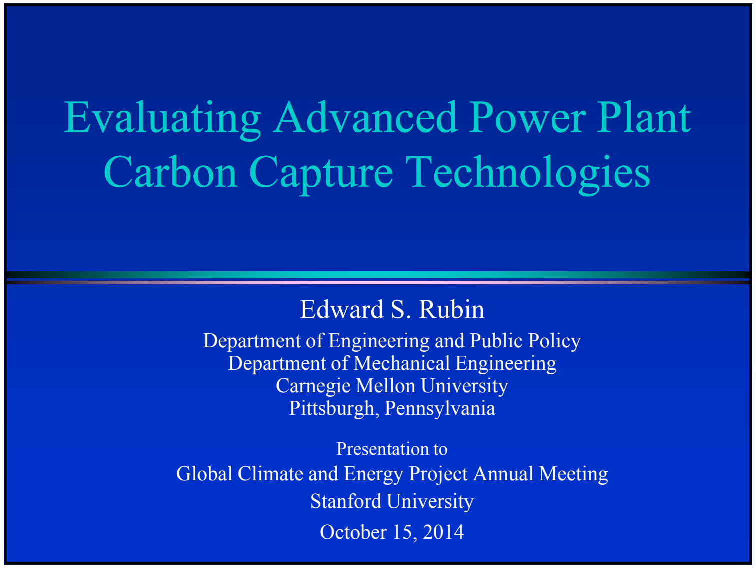

Evaluating Advanced Power Plant Carbon Capture Technologies

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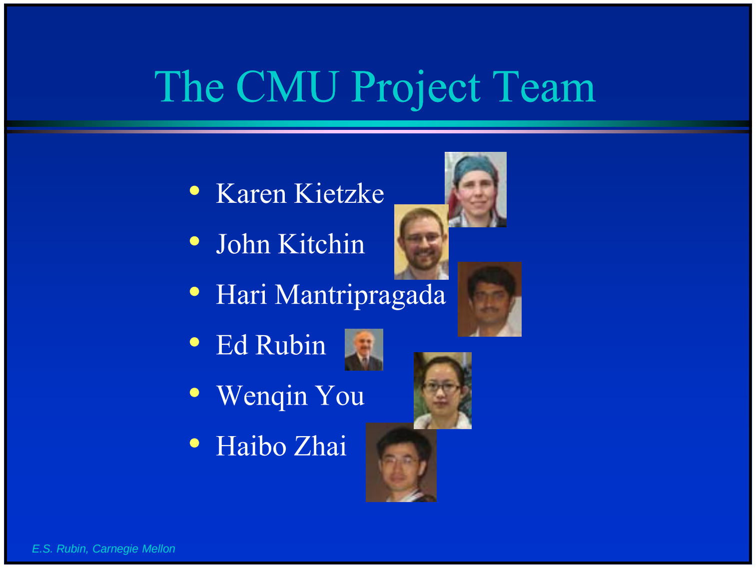
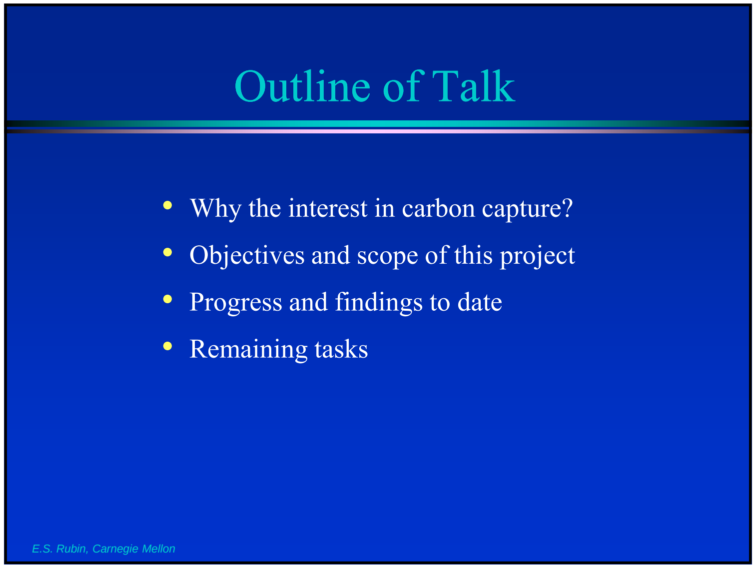
Presentation to
Global Climate and Energy Project Annual Meeting
Stanford University
October 15, 2014



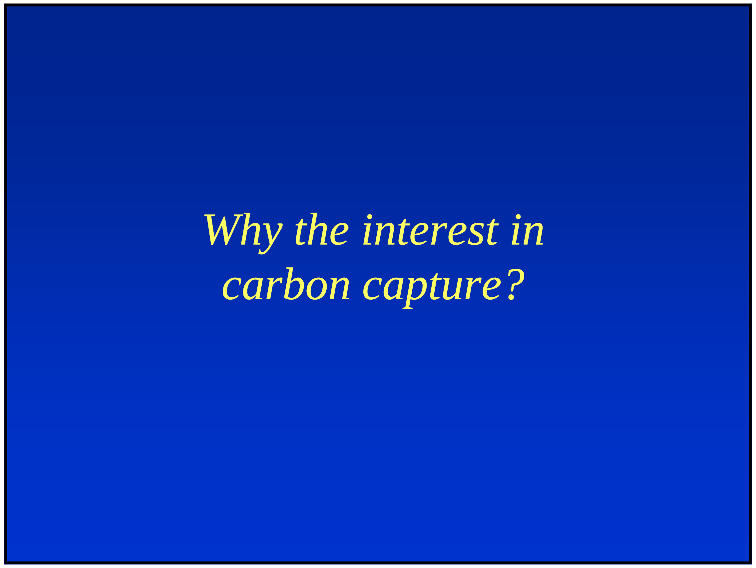
The CMU Project Team

- Karen Kietzke
- John Kitchin
- Hari Mantripragada
- Ed Rubin
- Wenqin You
- Haibo Zhai



Outline of Talk

- Why the interest in carbon capture?
- Objectives and scope of this project
- Progress and findings to date
- Remaining tasks

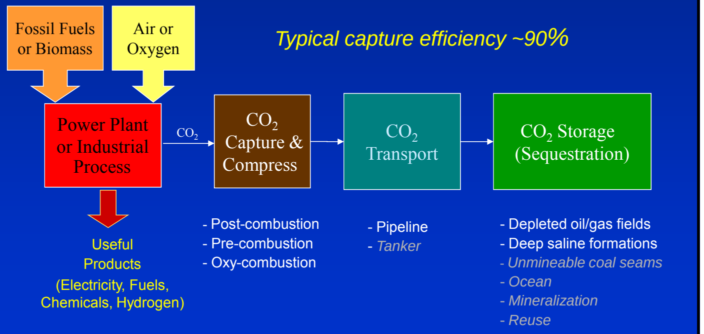


Why the interest in carbon capture?

