INTERNATIONAL TEST NETWORK FOR CO_2 CAPTURE: REPORT ON 8th WORKSHOP
(3–4th October 2005, Austin, Texas, USA)

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Report Number 2005/13
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INTERNATIONAL TEST NETWORK FOR CO_2 CAPTURE: REPORT ON 8th WORKSHOP

(3–4th October 2005, Austin, Texas, USA)

1. Overview of the network and past workshops

This workshop was the eighth in a series to discuss co-operation in development of MEA and related solvents to capture CO_2 from power plant flue gases. The previous events were in Gaithersburg, Calgary, Apeldoorn, Kyoto, Pittsburgh, Trondheim, and Vancouver. Copies of all the reports from and including the Apeldoorn meeting are available on CD (contact louise@ieaghg.org).

Carbon dioxide capture and storage is increasingly featuring in OECD countries' energy policies and R&D programmes as a potential contributor to climate mitigation strategies. It was a featured topic when the leaders of the G8 countries met in Scotland in July 2005. Post combustion capture allied to improved efficiency power plant looks likely to be a major element for new plant as markets develop – particularly so in developing countries where there is a clear preference for using the best established technologies for power generation. Retrofit to established plant is also technically feasible although less economically attractive for ageing, less efficient assets.

Over the five years in which this workshop series has existed, we are seeing more and more researchers coming into the field and some exciting new developments covering new solvent formulations, process engineering innovation and increasingly sophisticated process economic modelling. This report contains presentations on:

- significant scale pilot plant;
- first indicators of serious discussion about larger pilot plant on actual power stations; and
- a wish to facilitate the construction of a post-combustion capture demonstration at around the 300Mwe scale.

All these are signs that the technology is ready to move rapidly towards commercial deployment.

Some background on the most recent workshops in this series:-

Pittsburgh

Twenty-nine delegates attended. USA was the best represented followed by Japan and Canada. Research work taking place in eight countries was presented.

The Carnegie Mellon-Waterloo-Imperial College trio of process economic modellers had been co-operating to some extent and this was reflected in their presentations with a thought provoking idea from Imperial College about storing CO_2 during the day for regeneration during off-peak demand periods. Mitsubishi presented data comparing economic performance of KS-1 solvent retrofitted to a coal fired pf plant and to a natural gas combined cycle plant. Dutch, Norwegian, US and Japanese presentations on fundamental investigations ensured that the Workshop remained at the forefront in disseminating and exchanging latest work and ideas.

Trondheim

Norwegian University of Science and Technology (NTNU), Department of Chemical Engineering were the hosts. The thirty-eight registrants who attended included several post-grads and post-docs from NTNU itself. Drawn from eleven countries, the majority were understandably from Europe and for the first time the Network was glad to be able to welcome a delegate from Singapore.

The content showed a notable shift from previous workshops with more on fundamental laboratory investigations and a little less on process modelling.

Vancouver

This workshop was associated with the GHGT-7 conference and was for one day only. The opportunity was taken to allow students to present their work, in particular those who were unable to get a paper accepted for the conference platform. Thus, the majority of presentations dealt with studies of a fundamental nature. Numerically it was the best yet with around 60 attendees on the day. About half were graduate students or post doctoral workers. Ten countries were represented – Australia, Brazil (for the first time), Canada, Denmark, France, Japan, the Netherlands, Norway, UK and USA.

2. Austin Workshop

This was at the University of Texas at Austin and around 40 registrants were drawn from 10 countries. Sixty per cent were from the USA and Canada and one-third from Europe. There were also two attendees from Australia and one from Japan. Professor Gary Rochelle was host and his entire graduate school attended. The Agenda covered the usual modelling, process simulation and pilot studies and had side visits to the University's pilot unit and the laboratories associated with CO_2 capture.

This workshop was notable for the visit to a substantial pilot plant used to investigate CO_2 capture by solvents – centred on an absorber-stripper combination. There were 16 technical presentations about half of which were devoted to laboratory research and modelling including three from the "home" team. There were several on process economics – including material looking at "top-down" predicting of future capture costs and an attempt to model some of the effects of uncertainties in power plant systems operation on CO_2 capture economics.

Pilot Plant at the University of Texas

In the foreground is Ross Dugas to give an impression of scale

For the first time we had two Australian presenters – one looking broadly at the prospects for post combustion capture in Australia and the other at early results from university research.

There were several presentations about programmes of work rather than specific activities in detail. Amongst these the one on the EU funded CASTOR project and the pilot plant under construction at Elsam's power plant at Esbjerg was timely and assisted the introduction of Denmark as the venue for the next meeting. Gratifyingly, it was noted that NTNU in Norway and University of Texas have started to exchange research personnel. This network may have helped to promote that exchange.

The agenda and delegate list are appended as Annexes I and II, respectively.

3. Presentations by Attendees

Presentations were made as listed below. Copies of slides appear in the same order in Annex III.

1	John Topper	Introduction to 8th Workshop
2	Gary Rochelle	CO_2 Capture and Storage at University of Texas at Austin
3	John Davison	Overview of Recent Studies on CO_2 Capture
4	Ed Rubin	Estimating Future costs of CO_2 Capture Systems
5	Colin Alie	A Framework for Scheduling the Operation of Power Plants Incorporating CO_2 Capture
6	Babatunde Oyenekan	Modelling of Innovative Stripper Concepts
7	Amy Veawab and Andy Aroonwilas	CO_2 Capture by blended Alkanolamines
8	Eric Chen and Ross Dugas	Pilot Plant for CO_2 Capture
9	Kazuya Goto	Development of a new Chemical Absorption System for CO_2 Capture
10	Andrew Tobiesen	Experimental validation of a model for CO_2 post-combustion capture using MEA
11	Paul Broutin	Corrosion studies for CO_2 solvents
12	Erik da Silva	Chemical Understanding of Solvents for CO_2 Capture
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14	Sandip Chattopadhyay	Managing Climate Change and Securing a Future for the Midwest's Industrial Base
15	James Hoffman	Activities in CO_2 Capture
16	Louis Wibberley	PCC Post Combustion Demonstration in Australia
17	Sandra Kentish	CO2CRC Capturing CO_2 Down-Under
18	John Topper	Wrap-up session – future plans and projects

4. Next Meeting(s)

The next meeting will be as guests of the Danish power generation companies E2 and Elsam in Copenhagen on 16 June 2006. This date was chosen to be immediately before the GHGT-8 conference in Trondheim, Norway on 19-23 June 2006. There are regular daily flights from Copenhagen to Trondheim. The Agenda will concentrate on giving graduate students, who were unsuccessful in getting papers accepted for platform presentation in Trondheim, the opportunity to present to their peers.

Institute Francais du Petrole(IFP) have offered to host the 10th meeting in either Paris or Orleans in 2007.

5. Thanks and Acknowledgements

All participants wish to thank Professor Gary Rochelle and his assistant, Lane Salgado, at the University of Texas for facilitating arrangements for the meeting room, coffees, lunches, arrangements with the Crowne Plaza hotel and local transportation. There was a dinner on the intermediate night for which thanks are due to Shell for acting as sponsors.

6. Contacting the Co-ordinator

The IEA Greenhouse Gas R&D Programme co-ordinates the development of this network and arranges the workshops.

Queries about or copies of this report can be obtained by contacting:-

either John Topper john.topper@aol.com
or via the "feedback" facility in the IEA GHG website's home page http://www.ieagreen.org.uk

ANNEX I

Workshop Agenda

International Test Network for CO_2 Capture – Austin Workshop

Monday, 3rd October

0900	Welcome, Round the Table Introductions, Today's Agenda – John Topper for IEA Greenhouse Gas R&D Programme
0920	Carbon Dioxide Capture and Storage at University of Texas – Gary Rochelle
0950	**Session 1** – Systems Modelling and Process Economics – Paul Feron, Chair
a)	IEA GHG, "Overview of Recent Studies" – John Davison
b)	Carnegie Mellon University, USA, "Estimating Future Costs of CO_2 Capture" – Ed Rubin
c)	University of Waterloo, Canada, - An Update – Colin Alie
d)	University of Texas, USA, " Modelling of Innovative Stripper Concepts" – Babatunde Oyenekan
e)	University of Regina, Canada, "CO2 capture by blended Alkanolamines: experiments, modelling and simulation, cost analysis" – Amy Veawab and Andy Aroonwilas
1350	**Session 2** – Systems modelling and investigations – Gary Rochelle, Chair
a)	University of Texas, USA " Pilot Plant Results with Piperazine/Potassium Carbonate" – Eric Chen an Ross Dugas
b)	RITE, Japan, "Development of a new Chemical Absorption System for CO_2 Capture" – Kazuya Goto
c)	NTNU, Norway, " Absorber-Desorber Modelling" – Andrew Tobiesen
d)	IFP, France, " Solvent Corrosion studies (part of the EU Castor Project)" – Paul Broutin
e)	Sintef, Norway, "Chemical Understanding of Solvents for CO2 Capture" – Erik da Silva
1630	Visit to Pilot Plant

Tuesday, 4th October

0900	**Session 3** – Programmes on CO_2 Capture – Ed Rubin, Chair
a)	TNO, Netherlands, " Overview of the CASTOR Project" – Paul Feron
b)	Battelle, USA, " CO_2 Capture Related Activities at Battelle" – Sandip Chattopadhyay
c)	NETL, USA, "Activities in CO_2 Capture" – James Hoffman
d)	CSIRO, Australia, " Post-Combustion CO_2 capture; current work and intentions in Australia" – Louis Wibberley
e)	CO2CRC, Australia, "CO_2 Capture Down Under" – Sandra Kentish
1130	On-Campus Laboratory tour
1215	Wrap-up and Thanks session – John Topper
➢	Meeting Review
➢	An IEA Concept for a Post-Combustion demonstration Plant
➢	Next Meeting (adjacent to GHGT-8 Conference in Trondheim, 19-23 June 2006)
➢	News about a new Oxy-Fuel Network

ANNEX II

8th International Test Network for CO_2 Capture

3–4th October 2005, Austin, Texas, USA

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ANNEX III

PRESENTATIONS

The presentations are attached and can be accessed from the bookmark list

1	John Topper	Introduction to 8th Workshop
2	Gary Rochelle	CO_2 Capture and Storage at University of Texas at Austin
3	John Davison	Overview of Recent Studies on CO_2 Capture
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International Network for CO_2 Capture

Introduction to 8th Workshop, Austin

By

J M Topper

Managing Director IEA Environmental Projects Ltd

IEA Greenhouse Gas R&D Programme

- A collaborative research programme which started in 1991.
- Its main role is to evaluate technologies that can reduce greenhouse gas emissions.
- Aim is to:

Provide our members with informed information on the role that technology can play in reducing greenhouse gas emissions

Programme Members

International Network for CO_2 Capture

- ***AIM**: To establish a forum that will encourage practical work on CO_2 capture. Emphasis on use of MEA and derivative solvents*

- ***WHY CO-OPERATE?:***
  - *avoid duplication of effort*
  - *encourage development*
  - *minimise cost of participation*
  - *enhance technology credibility*
  - *share risks*

International Network for CO_2 Capture

Four Tasks Established **(Gaithersburg 2000)**

- A – Process Simulation
- B – Economic Assessment
- C – Process Innovation at Test Facilities
- D – Feasibility Study

IEA GHG to facilitate

International Network for CO_2 Capture

1st Workshop in Gaithersburg, USA (Spring 2000)

2nd Workshop, Calgary, Canada(November 2001)

3rd Workshop in Apeldoorn; Netherlands (Spring 2002)

4th Workshop in Kyoto, Japan (Autumn 2002)

5th Workshop in Pittsburgh, USA (June 2003)

6th Workshop in Trondheim, Norway, (Spring 2004)

7th Workshop in Vancouver, Canada, (Sept 2004)

8th Workshop at University of Texas, Austin, (Autumn 2005)

9th Workshop is expected to be attached to GHGT 8 in Trondheim, Norway, in June 2006,

International Network for CO_2 Capture

- We are now a well established club; 2/3 of the external registrants have been to two or more workshops
- Of those over 1/3 from N America; 1/3 from Europe + Japan, Australia.
- 10 different countries here today
- Excellent networking

International Network for CO_2 Capture

Today: Housekeeping Points

- Coffee breaks around 10.50 and 16 00
- Lunch, 12.50 – 13 40 followed by photos
- Afternoon session must finish no later than 16 00 to allow a break and then to the pilot plant by bus
- Dinner after the plant visit.
- ALL PRESENTERS ensure I get a copy of their presentation on data storage disc if you want it on the GHG website next week
- Tomorrow we finish at lunch time with transport back to hotel and/or airport

CO_2 Capture/Sequestration at The University of Texas at Austin

Sequestration

Dept of Petroleum & Geosystems Engineering
Prof. Steve Bryant et al.

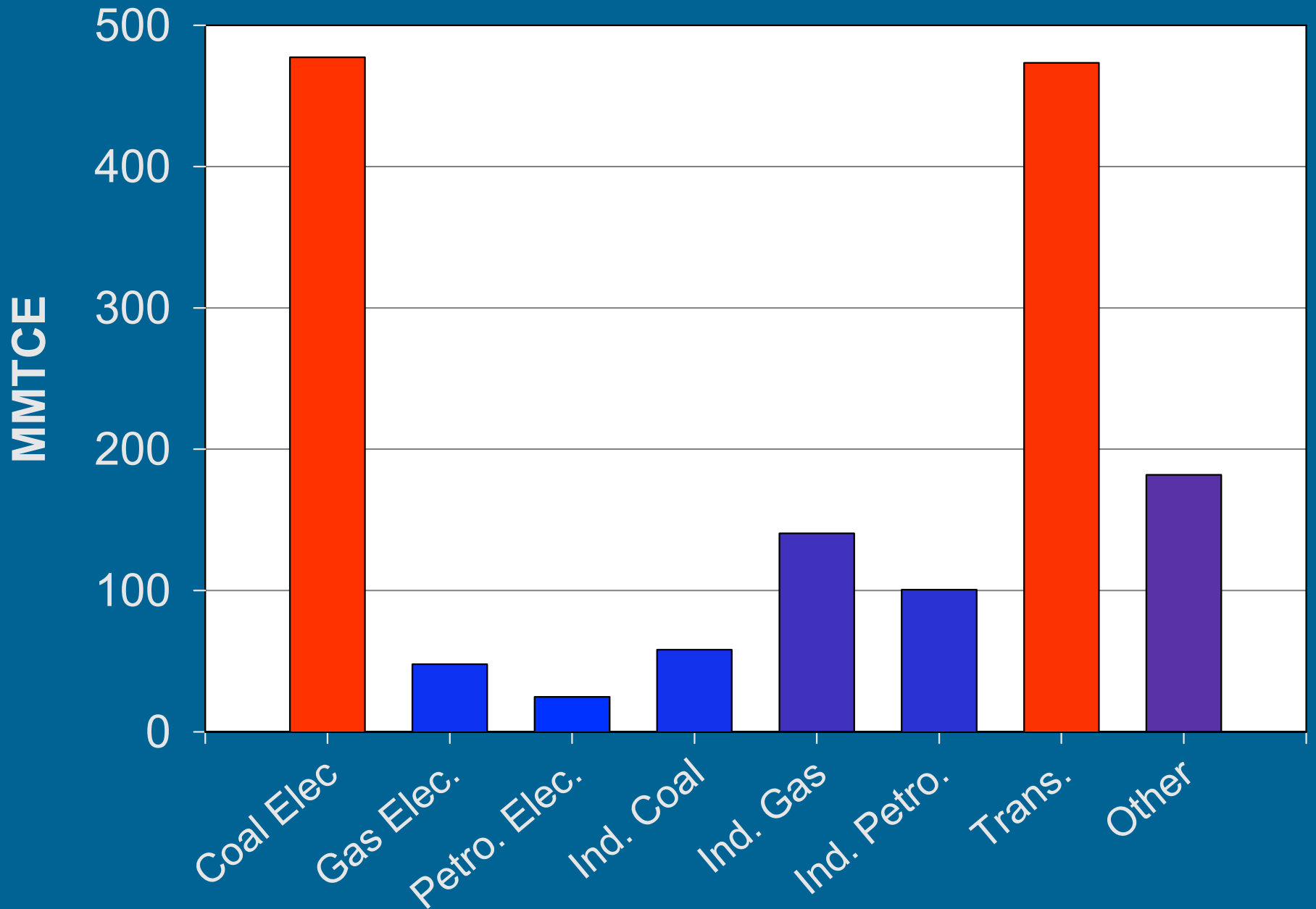
Bureau of Economic Geology
Dr. Susan Hovorka, Dr. Ian Duncan, et al.

Capture

Dept of Chem Eng/Separations Research Prog
Prof. Gary Rochelle, Dr. Frank Seibert - Absorption

Prof. Benny Freeman - Membranes

CO_2 Emissions by Source (1998)



Geological CO_2 Storage
Center for Petroleum & Geosystems Engin

- 5 Industrial sponsors

  Chevron, Exxon, ENI, CMG, Shell(pdg)

- Other Support

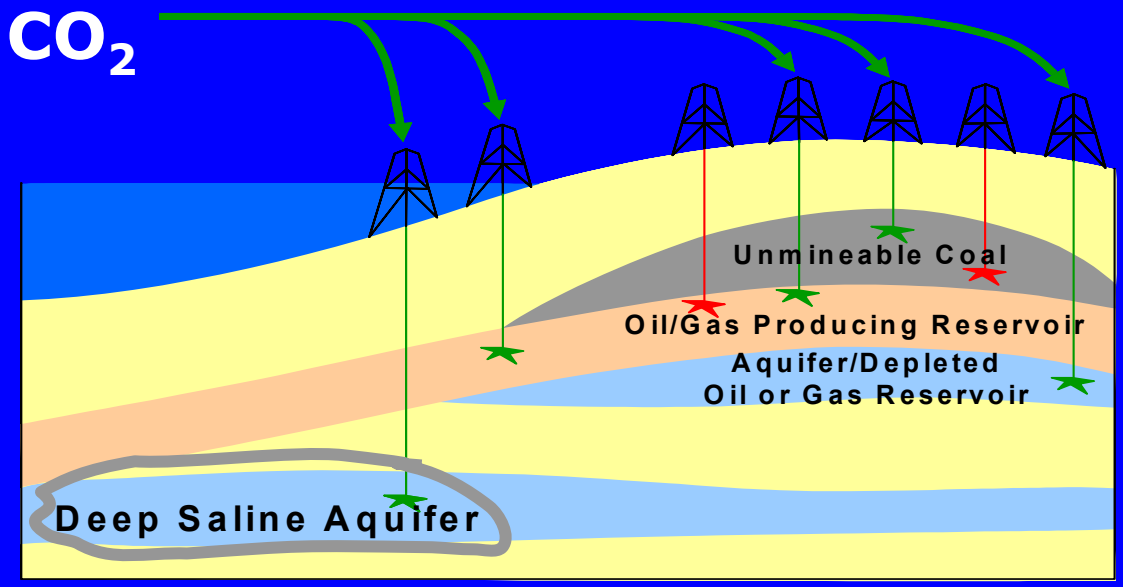
  Texas ATP, DOE(pending), CCP2

- Faculty: Bryant, Pope, Lake, Sepehrnoori

  Staff: 4 Grad students, 4 Researchers

Geological CO2 Storage JIP

- Objectives
  - Identify key mechanisms governing subsurface storage
  - Improve understanding of those mechanisms
  - Quantify time, length scales for storage in realistic aquifers
  - Establish framework for risk assessment (leakage)



Bureau of Economic Geology

- Funding – DOE, 7 industrial sponsors, etc.
- Susan Hovorka, Ian Duncan
  5 other professionals
- Regional Evaluation & Modeling
  - Gulf coast
- Field Experiment for CO_2 Sequestration
  - Frio brine pilot
- Sequestration
  - in Brine Formation
  - In Hydrocarbon Reservoirs

Gulf Coast Carbon Center

Main GCCC Results to Date

- Quantification of CO2 market for EOR in GIS (spatial inventory)
- Field demonstration (Frio I Project)
  - monitoring & modeling to measure CO_2 storage
  - assure public and environmental safety
- Demonstration of two phase trapping
- Development of enhanced screening for EOR
- Development of a cross-industry working group
- Publication and outreach

CO_2 Aqueous Absorption UT Austin - Research Funding

- DOE Contract for K_2CO_3/PZ
  - $1,565k - 5 yrs
  - With SRP, F. Seibert
  - 1 Subcontract with A. Veawab (Regina)
- Industrial Sponsors (10) – $200k/yr
- Separations Research Program (SRP)
  - 12 companies - $30k/yr
- 7 Graduate Students, 1 postdoc
- 1 Visiting researcher, NTNU (Norway)

CO_2 Capture by Aqueous Absorption

Rate/VLE Meas: MEA/PZ – Hilliard, Davis
(Okoye & Dang)
(K_2CO_3/PZ – Cullinane)
(DGA/MOR – Al-Juaied)

Amine Losses: Degradation – Sexton
(MEA - Goff, PZ – Alawode)
Volatility – McLees

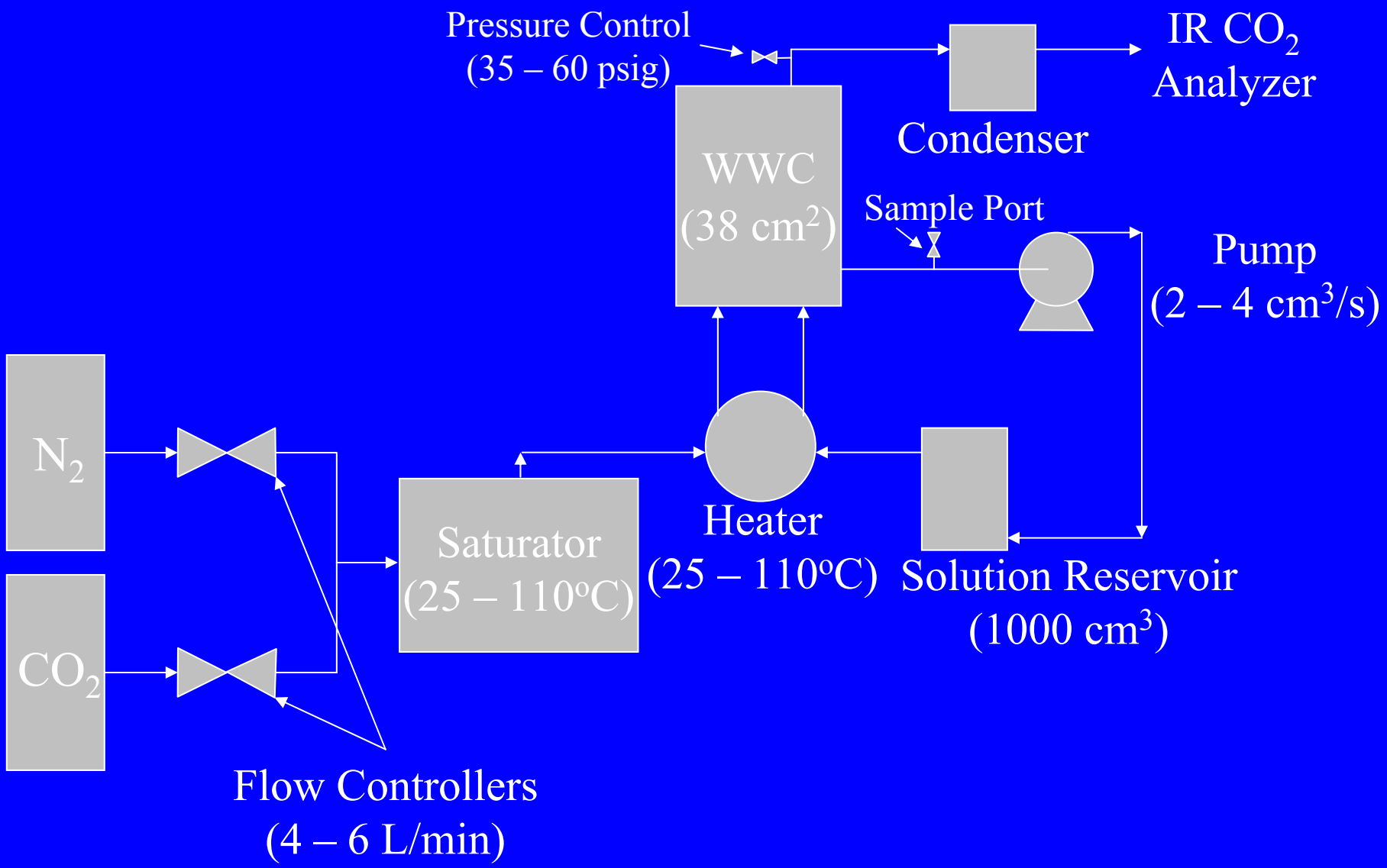
Modeling: Absorber – Kvamsdal
Stripper – Oyenekan (presenter)
Thermo - Hilliard

Pilot Plant: K_2CO_3/PZ – Chen (presenter)
MEA/PZ – Dugas (presenter)

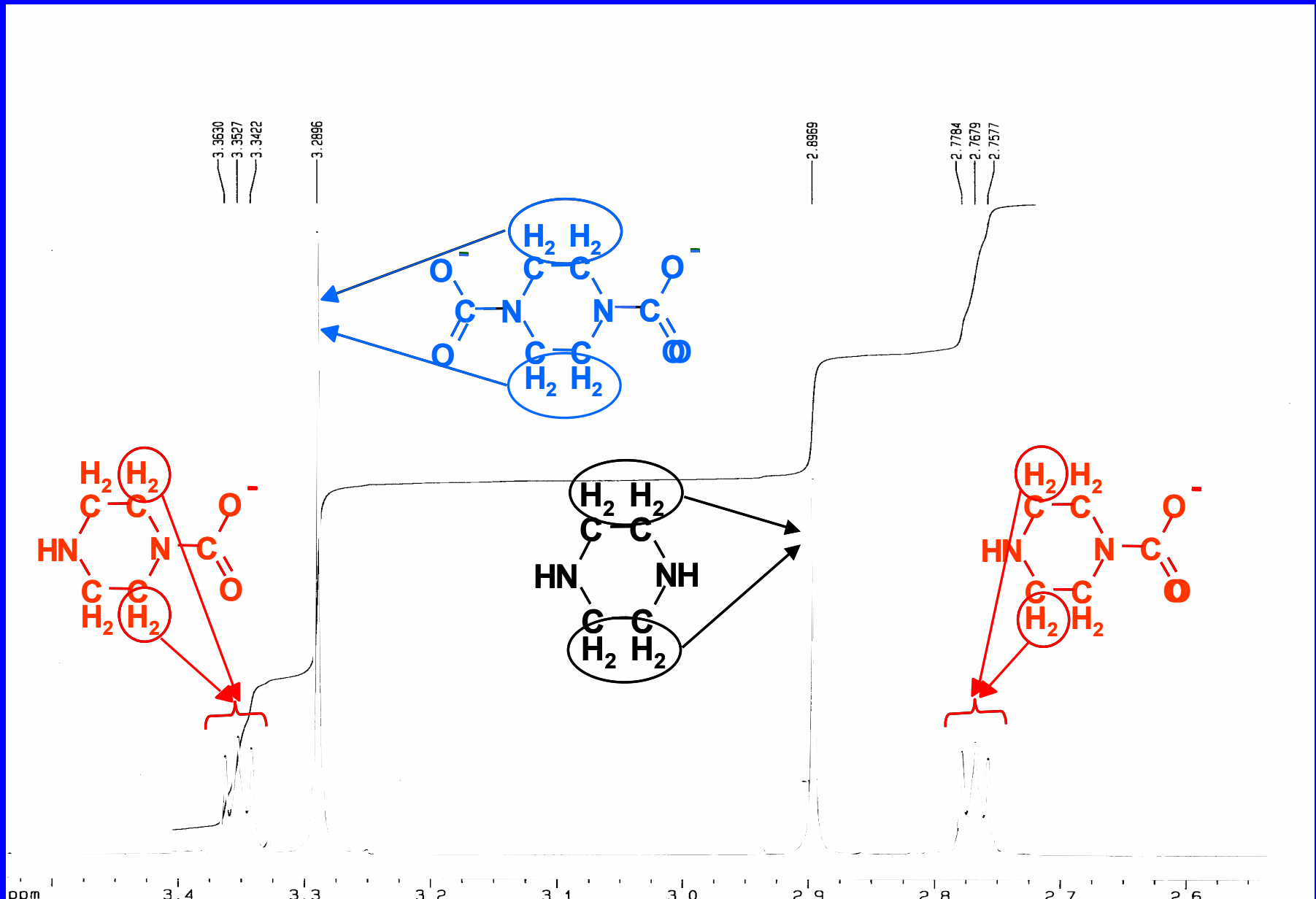
Thermodynamics

- Objectives:
  - Maximize CO_2 Capacity
  - Customize ΔH_{des}
  - Minimize Amine Volatility
- Experimental capabilities
  - CO_2 Solubility in Wetted Wall Column
  - Speciation by C^{13} and H^1 NMR
  - CO_2, Amine, H_2O VLE by Hot Gas FTIR
  - High T VLE, ΔH_{des} by collaboration with NTNU
- Model with Electrolyte NRTL – Rigorous G_{ex}

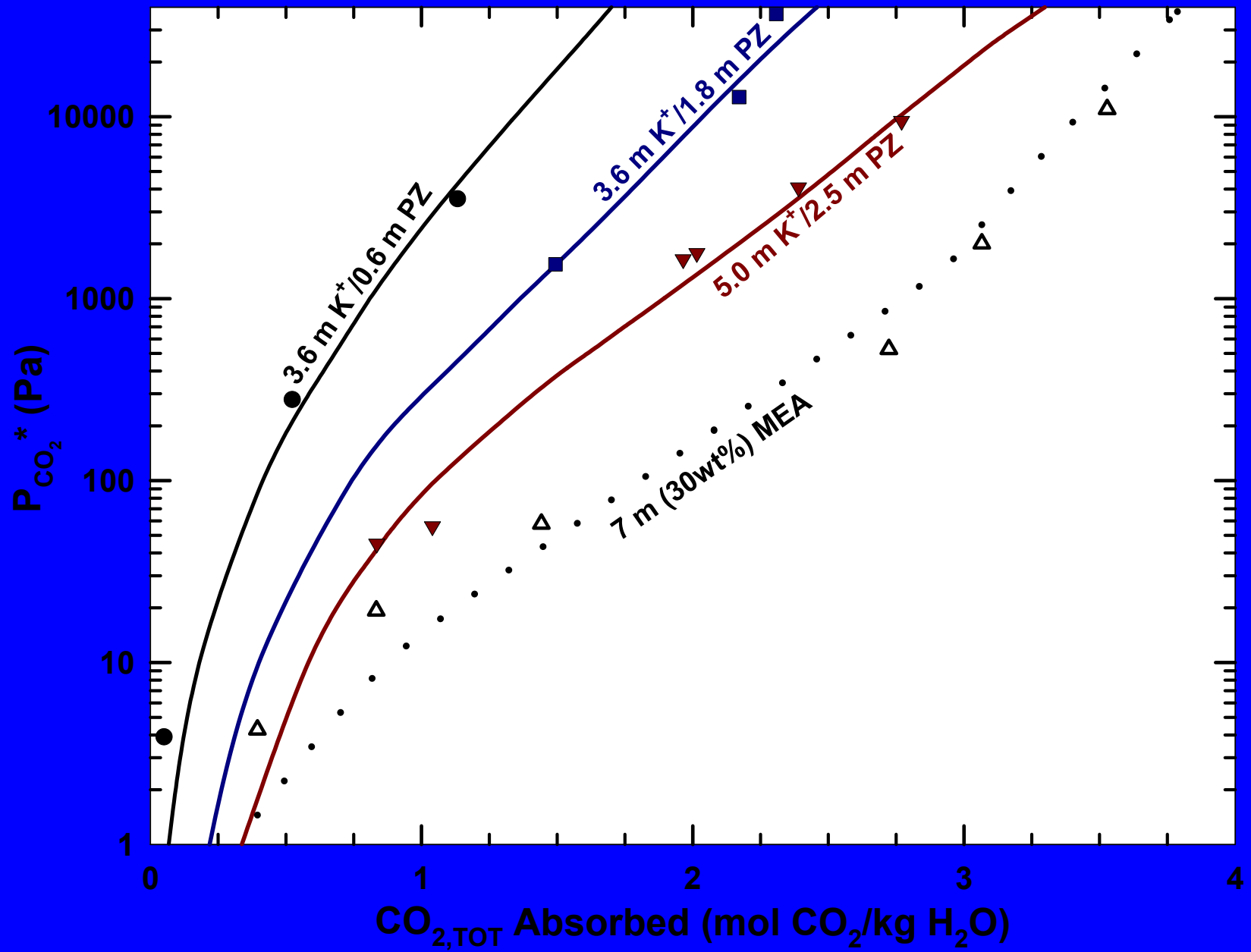
Wetted-Wall Column



PZ Speciation by H^1 NMR



Equilibrium in K^+/PZ at 60°C



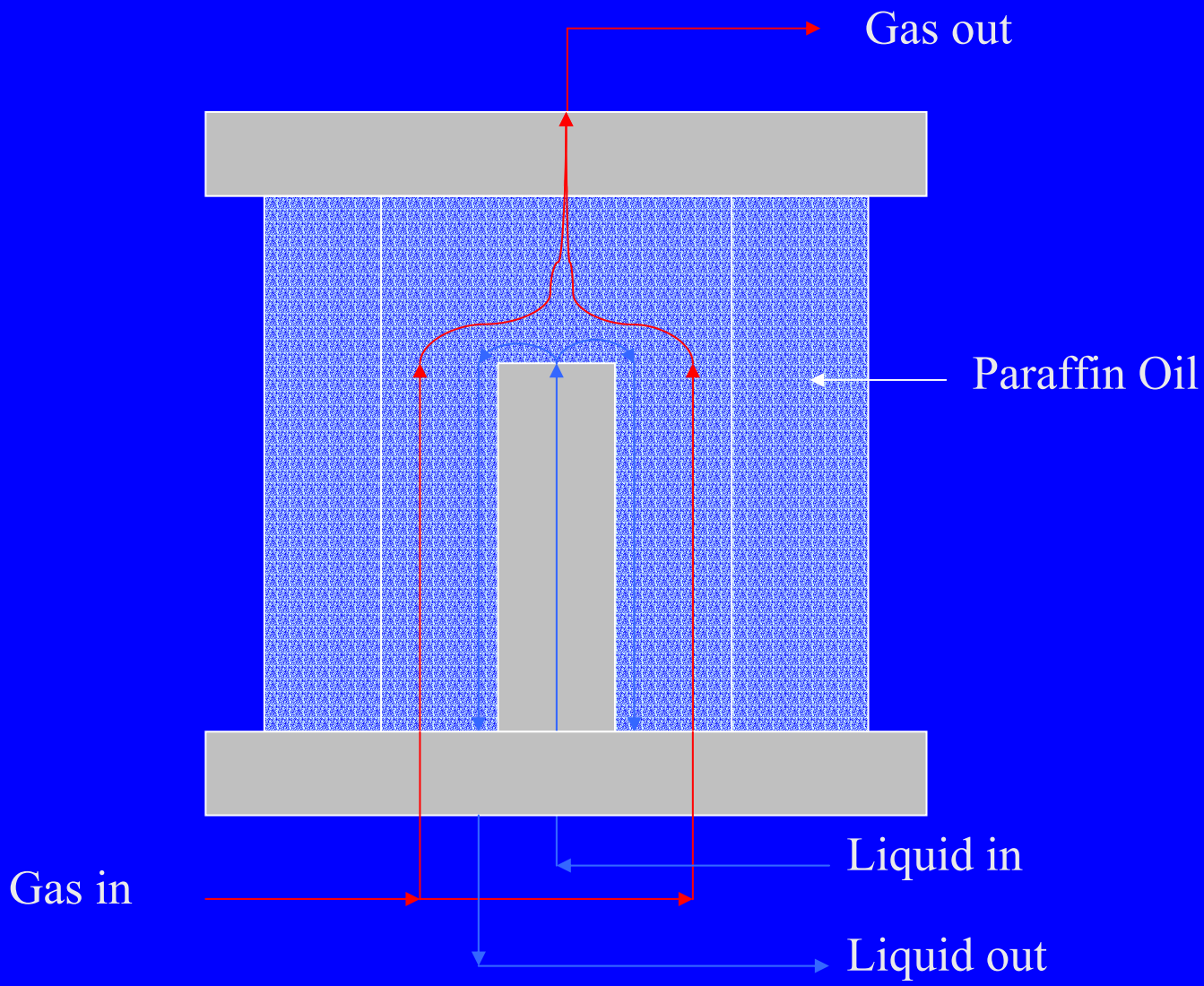
Mass Transfer with Reaction

- Objective: Enhance CO_2 Mass Transfer rates
  - Reduce packing height and pressure drop
  - Increase approach to saturation
- Measure Mass transfer with chemical reaction
  - in wetted wall column

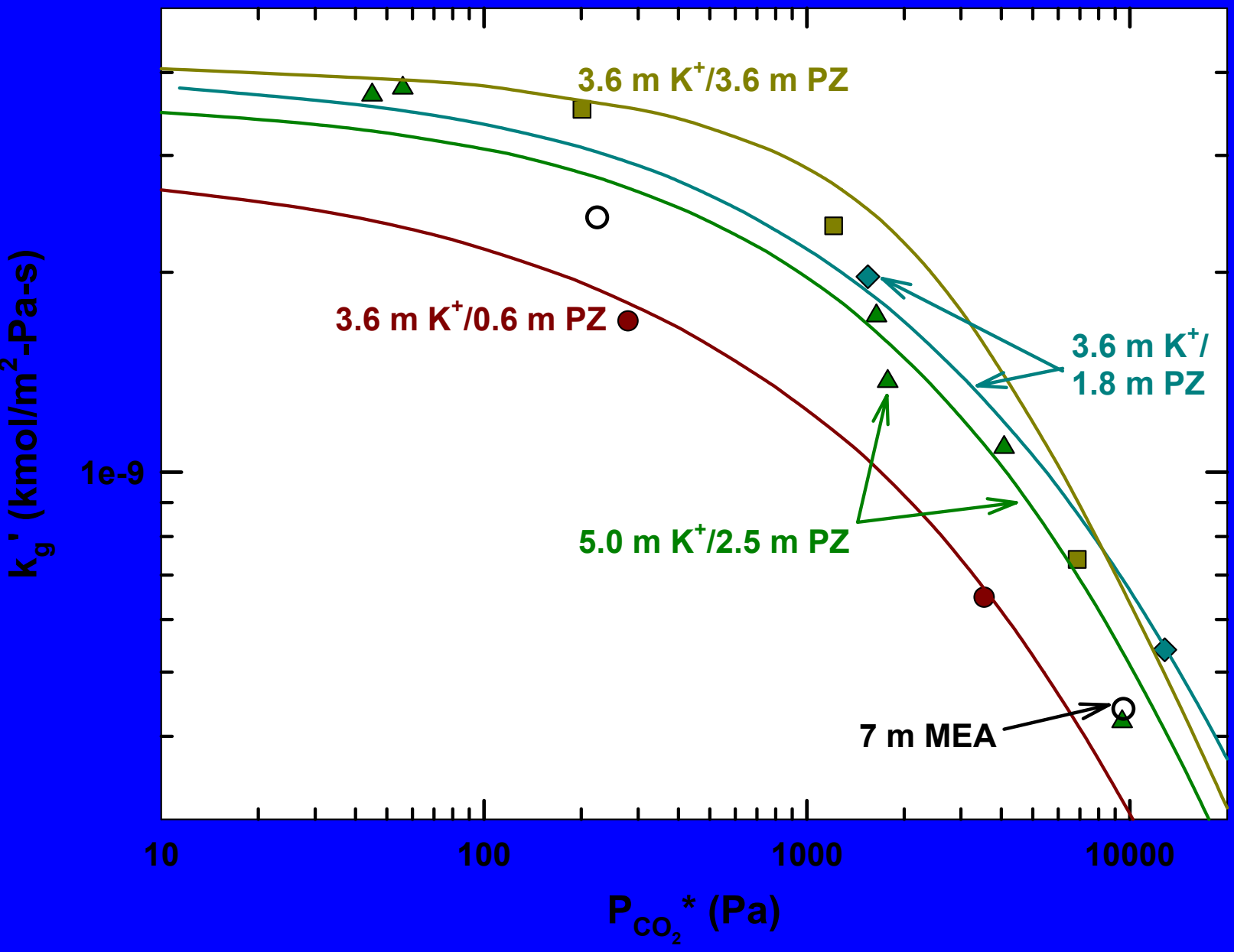
$$k_g^{'} = \frac{Flux}{\left(P_{CO_2,i} - P_{CO_2}^{*}\right)} = \frac{\sqrt{D_{CO_2}\left(k_{PZCOO^-}\left[PZCOO^-\right] + k_{PZ}\left[PZ\right]\right)}}{H_{CO_2}}$$

- Add piperazine to K_2CO_3 or MEA to get faster rates

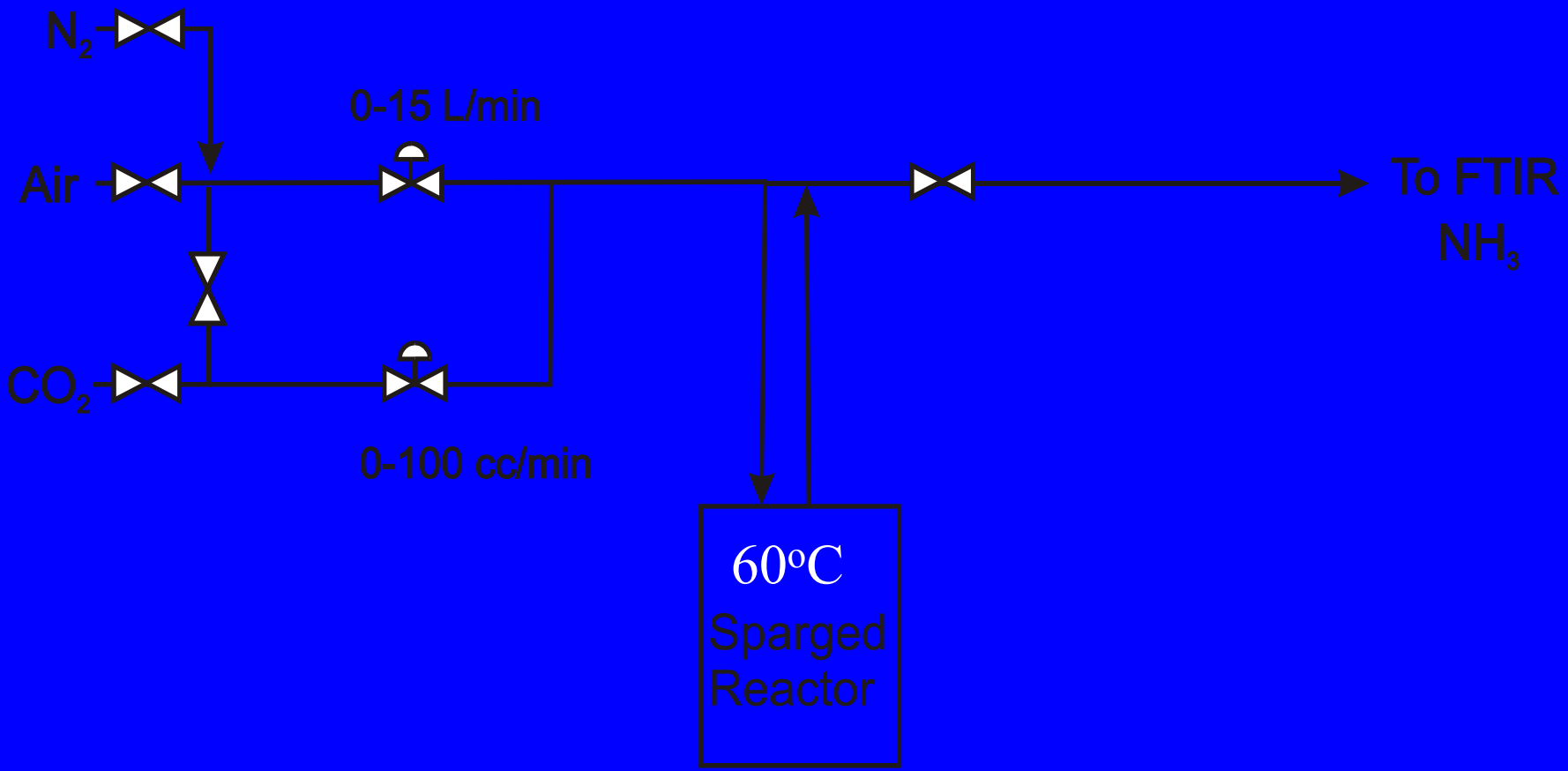
Wetted Wall Column



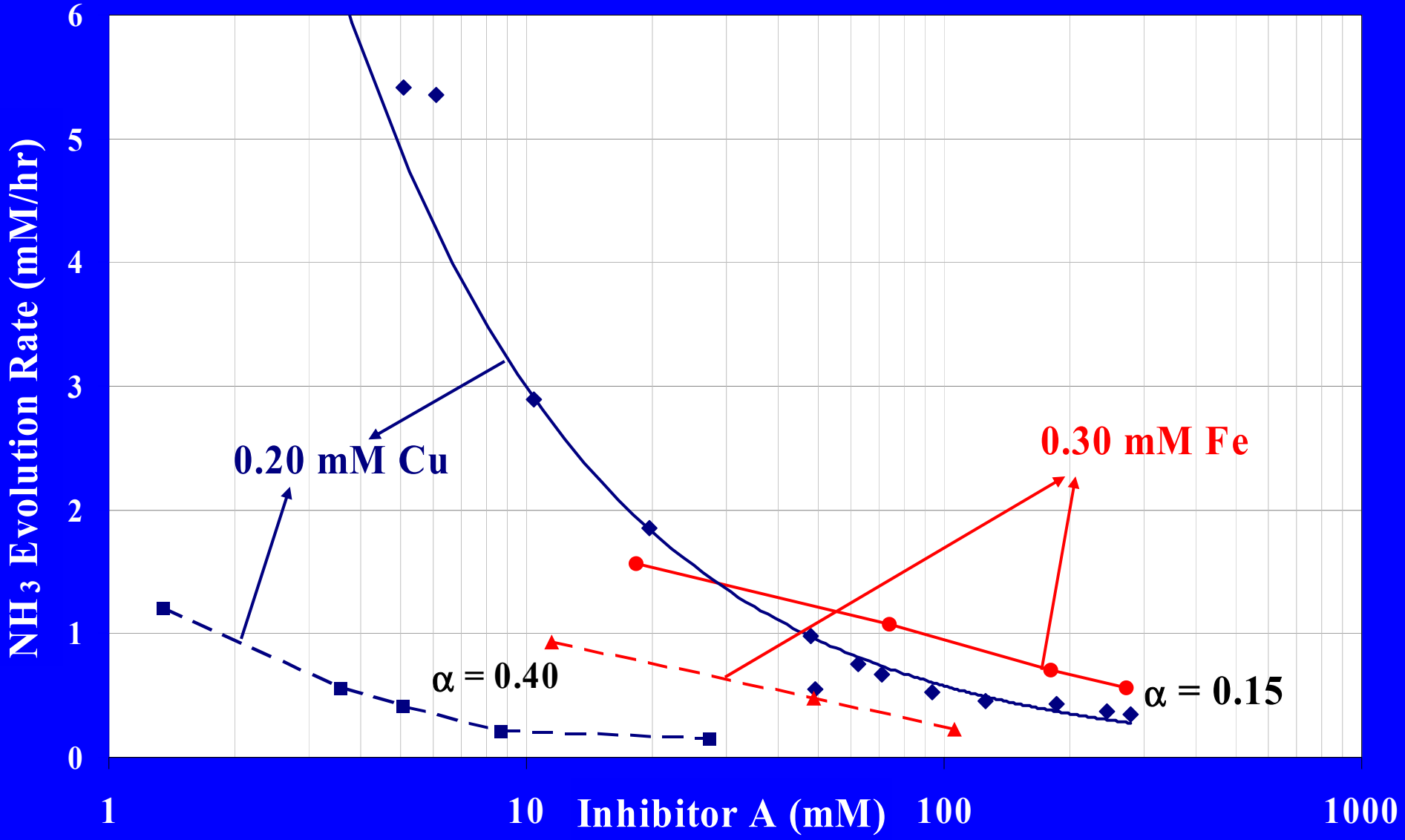
Normalized Flux at 60°C

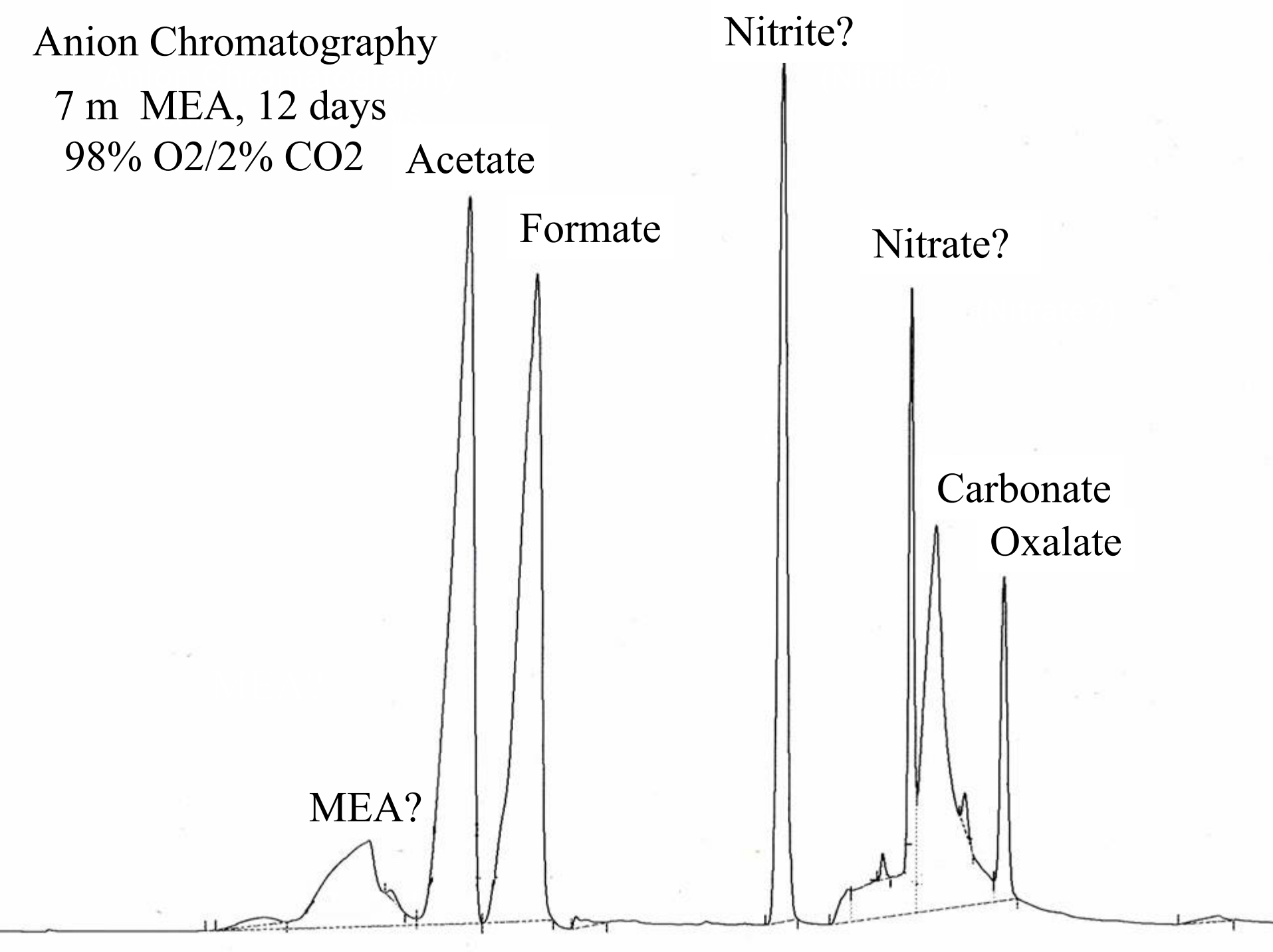


Degradation Experiment



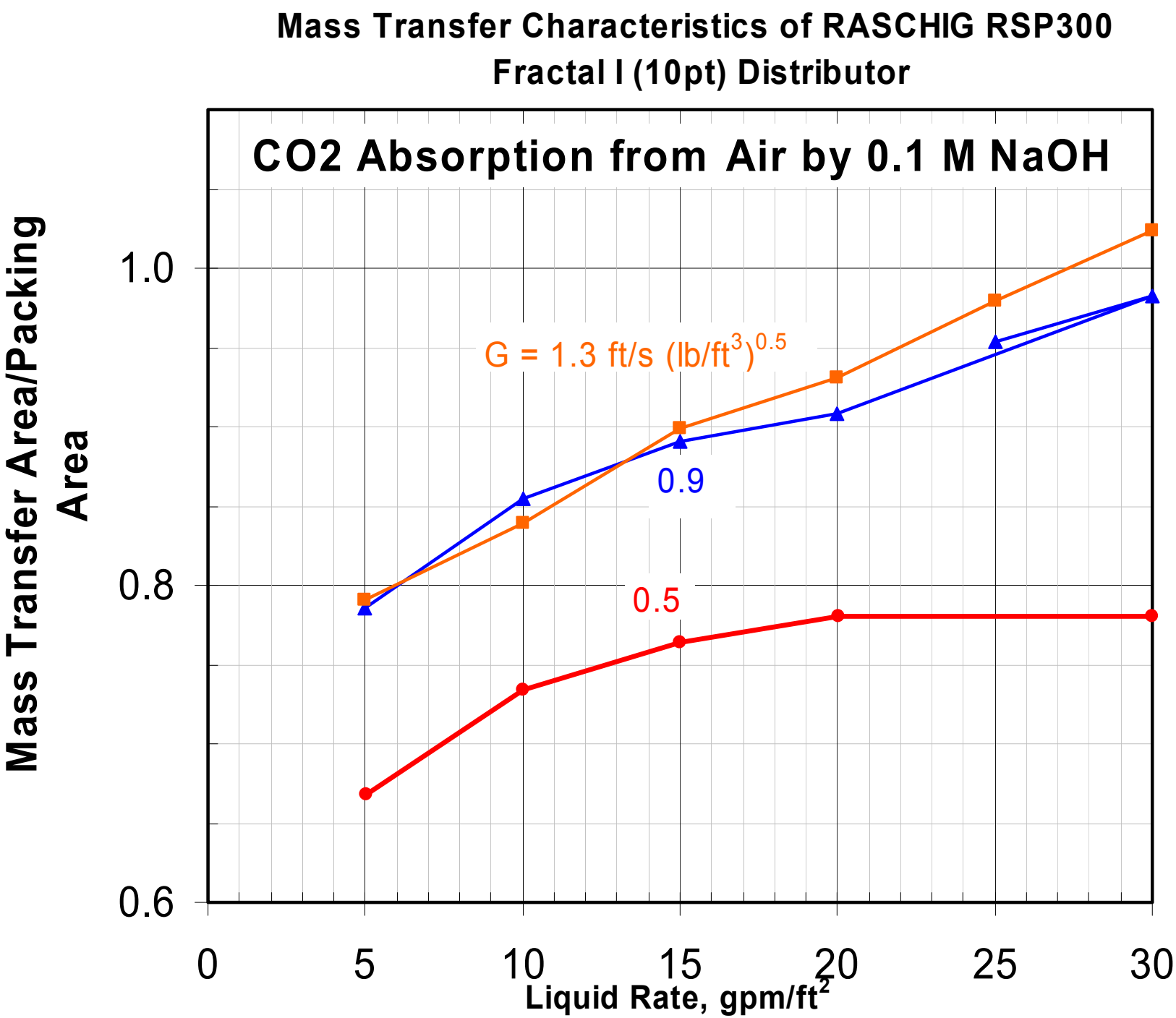
Oxidative Degradation of 7 m MEA, 60C, Air




Anion Chromatography
7 m MEA, 12 days
98% O2/2% CO2
Acetate
Formate
Nitrite?
Nitrate?
Carbonate
Oxalate
MEA?

Modeling and Pilot Plant Activities

- Develop Integrated Models
  - Absorber by Aspenplus/Ratefrac
  - Stripper by Aspenplus/ACM - Presentation
- Validate Models with Pilot Plant Presentation
- Test and Develop Packing
  - 16.8-inch x 10 ft PVC Absorber
  - Area by air/CO_2/NaOH
  - $k_g a$ by air/SO_2/NaOH
  - $k_l a$ by air/heptane/water


Mass Transfer Characteristics of RASCHIG RSP300
Fractal I (10pt) Distributor
CO2 Absorption from Air by 0.1 M NaOH
Mass Transfer Area/Packing Area
1.0
0.8
0.6
G = 1.3 ft/s (lb/ft3)0.5
0.9
0.5
0
5
10
15
20
25
30
Liquid Rate, gpm/ft2

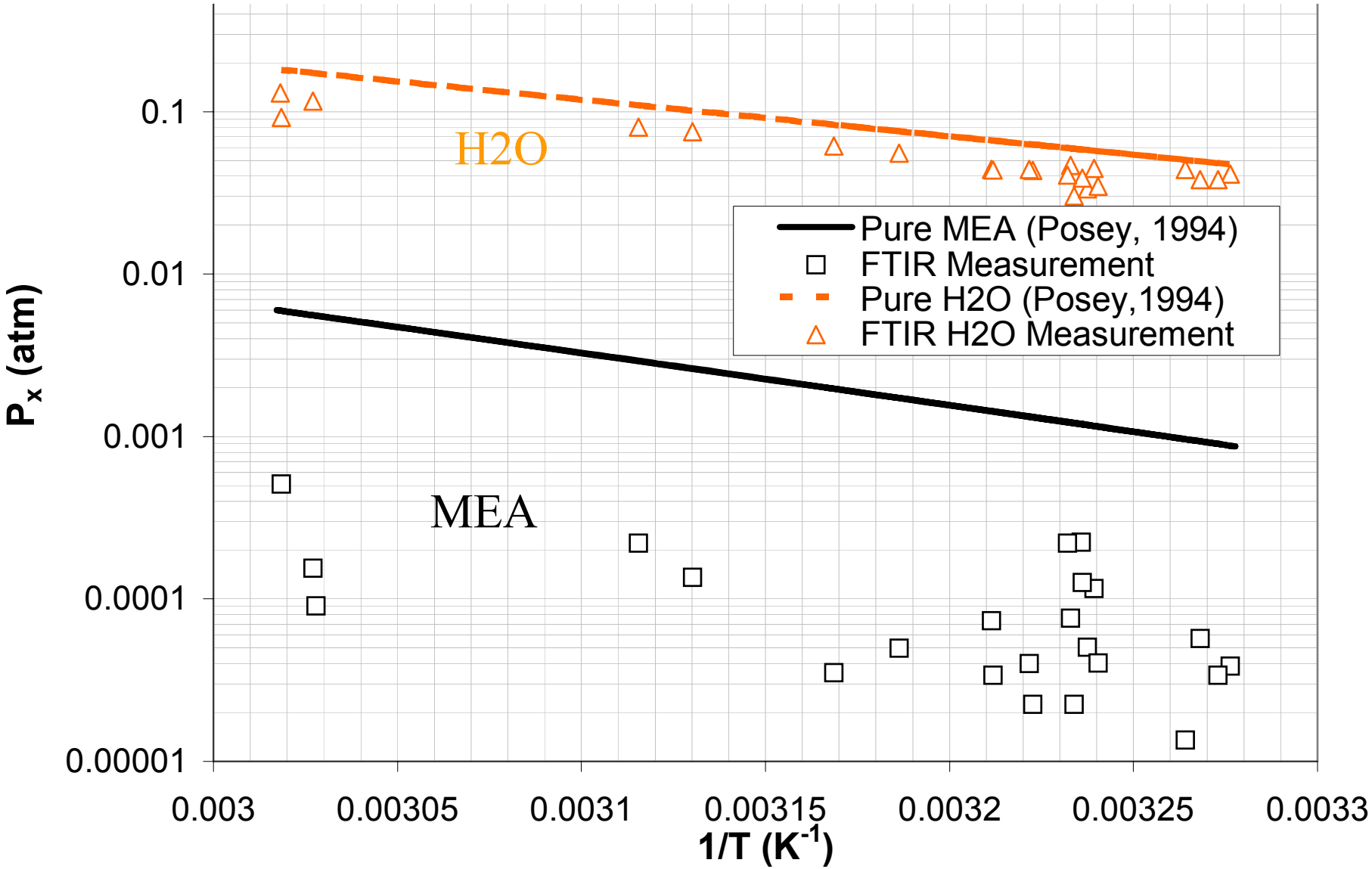
Important results

- Cullinane & Hilliard – K_2CO_3/PZ
  - Rates 1 – 3 times 7m MEA
  - ΔH=10-18 kcal/gmol, capacity equiv to MEA
- Goff & Alawode – MEA & PZ Oxidation
  - Catalyzed by Fe^{++},Cu^{++},V^{+5}
  - Frequently limited by O_2 mass transfer
  - Inhibited by sulfite, formadehyde, & A
- Chen & Dugas – 16.8-inch Pilot Plant
  - Detailed public data sets for MEA & K_2CO_3/PZ
  - Structured Packing effective in absorber & stripper
- Oyenekan & Jassim – Stripper Modeling
  - Vacuum stripping competitive
  - Multipressure stripping shifts Q to W
  - Optimum ΔH = 20-40 kcal/gmol (MEA)

Oxidative Degradation

- Objective: Minimize Solvent Degradation
- Measure oxidation catalyzed by metals
  - Fe^{++}
  - Cu^{+2},V^{+5} inhibit corrosion, catalyze degradation
  - Limited by oxygen mass transfer
- Quantify Degradation products
  - MEA → ammonia, organic acids, etc.
  - Piperazine → organic acids, etc.
- Minimize
  - Strip O_2 or add oxygen scavengers
  - Remove metals or add chelating agents
  - Add free radical inhibitors

MEA Campaign Hot FTIR



Prof. Benny Freeman
Dept of Chem Engin, Sep Res Prog

- Plasticization-resistant membranes for CO_2 removal
- Selective matls for acid gas removal from H_2
- Physical aging & chemical stability of high free volume glassy polymers & nanocomposites matls
- Interactions of basic nanoparticles and their influence upon gas transport properties
- Effect of substituent size and shape on gas transport properties of disubstituted polyacetylenes
- Physical aging of thin glassy polymer films

System Modeling in AspenPlus

Rate-Based contacting: RATEFRAC

Electrolyte Thermodynamics

Mass Transfer with Chemical Rxn

Simultaneous Heat Transfer

Flexible configuration and conditions

Pilot Plant Projects

Test and Develop Random and Structured Packing

- 16.8-inch x 10 ft PVC Absorber
- Area by air/CO_2/NaOH
- $k_g a$ by air/SO_2/NaOH
- $k_l a$ by air/heptane/water

Validate Models for K_2CO_3/PZ

- 16.8-inch x 20 ft Absorber/stripper
- Demonstrate atm & vacuum stripping
- Baseline MEA

Overview of Recent Studies on CO_2 Capture

John Davison

IEA Greenhouse Gas R&D Programme

8th International CO_2 Capture Network Meeting

Austin, Texas, 3-4 October 2005

Recent Completed Studies

- Post combustion capture (coal and gas)
  - Fluor
  - MHI
- IGCC (coal)
  - Foster Wheeler
- Oxy combustion (coal and gas)
  - Mitsui Babcock, Air Products and Alstom
- Capture retrofit to natural gas combined cycles
  - Jacobs

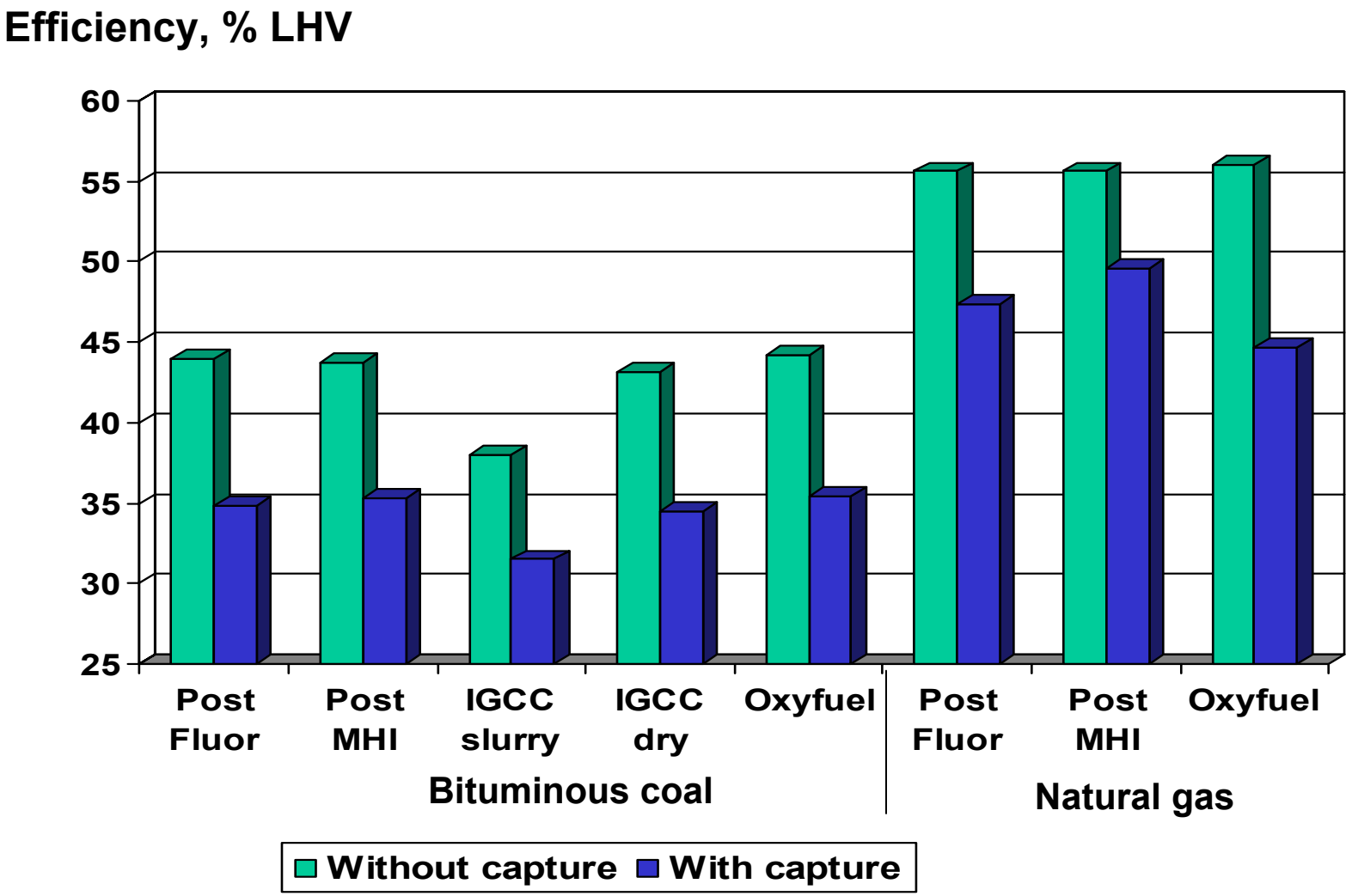
Study Basis

- Post combustion capture
  - Pulverised coal
    - 29 MPa, 600/620°C steam
  - GE 9FA gas turbine combined cycle
  - Fluor Econamine FG+ and MHI KS-1
- IGCC
  - Shell gasifier (dry feed, heat recovery boiler)
  - GE, formerly Texaco, gasifier (slurry feed, water quench gas cooling)
  - Selexol acid gas removal
  - GE 9FA gas turbine combined cycle

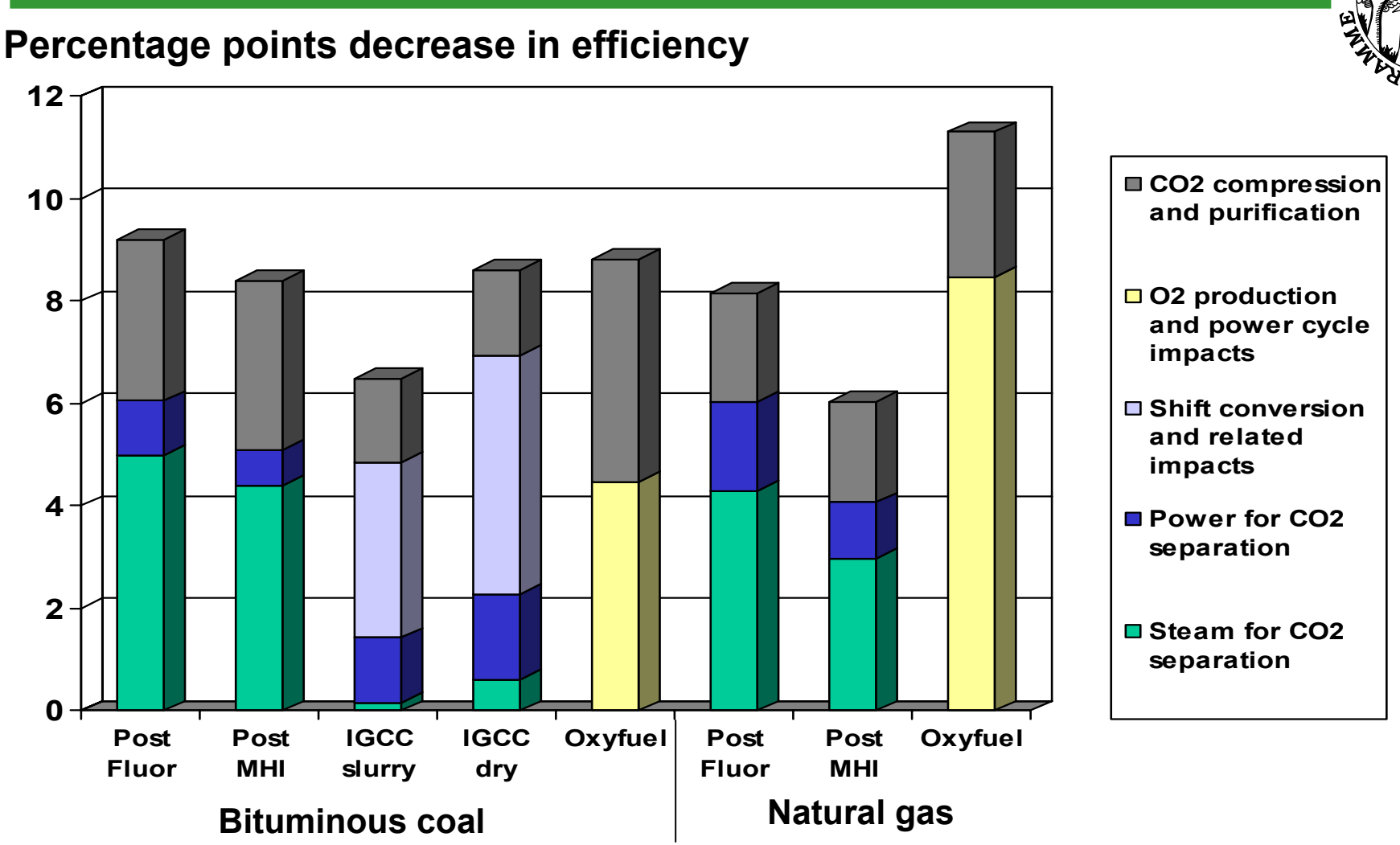
Study Basis

- Oxy-combustion
  - Cryogenic air separation
  - Pulverised coal
    - 29 MPa, 600/620°C steam
  - Gas turbine combined cycle
    - Gas turbine based on the same mechanical design parameters as the GE 9FA
    - Gas turbine inlet pressure 3 MPa

Power Generation Efficiency

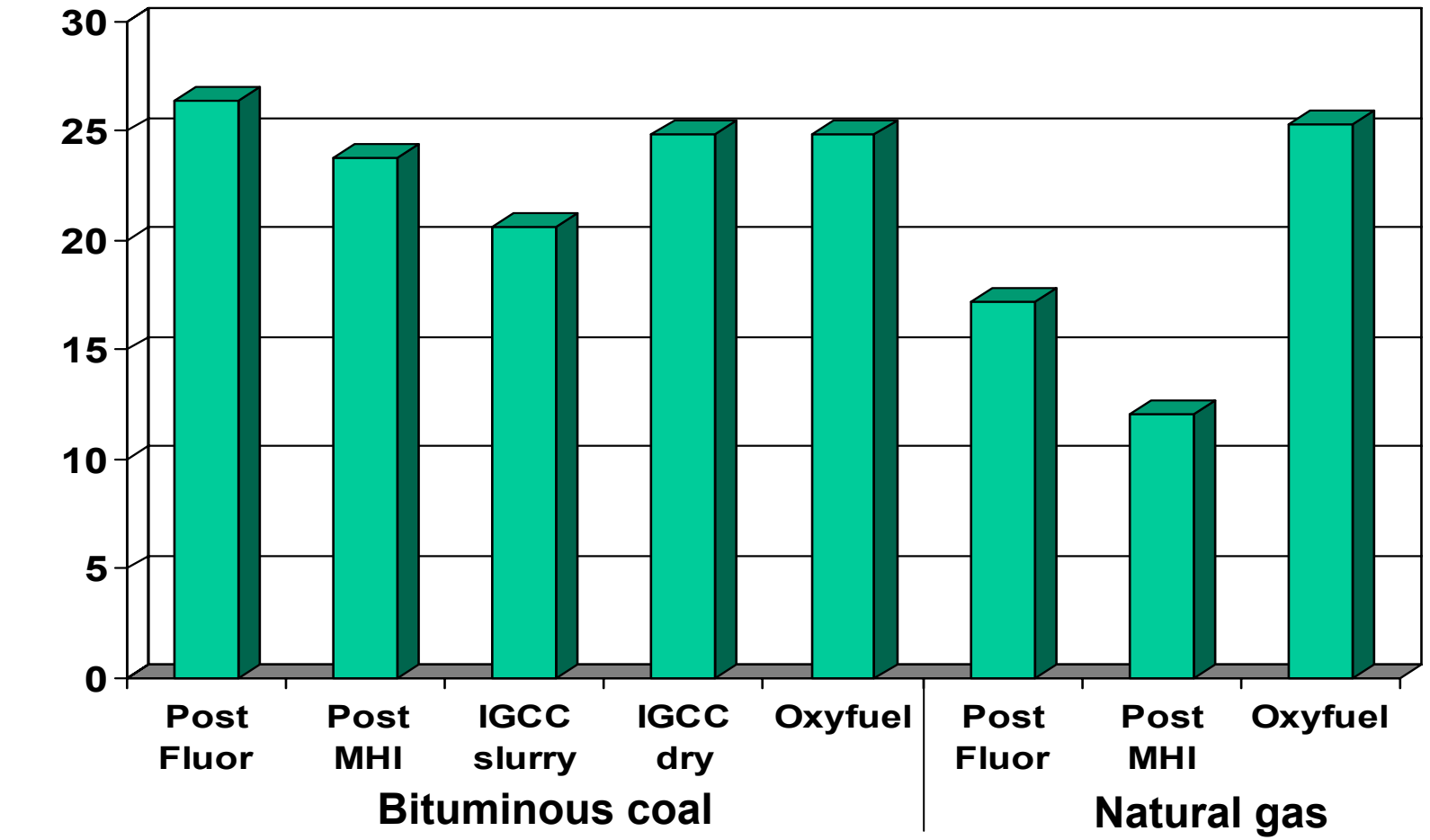


Efficiency Loss due to Capture



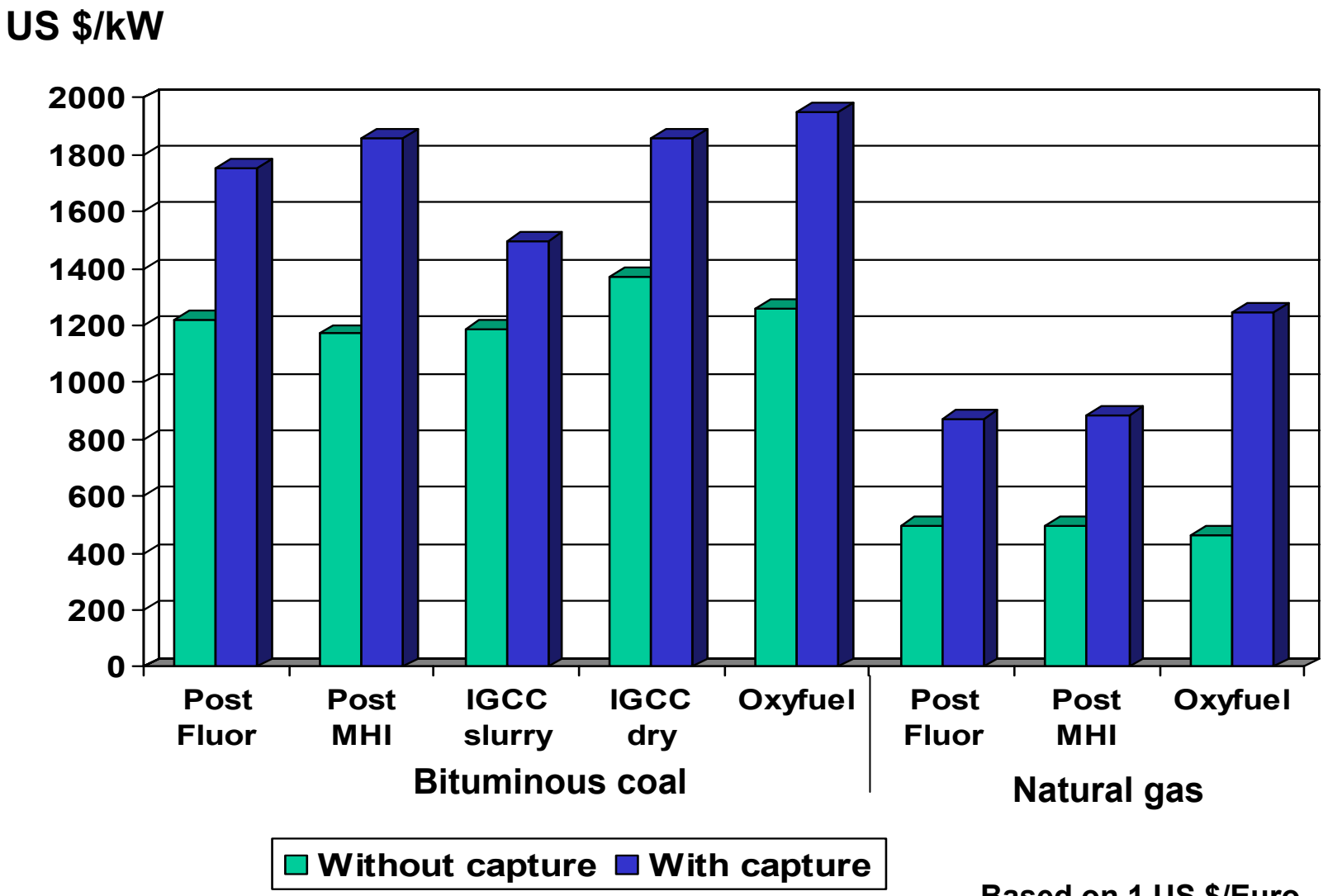
Plants with capture compared to same technology without capture

Increase in Fuel Consumption



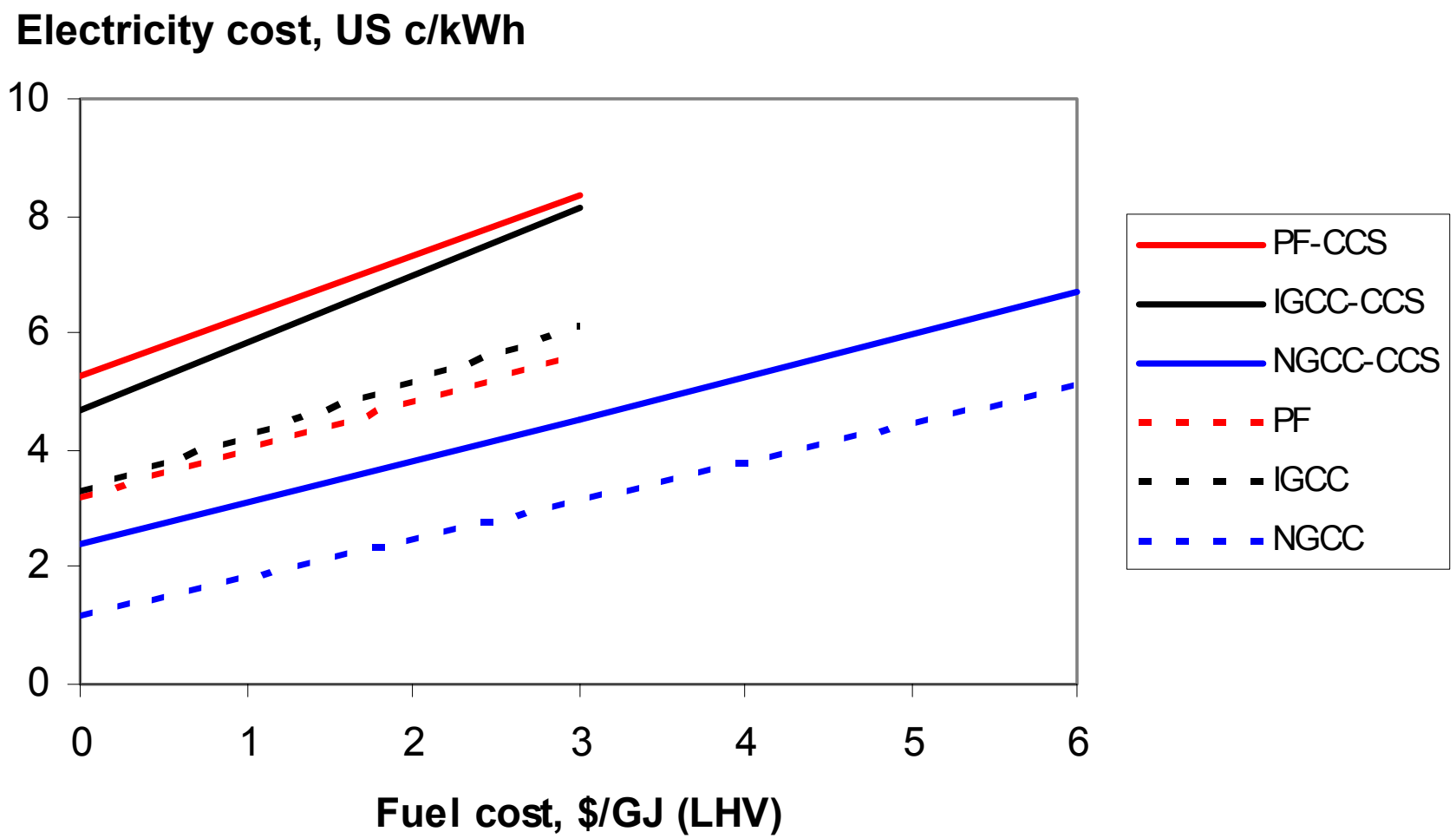
Plants with capture compared to same technology without capture

Capital Cost



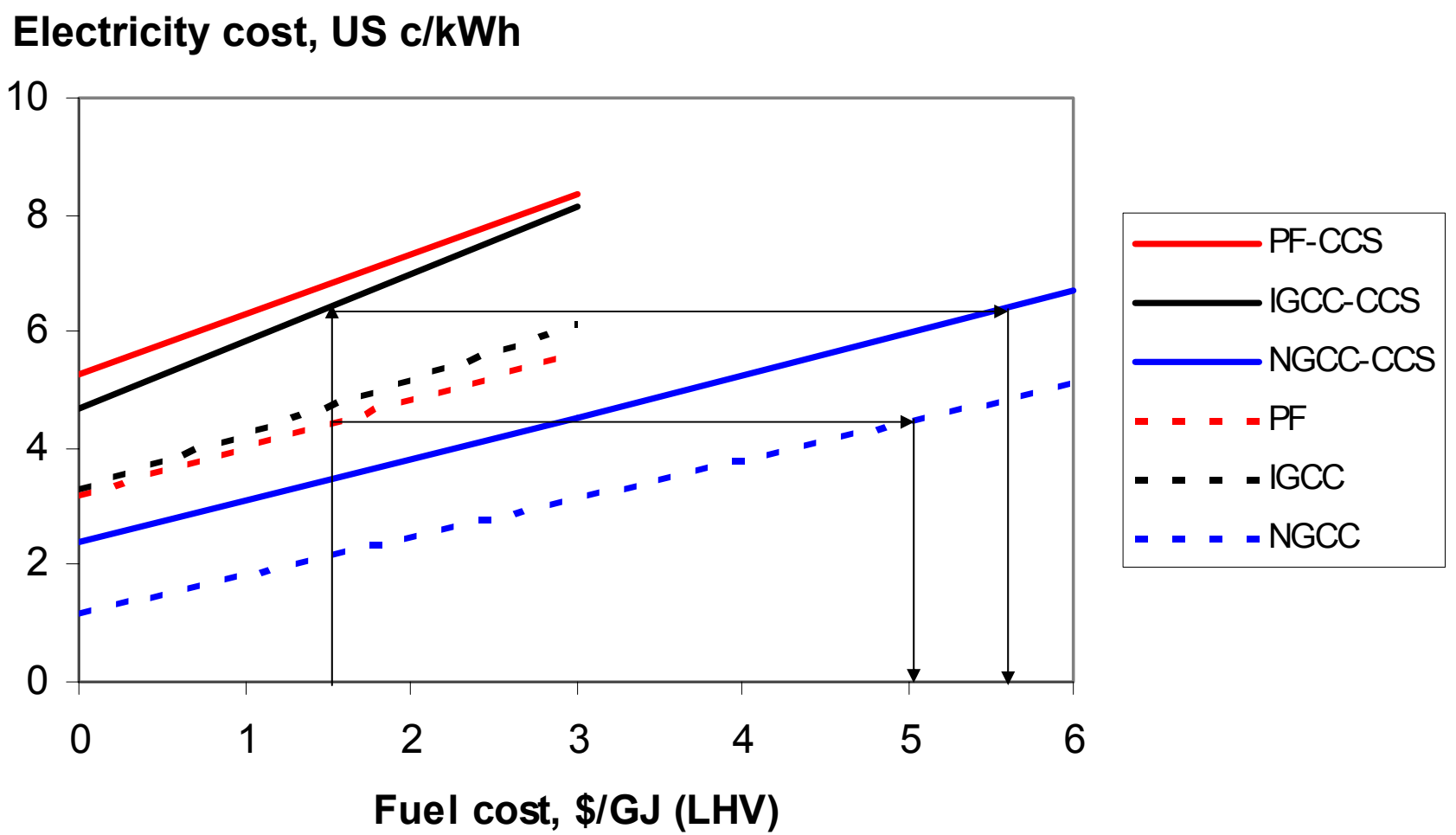
Based on 1 US $/Euro

Cost of Capture and Storage



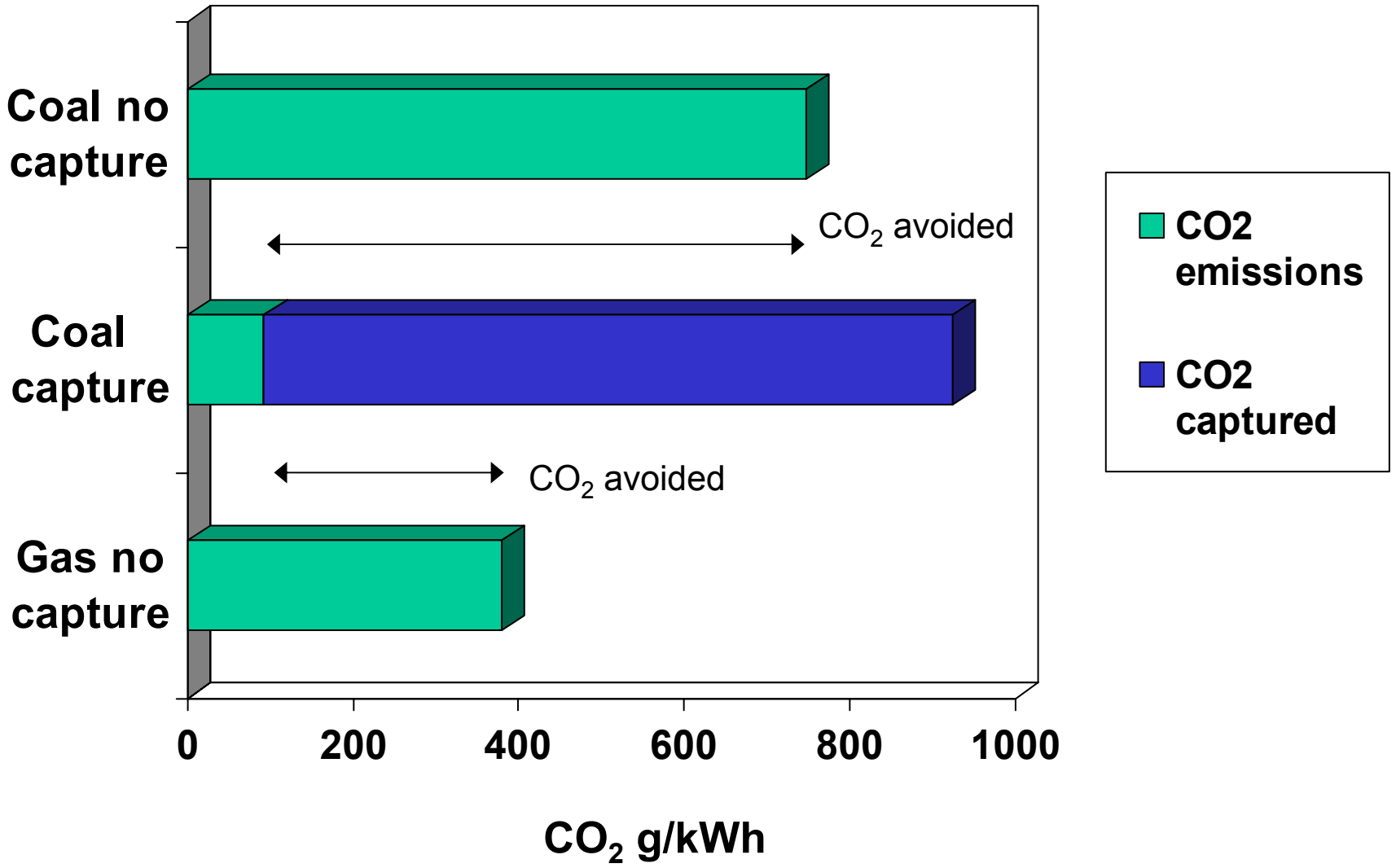
10% DCF, 25 year life, includes \$8/tonne CO_2 transport and storage cost

Cost of Capture and Storage



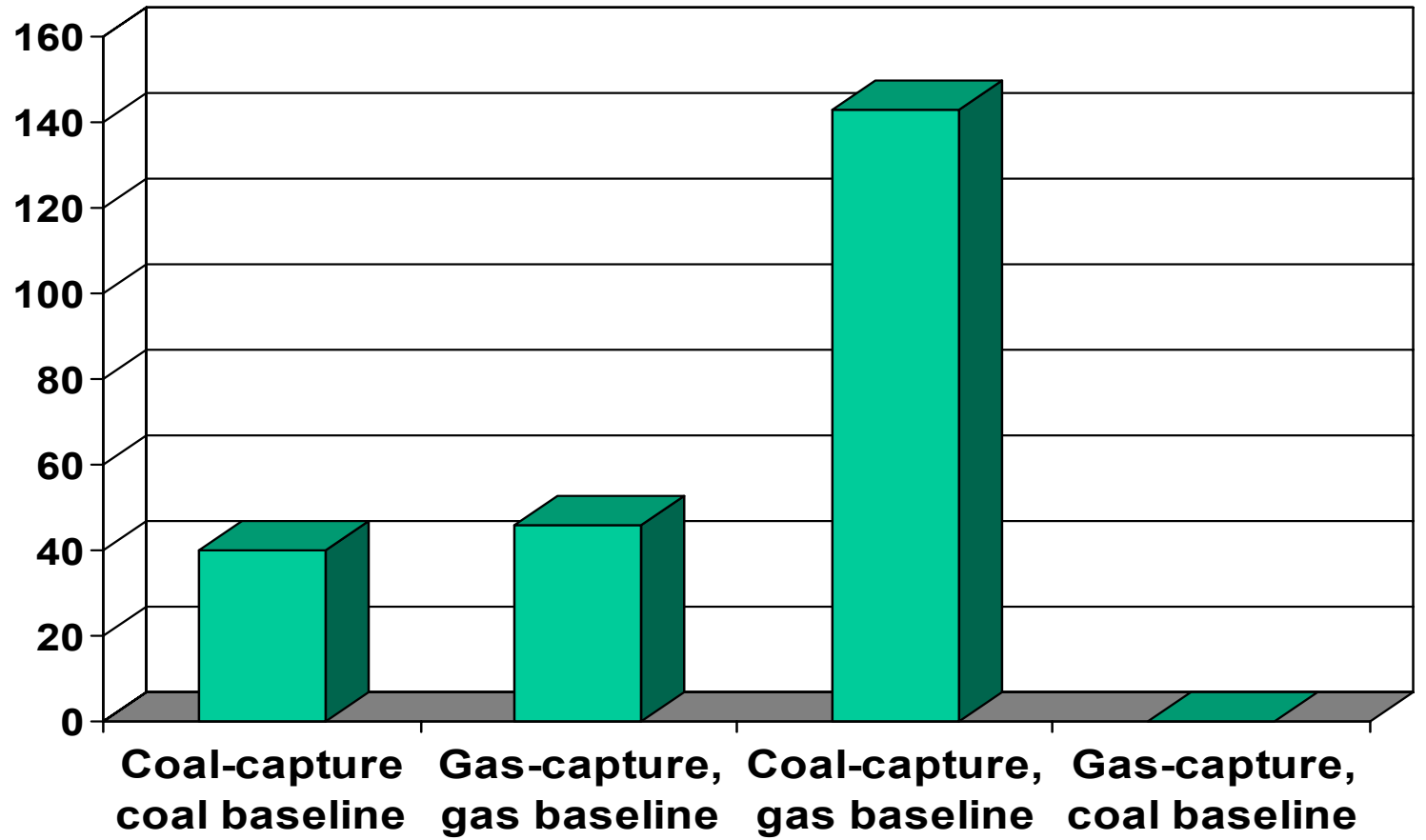
10% DCF, 25 year life, includes \$8/tonne CO_2 transport and storage cost

CO_2 Produced and Avoided



Cost per Tonne of CO_2

$ per tonne of CO_2 emissions avoided



10% DCF, Coal $1.5/GJ, Gas $3/GJ, $8/t CO_2 stored

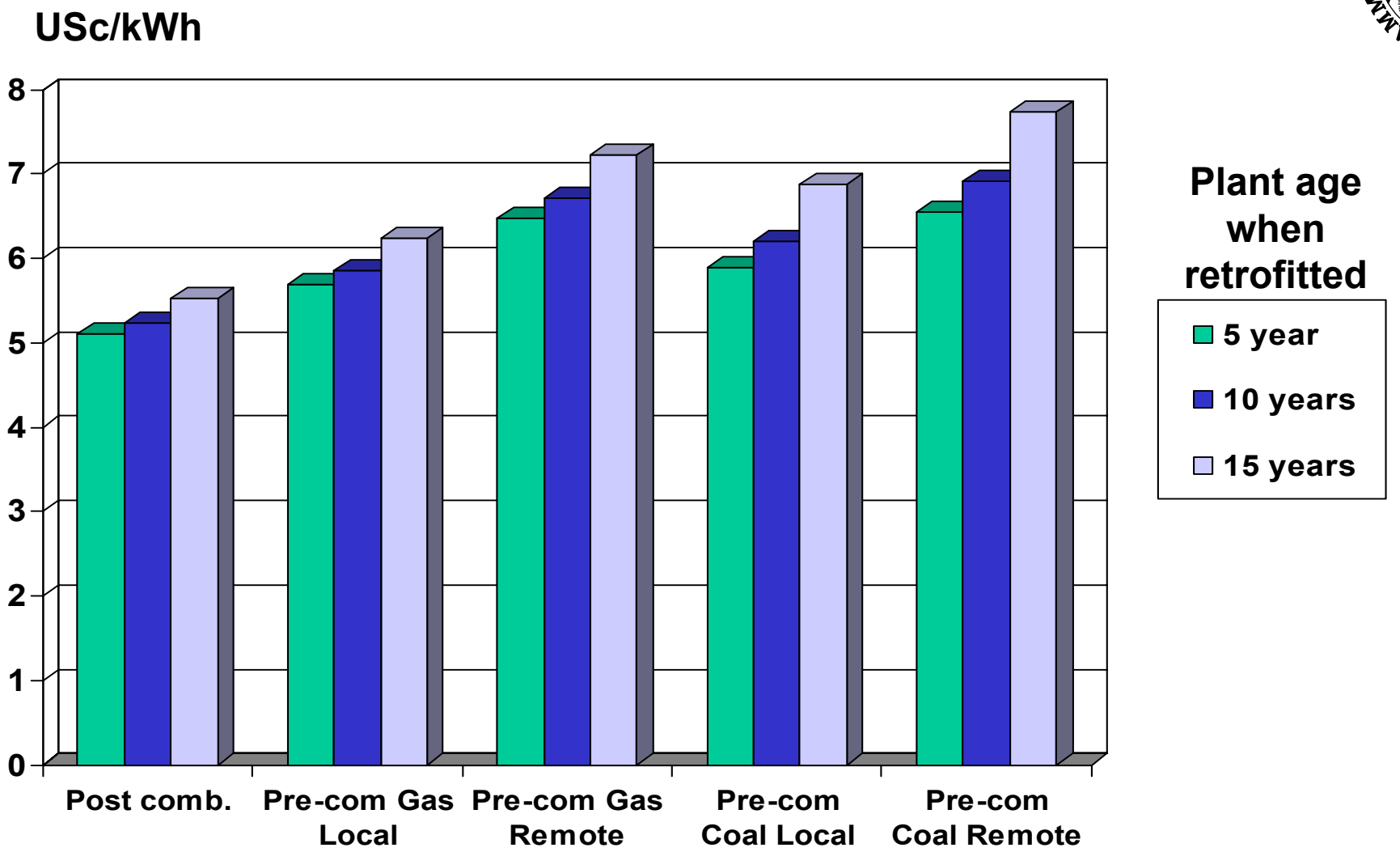
Capture Retrofit to GTCCs

- Study carried out by Jacobs Consultancy, Netherlands / UK

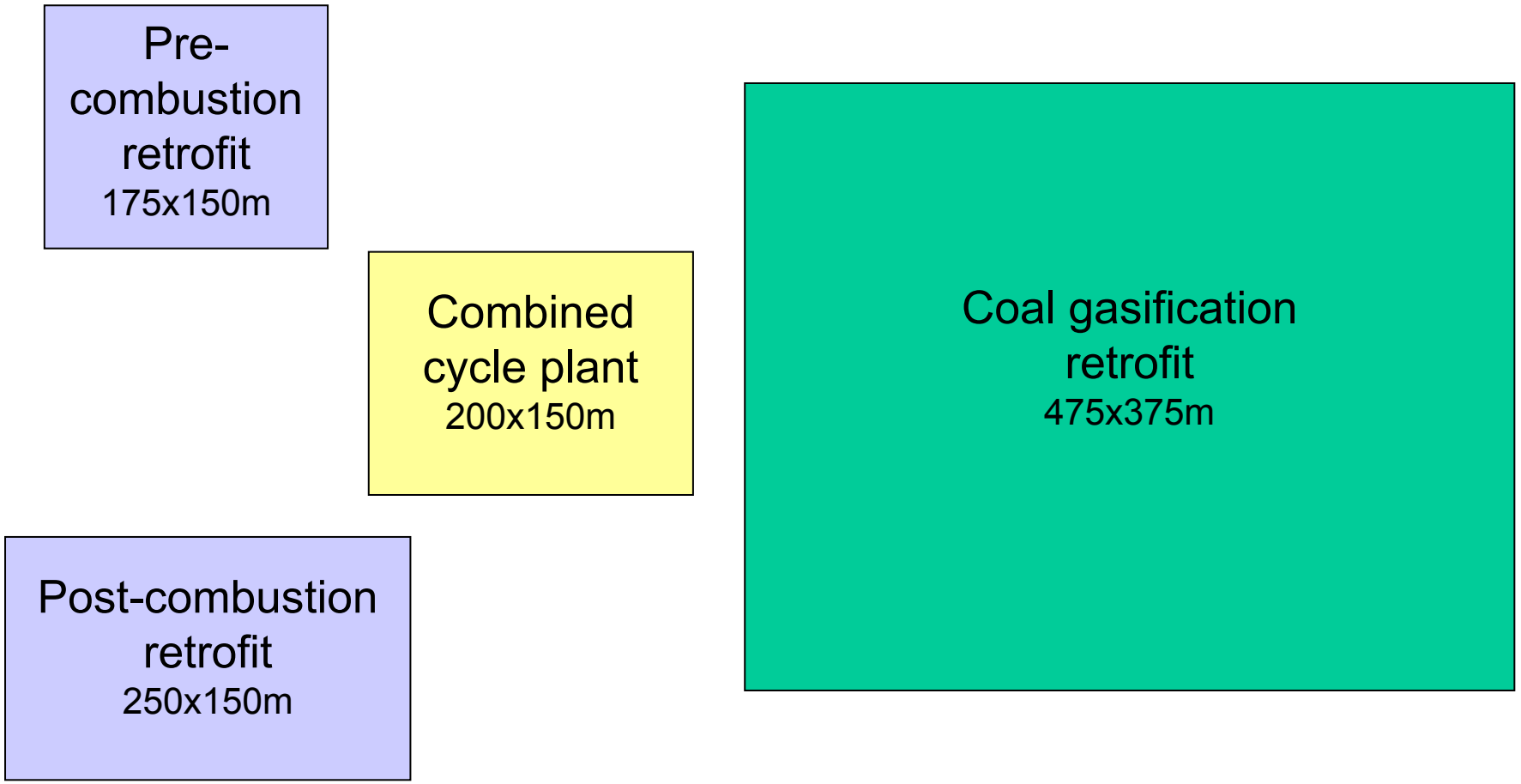
Retrofit cases assessed

- Post combustion capture
- Pre-combustion air blown reforming of natural gas
  - At the power plant site
  - At a remote site (40km form the power plant)
- Pre-combustion gasification of coal
  - At the power plant site
  - At a remote site

Cost of Electricity after Retrofit



Plant Area Requirement



Capture in Brown Coal Plants

- Study carried out by Foster Wheeler Italiana
- Based on German brown coal
  - 50.7% moisture
  - 7.1% ash (dry basis)
  - 0.45% sulphur (dry basis)
- Inland German site

Capture in Brown Coal Plants

Screening of technologies

- Post-combustion capture
  - Pulverised coal
  - Atmospheric pressure circulating fluidised bed
  - Pressurised circulating fluidised bed combustion
- Oxyfuel (pulverised coal)
- IGCC
  - Shell gasifier (oxygen, entrained, dry feed, heat recovery boiler)
  - Future Energy gasifier (oxygen, entrained, dry feed, water quench)
  - Foster Wheeler gasifier (air, fluidised bed, dry feed, heat recovery boiler)

Capture in Brown Coal Plants

Main conclusions

- Little difference between the performance and costs of leading post-combustion, pre-combustion and oxyfuel processes
- Dry feed gasifiers are necessary for IGCC
  - GE gasifier is not well suited for very low rank coal
- Compared to bituminous coal power plants:
  - Thermal efficiencies, LHV basis, are similar
  - 20% more CO_2 has to be captured per kWh_e
  - Cost of avoiding CO_2 per kWh is slightly higher
  - Cost per tonne of CO_2 avoided is slightly lower

Medium Scale CO_2 Capture

Large point sources

Large scale power generation
Oil refineries and chemicals production
Iron and steel production
Cement production

Medium point sources

Medium scale industry
Large commercial and institutional
Combined heat and power

Small sources

Residential
Small commercial and industrial

Medium Scale CO_2 Capture

- Is capture realistic for medium scale sources?
  - Question asked during the writing of the IPCC Special Report on CCS
  - It is likely to be more expensive than large scale capture but may be cheaper than other emission reduction techniques for these sources
- Study being carried out by Ecofys / ECN
  - Identify characteristics of medium scale sources
  - Identify appropriate capture technologies
  - Estimate cost and performance sensitivities
- This study may be followed by a comparison with energy carriers

Environmental Impacts Study

- Assess the environmental impacts of the main solvent scrubbing processes
  - Pre-combustion scrubbing
  - Post-combustion scrubbing
  - Direct and indirect impacts
- Identify ways of reducing environmental impacts
- Assess the potential market for solvent scrubbing and overall environmental impacts
- Study being carried out by TNO

Leading Options Study

- This study aims to look beyond standardised cost and efficiency comparisons
- Identify the criteria which will affect the choice of technologies for power plants with capture
- Ask utilities, financiers etc. to rank the criteria
- Compare against the characteristics of the main power generation processes with capture
- Multi criteria analysis based on responses from different utilities
- Study contract awarded to Mott MacDonald

Leading Options Study

- Fuel and other resource consumptions
- Standardised capital and operating costs
- Environmental impacts
- Operating flexibility and future grid requirements
- Risks
  - Availability
  - Contractual issues
  - Safety etc.
- Diversity of suppliers
- Compatibility with utilities' operating experience
- Potential for future improvements

Possible Future Capture Studies

- Capture-ready plants
- Capture in iron and steel and cement production
- Co-production of hydrogen and electricity with CCS

IEA GHG Reports

- Reports are available free of charge within IEA GHG's member countries
- Draft reports are sent to expert reviewers
- Anyone interested in reviewing the on-going studies, please contact John Davison

Estimating Future Costs of CO_2 Capture Systems

Edward S. Rubin
Department of Engineering and Public Policy
Carnegie Mellon University
Pittsburgh, Pennsylvania

8th International CO_2 Capture Network Workshop
Austin, Texas
October 3, 2005

Motivating Question

- What will be the future costs of power plants with CO_2 capture?

