IEA GREENHOUSE GAS R&D PROGRAMME

INTERNATIONAL NETWORK FOR CO_2 CAPTURE: REPORT ON 11TH WORKSHOP

Report Number: 2008/07

Date: July 2008

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 26 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. The IEA Greenhouse Gas R&D Programme is one of these Implementing Agreements.

DISCLAIMER

This report was prepared as an account of work sponsored by the IEA Greenhouse Gas R&D Programme. The views and opinions of the authors expressed herein do not necessarily reflect those of the IEA Greenhouse Gas R&D Programme, its members, the International Energy Agency, the organisations listed below, nor any employee or persons acting on behalf of any of them. In addition, none of these make any warranty, express or implied, assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights, including any party’s intellectual property rights. Reference herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply an endorsement, recommendation or any favouring of such products.

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 financial support provided by VEO, Federal Ministry for Transport and Technology and Wien Energie for this meeting and the hospitality provided by the hosts EVN.

The coordinator of this network is Dr John Topper, IEA Greenhouse Gas R&D Programme.

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 11th Workshop, 2008/07, July 2008”.

Further information on the network activities or copies of the report can be obtained by contacting the IEA Greenhouse Gas R&D Programme at:

IEA Greenhouse Gas R&D Programme, Orchard Business Centre,
Stoke Orchard, Cheltenham Glos. GL52 7RZ. UK
Tel: +44 1242 680753 Fax: +44 1242 680758
E-mail: mail@ieaghg.org
www.ieagreen.org.uk

INTERNATIONAL NETWORK FOR CO_2 CAPTURE: REPORT ON 11th WORKSHOP

(20 - 21 May 2008, EVN, Vienna, Austria)

INTERNATIONAL NETWORK FOR CO_2 CAPTURE:
REPORT ON 11th WORKSHOP

(20-21st May 2007, EVN, Maria Enzersdorf, Vienna, Austria)

1. Overview of the network and past workshops

This workshop was the eleventh in a series to discuss co-operation in development of MEA and other 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, Copenhagen, and Lyon. Copies of previous reports after the Apeldoorn meeting are available on CD (contact Sian Twinning, sian@ieaghg.org).

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 technically feasible although economically unattractive for ageing, less efficient assets. Since the previous workshop in Lyon, progress has been made with pilot plant work in Europe, Japan, USA, Canada and Australia and announcements of new investigations and partnerships. Until the end of 2007 no announcements had been made about commercial sized demonstration plant. That changed with the announcement by the UK Government that it was establishing a competition to build a post combustion demonstration unit (could also be based on oxy fuel if using a retrofit design). Key features of the announcement are:-

- At least 300MWe in unit size
- Based on use of coal (with efficient supercritical technology implicit)
- Demonstrate the full carbon capture and storage (CCS) chain by 2014
- Dissemination of results/progress to other parts of the world (with major coal using developing countries in mind) will be an important part of the operation

At the time of the workshop in Vienna, 9 organisations had submitted expressions of interest in participation and at the time of writing this covering report, this had been reduced to 4. In the interim Vattenfall has also announced that it is undertaking investigations at the Vested aquifer, located about 30 km from the Nordjyllands power station in Denmark where it is intending to extend the plant. Sanction to proceed or not is expected in 2010. In USA it has become apparent that permissions to proceed with unabated coal plant are becoming almost impossible to obtain and there has been a number of announcements of intentions to build with CCS based on post combustion capture – in some cases associated with use of ammonia or chilled ammonia for CO2 capture.

This all amounts to a picture which has transformed the importance of the workshop series. In Calgary in 2001 there was a small group of 23 attendees comprising researchers and potential technology providers. Today we are dealing with operations at an increasing scale and with increasing confidence in the application of what might be termed 1st generation technology, as indicated by the many representatives from power generators at the later workshops. The registrations for this workshop in Vienna had to be closed before the meeting to keep within room limits of around 100 people.

This report contains presentations on a variety of developments including up dates on amines, use of ammonia as a solvent, and for the first time a panel session looking at potential future technologies, as the IEA Greenhouse Gas R&D Programme intends to keep the network focused on pre-commercial activity. There are many new lines of inquiry developing as research funding builds up and as the amine and ammonia based techniques move towards commercialisation.

2. Vienna, EVN workshop

The delegate list is appended as Annex I. There were 100 pre-registrants (including local EVN staff and Sponsors) and 16 countries were represented. Presentations are listed in section 3 below.

3. Presentations by Attendees

Presentations were made as listed below. Copies of slides appear in Annex II.

1	John Topper, for the IEA GHG R&D Programme, UK	Introduction to 11th Workshop
	Fundamental Studies	Chair: Prof Paitoon Tontiwachwuthikul, Univ of Regina, Canada
2	Thermal and Oxidative Degradation of Amines	Jason Davis, University of Texas, USA
3	Aqueous Concentrated Piperazine – a Fast, Stable, Effective Solvent	Stephanie Freeman, University of Texas, USA
4	Evaluation of Post Combustion Capture using Piperazine Promoted Potassium Carbonate in a Coal Fired Power Station	Jochen Oexmann, Hamburg Univ of Technology, Germany
	More Fundamental Studies	Chair: Dr Paul Feron, CSIRO, Australia
5	Liquid Speciation and reaction kinetics for CO2 Aqueous polyamine (DETO) solution	Ardi Hartono, NTNU, Norway
6	Ebulliometric determination of Vapour-Liquid Equilibria for pure alkanolamines and their aqueous solutions	Inna Kim, NTNU, Norway
7	Mass transfer in a small scale Flue Gas	Dr Patrick Huttenhuis, Procede Gas

	Absorber; Experimental Modelling	Treating, the Netherlands
	Studies and Programmes	Chair: Prof Alfons Kather, Hamburg Univ of Technology, Germany
8	Update on Activities at and by Univ Regina	Prof Paitoon Tontiwachwuthikul, Univ Regina, Canada
9	CCS at IFP: from MEA to New processes for Post Combustion Capture	Raynal Ludovic, IFP, France
10	Post Combustion work at CSIRO and in Australia	Dr Paul Feron, CSIRO, Australia
	CASTOR and Capture Ready	Chair: Prof Hallvard Svendsen, NTNU, Norway
11	Results from CASTOR Project	Jan Hopman, TNO, Netherlands
12	Performance Review of Castor Pilot Plant at Esbjerg	Jacob Knudsen, Dong Energy, Denmark
13	The Concept of Capture Ready and its Application to Post Combustion Capture	Jon Gibbins and Matthew Lucquiard, Imperial College, UK
14	Vattenfall's Proposed Demonstration Project at Nordjyllandsvaerket	Ole Biede, Vattenfall, Denmark
	Ammonia	Chair: George Offen, EPRI, USA
15	Use of Chilled Ammonia	Brice Freeman, EPRI, USA
	Developments by Technology Providers	Chair: Dr Jon Gibbins, Imperial College, UK
16	Activities by Babcock and Wilcox	Lisa Rumpf, B&W, USA
17	Latest Developments by Fluor	Satish Reddy, Fluor, USA
18	Cansolv Activities	John Sarlis, Cansolv, Canada
19	Coal Fired Plant and Multi-Pollutant Control	Masaki Iijima, MHI, Japan
20	**Panel Session: What Technical and Technology Developments are Next**	Chair John Topper for IEA GHG R&D Programme
20a	Introductory Presentation	Dr Robert Davidson; IEA Clean Coal Centre
20b	Short Presentations by	Hallvard Svendsen,
20c		Alfons Kather
20d		Jon Gibbins
20e		Paul Feron
	Speech only	Paitoon Tontiwachwuthikul

4. Next Meeting(s)

The 12th Network meeting will be at the International Test Centre at the University of Regina in Canada, currently scheduled for end of September 2009.

5. Thanks and Acknowledgements

All participants wish to thank Dr Adolf Aumueller of EVN and his staff, Martin Burboek in particular, for all their hard work in providing the meeting place and facilities, co-ordinating the event and the visit to the biomass gasification research plant visit on the afternoon of the second day. Also to the Sponsors for the splendid dinner on the intermediate evening, the lunches and coffee breaks. They were Wien Energie, Verband der Elektritzitatsunternehmen Osterreichs and the Federal Ministry for Transport Innovation and Technology.

Paitoon Tontiwachwuthikul, Paul Feron, Alfons Kather, Hallvard Svendsen, George Offen, Jon Gibbins 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 john.topper@iea-coal.org.uk or Sian Twinning sian@ieaghg.org or via the "feedback" facility in the IEA GHG website's home page http://www.ieagreen.org.uk

Annex 1 - 11th International CO$_2$ Capture Network Meeting Attendees

Mr Jim Craigen	ACARP/COAL21
Mr Guenter Gronald	Austrian Energy & Environment AG & CoKG
Ms Lisa Rimpf	Babcock & Wilcox Power Generation Group
Mr Hugo Rafael Garcia Andarcia	BASF SE
Mr Harvey Wen	Bechtel Corp.
Mr Alfred Maeir	BMWA
Mr John Sarlis	Cansolv Technologies Inc.
Mr Devin Shaw	Cansolv Technologies Inc.
Dr Paul Feron	CSIRO
Mr Kaare Helle	DNV
Mr Jacob Nygaard Knudsen	DONG Energy
Mr Willy van Well	DONG Energy
Mr Poul-Jacob Vilhelmsen	DONG Energy Power
Mr Jonas Alin	E.ON Engineering
Mr Bernd Schallert	E.ON Engineering GmbH
Mr Nick Booth	E.ON Engineering UK
Dr Tom Dalziel	E.ON UK
Mr Mohamed Kanniche	EDF R&D
Dr Abhoyjit Bhown	Electric Power Research Institute
Mrs M.L Thielens	Electrabel
Dr Sven Unterberger	EnBW Kraftwerke AG
Miss Angela Mangiaracina	Enel Serearch and exsperimentation
Dr Moetaz Attalla	Energy Technology
Mr Brice Freeman	EPRI
Dr George Offen	EPRI
Mr Martin Burböck	EVN AG
Dr Gerald Kinger	EVN AG
Mr Franz Klemm	EVN AG
Dr Adolf Amüller	EVN AVG
Dr Satish Reddy	Fluor Corp
Mr Jochen Oexmann	Hamburg University of Technology
Mr Alfons Kather	Hamburg University of Technology
Mr Sebastian Linnenberg	Hamburg University of Technology (TUHH)
Rui Sun	HIT
Dr Christian Bergins	Hitachi Power Europe GmbH
Dr Arthur Heberle	Hitachi Power Europe GmbH
Mr Robert Davidson	IEA Clean Coal Centre
Dr John Topper	IEA GHG
Mr Stanley Santos	IEA Greenhouse Gas R&D Programme
Dr PIERRE-LOUIS CARRETTE	IFP
Mr Marc Jacquin	IFP
Dr Ludovic RAYNAL	IFP

Dr Jon Gibbins	Imperial College
Ms Hannah Chalmers	Imperial College London
Mr Mathieu Lucquiaud	Imperial College London
Mr Nial MacDowell	Imperial College London
Dr Manoj Nagvekar	KBR
Dr Jae-Goo Shim	Korea Electric Power Research Institute
Mr Torsten Stoffregen	Linde-KCA-Dresden GmbH
Mr Masaki Iijima	MHI
Mr Nobuo Imai	Mitsubishi Heavy Industries Europe
Dr George Peridas	NRDC
Mr Ardi Hartono	NTNU
Mrs Inna Kim	NTNU
Mr Hallvard F. Svendsen	NTNU
Dr Namat Abu Al-Soof	OPEC
Mr Brian McCain	PB Power
Dr Peter W.J. Derks	Procede Gas Treating
Mr Patrick, J.G. Huttenhuis	Procede Gas Treating
Mr Nick, A.M. Ten Asbroek	Procede Gas Treating
Mr Geert, F. Versteeg	Procede Group BV
Dr Laurent NORMAND	PROSERNAT
Dr Kazuya Goto	Research Institute of Innovative Technology for the Earth (RITE)
Dr John Sidders	RWE Npower PLC
Mr Yohei Tsujimoto	Sanki Engineering Co., Ltd.
Mr Yohei Tsujimoto	Sanki Engineering Co., Ltd.
Mr Mark Claessen	Shell Global Solutions
Mr Jiri van Straelen	Shell Global Solutions
Dr Vladimir Danov	Siemens AG
Dr Karl Anders Hoff	SINTEF Materials and Chemistry
Dr Thor Mejdell	SINTEF Materials and Chemistry
Dr Gelein De Koeijer	StatoilHydro
Mr Bart Vandeputte	Taminco
Mr Cyril THEBAULT	The CO2 European Test Centre Mongstad
Mr Jason Davis	The University of Texas at Austin
Ms Stephanie Freeman	The University of Texas at Austin
Mr Jan Hopman	TNO
Mr Kiyoshi Miyaike	Toshiba
Mr Yukio Ohashi	Toshiba Corporation
Dr Claude PREBENDE	TOTAL
Dr Shujuan Wang	Tsinghua University
Mr Kevin Brechtel	Universität Stuttgart - Institute of Process Engineering and Power Plant
Mrs Paula Galindo Cifre	Universität Stuttgart - Institute of Process Engineering and Power Plant
Mrs Elizabeth Heischkamp	University of Duisburg-Essen, LUAT
Prof Christopher Rayner	University of Leeds
Mr David Wappel	University of Leoben
Dr Paitoon Tontiwachwuthikul	University of Regina
Prof Markus Haider	University of Vienna

Prof Albert Hackl	University of Vienna
Prof Andreas Werner	University of Vienna
Mr Wilmersdorf	University of Vienna
Mr Ole Biede	Vattenfall A/S
Mr Marius Noer	Vattenfall A/S
Mr Moritz Köpcke	Vattenfall Research and Development AB


Schonbrunn Palace, Vienna

11th International Post-Combustion CO_2 Capture Network Meeting

20th-21st May 2008

EVN, Vienna, Austria

Organised by

IEA Greenhouse Gas R&D
Programme and EVN

Sponsored by
Wien Energie
VEO
Federal Ministry for Transport,
Innovation and Technology

EVN

VEO
VERBAND DER
ELEKTRIZITÄTSUNTERNEHMEN
ÖSTERREICHS

bmvit
Bundesministerium
für Verkehr,
Innovation und Technologie

WIEN ENERGIE
WIENSTROM

20th May 2008 Day 1

08.00 Delegates meet in lobby of Intercity Hotel for bus pick up and transfer
08.15 Delegates meet in lobby of Hotel Marriot for bus pick up and transfer

09.00 Session 1– Introduction

Welcome: Austrian Ministry Official

Welcome: Dr Adolf Aumueller on behalf of EVN and the Sponsors

Welcome: Dr John Topper on behalf of IEA Greenhouse Gas R&D PRogramme

Session 2- Fundamental Studies - Chair Prof Paitoon Tontiwachwuthikul, U of Regina, Canada

09.30 to 09.55 Thermal and Oxidative Degradation of Amines: Jason Davis, University of Texas, USA

09.55 to 10.20 Aqueous Concentrated Piperazine - a Fast, Stable and Effective Solvent: Stephanie Freeman, University of Texas, USA

10.20 to 10.45 Evaluation of Post Combustion Capture using Piperazine Promoted Potassium Carbonate in a Coal Fired Power Station: Jochen Oexmann, Hamburg University of Technology, Germany

10.45 to 11.15 Break

Session 2– More Fundamental Studies - Chair Paul Feron, CSIRO, Australia

11.15 to 11.40 Liquid speciation and reaction kinetics for CO2 in aqueous polyamine (DETA) solution: Ardi Hartono, NTNU, Norway

11.40 to 12.05 Ebulliometric determination of Vapour-Liquid equilibria for pure alkanolamines and their aqueous solutions; Inna Kim, NTNU, Norway

12.05 to 12.30 Mass Transfer in a Small scale Flue Gas Absorber, Experimental Modelling: Dr. Patrick Huttenhuis, Procede Gas Treating, The Netherlands

12.30 to 13.45 Lunch followed by Group Photograph

Session 3—Studies and Programmes - Chair Prof Alfons Kather, Hamburg University, Germany

13.45 to 14.05 Update on Activities at and by University of Regina: Prof. Paitoon Tontiwachwuthikul, University of Regina Canada

14.05 to 14.30 CCS at IFP: From MEA to New Processes for Post Combustion Capture: Raynal Ludovic, IFP, France

14.30 to 14.55 Post Combustion Work at CSIRO and in Australia: Dr. Paul Feron, CSIRO, Australia

14.55 to 15.30 Break

Session 4—CASTOR and Capture Ready- Chair Prof. Hallvard Svendsen, NTNU, Norway

15.30 to 15.55 Results from CASTOR project: Jan Hopman, TNO, The Netherlands

15.55 to 16.20 Performance Review of CASTOR Pilot Plant at Esbjerg: Jacob Knudsen, Dong Energy, Denmark

16.20 to 16.45 Studies on the Concept of Capture Ready and its Application to Post Combustion Capture: Jon Gibbins and Mattew Lucquiard, Imperial college, UK

16.45 to 16.55 Vattenfall’s Demo project at Nordjyllandsværket: Ole Biede, Vattenfall, Denmark

16.55 Wrap Up Day 1 by Dr. John Topper

Close Day 1

17.00 Bus Transfer to Schottenheuriger at nearby Maria Enzersdorf for Dinner

21st May 2007 Day 2

08.00 Delegates meet in lobby of Intercity Hotel for bus pick up and transfer
08.15 Delegates meet in lobby of Hotel Marriot for bus pick up and transfer

Session 5 - Ammonia Chair George Offen, EPRI, USA

09.00 to 09.25 Update on Use of Chilled Ammonia: Brice Freeman, EPRI, USA

09.25 to 09.50 Use of Ammonia Based Processes with Coal Fired Plant: Frank Alix, Powerspan, USA

Session 6 – Developments by Technology Providers- Chair Dr. Jon Gibbins, Imperial College, UK

09.50 to 10.15 Activities by Babcock & Wilcox: Lisa Rumpf, B&W, USA

10.15 to 10.40 Latest Developments by Fluor: Satish Reddy, Fluor, USA

10.40 to 11.10 Break

11.10 to 11.35 Cansolv Activities: Colin Ryan /Devin Shaw, Cansolv, Canada

11.35 to 12.00 Coal Fired Pilot Plant and Multipollutant Control: Masaki Iijima, MHI, Japan

Panel Session: What Technical and Technology Developments are Next: Chair Dr. John Topper

12.00 to 13.00 Robert Davidson IEA CCC will provide a list of potential developments before panel members will each be asked to give a brief personal view followed by audience comment and Questions.

Panel Members:
Paul Feron
Paitoon Tontiwachwuthikul
Hallvard Svendsen
Jon Gibbins
Alfons Kather

13.00 Wrap Up by Dr. John Topper

13.00 Lunch

14.00 Departure from EVN by Bus 1 back to Hotels and Bus 2 to visit Biomass Gasification Experimental Unit at Durnrohr Coal Fired Power Station (North of Vienna)

BUNDESMINISTERIUM für WIRTSCHAFT und ARBEIT

FEDERAL MINISTRY of ECONOMICS and LABOUR

CCS

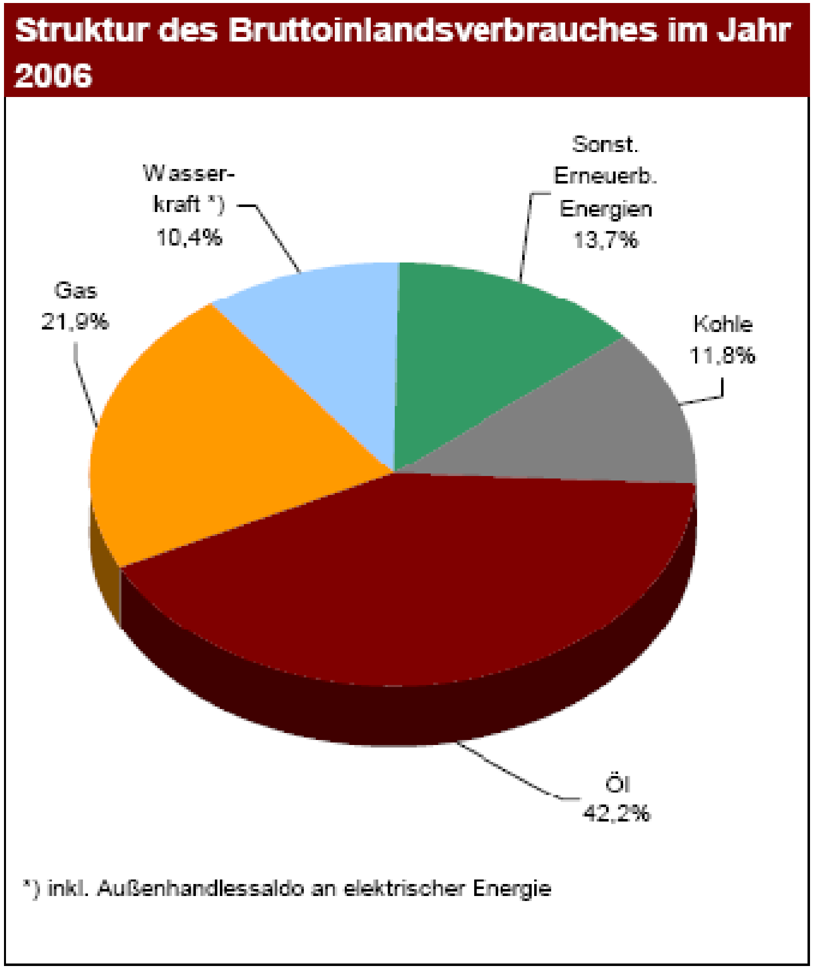
11th Meeting of the
INTERNATIONAL POST-COMBUSTION CO_2 CAPTURE NETWORK

Fundamental remarks, May 20th 2008,

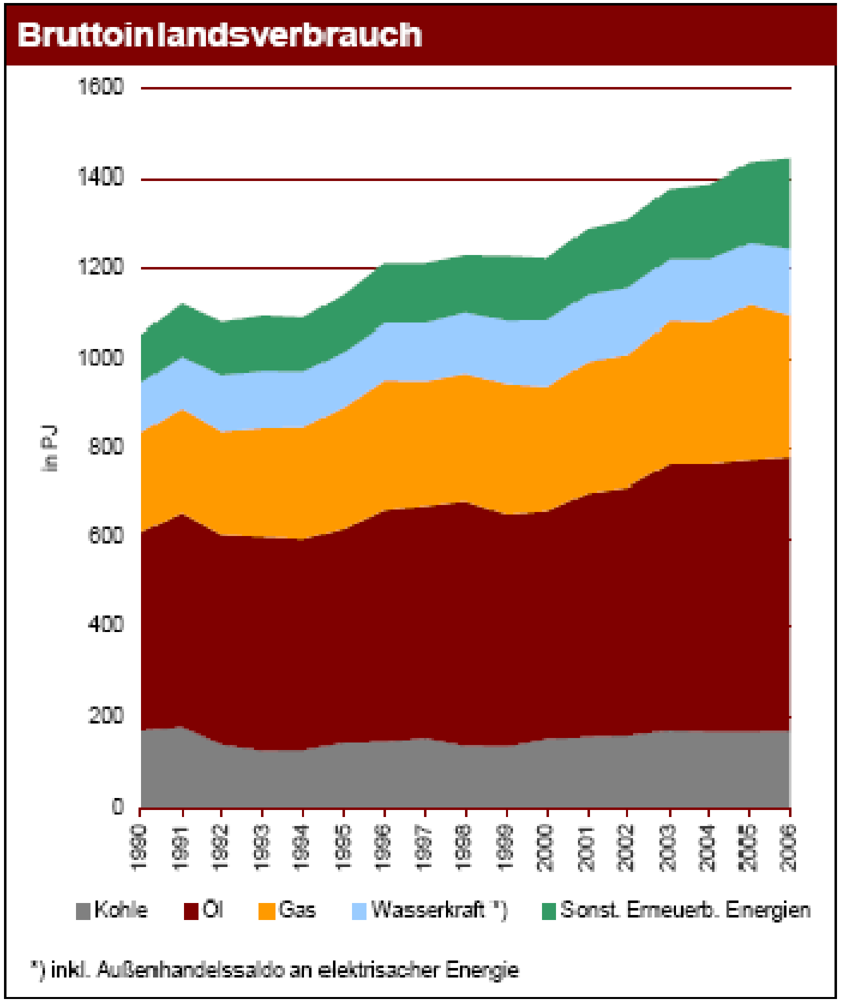
Alfred Maier

www.bmwa.gv.at

Total Primary Energy Supply Austria

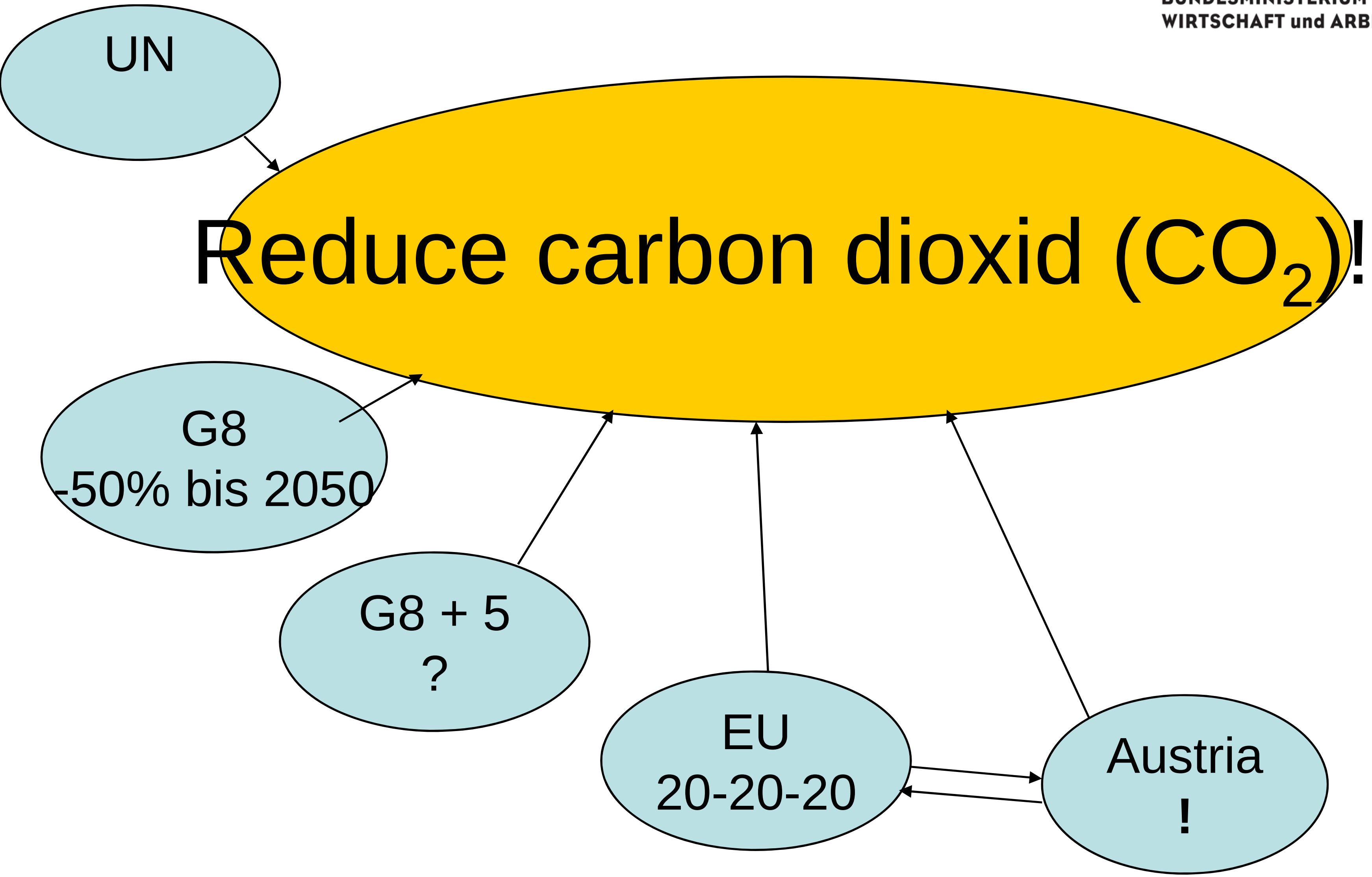

Struktur des Bruttoinlandsverbrauches im Jahr 2006

*) inkl. Außenhandlessaldo an elektrischer Energie


Bruttoinlandsverbrauch

*) inkl. Außenhandelssaldo an elektrisacher Energie

CO_2 and politics



Reduce carbon dioxid (CO_2)!

UN

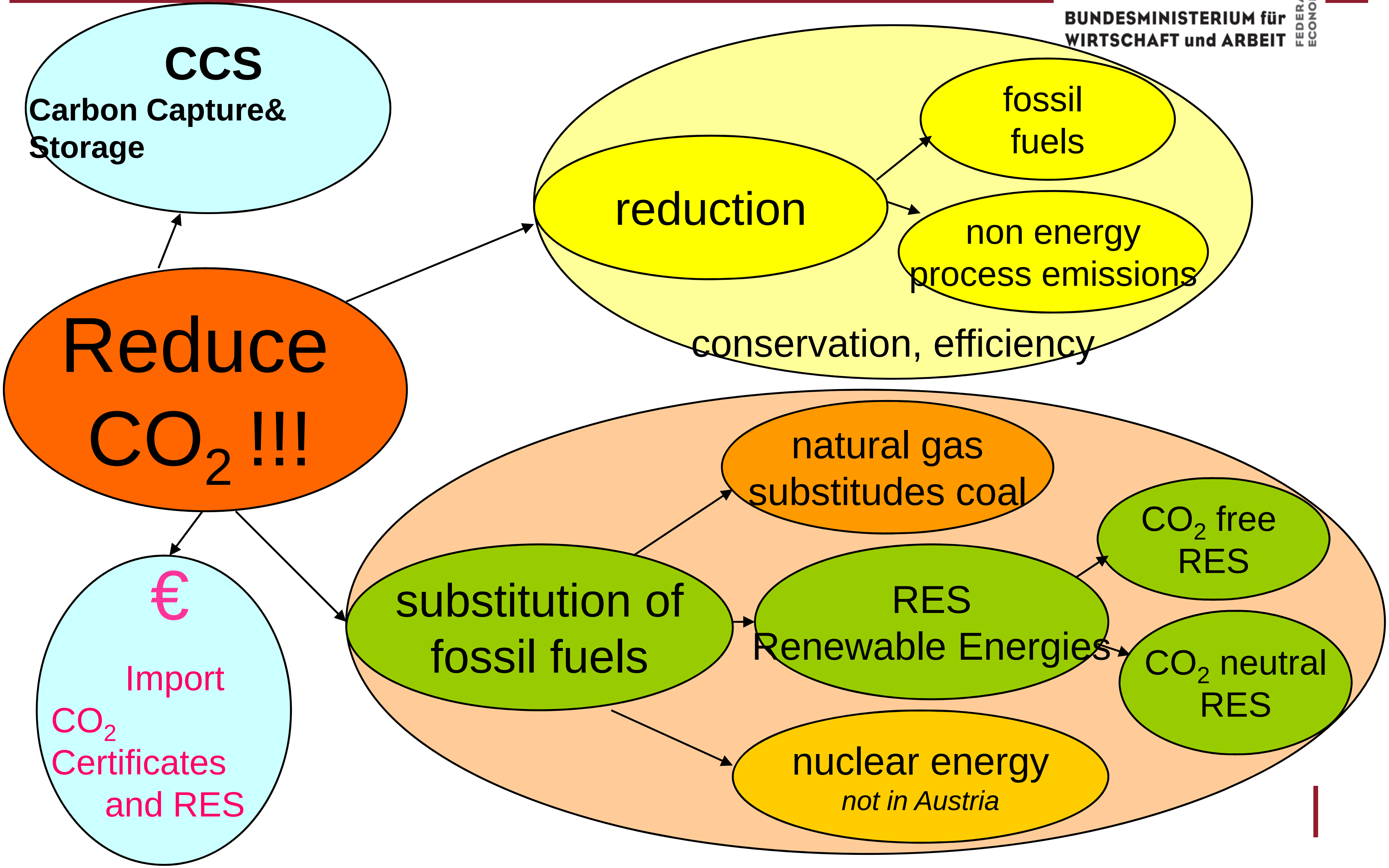
G8
-50% bis 2050

G8 + 5
?

EU
20-20-20

Austria
!

Strategies to reduce CO_2



CCS

Carbon Capture& Storage

Reduce CO_2 !!!

reduction

fossil fuels

non energy process emissions

conservation, efficiency

€

Import CO_2 Certificates and RES

substitution of fossil fuels

natural gas substitudes coal

RES Renewable Energies

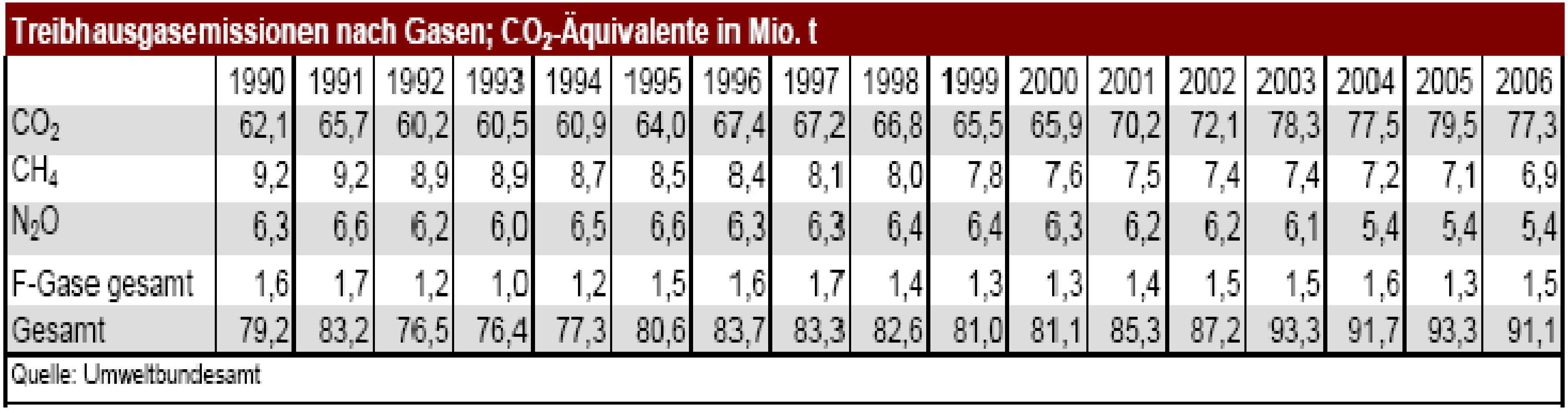
CO_2 free RES

CO_2 neutral RES

nuclear energy

not in Austria

CO$_2$ in Austria



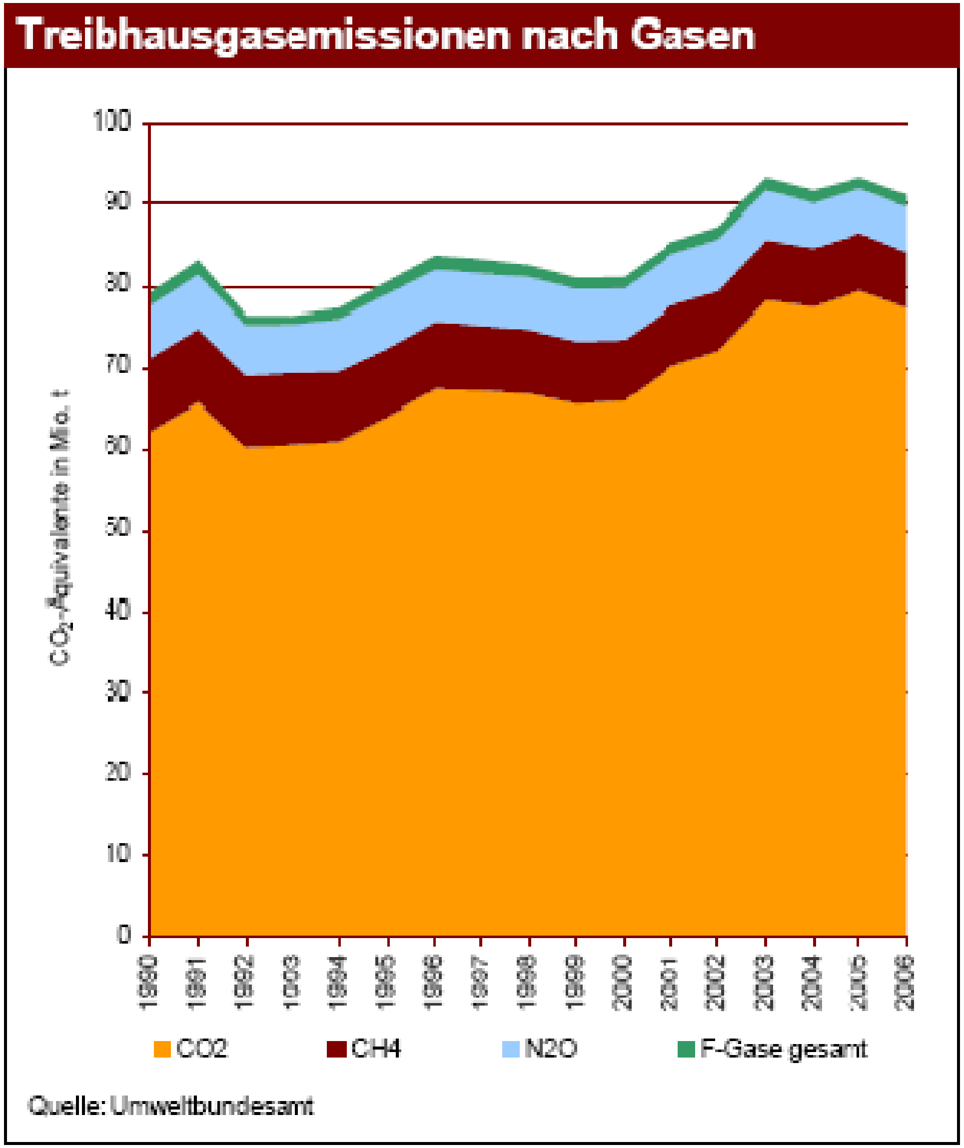
Treibhausgasemissionen nach Gasen; CO$_2$-Äquivalente in Mio. t

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
CO$_2$	62,1	65,7	60,2	60,5	60,9	64,0	67,4	67,2	66,8	65,5	65,9	70,2	72,1	78,3	77,5	79,5	77,3
CH$_4$	9,2	9,2	8,9	8,9	8,7	8,5	8,4	8,1	8,0	7,8	7,6	7,5	7,4	7,4	7,2	7,1	6,9
N$_2$O	6,3	6,6	6,2	6,0	6,5	6,6	6,3	6,3	6,4	6,4	6,3	6,2	6,2	6,1	5,4	5,4	5,4
F-Gase gesamt	1,6	1,7	1,2	1,0	1,2	1,5	1,6	1,7	1,4	1,3	1,3	1,4	1,5	1,5	1,6	1,3	1,5
Gesamt	79,2	83,2	76,5	76,4	77,3	80,6	83,7	83,3	82,6	81,0	81,1	85,3	87,2	93,3	91,7	93,3	91,1

Quelle: Umweltbundesamt

CO_2 in Austria

BUNDESMINISTERIUM für WIRTSCHAFT und ARBEIT
FEDERAL MINISTRY of ECONOMICS and LABOUR



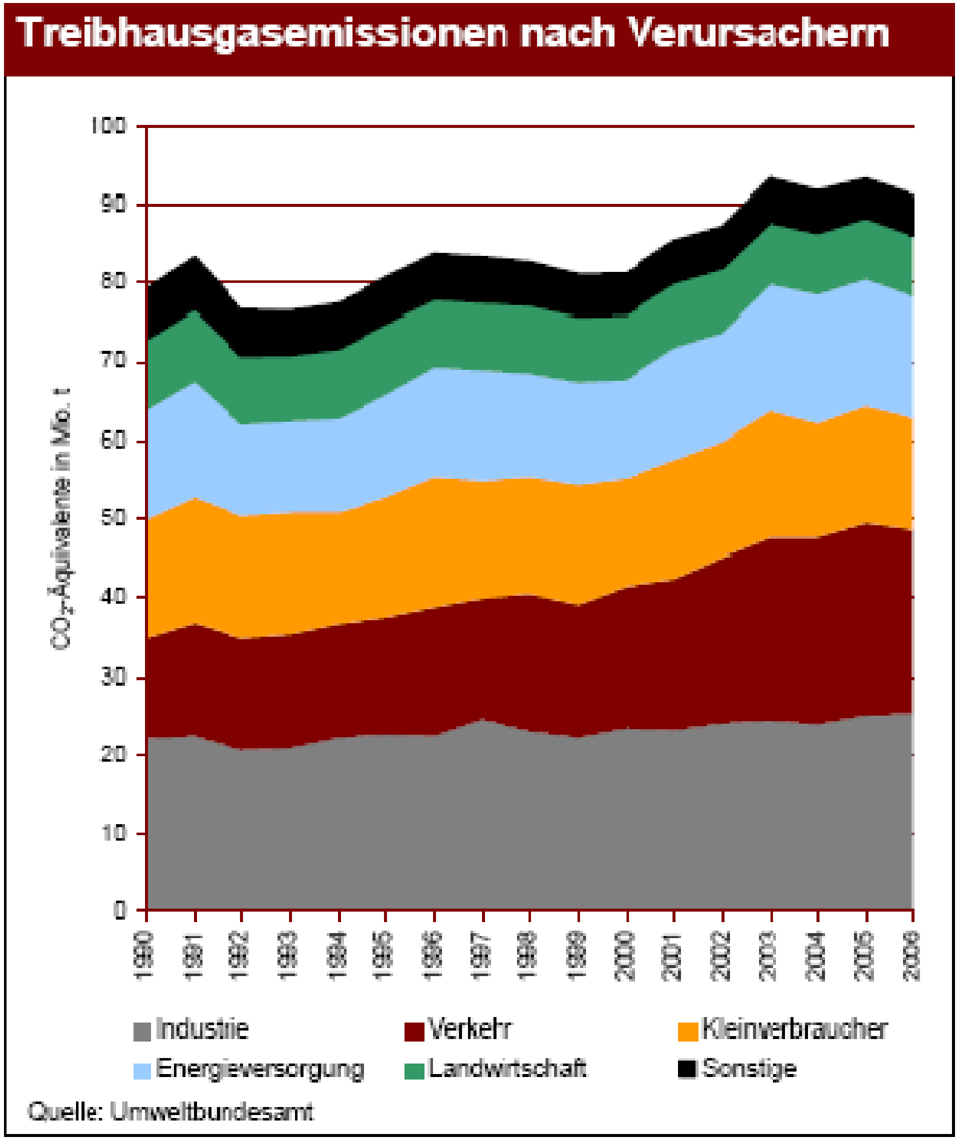
Treibhausgasemissionen nach Gasen

Quelle: Umweltbundesamt

CO$_2$ in Austria

BUNDESMINISTERIUM für
WIRTSCHAFT und ARBEIT

FEDERAL MINISTRY of
ECONOMICS and LABOUR



Treibhausgasemissionen nach Verursachern

Quelle: Umweltbundesamt

BUNDESMINISTERIUM für
WIRTSCHAFT und ARBEIT
FEDERAL MINISTRY of
ECONOMICS and LABOUR

Glück auf!

Thank you!

www.bmwa.gv.at

11th IEA GHG
Post Combustion CO_2 Capture Workshop

Welcome by Dr. Adolf Aumüller EVN AG

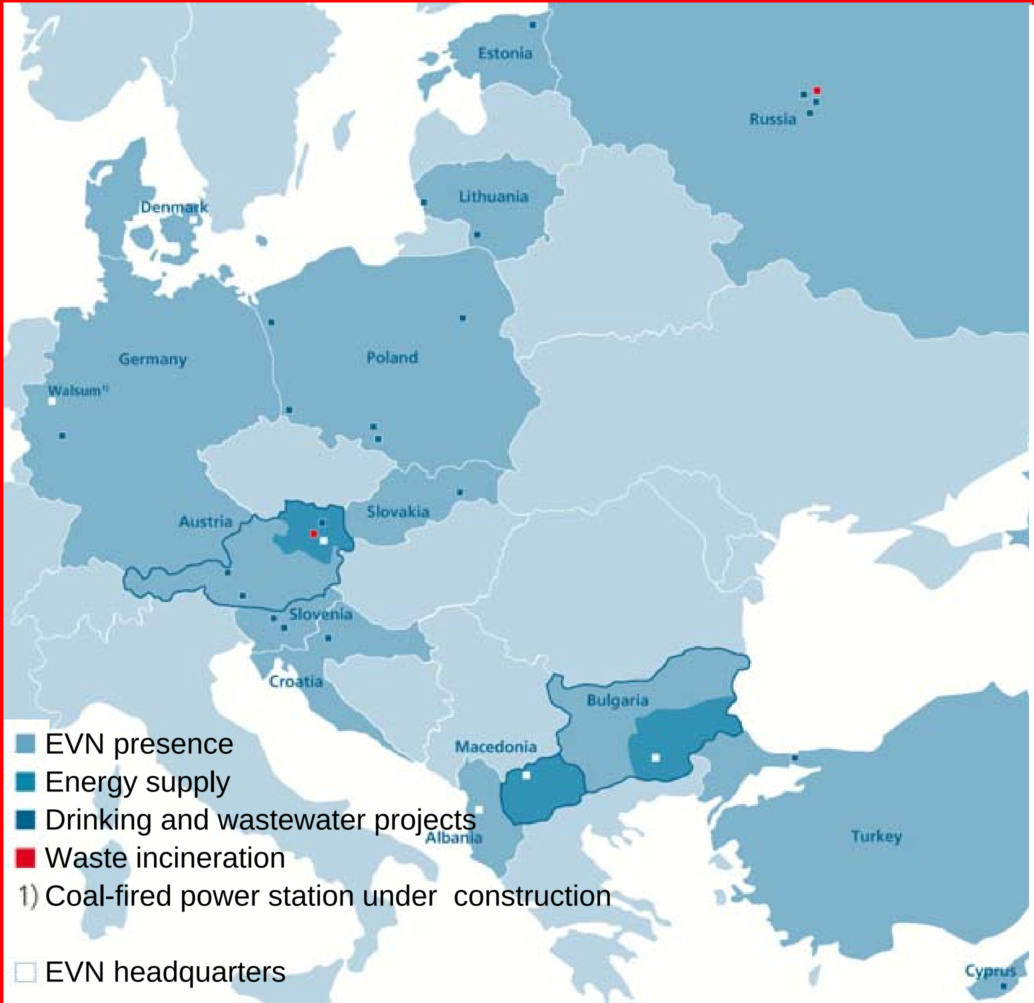
20th to 21st of May 2008

EVN Forum - Austria

EVN Company profile – fact sheet

EVN	EVN is a leading integrated energy and environmental service group serving customer in Lower Austria and Central and Eastern Europe
Business areas	Electricity, gas, heating, water, waste incineration
Countries	Austria, Bulgaria, Croatia, Cyprus, Estonia, Germany, Poland, Lithuania, Macedonia, Russia, Slovakia, Slovenia, Denmark, Turkey
Employees	9,535 (-4.4%) thereof ~ 75% in abroad
Revenue	2,233.1 EUR m (+7.8 %)
EBITDA	350.7 EUR m (-11.8 %)
EBIT	197.3 EUR m (+7.0 %)
Net results	227.0 EUR m (+2.3 %)
Credit Rating	Moody's: A1, stable Standard & Poor's: A, stable

EVN currently active in 14 CEE countries



Highlights

- 1 m electricity, gas, heat and water customers in Lower Austria
- 1.5 m electricity customers in Bulgaria
- 720,000 electricity customers in Macedonia
- 1,700 MW generation capacity (gas, coal, hydro, wind and biomass)
- Coal-fired power plant of 790 MW in Germany
- 131,000 km electricity network and 10,500 km gas pipelines
- Waste incineration plant of 300,000 tons p.a. in Lower Austria
- 70 drinking and waste water plants for 10 m people
- Waste incineration plant and drinking water facility in Moscow
- Substantial holdings in Austria’s second largest oil and gas producer and Austria’s leading hydro power producer
- Strong partner in EnergieAllianz and EconGas in Austria

EVN activities for CO_2-reduced electricity generation

- High efficient power plant technologies
  - Research activities for 700 °C power plant
  - Utilisation of high efficient power plant technologies for retrofits and new constructed power plants
- Technologies for the reduction of fossil primary usage
  - Biomass gasification (site visit 21st of May)
  - Utilisation of steam from a waste incineration to reduce the fossil primary consumption
- Utilisation of an ecological primary energy mix including wind, biomass and hydro
- Carbon capture storage - technologies
  - Participation in national and international research projects
  - Research projects for oxyfuel technology and post combustion capture technologies
  - Cooperation with Japanese electricity utility

Programme for 11th International Post Combustion CO_2 Capture Network Meeting

- Day 1: 20th of May
  - Results of fundamental studies
  - Results from different programmes which take place world wide
  - Results from CASTOR and Capture Ready – what is it?
- Day 2: 21st of May
  - Projects based on Ammonia
  - Developments by technology providers
  - Panel session: technology development – what´s next?

  - Visit to biomass gasification plant Dürnrohr

Thanks to co-sponsors

WIEN ENERGIE
WIENSTROM

bmvit
Bundesministerium
für Verkehr,
Innovation und Technologie

- Austrian Utility Association
- Wienstrom GmbH
- Federal Ministry for Transport, Innovation and Technology

EVN

International Network for CO_2 Capture

Introduction to 11th Workshop, EVN Forum

Maria Enzersdorf, Austria

By

J M Topper

Managing Director IEA Environmental Projects Ltd

IEA Greenhouse Gas R&D Programme

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

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

IEA Greenhouse Gas R&D Programme

OPEC Organization of the Petroleum Exporting Countries

ALSTOM B&W BG GROUP bp CEZ GROUP Chevron ConocoPhillips

EniTecnologie e·on EPRI ExxonMobil REPSOL YPF

RWE Schlumberger Statkraft STATOIL TOTAL VATTENFALL

International Network for CO_2 Capture

- ***AIM*: *To establish a forum that will encourage practical work on CO_2 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***

International Network for CO_2 Capture

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

International Network for CO_2 Capture

1st Workshop in Gaithersburg, USA (Spring 2000)	
2nd Workshop, Calgary, Canada(November 2001)	23 people
3rd Workshop in Apeldoorn; Netherlands (Spring 2002)	24 people
4th Workshop in Kyoto, Japan (Autumn 2002)	34 people
5th Workshop in Pittsburgh, USA (June 2003)	33 people
6th Workshop in Trondheim, Norway, (Spring 2004)	40 people
7th Workshop in Vancouver, Canada, (Sept 2004)	69 people
8th Workshop in Austin, USA (Autumn 2005)	41 people
9th Workshop at offices of E2, Copenhagen (June 2006)	52 people
10th Workshop at IFP in Lyon, France (May 2007)	62 +11 people
11th Workshop in EVN Forum, Austria (May 2008)	90+ people
12th Workshop in Univ Regina, Canada (September 2009?)	
13th Workshop/Conference probably Australia 2010	

GHGT-9

- Omni Shoreham Hotel, Washington D.C.
- 16th – 20th 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

International Network for CO_2 Capture

- We are now a well established club
- 16 countries here today
- Excellent networking; very popular.

Today: Housekeeping Points

- Coffee breaks around 10.45 and 14 55
- Lunch, 12 30 – 13 30 followed by photos
- Afternoon session will finish at around 17 00
- Dinner this evening by bus to the heuriger
- ALL PRESENTERS ensure Stanley Santos gets a copy of their presentation on data storage stick if you want it on the GHG website next week
- Tomorrow we finish with a panel session and lunch
- Visit to power station follows.
- Mobile phones off or on vibrating alert

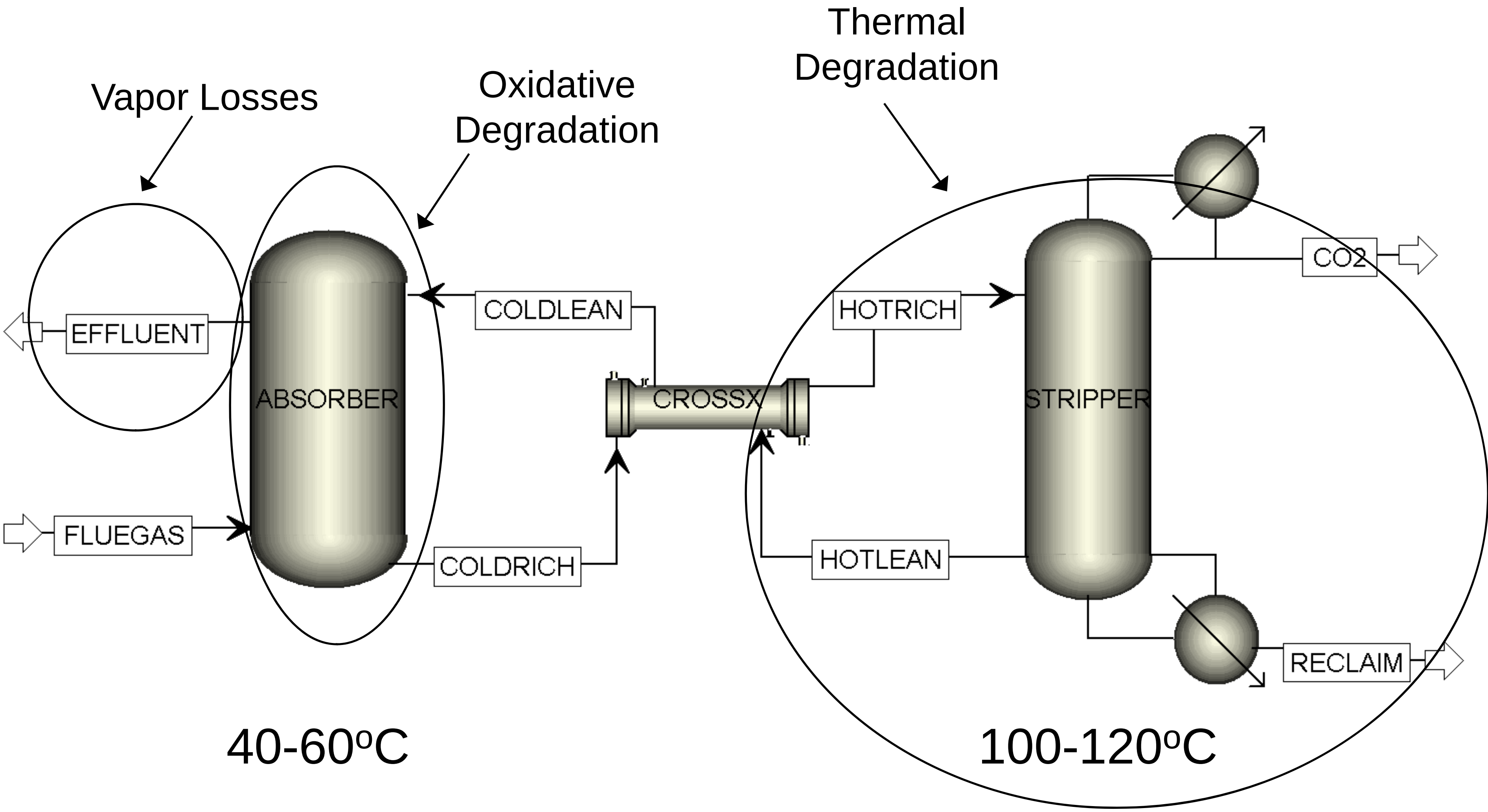
Thanks to EVN and all co-sponsors

- To EVN for local organisation, offering the meeting room and visit to their facilities
- And especially to Federal Ministry of Transport Innovation and Technology for Sponsoring the Dinner this evening.
- And to the Austrian Utility Association
- And to Wienstrom GmbH

Amine Degradation

Jason Davis - Thermal
Andrew Sexton - Oxidative
The University of Texas at Austin

Amine Losses



Vapor Losses

Oxidative Degradation

Thermal Degradation

40-60°C

100-120°C

Degradation Issues

- Solvent make-up costs can be a significant operating cost
- Trade off between energy/capital costs and solvent degradation
- Environmental implications of amine waste disposal
- System performance including corrosion and foaming

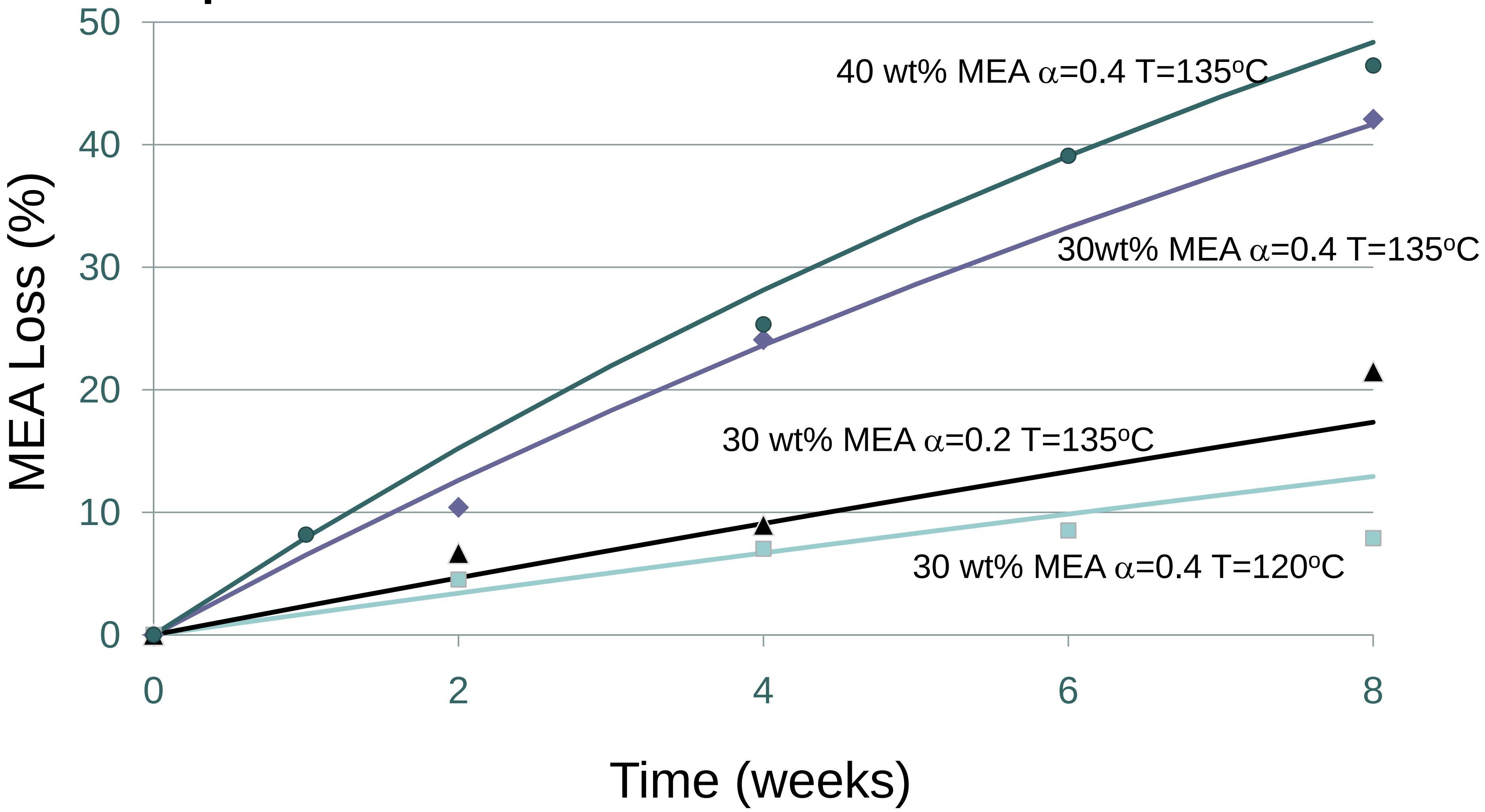
Thermal Degradation

- Experimental Set-up
- MEA Degradation
  - Varied amine concentration, loading and temperature
  - Regressed data
  - Identified unknowns
- Amine Screening
  - One set of conditions

Thermal Degradation Experimental

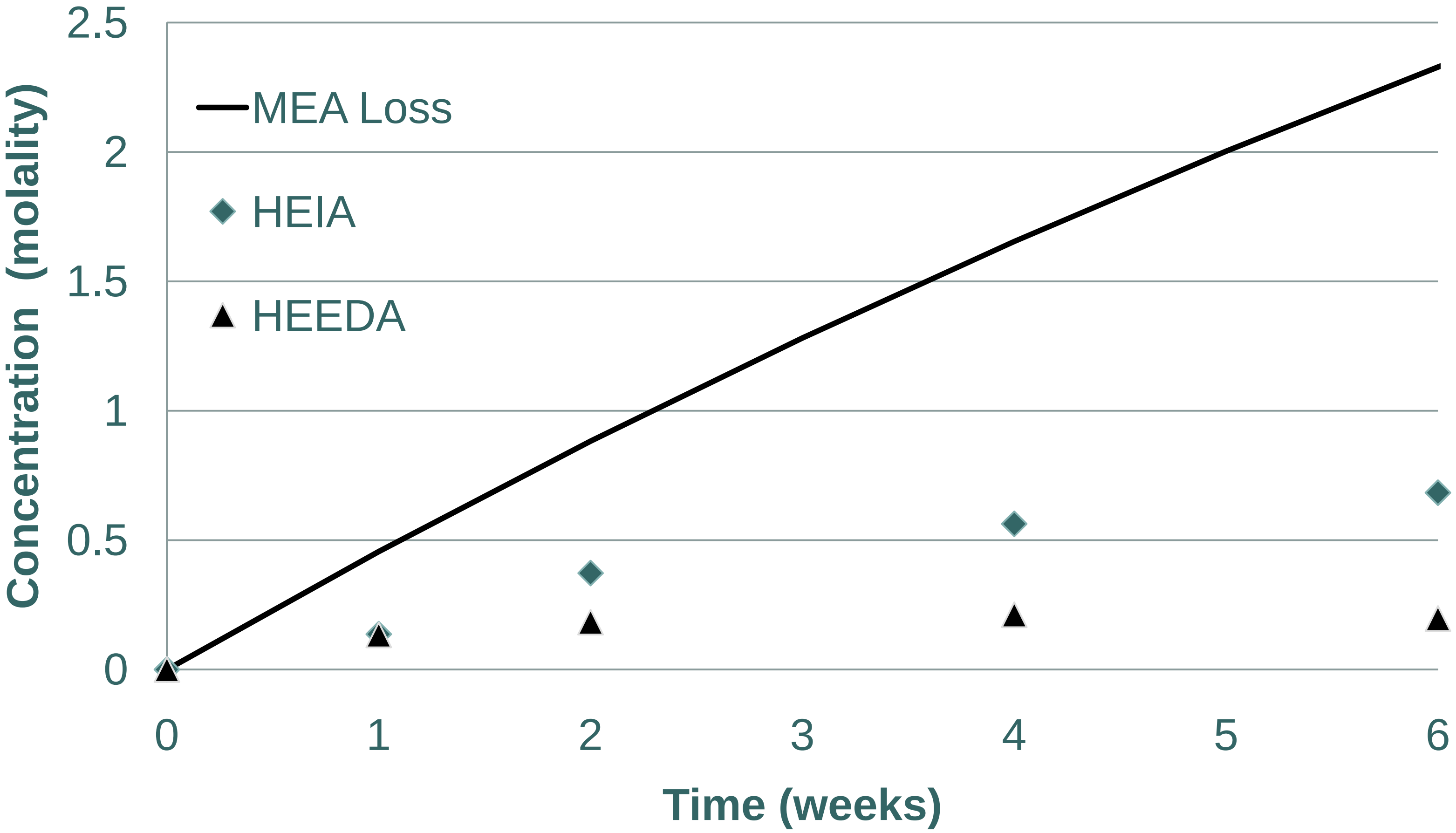
- 10mL stainless steel sample containers filled with differing amine solutions
- Placed in forced convection ovens at set temperatures
- Analyzed for ionic products (amines) with IC and nonionic products with HPLC
- GC provided unreliable results with several solvent systems (overpredicted rates in all cases)

MEA Results



40 wt% MEA α=0.4 T=135°C
30wt% MEA α=0.4 T=135°C
30 wt% MEA α=0.2 T=135°C
30 wt% MEA α=0.4 T=120°C
MEA Loss (%)
0
10
20
30
40
50
Time (weeks)
0
2
4
6
8

MEA Degradation Products



7 molal MEA at 135^{o}C and a loading of 0.4

MEA Conclusions

- Thermal degradation quadruples every 15^{o}C
- CO_2 loading increase degradation more than 1st order
- Amine concentration increases degradation more than 1st order
  - Increasing the concentration from 15 to 40wt% would also increase the BP by 4^{o}C and degradation by 40%
- Analysis with ASPEN models showed
  - Highest degradation rates found at the bottom of the stripper where temperatures were highest
  - Lowering the stripper pressure/temperature is the surest way to decrease degradation
  - 30wt% MEA with average loading of 0.4 at atmospheric pressure yields <0.15kg MEA/ton CO_2

Thermal Screening (T=135^{o}C α=0.4 t=4wks)

Amine	Concentration (molality)	Remaining Amine Peak (%)
PZ	3.5	100
AMP	3	97
DGA	7	93
MEA / PZ	7 / 2	88 / 68
MEA	7	76
MDEA	50 wt%	71
EDA	3.5	64
DETA	2.3	9
HEEDA	3.5	3

Thermal Screening Conclusions

- Most amines degraded thermally under the specified conditions
- MEA mainly converted to nonionic products
- Piperazine degradation could not be detected under these conditions
- Industrially, MDEA does not significantly degrade but under these conditions it does shift to other amines
- In a blended system of MEA and PZ, both MEA and PZ did degrade in significant quantities

Oxidative Degradation (Andrew Sexton)

- Experimental setup
- Analytical
- High gas flow and low gas flow experiments
- Liquid and vapor phase products
- Relative rates of various amines

Experimental

- High gas flow apparatus
  - CO_2/O_2 mixture introduced by bubbling into bottom of reactor with agitation
  - Vapor phase analysis with FTIR
  - Liquid phase analysis with IC
- Low gas flow apparatus
  - CO_2/O_2 mixture introduced in headspace of reactor
  - Vortexing at high agitation rates used for vapor / liquid mixing
  - No vapor phase analysis

Analytical

- FTIR used to detect ammonia, amine volatility, NO_x, CO, acetaldehyde, formaldehyde
- Cationic IC for amine losses and anionic IC for heat stable salt products
  - Caustic addition used to measure for amide production
- HPLC with electrochemical detection for amino acids and UV detection for aldehydes

30 wt% MEA with 1mM Fe	High Gas Flow – Vapor (mM/hr)	High Gas Flow – Liquid (mM/hr)	Low Gas Flow (mM/hr)
Formate		0.181	0.289
Formamide		0.485	0.352
Acetate		0.018	0.002
Oxalate		0.003	0.020
Oxamide		0.092	0.090
Nitrite/Nitrate		0.0367	0.265
NH3	1.935		
NOx	0.154		
CO	0.027		
CH4 / C2H4	0.053		
Formaldehyde	0.010		
Acetaldehyde	0.011		
Methanol	0.025		
MEA	1.060		

Rate Comparisons

System	Iron (mM)	Inhibitor “A” (mM)	Carbon (mM/hr)	Nitrogen (mM/hr)
7m MEA	0.1	0	0.51	0.51
7m MEA	0.1	100	0.10	0.04
5m PZ	5	0	0.046	0.040
3m Amp	0.1	0	0.015	0.004
Glycine	1	0	0.026	0.001
EDA	1	0	0.065	0.042

Oxidative Conclusions

- MEA oxidative degradation is much faster than other amines tested when uninhibited
- AMP oxidative degradation is slower than other amine systems tested
- For MEA, amides of oxalate and formate are present in significant quantities
- Vapor phase FTIR shows NO_X and CO emissions present for uninhibited MEA systems

Conclusions

- MEA thermal degradation has been quantified over a wide range of conditions
- Most amines thermally degrade, but there is a wide variation in rates
- Thermally stable amines can degrade when used in a blended system
- MEA oxidative degradation was an order of magnitude faster than AMP and PZ under similar conditions
- Amides of common oxidative degradation products have been found at significant quantities
- NOx and CO emissions were found in the vapor phase analysis at absorber conditions

QUESTIONS?

jdavis@che.utexas.edu

IEA GHG – 11th Meeting of the Post-Combustion
CO_2 Capture Network

Aqueous Concentrated Piperazine – a Fast, Stable, and Effective Solvent

Stephanie Freeman, Marcus Hilliard, Andrew Sexton,
Ross Dugas, and Gary T. Rochelle

The University of Texas at Austin

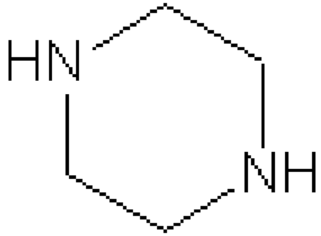
March 20-21st ○ EVN Forum ○ Vienna, Austria

Outline

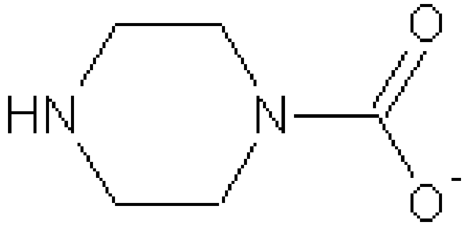
- Introduction to Concentrated Piperazine
  - Previous Work
  - Solid-Liquid Equilibrium
  - Volatility
  - Viscosity
- Energy Performance
  - Vapor-Liquid Equilibrium
  - Kinetics of CO_2 Absorption
- Degradation
  - Oxidative
  - Thermal
- Conclusions

Previous work with Piperazine (PZ)

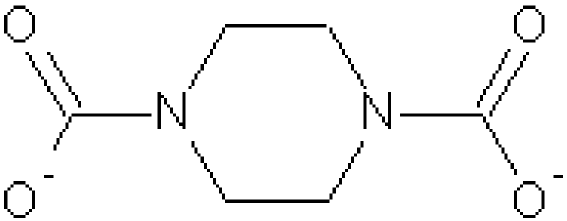
- Piperazine has been used as a promoter at concentrations up to 4 m
  - 7 m MDEA / 2 m PZ
  - 2.5 m K_2CO_3 / 2.5 m PZ



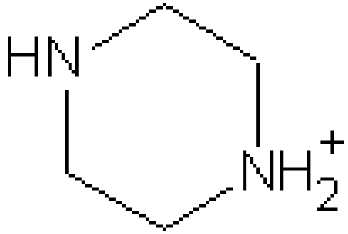
PZ



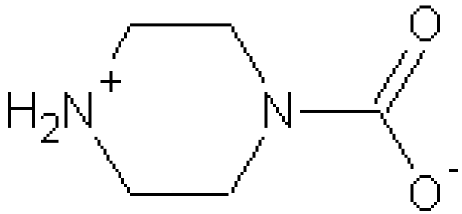
PZ COO^-



PZ $(COO^-)_2$



H^+PZ

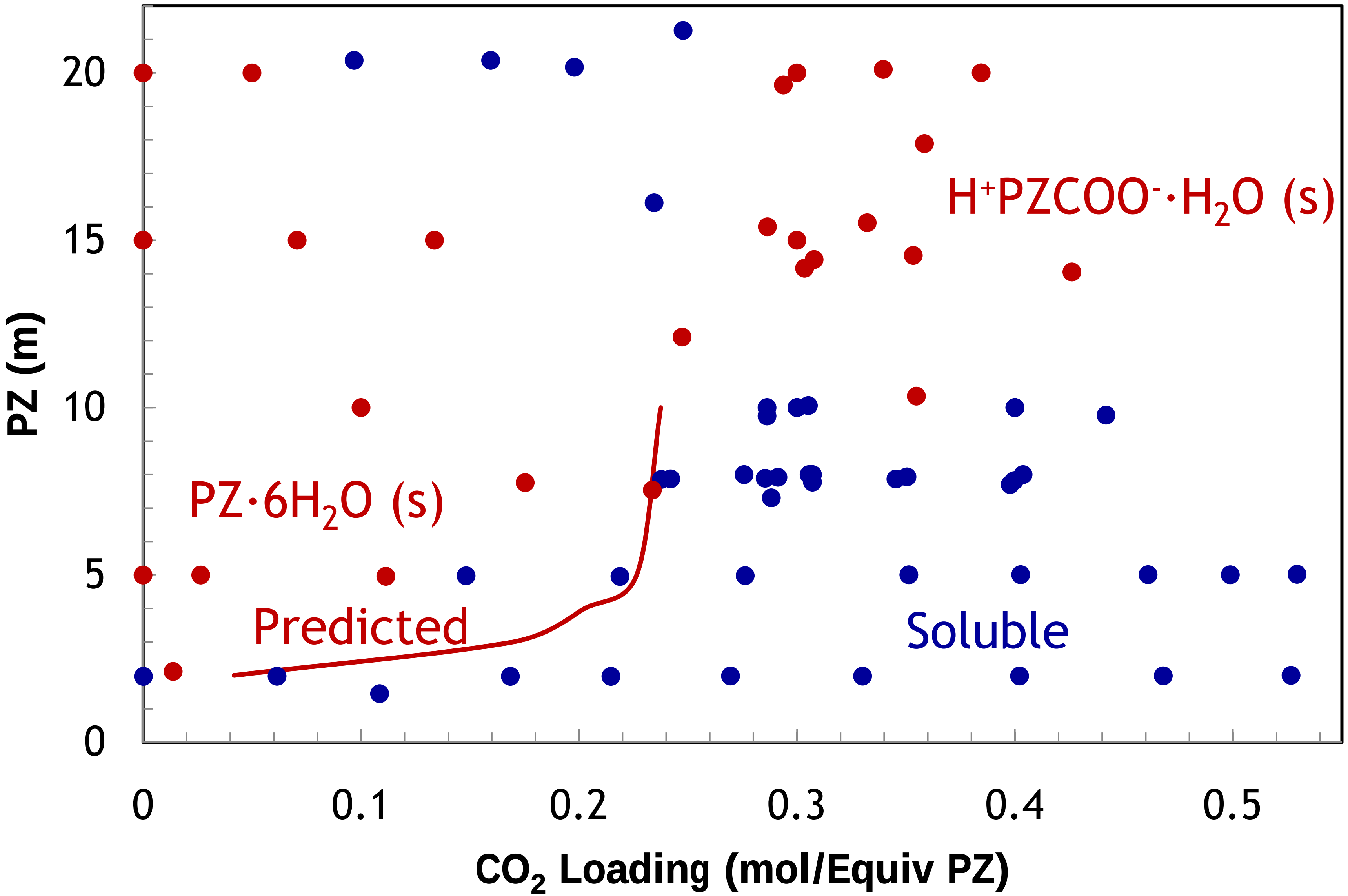


H^+PZ COO^-

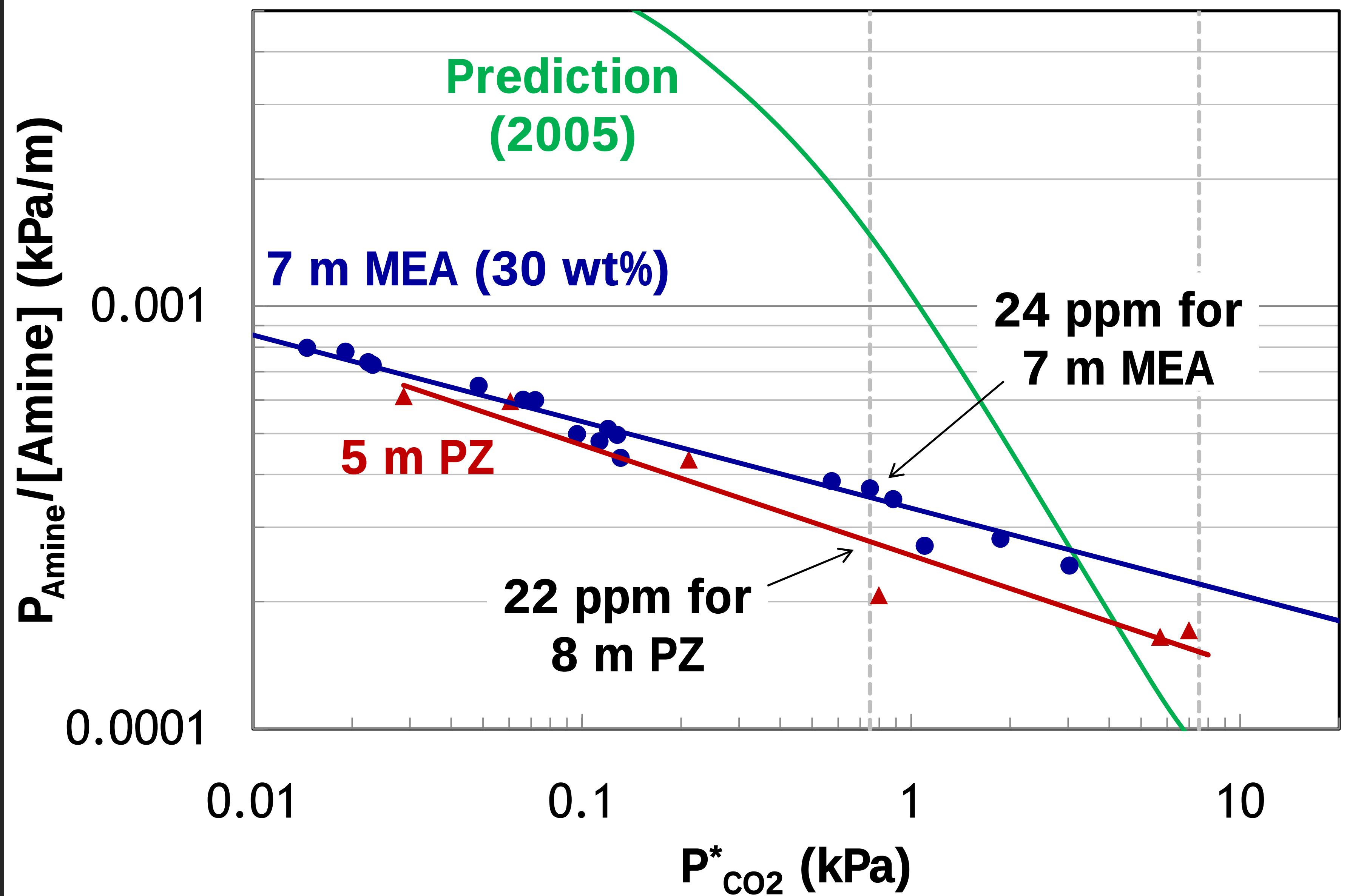
Introduction

- Why didn't we consider PZ before?
  - Solubility = 1.75 m PZ
    - PZ has low capacity at 1.75 m PZ
  - Boiling point is lower than MEA
    - Expected volatility is greater than MEA
- What's New?
  - We can prepare 8 m solutions at useful loadings
  - Non-ideality results in volatility equivalent to MEA

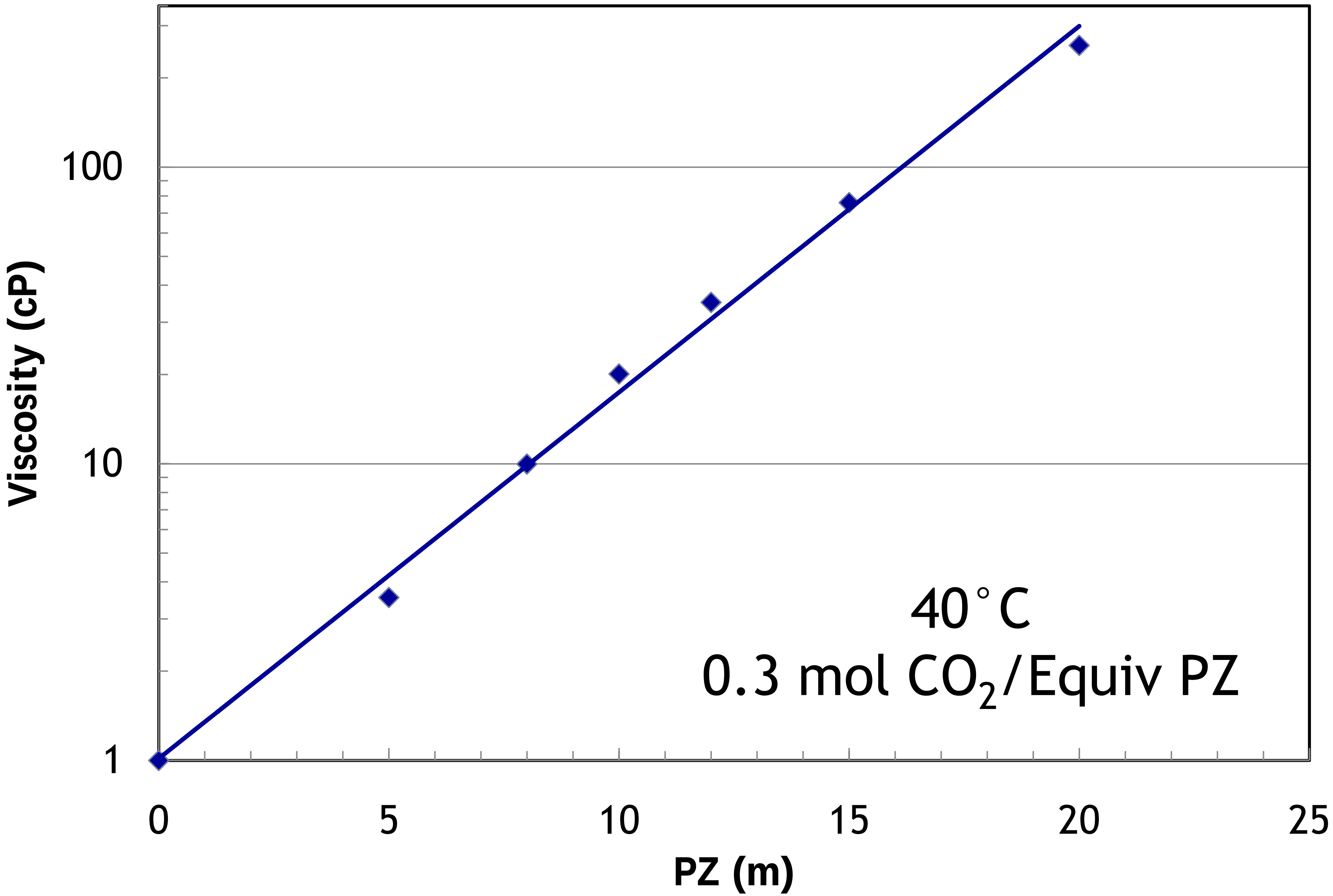
Solid Solubility at 21°C



Normalized Amine Volatility at 40°C

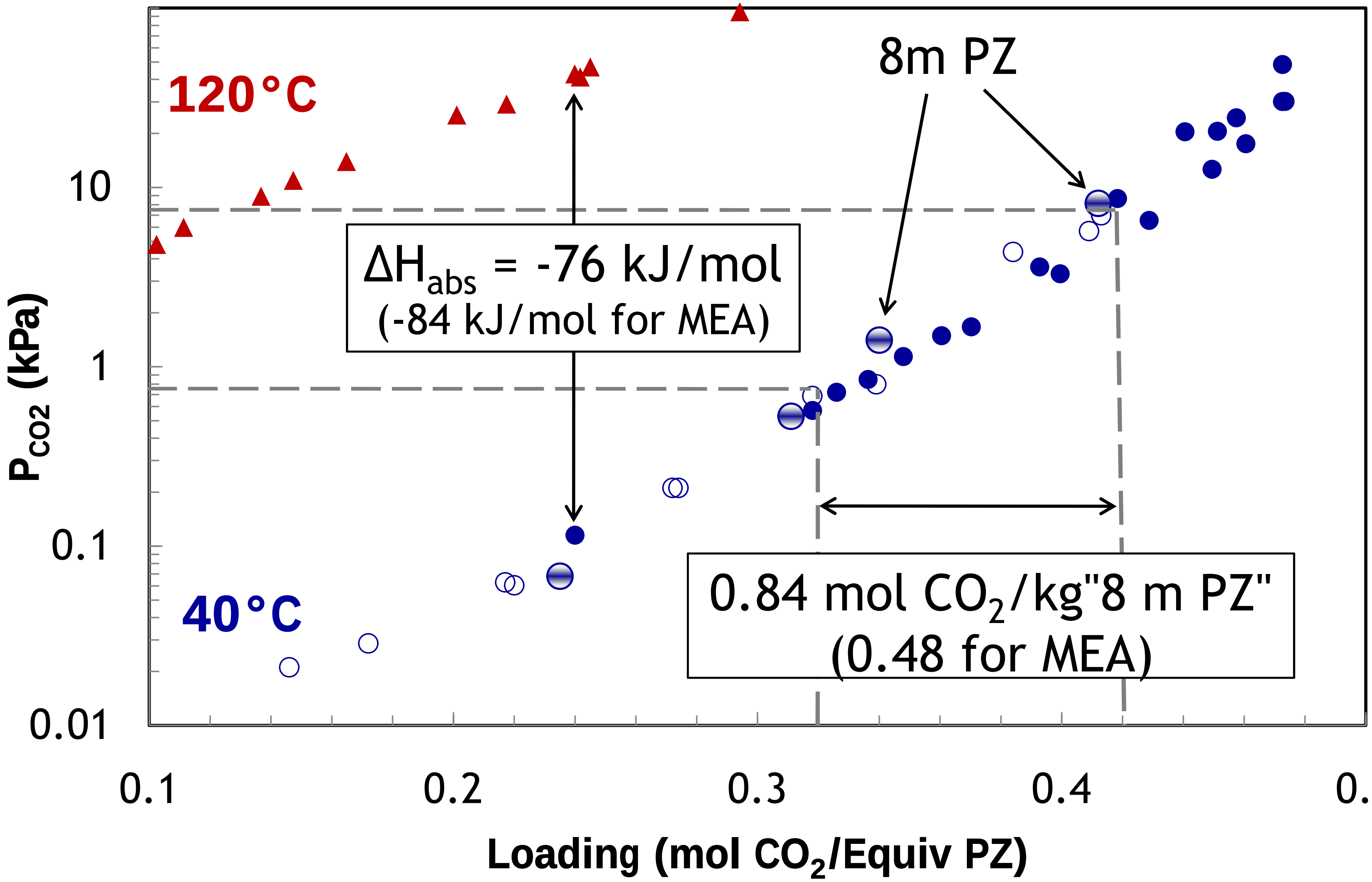


PZ is highly viscous above 8 m



Thermodynamics of PZ-H_2O-CO_2

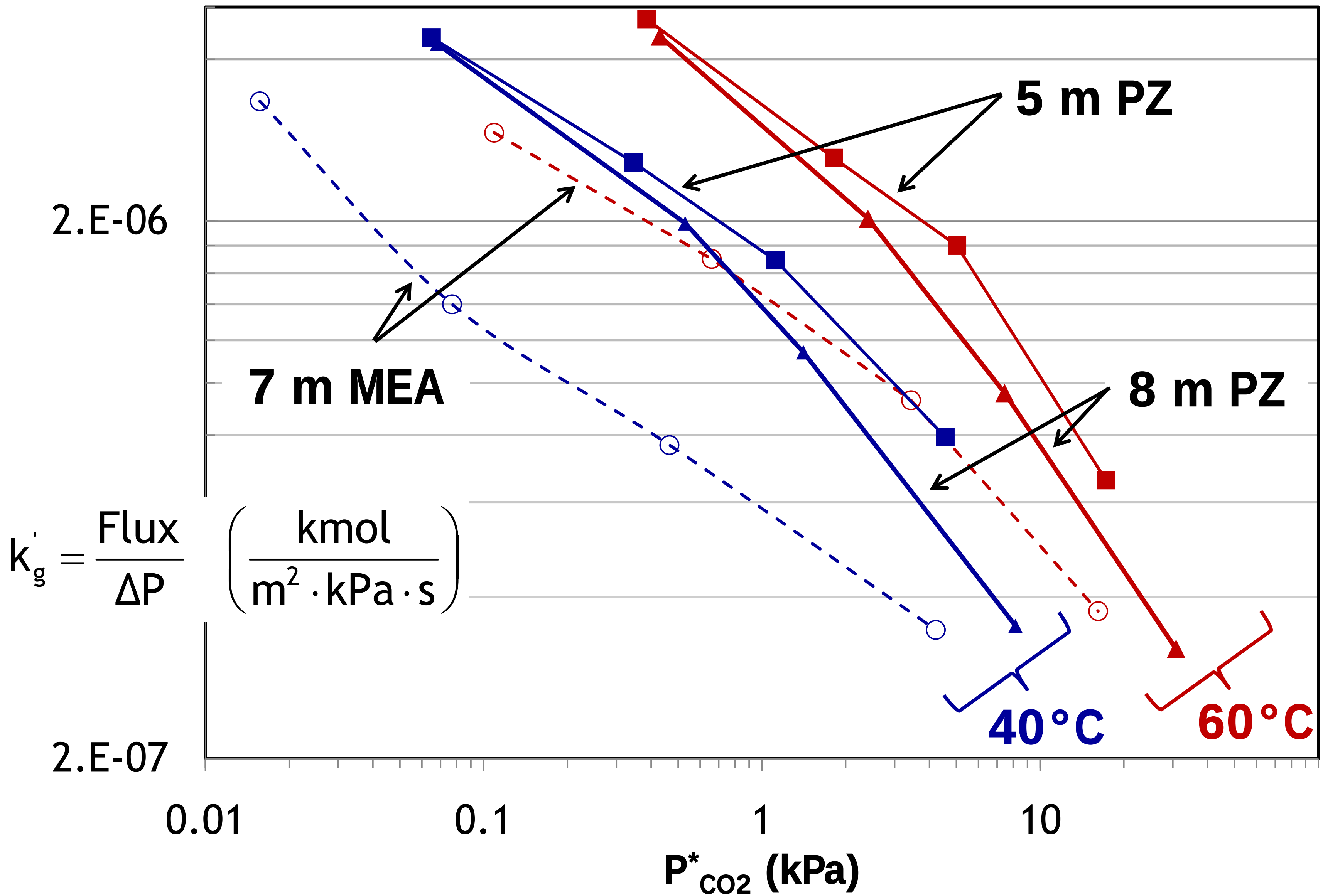
4.0 m (Ermatchkov 2006), 3.6 to 8.0 m (This Work)



ΔH_{abs} = -76 kJ/mol
(-84 kJ/mol for MEA)

0.84 mol CO_2/kg"8 m PZ"
(0.48 for MEA)

5 to 8 m PZ Doubles Rate of CO_2 Absorption



$$k_g' = \frac{\text{Flux}}{\Delta P} \left(\frac{\text{kmol}}{m^2 \cdot \text{kPa} \cdot s} \right)$$

Simple Stripper Energy Requirement

- Interpolated from Oyenekan (2007)
- CO_2 product delivered at 10 MPa

	7 m MEA	8 m PZ	Ideal
ΔH_{abs} (kJ/mol)	84	76	
CO_2 Capacity (mole/kg soln)	0.46	0.84	
Rich P_{CO2} at 40°C (kPa)	5	7.5	12
Equiv Work (kJ/mole)	30.9	28.2	18

Degradation Products

- Anion and cation chromotgraphy (Dionex)
- HPLC for molecular products
- Primary degradation products:
    - Amines: Ethylenediamine (EDA)
    - Amides: formamide, oxamide
    - Carboxylic acids: formate, oxalate
    - Nitrite and nitrate
    - (Ammonia)
- Total acid = acid + amide

PZ is resistant to Oxidation

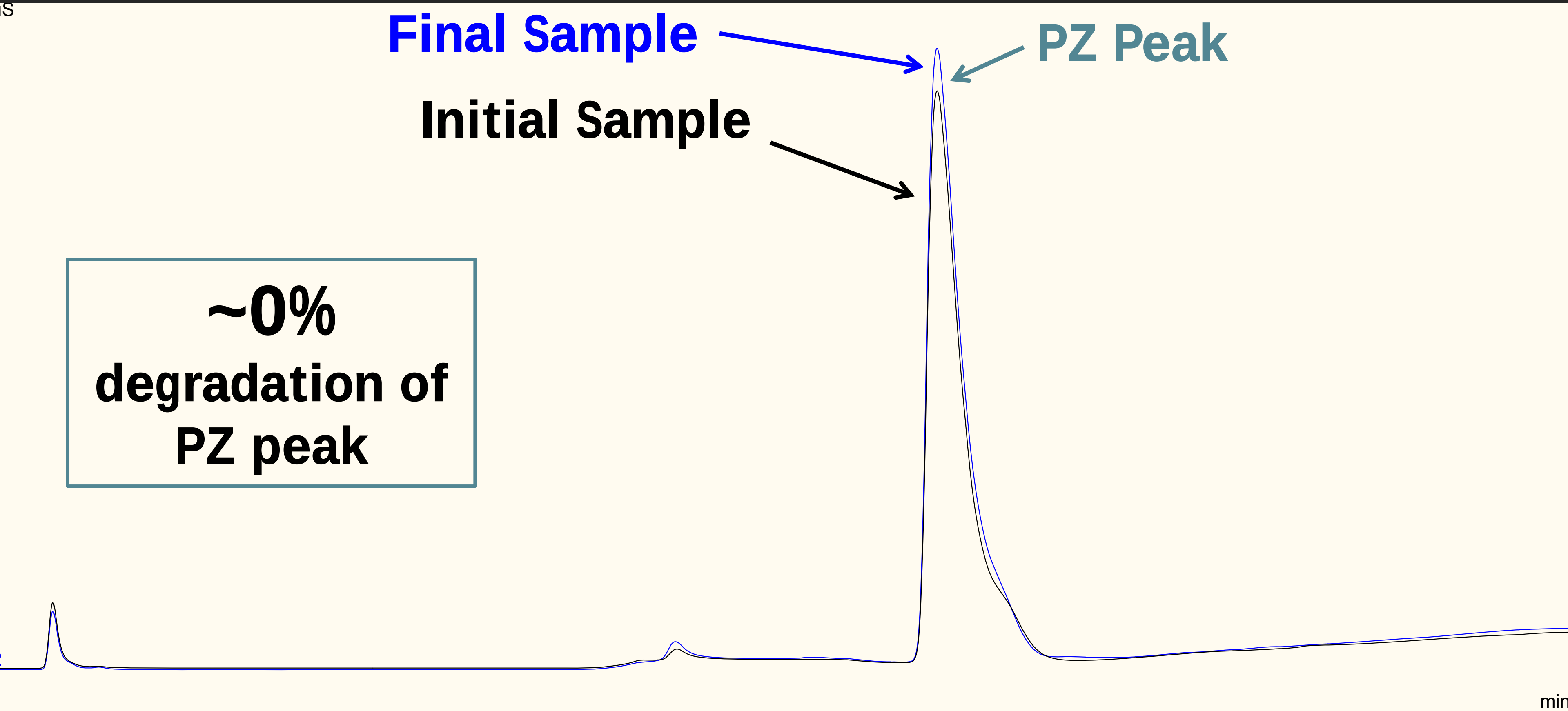
- 55°C, 100 mL/min O_2 w/ 2% CO_2 in 350 mL

AMINE	7 m MEA	10 m PZ	8 m PZ	10 m PZ
Additives **(mM)**	0.6 Fe	4.0 Cu	5.0 Cu 0.1 Fe 100 “A”	0.1 Fe 0.1 Ni 0.6 Cr
	Production Rates (mM/hr)			
Ethylenediamine	-	0.43	-	-
Total Formate	0.40	0.36	0.03	0.01
Total Oxalate	0.04	0.02	0.001	-
Nitrate/Nitrite	0.46	0.01	0.001	0.0003

Thermal Degradation of Piperazine

- SS bombs in forced convection ovens
- Degradation negligible up to 150°C
- Degradation not catalyzed by metals
  - Cu + Fe
  - Fe + Ni + Cr
  - Cu + Fe + Inhibitor "A"