Motivation for CCS

- Achieving global climate change goals will require <u>large</u> reductions in CO_2 emissions from power plants and other major sources of GHGs
- CCS is the <u>ONLY</u> way to get large CO_2 reductions from the fossil fuels that currently provide most of our energy—a potential bridging technology to a *sustainable* energy future
- CCS is a major component of cost-effective strategies for climate change mitigation—without it, global costs are trillions of dollars higher (IPCC)

Schematic of a Carbon Capture and Storage (CCS) System



Typical capture efficiency ~90%

Fossil Fuels or Biomass

Air or Oxygen

Power Plant or Industrial Process

CO_2

CO_2 Capture & Compress

CO_2 Transport

CO_2 Storage (Sequestration)

Useful Products

(Electricity, Fuels, Chemicals, Hydrogen)

- Post-combustion
- Pre-combustion
- Oxy-combustion

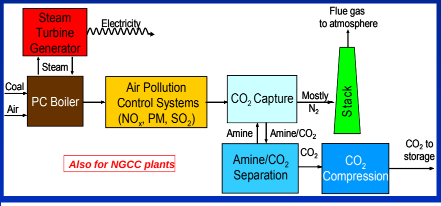
- Pipeline
- *Tanker*

- Depleted oil/gas fields
- Deep saline formations
- *Unmineable coal seams*
- *Ocean*
- *Mineralization*
- *Reuse*

CO_2 Capture from Power Plants

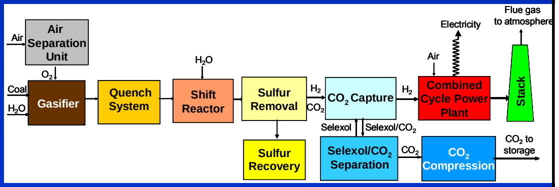
(current technology)

Post-Combustion Capture



Also for NGCC plants

Pre-Combustion Capture



Examples of CO_2 Capture Systems

Gas-fired power plant

(Source: Flour Daniel)

Coal-fired power plant

(Source: (IEA GHG)

H_2 production plant

(Source: Chevron-Texaco)

Large-scale Demonstration Projects

- Sask Power Boundary Dam project (Canada)
- 110 MW coal-fired unit
- Post-combustion capture +EOR
- 90% capture (~ 1 Mt CO_2/yr)
- Now operating (Sept 2014)

Sask Power, 2014

- Southern Co. Kemper County IGCC project (Mississippi)
- 582 MW coal-fired unit
- Pre-combustion capture +EOR
- ~ 65% capture (3.5 Mt CO_2/yr)
- Startup in 2015

Kemper, 2014

Cost of CCS for New Power Plants Using Current Technology

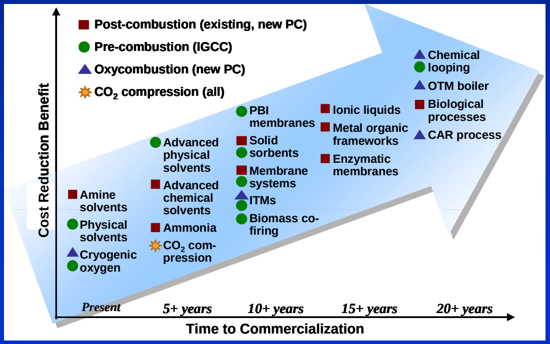
Increase in levelized cost for 90% capture

Incremental Cost of CCS ***relative to same plant type*** without	Supercritical Pulverized Coal Plant	Integrated Gasification Combined Cycle Plant	Natural Gas Combined Cycle
% Increases in power generation cost (\$/kWh)*	**~ 60–80%**	**~ 30–50%**	**~ 30–45%**

- ***Capture accounts for most (~80%) of the total cost***

**Added cost to consumers will be much smaller, reflecting the CCS capacity in the generation mix at any given time. Retrofit of existing plants typically has a higher cost*

R&D Programs Seek to Develop Lower-Cost Technologies



Source: USDOE, 2010

GCEP Projects on Advanced Carbon Capture Technologies

- In Fall 2011, GCEP issued RFP for advanced carbon capture and separation technologies and alternative processes that:
  - Have an excellent scientific basis rooted in the fundamentals;
  - Enables a step-out or game-changing improvement;
  - Could have large global impact in a 10 to 50 year timeframe; and
  - Is on a pathway to meet or exceed all performance criteria listed in RFP.
- Three projects were selected for funding in 2012:

Capture Material	Application	Research Group
Metal organic frameworks	Post-combustion	Northwestern University (R. Snurr, PI)
New AC sorbents	Post-combustion	Stanford University (J. Wilcox, PI)
Ionic liquids	Pre-combustion	University of Notre Dame (J. Brannecke, PI)

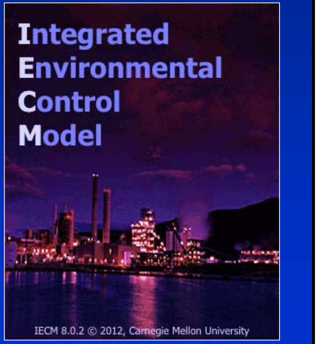
Objectives and scope of this project

A Systems Analysis Framework for Technology Assessments

- In response to a subsequent GCEP RFP, our group at Carnegie Mellon was selected to provide a systems analysis framework that could be used to:
  - Quantify key performance metrics for carbon capture systems in the context of a complete power plant system
  - Perform case studies of GCEP-supported technologies
  - Allow comparative analyses of capture technology options
  - Identify if an approach "has the potential to be a breakthrough when applied in a full-scale power generation system"

Our Approach:
Build on the IECM Framework

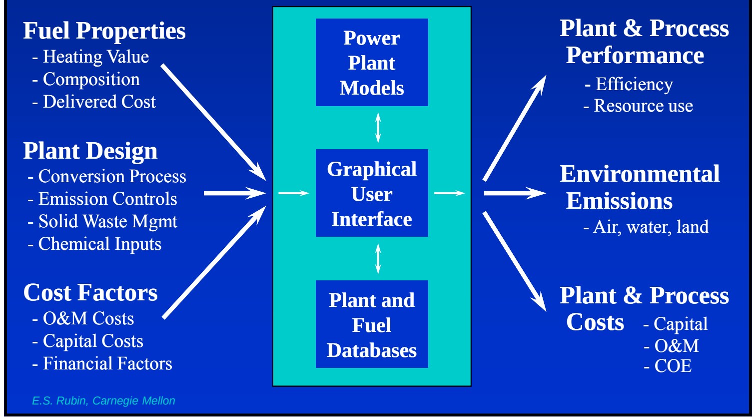
- A desktop/laptop computer simulation model developed for DOE/NETL
- Provides systematic estimates of <u>performance, emissions, costs</u> and <u>uncertainties</u> for preliminary design of:
  - PC, IGCC and NGCC plants
  - All flue/fuel gas treatment systems
  - CO_2 capture and storage options (pre- and post-combustion, oxy-combustion; transport, storage)
- Free and publicly available at: **www.iecm-online.com**



IECM Modeling Approach

- Process Performance Models
- Engineering Economic Models
- Systems Analysis Framework
- Advanced Software Capabilities
  - Probabilistic analysis capability
  - User-friendly graphical interface
  - Graphical analysis capabilities
  - Easy to add or update models

IECM Software Package



Fuel Properties
- Heating Value
- Composition
- Delivered Cost

Plant Design
- Conversion Process
- Emission Controls
- Solid Waste Mgmt
- Chemical Inputs

