NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL In-house Postcombustion Sorbent-Based Carbon Dioxide Capture Research

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Annual IEP Contractors Meeting

March 24, 2009

CO_2 Capture Sorbent Research

Timeline

Effort Start Date: FY2005
Effort End Date: FY2010

External Partners

MATRIC
TVA
Fuji Silysia
Georgia Tech
University of Hartford
Sud Chemie

Thermogravimetric unit

Overall Postcombustion Sorbent Research Approach

- **Immobilized Amine Sorbent Development**
  - McMahan Gray

Reactor Design Effort
- James Hoffman

- **Encapsulated Sorbent Development**
  - Ranjani Siriwardane

- **Novel Sorbent Concepts**
  - Carnegie Mellon University
  - West Virginia University
  - NETL / Parsons

Overall Research Objectives

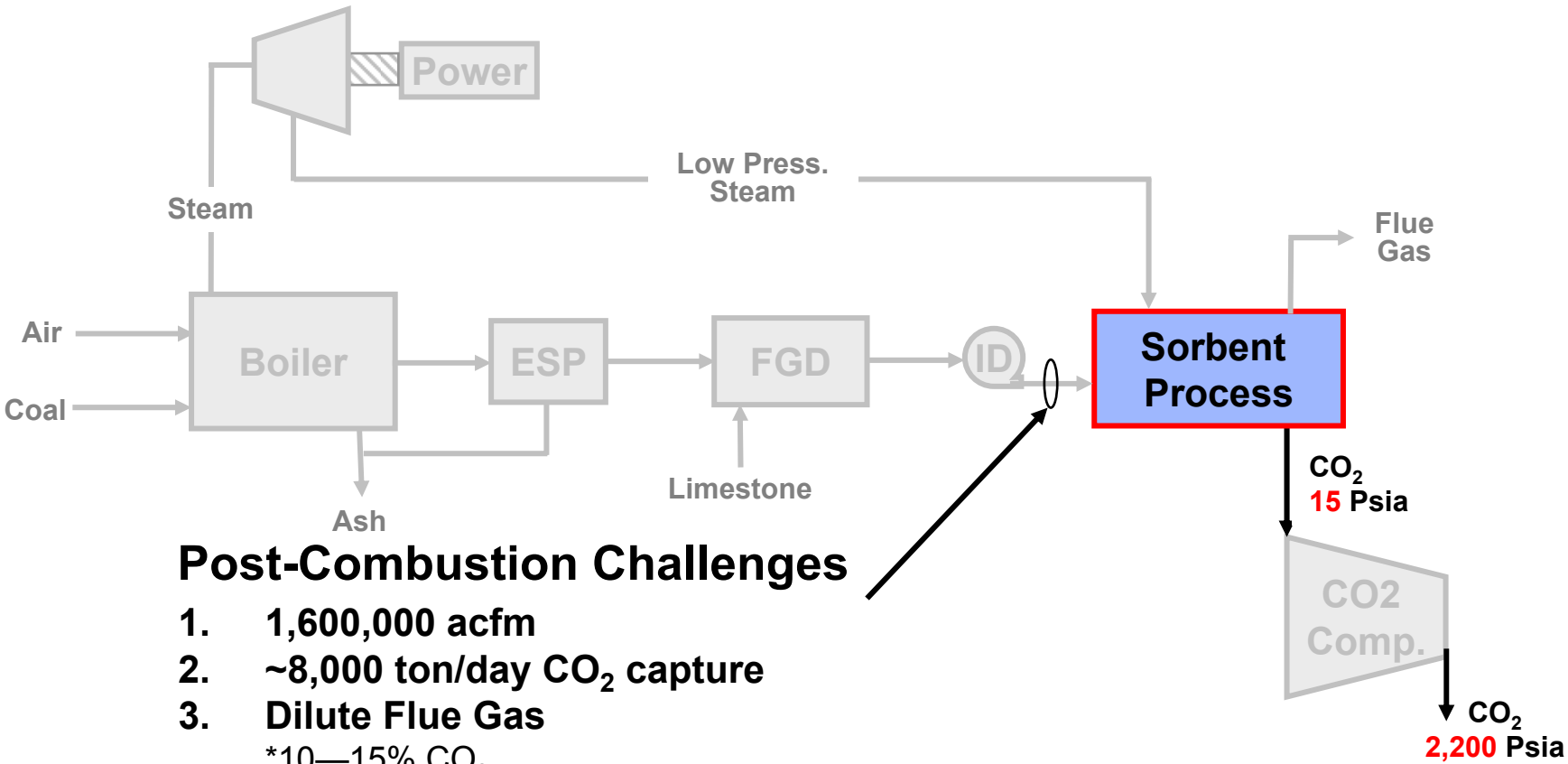
- To develop solid, durable, regenerable sorbents that have a high selectivity and high adsorption capacity for CO_2 at conditions suitable for post-combustion capture.

- To ensure that engineering and reactor design issues are addressed in the sorbent development.

- To ultimately meet the programmatic goal for energy conversion systems that can remove 90% CO_2 while keeping the increase in cost of energy service below 35%.

Postcombustion CO_2 Capture With Sorbent

Where does it fit?



Post-Combustion Challenges

1. **1,600,000 acfm**
2. **~8,000 ton/day CO_2 capture**
3. **Dilute Flue Gas**
   *10—15% CO_2
4. **Low Pressure —17 psia**
   *Decreased separation driving force
5. **High moisture content**
6. **Thermal need for regeneration**

Discussion Today

- **Background**
  - **Preliminary Systems Analysis For Amine-Based Solid Sorbents**
  - **MATRIC Corporation Study**
- **Sorbent Development**
  - **Immobilized Amine Sorbent**
  - **Encapsulated Sorbent**
- **Reactor Design**
- **Future**

BACKGROUND: Preliminary Systems Analysis Amine Enriched Sorbent Advantages*

Higher CO_2 carrying capacity per weight or volume of sorbent

Uses less energy for regeneration

- ↓ Heat Capacity (Do not need to heat water)
- Use less stripping steam to regenerate CO_2

Amine Enriched Sorbents

Heat Capacity (Btu/lb-°F)	0.3
ΔT Regeneration	80°F

Regeneration Energy (Btu/lb CO_2)		
Sensible		183
Reaction	+	600*
Vaporization	+	0
Total	=	783

VS.

30% MEA

Heat Capacity (Btu/lb-°F)	0.9
ΔT Regeneration	105°F

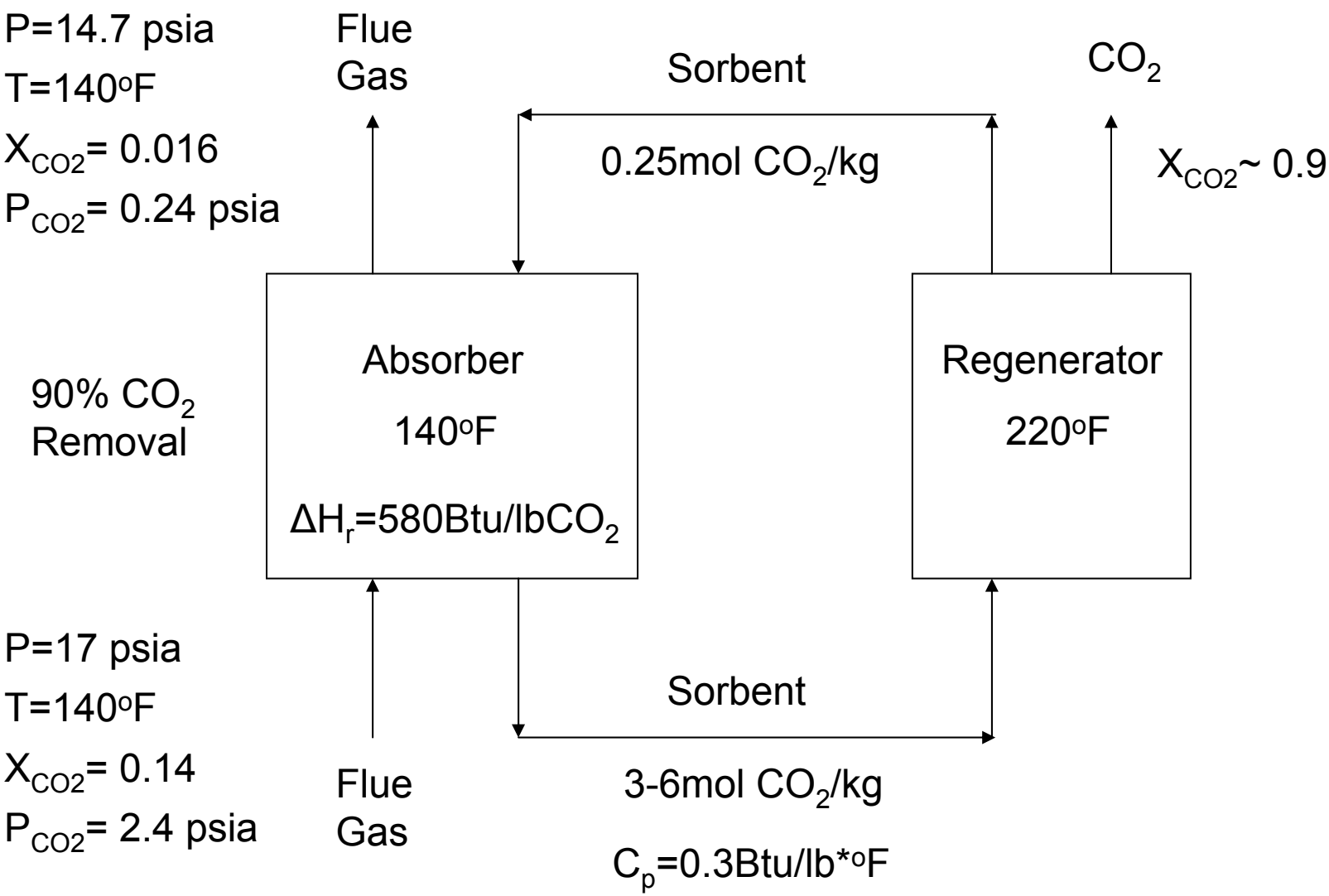
Regeneration Energy (Btu/lb CO_2)		
Sensible		941
Reaction	+	703
Vaporization	+	290
Total	=	1,934

Reference:
* Tarka, T. and J. Ciferno, Amine-Enriched Solid Sorbent for CO2 Capture: Systems Analysis and Design, Internal NETL Presentation, September 2005.

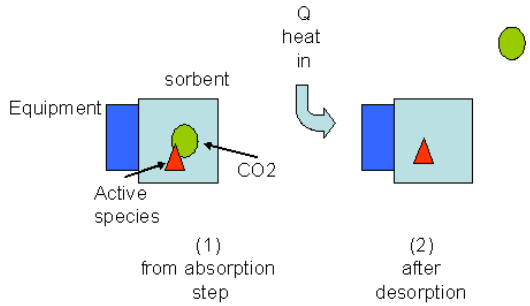
BACKGROUND: MATRIC Study

- MATRIC organization was tasked to perform spreadsheet calculations for a hypothetical sorbent (similar to the ones currently investigated) in various candidate reactor schemes.
- Experimental data requirements with identifiable gaps were determined to carryout a conceptual process design.
- Reactor heat management deemed important; moisture may have an impact.
- Performance goals paralleled program goals.
- Sensitivity analysis was done with respect to certain sorbent parameters.
- Target success criteria established for sorbents.

