

### International Network for CO<sub>2</sub> Capture: Report on 9<sup>th</sup> Workshop

(16th June 2006, Copenhagen, Denmark)



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#### **ACKNOWLEDGEMENTS AND CITATIONS**

The IEA Greenhouse Gas R&D Programme supports and operates a number of international research networks. This report presents the results of a workshop held by one of these international research networks. The report was prepared by the IEA Greenhouse Gas R&D Programme as a record of the events of that workshop.

The international research network on post combustion capture is organised by IEA Greenhouse Gas R&D Programme. For the 9<sup>th</sup> meeting we wish to acknowledge the support and hospitality provided by Energie E2 who acted as hosts for the meeting in Copenhagen.

The series of workshops is co-ordinated for the IEA Greenhouse Gas R&D Programme by Dr J M Topper, who is the managing director of the Operating Agent for the Programme Johnmtopper@aol.com or john.topper@iea-coal.org.uk. An alternative contact is John Gale, IEA Greenhouse Gas R&D Programme johng@ieaghg.org.

The report should be cited in literature as follows:

"IEA Greenhouse Gas R&D Programme (IEA GHG), International Network for  $CO_2$  Capture: Report on 9<sup>th</sup> Workshop, 2006/11, June 2006".

Further information on the network activities or copies of the report can be obtained by contacting the IEA GHG Programme at:

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#### **Table of Contents**

11

1.	Overview of the network and past workshops	
2.	Copenhagen Workshop	2
3.	Presentations by Attendees	2
4.	Next Meeting(s)	3
5.	Thanks and Acknowledgements	3
6.	Contacting the Co-ordinator	3
ANNEXES		
Ι	Workshop Agenda	4
II	Delegate List and Contact Details	6

**III** Slide Presentations

#### INTERNATIONAL NETWORK FOR CO<sub>2</sub> CAPTURE: REPORT ON 9<sup>th</sup> WORKSHOP

#### (16th June 2006, Copenhagen, Denmark)

#### 1. Overview of the network and past workshops

This workshop was the ninth 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, Vancouver and Austin. Copies of previous reports after the Apeldoorn meeting are available on CD (contact <u>louise@ieaghg.org</u>).

Carbon dioxide capture and storage is now established in OECD countries' energy policies and R&D programmes as a potential contributor to climate mitigation strategies. 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. Since the previous workshop a number of generators in Europe and Canada have expressed interest in the possibilities of demonstrating the technology at full scale and a major pilot plant operation under the EU CASTOR programme has commenced at a power station near Esbjerg in Denmark. About a quarter of the workshop participants used the opportunity to visit this new facility on the day previous to the workshop – thanks from all participants to Elsam for hosting this visit.

Over the six 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 a variety of fundamental developments including for the first time a presentation on the opportunities of using spray absorption of  $CO_2$ . There is also our first report on possible environmental impacts, although it must be borne in mind that this arises from experience at Statoil's Sleipner capture operations in the North Sea.

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

#### 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.

#### Austin

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 ranging 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.

#### 2. Copenhagen Workshop

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 - for the IEA GHG R&D Programme	Introduction to 9th Workshop
2	Ole Biede - E2 and Jacob Knudsen - Elsam, Denmark	Carbon Dioxide Capture and Storage activities in Denmark
3	J P Brouwer, P H M Feron, N A M ten Asbroek - Department of Separation Technology, TNO-Science and Industry, The Netherlands	CO <sub>2</sub> absorption using precipitating amino acids in a spray tower
4	Kazuya Goto - RITE, Japan	Novel Absorbents for CO <sub>2</sub> Capture from Gas Stream
5	Marcus Hilliard, John McLees and Gary T Rochelle - University of Texas, USA	Volatility of MEA and Piperazine
6	Babatunde A Oyenekan and Gary T Rochelle - University of Texas, USA	Rate modeling of Stripper Performance
7	Amy Veawab and Andy Aroonwilas - University of Regina, Canada	Energy Requirement for Solvent Regeneration in CO <sub>2</sub> Capture Plants
8	Jon Gibbins - Imperial College, UK	Making New Power Plants 'Capture Ready'
9	Louis Wibberley - CSIRO, Australia	Australian National Post Combustion Capture and Storage Demonstration Project

10	Barry Hooper - CO2 CRC, Australia	Dwarfing Sleipner! Large Scale CCS projects and other CO2CRC activities
11	Gelein de Koeijer - Statoil, Norway	Increased Interest in Environmental Impacts of Amines
12	Nick ten Asbroek - TNO, The Netherlands	Overview of activities in CASTOR, ENCAP, CATO and Dynamis at TNO
13	Dick Rhudy - EPRI, USA	CO <sub>2</sub> Testing Program: An Industry/EPRI Initiative to Develop CO <sub>2</sub> Capture and Storage Test Capabilities
14	Dennis Leppin - Gas Technology Institute, USA	GTI's Acid Gas Treating Pilot Plant (AGTPP) Relocation and Integration with FlexFuel Facility
15	Tsuyoshi Oishi,- MHI, Japan	Mitsubishi CO <sub>2</sub> Recovery Technology from Flue Gas: Experience and R&D Facilities

#### 4. Next Meeting(s)

The 10<sup>th</sup> Network meeting will be as guests of IFP, Institute Français du Pétrole, in Lyon in May or June of 2007. In 2008 GHGT9 conference will be in Washington DC, provisionally in early November. It is expected that the 11<sup>th</sup> Network meeting will be either before or after this conference.

#### 5. Thanks and Acknowledgements

All participants wish to thank Ole Biede of E2 for all the hard work of co-ordinating the event and the pilot plant visit on the previous day. The Danish power industry will have been reorganised by the time this report is made generally available and Ole will be in Dong. We wish him well under new ownership. The E2 offices were an excellent venue for the meeting and we all enjoyed further E2 hospitality at the dinner in the Tivoli area on the evening of 16<sup>th</sup> June.

#### 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:-

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

#### ANNEX I

1

#### **Workshop Agenda** 9<sup>th</sup> International Network for CO<sub>2</sub> Capture Copenhagen Workshop

<u>Friday, 16<sup>th</sup> June 2006</u>				
0900	Welcome, Round the Table Introductions, Today's Agenda – John Topper for IEA Greenhouse Gas R&D Programme			
0915	Hosts Address – "Carbon Dioxide Capture and Storage activities in Denmark" including description of pilot plant and it's programme of work			
Morning Chair – Gary Rochelle				
0950	Jan-Peter Brower – TNO, Netherlands: "CO <sub>2</sub> absorption using precipitating amino acids in a spray tower"			
1015	Coffee Break			
1045	Kazuya Goto – RITE: "Novel absorbents for CO <sub>2</sub> capture from gas streams"			
1110	Marcus Hilliard – University of Texas, USA: "Volatility of monoethanolamine and piperazine"			
1135	Babatunde Oyenekan, – University of Texas, USA: "Rate modelling of stripper performance"			
1200	Amornvadee Veab and Adisorn Aroonwilas – University of Regina, Canada: "Energy requirements for solvent regeneration in CO <sub>2</sub> capture plants"			
1225	Lunch and Group photo			
Early Afternoon Chair – Jon Gibbins				
1345	Jon Gibbins – Imperial College, UK: "Capture ready design and facilities"			
1410	Louis Wibberley – CSIRO, Australia: "Proposal for LETF funding from Australian Government on Post Combustion Capture"			
1435	Barry Hooper – CO2CRC, Australia: "Dwarfing Sleipner! Large scale CCS and other CO2CRC projects"			
1500	Coffee Break			
Late Afternoon Chair – John Topper				
1530	Gelein de Koeijer – Statoil, Norway: "Increased interest in Degradation of			

	Amines"
1555	Nick ten Asbroek – TNO, Netherlands: "An overview of activities in CASTOR, CATO, ENCAP and DYNAMIS"
1620	Richard Rhudy – EPRI, USA "Plans for post combustion pilot plant at EPRI
1635	Denis Leppin – GTI, USA: "The GTI Flex Fuel test Stand"
1650	Tsuyoshi Oishi – MHI, Japan: "KS 1 solvent – Commercial Experiences"
1705	Wrap up, conclusions, next meeting – John Topper

#### ANNEX II

### 9<sup>th</sup> International Network for CO<sub>2</sub> Capture

### 16<sup>th</sup> June 2006, Copenhagen, Denmark

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#### ANNEX III

#### PRESENTATIONS

The powerpoint presentations follow in the same order as listed in section 3 of this report and can be accessed from the bookmark list



### Introduction to 9th Workshop, Copenhagen

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



www.ieagreen.org.uk



- AIM: To establish a forum that will encourage practical work on CO<sub>2</sub> 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



## Four Tasks Established (Gaithersburg 2000)

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

IEA GHG to facilitate

1<sup>st</sup> Workshop in Gaithersburg, USA (Spring 2000)
2<sup>nd</sup> Workshop, Calgary, Canada(November 2001)
3<sup>rd</sup> Workshop in Apeldoorn; Netherlands (Spring 2002)
4<sup>th</sup> Workshop in Kyoto, Japan (Autumn 2002)
5<sup>th</sup> Workshop in Pittsburgh, USA (June 2003)
6<sup>th</sup> Workshop in Trondheim, Norway, (Spring 2004)
7<sup>th</sup> Workshop in Vancouver, Canada, (Sept 2004)
8<sup>th</sup> Workshop in Austin, USA (Autumn 2005)
9<sup>th</sup> Workshop at offices of E2, Copenhagen



We are now a well established club; 2/3 of the non-Danish registrants have been to two or more workshops

Of those almost 1/2 from N America; 1/3 from Europe + 2 from Japan, 6 or 7 from Australia.

> 10 different countries here today

Excellent networking

**Today: Housekeeping Points** 

- Coffee breaks around 10.15 and 15 00
- Lunch, 12.30 13 30 followed by photos
- Afternoon session will finish at around 17 30 and by bus back to hotel(s)
- Dinner this evening in the Tivoli area E2 to provide details. Need to check numbers & partners
- ALL PRESENTERS ensure I get a copy of their presentation on data storage stick if you want it on the GHG website next week
- Mobile phones off or on vibrating alert



# And one issue that IEA GHG would like raised now and in future workshops

# ENVIRONMENTAL IMPACTS OF AMINE SOLVENTS USAGE AND THE BY PRODUCTS OF CAPTURE



# Thanks to E2 and Elsam

- To E2 for local organisation
- And for Sponsoring the Dinner this evening
- To Elsam for the pilot plant and power station visit yesterday

# 9th International CO<sub>2</sub> Capture Network ENERGI E2, Copenhagen, June 16, 2006

# Carbon Dioxide Capture and Storage activities in Denmark

# Ole Biede, ENERGI E2 A/S

# Jacob Knudsen, Elsam Engineering







9th International CO<sub>2</sub> Capture Network ENERGI E2, Copenhagen, June 16, 2006

- Practical details
- ENERGI E2 and Reorganization of the Danish Power Companies
- CO<sub>2</sub> Capture and Storage activities in Denmark
- CASTOR Project (<u>Capture and Storage of CO<sub>2</sub></u>)
- Pilot Plant
- Results from the Pilot Plant







9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 Practical details - overview

- Coffee breaks 10.15 and 15.00
- Lunch buffet 12.30
- Restrooms
- Dinner in Tivoli, Restaurant Påfuglen 19.30
  - Number of participants
    - Accompany: Keith Harrison, Bob Stobbs, John Topper
  - Dietary requirements
    - No beef: Andy Aroonwilas, Amy Weawab
  - Tickets
  - Map
  - Tivoli closes at 00.30







9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 Practical details - maps









9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 Practical details - Tivoli









9th International CO<sub>2</sub> Capture Network E2, Copenhagen, June 16, 2006

# ENERGI E2 and Reorganization of the Danish Power Companies







### 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 ENERGI E2

- ENERGI E2 is a leading Danish energy production and trading company
- E2 owns and operates 17 power and combined heat and power plants in Eastern Denmark and has several activities internationally
- E2's head office is located in Copenhagen with approximately 400 employees
- In total E2 has 1450 employees
- Total production capacity:
   4.800 MW electricity, 2.850 MJ/s heat and 1.800 MJ/s steam.





