# 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

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

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# Company Background


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## 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**


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# Project Overview


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# *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%


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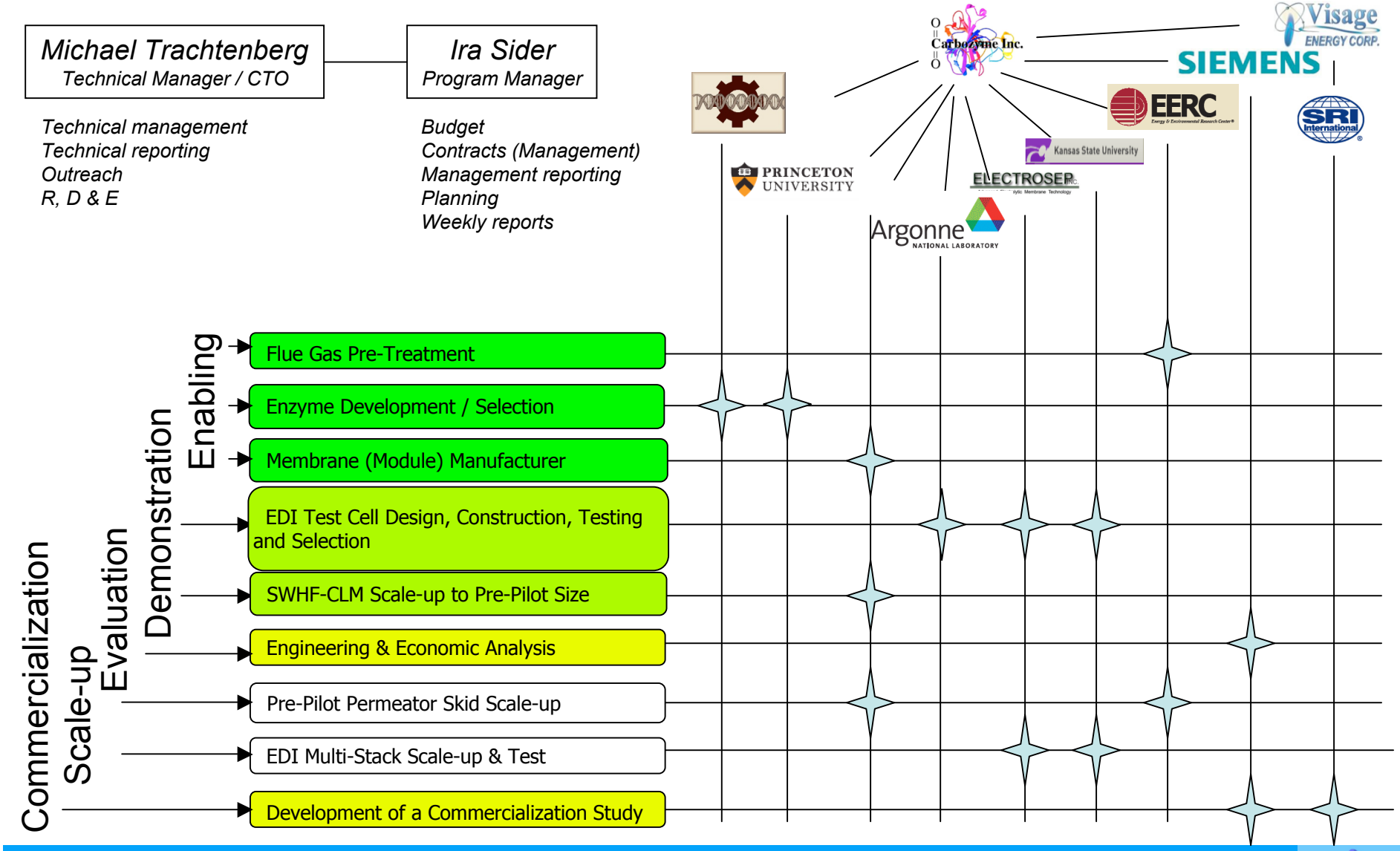
# *Project Participants*

**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*





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# Technology Fundamentals & Background

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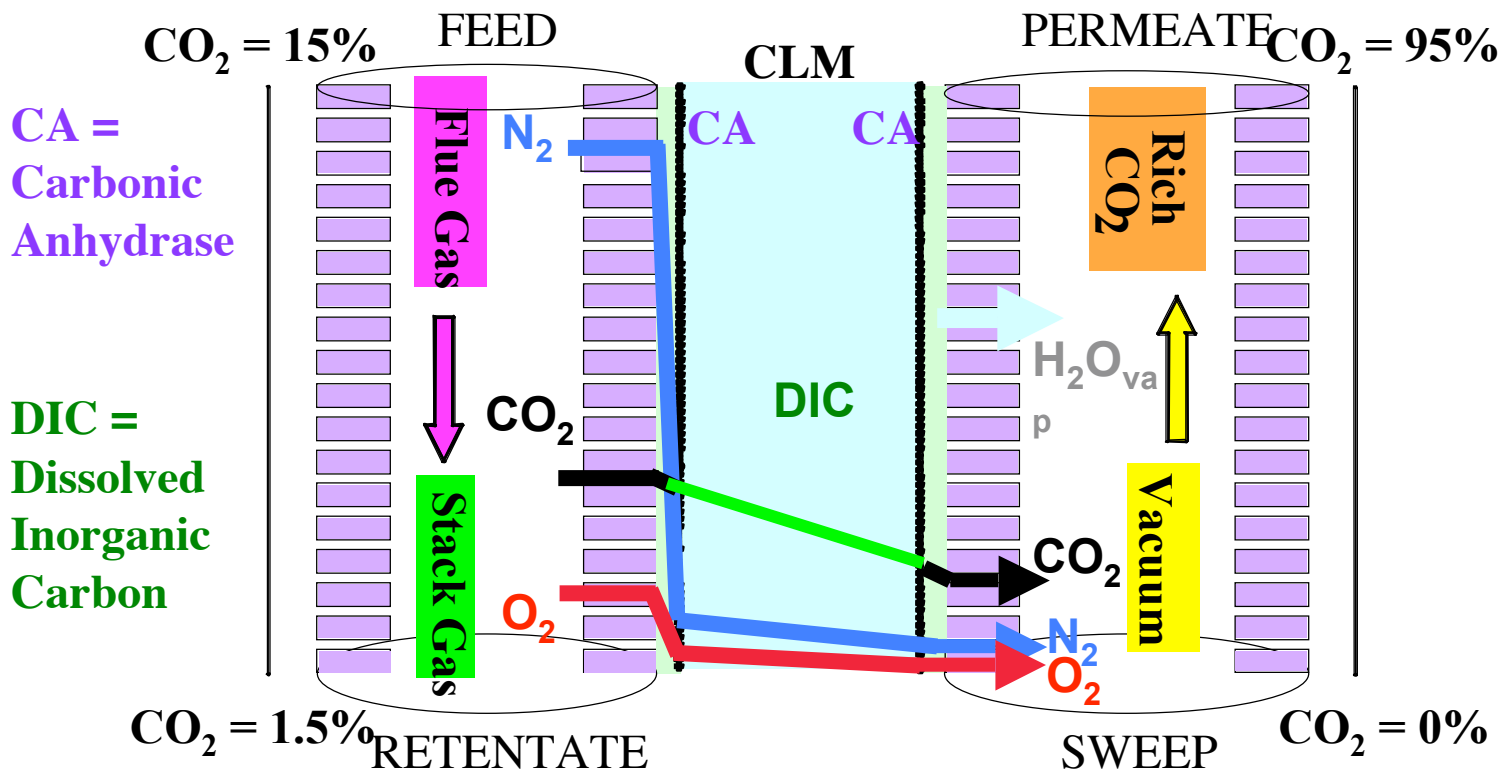
# Fundamental Permeator Design