Cost Factors
- O&M Costs
- Capital Costs
- Financial Factors

Power Plant Models

Graphical User Interface

Plant and Fuel Databases

Plant & Process Performance
- Efficiency
- Resource use

Environmental Emissions
- Air, water, land

Plant & Process Costs
- Capital
- O&M
- COE

Technologies Currently in IECM

CO_2 Capture & Storage Systems*	Coal Combustion Plants		Gasification Plants (IGCC)	IGCC and NGCC Plants
Post-Combustion Capture Conv. Amine; Adv. amines (FG+); Chilled ammonia; Membrane systems; Aux. NG steam or power gen. (optional) Oxy-Combustion Capture Flue gas recycle; ASU; Chemical processing units Pre-Combustion Capture Water gas shift + Selexol CO_2 Compressor CO_2 Transport Pipelines (6 U.S. regions); Other (user-specified) CO_2 Storage Deep saline formation; Geol.Storage w/ EOR; Other (user-specified)	Boiler/Turbine Systems Subcritical; Supercritical; Ultra-supercritical Furnace Firing Tangential; Wall; Cyclone Furnace NOx Control LNB; SNCR; SNCR+LNB; Gas reburn Flue Gas NOx Removal Hot-side SCR Mercury Removal Carbon/sorbent injection	Particulate Removal Cold-side ESP; Fabric filter (Reverse air; Pulse jet) SO_2 Removal Wet limestone (Conv.; F. oxidation; Additives); Wet lime; Lime spray dry Solids Management Ash pond; Landfill; Co-mixing; useful byproducts Cooling and Wastewater Systems Once-thru cooling; Wet cooling tower; Dry cooling; Chemical treatment; Mech. treatment	Air Separation Unit Cryogenic Slurry Preparation & Coal Pretreatment Gasification Slurry-fed gasifier (GE-Q); Dry-fed gasifier (Shell) Syngas Cooling and Particulate Removal Mercury Removal Activated carbon H_2S Removal Selexol; Sulfinol Sulfur Recovery Claus plant; Beavon-Stretford unit	Gas Turbine GE 7FA; GE 7FB Heat Recovery Steam Generator Steam Turbine Boiler Feedwater System Process Condensate Treatment Cooling Water System Once-through; Wet cooling tower; Dry cooling Aux. Equipment

*Additional capture options under development include solid sorbent and calcium looping systems for post-combustion (PC or NGCC plants), a chemical looping system for IGCC, and an advanced oxy-combustion system

GCEP Criteria for Advanced Carbon Capture Systems

We are working with the three GCEP-funded research teams to develop process performance and cost models that can be used to assess new process concepts relative to specific GCEP criteria:

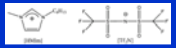
- Capture and separate ≥ 90% of power system CO_2
- Energy penalty ≤ 10% of overall power system output
- Minimal lifecycle environmental impacts and water demand
- Uses only earth-abundant and non-toxic constituents

- Incremental cost ≤ 15% of overall power system cost
- Reliability comparable to other power plant components
- Lifetime equal to the associated energy generation system
- Potential for low-cost integration & deployment at large scale

Performance models

Capture Materials Modeled

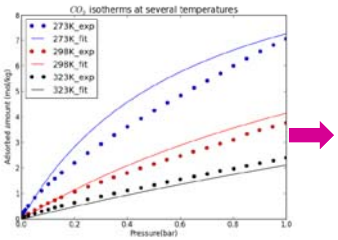
- All university research groups are still developing their novel capture materials
- For preliminary analysis we use surrogate materials suggested by each of the GCEP research groups:
  - MOFs: Zeolitic Imidazolate Frameworks (ZIF-78); also, Mg_2-(dobdc) – MOF-74
  - Activated Carbon: SU_AC
  - Ionic Liquids: 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hmim][Tf2N])



Post-combustion capture

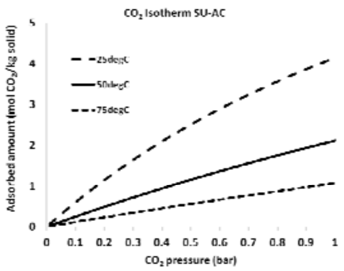
using novel sorbents

Examples of Sorbent Isotherms: SU_AC



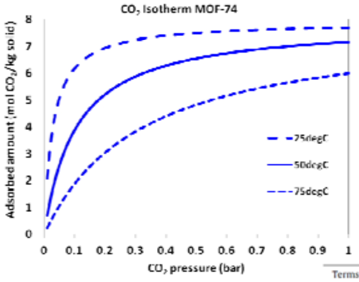
Activated Carbon	CO_2	N_2
m1 (gmol/kg)	11.89	1.05
bo1 (1/bar)	4.28 (-6)	2.1 (-3)
Q1 (kJ/gmol)	29.084	14.0

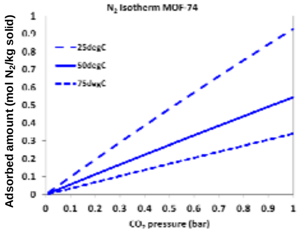
Langmuir Model Fit



Source: Based on data from J.Wilcox, 2014

Sorbent Isotherms: MOF-74





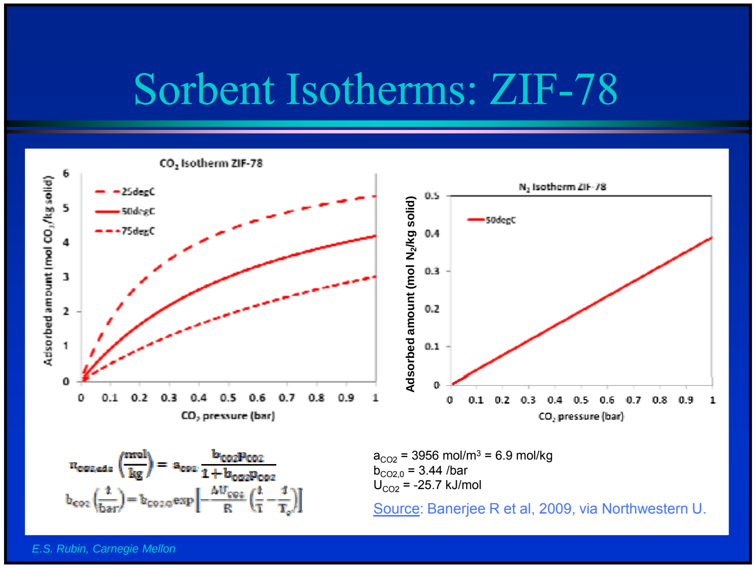
$$N_{ads,i} = \frac{m_1 b_i P_i}{1 + b_i P_i} + \frac{m_2 d_i P_i}{1 + d_i P_i}$$

$$b_i = b_{0i} \exp\left(\frac{Q_1}{RT}\right)$$

$$d_i = d_{0i} \exp\left(\frac{Q_2}{RT}\right)$$

Terms	Mg-MOF-74ᶜ	
	CO_2	N_2
m_1 (gmol/kg)	6.8	14
m_2 (gmol/kg)	9.9	-
b_{0i} (1/bar)	2.44E−06	4.96E−10
Q_1 (J/gmol)	42,000	18,000
d_{0i} (1/bar)	1.39E−05	-
Q_2 (J/gmol)	24,000	-