5 m PZ at 135°C, 8 wks, α=0.5



Final Sample

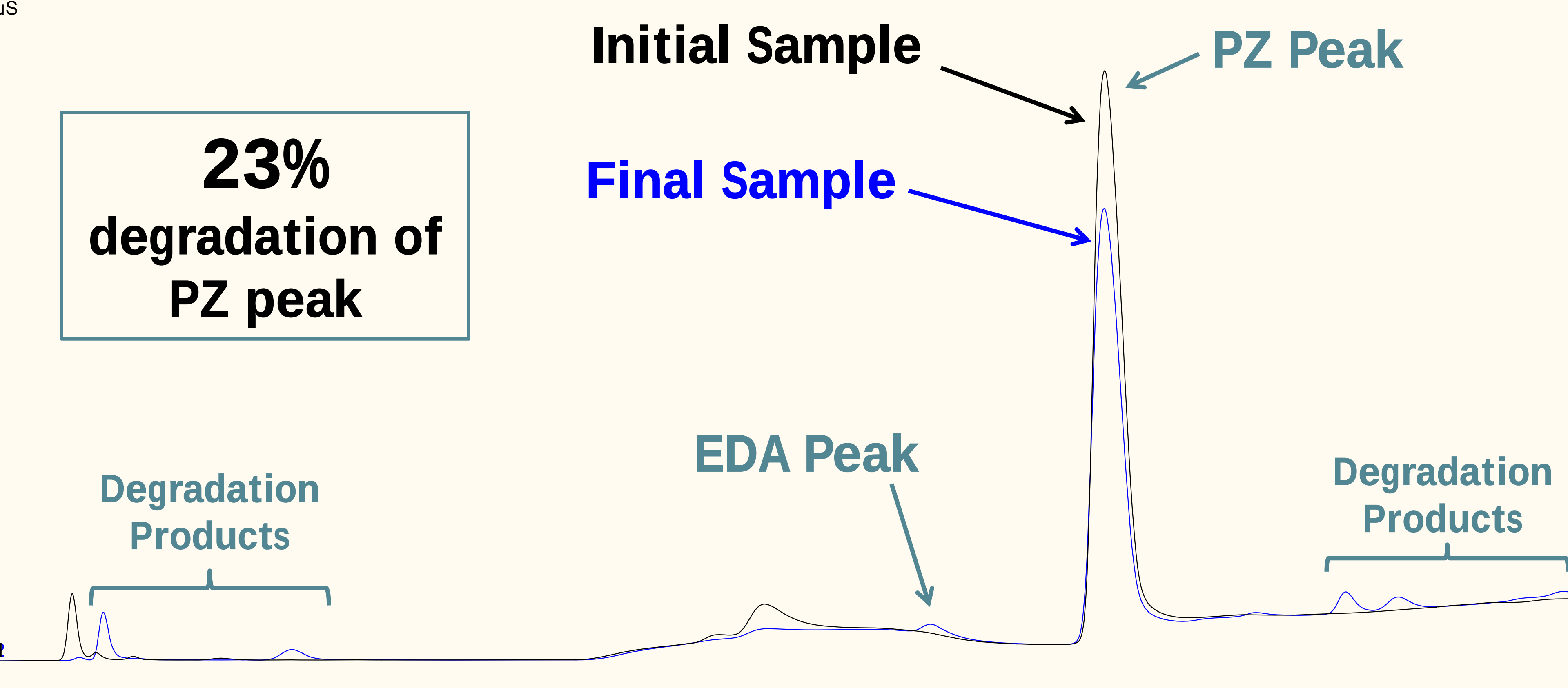
PZ Peak

Initial Sample

~0%
degradation of
PZ peak

8 m PZ at 175°C, 5 wks, α=0.3

23%
degradation of PZ peak



Initial Sample

Final Sample

PZ Peak

EDA Peak

Degradation Products

Degradation Products

Conclusions

- 8 m PZ is soluble at 0.25-0.4 mol CO_2/Equiv PZ
- Viscosity becomes prohibitive above 8 m PZ
- PZ volatility less than predicted & equiv to MEA
- CO_2 capacity is double that of 7 m MEA
- CO_2 absorption rate is double that of 7 m MEA
- Thermal degradation of PZ is negligible
- Oxidative degradation
    - Negligible with Fe, Cr, Ni, V, and Cu/“A”
    - Significant with Cu alone

Alfons Kather

Jochen Oexmann

Evaluation of Post-Combustion CO_2-Capture using Piperazine-Promoted Potassium Carbonate in a Coal Fired Power Station

TUHH
Technische Universität Hamburg-Harburg
Institute of Energy Systems
Prof. Dr.-Ing. A. Kather

11th Workshop of the Post-Combustion CO_2-Capture Network
Vienna, 21st May 2008

Agenda

Technische Universität Hamburg-Harburg

- **CO_2-Capture with K_2CO_3/PZ**
  - Thermodynamic model
  - Boundary conditions
- **CO_2-Compression**
- **Power Plant Integration**
- **Results**
  - Specific reboiler heat duty
  - Specific power loss of overall integrated process
- **Column Design**
  - Absorber and desorber sizes
- **Comparison to MEA**
- **Summary and Outlook**

K_2CO_3 / PZ as an Alternative Solvent for PCC

- **CO_2-capture process with MEA is considered the reference in post-combustion CO_2-capture, as**
    - Experience from commercial processes exist
    - Drawbacks: corrosivity, degradation and large regeneration heat duty
- **Potassium Carbonate (K_2CO_3)**
    - Cheap
    - Non-volatile
    - Non-toxic
    - But: low rate of absorption at atmospheric pressure
- **Promotion with Piperazine (PZ)**
    - Two amine functional groups ⇨ large capacity + high rate of absorption
    - Less sensitive towards O_2, SOx and NOx than MEA

Thermodynamics

- **Chemical absorption of CO_2 with K_2CO_3/PZ described by reaction scheme:**

$$2\,H_2O \longleftrightarrow H_3O^+ + OH^-$$

$$CO_2 + 2\,H_2O \longleftrightarrow H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-}$$

$$PZH^+ + H_2O \longleftrightarrow PZ + H_3O^+$$

$$\boxed{\begin{array}{c} PZ + HCO_3^- \longleftrightarrow PZCOO^- + H_2O \\ PZCOO^- + HCO_3^- \longleftrightarrow PZ(COO^-)_2 + H_2O \end{array}}$$

rate of absorption

$$HPZCOO + PZ \longleftrightarrow PZCOO^- + PZH^+$$

$$K_2CO_3 \longrightarrow 2\,K^+ + CO_3^{2-}$$

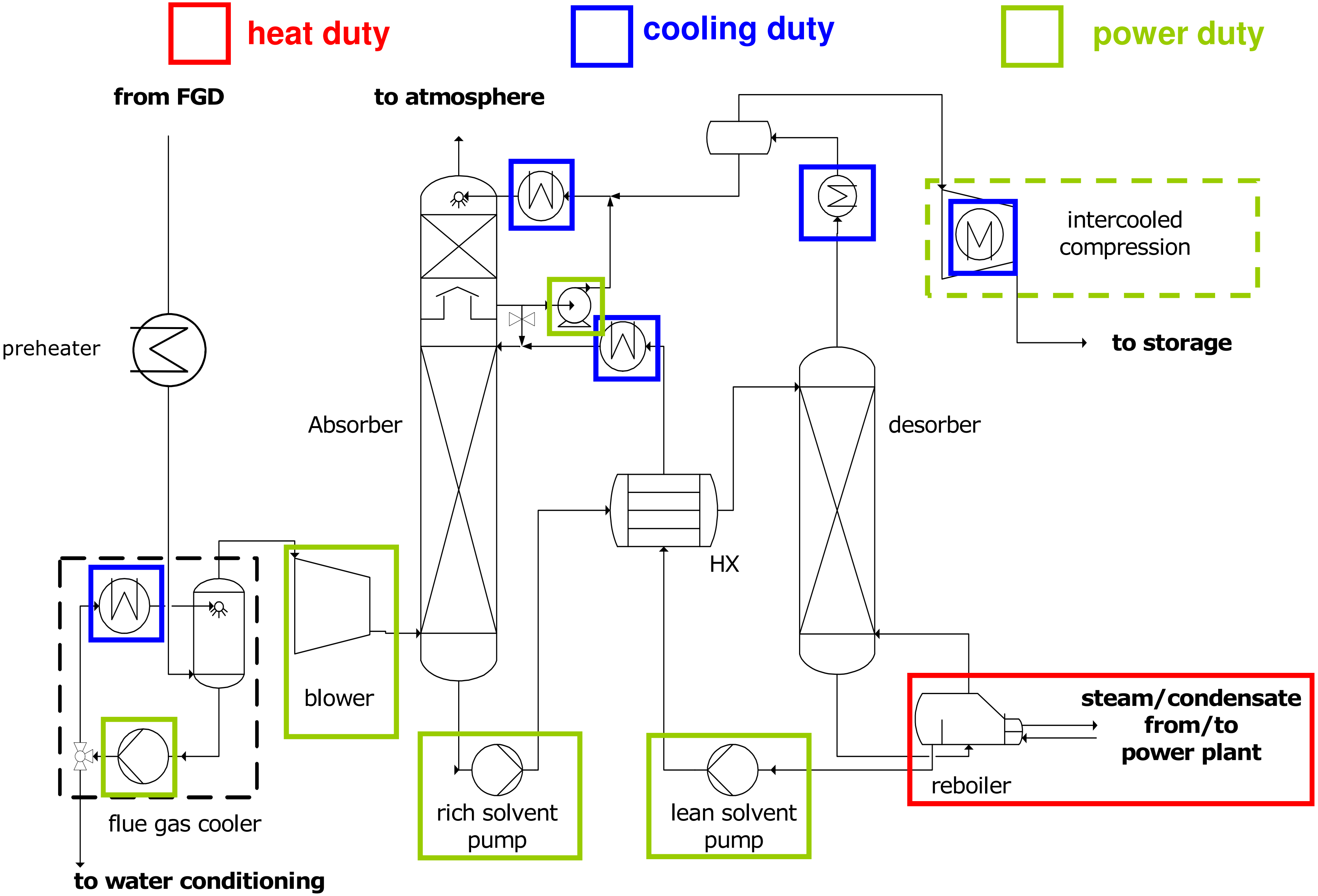
$$KHCO_3 \longrightarrow K^+ + HCO_3^-$$

- **Carbamate reactions dominant for overall absorption rate**

- **Electrolyte Non Randomness Two Liquid Model (eNRTL) in ASPEN Plus**
- **eNRTL parameters regressed by *Hilliard (2007)***

Interfaces to Power Plant

TUHH
Technische Universität Hamburg-Harburg

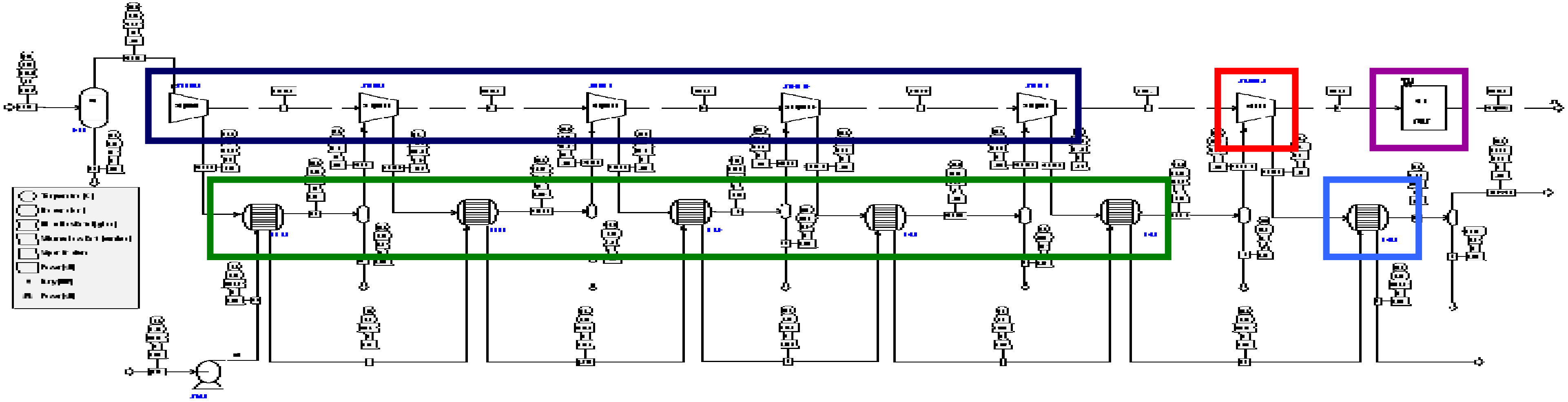


Boundary Conditions

• Flue gas mass flow	577 kg / s	
• Flue gas temperature from FGD	47 °C	
• Flue gas temperature at absorber inlet	62 °C	
• Flue gas CO_2 concentration	14.2 vol% (wet) 15.9 vol% (dry)	
• Absorber solvent inlet temperature	40 °C	
• Lean-rich heat exchanger LMTD	5 K	
• Reboiler temperature difference	10 K	
• CO_2 condition at compressor outlet	40 °C / 110 bara	
• Analysed solvents	2.5 m K_2CO_3 / 2.5 m PZ	$(S_{2.5,2.5})$
	3.2 m K_2CO_3 / 1.6 m PZ	$(S_{3.2,1.6})$
	4.8 m K_2CO_3 / 0.6 m PZ	$(S_{4.8,0.6})$
	3.0 m K_2CO_3	$(S_{3.0})$
• Lean Loading	*varied for minimisation of reboiler duty*	

CO_2-Compression

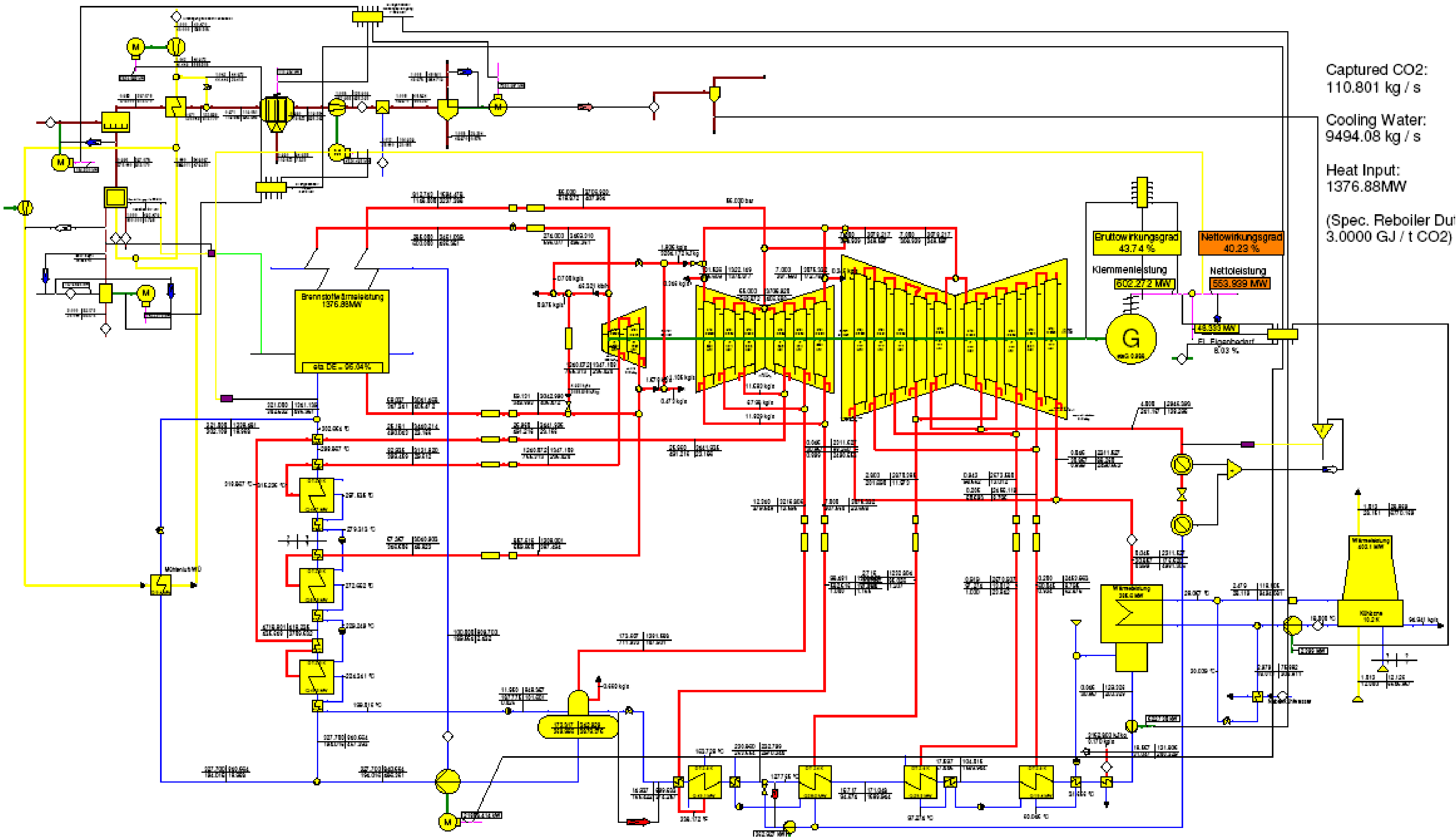
- **Simulation tool: *ASPEN Plus***
- **Technical data**
  - 2 parallel trains of similar geartype compressors with **5 radial stages** (η_i= 0,84....0,87)
  - 1 **booster** unit (outlet pressure 110 bar; η_i = 0,82)
  - **electric drive**
  - **intercooler** with water draw off after each stage ($\Delta p_{\text{hot side}}$ = 100 mbar)
  - **aftercooler** (outlet temperature 40 °C)



Reference Power Plant North-Rhine-Westphalia

TUHH
Technische Universität Hamburg-Harburg

- 600 MW_{el} hard coal fired power plant in EBSILONProfessional: η_{net} = 45.6 % (LHV)



Captured CO2:
110.801 kg / s

Cooling Water:
9494.08 kg / s

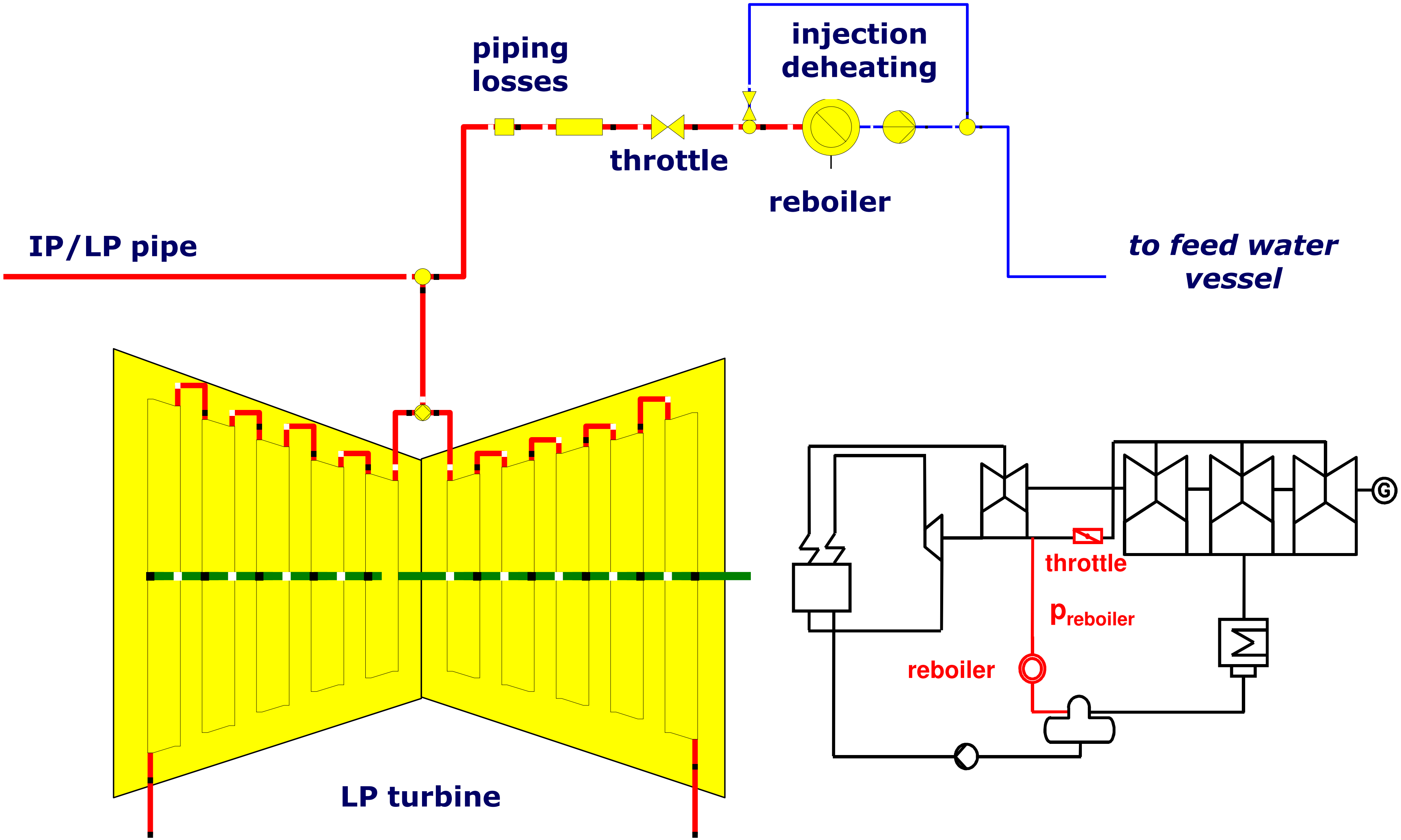
Heat Input:
1376.88MW

(Spec. Reboiler Du
3.0000 GJ / t CO2)

11th Workshop of the International
Network for CO_2 Capture, May 2008, Vienna

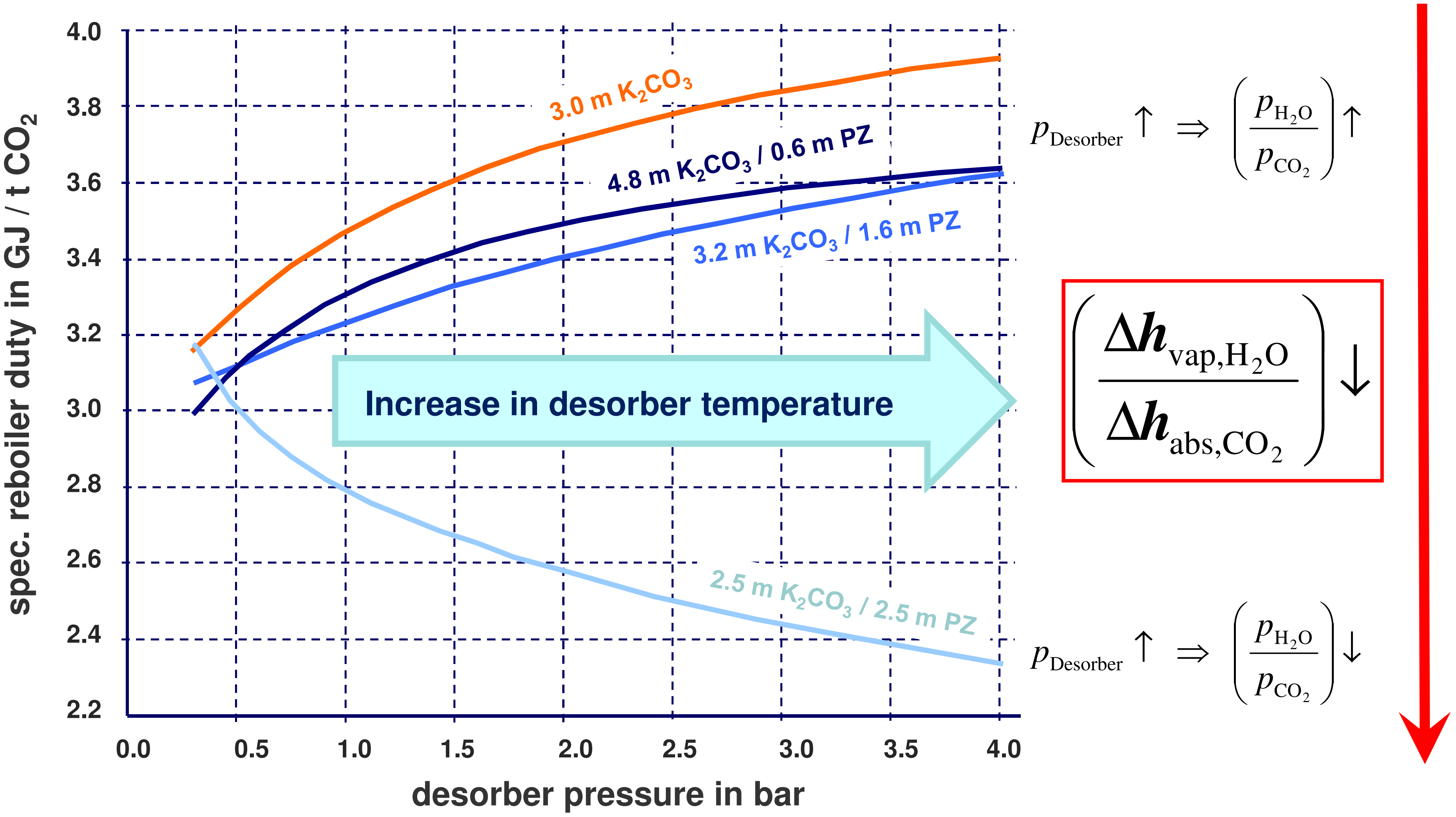
►Power plant integration

Heat for Solvent Regeneration



Effect of Desorber Pressure @ 90 % CO_2-Capture Rate

TUHH
Technische Universität Hamburg-Harburg



$$p_{\text{Desorber}} \uparrow \;\Rightarrow\; \left(\frac{p_{H_2O}}{p_{CO_2}}\right)\uparrow$$

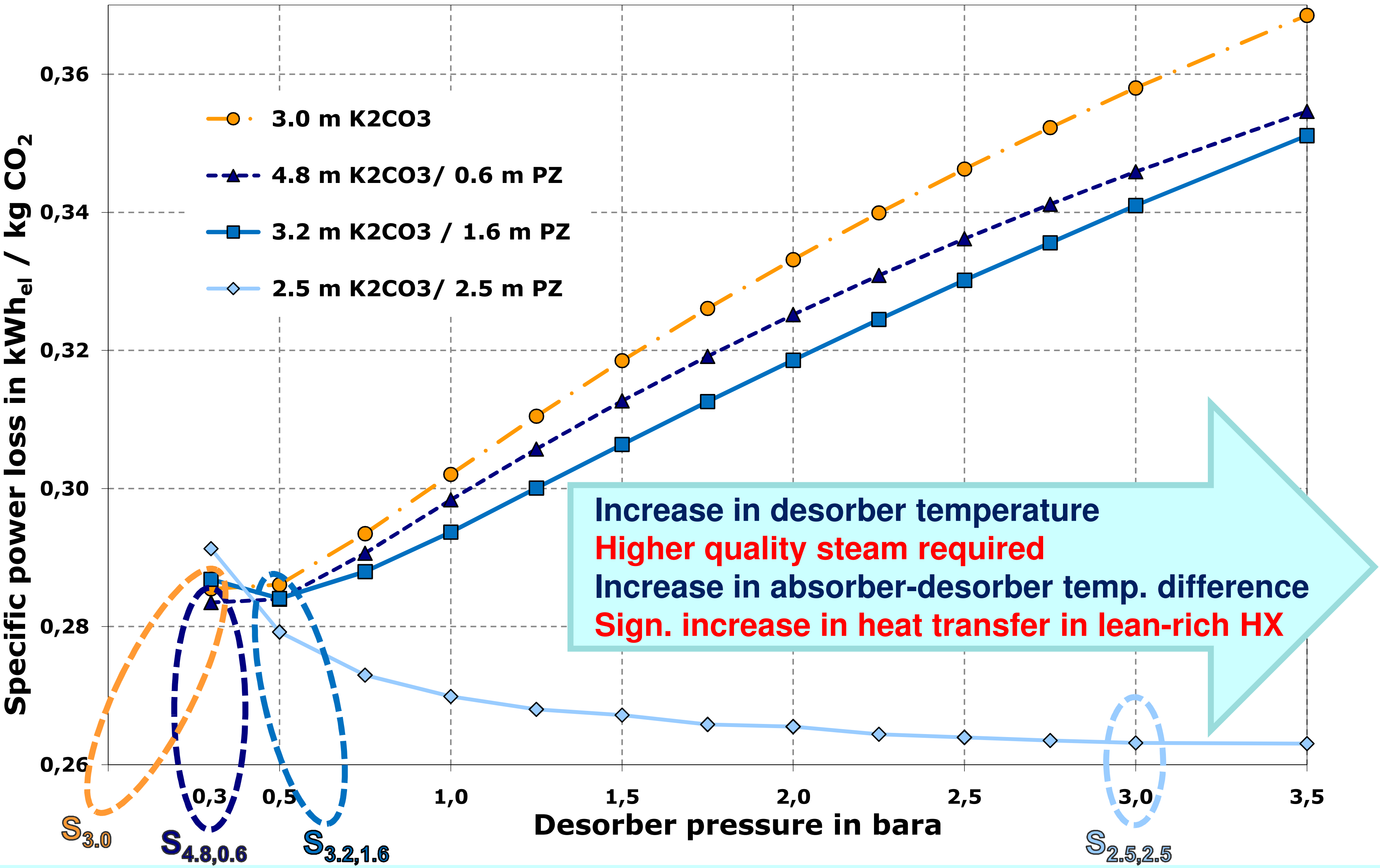
$$\boxed{\left(\frac{\Delta h_{\text{vap},H_2O}}{\Delta h_{\text{abs},CO_2}}\right)\downarrow}$$

$$p_{\text{Desorber}} \uparrow \;\Rightarrow\; \left(\frac{p_{H_2O}}{p_{CO_2}}\right)\downarrow$$

High heat of absorption solvents ($S_{2.5,2.5}$) profit from temperature swing

Overall Energy Requirement @ 90 % CO_2-Capture Rate

TUHH
Technische Universität Hamburg-Harburg



Increase in desorber temperature
Higher quality steam required
Increase in absorber-desorber temp. difference
Sign. increase in heat transfer in lean-rich HX

Results

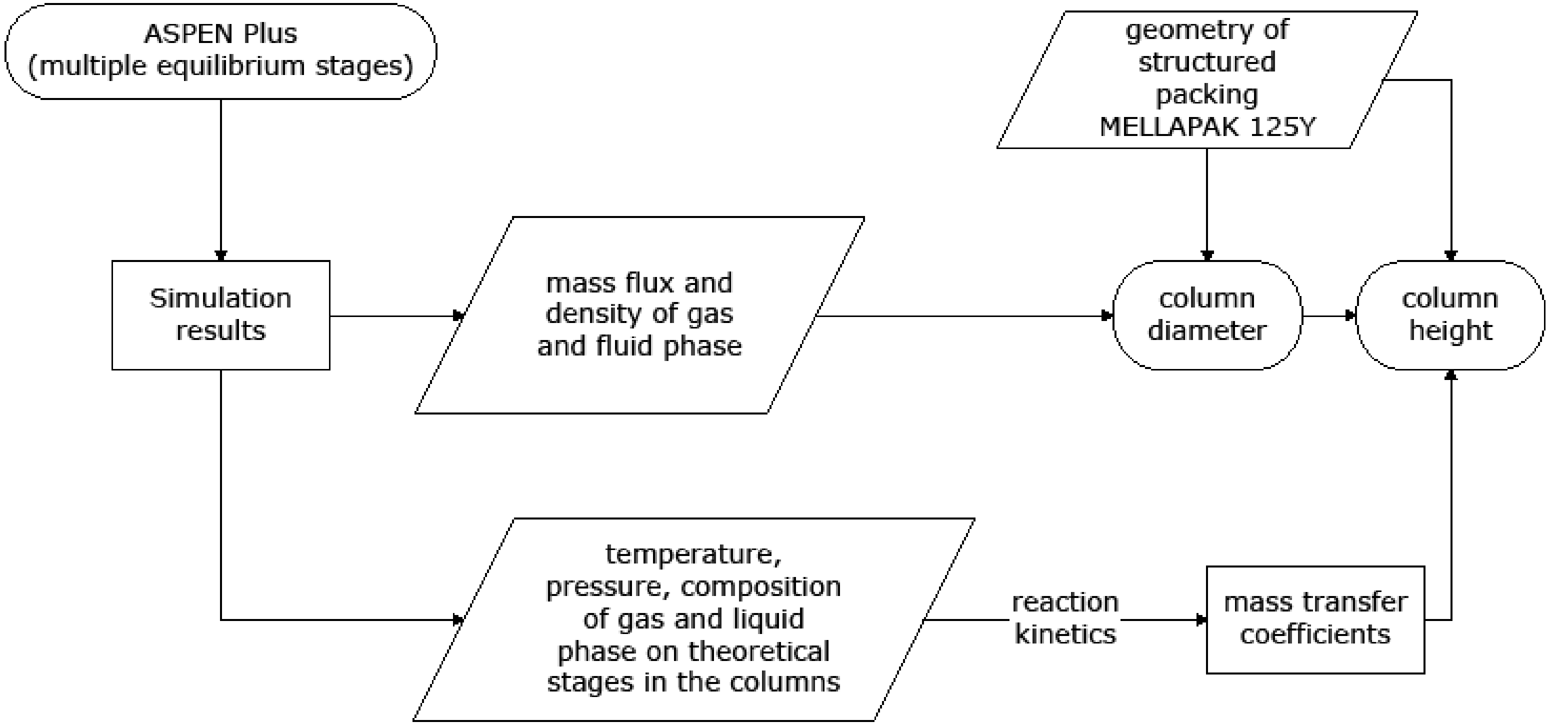
		$S_{2.5,2.5}$	$S_{3.2,1.6}$	$S_{4.8,0.6}$	$S_{3.0}$
CO_2-capture rate	**Desorber pressure (bara)**	3.0	0.5	0.3	0.3
90 %	**Spec. reboiler duty (GJ / t CO_2)**	2.44	3.12	3.00	3.16
70 %		2.07	2.68	2.57	2.92
50 %		2.05	2.65	2.52	2.92
90 %	**Spec. power loss (kWh / t CO_2)**	263.2	341.0	345.9	358.0
70 %		243.5	300.1	307.7	334.6
50 %		252.5	304.1	312.3	343.3
90 %	**Solvent circulation (kg / s)**	9581	6705	4512	4350
70 %		9326	7491	5412	4596
50 %		7163	6169	4535	3442

smaller pick-up range

$S_{2.5,2.5}$ shows lowest reboiler duty and power loss also for CO_2-capture rates below 90 %

Column Design

- Multiple equilibrium stages in ASPEN Plus
- Results from simulation runs used to determine required packing diameter and height considering kinetic data by *Cullinane and Rochelle (2006)*
- Structured packing MELLAPAK 125Y, maximum column diameter 12.8 m



ASPEN Plus
(multiple equilibrium stages)

geometry of structured packing MELLAPAK 125Y

Simulation results

mass flux and density of gas and fluid phase

column diameter

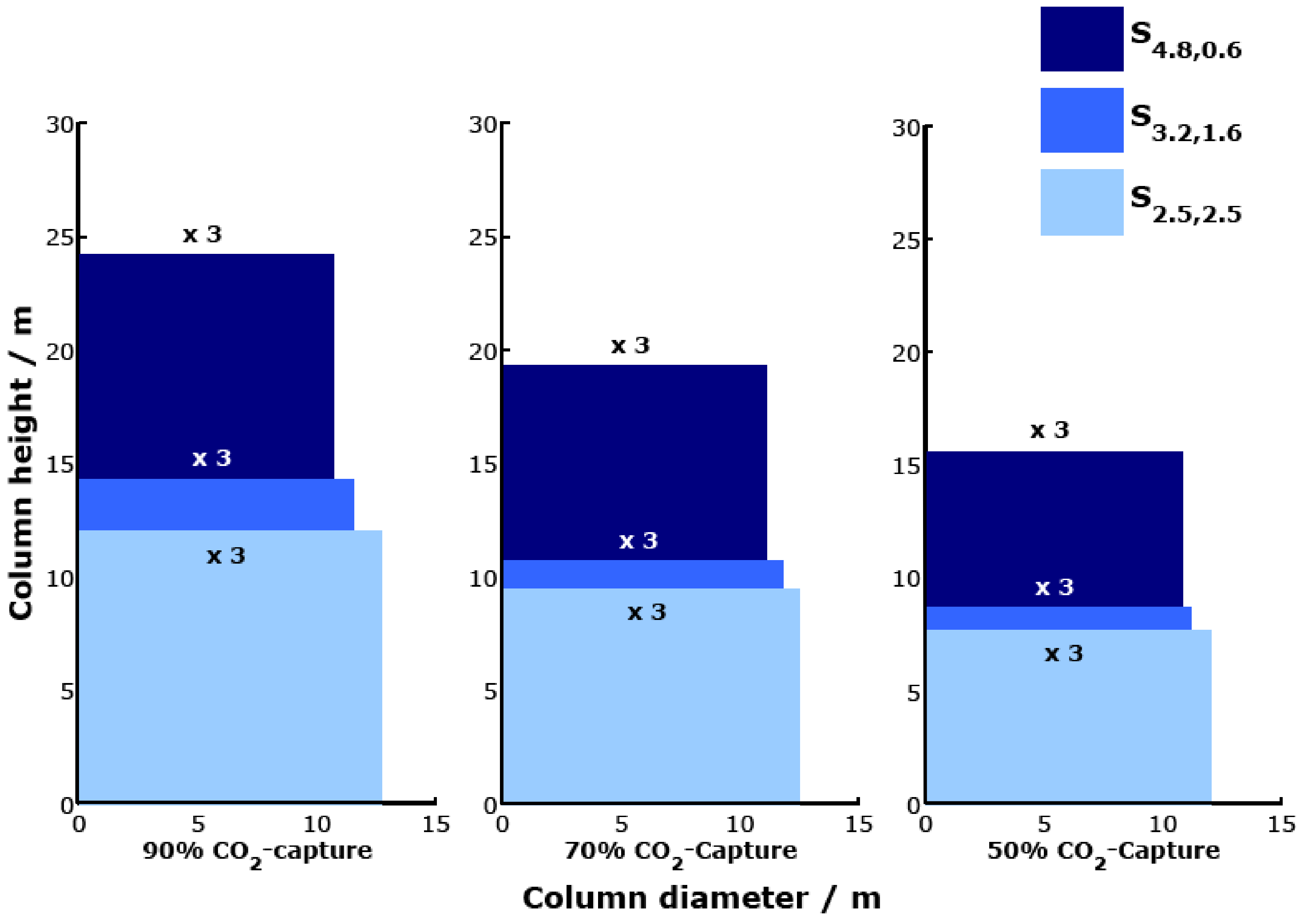
column height

temperature, pressure, composition of gas and liquid phase on theoretical stages in the columns

reaction kinetics

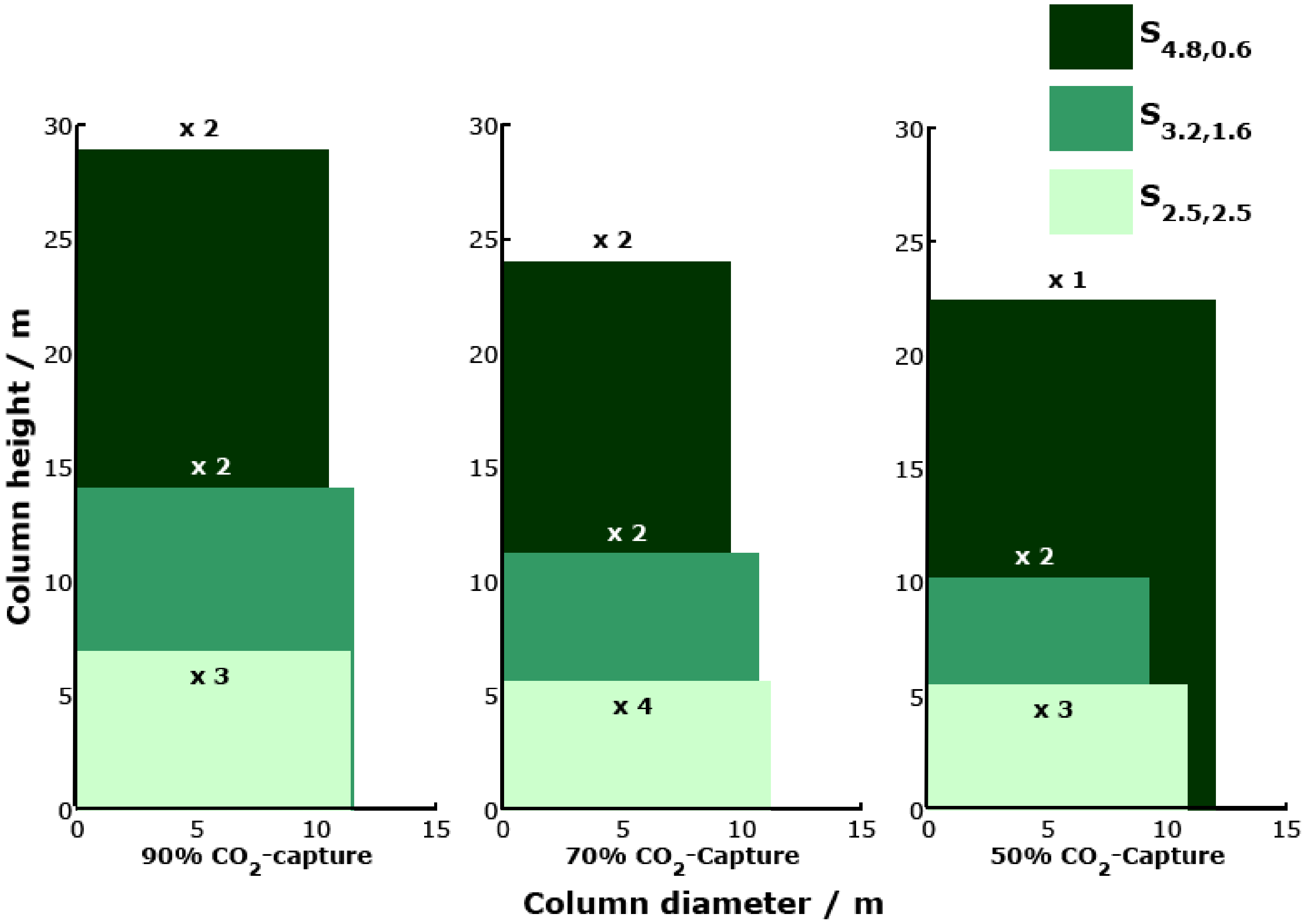
mass transfer coefficients

Absorber Sizes



Increasing height with lower PZ concentration due to reduced reaction kinetics.

Desorber Sizes



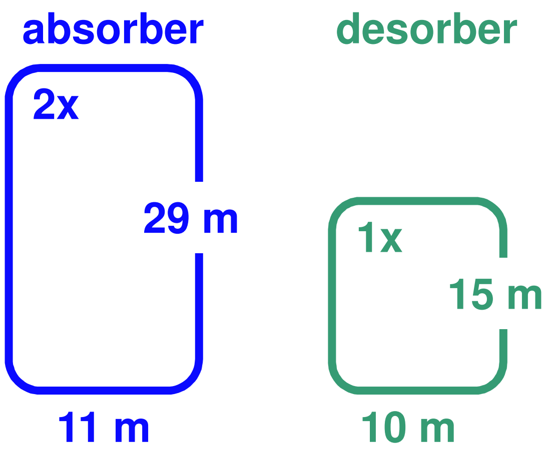
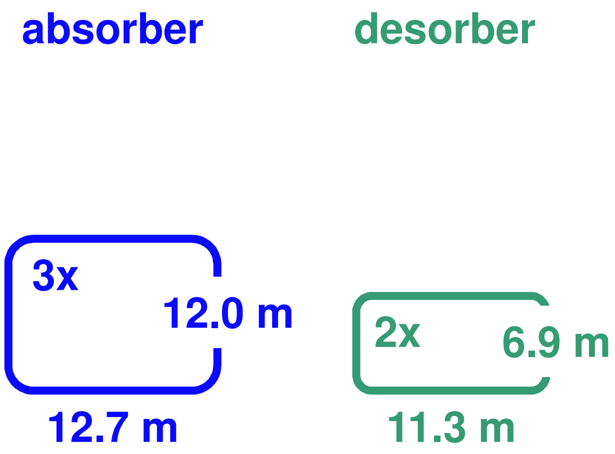
More columns with higher PZ concentration due to larger solvent circulation rate.

Comparison to MEA

- Results from *Abu-Zahra et al. (2007)* for a MEA process are applied to the same power plant and CO_2-compression model as used in this work
- Same methodology for process simulation, column sizing and cost estimation was applied in both works
- Comparison of energetic performance of integrated capture process, column sizes and specific column investment costs
- Boundary conditions:

	MEA	*2.5 m K_2CO_3 / 2.5 m PZ*
▸ Solvent concentration (wt%)	**30**	**22.1 / 13.8**
▸ CO_2-capture rate (%)	**90**	**90**
▸ Desorber pressure (bara)	**2.1**	**3.0**
▸ Reboiler temperature (°C)	**128**	**125**
▸ Lean loading (mol CO_2^{tot} / mol solvent)	**0.32**	**1.01**
▸ Pick-up range (mol CO_2 / mol solvent)	**0.17**	**0.09**
▸ Specific solvent flow (m^3 / t CO_2)	**27.8**	**74.4**

Comparison to MEA: Results

	MEA (Abu-Zahra et al.)	*K_2CO_3/PZ (this work)*
spec. reboiler duty (GJ / t CO_2)	3.3	2.4
spec. power loss (kWh / t CO_2)	342	288
Δ net efficiency (%pts., LHV)	-11.3	-9.5
columns	 absorber: 2x, 29 m, 11 m desorber: 1x, 15 m, 10 m	 absorber: 3x, 12.0 m, 12.7 m desorber: 2x, 6.9 m, 11.3 m
absolute and spec. column invest. costs	10.9 M€ 352 € / (t CO_2 / h)	8.84 M€ 288.3 € / (t CO_2 / h)

Summary

- **Preliminary evaluation of K_2CO_3/PZ process was performed**
- **Influence of key parameters such as solvent composition, loading, desorber pressure and capture rate was analysed**
- **2.5 m K_2CO3 / 2.5 m PZ at 3 bara desorber pressure shows energetic advantageous over other solvent compositions**
- **Comparison of this solvent to a reference MEA-process from literature**
  - The application of K_2CO_3/PZ bares the potential of significantly reducing the heat required for solvent regeneration
  - Relatively low pick-up ranges at the optimal lean loading lead to large solvent circulation rates and thus to larger column diameters and/or number of required columns
  - Promotion with PZ and enhanced kinetics can lead to significantly smaller column heights
  - Even though larger column diameters or more columns are needed, overall investment costs turn out to be lower than in the MEA case

Outlook

- **Re-simulation with new eNRTL parameter set by *Hilliard (2008)***
  - Fixed inaccuracies in calorimetry for H_2O-K_2CO_3-PZ-CO_2
  - Detailed parameter regression for H_2O-MEA-CO_2
- **Own calculations for MEA to compare K_2CO_3/PZ to MEA on a fair and unbiased basis**
- **Component pre-engineering design for all major components**
- **Detailed economic evaluation**
  - CAPEX, incl. investment costs for all major components, installation, engineering and construction
  - OPEX, e.g. for solvent make-up and maintenance
  - Determination of CO_2-avoidance costs (€ / t CO_2) and CoE (€ / kWh)

▶Conclusion

Thank you for your attention!

Questions?

NTNU

Innovation and Creativity

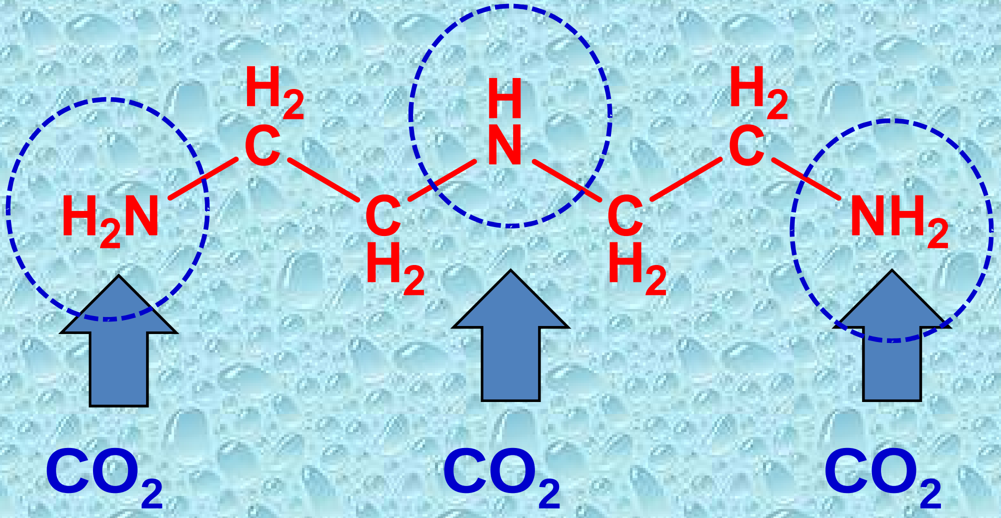
Liquid speciation and reaction kinetics determination in aqueous polyamine (DETA) solution with CO_2

Ardi Hartono and Hallvard F. Svendsen
Norwegian University of Science and Technology (NTNU)
Trondheim, NORWAY

Outline

- Review on DETA
- Liquid speciation in DETA/CO_2 system
  - Chemistry
  - Qualitative & Quantitative NMR Work
- Reaction Kinetics of DETA with CO_2
  - Zwitterion & Termolecular Mechanism
  - Experimental set up
  - Parameters
  - Determination of kinetic rate constants
  - Result
- Conclusion

Review on DETA



Possible as a promising solvent:

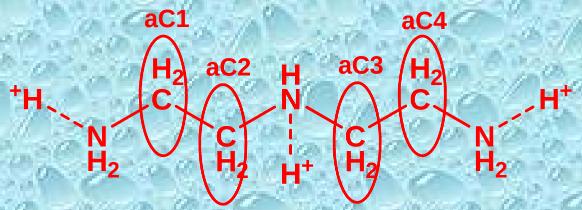
- **Higher loading capacity**
- **Faster absorption rate**
- *Lower heat of absorption*

Chemistry : Characterization with NMR

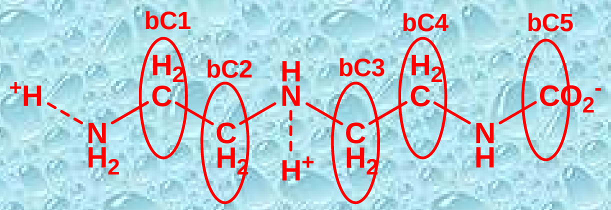
A. H_2O, H_3O^+, OH^-

B. CO_2, HCO_3^-, CO_3^{2-}

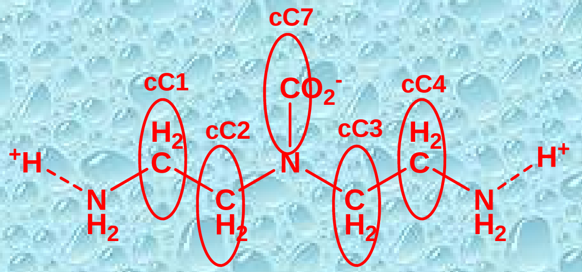
A. Group I :DETA, $DETAH^+_{(p)}$, $DETAH^+_{(s)}$
$DETAH_2^{2+}{}_{(pp)}$,$DETAH_2^{2+}{}_{(ps)}$, $DETAH_3^{3+}$



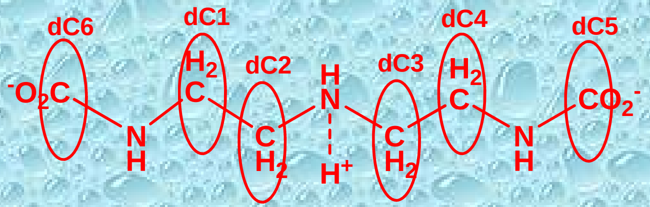
B. Group II: $DETACO_2^-{}_{(p)}$, $DETAH_{(p)}CO_{2\,(p)}$,
$DETAH_{(s)}CO_{2\,(p)}$, $DETAH_{2(ps)}CO_2^+{}_{(p)}$



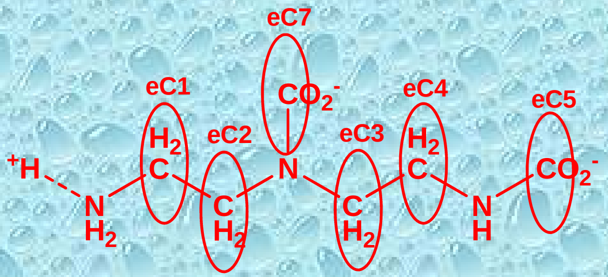
C. Group III: $DETACO_2^-{}_{(s)}$, $DETAH_{(p)}CO_{2(s)}$,
$DETAH_{2(pp)}CO_2^+{}_{(s)}$



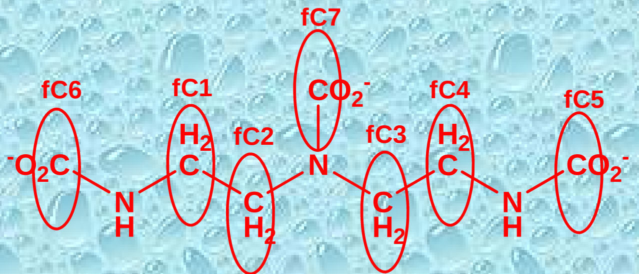
D. Group IV: $DETA(CO_2)_2^{2-}{}_{(pp)}$,
$DETAH_{(s)}(CO_2)_2^-{}_{(pp)}$



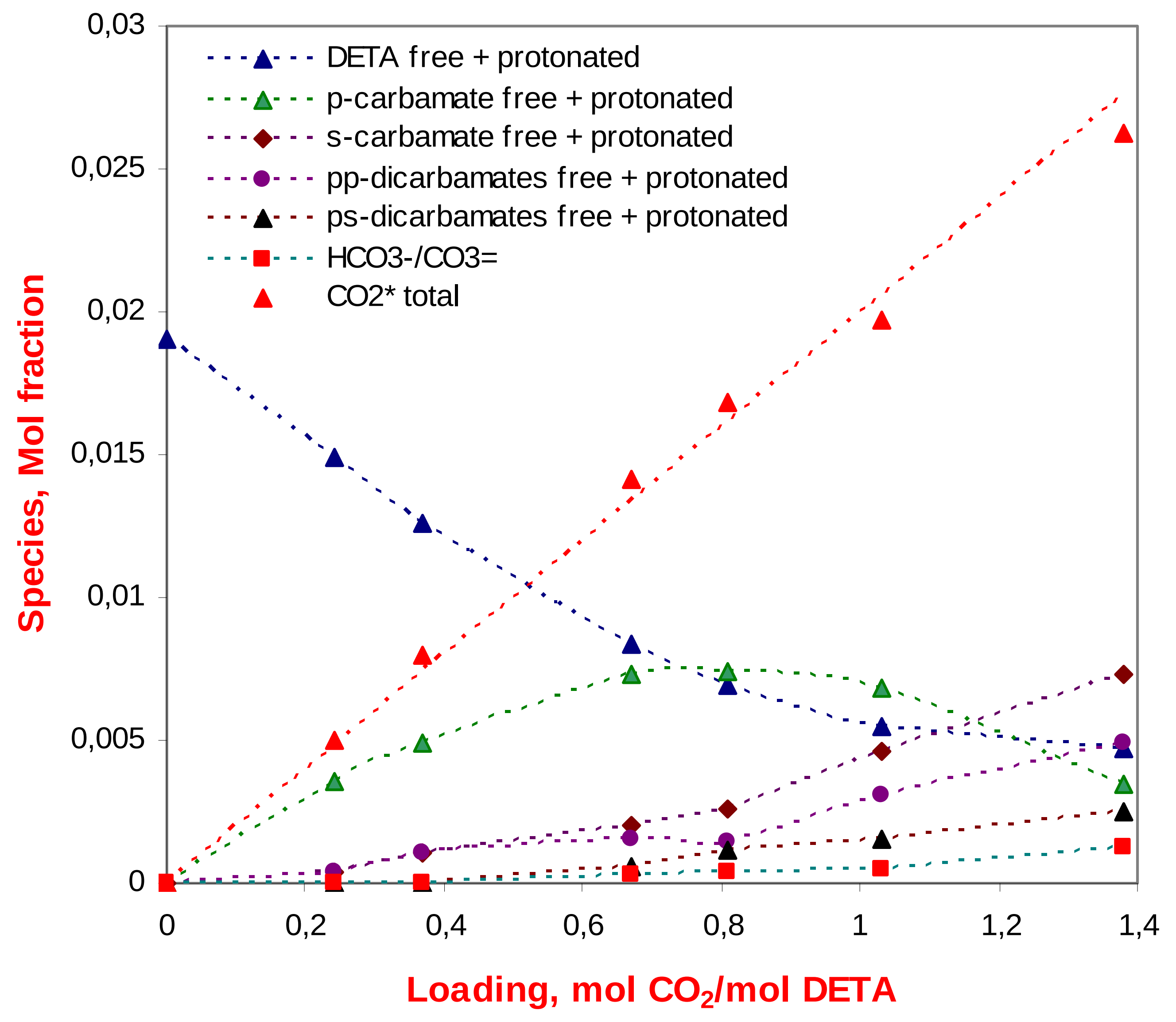
E. Group V: $DETA(CO_2)_2^{2-}{}_{(ps)}$, $DETAH_{(p)}(CO_2)_2^-{}_{(ps)}$



F. Group V: $DETA(CO_2)_3^{3-}$



Qualitative & Quantitative NMR Work



Reaction Kinetics of DETA with CO_2

Species at very low loading

Main reaction

$CO_2 + 2H_2O$ Û $HCO_3^- + H_3O^+$

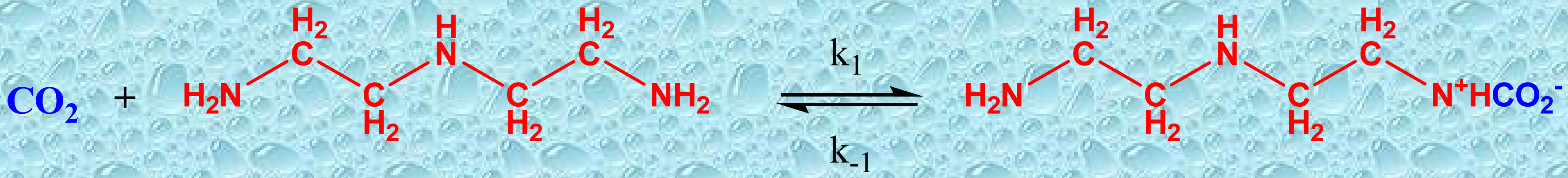
$CO_2 + \mathit{OH}^-$ Û HCO_3^-

$DETA + CO_2 + H_2O$ Û $DETACO^-_{2(p)} + H_3O^+$

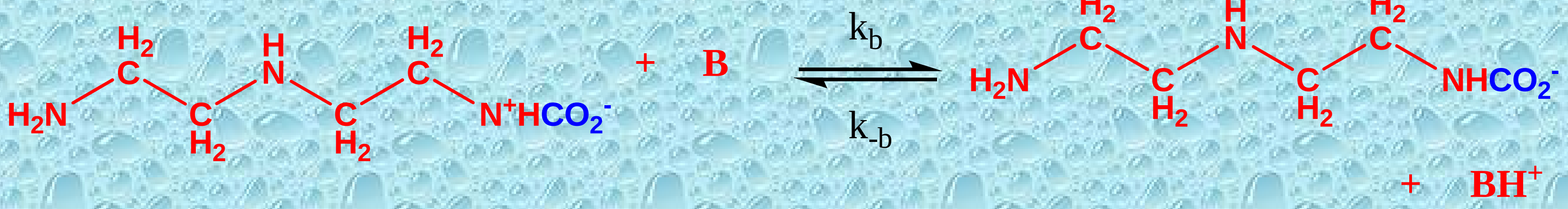
Mechanism of the forward reaction rate

I. Zwitterion Mechanism (Caplow, 1968; Danckwert, 1979)

i). Formation of a zwitterion



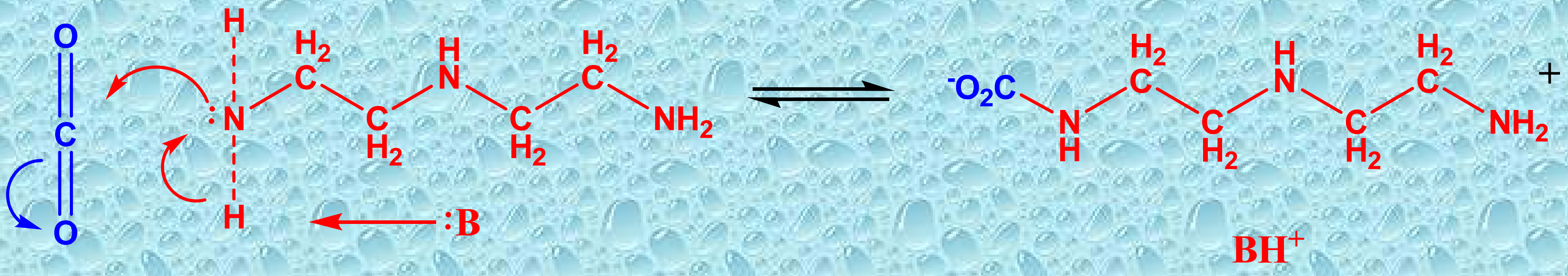
ii). Deprotonation of a zwitterion by base(s)



$$\left(-r_{CO_2}^{Z}\right)=\frac{k_1[\text{DETA}][CO_2]}{1+\frac{k_{-1}}{\sum k_b[B]}}$$

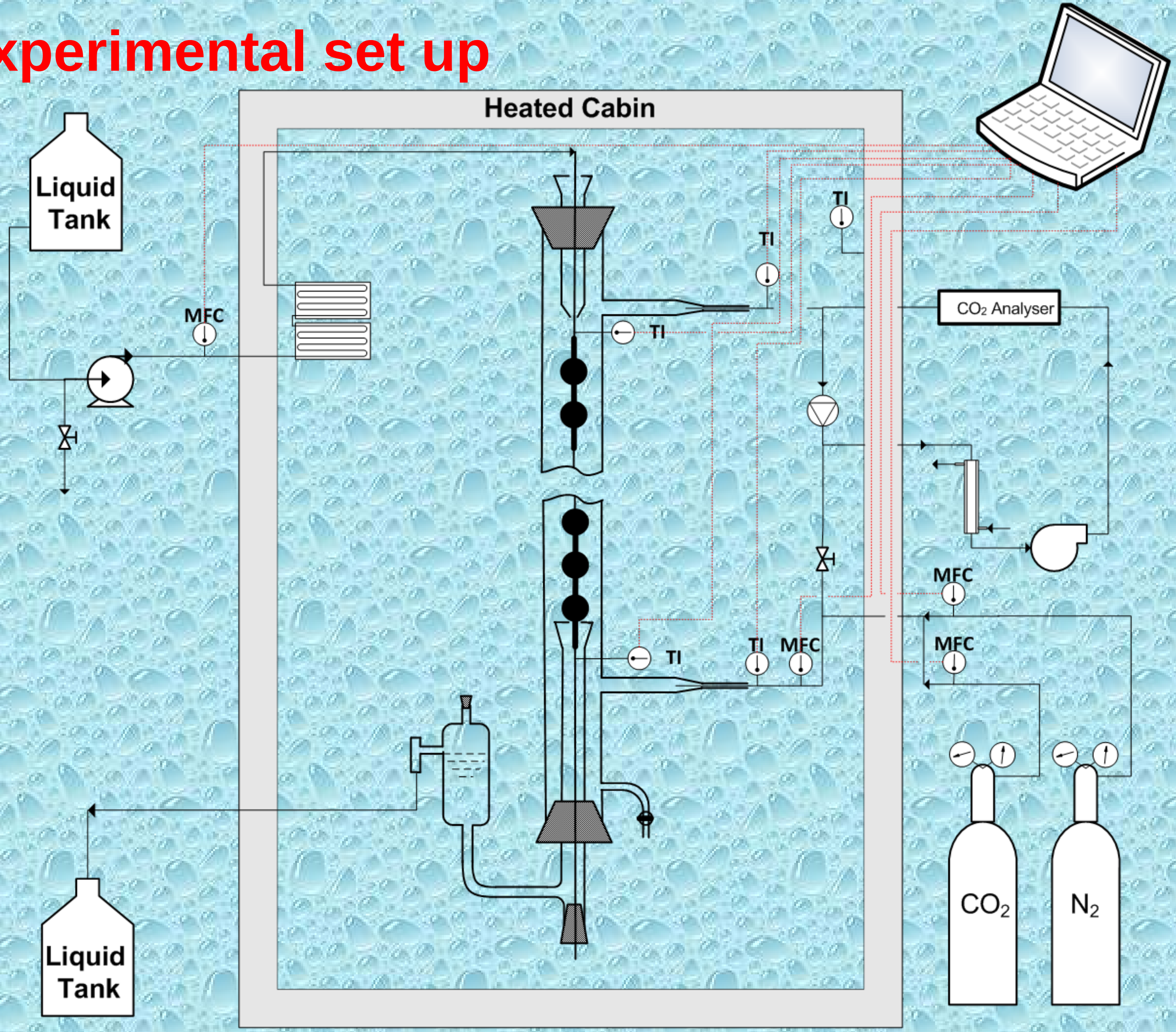
II. Termolecular Mechanism

(Crooks & Donnellan, 1989; da Silva & Svendsen, 2004)



$$\left(-r^{T}_{CO_2}\right) = \left\{k^{T}_{DETA}[DETA] + k_{H_2O}[H_2O] + k^{T}_{OH^-}\left[OH^-\right]\right\}[DETA][CO_2]$$

Experimental set up



Parameters

Physiochemical properties:

$$\rho_{DETA} = f(C,T) \qquad H_{N_2O\text{-}DETA} = f(C,T)$$

this work

$$m_{DETA} = f(C,T) \qquad pKa_{DETA} = f(C,T)$$

$$D_{CO_2-DETA} = D_{CO_2-H_2O}\left(\frac{\mu_{H_2O}}{\mu_{DETA}}\right)^{0.8}$$

The liquid-side mass transfer coefficient

$$\frac{k_L}{D} = 17.92\left(\frac{4\Gamma}{\mu}\right)^{1.0}\left(\frac{\mu}{\rho D}\right)^{0.5}$$

Vishwas, 2004; Hartono, et.al., 2006

The gas-side mass transfer coefficient

$$\frac{k_g d}{D_{CO_2}} = 0.12\,\mathrm{Re}^{0.79}\,Sc^{0.44}$$

Ma'mun, et.al., 2007

Determination of kinetic rate constants

$$N_A = \frac{1}{\frac{1}{\mathrm{E_A} k_L} + \frac{RT}{Hk_g}} \left(C_A^* - C_{A,b} \right)$$

$$E_A = \sqrt{1 + Ha^2} \qquad Ha = \sqrt{\frac{k_{obs} D_A}{k_l}} \qquad 3 < Ha << E_{A\infty}$$

$$k_{obs} = \frac{k_l}{D_A [DETA]_o} \left[\frac{k_L}{\frac{C_A^*}{N_A} - \frac{RT}{Hk_g}} \right]^2$$

Apparent kinetic rate constants

$$k_{app} = k_{obs} - k_{OH^-}\left[OH^-\right]$$

$CO_2 + OH^- \Leftrightarrow HCO_3^-$

$DETA + CO_2 + H_2O \Leftrightarrow DETACO_{2(p)}^- + H_3O^+$

Zwitterion Mechanism

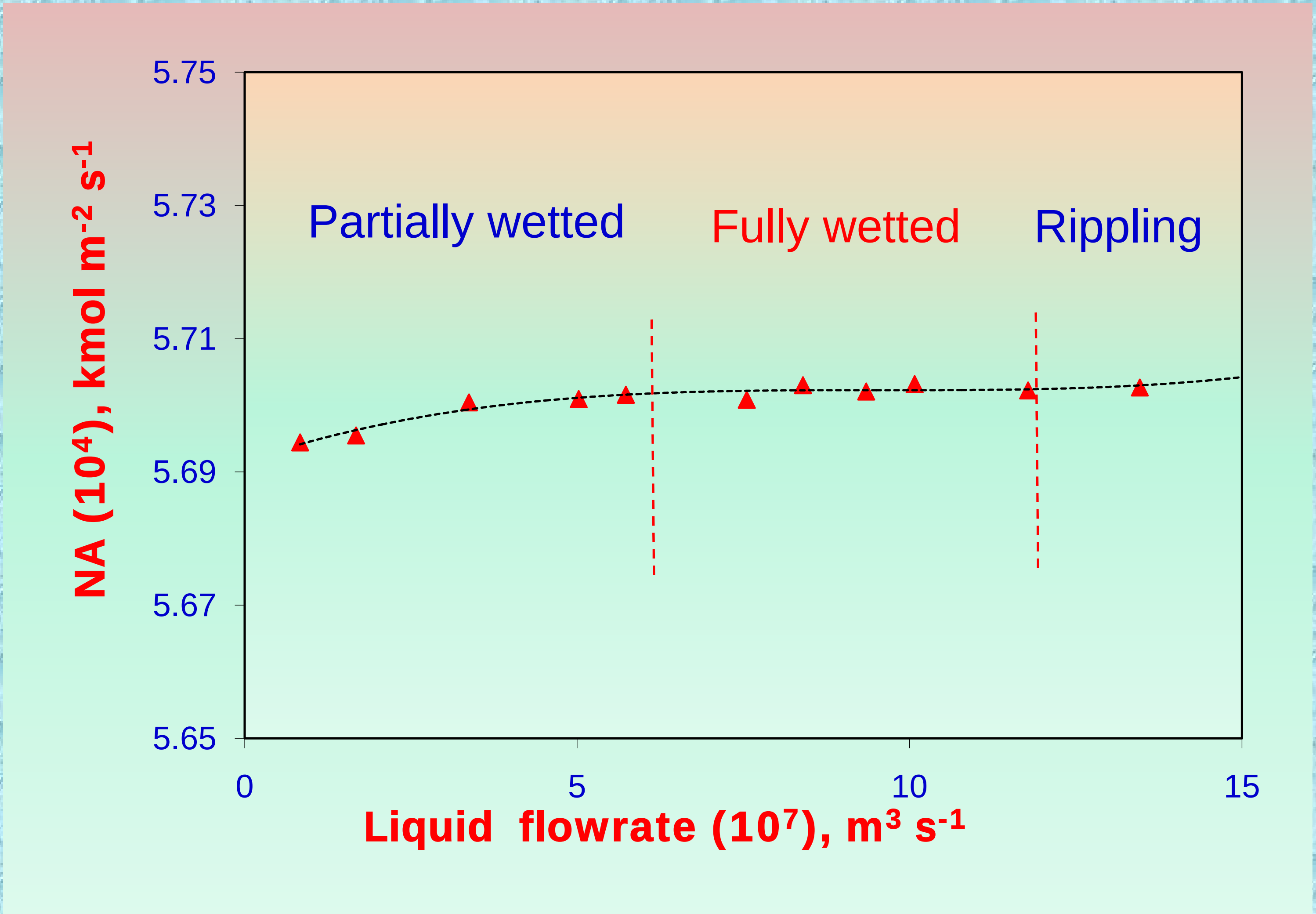
$$k_{app} = \frac{\left[DETA\right]}{\dfrac{1}{k_1} + \dfrac{1}{\left\{k^Z_{DETA}\left[DETA\right] + k^Z_{H_2O}\left[H_2O\right] + k^Z_{OH^-}\left[OH^-\right]\right\}}}$$

Termolecular Mechanism

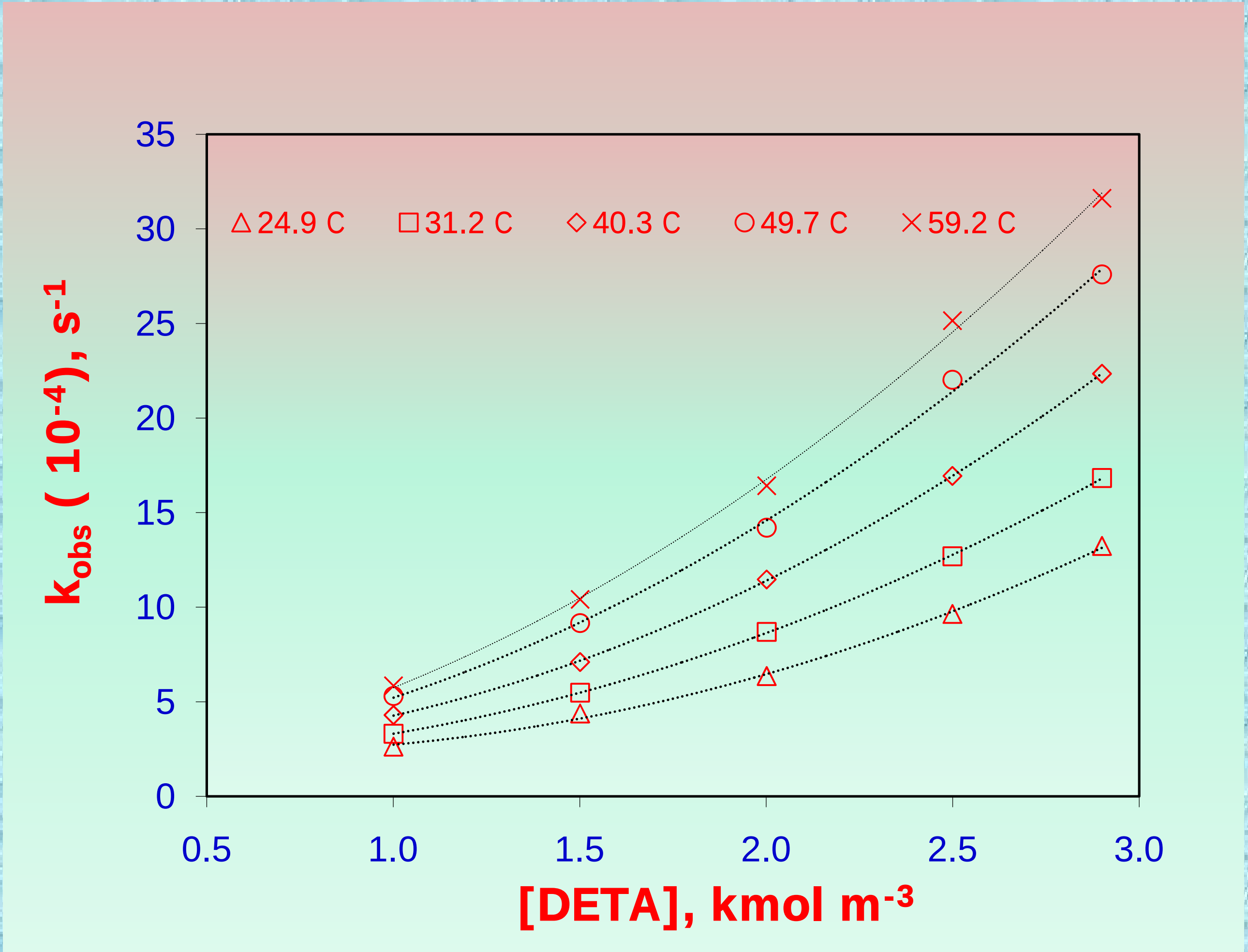
$$k_{app} = \left\{k^T_{DETA}\left[DETA\right] + k^T_{H_2O}\left[H_2O\right] + k^T_{OH^-}\left[OH^-\right]\right\}\left[DETA\right]$$

Results

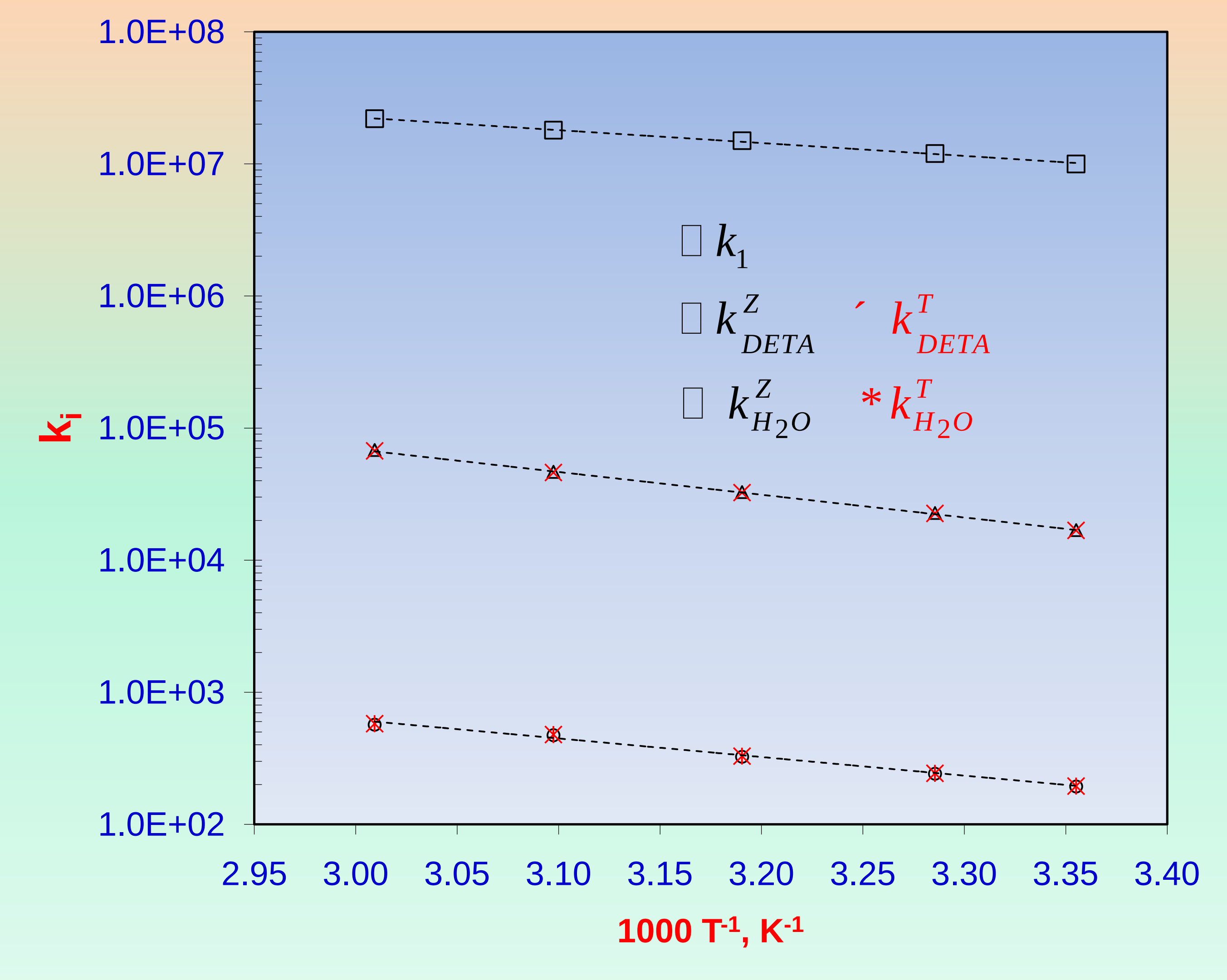
Effect of liquid flow rate on the average absorption flux of CO_2



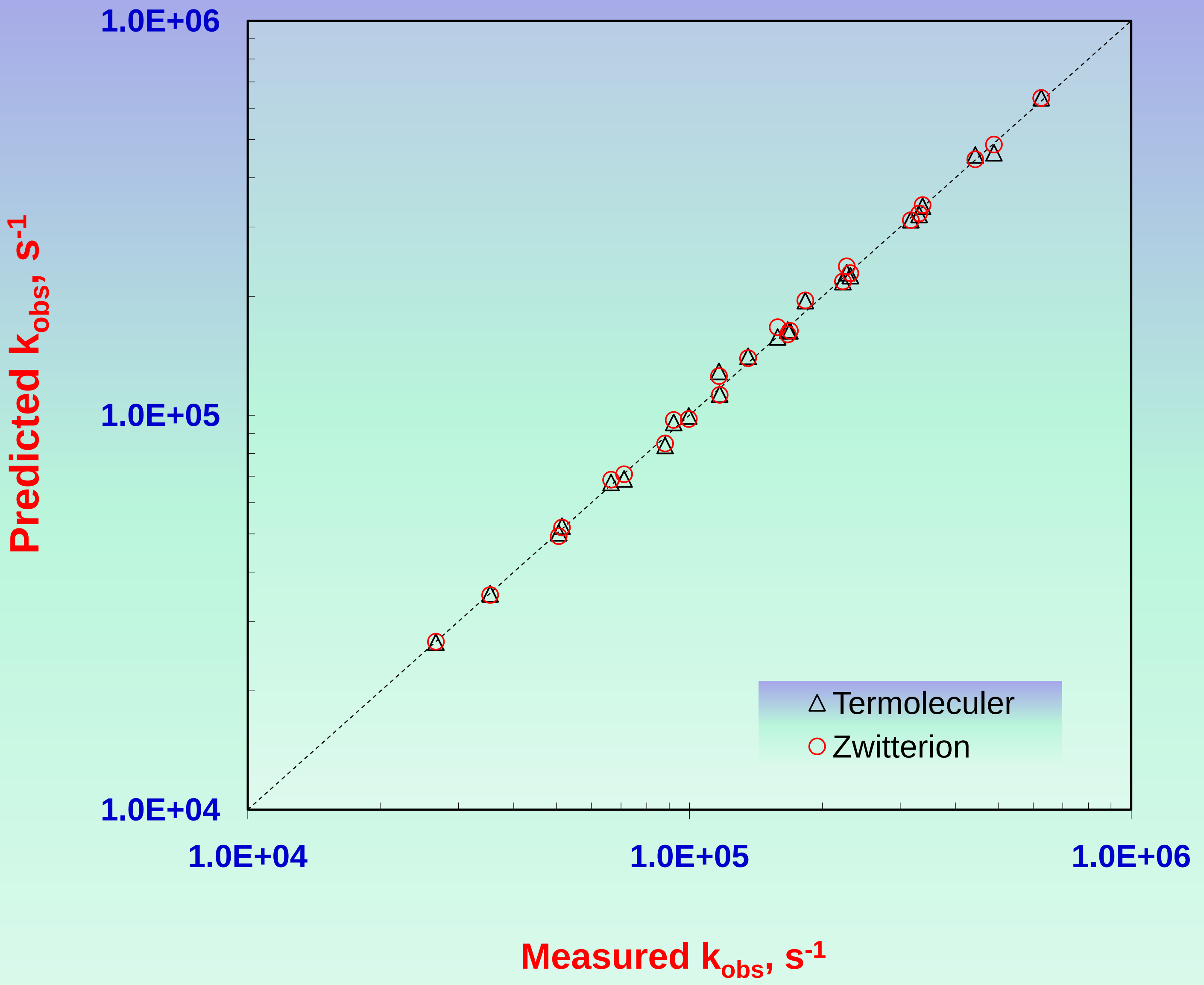
Effects of DETA concentration on k_{obs} over the range of temperatures



Relationship between k_i and 1/*T*



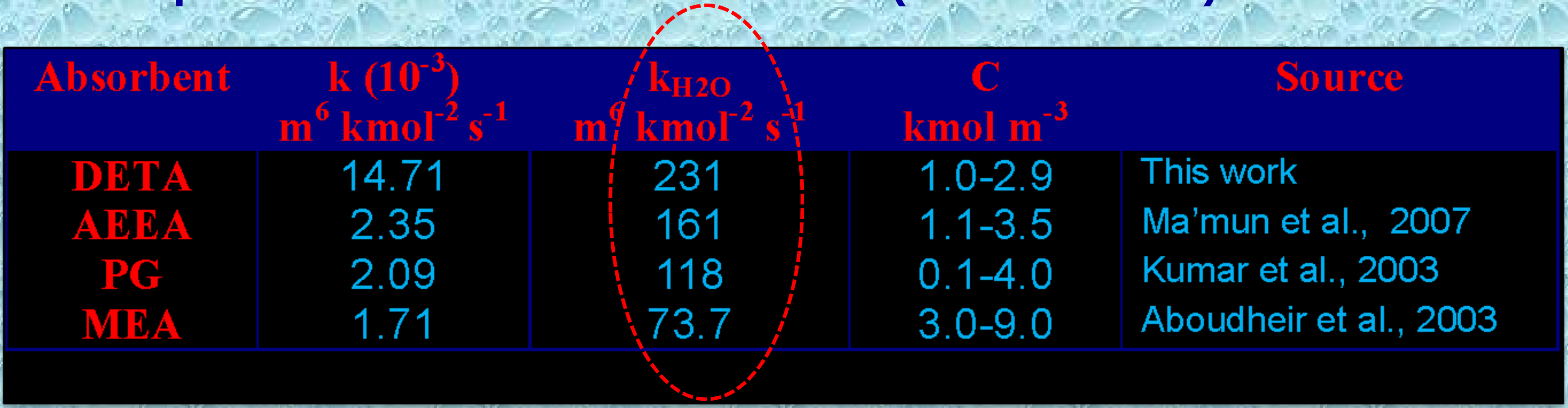
Measured and Predicted k_{obs}



Kinetic rate constants

Zwitterion		Termolecular	
k_1	$1.9268\ 10^{10} \exp(-2249.6/T)$		
$K^{Z}_{DETA} = \frac{k_2 k_{DETA}}{k_{-1}}$	$1.0827\ 10^{10} \exp(-3983.0/T)$	k^{T}_{DETA}	$1.0191\ 10^{10} \exp(-3967.0/T)$
$K^{Z}_{H_2O} = \frac{k_2 k_{H_2O}}{k_{-1}}$	$9.2721\ 10^{6} \exp(-3211.2/T)$	$k^{T}_{H_2O}$	$1.0405\ 10^{7} \exp(-3243.9/T)$

In comparison with literatures at 25°C (Termolecular)



Absorbent	k (10^{-3}) $m^6\ kmol^{-2}\ s^{-1}$	k_{H_2O} $m^6\ kmol^{-2}\ s^{-1}$	C $kmol\ m^{-3}$	Source
DETA	14.71	231	1.0-2.9	This work
AEEA	2.35	161	1.1-3.5	Ma'mun et al., 2007
PG	2.09	118	0.1-4.0	Kumar et al., 2003
MEA	1.71	73.7	3.0-9.0	Aboudheir et al., 2003

$$k_{app} = \left\{k^{T}_{DETA}[DETA] + k^{T}_{H_2O}[H_2O] + k^{T}_{OH^-}\left[OH^-\right]\right\}[DETA]$$

Conclusions

- The carbamate species at very low loading is predominantly the primary carbamate
- Both the Termolecular and the Zwitterion mechanism gave very good agreement to the experimental data
- Based on the Zwitterion mechanism, the rate determining step is deprotonation of zwitterion
- In comparison to literature data (AEEA, MEA, PG), DETA has a higher reaction rate

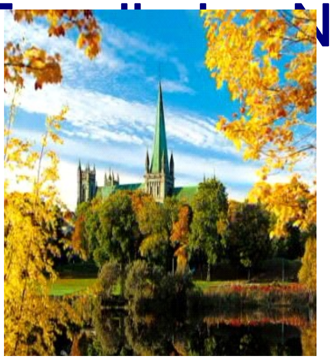
Future Work

$$k_{app} = \left\{k_{DETA}^{T}\gamma_{DETA}\left[DETA\right] + k_{H_2O}^{T}\gamma_{H_2O}\left[H_2O\right] + k_{OH^-}^{T}\gamma_{OH^-}\left[OH^-\right]\right\}\gamma_{DETA}\left[DETA\right]$$

Thank you for your attention

Ebulliometric Determination of Vapour-Liquid Equilibria for Pure Alkanolamines and their Aqueous Solutions

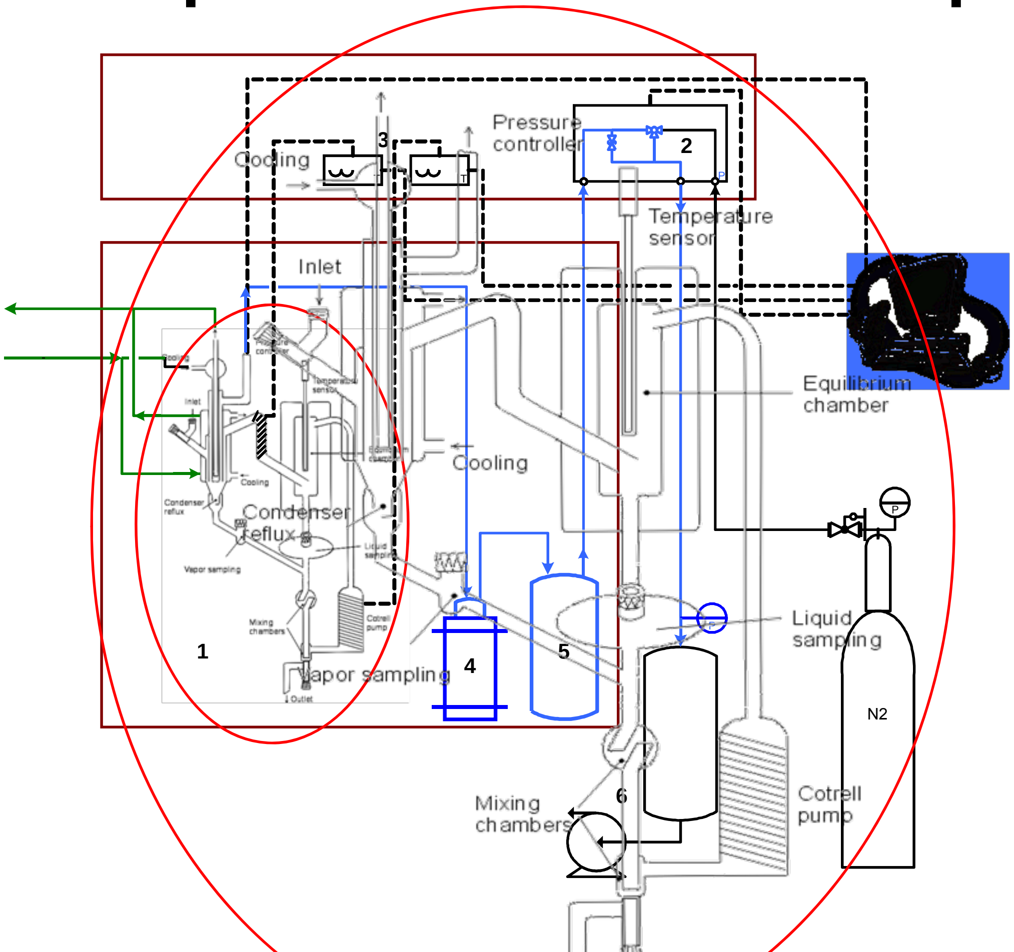
Inna Kim and prof. Hallvard F. Svendsen
NTNU, Trondheim, N



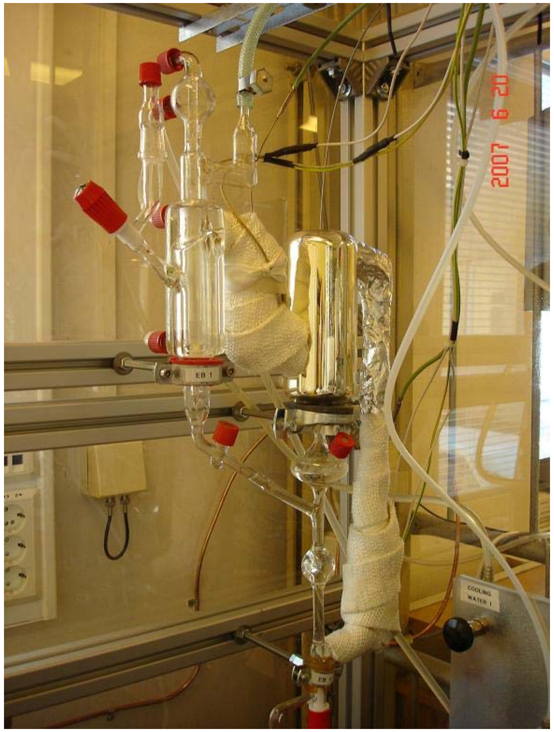
Outline

- Experimental set-up and procedure
- Results:
  - Pure components
  - Binary aqueous solutions
  - Ternary aqueous solutions
- Thermodynamic consistency test
- Summary

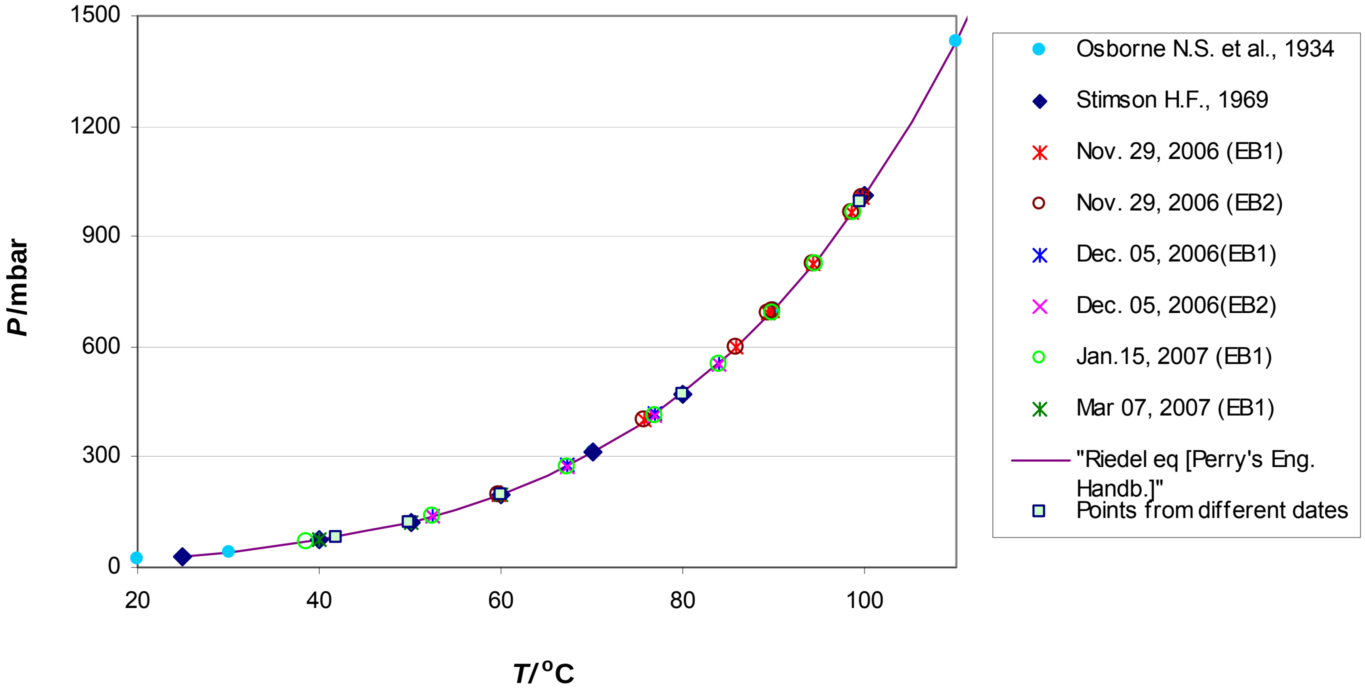
- Experimental set-up



1 - ebulliometer; 2 - pressure controller; 3 – thermocouples;
4 - cold trap; 5 - buffer vessel; 6 - Vacuum pump



Vapour pressure: H_2O (RMS* = 0.59)