ENERGI

### 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 ENERGI E2 – power plants



### 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 ENERGI E2 - international



### 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 ENERGI E2, Avedøre Power Station









9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 Reorganization of the Danish Power Companies








9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 Reorganization of the Danish Power Companies

Fordeling af produktionsanlæg i Danmark









9th International CO<sub>2</sub> Capture Network E2, Copenhagen, June 16, 2006

# CO<sub>2</sub> Capture and Storage activities in Denmark

# Kalundborg

- CENS
- EU-projects: CO2store, ENCAP, Castor







Geological Survey of Denmark and Greenland, GEUS

Saline aquifer storage of  $CO_2$  from major point sources – a Danish case study











Elsam-project:

CENS:  $\underline{CO}_2$  for  $\underline{E}$ nhanced Oil Recovery in the  $\underline{N}$  orth  $\underline{S}$  ea









## Esbjergværket today









## Esbjergværket with CO<sub>2</sub> capture









# Conclusions from the CENS-study:

- Technology for CO<sub>2</sub>-capture is commercially available
  No economic basis for EOR (2001)
- Lack of experience from coal-fired full-scale power plants
- Pilot / demonstration plants on coal flue gas needed

# **Participation in CASTOR**



9th International CO<sub>2</sub> Capture Network, ENERGI E2, Copenhagen, June 16, 2006

# CASTOR Project "<u>Capture and Storage of CO<sub>2</sub>"</u>







9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Objectives / Targets

- Reduce the cost of CO<sub>2</sub> post-combustion capture
- Contribute to the feasibility & acceptance of the geological storage concept
- Validate the concept on real site(s)
  - Pilot plant testing for capture
  - Detailed studies of future storage projects
- Duration: 4 years (February 2004 January 2008)
- Budget: ~16 M€ (EU funding: 8.5 M€)







9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Main Components









9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Consortium Participants

# 28 participants from 11 countries

#### R&D

IFP (FR) ST TNO (NL) GE SINTEF (NO) RE NTNU (NO) EN BGS (UK) RC BGR (DE) BRGM (FR) GEUS (DK) IMPERIAL (UK) OGS (IT) TWENTE U. (NL) STUTTGARTT U. (DE)

#### Oil & Gas

STATOIL (NO) GDF (FR) REPSOL (SP) ENITecnologie (IT) ROHOEL (AT)

## **Power Companies**

VATTENFALL (SE) ELSAM (DK) ENERGI E2 (DK) RWE (DE) PPC (GR) POWERGEN (UK)

#### **Manufacturers**

ALSTOM POWER (FR) MITSUI BABCOCK (UK) SIEMENS (DE) BASF (DE) GVS (IT)

Co-ordinator : IFP







9th International CO<sub>2</sub> Capture Network, ENERGI E2, Copenhagen, June 16, 2006

# **Castor Pilot Plant**







9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Time schedule

- February 2004
- September 2004
- February 2005
- July 2005
- October 2005
- January 2006
- March 2006
- August 2006
- Fall 2006:
- Summer 2007
- January 2008

- : Castor project starts
- : Invitation for tender issued
- : Contract awarded TPI, Italy
- : Erection start
- : Commissioning start
- : Start Test Phase 1, 1000 h on 30% MEA
- : End Test Phase 1
- : Start Test Phase 2, 1000 h on 30% MEA

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- : Start Test Phase 3, 4000 h on Castor1
- : Start Test Phase 4, 4000 h on Castor2
- : End of Castor













9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Esbjergværket unit 3





## 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Pilot plant



Sea Water Out















## 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 **CASTOR – Pilot plant**

Engineering





Sea Water Out











## 9th Int. CO<sub>2</sub> Capture Network, Copenhagen 2006 CASTOR – Pilot plant





Elsam

Engineering



Sea Water Out










#### 9th Int. CO2 Capture Network, Copenhagen 2006, CASTOR - Pilot plant



Engineering





9th International CO<sub>2</sub> Capture Network E2, Copenhagen, June 16, 2006

# Results from the Pilot Plant







# **Objectives - 1000 hours MEA campaign**

- Functional test of the pilot plant
- Gain of operating experience
- Information on operating costs (e.g. energy & solvent consumptions)
- Verification of theoretical models







# Test program – 1000 hours MEA campaign

Test 1 – 500 hours of continuous operation (10/01/06 - 01/02/06)

- Continuous operation at the nominal conditions, achieving 90% CO<sub>2</sub> capture
- Corrosion tests (IFP)
- Test 2 Parametric study (07/02/06 -15/02/06)
  - a) Load following capability
  - b) Minimizing the solvent flow
  - c) Changing the regeneration temperature
  - d) Optimizing the regeneration conditions
- Test 3 Special interest experiments (20/02/06 02/03/06)
  - a) Absorber pressure drop (IFP)
  - b) SO<sub>2</sub> injection incl. extended gas and solvent analyses (RWE & TNO)







# Test 1 - Summary

- Continuous operation from Jan 10<sup>th</sup> to Feb 1<sup>st</sup>
- Plant operated at settings recommended by the contractor:
- **18** outages during the test. Total down time:  $\approx$ 20 hours
- Causes: High SO<sub>2</sub>, high levels, plugging of sea water filter
- Frequent plugging of solvent filter (gypsum, fly ash)
- Fresh MEA added to compensate for losses
- No reclaiming during the test







# Test 1 – Settings









### Test $1 - CO_2$ recovery



Average (26/01/06 - 01/02/06):

• Flue gas flow: 4170 Nm<sup>3</sup>/h (12.4% CO<sub>2</sub>) • CO<sub>2</sub> recovery: 92.5% • CO<sub>2</sub> production: 850 kg/h







### Test 1 – Absorber & Stripper temperatures









# Test 1 – MEA % and CO<sub>2</sub> loadings



#### Average value:

•MEA: 25.7 %

- Lean loading: 0.24
- Rich loading: 0.37 (not reliable)







# Test 1 - Balances

#### Material balances (26/01/06 - 01/02/06)

	Stream	avg. value
CO <sub>2</sub> balance:	CO <sub>2</sub> absorbed - gas side	846
(kg/h)	CO <sub>2</sub> desorbed - gas side	885
	CO <sub>2</sub> absorbed - solvent	687
H <sub>2</sub> O balance:	H <sub>2</sub> O condensed from flue gas	246
(kg/h)	Make up H <sub>2</sub> O to abs. wash	60
	H <sub>2</sub> O input with CO <sub>2</sub> product	-12.3
	Drain of stripper condensate	n.d.
	Total:	+ 294

#### Energy balance (26/01/06 - 01/02/06)

Heat (MJ/ton CO <sub>2</sub> )	avg. value	
Heat input from steam	4400	
Heat from flue gas	720	
Cooling water	-4930	
Distribution of cooling duty (%)*	7.5 / 67 / 25.5	
Total energy balance	+170 (3.3 %)	

\*Distribution of cooling duty between abs. wash, MEA/H $_2$ O cooler, and condenser







### Flue gas pollutants - 1000 hours MEA Test



	O <sub>2</sub> (% vol)	NO <sub>x</sub> (ppm)	SO <sub>2</sub> (ppm)	Dust (mg/Nm <sup>3</sup> )
Average – 10. Jan 20. Feb.	6,0	187	7,6	3,5
Design criteria	-	65	10	10







# **Solvent consumption & degradation**

### Findings

- MEA consumption during Test 1: 2.4 kg/ ton CO<sub>2</sub>
- Nearly complete absorption of SO<sub>2</sub> (50% as SO<sub>4</sub><sup>2-</sup>)
- $\approx 1$  % of NO<sub>x</sub> absorbed ad NO<sub>3</sub><sup>-</sup>
- Solvent saturated with gypsum
- MEA loss by degradation probably more significant than slip

Degradation & absorption of NO<sub>x</sub> & SO<sub>2</sub>



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# Upcoming activities at Esbjerg pilot plant

- Additional campaign with MEA (Summer 2006)
- Campaign with new solvent "Castor 1" (Autumn 2006 2007)
- Campaign with new solvent "Castor 2" (2007)







# CO<sub>2</sub> absorption using precipitating amino acids in a spray tower

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9th International CO<sub>2</sub>-Capture Network Meeting 16 June 2006



### Overview

- Introduction to the Decab process
- Selection of contactor type
- Experimental set-up
- First results
- Preliminary design considerations
- **Conclusions + future work**



### **Introduction to the Decab process**

- **CORAL** =  $\underline{CO}_2$ - $\underline{R}$ emoval  $\underline{A}$ bsorption  $\underline{L}$ iquid
- Mixtures of amino-acids, alkali salts and amines
- Stable operation with polyolefin membranes
- Better oxygen stability
- Less corrosive
- No losses of active components
- Neutralized amino acids: very suitable for membrane gas absorption (no leakage through membrane, no vapour pressure, good thermal stability)



### Chemistry

• Preparation by neutralization of amino acid with KOH (up to 6 M, thus high loadings possible), equilibria:

 $HOOC-R-NH_{2}$   $\uparrow\downarrow$   $-H^{+} \qquad -H^{+}$   $HOOC-R-NH_{3}^{+} \leftrightarrow ^{-}OOC-R-NH_{3}^{+} \leftrightarrow ^{-}OOC-R-NH_{2}$   $low pH \qquad neutral - mildly acid pH \qquad high pH$ 

• Solubility of neutral species is limited  $\rightarrow$  salt formation during absorption



#### **Reactions with \overline{CO}\_2 (similar to "normal" amine systems):**





**Equilibria may be positively influenced by precipitation during absorption** (removal of acid from solution)



By increasing temperature, amino acid redissolves, effectively driving out  $CO_2$   $\Rightarrow$  lower top temperatures in stripper may be applied This necessitates use of an integrated heat exchanger though



#### **Conceptual process design:**







High cyclic loadings and low stripper top temperature are possible

- $\rightarrow$  Possible 40-50% reduction of energy consumption (compared to MEA)
- $\rightarrow$  Reduction of capital costs



### What contactor?

#### • Contactor must be able to handle slurries!

Contactor	$a [m^2/m^3]$	ε[-]	$k_1 * 10^4 [m/s]$
Bubble column	20	0.02	1-4
Spray column	60	0.95	1-3
Packed column	100	0.92	0.5-2
Tray column	150	0.85	1-4
Stirred tank	200	0.10	0.2-1
Hollow fibre module	3000		0.1-0.5

- Interfacial area is important for efficiency
- Typical absorption regime for Coral: chemical enhancement (E=Ha), thus k<sub>L</sub> not very important for flux
- MEA at high  $CO_2$ -concentrations: amine diffusion control, i.e.  $E=E_{\infty}$



• Spray columns are widely used in flue gas desulphurization

#### • Advantages:

- Low pressure drop
- High capacities, suitable for power plants
- Robust system, capable of handling slurries

#### • Drawbacks:

- Backmixing
- Recycle of solvent may be required for high G-L interface. This is unwanted! We want countercurrent flow!





# **Experimental set-up (absorption)**





### **First results**

- Absorption at 50-55°C; feed gas = 15% CO<sub>2</sub>
- Variation of
  - Coral concentration
  - Gas flworate
  - Liquid flowrate

$$k_{ov} = \frac{r_{abs}}{aV\left(\frac{P_{CO_2} - P_{CO_2}^*}{RT}\right)}$$



• K<sub>ov</sub> based on interpolated equilibrium pressures and estimated GL-surface area (including wetted wall!)



#### **Absorption rates**





#### **Overall mass transfer coefficients**





#### **Overall mass transfer coefficients**





### **Preliminary design considerations**

- Liquid recycling is detrimental to driving force! (increase of top loading)
- There exists an optimum recycling rate (increasing rate gives increasing a, but also increasing α<sub>top</sub> and thus P<sub>CO2.eq</sub>)
- Ways to deal with this:
  - Accept lower removal, i.e. an estimated efficiency of 70-80% instead of 90% (based on H=40 m, 12% CO<sub>2</sub> in feed gas and measured k<sub>ov</sub> as function of loading for countercurrent column)
  - Dual loop system: two column sections with separate absorbent circuits. Leads to loss in loading (not yet quantified).





### Conclusions

- CO<sub>2</sub>-absorption using precipitating amino acids in a spray tower is technically feasible (~75% CO<sub>2</sub> removal)
- Existing tower designs (for desulphurisation) can be used
- Potential for large capital and energy savings
- Liquid recycling may be required to obtain sufficient interfacial area; possibly dual loop system improves performance



### To do

- More flux measurements at increased flowrates
- Equilibrium measurements at absorption temperature
- **Desorption experiments**





9<sup>th</sup> International CO<sub>2</sub> Capture Network

# Novel Absorbents for CO<sub>2</sub> Capture

### From Gas Stream

Copenhagen, Denmark 16 June, 2006

#### RITE

Research Institute of Innovative Technology for the Earth Kyoto, Japan (URL: http://www.rite.or.jp)



### 1. Outline of COCS project

### 2. Development of new absorbents

- 1) Ideas to find new absorbents
- 2) Fundamental research
- 3) Evaluation of new absorbents



- · COCS Project:( <u>Co</u>st-Saving  $CO_2$  <u>C</u>apture <u>System</u>)
  - Financial Support by METI
  - Collaboration with 3-Japanese Companies
- Target of COCS Project

CO<sub>2</sub> Separation by Chemical Absorption and Storage

- Reduce CO<sub>2</sub> Capture Cost by less than 1/2



### **Concepts of COCS Project**






1. Develop new absorbents and absorption system for lower-energy CO<sub>2</sub> capture

2. Evaluate new CO<sub>2</sub> capture system for steel plant
1) Utilization of low-grade waste heat
2) Removal of CO<sub>2</sub> from high CO<sub>2</sub> concentration discharged gas by bench plant study



	'04	'05	'06	ʻ07	ʻ08
- New absorbents					
- Utilization of waste heat					
- Bench plant study					







**Today's Contents** 

- 1. Outline of COCS project
- 2. Development of new absorbents
  - 1) Ideas to find new absorbents
  - 2) Fundamental research
  - 3) Evaluation of new absorbents



Desirable characteristics:

- Low energy use for CO<sub>2</sub> capture
- High absorption/desorption rate
- High capacity of CO<sub>2</sub> capture
- Low volatility and high stability



1. Low energy use for CO<sub>2</sub> capture

2. High absorption/desorption rate

(1) Secondary/Tertiary amine (2) Effect of steric hindrance





1. High capacity of CO<sub>2</sub> capture

2. Low volatility and high stability

(1) High density of amino group (2) Position and number of OH-







(First stage)	<ul> <li>Screening</li> <li>Vapor-liquid equilibrium</li> <li>Heat of absorption</li> </ul>
(Second stage)	<ul> <li>Corrosion</li> <li>Kinetics</li> <li>Volatility</li> <li>etc.</li> </ul>