Source: Maring and Webley., 2013



Sorbent Isotherms: ZIF-78

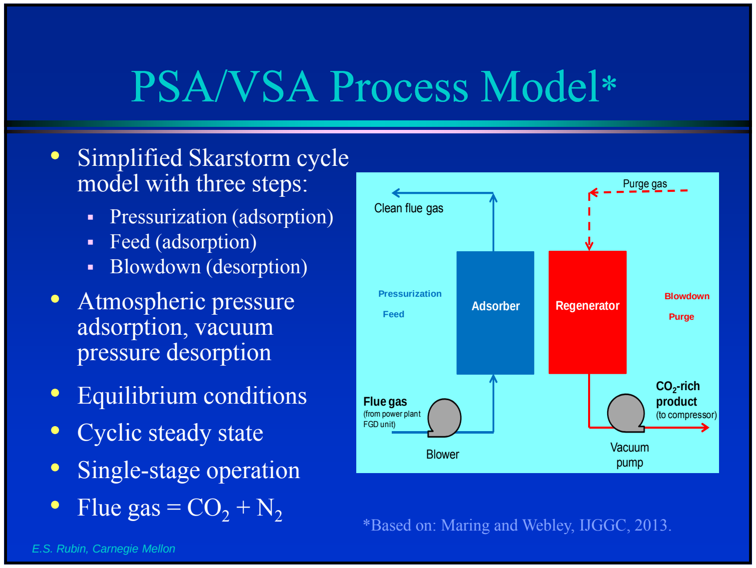
$$n_{CO2,ads}\left(\frac{mol}{kg}\right) = a_{CO2}\frac{b_{CO2}P_{CO2}}{1+b_{CO2}P_{CO2}}$$

$$b_{CO2}\left(\frac{1}{bar}\right) = b_{CO2,0}\exp\left[-\frac{\Delta U_{CO2}}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right]$$

a_{CO2} = 3956 mol/m^3 = 6.9 mol/kg
$b_{CO2,0}$ = 3.44 /bar
U_{CO2} = -25.7 kJ/mol

Source: Banerjee R et al, 2009, via Northwestern U.

E.S. Rubin, Carnegie Mellon

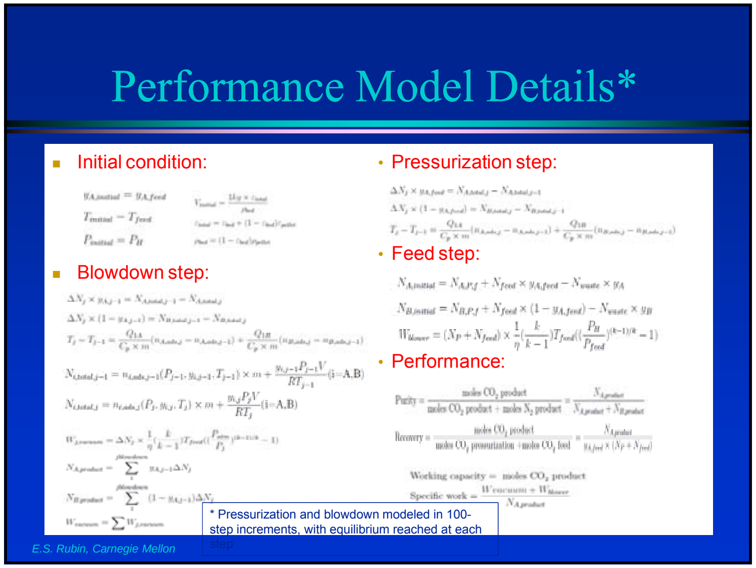


PSA/VSA Process Model*

- Simplified Skarstorm cycle model with three steps:
  - Pressurization (adsorption)
  - Feed (adsorption)
  - Blowdown (desorption)
- Atmospheric pressure adsorption, vacuum pressure desorption
- Equilibrium conditions
- Cyclic steady state
- Single-stage operation
- Flue gas = $CO_2 + N_2$

*Based on: Maring and Webley, IJGGC, 2013.

E.S. Rubin, Carnegie Mellon



Performance Model Details*

- Initial condition:

$$y_{A,initial} = y_{A,feed} \qquad V_{initial} = \frac{M_{ZIF}\times\varepsilon_{total}}{\rho_{bed}}$$
$$T_{initial} = T_{feed} \qquad \varepsilon_{total} = \varepsilon_{bed} + (1-\varepsilon_{bed})\varepsilon_{pellet}$$
$$P_{initial} = P_H \qquad \rho_{bed} = (1-\varepsilon_{bed})\rho_{pellet}$$

- Blowdown step:

$$\Delta N_j \times y_{A,j-1} = N_{A,total,j-1} - N_{A,total,j}$$
$$\Delta N_j \times (1-y_{A,j-1}) = N_{B,total,j-1} - N_{B,total,j}$$
$$T_j - T_{j-1} = \frac{Q_{1A}}{C_p\times m}(n_{A,ads,j} - n_{A,ads,j-1}) + \frac{Q_{1B}}{C_p\times m}(n_{B,ads,j} - n_{B,ads,j-1})$$
$$N_{i,total,j-1} = n_{i,ads,j-1}(P_{j-1}, y_{i,j-1}, T_{j-1})\times m + \frac{y_{i,j-1}P_{j-1}V}{RT_{j-1}}(i{=}A,B)$$
$$N_{i,total,j} = n_{i,ads,j}(P_j, y_{i,j}, T_j)\times m + \frac{y_{i,j}P_jV}{RT_j}(i{=}A,B)$$
$$W_{j,vacuum} = \Delta N_j \times \frac{1}{\eta}\left(\frac{k}{k-1}\right)T_{feed}\left(\left(\frac{P_{atm}}{P_j}\right)^{(k-1)/k} - 1\right)$$
$$N_{A,product} = \sum_{1}^{jblowdown} y_{A,j-1}\Delta N_j$$
$$N_{B,product} = \sum_{1}^{jblowdown} (1-y_{A,j-1})\Delta N_j$$
$$W_{vacuum} = \sum W_{j,vacuum}$$

- Pressurization step:

$$\Delta N_j \times y_{A,feed} = N_{A,total,j} - N_{A,total,j-1}$$
$$\Delta N_j \times (1-y_{A,feed}) = N_{B,total,j} - N_{B,total,j-1}$$
$$T_j - T_{j-1} = \frac{Q_{1A}}{C_p\times m}(n_{A,ads,j} - n_{A,ads,j-1}) + \frac{Q_{1B}}{C_p\times m}(n_{B,ads,j} - n_{B,ads,j-1})$$

- Feed step:

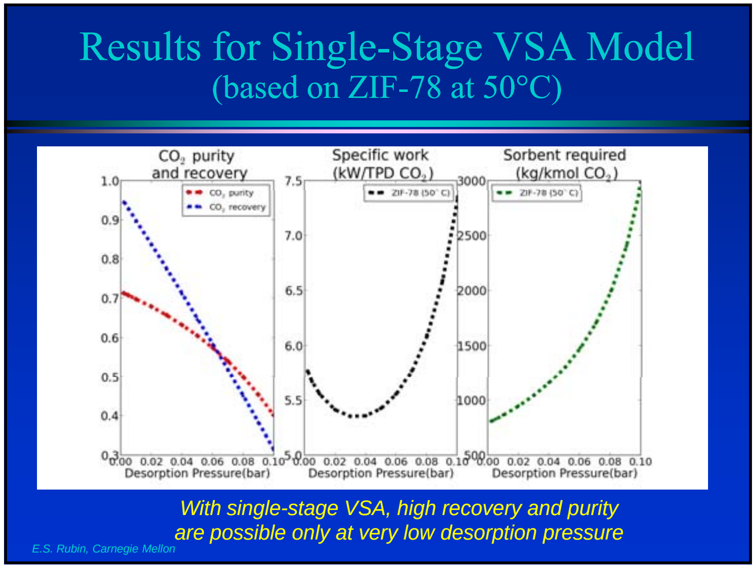
$$N_{A,initial} = N_{A,P,f} + N_{feed}\times y_{A,feed} - N_{waste}\times y_A$$
$$N_{B,initial} = N_{B,P,f} + N_{feed}\times(1-y_{A,feed}) - N_{waste}\times y_B$$
$$W_{blower} = (N_P + N_{feed})\times\frac{1}{\eta}\left(\frac{k}{k-1}\right)T_{feed}\left(\left(\frac{P_H}{P_{feed}}\right)^{(k-1)/k} - 1\right)$$

