

### INTERNATIONAL NETWORK FOR CO<sub>2</sub> CAPTURE: REPORT ON 10<sup>TH</sup> WORKSHOP

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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  $CO_2$  Capture is organised by IEA Greenhouse Gas R&D Programme. The organisers acknowledge the hospitality provided by the hosts IFP.

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  $10^{th}$  Workshop, 2007/08, July 2007".

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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# Group photo of the attendees at the $10^{th}$ International Post-Combustion $CO_2$ Capture Network Meeting



#### INTERNATIONAL NETWORK FOR CO<sub>2</sub> CAPTURE: REPORT ON 10<sup>th</sup> WORKSHOP

#### (24-25<sup>th</sup> May 2007, IFP, Lyon)

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

This workshop was the tenth in a series to discuss co-operation in development of MEA and related solvents and associated techniques to capture  $CO_2$  from power plant flue gases. The previous events were, in Gaithersburg, Calgary, Apeldoorn, Kyoto, Pittsburgh, Trondheim, Vancouver, Austin, and Copenhagen. Copies of previous reports after the Apeldoorn meeting are available on CD (contact <u>sian@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. Retrofit to established plant is also technically feasible although less economically attractive for ageing, less efficient assets. Since the previous workshop in Copenhagen, considerable progress has been made with the pilot plant at Esbjerg which was the subject of a side visit at that meeting. Others, notably in Australia and Italy have announced intentions to construct and operate pilot/small demonstration units. In Norway the technique has been used for some years for CO2 separation at Statoil's Sleipner gas field and there are clear intentions to do so again at other gas production or gas fired power units. However, no one anywhere in the world has announced a demonstration unit on a coal fired power plant – for which there is an urgent need when considering forward intentions to build new pulverised coal plant in China, India, USA, Europe, S Africa and S E Asia.

Over the seven 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. For the first time some potential attendees had to be turned away because of demand for places at the workshop. Attendees came from 13 countries, including China for the first time.

This report contains presentations on a variety of developments including up dates on amines, use of ammonia as a solvent, a process for combining CO2 and SO2 capture in one unit, a new solvent which facilitates phase separation and so reduces regeneration heat loads, and a set of reports on activities in different countries etc.

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

#### 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 CO2 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 CO2 capture economics.

#### Copenhagen

About a quarter of the attendees arrived a day early and visited the CASTOR, EU Project post combustion pilot plant operating at 1t/h CO2 scale on a flue gas slip stream at what is now a Dong Energy power station in Esbjerg. This was in early stages of operation using MEA to provide a baseline against which to judge other solvents. Fifteen presentations at the workshop, as usual, covered fundamental research investigations, process modelling, "capture ready" considerations and something on pilot plant work and commercialisation. The latter is key to wider process and it seems that none of the likely process licensors were quite yet in a position to offer full commercial guarantees.

#### 2. Lyon, IFP 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, UK	Introduction to 10th Workshop
2	Paul Broutin, IFP, France	The Scientific and Technical Challenges of IFP
3	Ross Dugas et al, University of Texas, USA	7m MEA & 7m MEA/2m PZ Kinetics, Thermodynamics & Degradation
4	Inna Kim, NTNU, Norway	Enthalpy of absorption of CO2 in the aqueous solutions of amines
5	P J G Huttenhuis et al, Procede BV, Netherlands	Performance of Aqueous MDEA Blends for CO2 Removal from Flue Gases
6	Jochen Oexemann, Technical University of Hamburg-Harburg, Germany	Optimisation and Integration of CO2 Capture by Wet Chemical Absorption Process
7	Kazuya Goto, RITE, Japan	Development of New Amine Absorbents in

		COCS project
8	Leo Hakka, CANSOLV, Canada	Integrated Regenerable SO2/CO2 Capture
9	Karl A Hoff, SINTEF, Norway	Reducing the Environmental impact of Acid gas Control Technologies - REACT
10	Rene van Gilswijk, TNO, Netherlands	Environmental impact of CO2 capture in power plants
11	Richard Rhudy, EPRI and Sean Black, Alstom, USA	Chilled Ammonia Process Update
12	Shujian Wang, Tsinghua University, China	Ammonia Scrubbing Technology for CO2 Capture
13	M Jacquin et al, IFP, France	New Solvent for CO2 Capture with Low Energy of Regeneration
14	Xiaohui Zhang, Shell, Netherlands	Study on Multiphase CO2 Capture with Immobilized Activator
15	J. Knudsen et al, Dong Energy, Denmark	CASTOR pilot plant – results and implications for Scale Up
16	Paul Webley, Monash University, Australia	Overview of the CO2CRC Capture Program
17	Phillippe Delage, Alstom & Paul Broutin, IFP, France	Integrated CO2 Capture Study for a Coal Fired Power Station
18	Hallvard Svendsen, NTNU, Norway	Learning from CASTOR: solvent, pilot plant and modeling work
19	Hamid-Reza Mirza, University of Waterloo, Canada	A Multi-period Optimisation Model for Energy Planning with CO2 Emissions Considerations
20	Gelein de Koeijer, Statoil, Norway	Halten CO2 and Mongstad in Norway– Gas Fired Projects with Post Combustion CO2 Capture
21	Graeme Puxty, CSIRO, Australia	Current CO2 PCC Research and Development Activity

### 4. Next Meeting(s)

The 11<sup>th</sup> Network meeting has to be confirmed. Discussions are in hand to hold it in Beijing, China in April/May 2008.

### 5. Thanks and Acknowledgements

All participants wish to thank Paul Broutin of IFP and his associates and staff for all the hard work of co-ordinating the event and the pilot plant and research facilities visit on the afternoon of the first day: also for the splendid dinner on the intermediate evening.

Prof Paitoon Tontiwachwuthikul, Univ of Regina, John Davison IEA GHG, Prof Gary Rochelle, Univ of Texas are all thanked for Chairing various sessions

#### 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 <u>john.topper@iea-coal.org.uk</u> or via the "feedback" facility in the IEA GHG website's home page <u>http://www.ieagreen.org.uk</u>



# **10th International Post-Combustion CO<sub>2</sub> Capture Network Meeting**

24th-25th May 2007 IFP Lyon, France

Organised by

IEA Greenhouse Gas R&D Programme.

Sponsored by

IFP





### 24th May 2007 Day 1

08.15 Delegates meet in lobby of two hotels for bus pick up and transfer

### 09.00 Session 1 - Introduction

Welcome, Round the Table Introductions, Today's Agenda: John Topper; IEA GHG R&D Programme, UK.

Host Address: The Scientific & technical challenges of IFP: Paul Broutin: IFP, France

09.45 Session 2-Use of Amines - Chair Prof Paitoon Tontiwachwuthikul, University of Regina, USA

7m MEA &7m MEA/2m PZ Kinetics, Thermodynamics & Degradation: Ross Dugas; University of Texas, USA

Enthalpy of Absorption of CO<sub>2</sub> in the Aqueous Solutions of Amines: Inna Kim, NTNU, Norway

Performance of Aqueous MDEA Blends for CO<sub>2</sub> Removal from Flue Gases: PJG Huttenhuis, Procede BV, Netherlands.

#### 10.45 to 11.15Break

Optimisation and Integration of CO<sub>2</sub> Capture by Wet Chemical Absorption Process: Jochen Oexemann, Hamburg University of Technology, Germany

Development of New Amine Aborbents in COCS Projects: Goto Kazuya, RITE, Japan

Integrated Regenerable SO<sub>2</sub>/CO<sub>2</sub> Capture: Leo Hakka, CANSOLV, Canada

12.20 Session 3—Environmental Impacts - Chair John Davison, IEA GHG, UK

Reducing the Environmental Impact of Acid gas Control Technologies-REACT: Karl A Hoff; SINTEF, Norway

Environmental Impact of CO<sub>2</sub> Capture in Power Plants: Rene van Gijlswijk; TNO, Holland

13.00 Lunch followed by Group Photograph

**14.00 Session 4**—Other Solvents and Technologies for Post Combustion Capture - Chair Paul Broutin, IFP, France

Chilled Ammonia Process Update: Richard Rhudy, EPRI USA and Sean Black, ALSTOM, USA

Ammonia Scrubbing for CO<sub>2</sub> Capture: Shujuan Wang, Tsinghua University, China.

New Solvent for CO<sub>2</sub> Capture with Low Energy Regeneration:Marc Jacquin, IFP, France

Study on Multiphase CO<sub>2</sub> Capture with Immobilised Activator: Xiaohui Zhang, Shell, The Netherlands

15.15 to 15.45 Break Visit to IFP Laboratories and Facilities

**Close Day 1** 17.00Return to hotels by bus transfer



### 25th May 2007 Day 2

08.30 Delegates meet in lobby of two hotels for pick up and transfer

09.15 Session 5— Pilot Plant Work - Chair Prof. Gary Rochelle, University of Texas, USA

Pilot Plant Results and Implications for Scale Up: Jacob Knusden, Dong Energy, Denmark

Overview of CO2CRC Capture Programme: Paul Webley, CO2CRC

Integrated CO<sub>2</sub> Capture Study for a Coal Fired Station; Philippe Delage (ALSTOM Power) & Paul Broutin (IFP)

### 10.30 to 11.00 Break

**Session 6**- International Perspectives and Activities - Chair Dr. John Topper, IEA GHG, Learning from CASTOR; solvent, pilot plant and modeling work: Hallvard Svendsen, EU CASTOR

A Multi-period Optimisation Model for Energy Planning with CO<sub>2</sub> Emissions Considerations: Hamid Raza Mirza, University of Waterloo, Canada

Halten CO<sub>2</sub> and Mongstad in Norway– Gas Fired Projects with Post Combustion CO<sub>2</sub> Capture: Gelein de Koeijer, Statoil, Norway

Current CO<sub>2</sub> PCC Research and Development Activity: Graeme Puxty, CSIRO Australia

### 12.45 Discussion and Wrap Lead by John Topper

#### 13.00 Lunch

14.00 Bus transfer back to hotels.



# 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 has been on use of MEA and derivative solvents. Now looking to broaden this
- WHY CO-OPERATE?:
  - avoid duplication of effort
  - encourage development
  - minimise cost of participation
  - enhance technology credibility
  - share risks



### Three technical elements to the Network

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

IEA GHG facilitates

The build up of international contacts has led to significant collaboration and exchange

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 (June 2006) 10<sup>th</sup> Workshop at IFP in Lyon, France (May 2007) 11<sup>th</sup> Workshop ?? Offer from CSIRO, Australia ?? Or back-to-back with GHGT9 in Washington USA in 2008??? WE MAY MAKE A SMALL CHARGE IN

### IEA Greenhouse Gas R&D Programme

# GHGT-9

- Omni Shoreham Hotel, Washington D.C.
- 16<sup>th</sup> 20<sup>th</sup> November 2008
- Organised by MIT, USDOE and IEA GHG
- Major sponsors: USDOE
- Planning on 1500 participants
- Dinner to be held at Smithsonian National Aerospace Museum





- We are now a well established club
- > 13 countries here today including for the first time China
- Good representation from other far away countries, Japan, Australia, USA, Canada
- Excellent networking; very popular, had to turn away 10+

**Today: Housekeeping Points** 

- Coffee breaks around 10.45 and 15 15
- Lunch, 13 00 14 00 followed by photos
- Afternoon session will finish at around 15 45 followed by tour of IFP and by bus back to hotel(s)
- Dinner this evening at 19 30at La Cuvee Need to check numbers
- ALL PRESENTERS ensure I get a copy of their presentation on data storage stick if you want it on the GHG website next week
- Tomorrow we finish with lunch apologies for wrong date on Agenda
- Mobile phones off or on vibrating alert



- Thanks to IFP
- To IFP for local organisation, offering the meeting room and visit to their facilities
- And for Sponsoring the Dinner this evening and one of the lunches

# The scientific & technical challenges of IFP

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Innovation Energy

Environment





### Research and development







A public R&D, training and information body

Mission: to develop the transport energies of the 21st century

IFP provides public players and industry with innovative solutions in its focal areas: energy, transport, environment

As an applied research center, it ensures transfer between fundamental research and industrial development





1,720 people\*, of which 65% in R&D based in Rueil-Malmaison and Lyon

219 doctoral and post-doctoral researchers

More than 50 professions represented: from geological engineers to motor engineers

A very high-quality technical environment (testing resources, equipment)

### IFP in a nutshell

Status: State-owned industrial and commercial establishment (EPIC)

Funding: State budget and resources provided by private French and foreign partners

Budget for 2007: €301.5 million including €241.3 million for R&D

More than 12,000 active patents

More than 200 scientific publications every year





# INDUSTRIAL OUTLETS FOR R&D RESULTS



Technip

3 %

### Stakes held in listed companies

**Compagnie Générale** 

de Géophysique 8 %







### Preparing for the energy transition

**5** complementary strategic priorities **DIVERSIFIED** FUEL-EFFICIENT CONTROLLED **EXTENDED CLEAN FUELS RESERVES** REFINING **VEHICLES** CO<sub>2</sub> Pushing back the Converting as **Diversifying fuel** Developing Capturing and boundaries in oil much raw material clean, fuelsources storing CO<sub>2</sub> to efficient vehicles as possible into and gas combat the exploration and transport energy greenhouse effect production

IFP's research programs are structured around these 5 priorities





**IFP** 



### Research and development





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# RESEARCH AND DEVELOPMENT

# **Extended Reserves**

### EXTENDED RESERVES



Because oil will continue to be the world economy's leading source of energy for several decades to come, especially in the transport and chemicals sectors

Because ongoing research will lead to a significant increase in available oil and gas reserves

Because the era of cheap energy is now in the past, the high added value technological exploitation of oil and gas has now become economically viable

### 3 R&D themes

- Increasing the success rate in exploration
- Improving the recovery ratio in reservoirs
- Developing fields in extreme environments





# **Challenges of extended reserves**



- seismic imaging of complex geological structures
- basin modelling



- upscaling: from pore to reservoir enhanced recovery
- reservoir modelling: management of uncertainties
- monitoring
- complex well architectures and productivity



# **RESEARCH AND DEVELOPMENT**

# **Clean Refining**



Converting as much raw material as possible into transport energy To develop industrial facilities capable of producing highquality light fuels from increasingly heavy crudes

To improve the quality of products and yields

► To reduce the impact of refining on the environment by limiting CO<sub>2</sub> emissions

### 3 R&D themes

- The production of high-quality fuels
- The conversion of heavy crudes, residues and distillates
- The production of petrochemical intermediates





### develop clean and highly efficient processes



### **DESIGN AND CONTROL**

- Multi-purpose and structured reactors
- Micro-technologies
- On-line analysis systems
- Real-time modelling

### **CATALYSTS AND ADSORBENTS**

- Molecular modelling
- High-flow experiments
- Nanotechnologies to optimize structure, texture and functioning



DISCHARGES

- Supercritical solvents
- Ionic liquids





# RESEARCH AND DEVELOPMENT

# Fuel-efficient vehicles

FUEL-EFFICIENT VEHICLES

Developing clean, fuel-efficient vehicles Because it is necessary to reduce the fuel consumption of vehicles and their impact on the environment

Because it is necessary to develop powertrain systems suitable for alternative energies (natural gas, biofuels) along with innovative solutions, such as thermal/electrical hybrid vehicles

### 4 R&D themes

 Development of highly efficient engine technologies (conventional and hybrid powertrains)

