INTERNATIONAL NETWORK FOR CO_2 CAPTURE: REPORT ON 12th MEETING

Report: 2010/ 2

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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 28 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. IEAGHG is one of these Implementing Agreements.

DISCLAIMER AND ACKNOWLEDGEMENTS

IEAGHG 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 IEAGHG as a record of the events of that workshop.

The 12th international research network meeting on CO$_2$ Capture was organised by IEAGHG in co-operation with University of Regina. The organisers acknowledge the financial support provided by the sponsors for this meeting and the hospitality provided by the hosts The Regina Inn Hotel and Conference Centre.

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Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

International Network for CO_2 Capture: Report on 12th Meeting

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29-30th September 2009, University of Regina, Regina, Canada

B&W power generation group
RWE The energy to lead
University of Regina Engineering Office of Energy and Environment
IPAC CO2
ITC
SaskPower
HTC Purenergy
DOOSAN Doosan Babcock Energy
Stokes Research Inc.
Saskatchewan Ministry of Energy and Resources
Stantec

Executive Summary

This meeting was the twelfth 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, Lyon and Vienna.

The programme of the 12th meeting was well received by the participants. 2 days in “class room” with 30 technical presentations and 20 posters. The meeting covered:

- The fundamental studies: This session covered topics related to fundamental work on amine based solvents, the development of new solvents with lower heat demand for stripping and the use of inhibitors to minimise solvent degradation and corrosion. In addition, the development of future capture technologies including ionic liquids and solid sorbents was presented.
- Pilot plant and scale up, this was the biggest session with 9 presentations. This showed the increasing interest in pilot plant and large scale demonstration.
- Capture process modelling: this session presented both fundamental thermodynamics and process modelling.
- Environmental impacts of post combustion capture, which is a topic of increasing attention and interest, were discussed in two dedicated presentations.

The interest and interaction of the participants varied from one topic to another. It was clear that the main interest of the participants were in the pilot plant and demonstration results and the newly developed capture processes and solvents. For many of the delegates, the level and details of the presented results of the pilot plant experimental work were limited and below expectation. This was due to the fact that most of the pilot and demonstration plant are still either in the first testing phase or in the planning and construction phases. However, for the coming meetings, it is important to keep and increase the focus on the pilot plants and large demonstration projects and results. In addition, more time should be given for these presentations, to encourage more results sharing and more discussions.

Different technologies were presented in this meeting, which could be considered as 2nd or 3rd generation technologies; for example, ionic liquids, the membrane technologies and the calcium-based process. It is important for future meeting to keep track of future development and R&D activities related to 2nd/3rd generation capture technologies.

Two dedicated presentations focused on the environmental impact of post combustion capture, which is considered an important issue to solve before full scale capture process deployment. The expected emissions of amines, additives and their degradation products with flue gas stream and waste product streams is a continued concern for the deployment of full scale CO_2 post combustion capture using amines.

The next network meeting is tentatively scheduled for spring 2011, with two offers to host this meeting being received by IEAGHG. The host and timing of the next meeting will be discussed further.

The format of the next meetings needs to be discussed and decided upon. Looking to the increased number of participants and interest in presenting during the workshop supports the idea of moving to conference type proceedings (based on presentations rather than written papers) with parallel sessions. Some long term attendees would like to see the single session approach retained even if this means limiting participation mostly to specifically invited people. During the wrap up these alternatives were put to the audience and a show of hands requested. The result was a roughly even split, so it becomes a matter purely for IEAGHG staff and members to determine.

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REPORT ON 12th Meeting

(29-30th September 2009, University of Regina, Regina, Canada)

1 Introduction

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Carbon dioxide capture and storage (CSS) 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 improve efficiency power plant looks likely to be a major element for new plants as markets develop. Retrofit to established plants is technically feasible although economically unattractive for ageing, less efficient assets.

Over the years in which this network series has existed, the interest in post combustion capture, the number of pilot plants and demonstrations projects and plans have increased. This 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 Regina had to be closed before the meeting to keep within room limits of around 150 people.

This report contains summaries of the presentations on a variety of developments including updates on amines, use of ammonia as a solvent, ionic liquids, solid sorbents, pilot plant and demonstration projects, modelling activities and environmental impacts of post combustion capture. In addition, the overall meeting evaluation and the major learning points from the meeting are summarised at the end of the report.

2 Programme

The programme of the meeting consisted of five oral presentation sessions in parallel to a poster session, which was added for the first time due to the high number of submitted abstracts and interest in presenting during the meeting.

The meeting agenda included:

- The fundamental studies: This session covered topics related to fundamental work on amine based solvents, the development of new solvents with lower heat demand for stripping and the use of inhibitors to minimise solvent degradation and corrosion. In addition, the development of future capture technologies including ionic liquids and solid sorbents was presented.
- Pilot plant and scale up, this was the biggest session with 9 presentations. This showed the increasing interest in pilot plant and large scale demonstration.
- Capture process modelling: this session presented both fundamental thermodynamics and process modelling.
- Environmental impacts of post combustion capture, which is a topic of increasing attention and interest was presented in two dedicated presentations.

3 Presentations Summaries and Discussion

3.1 Session one and sponsors

3.1.1 Welcome and introduction, John Topper, IEAGHG

The meeting was opened by John Topper, who welcomed the delegates on behalf of IEAGHG, extended thanks to the delegates, sponsors and organisers of the workshop for sharing their knowledge of CO_2 post combustion capture work currently undertaken around the world and hoped that the meeting would be beneficial, and include meaningful discussions.

John followed with a short introduction to the IEAGHG, explaining the background of the programme and its members and sponsors. The background and origination of the network was explained, touching briefly on the main aims of the network and the reasons for international cooperation in the CO_2 post combustion area. In 2000 the first international network for CO_2 capture took place in Gaithersburg in USA. Following the success of the workshop in Gaithersburg, 11 meetings of this series were organised in the following years. The interest of the network grew from the first meeting with 22 delegates to the 12th meeting. Almost 150 delegates from 18 countries (including major developing countries such as, India, China, Saudi Arabia and United Arab Emirates) joined the 2 day programme with more than 30% of the delegates came from North America.

John thanked the sponsors for the financial support of the workshop and the organising team from University of Regina and IEAGHG for their effort.

Some thoughts on the timing and format of the next time meeting were presented by John. The proposal was to have the next network in 2011 to avoid conflict with GHGT-10. The idea of either keeping the current single session format or move to parallel sessions while keeping the presentation format for was opened for discussion and debate during the workshop.

3.1.2 Post combustion capture research by the university of Regina and ITC, Paitoon Tontiwachwuthikul, University of Regina

Paitoon started the presentation with the reasons to apply CCS and how it could contribute to the overall reduction of CO_2 emissions. In addition, the speaker presented the reasons for the use of reactive solvents for CO_2 post combustion capture:

- Theoretical issues: the mass transfer of CO_2 in liquid is 10 to 100 times faster than other mediums
- The technology is proven and in use in gas processing
- The technology is available today
- The cost of technology is 25-60 \$/ton CO_2, depending on situation and location

The testing facilities at the University of Regina varied from research facilities and multi-purpose technology development pilot to technology demonstration plant at Boundary Dam power station near Estevan, Saskatchewan, Canada. These facilities serve the purposes of new solvent development and capture process development and optimisation. The scope of the research activities at University of Regina and ITC are:

- Fundamental: solvent development, solvent stability studies and membrane development.
- Bench testing facilities: solvent and membrane testing
- Pilot plant: technology testing on pilot scale and process optimisation
- Demonstration: technology testing on pre-commercial field demonstration plant

The research activities at the University of Regina resulted in the development of new chemicals for CO_2 absorption. These new solvents have superior performance in terms of higher absorption capacity and cyclic capacity, lower regeneration energy and lower circulation rate. Among others, the 4-diethylamine-2-butanol (DEAB) is found to have better solubility and cyclic capacities than both MEA and MDEA.

The capture testing facilities and pilot plants at University of Regina and Boundary Dam power station are used to optimise solvent circulation, maximise heat transfer between streams, optimise CO_2 loading and optimise the process configuration. Optimising the advanced capture technology, provided by University of Regina, resulted in a capture process with steam consumption of 1 kg steam/kg CO_2. This was based on energy efficient solvent, process optimisation and process configuration optimisation. The degradation seemed not be an issue and emissions were limited.

3.1.3 SaskPower's Carbon Capture Demonstration Projects, Michael Monea, SaskPower

The interest of SaskPower in CCS came from their mission of providing the people of Saskatchewan with safe, reliable and sustainable power. The Boundary Dam project is a fully integrated power plant with CO_2 capture and EOR. This demonstration project was established to demonstrate a cost effective, environmentally sustainable, long-term model of existing coal-fired electricity generation.

A decision to construction an integrated 180 MWe power plant with CO_2 capture and EOR project is expected in the fourth quarter of 2010 and the plant is expected to be in service in 2013. The choice of the capture technology will be made late in 2009 out of the short listed three providers: Cansolv Technologies, Fluor Canada and Powerspan. The concept idea is to have the carbon dioxide capture plant at SaskPower's Shand coal-fired power plant near Estevan with 600 tonnes CO_2 per day. The captured CO_2 will be available to the Saskatchewan Montana project.

3.1.4 Update on the state of the art B&W RSAT™ pilot plant and development activities, Ruyu Zhang, B&W

The RSAT CO_2 scrubber is waiting for the next step of field demonstration. It was tested in both lab scale pilot with 0.02 tonne CO_2/day and large pilot scale with 7 tonne CO_2/day. The development activities of this project started with a wetted-wall column in the laboratory up to pilot scale and used simulation tools for experimental results validation.

The large pilot plant (7 tonne CO_2/day) has an absorption tower with 0.61 m diameter and 20 m height with 7.6 m height of active packing material. The baseline test campaign using 30-wt% MEA has been completed. The research activities will continue aiming to find potential advanced solvents and advanced optimised process flow sheet. The design and cost estimation for a large scale (1500 tonne CO_2/day) field demonstration are in progress and waiting to identify partners in 2010-2011.

3.1.5 HTC Purenergy and Doosan Babcock energy post combustion capture technology, Lionel Kambeitz, HTC

HTC was founded in 1997 with core business activities focusing on CO_2 capture, CO_2 EOR and CO_2 storage. The CO_2 capture activities include: technology licensing, OEM supplier and engineering services. In addition, CO_2 EOR and storage include: oil field analysis, oil field economics and project validation, CO_2 compression and injection, geological profiling, risk assessment, CO_2 audit and monitoring and carbon credit validation.

HTC collaborates with Doosan Babcock Energy, Doosan heavy Industries and Construction and University of Regina. The international test centre of CO_2 capture (ITC) is a main partner of HTC and considered to be the home of HTC's technical centre.

CCS Purenergy system is a pre-engineered, modularly designed and constructed with 1000 ton/day CO_2 capture system with future possibility of scaling it up to 3000 tons/day. The concept of the Purenergy system is to make CO_2 capture commercially ready with guaranteed process performance.

3.1.6 CCS and climate change research in Canada, Malcolm Wilson, University of Regina

Malcolm gave an overview of the CCS and climate change related activities in Canada. At the federal level, 1 billion CAD reserved for research, demonstration and renewable projects. On the states' level, Alberta has 2 billion CAD for three chosen projects: Enhance/Northwest for the Alberta carbon trunk line, EPCOR/Enbridge for IGCC power plant and shell Canada energy/Chevron Canada Ltd./Marathon Oil Sands L.P. for a fully integrated CCS project. In Saskatchewan, the regulations are under development for technology fund development. In addition, University of Regina, ITC, PTRC and SaskPower are the main players in the CCS research field.

AQUISTORE is a collaborative effort among government, industry and research institutions to demonstrate that storage of CO_2 in deep geologic formations is a safe, effective solution for greenhouse gas emissions reduction. This is a five year project (2009-2013) with 100 million CAD budget. The project's capture capacity is 600 tonnes/day CO_2 and will be increased to 1600 tonnes/day when a second reformer is included. The captured CO_2 will be transported using pipelines to the injection site where it will be stored in deep saline aquifer at least 2000 m below surface. A carbon tax of 10 CAD was applied in British Columbia in 2008 escalating to 30 CAD on 2012. A new CCS research centre was formed in Nova Scotia.

3.1.7 Stoke research introduction and welcome, Janice Stokes, Stoke research Inc.

Janice Stokes, CEO of Stokes Research Inc. welcomed the delegates, thanked the host and the organisers of the meeting and introduced Stoke Research Inc. Since 2005 Stokes Research Inc. has continued to provide services to a diverse client group that include academic, community-based, Aboriginal, and governmental organisations committed to innovation in their respective fields. The firm has successfully completed projects ranging from innovation technology to innovation social economy initiatives.

Stokes Research Inc. provides national and international consulting services in areas such as:

- Innovation and Commercialisation Projects
- Sustainable Energy Demonstration Initiatives
- Innovation Social Economy Projects
- Feasibility Studies & Reporting
- Community-based Organisation Planning
- Workshop Facilitation & Conference Management

3.1.8 Post combustion capture development programme of RWE, Hotchkiss, Whitehouse, Moser and Schmidt, RWE

Post combustion capture is one part of RWE's CO_2 mitigation strategy for power plants. In its strategy, RWE focuses on the power plant efficiency increase to values above 50% and considering both IGCC and post combustion capture to make their power plants nearly CO_2-free.

RWE aims to access the best available post combustion capture technology for commercial application from 2020. Before that, techno-economic evaluation studies, promising technologies pilot plant testing and post-combustion capture demonstration projects are key factors in decision making.

The cooperation between RWE power, BASF and Linde aims to develop an advanced amine-based CO_2 scrubbing process (pilot plant and demonstration). In addition, RWE npower realised the generic test facility at Didcot. The goals for commercial full-scale application from 2020 are post combustion capture efficiency loss less than 10% points and the cost for CCS less than CO_2 certificate price. The testing programme at the pilot plant Niederaussem started in July 2009. 7.2 tonne CO_2/day can be captured (related to a capture rate of 90%). The basis of design for full scale/demo plant was worked out in 2009 and will be updated in 2010, with a decision on a demo plant at the end of 2010.

Didcot amine test rig will have capacity of 50 kg/hr CO_2 using an 8 m column height. The test programme will start with MEA as a referee case followed by alternative solvents e.g. MDEA, hindered amines and blends.

RWE does not see an obvious best technology. The combination of process optimisation and experimental work will provide valuable understanding of the capture technology. The pre-selection of the most promising technologies, individual collaboration with technology providers and generic test facilities will boost the development.

3.1.9 Impacts of post combustion capture on plant performance-a case study, Chris van Driel, Stantec

Chris discussed in this presentation the existing plant performance of the Boundary Dam power plant in Saskatchewan as a study case. In addition, Chris pointed out the importance of using modelling tools for process evolution, integration and development. In this work, the software packages GateCycle™ and ProMax were used to model a fully integrated power plant and capture plant.

The options of upgrading the boiler by considering the possibility to increase steam conditions (P, T) and the steam turbine by improving the stage efficiencies, increasing the steam operating temperature and evaluating the possibility to employ condensate from heat recovery were evaluated to improve the overall power plant efficiency. A combination of boiler and turbine improvements, coupled with heat recovery, revealed the potential to increase the plant efficiency by over 10%.

Process implications (e.g. flue gas water consumption and heat recovery) were evaluated. Increased heat recovery can improve cycle efficiency and reduce water consumption. Risk assessment studies (e.g. prior experience in amine systems, HAZID, HAZOP) showed that increased integration represents increased risks, which require proper threat and consequence identification for mitigation.

3.2 Session two: Fundamental studies

This session discussed the development of new absorption solvents and the methods of evaluating the behaviour of the new development solvents and processes. In addition, overviews of the research activities in different institutes were presented.

3.2.1 Concentrated Piperazine: a new standard solvent, Gary Rochelle, the University of Texas at Austin

Piperazine is considered as one of the solvent alternatives for CO_2 capture. 8 molar Piperazine (40-wt %) could be a competitive solvent for CO_2 capture for the following reasons:

- The regeneration energy requirement is estimated 10-20% lower than MEA solvent.
- The CO_2 mass transfer rate is two times higher than the MEA case
- The solvent capacity is 1.8 times the MEA solvent capacity
- The stripper operating pressure is high (6-15 atm)
- Piperazine is stable up to 150 ^{o}C.
- Oxidatively stable, especially with an inhibitor.
- Soluble at 0 ^{o}C at operating loading
- Good opportunities for reclaiming

The solvent development road map at University of Texas consists of three major parts:

1- Solvent properties: the solvent chemistry, viscosity, solubility, CO_2 solubility, solvent loading capacity, heat of desorption and solvent thermal stability
2- Solvent management: solvent volatility (< 20 ppm at lean conditions), oxidation (3 times less than MEA), corrosion and reclaiming by existing options (thermal or distillation reclaiming).
3- Pilot plant tests: the pilot plant experiments evaluated the mass transfer rate and the energy requirement. The pilot plant tests resulted in 10-20 % lower energy requirement comparing to MEA process.

3.2.2 Accurate screening of candidate solvents by the wetted wall column, Xi Chen, the University of Texas at Austin

Developing new solvents requires accurate screening and testing techniques. While testing these newly developed solvents, it is important to cover the range of real process conditions (temperature, CO_2 content and solvent capacity). In this work, wetted wall column (WWC) was selected for the solvent screening. The reasons behind this selection included:

- WWC is more representative of commercial packing than laminar jet or stirred cell.
- It gives more accurate VLE and mass transfer rate in loaded solution
- WWC is adequate for design of absorber and stripper.

Different types of solvents were tested in this work: primary amines (MEA, EDA and DGA), Piperazine and derivatives (PZ, HEP and AEP), hindered amines (AMP and 2-PE) and promoted tertiary amine (MDEA/PZ). These tests focused on measuring CO_2 solubility, solvent capacity, enthalpy of CO_2 absorption, reaction rate of amine with CO_2 (k_2) and absorption/desorption rates (kg). The solvent screening results were summarised in the table below.

Amine	Concentration (m)	CO_2 Capacity@ $P_{CO2,lean}$=0.5kPa (mol/kg (water+amine))	k_g @P_{CO2}=5kPa ($\times 10^{7}$ mol/s·Pa·m^{2})	ΔH_{abs}@P_{CO2} =1.5kPa (kJ/mol)
MDEA/PZ	7/2	0.71	5.7	67

PZ	8	0.79	5.3	70
MEA	7	0.47	3.1	82
HEP	7.7	0.68	2.9	69
MEA	11	0.52	2.5	84
DGA®	10	0.38	2.4	81
AEP	6	0.66	2.3	72
2-PE	8	1.23	2	73
AMP	4.8	0.96	1.7	73
EDA	12	0.78	1.6	80

3.2.3 IFP solutions for lowering the cost of post-combustion carbon capture from HiCapt+™ to DMX™ and future steps, Eric Lemaire and Ludovic RAYNAL, IFP

HiCapt+^{TM} is a process developed by IFP. This process uses high concentration of MEA (40-wt %) with corrosion and degradation inhibitors. Three major tests were done to come over the challenges of process operation at high MEA concentration: corrosion studies (various materials and different inhibitors were evaluated and tested), hydrodynamics and mass transfer (Kg, Kl, efficient interfacial area, pressure drop and liquid hold-up) and oxidative degradation (heat stable salts effects and screening tests for inhibitors, which included more than 130 products).

The HiCapt+^{TM} process showed some improvement comparing to conventional MEA process. The solvent flow rate was 25 % lower than MEA, regeneration energy was 3.1-3.3 GJ/tonne CO_2, solvent degradation was negligible and the total CAPEX and OPEX were 15 % lower than 30-wt% MEA process. This improved process will be tested in ENEL pilot plant (2.25. tonne CO_2/hr) by 2010.

DMX^{TM} is a new carbon capture process aiming for high solvent capacity, low heat of regeneration, good solvent kinetics and low temperature degradation. DMX^{TM} enables an energy penalty for the power plant reduction of about 3%-pts compared to the standard 30%wt MEA process. This process was proven at lab scale and will be tested in pilot plant by 2011-2013. In addition, IFP is working on long term development for 3rd generation carbon capture process. This development line includes new processes (amine blends, adsorption and ionic liquid) and new technologies (membrane contractors and high performance pickings).

3.2.4 Interactions of CO_2 with aqueous amine solutions-the molecular view, Marcel Maeder, the University of Newcastle

The understanding of the interaction mechanism of CO_2 with the amine molecules and the type of molecules that will be formed from these interactions is an important method for the understanding and developing of new capture solvents.

In this presentation, Marcel explained the interaction of CO_2 with amine groups (RNH2) and the mechanism of carbamate formation. H-NMR and stopped-flow kinetics using pH indicator measurement techniques were used to analyse the kinetics and the mechanism of CO_2 interactions with aqueous amine solutions. The formation of carbamates occurs in three parallel reactions of the amines with CO_2 (dissolved), with H_2CO_3 and with HCO_3^-. A couple of examples were presented in this work including the basic reactions of CO_2 with the amine groups of, Ammonia and Morpholine.

Together with the understanding of the interaction mechanism and products, it is important to integrate the complete model for absorption/desorption process with the process chemistry. Future work will include additional amines (e.g. Piperazine), reaction enthalpies (calorimetry), mixed amine solvents and microscopic analysis at gas-liquid interface (diffusion and PH-profiles).

3.2.5 Ionic liquids for post combustion CO_2 absorption, David Wappel, University of Leoben

This work aimed to investigate the ability of various task specific ionic liquids (ILs) as potential CO_2 capture solvents for post combustion capture and to compare these ILs to the reference solvent MEA. Ionic liquids have the advantages of the possibility for application without any solvent, myriad different structures and variation possibilities of anion and cation and non measurable vapour pressure. On the other hand, it has the disadvantages of high viscosity, current high cost and limited experience.

Screening experiments were designed to investigate the performance of CO_2 absorption with a small quantity of liquid and to benchmark this performance with reference solvents (MEA and K_2CO_3). 80 different ionic liquids or ionic liquid-blends were tested. Measurements for the ionic liquids viscosity vapour liquid equilibrium and enthalpy of absorption. Pilot plant testing will investigate the long term stability of ILS, corrosion problems, absorption kinetics and overall plant performance. The pilot plant tests were done using MEA as a benchmarking solvent and the ionic liquids tests are scheduled for late 2009.

The ionic liquids showed a potential for post-combustion capture with slightly better energy requirement and higher solvent flow rate compared to MEA. The main remaining drawbacks of ionic liquids are the high viscosity of pure ionic liquids, slow kinetics, lack of operational experience and the high price.

3.2.6 Latest research on fundamental studies of CO_2 capture process technologies, Raphael Idem, University of Regina

Raphael presented an overview of fundamental research activities of CO_2 capture technologies at the University of Regina. These activities included corrosion studies, kinetics studies and the work on reducing the heat requirement.

The objectives of the corrosion studies were to study the effect of operating parameters on the corrosion rate of carbon steam in MEA-H_2O-CO_2-O_2-SO_2 system and to screen corrosion inhibitors for carbon steel in this solvent system. The corrosion studies included experimental tests for different ranges of oxygen concentration in the feed gas (0-100%), a wide range of SO_2 concentrations (0-204 ppm), different CO_2 loading (0-0.5 mol/mol) and temperature range of 303-353 K. Corrosion rates increased with temperature and the effect of the concentrations of the different components on corrosion rate was that $[CO_2]>>[MEA]>[SO_2]>[O_2]$. Different inhibitors with different concentrations were tested.

Reducing the steam consumption for solvent regeneration was achieved by more energy efficient solvent and advanced process configuration and optimisation. The thermal energy requirement was reduced to almost 1.6 GJ/tonne CO_2. For the kinetics of CO_2 absorption studies, a 2-D model for CO_2 absorption in laminar jet absorber was established. Concentration profiles for all the species in both the radial and axial directions were obtained.

3.3 Session three: Pilot plant work and scale up

This session covered the activities related to pilot plant experimental results and plans for future demonstration plants. This was the biggest session with 9 presentations. This shows the increasing interest in pilot plant and large scale demonstration.

3.3.1 First results from start-up at pilot plant Niederaussem, RWE, Peter Moser, Sandra Schmidt , BASF, Hugo Garcia, Georg Sieder, Linde, Christine Foerster, Torsten Stoffregen

The Niederaussem pilot plant is operated under cooperation between BASF (solvents and chemicals development), Linde (engineering, system optimisation and scale up) and RWE (power producer, process integration and operation). Parallel to the solvent development of BASF, in 2007 the design, engineering and procurement of the pilot plant started. The capture capacity of the pilot plant is about 300 kg CO_2/hr.

The pilot plant tests and operation started with the MEA as a reference solvent in July 2009. Two improved solvents (solvent 1 and 2) will be tested in two separate campaigns in 2010. Along with these solvents and process operation tests, a material and component tests will be carried out.

Process variation and parametric studies were achieved in the first campaign by varying the stripper pressure and solvent flow rate. These test results showed a good agreement with simulation results. In addition, the first campaign illustrated a good, stable and smooth operational performance of the plant.

3.3.2 Post-combustion capture pilot plant operation I Australia and China, Paul Feron, CSIRO

Within the integrated post combustion capture R&D programme within CSIRO, three pilot plants were established in 2008. The results and the status of two of these pilot plants were presented in this session.

The PCC pilot plant at Loy Yang power was commissioned in July 2008 with a design CO_2 capture capacity of 50 kg/hr. The testing plan started with MEA solvent campaign and in a later stage to test novel solvent and to study the applicability for integration between the post combustion capture and new/existing power station. Experimental operation was carried out in the pilot to determine optimum operating conditions. GASMET Continuous Emission Monitoring System (CEMS) was used to monitor and analyse the chemical emissions from the capture plant. The MEA exit concentration during the campaign (without water wash) was tested and the measured values varied between 20 to 200 ppmv during the testing campaign. The MEA exit concentration increased with increasing the absorber temperature. The measured NH_3 exit concentration during the campaign varied between 10 to 65 ppmv.

CSIRO post combustion capture pilot plant activities in China were divided into four phases: phase 1, pilot plant at Huaneng Beijing Cogeneration plant. The 2nd phase will focus on a pilot plant at a second location, the 3rd phase will focus on technology scale up and international industry implementation and the 4th phase is the outreach programme, which will be concluded with a seminar in China in 2010/2011. The pilot plant was commissioned and successfully operated since July 2008 with a total of 1000 ton CO_2 produce from the flue gas since the start up.

3.3.3 Cansolv technologies: the value of integration, P. Just, Cansolv

Cansolv is aiming for a CO_2 capture process with minimum oxidative and thermal degradation, low specific regeneration energy, minimum effluent, high CO_2 product purity and SO_2 compatible. The Cansolv CO_2 capture process has more than 6000 hours of pilot operation in different world wide pilot plants.

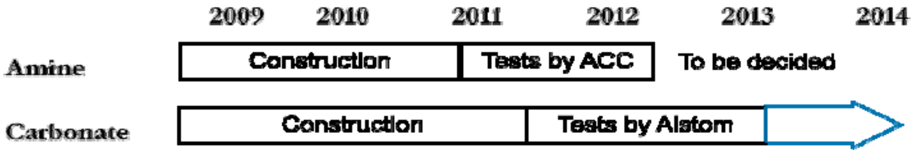
The concept of SO_2/CO_2 capture Integrating will help in heat recovery and integration. The heat recovery in the integrated process could benefit from the latent energy available in the lean amine exiting the stripper, heat integration with Cansolv SO_2 FGD process and heat recycle from FGD by product conversion (SO_2 to acid). The SO_2/CO_2 capture integrated process will be demonstrated in a large scale pilot plant (50 tonne CO_2/day). This demonstration plant is currently in a detailed engineering and procurement phase and the start up is planned for the start of 2011. The objectives of this demonstration plant are to confirm specific heat consumption, evaluate scale-up effects and to prove SO_2 compatibility of CO_2 solvent.

Integrating the Cansolv CO_2 capture process and ultra supercritical boiler has been investigated. The results showed a net overall plant efficiency of 42.3% compared to the benchmark process net efficiency of 36.8%. In addition, the relative specific investment costs increased by 50% in cases of Cansolv process integrated with USC700 boiler compared to 70% for the benchmark process with USC600 boiler.

3.3.4 Status of European CO_2 Technology Centre Mongstad, Gelein de Koeijer, StatoilHydro

The European Technology Centre Mongstad (TCM) is expected to be an important driving force in the qualification of large scale capture technologies and development of improved technologies. TCM is approved and still under construction. It is based on two industrial scale post combustion CO_2 capture technologies (amine and chilled ammonia technologies), each with access to two real industrial flue gases.

TCM is aiming to develop technologies for CO_2 capture, reduce financial and technical risks related to large scale CO_2 capture deployment and to demonstrate CO_2 capture technology owned and marketed by vendors. Two capture technology providers have signed contracts for TCM: Aker clean carbon SA for amine technology and Alstom Norway AS for Chilled Ammonia technology. The concept of TCM is to have these two capture technologies integrated with different sources of CO_2 with a total capacity of 100 ktonnes CO_2/year. The TCM construction and tentative test schedule is:



3.3.5 Evaluation of process improvements in pilot scale activities under the EU CESAR project, Jacob Knudsen, Dong energy

CESAR is a 3-year EU project aiming to reduce the cost of CO_2 post-combustion capture. A major activity within the CESAR project is the pilot plant testing in Esbjerg. The pilot plant tests are aiming to evaluate the potential of advanced absorption/desorption process, determine the performance and requirement of novel solvents in real flue gas conditions and monitor actual solvent degradation, emissions, by products and corrosions.

The pilot plant was constructed within the CASTOR project with a total capacity of 1000 kg CO_2/hr. Within the CESAR project; a couple of process modifications were introduced to improve the capture process. These modifications included among others, absorber inter-cooling, exchange the absorber random packing with structured packing, the expansion of the lean/rich cross flow heat exchanger and the installation of vapour recompression.

Before testing novel solvent, the modified capture process was tested using MEA solvent as a benchmark. The MEA test campaign included parametric variation (solvent flow rate optimisation, effect of absorber inter-cooling, effect of vapour recompression, variation of CO_2 removal percentage and variation of stripper pressure) and continuous long term process operation. The MEA benchmark test campaign has indicated that:

- Reducing the ΔT of the solvent cross flow heat exchanger from ≈7.5 to 4.5 ^{o}C leads only to minor saving in reboiler steam consumption (≈ 0.1 GJ/ton CO_2), however, it allows for lower reboiler temperatures (i.e. higher L/G) at reduced penalty
- Absorber inter-cooling seems to have only marginal effect on reboiler steam consumption with MEA, however, as a co-benefit the absorber ΔP is reduced
- Vapour re-compression may lower reboiler steam consumption substantially (3.6 to 2.8 GJ/ton) on account f increased power consumption. A full cost benefit analysis is required to determine the true benefits.

3.3.6 Environmental impacts of atmospheric emissions from amine based post-combustion CO_2 capture, Moetaz Attalla, CSIRO

Atmospheric emissions and the corrosion and degradation products are major challenges to the large scale deployment of CO_2 post combustion capture. Studying the expected environmental impacts of solvent-based capture process requires answering a couple of valid questions. What happens when there is amine slip from the capture plant? What will happen to the emitted chemical? How can we develop safe levels or environmental thresholds for amines? How much amine can be released to the environment?

Research programmes on emissions being undertaken at the energy centre, includes:

1- Oxidative/thermal mechanisms of amine degradation in the capture plant
2- The fate of slipped amine and amine degradation products in the troposphere
3- Under what atmospheric conditions amine catalysed smog-inducing photochemistry and photo-oxidation
4- Whether secondary or tertiary amines form nitrosamines in the atmosphere
5- Develop new screening methods for assessing atmospheric amine impacts
6- Develop dispersive models with a clearer understanding of amine atmospheric chemistry

Solvent degradation studies are being conducted using absorber packed column with MEA, plastic packing and metal salts as baseline case. The future tests will include CS, SS packing, effects of NOx/SOx and novel solvents.

The CSIRO Smog chamber facility aims to study the chemical basis for O_3, NO_2, aerosol and other oxidation formation. Provide necessary data to develop and test chemical mechanisms for different range of conditions. Identify the appropriate chemical reaction paths for ozone and SOA formation using explicit mechanisms. The data obtained are used to update and develop advanced techniques that can be used for air quality modelling and assessment.

The power plant emissions and regional transport of pollutants were modelled. In addition, the molecules that should be monitored close to post combustion capture plant were identified (ex. Ammonia, acetic acid, oxoacetic acid).

3.3.7 Chilled Ammonia – pilot testing at the We Energies Pleasant Prairie power plant, Sean Black, Alstom

The principle of chilled ammonia depends on cooled flue gas being treated with ammonium carbonate in solution, which reacts with CO_2 to form ammonium bicarbonate. By raising the temperatures, the reaction will be reversed and CO_2 is released. The main advantages of chilled ammonia are: energy efficient capture of CO_2, high CO_2 purity, tolerant to oxygen and flue gas impurities, stable reagent, no degradation possible, no emission of trace contaminants, low cost and globally available reagent.

The chilled ammonia process field pilot at We Energies was designed to capture 1600 kg CO_2/hr and operations commenced in June 2008. With over 7000 hours operation, 90% removal of CO_2 has been achieved, empirical data collected from pilot to date supports proof of concept and initial data on steam (1.21 GJ/tonne CO_2) and electrical energy consumption was consistent with expectations. The operation achieved low ammonia emissions and high purity CO_2 with low concentrations of ammonia (app 5 ppm), water (app 0.25 %) and other impurities.

The future steps will include: a complete parametric testing programme for absorber, support completion of EPRI's gas and liquid analysis test series, conduct long term tests at stable operating conditions and continue programme at 10 x scales at AEP Mountaineer.

3.3.8 Development of amine absorbents for post-combustion capture, Ji-Hyun Lee, KEPRI

A-COS project is a six year project leaded by KEPRI aiming to develop post combustion CO_2 separation technology by alkanolamine absorbents at a coal fired power station, develop absorbents with improved regeneration energy compared to MEA and operate capture process demonstration plants in large scale facilities by 2015-2020.

The testing and research facilities at KEPRI included solvent fast screening facilities, V-L equilibrium measurement, degradation and corrosion tests, reaction calorimetry, CFD and molecular simulation, bench unit and pilot plant (2 tonne/day), which started in 2002.

The solvent development of KoSol series resulted in improvement compared to MEA. The regeneration energy was reduced to 2.9 GJ/tonne CO_2 and the KoSol is found less corrosive than MEA. In the future, advance solvents will be applied to 2 TPD pilot plant and process optimisation and innovation (gas distributor and pre-contactor) will continue.

3.3.9 Hazelwood/H3 capture demonstration project, Geoff Stevens, University of Melbourne, CO2CRC

Hazelwood/H3 capture project will test three CO_2 capture technologies (solvent, membrane and adsorbent) with Australian brown coal flue gases and evaluate them for larger scale capture. A 30 meter high solvent absorption column with a capacity of 25 tonne CO_2/day (expandable to 50 tpd) has been installed by International Power with the purpose to test and evaluate new and improved solvents. This demonstration project was commissioned in late 2008 to separate CO_2 from flue gas stream using amino acid based technology, where CO_2 is converted to an inert material (calcium carbonate).

The membrane gas absorption technology is one of the future technological options. In this process, a membrane separates flue gas from liquid solvent and the CO_2 is absorbed by the solvent via pores on the membrane. This technology was tested using a hollow fibre polypropylene contractor with approximately 8 m^2 surface area between the solvent and flue gas. Initial performance of CO_2 loading into the solvent of 0.127 mol/mol resulted in 85% of the CO_2 in the flue gas being absorbed.

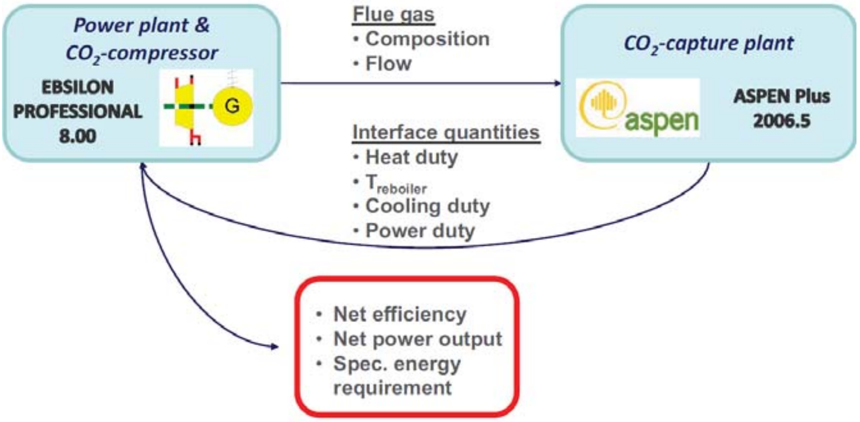
In addition, the ongoing research activities on adsorbent research and development in both the laboratory and real life experiments.

3.4 Session four: Modelling and plant studies

3.4.1 Design considerations of post combustion CO_2 capture process during part load operation of coal fired power plants, Sebastian Linnenberg, Hamburg University of Technology

The operation load of power plants depends on the time of the day, the day of the week and the season on the one side and grid feed-in of power from renewable energy systems (e.g. wind energy) on the other. Therefore, power plants are not always being operated to the design point, which will influence the efficiency of the power plant, flue gas composition and volume flow and will affect the CO_2 capture unit and the overall process.

A state-of-the-art supercritical power plant with a net output capacity of 1045 MWe and a net efficiency of 45.6% was modelled using EBSILON Professional. The CO_2 capture conventional process using 30-wt% MEA was modelled using the rate based approach in ASPEN Plus simulation tool. These two models were integrated allowing interaction between the input and the output of these two models, as shown below.



The effect of different part load cases (40%-100%) on the power plant, the CO_2 capture process and the integrated overall process was analysed. At different loading, the L/G has to be optimised with respect to the integrated overall process to achieve the minimal efficiency loss. At power plant partial load, the flue gas volume flow was decreased, while the flue gas composition changed (O_2 increases and CO_2 decreases). The net efficiency penalty of the integrated overall process was increased for lower loads (10.3 percentage points at full load and 12.6 percentage points at 40% load).

3.4.2 Optimised integration of post combustion CO_2 capture process in Greenfield power plants, Jochem Oexmann, Hamburg University of Technology

A study on optimised integration of post combustion capture focus on Greenfield was presented. Modelling and simulation tools were used to model and optimise the power plant and the capture plant. The reference power plant (600 MWe, 45.6% efficiency and 100% load) was modelled using EBSILON Professional. The reference 30-wt% MEA capture process with an optimistic performance was modelled using ASPEN Plus (3.3 GJ/tonne CO_2 @ 124 ^oC, 90% capture). CO_2 compression process with 8-stage compressor and inter-cooling was modelled using EBSILON Professional to deliver the CO_2 at 110 bar and 40 ^oC.

For each design case, steam bleed pressures of pre-heat train and reboiler condensate return point were optimised. The analysis included the basic integration (evaluate impact of IP/LP crossover pipe pressure) and process optimisation (waste heat recovery). Out of this study the following was concluded:

- Design point and part-load efficiency strongly depend on IP/LP pressure. The efficiency was decreased by 0.9 points at excess of 2.2 bar. The slope of part-load efficiency improved with increased crossover pipe pressure.
- By optimising the waste heat recovery, up to 0.9% points advancement in overall net efficiency. Increasing degree of integration resulted in potentially lower availability and operability. Most cost effective option has to be evaluated.

3.4.3 Retrofitting post combustion capture to existing power plant, Jon Gibbins, Mathieu Lucquiaud, Imperial College London

This study investigated using CO_2 post combustion as a retrofit option and the influence of the reference power plant efficiency on the capture costs. Different options for efficient, flexible and upgradable retrofit were examined. Implementing CCS will result in less generated electricity, extra costs (CAPEX and OPEX) for the capture plant and higher risks. On the other hand, emissions will be cut and there will be no need for emission allowance purchase. This study concluded that power plant efficiency does not affect capture costs but capture plant efficiency and costs do.

For process operational flexibility the options of solvent storage, part-load and arbitrage between carbon and electricity prices for simply venting CO_2 to atmosphere were investigated. In retrofit consideration, it is important for 1st generation plants to be upgradeable with better solvent to avoid stranded plant asset. This requires appropriate absorber design, regeneration system and steam turbine design. Floating pressure retrofit trade-offs, reinforce the very last blades of IP turbine by upgrading materials with higher tensile strength (10% gain by using LP last stage alloy for IP last stage. Blade design could be improved by lengthening the blade chord and increase bending modulus with thicker blades.

3.4.4 Using fundamental advanced thermodynamics to model CO_2 capture using aqueous ammonia, Victor Darde, Denmark technical University

Aqueous ammonia could be used as an alternative to the conventional MEA capture solvent. The process can be operated at ambient temperature or at low temperature (chilled ammonia process). The aqueous ammonia process is similar to MEA process but low temperature of absorption is needed to prevent ammonia evaporation, no degradation or corrosion issues, the pure CO_2 stream is available at high pressure and the heat consumption is decreased.

The Thomsen and Rasmussen (1999) model is valid for CO_2-NH_3-H_2O mixture. It uses extended UNIQUAC and valid up to 110 ^oC with about 2000 experimental data point on this system (e.g. binary VLE, ternary VLE, SLE and enthalpy). This thermodynamic model was upgraded using temperature correlation for the Henry constants for NH_3 and CO_2 and calculating the residual enthalpy of the gas phase with SRK. New data was added (e.g. VLE at higher temperature, enthalpy data, speciation data and heat capacity data). In conclusion, the model was upgraded by extending the validity of the temperature range and using a new kind of experimental data for parameters estimation. The upgraded model described the thermodynamic properties of NH_3-CO_2-H_2O accurately.

The heat requirement in the desorber was estimated assuming a reference ammonia process with 12% ammonia initial mass fraction, 0.33 lean loading, 0.67 rich loading, 110 ^oC regeneration temperature and 100 ^oC rich solvent inlet temperature to the stripper. The results showed significantly low values of heat consumption lower than 2 GJ/tonne CO_2 captured. Process optimisation was required to minimise the heat consumption and additional energy saving was achieved during CO_2 compression. On the other hand, additional heat/cooling power was needed to heat up the CO_2-rich stream, for chilling the flue gas and the solvent and to recover the vaporised ammonia.

This work will continue to evaluate the overall capture process. The thermodynamic model will be implemented in ASPEN Plus and process will be further optimised. Studies of process integration with the power plant and experimental measurement of the kinetic rate of absorption of carbon dioxide by ammonia solvent are planned.

3.4.5 Modelling of relationships among key parameters in CO_2 capture process, Christine Chan, University of Regina

The objectives of this work were to study the nature of relationships among key parameters of the CO_2 capture process and to focus on parameters that affect CO_2 production rate. Two modelling approaches were considered: the statistical regression (linear and non-linear) and the combination of artificial neural networks (ANN) and sensitivity analysis. The regression analysis procedure consisted of three major steps: correlation analysis, regression analysis and assessment of regression model. The modelling processes for CO_2 capture looks as follow:

The statistical regression models were based on four assumptions:

1. There is no multicollinearity between the predictor variables
2. The residuals are randomly distributed
3. The residuals are from a normal distribution
4. The relation between each conditional variable and the consequent variable is linear

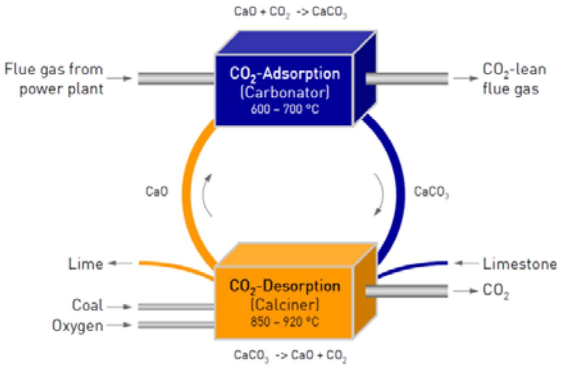
The statistical study showed that the 4 assumptions were satisfied, 3 linear models and 1 non-linear model were developed and the R statistic on each model showed that prediction accuracy of the model was acceptable.

In the artificial neural networks (ANN) approach, input parameters included among others: absorber in gas actual flow, input absorber fluid CO_2 gas, lean amine to absorber flow rate, reboiler pressure, steam from reboiler flow rate and amine concentration. The ANN output parameters were: CO_2 production rate, heat duty, absorption efficiency and lean loading. The modelling procedure started with constructing the artificial neural network models, conducting sensitivity analysis on the model results, experts' validation and reformulating the neural network model.

Four ANN models were developed and the significance of each input parameter to the output parameter was revealed using sensitivity analysis. The advantage of ANN was that the irregular non-linear relations among the parameters can be modelled. On the other hand, ANN is a black box and cannot explicate the relationships among the parameters.

3.4.6 Development of a Calcium based CO_2 capture process for coal fired power plants, Sven Unterberger, EnBW

EnBW included the different capture routes in the CCS R&D road map. However, EnBW focus on post combustion capture due to the possibility of retrofit, retain proven power plant technology and it is the closest capture technology to commercial availability. Three major technologies were included in the EnBW activities overview in relation to post combustion capture: Amine scrubbing (pilot plant-Esbjerg Dk), Chilled ammonia (pilot plant-EPRI/Alstom USA) and solid sorbents – calcium cased process (feasibility study TUD/ University Stuttgart /COORETEC, test rig at University Stuttgart). The calcium-based CO_2 capture process scheme, which was the focus of this session, is shown below:



The benefits of this technology are: retrofit option for existing power plants, host power plant remains unmodified, sorbent material well known and utilisation of purge stream in cement industry and/or flue gas desulphurisation. On the other hand, it has the drawbacks of the behaviour and deactivation of limestone are not fully understood and possibly further flue gas treatment is needed (CO_2 quality). The economic evaluation showed that the calcium-based process is competitive with other capture technologies with overall CO_2 avoided cost almost 50% lower than the amine scrubbing process. This process could be considered as a 2nd generation post-combustion capture technology, with the need for further R&D activities and process demonstration in pilot plant scale (5-20 MW).

3.4.7 Impact of carbon capture on power plant emissions, Harvey Wen, Ram Narula, Bechtel Power Corp.

The chemical emissions and waste products are considered to be of the major challenges for large scale solvent-based process deployment. These additional emissions and waste product are expected as result of solvent reaction with flue gas contaminants (O_2, SOx, NOx, Hg, Chlorides, particulates and heavy metals) or due to process operational conditions (thermal degradation).

For example, the MEA/oxygen reaction will form different types of acids (acetic acid, formic acid and oxalic acid). In addition, MEA reacts with SO_2 to form thiovanic acid. Moreover, the thermal degradation of MEA could result in by-products like hydroxyethylethylenediamine (HEED) and heat stable salts. Amine components are expected to evaporate from the top of the absorber and products like ammonia will be produced by the decomposition of amines. This study compared the different emissions with and without introducing the capture process and the resulted were summarised in the following table.

	Without CO_2 capture	**With amine CO_2 capture**
CO_2 emission, t/d	16100	1610

SO_2 emissions at stack	25-80 ppmv	< 1 ppmv
SO_3/H_2SO_4 emission at stack	< 5 ppmv	< 1 ppmv
NOx emission at stack	40 ppmv	40 ppmv
Amine vapour	0	< 2.5 ppmv
NH_3	3 ppmv	10 ppmv
Amine sludge, t/d	0	36

Different types of waste streams (solid, liquid and gas) need to be evaluated and considered before large scale deployment of the capture process. In addition, power plants permits must take into account the additional wastes and emissions created by CCS.

3.5 Session five: Commercial and other

3.5.1 MHI's recent post combustion CO_2 capture achievements and developments, Hiroshi Tanaka, MHI

MHI provides an advanced amine solvent (KS-1), which has high CO_2 loading, low solvent degradation and low corrosion. In addition, MHI developed an improved CO_2 recovery process with 15% steam consumption reduction over MHI's conventional process. This improved process, which has been demonstrated at MHI's Nanko pilot plant and integrated in a commercial plant, utilizes lean solvent steam condensate heat for regeneration inside the stripper.

MHI has multiple commercial CO_2 capture plants, which varies in capacity from 200 Mt/d up to 450 t/d. A couple of these commercial plants are in operation and others are planned for future installation. Beside the commercial plants, MHI has a long term CO_2 capture demonstration plant using KS-1 solvent to remove CO_2 from a coal fired power plant with a capacity of 10 t/d. This demonstration plant achieved more than 90% CO_2 recovery.

MHI is working on various process improvements aiming for further reduction on the heat requirement, the total capture costs and environmental emissions. A new heat optimisation system in CO_2 recovery process can achieve approximately 10% steam consumption reduction over MHI's improved process. In addition, medium scale demonstration of post combustion capture, including US demonstration (500 t/d) is under construction and are expected on stream in 2011.

3.5.2 Pilot plant approach for scale up of CO_2 capture process using amine solvents, Ahmad Abudheir, University of Regina

Three main methods are available to scale up: Brute force, rate based modelling and technology qualification (combined measurement, modelling and large pilot and demonstration). HTC scale up strategy is based on building comprehensive rate based models, using and modifying commercially available software's and validating these rate models using laboratory pilot plant and commercial plant results.

For absorption column design, the hydrodynamics, mass transfer coefficient, physical and chemical equilibrium and the enhancement by reaction kinetics need to be predicted or measured accurately. In addition, the absorption is a reactive process inherently operating under non-equilibrium condition and hence, rate based model is a must.

The key data for the design and simulation of CO_2 capture process include among others the physical properties (e.g. density, viscosity, solubility and diffusivity), chemical properties (e.g. VLE, reaction rate and heat of reaction), operation conditions (e.g. temperature, pressure, flow rates and concentrations) and boundary conditions of the process (e.g. inlet, outlet and geometry).

The models for CO_2 capture process, which were developed within UR, ITC and HTC, were validated using different pilot plant experimental data and showed a very good agreement with the actual column data.

4 What have we learnt from the 12th meeting of the international post combustion capture network?

The learning and new knowledge shared during the meeting varied by topic, presentation and institutes. However, there were few learning issues to point out.

- New capture technologies and improved solvents:
    - A new solvent as well as an advanced process configuration and optimization for CO_2 capture have been developed by University of Regina, with thermal energy requirement of 1.6 GJ/tonne CO_2
    - Concentrated Piperazine was tested at University of Texas, with 10-20% lower energy requirement compared to MEA
    - HiCapt+^{TM} process was developed by IFP with 3.1-3.3 GJ/tonne CO_2 energy requirement
    - KoSol solvent series by KEPRI, resulted with energy requirement of 2.9 GJ/tonne CO_2
    - The Calcium based CO_2 capture process is considered as a promising 2nd generation technology by EnBW
    - Ionic liquids are considered promising 2nd/3rd generation capture technologies and have been tested by University of Leoben.

- Pilot plant and large scale demonstration results and plans:
    - 180 MWe power plant with CO_2 capture and EOR by SaskPower is waiting for construction decision in 2010
    - B&W finished the design for a 1500 tonne/day CO_2 demonstration plant and is waiting to identify partners in 2010-2011
    - AQUISTORE is a five year collaborative Canadian project (2009-2013) with capture capacity of 600 tonne/day with the potential to be increased to 1600 tonne/day

- RWE together with BASF and Linde succeeded in the pilot plant operation, which started in July 2009. The current plan to make a decision on a demo plant by 2010 with the goal of full scale demonstration in 2020
- IFP is planning to test their improved process (DMX^{TM}) in a pilot plant by 2011-2013
- Cansolv is currently in the detailed engineering phase for their demonstration plant for the SO_2/CO_2 capture integrated process and the start up is planned for 2011
- The European Technology Centre Mongstad is currently under construction and the capture tests for both the amine and the chilled ammoniac processes are planned for 2011-2012.
- The EU CESAR project pilot plant modifications together with the first MEA test campaign were finished. It was concluded that the major process modification that improved the capture process requirement was the vapour re-compression, which resulted in energy requirement of 2.8 GJ/tonne CO_2
- The Alstom chilled ammonia pilot at We Energies commenced in June 2008. The first results supported the proof of concept with initial steam requirement of 1.21 GJ/tonne CO_2
- KEPRI developed solvent (KoSol) was tested in a 2 tonne/day pilot plant. The current plans are to go for the 2nd testing stage with a 50 tonne/day pilot and the 3rd stage with 50-500 MWe demonstration plant by 2015-2020
- Hazelwoor/H3 capture demonstration project (University of Melbourne, CO2CRC) was commissioned by late 2008. The project will illustrate three different capture technologies (solvent, membrane and adsorbent).
- MHI medium scale demonstration of post combustion capture, including US demonstration (500 t/d) is under construction and expected to stream in 2011

- Capture process modelling, integration and chemical emissions:
  - According to Stantec, a combination of boiler and turbine improvement, coupled with heat recovery revealed the potential to increase the plant efficiency by 10%. In addition, risk assessment studies showed that increased integration represented increased risks.
  - The understanding of the molecular interaction is an important tool in solvent development. In addition, according to University of Newcastle, this understanding of the molecular interaction should be combined with capture process integrated models
  - Atmospheric emissions, corrosion and solvent degradation are major challenges to the large scale deployment. CSIRO conducted solvent degradation studies and used Smog chamber facilities to study the chemical emissions and mechanisms of formation
  - Integrated models of the capture process with power plant provide a good overview of process integration and demonstrate the effect of process parameters like part load operation. Hamburg University concluded that at different power plant loading, the capture process needed to be optimised and the net efficiency penalty was increased for lower power plant loads
  - By optimising the waste heat recovery, in the work done by Hamburg University, only up to 0.9% point advancement in overall net efficiency was achieved

- Imperial College found that the power plant efficiency does not affect capture costs but capture plant efficiency and costs do
- Thermodynamic modelling is an important tool for process understanding and overall evaluation. The thermodynamic model for CO_2-ammonia system was upgraded and modified by the Denmark Technical University
- Bechtel showed that the amine vapour and ammonia emissions will increase after the deployment of amine capture process. On the other hand, the SO_2 emissions will decrease and NOx emissions will not be affected
- In the presentation by University of Regina, the necessity of selecting the correct models, physical, chemical and thermodynamic properties and the accuracy of the experiments were stressed as important parameters in designing the capture process.

5 Network meeting evaluation

The programme of the meeting was well received from participants. 2 days in “class room” with 30 technical presentations and 20 posters. Podium slots were much valued, and it was necessary to move too many into the poster session (1st time we have had one).

The interest and interaction of the participants varied from one topic to another. It was clear that the main interest of the participants was in the pilot plant and demonstration results and the new developed capture processes and solvent. For many of the delegates, the level and details of the presented results of the pilot plant experimental work were limited and below expectation. This is due to the fact that most of the pilot and demonstration plants are still either in the first testing phase or in the planning and construction phases. However, for the coming meetings, it is important to keep and increase the focus on the pilot plants and large demonstration projects and results. In addition, more time should be given for these presentations, to encourage more results sharing and more discussions.

Three technologies were presented in this meeting, which could be considered as 2nd or 3rd generation technologies; ionic liquids, the membrane technologies and the calcium-based process. It is important for future meetings to keep track of future development and R&D activities related to 2nd/3rd generation capture technologies.

Two dedicated presentations focused on the environmental impact of post combustion capture, which is considered as an important issue to solve before full scale capture process deployment. The expected emissions of amines, additives and their degradation products with flue gas stream and waste product streams is a continued concern for the deployment of full scale CO_2 post combustion capture using amines. Due to the importance and the increased interest in this topic, a dedicated workshop on environmental impact of post combustion capture is established and the first meeting will be held in Oslo 16th February, 2010.

5.1 Participants

More than 150 registrants, 140 approximately turned up. 18 countries represented – 50% from North America, 35% from Europe, good presence from Australia, Japan and Korea. China, Saudi Arabia and United Arab Emirates were also represented.

Comments:

- Comparing to previous network meeting, this one had the largest number of registrants and participants. This large number of participants resulted from the increased interest in the post combustion capture and due to the fact that this meeting took place in North America with 50% of the participants was from North American companies.
- The increased interest and number of delegates should be considered when discussing the format of the next meeting.

5.2 Venue/Accommodation/Catering

The venue selected by the organisers was excellent and none of the associated facilities could be faulted. The accommodation and services during the meeting were good.

5.3 Meeting programme

The programme covered different aspects of post combustion capture development and projects. The programme was balanced by introducing experimental results and modelling activities. In addition, the given session for the fundamental research and the development of future technologies was fruitful and interesting.

Comments:

- For the future meeting, it is important to keep and increase the focus on the pilot plant and demonstration projects.
- Next meeting should keep an eye on the capture process development and 2nd/3rd generation technologies.

5.4 The visit to the ITC facilities

The visit to the ITC facilities is appreciated and acknowledged by the organisers and the delegates. However, there was a problem arising from the University of Regina requiring visitors to sign a non-disclosure agreement. This should have been sent out to attendees well before the meeting but was only available on 28 Sept. The terms worried some delegates who declined to go on their intended visit.

Comments:

- Keep such a visit as part of future activities, once possible.

- Any confidentiality requirement or arrangement for such a visit in the future should be communicated with the IEA GHG's team and participants well in advance.

6 Next Meeting(s)

This is tentatively scheduled for spring 2011 to avoid GHGT10 and the oxyfuel conference OCC2 in Sept 2011 in Australia. While receiving two offers to host this event, the exact time and location of the next meeting will be decided later on.

7 Format of future meetings

Over the years the attendance has grown to the point where the meeting is at maximum size to remain as a workshop. Assuming further growth in interest by 2011 there are likely to be over 200 registrants if open to all. There would be perhaps 70-80 offers of presentations. This implies a move to conference type proceedings (based on presentations rather than written papers) with parallel sessions. Some long term attendees would like to see the single session approach retained even if this means limiting participation mostly to specifically invited people. During the wrap up these alternatives were put to the audience and a show of hands requested. The result was a roughly even split, so it becomes a matter purely for GHG staff and members to determine.

For the future meetings format, the following are suggested for consideration:

- To establish a steering committee for the network including members from both the R&D and industry.

- To keep the format of the network as abstract and presentation rather than writing full articles, even if it has been changed to a multiple session conference format.

- To evaluate the submitted abstracts by the steering committee in advance and promote a certain number of abstract to go for oral presentations depending on the quality, the focus of the network, the future agreed format and the possible number of oral presentations.

- To direct the main focus of the network to the pilot plant tests, large scale demonstration experiments and future planning for full scale deployment. While keeping a modest programme for fundamental research and 2nd/3rd generation capture technologies.

8 Thanks and Acknowledgements

IEAGHG coordinators and all participants wish to thank Professor Paitoon Tontiwachwuthikul and the staff of University of Regina, Malcolm Wilson, Victoria Muzychuk, Elsa Johnston and Danielle Riemer, for all their hard work in hosting the meeting, co-ordinating the event and the visit to the ITC facilities. Also the Sponsors are acknowledged for the splendid dinner and the financial support. They were Saskatchewan Ministry of Energy and resources, SaskPower, IPAC-CO2, Stokes Research, HTC Purenergy, Doosan Babcock, ITC, University of Regina, Stantec, RWE and Babcock and Wilcox.

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9 Contacting the Co-ordinator

The IEA Greenhouse Gas R&D Programme (IEAGHG) co-ordinates the development of this network and arranges the workshops. Queries about or copies of this report can be obtained by contacting:-

Mohammad Abu Zahra mohammad.abuzahra@ieaghg.org, 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.ieaghg.org

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Office of Energy and Environment (U of R), SaskPower, ITC, IPAC-CO2, B&W,
RWE, Stokes Research Inc., HTC Purenergy, Doosan Babcock Energy, Stantec.

12th Meeting of the International
Post-Combustion CO_2 CaptureNetwork

12th Meeting of the International Post-Combustion CO_2 Capture Network

Administrative Guide

28th September 2009

15.00 – 19.00	Registration: Cannington Room
15.00 – 19.00	Poster Session Set Up: Cannington Room
18.00 – 21.00	Ice-Breaker and Reception: Kenosee Room

Day 1 - 29th September 2009

8.00 Registration and Breakfast: Canningham Room

9.00 Session 1 – Welcome and Sponsors

Welcome on behalf of the IEA Greenhouse Gas R&D Programme – John Topper, IEA GHG

Post Combustion Capture Research by the University of Regina and the International Test Centre for CO_2 Capture (ITC): Pilot Plant Studies and Economic Evaluations - P Tontiwachwuthikul, R Idem & D Gelowitz, University of Regina, Canada

9.40 Sponsors presentations – Chair Paitoon Tontiwachwuthikul

SaskPower's Carbon Capture Demonstration Projects; Michael J. Monea, Vice-President, Integrated Carbon Capture & Storage, Canada

Update on the State of the Art B&W RSAT™ Pilot Plant & Development Activities; Rouyu Zhang, B&W, USA

HTC Purenergy & Doosan Babcock Energy Post Combustion CO_2 Capture Technology, Design and Integration Approach; Lionel Kambeitz, HTC Purenergy, Canada

10.40 Coffee Break

Session 2 – Fundamental Studies – Chairs Paul Feron & Mike Monea

11.00 Concentrated piperazine: Degradation, Modelling and Pilot Plant Results; Gary Rochelle, Univ Texas, USA

11.25 Accurate Screening of Candidate Solvents by the Wetted Wall Column; Xi Chen, Univ Texas, USA

11.50 IFP Solutions for Lowering the Cost of Post-Combustion Carbon Capture from HiCapt+ to Demixing Solvents and Future Steps; Eric Lemaire and Ludovic Raynal, IFP, France

12.15 Interactions of CO_2 with Aqueous Amine Solutions—the Molecular View; Marcel Maeder et al, University of Newcastle and CSIRO, Australia

12.40 Group Photograph and Lunch

14.00 Ionic Liquids for Post Combustion CO_2 Absorption; David Wappel et al, University of Leoben, Austria

14.25 Latest Research on Fundamental Studies of CO_2 Capture Process Technologies at the Process Systems Laboratory, University of Regina; R Idem, P Tontiwachwuthikul, and D Gelowitz, University of Regina, Canada

Session 3 – Pilot Plant Work and Scale Up – Chairs Gary Rochelle & Kevin McCauley

14.50 First Results from the Start up of a Post Combustion Pilot Plant at Niederaussem; Peter Moser et al, RWE Power, Germany and Christine Foerster and Torsten Stoffregen, Linde, Germany

15.15 Post-Combustion Capture Pilot Plant Operation in Australia and China; Paul H.M. Feron, Energy Transformed Flagship, CSIRO Energy Technology, Newcastle, Australia

15.40 Coffee Break

16.00 Integration of Cansolv CO_2 Capture with Coal-Fired Power Plants Using Supercritical Boilers; P E Just, Cansolv, Canada, and Yasaman Mirfendereski and Frank Geuzebroek, Shell, Netherlands

16.25 Status of European CO_2 Technology Test Centre Mongstad; Gelein de Koeijer, Statoil Hydro, Norway

16.50 Evaluation of Process Improvements in Pilot Scale Activities Under the EU CESAR Project; Jacob Knudsen, Dong, Denmark

17.15 End Day 1

Group Workshop Dinner
Location: The Terrace Building, 10 Research Drive
18.00 Cocktails
18.30 Dinner

* Transportation will be provided. see Administrative Notes.

Day 2 – 30th September

8.00 Breakfast: Canningham Room

Sponsors Presentations – Chair John Topper

9.00 CCS and Climate Change Research in Canada; Malcolm Wilson, University of Regina, Canada

9.10 Statement by Janice Stokes, Stokes Research Inc., Canada

9.20 Post-Combustion Capture Development Programme of RWE—A Group-Wide Approach to Implementing Technology; Hotchkiss, Whitehouse, Moser and Schmidt

9.45 Impacts of Post Combustion CO_2 Capture on Plant Performance—A Case Study; Chris van Driel, Anindo Dey, David Cameron, Stantec, Canada

Session 3 – Cont'd Pilot Plant Work and Scale Up – Chair Peter Douglas & Malcolm Wilson

10.10 ECO_2 Ammonia Based Post Combustion Capture Trials at the R E Burger Plant in Ohio; Chris McLarnon, Powerspan, USA

10.35 Chilled Ammonia—Update on Joint Investigations by Alstom and EPRI; Sean Black, Alstom, USA

10.55 Coffee Break

11.15 Development of Amine Absorbents for Post Combustion Capture; Ji Hyun Lee, Korea Electric Power Institute, Korea

11.40 The Hazelwood/H_3 Capture Demonstration Project; Geoff Stevens, University of Melbourne, Barry Hooper, CO_2CRC and Tony Innocenzi, International Power, Australia

Session 4 - Modelling and Plant Studies – Chairs Lionel Kambeitz & Richard Hotchkiss

12.05 Design Considerations of Post Combustion CO$_2$ Capture Process During Part Load Operation of Coal Fired Power Plant; Sebastian Linnenberg, Jochen Oexmann and Alfons Kather, Hamburg University of Technology, Germany

12.30 Lunch

13.50 Optimised Integration of Post Combustion CO$_2$ Capture Process in Greenfield Power Plants; Jochen Oexmann, Imo Pfaff, Sebastian Linnenberg, Alfons Kather, Hamburg University of Technology, Germany

14.15 Retrofitting Post Combustion Capture to Existing Power Plants; Jon Gibbins, Mathieu Lucquiaud, Jia Li and Hannah Chalmers, Imperial College, UK

14.40 Dynamic Simulation and Control of MEA Absorption Processes for CO$_2$ Capture from Fossil Fuel Power Plant; Noorlisa Harun, Peter L. Douglas, Eric Croiset, Luis Ricardez-Sandoval, Atchariya Chansomwong, University of Waterloo, Canada

15.05 Modelling of Relationships Among Key Parameters in CO$_2$ Capture Process; Christine Chan et al, University of Regina, Canada

15.30 Coffee Break

15.50 Development of a Calcium Based CO$_2$ Capture Process for Coal Fired Plants; Sven Unterberger et al, EnBW and University of Stuttgart, Germany

16.15 Impacts of Carbon Capture on Power Plant Emissions; Ram Narula and Harvey Wen, Bechtel Power, USA

Session 5 – Commercial and Other – Chairs Jon Gibbins & Janice Stokes

16.40 MHI's Recent Post Combustion CO$_2$ Capture Achievements and Developments; Hiroshi Tanaka, Masaki Iijima and Ronald Mitchell, MHI, Japan

17.05 Pilot Plant Approaches for Scale Up of CO$_2$ Capture Processes using Amine Solvents; Aboudheir and Elgarni, HTC Purenergy, and Tontiwachwuthikul and Idem, University of Regina, Canada

Wrap Up Session

17.30 Wrap Up—What and Where Next; John Topper, IEA GHG

17.45 Meeting adjourns

Poster Session

Posters will be available for viewing throughout the entire conference. Those who are participating in the poster session will be available to answer questions during any breaks at the conference.

Poster set up is at 15.00 on Monday September 28, 2009 in the Cannington room. Please check in with the Registration Desk when you arrive. Volunteers are available to assist you with setting up your poster.

P1 Steady State and Dynamic Modelling for a Hybrid Approach to Post Combustion Capture; Peter Stephenson (RWE npower), Jing Tian (RWE npower), Stevan Jovanovich (BOC Linde) and Xiaoping Tian (BOC Linde)

P2 Are Solid Sorbents a Viable Option for Post Combustion CO_2 Capture; Sharon Sjostrom, ADA Environmental Solutions, USA

P3 Using Fundamental Advanced Thermodynamics to Model CO_2 Capture Using Aqueous Ammonia; Victor Darde1, 2, Kaj Thomsen1, Willy J.M. van Well2 and Erling H. Stenby1, 1Dept of Chemical & Biochemical Engineering, Technical University of Denmark, 2Chemical & Materials Department, DONG Energy Power, Denmark

P4 Research Highlights in Post Combustion CO_2 Capture; Amr Henni, Saudi Aramco-R&DC Centre- Dhahran, Saudi Arabia

P5 Post Combustion Capture-Ready Options and Barriers; Adina Bosoaga, Mott McDonald, UK

P6 A Pilot Plant Study for CO_2 Capture by Aqueous Ammonia Applied to Blast Furnace Gas in Iron and Steel Making Process; Je Young Kim, Kunwoo Han, and Hee Dong Chun, Research Institute of Industrial Science & Technology, Republic of Korea

P7 Recent Development of CO_2 Capture Technology; Takashi Nojo, Yasuyuki Yagi and Masahiko Tatsumi, Kansai Electric Power

P8 Murphree Efficiency for Calculating Column Height in CO_2 Absorption from Atmospheric Gas Using Amines; Lars Erik Oi, Norway

P9 Post Combustion Carbon Capture Technologies Pilot Plant Trials on a Coal Fired Power Station; Scholes et al CO_2CRC, Australia

P10 Studies on Corrosion Inhibitors for Amine Based Solvents for CO_2 Absorption from Power Plant Flue Gases containing CO_2, O_2 and SO_2; Kladkaew, Saiwan, Thailand with Idem and Tontiwachwuthikul, ITC Regina, Canada

P11 Oxidation Inhibitors for Aqueous MEA Solutions used in a Post-Combustion CO_2 Capture Process; Pierre-Louis Carrette et al IFP, France

P12 Preliminary Screening for Optimum CCS Plant Design; Walid ElMoudir, Univ of Regina and HTC Purenergy Inc, Raphael Idem, University of Regina, and Ahmed Aboudheir; HTC Purenergy Inc, Canada

P13 An Architectural Framework for Developing Intelligent Applications for the Carbon Dioxide Capture Process; C. Luo, Q. Zhou, C.W. Chan, University of Regina, Canada

P14 HiCapt+ : A Step Forward for Industrial Post-Combustion CO_2 Capture in Flue Gases; Laurent Normand, PROSERNAT, France, Eric LEMAIRE, IFP, France, and Christian Streicher, PROSERNAT, France

P15 Environmental Impact of Atmospheric Fugitive Emissions from Amine Based Post Combustion CO_2 Capture; Moetaz I. Attalla, Merched Azzi, Phil Jackson, Dennis Angove, Energy Transformed Flagship, CSIRO Division of Energy Technology, Australia

P16 3D Visualization of the Carbon Capture Units; S. Guo, C.W. Chan, P. Tontiwacwuthikul, University of Regina, Canada

P17 New Developments in Post-Combustion Capture Models in the IECM; Peter Versteeg, Carnegie Mellon University

P18 Sensitivity Study on Bed Height of Amine-CO_2 Absorption Process; Anothai Setame teekul, HTC Purenergy, Canada

P19 Sensitivity and Optimization Study of Amine Based CO_2 Capture Process; Salim Kadiwala, Ahmed Aboudheir, HTC Purenergy, Canada

P20 Pilot Plant Study on CO_2 Capture Using Simulated NGCC Flue Gas and Formulated Solvent; Aihua Yang, Anothai Setameteekul, Salim Kadiwala, Ahmed Aboudheir, HTC Purenergy, Canada

P21 Reduction of the Energy Penalty of a Coal-Fired Power Plant by using a Novel Solvent together with an Improved CO_2 Capture Process for Post-Combustion Capture and Compression; Irene Bolea, Centro de Investigación de Recursos y Consumos Energéticos (CIRCE), Universidad de Zaragoza, Spain, Teerawat Sanpasertparnich, Raphael Idem, Paitoon Tontiwachwuthikul, David deMontigny, and Phairat Usubharatana, International Test Centre for CO_2 Capture, University of Regina, Canada

P22 Vapour-liquid equilibria determination of CO_2-H_2O-amine systems; Danlu Tong, Martin Trusler, Geoffrey Maitland, Jon Gibbins, Paul Fennell, Imperial College, London, UK

Administrative Notes

Welcome to the 12th Meeting of the International Post-Combustion CO_2 Capture Network. Please find below a brief explanation of the conference logistics.

Location of Sessions and Meals

All conference session are held at the Regina Inn Hotel. All session meals during the conference will take place in the Cannington room. Please refer to the Floor Plan.

Registration

Conference registration is open 15.00 – 19.00 on Monday September 28. And will open again at 8.00 on Tuesday September 29. The registration table is located outside the doors to the Cannington Room.

Evening Reception

The reception on September 28, 2009 will take place at 6pm in the Regina Inn Hotel in the Kenosee room.