Analytical Method

Two Approaches to Estimating Future Technology Costs

- *Method 1:* Engineering-Economic Modeling
  - Based on process models and expert elicitations (e.g., see Rao, et.al, *Energy Policy*, 2005)
- *Method 2:* Historical "Experience Curves"
  - Based on observed trends for analogous technologies or systems
- *This study uses the latter approach*

Power Generation Systems Studied

- PC plant with amine capture
- NGCC plant with amine capture
- IGCC plant with shift + Selexol
- PC plant with oxyfuel combustion

Part I:

Retrospective Case Studies

Research Methods

- Study historical cost trends for selected technologies relevant to CO_2 capture plants
- Estimate “learning rates” for those technologies
- Apply results to components of plants with capture
- Aggregate components to estimate total plant cost trends and their dependence on key assumptions

Retrospective Case Studies

- Flue gas desulfurization systems (FGD)
- Selective catalytic reduction systems (SCR)
- Gas turbine combined cycle system (GTCC)
- Pulverized coal boilers (PC)
- Oxygen production plants (ASU)
- Hydrogen production plants (SMR)
- Liquified natural gas plants (LNG)

Learning Curve Formulation

General equation:

$$y_i = a x_i^{-b}$$

where,

y_i = time or cost to produce i^{th} unit

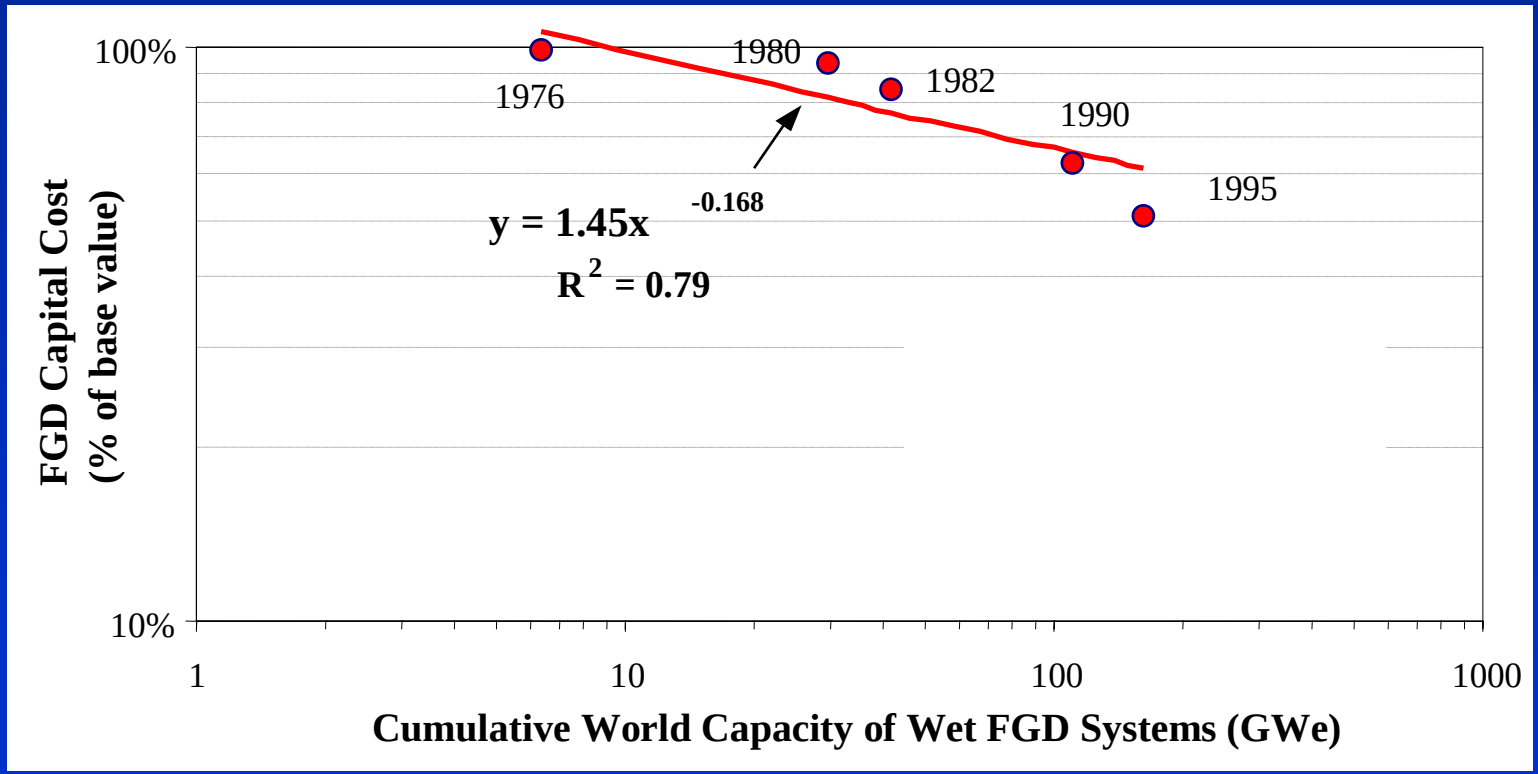
x_i = cumulative production thru period i

b = learning rate exponent

a = coefficient (constant)

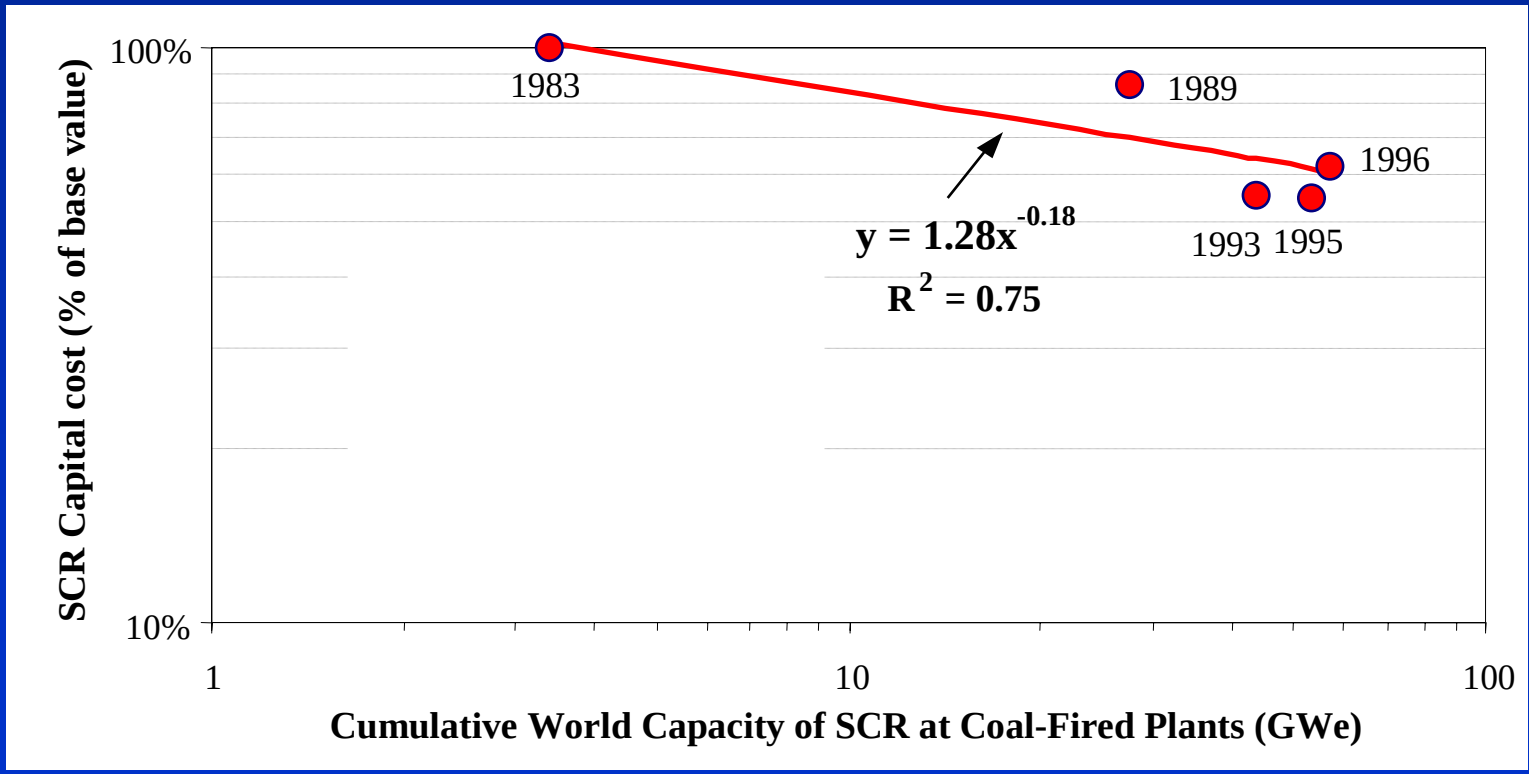
Percent cost reduction for a doubling of cumulative output is called the "learning rate" = $(1 - 2^{-b})$

FGD System Capital Costs



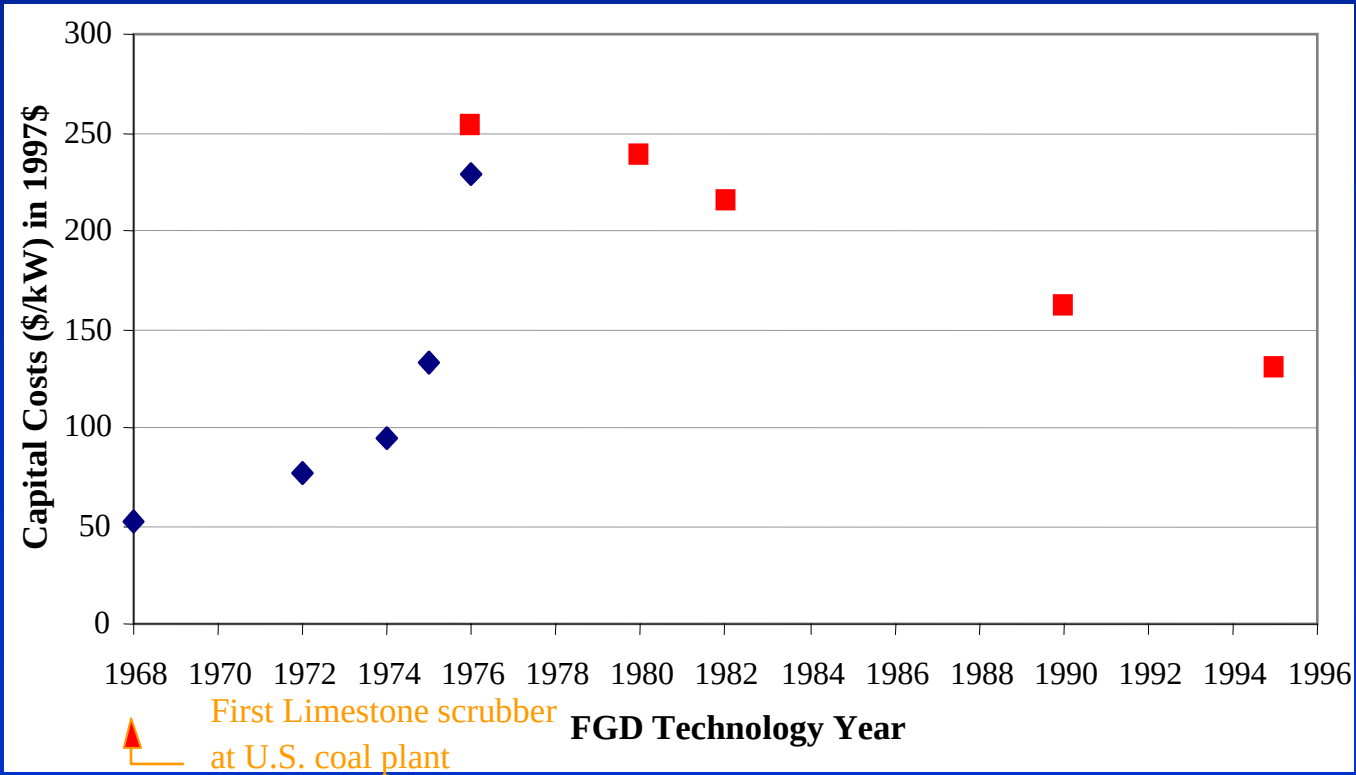
(Based on 90% SO_2 removal, 500 MW plant, 3.5%S coal)

SCR System Capital Cost

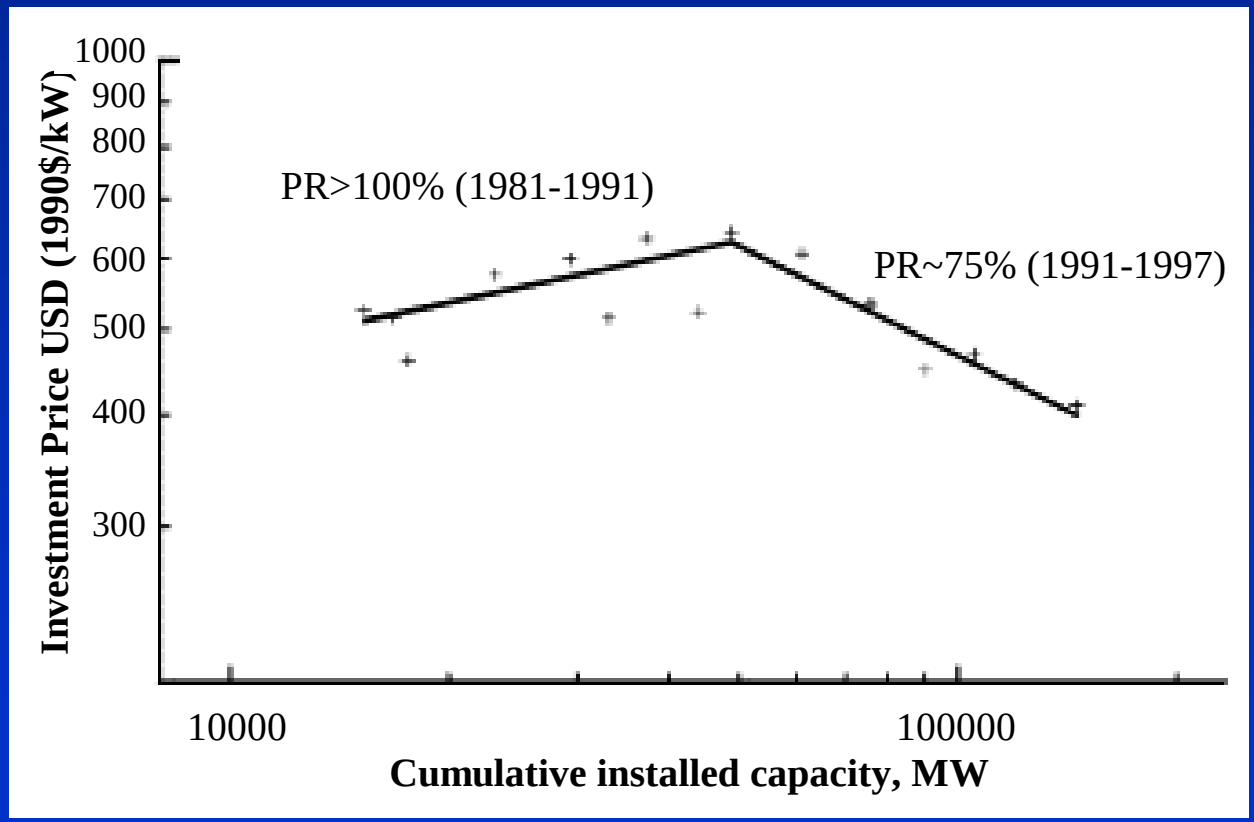


(Based on 80% NO_x removal, 500 MW plant, medium S coal)

Early Trend of FGD Cost

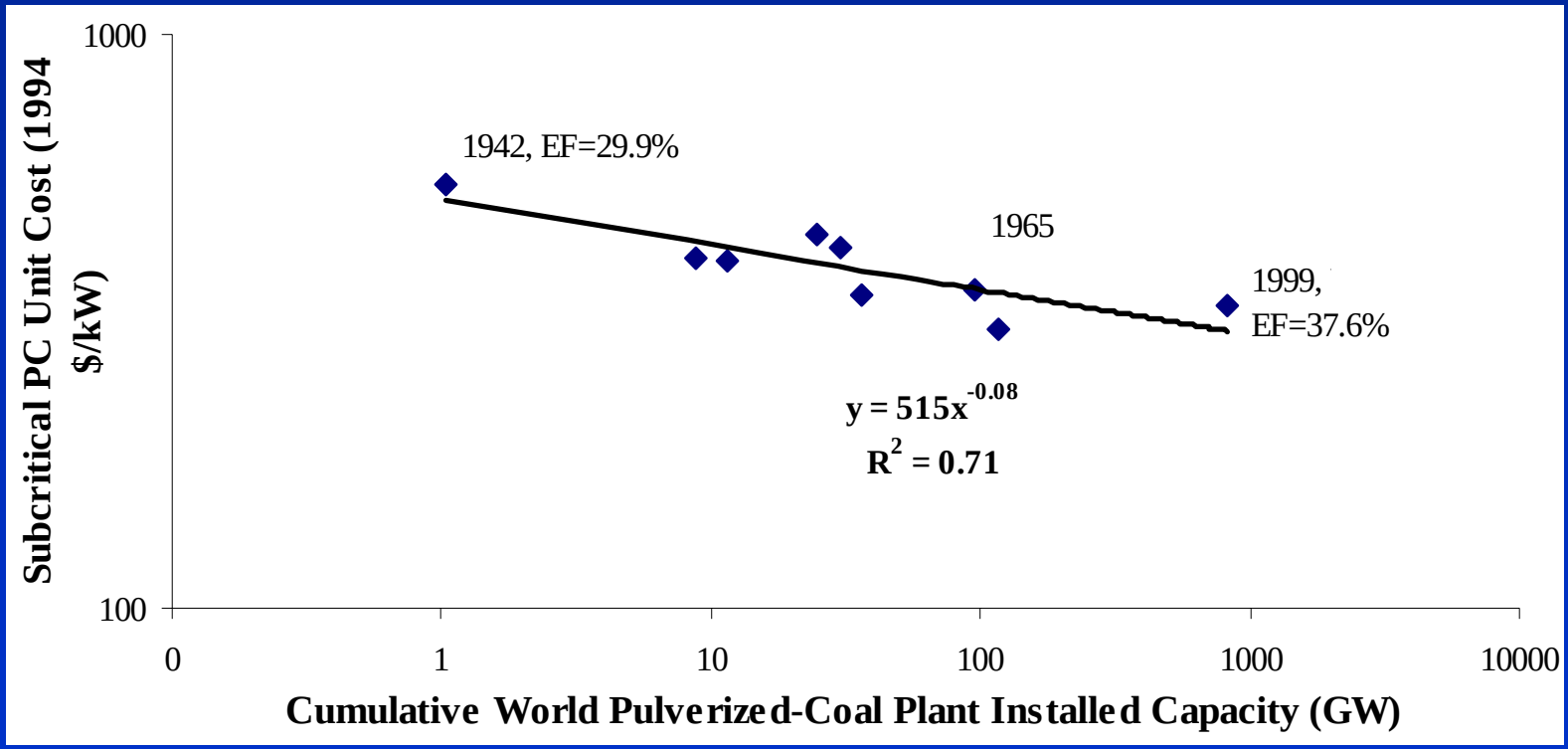


GTCC Capital Cost

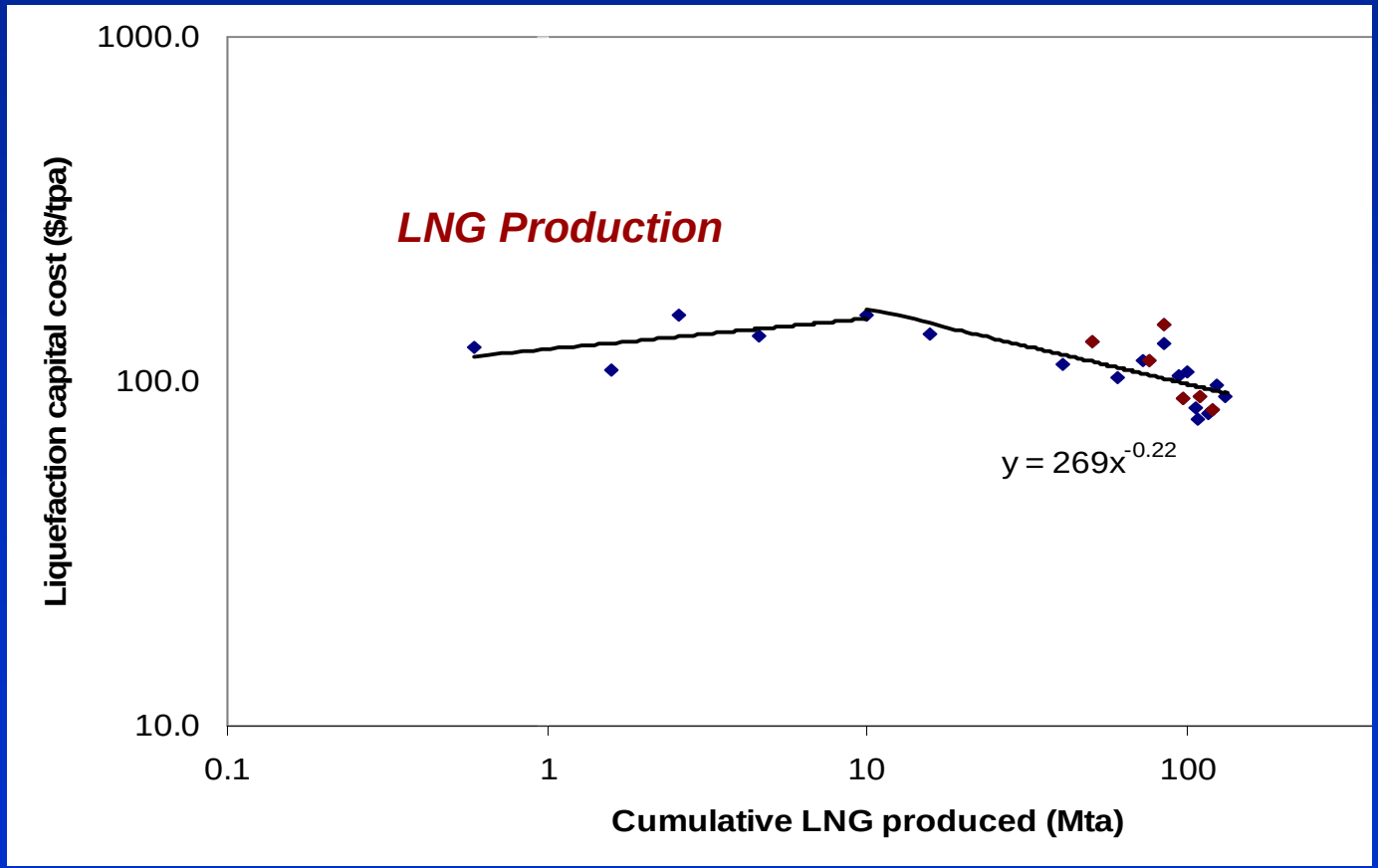


Source: Colpier and Cornland (2002).

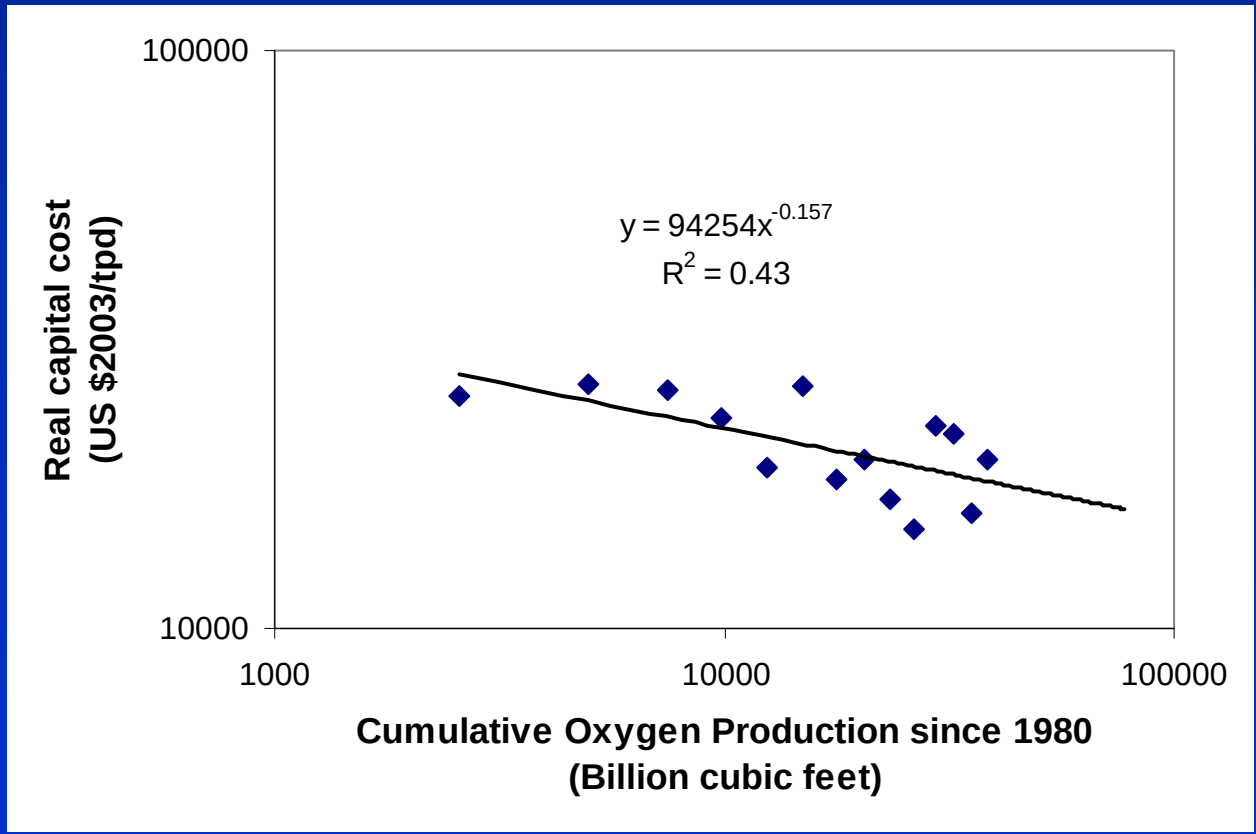
PC Boiler Capital Cost



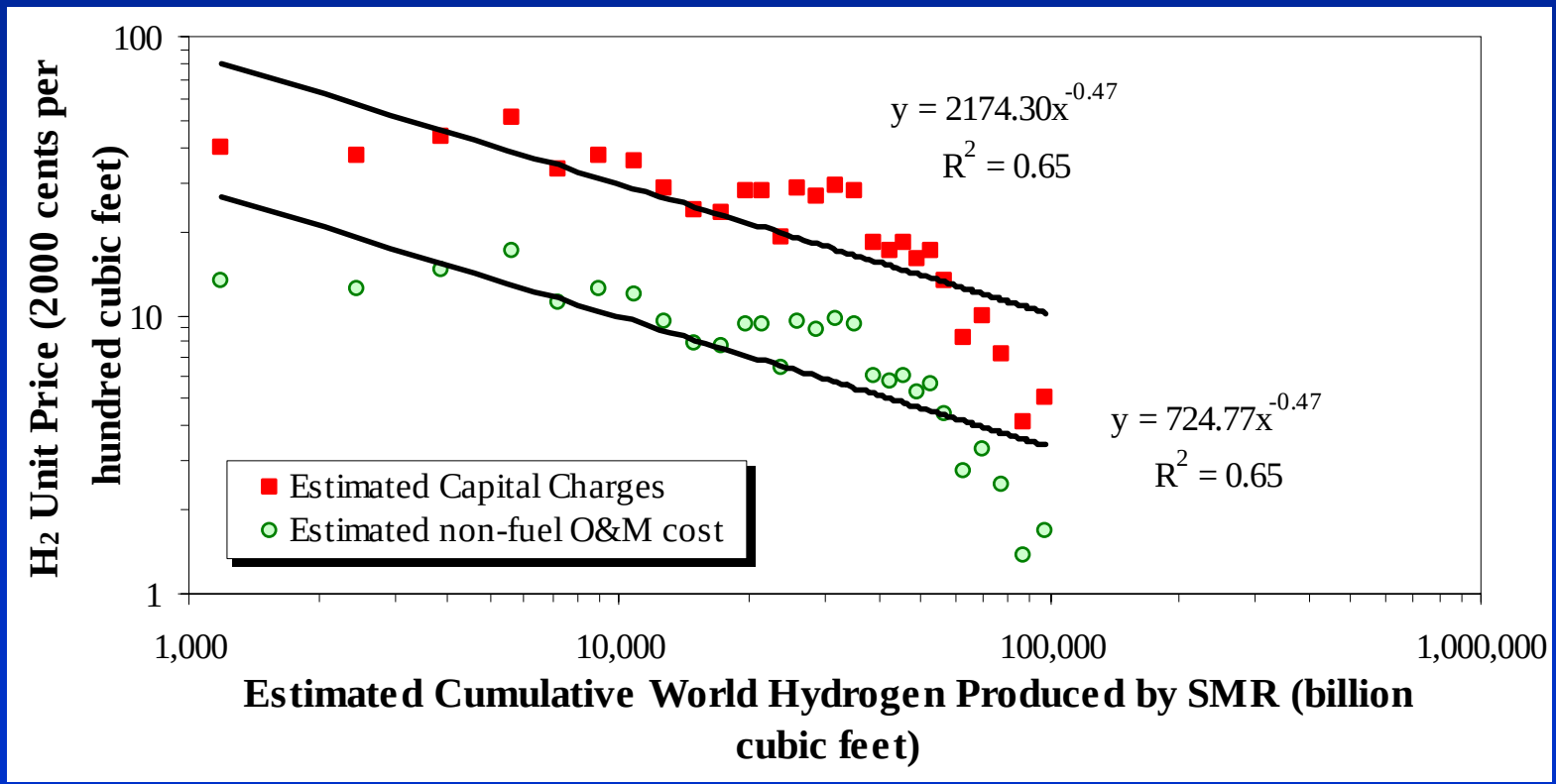
LNG Plant Capital Cost



Oxygen Plant Capital Cost



Hydrogen Production Cost



Case Study Learning Rates

Technology	Learning Rate	
	Capital Cost	O&M Cost
Flue gas desulfurization (FGD)	0.11	0.22
Selective catalytic reduction (SCR)	0.12	0.42
Gas turbine combined cycle (GTCC)	0.10	0.06
Pulverized coal (PC) boilers	0.05	0.07-0.30
LNG production	0.14	0.12
Oxygen production	0.10	0.05
Hydrogen production (SMR)	0.27	0.27

Part II:

Applications to Power Plants with CO_2 Capture

Methodology

Power Plant Components

NGCC Plant

- GTCC (power block)
- CO_2 capture (amine system)
- CO_2 compression
- Fuel cost

PC Plant

- PC Boiler/turbine-generator area
- AP controls (SCR, ESP, FGD)
- CO_2 capture (amine system)
- CO_2 compression
- Fuel cost

IGCC Plant

- Air separation unit
- Gasifier area
- Sulfur removal/recovery
- CO_2 capture (WGS/selexol)
- CO_2 compression
- GTCC (power block)
- Fuel cost

Oxyfuel Plant

- Air separation unit
- PC boiler/turbine generator area
- AP controls (ESP, FGD)
- CO_2 distillation
- CO_2 compression
- Fuel cost

Current Plant Costs

(based on IECM v. 5.0.2)

Plant Type & Technology	Capital	Plant O&M	COE
NGCC Plant	**915** $/kW	**36.9** $/MWh	**57.5** $/MWh
GTCC (power block)	72 %	6 %	30 %
CO_2 capture (amine system)	24 %	7 %	13 %
CO_2 compression	4 %	0 %	2 %
Fuel	0 %	0 %	56 %
PC Plant	**1,962** $/kW	**29.3** $/MWh	**73.4** $/MWh
PC Boiler/turbine-generator area	65 %	19 %	47 %
AP controls (SCR, ESP, FGD)	12 %	14 %	13 %
CO_2 capture (amine system)	18 %	25 %	21 %
CO_2 compression	4 %	1 %	3 %
Fuel	0 %	0 %	16 %
IGCC Plant	**1,831** $/kW	**21.5** $/MWh	**62.7** $/MWh
Air separation unit	18 %	8 %	14 %
Gasifier area	27 %	17 %	24 %
Sulfur removal/recovery	6 %	3 %	5 %
CO_2 capture (WGS/selexol)	11 %	7 %	10 %
CO_2 compression	4 %	2 %	4 %
GTCC (power block)	34 %	9 %	25 %
Fuel	0 %	0 %	18 %
Oxyfuel Plant	**2,404** $/kW	**24.2** $/MWh	**78.3** $/MWh
Air separation unit	32 %	13 %	26 %
PC boiler/turbine generator area	53 %	23 %	43 %
AP controls (ESP, FGD)	6 %	11 %	7 %
CO_2 distillation	7 %	6 %	7 %
CO_2 compression	3 %	2 %	2 %
Fuel	0 %	0 %	14 %

Learning Rate Analogs

Plant Type & Technology	FGD	SCR	GTCC	PC boiler	LNG prod	O2 prod
NGCC Plant						
GTCC (power block)			x			
CO_2 capture (amine system)	x					
CO_2 compression						
PC Plant						
PC Boiler/turbine-generator area				x		
AP controls (SCR, ESP, FGD)	x	x				
CO_2 capture (amine system)	x					
CO_2 compression						
IGCC Plant						
Air separation unit						x
Gasifier area					x	
Sulfur removal/recovery	x	x				
CO_2 capture (WGS/Selexol)	x	x				
CO_2 compression						
GTCC (power block)			x			
Oxyfuel Plant						
Air separation unit						x
PC boiler/turbine generator area				x		
AP controls (ESP, FGD)	x					
CO_2 distillation						
CO_2 compression						

Current Capacity of Components

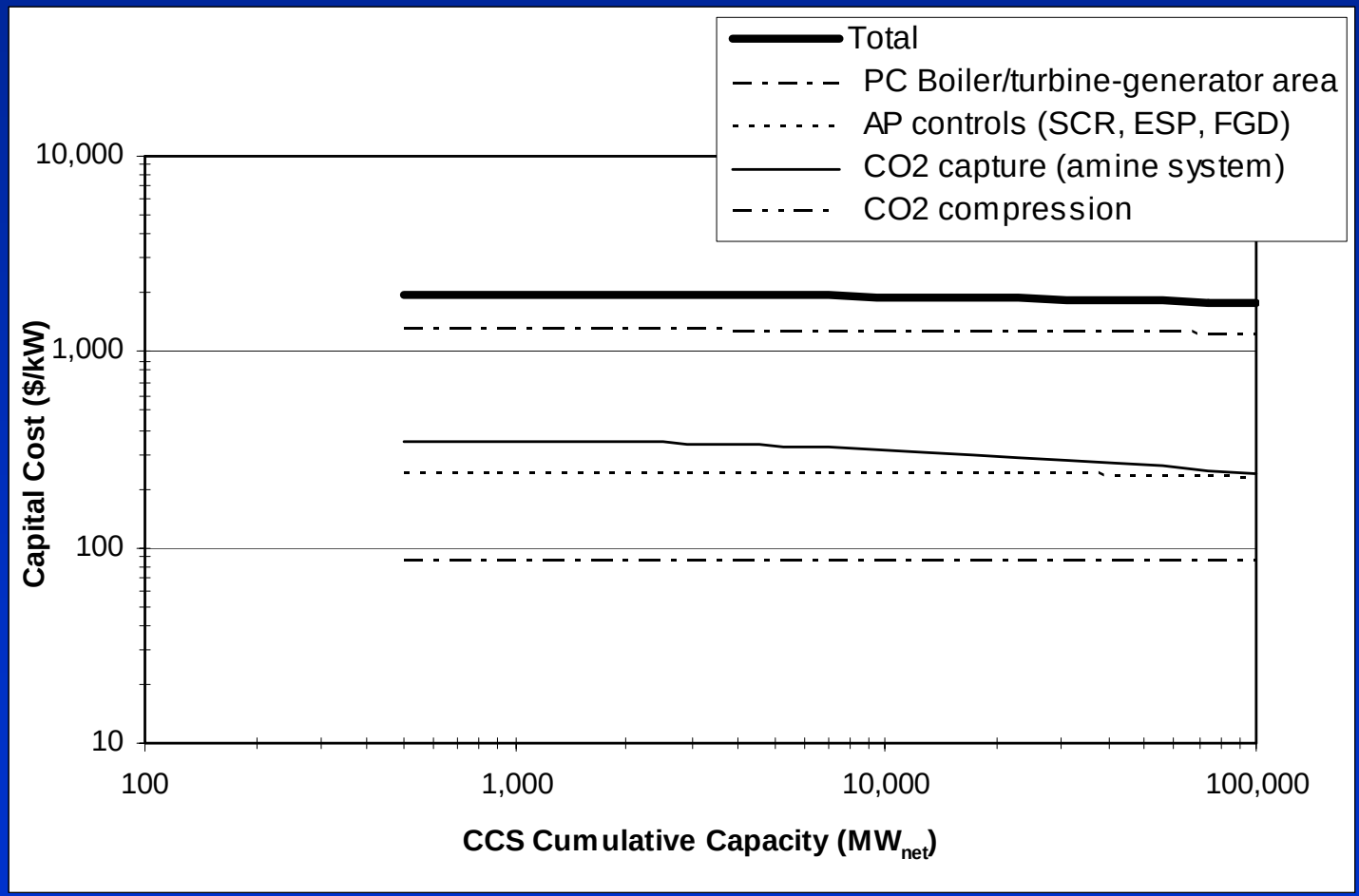
Plant Type & Technology	Current Capacity (MW net)
NGCC Plant	
GTCC (power block)	240,000
CO_2 capture (amine system)	10,000
CO_2 compression	10,000
PC Plant	
PC Boiler/turbine-generator area	120,000
AP controls (SCR, ESP, FGD)	230,000
CO_2 capture (amine system)	10,000
CO_2 compression	10,000
IGCC Plant	
Air separation unit	50,000
Gasifier area	10,000
Sulfur removal/recovery	50,000
CO_2 capture (WGS/Selexol)	10,000
CO_2 compression	10,000
GTCC (power block)	240,000
Oxyfuel Plant	
Air separation unit	50,000
PC boiler/turbine generator area	120,000
AP controls (ESP, FGD)	230,000
CO_2 distillation	10,000
CO_2 compression	10,000

When Does Learning Begin for New Plants with Capture?

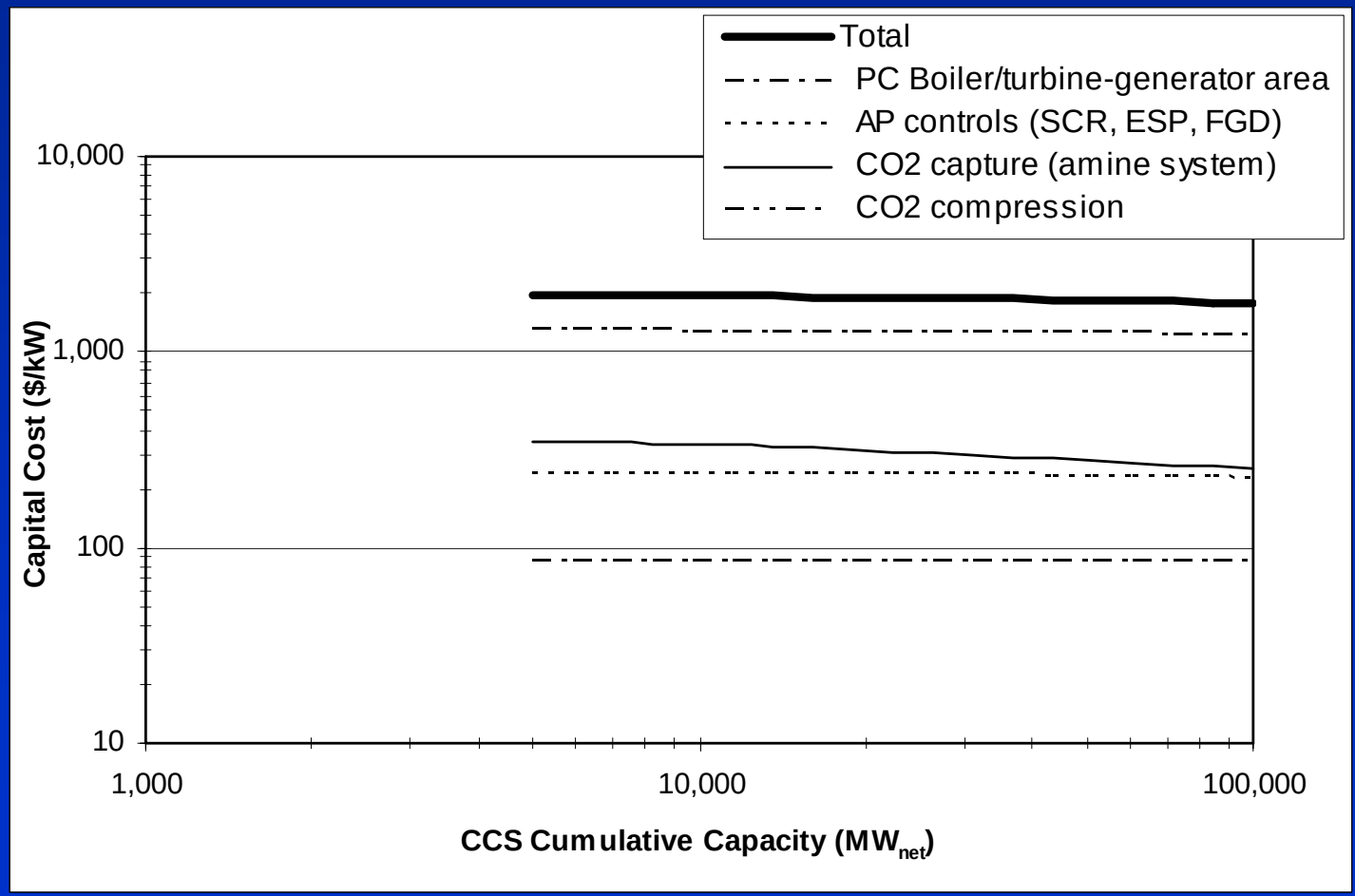
Plant Type	Cumulative CCS Capacity (MW)		
	Learning Begins at:		Learning Projected to:
	1st Plant	Nth Plant	
NGCC Plant	432	5,000	100,000
PC Plant	500	5,000	100,000
IGCC Plant	490	7,000	100,000
Oxyfuel Plant	500	10,000	100,000

Preliminary Results

Capital Cost of PC Plant: *Learning Begins at 1st 500 MW Plant*



Capital Cost of PC Plant: *Learning Begins at 5000 MW*



PC Plant Results

(*Learning Begins at 1st 500 MW Plant)*

Parameter	Capital Cost	O&M Cost	COE
Learning Rate	**0.026**	**0.068**	**0.042**
Initial Cost	1962 $/kW	29.3 $/MWh	73.4 $/MWh
Final Cost	1764 $/kW	21.1 $/MWh	60.8 $/MWh
Cost Reduction	10.1 %	28.0 %	17.2 %

PC Plant Results

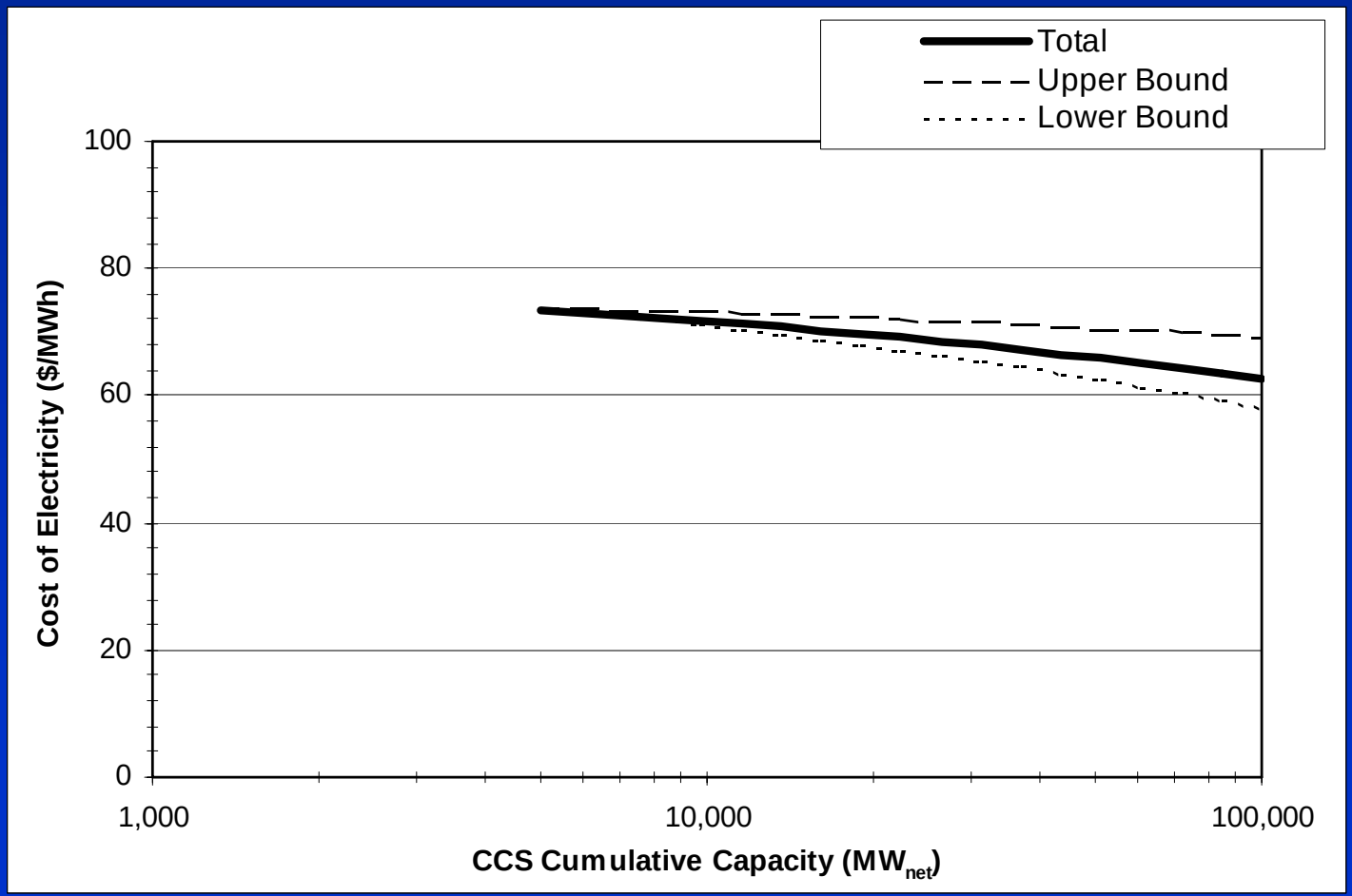
(*Learning Begins at 5000 MW*)

Parameter	Capital Cost	O&M Cost	COE
Learning Rate	**0.026**	**0.068**	**0.042**
Initial Cost	1962 $/kW	29.3 $/MWh	73.4 $/MWh
Final Cost	1783 $/kW	22.7 $/MWh	62.8 $/MWh
Cost Reduction	9.1 %	22.4 %	14.4 %

Learning Rate Uncertainty

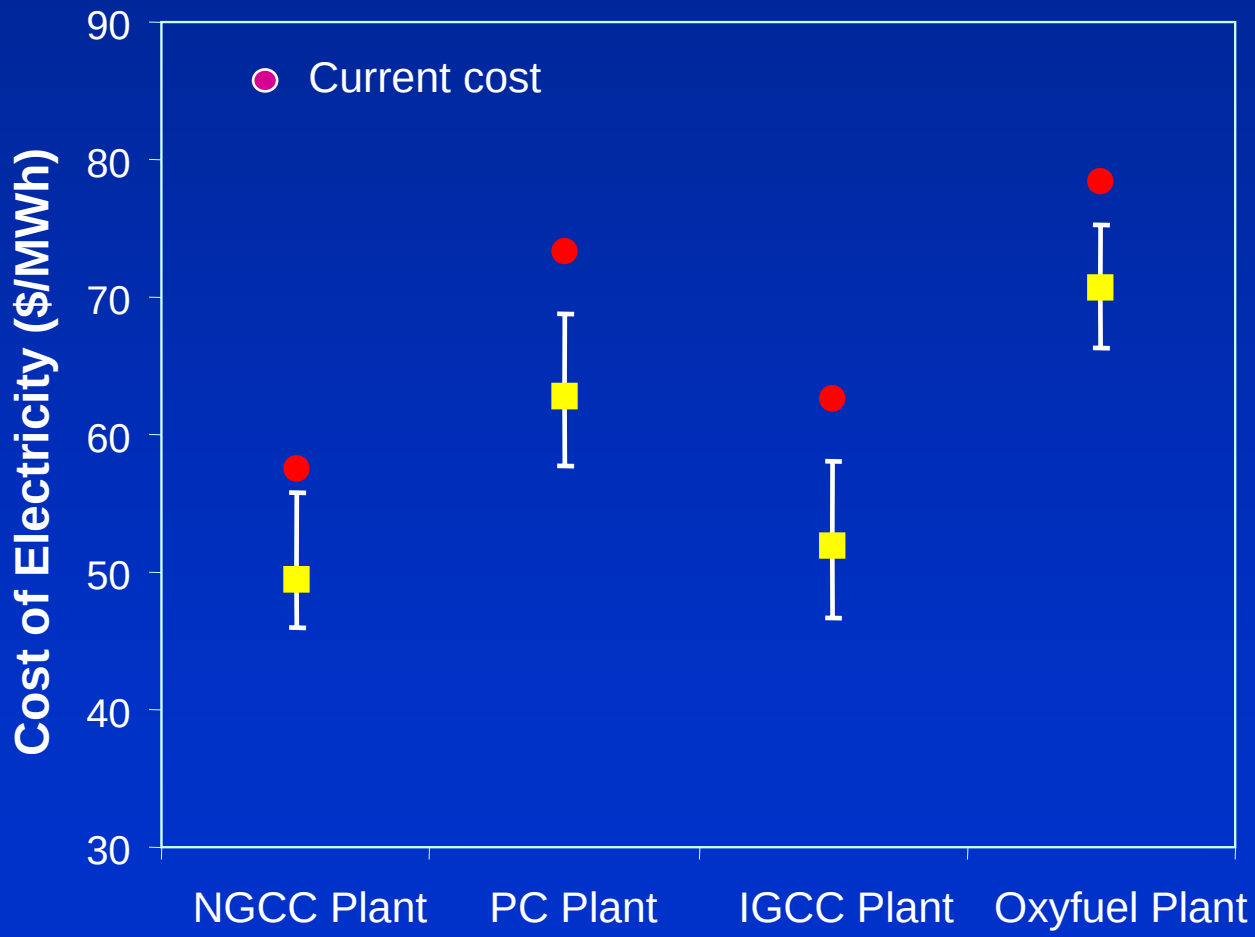
	Learning Rates Ranges	
PC Plant with Capture	**Capital Cost**	**O&M Cost**
PC boiler/turbine-generator area	0.03 - 0.09	0.07 - 0.30
AP controls (SCR, ESP, FGD)	0.06 - 0.18	0.10 - 0.30
CO_2 capture (amine system)	0.06 - 0.17	0.10 - 0.30
CO_2 compression	0.00 - 0.10	0.00 - 0.10
Fuel cost	0.00 - 0.00	0.00 - 0.05

Effect of Component Learning Rate Uncertainties on Total PC Plant Cost



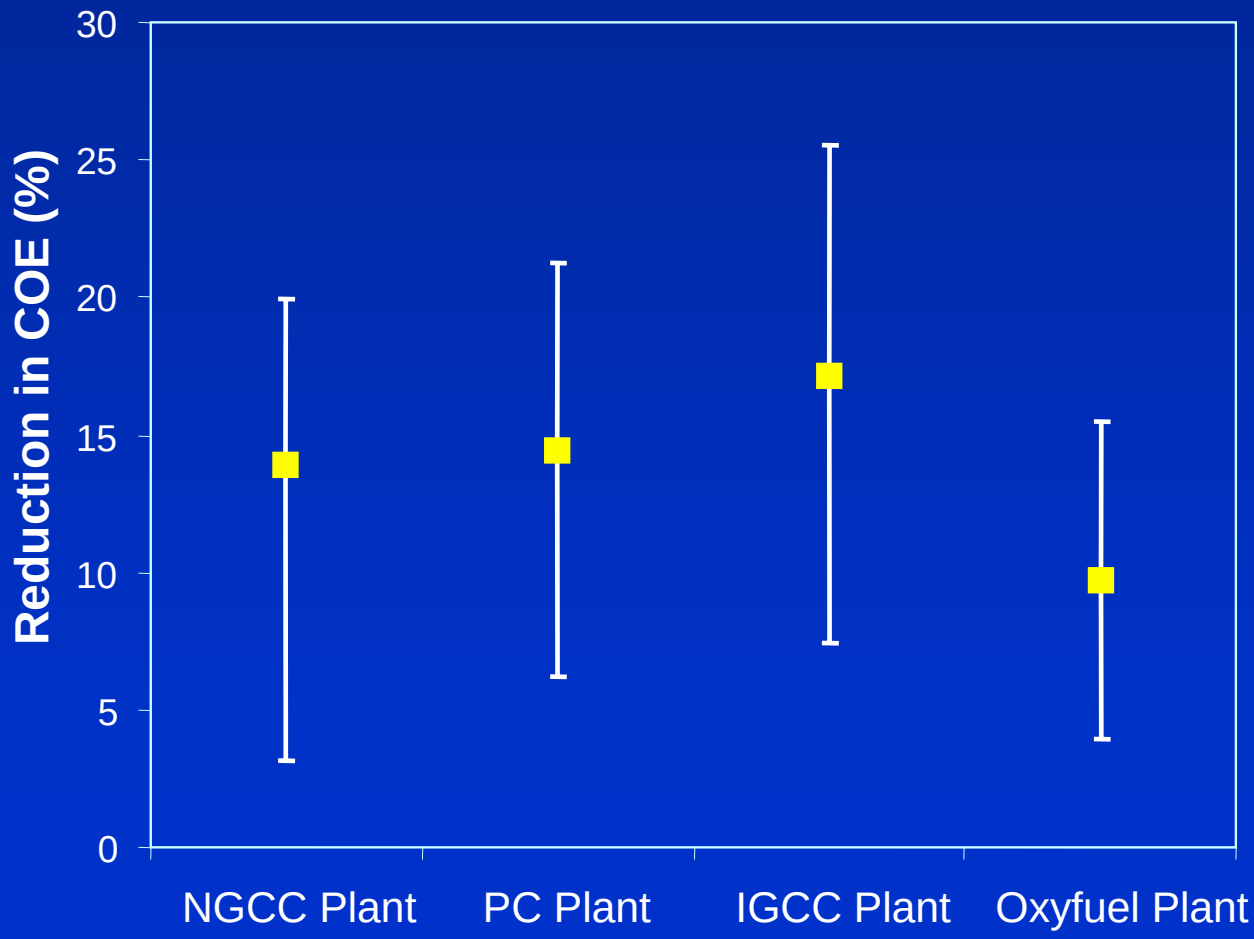
Cost of 4 Capture Plant Types

(before and after 100 GW of capacity)



Cost Reductions for 4 Plant Types

(before and after 100 GW of capacity)



E.S. Rubin, Carnegie Mellon

Conclusions

- Future reductions in the cost of CCS plants will require not only sustained R&D, but also full-scale deployment to foster learning-by-doing
- The magnitude of future cost reductions is uncertain; this study suggests that for comparable levels of installed capacity the largest cost reductions will be seen for IGCC plants, which is not currently as mature as combustion-based plants for electric power generation
- Current cost estimates for all large-scale power plants with CCS should be taken with a “grain of salt” until verified by full-scale projects

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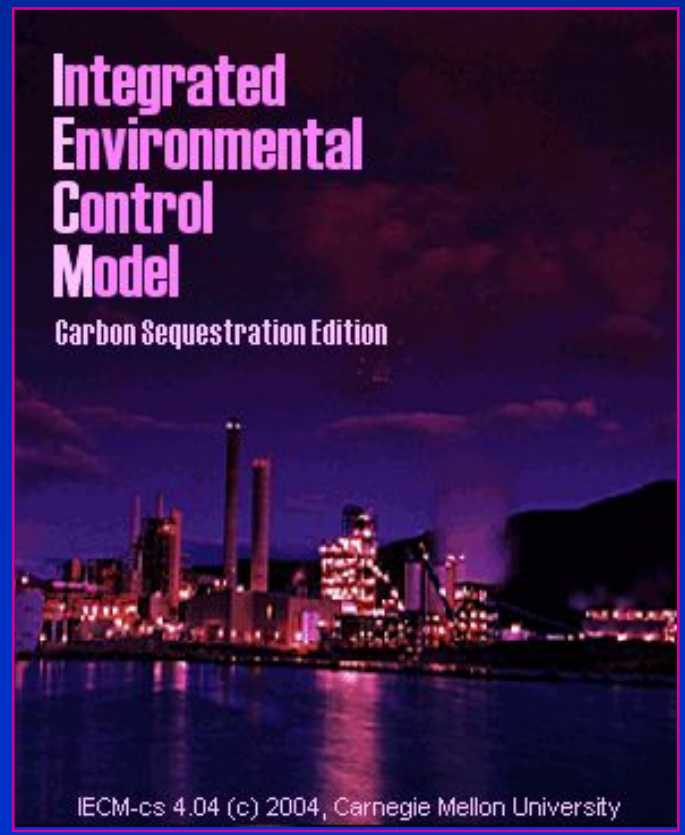
- Leo Schrattenholzer
- Dale Simbeck

IECM v.5.0.2 is Now Available

- **Free Web Download :**
  - www. iecm-online.com
- **Technical Support:**
  - PED.modeling@netl.doe.gov
- **Other Inquires:**
  - mikeb@cmu.edu
  - rubin@cmu.edu



A Generalized Framework for Scheduling the Operation of Power Plants Incorporating CO_2 Capture

Colin Alie

October 3nd, 2005

Department of Chemical Engineering
University of Waterloo
Waterloo, Ontario N2L 3G1
CANADA

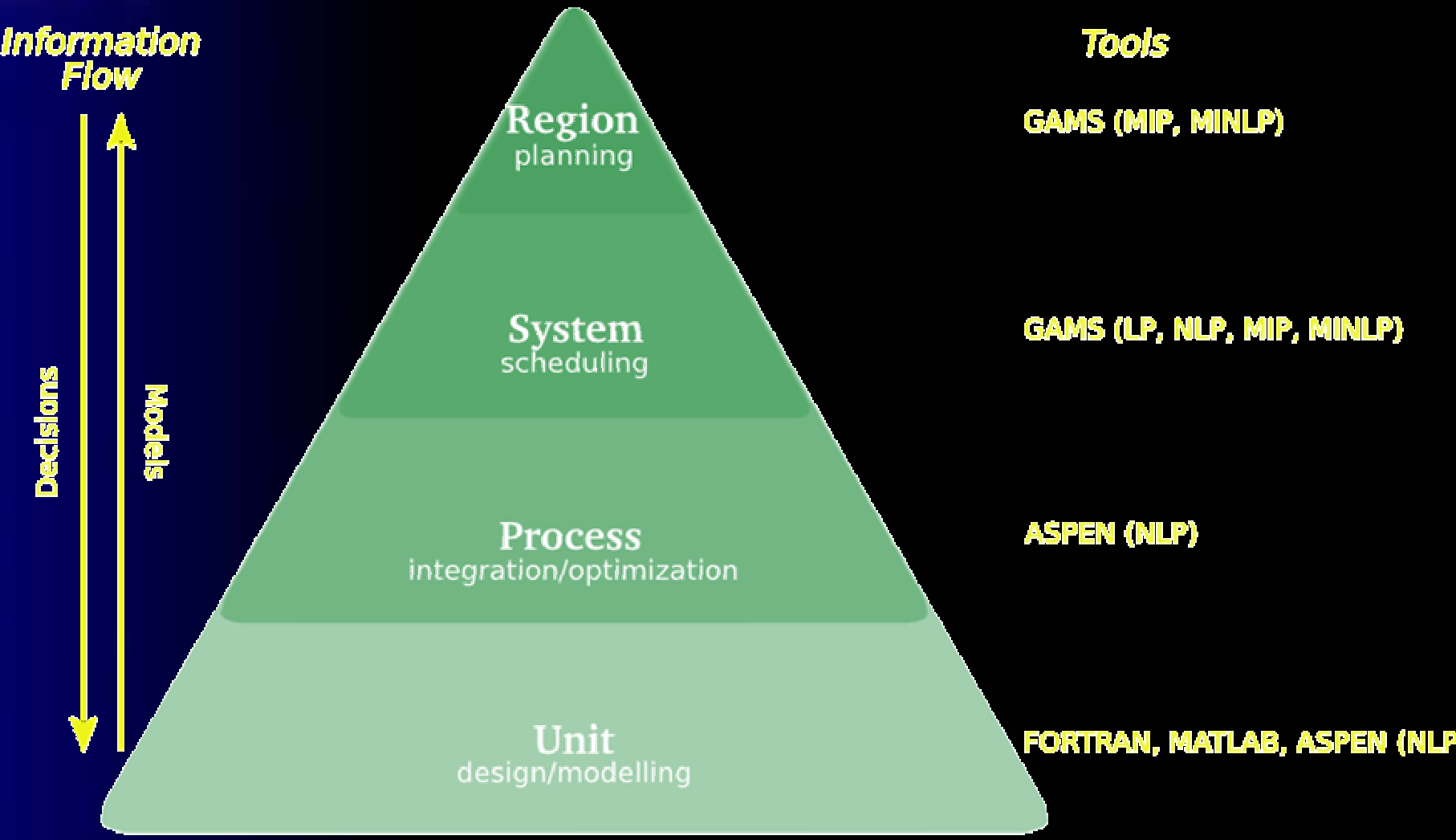
Presentation outline

- Brief review of research activities within CO_2 mitigation group
- New research direction: power system scheduling
  - Motivation
  - Model formulation
  - Anticipated benefits
- Summary and closing comments

University of Waterloo CO_2 mitigation activities

- Unit level:
  - SOFC modelling
- Process level:
  - O_2/CO_2 recycle combustion
  - ZECA process modelling
  - IGCC with CO_2 capture
  - modelling CO_2 capture from cement plant using MEA
  - modelling CO_2 capture from power plant using CO_2 selective membrane
  - optimal integration of CO_2 capture with MEA absorption and existing power plant
- Region level:
  - minimum cost configuration of a fleet of power plants within CO_2 constrained environment

UW CO_2 mitigation activities (cont…1)



Status of CO_2 capture work

- Completed integration of power plant steam cycle and CO_2 capture process.
- Next step is determining minimum cost design operating conditions.
- Challenge is that traditional approach for analyzing economics of CO_2 capture appears inadequate.

Traditional approach

$$\text{Cost of } CO_2 \text{ Avoided} = \frac{COE_{cap} - COE_{ref}}{CIE_{ref} - CIE_{cap}}$$

COE	cost of electricity	$/MWh
CIE	CO_2 emissions intensity	tonnes CO_2/MWh

subscripts:

cap	with capture
ref	reference case (without capture)

Traditional approach (cont…1)

$$COE = \frac{TCR \cdot FCF + FOM}{CF \cdot 8760 \frac{hours}{year} \cdot P} + VOM + HR \cdot FC$$

COE	cost of electricity	$/MWh
TCR	total capital requirement	$
FCF	fixed charge factor	hour/year
FOM	fixed operating and maintenance	$/year
CF	capacity factor	
P	nominal plant output	MW
VOM	variable operating and maintenance	$/year
HR	plant heat rate	Btu/kWh
FC	fuel cost	$/Btu

Parameter selection: $CF \cdot 8760 \frac{hours}{year} \cdot P$

- First inclination is to select CF so as to maximize power generation but…
  - in a deregulated (*i.e.*, competitive) market, unit commitment and dispatch depends upon marginal cost of generation.
  - without CO_2 capture, coal plants are often run at less than full capability

$$CF_{ref} < 1.0 - \frac{planned\ downtime}{8760 \frac{hours}{year}}$$

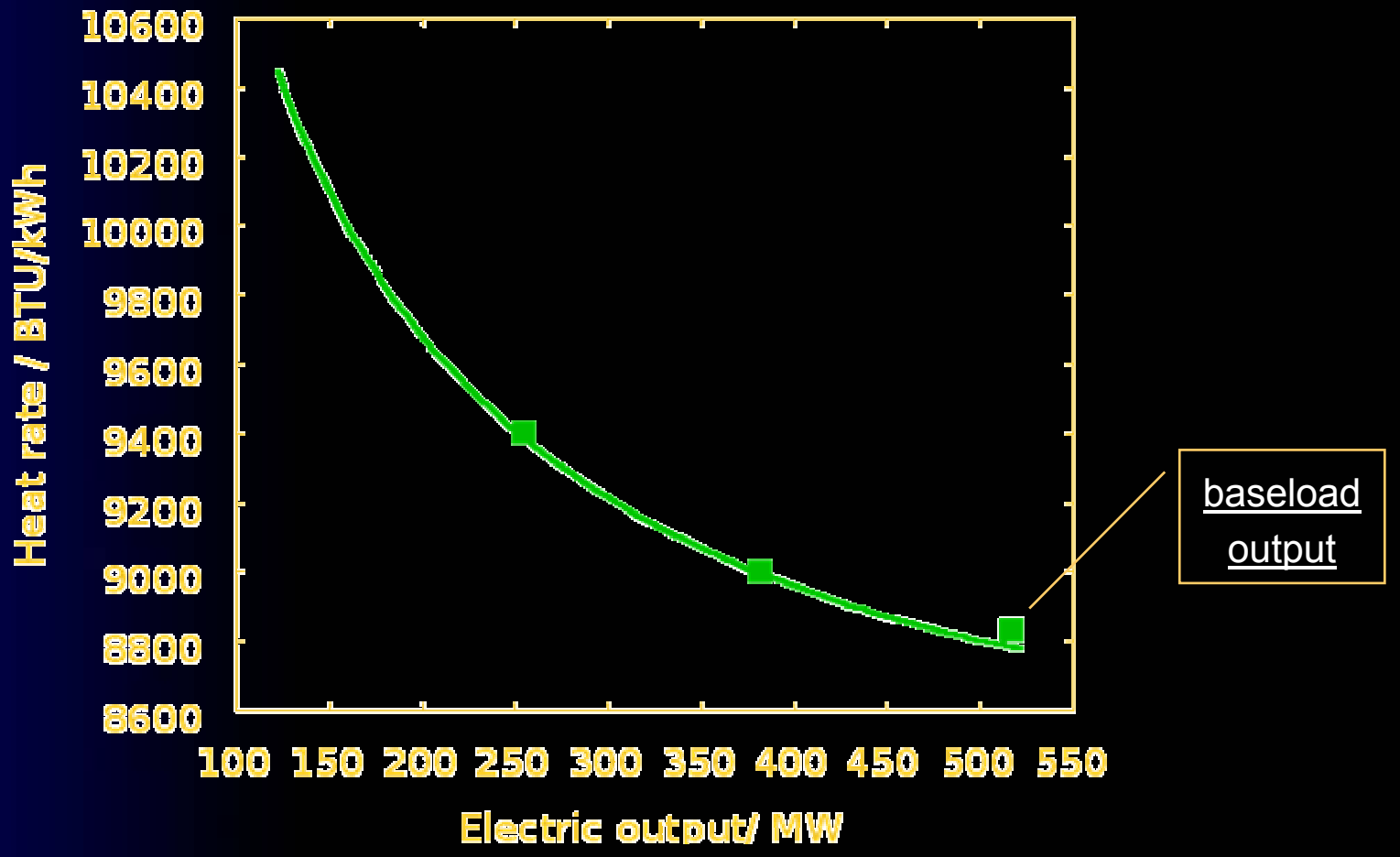
  - so, with CO_2 capture, marginal cost of power generation will increase; capacity factor will decrease (how much?)

$$CF_{cap} < CF_{ref}$$

- Selection of P is also problematic…more on this later.

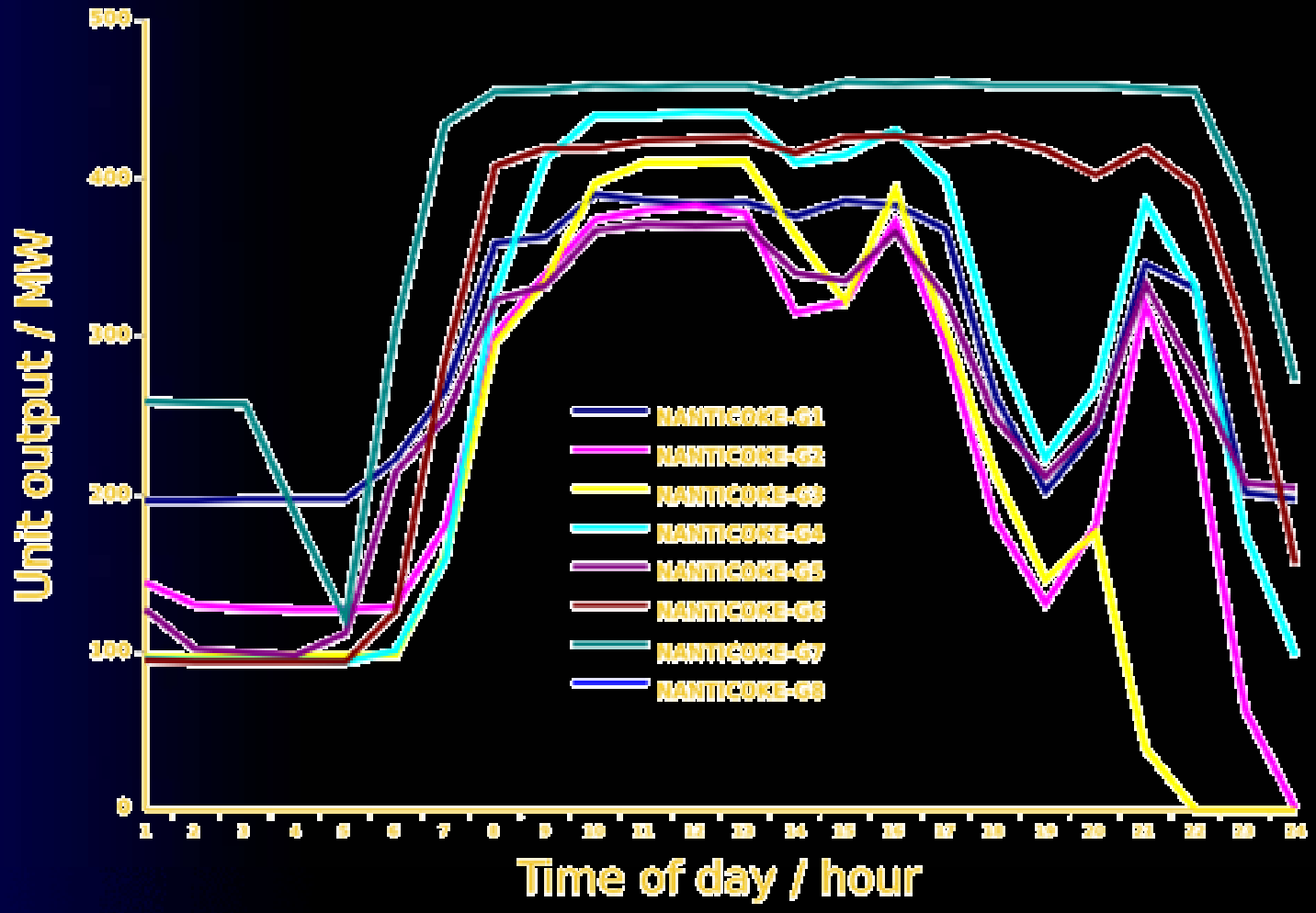
Parameter selection: *HR*

- First inclination is to choose *HR* at baseload...



Parameter selection: HR (cont…1)

- …but that appears not be reasonable assumption.



Traditional approach (cont…2)

$$\text{Cost of } CO_2 \text{ Avoided} = \frac{COE_{cap} - COE_{ref}}{CIE_{ref} - CIE_{cap}}$$

- Current lack of *a priori* knowledge of CF and HR for power plant with CO_2 capture precludes estimation of COE_{cap}.
- As will be shown, CIE_{cap} is an equally elusive target...

Traditional approach (cont…3)

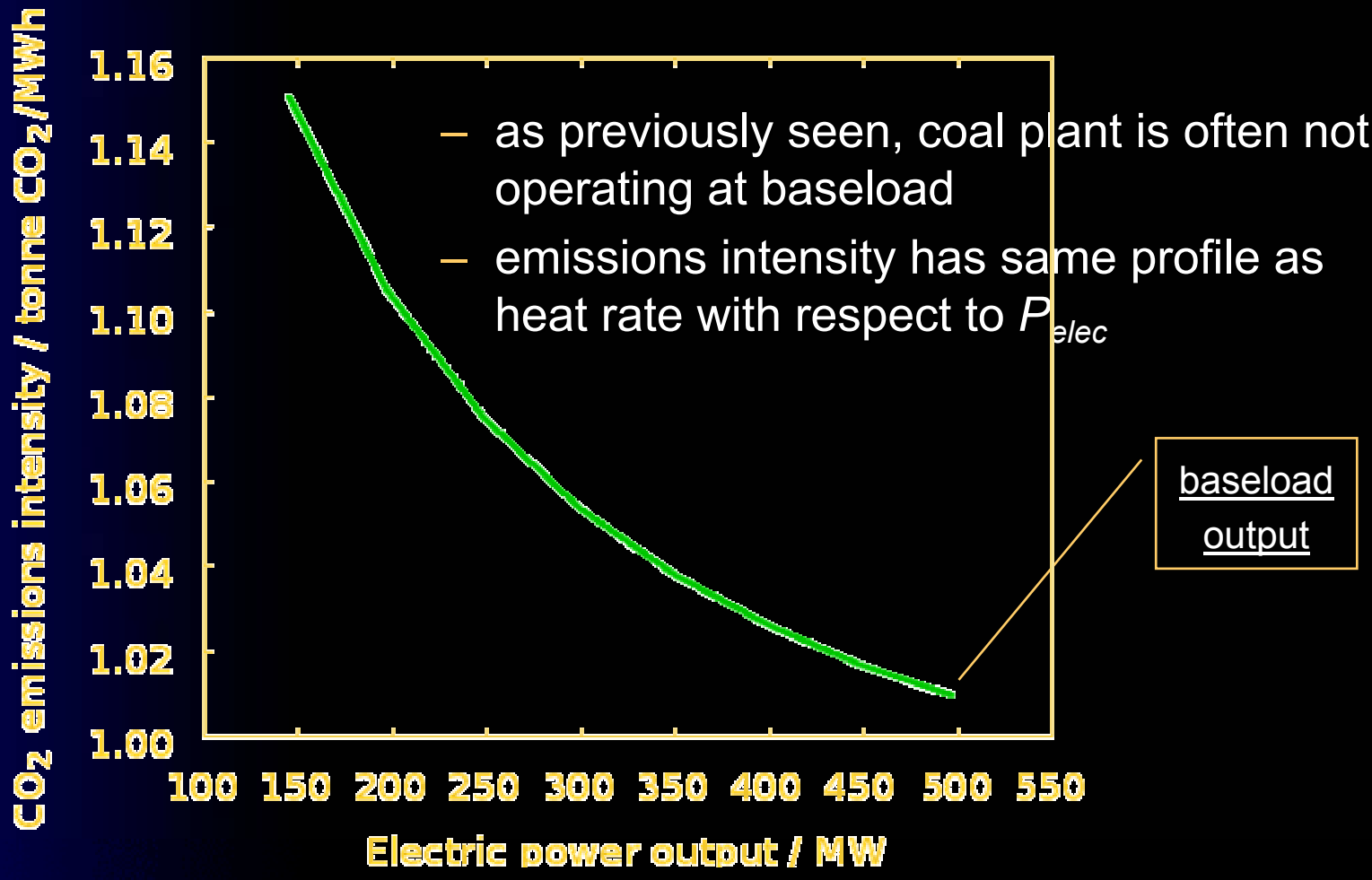
$$CIE_{ref} = \frac{m_{CO_2}}{E_{elec}}$$

$$CIE_{cap} = \frac{x\left(\dot{m}_{CO_2}\right)_{ref}}{(1-y)\left(P_{elec}\right)_{ref}}$$

CIE	CO_2 emissions intensity	tonnes CO_2/MWh
m	total CO_2 emissions	tonnes CO_2
$\dot{m}$	CO_2 emissions	tonnes CO_2/h
E	electric energy generated	MWh
P	electric power output	MW
x	fraction of CO_2 recovered	
y	power plant de-rate; $y=f(x)$	

Parameter selection: $\dot{m}_{CO_2}$

- First inclination is to choose $\dot{m}_{CO_2}$ at baseload…



Parameter selection: x

- First inclination is to choose *x* reasonably large (e.g., 0.85)

- However, x varies in some currently unpredictable manner as a function of forecasted demand:
  - at high demand, value of electricity exceeds value of capturing CO_2 (how often?) and x will decrease
  - after prolonged CO_2 emitting period, value of capturing CO_2 will increase (how often?) and x will increase

- Also, because of varying plant dispatch, specifying the power output in terms of P_{ref} in expression for CIE_{cap} doesn't make sense.

Traditional approach: Summary

$$\text{Cost of } CO_2 \text{ Avoided} = \frac{COE_{cap} - COE_{ref}}{CIE_{ref} - CIE_{cap}}$$

- Current lack of a priori knowledge of CF and HR for power plant with CO_2 capture precludes estimation of COE_{cap}.
- Reasonable procedure for estimating CIE_{cap} is not available.

Novel approach for CO_2 capture evaluation

- Proposed methodology:
  - dynamic electricity system model
  - incorporating CO_2 capture, transportation, and storage
  - unit commitment
  - economic dispatch
  - CO_2 emission limits
- Formulation of simple model
- Anticipated benefits

Model formulation

- Objective function

$$z = \sum_{i \varepsilon N} \sum_{k \varepsilon T} C_i\left(P_{i,k}\right) + u_{i,k} C_i^{start} + v_{i,k} C_i^{stop}$$

- Minimum up-time, minimum down-time

$$\left(t_{i,k-1}^{on} - \tau_i^{on}\right)\left(w_{i,k-1} - w_{i,k}\right) \geq 0$$

$$\left(t_{i,k-1}^{off} - \tau_i^{off}\right)\left(w_{i,k} - w_{i,k-1}\right) \geq 0$$

- Regional supply/demand balance

$$\sum_{i \varepsilon N_r} P_{i,k} + \sum_{s \varepsilon A_r} \left[T_k^{s,r} - L_k\left(T_k^{s,r}\right)\right] = D_{r,k} + \sum_{d \varepsilon A_r} T_k^{r,d}$$

- Regional security constraint

$$\sum_{i \varepsilon N_r} w_{i,k} P_i^{max} + \sum_{s \varepsilon A_r} \left\{\left(T^{s,r}\right)^{max} - L_k\left[\left(T^{s,r}\right)^{max}\right]\right\} = D_{r,k} + \sum_{d \varepsilon A_r} T_k^{r,d} + R_k$$

Model formulation (cont…1)

- Ramping constraints

$$P_{i,k-1}^{turbine}\,\rho_i^{down} \le P_i^{turbine} \le P_{i,k-1}^{turbine}\,\rho_i^{up}$$

- CO_2 emissions from power plant

$$E_{i,k} = P_{i,k} \cdot e_i\left(P_{i,k}\right) \times \left(1 - x_{i,k}\right)$$

- CO_2 capture plant de-rate

$$P_{i,k} = \begin{cases} P_{i,k}^{turbine} - P_{i,k}^{capture}\left(P_{i,k}^{turbine}, x_{i,k}\right) & i \,\varepsilon\, N_{coal} \\ P_{i,k}^{turbine} & otherwise \end{cases}$$

- Aggregate CO_2 emissions constraint

$$\sum_{k \varepsilon T} \sum_{i \varepsilon N} E_{i,k} \le E^{max}$$

Model formulation (cont…2)

- CO_2 transportation and storage

$$\sum_{i \varepsilon N_r} E_{i,k} + \sum_{s \varepsilon S_r} T_k^{s,r} = \sum_{d \varepsilon D_r} T_k^{r,d} + D_{r,k}$$

- Decision variables are bounded:
  - minimum and maximum power output from each plant
  - electricity transmission capacity limits
  - CO_2 recovery
  - CO_2 pipeline and injection constraints

Anticipated benefits of the model

- Ascertain the CO_2 recovery required in each time period to meet the emissions constraints.
- Determine the value/cost of CO_2 capture processes for reducing CO_2 emissions.
- Understand the impact that CO_2 emissions constraints have on the dynamic operation of the electricity system.