- Performance:

$$\text{Purity} = \frac{\text{moles } CO_2 \text{ product}}{\text{moles } CO_2 \text{ product} + \text{moles } N_2 \text{ product}} = \frac{N_{A,product}}{N_{A,product}+N_{B,product}}$$
$$\text{Recovery} = \frac{\text{moles } CO_2 \text{ product}}{\text{moles } CO_2 \text{ pressurization} + \text{moles } CO_2 \text{ feed}} = \frac{N_{A,product}}{y_{A,feed}\times(N_P+N_{feed})}$$
$$\text{Working capacity} = \text{moles } CO_2 \text{ product}$$
$$\text{Specific work} = \frac{W_{vacuum}+W_{blower}}{N_{A,product}}$$

* Pressurization and blowdown modeled in 100-step increments, with equilibrium reached at each step

E.S. Rubin, Carnegie Mellon



Results for Single-Stage VSA Model
(based on ZIF-78 at 50°C)

With single-stage VSA, high recovery and purity are possible only at very low desorption pressure

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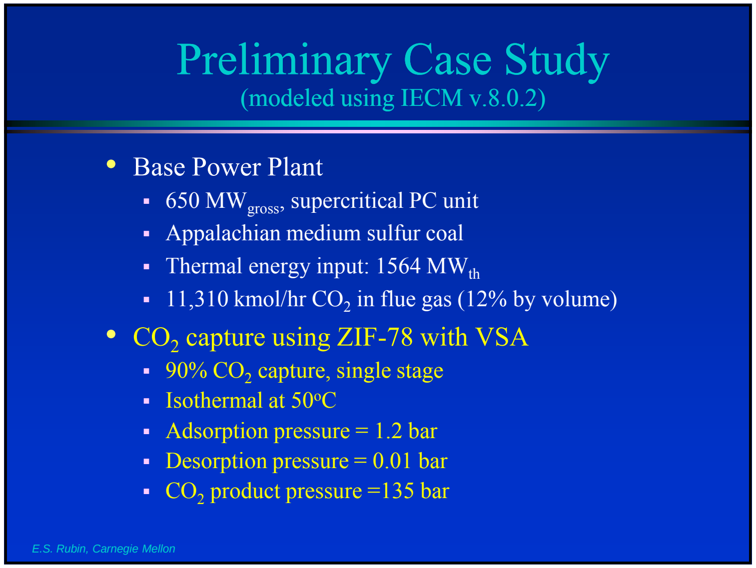
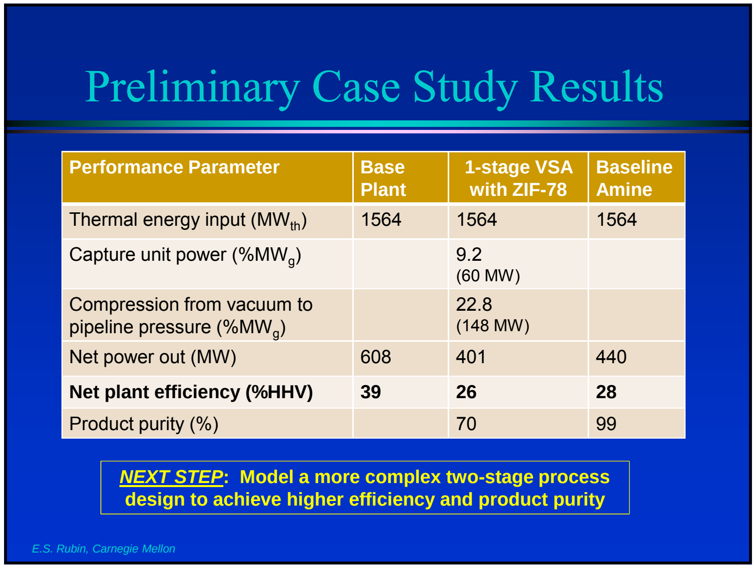


Preliminary Case Study
(modeled using IECM v.8.0.2)

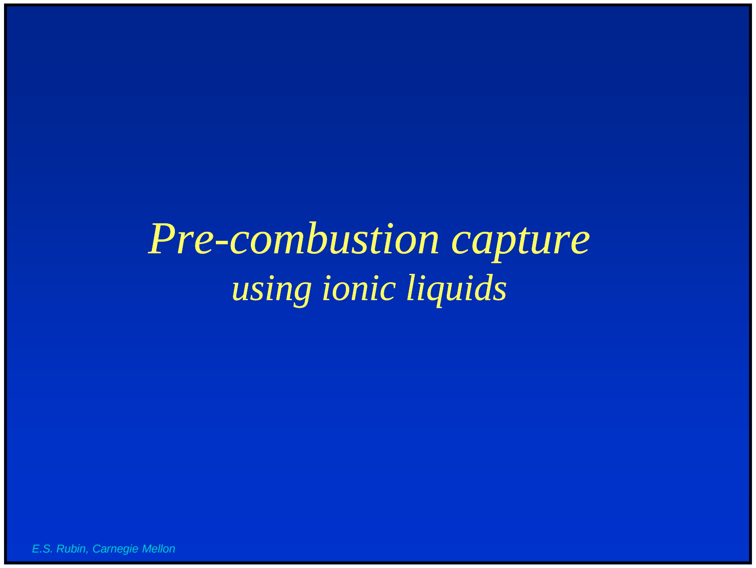
- Base Power Plant
  - 650 MW_{gross}, supercritical PC unit
  - Appalachian medium sulfur coal
  - Thermal energy input: 1564 MW_{th}
  - 11,310 kmol/hr CO_2 in flue gas (12% by volume)
- CO_2 capture using ZIF-78 with VSA
  - 90% CO_2 capture, single stage
  - Isothermal at 50°C
  - Adsorption pressure = 1.2 bar
  - Desorption pressure = 0.01 bar
  - CO_2 product pressure =135 bar



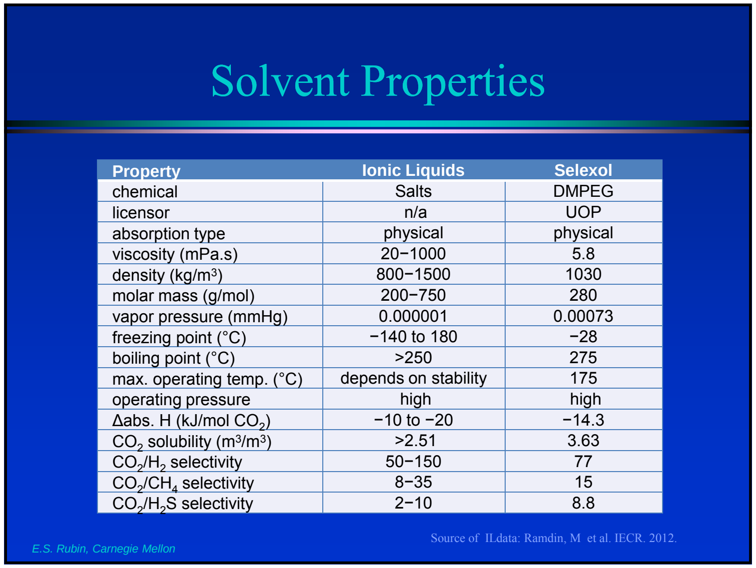
Preliminary Case Study Results

Performance Parameter	Base Plant	1-stage VSA with ZIF-78	Baseline Amine
Thermal energy input (MW_{th})	1564	1564	1564
Capture unit power (%MW_g)		9.2 (60 MW)	
Compression from vacuum to pipeline pressure (%MW_g)		22.8 (148 MW)	
Net power out (MW)	608	401	440
Net plant efficiency (%HHV)	**39**	**26**	**28**
Product purity (%)		70	99