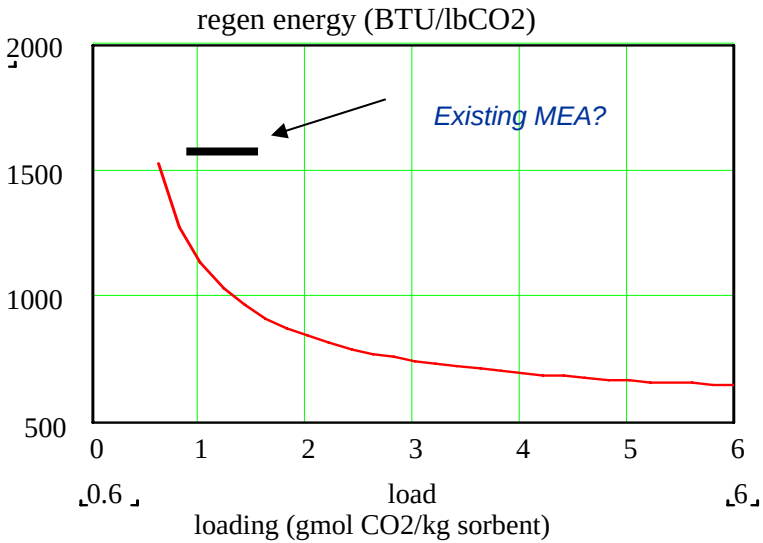
Conceptual CO_2 Removal Process



Regeneration Energy for Solid Sorbents TSA



$$\frac{Q}{m_c} = \underbrace{\frac{m_e}{m_c}\cdot C_e\cdot\Delta T}_{\text{Heating the "equipment"}} + \underbrace{\frac{B}{L}\cdot C_s\cdot\Delta T}_{\text{Heating The sorbent}} + \underbrace{C_{p.c}\cdot T_2 - C_s\cdot T_1}_{\text{Enthalpy change between gaseous } CO_2 \text{ and sorbent}} + \underbrace{\frac{Q_r}{m_c}}_{\text{Heat of reaction}}$$



For a given ΔT, regeneration energy may be reduced by:

1. ***increasing CO_2 capture loading (L)***
2. ***decreasing specific heat of the sorbent (C_S)***
3. ***Find a sorbent with lower heat of reaction Q_r.***

BACKGROUND: MATRIC Study Success Criteria

- The initial performance target for a CO_2 capture technology with sorbents is a reduction of no less than 30-50 percent of the energy required for a wet (MEA) process.
- The sorbent should achieve a minimum delta loading of 3.0 moles CO_2/kg of sorbent.
- The sorbent must adsorb and desorb CO_2 within the temperature envelope of 40 to 110 ^oC in the presence of water at atmospheric pressure.
- The sorbent must demonstrate stability and retain the CO_2 capture capacity during multi-cycling between the absorption and regeneration steps.
- The sorbent must be durable within the operating parameters of the selected reactor design.
- The sorbent must perform in the presence of water and other flue gas constituents.

Sorbent Path Forward: Critical Information Required

- Isotherms (Δ loadings) between rich loading (absorption) and lean loading (regeneration)
- ΔH_r for absorption
- C_p for sorbent
- Role of H_2O in process
- Role of trace components (SO_2 and NO_x)
- Kinetics

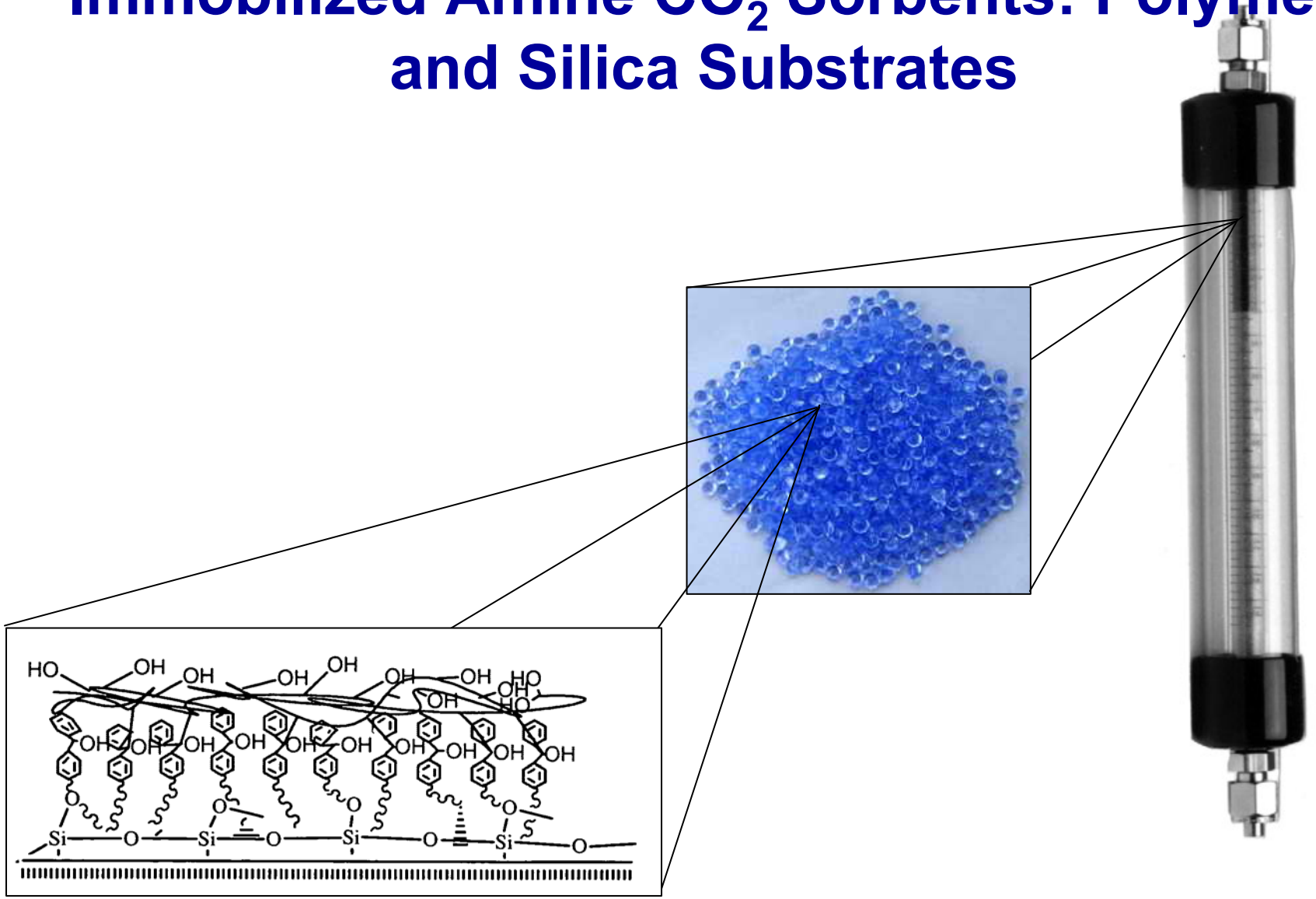
Discussion Today

- Background
- Sorbent Development
  - Immobilized Amine Sorbent
  - Encapsulated Sorbent
- Reactor Design
- Future

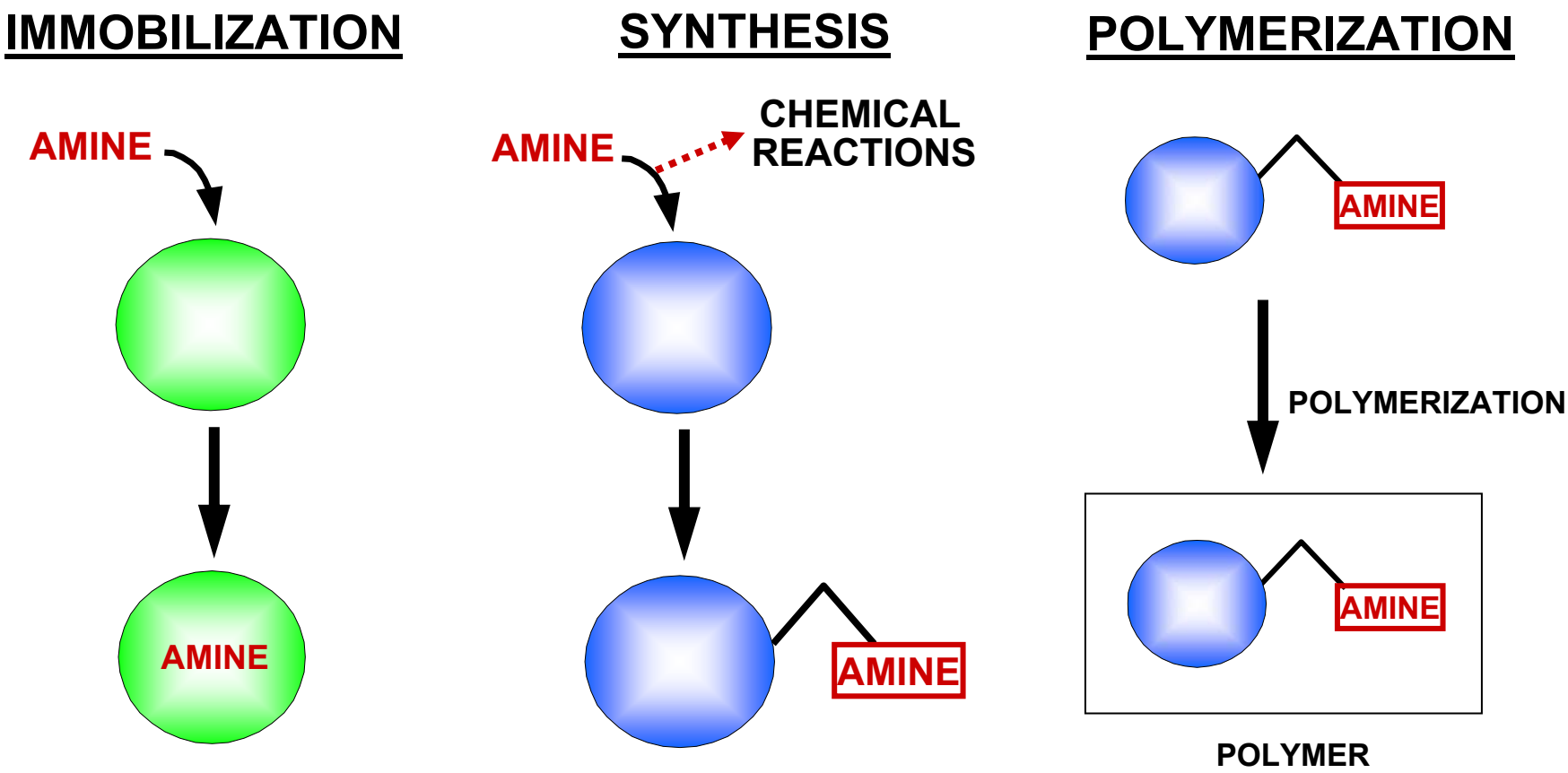
Experimental Facilities Available

- **Thermogravimetric analyzers and calorimeters**
- **Laboratory-scale packed bed reactors (1-gram)**
  - Flow 15-200 sccm simulated flue gas
  - CO_2 content 10-15%
  - Temperature 40-140°C
  - Mass spectrometer
- **Bench-scale packed bed reactors (30-50 gram)**
  - Flow 1.5-liter/min simulated gas
  - Same composition and temperature ranges as lab-scale
  - CEMS for gas analysis
  - Solid diluent (sand) used to manage exotherm
- **QA/QC**
  - Gas lag in process lines considered in data analysis
  - Consistent results between units desired—cross check
  - Mass closures in laboratory and bench-scale units
  - Regeneration typically temperature swing under inert gas

Immobilized Amine CO_2 Sorbents: Polymer and Silica Substrates



Pathways to Solid Amine Sorbents



Sorbent Development—Polyethylenimine (PEI)

Polymer Molecular Weights

PEI 423, PEI 600, and PEI 2500

$NH_2(CH_2CH_2\text{-}NH)_nH$ and

$$H_2N\text{—}(CH_2H_2N)_x\text{—}(CH_2CH_2NH)_y\text{ —}$$
$$|$$
$$CH_2CH_2NH_2$$

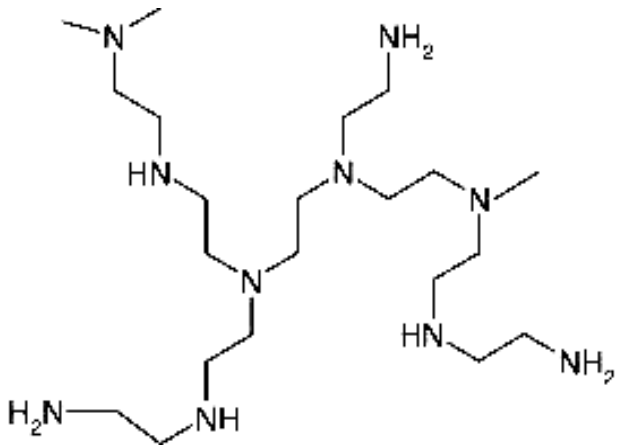
Chemical structure of polyethylenimine, a highly branched compound having two carbons per nitrogen with a ratio of 1:2:1 between primary, secondary, and tertiary amine groups.

