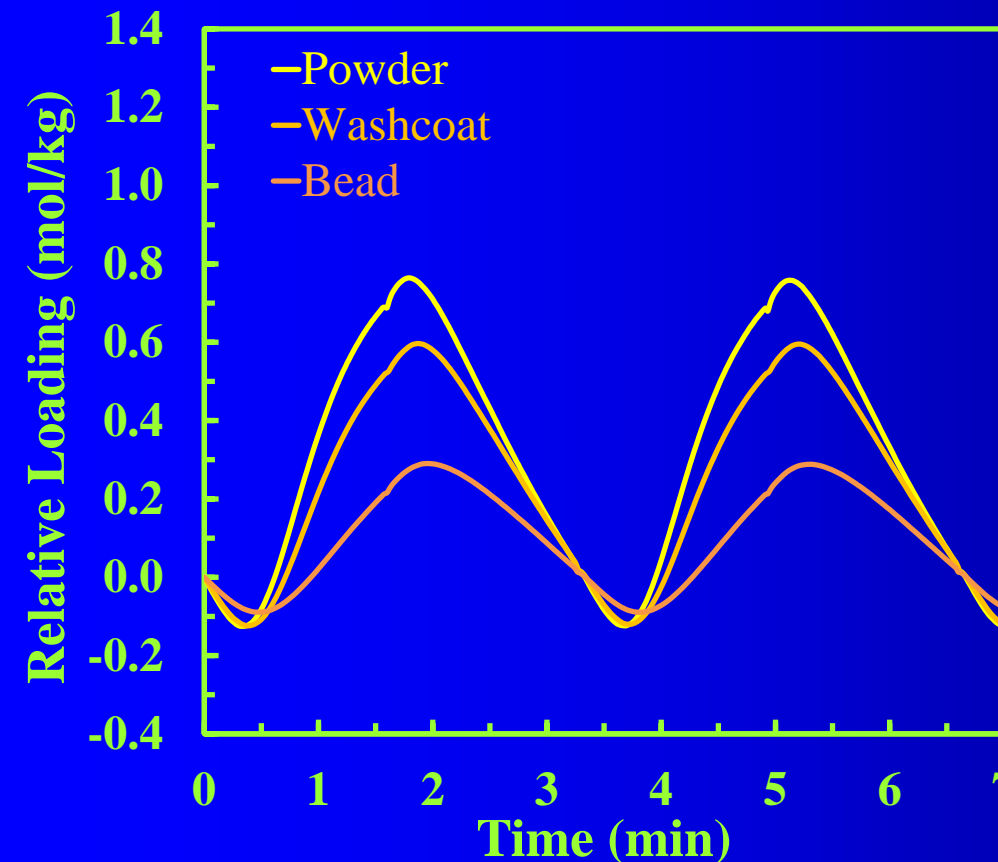
| | | | | | | |
|------------|---------|------|-----|---------|-------|---------|
| 7/2/2012 | HV | Spot | Sig | WD | Mag | Scan |
| 1:52:19 PM | 30.0 kV | 6.0 | SE | 10.9 mm | 1000x | 28.40 s |