Group Workshop Dinner

Dinner is being held at The Terrace Building, 10 Research Drive at the University of Regina. Cocktails will be served starting at 18.00 and the meal will be ready for 18.30. Transportation for this event is provided. Please see the Transportation Section of the Administrative Notes. Pick-ups to return you to the Regina Inn will begin at 20.30 and will continue until 21.30. You may leave at any point during this schedule on the provided buses.

Transportation and Tours

Transportation is offered for all delegates for any event that is part of the conference. There will be bus transportation for those attending the Tours of ITC on September 28, 2009 and October 1, 2009. There will be a bus that will pick you up directly in front of the Regina Inn Hotel. The schedule of bus pick-ups in relation to tour time is listed below.

There is also transportation offered for all delegates on September 29, 2009 for the dinner at 10 Research Drive. There will be two buses arriving at 17.45 directly in front of the Regina Inn Hotel. You will receive an assigned bus number located behind your name tag at registration. This will correlate to the bus that you will be boarding to take you to the dinner event. Please wait in the designated area in the lobby for your bus, there will be volunteers to help with coordinating the transportation and to answer any questions.

ITC Tour Bus Pick Up Schedule at Regina Inn:

September 28, 2009
Tour 1 – 14.45
Tour 2 – 15.45
Tour 3 – 16.30

October 1, 2009
Tour 4 – 8.45
Tour 5 – 9.45
Tour 6 – 10.45

Food Allergies or Dietary Restrictions

If you did not indicate any food allergies or dietary restrictions on your registration form, please advise conference staff so appropriate adjustments can be made. For those who have already advised conference staff of any dietary restrictions via the registration form, your restrictions have been taken into consideration, and you need only make yourself known to the staff during plate-service meals.

Photography

A group photo will be taken prior to lunch on Tuesday September 29. We ask that conference participants remain in the room after Session 2 breaks for lunch.

Information/Registration Desk

An information/registration desk is available throughout the conference. It is located outside of the doors to the Cannington room. Conference staff will be available to assist you with any questions and concerns.

Hotel Check-out Times

For those staying at the Regina Inn, check-out time is 12.00. If you require a later check-out time, please make arrangements with the Front Desk.

Name Tags

All delegates are provided with a name tag. Please wear your name tags during the conference, as name tags are required for admission to the conference sessions and for meals.

Cellular Phones and other Electronic Devices

Please turn your cellular phone, Blackberry, or pager off or turn the ringer to silence during conference proceedings.

Smoking Area

Smoking is not allowed inside the hotel during the conference. A designated smoking area is located directly outside of the hotel lobby front doors.

Parking

For those requiring parking, the hotel has a pay parkade located at the rear of the hotel off of Osler Street. There is also metered parking available around the parameter of the hotel block.

Aboudheir, Dr Ahmed
HTC Purenergy
E-Mail: aaboudheir@htcenergy.com

Abu Zahra, Mr Mohammad
IEA GHG Programme
E-Mail: mabuzahra@yahoo.com

Agarwal, Mrs Deepika
University of Regina
E-Mail: agarwald@uregina.ca

Ali, Dr Tariq
Masdar Institute of Science and Technology
E-Mail: tali@mist.ac.ae

Aramaki, Mr Satoshi
Japan CCS Co., Ltd.
E-Mail: satoshi.aramaki@japanccs.com

Aroonwilas, Dr Adisorn
University of Regina
E-Mail: aroonwia@uregina.ca

Ash Richard, Ms Gillian
SaskPower
E-Mail: gashrichard@saskpower.com

Attalla, Dr Moetaz
CSIRO
E-Mail: moetaz.attalla@csiro.au

Azzi, Dr Merched
CSIRO
E-Mail: merched.azzi@csiro.au

Ball, Mr Max
SaskPower
E-Mail: mball@saskpower.ca

Bhown, Dr Abhoyjit
Electric Power Research Institute
E-Mail: abhown@epri.com

Biede, Mr Ole
Vattenfall A/S
E-Mail: ole.biede@vattenfall.com

Black, Mr Sean
Alstom
E-Mail: sean.black@power.alstom.com

Bohm, Mr Mark
Suncor Energy
E-Mail: mbohm@suncor.com

Bonnin-Nartker, Mrs Purusha
The Babcock & Wilcox Company
E-Mail: epbonnin-nartker@babcock.com

Booth, Mr Nick
E.ON Engineering
E-Mail: nick.booth@eon-engineering.com

Bosoaga, Dr Adina
Mott MacDonald
E-Mail: adina.bosoaga@mottmac.com

Brunskill, Mr Brian
Helix Geological Consultants
E-Mail: brianbrunskill@sasktel.net

Bryant, Mr Mark
Doosan Babcock Energy
E-Mail: mhamil@doosanbabcock.com

Burns, Dr Robert
University of Newcastle
E-Mail: Robert.Burns@newcastle.edu.au

Cameron, Mr David
Stantec Consulting Ltd.
E-Mail: jana.masse@stantec.com

Carles, Miss Patricia
Air Liquide
E-Mail: patricia.carles@airliquide.com

Carrette, Dr Pierre Louis
IFP
E-Mail: P-Louis.CARRETTE@ifp.fr

Chan, Dr Christine
University of Regina
E-Mail: christine.chan@uregina.ca

Chen, Mr Xi
University of Texas at Austin
E-Mail: xi@che.utexas.edu

Chisholm, Mr Robert
Stantec Consulting Ltd
E-Mail: bob.chisholm@stantec.com

Choi, Mr Yunsik
KOPEC (Korea Engineering Power Company, Inc.)
E-Mail: cys0406@kopec.co.kr

Corless, Mr Tony
Scottish Power
E-Mail: Tony.Corless@scottishpower.com

Dai, Mr Jianjun
University of Calgary
E-Mail: jdai@ucalgary.ca

Darde, Mr Victor
DTU / DONG Energy
E-Mail: vid@kt.dtu.dk

Davidson, Mr Robert
IEA Clean Coal Centre
E-Mail: robert@iea-coal.org.uk

De Koeijer, Dr Gelein
StatoilHydro - European CO2 Technology Centre
E-Mail: gdek@statoilhydro.com

DeMontigny, Dr David
University of Regina
E-Mail: david.demontigny@uregina.ca

Dey, Anindo
Stantec Consulting Ltd.
E-Mail: n/a

Eimer, Prof Dag
Telemark University College
E-Mail: dag.a.eimer@tel-tek.no

Elgarni, Dr Mohamed
HTC Purenergy
E-Mail: melgarni@htcenergy.com

Elmoudir, Mr Walid
HTC Purenergy
E-Mail: wel-moudir@htcenergy.com

Eswaran, Dr Sandhya
Hitachi Power Systems America, Ltd
E-Mail: sandhya.eswaran@hal.hitachi.com

Feron, Dr Paul
CSIRO Energy Technology
E-Mail: paul.feron@csiro.au

Fujioka, Dr Yuichi
Research Institute of Innovative Technology for the Earth (RITE)
E-Mail: fujioka@rite.or.jp

Gayheart, Mr Jeb
The Babcock & Wilcox Company
E-Mail: jwgayheart@babcock.com

Gelowitz, Mr Don
University of Regina
E-Mail: don.gelowitz@uregina.ca

Gibbins, Dr Jon
Imperial College
E-Mail: j.gibbins@imperial.ac.uk

Gjernes, Mr Erik
Gassnova
E-Mail: eg@gassnova.no

Goel, Mrs Malti
n/a
E-Mail: malti_g@yahoo.com

Goto, Dr Kazuya
Research Institute of Innovative Technology for the Earth (RITE)
E-Mail: goto.ka@rite.or.jp

Gronald, Mr Guenter
AE&E Austria
E-Mail: guenter.gronald@aee-austria.at

Gupta, Mr Anil
CH2M hill
E-Mail: Anil.Gupta@ch2m.com

Gupta, Dr Himanshu
ExxonMobil
E-Mail: himanshu.gupta@exxonmobil.com

Han, Dr Kunwoo
Research Institute of Industrial Science & Technology
E-Mail: khan@rist.re.kr

Hart, Mr Allan
HTC Purenergy Inc.
E-Mail: ahart@htcenergy.com

Henni, Dr Amr
Saudi Aramco
E-Mail: amr.henni@aramco.com

Herscovitch, Mr Robert
Sulzer Chemtech Canada Inc
E-Mail: robert.herscovitch@sulzer.com

Hirota, Mr takeshi
Research Institute of Innovative Technology for the Earth (RITE)
E-Mail: hirota@rite.or.jp

Hotchkiss, Mr Richard
RWE npower
E-Mail: richard.hotchkiss@rwenpower.com

Ibrahim, Dr Hussameldin
HTC Purenergy
E-Mail: hibrahim@htcenergy.com

Idem, Dr Raphael
University of Regina
E-Mail: raphael.idem@uregina.ca

Iso, Dr Yoshiyuki
IHI INC.
E-Mail: yoshiyuki_iso@ihi.co.jp

Jensen, Mr Jørgen Nørklit
DONG Energy Power
E-Mail: jornj@dongenergy.dk

Johnston, Ms Elsa
Office of Energy and Environment
E-Mail: elsa.johnston@uregina.ca

Just, Dr Paul-Emmanuel
Cansolv Technologies Inc
E-Mail: paul-emmanuel.just@shell.com

Kadiwala, Mr Salim
HTC Purenergy
E-Mail: skadiwala@htcenergy.com

Kambeitz, Mr Lionel
HTC Purenergy
E-Mail: lkambeitz@htcenergy.com

Kanniche, Mr Mohamed
EDF R&D
E-Mail: mohamed.kanniche@edf.fr

Kim, Mr Jaehyung
KOPEC (Korea Engineering Power Company, Inc.)
E-Mail: jhk@kopec.co.kr

Kinger, Dr Gerald
EVN AG
E-Mail: gerald.kinger@evn.a

Kitamura, Mr Hideo
Toshiba Corporation
E-Mail: hide.kitamura@toshiba.co.jp

Knisley, Mr Daniel
Saskpower
E-Mail: dknisley@saskpower.c

Knudsen, Dr Jacob Nygaard
DONG Energy
E-Mail: jackn@dongenergy.dk

Koepcke, Mr Moritz
Vattenfall Research and Development AB
E-Mail: moritz.kopcke@vattenfall.com

Kotdawala, Mr Rasesh
Alstom Power
E-Mail: rasesh.kotdawala@power.alstom.com

Krutka, Holly
ADA-ES, Inc
E-Mail: pattieg@adaes.com

Kundra, Mr Pawan
HTC Purenergy
E-Mail: pkundra@htcenergy.com

Lee, Mr Ji Hyun
Korea Electric Power Research Institute
E-Mail: leejha@kepri.re.kr

Lemaire, Dr Eric
IFP
E-Mail: Eric.LEMAIRE@ifp.fr

Liang, Mr. Zhiwu W.
University of Regina
E-mail: Zhiwu.Liang@uregina.ca

Linnenberg, Mr Sebastian
Hamburg University of Technologie
E-Mail: linnenberg@tuhh.de

Lucquiaud, Mr Mathieu
Imperial College London
E-Mail: m.lucquiaud@imperial.ac.uk

Luo, Mr Chuansan
University of Regina
E-Mail: crazyluo@hotmail.com

Maeder, Prof Marcel
University of Newcastle
E-Mail: marcel.maeder@newcastle.edu.au

Maneeintr, Dr Kreangkrai
Kyushu University
E-Mail: kreangkrai@mine.kyushu-u.ac.jp

Mather, Mr Richard
RWE npower
E-Mail: richard.mather@rwenpower.com

Mccauley, Mr Kevin
Babcock & Wilcox
E-Mail: kjmccauley@babcock.com

Mccool, Dr Ben
Algenol Biofuels
E-Mail: ben.mccool@algenolbiofuels.com

Mclarnon, Mr Chris
Powerspan Corp.
E-Mail: nbrown@powerspan.com

Melaaen, Prof Morten Chr.
Telemark University College
E-Mail: Morten.C.Melaaen@hit.no

Mitrovic, Milenka
NRCan
E-Mail: Milenka.Mitrovic@NRCan-RNCan.gc.ca

Mohr, Dr Rebecca
Air Products and Chemicals, Inc.
E-Mail: mohrrj@airproducts.com

Monea, Mr Michael
SaskPower
E-Mail: mmonea@saskpower.com

Mori, Mr Noriyuki
Central Research Institute of Electric Power Industry
E-Mail: silvia@criepi.denken.or.jp

Morton, Mr Frank
Southern Company
E-Mail: fcmorton@southernco.com

Moser, Dr Peter
RWE Power
E-Mail: Peter.Moser@rwe.com

Muzychuk, Ms Victoria
Office of Energy and Environment
E-Mail: victoria.muzychuk@uregina.ca

Nagvekar, Dr Manoj
KBR
E-Mail: Manoj.Nagvekar@kbr.com

Nam, Dr SungChan
Korea Institute of Energy Research
E-Mail: scnam@kier.re.kr

Narula, Mr Ram
Bechtel Power Corporation
E-Mail: rnarula@bechtel.com

Normand, Mr Laurent
PROSERNAT
E-Mail: lnormand@prosernat.com

Oda, Mr Naoki
Babcock-Hitachi K.K.
E-Mail: naoki.oda.hg@hitachi.com

Oexmann, Mr Jochen
Hamburg University of Technology, Institute of Energy Systems
E-Mail: oexmann@tuhh.de

Oi, Mr Lars Erik
Telemark University College
E-Mail: lars.oi@hit.no

Oki, Dr Yuso
Central Research Institute of Electric Power Industry
E-Mail: oki@criepi.denken.or.jp

Panigrahy, Mr Bhabani
University of Regina
E-Mail: panigrab@uregina.ca

Parsons, Mr Ted
Babcock & Wilcox Company
E-Mail: trparsons@babcock.com

Peridas, Dr George
Natural Resources Defense Council
E-Mail: gperidas@nrdc.org

Poling, Mr Christopher
The Babcock & Wilcox Company
E-Mail: cwpoling@babcock.com

Prashad, Miss Alana
Innovation Norway
E-Mail: alana.prashad@innovationnorway.no

Prebende, Dr Claude
TOTAL
E-Mail: claude.prebende@total.com

Raynal, Dr Ludovic
IFP
E-Mail: ludovic.raynal@ifp.fr

Rhudy, Mr Richard
EPRI
E-Mail: rrhudy@epri.com

Richard, Mike
Stantec Consulting Ltd.
E-Mail: mike.richard@stantec.com

Rochelle, Mr Gary
University of Texas
E-Mail: gtr@che.utexas.ed

Saiwan. Ms. Chintana
Chulalongkorn University, Thailand/ ITC
E-mail: Chintana.sa@chula.ac.th

Sanpasertparnich, Mr. Teerawat
University of Regina/ ITC
E-mail: sanpaset@uregina.ca

Santos, Stanley
IEA GHG
E-Mail: stanley@ieaghg.org

Sasaki, Mr Takashi
Japan CCS Co., LTD.
E-Mail: takashi.sasaki@japanccs.com

Schmidt, Mrs Sandra
RWE Power
E-Mail: Sand.Schmidt@rwe.com

Schöffel, Dr Klaus
Gassnova SF
E-Mail: ks@gassnova.no

Setameteekul, Ms Anothai
HTC Purenergy
E-Mail: asetameteekul@htcenergy.com

Shaw, Mr Devin
Cansolv Technologies Inc.
E-Mail: devin.shaw@cansolv.com

Sieder, Dr Georg
BASF SE
E-Mail: georg.sieder@basf.com

Singh, Surindar
AERI
E-Mail: n/a

Sit, Dr Song P.
EnCana FCCL Oil Sands Ltd
E-Mail: Song.Sit@EnCana.com

Smith, Mr Dave
SaskPower
E-Mail: dsmith@saskpower.com

Spangler, Prof Lee
Montana State University
E-Mail: spangler@montana.edu

Stevens, Prof Geoff
Co-operative Research Centre for Greenhouse Gas Technologies
E-Mail: swatts@co2crc.com.au

Stoffregen, Mr Torsten
Linde-KCA-Dresden GmbH
E-Mail: torsten.stoffregen@linde-kca.com

Stokes, Ms Janice
Stokes Research Inc.
E-Mail: jstokes@accesscomm.ca

Sugavanam, Mr Kumar
BASF Corporation
kumar.sugavanam@basf.com

Supap, Dr Teeradet
University of Regina
E-Mail: teeradet.supap@uregina.ca

Tanaka, Mr Hiroshi
Mitsubishi Heavy Industries, Ltd.
E-Mail: hirosi_tanaka@mhi.co.jp

Tong, Miss Danlu
Imperial College
E-Mail: danlu.tong07@ic.ac.uk

Tontiwachwuthikul, Dr Paitoon
University of Regina
E-Mail: paitoon.tontiwachwuthikul@uregina.ca

Topper, Dr John
IEA GHG
E-Mail: john.topper@iea-coal.org.uk

Uchiyama, Mr Masao
Toyo Engineering Corporation
E-Mail: uchiyama@pl.toyo-eng.co.jp

Unterberger, Dr Sven
EnBW Kraftwerke AG
E-Mail: s.unterberger@enbw.com

Uttaranakorn, Ms Jirayu
University of Regina
E-Mail: jirayu.uttaranakorn@uregina.ca

Vandriel, Chris
Stantec Consulting Ltd.
E-Mail: n/a

Veawab, Dr Amornvadee
University of Regina
E-Mail: veawab@uregina.ca

Versteeg, Mr Peter
Carnegie Mellon University
E-Mail: plv@andrew.cmu.edu

Wang, Dr Shujuan
Tsinghua University
E-Mail: wangshuj@tsinghua.edu.cn

Wappel, Mr David
University of Leoben
E-Mail: david.wappel@unileoben.ac.at

Wen, Mr Harvey
Bechtel Power Corporation
E-Mail: hwen@bechtel.com

Wilson, Dr Malcolm
Office of Energy and Environment
E-Mail: malcolm.wilson@uregina.ca

Wright, Mr Connor
University of Regina
E-Mail: wright4c@uregina.ca

Yang, Ms Aihua
HTC Purenergy
E-Mail: ayang@htcenergy.com

Yokoyama, Mr Koichi
Babcock-Hitachi K. K.
E-Mail: koichi.yokoyama.ds@hitachi.com

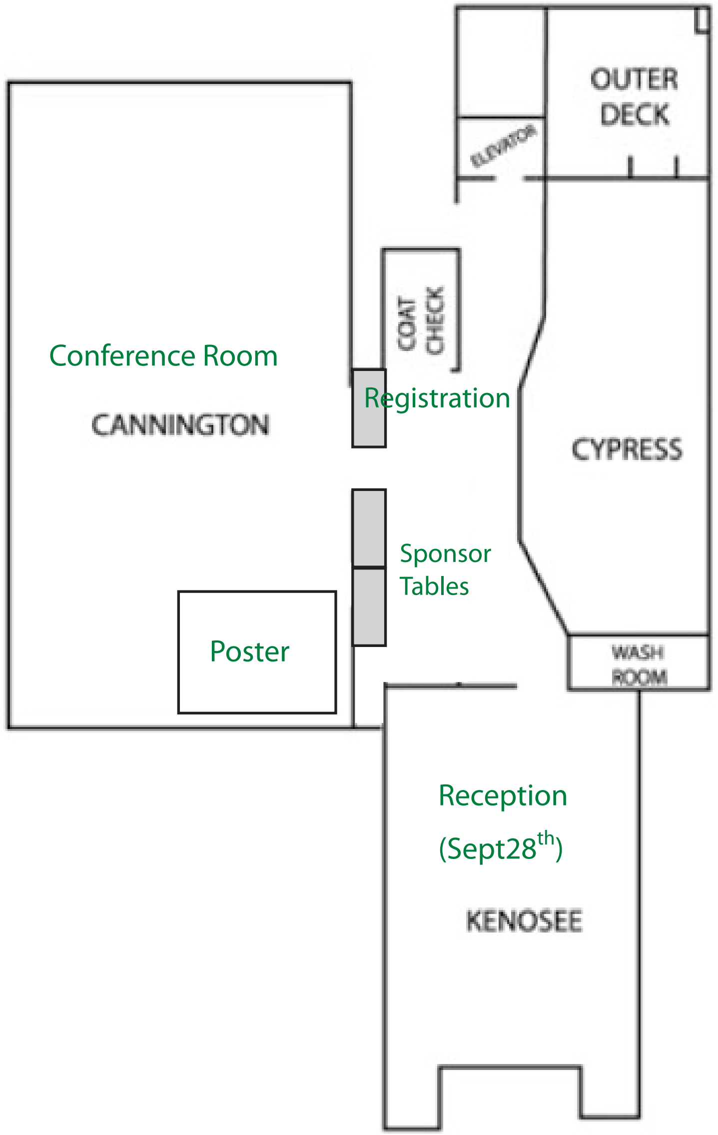
Zanganeh, Dr Kourosh
CanmetENERGY/ NRCan
E-Mail: kzangane@nrcan.gc.ca

Zarzour, Mr Othman
Abu Dhabi Future Energy Company (MASDAR)
E-Mail: ozarzour@masdar.ae

Zhang, Mrs Ruby
The Babcock & Wilcox Company
E-Mail: rzhang@babcock.com

Zhou, Miss Qing
University of Regina
E-Mail: sunny_energy@hotmail.com

MEZZANINE LEVEL



International Network for Post Combustion CO_2 Capture

Introduction to 12th Workshop, University of Regina

Saskatchewan, Canada

By

J M Topper

Managing Director Operating Agency for IEA GHG

IEA Greenhouse Gas R&D Programme

- A collaborative research programme founded in 1991
- Aim: *Provide members with definitive information on the role that technology can play in reducing greenhouse gas emissions.*
- Producing information that is:
  - Objective, trustworthy, independent
  - Policy relevant but NOT policy prescriptive
  - Reviewed by external Expert Reviewers
  - Subject to review of policy implications by Members
- Implementing Agreement set up under IEA

Contracting Parties and Sponsor Organisations of IEA GHG

International Network for Post Combustion CO_2 Capture

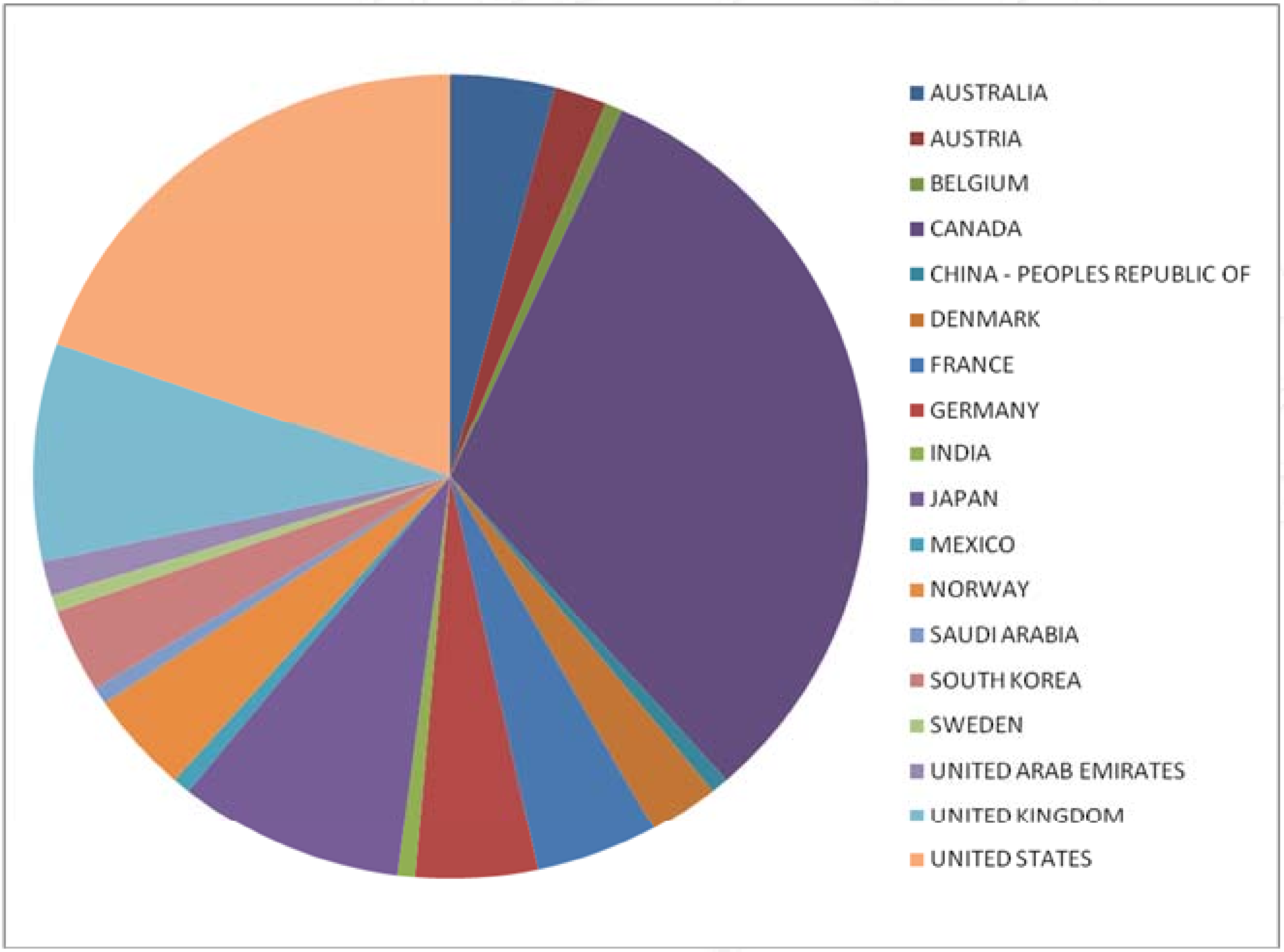
- ***AIM**: To establish a forum that will encourage practical work on Post Combustion CO_2 capture.*

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

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)	73 people
11th Workshop in EVN Forum, Austria (May 2008)	100 people
12th Workshop in Univ Regina, Canada (September 2009)	150 people

18 Countries Represented



B&W
power generation group

RWE
The energy to lead

UNIVERSITY OF
REGINA
ENGINEERING

IPAC
CO2

SaskPower

Office of Energy
and Environment

Saskatchewan
Ministry of
Energy and
Resources

DOOSAN
Doosan Babcock Energy

Stokes Research Inc.

ITC

HTC
purenergy

Stantec

Thanks to Organising Team

- University of Regina
  - Dean Paitoon Tontiwachwuthikul
  - Malcolm Wilson
  - Victoria Muzychuk
  - Elsa Johnston
  - Danielle Riemer
- IEA GHG
  - Stanley Santos and Mohammad Abu Zhara
  - Andrea Lacey

Conduct of the Meeting

- Session Co – Chairs please get together and decide how you want to share responsibility
- No- bios; just title,name and affiliation
- Speakers in technical sessions have 25 minutes including changeover time and Q&A. Please comply as it is unfair to others if you do not.
- PRESENTERS ensure Mohammad Abu Zhara (Mo) gets a copy of their presentation if you want it on the GHG website next week – in pdf format. Happy also to include posters as pdf files.
- Stanley Santos will act as MC with occasional announcements and hurry up messages

Today: Housekeeping Points

- Poster session runs through the conference – please take time to visit and talk to the authors
- Coffee breaks around 10 40 and 15 40; only 20 minutes
- Lunch, 12 40 – 14 00 preceded by group photos
- Afternoon session will finish at around 17 15
- Dinner this evening: Terrace Building, 10 Research Drive. Bus Pick up at 17 45.
- Mobile phones off or on vibrating alert

Next Time

- Want opinions about what to do next time, when and where.
- Will come back to this in the final wrap-up. Please talk to me or Stanley or Mo in next two days or by email afterwards
- Some thoughts:-
  - Too big now to continue in single session workshop format
  - GHG already runs world class GHGT conference series so can only manage big events in alternate years – next in 2011
  - Retain presentation format but with parallel sessions?
  - Would like an Asian host but failing this happy to take it back to Europe
  - Need a good side visit

GHGT-10
Amsterdam, 19th to 23rd September 2010

GHGT10

Call for Papers

10th International Conference on
Greenhouse Gas Control Technologies

The RAI, Amsterdam, The Netherlands.
19–23 September 2010

www.ghgt.info

- Key Diary Dates:
  - 15th September 2009 - Web site Open
  - 15th December 2010 - Abstract submission
  - 18th May 2010 - Notifications
  - 31st August 2010 - Paper submission date
  - 19th - 23rd September - 2010 Conference

Concentrated Piperazine
A new standard solvent

by

Gary T. Rochelle
gtr@che.utexas.edu
Luminant Carbon Management Program
Department of Chemical Engineering
The University of Texas at Austin

September 30, 2010

Why 8 m (40 wt% Piperazine?

- 10-20% less energy than 30 wt% MEA
  - – 2 x CO_2 mass transfer rate
  - – 1.8 x capacity
  - – High P (6 – 15 atm) Stripper, stable to 150°C
- Oxidatively stable, esp. with Inhibitor A
- Less volatile than 7 m MEA
- Soluble at 0^oC at operating loading
- Good Opportunities for Reclaiming

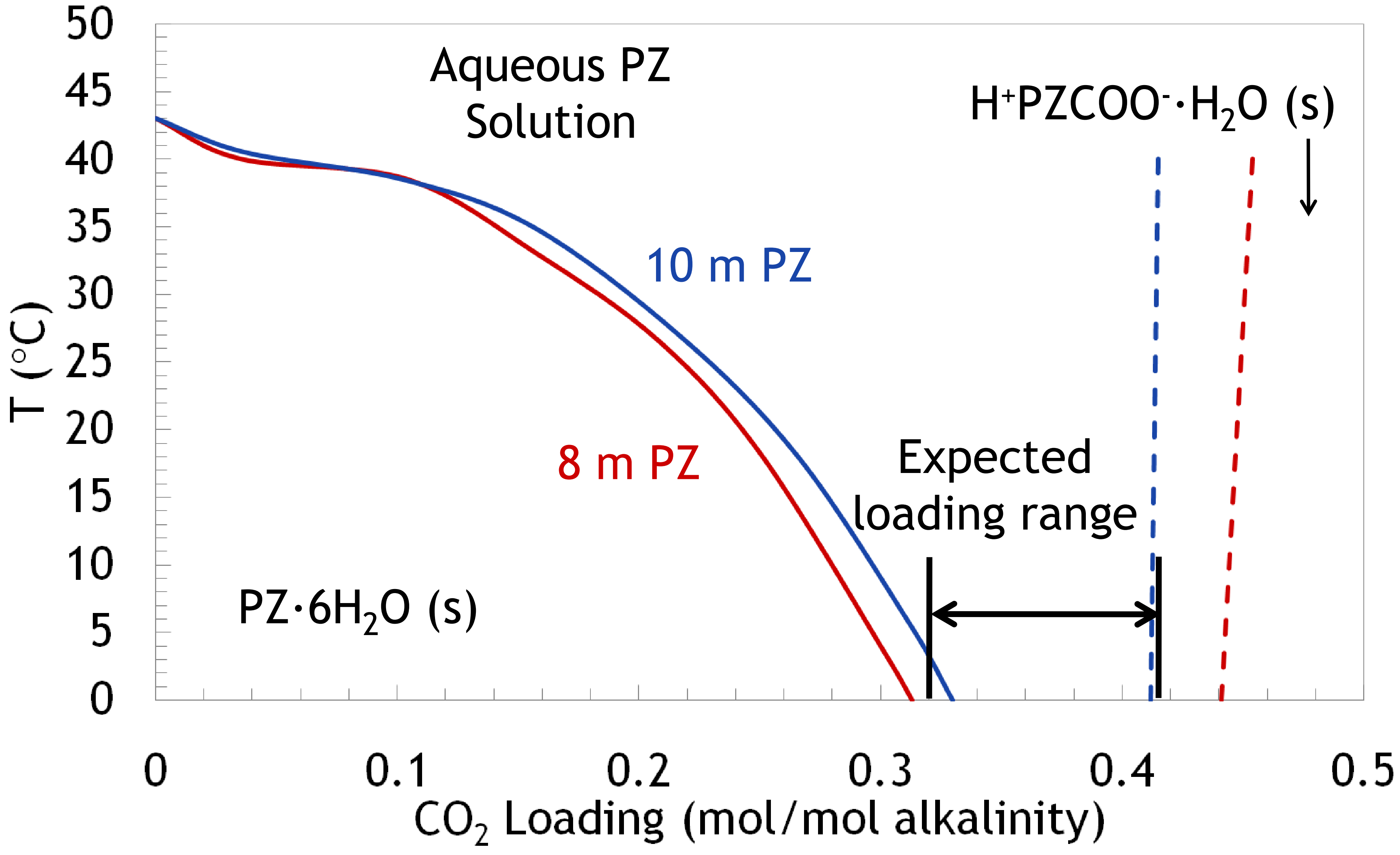
Roadmap

- Energy Properties
- Solvent Management
- Pilot Plant

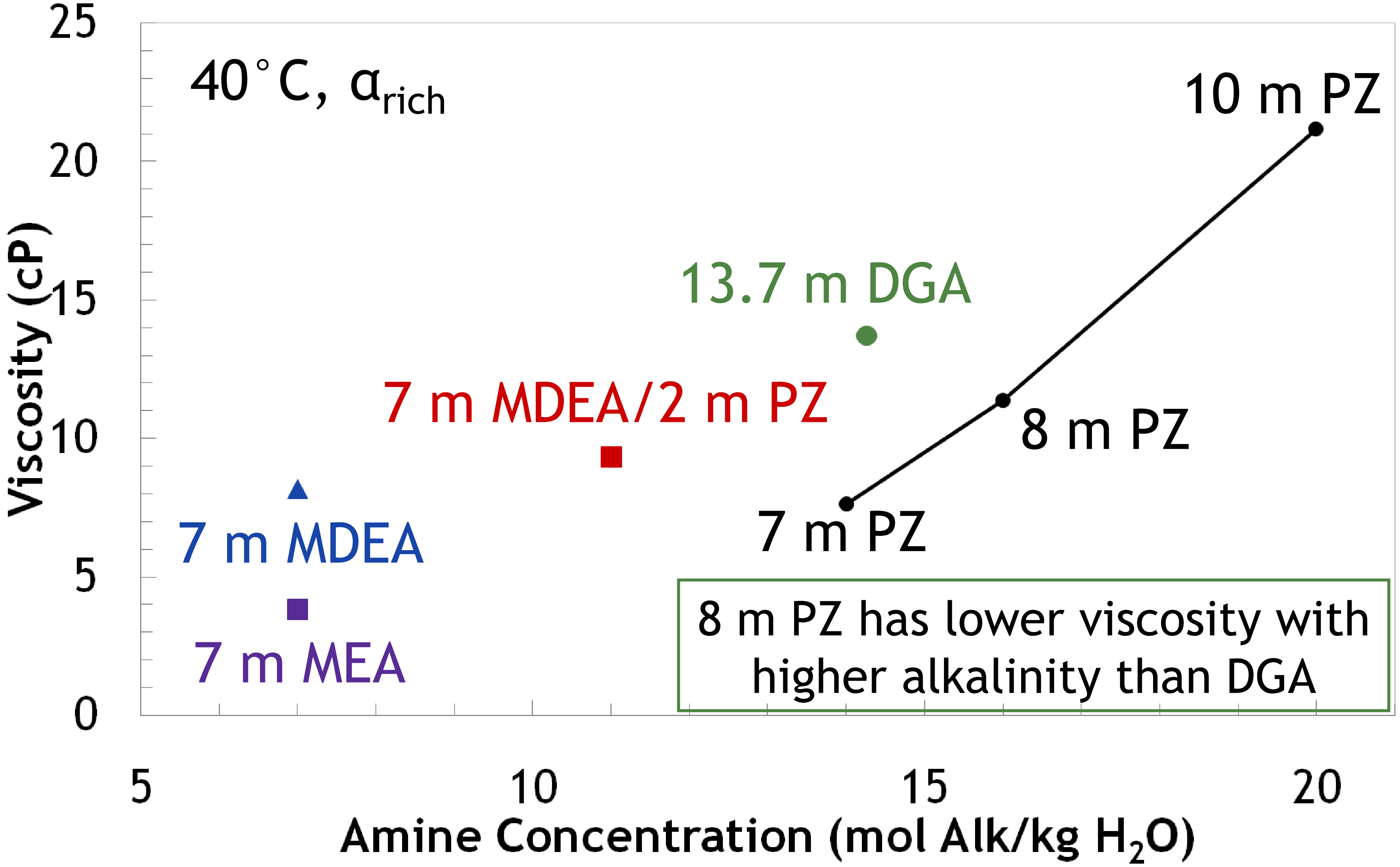
Energy Properties

- Chemistry – 2 active amines per molecule
- Viscosity & Solubility allow 8 m PZ when loaded
- CO_2 solubility
  - Capacity – 0.84 moles/kg solvent
  - Heat of Desorption – 76 kJ/mole
- Thermal Stability to 150^oC
- 2-stage heated flash reduces energy 15%

Solubility Envelope for PZ

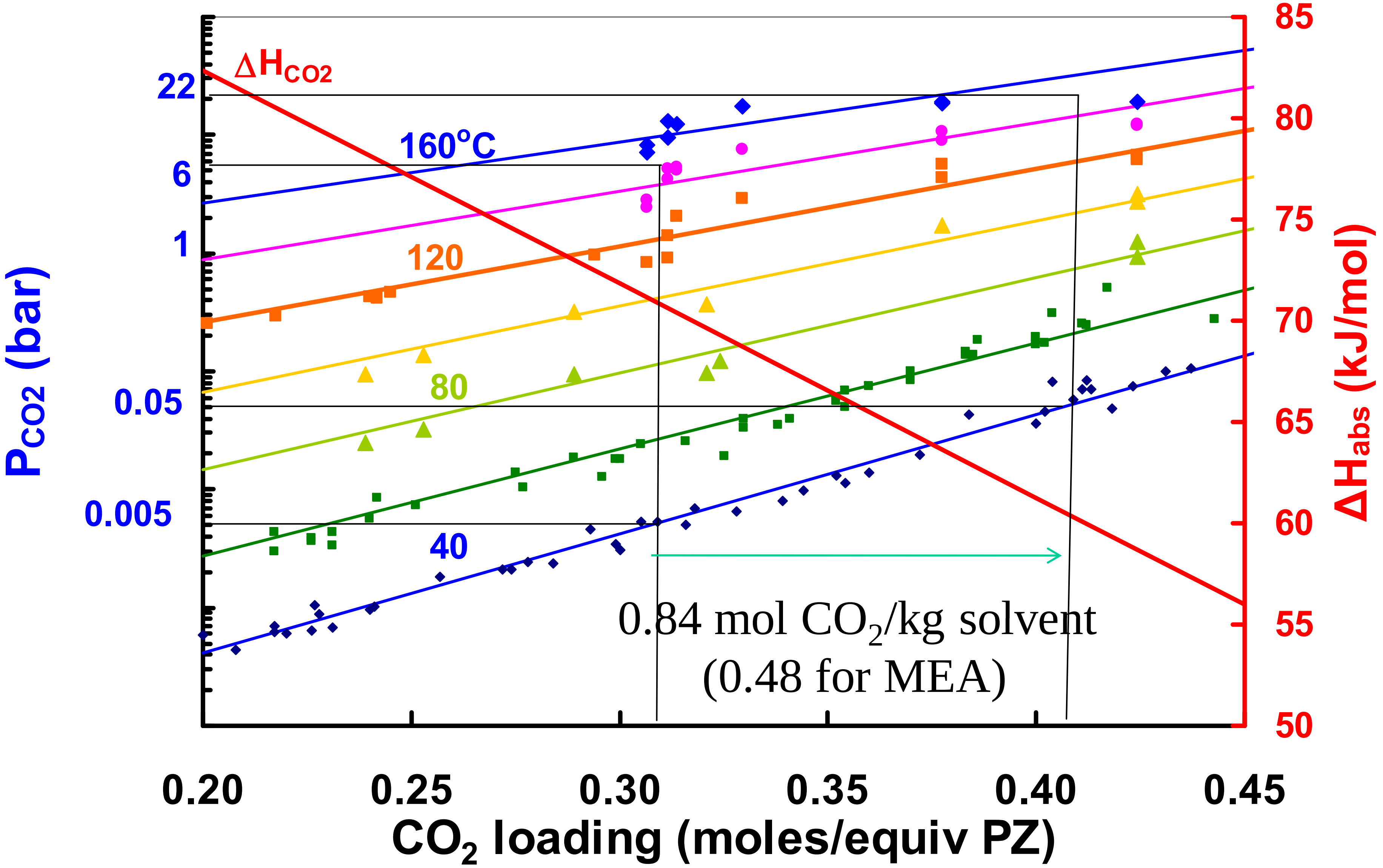


Viscosity Comparison



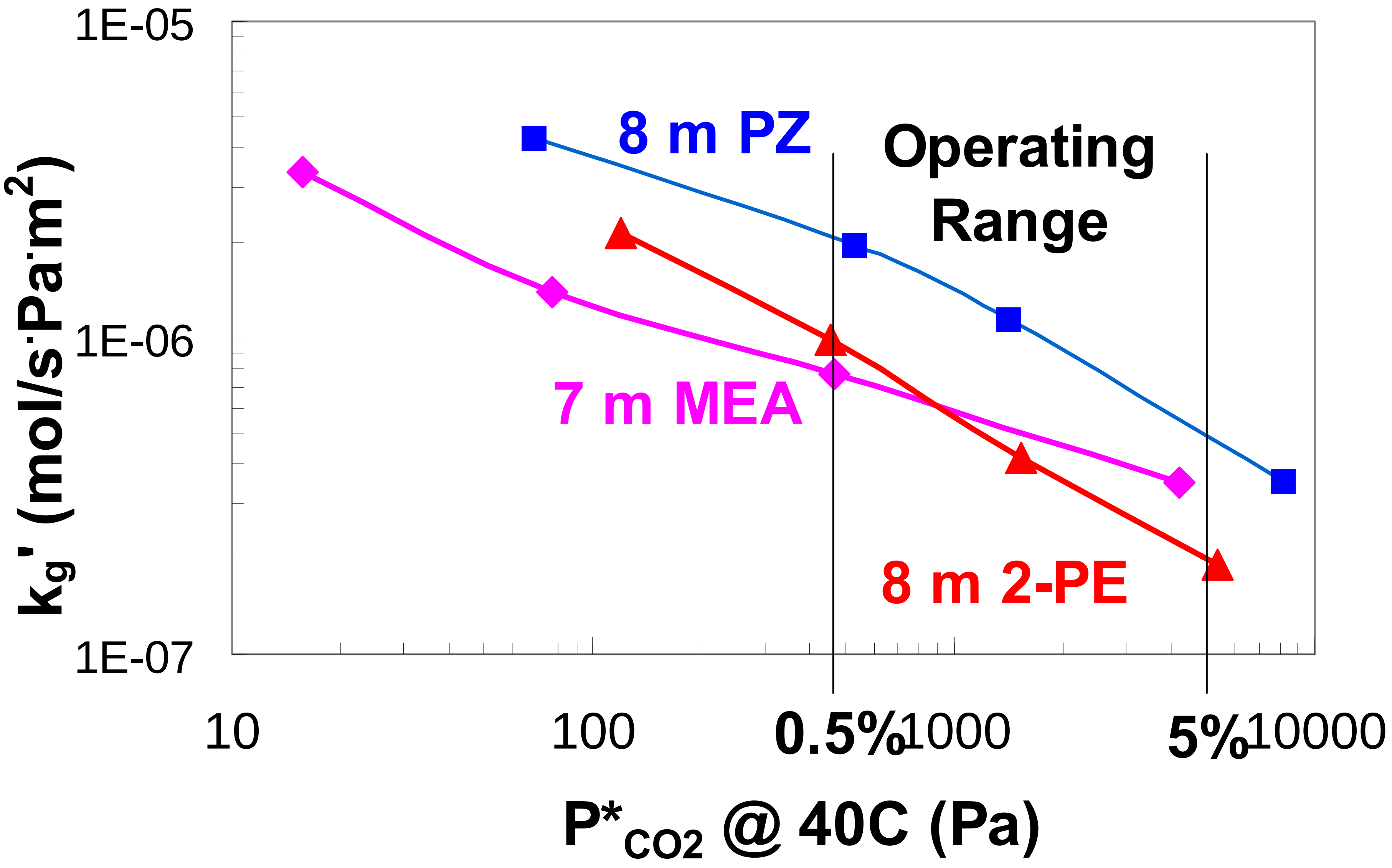
8 m PZ has lower viscosity with higher alkalinity than DGA

CO_2 solubility in Aqueous PZ

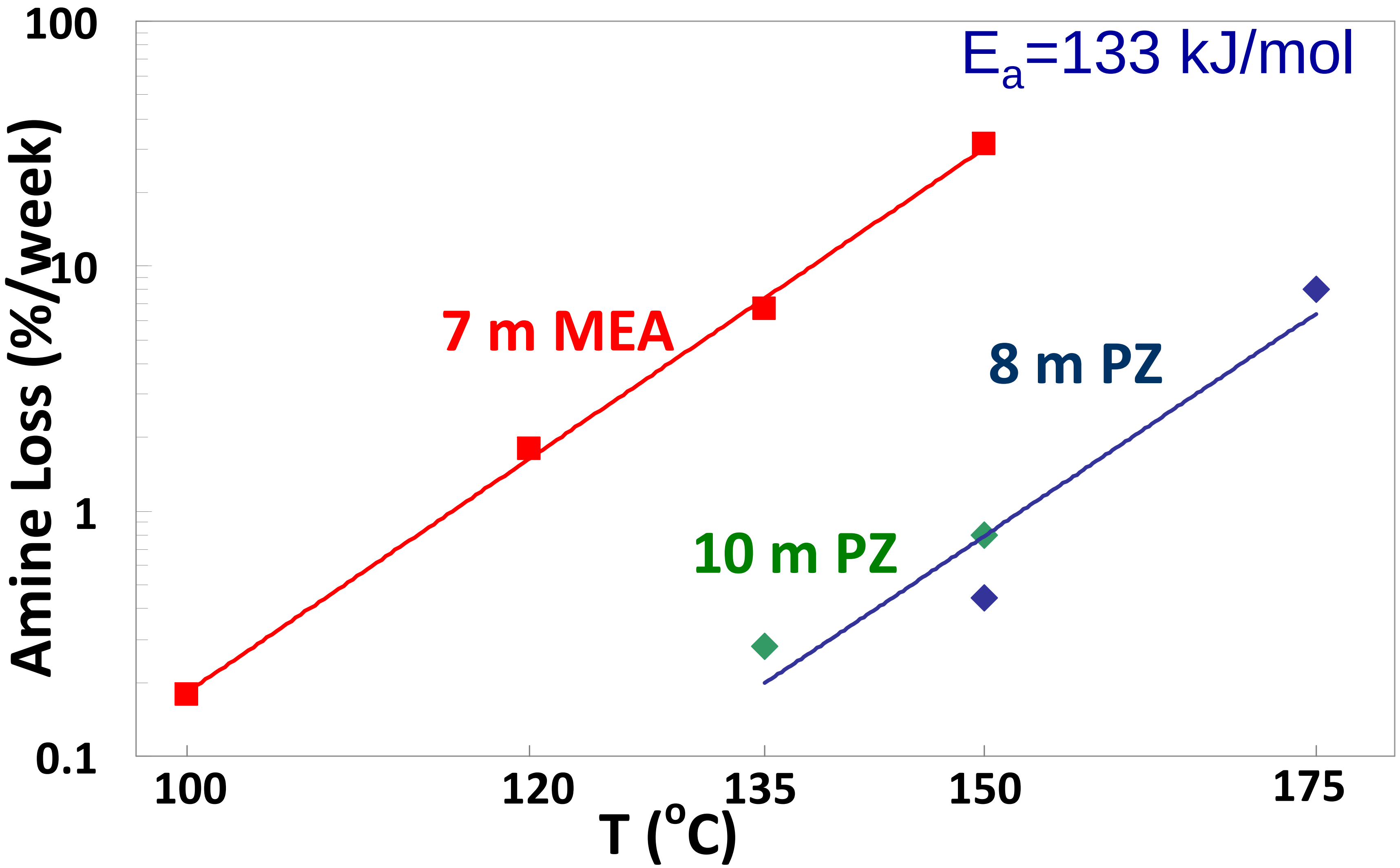


0.84 mol CO_2/kg solvent
(0.48 for MEA)

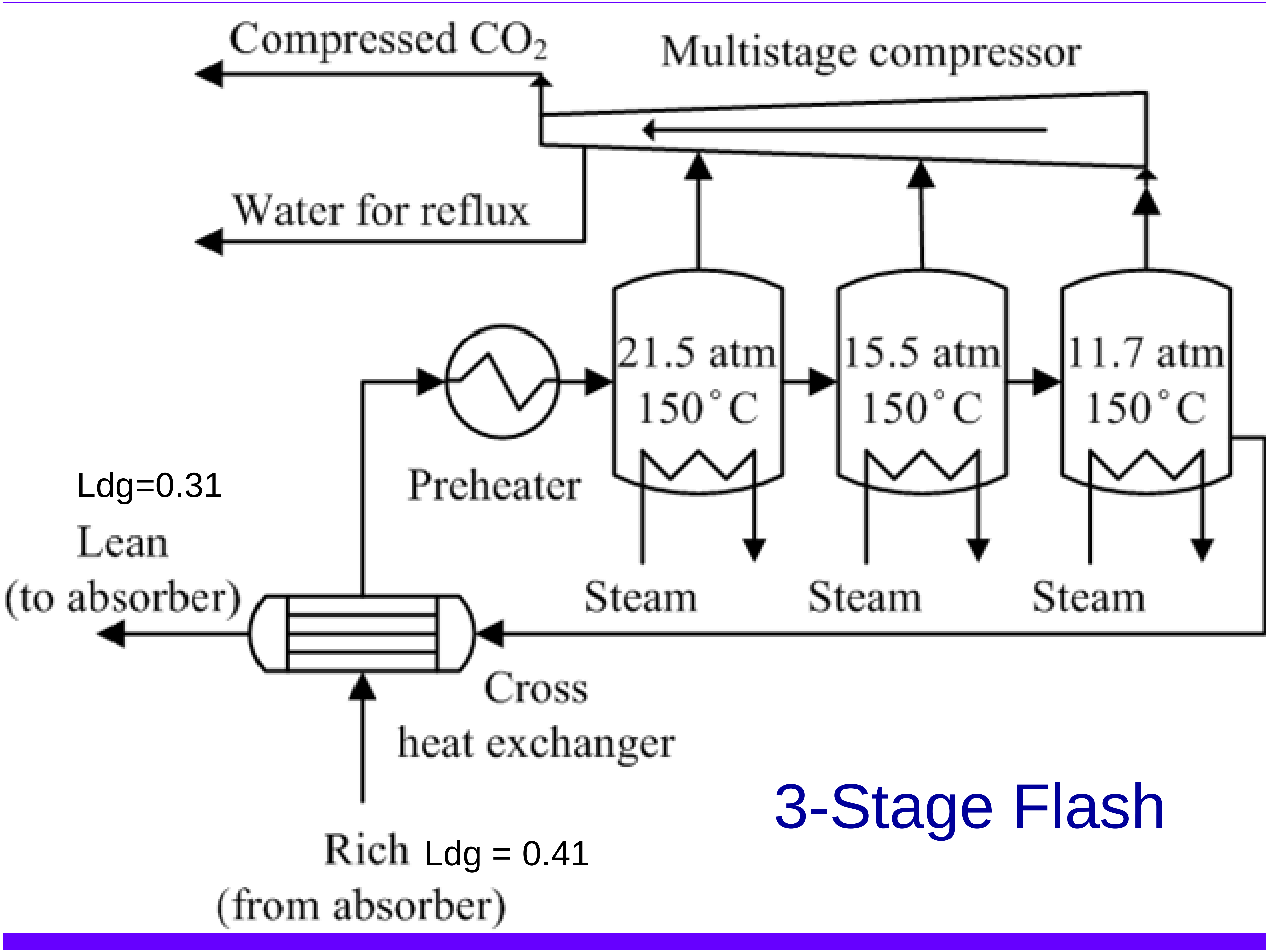
CO_2 Absorption Rate, 40°C



Thermal Degradation at Rich Loading



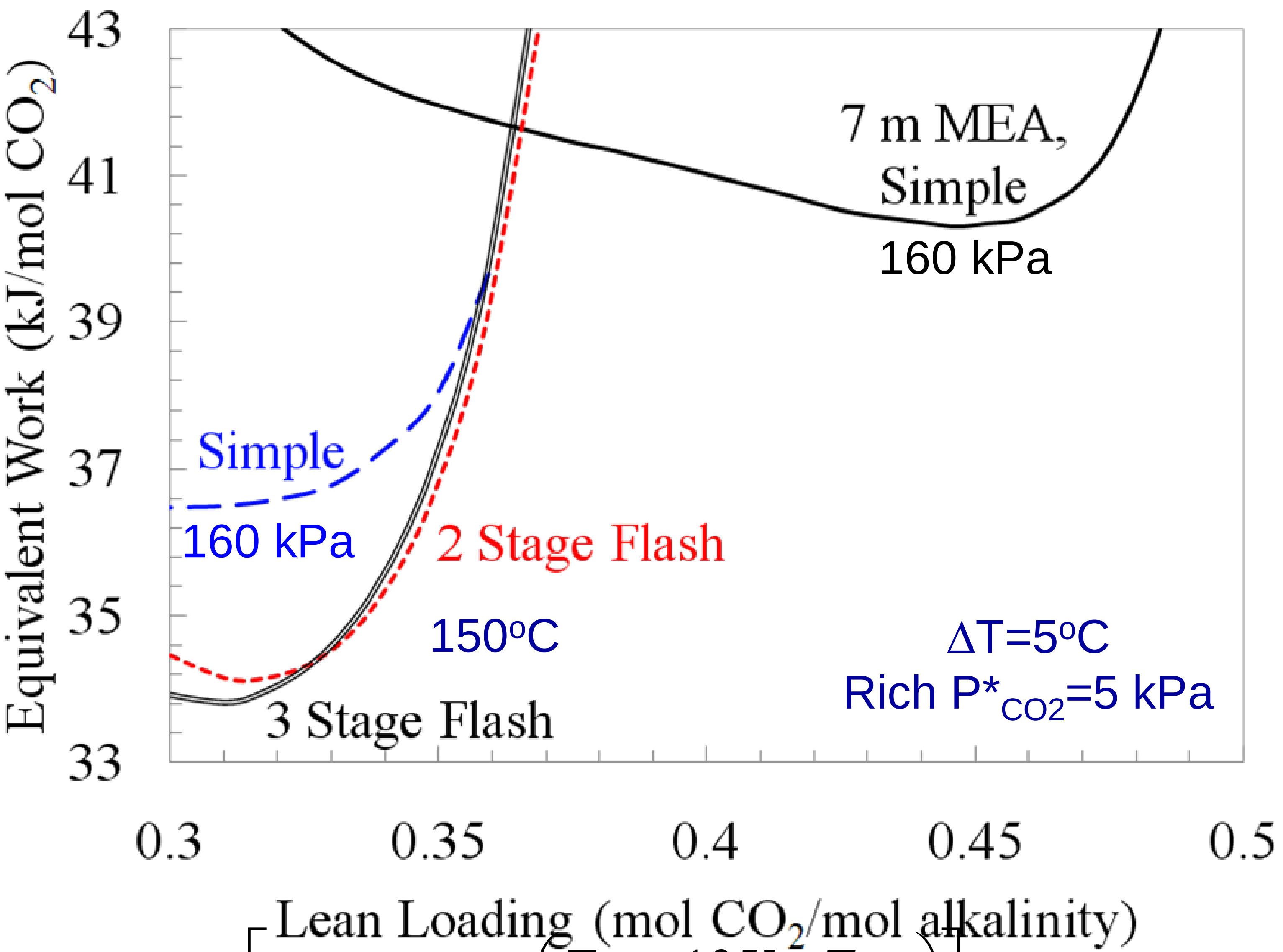
3-Stage Flash



Ldg=0.31

Rich Ldg = 0.41

Stripping 8 m PZ

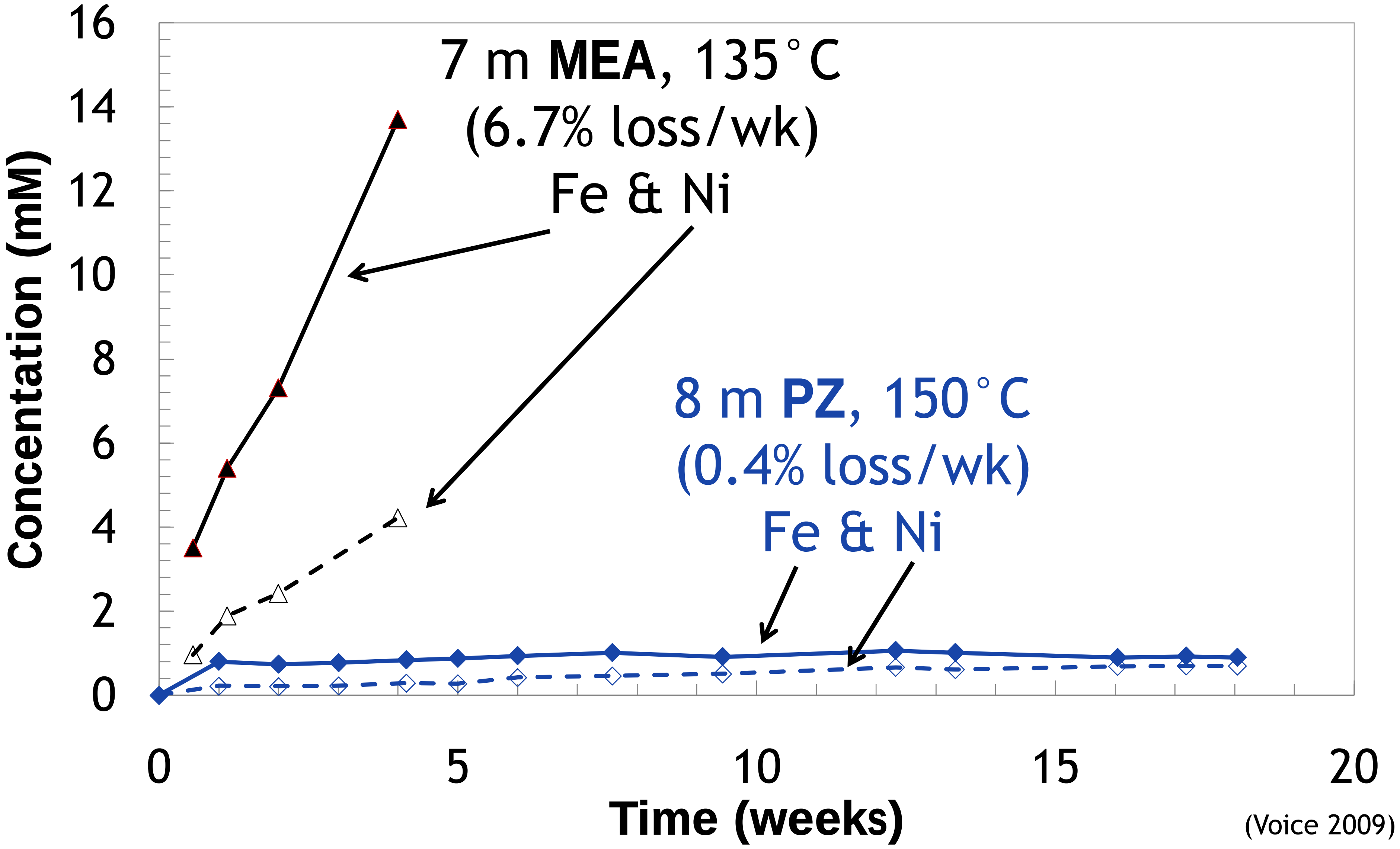


$$W_{eq} = \left[\sum 0.75 \cdot Q_{reb} \left(\frac{T_{reb} + 10K - T_{sink}}{T_{reb} + 10K} \right) \right] + W_{pump/comp}$$

Solvent Management

- Volatility <20 ppm at lean conditions
  - Air Impacts minimized by Water Wash
- Oxidation 3 x less than MEA
  - Eliminated by inhibitor A
- 316 SS resistant to corrosion
- Piperazine easily reclaimed by existing options

SS316 corrosion in thermal degradation experiments



(Voice 2009)

Reclaiming concepts

- Traditional Thermal or distillation Reclaiming
  - Atm or vacuum
  - PZ more volatile than MEA
  - PZ thermally stable
- Inhibitor A recovered from conc soln by supplier
- Ion Exchange or electrodialysis as with MEA
- K_2SO_4 crystallization with addition of KOH
  - 0.17 m sulfate solubility

Pilot Plant

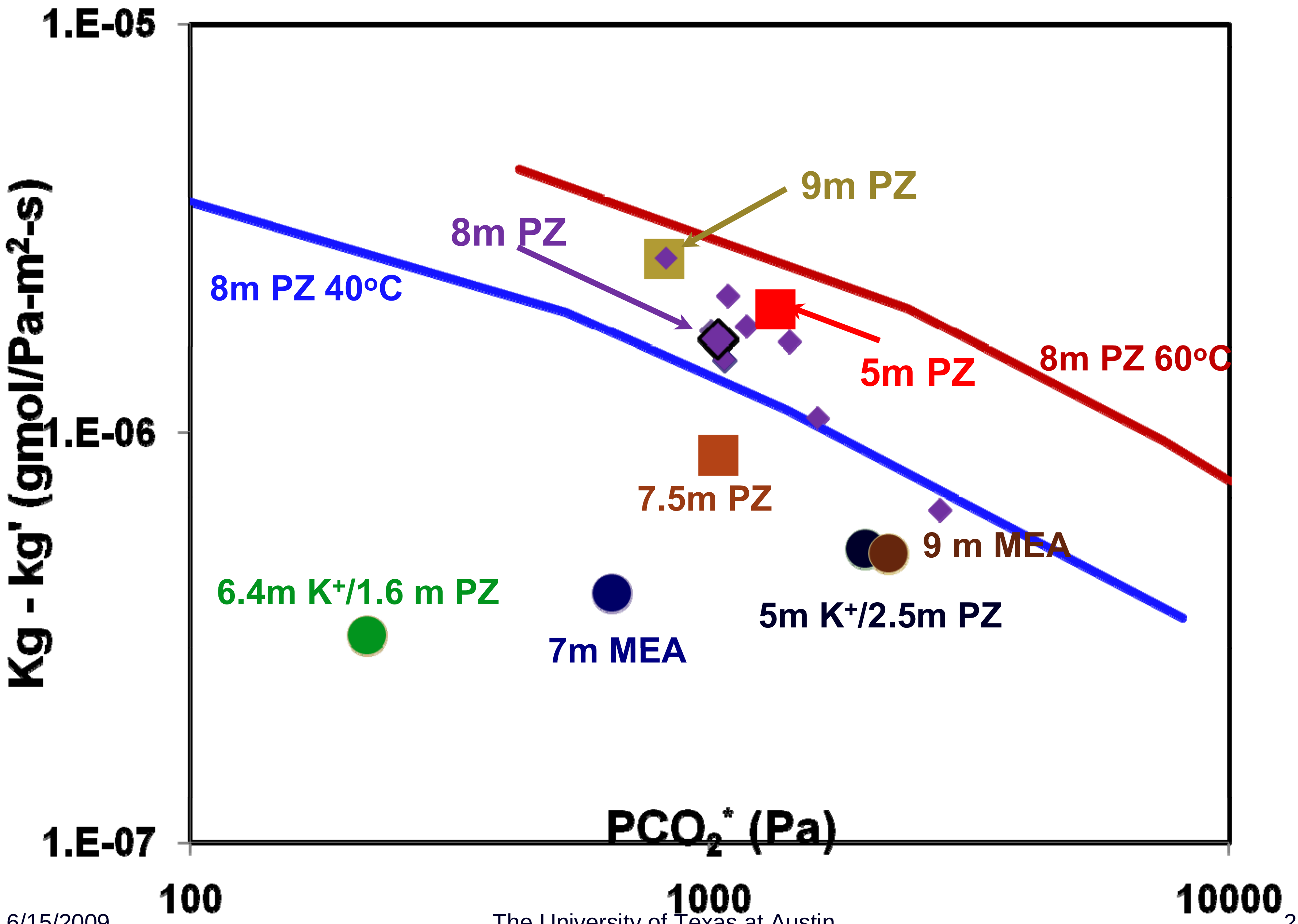
- Results in 0.1 MW with air/CO_2
  - Mass Transfer Rate
  - Energy
- Plans for 0.1 MW with high P 2-stage flash

Selected Pilot Plant Runs, 8 m PZ
20 ft Mellapak 2X, 200m^2/m^3

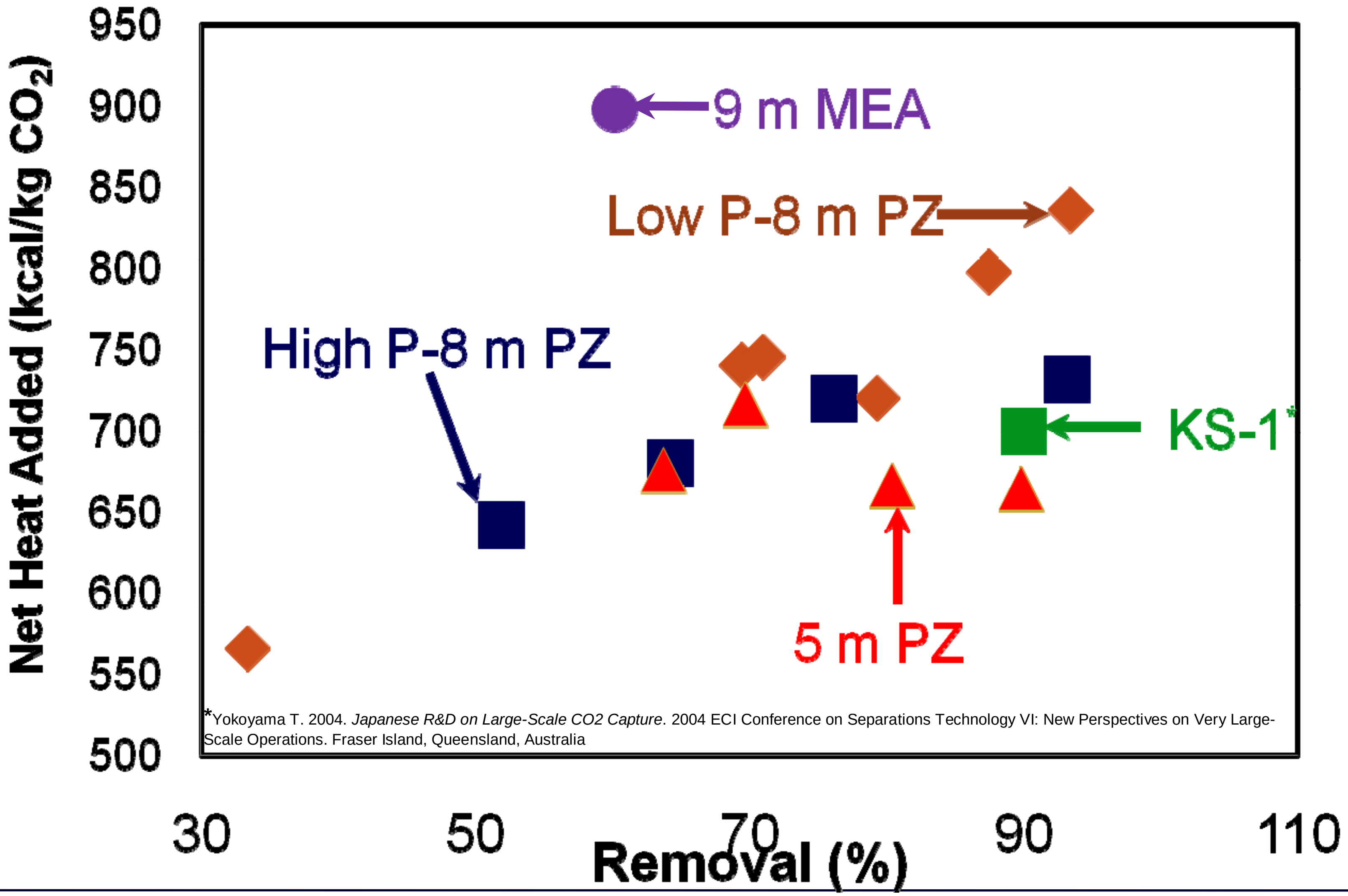
Gas (acfm)	Liq (gpm)	P_{STRP} (psia)	Rem (%)	Lean Ldg	Rich Ldg
350	18	51	93.2	0.27	0.34
350	15	20	93.4	0.25	0.33
350	18	20	79.3	0.30	0.36
350	15	60	76.1	0.31	0.36

Loading = mol CO_2/Total Alkalinity

Wetted wall kg' & Pilot plant K_G



Stripper Performance



*Yokoyama T. 2004. *Japanese R&D on Large-Scale CO2 Capture*. 2004 ECI Conference on Separations Technology VI: New Perspectives on Very Large-Scale Operations. Fraser Island, Queensland, Australia

Conclusions

- 10-20% less energy than 30 wt% MEA
  - Double the CO_2 mass transfer rate
  - 1.8 x capacity
  - High P (6 – 15 atm) Stripper, stable to 150°C
- Oxidatively stable, esp. with Inhibitor A
- Less volatile than 7 m MEA
- Soluble at 0^oC at operating loading
- Good Opportunities for Reclaiming

Accurate Screening of Candidate Solvents by the Wetted Wall Column

Xi Chen, Ross Dugas, Fred Closmann,
Shan Zhou, Gary T. Rochelle

The University of Texas at Austin

12th MEETING of the INTERNATIONAL POST-COMBUSTION
CO_2 CAPTURE NETWORK

Sep 29, 2009

Regina, Canada

Outline

- Background
    - Research needs
    - Literature review
- Apparatus
    - Wetted Wall Column (WWC)
- Results:
    - CO_2 solubility, CO_2 capacity, Heat of absorption
    - Absorption/Desorption Rates
- Conclusions

Research Needs

- Previous amine capacity & kinetics studies:
  - Low amine concentration (< 3 M)
  - Zero or very lean CO_2 loading
  - Narrow temperature range (25~60 ^{o}C)
- Typical industrial conditions for CO_2 capture
  - Absorber: 40-60 ^{o}C
  - Stripper: 80-120 ^{o}C
  - 12% CO_2 in flue gas at 1atm and 90% removal: CO_2-loaded amine solvent ($P^*_{CO2,lean}$=0.5 kPa and $P^*_{CO2,rich}$=5 kPa)
- Previous amine screening efforts
  - Simple gas sparging: Absorption rate affected by solution property (density, viscosity & surface tension etc.)
  - CO_2 capacity for industrial conditions not available

Why WWC for Screening?

- More representative of commercial packing than laminar jet or stirred cell.
- More accurate VLE and mass transfer rate in loaded solution.
- Adequate for design of absorber and stripper.

