EERC Energy & Environmental Research Center

SIEMENS

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OTTER TAIL POWER COMPANY

MONTANA-DAKOTA UTILITIES CO.
A Division of MDU Resources Group, Inc.

GREAT RIVER ENERGY

Development of Biomimetic Membranes for Near-Zero Power Plant Emissions

DE-FC26-07NT43084

Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting
March 24 -26, 2009 - Pittsburgh, PA

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

DEPARTMENT OF ENERGY • UNITED STATES OF AMERICA

Argonne NATIONAL LABORATORY

Kansas State University

ELECTROSEP INC.
Advanced Electrolytic Membrane Technology

Visage ENERGY CORP.

SRI International

Cogentrix

LIGNITE

OLI systems, Inc.

NJCST New Jersey Commission on Science & Technology
NJ Commission on Science & Technology

Michael C. Trachtenberg, PhD
Carbozyme, Inc - CEO, CTO

Carbozyme Inc.

Company Background

Corporate Focus: Gas Separation, Enrichment, Capture and Processing for Applications in Energy and Environment

History	– Founded in 1995
IP	– Three patents received; over ten applications under review
Know-How	– More than a decade of know-how in CO_2 Capture
In-house Personnel	– 7 PhDs, 3 Masters, 1 PE, 2 staff
Management	– Team has prior experience with start-up technology ventures, including a successful IPO

More than a Decade of Research in CO_2 Capture

Project Overview

Funding

- *$7,031243 Total*
  - *$5,593,981 DOE Share*
  - *$1,437,262 Non-DOE Share*

Project Performance Dates

- 3/28/07 - 7/28/10

Cost Share

- Carbozyme
- Lignite Council of North Dakota
- OtterTail Power Company
- Montana-Dakota Utilities Co.
- Great River Energy
- Cogentrix
- OLI Systems, Inc.
- New Jersey Commission on Science and Technology

Project Objectives

- Demonstrate the ability of an enzyme-based, contained liquid membrane (SWHF-CLM) to extract CO_2 from a variety of flue gas streams, including various ranks of coal and natural gas
- Evaluate a state-of-the-art electrodialytic (EDI) method for CO_2 capture and compare its performance with that of the SWHF-CLM
- Carry out engineering and economic analyses / comparisons

Successful Performance = DOE target values, at least 90% separation, and 95% purity in the captured flue gas stream with a COE of less than 35%

Carbozyme

Solutions for Affordable Clean Energy™

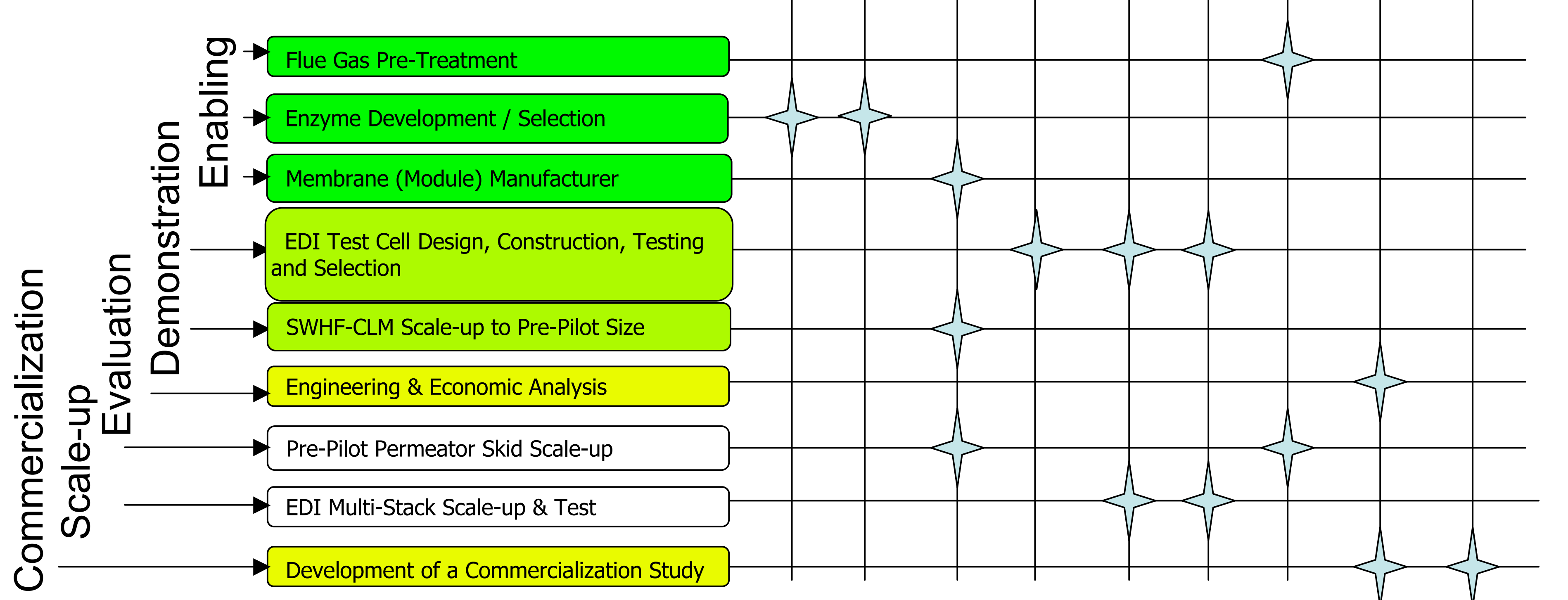
Project Participants

Michael Trachtenberg
Technical Manager / CTO

- *Technical management*
- *Technical reporting*
- *Outreach*
- *R, D & E*

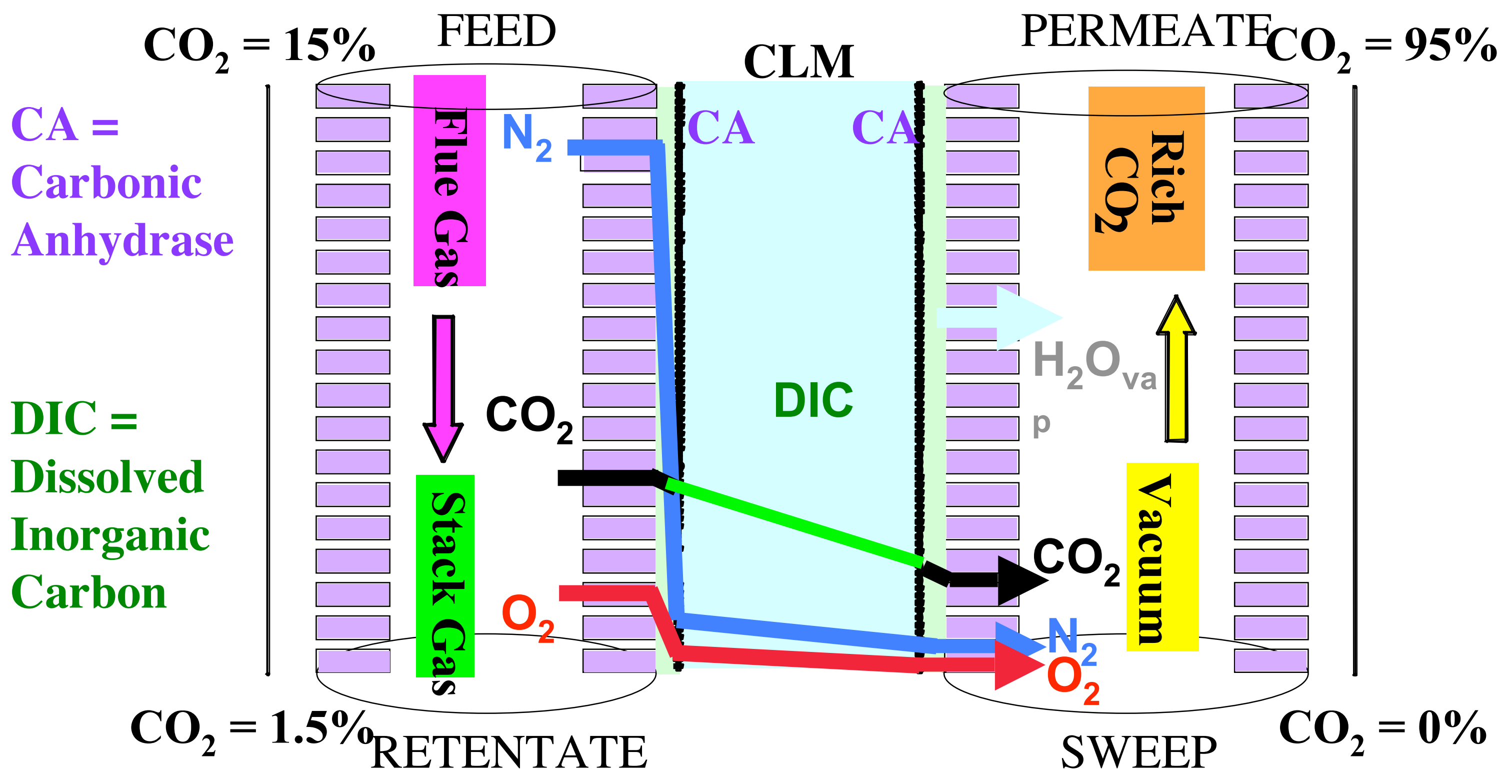
Ira Sider
Program Manager

- *Budget*
- *Contracts (Management)*
- *Management reporting*
- *Planning*
- *Weekly reports*