Absorbent : 50 ml Absorption time : 60 min Photo. Screening apparatus with six glass reactors









CO<sub>2</sub> conc. in liquid phase:

TOC (Total Organic Carbon analyzer)

CO <sub>2</sub> / N <sub>2</sub> gas:	20/80 %	
Gas flow rate:	700 ml/min	
Absorbent :	700 ml	
Temperature :	40 - 120 °C	
Pressure :	0.1 - 1 MPa	





### **Heat of Absorption**



#### **Measurements:**

- Differential reaction calorimeter
- ≻Semi-batch process
- ≻250ml reactor





Thermo couple Heater CO<sub>2</sub> inlet Reactor

#### (SETARAM DRC)







**Theoretical study:** 

Analysis of reaction energy of the following reaction as heat of absorption

Amine +  $CO_2$  +  $H_2O \rightarrow Protonated Cation + HCO_3^-$ 

Semi-empirical molecular orbital model, PM3 (Spartan '04 for Windows)

Solvation energy Cramer/Truhlar SM5.4 model













(Extensive research for absorbent evaluation)

- Estimation of CO<sub>2</sub> capture energy

## **Estimation of CO<sub>2</sub> Capture Energy**



### CO<sub>2</sub> capture energy:

$$Q = Q_R + Q_H + Q_V$$

#### Heat consumption in stripper:

(1) Reaction heat of stripping CO<sub>2</sub>

$$Q_R = fl(m_{top}, m_{bottom}, H_R)$$

(2) Sensible heat of absorbent

$$Q_H = W_S \cdot Cp \left( T_{top} - T_{bottom} \right)$$

(3) Latent heat of vapor at stripper top

$$Q_V = f2(W_{H2O}, H_{H2O}, T_{top})$$









Absorbent	Solvent A	<b>MEA30%</b>
Heat of absorption	84	91
H <sub>R</sub> [kJ/mol-CO <sub>2</sub> ]		
CO <sub>2</sub> loading at absorber bottom	0.64	0.50
m <sub>0</sub> [mol <sub>-CO2</sub> /mol <sub>-absorbent</sub> ]		
Total gas pressure in stripper	186	186
P <sub>t</sub> [kPa]		
Temp. at stripper top	90	90
T <sub>top</sub> [°C]		
Temp. at stripper bottom	110	120
T <sub>bottom</sub> [°C]		







#### Bench-scale plant facility with mixed gas (KEPCO)

	Diameter (m)	Height (m)
Absorber:	0.1	2.3
Stripper:	0.1	1.8

#### **Experimental condition**

Gas volume	6.5 m³/h
L/G	3.0 L/m <sup>3</sup>

### CO<sub>2</sub> capture energy [MJ/kg<sub>-CO2</sub>]

	Solvent A	30% MEA
Experiment	3.0	4.0
Calculation	2.8	3.9



#### Results :

- 1) Definition of the target absorbent.
- 2) Development of the new absorbents with higher-performance than MEA.

### Future Work :

- Develop higher-performance absorbents.
- Utilize low-grade waste heat.
- Study on process research with bench plant facility.



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.

# Volatility of MEA and Piperazine

Department of Chemical Engineering The University of Texas at Austin Austin, Texas 78712 USA Marcus Hilliard, John M<sup>c</sup>Lees, Dr. Gary T. Rochelle June 16, 2006

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# Outline

Background
Method: Multi-component VLE

Analysis: FT-IR
Modeling: NRTL

Results: Amine Volatility and γ<sub>i</sub>

# Background

Why is Amine Volatility Important in CO<sub>2</sub> Capture?

What is the Motivation for Studying Amine Volatility in Blended Amine Systems?



# Solvent - CO<sub>2</sub> Capture

- 30 wt% MEA Mature technology
  - K<sub>2</sub>CO<sub>3</sub>/PZ
  - MEA/PZ
    - Increased in capacity and faster rates
- Hilliard (2005) Aspen Plus ENRTL Model
  - Motivation for Modeling
    - Capacity
    - Heat of Desorption
    - Complex MT with Chemical Reactions Speciation
    - Cost of Amine Make-up or Recovery Amine Volatility







**Experimental Apparatus Benchmark - DIPPR** 



**Experimental Apparatus Benchmark – MEA Study** 

# **Aspen Plus - NRTL Model**



- $c_{ion} \rightarrow 0$ : ENRTL reduces to NRTL
- Developed by Renon and Prausnitz (1968)

$$\begin{aligned} \frac{G^{E}}{RT} &= x_{1}x_{2} \left( \frac{\tau_{21}e^{-\alpha_{21}\tau_{21}}}{x_{1} + x_{2}e^{-\alpha_{21}\tau_{21}}} + \frac{\tau_{12}e^{-\alpha_{12}\tau_{12}}}{x_{2} + x_{1}e^{-\alpha_{12}\tau_{12}}} \right) & 1 = H_{2}O \\ 2 &= \text{Amine} \end{aligned}$$

$$\tau_{ij} &= A_{ij} + \frac{B_{ij}}{T} + C_{ij}\ln T + D_{ij}T \qquad \tau_{ii} = \tau_{jj} = 0 \end{aligned}$$

$$\ln \gamma_{2} &= x_{1}^{2} \left[ \tau_{12} \left( \frac{e^{-\alpha_{12}\tau_{12}}}{x_{2} + x_{1}e^{-\alpha_{12}\tau_{12}}} \right) + \frac{\tau_{21}e^{-\alpha_{21}\tau_{21}}}{\left(x_{1} + x_{2}e^{-\alpha_{21}\tau_{21}}\right)^{2}} \right] \end{aligned}$$

## Aspen's Data Regression Package

- Maximum Likelihood Principle



- Determining the parameter values were carried out using an algorithm derived by Britt and Luecke (1973)
- Objective function based on the following assumptions:
  - Where all variables are adjusted and weighted by the standard deviation (i.e. experimental data are not error free)
  - Not Simple least squares regression.

$$Q = \sum_{i}^{N_i} \sum_{j}^{N_j} W_{U_j} \left( \frac{U_{j,adj} - U_{j,obs}}{\sigma_{U_j}} \right)^2$$

where the summation is over all of the measured variables,  $N_i$ , for all of the data points,  $N_i$ .
# Absolute Average Relative Deviation for the H<sub>2</sub>O-MEA-PZ systems

	•	$MEA/H_2O: 3$ parameters	No.	Name	Data type	# Papers	AARD (%)
010010		$A_{\mu O/MEA} = B_{\mu O/MEA}$	1	MEA/H <sub>2</sub> O	TPx	3	3.0
					Y <sub>MEA</sub>	4	6.4
	•	$A_{MEA/H_2O}$				This work	17.6*
		$PZ/H_2O: 4$ parameters			$Y_{H2O}$		10.6*
		$A_{H_2O/PZ}$ $B_{H_2O/PZ}$ $C_{H_2O/PZ}$			$\Delta T_{ m f}$	1	5.9
	•0000				$\Delta H_{mix}$	2	7.1
		$A_{_{PZ/H_2O}}$			C <sub>p</sub>	3	6.2
		$MEA/PZ/H_2O: 2$ parameters	2	PZ/H <sub>2</sub> O	$Y_{PZ}$	This work	23.0*
	10	2 I			Y <sub>H2O</sub>		5.4*
	0	A <sub>MEA/PZ</sub>			TPx	1	0.4
		A <sub>PZ / MEA</sub>	3	MEA/PZ/H <sub>2</sub> O	$\mathbf{Y}_{\mathrm{MEA}}$	This work	11.1*
	Г С				$Y_{PZ}$		13.0*
					$Y_{H2O}$		3.0*
	01	-1				010	10011
	0	1000011					

## **Measured multi-component VLE**

•MEA-H<sub>2</sub>O Study - 3.5, 7, 23.8 m MEA

•PZ-H<sub>2</sub>O Study - 0.9, 1.8, 2.5, 3.6, 5.0 m PZ

•MEA-PZ-H<sub>2</sub>O Study - 3.5, 7 m MEA + 1.8, 3.6 m PZ



#### Experimental Results for 7 m MEA + 3.6 m PZ Study

#### **Regressed Results for MEA/H<sub>2</sub>O**



#### **Excess Enthalpy (kJ/mol) for MEA at Infinite Dilution in Water**

$$\Delta H^{E} = R \frac{d \ln \gamma_{MEA}^{\infty}}{d1/T}$$

For a temperature range from 25 to 80 °C:

$\Delta H^{E}$	Source
-12.61	Touhara (1982)
-11.43	Kim et al. (1987)
-11.92 to -10.66	Austgen (1991)
-12.79 to -10.13	Posey (1996)
-14.28 to -14.28	This work





#### **Regressed Results for PZ/H<sub>2</sub>O Study**

#### **Excess Enthalpy (kJ/mol) for PZ at Infinite Dilution in Water**

$$\Delta H^{E} = \Delta H_{sol} = \left(\Delta H_{dis} - \Delta H_{fus}\right)$$
$$\Delta H^{E} = R \frac{d \ln \gamma_{PZ}^{\infty}}{d1/T}$$

For a temperature range from 25 to 80 °C:

$\Delta H^E$	Source
-44.1 to -38.5	$\Delta H_{dis}$ - $\Delta H_{fus}$
-55.54 to -39.25	Hilliard (2005)
-47.28 to -34.71	This work

# Conclusions

- Relative Volatility of MEA & PZ is ~ unity
- PZ activity coefficients are 567% lower than UNIFAC predictions
- Simultaneous regression may help improve Sequentially regressed parameters
- In 7 m MEA/3.6 m PZ at 40 °C
  - $-P_{PZ} = 2.676 Pa$
  - $-P_{MEA} = 7.708 Pa$
- ΔH<sup>E</sup> at Infinite Dilution from 25 to 80 °C
  - PZ: -14.28 kJ/mole
  - MEA: -47.28 to -34.71 kJ/mole
- Confident in this apparatus to generate new VLE data

# Thank you for your attention.

**Any questions?** 

## Rate Modeling of Stripper Performance

By

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9<sup>th</sup> International Post Combustion CO<sub>2</sub> Capture Network Meeting Copenhagen, Denmark June 16, 2006.

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# Outline

- Introduction
- Scope of work
- Rate Modeling
  - Mass transfer mechanisms
  - Aspen Custom Modeler Model Description
- Results
- Conclusions

# Typical Absorber/Stripper Configuration





#### Modeling approaches

- Equilibrium Stage Model (Oyenekan & Rochelle, 2006)
- Mass transfer with reaction in boundary layer and liquid diffusion (This work)
- Mass transfer with equilibrium reactions Weiland et al. (1982), Freguia & Rochelle (2002), Tobiesen et al. (2005)

#### Mass transfer with reaction in boundary layer and liquid diffusion (CO<sub>2</sub> in amines, K<sub>2</sub>CO<sub>3</sub>,PZ/K<sub>2</sub>CO<sub>3</sub>)



# Mass transfer with equilibrium reactions (Stripper conditions $- CO_2$ in amines ??)





Hydraulics –  $k_la,k_ga,a = f(internals,L,G,\rho,\mu,\sigma)$ ( $k_la,k_ga$  - ONDA (1968); a – SRP tests Overall mass transfer coefficient, K<sub>G</sub> Combined reaction

$$\frac{1}{\mathrm{K}_{\mathrm{G}}} = \frac{1}{\mathrm{k}_{\mathrm{g}}} + \frac{\mathrm{H}_{\mathrm{CO2}}}{\sqrt{\mathrm{k}_{2}[\mathrm{Am}]_{\mathrm{i}}\mathrm{D}_{\mathrm{CO2}}}} + \frac{1}{\mathrm{k}_{1},_{\mathrm{prod}}} \left(\frac{\Delta \mathrm{P}_{\mathrm{CO2}}}{\Delta [\mathrm{CO}_{2}]_{\mathrm{T}}}\right)^{\mathrm{T}}$$

#### Equilibrium reaction

$$\frac{1}{K_{G}} = \frac{1}{k_{g}} + \frac{1}{k_{1,\text{prod}}} \left( \frac{\Delta P_{\text{CO2}}}{\Delta [\text{CO}_{2}]_{\text{T}}} \right)^{*}$$

# Rate Model for k<sub>g</sub>'

Rigorous rate model (Bishnoi,2000) based on eddy diffusivity theory.

Model integrates the series of differential equations

- Thermodynamics in bulk liquid
- Diffusion across liquid film
- Reaction in the boundary layer

Non-linear regression (Cullinane,2005)

- Rate constants
- Diffusion coefficients

#### Aspen Custom Modeler (ACM) Model Features

- 10 segments, IMTP #40,equilibrium reboiler
  Rigorous thermo (E-NRTL, Chen et al. 1986) VLE (regressed from Cullinane,2005)
- Mass transfer with combined reaction (approx.)
- Account for flash and reboiler mass transfer
- Well mixed L & V phases
- Negligible vaporization of solvent
- Reaction takes place in the liquid phase
- Accounts for unequal flux of  $CO_2$  and  $H_2O$

Performance of Strippers Concept of Equivalent Work (W<sub>eq</sub>) Why W<sub>eq</sub> ?

