Eighth Annual Conference on
Carbon Capture & Sequestration

Session: Capture/Sorbents (1)

Capture of CO_2 by the Carbozyme Permeator

Robert M. Cowan, David A. Smith, Haibin Chen, Xiaoqiu Wu,
Randall S. Reali, Yla A. Angso, Michael C. Trachtenberg

May 4 -7, 2009 • Sheraton Station Square • Pittsburgh, Pennsylvania

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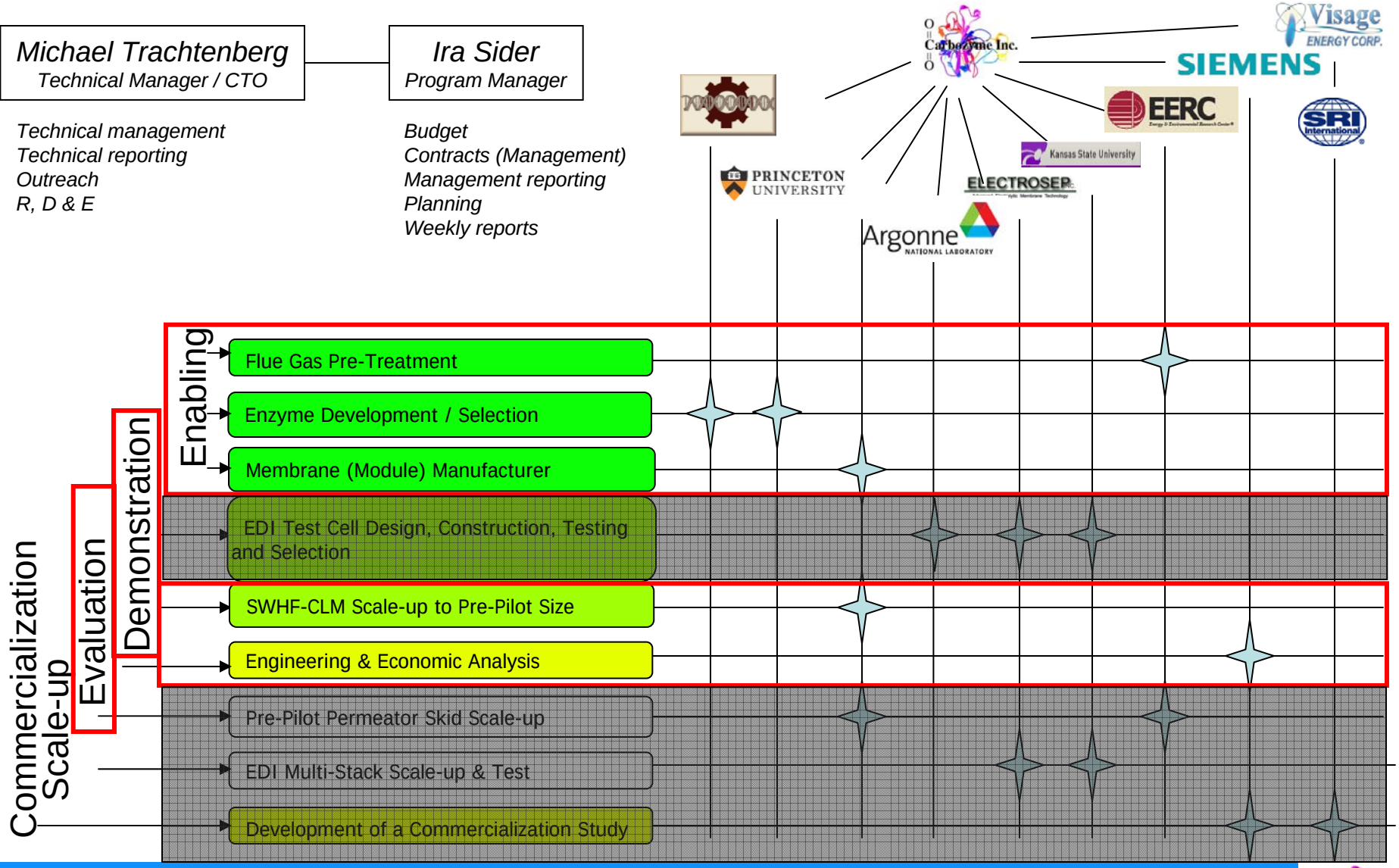
Participants

Michael Trachtenberg
Technical Manager / CTO

Technical management
Technical reporting
Outreach
R, D & E

Ira Sider
Program Manager

Budget
Contracts (Management)
Management reporting
Planning
Weekly reports



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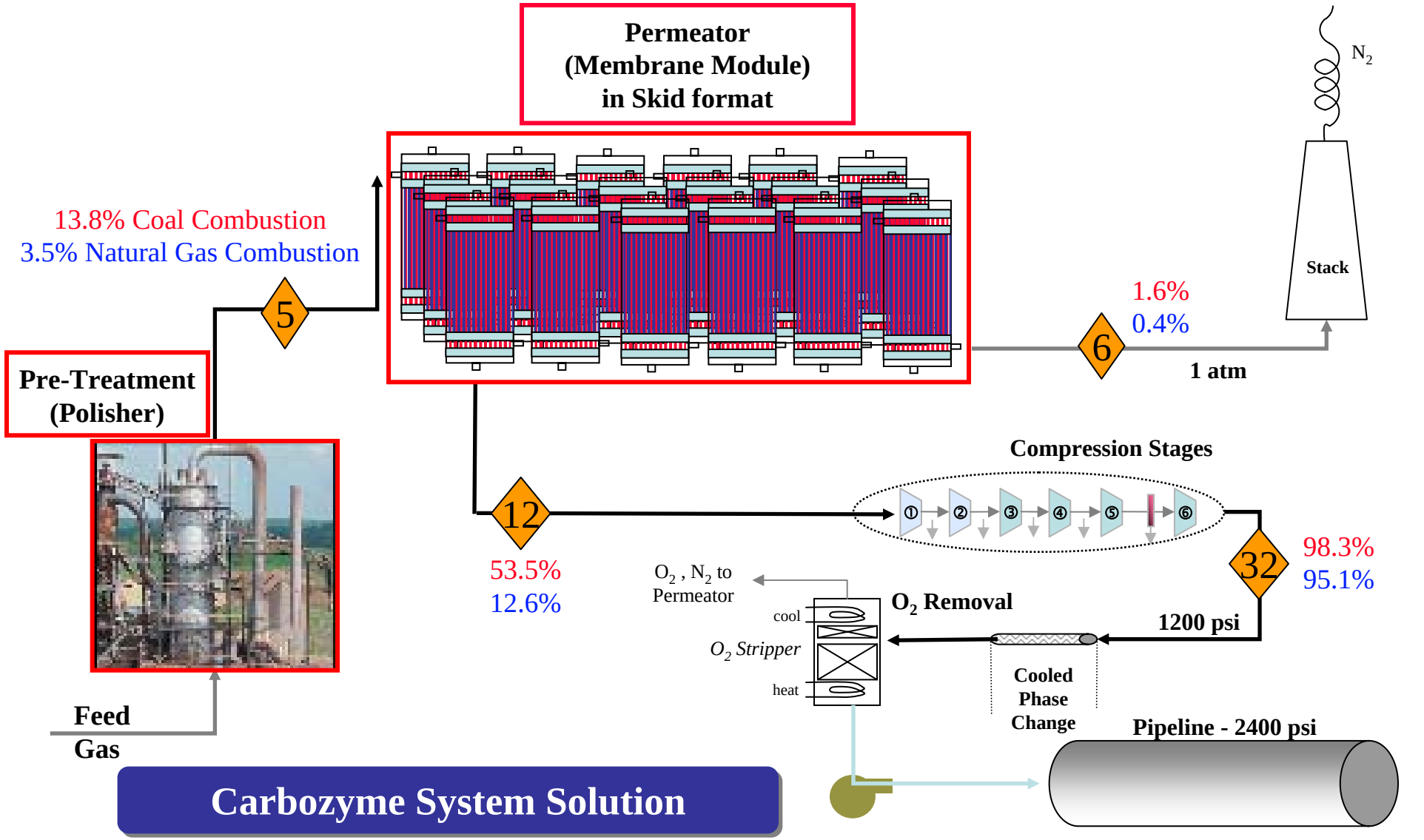
CO_2 Scrubber - Detailed Process Flow