Technology Fundamentals & Background

Permeance selective separation through a liquid membrane

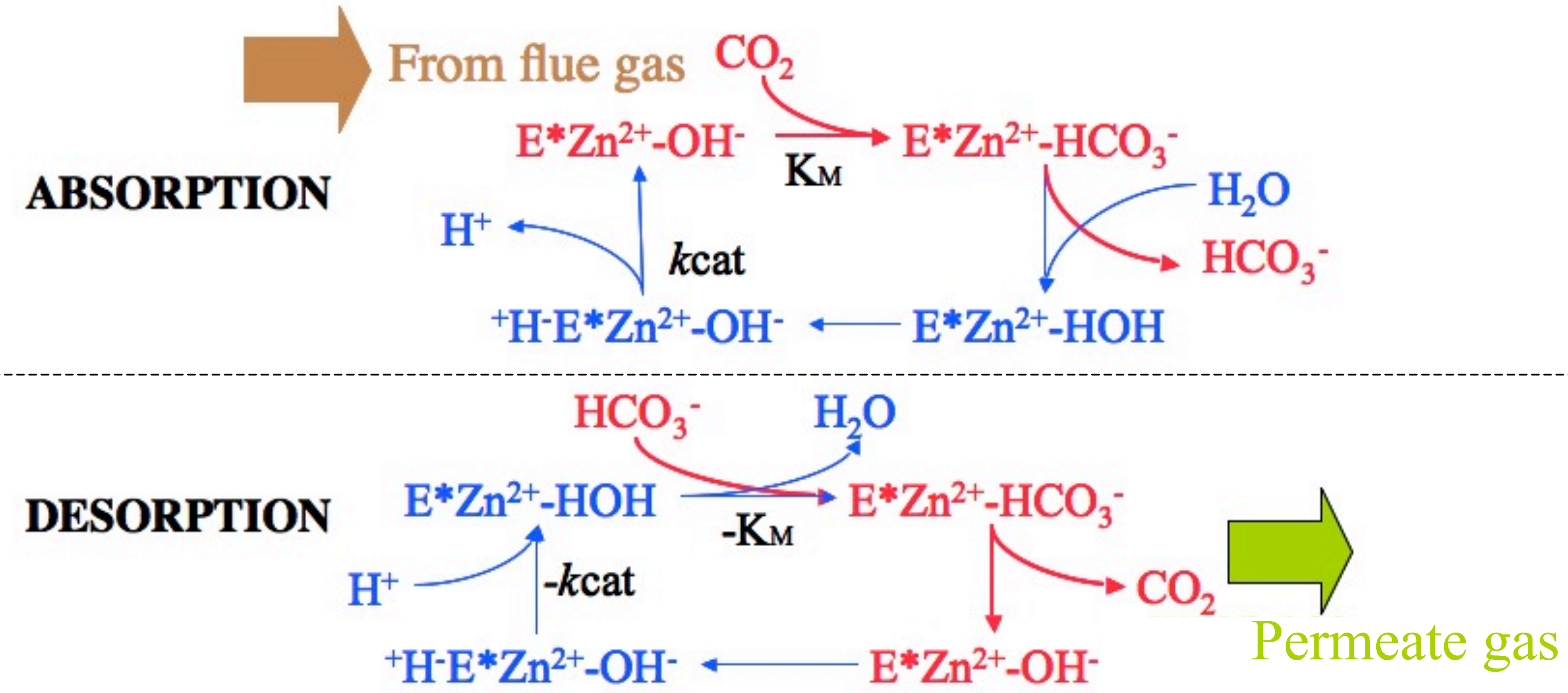


$$CO_{2(g)} \overset{H_2O}{\longleftrightarrow} CO_{2(d)} \underset{CA}{\overset{H_2O}{\longleftrightarrow}} \begin{matrix} H^+ \\ HCO_3^- \end{matrix} \longleftrightarrow \begin{matrix} 2\,H^+ \\ CO_3^= \end{matrix}$$

Carbozyme Inc.

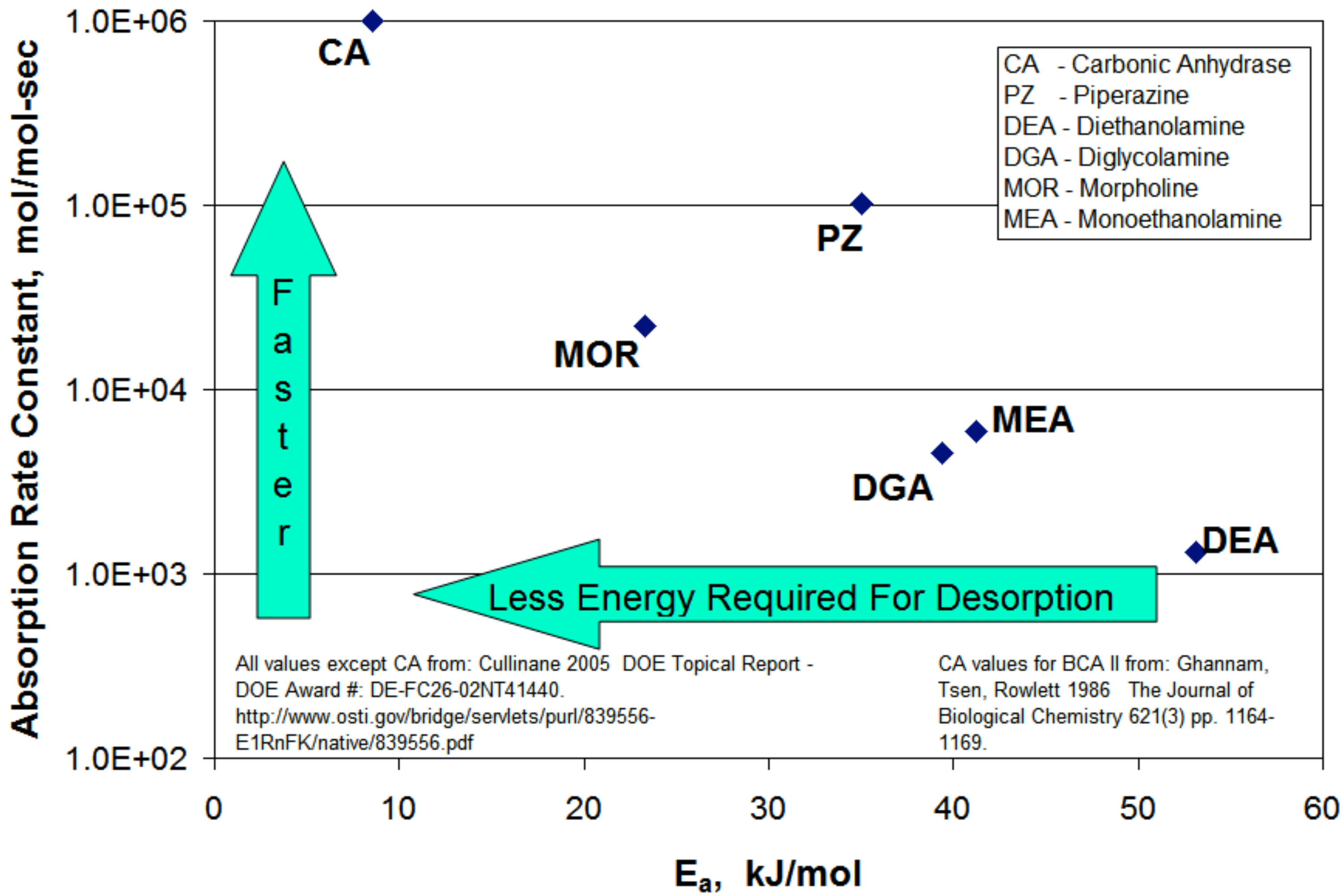
CA splits H_2O to provide an OH^- reaction center = fast absorption