- Development of pollutant after-treatment technologies

Development of electronic control strategy and onboard software

 Validation and specification of alternative fuels with low CO<sub>2</sub> emissions (in particular biofuels and NGV)



# **Challenges for fuel-efficient vehicles**





# **Diversified fuels**

DIVERSIFIED FUELS

Díversífying fuel sources Because oil and gas are non-renewable sources

To bring a range of energy options that could complement hydrocarbons for transport and petrochemicals

### 3 R&D themes

- The production of first- and second-generation biofuels
- The use of natural gas and coal to produce synfuels
- Hydrogen production





### **Challenges for diversified fuels**







### Thermochemical treatment Biomass to Liquid Esters of vegetable oils

- Cellulases for ethanol production
- Production of hydrogen

COAL • Liquefaction and upgrading of the liquids


#### **RESEARCH AND DEVELOPMENT**

### Controlled CO<sub>2</sub>



Capturing and storing CO<sub>2</sub> (CCS) a solution to limit the greenhouse effect Because IFP places sustainable development at the heart of its work

Because IFP has all the expertise and technological skills required to be present at all stages from capture to storage

Because the bulk of CO<sub>2</sub> emissions result from energy use

#### 3 R&D themes

- $-CO_2$  capture
- Transporting and injecting CO<sub>2</sub>
- Geological storage of CO<sub>2</sub>





#### **Challenges for controlled CO<sub>2</sub>**



#### Capture

- Solvent scrubbing processes
- Adsorption
- Oxyfuel
- Chemical-Looping
- Precombustion

Develop effective, reliable low-cost capture processes Prove the feasability of storage

#### Storage

- Modelling of CO<sub>2</sub> injection
- •Control of CO<sub>2</sub>/rock interactions
- Monitoring of storage units
- Modelling of long-term storage





© IFP



#### Dinner at Restaurant "La cuvée"

- Dinner hosted by IFP scheduled at 08:00
- Address: Corner Street Sala and Street Auguste Comte (Lyon 2ème)
- Departure at 07:30 from the lobbies of collège hotel and AXOTEL
- Thank you for filling the sheet in order to confirm your participation





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## 7m MEA & 7m MEA/2m PZ Kinetics, Thermodynamics & Degradation

By: Ross Dugas Marcus Hilliard Andrew Sexton Jason Davis Nidhi Mathur

May 24, 2007

# Scope of the Presentation

- Introduction to MEA/PZ
- Kinetics and Thermodynamics
  - Apparatus
  - Results
  - Conclusions
- Oxidative Degradation
- Thermal Degradation

# Why use 7m MEA/2m PZ?

Faster rates – kinetics
Less packing
Richer solutions

lower energy requirements

Increased capacity – VLE

Lower flow rates
Smaller heat exchangers, pumps

# **Kinetics and Thermodynamics**

Ross Dugas Marcus Hilliard





















# Kinetics and Thermodynamics Conclusions

- VLE measurements from Dugas, Hilliard, and Jou (1995) matched for 7m MEA over a wide range of CO<sub>2</sub> loadings. Dugas and Hilliard agree for 7m MEA/2m PZ.
- 7m MEA/2m PZ has 45% greater CO<sub>2</sub> capacity (40°C from 100-3000 Pa, molality basis).
- MEA and PZ volatility have been quantified.
- Discrepancies in Dugas and Aboudheir (2002) rate data can probably be explained by mass transfer phenomenon.
- 7m MEA/2m PZ shows faster rates than 7m MEA

# **Oxidative Degradation**

Andrew Sexton

#### Modified Low Gas Flow Apparatus



## Ion Chromatography Analysis Methods

- Dionex ICS-2500 System
- Anion: AS15 Ionpac Column & ASRS 4-mm Suppressor
  - Linear gradient of NaOH eluent
  - 1.60 mL/min, 30°C
- Cation: CS17 Ionpac Column & CSRS 4mm Suppressor
  - Constant methanesulfonic acid (MSA) eluent
  - 0.40 mL/min, 40°C





#### Degradation Product Formation Rates (mM/hr)

Distinguishing Conditions	7m MEA, 250 ppm Cu	7m MEA/2m PZ, 5 ppm Fe, 250 ppm Cu	7m MEA/2m PZ, 5 ppm Fe
Formate	0.39	2.35	0.04
Acetate	0.01	0.02	-
Oxalate	0.04	0.09	-
Glycolate	0.10	0.03	-
Nitrate	0.15	0.13	0.02
Nitrite	0.31	-	0.003
EDA	-	0.03	0.008
<b>Total Carbon</b>	0.69	2.67	0.056
Total Nitrogen	0.46	0.18	0.039

#### **Oxidative Degradation Conclusions**

- Confirmed formate, glycolate, oxalate as significant degradation products
- Discovered nitrate, nitrite, and ethylenediamine as significant products
- MEA/PZ relatively stable at low catalyst concentration
- Cu catalyzes MEA/PZ more than MEA by itself

# Thermal Degradation Jason Davis Nidhi Mather

# MEA/PZ Thermal Degradation

- Thermal degradation is a known loss mechanism for MEA and DEA at stripper conditions
- No literature on thermal degradation for piperazine or piperazine blend systems
- Less thermal degradation expected for piperazine because no alcohol group

## Method

 Solutions loaded with CO<sub>2</sub> and placed into a set of 5x10ml stainless steel sample bombs

- Sample containers loaded into forced convection oven and each one removed at desired time interval
- Samples analyzed with GC and titration to determine the amount of MEA and piperazine remaining

# PZ Systems ( $\alpha$ =0.4)



# MEA/PZ Systems ( $\alpha$ =0.4)



# MEA Systems ( $\alpha$ =0.4)



# Thermal Degradation Results

- Piperazine reaches equilibrium with its degradation product in a short time according to the GC results
- This equilibrium product comprises a large percentage of the original piperazine
- No losses are detected via pH titration
- The degradation products retain alkalinity and may be reversible back to piperazine

# Questions?

Dr. Gary Rochelle gtr@che.utexas.edu Ross Dugas ross@che.utexas.edu

# Enthalpy of absorption of CO<sub>2</sub> in the aqueous solutions of amines

Inna Kim and Hallvard F. Svendsen

The Norwegian University of Science and Technology (NTNU), Norway
## Outline

- Background
- Experimental set-up and results
- **D** Prediction of  $\Delta H_{abs}$  from K-values
- Conclusions

### Enthalpy(Heat) of absorption, $\Delta H_{abs}$ [Lee L.L., 1994]

due to chemical reaction (for the *n*-th reaction):

$$\frac{\partial \ln K_{eq.\,for\,n}}{\partial T} = \frac{\Delta H_r^o}{RT^2}$$

due to dissolution of the acid gas  $(CO_2)$  into the liquid (release of the kinetic energies)

$$\frac{\partial \ln k_{H_i}}{\partial T} = \frac{\partial H^o_{i(aq)} - \partial H^o_{i(gas)}}{RT^2} = \frac{\Delta H_{dissol}}{RT^2}$$

due to non-ideal mixing (preferential solvation and energetic changes with temperature) (for the *i*-th species)

$$\frac{\partial \ln \gamma_i}{\partial T} = \frac{H_{i(aq)}^o - H_{i(aq)}}{RT^2} = \frac{\Delta H_i^e}{RT^2}$$

## Integral and differential $\Delta H_{abs}$

 Integrated over some loading interval (direct measurement)



 Calculated using Gibbs-Helmholz equation:

$$\left[\frac{d\ln(f_{CO_2})}{d(1/T)}\right]_{x_{CO_2}} = \frac{\Delta H_s}{R}$$

- $f_{CO2}$  fugacity of CO<sub>2</sub>  $x_{CO2}$  – mole fraction of CO<sub>2</sub>
  - > Assumption:  $f_{CO_2} = P_{CO_2}$
  - Disadvantage: differentiation [Lee et al.,1974]

# Differential enthalpy of absorption from equilibrium data \*:



VLE data: In(p<sub>CO2</sub>) vs 1/T:

- a) Fitted with a line,
- b) Fitted with a 2<sup>nd</sup> order polynomial



\* [Hoff K.A., Mejdell T., Svendsen H., 2005]

## Experimental part

Measuring of semi-differential enthalpy of absorption of  $CO_2$  in a reaction calorimeter

## **Experimental set-up**



## Semi-differential $\Delta H_{abs}$ (an example of on-line recorded data)



### Semi-differential $\Delta H_{abs}$ for 30 wt% MEA



### Integral $\Delta H_{abs}$ for 30wt% MEA



# Estimation of the saturation loading point in the example of 30wt% MEA



10th International network for CO<sub>2</sub> capture, 24-25 May, 2007, IFP Lyon, France

# Semi-differential $\Delta H_{abs}$ for 30 wt% MDEA solution



## Semi-differential $\Delta H_{abs}$ for MDEA



\*\*[Oscarson et al.,2000]

### Integral $\Delta H_{abs}$ for 30 and 40wt% MDEA



# Measured integral $\Delta H_{abs}$ for 30wt% MDEA solution at 80oC



## Modelling

Prediction of the enthalpy of absorption from K-values

# The main reactions in the $CO_2$ /alkanolamine/water system:

$$2H_{2}O = H_{3}O^{+} + OH^{-}$$

$$K_{w} = \frac{a_{H,0^{+}} \cdot a_{OH^{-}}}{a_{w}^{2}} = \frac{x_{H,0^{+}} \cdot x_{OH^{-}}}{x_{w}^{2}} \cdot \frac{\gamma_{H,0^{+}} \cdot \gamma_{OH^{-}}}{\gamma_{w}^{2}}$$

$$2H_{2}O + CO_{2} = H_{3}O^{+} + HCO_{3}^{-}$$

$$K_{co_{2}} = \frac{a_{H,0^{+}} \cdot a_{Hco_{3}^{-}}}{a_{co_{2}^{-}} \cdot a_{w}^{2}} = \frac{x_{H,0^{+}} \cdot x_{Hco_{3}^{-}}}{x_{co_{2}^{-}} \cdot x_{w}^{2}} \cdot \frac{\gamma_{H,0^{+}} \cdot \gamma_{Hco_{3}^{-}}}{\gamma_{co_{2}^{-}} \cdot \gamma_{w}^{2}}$$

$$H_{2}O + HCO_{3}^{-} = H_{3}O^{+} + CO_{3}^{-}$$

$$K_{hco_{3}^{-}} = \frac{a_{H,0^{+}} \cdot a_{Co_{3}^{-}}}{a_{Hco_{3}^{-}} \cdot a_{w}} = \frac{x_{H,0^{+}} \cdot x_{Co_{3}^{-}}}{x_{Hco_{3}^{-}} \cdot x_{w}} \cdot \frac{\gamma_{H,0^{+}} \cdot \gamma_{Hco_{3}^{-}}}{\gamma_{Hco_{3}^{-}} \cdot \gamma_{w}}$$

$$H_{2}O + RR'NH = RR'NH_{2}^{+} + OH^{-}$$

$$K_{RR'NH_{2}^{-}} = \frac{a_{H,0^{+}} \cdot a_{RR'NH}}{a_{RR'NH_{2}^{-}} \cdot a_{w}} = \frac{x_{H,0^{+}} \cdot x_{RR'NH}}{x_{RR'NH_{2}^{-}} \cdot x_{w}} \cdot \frac{\gamma_{H,0^{+}} \cdot \gamma_{RR'NH}}{\gamma_{RR'NH_{2}^{-}} \cdot \gamma_{w}}$$

$$RR'NH + HCO_{3}^{-} = RR'NCOO^{-} + H_{2}O$$

$$K_{RR'NCOO^{-}} = \frac{a_{Hco_{3}^{-}} \cdot a_{RR'NH}}{a_{RR'NCOO^{-}} \cdot a_{w}}} = \frac{x_{Hco_{3}^{-}} \cdot x_{RR'NH}}{x_{RR'NCOO^{-}} \cdot x_{w}} \cdot \frac{\gamma_{Hco_{3}^{-}} \cdot \gamma_{RR'NH}}{\gamma_{RR'NL_{2}^{-}} \cdot \gamma_{w}}$$

$$CO_{2(g)} = CO_{2(aq)}$$

$$\phi_{co_{3}}y_{co_{3}}P = H_{co_{3}}x_{co_{3}}\gamma_{co_{3}}$$

### Enthalpy of reaction from K-values

$$\ln K = A + \frac{B}{T} + C \ln T + DT \qquad \Delta H_{j} = \Delta H_{j}^{o} + \Delta H_{j}^{ex}$$
$$\Delta G_{r}^{o} = -RT \ln K \qquad \Delta H_{j}^{o} = RT^{2} \left(\frac{\partial \ln K_{j}}{\partial T}\right)_{p}$$
$$\frac{\partial \left(\Delta G_{r}^{o}/T\right)}{\partial T}\right)_{p} = -\frac{\Delta H_{r}^{o}}{T^{2}} = -R \left(\frac{\partial \ln K}{\partial T}\right)_{p} \qquad \Delta H_{j}^{ex} = RT^{2} \left(\frac{\partial \ln(\Pi \gamma_{i})}{\partial T}\right)_{p}$$

## Calculation of the overall $\Delta H_{abs}$ [Merkley, 1987]

$$\Delta H_{abs} = \sum \Delta n_i \Delta H_j$$

 $\begin{aligned} 1. \ H_2 O \Leftrightarrow H^+ + OH^- \\ 2. \ H_2 O + CO_{2(aq)} \Leftrightarrow H^+ + HCO_3^- \\ 3. \ HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \\ 4. \ MDEAH^+ \Leftrightarrow MDEA + H^+ \\ 5. \ CO_{2(g)} \Leftrightarrow CO_{2(aq)} \end{aligned}$ 

 $\Delta n_{1} = [OH^{-}]_{f} - [OH^{-}]_{i}$   $\Delta n_{2} = [HCO_{3}^{-}]_{f} - [HCO_{3}^{-}]_{i} + [CO_{3}^{2-}]_{f} - [CO_{3}^{2-}]_{i}$   $\Delta n_{3} = [CO_{3}^{2-}]_{f} - [CO_{3}^{2-}]_{i}$   $\Delta n_{4} = [MDEA]_{f} - [MDEA]_{i}$   $\Delta n_{5} = [CO_{2}]_{f} - [CO_{2}]_{i}$ 

### Comparison of equilibrium constants



### Comparison of $\Delta H$ of reactions



# Experiment vs model for 30 wt% MEA solution



## Conclusions

- Direct calorimetric measurements provide an accurate means of obtaining the enthalpy of absorption for acid gases in solution as function of *temperature* and *loading*
- □ By keeping the delta in loading between each new equilibrium, rather low (~0.05), it is possible to obtain values of  $\Delta H_{abs}$  semi-differential in loading
- It seems to be possible to predict the enthalpy of absorption from the equilibrium data (K-values). The model may be used to predict the equilibrium constants from the experimental enthalpy data.
- The activity coefficient contributions will be taken into account via excess enthalpies.

## Acknowledgement

This work has been financially supported by the European Commission through the CASTOR Integrated Project (Contract no. SES6-CT-2004-502856).

Thank you for your attention !

