Development and Evaluation of A Novel Integrated Vacuum Carbonate Absorption Process

(Agreement No.: DE-FC26-08NT0005498; Project Manager: Robert Patton)

Yongqi Lu

Illinois State Geological Survey

Institute of Natural Resource Sustainability

University of Illinois at Urbana-Champaign

Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting

March 24-26, 2009 · Pittsburgh, PA

Lead Contractor

Illinois State Geological Survey/ University of Illinois

- *~200 scientists and technical support staff*
- *Basic and applied research and service in earth science and related subjects*
- *Energy & Environmental Engineering section focuses on development and evaluation of advanced coal utilization and pollution control technologies*
- *Lead organization of the Midwest Geological Sequestration Consortium (MGSC) Partnership*

Presentation Outline

Project Overview

Technology Background

Project Objective

Scope of Work and Methodology

Plans for Pilot-Scale Test/ Commercialization

Funding Profile

- *DOE funding: $691 K*

- *Cost share: $457 K (40% of total cost)*
  - *UIUC-ISGS: $239 K*
  - *Calgon Carbon Corporation: $100 K*
  - *Illinois Office of Coal Development (OCD) / Illinois Clean Coal Institute (ICCI): $118 K*

- *Project duration: 3 years (October 2008 – September 2010)*

Research Participants /Personnel

- Participants
  - Illinois State Geological Survey-UIUC
  - Department of Civil & Environmental Engineering, UIUC
  - Calgon Carbon Corporation
  - OCD/ICCI

- Personnel
  - 3 research chemical engineers
  - 1 professor
  - 1 post-doctoral research associate
  - 1 visiting scholar
  - 2 graduate students
  - 1 industrial R&D representative

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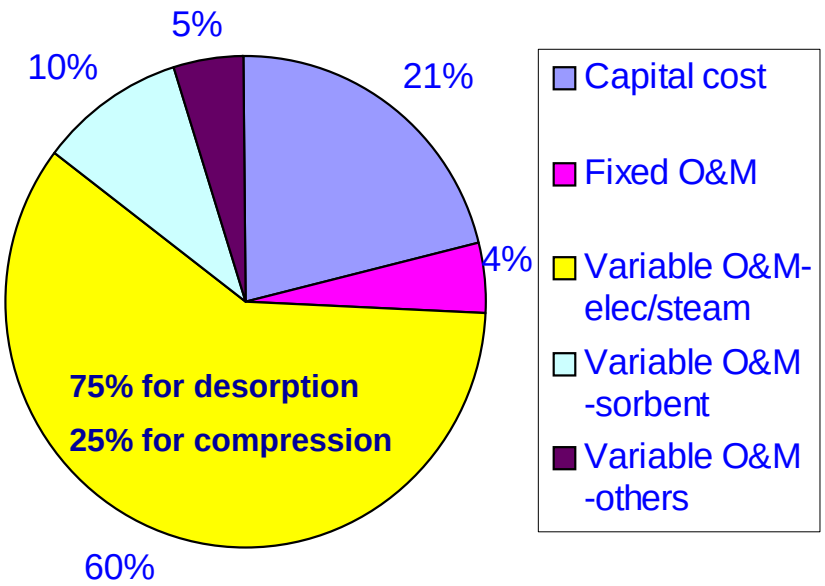
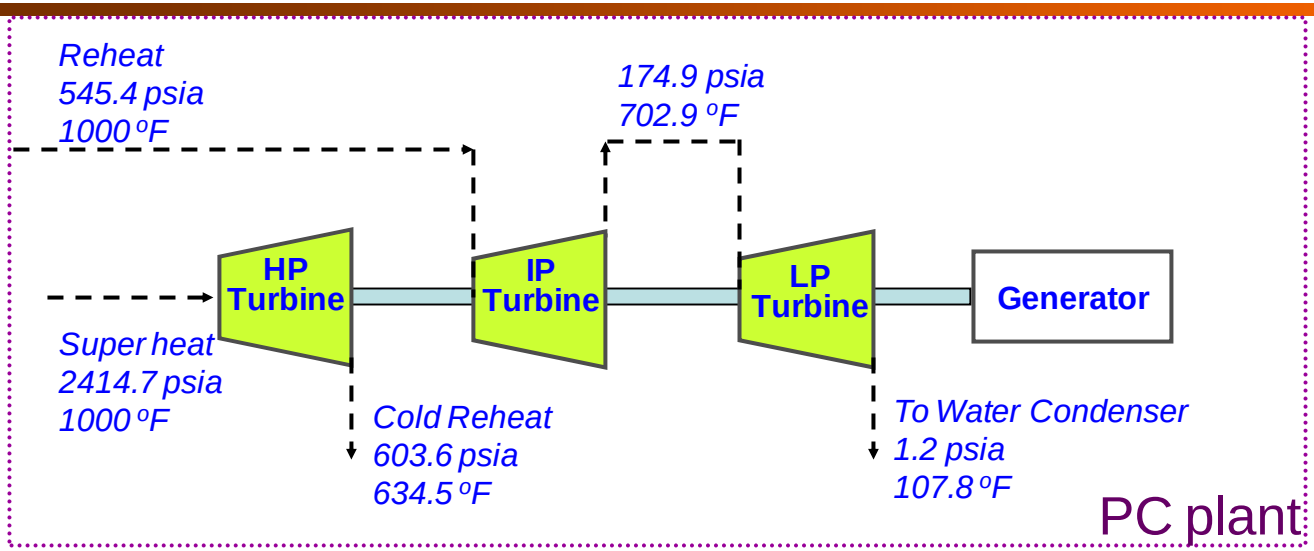
Absorption-Based Technology