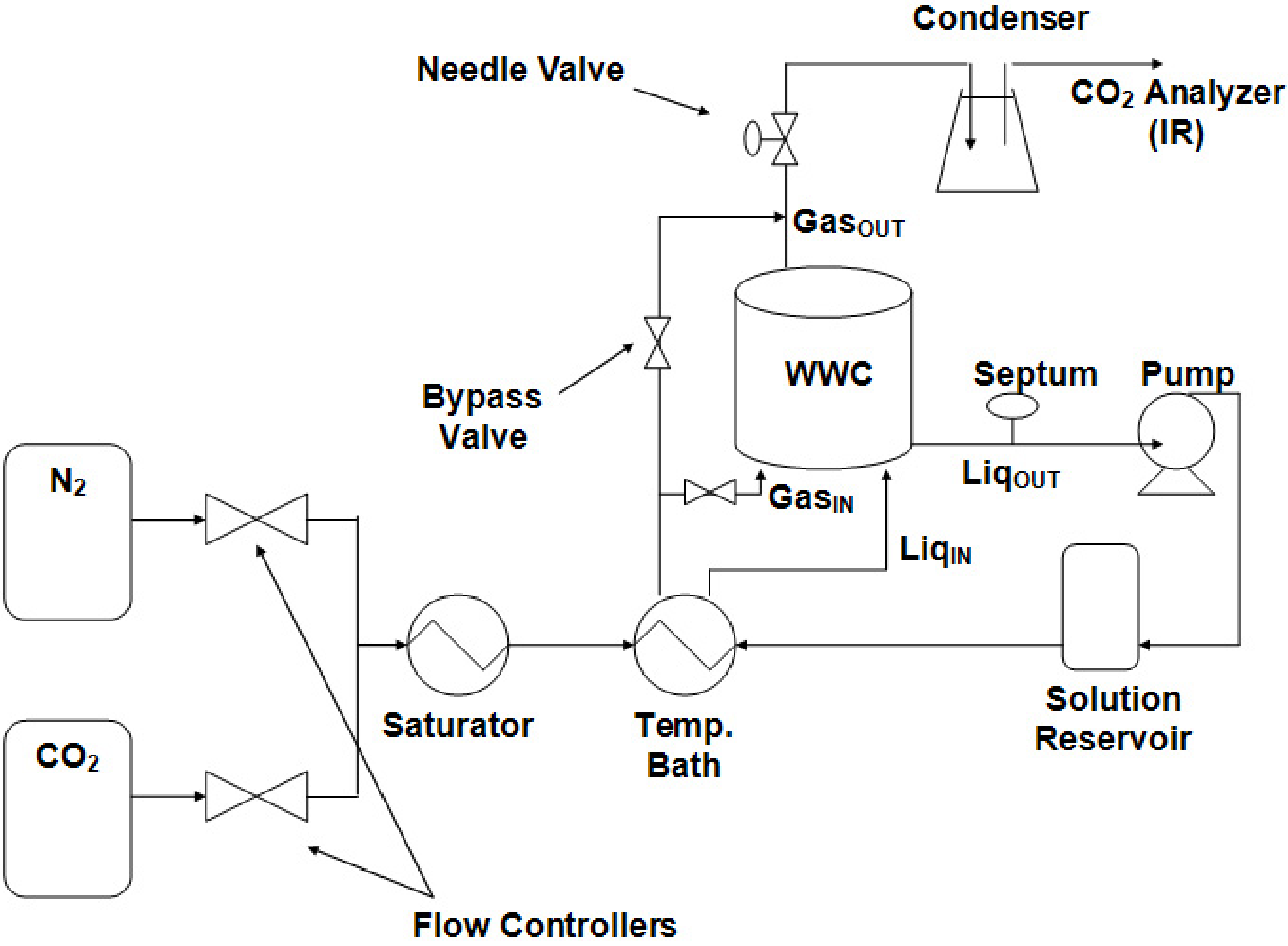
Previous work with WWC

Literature	**Solvents**	**$[\text{Amine}]_{max}$ (molality)**
Dugas 2009	MEA/PZ	13
Cullinane 2005	K^+/ PZ	4
Al-Juaied 2004	DGA / Morpholine	18
Bishnoi 2000	MDEA/PZ	8
Pacheco 1998	MDEA/ DGA	12
Mashewa 1995	MDEA/DEA	9

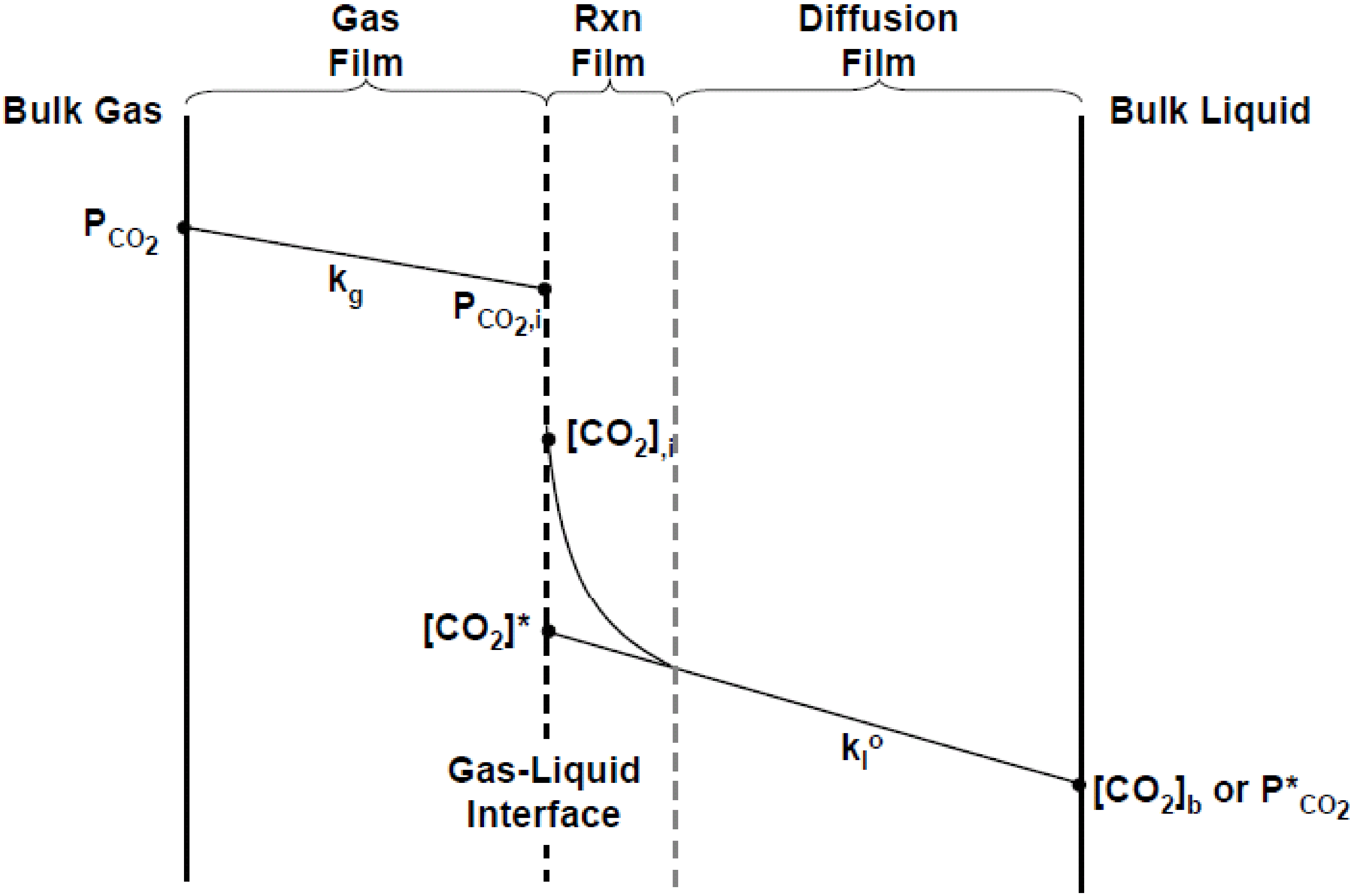
Scope of this work

		Conc. (m)	Viscosity@ $40^{o}C$& P^*_{CO2} =5kPa (cP)
Primary Amines	Ethanolamine (MEA)	7	2.5
	Ethylenediamine (EDA)	12	14
	Diglycolamine® (DGA®)	10	n/a
Piperazine & derivatives	Piperazine (PZ)	8	10
	N-(2-hydroxyethyl)piperazine(HEP)	7.7	17
	1-(2-Aminoethyl)piperazine (AEP)	6	23
Hindered Amines	2-amino-2-methyl-1-propanol (AMP)	4.8	4
	2-piperidineethanol (2-PE)	8	24
Promoted Tertiary Amine	Methyldiethanolamine (MDEA)/ Piperazine (PZ)	7/2	8

Wetted Wall Column



$$R_1 = \frac{1}{k_g} \qquad R_2 = \frac{H_{CO_2}}{E k_l^0} \qquad R_3 = \frac{1}{k_{l,PROD}^0} \frac{\partial P_{CO_2}^*}{\partial [CO_2]_T}$$



$$\frac{1}{K_G} = \frac{1}{k_g} + \frac{H_{CO_2}}{Ek_l^0} + \frac{1}{k_{l,PROD}^0}\frac{\partial P_{CO_2}^*}{\partial [CO_2]_T} = \frac{1}{k_g} + \frac{1}{k_g^{'}}$$

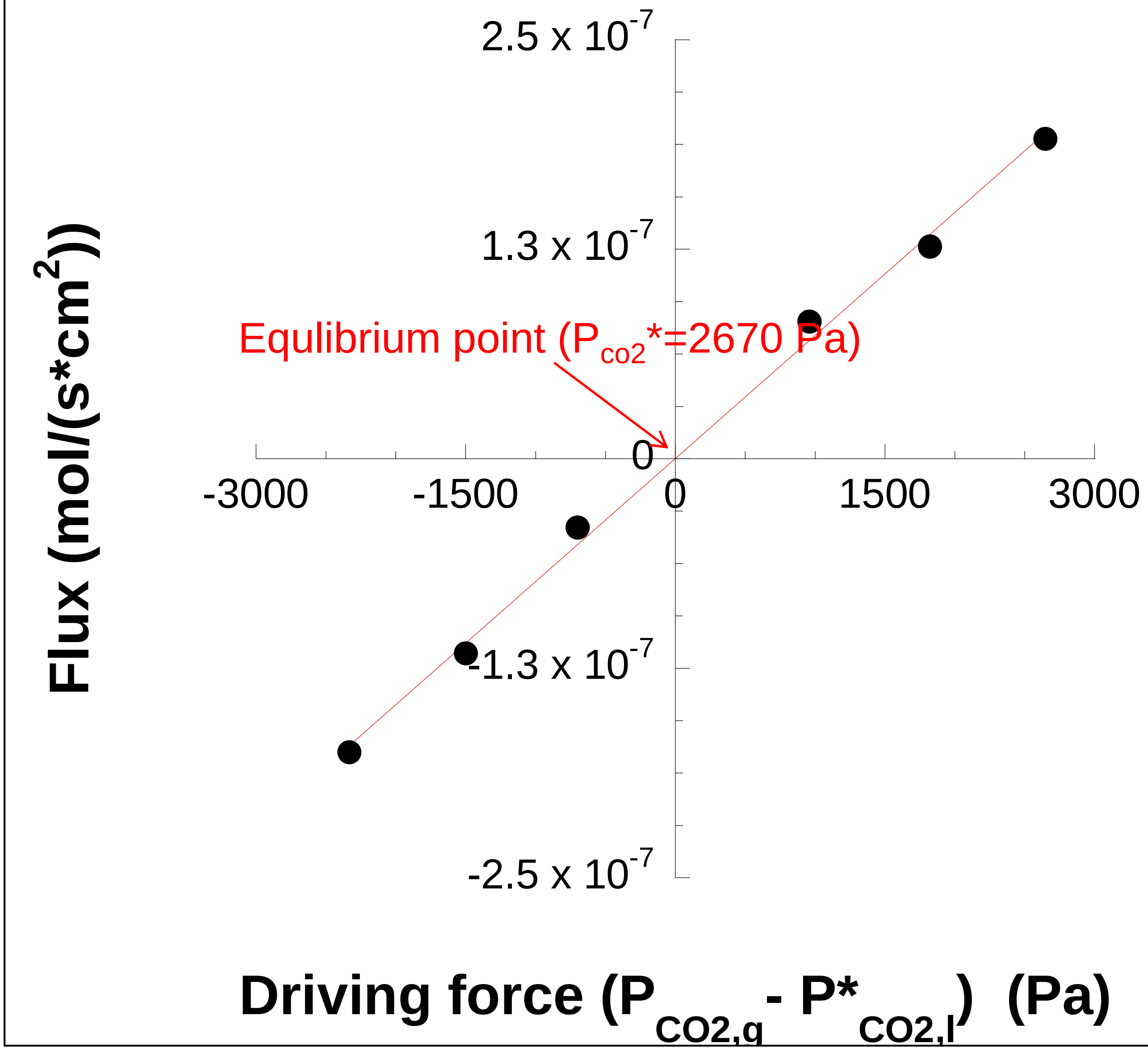
$$N_{CO_2} = K_g(P_{CO_2,g} - P_{CO_2,l})$$

$$= k_g^{'}(P_{CO_2,i} - P_{CO_2,l})$$

$$\Rightarrow \boxed{k_g^{'}} = \frac{N_{CO_2}}{P_{CO_2,i} - P_{CO_2,l}}$$

$$\approx \boxed{\frac{\sqrt{D_{CO_2}k_2[Am]_b}}{H_{CO_2}}}$$

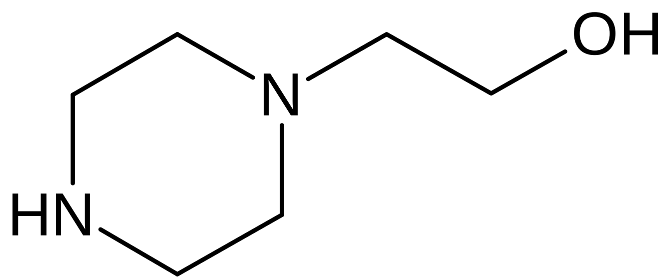
10m DGA® @ 60°C,
CO_2 ldg= 0.4 mol/mol alka

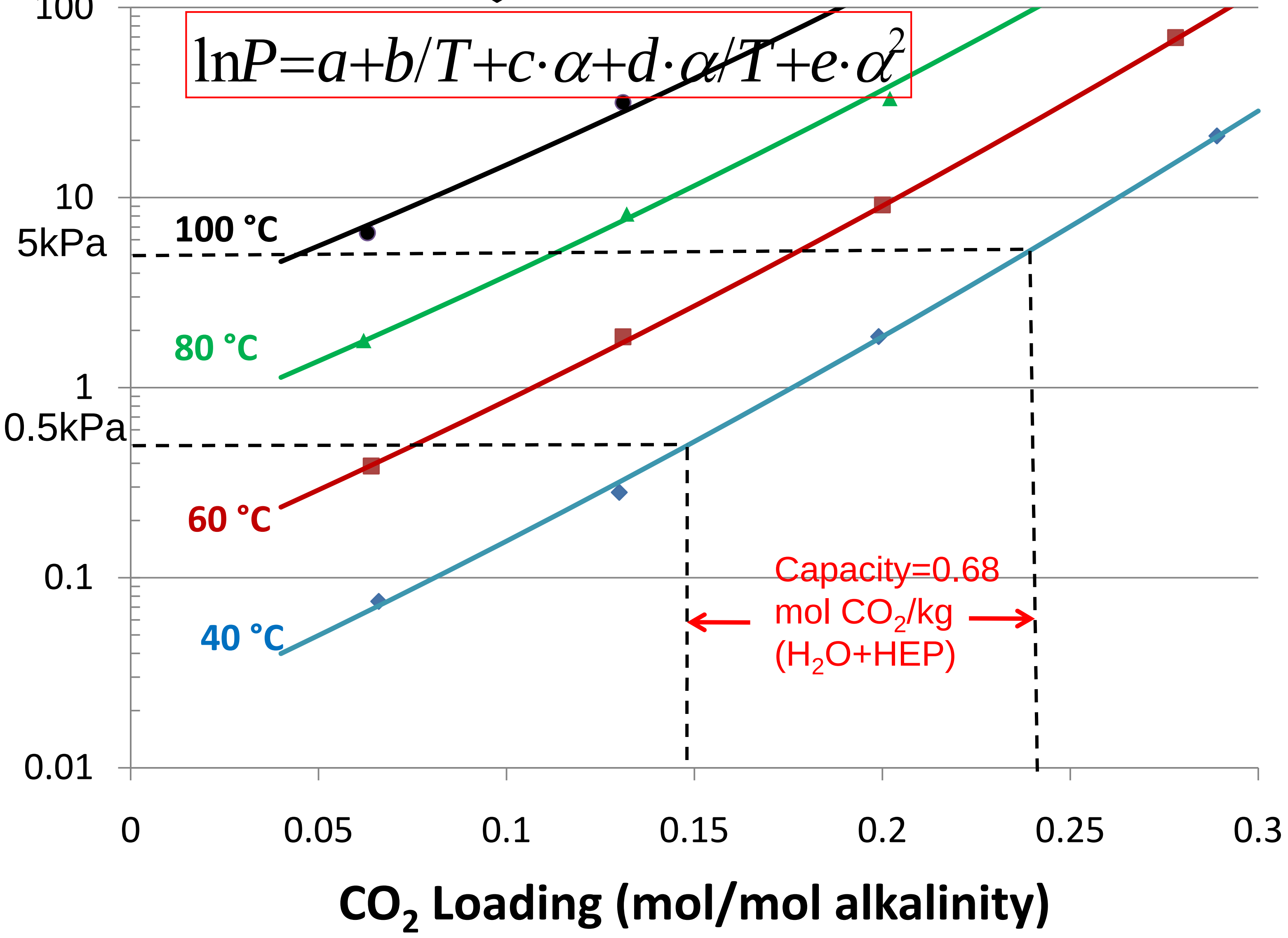


Equlibrium point (P_{co2}*=2670 Pa)

PIPERAZINE DERIVATIVES

CO_2 Solubility
7.7m HEP

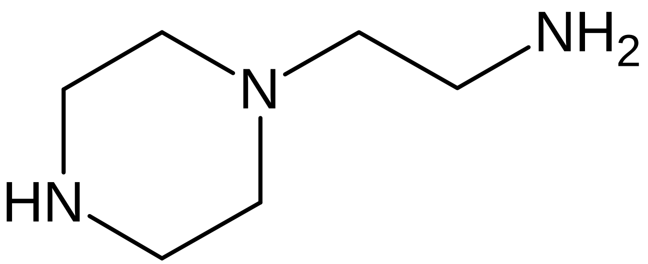


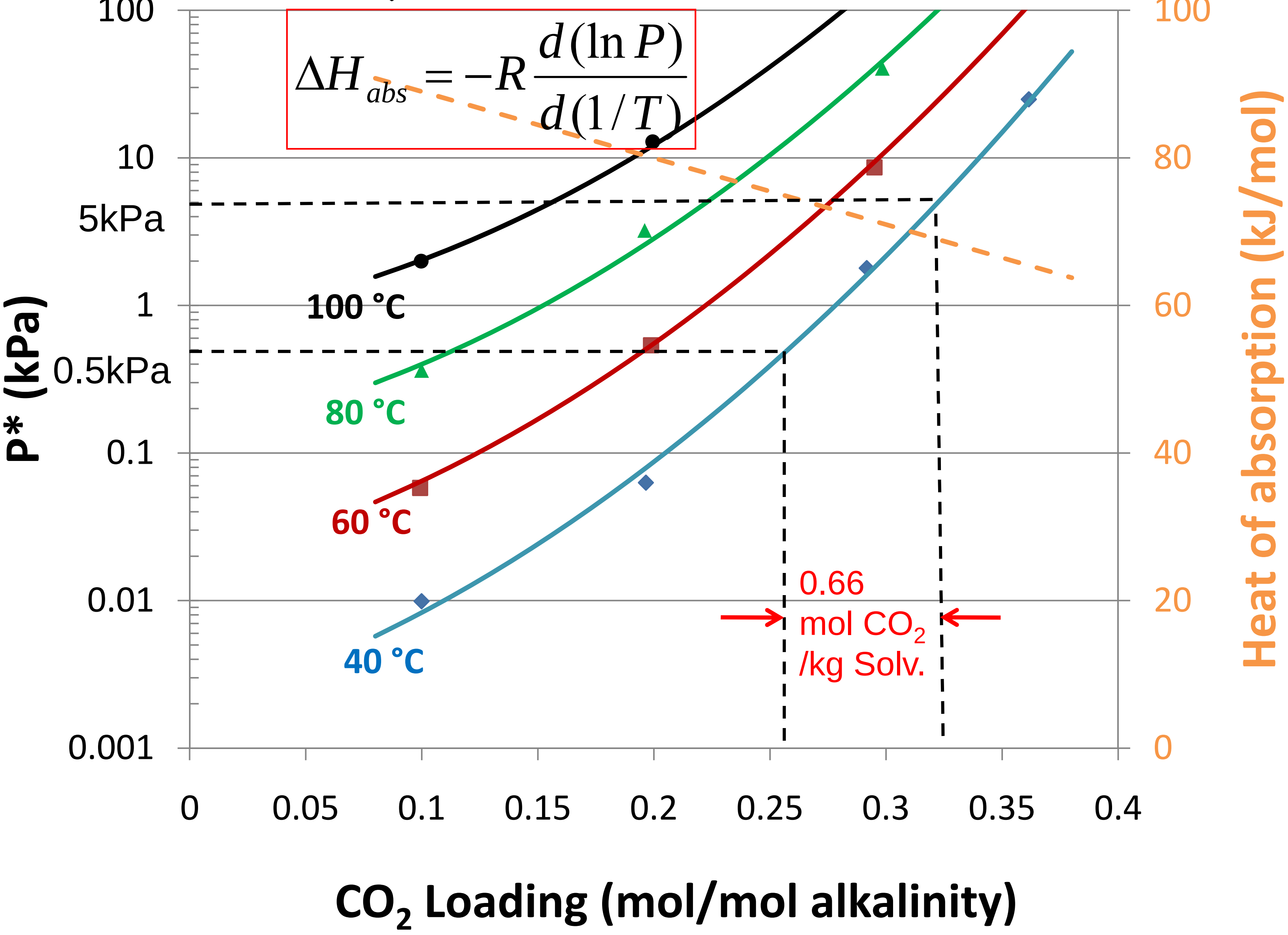


$$\ln P = a + b/T + c\cdot\alpha + d\cdot\alpha/T + e\cdot\alpha^2$$

Capacity=0.68 mol CO_2/kg (H_2O+HEP)

6m AEP



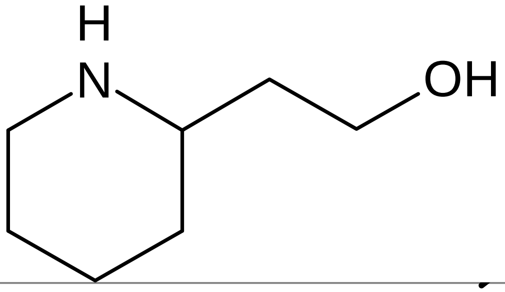


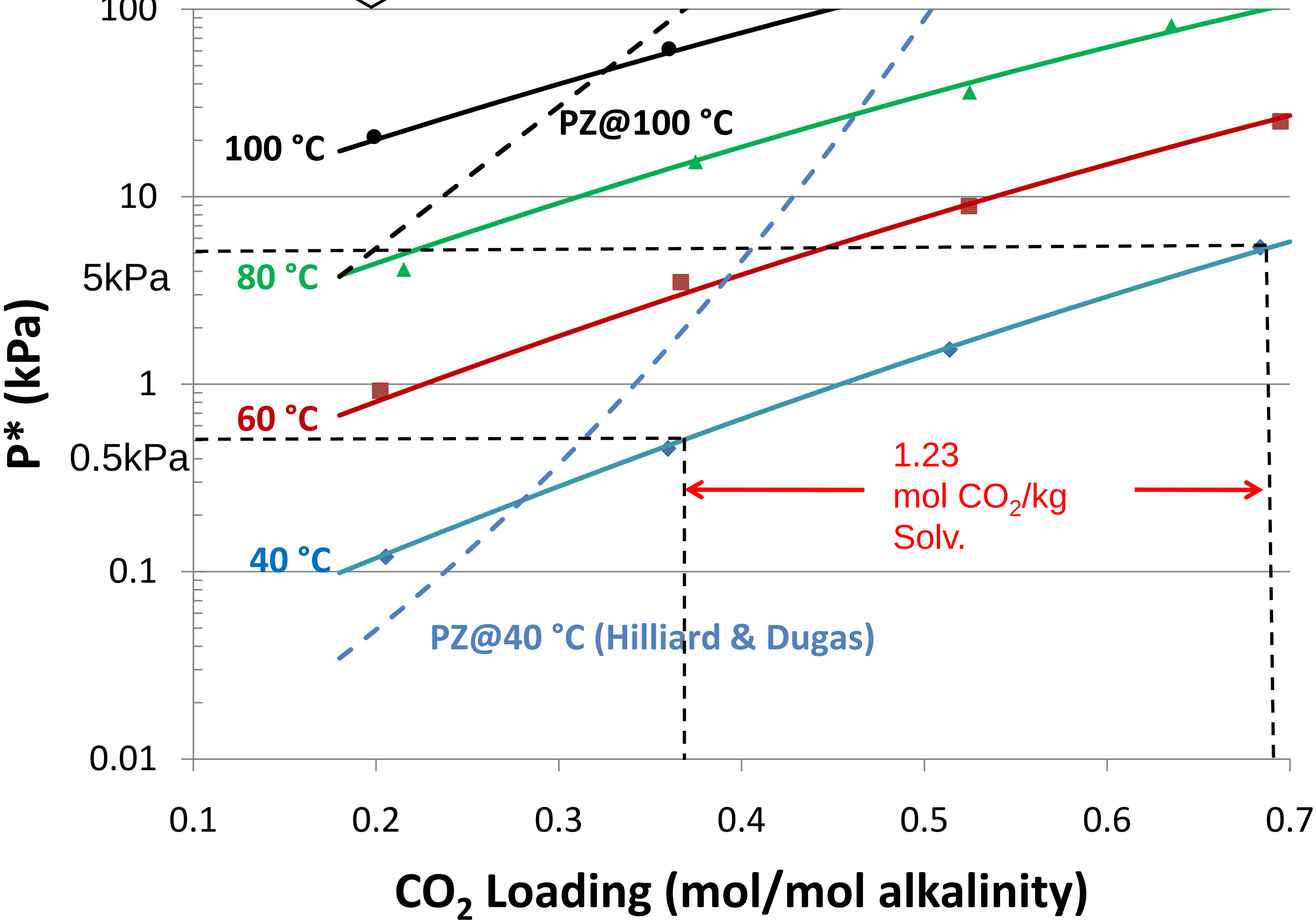
$$\Delta H_{abs} = -R\frac{d(\ln P)}{d(1/T)}$$

0.66 mol CO_2 /kg Solv.

HINDERED AMINE

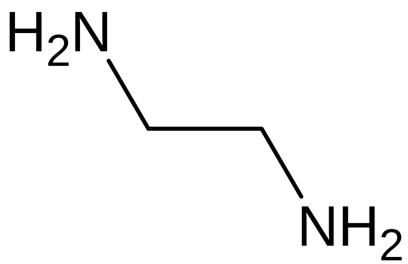
8m 2-PE


H
N
OH

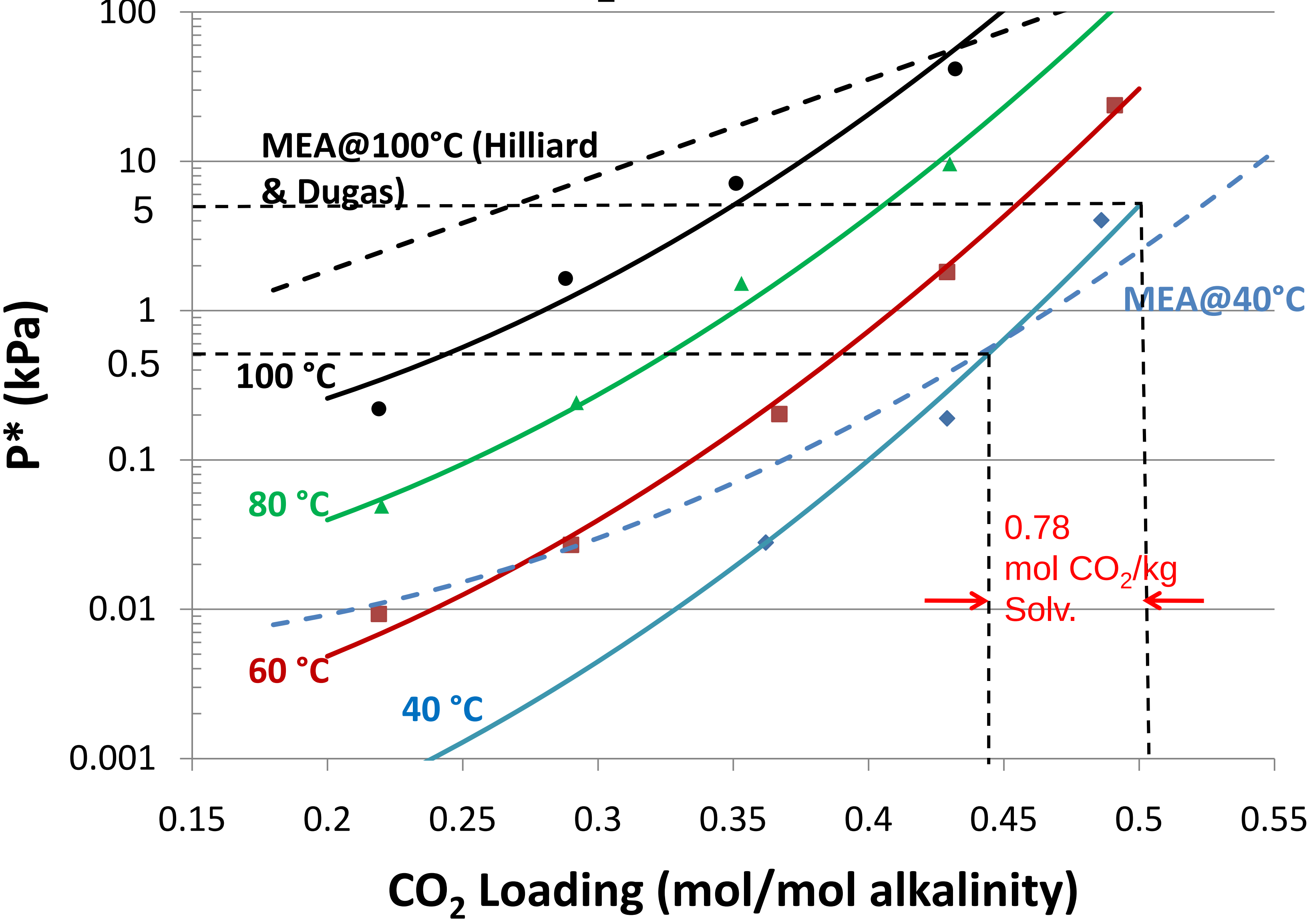

100
10
5kPa
1
0.5kPa
0.1
0.01
P* (kPa)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
CO₂ Loading (mol/mol alkalinity)
100 °C
PZ@100 °C
80 °C
60 °C
40 °C
PZ@40 °C (Hilliard & Dugas)
1.23
mol CO₂/kg
Solv.

PRIMARY AMINE

12m EDA



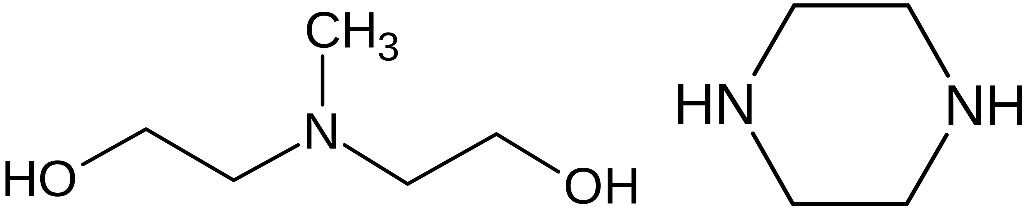
H_2N
NH_2

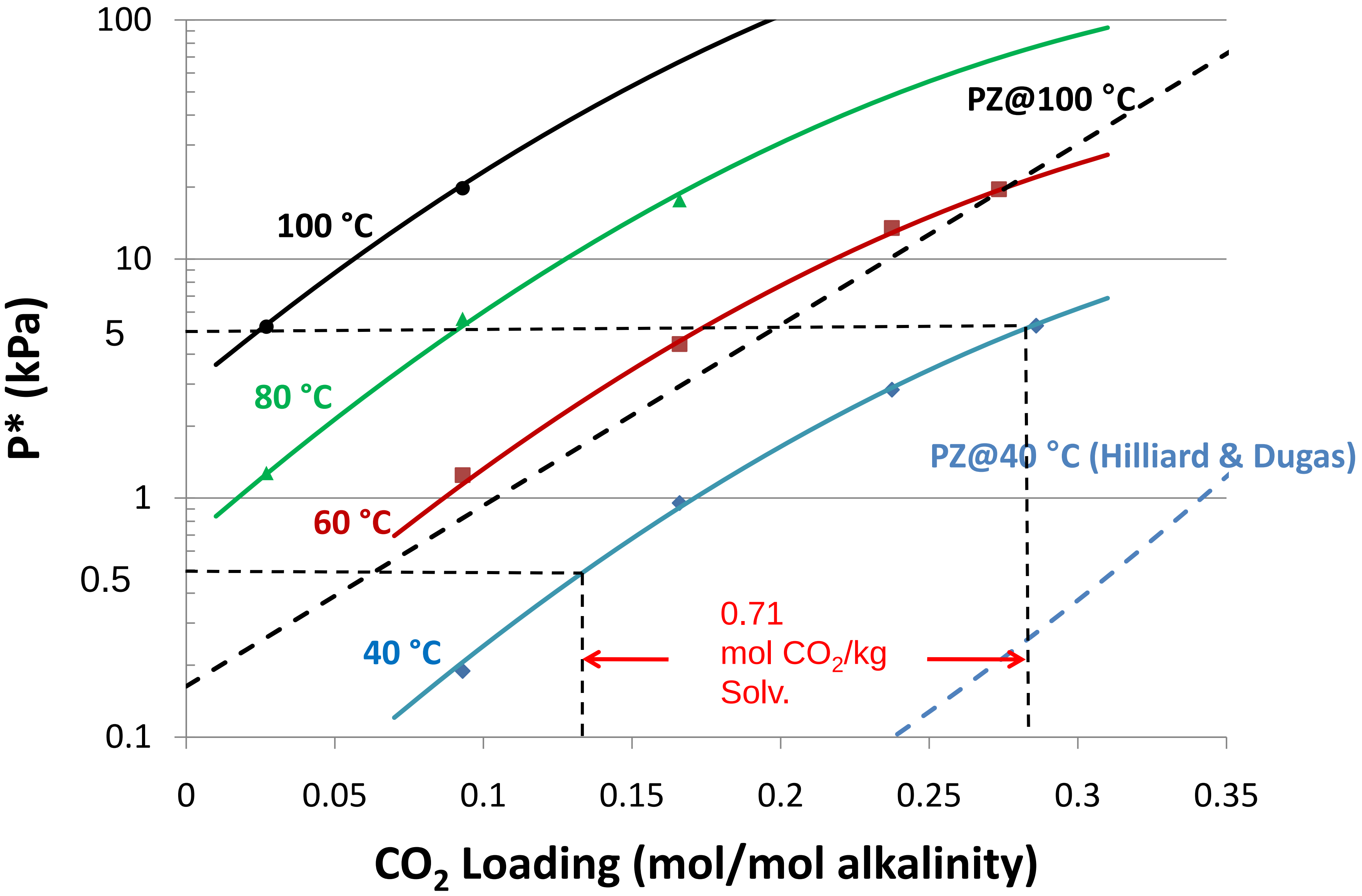


100
10
5
1
0.5
0.1
0.01
0.001
P* (kPa)
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
CO_2 Loading (mol/mol alkalinity)
MEA@100°C (Hilliard & Dugas)
100 °C
80 °C
60 °C
40 °C
MEA@40°C
0.78 mol CO_2/kg Solv.

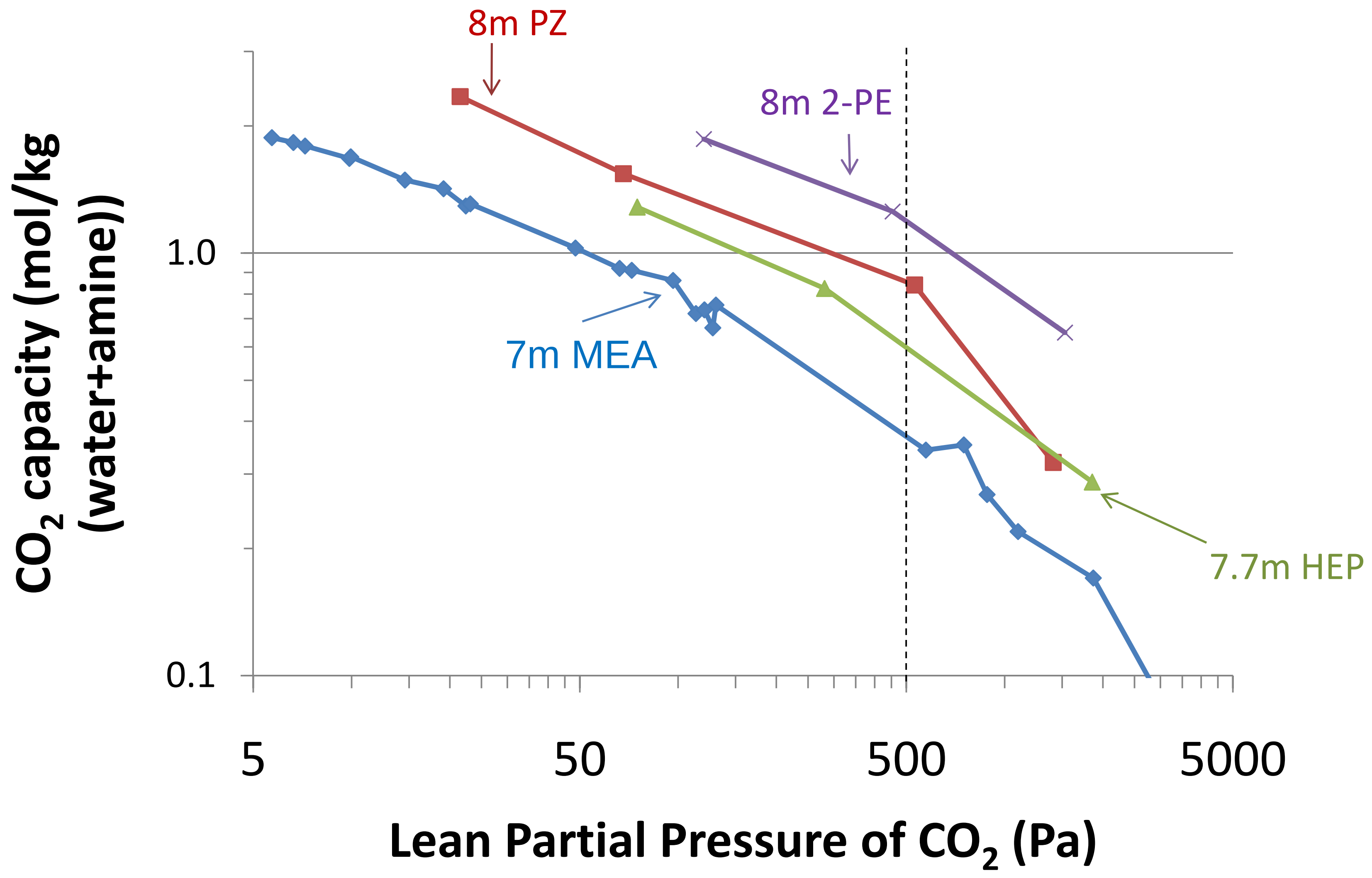
PROMOTED TERTIARY AMINE

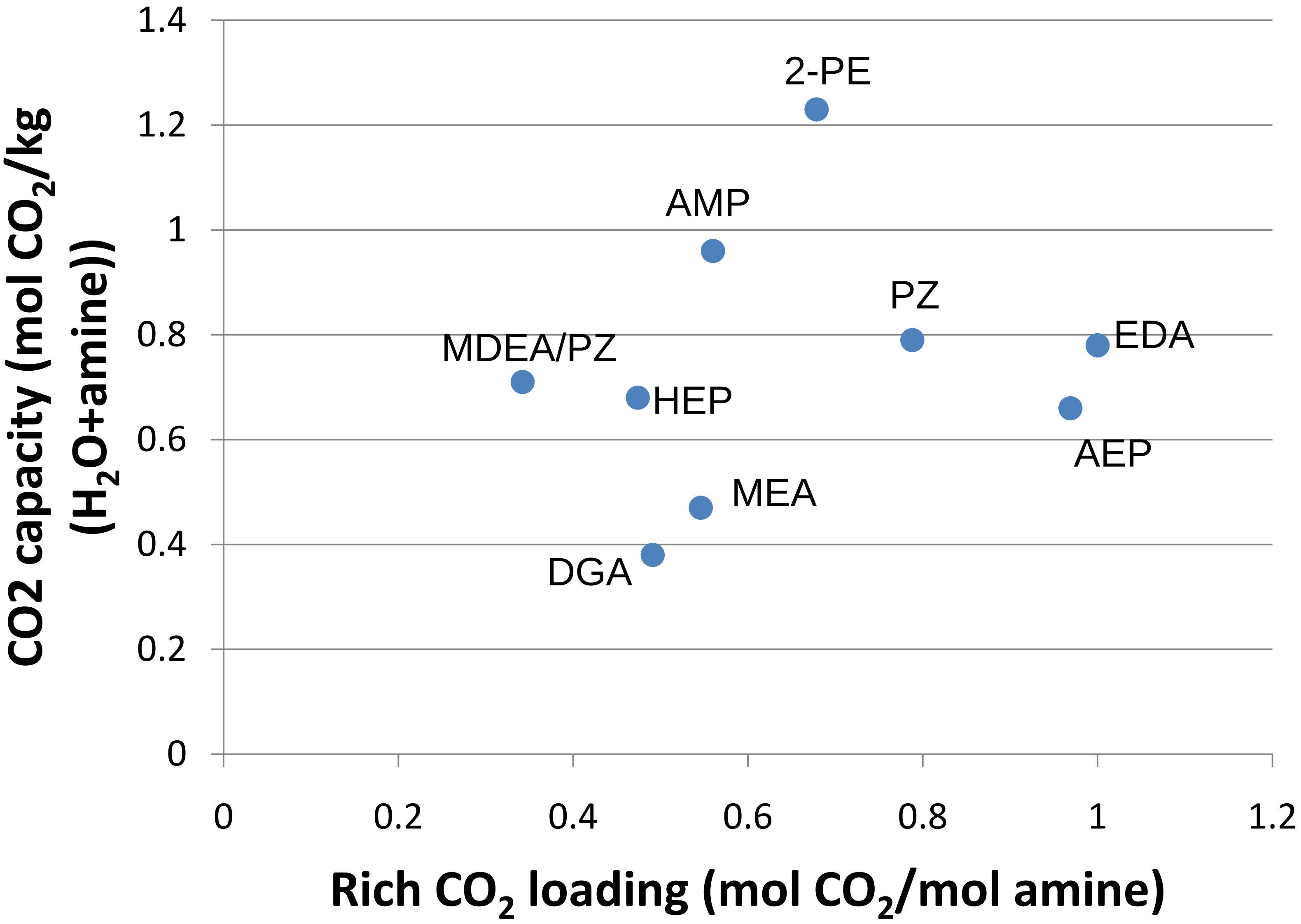
7m MDEA/2m PZ


CH3
HO
N
OH
HN
NH

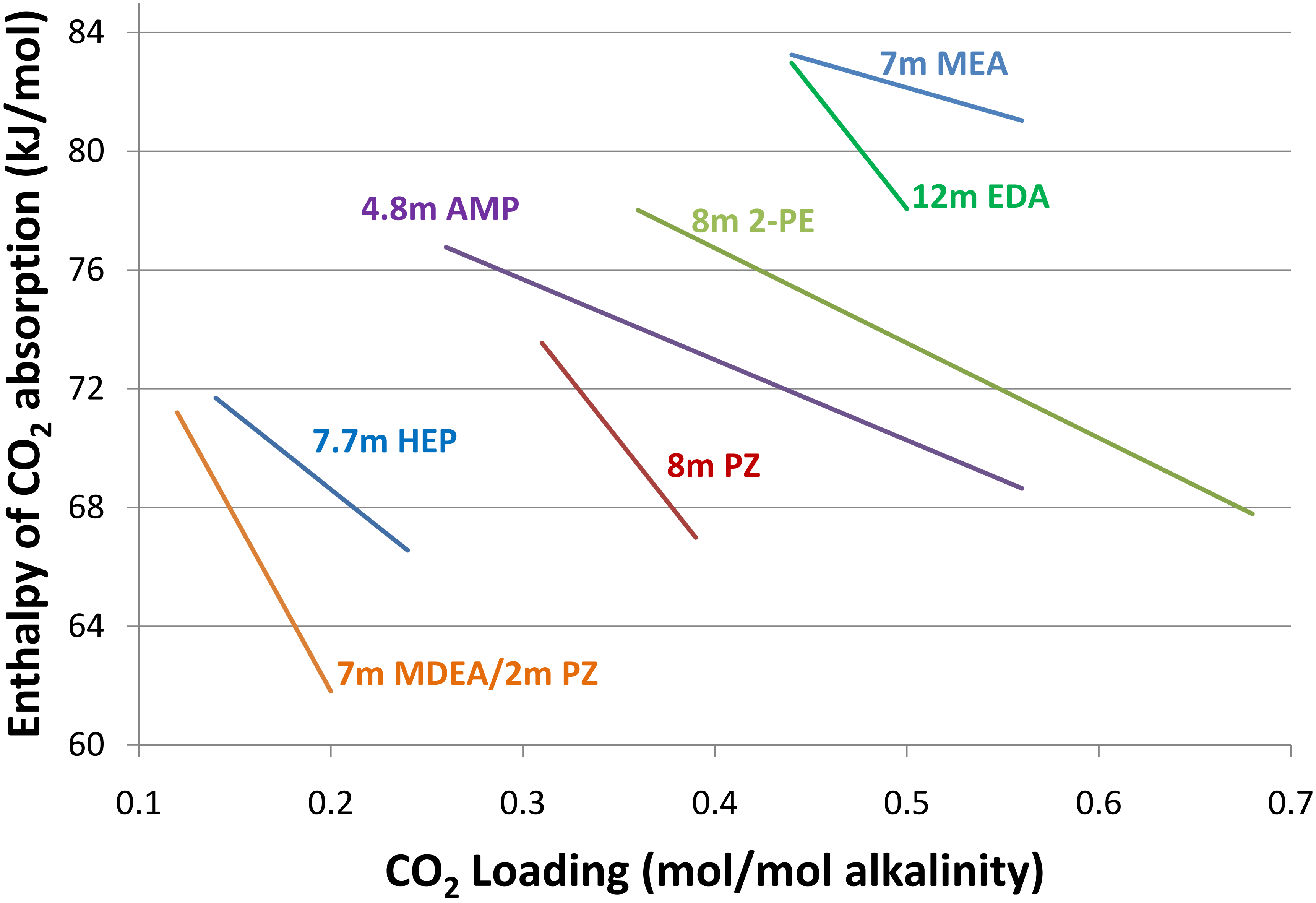

P* (kPa)
100
10
5
1
0.5
0.1
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
CO2 Loading (mol/mol alkalinity)
100 °C
80 °C
60 °C
40 °C
PZ@100 °C
PZ@40 °C (Hilliard & Dugas)
0.71
mol CO2/kg
Solv.

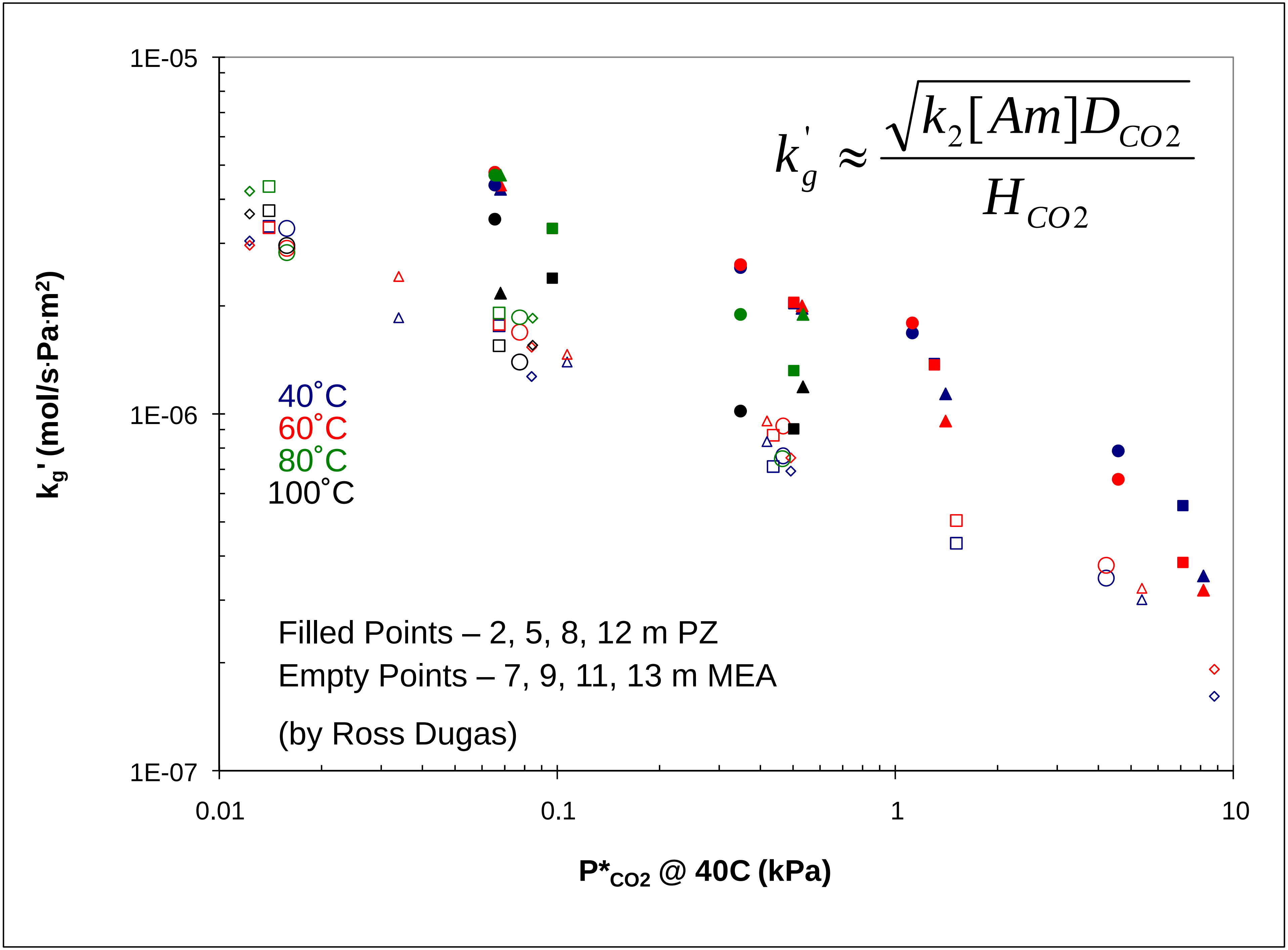
CO_2 Capacity for 5kPa Rich Solution



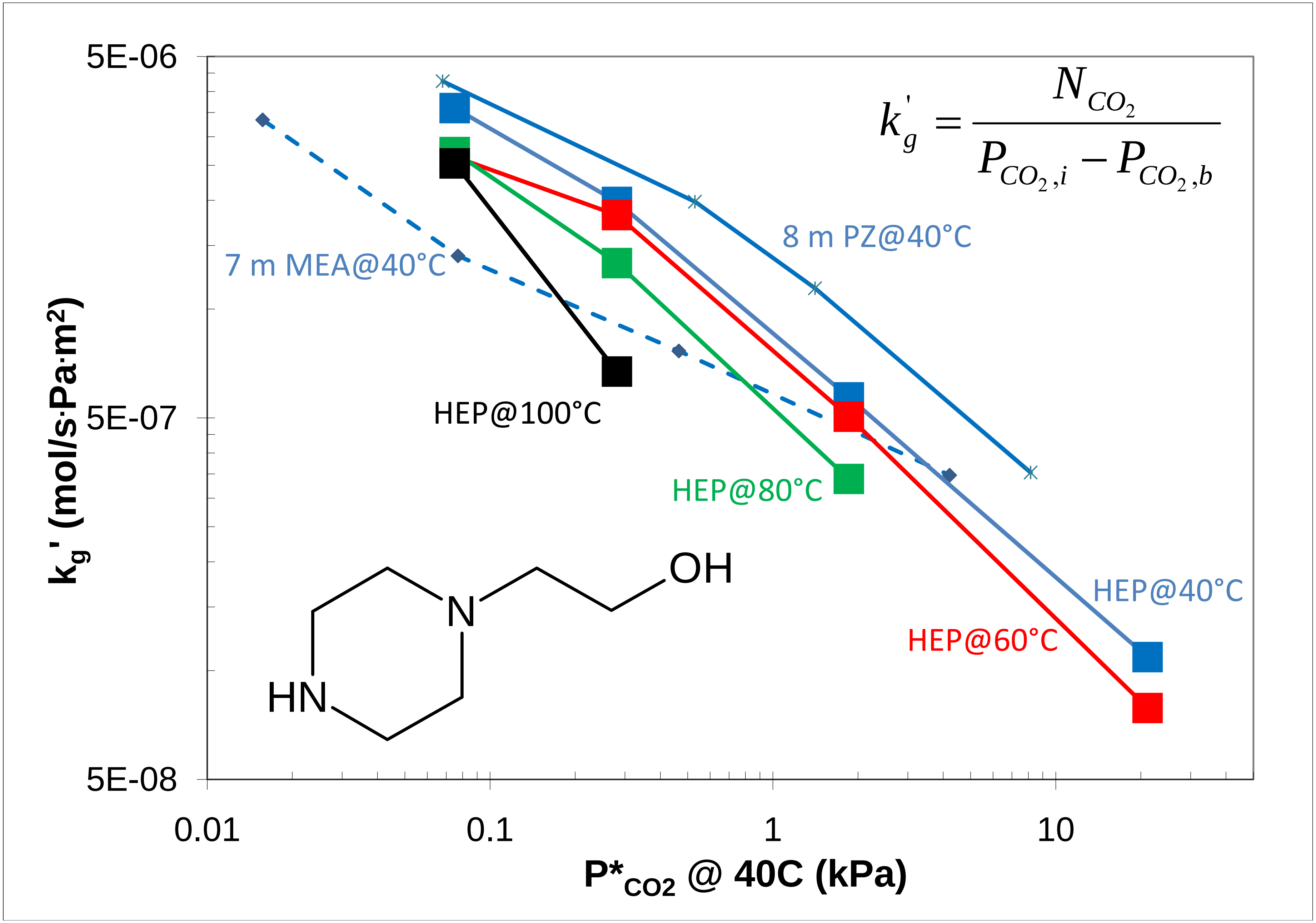

2-PE
AMP
PZ
EDA
MDEA/PZ
HEP
AEP
MEA
DGA
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
CO2 capacity (mol CO$_2$/kg (H$_2$O+amine))
Rich CO$_2$ loading (mol CO$_2$/mol amine)

Enthalpy of CO_2 Absorption



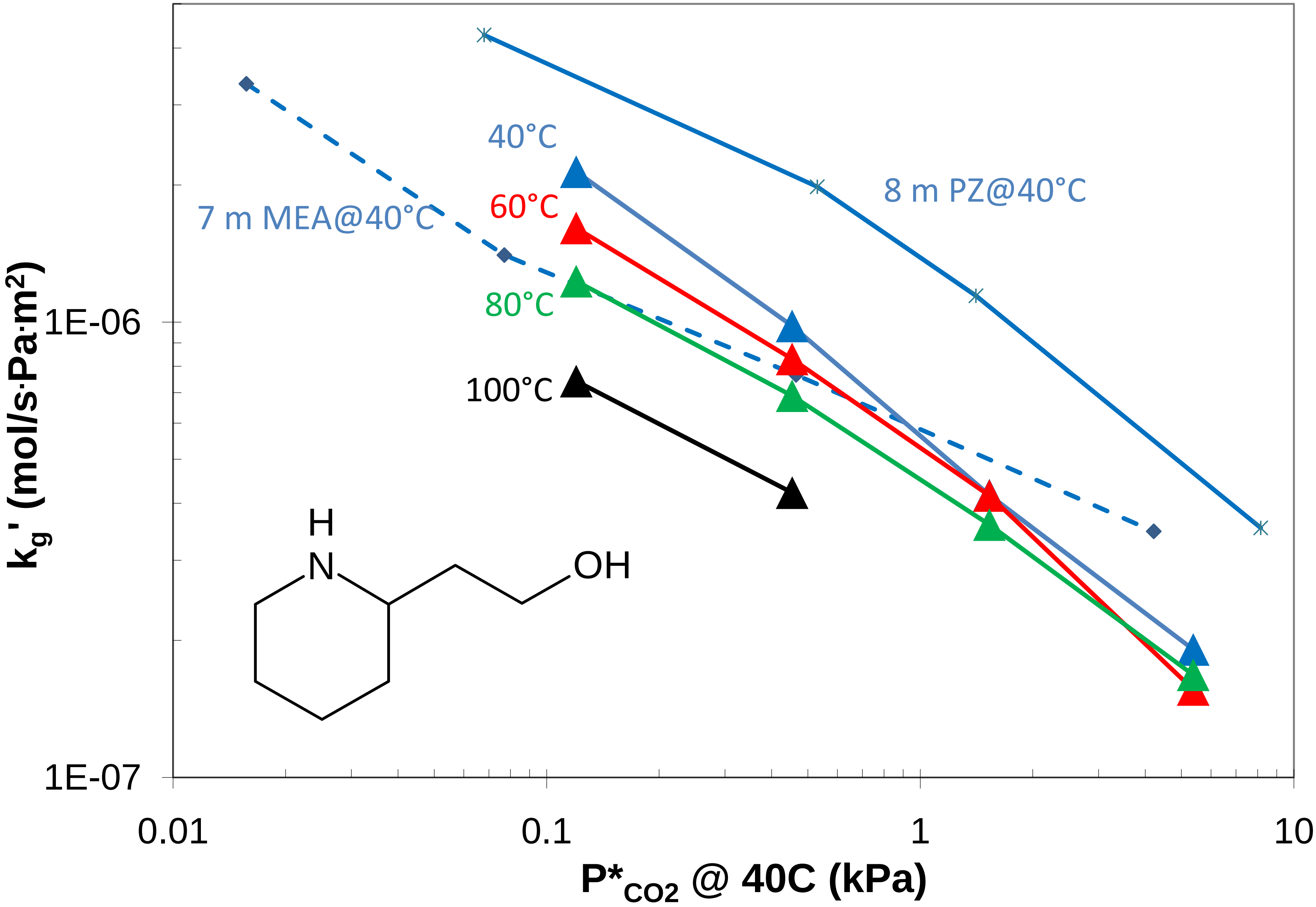

$k_g' \approx \frac{\sqrt{k_2[Am]D_{CO2}}}{H_{CO2}}$
40°C
60°C
80°C
100°C
Filled Points – 2, 5, 8, 12 m PZ
Empty Points – 7, 9, 11, 13 m MEA
(by Ross Dugas)
k_g' (mol/s·Pa·m²)
1E-05
1E-06
1E-07
0.01
0.1
1
10
P^*_{CO2} @ 40C (kPa)

Absorption/Desorption rates for 7.7m HEP

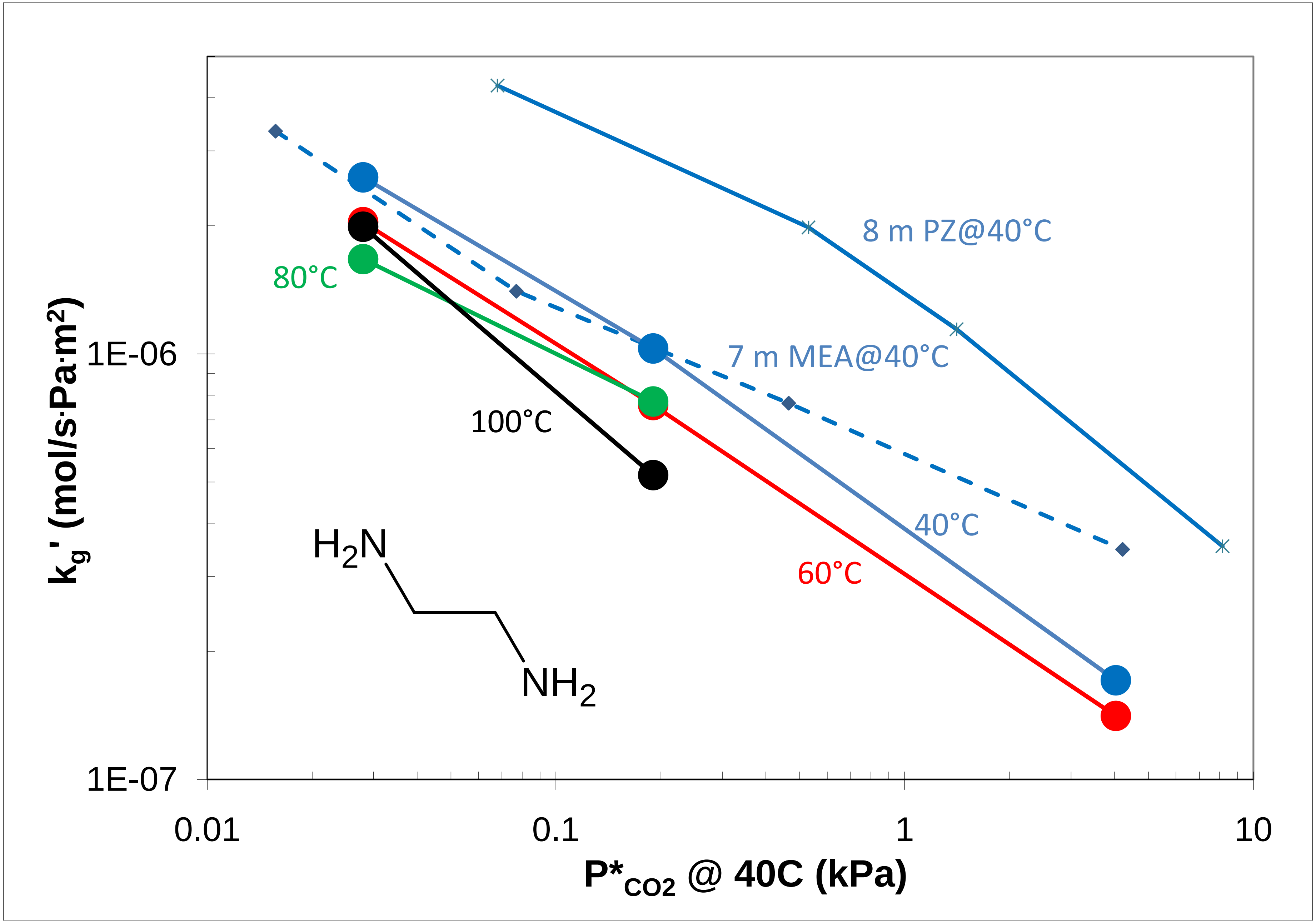


$$k_g' = \frac{N_{CO_2}}{P_{CO_2,i} - P_{CO_2,b}}$$

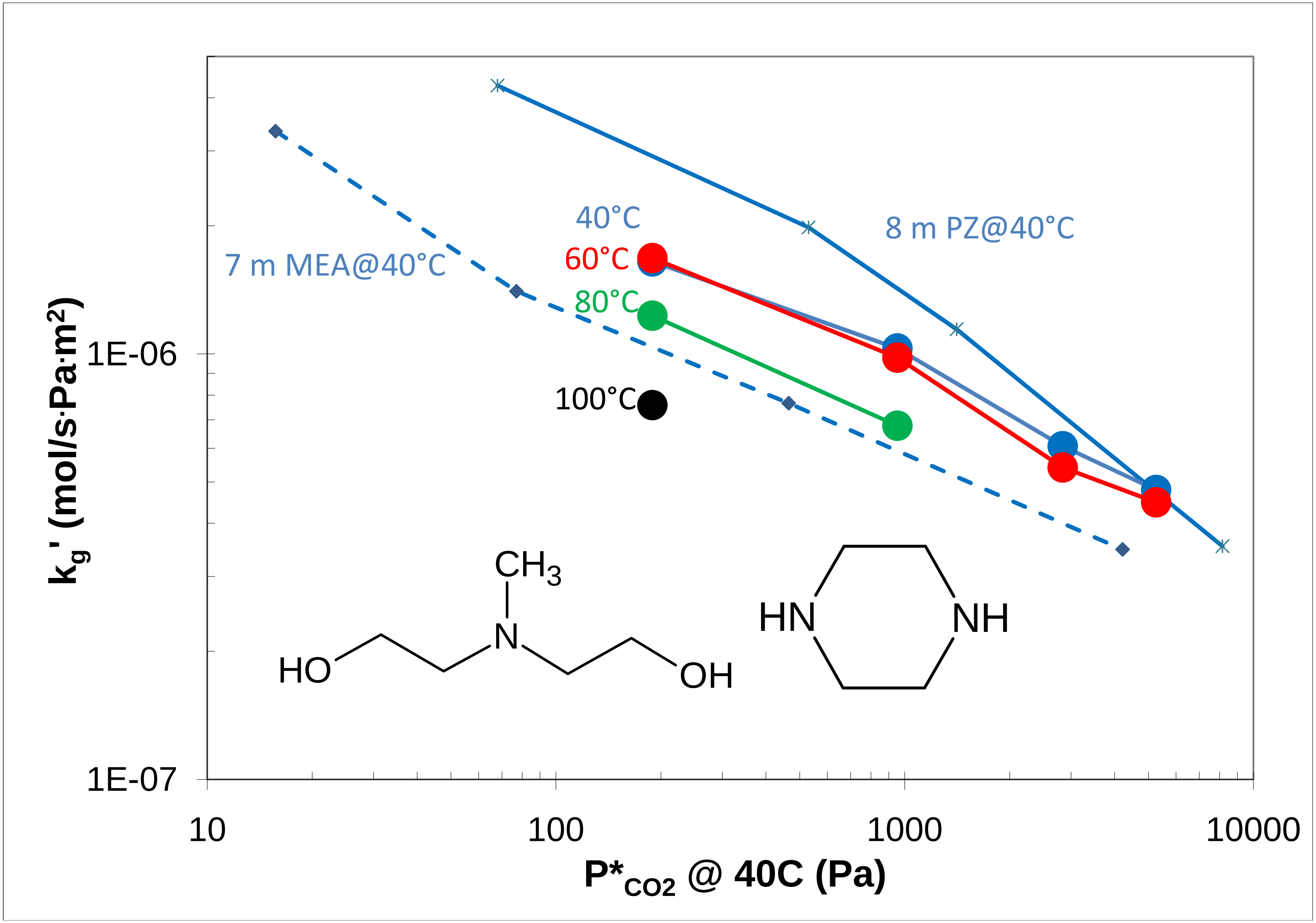
8m 2-PE


40°C
60°C
80°C
100°C
8 m PZ@40°C
7 m MEA@40°C
H
N
OH
1E-06
1E-07
0.01
0.1
1
10
k_g' (mol/s·Pa·m²)
P^*_{CO2} @ 40C (kPa)

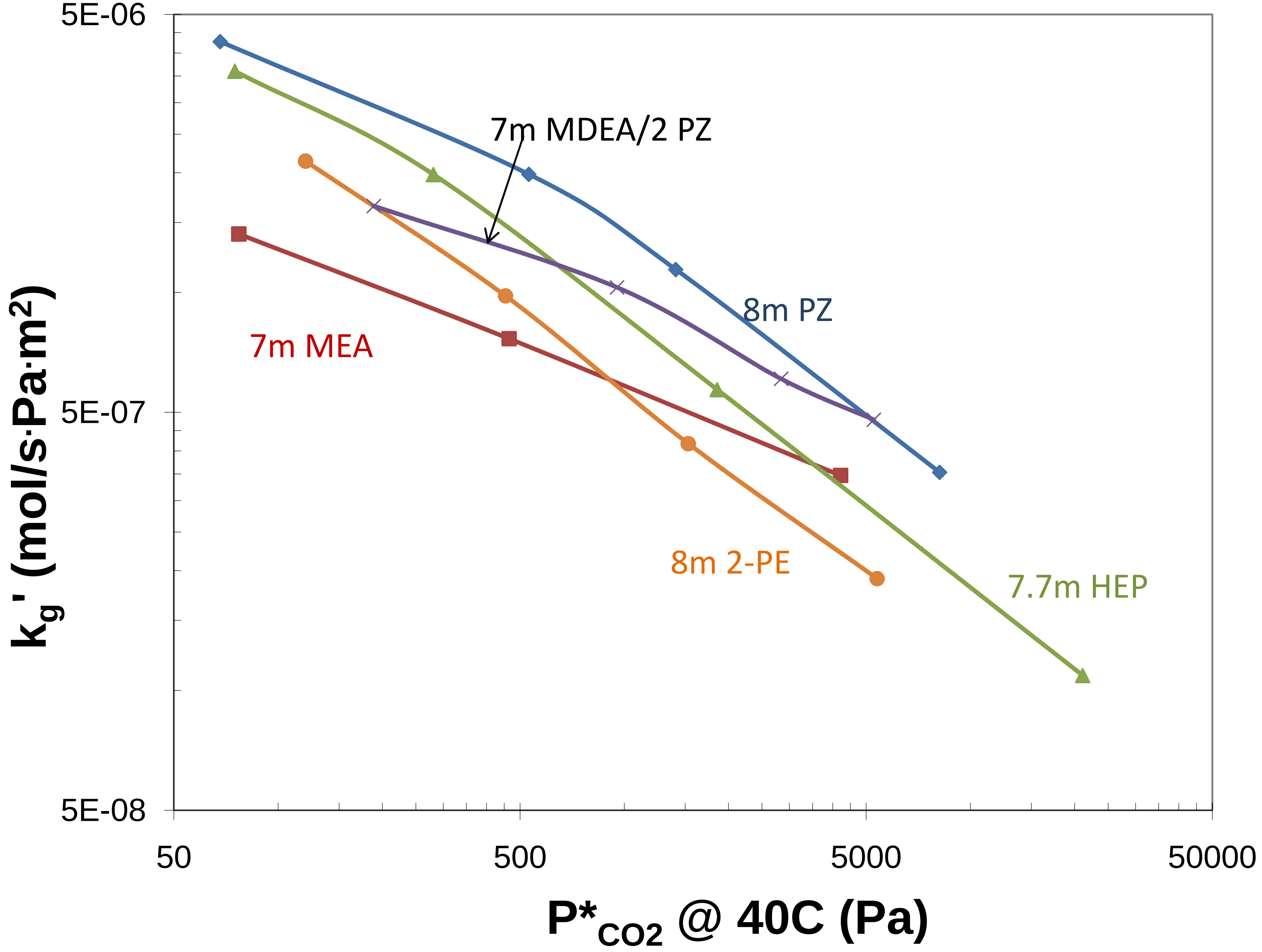
12m EDA


8 m PZ@40°C
7 m MEA@40°C
80°C
100°C
40°C
60°C
H_2N
NH_2
k_g' (mol/s·Pa·m²)
1E-06
1E-07
0.01
0.1
1
10
P^*_{CO2} @ 40C (kPa)

7m MDEA/2m PZ

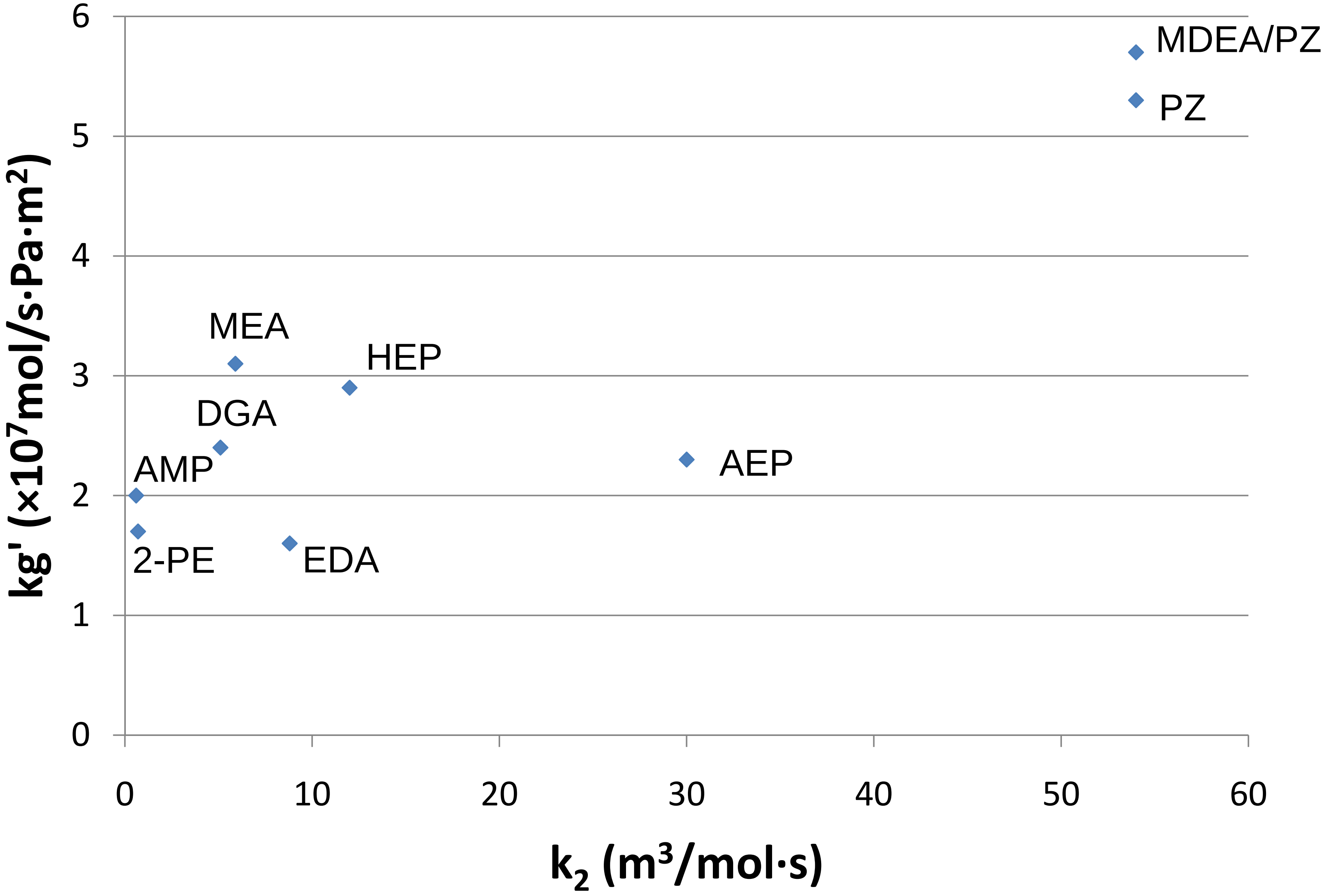


8 m PZ@40°C
7 m MEA@40°C
40°C
60°C
80°C
100°C
1E-06
1E-07
10
100
1000
10000
k_g' (mol/s·Pa·m²)
P^*_{CO2} @ 40C (Pa)
CH$_3$
N
HO
OH
HN
NH


5E-06
5E-07
5E-08
50
500
5000
50000
kg' (mol/s·Pa·m²)
P*CO2 @ 40C (Pa)
7m MDEA/2 PZ
8m PZ
7m MEA
8m 2-PE
7.7m HEP

Apparent second order reaction rate of amine with CO_2

Amine	k_2 (m^3/mol·s)	Source
PZ	54	(Bishnoi and Rochelle 2000)
AEP	30	(Bishnoi 2000)
HEP	12	(Bishnoi 2000)
EDA	8.8	(Sada et al. 1977)
MEA	5.9	(Blauwhoff et al. 1984)
DGA	5.1	(Pacheco 1998)
AMP	0.7	(Saha and Bandyopadhyay 1995)
2-PE	0.6	(Xu et al. 1993)
MDEA	0.005	(Versteeg and Van Swaaij 1988)



6
5
4
3
2
1
0
kg' (×10⁷mol/s·Pa·m²)
MDEA/PZ
PZ
MEA
HEP
DGA
AMP
AEP
2-PE
EDA
0
10
20
30
40
50
60
k₂ (m³/mol·s)

Conclusions

Fast solvents

Amine	Conc (m)	CO_2 Capacity@ $P_{CO2.lean}$=0.5kPa (mol/kg (water+amine))	k_g' @P_{CO2} =5kPa (×10^7mol/s·Pa ·m^2)	ΔH_{abs}@P_{CO2} =1.5kPa (kJ/mol)
MDEA/PZ	7/2	0.71	5.7	67
PZ	8	0.79	5.3	70
MEA	7	0.47	3.1	82
MEA	11	0.52	2.5	84

Slow solvents

Amine	Conc. (m)	CO_2 Capacity@ $P_{CO2,lean}$=0.5kPa (mol/kg (water+amine))	k_g' @P_{CO2} =5kPa (×10^7mol/s·Pa·m^2)	ΔH_{abs}@P_{CO2} =1.5kPa (kJ/mol)
MEA	7	0.47	3.1	82
HEP	7.7	0.68	2.9	69
DGA®	10	0.38	2.4	81
AEP	6	0.66	2.3	72
2-PE	8	1.23	2	73
AMP	4.8	0.96	1.7	73
EDA	12	0.78	1.6	80

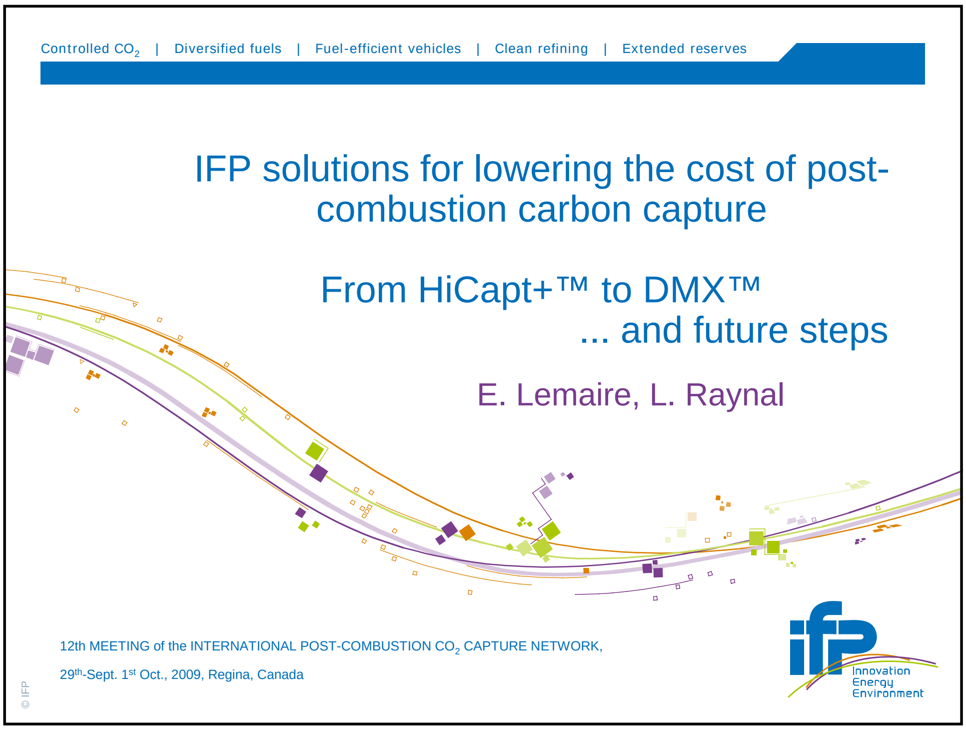
Acknowledgement

- Luminant Carbon Management Program
- Industrial Associates Program for CO_2 Capture by Aqueous Absorption

Accurate Screening of Candidate Solvents by the Wetted Wall Column

Questions?