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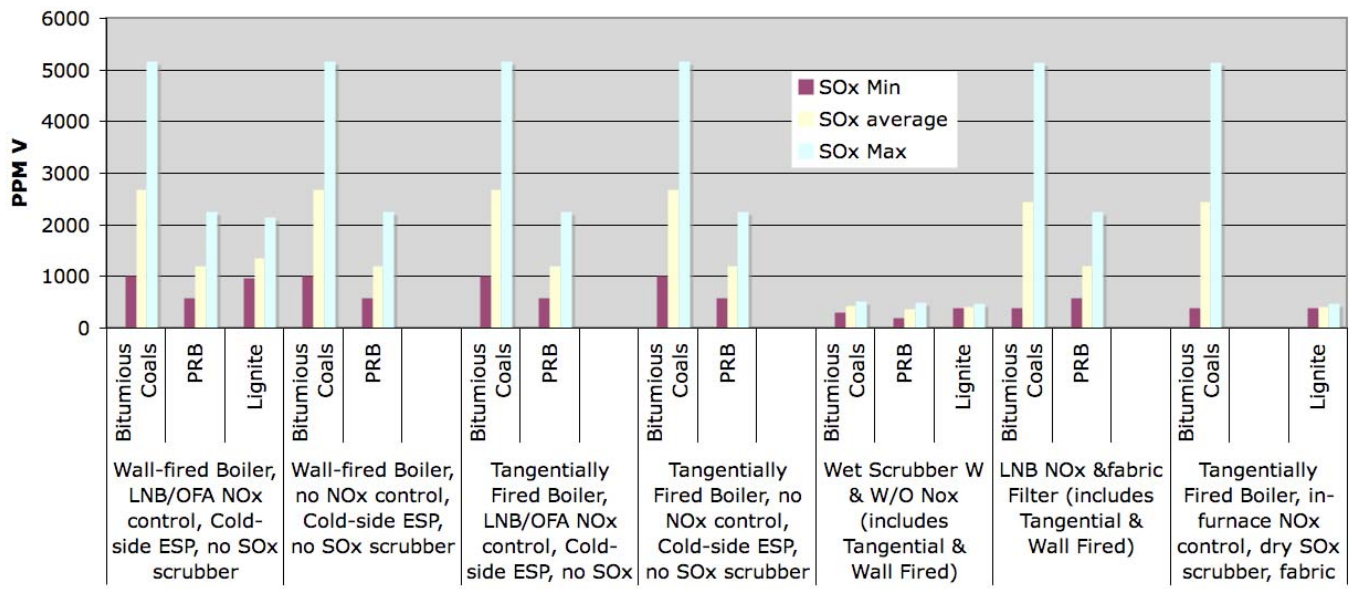
Flue Gas Pretreatment

- Last year our presentation focused strongly on identification of pretreatment needs
  - Conclusion: the most critical need was for removal of SO_X
  - The flue gas source range is
    - 330 to 1,000 ppmv for typical dry and wet scrubbed flue gas and/or low sulfur coals
    - 2000 to over 5000 ppmv for non-scrubbed high sulfur coals
- The Carbozyme acceptance standard for SO_X is 7 ppmv (20 ppmw) to sustain a 3-month lifetime of the liquid membrane solution

SO_X in Exhaust of Coal Fired Boilers



EERC Analysis using Integrated Environmental Control Model

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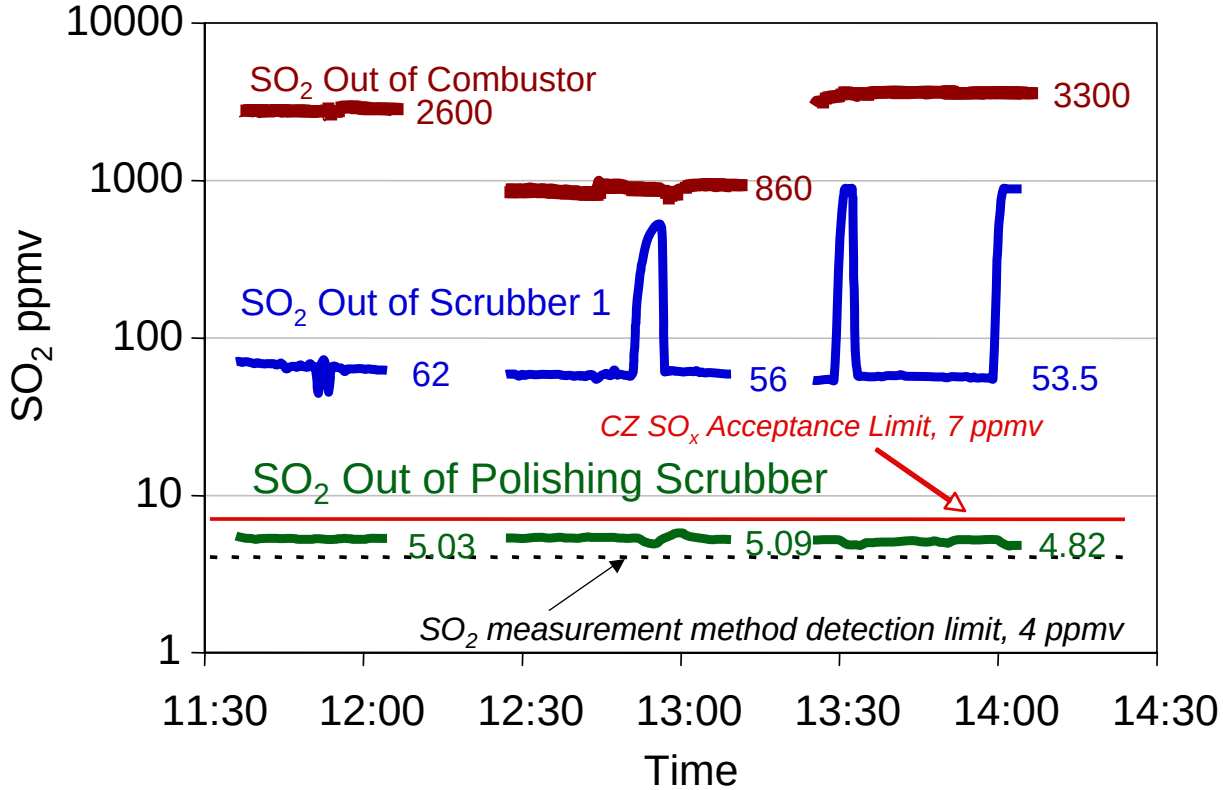
SO_X Scrubbing at EERC

- The wet lime slurry scrubber, built at EERC, meets the Carbozyme Acceptance Standard
  - EERC CEPS fired on SO_2 spiked natural gas to low, moderate, and high levels - 860, 2600 & 3300 ppmv
  - Pollution Control System on CEPS = SCR, Fabric Filter, Wet Scrubber 1, Polishing Scrubber ($CaCO_3$ slurry)



Lime slurry and ceramic Intalox saddle packing for the polishing scrubber. Packed tower used due to small scale of the test unit.

Target - <7ppmv (20ppmw) - Required Performance Achieved

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Requirements

- *Catalyst*
  - *High temperature*
  - *Interfacial localization*
  - *Stable*
  - *Long-lived*
  - *Remove & replace*
- *Apparatus*
  - *Maximize surface/volume*
  - *Minimize pressure loss*
  - *Avoid foaming*
  - *Avoid dead & flood zones*
- *Carrier fluid*
  - *Maximize capacity*
  - *Minimize corrosiveness*
- *Energy*
  - *Minimize total energy*
  - *Minimize use of high value energy - plant derating*
  - *Maximize plant independence*
- *Water*
  - *Minimize usage*
  - *Maximize recycle*

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Facilitated Absorption Design Options

Chemically Facilitated Absorption CO_2 Capture Method Options

	Chemistry	Description	Intermediate	Mass Transfer	Surface Area (m^2/m^3)	Operation	Energy	Cost	Benefit	Format
Enzyme	Interfacial catalyst + Bulk ionic carrier	Liquid Membrane w/ Immobilized Catalyst	Carbonates	Liquid membrane with immobilized catalyst - HFCLM	600 - 3000	Continuous	Vacuum Swing (VSA)	Vacuum; CO_2 recovered at <1atm	Minimal pumping; single vessel	Liquid Membrane
Enzyme	Immobilized catalyst + Bulk ionic carrier	Immobilized Catalyst / Bulk Fluid Desorber	Carbonates	Absorber/Stripper Tower	300	Continuous	Temperature Swing (TSA)	Low value heat	CO_2 recovered at >1atm	Tower
Enzyme	Dissolved catalyst + Immobilized buffer / ionic carrier	Bulk fluid w/ Ion Exchange beads	Carbonates	Absorber/Stripper Tower		Swing-bed	Temperature Swing (TSA)	Low value heat	CO_2 recovered at >1atm	Tower
Amine	Dissolved catalyst + Bulk ionic carrier	Modern Bulk Fluid - Mixed Amines	Carbonates or carbamates	Absorber/Stripper Tower	100 - 250	Continuous	Temperature Swing (TSA)	High value heat	CO_2 recovered at >1atm	Tower
Amine	Dissolved reactant	Bulk Fluid - Amines / Ammonia	Carbamates or carbonates	Absorber/Stripper Tower	100 - 250	Continuous	Temperature Swing (TSA)	High value heat	CO_2 recovered at >1atm	Tower
Amine	Interfacial reactant	Solid Sorbent - Carbonates or Amines	Carbonates	Liquid film "solid" bead or immobilized sorbent - beads, fibers or sheets in the gas stream	100 - 600	Swing-bed or Continuous	Temperature Swing (TSA) Pressure (Vacuum) Swing (P/VSA) Humidity Swing (HSA)	Solids handling; Vacuum; CO_2 recovered at <1atm	Minimal liquid	Film