#### Performance of Aqueous MDEA Blends for CO<sub>2</sub> Removal from Flue Gases





**P.J.G. Huttenhuis, E.P. van Elk, G.F. Versteeg Procede Group B.V., The Netherlands** 

10<sup>th</sup> MEETING of the INTERNATIONAL POST-COMBUSTION CO<sub>2</sub> CAPTURE NETWORK

24 May 2007, Lyon, France



#### Content

- Introduction;
- Rate based model;
- Results;
- Conclusions & Future work.
- Acknowledgement



• Experience with Post Combustion CO<sub>2</sub> capture :

- Fluor Econamine process (30 wt.% MEA);
- Kerr-McGee / ABB Lummus Crest process (15-20 wt. % MEA).
- Major challenges are: required scale and capture costs:

CAPACITY [tonne CO <sub>2</sub> /hr]		CAPTURE COSTS [€/tonne CO <sub>2</sub> ]	
Current	Goal	Current	Goal
35	<b>400</b> <sup>1)</sup>	50-60	20-30

1) 500 MW Coal fired plant



#### • Typical flowsheet:



10<sup>th</sup> CO<sub>2</sub> capture meeting; IFP; Lyon

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#### Main problems with this technology are:

- Degradation due to the presence of oxygen;
- Corrosion;
- High absorber costs;
- High regeneration costs;
  - $\rightarrow$  ± 70 % of operational costs (4 GJ / tonne CO<sub>2</sub>).

#### → Better Solvents required



#### • New solvent developments by several research programs:

- KS-1 : low regeneration energy (MHI);
- Amino acids: low volatility (TNO and University of Twente);
- K<sub>2</sub>CO<sub>3</sub> activated with PZ: low volatilty and no degradation (University of Texas);
- Mixed amines (MEA : MDEA; 4 : 1); lower regeneration energy (University of Regina).
- This work:

 $\rightarrow$  study of performance of aqueous MDEA activated with different accelerators (primary and secondary amines) in the absorber.



• MEA (primary amine) versus MDEA (tertiary amine):

	MEA	MDEA
Stoichiometry (amine-CO <sub>2</sub> )		1:1
Heat of absorption [MJ/kg CO <sub>2</sub> ]		1.1
Reaction rate constant @ 298 K [m <sup>3</sup> .mol <sup>-1</sup> .s <sup>-1</sup> ]		<b>5.10</b> -3
Volatility [P <sub>amine</sub> in kPa @ 373 K]	6.7	0.3
Corrosion rate [mili-inch/year]	136	68



- Tray to tray procedure (Blauwhof 1985);
- Series of ideal CISTR's;
- No pressure drop and back mixing;
- Constant heat and mass transfer parameters (k<sub>l</sub>, k<sub>a</sub>, a, h<sub>l</sub>, C<sub>p</sub>);
- Physical parameters only function of temperature (ρ, μ, D, K, m);
- limited to blend of two amines;
- ideal vapour / liquid phase (fugacity = 1).







#### • Process design:

- Hydrodynamics;
- Mass transfer parameters;
- Kinetics (enhancement);
- VLE (physical and chemical).

#### Flux according film model:





• Involved chemical reactions:

all amine systems:  $2H_2O \leftrightarrow H_3O^+ + OH^ CO_2 + 2 H_2O \leftrightarrow HCO_3^- + H_3O^+$   $HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$  $R_1R_2R_3N + H_2O \leftrightarrow R_1R_2R_3H^+ + OH^-$ 

(water ionization) (bicarbonate formation) (carbonate formation) (amine protonation)

for primary / secondary amines only ( if  $R_1$  and/or  $R_2$  is a hydrogen atom):  $2R_2R_3NH + CO_2 \leftrightarrow R_2R_3NCOO^- + R_2R_3NH_2^+$  (carbamate formation)



#### • CO<sub>2</sub> Solubility





#### Results

#### Input data for absorber simulations:

- Flue gas flow is 500 Nm<sup>3</sup>/s with 12 % CO<sub>2</sub> (typical coal fired);
- 90 % CO<sub>2</sub> removal;
- Absorber temperature is 40 °C;
- $K_a$  is 5.10<sup>-2</sup> and  $k_l$  is 2.10<sup>-4</sup> m/s;
- 3 M aqueous amine (> 90 % MDEA + make up accelerator);
- Simulated accelerators: MEA; DGA (primary) and DEA, MMEA, DIPA (secondary).



#### **Results**

#### Influence number of trays on column length:



Minimum number of calculated trays should be at least 30 to assure plugflow in the column.


## Influence type of accelerator (5 mole %) on column length:



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### Influence amount of accelerator on column length:





### **Influence MEA concentration on calculated enhancement:**





### Speciation in 3 M amine (resp. 1 % and 10 % MEA):



[MEA]	Liquid flow [m³/s]	Rich loading [mole CO <sub>2</sub> /mole amine]
1 %	5.82	0.148
10%	4.74	0.179



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# **Conclusions & Future work**

- MEA seems a very good accelerator;
- Small amount of MEA added to an aqueous MDEA blend results in a significant shorter column;
- Aqueous blends of MDEA/MEA may be competitive with aqueous MEA (lower regeneration, less corrosion, better stoichiometry);
- Model can provide good insight in solvent behavior in the absorber.



# **Conclusions & Future work**

- Study influence of tertiary amine type on absorption performance;
- Incorporation of desorber and other unit operations to study regeneration energy;
- Extension to more accurate thermodynamic models, like E-EOS models.



# Acknowledgement

- This work has been carried out as part of the CAPTECH project;
- CAPTECH is sponsored by the Dutch Ministry of Economic Affairs and is part of the EOS Long Term (Energy Research Strategy) research program.



# Thank you!



Institute of Energy Systems Prof. Dr.-Ing. A. Kather

Dipl.-Ing. J. Oexmann

# **Optimisation & Integration of CO<sub>2</sub>-Capture by Wet Chemical Absorption Process**

**Research Activities at the Institute of Energy Systems** 



10<sup>th</sup> Workshop of the International Network for CO<sub>2</sub> Capture Lyon, 24<sup>th</sup> May 2007

### Contents



# **1. PCC Research Activities at the IET**

## 2. Modelling and Simulation

- CO2 Capture
- CO2 Compression
- Power Plant Island
- Overall Process

# 3. Cost Estimation

- ► CAPEX
- ► OPEX

# 4. Outlook





#### • Modelling and simulation of sub-processes

- ► CO<sub>2</sub> capture
- CO<sub>2</sub> compression
- Power plant process
- Analysis of the overall process under realistic boundary conditions
- Focus on CO<sub>2</sub>-capture by wet chemical absorption
- Evaluation of most promising solvents and their respective processes
- Analysis of novel process configurations
- Integration in power plant process and optimisation of overall process



#### • Softwaretools

- ► CO<sub>2</sub>-capture and compression: *ASPEN Plus*
- Power plant process: EBSILON Professional
- ► Input, cost estimation and overall process analysis: *MS Excel*
- Linking ASPEN<sup>+</sup> ↔ Excel ↔ EBSILON
  - Enables the analysis of the overall process in a closed manner
  - Object Linking and Embedding (OLE) and Visual Basic for Applications (VBA)
  - Cost estimation by directly linking the characteristic design parameters to results of process simulations

#### • Aim

Establish a unified and realistic basis in order to compare solvent and process alternatives for post-combustion CO<sub>2</sub>-capture & to identify the most promising option

#### **Post-Combustion CO<sub>2</sub>-Capture: Overview**





- 1. CO<sub>2</sub> Capture
- 2. CO<sub>2</sub> Compression
- 3. Power Plant Process
- 4. Overall Process

Source: Advanced Fossil Power Systems Comparison Study - NETL Modelling of CO<sub>2</sub>-Capture



- Simulation tool: ASPEN Plus
- Solvent: aqueous monoethanolamine (MEA) solution, 30 wt.-%
- Property method: *ELECNRTL* electrolyte non randomness two liquid model
- Insert for H<sub>2</sub>O MEA H<sub>2</sub>S CO<sub>2</sub> system: emea
  - ► Parameters tested against real life data for T < 125°C and x<sub>MEA</sub> < 50 wt.-%</p>
  - ► To be updated with data by Jou et al. (1995)

#### • Absorber & Desorber:

- Equilibrium (ASPEN: RadFrac vs. RateSep)
- Pressure drop: 100 mbar



#### • Simulation tool: ASPEN Plus



#### • Absorber & Desorber:

- Equilibrium (ASPEN: RadFrac vs. RateSep)
- Pressure drop: 100 mbar

### **Post-Combustion CO<sub>2</sub>-Capture: Overview**





CO<sub>2</sub> - Capture

- **CO**<sub>2</sub> **Compression**
- **Power Plant Process**
- **Overall Process**

### CO<sub>2</sub>–Compression Train



• Simulation tool: ASPEN Plus

#### • Technical data

- 2 parallel trains of similar geartype compressors with **5 radial stages** ( $\eta_i$ = 0,84....0,87)
- 1 **booster** unit (outlet pressure 110 bar;  $\eta_i = 0.82$ )
- electric drive (η<sub>el</sub> = 0,975)
- intercooler with water draw off after each stage ( $\Delta p_{hot side}$  = 100 mbar)
- aftercooler (outlet temperature 40°C)



### CO<sub>2</sub>-Compression Power Duty (1)





10<sup>th</sup> Workshop of the International Network for CO<sub>2</sub> Capture, May 2007, Lyon

► Modelling and Simulation: CO<sub>2</sub>-compression

### CO<sub>2</sub>-Compression Power Duty (1)





including all sub-processes: CO<sub>2</sub>-capture, CO<sub>2</sub>-compression and power plant process



-7.2 MW<sub>el</sub>

#### **Post-Combustion CO<sub>2</sub>-Capture: Overview**





<sup>1.</sup> CO<sub>2</sub> - Capture

- $CO_2$  Compression
- Power Plant Process
- 4. Overall Process

Source: Advanced Fossil Power Systems Comparison Study - NETL



#### Hard Coal: 600 MW (Reference Power Plant North-Rhine Westphalia)



#### **Post-Combustion CO<sub>2</sub>-Capture: Overview**





### **Overall process: LMTD & FG cooler**









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#### **Capital Expenditure - CAPEX**





Increase in specific investment costs (P<sub>el,gross</sub> = 1100 MW): approx. + 60 %

### **Operational Expenditure - OPEX**





#### **Costs of Utilities for CO<sub>2</sub> Scrubber**



- ▶ single circuit FGD: up to 95 %
- ▶ dual circuit FGD: up to 98 %
- addition of adipic acid in FGD: over 99,5 %



#### • MEA loss because of

- ▶ oxidisation
- thermal degradation
- slip to flue gas
- quantitative destruction by SO<sub>2</sub> and NO<sub>2</sub>
- Minimizing MEA loss by higher FGD efficiency

FGD efficiency	MEA loss
90 %	73 %
97 %	44 %
99 %	39 %

# Decrease of total OPEX (P<sub>el,gross</sub> = 1100 MW): approx. 12 %

### **Outlook (1)**



• Evaluation of the overall process to establish a unified and realistic basis for comparing solvent and process alternatives for post-combustion CO<sub>2</sub>-capture and identifying the most promising option

#### Alternative organic solvents

- Primary, secondary and tertiary amines and amie blends (e.g. Diglycolamin DGA, Diethanolamin DEA, Methyl-Diethanolamine MDEA)
- Sterically hindered amines (z.B. Amino-Methyl-Propanol AMP)

#### • Anorganic solvents and respective processes

- Chilled ammonia
- Potassium carbonate (potash) + promoter (e.g. piperazin, DETA)

#### **Outlook (2)**



#### • Heat integration of capture and compression into power plant process

- Heat duty and temperature levels depend on solvent, the associated process and the (optimised) configuration
- e.g.: cooled absorber for the chilled ammonia process
- Novel process configurations to optimise CO<sub>2</sub>-capture process
  - ▶ e.g.: split-flow, intercooled absorber, vacuum stripping, multi pressure stripping

#### Co-capture process

 Potential synergies and cost reductions associated with simultaneous capture of CO<sub>2</sub> and SO<sub>2</sub> (e.g. CANSOLV process), NO<sub>x</sub> and Mercury.

#### • Techno-economic analysis of all promising options



# Thank you for your attention!



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

# Development of New Amine Absorbents in COCS project

Lyon, France 24 May, 2007

# RITE

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



• COCS Project: (<u>Cost-Saving CO<sub>2</sub> Capture System</u>)



# Schedule and collaboration







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



CO2 capture energy (Q):  $Q = Q_R + Q_H + Q_V$ 










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



About 100 single amine solvents:

- Primary amines MAE MEA HN EAE AMP - Secondary amines PAE nBAE - Tertiary amines 'nн ОН DIPA DEA - Piperazine DMAE DEAE Ю - Piperidine (PR) сH **MDEA** DMA2P  $\mathbf{PZ}$ HD\_ - Poly-alykylene poly-amines 2AMPZ HN (TEPA, etc) TEA 2MPZ

Blended amine solvents:

- Mixture of 2 or 3 amines with different features









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

TOC (Total Organic Carbon analyzer)

$CO_2 / N_2$ gas:	20/80 %
Gas flow rate:	700 ml/min
Absorbent :	700 ml
Temperature :	40 - 120 °C
Pressure :	0.1 - 1 MPa





# **Calorimetry of CO2 absorption**



#### Measuring instrument:

- Calorimeter
   (RC-1e, Mettler
   Toledo)
- 1L reactorMeasuring condition:
- Semi-batch process (Absorption heat)
- Solvent: 500ml
- Gas: 100%CO2 250ml/min
- Temp: 40°C (Constant temp analysis)









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

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

Reboiler: Electric heater (0.6~2.1kW)

Experimental conditionGas volume6.5 m³/hL/G2~4 L/m³Stripper0.12~0.19MPa







### Summary



#### Results :

- Single and blended amine solvents were examined through lab-experiments.
- New absorbents showed higher-performance than MEA.

Research issues in the last 2 years of COCS project :

- Develop higher-performance absorbents.
- Evaluate CO2 capture in the steel works by new absorbents and waste heat use.