Favorable Characteristics

High boiling point

Low vapor pressure

Low viscosity



Supports

- **Macroporous Resin of Methacrylate-Type—Diaion® HP2MG**
  - Based on a methacrylic ester copolymer (Tg: 105,120 & 115°C)
  - relatively hydrophilic nature
  - Successfully applied in removing CO_2 and water in space life support systems

- **Commercial Catalyst Support (Silica gel)—Cariact® Q and G series**

Catalyst Support
Silica Gel

Support Characteristics

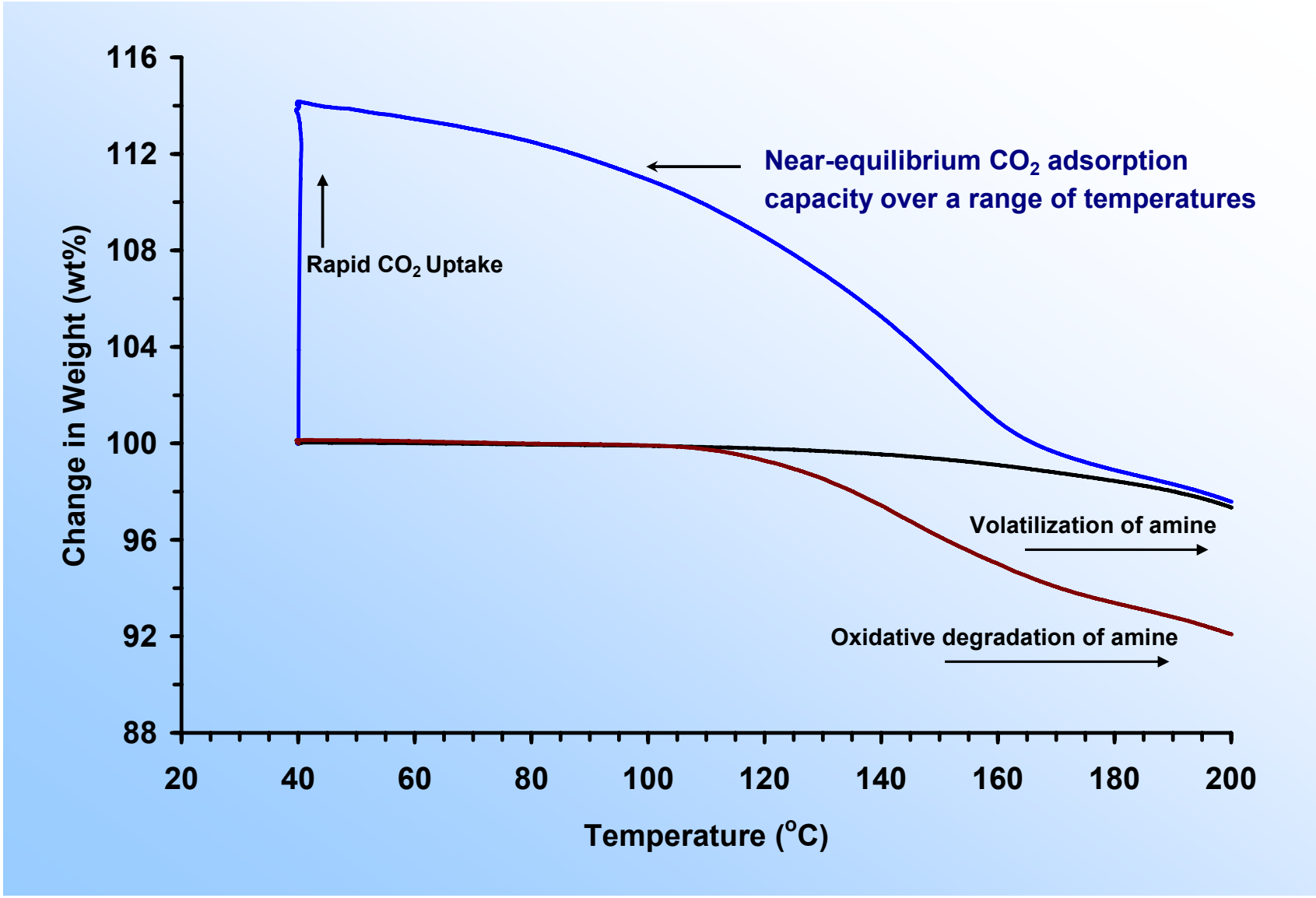
- *High Purity*
- *Selectable Particle size*
- *Controlled pore diameter*
- *Water and attrition resistance*

Table 1. Characterization of Supports by N2 physisorption at 77 K

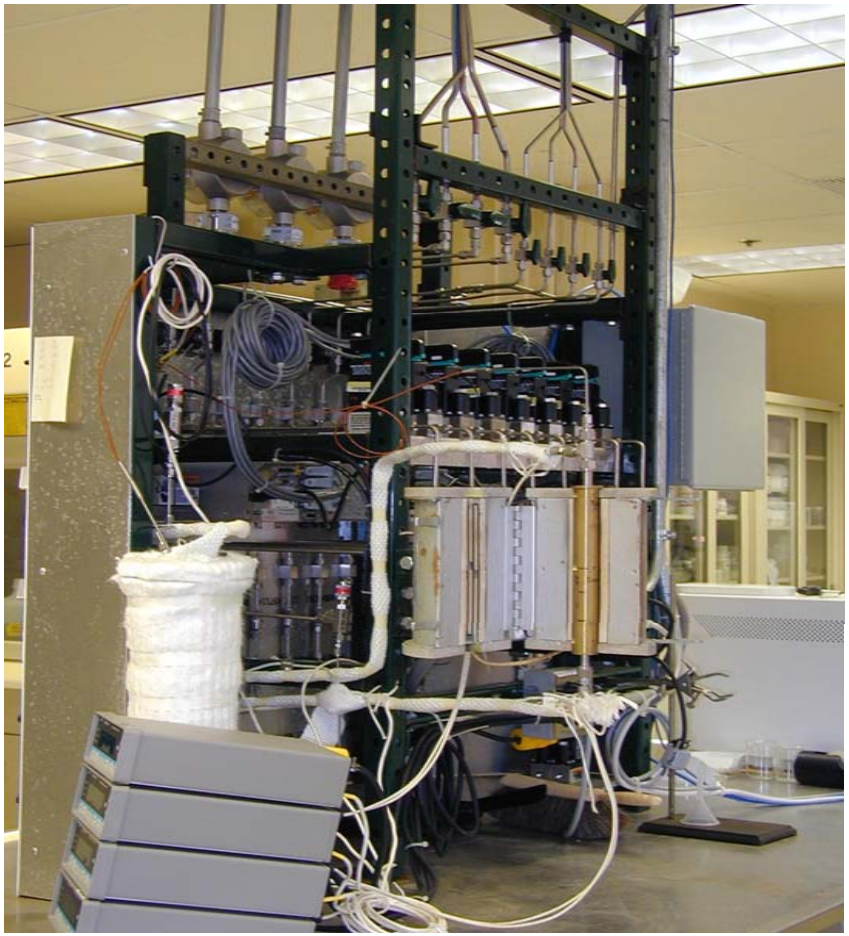
Support	S_{BET} (m^2/g)	V (cm^3/g)	D_{BJH}, (Å)	*Particle diameter, (µm)*
Diaion® HP2MG[1]	579	1.12	104	425-850
Cariact® G10[2]	300	1.3	100	45-150

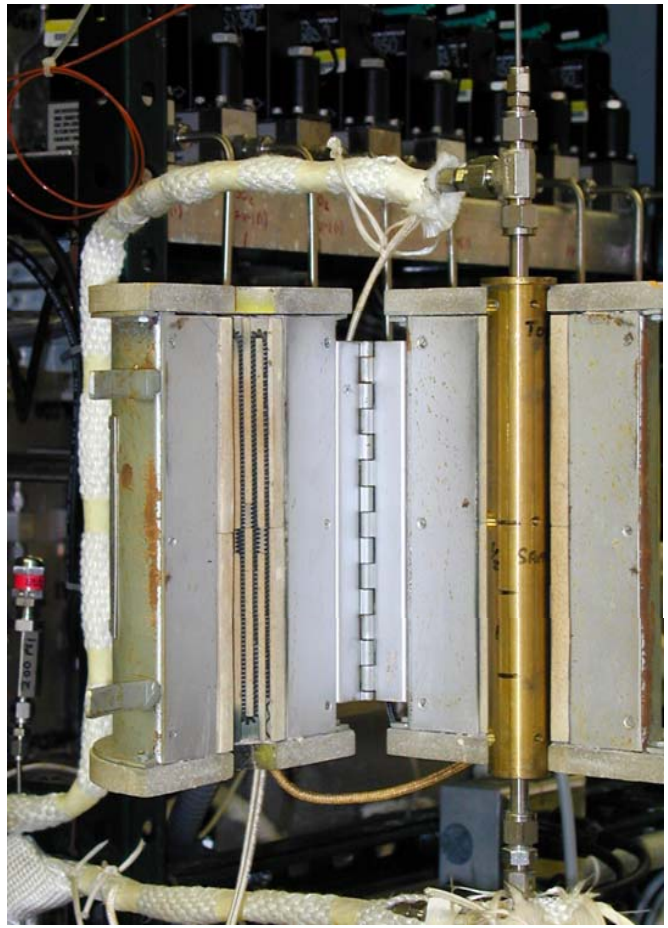
[1] Measured values in our study
[2] obtained from Fuji Silysia Chemical Ltd. brochure

Absorption & Stability—PEI supported PMMA

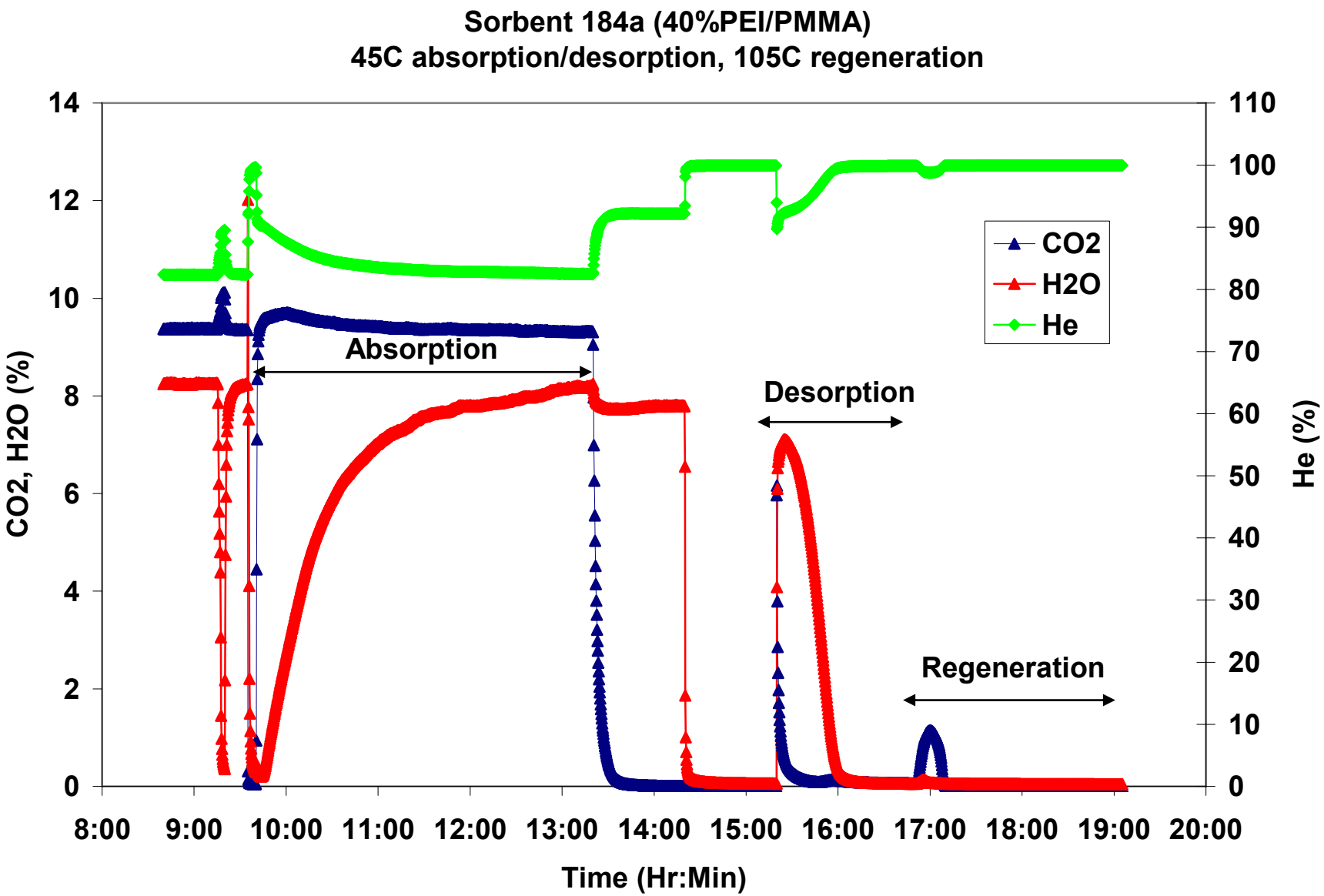


Laboratory Scale Reactor





Typical Experiment (Wet) on 40%PEI/PMMA



Moisture Impact on Sorbent with Polymer Substrate

PEI/PMMA			
Temperature – 60°C (140°F)	CO_2 Capacity mol/kg sorbent	H_2O Capacity mol/kg sorbent	H_2O Closure %
10% CO_2, 7.7% H_2O, He	1.9	4.4	90
10% CO_2, 16.5% H_2O, He	1.8	14.7	99
Temperature – 45°C (113°F)			
10% CO_2, 8.3% H_2O, He	2.4	17.8	92