Hybrid design achieves benefits of membranes and chemical facilitation

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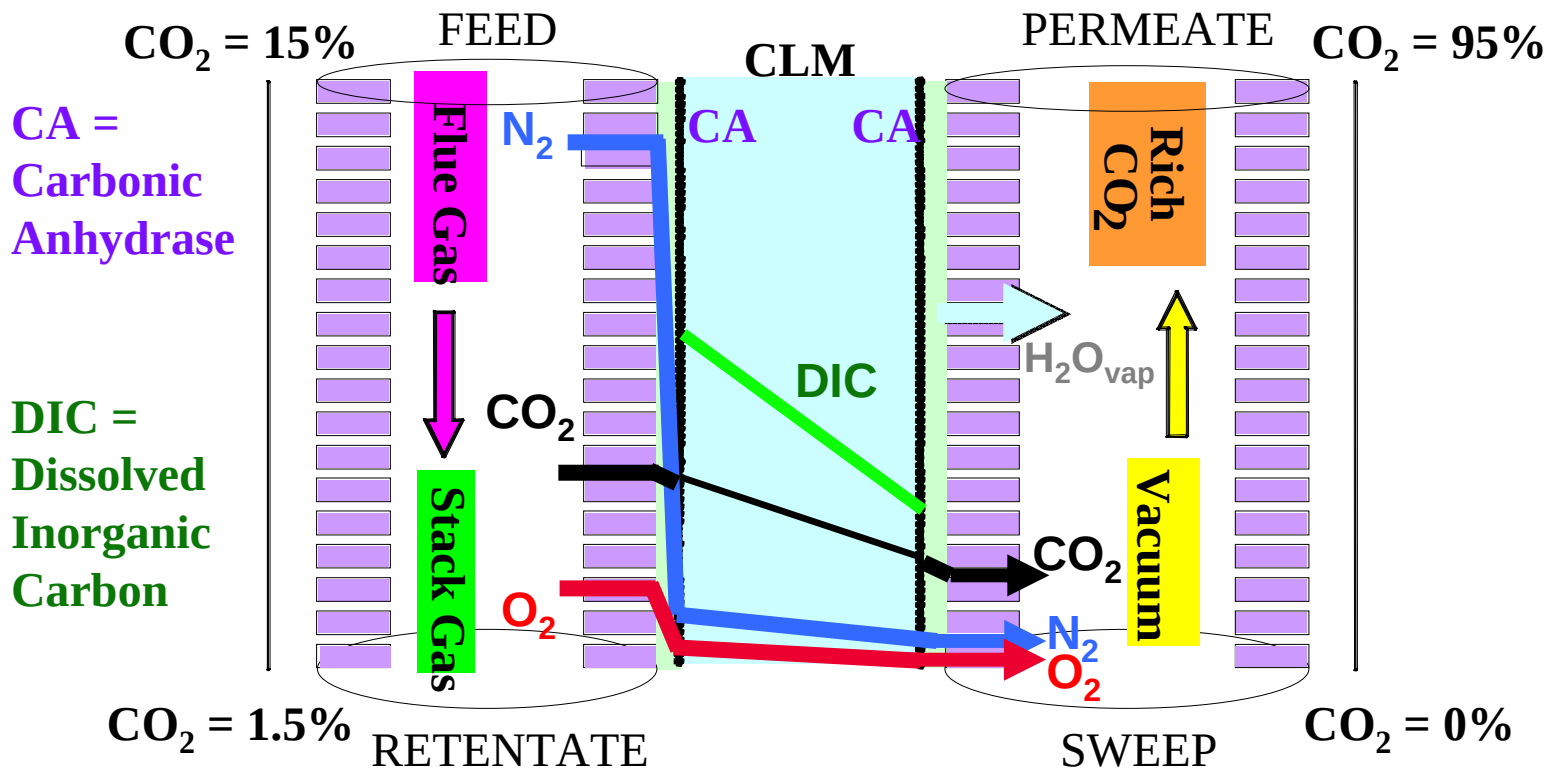
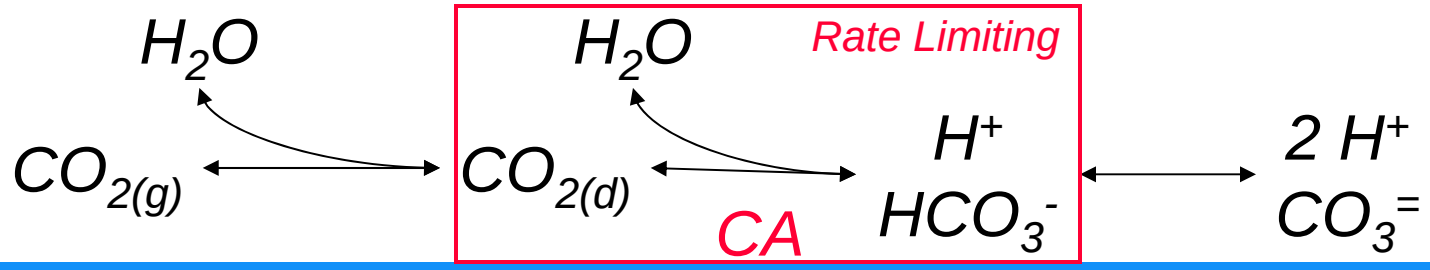
Selective Separation through a Liquid Membrane





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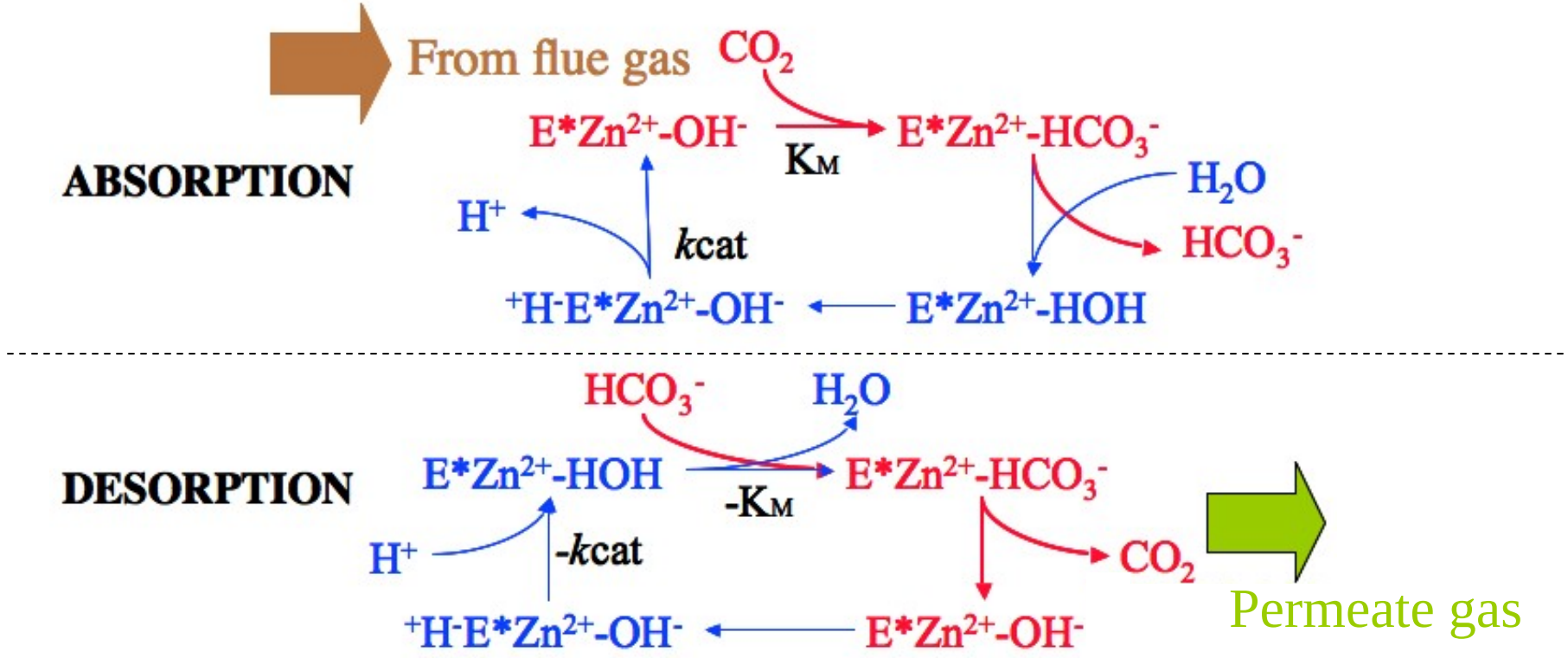
Enzyme Chemistry

