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UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

# CO<sub>2</sub> Capture Research at AETI/ ISGS/ INRS/ UIUC: Process Development for Minimizing CO<sub>2</sub> Desorption Energy and Compression Work

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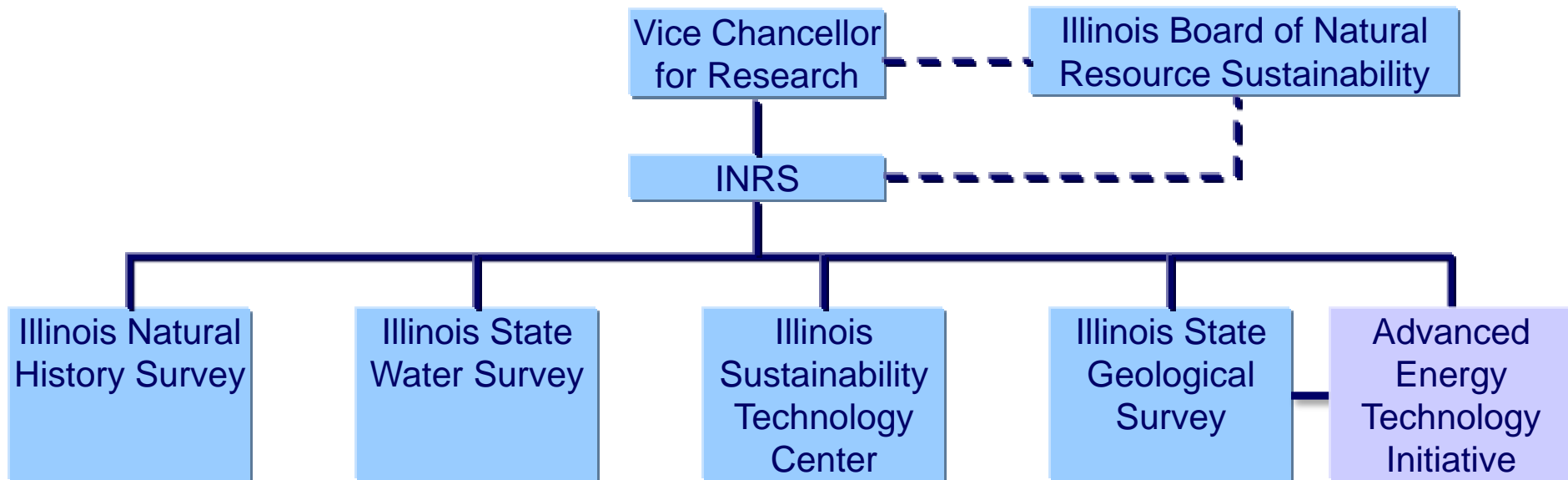
UK-US CCS R&D Workshop

Hilton Pittsburgh, PA  
May 10 and 12<sup>th</sup>, 2010



## □ Institute of Natural Resource Sustainability (INRS)

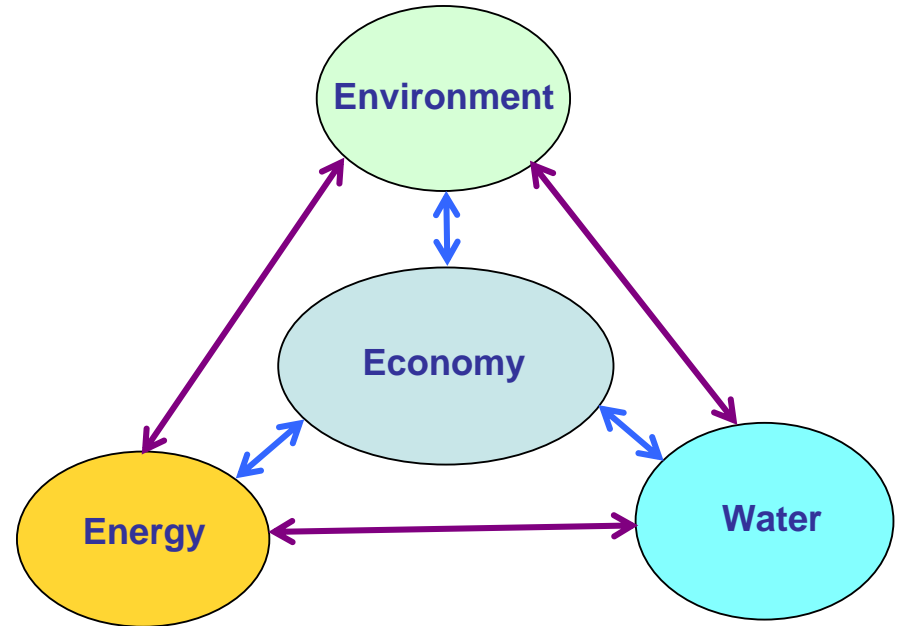
>600 scientists and technical support staff; annual budget of \$50 million; basic & applied research and service in resource sciences and related subjects



## ❑ Advanced Energy Technology Initiative (AETI)

AETI focuses on development of advanced resource utilization and pollution control technologies

- Carbon capture & sequestration
- Water-energy Nexus
- Air toxics control
- Nano science and engineering



Pillars of Economic Growth

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## Presentation Outline

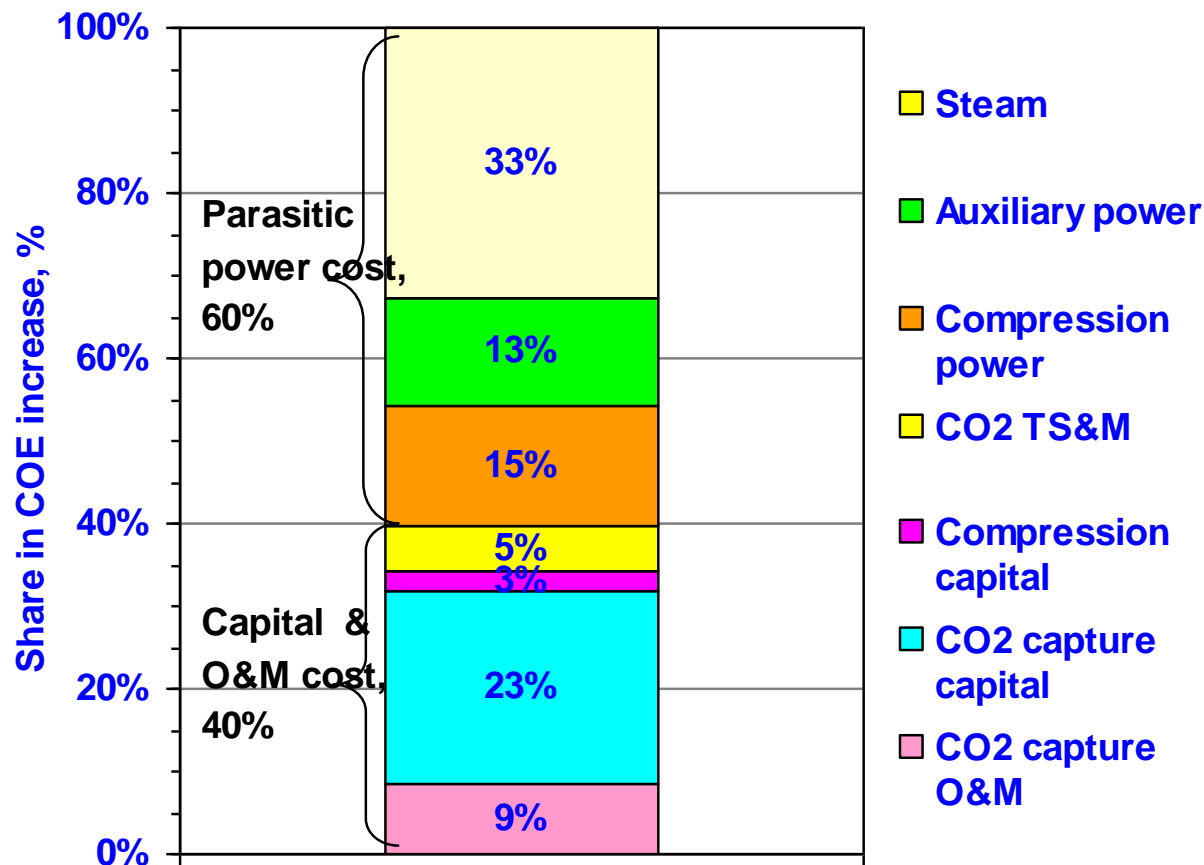
- ❑ Technical challenges in CO<sub>2</sub> capture
- ❑ Minimizing energy use for post-combustion CO<sub>2</sub> capture
  - Use of low quality steam
  - Phase change-enabled high pressure stripping
- ❑ Minimizing energy use for pre-combustion CO<sub>2</sub> capture
- ❑ Summaries