## Permeance selective separation through a liquid membrane




$$H_2O \qquad H_2O$$

$$CO_{2(g)} \longleftrightarrow CO_{2(d)} \xleftrightarrow{CA} H^+ + HCO_3^- \longleftrightarrow 2\,H^+ + CO_3^=$$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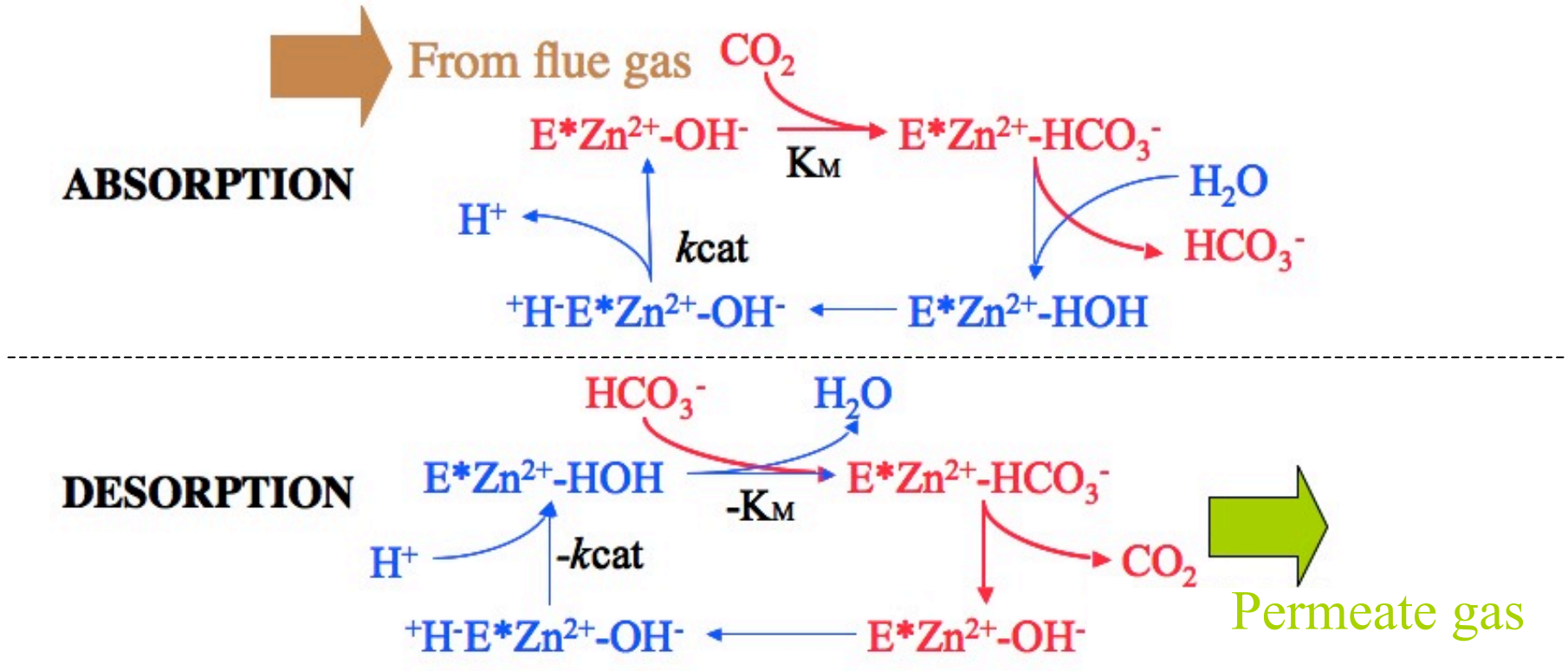
CA splits $H_2O$ to provide an $OH^-$ reaction center = fast absorption

CA also catalyzes the reverse reaction = fast desorption





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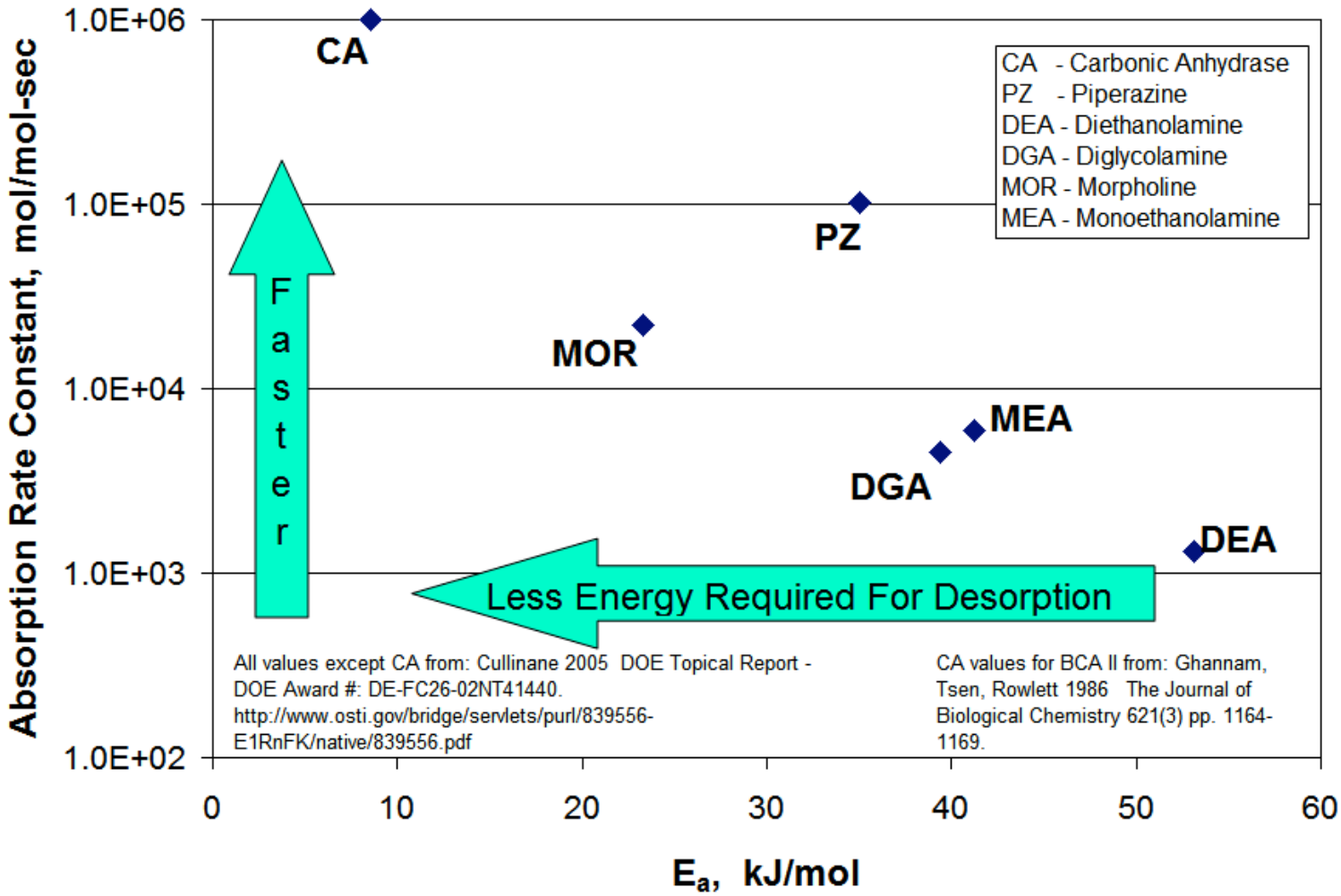
# *CA vs. Amine – Rate vs. Energy*