Water is a solvent and a reactant

CA splits H_2O to provide an OH^- reaction center = fast absorption

CA also catalyzes the reverse reaction = fast desorption



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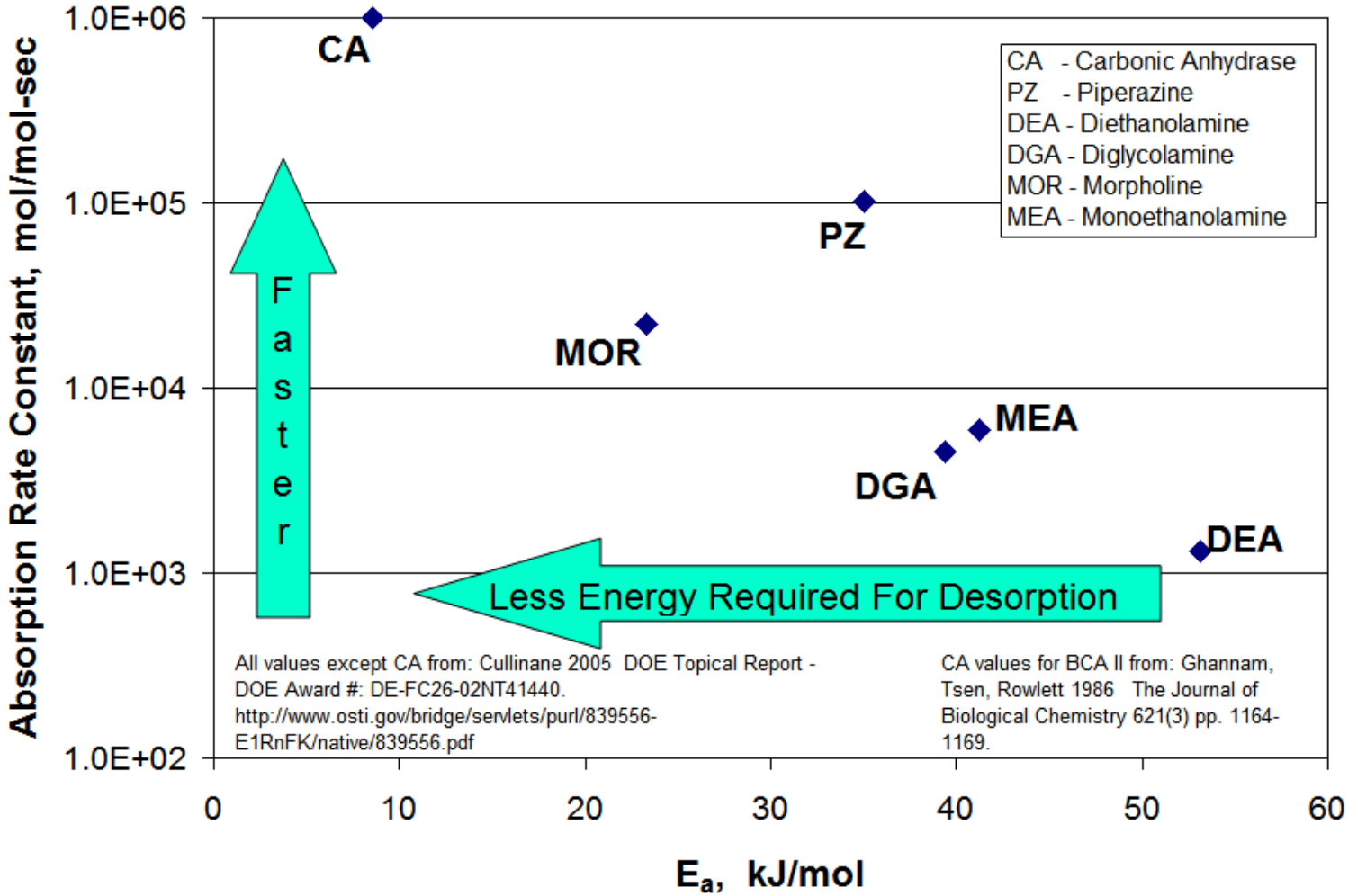
CA vs. Amine – Rate vs. Energy

CA - the most efficient, lowest energy catalyst



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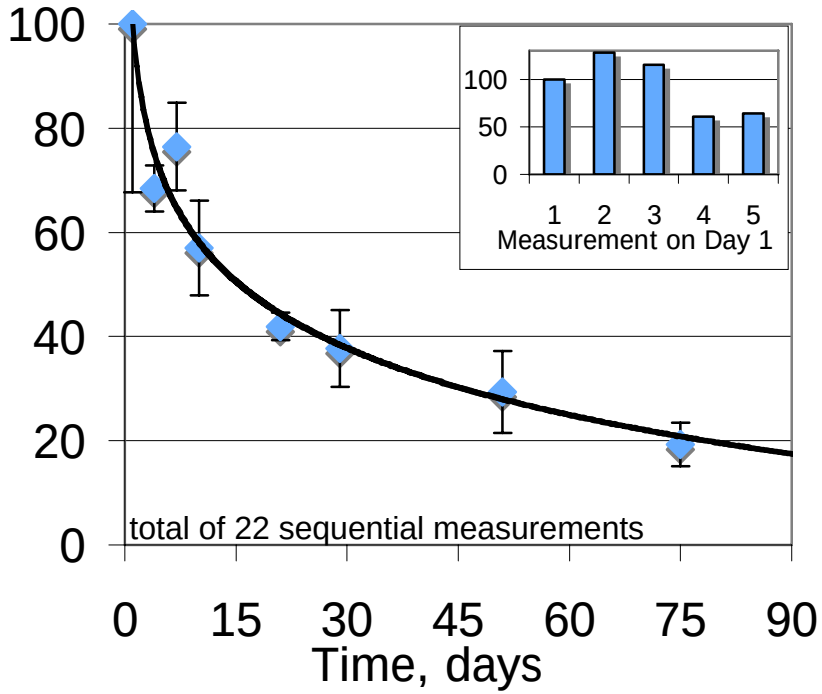
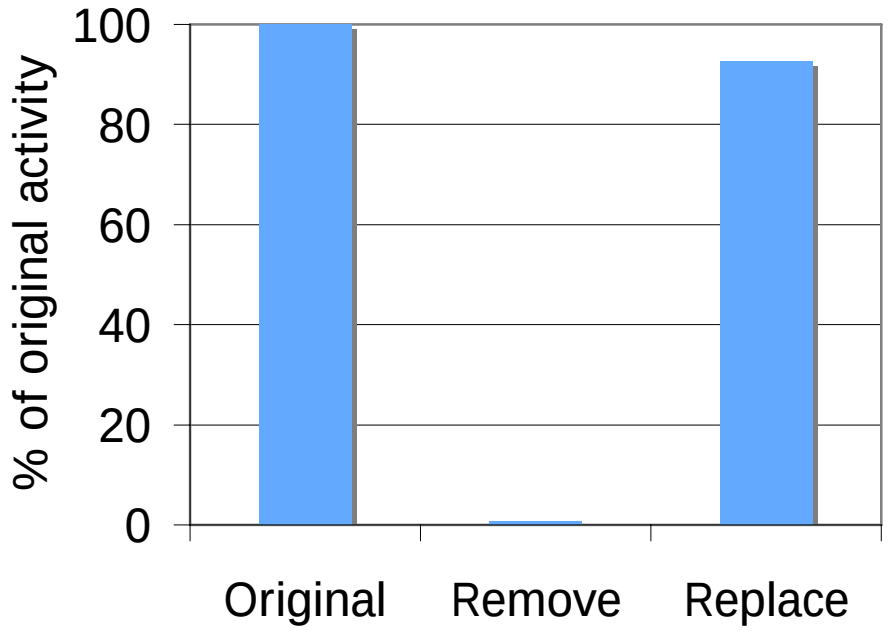
Enzyme Stability & Immobilization

Stability of Immobilized Enzyme Activity



Immobilized Enzyme Removal and Replacement



Immobilized enzyme is stable but easily managed

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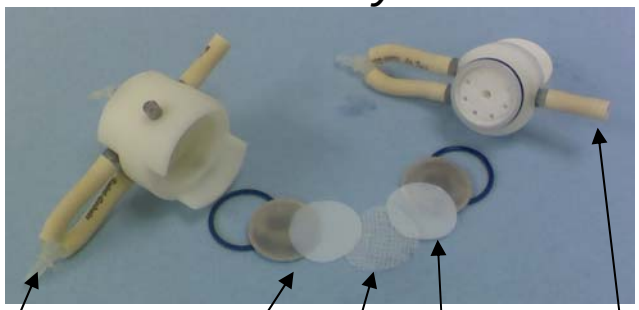
Enzyme Performance Verification

Very Small Permeator

Used to:
- *Test and select enzymes*
- *Optimize CLM chemistry*
- *Test immobilized enzyme*



feed flow path

membrane

CLM spacer

membrane

permeate flow path

Small HF Module

Used to test: (0.033 m²)
- *in-situ immobilization procedure*
- *immobilized enzyme*