TGA Runs at 70 °C

Cycle: 100 s Stream with CO₂ / 100 s Pure N₂

15% CO₂ in N₂ / 100 % N₂

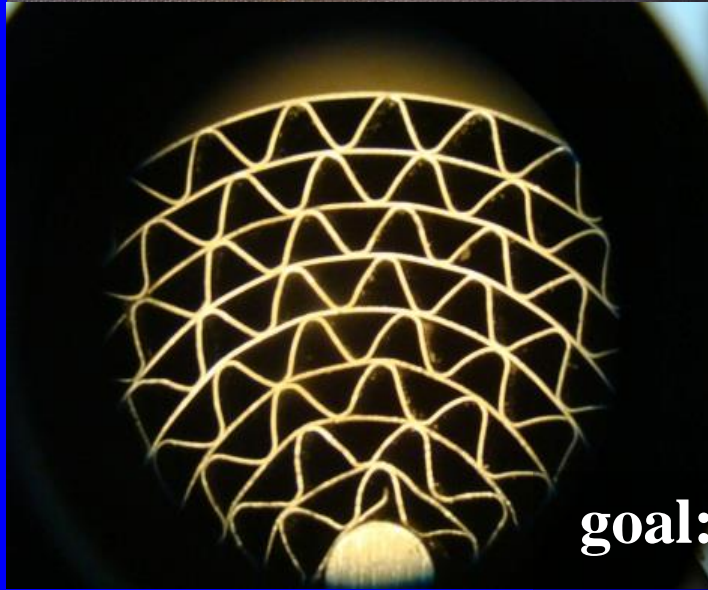
100% CO₂ / 100 % N₂



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