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

and carried out with collaboration from four companies:

- Nippon Steel Co. (NSC)
- Nippon Steel Engineering Co. (NSE)
- Mitsubishi Heavy Industries, Ltd. (MHI)
- The Kansai Electric Power Co., Inc. (KEPCO)



#### Integrated Regenerable SO<sub>2</sub> and CO<sub>2</sub> Capture

#### 10th MEETING of the INTERNATIONAL POST-COMBUSTION CO<sub>2</sub> CAPTURE NETWORK

**IFP, Lyons, France,** May 24-25, 2007

Leo Hakka, Chief Technology Officer

## **Cansolv Technologies at a Glance**

- Founded in 1997 (spin-off UCC SO<sub>2</sub> program
- 42 employees
- Seven SO<sub>2</sub> plants commissioned since 2002 in Europe, US, Canada, India
- Two SO<sub>2</sub> scrubbers under construction (Canada, China), four in design (South America, China, US)
- R&D focused on flue gas clean-up
- Business model: technology developer, licensor, special equipment & solvent supply



### **Technology Focus**



- Core platform process is CANSOLV SO<sub>2</sub> Scrubbing Selective amine scrubbing in an oxidative environment
- The Cansolv breakthrough in operating costs:
  - »low salt formation
  - »low amine degradation
  - »low heat of regeneration
- R&D Focus in 2000-2007 on developing high performance solvents for NOx, Hg & CO<sub>2</sub> absorption
- Commercialization Focus in 2005-2007: optimizing processes:

»CO<sub>2</sub> - SO<sub>2</sub>

# **Cansolv Commercial Units**



Application	Location	Appl.	Size (Nm3/hr)	Size MW <sub>equiv.</sub>	SO <sub>2</sub> Content	Emissions	Phase
Sulfur tail gas	Belgium	SO <sub>2</sub>	18,000	n/a	1 %	<30 ppm	Oper. since 2002
Zinc smelt. gas	Canada	SO <sub>2</sub>	5,600	n/a	8%	30 ppm	Oper. since 2002
Acid Tail Gas	US	SO <sub>2</sub>	45,000	n/a	3000 ppm	15 ppm	Oper. since 2002
FCCU Flue Gas	US	SO <sub>2</sub>	640,000	175	800 ppm	25 ppm	Oper. since 2006
Coker Flue gas	US	SO <sub>2</sub>	375,000	100	2000 ppm	25 ppm	Oper. since 2006
Lead Smelt.Gas	India	SO <sub>2</sub>	20,000	n/a	1 to 11 %	150 ppm	Oper. since 2005
Sulfur tail gas	US	SO <sub>2</sub>	32,000	n/a	4%	200 ppm	Oper. since 2006
Catalyst Roaster	Canada	SO <sub>2</sub>	48,000	n/a	9600 ppm	150 ppm	Forecast start 2007
Copper Smelter	China	SO <sub>2</sub>	42,000	n/a	19000 ppm/ 900 ppm	150 ppm	Forecast start 2007

# **CO<sub>2</sub> CAPTURE BACKGROUND**



- Amine scrubbing is the consensus benchmark process for CO<sub>2</sub> capture
- The deficiencies of current processes are high energy consumption, amine degradation by oxygen and inability to tolerate SO<sub>2</sub> in the feed gas
- The CANSOLV DeSO<sub>x</sub> process has very low energy use

and amine degradation

# CO<sub>2</sub> CAPTURE



- Building on this experience, CTI has demonstrated a novel CO<sub>2</sub> solvent at Laboratory & Pilot scale
- The solvent is fully stable to SO<sub>2</sub> simplifying feed gas preparation for CO<sub>2</sub> capture
- The proprietary solvent combined with engineering process optimization has resulted in a superior process

## CO<sub>2</sub> Capture Cont'd



Cansolv CO<sub>2</sub> Absorbent performance properties:

»Low regeneration energy: 60% of MEA
»Very low degradation compared to MEA
»Degraded material similar to original so it retains scrubbing capacity
»Fast kinetics: similar to primary amines
»Stable to SO<sub>2</sub>

# **Cansolv CO<sub>2</sub> Capture Flowsheet**





### **Cansolv Multipollutant Pilot Plant**



- New pilot unit commissioned on coal fired industrial boiler on Nov. 1<sup>st</sup> 2004.
- Four pilot tests on SO<sub>2</sub>, CO<sub>2</sub>, NOx and Hg
- Currently operating at Stavanger on CO<sub>2</sub> capture



# **CANSOLV Pilot Plant**





# **Costs for CO<sub>2</sub> Project Vary Project to Project**



- Capture and Compression
- Transmission
- Storage
- Total Cost Range

USD 25 - 35/t USD 5 - 10 USD 5 - 10 USD 35 - 55/t Source - IEA Greenhouse Gas R&D

- Capture and Compression
- Transmission
- Storage
- Total Cost Range

USD 15 - 75/t USD 1 - 8/t USD 0.5 - 8/t USD 16.5 - 91/t

Source - IPCC

**Costs are highly Project Specific** 

# **CANSOLV CO<sub>2</sub> Cost Basis**



#### **Utility Costs**

<ul> <li>Steam (3.5 barg)</li> </ul>	\$5.56/t
<ul> <li>Electricity</li> </ul>	<b>\$0.06/t</b>
<ul> <li>Cooling Water</li> </ul>	<b>\$0.04/t</b>
Cost of Canital	12%: 25 years

#### **300 MW Power Plant Feed Basis**

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- Inlet CO2 Content 11%
- CO2 Removal
- CO2 Captured (t/day)
- Flue Gas Flow

5,600

90%

**1.2 MM Nm3/hr** 

# CANSOLV Costs - 2.0 MMt/yr CO<sub>2</sub> 300 MW Plant - US Gulf Coast Basis



Capital Cost	<b>USD 180 MM</b>
»Cost of Capital @ 12%, 25 years	USD 12.30/t
<b>Operating Cost</b>	
» Maintenance and Labor	<b>USD 1.2 MM</b>
» Steam	<b>USD 12.2 MM</b>
» Cooling Water	<b>USD 2.5 MM</b>
» Electricity	<b>USD 2.1 MM</b>
» Solvent and Chemicals	<b>USD 1.0 MM</b>
» Total Op Cost	<b>USD 19.0 MM</b>
Sum of Capital and Op Cost	USD 22.3/t
<b>Compression Cost</b>	<b>USD 5.0/t</b>

# **Excerpt from OilGas 24 Scandinavian Oil and Gas Magazine**



Statoil, Shell assemble carbon frontrunners

courtesy Statoil

A mobile carbon-scrubbing construction will be tested in May at the Shell-Statoil carbon-dioxide project at Risavika, just outside Stavanger, it was learned Tuesday.

Canadian supplier Cansolv is one of three suppliers to the full-scale Halten CO2 project at Tjeldbergodden central Norway. Mitsubishi Heavy Industries and Fluor are the other carbon sequestration companies employed in the tests.

The companies are vying for a contract to stop 2.5 million tonnes a year from flowing into the atmosphere at a future 850 Megawatt gasplant on the Tjeldbergodden site...

... Cansolv is dwarfed by the two industrial giants, but "sits on solid knowledge on the separating of carbon from natural gas", although the plan is to separate 85 percent of the C02 from the power plant's exhaust passages.

 http://www.oilgas24.com/bm/Gas/statoil-shell-assemble-carbonfrontrunners.shtml

### **CO<sub>2</sub> Readiness to Commercialize**



- Identification of solvent classes -- Start 2000
- 4 field pilot tests -- March April & Nov. 2004; July & Aug, 2006; May - Aug. 2007
- 50 TPD demo plant design 2007
- Demo construction & start-up 2008
- Full commercial project engineering start 2007

# **CANSOLV Integrated SO<sub>2</sub> and CO<sub>2</sub>**



- Technology developed for fuel value based projects
- Takes advantage of cost differential between premium fuels and low value, high sulfur fuels
- Integrates absorbers into one vessel
- Integrates SO<sub>2</sub> regeneration with CO<sub>2</sub> regeneration
- The same solvent can be used for SO<sub>2</sub> and CO<sub>2</sub>
- Eliminates need for caustic polishing prior to CO<sub>2</sub> capture
- Cross-contamination of circuits of no concern

### **CANSOLV CO<sub>2</sub> and SO<sub>2</sub> Capture With Regeneration Steam Integration**





17

### Conclusions



- Cansolv Scrubbing Technologies are ready for application
- Experienced in regenerable amine flue gas treatment for SO<sub>2</sub>
- Developed more stable and energy efficient solvents for CO2
- Demonstrated at rates up to 700,000 Nm3/hr equivalent to 165 Mwe
- Piloting for specific applications is underway

# Reducing the Environmental impact of Acid gas Control Technologies -REACT

Karl Anders Hoff, Eirik Falck da Silva Odd Gunnar Brakstad and Kristin Rist Sørheim SINTEF Materials and Chemistry



# **Amine emissions**

- Evaporation losses.
- Emission of waste material from the solvent reclaimer.
- Condensate drainage in order to fulfill the water balance.





# **Classification of chemicals**

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

Commercial chemical solvents like MDEA/piperazine are classified as red
 Pollution authorities require these to be replaced by green or yellow alternatives for <u>offshore</u> application



# REACT

- Determine experimentally the ecotoxicity and biodegradability of a wide set of process chemicals.
- Develop understanding of degradation processes in both process and environmental conditions.
- Chemicals identified as promising shall be characterized by measurement of thermodynamical and kinetic data.
- New solvents will be implemented in a process modeling tool and simulations performed to assess the process performance and energy requirements.



# REACT





# **Solvent selection criteria**

- Regeneration energy requirement
- Rate of reaction/Mass transfer
- Cyclic capacity
- Molecular weight (per active site)
- Foaming properties
- Water solubility
- Molecular transport properties
- Vapor pressure
- Corrosivity
- Chemical stability
- Toxicity
- Cost and availability



# **Selection of chemicals for testing**

- 28 Candidates for first test campaign selected from
  - Alkanolamines known to be in commercial operation (MEA, MDEA, AMP, DEA etc.)
- New candidates deemed promising based upon earlier experience + molecular modeling studies
  - Cyclic amines
  - Linear polyamines
  - Sterically hindered amines
- A large database is required in order to correlate results with molecular structure!


# **Ecotoxicity studies**

- Ecotoxicity tests recognized by OSPAR and by Norwegian Pollution authorities
  - Phytoplankton: Skeletonema costatum (ISO/DIS 10253) all chemicals
  - Marine biodegradation test (OECD 306) all chemicals
  - Bioaccumulation testing calculations
  - Other bioassay studies
    - Microtox assay all chemicals
    - Response studies in Calanus finnmarchicus method development on selected chemicals



# Test methods Algae test (*Skeletonema costatum*)







# **Skeletonema – EC-50 results**

Skeletonema - EC50





. . . . . .

# Test methods Marine biodegradation test (BOD)



🕥 SINTEF





. . . . . .

# **Summary of results**





# **Bioaccumulation test**

- Chemical test to determine the distribution of a chemical between two immiscible phases; octanol and water
- The calculations were based on the difference between free energy of solvation in water (dGs<sub>water</sub>) and in the water-immiscible solvent octanol (dGs<sub>octanol</sub>).

$$Log P_{OW} = \frac{dGs_{water} - dGs_{oc \tan ol} x1000}{2.303 x 1.987 x 298}$$

Results: No tested chemicals were bioaccumulating (all water-soluble)



# **Calanus response studies**

- Calanus finnmarchicus-essential organism in the Atlantic ecosystem
- Cf are available as cultures in Trondheim

Calanus exposed to chemicals in sublethal concentration

Responses determined as up- or down-regulated gene activities in the organisms

Determination of essential toxicity responses/mechanisms caused by the chemicals





# Conclusions

- The amines tested show a relatively large span in both ecotoxicity and biodegradability
- Most tertiary and sterically hindered amines are red
- Of the candidates identified as yellow, several are promising activators
- Amines vulnerable to oxidation in post combustion plants (like MEA) also have a high biodegradability
- For natural gas sweetening the gas is not oxidative and it may thus be possible to find a candidate solvent fulfilling the requirements
- The relevance of these results for large scale post-combustion CO2 capture needs to be investigated further!



# **Acknowledgements**

 The REACT project is funded by the Research Council of Norway, through the strategic PETROMAKS programme
Co-funded by Shell Technology Norway and Statoil ASA





## Environmental impact of CO<sub>2</sub> capture in power plants Study carried out on behalf of IEA-GHG R&D Programme

Rene van Gijlswijk (TNO) Paul Feron (TNO) John Davison (IEA-GHG)

### **TNO | Knowledge for business**



## Environmental impact of CO<sub>2</sub> capture in power plants

- Objectives
- Methodology
- Results
- Conclusions
- Recommendations

## Objectives

Determining environmental impact of:

Electricity production in power plant

- With and without solvent absorption CO<sub>2</sub> capture
- Coal and natural gas based
- Direct fired and reformed/gasified



## **Environmental impact**

Accounted for:

- Direct, process related impact
  - Example power generation: emissions to air
  - Example CO<sub>2</sub> capture: emissions of solvent and degradation products
- Indirect impact: chain effects
  - Example power generation: depletion of fossil fuel, emissions during production of fuel
  - Example CO<sub>2</sub> capture: production of solvent, 'energy penalty', final waste sludge
- >> "Cradle to grave" approach: Life-Cycle Assessment (LCA)

Linear model (time and place of e.g. releases are disregarded)



## System boundaries

Starting point: production of 1 MWh of electricity in coal or natural gas fired power plant

### Processes regarded:

- Mining, separation, cleaning and grinding of fuel
- Fuel conversion (some scenarios)
- Power generation
- Flue gas cleaning
- Solvent production
- CO<sub>2</sub> scrubbing processes
- Avoided CO<sub>2</sub> emission
- Compression
- Treatment of waste

### Excluded:

- CO<sub>2</sub> transport and storage
- Additives in solvents (data gap)





Inventory





Impact assessment

Use of raw materials and emissions to air, water, soil are translated to ...

 Depletion of abiotic resources (minerals, fossil fuels)

... using substance-specific effect factors

- Global warming
- Ozone depletion
- Acidification

- Eutrophication
- Human toxicity
- Ecotoxicity (2)
- Summer smog

Impact categories

(CML-LCA2 methodology [Guinée et al., 2001])

#### Lyon, May 24, 2007



7 Methodology

Result of former sheet: one environmental profile per case = nine figures, each representing an impact category

### Enables us to identify:

- to which environmental problems the case contributes most (normalization step required)
- on a per impact category basis: which case causes less environmental burden

Direct total comparison of cases is not possible without weighing



Weighing: 9 impact categories >> single environmental indicator

That enables direct comparison of the cases (but introduces additional uncertainty)

Shadow price methodology:

Marginal cost [per unit of environmental burden] that is paid for the 'last' most expensive kg of mitigation to reach Dutch policy goals for a certain impact category

### Source: [TNO, CE]

9 Methodology



## Cases

No.	Abbrev.	Fuel	Description
1	NGCC	Natural gas	Direct fired
2	NGCC+	Natural gas	Direct fired, post combustion CO <sub>2</sub> capture
3	POCC	Natural gas	Partial oxidation
4	POCC+	Natural gas	Partial oxidation, precombustion CO <sub>2</sub> capture
5	USCPF	Pulverized coal	Direct fired
6	USCPF+	Pulverized coal	Direct fired, post combustion CO <sub>2</sub> capture
7	IGCC	Pulverized coal	Gasification
8	IGCC+	Pulverized coal	Gasification, precombustion CO <sub>2</sub> capture

## Information sources

Data power plants and solvent scrubbing: Studies carried out on behalf of IEA-GHG by:

- Fluor
- Foster Wheeler
- Jacobs Consultancy

Background data: (production of chemicals, waste treatment, aux.)