Compare stripper configurations on same basis.
Compare Q and W.

$$= 0.75 \, \text{Q}_{\text{reb}} \left[ \frac{(\text{T}_{\text{reb}} + 10) - 313}{(\text{T}_{\text{reb}} + 10)} \right] + \text{W}_{\text{comp}} + \text{W}_{\text{pump}}$$

75% Adiabatic Efficiency in Compressor Wcomp to 1000 kPa 65% Efficiency in Pumps

#### Conditions

- 5m K<sup>+</sup>/2.5m PZ
- L = 30 gpm
- Loading (mol  $CO_2$ /mol TAlk) Rich = 0.560, Lean = 0.467
- 80% flood

#### "Short & Fat" vs "Tall & Skinny" Column (Fixed volume of packing = 0.858 m<sup>3</sup>)

Reboiler P	% flood	D	Н	Q <sub>reb</sub>	W <sub>comp</sub>	Total W <sub>eq</sub>
kPa		m		kJ/mol		
	80	0.33	9.8	190	18	33.7
30	30	0.51	4.2	155	15	30.9
	80	0.20	26.8	138	7.6	35.3
160	30	0.33	10.2	128	7	33.3

#### McCabe-Thiele Plot for Vacuum Stripper



#### McCabe-Thiele Plot for Simple Stripper



# Mass Transfer Mechanisms In Simple Stripper

Mole fraction units (x 10 <sup>5</sup> ) kmol/m <sup>2</sup> -s	P =	30 kPa	P = 160 kPa		
	Rich End	Lean End	Rich End	Lean End	
k <sub>y</sub> '	1.5	3.7	22.8	37.7	
K <sub>y</sub>	1.5	3.5	19.8	28.0	
Gas res.(%)	2	3	14	25	
Kinetic res.(%)	89	60	17	25	
Diffusion res.(%)	9	37	69	50	

#### Conclusions

- Stripper operation is liquid film controlled.
- The stripper operation is kinetics controlled at 30 kPa and diffusion controlled at 160 kPa.
- For vacuum operations, a 'short and fat' stripper may be more attractive than a 'tall and skinny' one. The ΔP is also less with a 'short and fat' stripper.
- A vacuum (30 kPa) stripper requires less W<sub>eq</sub> (~7%) when run at the same % flood than a simple (160 kPa) one.

#### **Energy Requirement for Solvent Regeneration in CO<sub>2</sub> Capture Plants**

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Presented at the 9<sup>th</sup> International CO<sub>2</sub> Capture Network, Copenhagen. June 16, 2006





Introduction/ motivation
Research Objective
Methodology
Results & Discussion
Conclusions
Acknowledgement



# **Amine Treating Plant for CO<sub>2</sub> Capture**



<text>

## **Utility & Energy Consumption**



Steam consumption: • 4,000-5,000 kJ/kg CO<sub>2</sub>

Steam cost:

• 70-80% of operating cost

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



## **Solvent Regeneration**



#### Energy utilization: (Steam)

- Heat of reaction (CO<sub>2</sub> Amine)
- Heat capacity (increase in Temp.)
- Heat of water vaporization

#### **Cost reduction:**

- Energy-efficient solvents
- Process modifications

#### **Research Objectives**

- To evaluate reboiler heat duty of different solvent types under different operating conditions
- To correlate relationships between process parameters and reboiler heat-duty
- □ To establish a strategy for process cost reduction



## **Experiments (Flow-Through Gas Stripping System)**







# **Experiments**

Single Alkanolamine	<ul> <li>MEA (Monoethanolmine)</li> <li>DEA (Diethanolamine)</li> <li>MDEA (Methyldiethanolamine)</li> </ul>
Blended Alkanolamine	<ul> <li>MEA-MDEA</li> <li>DEA-MDEA</li> </ul>
Mixing Ratio	□ 1 : 2
(mol : mol)	□ 1 : 1
Rich CO <sub>2</sub> Loading	□ 0.3 mol/mol
	□ 0.5 mol/mol
Solvent Concentration	$\Box$ 4.0 kmol/m <sup>3</sup>
	$\Box$ 5.0 kmol/m <sup>3</sup>
IVERSITY OF	$\Box$ 7.0 kmol/m <sup>3</sup>


# **Experimental Validation**

	lean CO <sub>2</sub> loading (mol/mol)		
Reboiler heat-duty (kJ/kg CO <sub>2</sub> )			
	literature <sup>a</sup> (1-4 tonnes/day units)	this study	
3,800	0.28 - 0.35	0.30 (at 3,767 kJ/kg CO <sub>2</sub> )	
4,800	0.23 – 0.29	0.25 (at 4,849 kJ/kg CO <sub>2</sub> )	
5,400	0.20 - 0.24	0.23 (at 5,203 kJ/kg CO <sub>2</sub> )	

<sup>a</sup> Estimated values from the work by Wilson et al. (2004)



### Methodology (Energy model simulation)

- Process flow model
- Design & property sub-models





# **Mechanistic Model**

#### (Mass-transfer & Hydrodynamics)



### **Effect of Lean-CO<sub>2</sub> Loading**



REGINA

Rich Loading: 0.5 mol CO<sub>2</sub> / mol DEA, Concentration: 4 kmol/m<sup>3</sup>

# Effect of Lean-CO<sub>2</sub> Loading (con't)

#### **Unfavorable Region**

#### **Favorable Region**





# **Simulation Results**





# Simulation Results (Effect of Reboiler Temp.)





# Simulation Results (Effect of Regen Feed Temp.)





### **Effect of Rich-CO<sub>2</sub> Loading**



0.3 mol/mol Rich CO<sub>2</sub> Loading > 0.5 mol/mol Rich CO<sub>2</sub> Loading REGINA Solution: MEA, Concentration: 5 kmol/m<sup>3</sup>

# Effect of Rich-CO<sub>2</sub> Loading (con't)





### **Effect of Solvent Concentration**





Solution: MEA, Rich Loading: 0.5 mol CO<sub>2</sub> / mol solution

# Effect of Solvent Concentration (con't)



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



Solution: MEA, Rich Loading: 0.5 mol CO<sub>2</sub> / mol solution

# **Effect of Single Alkanolamine**



### MEA > DEA > MDEA



Rich Loading: 0.5 mol CO<sub>2</sub> / mol solution, Concentration: 4 kmol/m<sup>3</sup>

# **Effect of Blended Alkanolamine**



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



Rich Loading: 0.5 mol CO<sub>2</sub> / mol solution, Concentration: 4 kmol/m<sup>3</sup>

# Effect of Blended Alkanolamines (con't)





# Effect of Blended Alkanolamines (con't)



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



Rich Loading: 0.5 mol  $CO_2$  / mol solution, Concentration: 4 kmol/m<sup>3</sup>

# Effect of Blended Alkanolamines (con't)





# Conclusions

Reduction in reboiler heat-duty can be achieved by operating the plants at:

- High rich-CO<sub>2</sub> loading
- Favorable range of lean-CO<sub>2</sub> loading
- Low reboiler temperature
- High lean-regen. feed temperature
- Blended MDEA-based solvents

Reduce excess water vapor at the regenerator top Approach heat of reaction



# **Split-Flow Configuration**

#### Scheme feature:

- Division of rich-solution from the absorber into two streams.
- Reduce the associated latent heat required during solvent regeneration.



# McCabe-Thiele Diagram (Typical Process)





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REGINA



### **Process Simulation**

### Simulation conditions:

Column **Packed type** 1,000 tonne CO<sub>2</sub>/day Process capacity **CO<sub>2</sub> capture efficiency** 95% Absorption solvent **Aqueous MEA solution** Solvent concentration **5.0 kmol/m<sup>3</sup>** 0.50 mol CO<sub>2</sub>/mol MEA □ CO<sub>2</sub> content before regen. 0.17-0.22 mol CO<sub>2</sub>/mol MEA □ CO<sub>2</sub> content after regen. up to 120°C Reboiler temperature



# Simulation Results (Case I)

#### **Result representation:**

**Split-flow:** 

- Dimension of absorption column
- Height of regeneration column
- Reboiler heat duty (energy input)

#### **Case I:** Reboiler temp. = 110°C, CO<sub>2</sub> content after regen. = 0.17 mol/mol

53 - 62 % energy saving

Process	Specific absorber size	Specific NTU <sub>Regen</sub>	Reboiler heat duty (Btu/lb mol CO <sub>2</sub> )
Typical amine process	1.00	1.0	144,000 (7,600 kJ/kg)
Split-flow (Operation I-CI)	1.05	4.2	55,000 (2,900 kJ/kg)
Split-flow (Operation II-CI)	1.01	3.4	59,000 (3,100 kJ/kg)
Split-flow (Operation III-CI)	0.99	2.0	67,000 (3,500 kJ/kg)



### Simulation Results (Cases II & III)

#### **Case II:** Reboiler temp. = 110°C, CO<sub>2</sub> content after regen. = 0.22 mol/mol

Process	Specific absorber size	Specific NTU <sub>Regen</sub>	Reboiler heat duty (Btu/lb mol CO <sub>2</sub> )
Typical amine process	1.00	1.0	83,000 (4,400 kJ/kg)
Split-flow (Operation I-CII)	0.73	3.0	68,000 (3,600kJ/kg)
Split-flow (Operation II-CII)	1.09	2.0	69,000 (3,600 kJ/kg)

**Case III:** Reboiler temp. = 120°C, CO<sub>2</sub> content after regen. = 0.17 mol/mol

Process	Specific absorber size	Specific NTU <sub>Regen</sub>	Reboiler heat duty (Btu/lb mol CO <sub>2</sub> )
Typical amine process	1.00	1.0	78,000 (4,100 kJ/kg)
Split-flow (Operation I-CIII)	1.01	1.9	64,000 (3,400 kJ/kg)

18 % energy saving

Split-flow:



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9th International CO2 Capture Network – Agenda 16 June 2006 Offices of E2, Copenhagen, Denmark

# MAKING NEW POWER PLANTS 'CAPTURE READY'

Jon Gibbins Energy Technology for Sustainable Development Group Mechanical Engineering Department Imperial College London BCURA, DTI, IEA GHG, TSEC Programme - UKCCSC



**CHINA: EXAMPLE OF** POTENTIAL 'CARBON LOCK-IN'

Guo Yuan and Zhou Dadi, Low emission options in China's electric power generation sector, ZETS Conference, Brisbane, Feb 2004.

UK: EXAMPLE OF POTENTIAL 'CARBON LOCK-IN' AND 'GAS LOCK-IN'

Lowest cost generation as a function of gas and carbon prices

Coal price: £1.4/GJ 25 year plant life, 10% IRR





# THE GLENEAGLES COMMUNIQUÉ

14. We will work to accelerate the development and commercialization of Carbon Capture and Storage technology by:

(a) endorsing the objectives and activities of the Carbon Sequestration Leadership Forum (CSLF), and encouraging the Forum to work with broader civil society and to address the barriers to the public acceptability of CCS technology;

(b) inviting the IEA to work with the CSLF to hold a workshop on short-term opportunities for CCS in the fossil fuel sector, including from Enhanced Oil Recovery and  $CO_2$  removal from natural gas production;

(c) inviting the IEA to work with the CSLF to study definitions, costs, and scope for 'capture ready' plant and consider economic incentives; (E.ON, Mitsui Babcock, Imperial IEA GHG project)

(d) collaborating with key developing countries to research options for geological  $CO_2$  storage; and

(e) working with industry and with national and international research programmes and partnerships to explore the potential of CCS technologies, including with developing countries.

### UK PARLIAMENT SCIENCE & TECHNOLOGY SELECT COMMITTEE, 2006

"We recommend that Government makes capture readiness a requirement for statutory licensing of all new fossil fuel plant. This would compel the developer to demonstrate that <u>consideration has</u> <u>been given in the planning and design of the plant</u> <u>to facilitating subsequent addition of suitable</u> <u>carbon dioxide capture technology</u>, as and when it becomes available and economic." GENERAL PRINCIPLES FOR CAPTURE READY Easy requirements:

a) Space on site and in critical access locations to build CO<sub>2</sub> capture plant and make connections.

**b)** Design study for adding CO<sub>2</sub> capture.

### **Challenging requirements:**

c) Optional pre-investments to reduce future costs, improve performance etc.

- Extra/modified equipment
- Plant siting to reduce storage costs
- Choice of base plant



Statoil/Shell 860 MW gas fired power plant, Draugen, Norway





### HOW MUCH MONEY IS IT WORTH SPENDING NOW TO SAVE MONEY WHEN CAPTURE IS ADDED?



When uncertainty is taken into account future cost savings of 2:1 - 10:1 required i.e. Capital cost can be 2-10 times as much, if it is not incurred until capture is fitted

### **IDEAL CAPTURE READY FOSSIL FUEL PLANT**

1. Prior to capture: no additional expenditure, no performance penalties vs. industry standard plant.

2. After capture added: no additional expenditure, no performance penalties vs. industry standard plant.

3. Sited with access to viable CO<sub>2</sub> storage.

### **NO CHOICE FOR BASE PLANT:**

- Gasifier-based polygeneration plants e.g. electricity + hydrogen, liquid fuels
- Natural gas combined cycle plant (NGCC) can be capture ready and gasifier ready

### CHOICE FOR BASE PLANT:

Coal power plants
IGCC

higher cost & risk without capture, some cost penalty to be capture ready industry standard with capture

#### **Supercritical PC** industry standard without capture minimal cost to be capture ready higher capture cost & risk

#### COMPARISON OF ELECTRICITY COSTS FOR POWER PLANTS BUILT WITH CAPTURE IEA GHG 2006-8


Plant type (net electrical output approx		Supercrit		Supercrit	New
800MW)		Coal	precom	postcom	precom
Total plant cost	£/kW	880	1258	. 317	700
· · · ·	£/kW			1408	
Efficiency (LHV)	% LHV	44.0%	33.5%	35.5%	42.0%
% CO2 captured		0%	85%	85%	85%
Fuel cost (LHV)	£/GJ	1.4	1.4	1.4	1.4
Operating hours	hrs/yr	8000	8000	8000	8000
Discount rate	%	10%	10%	10%	10%
Plant life	years	25	25	15	25
CO2 storage cost (part of 10MtCO2/yr					
aquifer/gas field storage system)	£/tonne CO2	5.5	5.5	5.5	5.5
EU ETS CO2 Emission Allowance cost	£/tonne CO2	25	25	25	25
Cost of electricity					
Capital	p/kWh	1.21	1.73	0.52	0.96
Operating expenditure	p/kWh	0.38	0.44	0.56	0.44
Fuel	p/kWh	1.15	1.50	1.42	1.20
CO2 storage costs	p/kWh	0.00	0.45	0.43	0.36
Emission allowance costs	p/kWh	1.85	0.36	0.34	0.29
Cost of electricity inc. EU ETS	p/kWh	4.58	4.49	3.27	3.25
Marginal cost of generation	p/kWh	3.18	2.54	2.47	2.07

#### **CAPTURE READY REQUIREMENTS**

- Post-combustion ready (PC and NGCC) space for absorber (plus FGD if needed) suitable IP/LP crossover steam pressure allow for rapid technology changes
- Gasifier ready NGCC gas turbine for H<sub>2</sub> space on site? or pipeline to remote site
- Capture ready IGCC layout and space but cannot integrate before <u>and</u> after capture, unless other uses for gas, steam, etc.
- Oxyfuel PC space for ASU duct access, air heater & fan capacity

### **CONCLUSIONS AND ISSUES**

• Capture ready not a substitute for capture.