# Cost Breakdown of Baseline MEA Process for CO<sub>2</sub> Capture

## □ DOE/NETL baseline MEA process

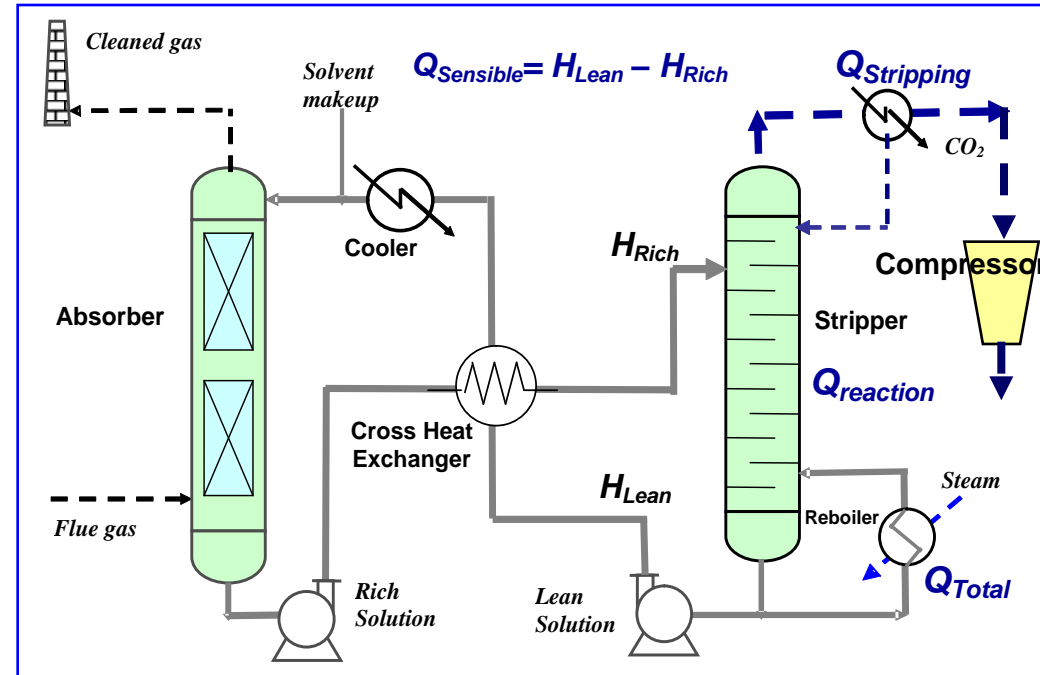
- 86% increase in Cost of Electricity (COE)
- 60% of total cost contributed by parasitic power loss



# Parasitic Power Consumption of CO<sub>2</sub> Capture Process

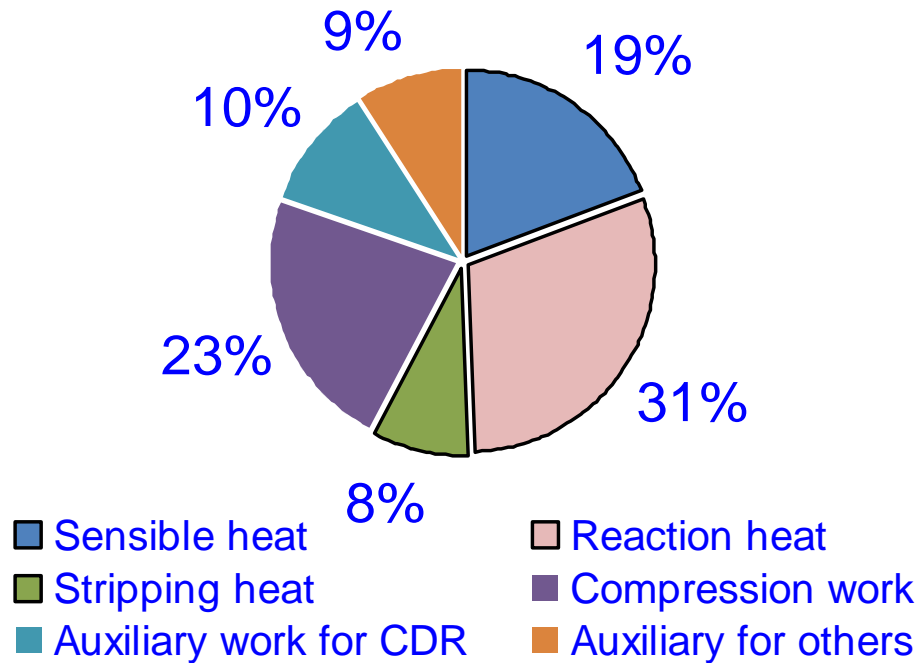
## Energy use components

- ❑ CO<sub>2</sub> desorption (steam use)
  - Heat of absorption (rxn heat)
  - Sensible heat (heat for  $\Delta T$  between CO<sub>2</sub>-rich and lean solvents)
  - Stripping heat (water vaporization)
- ❑ CO<sub>2</sub> compression work
  - Work for CDR
  - Others