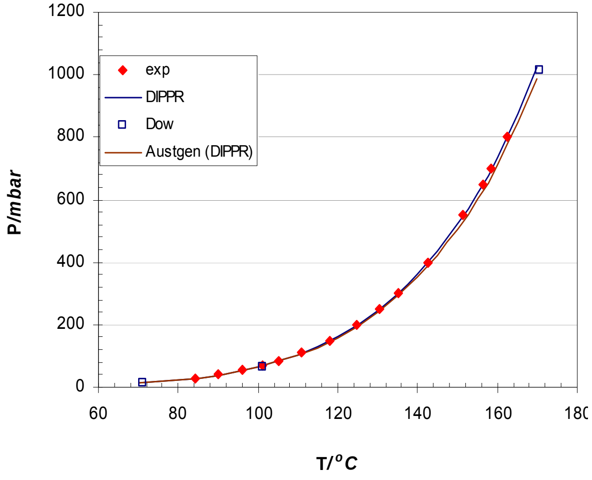
---

* Root Mean Square (RMS) deviation = $\sqrt{(\Sigma(Y_{exp}-Y_{pred})^2)}/n$

Vapour pressure of pure components

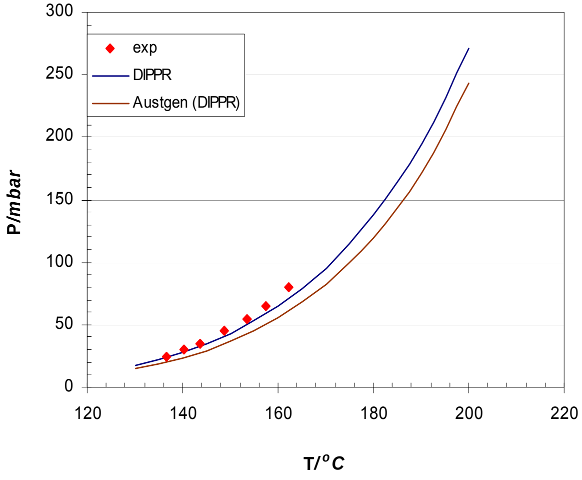
MEA

(RMS = 1.716)



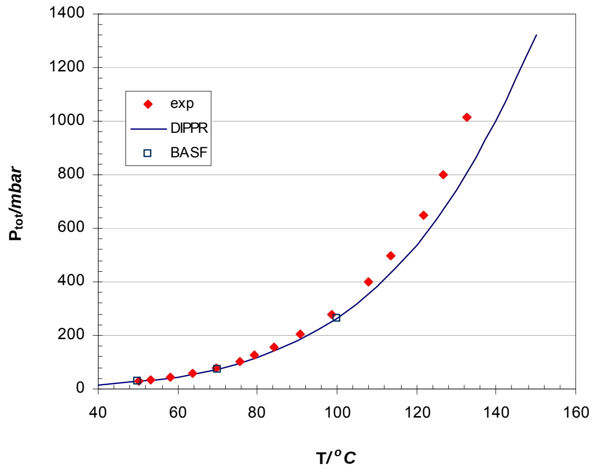
MDEA

(RMS = 5.934)



MAPA*

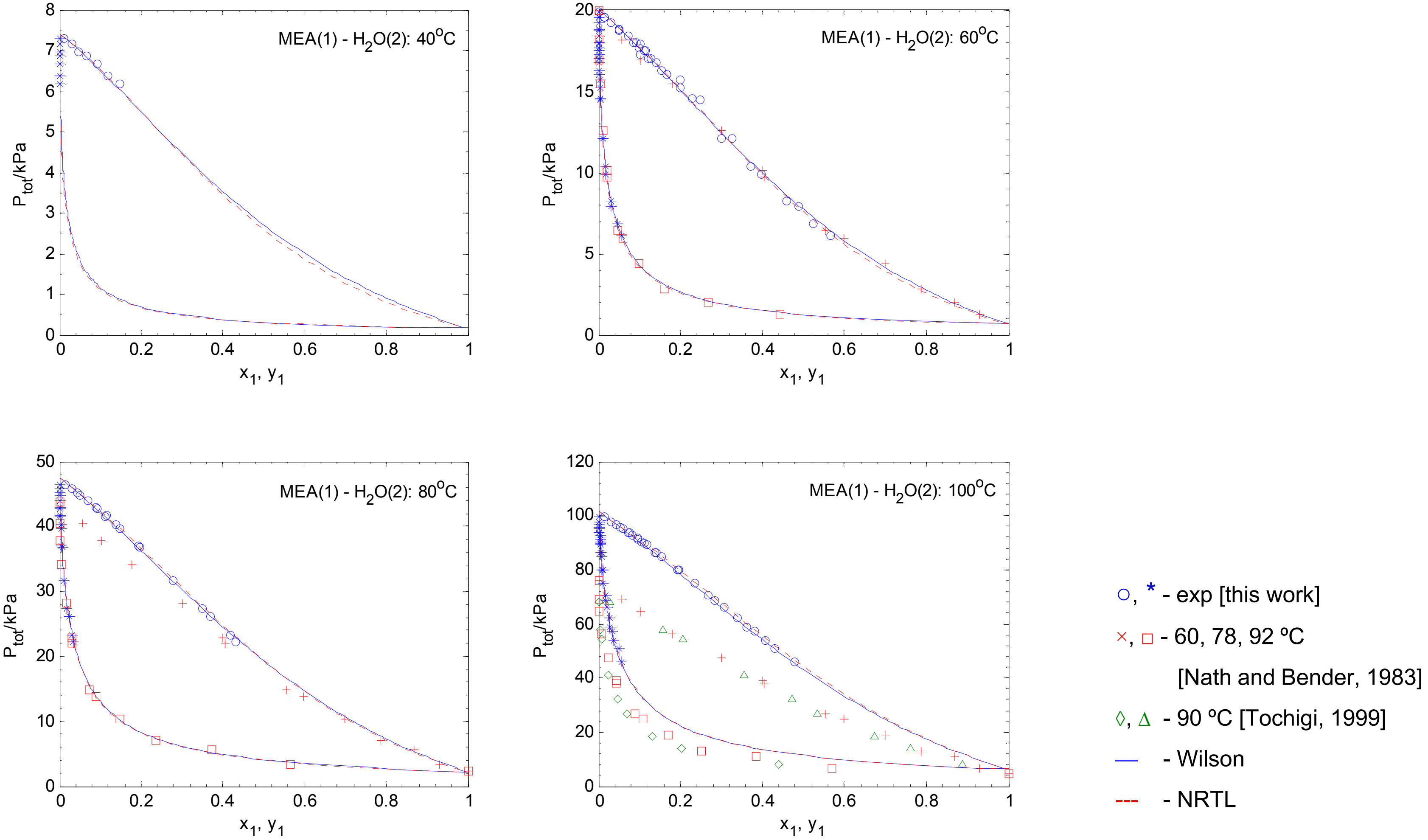
(RMS = 70 (4.16))



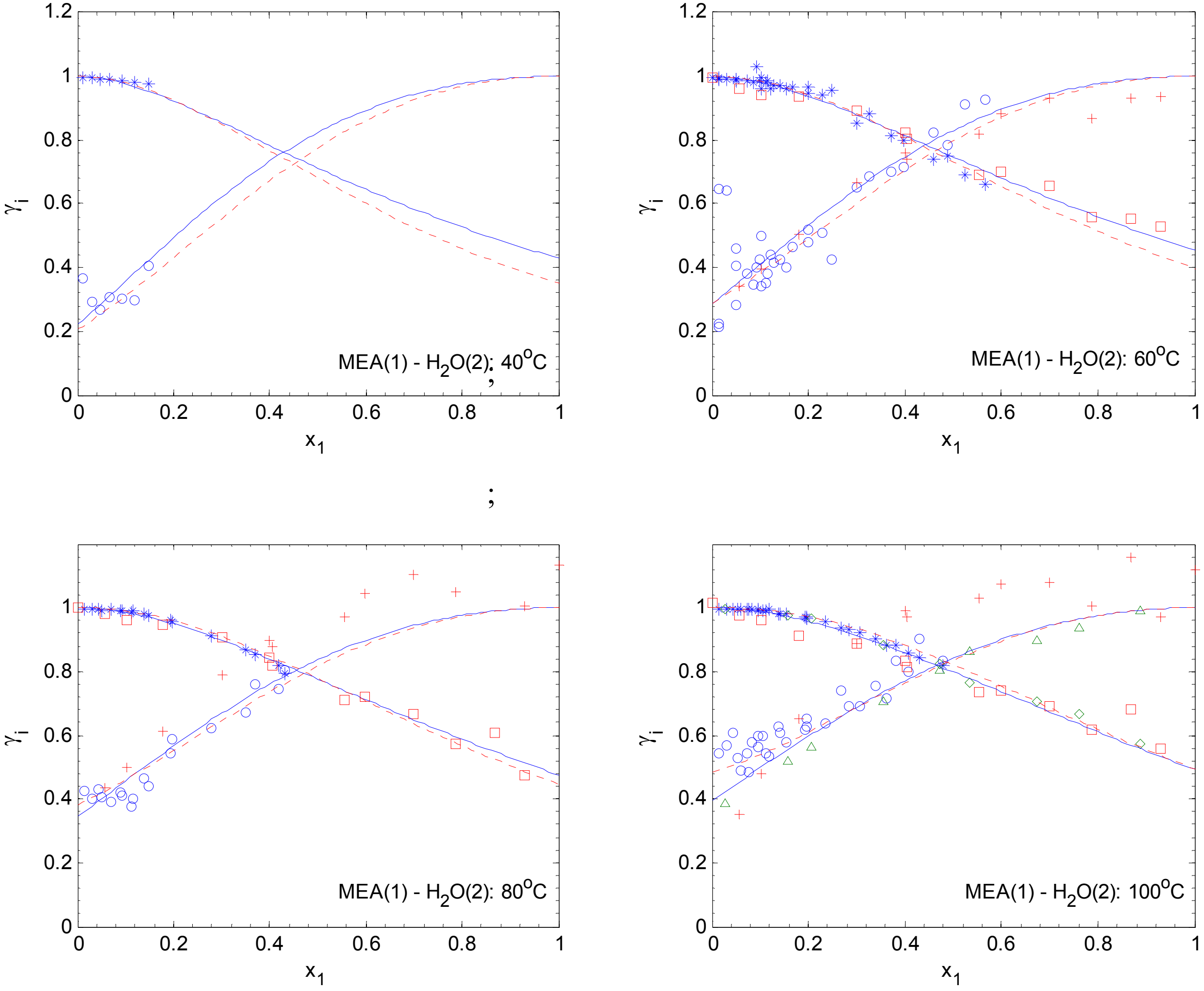
---

*Methylaminopropylamine, $CH_3NHCH_2CH_2CH_2NH_2$, (CAS No. 6291-84-5)

P_{tot}-xy diagram: MEA(1)+H_2O(2)



Activity coefficients: MEA(1)+H_2O(2)



MEA (1) – H_2O (2)	
	Wilson
λ_{12}	3506
λ_{21}	-5682
	NRTL*
a_{12}	-0.488
b_{12}	-699.6
a_{21}	2.83
b_{21}	89.272
α_{12}	0.2

* Temperature dependent parameters: $\tau_{12}= a_{12}+b_{12}/T$; $\tau_{21}= a_{21}+b_{21}/T$

○, * - exp [this work]

×, □ - 60, 78, 92 ºC [Nath and Bender, 1983]

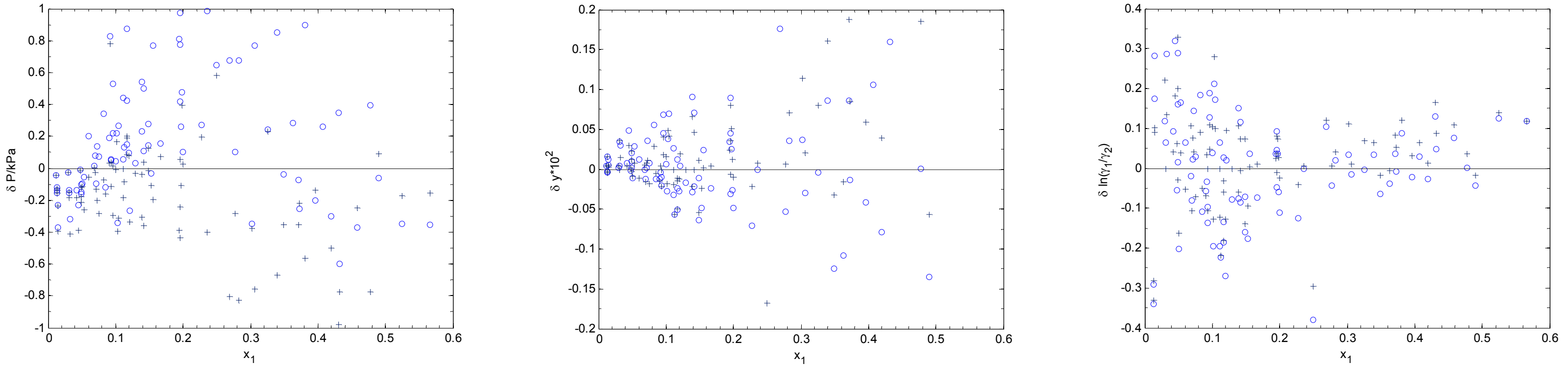
◊, Δ - 90 ºC [Tochigi, 1999]

— - Wilson

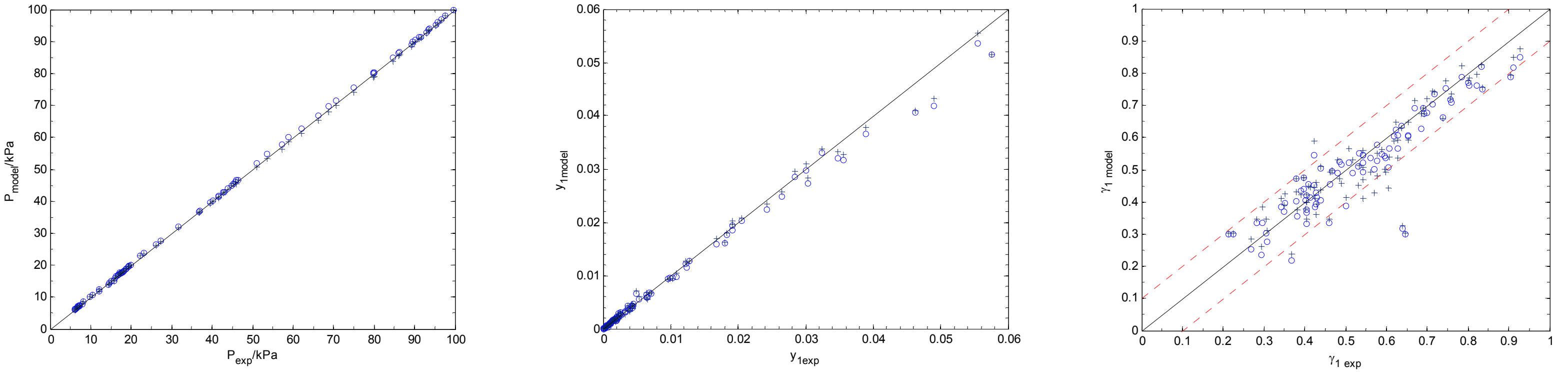
--- - NRTL

Pressure, vapour phase composition and activity coefficients (MEA): residuals (a), model vs experiment (b)

(a)



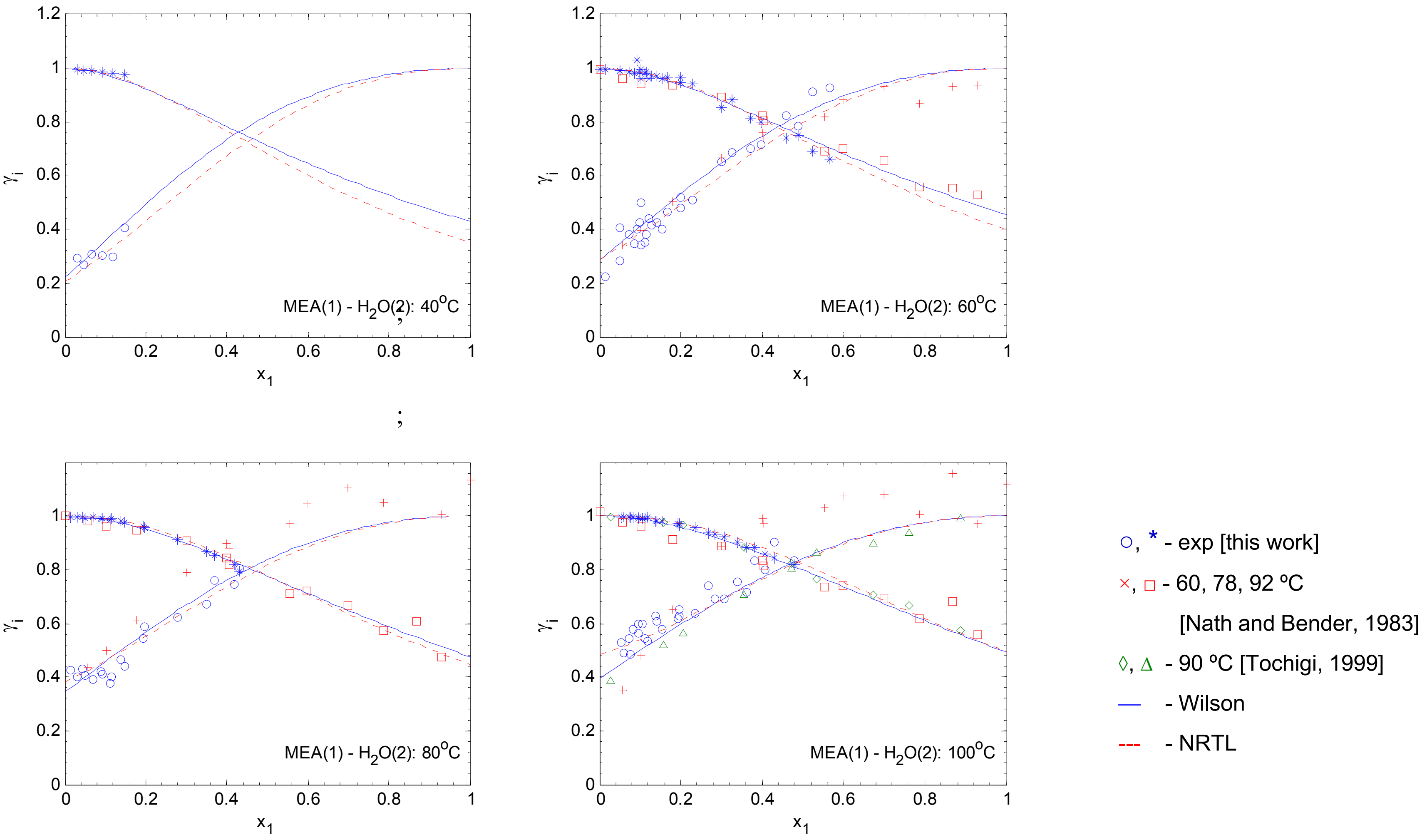
(b)



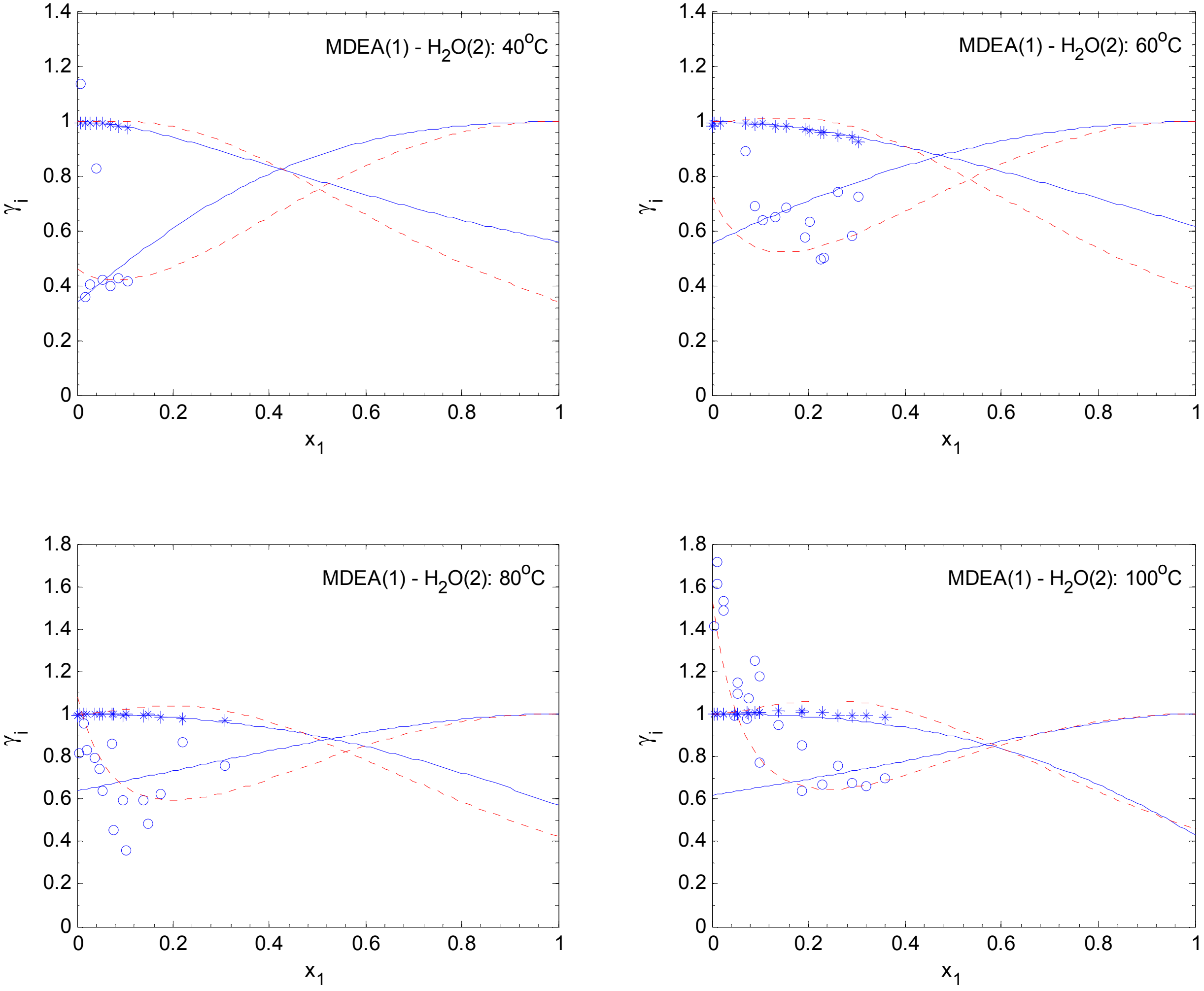
○ - NRTL ; + - Wilson

- Results : binary aqueous solutions

Activity coefficients: MEA(1)+H_2O(2)



Activity coefficients: MDEA(1)+H_2O(2)



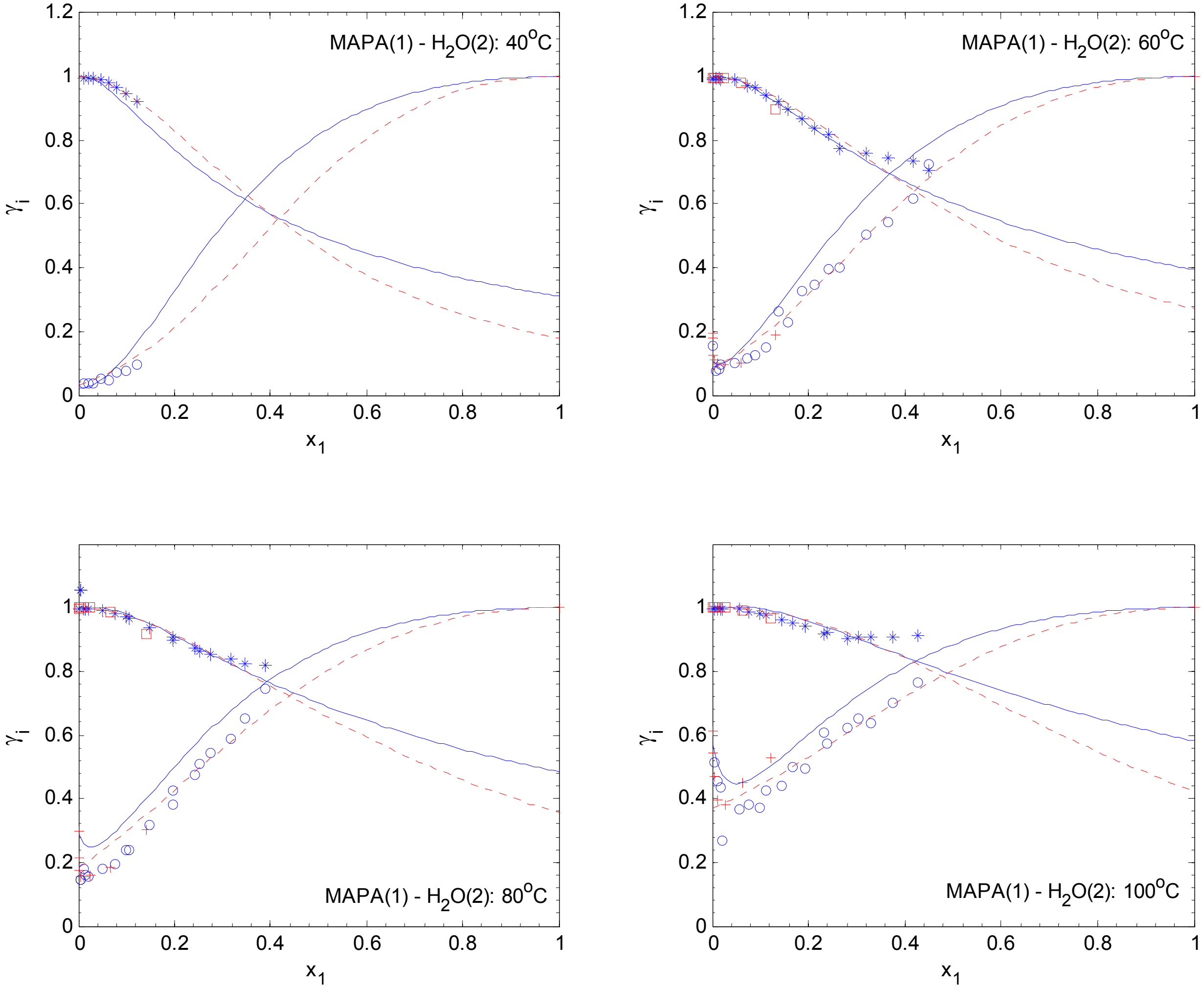
MDEA (1) – H_2O (2)	
	Wilson
λ_{12}	18784
λ_{21}	-20107
	NRTL*
a_{12}	-1.193
b_{12}	-531.72
a_{21}	7.281
b_{21}	-909.68
α_{12}	0.2

○, * - exp [this work]

— - Wilson

--- - NRTL

Activity coefficients: MAPA(1)+H_2O(2)



MAPA (1) – H_2O (2)	
	Wilson
λ_{12}	14375
λ_{21}	-10167
	NRTL*
a_{12}	-1.783-
b_{12}	-290.91
a_{21}	13.776
b_{21}	-3912.66
α_{12}	0.2

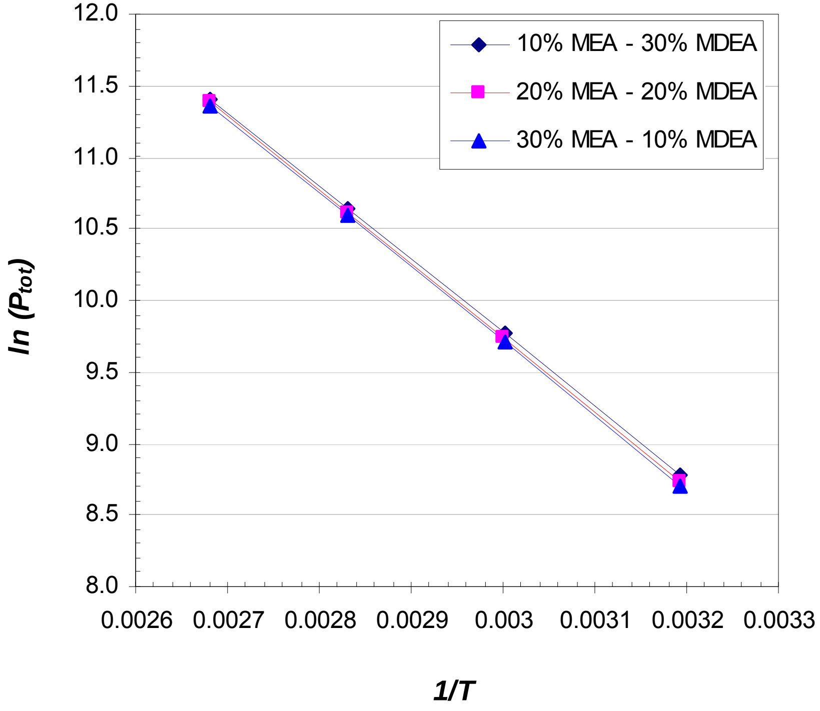
○, * - exp [this work]

×, □ - 50, 70, 100 ºC [BASF]

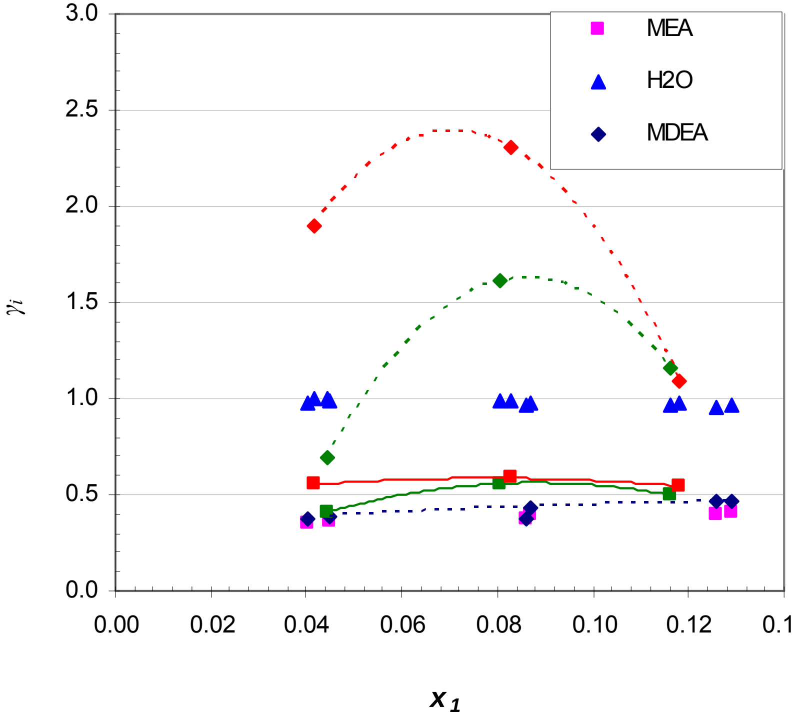
— - Wilson

--- - NRTL

MEA(1)+MDEA(2)+H_2O(3) system



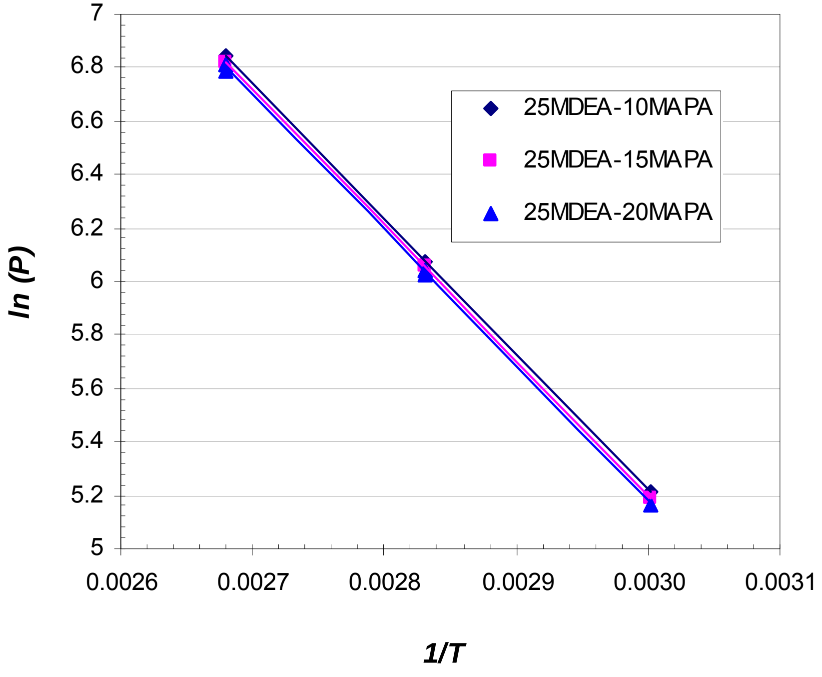
(a) Total pressure vs temperature and composition



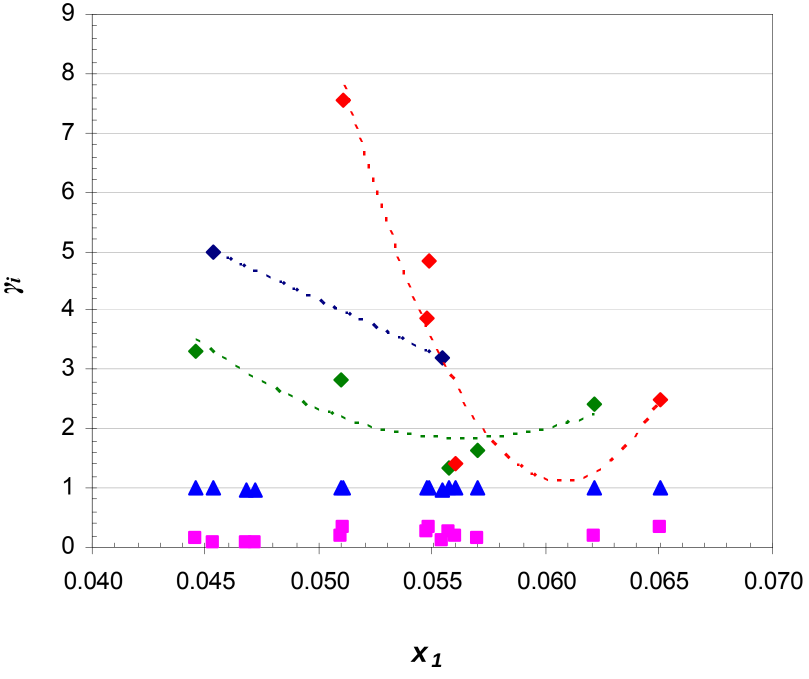
(b) Activity coefficients vs composition:

■ - MEA (red – 100ºC, green – 80ºC); ▲ - H_2O;
♦ - MDEA (red – 100ºC, green – 80ºC),

MDEA(1)+MAPA(2)+H_2O(3) system



(a) Total pressure vs temperature and composition



(b) Activity coefficients vs composition:

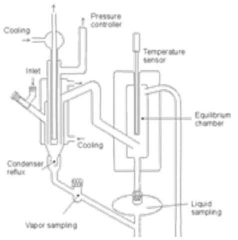
♦ - MDEA (red – 100ºC, green – 80ºC),

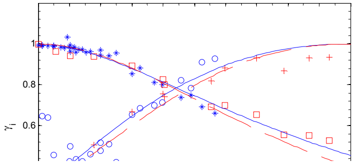
■ - MAPA; ▲- H_2O

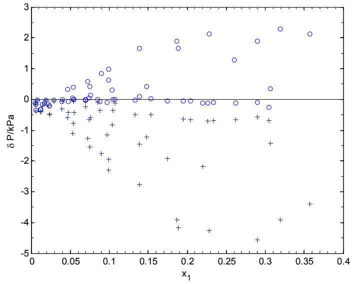
Summary

- Ebulliometry – a simple and fast method for measuring VLE.
- VLE of pure components and binary and ternary aqueous solutions was measured. Accuracy of the results is limited by purity of the substances used and by the precision of the analytical methods used for the sample analyses
- Activity coefficients were calculated and fitted to Wilson and NRTL models
- Thermodynamic consistency test shows that measured data are consistent

** The results were submitted for publication to the J. Chem. Eng. Data*







Acknowledgements

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

the ***BIGCO2*** project, performed under the strategic Norwegian research program Climit. The authors acknowledge the partners: Norsk Hydro, Statoil, GE Global Research, Statkraft, Aker Kværner, Shell, TOTAL, ConocoPhillips, ALSTOM, the Research Council of Norway (178004/I30 and 176059/I30) and Gassnova (182070) for their support

THANK YOU

FOR YOUR ATTENTION !

Questions?

Mass Transfer in a Small Scale Flue Gas Absorber – Experimental and Modeling

P.J.G. Huttenhuis, E.P. van Elk, S. Van Loo, G.F. Versteeg
Procede Gas Treating B.V., The Netherlands

11th MEETING of the INTERNATIONAL POST-COMBUSTION CO_2 CAPTURE NETWORK

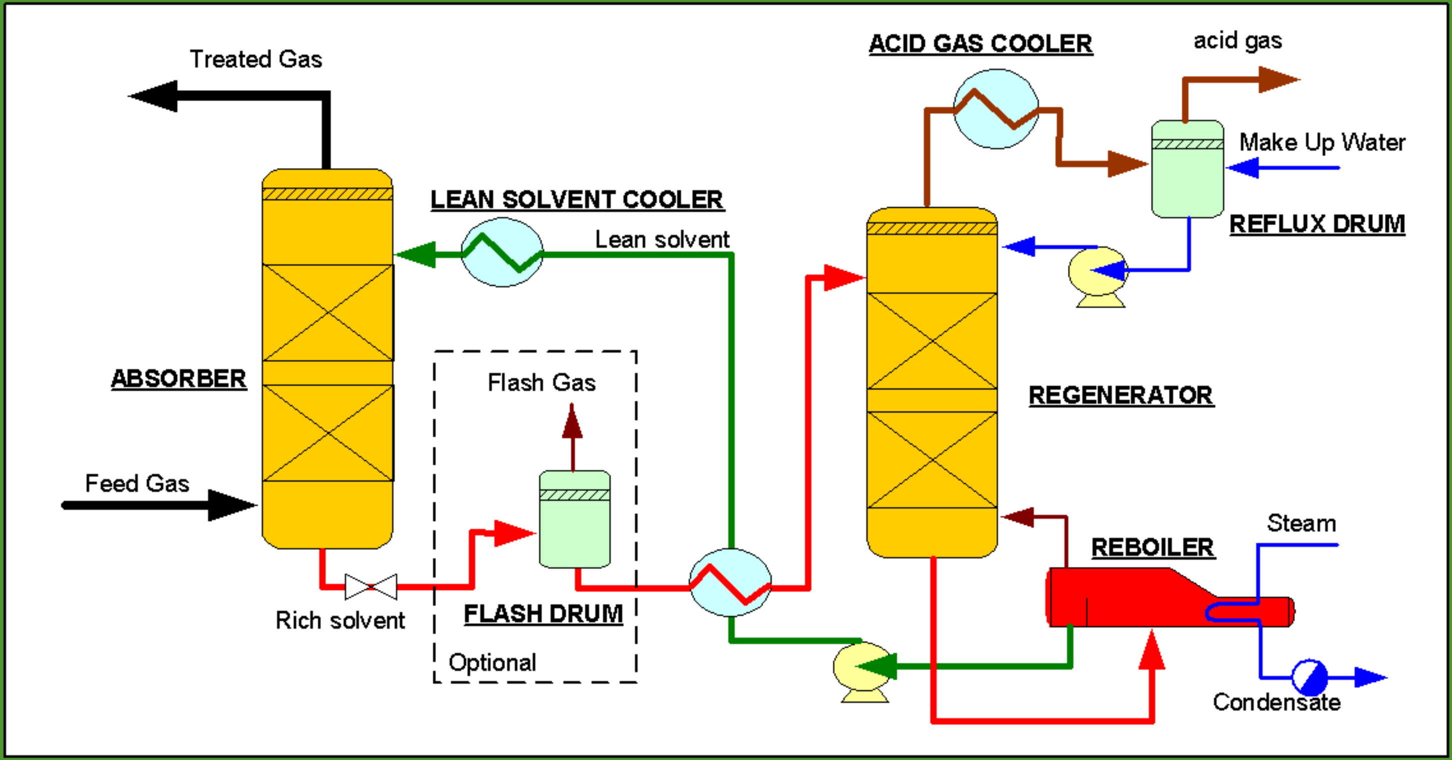
20 May 2008, Vienna, Austria

Content

- Introduction;
- Shell ASAP unit;
- Rate based model;
- Results and Discussion;
- Conclusions & Future work.

Introduction

Typical flowsheet:



Introduction

Main problems with this technology are:

- Degradation due to the presence of oxygen;
- Corrosion;
- High absorber costs;
- High regeneration costs → ± 70 % of operational costs (4 GJ / tonne CO_2).

→ Better solvents required.

This Work:

→ Study of performance of aqueous MDEA and comparison with pilot plant data of an absorber – desorber.

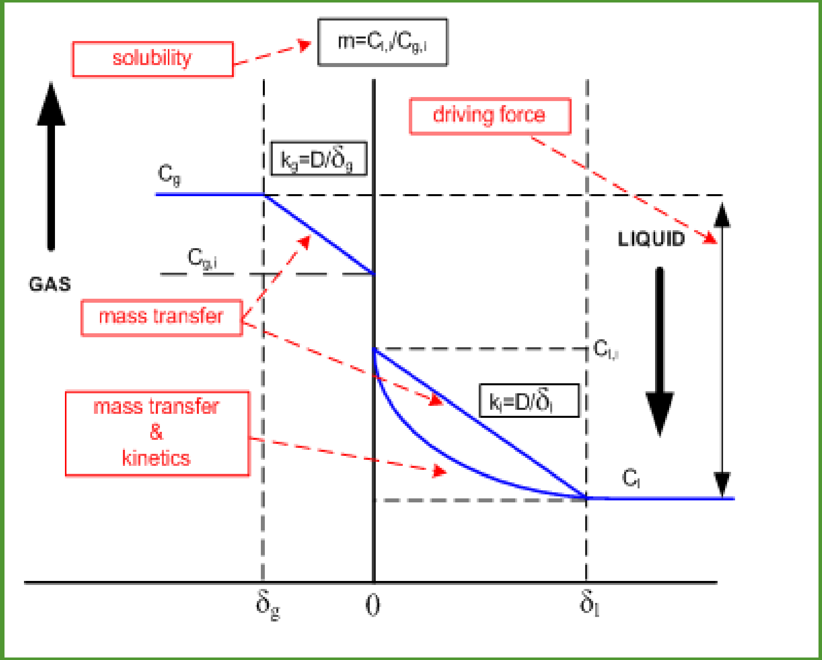
Introduction

- **Process design:**
  - **Hydrodynamics (a);**
  - **Mass transfer parameters (k_L and k_G);**
  - **VLE (physical and chemical);**
  - **Kinetics (enhancement).**

- **Accurate prediction of fundamentals required;**

- **Rate based model required because absorber is not operating at equilibrium conditions.**

Film model



Introduction

- **Kinetics tertiary amines:**

$$CO_2\,(g) + R_3N(l) + H_2O(l) \xleftarrow{k_{-1}}\xrightarrow[k_2]{} HCO_3^-\,(l) + R_3NH^+\,(l) \qquad (1)$$

Reaction with tertiary amine is slow and has a low regeneration energy;

$$R_{CO_2} = k_2[CO_2][R_3N] \quad \text{mole.m}^{-3}.\text{s}^{-1}$$ **(second order reaction)**

- **Kinetics primary-secondary amines:**

Reaction with primary / secondary amine (carbamate formation) is fast and has higher regeneration energy;

Reaction is complex and can be described with zwitterion mechanism:

$$CO_2\,(g) + R_1R_2NH\,(l) \xleftarrow{k_{-1}}\xrightarrow[k_2]{} R_1R_2NH^+COO^-\,(l) \qquad (2a)$$

$$R_1R_2NH^+COO^-\,(l) + B\,(l) \xleftarrow{k_{-b}}\xrightarrow[k_b]{} R_1R_2NCOO^-\,(l) + BH^+\,(l) \qquad (2b)$$

$$R_{CO_2} = \frac{[CO_2][R_1R_2NH]}{\frac{1}{k_2} + \frac{k_{-1}}{k_2 \sum k_b[B]}} \qquad \text{mole.m}^{-3}.\text{s}^{-1}$$

Introduction

- **Mass transfer:**

$$J_{CO_2} = \frac{C_{CO_2,G} - \dfrac{C_{CO_2,L}}{m}}{\dfrac{1}{k_G} + \dfrac{1}{mk_L E_{CO_2}}}$$

$$Ha = \frac{\sqrt{k_{ov} D_{CO_2}}}{k_L}$$

$$E_{CO_2,\infty} = 1 + \frac{D_{am}[Am]}{\nu_{am} D_{CO_2}[CO_2]}$$

Pseudo first order regime:

$E_{CO2}=Ha$ if $2 < Ha << E_{CO2,\infty}$

Diffusion limited regime:

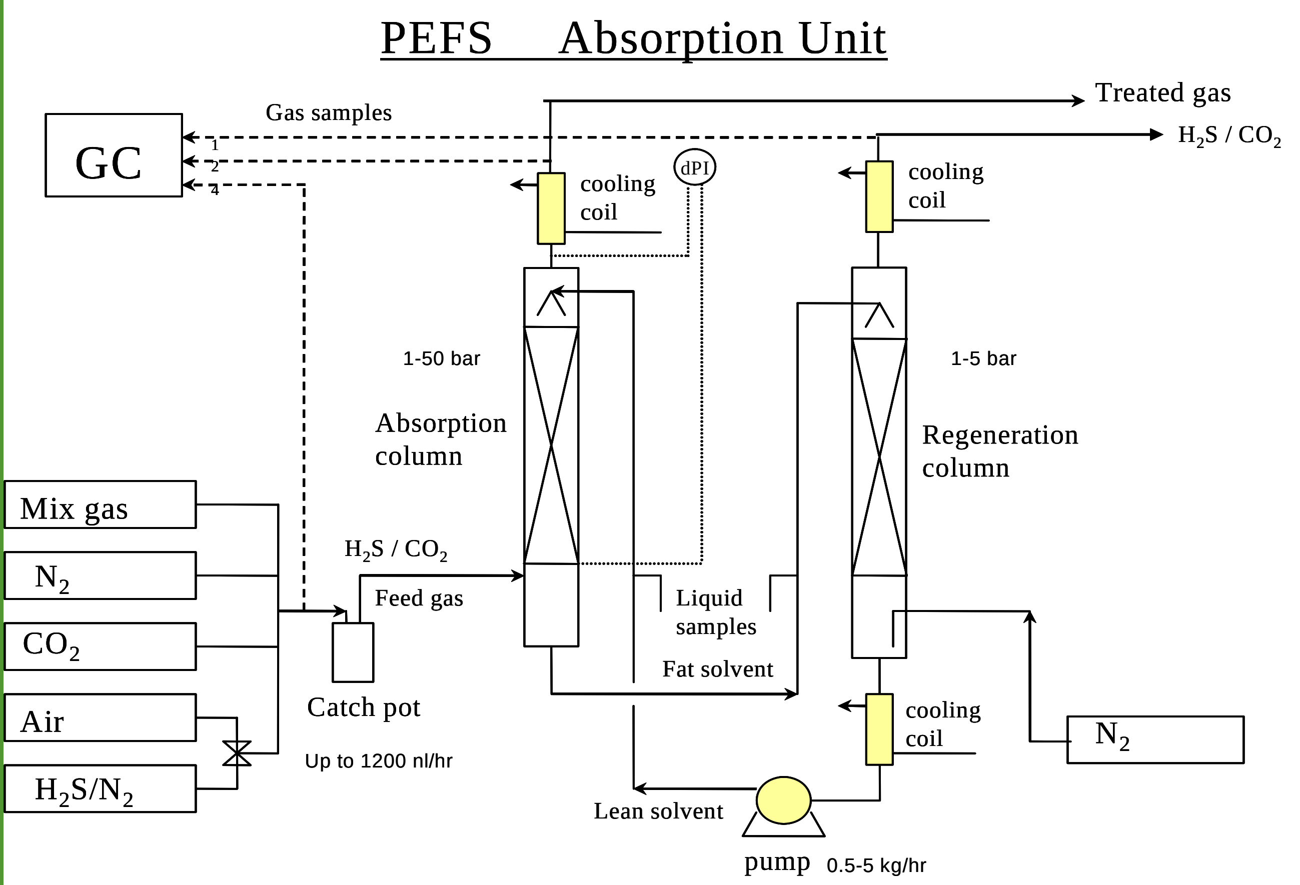
$E_{CO2}=E_{CO2,\infty}$ if $2 < E_{CO2,\infty} << Ha$

Shell ASAP unit

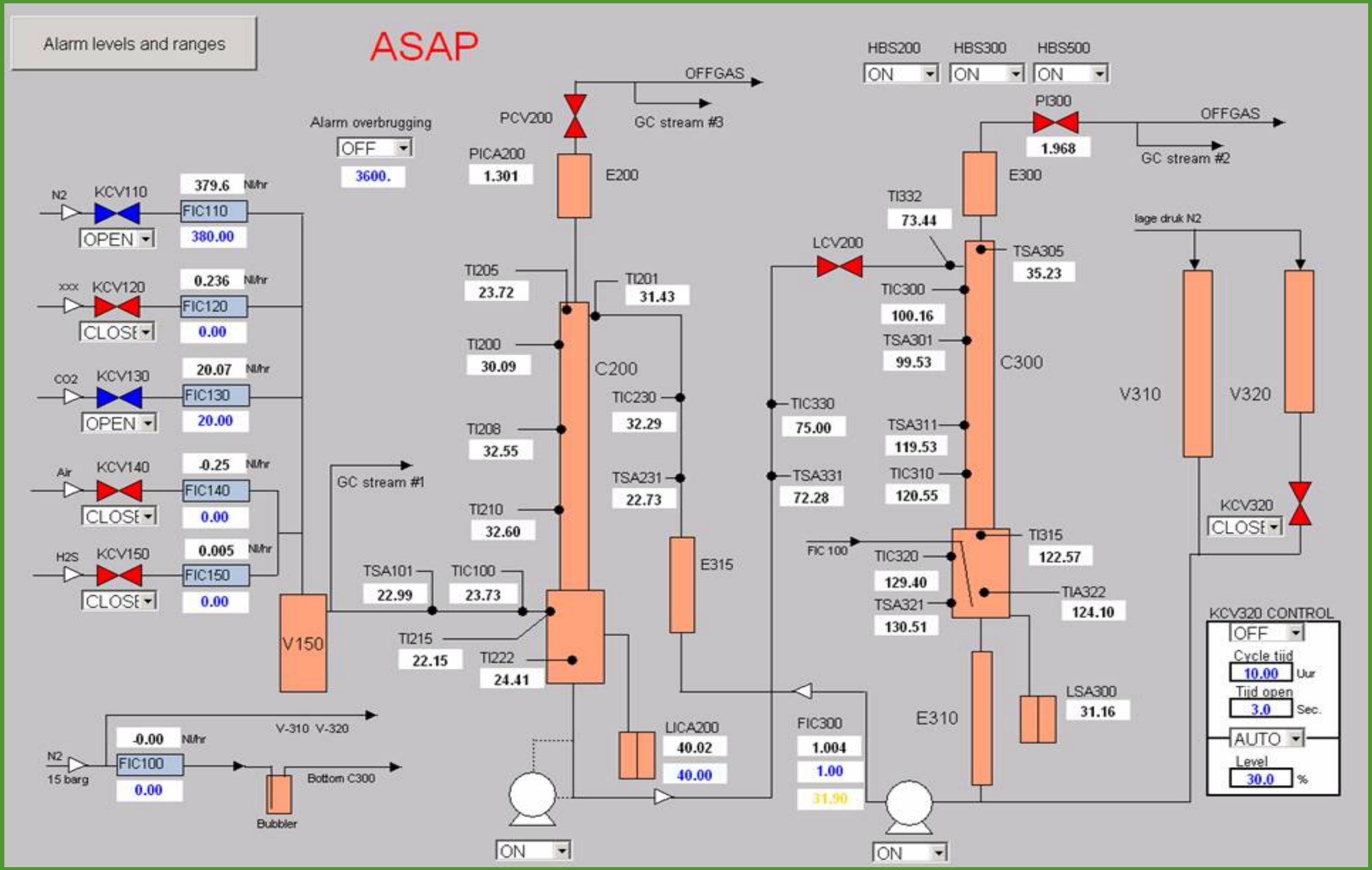
- ASAP Unit (Amine Screening APparatus) is developed by Shell Global Solutions - Amsterdam;
- Designed to test the performance of different solvents;
- Gas flow up to 1.3 Nm^3/hr;
- Liquid flow up to 6 kg/h;
- D=2.5 cm, L=1.45 m;
- Sulzer EX laboratory packing; area is 1735 m^2/m^3.

- Following solvent have been tested and simulated:
  - 50 wt.% MDEA → solvent circulation is 80 m^3 solvent / tonne removed CO_2.

Shell ASAP unit



Shell ASAP unit



HBS200 ON
HBS300 ON
HBS500 ON

Alarm overbrugging OFF
3600.

N2 KCV110 OPEN; FIC110 379.6 Nl/hr; 380.00
xxx KCV120 CLOSE; FIC120 0.236 Nl/hr; 0.00
CO2 KCV130 OPEN; FIC130 20.07 Nl/hr; 20.00
Air KCV140 CLOSE; FIC140 -0.25 Nl/hr; 0.00
H2S KCV150 CLOSE; FIC150 0.005 Nl/hr; 0.00
N2 FIC100 -0.00 Nl/hr; 0.00

PICA200 1.301
TI205 23.72
TI201 31.43
TI200 30.09
TI208 32.55
TIC230 32.29
TSA231 22.73
TI210 32.60
TSA101 22.99
TIC100 23.73
TI215 22.15
TI222 24.41
LICA200 40.02; 40.00
ON

PI300 1.968
TI332 73.44
LCV200
TSA305 35.23
TIC300 100.16
TSA301 99.53
TIC330 75.00
TSA331 72.28
TSA311 119.53
TIC310 120.55
FIC 100
TI315 122.57
TIC320 129.40
TSA321 130.51
TIA322 124.10
FIC300 1.004; 1.00; 31.90
LSA300 31.16
ON

KCV320 CLOSE

KCV320 CONTROL
OFF
Cycle tijd 10.00 Uur
Tijd open 3.0 Sec.
AUTO
Level 30.0 %

Rate Based Model

Two (rate based) models are under development at Procede:

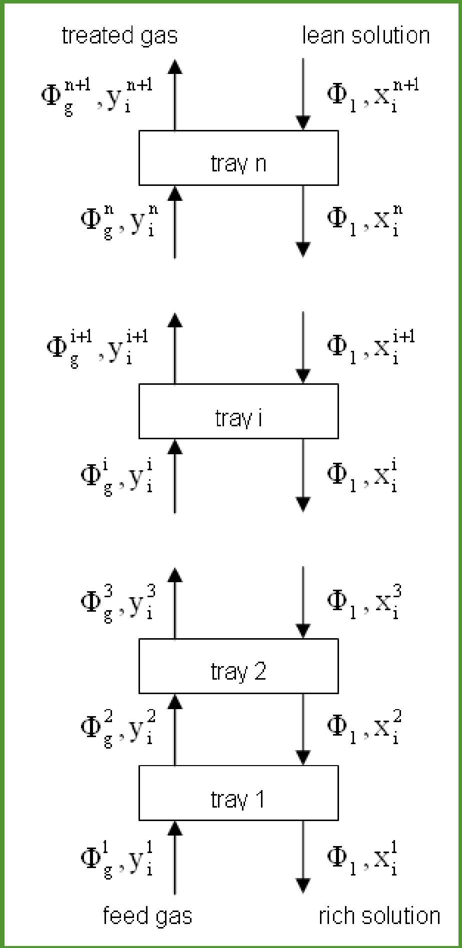
1. **Top down model (SimCol):**
   → Unit operations;
   → Mass transfer + kinetics;

2. **Bottom up model (Pro2Sim):**
   → Fundamentals (equilibrium, flash and rate models);
   → Unit operations;

In this work SimCol is used to describe the absorber of the ASAP unit located at the Shell laboratories in Amsterdam.

Rate Based Model

- Flux model for mass transfer;
- Ideal vapor / liquid phase (fugacity = 1);
- Tray to tray procedure (Blauwhof 1985);
- Series of ideal CISTR's;
- No pressure drop and back mixing;
- Constant heat and mass transfer parameters (k_L, k_G, a, h_L, C_P);
- Physical parameters only function of temperature (ρ, μ, D, K, m);
- Limited to blend of two amines.



Rate Based Model

Following input data are required:

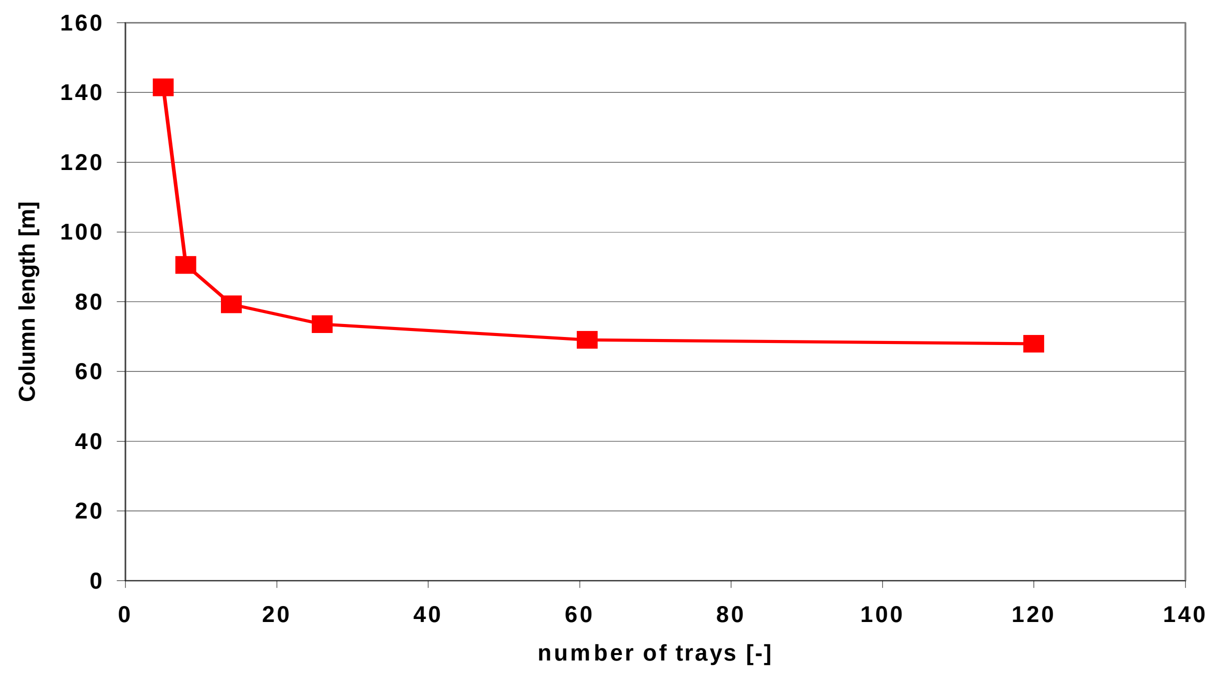
- Solvent type;
- Gas and liquid temperatures;
- In- and outlet CO_2 concentrations;
- Lean solvent concentration;
- Mass transfer parameters: k_G, k_L and a;
- Physical properties (density and heat capacity);
- Reaction and absorption enthalpy;

Output:

- Required absorber dimensions;
- Temperature profile in absorber;
- Concentration profile in column;
- Speciation of the liquid.

Model results and Discussion

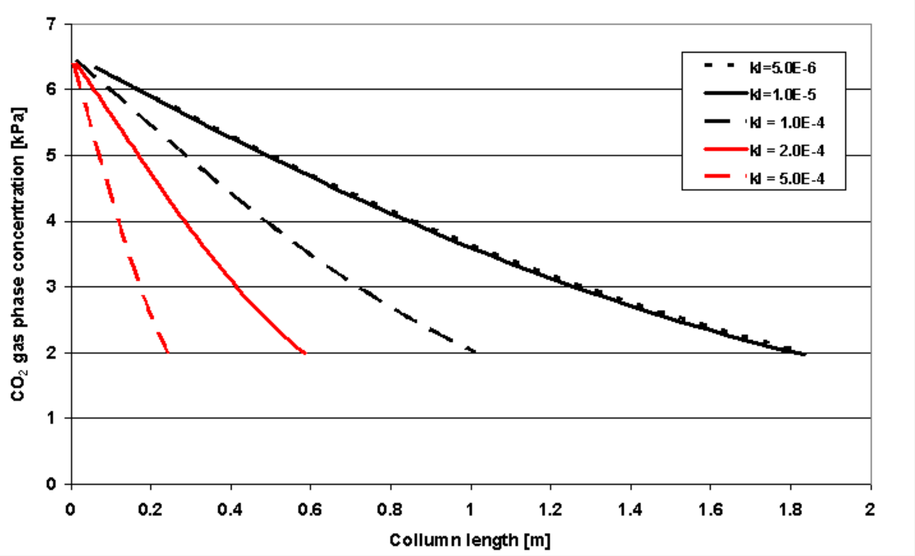
Influence number of trays :



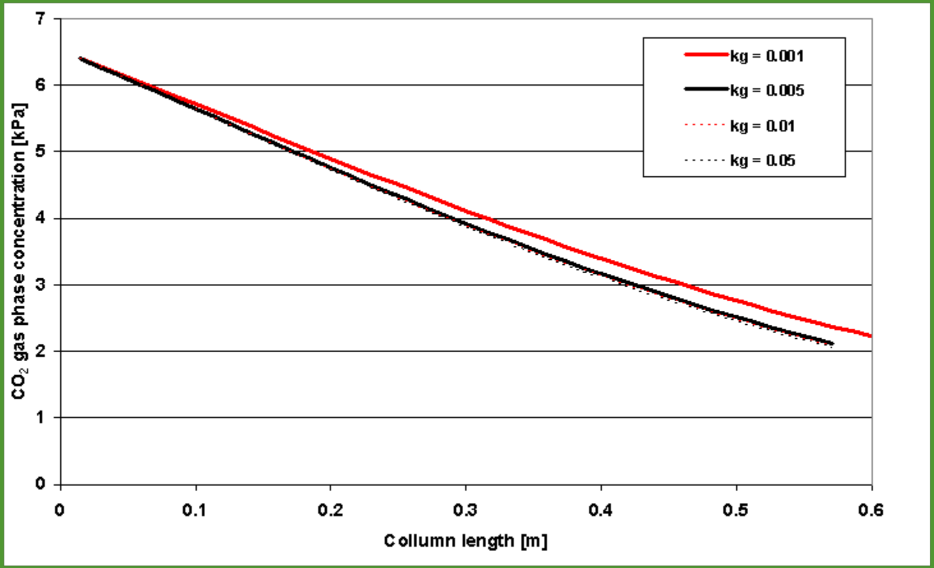
Minimum number of calculated trays should be at least 30 to assure plugflow in the column.

Model Results and Discussion

Influence k_L:



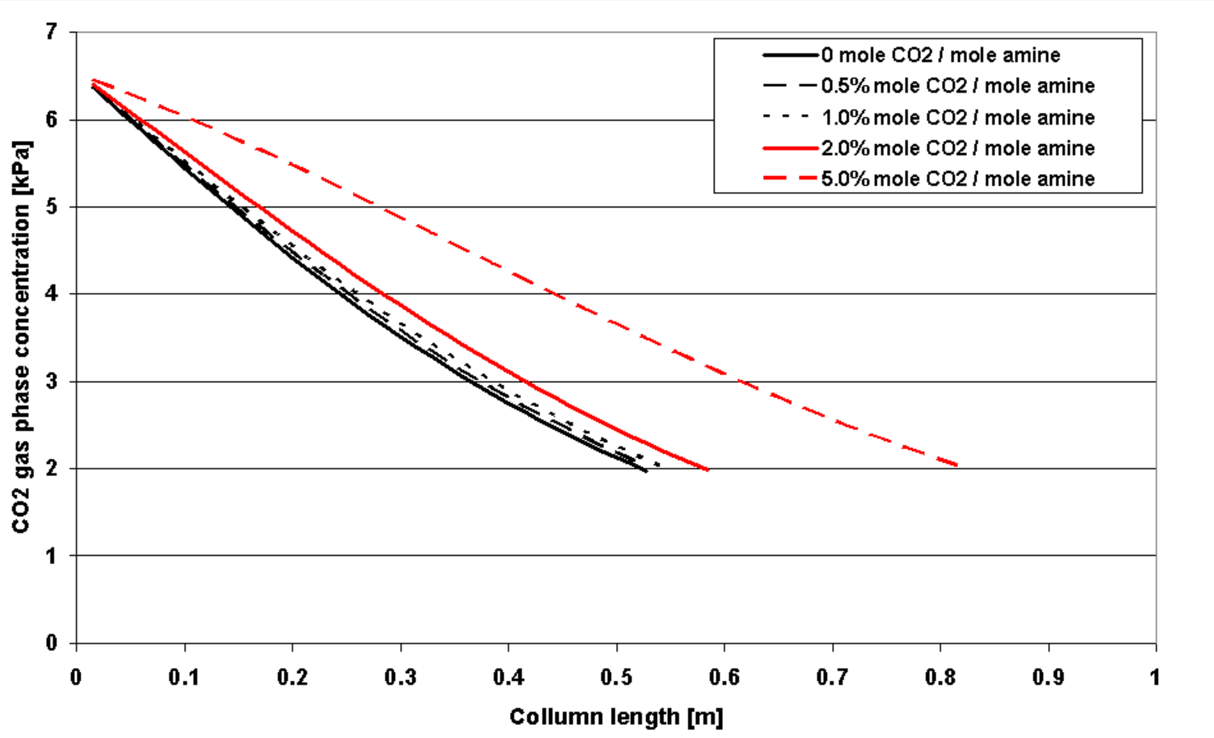
Influence k_G:



Conclusion: Mass-transfer is generally k_L limited and not k_G.

Model Results and Discussion

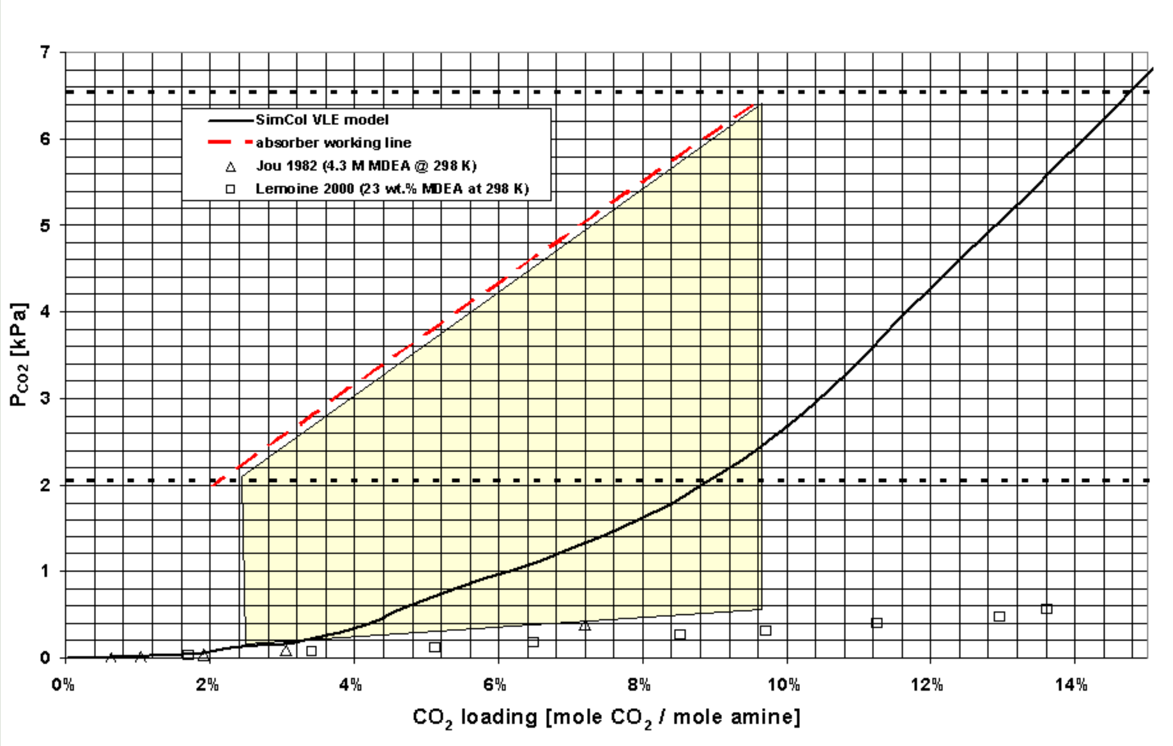
Influence lean loading:



Conclusion: Mass-transfer is highly depended on lean loading.

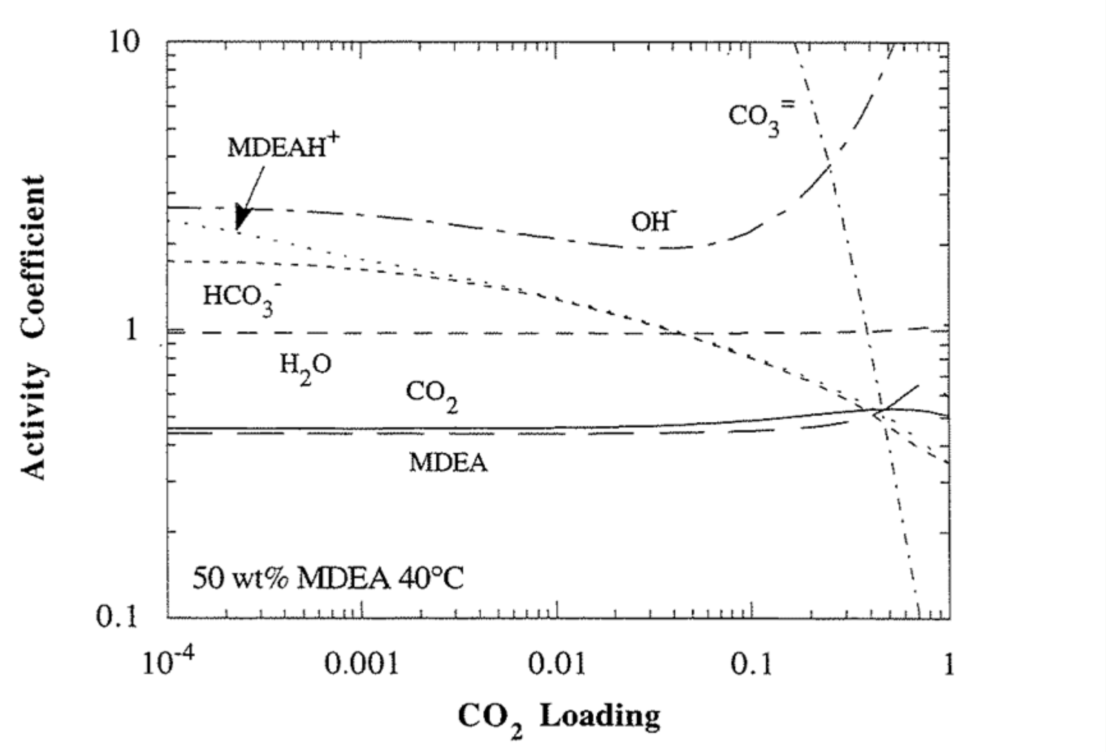
Model Results and Discussion

Driving force in absorber:



Model Results and Discussion

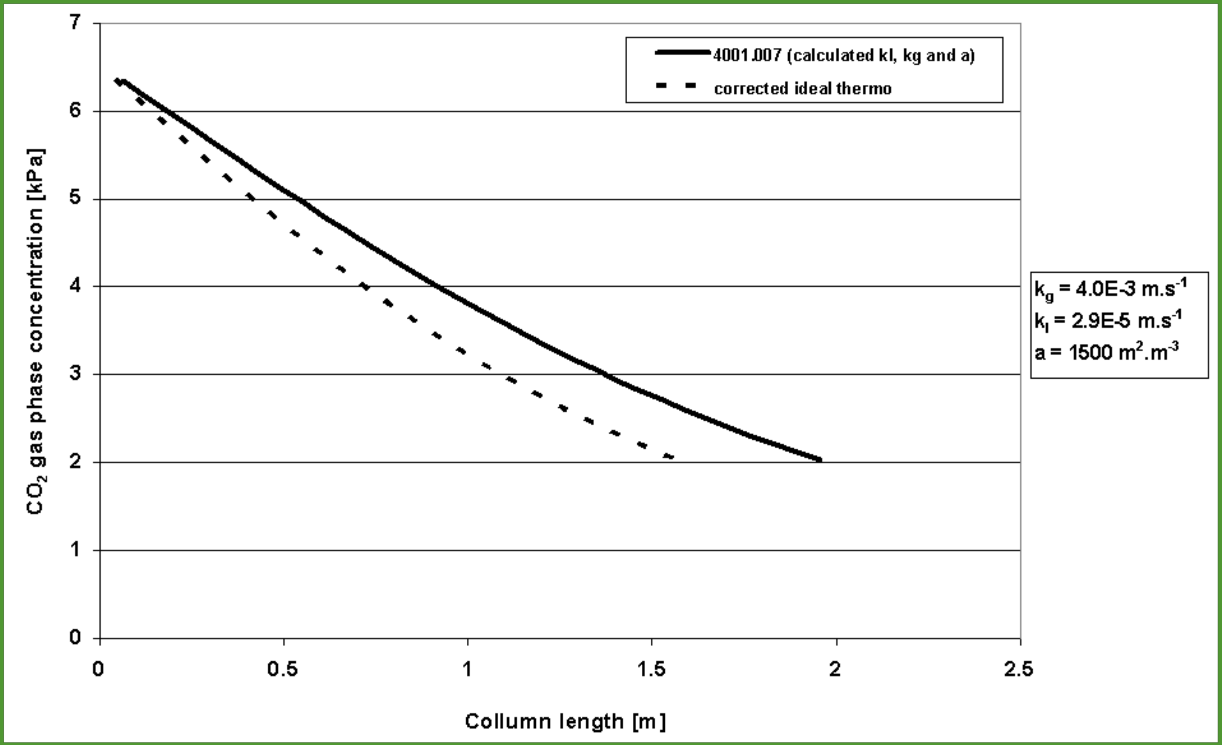
Calculated activity coefficient in CO_2 loaded 50 wt.% MDEA at 40 °C as calculated by electrolyte NRTL model:



Ref: PhD –thesis Posey (1996) University of Texas.

Model Results and Discussion

Calculated column length:

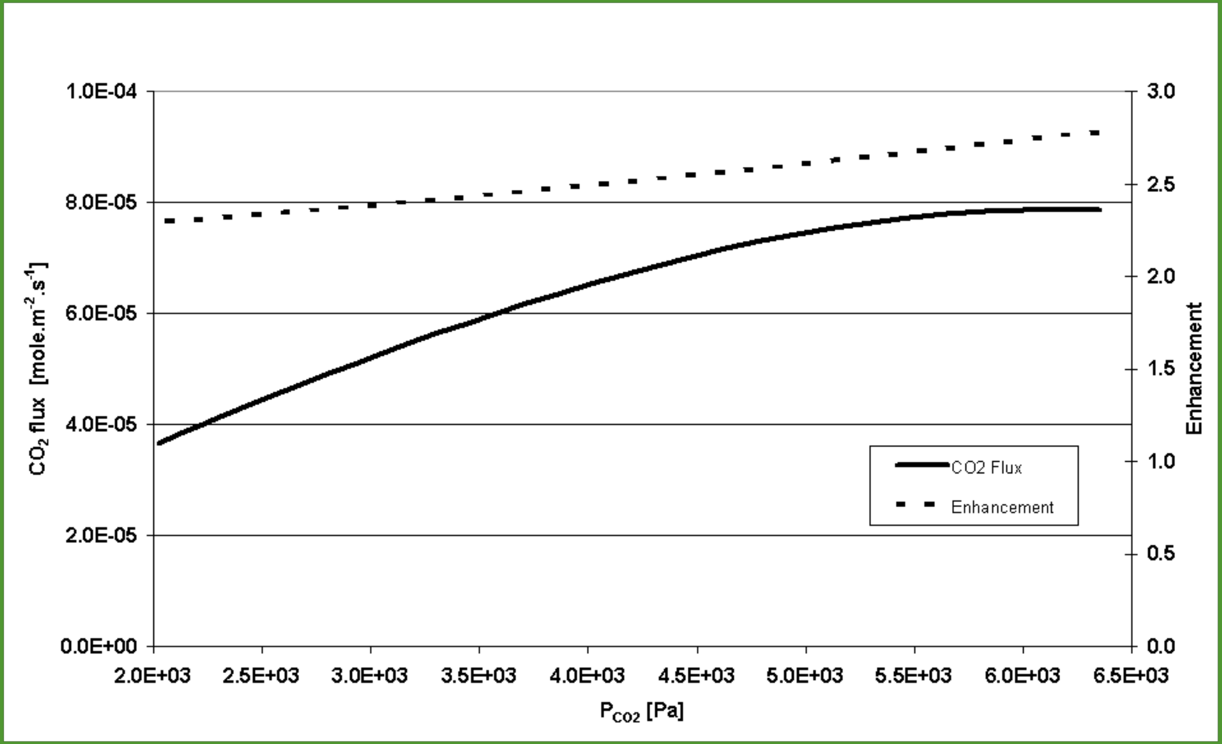


$k_g = 4.0E\text{-}3\ m.s^{-1}$
$k_l = 2.9E\text{-}5\ m.s^{-1}$
$a = 1500\ m^2.m^{-3}$

Calculated length; good agreement with experiments (1.45 m).

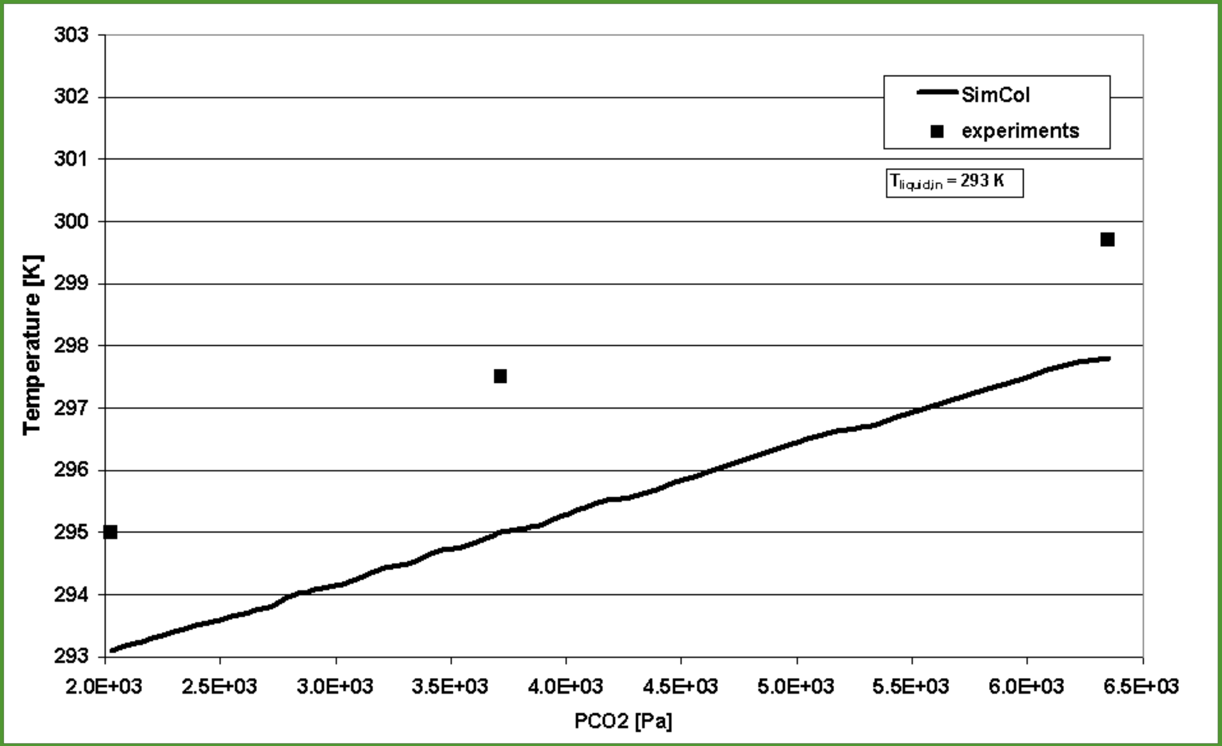
Model Results and Discussion

Flux and chemical enhancement:



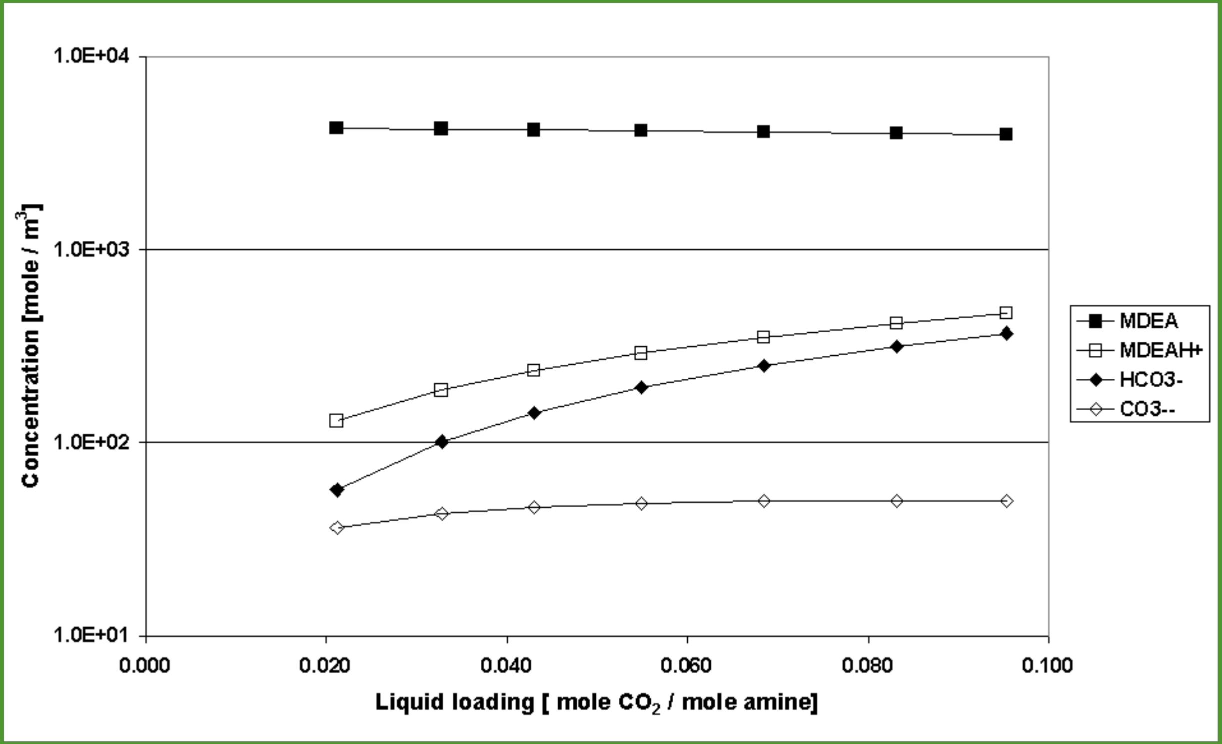
Model Results and Discussion

Temperature profile:



Model Results and Discussion

Speciation in liquid phase:



Conclusions & Future work

- SimCol can be used for qualitatively absorber calculations;
- Simple thermodynamic and enthalpy model not sufficient for accurate calculations → Extension to more accurate thermodynamic models, like E-EOS models;
- Good prediction for MDEA experiments; other solvents will be studied.

Acknowledgement

- Shell Global Solutions for the experimental part of this work;

- 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!

CCS at IFP

from MEA to New Processes for CO_2 Post-Combustion Capture

L. Raynal, E. Lemaire, P. Broutin (IFP)

& L. Normand (Prosernat)

11th MEETING of the INTERNATIONAL POST-COMBUSTION CO_2 CAPTURE NETWORK,

20th-21st May, 2008, Vienna, Austria

Innovation
Energy
Environment

Outlook

- **IFP & CCS**

- MEA process

- New processes

- Conclusion

© IFP

IFP

IFP in a nutshell

- 1,735 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)

- 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 12,500 active patents
- More than 200 scientific publications every year

** mean workforce, full-time equivalent*

Innovation
Energy
Environment

IFP

Preparing for the energy transition

5 complementary strategic priorities

CONTROLLED CO_2	DIVERSIFIED FUELS	FUEL-EFFICIENT VEHICLES	CLEAN REFINING	EXTENDED RESERVES
Capturing and storing CO_2 to combat greenhouse effect	Diversifying fuel sources	Developing clean, fuel-efficient vehicles	Converting as much raw material as possible into energy for transport	Pushing back the boundaries in oil and gas exploration and production

IFP's research programs are structured around these 5 priorities

Research and development

Controlled CO_2

CONTROLLED CO_2

Capturing and storing CO_2 to combat 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 intervene at all stages in the process, from capture to storage
- Because the bulk of CO_2 emissions result from energy use

3 R&D themes

- CO_2 capture
- Transporting and injecting CO_2
- Geological storage of CO_2

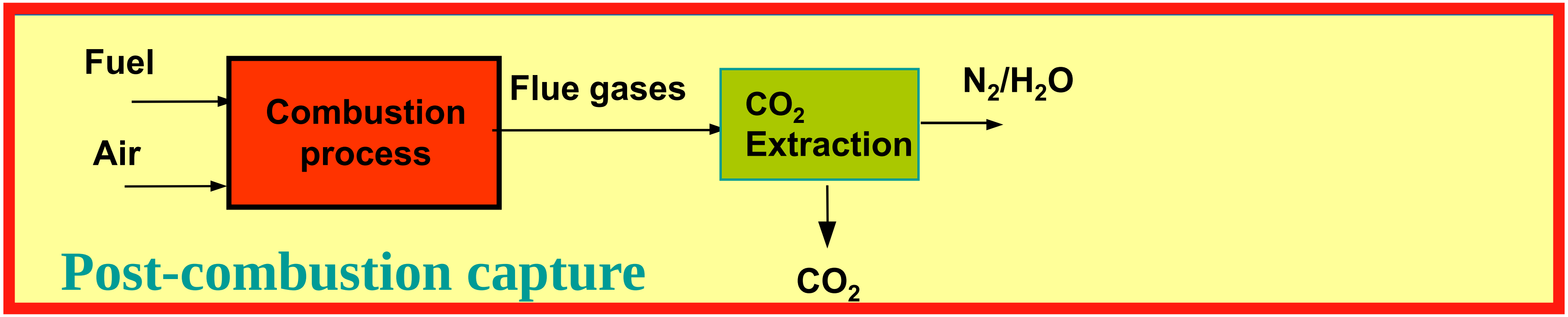
Industrial Outlets

PROSERNAT
IFP Group Technologies

geogreen

ifp
Innovation
Energy
Environment

Energy production with CO_2 capture



Fuel

Air

Combustion process

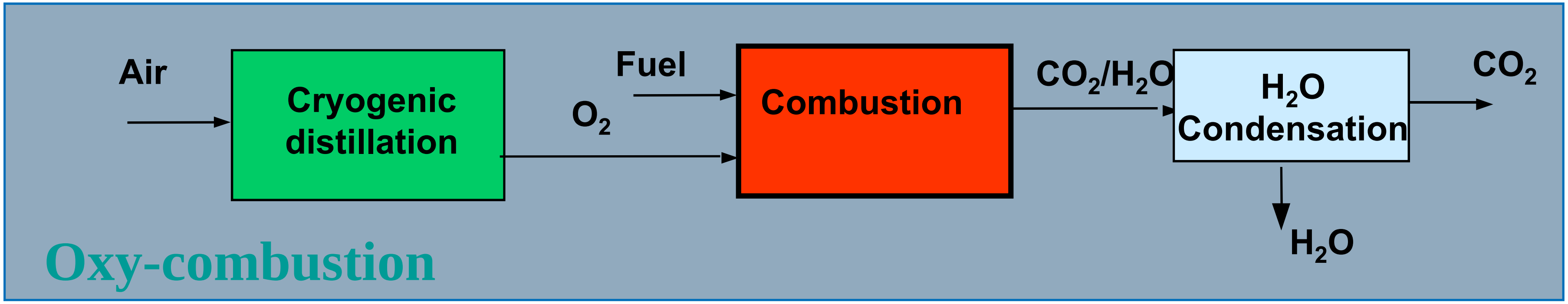
Flue gases

CO_2 Extraction

N_2/H_2O

CO_2

Post-combustion capture



Air

Cryogenic distillation

Fuel

O_2

Combustion

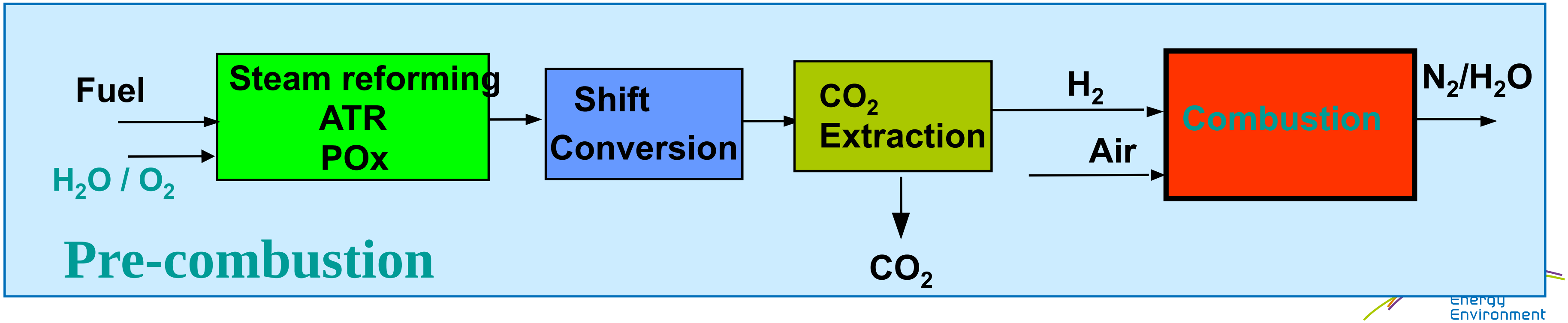
CO_2/H_2O

H_2O Condensation

CO_2

H_2O

Oxy-combustion



Fuel

H_2O / O_2

Steam reforming ATR POx

Shift Conversion

CO_2 Extraction

H_2

Air

Combustion

N_2/H_2O

CO_2

Pre-combustion

Outlook

- IFP & CCS
- **MEA process**
- New processes
- Conclusion

The MEA+ process

- **The MEA process = BAT**
  - only proven technology for demos and first generation CO_2 ready power plants
  - second generation will not be ready before at least 5 years for industrial demos/applications
- **The MEA+ process @ IFP**
  - Demonstration and knowledge partly acquired within CASTOR project
  - Huge experience with gas treatment processes commercialized by Prosernat (Technologies and equipment supplier to the natural gas industry, an IFP fully owned subsidiary)
  - => IFP process for minimum costs
    - optimized formulation (corrosion, degradation)
    - optimized design (column size)

Innovation
Energy
Environment

Optimized formulation

- **standard MEA**
- **Oxygen & Thermal Degradation**

(schematic reaction) MEA $+O_2 \longrightarrow$ HSS $+$ NH_3

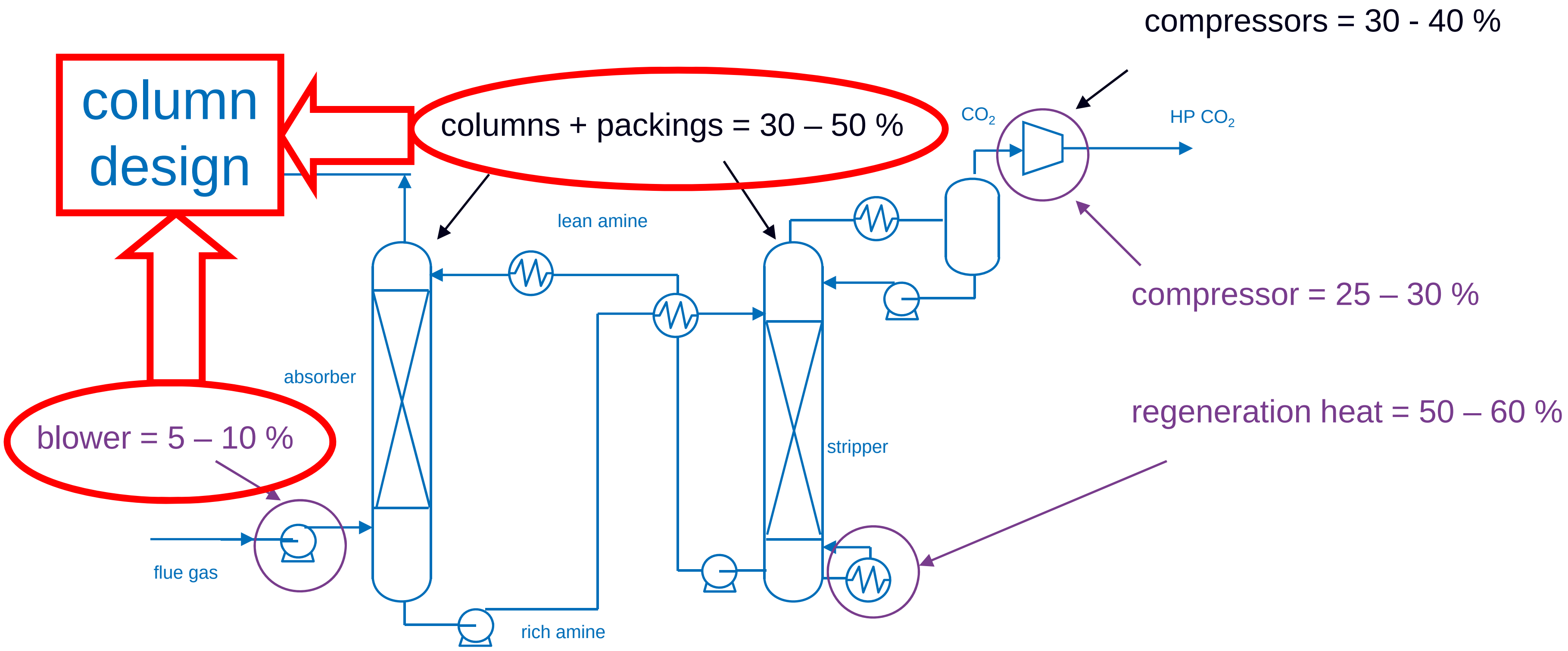
  - **HSS formation, corrosion, slower reactivity, ammonia specification**
  - **solvent consumption**
  - **= > tests and screening for inhibitors**

- **Corrosion**
  - **comparison and evaluation off various material**
  - **use of Castor data (monitoring done by IFP)**
  - **= > tests and screening for inhibitors**

AISI 1018 carbon steel coupon after 3 weeks exposure in the lean solvent outlet of the regenerator.