Xi Chen
xi@che.utexas.edu



Controlled CO_2 | Diversified fuels | Fuel-efficient vehicles | Clean refining | Extended reserves

IFP solutions for lowering the cost of post-combustion carbon capture

From HiCapt+™ to DMX™
... and future steps

E. Lemaire, L. Raynal

12th MEETING of the INTERNATIONAL POST-COMBUSTION CO_2 CAPTURE NETWORK,

29th-Sept. 1st Oct., 2009, Regina, Canada

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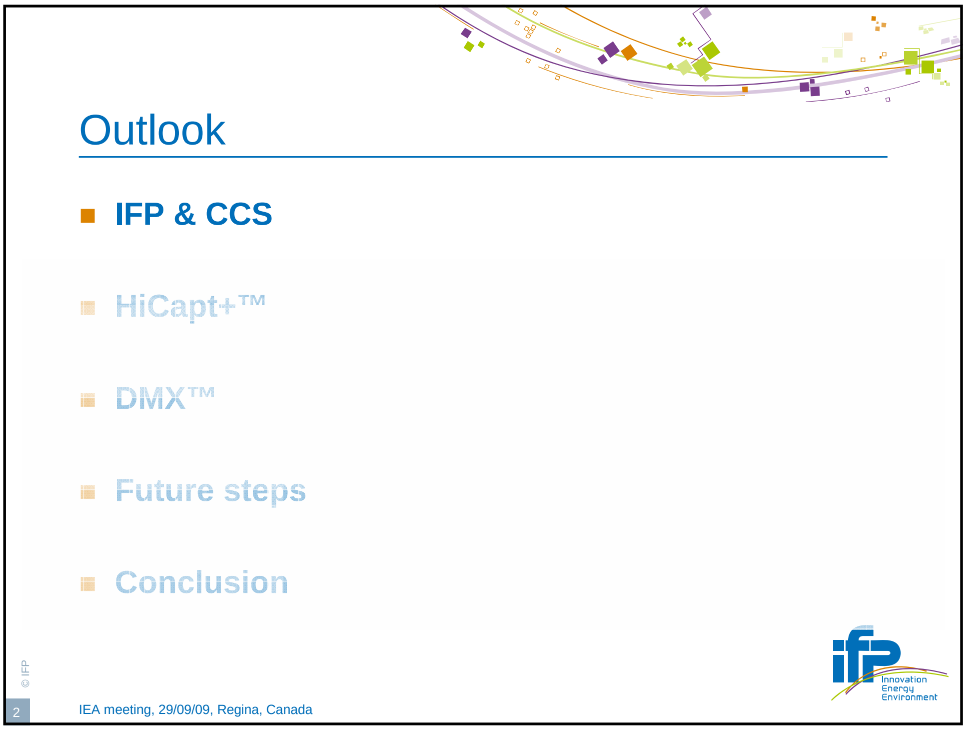


Outlook

- **IFP & CCS**
- HiCapt+™
- DMX™
- Future steps
- 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*

ifp Innovation Energy Environment

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

Outlook

- IFP & CCS
- **HiCapt+™**
- DMX™
- Future steps
- Conclusion

State of the art : Post combustion CO_2 capture

- **Standard process : MEA at 30 % wt**
  - **proven with the Castor pilot**
    - **Reliable, safe, no impact on power plant operation**
  - **Cost evaluated around 50 to 65 €/t CO_2 avoided**
  - **Energetic penalty for the power plant : - 10.5 pts on the yield**
  - **High sensibility to O_2 : degradation**
    - **corrosion**
    - **reactivity down**
    - **solvent consumption (~ 2 batches / year)**
    - **ammonia specification (>25 mg/Nm3 in the flue gas)**

New solution : HiCapt+™

- **Goal : enhance 1st generation process**
  - **based on knowledge of MEA 30 % wt : HiCapt™ process**
  - **keep reliability and robustness**
  - **Two ways to increase performances :**

↗ MEA concentration

Degradation inhibitors

HiCapt+™ process

- **HiCapt+™ (40 %wt MEA) : some challenges to reach so high concentration**
  - **Corrosion**

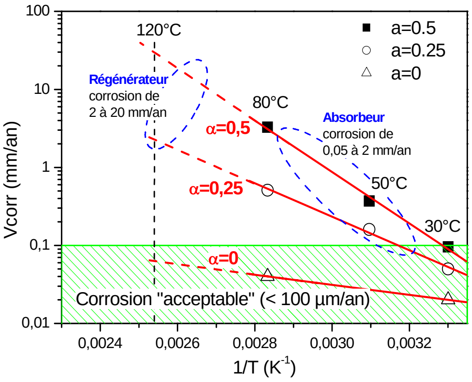
AISI 1018 carbon steel coupon after 3 weeks exposure in the lean solvent outlet of the regenerator.

  - **Hydrodynamic**

  - **Degradation**

Corrosion studies

- **Very high corrosion for MEA solvent**
- **Corrosion studies**
  - **evaluation of various materials**
    - **Very good results for stainless steel**
  - **use of Castor data (monitoring done by IFP)**
  - **tests and screening of inhibitors**



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Hydrodynamic and mass transfer

- **Characterization of parameters for each internal :**
  - **kg : gas transfer coefficient**
  - **kl : liquid transfer coefficient**
  - **ae : efficient interfacial area**
  - **pressure drop**
  - **liquid hold-up**

$$\phi_{CO2} = \frac{1}{\frac{1}{k_G} + \frac{He}{E.k_L}}.a_e.\left(P_{CO2} - He.C_{CO2}{}^{0}\right)$$

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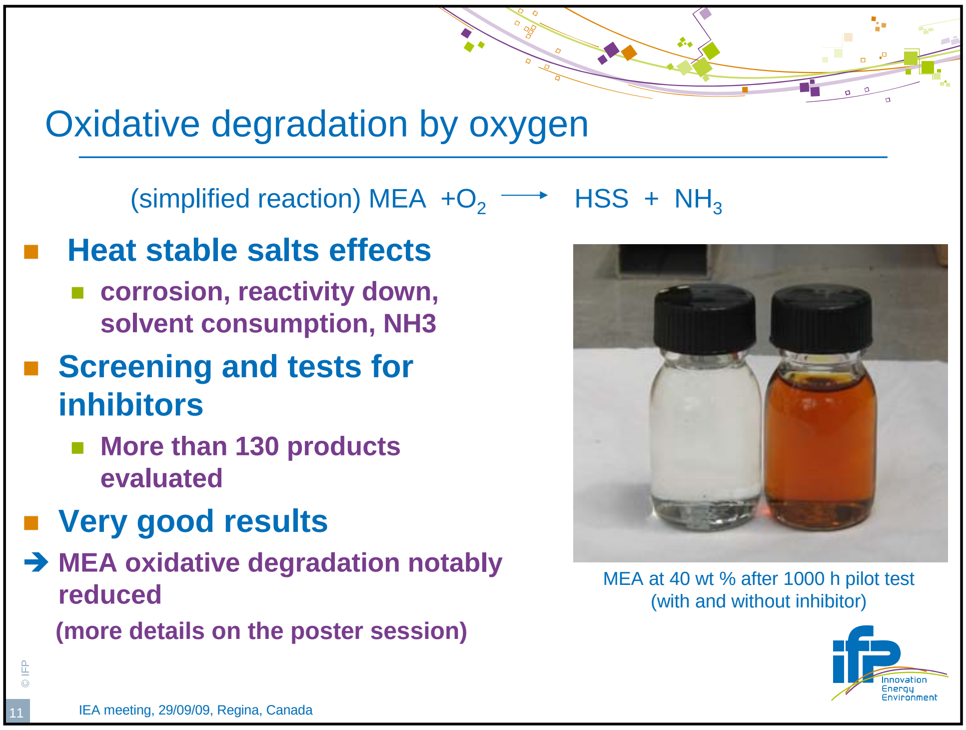


Oxidative degradation by oxygen

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

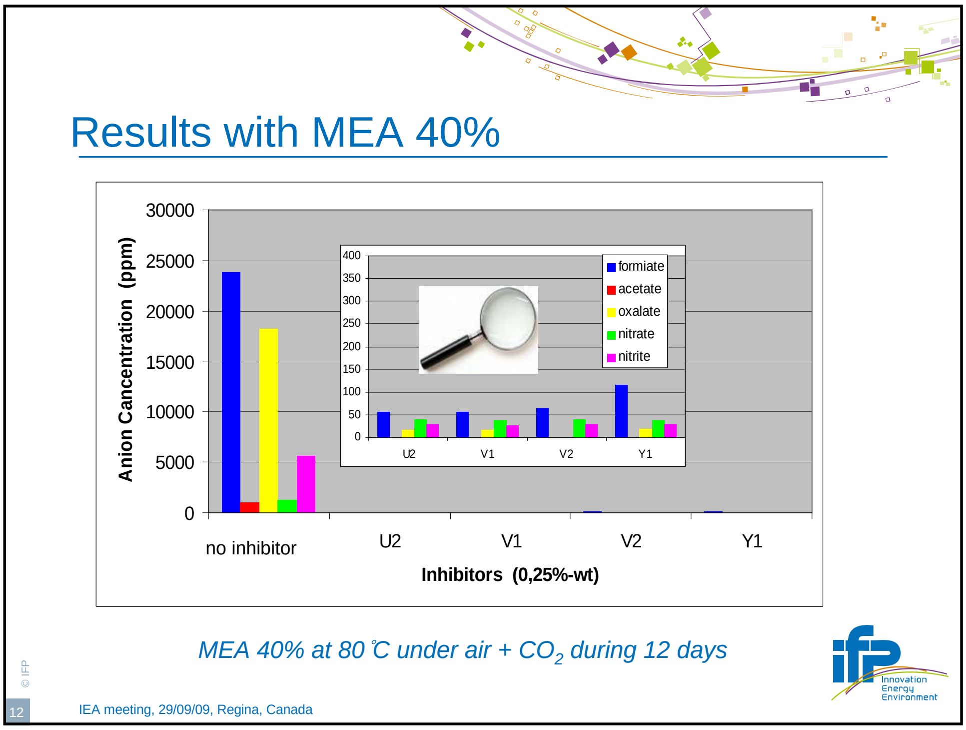
- **Heat stable salts effects**
  - **corrosion, reactivity down, solvent consumption, NH3**
- **Screening and tests for inhibitors**
  - **More than 130 products evaluated**
- **Very good results**

➔ **MEA oxidative degradation notably reduced**

(more details on the poster session)

MEA at 40 wt % after 1000 h pilot test
(with and without inhibitor)

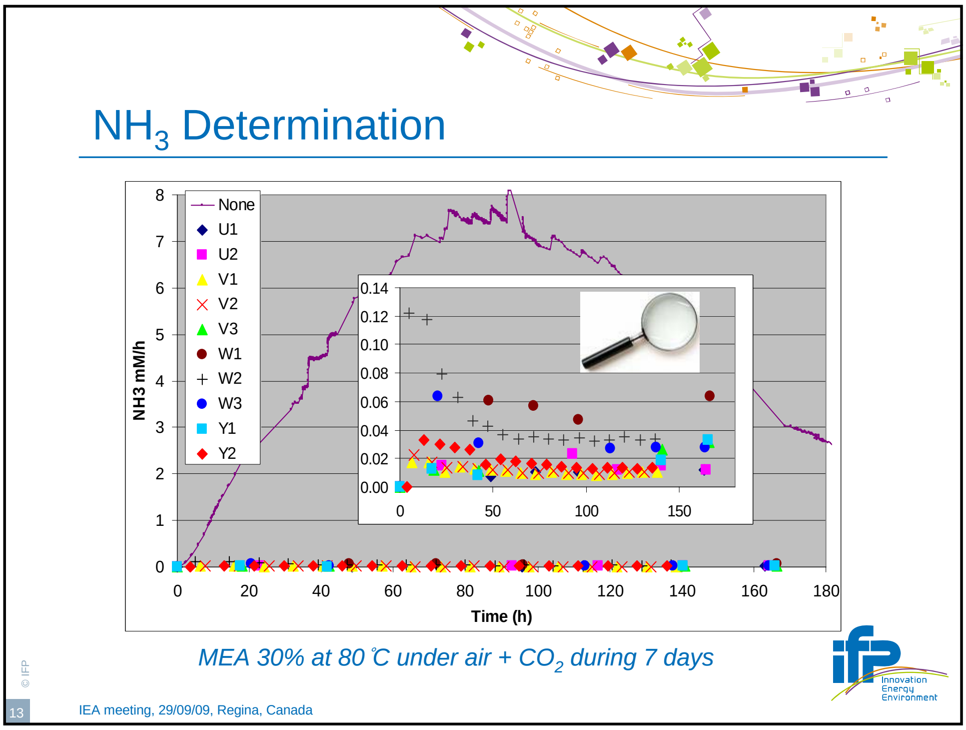
© IFP



Results with MEA 40%

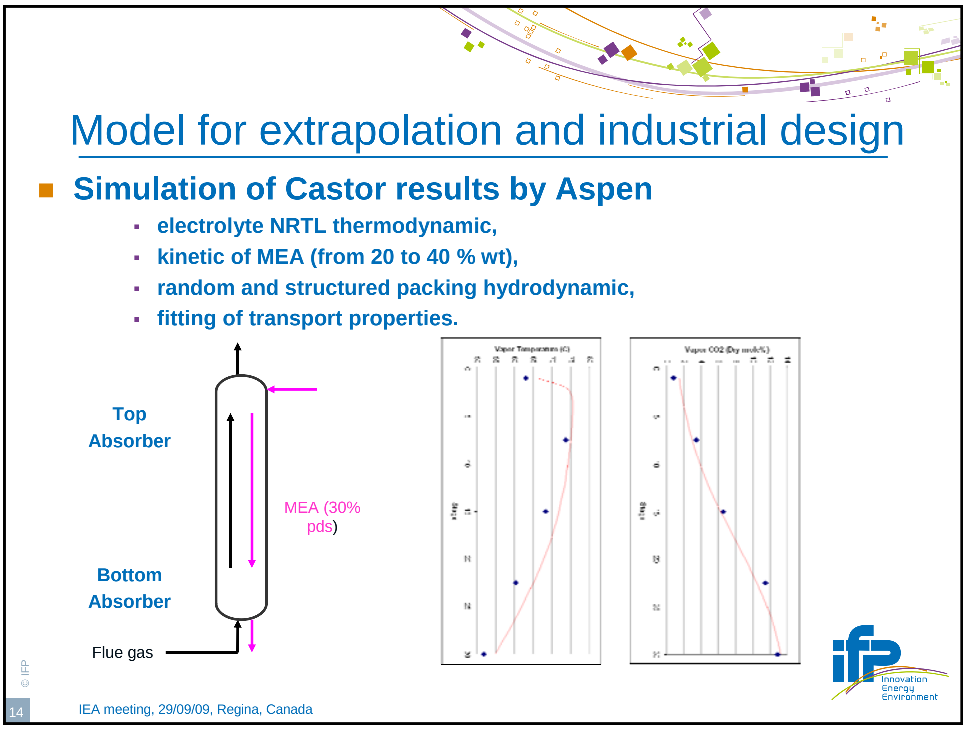
MEA 40% at 80 °C under air + CO_2 during 12 days

© IFP



NH$_3$ Determination

MEA 30% at 80 ℃ under air + CO$_2$ during 7 days



Model for extrapolation and industrial design

- **Simulation of Castor results by Aspen**
  - **electrolyte NRTL thermodynamic,**
  - **kinetic of MEA (from 20 to 40 % wt),**
  - **random and structured packing hydrodynamic,**
  - **fitting of transport properties.**

Post combustion CO_2 capture : ENEL pilot plant

ENEL Site :
Coal power plant in Brindisi
(4 x 660 MWe)

Pilot Main Data :
Flue gas : 10 000 Nm3/h
CO2 captured : 2.25 t/h
Start-up: 2010

ENEL/ IFP collaboration :
Classical MEA process
HiCapt+™ process

HiCapt+™ performances

- **Process with 40 % wt MEA + oxydative inhibitor**
  - **Solvent flow rate : – 25 % compare to MEA 30 % wt**
    - **OPEX cost decrease : pump and regeneration**
  - **3.1 to 3.3 GJ/t CO_2 avoided (depending on CO_2 partial pressure of the flue gas)**
  - **Negligible solvent degradation**
    - **OPEX cost reduction and easier operation (reclaiming)**
- **(CAPEX + OPEX) : - 15 % compare to 30 % wt MEA**

HiCapt+™ is a reliable and efficient process licensed by PROSERNAT with demonstration in ENEL pilot by 2010

Outlook

- IFP & CCS
- HiCapt+™
- **DMX™**
- Future steps
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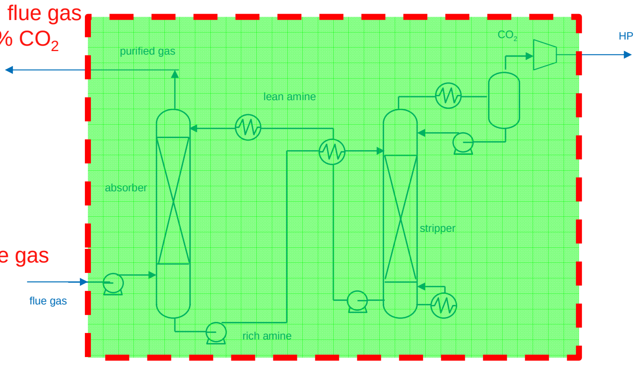
Targets for a new CC process

Avoided CO_2 costs : = 44 €/t - 65 €/t

Opex (2/3) + Capex (1/3)

treated flue gas
-90 % CO_2



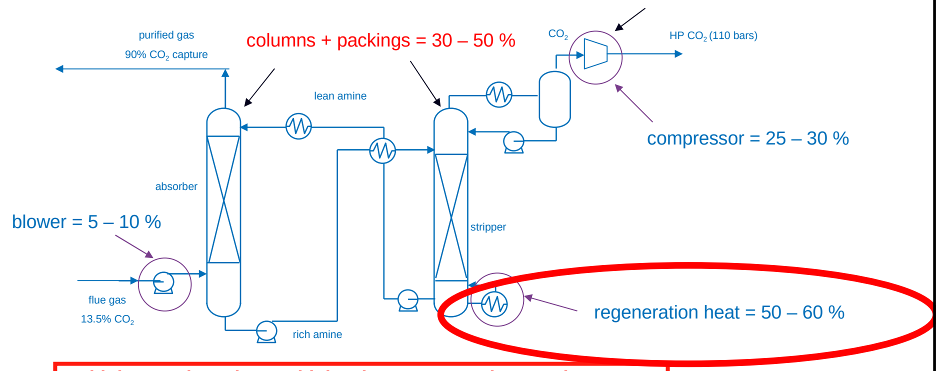
CO_2 @ 110 bars
y > 95 %

flue gas

Objective : propose a new CO_2 capture process with a significant decrease in avoided CO_2 costs

New process : main targets 1/3

Opex (2/3) + Capex (1/3)



compressors = 30 - 40 %

columns + packings = 30 – 50 %

compressor = 25 – 30 %

blower = 5 – 10 %

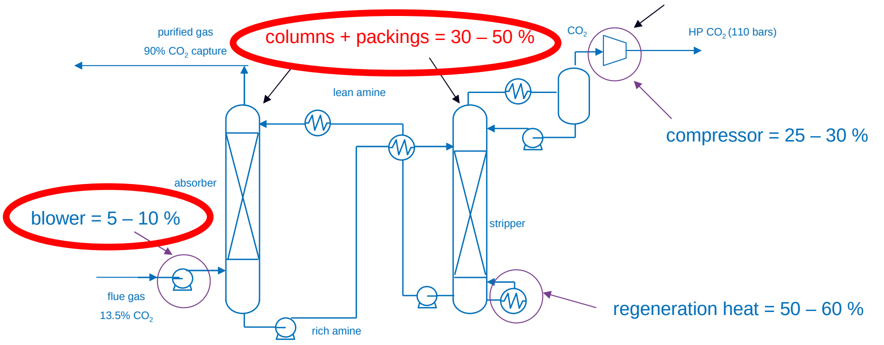
regeneration heat = 50 – 60 %

1 : high capacity solvent with low heat regeneration requirements

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

New process : main targets 2/3

Opex (2/3) + Capex (1/3)



compressors = 30 - 40 %

columns + packings = 30 – 50 %

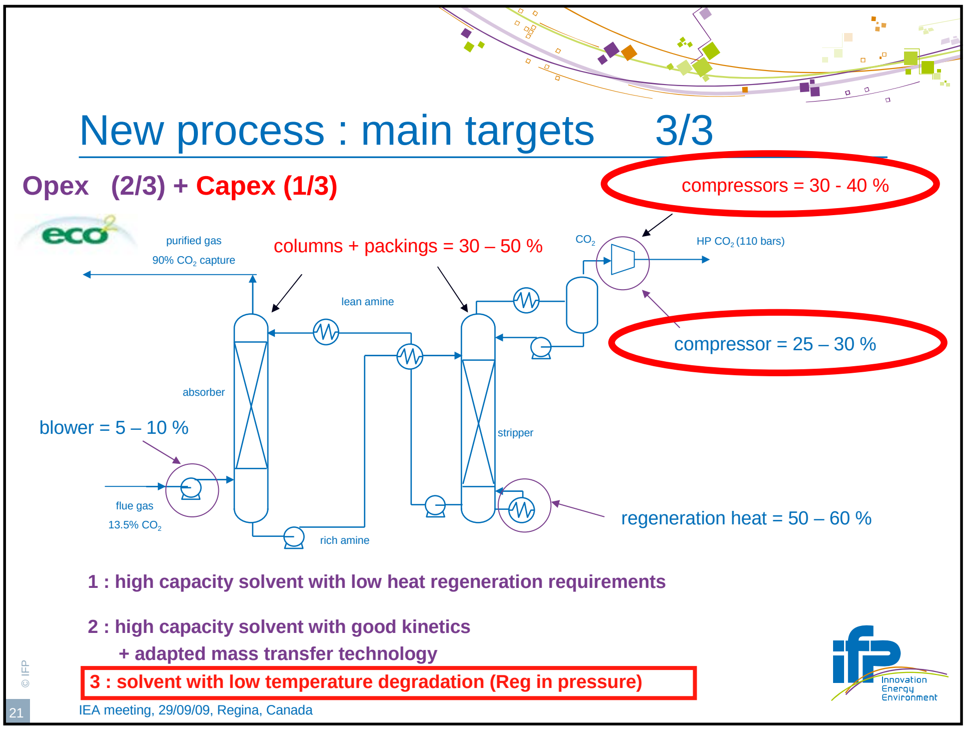
compressor = 25 – 30 %

blower = 5 – 10 %

regeneration heat = 50 – 60 %

1 : high capacity solvent with low heat regeneration requirements

2 : high capacity solvent with good kinetics
+ adapted mass transfer technology



New process : main targets 3/3

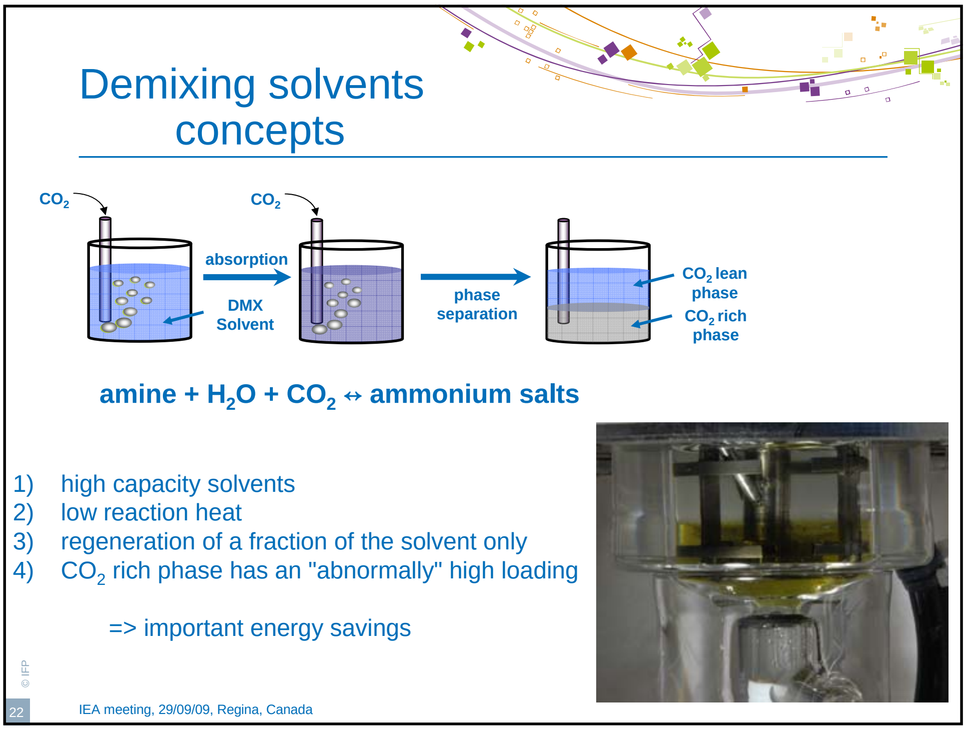
Opex (2/3) + Capex (1/3)

1 : high capacity solvent with low heat regeneration requirements

2 : high capacity solvent with good kinetics
+ adapted mass transfer technology

3 : solvent with low temperature degradation (Reg in pressure)

© IFP



Demixing solvents concepts

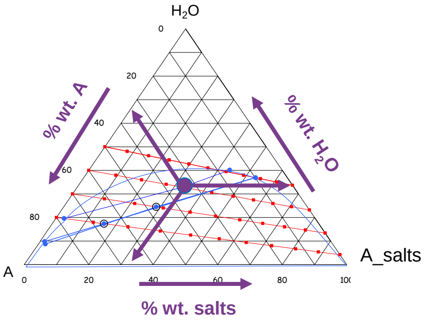
amine + H_2O + CO_2 ↔ ammonium salts

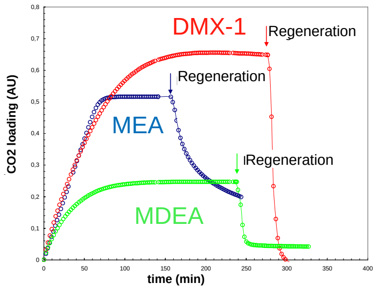
1) high capacity solvents
2) low reaction heat
3) regeneration of a fraction of the solvent only
4) CO_2 rich phase has an "abnormally" high loading

=> important energy savings

© IFP

Demixtion – absorption / desorption tests

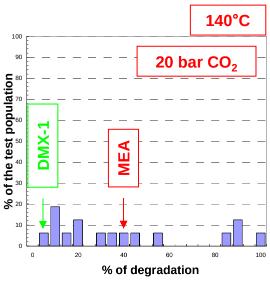


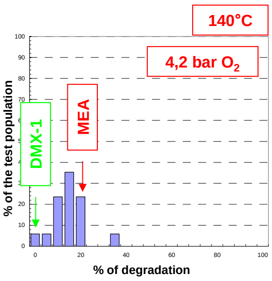


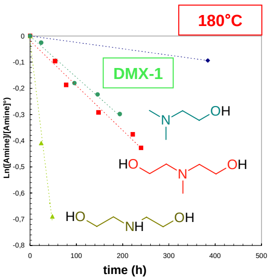
Thermal degradation

- Very low thermal degradation, little influence of CO_2 or/and 0_2 concentration (DMX-1 vs 17 molecules)

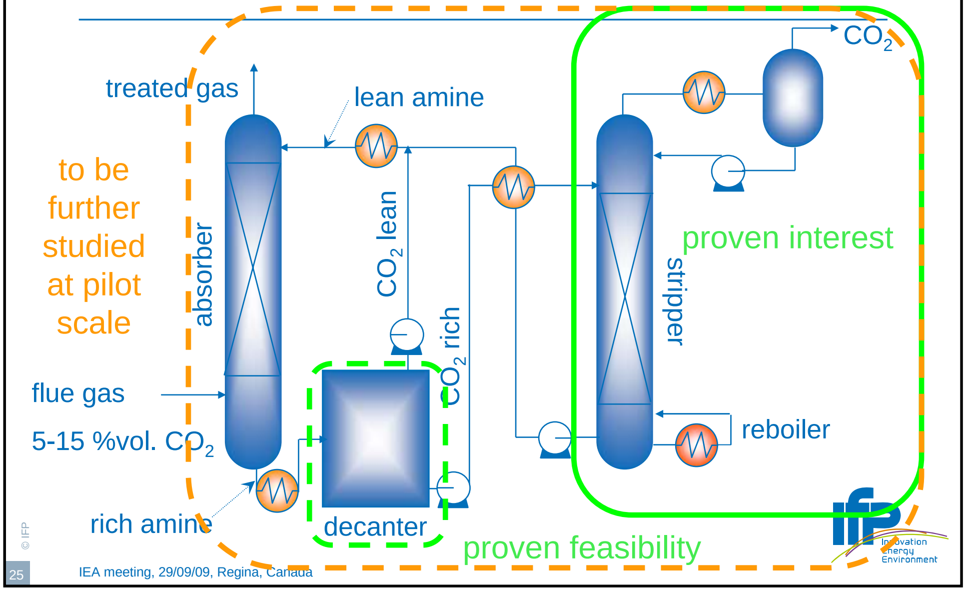
=> possibility to increase temperature at stripper and therefore possibility to increase pressure at stripper



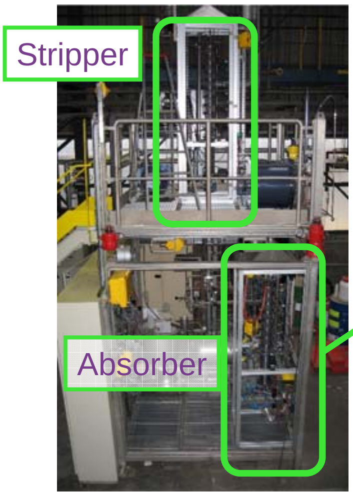




DMX™ Process



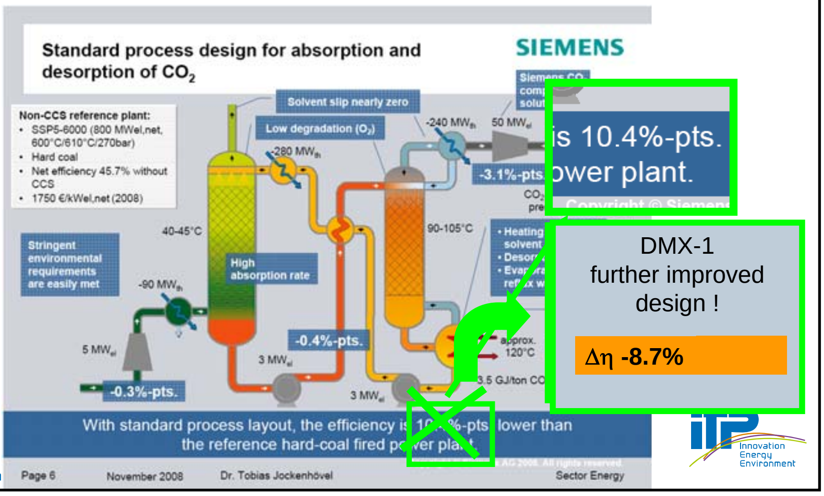
Small scale pilot test campaign



work in progress !

DMX™ Process
What perfomances ?

- **Difficulty to compare from one process to another (CO2 cost, Capex, Opex, energy savings ....) => efficiency loss**



Standard process design for absorption and desorption of CO_2

Non-CCS reference plant:
- SSP5-6000 (800 MWel,net, 600°C/610°C/270bar)
- Hard coal
- Net efficiency 45.7% without CCS
- 1750 €/kWel,net (2008)

is 10.4%-pts.
ower plant.
Copyright © Siemens

DMX-1
further improved
design !

Δη -8.7%

With standard process layout, the efficiency is 10.4%-pts lower than the reference hard-coal fired power plant.

Page 6 November 2008 Dr. Tobias Jockenhövel Sector Energy

Outlook

- IFP & CCS
- HiCapt+™
- DMX™
- **Future steps**
- Conclusion

Other works for 3rd generation CC process

- **Long term developments**
- **New processes**
  - **amine blends**
  - **original solvents with new chemistry**
  - **hydrates**
  - **adsorption : functionnalized adsorbents – MOF**
  - **ionic liquids**

- **New technologies**
  - **membrane contactors**
  - **high performance packings**

- **IFP Collaborations (ANR, EU ...)**

Outlook

- IFP & CCS

- HiCapt+™

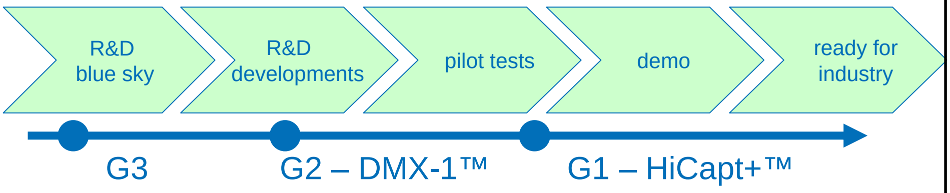
- DMX™

- Future steps

- **Conclusion**

IFP solutions

- **1st generation process : HiCapt+™**
  - **ready for demo => Enel**
  - **2010 : commercialization**



R&D blue sky

R&D developments

pilot tests

demo

ready for industry

G3

G2 – DMX-1™

G1 – HiCapt+™

- **2nd generation process : DMX-1™**
  - **proven interest at lab scale**
  - **2011- 2013 : pilot test campaign**

- **3rd generation process ...**

Thank you !

Innovating for energy

www.ifp.fr

Eric.Lemaire@ifp.fr
Ludovic.Raynal@ifp.fr

Interactions of CO_2 with Aqueous Amine Solutions – the Molecular View

Marcel Maeder, Xiaoguang Wang, Will Conway, Debra Fernandes, Robert Burns, Nichola McCann
Department of Chemistry, The University of Newcastle
Callaghan, NSW 2308, Australia

Graeme Puxty, Moetaz Attalla
CSIRO Energy Transformed Flagship, CSIRO Energy Centre
Mayfield West, Newcastle NSW 2300, Australia

Chemical Engineers – Chemists

Chemical Engineers see:

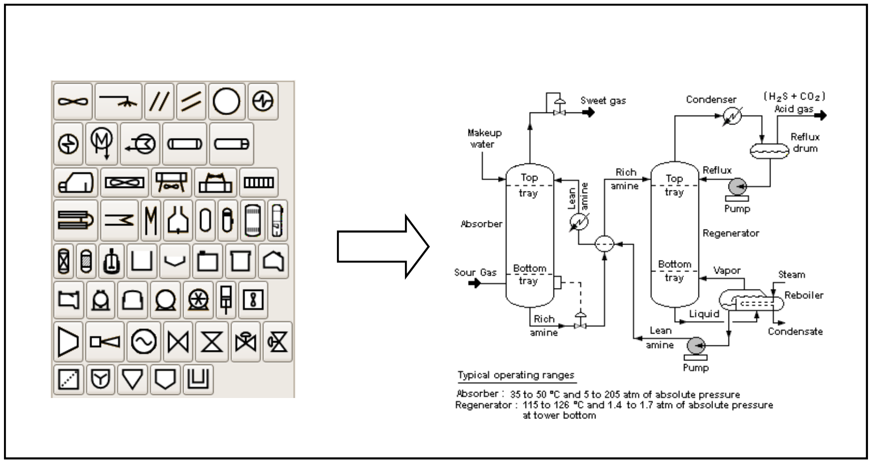
- reactors
- pumps
- heat exchangers
- etc.

that interact to form chemical plants

Chemists see:

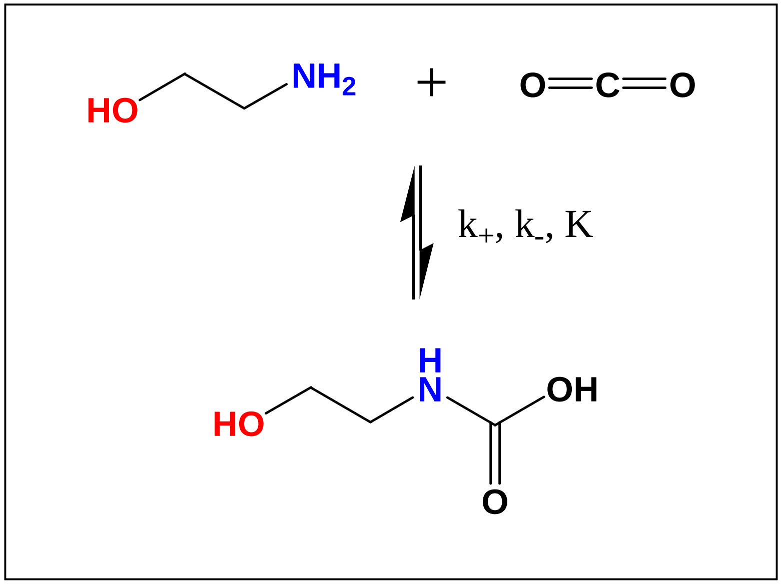
molecules

that interact to form new molecules

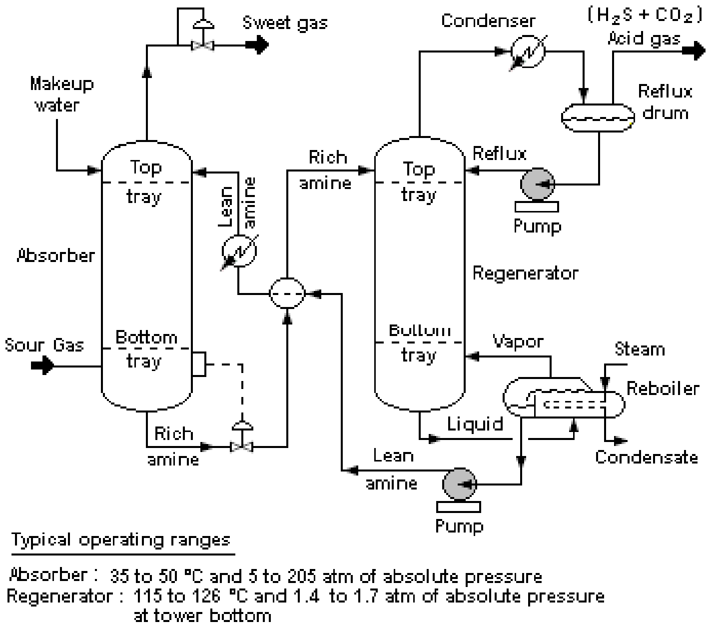


Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure at tower bottom



Chemical Engineers + Chemists



Typical operating ranges

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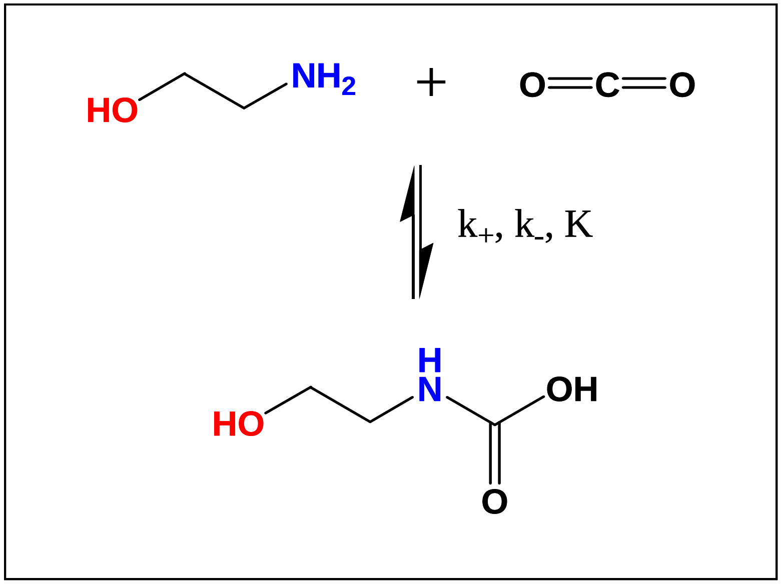
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure
at tower bottom



First questions a chemist is asking:

- **What are the molecules that interact in PCC ?**
- **How do they interact with each other ?**

What are the molecules that interact in PCC ?

{CO_2}

$CO_2(aq)$, H_2CO_3
HCO_3^-, CO_3^{2-}

amine, **{RNH_2}**

RNH_2, RNH_3^+

carbamate, **{$RNHCO_2^-$}**

$RNHCO_2^-$, $RNHCO_2H$

How is the carbamate formed?

$\{CO_2\}$

$CO_2(aq)$, H_2CO_3
HCO_3^-, CO_3^{2-}

+

amine, $\{RNH_2\}$

RNH_2, RNH_3^+

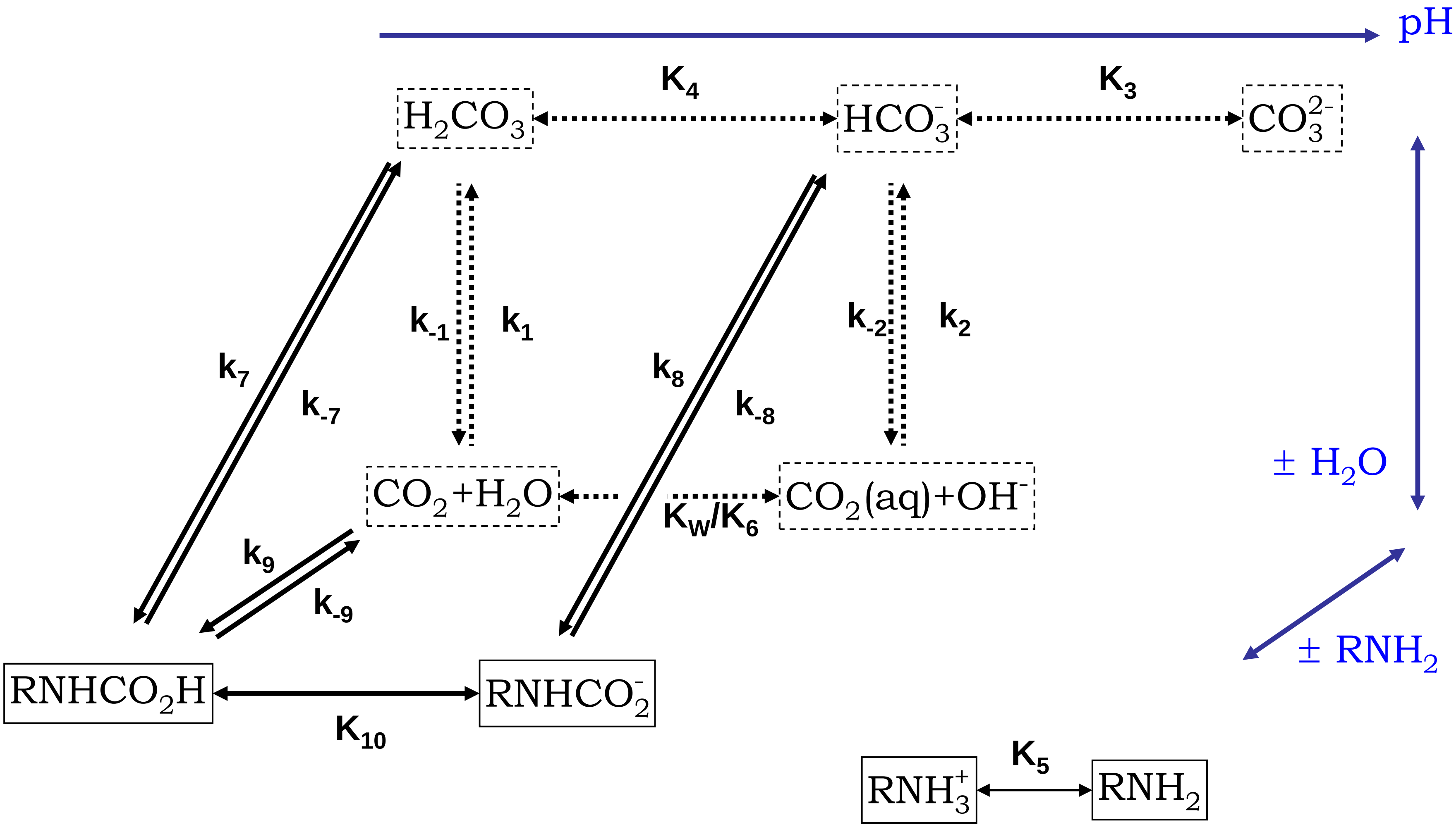
$\rightleftharpoons$

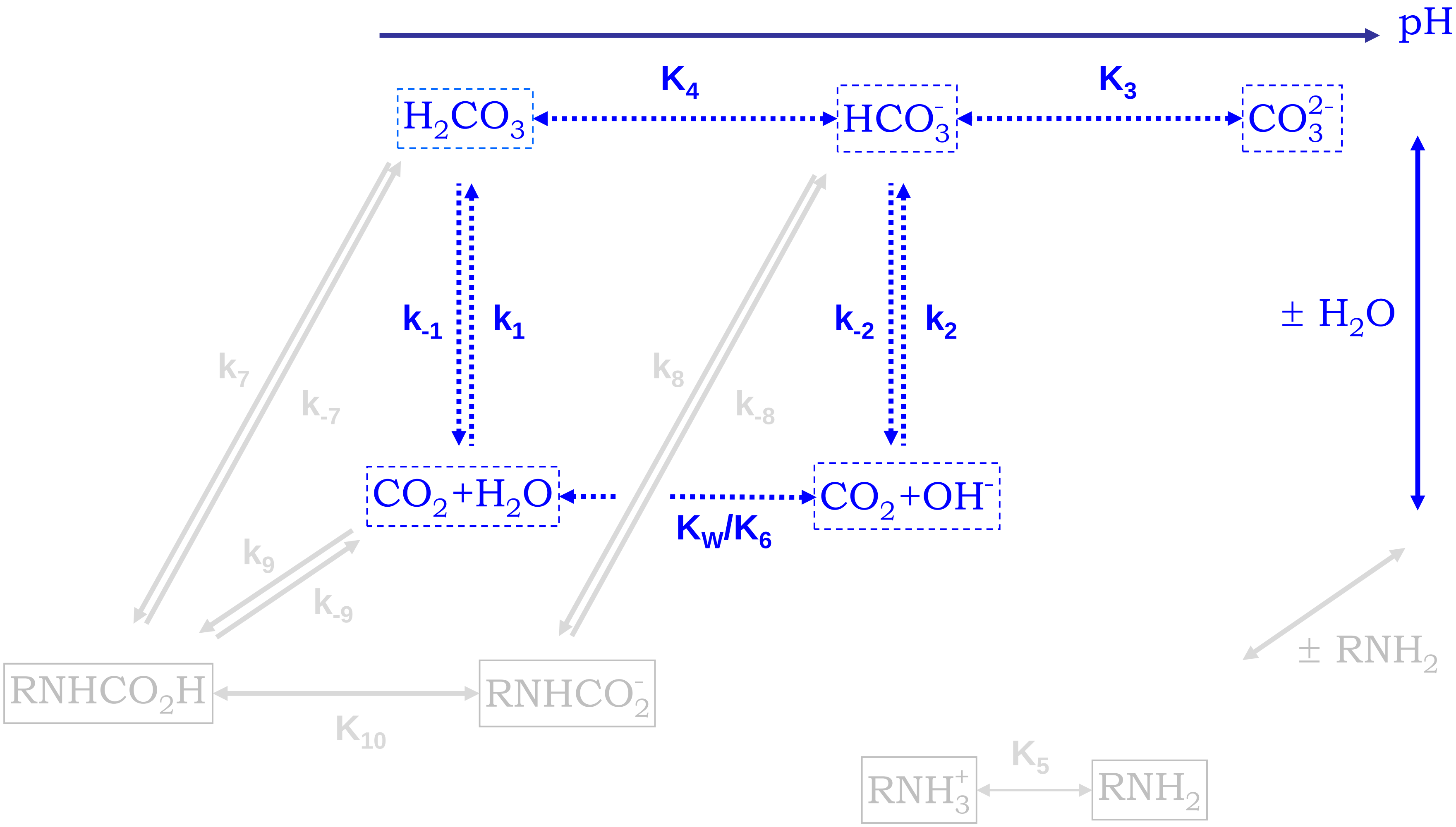
carbamate, $\{RNHCO_2^-\}$

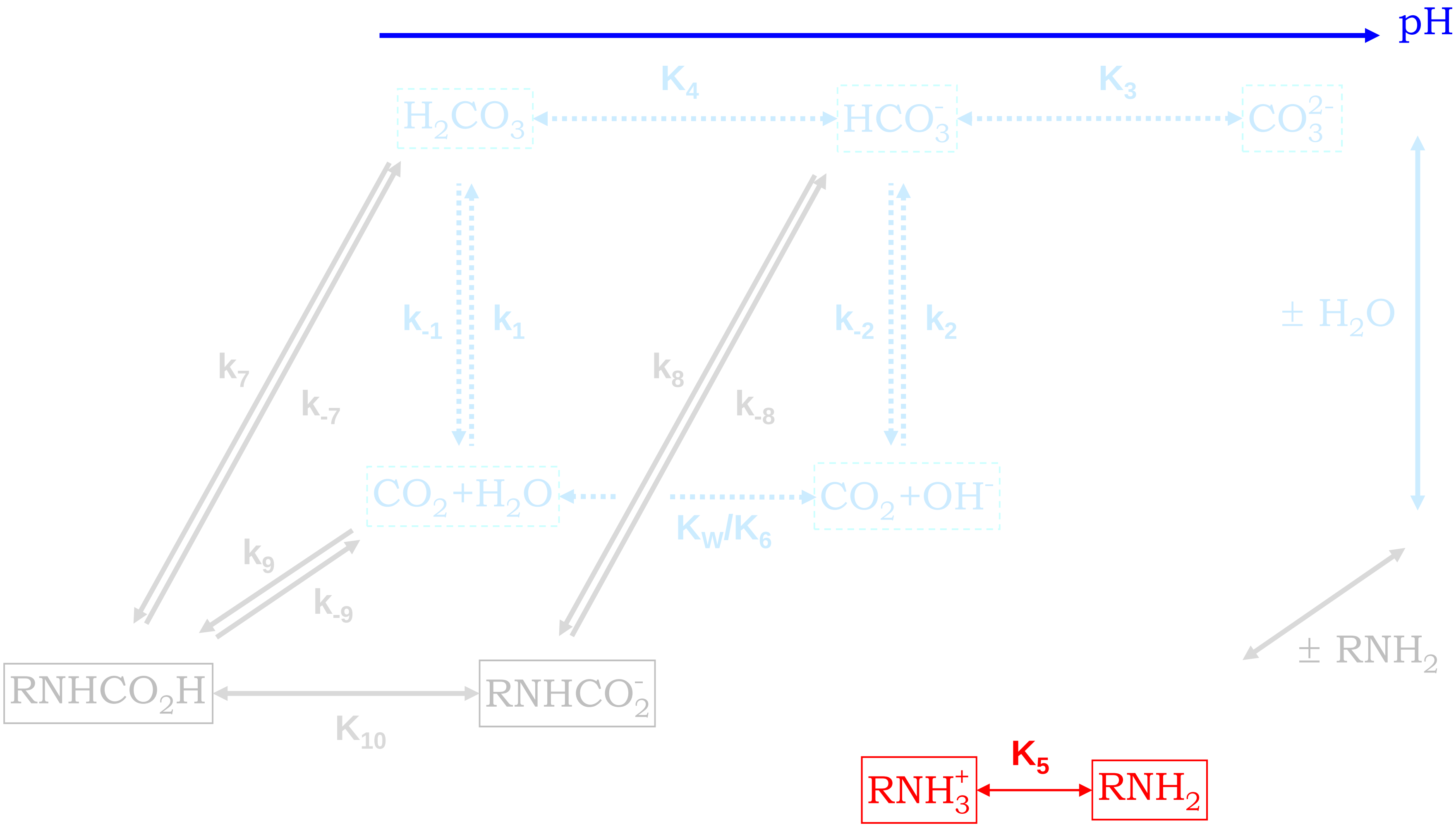
$RNHCO_2^-$, $RNHCO_2H$

1 molecule + **1 molecule** $\rightleftharpoons$ **1 molecule**

$$\left\{\begin{matrix} CO_2(aq) \\ H_2CO_3 \\ HCO_3^- \\ \cancel{CO_3^{2-}} \end{matrix}\right\} + \left\{\begin{matrix} RNH_2 \\ \cancel{RNH_3^+} \end{matrix}\right\} \rightleftharpoons \left\{\begin{matrix} RNHCO_2^- \\ RNHCO_2H \end{matrix}\right\}$$


pH
K_4
K_3
H_2CO_3
HCO_3^-
CO_3^{2-}
k_{-1}
k_1
k_{-2}
k_2
k_7
k_{-7}
k_8
k_{-8}
CO_2+H_2O
K_W/K_6
$CO_2(aq)+OH^-$
± H_2O
k_9
k_{-9}
± RNH_2
$RNHCO_2H$
K_{10}
$RNHCO_2^-$
K_5
RNH_3^+
RNH_2


pH
K_4
K_3
H_2CO_3
HCO_3^-
CO_3^{2-}
k_{-1}
k_1
k_{-2}
k_2
± H_2O
k_7
k_{-7}
k_8
k_{-8}
CO_2+H_2O
CO_2+OH^-
K_W/K_6
k_9
k_{-9}
± RNH_2
$RNHCO_2H$
$RNHCO_2^-$
K_{10}
K_5
RNH_3^+
RNH_2


pH
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K_3
CO_3^{2-}
k_{-1}
k_1
k_{-2}
k_2
± H_2O
k_7
k_{-7}
k_8
k_{-8}
CO_2+H_2O
CO_2+OH^-
K_W/K_6
k_9
k_{-9}
± RNH_2
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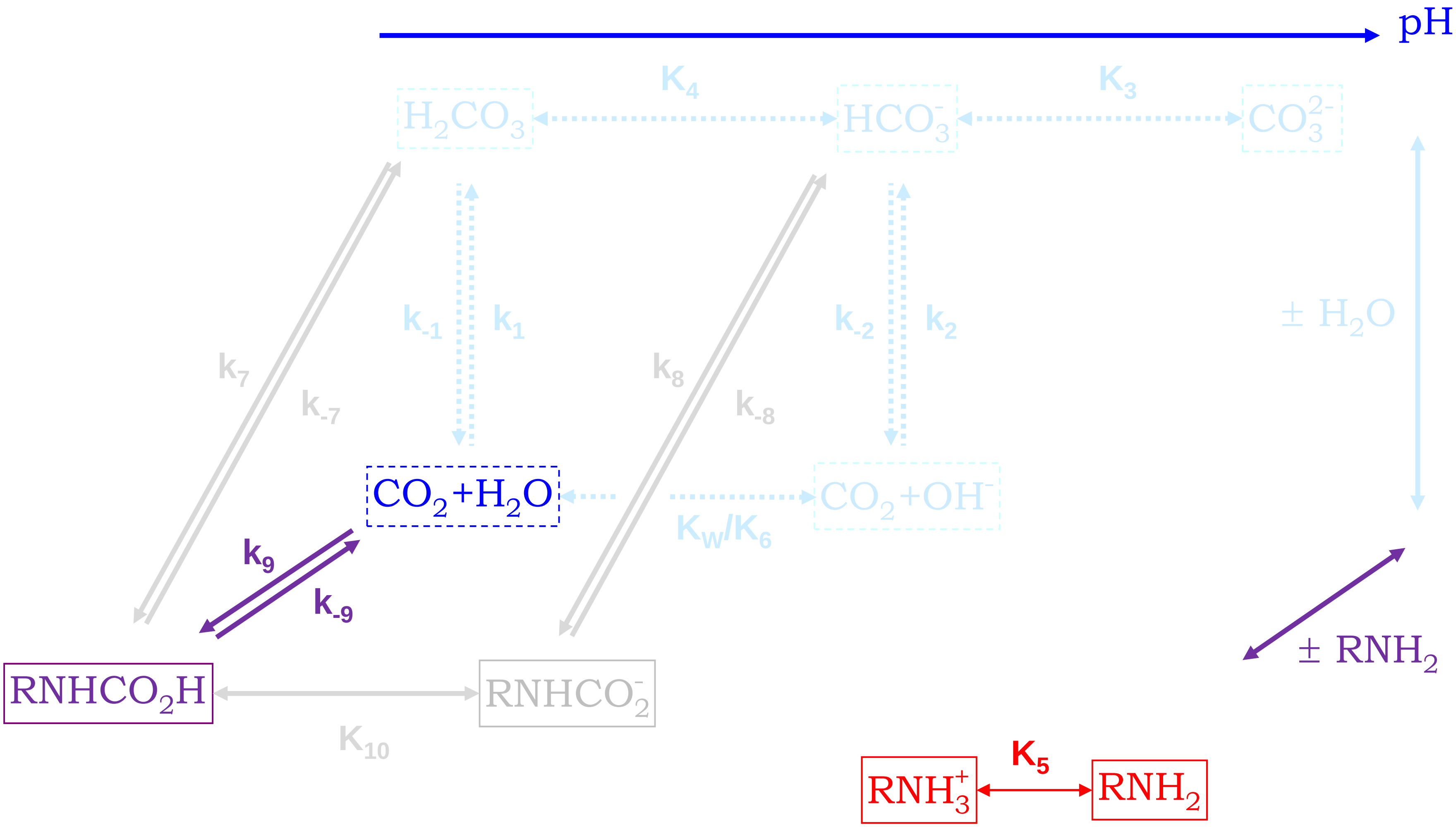
$RNHCO_2^-$
K_{10}
K_5
RNH_3^+
RNH_2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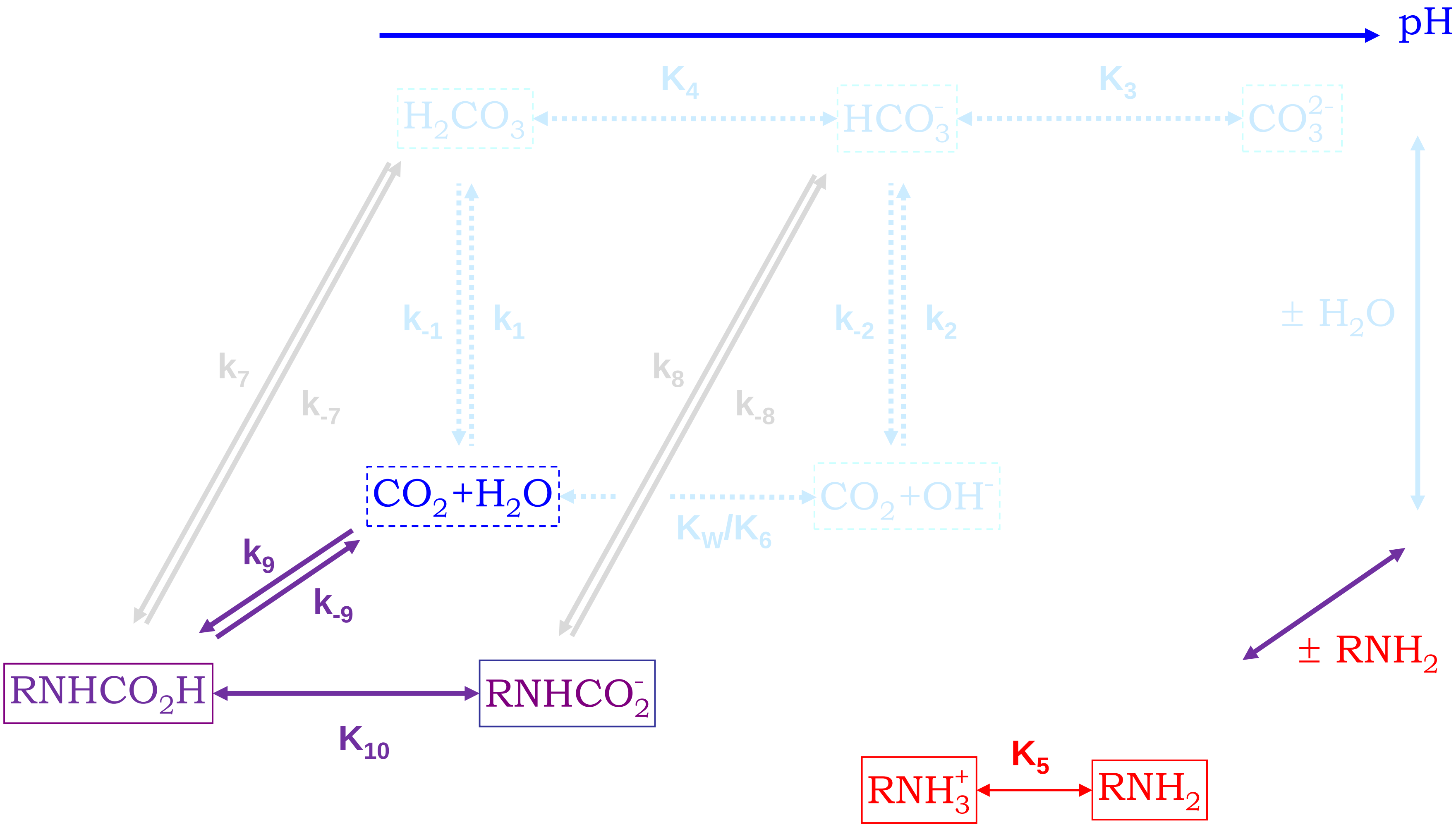
HCO_3^-
CO_3^{2-}
k_{-1}
k_1
k_{-2}
k_2
± H_2O
k_7
k_{-7}
k_8
k_{-8}
CO_2+H_2O
CO_2+OH^-
K_W/K_6
k_9
k_{-9}
± RNH_2
$RNHCO_2H$
$RNHCO_2^-$
K_{10}
K_5
RNH_3^+
RNH_2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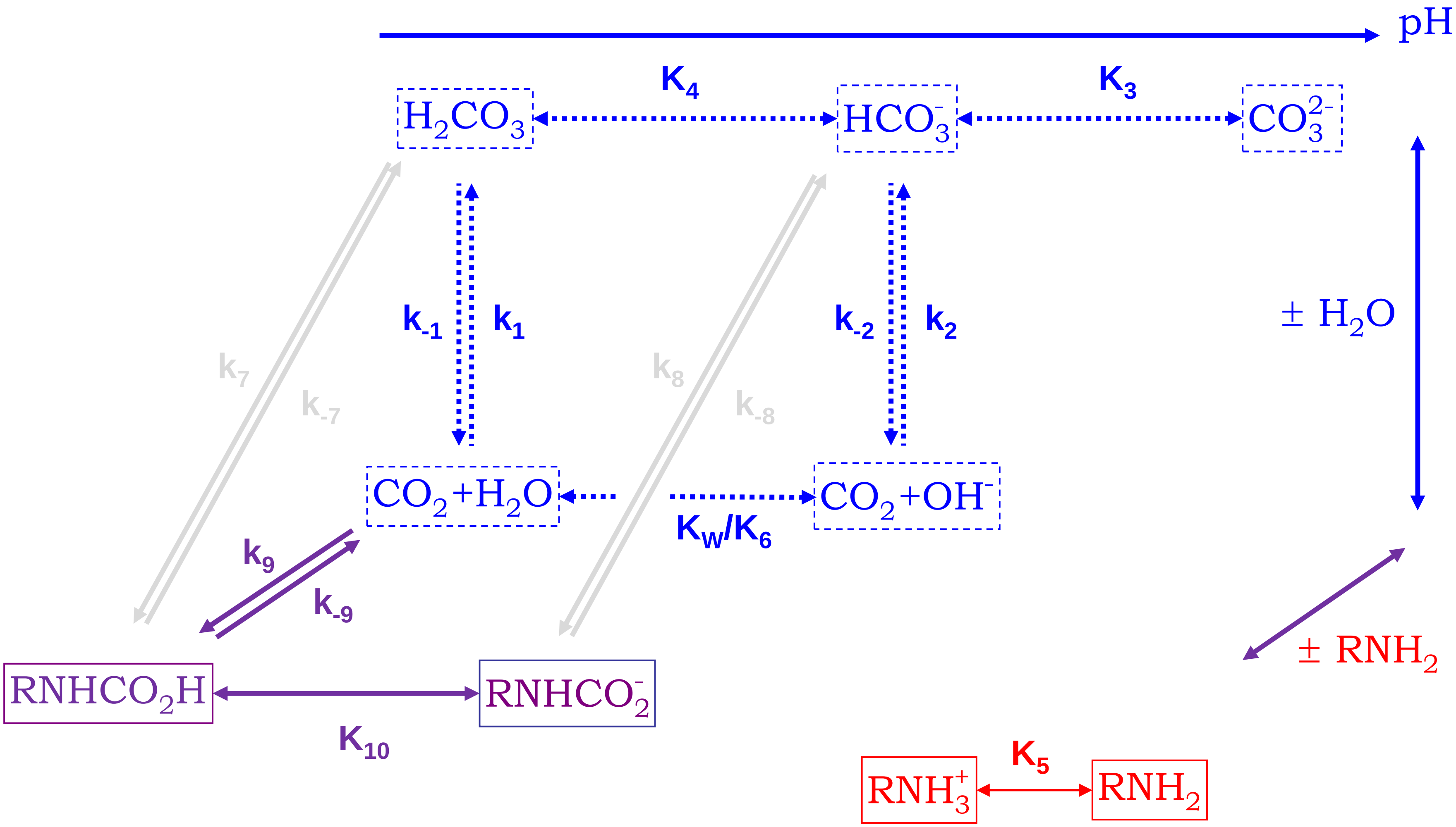
HCO_3^-
CO_3^{2-}
k_{-1}
k_1
k_{-2}
k_2
$\pm H_2O$
k_7
k_{-7}
k_8
k_{-8}
CO_2+H_2O
CO_2+OH^-
K_W/K_6
k_9
k_{-9}
$\pm RNH_2$
$RNHCO_2H$
$RNHCO_2^-$
K_{10}
K_5
RNH_3^+
RNH_2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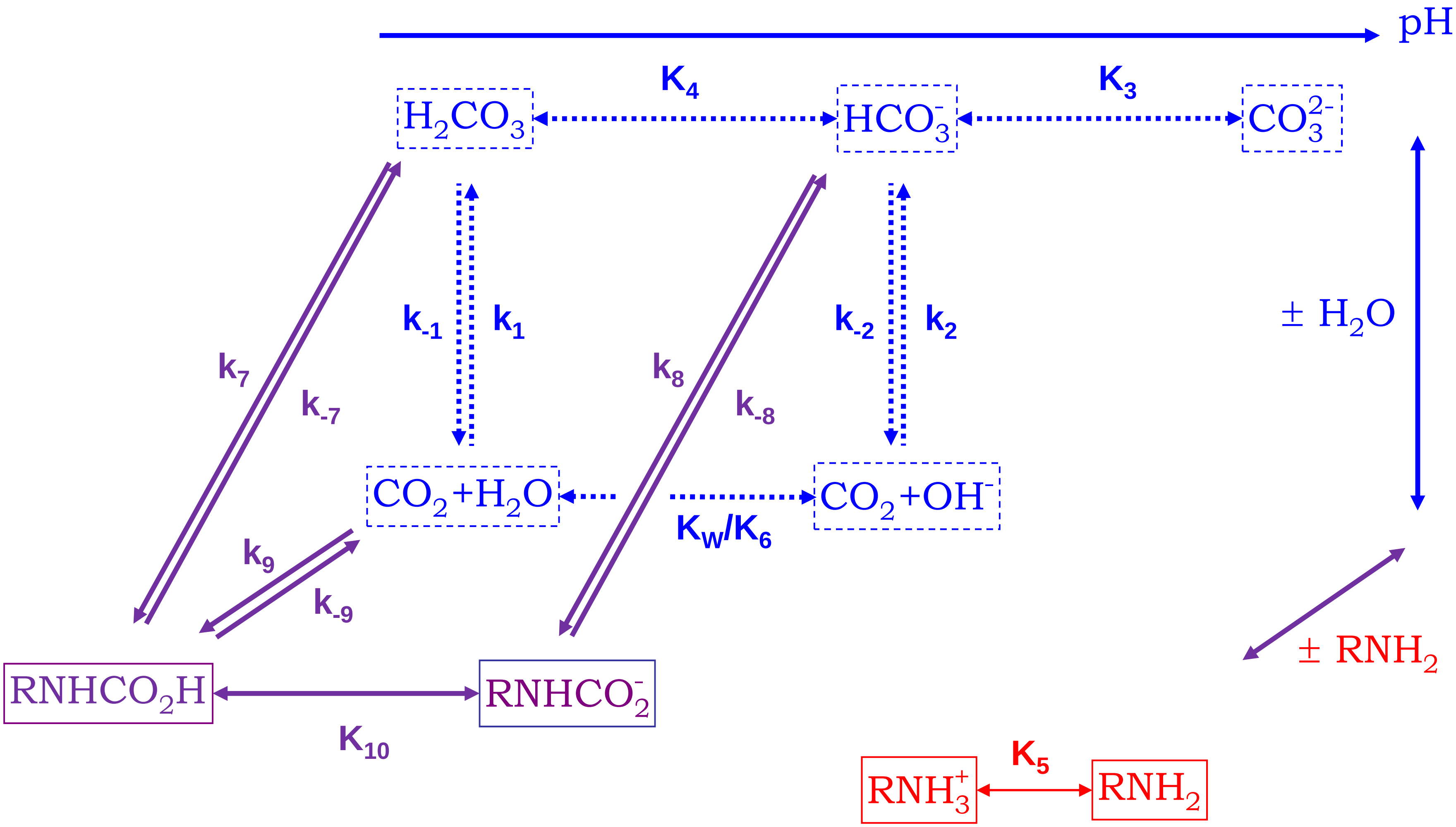
K$_3$
H_2CO_3
HCO_3^-
CO_3^{2-}
k$_{-1}$
k$_1$
k$_{-2}$
k$_2$
± H_2O
k$_7$
k$_{-7}$
k$_8$
k$_{-8}$
CO_2+H_2O
CO_2+OH^-
K$_W$/K$_6$
k$_9$
k$_{-9}$
± RNH_2
$RNHCO_2H$
$RNHCO_2^-$
K$_{10}$
K$_5$
RNH_3^+
RNH_2


pH
K$_4$
K$_3$
H$_2$CO$_3$
HCO$_3^-$
CO$_3^{2-}$
k$_{-1}$
k$_1$
k$_{-2}$
k$_2$
± H$_2$O
k$_7$
k$_{-7}$
k$_8$
k$_{-8}$
CO$_2$+H$_2$O
CO$_2$+OH$^-$
K$_W$/K$_6$
k$_9$
k$_{-9}$
± RNH$_2$
RNHCO$_2$H
RNHCO$_2^-$
K$_{10}$
K$_5$
RNH$_3^+$
RNH$_2$