# Parasitic Power Consumption of MEA-Based Process

Energy use breakdown



## Energy intensive

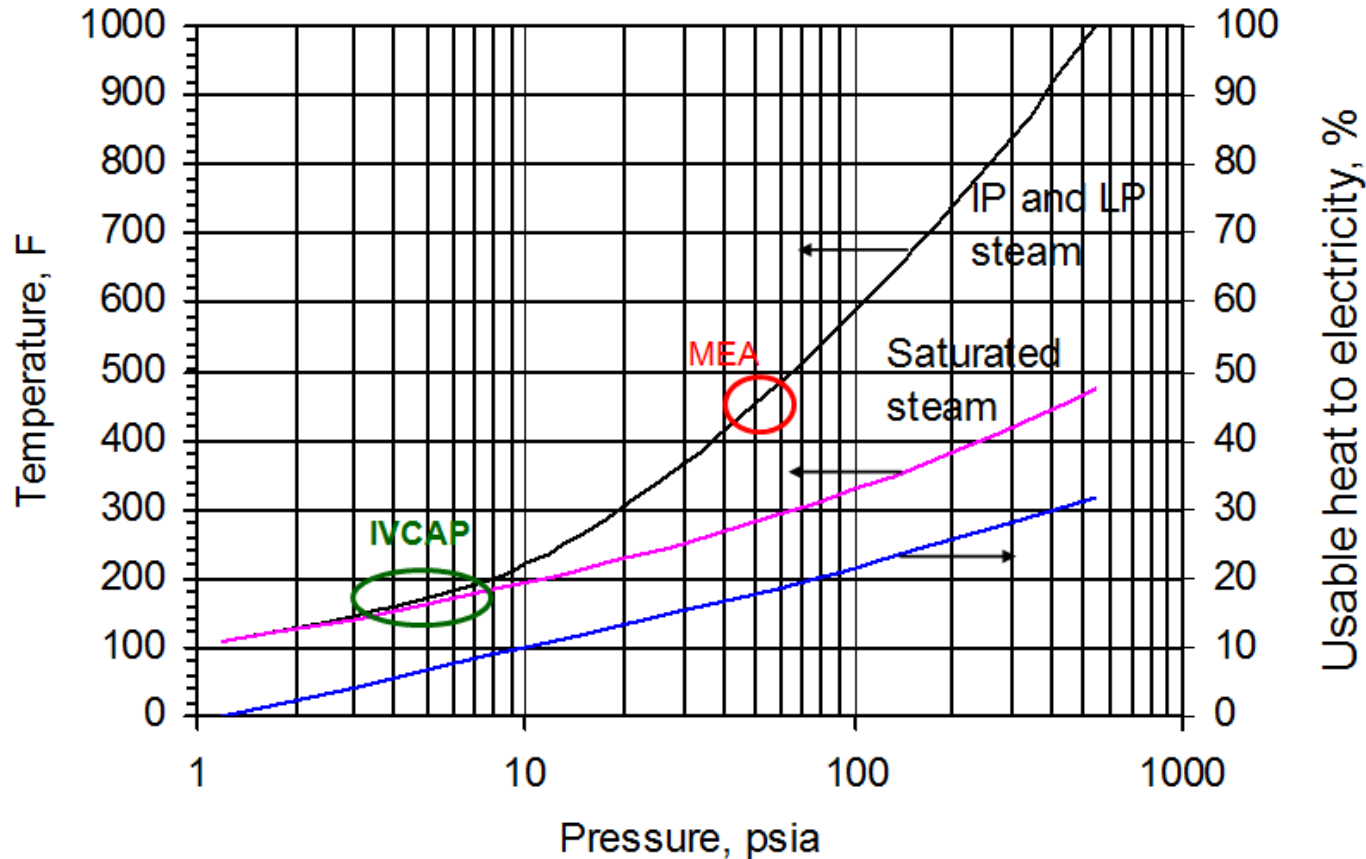
- High heat of reaction
- Low working capacity (high L/G and sensible heat)
- Low pressure stripping (high stripping heat + high compression work)

## Other disadvantages

- Pretreatment requirement for contaminants such as SO<sub>x</sub>, NO<sub>x</sub>
- Degradation (thermal, oxidative)
- Corrosion

# 1. Use of Low-Quality Steam for Solvent Regeneration

- ❑ Lower quality steam → less electricity loss
- ❑ lower stripping temperature allows use of lower quality steam