=> original IFP formulation MEA+ 30%wt + additives

Optimized design



compressors = 30 - 40 %

column design

columns + packings = 30 – 50 %

compressor = 25 – 30 %

regeneration heat = 50 – 60 %

blower = 5 – 10 %

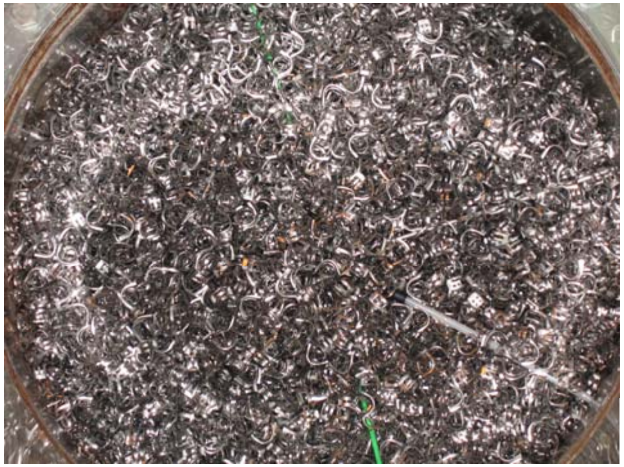
Capex

Opex

column design :

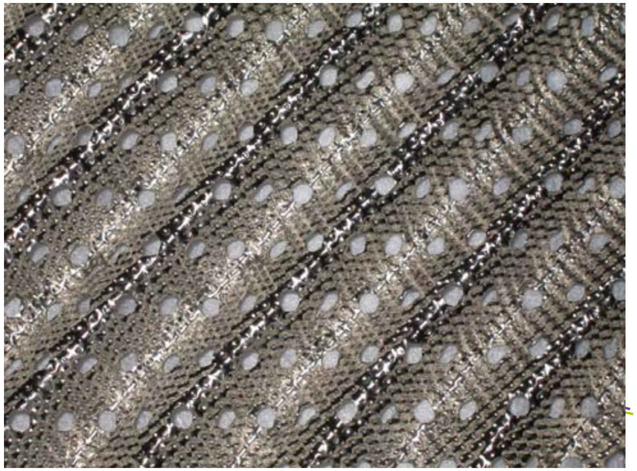
- optimum packing / distribution
- minimum pressure drop
- maximum mass transfer characteristics

Experiments (1/2)
Large scale experimental facilities



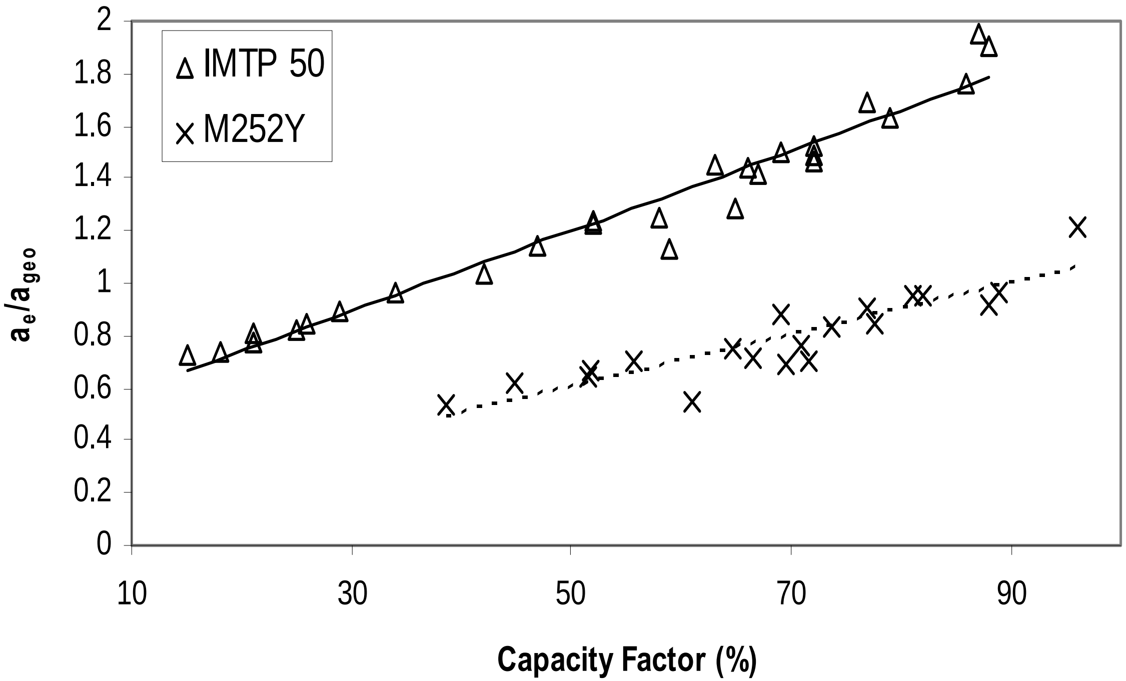
IMTP 50

Mellapak
252 Y



Experiments (2/2)
Results - Mass Transfer Measurements

- **comparison between random & structured packing**
- **=> strong differences in behaviour**



CFD calculations (1/2) strategy

Geometry :

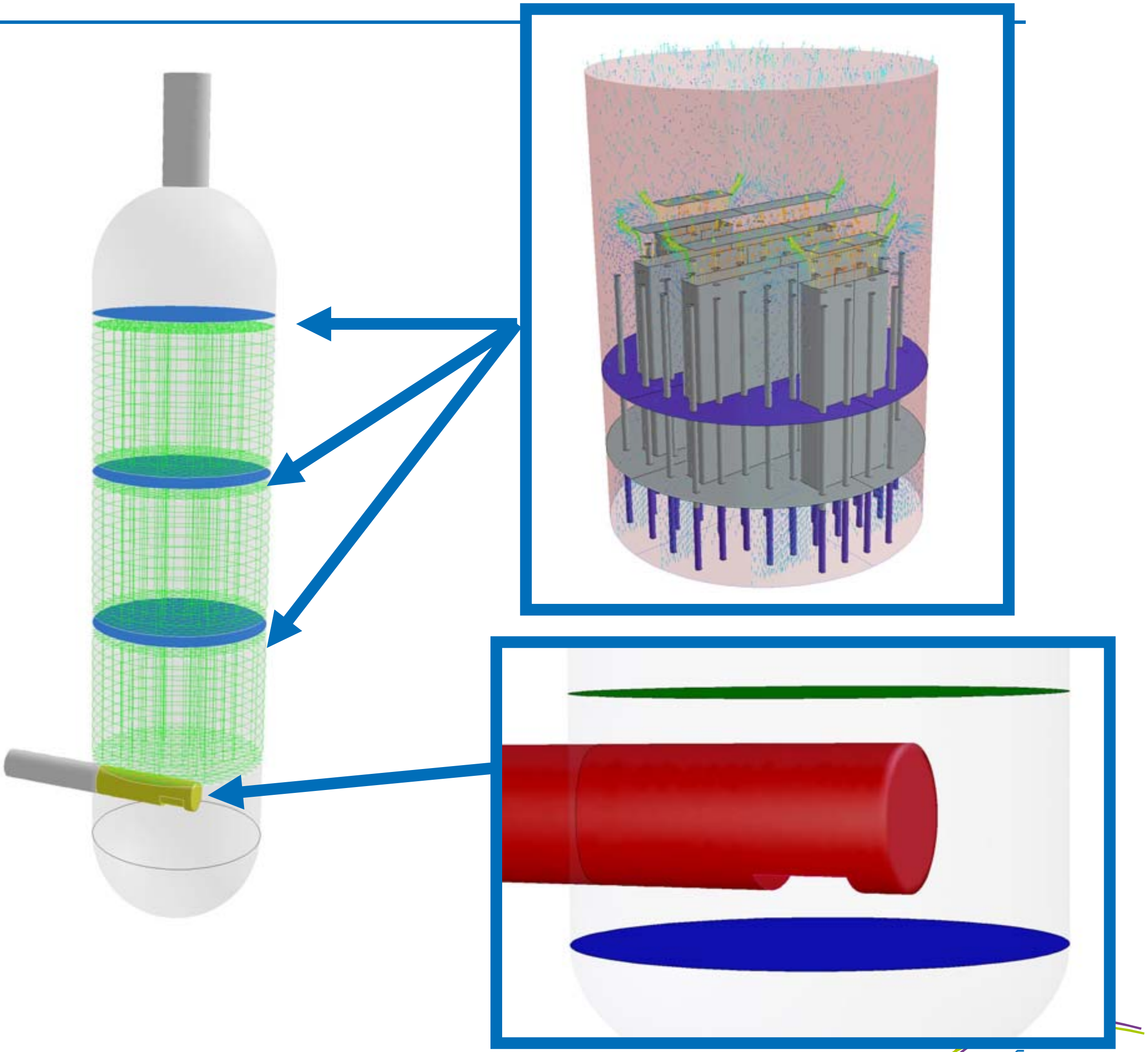
the whole column
3D calculations

Outputs :

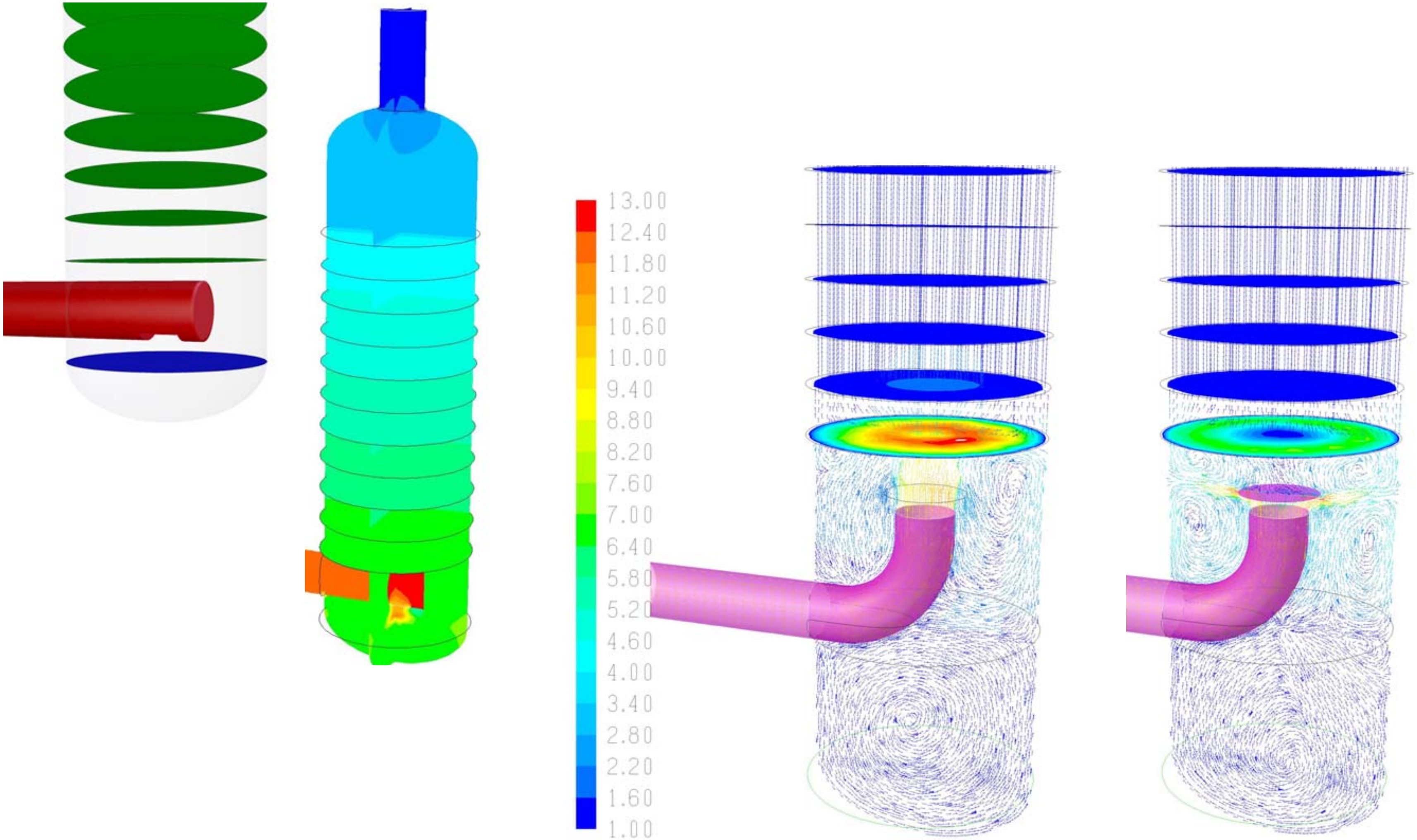
tests of design

Inputs :

local information on
packings < experiments



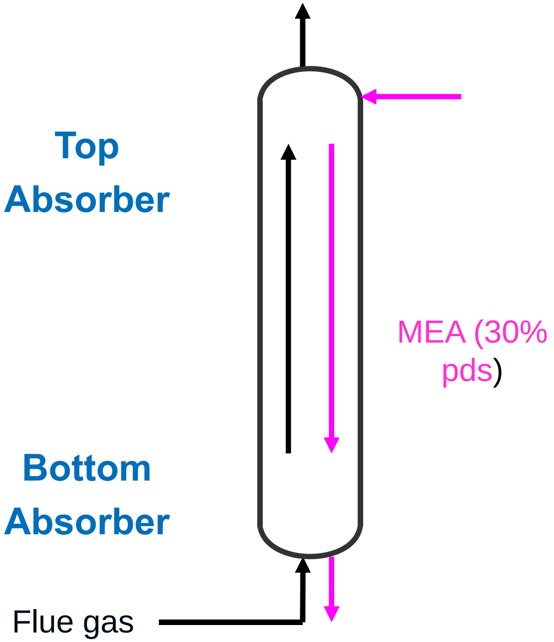
CFD calculations (2/2)
Results – tests of gas distributors



Validation
Process simulation

IFP Simulation of Castor results

- electrolyte NRTL thermodynamic
- IMTP 50 random packing characteristics (IFP data)

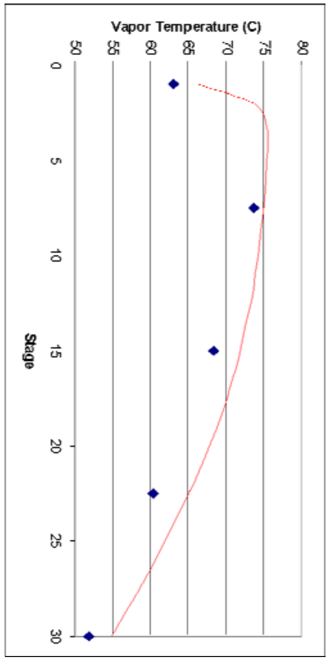


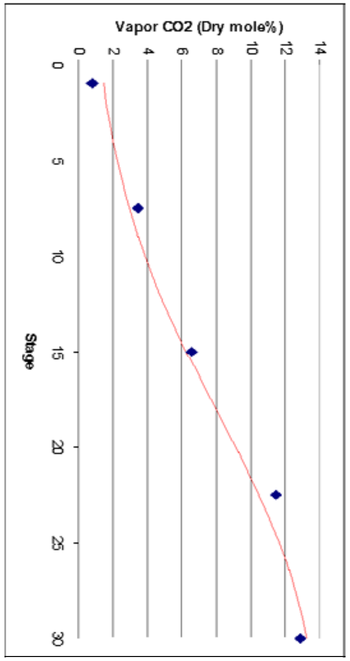
Top Absorber

Bottom Absorber

MEA (30% pds)

Flue gas

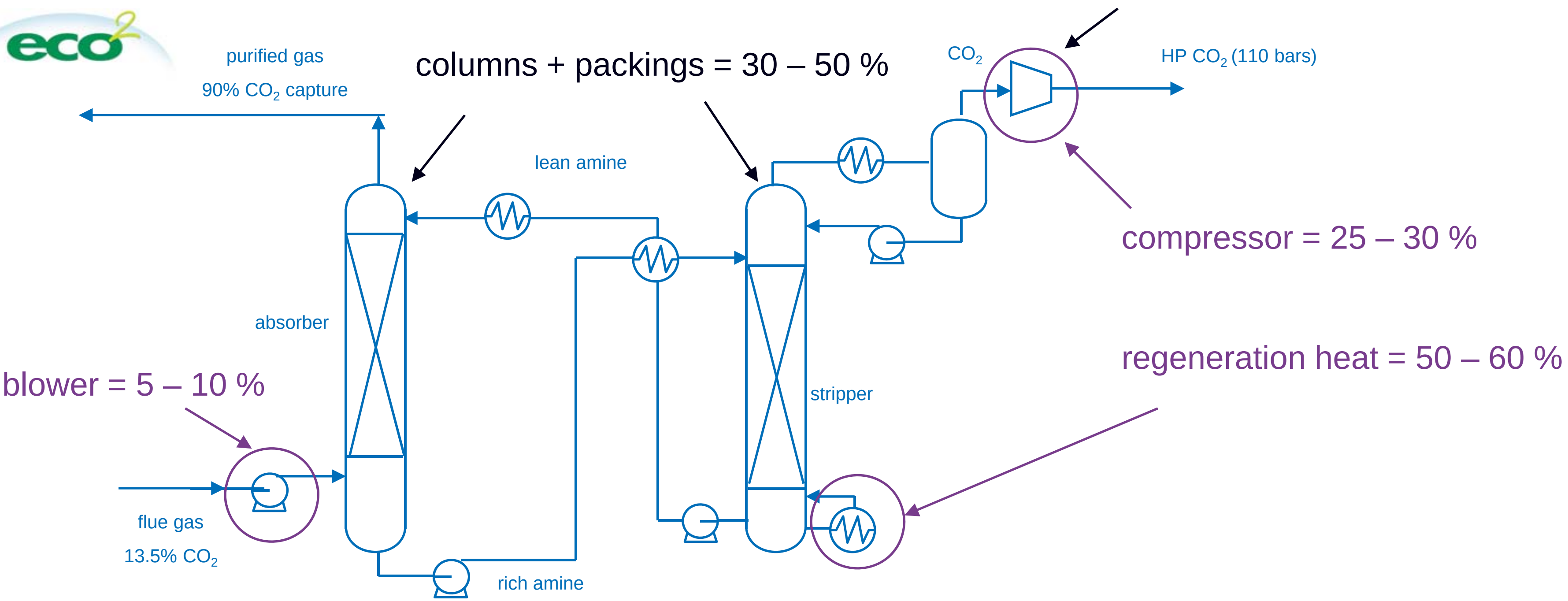




MEA process cost

from the IFP – Alstom éCO$_2$ study, a project sponsored by Ademe
case of a CFB Coal fired power station, 1400 MW_th, 630 MW_é

compressors = 30 - 40 %



columns + packings = 30 – 50 %

compressor = 25 – 30 %

regeneration heat = 50 – 60 %

blower = 5 – 10 %

	Reference power plant	**plant with CCS (MEA)**
Net efficiency	**45 %**	**34.5 %**
Cost of electricity	**38 €/MWh**	**66 €/MWh**
Cost of CO$_2$ avoided		**44 €/t**

Outlook

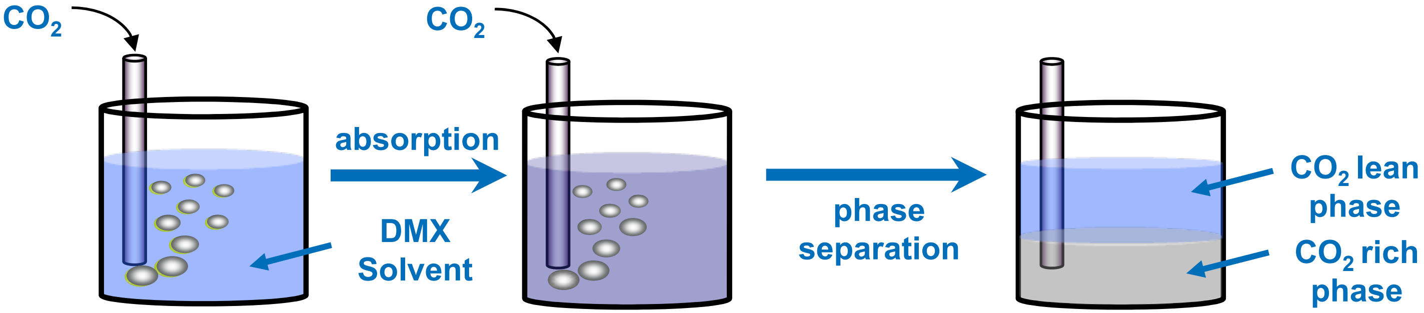
- IFP & CCS

- MEA process

- **New processes**

- Conclusion

New concepts
Demixing solvents



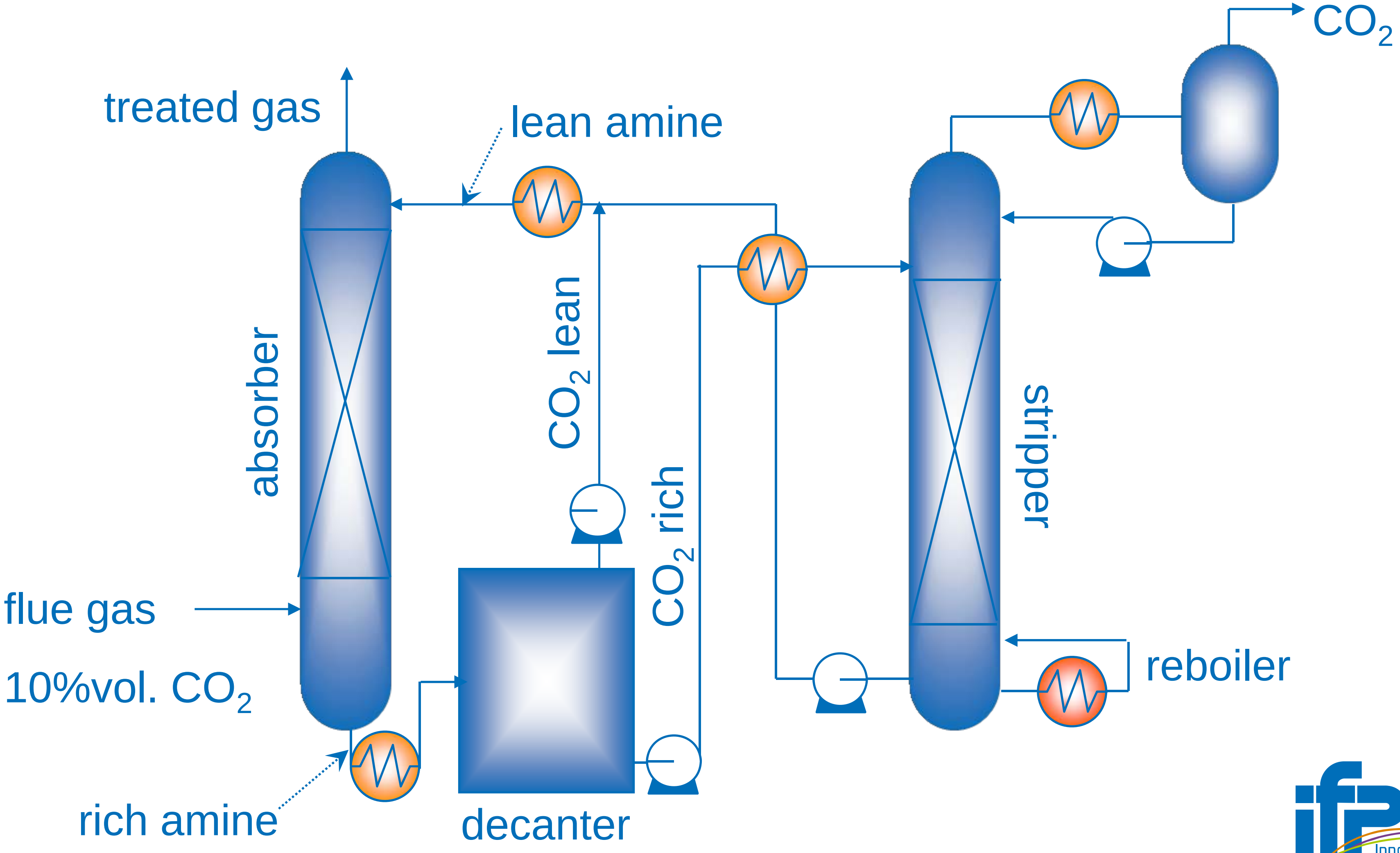
amine + H_2O + CO_2 ↔ ammonium salts

1) high capacity solvents
2) regeneration of a fraction of the solvent only
3) CO_2 rich phase has an "abnormally" high loading

=> important energy savings

© IFP

Process with DMX solvents



New concepts
Hydrates formation

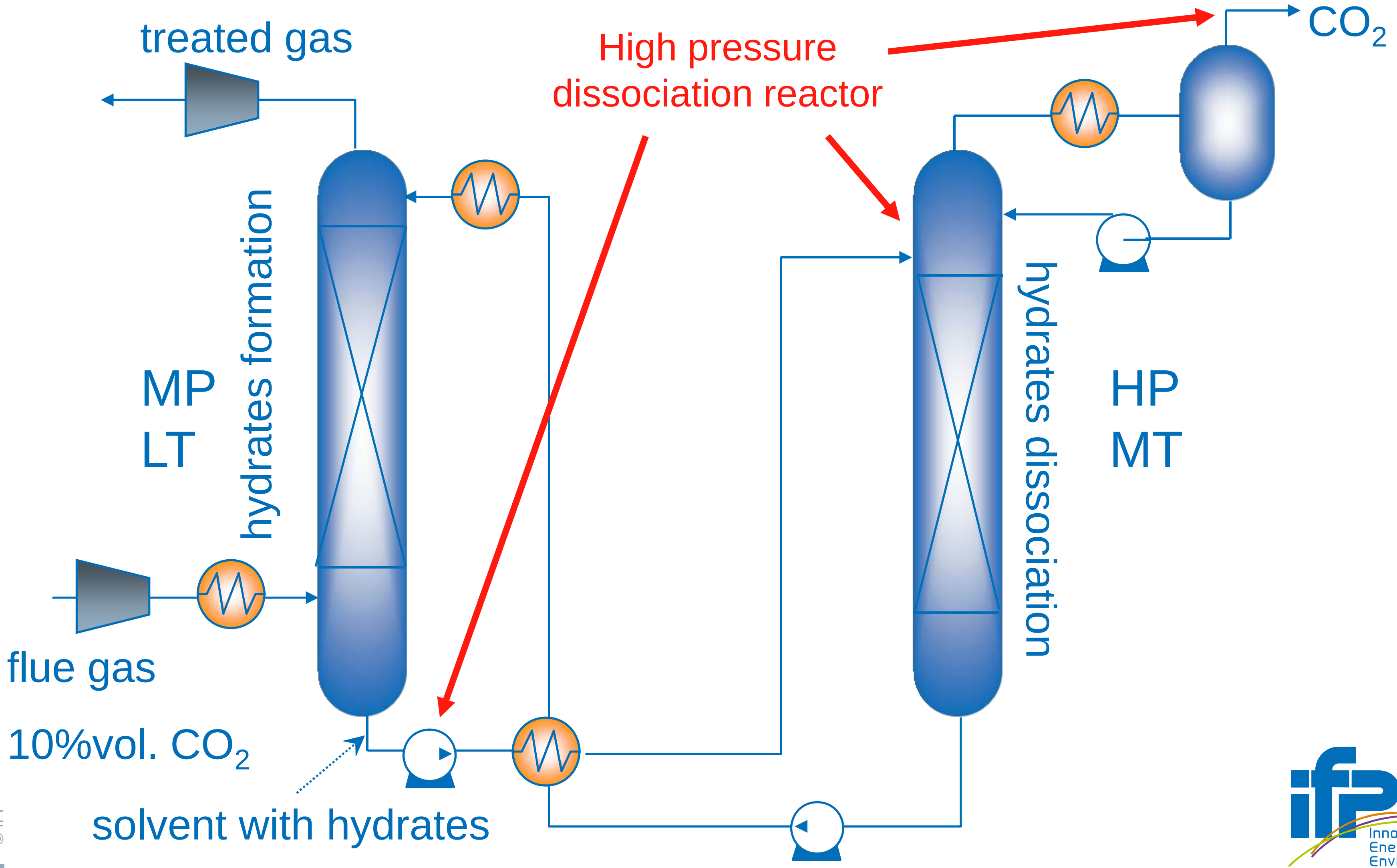
- **Hydrates**
  - **natural selectivity towards CO_2 hydrates formation**
  - **HP, LT**

  => needs for a promoter (TBAB, THF...)

  - **natural formation of agglomerates which leads to plugging**

  => original IFP formulation : water in oil emulsion with a proprietary anti-agglomerate

Process Hydrates



treated gas

High pressure dissociation reactor

CO_2

MP
LT

hydrates formation

hydrates dissociation

HP
MT

flue gas

10%vol. CO_2

solvent with hydrates

Other works

- **New processes**
  - **amine blends**
  - **adsorption : functionnalized adsorbents – MOF**
  - **ionic liquids**
  - **original solvents ...**
- **New technologies**
  - **membrane contactors**
  - **high performance packings**

- **IFP Collaborations**
  - **Castor, Cesar, Caprice, Acacia, Axelera, Gascogne, CapCO2, éCO2, ...**
  - **+ Encap, Coach, Decarbit, Dynamis, Cachet, ...**

Energy savings

from the IFP – Alstom éCO$_2$ study, a project sponsored by Ademe
case of a CFB Coal fired power station, 1400 MW_th, 630 MW_é

- **MEA+**

  => loss of 150 MWe

- **Demixing solvents**
  - **+ : lower L flowrate, lower reboiler duty, lower stripping**

  => loss of 130 – 90 MWe

- **Others**
  - **many ideas but many work to do before any estimation !**
  - **will not be ready for commercialization before 7-10 years**

Outlook

- IFP & CCS
- MEA process
- New processes
- **Conclusion**

Conclusion / future work

- **MEA +**
  - **A first industrial process for now**
  - **advanced MEA**
  - **ready for pilotes, demos and more ...**

- **Next generation processes**
  - **energy loss reduction by at least 30 %**
  - **original concepts (DMX solvents, Hydrates, ...) need further investigations (solvents characteristics, thermodynamics, kinetics, degradation; process studies ...)**
  - **proposition for pilote tests for 2010-2012 +**

Thank you !

www.ifp.fr

Ludovic.Raynal@ifp.fr

Innovation
Energy
Environment

Post-Combustion Capture (PCC) R&D and Pilot Plant Operation in Australia

IEA GHG 11th Post Combustion CO_2 Capture Network Meeting

Vienna, Austria, 20-21 May 2008

National Research FLAGSHIPS

CSIRO

Overview

- Clean Coal Technologies in Australia
- PCC in Australia
  - The Need
  - The Issues
- PCC programme at CSIRO
  - Pilot plant activities
  - Research activities

Australia’s Greenhouse Gas Emissions

- Australia emitted 559 M tonnes CO_2 equiv. (2005)
- Australia has signed the Kyoto Protocol. Committed to the Kyoto target of a 108% increase over 1990 emissions (to 2012) – currently on track
- Australia’s greenhouse gas intensity (per capita) at ~27 tonnes CO_2 – equiv. per capita is among the highest in the world
- Australia’s greenhouse gas intensity (per $ of GDP) is 0.7 kg CO_2

Importance of Coal to Australia

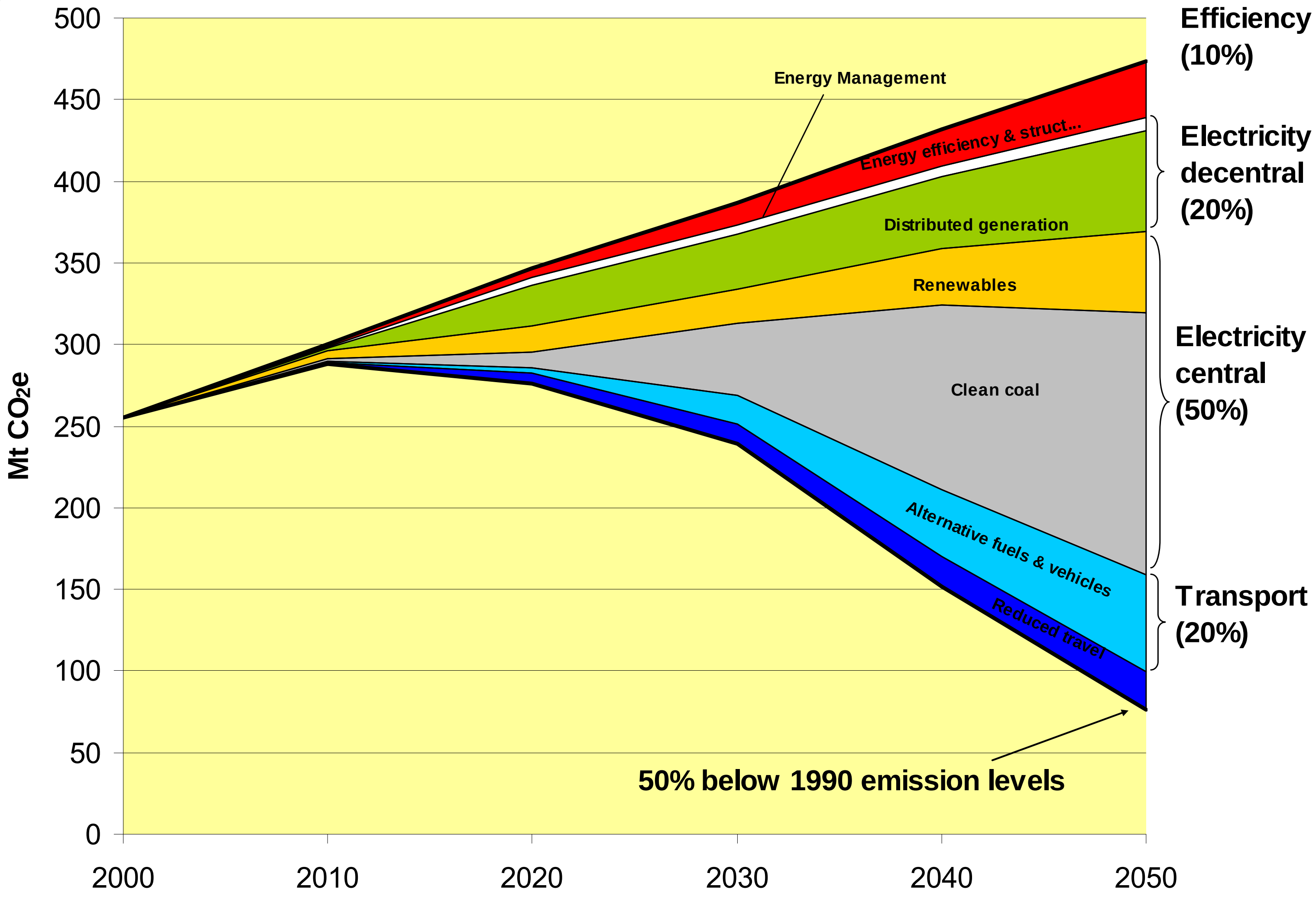
- Black coal is Australia's largest commodity export and is worth $25 billion (AUD) per annum

- Australia is the world's largest exporter of coal

- Electricity generation accounts for ~35% of Australia's net GHG emissions

- Australia's electricity derives mainly from coal (57% black coal, 30% brown coal)

Emission reduction pathway for Australia



Source: Energy Futures, Paul Graham, CSIRO

Australian Research Organisations in CCT

- Cooperative Research Centre for Coal in Sustainable Development (CCSD)
- Centre for Low Emission Technologies (cLET)
- Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC)
- Australian Coal Association Research Program (ACARP)
- Energy Transformed Flagship of the Commonwealth Scientific and Industrial Research Organisation (ETF-CSIRO)

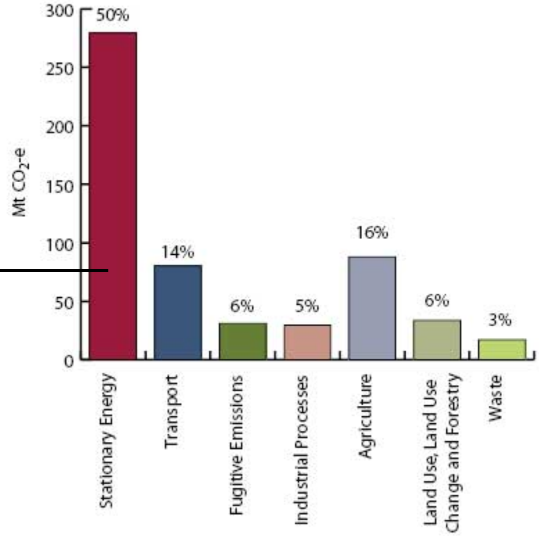
- *Until 2006 there was also a CRC for Clean Power from Lignite*

Clean Coal Technology Pilot and Demonstration Projects

1. IDGCC (HRL)
2. Monash Energy -Gasification/ GtL/ CSS
3. Stanwell IGCC/ CSS - *ZeroGen* Project
4. CS Energy Oxyfuel Project
5. International Power - Lignite Power Repowering, Drying and Capture
6. Gorgon
7. Zero Carbon - Fairview
8. CO2CRC Otway Basin Project
9. Kwinana Project
10. Latrobe Valley PCC Project
11. Moombah Carbon Storage
12. APP - Post Combustion Capture Project
13. APP - Enhanced Coal Bed Methane Project

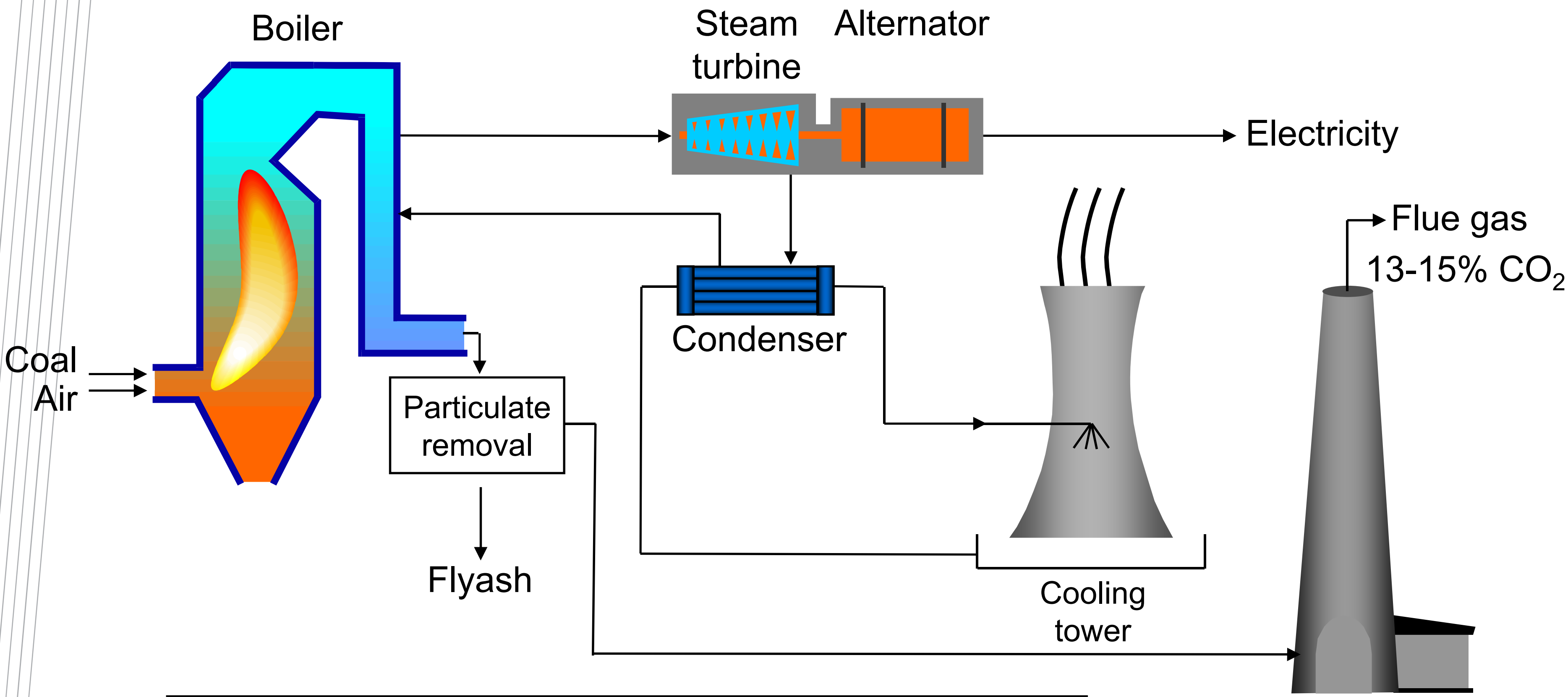
The Need for PCC in Australia

- Potential for substantial impact on very high GHG intensity of nations with a heavy reliance on coal for power generation
- Offers ultimate long-term objective of near-zero CO_2-emissions
- Addresses the risk of having major stranded generation assets (if a high cost is applied to carbon emissions)
- PCC potentially offers cost competitive route to low GHG emission electricity from coal for existing and new power stations



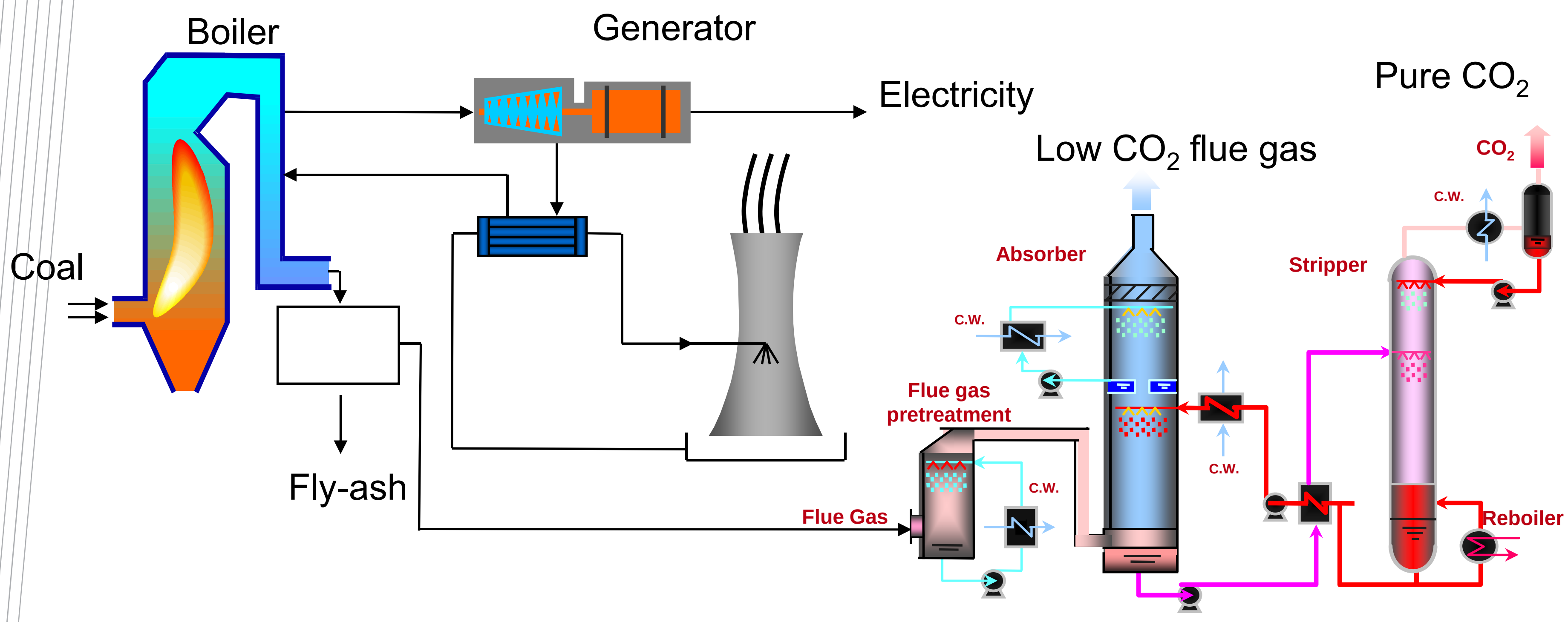
80% of energy from burning coal

PF Power Plant



Coal Type	Thermal Efficiency (%)	CO_2 Emissions (kg/MWh)
Black	36 - 41	1000 - 800
Brown	28 - 32	1300 - 1100

PF Power Plant with Post Combustion Capture



Thermal efficiency 28 - 33%
CO_2 emissions <100 kg/MWh

11th PCC network meeting, IEA GHG R&D programme, 20-21 May 2008, Vienna, Austria

National Research FLAGSHIPS CSIRO

PCC application in Australian coal fired power stations

- Generation capacity ~ 28 GW
- Electricity production 170 TWH/a
- Average generation efficiency
  - Black coal: 35.6% - 0.9 tonne CO_2/MWh
  - Brown coal: 25.7% - 1.3 tonne CO_2/MWh
- CO_2-emissions ~ 170 Mtonne CO_2/a from ~ 60 flue gas streams
- SO_2 levels:
  - Black coal: 200 - 600 ppm
  - Brown coal: 100 - 300 ppm
- NO_x levels:
  - Black coal: 300-700 ppm
  - Brown coal: 100-200 ppm
- Flue gas temperature
  - Black coal: 120 ^oC
  - Brown coal: 180 ^oC
- Cooling water: 1.5-3.0 m^3/MWh

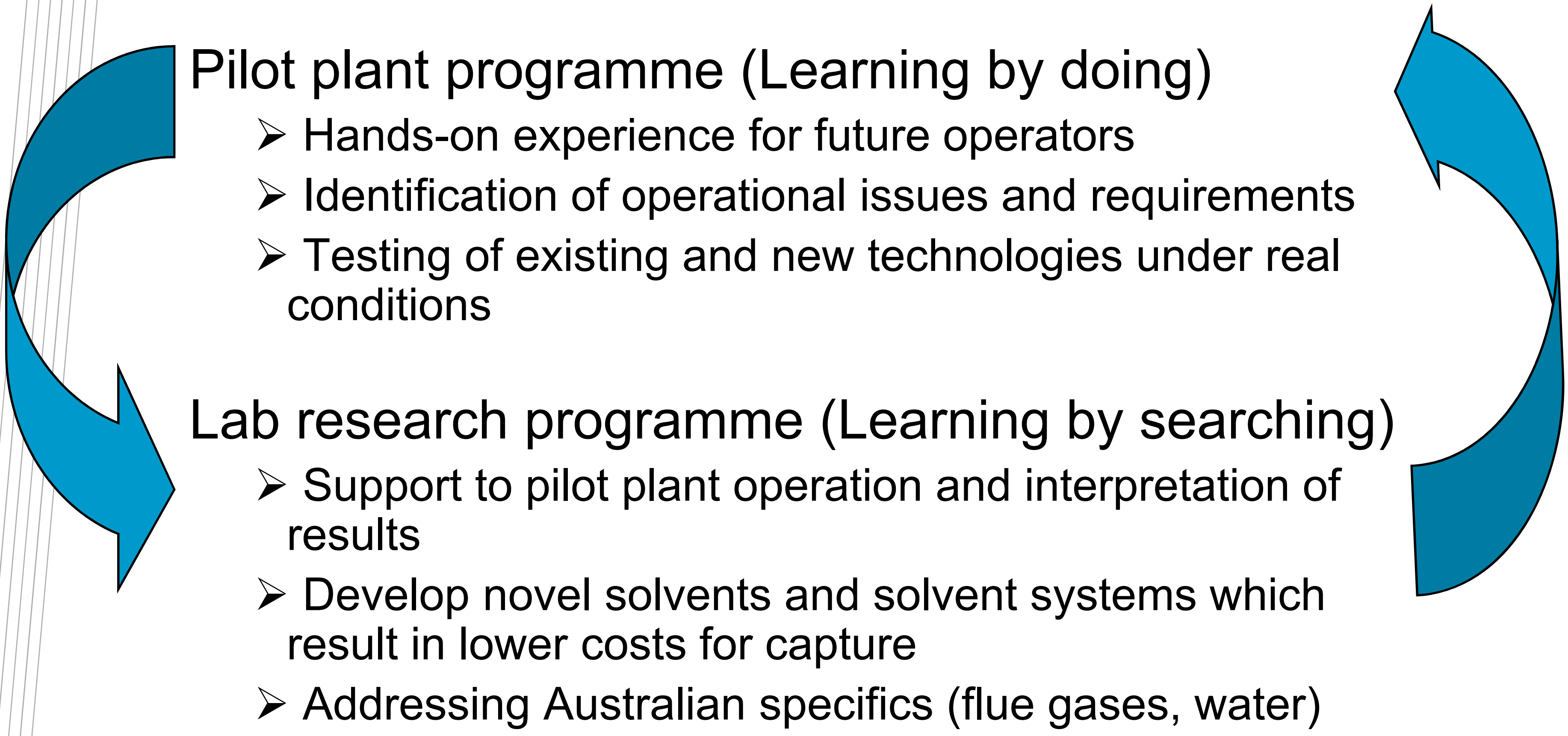
Data used from CCSD – technology assessment report 62

Known issues with PCC

- High cost: around $30/t CO_2 captured
- Electricity cost increase from $30/MWh to $50/MWh for an 85% reduction in GHG
- Loss of generation efficiency around 20-30% to capture 90% of CO_2
- Not demonstrated in integrated power plants scale
- Sensitive to O_2, SOx and other flue gas constituents
- Large increase in cooling water requirement

PCC programme at CSIRO

Integrated PCC R&D Programme



Pilot plant programme (Learning by doing)

- Hands-on experience for future operators
- Identification of operational issues and requirements
- Testing of existing and new technologies under real conditions

Lab research programme (Learning by searching)

- Support to pilot plant operation and interpretation of results
- Develop novel solvents and solvent systems which result in lower costs for capture
- Addressing Australian specifics (flue gases, water)

Confirmed Pilot Plants

Delta electricity

- APP support
- Munmorah Power Station
- Black coal
- Ammonia based
- No FGD/DeNox

CHINA HUANENG

- APP support
- Gaobeidian Power Station
- Black coal
- Amine based
- FGD/DeNox installed

LOY YANG power

Latrobe Valley Post Combustion Project

- ETIS support
- Loy Yang Power Station
- Lignite
- Amine based
- No FGD/DeNox

Pilot plant locations

Gaobeidian power station

Latrobe Valley Post-Combustion Capture Project

Victoria
The Place To Be

Energy Technology Innovation Strategy

LOY YANG power

National Research FLAGSHIPS

CSIRO

CO2CRC

International Power

Project activities and actors

- New solvent development research – CSIRO/CO2CRC
- Membrane research 10 tpa – CO2CRC
- Adsorbent research at 100 tpa – CO2CRC
- Solvent testing in 1000 tpa test facility – CSIRO/Loy Yang Power
- Solvent testing in 10000 tpa demonstration plant – CO2CRC/International Power Hazelwood
- Process and energy integration studies - all
- Technical and economical studies - all

Scope of pilot plant experiments at LYP

➢Technical and economical scale-up information about CO_2 capture plant based on operation on flue gas from brown coal combustion

➢This includes determining the following interrelationships:

- CO_2 capture energy consumption
- CO_2 capture efficiency
- Solvent CO_2 loading
- Solvent and flue gas flow rates
- Regeneration temperature and pressure
- Absorption temperature
- Solvent consumption and degradation rates
- Fouling and corrosion
- Effectiveness of the conditioning stage
- Reagent loss rate both to acid gas and to release with flue gas
- System water consumption

Loy Yang Power Station, Victoria

- The power station is capable of generating 2,200 megawatt.
- Loy Yang mine is the largest producing open cut brown coal mine in the southern hemisphere.
- Loy Yang Power supplies one third of Victoria's electrical energy needs.
- The Loy Yang open cut coal mine excavates approximately 30 million tonnes of brown coal each year.
- There are 168,000 million tonnes of accessible brown coal beneath the Latrobe Valley, or in excess of 1,300 years supply at current rates of usage.

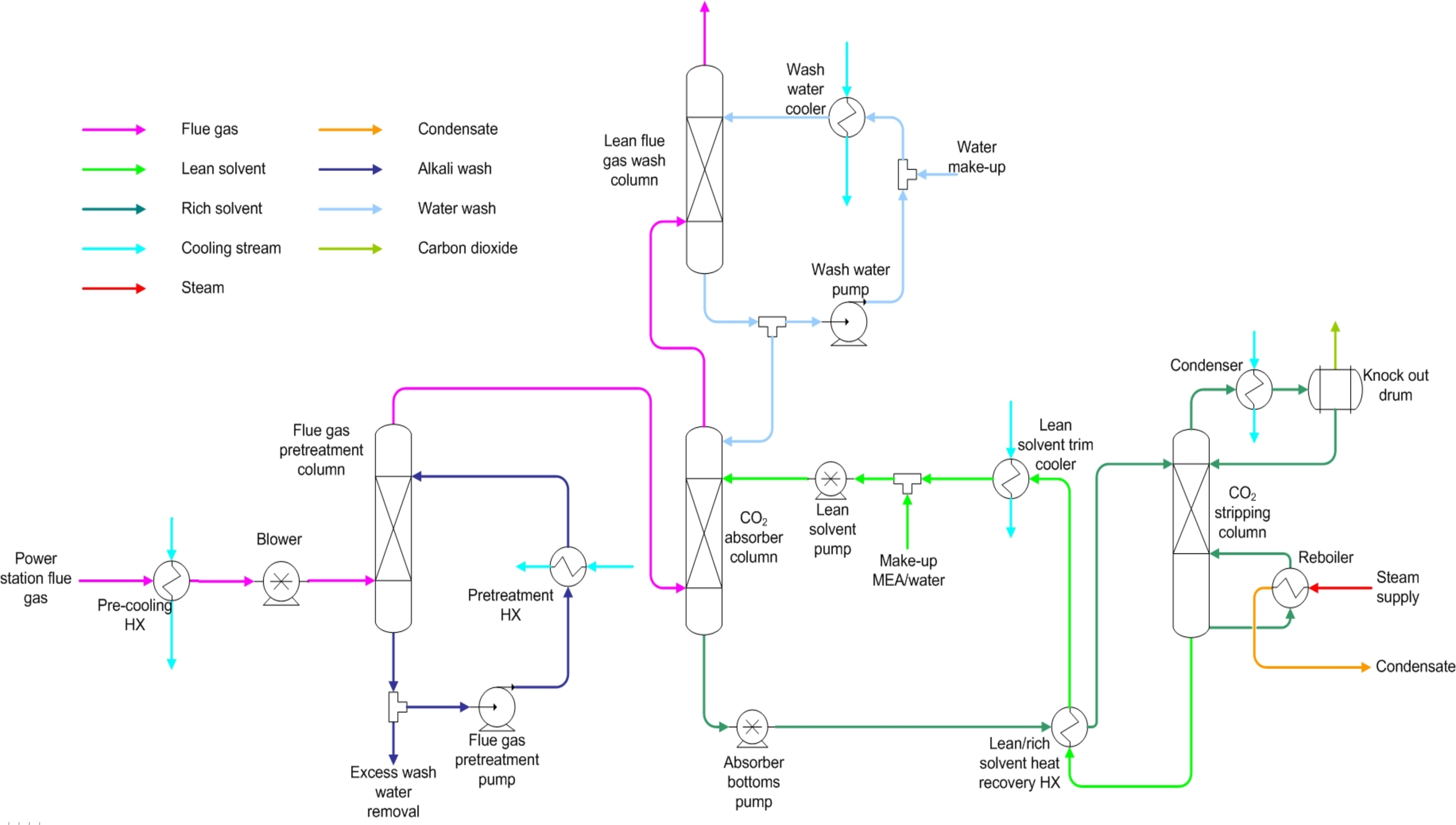
LYP Pilot plant design

- Use of two columns with a specified single column design CO_2 capacity of 100 kg/hr as a minimum (85% removal)
- Based on local flue gas composition (11% CO_2)
- Based on the use of MEA (30%)
- Operate with reboiler temperatures 100 - 120°C
- Operate with stripper pressures 1 - 2 bar
- Be able to determine thermal and electrical energy requirements of the pilot plant
- Be able to determine emissions to atmosphere and CO_2-product quality

Pilot plant design process

- Process modelling based on Winsim and Aspen Plus providing heat and mass balance -> basis for design
- Sizing and costing of major equipment both internally and by external contractors
- Frame/skid design
- Detailed design including piping
- Process and Instrumentation
- Control logic

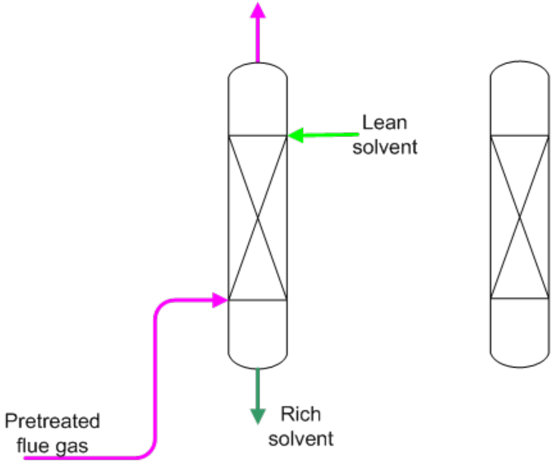
Simplified Pilot plant flow sheet



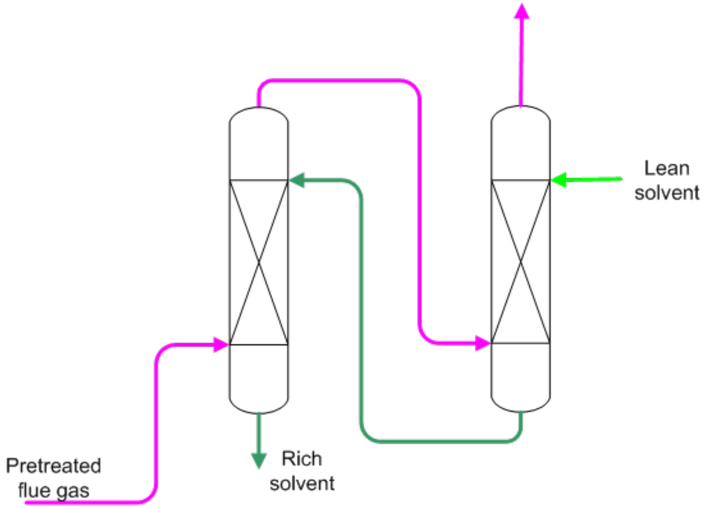
11th PCC network meeting, IEA GHG R&D programme, 20-21 May 2008, Vienna, Austria

National Research FLAGSHIPS CSIRO

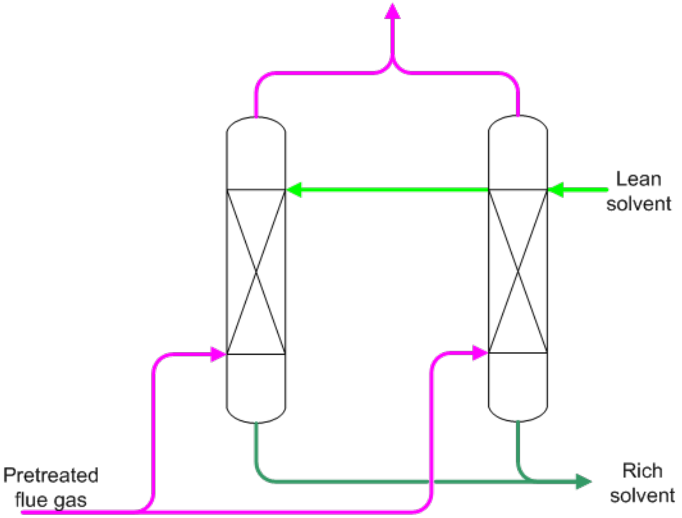
Two absorbers for added flexibility



Single column operation with other column on standby or changed out for new experiment



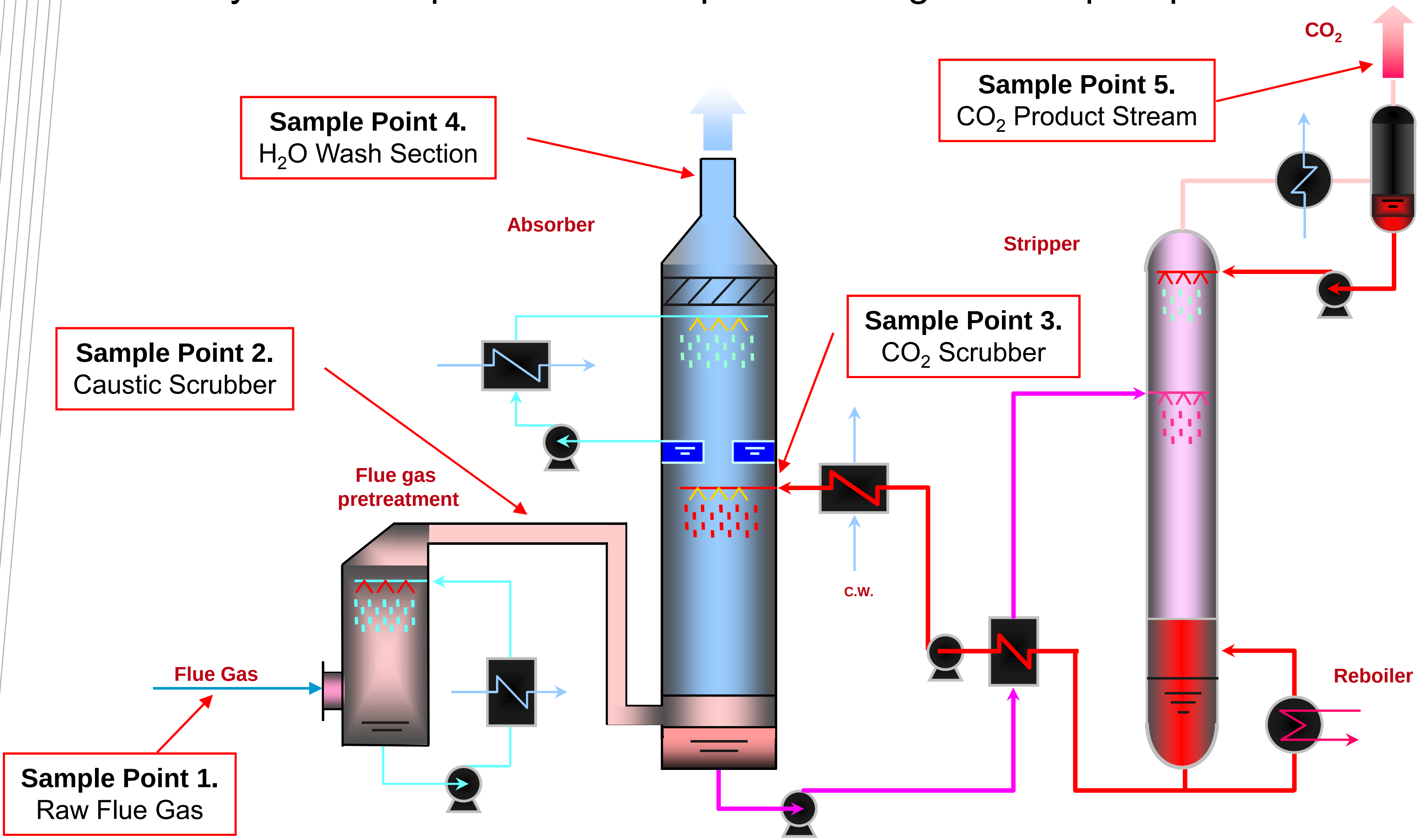
Series operation for higher packing heights



Parrallel operation for larger equivalent column diameter

Pilot Plant Gas Analysis

Gas analysis will be performed at 5 points throughout the pilot plants.



CO_2

Sample Point 5.
CO_2 Product Stream

Sample Point 4.
H_2O Wash Section

Absorber

Stripper

Sample Point 3.
CO_2 Scrubber

Sample Point 2.
Caustic Scrubber

Flue gas pretreatment

C.W.

Flue Gas

Reboiler

Sample Point 1.
Raw Flue Gas

Diagram adapted from MHI.

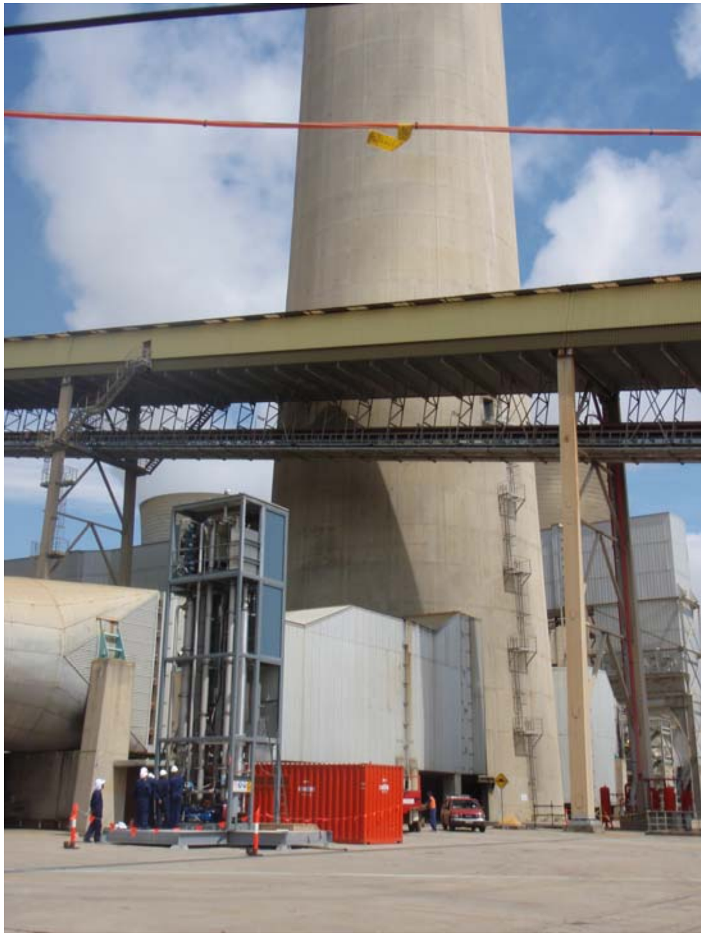
Loy Yang Pilot Plant Program

Collaboration Partners

- Loy Yang Power
- Victorian Government (Energy Technology Innovation Strategy - ETIS)

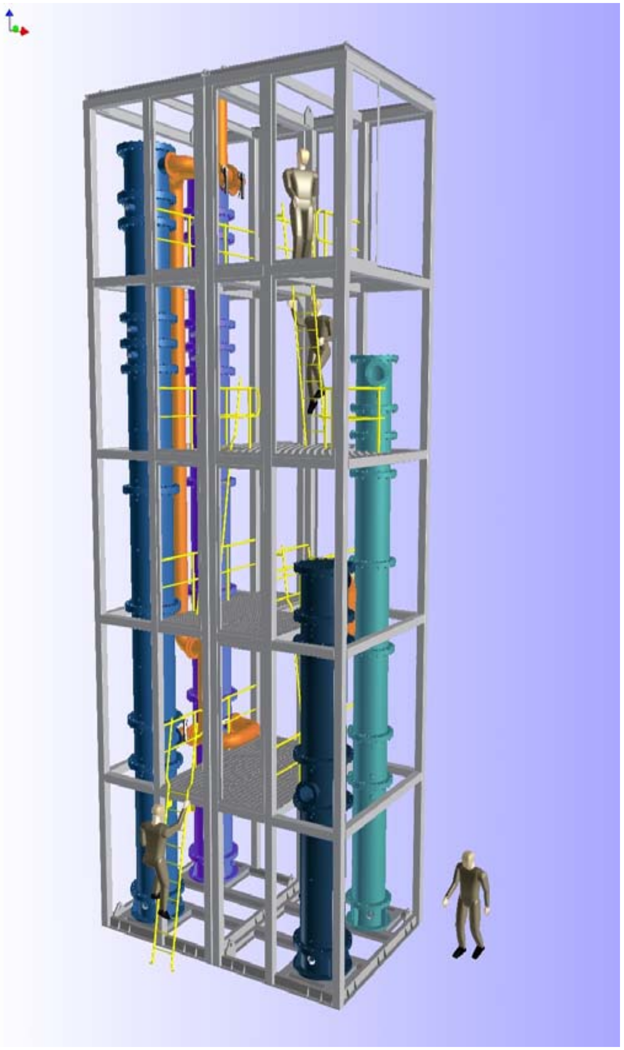
Project Milestones

- Establishment of pilot plant on site Jan 2008
- Official opening 29 April 2008
- Pilot plant operational - May 2008
- Experimental program – Jun 2008 – Dec 2009



Munmorah Pilot Plant

- Collaboration Partners
  - DELTA Electricity
  - Department of Resources, Energy, & Tourism (Asia Pacific Partnership program)
- Project Milestones
  - Detailed design complete – Feb 2008
  - Construction complete – June 2008
  - Commissioning and experimental program – July 2008 – July 2010



Australian Government
Department of Industry, Tourism and Resources

Delta electricity

Development Pathway for PCC

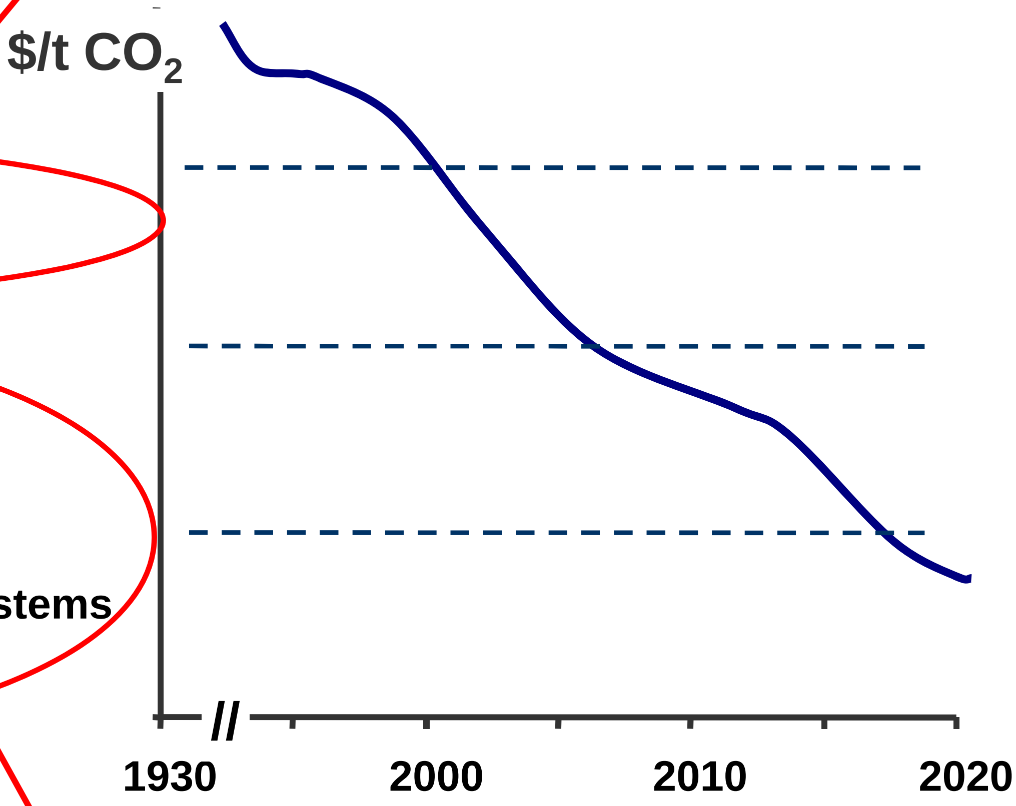
Current best technology

Generation I: **MEA (chemicals)**

Generation II: **Improved “MEA” (EOR, chemicals)**

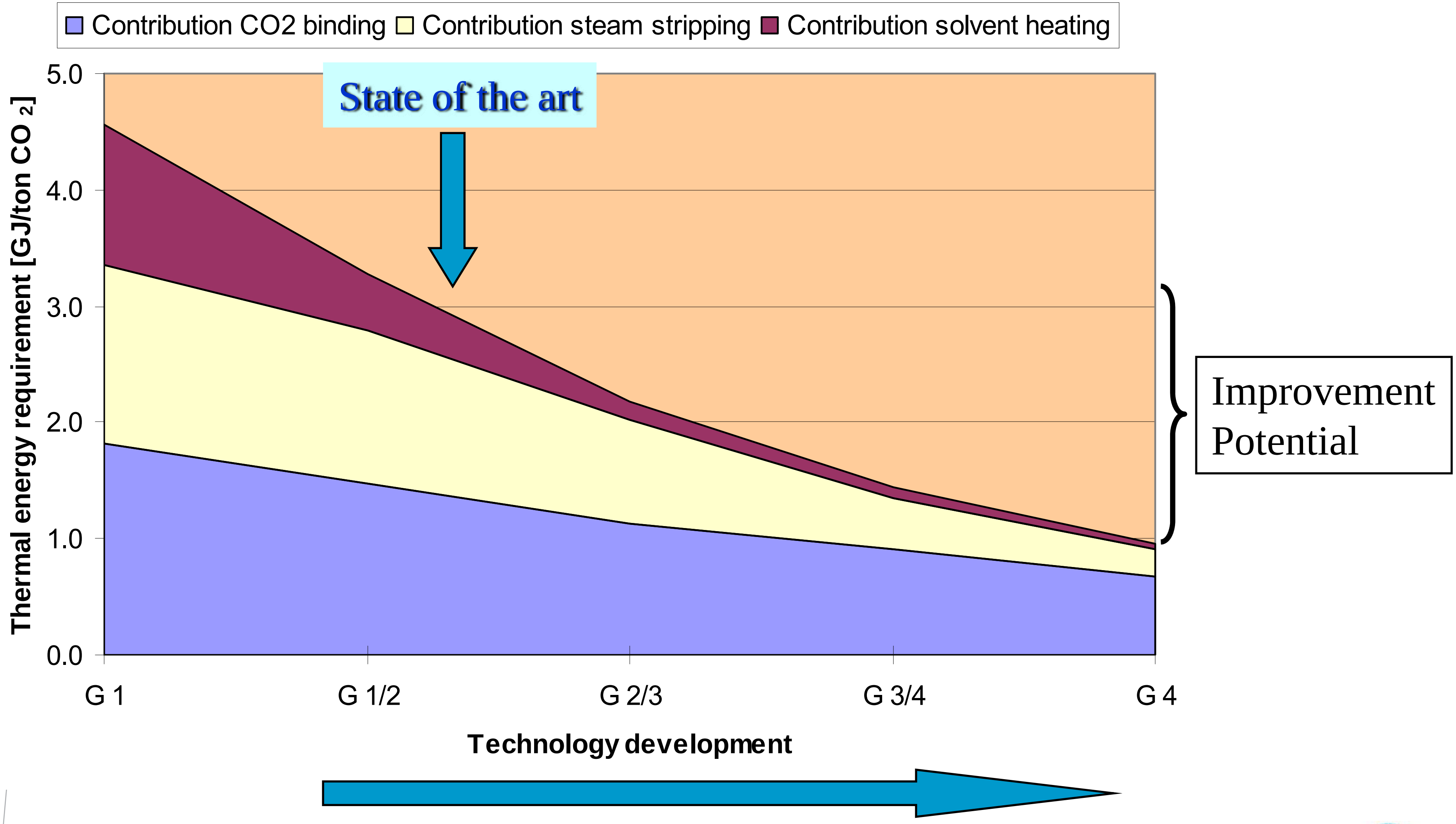
Generation III: **Novel solvents (PCC-CS)**

Generation IV: **Novel capture systems (PCC-CS)**

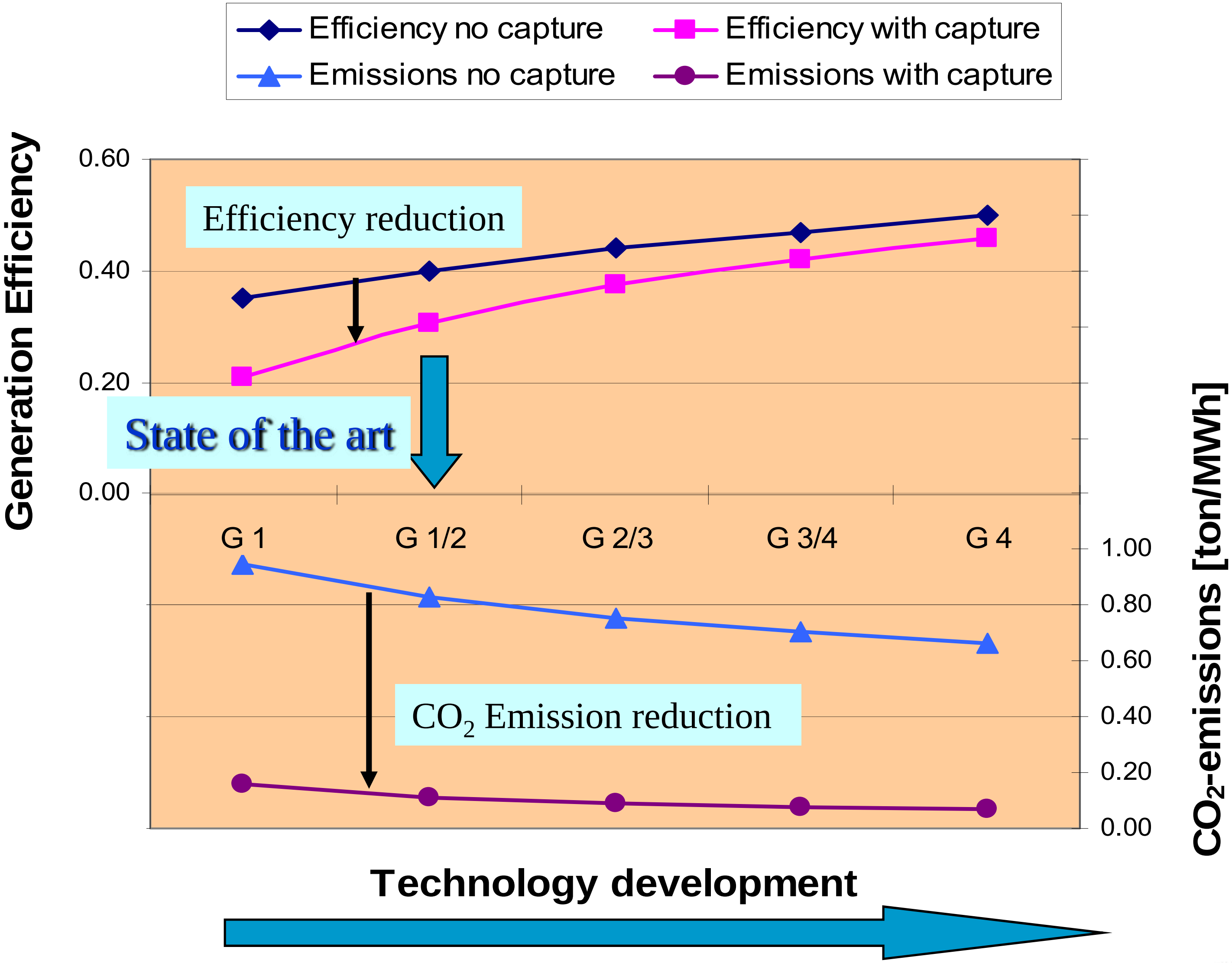


Focus of the lab research

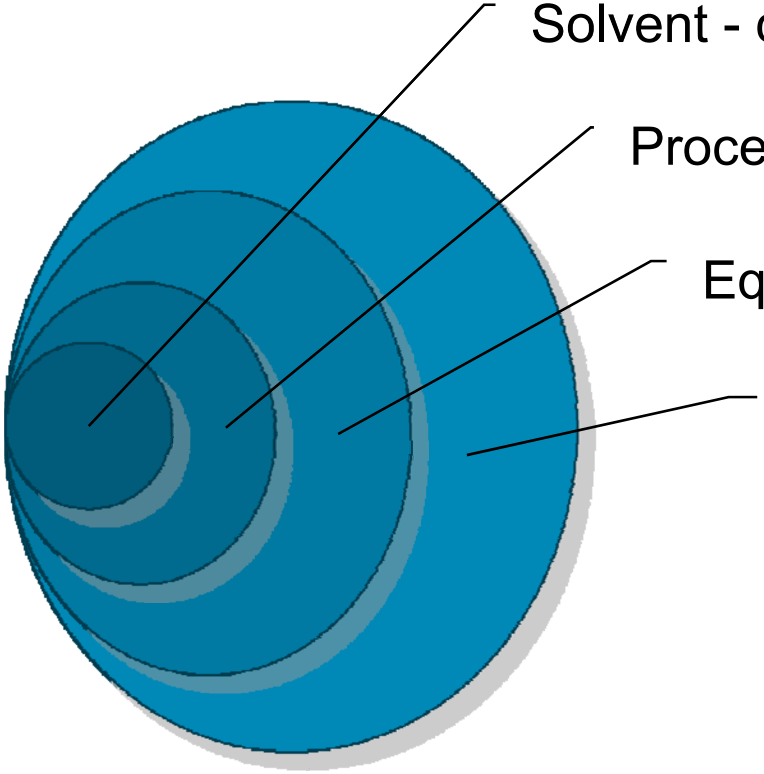
PCC Technology Development Scenario



Efficiency and CO_2 Emissions



Research: Solvent system development



Solvent - chemistry

Process design - flow sheet

Equipment - hardware

Integration - thermodynamics

A holistic approach is essential!

PCC Research programme overview

1. Solvent development focuses on new chemicals or chemical formulations for reversible binding of CO_2
2. Solvent process development involves the development of alternative processes, novel process flow sheets, inclusion of other separation processes such as membrane technology to improve the solvent process performance
3. Equipment development is particularly aimed at reducing the equipment sizes and the physical footprint of capture technology and hence reducing investment costs
4. Optimal power plant integration is required to have minimal impact of the capture process on the power plant, including the usual of solar energy

Solvent development programme

Over 100 amines

Commercially available amines

Amine synthesis

Screening of CO_2 absorption capacity and initial rate

Modelling of CO_2-amine interactions

Identification of outstanding performers

Absorption kinetics (wetted-wall)

Vapour-liquid equilibria and kinetics (stirred batch reactor)

Solution phase reactions and speciation (NMR and FTIR)

Reaction enthalpies (calorimeter)

Identification of outstanding performers

Laboratory pilot-plant testing

Corrosion

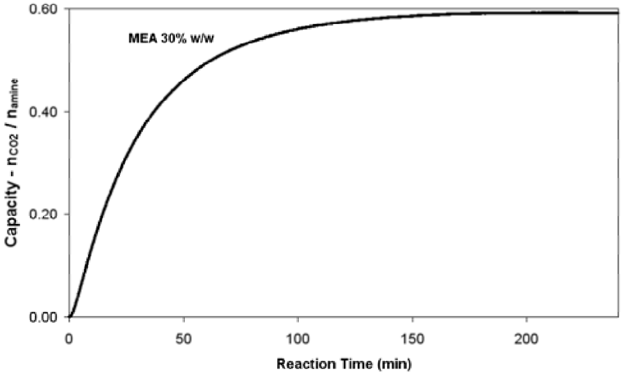
Oxidation

Impact of SO_x and NO_x

Pilot-plant testing

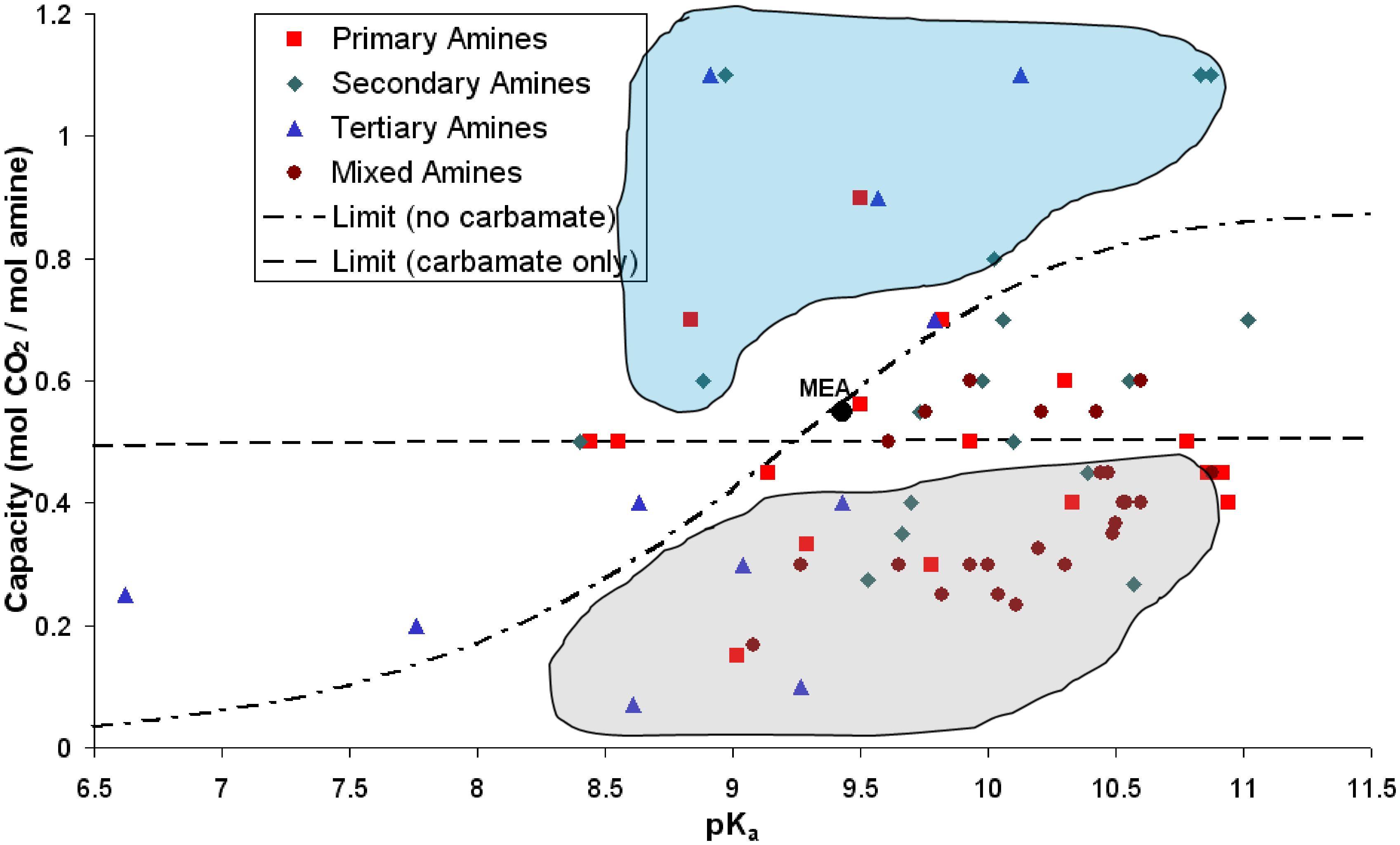
Screening of Capacity and Initial Rate

Gravimetric method used to measure CO_2 absorption and initial absorption rate on µL scale



Traditional absorption method used on the mL scale

Modelling + Screening



G III-IV - R&D Directions

- Advanced amines
  - Formulated mixtures, multiple amine groups
- Non-aqueous solvents
  - Ionic liquids
- Phase change solvents
  - Slurries, emulsions
- Modified process concepts
  - Intervolving, heat exchange integration in stripper, integration of compression, split flow
- Novel process components
  - Membrane contactors, heat pumps
- Robust solvents
  - Ammonia, carbonates
- Biomimetic approaches
  - Enzymes for solvent process improvements

CSIRO Energy Technology
Paul H.M. Feron
PCC Science Leader

Phone: +61 (0)2 4960 6022
Email: paul.feron@csiro.au
Web: www.csiro.au

www.csiro.au

Thank you

Contact Us

Phone: 1300 363 400 **or** +61 3 9545 2176
Email: Enquiries@csiro.au **Web:** www.csiro.au

National Research
FLAGSHIPS

CSIRO

Results from CASTOR project

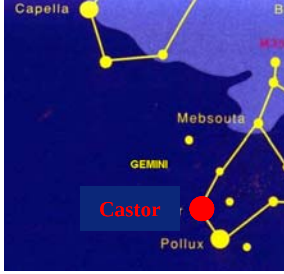
International Post-Combustion CO2 Capture Network
Vienna, 2008.05.20&21

TNO | Knowledge for business

Jan Hopman

Energy/CO_2
TNO Science & Industry

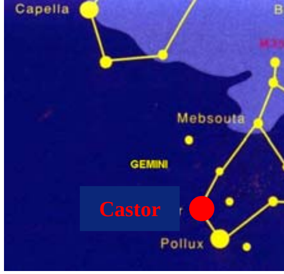
E: jan.hopman@tno.nl
T: +31 15 269 2196



CASTOR-SP2 objectives (2004)

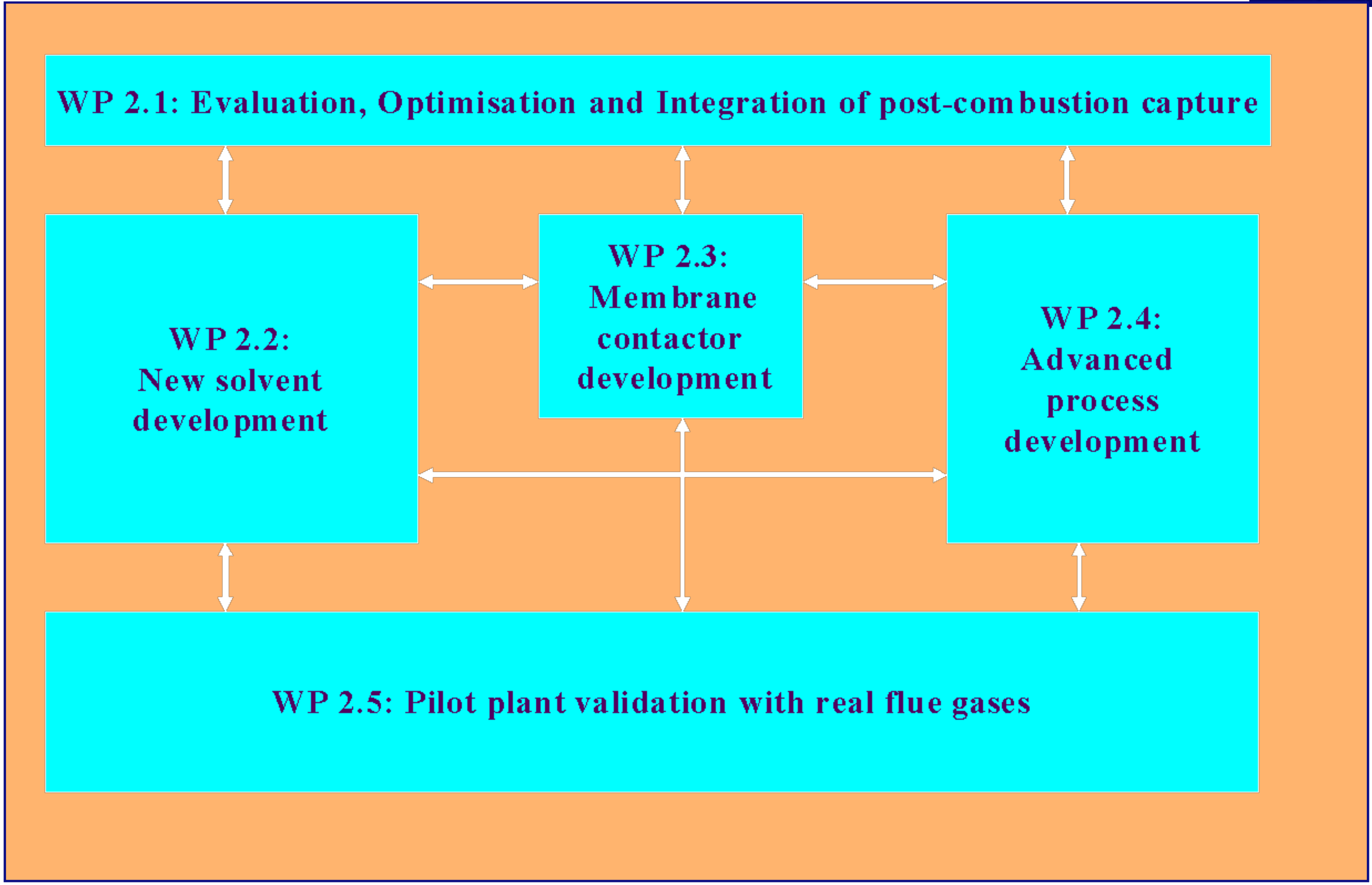
- Development of absorption liquids, with a thermal energy consumption of **2 GJ/tonne CO_2** at 90% recovery rates (4 GJ/tonne CO_2 with reference process)
- Resulting costs per tonne CO_2 avoided not higher than **20 to 30 €/tonne CO_2**, depending on the type of fuel (40 to 50 €/tonne CO_2 with reference process)
- **European pilot plant** tests showing the reliability and efficiency of the post-combustion capture process

CASTOR-SP2 Members



- Knowledge
  - IFP
  - NTNU
  - SINTEF
  - TNO
  - USTUTT
- Industrial
  - Alstom-Power
  - BASF
  - DONG Energy
  - Doosan-Babcock
  - Electrabel
  - EON-Engineering (D,UK)
  - Gaz de France
  - PPC
  - RWE
  - SIEMENS
  - StatoilHydro
  - Vattenfall

CASTOR-SP2: work-packages



WP 2.1: Evaluation, Optimisation and Integration of post-combustion capture

WP 2.2: New solvent development

WP 2.3: Membrane contactor development

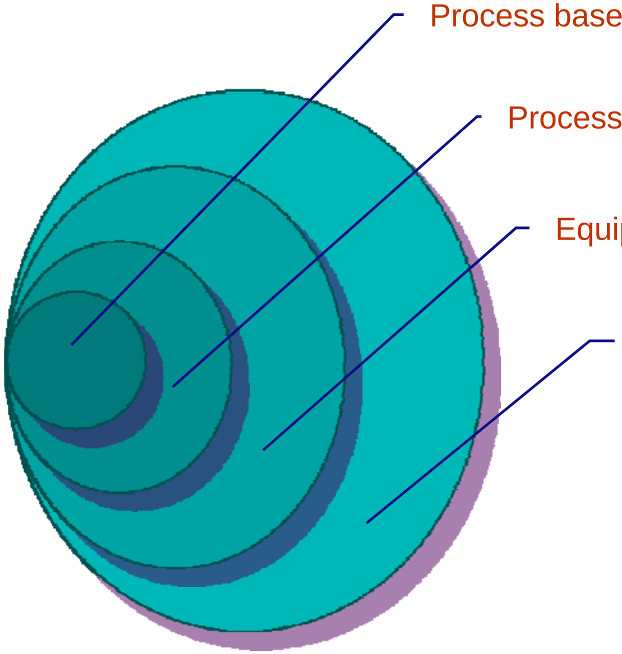
WP 2.4: Advanced process development

WP 2.5: Pilot plant validation with real flue gases

WP2.1: Base cases & Integration

- Integration Carbon Capture in Power Plants for following base cases:
  1. 393 MWe CCGT (Siemens)
  2. 600 MWe bituminous (Doosan Babcock)
  3. 1000 MWe lignite (RWE/Alstom)
  4. 380 MWe lignite (PPC)

- Economic models for each base case



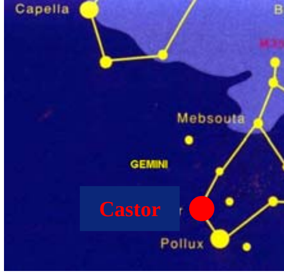
Process base case definition

Process modelling – flow sheeting tools

Equipment design and process integration

Economic evaluation and analysis

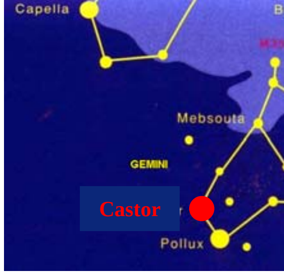
WP2.1: Base cases & Integration



Conclusions:

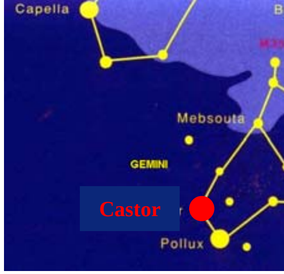
- A **techno-economical model** has been developed, which enables process analysis, optimization and integration.
- The **optimum flue gas CO_2 recovery** from coal fired power station lies in the range 80% - 95%.
- **Process integration and heat recovery** results in 15-20% heat recovery, which could save 0.4-1.6 percentage points from the overall efficiency penalty using MEA.
- Using improved **CASTOR2 solvent** results in extra 1.2-2.1 percentage points savings.