The complete reaction scheme

$$CO_2(aq) + RNH_2 \rightleftarrows RNHCO_2H$$
$$H_2CO_3 + RNH_2 \rightleftarrows RNHCO_2H$$
$$HCO_3^- + RNH_2 \rightleftarrows RNHCO_2^-$$
$$RNHCO_2^- + H^+ \longleftrightarrow RNHCO_2H$$

Reactions involving carbamates

+

$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3$$
$$CO_2(aq) + OH^- \rightleftarrows HCO_3^-$$
$$CO_3^{2-} + H^+ \longleftrightarrow HCO_3^-$$
$$HCO_3^- + H^+ \longleftrightarrow H_2CO_3$$
$$RNH_2 + H^+ \longleftrightarrow RNH_3^+$$

Other, known reactions

To be determined:

- **6 rate constants**
- **1 equilibrium constants**
- **- 3 due to microscopic reversibility**

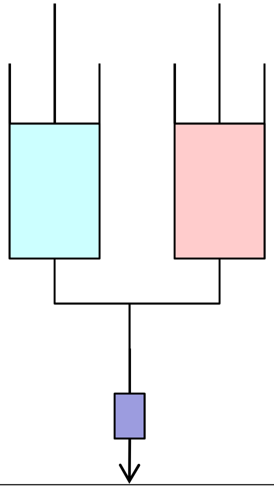
Measurement techniques

- $p(CO_2)$ partial pressure in gas phase (slow)
- $Ba(CO_3)$ precipitation (slow)
- Conductometry (fast, not specific)
- **pH, indicator (fast)**
- NMR
  - ^{13}C-NMR (slow, not quantitative)
  - **^{1}H-NMR (intermediate, quantitative)**

Example 1:

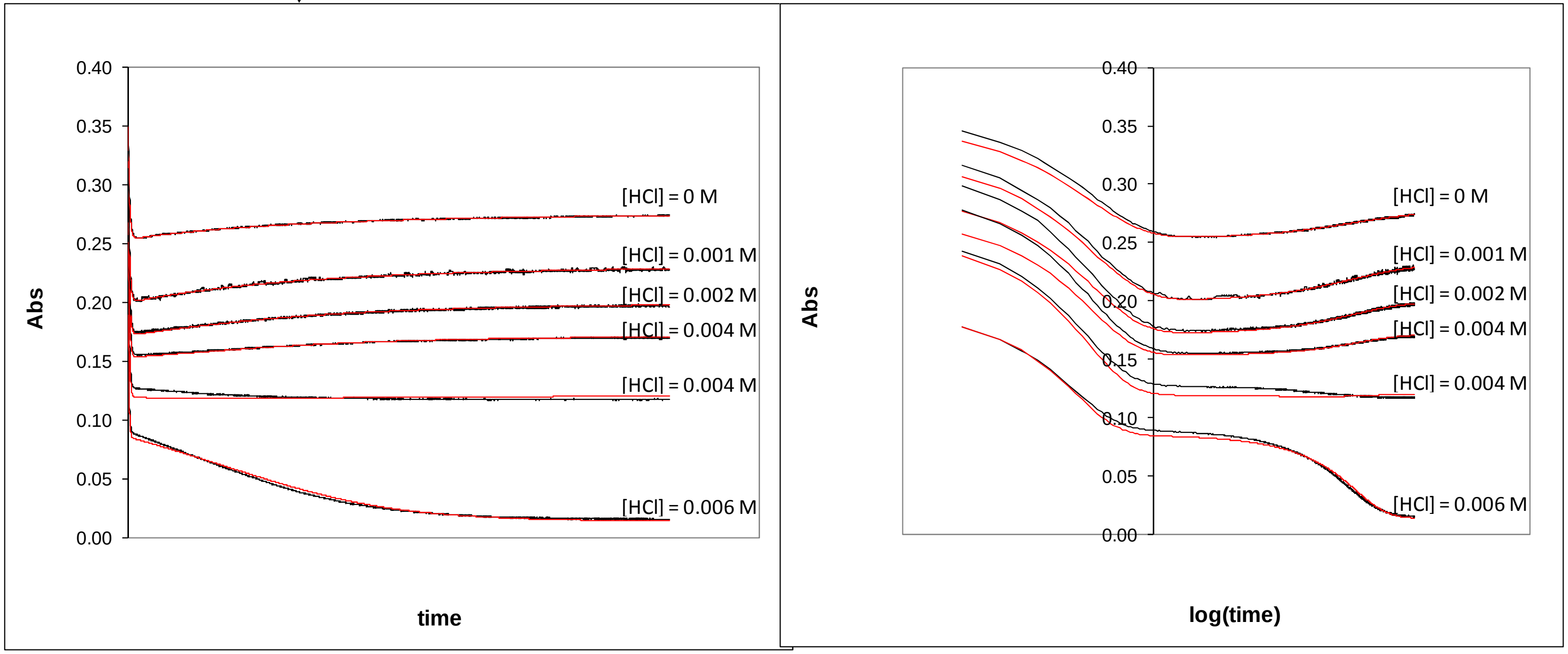
Ammonia, NH_3

Measurements, stopped-flow

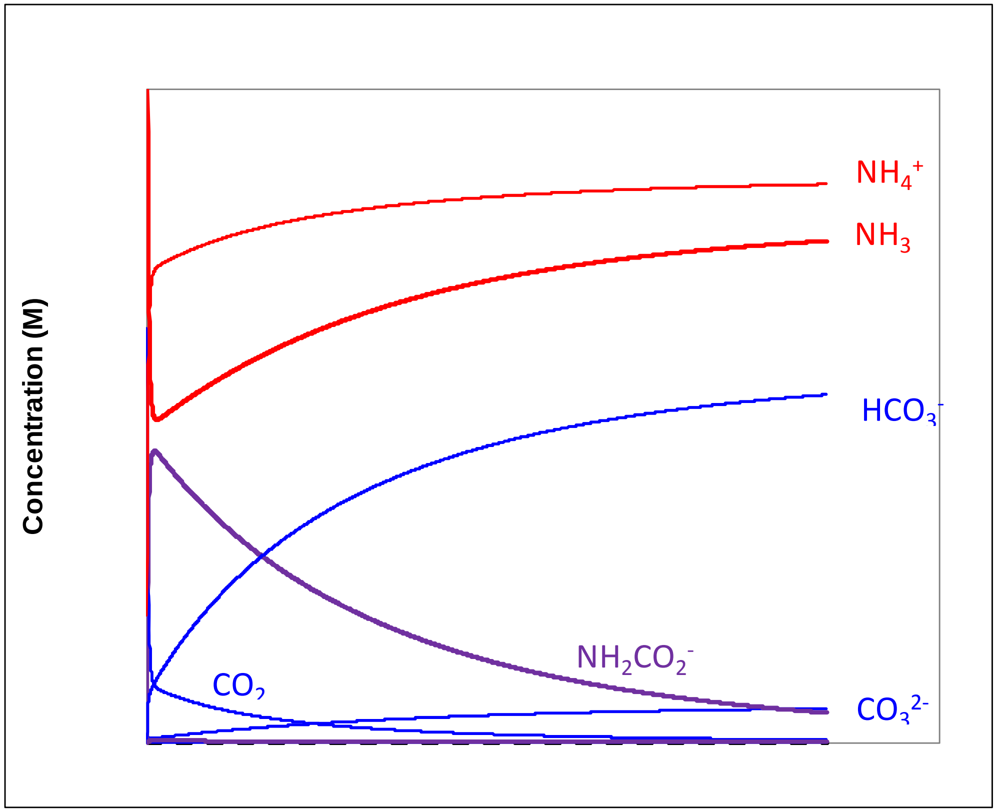


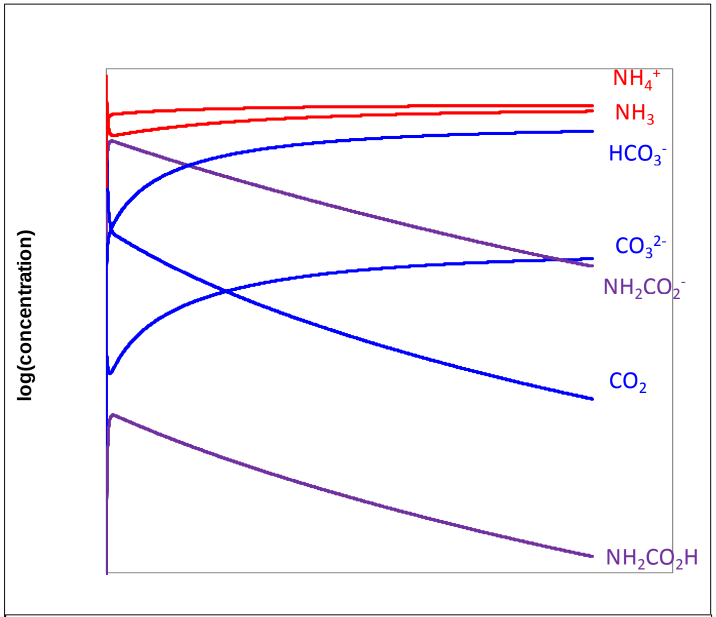
$[CO_2]$ = 0.0xx M

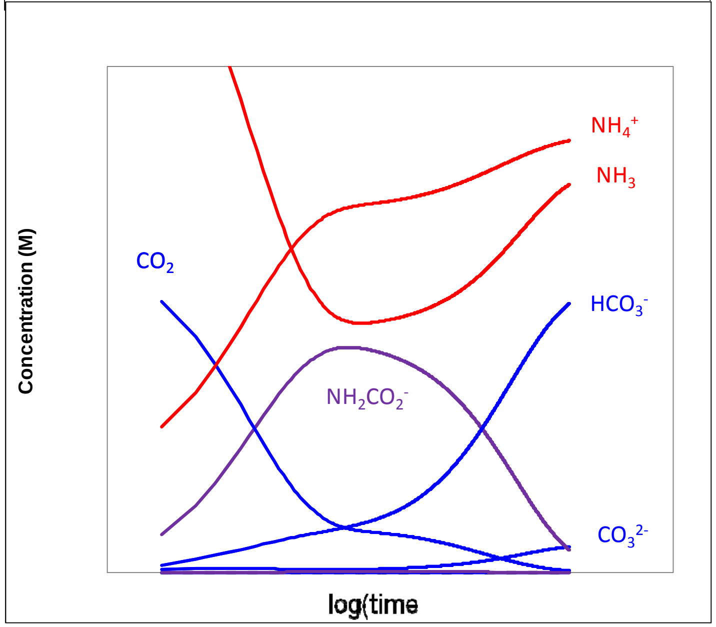
$[NH_3]$ = 0.0xxM
[HCl] = …
[ThB] = 1.5×10^{-5} M



Analysis:
$NH_3 + CO_2$





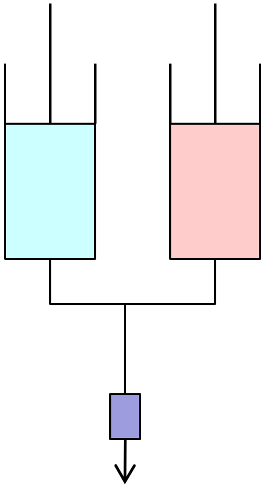


Analysis: $NH_2COO^- + H^+$

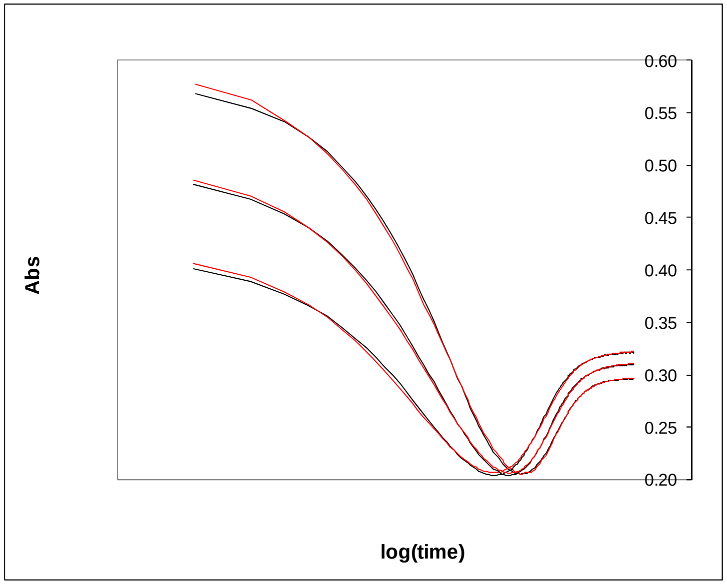
$[NH_3]$ = 0.0xx M
$[HCO_3^-]$ = 0.yy M

equilibration

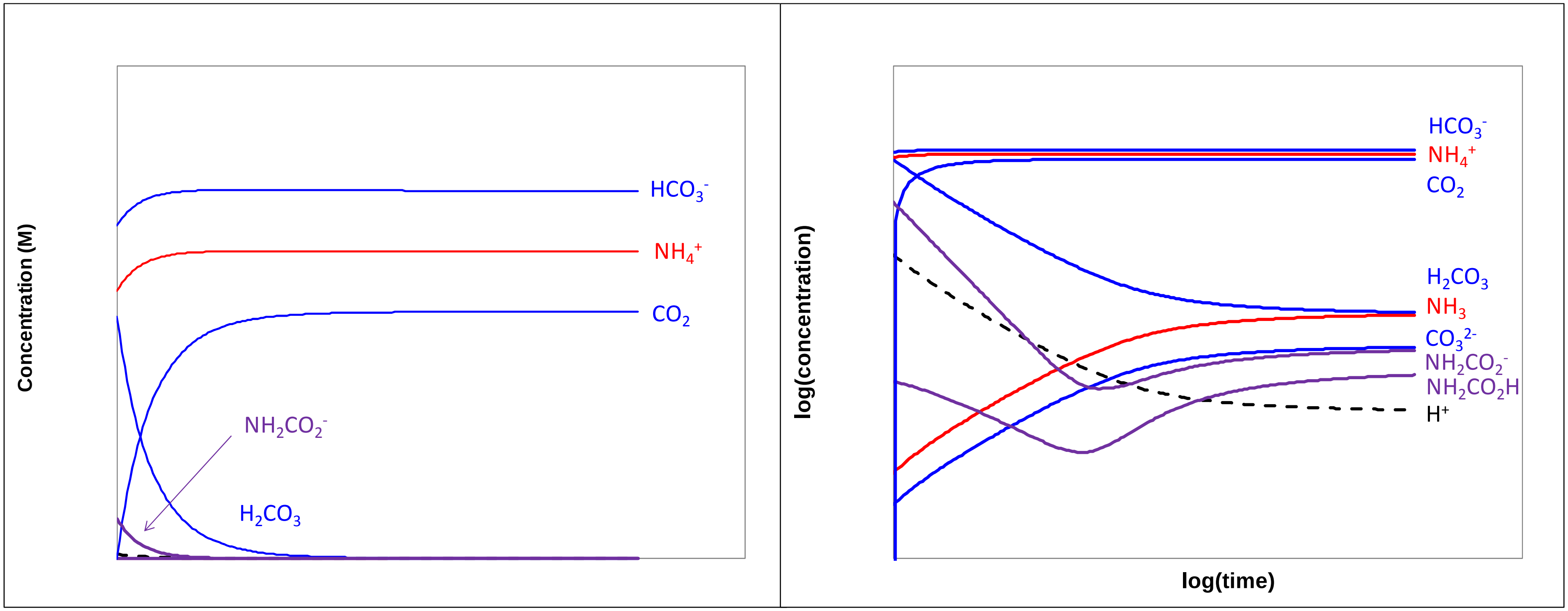
$[NH_3]$ = … M
$[HCO_3^-]$ = … M
$[NH_2COO^-]$ = … M



[HCl] = 0.09 M
[MeOr] = 5×10^{-5} M
[AlRed] = 1×10^{-4} M

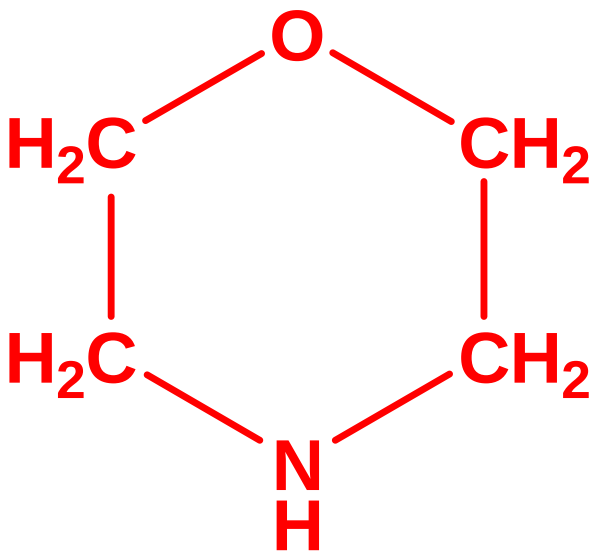


Analysis: $NH_2COO^- + H^+$

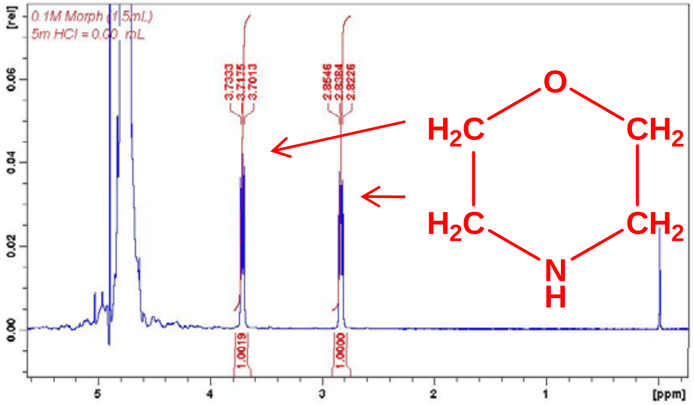


Example 2:

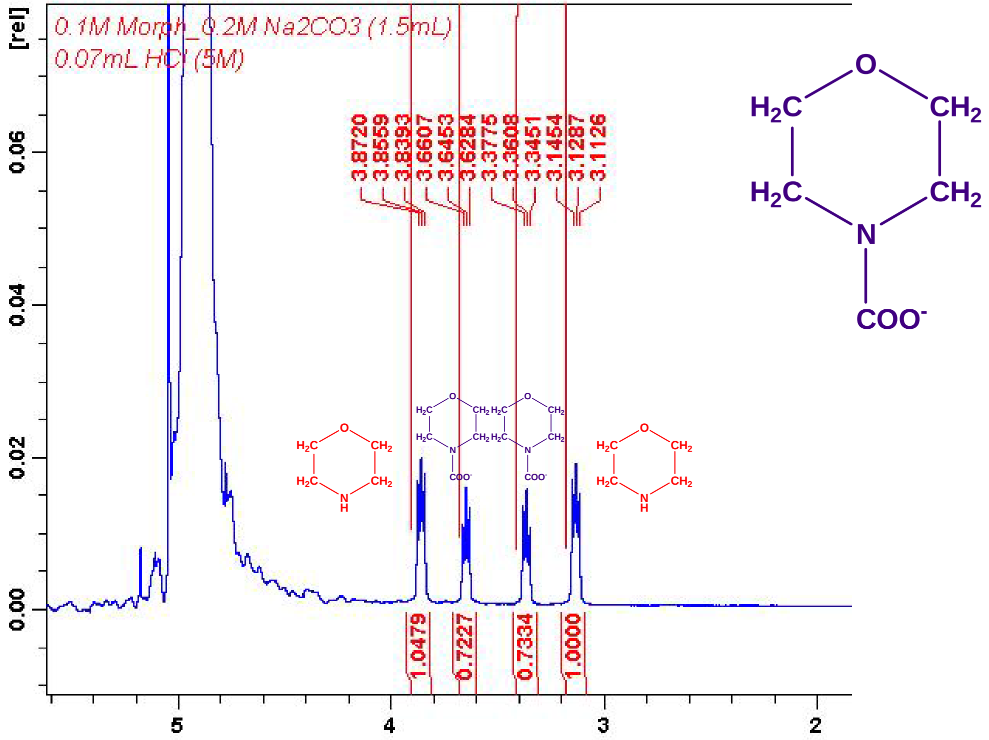
morpholine



^{1}H-NMR spectra



morpholine

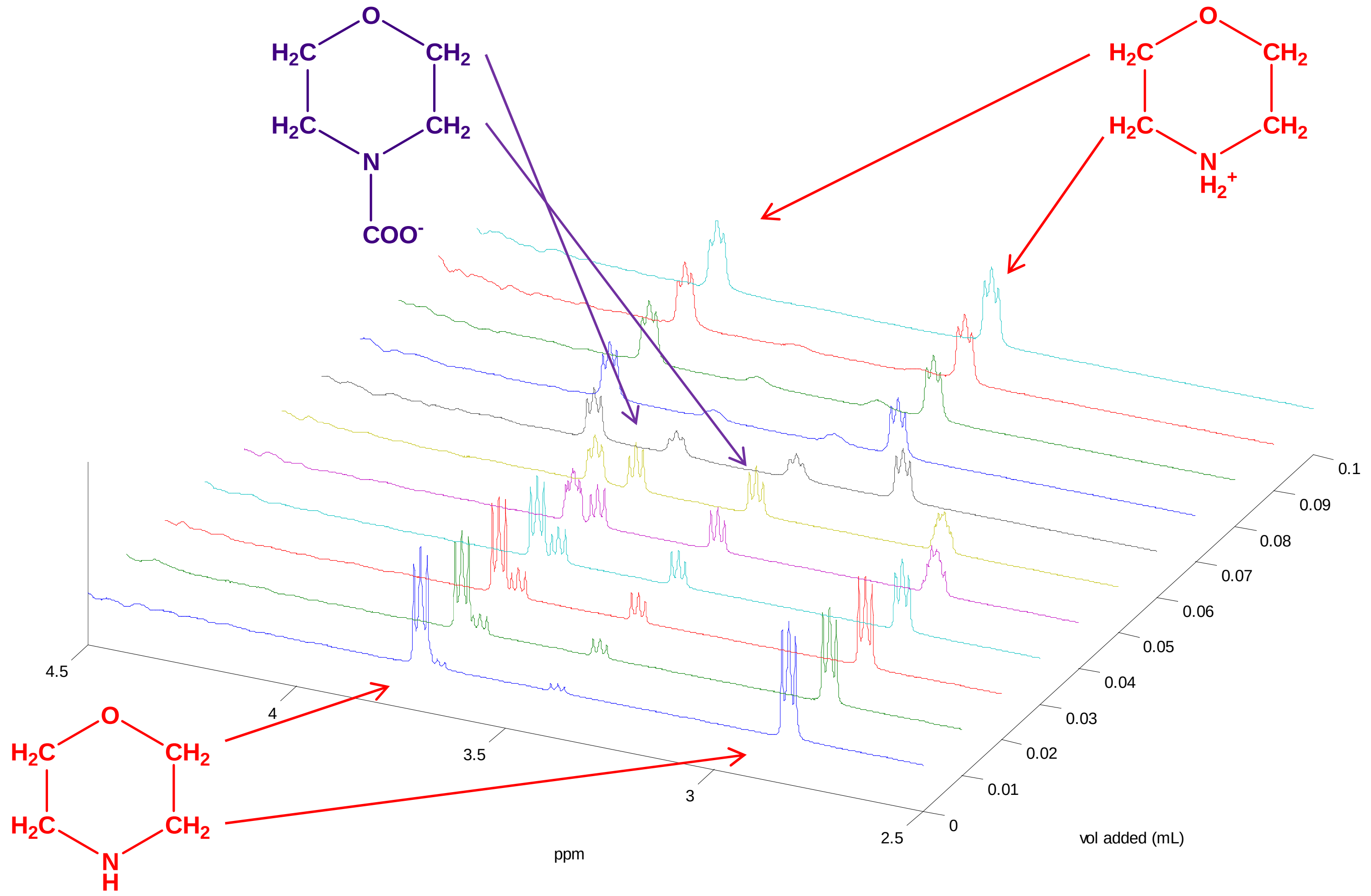


morpholine

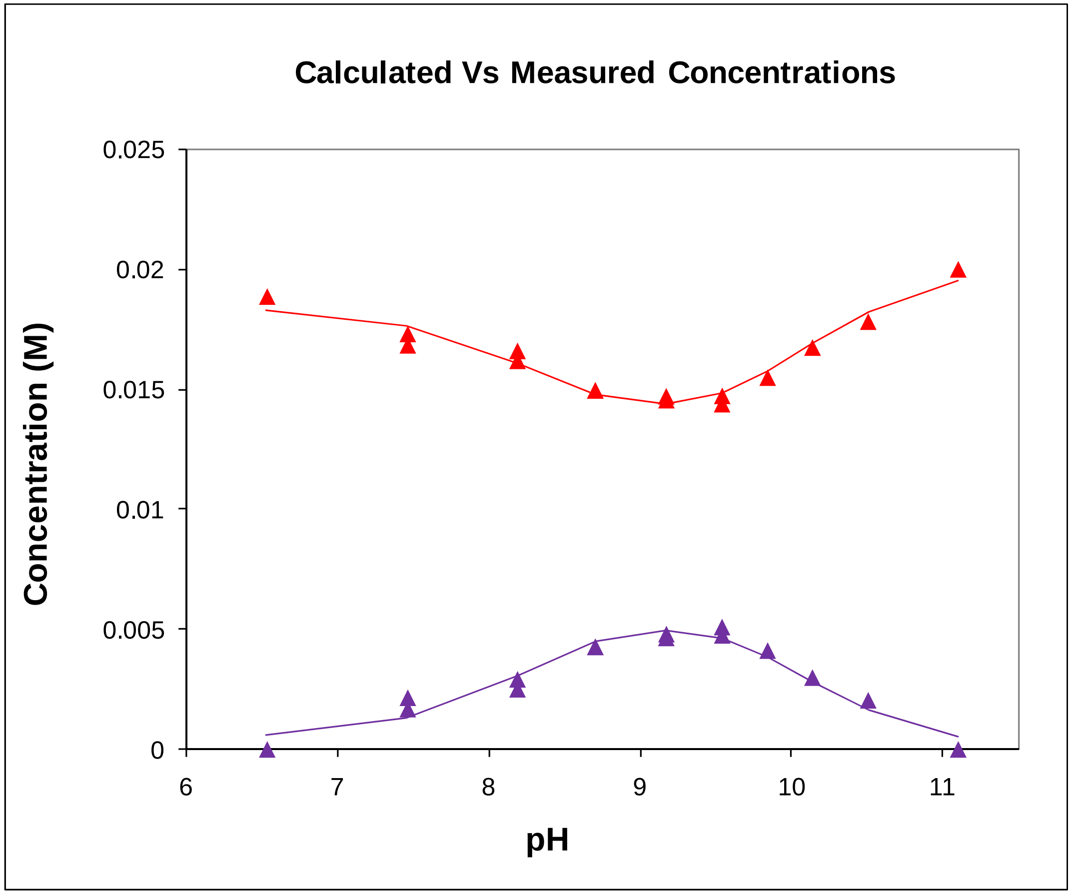
+

carbamate

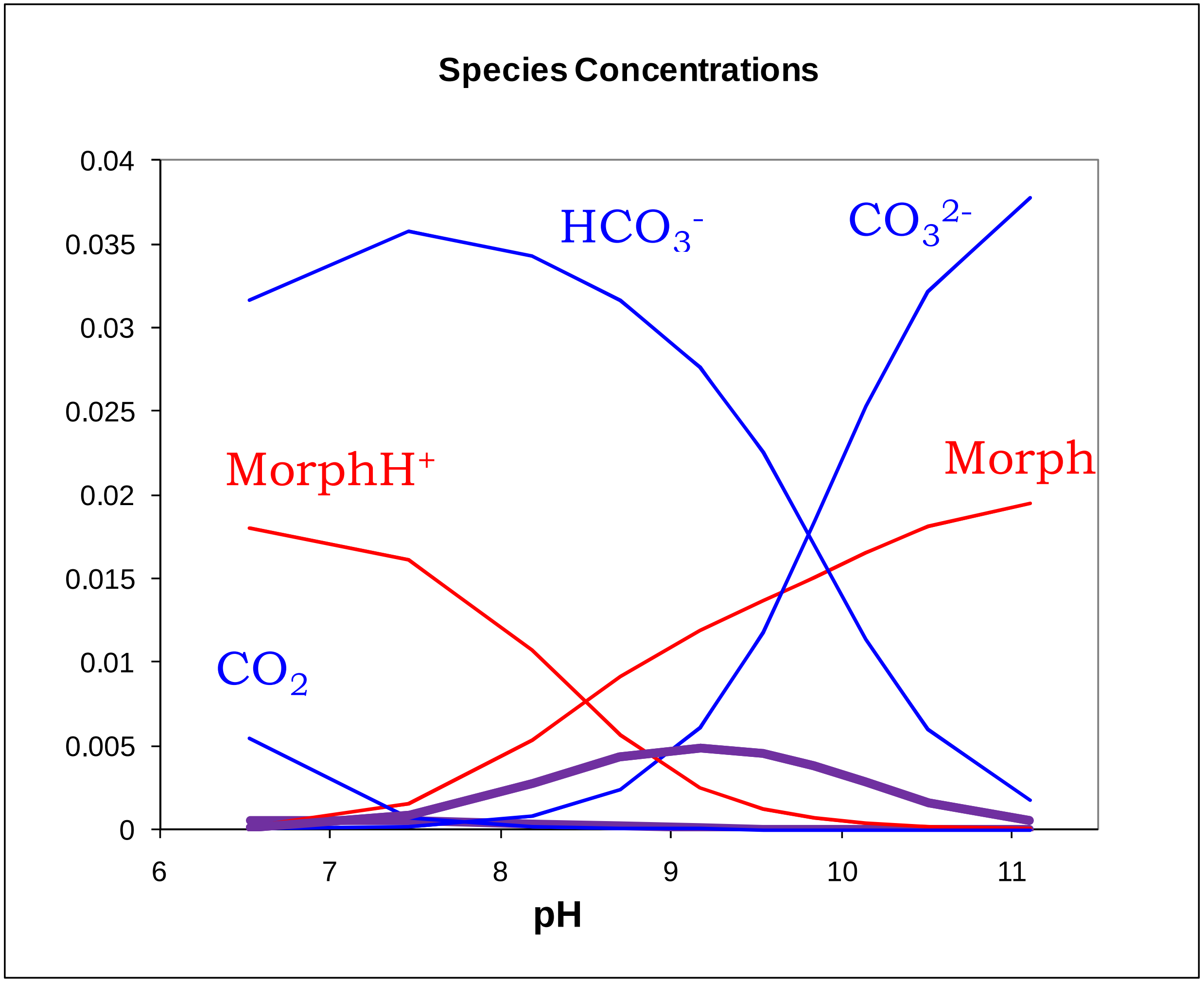
^{1}H-NMR spectra of Morpholine at 25˚C
(Morpholine/Na_2CO_3 1/2 with different volumes of 5M HCl)



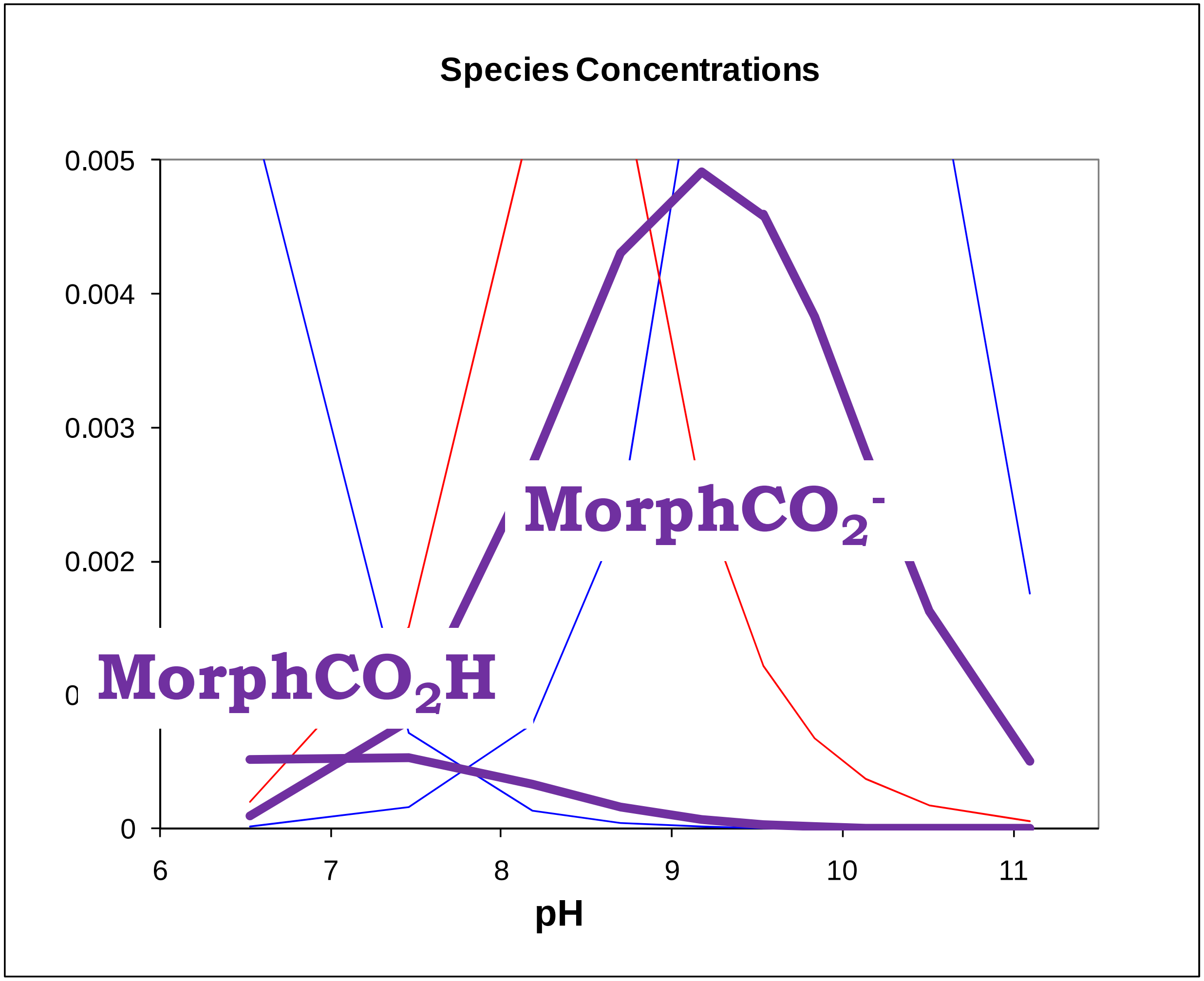
Analysis of the data



Result of the Analysis



carbamate and carbamic acid



Results for morpholine

Reaction	Kinetics	Equilibrium constants
$H_2CO_3 + NH_3 \xrightleftharpoons[k_{-7}]{k_7} NH_2COOH + H_2O$	$k_7 = 13.5\ M^{-1}s^{-1}$ $k_{-7} = 6.9\times10^{-5}\ s^{-1}$	$\log K_7 = 5.3$
$HCO_3^- + NH_3 \xrightleftharpoons[k_{-8}]{k_8} NH_2COO^- + H_2O$	$k_8 = 6.2\times10^{-4}\ M^{-1}s^{-1}$ $k_{-8} = 7.9\times10^{-5}\ s^{-1}$	$\log K_8 = .9$
$CO_2(aq) + NH_3 \xrightleftharpoons[k_{-9}]{k_9} NH_2COOH$	$k_9 = 4\times10^{3}\ M^{-1}s^{-1}\ \$$ $k_{-9} = 14\ s^{-1}$	$\log K_9 = 2.5$
$NH_2COO^- + H^+ \xleftrightarrow{K_{10}} NH_2COOH$		$\log K_{10} = 7.9$

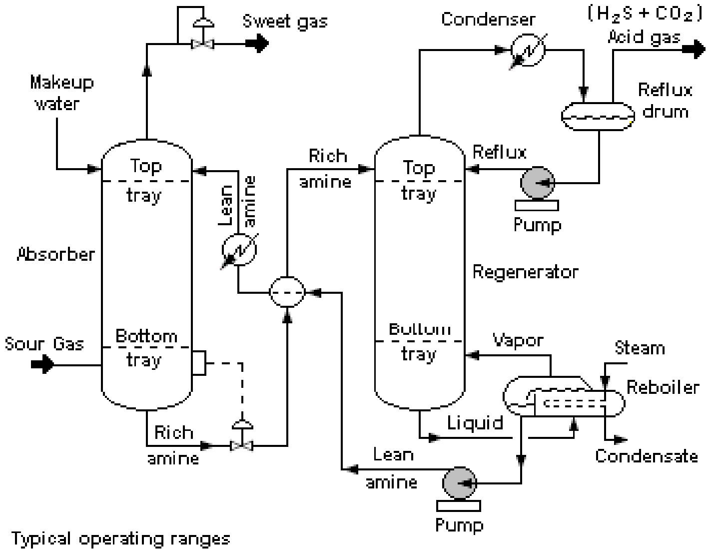
Published results for morpholine

Rate constant, M^{-1} s^{-1}	**literature**
20000	Sharma, M. M. *Trans. Faraday Soc.* **1965,** *61*, 681-687.
20520	Alper, E. *Chem. Eng. J.* **1990,** *44*, 107-111.
6100 (303 K)	Littel, R. J.; Versteeg, G. F.; Van Swaaij, W. P. M. *Chem. Eng. Sci.* **1992,** *47*, 2037-2045.
22259	Al-Juaied, M.; Rochelle, G. T. *Chem. Eng. Sci.* **2006,** *61*, 3830-3837.
4000	Our work

Back to the original question:

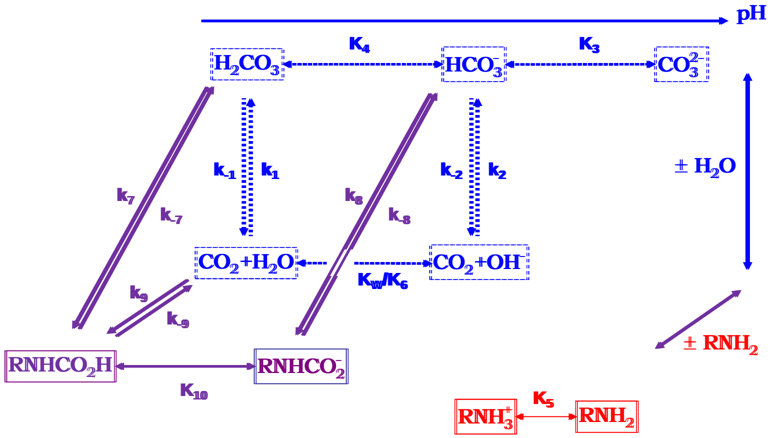
Is it worth the effort of determining such a complex mechanism, rather than being satisfied with an empirical function which might be sufficient for the purpose?

Complete Model for Absorber and Stripper



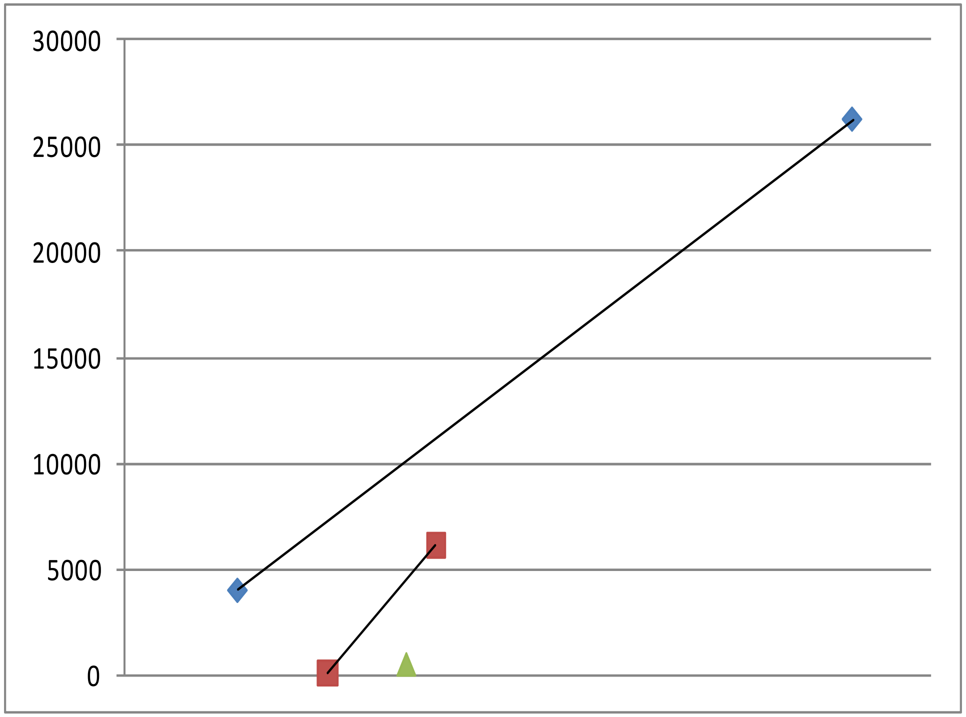
Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure at tower bottom



Bringing results together

$$CO_2(aq) + RNH_2 \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} RNHCOOH$$



k_9 vs pKa of different types of amines

Future steps

- Additional amines
  - e.g. piperazine which forms bi-carbamate (challenge)
  - many other amines
- Reaction enthalpies, calorimetry
- Mixed amine solvents
- Microscopic analysis at gas-liquid interface
  - diffusion
  - pH-profiles

Acknowledgments

- University of Newcastle
  - Financial support
  - Scholarships
- CSIRO Energy Transformed Flagship Grant
  - Financial Support

Thank you for your attention !


Positive proof of global warming.

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Ionic Liquids for Post Combustion CO_2-Absorption

12th MEETING of the
INTERNATIONAL POST-COMBUSTION CO_2 CAPTURE NETWORK

David Wappel(1), Guenter Gronald(2), Roland Kalb(3) and Josef Draxler(1)

1) University of Leoben, Institute of Process Technology and Industrial Environmental Protection, Austria

2) AE&E Austria GmbH & Co KG

3) proionic Production of Ionic Substances GmbH

29th September - 1st October 2009
Regina, Canada

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proionic

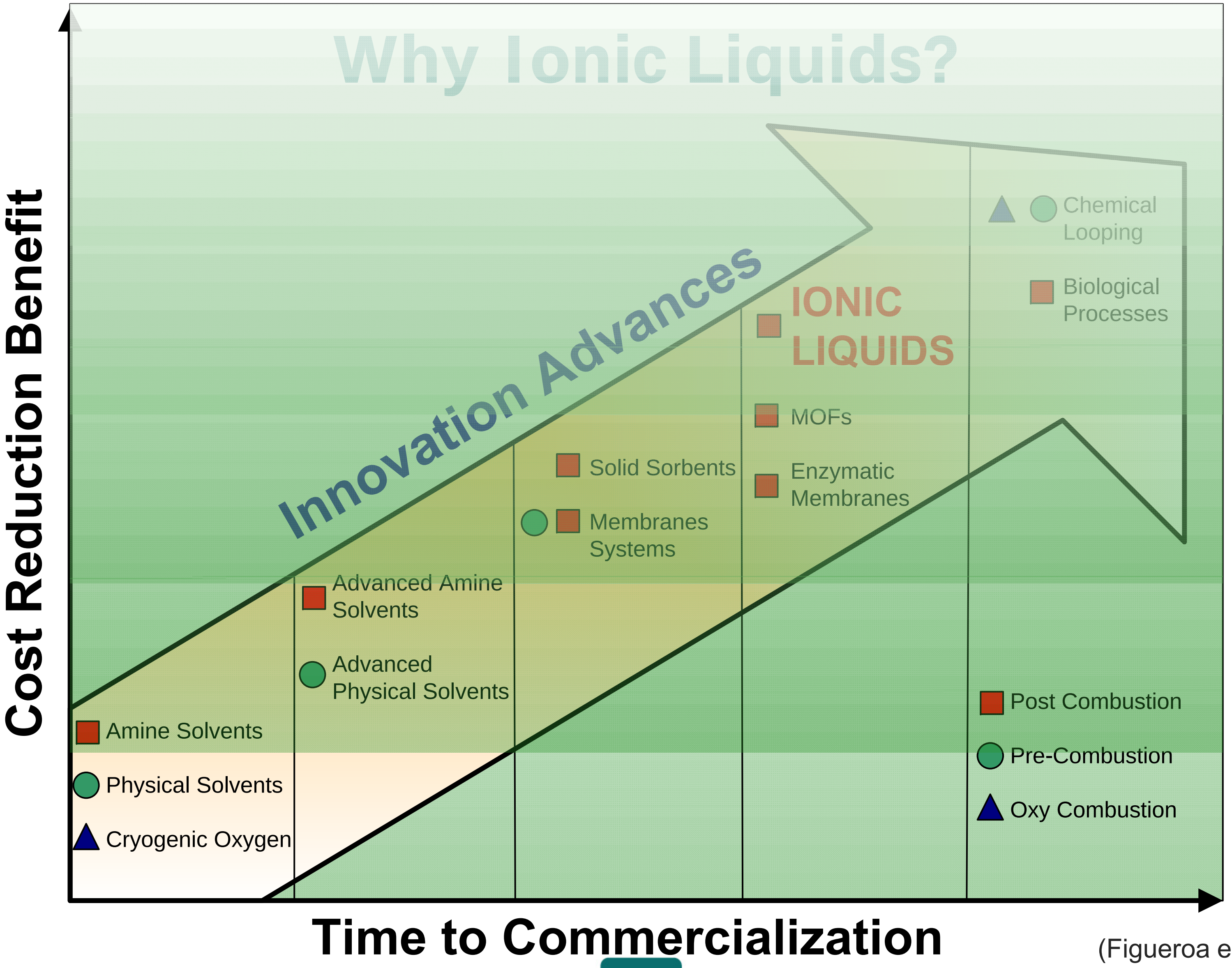
Target of the Work

- To investigate the ability of various task specific ionic liquids (ILs) as potential CO_2 capture solvents for PCC
- Comparison of one selected task specific ionic liquid to the reference solvent MEA

Content of the Work

- Laboratory Work:
  - Screening of ionic liquids for a quick evaluation of the CO_2 absorption performance
  - Vapor-liquid equilibrium measurements
  - Calculation of the enthalpy of absorption
  - Calculation of the energy demand for stripping
- Pilot Plant Testing:
  - Direct comparison of MEA and IL under real flue gas conditions

Why Ionic Liquids?



Cost Reduction Benefit

Time to Commercialization

Innovation Advances

■ Amine Solvents

● Physical Solvents

▲ Cryogenic Oxygen

■ Advanced Amine Solvents

● Advanced Physical Solvents

■ Solid Sorbents

● ■ Membranes Systems

■ IONIC LIQUIDS

■ MOFs

■ Enzymatic Membranes

▲ ● Chemical Looping

■ Biological Processes

■ Post Combustion

● Pre-Combustion

▲ Oxy Combustion

(Figueroa et al. 2008)

Ionic Liquids

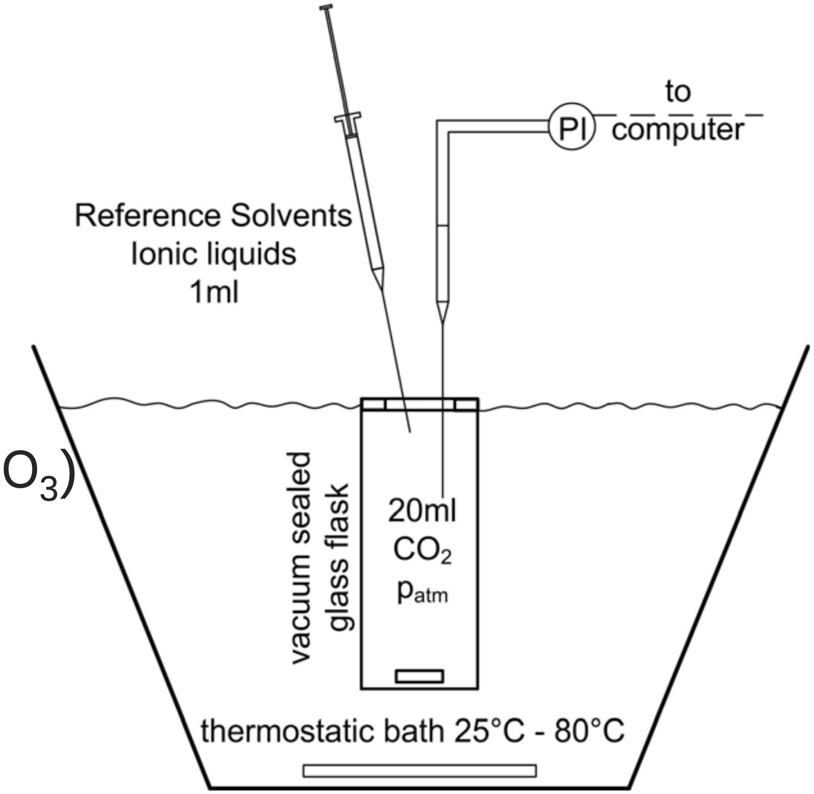
- “Ionic liquids are salts with a melting temperature below the boiling point of water. Most ionic liquids have an organic cation and an inorganic anion. “

  (Wasserscheid und Welton, 2008)

- Advantages:
  - Application without any solvent possible
  - Myriad different structures and variation possibilities of anion and cation
  - Non measurable vapor pressure
- Disadvantages:
  - High Viscosity
  - Currently high costs
  - Little Experience

Screening Experiments

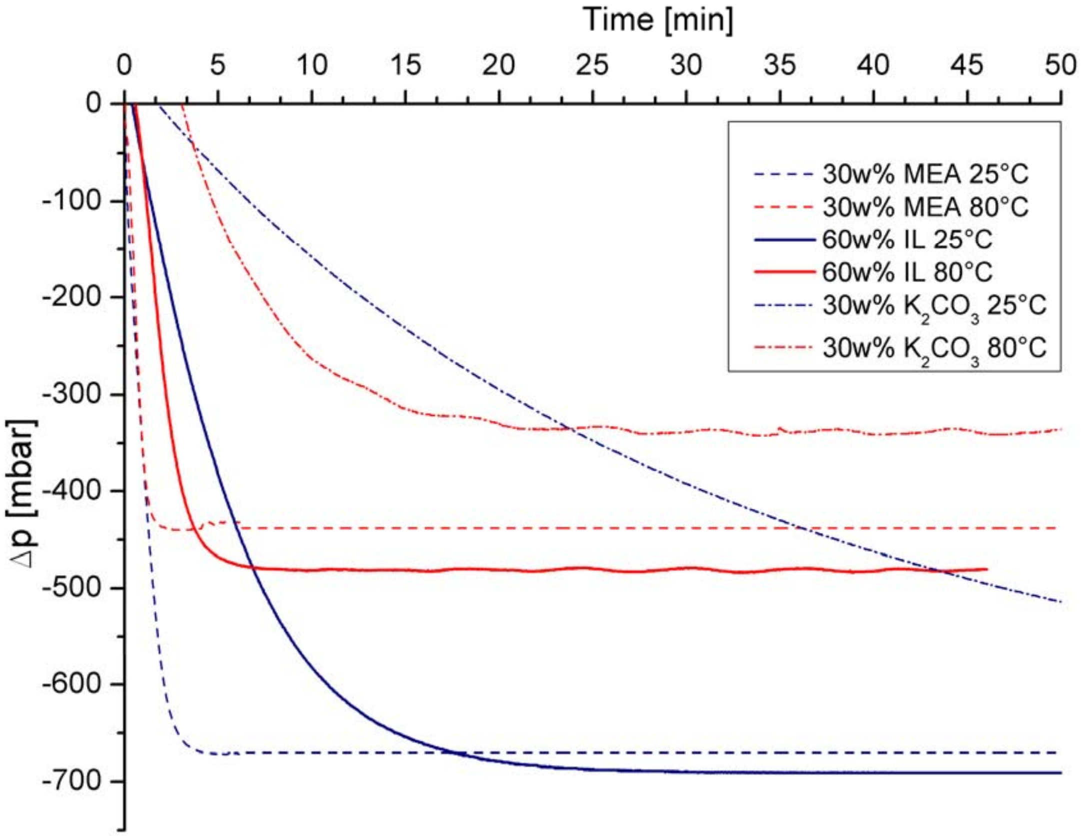
- Fast investigation of CO_2 absorption performance with a small amount of liquid.
- Reference solvents
  - 30w% Monoethanolamine (MEA)
  - 30w% Potassium Carbonate (K_2CO_3)
- Test of CO_2 absorption at 25°C and 80°C
- Qualitatively determination of the absorption kinetics



Screening Experiments

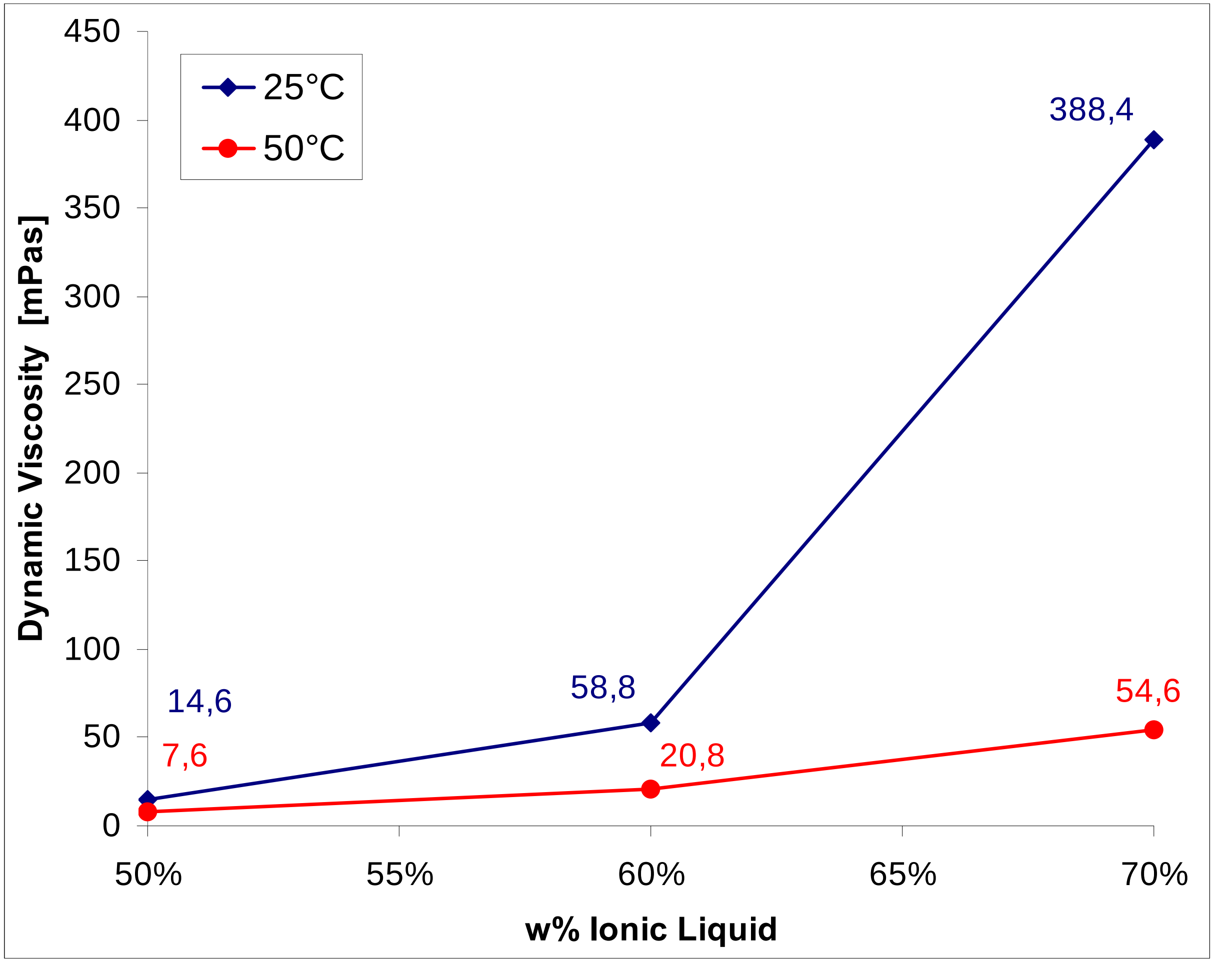
- 80 different ILs or IL-blends were tested
- Pure ILs (without additive)
    - High viscosity
    - Low CO_2 absorption performance
    - Slow absorption kinetics
- Water as an additive
    - Better absorption performance

Screening Experiments



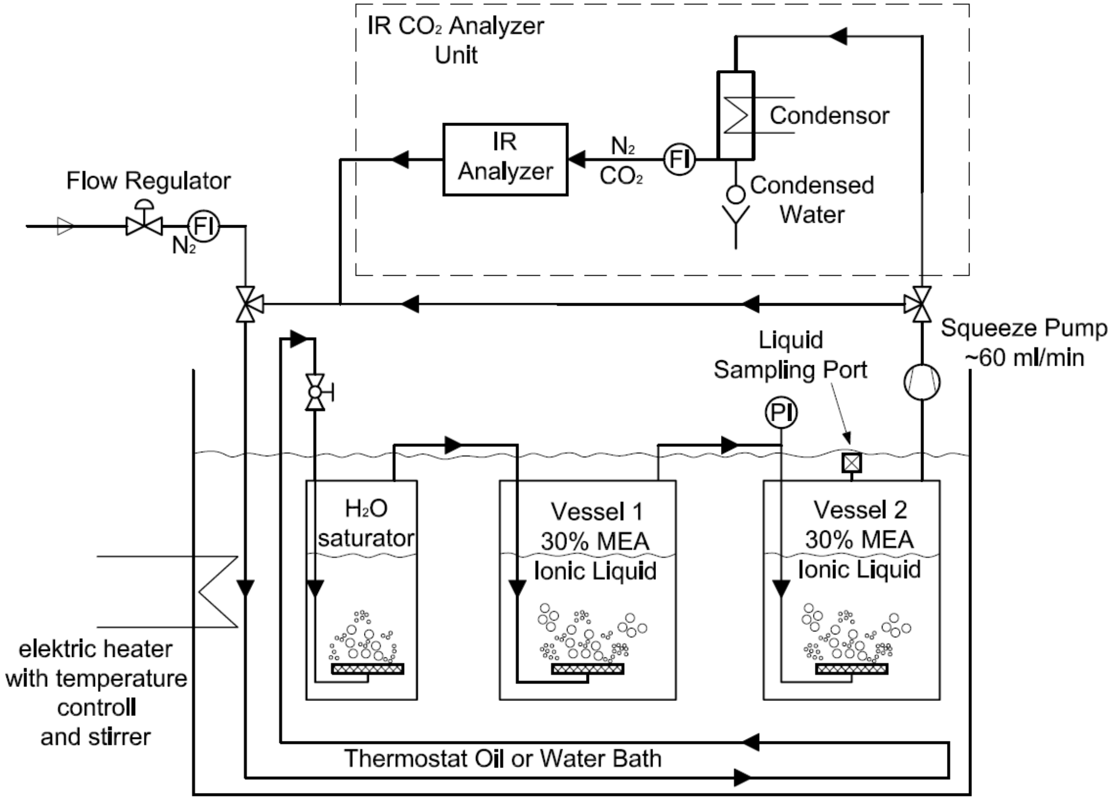
Solvent		30w% MEA in water	48w% IL 8 in water	30w% K_2CO_3 in water
Δp_{25}	[mbar]	-676	-691	-645
Δp_{80}	[mbar]	-438	-480	-343
t_{25}	[sec]	250	1600	5000 - 7000
t_{80}	[sec]	150	400	1800

Viscosity of the ionic liquid water blend depending on the water content



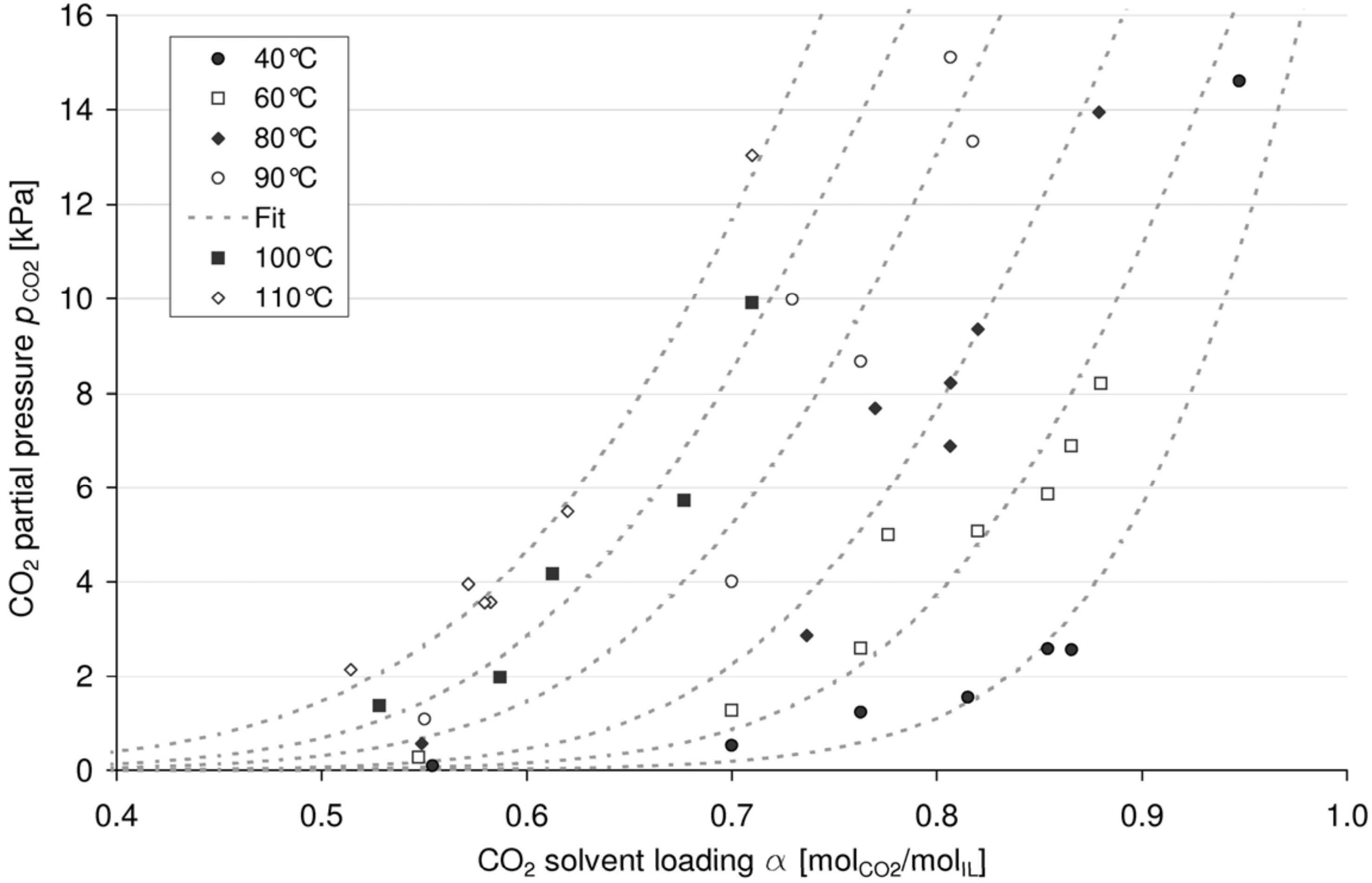
Vapor-Liquid Equilibrium (VLE) Measurements

- Basis for energy demand calculation
- Validation with MEA and comparison with the literature
- VLE Measurements of IL between 40°C und 110°C



Austgen et al. (1991) and Ma'mum et al. (2005; 2007)

Vapor-Liquid Equilibrium Curves



Enthalpy of Absorption ΔH_{abs}

- Changing of equilibrium with temperature expressed with van‘t Hoff equation

$$\frac{d\ln k}{dT}=\frac{\Delta H_{Abs}}{R\cdot T^{2}} \quad\longrightarrow\quad \Delta H_{Abs}=R\cdot\left(\frac{\partial\ln p_{CO2}}{\partial\left(\frac{1}{T}\right)}\right)_{\alpha}$$

- For the analyzed ionic liquid

$$\Delta H_{Abs}=41.1\ \pm 3.2\frac{kJ}{mol}$$

Energy Demand for the CO_2 Stripping

- Calculation for 30w% MEA and 60w% IL
  - Validation of model with MEA literature
    - Different process parameters: Mean deviation only 1,3%
  - Standard process parameters

CO_2-Concentration Flue Gas	13,3	vol%
CO_2 Capture Rate	90	%
IL Concentration	60	w%
MEA Concentration	30	w%
Temperature Absorber	40	°C
Desorption Temperature	110	°C

Energy Demand for the CO_2 Stripping

- Simplifications
  - No temperature dependency of enthalpy of absorption
  - Comparison of standard PCC process with obtained VLE data – not very detailed optimization of the CO_2 absorption process
  - Calculations are based on equilibrium conditions – no kinetic effects

Energy Demand for the CO_2 Stripping

		60w% Ionic Liquid in water **Equilibrium data from experiment**		**30w% MEA in water** **Calculation**	
Stages absorption		2	2	2	2
Stages desorption		4	8	4	8
Solvent loading inlet absorber	[$mol_{CO2}/mol_{Solvent}$]	0,65	0,68	0,242	0,242
Heat of absorption Dh_{abs}	[kJ/mol_{CO2}]	41,1	41,1	82	82
Solvent flow rate required	[m^3/ton_{CO2}]	36	40	14,5	14,5
Thermal heat requirement	**[GJ/ton_{CO2}]**	**4,18**	**3,43**	**4,78**	**4,12**

Laboratory Work Summery

- Ionic Liquids have a potential for post-combustion CO_2 capture
  - Energy demand is slightly better than MEA
  - Solvent Flow rate is higher than for MEA solution

- Drawbacks of ILs
  - High viscosity of pure ionic liquids
  - Slower kinetics
  - No operational experience for PCC
  - High price (production of small amounts)

Pilot Plant Testing

- Maintain operational experience
  - Long term stability (Degradation)
  - Corrosion
  - Absorption kinetics
  - Pilot plant performance

- Small pilot plant for post combustion CO_2 capture
  - Direct comparison of MEA and IL

CO_2 Pilot Plant

- Hard coal fired power plant
- Characteristics
  - V_{Gas} = 20 Nm³/h
  - d_{Abs} = 15 cm
  - d_{Des} = 12 cm
  - Fully instrumented
  - Fully balanceable

CO_2 Pilot Plant Testing

- Experiments with 30w% MEA solution
  - Stable conditions
  - Demonstrate the functionality of the pilot plant
  - Average capture rate of 85-90%
  - Energy demand ~ 4.2 GJ/t_{CO2}

- Ionic liquid tests are scheduled in October 2009

- Direct comparison of MEA and IL considering energy demand and capture performance at “real conditions”

Acknowledgement

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Thanks for your attention !!