Flat sheet & hollow fiber immobilized enzyme test beds

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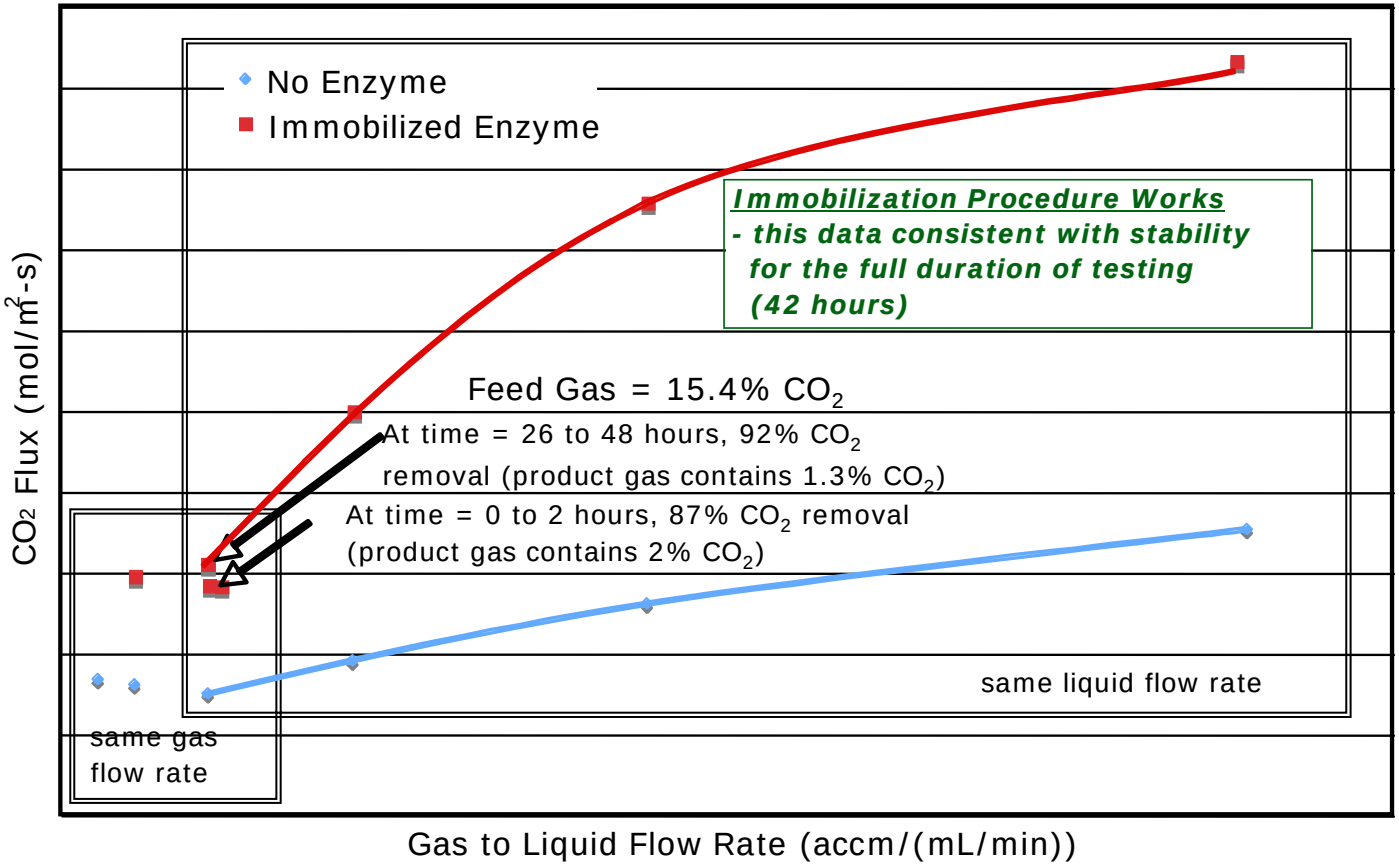
Test of Immobilized Enzyme



>150 module volumes of CLM buffer were flushed through without loss of activity

In-situ immobilization in module works and immobilization is stable

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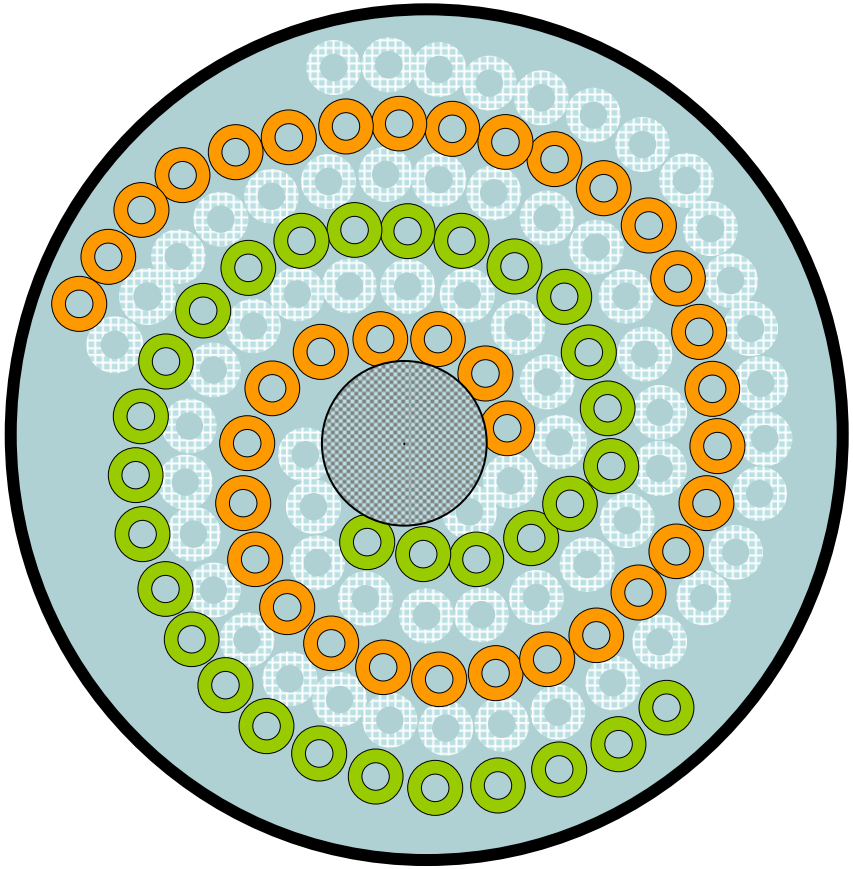
Spiral Wound Permeator



Spacer material provides controlled thickness for liquid membrane "contained" between the feed/retentate and permeate fibers

- Spacer material
- Feed/retentate fibers
- Permeate fibers
- Fabrication support

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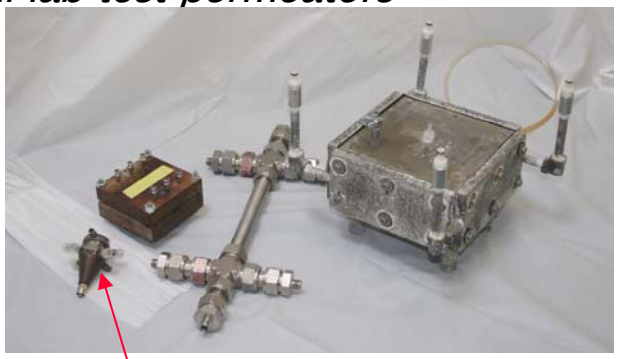
Permeator Modifications / Scale-up

BEFORE CURRENT PROJECT

Small lab test permeators

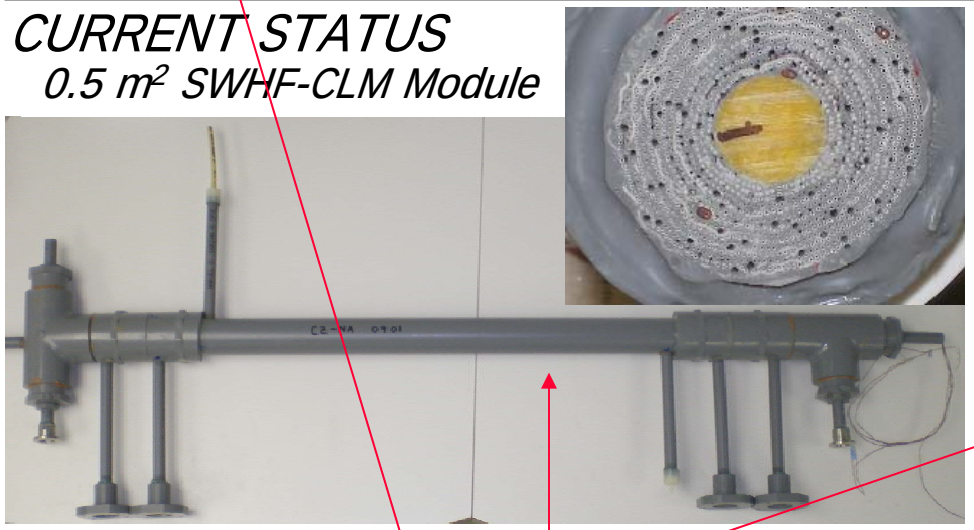


0.05 m² permeator

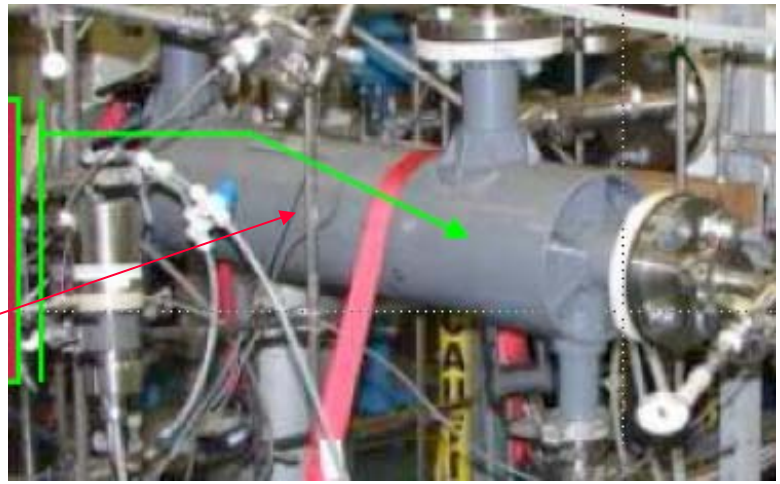
$2.8*10^{-4}$ to $1.9*10^{-1}$ m²

CURRENT STATUS

0.5 m² SWHF-CLM Module



11 m² permeator



Size increase from start: 1,768; 38,797; 162,241

46 m² module has been designed

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Test Results

- TARGET
  (DOE CCS Goals)
  - 90% removal of CO_2 from a 15% CO_2 feed
  - 95% CO_2 dry product gas
  - Flue gas at design load
  - Operating temperature near adiabatic for flue gas
  - Permeate pressure as high as possible