WP2.2: New solvents objectives



- To make a **preliminary selection** of suitable solvents as alternatives to the state-of-the-art monoethanolamine solutions
- To **characterise** selected solvent alternatives to enable design studies and to assess potential to reduce CO2 capture costs
- To determine the **degradation** of selected solvents as a result of flue gas components
- To assess **corrosion rates** for selected solvents
- To define and **validate** mass transfer models and pressure drop models for the absorber and for the desorber, suitable for extrapolation purposes

WP2.2: New solvents



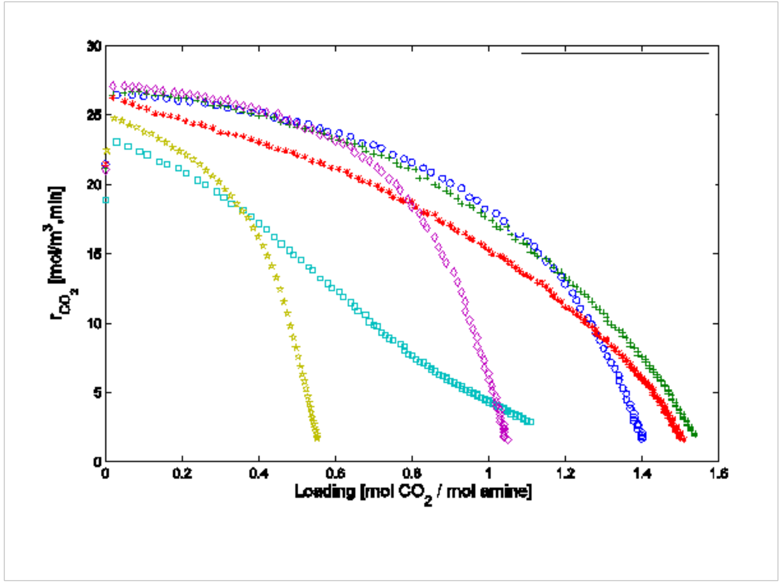
- 30 solvents investigated

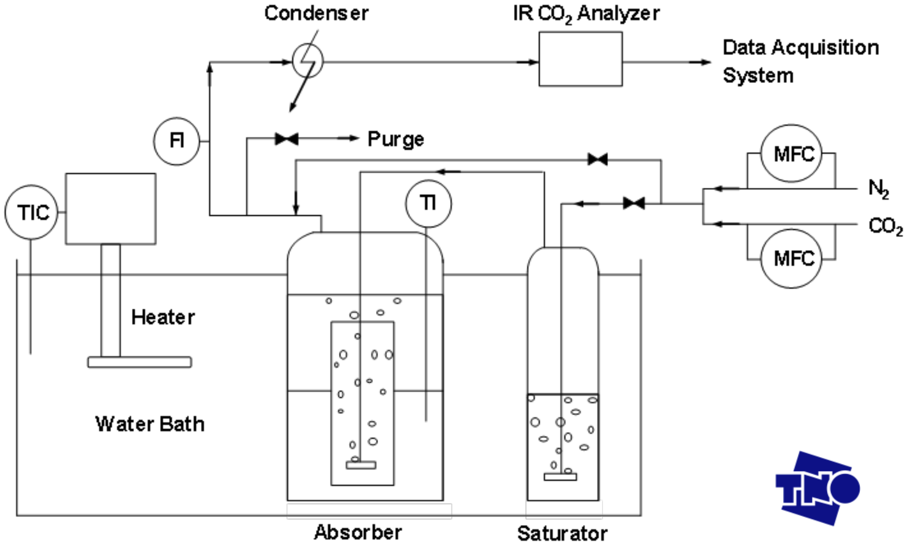
- Models developed and validated

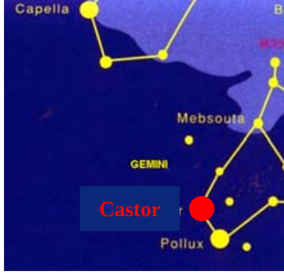
- Three solvents tested at CASTOR-pilotplant-Esbjerg:
  1. MEA
  2. CASTOR-1 solvent
  3. CASTOR-2 solvent

WP2.2 Solvent selection (SINTEF/NTNU)

- Background
  - Examination of literature and patents
  - Steric hindered primary and secondary amines
  - Polyamines
  - Partial loading of polyamines with acid (polyamine salts)
- 30 solvent were chosen for pre-selection
- Screening tests
- Equilibrium data at 40 and 120 C.







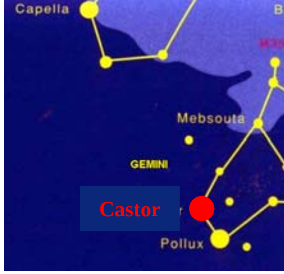
Solvent Characterisation

- Gas-liquid equilibrium
- Determination of suitable lean and rich loading
- Calculation of thermal energy requirements
- Calorimetric measurement of heat of absorption
- Reaction kinetics – estimation of absorber heights
- Viscosity, diffusivity, solubility
- Corrosiveness

Solvent test facilities

Miniplant (USTUTT)

Esbjerg Pilotplant (DONG)



WP2.3: Membranes

Objectives:

- Conceptual design of membrane absorber & desorber
- To determine membrane performances
- To validate performances under realistic conditions

Results:

- Membrane desorber
  - Conceptual design
  - Lab tests
- Membrane absorber
  - Flue gas exposure test with 3 membranes
  - Flue gas test with hollow fiber membrane module

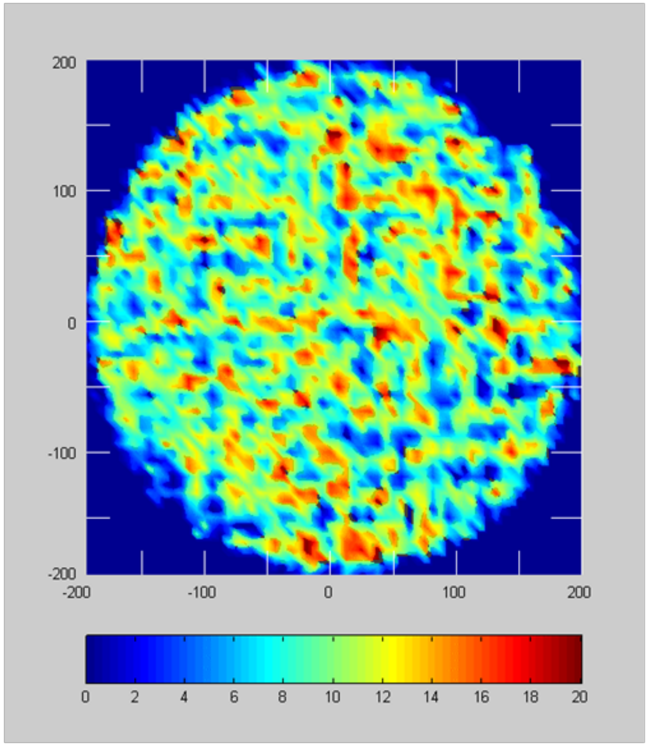
WP2.3: Membranes

- Three membrane types developed and tested:
  - Transversal flow module
  - Flat membrane module
  - Fibre module

- Practical data generated:
  - Filter recommended

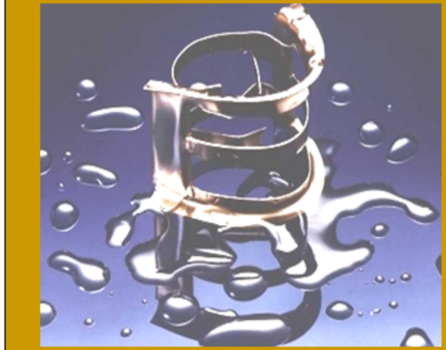
WP2.4: Advanced processes

- Process optimization of the absorption / desorption loop (Gaz de France, IFP)
- Packing material characterization (IFP)
  - Two packings fully characterized (IMTP50 & ME252Y)
  - Hydrodynamic test on pilot plant (Esbjerg) equipped with IMTP50.

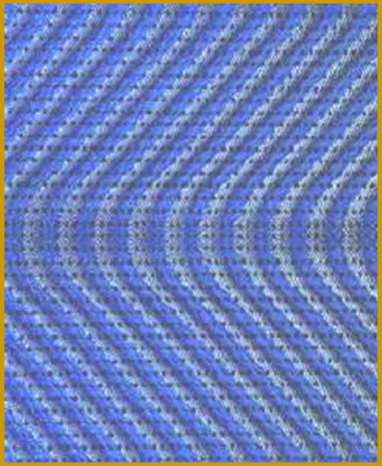


WP2.4: Advanced processes

- Process optimization of the absorption / desorption loop (Gaz de France, IFP)
- Packing material characterization (IFP)
  - Two packings fully characterized (IMTP50 & ME252Y)
  - Hydrodynamic test on pilot plant (Esbjerg) equipped with IMTP50.



New generation random packing
IMTP50 (Koch-Glitsch)

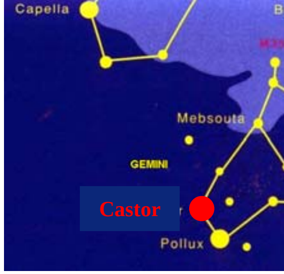


HC structured packing
Mellapak 252 Y (Sulzer)

WP2.5: Pilotplant tests

- CASTOR pilot-plant at DONG-Esbjerg
  - Presentation by DONG
- Four test runs:
  - MEA-1
  - MEA-2
  - CASTOR-1 solvent
  - CASTOR-2 solvent

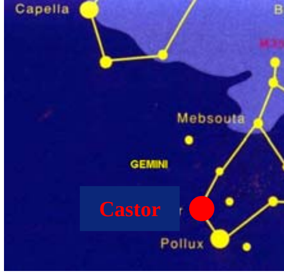
CASTOR-SP2: Conclusions - 1



1. Development of absorption liquids, with a thermal energy consumption of 2 GJ/tonne CO_2 at 90% recovery rates
   - Reference process: ~4GJ/tonne CO2
   - With CASTOR2 solvent: down to 3.5GJ/tonne CO2 (12%)
   - With integration: down to 3.2 GJ/tonne CO2 (20%)

2. Resulting costs per tonne CO_2 avoided not higher than 20 to 30 €/tonne CO_2, depending on the type of fuel
   - Reference process: 40-50 €/tonne CO2
   - With MEA process optimization: 35-37 €/tonne CO2 (2005 ref)

- First steps to the ambitious goals are made

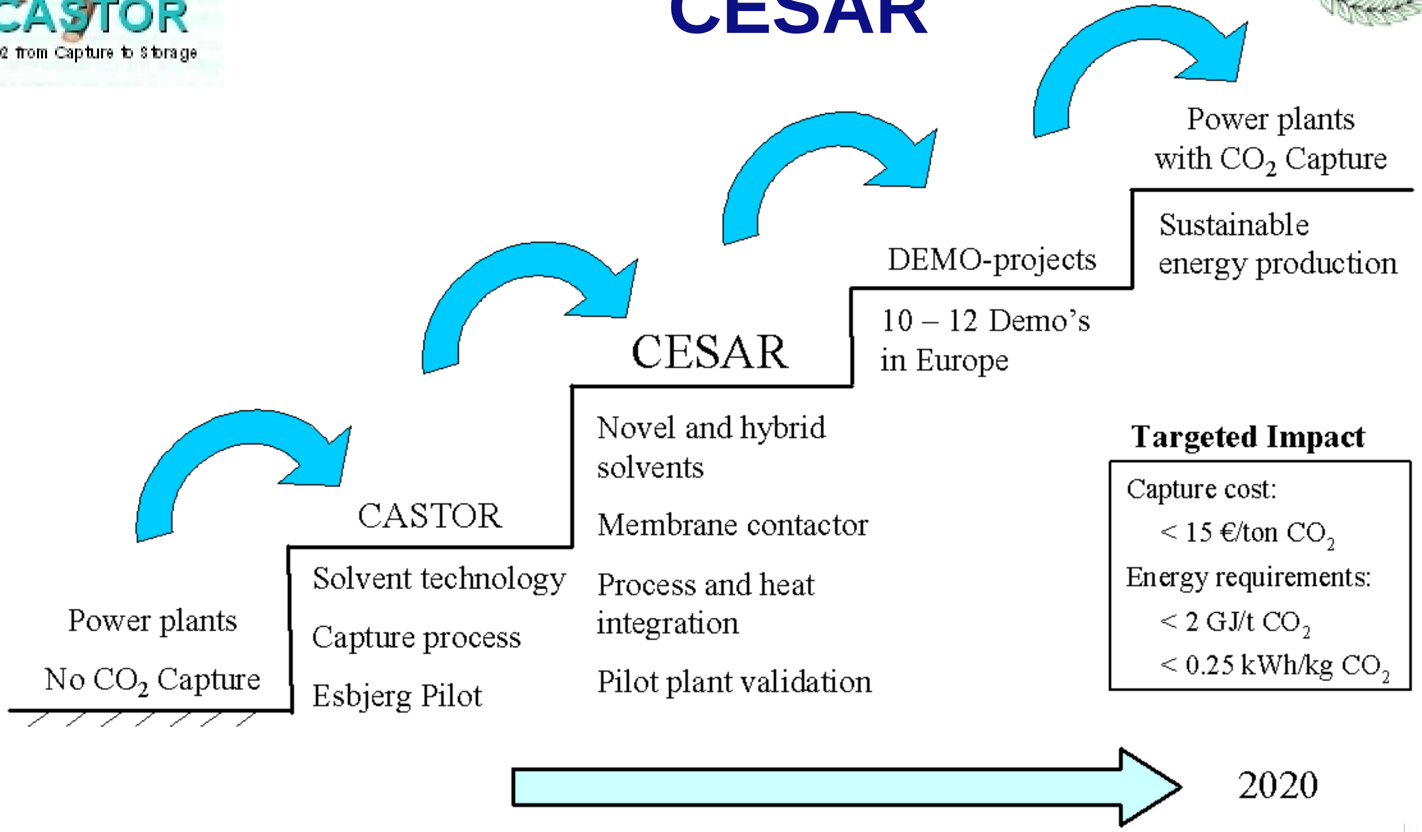


CASTOR-SP2: Conclusions - 2

3. European pilot plant tests showing the reliability and efficiency of the post-combustion capture process
    - Operational pilot plant
    - Validation procedures
    - Validation experience
    - Validation results
    - Environmental awareness
    - Queue of requests from industry

- CASTOR made validation basis for Post-Combustion-Capture development

CESAR



Power plants

No CO_2 Capture

CASTOR

Solvent technology

Capture process

Esbjerg Pilot

CESAR

Novel and hybrid solvents

Membrane contactor

Process and heat integration

Pilot plant validation

DEMO-projects

10 – 12 Demo's in Europe

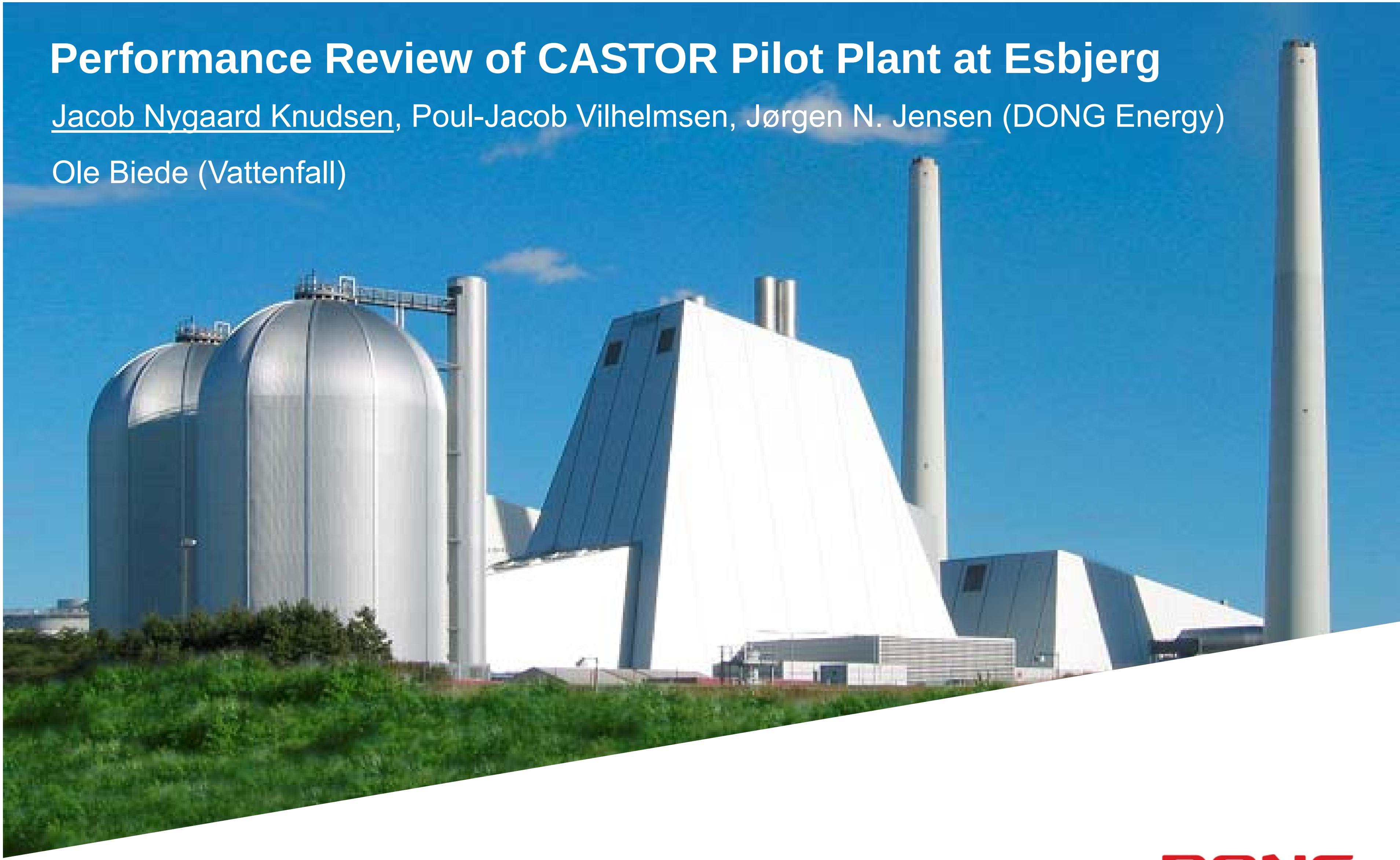
Power plants with CO_2 Capture

Sustainable energy production

2020

Targeted Impact

Capture cost:
< 15 €/ton CO_2
Energy requirements:
< 2 GJ/t CO_2
< 0.25 kWh/kg CO_2



Performance Review of CASTOR Pilot Plant at Esbjerg

Jacob Nygaard Knudsen, Poul-Jacob Vilhelmsen, Jørgen N. Jensen (DONG Energy)

Ole Biede (Vattenfall)

CASTOR Pilot Plant Objectives

The test facility shall

- Prove long-term stable operation on coal flue gas
- Act as a test facility for dedicated tests (e.g. test of novel solvents)

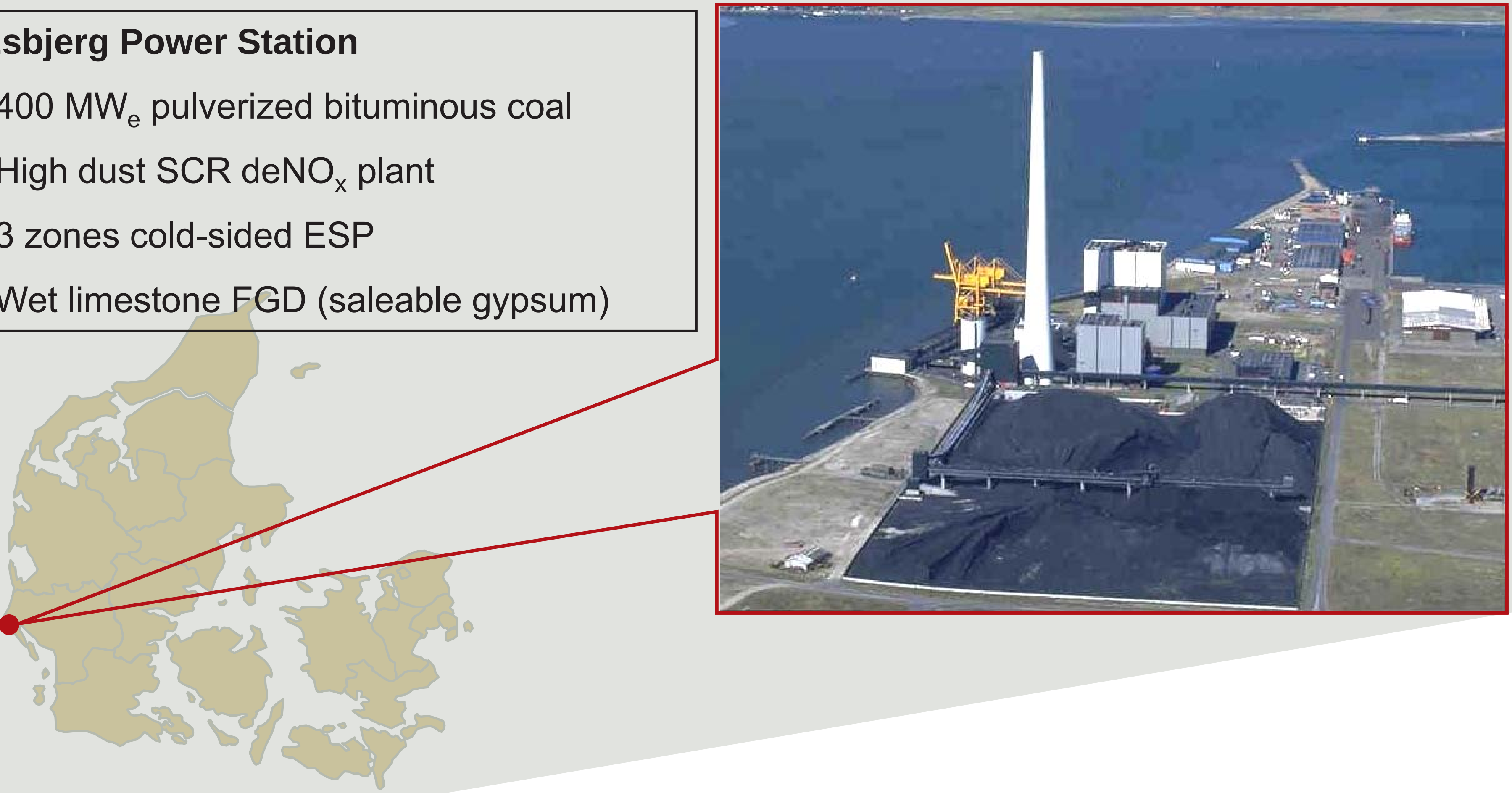
Provide information about

- Operation costs
- Maintenance costs
- Reliability
- Operation flexibility
- Environmental issues
- Engineering experience

Esbjerg Power Station (ESV)

Esbjerg Power Station

- 400 MW_e pulverized bituminous coal
- High dust SCR deNO_x plant
- 3 zones cold-sided ESP
- Wet limestone FGD (saleable gypsum)



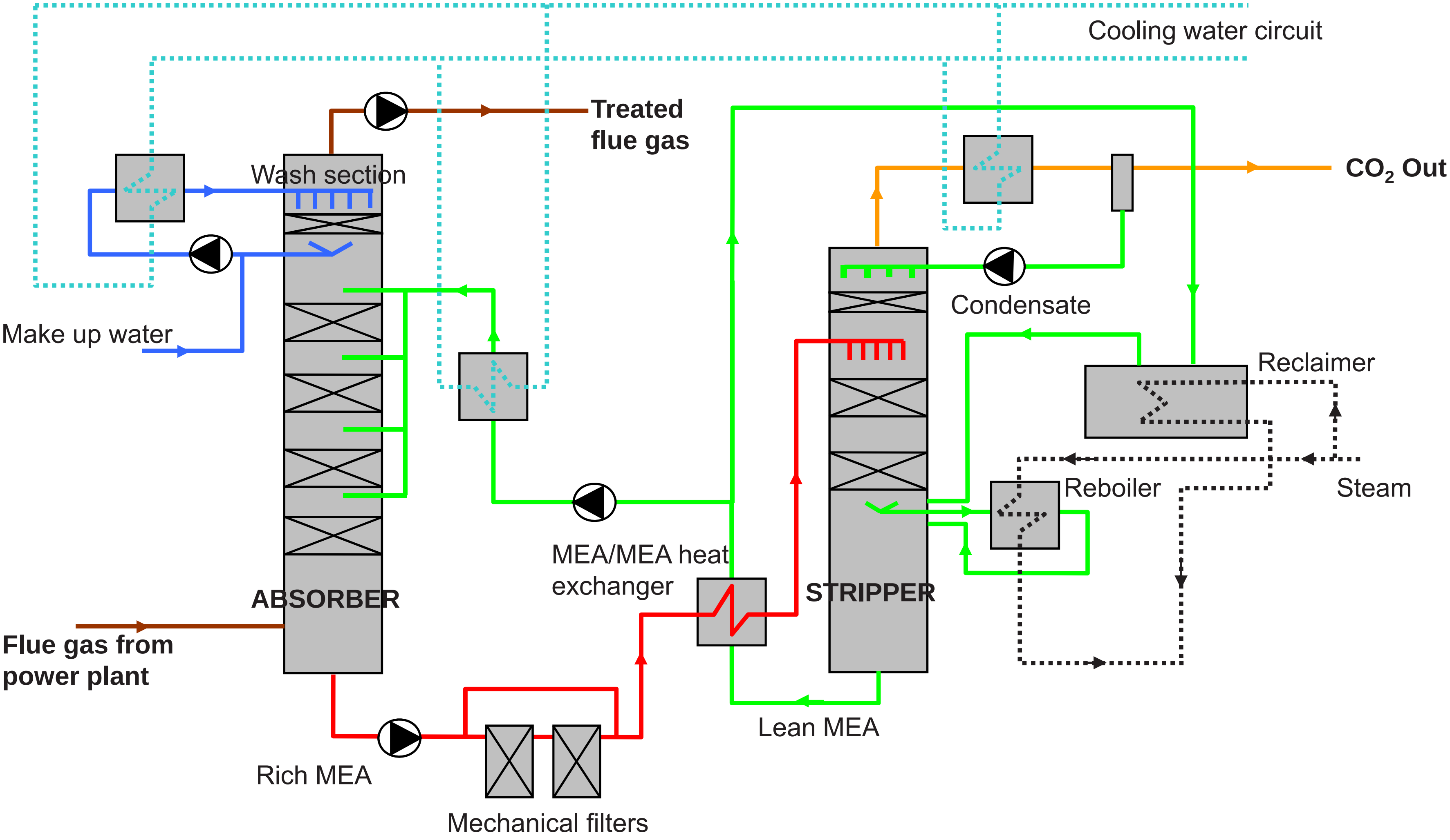
CASTOR Pilot Plant Specifications

- Pilot plant erected and commissioned during 2005
- Design of pilot plant based on a commercial CO_2 production plant (MEA)
- Pilot plant operates on a slip stream taken directly after the wet FGD
- Design flue gas conditions: ~47°C saturated, <10 ppm SO_2, <65 ppm NO_x, <10 mg/Nm^3 dust

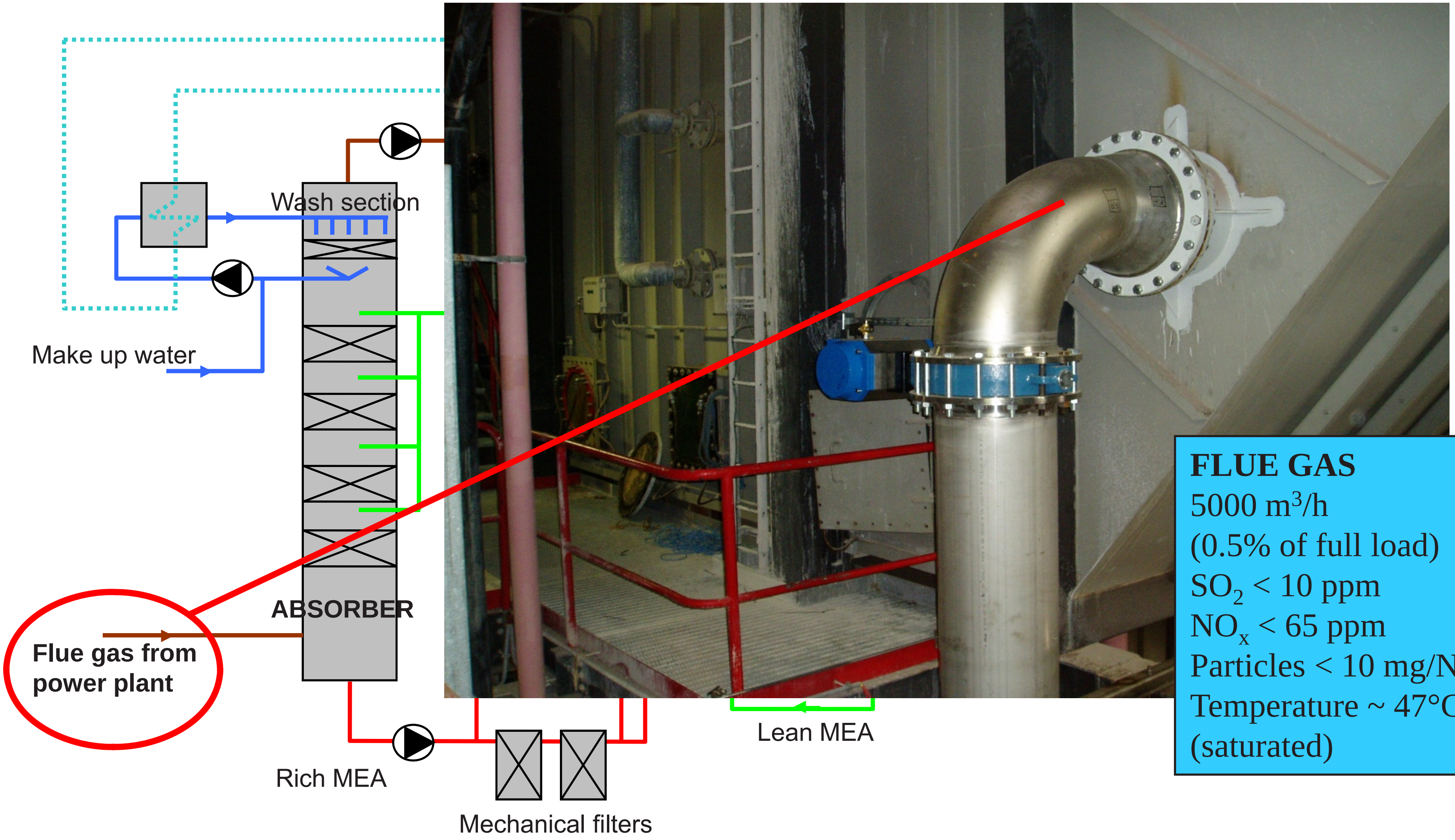
Key design parameters

Parameter	*Design value*
Flue gas capacity	5000 Nm^3/h
CO_2 production (at 12% CO_2)	1000 kg/h
Absorption degree	90%
Max solvent flow	40 m^3/h
Max stripper pressure	2 bar_g
Max steam pressure	3.5 bar_g

CASTOR Pilot Plant Flow Diagram

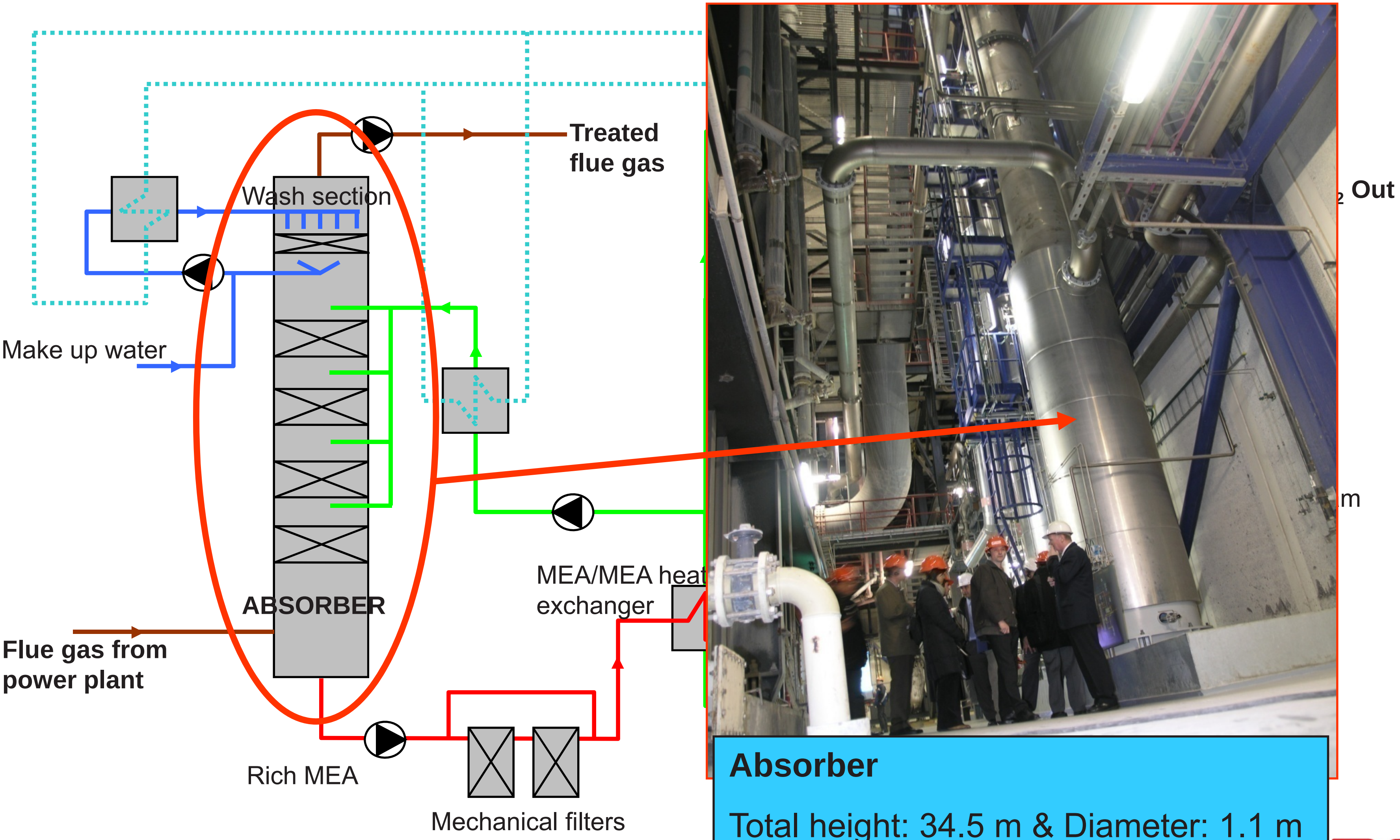


CASTOR Pilot Plant



FLUE GAS
5000 m^3/h
(0.5% of full load)
$SO_2 < 10$ ppm
$NO_x < 65$ ppm
Particles < 10 mg/Nm^3
Temperature ~ 47°C
(saturated)

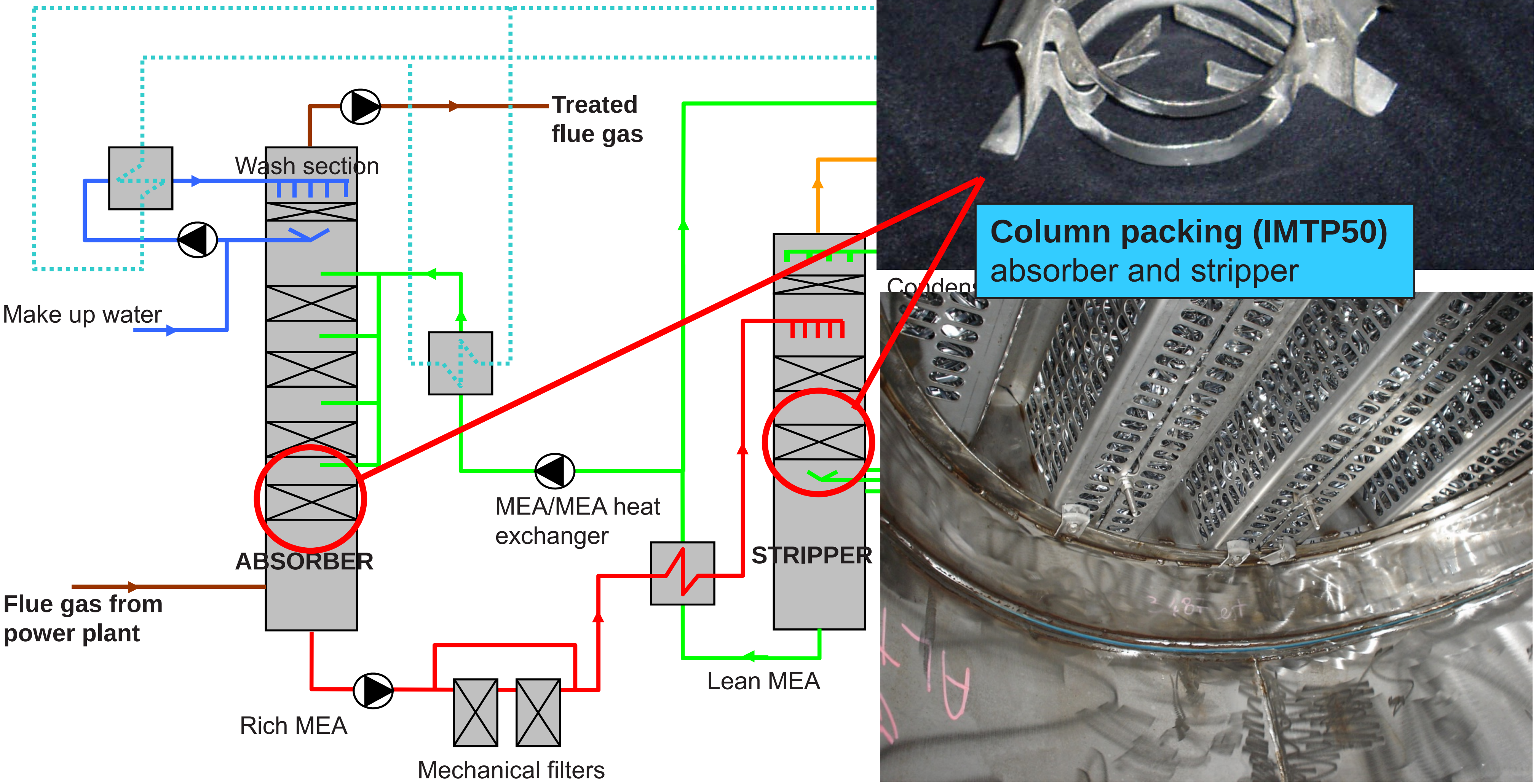
CASTOR Pilot Plant



Absorber

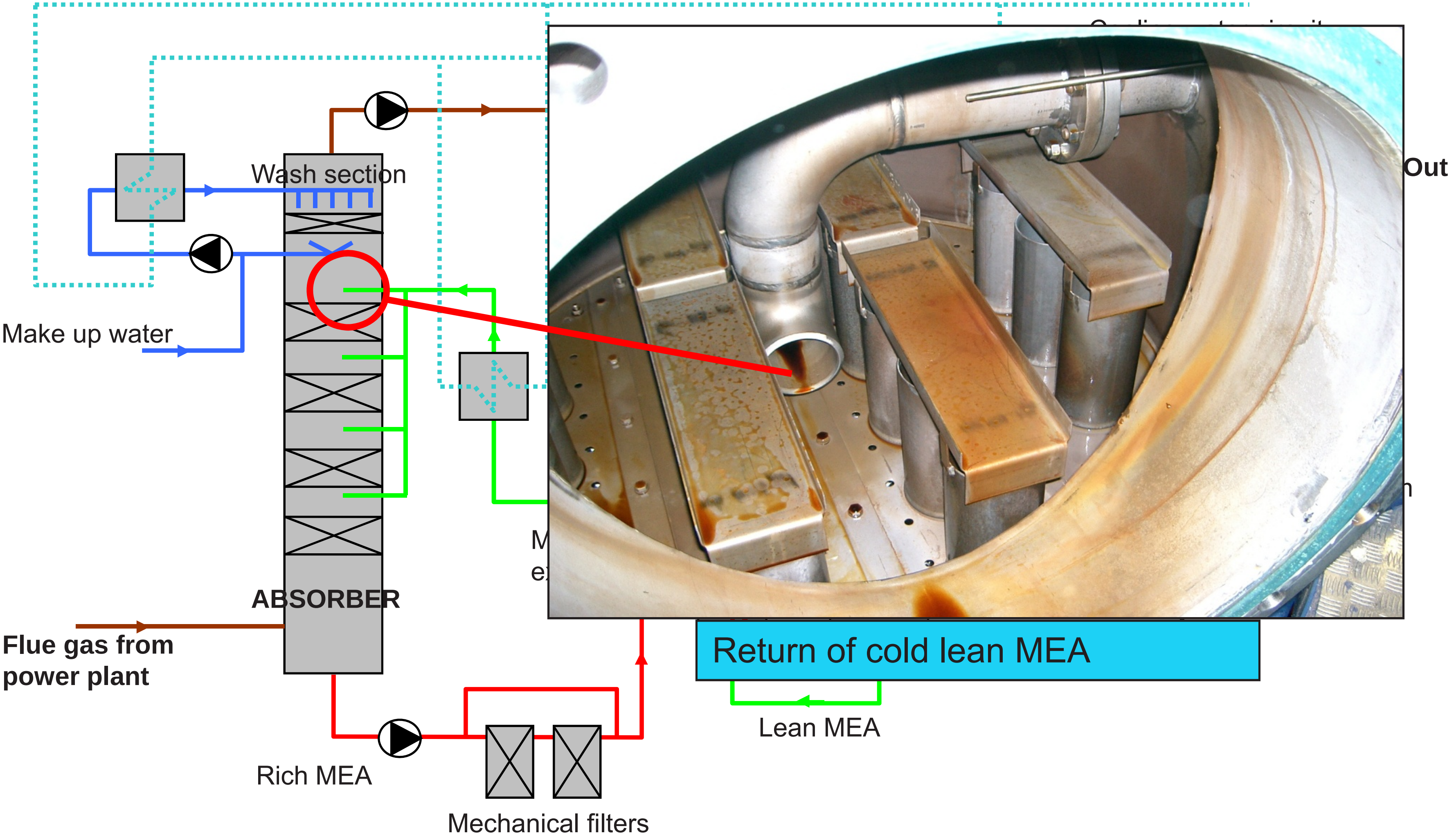
Total height: 34.5 m & Diameter: 1.1 m
Sump + 4 beds + 1 wash section

CASTOR Pilot Plant



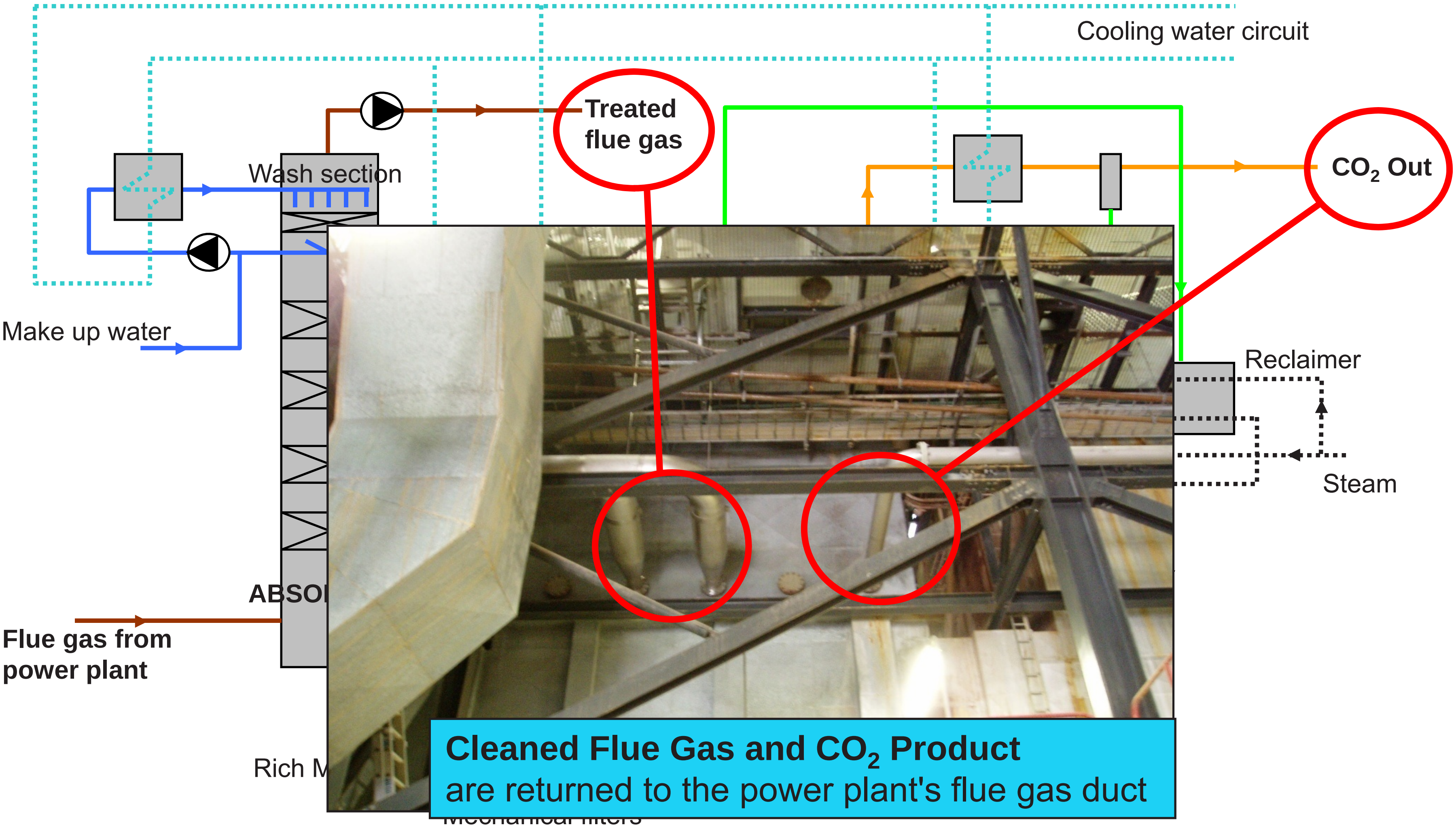
Column packing (IMTP50)
absorber and stripper

CASTOR Pilot Plant



Return of cold lean MEA

CASTOR Pilot Plant



Cleaned Flue Gas and CO$_2$ Product
are returned to the power plant's flue gas duct

CASTOR Pilot Plant Test Programme

Four test campaigns have been conducted in CASTOR:

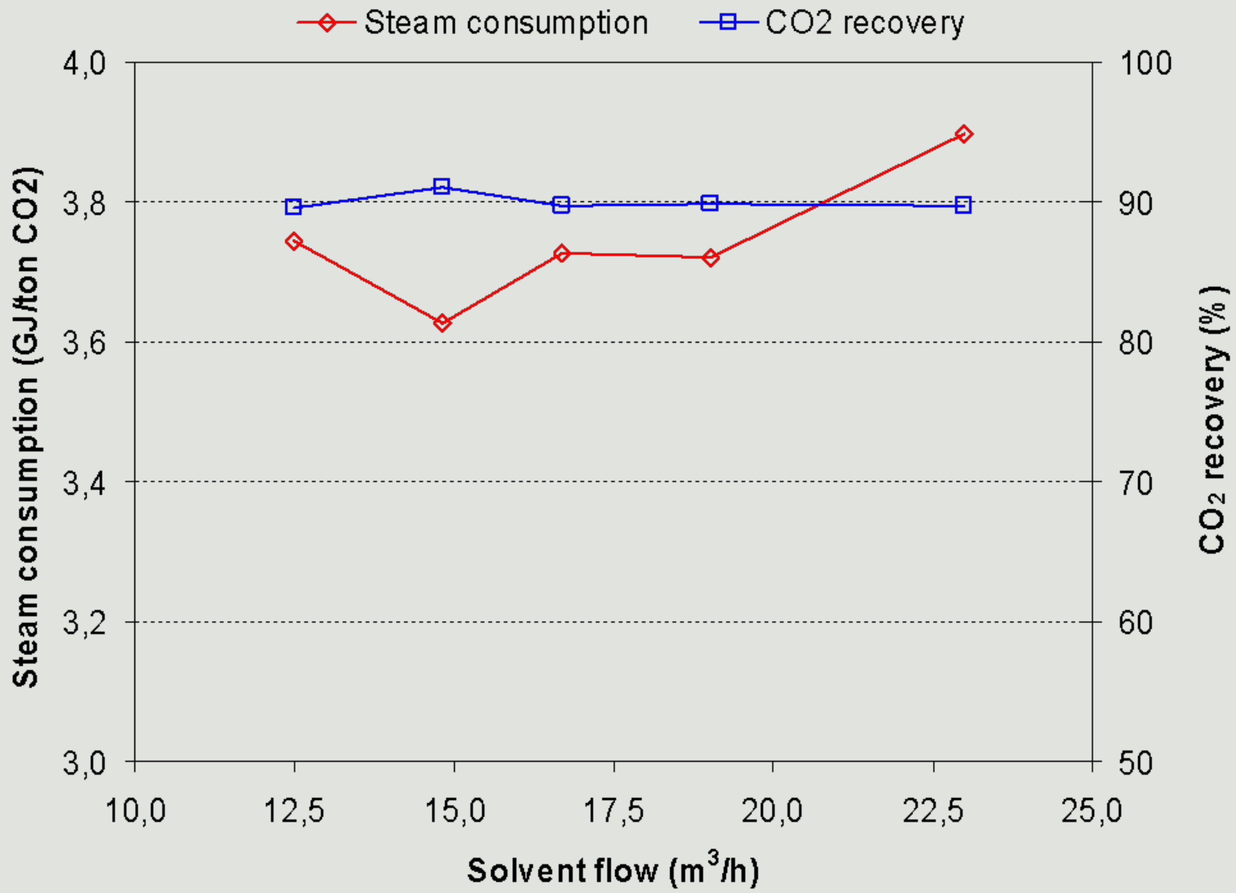
- 1000 hours using standard solvent ”30%-wt. MEA” (Jan. – Marts 2006)
- 1000 hours using standard solvent ”30%-wt. MEA” (Dec. 2006 – Feb. 2007)
- 1000 hours using novel solvent ”CASTOR 1” (April – June 2007)
- 1000 hours using novel solvent ”CASTOR 2” (Sep. – Dec. 2007)

Outline of Test Campaigns

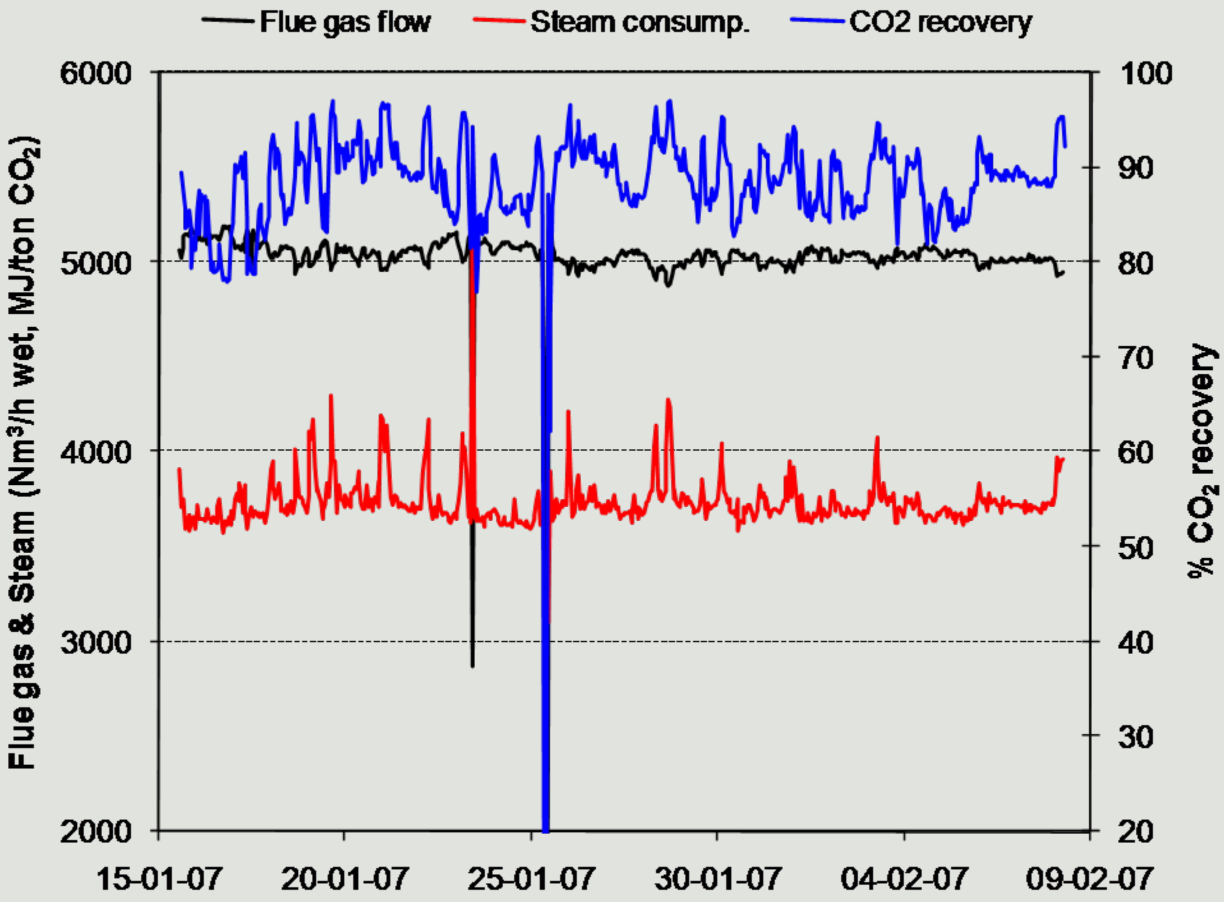
- **Test 1 – Parameter variation**
  - a) Optimisation of solvent flow rate (at 90% capture)
  - b) Variation of reboiler steam input at optimum solvent flow
  - c) Variation of stripper pressure (at 90% capture)
- **Test 2 – 500 hours of continuous operation**
  - Operation at ”optimised” conditions
  - Achieving 90% CO_2 capture (on average)
  - Quantification of solvent consumption and degradation
  - Characterisation of corrosion behaviour
- **Test 3 – Miscellaneous tests**
  - Absorber pressure drop measurements
  - Emission measurements
  - Etc.

2nd MEA Test: Solvent Flow Rate Optimisation

Specific steam consumption and CO_2 recovery at stripper pressure 0.85 bar_g and flue gas flow ≈5000 Nm^3/h



2nd MEA Test: 500 Hours of Continuous Operation

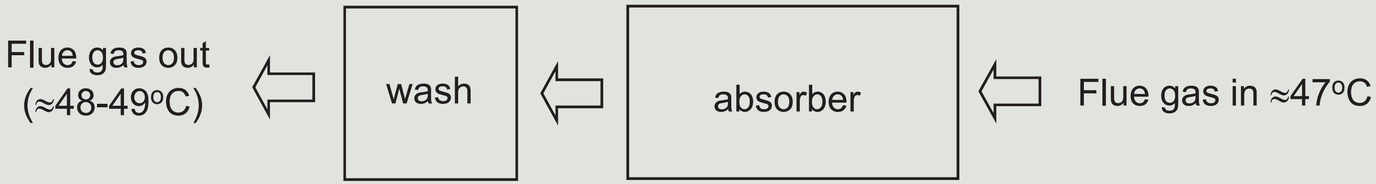


Average steam consumption: ≈3.7 GJ/ton CO_2

Average CO_2 capture: 88 %

2nd MEA Test: Emission Measurements

- Very low emission of MEA and other alkanolamines
- Detectable emissions of the more volatile degradation products: NH_3 (25 mg/Nm^3), acetaldehyde, acetone, formaldehyde
- The water wash must be operated at temperatures similar to that of the flue gas in order to achieve a neutral water balance => difficult to remove volatile degradation products e.g. NH_3



Flue gas out
(≈48-49°C)

wash

absorber

Flue gas in ≈47°C

Overview of Operating Experience with CASTOR 1 & 2

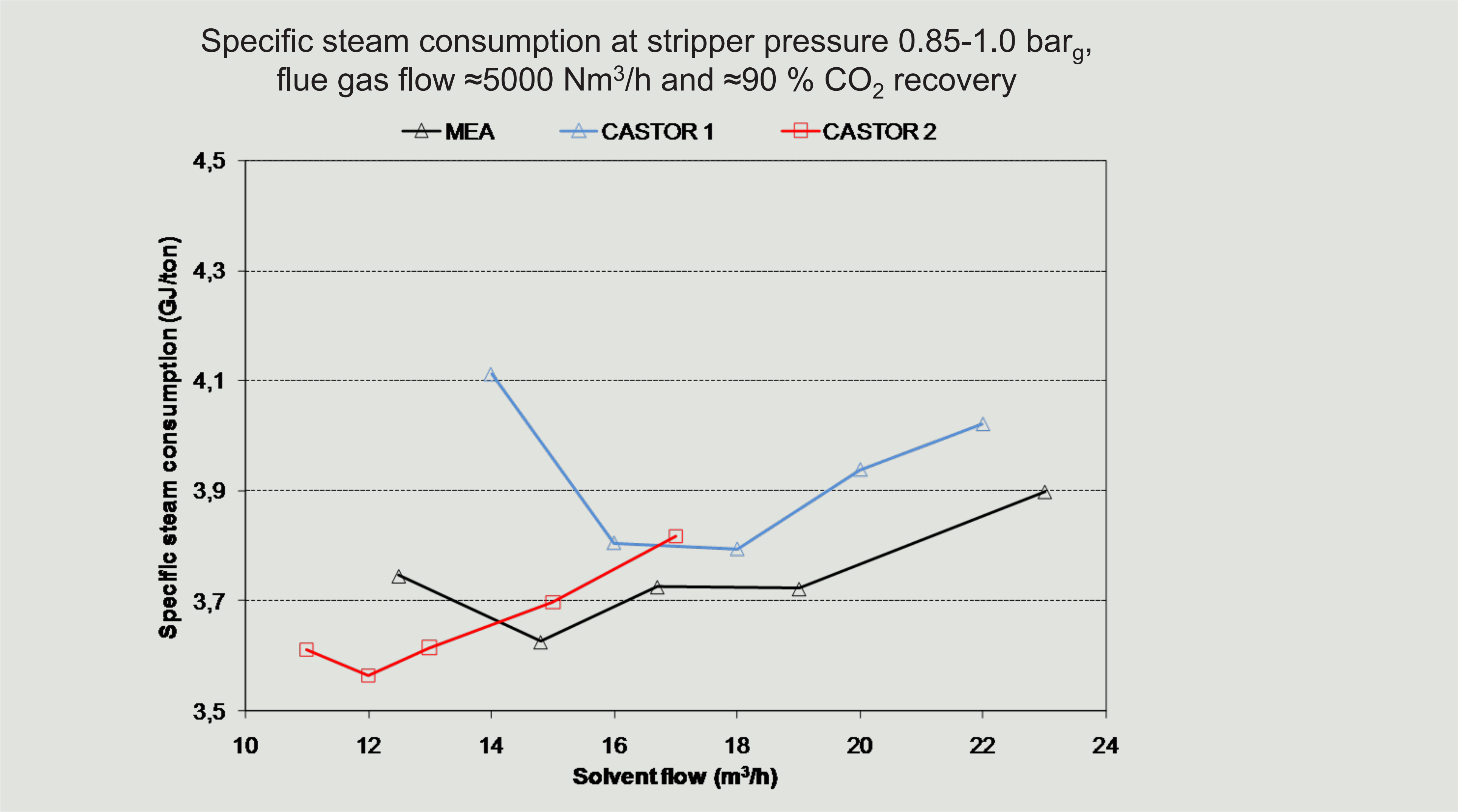
General operating experience with CASTOR 1

- Initially, the operation with CASTOR 1 was complicated by foaming. The problems diminished when a proper antifoam agent was added
- Difficult to reach high CO_2 loadings of solvent because of relatively slow kinetics
- => Difficult to obtain 90% CO_2 recovery
- => No improvement in regeneration energy compared to MEA

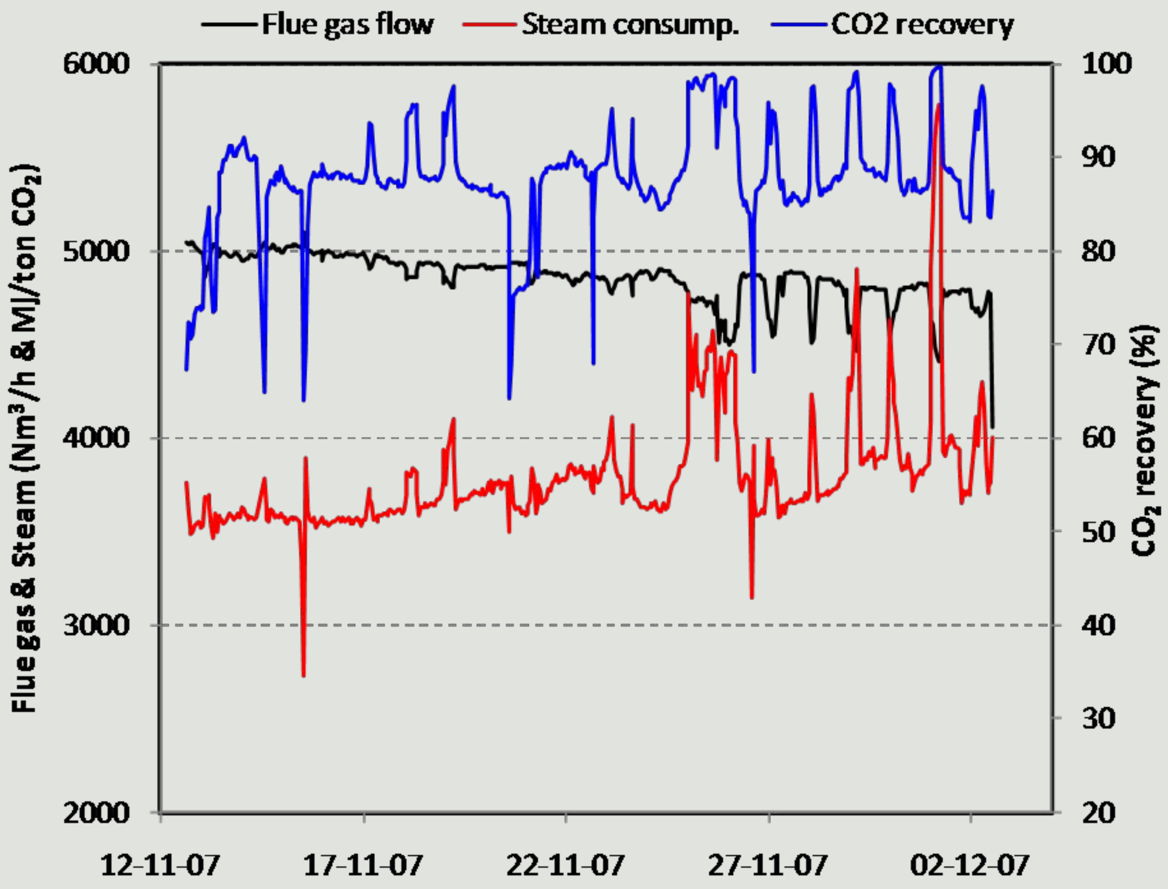
General operating experience with CASTOR 2

- Stable operation (antifoam agent applied right from beginning)
- Possible to reach relatively high CO_2 loadings
- Small improvement in regeneration energy compared to MEA
- 90% CO_2 recovery can be reached
- Loss of solvent!

Comparison of Regeneration Energies with MEA, CASTOR 1 & 2


Specific steam consumption at stripper pressure 0.85-1.0 bar_g, flue gas flow ≈5000 Nm^3/h and ≈90 % CO_2 recovery

CASTOR 2 Test: 500 Hours of Continuous Operation



Steam consumption: First 5 days ≈3.5 GJ/ton CO_2 Average CO_2 capture: 88 %

VATTENFALL

DONG energy

MEA & CASTOR 1 & 2 Tests: Flue Gas Impurities & Corrosion

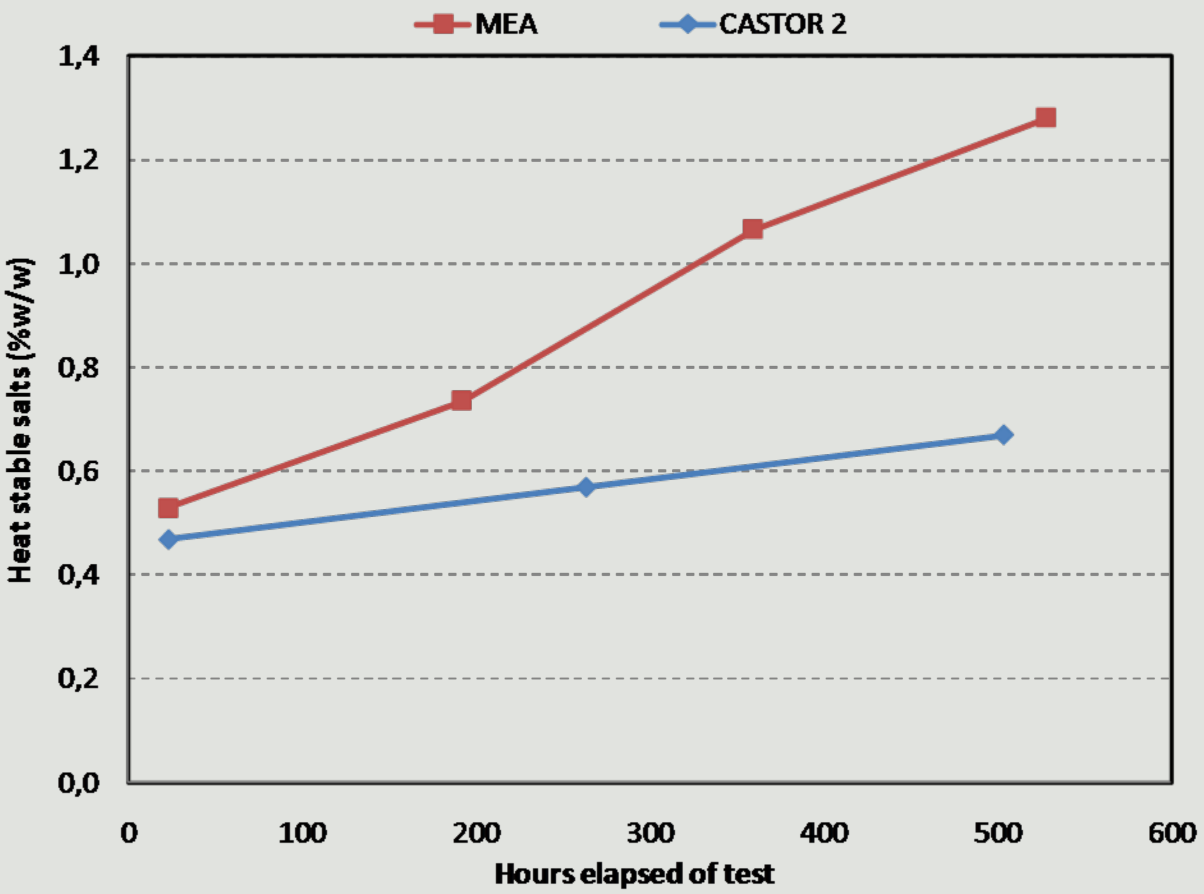
Flue gas impurities

- Typically, good balance between SO_2 input & sulphur uptake
- Fouling of packings and process equipment seems low
- 1–300 ppm: Cl, Ca, K, Mg, Na, P & Si
- < 1 ppm: Cr, Cu, Hg, Mo, Ni, Pb & V

Corrosion studies

- MEA: High corrosion rate for carbon steel at regenerator, low with stainless. Low corrosion with carbon and stainless steels at absorber
- CASTOR 1 & 2: Low corrosion with carbon and stainless steels at all positions

Growth in Degradation Products during 500 hours Tests



Summary CASTOR 2 vs. MEA

Improvements with CASTOR 2 compared to MEA

- Decreased regeneration energy 3.7 => 3.5 GJ/ton CO_2 (further improvement is plausible)
- Increased CO_2 carrying capacity i.e. reduced pumping works
- Degradation rate significantly reduced
- Low corrosiveness

... and the drawbacks

- Possible loss of solvent by physical mechanisms (entrainment & evaporation)
- Cost of solvent

Conclusions

Four 1000 hours test campaigns with MEA and novel solvents have been conducted at the CASTOR pilot plant in Esbjerg. The campaigns have indicated that:

- Stable operation on coal-derived flue gas is possible
- The impact of flue gas impurities can be handled
- Regeneration energy with MEA: ≈3.7 GJ/ton CO_2 at 90 % CO_2 removal
- MEA emission very low, but detectable emissions of volatile degradation products (e.g. NH_3, acetaldehyde, acetone)
- Small improvement in regeneration energy with CASTOR 2: ≈3.5 GJ/ton CO_2 at 90 % CO_2 removal (further improvement plausible)

Implications for further work:

- Possible to develop solvents with greater chemical stability and that are less corrosive
- Possible to develop solvents with improved regeneration energy compared to MEA, however, difficult to obtain major improvements with solvent alone

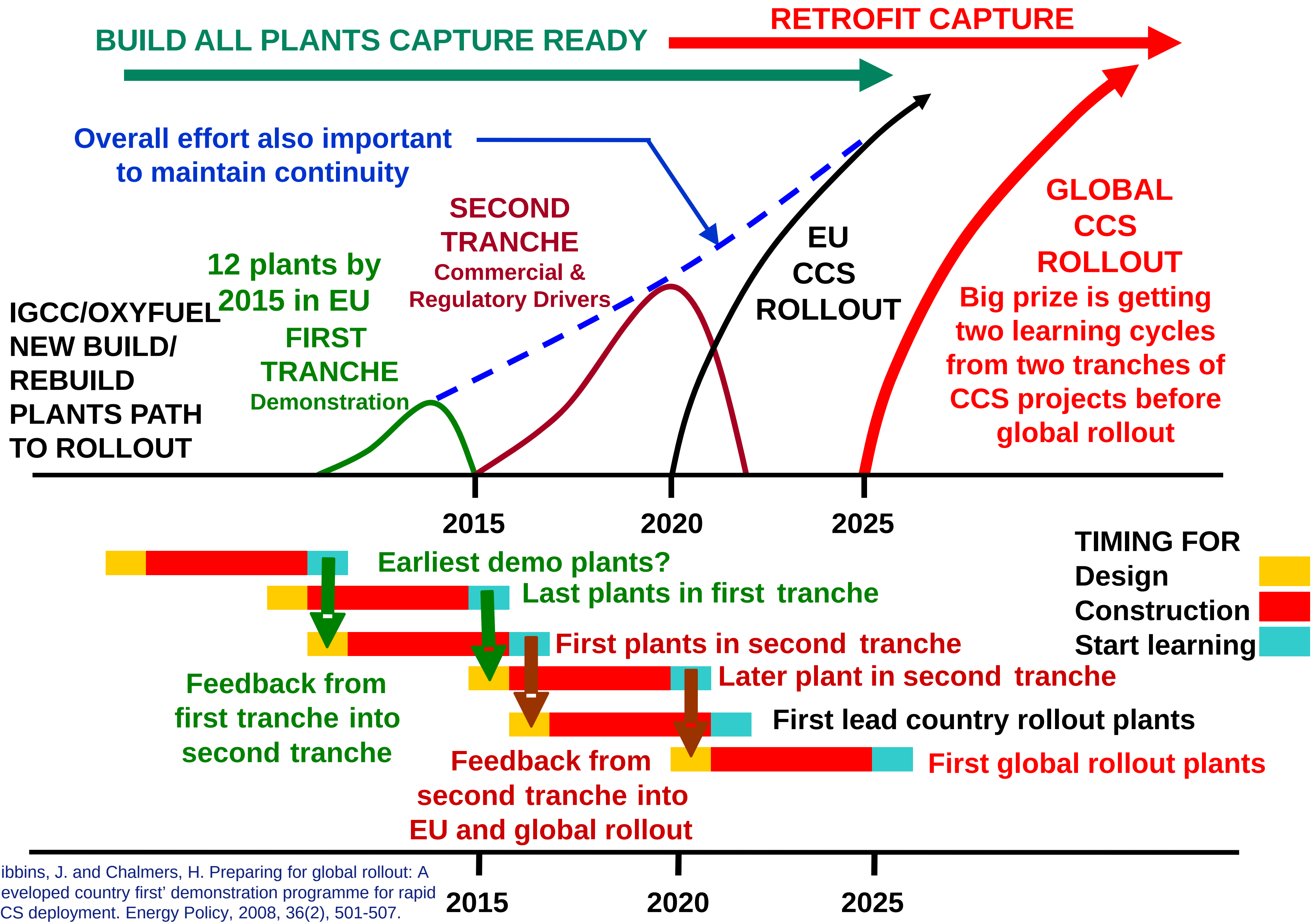
Imperial College
London

11th MEETING of the
INTERNATIONAL POST-COMBUSTION CO2 CAPTURE NETWORK
Date: 20th-21st May, 2008, Vienna, Austria
Organised by IEA Greenhouse Gas R&D Programme, Hosted by EVN

Studies on the Concept of Capture Ready and its Application to Post Combustion Capture

Jon Gibbins, Mathieu Lucquiaud & Hannah Chalmers
Energy Technology for Sustainable Development Group
Mechanical Engineering Department
Imperial College London, SW7 2AZ, UK
j.gibbins@imperial.ac.uk

CCS - Sequencing the Deployment – the Big Picture



RETROFIT CAPTURE

BUILD ALL PLANTS CAPTURE READY

Overall effort also important to maintain continuity

SECOND TRANCHE
Commercial & Regulatory Drivers

12 plants by 2015 in EU

FIRST TRANCHE
Demonstration

IGCC/OXYFUEL NEW BUILD/ REBUILD PLANTS PATH TO ROLLOUT

EU CCS ROLLOUT

GLOBAL CCS ROLLOUT
Big prize is getting two learning cycles from two tranches of CCS projects before global rollout

2015 2020 2025

Earliest demo plants?

Last plants in first tranche

First plants in second tranche

Later plant in second tranche

First lead country rollout plants

First global rollout plants

Feedback from first tranche into second tranche

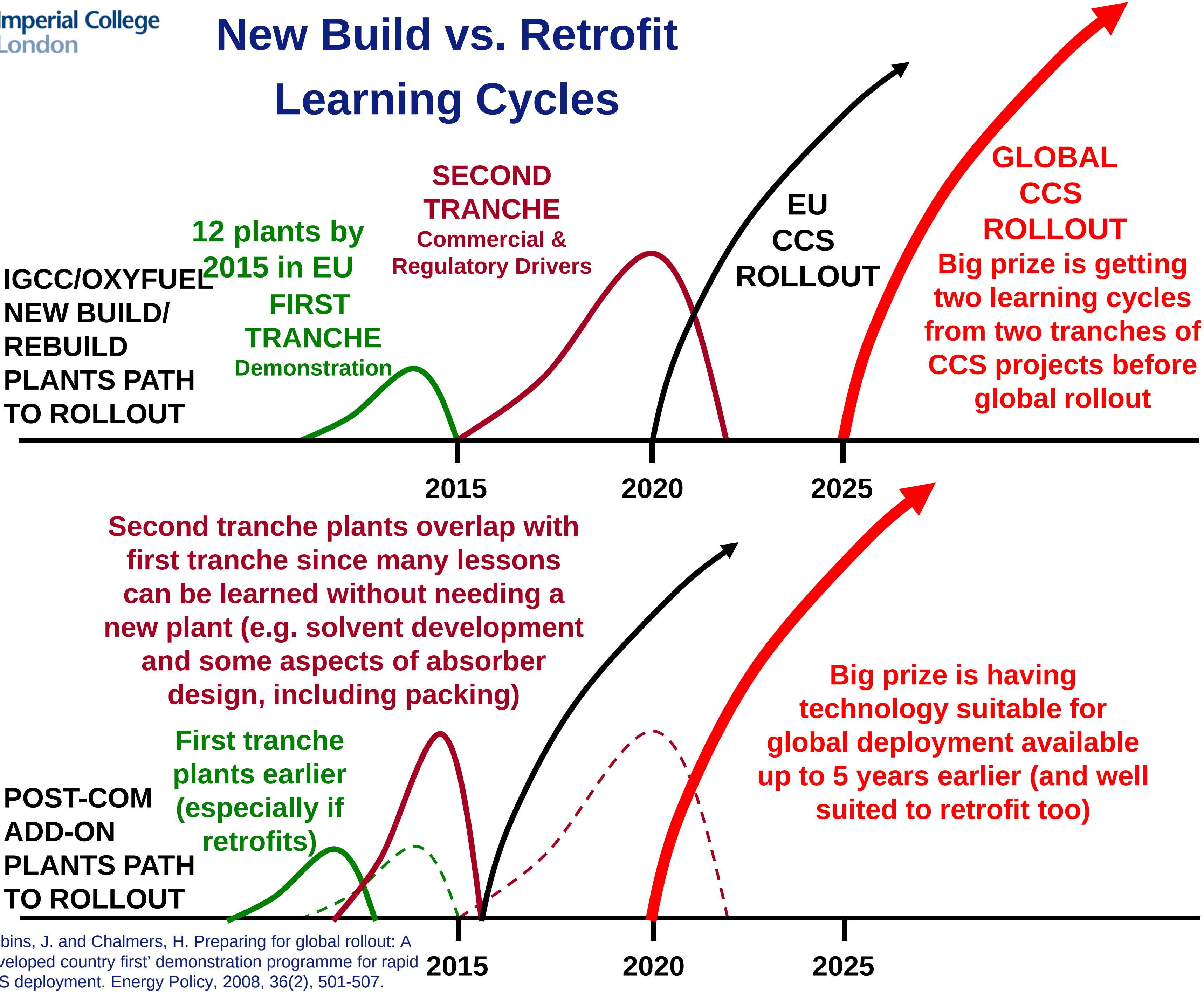
Feedback from second tranche into EU and global rollout

TIMING FOR
Design 🟨
Construction 🟥
Start learning 🟦

2015 2020 2025

Gibbins, J. and Chalmers, H. Preparing for global rollout: A ‘developed country first’ demonstration programme for rapid CCS deployment. Energy Policy, 2008, 36(2), 501-507.

New Build vs. Retrofit Learning Cycles



IGCC/OXYFUEL NEW BUILD/ REBUILD PLANTS PATH TO ROLLOUT

12 plants by 2015 in EU

FIRST TRANCHE
Demonstration

SECOND TRANCHE
Commercial & Regulatory Drivers

EU CCS ROLLOUT

GLOBAL CCS ROLLOUT
Big prize is getting two learning cycles from two tranches of CCS projects before global rollout

2015
2020
2025

Second tranche plants overlap with first tranche since many lessons can be learned without needing a new plant (e.g. solvent development and some aspects of absorber design, including packing)

POST-COM ADD-ON PLANTS PATH TO ROLLOUT

First tranche plants earlier (especially if retrofits)

Big prize is having technology suitable for global deployment available up to 5 years earlier (and well suited to retrofit too)

2015
2020
2025

Gibbins, J. and Chalmers, H. Preparing for global rollout: A ‘developed country first’ demonstration programme for rapid CCS deployment. Energy Policy, 2008, 36(2), 501-507.

Two actions to get ready for CCS rollout

1. Get through two learning cycles of CCS as quickly as possible – plus all the other support activities

2. Make all new fossil fuel plants capture ready – and move towards replacing fossil fuels in buildings and transport with electricity (or hydrogen)

Why to make plants capture-ready

- Not able to justify capture now
- May want to capture CO_2 in the future
- Society – avoid carbon-lock in
- Owner – cap carbon costs
  license to operate
- Regulator – lowest cost for electricity
  now?
  and in the future?

Responsibilities map onto hows:

Society

Reasonably-justified plan for the future

Must:

- Have access to geological storage
- Have space and access for capture equipment
- Have reasonable confidence it will work

e.g. Have to re-permit for CO_2 after ten years?

~~Also~~ Must consider:

Regulator ↔ **Owner**

but different interests?

- Up-front expenditure with savings later,

e.g. Bigger, better equipment?

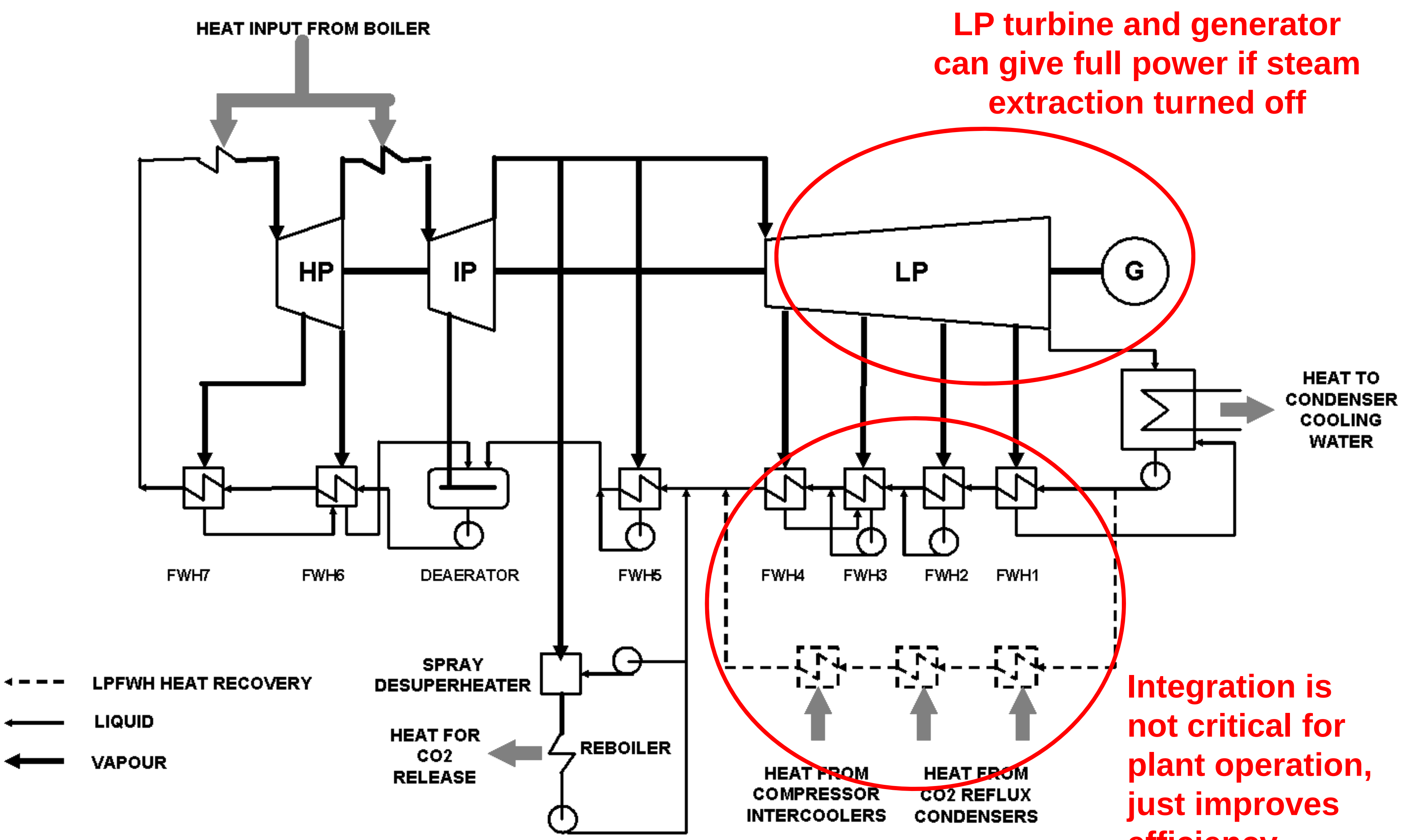
Cheaper/better CO_2 storage?

& auditors, bank’s engineers etc.

Detailed studies for immediate action, protect investment value

Imperial College London

Typical heat integration options for post-combustion capture retrofit



LP turbine and generator can give full power if steam extraction turned off

Integration is not critical for plant operation, just improves efficiency

Post-combustion capture-ready designs

- Post-com capture - must be demonstrated on coal & at scale
- Many future developments likely
- Should not lock in to known technology
- Likely common requirements, can be met at low cost:
  - Reasonable evidence for access to storage
  - Conceptual capture retrofit feasibility study
  - Space – large volumes of gas to handle, building work
  - Clean and probably cool flue gas
  - Pressure drop
  - Provision for extra instrumentation and control, other services
  - Extra cooling (efficiency penalty)
  - Some electricity for capture/compression plant
  - Some steam for temperature swing solvents

  Steam pressure (saturation temperature) and flow rate?