- Ecoinvent 2000 version 1.2 (commercially available) Preparation of fuels, production of base chemicals
- TNO modelling waste treatment
- Toxicity of solvent releases: Radboud University Nijmegen

Methodology: Life Cycle Assessment – CML (University of Leiden) Shadow prices – TNO, CE



## NGCC (natural gas, direct fired), with & without capture



12 Results

## POCC (natural gas, reformer), with & without capture



All impact categories (except global warming): increased fuel consumption

Lyon, May 24, 2007



## USCPF (pulverized coal, direct fired), with & without capture



14 Results

## IGCC (pulverized coal, gasification), with & without capture



All impact categories (except global warming): increased fuel consumption

## Net CO<sub>2</sub> reduction

- Additional fuel consumption, production solvent etc. decrease the effective CO<sub>2</sub> reduction
- Calculated with CO<sub>2</sub> scrubbing efficiency approx. 85%
- Net CO<sub>2</sub> emission reduction (in GWP<sub>100</sub>):

NGCC	80%
POCC	79%
USCPF	73%
IGCC	72%



## Weighed results: environmental indicator (1)



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Results

## Weighed results: environmental indicator (2)



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## Conclusions (1)

• Additional environmental impact of CO<sub>2</sub> capture:

- energy consumption of stripper and reclaimer
- production of solvent
- Environmental benefits of CO<sub>2</sub> capturing:
  - avoided CO<sub>2</sub> emission, obviously
  - decrease of acidification and summer smog (USCPF plant)
- Based on information available: solvent releases and reclaimer waste disposal play minor role – though, more research desirable

## Conclusions (2)

Based on weighed results,

- fitting new power plants with CO<sub>2</sub> capturing leads to a net positive environmental impact (over current state of the art)
- remaining impact is slightly less for reformer/gasification plants
- natural gas fired plants have lower shadow costs than PC fired plants, even lower than PC with capture
- natural gas fired plants: impact dominated by global warming (and human toxicity)
- pulverized coal fired power plants: impacts dominated by global warming and acidification due to direct emissions and coal preparation



## Recommendations

How to achieve reduction of environmental impact of CO<sub>2</sub> scrubbing ?

- development of more energy efficient solvents and solvent processes compared to MEA
- reduction of solvent consumption
- development of alternative capture processes not requiring any additional consumables (chemicals)

Publicly available information on env.impact of CO<sub>2</sub> scrubbing is scarce; more information is desirable regarding:

- Emissions to air of solvent and decomposition products; amount and composition of 'cocktail'
- Characterization of waste streams; amount and composition



## Questions?

Lyon, May 24, 2007



## Shadow price: how is it established?



In a virtual market, demand for environmental damage limitation and supply of emission mitigation by measures will result in an equilibrium price for environmental quality. If a government's emission objective crosses the equilibrium point, the shadow price is optimal and equal to the equilibrium price.

# Shadow prices

Environmental Impact Category	Equivalent unit	Shadow price [€ / kg equivalent]	Damage [billion €]	Source
Abiotic depletion – ADP	Sb eq	€0	0.0	TNO
Climate change – GWP100	CO <sub>2</sub> eq	€ 0.05	11.5	CE
Ozone layer depletion – ODP	CFC11 eq	€ 30	0.03	CE
Human toxicity – HTP	1,4-DCB eq	€ 0.08	4.0	TNO
Fresh water aquatic ecotoxicity – FAETP	1,4-DCB eq	€ 0.04	0.1	TNO
Terrestrial ecotoxicity – TETP	1,4-DCB eq	€ 1.3	0.9	TNO
Photochemical oxidation – POCP	$C_2H_2$ eq	€2	0.4	CE
Acidification – AP	SO <sub>2</sub> eq	€4	2.8	CE
Eutrophication– EP	PO <sub>4</sub> eq	€9	0.5	CE

Д.





# **Chilled Ammonia Process Update**

Richard Rhudy, EPRI Sean Black, ALSTOM CO<sub>2</sub> Capture Network May 24, 2007 Lyon, France



# Schematic of the Chilled Ammonia **Process**




## **Advantages of Ammonia**

- Energy efficient capture of CO<sub>2</sub>
- High capacity for CO<sub>2</sub> per unit of solution
- High pressure regeneration
- Low heat of reaction
- Low cost reagent
- No degradation during absorption-regeneration
- Tolerance to oxygen and contaminants in gas

### **Ammonia Process Innovations**

- Cooling the flue gas to 0-10°C
  - Condensing  $H_2O$  and eliminating residual contaminants
  - Reducing flue gas volume and increasing CO<sub>2</sub> concentration
- Operating the absorber at 0-10°C for high CO<sub>2</sub> capture efficiency with low NH<sub>3</sub> emission
- Regeneration at >120°C and >20 bar to generate high pressure CO<sub>2</sub> stream with low moisture and ammonia concentration

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## Chilled Ammonia Scrubber Development Program

- Step 1 Small bench scale testing at SRI International
  - Work co-funded by ALSTOM, EPRI and Statoil
- Step 2 Large bench scale testing at SRI International
  - Work co-funded by ALSTOM, EPRI and Statoil
- Step 3 Field pilot testing at We Energies
  - Work co-funded by ALSTOM and EPRI
- Step 4 Commercial Demonstration at AEP Mountaineer

### Step 1 – Small Bench Scale Testing Key Objectives

- Establish thermodynamic potential
  - Testing of absorber and regenerator
- Generate data to support initial techno-economic analysis
- Identify key issues to be addressed in later development stages

### **Small Bench Scale Testing Picture of Absorber System**





### **Small Bench Scale Testing** 10" D, 6ft H, Bubbler reactor





### **Small Bench Scale Testing Techno-Economic Analysis**

	Supercritical PC Without CO <sub>2</sub> Removal	SCPC With MEA CO₂ Removal Parsons Study	SCPC With NH <sub>3</sub> CO <sub>2</sub> Removal Current Study
Total power plant cost, M\$	528	652	648
Coal Feed rate, lb/hr	333,542	333,542	333,542
Coal heating value, Btu/lb (HHV)	11,666	11,666	11,666
Boiler heat input, MMBtu	3,891	3,891	3,891
LP Steam extraction, lb/hr for reboiler	0	1,215,641	179,500
Steam Turbine Power, kWe	498,319	408,089	478,319
Generator loss, kWe	(7,211)	(5,835)	(7,018)
Gross plant, kWe	491,108	402,254	471,301
Plant Auxiliary Load (IDF, FGD, BFW pumps, Water pumps, Cooling Towers, CO2 unit, Chillers, CO2 compressor, BOP), kWe	(29,050)	(72,730)	(56,050)
Net Power Output	462,058	329,524	415,251
Avoided Cost, \$/ton CO2	Base	51.1	19.7



### **Step 2 - Large Bench Scale Testing** Key Objectives

- Demonstrate potential to achieve 90% CO<sub>2</sub> capture efficiency for 3.5, 8, 15% CO<sub>2</sub> concentrations
- Demonstrate low ammonia emission
- Measure mass transfer
- Optimization of absorber design and operating conditions
- Provide data to support the design of the 5 MW pilot

### Large Bench Scale Testing Process Flow Diagram for Absorber System



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## Photo of the Absorber and Water Wash System



### **Large Bench Scale Testing** Photo of the CO2 Gas Delivery System



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### **Large Bench Scale Testing Photos of Chiller and Dry Condensing System**







### Large Bench Scale Testing Key Conclusions of Absorber Testing

- Rate of CO<sub>2</sub> absorption/mass transfer is acceptable
- Absorber operates at low recycle rate and low pressure drop
- Generated bicarbonate solids are easy to handle
  - No fouling or scaling has been observed
- NH<sub>3</sub> emission from absorber is acceptable
  - Agrees well with equilibrium modelling
- Water wash performance is good
  - Low NH<sub>3</sub> emissions are obtained
  - Acid wash reduces emission to extremely low levels



### **Large Bench Scale Testing Schematic and Photo of the Batch Regeneration System**







### **Step 3 - Field Pilot at We Energies** Key Objectives

- Validate operation of the entire system on actual flue gas
- Measure heat of reaction to compare against theoretical values
- Develop and evaluate the process control logic and operating system
- Operate the system in long-term tests to identify O&M issues and establish system reliability
- EPRI to develop a techno-economic analysis to scale up the system for commercial applications

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ALST

### **Field Pilot at We Energies Project Summary**



### Field Pilot at We Energies Proposed Pilot Location





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## **Field Pilot Duct Tie-In Locations on** Unit 2







### Field Pilot at We Energies 3-D View of Proposed Pilot





#### Questions





# Ammonia scrubbing technology for CO<sub>2</sub> capture

Wang Shujuan Department of Thermal Engineering Tsinghua University May 24, 2007

## Our group-ECANE





**Prof. Xuchang Xu** 



**Prof. Changhe Chen** 



Yan Li



Yuqun Zhuo



**Huiling Tong** 



Shujuan Wang





- Introduction
- Ammonia Scrubbing: general
- Ammonia Scrubbing: Tsinghua University
- Solar energy used for CO<sub>2</sub> capture
- Conclusions



## Introduction: primary energy consumption of China (Mtce)



1980-1984: low increasing of energy consumption due to decreasing proportion of secondary industry

1985-1996:accelerating increasing of energy consumption due to the light industry expansion

1996-2000: energy consumption increasing fluctuation

2000-2005: acceleating increasing of energy consumption





#### Primary energy consumption mix



#### Main indicators comparison









## **Carbon emission and intensity**



Carbon emission: 1980 387MtC, 2005 1376MtC, AGR 5.2% Intensity: 1980 2.35KgC/US\$, 2005 0.81KgC/US\$, ADR 4.2%



- $(NH_4)_2CO_3 \leftrightarrow CO_2 + 2NH_3 + H_2O$
- $NH_4HCO_3 \leftrightarrow CO_2 + NH_3 + H_2O$
- $\square (NH_4)_2CO_3 + CO_2 + H_2O \leftrightarrow 2NH_4HCO_3$  $\blacksquare 2NH_4HCO_3 \leftrightarrow (NH_4)_2CO_3 + CO_2 + H_2O$
- $\square \text{ NH}_4\text{HCO}_3 + \text{NH}_4\text{OH} \leftrightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}_3$
- $\Box \operatorname{NH}_3 + \operatorname{H}_2 O \leftrightarrow \operatorname{NH}_4 OH$
- $\Box \text{ NH}_2\text{COONH}_4 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4\text{HCO}_3 + \text{NH}_3$
- $\Box CO_2 + NH_3 \leftrightarrow NH_2COONH_4$
- $CO_2 + NH_3 + H_2O \leftrightarrow NH_4HCO_3$

## Ammonia scrubbing technology: general





## Ammonia scrubbing technology: general

### Comparing with MEA

- Loading capacity
  - $\square$  NH<sub>3</sub>: 1kgCO<sub>2</sub>/kg NH<sub>3</sub>
  - □ MEA: 0.35kgCO<sub>2</sub>/kg MEA
- Removal efficiency
  - □ NH<sub>3</sub>: 99%
  - □ MEA: 94%
- Byproducts recoverability
  - □ NH<sub>3</sub>: easy
  - MEA: difficult



### Ammonia scrubbing technology: general



#### Economic assessment by NETL



图1 电价上升的百分比







#### Semi-batch reactor







# Ammonia scrubbing technology: Tsinghua



#### Continuous reactor











Combined removal of CO<sub>2</sub>/SO<sub>2</sub>







CO2 removal efficiency as a function of reaction time for various  $CO_2$  concentrations. The operating conditions were at  $CO_2$  inlet concentration of 10%, 12%, 14% (v/v), water bath temperature of 28°C, and ammonia concentration of 0.140mol/l.

CO2 removal efficiency as a function of reaction time for various ammonia solution concentrations. The operating conditions were at  $CO_2$  inlet concentration of 12%(v/v), water bath temperature of 28°C




 $CO_2$ ,  $SO_2$  removal efficiency as a function of reaction time.

Operation conditions: temp. of water bath 45°C , temp. of water steam 50°C

Concentration of  $SO_2$  is 3000ppm, concentration of  $CO_2$  is 10%

 $CO_2$ ,  $SO_2$  removal efficiency as a function of reaction time.

Operation conditions: temp. of water bath 55°C , temp. of water steam 50°C

Concentration of  $SO_2$  is 2500ppm, concentration of  $CO_2$  is 12%

# Ammonia scrubbing technology: Tsinghua Life Cycle CO<sub>2</sub> Emissions

**Combined System** 

Separated System





# Ammonia scrubbing technology: Tsinghua System Simulation

- Absorption Column
  - □ Aspen Plus<sup>™</sup> unit: RADFRAC
  - 10 equilibrium stages
  - □ No condenser or roboiler
- Desorber Column
  - □ Aspen Plus<sup>™</sup> unit: RADFRAC
  - 2 equilibrium stages
  - No condenser
  - Reboiler: Kettle
- Adopted Property
   ELECNRTL

# Ammonia scrubbing technology: Tsinghua System Simulation













# Solar energy used for CO<sub>2</sub> capture

 $CO_2 + 2NH_3 \leftrightarrow NH_2COONH_4$ 









## Combined removal of CO<sub>2</sub>/SO<sub>2</sub>/NO<sub>x</sub>/Hg









## Ammonia based membrane contactor







Carbon sequestration in ecosystem

- Carbon existing form, and transform between and dependence on different forms
- Carbon distribution among soil, plant, water, atmosphere, when ammonia bicarbonate is used as fertilizer
- □ The impact of ammonia bicarbonate on soil









# New Solvent for CO<sub>2</sub> Capture with Low Energy of Regeneration

P.-L. Carrette, R. Cadours, P. Boucot, P. Mougin, M. Prigent, A. Gibert., <u>M. Jacquin</u>

Innovatior Energy

Environment



How to reduce CO<sub>2</sub> emissions ?

- Pre-Combustion Capture
- Oxy-Combustion
- Post-Combustion Capture (advanced technology)
  - High flow rate of flue gas
  - → Low  $CO_2$  partial pressure
  - →■ 90 % CO<sub>2</sub> capture

Chemical Solvent ≡

High Energy Requirement

• Reference Case (30%wt. MEA) : E ~ 3,9 GJ/t<sub>CO2</sub>

→ Targeted Solvent : E ~ 2 GJ/t<sub>CO2</sub>







- ... is the sum of the energies needed to :
- heat the solvent to boiling point (sensible heat)
- break the chemical bond
   (enthalpy of reaction)
- generate the steam for CO<sub>2</sub> stripping (energy of stripping)





## State of the art

Primary Amine	<b>0</b> 00	$CO_{2(aq)} + 2 R_2 NH \longrightarrow R_2 NHCOO^- + R_2 NH_2^+$
Hindered Amine		$CO_{2(aq)} + 2 Z_2 NH \longrightarrow Z_2 NHCOO^- + Z_2 NH_2^+$ $H_2 O \qquad K_c = \frac{[Z_2 NCOO^-]}{[Z_2 NH][HCO_3^-]} < 0,1$
Tertiary Amine		$HCO_{3}^{-} + \mathbb{Z}_{2}NH$ $CO_{2(aq)} + \mathbb{R}_{3}N + H_{2}O \longrightarrow HCO_{3}^{-} + \mathbb{R}_{3}NH^{+} \qquad \kappa_{c} = 0$
	<b>O o o o o o o o o o o</b>	In a general manner, the enthalpy of reaction $\Delta H$ increases with pKa and Kc of the amine.
		At low $CO_2$ partial pressure, the cyclic capacity $\Delta \alpha$ increases with pKa and Kc of the amine. Then, the sensible heat is reduced.



## State of the art

MEA Primary		$CO_2 + 2 H_2N$ $OH$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$ $HO$
Amine	00	High Energy of Regeneration :
	• • •	• Low Sensible Heat / High Capacity : $\Delta \alpha \sim 0.25$
	00	• High Enthalpy of Reaction : $\Delta H \sim 80 \text{ kJ/mol}$
		High Energy of Stripping
MDEA Tertiary Amine		$CO_2 + H_2O + HO $ $N_1 \rightarrow HCO_3 + HO $ $N_1 \rightarrow OH$
	00	Lower Energy of Regeneration :
		• High Sensible Heat / Low Capacity : $\Delta \alpha \sim 0.15$
	00	• Low Enthalpy of Reaction : $\Delta H \sim 50 \text{ kJ/mol}$
		Low Energy of Stripping
	0 0	
	00	The sensible heat and enthalpy of reaction are closely
	00	related. An optimum can be found but how low is it?