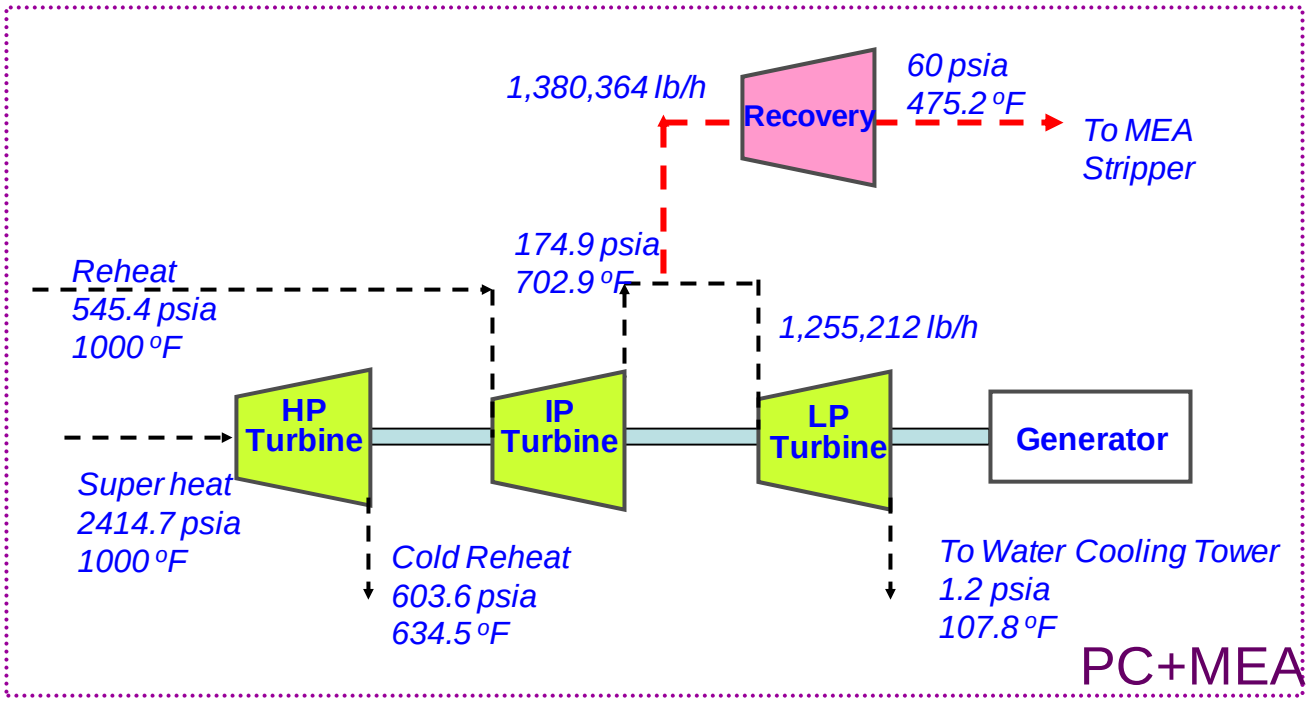
- *Electricity loss = ~27% of power plant output*
  - *¾ for stripping/desorption*
  - *¼ for compression*
  - *stripping + compression = 60% of CO_2 capture cost*



CO_2 avoidance cost breakdown (MEA solvent)

Steam Cycle in Power Plant

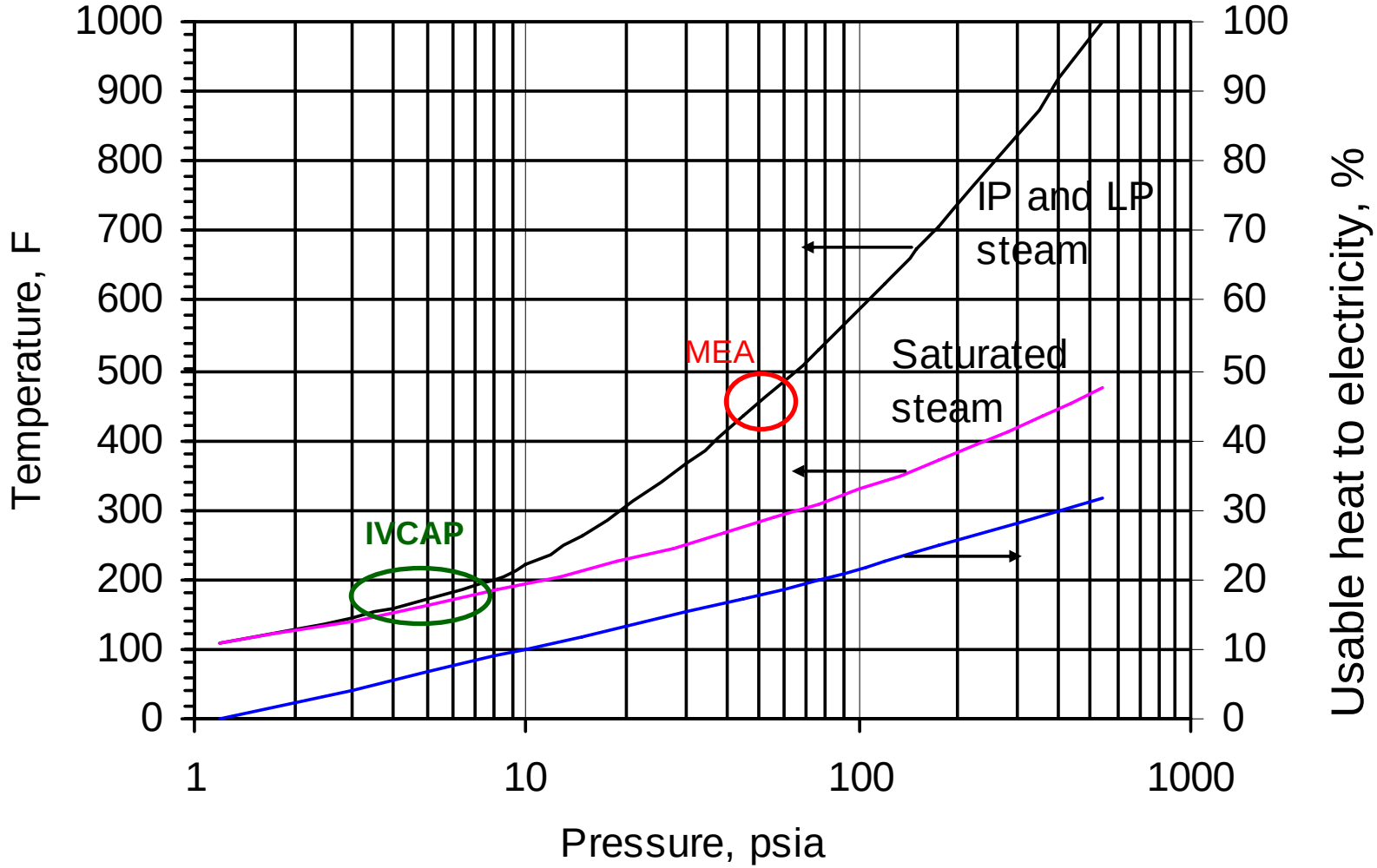




Turbine generations in a 528 MW (gross) plant

	PC	PC+MEA
HP	150.6	150.6
IP	124.7	124.7
LP	**252.3**	**120.2**
Recover		42.7
Total	527.6	438.2
Electricity loss		**89.4**