#### **Proposed** full-scale (~300 MWe and above) CCS projects

(Based on media reports, press releases and personal communication so indicative only!)

Company/ Project Name	Fuel	Plant output/cost	Capture technology	Start
Progressive Energy, Teeside, UK	Coal (petcoke)	800 MW (+ H2 to grid) (\$1.5bn)	IGCC + shift + precombustion	2009
BP/SSE DF1, Peterhead/Miller, Scotland	Natural gas	350 MW, (\$600M)	Autothermal reformer + precombustion	2010
Powerfuel/Kuzbassrazrezugol Hatfield Colliery, UK	Coal	~900 MW	IGCC + shift + precombustion	2010
BP DF2, Carson, USA	Petcoke	500 MW, (\$1bn)	IGCC + shift + precombustion	2011
Statoil/Shell, Draugen, Norway	Natural gas	860 MW	NGCC+ Post-combustion amine	2011
SaskPower, Saskatchewan Canada	Lignite coal	300 MW	PC+ Post-combustion or oxyfuel (to be determined Q3 2006)	2011
E.ON, Killingholme, Lincolnshire coast, UK	Coal (+petcoke?)	450 MW (£1bn)	IGCC + shift + precombustion? (may be capture ready)	2011
Stanwell, Queensland, Australia	Coal	275 MW	IGCC + shift + precombustion	2012
Futuregen, USA	Coal	275 MW	IGCC + shift + precombustion	2012
RWE, Germany Germany	Coal	450 MW (€1bn)	IGCC + shift + precombustion	2014
RWE, Tilbury, UK	Coal	~500 MW (£800m)	PC (supercritical retrofit) + post- combustion (may be capture ready)	2016

## **CONCLUSIONS AND ISSUES**

- Capture ready not a substitute for capture.
- Flexible approach needed for capture ready.
- Show-stoppers must be avoided: space, access to storage or H<sub>2</sub> supply; but significant expenditure not justified.
- Often no choice in base plant, or capture method but technology changing rapidly.
- Choice between IGCC and PC as capture ready; depends on technical developments.
- Choice between pre- and post-com for NGCC; depends on future gas and coal prices.
- 'Plan capture ready, build capture' also an option.

#### **APPENDIX**

#### CAPTURE READY IGCC PLANT FOR THE PURPOSES OF US GOVERNMENT SUPPORT:

"Qualifying IGCC projects must use coal, petroleum coke, or biomass for at least 65% of annual heat input, produce electricity for 65% of their useful output, <u>have a</u> <u>design determined by the Secretary to be capable of</u> <u>accommodating equipment for capturing carbon dioxide</u>, have an assured revenue stream to cover capital and operating costs approved by the Secretary and relevant PUC, and commence construction within 3 years of receiving a guarantee commitment." (EPACT, 2005)

	Baseline CVX	Operating CVX IGCC Plant	Pre-investment CVX IGCC	Pre-investment CVX IGCC
		Retrofitted for	Plant	Plant Retrofitted
	IGCC Plant	CO <sub>2</sub> Capture		for CO <sub>2</sub> Capture
	Dural Tasia	Derated 90%	Oversized Dual	0.00% Comburg
<b></b>	Dual Train	Capture	Irain	90% Capture
Performance				
Coal Flow, lb/hr	370,663	370,663	370,663	390,950
Total Oxygen Flow, lb/hr	375,574	375,574	375,574	393,747
Gas Turbine Power, kW	394,000	374,480	394,000	394,000
Expander Power, kW	13,950	11,090	13,950	11,600
Steam Power, kW	206,950	191,260	206,950	201,870
Total, kW	614,900	576,830	614,900	607,470
Total Auxiliaries, kW	105,620	152,000	105,620	158,620
Net Power, kW	509,280	424,830	509,280	448,850
HHV hast fficiency, %HHV	35.4	29.5	35.4	29.5
Heat Rate, Btu/kWh HHV	9,653	11,569	9,653	11,550
CO <sub>2</sub> Captured, lb/hr	N/A	839,372	N/A	885,381
Cost				
Total Plant Cost, 1,000 \$	\$589,896	\$678,196	\$619,600	\$682,953
Total Plant Cost, \$/kW	\$1,158	\$1,596	\$1,217	\$1,522
Delta Cost of Retrofit, 1,000 \$		\$88,300		\$63,353
Fixed Operating	\$10,806	\$11,560	\$11,055	\$11,586
Variable Operating	\$13,837	\$14,878	\$14,547	\$15,173
Fuel @\$1.35/MMBtu)	\$51,157	\$51,144	\$51,157	\$53,947
COE, \$/Mwh <sup>a)</sup>	\$45.74	\$59.32	\$47.09	\$57.23
COE based on TPC plus owners costs annualized at a rate of 15% and a 90% capacity factor				
+5% capital for $+5%$ capital for				
capture ready capture un- ready				

#### **Parsons Corporation Capture Ready IGCC**

Rutkowski, M., Schoff, R., Holt, N. and Booras, G., 2003, *Pre-Investment of IGCC for CO*<sub>2</sub> *Capture with the Potential for Hydrogen Co-Production*, Gasification Technologies 2003, San Francisco, CA, October 12-15, 2003. (http://www.gasification.org/Docs/2003\_Papers/29RUTK\_paper.pdf)

after capture

before capture

#### **PRE-COMBUSTION CAPTURE READY**

Problem for IGCC, if gas turbine is matched to gasifier and oxygen plant before shift and capture is added.

Possible alternative for IGCC – have shift from the start and recover the losses Gasification Heat Recovery (with Shift)



## Jacobs Engineering Capture Ready IGCC

	<b>_</b>	1		
	1A	1B	2A	2B
Coal Feed rate AR (t/h)	160	172	173	168
Steam Turbine (MW)	246.9	241.3	254.6	233.4
Gas turbine (single) (MW)	197.0	194.4	197.0	197.0
Power Output (nett) (MW)	559	489	576	472
Efficiency (%) LHV basis	42.2	34.3	40.3	34.0
Heat Rate (HHV) (Btu/kWh)	8384	10296	8777	10395
Capex \$MM	650.8	739.5	672.9	728.1
Capex \$/kW	1164	1511	1169	1542
5% extra fuel for capture ready IGCC	+2% capital for capture ready plant compared to plant built with capture			

Griffiths, J. and Scott, S., 2003, *Evaluation of Options for Adding CO<sub>2</sub> Capture to ChevronTexaco IGCC*, Gasification Technologies 2003, San Francisco, CA, October 12-15, 2003. http://www.gasification.org/Docs/2003\_Papers/28GRIF.pdf)

#### COMPARISON OF ELECTRICITY COSTS FOR POWER PLANTS BUILT WITH CAPTURE IEA GHG 2006-8

- USCPC industry standard without capture best efficiency, lowest capital cost
- IGCC without capture higher capital cost, availability issues
- USCPC with capture higher capital and operating costs
- IGCC with capture lowest capital and operating costs, lower efficiency (for lowest COE)
- USCPC with capture no experience
- IGCC with capture some chemical plant experience



#### PCC Ltd

### RIO TINTO





Louis Wibberley Principal Technologist CSIRO Energy Technology



# **Presentation outline**

- What's changed since Austin Oct 2005
- Australian context
  - different flue gases, water issues, brown coals
- Why PCC?
  - initially rejected in Australia in favour of IGCC and oxy-pf
- CSIRO's National PCC R&D Program
  - led to a proposal to Government and Industry for a National Demonstration Program
- PCC Ltd and the demonstration program
  - formed to enable large scale demonstration of PCC and storage, with the assistance of LETDF
  - combines the National R&D activities
- Current status

# Changes since Austin 10/2005

- CSIRO now has an established a PCC laboratory and pilot plant, with a number of research programs
  - joined University of Texas IRA
  - research programs established with RITE/MHI and University of Newcastle (others under development)
- CSIRO's proposal for a National PCC and storage RD&D program has been endorsed by industry, with PCC Ltd established as the entity to progress the National RD&D program
  - currently consists of Rio Tinto (lead organisation), Australian Coal Association and CSIRO, with other industry participants expected
  - developing consolidated program, including engineering for the demonstration phase
- Also several other projects involving PCC for gas and brown coal-based generation
  - PCC R&D is not the primary focus

# Why PCC?

- PCC concept now fully endorsed by Australian Utilities and State/Federal Governments mostly due to:
  - potential retrofit to existing plants (near ZETS)
  - can be integrated into new SCPF plants (near ZETS)
- Generators like high adaptability and resilience
  - partial retrofit, zero to full operation (market matching)
    - Australia has an increasing peak demand
    - provides a discretionary load
  - ability to use solar thermal energy
  - unique options for application to Victorian brown coal generation
- Low technology and commercial risk (vs IGCC and oxy-pf)
  - cost of electricity is broadly comparable with other LET options
  - reduced multiplier effect
- Cooling water and storage uncertainties are significant issues
- Strategic importance to developing nations with emerging large pf capacity, and for Australia's contribution to AP6

## CSIRO – National PCC Program Concept

- Five concurrent phases
  - semi-commercial scale facility (50,000 tpa) at host site
  - geo-sequestration demonstration into coal & adjacent strata (based on existing CSIRO studies)
  - pilot plant research and development
  - applied laboratory research and test capability for sorbent and membrane development, and energy integration (CSIRO, CO2CRC, CCSD, LigniteCRC)
  - international collaboration (AP6, CASTOR, MHI & RITE, Uni Texas, IEA, IPHE, CSLF)
- Managed by an industry-led consortium over 7 years (LETDF funding)
  - commencing in 2007
  - R&D supporting the demonstration, which will use best commercial technology

# PCC Ltd project overview

- PCC Ltd formed, led by Rio Tinto
- PCC demonstration at an Australian coal fired power station
  - 50,000 tpa CO<sub>2</sub> capture
  - 10,000 tpa CO<sub>2</sub> storage
- Total project cost = A\$61M
- Based on best commercially available solvent technology at the proposed scale.
- CO<sub>2</sub> storage into deep un-mineable coal or other geological formations
- Concurrent (separately funded) R&D and pilot program
  - integrated approach between R&D, pilot and demonstration programs

# Development pathway for PCC



## Project development process – milestones

- Engagement with domestic coal and utility industry
  - technical scope to be broadened
  - consideration of international activities and domestic fit
  - integrated National PCC Program concept
- Technical Review Meeting convened (3-5-2006)
  - 20 organisations represented
  - Australian coal suppliers
  - Australian black coal utilities
  - Australian based researchers
  - International PCC experts/researchers
- Project development Action Plan developed
- Formation of an Industry Advisory Group
  - coal supplier representation
  - Qld/NSW utility representation

## Project development process – overview

- Three initial areas of work:
  - complete a state of the art review of PCC in the Australian context
  - develop industry drivers and success criteria for PCC
  - assess other carbon capture and storage activities for linkages and fit
- Outputs will be consolidated to form the basis of an integrated national plan for PCC that covers R&D, pilot scale and demonstration scale components
- EPC company to develop pre-feasibility study for demonstration activity
- Continued engagement with potential sponsors move from technical engagement to commercial engagement

## Project development process – status

- State of the Art Review underway
  - scope developed from output of Technical Review Meeting and Industry Advisory Group
  - work being undertaken jointly by CSIRO and CO2CRC with IAG review (completion by early July)
- Industry drivers and success criteria to be documented during June
- Assessment of other capture and storage activities to be completed by end of June
- AusIndustry assessment process has gone well so far timing remains the challenge
- R&D led by CSIRO is progressing

# Pilot plant and R&D – overall objectives

- To support the demonstration program
  - pilot plant, laboratory and technical support (new solvents towards end of program)
- Goal science and engineering to reduce the cost of capture by 50%
  - costs need to be lower than the value of the avoided emissions (or use of alternative generation technologies)
  - incremental and step improvements needed at all stages:
    - reducing the amount and value of the energy used for capture
    - reducing the need for separate deNOx and deSOx plant
    - reducing overall equipment cost
    - production of by-products (Australia is sulphur impoverished)
    - inherent high adaptability/flexibility should be maintained
    - benefiting from the synergies with renewables

 leverage from, and contribute to, international efforts in PCC (from all forms of capture and gas processing)