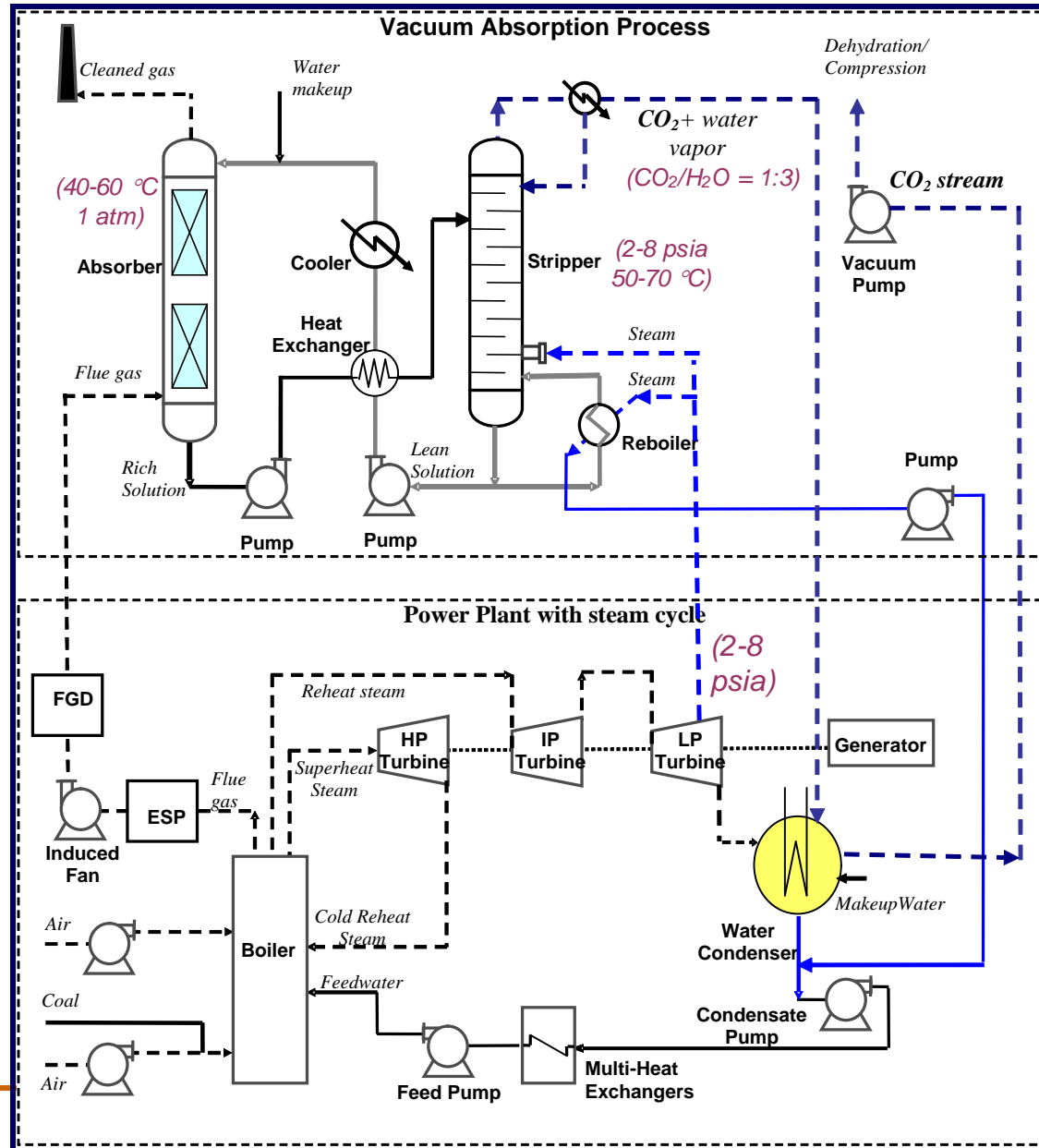


Superheated steam in power plant IP and LP turbines

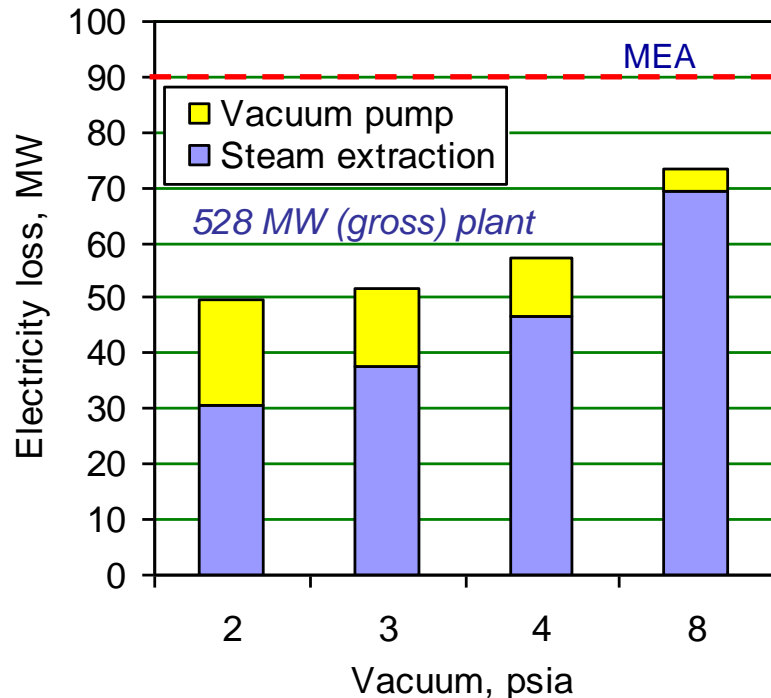


# Integrated Vacuum Carbonate Absorption Process (IVCAP)

- ▣ Low heat of absorption
  - $K_2CO_3 (PC) + CO_2 + H_2O = 2KHCO_3$   
 $(\Delta H_r = 600 \text{ kJ / kg})$
  - Weak affiliation with  $CO_2$  favors low T/P stripping
  
- ▣ Integration with power plant steam cycle
  - Vacuum stripping allows use of low quality steam (2-9 psia vs. ~60 psia for MEA)
  - Direct introduction of steam into stripper to reduce heat transfer  $\Delta T$



# Energy Use Performance of IVCAP



MW	PCP W/O CO <sub>2</sub>	PCP+ MEA	PCP+ Vacuum
Net output	492.86	358.93	390.07
Aux. electricity use	34.74	32.00	33.27
Steam extraction	0	89.43	37.81
Fan/pump in CO <sub>2</sub> capture process	0	11.82	12.84
CO <sub>2</sub> compression	0	35.42	39.65
Vacuum pump	0	0	13.96

\* A case study based on 3 pisa stripping pressure, 1%wt CO<sub>2</sub> lean loading, 20%wt PC, and L/G=1.2 (L/G)min.

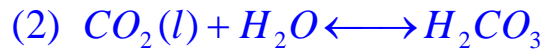
❑ Energy use in CO<sub>2</sub> desorption reduced by 20-45% compared to MEA

❑ Total energy use reduced 20%-30% compared to MEA



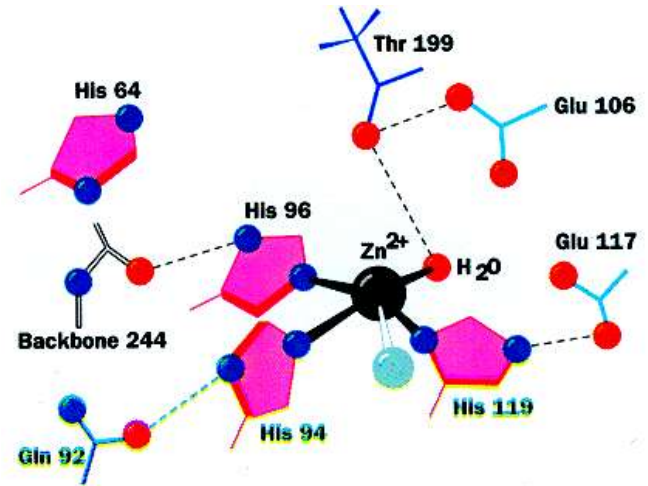
# Application of Biocatalyst in IVACP

- ❑ PC has a much lower CO<sub>2</sub> absorption rate compared to MEA



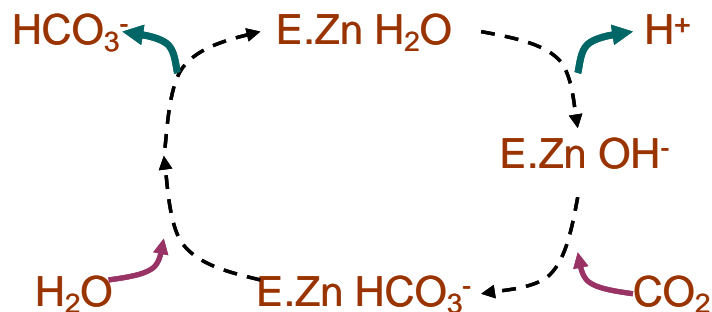
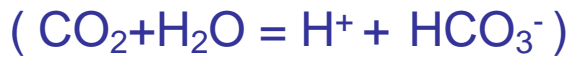
- ❑ Carbonic anhydrase (CA)

- Most effective catalyst for CO<sub>2</sub> hydration
- Turnover rate = 1.4 MM/s at pH = 9 and 25°C