Use of Low-Quality Heat



- *Low steam pressure → low potential to produce electricity*

Carbonate Vs. Amine Solvents

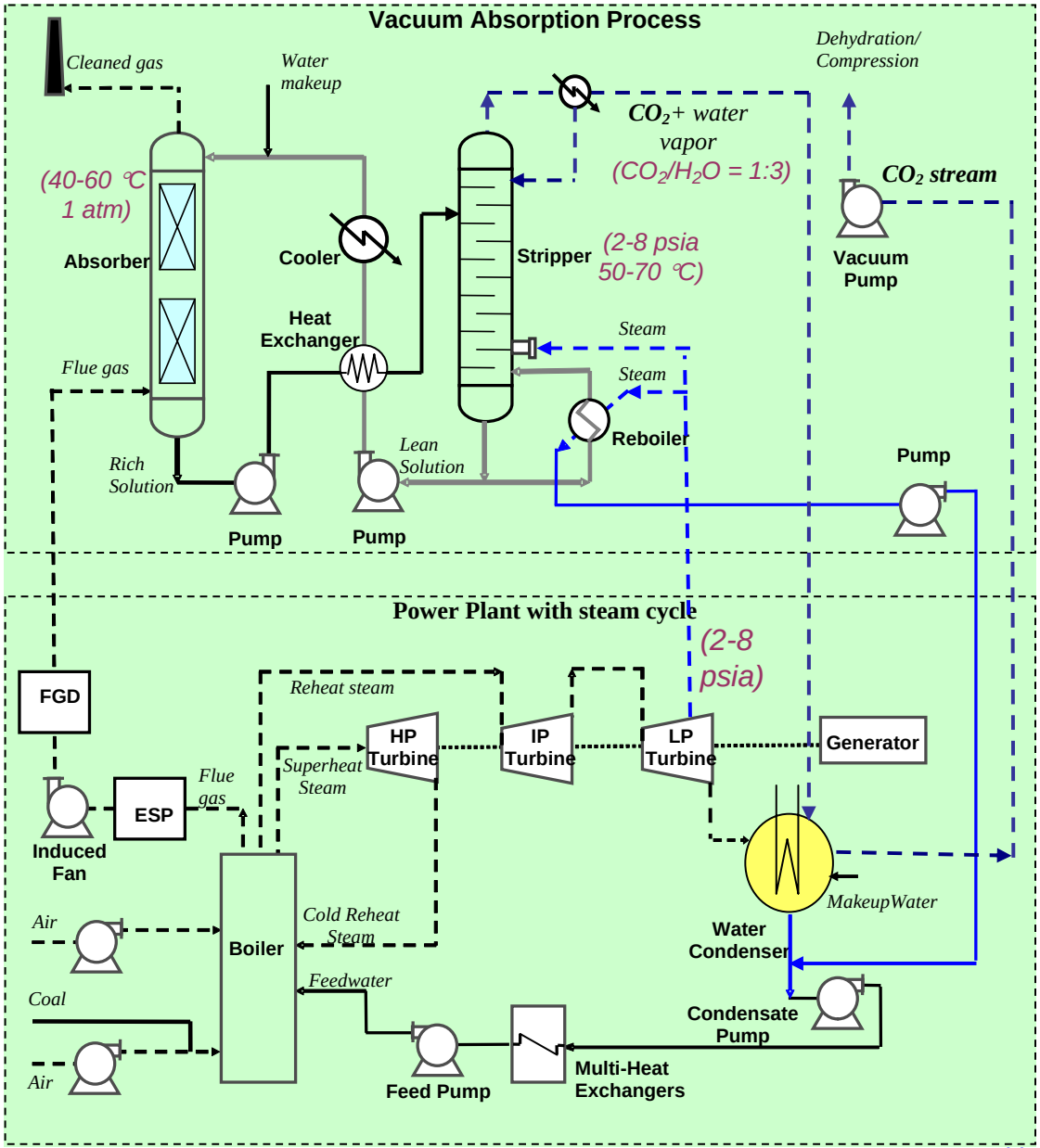
Solvent	Main Reaction	Heat of Absorption
Primary/secondary amines	$2RR'NH + CO_2 = RR'NCOO^- + RR'NH2^+$ (A)	MEA: 1,900 kJ/kg
Tertiary amine	$RR'R''N + CO_2 + H_2O = HCO_3^- + RR'R''NH^+$ (B)	MDEA: 1,200 kJ/kg
Carbonate	$CO_3^{2-} + CO_2 + H_2O = 2\ HCO_3^-$ (C)	600 kJ/kg

K_2CO_3 aqueous solution:

- *Low heat of absorption, high absorption capacity*
- *Weak affiliation with CO_2 favors low T/P stripping*