CA also catalyzes the reverse reaction = fast desorption



CA vs. Amine – Rate vs. Energy

CA - the most efficient, lowest energy catalyst

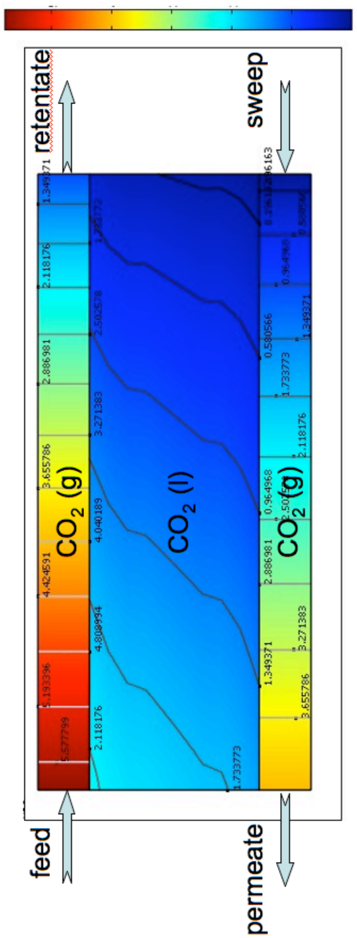


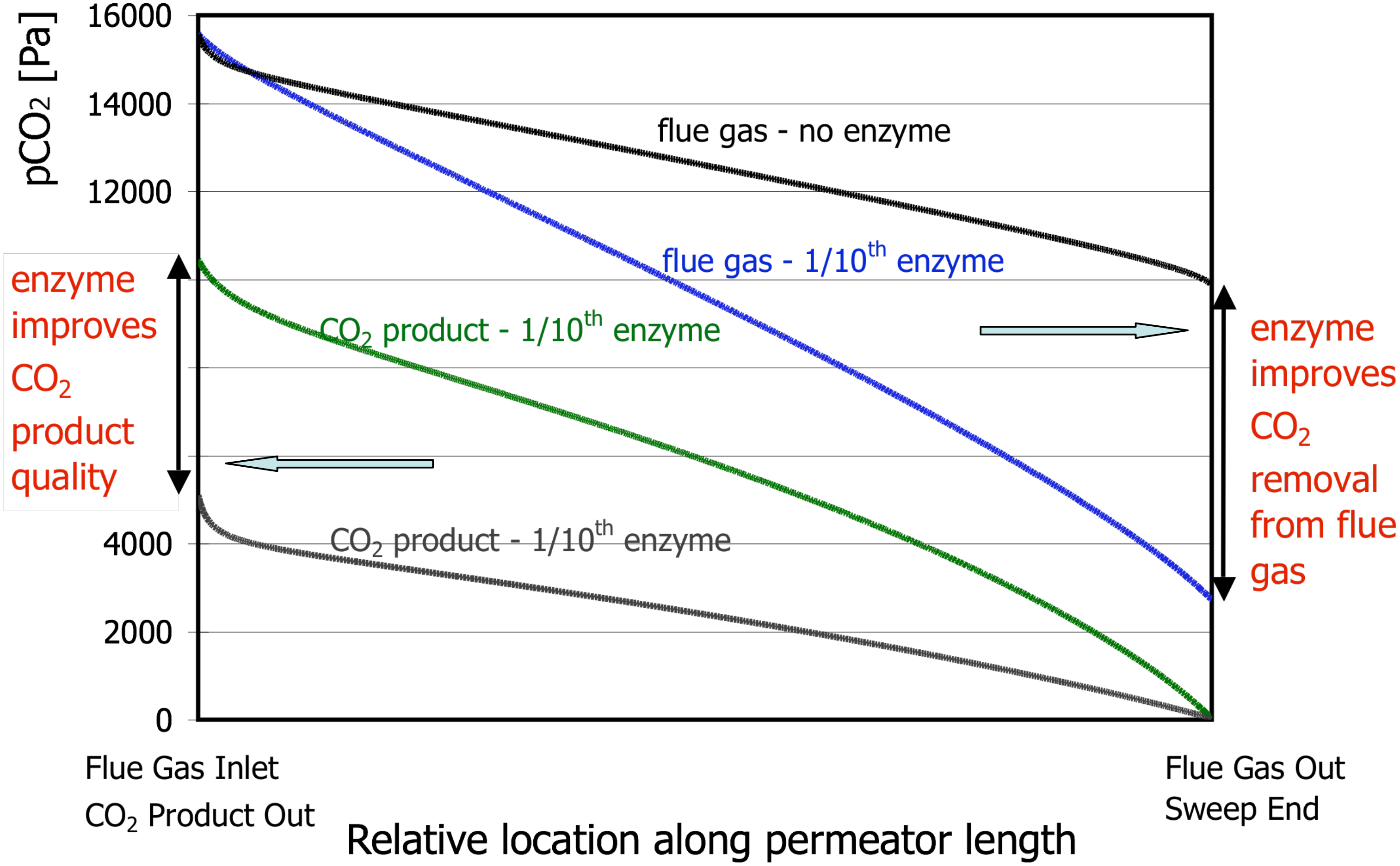
Enzyme Advantage

95% pure CO_2 product (dry)