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## New concept of solvent



### amine + H<sub>2</sub>O + CO<sub>2</sub> ↔ ammonium salts

- 1) regeneration of a fraction of the solvent
- 2)  $CO_2$  rich phase has an "abnormal" loading for a  $CO_2$  partial pressure of 0.1 atm.

Lower energy of regeneration



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## Process Design 1/ ABSORBER

Clauspol<sup>®</sup> : Claus tail gas treatment unit

 $H_2S$  elimination process in organic phase, leading to a phase separation of liquid sulfur produced (T>MP).

 $2 H_2 S + SO_2 \xrightarrow[T=125]{organic phase} 3 S_{(liquid)} + 2 H_2O$ 35 years experience in gas treatment 40 Clauspol<sup>®</sup> references worldwide

#### DMX : CO<sub>2</sub> capture unit

CO<sub>2</sub> capture process in postcombustion, leading to a phase separation of ammonium salt at a critical loading.

amine +  $H_2O$  +  $CO_2$   $\longrightarrow$  ammonium salts







(



## **Process Design 2/ DECANTER**

Clauspol<sup>®</sup> : Claus tail gas treatment unit

 $H_2S$  elimination process in organic phase, leading to a phase separation of liquid sulfur produced (T>MP).

 $2 H_2S + SO_2 \xrightarrow[T=125]{organic phase} 3 S_{(liquid)} + 2 H_2O$ 35 years experience in gas treatment 40 Clauspol<sup>®</sup> references worldwide

#### DMX : CO<sub>2</sub> capture unit

CO<sub>2</sub> capture process in postcombustion, leading to a phase separation of ammonium salt at a critical loading.

amine +  $H_2O$  +  $CO_2$   $\implies$  ammonium salts







0

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## **Process with DMX Solvent**



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## Process with DMX1





## Process with DMX2





## **Energy of regeneration**

Calculation of energy of regeneration, simple model based on :

- Vapor Liquid Equilibrium
- Analysis of liquid phases
- Enthalpy of reaction (calorimetric measurements)

	Enthalpy of	Sensible Heat	Energy of
	Reaction	∆T = 15°C	Stripping
	(GJ/t <sub>CO2</sub> )	(GJ/t <sub>CO2</sub> )	(GJ/t <sub>CO2</sub> )
MEA	<b>1.8</b>	<b>1.1</b>	~1
	(∆H ~ 80kJ/mol)	(Δα ~ 1.5mol/kg)	(Reflux Ratio~2)
DMX1	1.3	<b>1.2</b>	< 0.5
	(∆H ~ 60kJ/mol)	(∆CO <sub>2</sub> ~ 1.4mol/kg)	(Reflux Ratio<1)
DMX2	<b>1.4</b> (∆H ~ 63kJ/mol)	$\begin{array}{c} \textbf{0.5} \\ (\Delta \text{CO}_2 \sim \textbf{2.7mol/kg}) \end{array}$	< 0.5 (Reflux Ratio<1)

due to the "abnormal" loading for a  $CO_2$  partial pressure of 0.1 atm. and increase of the temperature



AIE – 05/24/2007 - Department of Separation - IFP

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## Conclusion

### Original concept combined with a standard technology :

Process close to standard amine treating processes

+ decanter

#### Interest of the concept :

Two solvents with energy of regeneration, lower than **2.5 GJ/t CO<sub>2</sub>** Complete economical analysis in progress

Still looking for improved performances...







## Study on Multiphase CO<sub>2</sub> Capture with Immobilised Activator

Xiaohui Zhang\*

David W. Agar University of Dortmund

24th May 2005, Lyon

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- Motivation
- CO<sub>2</sub>-capture technologies

## Section 2018 Section 2018 Section 2018

- G/L/S
- G/S
- L/S
- G/S S/L

## Sconclusions & Outlook



## CO<sub>2</sub> absorption in amine mixtures (conventional process)



Theoretical Background

slide 4













**Immobilised Amine** 



polystyrene, macroporous diameter: 0.5 – 1.0 mm density: 1.092 g/ml





gas  $\rightarrow$  solid  $\rightarrow$  liquid

gas  $\rightarrow$  liquid  $\rightarrow$  solid  $\rightarrow$  liquid

Mechanisms for gas-liquid-solid system

slide 9



Mechanisms for gas-liquid-solid system

slide 10



gas  $\rightarrow$  solid  $\rightarrow$  liquid

Mechanisms for gas-liquid-solid system

slide 11







**Experiments in a Aerated Stirred Tank Reactor** 

slide 13


**Results of the Aerated Stirred Tank Reactor** 

slide 14







**Experiments in a Gas-Solid Fixed-Bed Reactor** 

#### slide 16



**Results of the Gas-Solid Fixed-Bed Reactor** 

slide 17







**Experiments in a Liquid-Solid Fixed-Bed Reactor** 

slide 19

#### **Experimental Setup**





#### **Influence of Concentration**









Measured kinetic parameters at 298 K

Mass trans	fer process	k <sub>eff</sub> (10 <sup>-8</sup> m/s)	K <sub>eff</sub> a (10 <sup>-4</sup> 1/s)	assessment
Gas-solid	Adsorption	instantaneous	instantaneous	Instantaneous
Gas-liquid	Absorption	3600	1458	Slow 📈
Liquid-solid	Adsorption	15.4	6.2	Rate-limiting
Solid-liquid	Desorption/ regeneration	5.6	2.3	Rate-limiting



### **Comparision of the two mechanisms**

gas  $\rightarrow$  liquid  $\rightarrow$  solid  $\rightarrow$  liquid

gas  $\rightarrow$  solid  $\rightarrow$  liquid

н

н

solid





#### Periodic operation of trickle bed



**Results of the Periodic-Operated Fixed-Bed Reactor** 

slide 25



 the natural pulsing flow regime marginal effect







**Film-pore diffusion model** 

slide 28

#### Shrinking Core model or Unreacted-core model

Yagi, S., and Kunii, D. Chem. Eng. Sci., 16,364, 372, 380 (1961) Levenspiel O. Chemical Reaction Engineering, Wiley, New York, (1972)

#### Mass balance in the particle:

$$\varepsilon_{p} \frac{\partial C}{\partial t} = \frac{1}{r^{2}} \frac{\partial}{\partial r} \left( r^{2} D_{p} \frac{\partial C}{\partial r} \right) - \rho_{p} G(C, q)$$
$$\frac{\partial q}{\partial t} = G(C, q)$$

Mass balance in the fixed bed:

$$\varepsilon_{b} \frac{\partial C_{b}}{\partial t} = D_{b} \frac{\partial^{2} C_{b}}{\partial z^{2}} - \varepsilon_{b} V \frac{\partial C_{b}}{\partial z} - \left(\frac{3}{R}\right) \left(\frac{m_{p}}{\rho_{p}}\right) D_{p} \frac{\partial C}{\partial r}\Big|_{R}$$

#### Boundary condition:

Dp

K<sub>f</sub>

C<sub>b</sub>

 $\mathbf{C}_{\mathbf{s}}$ 

$$r = R; \quad k_f (C_b - C) = D_p \frac{\partial C}{\partial r} \Big|_{R}$$

adsorbed region

liquid film

CO2 free region

concentration-front



#### Measured kinetic parameters at 298 K

CO <sub>2</sub> Conc. [mol/m <sup>3</sup> ]	k_film [10 <sup>-5</sup> m/s]	D_pore [10 <sup>-9</sup> m²/s]	Bi = <u>k_film-d</u> 2D_pore
39.6	4.0	0.900	16.7
25.0	6.0	0.870	25.9
16.0	5.5	1.125	18.3

#### Pore diffusion is more limiting than film mass transfer







- Liquid phase on the surface and in the pore is ratelimiting step
- Centrifuge can only make the liquid on the surface away
- After vacuum the particle is totally free of liquid and reaction is much faster

# Summary

slide 32

### Summary

- Absorption can be accelerated by immobilised activators
- Chemical ,shuttle' mechanism *via* carbamate formation
- Higher mass transfer resistance in the liquid phase
- Centrifuge Reactor can only remove the surface liquid
- Enhancement of carbamate hydrolysis necessary
- Wettability Modification of Immobilised Amine
- Udea : Hydrophobic Immobilised Sterically Hindered Amines









#### **Research group:**

Prof. Dr. Agar Dr. M. Grünenwald Dr. Schubert M.Sci. Yudy Tan

#### **Diplom- & Masterstudenten:**

Jan Mackowiak Nuthakki Seshagiri Rao Yozi Bastian

#### **Techniker:**

Micheal Schlüter Julian Gies



## **Max-Buchner Stiftungen**







Thanks for your attention!

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#### Introduction

1 t/h CO<sub>2</sub> absorption pilot plant

- Build as a part of the EU sponsored CASTOR project
- Purpose: To validate the post combustion capture concept and to test novel solvents
- Location: Esbjerg Power Station, Denmark (DONG Energy)
- Pilot plant erected and commissioned during 2005

**Operation history** 

- First test campaign 1000 hours using 30 % MEA (Jan.-Mar. 2006)
- Second test campaign 1000 hours using 30% MEA (Dec.-Feb. 2006/07)
- Third test campaign using a novel solvent "CASTOR 1" (on-going)



#### Host: CASTOR pilot plant

**Esbjerg Power Station** 

- 400 MW<sub>e</sub> pulverized-coal
- Firing bituminous coals
- Wet-FGD + HD-SCR



#### **Pilot plant specifications**

- Pilot plant operates on a slip stream taken directly after the FGD
- Flue gas conditions: ≈47℃ saturated, <10 ppm SO<sub>2</sub>, <65 ppm NO<sub>x</sub>, <10 mg/Nm<sup>3</sup> dust

Key design parameters

Parameter	Design value
Flue gas capacity	5000 Nm <sup>3</sup> /h
CO <sub>2</sub> production (at 12% CO <sub>2</sub> )	1000 kg/h
Absorption degree	90%
Max solvent flow	40 m <sup>3</sup> /h
Max reboiler steam flow	2200 kg/h (3.5 bar)
Max stripper pressure	2 bar (g)





#### **Pilot plant flow diagram**





#### **Test programme 2<sup>nd</sup> MEA campaign**

- Test 1 Parameter variation (12/12/06 05/01/07)
  - a) Optimisation of solvent flow rate (at 90% capture)
  - b) Variation of reboiler steam input at optimum solvent flow
  - c) Variation of stripper pressure (at 90% capture)
- Test 2 500 hours of continuous operation (15/01/07 06/02/07)
  - Operation at "optimised" conditions
  - Achieving 90% CO<sub>2</sub> capture (on average)
  - Characterisation of corrosion behaviour
- Test 3 Emission measurements (06/02/07 07/02/07)
  - Operation at optimum flow rate (similar settings as Test 2)
  - Gas sampling at absorber and stripper outlets



#### **General results and improvements 2<sup>nd</sup> MEA campaign**

## Compared to the first MEA Campaign several improvements have been made:

- Plant operation at close to neutral water balance, thus no excess condensation of water from the flue gas
- Better quantification of steam requirements and good closure on energy balances
- Improved closure on CO<sub>2</sub> balances (gas and solvent side)
- More time allowed to reach steady state operation
- Fewer plant outages



#### **Summary 500 hours test**

- Continuous operation from Jan 15<sup>th</sup> to Feb 7<sup>th</sup> (550 hours)
- Plant operated at "optimised" settings
- 1 outages during the test (power plant failure). Total down time: ≈4 hours
- No MEA was added during campaign (MEA: 31 => 29 %-wt.)
- No reclaiming during the test (not necessary)



#### 500 hours test – CO<sub>2</sub> recovery and steam consumption



"Optimised" conditions MEA flow: 15.5 m<sup>3</sup>/h P<sub>stripper</sub>: 1.85 bar(a) T<sub>reboiler</sub>: 120.5°C

> **DONG** energy

#### **Results 500 hours test – Mass & Energy balances**

Stream avg. value CO<sub>2</sub> balance: CO<sub>2</sub> absorbed - gas side 960 (kg/h)CO<sub>2</sub> desorbed - gas side 1040 H<sub>2</sub>O balance: H<sub>2</sub>O condensed from flue gas -38 (kg/h)Make up  $H_2O$  to abs. wash 70  $H_2O$  input with  $CO_2$  product -13 Drain of stripper condensate n.d. Total: +20

Material balances (15/01/07 - 07/02/07)

Energy balance (15/01/07 - 07/02/07)

Heat (GJ/ton CO <sub>2</sub> )	avg. value
Heat input from steam	3.75
Heat from flue gas	-0.15
Cooling water	-3.39
Total energy balance	+0.21 (6 %)



#### 500 hours test – Solvent consumption & degradation

#### Results

- MEA consumption: 0.8 kg/ton CO<sub>2</sub>
- ΔHSS approx. 1 %-point during 500h test
- 1–110 ppm: Cl, Ca, K, Mg, Na, P & Si
- 1 ppm: Cr, Cu, Mo, Ni, Pb & V



Heat stable salts (HSS), iron & sulphur



#### **Implications for scale up – Some initial thoughts!**

- Emissions and water wash
- Process dynamics
- Particulate removal and solvent purification

#### **Implications: Emissions & water wash**

- Neutral water balance implies that temperatures of flue gas in and out should be similar
- Higher water wash temperature => higher emissions
- Addition of (external) make-up water in wash => higher flue gas outlet temperature to achieve neutral balance
- Emission measurements: ≈25 mg/Nm<sup>3</sup> NH<sub>3</sub>
- Implications: Additional water wash (adiabatic) or cool flue gas in direct contact cooler upstream absorber





#### **Implications: Process dynamics**



"Optimised" conditions MEA flow: 15.5 m<sup>3</sup>/h

DONG

energy

Doc. info
#### **Implications: Process dynamics (2)**

System response to step change in CO<sub>2</sub> inlet concentration





Doc. info

#### **Implications: Solvent purification**

- Amine scrubbers downstream limestone based FGDs will be exposed to fine particulate
- Complicated (and expensive) to remove fine particles with an in-stream filter
- Reclaiming by distillation removes particulates (only MEA process)
- Visual inspection of plant indicate very little deposition on packing and other surfaces
- Implications: Slipstream filtration of solvent







### Conclusion

A second 1000 hours campaign using 30 % MEA has been conducted at the CASTOR pilot plant in Esbjerg. The campaign indicated:

- Stable operation on coal-derived flue gas is possible
- Possible to operate at neutral water balance
- MEA: specific steam consumption of 3.75 GJ/ton CO<sub>2</sub> at 90% removal
- Neutral water balance may increase emissions
- "Optimal" operating conditions with respect to energy consumption may not be optimal in daily practice
- Slipstream filtration may be the best method to remove gypsum and fly ash particles

#### Acknowledgement

The pilot plan at ESV is sponsored by the CASTOR partners and the European Commission through the CASTOR project. The authors would like to express their gratitude to all the sponsors and the staff at ESV.