Patent-Pending IVCAP Process

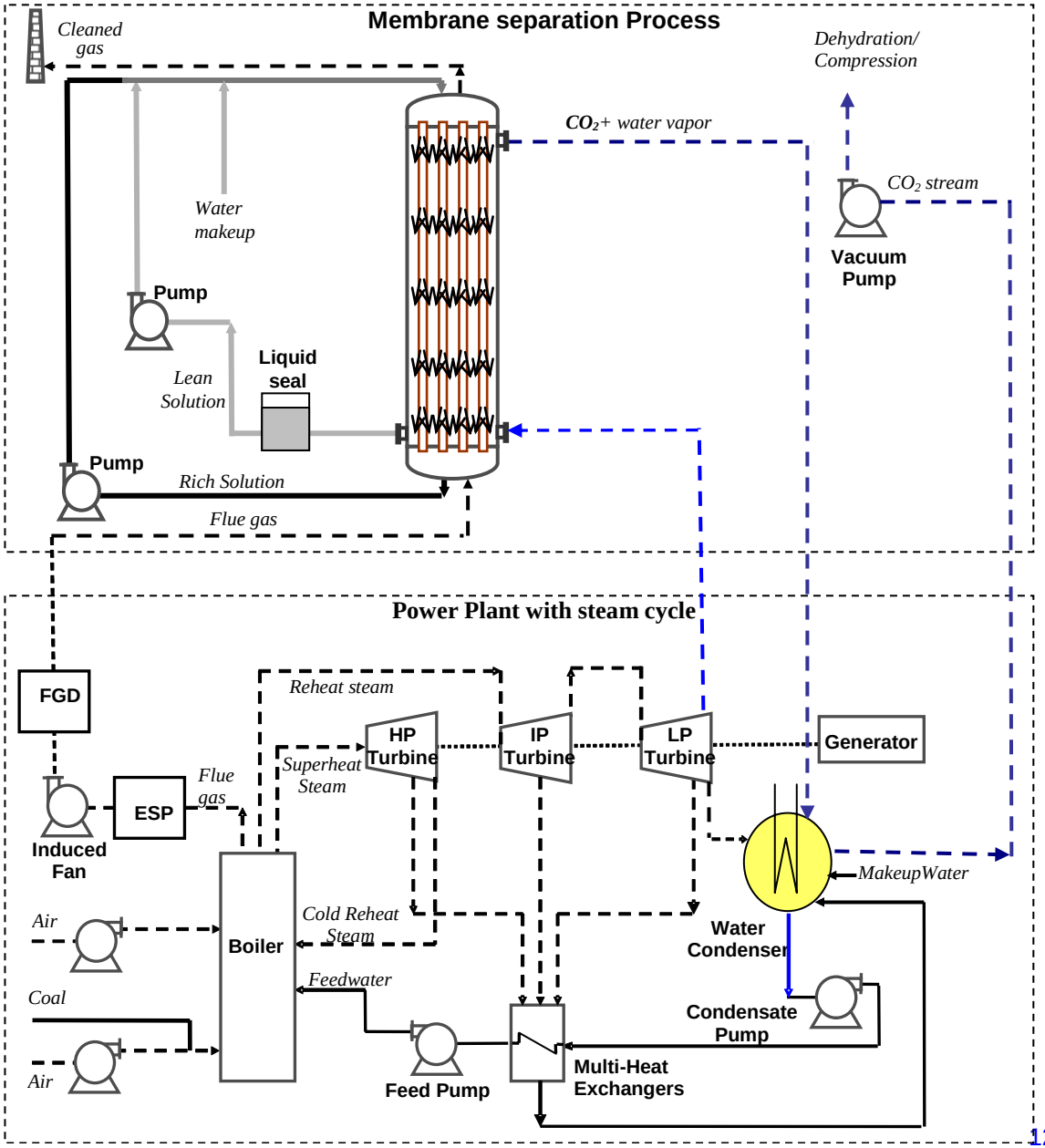
- *Integration with power plant steam cycle*
  - *Vacuum stripping allows the use of low quality steam*
  - *Direct introduction of steam into stripper to reduce heat transfer ΔT*



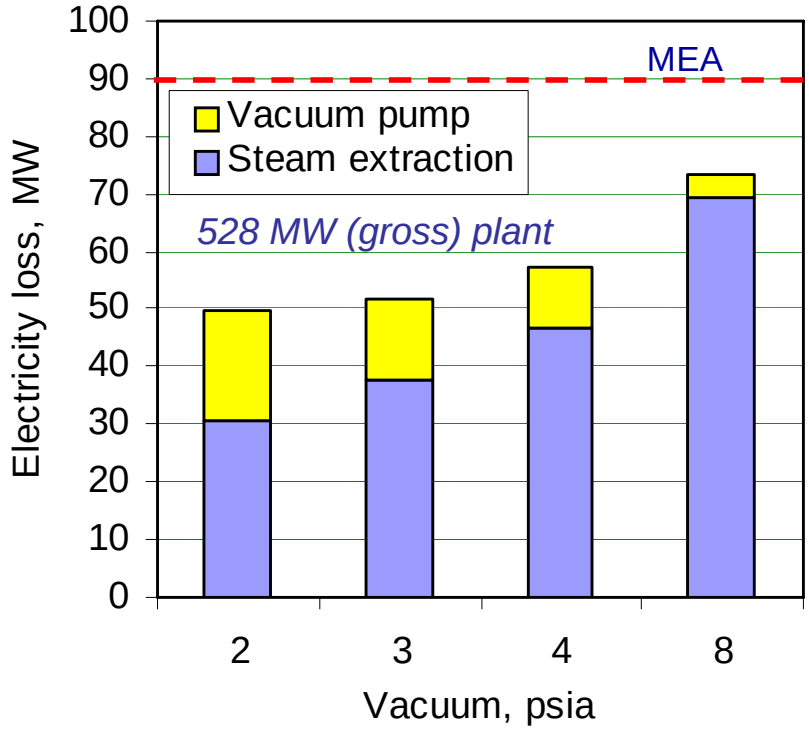
Integrated Vacuum Absorption Steam Cycle Gas Separation, Patent Application No. 60/798,489, May 2007.

IVCAP Configurations

- Packing bed-based absorption
- Membrane-based absorption
  - Membrane process with carrier solution permeation (vs. conventional membrane contactor)



Energy Use in IVCAP Stripper



(Compression, fan/pump electricity use not included in this figure)

(Simulation condition: Flue Gas: 130 °F, 14% CO_2; Solvent: 20wt% K_2CO_3; CO_2 lean loading: 0.16 mol/mol K_2CO_3; L/G ratio: 1.2 (L/G)min)

- *Energy use for stripping reduced by 20-45% compared to the MEA*

Preliminary Economic Analysis

Electricity, MWe	PC	PC+ Vacuum	PC+ MEA
CO_2 capture			
Steam extraction loss	0	37.8	89.4
Gas blower	0	10.0	10.0
Liquid pump	0	2.8	1.8
Vacuum pumps	0	14.0	0
CO_2 compression	0	39.7	35.4
Auxiliary energy in PC plant	34.7	33.3	32.0
Net output, MW	492.9	390.1	358.9

	MEA		IVCAP	
Annualized cost of CO_2 capture	Cost, M$/y	Share, %	Cost, M$/y	Share, %
Capital cost	24.3	31.0%	31.6	48.5%
Fixed O&M	5.0	6.3%	6.5	9.9%
Variable O&M - energy	32.6	41.5%	25.0	38.4%
Variable O&M - sorbent	11.3	14.4%	1.7	2.6%
Variable O&M - inhibitor	5.4	6.8%	0.3	0.5%
Subtotal	78.4	100.0%	65.1	100.0%
Net electricity, MW	358.9		390.1	
Loading factor, %	0.8		0.8	
Increase of electricity cost, c/kWh	3.3		2.5	
Reference CO_2 emissions, lb/kWh	1.9		1.9	
CO_2 emissions with control, lb/kWh	0.3		0.2	
CO_2 avoidance cost, $/ton	41.0		30.9	