Enzyme Concentration
1/10 Design Value

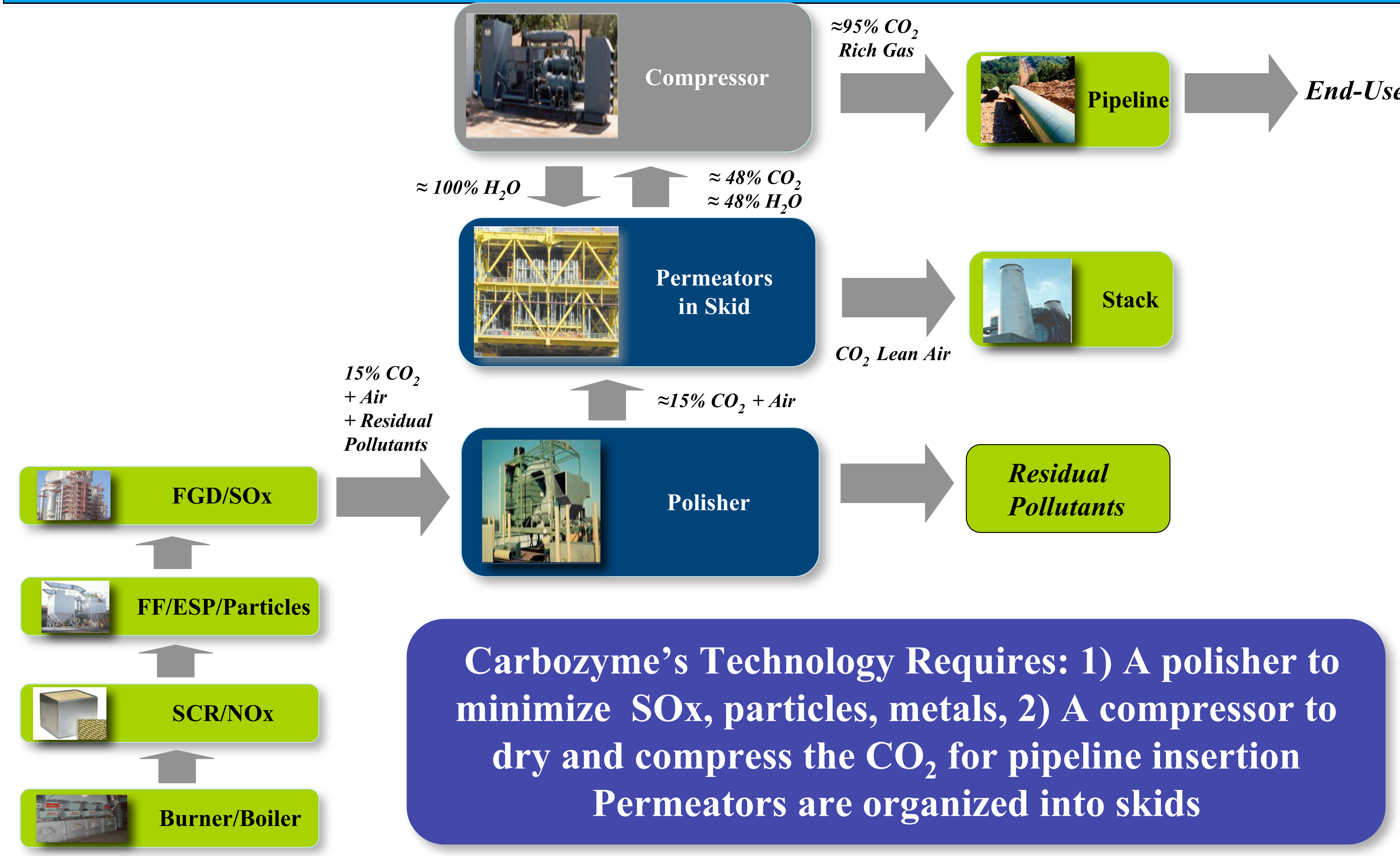
83% CO_2 removal





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

Process Overview

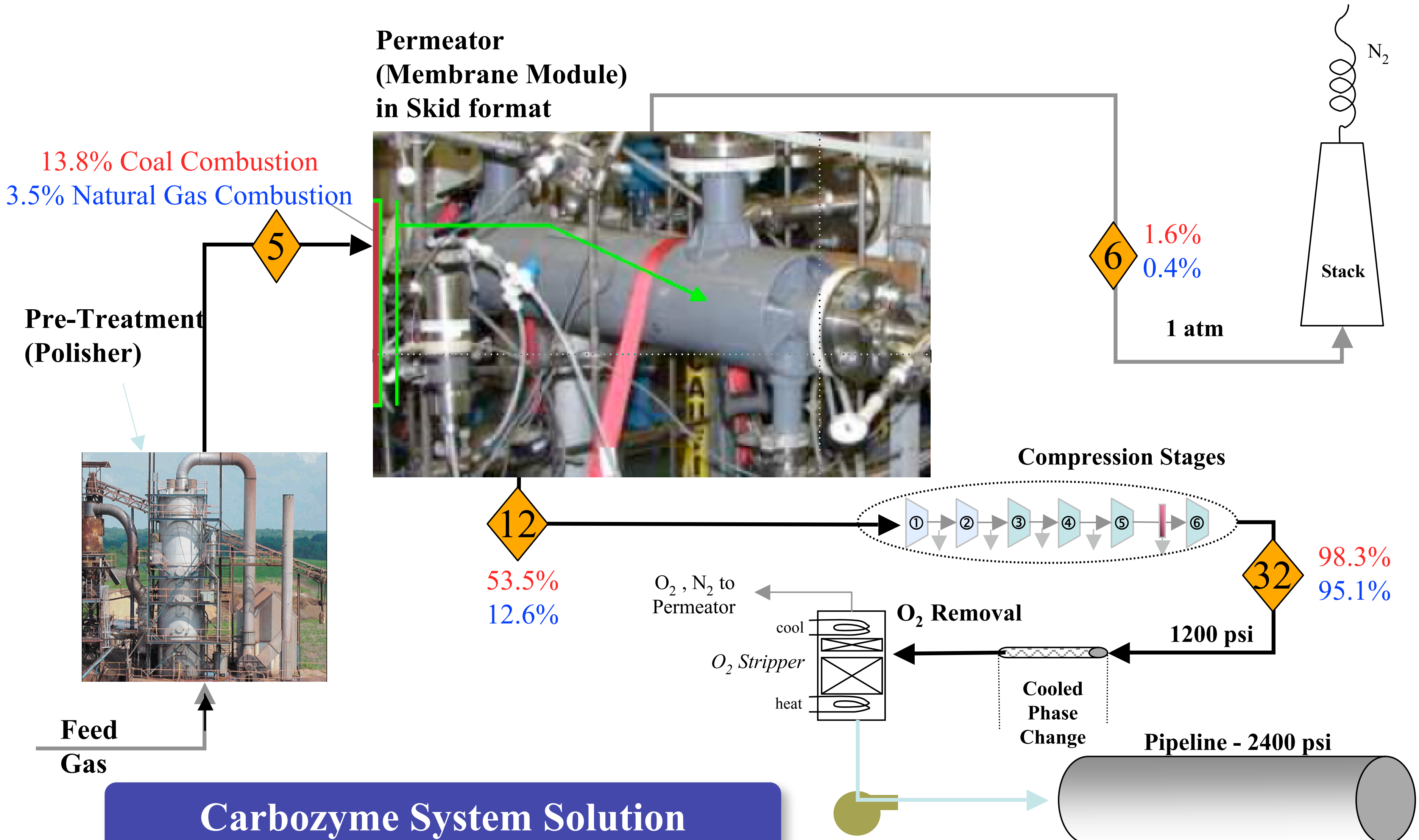


Carbozyme's Technology Requires: 1) A polisher to minimize SOx, particles, metals, 2) A compressor to dry and compress the CO_2 for pipeline insertion
Permeators are organized into skids

Key Components

- Polishing scrubber to remove SO_X to <7 ppmv
  - wet lime scrubber operated at near atmospheric pressure
  - Temperature = adiabatic quench temperature for flue gas (c.a. 50 - 55°C)
- SWHF-CLM Module to capture CO_2
  - Operated at temperatures within 10 - 15°C of the adiabatic quench temperature of the flue gas
  - Flue gas side operated at near atmospheric pressure with low pressure drop (~5 kPa)
  - Product CO_2 side operated at vacuum (pressures near 25 - 35 kPa) and low pressure drops
- Polishing and Compression - TBD

CO_2 Scrubber - Detailed Process Flow



Carbozyme System Solution

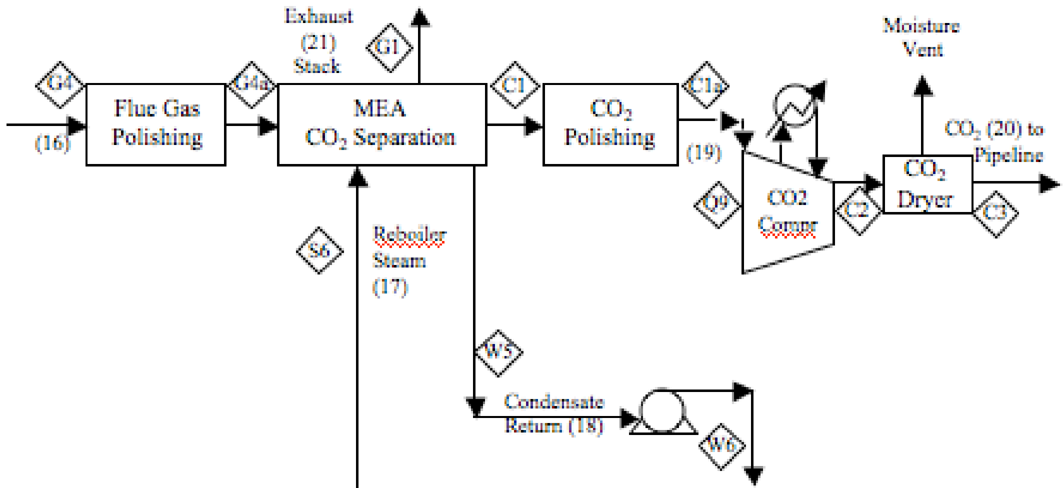
Advantages

	Importance
Enzyme Catalyst/Chemistry	▪ Environmentally safe - no use of toxic chemicals and no harmful by-products ▪ Enzyme catalyst greatly speeds the production of CO_2 at very low energy ▪ Enzyme is not subject to oxidation or formation of stable salts ▪ CLM has low nitrogen and oxygen solubility enhancing separation and purification
Mass Transfer Device	▪ Minimal fluid pumping, no heat exchangers ▪ Modular design allows factory manufacture ▪ Ease of installation with a wide variety of geometries and applicable to most plant footprints ▪ Scale-up is linear ▪ Very large pilot scale not needed
Energy Control	▪ Cost of CO_2 captured is less than $20 per tonne ▪ Operates over a moderate temperature range (55-65°C) ▪ Consumes 30-50% less energy relative to competing technologies ▪ System uses waste heat ▪ No high energy demanding chemicals ▪ Plant de-rating minimized ▪ Almost all water captured and recycled

CZ Technology has Sustainable Advantages Over Competing Technologies

Initial Performance / Economic Analysis

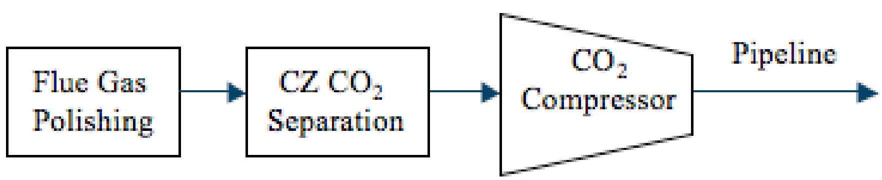
Competitors – MEA (Amine) Process Flow and Costs



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**	

Source: CZ Internal

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 .