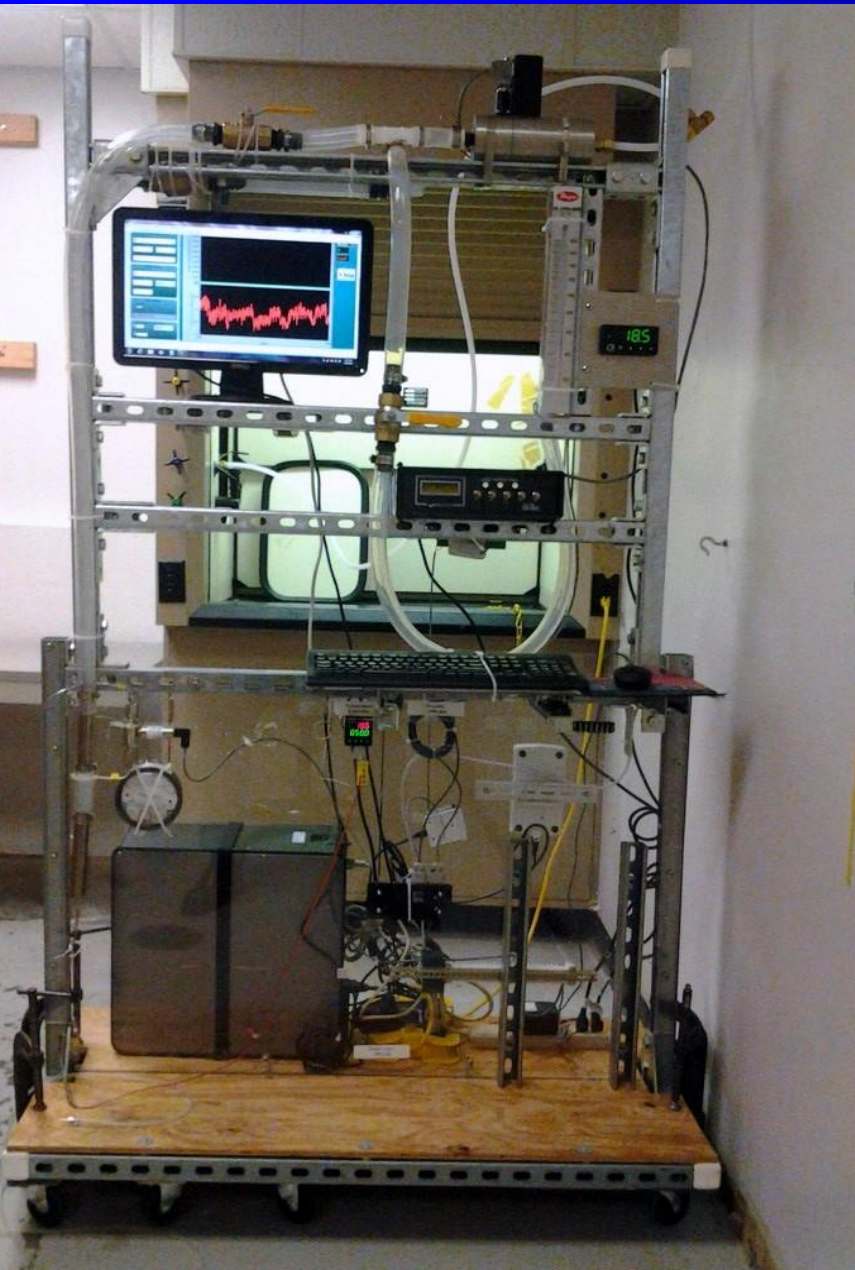
Corrugated Catacel Cores

1" x 6" x 400 cells/in²



goal: to increase corrugation to 800 cpsi

Structured and Beaded Media Pressure Drop