## CA - the most efficient, lowest energy catalyst





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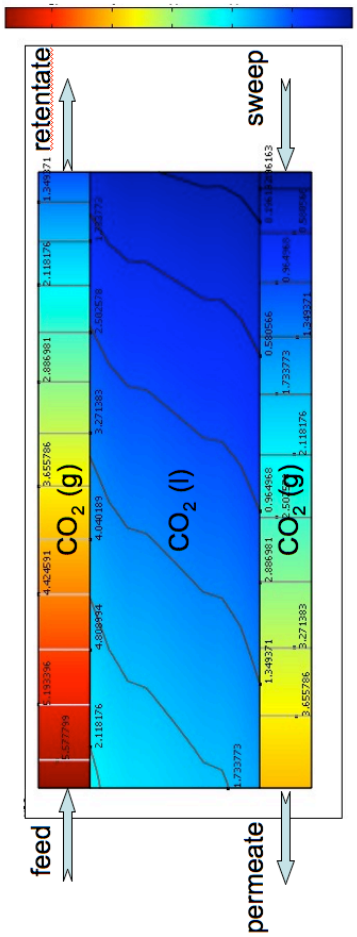
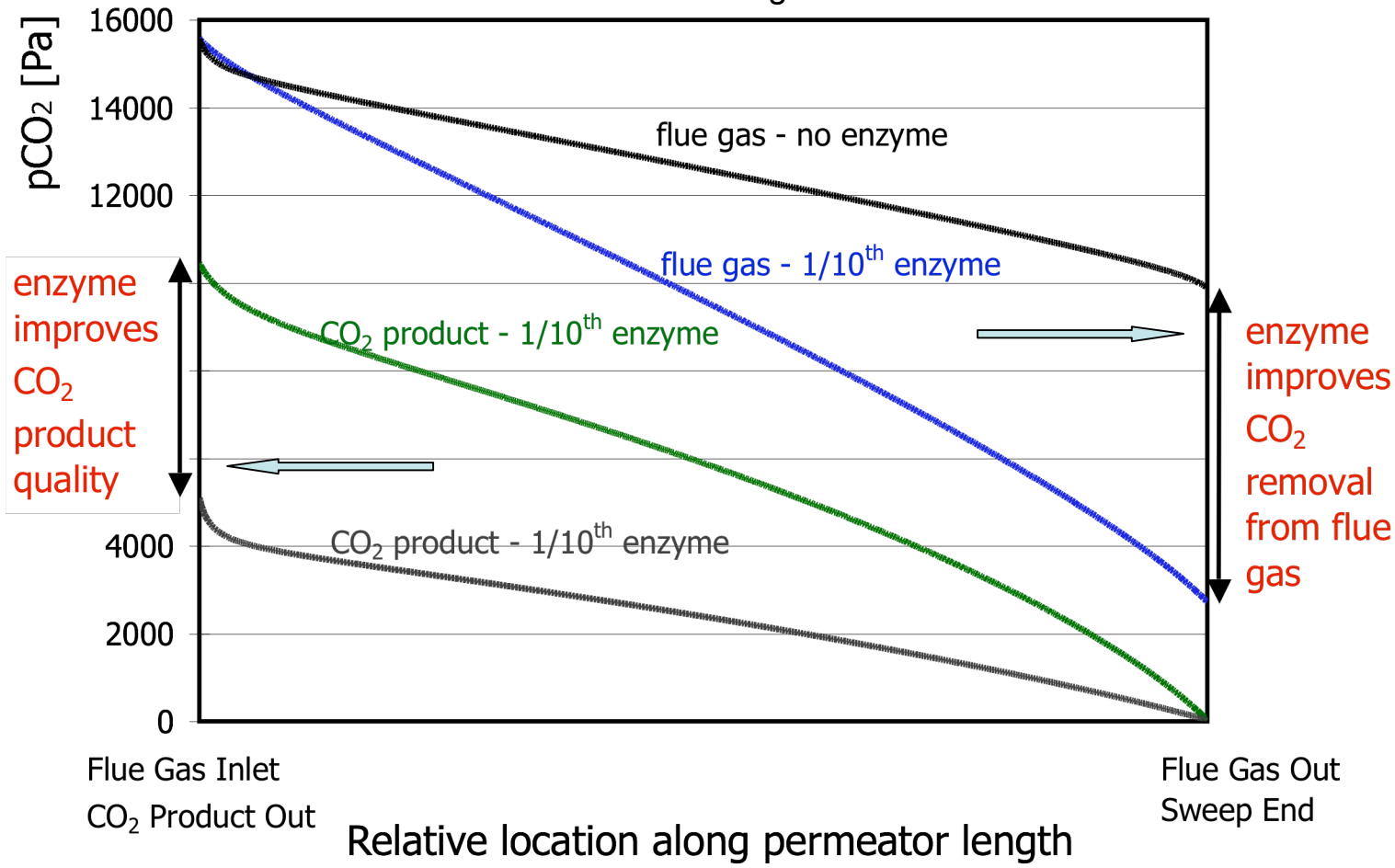
# *Enzyme Advantage*

*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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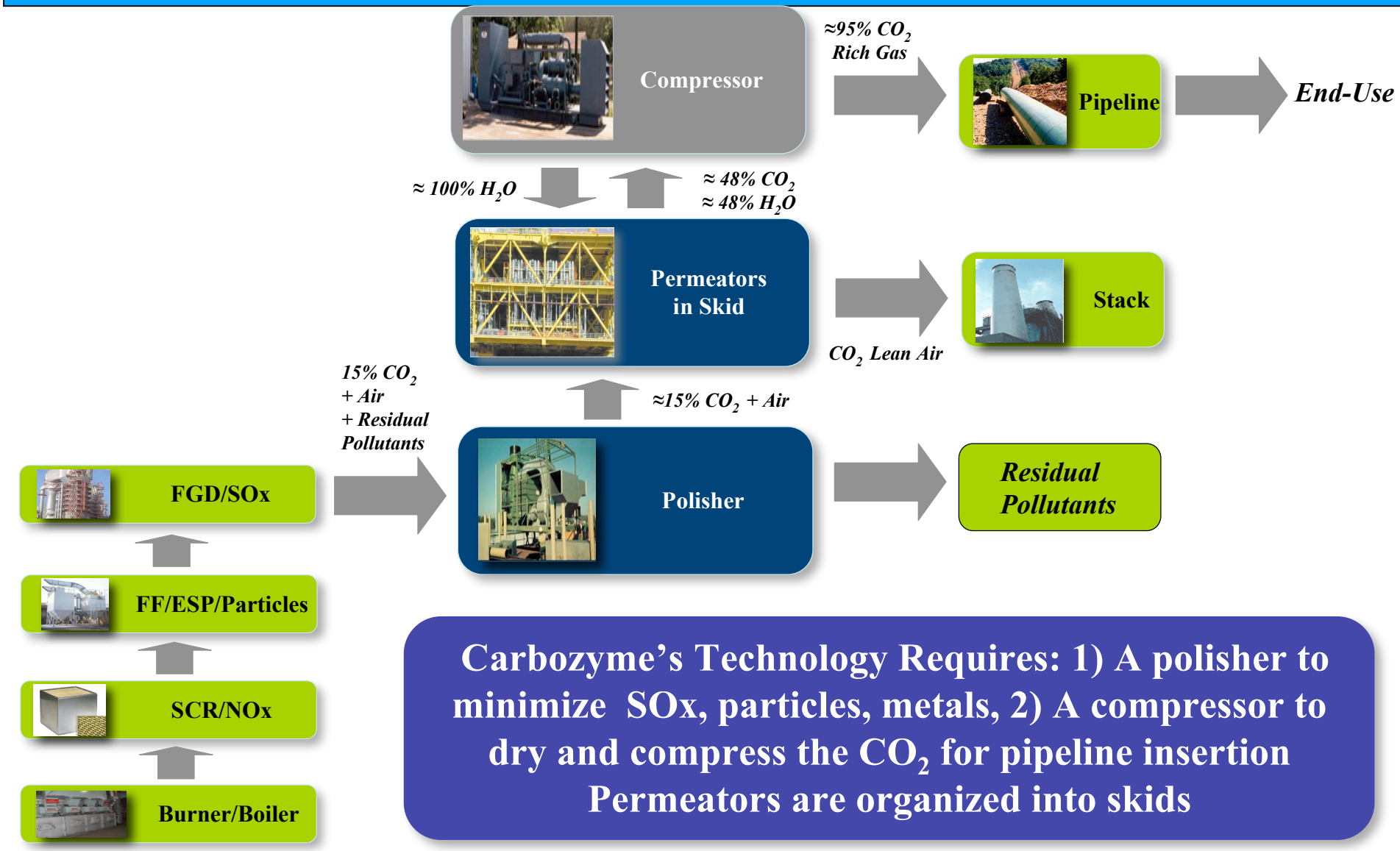
# Process Overview