Achievements

Area	Accomplishment
Flue Gas Stream Analysis & Conditioning	• Fabricated a polisher that exceeded acceptance requirements
Enzyme Selection	• Secured required enzyme from stable supplier
Enzyme Immobilization	• Demonstrated enzyme immobilization; remove & replace • Immobilized enzyme *in-situ*
Membrane Module	• Constructed and tested a 0.5m^2 SWHF-CLM; demonstrated performance close to DOE program objectives • Demonstrated a 0.5m^2 SWHF-CLM with immobilized enzyme • Fabricated an 11m^2 module containing spiral- bound hollow-fiber woven array sheets
Economic Analysis	• Developed an MEA base case engineering and economic analysis that can estimate overall Capex, LCOE, and CO_2 removal and avoided costs for CO_2 removal methods in SCPC plants
EDI	• Developed and tested a novel EDI cell for capturing CO_2

Critical SOPO Goals Achieved

Future Challenges

- *Production of modules (challenge and opportunity)*
  - *Potential demand far outstrips current supply*
  - *Industrial partners will need to find funding to expand manufacturing capacity*
- *Production of Enzyme (challenge and opportunity)*
  - *Cost of "purified" enzyme too high; working on methods to decrease cost of "purified" enzyme production*
  - *Fermentation capacity exists - funding for production of large batches will require commitment and funding*
- *Funding for construction of pilot plant and full scale facility*
  - *Carbozyme will have to partner with larger firms, or obtain government funds, to support the construction of future installations*

Progress and Current Status of Project

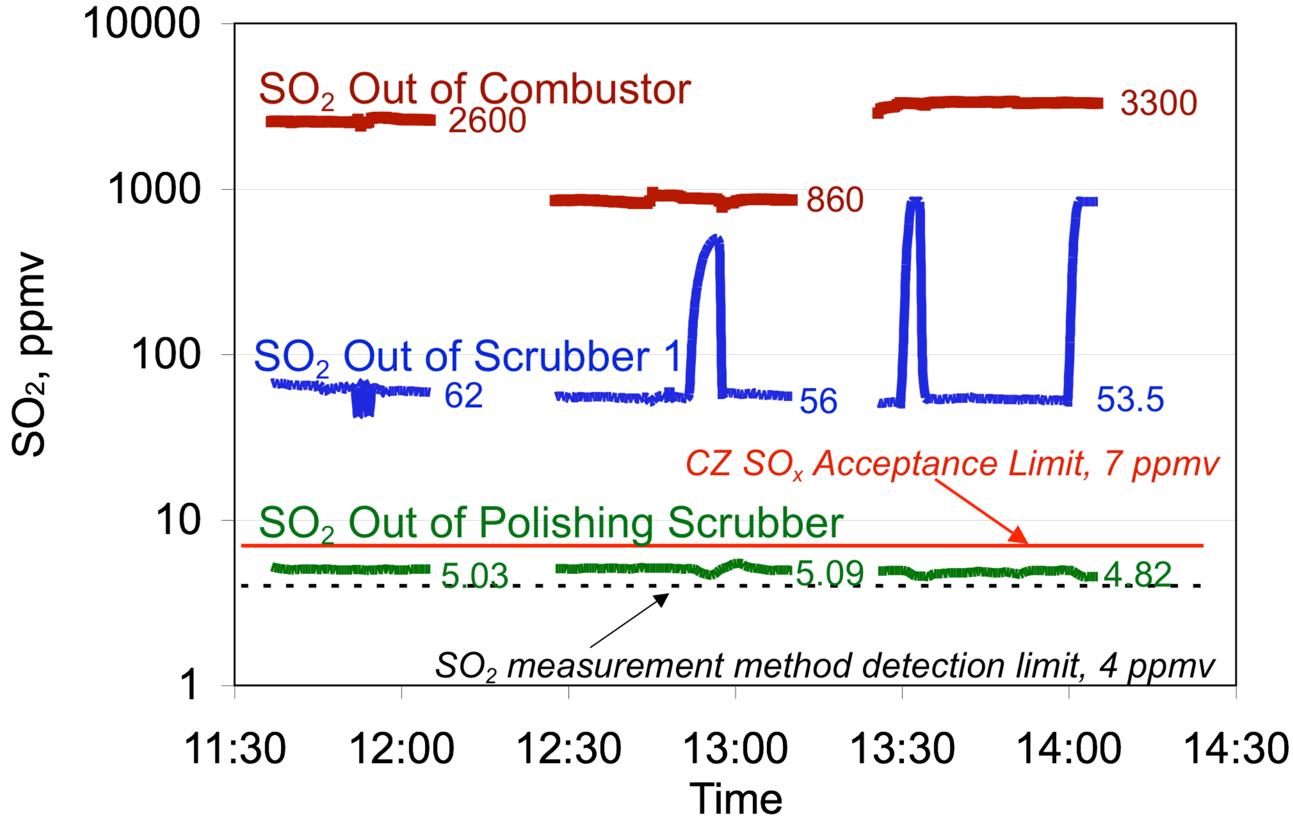
Data Acquisition and Control

- Gas Analysis
  - Extrel Questor V Residual Gas Analysis mass spectrometer
    - 16 port inlet valve
    - Custom pressure controlled inlet
    - Allows for analysis of low absolute pressure flows
    - Simultaneous analysis for CO_2, N_2, O_2, H_2O, Ar, SO_2, NO, NO_2, He

- Equipment Management
  - LabView
    - T, P, Flow, pH, Safety

EERC SOx Scrubbing

- EERC CEPS fired on SO_2 spiked natural gas to low, moderate, and high levels
- PCS on CEPS = SCR, Fabric Filter, Wet Scrubber 1, Polishing Scrubber ($CaCO_3$ slurry)



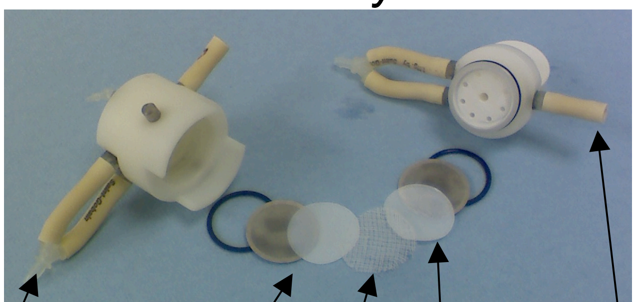
Lime slurry and ceramic Intalox saddle packing for the polishing scrubber. Packed tower used due to small scale of the test unit.

Required Performance Achieved (<7ppmv)

Enzyme Performance Verification

Very Small Permeator

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



feed flow path

CLM spacer

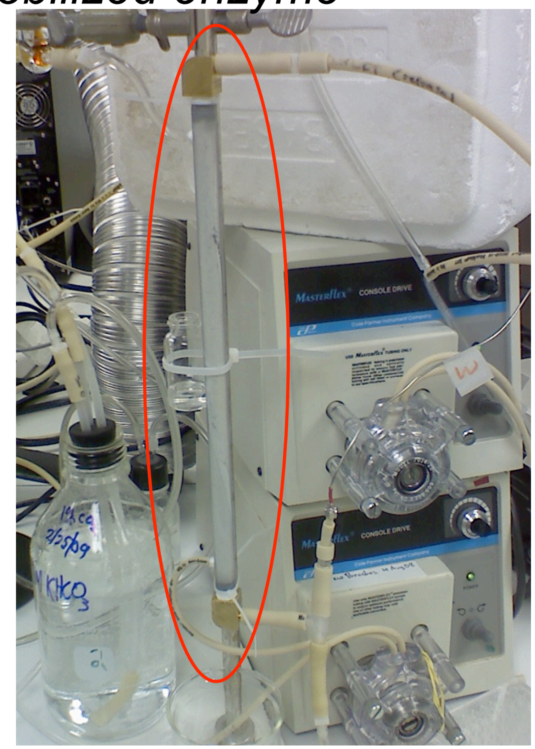
permeate flow path

membrane

membrane

Small HF Module

Used to test: *(0.033 m^2)*
- *in-situ immobilization procedure*
- *immobilized enzyme*