- IVCAP offers 25% lower avoidance cost than MEA process

(Analysis based on 20%wt K_2CO_3 solution and stripping pressure of 3 psia)

Presentation Outline

- *Project Overview*
- *Technology Background*
- ***Project Objective***
- *Scope of Work and Methodology*
- *Plans for Pilot-Scale Test / Commercialization*

Objective

- *Test the proof-of-concept of the IVCAP process*
- *Identify an effective catalyst for accelerating CO_2 absorption*
- *Identify an effective additive for reducing the stripping heat*
- *Evaluate a modified IVCAP process as a multi-pollutant control process for combined SO_2 and CO_2 capture*

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Research Focus 1:
Evaluation/Development of Catalysts for Promoting Absorption Rate

- *Solvents with lower heat of absorption tend to have lower absorption rates*

$$CO_2(l) + H_2O \underset{1}{\longleftrightarrow} H_2CO_3 \qquad (slowest\ step)$$
$$CO_2(l) + OH^- \underset{2}{\longleftrightarrow} HCO_3^-$$

$$H_2CO_3 \underset{3}{\longleftrightarrow} H^+ + HCO_3^-$$
$$HCO_3^- \underset{4}{\longleftrightarrow} H^+ + CO_3^{2-}$$

$$Overall: K_2CO_3 + H_2O + CO_2 = KHCO_3$$

Comparison of Reaction Rates without Catalysts

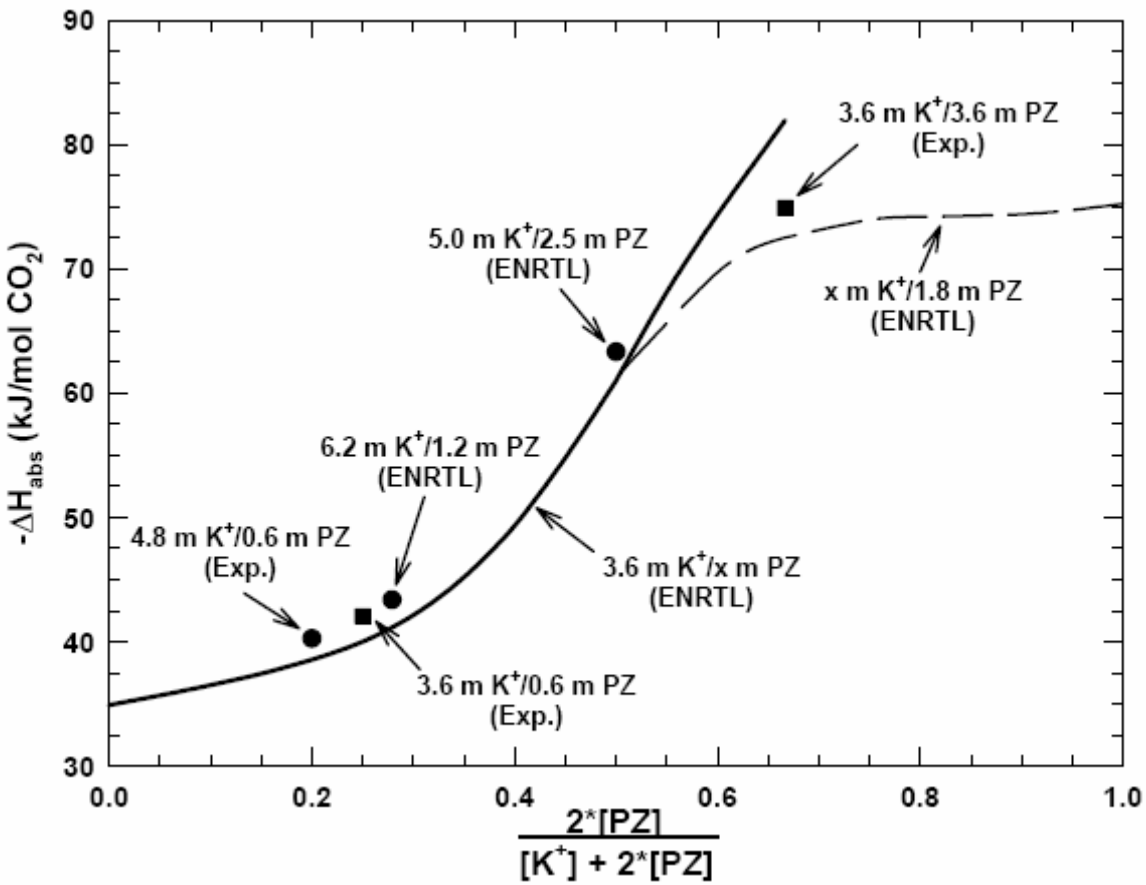
- *Without a catalyst, intrinsic rate of CO_2 in K_2CO_3 solution is 3-4 folder slower than in MEA.*

Reactions	Rate constants in literature	Rates, M s^{-1} ***
Rxn (1): CO_2 hydration with water	k'_{H2O} = 0.0375, 0.0358 s^{-1}	1.76 x10^{-4}
Rxn (2): CO_2 hydration with OH^-	K_{OH} = 8320, 8500 $M^{-1}s^{-1}$	3.91 x10^{-2}
Rxn (A) and (B): CO_2 hydration with amines	k_{am} = $M^{-1}s^{-1}$	
MDEA*	5.1, 5.0	1.20 x10^{-1}
TEA*	3.8	8.93 x10^{-2}
DMMEA*	7.5	1.76 x10^{-1}
DEMEA*	4.6	1.08 x10^{-1}
DEA**	110, 1500	2.59
DIPA**	54, 400	1.27
DGA**	4480, 4000	1.05 x10^{2}
MEA**	4700, 5868	1.10 x10^{2}

*Tertiary amines; ** Primary /secondary amines;
*** Rates based on the following assumptions: $[CO_2]$ = 0.0047 M, $[OH^-]$= 10^{-4} M, [amine] = 5 M

Catalyst vs. Mixture Solvent

- *A mixture solvent serves as a promoter rather than a catalyst*
- *Heat of absorption in a solvent mixture is higher than K_2CO_3 alone*



Effect of K+/PZ Ratio on the Heat of Absorption (40 to 70 ℃ average) at P_{CO2^*} = 3,000 Pa

Cullinane T. J., G.T. Rochelle, Fluid Phase Equilibria, 227(2), 2005: 197-213

Proposed Catalyst Research Work

- *Investigate catalytic methods to enhance CO_2 absorption rate in the K_2CO_3 solution*
  - *Evaluate and optimize activity of enzyme catalysts*
  - *Investigate enzyme Immobilization*
  - *Test other potential catalysts*