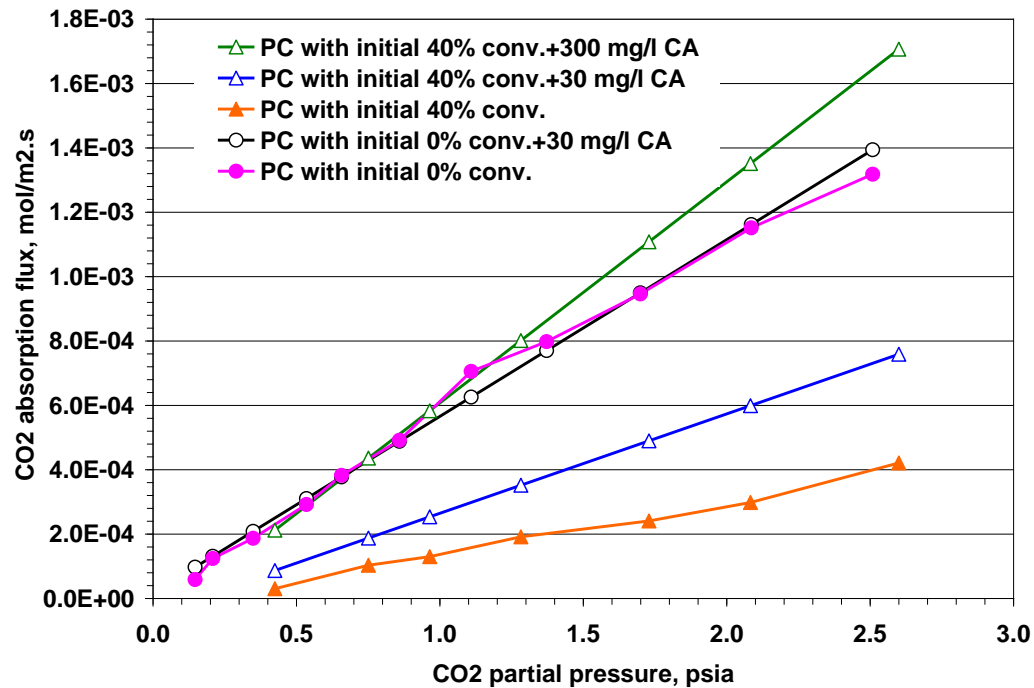
Molecular structure of CA

Catalytic mechanism



# Activity of CA Biocatalyst in PC Solution

- ❑ Rate into PC increases by 2-20 times at 300 mg/L CA
  - CA is more effective for PC with higher CO<sub>2</sub> loading
- ❑ Presence of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> in PC+CA resulted in <11% loss of initial CA activity



50 °C, 20%wt PC solution



# Biocatalyst Immobilization

## Advantages:

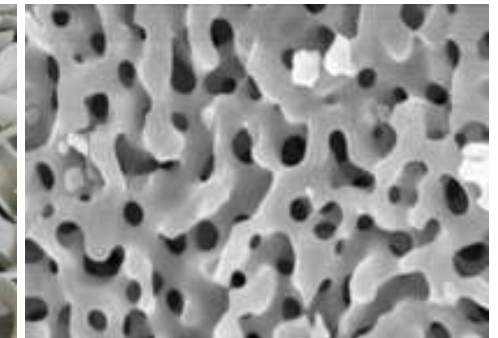
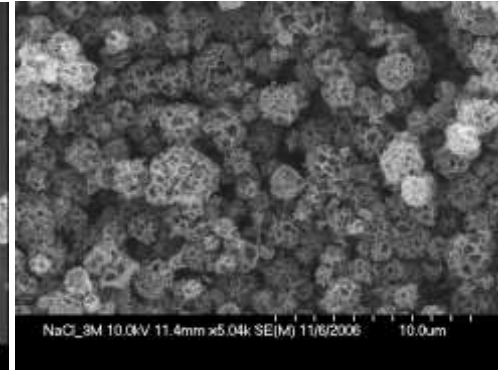
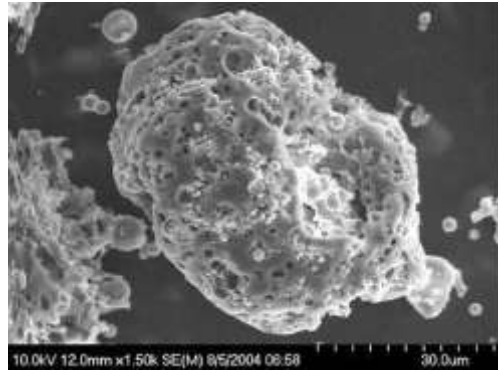
- Improve enzyme stability
- Reduce enzyme elution in a flow system

## Support materials

- Controlled pore glass (CPG, 100nm macro-pore, SA=25m<sup>2</sup>/g, 200-400 mesh)
- Activated carbon, celite, ceramic support materials are currently under investigation

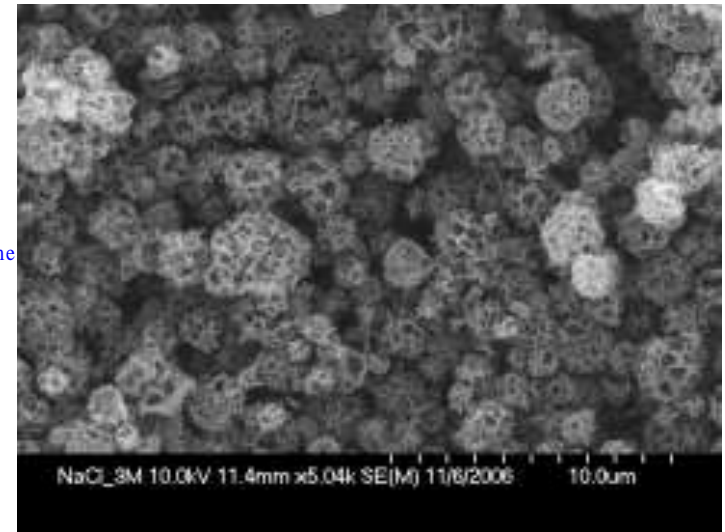
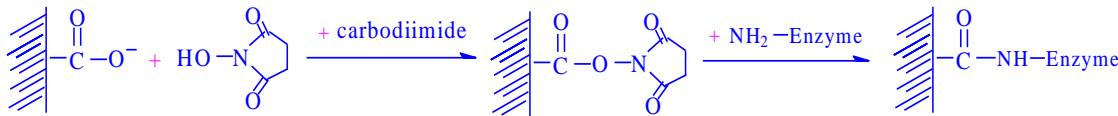
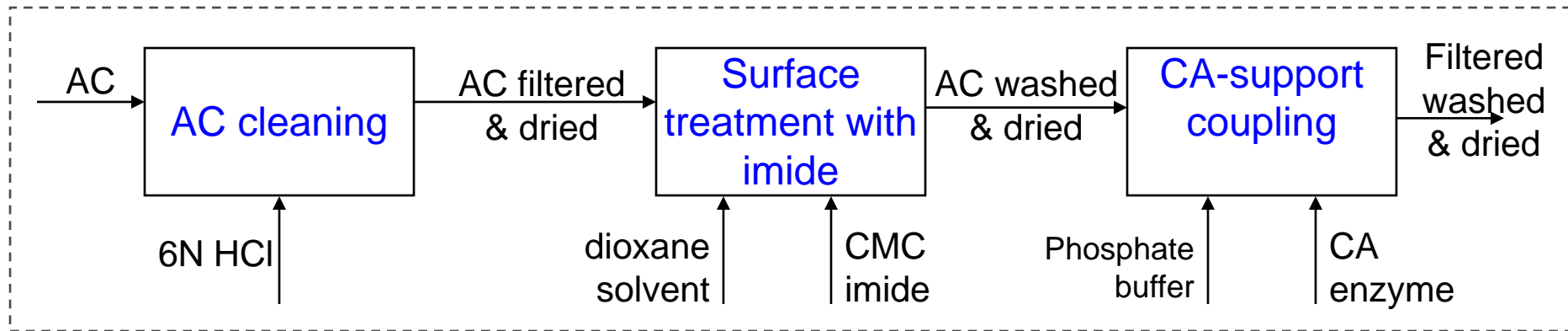
## CA enzymes

- A commercial pure CA used in developing immobilization methods
- Another technical-grade CA currently under investigation