CO$_2$ CAPTURE READY PLANTS

Technical Study

Report Number: 2007/4

Date: May 2007

E.ON
Robin Irons

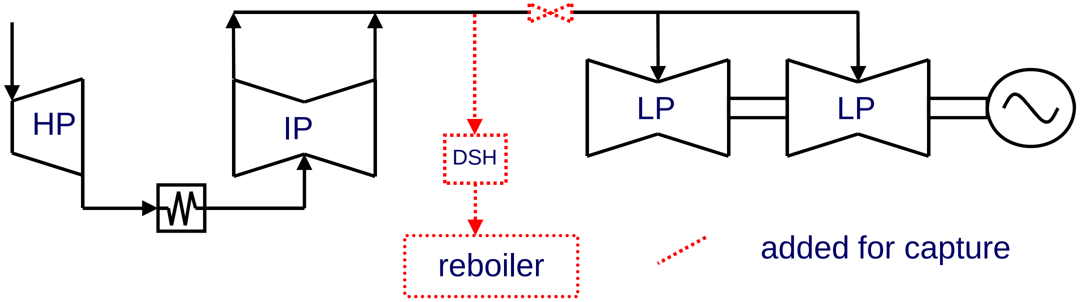
Doosan-Babcock
G. Sekkappan

Imperial
Mathieu Lucquiaud,
Hannah Chalmers
Jon Gibbins

Capture-ready steam turbine designs

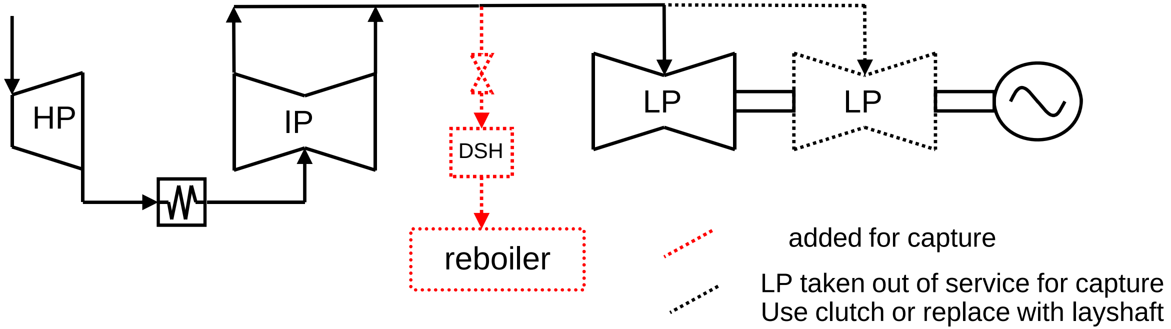
Lucquiaud & Gibbins, IEA GHG 2007-4

- Throttled LP turbine



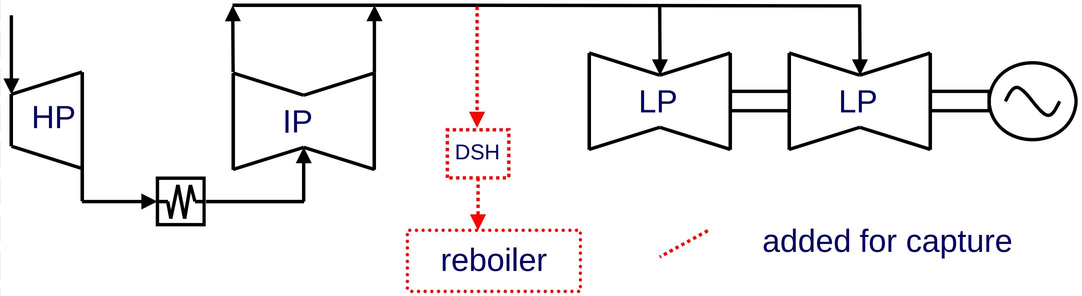
Simplest design, but losses in throttling valve. Initial pressure ~3.6 bar for amine, cannot be varied

- LP turbine taken out of service



Most efficient design, but cannot vary steam extraction flow. Initial pressure ~3.6 bar for amine, cannot be varied

- Floating IP/LP crossover pressure



Avoids all throttling losses at design extraction rate. Extraction pressure goes up with reduced flow rate

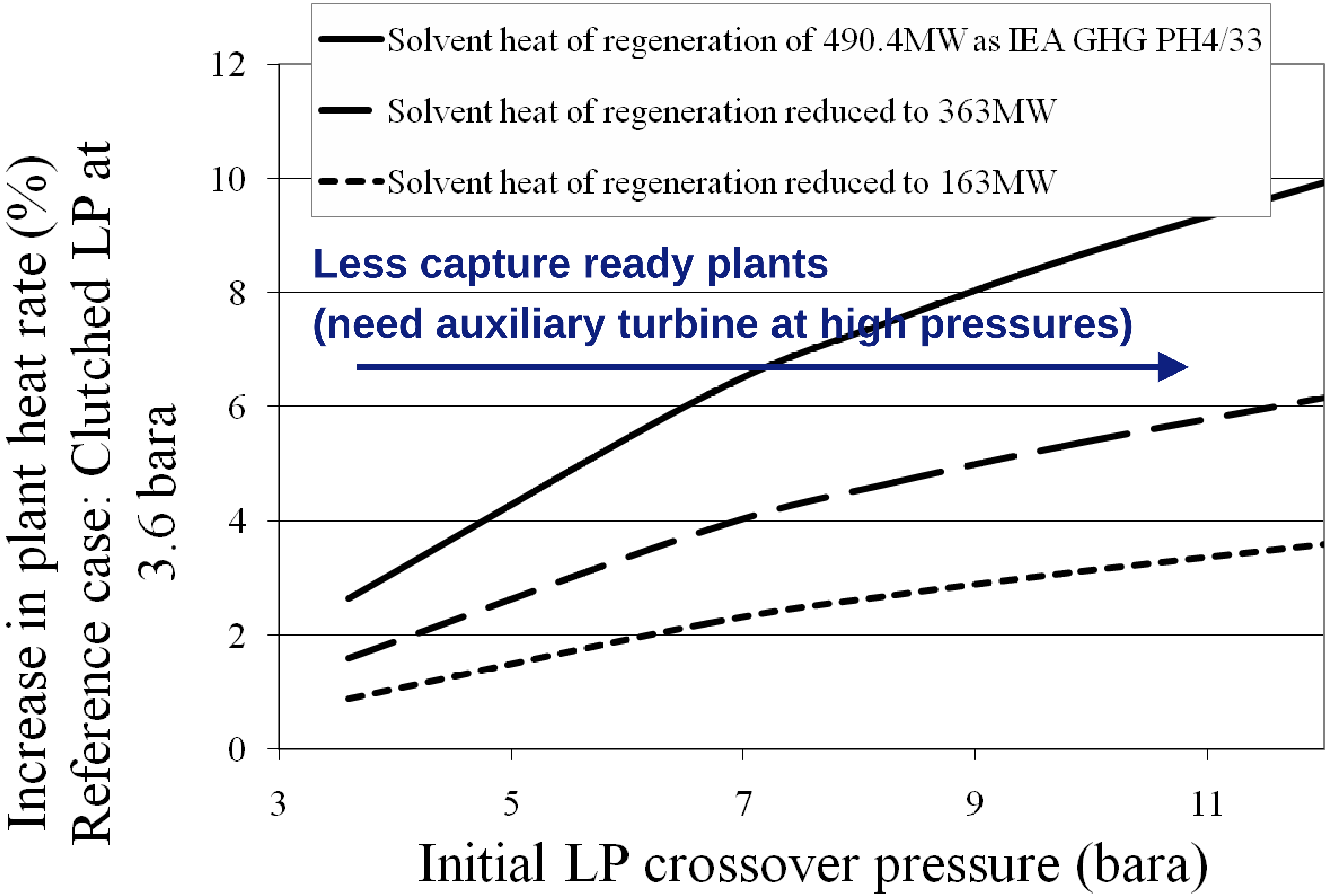
7 to 3.6 bar possible

Comparison of steam turbine performance

	New Coal plant without CCS	New build coal plant with CCS	Clutched LP turbine retrofit	Throttled LP turbine retrofit	Floating IP/LP crossover pressure
Efficiency without CCS (LHV basis)	45.3%		45.3%	45.3%	45.3%
Efficiency with CCS (LHV basis)		35.9%	35.9%	35.0%	35.5%
Additional capital costs			High	Negligible	Negligible

BUT efficiency at the time of retrofit is not the only criterion that matters
OPERABILITY => keep the light on when the capture plant trips
FLEXIBILITY => vary level of CO2 capture to provide additional services to the grid
UPGRADE => Maintain competitiveness with new CCS plants coming later online by upgrading the solvent

Penalty for throttling with elevated IP/LP pressures



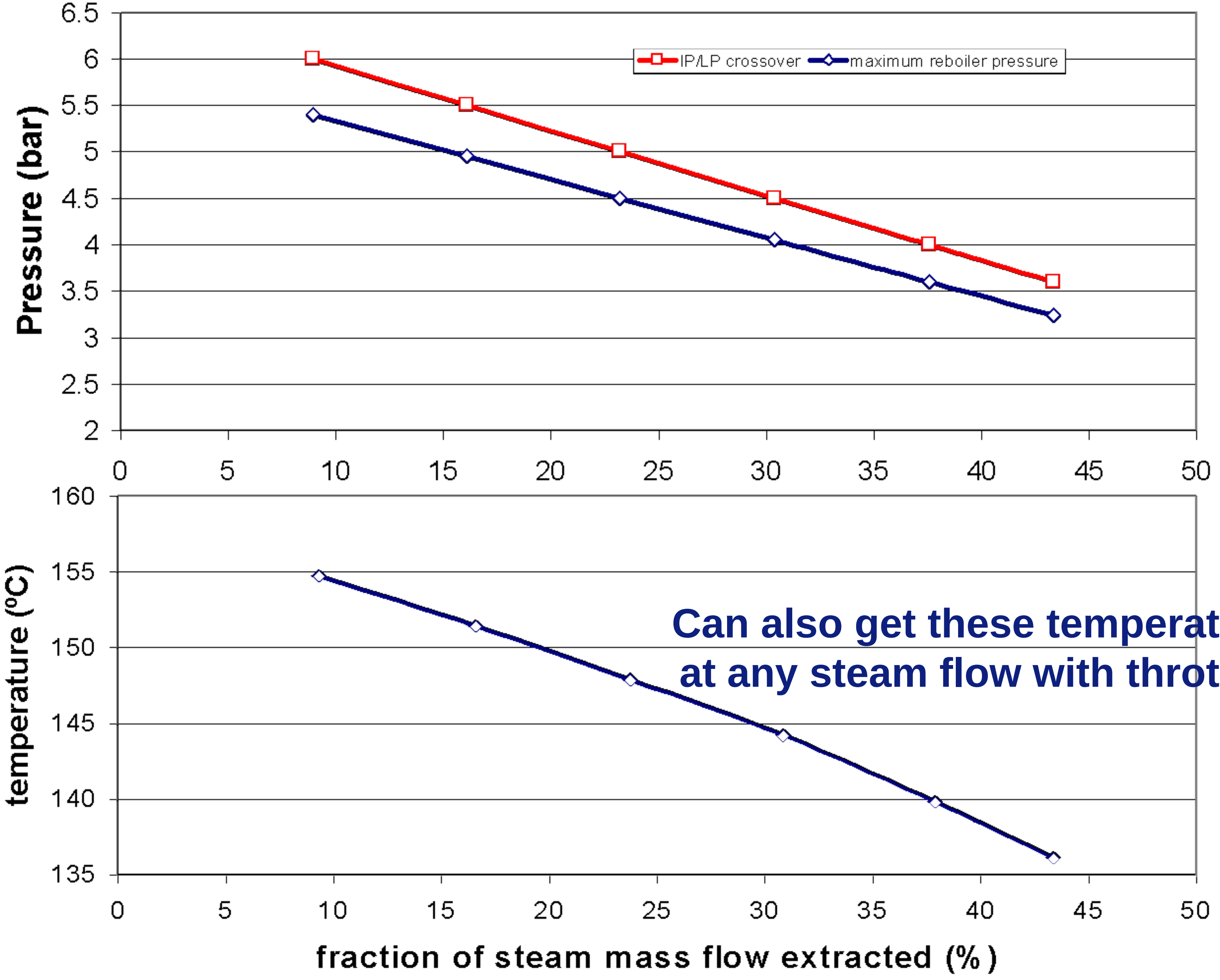
Less capture ready plants

(need auxiliary turbine at high pressures)

Comparison of steam turbine performance

	New coal plant without CCS	New build coal plant with CCS	Clutched LP turbine retrofit	Throttled LP turbine retrofit	Floating IP/LP crossover pressure
Operation without capture			Difficult. Would have to re-clutch the turbine	Easy. Divert steam to low pressure turbine	Easy. Divert steam to low pressure turbine
Dynamic response	Baseline	Depends on steam turbine design	Same or slower	Very fast	Fast
Upgrade with next generation of solvents		POSSIBLE	NO	POSSIBLE	POSSIBLE

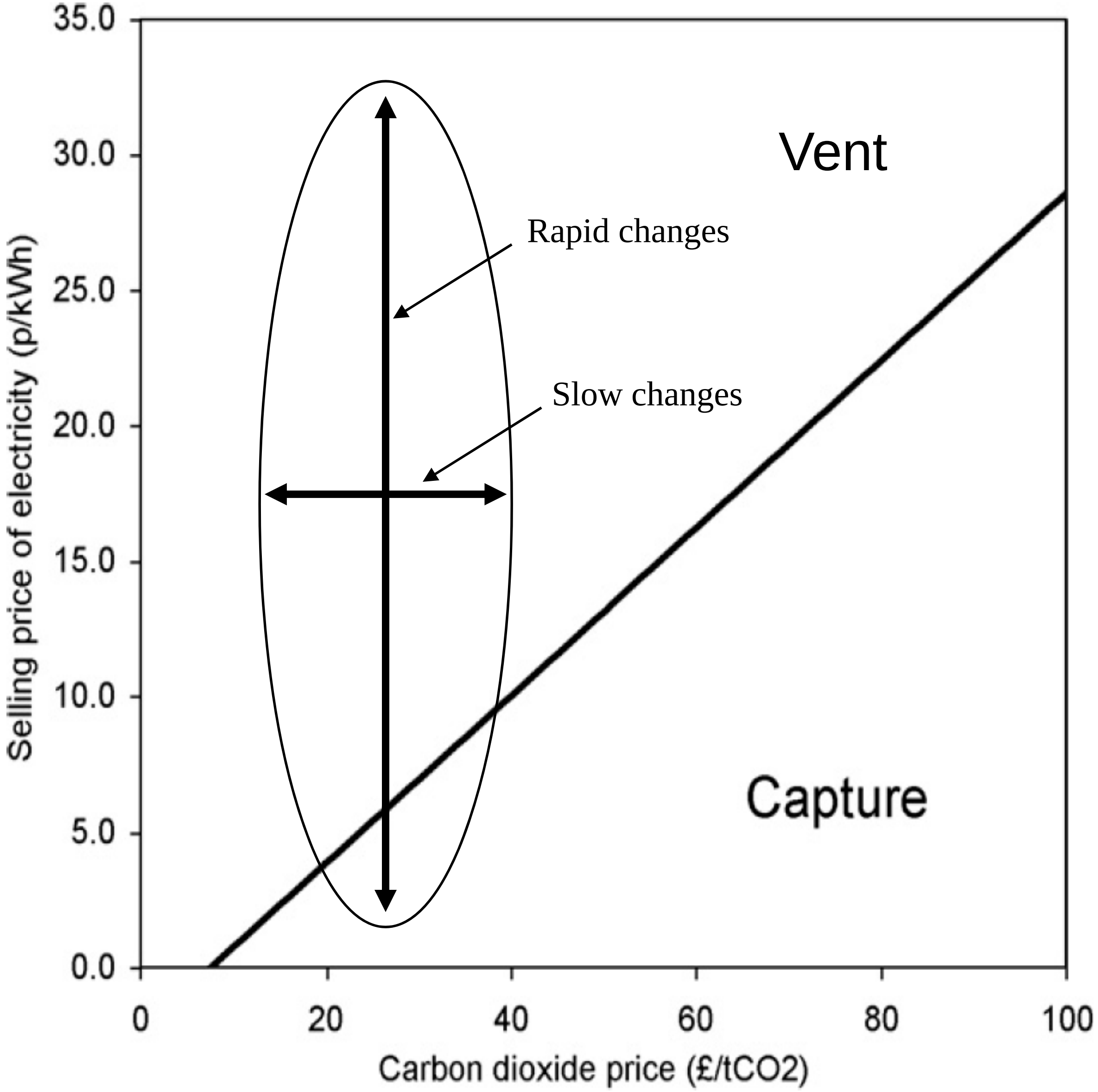
MAXIMUM PRESSURES AND TEMPERATURES FOR FLOATING IP/LP OPTION



Can also get these temperatures at any steam flow with throttling

Imperial College London

Steam flow rate (but not pressure) likely to vary anyway, for arbitrage between carbon and electricity prices for simply venting CO_2 to atmosphere



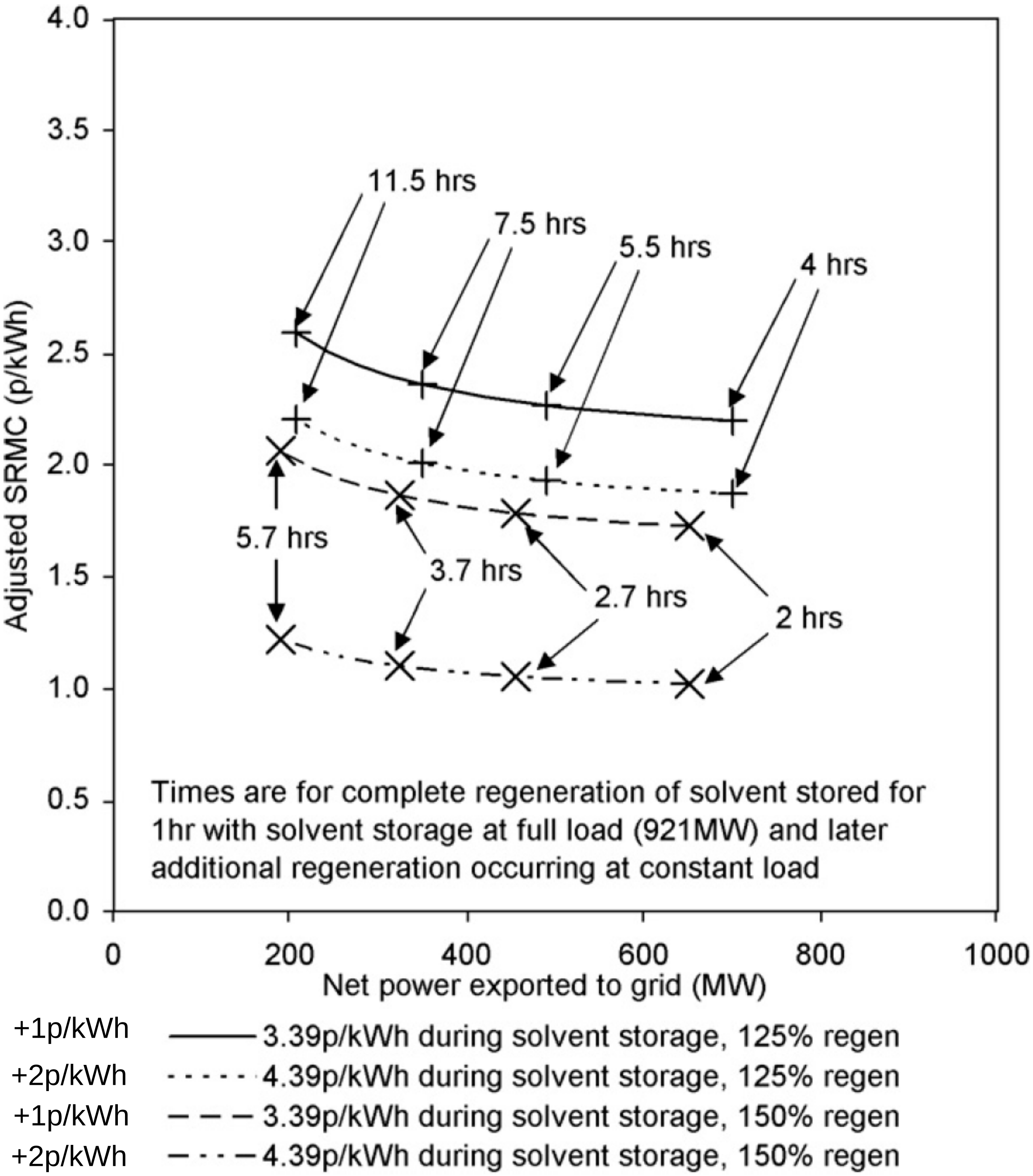
Plant output	750 MW
Coal price	£1.4/GJ
Carbon price	£25/tCO_2
CO_2 transport & storage	£5.5/tCO_2

Chalmers H, Gibbins J, Initial evaluation of the impact of post-combustion capture of carbon dioxide on supercritical pulverised coal power plant part load performance, Fuel (2007) (in press)

Reduced output and short run marginal cost of generation for solvent storage – generate more when prices high, less when prices low, improve load factor for capital recovery

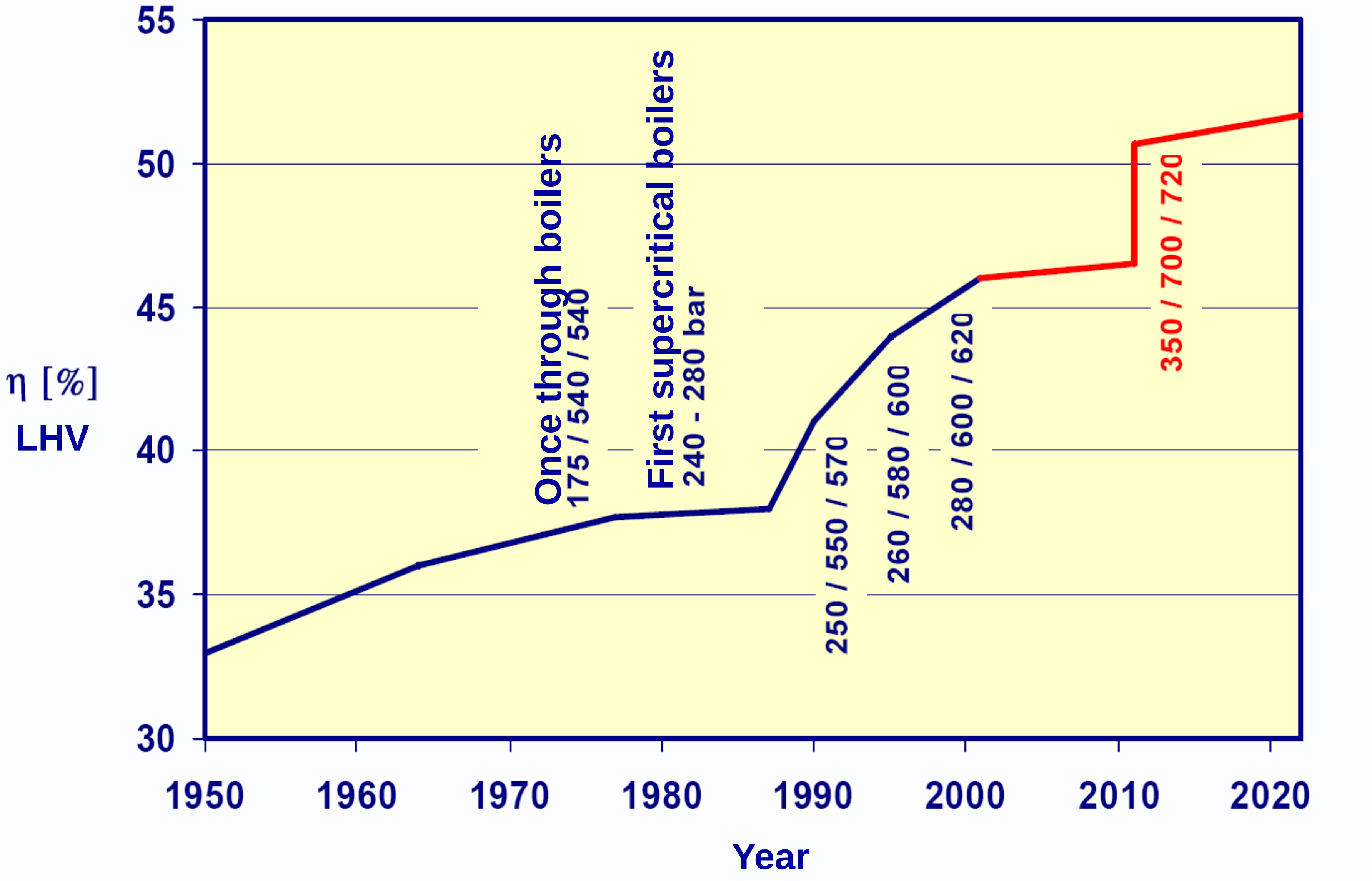
Plant output	750 MW
Coal price	£1.4/GJ
Carbon price	£25/tCO2
CO_2 transport & storage	£5.5/tCO2

Chalmers H, Gibbins J, Initial evaluation of the impact of post-combustion capture of carbon dioxide on supercritical pulverised coal power plant part load performance, Fuel (2007) (in press)



Imperial College London

Developments in EU steam plant efficiency



Epple, TU Darmstadt, http://www.dvv.uni-essen.de/download/pdf_30Fach/2004-11-12_DVV_Anlage7_Epple.pdf

Power plant efficiency for CR plants

Consequences for reduced CO_2 emissions

- Appears that overall coal sector efficiency or plant average efficiency (i.e. coal burned / electricity generated) is sometimes being compared with full load efficiency for new plants
- Part-load, start up etc. all reduce efficiency, but necessary
- Wind and other renewables plus nuclear need flexible plants to maintain continuous electricity supplies.
- Old, less efficient plants tend to run for less hours – effect of replacement not easy to judge

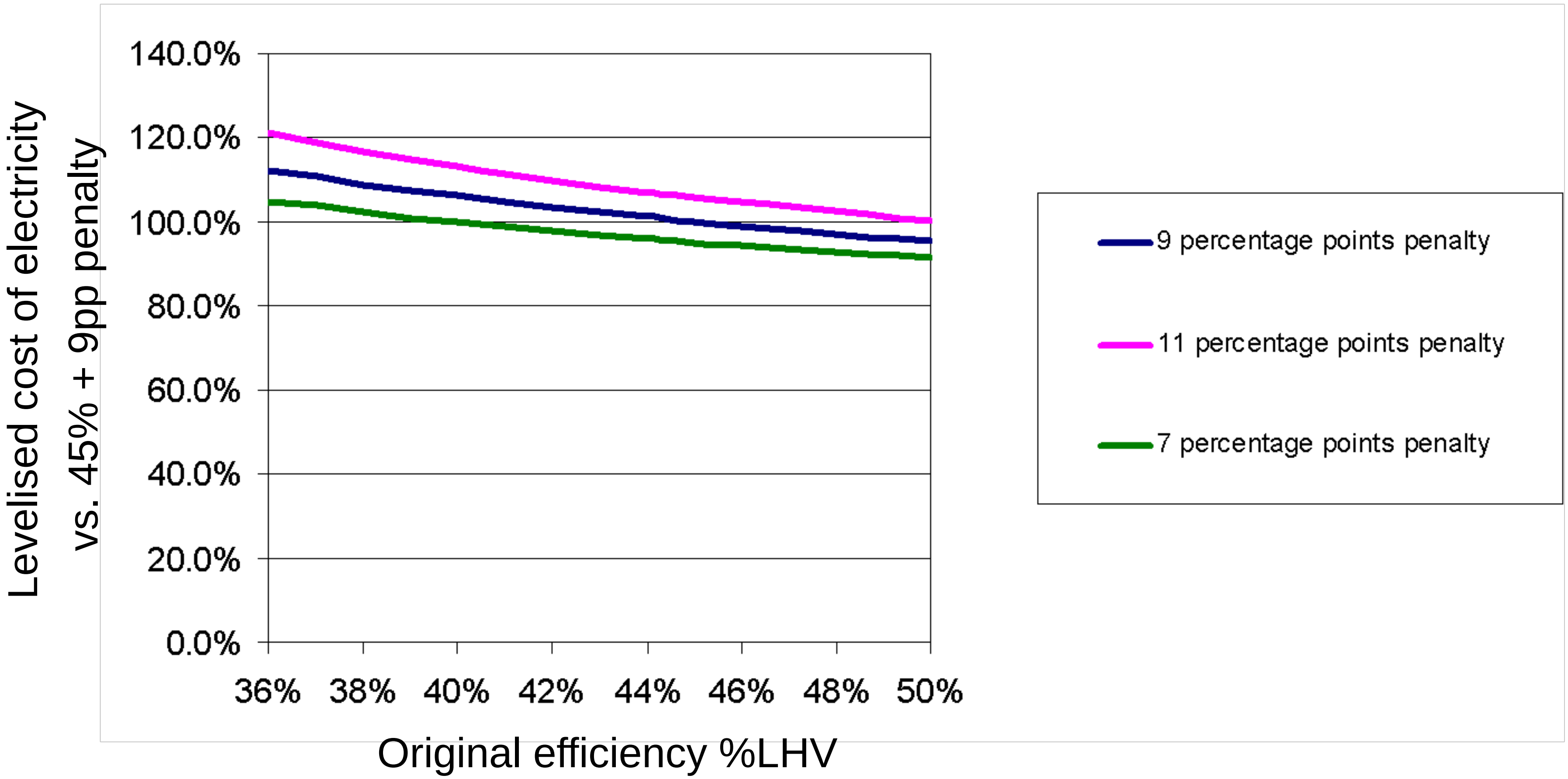
Consequences for subsequently retrofitting capture

- Small effect of original efficiency on cost of electricity, even smaller on cost of CO_2 abated, negligible effect on cost of CO_2 captured
- Capture plant performance probably more important
- Cost of electricity likely to be much lower from paid-off PC plants than from new plants, new capital costs swamp efficiency effects

Preliminary estimates on the effect of original plant efficiency on the levelised cost of electricity with capture retrofit

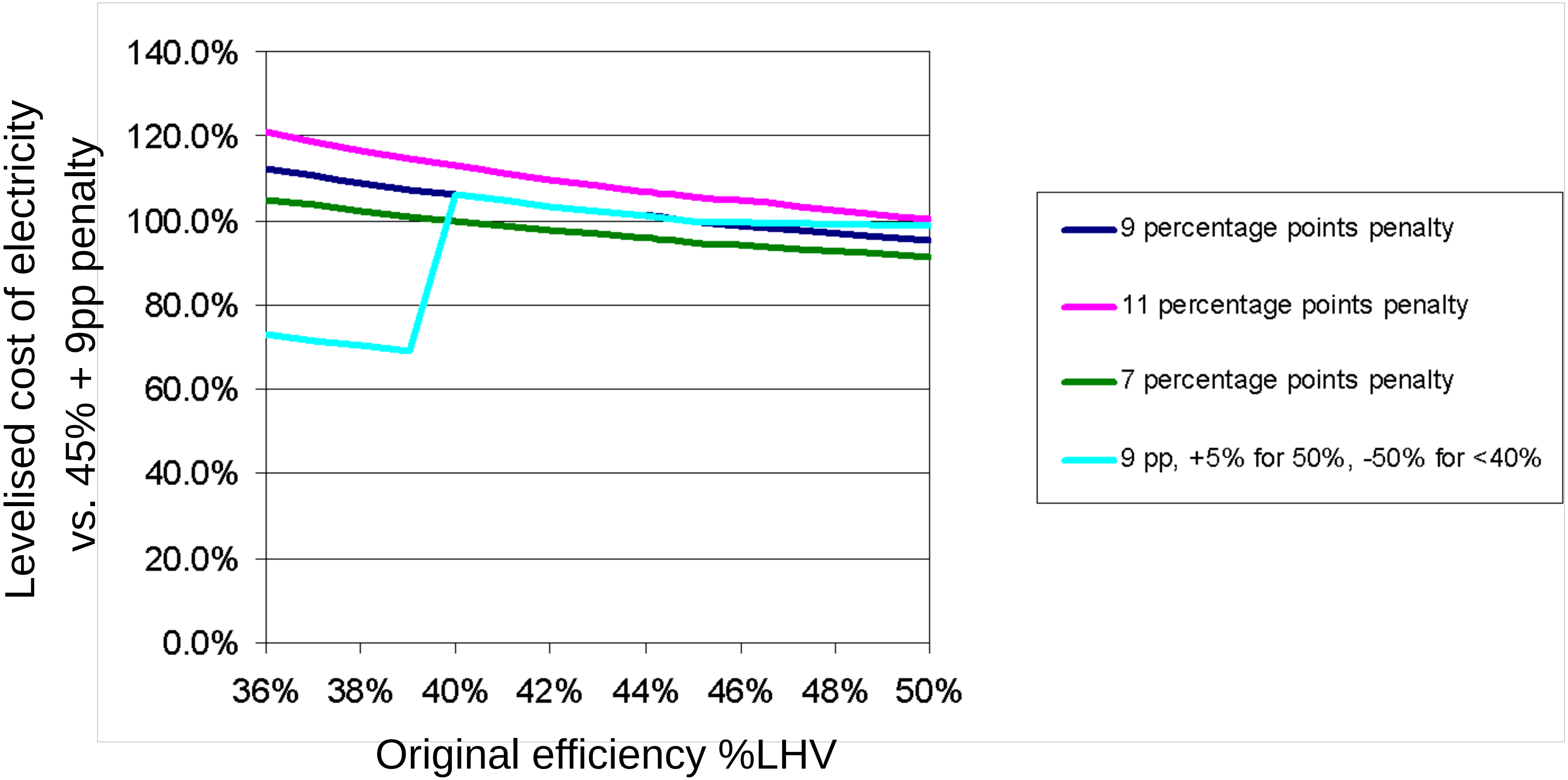
All plants assumed to have same original COE,

capture equipment capital costs ~ throughput$^{0.8}$



Preliminary estimates on the effect of original plant efficiency on the levelised cost of electricity with capture retrofit

-50% original COE for subcritical plant (<40%), assumed to be existing plants, + 5% COE for 50% LHV.



No new coal without CCS – CR an excuse for doing nothing

Issue in UK (and elsewhere in developed world) now is not whether or not plants are capture ready, but when will they have capture fitted.

Different positions:

- lobbying designed to stop coal (NGO and gas industry)
- gas performance standards – e.g. 500 kg/MWh in California
- timing not relevant – cap and market will force capture if needed
- planned transition by 2015 - 2025

Utilities appear ready to capture from power plants:

- if costs can be recovered
- if storage can be sorted out (beyond their direct control)

Oil companies appear to want bigger returns for ‘turnkey’ approach on projects they feel happy with.

If carbon market is not sufficient, government action needed:

- cost recovery mechanism for capture, transport & storage
- strategic planning for pipelines (and cost recovery for these)

Danger in rigid rules e.g. 90% capture, that reduce design and operational flexibility inherent in the carbon market

Possible that UK CCS activity stopped if no new coal plants are built

False Hope - Why carbon capture and storage won’t save the climate

Greenpeace, May 2008

“Capture ready” power stations

Proponents of CCS circumvent the fact that the technology is not ready, by proposing to build “capture ready” power stations. This term refers not to a particular type of technology but more a state of being for a power station. While there is no strict definition of “capture ready”, the IEA describes a capture ready plant as “[one] which can be retrofitted with CO_2 capture when the necessary regulatory or economic drivers are in place.”

This is sufficiently broad to make any station theoretically capture ready, and the term meaningless.

The concept of “capture ready” power stations allows new coal-fired power stations to be built today while providing no guarantee that emissions will be mitigated in the future. In lieu of delivering a concrete solution to fighting climate change, it banks on the promise of an unproven technology and risks locking us into an energy future that fails to protect the climate.

David Hawkins, NRDC - To say a power plant is ‘capture-ready’ is like saying you have a Ferrari-ready drive way on your house.

IEA GHG 2007/4 Summary of capture ready power plant considerations

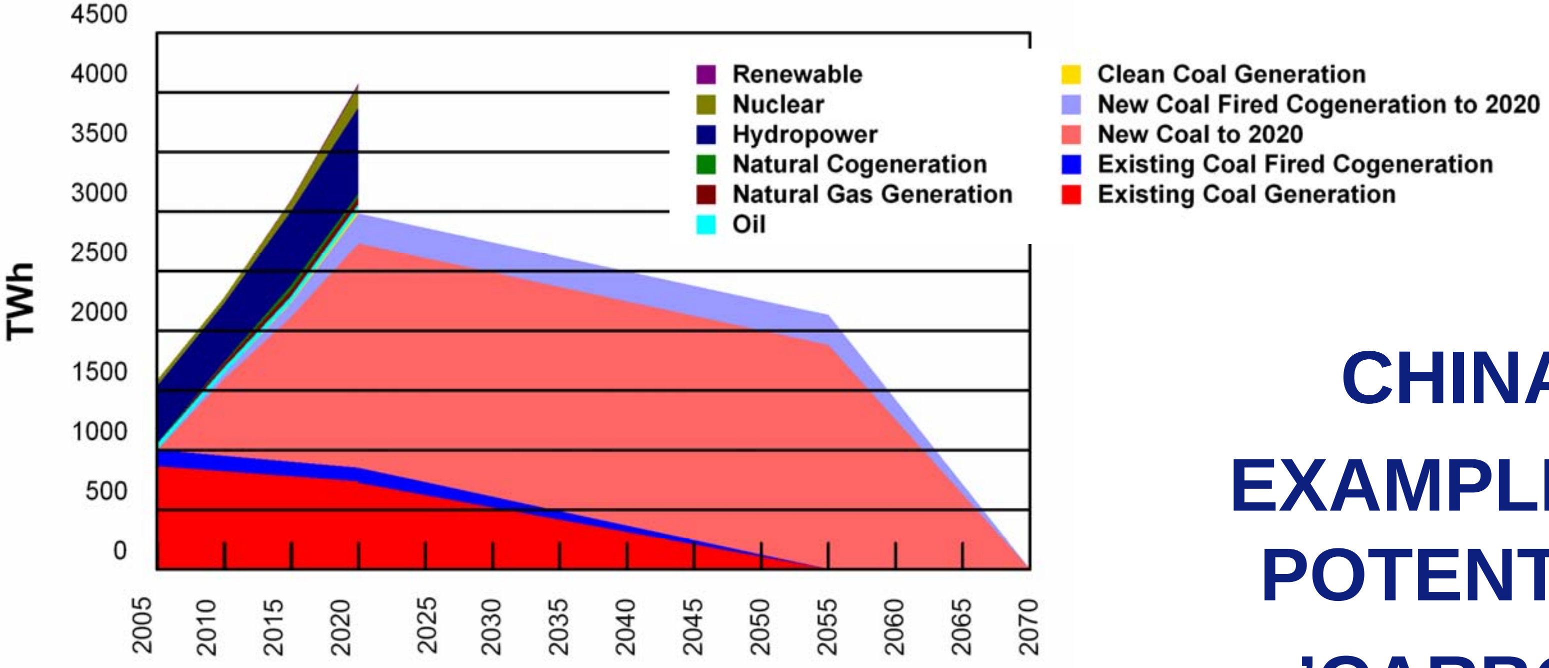
IEA GHG and the study contractors have produced the following ‘headline’ summary of capture ready considerations for power plants:

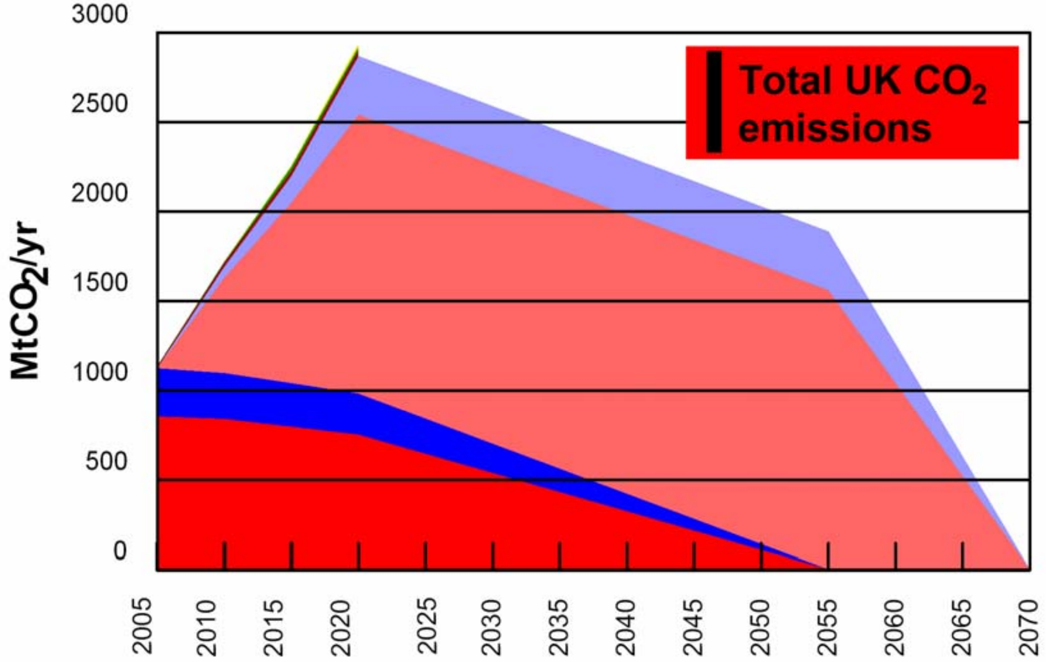
A CO_2 capture ready power plant is a plant which can include CO_2 capture when the necessary regulatory or economic drivers are in place. **The aim of building plants that are capture ready is to reduce the risk of stranded assets and ‘carbon lock-in’.**

Developers of capture ready plants should take responsibility for ensuring that all known factors in their control that would prevent installation and operation of CO_2 capture have been identified and eliminated.

This might include:

- A study of options for CO2 capture retrofit and potential pre-investments
- Inclusion of sufficient space and access for the additional facilities that would be required
- Identification of reasonable route(s) to storage of CO_2
- Competent authorities involved in permitting power plants should be provided with sufficient information to be able to judge whether the developer has met these criteria.





CHINA: EXAMPLE OF POTENTIAL 'CARBON LOCK-IN'

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

NZEC – Near Zero Emissions from Coal project Work Package 3 (WP3) – Case studies for Carbon Dioxide Capture

www.nzec.info

WP3 Partners

GreenGen (GG)
Institute of Engineering Thermophysics, Chinese Academy of Science (IET)
State Key Laboratory of Chemical Engineering, Tsinghua University (DCE)
Department of Thermal Engineering, Tsinghua University (DTE)
BP Clean Energy Research & Education Centre, Tsinghua University (THCEC)
Thermal Power Research Institute (TPRI)
North China Electric Power University (NCEPU)
Wuhan University (WHU)
Zhejiang University (ZJU)

Imperial College (Imp)
Alstom Power (Alstom)
BP (BP)
Univ. of Cambridge
Doosan Babcock (DB)
Shell (Shell)

NZEC - Description of tasks in WP3

Task 1: Initial Phase: Definition of basic conditions and reference basis

Task 2: Case Studies ***(similar scope to IEA GHG studies)***

Subtask 2.1: Oxyfuel

a) OX1 Oxyfuel, new build Capture-Ready, (Doosan Babcock, AP + ZJU)

b) OX2 Oxyfuel, capture retrofit to existing sub-critical plant combined with ASCBTR, (Doosan-Babcock)

Subtask 2.2: Post-combustion:

a) PC1 Post-combustion capture, new build, (Alstom + DCE)

b) PC2 Post-combustion capture, capture-ready, and retrofit (Alstom + DTE)

c) PC3 Super-critical with post-combustion capture by chemical absorption and membrane contactor (ZJU)

d) PC4 Possible post-combustion capture options for existing sub-critical and supercritical power plants (i.e. Chinese power plant fleet in 10-20 years time) (NCEPU)

(Plus other gasification, transport, technoeconomic comparison studies)

BERR PROJECT: CHINESE ADVANCED POWER PLANT CARBON CAPTURE OPTIONS (CAPPCCO)

Harbin Institute of Technology (Prof. Shaozeng Sun, Combustion Engineering Research Instititute – linked to MOST 863 project)

Cambridge University (David Reiner, Judge Business School)

1. Carbon capture characteristics database for existing & planned plants
2. Develop and assess capture options for planned new PC plants
3. Develop and assess capture options for existing PC plants
4. Special issues for adding carbon capture to Chinese power plants e.g. water requirements, cooling requirements, coal properties, capture performance under variable Chinese climatic conditions including likely performance of next-generation pollutant control technologies
5. Financing capture ready and capture retrofit

- Project started end 2007, 3 years
- Translation of 2007/4 post-com sections
- Stakeholder consultation – identify key questions

CO_2 Capture-Ready Ultra Mega Power Projects, India

The Government of India is developing nine Ultra Mega Power Projects (UMPPs), each of 4,000 MW capacity, through private competitive bidding. This report presents the results of an innovative study carried out by Mott MacDonald (MM) on behalf of the British Government*, combining new information available from three other first-of-kind studies, to identify and evaluate options for making the UMPPs “CO_2 Capture-Ready”.

The report builds .. on two studies commissioned by the IEA Greenhouse Gas R&D Programme (IEA GHG) – on capture-ready plants globally and on CO2 storage opportunities in the Indian subcontinent.

For a UMPP with estimated initial capital costs of USD 5 billion, the additional capital expenditure for design of a capture-ready plant is limited to 1% of the initial cost i.e. USD 50 million. ….. Retrofit of CCS to a UMPP of 4,000 MW gross capacity will capture18.8-19.5 Mt/year, at an 85% capture rate. The resulting abatement cost … is calculated at approximately USD 33/tCO2.

http://www.defra.gov.uk/environment/climatechange/internat/devcountry/india.htm

*Foreign and Commonwealth Office (FCO) under their Global Opportunities Fund Climate Change and Energy Programme

Incentives to retrofit CCS – shadow carbon price?

When adding capture to a power plant

Financial penalties:

Lost electricity revenue (but note – not a constant electricity price)

Additional CAPEX and OPEX

Financial gains:

Avoided EUA purchase for carbon captured

Additional payment per tonne of CO_2 stored

Together these make up the shadow carbon price for CCS for this project

Example for 800MW pulverised coal power plant:

	Original	CCS	Difference
Electricity	800MW	630MW	- 170MW
CO_2 emitted	560 t/hr	56 t/hr	- 504 t/hr
CO_2/MWh	700kg	89 kg	
CO_2 stored	0 t/hr	504 t/hr	+ 504 t/hr
CCS CAPEX & OPEX	0	??	+??

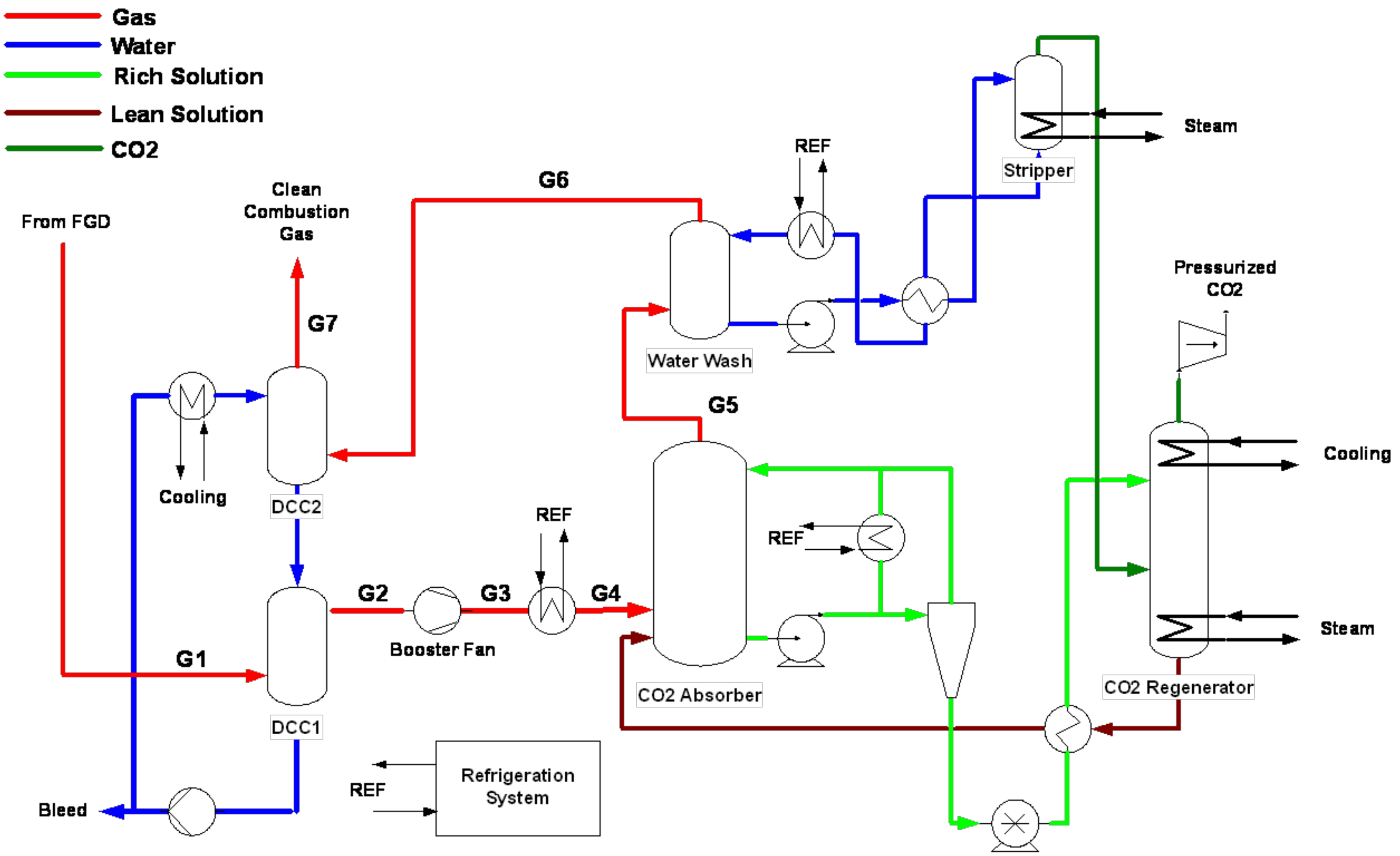
Summary

1. Two learning cycles before CCS proven – maybe 10 years – meanwhile make all non-CCS fossil fuel plants capture ready
2. Very effective and low cost CR options exist for PC plants
3. Electricity price varies drastically – flexibility for CCS plant design and operation fairly essential – rigidity will increase costs and restrict development
4. Plant efficiency has small effect on electricity costs with capture
5. Timing when capture is retrofitted now critical factor for CR plants in EU/USA – low cost CR for PC seen as an excuse
6. Carbon lock-in in China, India etc. still a very real risk, CR unlikely to increase number of plants built significantly but would help with subsequent retrofitting.
7. Additional payment per tonne CO2 captured and stored being considered, better than rigid performance standard

Chilled Ammonia Process Update

Brice Freeman – Project Manager
(650) 855-1050 or bfreeman@epri.com

Schematic of the Chilled Ammonia Process



Cooling and Cleaning

CO_2 Absorption

CO_2 Regeneration

Courtesy of Alstom

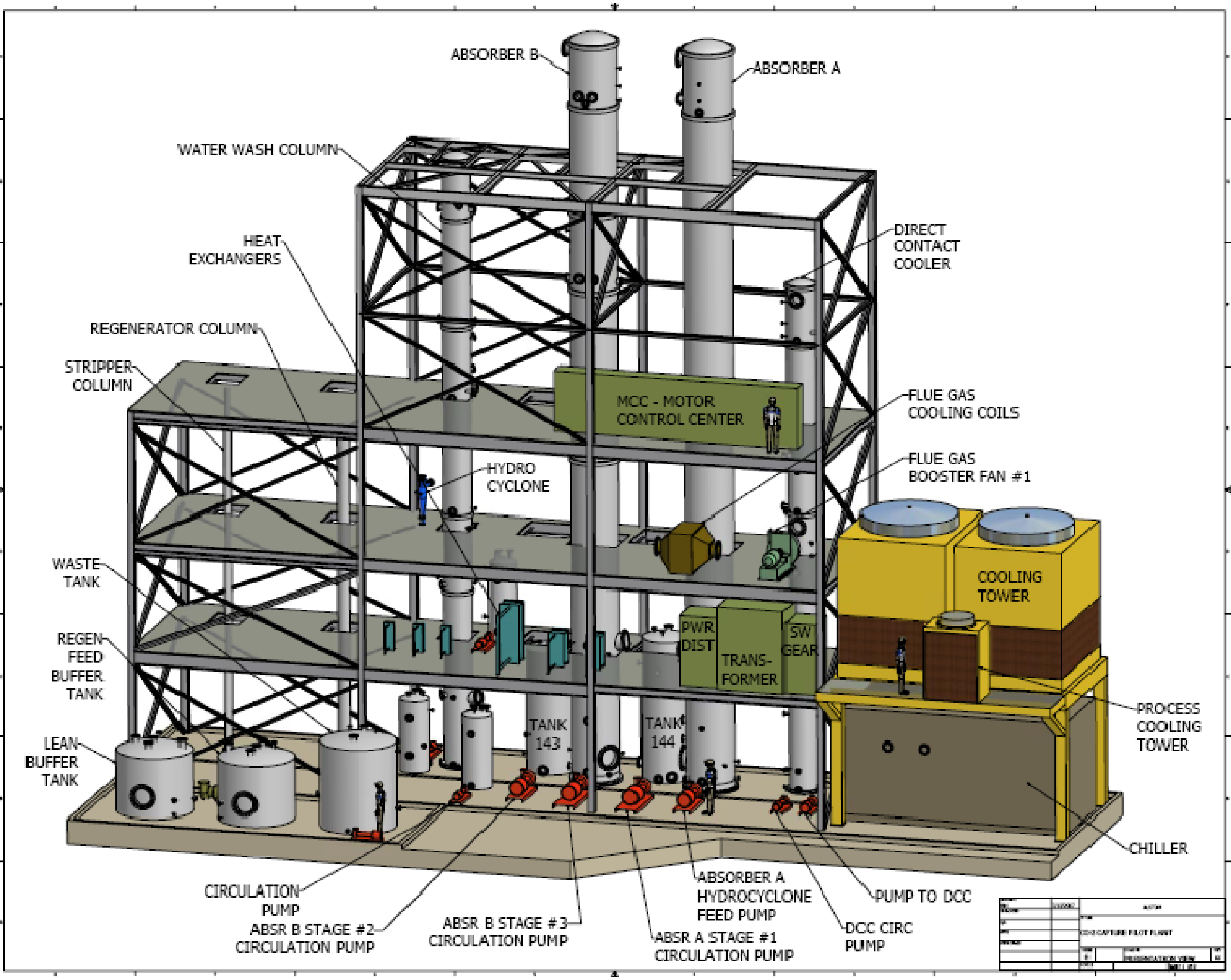
1.7 MW Chilled Ammonia CO_2 Capture

- 37 Executed pilot participant agreements
- Construction complete
- Commissioning underway
- May Plant outage
- Testing starting in June

Courtesy of Alstom

Phase 3 - Field Pilot at We Energies

3-D View of Pilot



Courtesy of Alstom

Phase 3 - Field Pilot at We Energies

Pilot Photos

Courtesy of Alstom

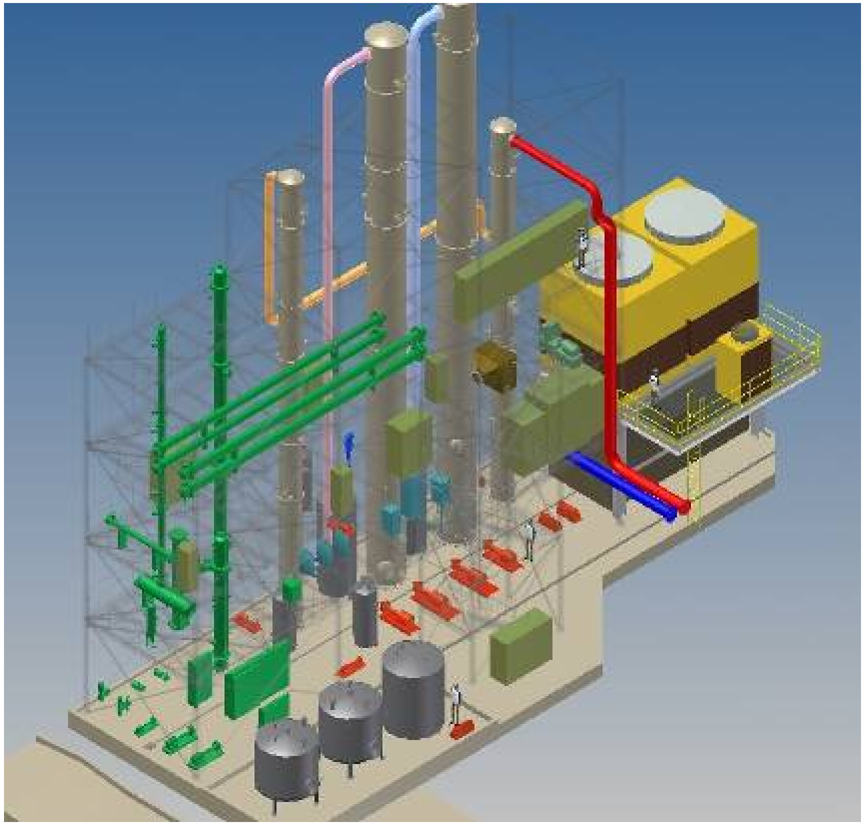
Overall EPRI Monitoring and Analysis at PPPP

Monitor pilot plant operations in sufficient detail to extrapolate the process to full scale (factor of ~400).

- Prepare material flow sheets (Process Characterization)
- Identify opportunities for thermal integration
  - Estimate process thermal requirements and the impact on the host power cycle
  - Estimate other utility and material operating costs
  - Estimate equipment requirements and capital costs
- Develop levelized costs (and uncertainties):
  - Process CO_2 removal costs (\$/tn CO_2)
  - Cost of electricity impact (\$/MWh)

Process Characterization Monitoring

- Utilities Required
  - Cooling Water
  - Chilled Water
  - Steam
  - Auxiliary Power
- Ammonia loss/make-up
- Process water loss/make-up
- Product CO_2 purity
- Fate of SO_2/SO_3, NOx, PM, Hg, HAPs



Questions?

Dick Rhudy, Technical Executive

650-855-2421 / rrhudy@epri.com

IEA Greenhouse Gas R&D Programme

11th MEETING of the INTERNATIONAL POST-COMBUSTION CO2 CAPTURE NETWORK

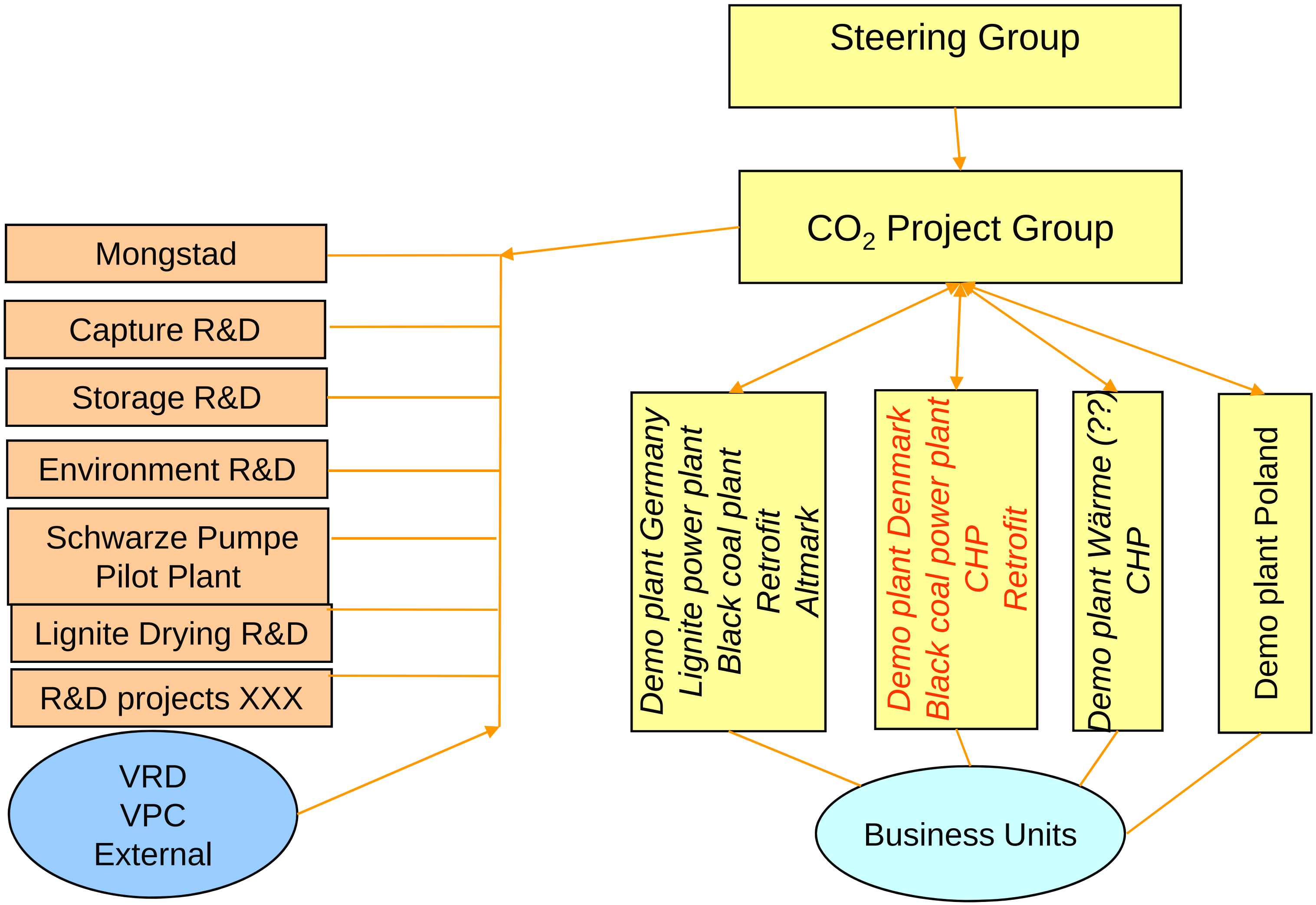
20th-21st May, 2008, Vienna, Austria

Vattenfall’s Demo project at Nordjyllandsværket

Capture, Transport & Aquifer Storage of CO_2

Ole Biede
Vattenfall A/S

Vattenfall's CO$_2$ free Power Plant Project



Steering Group

CO$_2$ Project Group

Mongstad

Capture R&D

Storage R&D

Environment R&D

Schwarze Pumpe
Pilot Plant

Lignite Drying R&D

R&D projects XXX

VRD
VPC
External

Demo plant Germany
Lignite power plant
Black coal plant
Retrofit
Altmark

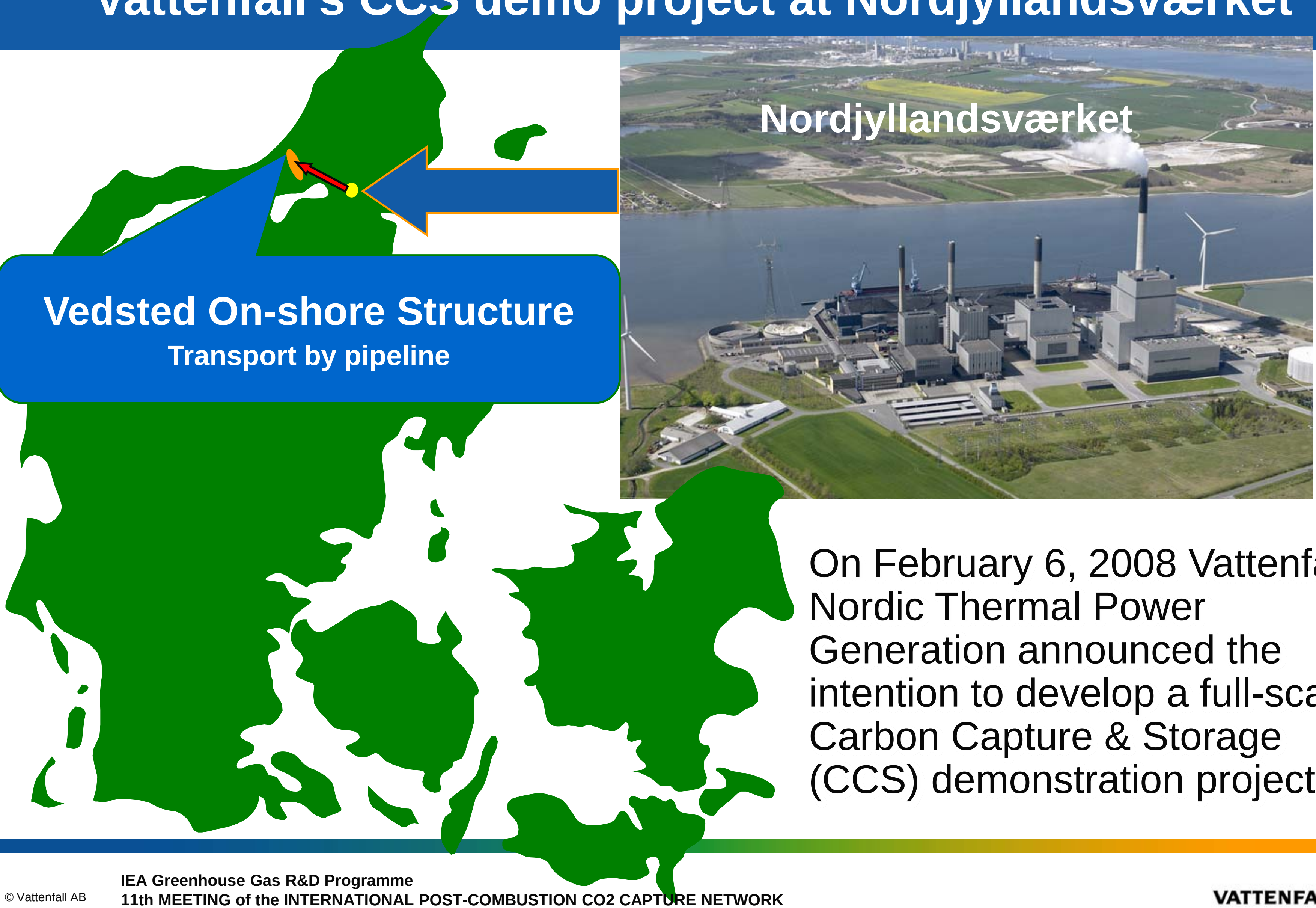
Demo plant Denmark
Black coal power plant
CHP
Retrofit

Demo plant Wärme (??)
CHP

Demo plant Poland

Business Units

Vattenfall's CCS demo project at Nordjyllandsværket



Vedsted On-shore Structure

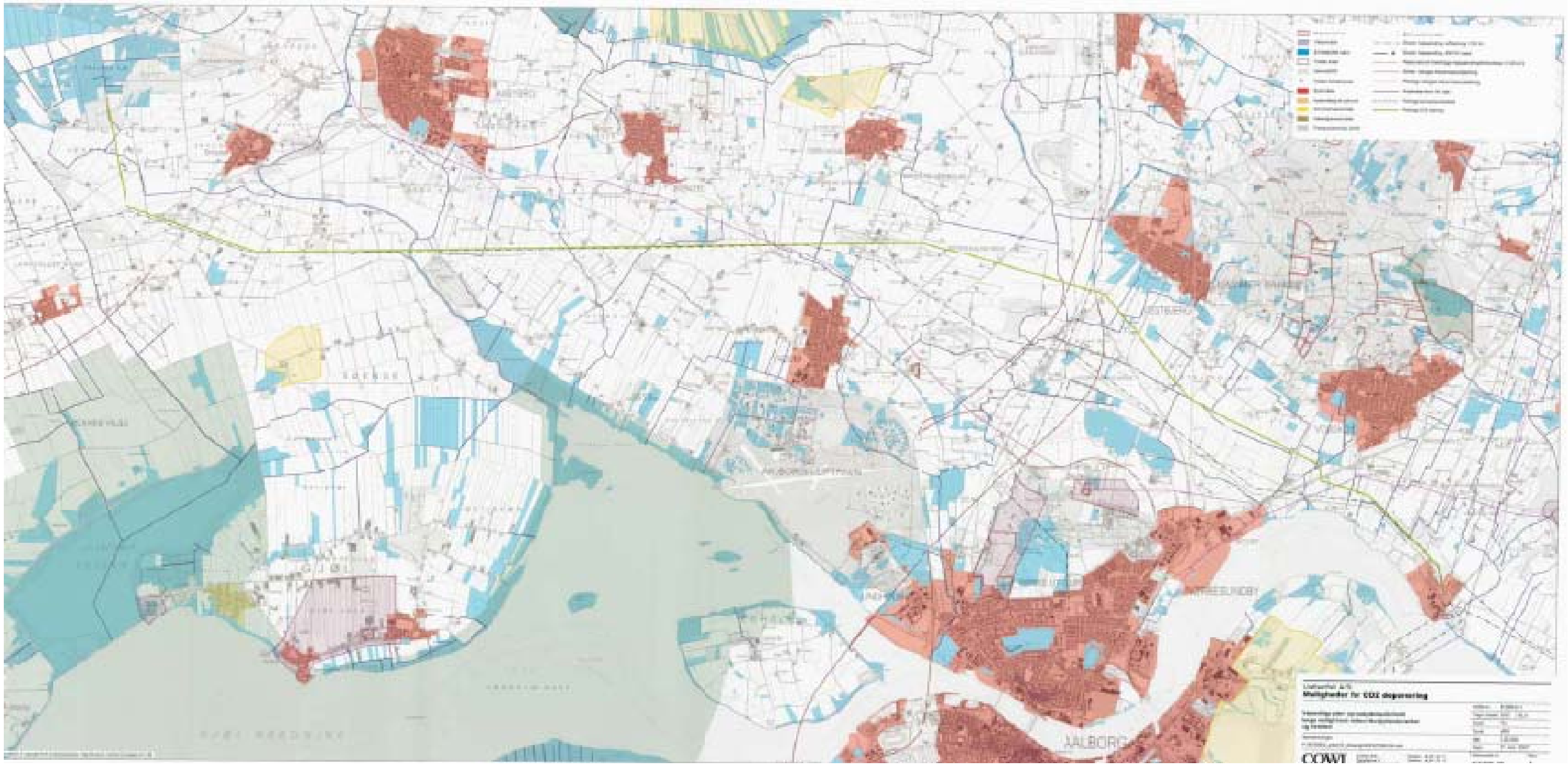
Transport by pipeline

On February 6, 2008 Vattenfall Nordic Thermal Power Generation announced the intention to develop a full-scale Carbon Capture & Storage (CCS) demonstration project

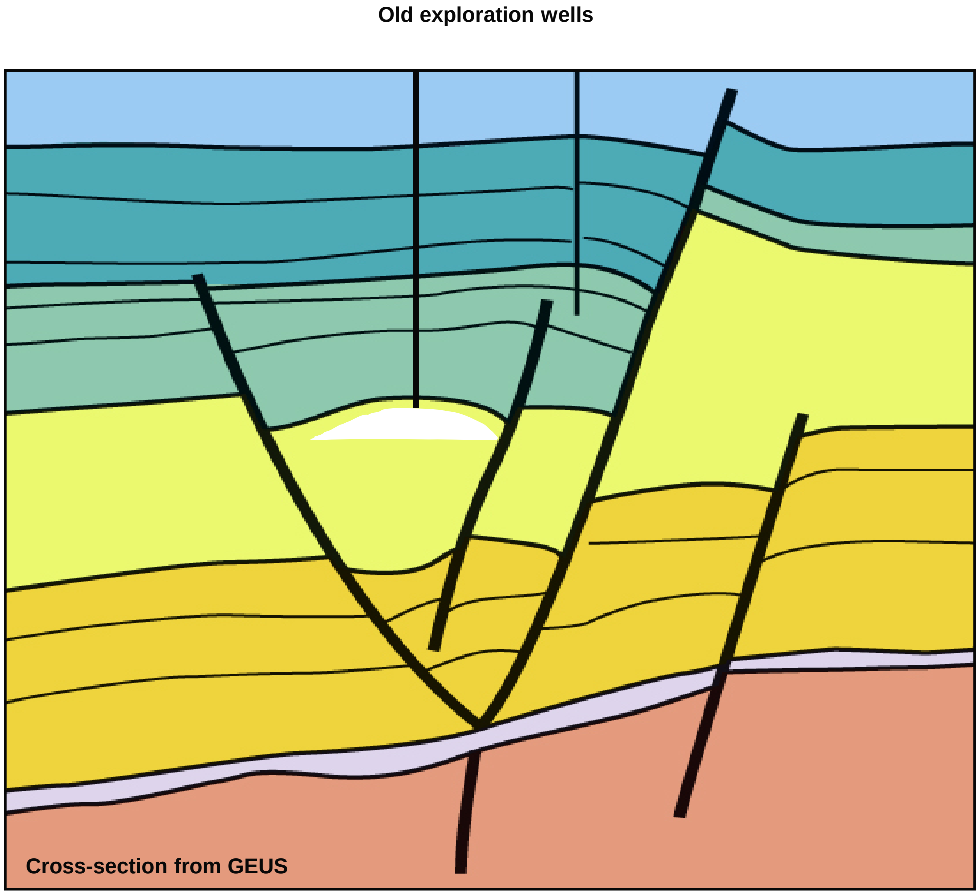
The power plant - Nordjyllandsværket

High efficient 410 MW bituminous coal-fired power unit
1.8 million tonnes of CO_2 per annum

Possible Pipeline Route ~ 30 km / Ø 400 mm



The Vedsted geological structure



Geological storage structure has been investigated by two old oil exploration wells and regional seismic lines

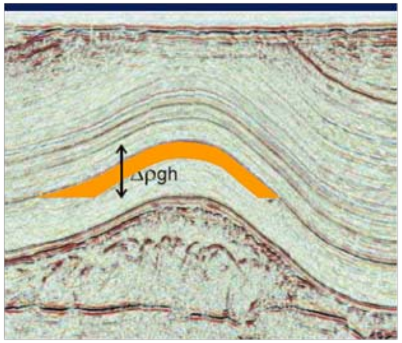
- Anticlinal closure within fault block
- Several sandstone reservoirs of good quality at depths 1200 - 2000 m
- Several thick claystone cap-rock intervals above the reservoirs, plus thick chalk section close to surface
- Expected storage capacity above 100 mil tons

Geology to be investigated for Vedsted

- The potential storage has to be investigated for
  - Structure (Is there a CO2 trap?)
  - Capacity
  - Possible injection rate
  - Tightness of cap rock

- The storage is proven in two steps
  - Seismic investigations (September 2008 to March 2009)
  - Test drillings (March 2009 to March 2010)

CO2 trap



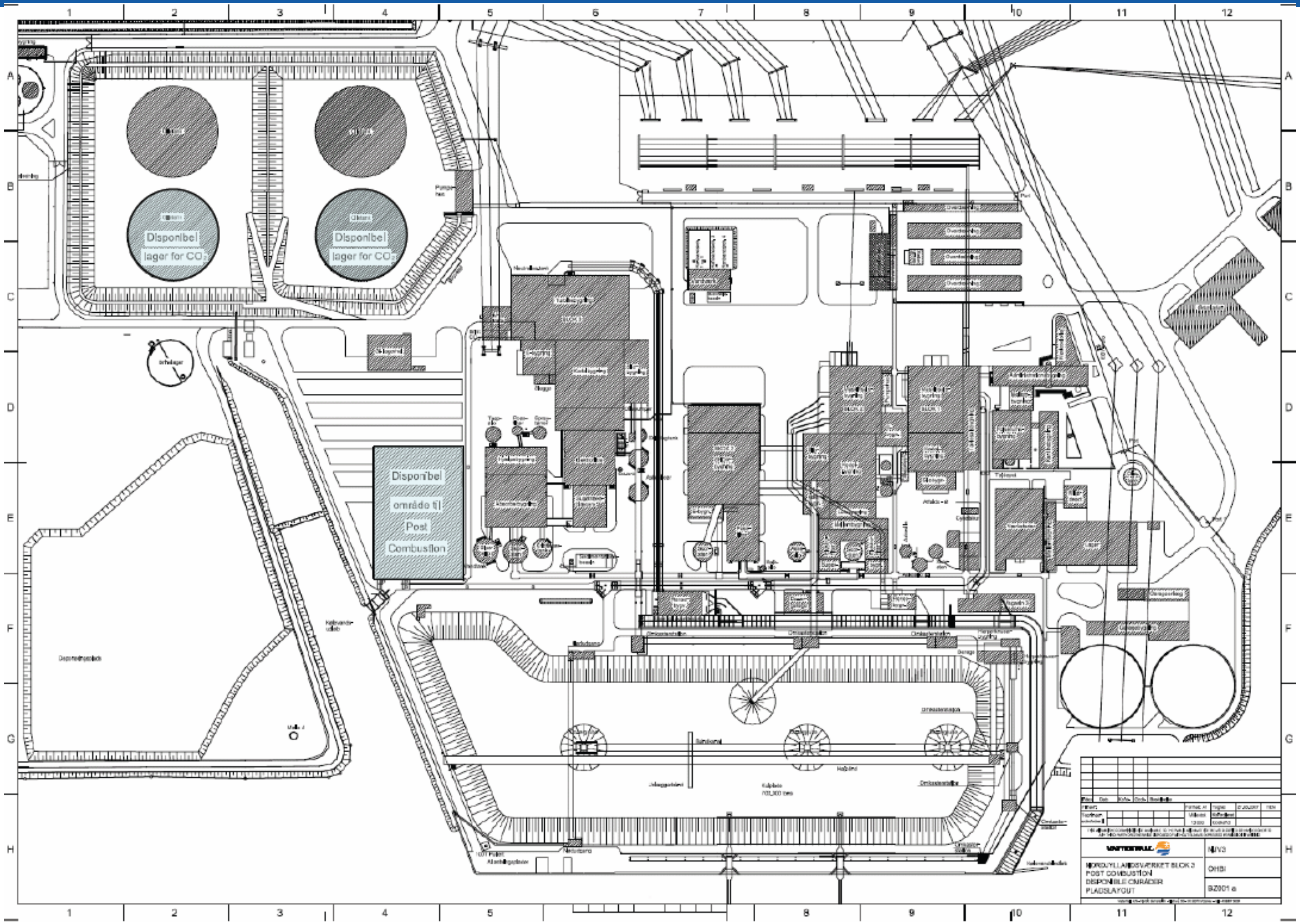
Seismic trucks.
Expected length of tests 150 – 200 km

Nordjyllandsværket - Main Technical Data

- Electrical output gross: 410 MW
- Max. output of district heat: 420 MJ/s
- Total efficiency in back pressure mode: 91 %
- Efficiency in condensing mode: 47 %

- Flue gas data before capture plant
  - CO2: 13 – 14 v-%
  - O2: 4.5 – 5 v-%
  - SOX: 15 – 25 mg/Nm3
  - NOX: 100 mg/Nm3
  - Temperature: 52ºC

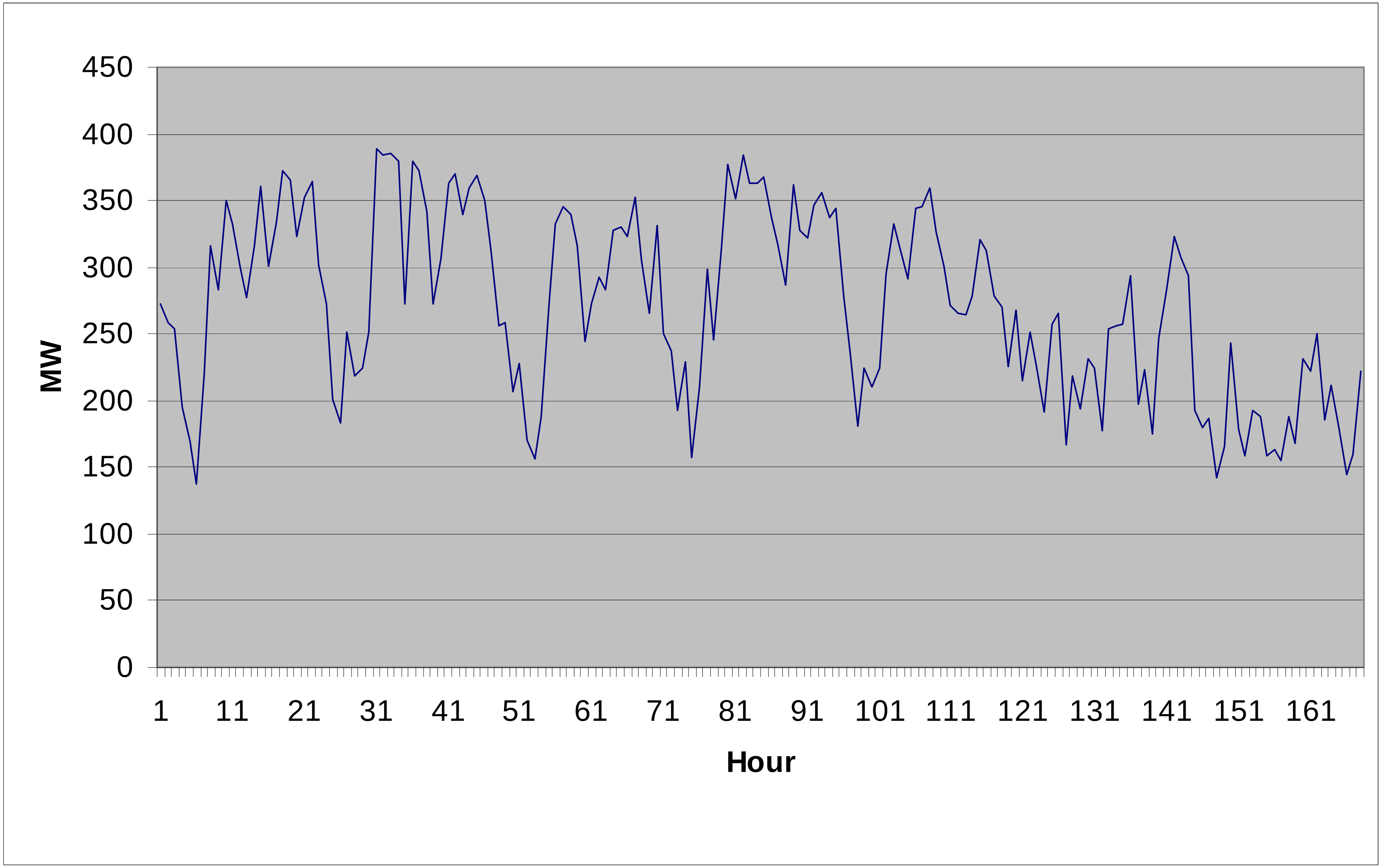
Nordjyllandsværket – layout



Capture plant - important performance issues

- Low energy and capacity loss
- Ability to maintain same district heating capacity as today
- High flexibility
  - big operation range (35 – 100% load)
  - high load change rate gradients (4% pr minute)
  - possibility to shut of capture plant to produce more electricity at peak loads

Nordjyllandsværket Unit 3 - Load week 34 2007



Timeline

- Seismic surveys 2008
- Test drilling 2009
- Capture project preparation 2008 - 2010
- Investment decision and Contract Award 2010
- Start of Operation late 2013

Thank you for the attention

11th Meeting International Post-Combustion CO_2 Capture Network

Vienna, Austria

2008 May 21

Lisa Rimpf
Research Engineer
Babcock & Wilcox Research Center

McDermott International, Inc.

J. Ray McDermott

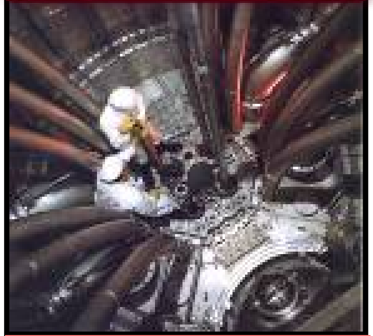
Providing solutions for offshore field development to the worldwide oil and gas industry

The Babcock & Wilcox Company

B&W Nuclear Operations Group

- **Government Reactors**
- **Weapons-Grade Uranium Management**

B&W Technical Services Group



- **Nuclear Research**
- **Nuclear Weapons Programs**

B&W Nuclear Power Generation Group

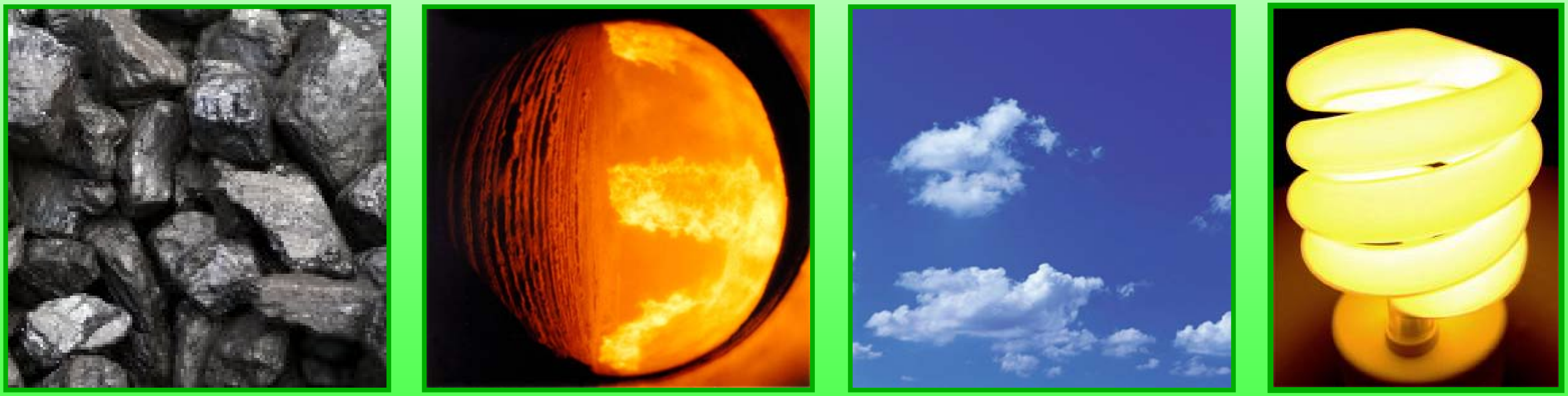
- **Nuclear Products**
- **Nuclear Services**
- **Nuclear Construction**

B&W Power Generation Group

- **Power Plant Design**
- **Field Engineering**
- **Construction Company**
- **Environmental Equipment**

Carbon Management Portfolio

- Post-Combustion Capture
- Oxycoal Combustion
- Advanced Ultra-Supercritical Boilers



Oxycoal Combustion Demonstration

- Managed and funded by B&W, American Air Liquide, Inc. and Utility Advisory Group
- Clean Environment Development Facility: Alliance, Ohio

AIR LIQUIDE

AEP

AES

BASIN ELECTRIC POWER COOPERATIVE

FirstEnergy

EPRI

minnesota power

MidAmerican ENERGY

MONTANA-DAKOTA UTILITIES CO.

SaskPower

PACIFICORP ENERGY

SOUTHERN COMPANY

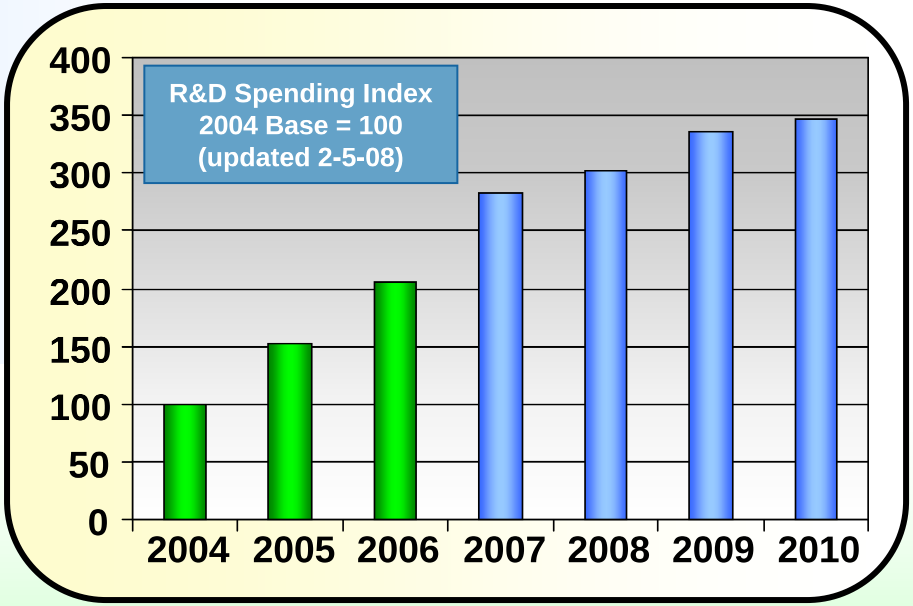
- 30 MW_t
- Coal
  - Eastern Bituminous
  - Sub-Bituminous: Powder River Basin
  - Saskatchewan Lignite
- Ready for Deployment

New Research Center

Significant enhancement of capabilities to develop, verify and deploy new, utility-focused technologies

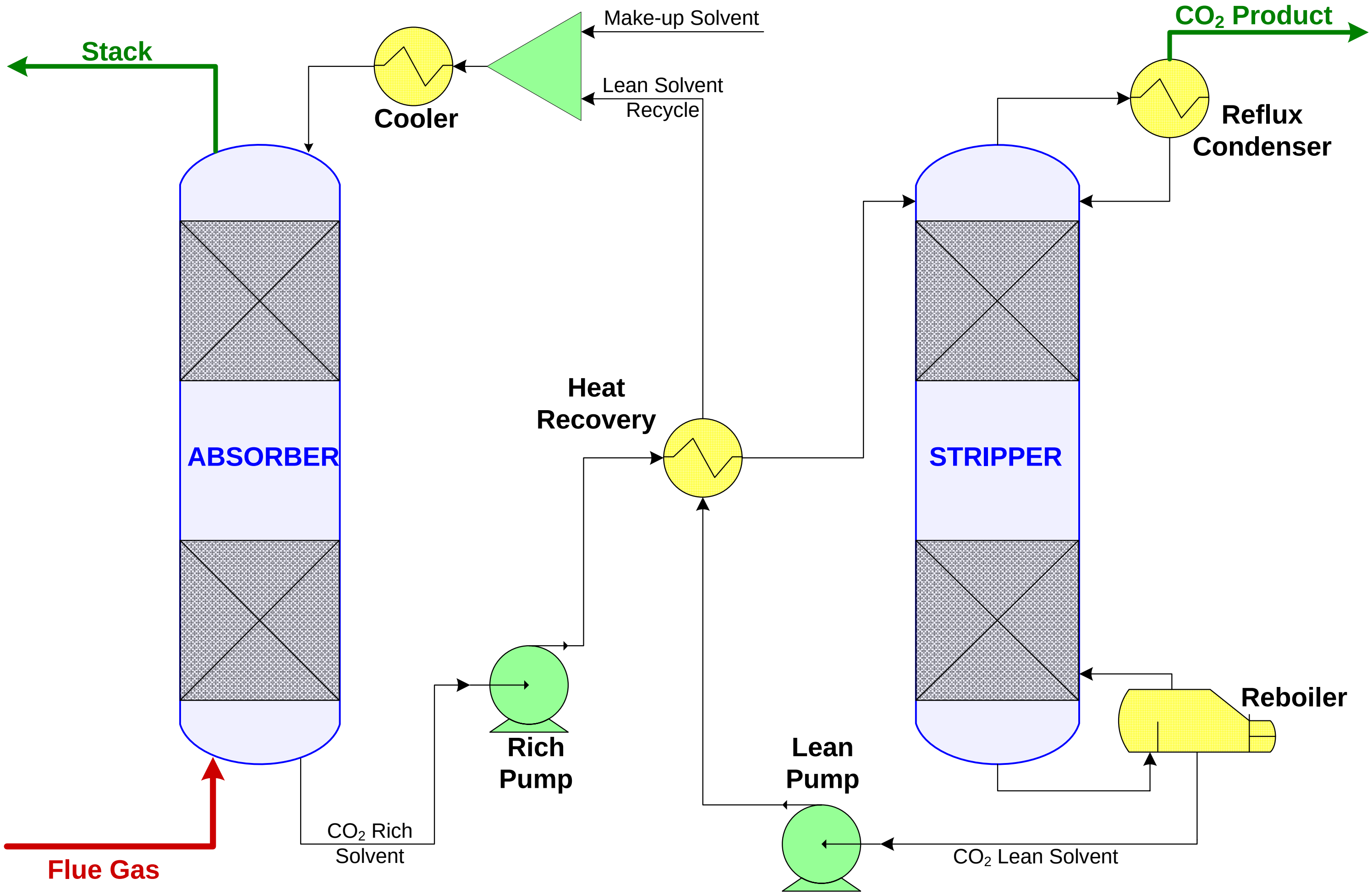
The Babcock & Wilcox Research Center
Inaugurated on August 15, 2007

This facility is dedicated to all past, present and future employees of The Babcock & Wilcox Research Center. Their technological expertise, commitment and inventive spirit fuel the innovation furnaces of our company. Through their efforts, we generate powerful solutions to improve our world, now and in the future.

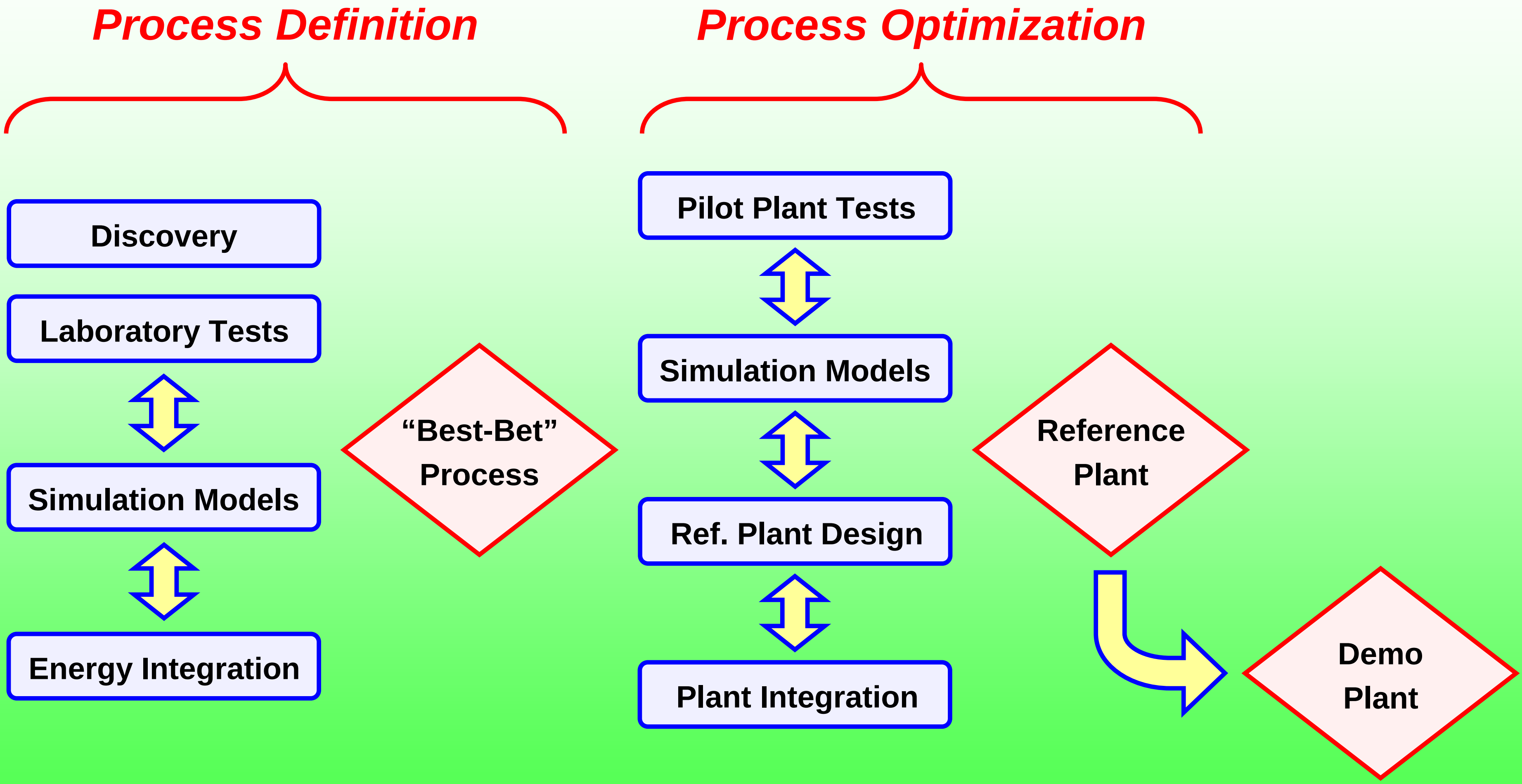


More than tripled research and development spending since 2004 to advance existing and novel technologies for <u>future</u> growth

Regenerable Solvent Absorption Technology RSAT™



RSAT Development Logic



Process Definition

Discovery

Laboratory Tests

Simulation Models

Energy Integration

"Best-Bet" Process

Process Optimization

Pilot Plant Tests

Simulation Models

Ref. Plant Design

Plant Integration

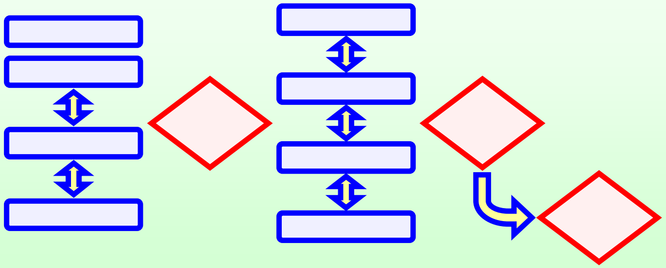
Reference Plant

Demo Plant

RSAT Development Progression

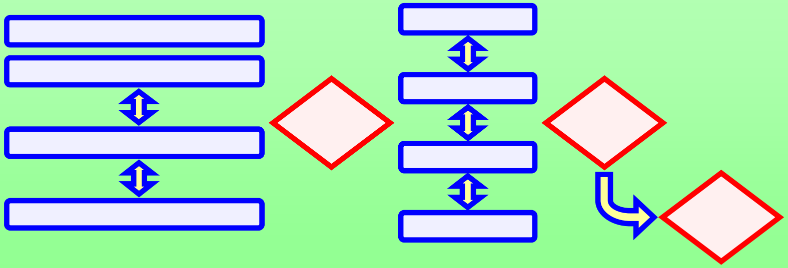
1st Generation

- Available solvents, promoters
- Process energy integration



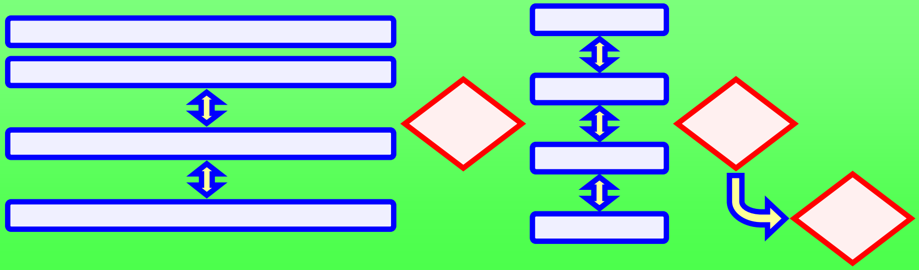
2nd Generation

- Novel solvents, promoters, catalysts
- Extensive process energy integration



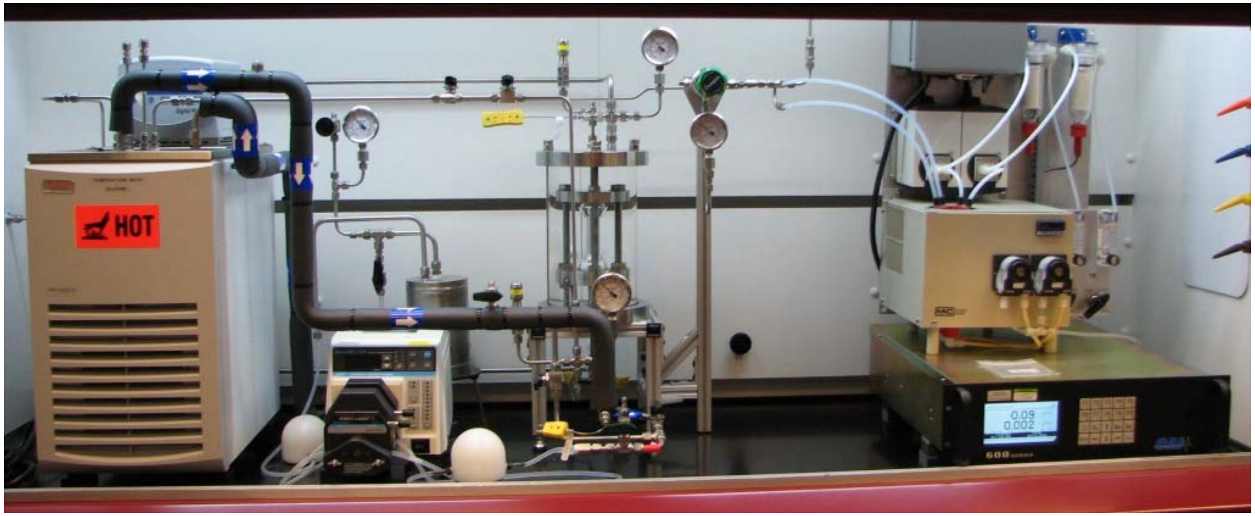
3rd Generation

- Optimized solvents, promoters, catalysts
- Full power plant energy integration



CO_2 Control Lab: Wetted-Wall Column

- Cylindrical Falling-Film Gas/Liquid Contactor
- Fundamental Evaluation:
  - Mass Transfer
  - Chemical Kinetics
- Data for Aspen Plus® Modeling
- Qualitative & Quantitative Comparison



CO_2 Control Lab: Glass Absorber/Regenerator

- **Solvent Characterization**
- **Feasibility Studies**
- **Integrated Process**
- **Glass Columns: Modular Construction**
  - **5cm Inner Diameter**
  - **1.5m Height**
  - **Random *or* Structured Packing**
- **Flow Rates: Flexibility**
  - **~ 0.9 kg/hour CO_2 Capture**
  - **~ 0.3 liters/min Solvent**

B&W RSAT Pilot Plant

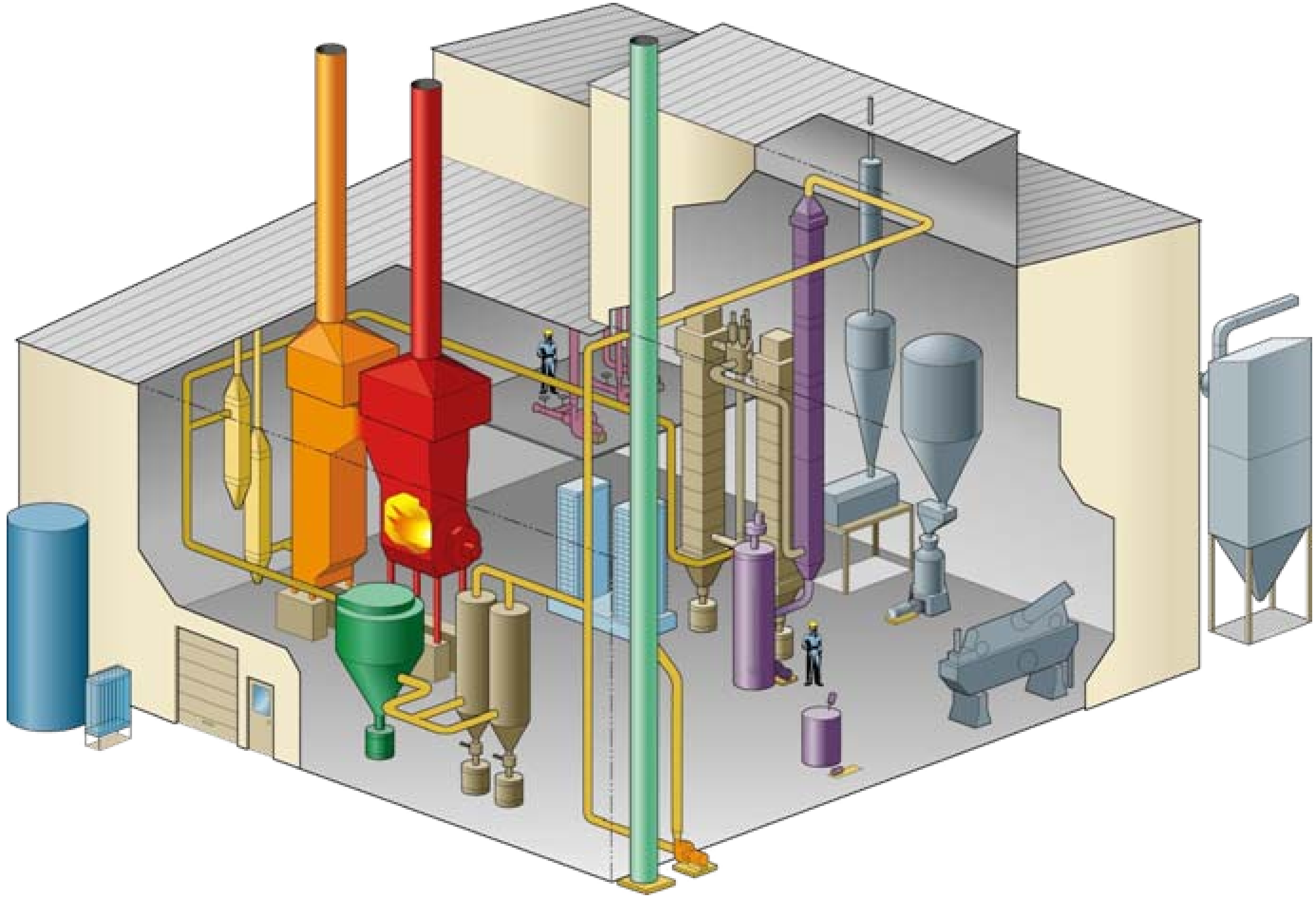
Features

- Fully integrated RSAT process
    - Flexible
    - Well instrumented
- Significant scale: 7 tonnes/day CO_2 (~0.9 MW_t)
- Operation on coal, or synthetic, flue gas

Absorber and Regenerator Columns

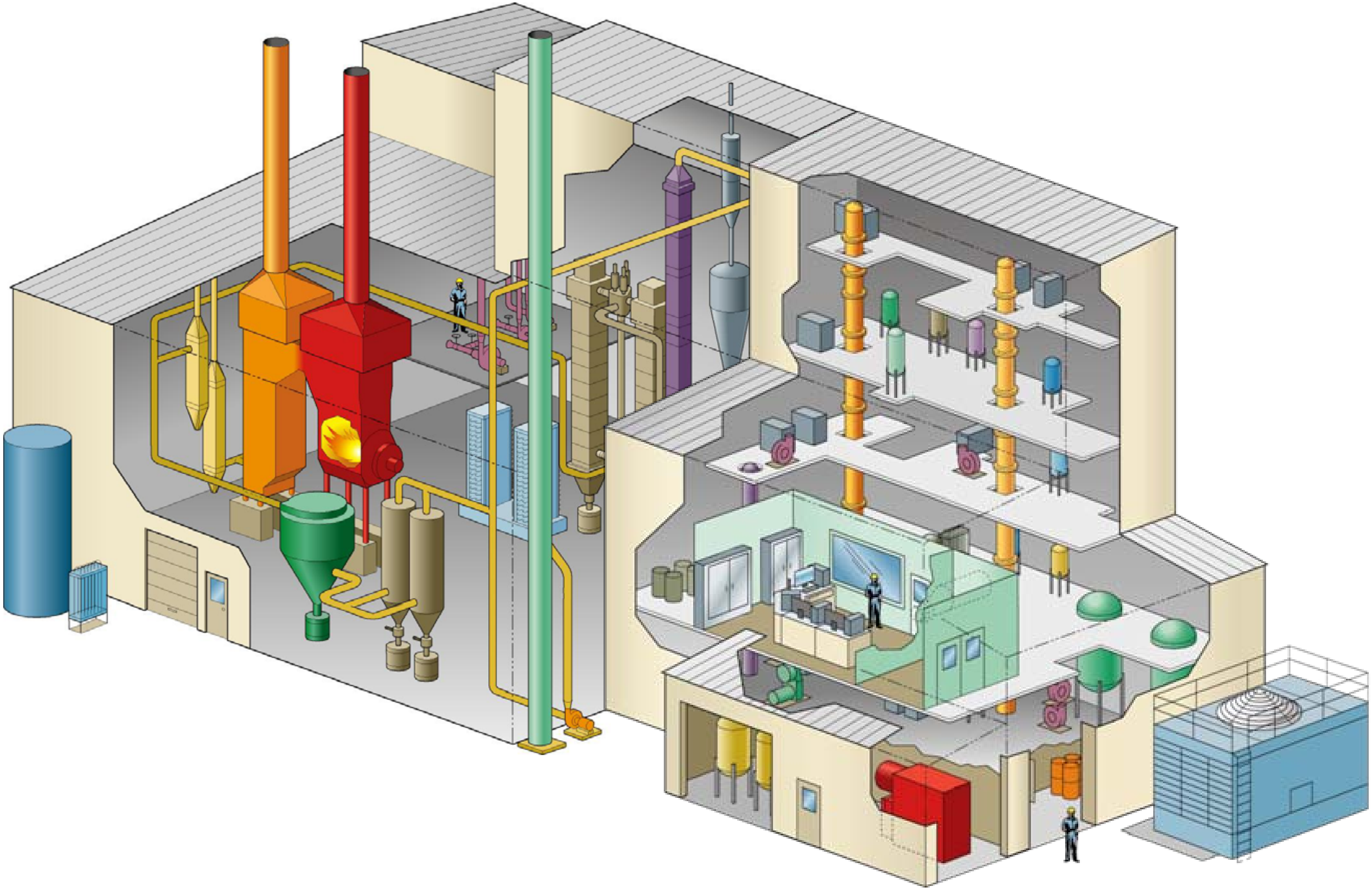
- 61 cm diameter x 20 m high
- Design pressure: 1.14 MPa @ 230 C
- Structured packing

Small Boiler Simulator (SBS)



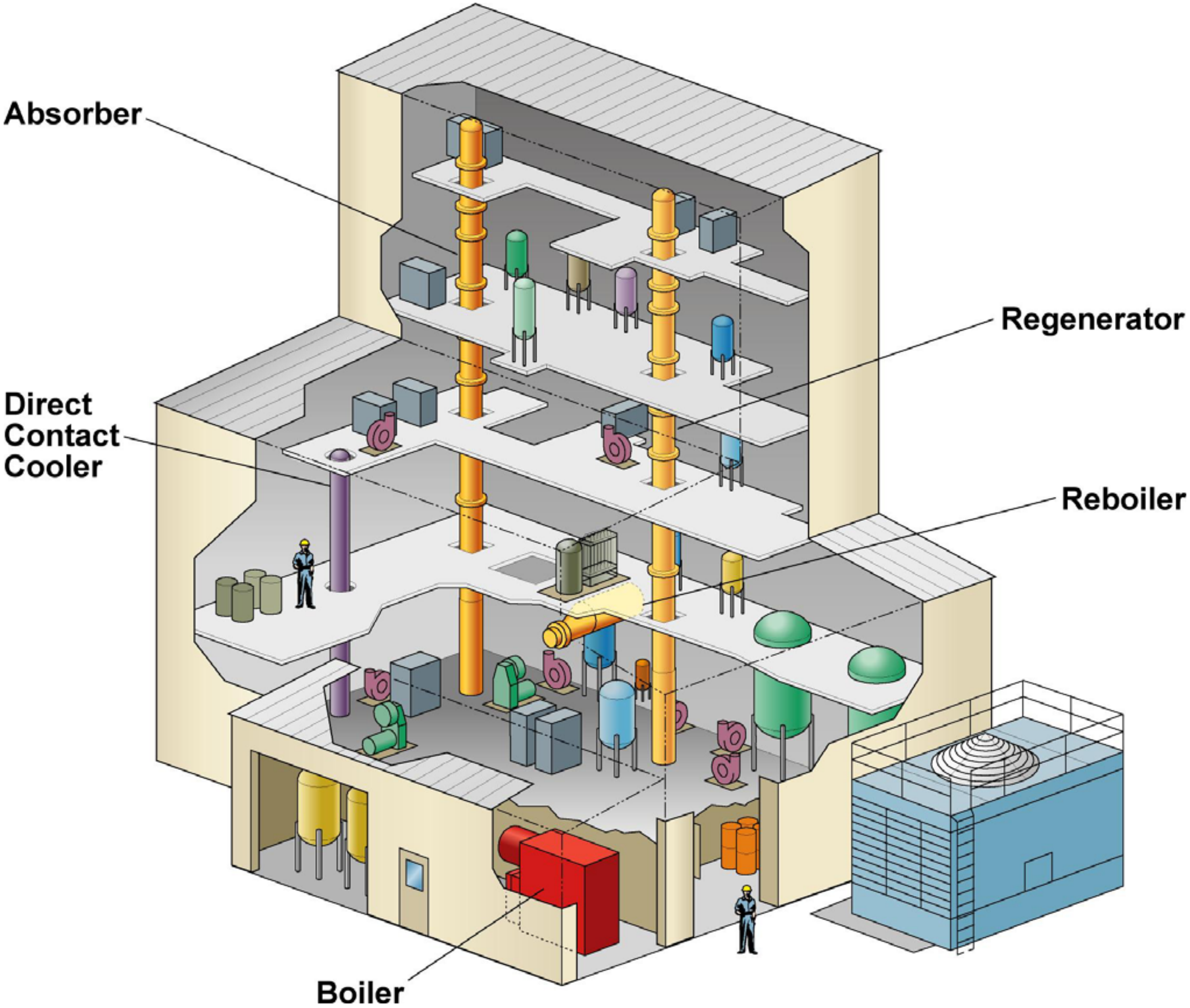
Replicates an electric utility power plant from the coal pile to the stack.