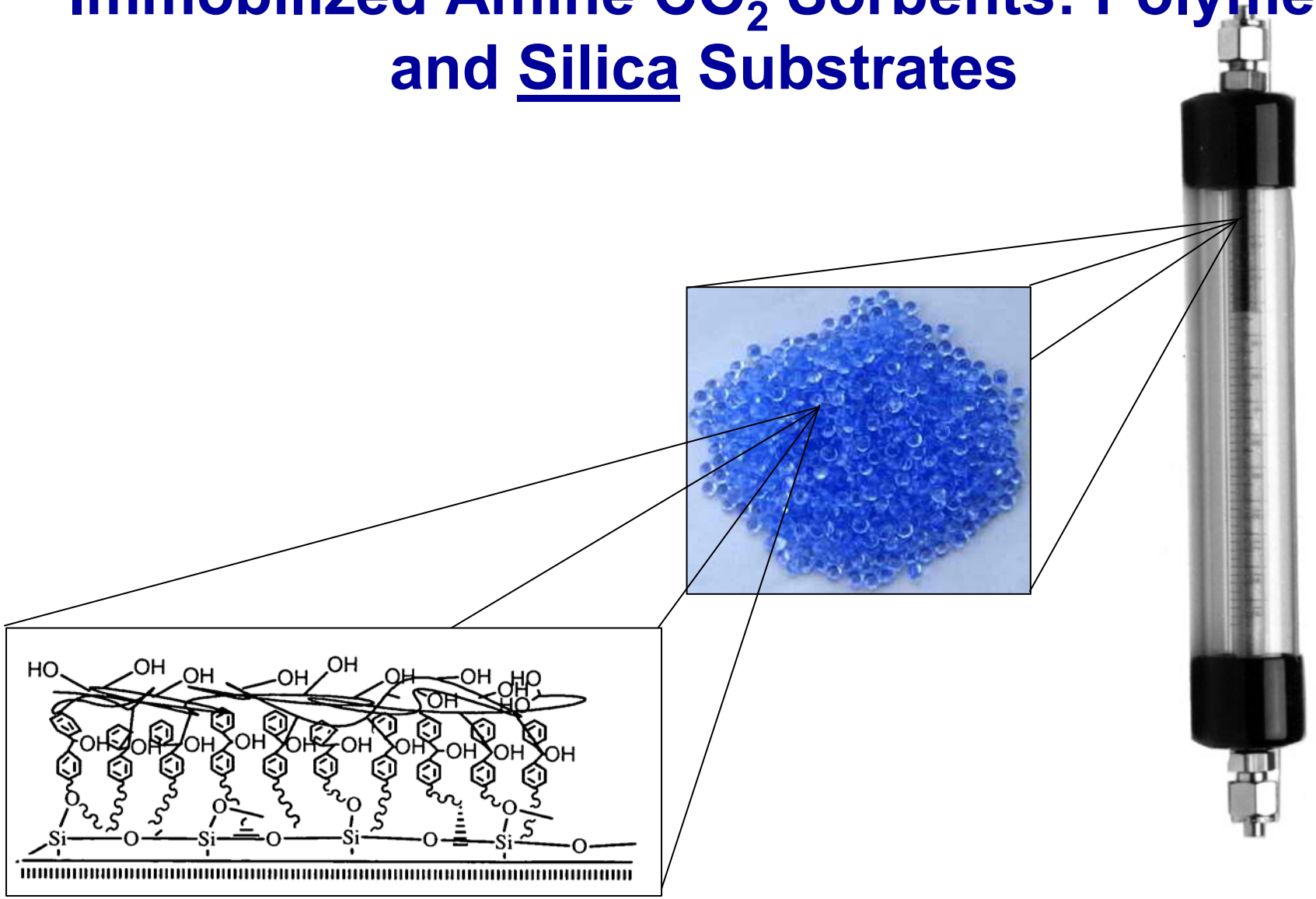
Calorimeter & Loadings

Table 4
Calorimeter & sorbent capacity

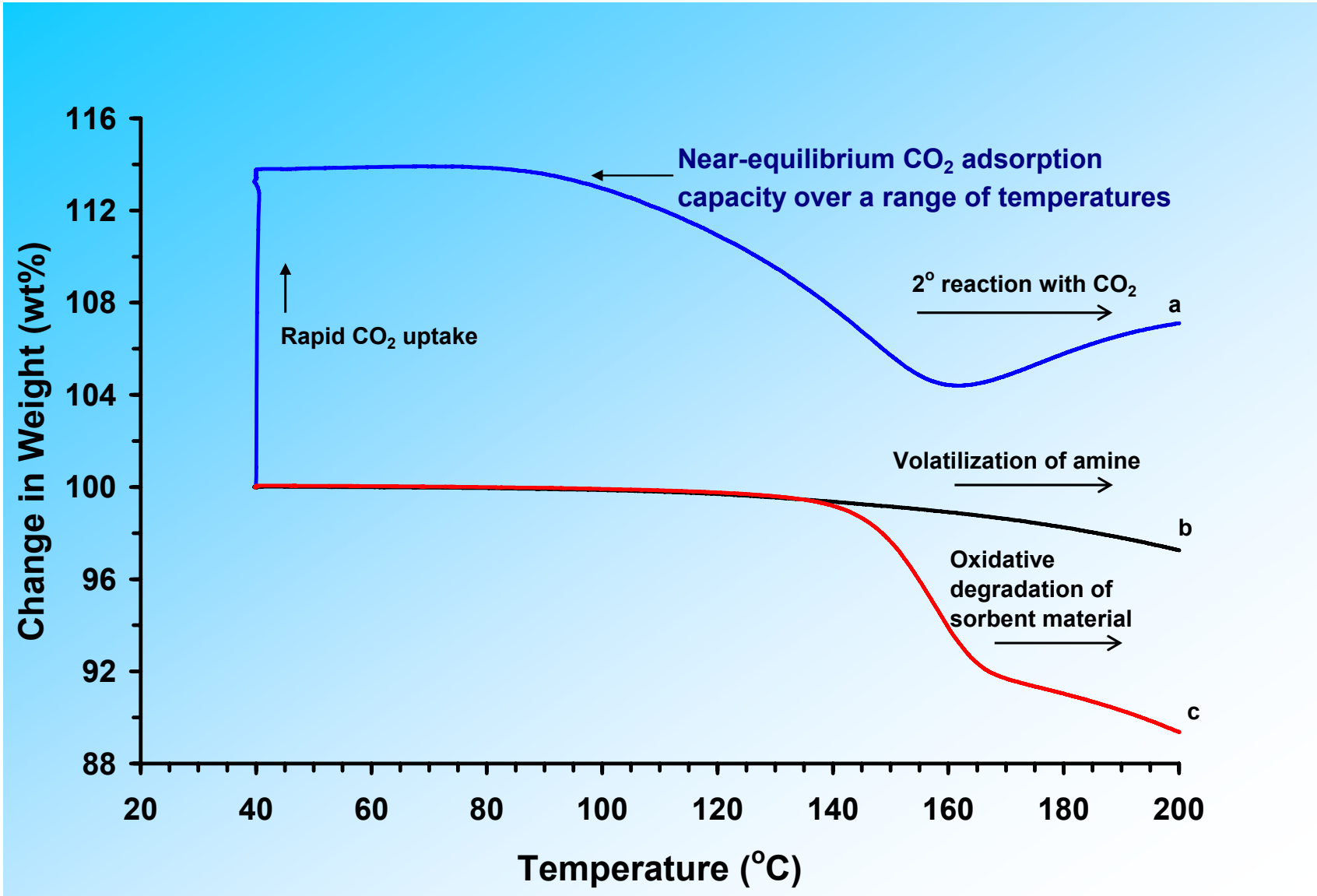
			PMMA				184a			
	Gas	T	CO2	Q	ΔH_r		CO2	Q	ΔH_r	
		ºC	mole/kg	J/g	kJ/ mol CO2	Btu/ lb CO2	mole/kg	J/g	kJ/ mol CO2	Btu/ lb CO2
ABS	10%CO2/N2 (Dry)	40					2.7			
(TGA)	100%CO2 (Dry)		0.51	9.7	19.0	186	3.3	141	42.7	418
	100%CO2 w 1%H2O		0.55	16	29.1	284	3.6	171	47.5	465
ABS	10%CO2/He (Dry)	45					2.3			600
(MS)	10%CO2/He (Wet)		0.1							
Matric										580

Preliminary measurements – being checked!

Immobilized Amine CO_2 Sorbents: Polymer and Silica Substrates



Absorption & Stability—PEI supported Silica

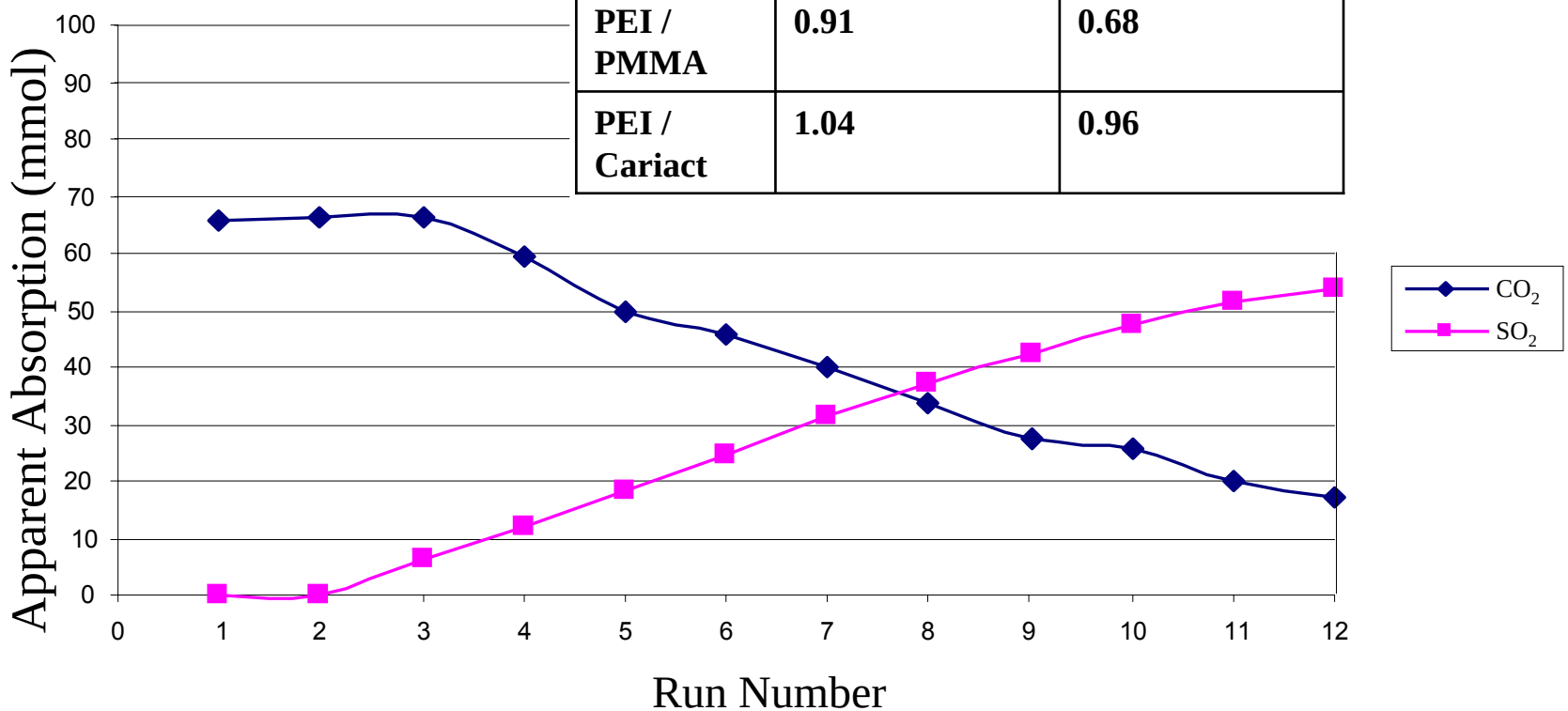


SO_2/NO_x Accelerated Exposure Tests

- 1000ppm SO_2 or 750ppm NO_x or 750ppm NO_2 in CO_2 + N_2 mixtures
- Bench-scale packed bed reactor
- 40% PEI on PMMA or silica was sorbent
- Minimum 10– absorption/desorption cycles
- Rate of poisoning established