**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**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# *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


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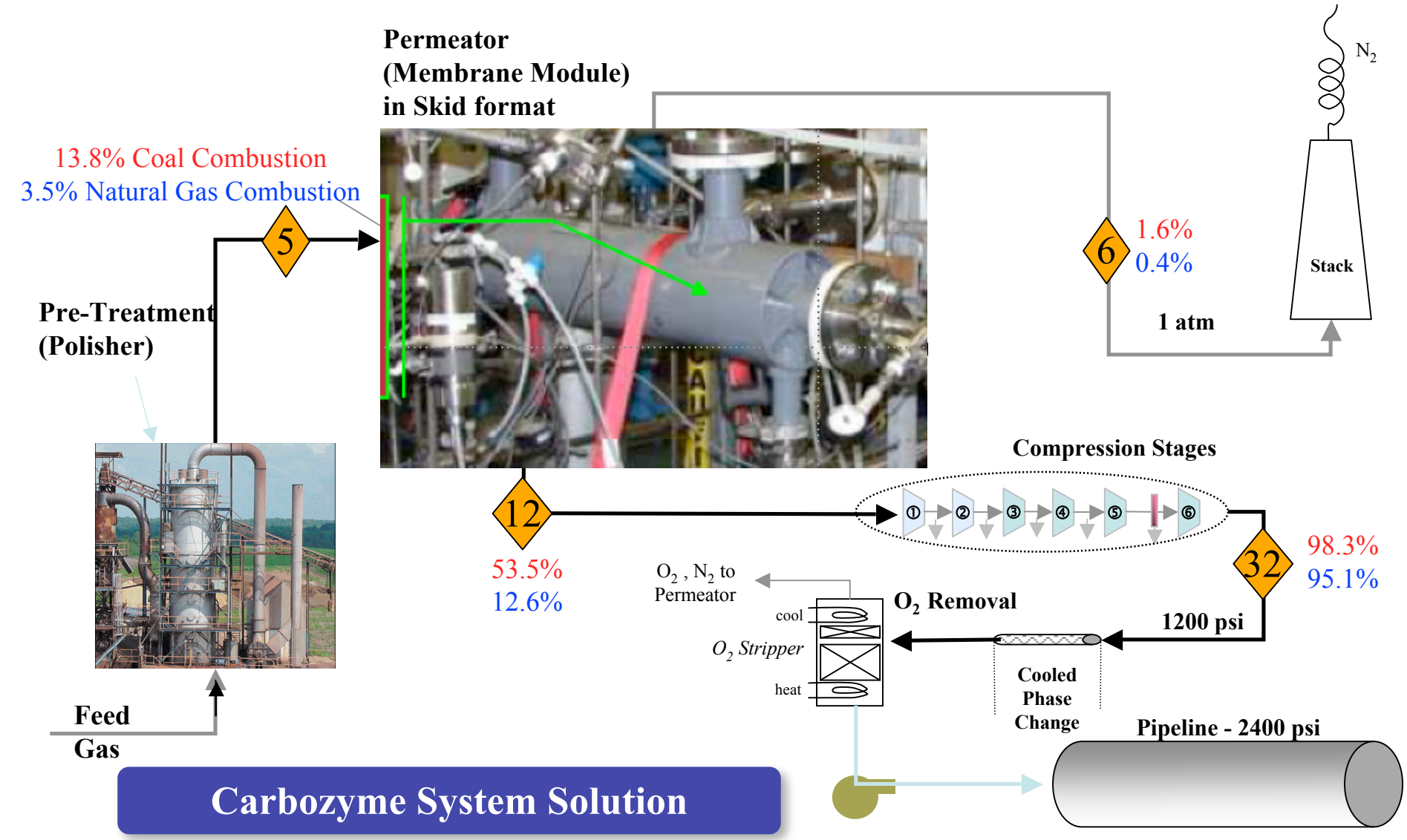
# $CO_2$ Scrubber - Detailed Process Flow




**Carbozyme System Solution**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# Advantages

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

**CZ Technology has Sustainable Advantages Over Competing Technologies**


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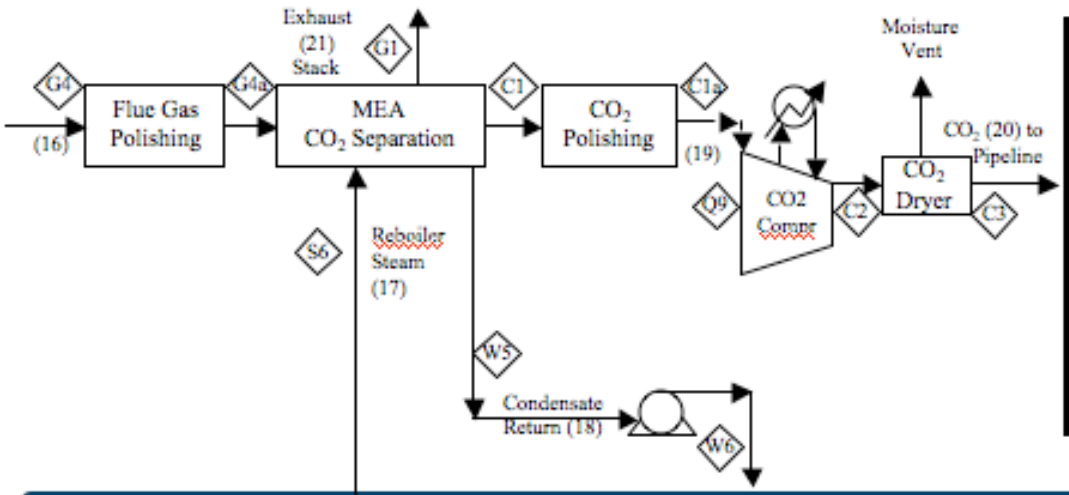
# *Initial Performance / Economic Analysis*

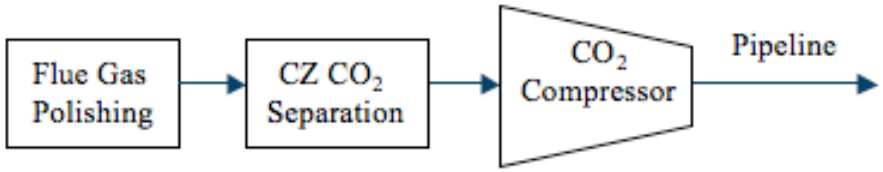
## Competitors – MEA (Amine) Process Flow and Costs




| 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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# *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<br>• Immobilized enzyme *in-situ* |
| Membrane Module | • Constructed and tested a 0.5m$^2$ SWHF-CLM; demonstrated performance close to DOE program objectives<br>• Demonstrated a 0.5m$^2$ SWHF-CLM with immobilized enzyme<br>• 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**


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# 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*

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# Progress and Current Status of Project


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# *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