Future work

- Data collection
  - primary sources (e.g. OPG)
  - secondary sources (e.g. Statistics Canada, Environment Canada)
  - process simulation using Aspen Plus
- Implementation of model using GAMS

Modeling of Innovative Stripper Concepts

by

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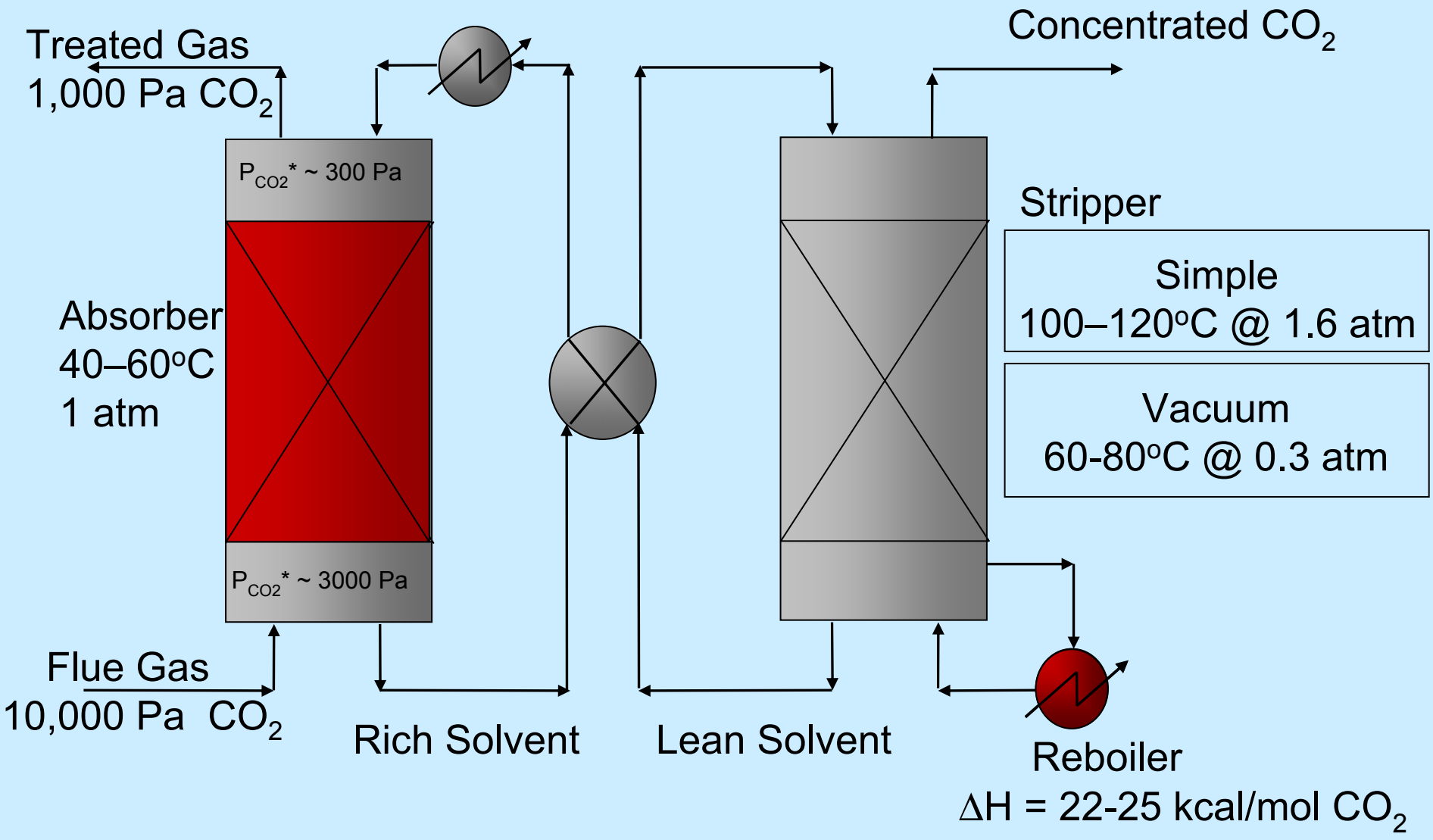
The University of Texas at Austin
October 3, 2005

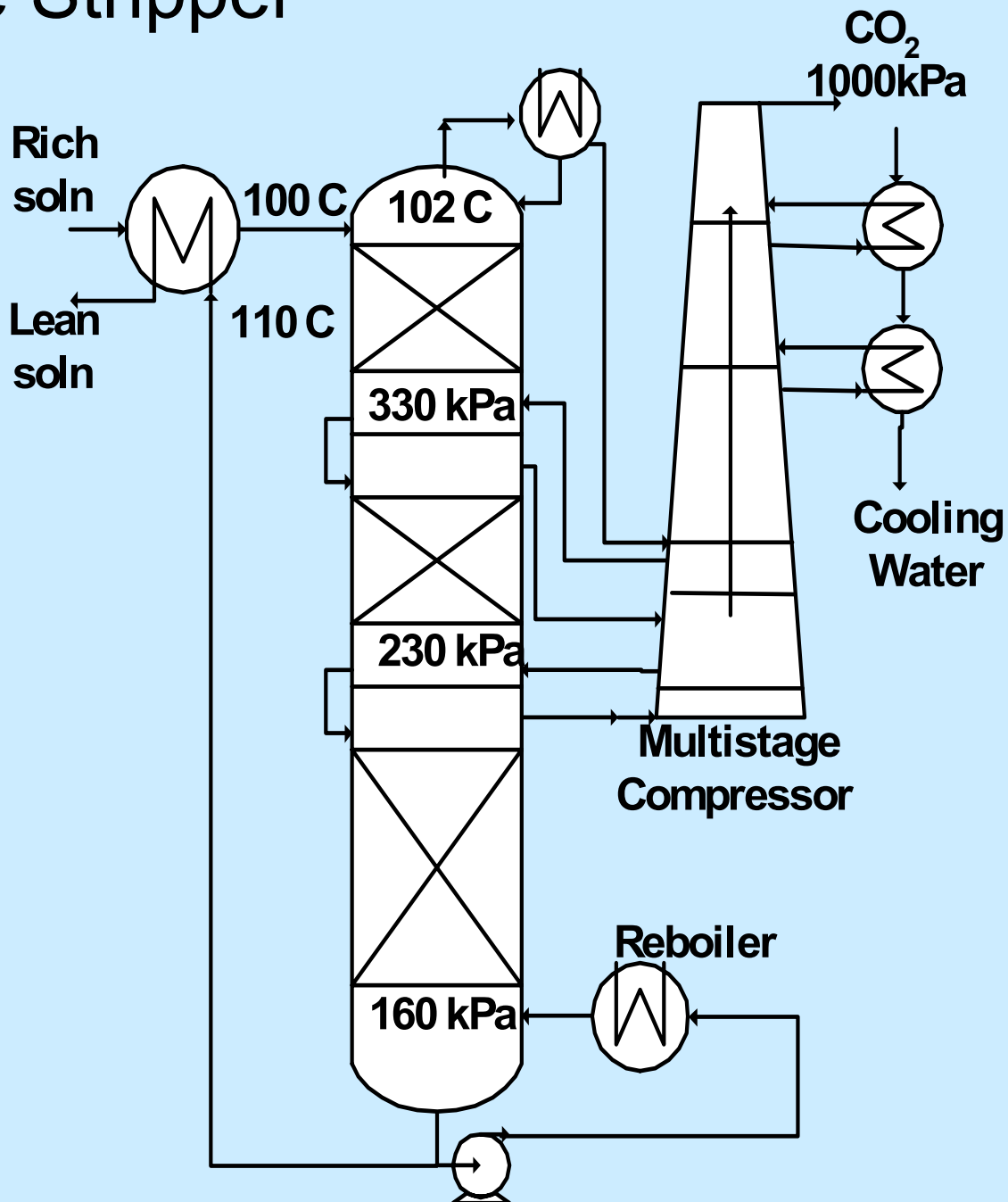
Outline

- Introduction
- Approaches to reducing energy
- Solvent alternatives
- Aspen Custom Modeler (ACM) Model
- Results
- Conclusions

Typical Absorption/Stripping System



Multipressure Stripper



Approaches to Reducing Energy

- Better Solvents
  - Low ΔH, High Rates,High Capacity

- Better Processes / Innovative Flowsheets
  - Different Configurations (Simple,Vacuum & Multi P)
  - Vary approach T (Cross exchanger area)

Solvents

7m (30wt%) MEA

- Reasonable rates
- High capital & energy
- Degradation & Corrosion

*5m K^+/2.5m PZ (*2.5m K_2CO_3/2.5m PZ)

- Developed by Cullinane
- 1-3 times faster than 7m MEA
- 1.5-2.5 less packing, ΔP savings

Solvents (Contd.)

Generic Solvents (ΔH, Capacity)

$$\ln P = a + b^{*}[CO_2]_T - \frac{\Delta H}{RT}$$

b = f (capacity) = 3.07 kg solution/ gmol CO_2

Aspen Custom Modeler (ACM) Model Description

Features

- Flash section, 10 sections, Reboiler
- Compression to 1000 kPa in 5 stages

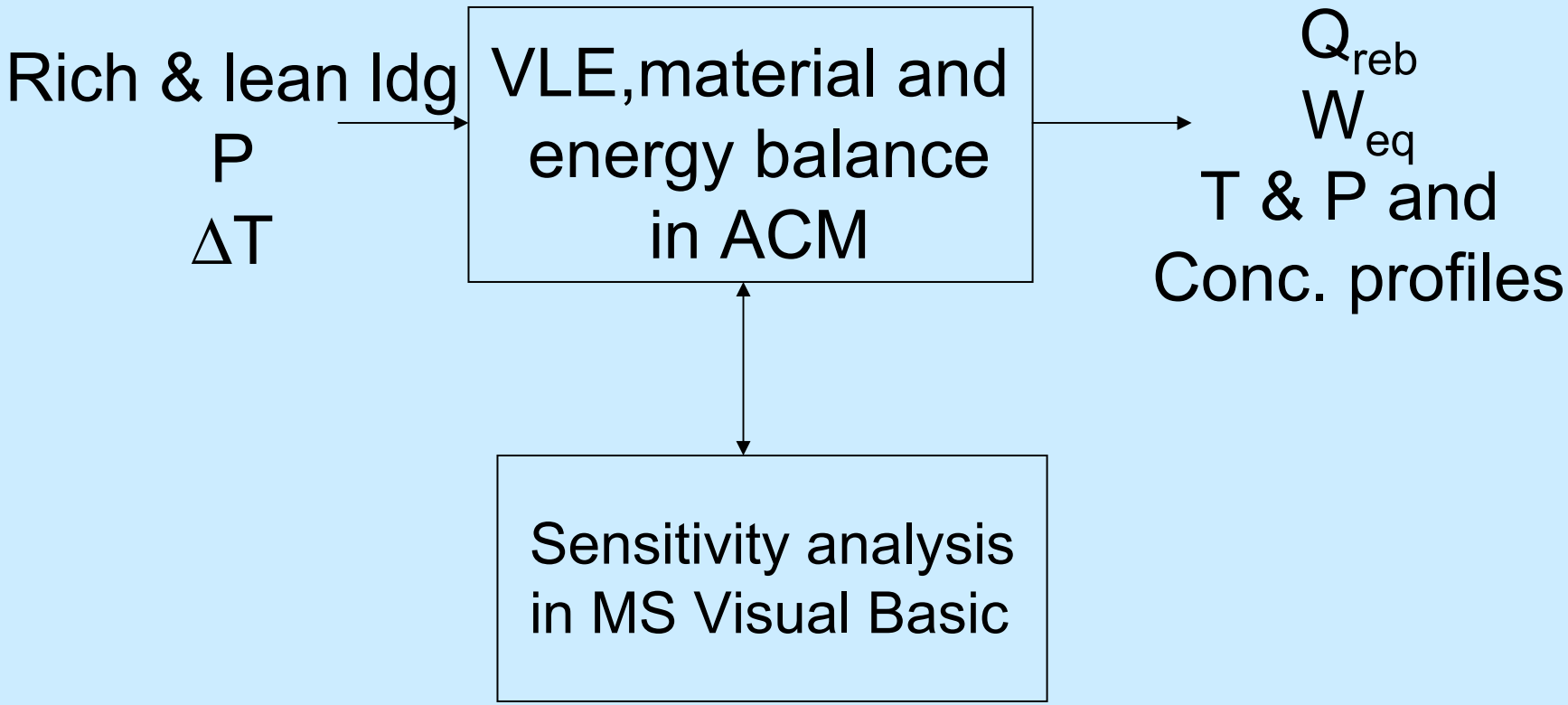
VLE

- 7m MEA (Freguia,2003)
- 5m K^+/2.5m PZ (Cullinane,2005)
- Generic Solvents (3 Parameter Expression)

Model Assumptions

- Well-mixed L & V phases
- 40%,100%,100% Murphree Eff. for CO_2, T and H_2O
- Equilibrium reboiler
- Negligible vaporization of solvent

MODEL


Rich & lean ldg
P
ΔT
VLE,material and energy balance in ACM
Q_{reb}
W_{eq}
T & P and
Conc. profiles
Sensitivity analysis in MS Visual Basic

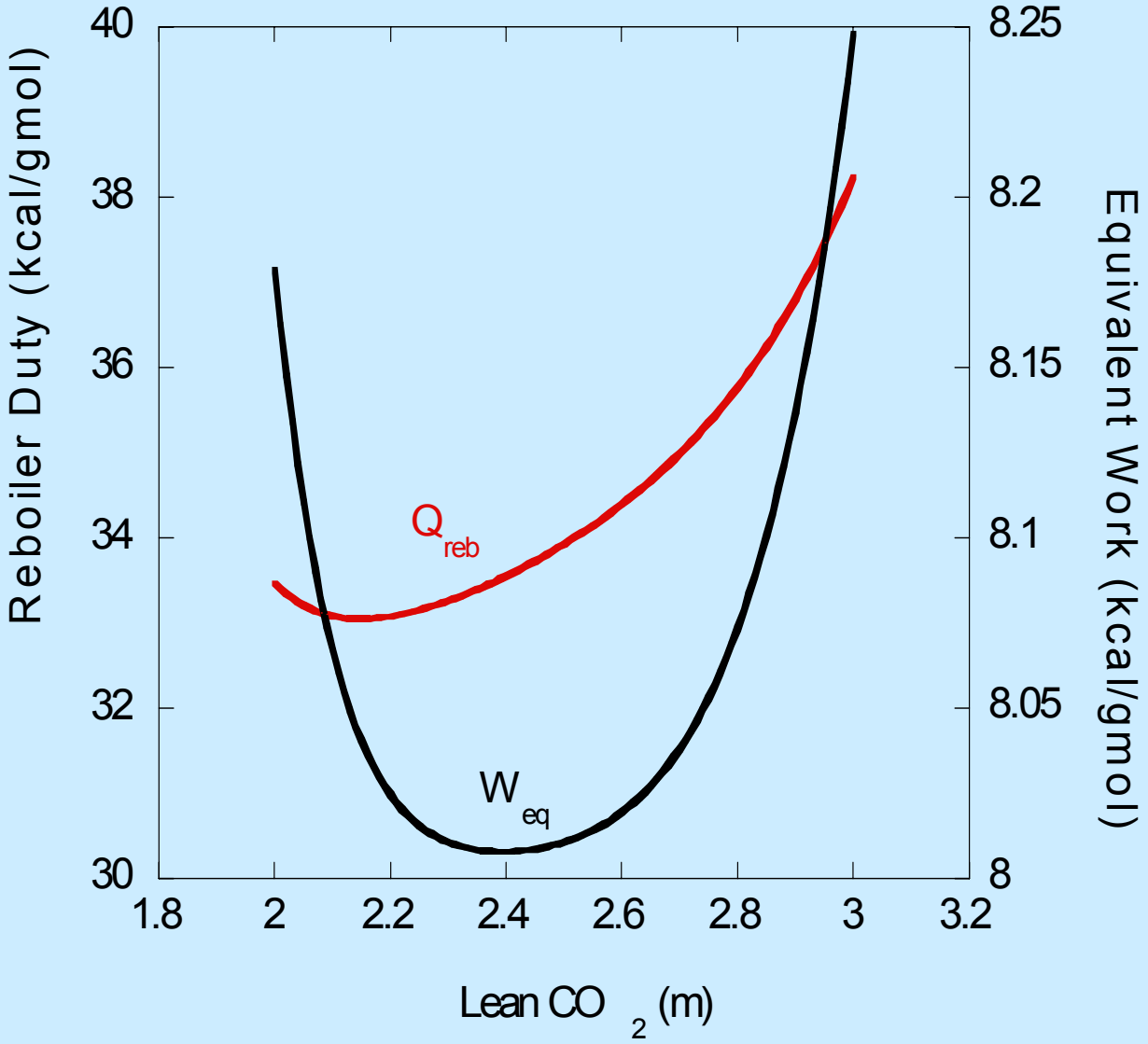
Performance of Strippers
Concept of Equivalent Work

$$W_{eq} = 0.75\, Q_{reb}\left[\frac{T_{cond} - T_o}{T_{cond}}\right] + W_{comp}$$

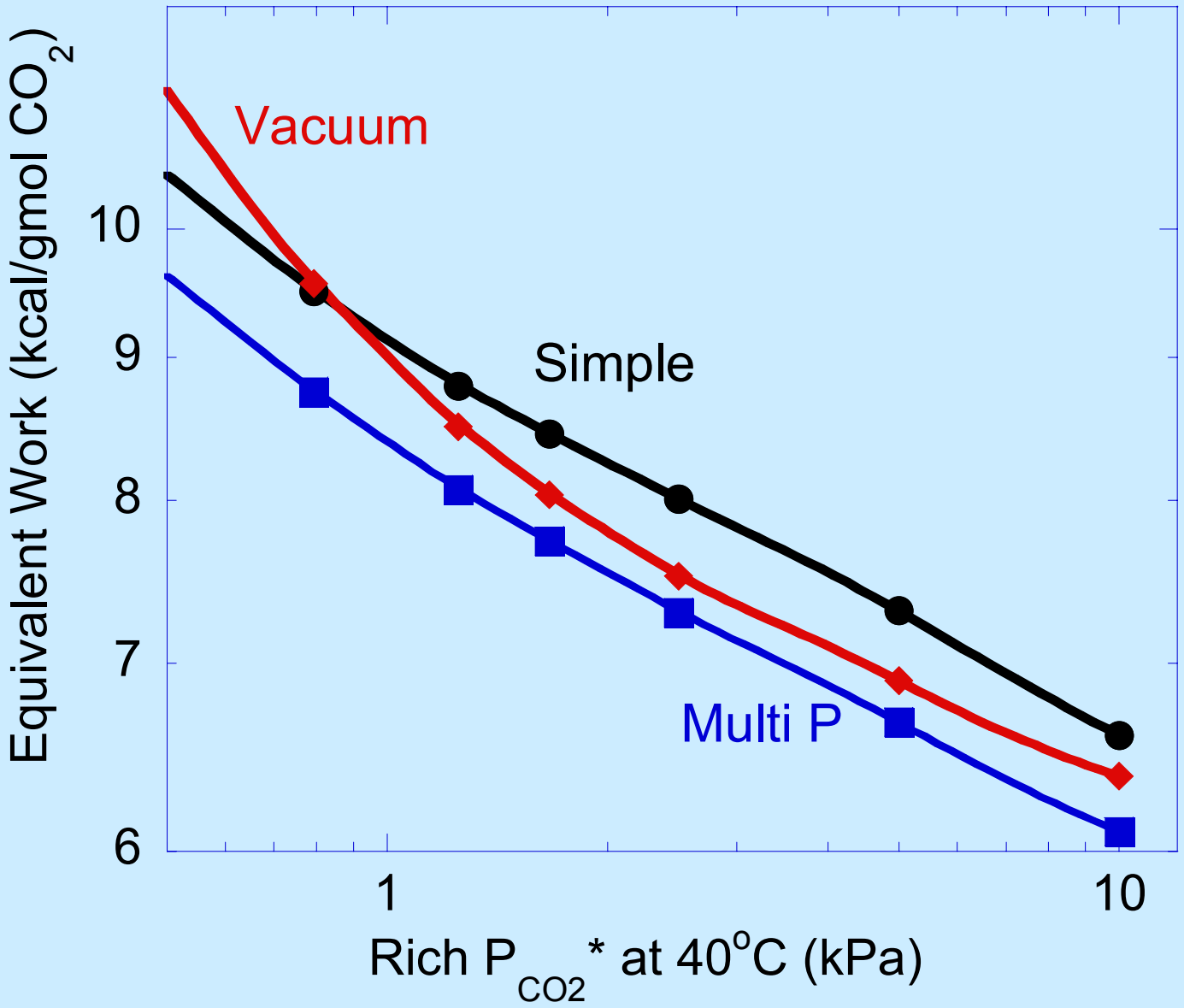
$$= 0.75\, Q_{reb}\left[\frac{(T_{reb} + 10) - 313}{(T_{reb} + 10)}\right] + W_{comp}$$

(75% Adiabatic Efficiency in Compressor)

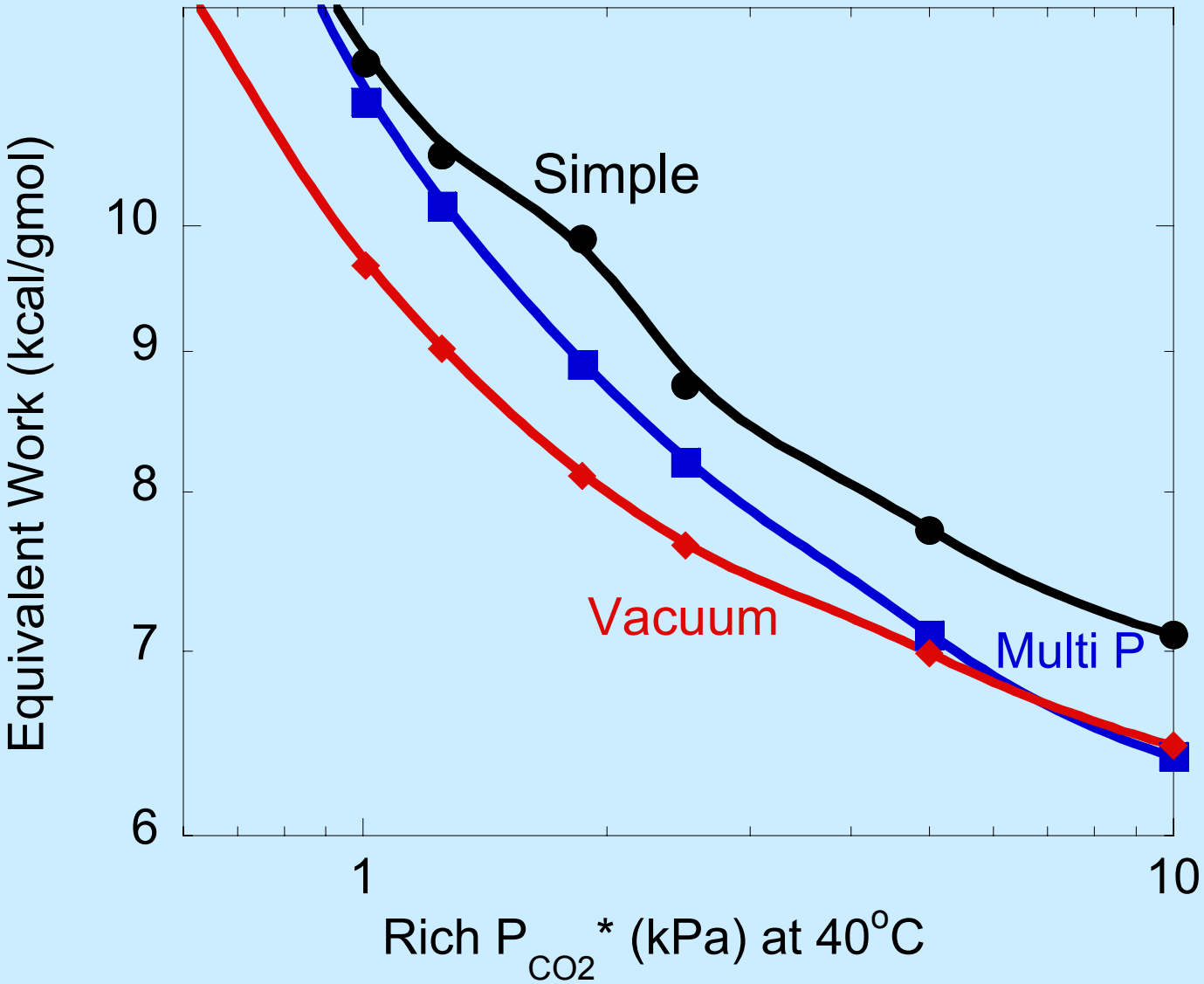
Optimized Lean Concentration for Minimum Equivalent Work with 7m MEA (Rich P_{CO2}* = 2.5 kPa @ 40°C)



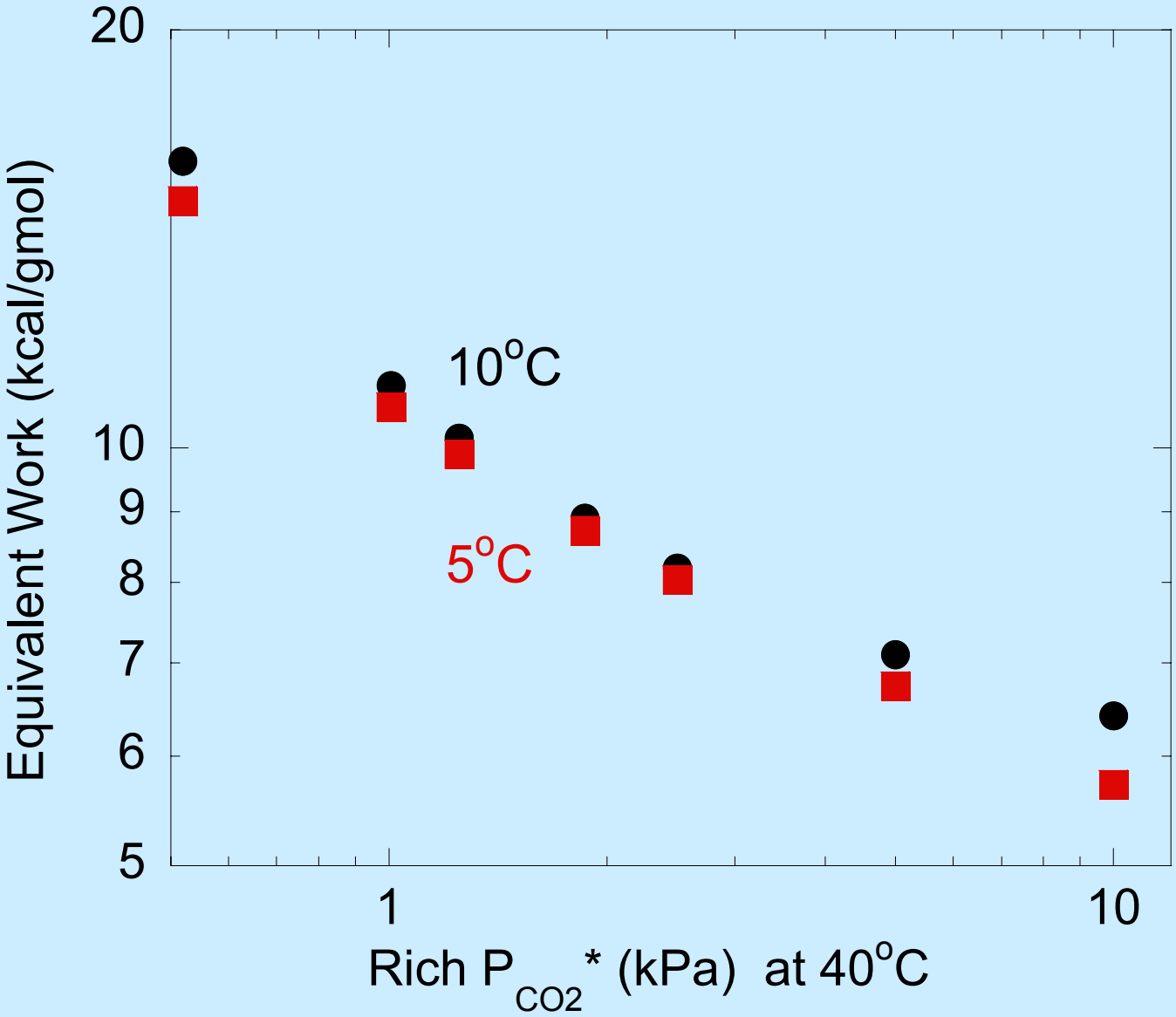
Total Equivalent Work for Different Configurations with 7m MEA ($\Delta T=10^{o}C$)



Total Equivalent Work for Different Configurations with 5m K^+/2.5m PZ ($\Delta T=10^oC$)

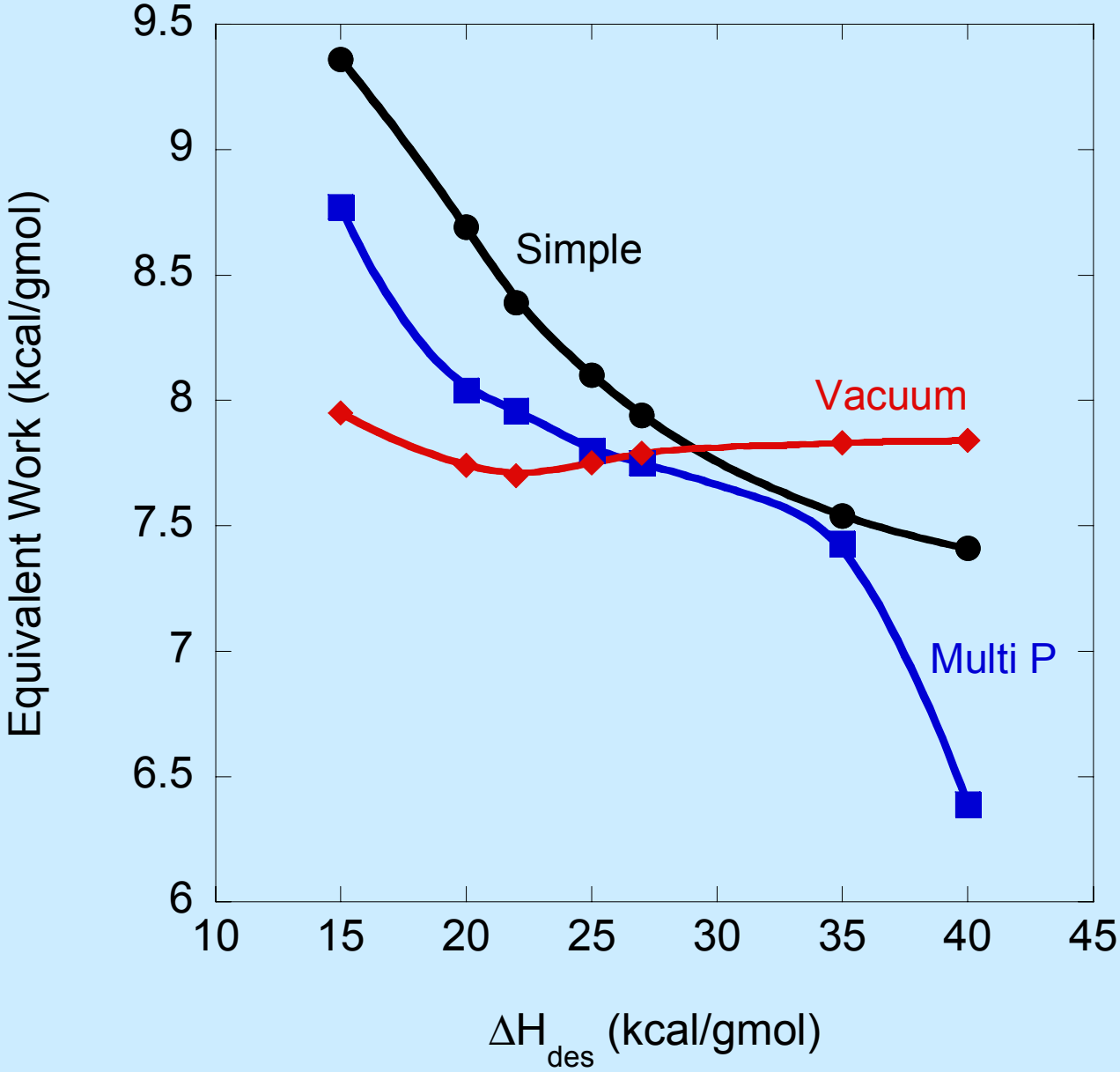


Total Equivalent Work for Different ΔT for 5m K^+/2.5m PZ for a Simple Stripper

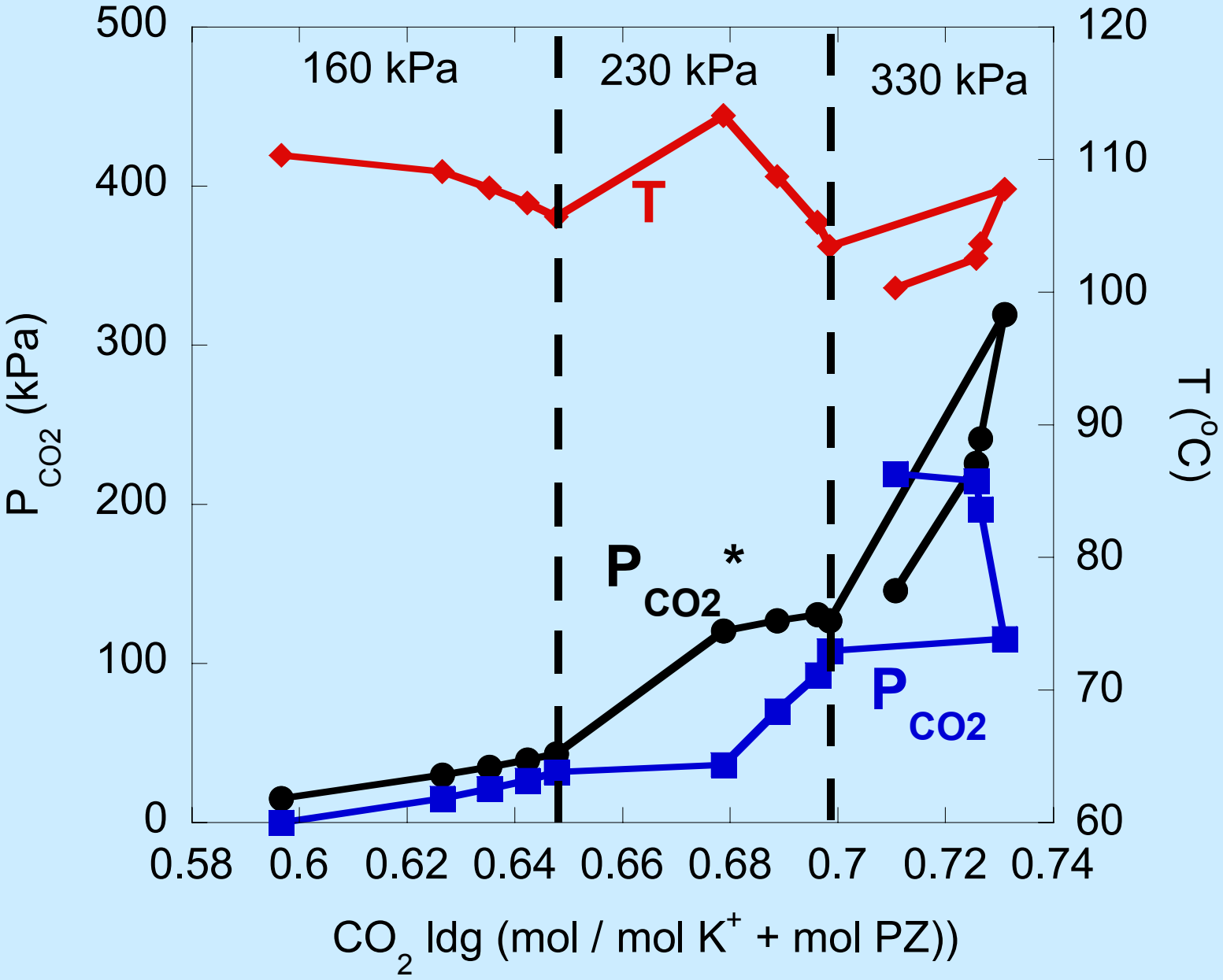


Total Equivalent Work for Generic Solvents

(Rich P_{CO2}^{*} = 2.5 kPa at 40°C, ΔT = 10°C)



McCabe-Thiele Plot for 5m K^+/2.5m PZ, Multipressure Stripper



Mass transfer Modeling

Flux of CO_2 from bulk liquid to bulk gas

Overall m.t. coefficient
f(equipment,fluid properties, hydraulics,composition,chemistry)
• accounts for reaction and diffusion

$$N_{CO2} = K_G (P_{CO2}^* - P_{CO2b})$$

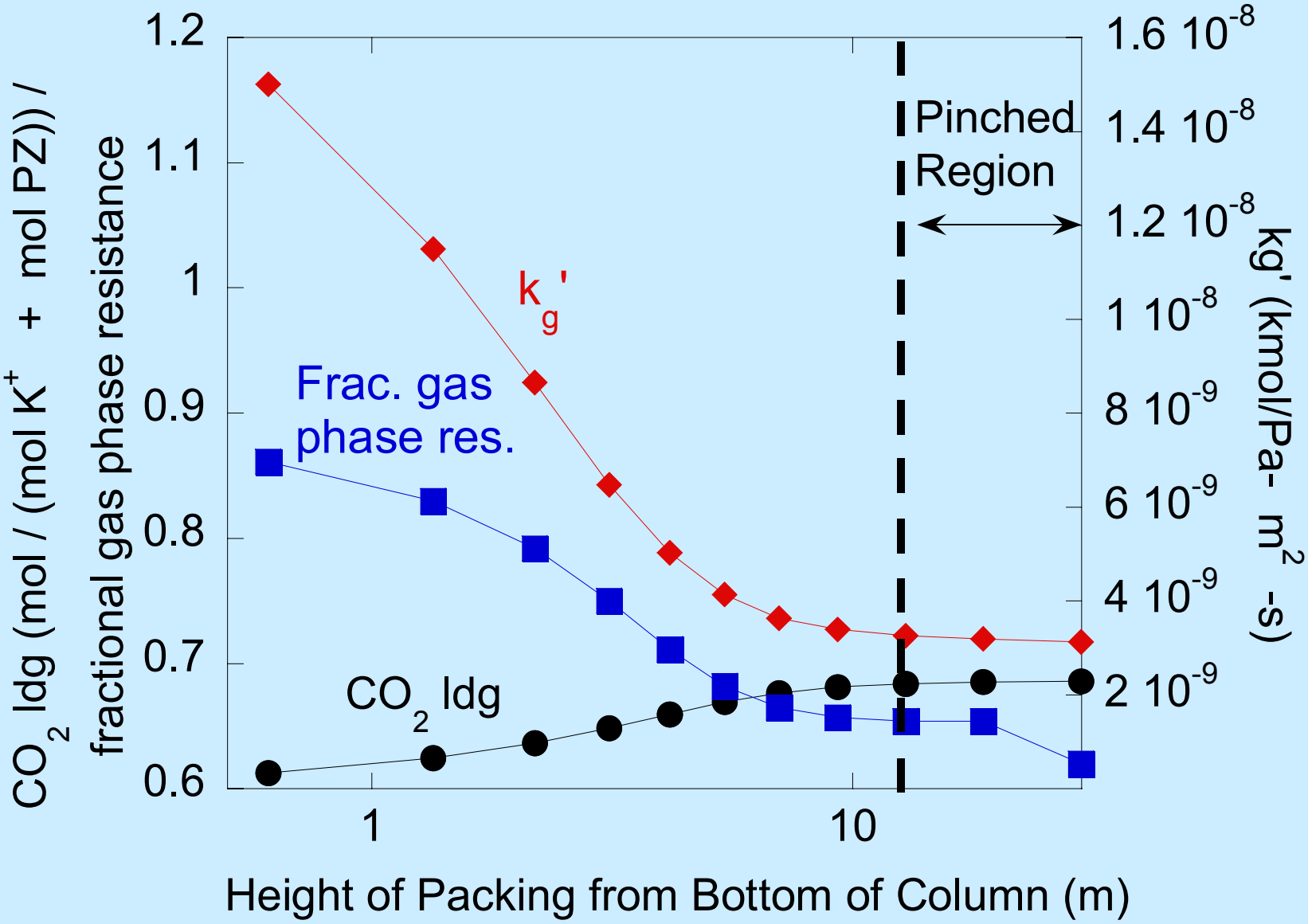
$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{1}{k_g'}$$

Driving force
f(thermodynamics i.e. VLE)

Gas-film controlled – k_g controls desorption rate
Liquid-film controlled – kinetics and diffusion control desorption rate

$$\text{Rate} = \text{Flux} * \text{Contact Area}$$
$$= K_G A (P_{CO2}^* - P_{CO2b})$$

Rate in Simple Stripper, 5m K^+/2.5m PZ



Conclusions

- Multi P stripper gives least W_{eq} at fixed absorber P_{CO2}* for 7m MEA
- Vacuum Stripper most attractive for 5m K^+/2.5m PZ
  - Lower T, Materials of Construction - FRP
- For 5m K^+/2.5m PZ, 5^{o}C cross exchanger offers 2-6% energy savings over 10^{o}C
- Generic solvents - Optimum ΔH = f (stripper configuration)
  - Vacuum $\leq$ 25 kcal/gmol CO_2, Multi P > 25 kcal/gmol CO_2

Acknowledgments

- US DOE (Award No. DE-FC26-02NT41440)
- Aspen Technologies
- Industrial Associates for CO_2 Capture
- Dr. Frank Seibert, Eric Chen and Ross Dugas
- UT CO_2 Capture Group Members
- SRP Staff

Questions ?

CO_2 Capture by Blended Alkanolamines:
Experiments, Modeling & Simulation, Cost Analysis

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Presented at the 8th International CO_2 Capture Network, Austin, Texas.
October 3-4, 2005

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CO_2 Capture

Why CO_2 Capture?

- Gas Treating and Purification *(Higher gas Quality)*
- Environmental Purpose *(Climate Change)*

Absorption Technology

- Reaction of CO_2 with chemical (Amine)

$$CO_2 + 2RR'NH \leftrightarrow RR'NH_2^+ + RR'NCOO^-$$

$$CO_2 + RR'NH + H_2O \leftrightarrow RR'NH_2^+ + HCO_3^-$$

$$CO_2 + RR'NCOO^- + 2H_2O \leftrightarrow RR'NH_2^+ + 2HCO_3^-$$

- Alkanolamine

Monoethanolamine (MEA)

Diethanolamine (DEA)

Methyldiethanolamine (MDEA)

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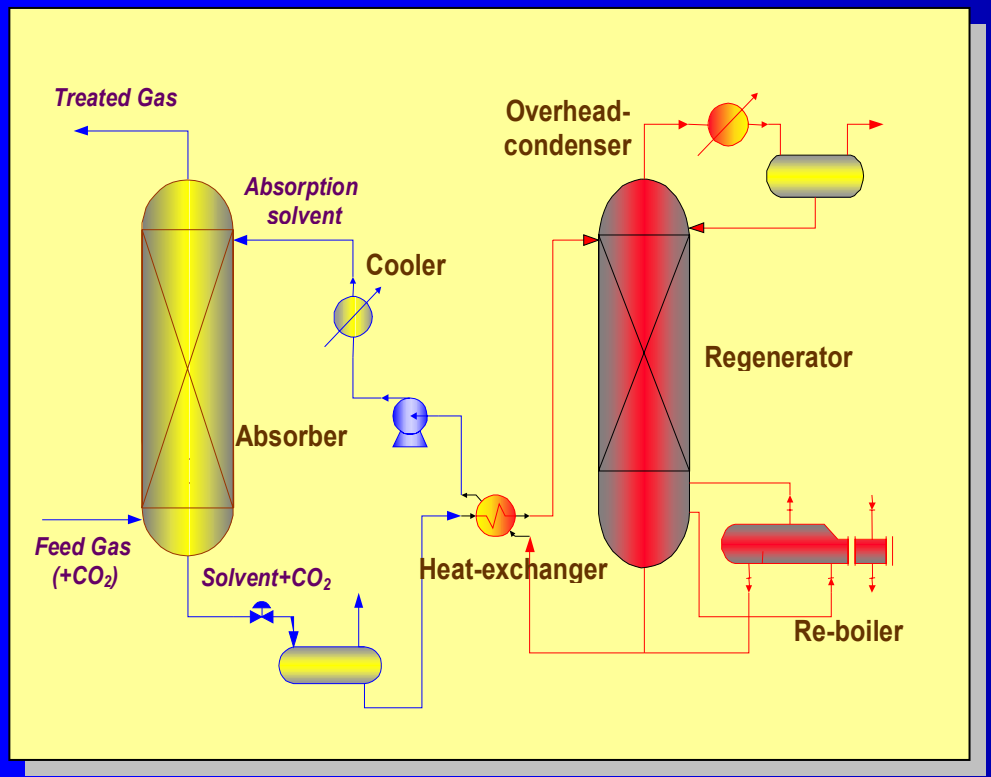
Absorption Process



- **Absorber:** CO_2 removal (40-60 °C)
- **Regenerator:** CO_2 release
  Solvent regeneration (100-120 °C)
- **Efficiency:** Up to 99+% removal
- **CO_2 product:** 95 – 99% CO_2
- **Energy source:** Steam at reboiler

- **Absorption solvent:** Aqueous solution of Monoethanolamine (MEA)

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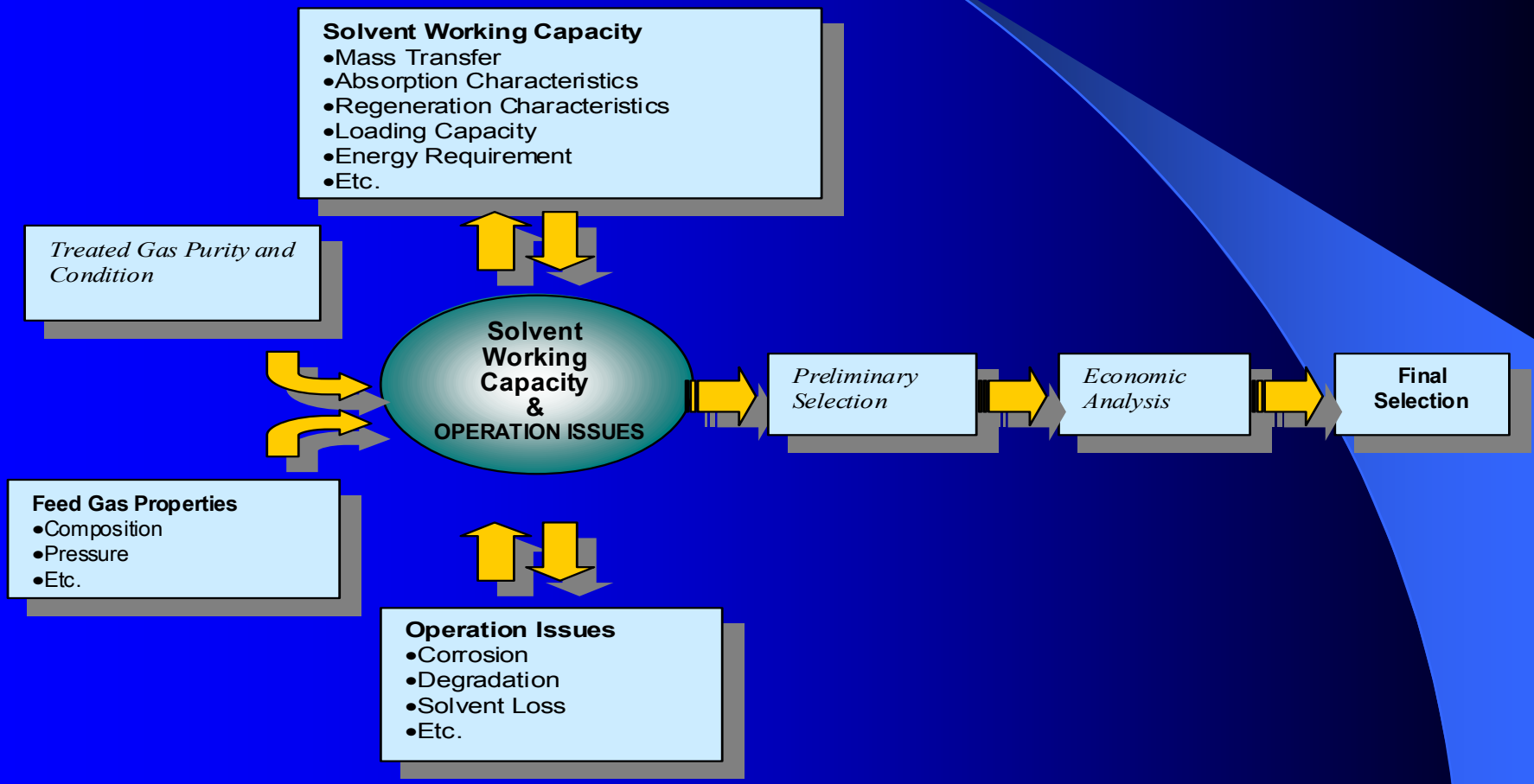
Solvent Selection



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Solvent Characteristics

	MEA	DEA	MDEA
Absorption efficiency or rate $r_{CO2} = k_2[CO_2][Amine]$	**k_2 ~ 6000 to 7500 m^3/kmol-s**	k_2 ~ 550 to 1600 m^3/kmol-s	k_2 ~ 5 m^3/kmol-s
Heat of reaction (kJ/mol CO_2)	85.6	76.3	60.9
Energy requirement for regeneration (kJ/kg CO_2)	Very high	Medium	**Very low**
Operational difficulties (corrosion problem)	High	Medium	**Low**
CO_2 solubility (mol CO_2/mol Amine)	0.5	0.5	**1.0**

Blended-alkanolamines

- **Low energy requirement with acceptable absorption rate**
- **MDEA-based solvent *(MEA-MDEA and DEA-MDEA)***

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Research Objectives

- Evaluate the overall performance of MEA-MDEA and DEA-MDEA processes in aspects of absorption efficiency and energy consumption for solvent regeneration

- Translate the performance to an overall cost-saving in relation to the MEA process

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Methodology

Technical Evaluation (Experiments)

- CO_2 absorption performance
- Energy requirement for solvent regeneration

Economic Analysis (Technical + Cost Model)

- Process design modeling and simulation
- Capital cost
- Operating cost
- Cost of CO_2 capture (\$/tonne CO_2)

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Absorption Performance

Mass-transfer efficiency → Absorption rate + hydrodynamics
→ Column height & diameter
→ Main portion of capital cost

Absorption column:

Diameter = 1”
Sulzer DX packing

Diameter = 4”
Mellapak 500Y

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Test Conditions

Experimental conditions

Pressure	Atm.
Gas phase	
CO_2 concentration:	10 - 15 %
Liquid phase	
Absorbent:	MEA, DEA, MDEA, MEA-MDEA, DEA-MDEA
Absorbent concentration:	3.0 – 5.0 kmol/m^3
Liquid load:	4.8 - 10.1 m^3/m^2-h
Temperature:	25 - 50 ^oC

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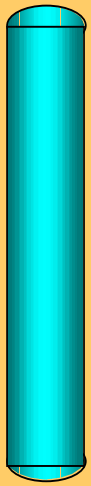
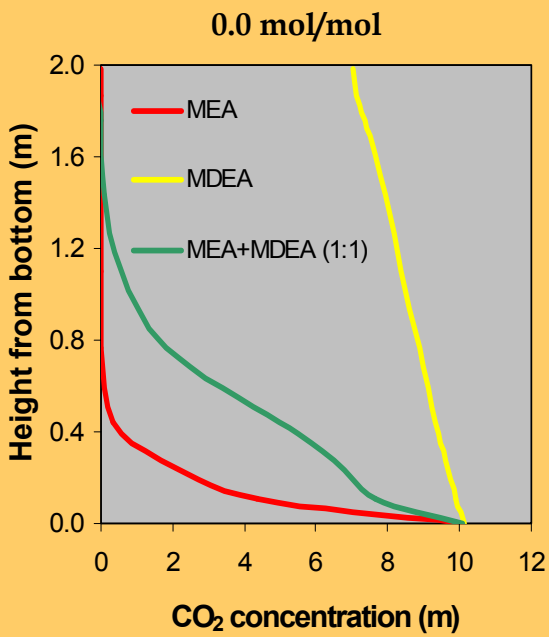
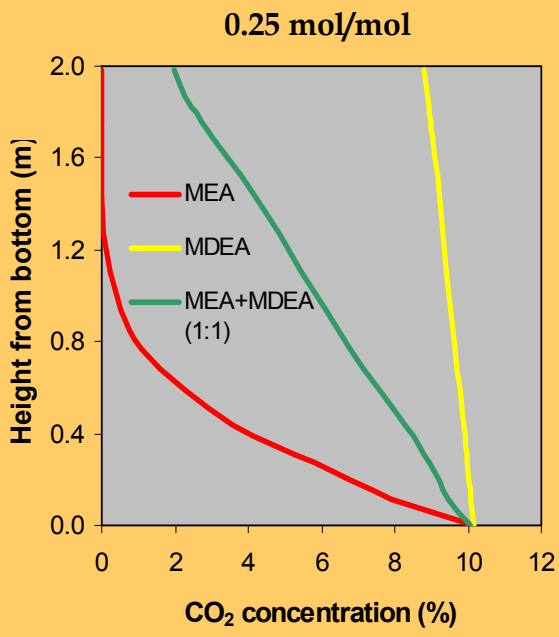
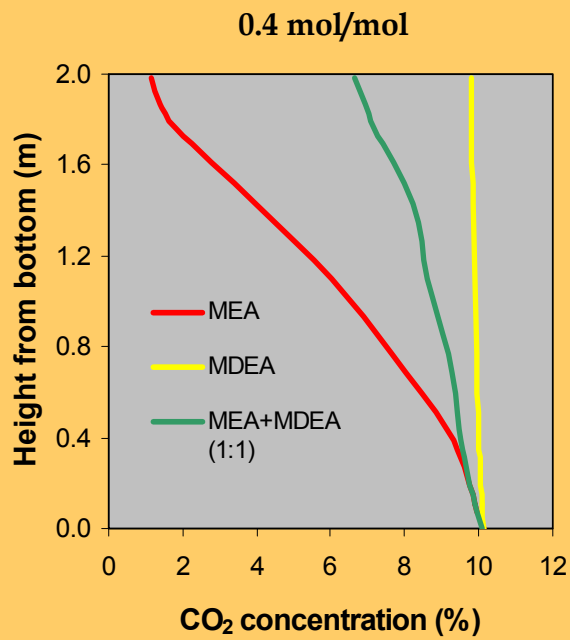
Efficiency of MEA-MDEA

- Profiles of MEA-MDEA lie between those of the precursors.
- The absorption behavior is influenced by variation in CO_2 loading.









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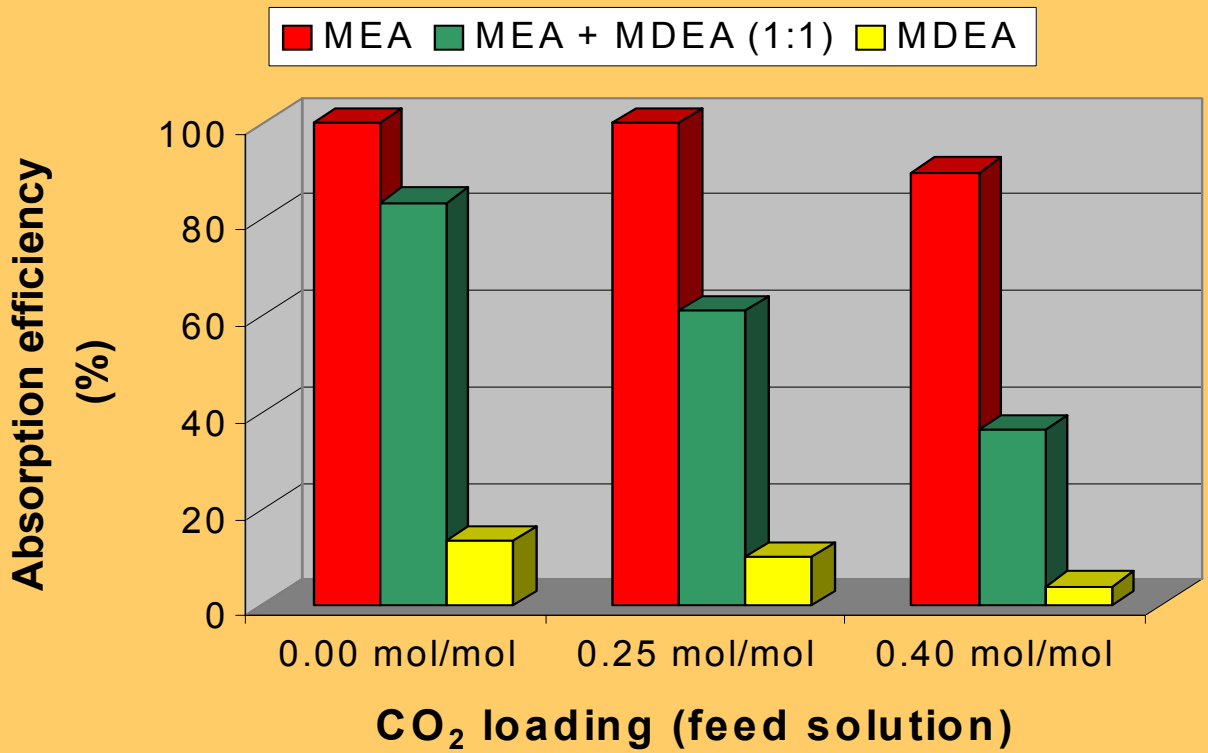
Efficiency of MEA-MDEA

$$\eta = \left[1 - \left(\frac{y_{out}}{1 - y_{out}}\right) \times \left(\frac{1 - y_{in}}{y_{in}}\right)\right] \times 100\%$$



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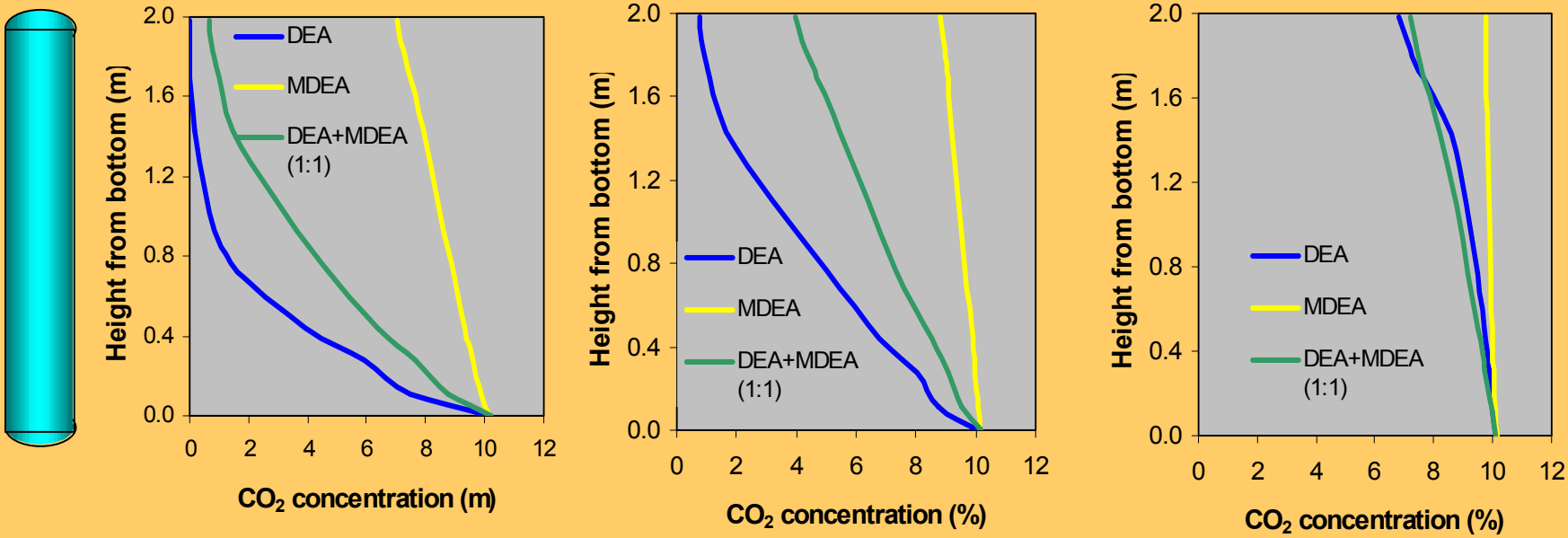
Efficiency of DEA-MDEA

- Profiles of DEA-MDEA are generally the combination of those of the precursors.



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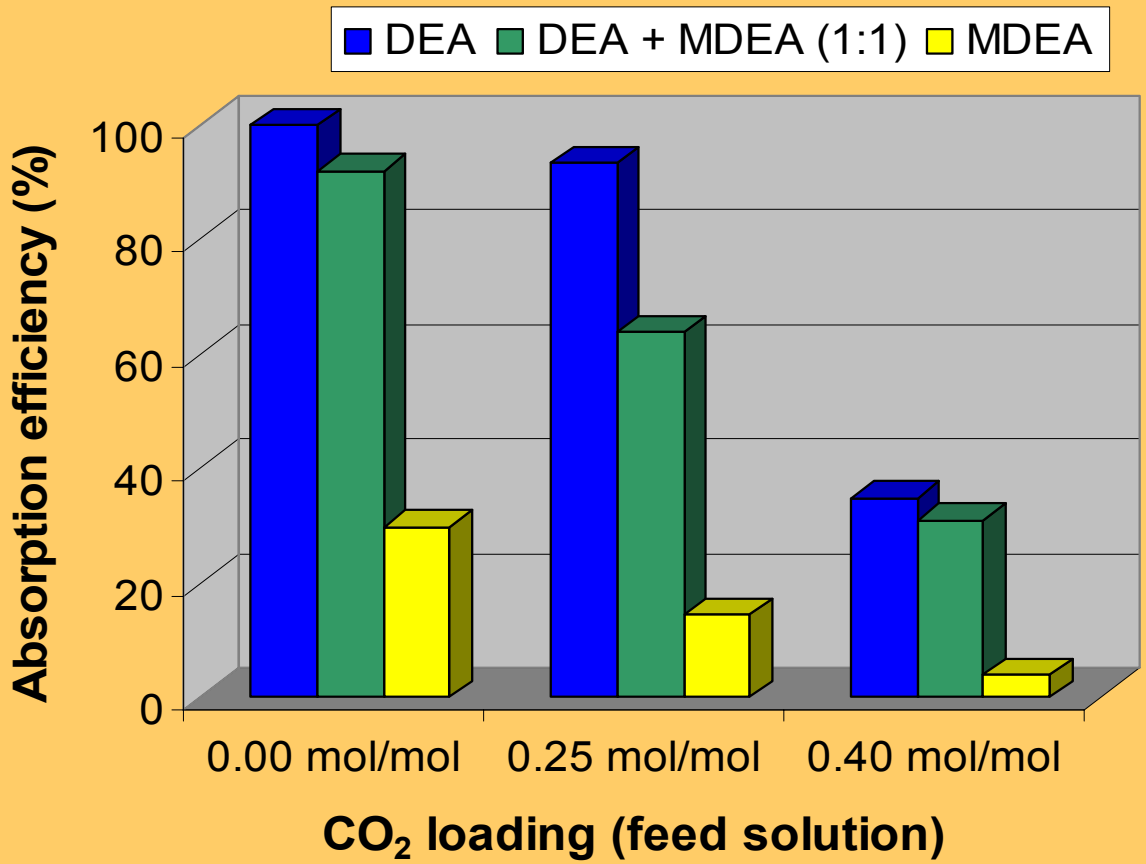
Efficiency of DEA-MDEA



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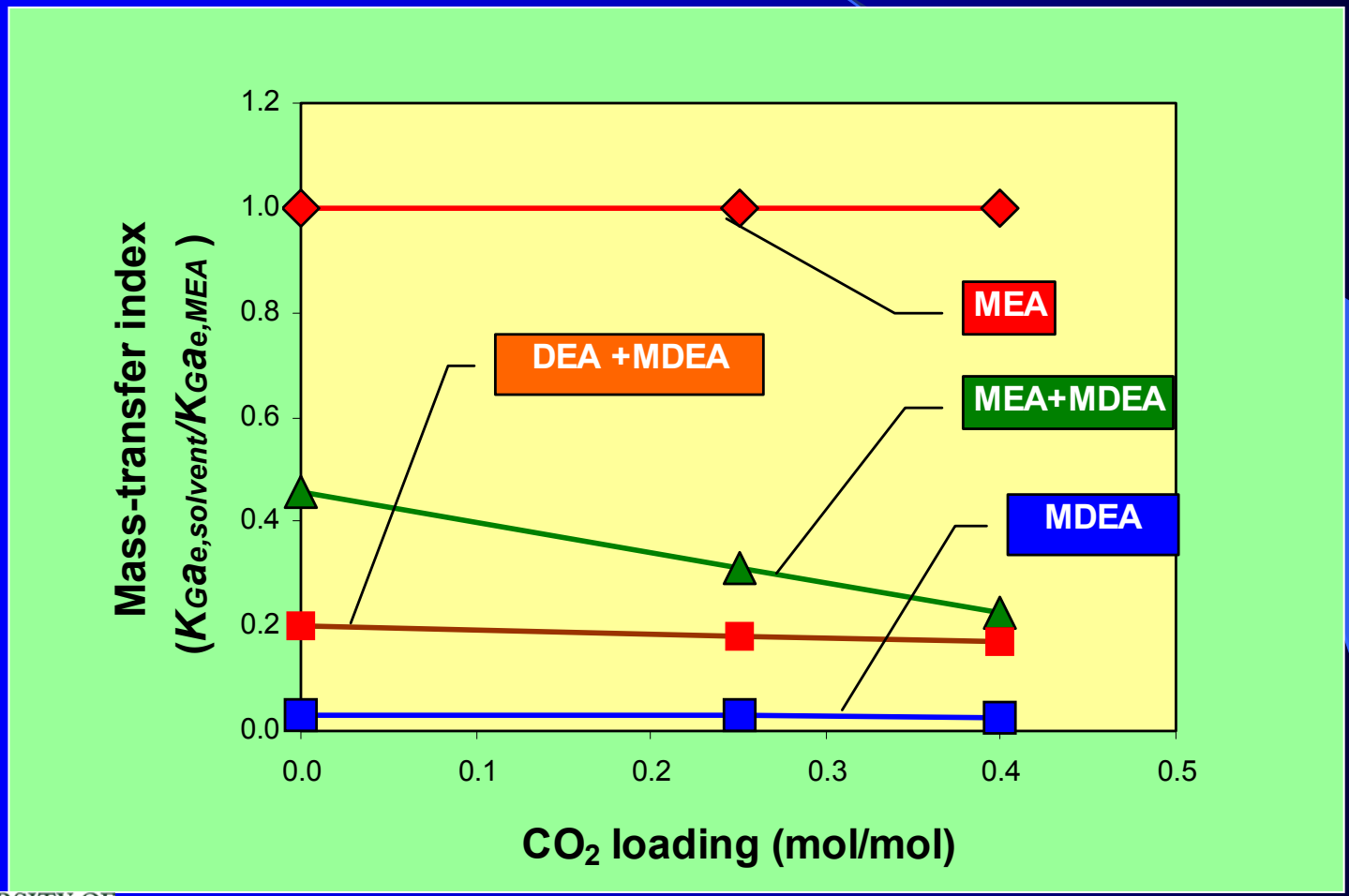
Mass-Transfer Index



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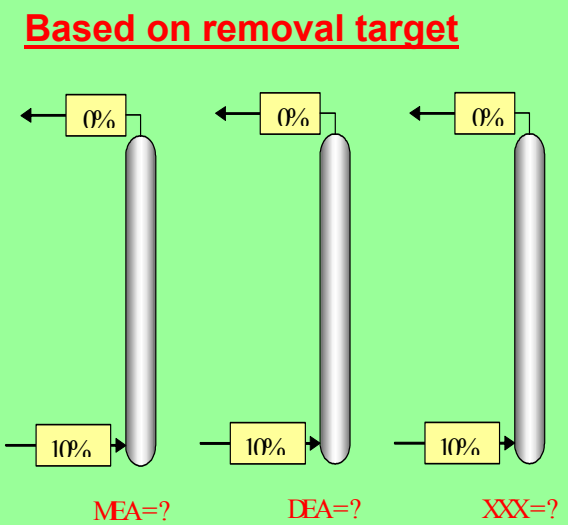
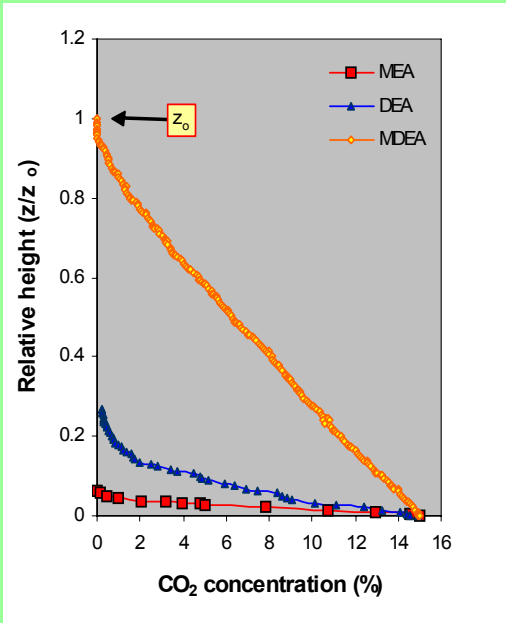
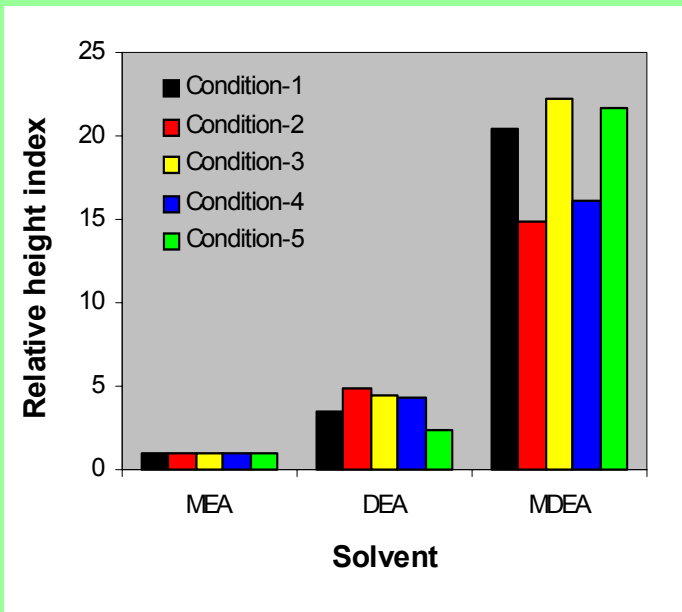
Absorber Height Index

- Column height required for a particular absorption task.
- Height index = absorber height for solvent-X / height for MEA
- MEA < DEA < DIPA << MDEA







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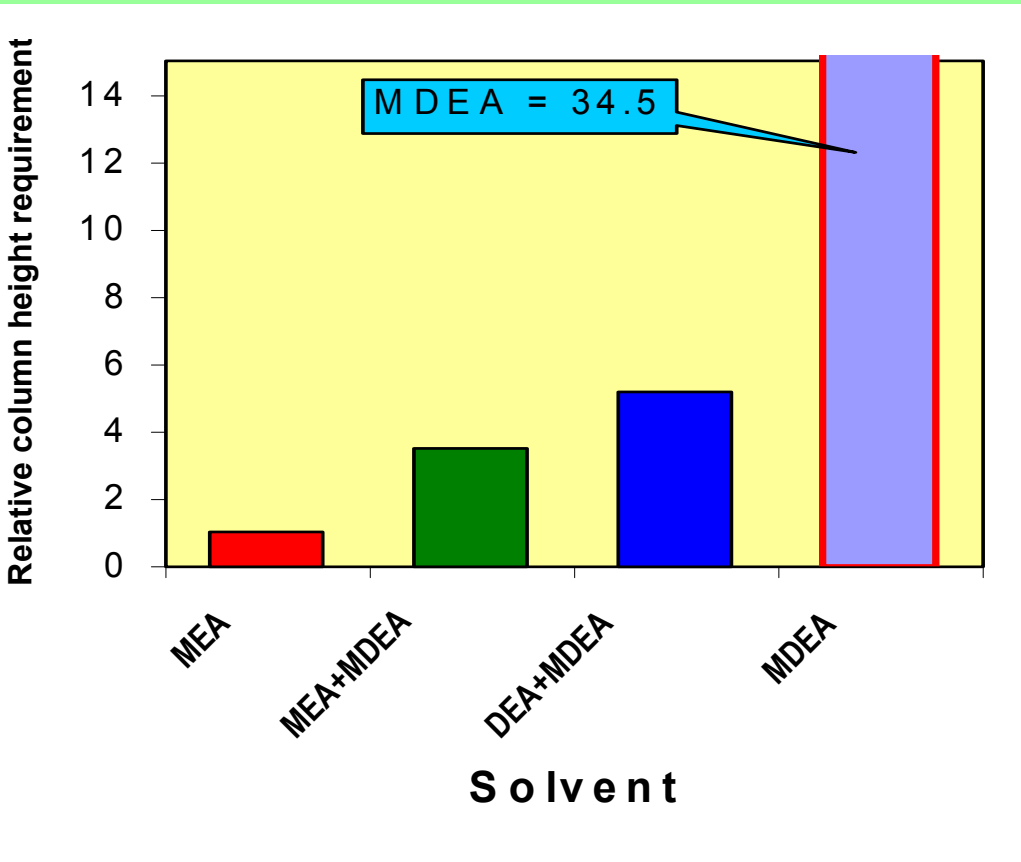
Absorber Height Index (Blend)



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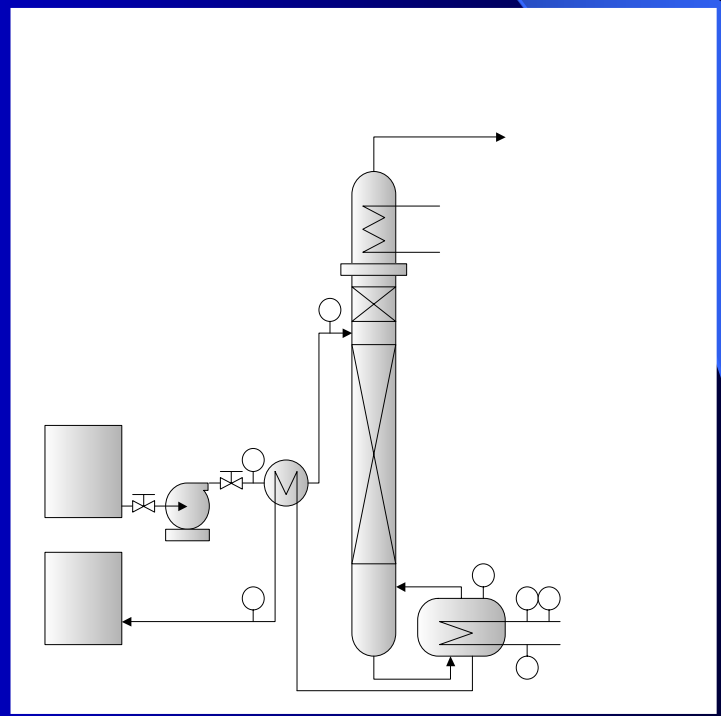
Solvent Regeneration

Energy requirement → **Heat of reaction + Sensible heat + Heat of water vaporization**

→ **Main portion of operating cost**

Reboiler heat duty

= **Energy consumed by process to recover one CO_2 unit**



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Test Conditions

Single Alkanolamine	• MEA (Monoethanolmine) • DEA (Diethanolamine) • MDEA (Methyldiethanolamine)
Blended Alkanolamine	• MEA-MDEA • DEA-MDEA
Mixing Ratio (mol : mol)	• 1 : 2 • 1 : 1 • 2 : 1
Rich CO_2 Loading	• 0.3 mol/mol • 0.5 mol/mol
Solvent Concentration	• 4.0 kmol/m^3 • 5.0 kmol/m^3 • 7.0 kmol/m^3

Experimental Validation

Reboiler heat-duty (kJ/kg CO_2)	lean CO_2 loading (mol/mol)	
	literature [a]	this study
3,800	0.28 – 0.35	0.30 (at 3,767 kJ/kg CO_2)
4,800	0.23 – 0.29	0.25 (at 4,849 kJ/kg CO_2)
5,400	0.20 – 0.24	0.23 (at 5,203 kJ/kg CO_2)

[a] Estimated values from the work by Wilson et al. (2004)

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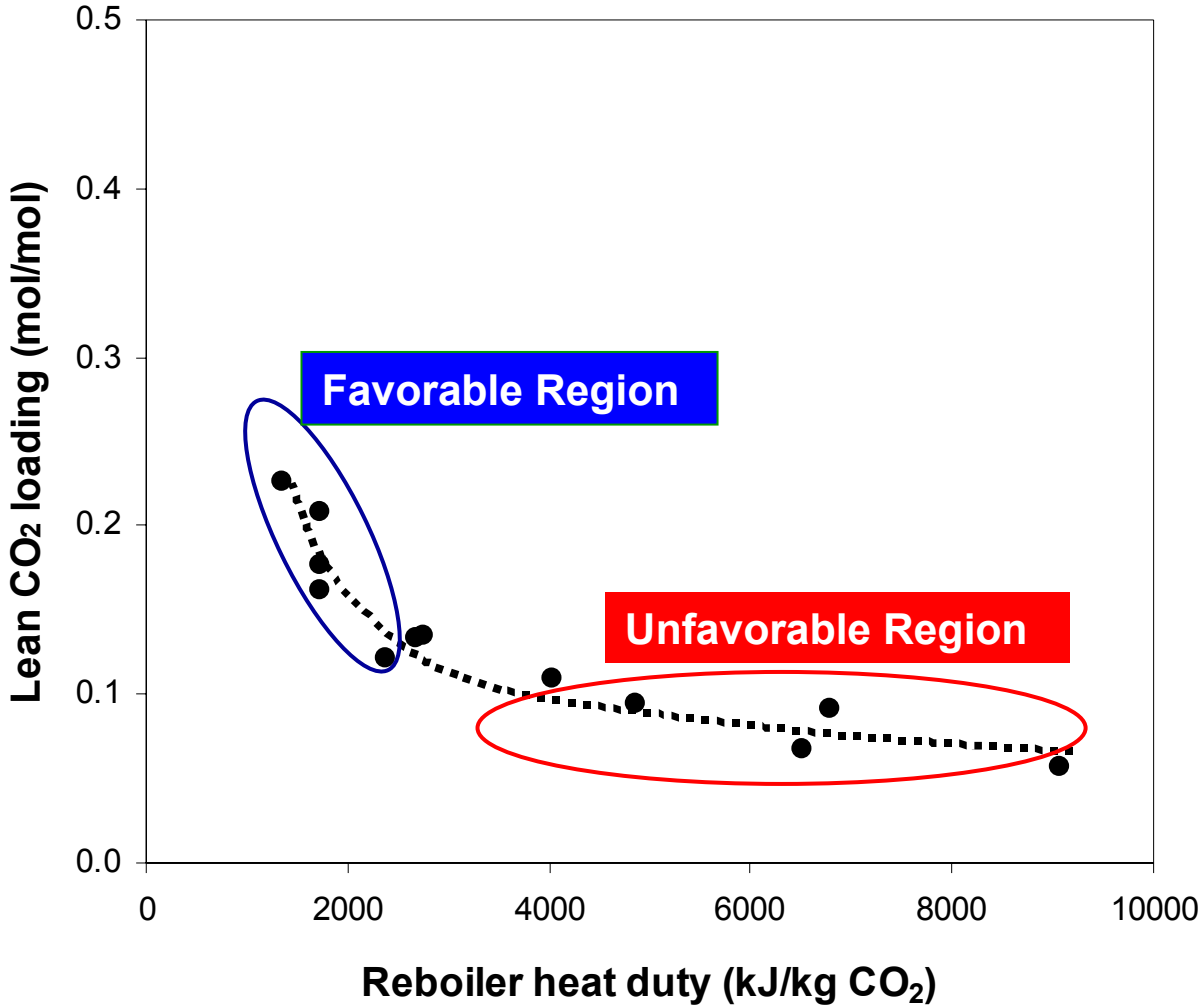
Effect of Lean CO_2 Loading



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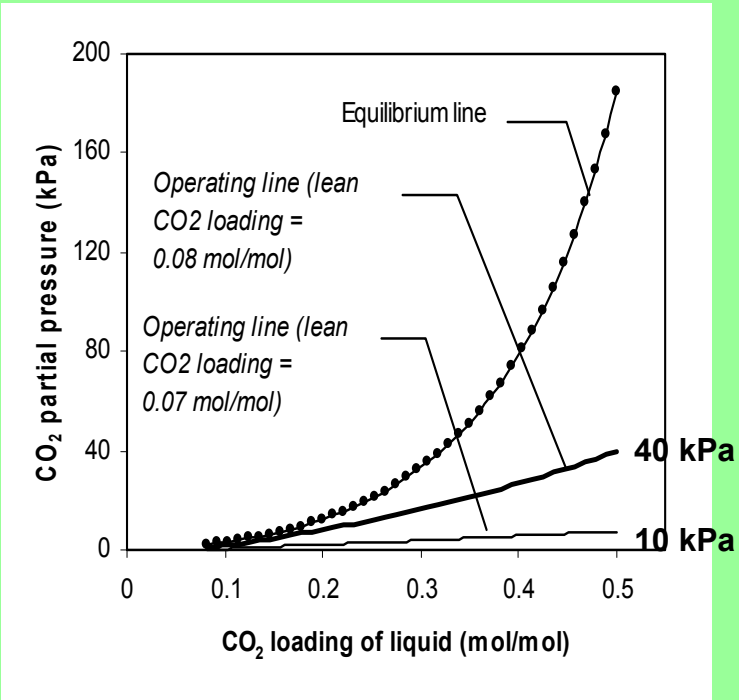
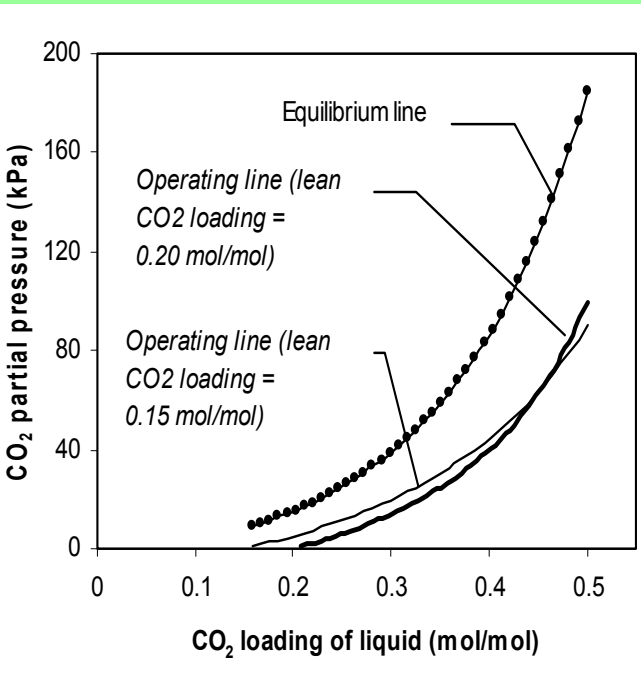
Rich Loading: 0.5 mol CO_2 / mol DEA, Concentration: 4 kmol/m^3

Effect of Lean CO_2 Loading

Unfavorable Region



Favorable Region



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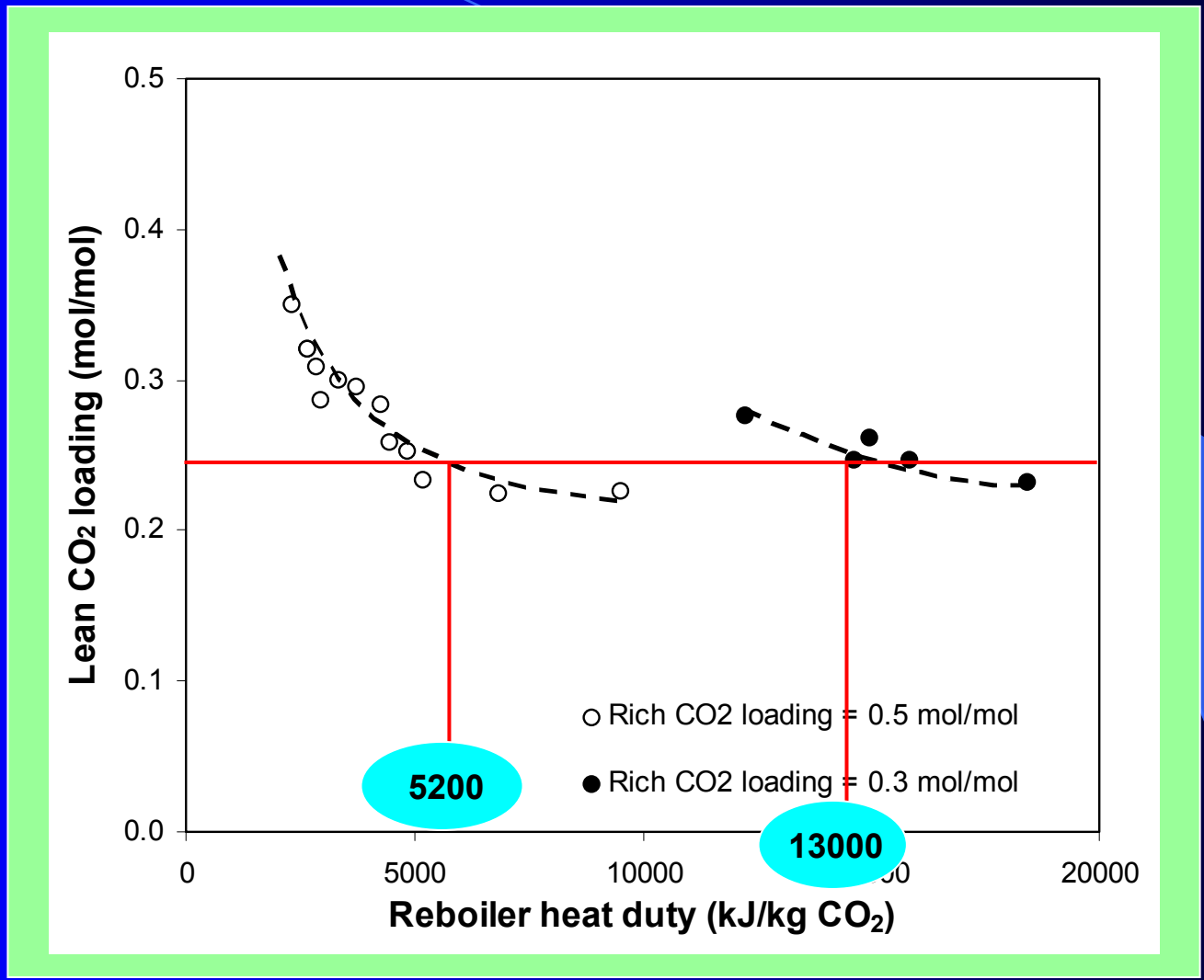
Effect of Rich CO_2 Loading



0.3 mol/mol Rich CO_2 Loading > 0.5 mol/mol Rich CO_2 Loading

Solution: MEA, Concentration: 5 kmol/m^3

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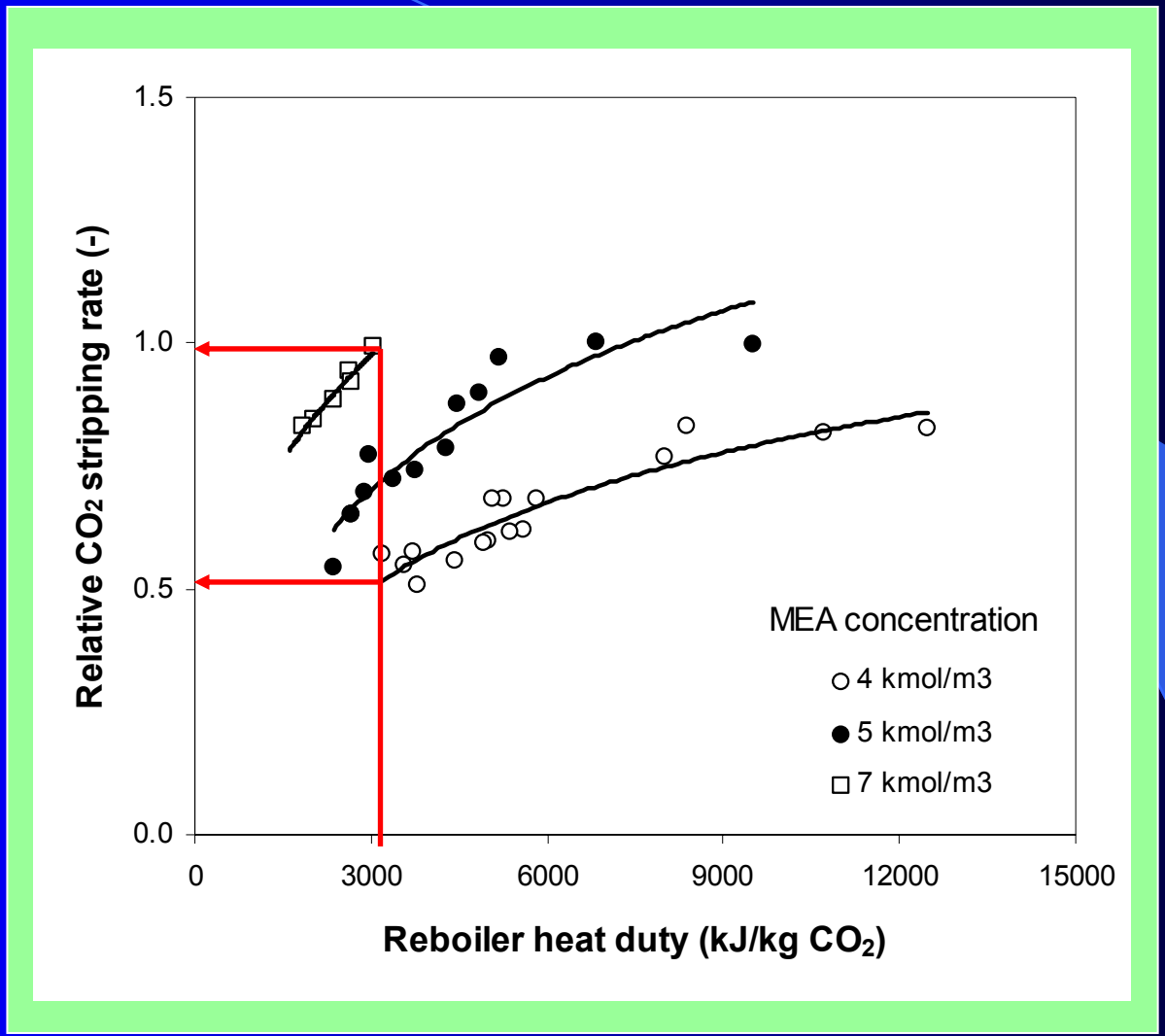
Effect of Solvent Concentration



4 kmol / m^3 > 5 kmol / m^3 > 7 kmol / m^3

Solution: MEA, Rich Loading: 0.5 mol CO_2 / mol solution

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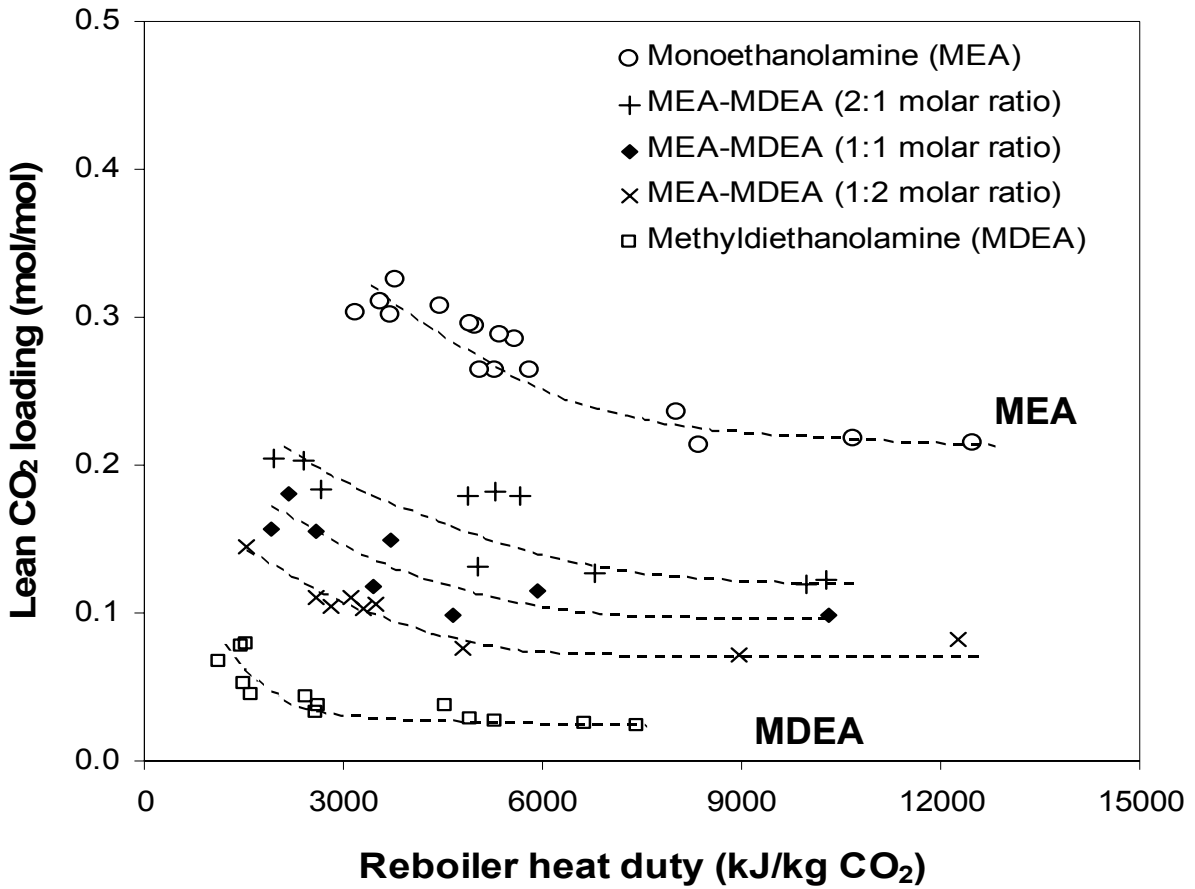
Blend Alkanolamine (MEA-MDEA)