# Large improvement potential for the capture stage



PCC Ltd

# Iterative R&D methodology





# Research program next 5 years

- Developing novel amines (and RTILs and other solvents) using molecular science
  - regeneration with low energy use
  - high absorption/desorption rate and regeneration at low temperature
  - tolerant of NOx, SOx, oxygen and ash trace elements
  - low volatility and high stability
  - low corrosiveness and toxicity
- Developing novel systems for Generation IV capture
  - expected to include a range of liquid and solid systems (*eg* ionic liquids with polymer support networks)
- Scaling up research results, using the transportable pilot plant on real flue gases

# Summary

- PCC offers a resilient strategy for coal-fired generation
  - near zero emission for coal fired plant (both existing and new)
  - high operational flexibility
  - low technology risk
  - competitive cost
- Therefore, a high degree of buy-in by power industry on the technical way forward has been achieved
  - technical challenges (but we know how to address them)
  - major blockers are political, as well as the fragmented nature of power generation industry
- Success with PCC development and demonstration for pf power generation is necessary to ensure the role of coal in Australia's fuel energy mix

# **Dwarfing Sleipner!**

Large Scale CCS projects and other CO2CRC activities

**Barry Hooper** 

IEA Capture Test Network Copenhagen 16<sup>th</sup> June 2006





#### **Presentation Outline**

- Background to the Cooperative Research Centre for Greenhouse Gas Technologies – aka CO2CRC
- CO2CRC Capture Program
- Review of Large Scale CCS Project Development
  - Background to LVCSA
  - Earth Science Studies
  - Reservoir Modelling
  - Techno-Economics
  - Storage Risk Assessment
  - Infrastructure Risk Assessment
  - Conclusion









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Total budget approximately \$140 million



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#### PROGRAM 2: CAPTURING CO<sub>2</sub> PROGRAM MANAGER: Barry Hooper

- 2.1 Characterising Australian Emissions Project Leader: Luke Murray
- 2.2 Enhanced Solvent Based Systems Project Leader: Prof G Stevens, Melbourne University
- 2.3 Innovative Membrane Systems Project Leader: Dr S Kentish, Melbourne University
- 2.4 Innovative Pressure Swing Adsorption Systems Project Leader: Dr A Chaffee/Dr Paul Webley, Monash University
- 2.5 Hydrate Formation & Cryogenic Distillation Systems Project Leader: Prof R Amin, Curtin University of Technology
- **2.6 Capture of CO<sub>2</sub> in Brines and Minerals** *Project Leader: Dr G Sparrow, CSIRO Minerals*
- 2.7 Metal Activated Conversion of CO<sub>2</sub> Project Leader: A/Prof M Buntine, University of Adelaide
- 2.8 Economic Modelling of Capture & Storage Systems Project Leader: G Allinson, UNSW
- 2.9 LDH Membranes

Project Leader: J da Costa, U of Qld



CO2CRC Programs


### **GHGT 8 Presentations**

### Papers

- CO2CRC Capture Program
- CCS Economics
- GAM Membranes
- Adsorbents Research
- LVCSA Geoscience
- LVCSA Risk Assessment

### • Posters

- Capture Economics
- LVCSA Economics
- Solvent Packings
- VSA for CO2 Capture
- Novel Materials for ESA
- OBPP Pilot Plant Capture
- LDH Material
  Development





### LVCSA Background

#### • The Problem

- New brown coal developments in Latrobe Valley, Victoria
- CO<sub>2</sub> emissions up to 50 Million tonnes/year
- Potential Solution
  - Offshore Gippsland Basin
  - Existing oil and gas fields (once depleted)
  - Deeper saline formations
- Injection Scenarios
  - Injection at several sites along regional migration pathways, sequentially & simultaneously, ramping up volume to 50 Mt/y
  - 1. Kingfish Field: 15 Mt/y for 40 years ← This presentation
  - 2. Fortescue Field: 15 Mt/y for 40 years
  - 3. Basin centre & northern gas fields: 20 Mt/y for 40 years



### **Geological Storage of CO<sub>2</sub>**



#### What do we need?

- RESERVOIR ROCK porous, e.g. sandstone
- SEAL ROCK nonporous, e.g. claystone

#### How does it work?

- CO<sub>2</sub> injected into porous reservoir rock
- CO<sub>2</sub> held in place by overlying non-porous seal rock

### **Geological Storage of CO<sub>2</sub>**



No pore spaces 500 μm

Nyanda-1, 1951.80



#### SEM image of mudstone seal rock (1/2 mm scale)

### **Geological Storage of CO<sub>2</sub>**



#### **CO<sub>2</sub> storage sites:**

- Several kilometres below surface
- Similar locations to oil and natural gas



### **Conceptual CO<sub>2</sub> Storage Scenario**



NOTE: Supercritical  $CO_2$  less dense than water. Post-injection,  $CO_2$  will move upwards through reservoir rock until trapped by impermeable seal rock

Conventional Structural <u>Trap / Depleted Field</u> •Proven seal potential •Few opportunities in Australia at present; more expected in next 20 years •Relatively small volume opportunities at present; larger potential volumes in next 20 years





### **Conceptual CO<sub>2</sub> Storage Scenario**



# Amount of CO<sub>2</sub> geologically stored influenced by:

- Rate of CO<sub>2</sub> migration
- Style of multiphase flow
- Rate of CO<sub>2</sub> dissolution
- Rate of chemical reaction with minerals

#### **Controlled by many variables, including:**

- Reservoir and seal structure
- Stratigraphic architecture
- Reservoir heterogeneity
- Faults/fractures
- Pressure/temperature conditions
- Hydrodynamics and chemistry of in situ formation fluids

(CO<sub>2</sub> concept models courtesy of Robert Root) UNSW







### **Site Characterisation Workflow**





### **Gippsland Basin, Southeast Australia**





### **Selected Site Scenarios**





### **Detailed Characterisation: Kingfish Field**

#### Location map of Gippsland Basin

Stratigraphic column



#### (after Bernecker & Partridge, 2001)



(modified after Power et al., 2001)

### **Sequence Stratigraphy**





### **Containment: Geomechanics**



#### Seismicallyresolvable faults

- 3 cut the top Latrobe unconf.
- 7 terminate within Latrobe Gp
- Most have moderate to high fault reactivation potential
- However, most not in immediate migration pathway



### **Containment: Hydrodynamics**





### **Numerical Flow Simulation**







- 15 Mt/y for 40 years
- Post-injection small shales 0–40 yrs



- 15 Mt/y for 40 years
- Post-injection small shales 40–400 yrs



#### **Simulation results:**

- Injection rate achievable – lower permeability or extensive shale barriers require more wells
- Migration time to the oil-bearing zone is 40–200 years for deep injection – less for shallow injection, more for wider shale barriers
- Storage capacity sufficient with deep injection – more CO<sub>2</sub> trapped as residual gas

- 15 Mt/y for 40 years
- Post-injection small shales 400–1140 yrs

### **Geoscience Conclusions**

Suitability of Kingfish Field/Gippsland Basin as CO<sub>2</sub> storage site:

- Complex stratigraphic architecture which slows vertical migration and increases residual gas trapping
- Non-reactive reservoir units with high injectivity
- Geochemically-reactive, low permeability reservoir just below regional seal to provide additional mineral trapping
- Several depleted oil fields to provide storage capacity coupled with transient flow regime that enhances containment
- Long migration pathways beneath competent regional seal
- Kingfish Field, in conjunction with other sites (e.g. Fortescue, northern gas fields), indicate that Gippsland Basin has sufficient capacity to store very large volumes of CO<sub>2</sub>.



# **Latrobe Valley Storage Economics**





### **Base Cases**

Five cases are examined -

- A Constant 2 MMtpa for 5 years
- B1 Constant 15 MMtpa for 40 years
- B2 = B1 with onshore capacity for 50 MMtpa
- C1 Ramp up from 15 MMtpa to 50 MMtpa for 40 years
- C2 Constant 50 MMtpa for 40 years



### **Study Area & Storage Process**





### Assumptions

- Costs as at Q1 2005.
- Real discount rate = 7%
- Project Life = 40 yrs
- Spare compressor trains (cycled)
- Capture not modelled
- New platforms for A, B and C cases
- Permeability = 150 millidarcies
- Fortescue and Central Deep properties the same as Kingfish



### **Capital Cost of Base Cases**





### Real (2005) Storage Cost and CO2 Avoided





# **Sensitivity Analyses**





### Permeability





### **Horizontal Wells**





### **Sparing Philosophy & Shallow Injection**





### **Sensitivities**





### **Summary**

- Base case (40 year) storage cost A\$10–12/t CO2 avoided
- Storage cost highly sensitive to permeability
- Costs can be reduced by -
  - Using horizontal wells
  - Not installing spare compressors
  - Injecting in shallower, higher permeability layers



### **Storage Risk Assessment**





### GEODISC KPI 1 Reservoir performance

- The following risk events could potentially affect containment:
  - leakage via permeable zones in seal,
  - leakage via faults,
  - leakage via wells,
  - regional scale over-pressurisation,
  - local scale over-pressurisation,
  - exceeding spillpoint,
  - earthquake,
  - misidentification of migration direction,
  - well-head failure, pipeline failure, compressor failure, and platform failure.









SIRC







## **Infrastructure Risk**




#### Figure 2-1 The QRA Process



#### **Frequency Analysis**





#### **Consequence Analysis**

#### Downwind Dispersion Distances for Three Pasquil Atmospheric Stability Classes





#### **Plume Calculations**





#### **Risk Analysis**





#### **Infrastructure Risk Findings**

- Demonstrated infrastructure risk for major CCS installation
- Installation poses no greater risk than similar pipeline facilities currently in operation in Australia
- All risks are considered manageable with conventional pipeline safety and mitigation methods incorporated into the design
- Examined the sensitivity of several pipeline parameters
  - Pressure
  - Impurities



#### Conclusions

#### • The findings from the project indicate that:

- the existing oil and gas fields could store more than two billion tonnes of CO2 once depleted;
- the regional seal rock is of good quality to store CO2;
- the geology, chemistry and hydrology are favourable for CO2 storage;
- CO2 will migrate very slowly through the reservoir rock over tens to hundreds of years;
- the unit cost of storage is low by world standards;
- risks are low and can be readily managed by proponents; and
- the targeted offshore injection sites are favourable for geosequestration.



Thank you

#### I'd be pleased to take questions





# **Increased Interest in Environmental Impacts of Amines**

Gelein de Koeijer

9<sup>th</sup> IEA GHG International CO<sub>2</sub> Capture Network

Copenhagen, 16-6-2006



## Reasons for increased interest

- Norwegian pollution control authorities required Statoil to give an assessment on possible substitutes for MDEA at the Snøhvit CO<sub>2</sub> capture site<sup>1</sup>
- Statoil and Shell are assessing the possibilities for building a CO<sub>2</sub> capture plant at Tjeldbergodden (Norway)
- Statoil's aim to produce oil & gas with zero harmful emissions



## Emissions from CO<sub>2</sub> capture plants



## Classification chemicals offshore Norway

	Classification
Water	Green
Chemicals on PLONOR list	Green
Hormone disturbing chemicals	Black
List over prioritised chemicals that are contained in "resultatmål 1 (prioritetslisten) St.meld. nr 25 (2002-2003)"	Black
Biodegradibility < 20 % and log Pow $\geq$ 5	Black
Biodegradibility < 20 % and toxicity EC50 or LC50 $\leq$ 10 mg/l	Black
Two out of three categories: Biodegradability < 60 $\%$	Red
log Pow $\geq$ 3, IEC50 or LC50 $\leq$ 10 mg/l	
Inorganic and EC50 or LC50 $\leq$ 1 mg/l	Red
Biodegradability < 20 %	Red
Other chemicals	Yellow





#### Amine based absorbents: general behaviour

#### **Red:**

Most tertiary amines (e.g. MDEA) Some common activators (e.g. Piperazine, AEEA) Some foam and corrosion inhibitors

#### Yellow:

Most primary and secondary amines (e.g. MEA) Some sterically hindered amines (e.g. Flexsorb) Some foam and corrosion inhibitors



#### **Historic emissions**





Red chemicals, tonnes

Source:http://www.olf.no/miljo/miljorapporter/?27221.pdf

Black chemicals, tonnes



## Uncertainties

- Are the current classifications based on the latest results and correct test method?
- Are all aspects of bio-degradibility and eco-toxicity taken into account in the classification tests?
- Are all emissions fairly assessed?
- Are the classification tests valid for the specific site?