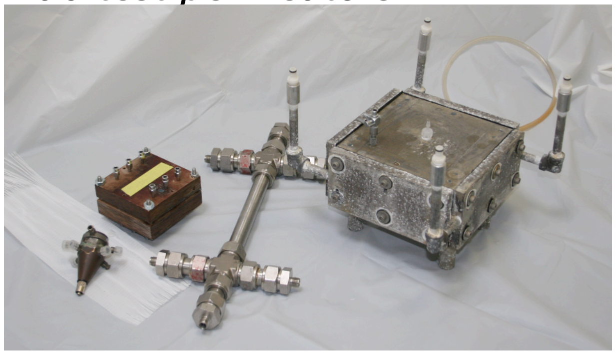


Flat sheet & hollow fiber immobilized enzyme test beds

Permeator Modifications / Scale-up

BEFORE CURRENT PROJECT

Small lab test permeators

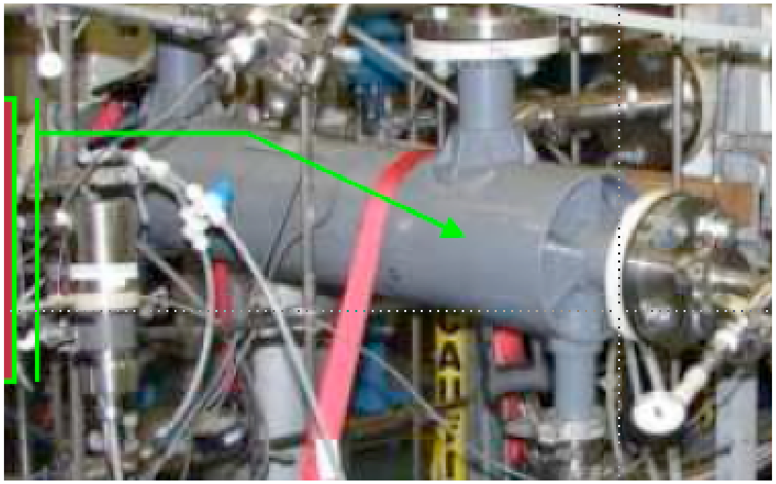


0.05 m^2 permeator

CURRENT STATUS

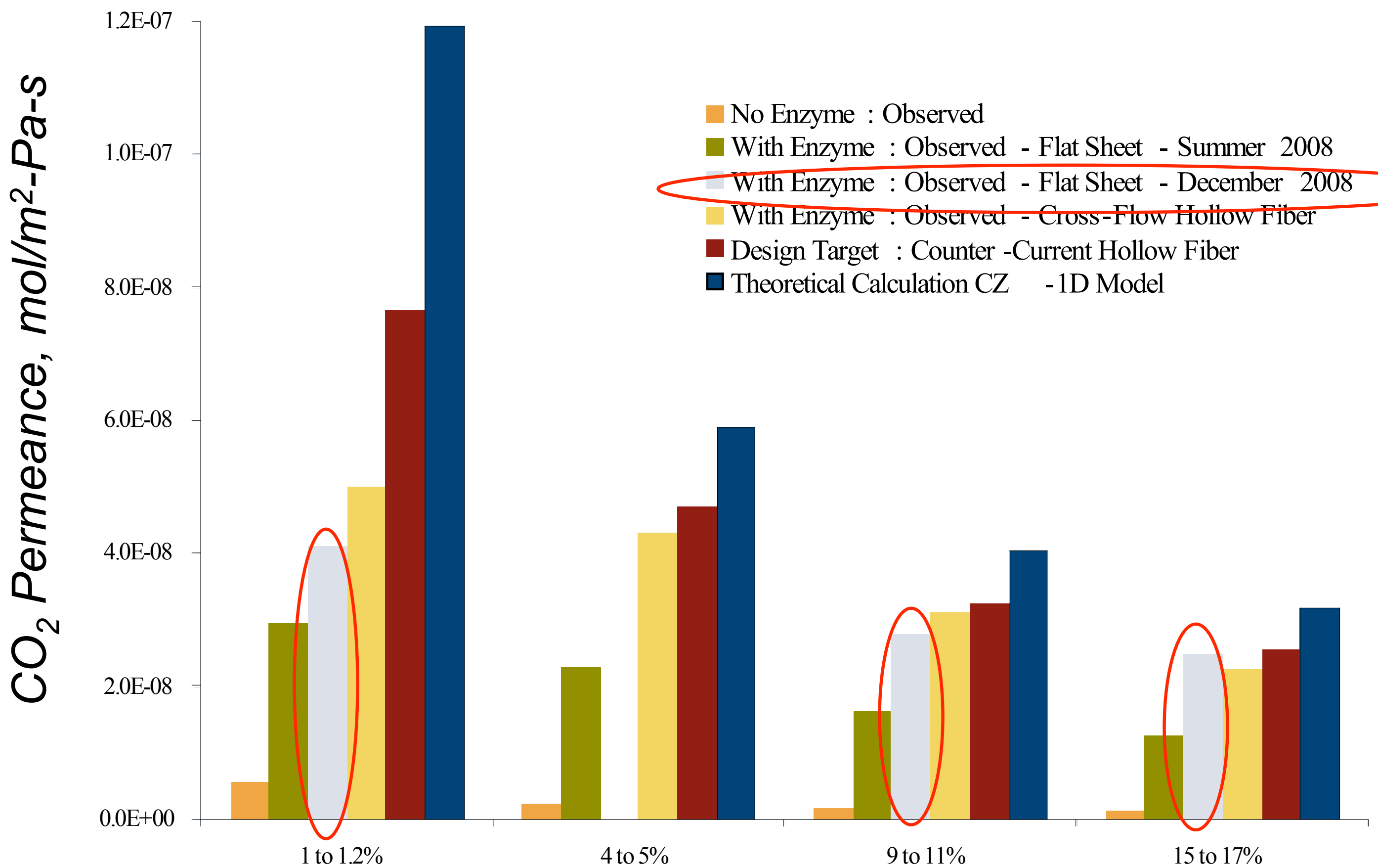