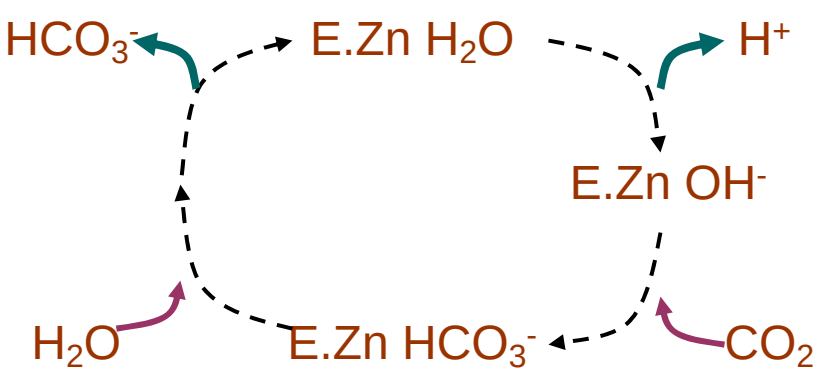
Carbonic Anhydrase (CA) Enzyme Catalyst

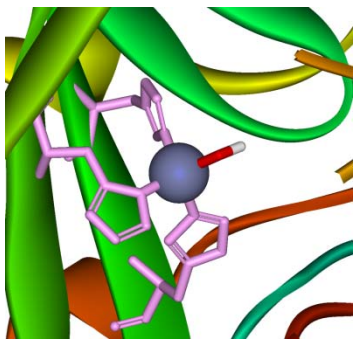
- *Most effective catalyst for CO_2 hydration*
- *Turnover rate of CA II =1.4 MM/s (at pH =9 and 25°C)*

(a) Ribbon diagram
Active site zinc ion (in gray) visible at center

Catalytic mechanism:

$$CO_2\,(l) + H_2O = H_2CO_3$$

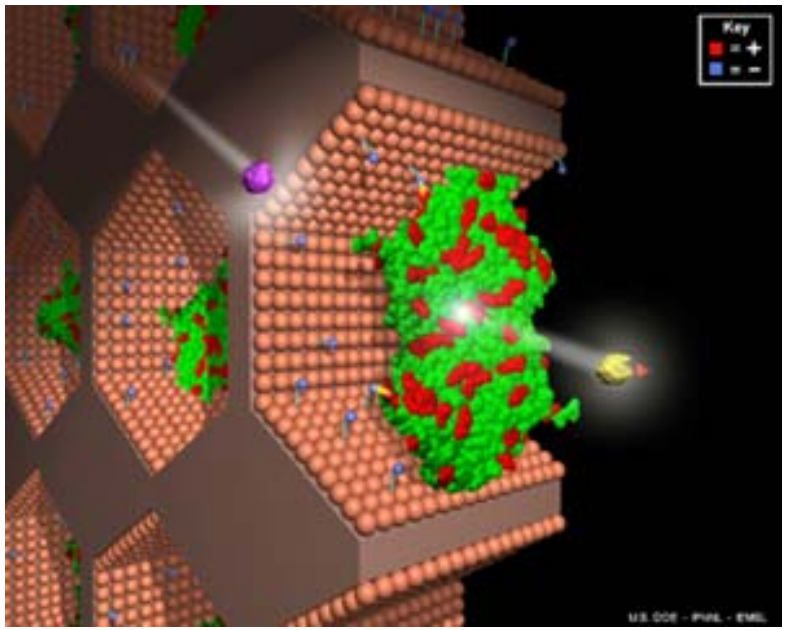


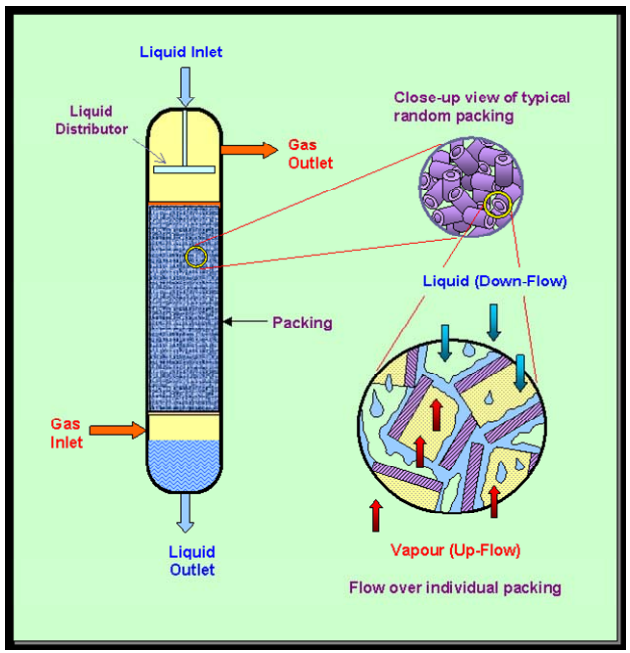


(b) Close-up view
3 histidine residues (in pink) and 1 hydroxide group (red and white) coordinating zinc ion (gray)

Enzyme Immobilization

- *Reduce enzyme leakage in a flow system*
- *Improve chemical stability of enzymes*
- *Improve thermal stability of enzymes*

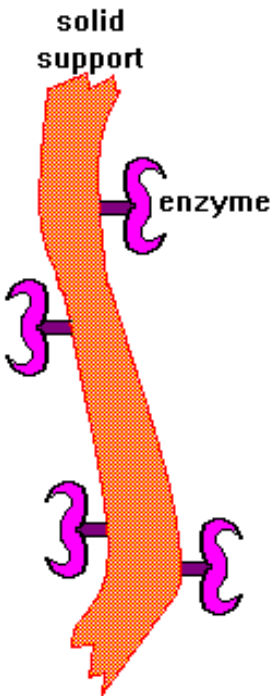




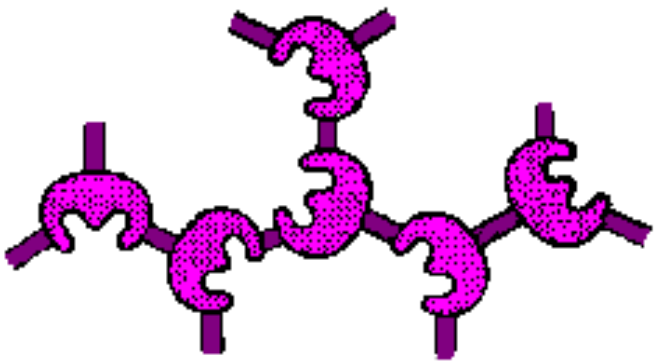
Methods and Materials for Immobilization