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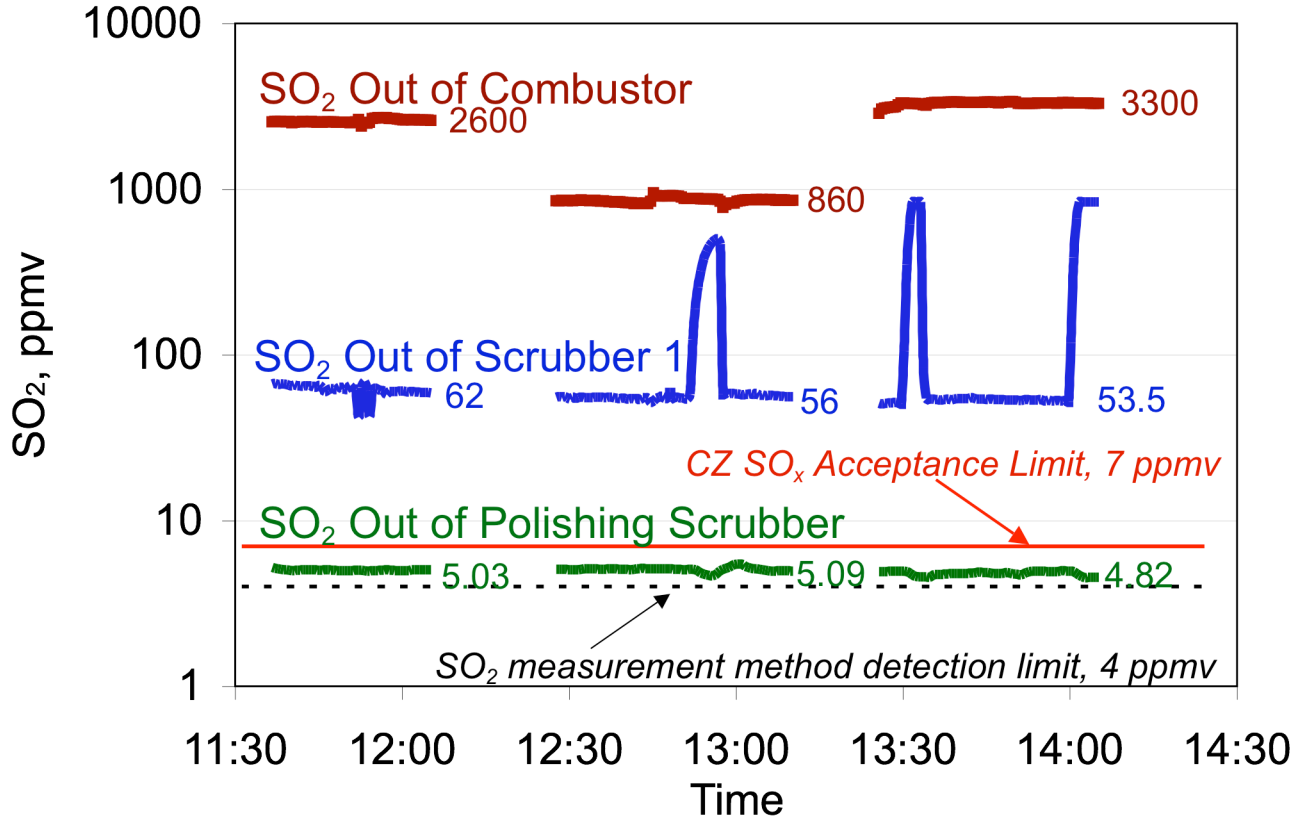
# *EERC SOx Scrubbing*

- 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)**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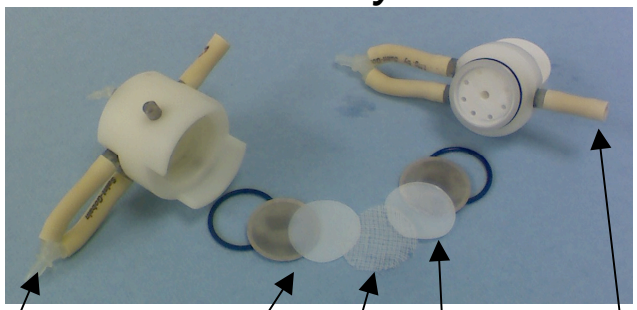
# Enzyme Performance Verification

## Very Small Permeator

*Used to:*

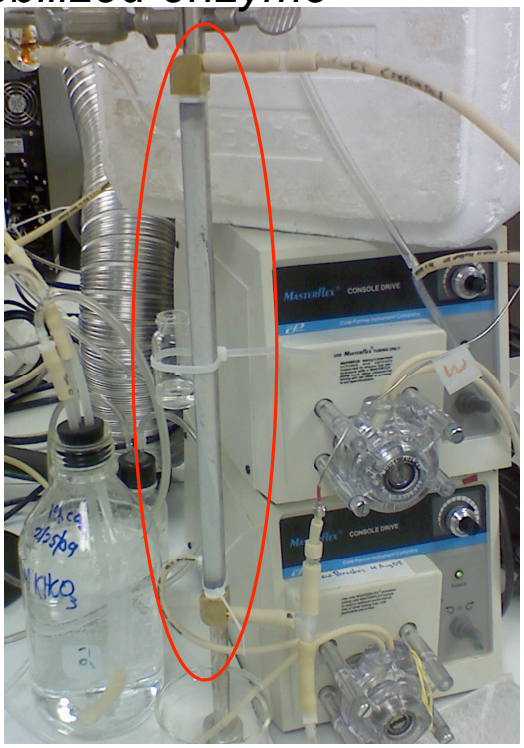
- *Test and select enzymes*
- *Optimize CLM chemistry*
- *Test immobilized enzyme*




## Small HF Module

*Used to test: (0.033 $m^2$)*

- *in-situ immobilization procedure*
- *immobilized enzyme*



**Flat sheet & hollow fiber immobilized enzyme test beds**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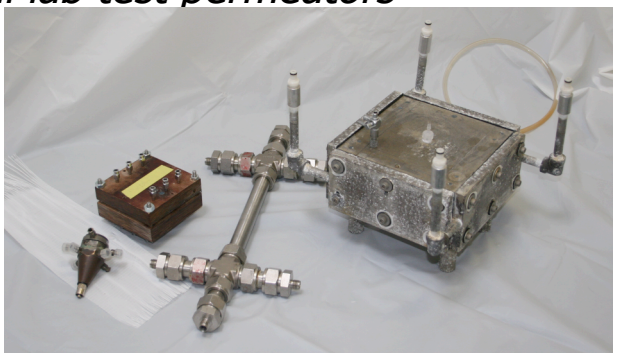
# Permeator Modifications / Scale-up