# CA Immobilization onto Carbon



Novel carbons developed at AETI-UIUC



# Comparison between Immobilized and Free CAs

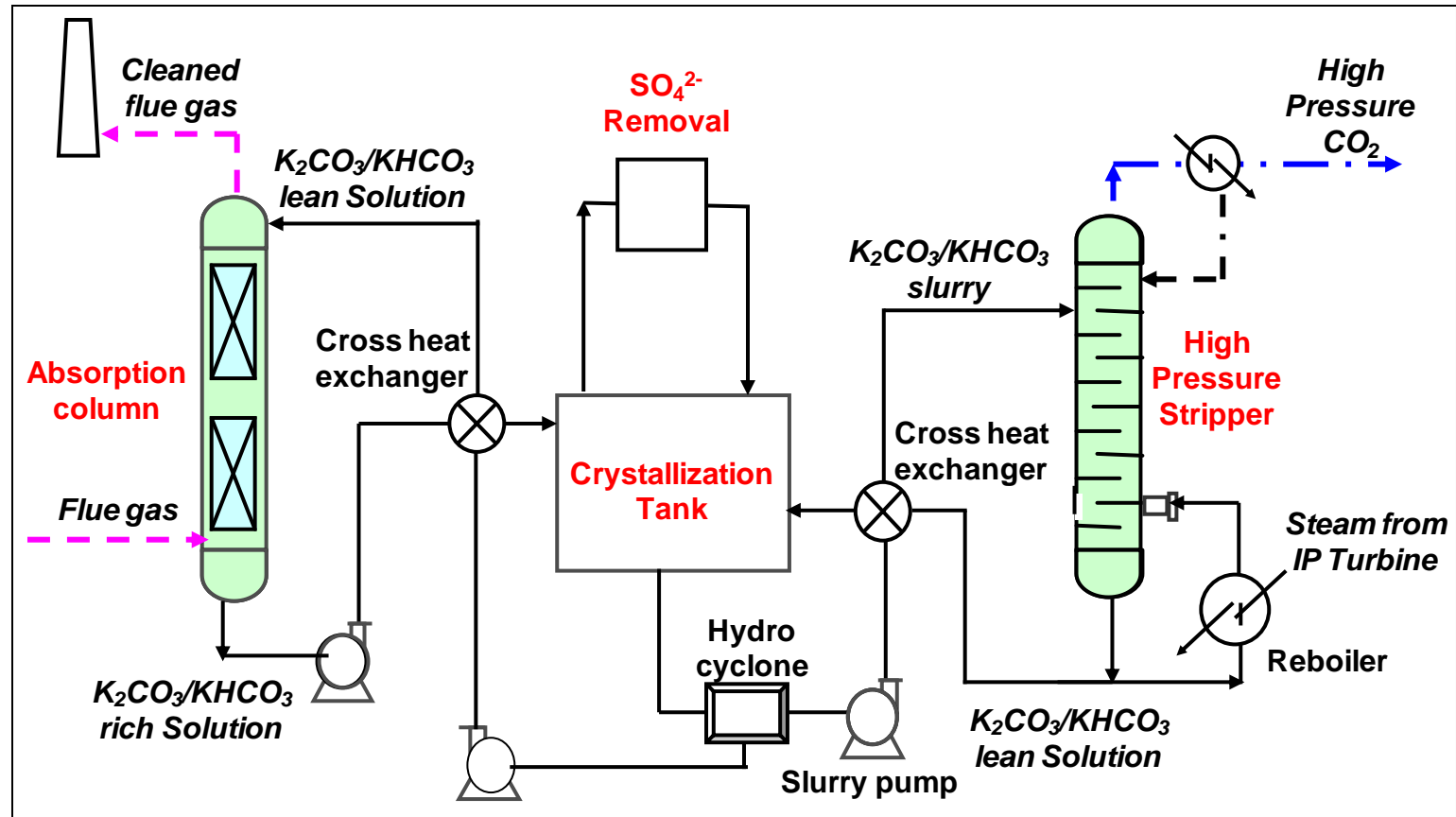
## □ Immobilization factor (IF)

$$IF = \frac{\text{Specific activity of immobilized enzyme}}{\text{Specific activity of free enzyme}}$$

	Activity (U/g CA-CPG, dry basis)	CA loading in dry CPG (mg/g)	Specific activity (U/g CA)	IF
CA-CPG air-dried	0.097	10.7	9.06	0.033
CA-CPG wet-stored	0.438	10.7	46.9	0.169
CA-CPG with aldehyde residue removal after CPG activation + wet-stored	0.822	6.32	124	0.470

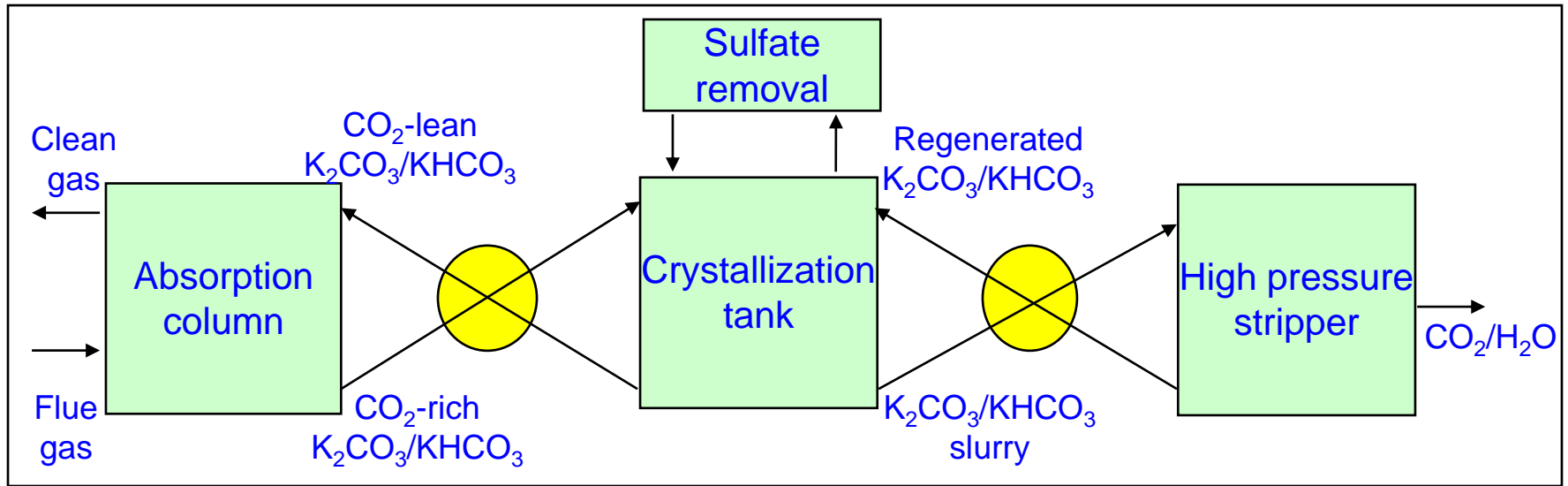


## 2. Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP)

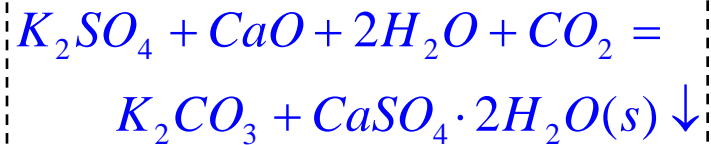


- ❑ Absorption at 70-80 °C
- ❑ Working capacity of 40%wt PC: 15-40% carbonate-to-bicarbonate conv.
- ❑ Crystallization at room temperature (30°C)
- ❑ Stripping of bicarbonate slurry at up to 20-40 atm