# Overview of the CO2CRC Capture Program

Paul Webley Monash University

Lead Researcher Cooperative Research Centre for Greenhouse Gas Technologies

10<sup>th</sup> International Post-Combustion CO2 Capture Network Meeting 24-25<sup>th</sup> May 2007 IFP Lyons, France









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## **CO2CRC** Participants



Supporting participants: Australian Greenhouse Office | Australian National University | | CANSYD | Meiji University | The Process Group | University of Queensland |



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**CO2CRC** Programs

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Initial LETDF project announcements

# -Over \$A 2 billion

- First tranche Wed 25<sup>th</sup> Oct
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• Linked to two separate ETIS LSDP/LETDF projects

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Post Combustion project is a joint project between Loy Yang Power and CO2CRC
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# **Scope of Program**







## **CO2 Capture by Adsorptive Processes**

- Adsorbents exist (and can be developed) to selectively adsorb CO2 from process streams
- CO2 is removed by reduction in pressure (regeneration)
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# CO2 Capture: Post Combustion – Major Challenges

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  - 3 beds, 1m x 8 cm i.d.

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allows prediction of the effect of operating and design variables

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# Handling Water?

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# **Summary - Post Combustion**

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  - Processing conditions
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## Acronyms

- ETIS = Energy Technology Innovation Strategy
- LETDF = Low Emissions Technology Demonstration Fund
- ECBM = Enhanced Coal Bed Methane
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# Integrated CO<sub>2</sub> capture study for a coal fired station

Philippe Delage (ALSTOM) & Paul Broutin (IFP)







#### • Introduction

- Bases of the study
- Integration study
- Conclusions







- Study sponsored by ADEME (French Environment and Energy Management State Agency)
- Identify major features for integration between CO<sub>2</sub> capture process and coal-fired power plant
- 2 integrated CO<sub>2</sub> capture processes studied on a CFB SC boiler
  - scrubbing with Mono Ethanol Amine solution,
  - oxyfiring CFB SC boiler







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- CFB supercritical boiler
- 270 bar / 600 °C life steam, 60 bar / 600 °C reheat steam
- Feedstock: International bituminous coal
- Seaside location (seawater @ 15 °C)
- $CO_2$  capture: 90 %
- CO<sub>2</sub> available at 110 barabs at battery limits







#### Reference Plant Performance (without capture)

Supercritical CFB Plant performance	Without capture
Fuel input, MW (LHV)	1400
Gross power output, MW	685
Ancillary power consumption and losses, MW	55
Net Power Output, MW	630
Thermal Efficiency, % (LHV)	44.9









# **Simulation methodology**

- ALPRO software from ALSTOM Power was used to simulate the power plant
- Hysys from Aspen Tech was used by IFP to simulate the CO<sub>2</sub> capture plant, the Air Separation Unit and CO<sub>2</sub> compression
- Iterative approach using the results from both softwares







- Introduction
- Bases of the study
- Integration study
- Conclusions







### Integration with steam cycle

- Integration has impact on steam cycle
- With postcombustion capture, the steam turbine is adapted to accomodate large quantity of extracted steam.
- With oxyfiring the heat is recovered without modification of the steam turbine.



ALSTOM steam turbine in ESBJERG power plant, Denmark (Net power output: 350 MW, District heating: 459 MJ/s)







#### **CFB with post-combustion capture**









#### **Major integration aspects / Post-combustion capture**

- Integration of the steam cycle
- Heat recovery from absorption/desorption loop
- Heat recovery from compression
- Flue gas sulphur & particulates removal
- Flue gas cooling
- Position of booster fan
- Electrical distribution







#### CO<sub>2</sub> capture system process flow diagram









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#### **Capture process heat recovery for post-combustion capture**

- Optimisation of the heat recovery from the capture process is the main target to improve efficiency
- Constraint: the condensate flow is reduced due to the steam extraction for amine regeneration
- Three main heat sources

Heat sources	Inlet Temperature (°C)	Outlet Temperature (°C)	Available heat (MJ/sec)	Heat recovered (MJ/sec)
Condenser top of the stripper	105	25	190	60
Lean solution sub-cooling	52	25	200	0
CO <sub>2</sub> compressors intercooling	108	25	60	0







#### **Optimisation of the absorption/desorption loop**

 The influence of the variation of the lean amine has been investigated. A lean loading of around 0.24 mol/mol appears to be the optimum value (using the Hysys software)









#### Optimisation of the absorption/desorption loop (continued)

- By a better heat integration with the absorption/desorption loop, the power necessary for the capture can be reduced by 5%.
- An additional 3% reduction can be achieved by cooling the flue gas to 30℃ instead of 40℃ at the inlet of the absorber.









#### Major integration aspects / oxyfiring

- Integration of the steam cycle
- Heat recovery from ASU
- Heat recovery from compression
- Flue gas sulphur & particulates removal
- CO<sub>2</sub> Recirculation rate
- Electrical distribution







#### **Capture process heat recovery for oxyfiring**

- Optimisation of the heat recovery from the compressors intercooling is main target to improve efficiency
- Two main heat sources

Heat sources	Inlet Temperature (°C)	Outlet Temperature (°C)	Available heat (MJ/sec)	Heat recovered (MJ/sec)
ASU compressors intercooling	110	25	91	68
CO <sub>2</sub> compressors intercooling 3 stages	140	25	55	48







#### Comparison of the performances

	Reference Plant (without capture)	CO <sub>2</sub> Capture by MEA scrubbing	Oxyfiring
Heat Input (LHV) (MW)	1400	1400	1400
Gross Power output, (MW)	685	604	708
Electrical consuption (MW)	55	118	198
Net Power (MW)	630	486	510
Net efficiency (%)	44.9	34.6	36.4
(/0)		(33.8 without integration and	(35.8 without integration)
		capture loop	
	19		





- Introduction
- Bases of the study
- Integration study
- Conclusions







## Conclusions

- Solutions for CO<sub>2</sub> capture are available,
- Economical comparison show the solutions to be close to each other,
- Integration is then a key factor of selection,
- Different type of expertises shall be combined to optimise the processes,
- Effective simulation has been made possible with in-house ALSTOM software ALPRO and IFP's knowledge in using simulation tools such as Hysys software.







# Thank You!









#### Learning from CASTOR: solvent, pilot plant and modeling work

#### Presented by Hallvard F. Svendsen , NTNU

10th MEETING of the INTERNATIONAL POST-COMBUSTION CO<sub>2</sub> CAPTURE NETWORK Date: 24th-25th May, 2007

IFP, Lyon, France

10

Norway

# 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 testing for capture (25 t  $CO_2$  / day)
  - Follow-up of ongoing storage projects

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# Consortium participants R&D Oil & Gas Power C

# R&DOiIFP (FR)STTNO (NL)GESINTEF (NO)RENTNU (NO)ENBGS (UK)RCBGR (DE)BRGM (FR)GEUS (DK)IMPERIAL (UK)OGS (IT)TWENTE U. (NL)STUTTGARTT U. (DE)

# Oil & GasPower ControlSTATOIL (NO)VATTENFAGDF (FR)ELSAM (DIREPSOL (SP)ENERGI E2ENITecnologie (IT)RWE (DE)ROHOEL (AT)PPC (GR)

#### 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)

Production:

104 Scientific reports (deliverables)

Two pilot plants ~10 kg  $CO_2/hr$  and  $1tCO_2/hr$ 

#### Co-ordinator : IFP

Department of Chemical Engineering


## **CASTOR** main components

Strategy for CO<sub>2</sub> Reduction

WP1.1 Development of CO<sub>2</sub> reduction strategies

WP1.2 Geological storage options for  $CO_2$  reduction strategy

Budget: 1 M€

CO<sub>2</sub> Post-Combustion Capture

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

WP2.2 Identification of most promising liquids

WP2.3 Design of membrane based processes

WP2.4 Advanced processes

WP2.5 Process validation in pilot plant

Budget: 10 M€

CO<sub>2</sub> storage performance & risk assessment studies

WP3.1 Field case "Casablanca"

WP3.2 Field case "Lindach"

WP3.3 Field case "K13b"

WP3.4 Field case "Snøhvit"

WP3.5 Preventive & corrective actions

WP3.6 Criteria for site selection and site management



## Solvent selection

- Approximately 30 candidate solvents • were selected for a screening study
  - Polyamines, alkanolamines, amino acid salts, mixed solvents

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Several new solvents were identified with both a higher rate of absorption and a higher absorption capacity than MEA





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#### **Reaction Rate versus Carbamate stability**





## Assessment of heat requirement: (MJ/kg CO<sub>2</sub>)



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## Estimating close to optimal loadings



•

#### Rich loading (easy)

90% of equilibrium loading with p<sub>CO2</sub> corresponding to coal or natural gas exhaust

#### Lean loading (more difficult)

- Heat limited regime.
- Stripping limited regime.





1

## Simplified equilibrium model

 The equilibrium data fitted to a sigmoidal + ramp function, describing the p<sub>CO2</sub> vs. loading

n 
$$p_{CO_2} = A\alpha + k_1 + \frac{B}{1 + k_2 \exp(-k_3\alpha)}$$



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## Heat of absorption

From equilibrium function with the Gibbs-Helmholtz equation:



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## Mass transfer performance

- The string of discs absorber works as a model contactor for the packed absorption column
- Similar liquid flow pattern as provided by a typical structured packing

$$H = \frac{G}{P_{tot}S} \int_{p_{CO_2}^{out}}^{p_{CO_2}^{in}} \frac{dp_{CO_2}}{K_G a(p_{CO_2} - p_{CO_2}^*)}$$





## **Typical results**

**Desorber energy** 

Packing height



30 % MEA is the only "optimized" solvent

Comparison should be refined by improved method for lean loading + effect of reactant concentration

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ЫΡ

+ 0.10 g/g

0.30 g/g MDEA

Tertiäre Amine Aktivatoren

ш

+ 0.10 g/g

0.30 g/g A

7

g/g

0.03

+

C

g/g

0.37

g/g

0.03

+

∢

g/g

37

o.

У

g/g

0.03

+ മ

g/g

37

Ö



Mixed amines



NTNU Norway

## **Corrosion tests**

- Preliminary tests in 30% MEA solvent
- Fixed temperature = **120℃**
- Variable parameter = gas load

• Variable parameter = gas load	Corrosion rate (µm/year)		
Gas load	AISI 1018	AISI 304	AISI 316
A/ SO <sub>2</sub> 10 ppm + NO 20 ppm + CO <sub>2</sub> 15% + N <sub>2</sub>	~ 0	0.4	1
B/ CO <sub>2</sub>	48	38	12
C/ CO <sub>2</sub> 75% + <b>O<sub>2</sub> 5%</b> + N <sub>2</sub> 20%	420±180	55±20	14±10

- Solvent saturation at ambient T° with gas C (CO  $_2$  75% + O $_2$  5% + N $_2$  20%)
- Temperature increase to 120°C, followed by pressur e adjustment to 2 bar (start of the test)
- 1 month weight loss test

	Corro	Corrosion rate (µm/year)		
Solvent composition	AISI 1018	AISI 304	AISI 316	
MEA 5M (30%)	420	55	14	
MEA 5M + inhibitor*	215	< 1	< 1	
degraded MEA 5M*	1300	< 1	< 10	
DETA 5M (60%)	615	9	7	
DEEA 2.5M	23	< 1	< 1	
Castor 1 solvent	< 5	< 1	< 1	



pressure vessel

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# Pilot plant corrosion monitoring



#### First run: 500h MEA 30%

- Solvent: MEA 30% + corrosion inhibitor
- Flue gas contain 6% O<sub>2</sub> (mean value)
- Reboiler average temperature: 109℃
- Bottom of the stripper average temperature: 106 ℃ Flue gas
- No reclaiming



Monitoring point	AISI 1018	AISI 316	
1- Lean solvent, absorber inlet	<b>240 µm/year</b>	0.53 µm/year	
2- Rich solvent, absorber outlet	0.26 µm/year	0.33 µm/year	
3- Rich solvent, stripper inlet	Coupons lost in the pilot plant		
4- Lean solvent, stripper outlet	3.7 mm/year	1.5 µm/year	
5- Flue gas, absorber outlet	0.26 µm/year	0.33 µm/year	
6- CO <sub>2</sub> gas, stripper outlet	5.3 µm/year	1 µm/year	

- → Corrosivity strongly depends on location (temperature / lean rich solvent...)
- → Considerable impact of temperature
- → Extreme corrosion probably linked with high HSS concentration (no reclaiming)
- → Poor efficiency of corrosion inhibitor for carbon steel
- → AISI 316 always corrosion resistant

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## Amine volatility and activity

Unloaded solutions:

- Vapour pressure (water wash)
- Need x-y data
- Basis for thermodynamic activity coefficient model
- Obtain water activity





## **Pilot scale facilities**





SINTEF/NTNU laboratory pilot, 10kg/h Esbjerg Industrial pilot, 1tCO2/h Univ. of Stuttgart pilot

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## **Experimental programme**

- 6 systems tested in Stuttgart and SINTEF/NTNU rigs
- 2 systems tested in Esbjerg pilot plant, will be 3
- Performance measurements
- Concentration profiles
- Temperature profiles
- Pressure drop measurements
- Degradation tests
- Measurements on effluents
- Corrosion tests
- Simulator validation



## **Description of simulation model**



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## SINTEF/NTNU pilot results:







#### Comparison experimental and simulated results absorber



#### Comparison experimental and simulated results desorber

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## Continuation in CAPRICE

## CAPRICE WP1

Benchmarking and validation of amine process performance

Objectives

•To obtain a set of validated performance data from pilot plant operation of the MEA solvent system

•To use this data for detailed validation of various simulation models including Hysys, Aspen, Protreat and an in-house code.

•A set of recommendations to limit and monitor corrosion and also to select the best material for the industrial plants.

•Proved a set of recommendations or guide lines at such a level of detail as required for obtaining satisfactory accuracy in the absorber, desorber and overall plant design.

•Provide a set of experimental condition where the highest experimental sensitivity is found as a basis for further test campaigns.



# Thank you



Department of Chemical Engineering

A Multi-period Optimization Model for Energy Planning With CO<sub>2</sub> Emission Consideration

Jniversity Of Waterloo Jepartment of Chemical Engineering

By: Hamid-Reza Mirza

Supervisors: Ali Elkamel, Peter Douglas, Eric Croiset

# **Presentation Outline**

- Introduction
- Research Objectives
- Model Description
- Future Work
- Closing Remarks



- Coal
- Gas/Oil
- Nuclear
- Renewable
  - Hydroelectric
  - Wind
  - Biomass





- Coal
- Gas/Oil
- Nuclear
- Renewable
  - Hydroelectric
  - Wind
  - Biomass





- Coal
- Gas/Oil
- Nuclear
- Renewable
  - Hydroelectric
  - Wind
  - Biomass





- Coal
- Gas/Oil
- Nuclear
- Renewable
  - Hydroelectric
  - Wind
  - Biomass





- Coal
- Gas/Oil
- Nuclear
- Renewable
  - Hydroelectric
  - Wind
  - Biomass





# Ontario's Capacity & Demand cont...



# Canada's GHG Emissions





10th International CO2 Capture Network

# **Research Objective**

- Taking into account time dependent parameters, such as future electricity demand and fuel price fluctuations, what is the optimal mix of electricity supply sources needed to:
  - satisfy electricity demand each year
    while meeting CO<sub>2</sub> emission targets
    at <u>minimum</u> cost



# The Pyramid



# Current Work

- Current work involves development of a deterministic multi-period planning model that will is implemented in GAMS.
- The model will take into account several time dependent parameters and variables that may change over time.