#### **Answer: Integrated HSE tools**



# Snøhvit LNG





## Assessing alternatives to MDEA

- Maximum loading of MDEA and alternative yellow amines
- Kinetics of MDEA and and alternative yellow amines
- Environmental tests of alternative yellow amines
- Test alternative yellow foam inhibitors



## Preliminary results: MDEA vs alternatives



**STATOIL** 

#### An industrial model for a CO<sub>2</sub> value chain in Norway







# Summary

- Knowledge on environmental aspects of CO<sub>2</sub> capture with amines is increasing at authorities
- Stricter requirements on environmental aspects for operators and suppliers
- Legislation is becoming clearer
- Statoil R&D will increase activity on environmental aspects of CO<sub>2</sub> capture with amines
- Integrated HSE tools are needed, and under development



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Source figure: SINTEF



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Translated from Miljørapport 2004 Oljeindustriens Landsforening, http://www.olf.no/miljo/miljorapporter/?27220.pdf



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CO<sub>2</sub> loading



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#### Overview of activities in CASTOR, ENCAP, CATO and Dynamis at TNO

**TNO | Knowledge for business** 



TNO Science & Industry Department of separation technology e-mail: <u>Nick.tenAsbroek</u> Internet: <u>www.tno.nl</u>

#### Overview

Post-combustion related activities:

- MGA Developments in CASTOR/CATO
- Post combustion CO<sub>2</sub> capture in EU-Dynamis
- Caprice
- Construction of hybrid-pilot in CATO

Chemical Looping Combustion related activities:

• Development of fixed bed CLC reactors in ENCAP and CATO



IEA - 9th International CO2 Capture Network - 16 June Copenhagen

#### **CASTOR** CO<sub>2</sub> CApture and STORage



Main activities

- CO<sub>2</sub>-storage, verification and monitoring (TNO NITG)
- Esbjerg pilot plant experimental program (TNO I&T)
- System modelling and economic optimalisation (TNO I&T)
- Development of MGA for absorption/desorption (TNO I&T)
  - Membrane selection (absorption/desorption)
  - MGA contactor development (absorption/desorption)
  - Basic design of absorption MGA installation



#### Principle CO<sub>2</sub> Membrane Gas Absorption



CO<sub>2</sub>, present in the flue gas, is selectively absorbed into a proprietary absorption liquid through a porous membrane

IEA - 9th International CO2 Capture Network - 16 June Copenhagen


# Advantages CO<sub>2</sub> MGA

- High selectivity
- Compact equipment
- Independent flow control
- No entrainment, flooding, channelling, foaming
- Not influenced by tilt
- Low liquid pumping power
- Flexibility in scale-up





### Future - Membrane Gas Absorption/Desorption



# MGA process development

- Breakthrough pressures of membranes with absorption liquids
- Liquid site mass transfer (with spacer)
  - Oxygen desorption tests →kL
- Membrane characterisation
  - $SO_2$  experiments  $\rightarrow$  km and kg





## Liquid-side mass transfer of membrane channel (kL) Oxygen-setup





### Liquid-side mass transfer of membrane channel (kL)





# Gas and membrane mass transfer resistance SO<sub>2</sub>-setup





# SO<sub>2</sub>-experiments

- Overall mass transfer coefficient
  - SO<sub>2</sub> reaction with KOH very rapid







 $1/\alpha g$ 



# Membrane desorption set-up at TNO







# Membrane desorption

- Membrane testing at various temperatures and pressures
- Membrane desorption process development





# Membrane absorption set-up at TNO





### Preliminary results of membrane absorption/desorption



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TT

### Membrane contactor development

#### Boundary conditions and choices for a membrane contactor

Module channel wide	1.0 meter		
Module channel length	3.0 meter		
Module total height	Approx. 1 meter		
Module gas channel height	2.0 mm (spacer filled)		
Module liquid channel height	1.0 mm (spacer filled)		
Number of gas channels	322		
Number of liquid channels	322		
Number of baffles liquid side	5 x (approach counter current)		
Gas speed	2.0 m/s		
Liquid speed	0.02 – 0.07 m/s		
Gas side pressure drop	3 – 4 kPa		
Liquid side pressure drop	20 - 60 kPa		
Membrane area per feed gas	Approx. 0.5 m <sup>2</sup> per m <sup>3</sup> /hour		
CO <sub>2</sub> capture ratio	90 %		
CO <sub>2</sub> content in flue gas	5 – 25 %		
Flue gas mass flow single channel	18 - 19 kg/h (at 2 m/s gas speed)		
Total module gas side mass flow	Around 6000 kg/h (at 2 m/s)		
Total module liquid side mass flow	15000 - 45000 kg/h (at 2 m/s) (depending on CO <sub>2</sub> inlet conc.)		
Weight module empty (approx.)	1400 kg (incl. heavy support mounting)		
Weight module filled (approx.)	2500 kg		



## Results CASTOR conventional absorber and MGA

Power plant		Gas fired combined cycle [393 MW <sub>e</sub> ] Conventional column	Gas fired combined cycle [393 MW <sub>e</sub> ] MGA	Bituminous coal fired power plant [600 MW <sub>e</sub> ] conventional column	Bituminous coal fired power plant [600 MW <sub>e</sub> ] conventional column
CO <sub>2</sub> product capacity	ton CO₂/hr	131	131	410	410
Equipment	Parameter				
Absorber column	Columns	2	1	2	1
	Dimension	Ф 10.7m x 29.5m	Ф 11.4m x 17.0m	Ф 10.9m x 28.1m	Ф 11.2m x 16.0m
	Packing	1605 m <sup>3</sup>	1.01 $E^6 m^2$	1448	9.31 $E^5 m^2$

Radial flow profile with flat sheet contactor

• Based on in-house measured data with Coral liquids

#### **Conclusions:**

• Significant lower footprint possible (drive for improved liquids)



### Large scale flat sheet modules by Keppel Seghers and TNO





# **DYNAMIS** Towards hydrogen production with CO<sub>2</sub> management



#### Program

- The EU HYPOGEN initiative for hydrogen economy
- Started march 2006
- To asses the options for full scale HYPOGEN Power Plant
- Full scale pilot to be build by industry post-2008
- Full production HYPOGEN Power Plant to go on stream by 2012

#### **Boundary conditions**

- Combined cycle power generation 400 MWe (approx. 700 MW)
- Hydrogen production 25-50 MW (flexible 0-100% hydrogen????)
- Hydrogen spec's according EU hydrogen infrastructure (2010)
- 90% CO<sub>2</sub> capture
- CO<sub>2</sub> capture cost of €25-30 per tonne CO<sub>2</sub>



### DYNAMIS

#### Post-combustion CO<sub>2</sub> capture options researched by TNO

Η,

Coal gasification with post-combustion CO2 capture split stream amine scrubbing of  $H_2$  producing WGS reactor



### CAPRICE

<u>C</u>O<sub>2</sub> capture using <u>A</u>mine <u>Processes</u>: <u>International Cooperation</u> and <u>E</u>xchange

- STREP currently under negotiation with EC
- Cooperation between CASTOR-partners and consortium around International Test Centre on CO<sub>2</sub> capture (University of Regina, Canada)
- Extending research efforts to other CSLF countries (China, Russia, Brasil)
- o Partnership
  - EU linked: <u>TNO</u>, NTNU, Stuttgart University, IFP, Elsam, E2, E.ON-UK, TIPS, Tsinghua University
  - Canada linked: <u>Energy Inet</u>, ITC, Un. of Regina, Alberta Research Council, Unifacs



### Caprice

#### Project activities:

- 1. Benchmarking and validation of amine processes
- 2. Membrane contactor validation studies
- 3. Development of tools for integration

#### Budget:

- Total 1.1 MEuro
- EC-contribution: 0.38 MEuro
- Equal effort by EU and CDN partnership

#### Key deliverables:

- Input to CSLF
- Action plan for further post-combustion R,D&D on global scale





### Construction of hybrid-pilot in CATO



Dutch post-combustion CO<sub>2</sub> capture pilot plant (250 kg/h)

- Budget around K€ 1000
- Start construction expected third quarter of 2006, finished second quarter 2007
- Location? (planned at a coal-fired power plant)
- First operation with conventional columns but with CORAL liquids
- Pilot to be upgraded with membrane contactors for SO<sub>2</sub> and CO<sub>2</sub> removal.



# Chemical Looping Combustion (CLC) in ENCAP and CATO



#### Important features of CLC

- Air and fuel are only contacted via an oxygen carrier (a metal/metal oxide, e.g. Ni/NiO, Fe/Fe<sub>2</sub>O<sub>3</sub>)
- No NOx formation (absence of flame)
- No dilution of  $CO_2$  with  $N_2 \rightarrow$  no energy penalty for separation





### Chemical Looping Combustion (CLC) in ENCAP and CATO

CLC has in theory high potential for Zero Emission Power Production:

- Theoretical high thermal efficiency
- Low CO<sub>2</sub> separation cost
- Fluidising Circulating Bed technology close to current standard

Current development status of CLC:

- Only applicable for gaseous/liquid fuels
- No integration with gas turbine
  - Risk of particle carry-over
  - Limited intermediate temperature stability
  - High particle cost (environmental concerns)

#### CLC is more expensive then post-combustion CO<sub>2</sub>capture



### Chemical Looping Combustion (CLC) in ENCAP and CATO

New developments on CLC:

• Integration of CLC-reactor with Combined Cycle Power Plant

Reactor concept for CLC:





### Chemical Looping Combustion (CLC) in ENCAP and CATO Fixed bed diffusive reactor





## Chemical Looping Combustion (CLC) in ENCAP and CATO Results of modelling work

# The formation of a reaction front in the packed bed around an active membrane based on diffusion



#### The temperature development at the exit of the diffusion reactor





### Chemical Looping Combustion (CLC) in ENCAP and CATO Future work on CLC

- Further development of fixed bed CLC reactors integrated with combined cycle power plant
- Development of new temperature stable intermediates
- Modelling of complete process
- Testing of pilot installation



# Conclusions

TNO focuses on CO<sub>2</sub> post-combustion capture!

- 1. Most developed CO<sub>2</sub> capture technology
- 2. High potential for further improvement
  - Development of improved liquids
  - Process integration and novel processes steps
  - Optimized and new contactors
  - Process modelling and economic optimisation

### Future development includes fixed bed CLC processes!









# **CO<sub>2</sub> Testing Program**

#### An Industry/EPRI Initiative to Develop CO<sub>2</sub> Capture and Storage Test Capabilities

Dick Rhudy

CO<sub>2</sub> Capture Network Meeting June 16, 2006

# **History of the CO<sub>2</sub> Testing Issue**

- Conceived of need for regional CO<sub>2</sub> Capture and Storage Test Centers as a necessary RD&D step
  - Several across country
  - Different power generation and storage depending on region
  - 10 MW (150 t CO<sub>2</sub>/d)
- Conducted engineering cost and site selection study on pulverized coal (PC) power plant systems
  - PC is the only type of generation available in near-term
  - 4 sites identified
  - High cost



# History of the CO<sub>2</sub> Testing Issue (cont.)

- Reviewed with EPRI BoD and Technical Review Committee
  - Identified need for better capture processes
- Decided to conduct study in two steps
  - 1-MW CO<sub>2</sub> capture pilot
  - 10-MW CO<sub>2</sub> capture and storage test facility
- Selected chilled ammonia process to test
- Alstom interest and collaboration
- Currently soliciting participation in 5-MW CO<sub>2</sub> capture pilot of chilled ammonia process

# **CO<sub>2</sub> Test Centers Current Plan**

A multi-phase testing program to develop costeffective and practical capture technologies

#### Phase 1

- 1-MW pilot plants
- Test solvent, solid and membrane capture technologies
- Test materials to be used for compression, transport and injection of flue-gas CO<sub>2</sub>

#### <u>Phase 2</u>

- 10-MW CO<sub>2</sub> Test Center (150 Tonnes/day)
- Capture and store CO<sub>2</sub> at substantial scale and real operating environments
- Future phases larger demos to scale-up to full plant

Determine the viability of combustion-based coal plants in a carbon constrained future

# **Project Schedule**

- Assembling funding in early 2006
- Start on engineering/ procurement in 2006
- Operation of pilot starting in 2007



# **First Capture Process to be Tested**

- Chilled ammonia
  - Under development by EPRI



# **Conventional Ammonia Scrubbing**

- Advantage
  - Potentially lower
     regeneration energy
- Challenges
  - -Ammonia volatility
  - -Poor kinetics in absorber



# Chilled Ammonia Process: Key Design Features

- Low temperature CO<sub>2</sub> Absorption--minimize NH3 emissions
  - Absorber operation at optimal temperature of 2-16C (35-60F)
- High concentration of Ammonium Carbonate/Ammonium Bicarbonate (AC/ABC)--improve CO<sub>2</sub> removal
  - High CO<sub>2</sub> loading per recycled slurry
- High pressure regeneration--saves energy



# **Chilled Ammonia Lab Tests**

- Phase 1 (2004)
  - Ammonia emission not an issue during absorption at 0-5C (32-40F)
  - High CO<sub>2</sub> absorption efficiency can be achieved in bubbler absorber
  - High pressure regeneration—at least
    20 Bar (300psi) is feasible



 – NH<sub>3</sub> and H<sub>2</sub>O concentration in regeneration gas stream is very low

# **Chilled Ammonia Lab Tests**

- Phase 2 (2005)
- Absorption
  - Measurements of absorption rates were completed
  - CO<sub>2</sub> removal in the 2" flow reactor was limited by mass transfer
  - A large scale absorber (1-2 ft) diameter needs to be built and tested to demonstrate high efficiency and high mass transfer rates


#### Chilled Ammonia Lab Tests (cont.)

- Phase 2 (2005)
- Regeneration
  - 800 psig was measured with regeneration simulation from ammonium bicarbonate
  - High pressure regeneration can be designed to regenerate ammonium carbonate at 125℃



# Chilled Ammonia Process Cost Prediction (Early Data Only)

Used Parsons Study for basis	Supercritical	Supercritical	Supercritical
	PC without	PC with	PC with NH <sub>3</sub>
	CO <sub>2</sub> Removal	$MEA CO_2$	CO <sub>2</sub> removal
		Removal	
Levelized cost of Power,	5.15	8.56	6.50
c/KWh			
% increase		66	26
Avoided Cost, \$/ton CO <sub>2</sub>	Base	51	20