David Wappel
david.wappel@unileoben.ac.at

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Latest Research on Fundamental Studies of CO_2 Capture Process Technologies

Raphael Idem, Paitoon Tontiwachwuthikul & Don Gelowitz
Faculty of Engineering
University of Regina, Regina
CANADA

www.uregina.ca

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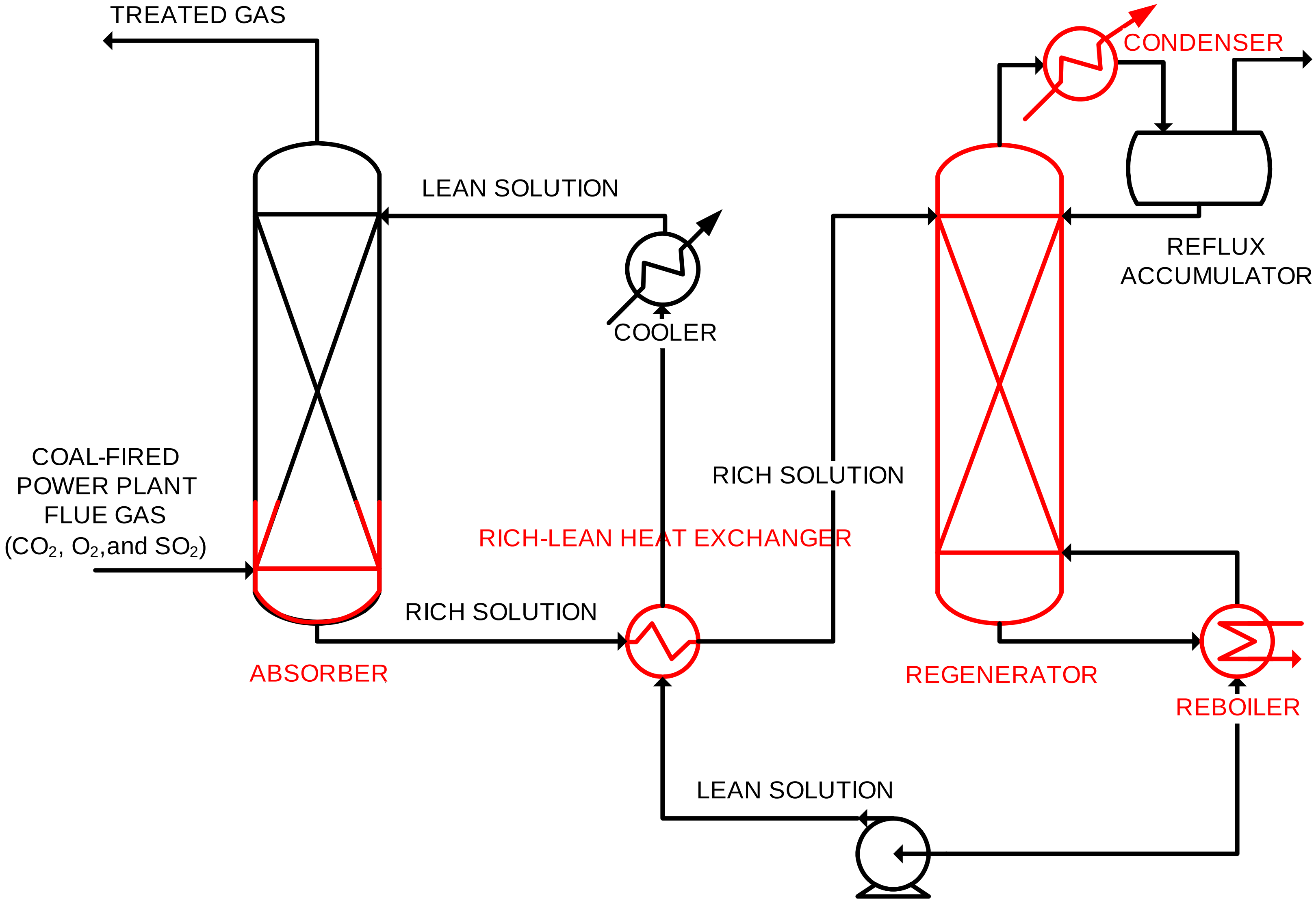
Presentation Outline

- Introduction
- Corrosion Studies
- Kinetic Studies
- Heat Duty Reduction
- Summary

Introduction



TREATED GAS

LEAN SOLUTION

CONDENSER

REFLUX ACCUMULATOR

COOLER

COAL-FIRED
POWER PLANT
FLUE GAS
(CO_2, O_2,and SO_2)

RICH SOLUTION

RICH-LEAN HEAT EXCHANGER

RICH SOLUTION

ABSORBER

REGENERATOR

REBOILER

LEAN SOLUTION

Corrosion Studies

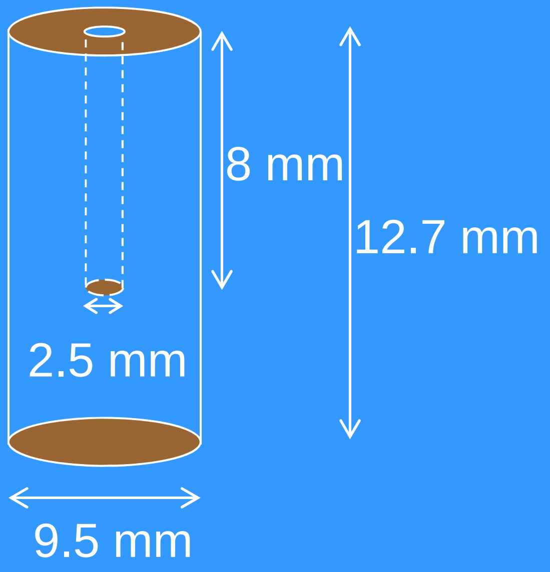
- Introduction & Background
- Research objectives
- Experiments
- Results & Discussion

Objectives

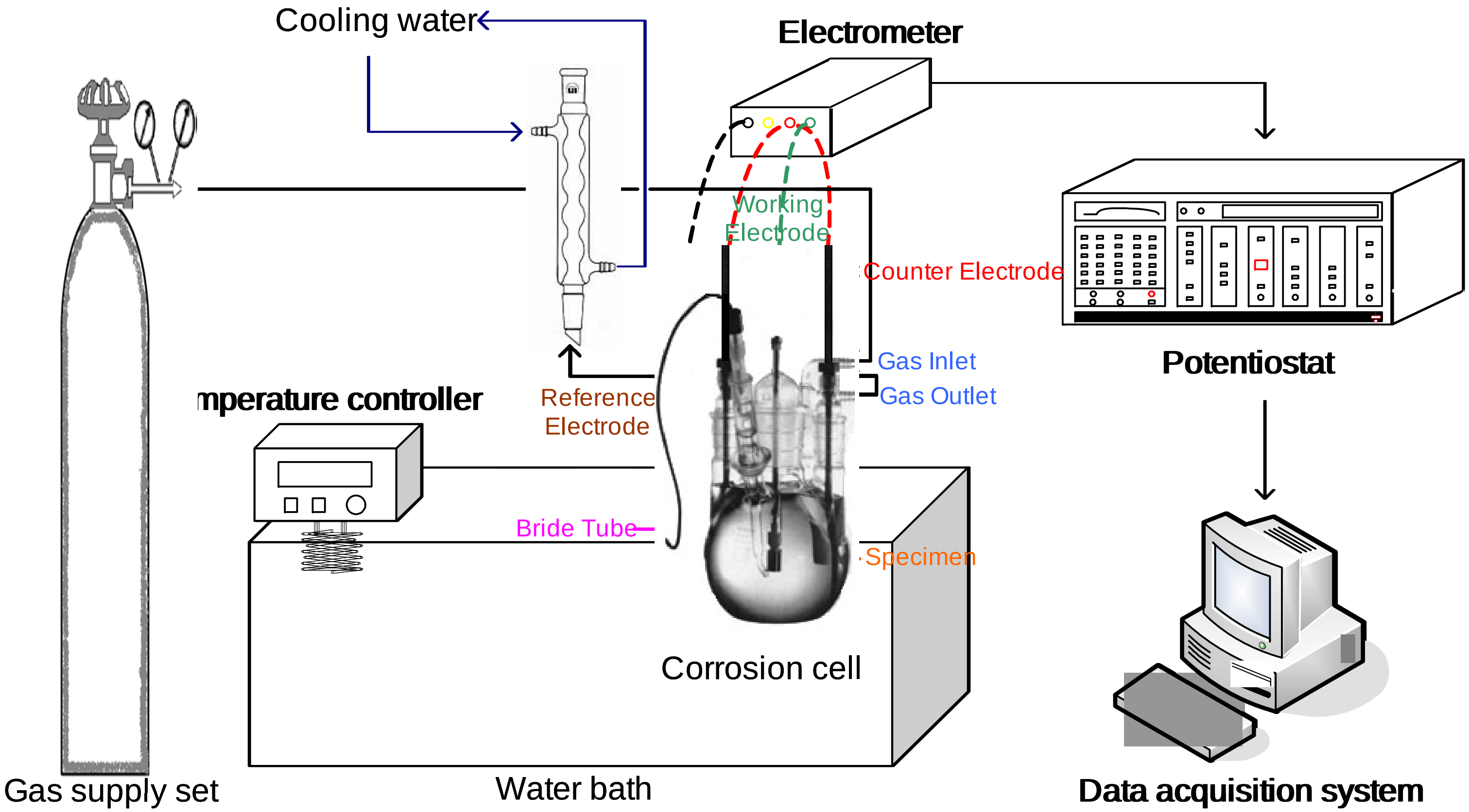
- To study the effect of operating parameters on the corrosion rate of carbon steel in MEA-H2O-CO2-O2-SO2 system
- To screen corrosion inhibitors for carbon steel in MEA-H2O-CO2-O2-SO2 system

Materials

- Specimens
  - Stainless steel-430
    - Validation of experiment (ASTM G-5)
  - Carbon steel-1020

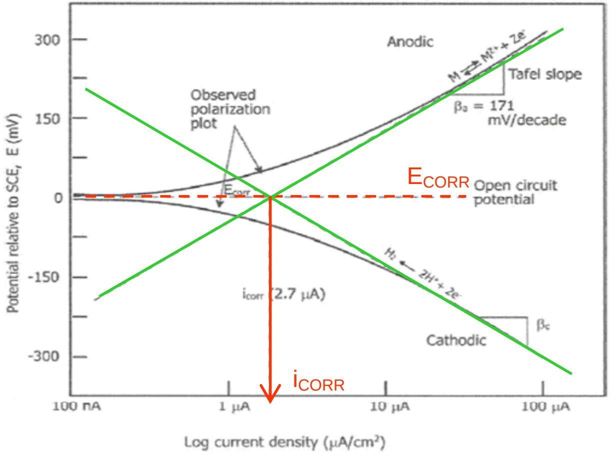


Experimental Setup

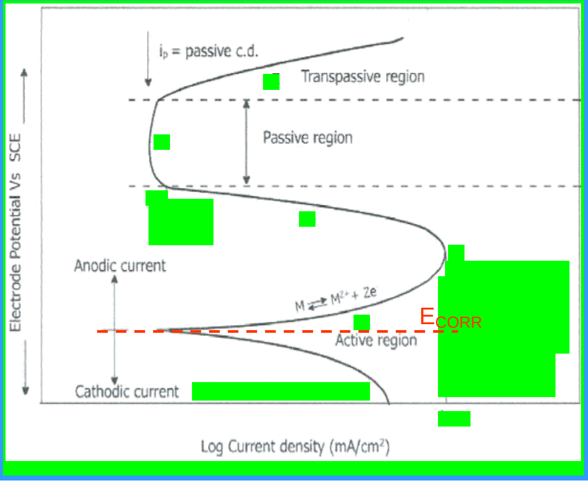


Corrosion analysis

Tafel Plot



Potentiodynamic polarization



β_A = Anodic Tafel Constant (mV/decade)

β_C = Cathodic Tafel Constant (mV/decade)

i_{CORR} = Corrosion Current (A)

Corrosion rate (mpy) = 0.13 i_{CORR} (E.W.) / (A)(d)

E.W. = equivalent weight of specimen
A = Area of specimen (cm^2)
d = density (g/ml)

The passivation behavior of the specimen in anode side

- Film formation

Experimental conditions

- Oxygen concentration in feed gas
  - 0 – 100%
- SO_2 concentration in feed gas
  - 0 – 204 ppm
- CO_2 loading
  - 0 – 0.5 mol/mol MEA
- MEA concentration
  - 1 – 7 kmol/m3
- Temperature
  - 303 - 353

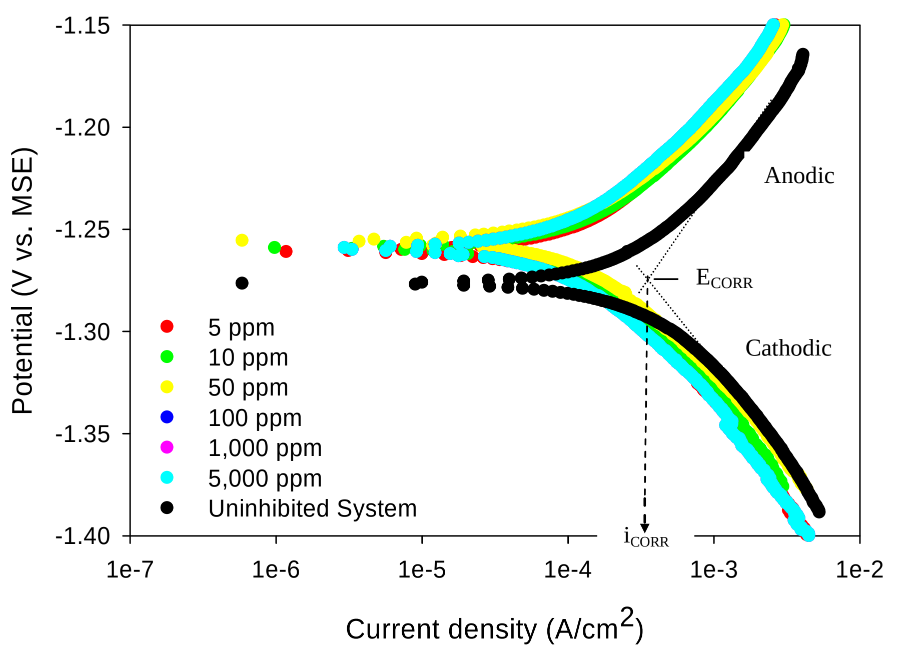
Corrosion Rate

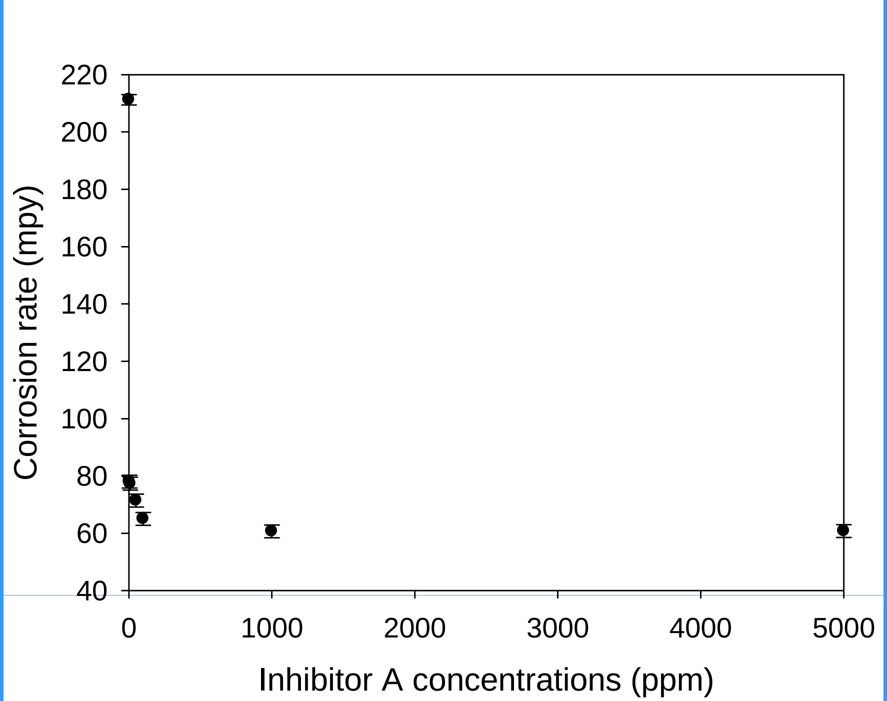
- All the parameters had effect on corrosion rate
- $[CO_2] >> [MEA] > [SO_2] > [O_2]$
- Corrosion rate increased with temperature had

Inhibitor Test Conditions

- MEA concentration
  - 7 kmol/m3
- Temperature
  - 353K
- CO_2 loading
  - 0.5 mol/mol MEA
- O_2-SO_2-N_2 gas mixture
  - 6%O_2 - 204ppm SO_2, (N_2 balance)
- Inhibitors: A, B, C, D, E, AD, BD. CD
- Inhibitor concentration
  - 0 – 10000 ppm

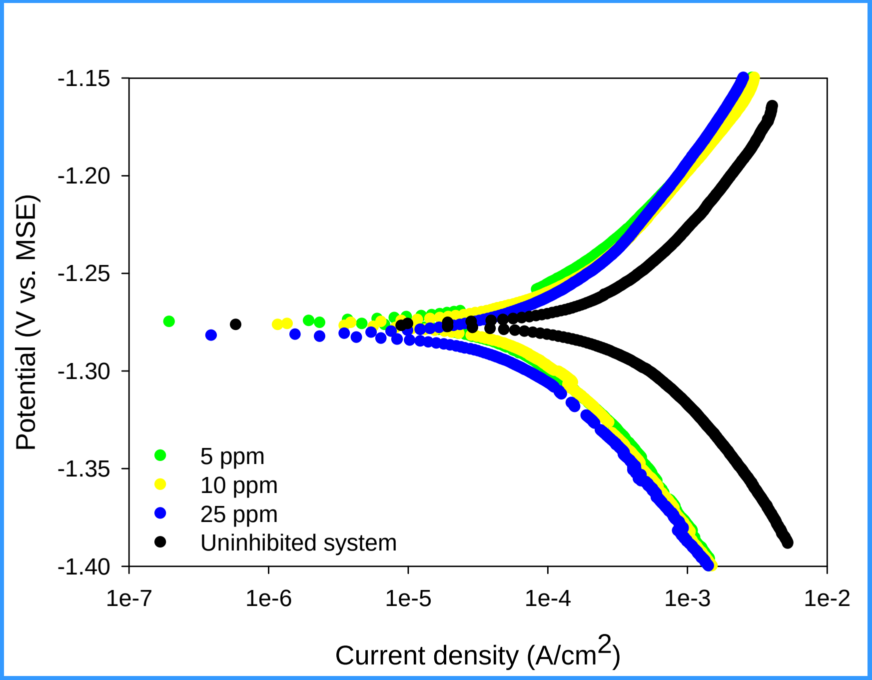
Inhibitor A

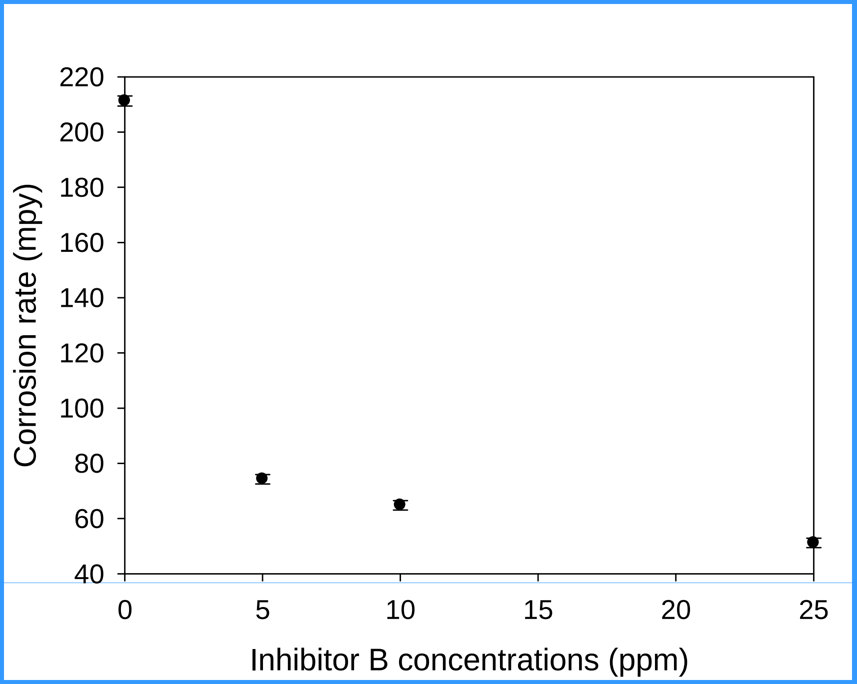




- The polarization curve of the inhibited system shows more suppression at anodic site indicating formation of dense protective film on the metal surface.
- The corrosion rate decreases as increasing the inhibitor A concentration from 0-1,000 ppm. Higher concentrations, 1000 – 5000 ppm yield no further reduction in corrosion rate.
- The maximum inhibition efficiencies of A is 71%.

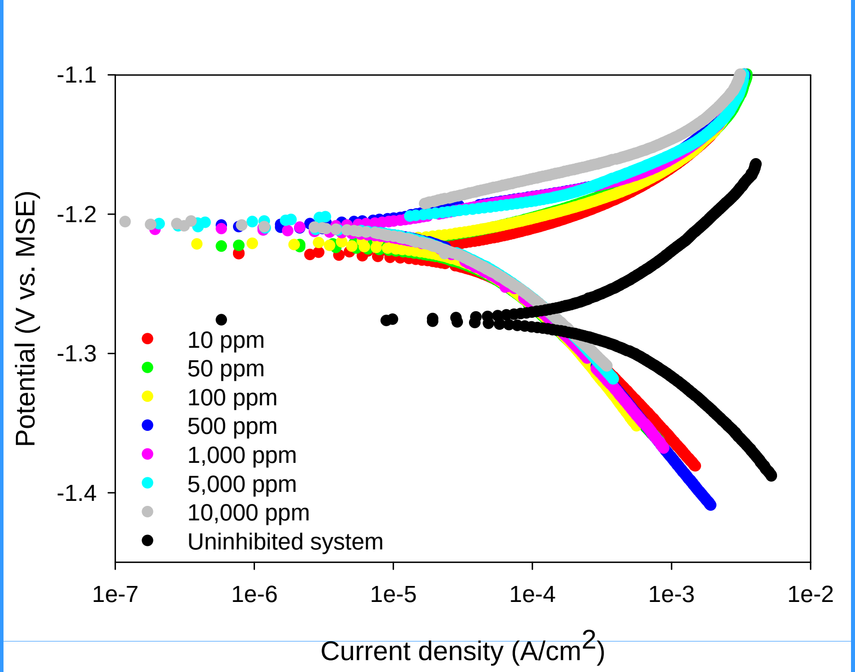
Inhibitor B

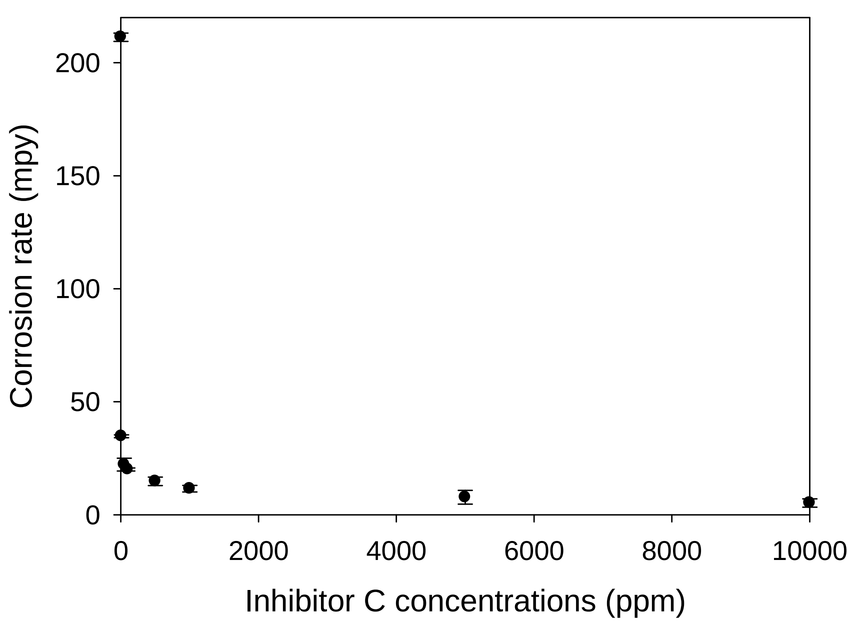




- The polarization curve of the inhibited system shows suppression at both anodic and cathodic site.
- The corrosion rate decreases as increasing the inhibitor B concentration from 0 - 25 ppm. Use of higher concentrations is limited due to the inhibitor solubility.
- The maximum inhibition efficiencies of B is 76%.

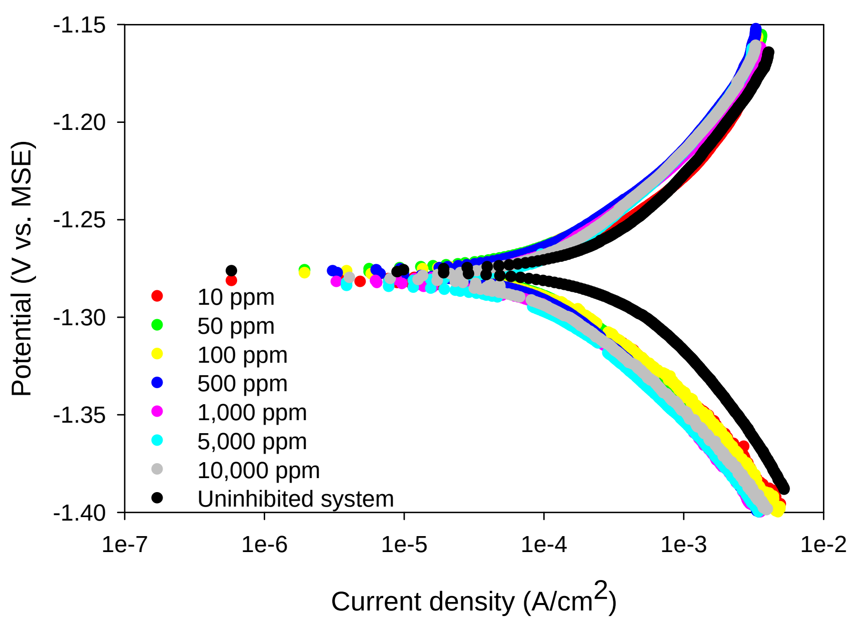
Inhibitor C

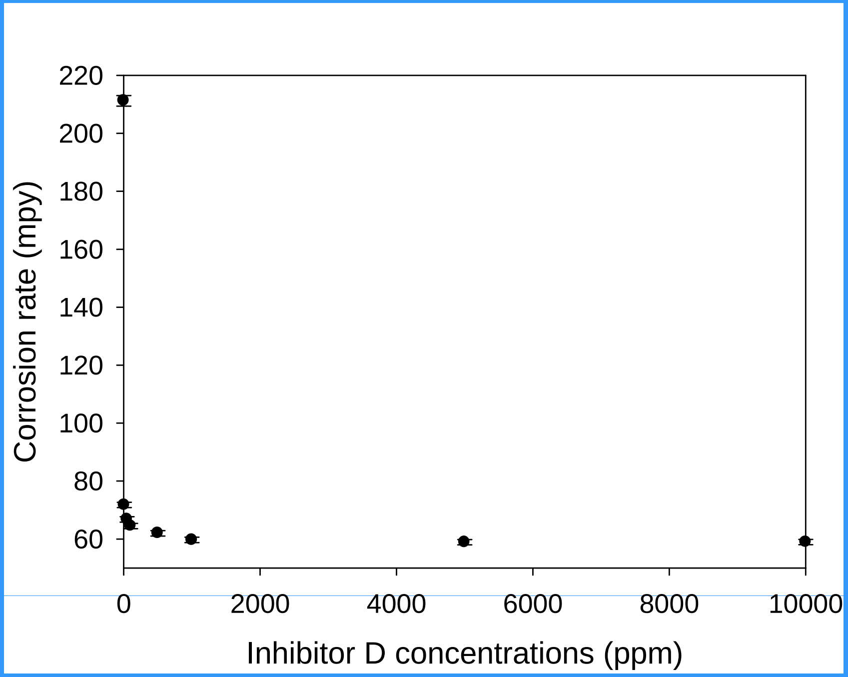




- The polarization curve of the inhibited system shows more pronounced effect at anodic site.
- The corrosion rate decreases as increasing the inhibitor C concentration from 0 - 1000 ppm. No further significant reduction in rate is observed at higher concentrations, 1000 – 10000 ppm. The optimum concentration is then considered at 1000 ppm.
- The maximum inhibition efficiencies of C is 95%.

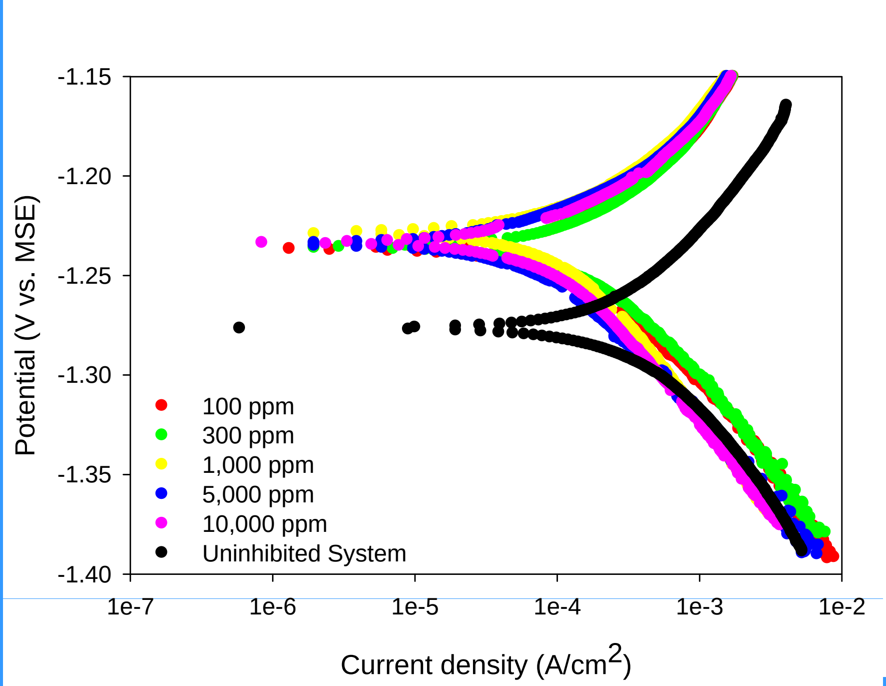
Inhibitor D

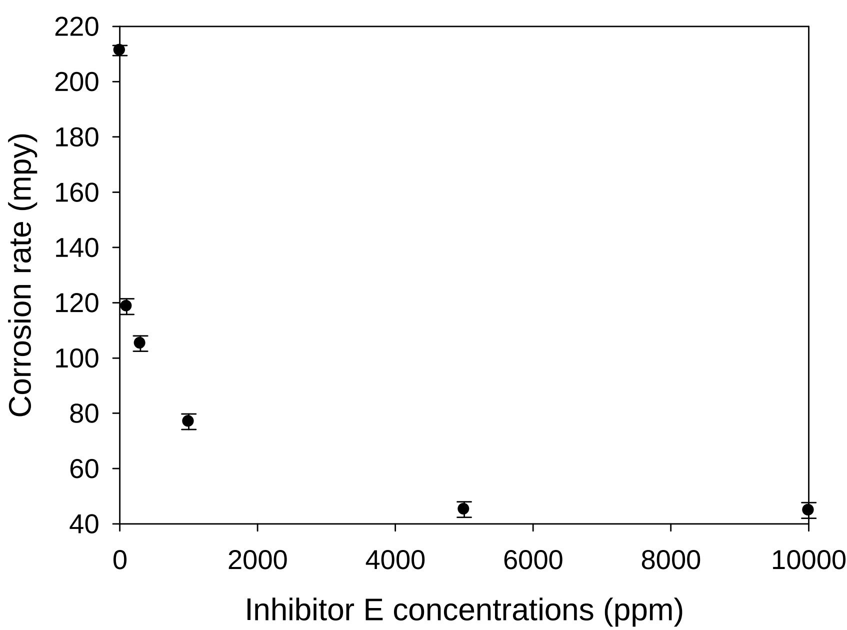




- The polarization curve of the inhibited system shows more significant effect at cathodic site in which H^+ is taken up by inhibitor D.
- The corrosion rate decreases as increasing the inhibitor D concentration from 0 - 1000 ppm. No further significant reduction in rate is observed at higher concentrations, 1000 – 10000 ppm. The optimum concentration is then considered at 1000 ppm.
- The maximum inhibition efficiencies of D is 72%.

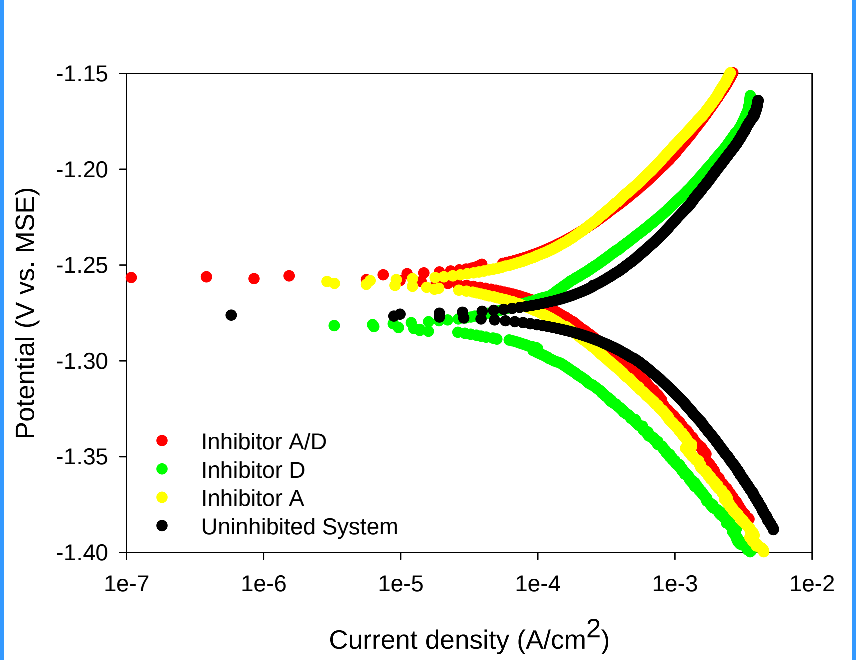
Inhibitor E

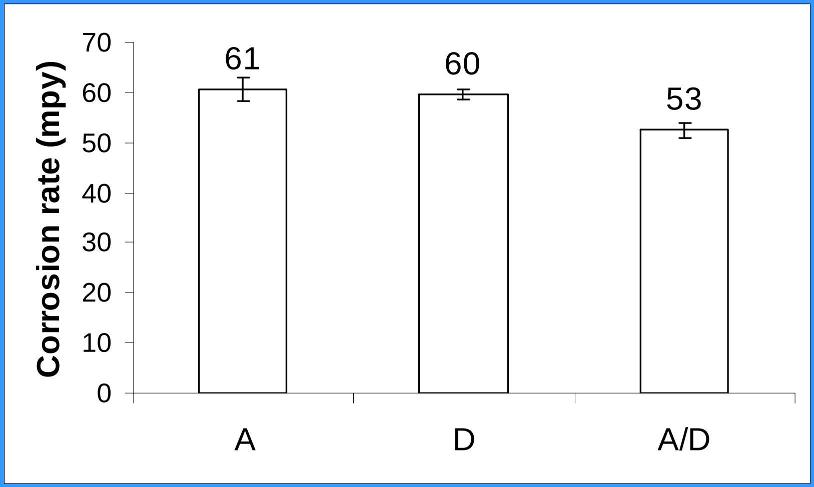




- The polarization curve of the inhibited system shows more significant effect at anodic site.
- The corrosion rate decreases as increasing the inhibitor E concentration from 0 - 5000 ppm. No further significant reduction in rate is observed at higher concentrations, 5000 – 10000 ppm. The optimum concentration is then considered at 5000 ppm.
- The maximum inhibition efficiencies of E is 79%.

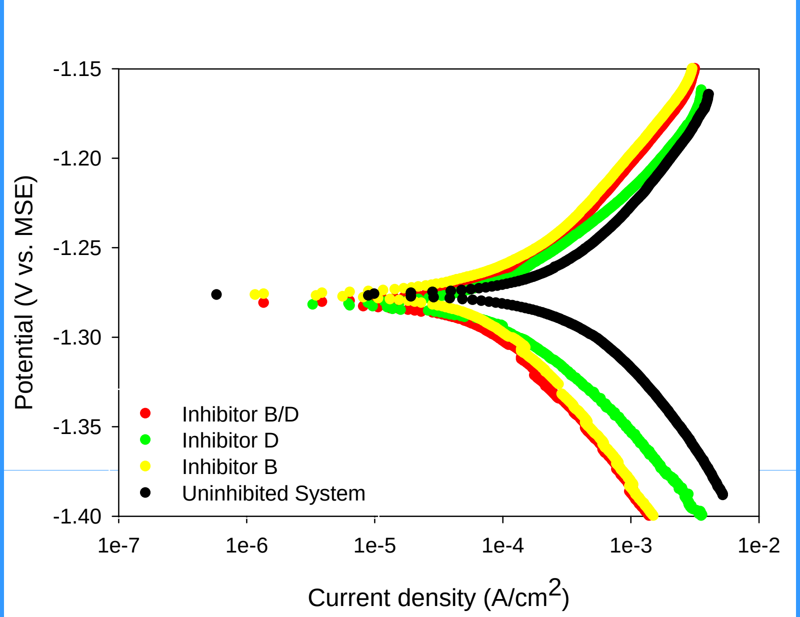
Inhibitor A/D

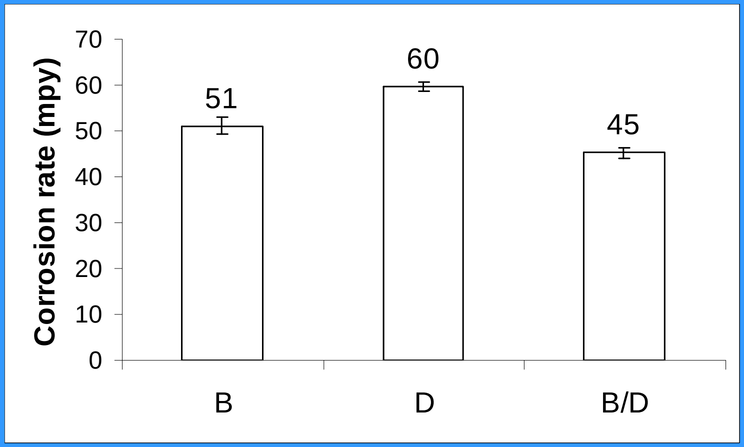




- The inhibitor A/D decrease the corrosion rate to 52 mpy corresponding to 75% inhibition efficiency, which is slightly more effective than the single inhibitor A or D alone

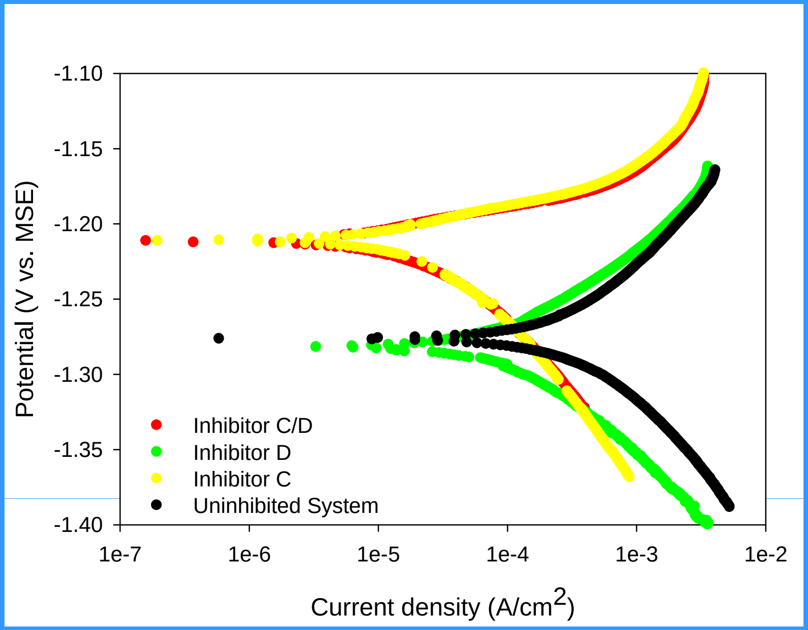
Inhibitor B/D

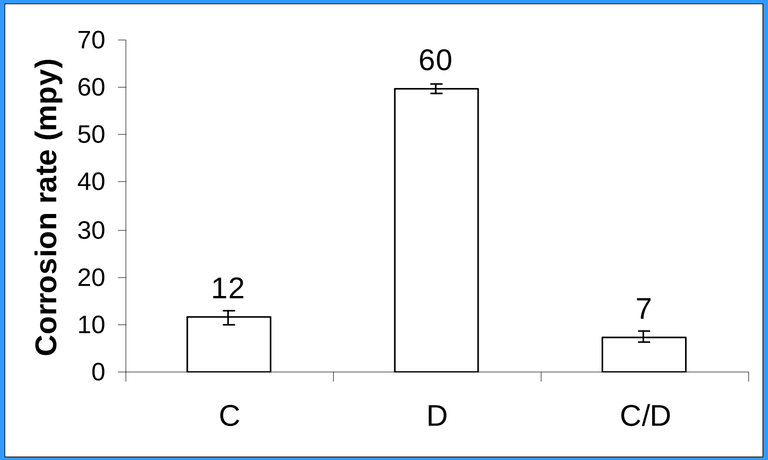




- Inhibitor B/D yielded the corrosion rate of 45 mpy and 79% of inhibition efficiency which is more effective than its parent inhibitors, where the inhibition efficiencies of B and D are 76 and 72% respectively.

Inhibitor C/D





- Inhibitor C/D yielded the corrosion rate of 7 mpy and 96% of inhibition efficiency where C and D alone gave 95 and 72% respectively.

Summary

- Inhibitor A, B, C, D, and E at the optimum concentration of 1,000, 25, 1,000, 1,000 and 5,000 ppm were respectively found to be the most effective in minimizing the corrosion of carbon steel in MEA-H_2O-CO_2 –O_2-SO_2 system, which give the inhibition efficiencies of 71, 76, 95, 72, and 79%, respectively.

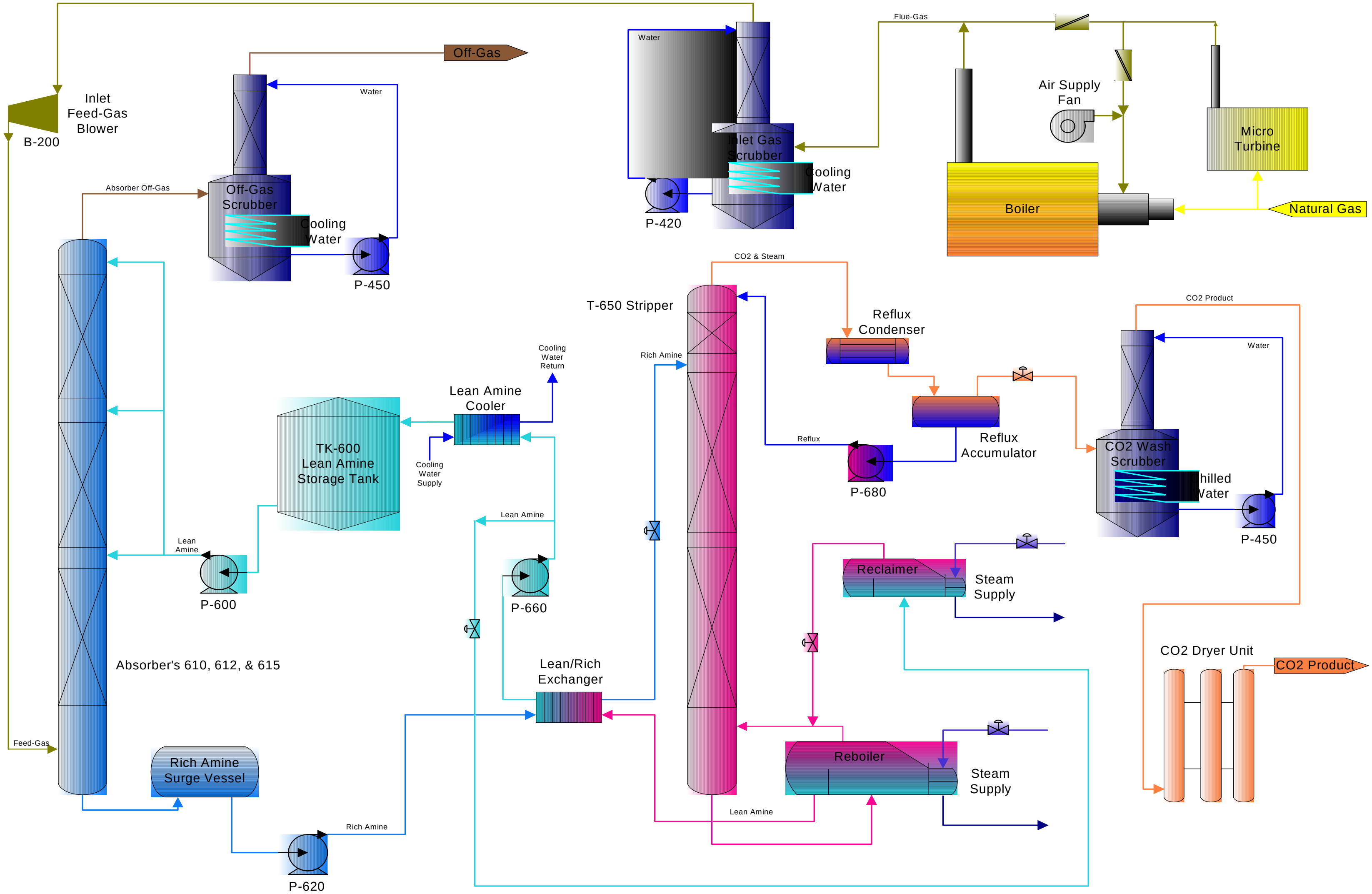
- Inhibitor A, B, C, and E minimize corrosion by adsorption on iron surface to form a dense film while inhibitor D eliminates $H^{+,}$ the corrosive species in the solution, to reduce corrosion.

- Blends of A/D, B/D, and C/D slightly enhanced the inhibitive effect of their individual compounds.

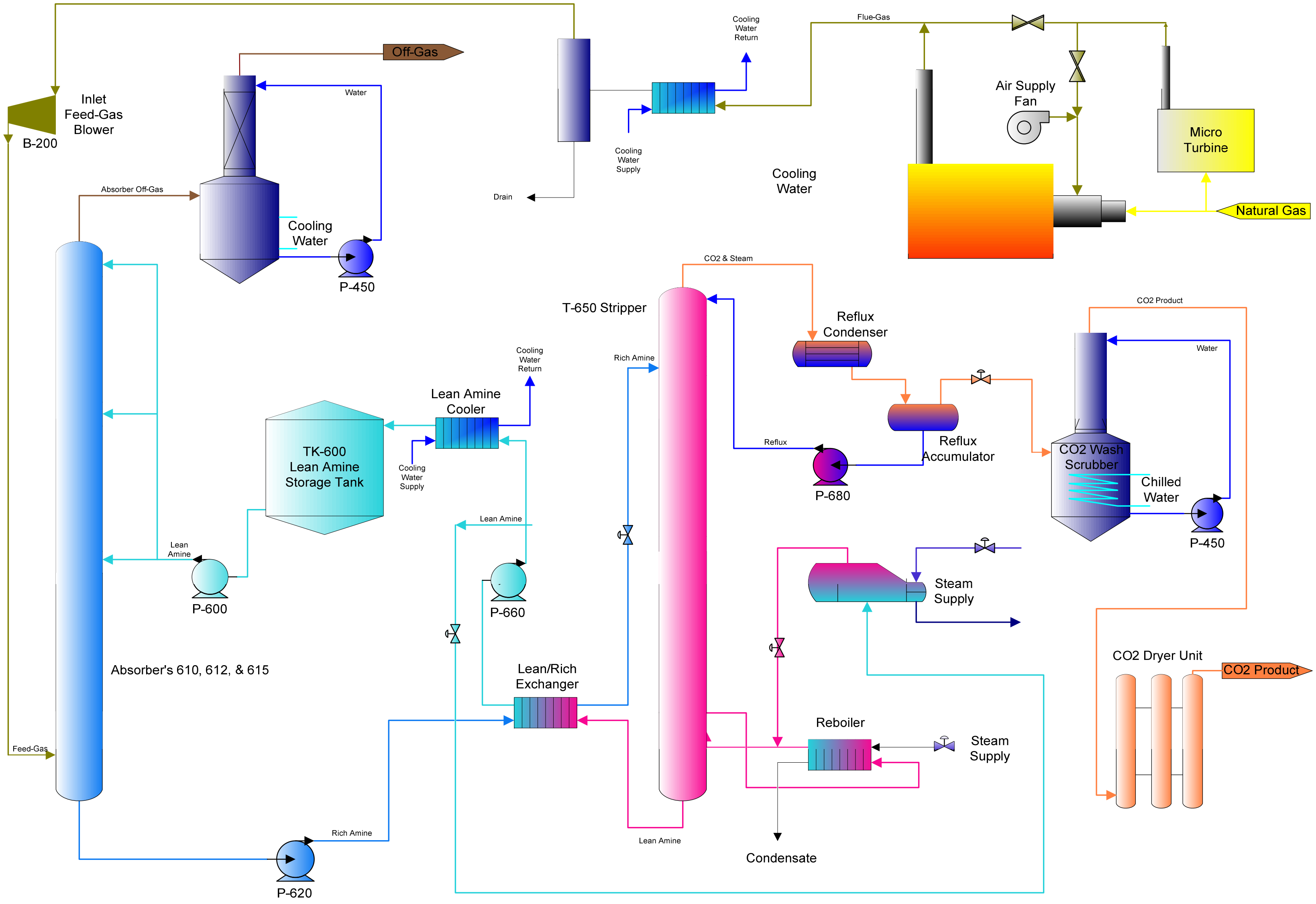
Heat Duty Reduction

Conventional Process Flow Diagram of UR Multipurpose CO_2 capture Plant

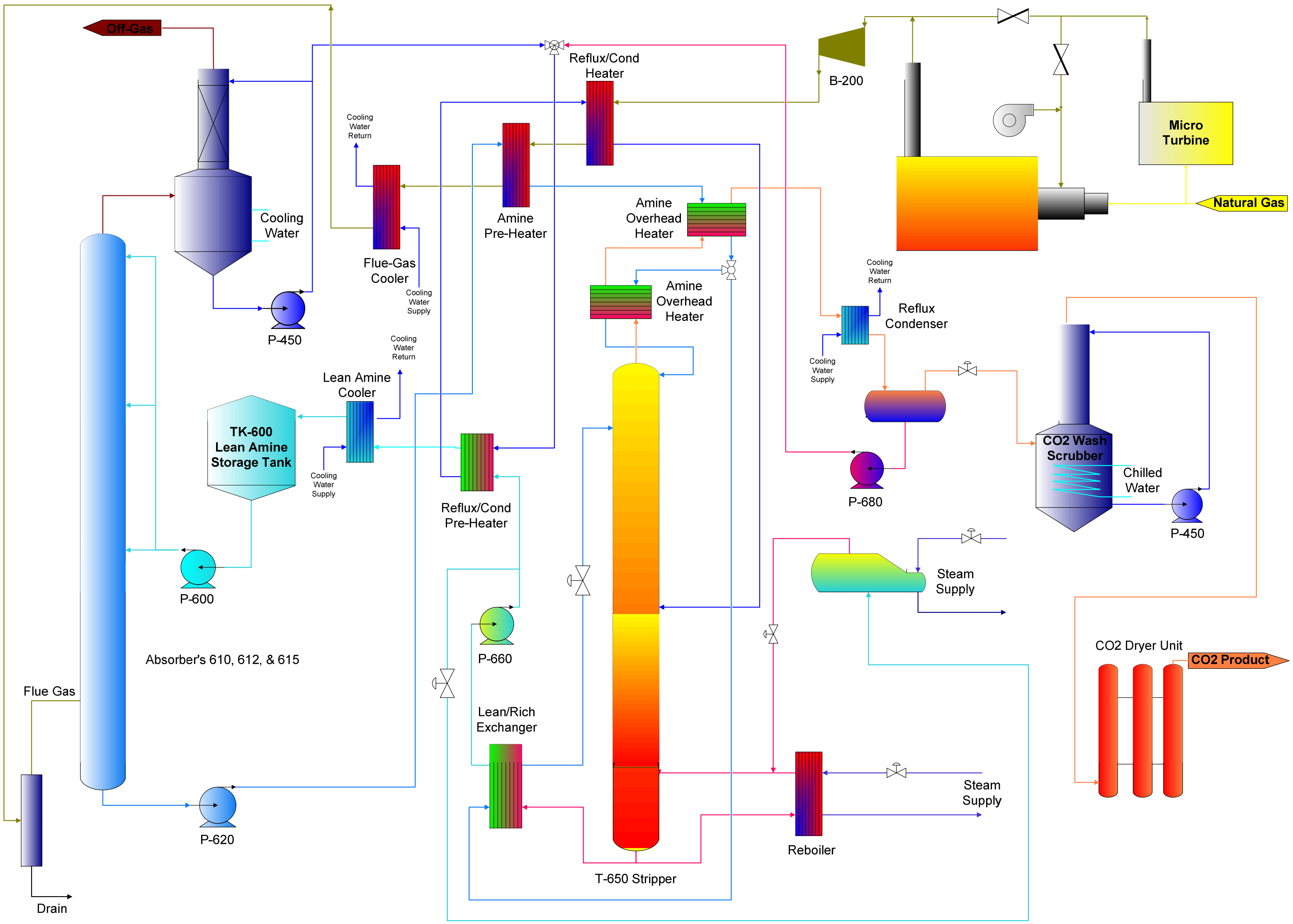
(Kettle Reboiler)



Process Flow Diagram of the Optimized UR Multipurpose CO$_2$ capture Plant (Plate Exchanger Reboiler)

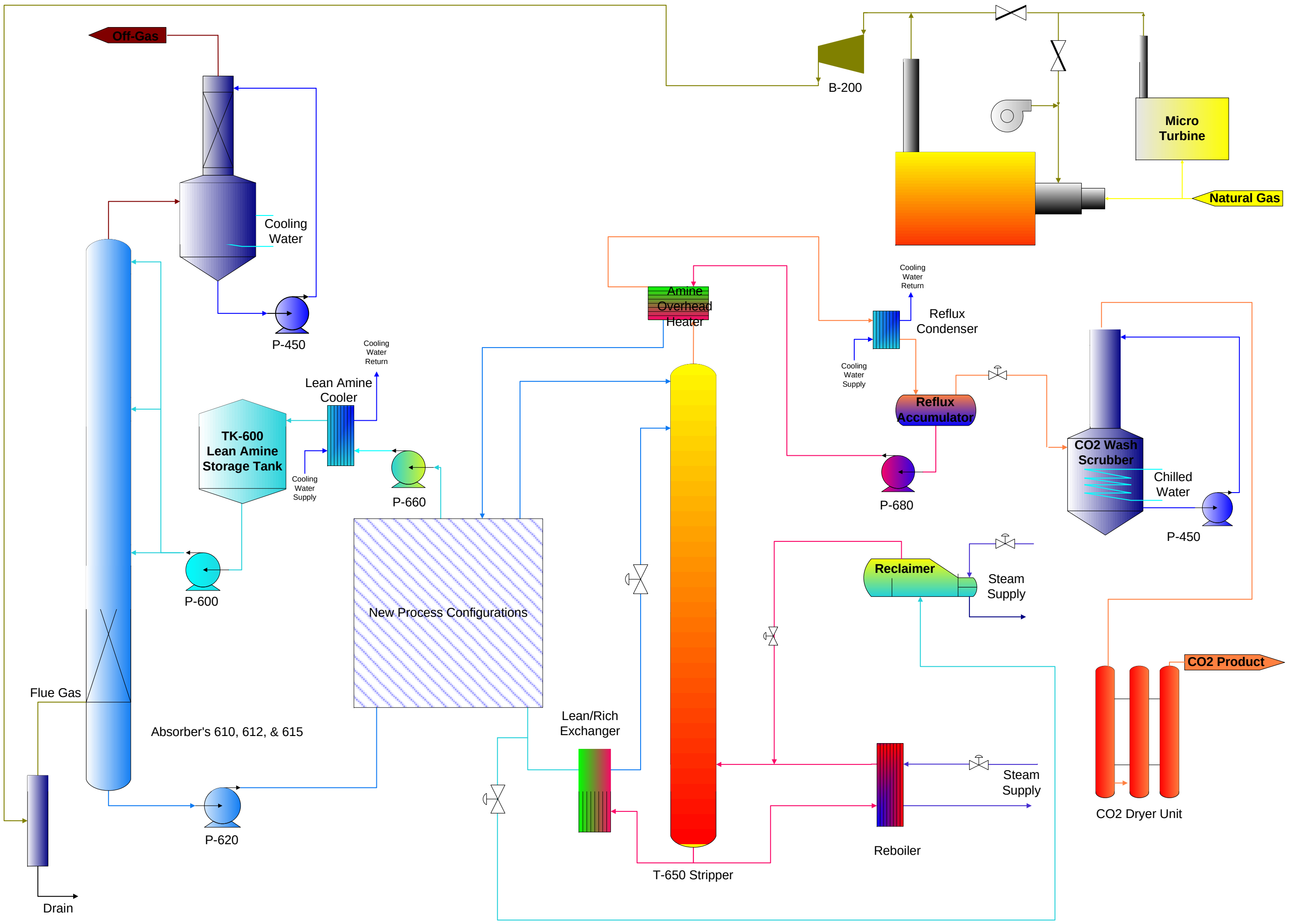


Process Flow Diagram of the Optimized Process Configuration of UR Multipurpose CO_2 capture Plant



Process Flow Diagram
for Advanced Process Configuration

UR CO_2 PILOT PLANT PROCESS FLOW DIAGRAM



Advances In CO_2 Capture Technology By University of Regina (ITC) – Selected Cases

	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	
Solvent	MEA	RS-2	MEA	RS-1	MEA	RS-2	RS-2	RS-3	
Configuration	Conventional	Conventional	Optimized	Optimized	Process Integration	Process Integration	Advanced Process Integration	Advanced Process Integration	
Method	Pilot Plant	Pilot Plant	Pilot Plant	Pilot Plant	Pilot Plant	Pilot Plant	Simulation	Simulation	
Inlet Gas Composition	10.8	11.0	8.0	8.0	12.2	12.1	10.8	10.8	%
Absorber Efficiency	91.3	90.5	90.2	90.6	93.1	91.0	90.2	90.0	%
CO2 Production	0.84	0.72	0.56	0.56	0.58	0.58	0.91	0.91	tonne/day
Steam Rate	81.9	60.7	33.0	32.0	32.9	26.9	29.0	27.0	kg/hr
Heat Duty	5.08	4.25	2.99	2.85	2.58	2.07	1.79	1.66	GJ/tonne
Steam Duty	2.35	2.02	1.43	1.35	1.21	0.98	0.80	0.74	kg steam/kg CO2
Lean Loading	0.2121	0.2495	0.2280	0.1780	0.2270	0.1835	0.3237	0.3592	mol/mol
Rich Loading	0.3967	0.3958	0.4290	0.4520	0.5024	0.4252	0.4793	0.5689	mol/mol

Notes:

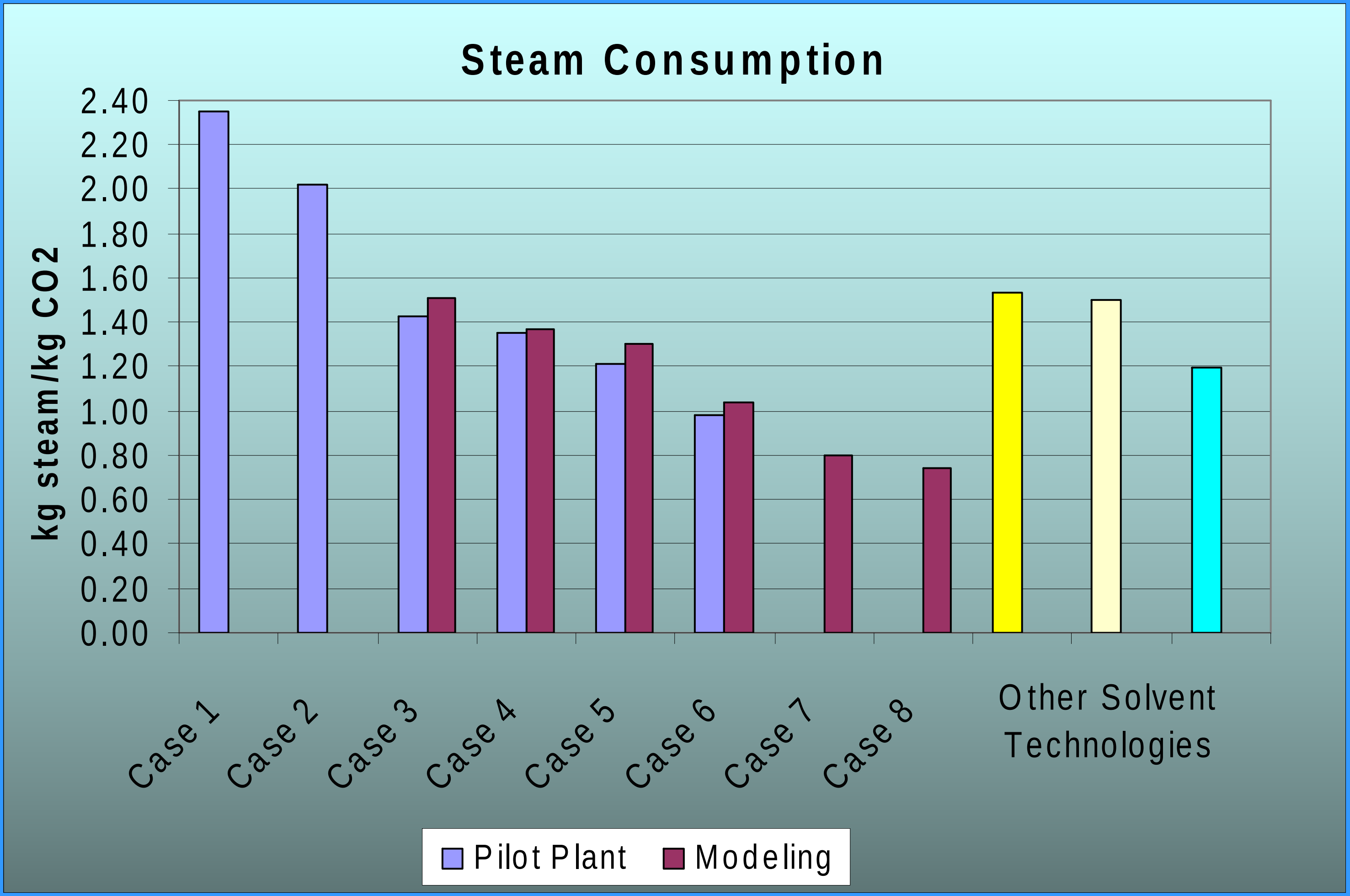
Conventional - Kettle Reboiler

Optimized - Plate Exchanger upgrade

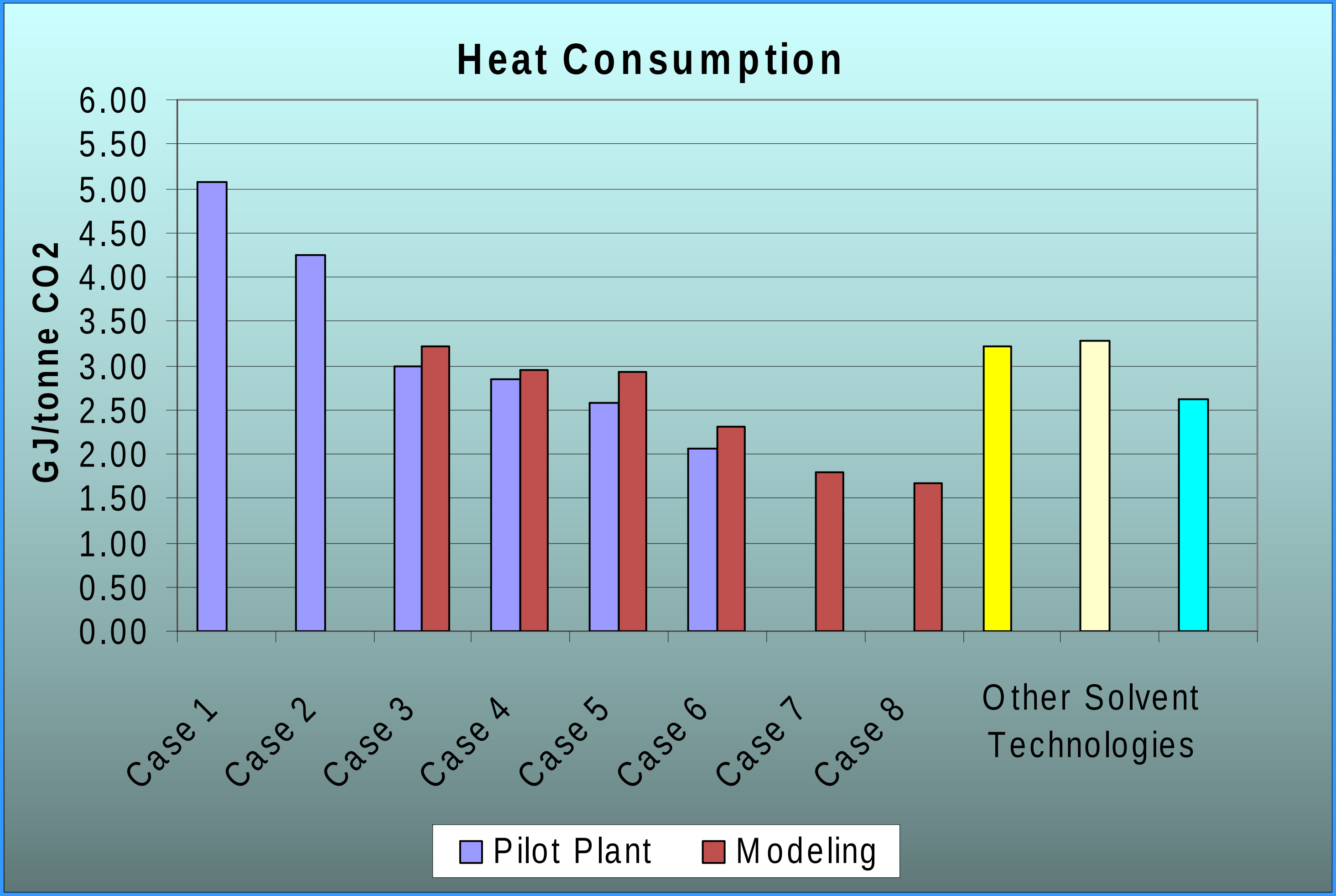
Process Integration - Modified process configuration

Advanced Process Integration - Advanced process configuration

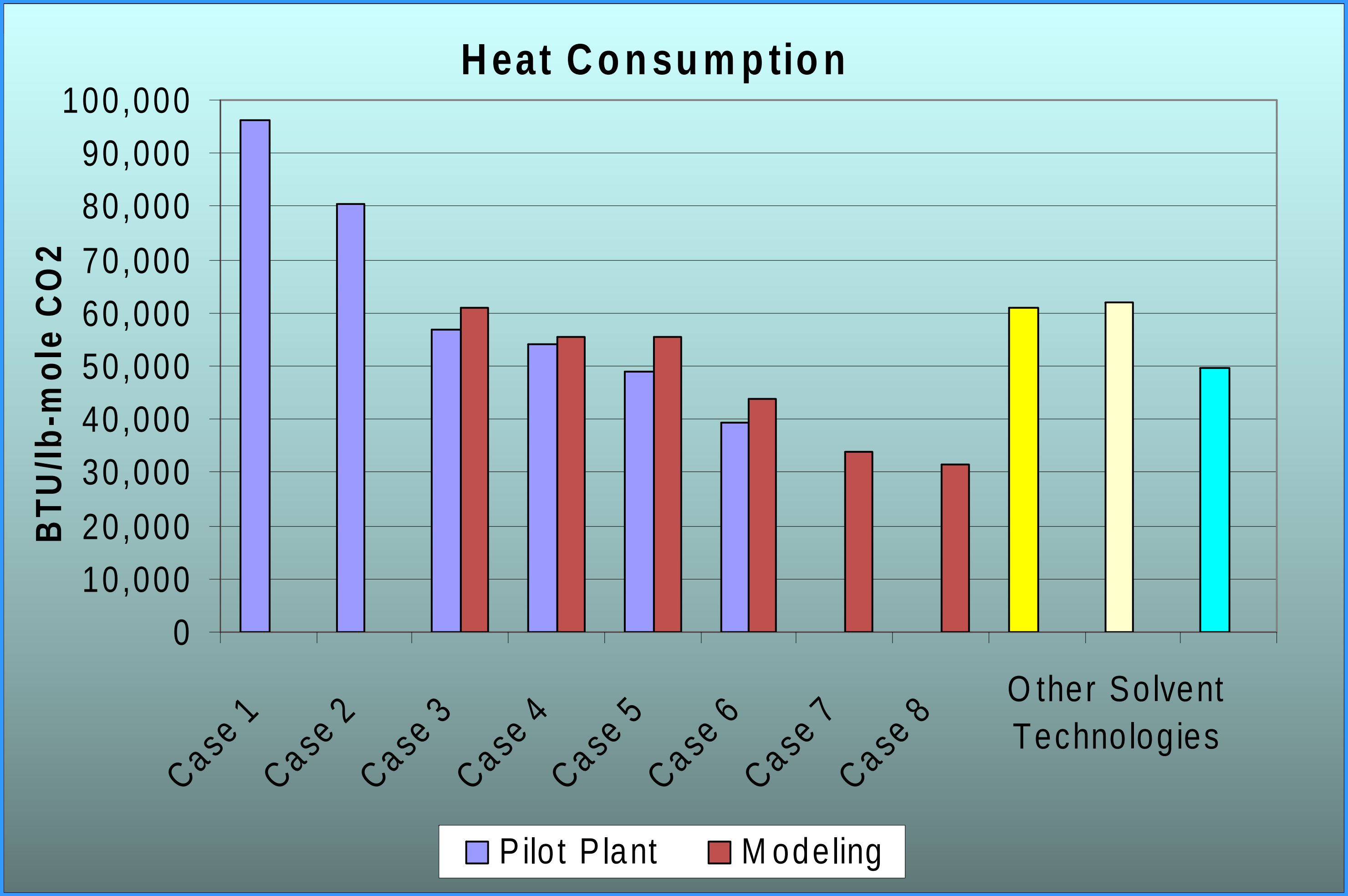
Advances In CO_2 Capture Technology By University of Regina (ITC)



Advances In CO_2 Capture Technology By University of Regina (ITC)



Advances In CO_2 Capture Technology By University of Regina (ITC)