## BEFORE CURRENT PROJECT

*Small lab test permeators*

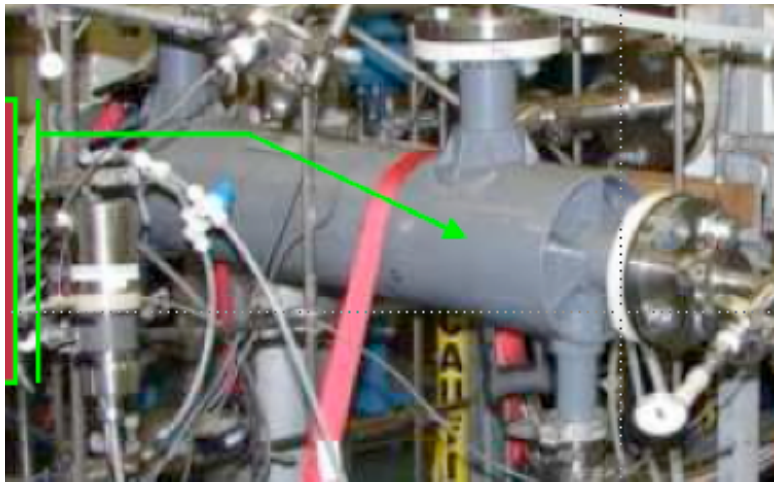


*0.05 m² permeator*

## CURRENT STATUS

*0.5 m² SWHF-CLM Module*

*11 m² permeator*



*46 m² module has been designed*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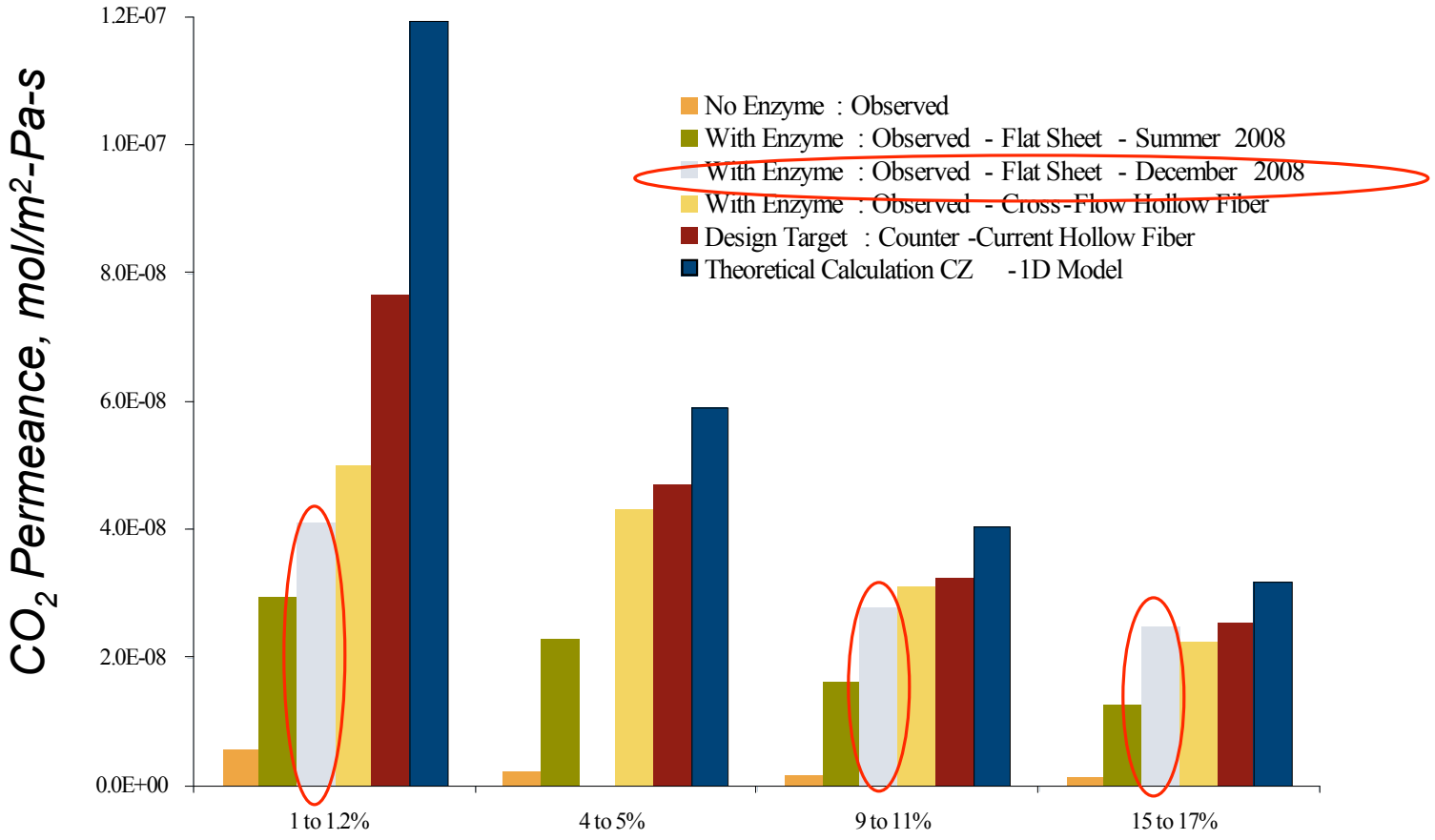
# *Preferred Enzyme Performance*




**Current performance is close to design target**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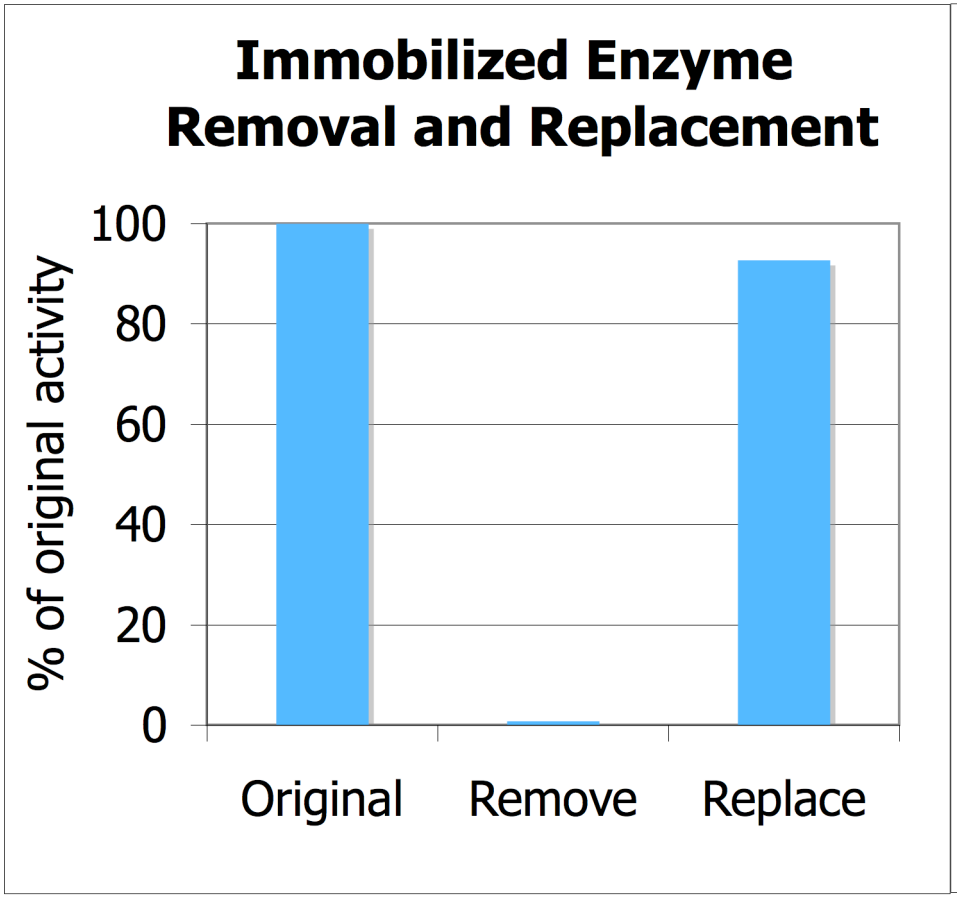
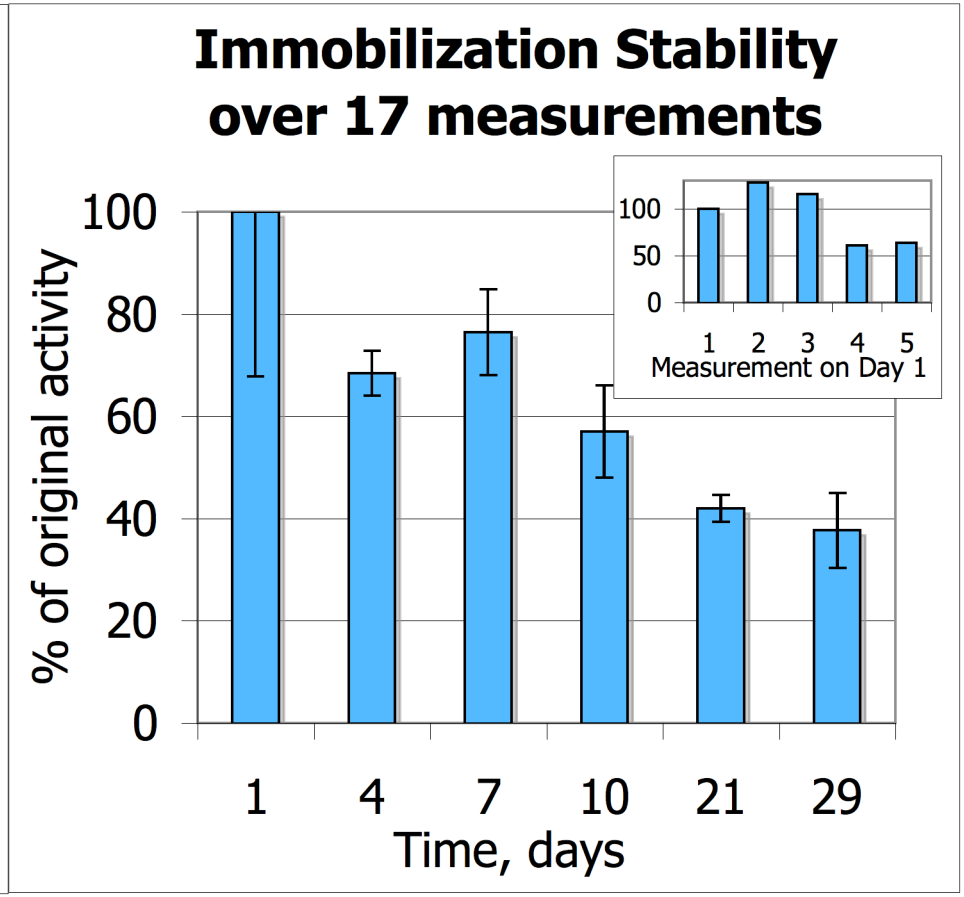
# *Enzyme Immobilization*