# Major Reactions



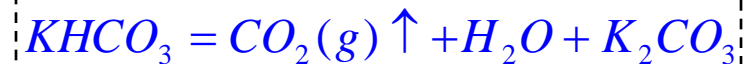
*SO<sub>4</sub><sup>2-</sup> reclamation*



*CO<sub>2</sub> absorption at 70–80°C*



*CO<sub>2</sub> desorption at ~ 150°C*

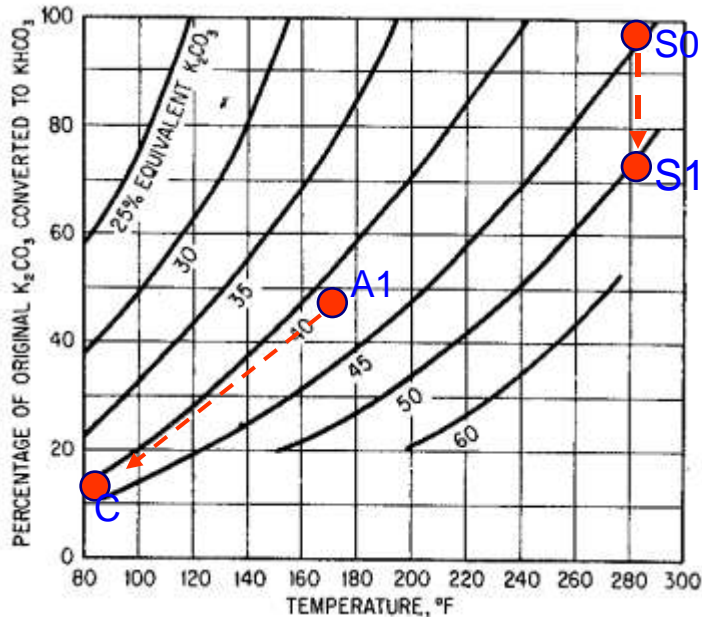


*Crystallization at 30°C*

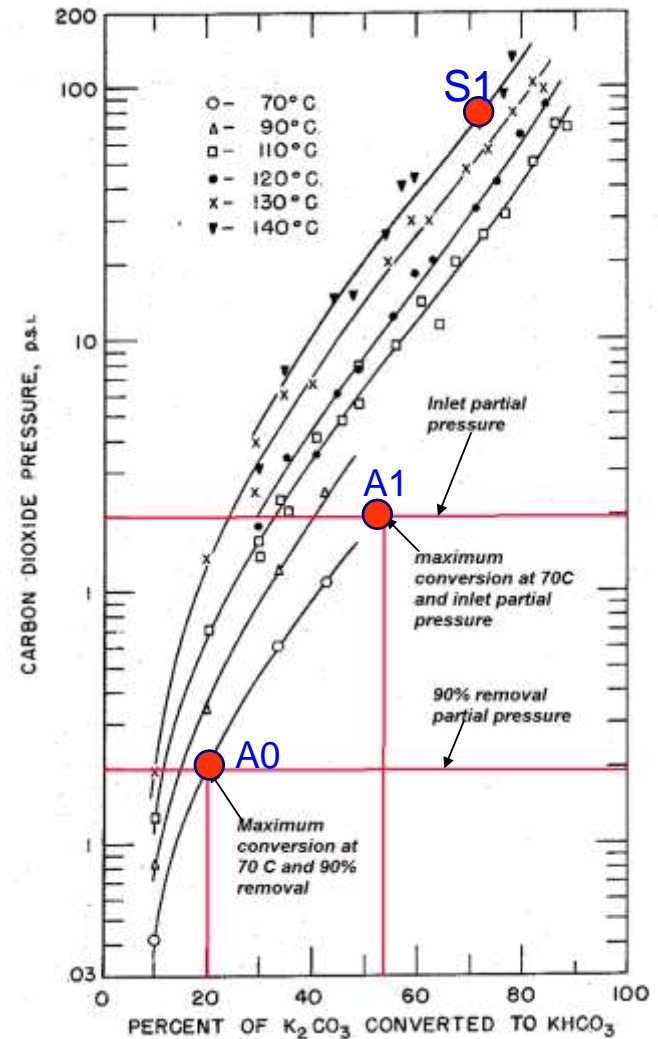


# Technical feasibility

- ❑ 90% CO<sub>2</sub> removal
- ❑ Crystallization prevented in absorber
- ❑ High pressure stripping at high T, high slurry concn., high conv.



Solubility of bicarbonate in carbonate solution



Vapor-liquid equilibrium of CO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> (40%wt) system



# Advantages of Hot-CAP Process

- ❑ High stripping pressure (20-40 atm)
  - low compression work
  - low stripping heat (low H<sub>2</sub>O/CO<sub>2</sub> pressure ratio)
- ❑ Low sensible heat
  - Comparable working capacity to MEA
  - Low Cp (1/2)
- ❑ Low heat of absorption
  - 7-17 kcal/mol CO<sub>2</sub> (crystallization heat incld.) vs. 21 kcal/mol for MEA
- ❑ Kinetics improved by using high concentration PC and high absorption temperature
- ❑ FGD may be eliminated
- ❑ No solvent degradation
- ❑ Less corrosiveness



# Energy Use Comparison with MEA

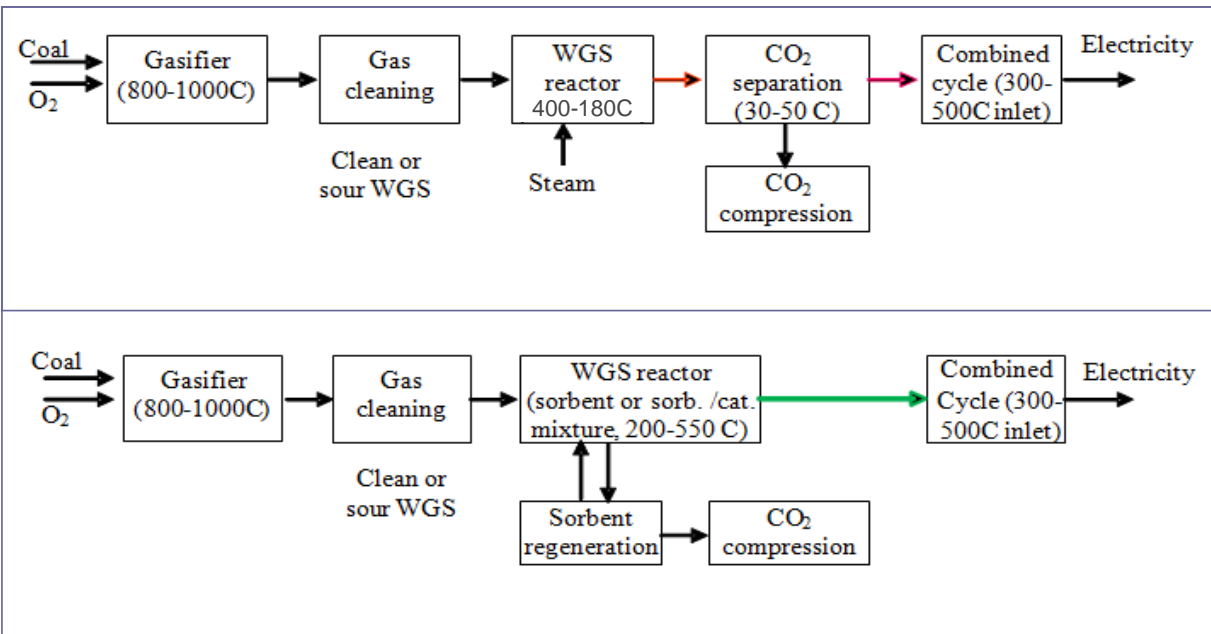
Items	MEA	Hot-CAP
Energy Consumption		
<b>CO<sub>2</sub> desorption</b>		
Heat of absorption (Btu/lbCO <sub>2</sub> )	825	600
Sensible heat (Btu/lbCO <sub>2</sub> )	600	300
Stripping heat (Btu/lbCO <sub>2</sub> )	270	30
Electricity equivalent (kWh/ kg CO <sub>2</sub> )	0.28	0.18
<b>Compression work</b> (kWh/ kg CO <sub>2</sub> )	0.09	0.03
Total electricity (kWh/kg CO <sub>2</sub> )	0.37	0.21
Operating		
Degradation (kg MEA/ ton CO <sub>2</sub> )	2	0
FGD Required	Y	N