- OBSERVED
  (Shakedown run)
  - 85.3% removal of CO_2 from a 15.4% CO_2 feed
  - 93.6% CO_2 dry product gas
  - 45.7% of design gas load
  - Low operating temperature
  - Low permeate pressure

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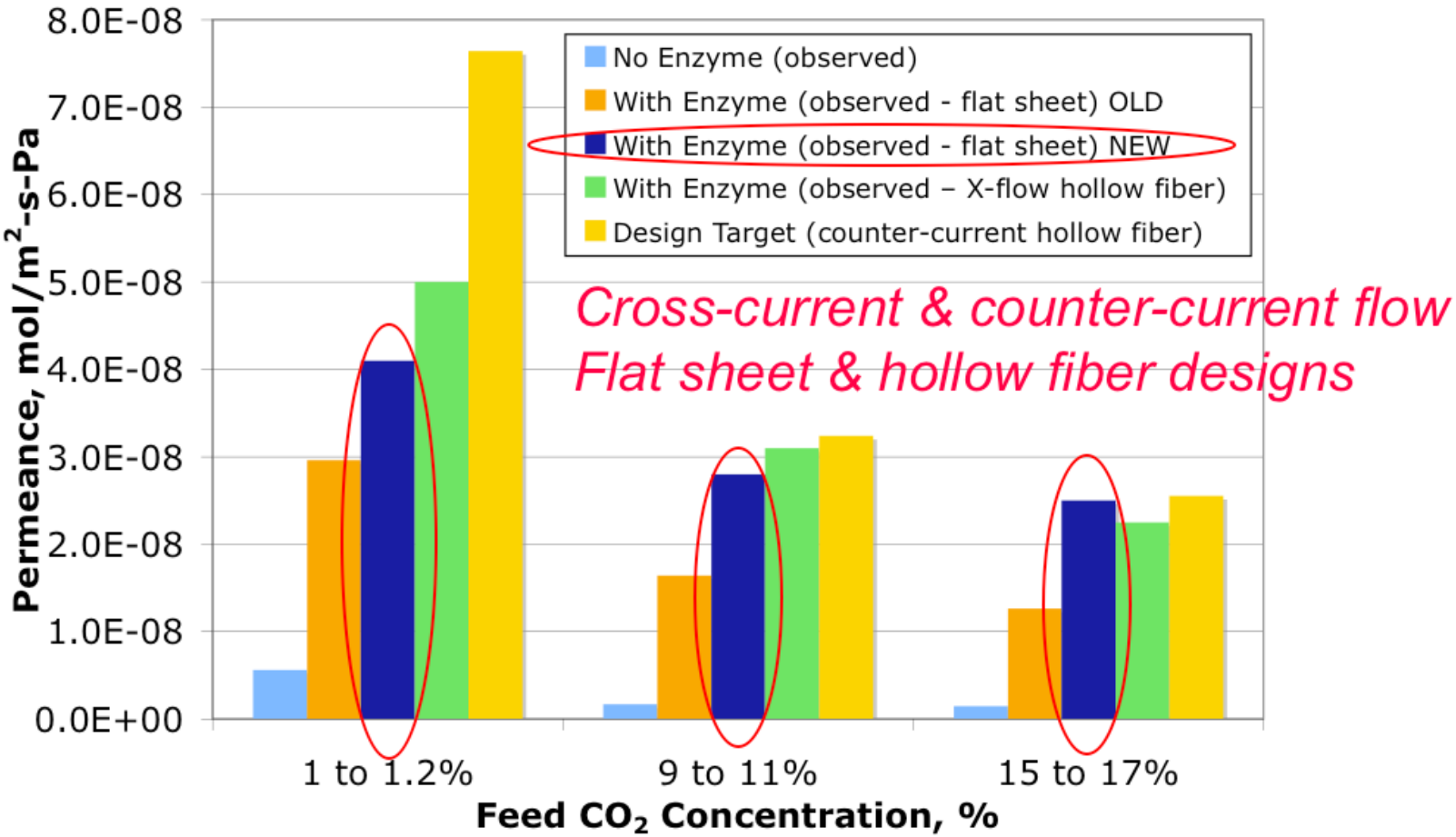
System Performance



Current enzyme performance is almost at design target

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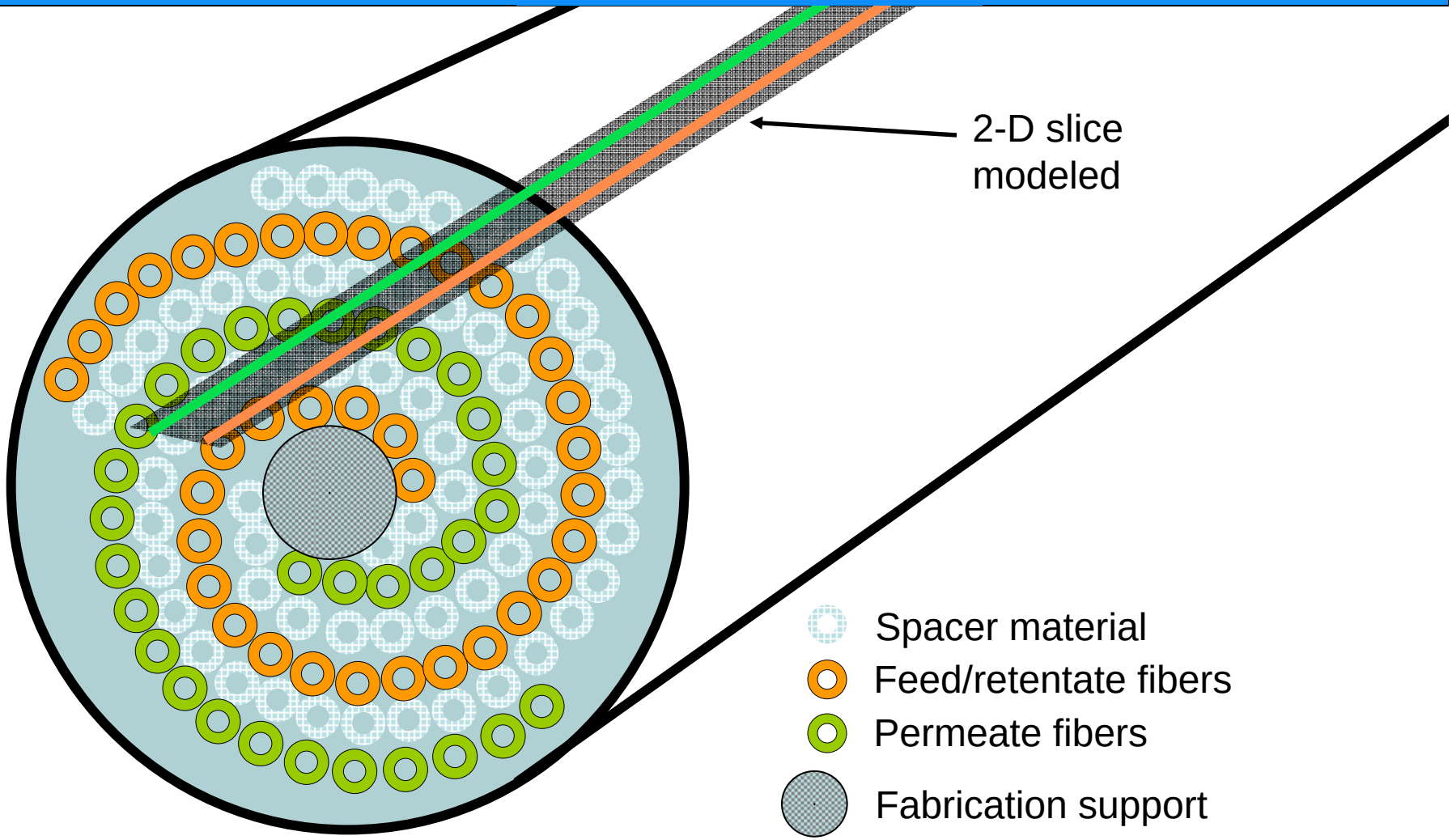
2-D model slice inside permeator