Source: Nexant

### **Chilled Ammonia Process Performance Prediction (Early Data Only)**

Used Parsons Study for	Supercritical	Supercritical	Supercritical
Basis	PC	PC With	PC With
	Without CO <sub>2</sub>	MEA CO <sub>2</sub>	NH <sub>3</sub> CO <sub>2</sub>
	Removal	Removal	Removal
LP Steam extraction, lb/hr	0	1,220,000	270,000
Power Loss, KWe	0	90,000	20,000
<b>GROSS POWER, KWE</b>	491,000	402,000	471,300
AUXILIARY LOAD,			
KWE			
Induced Draft Fan	5,000	19,900	10,000
Pumping CO <sub>2</sub> system,	0	1,900	5,000
Chillers	0	0	8,900
CO <sub>2</sub> compressor	0	30,000	9,500
NET POWER OUTPUT	462,000	330,000	415,000
% POWER REDUCTION		29	10

Source: Nexant

### Chilled Ammonia Looks Good to Test at 1 MW

- Data from Technology Innovation bench-scale work looks good
- Economics are very preliminary and supplier derived
- Appropriate for scale-up



### **CO<sub>2</sub> Capture Pilot Project Launch**

- In early February, PON released and participation solicitation initiated
- Initial calls made to potential anchor tenant members
- 16 companies have agreed to participate
- Funding from these members represents about 2/3 of the project funding



#### **Alstom Discussions**

- Based on
  - Common interests (e.g., we jointly bid the chilled ammonia project to DOE but was not selected)



- Alstom's desire to push scale-up and commercialize the chilled ammonia process
- Organizations agreed to collaborate on the construction and testing of a 5-MW pilot CO<sub>2</sub> test unit of this process
- Could accelerate our currently proposed scale-up at no cost to the EPRI funders
- Could move us to scale for CO<sub>2</sub> storage

#### **Alstom Collaboration Benefits**

- Enables us to leverage our funder's investment even more
- Allows us to accelerate both the development and commercialization path



- A 5-MW pilot is big enough to use commercial components (e.g., slurry pumps) designed for such an application
- Teaming with the company that views this technology as their offering of choice will accelerate its commercialization
- Can move into a size which allows CO<sub>2</sub> storage testing at least 2-3 years faster

#### Chemical Looping Combustion (CLC) in ENCAP and CATO

New developments on CLC:

• Integration of CLC-reactor with Combined Cycle Power Plant



Recirculation or stationary solids?

#### Chemical Looping Combustion (CLC) in ENCAP and CATO Fixed bed diffusive reactor



#### Chemical Looping Combustion (CLC) in ENCAP and CATO Results of modelling work

The formation of a reaction front in the packed bed around an active membrane based on diffusion



The temperature development at the exit of the diffusion reactor



IEA - 9th International CO2 Capture Network - 16 June Copenhagen

#### Chemical Looping Combustion (CLC) in ENCAP and CATO Future work on CLC

- Further development of fixed bed CLC reactors integrated with combined cycle power plant
- Development of new temperature stable intermediates
- Modelling of complete process
- Testing of pilot installation



IEA - 9th International CO2 Capture Network - 16 June Copenhagen

#### Conclusions

TNO focuses on CO<sub>2</sub> post-combustion capture!

- **1.** Most developed CO<sub>2</sub> capture technology
- 2. High potential for further improvement
  - Development of improved liquids
  - Process integration and novel processes steps
  - Optimized and new contactors
  - Process modelling and economic optimisation

#### Future development includes fixed bed CLC processes!



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# **Objective**

- > Develop a research capability for precombustion CO<sub>2</sub> removal
- Integrate an existing plant with a new coal gasifier test facility ("GTI Flex Fuel")
- > Test new technology applicable to IGCC acid gas removal
  - Solvents
  - Contactor devices, packing etc.



# **GTI's Pilot Plant Unit**

- Built in 1994 by Gastech Engineering, Tulsa, OK
- > Used extensively for the development of the Morphysorb process - last used in 1999
- > Needs reconditioning and modifications to meet syngas application requirements
- > Solvent Chillers need to be replaced/rented
- > 2005 State of Ilinois IDCEO has funded relocation/refurbishment project



Currently has a fluid bed gasifier, lock hopper fed using pre-sized and dried feedstocks

4 4

gti

### **Flex Fuel PFD**



# **Flex Fuel**

- > Various capabilities will be added in planned programs:
  - Entrained gasification (third party)
  - Acid gas removal (AGTPP)
  - Gas quench/gas cooling
  - Sulfur Capture (SulfaTreat)
  - Shift/COS Hydrolysis
  - Oxygen feed
  - Higher-pressure operation
- > Using syngas from ongoing tests will be best option if cost is major factor

# **AGTPP Pilot Plant Unit**

**Pilot Plant Specifications:** 

- Pressure, 1200 psig
- Circulation Rate, 5-15 gpm
- Feed Gas Flow Rates Up to 1 MMSCF/d
- Reboiler Capacity, 600,000 Btu/h
- Overall Dimensions, 12 x 12 x 60 ft.
- Contract to move this to GTI Fall 2006 – integrate with **FlexFuel gasifier - underway**









### Moving the Plant from Kinder Morgan's Zapata Plant





#### Site Preparation at GTI



Unit at GasTech Shop in Tulsa



# **New Rich/Lean Exchanger**



# **Case 1: High CO<sub>2</sub>**

- > Gas pressure: 400 psig
- > Gas Temperature: 90 F
- > Total gas flow:1925 lb/hr
- > Solvent Circulation: 30 gpm
- > Gas Composition

	Inlet Gas		Outlet Gas	
Gas Composition	mole %	lb/hr	mole%	lb/hr
H2O	0.76	11.48	2 ppm	0.00
CO2	23.54	867.61	3.38	94.97
H2S	1.37	39.09	1 ppm	0.00
CH4	4.67	62.76	5.92	60.61
NFM	0.00	0.00	0.00	0.00
NAM	0.00	0.00	0.00	0.00
CO	30.19	708.19	39.25	702.09
H2	31.71	53.54	41.34	53.23
N2	7.71	180.99	10.12	181.04
COS	0.05	2.30	20 ppm	0.01



### **Case 2—Low CO<sub>2</sub> in Feed Gas**

- > Gas pressure: 400 psig
- > Gas Temperature: 90 F
- > Total gas flow:1925 lb/hr
- > Solvent Circulation: 30 gpm
- > Gas Composition

	Inlet Gas		Outlet Gas	
Gas Composition	mole %	lb/hr	mole%	lb/hr
H2O	8.95	165.26	<2 ppm	0.00
CO2	6.98	315.01	2.10	79.88
H2S	0.93	32.51	0.00	0.00
CH4	4.58	75.36	5.30	73.57
NFM	0.00	0.00	1 ppm	0.00
NAM	0.00	0.00	1 ppm	0.00
CO	42.91	1231.91	50.52	1223.62
H2	34.46	71.20	40.67	70.89
N2	1.14	32.80	1.41	34.12
COS	0.03	1.91	13 ppm	0.07



# **AGTPP Modifications**

- > Replace high-pressure pump
- Replace Column with 16" diameter and need minimum of 30
  ft. packing height
- > Extend Regenerator Column (12" dia) to 50 ft. to increase number of stages to meet the lean solvent specification
- > Some piping changes to accommodate higher solvent rates
- > Replace lean/rich heat exchanger
- > Procure/rent solvent chiller
- > Replace Data acquisition/PLC



### **AGTPP Absorber Column Details**



- > 16" diameter column
- > ~35 ft packing
- > Structured Packing
- > Solvent Redistributor after 20 ft
- > Total Column height 50 ft

### **Regenerator Column (12" Dia)**

- > Structured packing
- > Column height ~50 ft
- > 45' of packing (two beds with redistributor)



# **Koch's Structured packing**

- > The new style FLEXIPAC® HC® (High Capacity) structured packing, incorporates a patented modification to the bottom and top edge of each individual corrugated sheet.
- > Lower Pressure Drop and up to 40% Higher Capacity than Conventional Structured Packing





#### **Relocation of AGTPP to Flexfuel Test Facility – Major Tasks**

- > Task 1 Relocation & Erection of Acid Gas Treating Pilot Plant Unit
- > Task 2 Installation of Acid Gas Treating Unit with Flex Fuel Testing Facility
- > Task 3 Acid Gas Treating Pilot Plant Unit Shakedown and Testing



# Task 1: Relocation & Erection of AGTPP

- > Task 1.1 -- Prepare Site at Flex-Fuel
- > Task 1.2 Prepare and Submit Permits
- > Task 1.3 -- Prepare Pilot Plant for Transfer
- > Task 1.4 -- Transport Pilot Plant to Des Plaines
- > Task 1.5 Install AGTPP at Flex Fuel Facility


# Task 2--Installation of Acid Gas Treating Unit at Flex Fuel Testing Facility

- > Re-Install process lines and run necessary utility lines
- > Install interconnecting gas piping from FFTF to AGTPP
- Install control / data system in FFTF Control Room and run control wires to AGTPP
- > Connect AGTPP unit to Flex Fuel electric switchgear
- > Check out of Instrumentation and Control System, and shake down unit
- > Fill AGTPP unit with chemicals and ready for testing



# Task 3 – Acid Gas Treating Pilot Plant Unit Shakedown and Testing

- > AGTPP Unit Shakedown
- > Prepare the test unit for experiments
- > Limited Testing



# **AGTPP Status (as of June 2006)**

- > Main module is expected to ready by end of June
- > Absorber Column fabrication and packing is complete
- > AGTPP Foundation pad is ready at GTI, Des Plaines, IL
- > FFTF and AGTPP piping tie-ins will be completed by August '06
- > AGTPP expected to be at GTI by July'06



# Conclusion

- > Funding will be needed to carryout any testing or development in the AGTPP
- > Please contact the author if you have a potential need for carrying out any testing or development

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> 9<sup>th</sup> International CO<sub>2</sub> Capture Network Copenhagen, Denmark 16 June, 2006

Mitsubishi Heavy Industries, Ltd.







#### **Commercial Scale Plants**

1. CO2 Recovery Plant in Malaysia



#### Plant Outline

200 ton/day
KS-1
Urea produo
October, 19
Petoronas F
(Kedah) Sdr

Location

Flue das source

Urea production ation October, 1999 Petoronas Fertilizer (Kedah) Sdn Bhd Kedah Darul Aman, Malaysia rce Stream reformer fluegas

#### Process Description

CO<sub>2</sub> is recovered from flue gas of steam reformer of ammonia plant and delivered to CO<sub>2</sub> compressor for urea synthesis. Recovered CO<sub>2</sub> is used to increase urea production. The first commercial plant for flue gas CO<sub>2</sub> recovery using this advance technology has been operating in Malaysia since October 1999 for Urea production. Performance of process is excellent in terms of low steam consumption, very low solvent degradation and low solvent loss.

#### **Commercial Scale Plants**

### 2. Commercial Project in Japan



#### **Plant Outline**

ClientA Chemical CompanyCapacity330 T/D (Max.)SolventKS-1Feed GasNatural Gas and Heavy Oil Fired<br/>BoilerUse of CO2General Use

#### Process Description

CO<sub>2</sub> is recovered from a natural gas fined boiler and a oil fired boiler. Flue gas is cooled and removed SO<sub>x</sub> (When CO<sub>2</sub> is recovered from oil fired boiler) before entering CO<sub>2</sub> absorber. CO<sub>2</sub> is liquefied and used for dry ice, beverages and welding.



#### **Commercial Scale Plants**

# 3. Coal Fired Long Term Demonstration Plant



#### Plant Outline

Client Solvent Capacity Feed Gas Start-up Location

Power Station, Japan KS-1 10 T/d Coal Fired Boiler 2006 Nagasaki, Japan

#### Process Description

This is the demonstration plant for CO<sub>2</sub> recovery from coal fired boiler flue gas. This demonstration plant was constructed 50% cost supported by Japanese Government. The plant is planning a long term operation for coal fired flue gas CO<sub>2</sub> recovery.



Commercial Scale Plants

4. Commercial Project in India

# **Under Construction**

#### Plant Outline

ClientIndian Farmers Fertilizer Co.SolventKS-1 SolventCapacity450 T/d x 2 unitsFeed GasNatural Gas and Naphtha<br/>Reformer Flue GasUse of CO2Urea ProductionStart-up2007MANY SUBSTICHIM

#### Process Description

 $CO_2$  is recovered from steam reformer flue gases.  $CO_2$  is compressed and then used for urea synthesis. Flue gas is cooled and then removed  $SO_x$  before entering  $CO_2$  absorber.

Delivery Record	Purpose	CO <sub>2</sub> Recovery Capacity (metric ton/day)	'99	'00	'01	<sup>'</sup> 02	03	'04	'05	' <b>0</b> 6	'07	'08	'09	'10
Malaysia, Petronas Fertilizer	Urea Production	200								 				
Japan, Chemical Company	General Use	330												
India, Fertilizer Company	Urea Production	450 × 2								~			•••••	
Abu Dhabi, Fertilizer Company	Urea Production	400				(Er	 nergy 	y Sav	 /ing   	Proc	ess)		•••••	
Japan, Coal-Fired Long-Term Demonstration Plant	R&D	10							Sta	art of	 f Tes	st		
			Start of commercial Operation											