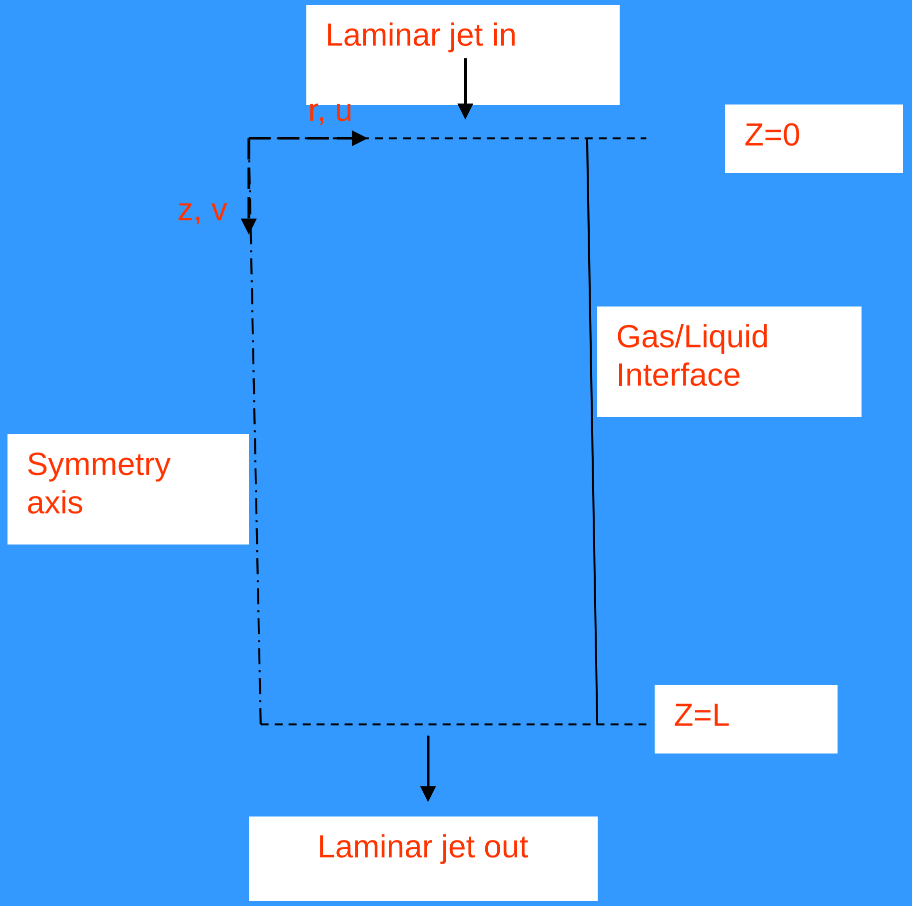
Summary

- The steam consumption for solvent regeneration can be reduced to <0.75 kg steam/kg CO_2 produced (<1.6 GJ/tonne) based on:
  - 90% Absorber Efficiency/Recovery
  - Energy Efficient Solvent
  - Process Optimization
  - Advanced Process Configuration Optimization

Kinetics of CO_2 Absorption

- Objectives
  - 2-Dimensional Modeling for laminar jet
  - Species Concentration profile along the jet

Schematic diagram of the Laminar Jet Absorber



Laminar jet in

Z=0

Gas/Liquid Interface

Symmetry axis

Z=L

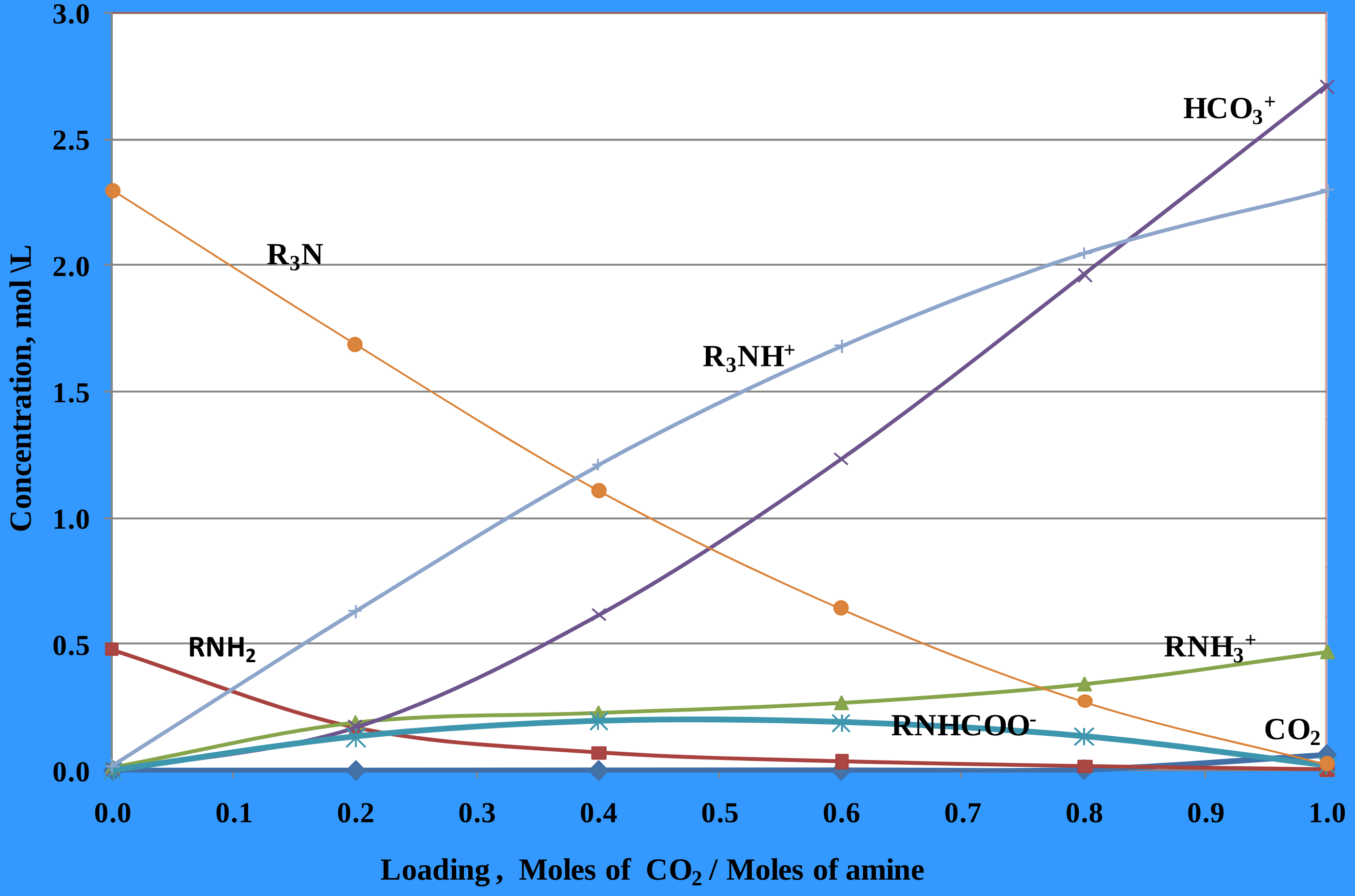
Laminar jet out

2-D Kinetics Model for MDEA-MEA Solution Using a Laminar Jet Absorber

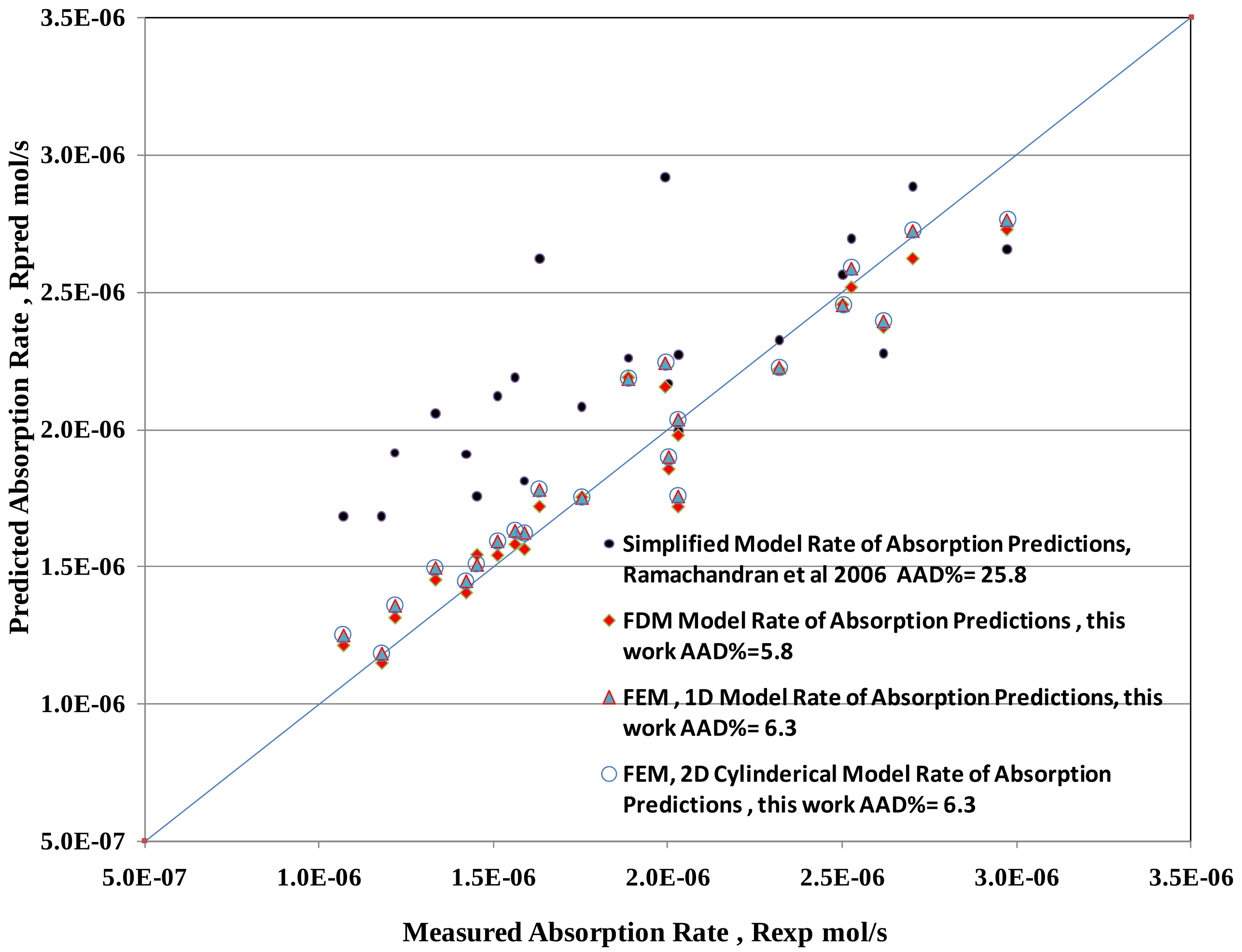
$$D\left[\frac{\partial^2 C}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}+\frac{\partial^2 C}{\partial z^2}\right]=vz\frac{\partial C}{\partial z}+\frac{\partial C}{\partial t}+R$$

- C1= [CO2],
- C2= [RNH2],
- C3= [RNH3+],
- C4= [HCO3-],
- C5= [OH -],
- C6= [CO-3],
- C7= [H+],
- C8= [RNHCOO-],
- C9 = [R3N]
- C10 = [R3NH+].

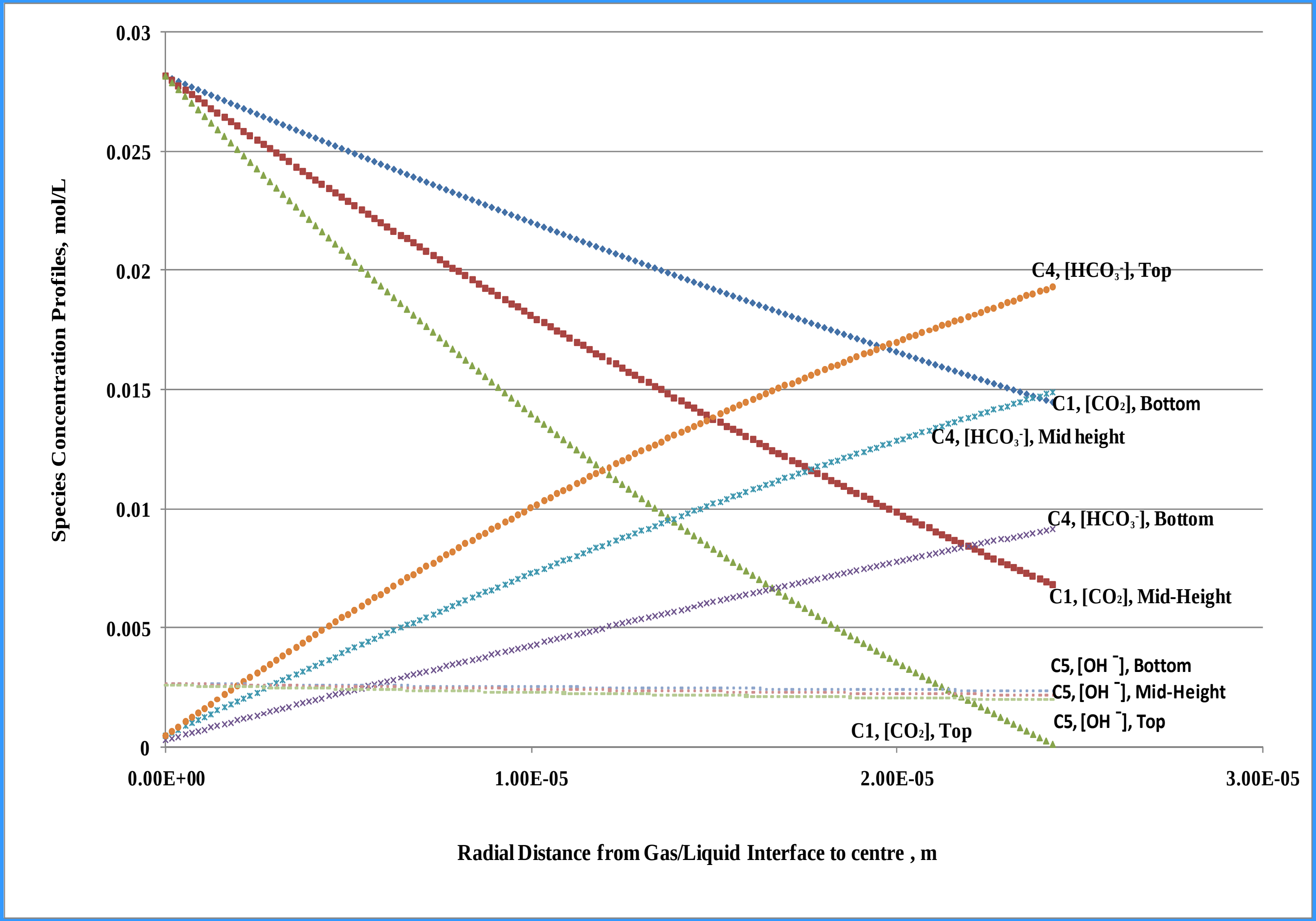
Liquid –phase speciation and concentration in aqueous MDEA-MEA (27/3wt. ratio) solution as a function of CO_2 loading (α) at 313K



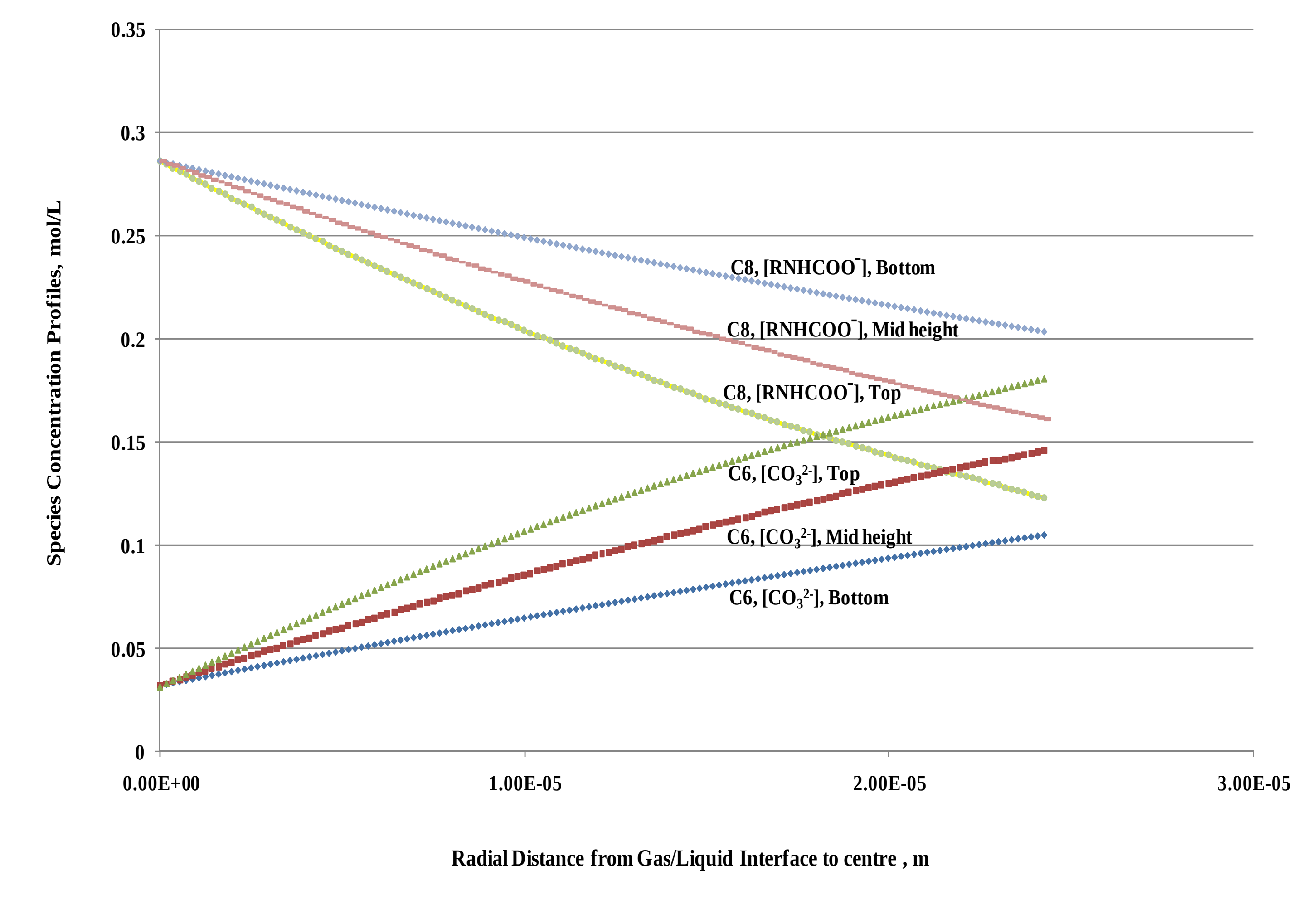
Parity Chart for comparison of all the kinetics model solved by FDM, FEM, and the simplified models for loaded 30 wt% MDEA_ MEA solution (temp. range of 298-333K).



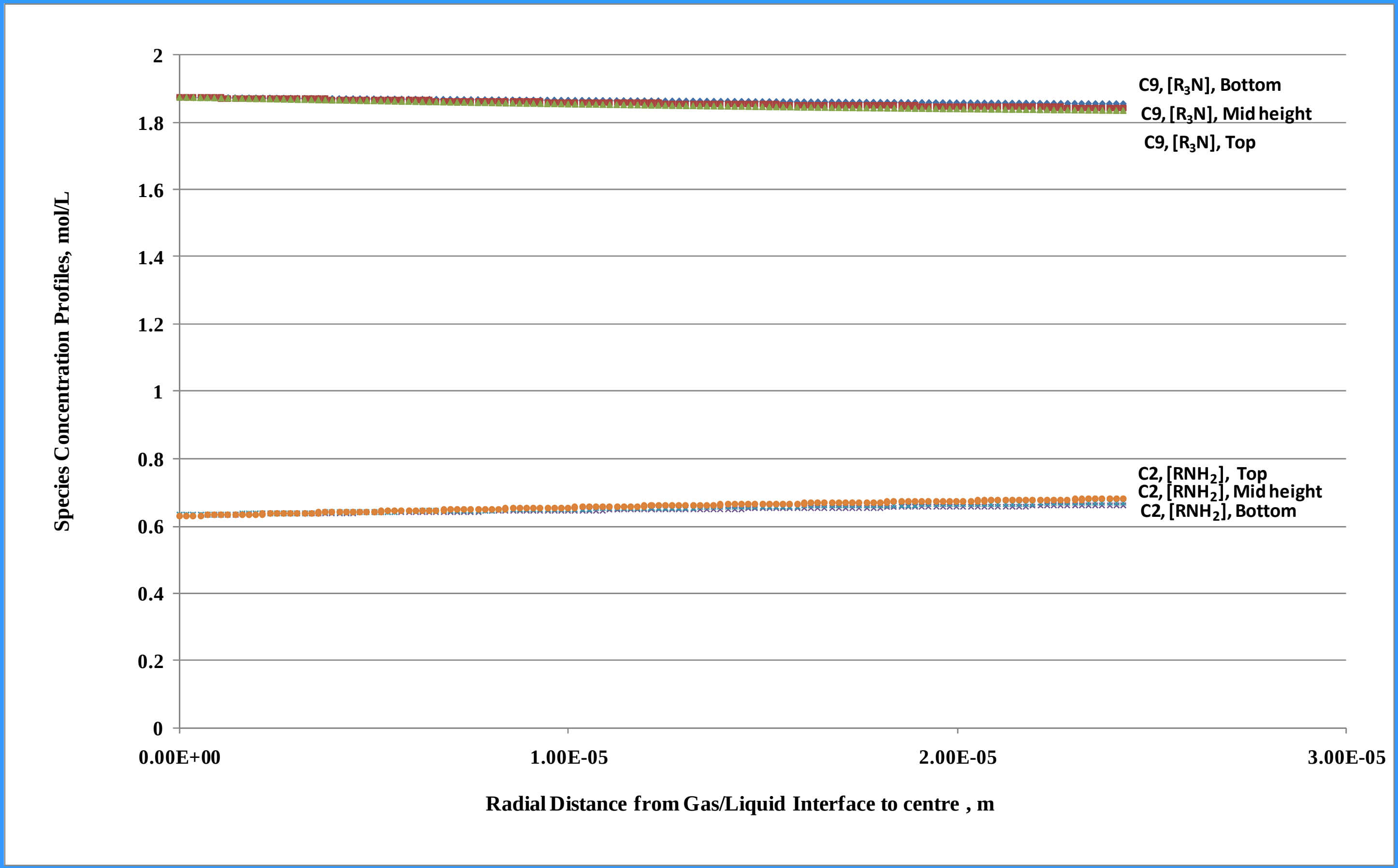
Radial concentration profiles for species C1, C4, and C5 based on 2-D comprehensive rate/kinetics model for top, mid height and bottom of laminar jet (aqueous solution of MDEA-MEA wt ratio of 23/7; CO_2 loading (α) of 0.1012 mol CO_2/mol amine at 298K)



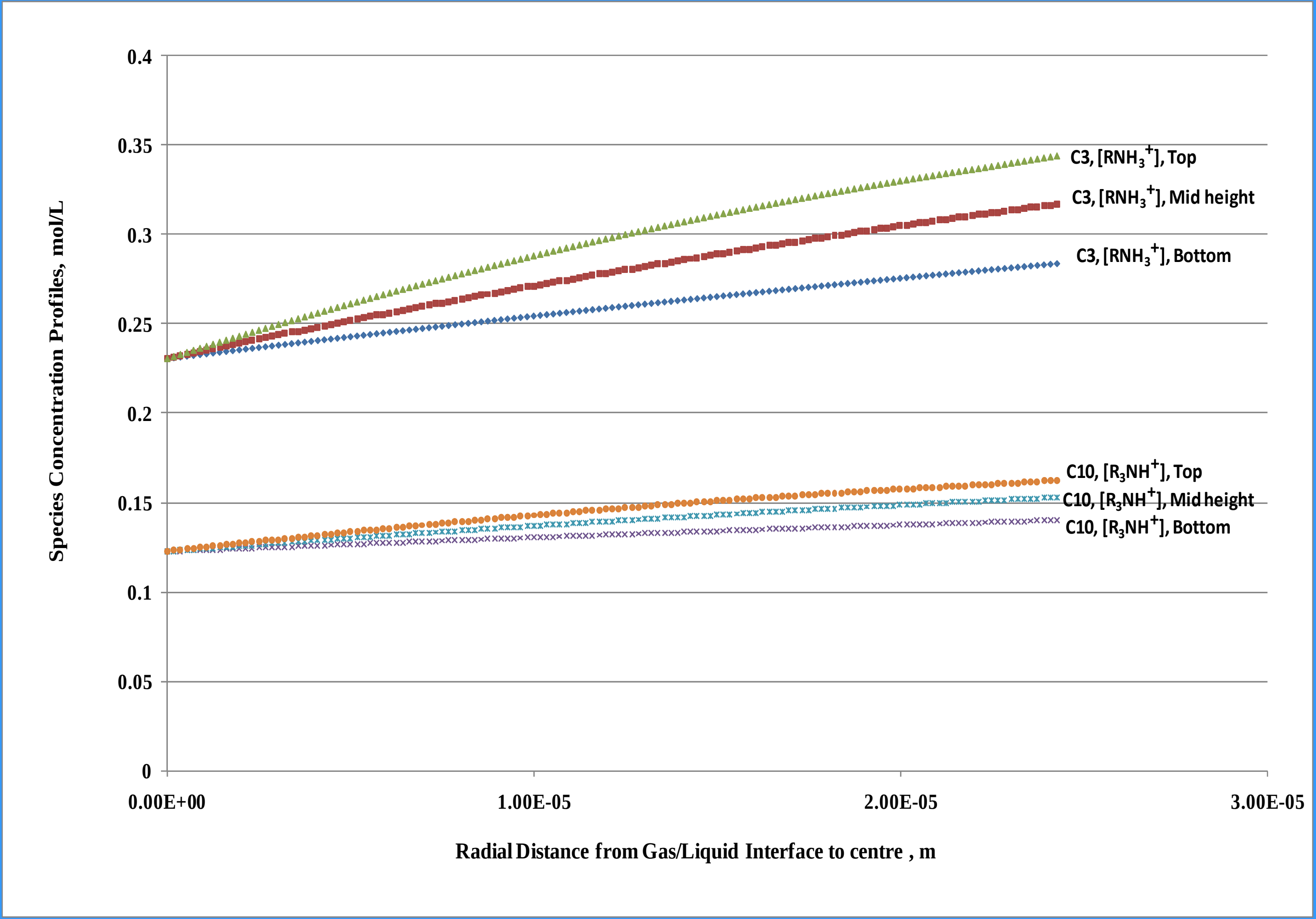
Radial concentration profiles for species C6 and C8 based on 2-D comprehensive rate/kinetics model for top, mid height and bottom of laminar jet (aqueous solution of MDEA-MEA wt ratio of 23/7; CO_2 loading (α) of 0.1012 mol CO_2/mol amine at 298K)



Radial concentration profiles for species C2 and C9 based on 2-D comprehensive rate/kinetics model for top, mid height and bottom of laminar jet (aqueous solution of MDEA-MEA wt ratio of 23/7; CO_2 loading (α) of 0.1012 mol CO_2/mol amine at 298K)



Radial concentration profiles for species C3 and C10 based on 2-D comprehensive rate/kinetics model for top, mid height and bottom of laminar jet (aqueous solution of MDEA-MEA wt ratio of 23/7; CO_2 loading (α) of 0.1012 mol CO_2/mol amine at 298K)



Summary

- 2-D Model for CO2 Absorption in laminar jet absorber
- Concentration profiles of all the species in both the radial and axial directions have been obtained
- Understanding of the correct sequence in which the reaction steps occur is enabled

Other Contributors to Presentation

- Mohamed Edali – PhD Student
- Nattawan Kladkaew – PhD Student
- Chintana Saiwan – Visiting Professor
- Teeradet Supap – Research Associate
- Ahmed Aboudheir - Collaborator

Acknowledgment

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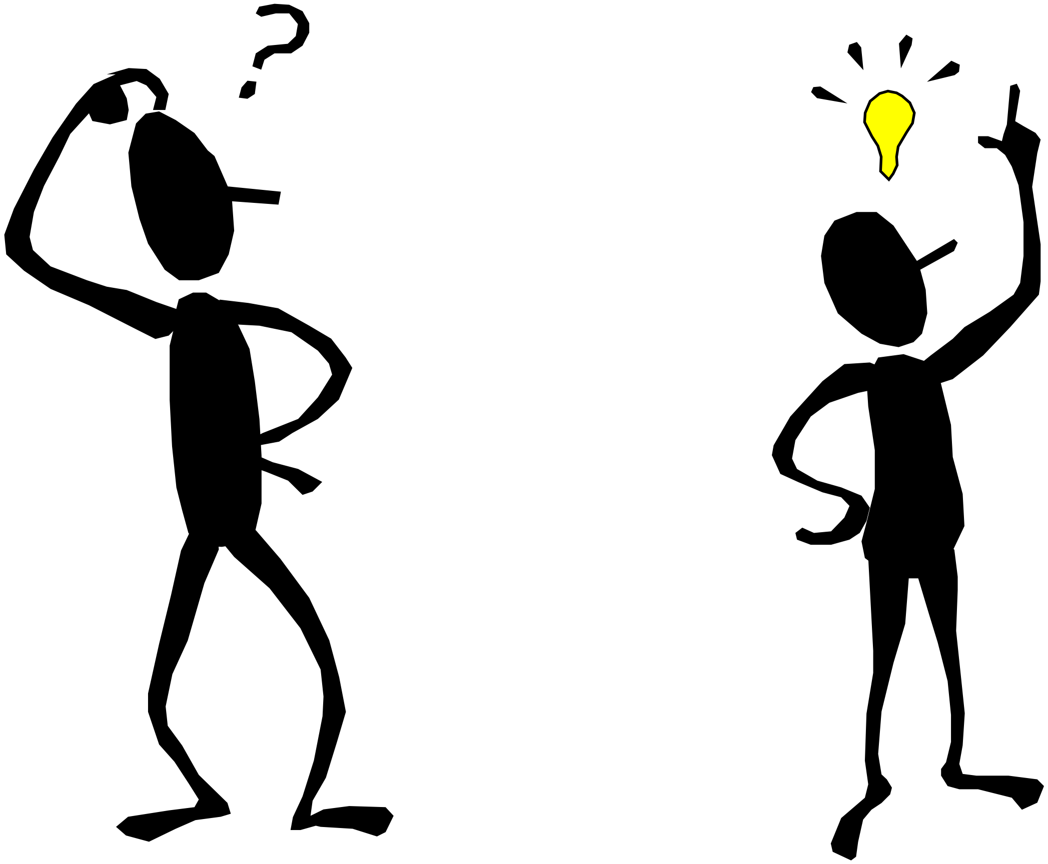
- RITE, Japan
- Alberta Energy Research Insitute
- RWE npower, UK
- EnCana, Canada
- Babcock & Wilcox, USA
- Stantec, Canada
- Natural Resources Canada
- Saskatchewan Industry & Resources

For more info >> www.CO2-research.ca



ITC

International Test Centre
for CO2 Capture

First Results from Start-up at Pilot Plant Niederaussem

Dr. Peter Moser (RWE), Sandra Schmidt (RWE),
Hugo Garcia (BASF), Dr. Georg Sieder (BASF),
Christine Förster (Linde-KCA), Torsten Stoffregen (Linde-KCA)

12th Meeting of the International Post-Combustion CO_2 Capture Network
29th September - 1st October 2009, Regina, Canada

RWE
The energy to lead

BASF
The Chemical Company

THE LINDE GROUP
Linde

sand.schmidt@rwe.com, torsten.stoffregen@linde-kca.com

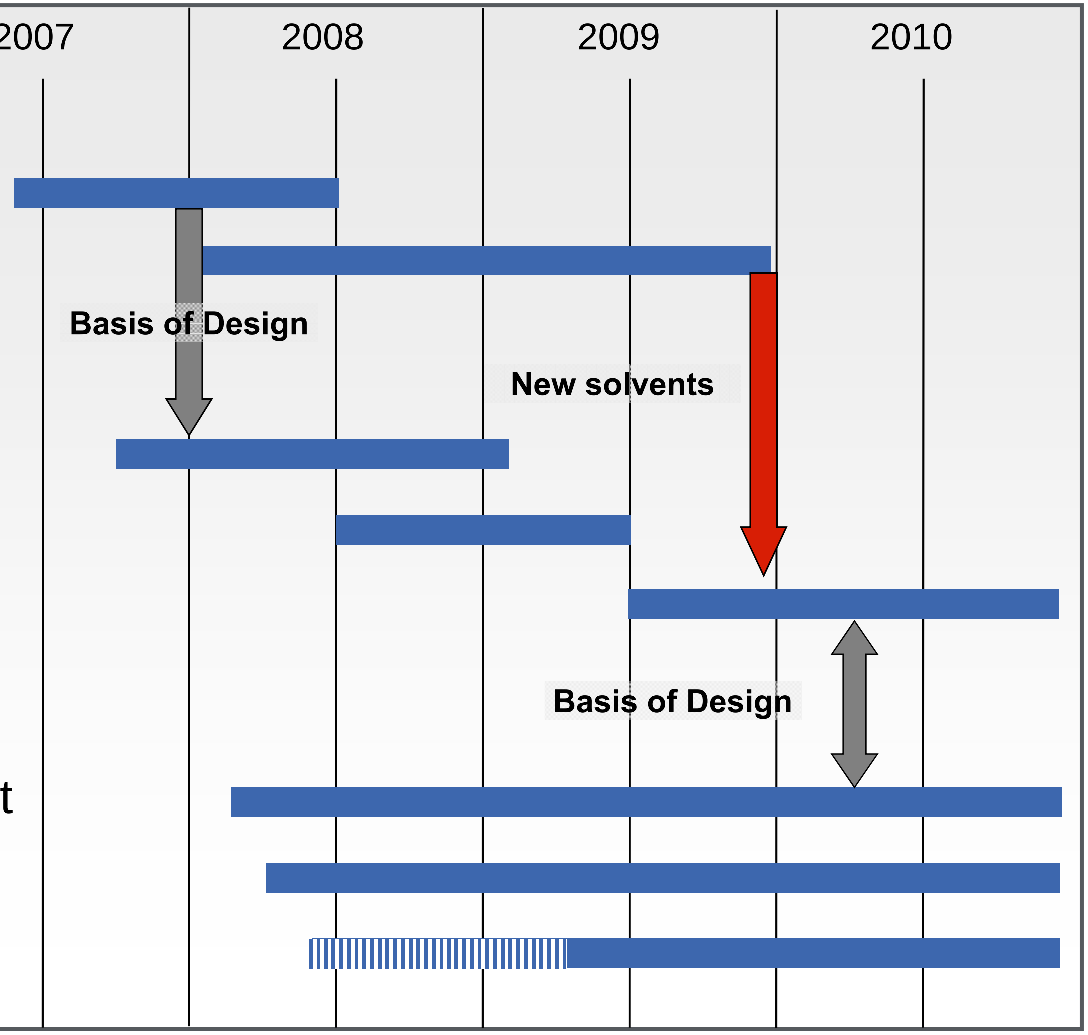
Cooperation BASF - Linde - RWE Power

The interdisciplinary approach – key to success:

- BASF – ”The Chemical Company“: development of new solvents and optimized process design
- Linde – “Engineering company”: engineering and construction of the pilot plant, system optimization, scale up
- RWE Power – “Power producer and utility”: plant integration, interface optimization, operation

Cooperation Roadmap

Development of a highly efficient amine based PCC process



Solvent Development BASF

- Screening
- Miniplant performance tests

CO_2 Capture Pilot Plant

- Engineering, Procurement
- Construction
- Operation

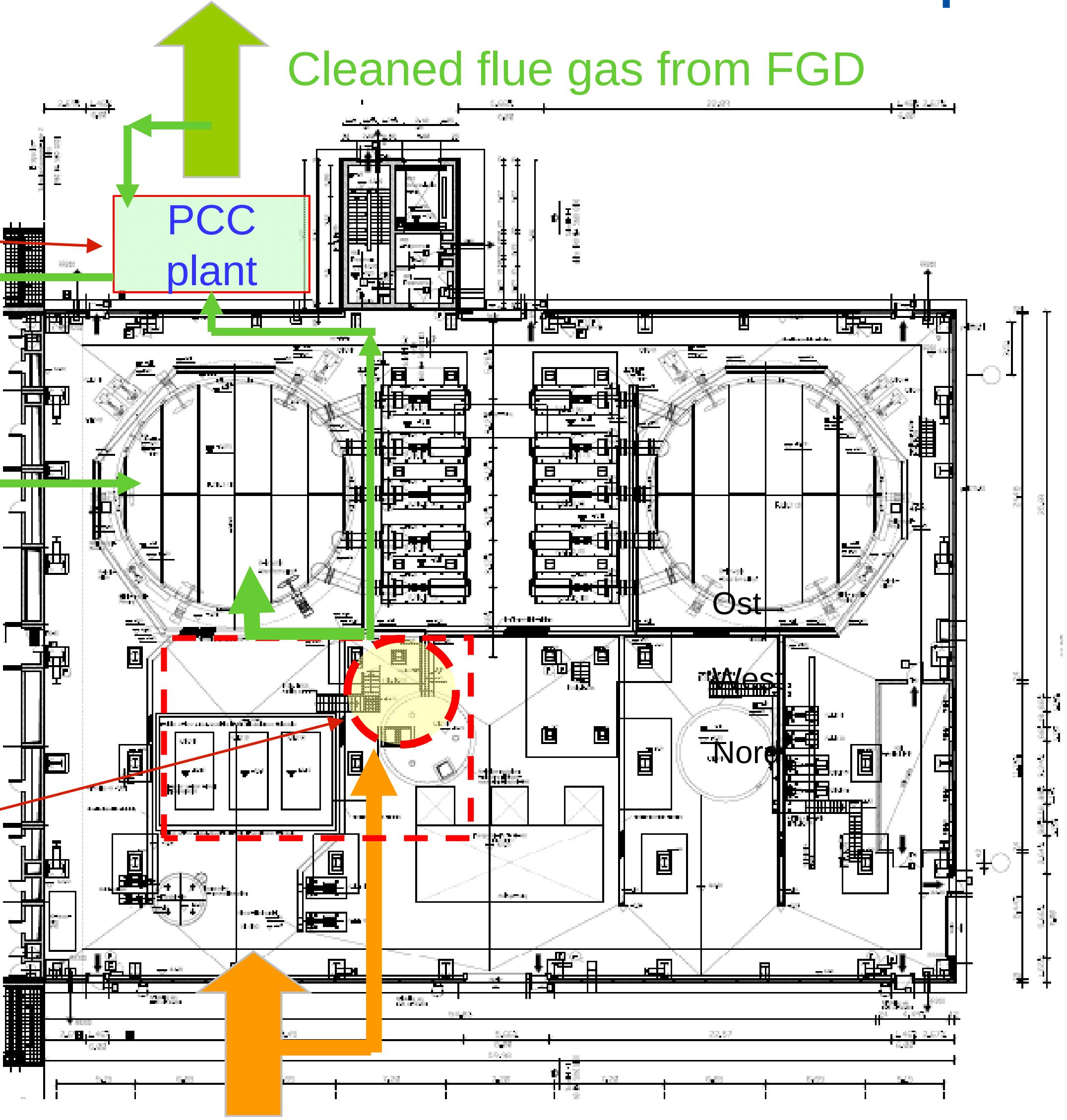
Working Group “PCC-Demo”

- Optimization of the PCC concept
- Scale up for a full-scale plant
- Designing of the demo plant

RWE Coal Innovation Centre - PCC and REAplus

PCC pilot plant

REAplus (High performance FGD)



Cleaned flue gas from FGD

PCC plant

Raw flue gas from 1000 MW unit BoA 1

PCC Pilot Plant Niederaussem/Germany

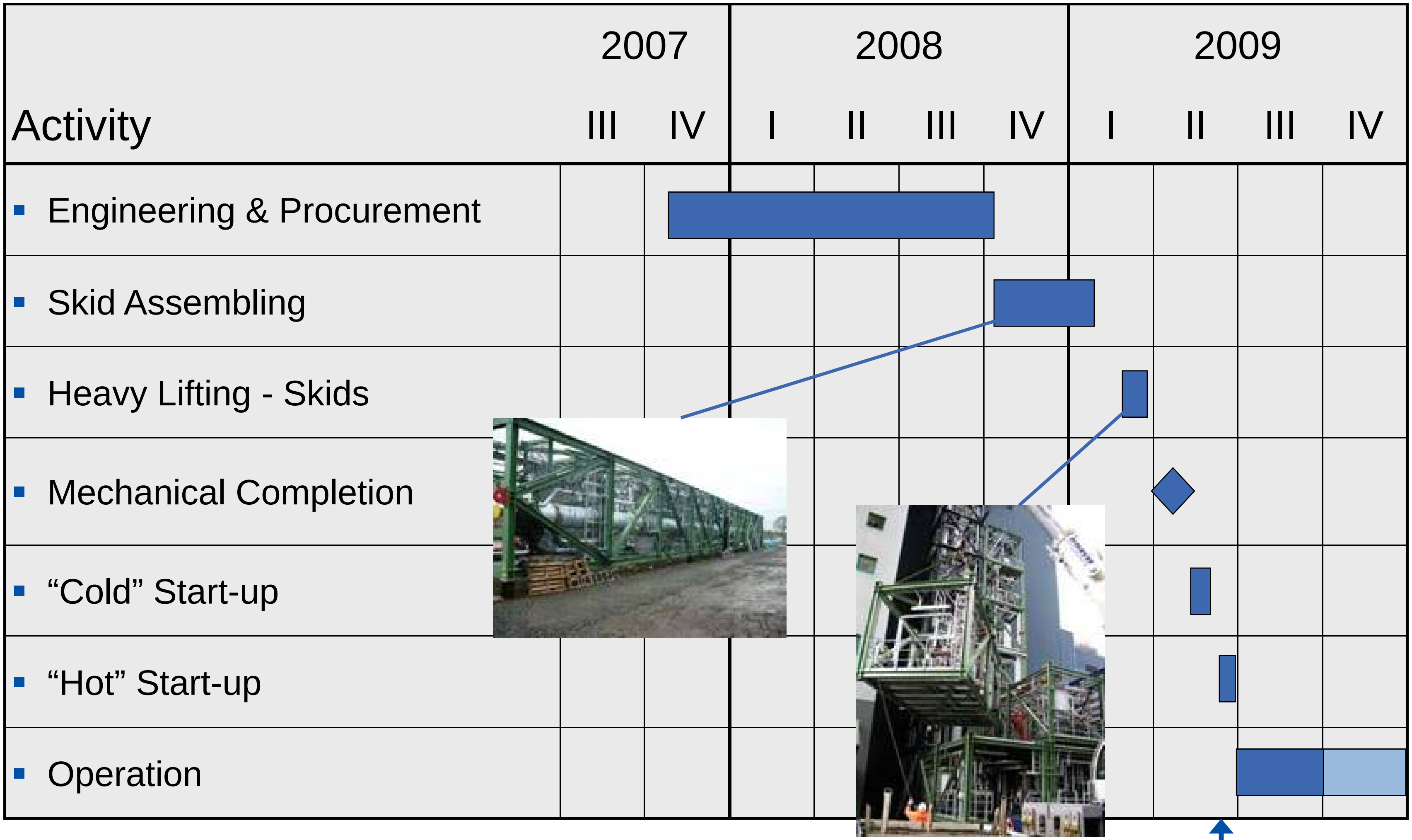
- Flue gas capacity: 1552 Nm^3/h
- CO_2-capture rate 90 %
- App. 300 kg CO_2/h

- Height: app. 40 m
- Area: app. 15 m x 20 m
- Design: 6 skids, 2 container
- Instrumentation: 240 measurements
- MOC testing: 15 different locations

- Budget RWE Power: 9 Mio. €
- 40% funding by BMWi

- Start-up: July 2009

Time Schedule - Pilot Plant Niederaussem

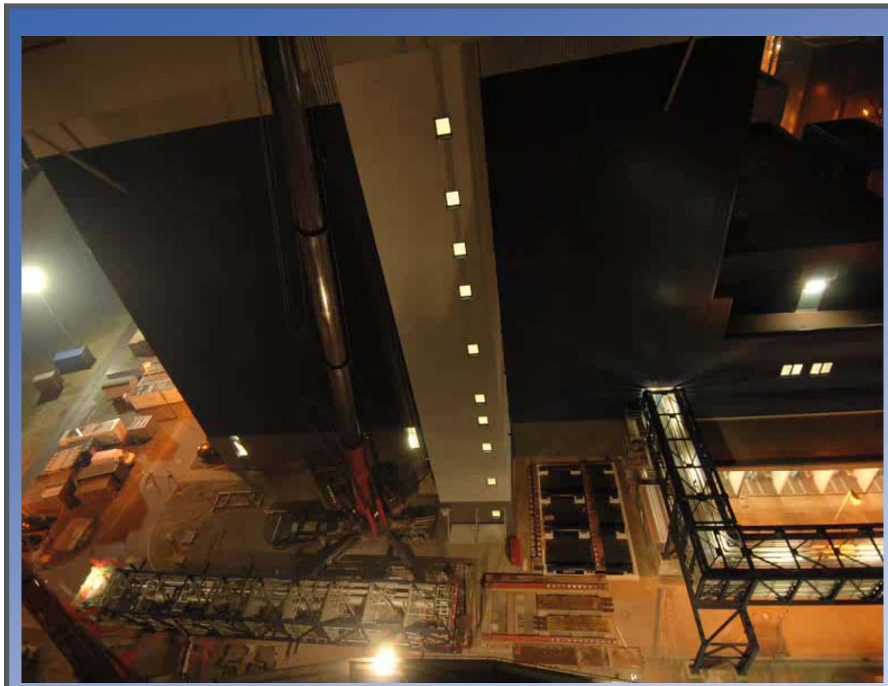


- Engineering & Procurement
- Skid Assembling
- Heavy Lifting - Skids
- Mechanical Completion
- “Cold” Start-up
- “Hot” Start-up
- Operation

First CO_2-capture from flue gas of a conventional power plant in Germany

PCC Pilot Plant Niederaussem - Construction

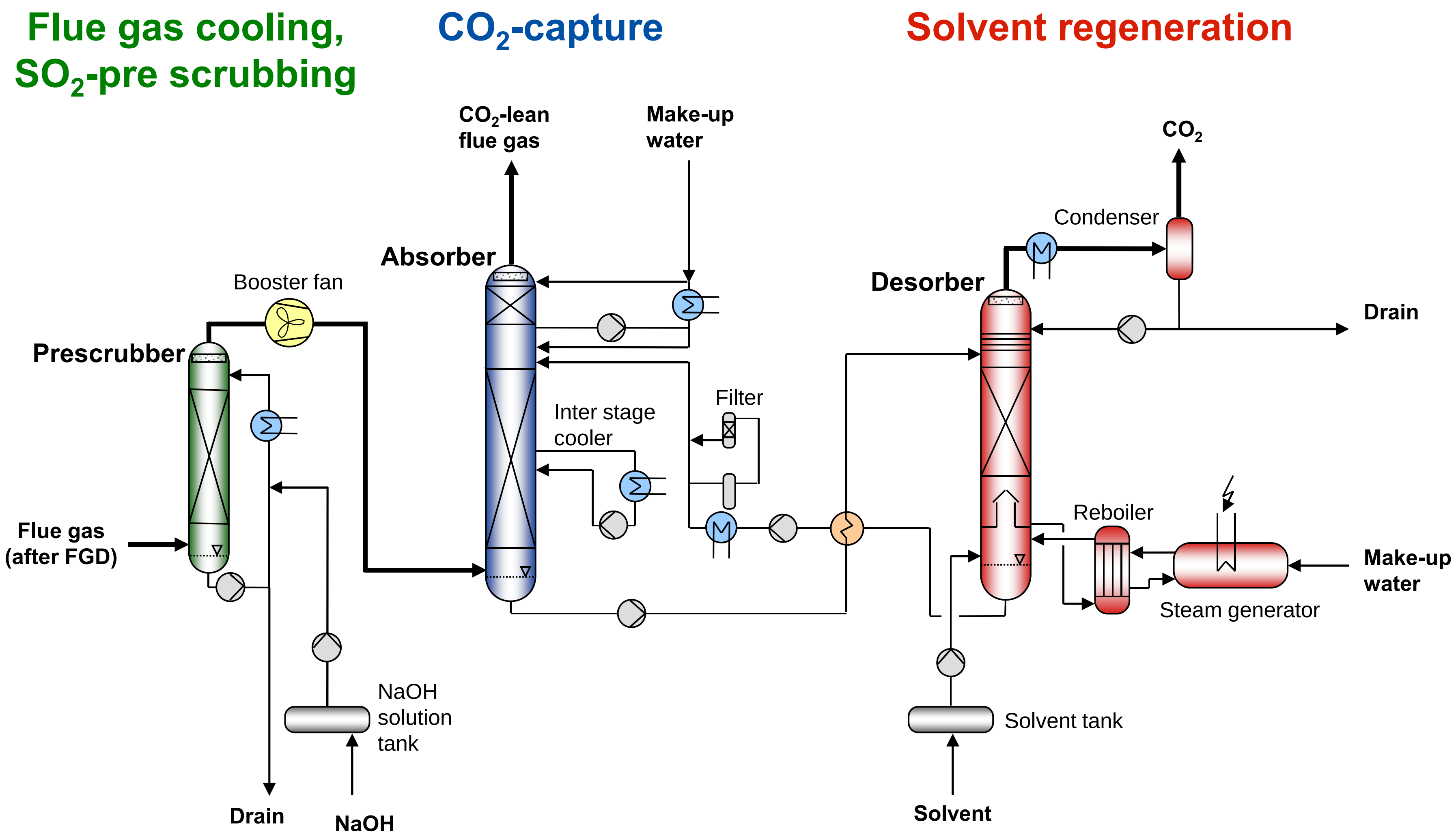
Erection of Skid 1 and Skid 2 in March 2009



Skid 1 – app. 80 t, 41 m
05.03.09

Skid 2 – app. 50 t, 25 m
06.03.09

Basic Process of the PCC Pilot Plant

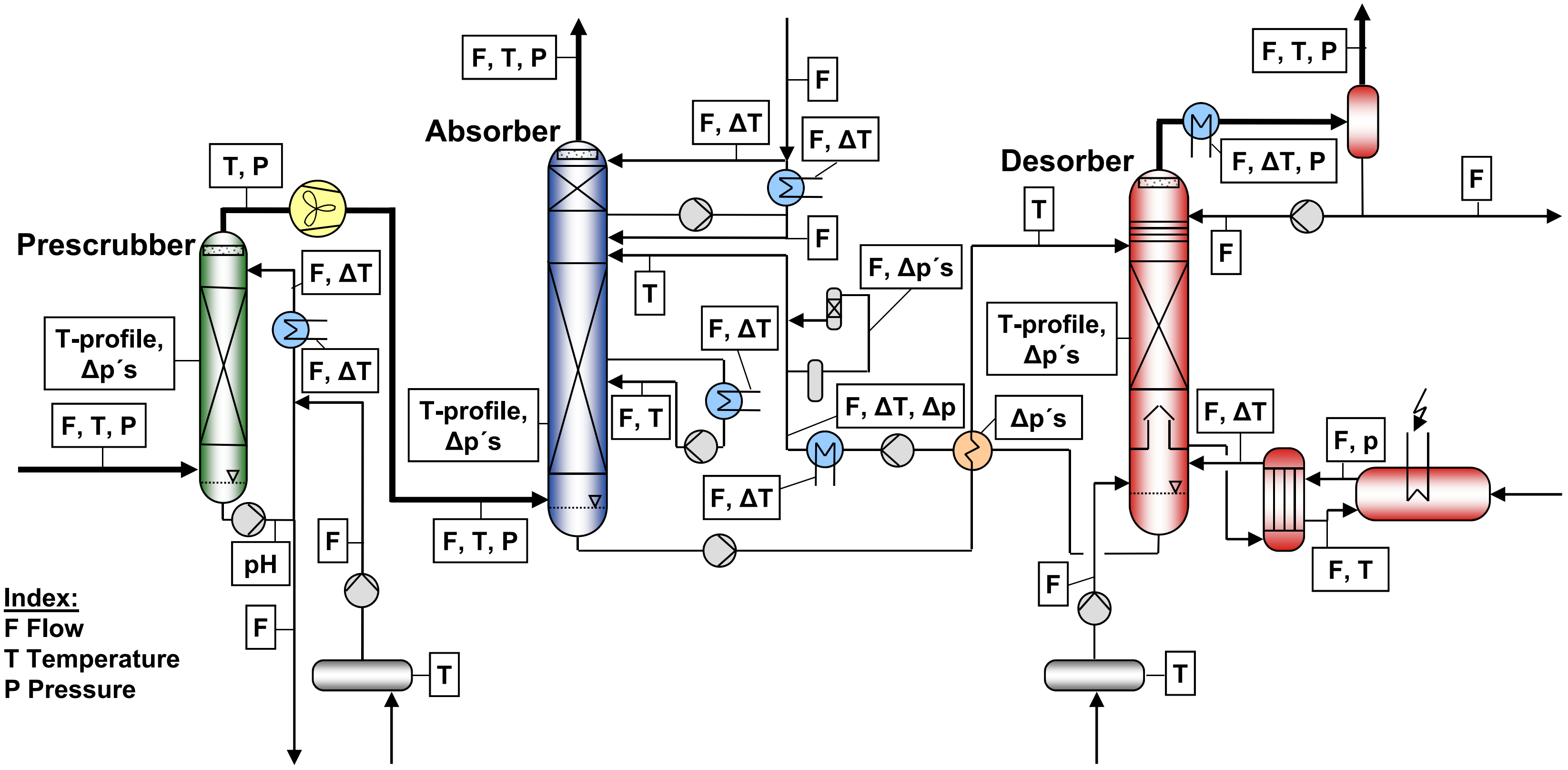


Measurement Equipment of the PCC Pilot Plant

Flue gas cooling, SO_2-pre scrubbing

CO_2-capture

Solvent regeneration



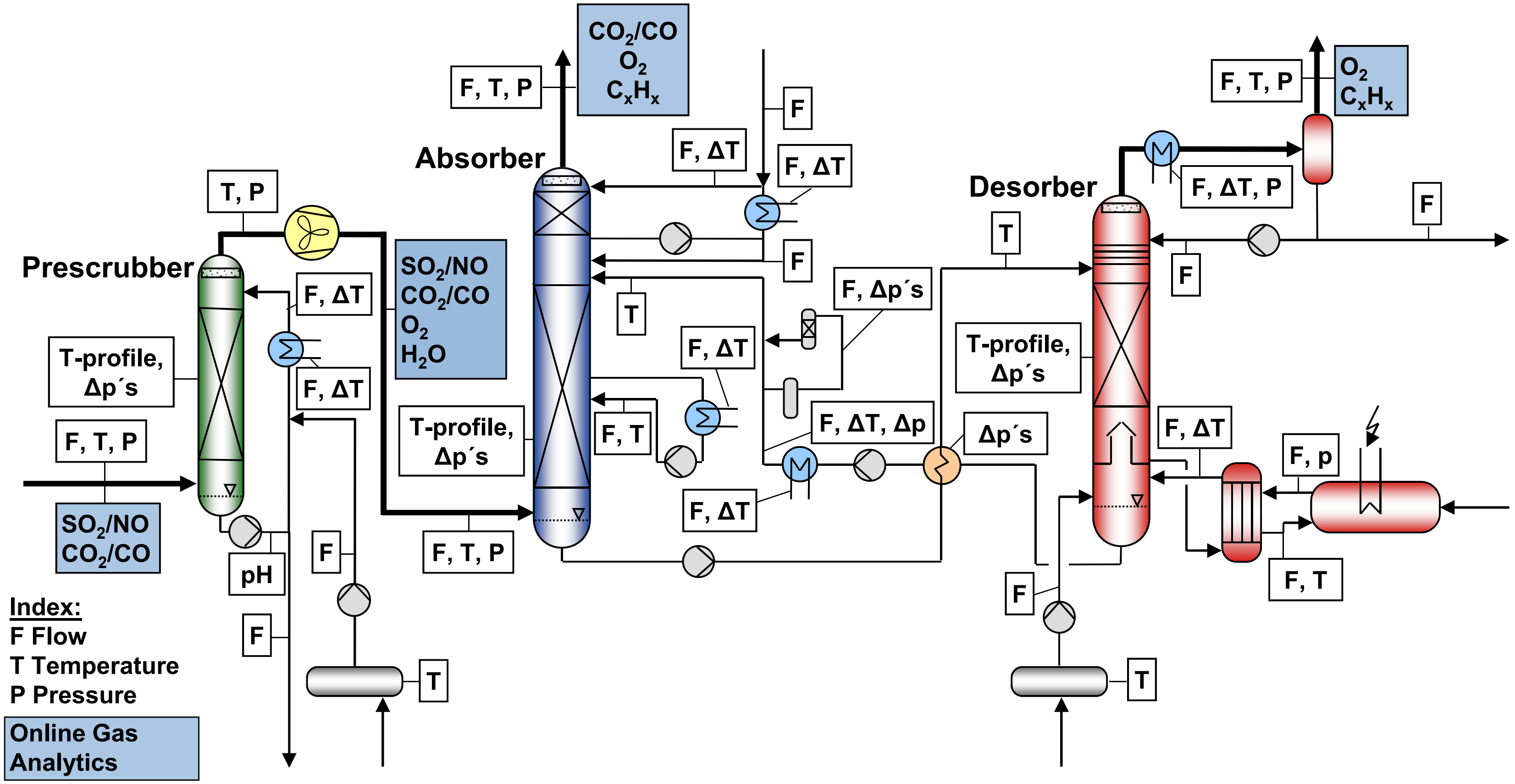
Index:
F Flow
T Temperature
P Pressure

Measurement Equipment of the PCC Pilot Plant

Flue gas cooling, SO_2-pre scrubbing

CO_2-capture

Solvent regeneration



Index:
F Flow
T Temperature
P Pressure

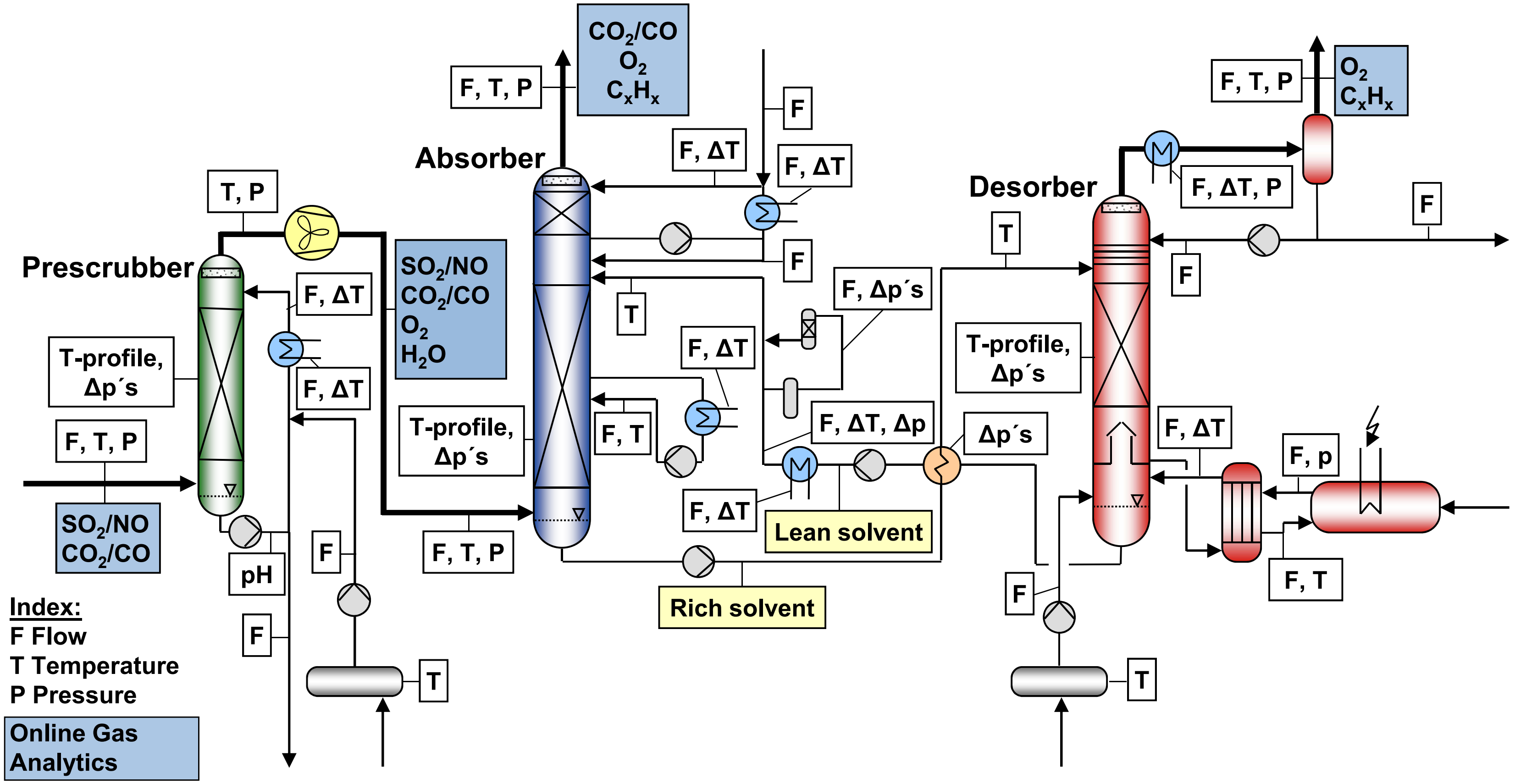
Online Gas Analytics

Measurement Equipment of the PCC Pilot Plant

Flue gas cooling, SO_2-pre scrubbing

CO_2-capture

Solvent regeneration

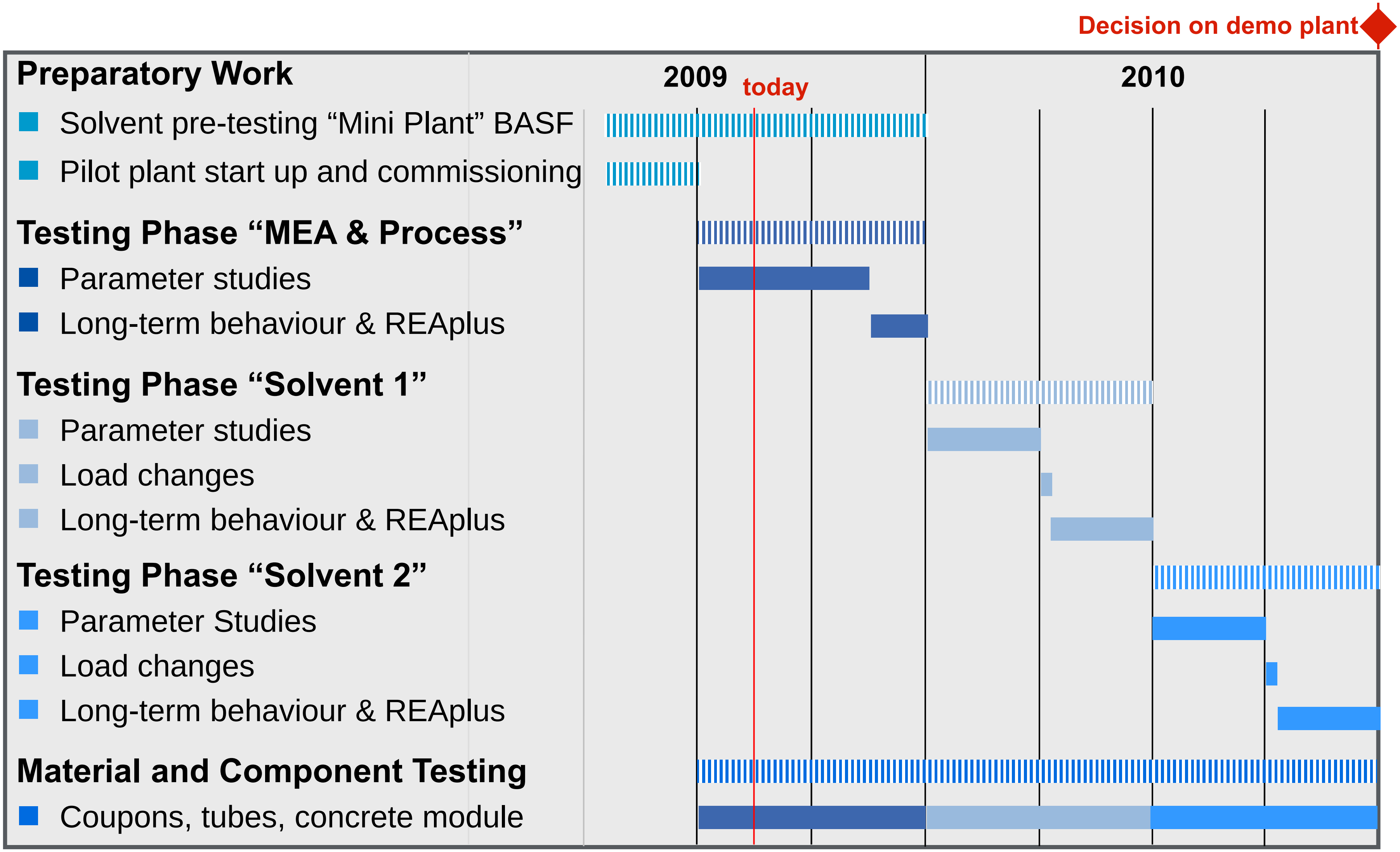


Index:
F Flow
T Temperature
P Pressure

🟦 Online Gas Analytics

🟨 Sampling point of daily solvent samples

Testing Programme Pilot Plant Niederaussem



Preparatory Work

- Solvent pre-testing “Mini Plant” BASF
- Pilot plant start up and commissioning

Testing Phase “MEA & Process”

- Parameter studies
- Long-term behaviour & REAplus

Testing Phase “Solvent 1”

- Parameter studies
- Load changes
- Long-term behaviour & REAplus

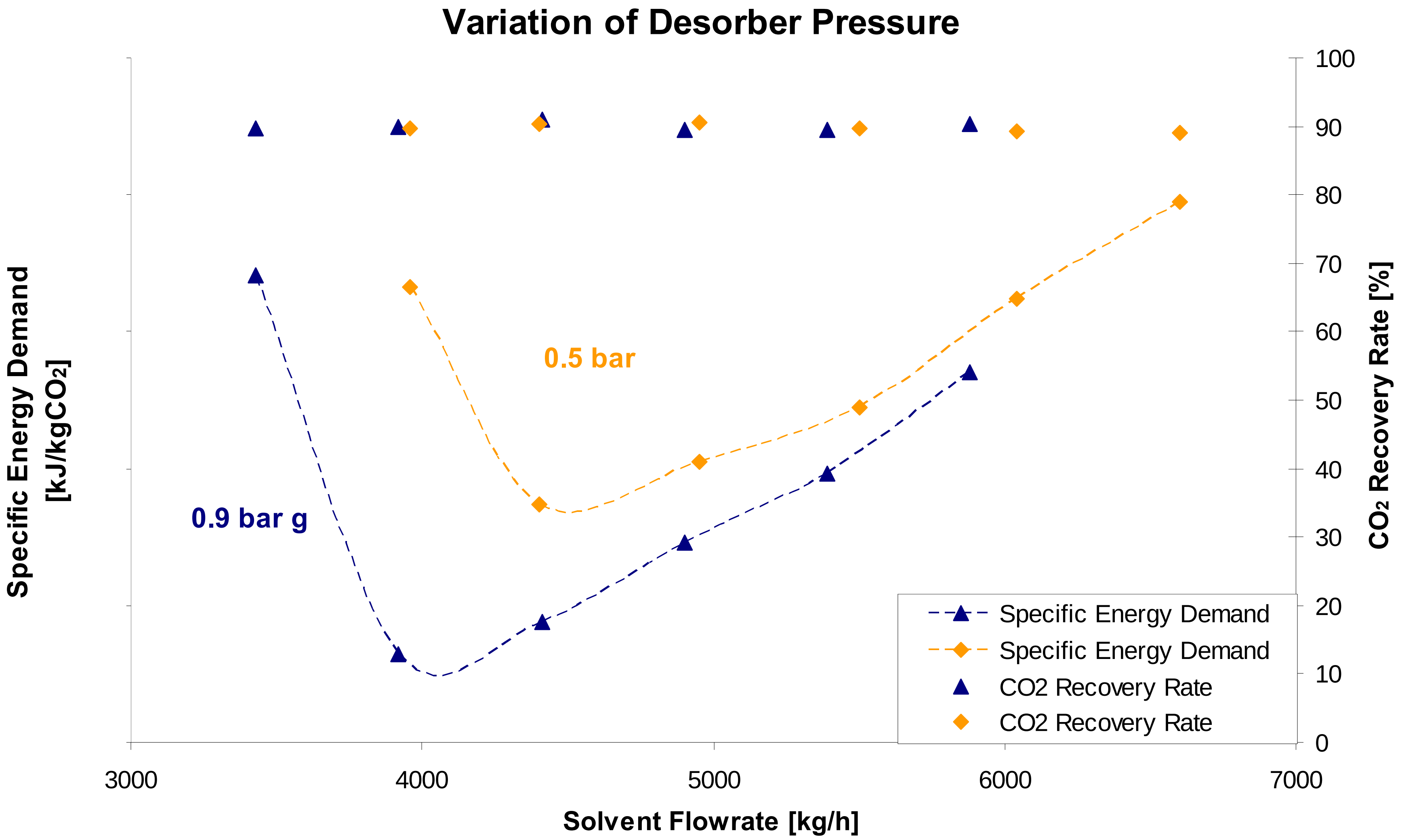
Testing Phase “Solvent 2”

- Parameter Studies
- Load changes
- Long-term behaviour & REAplus

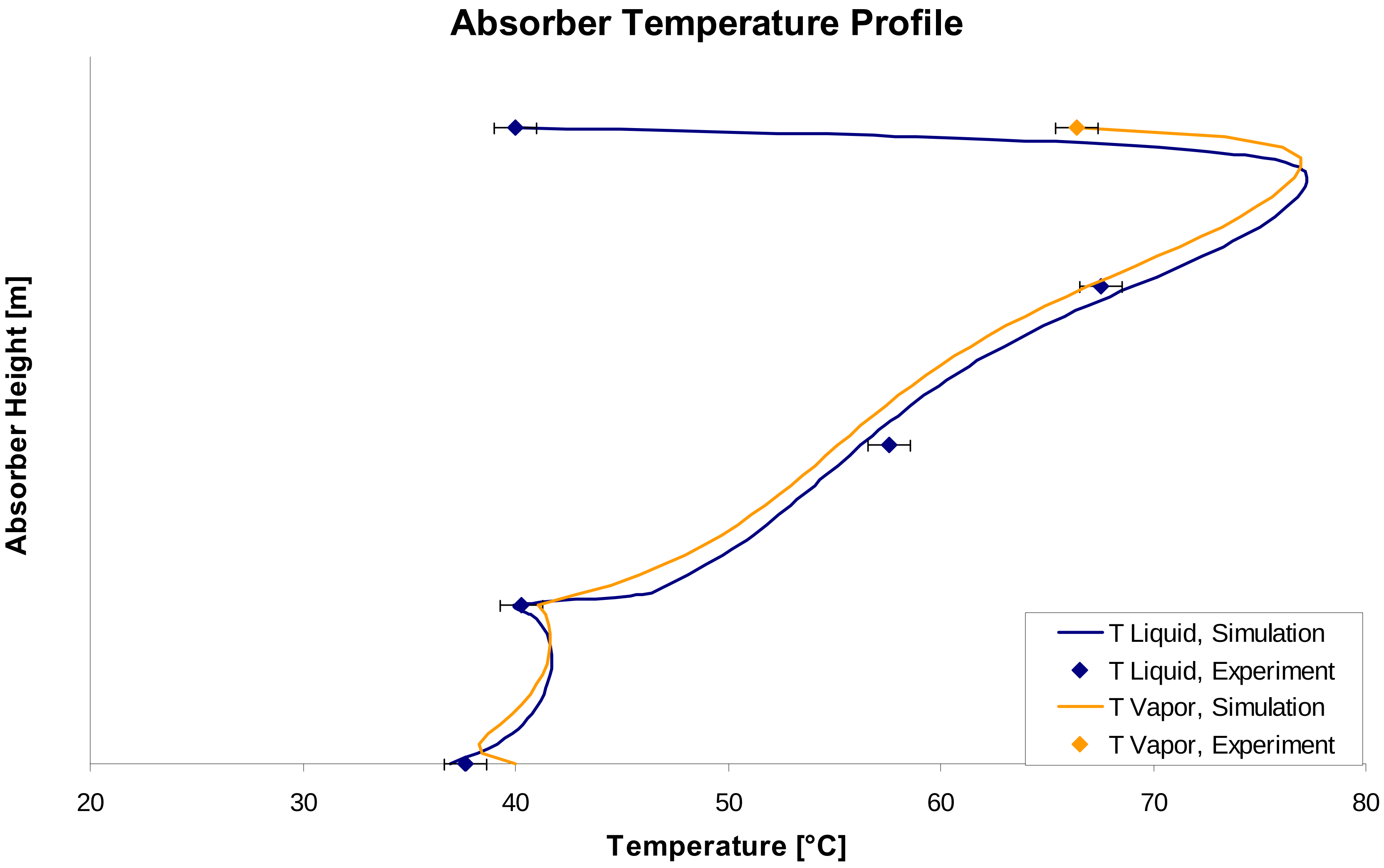
Material and Component Testing

- Coupons, tubes, concrete module

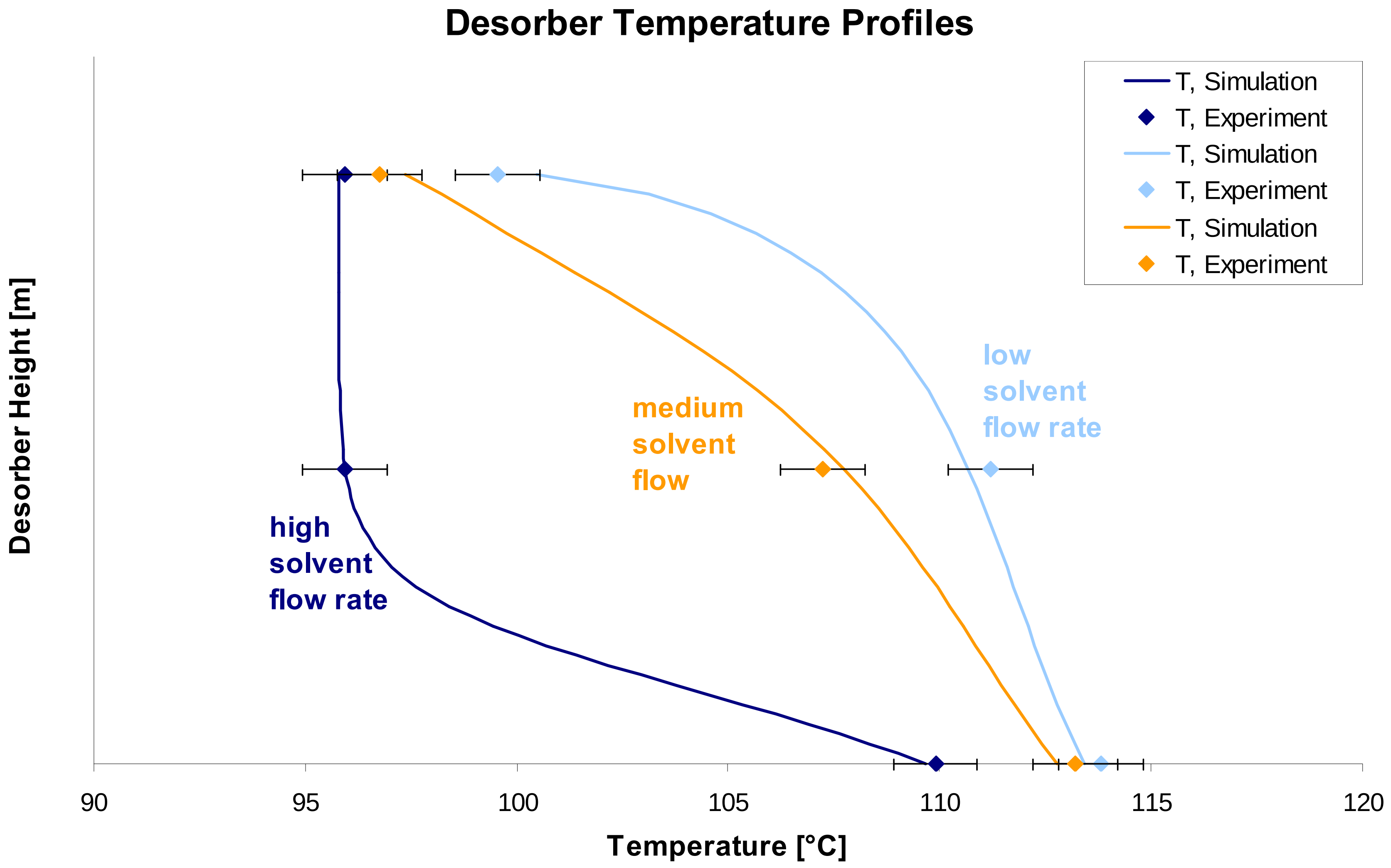
Parameter Study – Variation of Desorber Pressure
Capture rate and specific energy demand for MEA



Comparision of Tests and Simulation



Parameter Study – Variation of Flow Rate
Process optimisation



Conclusion and Next Steps

Conclusion:

- Successful start-up of the Pilot Plant in Niederaussem, Germany
- In operation since June 2009
- Start of the testing programme with the solvent MEA in July with parameter studies to confirm the process performance and to validate the simulation tool
- First results show a good performance of the plant
- Stable and smooth operability of the plant guarantees positive testing-measurements

Testing of the optimized process, new developed CO_2-solvents and equipment materials in the pilot plant in Niederaussem until end of 2010

Next steps:

- Technical and economic evaluation of the new amine process
- Results of the pilot plant will be used for the engineering of the demonstration plant

Thank you very much for your attention

RWE
The energy to lead

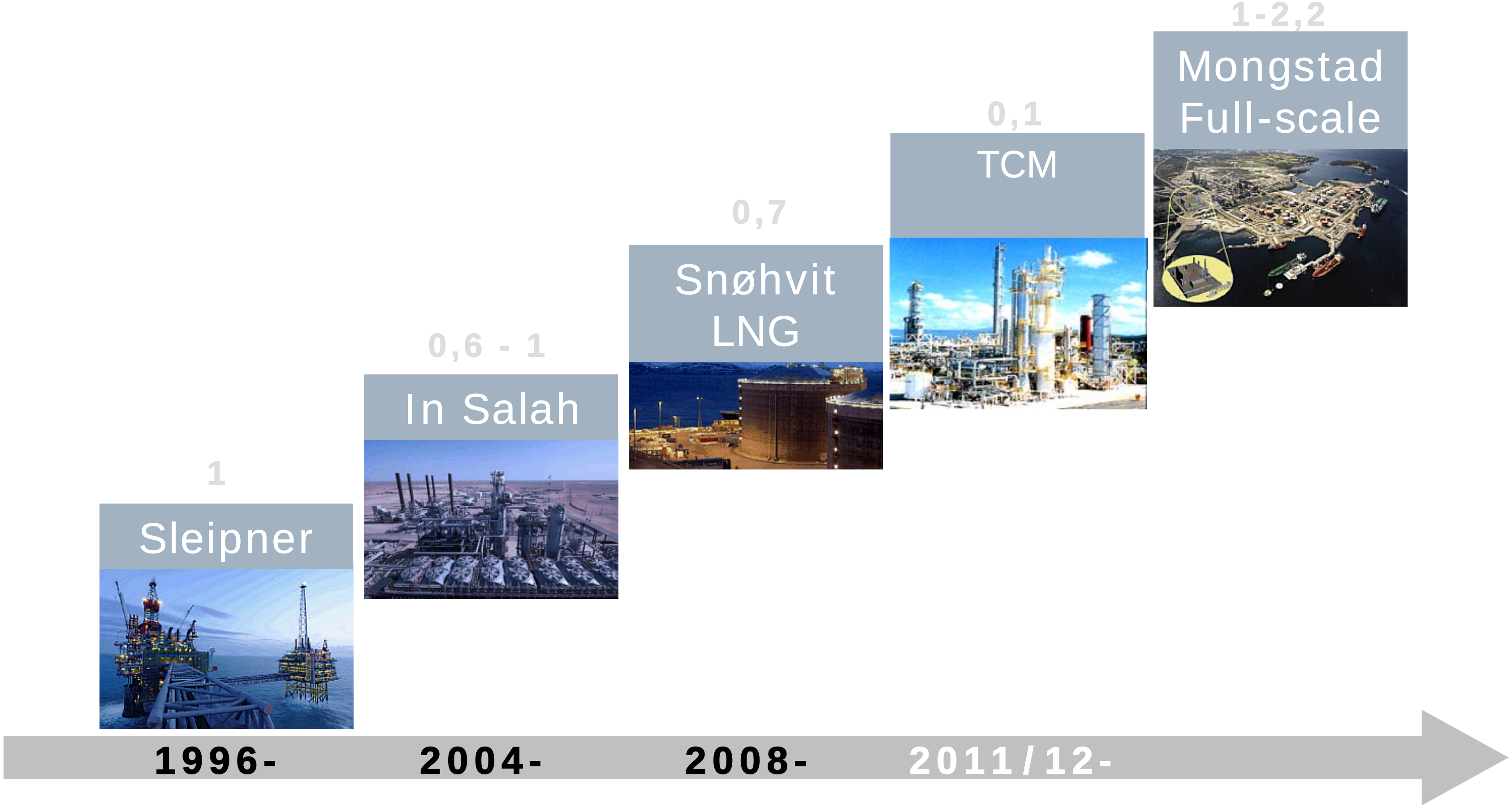
BASF The Chemical Company

THE LINDE GROUP Linde

Status of European CO_2 Technology Centre Mongstad

Dr. Gelein de Koeijer
Principle Researcher at StatoilHydro
IEA GHG 12th International Post Combustion Capture Network
29-09-2009, Regina, Canada

StatoilHydro's CCS projects
An industrial approach to climate change



1
Sleipner

0,6 - 1
In Salah

0,7
Snøhvit LNG

0,1
TCM

1-2,2
Mongstad Full-scale

1996-
2004-
2008-
2011/12-

StatoilHydro

The next big step: Mongstad CHP and refinery CCS

Why is this a big step?