0.5 m^2 SWHF-CLM Module

11 m^2 permeator

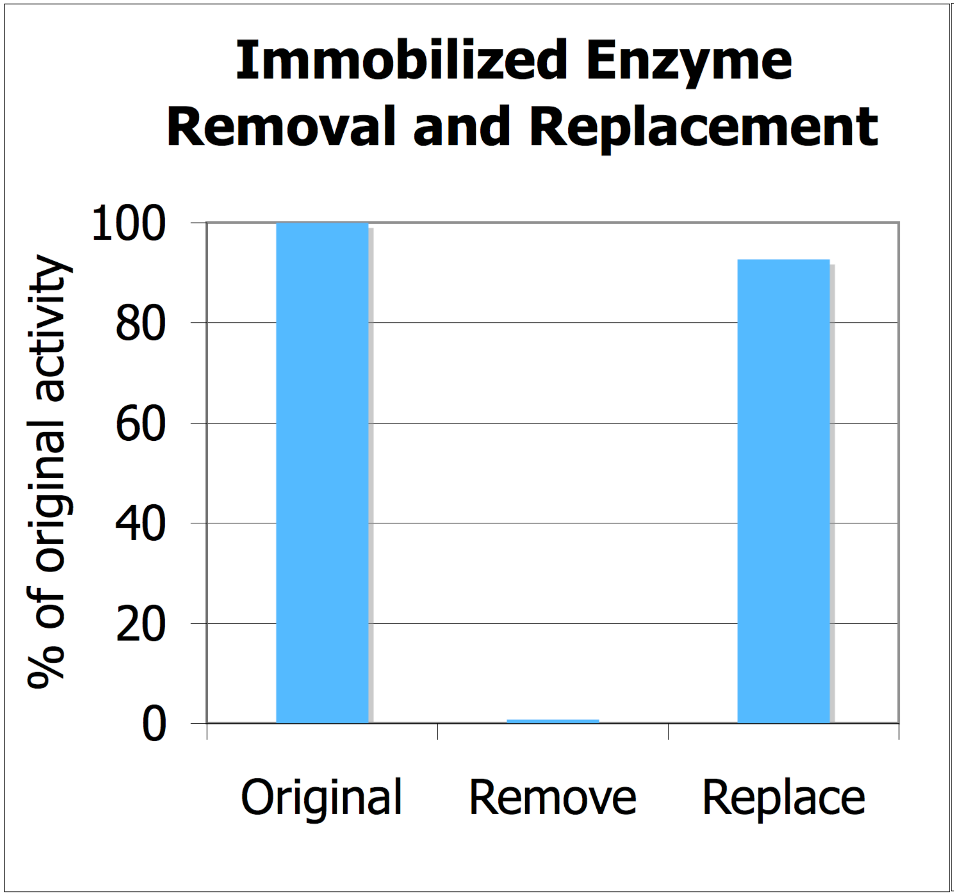


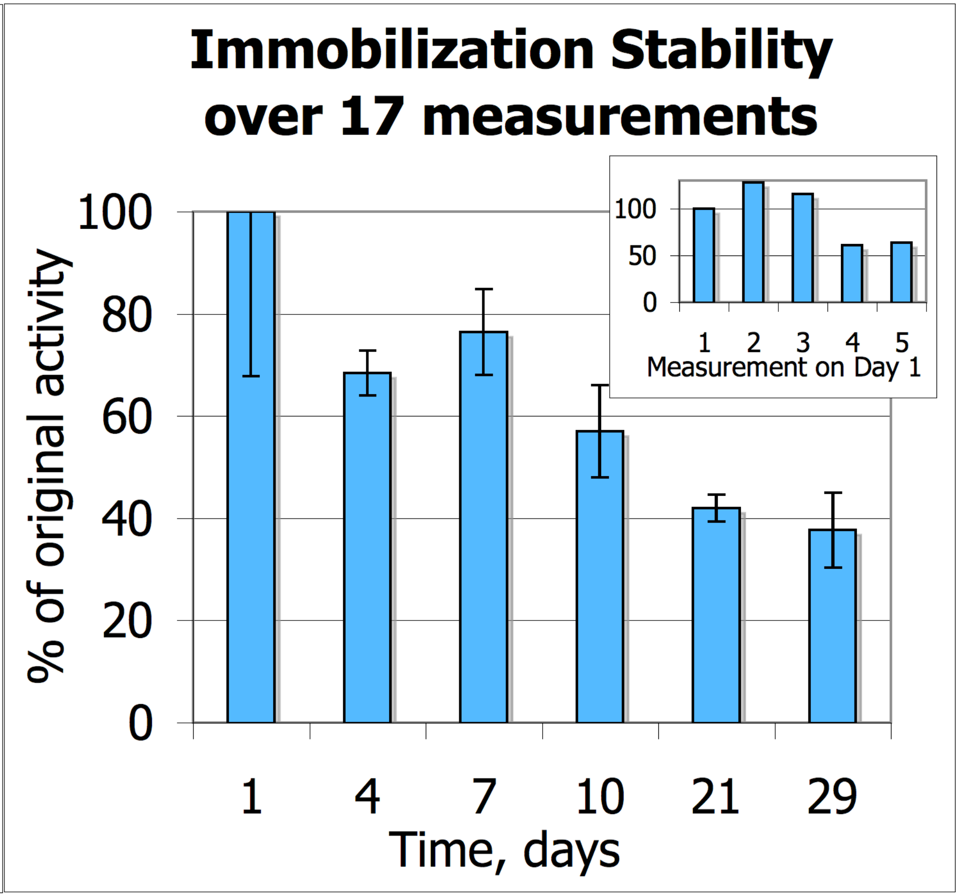
46 m^2 module has been designed

Preferred Enzyme Performance



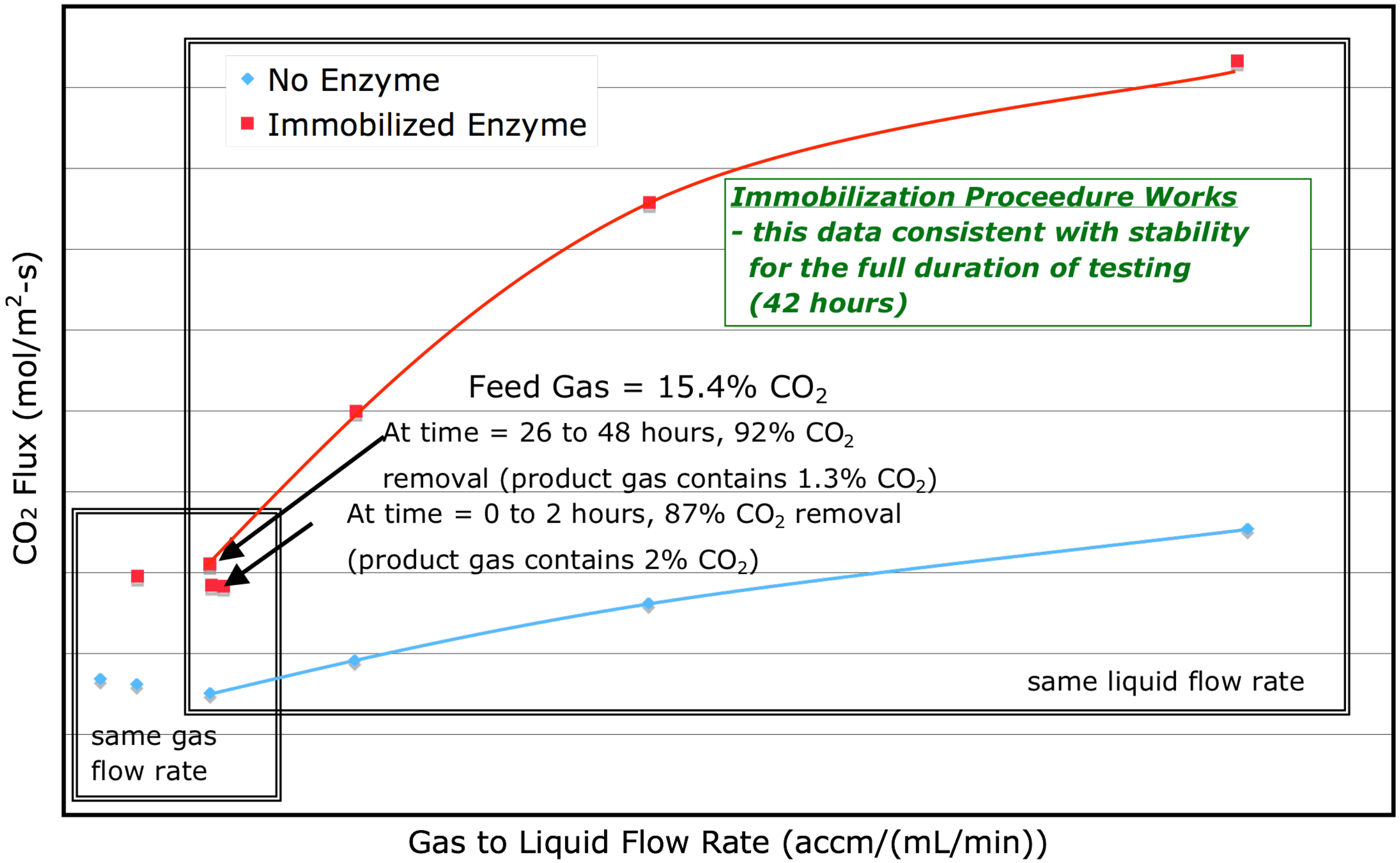
Current performance is close to design target