❑ Saving of 43% electricity loss compared to MEA



# 3. Engineered Adsorbents for Pre-Combustion CO<sub>2</sub> Capture

- ❑ Sorption-enhanced water-gas-shift (WGS) reaction
  - No or limited WGS catalyst ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ )
  - No gas cooling/reheating
  - No separate CO<sub>2</sub> unit required





**the ENERGY lab**  
PROJECT FACTS  
Carbon Separation

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**Evaluation of Dry Sorbent Technology for Pre-Combustion CO<sub>2</sub> Capture**

**Description**  
For this three-year project, Lurgi Group, Inc. and University of Illinois at Urbana-Champaign will investigate a dry sorbent process designed to combine the water-gas-shift (WGS) reaction with carbon dioxide (CO<sub>2</sub>) removal for coal gasification systems. Project objectives include determination of optimal CO<sub>2</sub> sorbent properties and operating conditions using a combination of computational and experimental methods. Laboratory tests will evaluate a number of sorbent types, identified as optimized based upon detailed engineering analyses considering key thermodynamic and molecular properties. Tests will focus on determining optimal results for CO<sub>2</sub> adsorption, including the presence of typical species impurities, as well as regeneration. Results will be used to evaluate the technical and economic feasibility of full-scale implementation of the dry sorbent technology.

**Primary Project Goal**  
The project will investigate a concept in which a dry sorbent technology is used to combine the WGS reaction with CO<sub>2</sub> removal for coal gasification systems. The project aims to improve upon the current state-of-the-art by developing high performance sorbents that are capable of achieving 90 percent CO<sub>2</sub> removal from high loading gasifiers, and operate at the high temperatures and pressures typically associated with systems of a WGS reactor. If successful, the sorbents developed as the program will improve or replace the carbon monoxide (CO) conversion catalyst currently used in WGS reactors and improve overall WGS thermal efficiency. The process also enables CO<sub>2</sub> capture and regeneration at high temperature and pressures, thus reducing energy efficiency impacts on the overall integrated gasification combined cycle (IGCC) plant. Program objectives include identification of optimal sorbents and operating conditions for CO<sub>2</sub> removal and regeneration and CO<sub>2</sub> conversion to gaseous form.

To meet the project objectives, a combination of process simulation modeling and sorbent materials and thermodynamic analysis will be used. Results from the computational study will identify suitable existing commercial or developing sorbents. In addition, the project team will use these results as a guide to synthesize a number of sorbent materials made from highly porous materials and carbon designed to exhibit properties for superior CO<sub>2</sub> sorption. A laboratory program will be conducted using process and temperature reactors to evaluate the sorbents at conditions simulating coal-derived syngas entering a WGS reactor. The tests will determine optimal process conditions for CO<sub>2</sub> removal and regeneration for different sorbent types and aspects of key design parameters. Results will be used in the form of an analysis to evaluate the technical and economic feasibility of the dry sorbent technology in a pre-combustion CO<sub>2</sub> mitigation process.



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**Funders**  
National Science Foundation, PhD  
University of Illinois at Urbana-Champaign

**Period of Performance**  
1/1/09 to 12/31/11

**Cost**

**Total Project Value**  
\$ 1,000,000

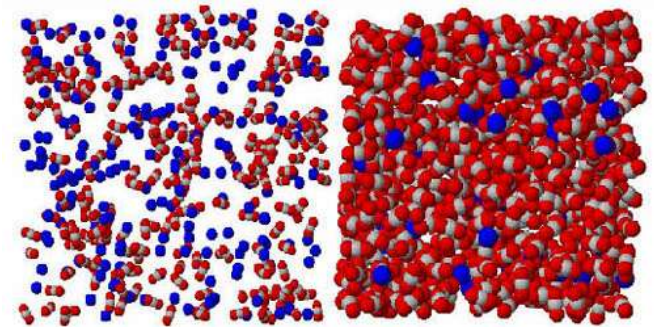
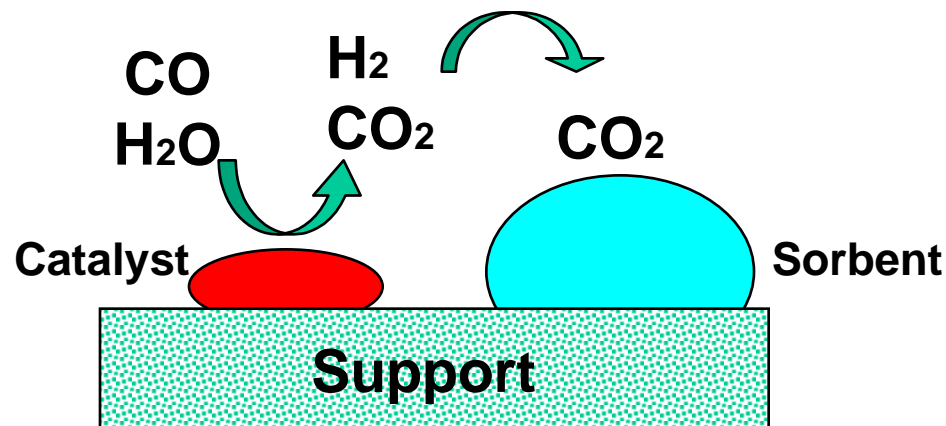
**SRD Group, Inc. Share**  
\$ 1,000,000 (100%)



# Engineered Adsorbents for Pre-Combustion CO<sub>2</sub> Capture

## □ Scope of Work

- Molecular and process simulation modeling to optimize sorbent properties
- Synthesis/characterization of sorbents
- Sorbent evaluation at WGS conditions using a high pressure and temperature reactor (HPTR) and high pressure TGA
- Techno-economic analysis and scale-up



# Summaries

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- ❑ Use of low quality steam provides one option for reducing solvent regeneration energy
- ❑ Compression work can be minimized by high pressure stripping
- ❑ Improving process reversibility and heat integration can further improve energy efficiency
- ❑ Availability of catalysts to accelerate CO<sub>2</sub> absorption into a solvent could enable applications of absorption processes that otherwise are limited by slow rates of reaction



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**Thank You!**

**Questions or Comments?**

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