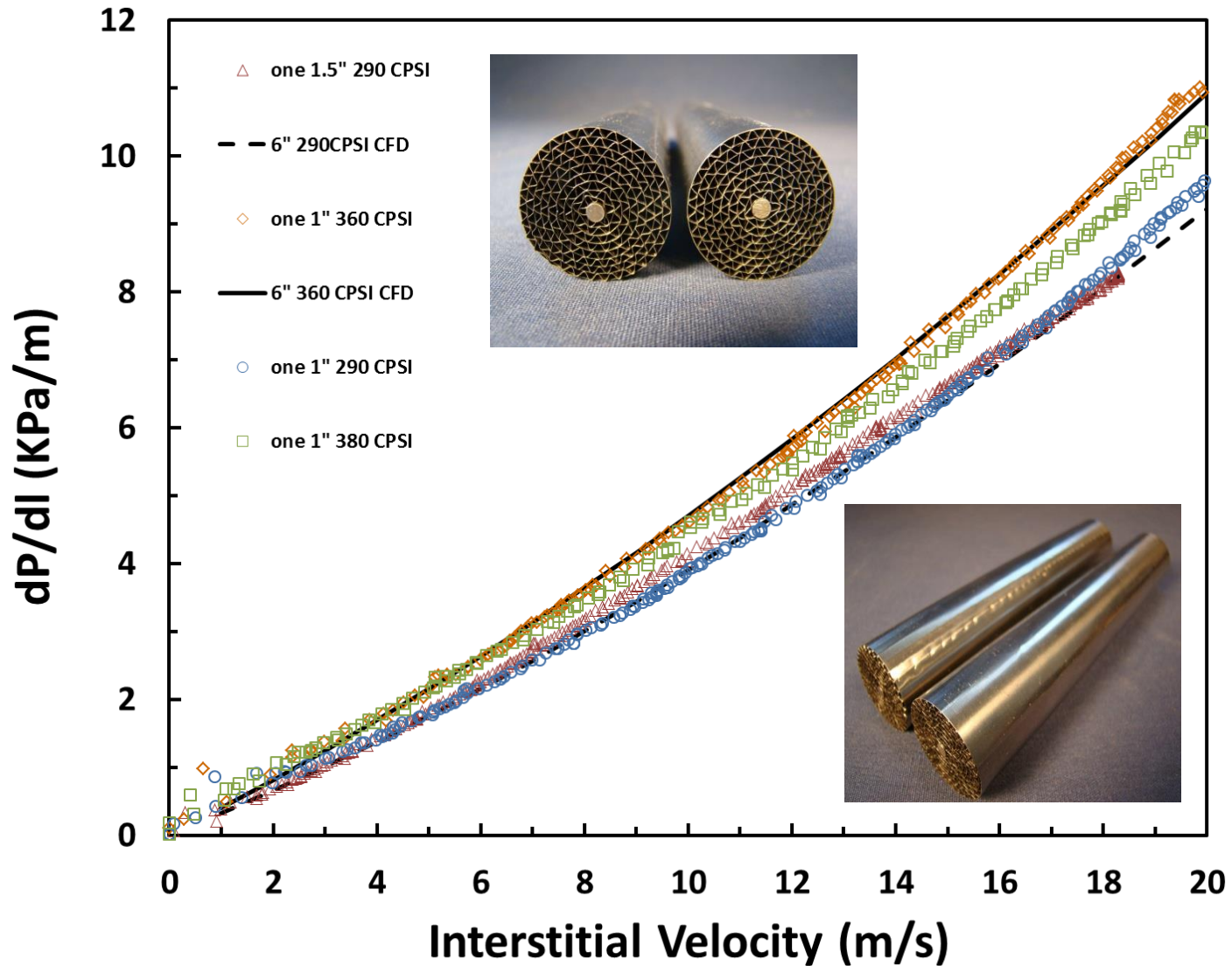
Pressure Drop Apparatus

$$Q_{\max} = 1000 \text{ SLPM}$$

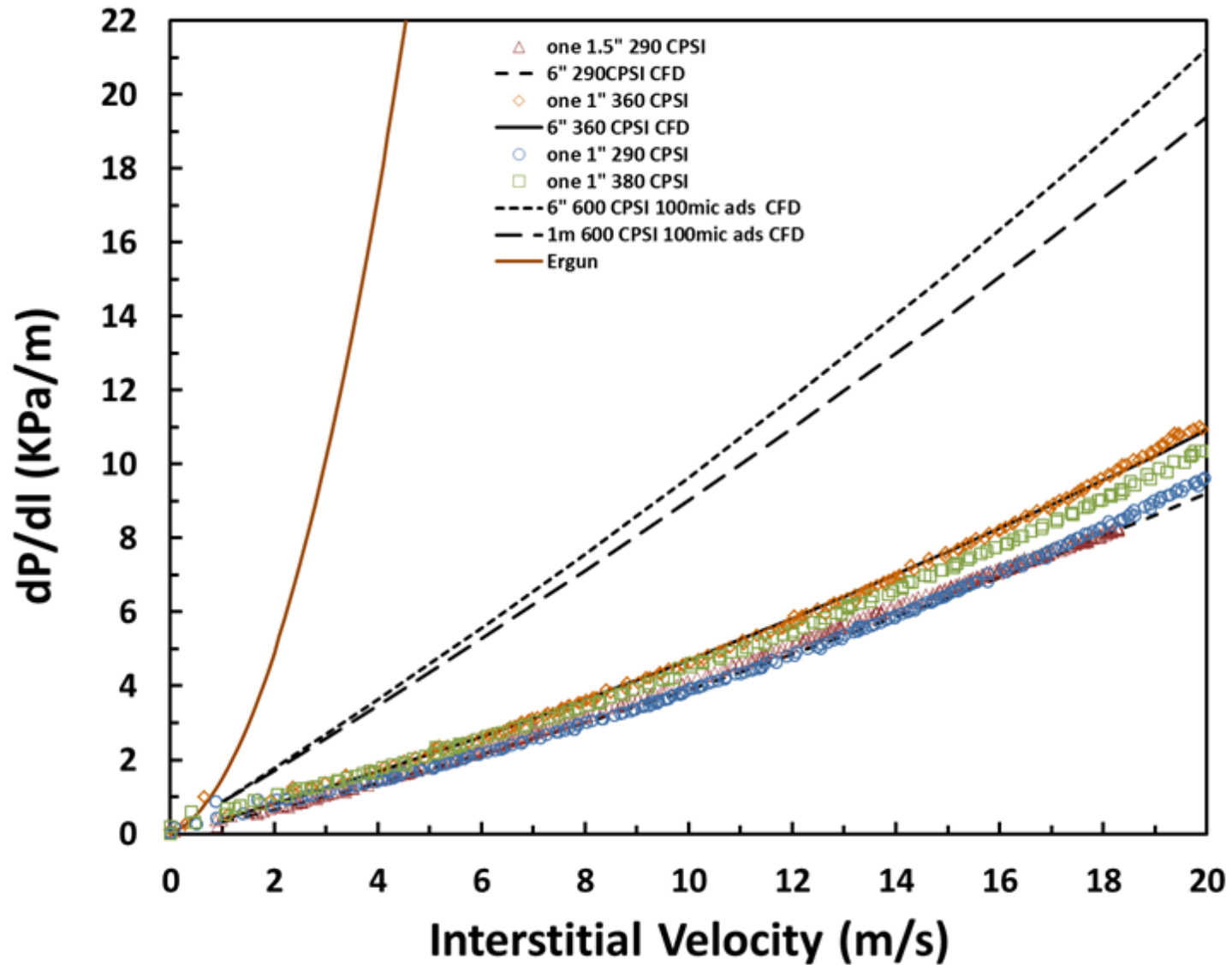
$$\Delta P_{\max} = 30, 70 \text{ or } 140 \text{ in H}_2\text{O}$$