RSAT Installation at SBS

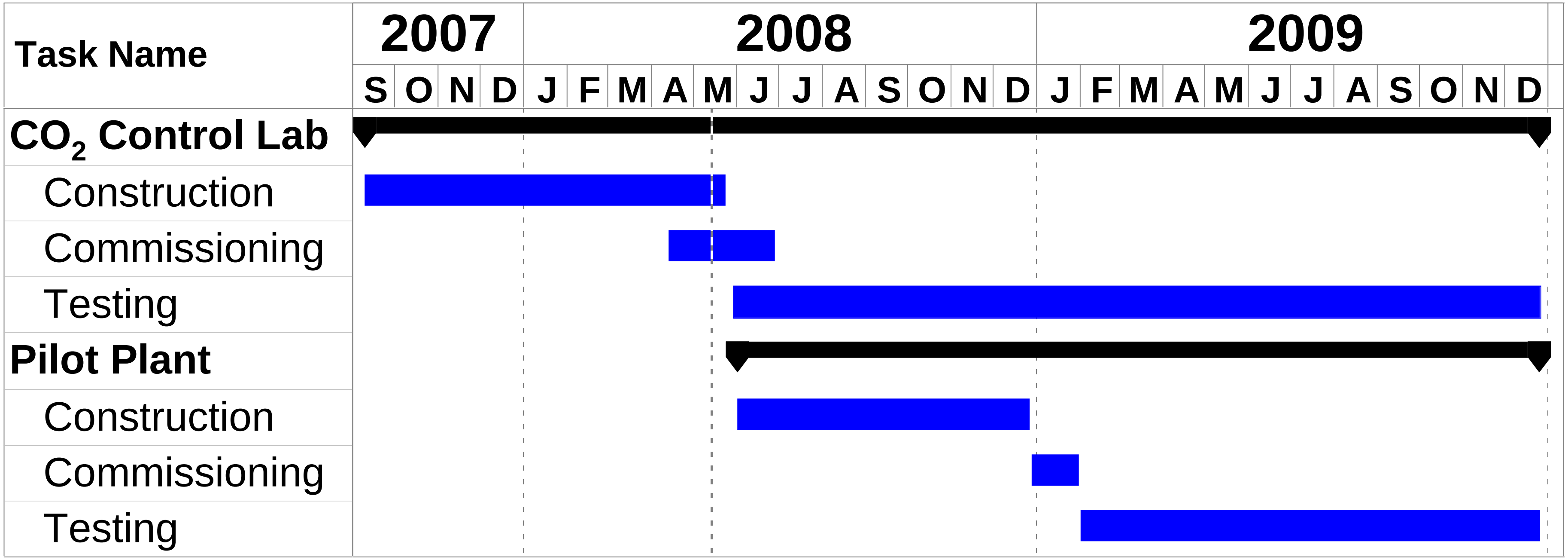


RSAT Pilot Facility

- **Modular Construction**
- **Auxiliary Steam Boiler**
- **Kettle Reboiler**
- **Solvent Storage**
- **Cooling Water Tower**
- **Control Room**



Schedule


Task Name
2007
2008
2009
S O N D J F M A M J J A S O N D J F M A M J J A S O N D
CO₂ Control Lab
Construction
Commissioning
Testing
Pilot Plant
Construction
Commissioning
Testing

"We are passionate about innovation and technology leadership"

B&W
power generation group

Econamine FG Plus^{SM} Technology for Post-Combustion CO_2 Capture

Satish Reddy

FLUOR®

Presented at: 11th Meeting of the International Post-Combustion CO2 Capture Network
May 20th - 21th, 2008, Vienna, Austria

Agenda

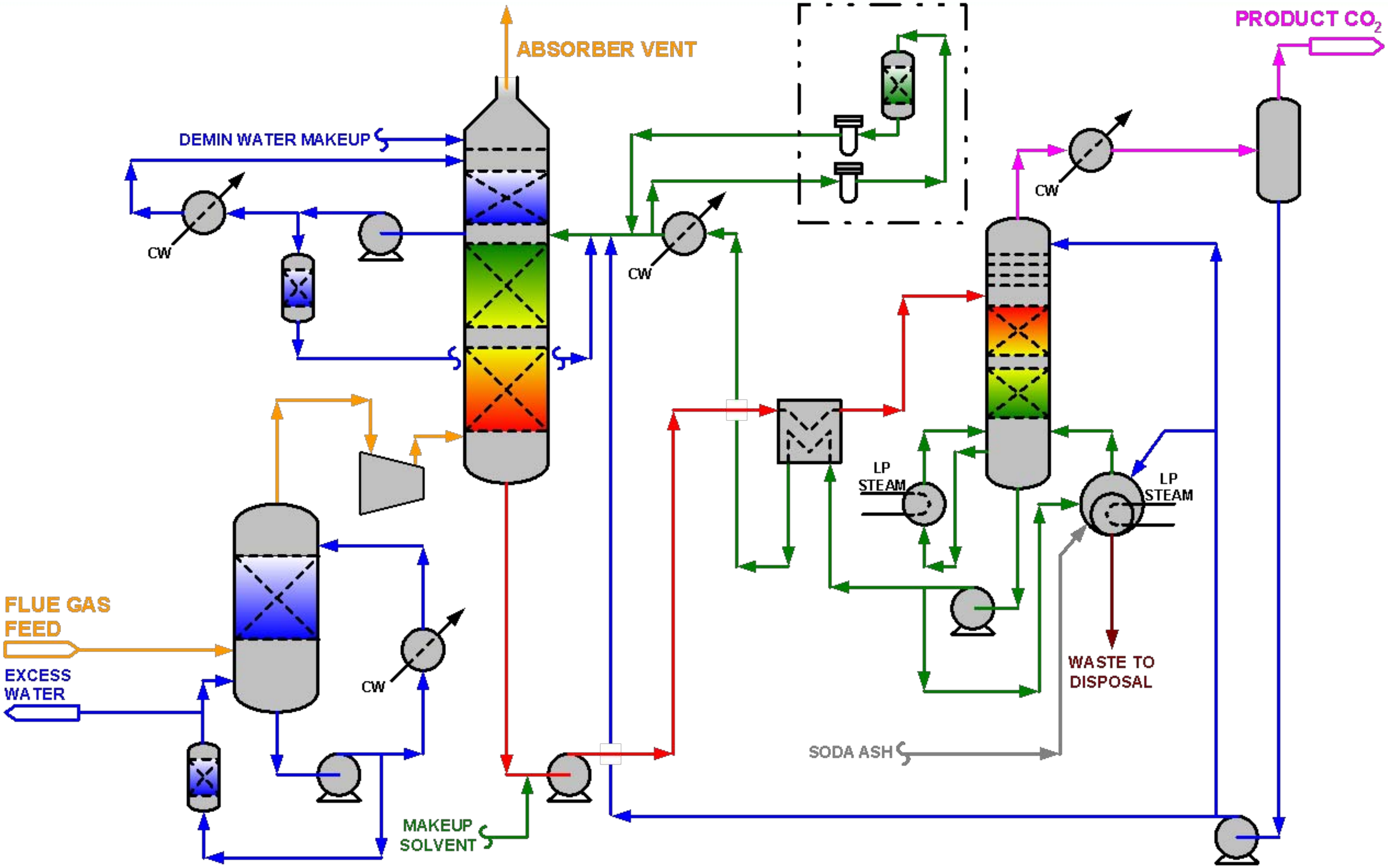
- Econamine FG+^{SM} technology background
- Commercial plant experience
- Enhancements to Econamine FG Plus^{SM} technology
- Strategies for CO_2 Capture from Large Power Plants

Econamine FG+^{SM} Technology

Econamine FG+^{SM} Technology Background

- Econamine FG+^{SM} (EFG+) technology permits large-scale CO_2 capture from low-pressure, oxygen containing streams, such as flue gases
- The EFG+ solvent is based on Monoethanolamine (MEA)
- Plant operating experience has shown that there is virtually no corrosion

Typical Econamine FG+ ^{SM} Flowsheet



FLUOR®

Commercial Plant Experience

FLUOR®

Commercial Experience

- World-wide licenses to date: 24 plants
- Plants/Licenses on order: 10
- CO_2 concentrations from 3% to 20% v/v
- O_2 Concentrations from 1 to 15% v/v
- Only process that has commercially demonstrated CO_2 recovery from a gas turbine exhaust (13 to 15% v/v O_2)
- Several units installed on boilers and steam reformers in Ammonia and Methanol plants

FLUOR®

Reference Plant: Florida Power and Light

Project Profile

- Plant location: Bellingham, MA
- Capacity 330 t/d
- CO_2 Concentration: 3.5% v/v
- O_2 Concentration: 13 to 14% v/v
- 100% air cooled
- Product Usage: Food-grade CO_2

FLUOR®

Bellingham Plant Ground View

Process Enhancements: Econamine FG Plus^{SM} Technology

Enhancements to Econamine FG Plus^{SM} Technology

- Fluor is continuously improving the EFG+ process to has lower energy consumption and solvent losses
- Menu of advanced features are available to customize each project:
  - Enhanced solvent formulation
  - Fluegas Pre-Treatment
  - Absorber Intercooling
  - Lean vapor compression configuration
  - Advanced reclaiming technologies
  - Heat integration with the power plant

Improved Solvent Formulation

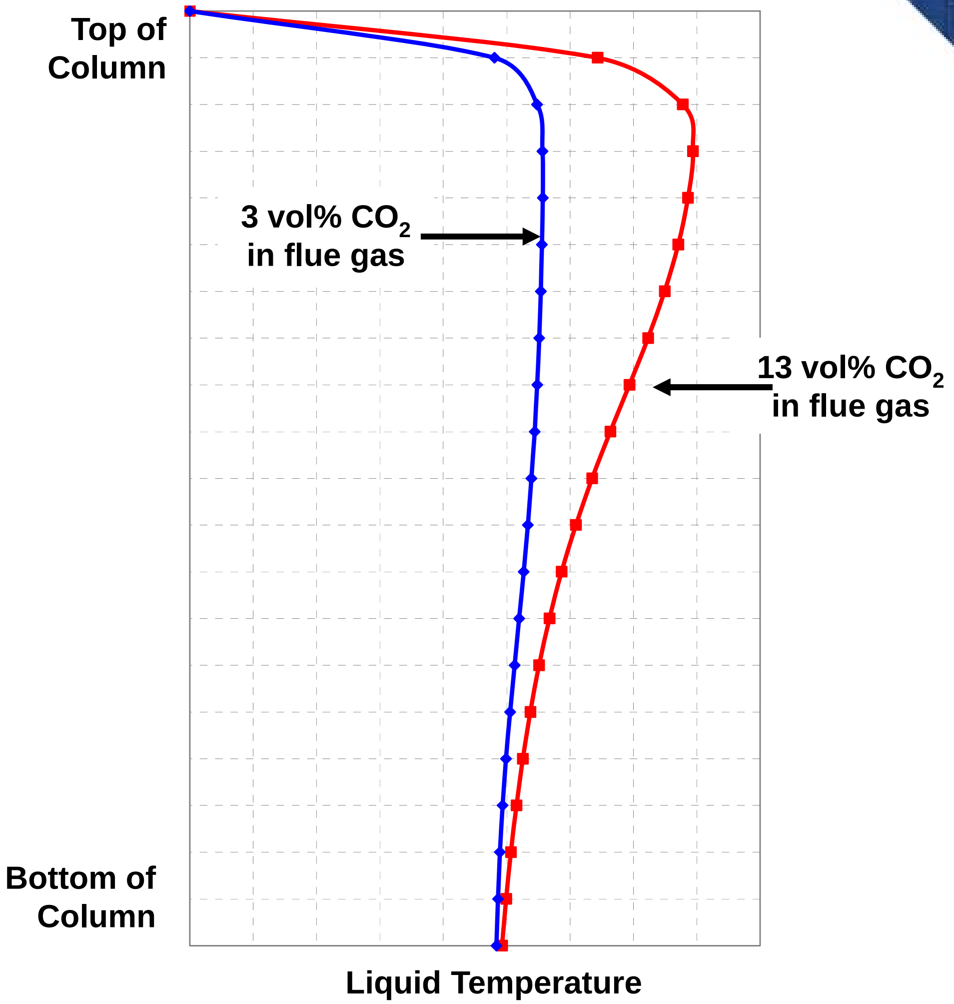
- Generic MEA based plants operate at low concentrations: 18-20 wt%
- Econamine FG operated with 30% MEA
- Econamine FG+ has an improved solvent designed with MEA concentration greater than 30 wt%
  - Increased reaction rates
    - Less absorber packing required
    - Lower capital cost
  - Higher solvent carrying capacity
    - Lower solvent circulation rates
    - Lower steam requirements
    - Lower capital cost on circulation equipment

Fluegas Pre-treatment

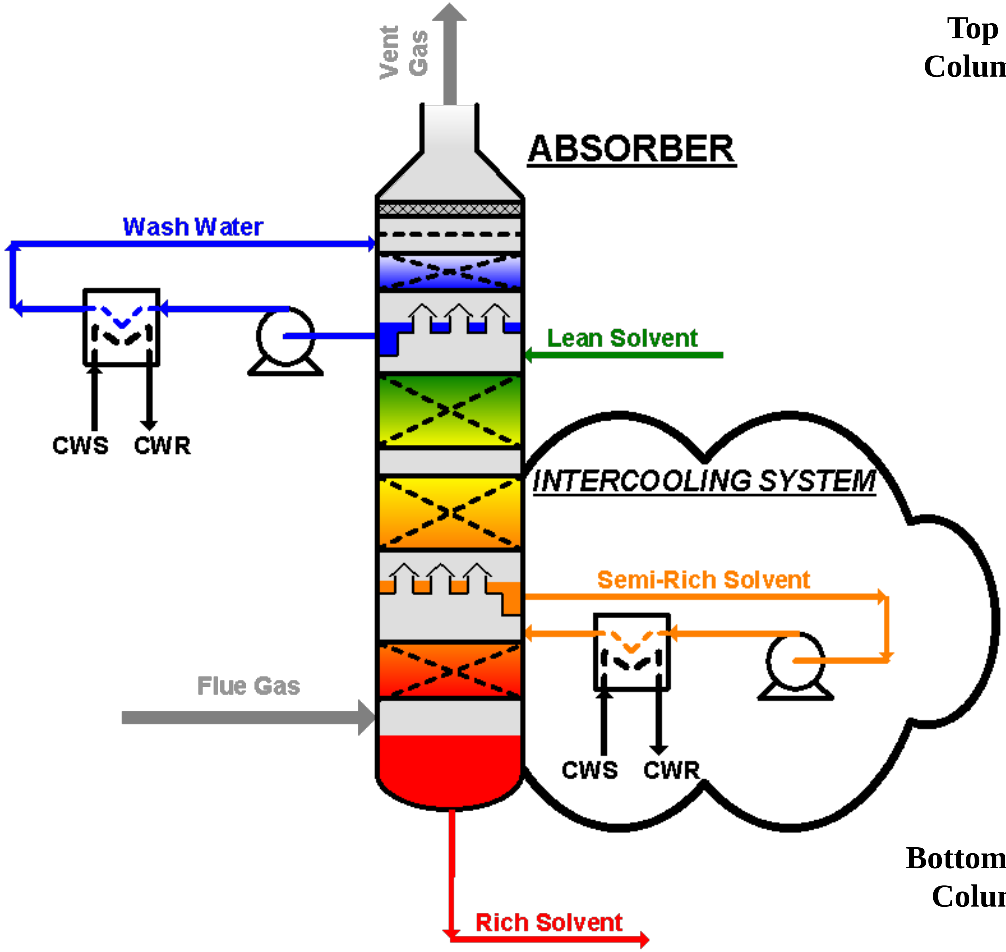
- Removal of SOx, NO_2 and particulate matter from fluegas is essential for minimizing solvent losses
- Fluor has developed SOx and NO_2 removal systems that are integrated with the Direct Contact Cooler (DCC)
  - Reduces capital cost
  - Minimizes plot Space
- A proprietary design of the DCC minimizes waste production by recovering combustion water

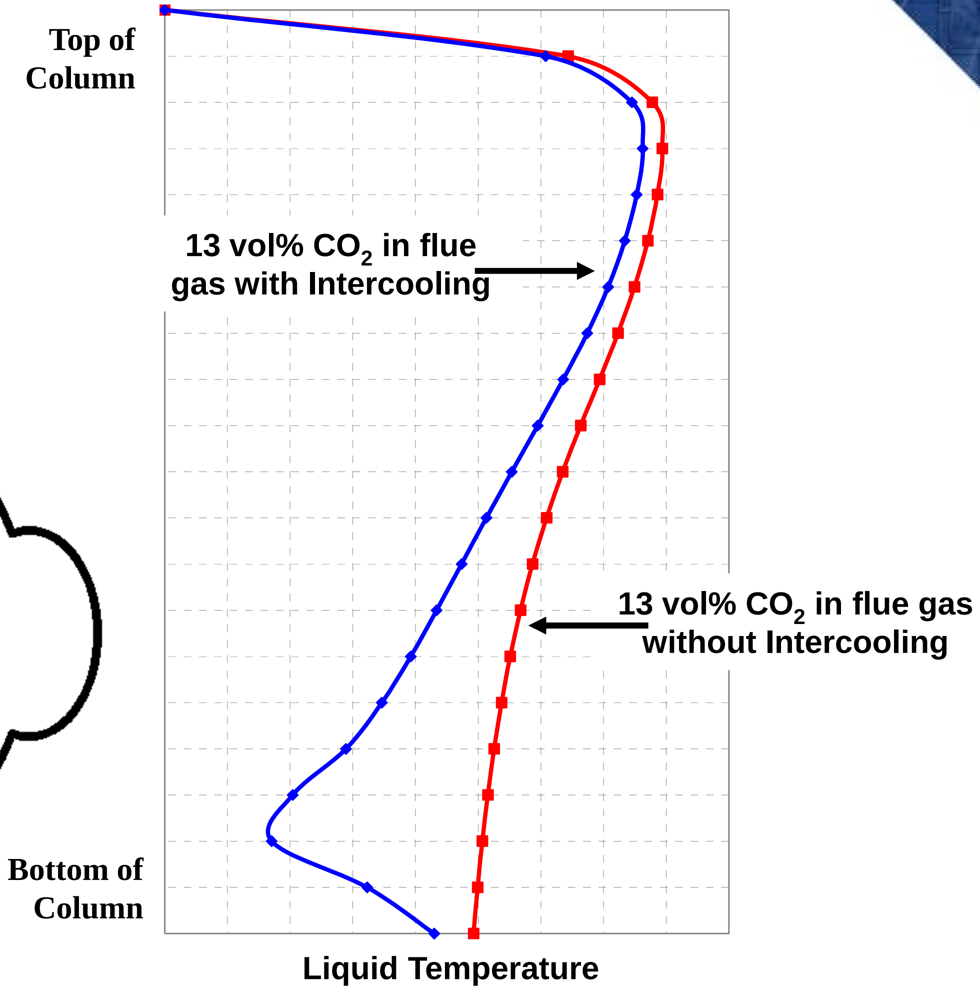
Absorber Intercooling

- Heat released in absorber due to heat of reaction
- Higher flue gas CO_2 concentrations lead to higher operating temperatures
  - Faster reaction kinetics
  - Lower solvent carrying capacity
- Optimum temperature profile
  - Higher temperature at top
  - Lower temperature at bottom



Absorber Intercooling



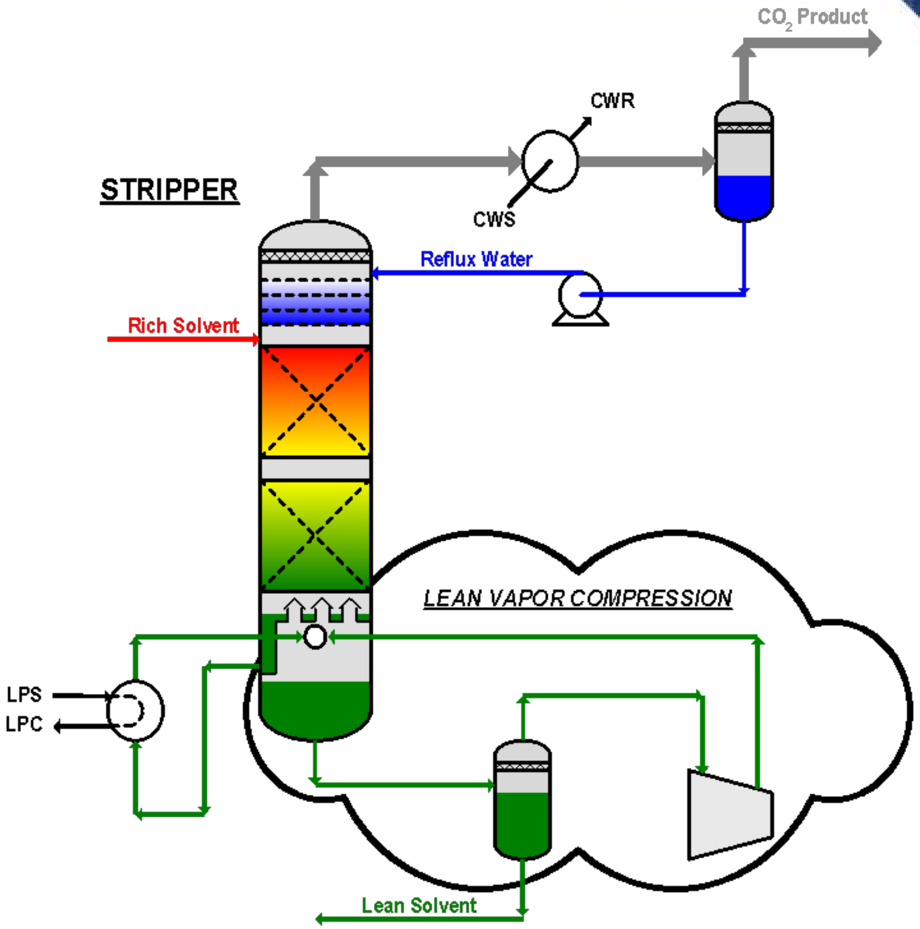


Absorber Intercooling Results

- Higher solvent carrying capacity at bottom of absorber
  - Lower solvent circulation rate
  - Lower steam consumption
  - Lower capital cost on circulation equipment
- Higher CO_2 absorption rate
  - Smaller absorber diameter
  - Lower capital cost
- Patent application pending

Lean Vapor Compression

- Lower steam consumption
- Lower cooling water requirement
- Patent application is pending



FLUOR®

Advanced Reclaiming Technologies

- Previously, EFG plants were designed with a thermal reclaimer
  - Degradation of solvent occurred because of high temperature and residence time
- New processes for low temperature reclaiming have dramatically reduce solvent losses
  - Ion-exchange reclaiming efficiently regenerates solvent from heat stable salts
  - A low-residence time, atmospheric reclaiming process to remove heat stable salts and minor amounts of degradation products that could form

Integration with Power Plant

- Three potential strategies exist for power plant integration
  - Flue gas reboiler
    - Eliminate steam demand
    - Reduces both size and cooling load on DCC
  - Vacuum condensate heating or district heating
    - Improves heat rate of the combined facility and reduces the cooling load on the EFG+^{SM} plant
  - Supplemental duct firing in Natural Gas Combined Cycle Power Plants (patent pending)
    - Raises steam for CO_2 Capture in the HRSG
    - Decreases flue gas O_2 concentration
    - Increases flue gas CO_2 concentration

FLUOR®

Strategies for CO_2 Capture from Large Power Plants

FLUOR®

Minimum Number of Process Trains

- Large-scale CO_2 sequestration projects often require multiple absorption trains, resulting in higher CAPEX and larger plot space
- Plot availability can also play a vital role in a project feasibility for retrofit application
- Fluor is focused on strategies to minimize the number of trains
  - Large diameter absorber design (20 m diameter)
  - 1000 MW coal based power plant requires two absorption trains
  - Plate and frame exchanger train minimization

Large Column Design

- Fluor has standardized the design of large absorbers to 20 meters in diameter. Experience from design of large vacuum columns (refining) has been applied.
- Gas and liquid distribution has been studied and optimized using Computational Fluid Dynamics (CFD)
- Optimum cross-sectional shape of the column for liquid distribution is circular
- Proprietary non-metallic construction has been developed and is being implemented in a demo plant
- The CAPEX of a non-metallic column is about 40% of the conventional absorber.
- Very rapid construction of the absorber is possible.

Fluegas Inlet: Design for Excellent Distribution

- Vapor mal-distribution should be avoided
- Primary considerations in the design of the absorber vapor inlet
  - Kinetic energy of incoming gas
  - Vertical clearance between vapor inlet and bottom absorption bed
- Ducting layout between Blower and Absorber plays key role

Large Reboiler Design

- Experience gained from designing reboilers in large refining and petrochemical applications
- Largest reboiler built by Fluor is used as a reference design
- Reference reboiler has a size in excess of 3000 m^2/shell

Reboiler Reference Design

Summary

- EFG+ is a proven, cost effective process for the removal of CO_2 from low-pressure, oxygen containing flue gas streams
- The EFG+ technology has a menu of advanced features that resulting in:
  - Low energy consumption (Typical 1270 Btu/lb CO_2 for USC Coal-based power plant; Texas Location)
  - Low solvent and chemical costs
  - Friendly environmental signature
  - Reduced footprint
- Reference designs are available for:
  - Absorbers to 20 m diameter
  - Reboilers with size in excess of 3000 m^2/shell

FLUOR®

Summary

The Econamine FG+ technology is ready for full scale deployment in:

- Gas and Coal-fired Power plants
- In refineries and fertilizer plants on large furnaces

Contacts

- Dr. Satish Reddy

  Executive Director, Process Technology
  Fluor Corp, Aliso Viejo, CA
  +1 949-349-4959
  satish.reddy@fluor.com

FLUOR®

Questions

Any Questions?

11th MEETING
of the
INTERNATIONAL POST-COMBUSTION CO2 CAPTURE NETWORK

Post Combustion Systems

Coal Fired Pilot Plant and Multipollutant Control

MITSUBISHI HEAVY INDUSTRIES, LTD.

Masaki Iijima

20th -21st May, 2008 Vienna, Austria

CONTENTS

1. MHI’s Commercial Achievements

MHI’s Operating Commercial CO2 Capture Plants

Malaysia

Client: Petoronas
Start-up: 1999~
CO2 Source:
Nat. Gas Reformer
Capacity: 200 t/d
Product: Urea

India

Client: IFFCO
Location: Aonla
Start-up: Dec 2006~
CO2 Source:
Nat. Gas Reformer
Capacity: 450 t/d
Product: Urea

Japan

Client: Chemical Co.
Start-up: 2005~
CO2 Source:
Nat. Gas Boiler
Capacity: 330 t/d
Product: General use

India

Client: IFFCO
Location: Phulpur
Start-up: Dec 2006~
CO2 Source:
Nat. Gas Reformer
Capacity: 450 t/d
Product: Urea

MHI’s Recently Awarded Commercial Projects

OTHER PROJECTS	Abu Dhabi	India	Bahrain	‘Asia’	China
Project Status	Under Construction	Under Construction	Under Construction	Under Construction	FEED Complete
Flue Gas Source	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Boiler
Expected on stream	2009	2009	2010	2010	TBC
CO2 Capture Capacity (T/D)	**400**	**450**	**450**	**340**	**800**

2. MHI’s long term 10 t/d CO2 capture demonstration tests from a coal fired boiler

Coal Fired Long Term Demonstration Plant

Plant Outline

Solvent : KS-1
Capacity : 10 T/D
Feed Gas : Coal Fired Boiler (14.1 v% CO_2)
Start-up : July 2006
Location : Nagasaki, Japan

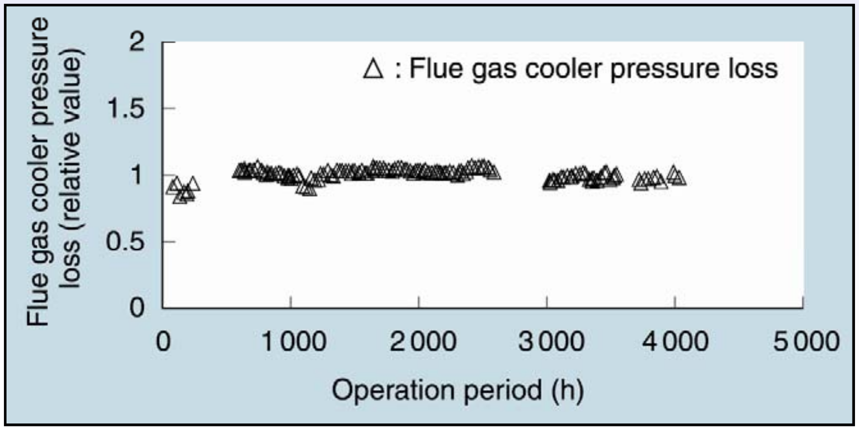
Operational experiences

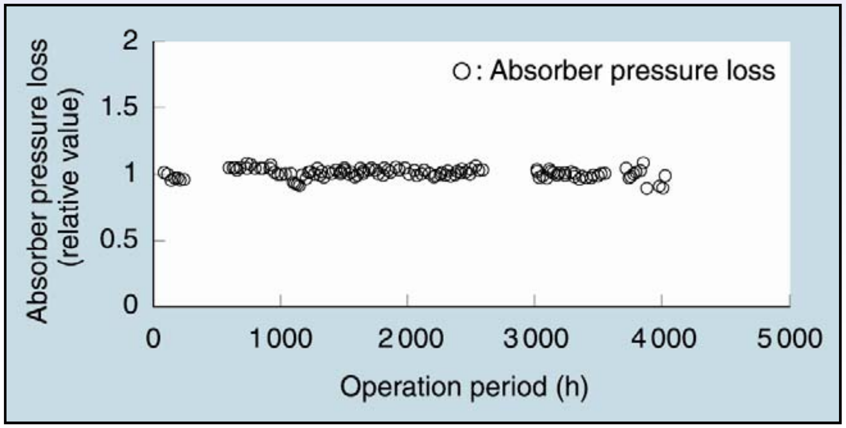
- Increased understanding of the effects of impurities on the system (dust, SOx, NOx, etc.)
- Identifying and incorporating countermeasures for each impurity
- >5,000 hours of operation and experience
- Test results exceeded expectations and will facilitate scale up CO2 capture for coal fired boilers
- Confirms that the MHI CO2 capture process can be applied to coal fired flue gas streams

2. MHI's long term 10 t/d CO2 capture demonstration tests from a coal fired boiler

Coal Fired Long Term Demonstration Plant - Results

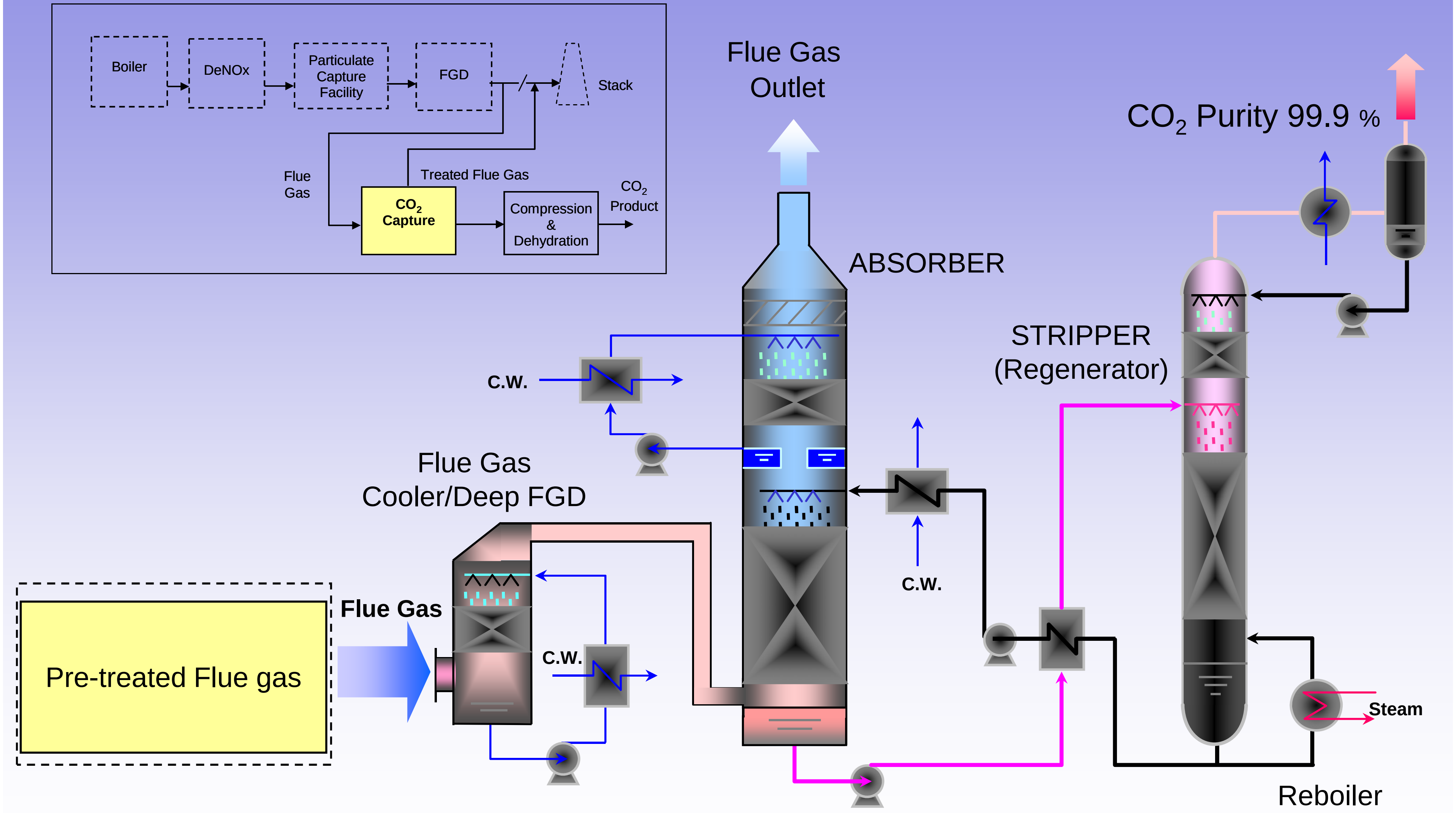
Test Item	Result
• Achieve long term stable operation	✓ >5000 hours of near continuous operation
• Confirm effect of various impurities on CO2 capture process & equipment	✓ Advanced know-how of the impacts of dust, SO2 and NOx
• Achieve high CO2 purity performance	✓ >99.9% achieved
• Confirm heat consumption required for CO2 recovery	✓ 730-820 kcal/kg-CO2 (Improved process reduced by a further 15%)
• Record pressure loss observed in the cooler and absorber	✓ No major pressure fluctuations
• Confirm process can be applied to coal fired flue gas	✓ Yes - KM-CDR Process can be applied to coal fired power stations





3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

Process Flow for Amine Absorption



Boiler
DeNOx
Particulate Capture Facility
FGD
Stack
Flue Gas
Treated Flue Gas
CO_2 Capture
Compression & Dehydration
CO_2 Product

Flue Gas Outlet
CO_2 Purity 99.9 %
ABSORBER
STRIPPER (Regenerator)
C.W.
Flue Gas Cooler/Deep FGD
C.W.
Flue Gas
C.W.
Pre-treated Flue gas
Steam
Reboiler

3. MHI’s CO2 Recovery Technology: Process Improvements & Heat Integration

MHI’s Flue Gas CO2 Recovery Improved Process

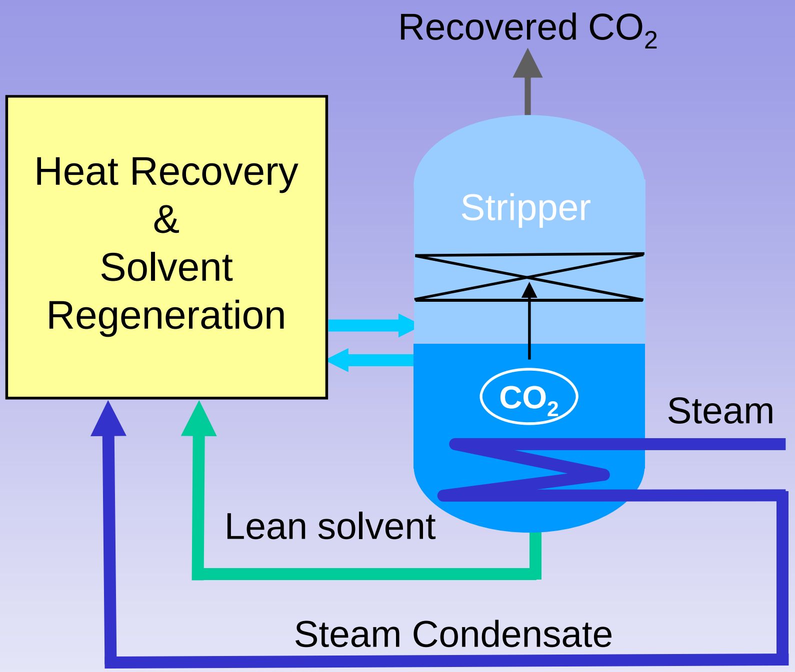
- 15% steam consumption reduction over MHI’s conventional process
- Advanced process demonstrated at MHI’s Nanko Pilot Plant & Commercial Plants
- Process Features
Utilize lean solvent and steam condensate heat for regeneration inside the stripper
- Performance

*Steam Consumption: 1.30 Ton Steam/ Ton CO2 (660 Kcal/ Kg CO2)

Note: Steam = 3 BarG Saturated

*Regeneration Energy less than 700 Kcal/ Kg CO2 can be guaranteed

Patent Application submitted in various countries



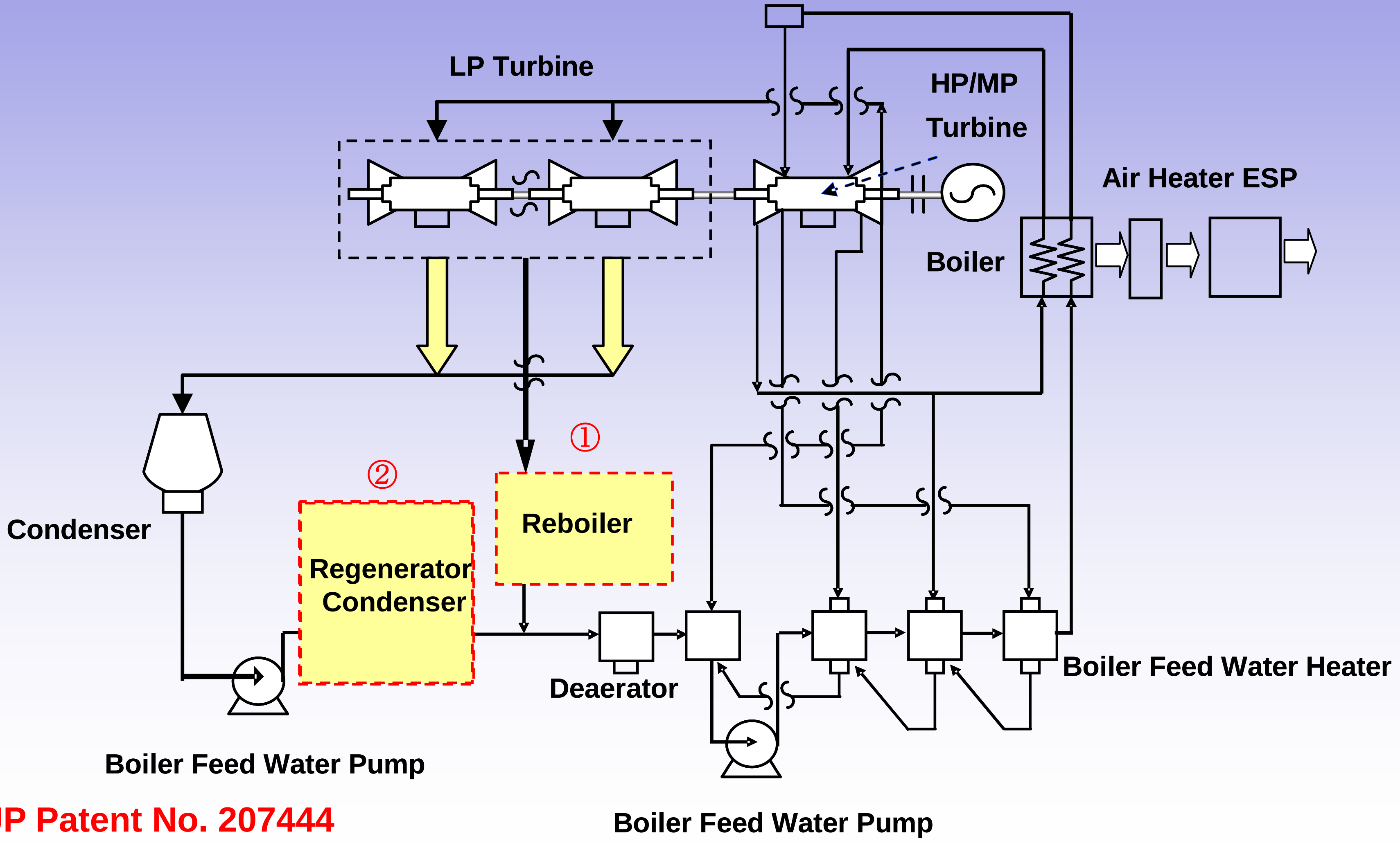
Advanced Amine Solvent ‘KS-1’

- High CO2 Loading
- Low Solvent Degradation
- Low Corrosion
- No Corrosion Inhibitor

MHI Heat integration Concept (Base Case)

① LP Steam extraction from the LP Turbine

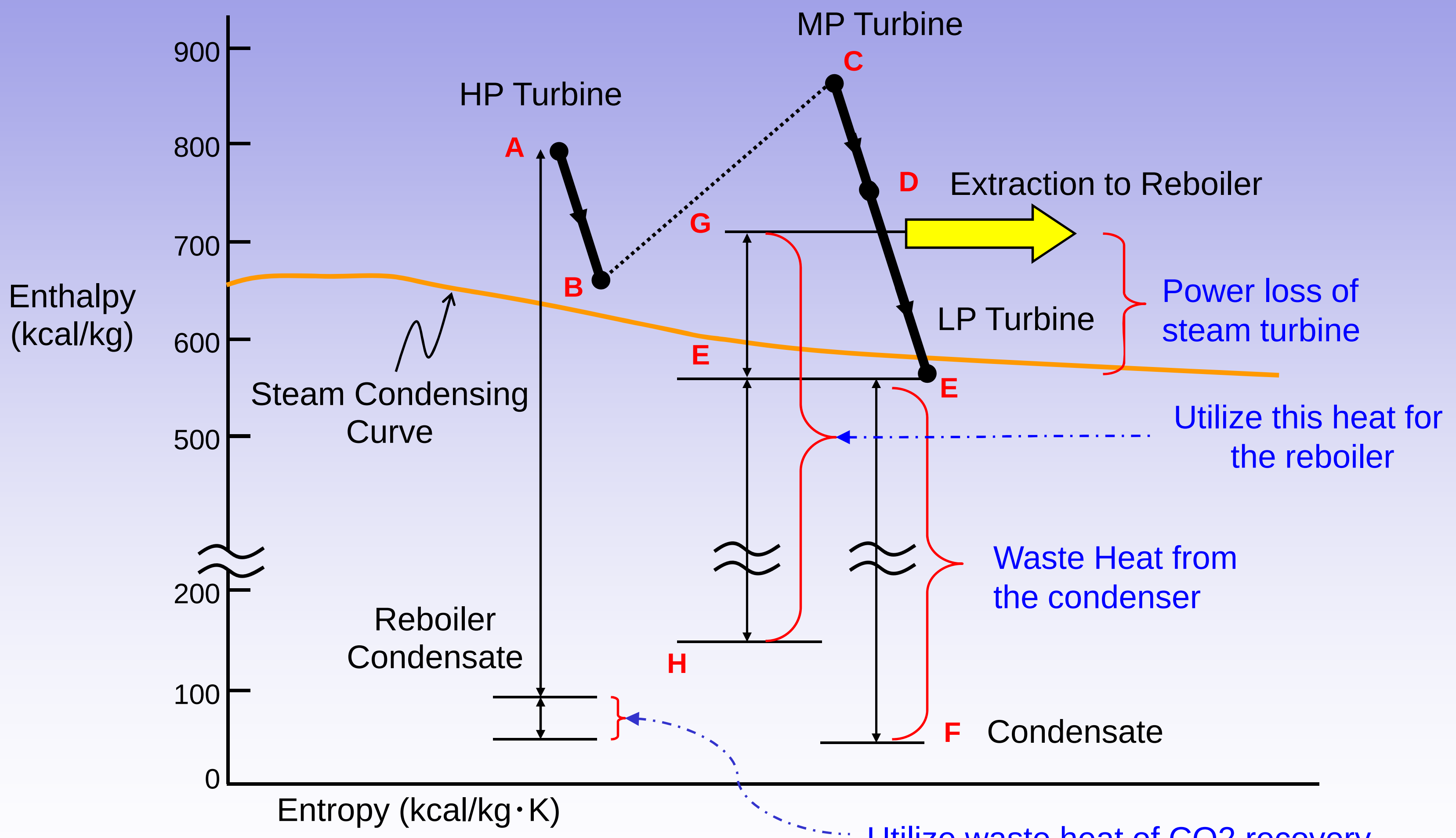
② Recovery of overhead condenser heat



JP Patent No. 207444

3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

MHI Heat integration Concept



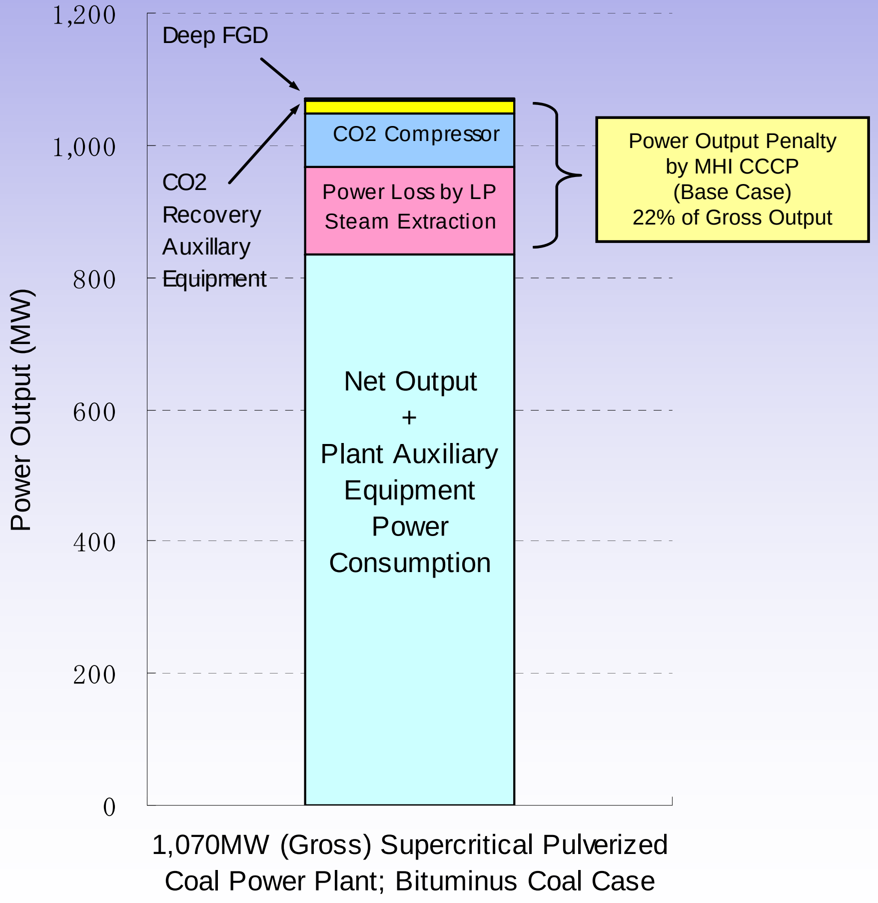
Utilize waste heat of CO2 recovery

3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

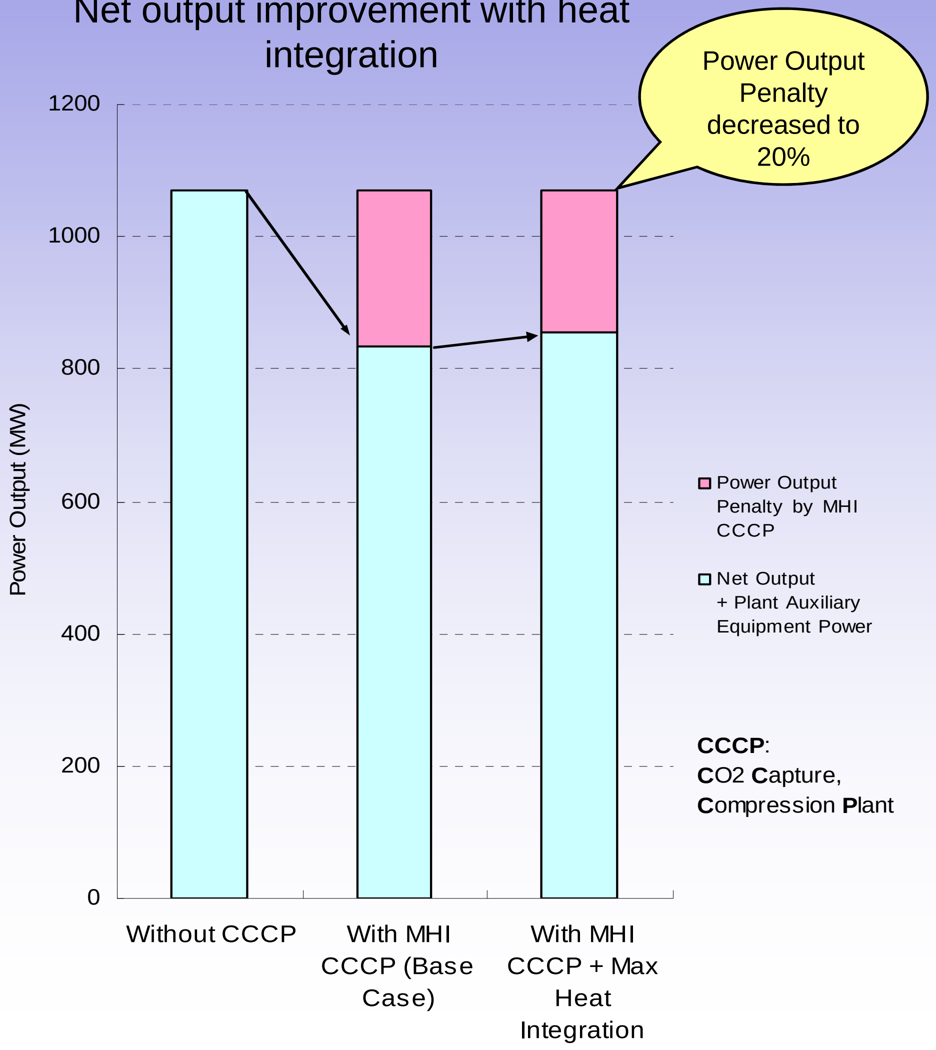
CO2 Recovery Plant Power Output Penalty Assessment and Heat Integration Options;

1) Base Case +
2) Recovery of Compression Heat
3) Recovery of Flue Gas Heat

Power output penalty of CO2 capture and compression without heat integration

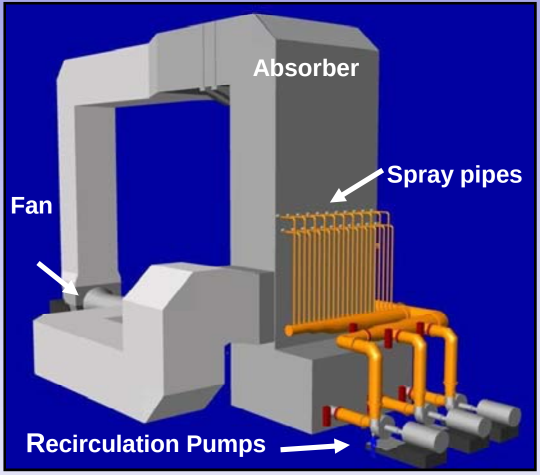


Net output improvement with heat integration



CCCP:
CO2 **C**apture,
Compression **P**lant

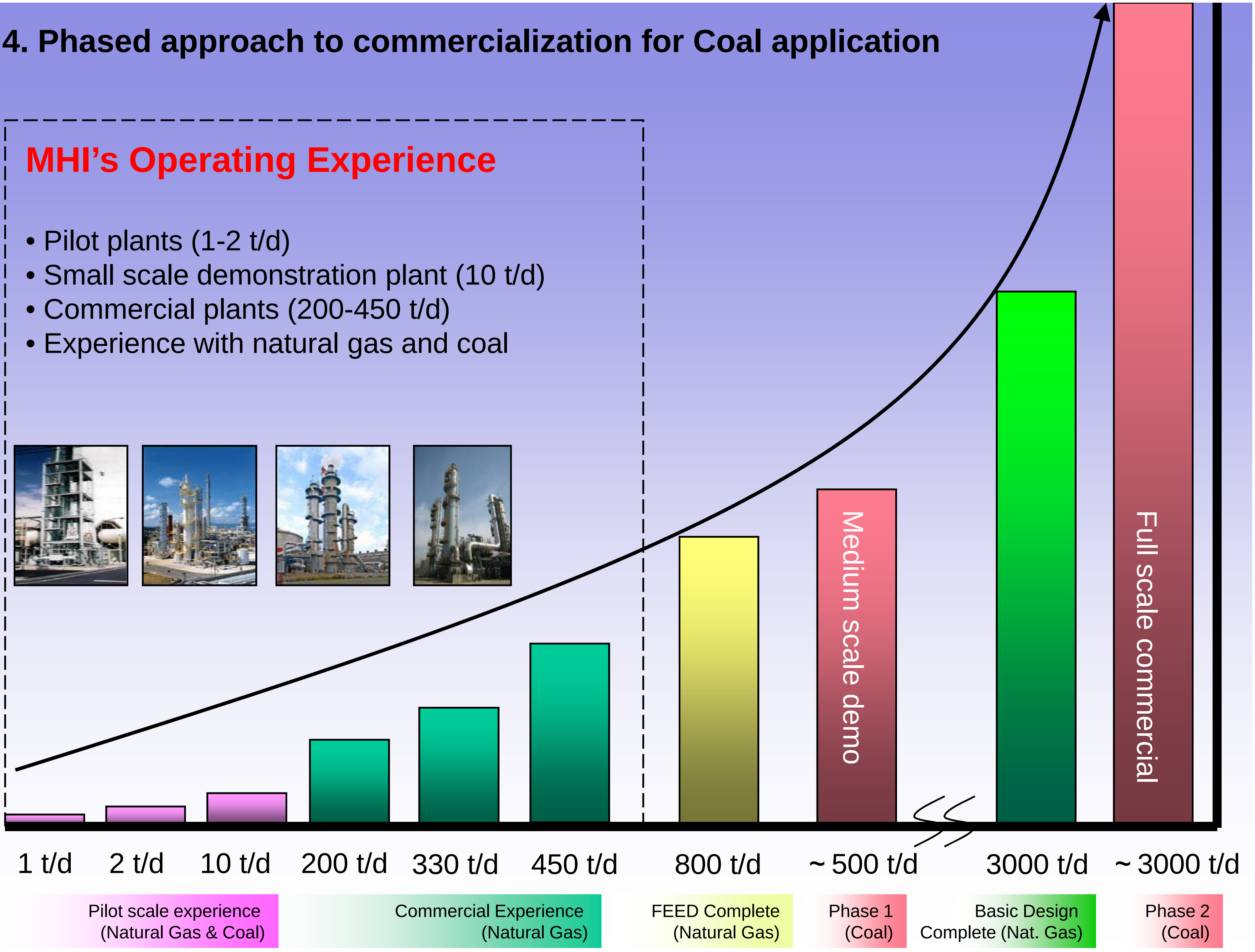
Multi-Pollutant Test Plant (FGD & CO2 Capture)
Absorber 1 by 1 Scale Test Facility (400 MW equivalent)



Commercial Scale Tests

- Q1 2008 – Extensive Liquid Distribution Tests
- Rectangular Absorber
- Panel Design

4. Phased approach to commercialization for Coal application

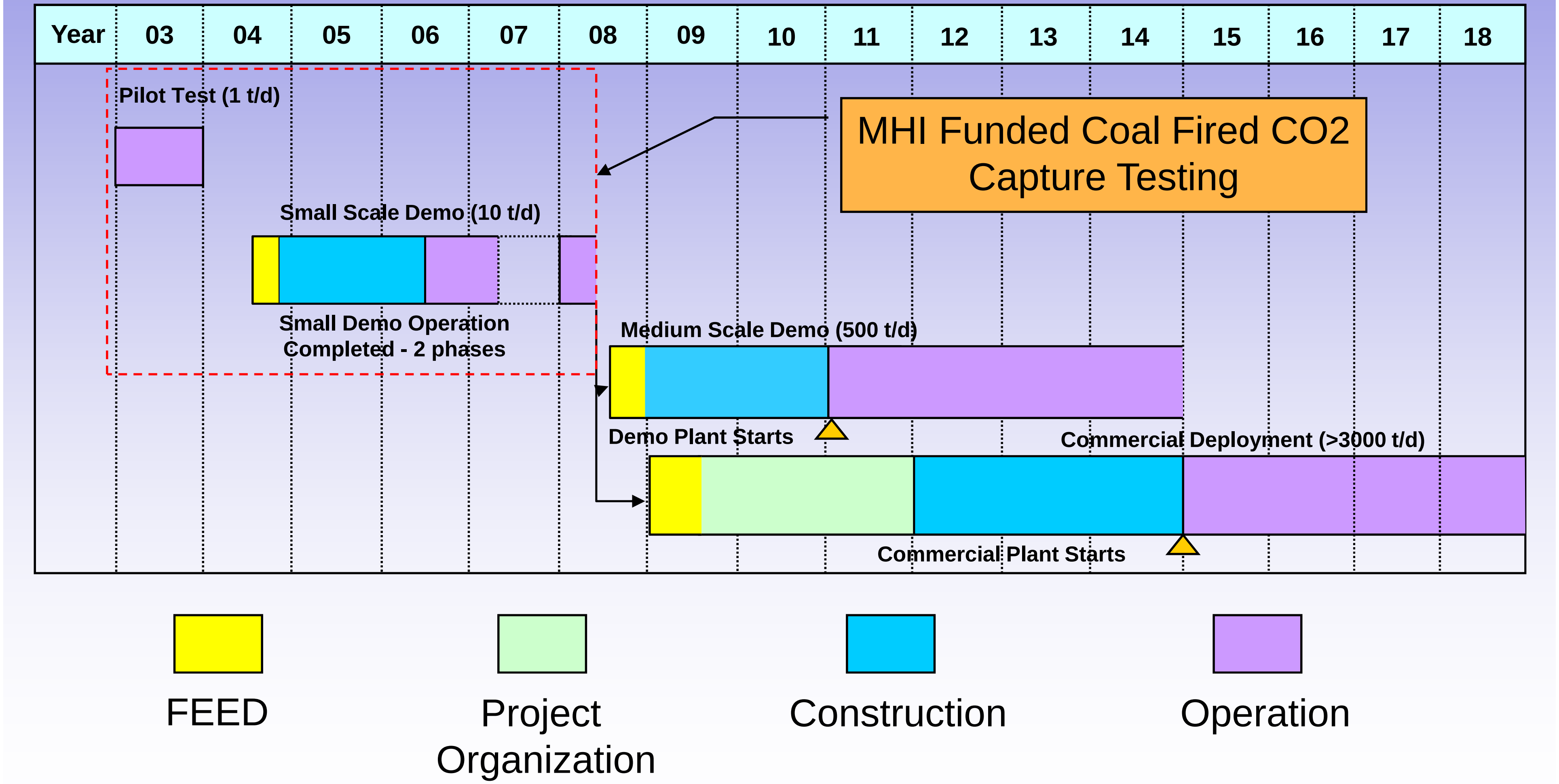


MHI’s Operating Experience

- Pilot plants (1-2 t/d)
- Small scale demonstration plant (10 t/d)
- Commercial plants (200-450 t/d)
- Experience with natural gas and coal

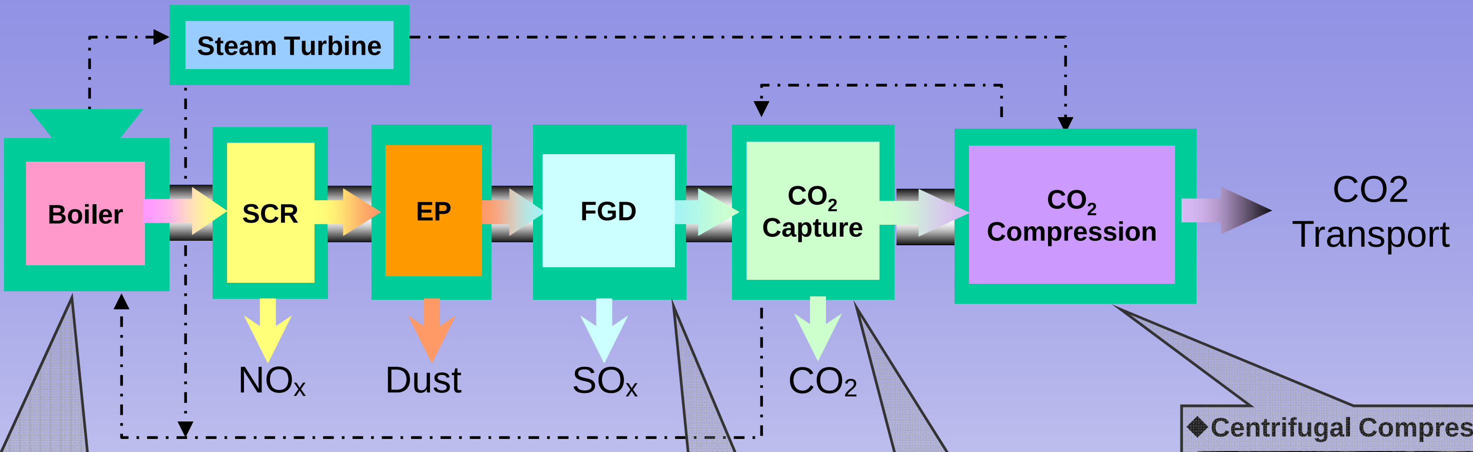
4. Phased approach to commercialization for Coal application

MHI's Conceptual Schedule for a Medium – Large Scale Coal Fired CO2 Capture Demonstration Plant



Note: This schedule is a conceptual figure only and shows MHI's roadmap for the future commercialization of this technology for coal fired boilers

5. MHI’s Scope in a CCS Project



Steam Turbine

Boiler

SCR

EP

FGD

CO$_2$ Capture

CO$_2$ Compression

CO2 Transport

NO$_x$

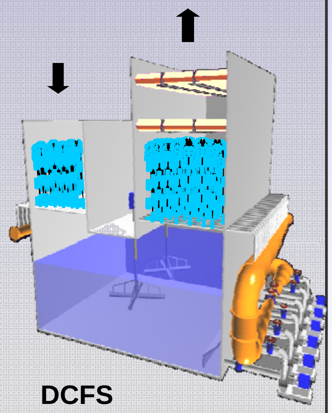
Dust

SO$_x$

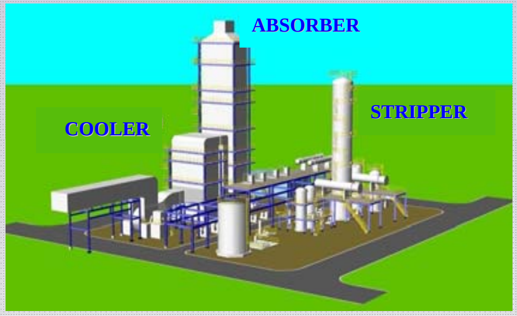
CO$_2$

◆Coal Fired Power Station

◆FGD



◆CO$_2$ Capture Plant



◆Centrifugal Compressors

MHI Can Supply All Technology – Efficient Integration

6. Conclusions

Need for Carbon Capture & Storage

① Coal will remain a dominant fuel for electric power generation

② Coal with CCS technology can play an important part in CO2 mitigation - regulatory certainty and political support is needed

③ Governments must continue to support CCS and a ‘suite’ of carbon mitigation strategies

④ Incentives for first stage commercial CCS plants are necessary to reduce technical and financial uncertainties

⑤ Post combustion CO2 capture technology offers many advantages and can be transferred to developing countries

⑥ Allows for future zero emission use of coal

Cansolv

Cansolv Activities
&
Technology Focus for CO_2 Capture

John Sarlis / Devin Shaw

IEA Meeting, Vienna, May 2008

Outline

- Company background
- Technology development strategy
- Technology developent status
  - Piloting Campaigns
- Next plans
  - Integrated SO_2 - CO_2 Capture

Cansolv Technologies at a Glance

- Founded in 1997 as Union Carbide spin-off
- Located in Montreal, Canada and Shenzhen, P.R.C.
- ***Global leader in amine based regenerable scrubbing for SO_2 and CO_2***
- Providing solutions for:
  - Oil & Gas applications : Sulfur plants, FCCs, Cokers
  - Industrial combustion applications: coal and bitumen boiler flue gas
  - Smelter applications (lead/zinc furnaces, copper anode furnaces)
  - Others: acid plant tail gas, incinerator off-gas

SO$_2$ Commercial Flue Gas Amine Plants

Application	Location	Flow (Nm3/hr)	Size MW_{equiv}	SO$_2$ Concentration		Operation since
				In	Out	
Incinerator Tail Gas	Belgium	12,000	3	1 %	<30 ppm	2002
SARP Acid Plant TG	US	40,000	10	5000 ppm	15 ppm	2002
FCCU CO Boiler Flue Gas	US	740,000	180	800 ppm	25 ppm	2007
Coker CO Boiler Flue Gas	US	430,000	120	2000 ppm	25 ppm	2006
Metallurgical Off-gas	India	33,700	8	0.1 to 12.5 %	150 ppm	2006
Claus plant tail gas	US	18,000	5	4%	200 ppm	2006
Anode Furnace Off-Gas	China	43,000	10	900 ppm-1.9%	100ppm	2007

1 unit in Commissioning

5 units in Engineering and Procurement

Technology Development Strategy

Cansolv

- SO_2 compatible
- Amine based
- Lower energy & degradation than benchmark
- Solvent,
  - stable
  - reasonable cost
  - easily sourced
  - good HS&EA properties

CO_2 Scrubbing - Comparison of Amines

- Amines broadly used for selective absorption of H_2S/CO_2
- Cansolv pioneered use of amines in oxidative environments

CANSOLV PROCESS	CONVENTIONAL AMINE
Diamine absorbent	MEA, DEA, MDEA
Tolerable to SO_2	Prone to degradation in presence of SO_2
Stainless steel metallurgy	Carbon steel metallurgy
Corrosion allowance minimal	Corrosion allowance important
No Fe S formation	Fe S formation
Only source of solids is feed gas	Fe S precipitation and scaling source of solids

Technology Development Plan

- Solvent screening in Lab
- Physical properties development;   1st Pass
- Piloting (actual commercial sites)
- Simulation development; A+, eNRTL, 1st Pass
- Cost Model; 1st Pass
- Intense physical/chemical properties & mass transfer development
- 2nd Pass Cost model
- Demonstration plant (integrated with SO_2 & Stand alone)
- Ongoing simulation model;
    - Rate based and Pilot plant validated

CO$_2$ CAPTURE EXPERIENCE

Over 5,000 hours of CO$_2$ Piloting

CO_2 CAPTURE EXPERIENCE

Cansolv

Application	Date	Site	CO_2 in the gas	Removal
Natural Gas Fired boiler	March-June 2004	Paprican, Montreal, Canada	8%vol	75%
Coal fired Boiler	November 2004	Pulp Mill Boiler, US	11.5%vol	65%
Coal fired Power Plant	July – Sept 2006	Saskpower, Poplar River, Canada	12% vol	90%
Blast Furnace	April 2007 - 2008	Japan	22% vol	90%
Natural Gas Fired Boiler	May - Sept 2007	Shell-Statoil, Norway	4.5%vol	85%
Cement Kiln	Jan – Feb 2008	Cal Portland, California	20%vol	90% and 45%

CTI CO_2 Capture Solvent Development

- Cansolv Solvents, buffer at the appropriate pKa
  - Cansolv DC101
  - Cansolv DC103
  - Cansolv DC103A
  - Cansolv DC103B

- Independent Testing Verification

- Third Party Assistance in Testing of Solvent Performance

- Baseline Comparison
  - MEA reference vs. Cansolv Solvents
  - Laboratory Experimentation
  - Piloting Campaigns

Cansolv CO_2 Piloting Campaigns

Pilot Testing - Example #1

Application: Coal-fired Power Plant

Dates: July 2006 – Sept 2006

Project Description: Saskpower

Site: Poplar River Power Plant, Canada

Inlet Gas Temperature = 40 - 50°C

Inlet CO_2 concentration: 12 vol % (wet)

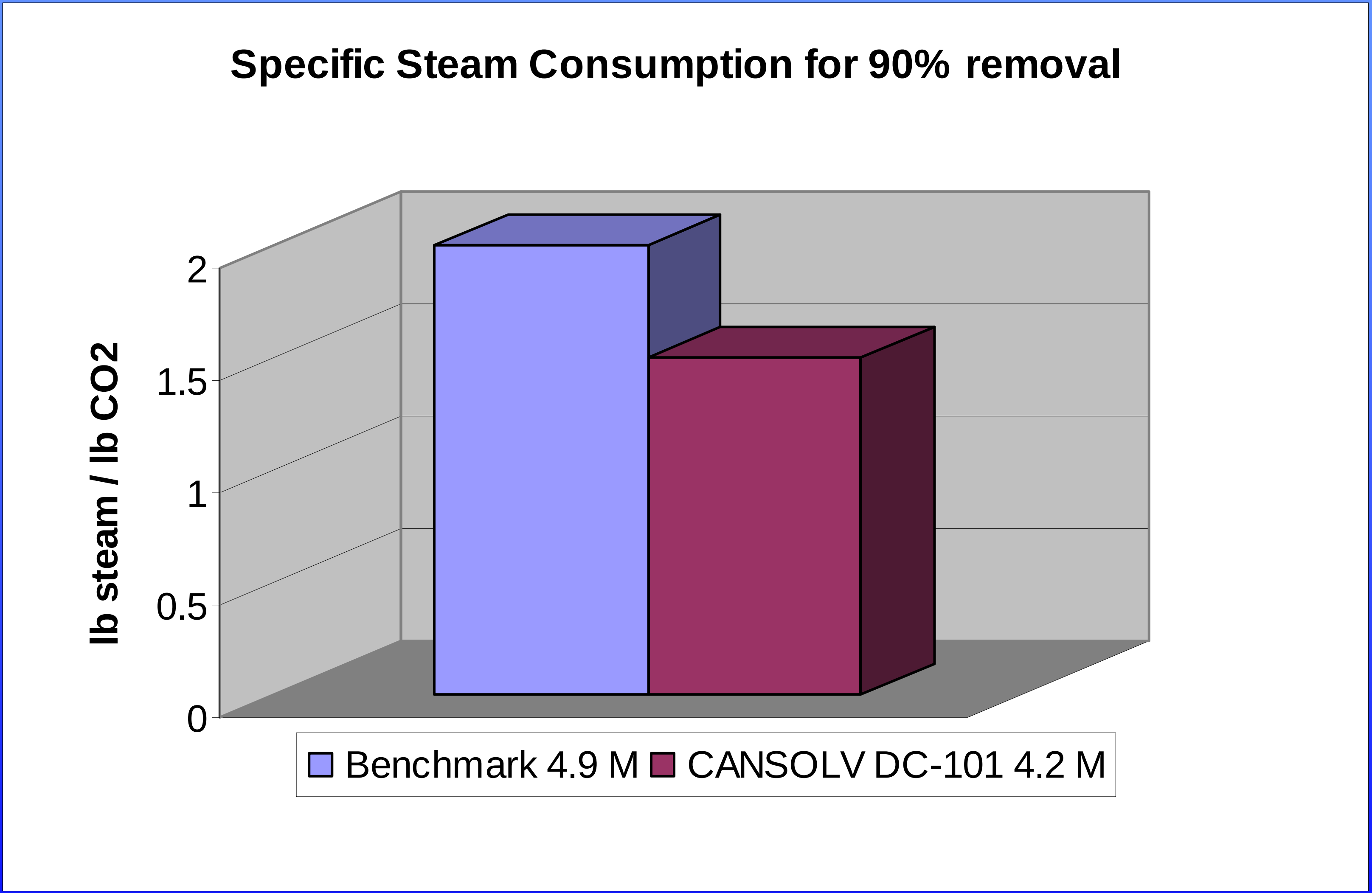
CO_2 Removal = 90%

O_2 inlet concentration = 6 vol %, **SO_2 inlet concentration = 15 ppm**

Gas flow = 65 scfm or 110 Nm^3/hr

Solvents tested: Benchmark (7 days) and CANSOLV DC101 (53 days)

Benchmark and DC-101 Optimal Conditions



Cansolv CO_2 Piloting Campaigns

Pilot Testing - Example #2

Application: Natural Gas Fired Boiler

Dates: May - Sept 2007

Project Description: Shell – Statoil
Site: Risavika Gas Center, Norway

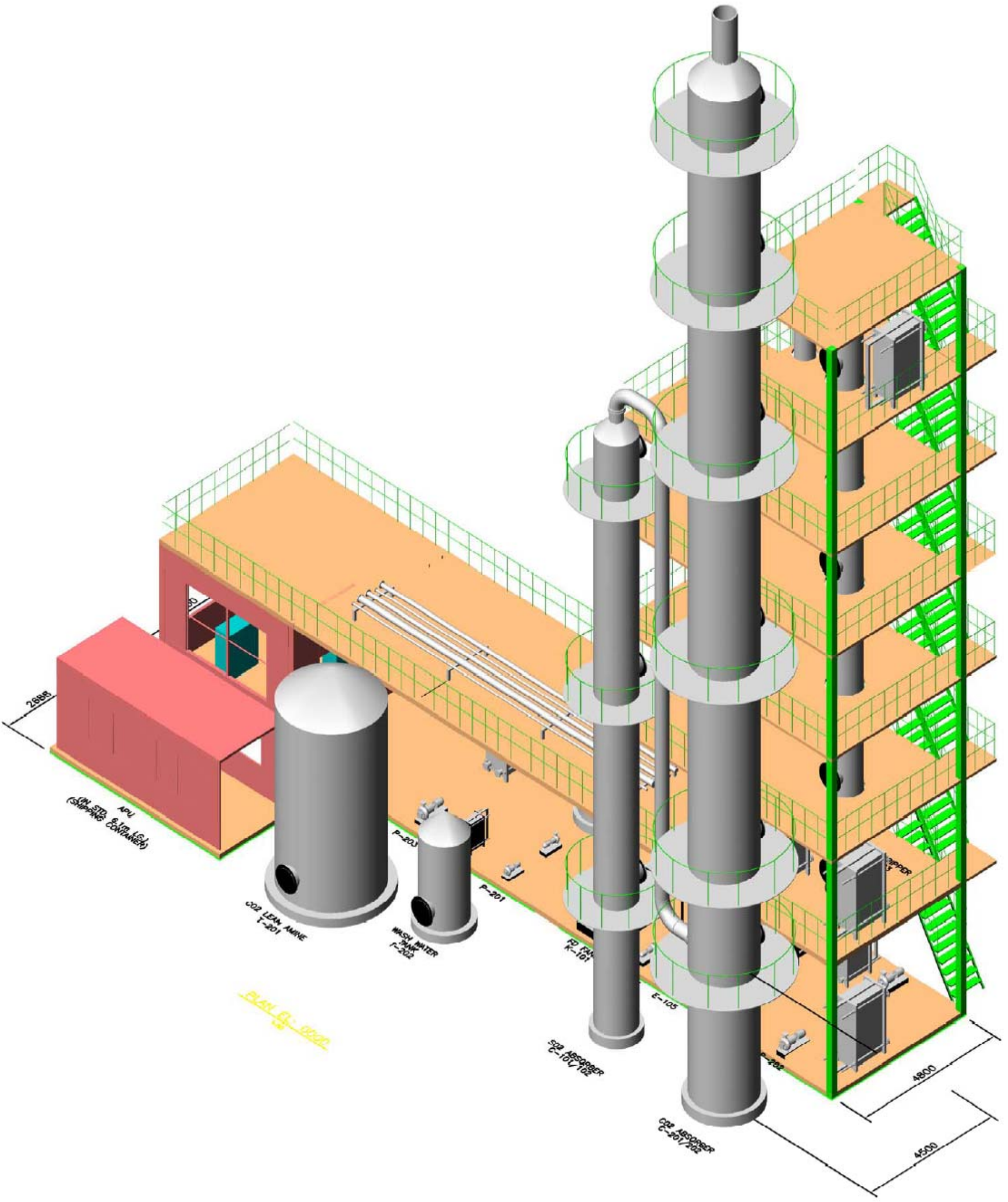
Inlet Gas Temperature ~ 50°C
Inlet CO_2 Concentration = 4.5 vol % (wet)
CO_2 Removal = 85 %

Solvents tested: DC-103 and DC-103A (100 days)

Optimization of DC-103 & DC-103A-B

SOLVENT		CANSOLV DC-103	CANSOLV DC-103A-B
	Units		
CO_2 Removal	%	**84**	**85**
Specific Steam Consumption, 2.5 Bar(g)	lb steam/lb CO_2	**1.34**	**1.55**
Gas Flow	SCFM	**120**	**140**
Gas Residence Time	seconds	**8.8**	**7.3**

Minimization of regeneration steam requirement



CANSOLV

Integrated

SO_2 Control and

CO_2 Capture **50 ton/day**

Demonstration Plant

Amine Based SO_2 and CO_2 Capture

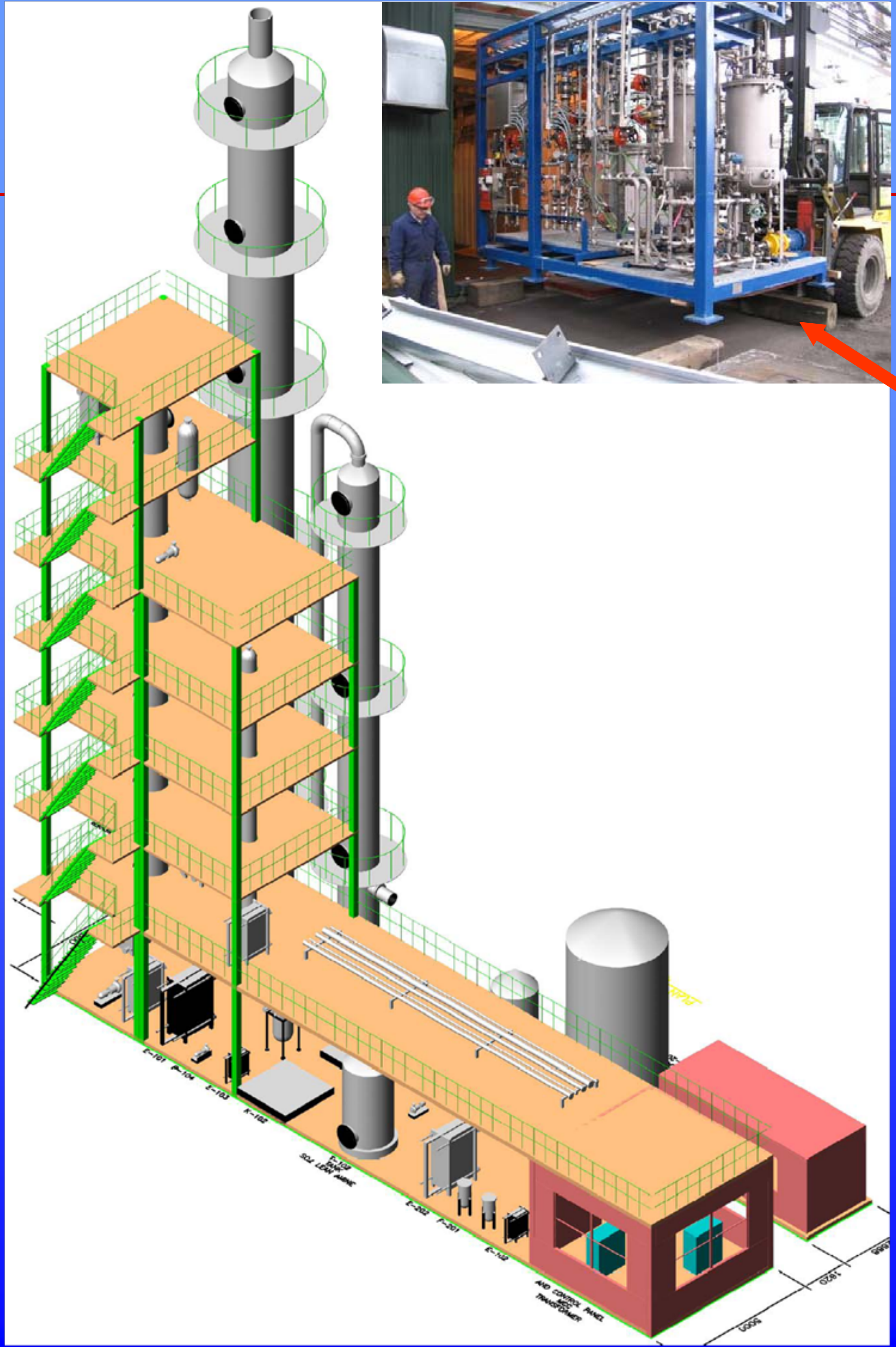
- **CANSOLV SO_2 Control**
  - Diamine operating pH 4.5 to 5.5
  - Regenerable ion HSO_3^-
  - Stripper overheads suitable for heat recovery
  - Low degradation
  - Heat stable salts removed by APU
  - Slips 99.99% of CO_2

- **CANSOLV CO_2 Capture**
  - Diamine operating pH 9 to 10
  - Regenerable ion HCO_3^-
  - Stripper overheads unsuitable for heat recovery
  - Low degradation
  - Heat stable salts removed by APU
  - Captures 99% of residual SO_2

Process & Heat Integration Potential

SO_2 / CO_2 Capture Demonstration Plant

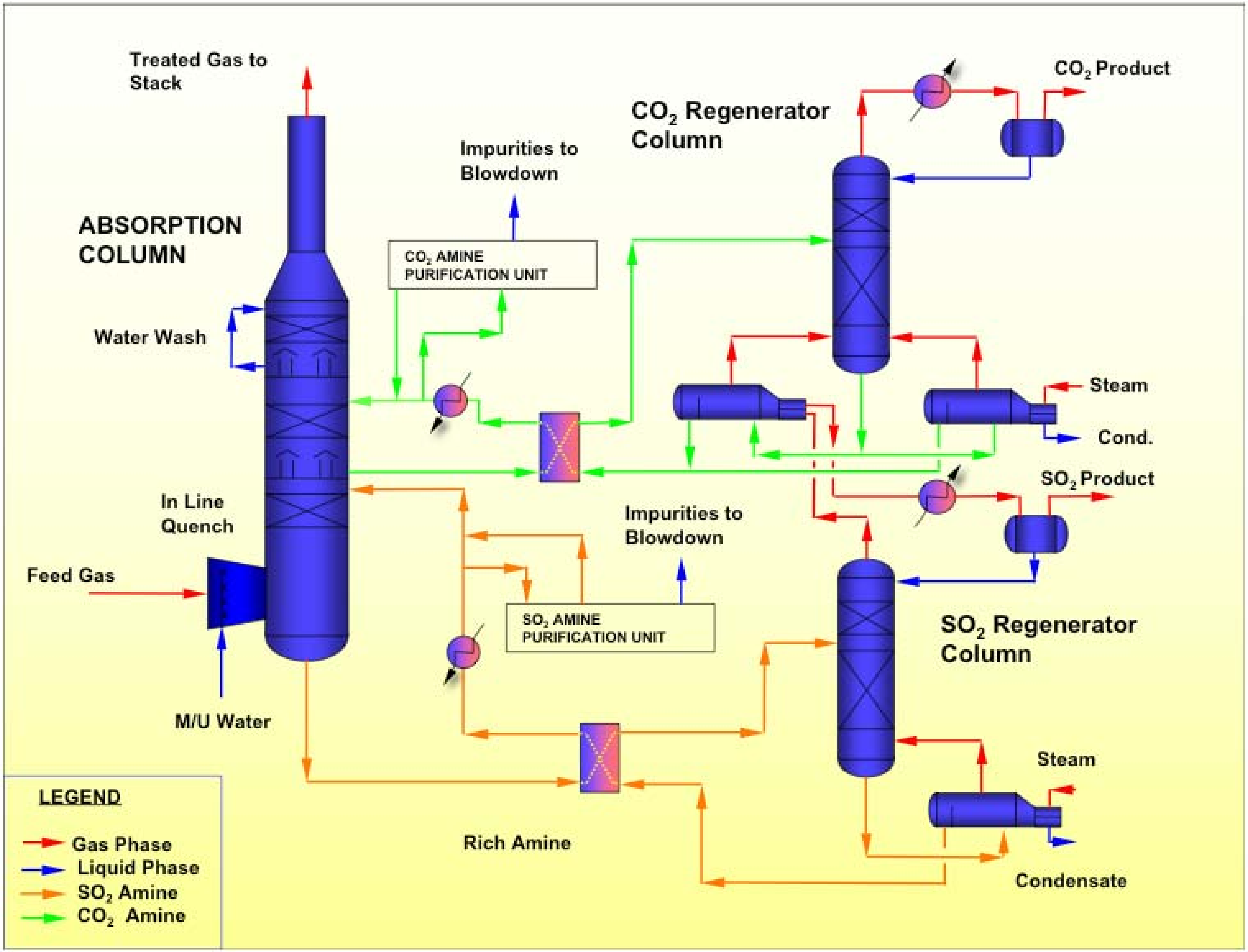
- 50 ton per day CO_2 capture capacity (3 MW)
- Currently in Engineering and Procurement Phase
- Heat integrated CANSOLV-SO_2 Control CANSOLV-CO_2 Capture Process
- Objectives:
  - confirm specific heat consumption
  - evaluate scale-up effects



CANSOLV – SO_2 CONTROL CO_2 CAPTURE DEMO PLANT

- Modular design
  (skid design experience)
- Sized for most road clearances
- Maximum pre-assembly
- MCC & control system on main skid
- Equipped for two mode heat recovery
- Modular design scalable to 400 tons / day

CANSOLV SO_2 - CO_2 CAPTURE DEMO PLANT



Demo Plant Performance

Cansolv

- Solvent designed for :
  - 1.3 tons steam per ton CO_2 (without heat integration)
  - 1.0 tons steam per ton CO_2 (with heat integration)
- Including Electricity and Capital costs → 15% savings

- Two mode heat recovery capability
  - »SO_2 overhead to CO_2 reboiler
  - »Heat recycling internal to CANSOLV CO_2 Process

- Instrumented for operating and capital cost optimization

CANSOLV CO_2 Capture System – CNN News Press Release

RWE Npower Forms Consortium For UK Carbon Capture Project

March 20, 2008: 06:48 AM EST

LONDON -(Dow Jones)- RWE npower, the U.K. arm of German utility RWE (RWE.XE), said Thursday that it had formed a consortium with five other companies to build a carbon capture and storage power plant, ahead of entering a competition to get U.K. government funding for the project.

In addition to RWE npower, the consortium comprises of chemical and gas provider BOC Gases PLC (BOCGAS.LA), flue gas desulfurization and combustion technology provider Cansolv Technologies, marine transportation company I.M. Skaugen AS (IMSK.OS), engineering and construction company The Shaw Group Inc. (SGR) and oil and gas exploration company Tullow Oil PLC (TQW.DB).

"RWE npower is currently developing proposals for entry by the end of March into the pre-qualification phase of the Government's CCS demonstration competition. The partnership structure will form part of its proposals," the company said.

-By Erica Herrero-Martinez, Dow Jones Newswires; +44 (0)20 7842 9353; erica.herrero-martinez@dowjones.com

- Thank You!!

- Questions ?

11th MEETING
of the
INTERNATIONAL POST-COMBUSTION CO2 CAPTURE NETWORK

Post Combustion Systems

Coal Fired Pilot Plant and Multipollutant Control

MITSUBISHI HEAVY INDUSTRIES, LTD.