MEA > MEA-MDEA (2:1) > MEA-MDEA (1:1) > MEA-MDEA(1:2) > MDEA

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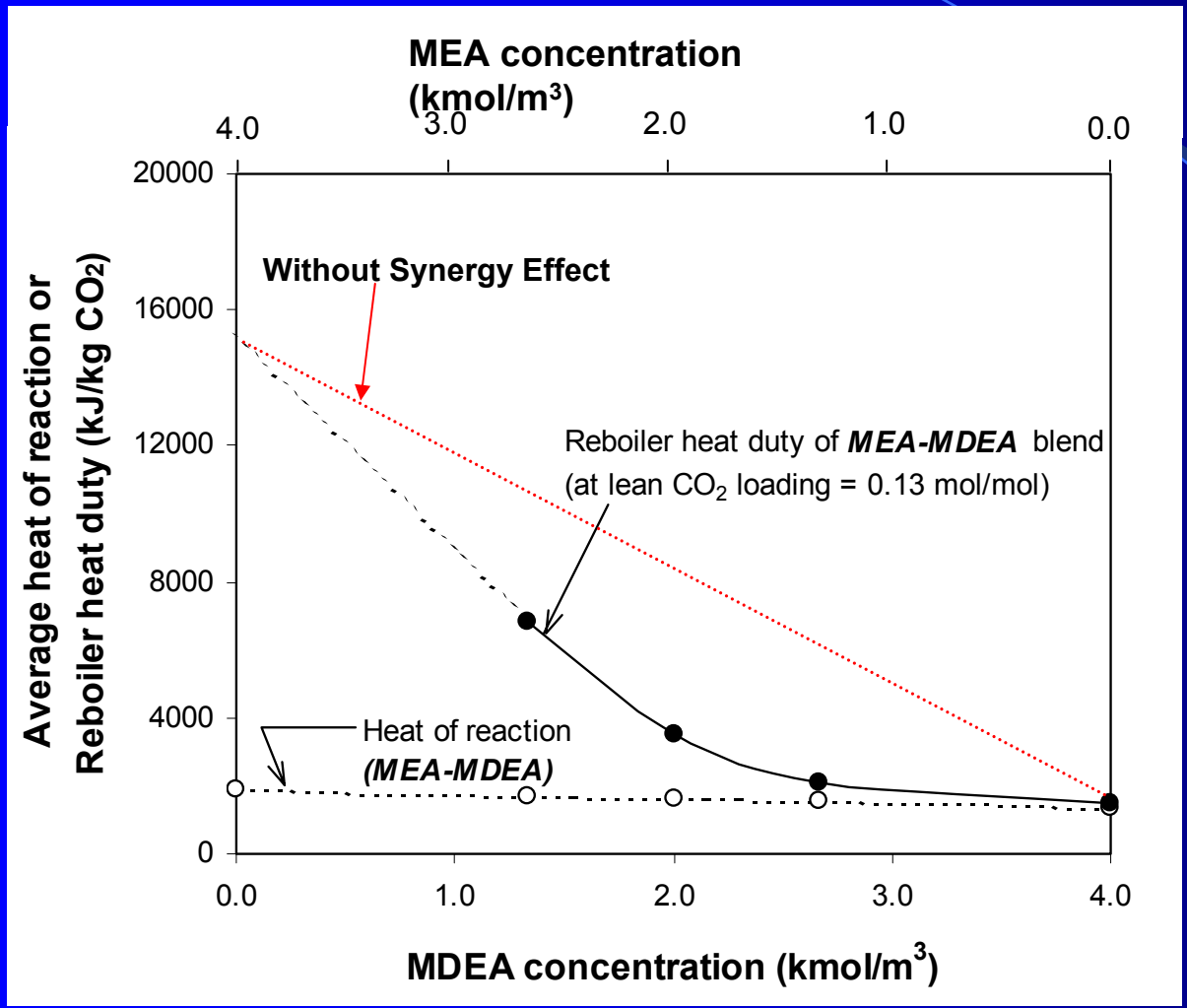
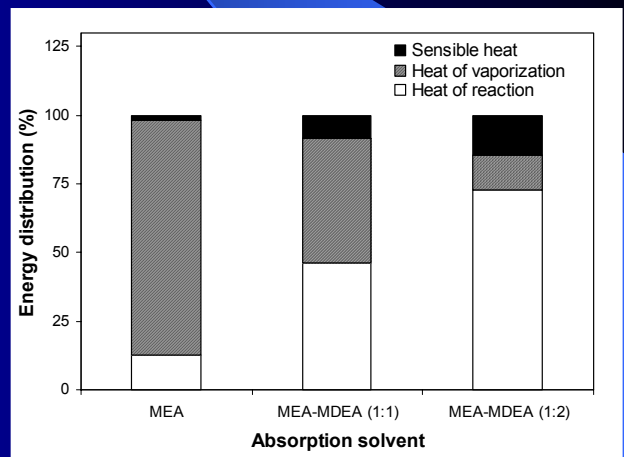
Rich Loading: 0.5 mol CO_2 / mol solution, Concentration: 4 kmol/m^3

Blend Alkanolamine (MEA-MDEA)



Energy Distribution



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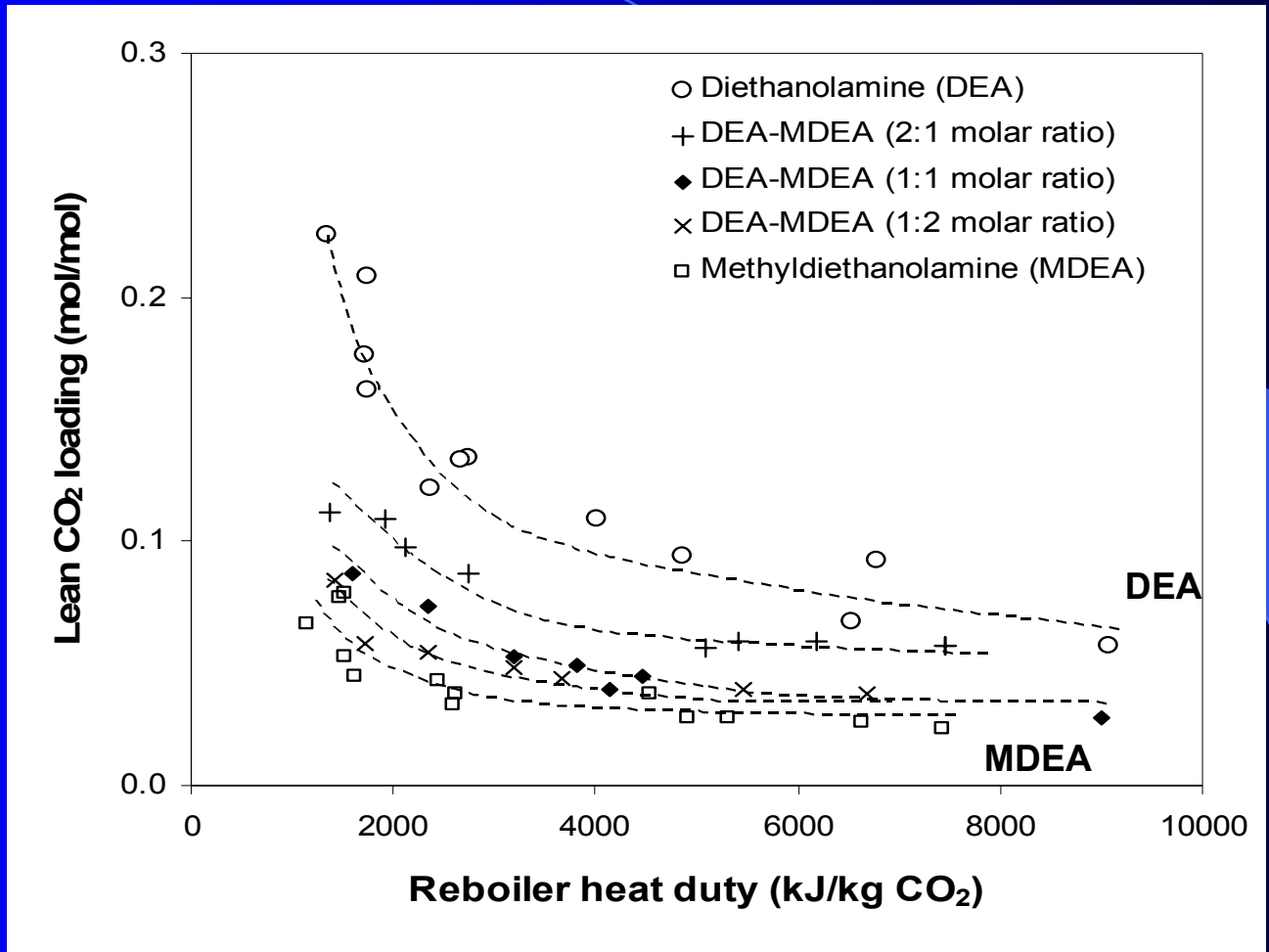
Blend Alkanolamine (DEA-MDEA)



DEA > DEA-MDEA (2:1) > DEA-MDEA (1:1) > DEA-MDEA (1:2) > MDEA

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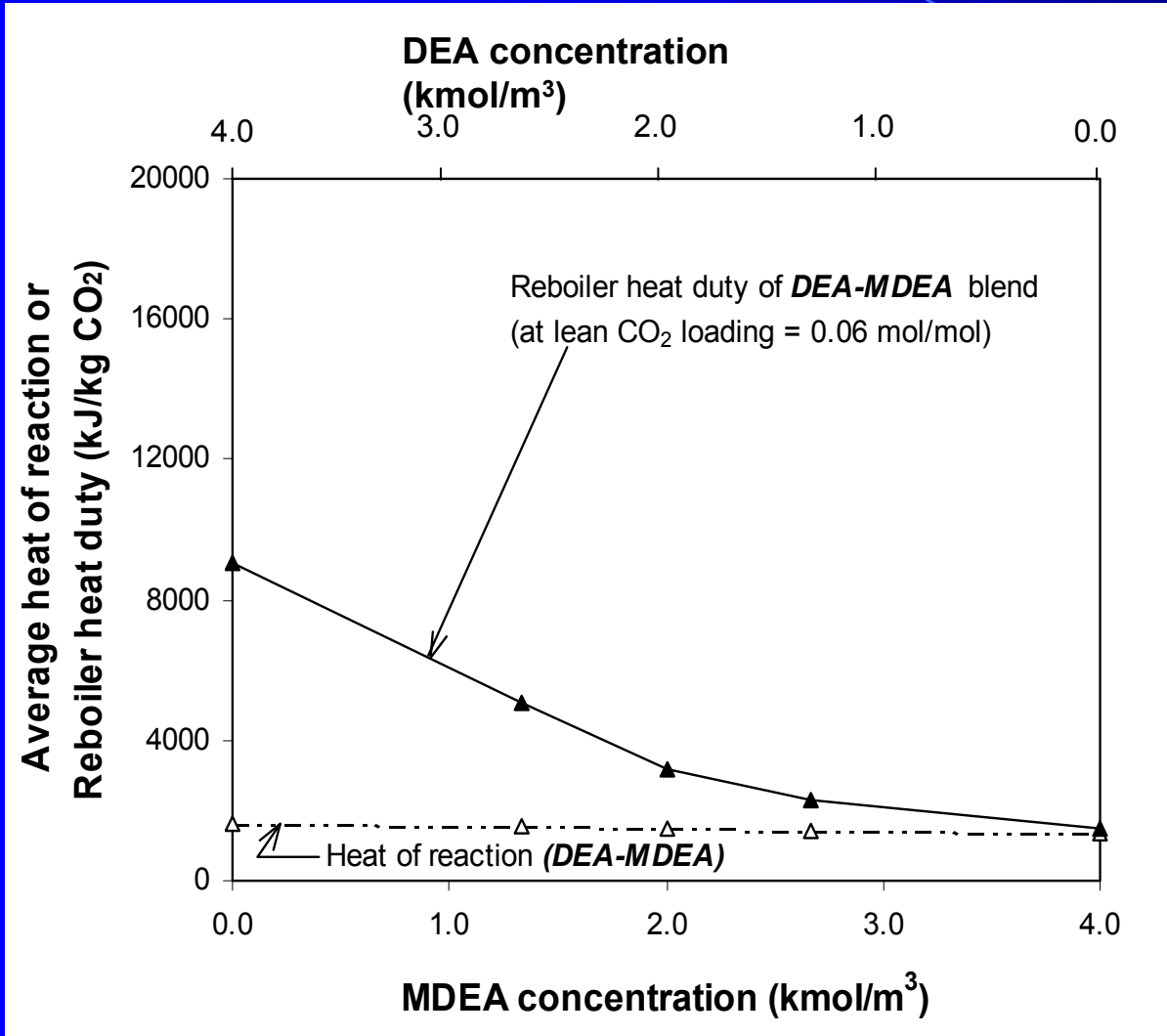
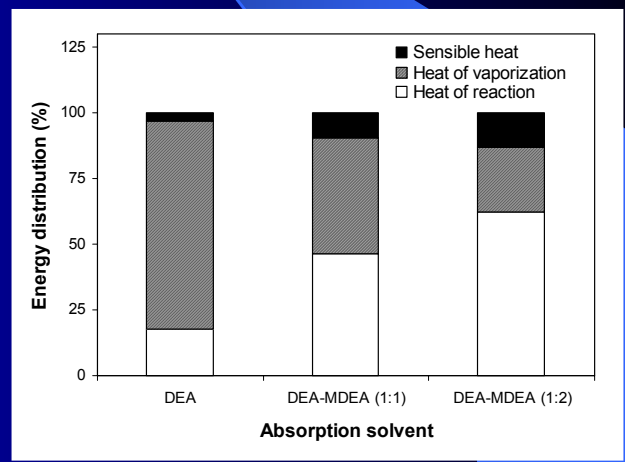
Rich Loading: 0.5 mol CO_2 / mol solution, Concentration: 4 kmol/m^3

Blend Alkanolamine (DEA-MDEA)



Energy Distribution



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Rate-Based Model (Modeling & Simulation)

(Mass-transfer & Hydrodynamics)

Input Information:
- Packing geometry
- Operating conditions

Liquid Distribution Model:
- Liquid distribution pattern
- Maldistribution

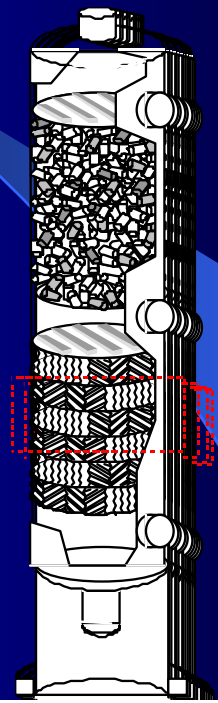
Thermodynamic Model:
- Vapor-liquid equilibrium (VLE)
- Speciation (from NRTL model)
- Mass-transfer driving force

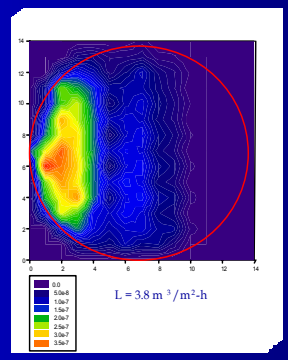
Interfacial Area Model:
- Dimensions of liquid rivulet
- Gas/liquid interfacial area (local region)

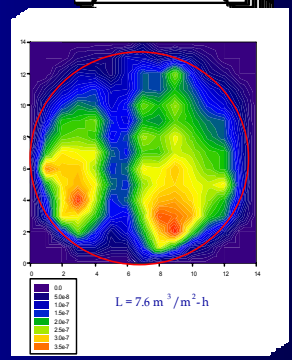
Mass-Transfer Model:
- Two-film theory
- Mass-transfer coefficient (k_G and k_L)
- Enhancement factor

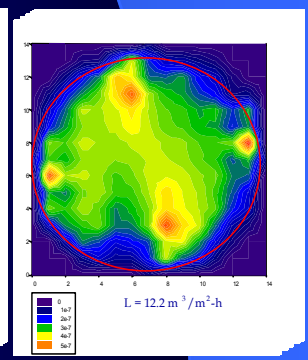
Column Design Procedure:
- Adiabatic absorption
- Mass balance
- Energy balance

Results:
- Performance of full-length column
- CO_2 concentration profile
- Temperature profile









- section at various liquid loads.

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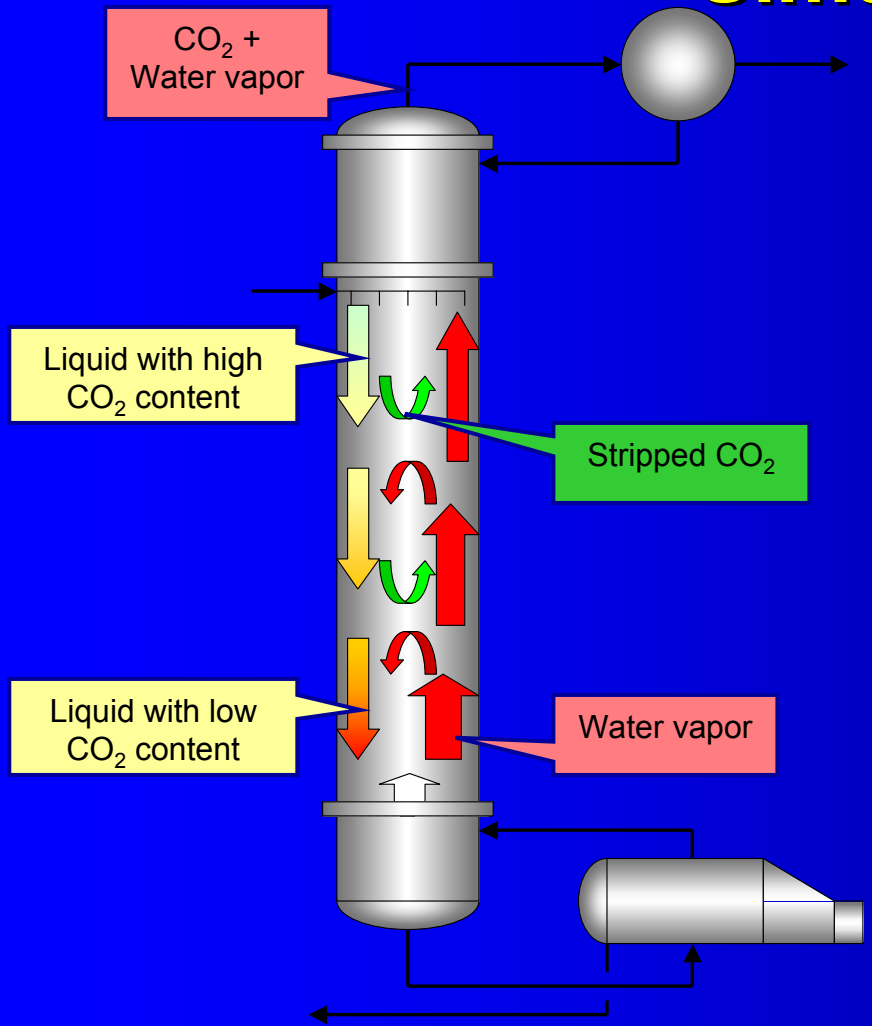
Solvent Regeneration (Modeling & Simulation)



Energy utilization: (Steam)

- Heat of reaction (CO_2 – MEA)
- Heat capacity (increase in Temp.)
- Heat of water vaporization

Solvent regeneration efficiency:

- High efficiency → Low CO_2 content (liquid)
- High efficiency → High water vapor
- High efficiency → High energy input
- Waste water vapor (Column Top)

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Process Simulation

Simulation conditions:

Absorption process	Packed absorber-regenerator
Process capacity	6,000 tonne CO_2/day
CO_2 capture efficiency	95%
Absorption solvent	Aqueous Alkanolamine
Solvent concentration	5.0 kmol/m^3
CO_2 content before regen.	0.50 mol CO_2/mol MEA
CO_2 content after regen.	0.17-0.22 mol CO_2/mol MEA
Reboiler temperature	110-120^oC

Simulation results:

- Dimensions of ABSORBER and REGENERATOR
- Heat Exchanger / Reboiler / Condenser / Cooler
- Pump / Blower / Storage Tank
- Temp. & Conc. Profiles / Equilibrium & Operating Lines

Design & Utility Consumption

Design & Electricity Consumption

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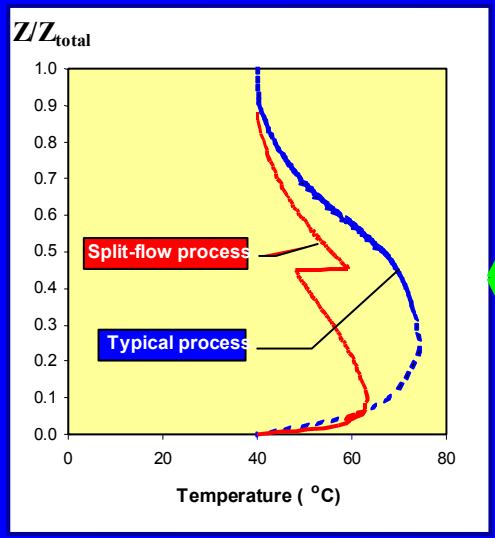
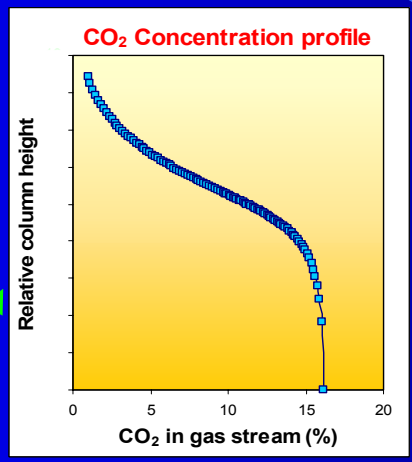
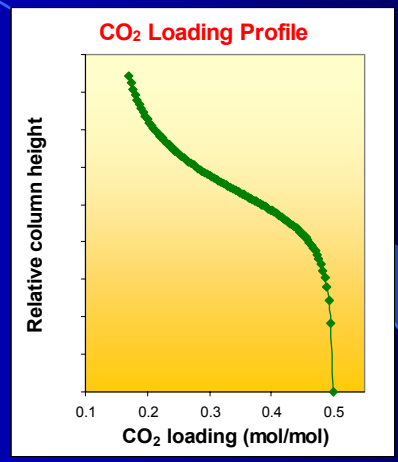
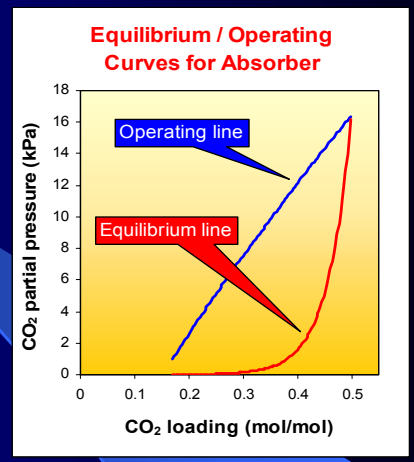
Simulation Results

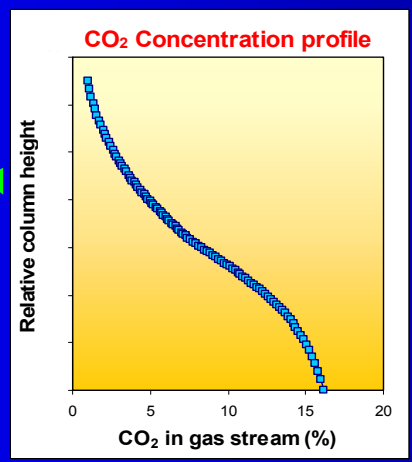


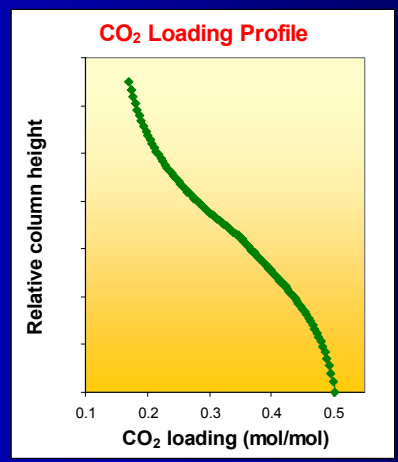


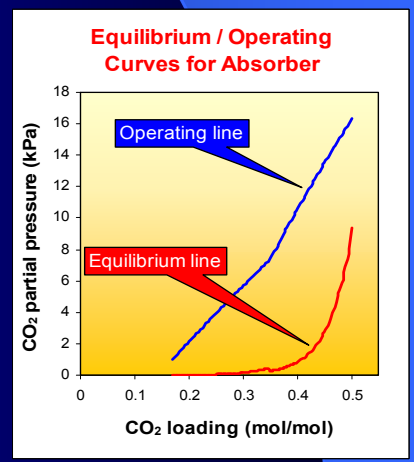




Typical process: High temperature at column bottom, low mass-transfer.







Split-flow: Lower temperature at column bottom, higher mass-transfer.

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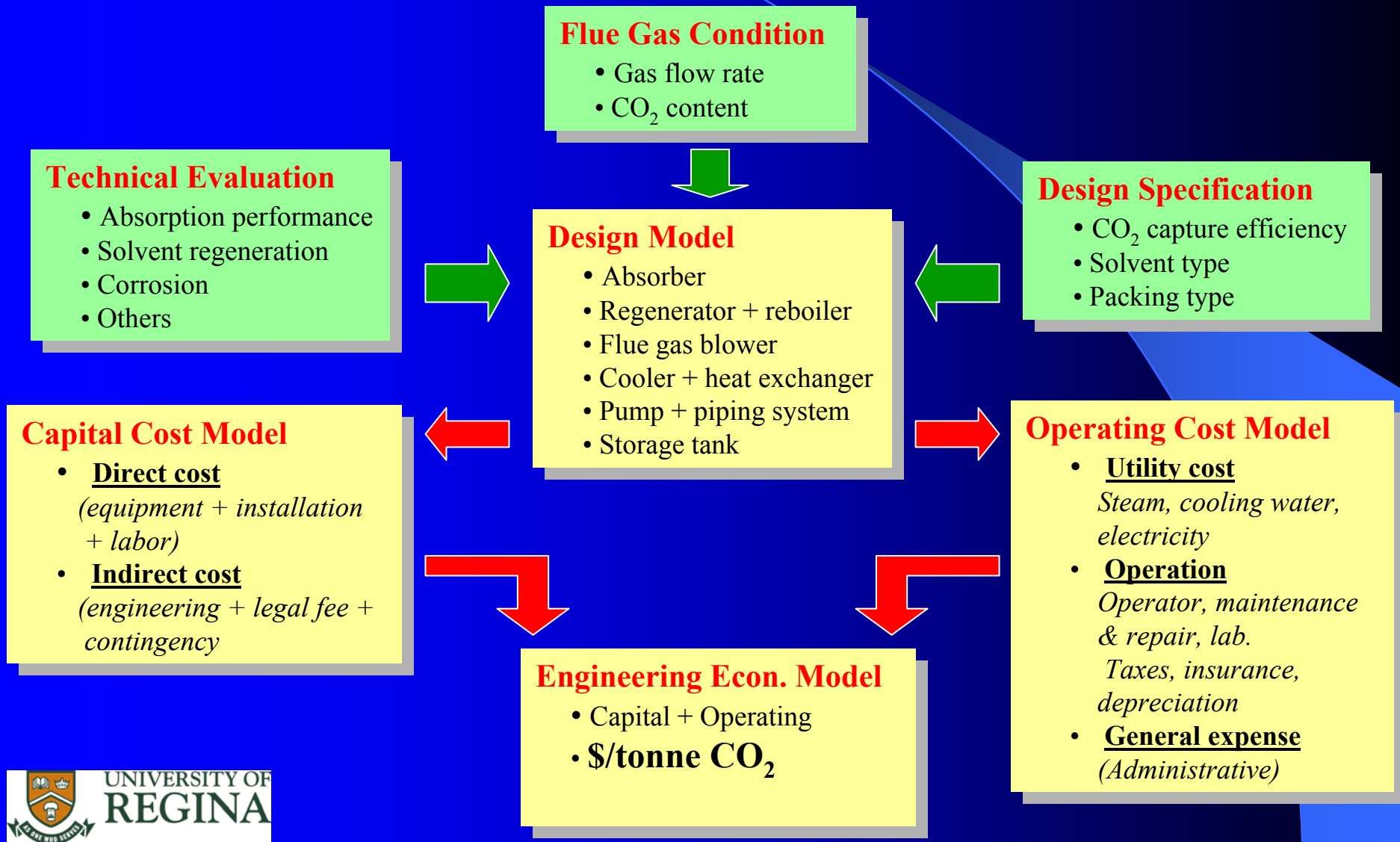
Economic Analysis (Technical + Cost Model)



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Case Study

Power Plant

Electricity generation	300 MW
Thermal efficiency	40 %
CO_2 emission	6,300 tonnes/day
CO_2 content in flue gas	15%

CO_2 Capture Process

Absorption process	Packed absorber-regenerator
CO_2 capture efficiency	95%
Absorption solvent	MEA, MEA-MDEA

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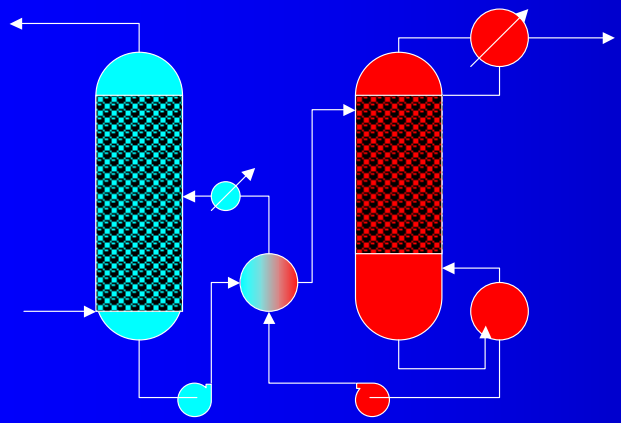
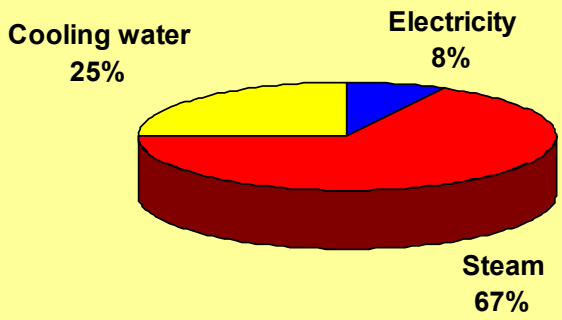
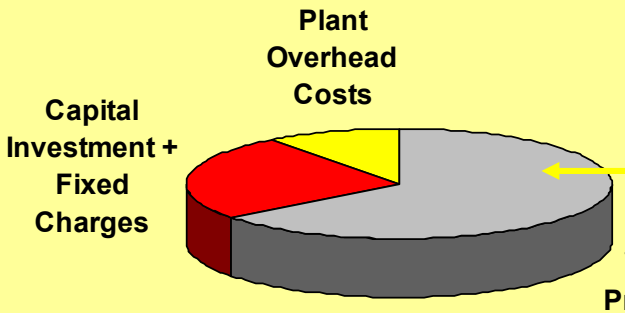
CO_2 Absorption by MEA (Base Case)



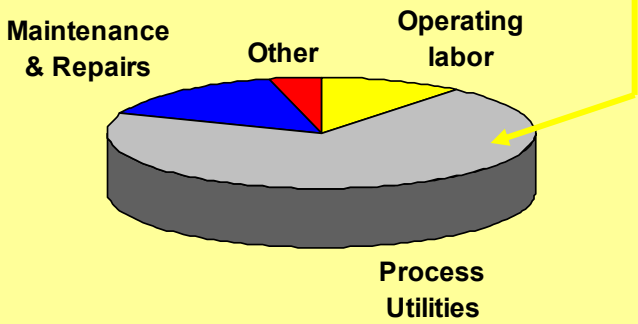
Utilities



Total Production Cost



Variable Production Cost



Production Cost Index = **1.00**

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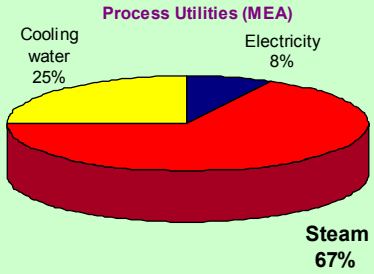
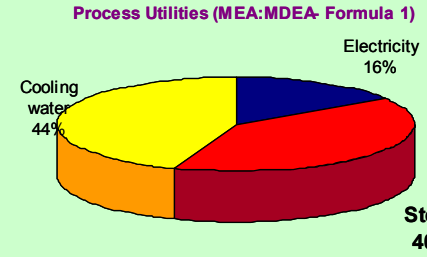
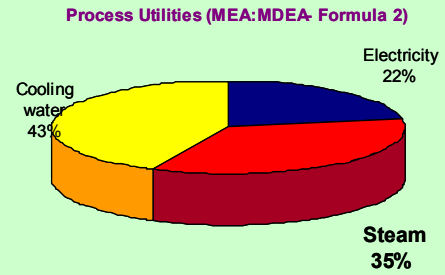
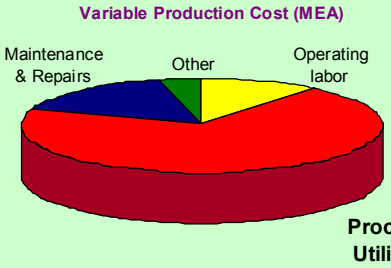
CO_2 Absorption by MEA-MDEA

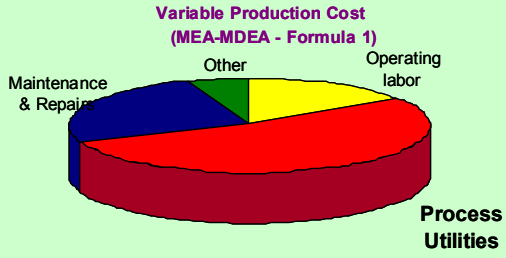
MEA (Base case)	MEA-MDEA (Formula 1)	MEA-MDEA (Formula 2)
Production cost index =1.00	Production cost index =**0.87**	Production cost index =**1.03**

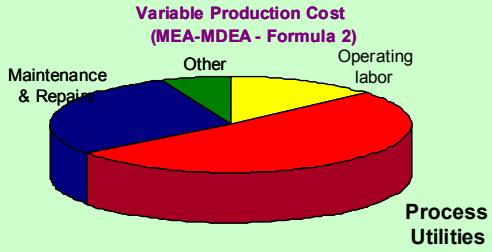


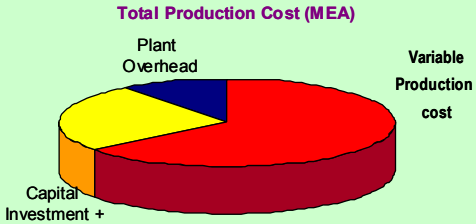


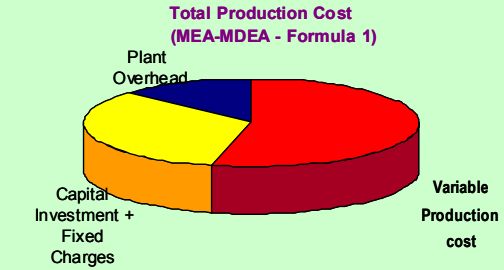


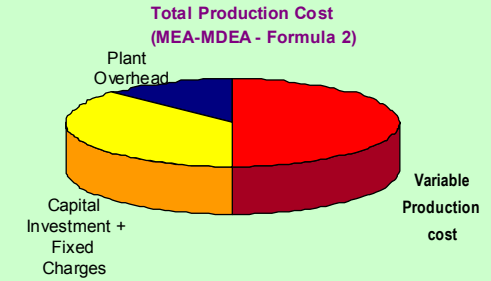












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Cost Comparison

	Steam for solvent regeneration	Capital Cost	Total CO_2 Capture Cost
MEA	100 %	100 %	100 %
MEA-MDEA (1)	33 %	113 %	87 %
MEA-MDEA (2)	30 %	150 %	103 %

Blended MEA-MDEA

- **Lower energy requirement**
- **Higher capital cost**

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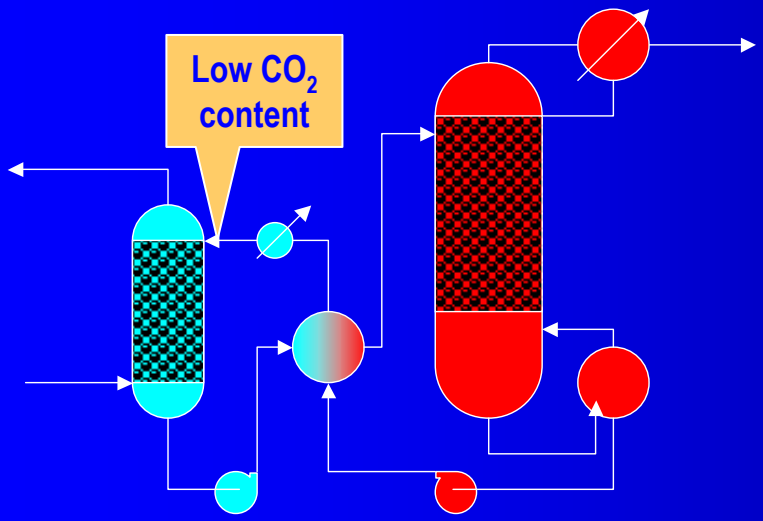
Design & Operation (Technical + Cost Model)

Technical Evaluation

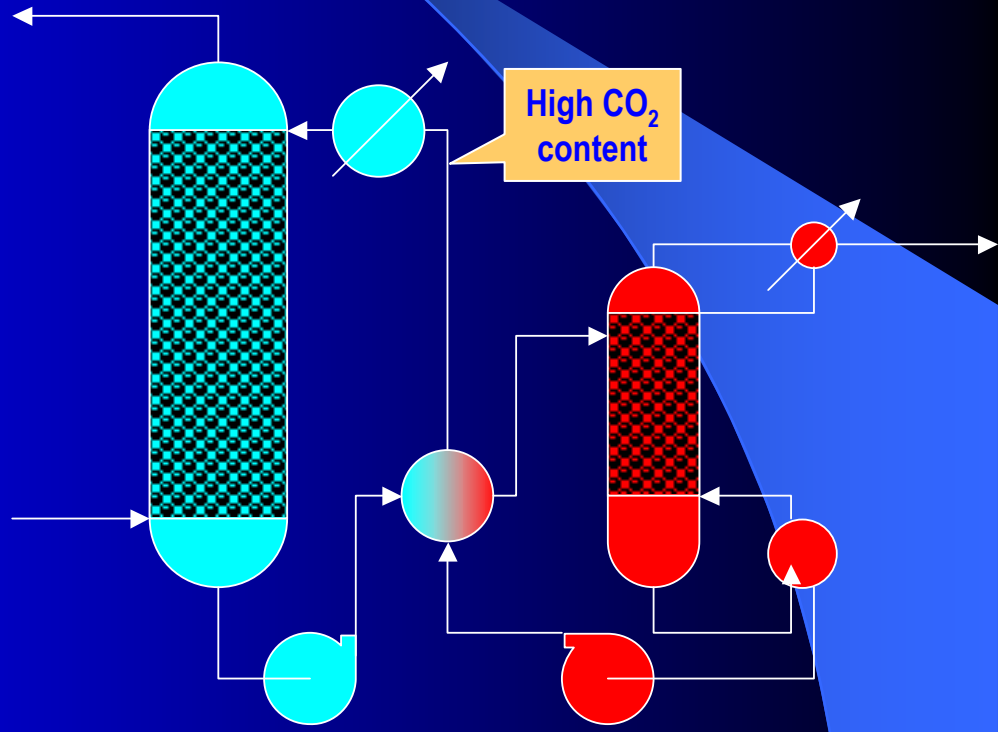
- Absorption performance
- Solvent regeneration
- Corrosion
- Others

= fn (operating conditions)

= fn (Temp., Conc., CO_2 content, % CO_2 in gas)



- Low capital cost
- High operating cost



- High capital cost
- Low operating cost

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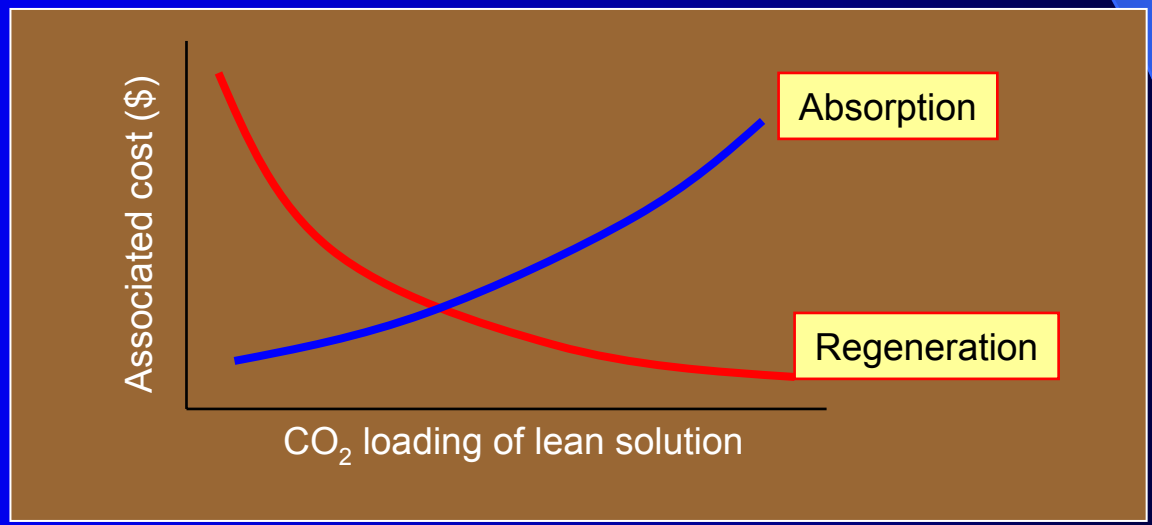
Trade-off Behavior for Cost Analysis

Absorption

- Leaner CO_2 loading
- Higher absorption efficiency
- Lower cost

Regeneration

Leaner CO_2 loading
Higher energy requirement
Higher cost



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Conclusions

- Blended MEA-MDEA and DEA-MDEA show a promising cost-saving opportunity in relation to MEA.
- The cost saving is primarily a result of lower steam cost.
- A favourable saving can however be achieved only when an appropriate mixing ratio of MEA-MDEA and DEA-MDEA as well as optimal operating conditions are applied.

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Acknowledgement

- Natural Sciences and Engineering Research Council of Canada (NSERC)
- Natural Resources Canada (NRCan)

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The University of Texas at Austin
Department of Chemical Engineering

Pilot Plant for CO_2 Capture

Eric Chen and Ross Dugas

IEA CO_2 Capture Workshop

October 3, 2005

Outline

- Background
- Scope of Work
- Pilot Plant Design
- Campaign 2 Results
- MEA Results
- Final Campaign
- Future Work

K_2CO_3 Promoted by Piperazine (PZ)

- New Solvent Developed by Cullinane (2005)
  - 5 m K^+/ 2.5 m PZ
  - CO_2 Absorption 1.5 – 3 Times Faster than 30 wt% MEA
  - Heat of Absorption 10-25% Less than MEA
- Implications
  - 1.5-2.5 less Packing and Pressure Drop

    OR
  - Closer Approach to Saturation - 10-20% Less Energy

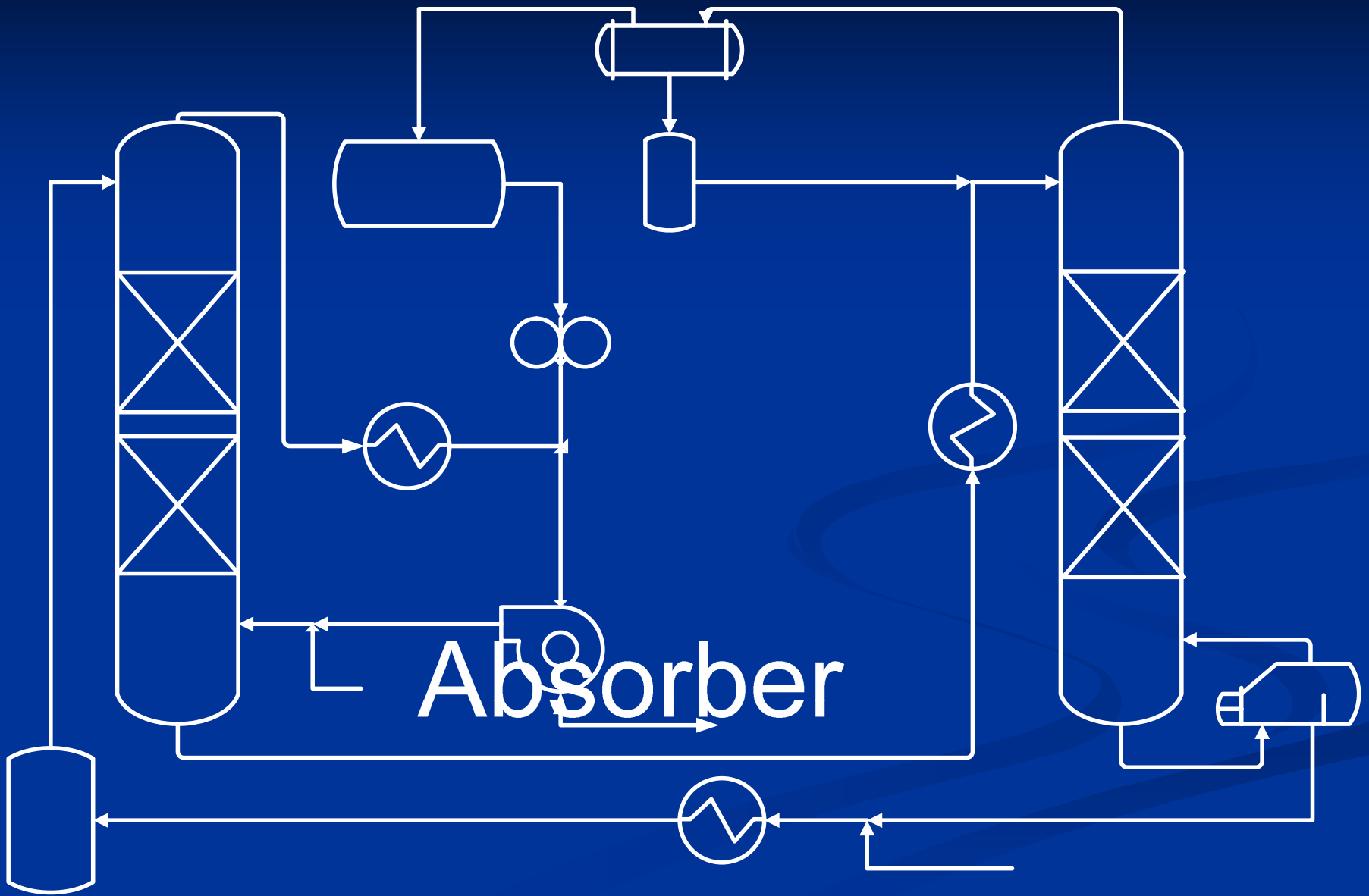
Research Objectives

- Develop & Validate Design Method for Scale-up from Bench-scale Measurements
  - CO_2 Absorption in Potassium Carbonate Promoted by Piperazine
  - Wetted Wall Column & Absorber Pilot Data
- Bench-mark K^+/PZ with 30wt% MEA in Pilot Absorber/Stripper
- Optimize Packing Selection (Random vs. Structured)
- Demonstrate Reliable Operation of Absorber/ Stripper System

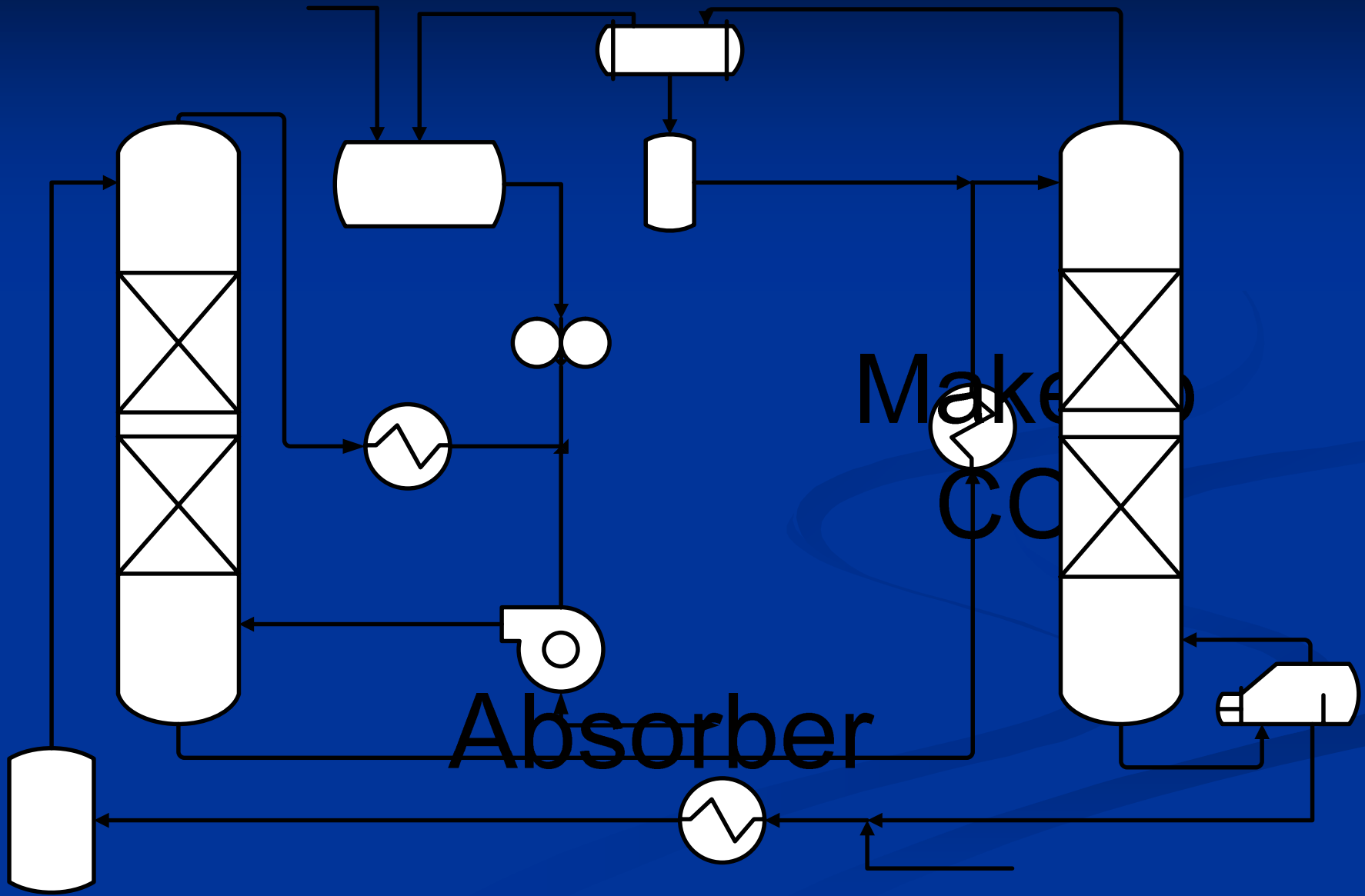
CO_2 Pilot Absorber/Stripper System

- Pickle Research Center
- Column ID – 43 cm
- Packed Height – 6.1 m in 2 beds (3.05 m each)
- Collector Plate & Redistributor in Between Packed Beds
- Multi-use facility (distillation/extraction)

Pilot Plant Schematic



Pilot Plant Schematic



SRP Pilot Plant Characteristics

- Gas Recycle
  - Variable CO_2 Inlet Concentration
  - Variable Inlet Gas Temperature/Water
- CO_2 Recycle – Constant Lean Loading
- Stripper Pressure – 0.3 to 4 atm
- Simple Packing Change-out

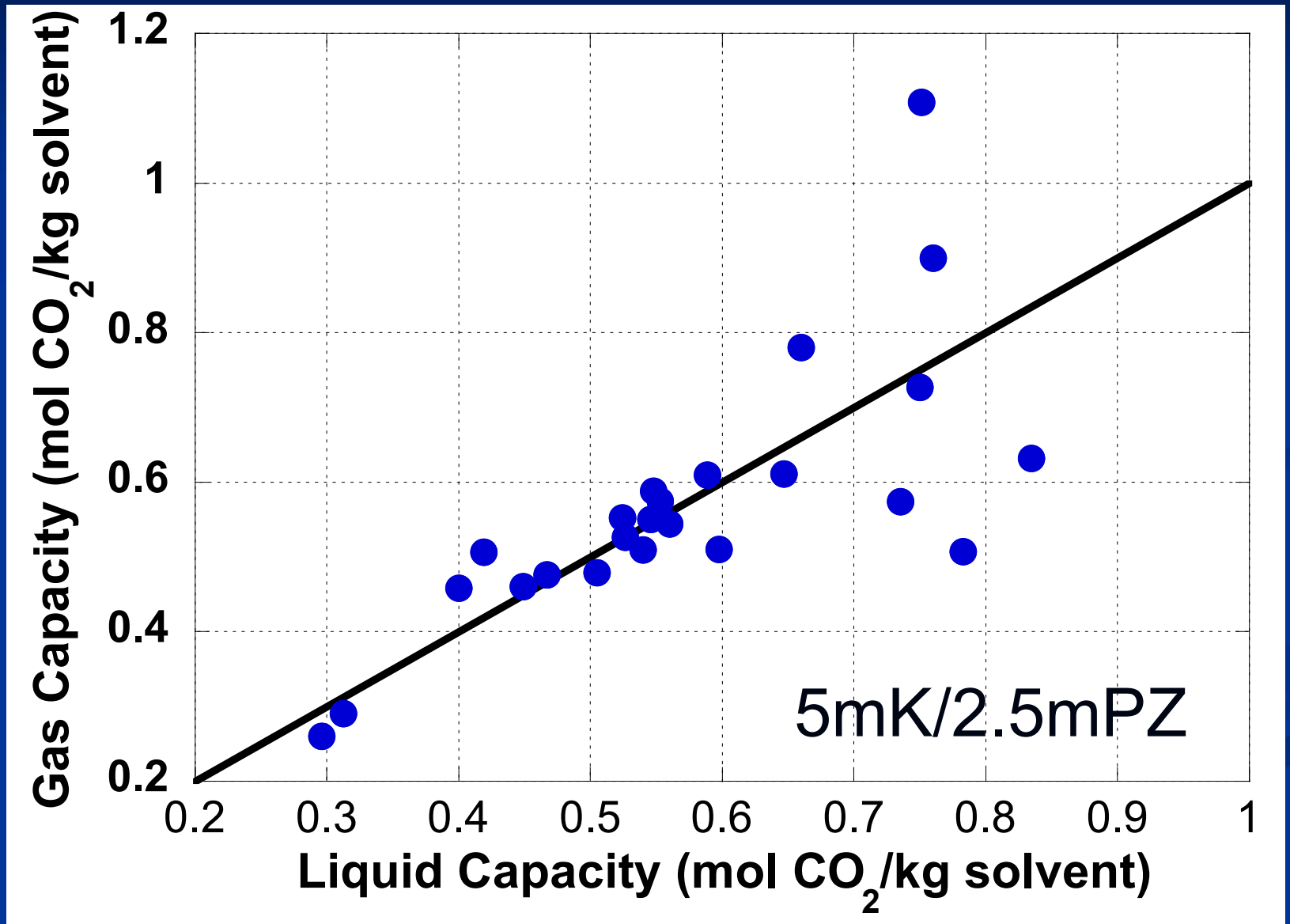
Pilot Plant Campaign Overview

Campaign	Solvent	Absorber Packing	Stripper Packing
1	5mK^+/2.5mPZ	Flexipac 1Y	Sieve Trays
2	5mK^+/2.5mPZ	Flexipac 1Y	IMTP#40
3	7 m MEA	Flexipac 1Y	IMTP#40
	7 m MEA	IMTP#40	Flexipac 1Y
4	5mK^+/2.5mPZ	Flexipac 2Y	Flexipac 2Y
	7.2mK^+/1.8mPZ	Flexipac 2Y	Flexipac 2Y

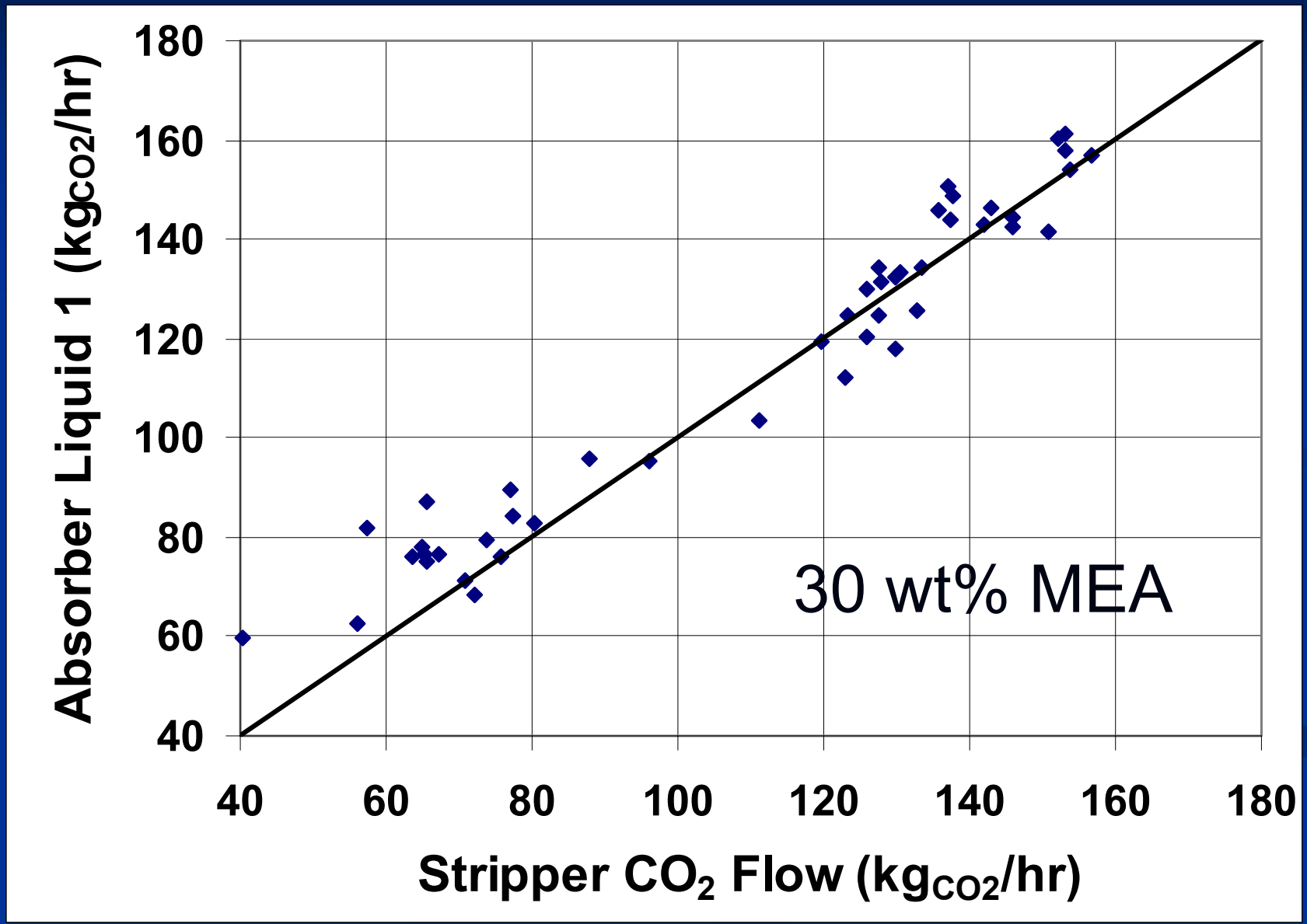
Analytical Methods

- CO_2 Gas Concentration
  - Vaisala (Absorber Inlet & Outlet)
  - Horiba (Absorber Middle and Outlet)
- CO_2 Loading
    - Total Inorganic Carbon (TIC)
    - Sample Bombs, Diluted with Chilled DI Water
- Water Balance – Online Density by MicroMotion™
- Titration – PZ, K, Total Alkalinity, MEA
- ICP – Potassium, Vanadium, Iron

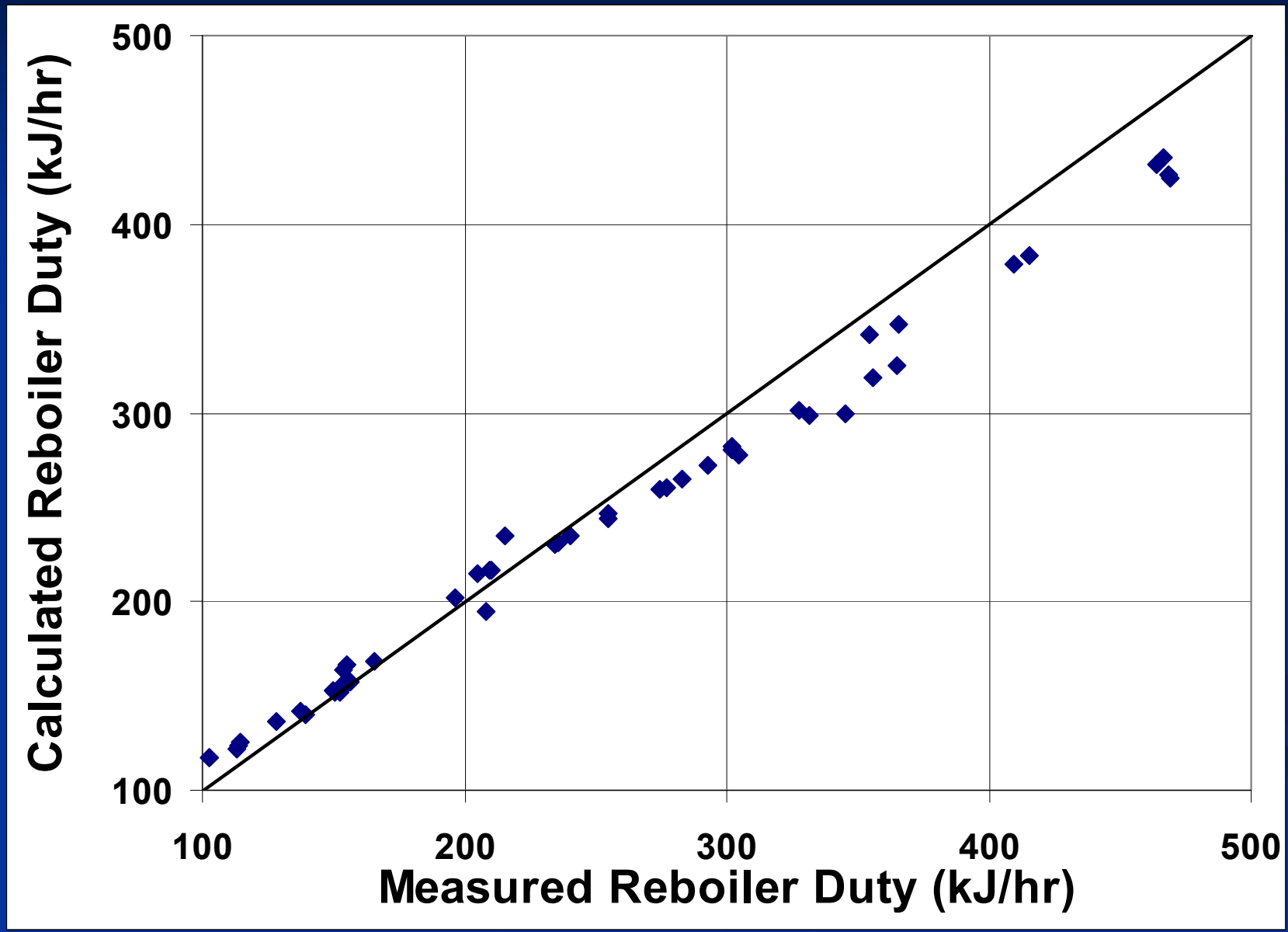
Campaign 2 - CO_2 Balance



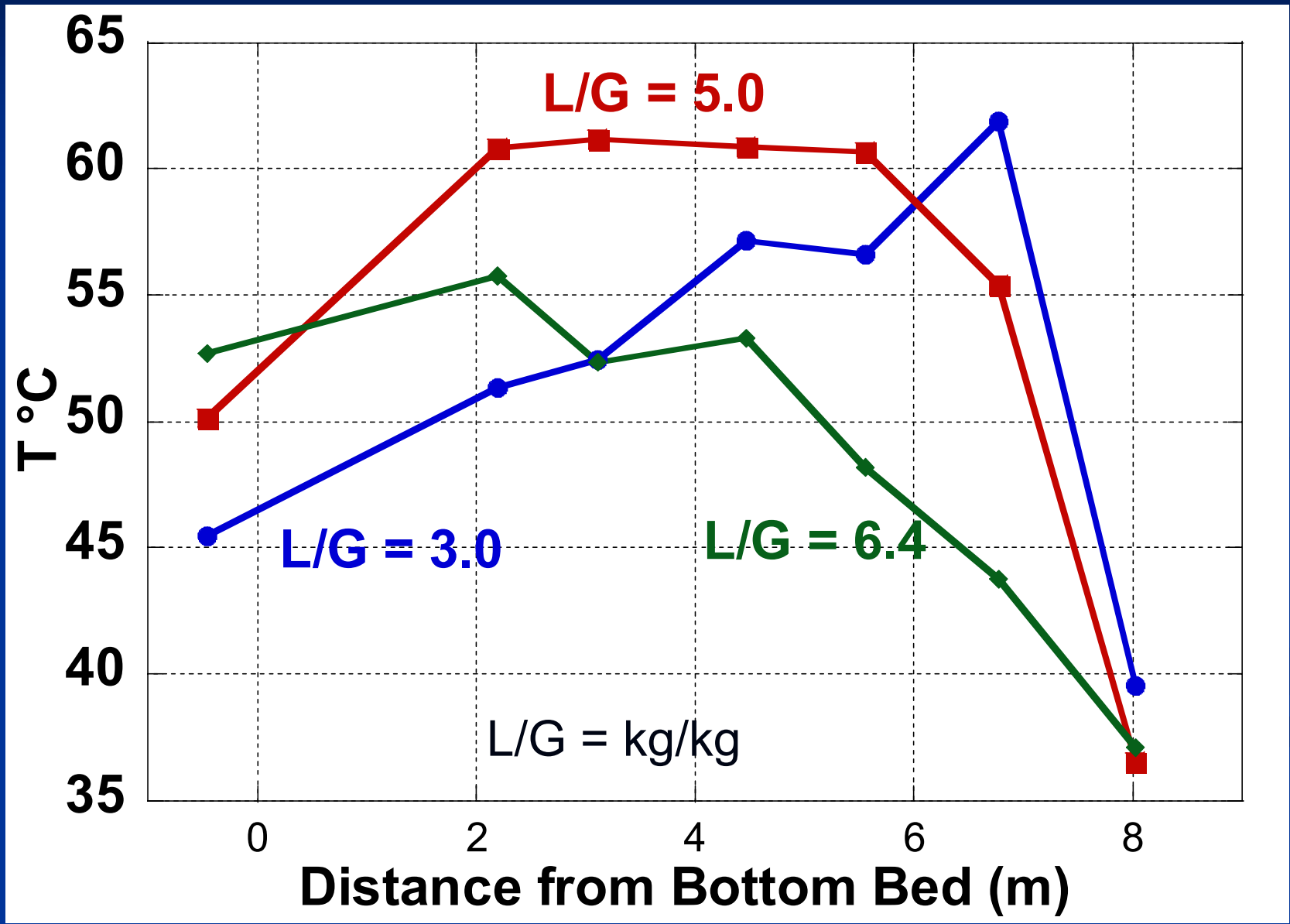
MEA Campaign - CO_2 Balance



MEA Campaign - Energy Balance



K^+/PZ Campaign 2 - Absorber Temperature Profiles (8 – 12.4% Inlet CO_2)



Absorber Rate Data Analysis

$$K_G a_{eff} = G \frac{CO_{2,IN} - CO_{2,OUT}}{\left(CO_2 - CO_2^*\right)_{LM}}$$

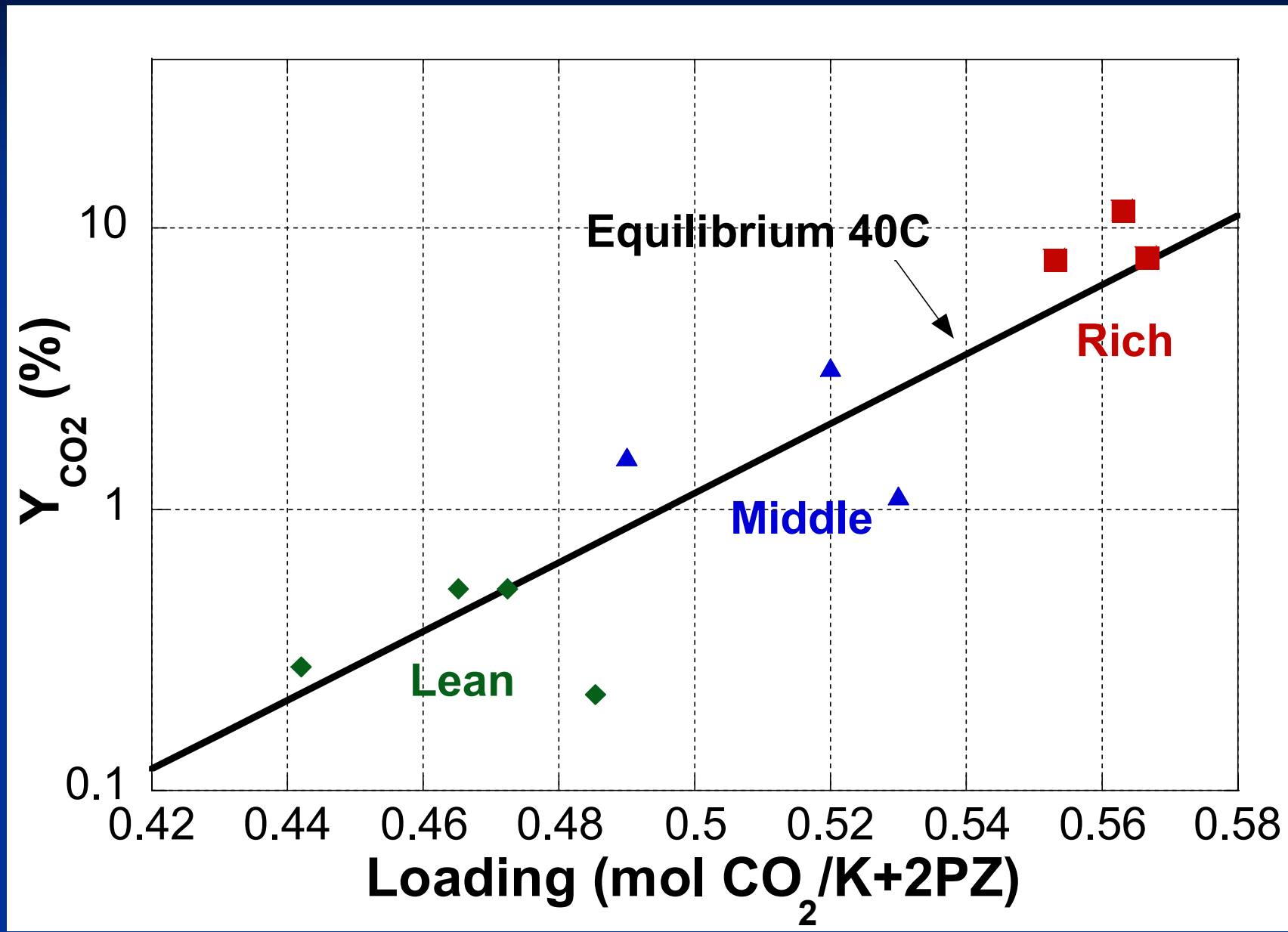
- G = Inlet Gas Rate
- a_{eff} = Correlated Effective Area from Hydroxide Data
- P_{CO2}^* from Model Fitted to Bench-scale VLE
- Calculated K_G for Top, Bottom and Overall Bed
- Validated Bench-scale VLE with Pinch Points
- Plot K_G against Average Loading Across Bed(s)

Absorber Rate Data Analysis

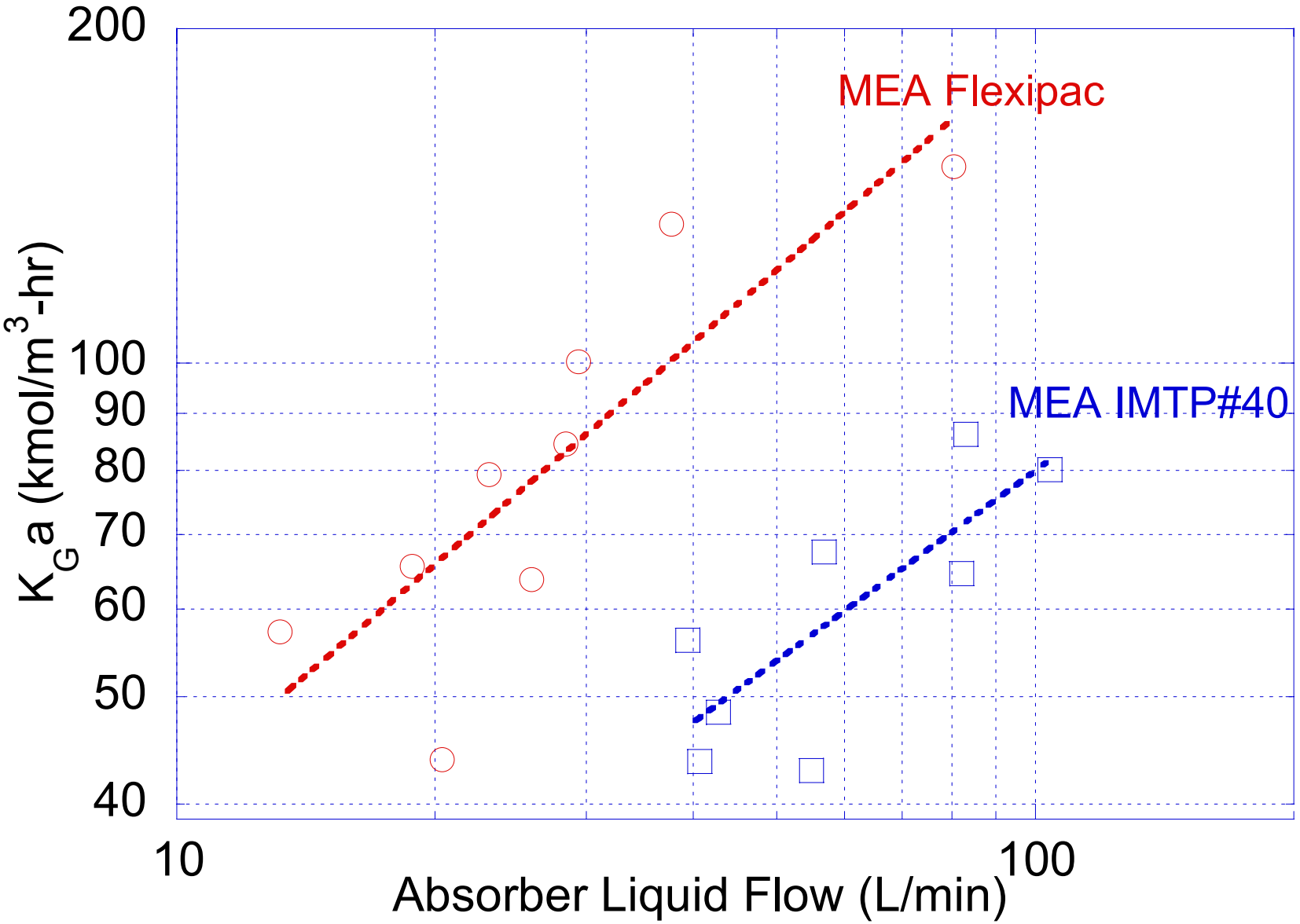
$$K_G a_{eff} = G \frac{CO_{2,IN} - CO_{2,OUT}}{\left(CO_2 - CO_2^*\right)_{LM}}$$

- G = Inlet Gas Rate
- a_{eff} = Correlated Effective Area from Hydroxide Data
- P_{CO2}^* from Model Fitted to Bench-scale VLE
- Calculated K_G for Top, Bottom and Overall Bed
- Validated Bench-scale VLE with Pinch Points
- Plot K_G against Average Loading Across Bed(s)

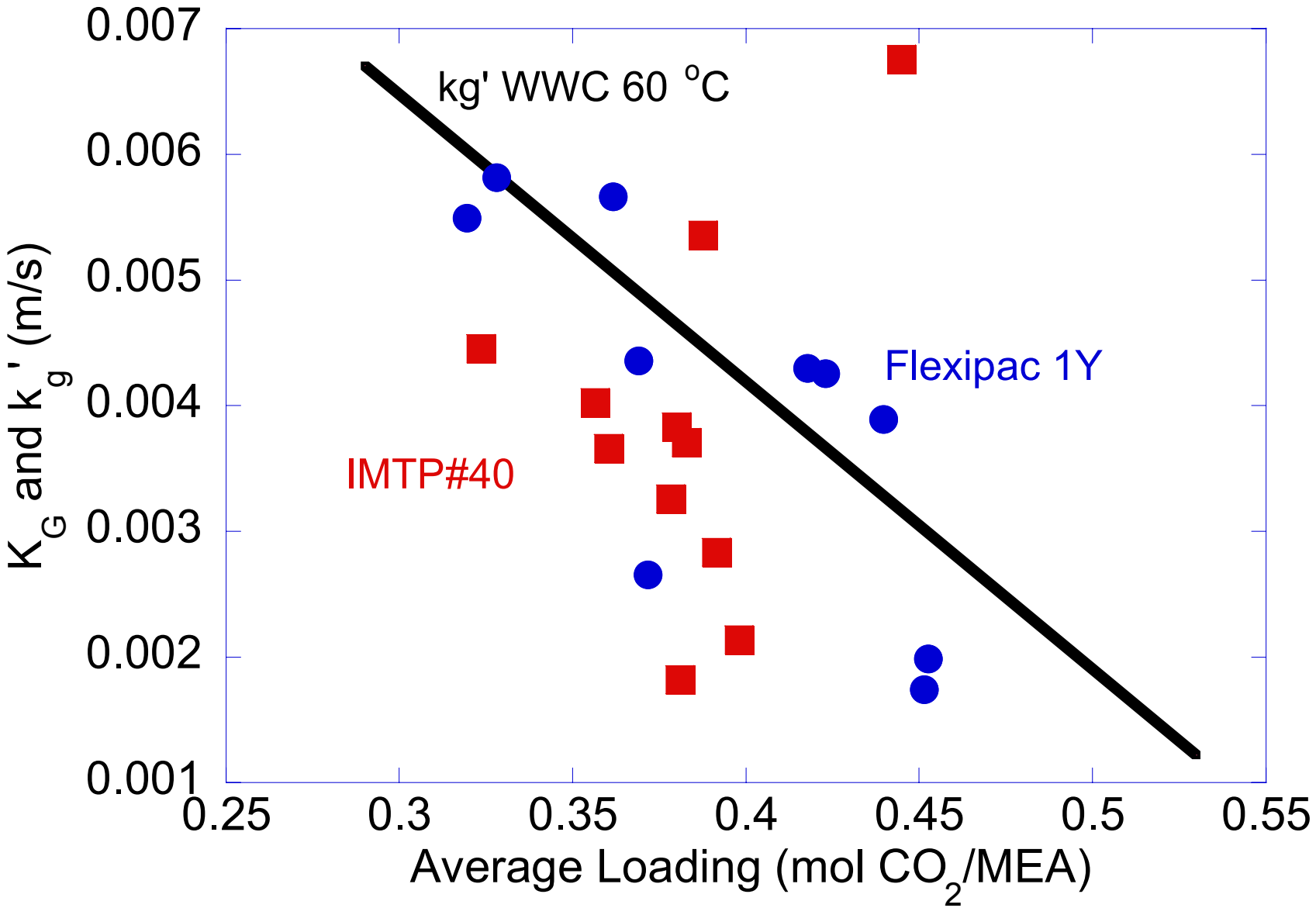
K^+/PZ Campaign 2 – VLE Pinch Analysis



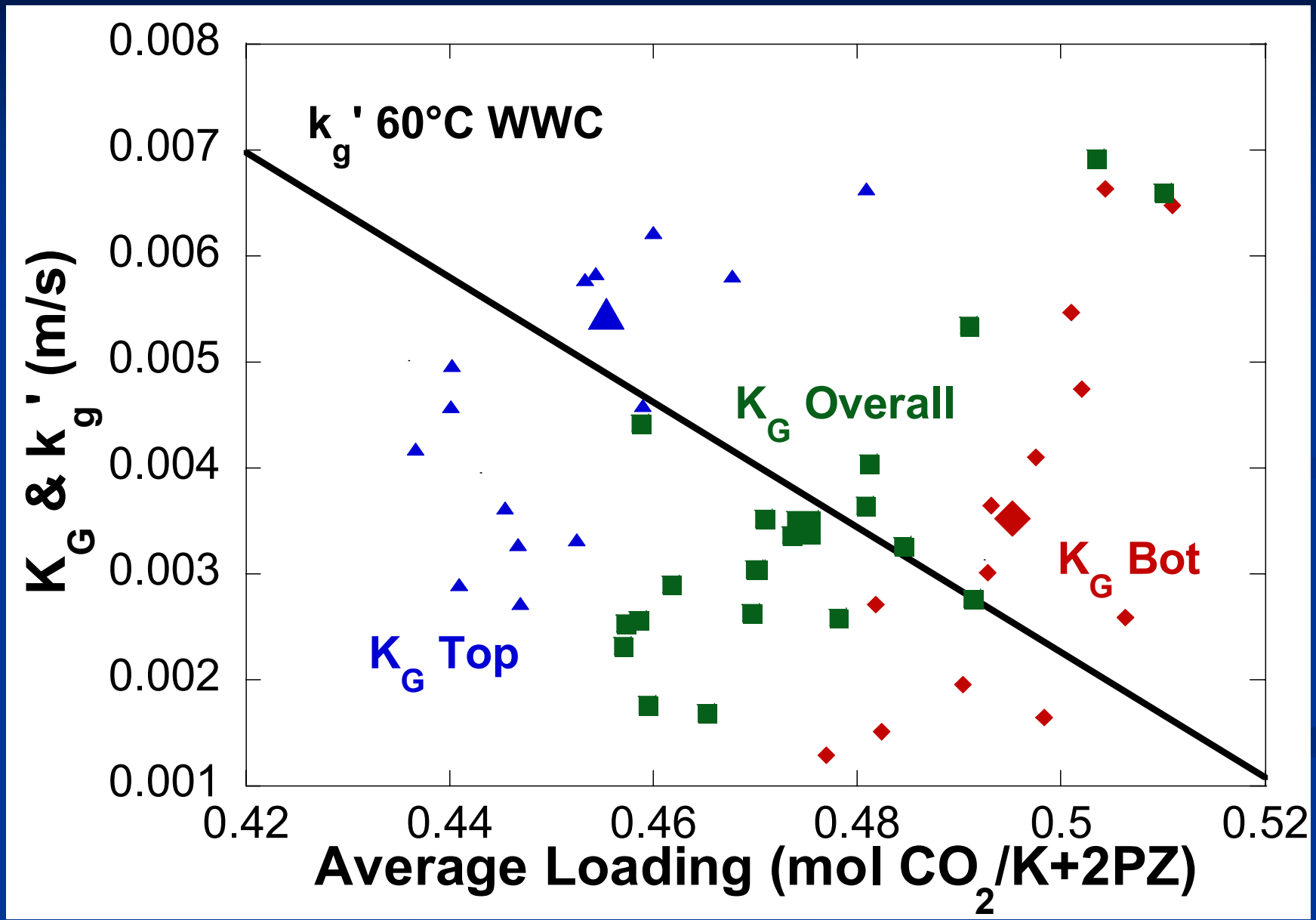
K^+/PZ MEA Rate Comparison



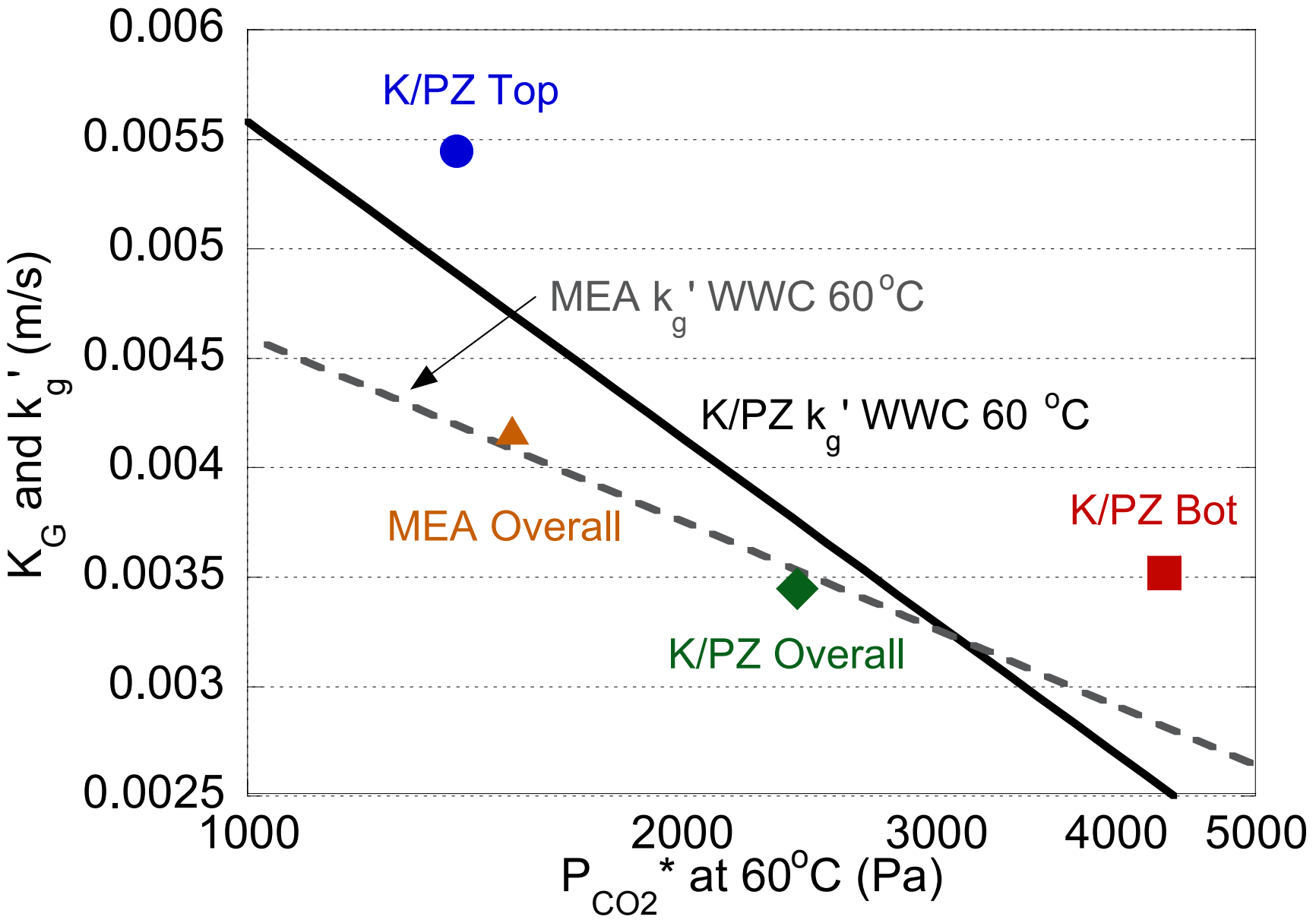
MEA Mass Transfer Results



K^+/PZ Campaign 2 – Mass Transfer Results



K^+/PZ MEA Rate Comparison



Pilot Plant Modification for Campaign 4 (C4)

- Inadequate Stripper Preheat - Cross-Exchanger (10^{o}C Approach)
- Variable Inlet Gas Temperature - Preheat with Steam Injection (40^{o}C)
- Foaming - Activated Carbon Filter
- Carbon Steel Reboiler - Stainless Steel (Replacement)
- FTIR – Inlet and Outlet (Volatility / CO_2 / H_2O)

Campaign 4 Summary

- Absorber/Stripper Packing – 6.1 m Flexipac 2Y (Structured)
- Solvent Systems
  - 5mK^+/2.5mPZ - Measure Performance with Optimized Packing (1.6 atm)
  - 7.2mK^+/1.8mPZ – (Vacuum)
    - Heat of Absorption ~50% Lower
    - Absorption Rate ~40% Lower than 5/2.5
    - Capacity 0-10% Higher than 5/2.5
- 12% Inlet CO_2
- 4 Lean Loadings for Each Solvent

Conclusions

- Flexipac 1Y – 2X's Better than IMTP#40
- 5mK^+/2.5mPZ CO_2 Absorption Rate Slightly Higher than MEA
- Matched Pilot to Bench-scale Data
  - VLE
  - Mass Transfer Coefficient
- Reliable and Publicly Available Data Set
- Temperature Bulge Varied from 18 to 33 °C with High CO_2

Support & Publications

- U.S. Department of Energy*
  - Detailed Quarterly Reports
    - http://www.osti.gov/bridge/basicsearch.jsp
    - Search for "CO2 capture by Absorption…"
- Industrial Associates Program for CO_2 Capture
  - http://www.che.utexas.edu/rochelle_group
- UT Separations Research Program
- EPA STAR Fellowship

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Development of a New Chemical Absorption System for CO_2 Capture

RITE

University of Texas, Austin, USA

3-4 October, 2005

Today's Contents

1. Outline of the "COCS" project

2. Fundamental research on new absorbents

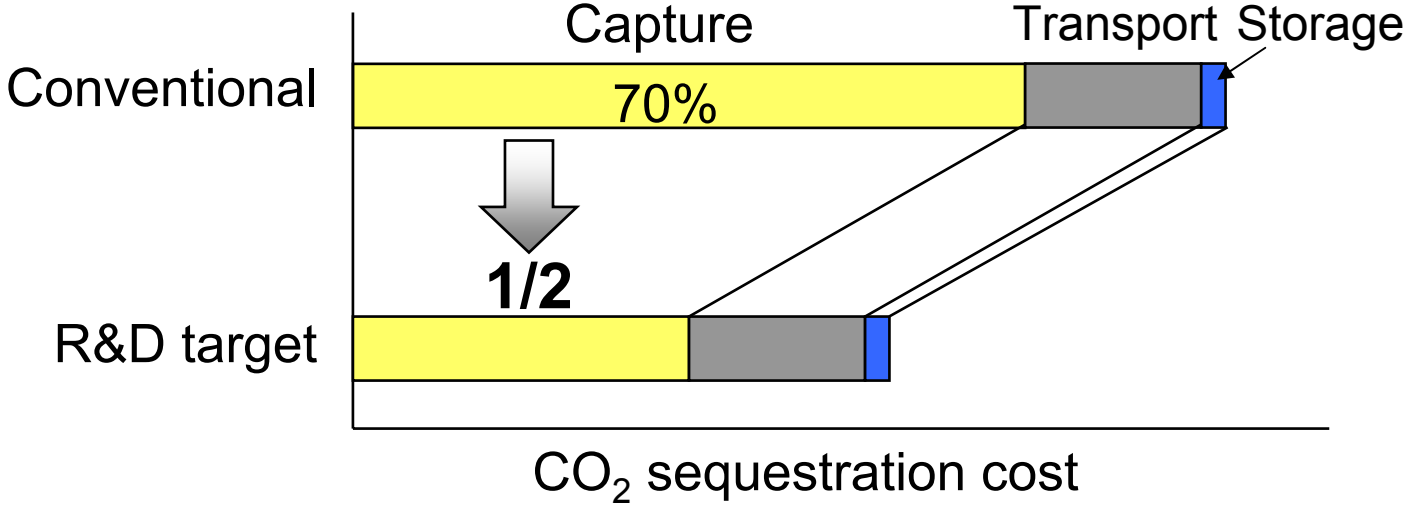
   - Ideas to find new absorbents
   - Research results in 2004

R&D Target of COCS Project

"COCS" Project: (Cost-Saving CO_2 Capture System)

Chemical Absorption Process

(Features: Immediate and Large-scale)

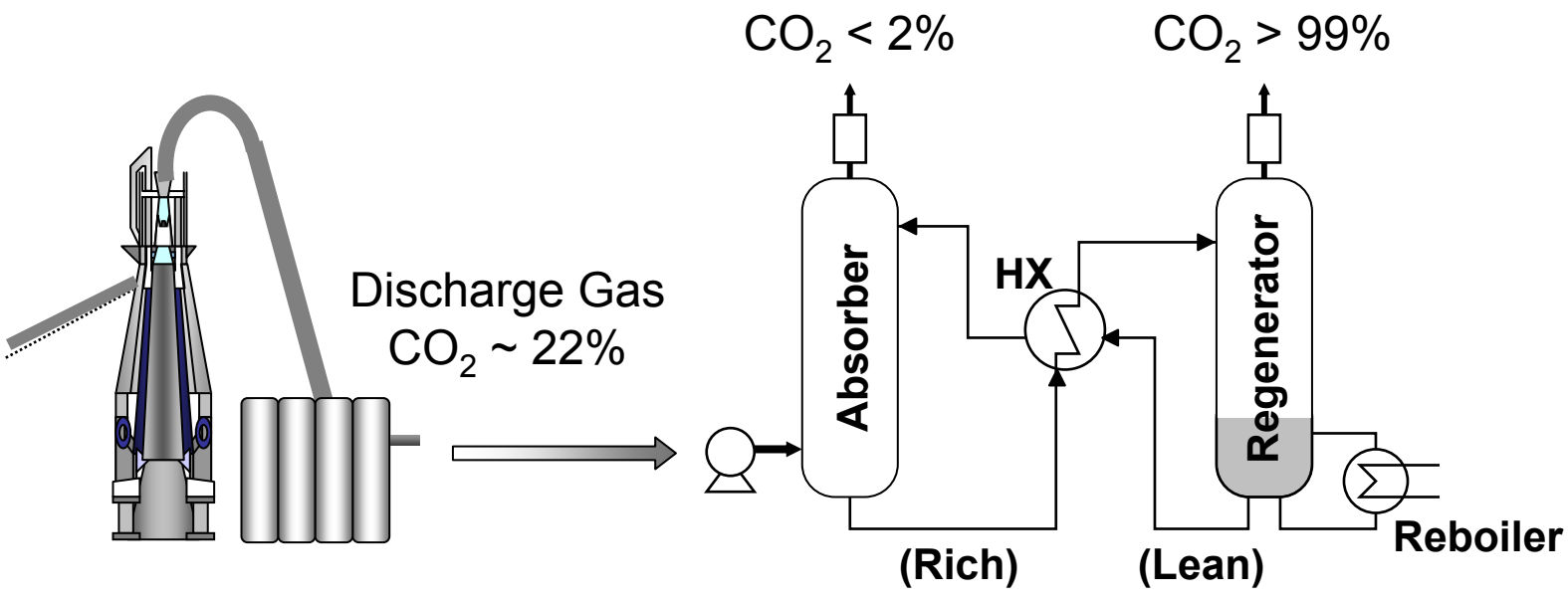


Concepts of COCS Project

RITE
Research Institute of Innovative Technology for the Earth

Steel Plant, etc.