Effect of SO_2 Contamination on PEI/PMMA

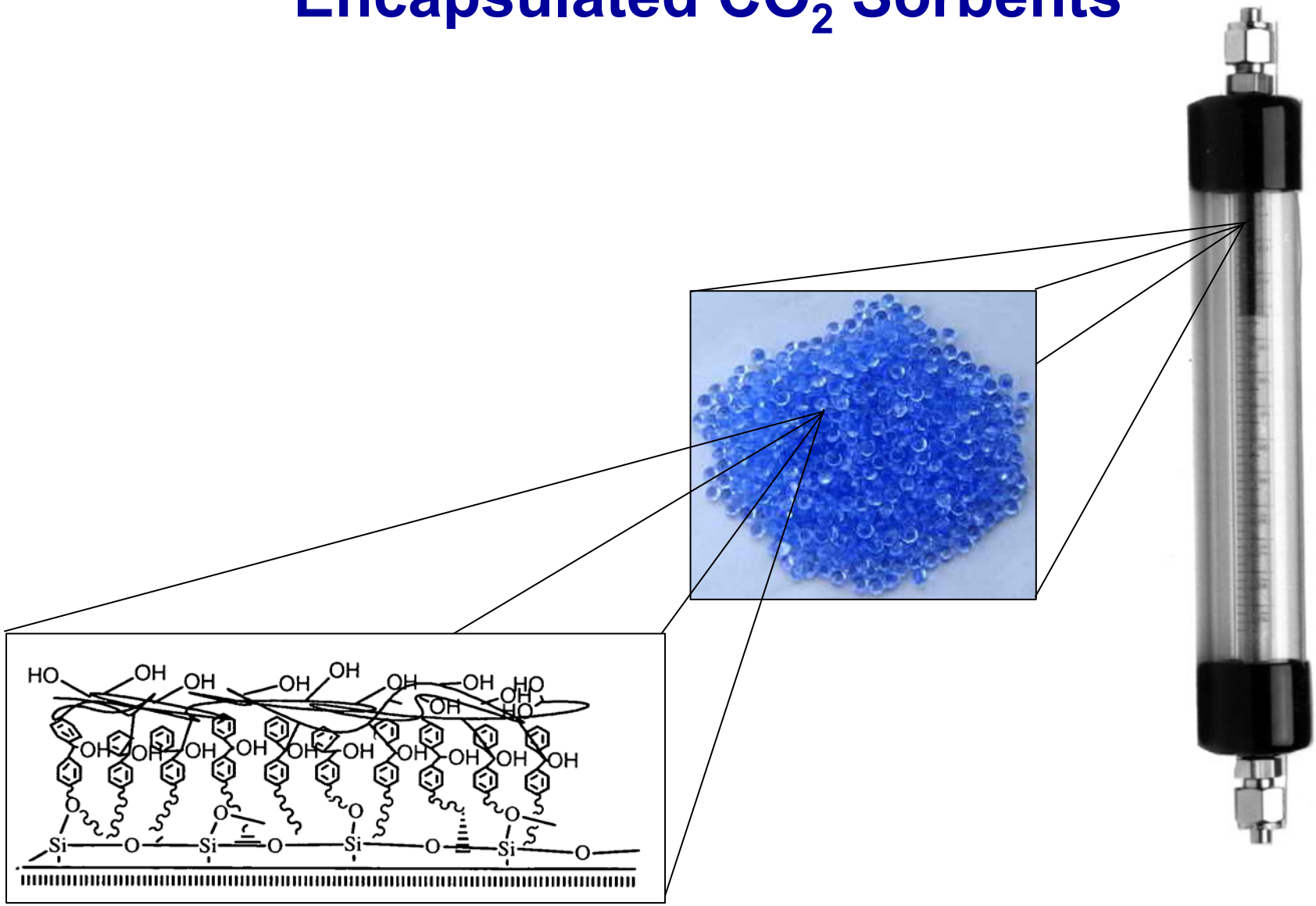
Sorbent	Δ CO_2 Capacity/ Cum SO_2 (mol/mol)	Δ CO_2 Capacity/ Cum NO_2 (mol/mol)
PEI / PMMA	**0.91**	**0.68**
PEI / Cariact	**1.04**	**0.96**



Summary for Immobilized Amine Sorbents

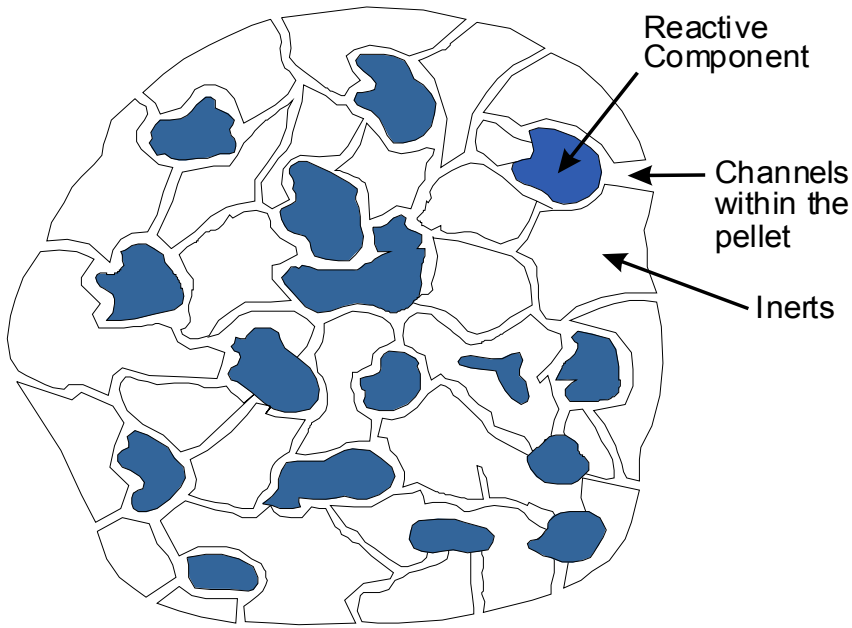
- **Polymer-based sorbent**
  - Loading near the 3-mol/kg target; CO_2 regeneration not an option
  - Heat of reaction within prescribed range
  - Showed oxidative degradation tendancies at temperatures near regeneration
  - Moisture adsorption may impact energetics
  - Candidate dropped from further consideration
- **Silica-based sorbent**
  - High loadings in the 3-4mol/kg range; CO_2 regeneration improbable
  - Stable at elevated temperatures
  - Candidate of choice
  - Additional information required
- **Both sorbents**
  - Susceptible to poisoning with SO_2 and NO_2; upstream cleaning required in process

Encapsulated CO_2 Sorbents



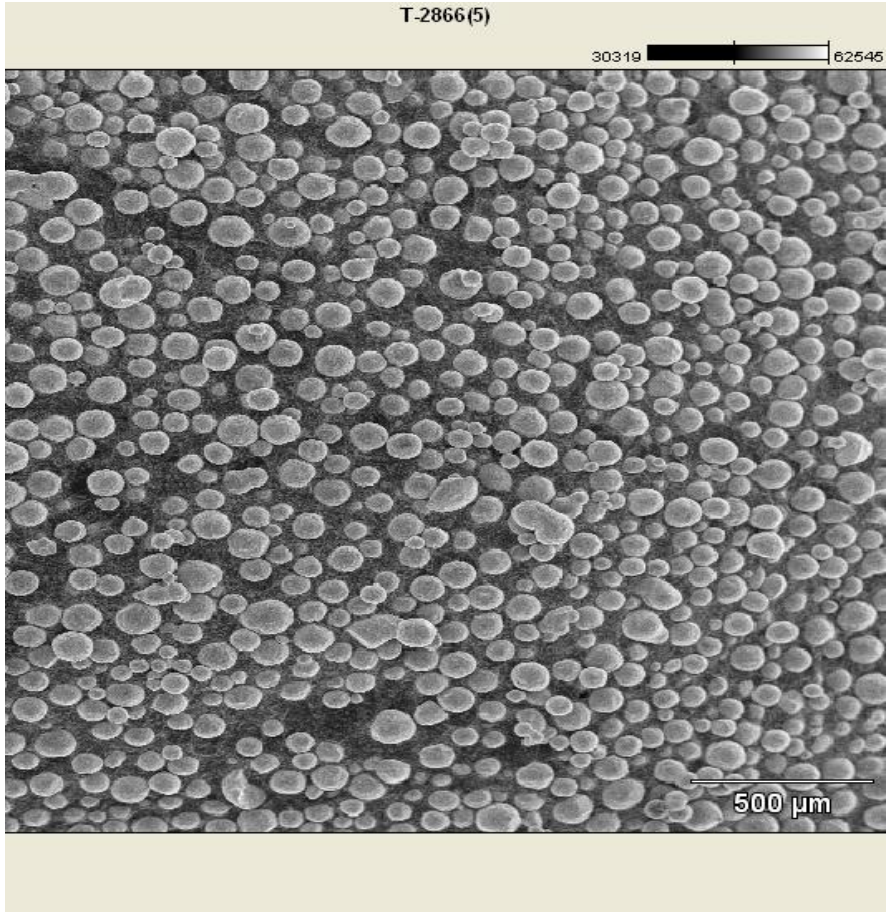
Encapsulated Amine-Based Sorbents

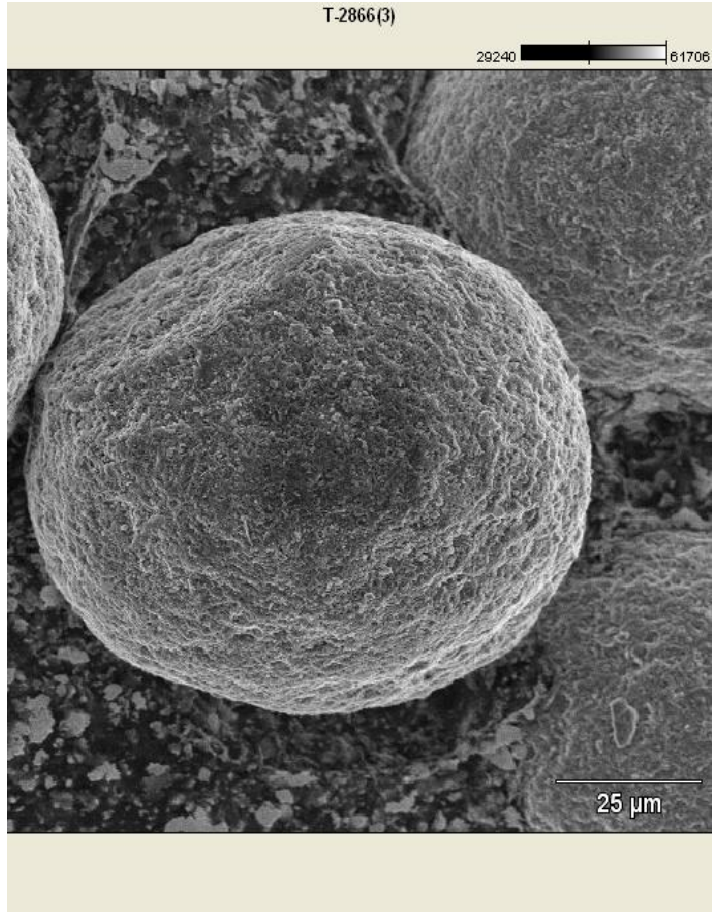
- **Polar liquid mixture containing amine and ethers/glycols were utilized**
- **Polar liquids trapped inside the unit layers of the clay**
- **Advantages**
  - Readily available materials – low cost
  - Easy preparation technique
  - No corrosion problems
  - No liquid wastes generated
- **U.S. Patent 6,908,497 issued for this work**