- *Supportive matrix:*
  - *Carbon-based materials*
  - *Inorganic gel materials*
  - *Polymer materials*

- *Method:*



Carrier-Binding

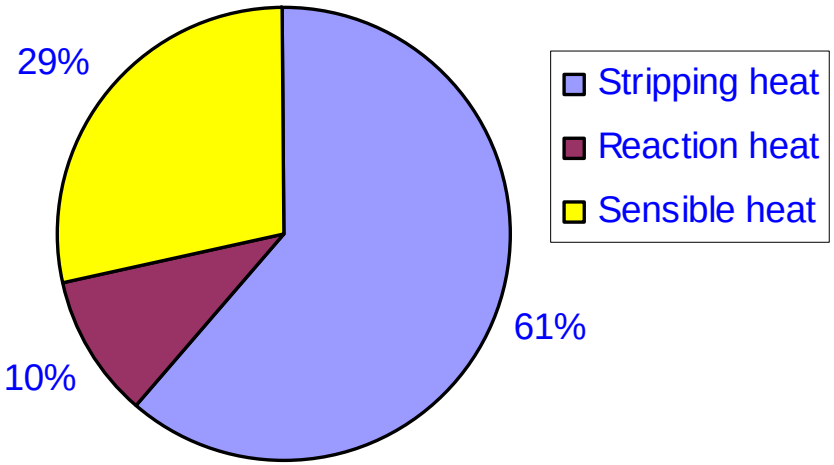


Cross-Linking

Research Focus 2:
Selection of Additives for Suppressing Water Vaporization in Stripper

- *More than 60% of the process heat in IVCAP is stripping heat*

- *Additives to suppress the water vapor saturation pressure lower stripping heat*

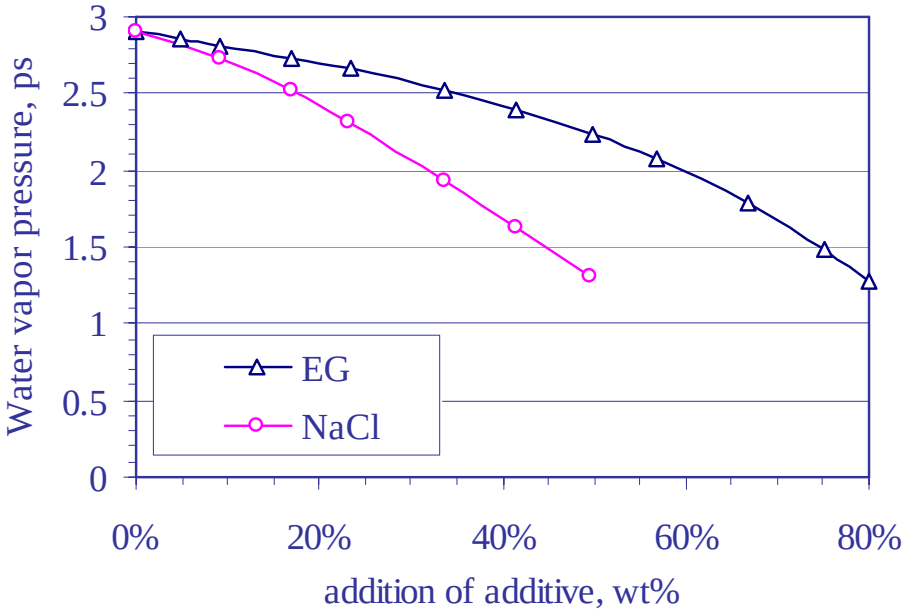


Heat use breakdown of IVCAP

Proposed Additive Research Work

- *Measurement of vapor-liquid phase equilibrium*
  - *CO_2-H_2O-K_2CO_3-$KHCO_3$ systems with and without additives*
  - *Temperature range of 25-70 °C*

- *Additives under consideration*
  - *Inorganic (Chloride, sulfate, others)*
  - *Glycols*



Examples of two additives: calculation results

Research Focus 3:
Combined SO_2 Removal in CO_2 Capture Process

- *Wet FGD is expensive*
  - *~15% of the cost of electricity*
  - *~40% FGD cost reduction equiv. to a saving of \$5/ton CO_2 (10%)*

- *IVCAP vs. MEA*
  - *A Separate wet FGD is required prior to the MEA process*
  - *Upgrading of the existing FGD is required to prevent the formation of irreversible HSS with MEA*
  - *Combining SO_2 removal with CO_2 capture is possible in IVCAP*