Immobilized enzyme is stable but easily managed

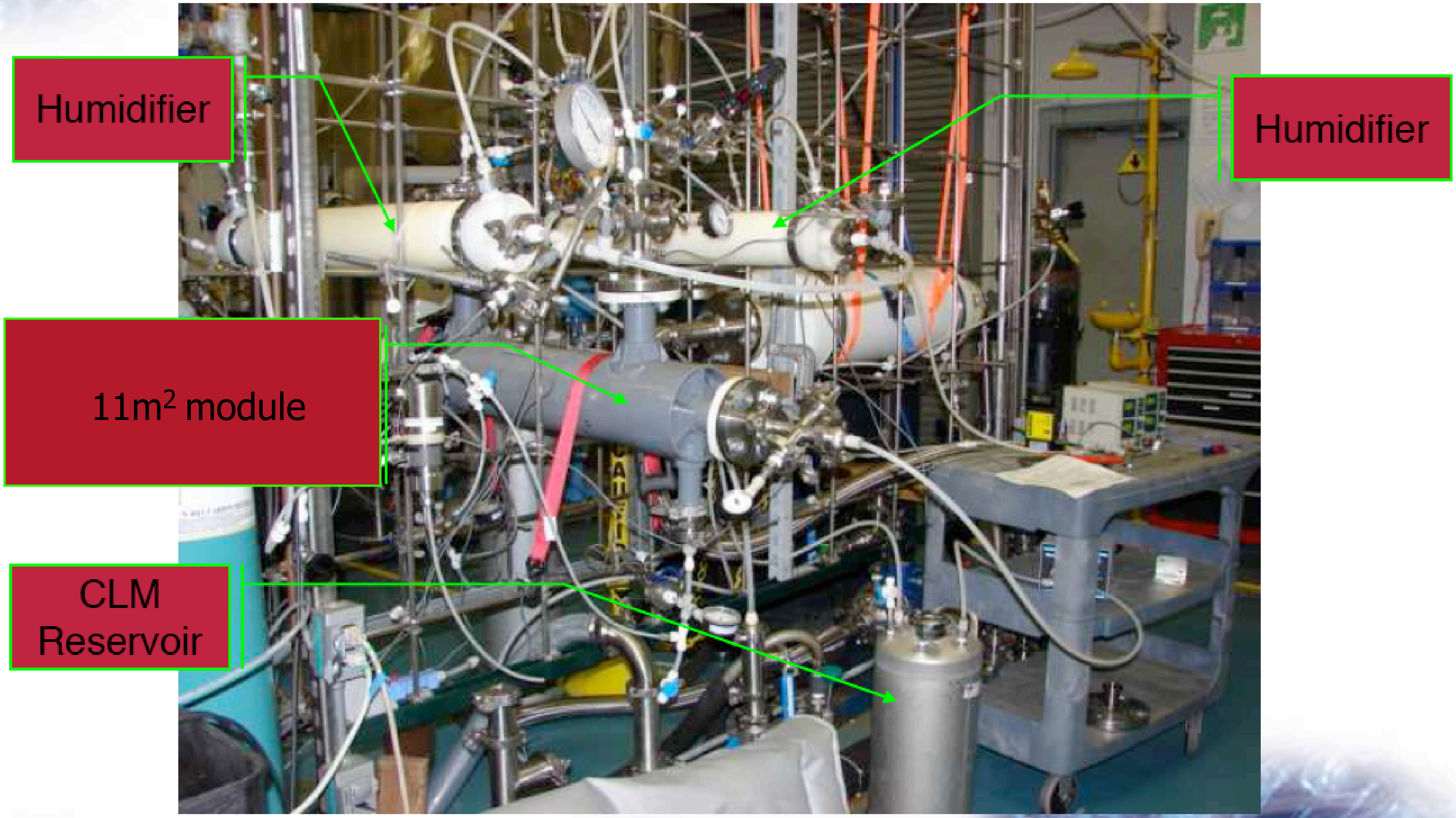
Test of Immobilized Enzyme



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

In-situ immobilization in module works and immobilization is stable

$11m^2$ SWHF-CLM Test Rig



EDI Results

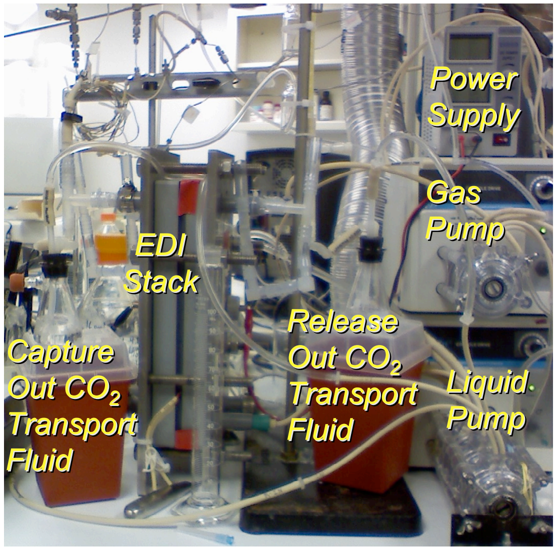
- Considered ~50 designs; Built and tested three designs
- No enzyme testing performed on 10 designs (smallest scale, 14 cm^2)
- Larger scale test rig - 195 cm^2 (14X scale-up)
- 195 cm^2 unit tested ± enzyme (at ANL and CZ)
- Demonstrated ability to obtain desired pH shifts
- Closed mass balance measurement
- Demonstrated concept validity
  - Combination of EDI and enzyme is complimentary
- Almost 90% CO_2 captured
- Patent application is in process through ANL
- Additional development is needed before EDI method for CO_2 capture is ready for scale-up

EDI Results

Run	Operation time	CO2 Adsorption Ratio	CO2 Descorption Ratio	Overall CO2 Captured	CO2 Captured Power Consumption (kWh/kg CO2)
					-
EDI w/o CA	60 min	77%	74%	56.6%	2.1
	120 min	70%	57%	39.9%	2.7
					-
EDI w/ CA	60 min	108%	69%	74%	**2.2**
	120 min	97%	92%	89%	**1.4**
	180 min	94%	83%	78%	**1.3**

- DOE – FE target is 90% capture. We are almost there after phase I of the project.
- Still need to improve electrical efficiency
  - Not close to performance expected from our models
  - We are seeking other resources to continue work

Summary for EDI CO_2 Capture and Release (steady state)			
	Relative Amount of CO_2 Produced		
Power Condition	**1**	**2**	**3**
No Enzyme			
Solution 1	1	1.2	1.67
Solution 2		1.5	2.67
Enzyme			
Solution 1	1.33	1.6	1.73
Solution 2		1.8	2.87



Progress for Future Testing / Development / Commercialization

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

- Fabricate 11m^2 modules with necessary modifications
- 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
- Analyze data and publish final report

Current Task Plan

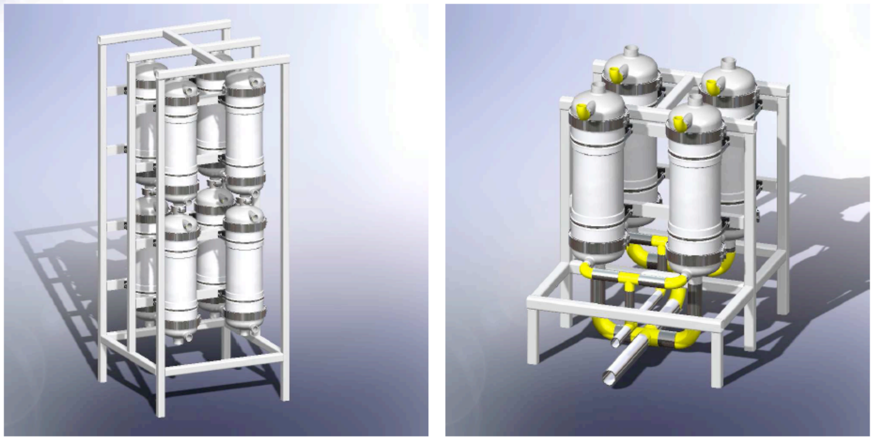
Pre-pilot Skid

- Fabricate 3x46m^2 modules
- Integrate modules into 3x46m^2 skid
- Model system to validate performance of multi-module configuration; 46m^2 module is base case
- Test 3x46m^2 MMS at EERC for 250h using natural gas, and polished flue gas derived from Lignite, Bituminous coals and Sub-bituminous coal
- Analyze data collected for 4 feed gas streams and compare results with the 3x46m^2 module and publish final report

Engineering and Economic Analysis

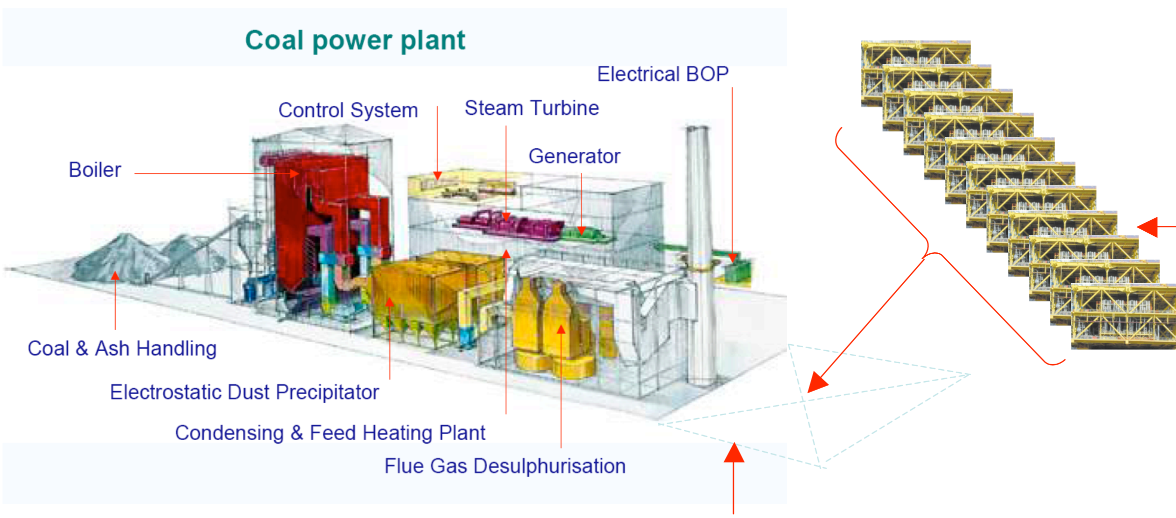
- Perform cost/performance analysis of 11m^2 system
- Perform cost/performance analysis of multi-module system

Scale-Up to 1t CO_2 /day capacity



Pilot Field Test

Natco



Carbozyme Modular Skids

Acknowledgements

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  - Carbozyme - Robert Cowan, David Smith, Xiaoqiu Wu, Haibin Chen, Randy Reali, Yla Angso, Nikolai Kocherginsky, Burt Waxman
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Questions?