NEXT STEP**: Model a more complex two-stage process design to achieve higher efficiency and product purity**



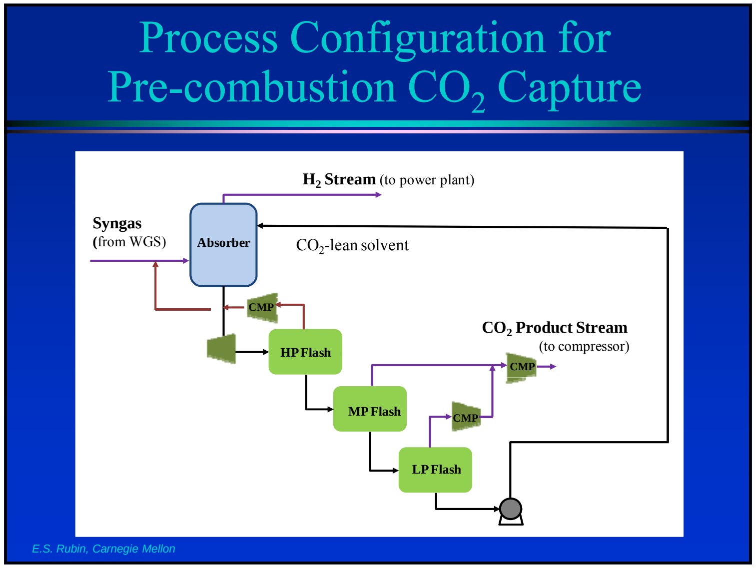
Pre-combustion capture
using ionic liquids



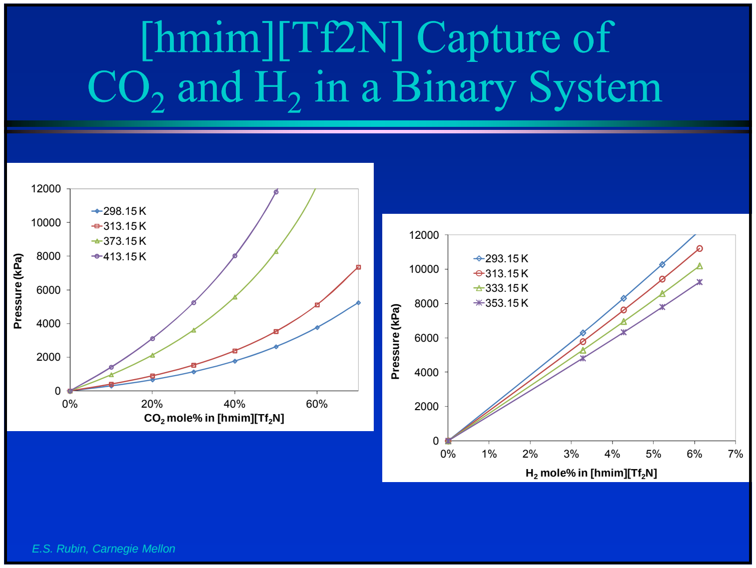
Solvent Properties

Property	Ionic Liquids	Selexol
chemical	Salts	DMPEG
licensor	n/a	UOP
absorption type	physical	physical
viscosity (mPa.s)	20−1000	5.8
density (kg/m³)	800−1500	1030
molar mass (g/mol)	200−750	280
vapor pressure (mmHg)	0.000001	0.00073
freezing point (°C)	−140 to 180	−28
boiling point (°C)	>250	275
max. operating temp. (°C)	depends on stability	175
operating pressure	high	high
Δabs. H (kJ/mol CO_2)	−10 to −20	−14.3
CO_2 solubility (m³/m³)	>2.51	3.63
CO_2/H_2 selectivity	50−150	77
CO_2/CH_4 selectivity	8−35	15
CO_2/H_2S selectivity	2−10	8.8

Source of IL data: Ramdin, M et al. IECR. 2012.



Process Configuration for Pre-combustion CO_2 Capture

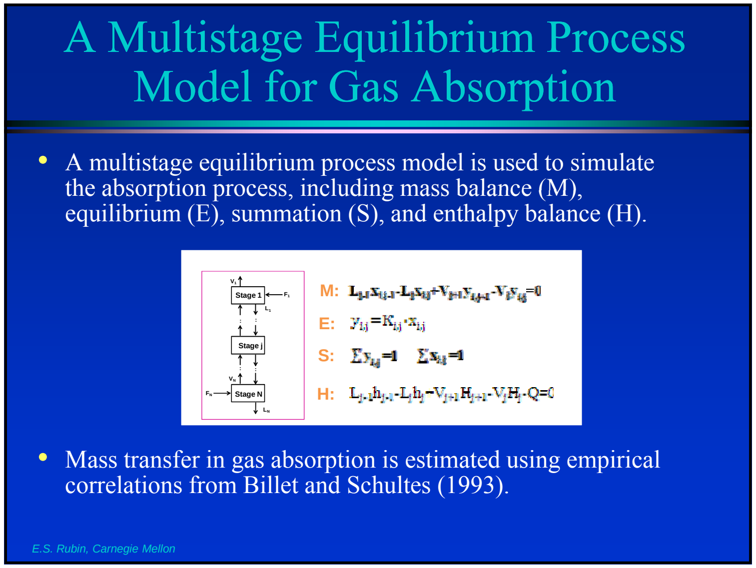


[hmim][Tf2N] Capture of CO_2 and H_2 in a Binary System

Preliminary Case Study

(modeled using IECM v.8.0.2)

- Base Power Plant
  - 651 MW_g IGCC plant
  - 26,500 kmol/hr syngas (32% CO_2 , 68% H_2)
- 90% CO_2 capture using IL (vs. Selexol)
  - Absorber: Temp = 30C, Pressure = 3000 kPa
  - Flash Drum Pressures for Stripping: high = 1000 kPa , medium = 500 kPa, low = 100 kPa
  - Flash temperature = 30C
  - Equipment Efficiency: compressor = 80%, pump =75%, hydraulic turbine = 80%
  - CO_2 product pressure =135 bar
  - 2 trains



A Multistage Equilibrium Process Model for Gas Absorption

- A multistage equilibrium process model is used to simulate the absorption process, including mass balance (M), equilibrium (E), summation (S), and enthalpy balance (H).