Spray Dried Formulations Suitable for Fluidized Beds Prepared in Collaboration with Sud Chemie

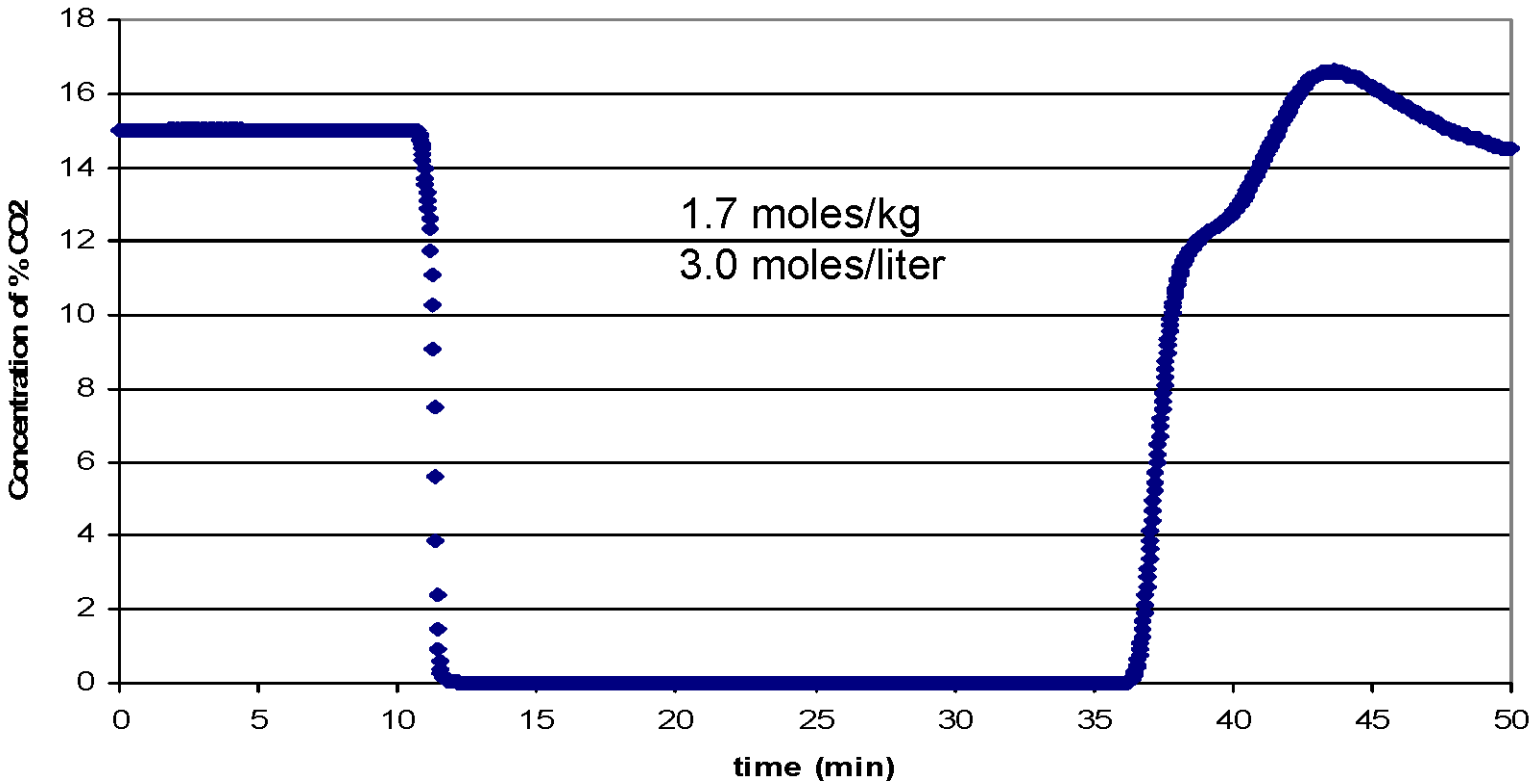
Average Particle Size 80 Microns



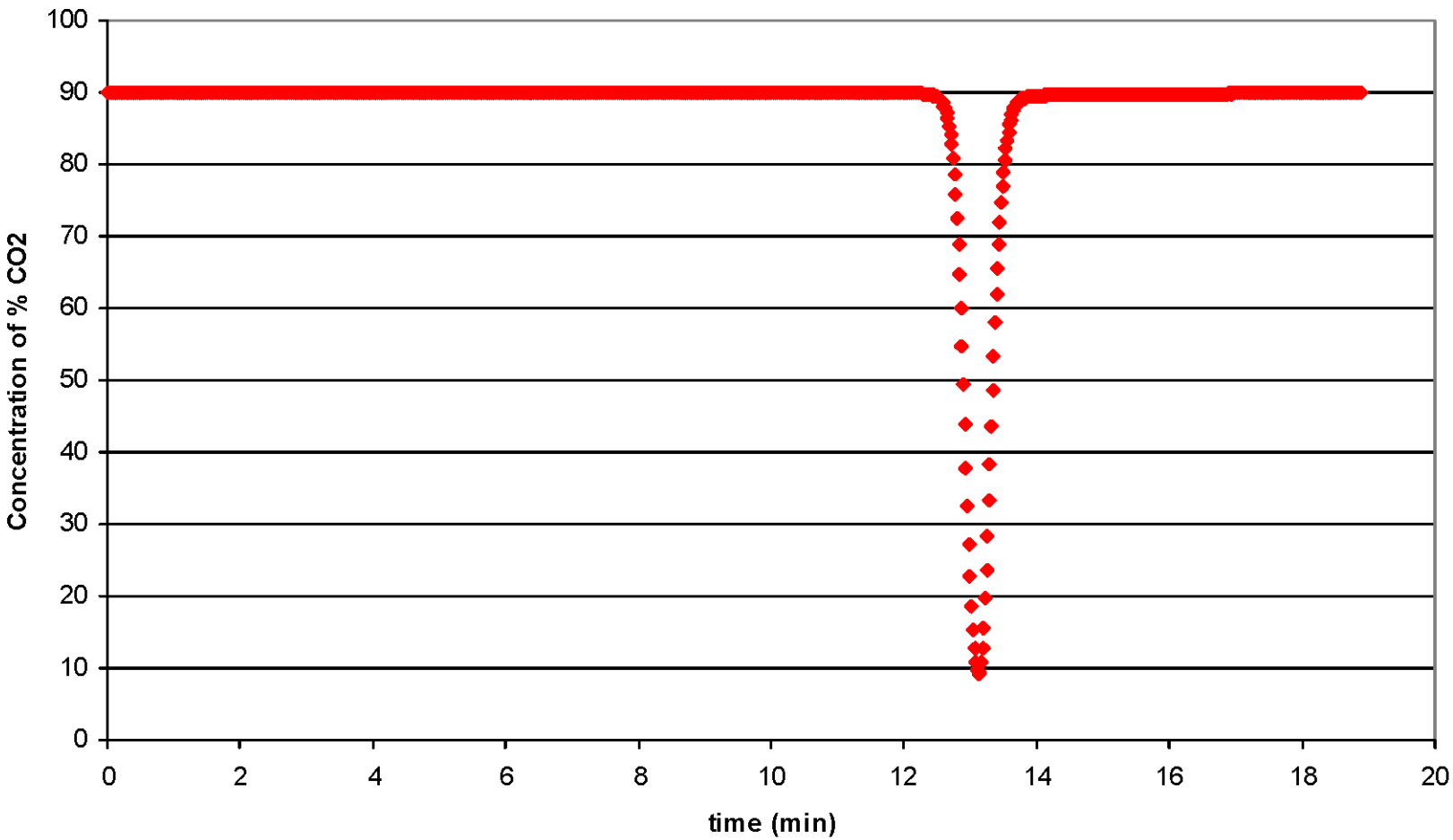


Delta CO_2 Loading Data for Sorption of CO_2 on Spray Dried Clay-Liquid Sorbent –

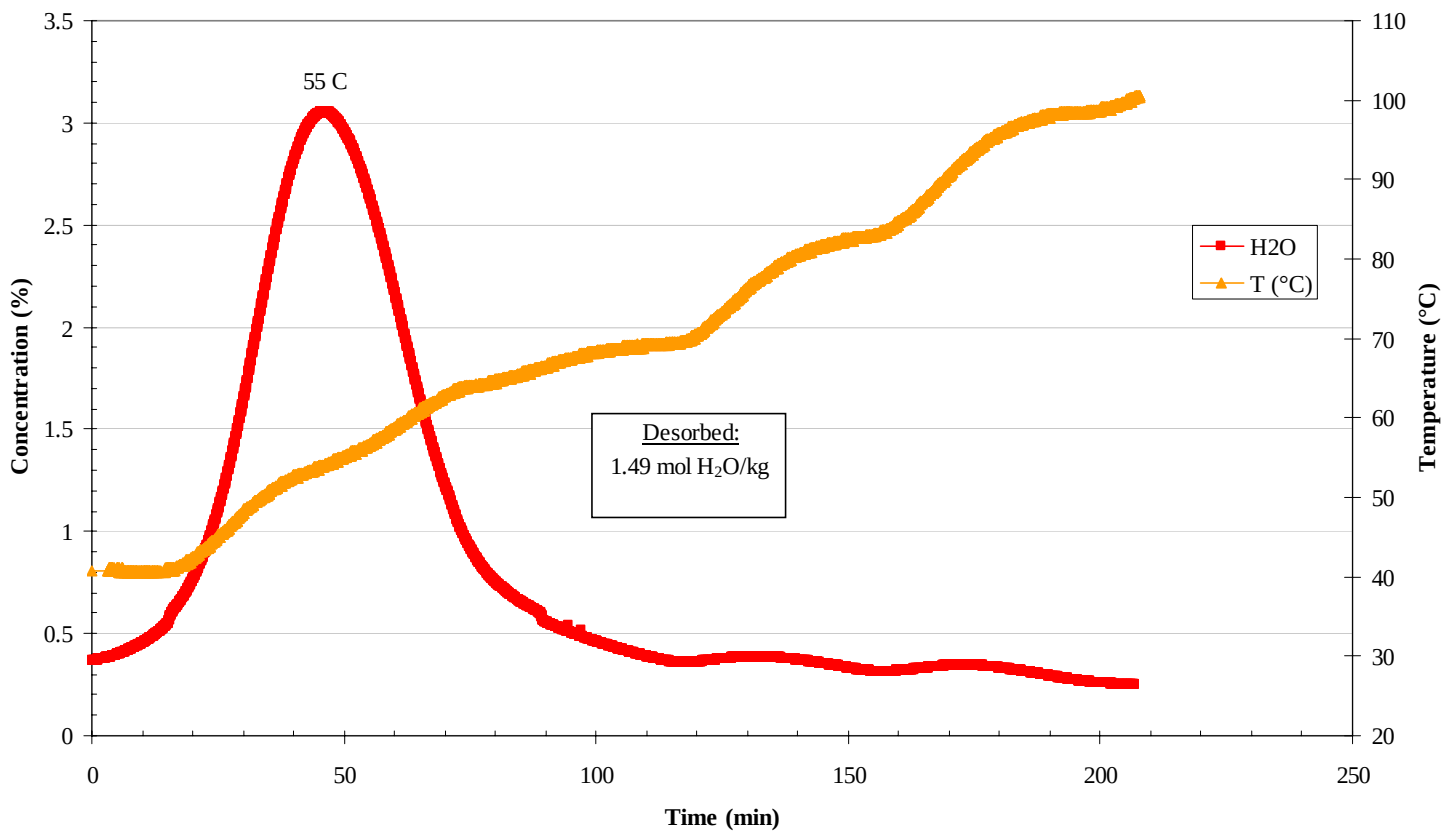
(15% CO_2, 3%O_2, 3% H_2O and 79% N_2, at 40 °C, 15 cc/min, in atmospheric reactor)



Spray Dried Sorbent from SudChemie Sorption at 100°C with 90% CO_2 in N_2



TPD Study of Water after Sorption of 7% H_2O, 17% CO_2, 3% O_2, and Nitrogen at 40°C