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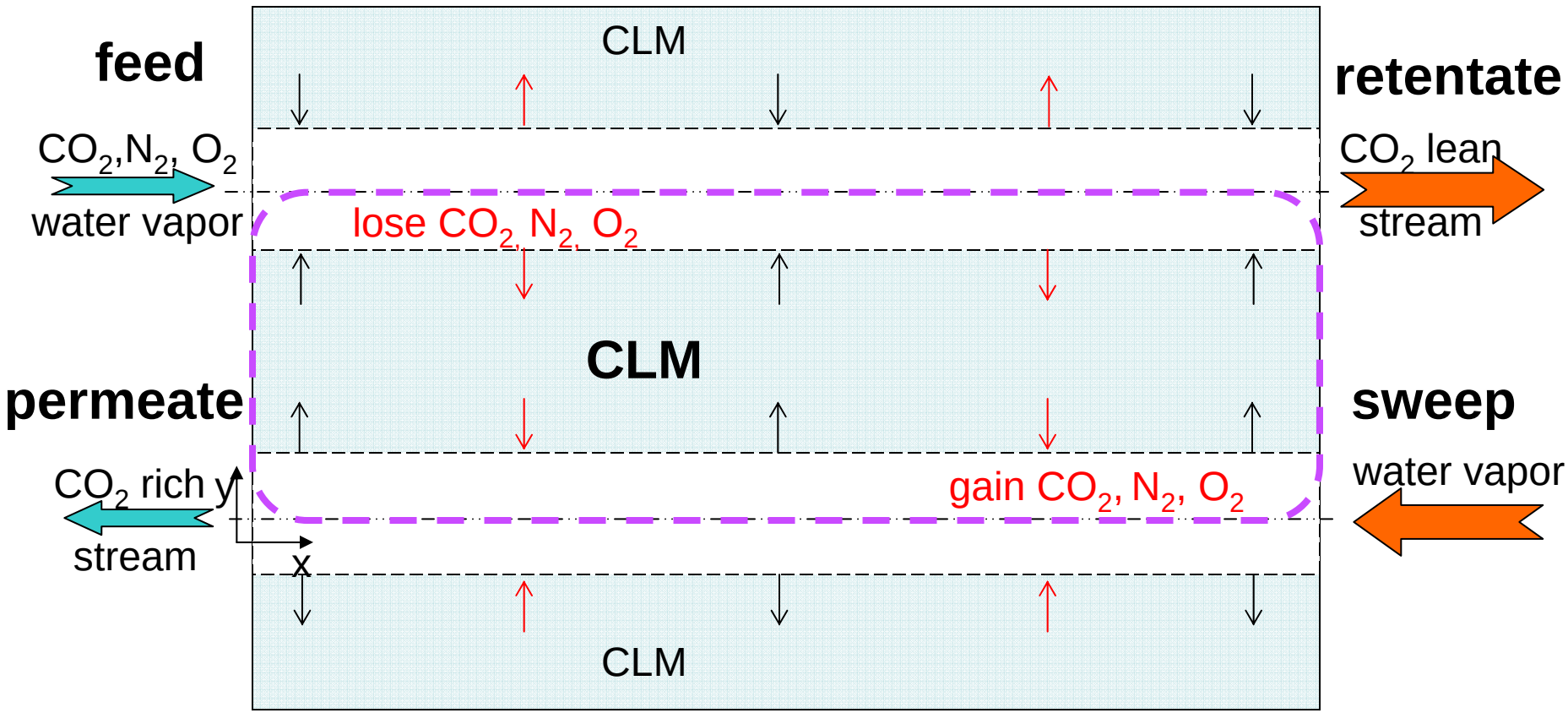
2-D Model Description



Indicates the 2-D slice modeled

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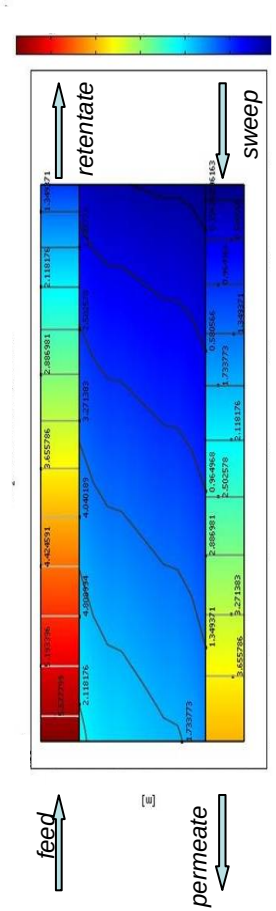
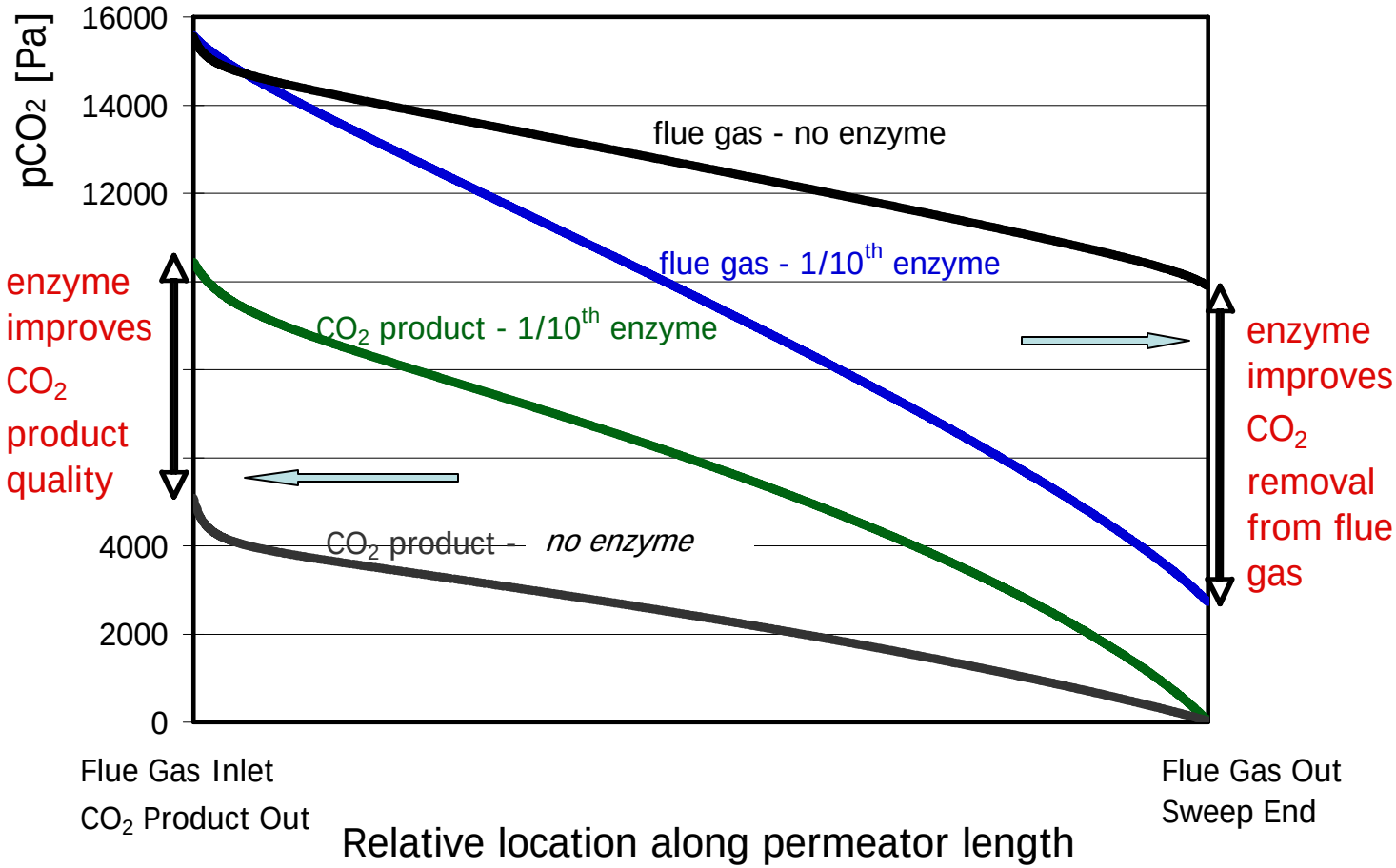
Modeling showing enzyme advantage

95% pure CO_2 product (dry)

Enzyme Concentration
1/10 Design Value

83% CO_2 removal





Counter current operation allows for high % removal and high purity permeate

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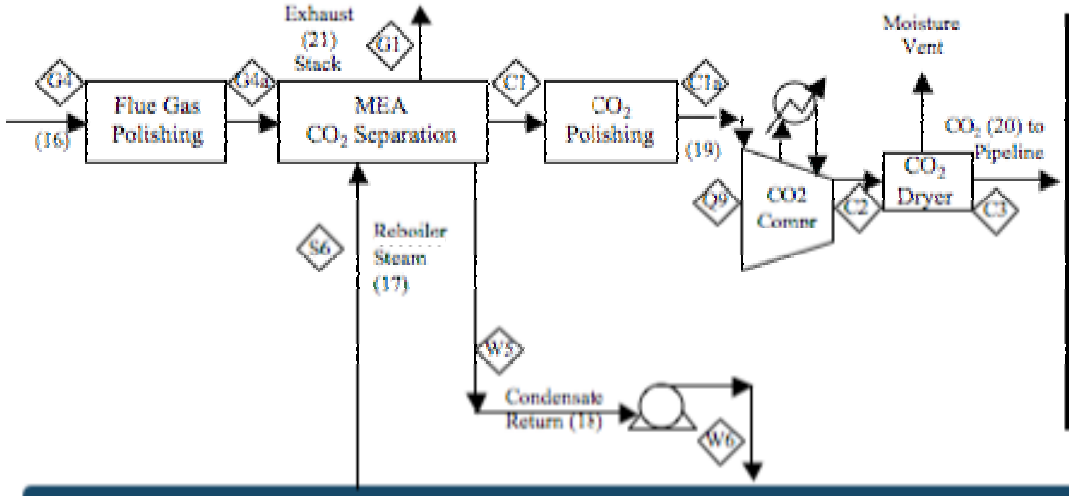
Initial Performance / Economic Analysis