Chemical Absorption



- High CO_2 conc.
- New absorbent
- Utilization of low-grade waste heat

⇒ Decrease of Capture Cost

Objectives of COCS Project

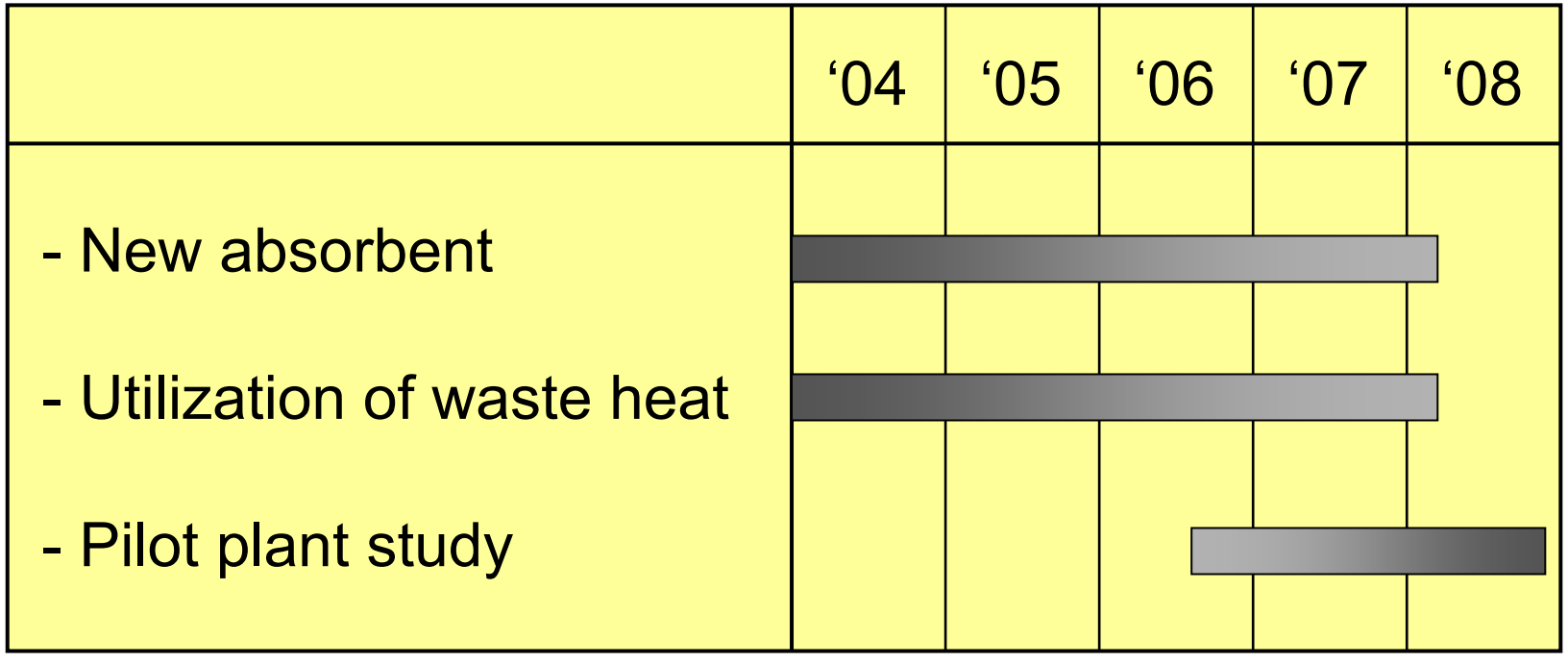
RITE
Research Institute of Innovative Technology for the Earth

1. Develop new absorbent for low-temperature and low-energy regeneration

2. Establish CO_2 capture system for steel plant
   1) Utilization of low-grade waste heat
   2) Removal of CO_2 from high CO_2 concentration discharged gas

3. Demonstrate total system by pilot plant study

Schedule of COCS Project



Fundamental Research on New Absorbents

- Screening
- Vapor-liquid equilibrium
- Heat of reaction
- Corrosion
- Kinetics
- Bench-scale experiment
- Molecular dynamics calculation

etc.

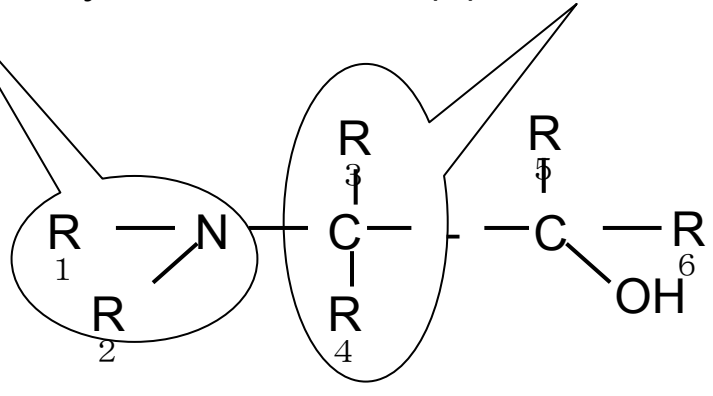
Ideas to Find New Absorbents (1)

Desirable characteristics of absorbents:

1. Regeneration with low energy use
2. High absorption/desorption rate
   and regeneration under low temperature

(1) Secondary/Tertiary amine

(2) Effect of steric hindrance



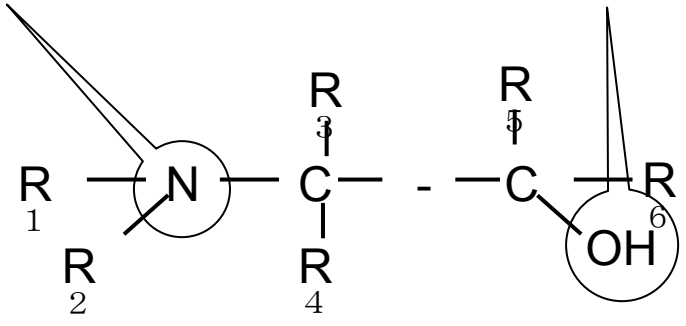
Ideas to Find New Absorbents (2)

Desirable characteristics of absorbents:

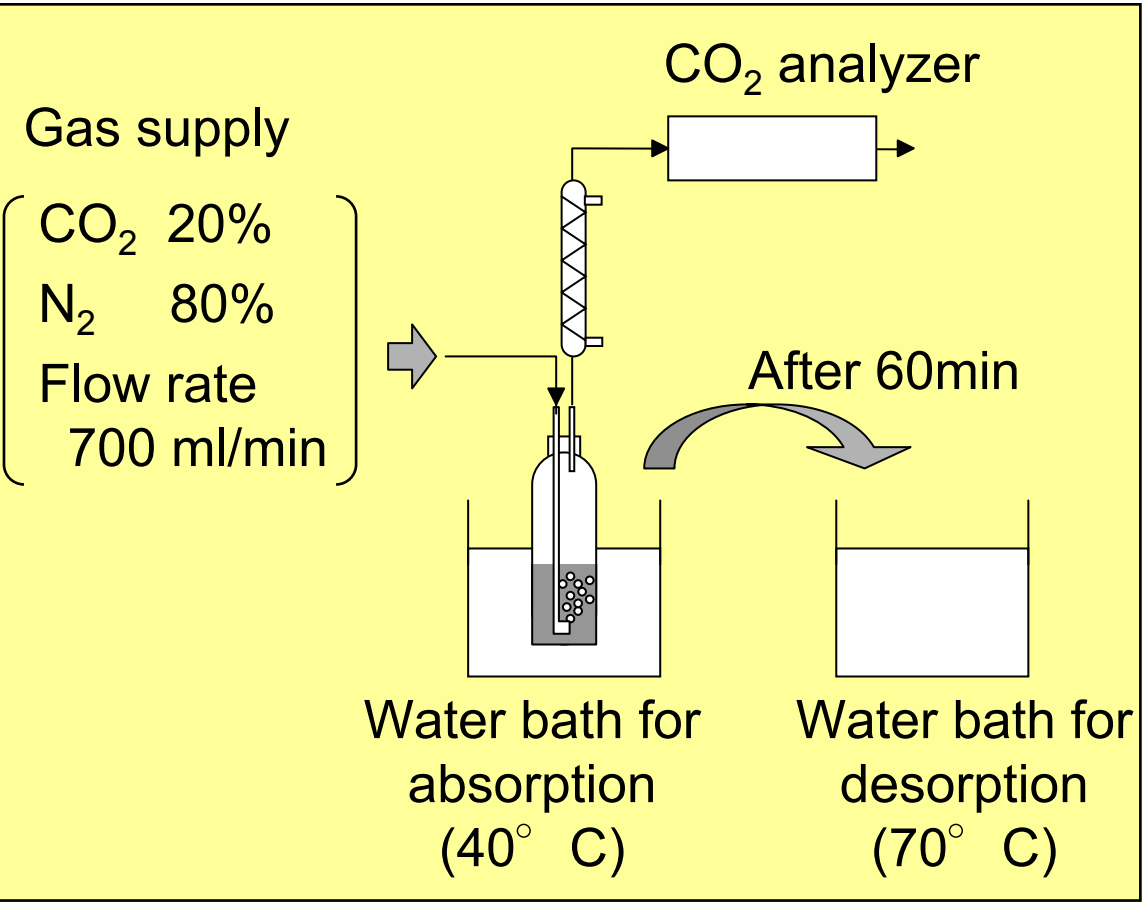
1. High capacity of CO_2 capture
2. Low volatility and high stability

(1) High density of amino group

(2) Position and number of OH-



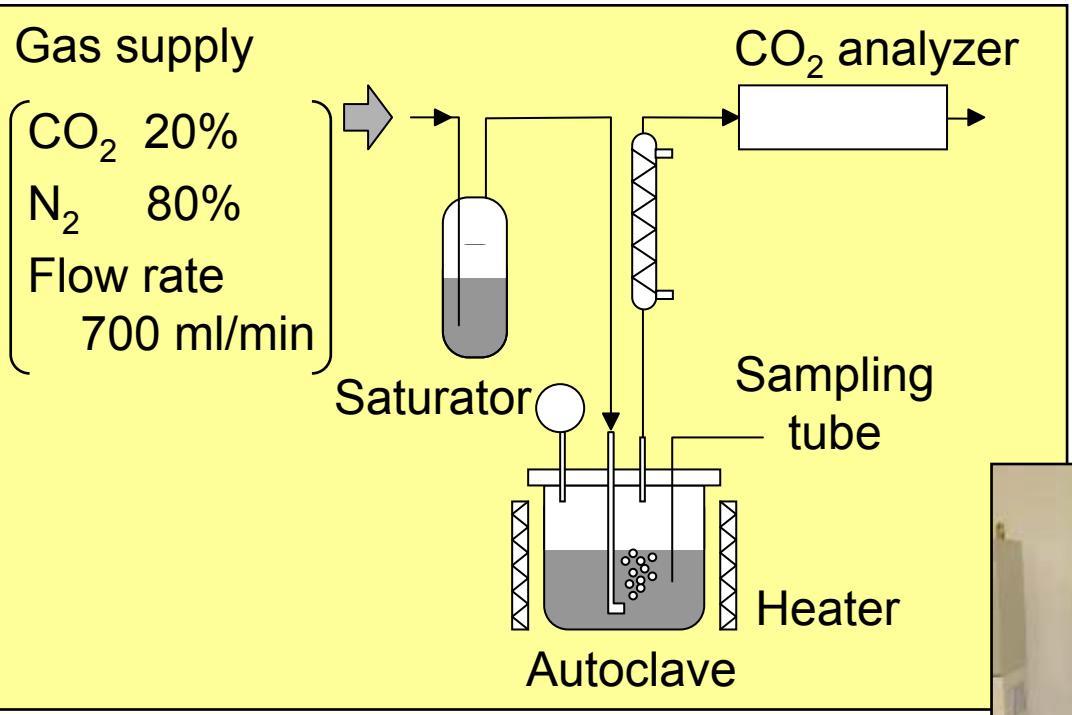
Screening Test Apparatus



Absorbent : 50 ml
Absorption time : 60 min

Photo. Screening apparatus with six glass absorbers

Vapor-liquid Equilibrium Apparatus



CO2 conc. in liquid phase

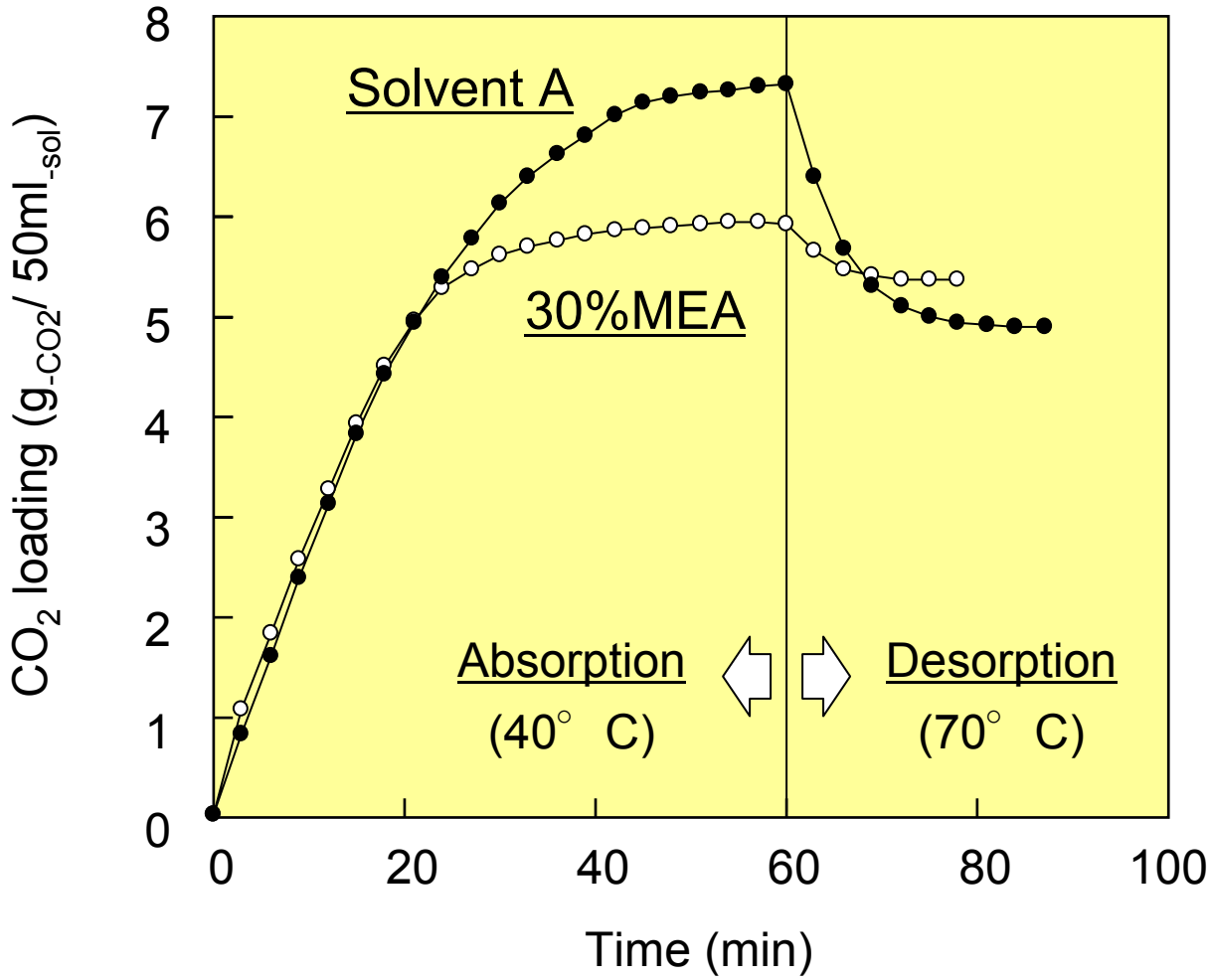
(Total organic carbon analyzer

Experimental condition

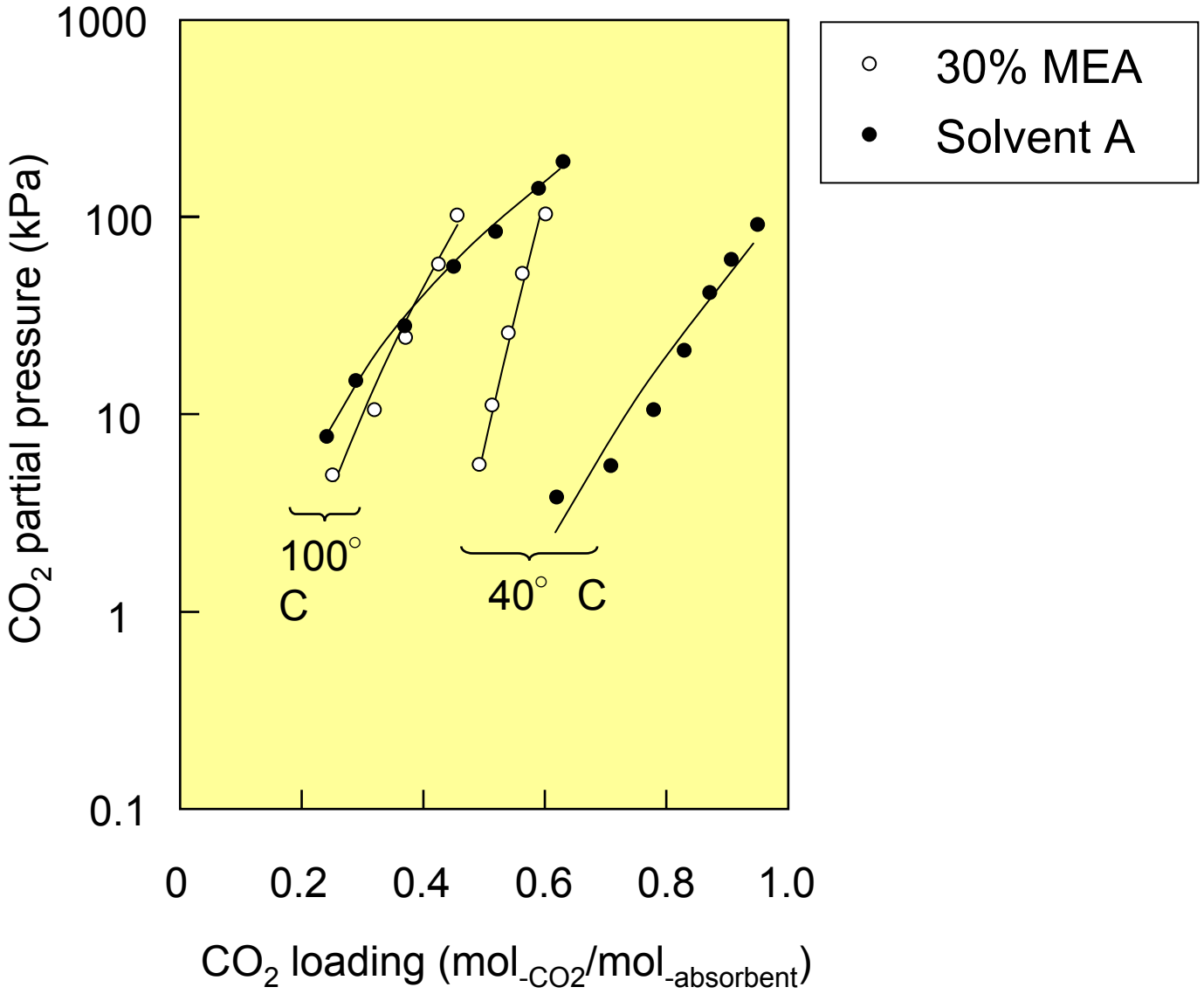
Absorbent :	700 ml
Temperature : 120 ° C	~
Pressure :	~ 1MPa

Capacity of CO_2 Capture

Solvent A : Newly-developed absorbent in 2004



Vapor-Liquid Equilibrium



Heat of Reaction

	Solvent A	30% MEA
kJ/mol_{-CO2}	74	85

(CO_2 loading : 0.5 $mol_{-CO2}/mol_{-absorbent}$)

(Experimental condition)

Apparatus : Adiabatic calorimeter
Absorbent : 200 ml
Gas : CO_2 100%
Gas flow rate : 200 ml/min

Corrosion

	Solvent A	30% MEA
Weight loss (mg/mm^2)	0.0063	0.0948
Corrosion rate (mm/year)	0.15	2.20

(Experimental condition)

Absorbent : 700 ml
CO_2 loading : Rich solvent (CO_2-saturated)
Test piece : Carbon steel (SS400), 25x20x2 mm
Testing time : 48 h
Temperature : 130 ° C

Summary

Results in 2004:

1) Start-up of the project and declaration of its objectives.
2) Development of the new absorbent with higher-performance than MEA.

Future Work :

- Develop higher-performance absorbents.
- Utilize low-grade waste heat.
- Demonstrate pilot plant study.

Sponsorship and Collaboration

COCS project is financially supported by Ministry of Economy, Trade and Industry (METI),

and carried out with collaboration from three Japanese companies:

- Nippon Steel Co.
- Mitsubishi Heavy Industries, Ltd.
- The Kansai Electric Power Co., Inc.

Experimental validation of a model for CO_2 post-combustion capture using monoethanolamine (MEA)

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Sintef Research , Department of Materials and Chemistry,
Sem Sælands Vei 2a, Norway

8th International CO_2 Capture Network
University of Texas, Austin
3-4 October 2005

Objective

- The objective of this work is to validate a rigorous simulation program with data from a pilot plant available in our labs.
- In order to properly understand the mechanisms associated with this removal technology, for accurate plant design, and for process improvement, precise modeling of this entire process is of importance.

Outline:

- Description of pilot plant
- Modeling aspects
- Simulation results absorber
- Preliminary simulation results desorber section
- Conclusions

Pilot plant [1]

- Processes about 150 Nm3/hr with a recovery rate of about a 10 kg/hr.
- Fully computerized
- Data was obtained during continuous operation over a time period of 3 months.
  - The lower range of the loading interval was utilized first, and later during testing, higher loading ranges were tested and so forth.
- 3 loading ranges for MEA.
- 0,18-0,30 range 1
- 0,31-0,40 range 2
- 0,41-0,45 range 3

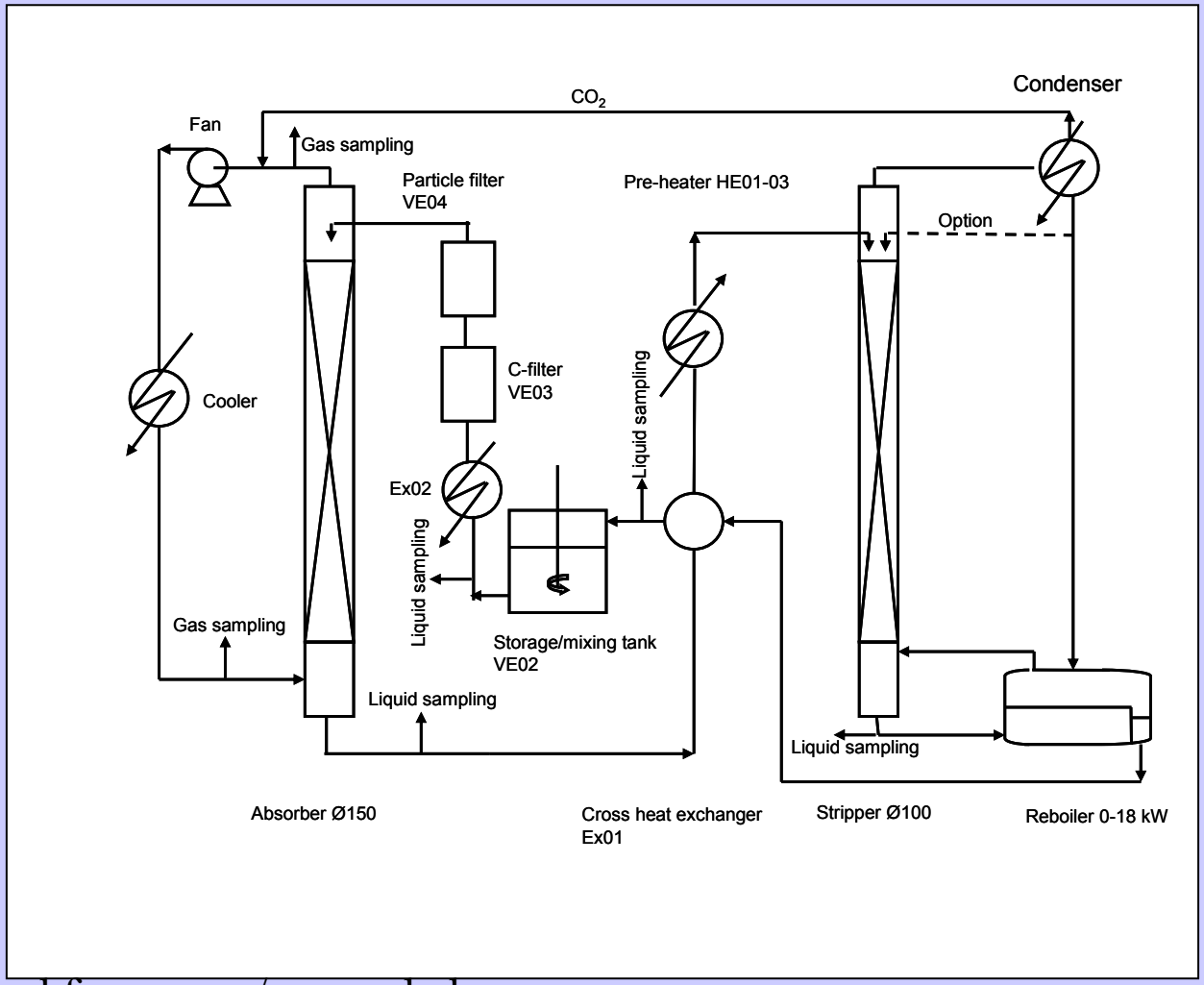
Pilot plant [2]: Process description

Data acquisition:

- Gas flow rate
- Liquid flow rate
- CO_2 flow rate
- Reboiler T,P
- Reb. Steam T,P
- CO_2 production
- Profiles in packing
- T,P pipes

Liquid Samples:

- Composition



- Remaining data found from mass/energy balance

Pilot plant [3]

Absorber characteristics

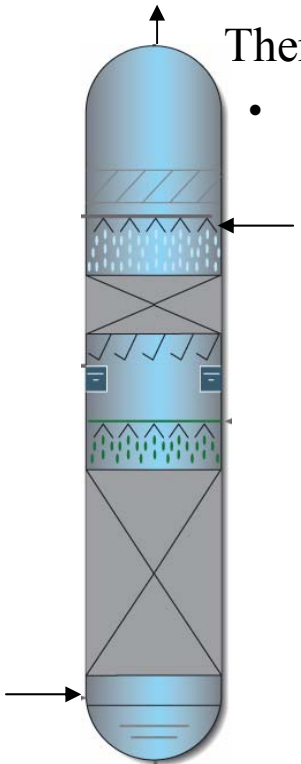
Column internal diameter (m)	0.15
Packing height (m)	4.36
Packing (structured):	Shulzer Mellapak 250Y

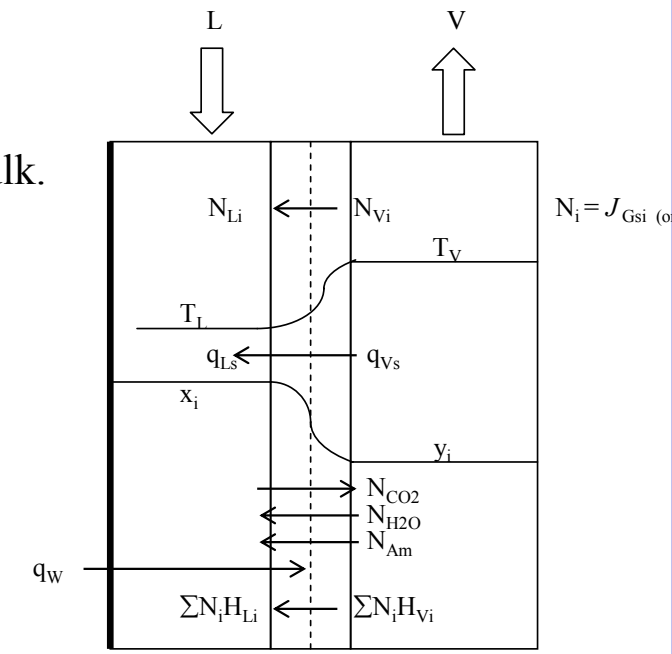
Parameter:	Value
MEA concentration wt% (15°C)	30.2
Rich solution loading max	0.45
Lean solution loading min	0.18
Temperature lean stream to absorber (°C)	40-43
Temperature rich stream out of absorber (°C)	47-50
Absorber pressure (kPa A)	~100
Condenser temperature (°C)	~25
Reboiler heat duty (kW)	3-13

Modeling approach [1]

In general:

- Flow model.
  - Includes separate equations for mass and energy transfer in the liquid an gas phases.
- G/L Interface model.
  - Sub-model that accounts for the rate of reaction on interfacial mass transfer.
- Thermodynamic model.
  - Sub-model giving the chemical reaction equilibrium relationship in the bulk liquid.
    - Dissociation of species in the liquid bulk.
    - Vapor-liquid of the acid gas species.





Modeling approach [2]

- Written in Fortran 90.
- A gas/liquid interface model is developed based on the penetration theory (transport equations for all reacting species) and solved using advanced numerical techniques
  - (MOL: stiff integrator, adaptive grid at the interface)
  - Simpler and faster interfacial models can also be used in the present simulator (Enhancement factor models). Must assume reaction regimes.
- Emphasis has been put on the adaptability of the code for different systems.
  - all subprograms within the main module are developed using standardized syntax and unit operations are modularized to ease changing spread sheet configuration if that is required

Model [3]: Base case model setup

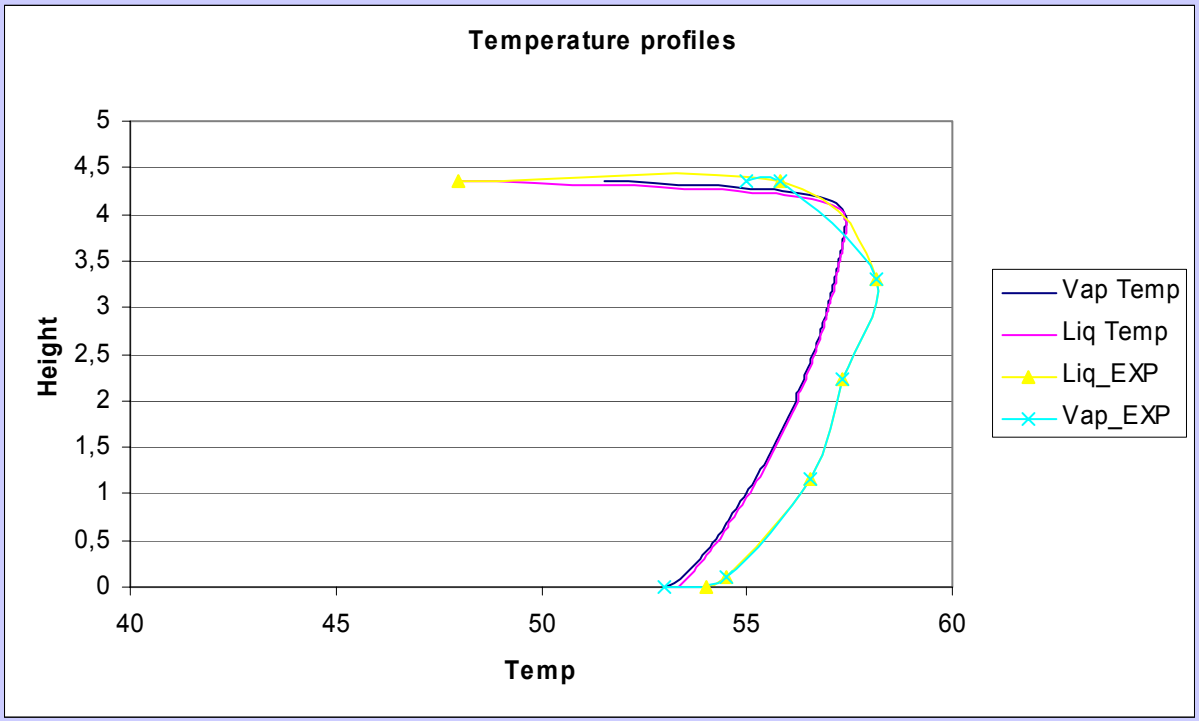
Routines	***Type***	***Validity***	***Reference***
Interfacial mass transfer model	Numerical penetration model (adaptive grid)	All reaction regimes	
Contact time routine	Lumped parameter	Ambient pressure	Billet (1995)
Equilibrium model data fit	Regression to VLE data from NTNU/Sintef Liquid phase speciation described with the use of a modified Kent-Eisenberg model	25-120˚C	NTNU/Sintef report

Model validation: Absorber

- The model was tested against all the obtained experimental data, which included 21 data acquisition periods, during the continuous pilot rig operation.
- The following data were used as basis:
  - The fully described incoming liquid stream and incoming gas stream to the absorber, *molar flow rate, F; xi and yi; T, p.*
  - The fully described outlet liquid stream and outlet gas stream of the absorber, *molar flow rate, F; xi and yi; T, p.*
  - 5 temperature probes through the absorber packing to capture the temperature profile.

Simulation Results:

Temperature profiles (loading ranges 1, 2, and 3)



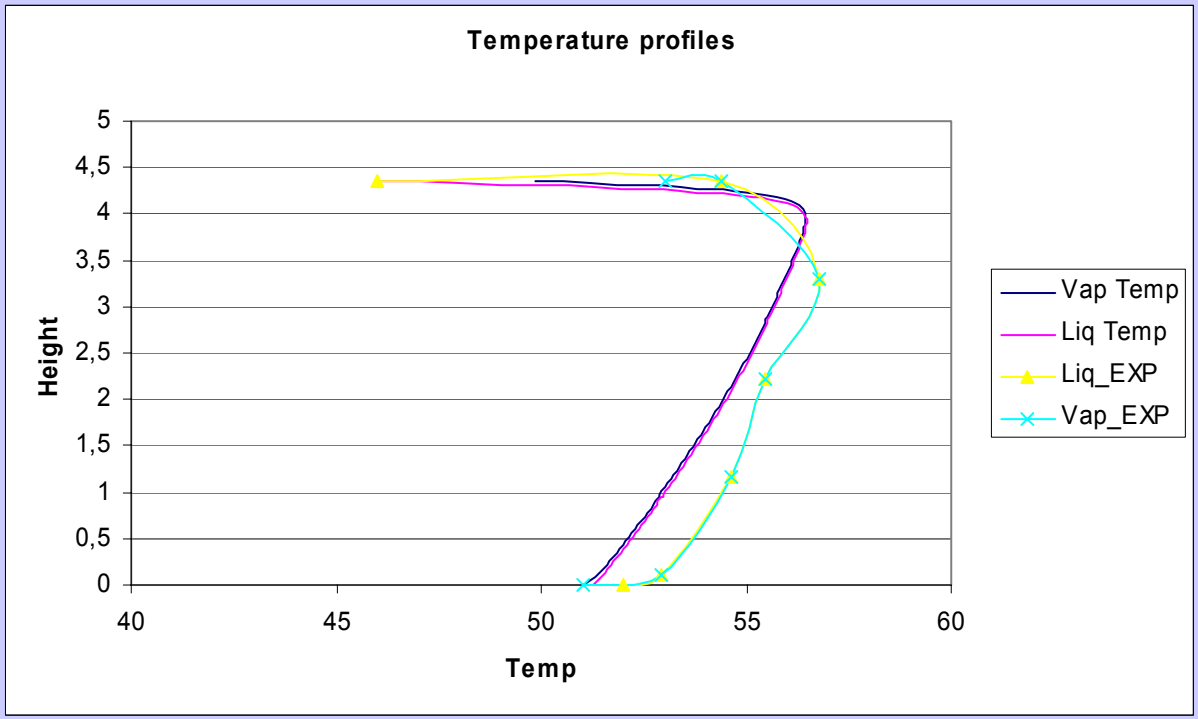
LOADING RANGE 1

Loading range 1 (14.03.2005 par 1): experiment: 0.217-0.333, simulated: 0.217-0.334

Loading exp		0,217	0,333	CO_2 transfer absorber: 4,561 kg
Loading sim	pen. model	0,217	0,335	CO_2 transfer absorber: 4,620 kg

Simulation Results:

Temperature profiles (loading ranges 1, 2, and 3)



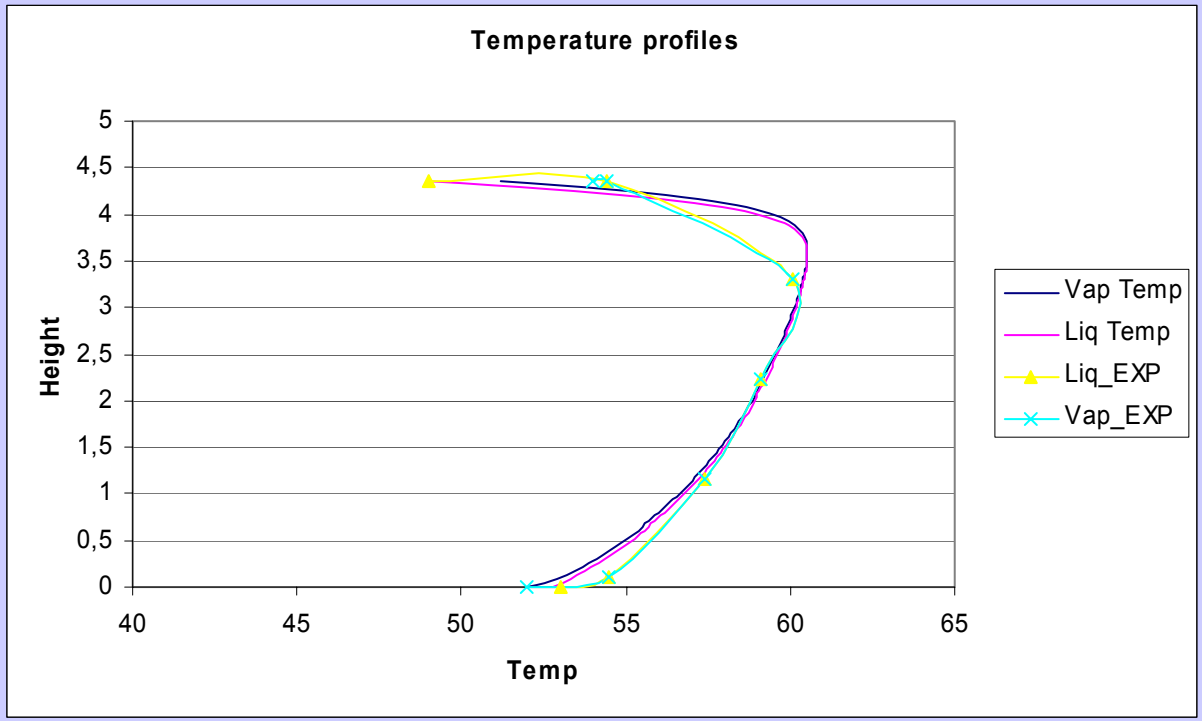
LOADING RANGE 2

Loading range 2 (16.03.2005 par 1): experiment: 0.307-0.400, simulated: 0.307-0.409

Loading exp		0,307	0,400	CO_2 transfer absorber: 3,819 kg
Loading sim	pen. model	0,307	0,409	CO_2 transfer absorber: 4,004 kg

Simulation Results:

Temperature profiles (loading ranges 1, 2, and 3)



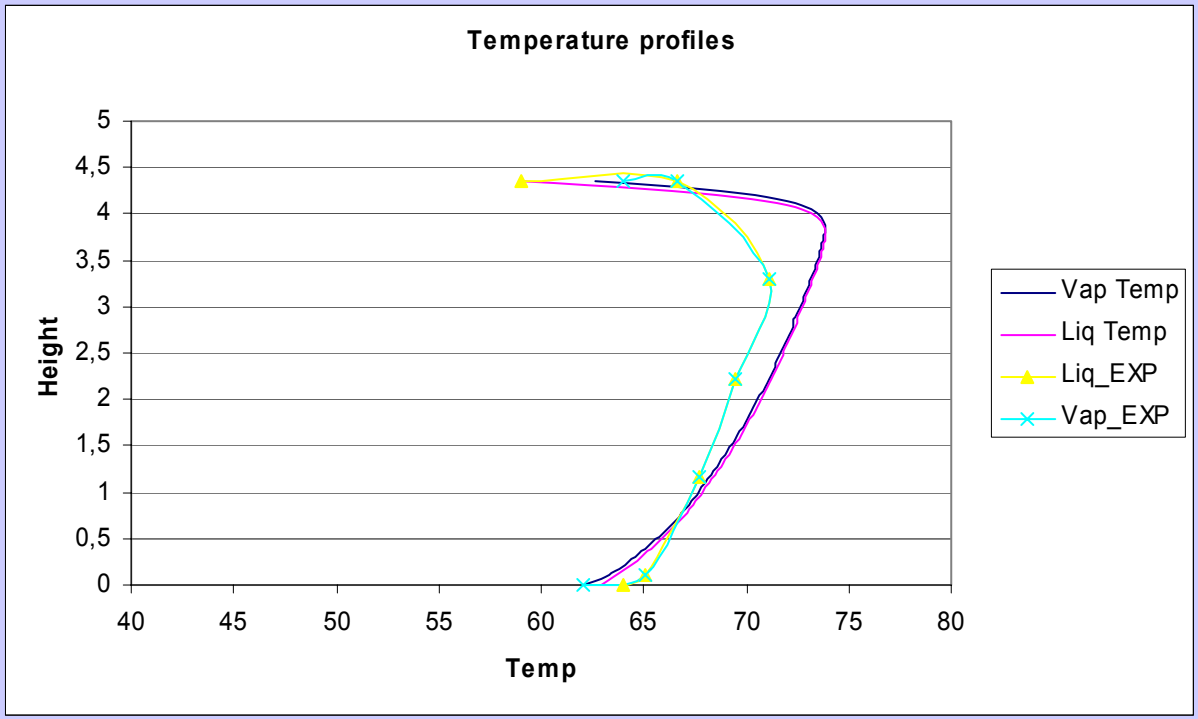
LOADING RANGE BETWEEN 1 and 2

Loading range between 1 and 2 (11.03.2005 par 1): experiment: 0.284-0.345, simulated: 0.284-0.347

Loading exp		0,284	0,345	CO_2 transfer absorber: 4,487 kg
Loading sim	pen. model	0,284	0,346	CO_2 transfer absorber: 4,522 kg

Simulation Results:

Temperature profiles (loading ranges 1, 2, and 3)

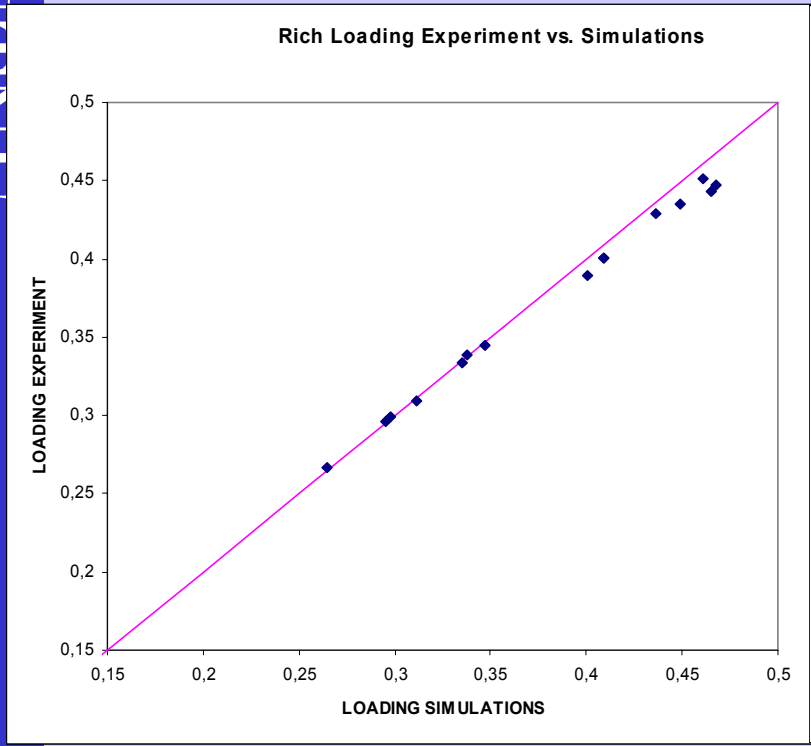


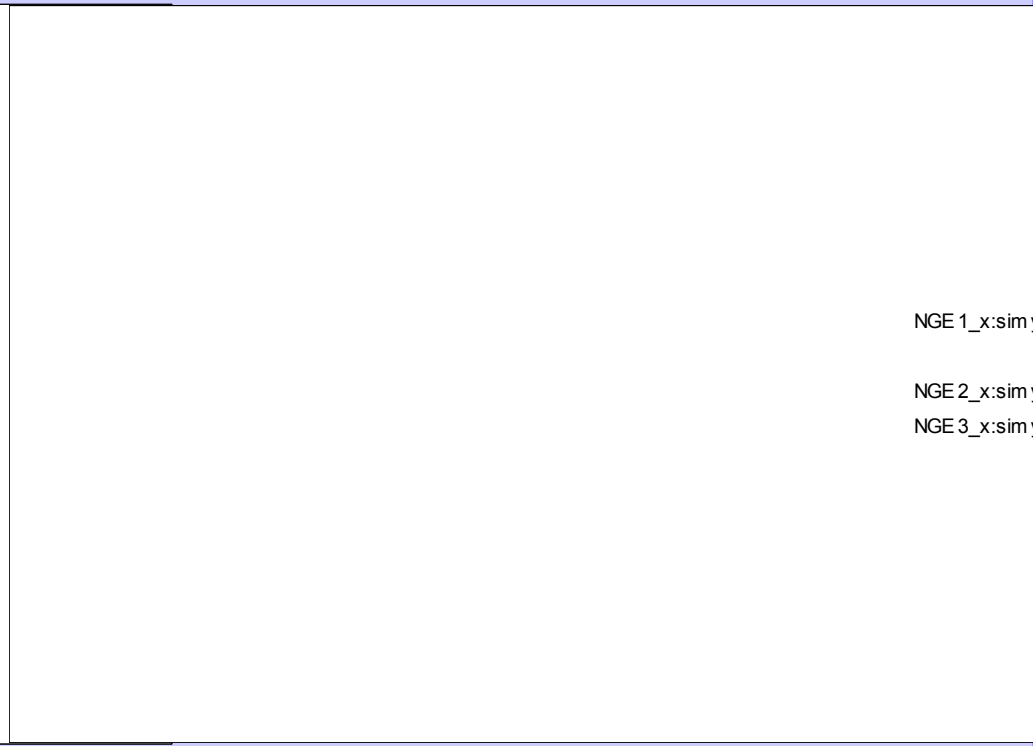
LOADING RANGE 3

Loading range 3 (17.03.2005 par 2): experiment: 0.357-0.434, simulated: 0.357-0.441

Loading exp		0,357	0,434	CO_2 transfer absorber: 9.404 kg
Loading sim	pen model	0,357	0,441	CO_2 transfer absorber: 10.079kg
Loading sim	Pseudo 1st order	0,357	0,449	CO_2 transfer absorber: 11.016kg

All obtained experimental data



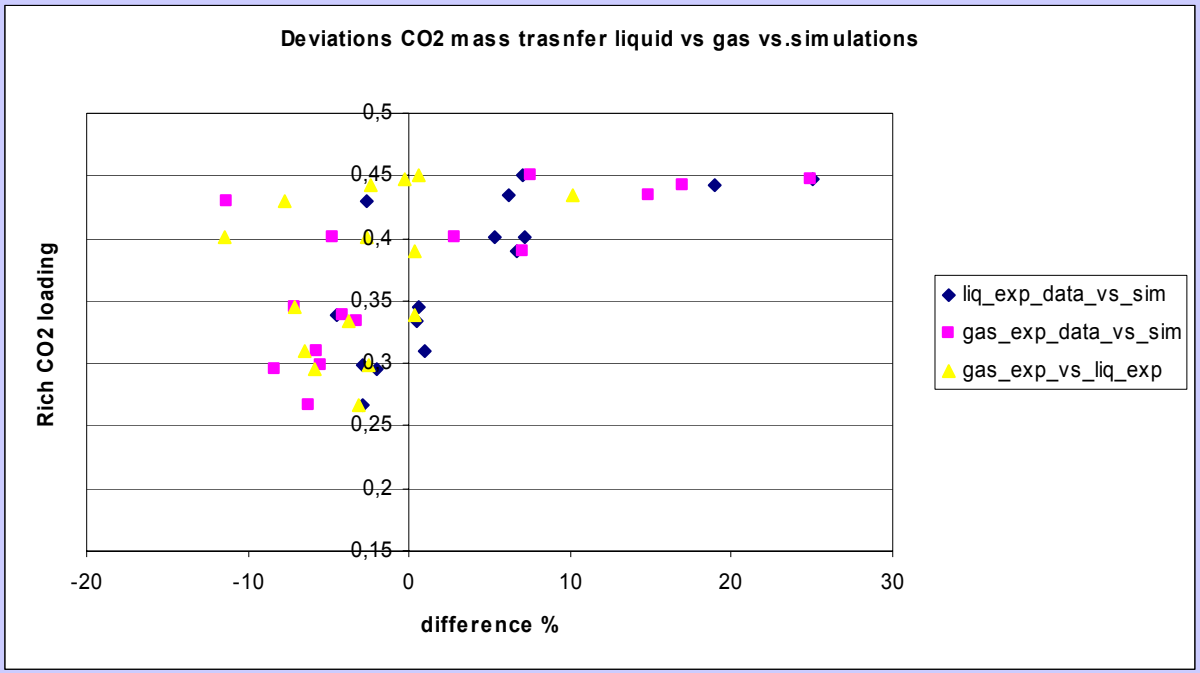


Rich loading from analysis

CO_2 mass transfer based on the liquid side

It is clear that the deviations start becoming larger as the loading range increases.
The 3 loading range indicated by the red crosses and black crosses

Deviations CO_2 mass transfer liquid/gas



- Since the experimental liquid and gas phase mass transfer rates are calculated independently, the measured differences and, thus, the variability can be found
- AAD - a measure of the variability of a dataset

Exp. data vs. BASE CASE Simulations	Exp liq/sim data	Exo gas/sim data	% error liq/gas
Absolute Average Deviation (%)	6,22	8,93	3,46

Sources of errors, model:

- The use of the complete numerical solution of the penetration model will account for the possible different reaction regimes.
  - Accounts for deviations from pseudo 1st order reaction
- The lumped parameter describing the contact time
  - describes all the hydrodynamic properties in the packing
  - the effective interfacial area
- Reaction rate expression less accurate at higher temperature
  - Arrhenius exponential extrapolation might not be valid, as shown by Aboudheir et al.
- Uncertainties associated with the equilibrium data.

  - Sensitivity tests should be carried out.
    - equilibrium data

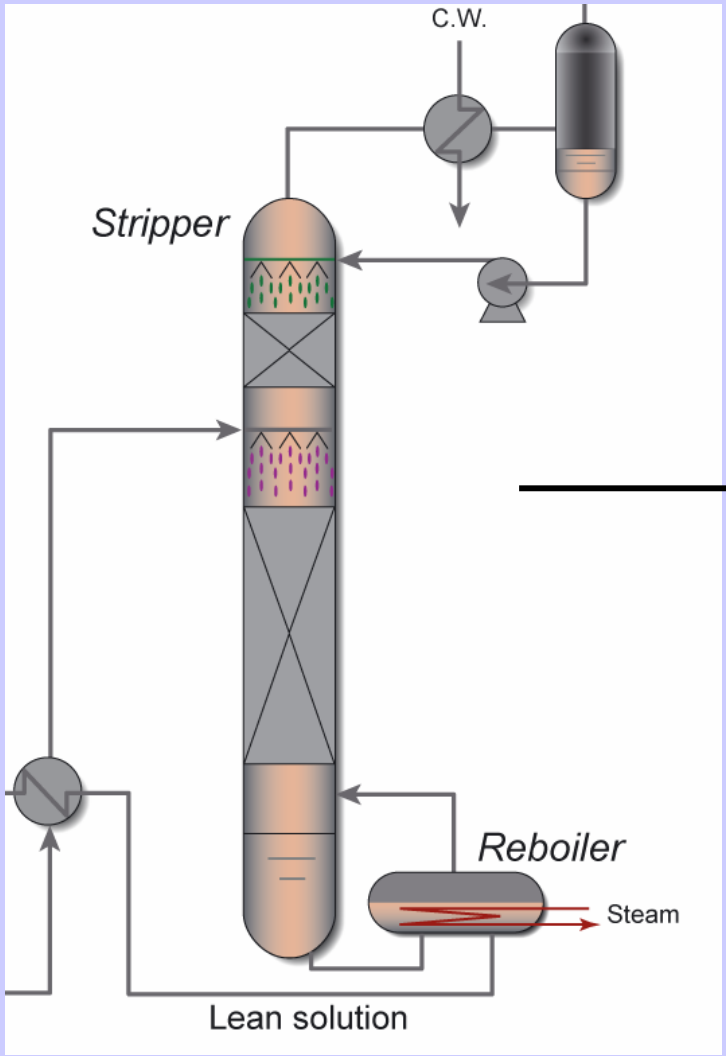
Correlation	*Phase*	*Function of*	*Notes and source*
Diffusion coefficients	Liquid: Reactants:	$T_{L,}$ viscosity	Versteeg et al. 1996 and Tamimi, Rinker and Sandall, 1994
	Liquid: Products		Hoff et al. 2003
	Vapor components: Absorber: N2 environment. Desorber: Steam environment.		Correlation from Fuller et al. (Reid et al., 2000)
Viscosity	Liquid_solution	x_i, T_L	Li & Lie, Hsu & Li, Toman (1990)
	Vapor mixture	T_L, y_i	Corresponding state. Chung et al., simple Mixing rule, (Wilke) Reid et al., 1986
Denisty	Liquid solution	T_L, w_i	Cheng et al., 1996
SRK	Vapor Abs: Ideal Desorber: SRK, solve EOS with newton-raphson		Reid et al., 2000
Enthalpy	Vapor	Tg, y_i	Reid et al., 2000 (ideal)
	Liquid solution	T_L, w_i,	Integrate CPL(T) Cheng et al and add contribution for CO_2 by subtracting heat of reaction from gas phase enthalpy.
Surface tension	Liquid solution		In-house
Heat of reaction CO_2	Liquid solution	T_L, xi	Aboudheir et al. 2003
Heat of vaporisation MEA	Liquid solution	T_L, xi	Difference between Hg and Hl
Heat of vaporisation H2O	Liquid solution	T_L, xi	Difference between Hg and Hl
	Vapor, MEA	T_L, xi	Nath and Bender, 1983
Henry parameter CO_2		Tl, xi,	Austgen et al., 1989

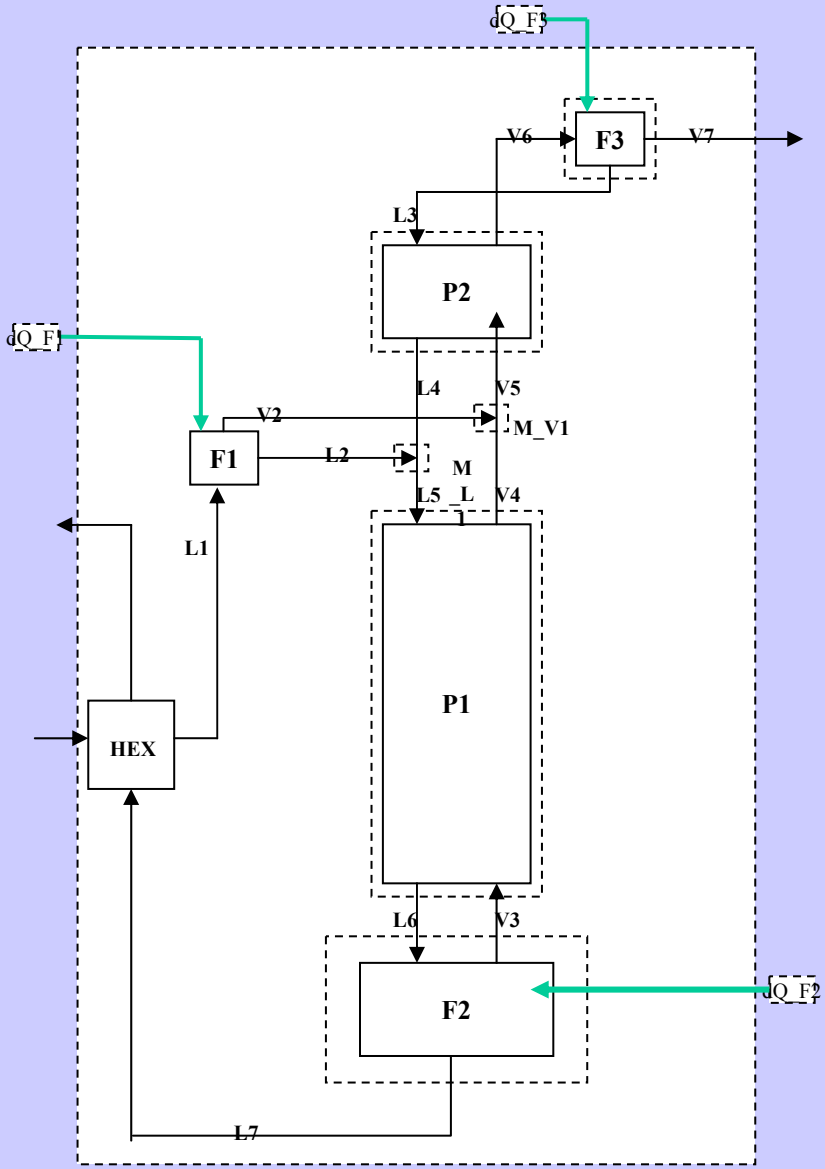
Sources of errors, experimental data:

- Errors in CO_2 calibration (flow meters etc)
- Errors analyzing CO_2 in solvent:
  - At the higher loading interval, there might be some CO_2 lost from the MEA due to flashing, avoid by using pressurized sample container
  - Also errors in the actual analysis, titration
- Errors in gas and/or solvent flow rates

Part 2: Modeling the desorber

Solving the process flow sheet:





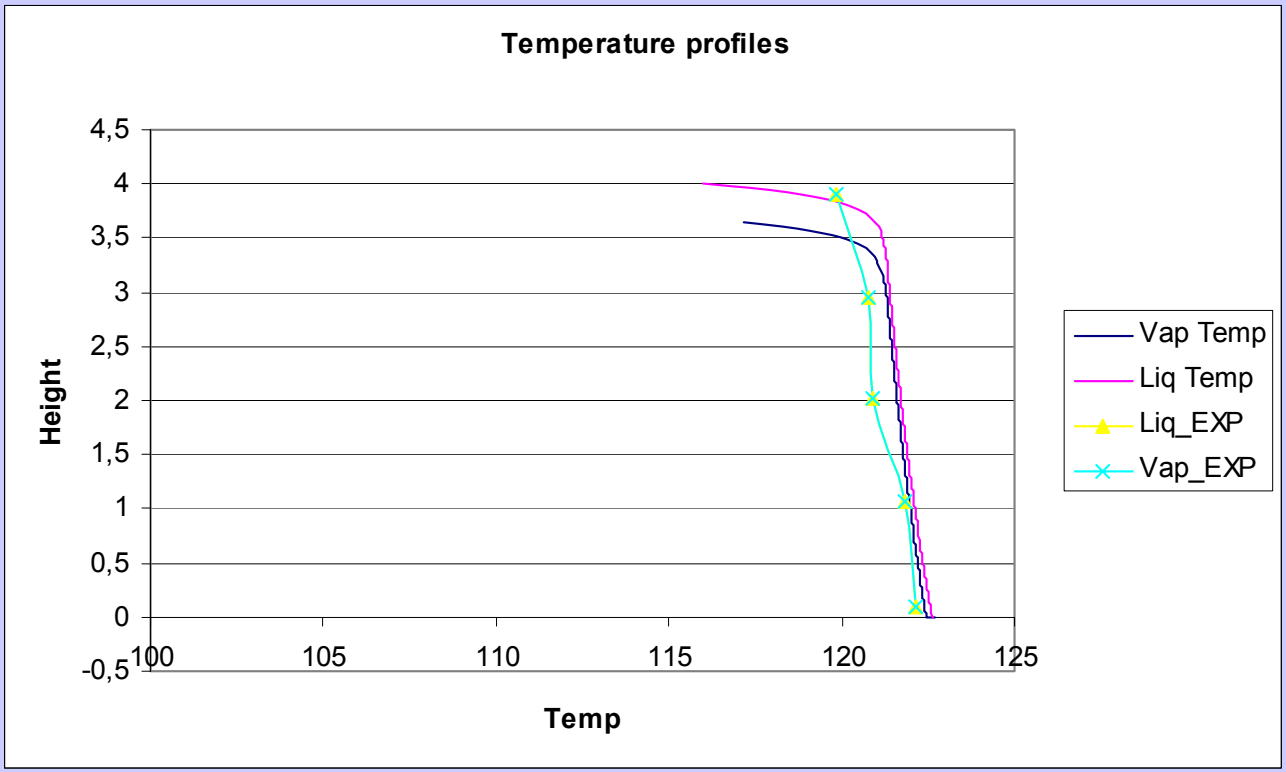
Problems when modeling the desorber:

1. Packing section
   - In terms of numerical stability, considerable more difficult to model
     - Gives rise to numerical solutions that exhibit narrow regions of very fast variation, large transfer gradients, thus, a stiff system of ode's
     - Fast reactions that occur as well as high heat transfer numbers
     - Need a robust mathematical routine for solving the packing
     - Progressively lower under-relaxation is used during the sequential iterations around the unit operations.
2. Recycle loops for material/energy balance.
   - Require good initial guesses
     - This is essential in order to obtain convergence when simulating parts of or the entire CO_2-loading range as well as obtaining a solution when using very low reflux rates i.e. low reboiler duties.
     - Upper and lower bounds for boilup flow rate must be carefully chosen.

Desorber base case setup

Routines	***Type***	***Validity***	***Reference***
Interfacial mass transfer model	Instantaneous reversible reaction		Astarita et al.
Equilibrium model data fit	NTNU/Sintef data (liquid phase speciation described with the use of a modified Kent-Eisenberg model	25-120˚C	NTNU/Sintef data

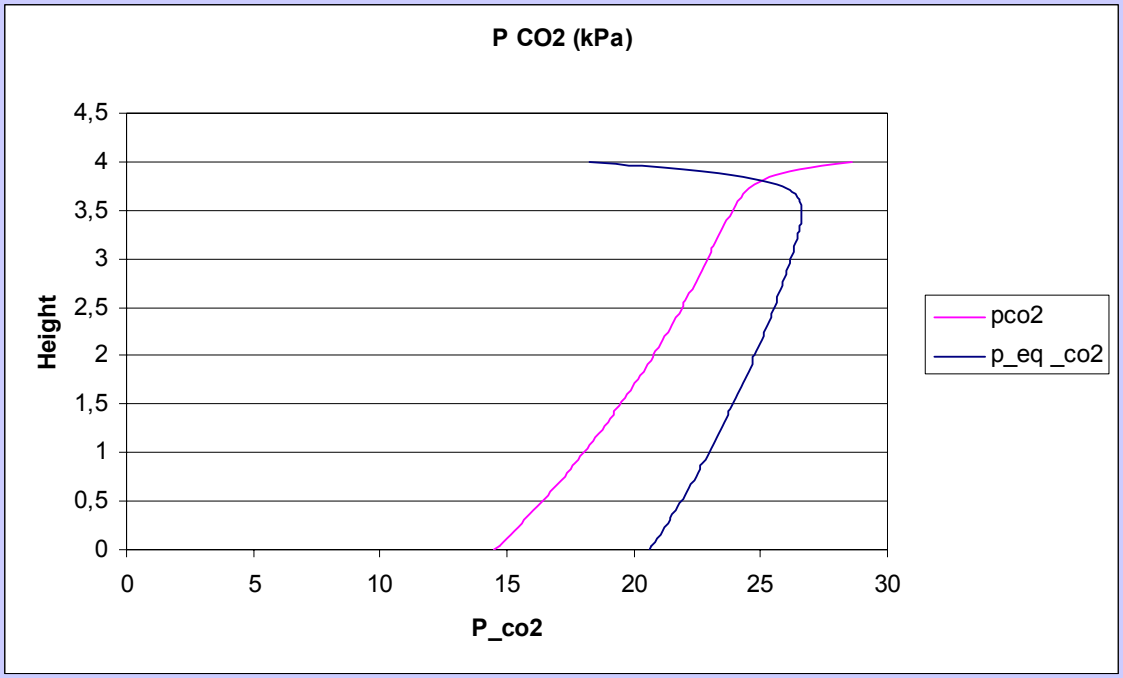
Preliminary results on the desorber side



Temperature profiles for the liquid and vapour phases as well as the experimentally obtained temperatures.

The measured profile must be taken as an average for the liquid and vapour temperatures as there is no way to determine which phase is in contact with the sensor at any time.

Preliminary results on the desorber side



Stripper packing profiles of the CO_2 partial pressure and equilibrium partial pressure.

- The rich amine entering the desorber is assumed to be at or below equilibrium because of an initial QP flash calculation prior to the inlet. Since the liquid inlet temperature is significantly below its bubble point, absorption should take place in the upper region. When sufficient sensible and latent heat has been added to the liquid phase, desorption occurs.

Preliminary results for desorber, reboiler and condenser

	020305, set nr 1.	
Rich loading	0,268	
Lean loading (out of reboiler)	0,182	
kg removed	4,438	kg/hr
Model:		
Steam consumption	**9,983**	MJ/kg CO_2
Experimental:		
Steam consumption	**10,95**	MJ/kg CO_2

- The absolute values are very high compared to what is found in commercial installations. Due to the low inlet rich loading.
- The fact that we have results spanning most of the interesting loading range adds to the validation value for the simulation model.

Conclusions:

- This work presents experimental absorber results from continuous operation of a well instrumented laboratory scale pilot rig using 30wt% MEA as solvent.
- The absorber simulations show good agreement with the experimental pilot rig data.
- Preliminary results for the desorber section shows good similarity to the experimentally obtained data.
- A stable solution strategy for making the overall regeneration part (and the subsequent overall spreadsheet) run towards convergence has been developed.

Acknowledgement

This work was supported financially by the Norwegian Research Council Klimatek Project through the SINTEF Project 661292.01 and by the European Commission through the CASTOR Integrated Project (Contract no. SES6-CT-2004-502856).

Corrosion experiments for CO_2 solvent

Paul Broutin
Jean Kittel
David Pasquier
François Ropital

8th International CO_2 Capture Network – University of Texas Austin
3rd October 2005

Overview

- IFP involvement within the CASTOR Project
- Objectives of the corrosion study
- Experimental methods on lab scale
- Corrosion experiments
- Discussion
- Future works

IFP involvement within the CASTOR Project

- Corrosion experimentation
- Optimisation of the process loop
- Characterisation of the gas/liquid contactors
- Follow-up of the CASTOR pilot
- Study of CO_2 storage in the Casablanca field
- Study of CO_2 storage in the Snøvhit field

Objectives of the corrosion study

Propose a lab corrosion test able to rank the corrosivity of different amine solutions

- Need to define:
  - Experimental conditions (vessels, Temperature...)
  - Gas composition and pressure (CO_2, O_2, impurities...)
  - Amine solution (concentration, CO_2 loading, fresh or degraded...)

Rank the different amine solutions

Experimental Methods on lab scale /1

- Based on NACE Standard TM 0169-95:
  "Lab corrosion testing of metals"
  - Section 2: Test specimens
    - *Size, Shape, surface finish...*
  - Section 3: Equipment and apparatus
  - Section 4: Test conditions
    - *Composition of test solution, solution velocity, duration...*
  - Section 5: Cleaning specimens after the test
    - *Mechanical, chemical and electrolytic cleaning methods*
  - Section 6/7: Evaluation of results / Calculation of corrosion rates

Experimental Methods on lab scale /2

Equipment and apparatus

- Pressure Vessel

Pressure control (up to 120 bars)

Temp regulation (up to 200°C)

Solution stirring (controlled velocity)

- Specimen holder / Stirrer

Experimental Methods on lab scale /3

Test Specimens

- Flat rectangular samples
  - 30mm x 30mm x 2mm
  - Polished to grade 600 SiC
  - Metal grades :
    - AISI 1028 (carbon steel)
    - AISI 304 / AISI 316 (SS)

Weight loss corrosion evaluation

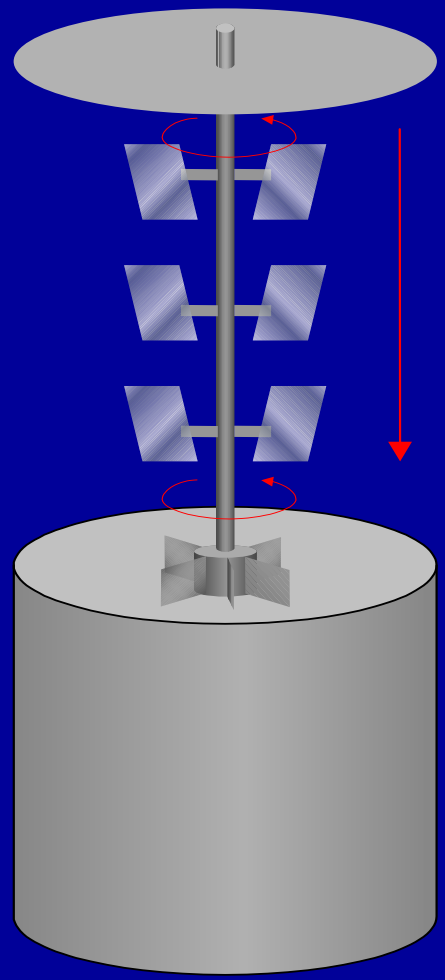
- U-Bends

Visual evaluation of Stress Corrosion Cracking

Experimental Methods on lab scale /4

- test duration
  - 1 month (base time)
- Solution composition
  - different CO_2 loading conditions
  - MEA 30% = model reference solvent
- Gas composition
  - different compositions can be tested (CO_2 + O_2 + N_2 + SO_2, NO...)
- Temperature
  - 120°C
- Pressure
  - Set at 2 bars (beginning of tests)
  - free to evolve during tests

Test conditions



Experimental methods on lab scale 5/

Evaluation of results / Corrosion analysis

- Visual inspection

– Corrosion scale aspect (color…)
– Cracking (U-Bends)

- Coupon cleaning

– Scale removal

- Weight-loss measurements

$$\text{Corrosion rate } (\mu\text{m/year}) = \frac{\Delta g(g)}{\text{area}(cm^2) \times \text{density}(g/cm^3)} \times \frac{365 \times 10^4}{\text{E.T.(days)}}$$

Corrosion experiments /1

- First objective: with the ref. solvent (MEA 30%), find experimental conditions:
  - Reproducible
  - Representative of real amine units
  - Able to rank different amine solutions

Corrosion experiments /2

Experimental parameters

- Amine solution
  - Saturated at ambient T° before the experiment
  - MEA 30% (reference solvent)
- Temperature: 120°C
- Pressure
  - 2 bars (equilibrium) at the start of experiments
  - Free evolution during the test
- Gas composition
  - Different blends containing CO_2, N_2, O_2, SO_2, NO

First Results on 30% MEA: gas free of O_2

- Gas composition
  - CO_2 15%, N_2 85%, SO_2 10ppm, NO 20ppm (close to absorption cond.)
  - Pure CO_2
- Corrosion rates (mean value of 3 tests in pure CO_2 loading)

AISI 304: < 30 µm/year **AISI 316: < 10 µm/year** **AISI 1028: 50 µm/year**

Weak degradation of amine solution (light yellow, ΔP = 0.5 bars)

Low corrosion (not representative of severe service conditions)

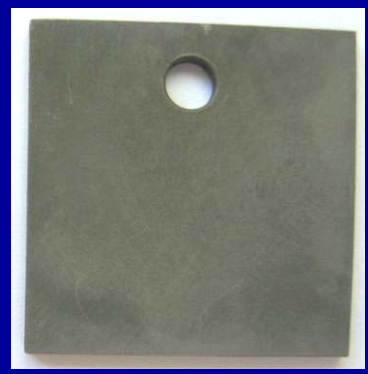
Comparison between different amines difficult

Second results on MEA 30%: gas with O_2

- Gas composition
  - CO_2 75%, O_2 5%, N_2 20%
- Corrosion rates (mean value of 2 independent tests)

304: <50 µm/year

316: <15 µm/year



1028: >400 µm/year

Evidence of amine degradation (dark colour, ΔP = 2 bars)

Clear discrimination between corrosion rates of different materials

Discussion /1

- Ideal situation
  - Work with degraded industrial solvent solutions
  - Not feasible except with solvents from Stuttgart pilot plant

- Alternative solution
  - Use "artificially degraded" amine solutions
  - Appropriate gas composition and charging conditions

Need to find realistic experimental conditions:

  - with relatively high corrosion rates (for comparison between solvents and materials)
  - with representative gas compositions
  - with some degradation of amine solution within the testing period

Discussion /2

- Without O_2 in charging gas:
  - Weak degradation of amine solution
    - Extremely low corrosion rate
  - Not representative of real service conditions

- With O_2 in charging gas:
  - More degradation of amine solution
    - Higher corrosion rate

Degradation product = major cause of corrosion

Discussion /3

- Reproducible and selective experimental procedure was established:
  - Saturation with a CO_2/Air mix 75:25 at ambient T° and atmospheric P
  - Stirring (400 rpm) then heating at 120°C
  - Adjust pressure at 2 bar with CO_2/Air mix 75:25

➡ **Ensures controlled amount of oxygen in the liquid/gas phases**

➡ **Degrades amines and increases corrosivity**

➡ **Allow ranking of different amine solutions**

Future Works /1

- Solvents ranking using the experimental procedure established with MEA:
  - Selected CASTOR solvents
- Impact of degradation products on corrosivity
  - Analysis of degradation products in the gas and liquid
  - Correlations between degradation products and corrosion rates
- Tests with degraded solvents
  - From Stuttgart pilot plant (MEA and CASTOR solvents)

Future Works /2

- Corrosion monitoring of the CASTOR pilot plant operated by ELSAM in Esbjerg (DK)

MP1- Lean solution inlet of the absorber

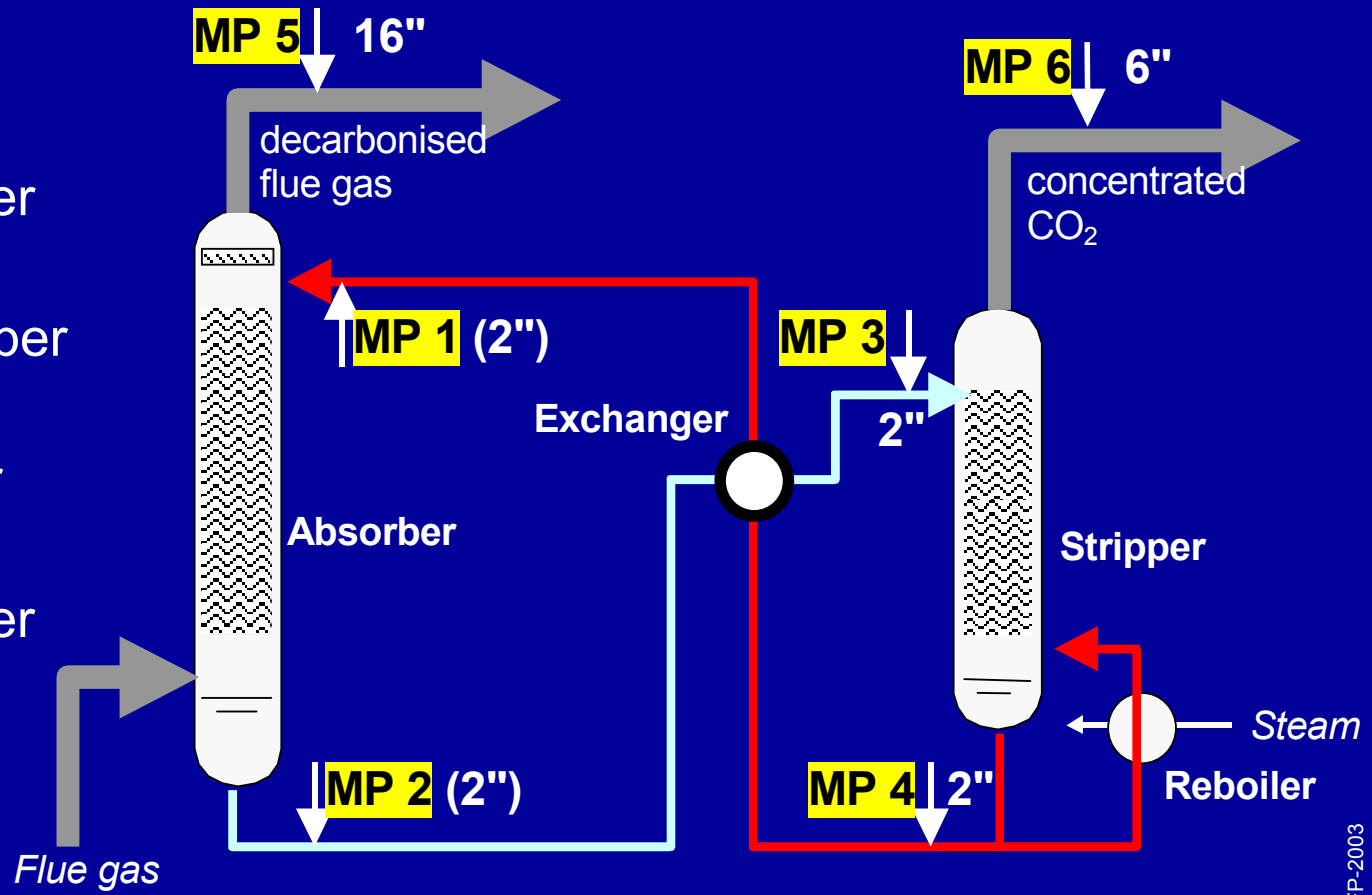
MP2- Rich solution outlet of the absorber

MP3- Rich solution inlet of the stripper

MP4- Lean solution outlet of the stripper

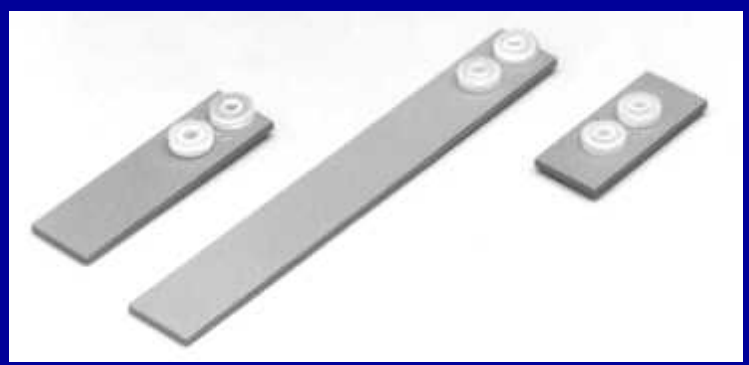
MP5- Absorber outlet

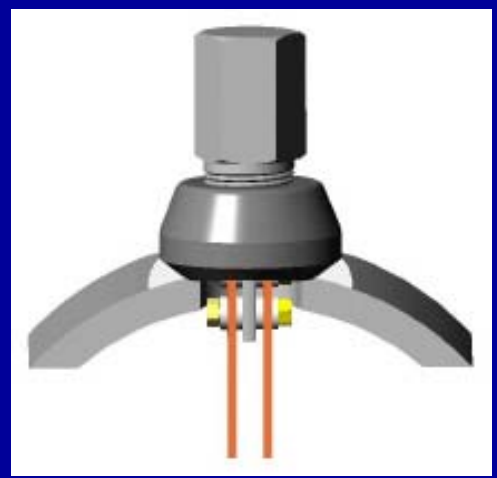
MP6- Stripper outlet



Future Works /3

- Installation of corrosion monitoring tools in the CASTOR pilot plant
  - Corrosion weight loss coupons
  - Periodic sampling / weighing for corrosion rate evaluation
  - Tests on MEA and CASTOR 1 solvent





Future Works /4

- Installation of the corrosion probes on the CASTOR pilot plant achieved

ACKNOWLEDGMENT

- This work is supported financially by the European Commission through the CASTOR Project

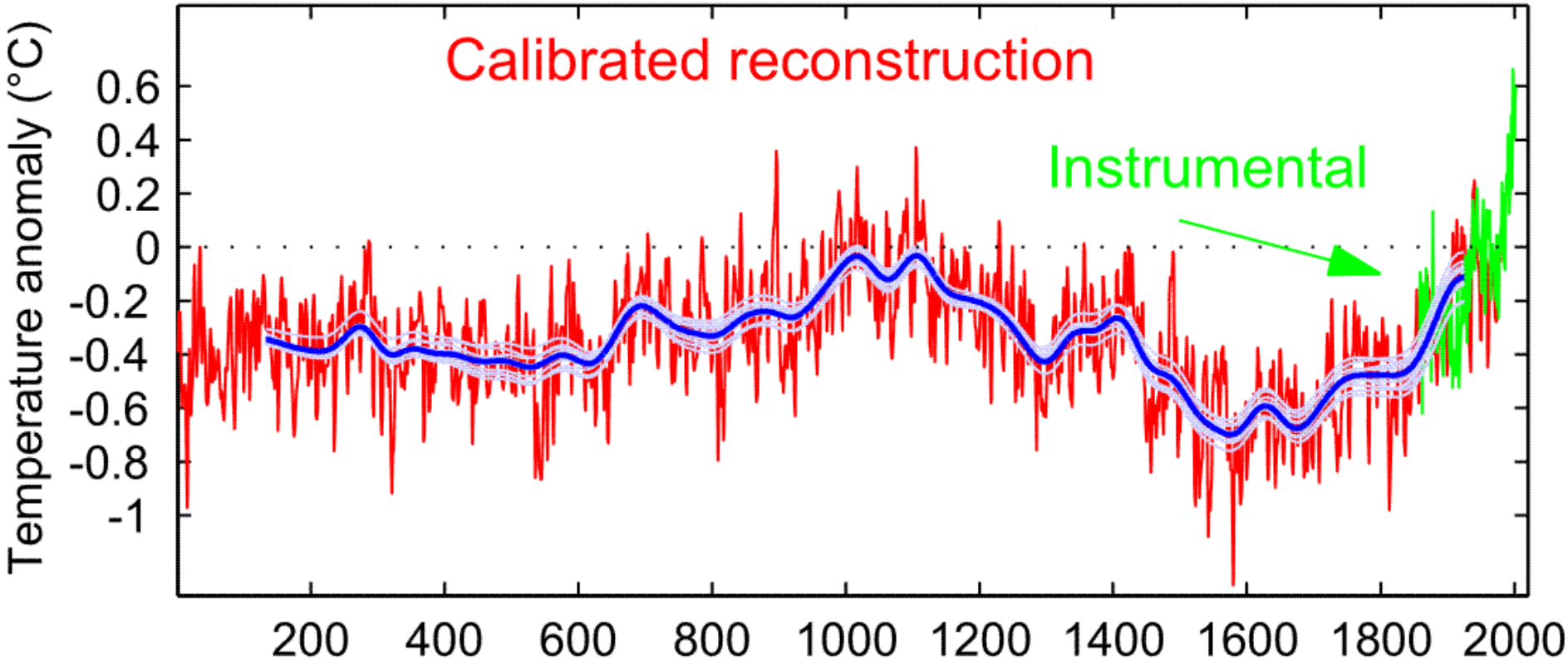
Chemical Understanding of Solvents for CO_2 Capture

Eirik Falck da Silva
3 October 2005

Outline

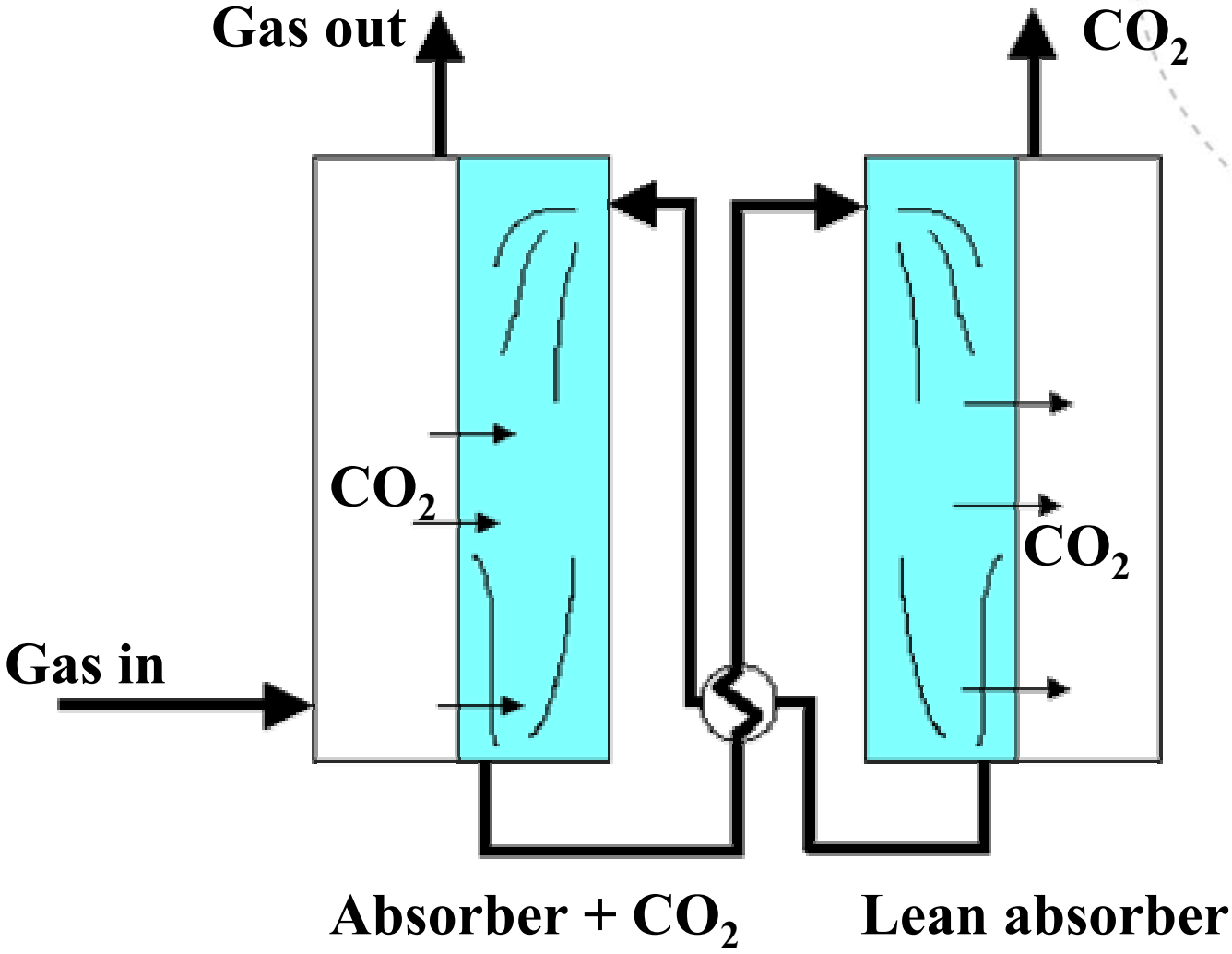
- Reactions and Equilibrium
- Liquid Simulation
- Degradation
- New Proposal

Global Warming



Moberg, Sonechkin, Holmgren, Datsenko and Karlen, Nature, 433, 2005

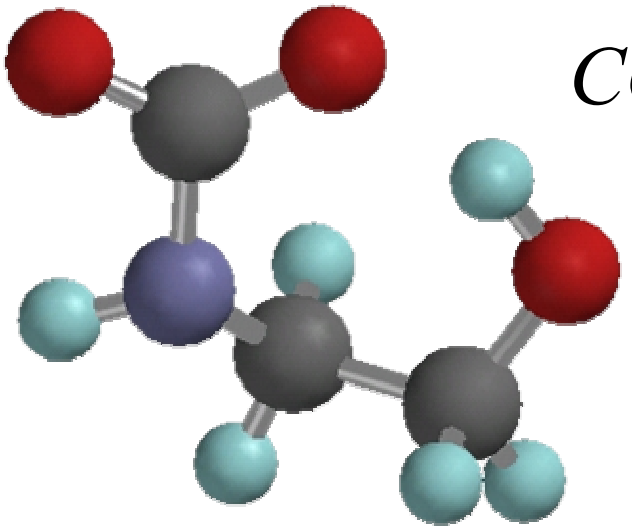
Chemical Absorption



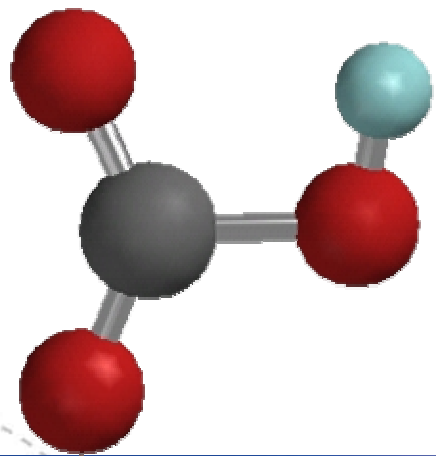
Computational Chemistry

- Quantum Mechanical Methods
- Molecular Simulation
- Solvation Models

Chemical Absorption

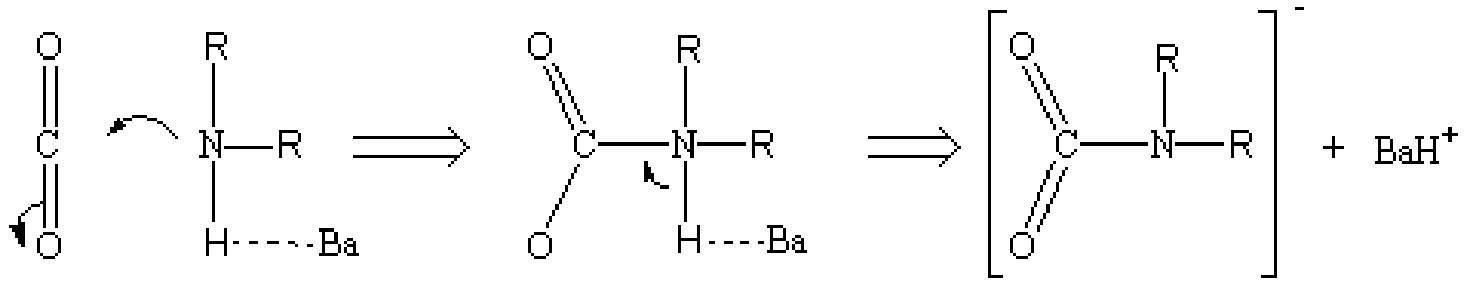


$$CO_2 + 2Am\ f \quad AmCO_2^- + AmH^+$$



$$CO_2 + H_2O + Am\ f \quad HCO_3^- + AmH^+$$

Reactions



$$Am + H_2O \; f \quad AmH^+ + OH^-$$

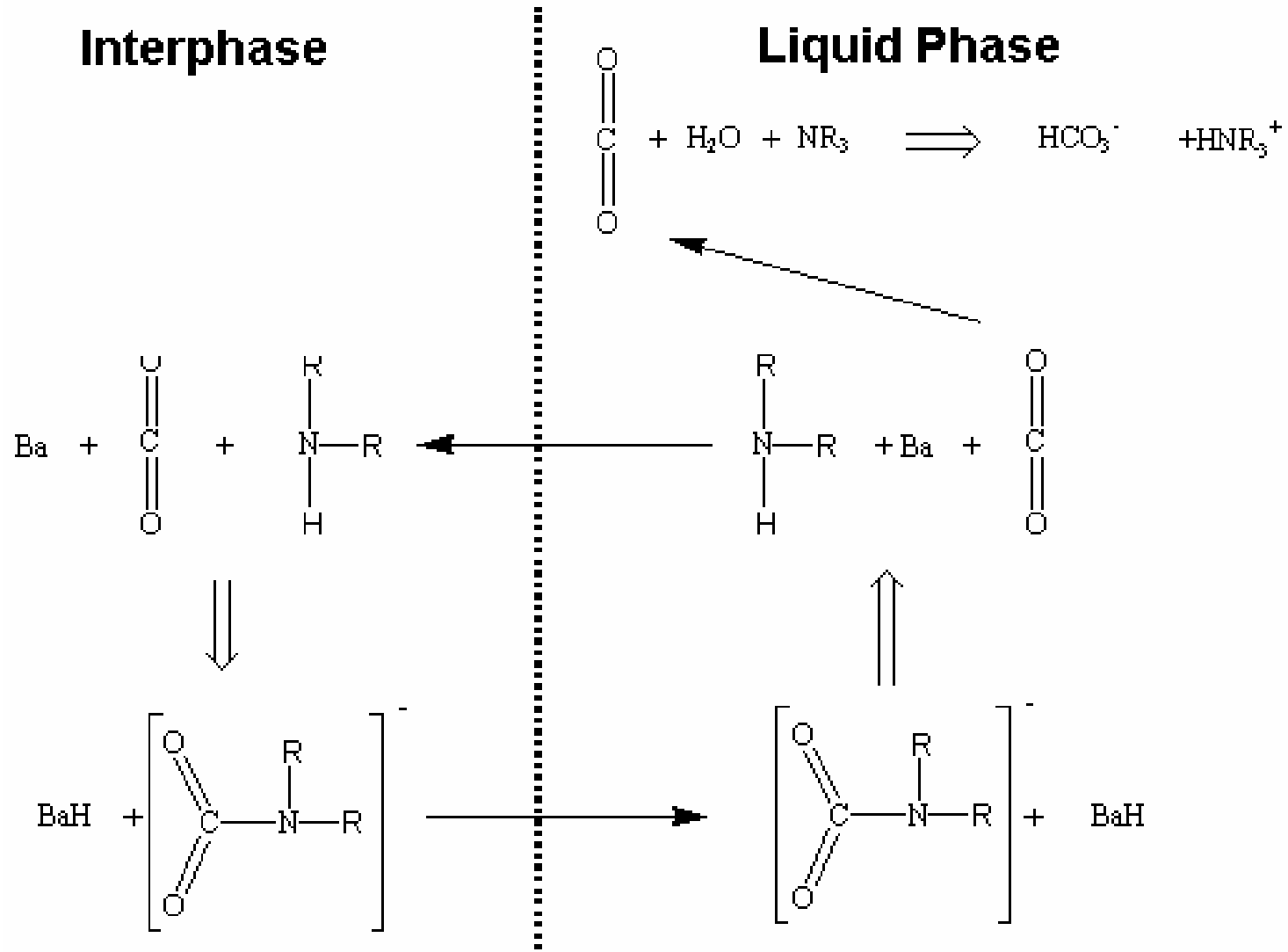
$$CO_2 + H_2O \; f \quad H_2CO_3$$

$$CO_2 + OH^- \; f \quad HCO_3^-$$

$$HCO_3^- + OH^- \; f \quad CO_3^{-2} + H_2O$$

+Shuttle-Mechanism

Shuttle-Mechanism



Main parameters:

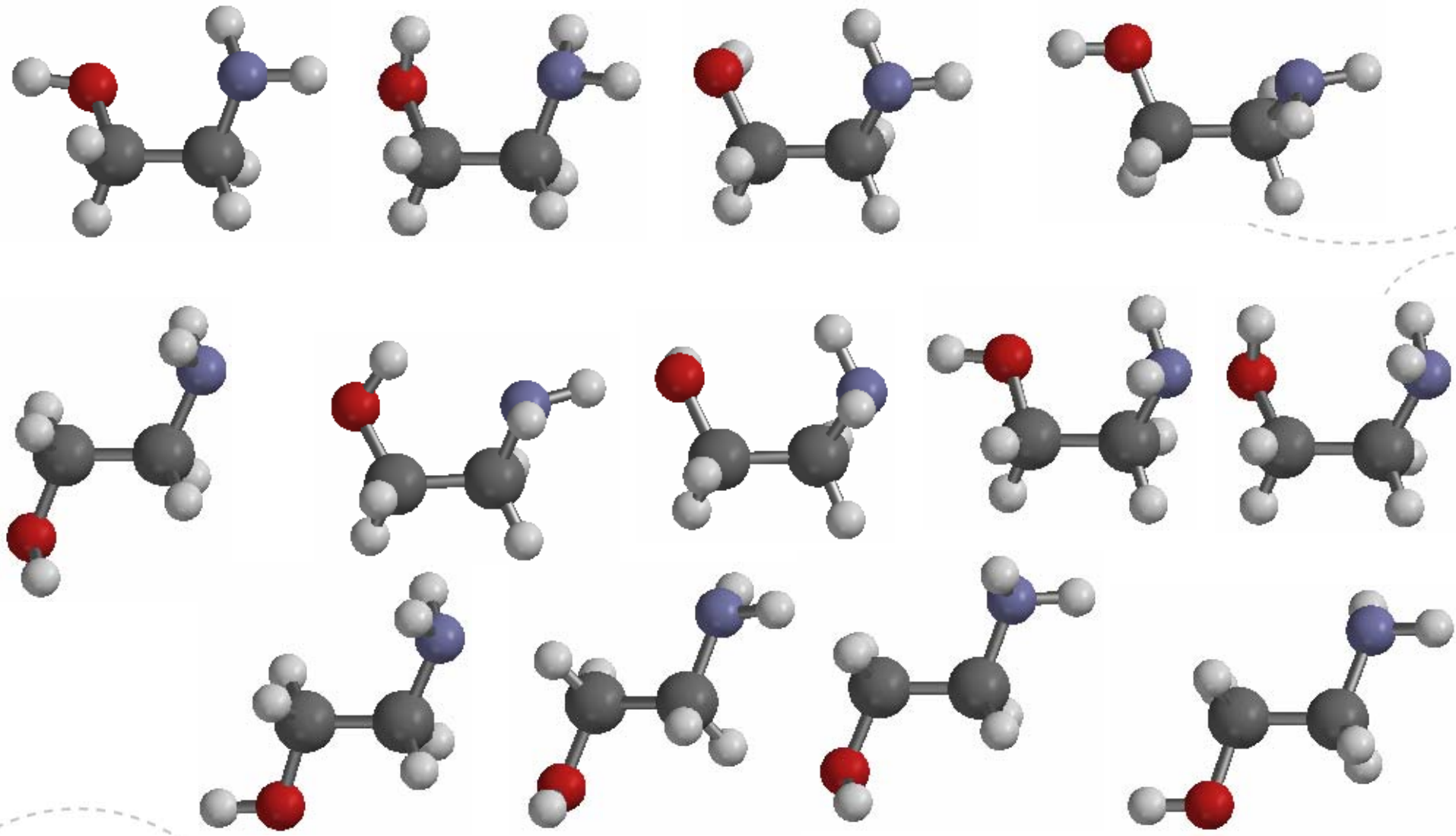
- Base-strength of amine:

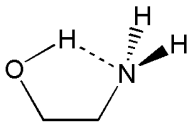
$$pK_a(T,c)$$

- Carbamate stability of amine:

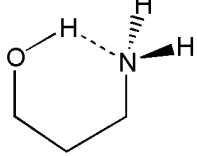
$$K_c(T,c)$$

Conformer selection





MEA



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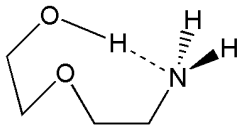

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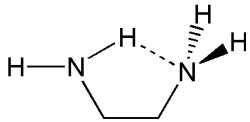

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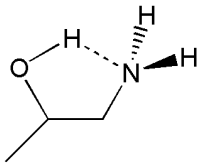

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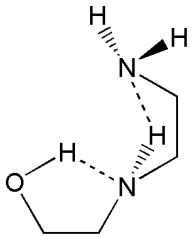

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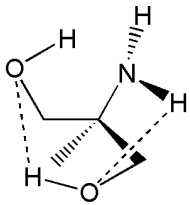

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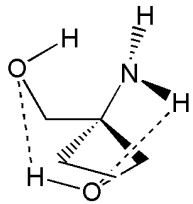

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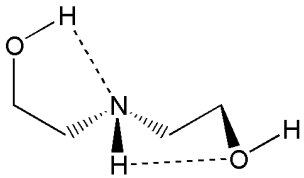

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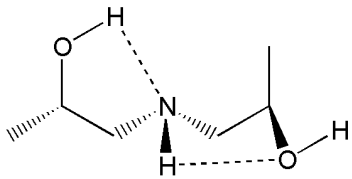

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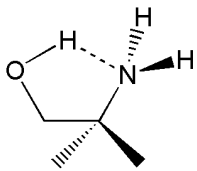

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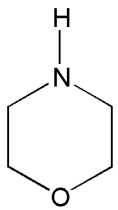

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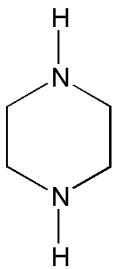
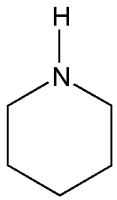


Piperazine



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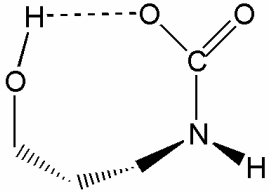

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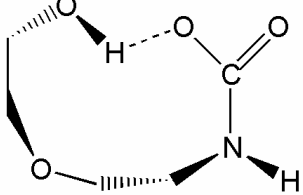

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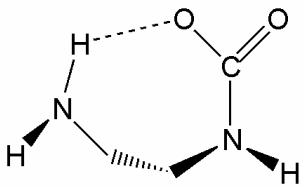

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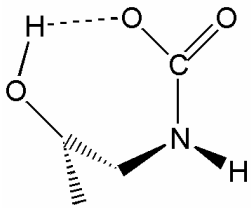

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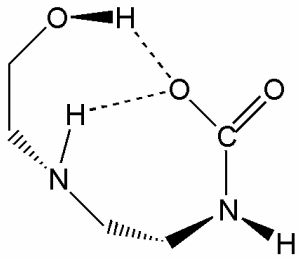

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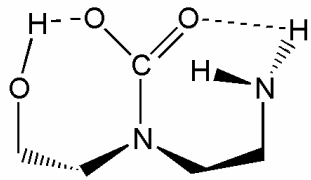

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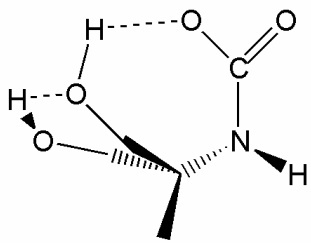

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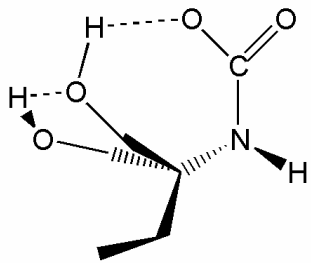

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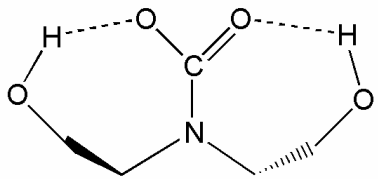

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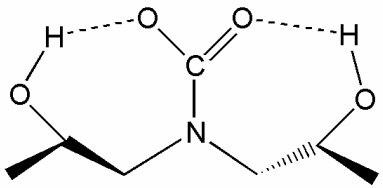

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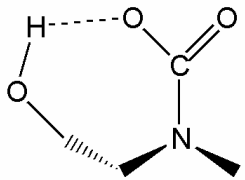

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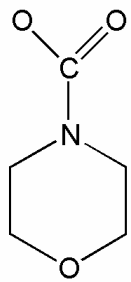
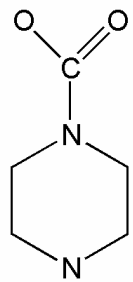


Morpholine



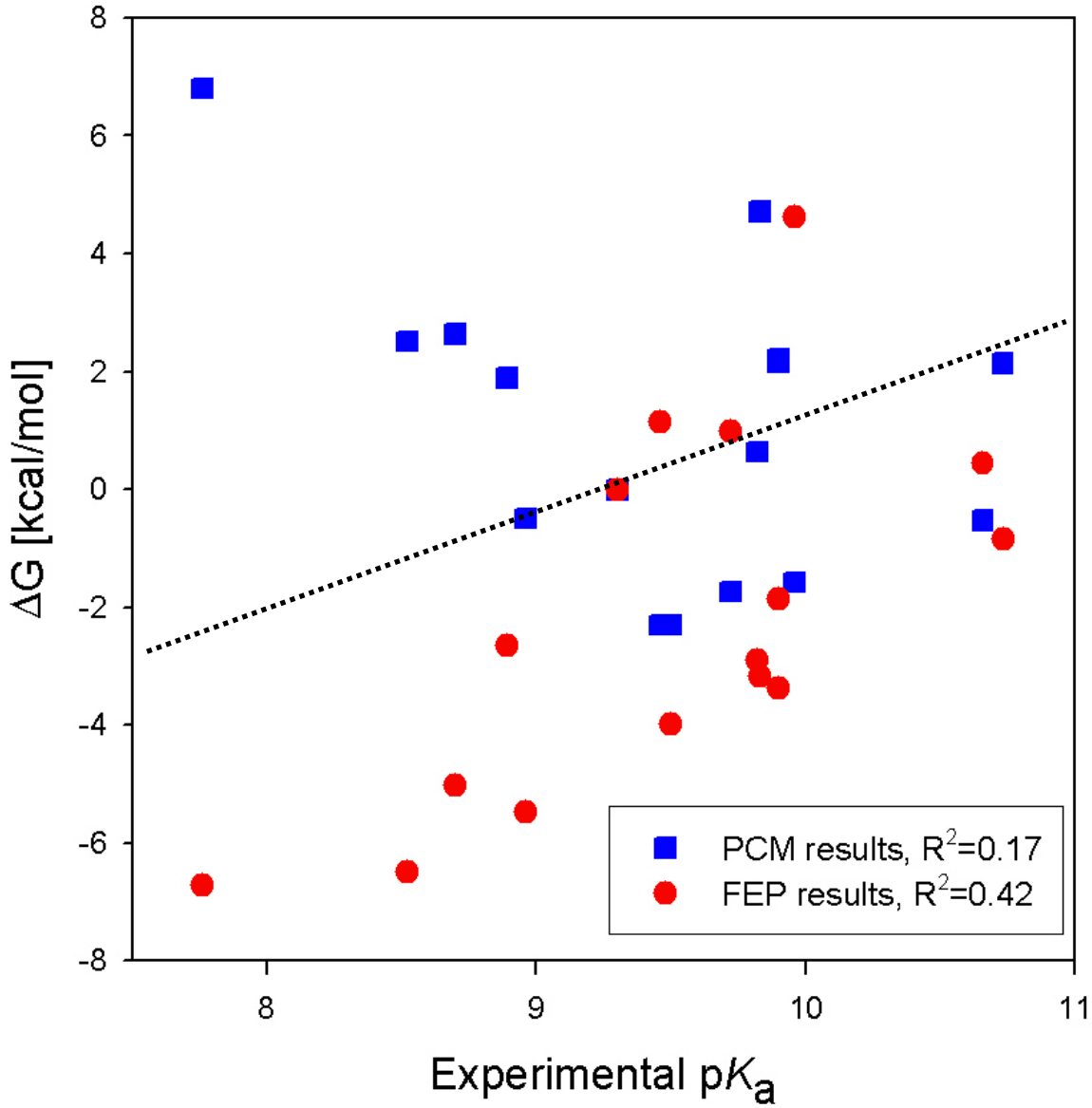
Piperazine

pK_a Model

Gas phase energies:

B3LYP/6-311++G(d,p)

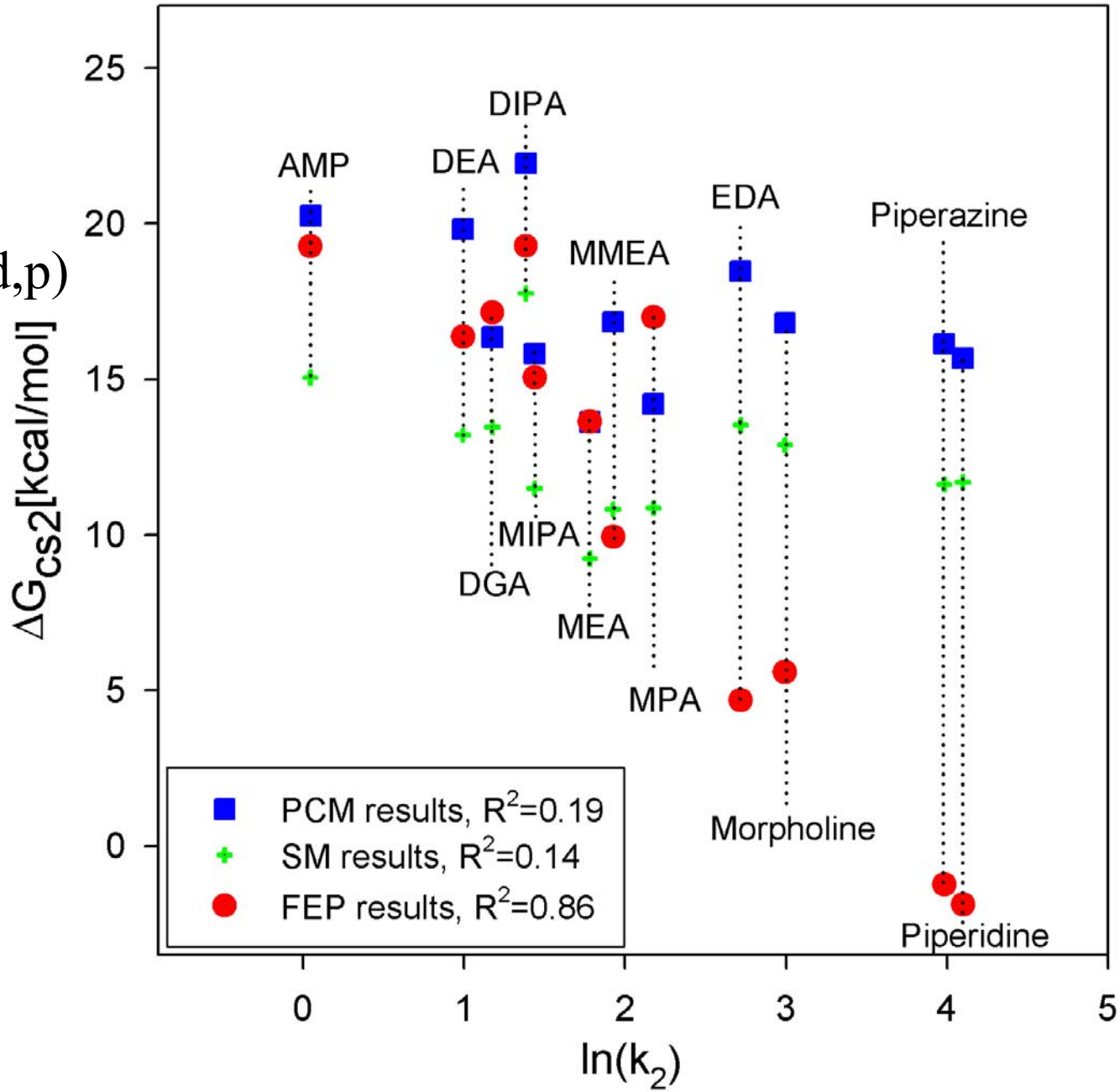
$$BH^+ + H_2O \; f \quad B + H_3O^+$$



K_c Model

Gas phase energies:

B3LYP/6-311++G(d,p)

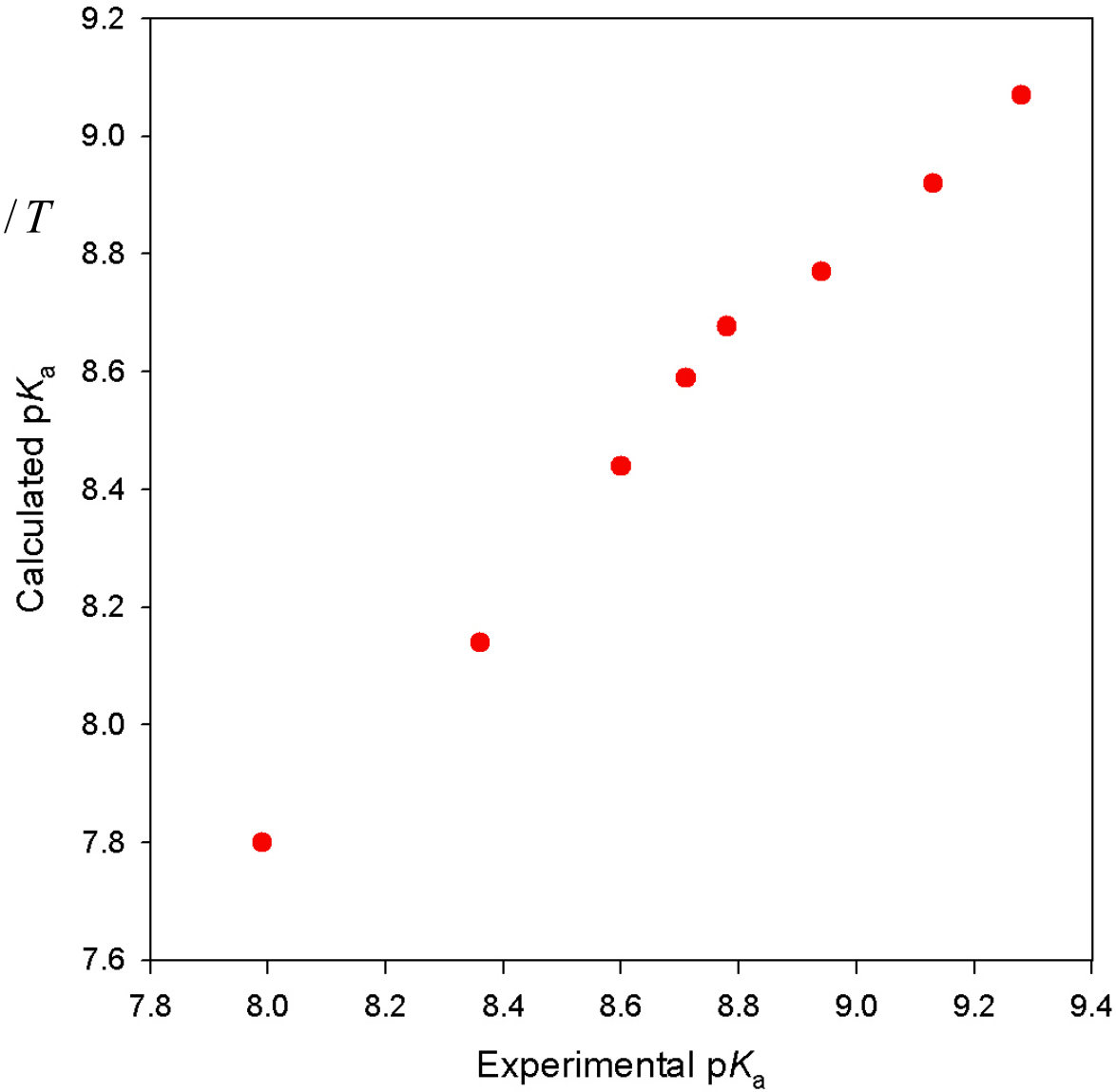


pK_a(T) Model

20°C ->60°C

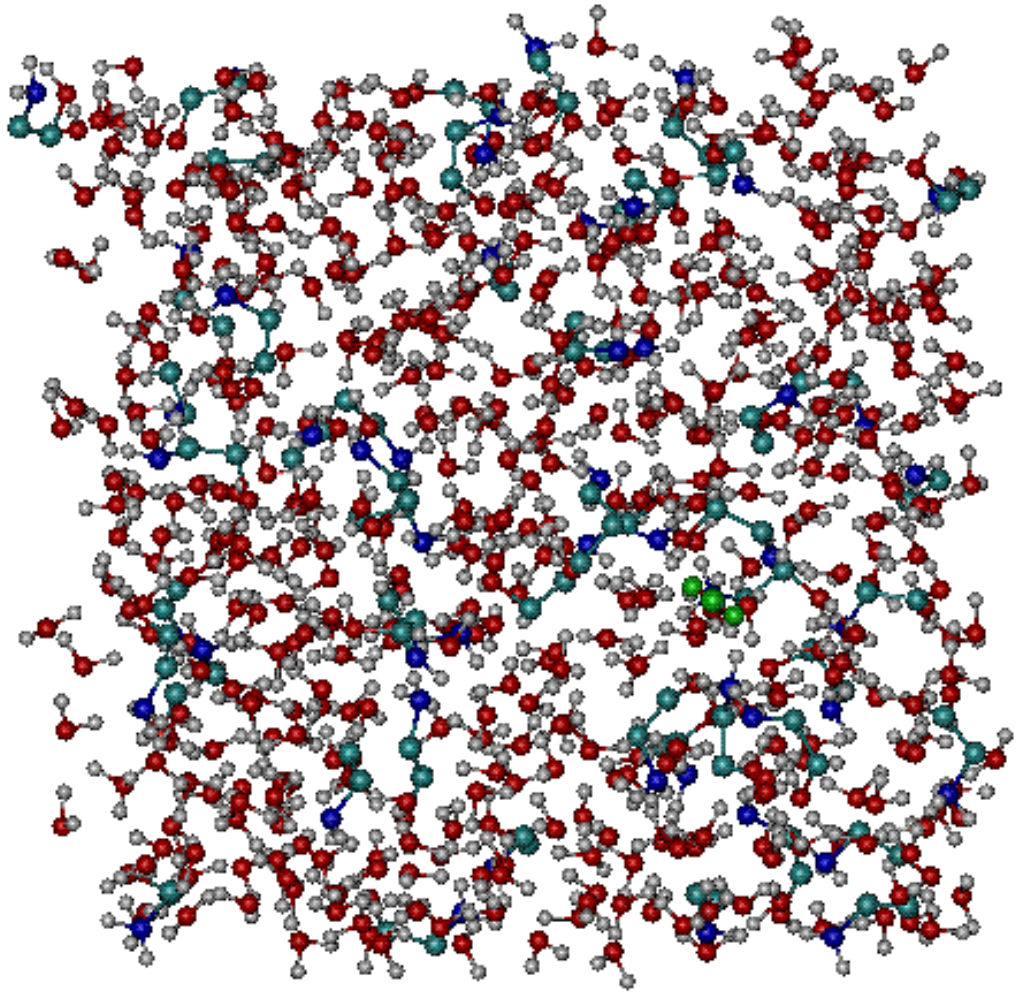
$$-d(pK_a)/dT = (pK_a + 0.052\Delta S^0)/T$$

HF/3-21G(d) level calculations used to determine entropies.



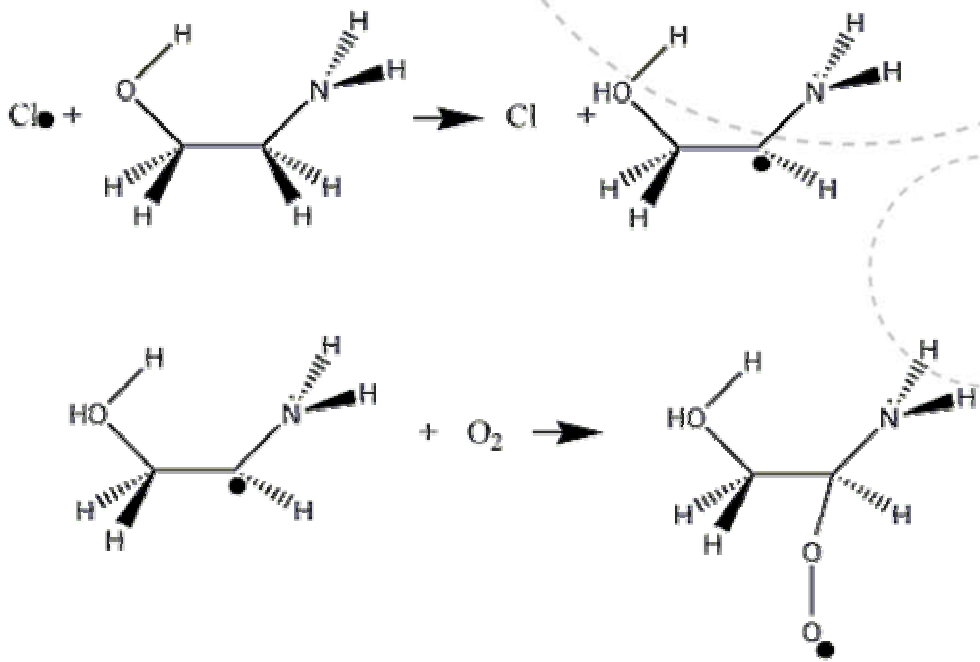
Liquid Structure

	MEAb	Experimental
$r(298.15K)$	**1.013** g/cm3	**1.012** g/cm3
$r(333K)$	**0.98** g/cm3	**0.984** g/cm3
$DH_{vap}(333K)$	**50.6** kcal/mol	**57.7** kcal/mol



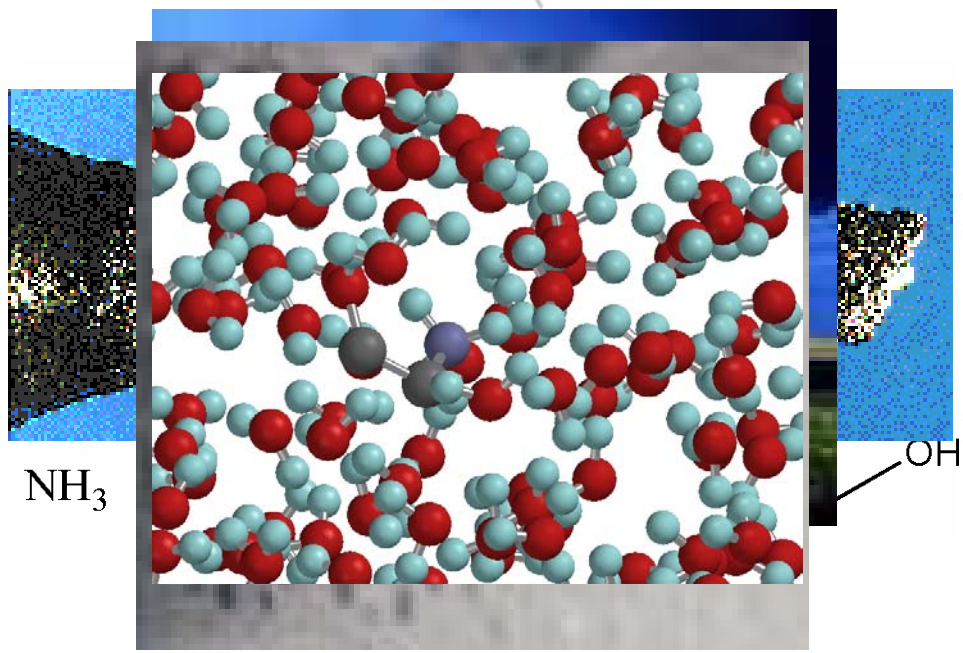
Degradation

Molecule	Reaction 1	Reaction 2
MEA	**-0.7**	**-75.9**
Piperazine	**7.5**	**-77.9**
MDEA	**-3.3**	**-68.4**

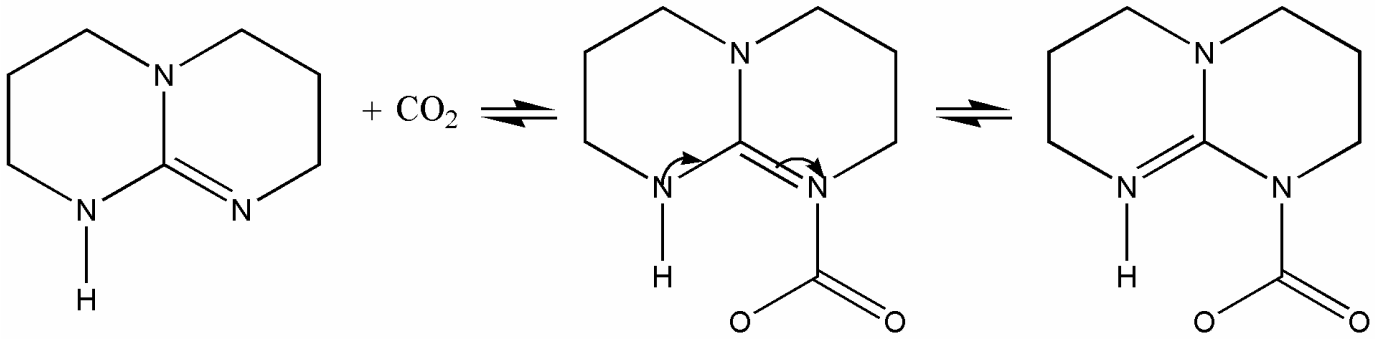


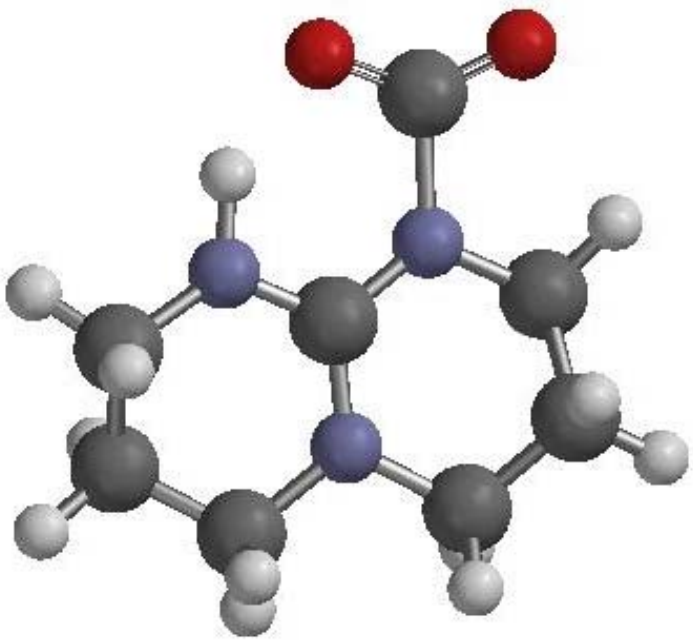
Other Properties

- Solvability
- Foaming
- Corrosion
- Environmental Issues
- Cost



Highly Nucleophile Solvents





Summary

- Reaction mechanisms of CO_2 absorption are well understood.
- Main equilibrium constants can be predicted with useful degree of precision.
- Liquid structure of amine-water-CO_2 can be modeled.

CASTOR

CO_2, from Capture to Storage

"A project overview and tasting"

Paul H.M. Feron (TNO)

Presentation at 8th IEA International Capture Test Centre network meeting
University of Texas, Austin, 4 October 2005

Presentation overview

- CASTOR “Executive” Summary
- Post-combustion capture R&D programme
  - Objectives
  - Methods
- Some preliminary results
  - Baseline studies and parametric modelling
  - Two other presentations
- Credits

CASTOR Objectives / targets

- Reduce the cost of CO_2 post-combustion capture
- Contribute to the feasibility & acceptance of the geological storage concept
- Validate the concept on real site(s)
  - Pilot testing for capture (25 t CO_2 / day)
  - Detailed studies of future storage projects

Consortium participants

R&D	Oil & Gas	Power Companies	Manufacturers
IFP (FR)	STATOIL (NO)	VATTENFALL (SE)	ALSTOM POWER (FR)
TNO (NL)	GDF (FR)	ELSAM (DK)	MITSUI BABCOCK (UK)
SINTEF (NO)	REPSOL (SP)	ENERGI E2 (DK)	SIEMENS (DE)
NTNU (NO)	ENITecnologie (IT)	RWE (DE)	BASF (DE)
BGS (UK)	ROHOEL (AT)	PPC (GR)	GVS (IT)
BGR (DE)		E.ON-UK (UK)	
BRGM (FR)			
GEUS (DK)			
IMPERIAL (UK)			
OGS (IT)			
TWENTE U. (NL)			
STUTTGARTT U. (DE)			

Co-ordinator: IFP

Chair of the Executive Board: Statoil

CASTOR Summary

- Budget: 15.8 M€
- EU funding: 8.5 M€
- Industrial funding: 2.2 M€
- Internal funding: 5.1 M€
- Duration: 4 years (2004-2008)
- 30 partners from 11 European countries

CASTOR main components

Strategy for CO_2 Reduction

WP1.1 Development of CO_2 reduction strategies

WP1.2 Geological storage options for CO_2 reduction strategy

Budget: 0,9 M€

Management Dissemination

WP0.1 Project Management

WP0.2 Dissemination & Training

Budget: 0,75 M€

CO_2 Post-Combustion Capture

WP2.1 Evaluation, optimisation & integration of post-combustion capture processes

WP2.2 Identification of most promising liquids

WP2.3 Designed of membrane based processes

WP2.4 Advanced processes

WP2.5 Process validation in pilot plant

Budget: 10,3 M€

CO_2 storage performance & risk assessment studies

WP3.1 Field case "Casablanca"

WP3.2 Field case "Lindach"

WP3.3 Field case "K13b"

WP3.4 Field case "Snohvit"

WP3.5 Preventive & corrective actions

WP3.6 Criteria for site selection and site management

Budget: 3,8 M€

CASTOR

Sub Project 2:
CO_2 Post-combustion Capture
Leader: TNO

Why develop post-combustion capture of CO_2? Why focus on absorption processes?

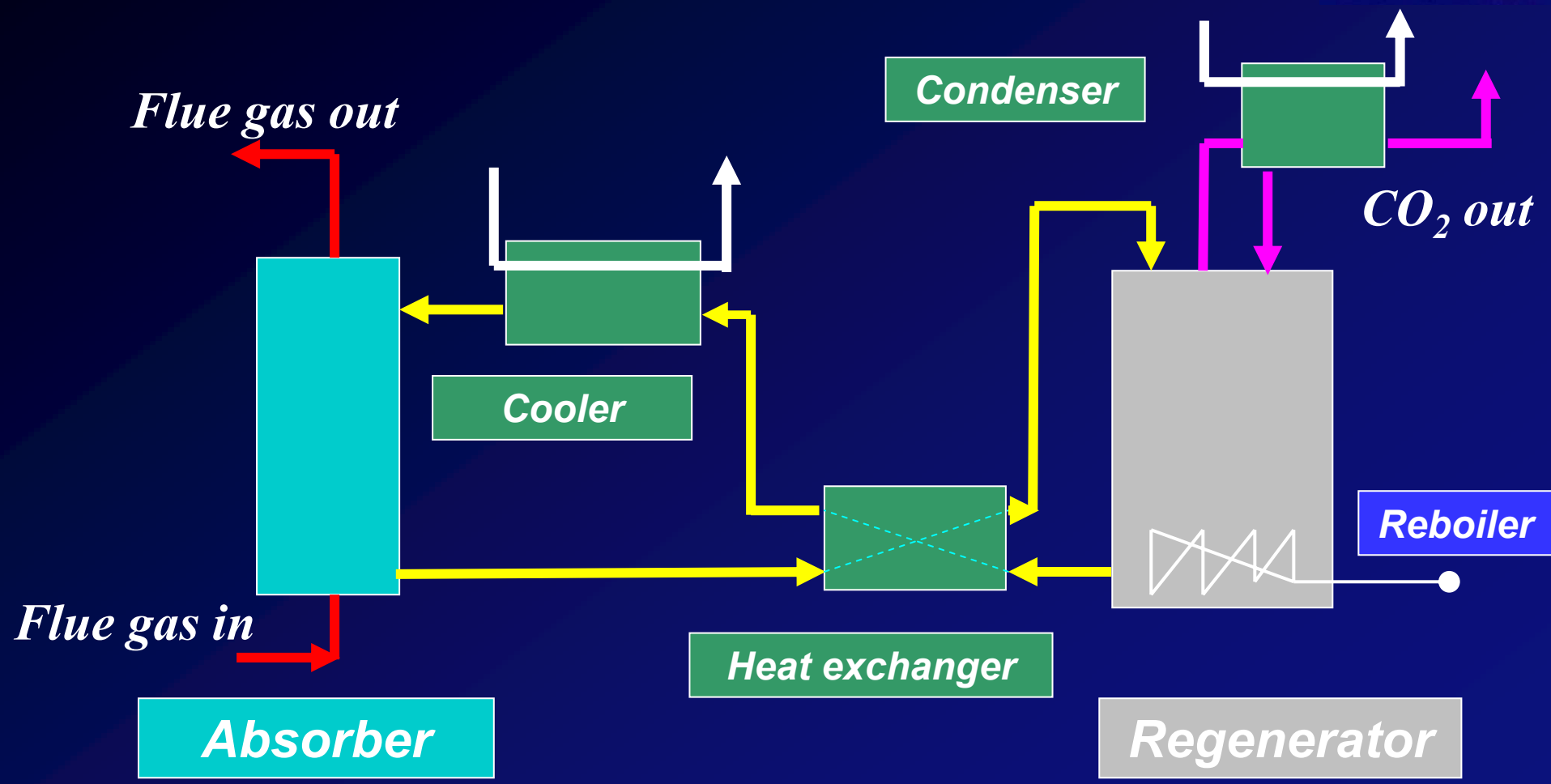
- Post-combustion capture is important because of large existing stock of power plants and boilers but also for new plants, as the cheapest ones will be conventional based on direct combustion of fuel with air

- Evaluation of post-combustion capture (membranes, absorption processes, adsorption processes, cryogenics) identified absorption processes as leading technology

- Europe is leading in solvent technologies for natural gas, but is trailing in solvent technologies for flue gas

➢ *Absorption technology is favoured but still expensive; therefore focus on novel absorption technology in SP2 to provide opportunity for European industry to prepare for future business*

Solvent process flow sheet
Aqueous ethanolamine solutions



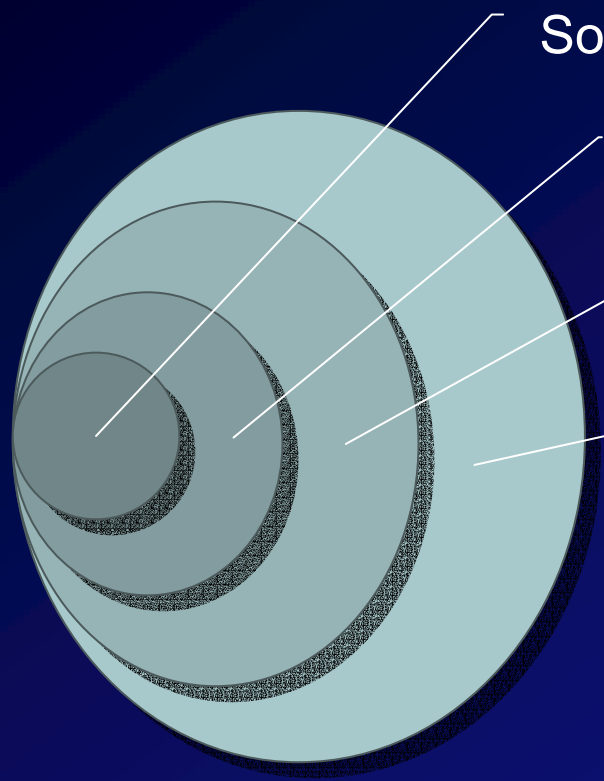
Issues for flue gas CO_2-capture technology

- Absorption technology is leading option but:
  - Power cost increases >50%
  - Generation efficiency decreases by 15 – 25%
- Absorption process break-throughs required
  - Energy requirements
  - Reaction rates
  - Contactor improvements
  - Liquid capacities
  - Chemical stability/corrosion
  - Desorption process improvements
  - Hence cost reductions
- Integration with power plant
  - Heat integration with other process plant (desorption)

Estimate of contributions to the capture costs

	Current costs contribution	Cost contribution by advanced process	Effected by
Investment costs			
Absorber	25 %	10 – 15%	Compact contactor Simplified cost-optimised contactors Membrane contactors
Rest of equipment (desorber, heat exchangers)	25 %	10 – 15 %	Halving of solvent flow rate Optimised operational conditions for advanced solvents
Total investment	*50 %*	*20 – 30 %*	
Operational costs			
Thermal energy	25%	10 – 15 %	Halving of energy consumption through use of advanced solvents (novel chemicals, additives with low vaporisation enthalpy) Integration of heat exchanger in desorber
Rest (cooling, electricity, chemicals)	25%	10 – 15 %	Halving of solvent flow rate Optimised operational conditions for advanced process technologies and solvents Solvent stability improvements
Total operation	*50 %*	*20 – 30 %*	
Total costs	**100%**	**40 – 60 %**	

Integrated approach in solvent process development for post-combustion capture



Solvent - chemistry

Process - flow sheet

Equipment - hardware

Integration - thermodynamics

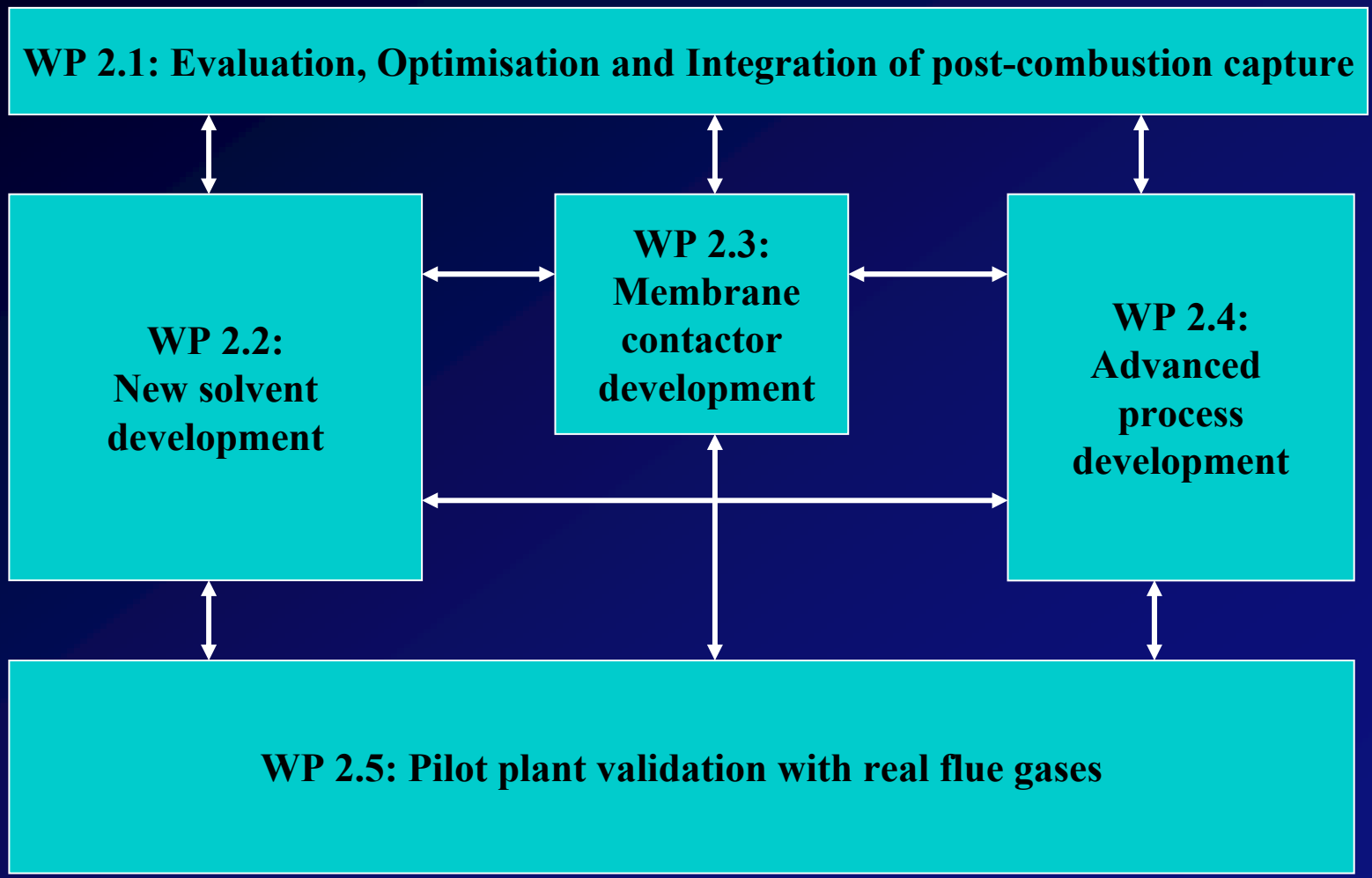
SP2. CO_2 post-combustion capture

- Overall Objectives
  - Development of absorption liquids, with a thermal energy consumption of 2.0 GJ/tonne CO_2 at 90% recovery rates
  - Resulting costs per tonne CO_2 avoided not higher than 20 to 30 €/tonne CO_2, depending on the type of fuel
  - Pilot plant tests showing the reliability and efficiency of the post-combustion capture process

R&D team in SP2

WP 1: Evaluation, optimisation, integration	**TNO**, Sintef, Vattenfall, Siemens, Alstom Power, Mitsui Babcock, Statoil, Gaz de France, PPC, E.On UK, RWE
WP 2: New solvents	**SINTEF**, NTNU, Stuttgart University, Twente University, BASF, IFP
WP 3: Membrane contactors	**TNO**, GVS
WP 4: Advanced process development	**IFP**, Sintef, NTNU, Statoil, Gaz de France
WP 5: Pilot plant validation	**Elsam**, Energie E2, TNO, Vattenfall, PPC, Statoil, RWE

SP2 – Work package structure



SP 2 planning

QTR	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
WP 1: Evaluation, optimisation, integration																
WP 2: New solvents																
WP 3: Membrane contactors																
WP 4: Advanced processes																
WP 5: Pilot plant validation																

Major technical results/deliverables

- New solvents resulting in less heat for regeneration
- Advanced processes resulting in lower power output losses
- Advanced equipment (membrane contactors) resulting in lower investment costs
- Pilot plant operating with real flue gas allowing hands-on-experience with absorption technology
- Methods for integration and optimisation resulting in lower power output losses

Experimental set-ups for solvent selection

Miniplant
Stuttgart Uni.

Degradation set up
Stuttgart Uni.

Equilibrium
Apparatus
SINTEF/NTNU

Corrosion test cell
IFP

Set-up for G/L mass transfer measurements

D=150 mm, H=2m
System model : CO_2/NaOH system

Large size pilot plant for hydrodynamics

- D=400 mm, H=2m
- System model : water+additives / air
- Gamma tomography system

Pilot plant in Denmark (Elsam/E2)

- Application in modern coal-fired power station: Esbjerg power station operated by ELSAM
- Capacity 1 ton/h CO_2
- Pilot plant will be largest test facility in the world
- EU test facility for post-combustion capture processes
- Testing will start with MEA to be followed by CASTOR solvents

Pilot plant ESV3 (Esbjerg - Denmark

Location

Esbjergværket

Elsam
essential energy

Capacity

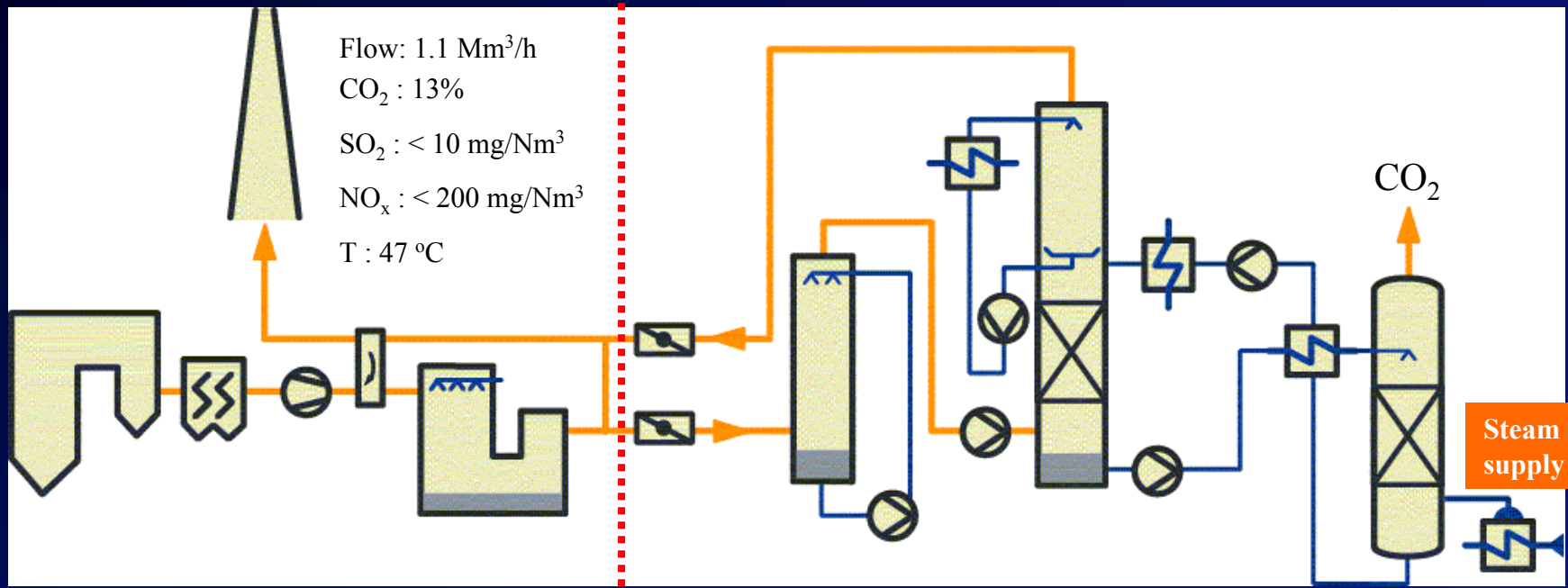
1 t/h CO_2 capture

5.000 Nm^3/h flue gas (coal combustion)

Pilot plant flow sheet

Power plant

Capture pilot plant



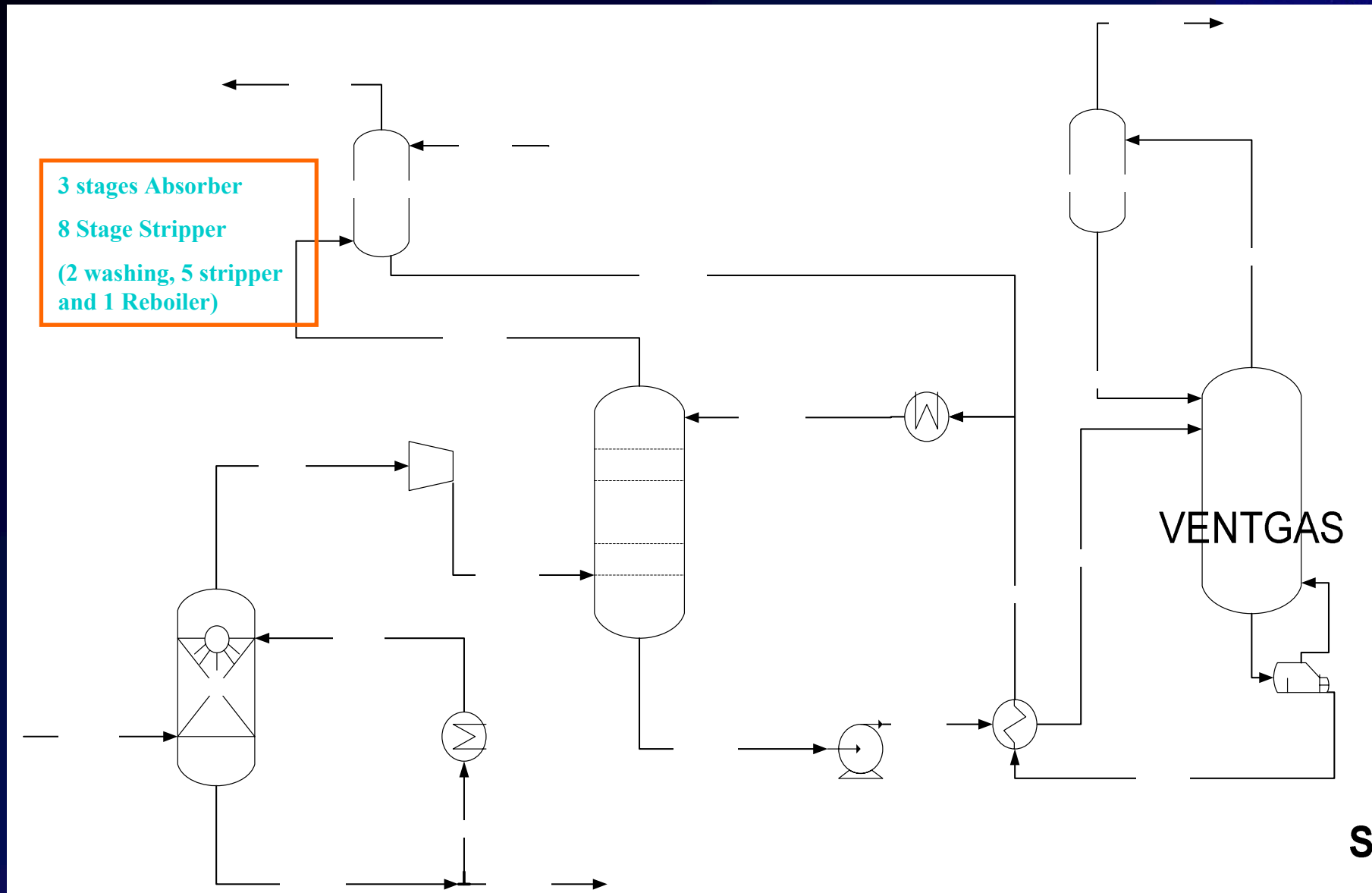
Power plant reference cases
2004 state-of-the-art (also for ENCAP)

- Natural gas fired 393 MW_e Gas Turbine Combined Cycle
- Bituminous coal fired PF 600 MW_e
- Lignite fired PF 1000 MW_e
- Lignite fired PF 380 MW_e

Baseline absorption process

- Solvent: Aqueous 30 % MEA solution
- Modelling tool: Aspen Plus using equilibrium stage model
- Flue gases:
  - Pulverised coal fired power station (500 MW_e)
- Absorber:
  - 3 stages
- Stripper:
  - 8 stages overall (one for reboiler, two for wash section)
  - Bottom: 1.8 bar; top: 1.5 bar
- Lean/rich loading: 0.242/0.484 mol/mol MEA
- 90 % CO_2 removal
- Specific thermal energy consumption: ~4 GJ/tonne CO_2

Process Flow Sheet

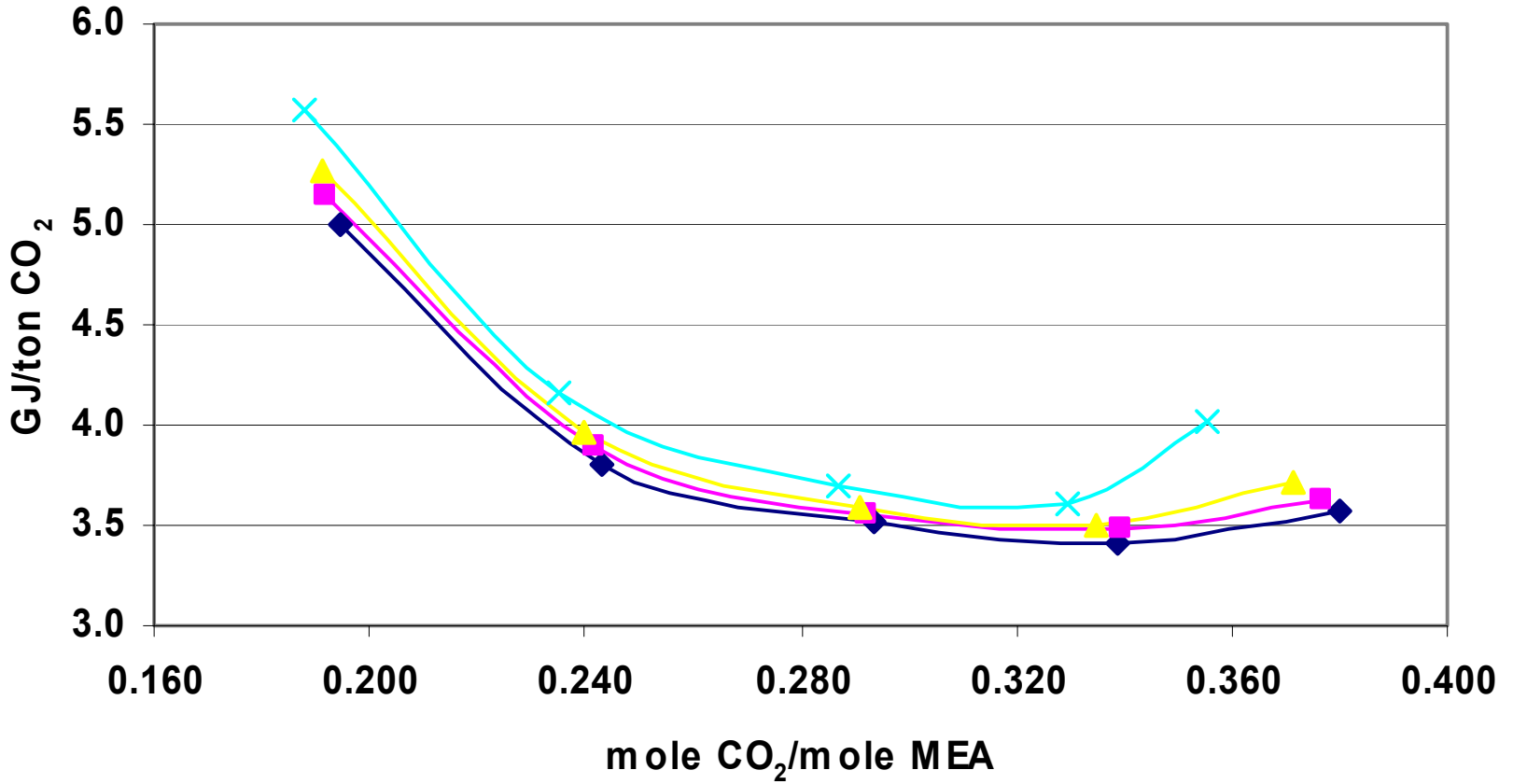


Parametric studies based on MEA-process

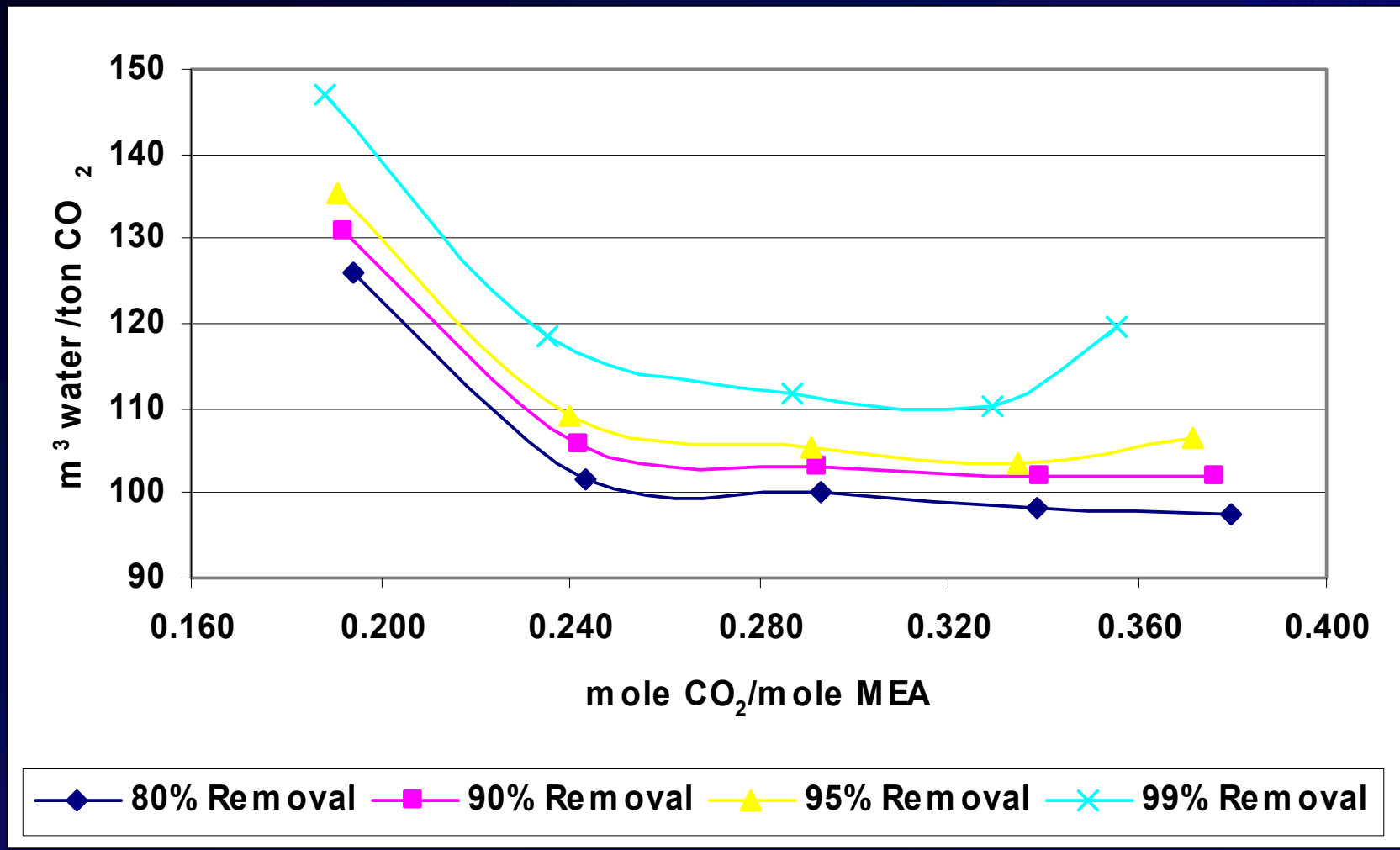
- Lean solvent loading/degree of regeneration as main variable
  - Different CO_2-removal
  - Different MEA-concentrations

- Assess the impact on:
  - Thermal energy requirement
  - Cooling water
  - Cost of electricity
  - Avoided costs

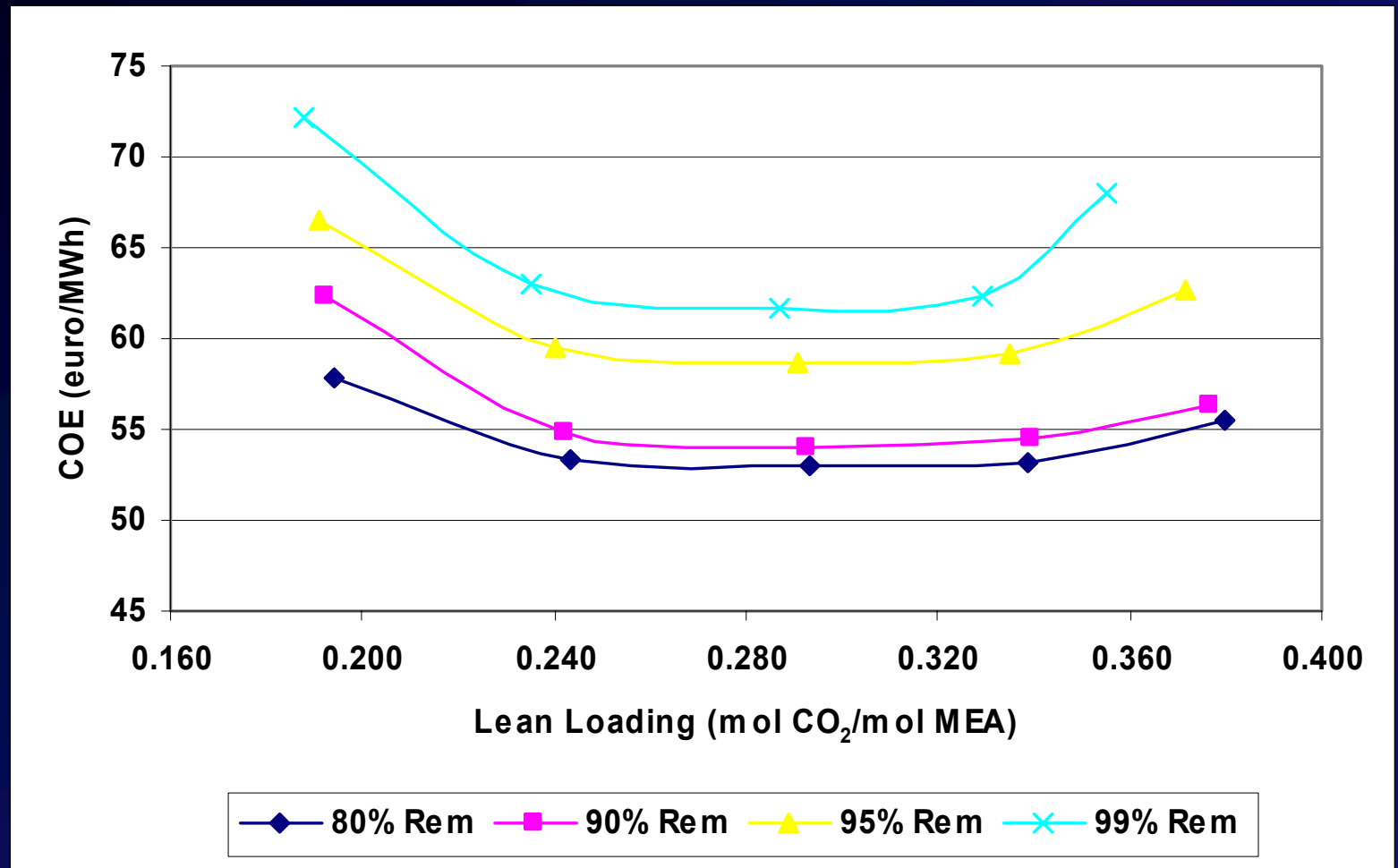
Effect of CO_2 removal and lean loading on thermal energy requirement



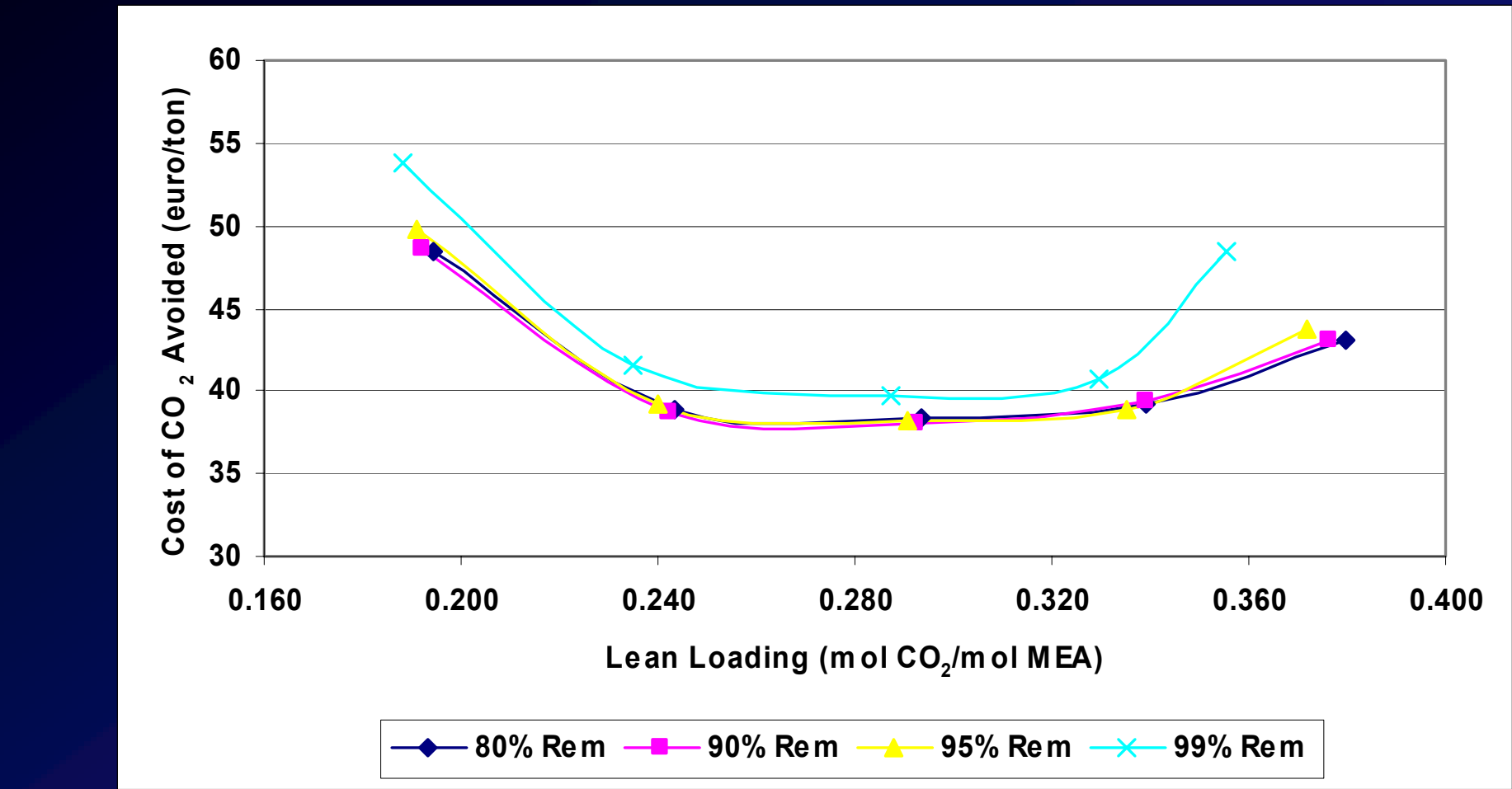
Effect of CO_2 removal and lean loading on cooling water requirement



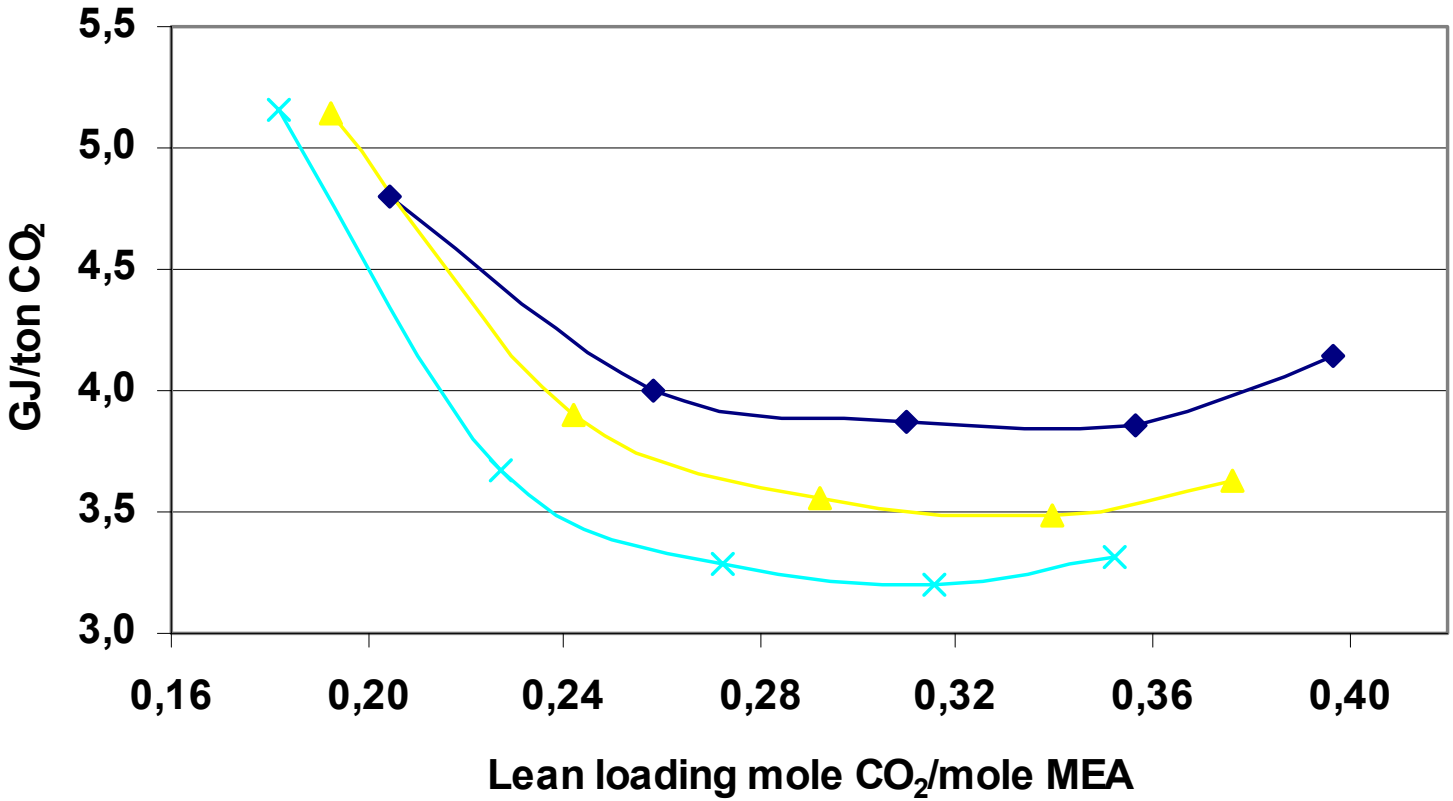
Effect of CO_2 removal and lean loading on cost of electricity (preliminary)



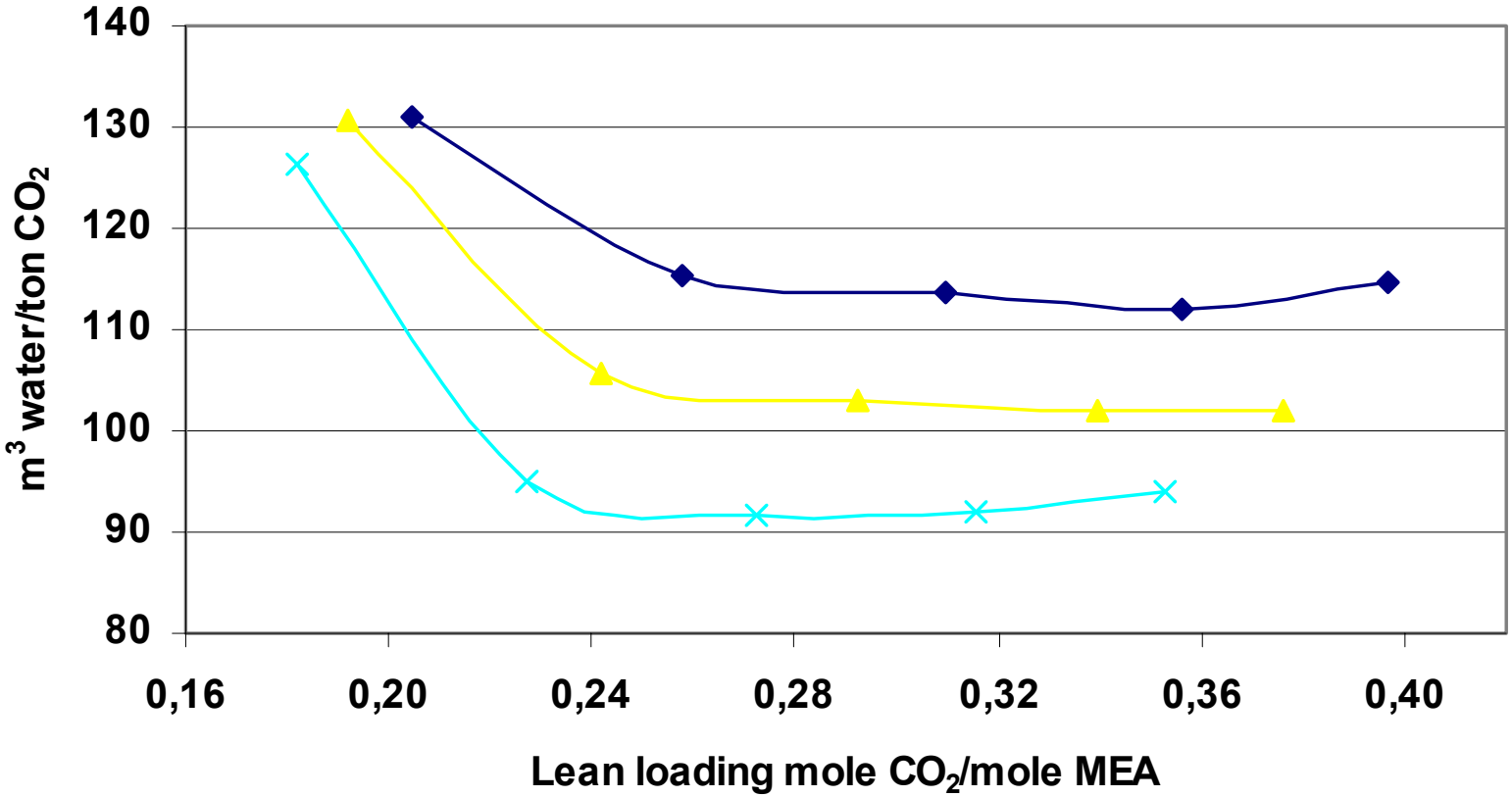
Effect of CO_2 removal and lean loading on avoided costs (preliminary)



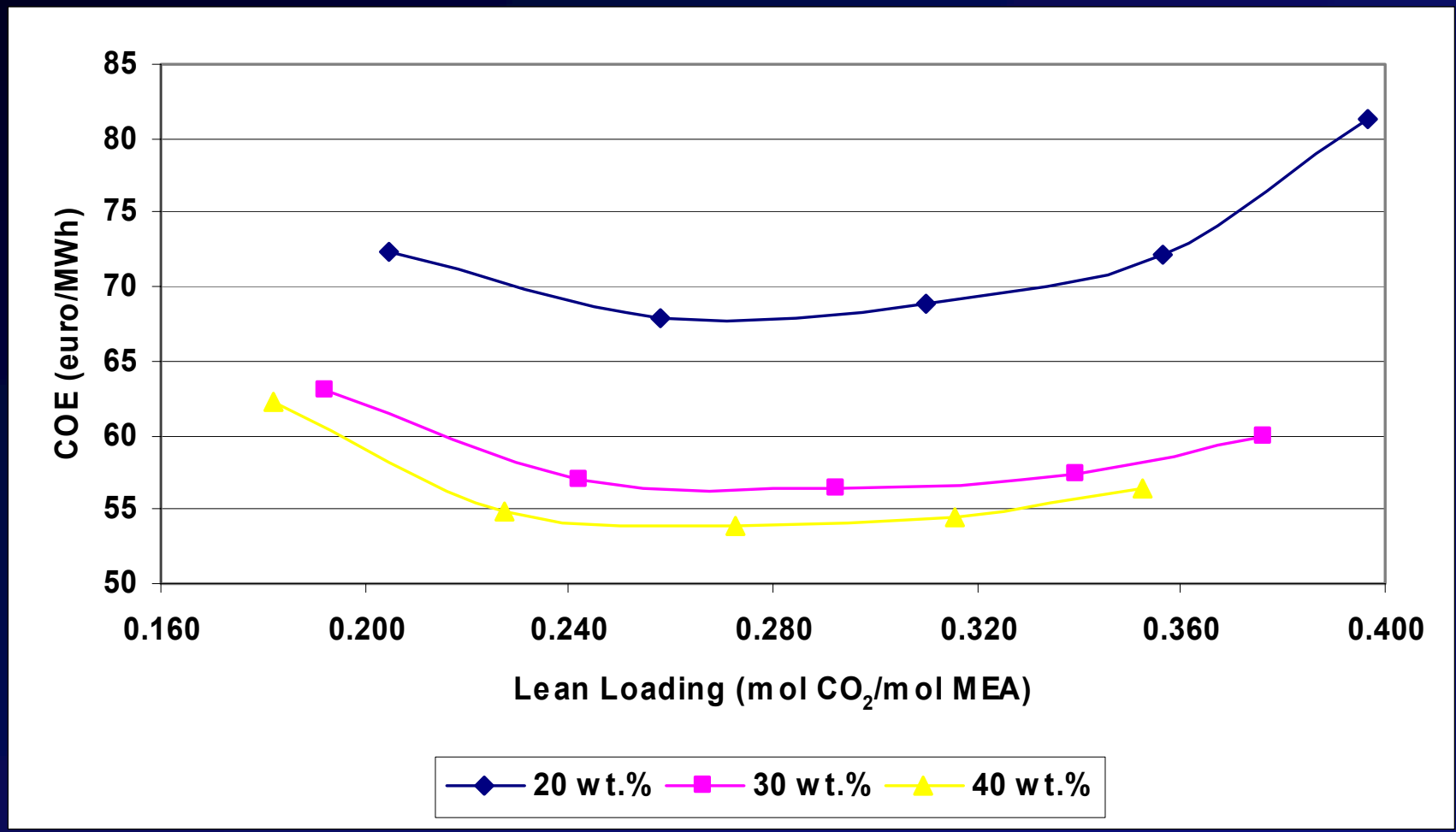
Effect of MEA-concentration and lean loading on thermal energy requirement



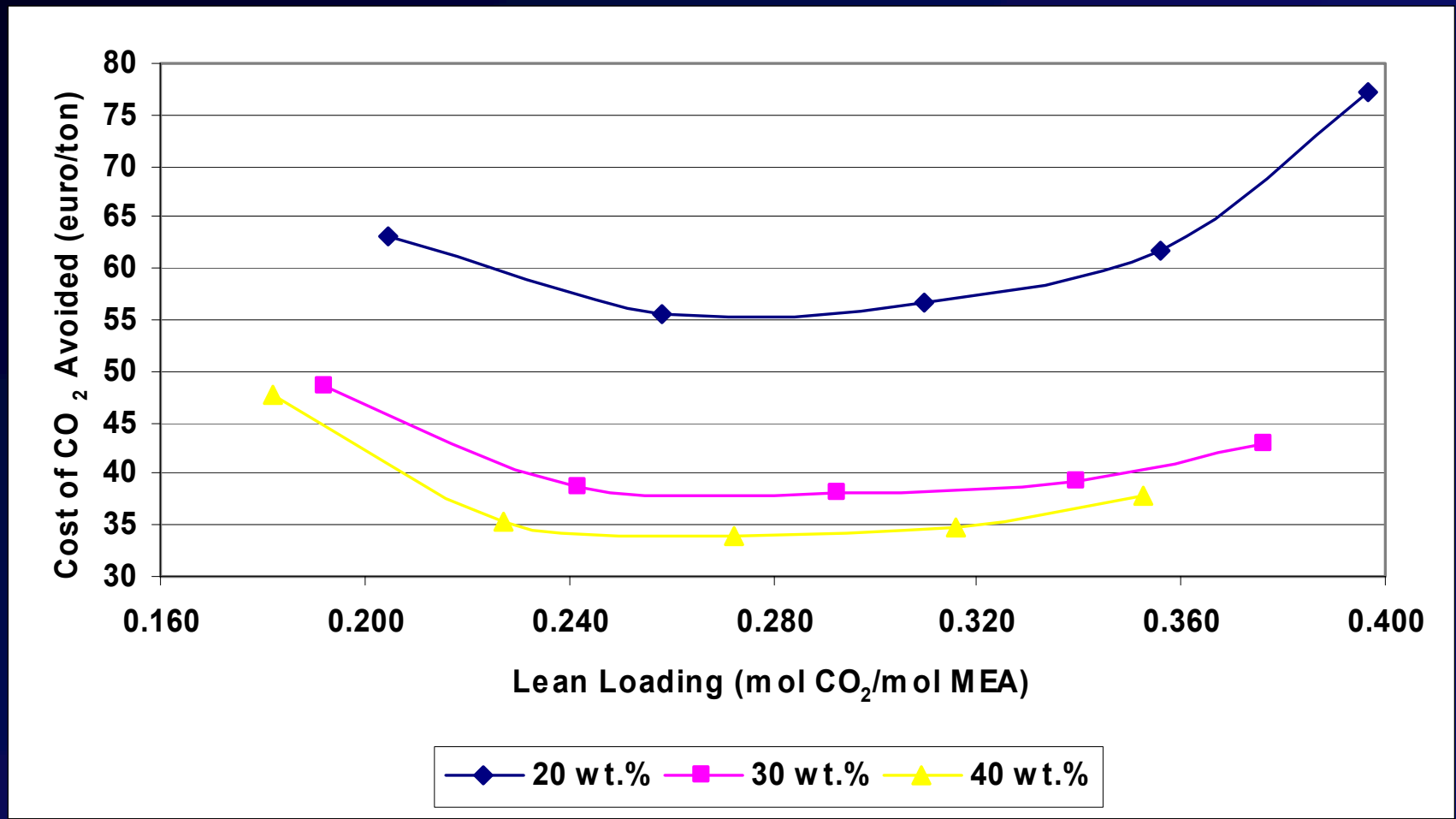
Effect of MEA-concentration and lean loading on cooling water requirement



Effect of MEA-concentration and lean loading on cost of electricity (preliminary)



Effect of MEA-concentration and lean loading on avoided costs (preliminary)



Thanks to SP 2 contributors!

- Alstom Power
- BASF
- Elsam
- Energie E2
- EON UK
- Gaz de France
- GVS
- IFP
- Mitsui Babcock
- NTNU
- PPC
- RWE
- Siemens
- SINTEF
- Statoil
- Stuttgart University
- TNO
- Twente University
- Vattenfall

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MRCSP
MIDWEST REGIONAL
CARBON SEQUESTRATION
PARTNERSHIP

Managing Climate Change and Securing a Future for the Midwest's Industrial Base

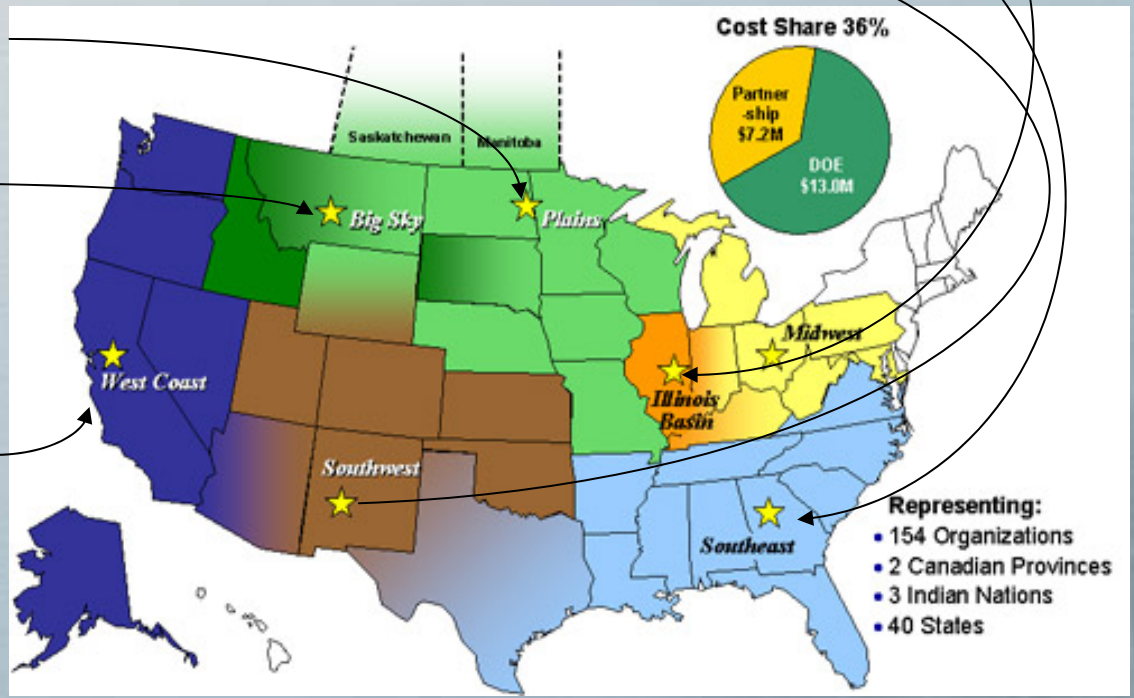
Sandip Chattopadhyay, Dave Ball, Neeraj Gupta, Bruce Sass, and Phil Jagucki

8th International CO_2 Capture Network
3-4 October 2005
University of Texas, Austin, USA

The MRCSP is One of Seven Regional Partnerships Across the U. S.

The other six are:

- Geological Carbon Sequestration Options in the **Illinois Basin**
- **Southeast** Regional Carbon Sequestration Partnership
- **Southwest** Regional Partnership for Carbon Sequestration
- **Plains** CO_2 Reduction Partnership
- **Big Sky** Regional Carbon Sequestration Partnership
- **West Coast** Regional Carbon Sequestration Partnership



See http://www.netl.doe.gov/coal/Carbon%20Sequestration/partnerships/index.htm for more information from NETL on the seven partnerships.

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MRCSP
MIDWEST REGIONAL CARBON SEQUESTRATION PARTNERSHIP

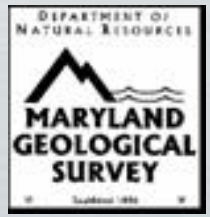
MRCSP Mission

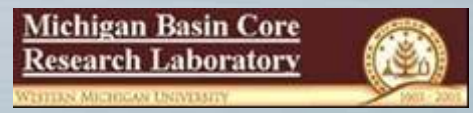
be the premier resource in its Region for identifying the technical, economic, and social considerations associated with CO_2 sequestration and creating viable pathways for its deployment.