Masaki Iijima

20th -21st May, 2008 Vienna, Austria

CONTENTS

1. MHI’s Commercial Achievements

MHI’s Operating Commercial CO2 Capture Plants

Malaysia

Client: Petoronas
Start-up: 1999~
CO2 Source:
Nat. Gas Reformer
Capacity: 200 t/d
Product: Urea

India

Client: IFFCO
Location: Aonla
Start-up: Dec 2006~
CO2 Source:
Nat. Gas Reformer
Capacity: 450 t/d
Product: Urea

Japan

Client: Chemical Co.
Start-up: 2005~
CO2 Source:
Nat. Gas Boiler
Capacity: 330 t/d
Product: General use

India

Client: IFFCO
Location: Phulpur
Start-up: Dec 2006~
CO2 Source:
Nat. Gas Reformer
Capacity: 450 t/d
Product: Urea

MHI’s Recently Awarded Commercial Projects

OTHER PROJECTS	Abu Dhabi	India	Bahrain	‘Asia’	China
Project Status	Under Construction	Under Construction	Under Construction	Under Construction	FEED Complete
Flue Gas Source	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Reformer	Nat. Gas. Boiler
Expected on stream	2009	2009	2010	2010	TBC
CO2 Capture Capacity (T/D)	**400**	**450**	**450**	**340**	**800**

2. MHI’s long term 10 t/d CO2 capture demonstration tests from a coal fired boiler

Coal Fired Long Term Demonstration Plant

Plant Outline

Solvent : KS-1
Capacity : 10 T/D
Feed Gas : Coal Fired Boiler (14.1 v% CO_2)
Start-up : July 2006
Location : Nagasaki, Japan

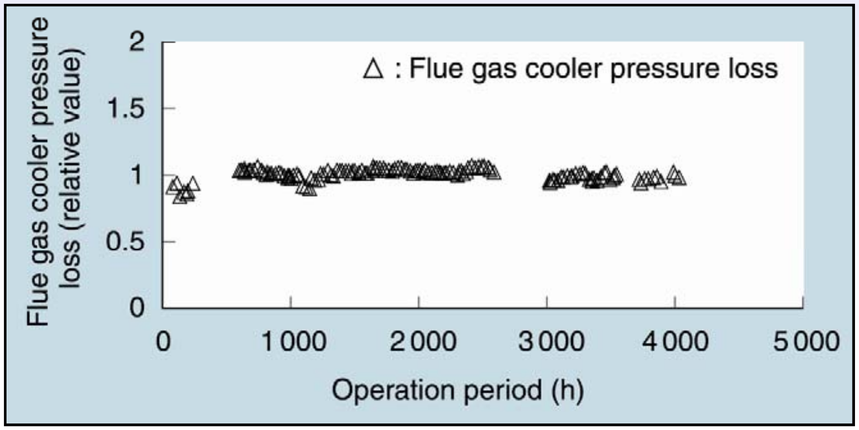
Operational experiences

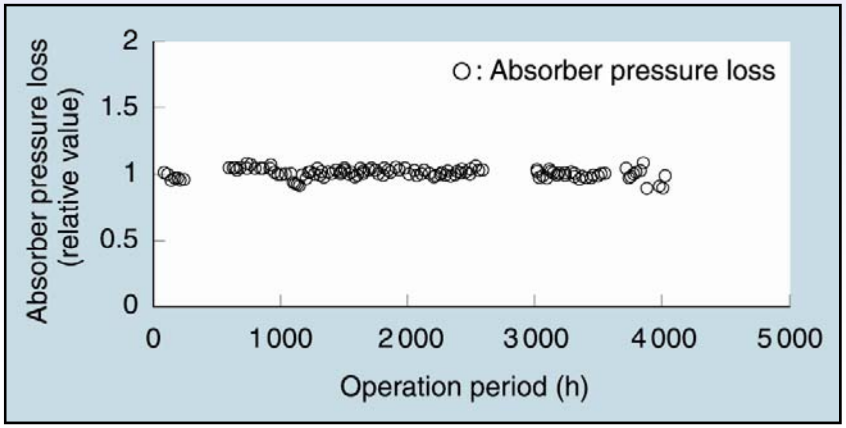
- Increased understanding of the effects of impurities on the system (dust, SOx, NOx, etc.)
- Identifying and incorporating countermeasures for each impurity
- >5,000 hours of operation and experience
- Test results exceeded expectations and will facilitate scale up CO2 capture for coal fired boilers
- Confirms that the MHI CO2 capture process can be applied to coal fired flue gas streams

2. MHI’s long term 10 t/d CO2 capture demonstration tests from a coal fired boiler

Coal Fired Long Term Demonstration Plant - Results

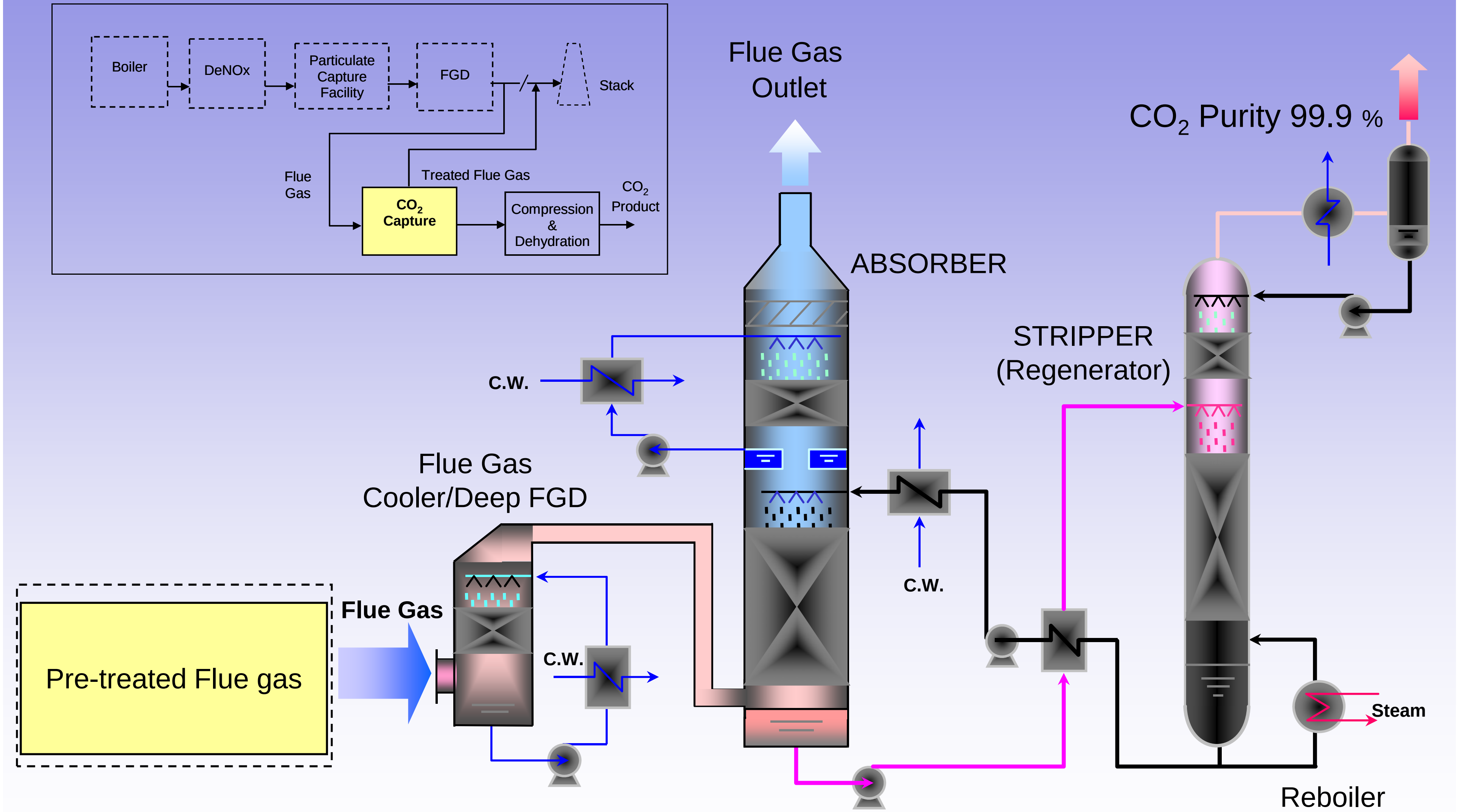
Test Item	Result
• Achieve long term stable operation	✓ >5000 hours of near continuous operation
• Confirm effect of various impurities on CO2 capture process & equipment	✓ Advanced know-how of the impacts of dust, SO2 and NOx
• Achieve high CO2 purity performance	✓ >99.9% achieved
• Confirm heat consumption required for CO2 recovery	✓ 730-820 kcal/kg-CO2 (Improved process reduced by a further 15%)
• Record pressure loss observed in the cooler and absorber	✓ No major pressure fluctuations
• Confirm process can be applied to coal fired flue gas	✓ Yes - KM-CDR Process can be applied to coal fired power stations





3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

Process Flow for Amine Absorption



3. MHI’s CO2 Recovery Technology: Process Improvements & Heat Integration

MHI’s Flue Gas CO2 Recovery Improved Process

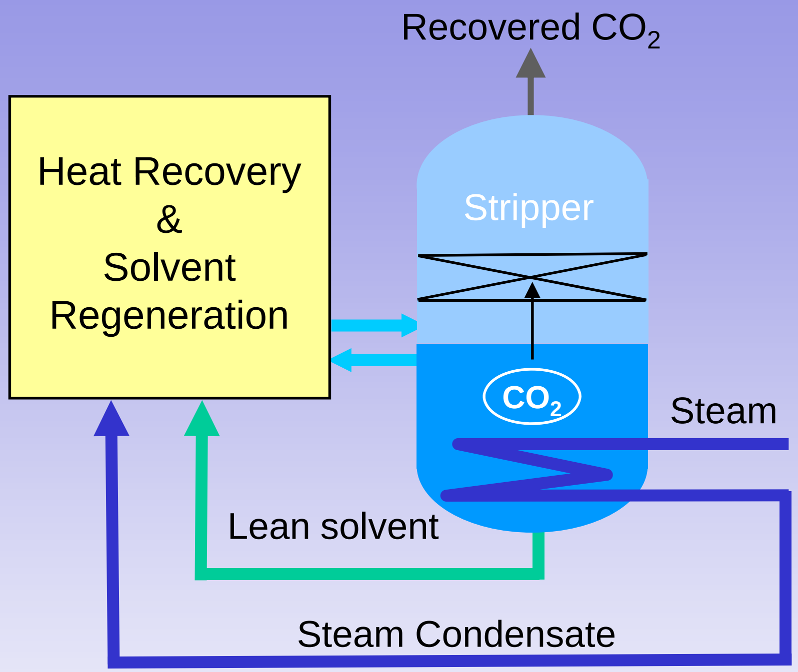
- 15% steam consumption reduction over MHI’s conventional process
- Advanced process demonstrated at MHI’s Nanko Pilot Plant & Commercial Plants
- Process Features
  Utilize lean solvent and steam condensate heat for regeneration inside the stripper
- Performance

*Steam Consumption: 1.30 Ton Steam/ Ton CO2 (660 Kcal/ Kg CO2)

Note: Steam = 3 BarG Saturated

*Regeneration Energy less than 700 Kcal/ Kg CO2 can be guaranteed

Patent Application submitted in various countries

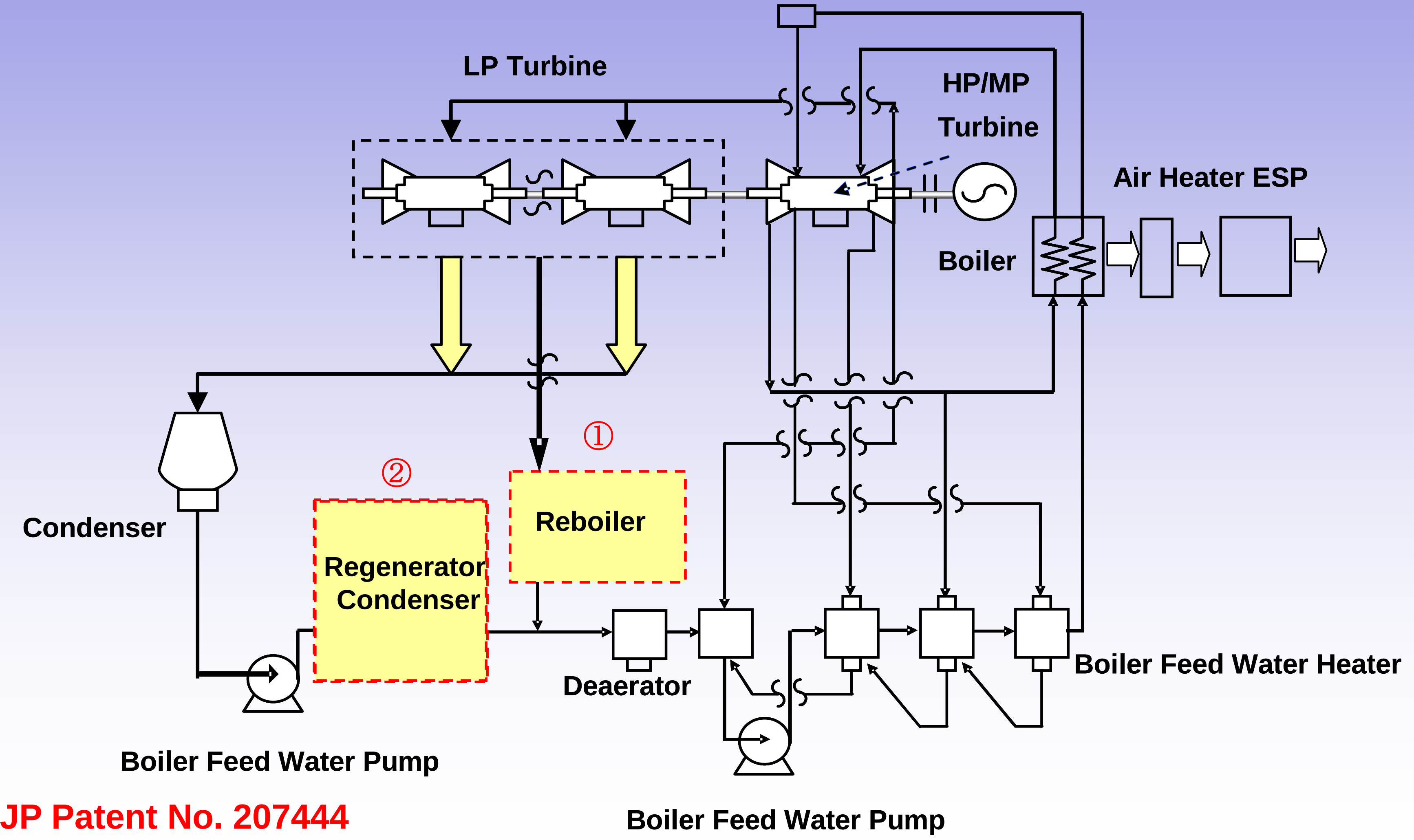


Advanced Amine Solvent ‘KS-1’

- High CO2 Loading
- Low Solvent Degradation
- Low Corrosion
- No Corrosion Inhibitor

MHI Heat integration Concept (Base Case)

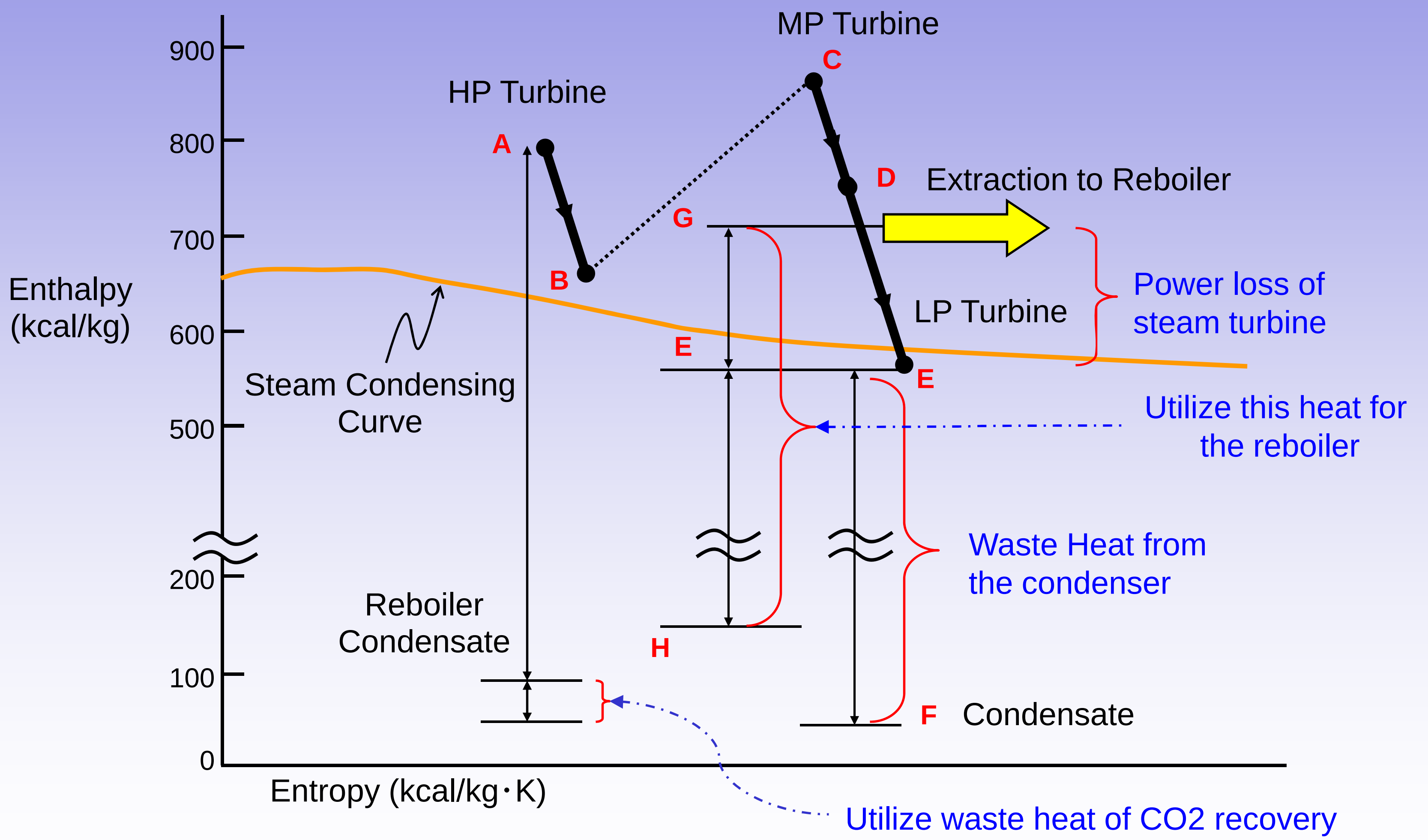
① LP Steam extraction from the LP Turbine
② Recovery of overhead condenser heat



JP Patent No. 207444

3. MHI’s CO2 Recovery Technology: Process Improvements & Heat Integration

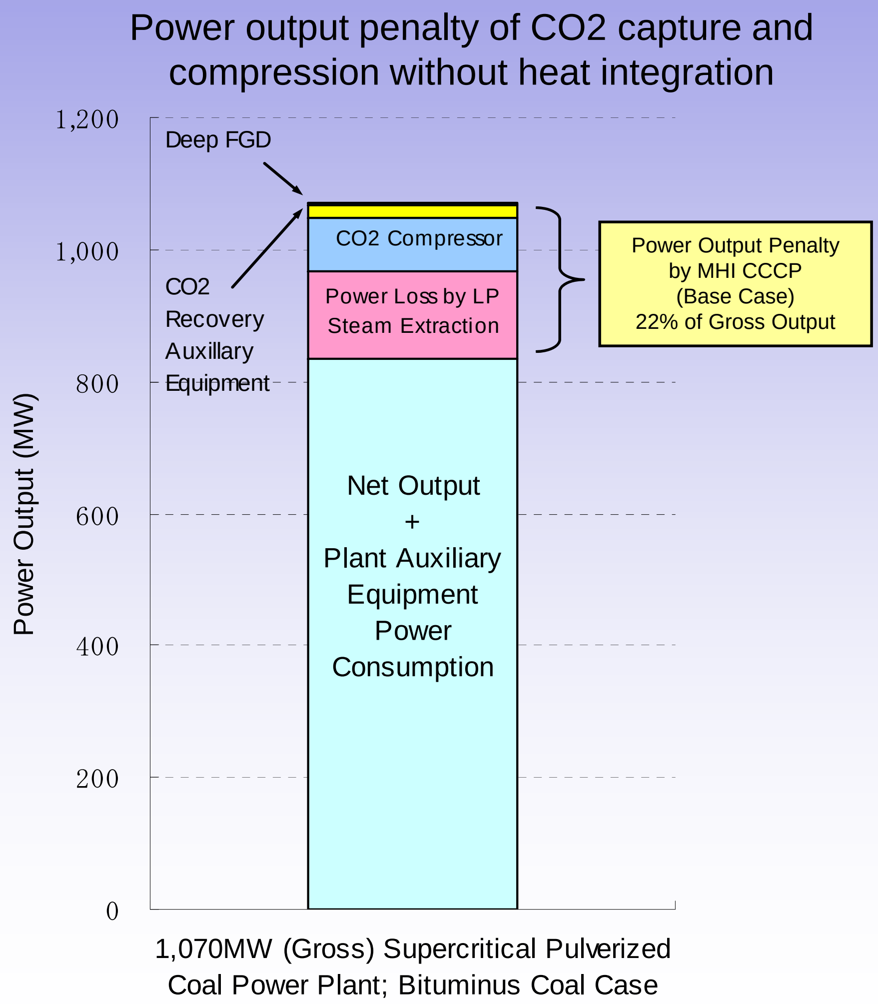
MHI Heat integration Concept

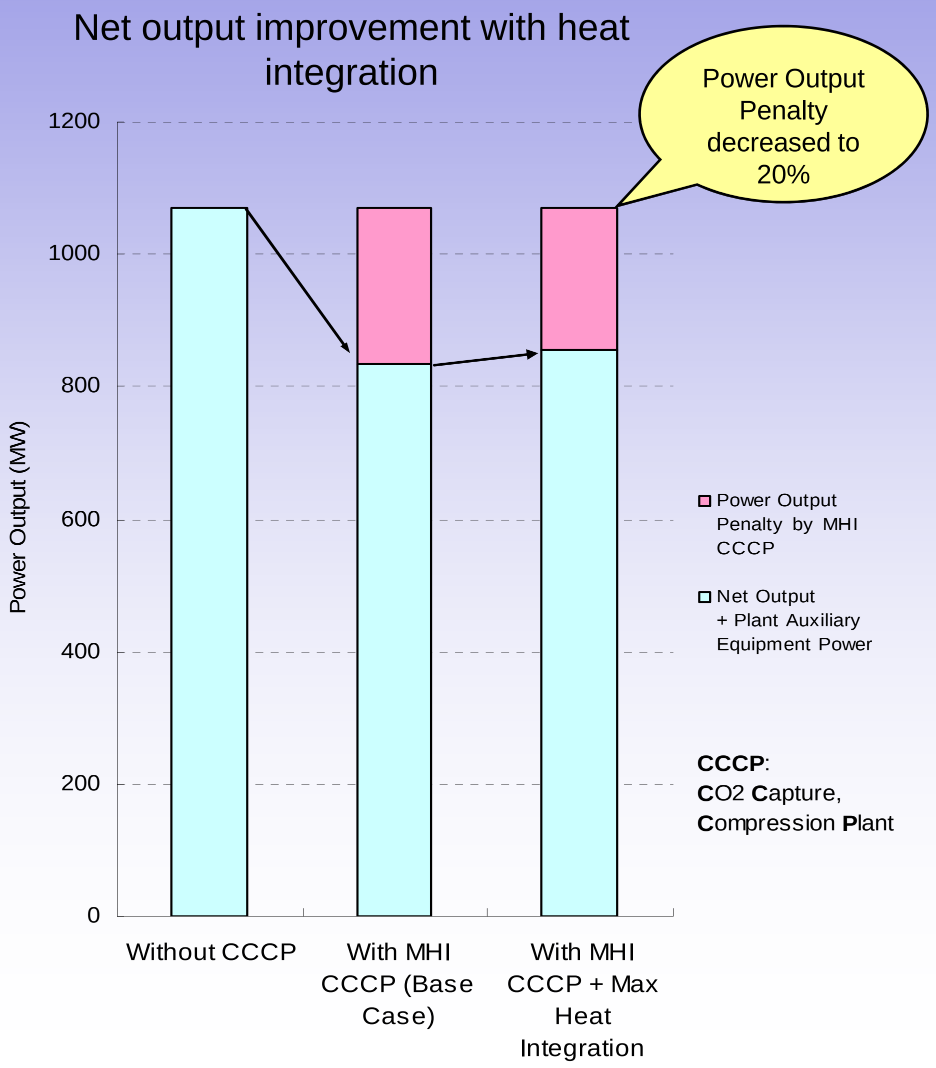


3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

CO2 Recovery Plant Power Output Penalty Assessment and Heat Integration Options;

1) Base Case +
2) Recovery of Compression Heat
3) Recovery of Flue Gas Heat

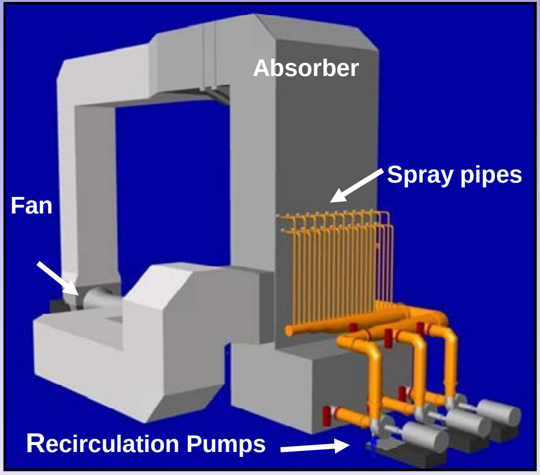

Power output penalty of CO2 capture and compression without heat integration


Net output improvement with heat integration

CCCP: **C**O2 **C**apture, **C**ompression **P**lant

3. MHI's CO2 Recovery Technology: Process Improvements & Heat Integration

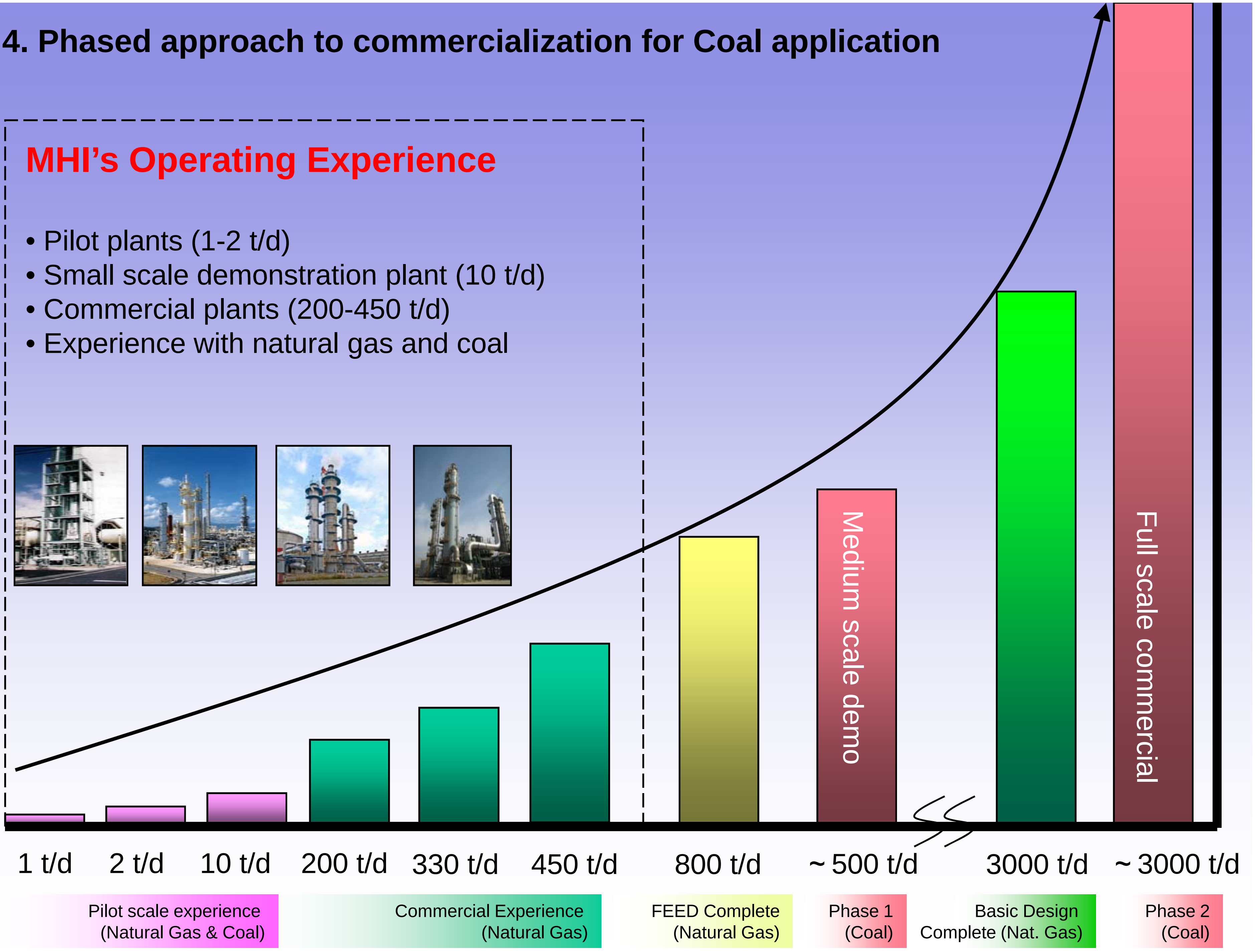
Multi-Pollutant Test Plant (FGD & CO2 Capture) Absorber 1 by 1 Scale Test Facility (400 MW equivalent)



Commercial Scale Tests

- Q1 2008 – Extensive Liquid Distribution Tests
- Rectangular Absorber
- Panel Design

4. Phased approach to commercialization for Coal application

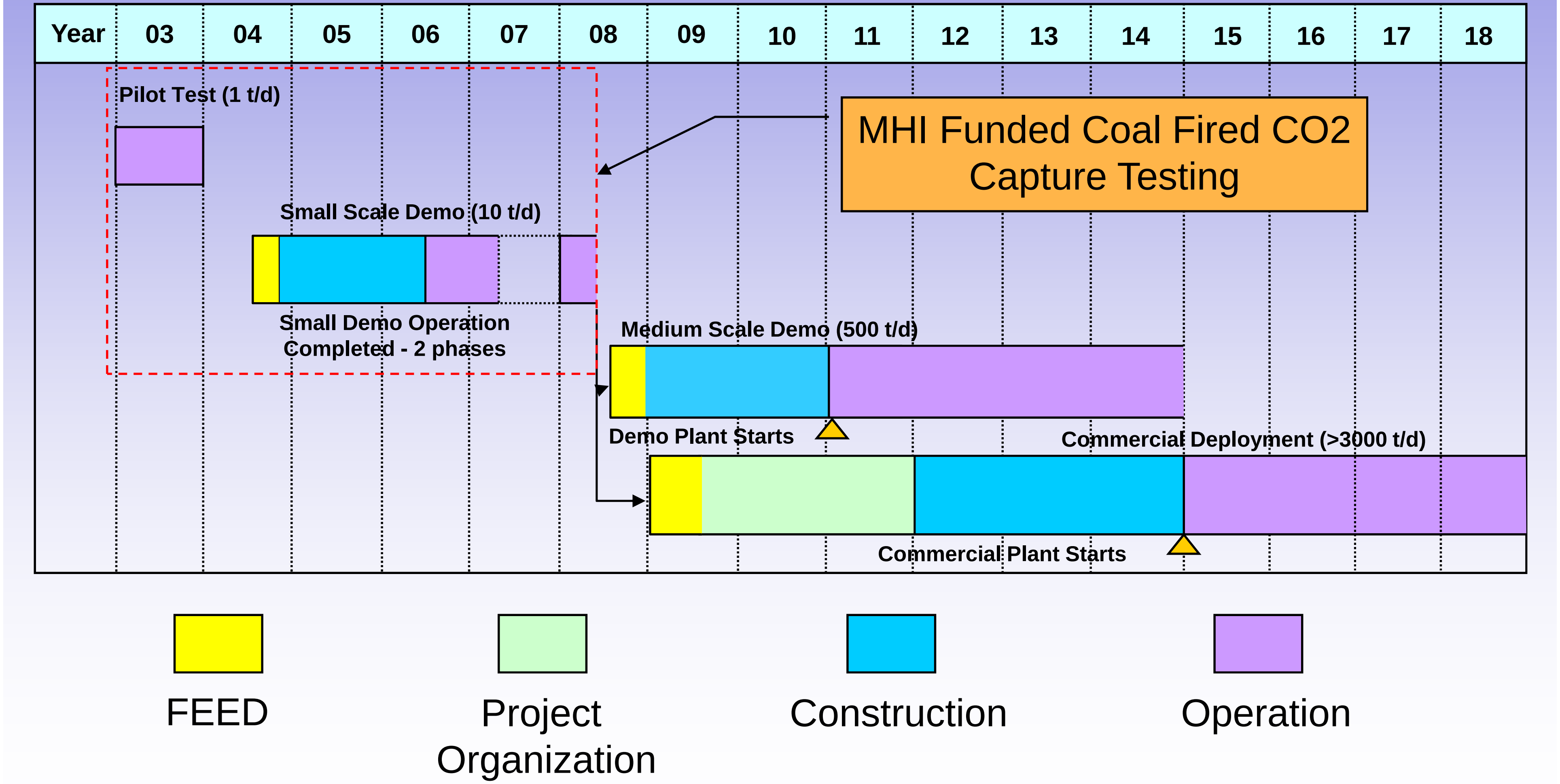


MHI's Operating Experience

- Pilot plants (1-2 t/d)
- Small scale demonstration plant (10 t/d)
- Commercial plants (200-450 t/d)
- Experience with natural gas and coal

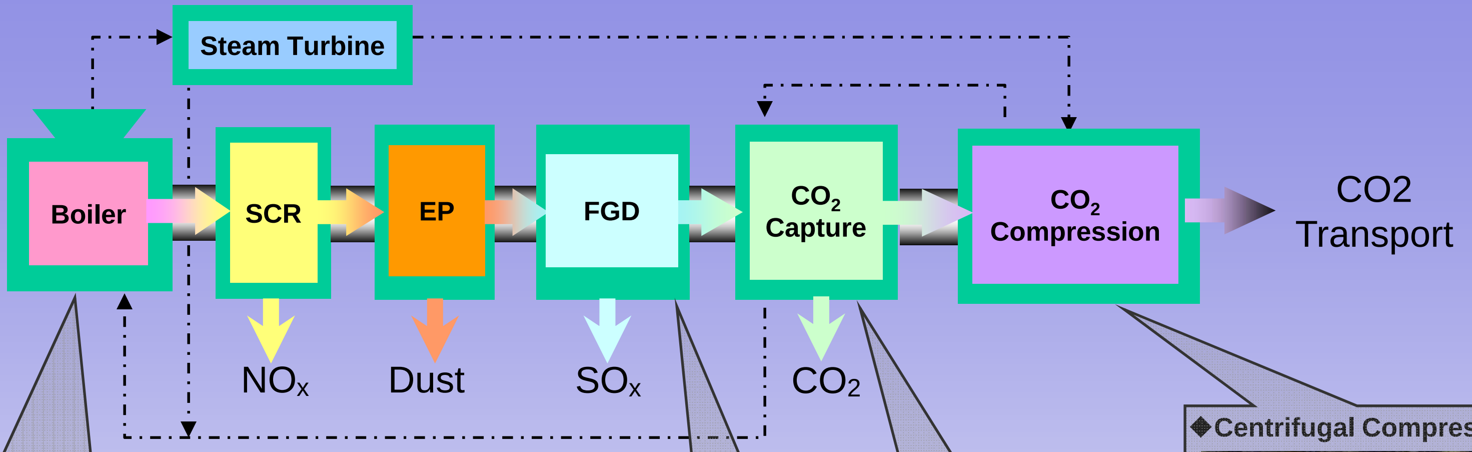
4. Phased approach to commercialization for Coal application

MHI’s Conceptual Schedule for a Medium – Large Scale Coal Fired CO2 Capture Demonstration Plant



Note: This schedule is a conceptual figure only and shows MHI’s roadmap for the future commercialization of this technology for coal fired boilers

5. MHI's Scope in a CCS Project



Steam Turbine

Boiler

SCR

EP

FGD

CO_2 Capture

CO_2 Compression

CO2 Transport

NO_x

Dust

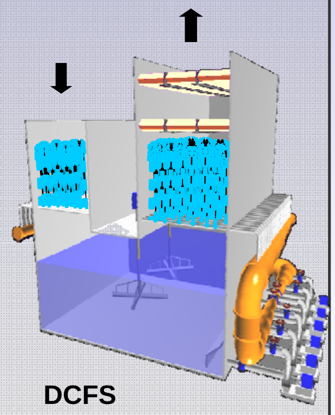
SO_x

CO_2

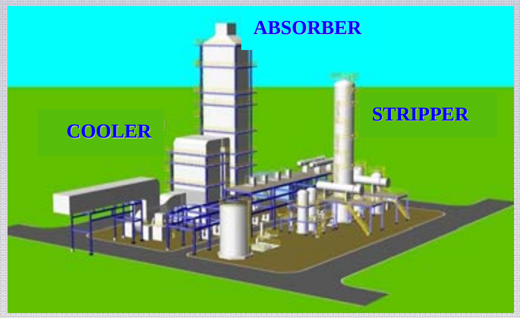
◆Centrifugal Compressors

◆Coal Fired Power Station

◆FGD



◆CO_2 Capture Plant



MHI Can Supply All Technology – Efficient Integration

6. Conclusions

Need for Carbon Capture & Storage

① Coal will remain a dominant fuel for electric power generation

② Coal with CCS technology can play an important part in CO2 mitigation - regulatory certainty and political support is needed

③ Governments must continue to support CCS and a ‘suite’ of carbon mitigation strategies

④ Incentives for first stage commercial CCS plants are necessary to reduce technical and financial uncertainties

⑤ Post combustion CO2 capture technology offers many advantages and can be transferred to developing countries

⑥ Allows for future zero emission use of coal

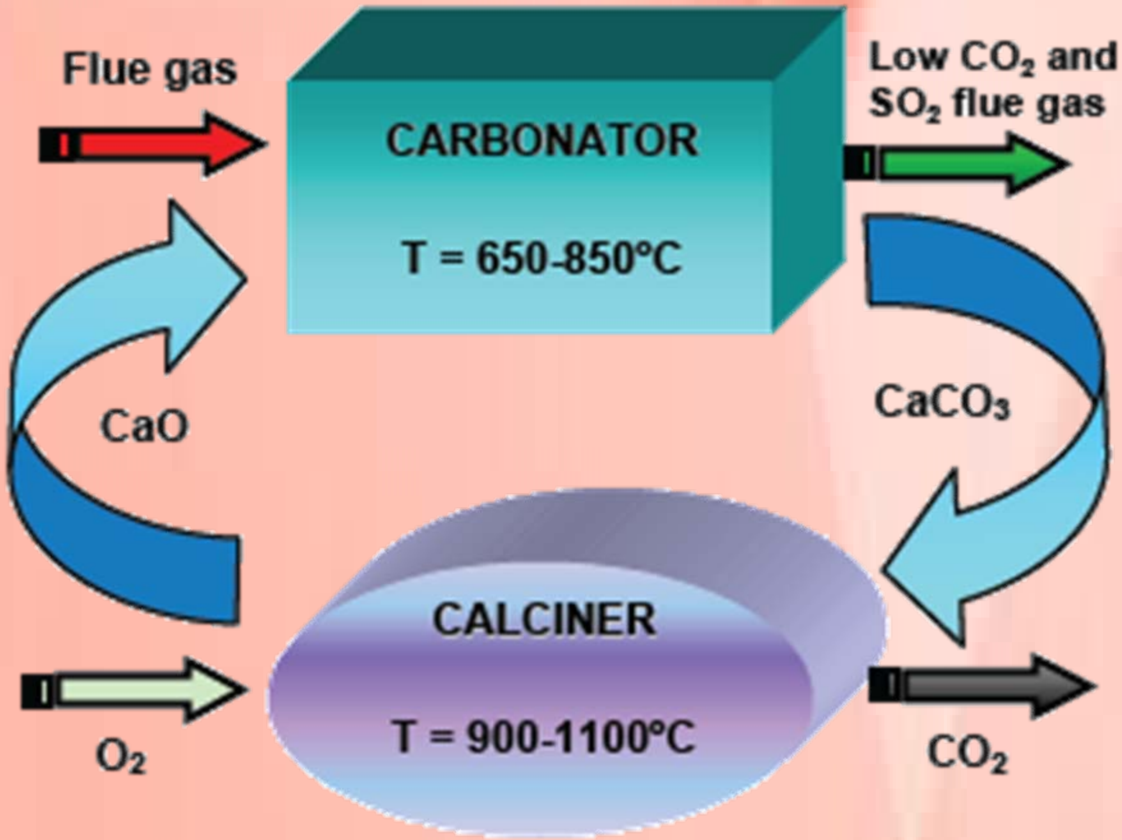
Potential CO_2 post-combustion capture systems

Robert Davidson
robert@iea-coal.org.uk

International Test Network for CO_2 Capture:
11th workshop
Maria Enzersdorf, Austria, 20-21 May 2008

www.iea-coal.org.uk
www.coalonline.org

Calcination/carbonation loop



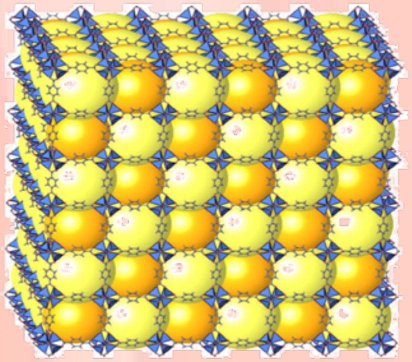
Alkali/alkaline earth compounds

- dolomites
- sodium carbonates
- potassium carbonates
- lithium compounds
- supported sorbents

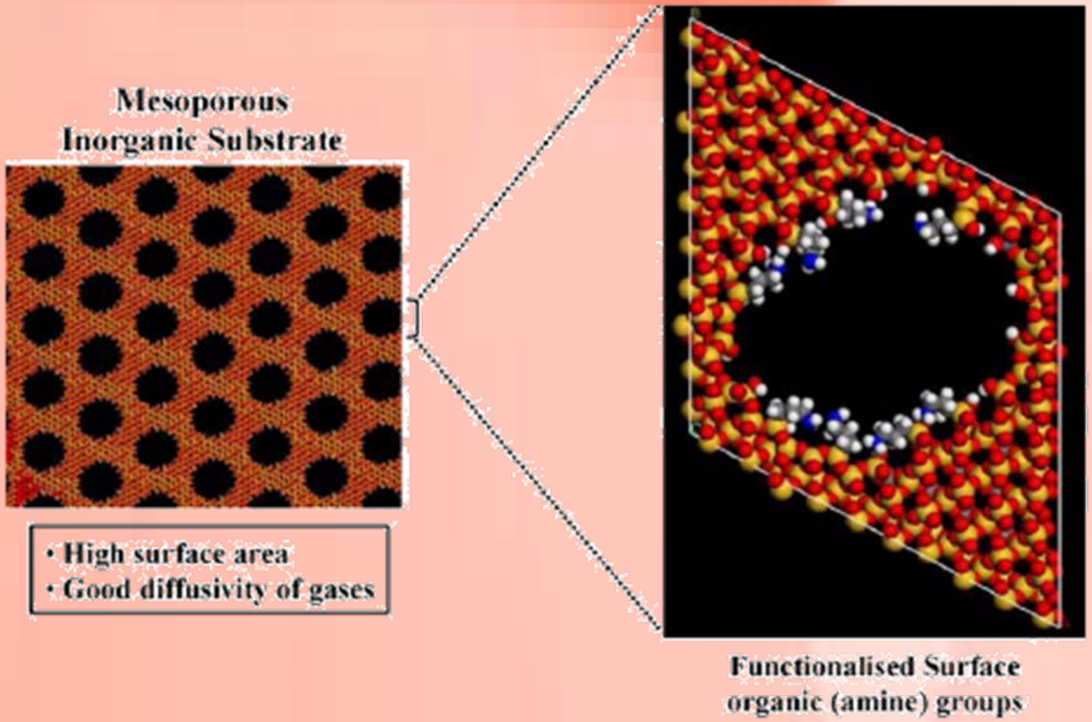
Physical microporous adsorbents

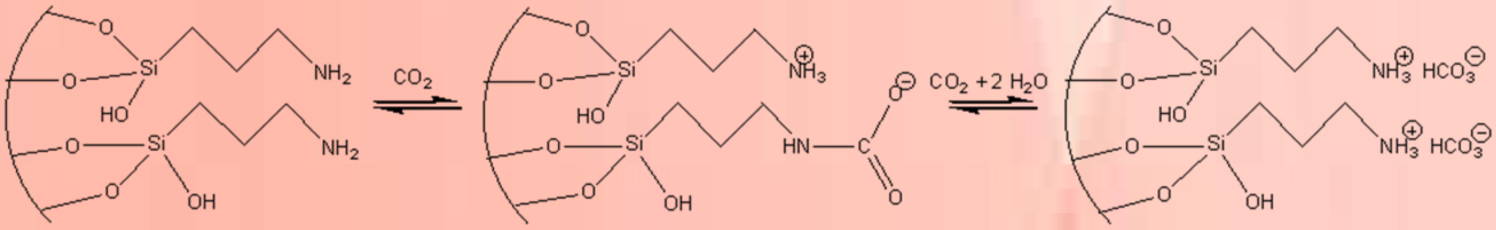
molecular sieves

- activated carbon
    - anthracite
- metal organic frameworks
- zeolites



CO_2 adsorption on immobilised amine adsorbents





Gas permeation membranes

- organic
  - glassy polymers
- inorganic
  - ceramic
  - metallic

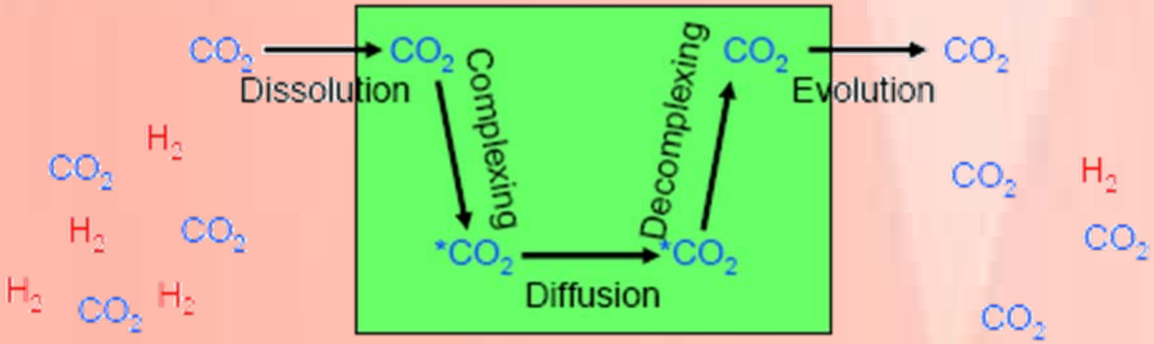
Polymeric membranes

- polyarylates
- polycarbonates
- polyimides
- polypyrrolones
- polysulphones
- copolymers and mixed polymers

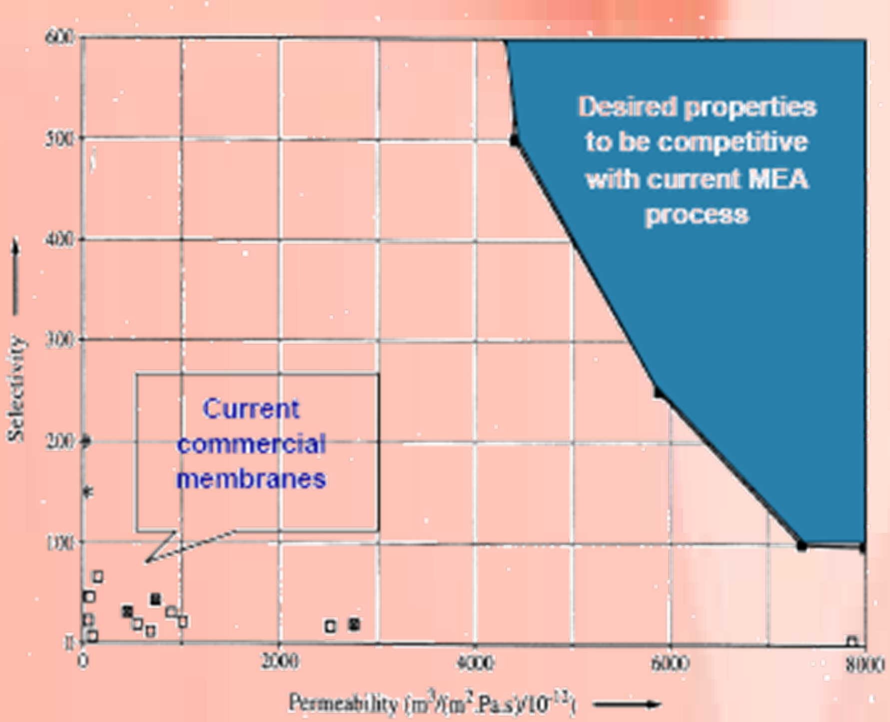
Facilitated transport membranes

reversible reactions between CO_2 and carriers in the membrane

inert gases such as N_2 do not react with the carriers



Membranes vs. MEA



Current economic performance of membrane separation process and its required quality to compete with current MEA processes

(Chen et al., 2006)

Summary

- dry regenerable sorbents
- physical microporous adsorbents
- amine modified substrates
- gas permeation membranes

... and a few more

- hydrates
- cryogenics
- photosynthesis of microalgae
- accelerated weathering of limestone

www.csiro.au

What is the next best thing in PCC?

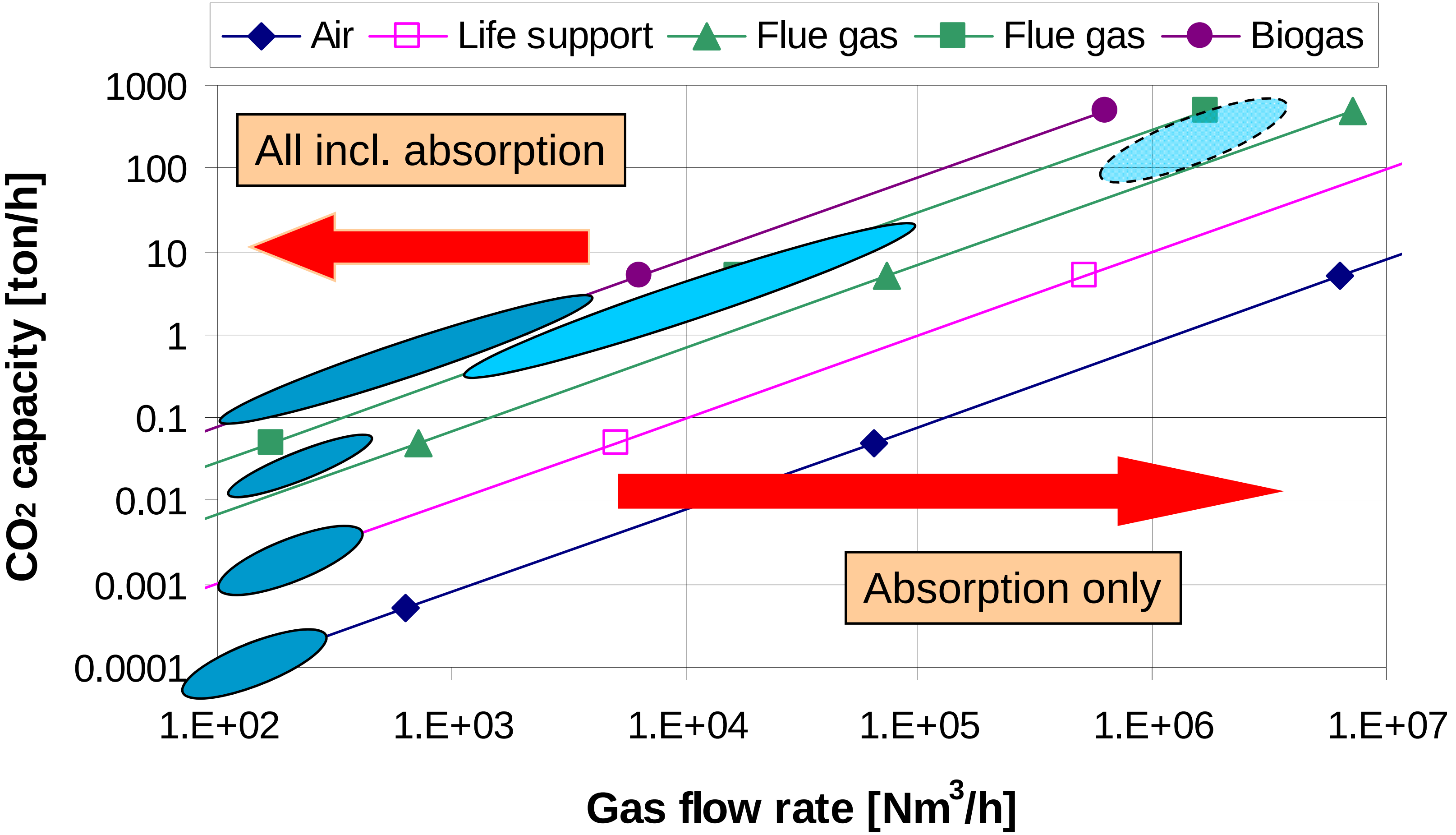
Energy Transformed Flagship

Paul Feron
IEA GHG 11th Post Combustion CO_2 Capture Network Meeting
Vienna, 20-21 May 2008

National Research
FLAGSHIPS

CSIRO

CO_2 separation at atmospheric pressure: Current technologies and markets



Panel discussion 11th IEA PCC network meeting, 20-21 May, Vienna, Austria

Novel PCC technologies

➢Requirements

- Quickly deployable at large capacities
- Need to be a lot better than absorption processes

➢Adsorption processes

- Use of circulating fluidised beds

➢Membranes

- Engineering designs for large capacities

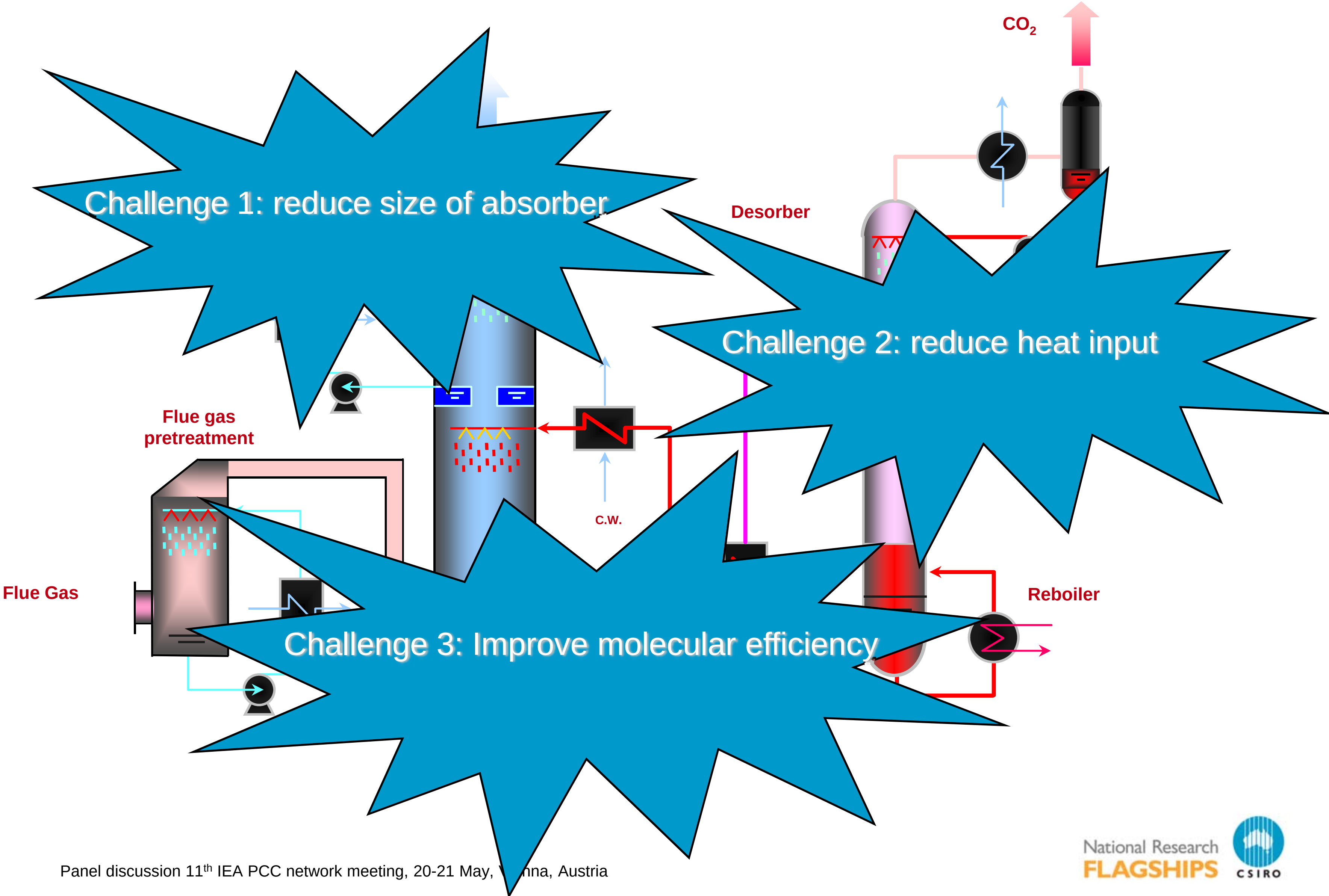
➢ Cryogenic technologies

- Engineering designs for large capacities

➢General

- Less material science, more engineering & equipment design
- Absorption processes likely to be improved through R,D&D

Three main challenges for PCC



Challenge 1: reduce size of absorber

Challenge 2: reduce heat input

Challenge 3: Improve molecular efficiency

Go for innovation in absorption processes!

- Advanced amines
  - Formulated mixtures, multiple amine groups
- Non-aqueous solvents
  - Ionic liquids
- Phase change solvents
  - Slurries, emulsions
- Modified process concepts
  - Intercooling, heat exchange integration in stripper, integration of compression, split flow
- Novel process components
  - Membrane contactors, heat pumps
- Robust solvents
  - Ammonia, carbonates
- Biomimetic approaches
  - Enzymes for solvent process improvements

NTNU
Norway

Department of Chemical Engineering

Remarks on post combustion CO_2 capture systems

Hallvard F. Svendsen, IEA GHG International Network Meeting 21 May 2008 , Vienna, Austria

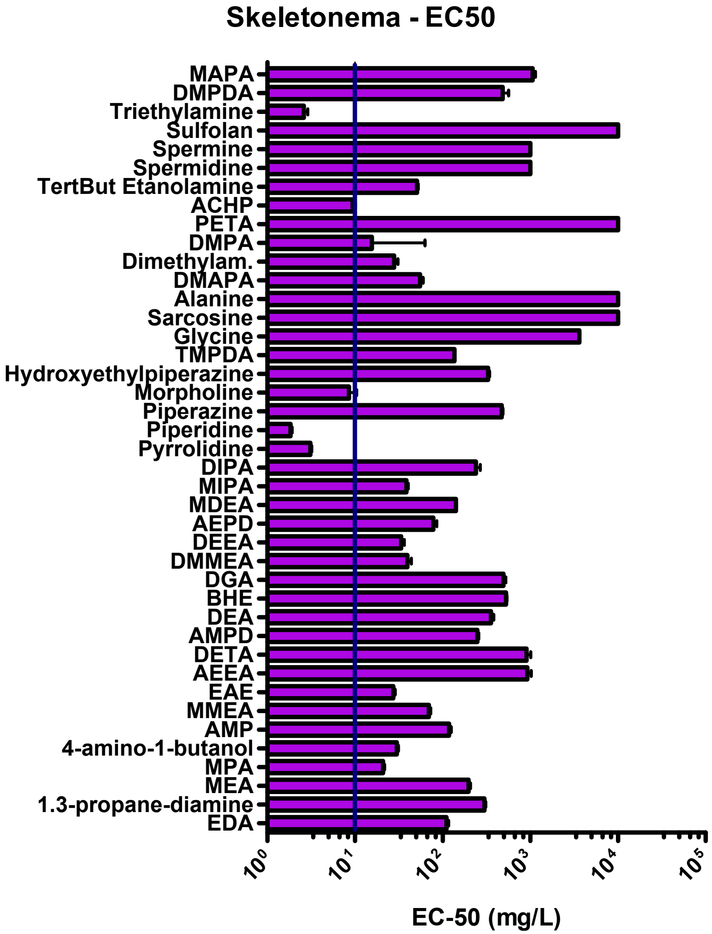
1) Environmental concerns
Categorization of chemicals
OSPAR Convention

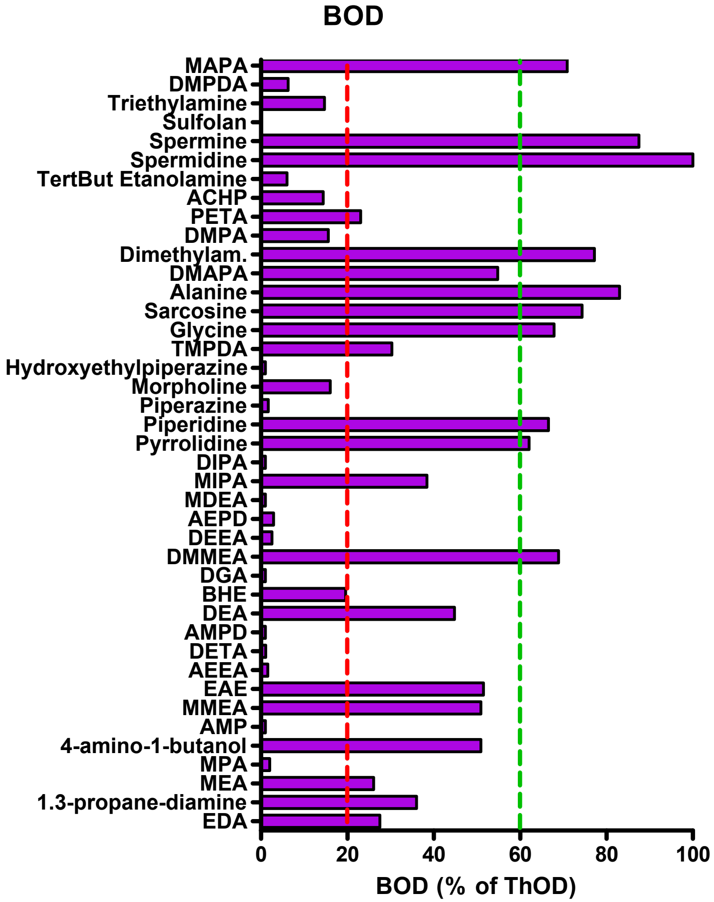
Category	*Criteria – Ecotoxicity tests*	*Actions*
Black	•Priority list (Stortingsmelding Nr. 25) •OSPAR List of Chemicals for Priority Action •Both low biodegradability and high bioaccumulation (BOD28 < 20 %, and Log $P_{OW} \geq 5$) •Low biodegradability and toxic (BOD28 < 20 %, and EC50 or LC50 ≤ 10 mg/L) •Compounds expected to be carcinogenic/mutagenic or harmful to reproduction	**Not discharged**
Red	•Inorganic chemicals with high toxicity (EC50 or LC50 ≤ 1 mg/L) •Organic chemicals with low biodegradability (BOD28 < 20 %) •Organic chemicals or mixtures which meet 2 of the 3 following criteria: Biodegradability < 60 %, bioaccumulation potential (Log $P_{OW} \geq 5$), or toxicity of EC50 or LC50 ≤ 10 mg/L	**Phased out or replaced**
Yellow	•Include compounds which based on their characteristics are not defined as RED or BLACK, and •NOT included in the PLONOR list	**Accepted**
Green	•Chemicals expected to have NO environmental effects •PLONOR list	**Testing not required**

Department of Chemical Engineering

Example results

Ecotoxicity and biodegradability for 41 solvents.





Phase change absorption systems

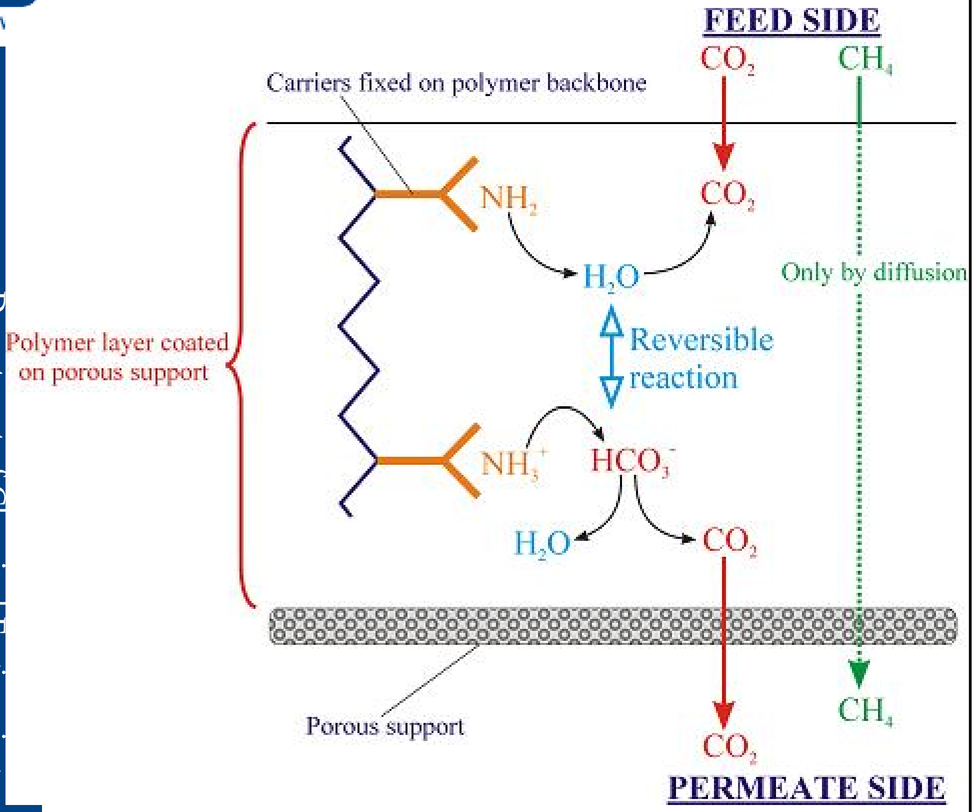
Precipitation:

- Alstom Chilled Ammonia
- Precipitating amino acid systems

Two liquid phases:

- IFP process

Facilitated Transport by a ”fixed-site-carrier” (FSC) membrane



Example gas mix: $CO_2 – N_2$

Example existing membrane

Cellulose Acetate (CA)

CO_2 flux: 0.15 m^3(STP)/(m^2 h bar)

Selectivity CO_2/N_2 : ~30

Comment:

The simple, polymeric membranes will never be an alternative for CO_2-N_2 separation in large volume gas streams such as flue gas

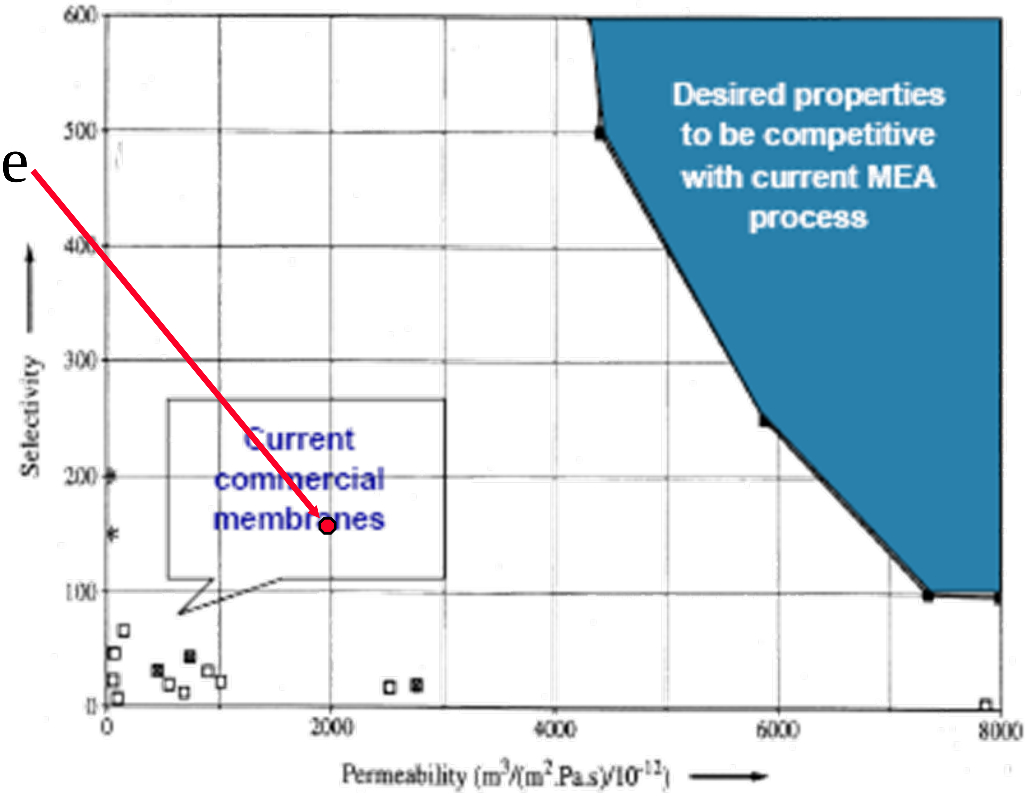
⇐The New FSC-membrane may be attractive for integrated solutions.

CO_2 flux → 0.70 m^3(STP)/(m^2 h bar)

Selectivity CO_2/N_2 : > 150

PCT: Hägg, MB, Kim TJ, Li,B.: WO2005/089907

FSC membrane



Other options:
Dual action, liquid filled membranes

Six rules for maximising the effectiveness of post combustion CO_2 capture systems

Jon Gibbins, Imperial College (GHGT7 paper, 2004)

1. Add heat to the steam cycle at as high a temperature as possible (i.e. be prepared to use best available steam conditions if commercially justified).

2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at as low a temperature as possible.

3. Produce as much electricity as possible from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.

4. Make use of waste heat from CO_2 capture and compression in the steam cycle.

5. Use the latest solvent developments.

6. Exploit the inherent flexibility of post-combustion capture.

Six rules for maximising the effectiveness of post combustion CO_2 capture systems

Jon Gibbins, Imperial College (GHGT7 paper, 2004)

1. Add heat to the steam cycle at as high a temperature as possible (i.e. be prepared to use best available steam conditions if commercially justified).

2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at as low a temperature as possible.

3. Produce as much electricity as possible from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.

4. Make use of waste heat from CO_2 capture and compression in the steam cycle.

5. Use the latest solvent developments.

6. Exploit the inherent flexibility of post-combustion capture.

2. Reject heat from the steam cycle, in the steam extracted for solvent regeneration, at as low a temperature as possible.
Part load steam extraction issues
Multiple steam tapping points?
Auxiliary turbines?

4. Make use of waste heat from CO_2 capture and compression in the steam cycle.
Feed water quality issues
Secondary heat recovery circuits?
Interaction with district heating

5. Use the latest solvent developments.
Capital costs plus flexibility, appropriate construction approach
Compatible upgraded solvents
Troubleshooting solvent additives – maintaining performance

6. Exploit the inherent flexibility of post-combustion capture.
Definite interest in this area now
Solvent storage
Compressor/pipeline interactions
Dynamic modelling including revenue optimisation

Post-Combustion CO_2-capture

Potential CO_2 post-combustion capture systems

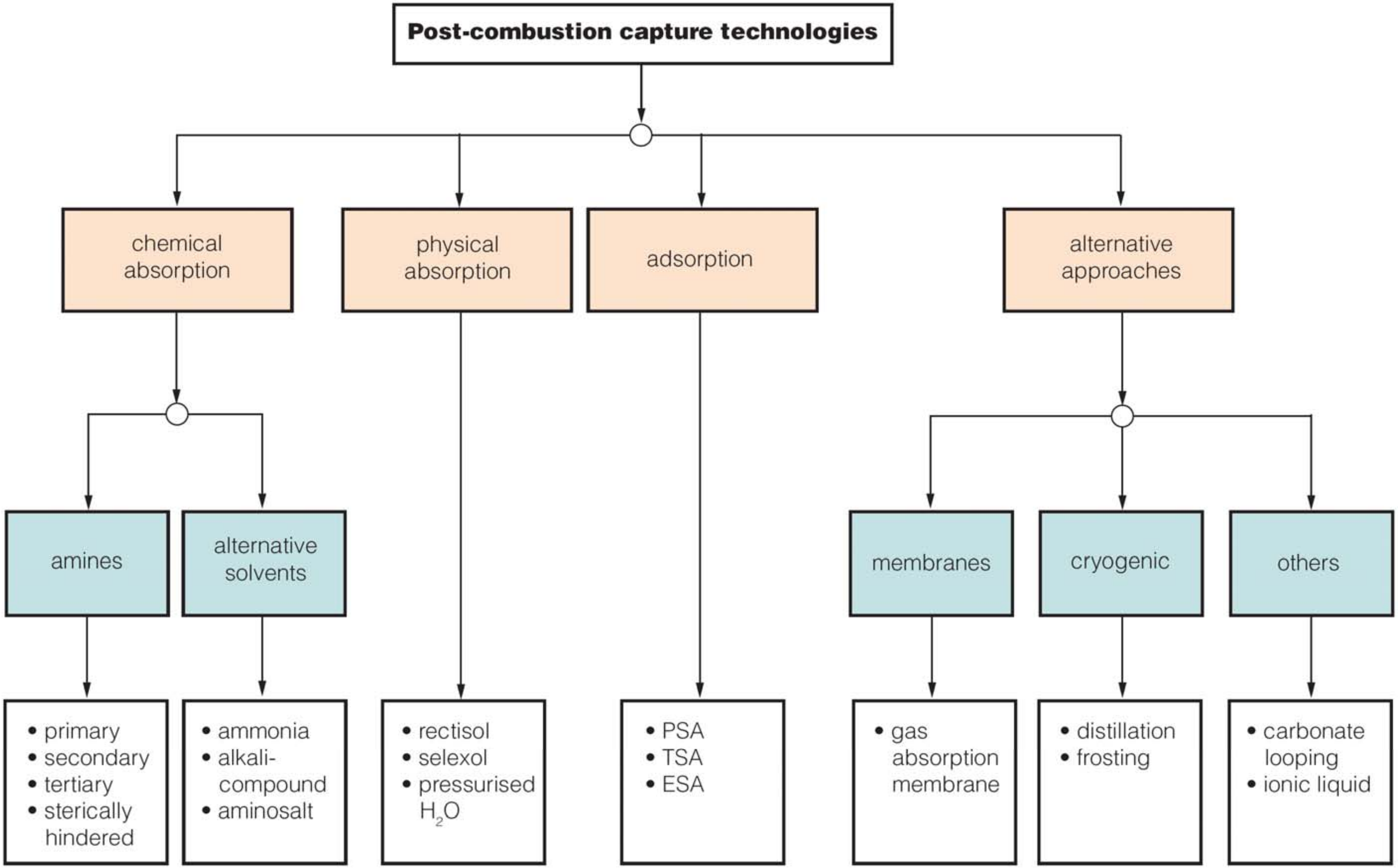
Challenges of future technology development

Alfons Kather

11th Post Combustion Network Meeting
Panel Session
Vienna, 21st May 2008

TUHH
Technische Universität Hamburg-Harburg
Institute of Energy Systems

PCC Technologies



Post-combustion capture technologies

chemical absorption

physical absorption

adsorption

alternative approaches

amines

alternative solvents

membranes

cryogenic

others

- primary
- secondary
- tertiary
- sterically hindered

- ammonia
- alkali-compound
- aminosalt

- rectisol
- selexol
- pressurised H_2O

- PSA
- TSA
- ESA

- gas absorption membrane

- distillation
- frosting

- carbonate looping
- ionic liquid

Competition for Deployment

- **PCC processes using wet chemical absorption compete for large scale deployment in the middle and long term with**
    - alternative PCC technologies, and
    - Oxyfuel & IGCC-CCS technologies.

Summary

	SPP-PCC	IGCC	SPP-PCC-CCS	Oxyfuel	IGCC-CCS
Availab./Reliability	**+**	**-**	**+**	●	**-**
		short-term			
Efficiency	46%	46%	**34%→36%**	**37%**	**38%**
CO_2 emissions (gCO_2/kW.h)	717	717	97→92	89	87
Fuel consumption*	base	base	+35%→+28%	+24%	+21%
		long-term			
Efficiency	50%	51%	**41%**	**42%**	**44%**
CO_2 emissions (gCO_2/kW.h)	660	647	80	79	75
Fuel consumption*	-8%	-10%	+12%	+10%	+5%

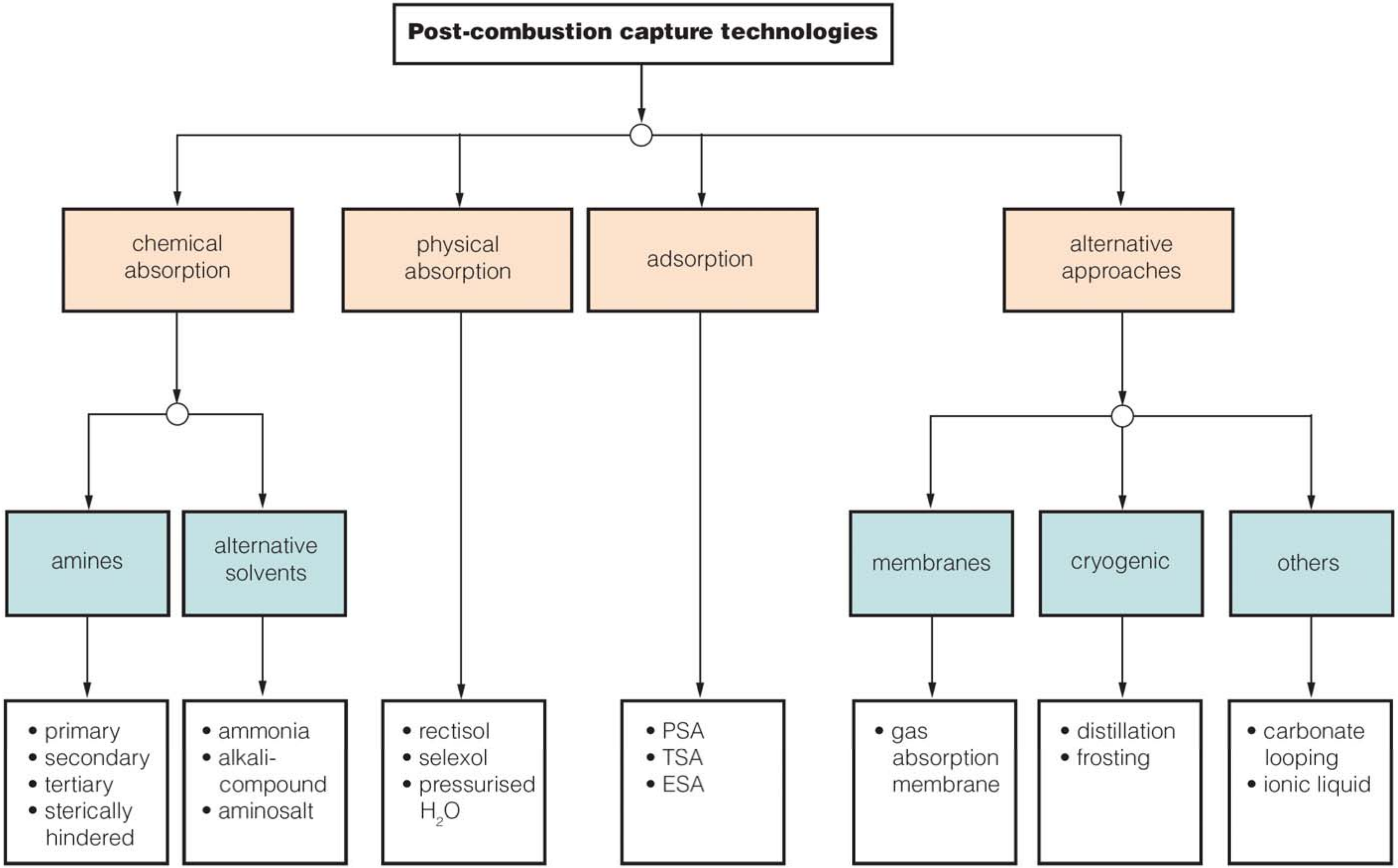
* relative to the reference plant (SPP-PCC with 46% efficiency)

Competition for Deployment

- **Of the three CCS technology paths, Post-Combustion CO_2-capture (PCC) using wet chemical absorption currently**
  - shows the largest efficiency decrease, and
  - has the potential of highest availability, reliability and flexibility.

►The integrated overall CO_2-capture process that shows the highest efficiency while offering acceptable levels of availability and reliability will prevail in this competition.

PCC Technologies



Post-combustion capture technologies

chemical absorption

physical absorption

adsorption

alternative approaches

amines

alternative solvents

membranes

cryogenic

others

- primary
- secondary
- tertiary
- sterically hindered

- ammonia
- alkali-compound
- aminosalt

- rectisol
- selexol
- pressurised H_2O

- PSA
- TSA
- ESA

- gas absorption membrane

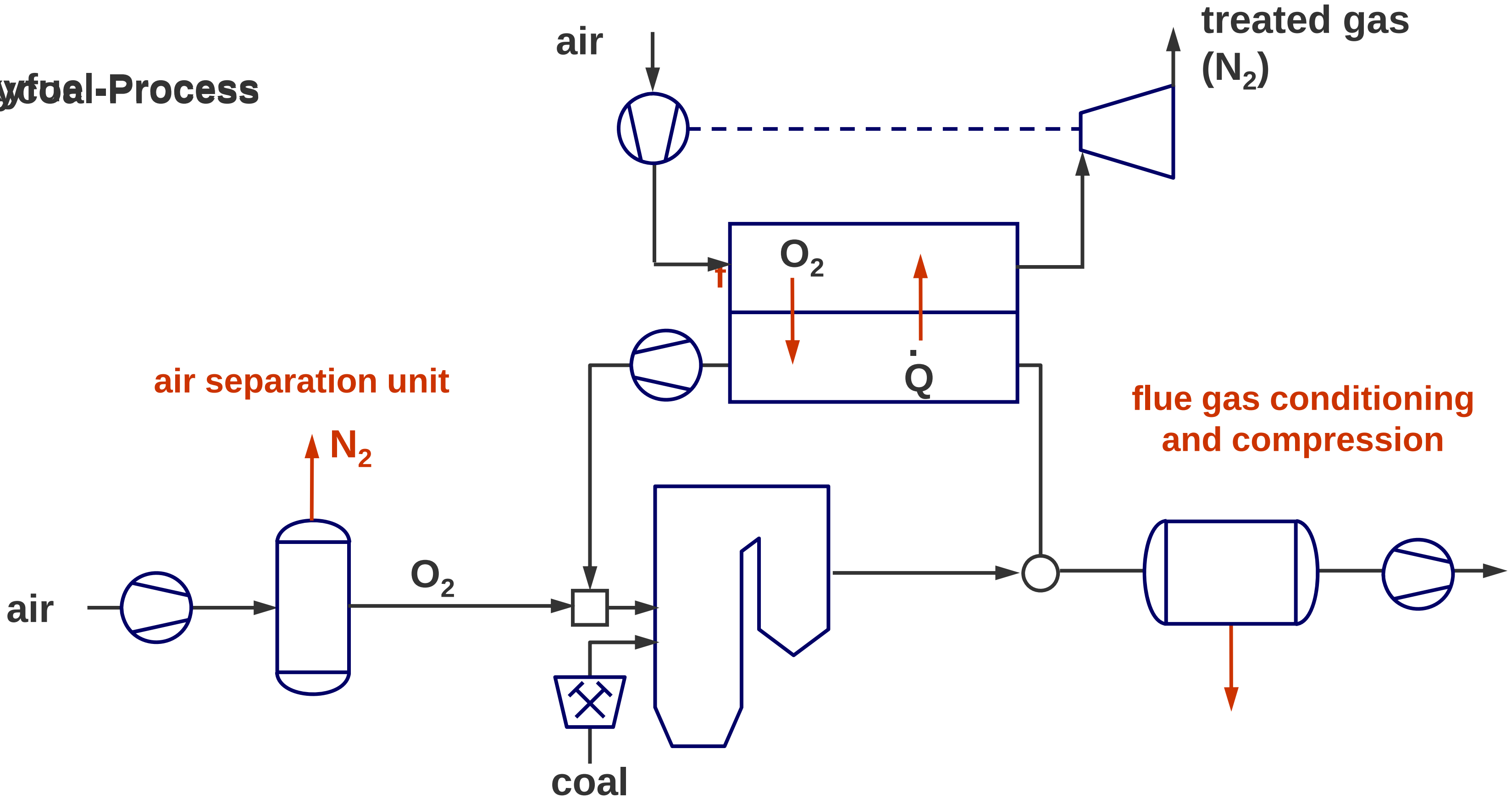
- distillation
- frosting

- carbonate looping
- ionic liquid

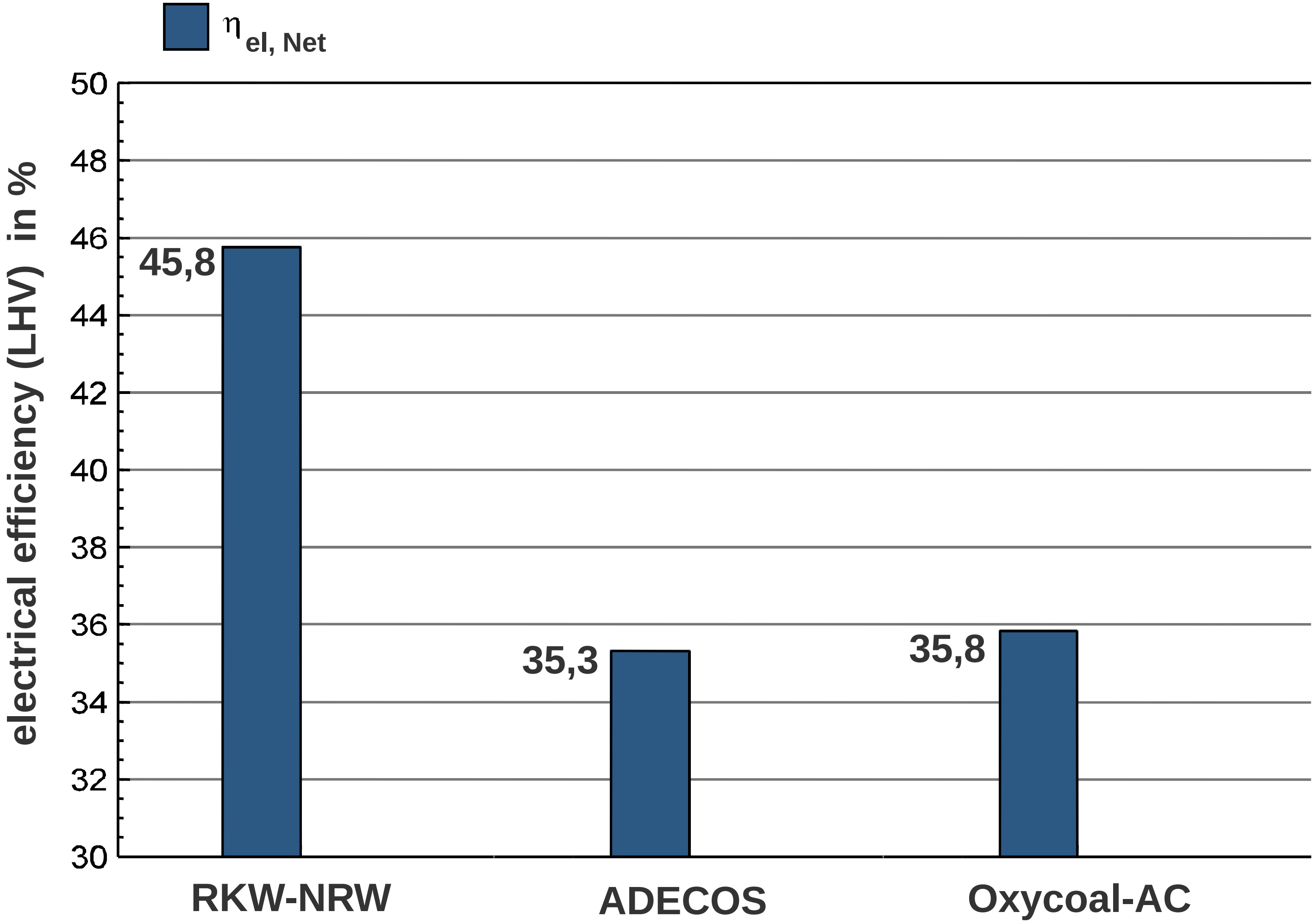
Oxyfuel vs. Oxycoal

Oxyfuel-Process

Oxycoal-Process



Comparison of efficiency and CO_2-emission



→ **Before doing detailed R&D the overall process has to be checked according to efficiency potential and reliability**

Conclusion

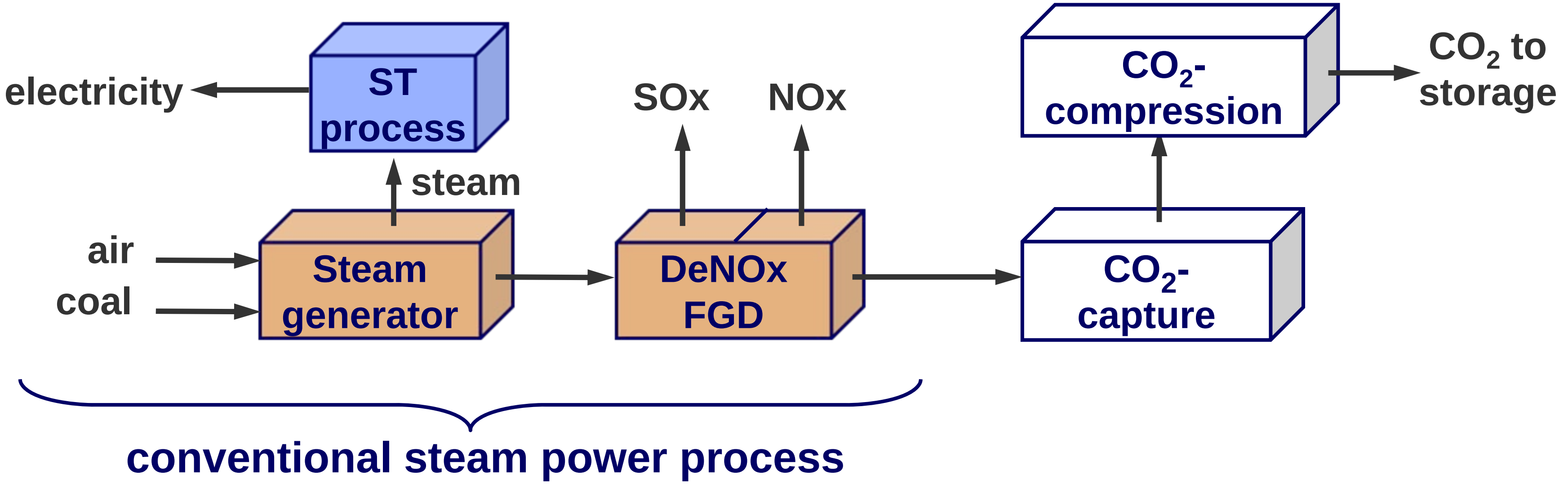
- The need for high efficiency and high levels of reliability and availability demands the consideration of the integrated overall process.

►Continuous and seamless communication among

- Chemists
- Chemical engineers
- Mechanical engineers

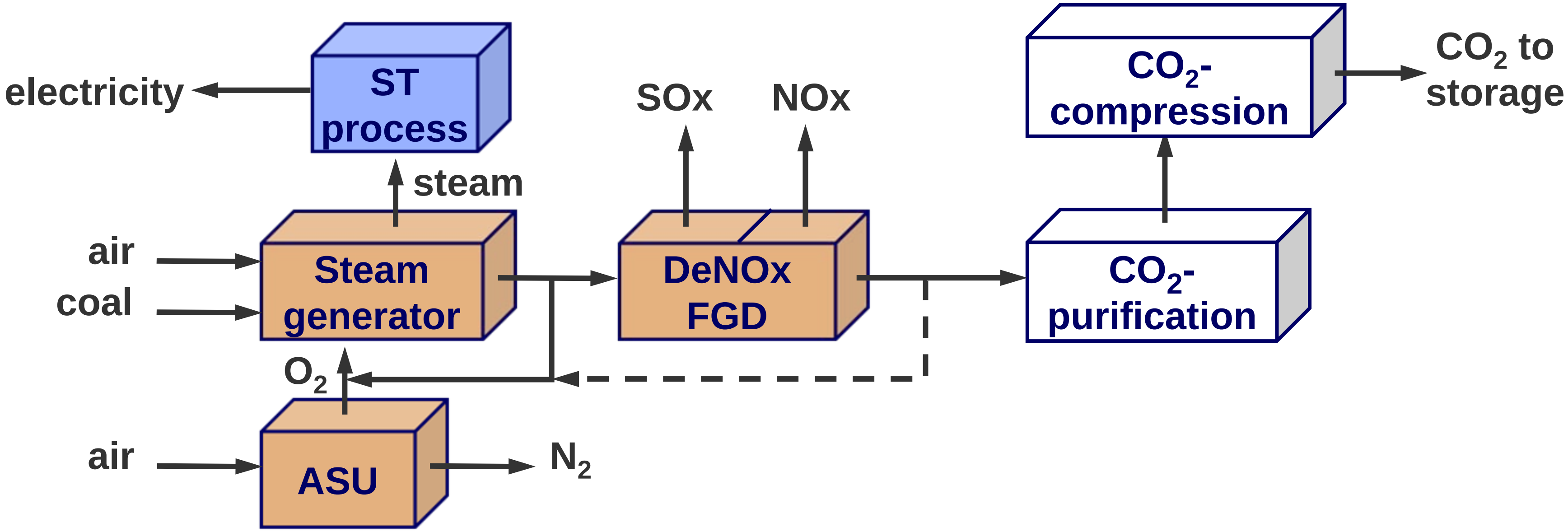
Thank you for your attention

Post-combustion capture (PCC) with chemical absorption



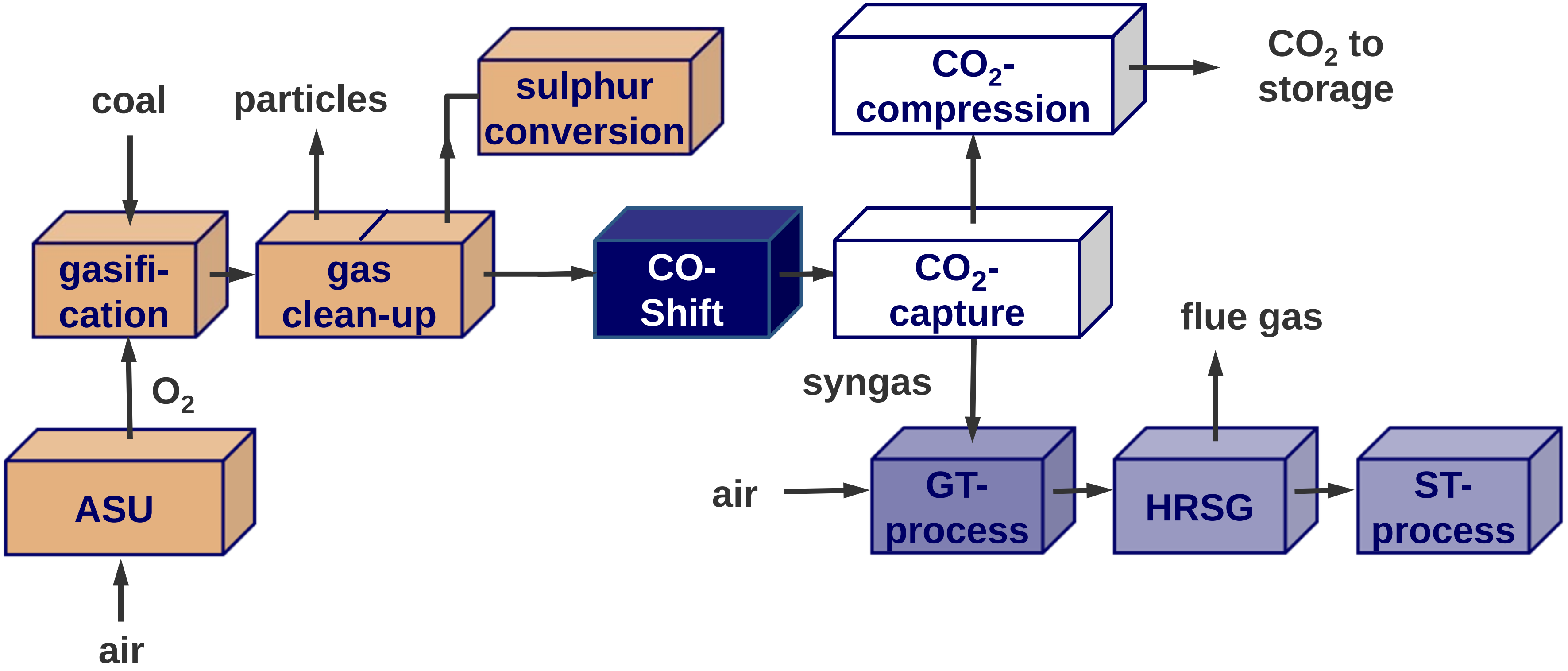
- \+ Commercial experience with chemical absorption from gas treating industry
- \+ Based upon proven steam power process ➔ reliability and availability
- \+ Small degree of integration, high flexibility
- − Highest efficiency decrease of the three CCS paths (~12%pts →10%)

Oxyfuel combustion



- + Possibly lower efficiency decrease than post-combustion capture (10.5%pts → 9%pts)
- O Based on proven steam power process but with many changes in the firing system
- − Impurities could present a knock-out criterion depending on transport and storage specifications → distillation ?

Pre-combustion capture (IGCC-CCS)



\+ Potential for smallest efficiency decrease (~8%pts)

\+ Flexibility with respect to fuel and products (polygeneration)

– Highly complex process configuration ➔ reliability?