Heat of Sorption Measurements

- **Heat of sorption = 650 Btu/lb of CO_2**

Data will be utilized for heat of regeneration calculations

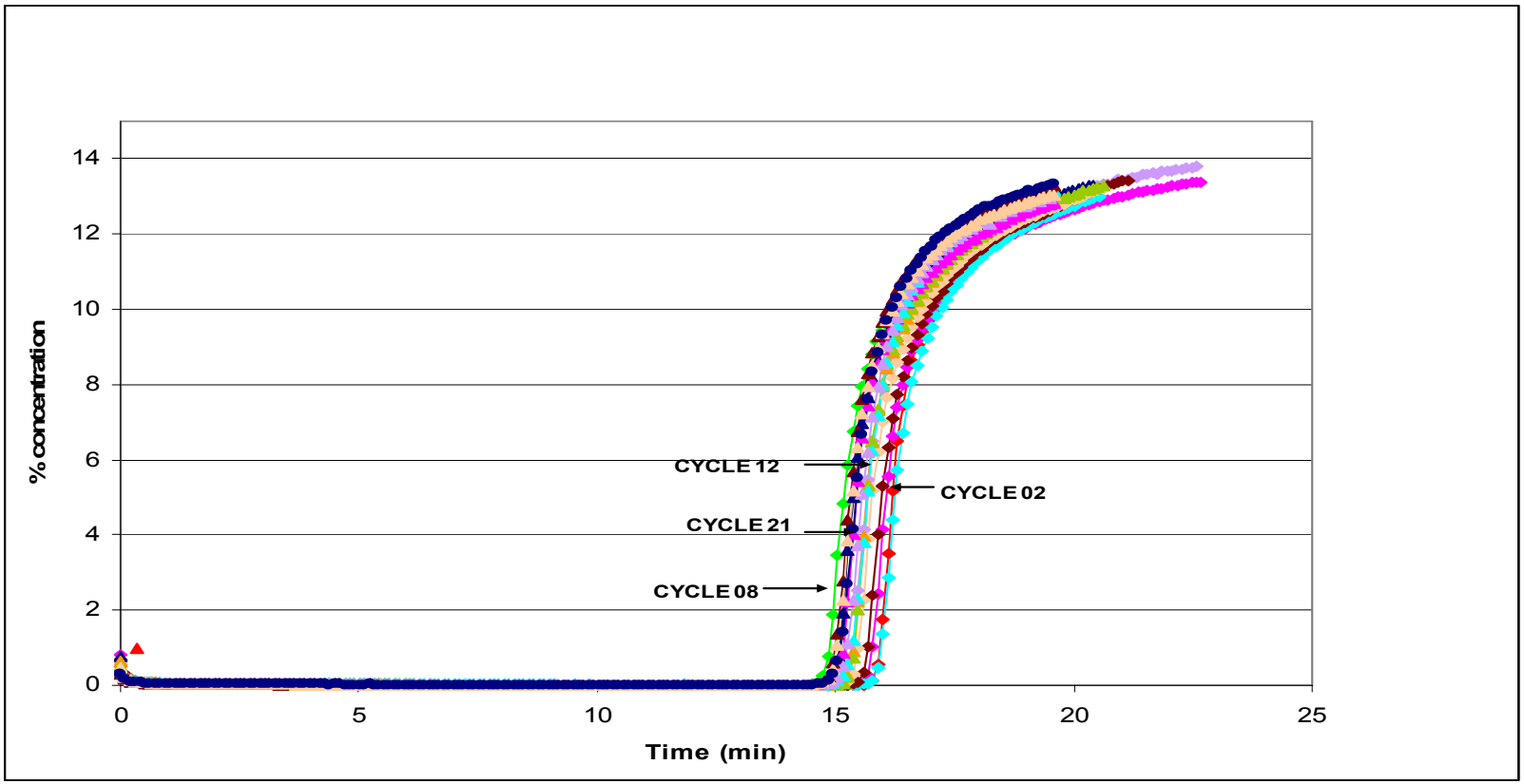
Preliminary data!
The heat of reaction (with water) is being repeated.

Setaram DSC111 Flow calorimeter

Sorbent Stability Tests
- 21 cycle test in the presence of SO_2

Sorption at 40 ^oC (15% CO_2, 3%O_2, 82% N_2, 20 ppm SO_2 and 3% H_2O, 15 cc/min, in atmospheric reactor)

Regeneration at 100 ^oC (Nitrogen)



Summary for Clay-Based Sorbent

- CO_2 capacity is reasonable (1.7mol CO_2/kg) with low specific heat.
- Regeneration in CO_2 is possible.
- Water/humidity investigation continuing with need to quantify heat of adsorption.
- More cycles needed for long-term stability with respect to SO_2.
- Expected low cost, easy to manufacture.
- Once parameters quantified, revisit spreadsheet calculations and systems analysis.

Discussion Today

- Background
- Sorbent Development
  - Immobilized Amine Sorbent
  - Encapsulated Sorbent
- **Reactor Design**
- Future

Reactor RD&D Challenges

Laboratory

- 0.1 ft^3 Reactor Volume
- 0.27 scf per minute

Technically possible?

Scale-up

Economically feasible?

500 MW Commercial Power Plant

- 57,000 ft^3 Reactor Volume
- 1,800,000 scf per minute

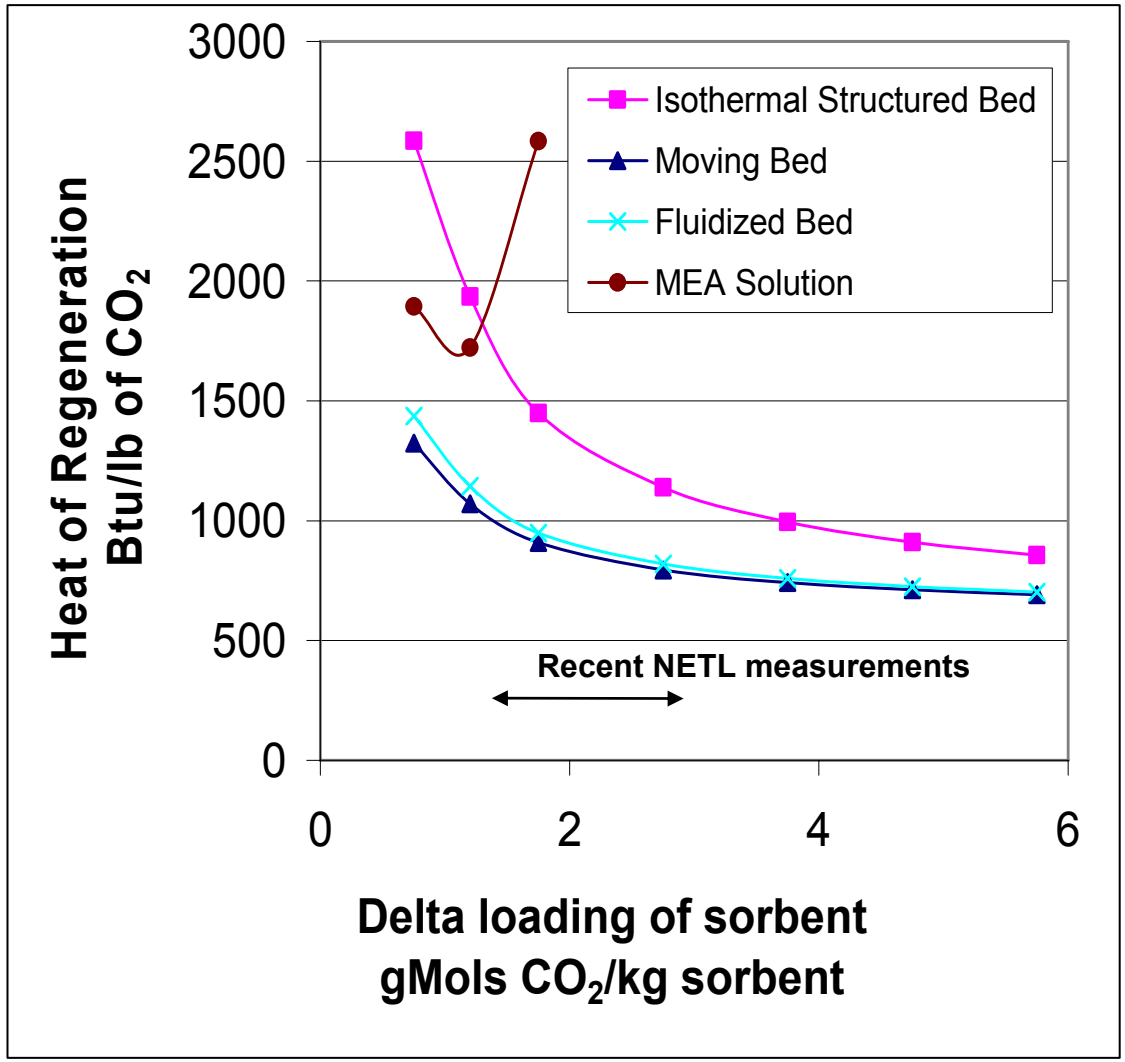
Candidate Reactor Designs[3]

- **Structured Bed Concept**
  - Fixed bed sorber, with internal heat removal
  - Internal heating of same bed for regeneration
- **Moving Bed Concept**
  - Moving bed sorber, with internal heat removal
  - Moving bed regenerator, with internal heating
- **Fluidized Bed Concept**
  - Fluid bed sorber, with internal heat removal
  - Moving bed regenerator, with internal heating
- **Fixed Bed Adsorber Concept**
  - Fixed bed sorber, adiabatic, multi-stage with interstage heat removal
  - Heating of same bed for regeneration with hot fluid stream
- **Transport Reactor**
  - Circulating fluid bed sorber
  - Circulating fluid or moving bed regenerator

3. Hoffman et al. "Factors in Reactor Design for Carbon Dioxide Capture with Solid, Regenerable Sorbents," Proceedings of the 33rd International Technical Conference Coal Utilization and Fuel Systems, 2008.

Regeneration Energy versus Sorbent Loading

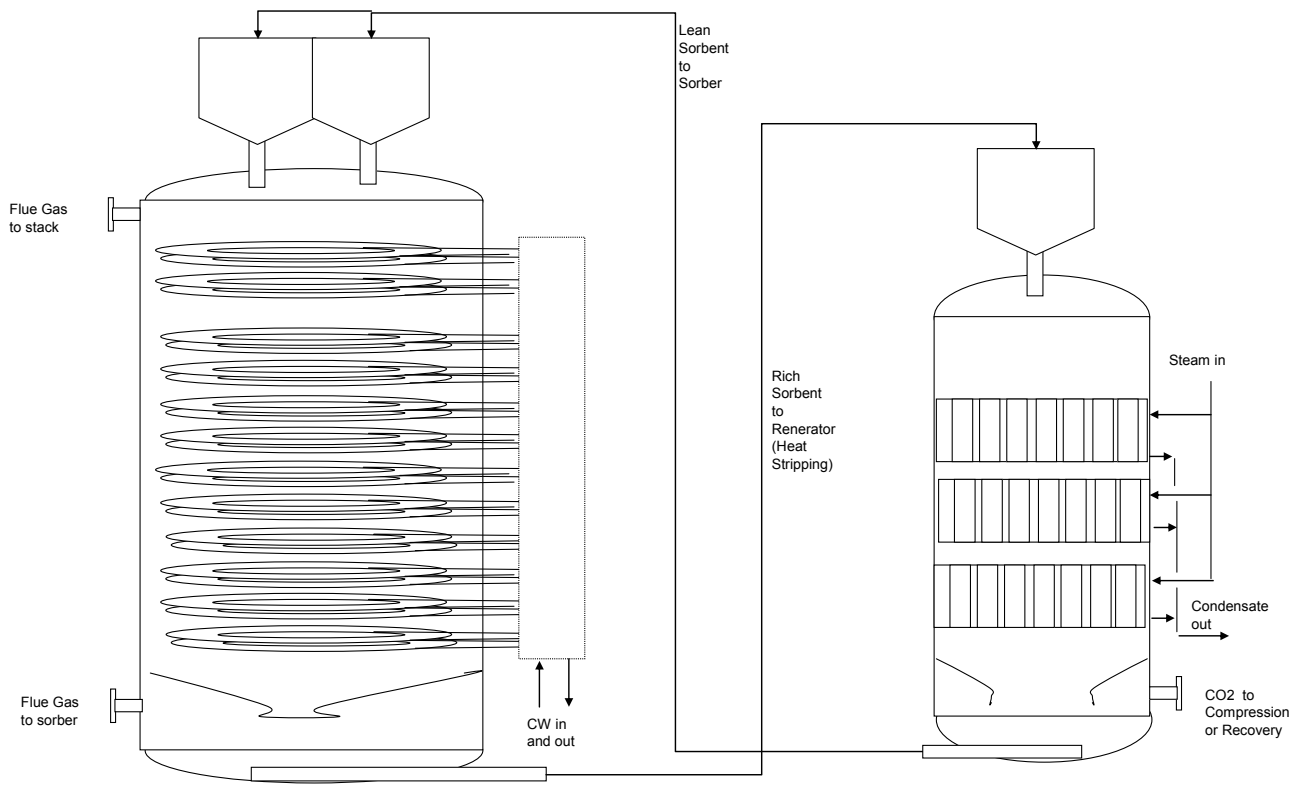
- **Includes:**
  - Heat of sorption
  - Sensible heat of sorbent and equipment vessel walls
- **Excludes:**
  - Pumping, compression, cooling, conveying materials