goal: $\Delta P_{\max} < 20 \text{ kPa/m}$ at
design velocity of 20 m/s

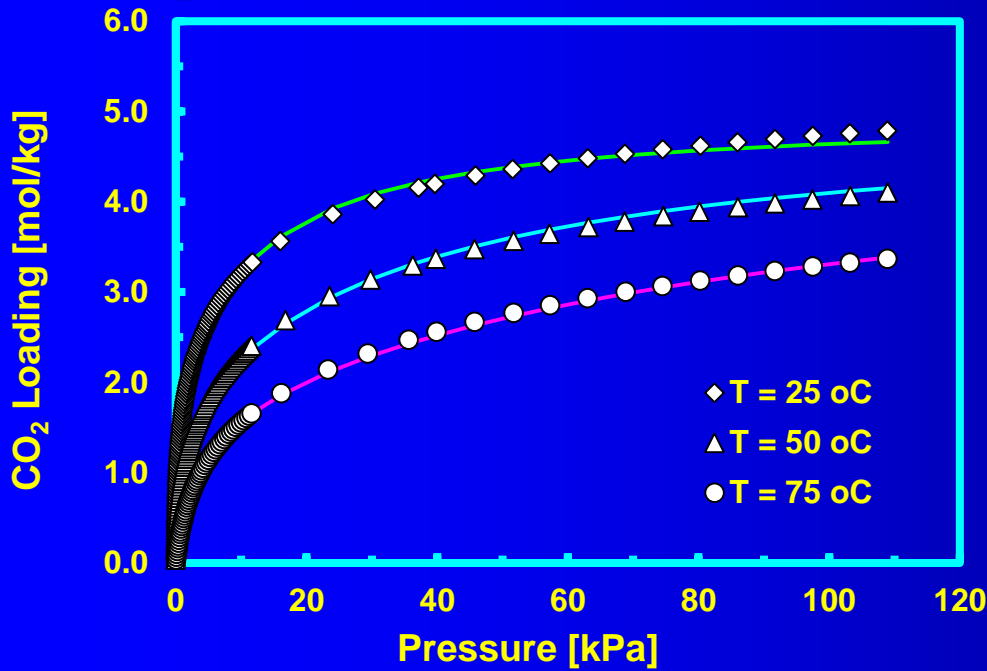
Structured and Beaded Media Pressure Drop