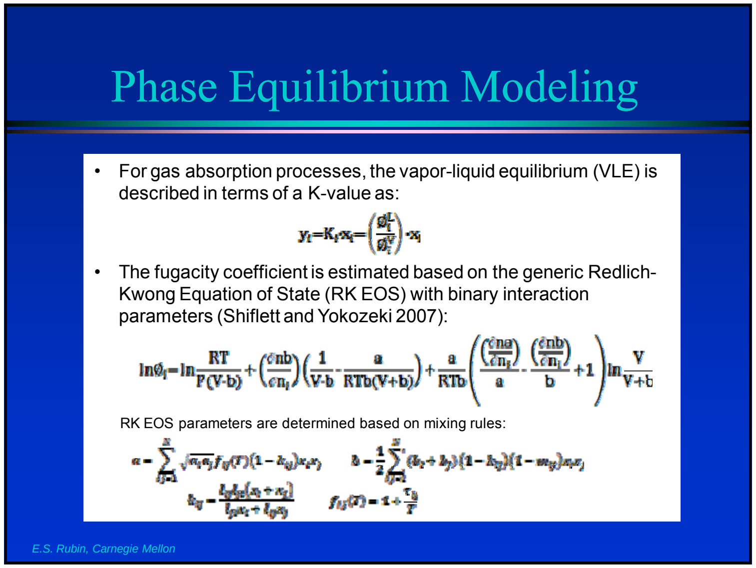
M: $L_{j-1}x_{i,j-1}-L_jx_{i,j}+V_{j+1}y_{i,j+1}-V_jy_{i,j}=0$

E: $y_{i,j}=K_{i,j}\cdot x_{i,j}$

S: $\Sigma y_{i,j}=1 \quad \Sigma x_{i,j}=1$

H: $L_{j-1}h_{j-1}-L_jh_j+V_{j+1}H_{j+1}-V_jH_j-Q=0$

- Mass transfer in gas absorption is estimated using empirical correlations from Billet and Schultes (1993).



Phase Equilibrium Modeling

- For gas absorption processes, the vapor-liquid equilibrium (VLE) is described in terms of a K-value as:

$$y_i = K_i x_i = \left(\frac{\phi_i^L}{\phi_i^V}\right) \cdot x_i$$

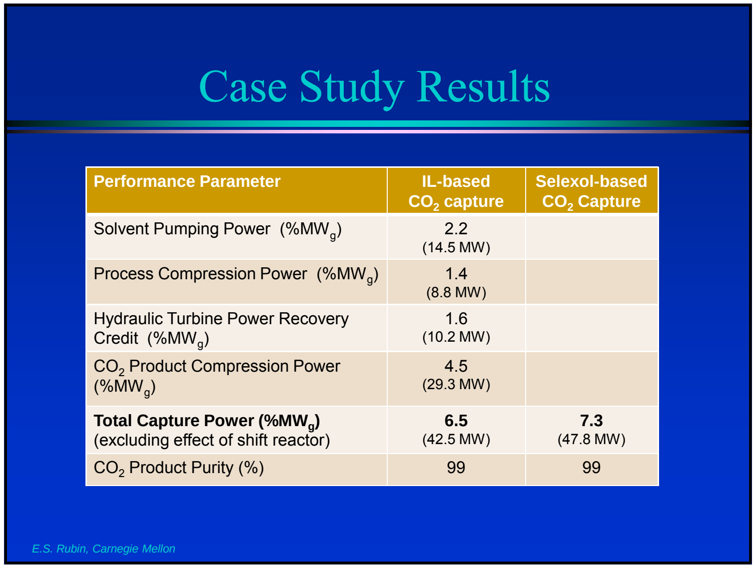
- The fugacity coefficient is estimated based on the generic Redlich-Kwong Equation of State (RK EOS) with binary interaction parameters (Shiflett and Yokozeki 2007):

$$\ln\phi_i = \ln\frac{RT}{P(V-b)} + \left(\frac{\partial nb}{\partial n_i}\right)\left(\frac{1}{V-b} - \frac{a}{RTb(V+b)}\right) + \frac{a}{RTb}\left(\frac{\left(\frac{\partial na}{\partial n_i}\right)}{a} - \frac{\left(\frac{\partial nb}{\partial n_i}\right)}{b} + 1\right)\ln\frac{V}{V+b}$$

RK EOS parameters are determined based on mixing rules:

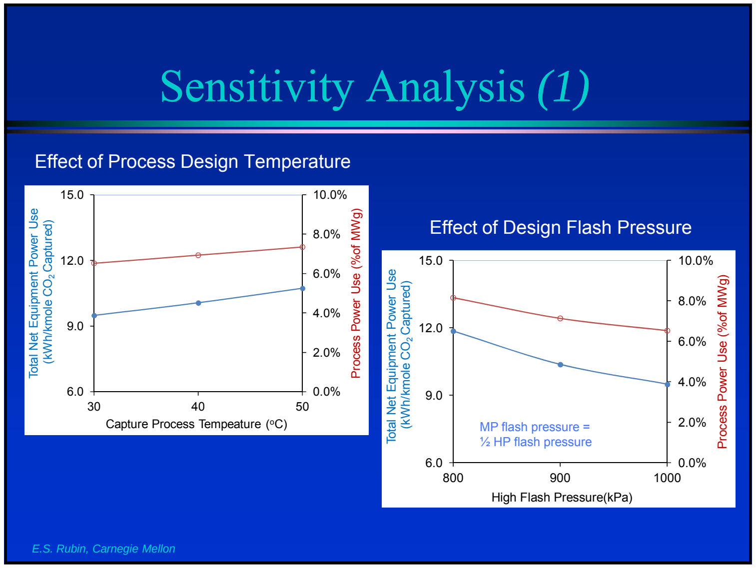
$$a = \sum_{i,j=1}^{N} \sqrt{a_i a_j}\, f_{ij}(T)(1-k_{ij})x_i x_j \qquad b = \frac{1}{2}\sum_{i,j=1}^{N} (b_i + b_j)(1-k_{ij})(1-m_{ij})x_i x_j$$

$$k_{ij} = \frac{l_{ij} l_{ji}(x_i + x_j)}{l_{ji} x_i + l_{ij} x_j} \qquad f_{ij}(T) = 1 + \frac{\tau_{ij}}{T}$$



Case Study Results

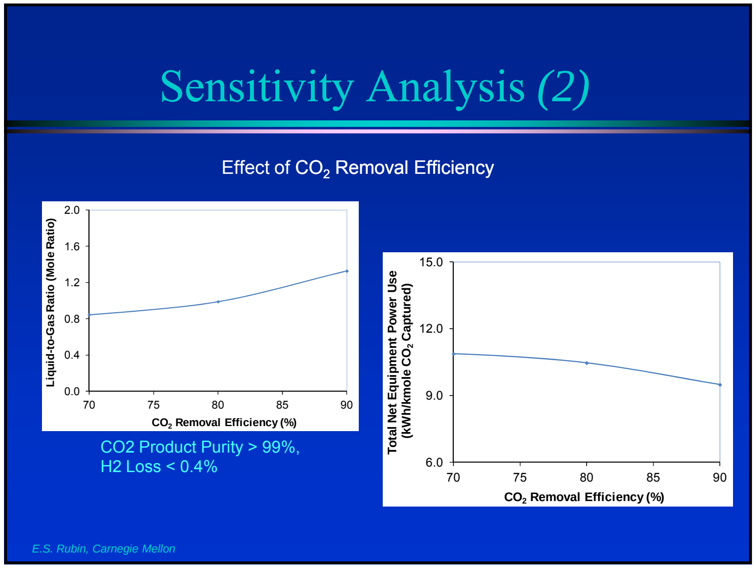
Performance Parameter	IL-based CO_2 capture	Selexol-based CO_2 Capture
Solvent Pumping Power (%MW_g)	2.2 (14.5 MW)	
Process Compression Power (%MW_g)	1.4 (8.8 MW)	
Hydraulic Turbine Power Recovery Credit (%MW_g)	1.6 (10.2 MW)	
CO_2 Product Compression Power (%MW_g)	4.5 (29.3 MW)	
Total Capture Power (%MW_g) (excluding effect of shift reactor)	**6.5** (42.5 MW)	**7.3** (47.8 MW)
CO_2 Product Purity (%)	99	99