Results depend on the reactor to handle the sorbent (examples next)

Moving Bed

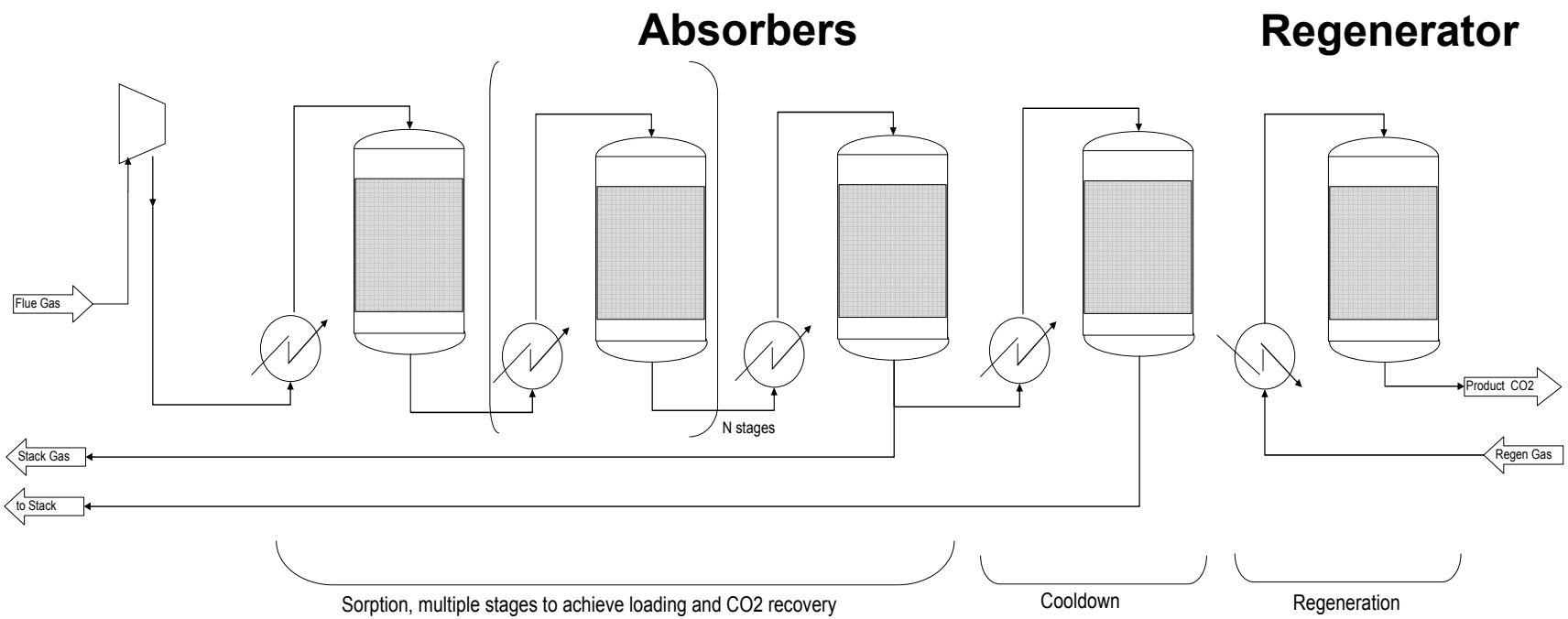
- CO_2 captured by solids flowing against flue gas.
- Heat removed by heat transfer tubes – lots of tubes!



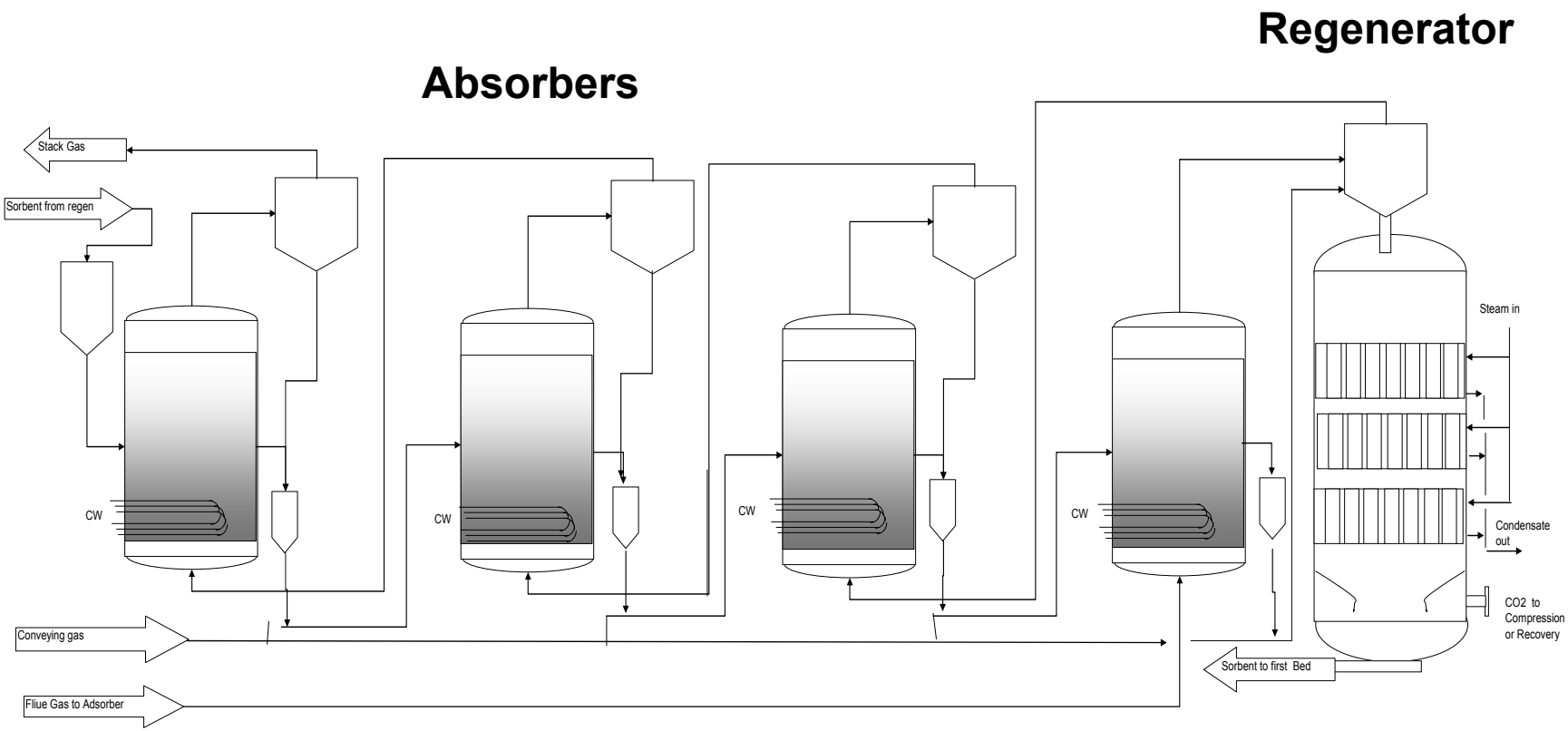
CO2 absorber

Sorbent regenerator

Fixed Bed Adiabatic Reactors



Fluid Bed / Moving Bed Reactors



System shown with 4 countercurrent beds, but the actual number is dependent on sorbent isotherm data.

Compressors are needed but not shown for flue gas and conveying gas

System shown is one of multiple parallel systems required for capacity of plant.

“Structured bed” (Disclosed to NETL, with Matric)

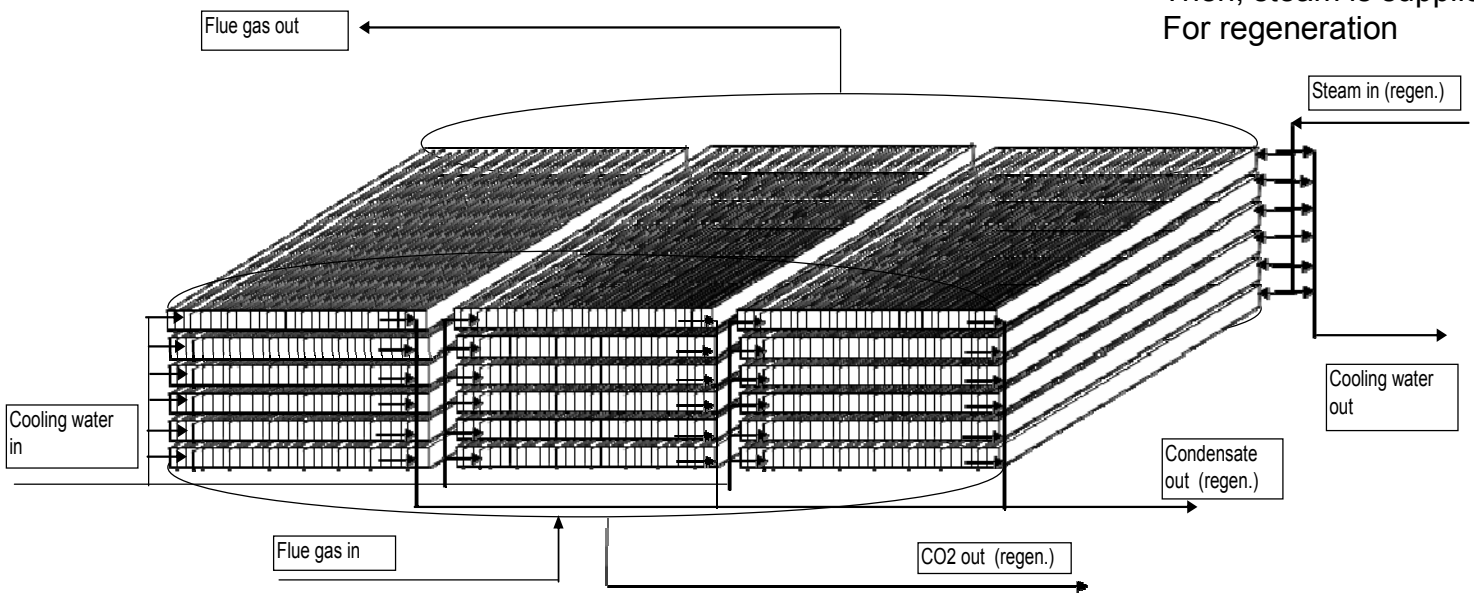
The sorbent
Is attached to
a heat exchanger.

The fuel gas is alternatively
Cycled for absorbing.
(water cools the HX)

Then, steam is supplied
For regeneration

Advantage: no circulating solids!

Disadvantage: alternating flows, no simple sorbent replacement



Summary Reactor Design and Path Forward

- **NETL labs: Sorbent performance**
  - Conclude information gathering: ΔH_r, C_p, moisture parameters, and eventual kinetics
- **NETL labs: Reactor Design**
  - Update MATRIC spreadsheets with above information to assure initial objectives met
- **NETL Computational Science Division:**
  - Reactor modeling (including transport reactor) and process integration with reactor concepts
- **Systems Analysis Group:**
  - Economic analysis of integrated process with reactor concepts. This will also validate performance and cost advantage of sorbent process (with final reactor design) over MEA process

Acknowledgement of CO_2 Sorbent Participants

- **NETL:**
  - A. Layne
  - M. Keller
  - K. Champagne
  - S. Hedges
  - J. Kleinhenz
- **MATRIC:**
  - D. Fisher
  - G. Keller
- **University of Pittsburgh:**
  - B. Morsi
  - W. Yang
- **Parsons:**
  - D. Hreha
  - K. Resnik
  - C. Robinson
  - R. Stevens
  - P. Zandhuis