Structured and Beaded Media Pressure Drop



CO₂ Isotherm on Adsorbent and Dual Process Langmuir Fit

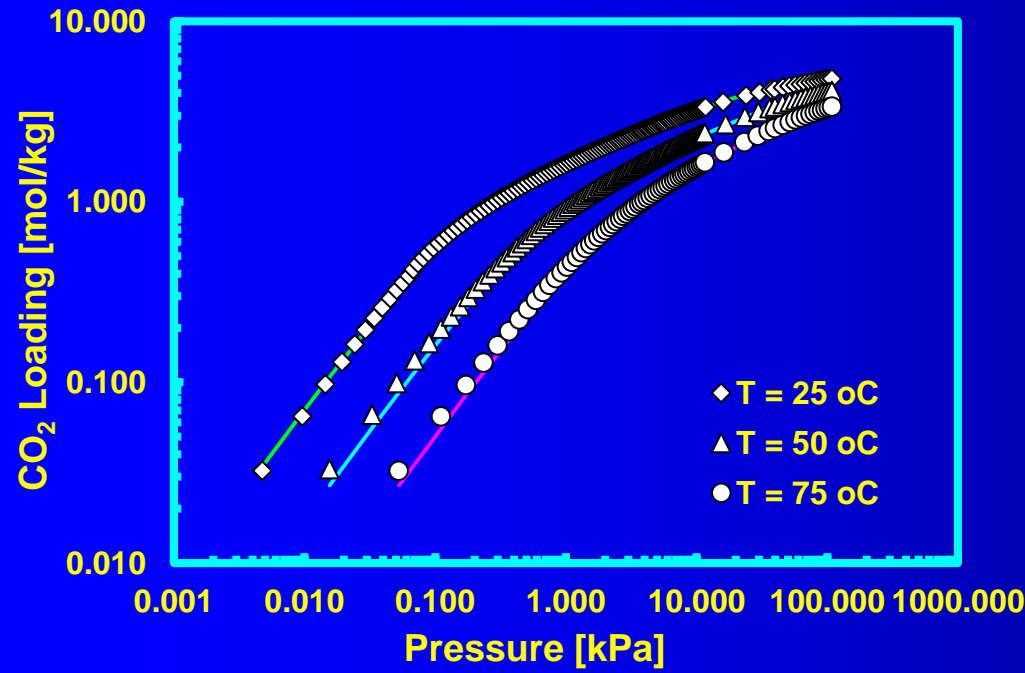


Dual Process Langmuir (DPL) Isotherm

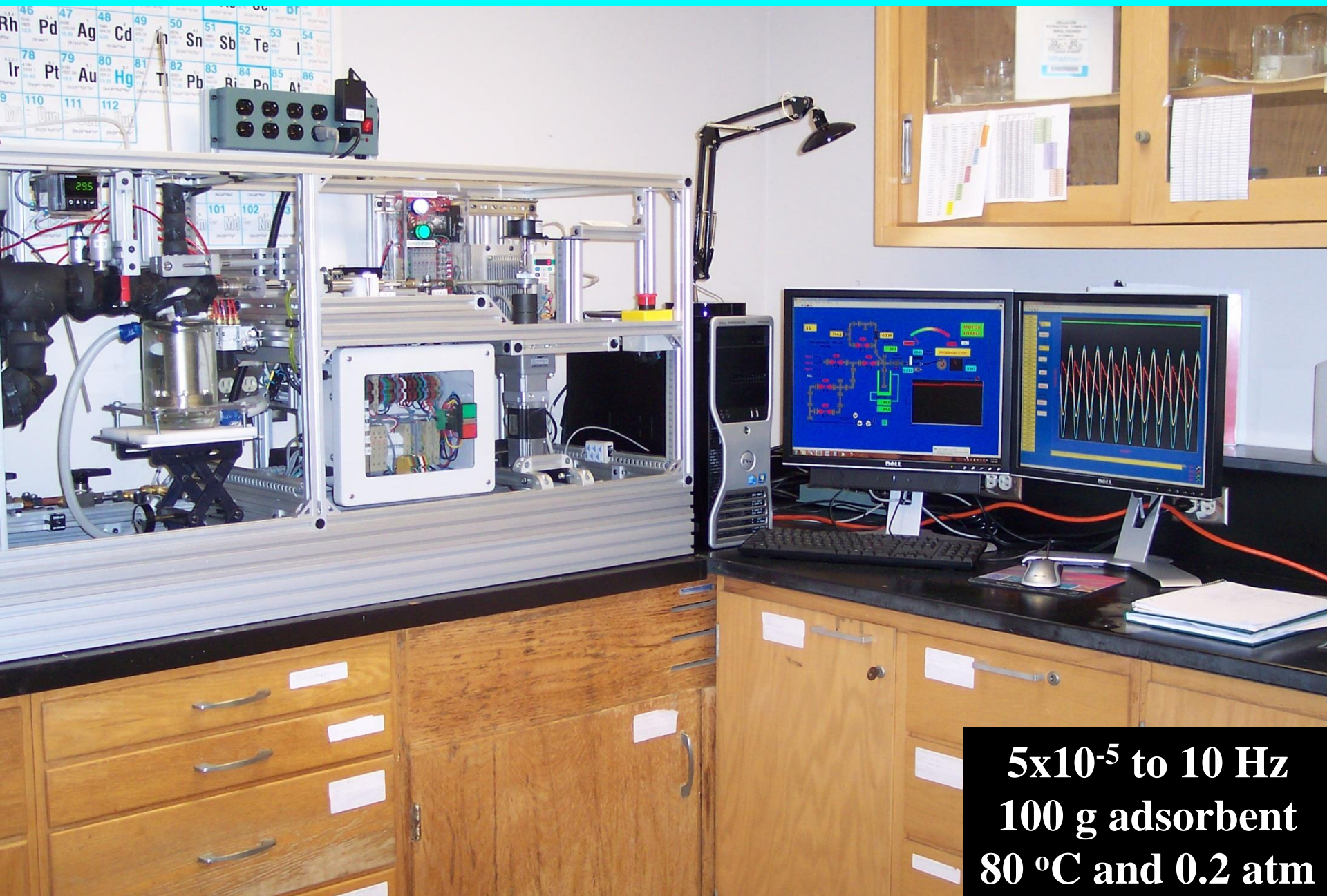
$$n_i = \left(\frac{n_{1,i}^s P y_i b_{1,i}}{1 + P y_i b_{1,i}} \right)_{site-1} + \left(\frac{n_{2,i}^s P y_i b_{2,i}}{1 + P y_i b_{2,i}} \right)_{site-2}$$