**Immobilized enzyme is stable but easily managed**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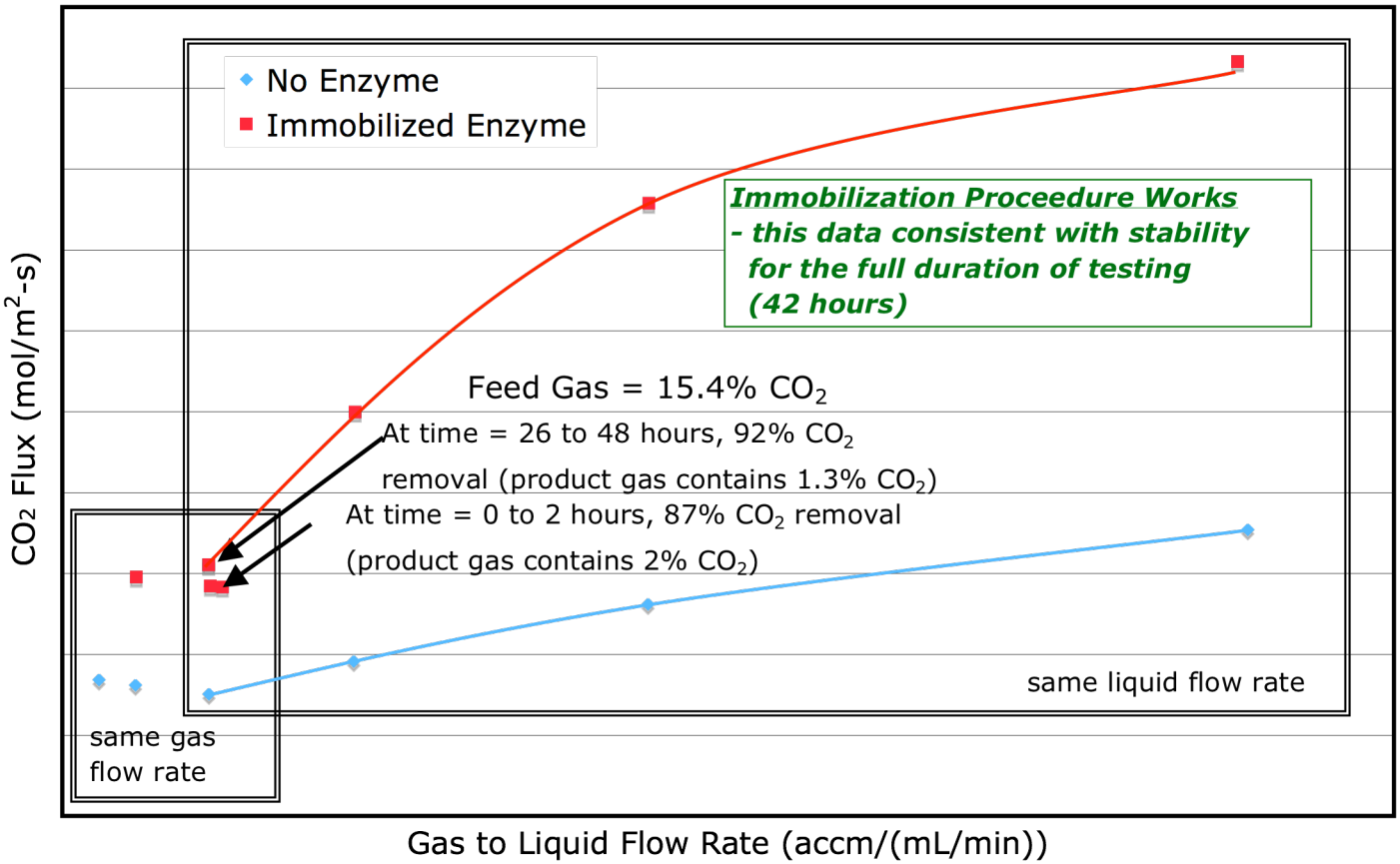
# Test of Immobilized Enzyme