Snapshot of the MRCSP

- **Who:** 38-member team led by Battelle:
  - Leading research organizations in our Region
  - Major energy and agricultural entities operating in our Region
  - Key government and non-government organizations
- **What:** Assessing carbon sequestration opportunities
  - Technical and economic potential
  - Public acceptance
- **Where:** Seven-State Region:
  - IN, KY, MD, MI, OH, PA, and WV
- **When:** Launched, fall of 2003; two year Phase I program
- **When:** MRCSP Proposal for Phase II Selected, 2005-2009
- **Why:** Part of national effort to develop robust, potentially large scale and cost effective strategies for mitigating anthropogenic CO_2 emissions

MRCSP Phase I Partner Listing





U.S. Department of Energy/NETL

Phase I Accomplishments

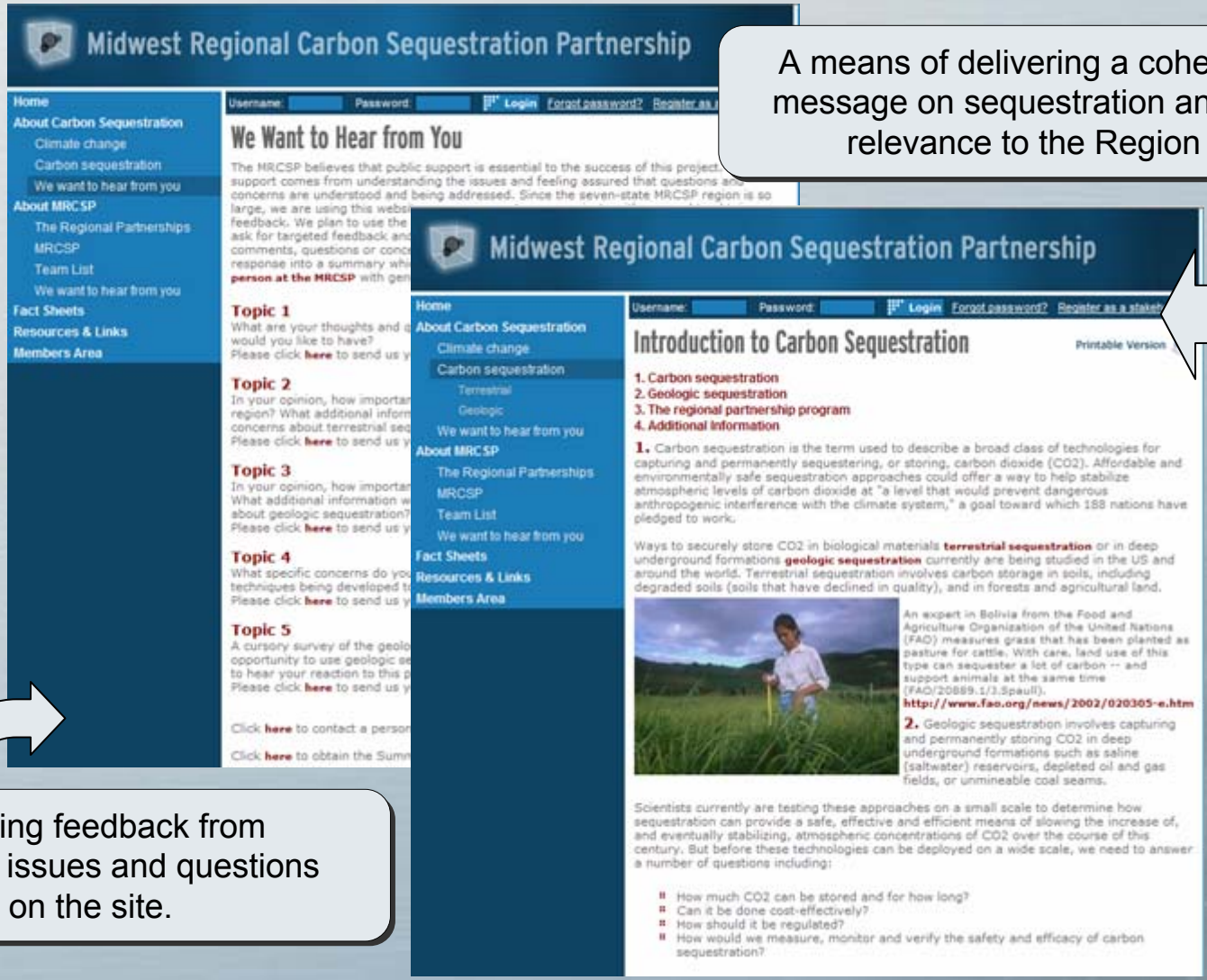
- First ever coherent mapping of the region's potential geological and terrestrial carbon sinks
  - Calculation methodologies developed and agreed to for calculating terrestrial and geological storage potential.
- An extensive outreach stakeholder database and an interactive web site (completed in January 2005) for obtaining feedback from the public
  - Number of web visits doubled as a result (from about 400/mo to over 900/mo).
  - Site is being used and evaluated as a cost effective vehicle to educate and poll the interests and knowledge of the public.
- Compilation of a multi-layer GIS source inventory
- State of the art assessment of capture technology and economics as it relates to large CO_2 sources in the region

Phase I Accomplishments (Continued)

- Acquired and reviewed applicable federal and state regulations affecting implementation of sequestration in the region
  - Focus groups with regulators have been completed in six of the seven MRCSP states (WV, OH, IN, MD, KY, and PA). A meeting in Michigan is planned soon.
- A detailed cost model used by Battelle in other studies has been adapted to the region's large point sources. A preliminary cost curve for the region has been prepared.
- A portfolio of Phase II demo opportunities has been defined (both geological and terrestrial). New members to join include Chicago Climate Exchange, Schlumberger, and Stanford University. Praxair and Air Liquide are also expected to join.
- Many presentations and meetings involving the public have been held in the various MRCSP states

In January 2005 we Upgraded our Website (www.mrcsp.org) to be Interactive

A means of delivering a coherent message on sequestration and Its relevance to the Region



While obtaining feedback from stakeholders on issues and questions posed on the site.

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MIDWEST REGIONAL CARBON SEQUESTRATION PARTNERSHIP

Our source GIS has multiple layers of information on over 600 CO_2 sources

Facility Type	Number of Facilities	Percent of CO2 Emissions
Ammonia	1	0.0
Cement	29	1.9
Ethanol	4	0.1
Ethylene	3	0.1
Ethylene Oxide	1	0.0
Gas Processing	33	1.8
Hydrogen	9	0.1
Iron and Steel	64	9.0
Refineries	18	2.6
Power Generation	455	84.4
Totals	**617**	**100.0**

Unit Type	Number of Units	Average Capacity	Average Vintage
Coal			
Bituminous	340	315	1964
Subbituminous	14	305	1973
Other	18	80	1987
IGCC	1	192	1995
Gas			
Combined Cycle	16	86	1991
Gas Turbine	4	51	1978
Steam Turbine	15	265	1969
Oil	10	368	1973

Bituminous coal fired power generation is clearly a major source in our region

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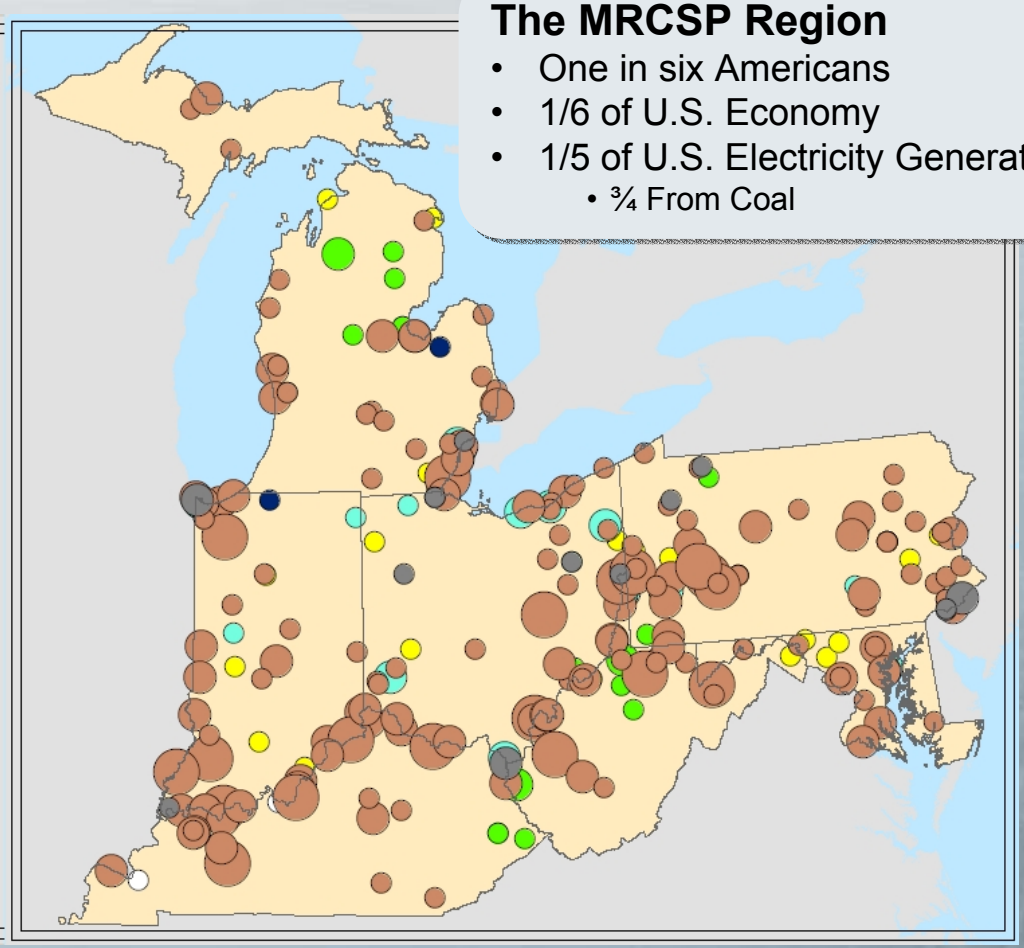
The MRCSP Region: The Nation's Engine Room

MRCSP
Large CO2 Point Sources
(100+ kt CO2/yr)

- Cement
- Ethanol
- Ethylene
- Gas processing
- Hydrogen
- Iron & steel
- Power
- Refineries

ktCO2/yr
- 100 - 2,000
- 2,000 - 10,000
- 10,000 - 20,000



The MRCSP Region
- One in six Americans
- 1/6 of U.S. Economy
- 1/5 of U.S. Electricity Generated
  - ¾ From Coal

- About 300 Large Stationary Point Sources
- Over 770 $MtCO_2$/year

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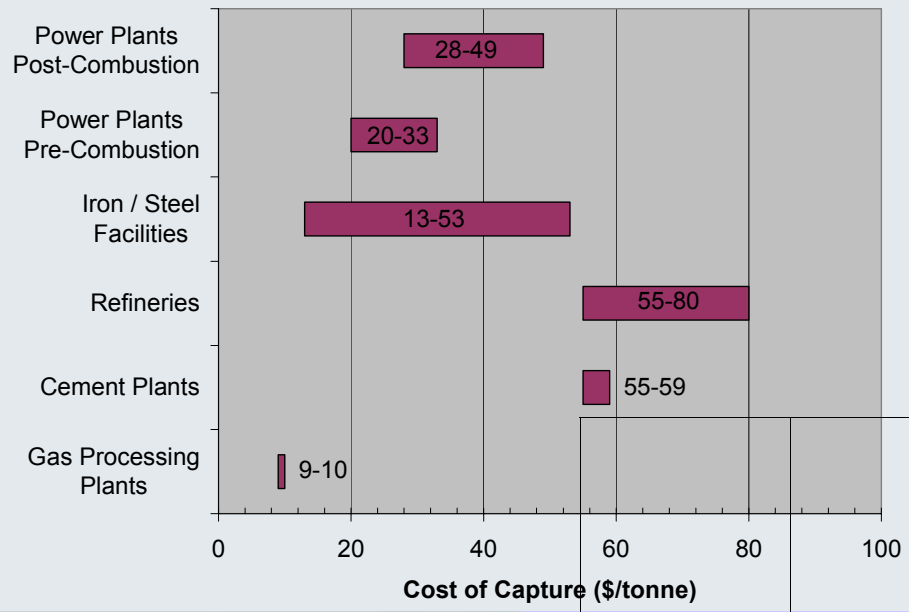
CONSOL has completed a detailed analysis of capture technologies for MRCSP

Technologies Considered

- Amine Scrubbing
- Alkaline Salt Scrubbing
- Ammonia Scrubbing
- Physical Absorption
- Gas Separation Membrane
- Gas Absorption Membrane
- Physical Adsorption
- Solid Chemical Absorption
- Cryogenic
- Hydrate Formation
- Electrochemical Separation
- Biochemical Separation
- Oxyfuel
- Chemical Looping Combustion

An Amine Capture Plant on a Gas Processing Plant
Photo provided by CONSOL Energy

The capture analysis includes economic analysis and a ranking of processes



Cost of capture is in the range of $20 to $50 per tonne of CO2 for most MRCSP sources

Capture technologies are ranked as:

- **"L" Likely,**
- **"A" Attractive, and**
- **"S" Speculative**

Source Type	Point of Capture	Amine Scrubbing	Ammonia Scrubbing	Physical Absorption	Gas Separation Membrane	Gas Absorption Membrane	Oxyfuel + Drying/Compression	Simple Drying/Compression
Power Plants Post-Combustion	Flue Gas	L	A	--	A	A	A	--
Power Plants Pre-Combustion	Shifted Syngas	--	--	L	A	--	--	--
Iron / Steel Facilities	Blast Furnace Gas (~60-70% of total CO_2)	L	--	L	A	S	--	--
Refineries	Heater/Boiler Flue Gas (~65-85% of total CO_2)	L	S	--	A	S	A	--
Cement Plants	Kiln Flue Gas	L	S	--	S	S	S	--
Gas Processing Plants	Vented CO_2	--	--	--	--	--	--	L

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Our regulatory analysis is showing no significant barriers but awareness and protocols are lacking

Activities

- Pertinent federal and state regulations have been compiled and reviewed
- Focus groups with various regulatory representatives are being held in each state

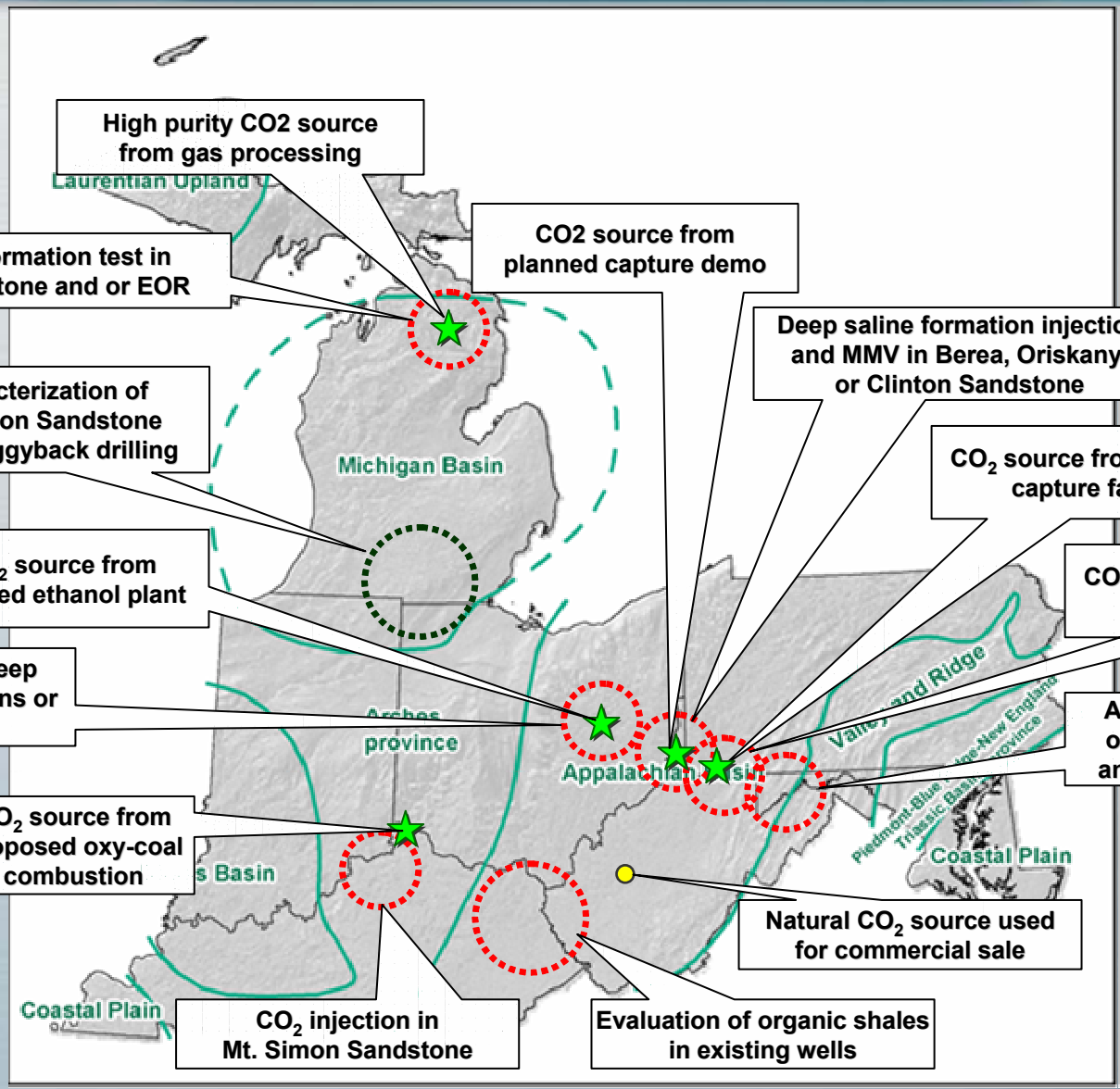
Findings to date

- Need for interagency coordination
  - So far there has been very little dialogue between various state agencies on sequestration
  - In fact, knowledge and awareness of sequestration technologies is low
  - It's clear that an integrated siting and permitting process is lacking.
- Terrestrial sequestration
  - Few constraints and many states are aware and interested. But jurisdiction is dispersed over various agencies
    - e.g. DNR for forests, minelands, and wetlands; Agriculture for croplands and conservation
  - Monitoring and verification protocols need further refinement.

Regulatory analysis (continued)

- CO_2 pipelines
  - No major regulatory hurdles. Several states indicate that they would allow eminent domain for CO_2 pipelines (others are uncertain).
  - Joint federal and state pipeline regulations are already in place. However there is modest experience with CO_2 pipelines in the MRCSP region
- Geologic sequestration
  - How long-term liability will be handled is uncertain
  - In the absence of specific statutes, the UIC program developed for ensuring safe drinking water will apply.
  - State regulators confirm that pilot projects will be permitted under the UIC
  - Most agree that the UIC program can be adapted to better meet the needs of sequestration if new regulations are not forthcoming
  - Property rights issues are still unresolved. A legal means for creating large underground storage fields needs to be created
  - All MRCSP states but one have statutes for creating unitized oil and gas fields but these are insufficient for carbon sequestration.

Phase II Geologic Field Validation Tests



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Carbon Capture and Storage Tests in The Ohio River Valley Region – Mountaineer Project

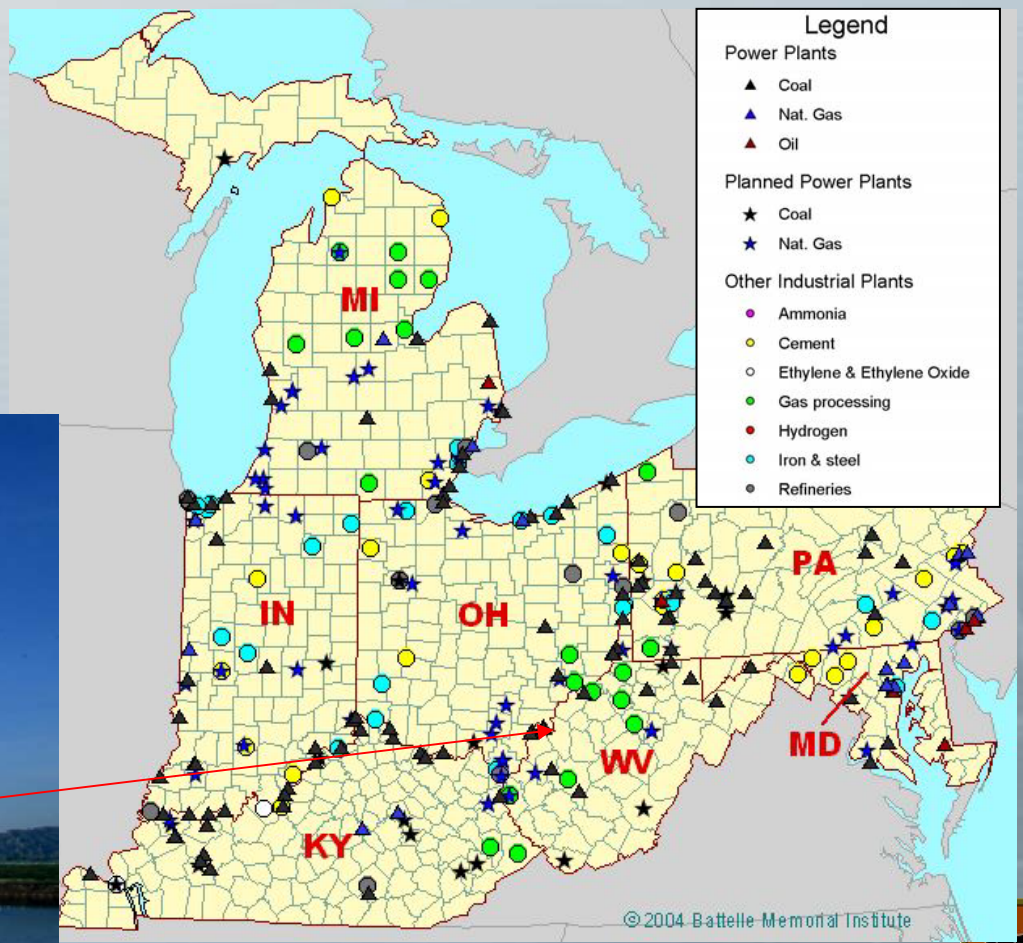
NETL AEP bp MAKING OHIO COAL THE CLEAN CHOICE Pacific Northwest National Laboratory Operated by Battelle for the U.S. Department of Energy Schlumberger

Ohio River Valley CO_2 Storage Project – Key Motivations

- A large number of CO_2 sources lie in the Ohio River Valley region and it is important to determine the CO_2 storage opportunities in this region
- Systematic field tests and regional geologic data are essential for understanding storage potential and building stakeholder confidence
- The objective of this project is to characterize the CO_2 storage potential in geologic reservoirs in the region and demonstrate safe and cost effective strategies for enhancing injection potential
- During the last two years characterization of a test well, seismic survey, and reservoir simulations etc have been conducted
- We are now working on site design and permitting feasibility aspects:
  - Development of a capture and local transport system design
  - Design for injection and monitoring systems
  - NEPA assessment and underground Injection permitting
  - Enhanced regional geologic framework
  - Building on the foundation of stakeholder outreach

Project Motivation – Why the Ohio River Valley Region?

- Mountaineer Plant - 1,300-MW, flagship, coal-fired plant with installed SCR for NOx control and FGD for SOx under construction
- Numerous other sources in the region and high potential for additional sources



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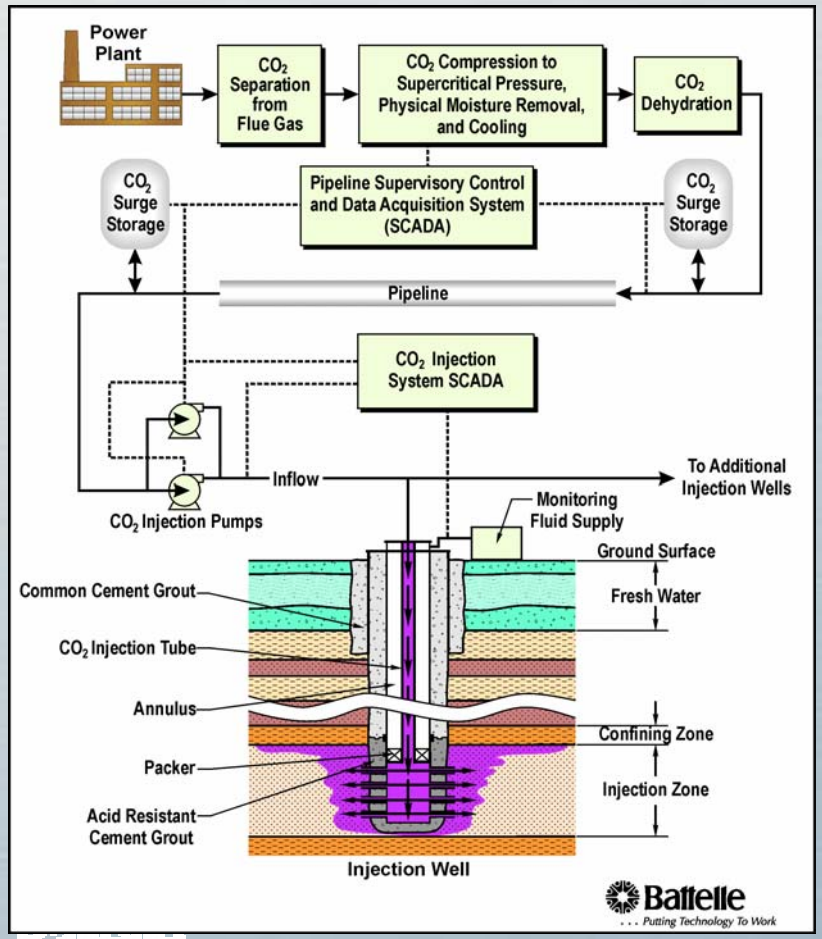
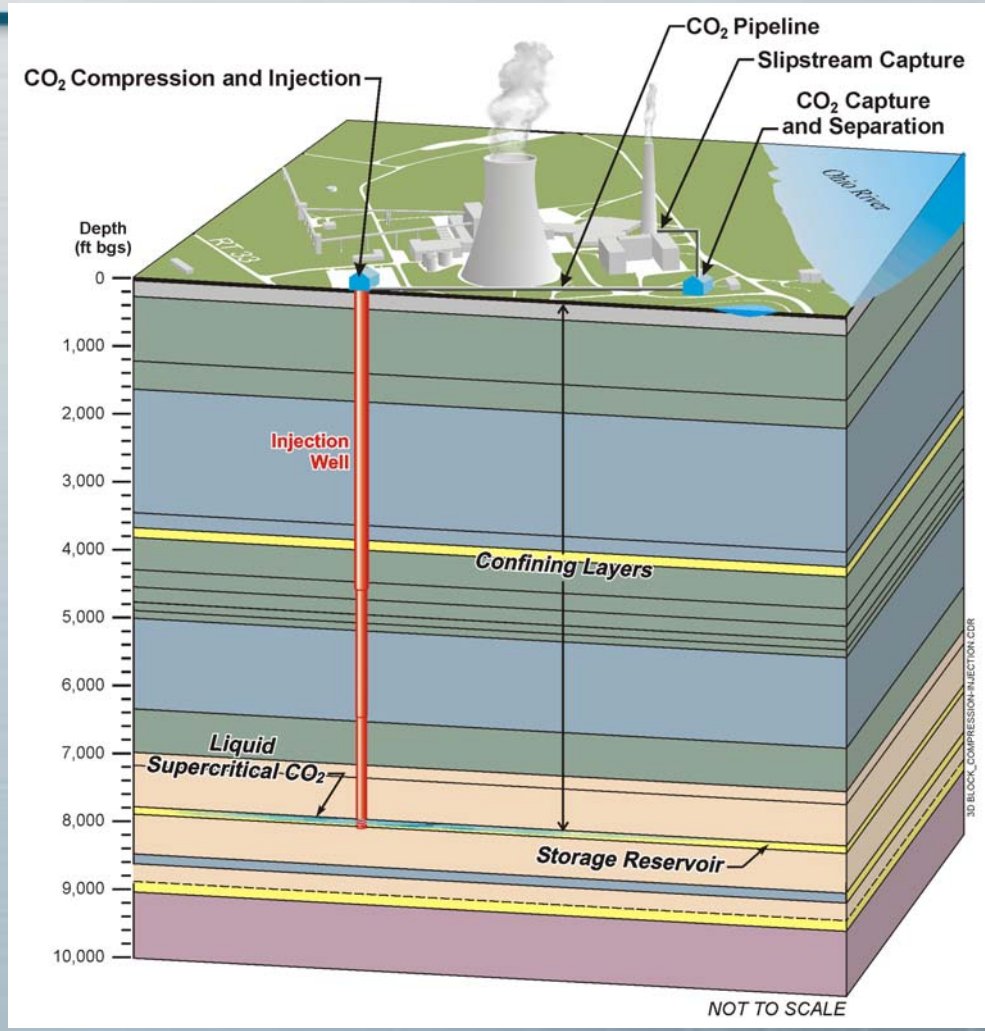
Geologic Sequestration System Components and Mountaineer Plant





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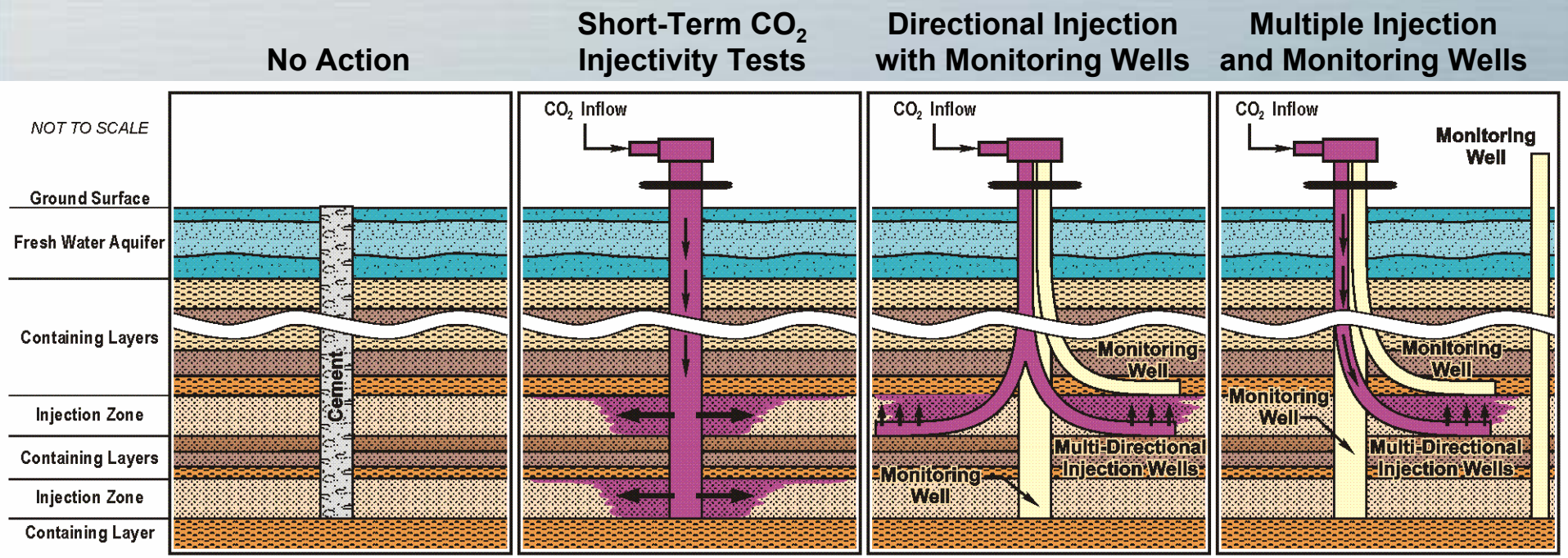
What is Next –
Design Feasibility for Injection Tests

- Options for an injection/monitoring program at the site are being evaluated
- The next logical steps include system design, permitting, and monitoring plan
- This decision to proceed to injection will be made by project sponsors based on the outcome of the complete design feasibility study



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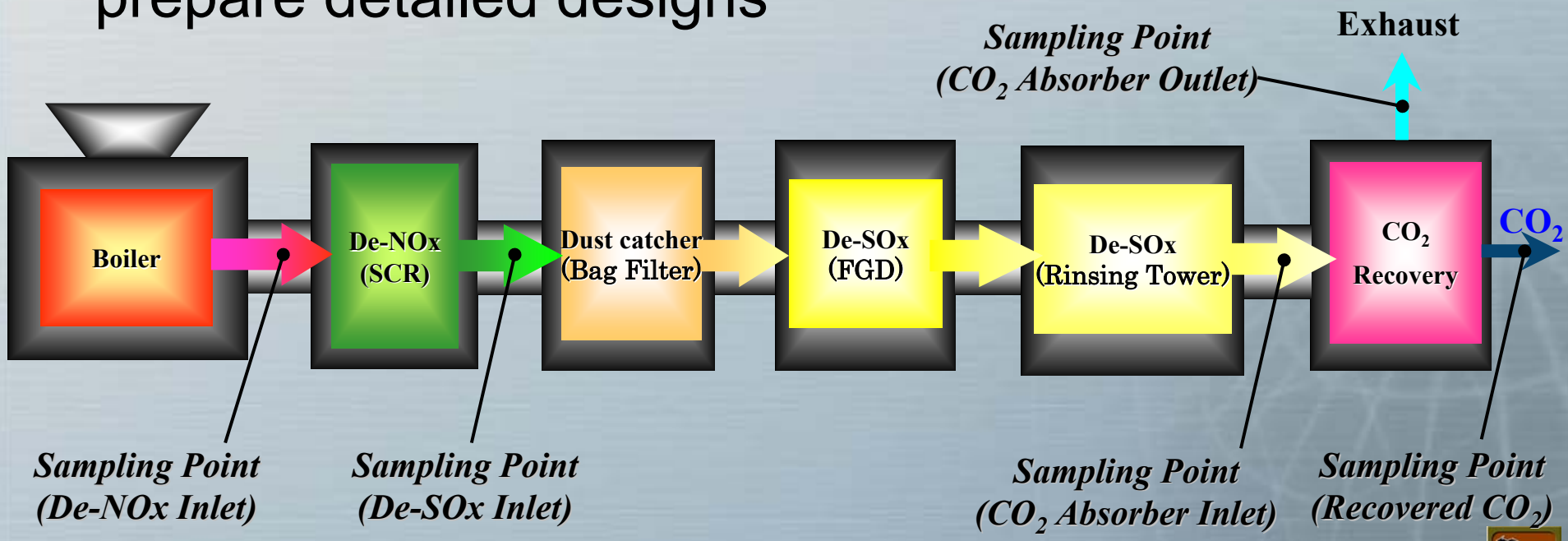
Process Flow of CO_2 Recovery Pilot Plant

- High-sulfur coal tested for capture optimization
- Preliminary basic design has been prepared
- Collaboration with capture vendors is underway to prepare detailed designs



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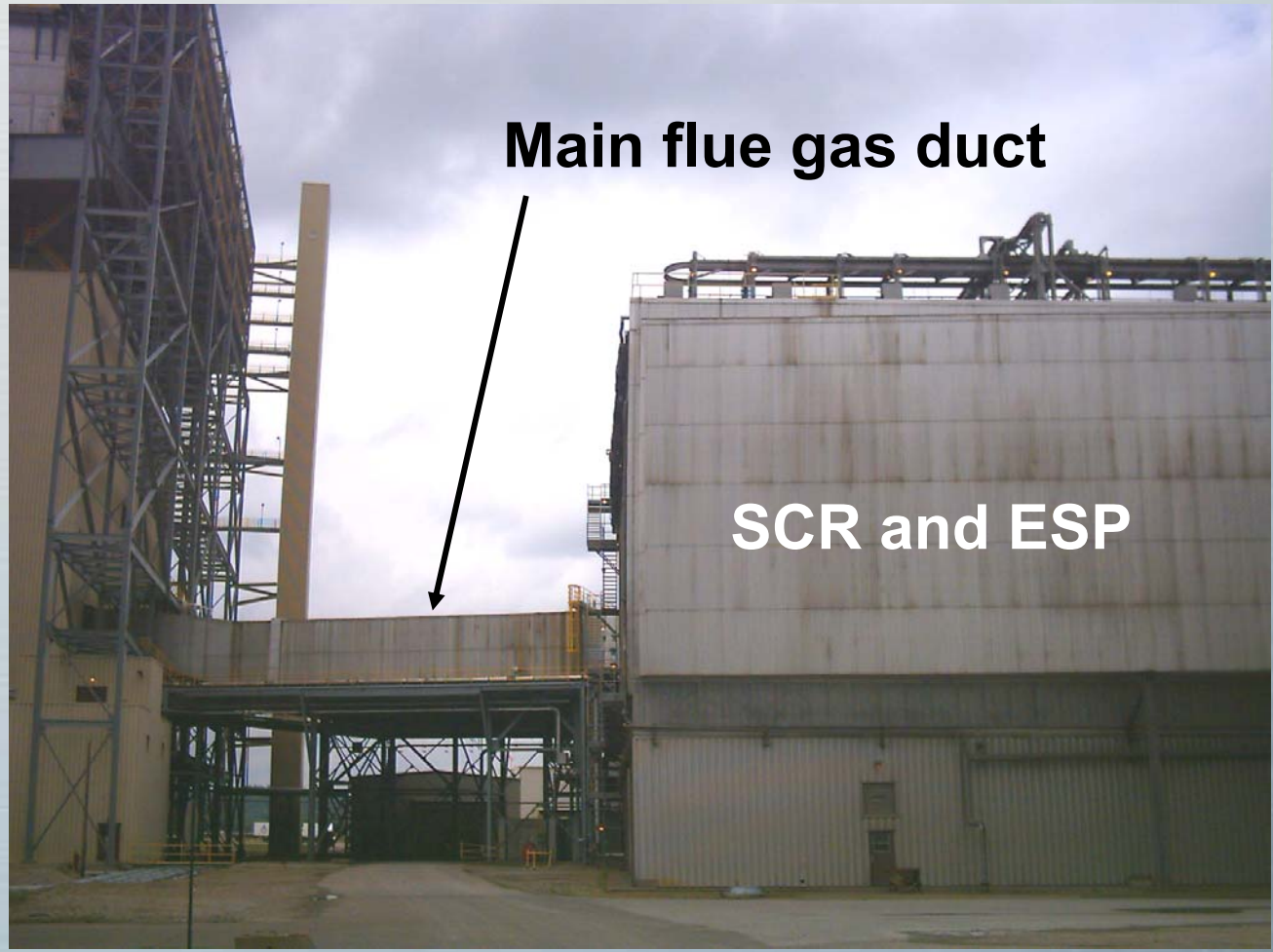
Considerations for a Pilot CO_2 Injection Test at Mountaineer Plant

- CO_2 capture unit should be modular so that is possible to transport the unit to different demonstration sites.
  - Skid-mounting may be preferred for ease in shipping and assembling.
- The system should be constructed so that it can withstand repeated disassembly and reassembly.
  - However, the period of usage may be limited. Therefore, the materials used in construction may not have to be the most durable.

Mountaineer Plant

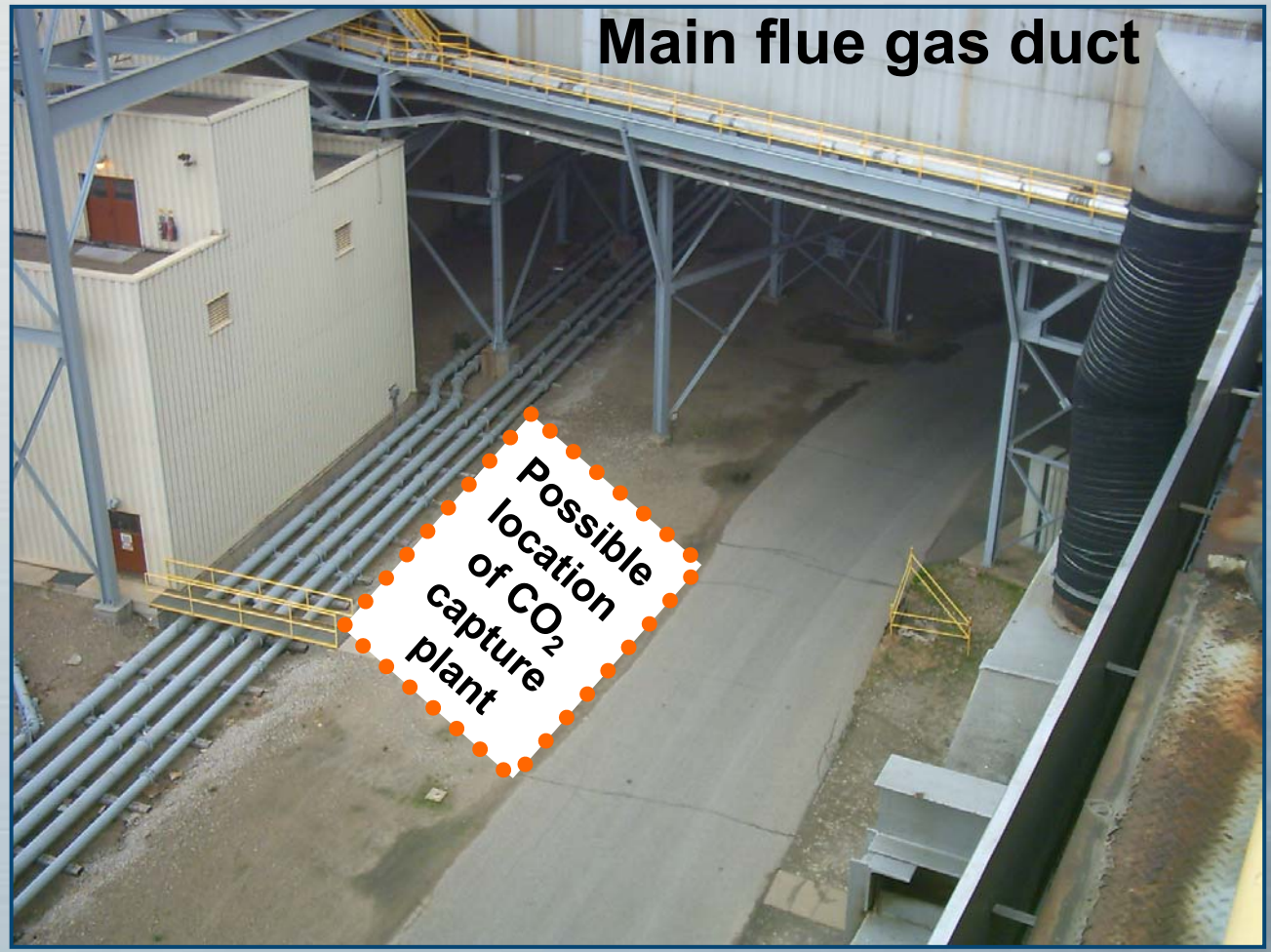


Mountaineer Power Plant: Showing New FGD Unit

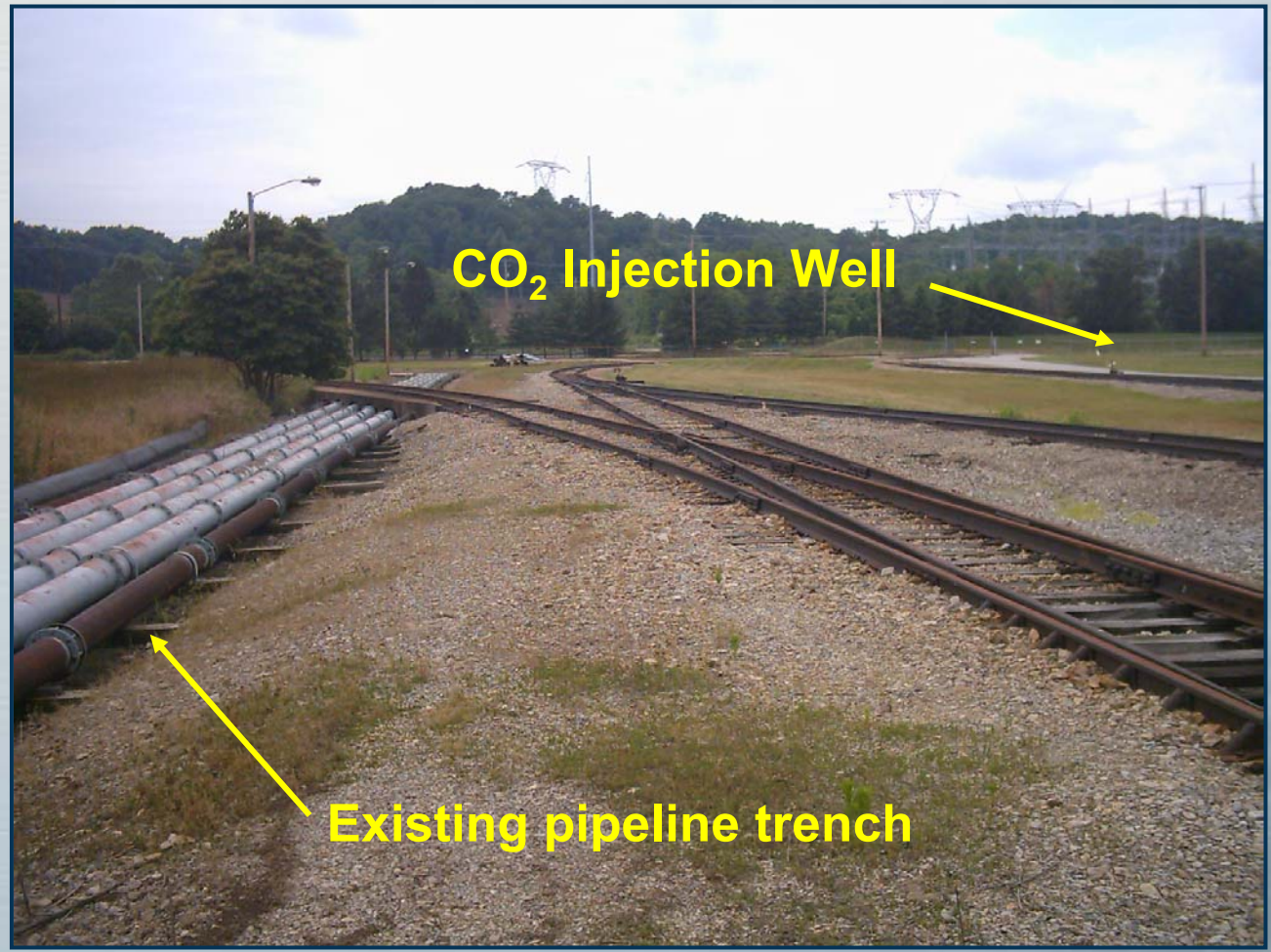
Duct for flue gas slip stream

Similar overhead raceway to support slipstream duct

Mountaineer Plant – Example of Capture Siting



Considerations for a Pilot CO_2 Injection Test at Mountaineer Plant



Summary

- Deployment of geologic sequestration requires research at multiple spatial scales
- Joint industry-government R&D efforts to secure a future for fossil fuels and secure a future for region's fossil-fired generation fleet in a greenhouse gas constrained world are essential
- Substantial improvement in understanding features of relevant geologic formations in Midwestern USA
- There is simply no substitute for the experience gained by actually working in the field
- An expanded collaboration and support from the oil and gas industry is critical for a successful implementation
- Significant technical progress has been made to initiate a first-of-a-kind integrated demonstration of capture, local transport, storage, and monitoring test at a major power plant.

Capture of CO_2 from Point Sources: NETL In-House Research Activities

James Hoffman
U.S. Department of Energy
National Energy Technology Laboratory
P.O. 10940
Pittsburgh, PA 15236

8th International CO_2 Capture Network Meeting
Oct 3-4, 2005
University of Texas
Austin, Texas

Presentation Outline

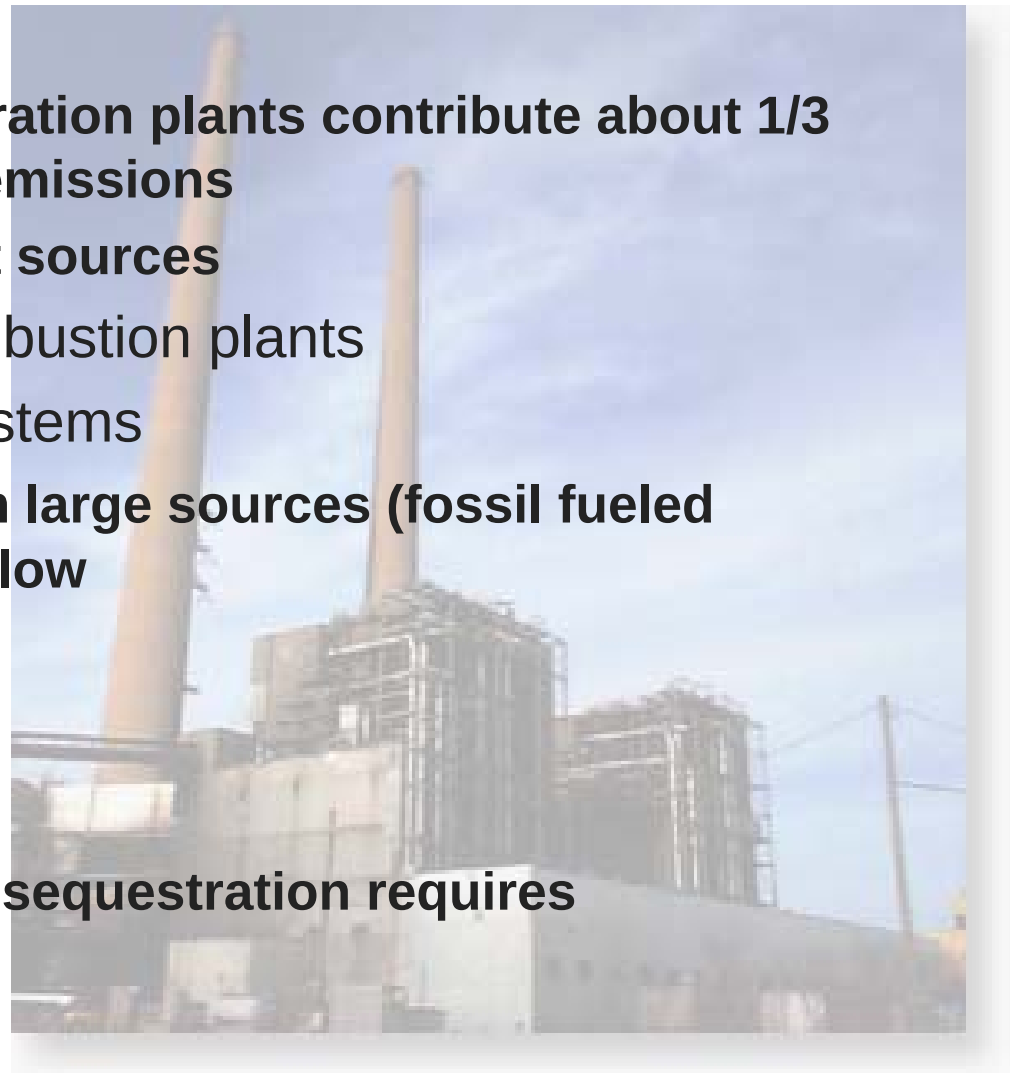
- **Introduction of CO_2 capture & separation activities at NETL.**
- **Pilot-scale tests (MCCF) and supplementary bench-scale tests (packed-bed reactor) using molecular sieve 13X to separate/capture carbon dioxide from flue gas.**
- **Future activities.**

Carbon Sequestration Program*

- **Implements the President's Global Climate Change Initiative of 18% reduction in GHG intensity by 2012.**
- **Carbon dioxide capture drives the cost of sequestration systems.**
- **Capture program goals**
  - By 2007, develop technologies that result in less than 20% increase in cost of energy services.
  - By 2012, develop technologies that result in less than 10% increase in cost of energy services.

*Carbon Sequestration Technology Roadmap and Program Plan - May 2005

POINT SOURCES OF INTEREST



- **Fossil-fuel power generation plants contribute about 1/3 of anthropogenic CO_2 emissions**
- **Power generation point sources**
  - Pulverized-coal combustion plants
  - Advanced power systems
- **CO_2 concentration from large sources (fossil fueled power plants) typically low**
- **Capture step**
  - Post-combustion
  - Pre-combustion
- **Storage step in carbon sequestration requires concentrated CO_2**

RECENT ADVANCES IN CARBON DIOXIDE CAPTURE AND SEPARATION TECHNIQUES FOR POWER GENERATION POINT SOURCES

Henry Pennline et. al.
U.S. Department of Energy
National Energy Technology Laboratory
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Prepared for presentation at the
2005 AIChE Annual Meeting
November, 2005
Cincinnati, Ohio

Novel In-House CO_2 Capture Technologies

AA
- Aqua Ammonia Process for Multicomponent Removal (J. Yeh)

MEM
- Hybrid Membranes for CO_2 Separation (D. Luebke)

SOL
- Solvents for CO_2 Capture (K. Jones & B. Morsi)

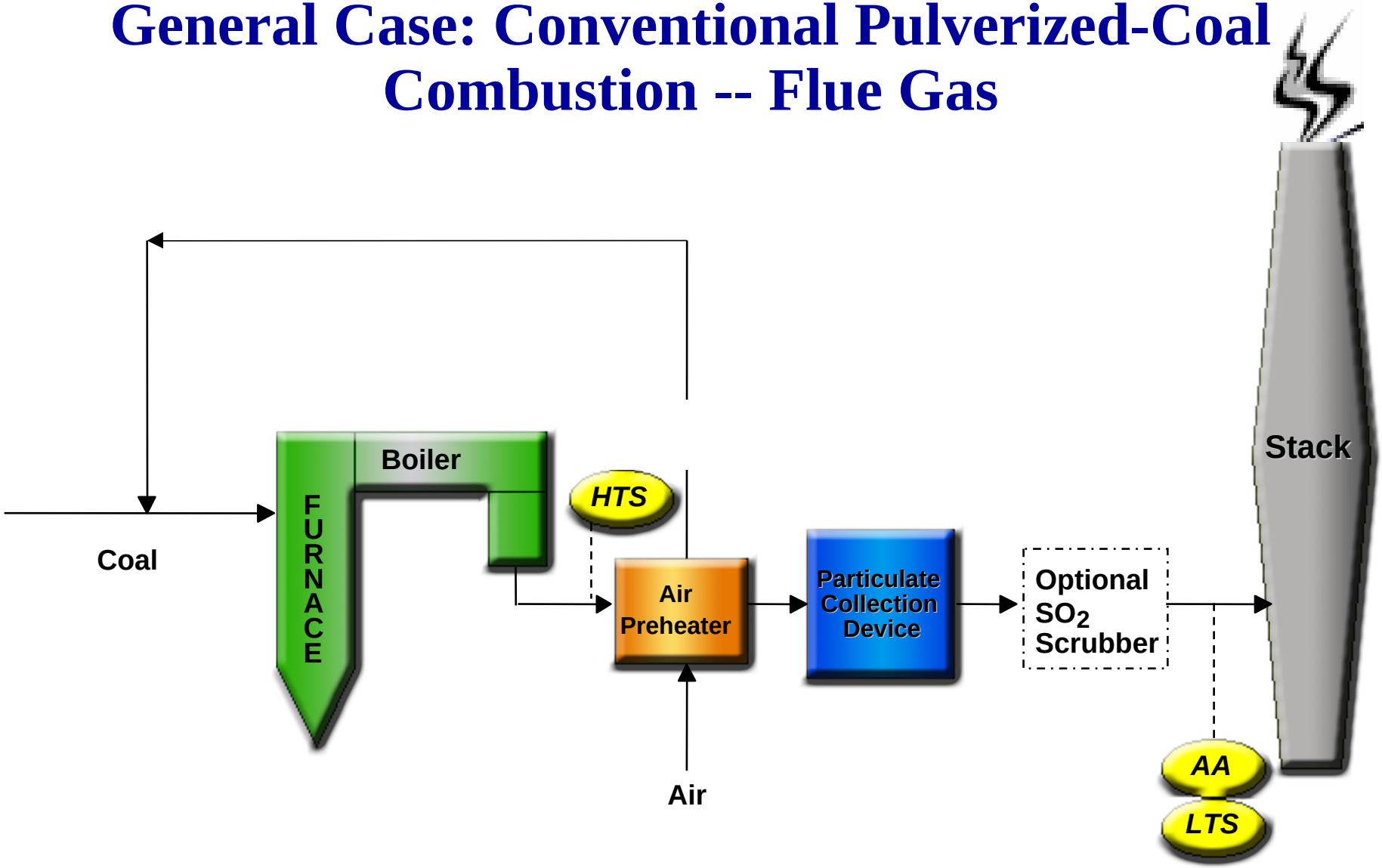
- Regenerable Sorbent Capture Techniques

LTS
– Low temperature (<300°F)
  - amine-based (M. Gray & D. Fauth)
  - zeolites (R. Siriwardane)

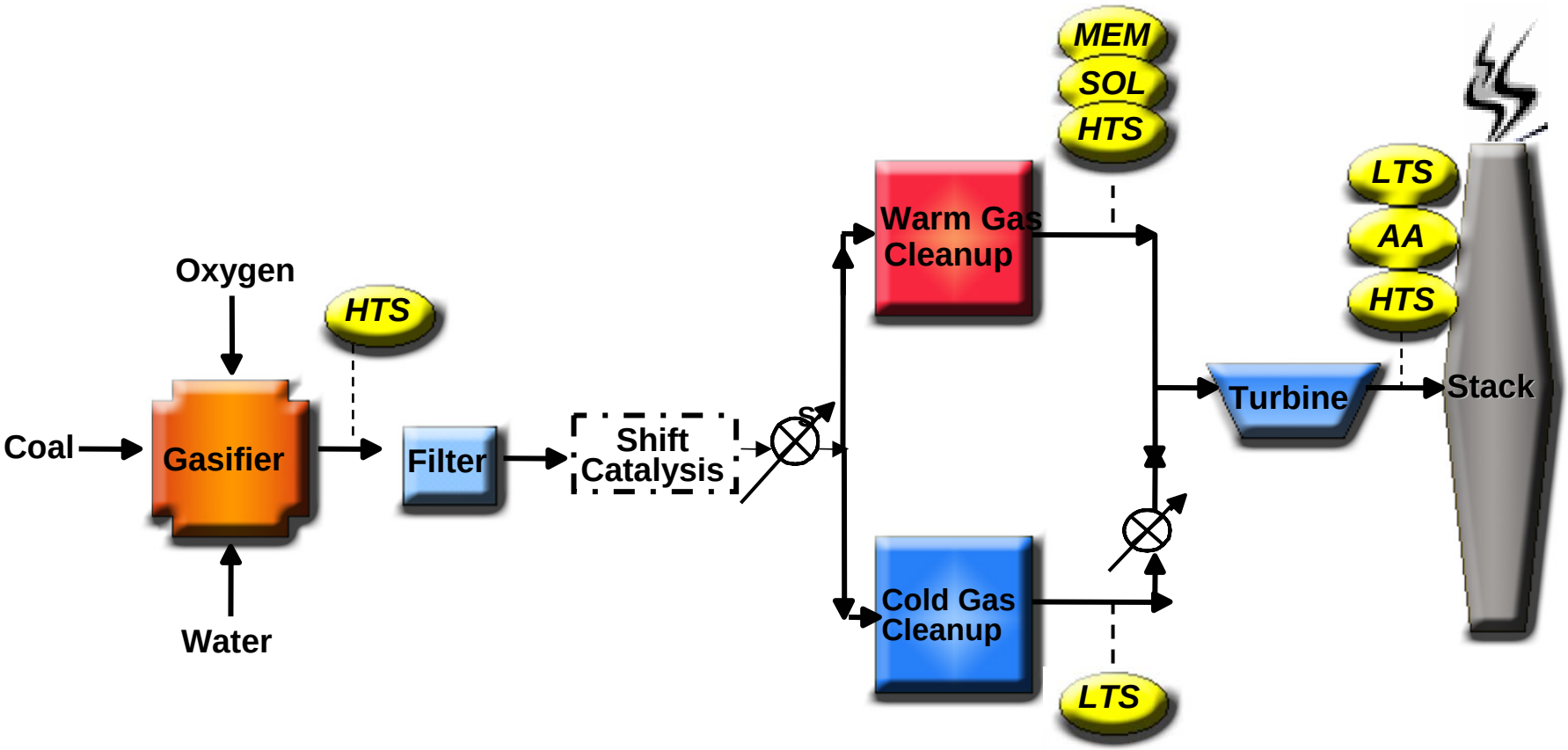
HTS
– High temperature (>300°F)
  - alkali/alkaline earth-based (R. Siriwardane)

NETL

General Case: Conventional Pulverized-Coal Combustion -- Flue Gas



General Case: Advanced Gasification/ IGCC -- Fuel Gas

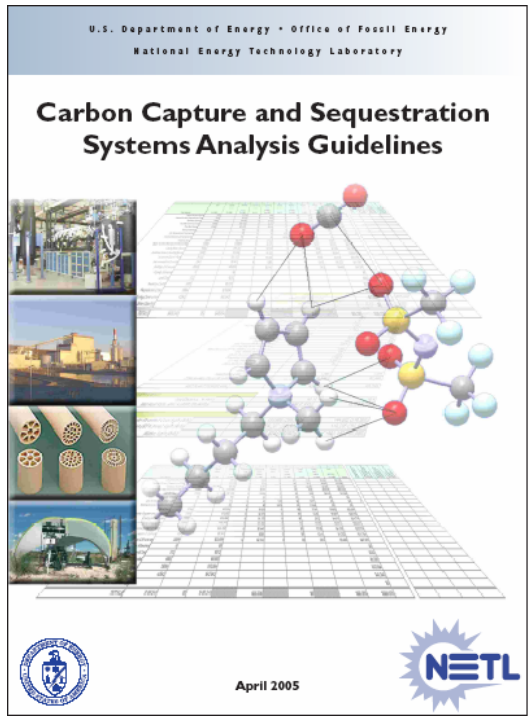


Systems Analysis

- **Commissioned for all in-house capture projects**
- **Prime use**
  - Determine if technology has the opportunity of meeting program goals
  - Research tool to gauge what parameters have the most impact
- **Must be repetitive process**

Common System Analysis Guidelines

- **Released April 29, 2005**
- **Available on the NETL website**
- **Purpose:**
  - Have NETL funded capture and separation technology projects:
    - Report System and Economic Analysis on a common and transparent basis.
    - Emphasize the need for technology developers to consider commercialization pathways for their technologies.
    - Provide performance and cost sensitivity analysis through scaling curves relative to plant size (200 to 1000 MW).



Capture of Carbon Dioxide Using Zeolitic Molecular Sieve

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8th International CO_2 Capture Network Meeting
Oct 3-4, 2005
University of Texas
Austin, Texas

Technical Approach

- **Investigate use of physical adsorbent for CO_2 capture.**
- **Identify key parametric impacts on bench-scale packed bed reactor using molecular sieve 13X to separate/capture carbon dioxide from flue gas.**
- **Test adsorption technique in pilot-scale Modular Carbon Dioxide Capture Facility (MCCF).**

Experimental Procedure

- **Adsorption**

  Pass flue gas mixture through sorbent bed, causing physical adsorption of CO_2 onto the solid.

- **Desorption**

  Cease flow of flue gas mixture through sorbent bed. Initiate flow of sweep gas through bed, causing physical desorption of CO_2 from the solid.

- **Thermal Regeneration**

  Raise bed temperature while maintaining flow of sweep gas through bed, causing additional gas desorption.

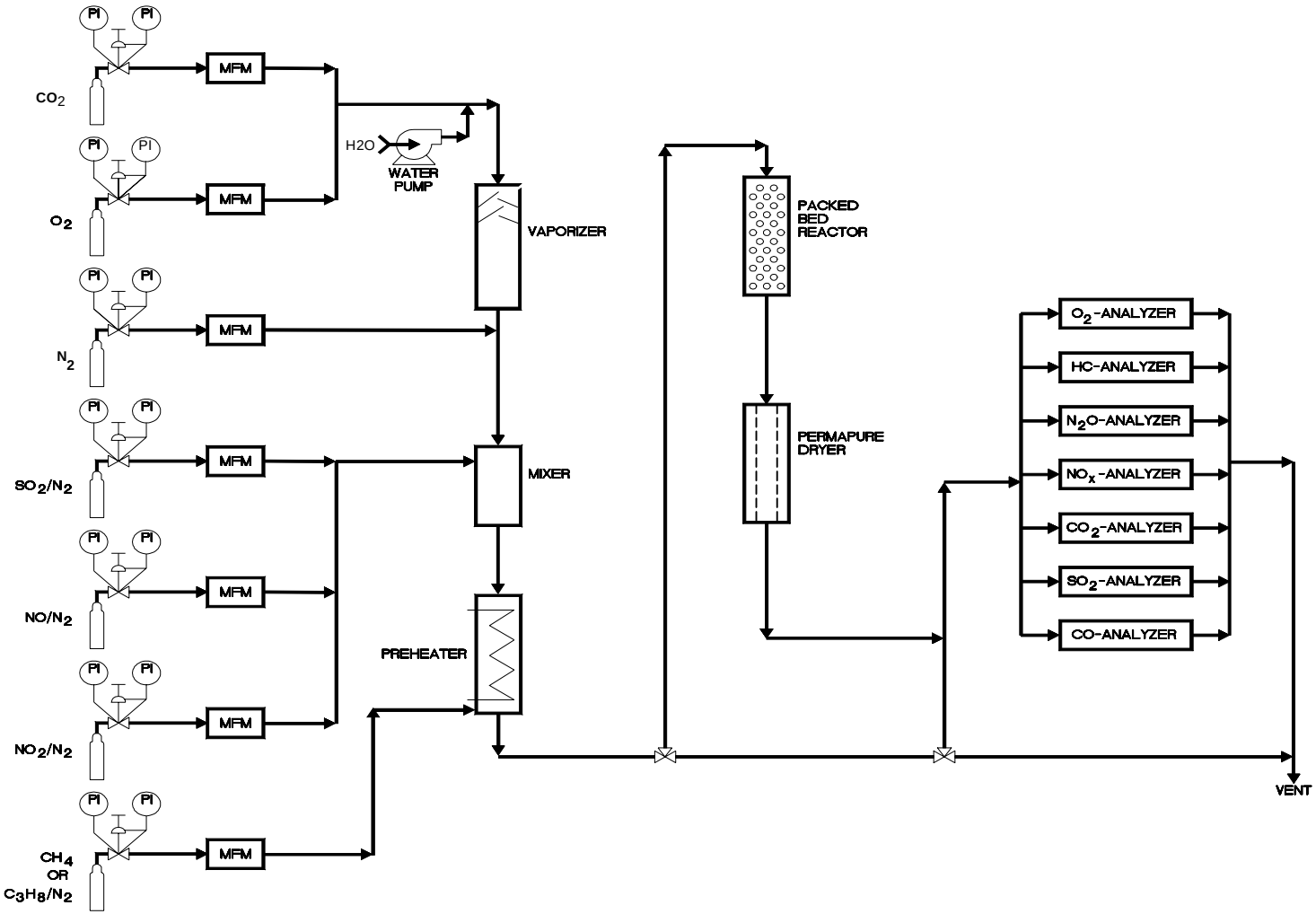
Facility Descriptions

	Packed Bed	MCCF
Reactor	Cylindrical	Rectangular
Bed Cross Section	40 mm ID	8 ft (h) x 1 ft (w)
Bed Depth	~ 3 in	5 in
Material	quartz	316 ss
Sample Inventory	60 g	150 lb
Pressure	5-7 psig	Sub-atmospheric (Neg 5-10 inches W.C.)
Flue Gas		
Source	Simulated (cylinders)	Natural Gas Furnace
Flowrate	1.5 slpm	100 scfm
Typical Flue Gas Composition (Dry)	16%CO_2 /3.5%O_2 / bal N_2	9%CO_2 /4%O_2 / bal N_2 ~100 ppm NO_x
Regeneration		
N_2 Sweep Gas Flowrate	1.25 slpm	50 lb/hr
N_2 Heat Gas Flowrate	---	200 lb/hr

Zeolite 13X

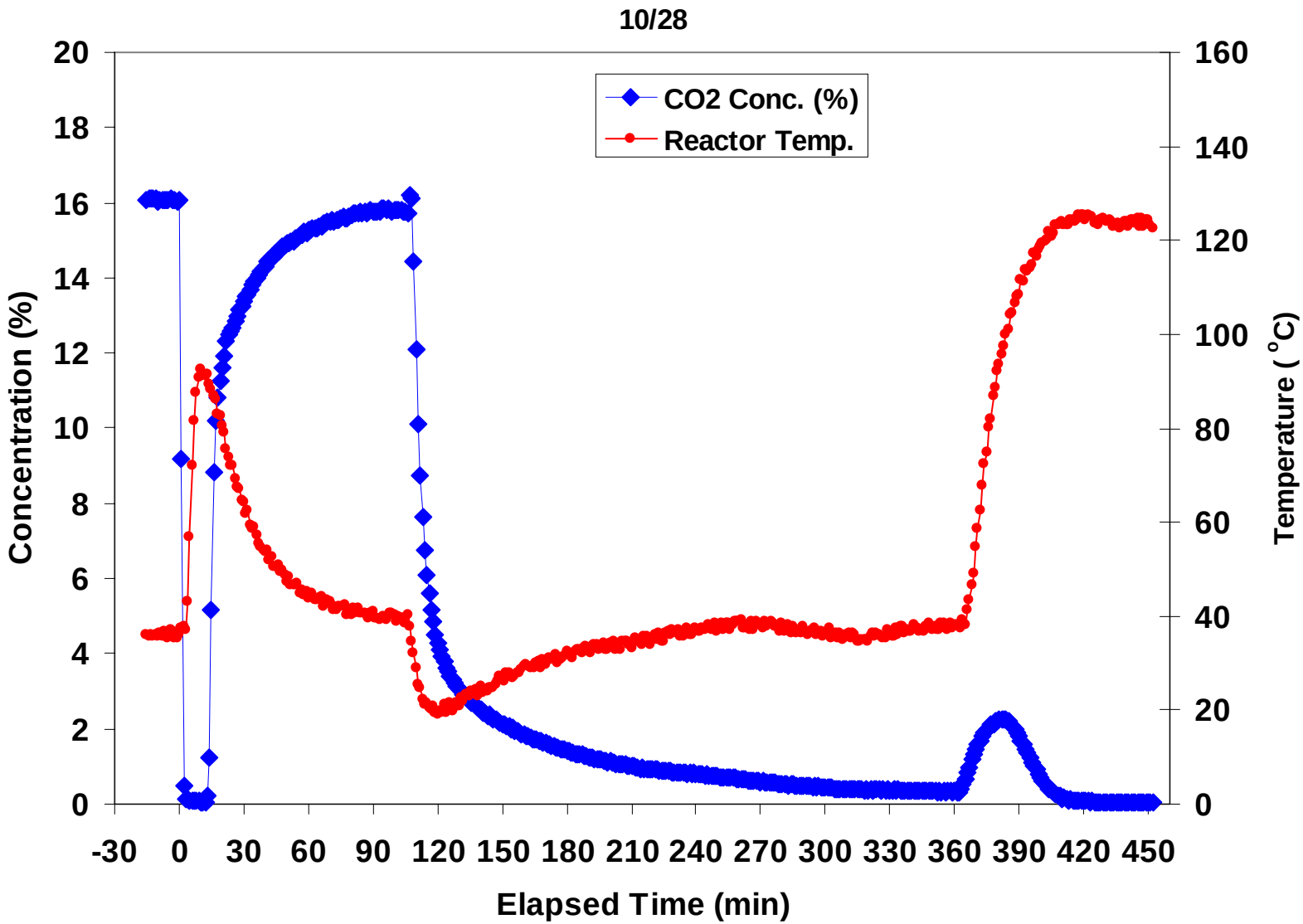
- **Zeochem Molecular Sieve consists of spherical pellets (8 x 12 mesh) obtained from Sud Chemie.**
- **Molecular sieve composed mainly of sodium aluminosilicate with 10 angstrom average pore diameter.**
- **Surface area of 380 m^2/g (BET) & 600 m^2/g (Langmuir).**

Packed-Bed Reactor Schematic

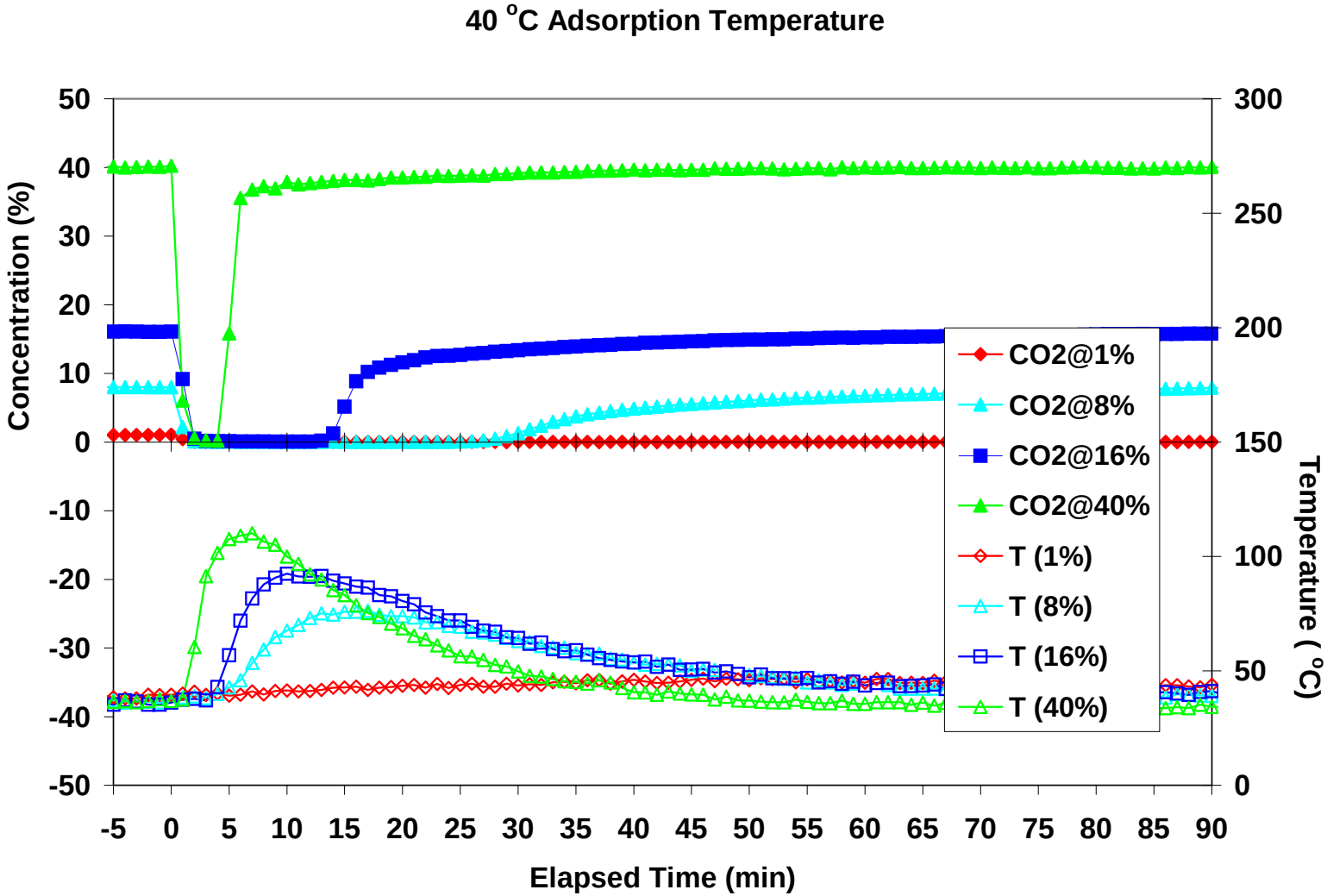


Packed-Bed Reactor

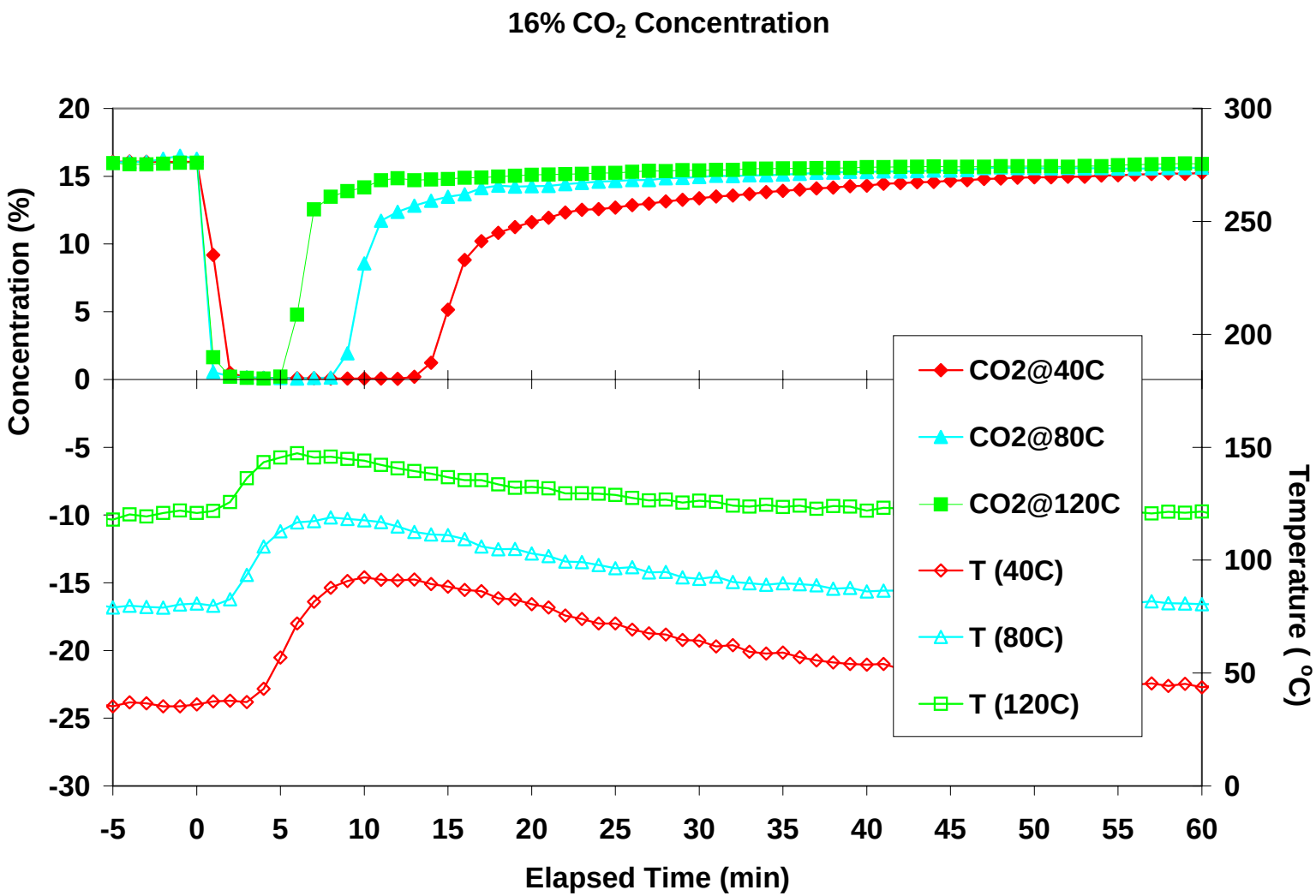
Typical packed-bed experiment for CO_2 adsorption/regeneration.



Effect of CO_2 Concentration



Effect of Temperature



Packed-Bed Experimental Summary

Adsorption

- **Molecular sieve 13X demonstrated 3.5 mol CO_2/kg sorbent capacity at baseline conditions.**
- **Lower temperatures and higher CO_2 partial pressures improve adsorption.**
- **Moisture strongly adheres to zeolite.**
- **Adsorption capacities could be maintained in cycling tests.**

Regeneration

- **Spent zeolite can be regenerated at 120°C for 3 hours after dry adsorption conditions.**
- **Moisture presence (2-4%) in adsorption requires high temperature (350°C) of regeneration.**
- **Carbon dioxide sweep inhibits low temperature regeneration.**

MCCF

Modular CO_2 Capture Facility (MCCF)

Goal

- **To facilitate commercial readiness of advanced, cost-effective capture and separation technologies. Technologies range from conceptual to verification at large scale.**

Objectives

- **To develop a modular facility capable of investigating various capture technologies.**
- **To select candidate technologies for investigation.**
- **To ultimately provide experimental information from which further engineering scale-up decisions can be made.**

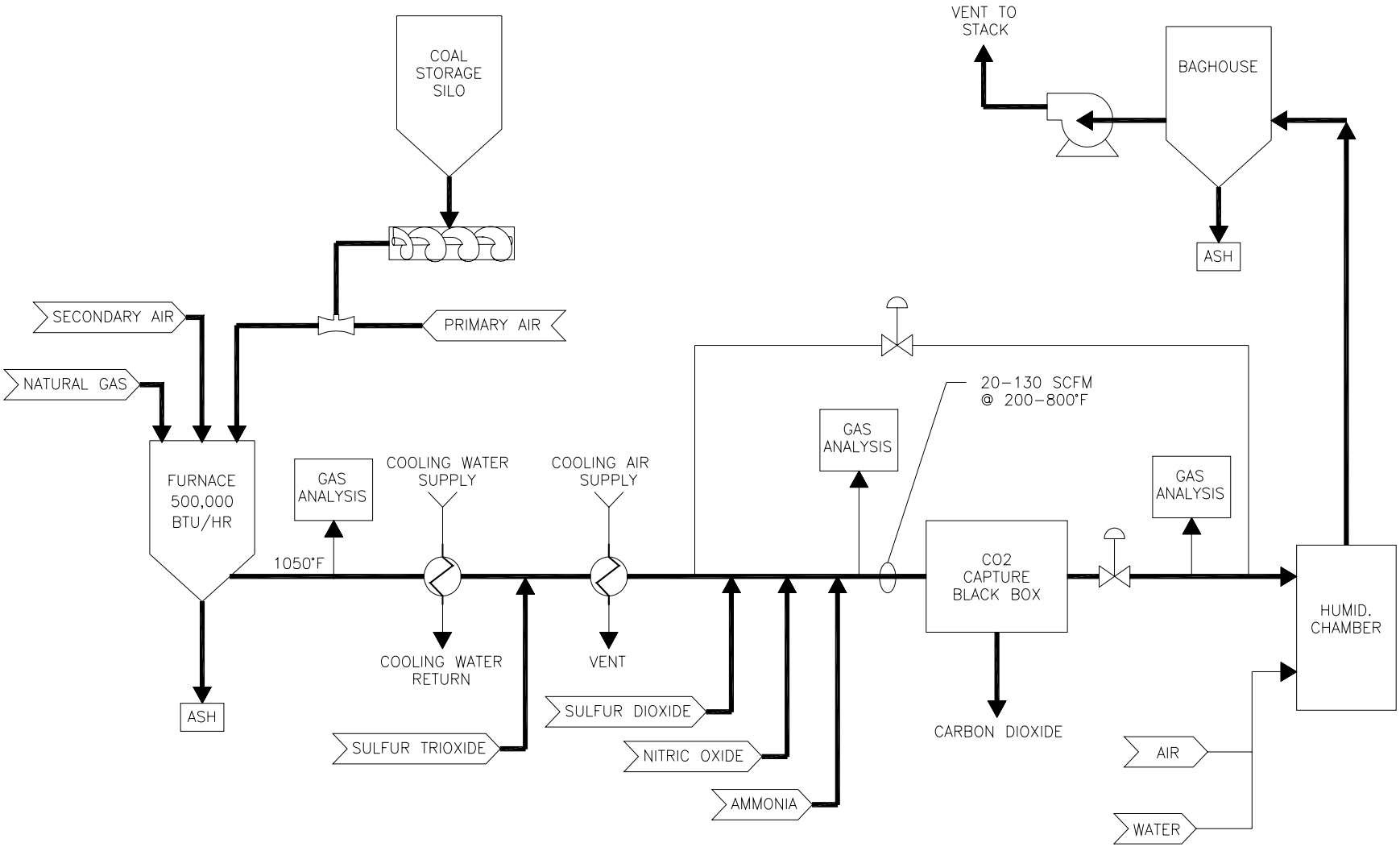
MCCF History

- Timing appropriate in programmatic scheme of carbon sequestration. Project began as scoping exercise.
- Internal assessment
  - NETL experienced with flue gas and fuel gas cleanup
  - Facility existed in part
  - Air toxics sampling available
- In-house projects screened to determine process parameter design ranges.
- *Ad hoc* committee formed of personnel familiar with DOE-sponsored research and other outside capture development.
- PFDs developed with “black box” technology for either flue gas or fuel gas applications.

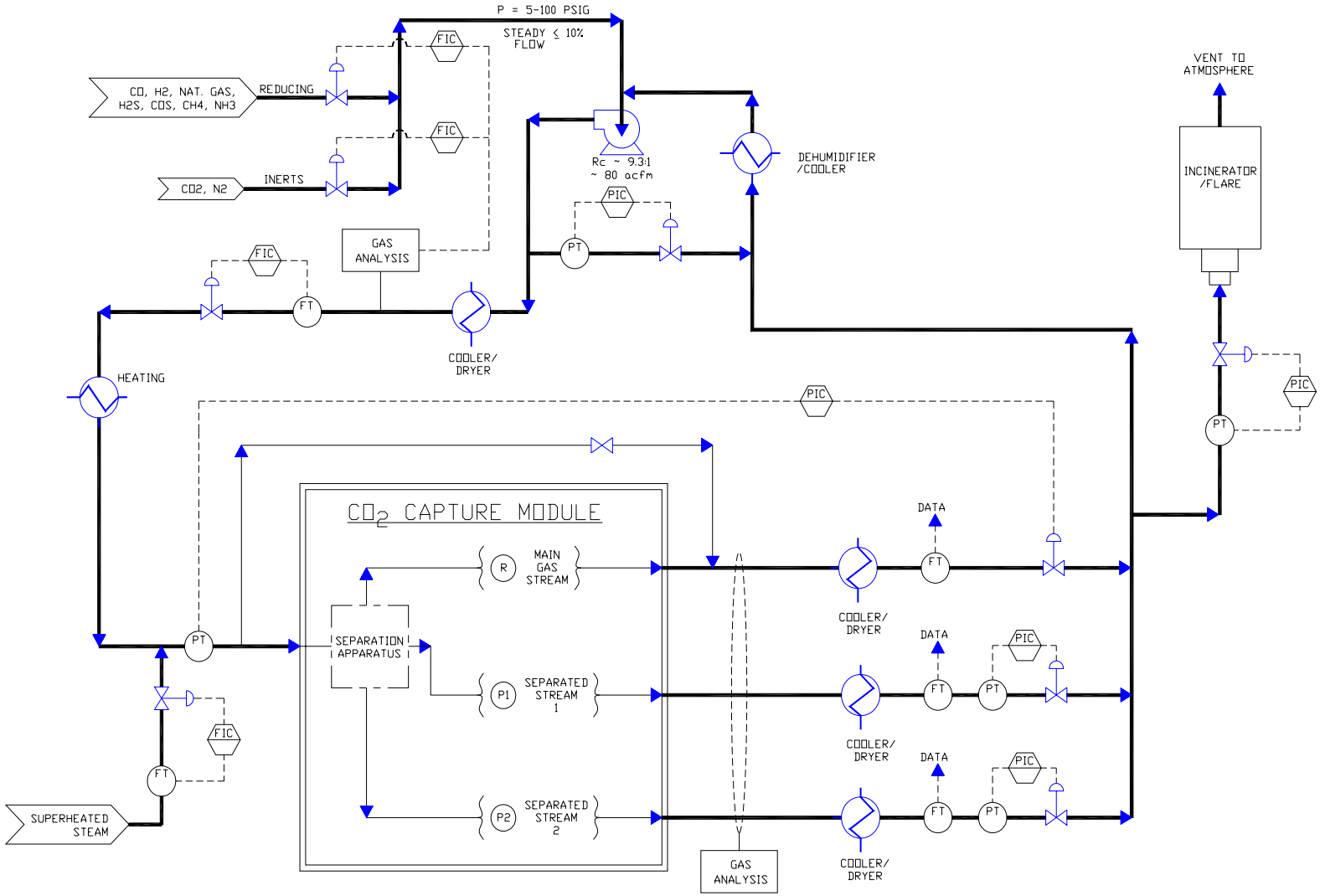
Uniqueness of MCCF

- Capture technology can be evaluated in actual flue gas.
  - Coal or natural gas combustion
  - Spike gases (SO_2, NO_x, etc.)
- Pilot-scale.
- Future capability of simulated fuel gas.
- Cross-comparision of technologies using same facility (“apples to apples”).
- Unbiased assessment.

CO_2 Capture Facility – Flue Gas



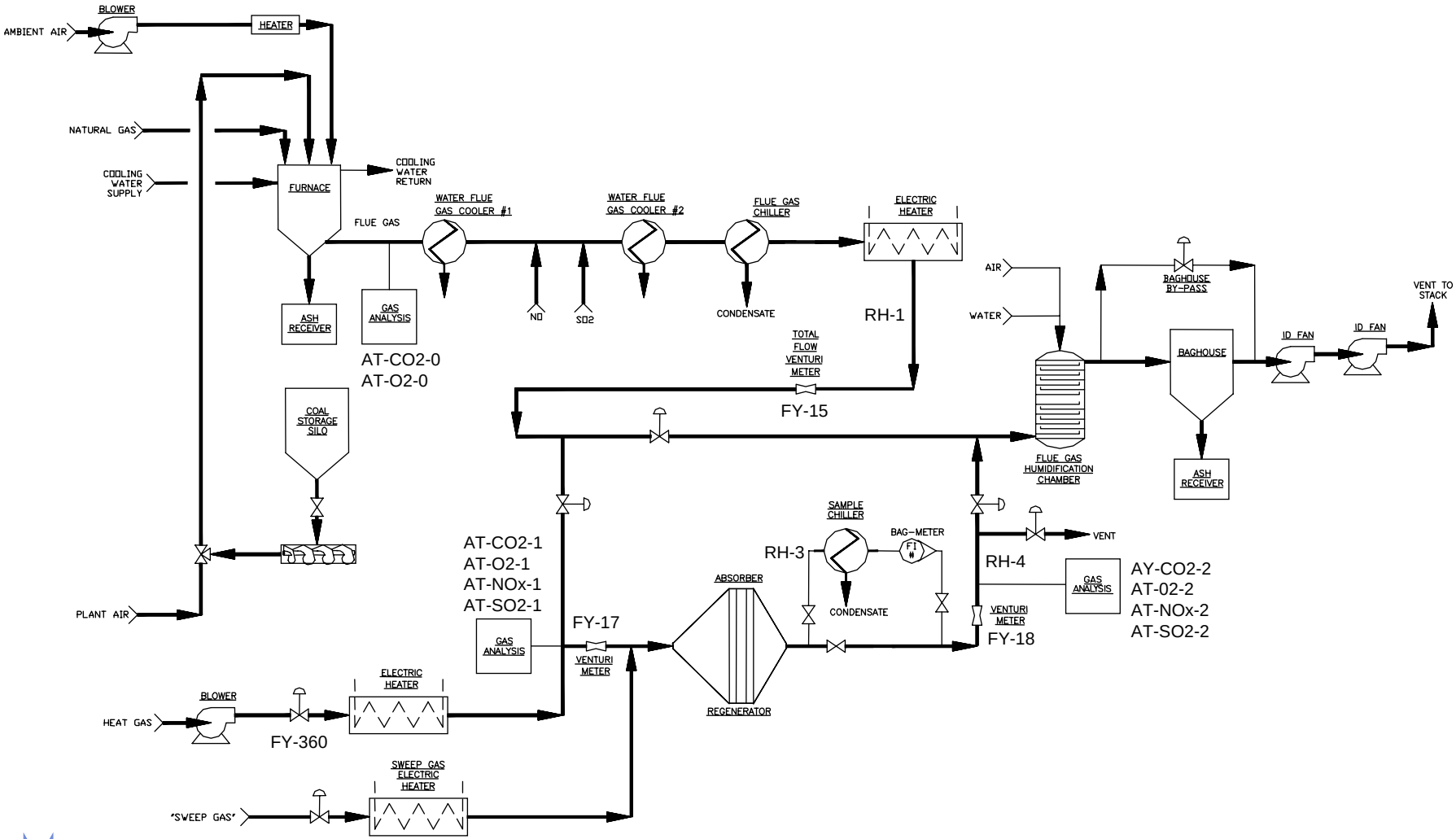
CO_2 Capture Facility – Fuel Gas



Why test Zeolite 13X in MCCF?

- Prior studies using zeolites as a physical adsorbent for CO_2.
  - Yokosuka Thermal Power Plant (TEPCO & Mitsubishi Heavy Industries).
    - PSA/TSA employed to remove CO_2 from flue gas.
  - NETL investigations (Siriwardane)
    - PSA/TSA bench-scale studies with molecular sieves.
- Material was commercially available in sufficient quantity for pilot-scale tests.
- Timing/schedule
  - Allow design/shakedown of MCCF and establish baseline performance for commercially available technology.

MCCF process flow diagram

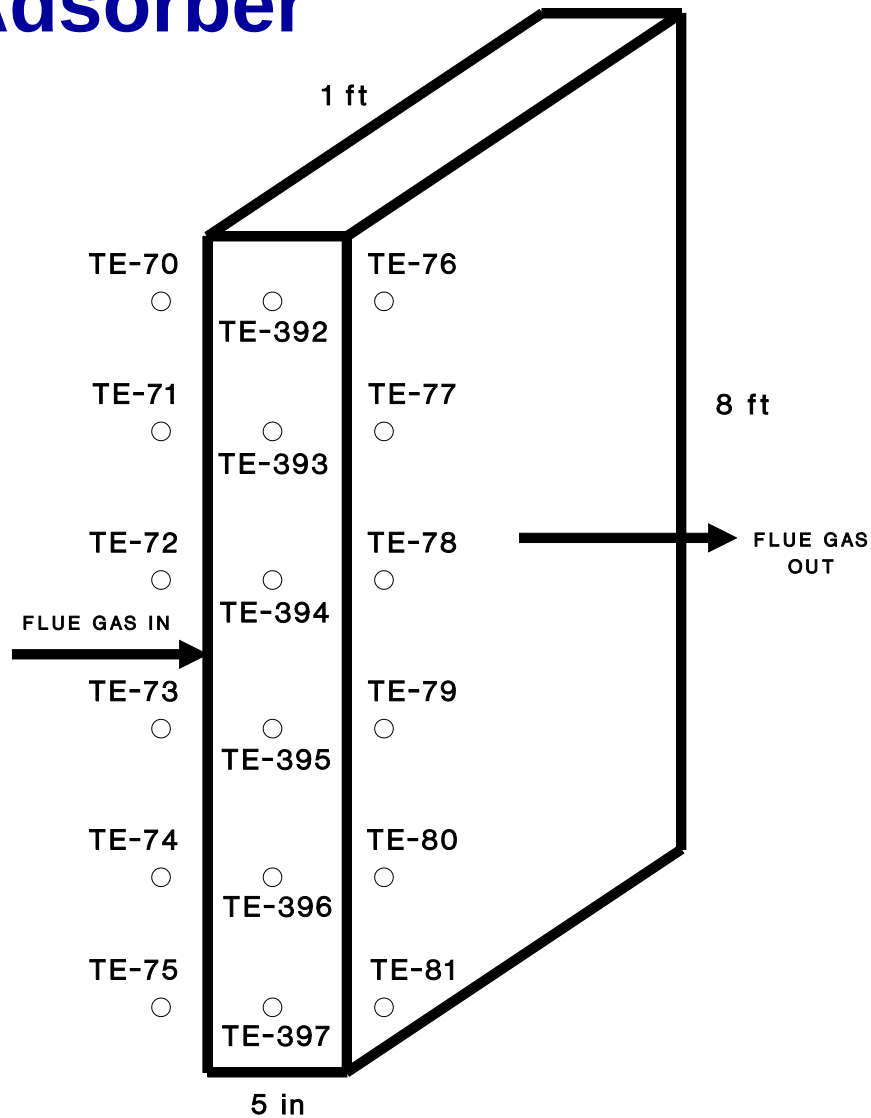


Modular CO_2 Capture Facility

Natural Gas-Fired Furnace

Adsorber/Regenerator

MCCF Adsorber



Absorber Thermocouple Port Locations

MCCF Experimental Procedure

- **Combustion**

  Generate flue gas from natural gas firing in combustor. Flue gas is passed through chiller to reduce moisture content (to ~1%) and then reheated and sent to adsorber.