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

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



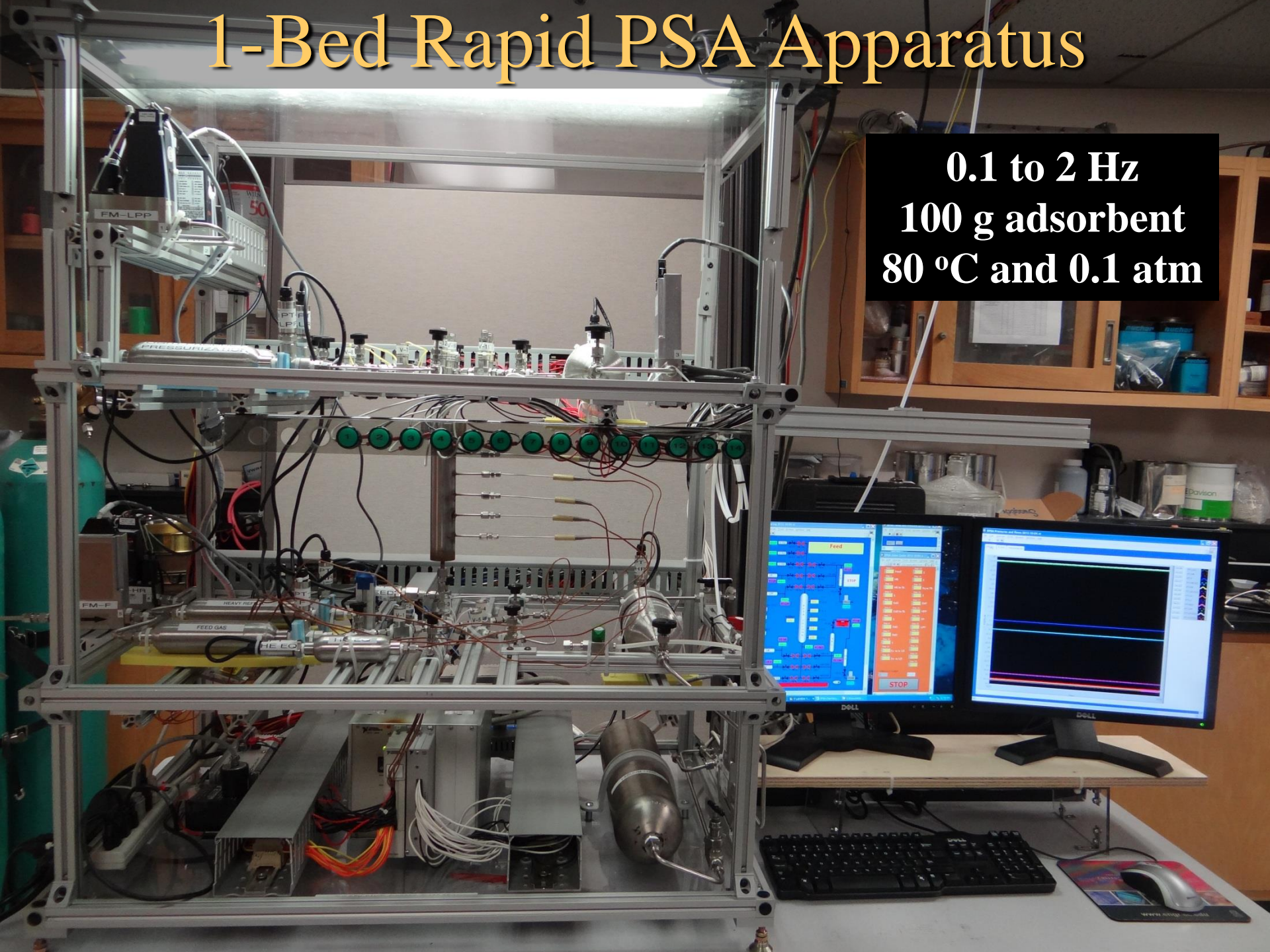
Volumetric Frequency Response Apparatus



5×10^{-5} to 10 Hz
100 g adsorbent
80 °C and 0.2 atm

1-Bed Rapid PSA Apparatus

0.1 to 2 Hz
100 g adsorbent
80 °C and 0.1 atm



1-Bed PSA System

Rapid Complex PSA Cycle Schedule Analysis

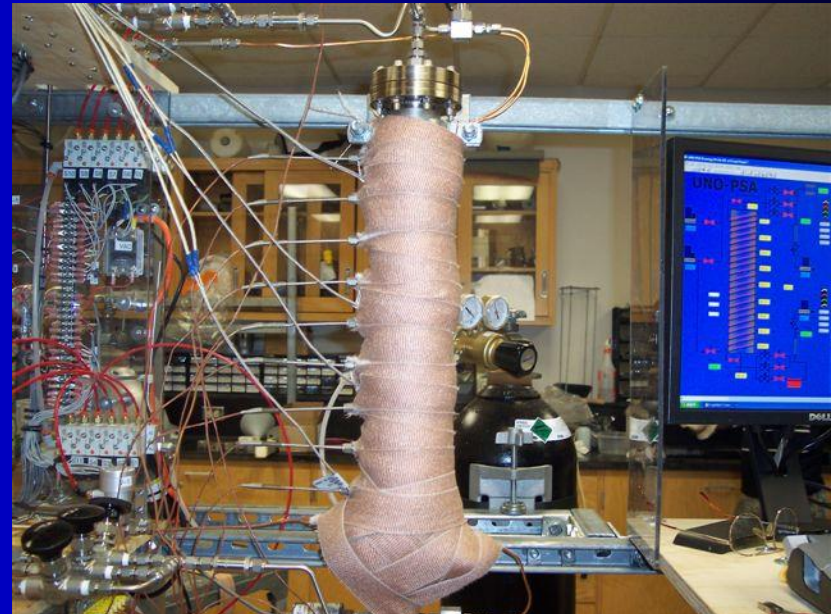


PSA Process Simulator Validation with 1-Bed PSA Experiment

| | CO ₂ Feed Concentration in N ₂ (%) | Feed Throughput (L STP/hr/kg) | T (°C) | Cycle Time (sec) | CO ₂ Purity (%) | CO ₂ Recovery (%) | N ₂ Purity (%) | N ₂ Recovery (%) |
|------------|--|-------------------------------|--------|------------------|----------------------------|------------------------------|---------------------------|-----------------------------|
| Experiment | 15 | 150 | 25.2 | 900 | 94.1 | 90.9 | 93.7 | 96.0 |
| Model | 15 | 150 | 25.4 | 900 | 93.2 | 91.5 | 93.5 | 97.1 |



VS



5-Bed CO₂ Capture PSA System

Under Construction

Suitable for Power Plant Demonstration



4-Bed PSA System



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