Sensitivity Analysis *(1)*

Effect of Process Design Temperature

Effect of Design Flash Pressure



Sensitivity Analysis *(2)*

Effect of CO_2 Removal Efficiency

CO2 Product Purity > 99%,
H2 Loss < 0.4%

Preliminary Conclusions
Related to Process Performance

- Novel sorbent materials should seek high selectivity to achieve high capture efficiency and high purity
- Data are needed on sorbent behavior in the presence of water and impurities such as sulfur
- Mixed gas isotherms are needed to give more accurate performance estimates

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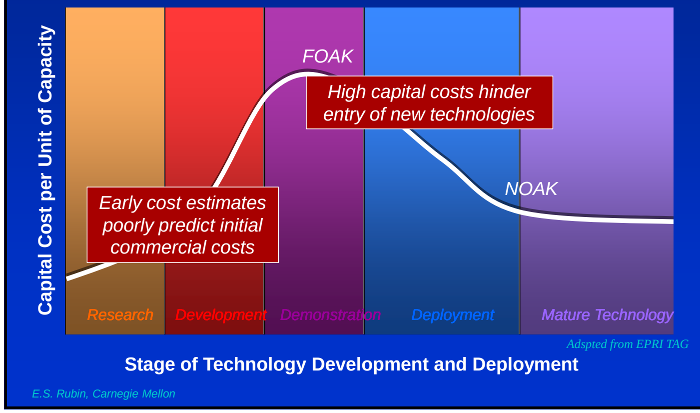
Process Cost Models

Cost Models for New Technologies are Under Development

- CAPITAL COSTS
  - Direct equipment costs
  - Indirect costs (related to PFC)
    - General facilities capital
    - Engineering & home office fees
    - Process contingency cost
    - Project contingency cost
    - Interest during construction
    - Preproduction (startup) cost
    - Royalty fees
    - Inventory capital
  - Total Capital Requirement
- O&M COSTS
  - Variable costs
    - Chemicals
    - Fuels
    - Waste disposal
    - Byproduct credits
    - Other
  - Fixed costs
    - Labor
    - Maintenance
  - Total O&M Cost
- Financial Factors

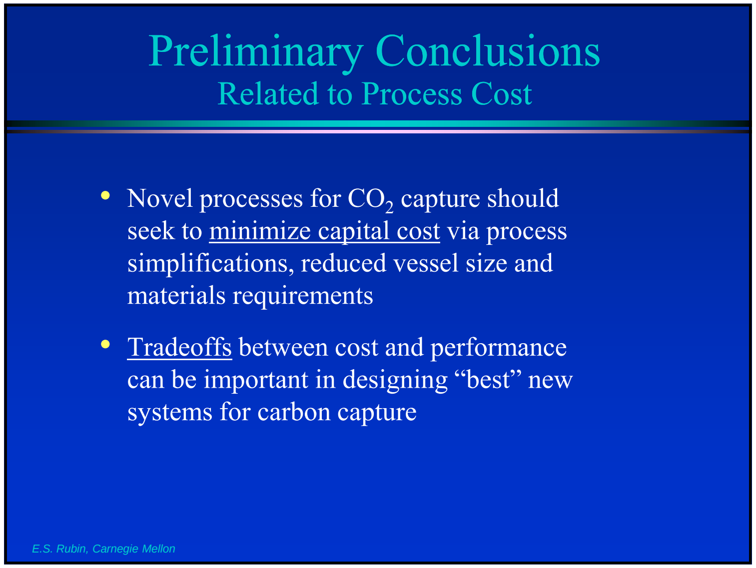
The Challenge for New Technologies:
Typical Cost Trend of a New Technology



High capital costs hinder entry of new technologies

Early cost estimates poorly predict initial commercial costs

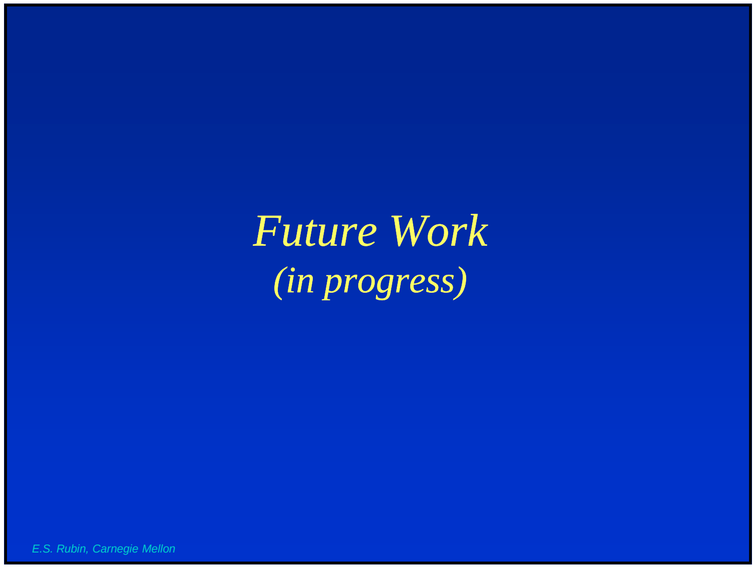
Adspted from EPRI TAG



Preliminary Conclusions

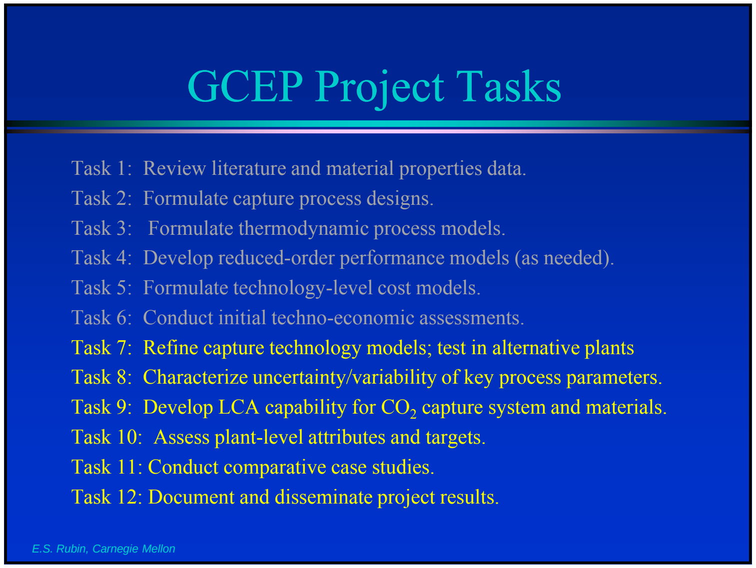
Related to Process Cost

- Novel processes for CO_2 capture should seek to minimize capital cost via process simplifications, reduced vessel size and materials requirements
- Tradeoffs between cost and performance can be important in designing "best" new systems for carbon capture



Future Work

(in progress)



GCEP Project Tasks

Task 1: Review literature and material properties data.
Task 2: Formulate capture process designs.
Task 3: Formulate thermodynamic process models.
Task 4: Develop reduced-order performance models (as needed).
Task 5: Formulate technology-level cost models.
Task 6: Conduct initial techno-economic assessments.
Task 7: Refine capture technology models; test in alternative plants
Task 8: Characterize uncertainty/variability of key process parameters.
Task 9: Develop LCA capability for CO_2 capture system and materials.
Task 10: Assess plant-level attributes and targets.
Task 11: Conduct comparative case studies.
Task 12: Document and disseminate project results.

Thank You

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