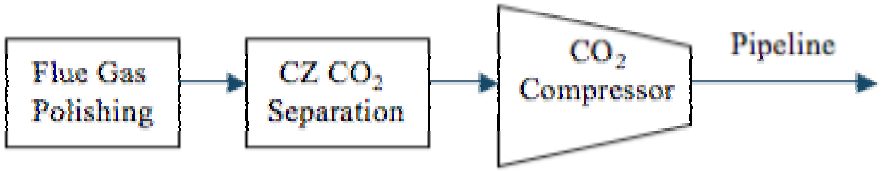
Competitors – MEA (Amine) Process Flow and Costs



MEA First Round Estimates		
Cost	Levelized	First-year
CO_2 Removal Only[1] ($/tonne)	$45.00	$41.37
CO_2 Avoided[1] ($/tonne)	$67.46	$62.02
Additional Cost of Electricity[2] ($/kWh – Net)	1.70 cents	

Source: Siemens

Carbozyme Process Flow and Costs



Carbozyme First Round Estimates		
Cost	Levelized	First-year
CO_2 Removal Only[1] ($/tonne)	~$15.00	NA
CO_2 Avoided[1] ($/tonne)	~$30.00	NA
Additional Cost of Electricity[2] ($/kWh – Net)	**1.15 cents**	

1 Total costs (OpEx + CapEx)
2 Operating costs only (excludes equipment cost)
Reference: Cost and Performances Baseline for Fossil Energy Plants, DOE/NETL-2007/1281 pgs 349, 373.

Source: CZ Internal

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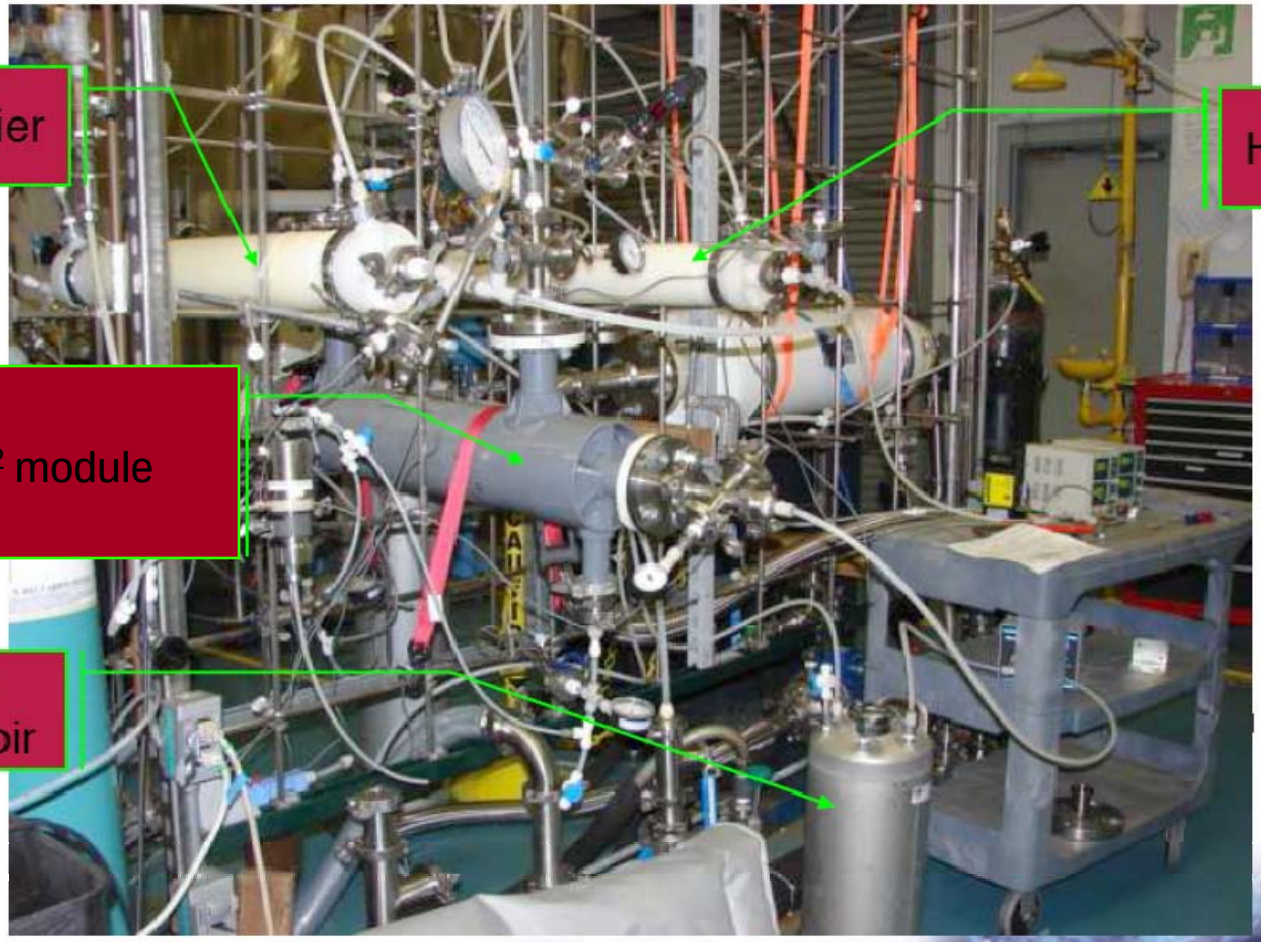
11m² SWHF-CLM Test Rig



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Scale-Up to 1t CO_2 /day capacity

Enzyme

- Fine-tune HF activation approach to ease commercialization
- Fine-tune immobilization methods for improved enzyme stability, greater retained activity, enhanced remove and replace and *in situ*
- Demonstrate 90d duration immobilized enzyme at design conditions

SWHF-CLM Scale-Up

- Assemble 11m^2 system
- Test 11m^2 system for 2,000hr using spiked natural gas
- Model system to predict and confirm performance of 11m^2 system
- Test system for 250hr for each of 3 ranks of coal - lignite, bituminous, sub-bituminous
- Analyze data and publish final report

Engineering and Economic Analysis

- Perform cost/performance analysis of 11m^2 system
- Perform cost/performance analysis of multi-module system

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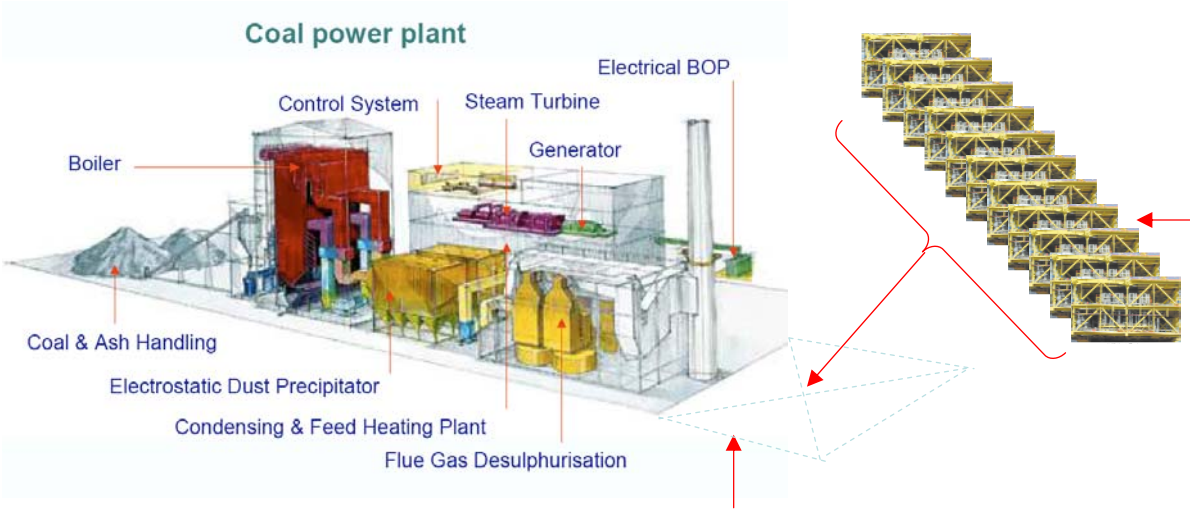
Pilot Field Test

Natco



Carbozyme Modular Skids

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Acknowledgements

- DOE Project Manager - Jose D Figueroa
- Team Members
  - Carbozyme - Robert Cowan, David Smith, Xiaoqiu Wu, Haibin Chen, Randy Reali, Yla Angso, Nikolai Kocherginsky, Burt Waxman
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  - Siemens - Dennis Horazak
  - Visage Energy - Will Johnson, Daryl-Lynn Robinson, George Hu
  - SRI - Kevin O'Brien
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