- **Adsorption (100°F/38°C)**

  Pass flue gas mixture through sorbent bed, causing physical adsorption of CO_2 onto the solid.

- **Desorption (248°F/120°C)**

  Bypass flow of flue gas around sorbent bed. Initiate flow of N_2 sweep gas through bed, causing physical desorption of CO_2 from the solid.

- **Thermal Regeneration (660°F/350°C)**

  Raise bed temperature while maintaining flow of N_2 sweep gas through bed, causing additional gas desorption and thermal regeneration of the sorbent. Introduce additional flow of N_2 heat gas to enhance swinging bed temperature to elevated level.

MCCF Measurement Stations

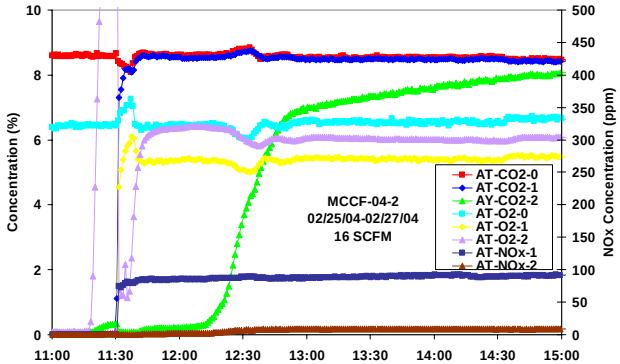
- **Continuous emission monitors (CEMs) are used to measure gas composition at the furnace exit, the adsorber inlet, and the adsorber outlet.**

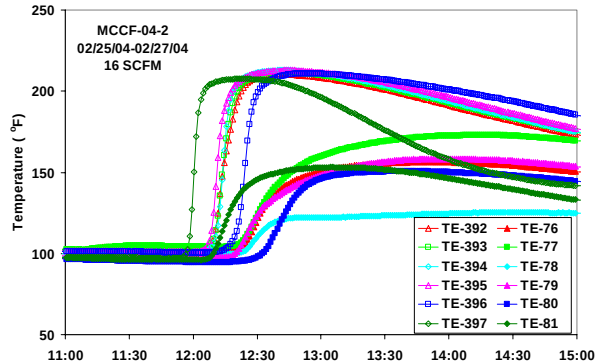
- **Gas flowrate is measured between the chiller and reheater, and at the adsorber inlet and exit locations. A slip stream of the adsorber exit can be sent through a bagmeter to determine total sampled gas volume.**

- **Regenerative flow inputs (N_2 sweep gas and heat gas streams) are metered independently.**

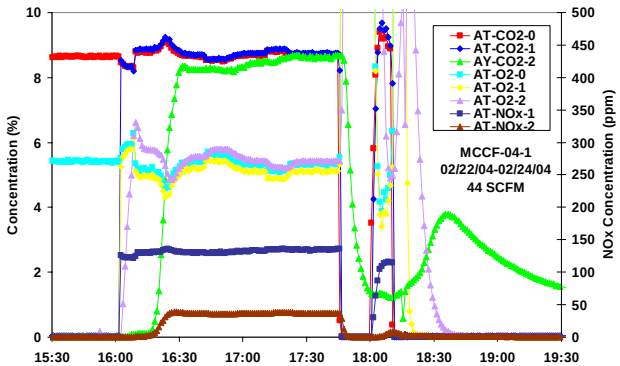
Effect of Flue Gas Flowrate

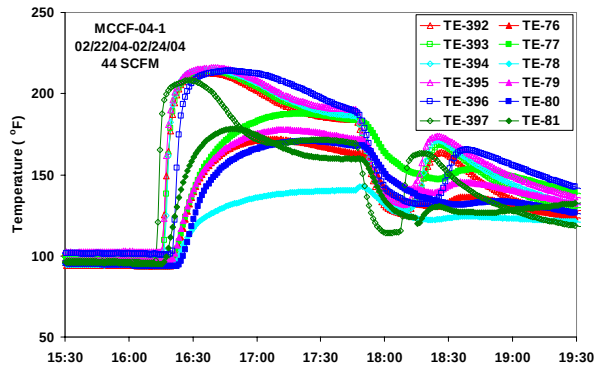
16 scfm



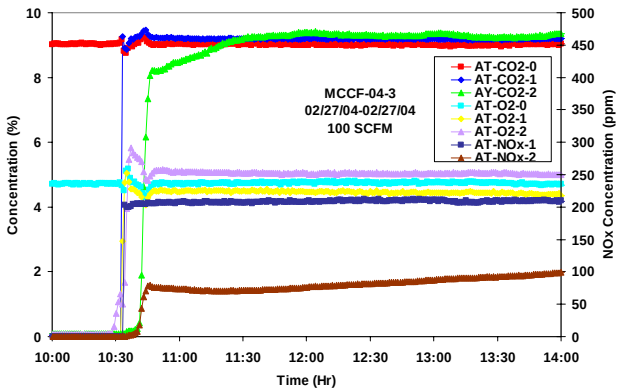


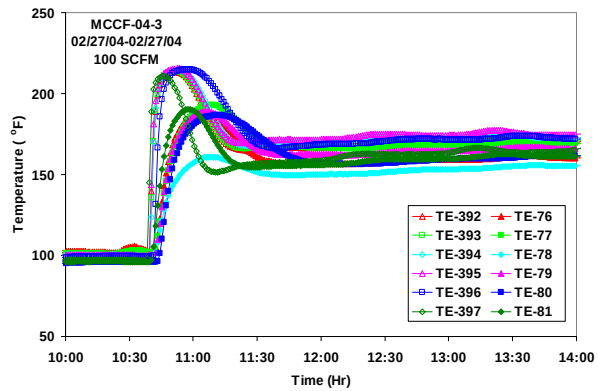
44 scfm





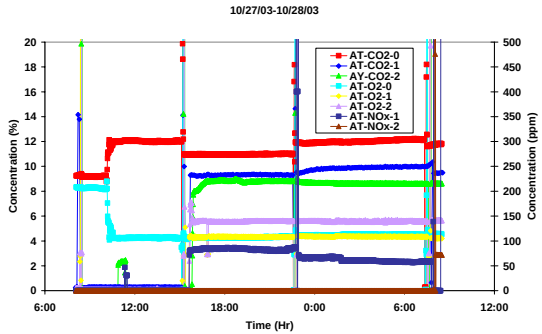
100 scfm

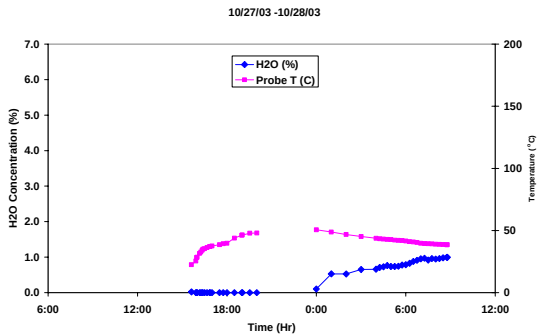


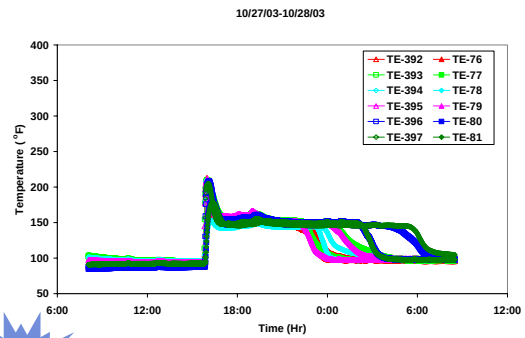


Effect of Flue Gas Moisture

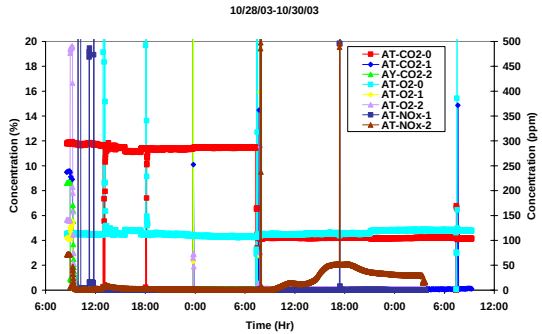
Cycle 1 Adsorption

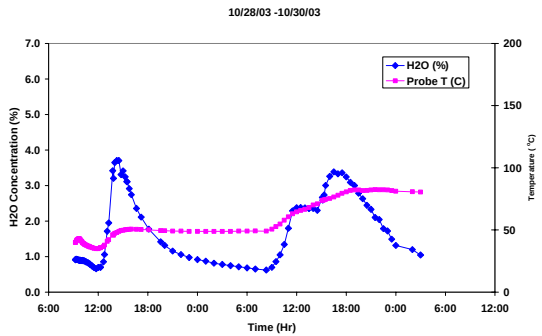


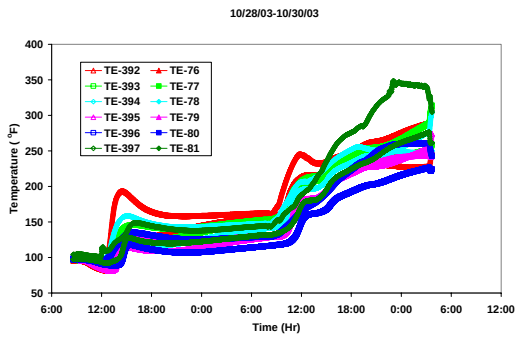




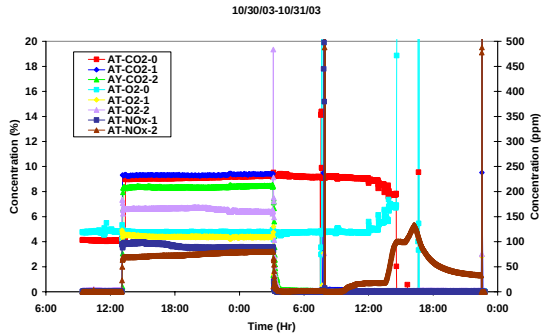
Cycle 1 Regeneration

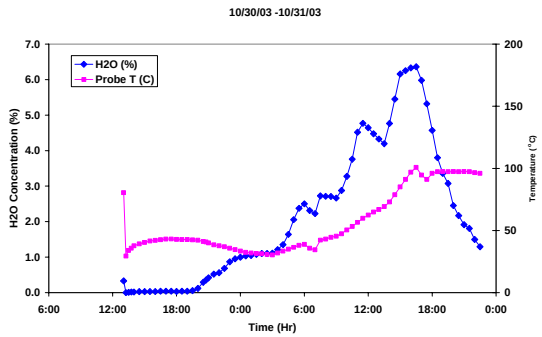


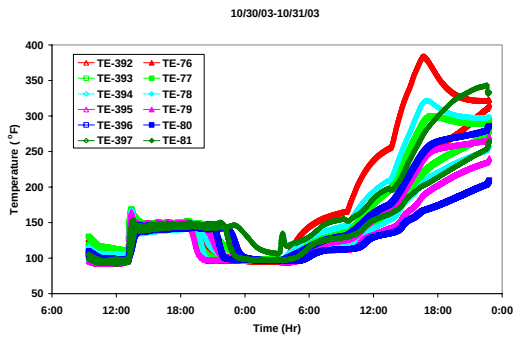




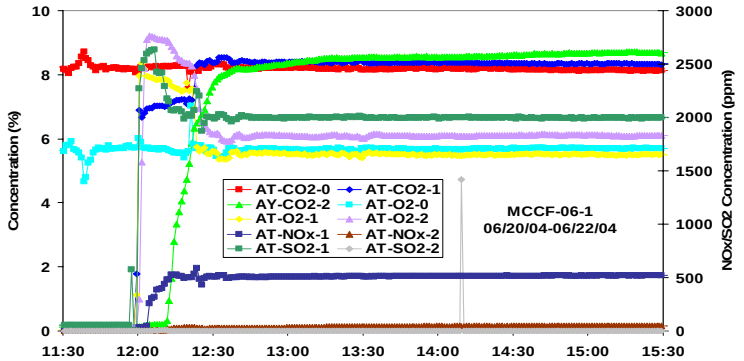
Cycle 2 Adsorption/Regeneration

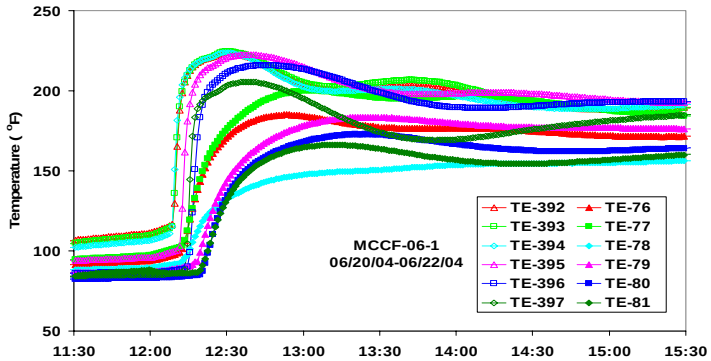


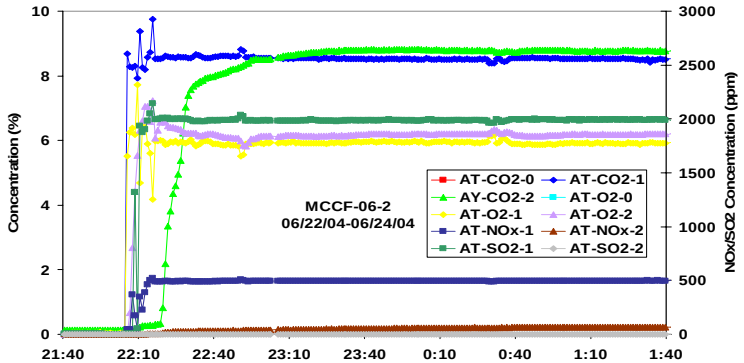


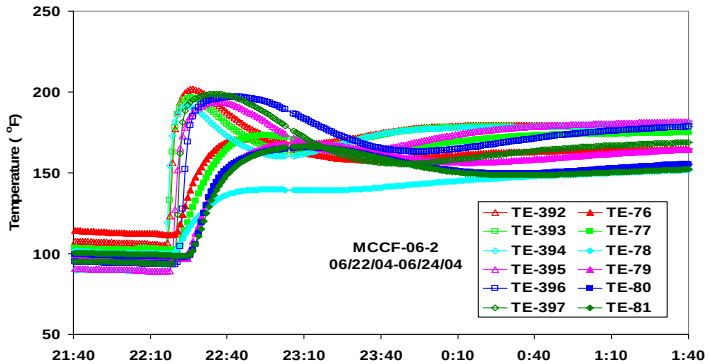


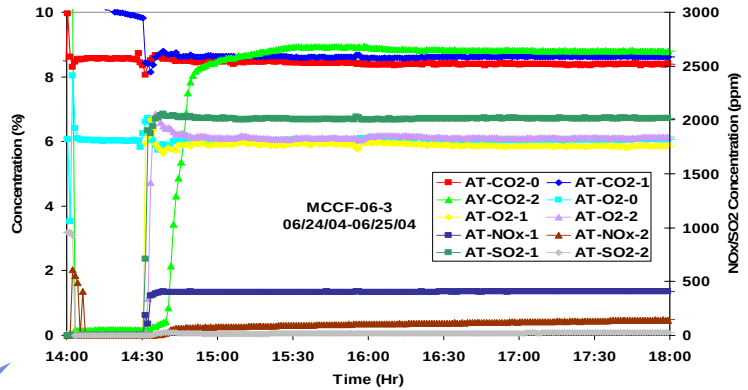
Effect of SO_2 & NO_x During Adsorption

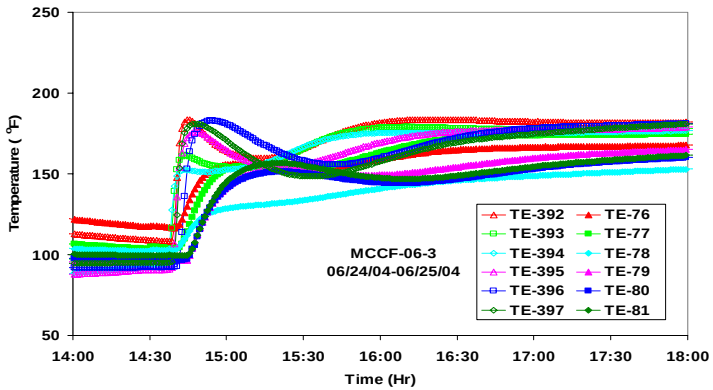




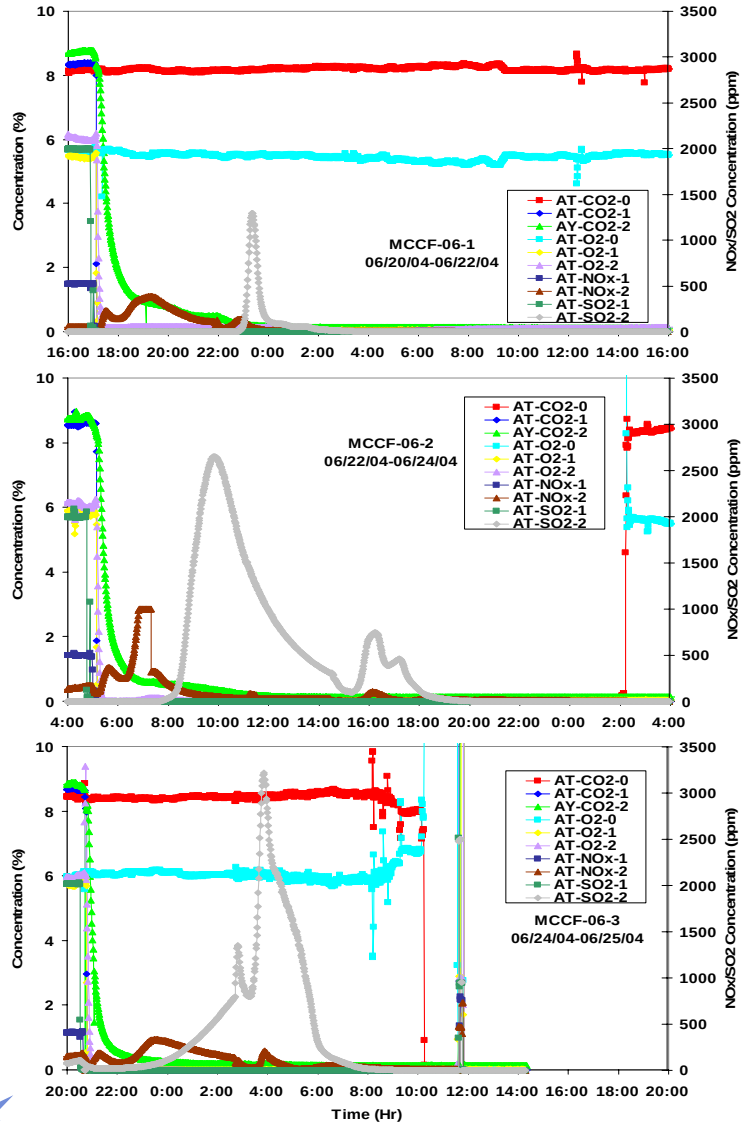


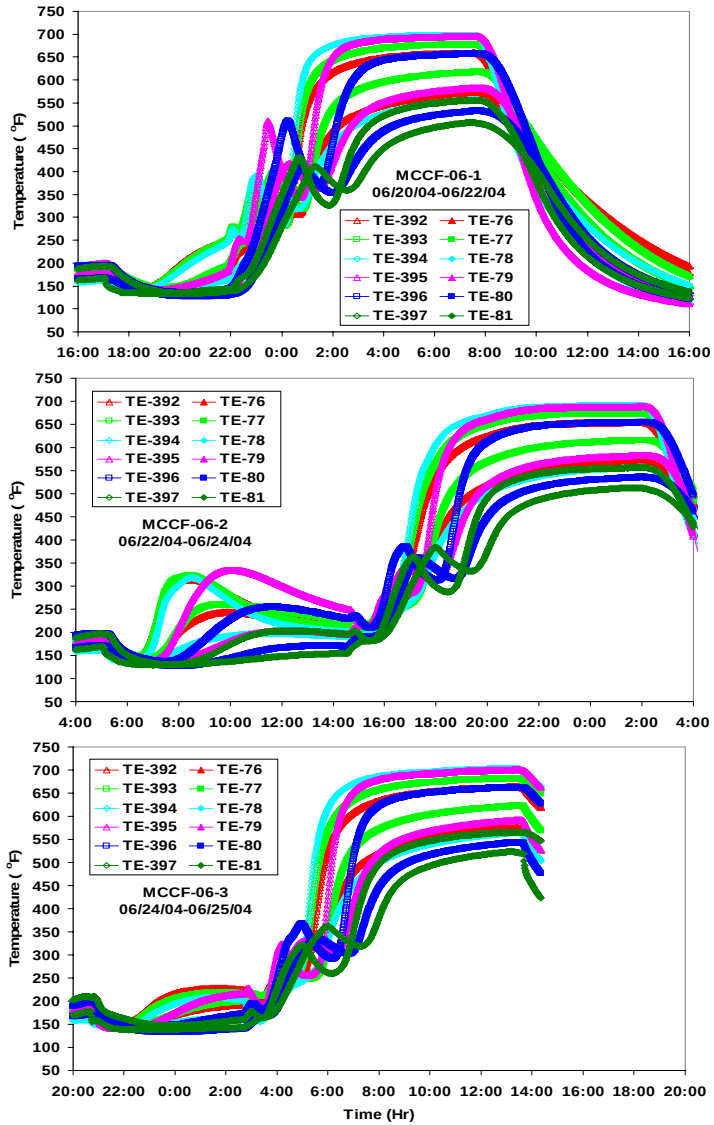






Desorption/Regeneration of SO_2/NO_x





MCCF Experimental Summary

- **Molecular sieve 13X was able to adsorb CO_2 from flue gas at baseline conditions (40°C at atmospheric pressure).**
- **CO_2 breakthrough time is related to molar flux, but little difference in CO_2 capacity (1.3-1.7 mol CO_2/kg sorbent).**
- **Moisture impacts adsorption.**
- **NO_x and SO_2 are adsorbed onto sorbent and deleteriously impacts sorbent. Desorption is minimal at high regeneration temperature (350°C).**
- **A high temperature of regeneration (350°C for 3 hr) is required after adsorption of CO_2 from moisture containing flue gas.**
- **Combination of PSA with TSA may be optimal mode of regeneration for this technology.**

Potential MCCF Future Activities

- **Membranes**
  - **molecular gate (RITE)**
- **Chemical Sorbents by NETL In-House Researchers**
  - **amine-enriched (M. Gray)**
  - **alkali and alkaline earth (R. Siriwardane)**
- **System studies will help guide the design of the reactor system to be used for pilot-scale evaluation**

PCC Demonstration Program in Australia

Louis Wibberley

CSIRO Energy Technology

Contents

- Background – how and why PCC has been given a low priority (until recently)
- Current status – playing catch-up and have proposals for major initiatives
- Why Australia needs to do this - rather than fast-follower or buy-in
- Objectives and components of CSIRO's proposal for a National PCC Program
- CSIRO's PCC pilot plant
- Current status
- Concluding comments
- Other non-PCC but related CSIRO work towards low emissions electricity

Background (2005)

- Solvent-based PCC has received scant consideration - until recently
  - based on adverse findings of studies in the late 90's (relative to doing nothing)
  - expected that novel separations may be developed (from gas sep for IGCC)
- PCC was considered for COAL21, but rejected as a main focus area
  - "there are cleverer ways"
  - IGCC is the "only show in town" (reluctant consideration of oxy-pf for retrofit option)

  Main projects being developed under COAL21 Action Plan
  - IGCC: (250) 180 MWso IGCC (with capture and storage into aquifers)
  - Oxy-pf: retro fit of (30) 13 MWso 1960's pf plant (capture, but no storage)
  - CTL: large project involving gasification, cogeneration, capture, storage into DOW
- Limited industry direction to R&D by Co-operative Research Centres
  - mostly small activities for advanced separation techniques; PCC with methanol, aqueous ammonia process (CCSD), "watching briefs" and "no development of new liquid solvents"- funding focus for gas processing for NG and IGCC

Currently

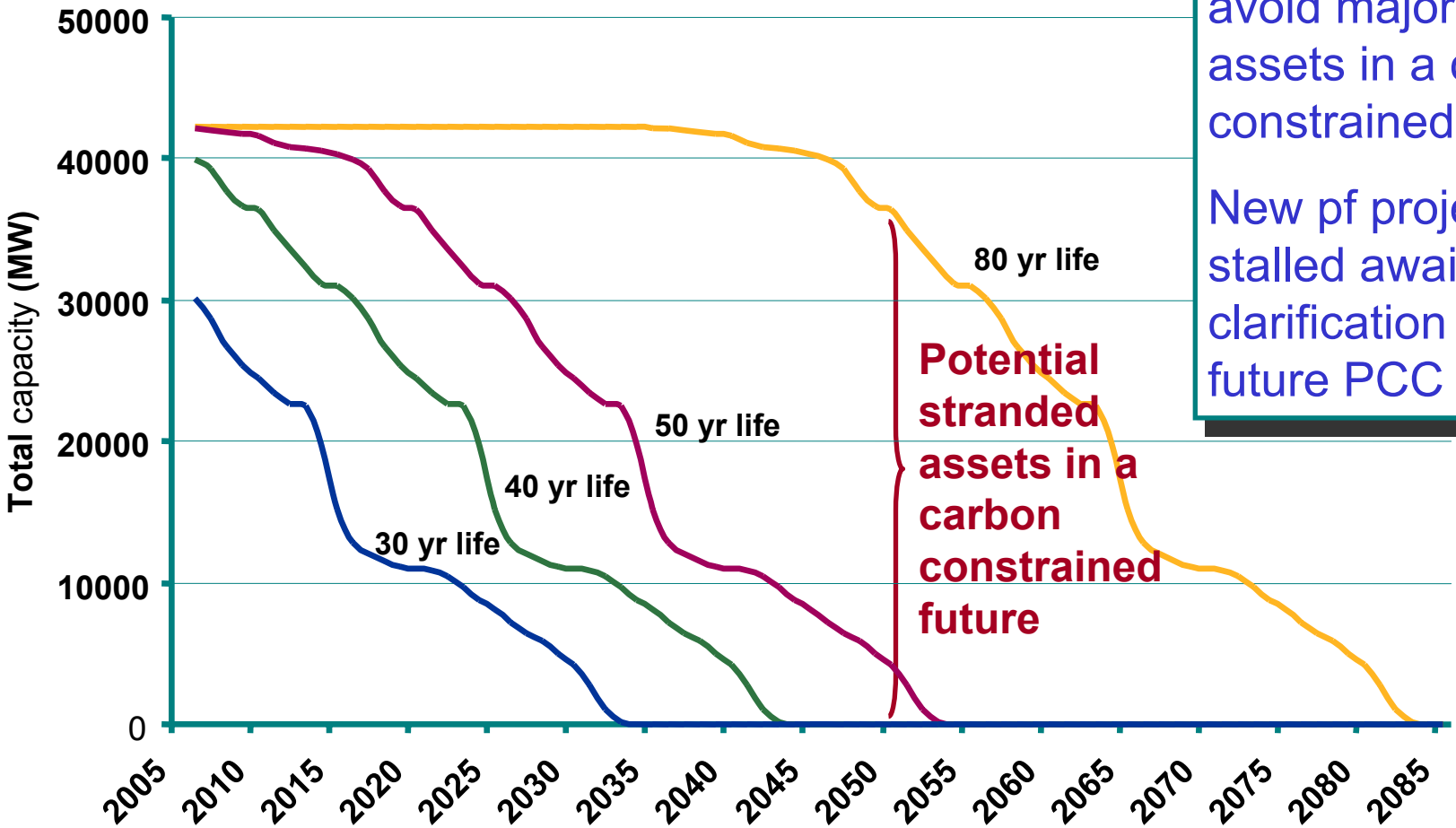
- Rapidly changing attitude by industry
  - PCC is now benefiting from concerns over the high cost of alternative LET fund demonstration proposals
  - and positive overseas developments
- 2004 CSIRO started a program involving a proposal for a large demonstration project has been developed with industry
  - several iterations, 2 or 3 favoured options, dependant on existing LETDF proposals
  - leverage for several new projects requiring capture or storage
- Increasing interest by CRCs and others
  - CCSD - new project to look at retro-fit issues and opportunities for existing pf plant
  - CO2CRC – all things capture, but change of emphasis (Sandra will cover)
  - CRC for Clean Power from Lignite – developing
  - HRL considering PCC for IDGCC

Why Australia needs a PCC Demonstration Program

- A cost effective Australian demonstration of capture and storage is required
  - PCC is the lowest cost option for different locations and host plants
  - Implementation with less risk and with smaller hurdles
- Australian power plants are different
  - we are heavily dependent on them
  - existing capacity has no NOx or SOx control equipment - requires new sorbents and new process design to minimise costs (will also decrease cost of new plant)
  - Victorian lignites are unique and will need a novel PCC process
- Large CBM reserves
  - facilitates LET with CBM and storage into coal
  - site specific GCC+PCC+CO2Seq+Enhanced CBM
- Most Australian plants have a high potential to use heat from solar thermal
  - new sorbents with lower regeneration temperatures could be needed
- A strong need to “learn and evaluate by doing”

CSIRO

Drivers and dilemmas



PCC is required to avoid major stranded assets in a carbon constrained world

New pf projects are stalled awaiting clarification on viable future PCC (& storage)

CSIRO

Objectives of the National PCC Program (proposed)

1. Semi-commercial scale facility (50,000 tpy) at host site
   - main purpose is to demonstrate capture,
   - capable of providing CO_2 for sequestration projects of others
   - relocatable components for use at several sites across Australia
2. Pilot plant research and development
3. Applied laboratory research and test capability for sorbent and membrane development, and energy integration (CSIRO, CO2CRC, CCSD, cLET, Lignite CRC)
4. International collaboration (APP, CSLF)

The National PCC Program would be undertaken by a consortium of industry, research and Government to develop and fund the 5 year program (possible *LETDF project*)

1

the

PCC demonstration project

- industry lead consortium
- commercial scale operation on slip stream
- 100 – 200 t/day
- new technology combination to handle NOx/SOx
- some facility to handle modifications to the base process
- with LETDF support
- linked storage projects

Linked storage demonstration projects

2

Pilot trials

Pilot scale testing
(1 – 10 t/day)
Slip stream operation at power station sites

CSIRO-NPPC facility
CASTOR
ITC
MHI-KEPCO

4

Collaborative, contract International R&D

3

Research

Fundamentals
Desktop studies
Laboratory scale testing
(<1,000 kg/day)

CSIRO
CRCs
cLET
RITE and others

CSIRO Post Combustion Capture Facility

www.csiro.au

- Refurbishment of existing fixed equipment
  - 2x 200 mm absorbers, allowance for sequential SOx-CO_2 removal, assistance by MHI
- Relocatable for pf slip stream operation
  - 3 pf stations in program
- Solar thermal integration
  - CSIRO National Solar Energy Centre
  - Liddell Solar Thermal demonstration
  - CO_2 capture from solar reforming

0.1 – 2 tpd (3 columns)

CSIRO

Current status

- Engagement with key industry groups to build program and consortium
  - industry led steering committee to develop proposal for LETDF
  - 2 (maybe 3) other LETDF project proposals underway to use PCC for capture and storage trials
  - commitments being delayed due to alignments with IGCC and oxy-pf
- CSIRO CO_2 capture facility relocated and being refurbished at CET Newcastle into a relocatable facility
  - collaborative agreements established for laboratory and pilot testing of 2 new sorbents on pf side-streams
  - agreements with 3 power companies for slip stream trials
- Studying pf-PCC energy integration requirements and opportunities under CCSD program
  - 3 Australian power plants being used as case studies

Concluding comments

- Australia industry, research and Government is now firmly committed to PCC as the 3rd option for achieving low emissions through
  - increased research, pilot scale and semi-commercial scale activities
- While it is recognised that we should access the best from others, it will be important to develop specific expertise and technologies relevant to Australian situation
- PCC is a priority area for the CSIRO Energy Transformed Flagship Program, and has become a “National Imperative”
  - wants to avoid commercial issues getting in the way of “National-good”
  - it is expected this initiative will form part of Australia’s contribution to the Asia Pacific Partnership

Supporting information – portfolio of related LET projects

- CSIRO is also actively evaluating alternative approaches to achieving lower emissions:
  - low cost gasification-based cycles with capture
  - efficient smaller scale (30-100 MW) power cycles suitable for dispersed generation (especially mine-mouth)
  - attaining high efficiency from high moisture coals and lignites without pre-drying or dewatering
  - ultra high efficiency power cycles without capture
  - ultra clean coal-based fuels
  - underground gasification of coal
  - fundamentals of CO_2 storage and ECBM
  - solar thermal energy for power production (direct, reforming and ORC)
- CSIRO Energy Technology also is a large contributor across other areas, through collaborative centres (CCSD, cLET and the CO2CRC)

CO2CRC
Capturing CO_2 Down Under

Sandra Kentish
Research Project Leader
Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC)

4th October 2005

Outline of presentation

- Overview of CO2CRC
- Capture Program
  - Absorption Projects
    - Characterisation of novel packings
    - Absorption Energy Demand simulations
    - Surface Treatments of Membranes
  - Other Projects
    - Polymeric and nanoporous carbon membranes
    - Inorganic membranes
    - Adsorption Systems
    - Techno-economics

CO2CRC

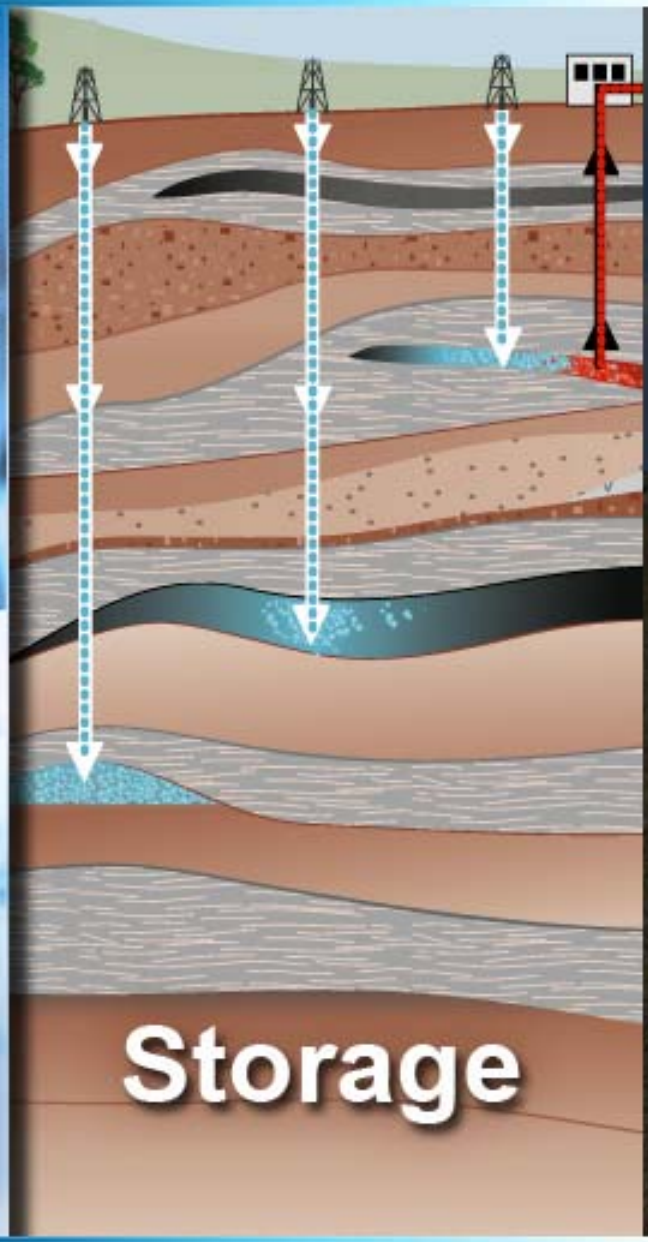
- Cooperative Research Centre (CRC) for Greenhouse Gas Technologies
  - Research collaboration between
    - Australian Government
    - Industrial Partners
    - Research Institutions
  - Funded for 7 years to work on specific industrially relevant work. Can be renewed for further periods.
- Started 2 years ago following 4 years work on geological issues (GEODISC)

CO2CRC Partners:

Australian Government

Geoscience Australia
Australian Greenhouse Office
Department of Industry, Tourism and Resources

RIO TINTO



CO2CRC

CO2CRC Capture Program research teams

CO2CRC Capture Program research teams

The University of Melbourne

Performance of Novel Equipment for Absorption Systems

Surface Modification of Membranes for Gas-Liquid Membrane Contactors

Performance of Polymeric Membranes

New Polymer membranes for CO_2 removal

Membrane Units for Gas to Liquid Technology

(Solvent development & membranes)

THE UNIVERSITY OF MELBOURNE

CO2CRC

Novel Random Packings

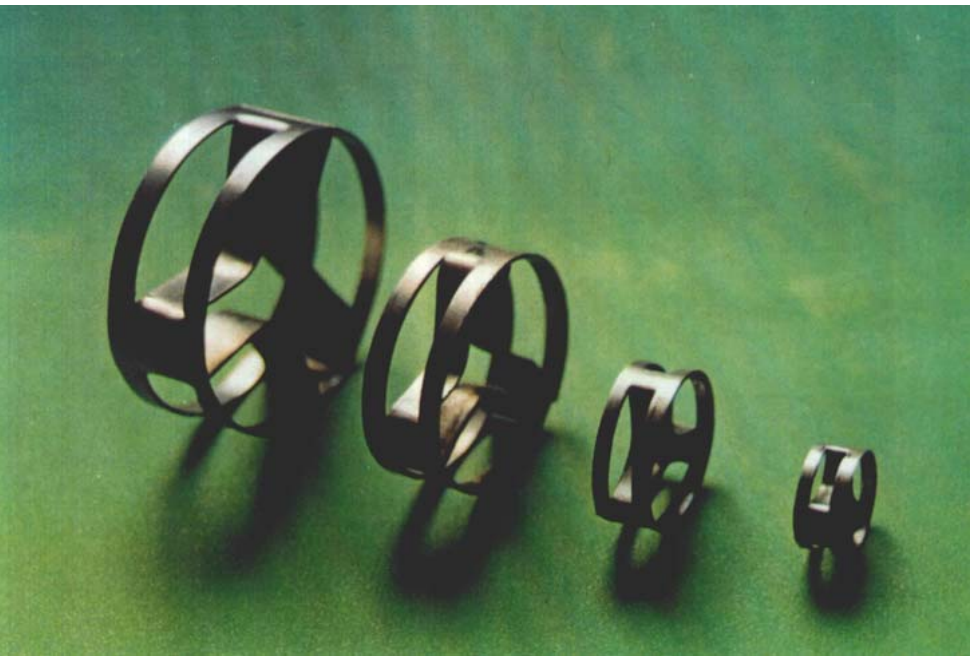
(G. Stevens, H. Habaki, J. Perera, S. Kentish)

Collaboration with Tsinghua University (Prof. Weiyang Fei)

Random packings with low height/diameter ratio have improved capacity and mass transfer efficiency

(Sun et al., 2001, Fei et al., 2002)

Super Mini Ring



Packing	Aspect Ratio	Specific Area
13 mm SMR	0.35	420 m^{-1}
13 mm Pall Ring	1	360 m^{-1}

Experimental Comparison to Pall Rings:

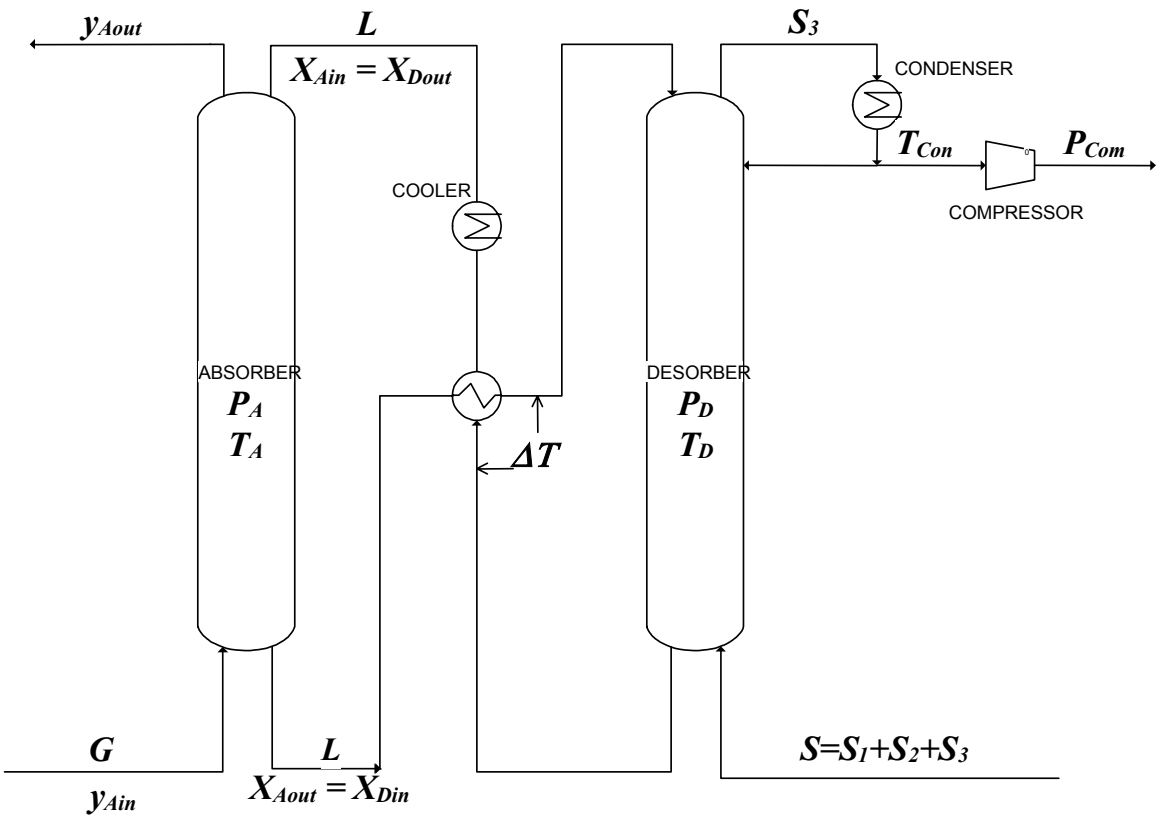
- No change in gas phase holdup
- Reduction of 20% in column height
- Reduction of 15-20% in pressure drop

CO2CRC

Simulations of Energy Demand

(J.Draxler - University of Leoben, Austria, G.Stevens, S.Kentish)

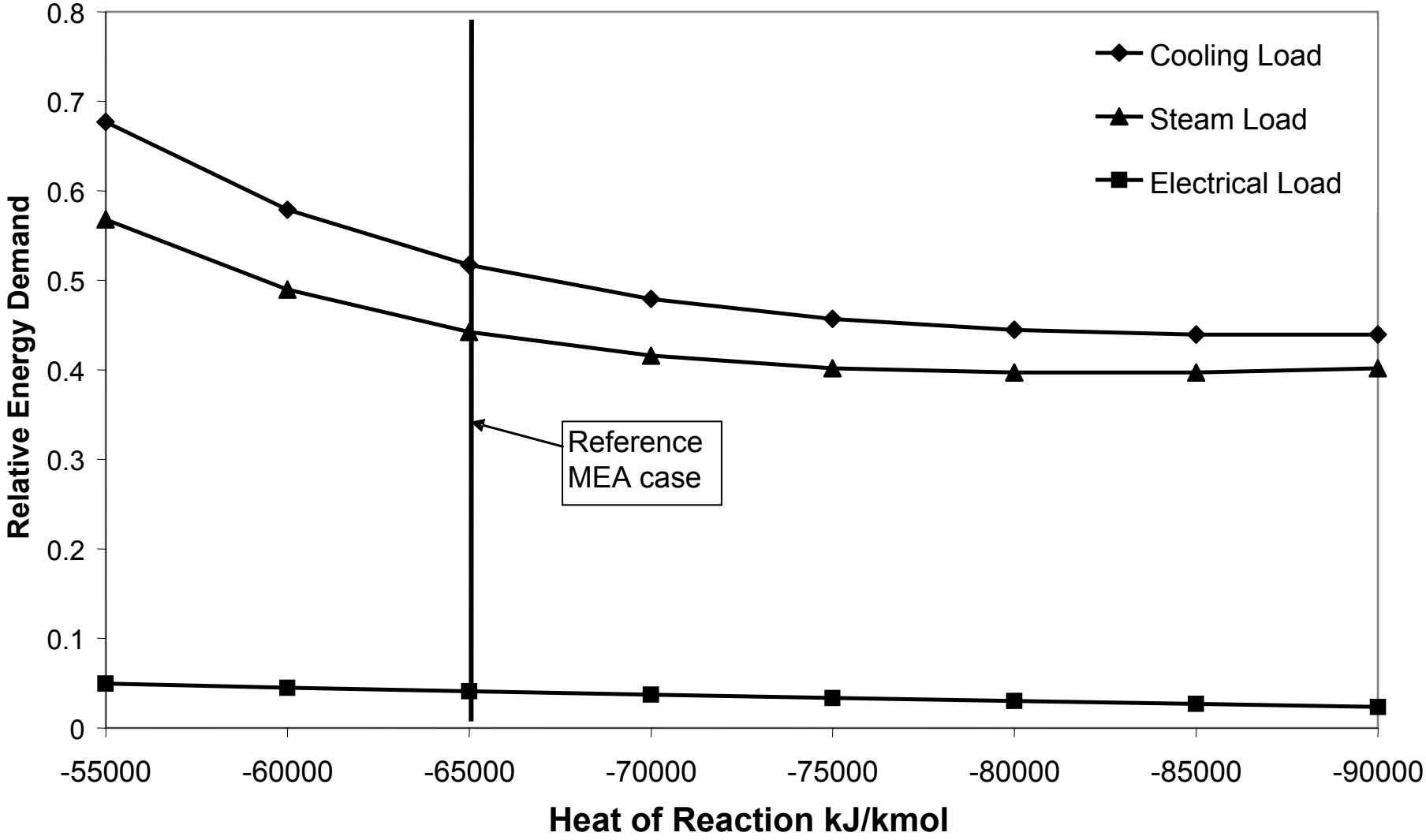
- **Simulation of idealised CO_2 absorption/desorption process**



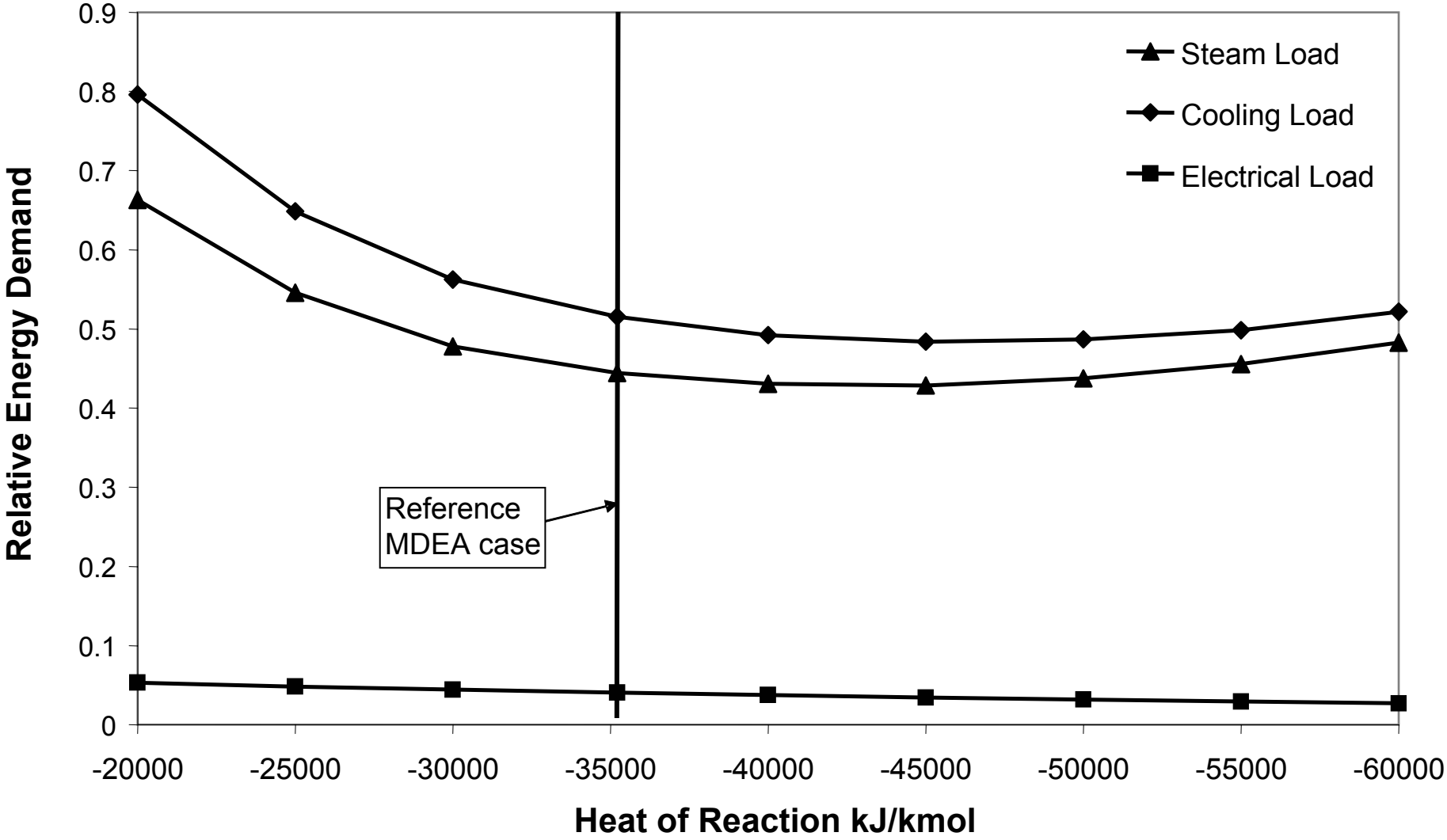
Simulation Results

	Reference MEA Case	Reference MDEA Case	Reference K2CO3 case	Literature
Steam ($kg/kg\ CO_2$)	1.9	2.0	2.0	2 - 2.3 (MEA, Geuzebook et al. (2002)) 1.92 (MEA, Simmonds et al. (2002)) 1.5 (KS-1, Mimura et al. (1995))
Cooling (kJ/ kg CO2)	4800	5000	5200	3000 (MEA, Simmonds et al. (2002))
Electrical kJ/kg Co2)	380	400	440	

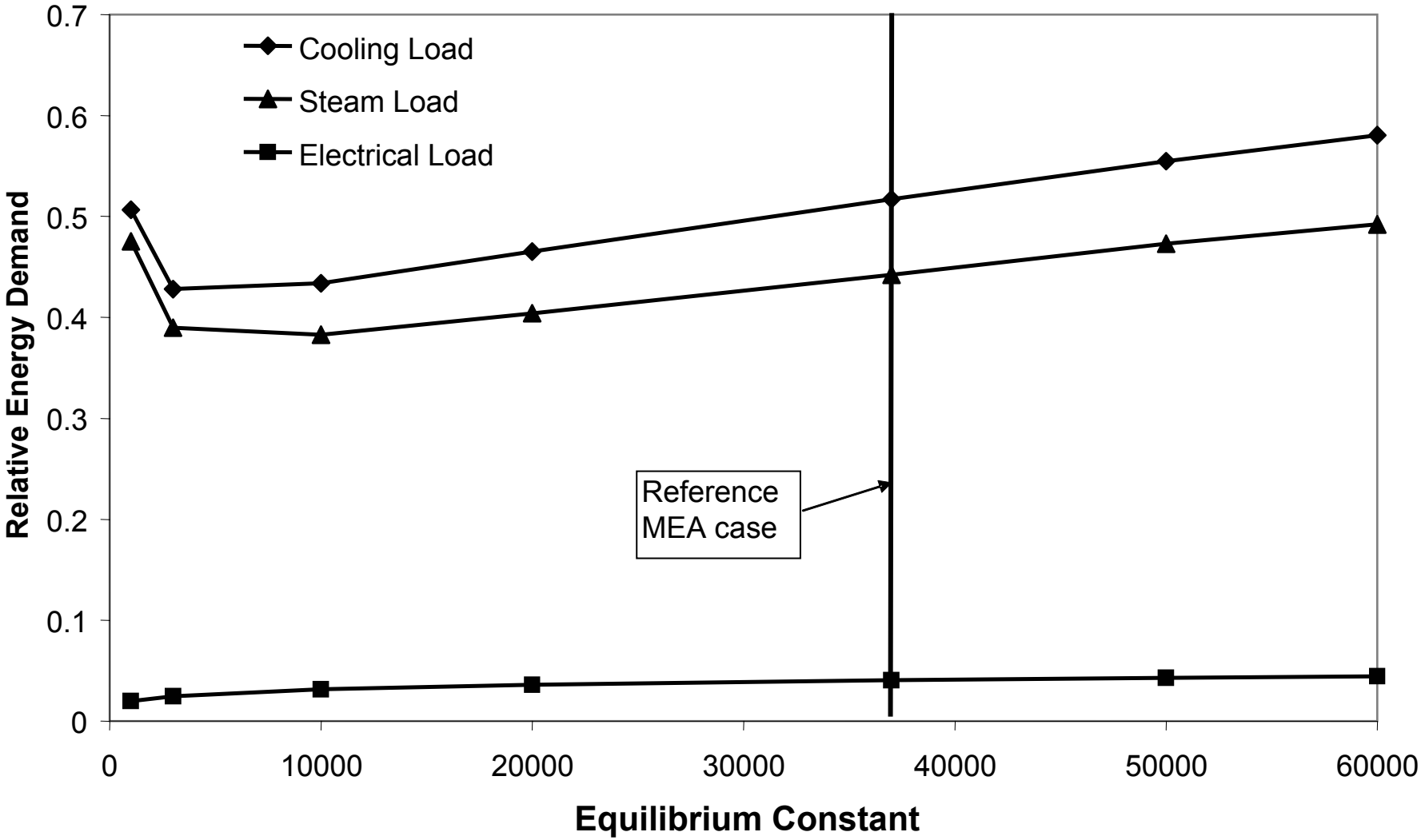
Primary and Secondary Amines



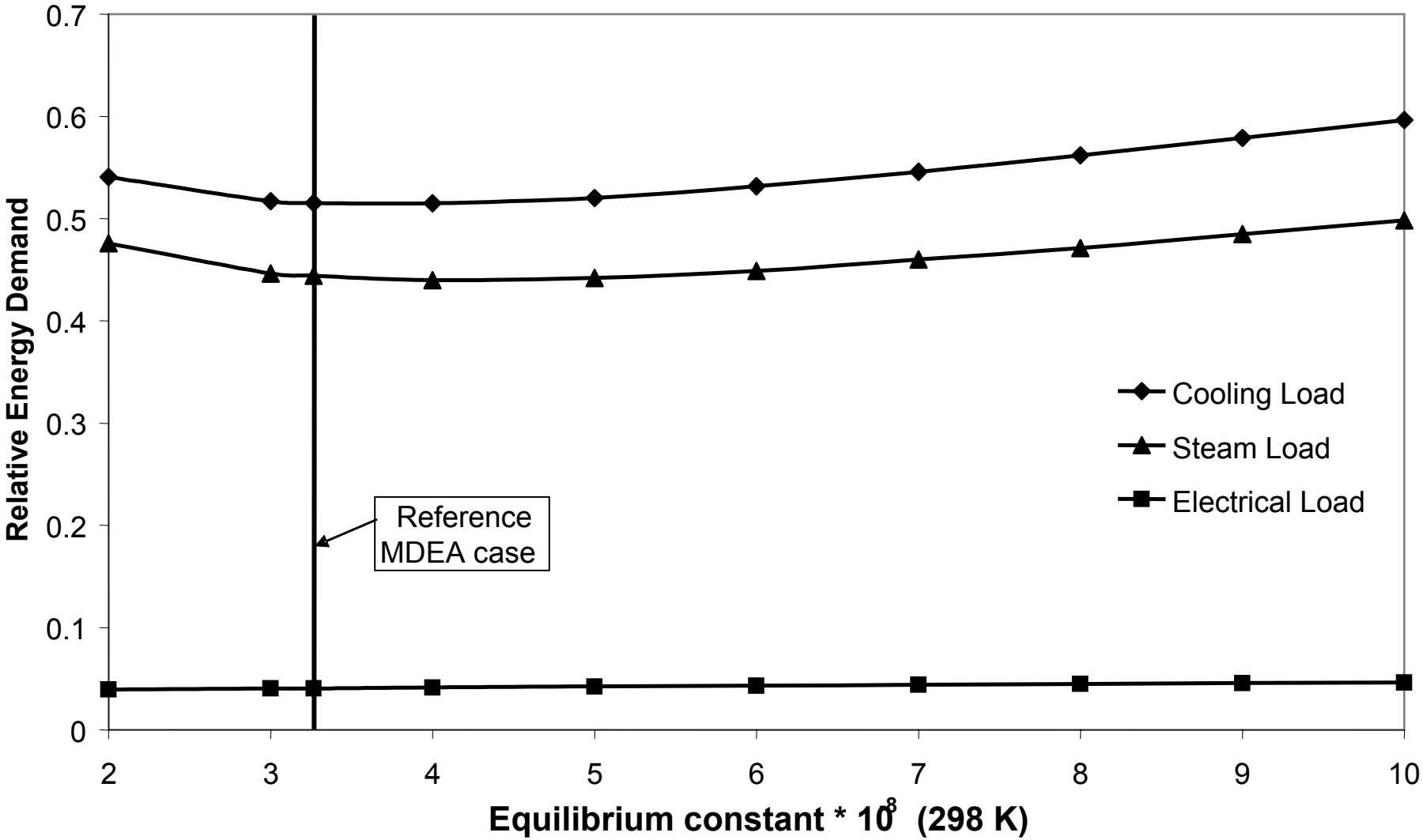
Tertiary Amines



Primary and Secondary Amines



Tertiary Amines



Conclusions

- New aqueous-based solvent formulations alone are unlikely to lead to a significant reduction in overall energy consumption
- Existing aqueous-based solvents (particularly KS-1) provide close to the minimum possible energy demand
- Solvent design may lead to improved reaction kinetics and reagent stability

Membrane Gas Absorption

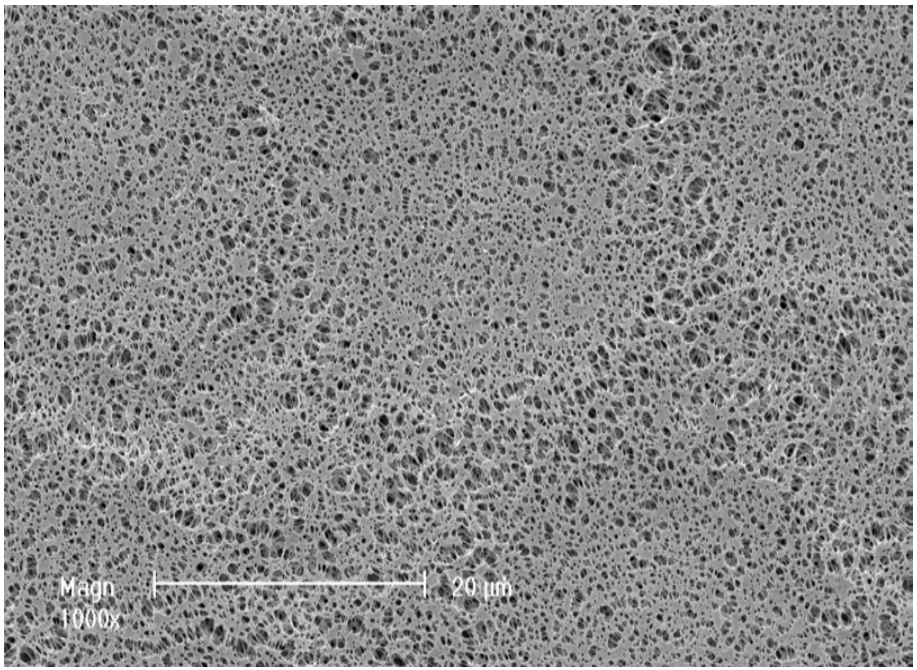
(J. Franco, J. Perera, G. Stevens, S. Kentish)

Key problem with MGA:

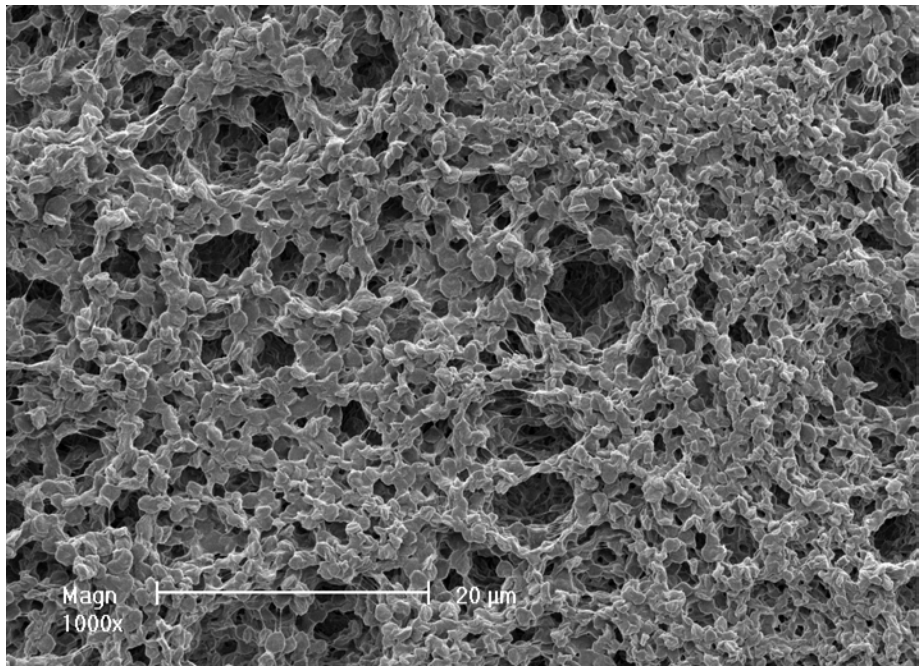
- **Pore wetting increases mass transfer resistance**
  - **Stagnant liquid in pores**
  - **2% pore wetting → membrane mass transfer resistance greater than 60% of total resistance**
  - **Pore wetting can be reduced by decreasing wettability of membrane**

Chemical Treatment of Polypropylene Membrane

Untreated (avg pore size 0.8 µm)

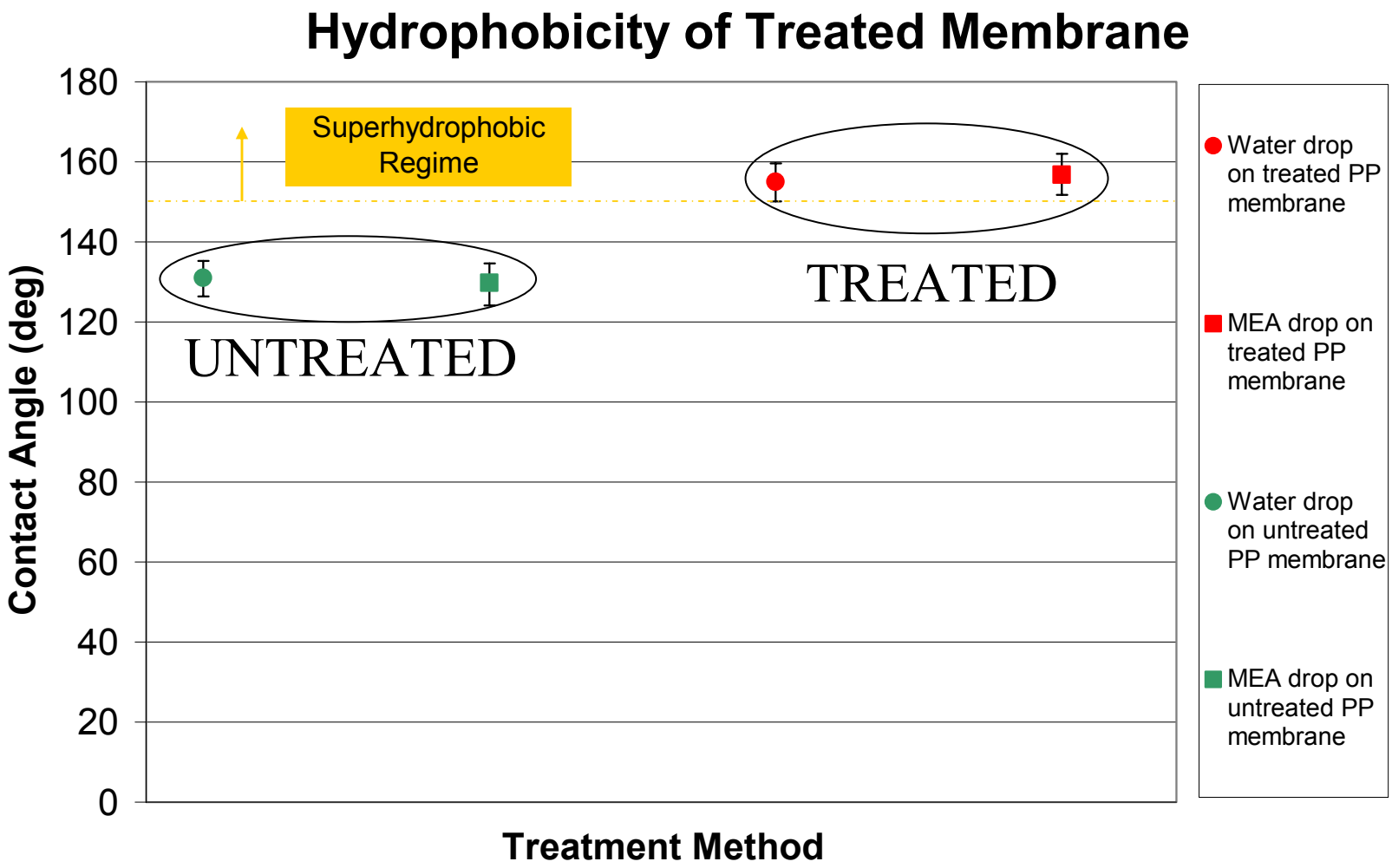


Chemically Treated (avg pore size 2 µm)



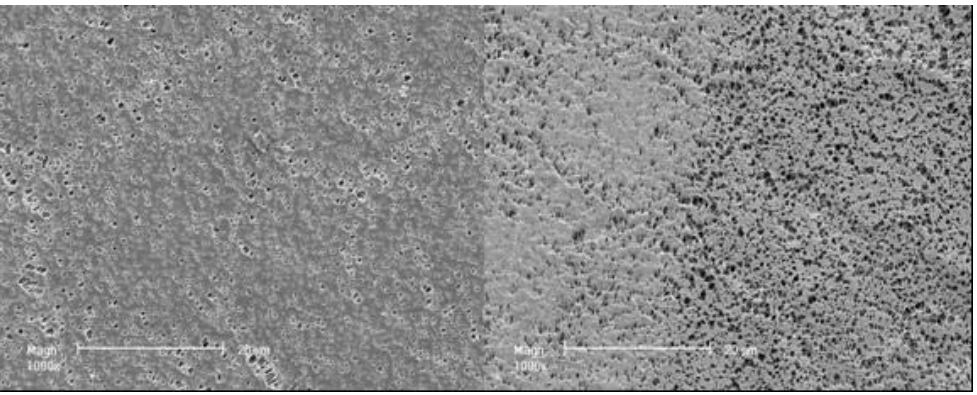
1000×Magnification

Chemical Treatment of Membrane



Effects of Chemical Treatment

- **After Exposure to MEA Solution (20 wt%, 2 days)**
  - **Hydrophobicity remains better than PTFE**
  - **Less distortion to membrane surface morphology than untreated membrane**

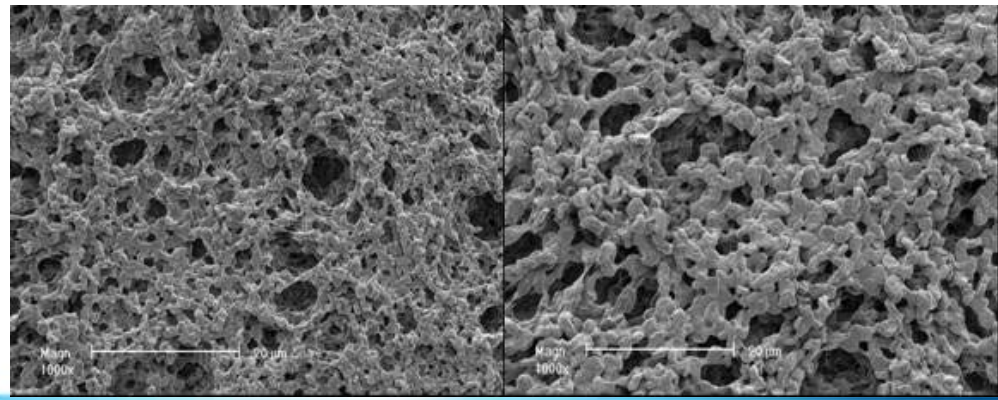


Before After

Untreated Membrane

Treated Membrane

Before After

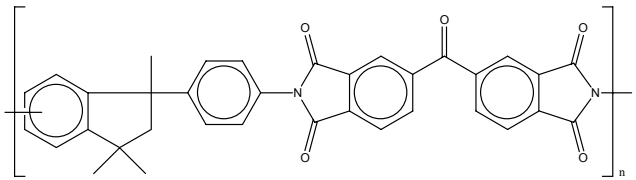


Polymeric Membranes

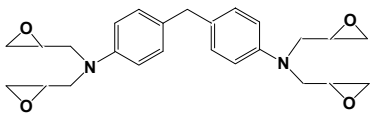
(X. Duthie, C. Powell, S. Kentish, G. Qiao, G. Stevens, K. Nagai – Meiji University, Japan)

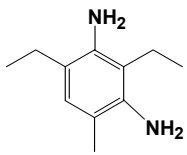
- **Characterisation of existing membrane materials**
- **Development of new polymers**

- **Matrimid (BTDA-DAPI)**

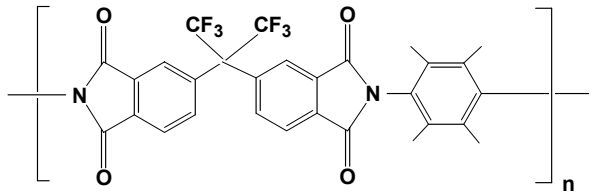


- **Polyimide/diamine/epoxy blends**





- **6FDA – TMPDA (6FDA-Durene)**

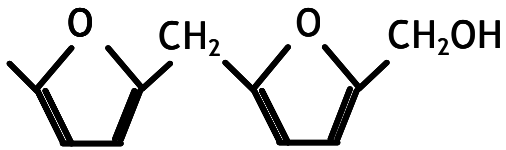


- **Others under Development**

Nanoporous Carbon Membranes

(C. Anderson, S. Kentish, G. Stevens, D. Trimm, S. Sandler)

- **Poly furfural alcohol coated on porous stainless steel**
- **High temperature carbonisation under argon**

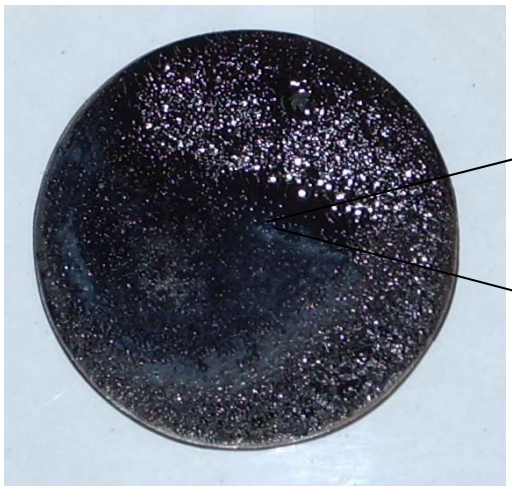


Polymer (PFA)

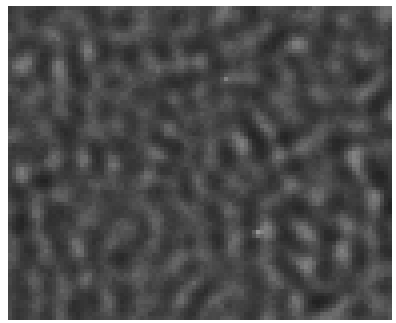
Heat

$H_2O + FA + CO_2 + CO + CH_4 +$ **Nanoporous Carbon**

Membrane with 3 Coats



HRTEM Image (Pore Size 3 – 8 Å)



CO2CRC Capture Program research teams

The University of New South Wales

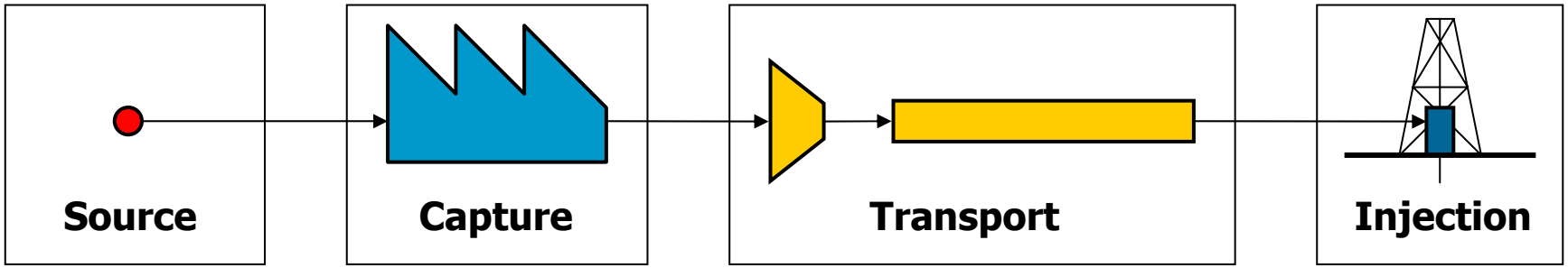
Economic modeling of CO_2 capture systems

(Techno-economic modeling & Membrane Systems)

THE UNIVERSITY OF NEW SOUTH WALES

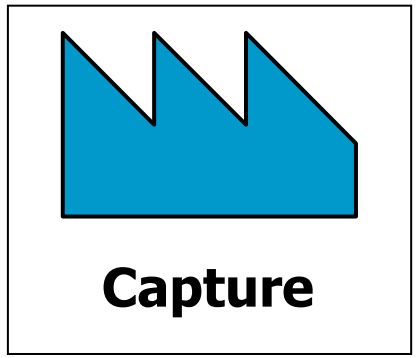
CO2CRC

From End to End



- Encompasses entire process from source to sink.
- Can be used to model several sources and sinks
- Gives process and design results
- Costs based on actual equipment, updated regularly
- Generates cash flow before and after tax

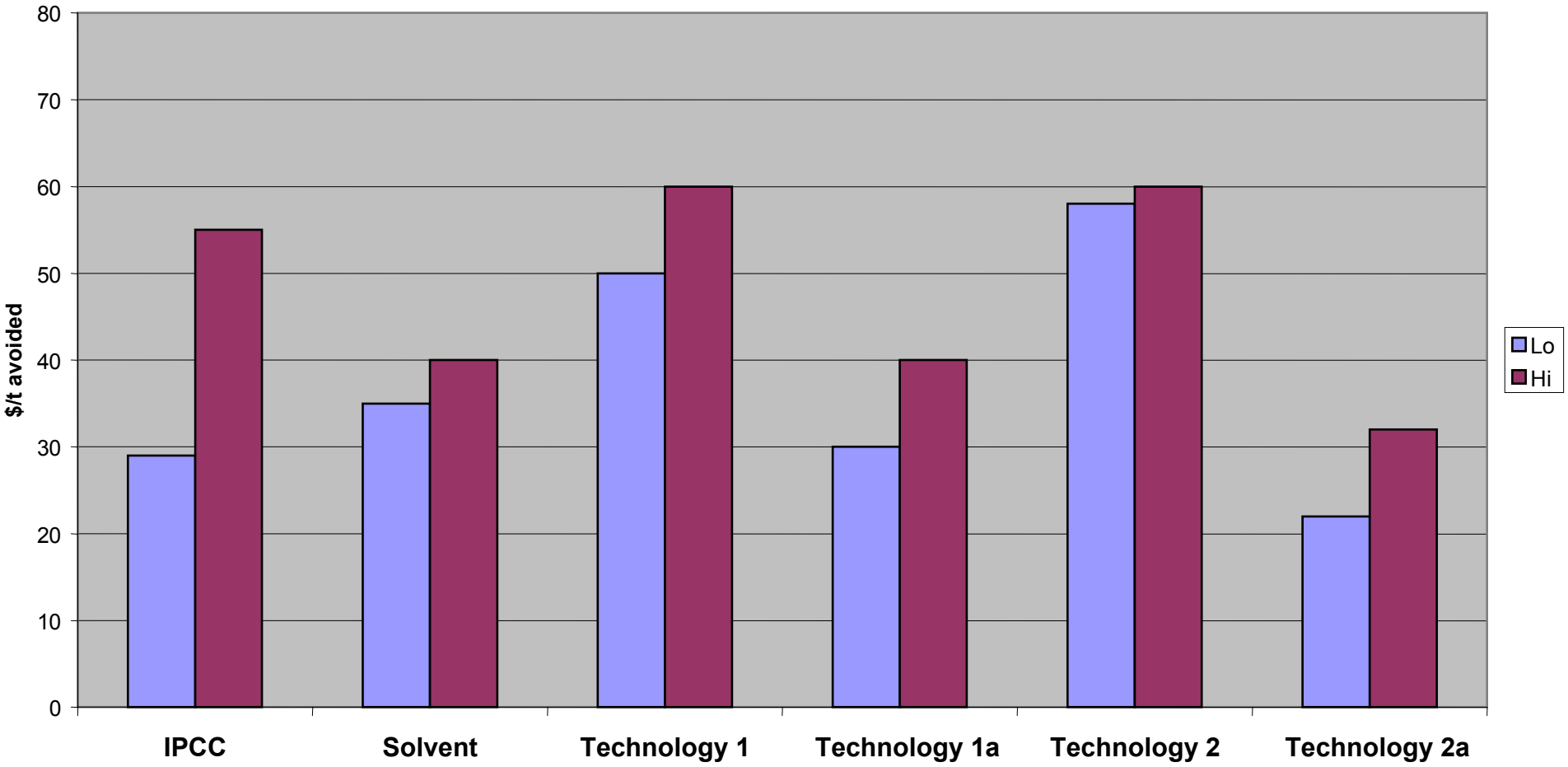
CO2CRC



- Multiple capture technologies
  - Solvent Absorption*
  - Gas Separation Membranes*
  - Pressure Swing Adsorption*
  - Cryogenic Separation
  - Oxy fuel

*Customisable

Capture Costs (USD)
Black Coal PC
Preliminary



CO2CRC Capture Program research teams

Monash University

Adsorption Process Development for CO_2 Capture

Materials for CO_2 Separation by pressure-swing absorption

Inorganic - Organic Hybrid Membranes for CO_2 Separation

Electrically Regenerable Monolithic Adsorbent Carbons

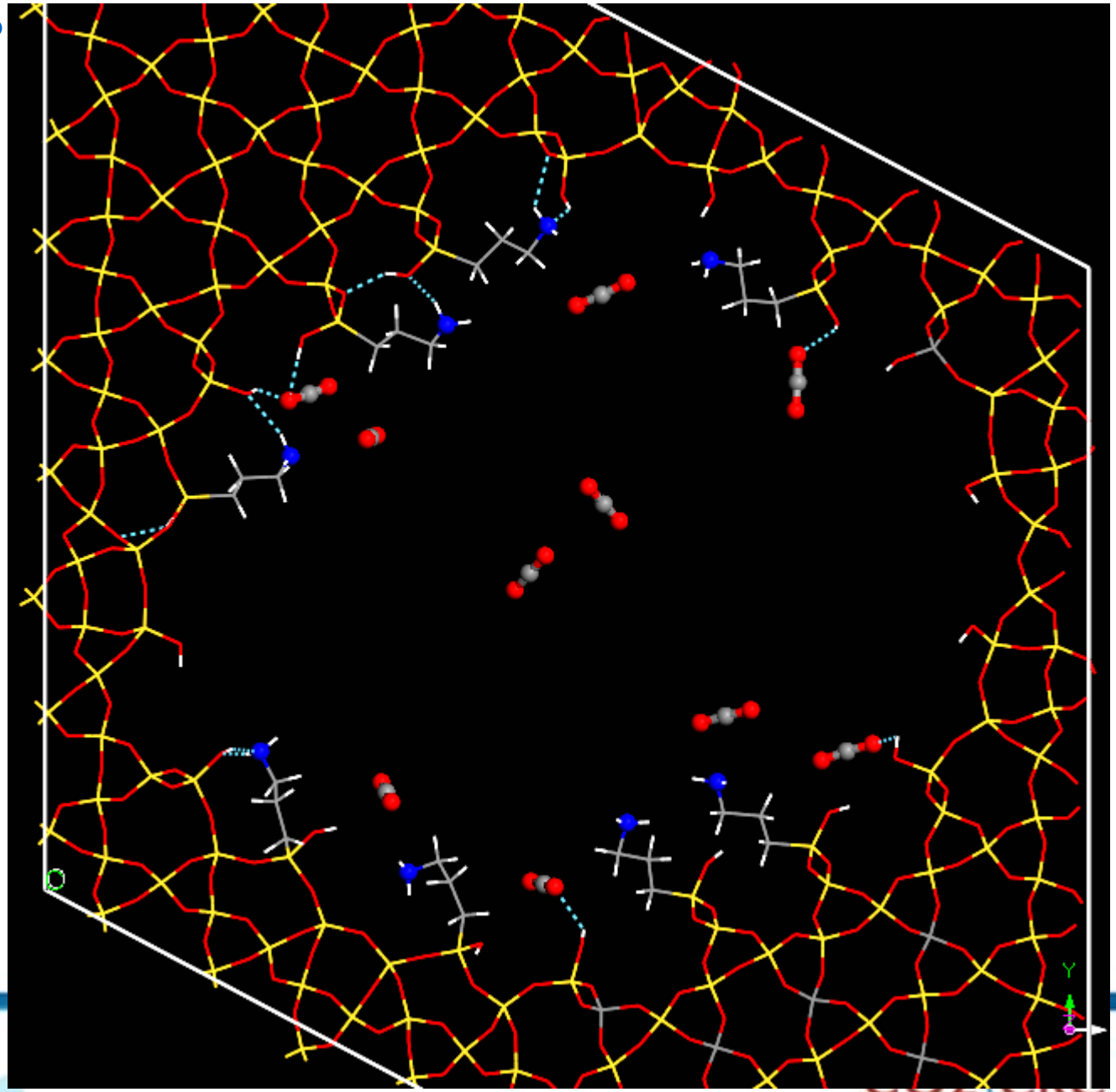
(Adsorbents and adsorption systems)

MONASH University

CO2CRC


21. 8. 2001

33Opt_5OH8APTS plus 10 CO2



CO2CRC Capture Program research teams

The University of Queensland

Scale up of Layer Double Hydroxide (LDH) Membranes for CO_2 Capture

(Inorganic membranes)

THE UNIVERSITY OF QUEENSLAND

CO2CRC

CO2CRC Capture Program research teams

Curtin University of Technology

Hydrate formation and cryogenic capture systems

(Cryogenics and hydrates)

curtin
University of Technology
Western Australia

CO2CRC

Conclusions

- CO2CRC Capture Program is now 2 years into a 7 year program
  - Wide range of leading Australian research groups
  - Capability established in all major technologies
  - Generation of results has commenced

WRAP UP SESSION

- Meeting Review
- An IEA Concept for a Post – Combustion Demonstration Plant
- GHGT 8 in Trondheim
- 9th Meeting of the International CO_2 Capture Network
- A new Network on Oxy-Fuel

Introduction: CCS Demonstration

- Storage demonstrated at 1 million tCO_2/year scale (Sleipner, Weyburn, In Salah)
- CO_2 capture demonstrations:
  - Pre-combustion route
  - Solvents used in reducing atmosphere
- Post-combustion capture done at small commercial-scale but not for climate change reasons.

Why a post-combustion capture demonstration?

- Most coal-fired power plant being built is based on steam boiler/turbine technology.
  - Massive number of orders in China including supercritical plant.
  - Much capital replacement of existing plant expected.
- Pre-combustion capture well covered by Future-Gen and HypoGen/Dynamis.

Post-Combustion CO_2 Capture

- Warrior Run power Station, USA
- 180 MWe coal fired circulating fluidised bed combustor
- 150 t/d of CO_2 captured from a slipstream
  - About 5% of the total
- Largest gas fired capture plant: 800t/d

Elsam's Esjberg Power Plant

A modern pf-fired power station with a supercritical steam cycle

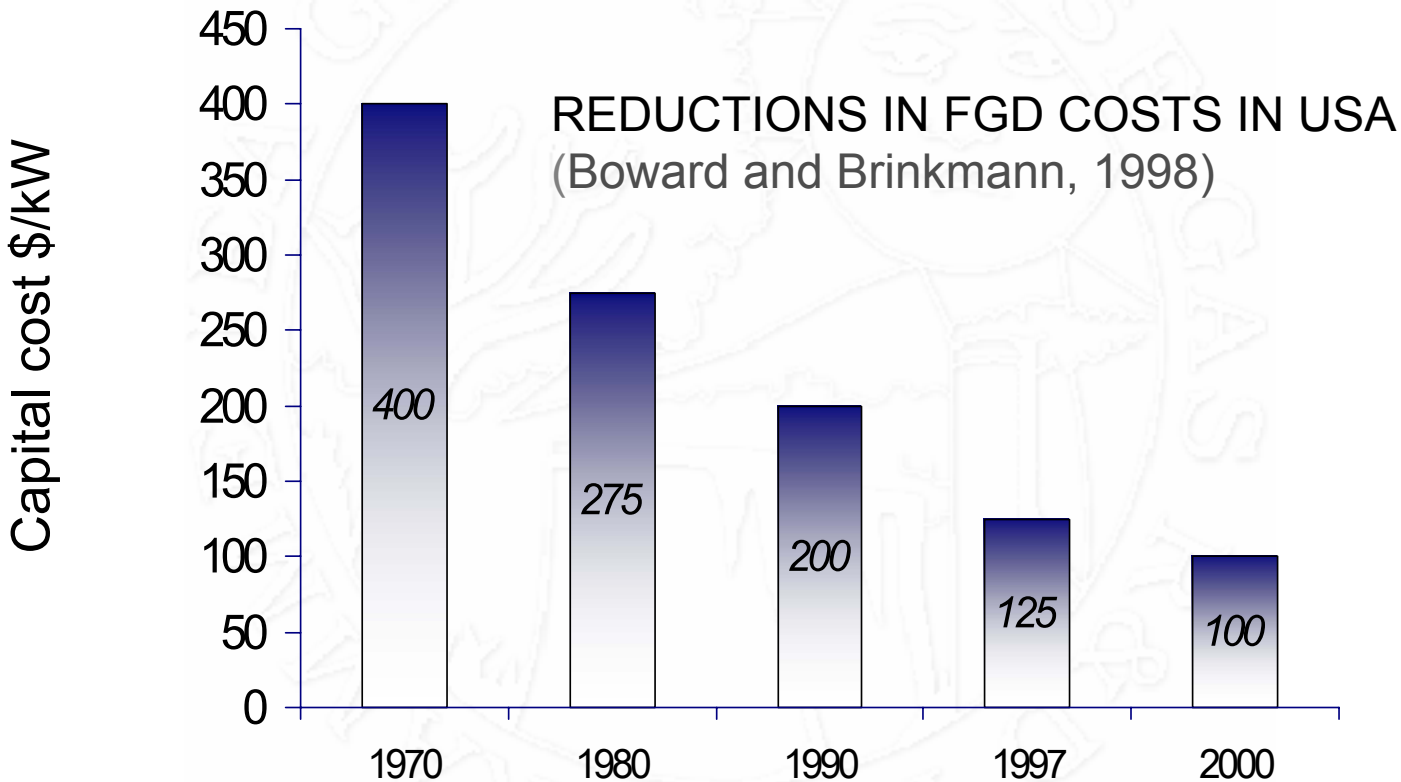
Elsam's Esjberg Power Station

Artist's impression showing added CO_2 capture unit

Objective: of Demonstration

- Demonstrate that a high percentage of the CO_2 produced can be reliably captured without serious impact on power station reliability and operability.
- Further requirements:
  - Demonstrate integrated operation.
  - Satisfactory solvent life and performance.
  - Environmentally acceptable treatment of degradation products.

Solvent Capture of CO_2 – Learning by doing parallels with FGD ?



Original slide from IEA Clean Coal Centre

Proposed CCS demonstration

- Under IEA aegis – Government and Industry Participation
- IEA Grimethorpe PFBC set precedent

The Proposed Facility

- Probably stand-alone but could be one stream on a large unit.
- At least 300MWe to justify supercritical operation.
- High efficiency SOx and NOx clean-up required.
- Approximately 6,000 tpd CO_2 to be stored (about 2x size of Sleipner).

Solvent Suppliers and the Demonstration

- At least 2 potential suppliers of the solvent.
- Will enable detailed design to be carried out.
- Will highlight solvent-suppliers'/ technology-vendors' level of confidence.
- Input from pilot-scale activities we hope will be available:
  - EU Castor – 25 tpd
  - MHI, Nagasaki -10 tpd
  - ITC Boundary Dam – 4 tpd

Post-demonstration options

- Following 2-3 years of demonstration, options include:
  - Continue to capture CO_2 – commercial incentive would need to be there.
  - Operate without capture – would need assurance in advance this was an option
  - Extend life as a demonstration/test facility
  - Allow for possible future conversion to an oxyfuel facility

Proposed Organisation

- Early development of interest and project definition by IEAGHG. (YEAR 1)
- Preliminary design, site selection, consortium development by new Annex to existing IEA Implementing Agreement. (YEARS 2&3)
- Separate IEA Implementing Agreement for participants (YEAR 4)

CONCLUSIONS

- Post-combustion capture is a major missing-link in planned CCS demonstrations.
- At best, it will take 5 years to establish a demonstration
- A decision to build could be made in 2010.
- Operation could start 2012.

IEA Greenhouse Gas R&D Programme

GHGT-8

Trondeim, Norway

19th – 22nd June 2006

Organised by IEA GHG in conjunction with:

NTNU

SINTEF

www.GHGT8.no

Trondheim

3rd Largest City in Norway – 150,000 inhabitants

1000 years of history - Capital in Middle Ages

Getting there

- Regular flights from:
  - Oslo, Norway
  - Amsterdam, Netherlands
  - Copenhagen, Denmark






GHGT-8 Venue

NTNU Campus

- 20 minutes walk from city centre
- Shuttle bus to run during conference
- Hotels in city centre
- Student accommodation on campus

Outline Programme

Sunday (18th)	Monday (19th)	Tuesday (20th)	Wednesday (21st)	Thursday (22nd)
Free	Plenary Lectures	Parallel Technical Sessions	Parallel Technical Sessions	Parallel Technical Sessions
	Lunch			
	Parallel Technical Sessions	Parallel Technical Sessions	Parallel Technical Sessions	Round Table and Closing Ceremony
Registration and Opening Reception			Poster Session	
	Social Evening	Dinner	Social Activities	

Key Dates

- Call for Papers: 24/06/2005 CLOSED
- Deadline for abstracts: 23/09/2005 CLOSED
- Notification to authors: 16/12/2005
- Abstracts on line: 27/01/2006
- Registration open: 27/01/2006
- Paper submission deadline: 21/04/2006
- Papers on web: 26/05/2006

Details

- Expected attendance –700+
- No. of technical papers presented – 230
- No. of posters – 100+
- All papers and poster to be 8 pages long
- Papers will be posted on web site until proceedings issues
  - Abstract book at conference
- Proceedings – CD ROM
- Special edition of technical journal to be published with selected papers from GHGT-8

Anticipated Registration Fees

- Main fee: 600€*
- Includes:
  - Attendance at conference, dinner and receptions & all meals during conference
  - Free use of shuttle buses
  - Copy of abstract book & proceedings
- Reduced registration fee for students: 250€*

***Prices quoted subject to confirmation outcome depends on sponsorship income agreed**

Sponsorship So Far

- Main sponsors:
  - Gasanova, Statoil, Hydro, Research Council of Norway and EC
- Sponsors:
  - CCP2, BP, NEDO/RITE
- Supporters:
  - Chevron, IFP, Schlumberger,

9th International CO2 Capture Network

- Denmark just before GHGT8 as guests of E2
- Easy connections; Copenhagen to Trondheim
- Friday 16th and Saturday 17th June
- Can opt to see a local power station (E2 Avedore) or a full day trip to Esbjerg to see Elsam's CO2 capture pilot plant; visits must be on Friday?
- Or a one day workshop on Saturday with no side visit
- Any volunteers as hosts for 10th meeting in 2007?

Oxy-Fuel Combustion Research Network

- 29-30th November – similar format to this workshop
- Cottbus, Germany
- Vatenfall as host
- Visit to Schwarze Pumpe power plant
- Radisson SAS Hotel in Cottbus
- Contact for registration stanley@ieaghg.org or johnmtopper@aol.com
- Registrants so far from Europe, USA, Canada, Australia, Japan
- Agenda is filling up fast