Absorption

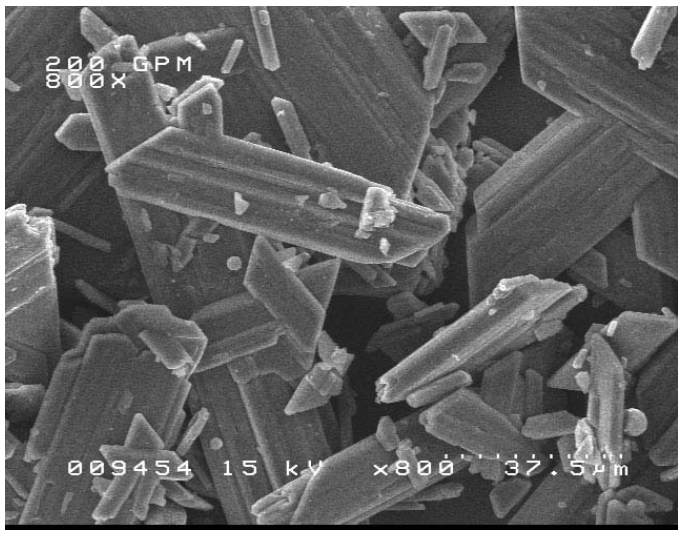
$$CO_2 + H_2O + K_2CO_3 = KHCO_3$$

$$SO_2 + 1/2H_2O + K_2CO_3 = K_2SO_4 + CO_2$$

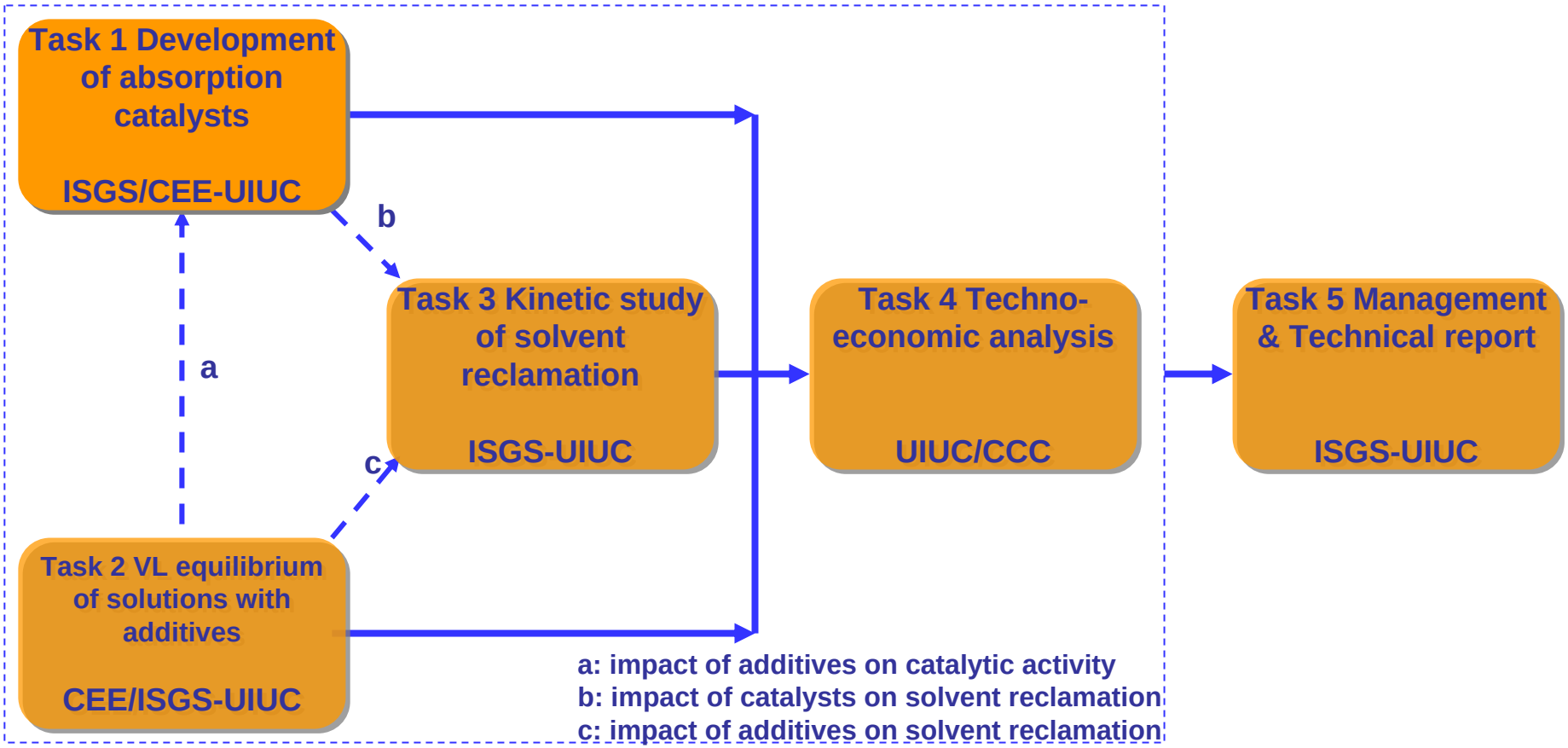
Sulfated solvent needs to be reclaimed

Proposed Research for Combined CO_2/SO_2 Capture Process Development

- *A unique process is proposed for combined SO_2/CO_2 capture*
- *Kinetic measurement of reclamation reactions of solvent consumed for desulfurization in the combined process*
  - *Evaluation of reclamation reagents*
  - *Parametric tests*
  - *Batch and semi-continuous tests*



Summary of Scope of Work



Project Schedule

Months after contract award	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Task 1. Development of absorption catalysts																																				
1.1 Experimental set up																																				
1.2 CA activity									a	A																										
1.3 Inorganic catalysts												b	B																							
1.4 CA immobilization																		c																		
1.5 Impact of additives from task2																						d														
Task 2. V-L equilibrium Measurement																																				
2.1 Experimental set up																																				
2.2 Reference solutions																e																				
2.3 Solutions with additives																				f	C															
3. Kinetic study of solvent reclamation																																				
3.1 Batch test																								g												
3.2 Semi-continuous test																													h							
3.3 Impacts of catalysts and additives from tasks 1 and 2																															i					
Task 4. Techno-economic analysis																																				
4.1 Process simulation																																	j			
4.2 Cost analysis																																		k		
Task 5. Management &Reporting			Q			Q			Q			Q			Q			Q			Q			Q			Q			Q			Q			F

Project Milestone Log

- *Milestones:*

a: *Activity data of CA enzymes*

b *Reactivity data of other selected catalysts*

c: *Immobilization method development and testing of immobilized enzymes*

d: *Impacts of additives on enzyme activity*

e, f: *V-L equilibrium data of solutions with and w/o additives*

g, h: *Kinetic data of the batch and semi-continuous crystallization tests*

i: *Impacts of selected catalysts and additives*

j, k: *Process simulation and techno-economic evaluation for a conceptual 500 MW power plant*

- *Decision points*

A: *The absorption rate of CA enzyme-promoted solution comparable to primary amine*

B: *Comparison of CA enzyme activity with other catalysts*

C: *Selection of an additive with minimal water evaporation*

Project Updates

- ***Development of absorption catalysts***
  - *Semi-batch experimental setup*
  - *Test plan matrix*
  - *Measurement/ anslysis methods*
  - *Parametric tests of catalyst activity*

CSTR experimental system at ISGS/UIUC

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Pilot-Scale IVCAP

- *Obtain proof-of-concept and scale-up data*
- *Seek federal (such as through RFPs) and industrial support for a pilot-scale test (0.3-3 MWe)*
- *A potential utility site has been identified*
- *Potential support from Illinois Office of Coal Development / Illinois Department of Commerce and Economic Opportunity*
- *Identify industrial partners for pilot-scale demonstration*

Summary

- *IVCAP offers ~25% lower electricity loss (absorption + compression) compared to MEA process*
- *More cost savings with combined SO_2 removal*
- *Key process parameters are an effective catalyst and vacuum degree of the stripper*
- *Scale up data are being collected to advance the technology for a pilot-scale demonstration*