# **Power Generating Options**

- Existing Power Stations
  - The model considers the option to:





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# CO2 Storage in Ontario



- Two potential reservoirs = Lake Huron and Lake Erie
- Economic estimates (Shafeen, Croiset, Douglas, 2003)



# Power Generating Options cont...

- New Power Plants
  - The power generating technologies considered are:
    - Pulverized coal (PG)CCS
    - Natural Gas Combined Cycle (NGCCCS)
    - Integrated Gasification Combined Cycle (IGCC)S
    - New Nuclear


## Model Inputs

- Forecasted energy demand
- Fixed O&M cost
- Variable O&M cost
- Fuel price fluctuations
- Capital cost of new plants
- Construction lead time
- Energy conservation initiatives
- Annual CO<sub>2</sub> emission targets
- Cost carbon capture and storage
- Annual budget (if specified)
- Cost of CO<sub>2</sub> credits





## **Objective Function**

 $OF = \sum \sum \sum F_{ijt}^F C_{ij}^F \boldsymbol{x}_{ijt} + \sum \sum F_{it}^{NF} C_i^{NF} \boldsymbol{y}_{it}^{NF} + \sum \sum \sum \sum V_{ijt}^F \boldsymbol{\mathcal{E}}_{ijlt}^F P_{lt} + \sum \sum \sum V_{it}^{NF} \boldsymbol{\mathcal{E}}_{ilt}^{NF} P_{lt} + \sum \sum V_{it}^{NF} \boldsymbol{\mathcal{E}}_{ilt}^{NF} P_{lt} + \sum \sum V_{it}^{NF} \boldsymbol{\mathcal{E}}_{ilt}^{NF} P_{lt} + \sum \sum V_{it}^{NF} \boldsymbol{\mathcal{E}}_{ijt}^{NF} P_{lt} + \sum V_{it}^{NF} \boldsymbol{\mathcal{E}}_{ijt}^{NF} P_{it} + \sum V_{it}^{NF} P$ i∈F  $i \in NF t$  $i \in NF \ l$  $i \in F$  i Fixed O&M cost of existing power plants *VariableO&M* cost of existing power plants  $\sum \sum U_{jt} G_{ij}^F \mathbb{Z}_{ijlt}^F P_{lt} + \sum \sum R_{it} h_{it} + \sum \sum S_{it}^{new} C_i^{new} n_{it} + \sum \sum F_{it}^{new} C_i^{new} y_{it}^{new} +$  $i \in P^{new}$ i∈F *retrofit* cost for Fixed O&M cost of new Fuel cost for fossil fuel plants capital cost for new *fuel switching* power plant power plant  $\sum \sum V_{it}^{new} \mathbf{E}_{ilt}^{new} P_{lt} + \sum \sum \sum U_{it} G_i^{new} \mathbf{E}_{ilt}^{new} P_{lt} + \sum (\mathbf{Cre})_t (\mathbf{CCost})_t +$  $i \in P^{new}$  1  $i \in P^{new}$  l *VariableO*&M cost of new Fuel cost for new Cost of purchasin g CO2 emission credits power plant power plant  $\sum \sum Q_i (CO2)_{ij} \mathcal{E}_{ikt} \mathbb{Z}_{ijkt}^F \mathcal{Z}_{ijkt} P_{lt} + \sum \sum \sum Q_i (CO2)_i \mathcal{E}_{ikt} \mathbb{Z}_{ilt}^{new} P_{lt}$  $i \in P^{new-cap}$  l  $i \in F$  j k lCarbon capture and storage cost Carbon capture and storage cost for existing power plants for new power plants i: POWER PLANT j: FUEL (COAL/NG) k: CAPTURE PROCESS I: LOAD (BASE/PEAK)

+ TIME (vare)

## Model Output

- Output data from each boiler:
  - Energy production for each year
  - CO<sub>2</sub> Emissions for each year
  - Whether Carbon Capture should be put online, and in which year
  - What type of Carbon Capture technology to install
  - CO2 storage site
  - Whether fuel-switching should be implemented, and in which year
- Year in which construction of new power plant should commence
- Annual expenditure for entire fleet
- Annual Cost of Electricity (COE)
- Annual out-of-province imports



10th International CO2 Capture Network

## **Model Statistics**

#### **Current Model**

#### Previous Model (Haslenda's)

SINGLE EQUATIONS: SINGLE VARIABLES: DISCRETE VARIABLES : 9,950

42,20**SINGLE** 25,52**EQUATIONS**: 1,325 SINGLE VARIABLES: 706 DISCRETE VARIABLES: 265

#### GENERATION TIME = 26 Hours

GENERATION TIME = 0.031SEC



# Summary

- A deterministic multi-period model has been developed for energy planning
- Model finds the optimal mix of electricity supply sources needed to satisfy electricity demand each year, while meeting CO2 emission targets, at a minimum cost
- Model takes into account several timedepending variables and parameters



## Future Work

- Examine other case studies
- Consider additional pollutants (NOx, SO<sub>2</sub>, Hg)
- Extend the current deterministic model into a stochastic formulation
- CCS pipeline network optimization



# **Closing Remarks**

- Research supervisors:
  - Eric Croiset
  - Peter Douglas
  - Ali Elkamel
- Financial support:
  - Ontario Power Generation (OPG)
  - NRCan
  - NSREC



End of Presentation

## **QUESTIONS & ANSWERS**

10th International CO2 Capture Network

## Halten CO<sub>2</sub> and Mongstad in Norway– Gas Fired Projects with Post Combustion CO<sub>2</sub> Capture

Dr. Gelein de Koeijer

Statoil R&D, Trondheim, Norway

10th MEETING of the IEA GHG INTERNATIONAL POST-COMBUSTION CO<sub>2</sub> CAPTURE NETWORK 24<sup>th</sup>-25<sup>th</sup> May, 2007, IFP, Lyon, France



### **Norway as a "CO<sub>2</sub> laboratory"**



#### Halten $CO_2$ - An industrial model for a $CO_2$ value chain







### Ongoing: Technology qualification by competition

- Fluor Daniel
- Mitsubishi Heavy Industries
- Cansolv Small pilot at Risavika near Stavanger



#### Mongstad CHP station Technical concept



**Energy efficiency CHP station : 70-80%** 



## Statoil- Government agreement:

Towards full scale CO<sub>2</sub> management at Mongstad in two stages - and wide international employment of technology developed at the Test Centre







ww.csiro.au

#### Current CO<sub>2</sub> PCC Research and Development Activity CSIRO Energy Technology, Australia

Graeme Puxty Friday, 25<sup>th</sup> May 2007



#### **CSIRO Energy Technology**



Laboratory

Molecular Modelling

Introduction

- 6 500 research scientists/engineers and support staff
- Over 100 sites around the country
- Division of Energy Technology:
  - Renewables

Pilot Scale

- Low emission fossil fuels
- Energy storage
- Distributed energy management and supply

Outlook

# PCC Research and Development in Australia

 PCC recognised by industry and government as a necessary transition technology for large reductions in CO<sub>2</sub> output in the short-medium term and to avoid stranded assets



# PCC Research and Development in Australia

 PCC from Australian coal fired power stations poses a number of challenges compared to existing PCC technology (ammonia production)



Bayswater power station, 4×660 MW

- →  $\approx$  90 000 m<sup>3</sup>min<sup>-1</sup> (**31** tmin<sup>-1</sup> CO<sub>2</sub>) flue gas @ 120 °C (0.6 tmin<sup>-1</sup> CO<sub>2</sub> currently with commercial systems)
- → ≈ 10-15% CO<sub>2</sub>
- $\rightarrow$  ≈ 3-5% O<sub>2</sub> (oxidative degradation of solvent)
- → ≈ 80-87% N<sub>2</sub>
  - → ≈ 500-900 ppmv SO<sub>x</sub> (HSO<sub>3</sub><sup>-</sup>+H<sup>+</sup> → heat stable salts)
  - →  $\approx$  5-30 ppmv NO<sub>x</sub> (?)
    - ➤ ≈ 0.35 mgm<sup>3</sup> fly ash (some trace elements enhance oxidation, ?)

## Properties vary between black and brown coal

# PCC Research and Development in Australia

#### Other issues associated with PCC:

- High cost (presently around \$35 / t CO<sub>2</sub> captured and compressed, equivalent to around \$33 / MWh for an 85% reduction in GHG)
- Loss of generation efficiency around 20-25% to capture 90% of  $\mathrm{CO}_2$
- Like all zero emission technology options, PCC needs R&D to increase efficacy, efficiency and drive down costs
  - Increase CO<sub>2</sub> cyclic capacity
  - Maintain fast rate of CO<sub>2</sub> uptake/release
  - Reduce regeneration energy requirements
  - Reduce vapour pressure
  - Resistance to oxidation
  - Resistance to SO<sub>2</sub>, NO<sub>x</sub> and fly ash

#### **Overview of CSIRO Capture Activities**

•	<b>CSIRO</b> led national PCC research, development and
	demonstration program established

 Laboratory scale research underway across a range of technology options

Generation II-III systems

- Traditional amine/ammonia liquid solvents
- Novel amines, solvent systems and promoters (off the shelf and synthesised)
- Enzyme catalysis of absorption/stripping
- Ionic liquids
- Solid phase absorbents

Generation IV systems

- Molecular modelling of solvent systems and their behaviour using experimentally determined parameters for intelligent solvent design
- Two portable pilot scale demonstration plants being constructed and will be installed at power stations for an initial testing campaign in 2007

#### Solvent PCC – Generation II-III Systems



#### Solvent PCC Activities – Generation II-III Systems



#### Laboratory – Synthesis (G II-III)

- Division of Molecular & Health Technologies synthesising new solvent molecules
- Testing PCC performance of existing and new molecules
  - Quantitative Structure Activity Relationship used to determine important molecular parameters
  - Molecular modelling used to model kinetic and thermodynamic behaviour of existing and new molecules
  - Both used to intelligently design new solvent molecules



#### Laboratory – Micro Scale TGA (G II-III)

#### Microscale TGA measurements of solvents

- Microgram quantities required so appropriate for screening newly synthesised molecules
- CO<sub>2</sub> uptake measured as a mass increase



Introduction

Laboratory

Molecular Modelling

Pilot Scale

Outlook

#### Laboratory – Micro Scale TGA (G II-III)



#### Laboratory – Micro Scale TGA (G II-III)



#### Laboratory – Macro Scale (G II-III)

#### Macro-scale absorption apparatus



Introduction

Molecular Modelling

Outlook

### Laboratory – Macro Scale (G II-III)



#### Laboratory – Macro Scale (G II-III)



#### Laboratory – Enzyme Catalysis (G IV)

- Use enzymes such as carbonic anhydrase to catalyse CO<sub>2</sub> absorption desorption
  - Fast reaction rates
  - Low energy requirements
  - Large scale production by fermentation
  - Biodegradable and environmentally safe
  - Degraded/inhibited by high temperature and contaminants

#### Work in early stage – preparation of suitable enzymes for testing

#### Laboratory – Enzyme Catalysis (G IV)



#### Laboratory – Ionic Liquids (G IV)

• Develop functionalised ionic liquids for PCC applications



*E.D. Bates et al., J. Am. Chem. Soc. 124*(2002) *926* 

#### • Properties of existing ionic liquids:

- Low enthalpy of absorption/desorption
- Chemically inert and robust
- No vapour pressure
- Low absorption capacity
- Work in early stage screening existing ionic liquids for capacity

Outlook

#### Laboratory – Ionic Liquids (G IV)



#### Laboratory – Solid Phase Adsorbents (G IV)

- Nano-structured carbon fibre composites for CO<sub>2</sub> capture
  - Capture in a dry process
  - Will work in high dust environments
  - Low pressure drop
  - Low energy requirements
  - Absorption/desoprtion by pressure swing
  - Low absorption capacity

 Work at an early stage – fabrication process developed and testing to identify crucial properties under way

#### Laboratory – Solid Phase Adsorbents (G IV)



#### Molecular Modelling (G II-III)

- Comprehensively model all chemical steps involved in CO<sub>2</sub> absorption/desorption
- This requires information about:
  - The mechanism of all chemical steps
  - Rate constants and activation parameters (E<sub>a</sub>) of kinetically "slow" steps
  - Equilibrium constants of kinetically fast steps (e.g. protonations)
  - Enthalpies of all steps
- With this information you can model CO<sub>2</sub> capacity, cyclic capacity, the kinetics of uptake/desorption and energy requirements
- You can predict the behaviour of potential solvents from determination of a few parameters
# Molecular Modelling – Amines (G II-III)



Outlook

## Molecular Modelling – Amines (G II-III)



# Molecular Modelling – Amines (G II-III)

#### Improving on MEA

- Vary theoretical properties of solvent to find optimal parameters
  - Cyclic capacity (α<sub>loaded</sub>-α<sub>lean</sub>) of MEA-type amine could be doubled and energy requirements reduced by increasing basicity and reducing carbamate stability
  - Even greater improvements when considering di/tri-amines, base-amine mixtures, ...



# Molecular Modelling – Parameter Determination (G II-III)



# Pilot Scale – Transportable Pilot Plant

#### Multiple transportable pilot plants

- 1,000 tpa
- Pre-wash column for optional SO<sub>x</sub> / NO<sub>x</sub> scrubbing
- Dual 200 mm absorbers
- Single stripper column

#### Relocatable for slip stream operation

 Several power stations in program burning black and brown coal

#### Modular construction

- Plans for testing different packing types and novel membrane contactors
- Testing of alternative solvents (e.g. chiller being added to test chilled ammonia as a solvent)



CSIRO's transportable PCC Pilot Plant

Molecular Modelling

Outlook

# **Outlook – Generation II-III Systems**

- NMR measurements of liquid phase amine/ammonia-CO<sub>2</sub> reactions
  - Carbamate formation kinetics and stability constant determination
  - Determination of carbamate formation pathway (via CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup>, ...)

#### Calorimetry for enthalpy determination

- Use calorimetry to determine enthalpy of individual reaction steps
- Will combined with NMR results to provide all parameters required for molecular models

#### Detailed models of pilot plant being developed in Aspen

- Coupling dynamic chemistry with a detailed plant model
- Will allow new solvent options to be simulated prior to running in the pilot plant
- Measurements from the pilot plant will be fed back to the model

# **Outlook – Generation II-III Systems**

- Novel absorption/desorption cycling apparatus
- Wetted-wall reactor for reaction kinetics measurements
- Oxidation apparatus
  - Gas in-flow, reactor and spectroscopic flow-cell combined to monitor oxidation of solvents



Outlook

# **Future Projects**

	Future Projects
	AP6 & CSIRO 2007-2011 Laboratory and pilot scale work on amine/ammonia based systems Use of solar thermal for desorption Technology exchange with India, China, Japan and the USA
Generation II-III	Loy Yang Power & The Victorian Government 2007-2009 Laboratory and pilot scale work on amine/ammonia based systems Focused on brown coal
	Australian Coal Association (Stage 1) 2007-2009 Site selection and evaluation for large scale capture and storage demonstration
	Australian Coal Association (Stage 2) 2009-2014 50 ktpa capture and demonstration facility
Generation IV	CSIRO 2007-2017 Enzymes, ionic liquids and adsorbents
Generation V	CSIRO 2007-2017 Value adding CO <sub>2</sub> : Algal/biomass growth to fuel, Solar CO <sub>2</sub> splitting

Introduction

### The Team



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# Thank you

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