***>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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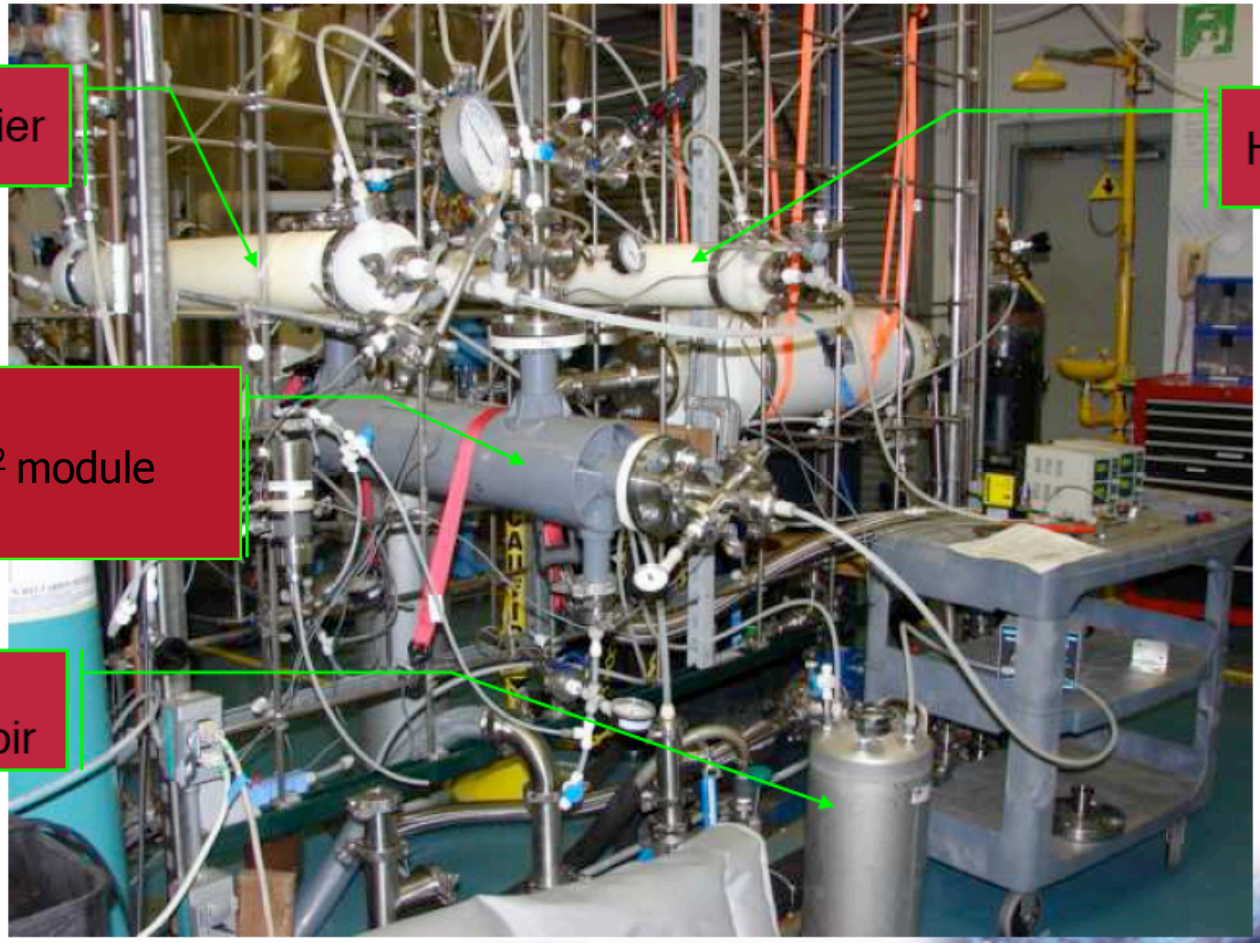
# *11m² SWHF-CLM Test Rig*

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# *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

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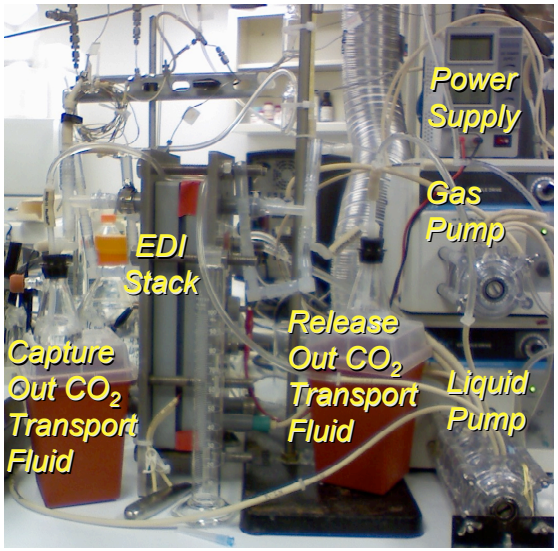
# EDI Results

| 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 |

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# Progress for Future Testing / Development / Commercialization


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# *Current Task Plan*

## 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


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# *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

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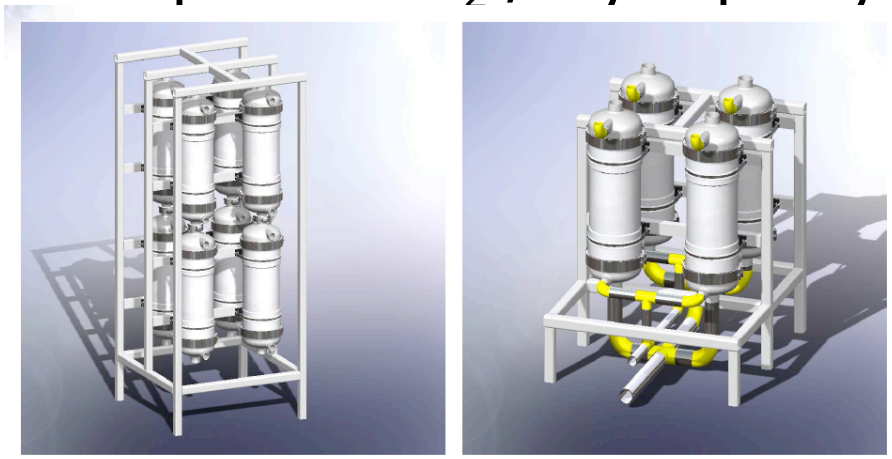
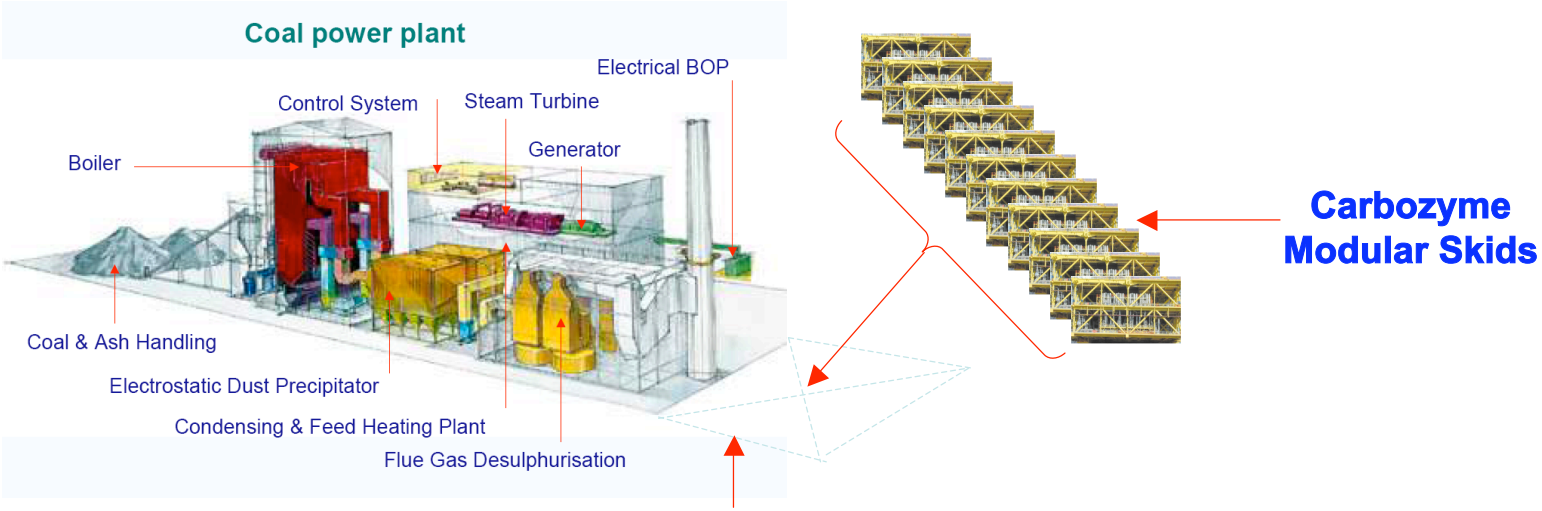
## Scale-Up to 1t $CO_2$ /day capacity



## Pilot Field Test

*Natco*





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# *Acknowledgements*


- DOE Project Manager - Jose D Figueroa
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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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  - SRI - Kevin O'Brien
  - Argonne National Laboratory - YuPo Lin, Seth Snyder
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  - ElectroSep - Paul Parisi


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