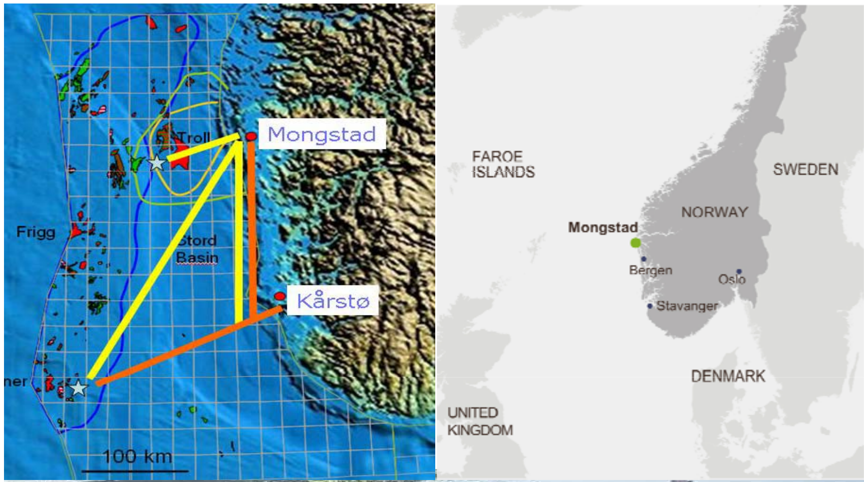
- Cleaning flue gases is less mature and more costly compared to removing CO_2 from natural gas

Two plants planned:

- Technology centre - StatoilHydro operator for execution and operation
- Full scale CCS – possible for both CHP and refinery

Financing:

- Technology centre:
  - StatoilHydro: 20%
  - Shell: 2.44%
  - The Norwegian State through Gassnova SF : 77.56%
- Full-scale: Norwegian State 100%



TCM is under construction!

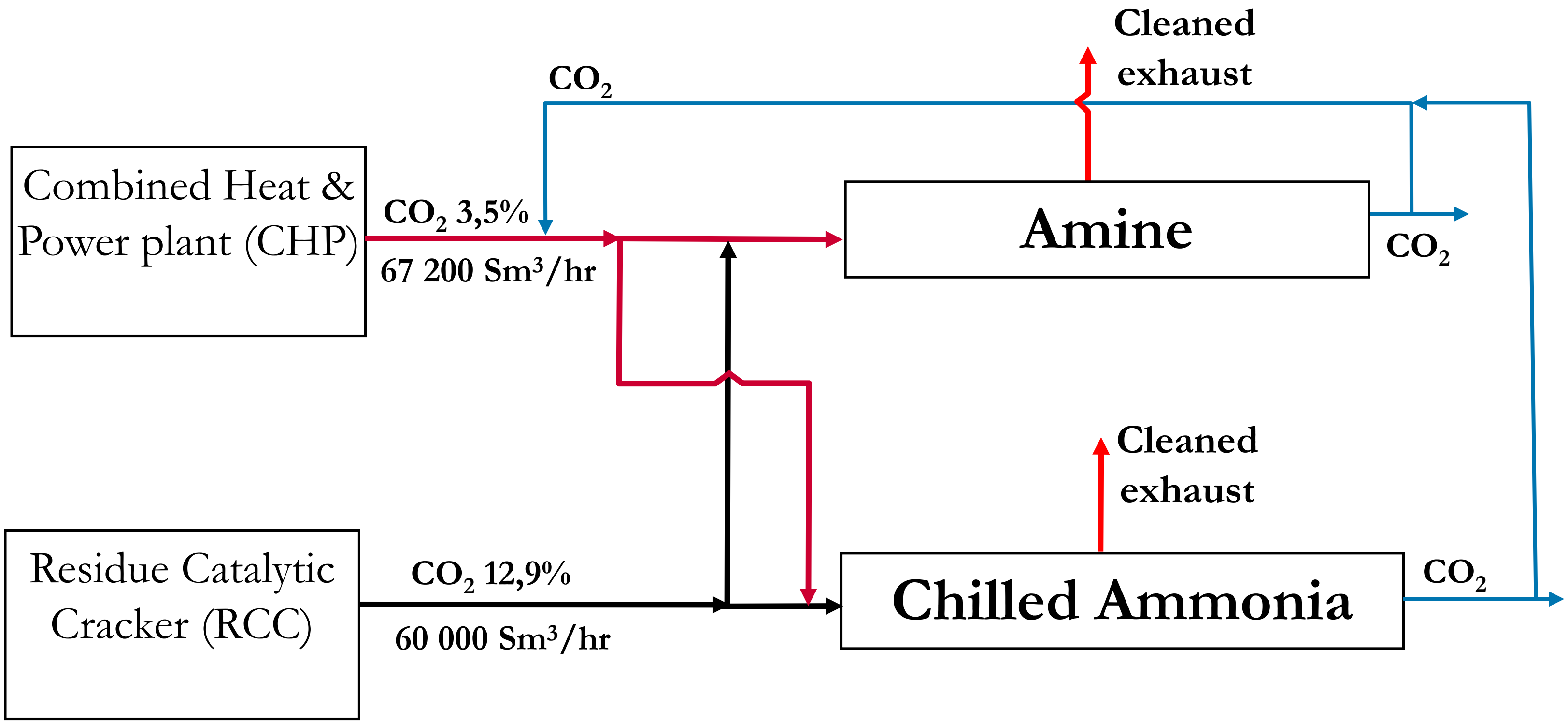
TCM Ambitions

- Develop technologies for CO_2 capture capable of wide national and international deployment
- Reduce cost and technical, environmental and financial risks related to large scale CO_2 capture
- Test, verify and demonstrate CO_2 capture technology owned and marketed by Vendors
- Encourage the development of technology and vendors

Contracts until now

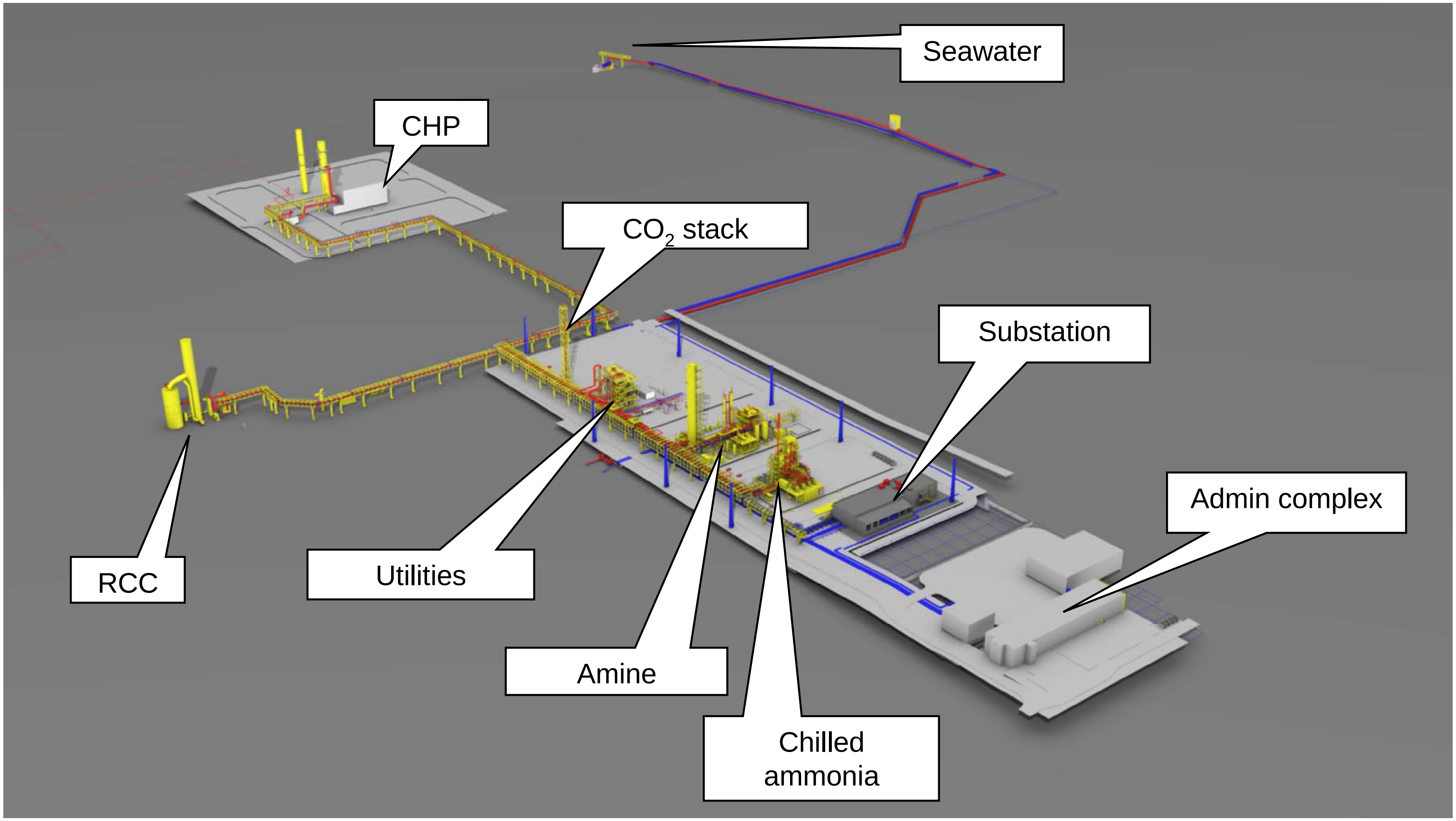
Civil Works	Vassbakk og Stol AS
Administration Buidling	Larsen Atterås og Brosvik AS (LAB)
Utility Systems/Infrastructure	Aibel AS
Amine Technology	Aker Clean Carbon AS
Chilled Ammonia Technology	Alstom Norway AS
Concrete works	AF Gruppen AS

Overall Concept and Functional Requirements



Total capacity 100 ktonnes CO_2 per year

Plot plan (Movie)



Key advantages of TCM test facility

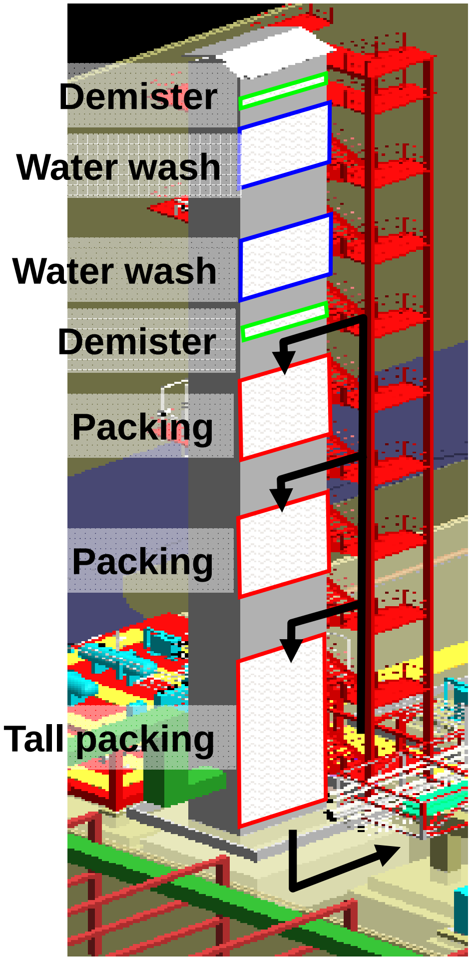
- Testing at industrial scale, i.e. 60,000 Sm^3/h of flue gas
- Tied-in with two industrial flue gas sources (one resembles coal flue gas)
- Have high degree of flexibility and features for future testing and modifications
- Resembles large-scale design

TCM can test effects that depend on scale with a higher accuracy and with a larger variety of flue gasses

Functional Requirements

- The captured CO_2 product shall meet the following requirements at battery limit:
    - Minimum CO_2 purity 99.9%
    - Acceptable quality for discharge to air
- The solution shall have suitable scale up properties to a full-scale plant
- Limited lifespan for test facilities (minimum 5 years of operation)
    - Design life for technologies: 10 years
    - Design life for infrastructure: 25 years
- 10-20% design margins in flue gas conditioning systems to test limitations in CO_2 capture units
- 50% turndown in CO_2 capture plants
- Space allocation for future installation of flue gas mixer
- Provisions for future process modifications
- The Amine and Carbonate units may be operated independent of each other

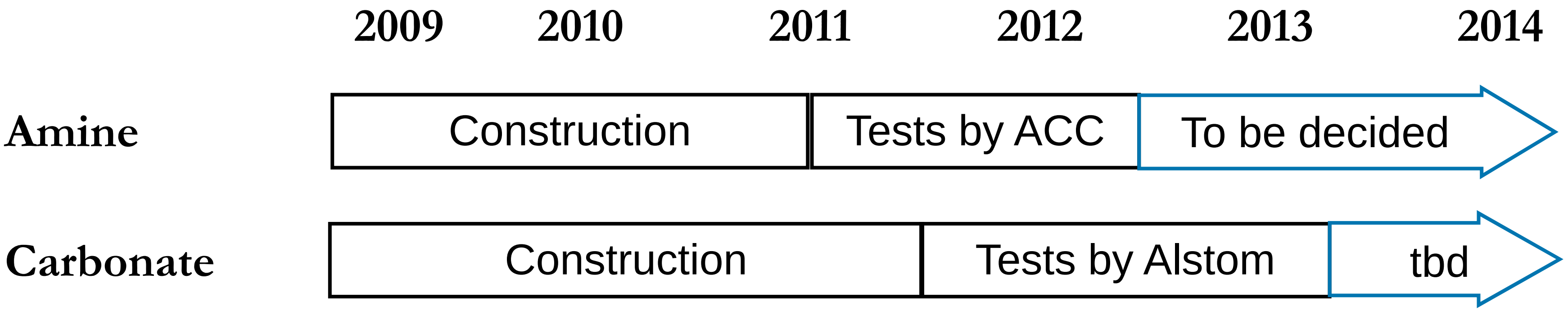
Example: TCM's requirements and ACC's technology



- Rectangular
- ~60 m tall
- Concrete with liner – slip formed
- Structured packing
- ACC's new washing technology - to be decided
- Extensive measurements – HSE focus
- Prepared for future improvements:
  - 4 beds
  - Change/removal of beds & demisters
  - Different heights
  - Inter-stage cooler
  - Split flow

Aker CleanCarbon™

Tentative test schedule



Key messages

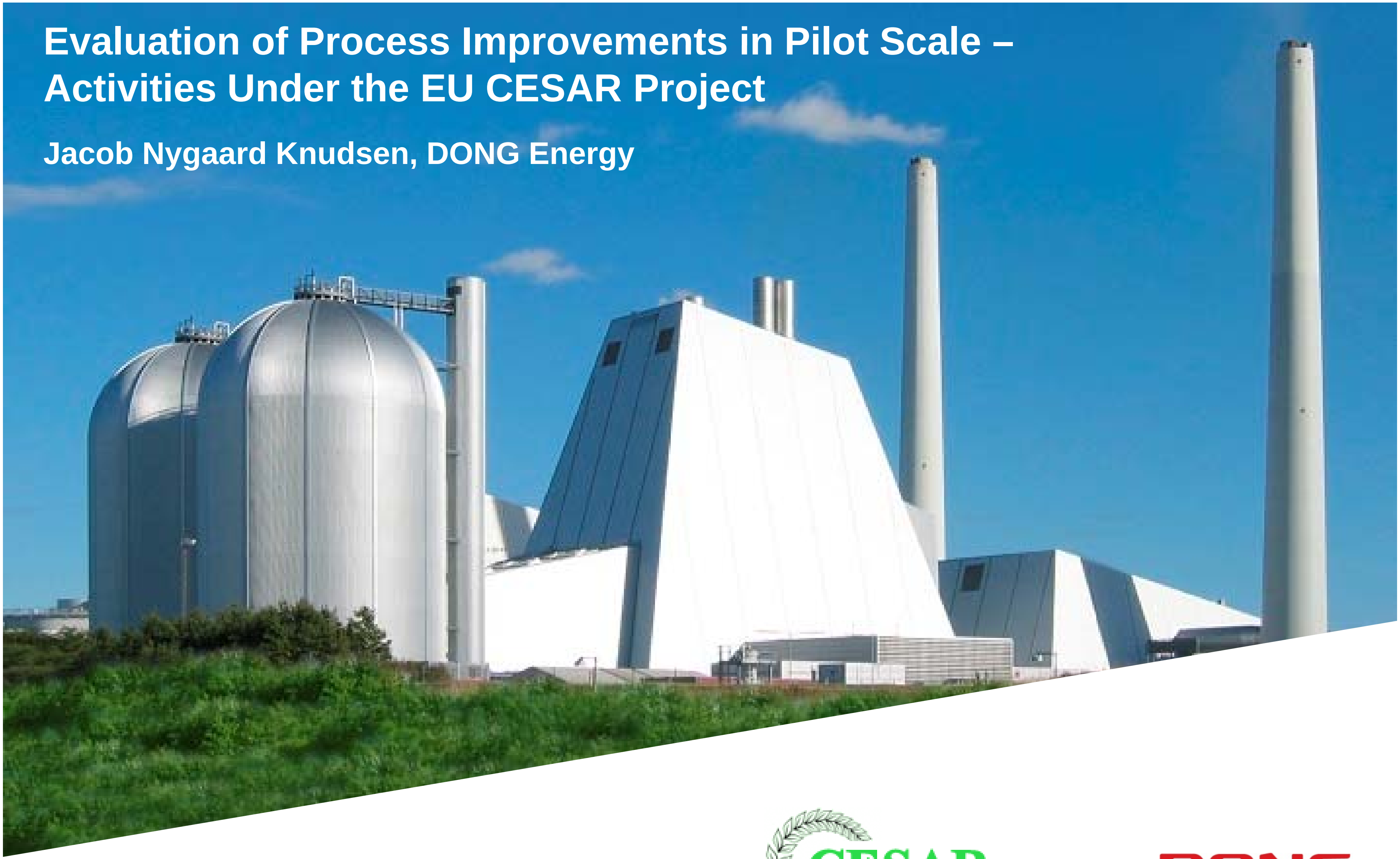
- **European CO_2 Technology Centre Mongstad will be an important driving force in the qualification of large-scale capture technology and development of improved technology**
- **TCM is approved and under construction**
- **TCM is based on two industrial scale post combustion CO_2 capture technologies, each with access to two real industrial flue gases**
- **TCM's plants will have a large degree of flexibility which gives many opportunities for the test program**
- **More information in GHTG-9 article and www.tcmda.no**

Thank You !

www.statoilhydro.com

StatoilHydro

12th Meeting of the International PCC Network – Regina, Canada 29 Sep – 1 Oct 2009



Evaluation of Process Improvements in Pilot Scale – Activities Under the EU CESAR Project

Jacob Nygaard Knudsen, DONG Energy

CESAR Enhanced Separation & Recovery

DONG energy

CESAR Project Consortium

CESAR: CO$_2$ Enhanced Separation And Recovery

- 3-year EU project (2008 – 2011) in the 7th Framework Programme
- Aim: To reduce the cost of CO$_2$ post-combustion capture

R&D

IFP (FR)
TNO (NL)
SINTEF (NO)
NTNU (NO)
POLYMEN (FR)
CNRS (FR)
U. KAISERSLAUTERN (DE)

Oil & Gas

STATOILHYDRO (NO)
GDF (FR)

Power Companies

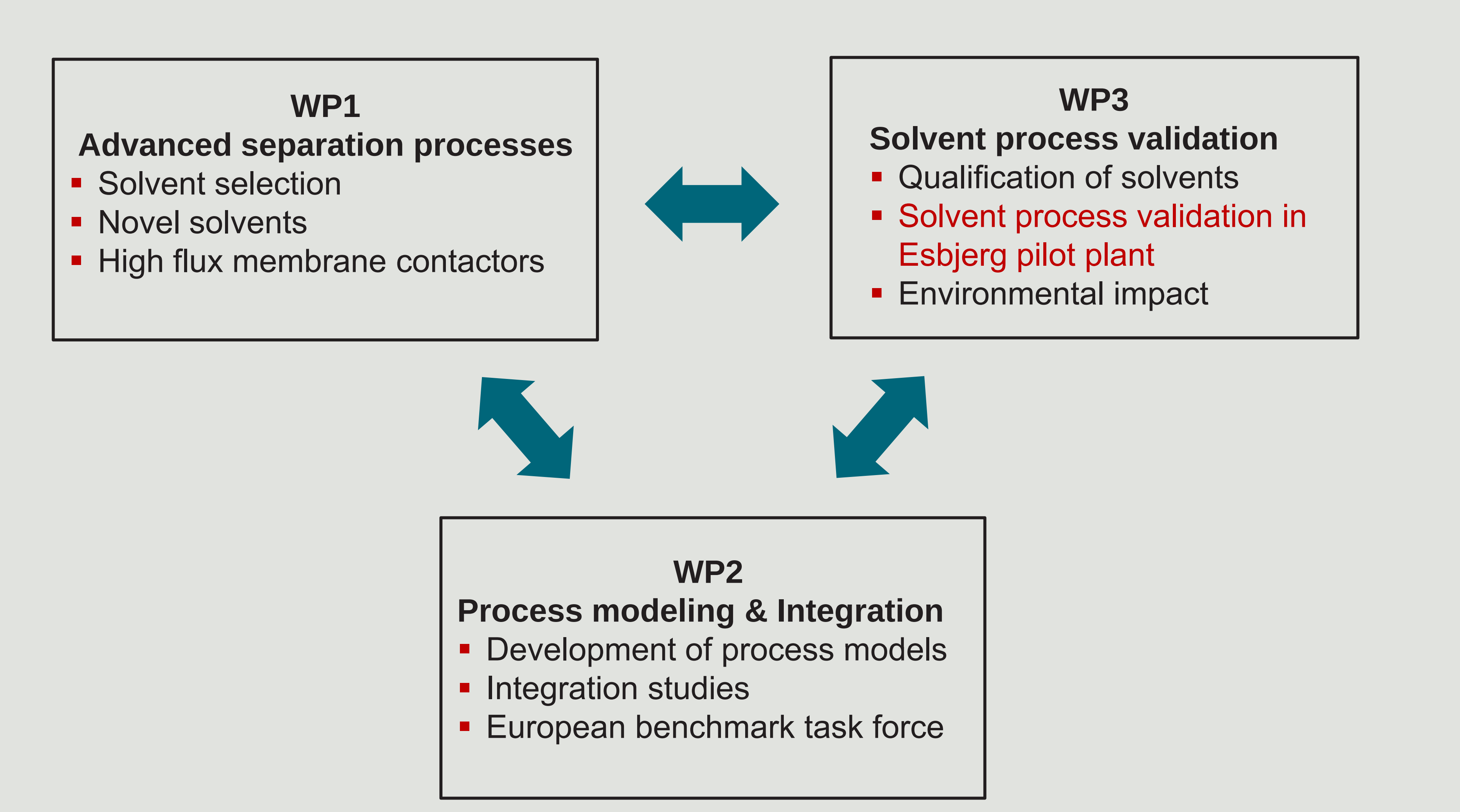
DONG Energy (DK)
VATTENFALL (SE/DK)
E.ON (DE/UK)
ELECTRABEL (BE)
RWE (DE/UK)
PPC (GR)
POWERGEN (UK)

Manufacturers

ALSTOM POWER (SE)
DOOSAN BABCOCK (UK)
SIEMENS (DE)
BASF (DE)

Coordinator: TNO

Outline CESAR Project



WP1
Advanced separation processes

- Solvent selection
- Novel solvents
- High flux membrane contactors

WP3
Solvent process validation

- Qualification of solvents
- Solvent process validation in Esbjerg pilot plant
- Environmental impact

WP2
Process modeling & Integration

- Development of process models
- Integration studies
- European benchmark task force

CESAR
Enhanced Separation & Recovery

DONG
energy

CESAR Objectives of Pilot Plant Testing in Esbjerg

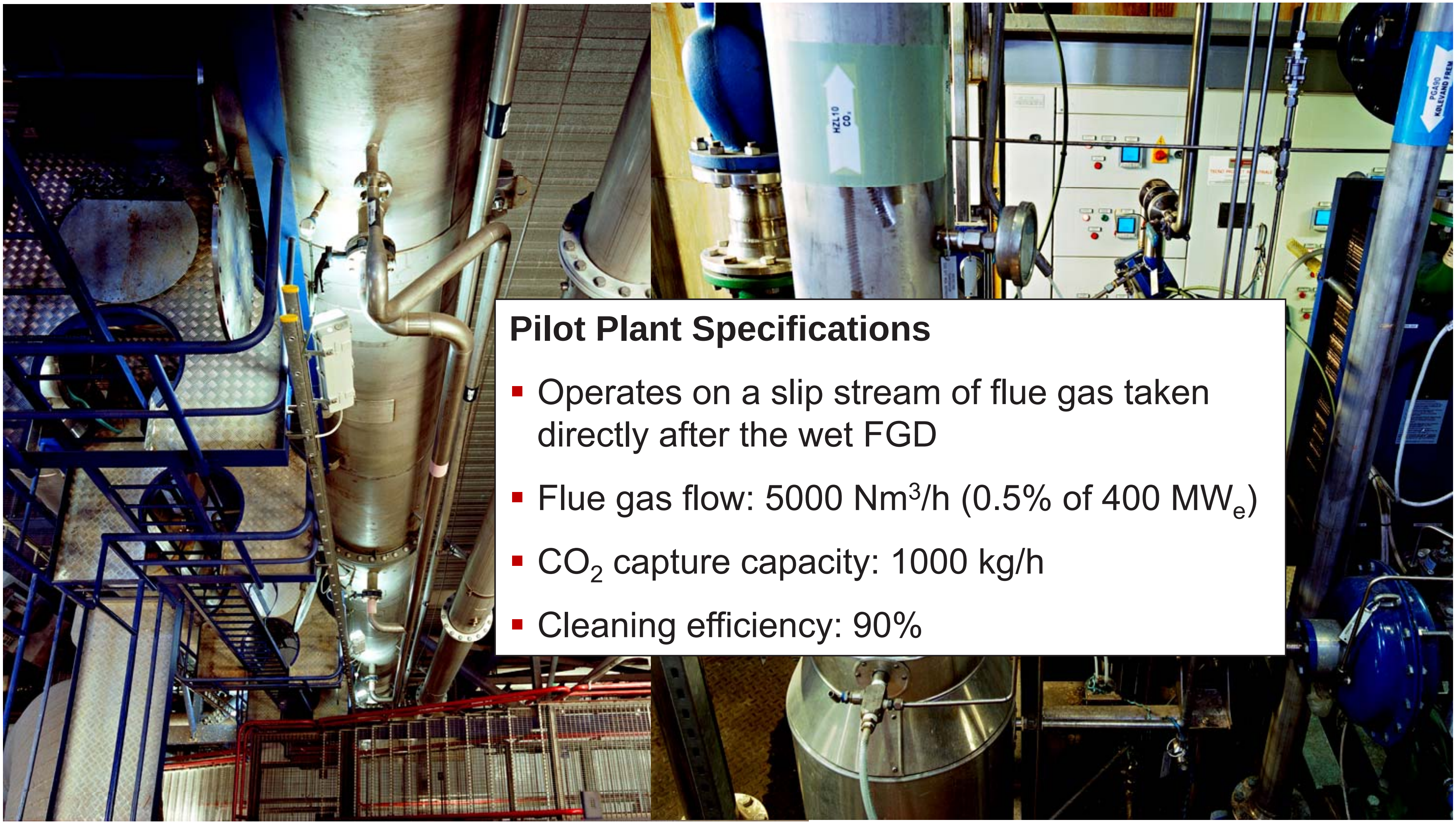
- Evaluate the potential of advanced absorption/desorption process configurations in pilot-scale
- Determine the performance of novel solvents in realistic operation conditions for future full-scale application in coal-fired power plants
- Measure energy requirement and temperature levels for regeneration of the novel solvents
- Monitor actual solvent degradation, losses and by-products, corrosion, fouling and emissions for novel solvents

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)

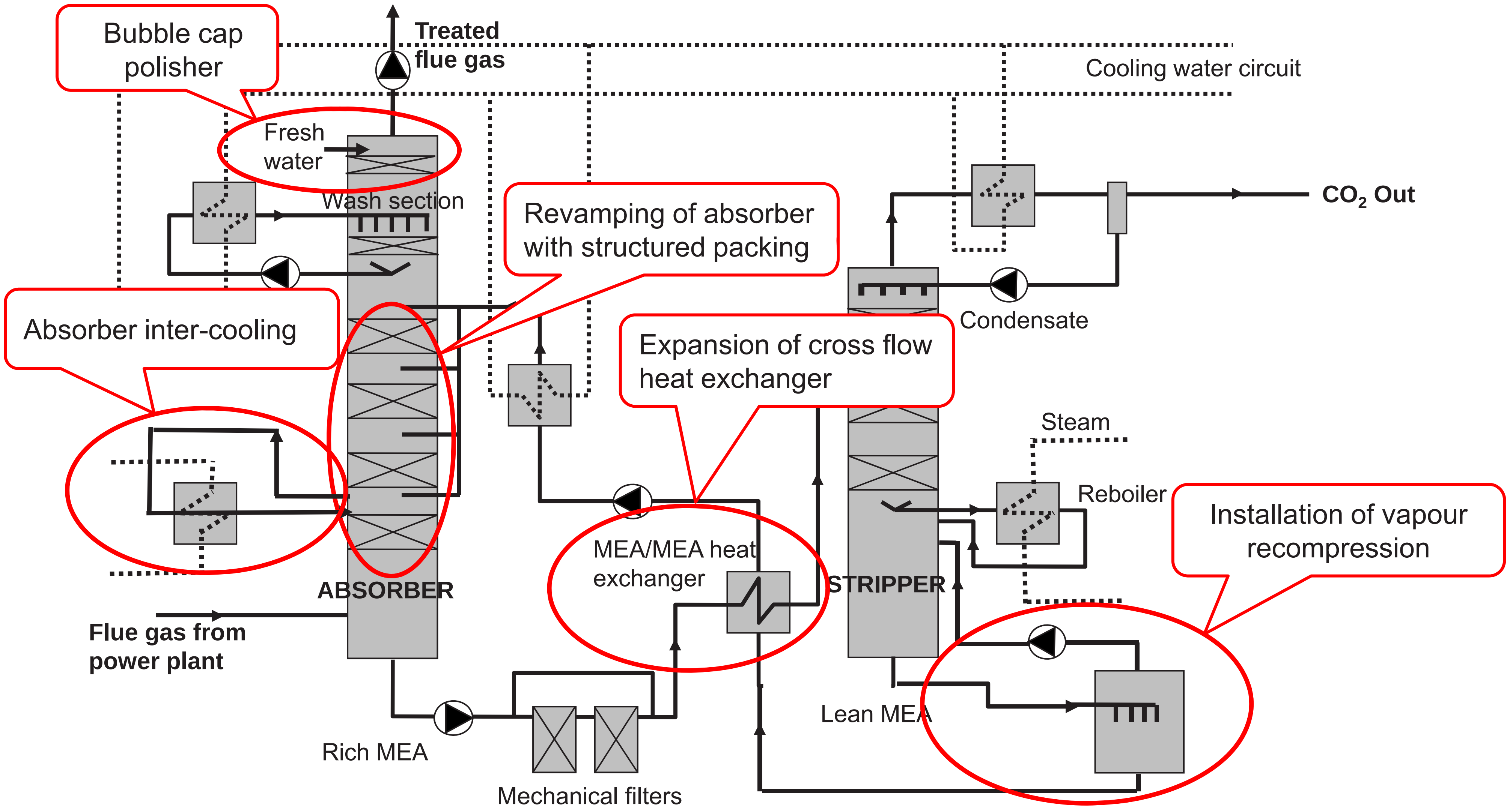
The CO_2 Capture Pilot Plant at Esbjerg Power Plant



Pilot Plant Specifications

- Operates on a slip stream of flue gas taken directly after the wet FGD
- Flue gas flow: 5000 Nm^3/h (0.5% of 400 MW_e)
- CO_2 capture capacity: 1000 kg/h
- Cleaning efficiency: 90%

Esbjerg Pilot Plant Flow Diagram



Bubble cap polisher

Revamping of absorber with structured packing

Absorber inter-cooling

Expansion of cross flow heat exchanger

Installation of vapour recompression

CESAR Pilot Plant Modifications: Inter-cooler & Flash Vessel

Absorber inter-cooler skid

Flash vessel for vapour recompression

Pilot Plant Operation History and Outlook

Four test campaigns have been conducted during CASTOR and three more are scheduled for the CESAR project:

- 1000 hours using standard solvent ”30%-wt. MEA” (Jan – Mar 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)

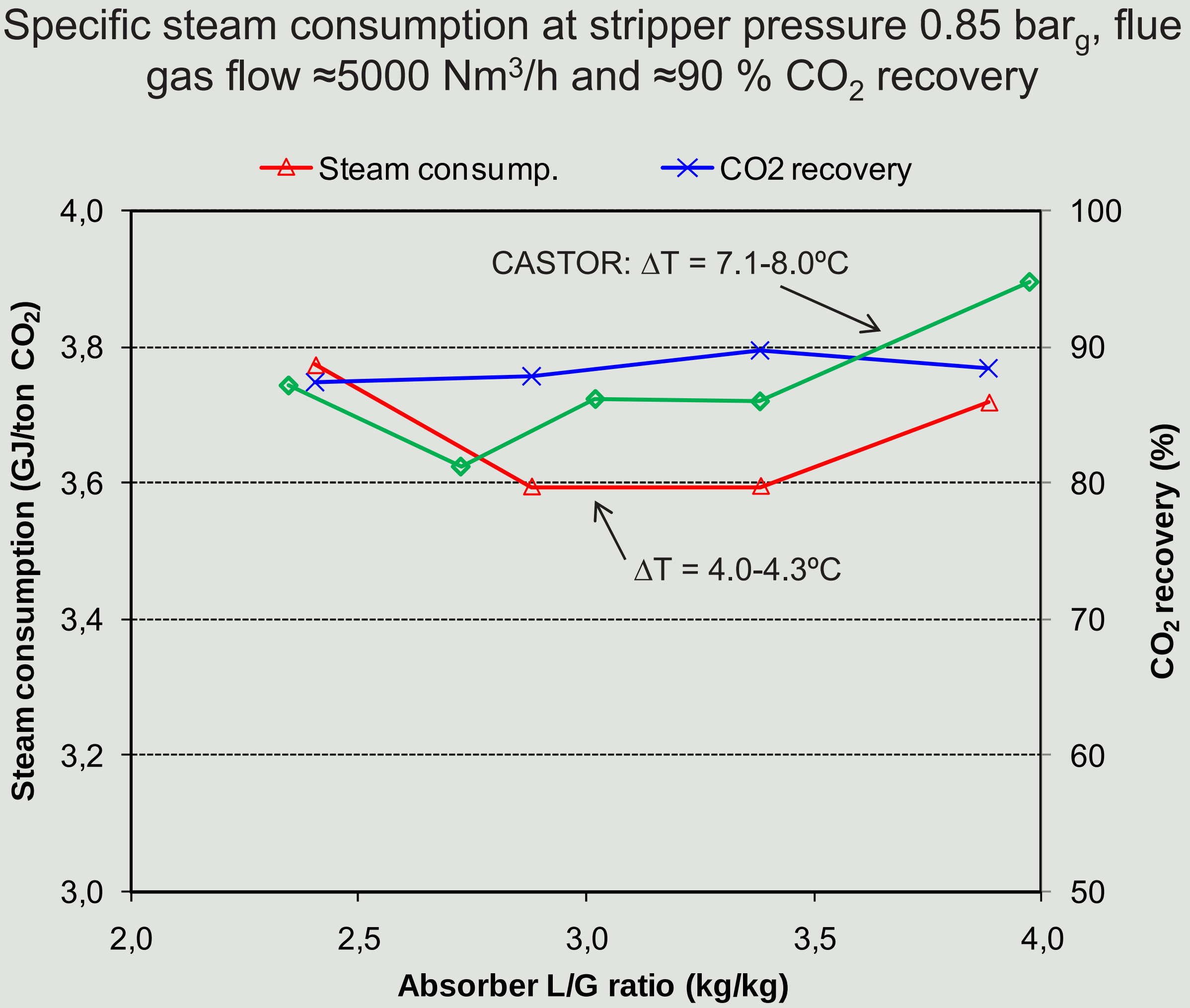
CASTOR

- >1000 hours using standard solvent ”30%-wt. MEA” (Mar 2009 – July 2009) in modified pilot plant
- >1000 hours using novel solvent ”CESAR 1” (Oct 2009 – Dec 2009) in modified pilot plant
- >1000 hours using novel solvent ”CESAR 2” (Feb 2010 – Jun 2010) in modified pilot plant

Outline of CESAR MEA Test Campaign

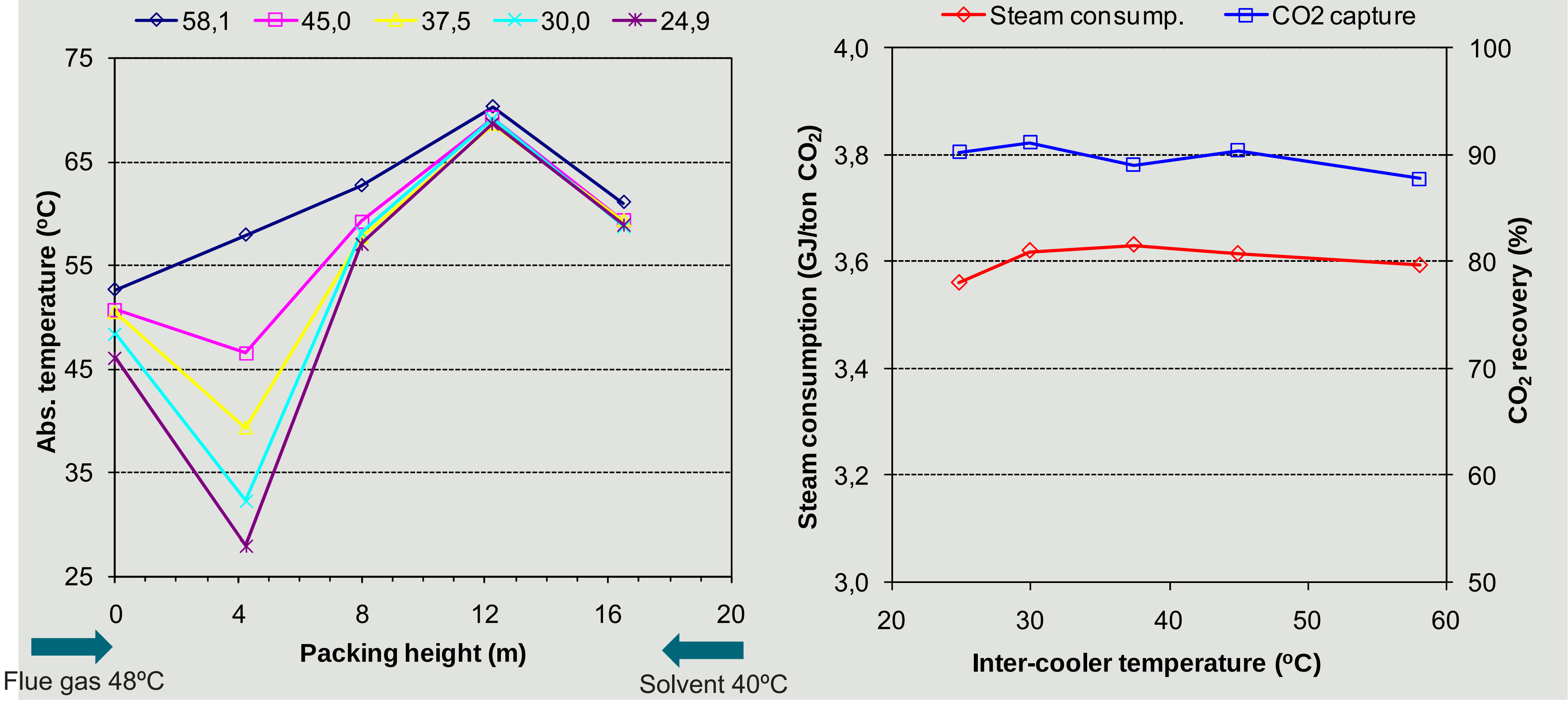
- **Test 1 – Parameter variation**
  - a) Optimisation of solvent flow rate (at 90% capture)
  - b) Effect of absorber inter-cooling
  - c) Effect of vapour re-compression
  - d) Variation of CO_2 capture percentage
  - e) Variation of stripper pressure
- **Test 2 – 500 hours of continuous operation**
  - Operation at ”optimised” conditions and achieving 90% CO_2 capture (on average)
  - Quantification of solvent consumption and degradation
  - Characterisation of corrosion behaviour
- **Test 3 – Miscellaneous tests**
  - Transient test & load following capability
  - Emission measurements
  - Etc.

Optimisation of Absorber L/G with Improved Cross Flow HX



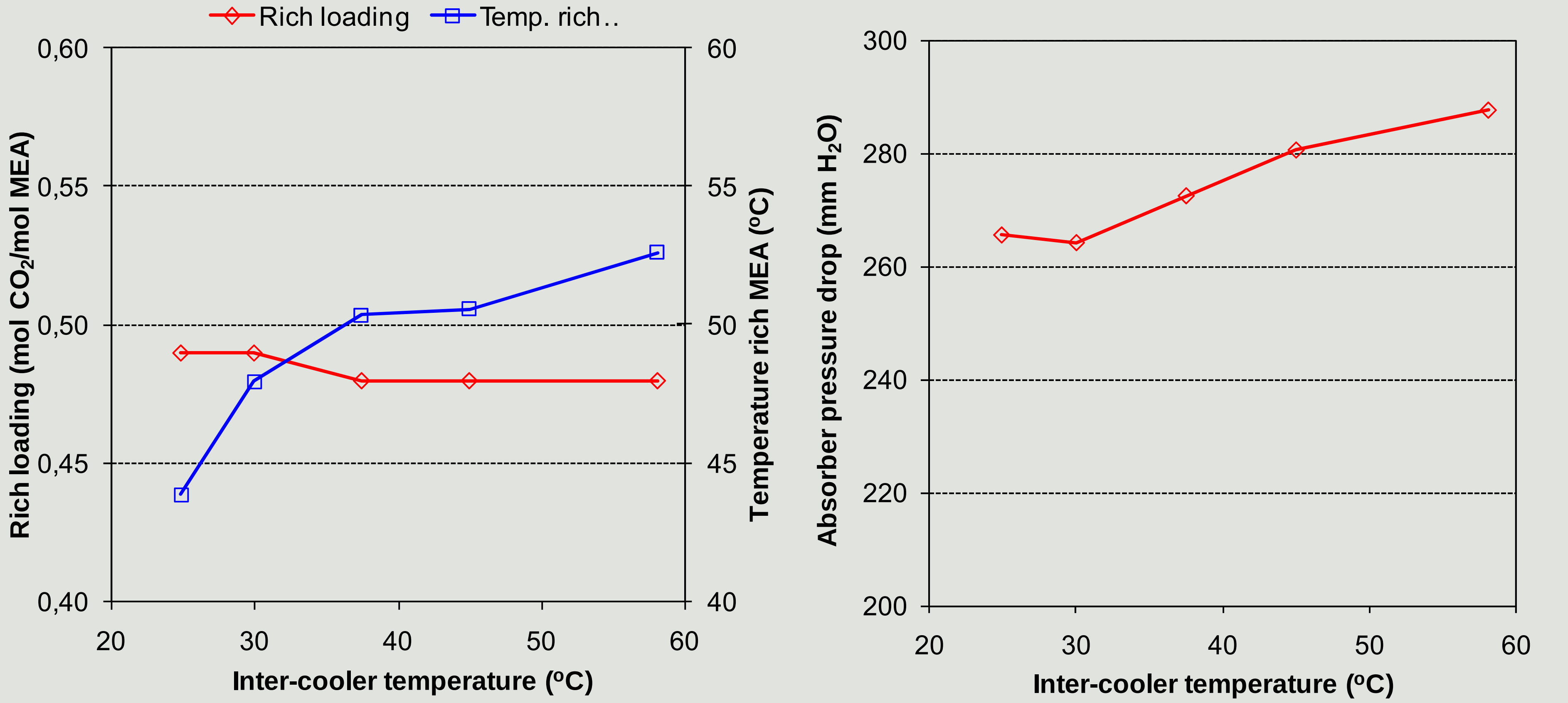
Effect of Process Modifications: Absorber Inter-cooling (1/2)

Flue gas flow ≈5000 Nm^3/h, L/G ≈3 kg/kg, Stripper pressure =0,85 barg,
CO_2 capture ≈90%



Effect of Process Modifications: Absorber Inter-cooling (2/2)

Flue gas flow ≈5000 Nm^3/h, L/G ≈3 kg/kg, Stripper pressure =0,85 barg,
CO_2 capture ≈90%

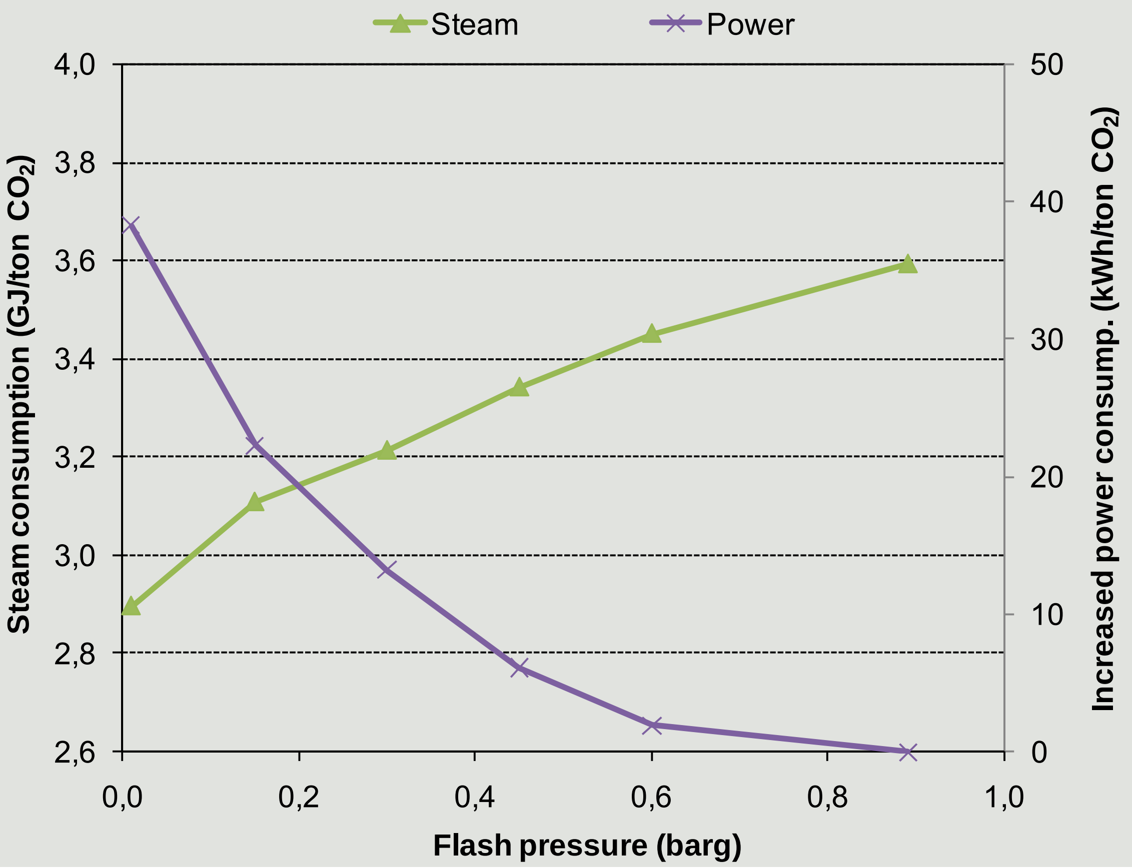


CESAR Enhanced Separation & Recovery

DONG energy

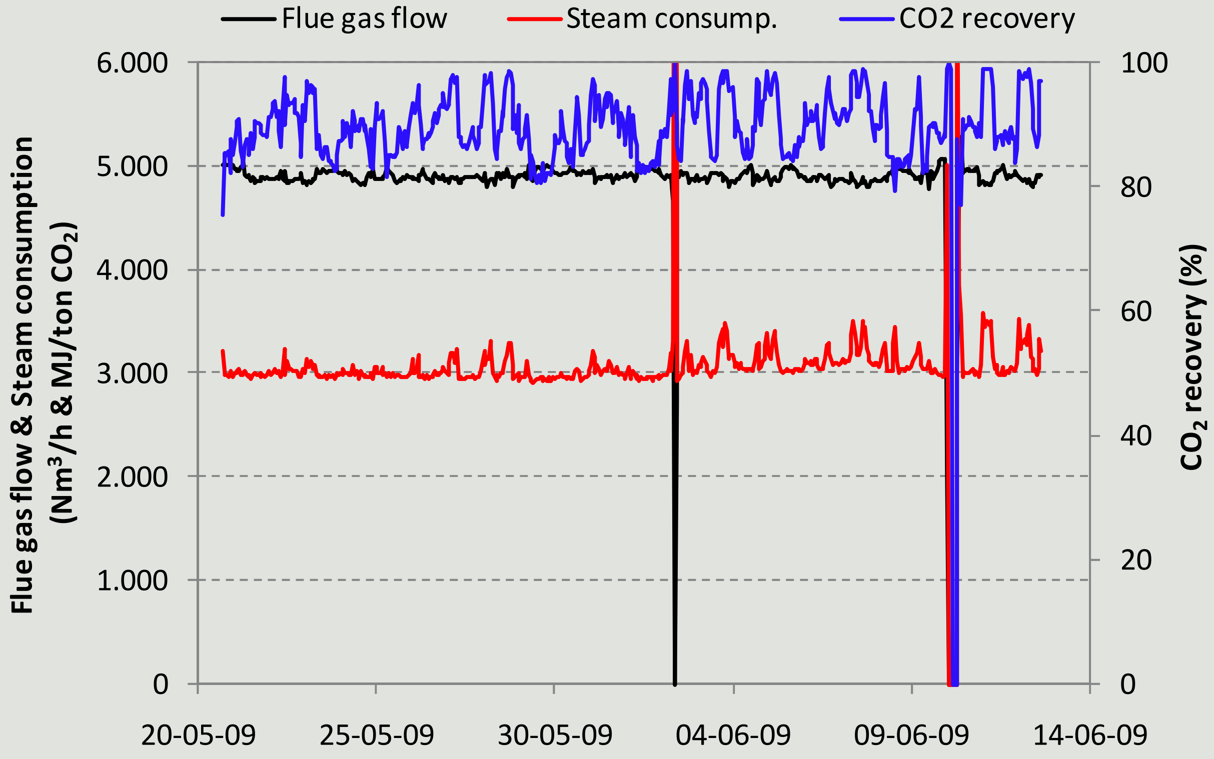
Effect of Process Modifications: Lean Vapour Re-compression

Flue gas flow ≈5000 Nm^3/h, L/G ≈3 kg/kg, Stripper pressure =0,85 barg, CO_2 capture ≈90%, no inter-cooling



CESAR MEA Test: 500 Hours of Continuous Operation

L/G ≈3 kg/kg ,stripper pressure 0.85 bar_g with inter-cooling and vapour re-compression

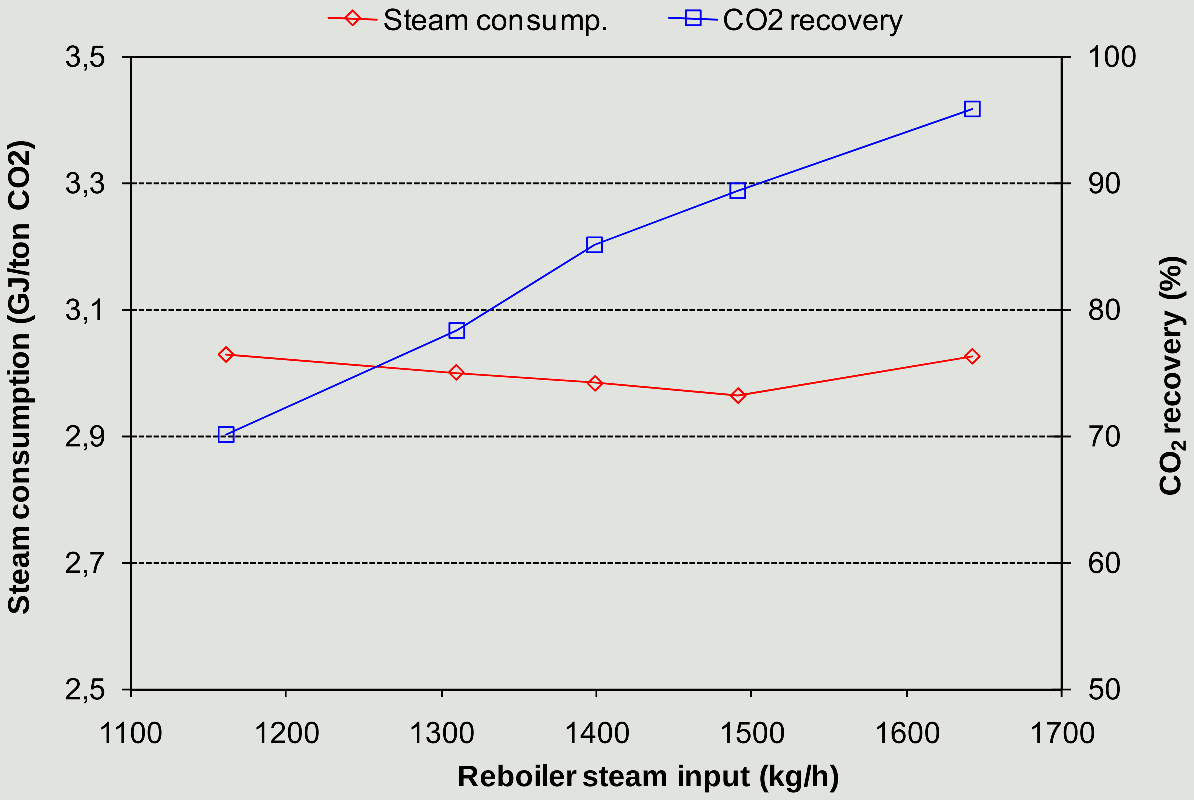


Average steam consumption: ≈3.07 GJ/ton CO_2 (+ 24 kWh/ton CO_2) Average CO_2 capture: 90 %

(Result from CASTOR: ≈3.7 GJ/ton CO_2)

Influence of Reboiler Steam Input

Flue gas flow ≈5000 Nm^3/h, L/G ≈3 kg/kg ,stripper pressure 0.85 bar_g
with inter-cooling and vapour re-compression



Conclusions

Several process upgrades have been introduced at the Esbjerg CO_2 capture pilot plant . A benchmark campaign using 30% MEA has among others indicated that:

- Reducing the ΔT of the solvent cross flow heat exchanger from ≈7.5 to 4.5ºC leads only to minor saving in reboiler steam consumption (≈ 0.1 GJ/ton CO_2), however, it allows for lower reboiler temperatures (i.e. higher L/G) at reduced penalty
- Inter-cooling seems to have only marginal effect on reboiler steam consumption with MEA, however, as a co-benefit the absorber ΔP is reduced
- Vapour re-compression may lower reboiler steam consumption substantially (3.6 to 2.8 GJ/ton) on account on increased power consumption. A full cost benefit analysis is required to determine the true benefits

Acknowledgements

The pilot plant in Esbjerg is sponsored by the CESAR partners, the European Commission through the CESAR project, and the CLEO project sponsors: Aker Clean Carbon, EDF, EnBW, Enel & Hitachi Power Europe

www.csiro.au

Environmental Impacts of Atmospheric Emissions from Amine-based Post-Combustion CO_2 Capture

Energy Transformed Flagship

Moetaz Attalla, Merched Azzi, Phil Jackson and Dennys Angove

29th September 2009

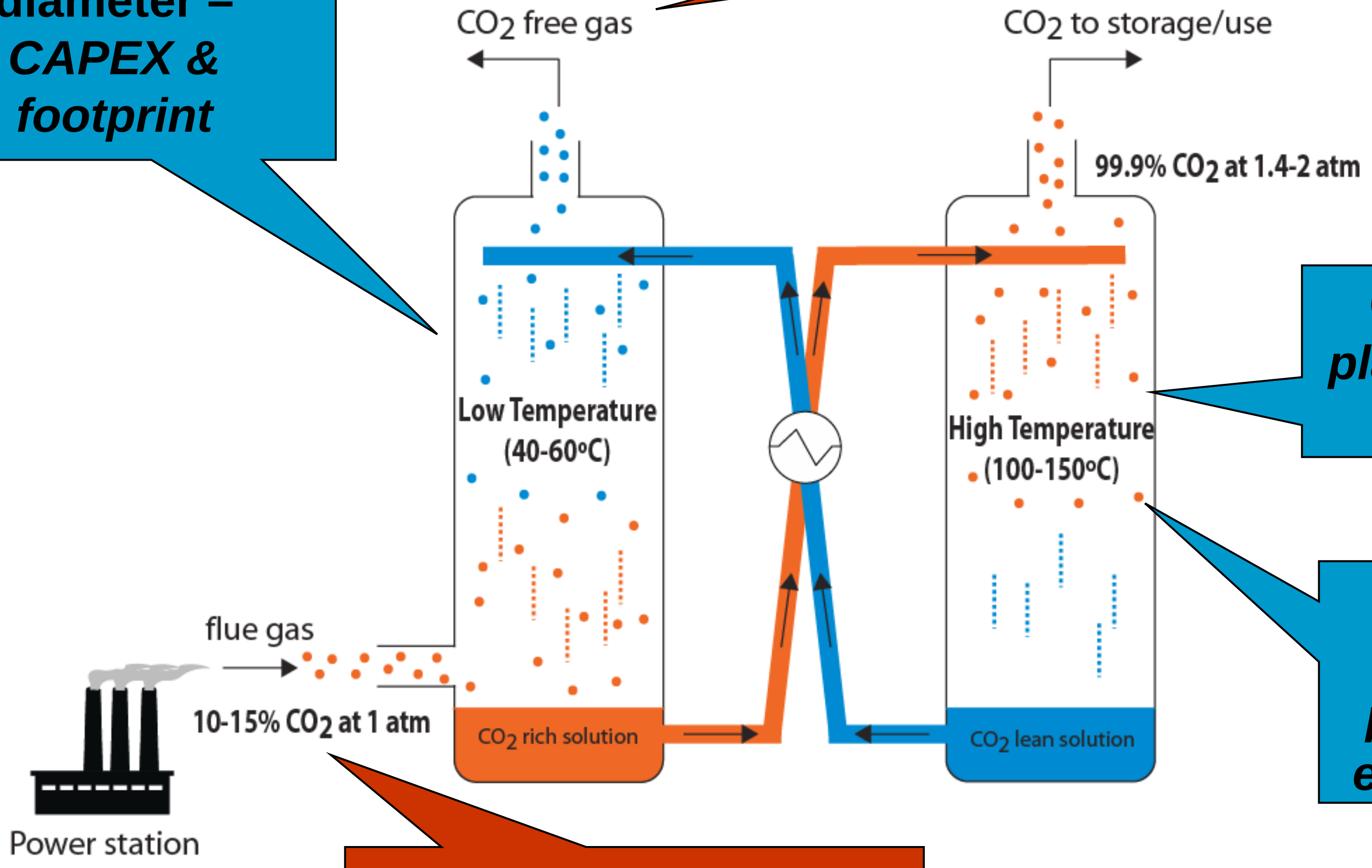
National Research
FLAGSHIPS
CSIRO

CSIRO Energy Centre

CSIRO’s Energy Research At Newcastle

- Renewable Energy Systems
  - Solar Thermal
  - Vibration Energy Harvesting
  - Organic Photovoltaics
- Improving Energy End Use
  - Distributed Energy
  - Self Learning Smart Agent Technologies
  - Energy Storage
- Carbon Capture and Storage
  - Geosequestration (ECBM,..)
  - Post Combustion Capture Technologies

The Scientific Challenges…….



Atmospheric emissions – *environmental impacts*

Column height & diameter – *CAPEX & footprint*

Corrosion – *plant downtime and repair*

Heat for desorption – *power station energy penalty*

Flue gas impurities – *solvent degradation*

Identifying potential impacts when solvent-based carbon capture is deployed….

- **Solvent-based carbon capture plants using amines can mitigate stationary-source CO_2 emissions, BUT……**

- **What happens when there is amine "slip" from the capture plant?**

- **What is the atmospheric fate of the lost amine molecules?**
- **Are they deposited close to the emission source, or does atmospheric chemistry convert them into deleterious molecules, harmful to people and the environment?**

- **How can we develop safe levels or environmental thresholds for amines?**

- **What are safe levels of exposure to amines?**

- **How much amine can be "released" to the environment before authorities need to act?**

Identifying potential impacts when solvent-based carbon capture is deployed….

- **Most, but not all, capture amines have large dipole moments and are strongly hydrophilic eg ammonia**

- **Ammonia undergoes atmospheric chemical reactions, and other highly polar molecules, tend to promote aggregation and particulate formation (SOA) that impact on climate change**

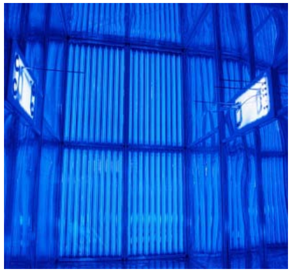
- **The degradation products of larger capture amines *in the capture plant* include amides and aldehydes – volatiles implicated in photochemical smog formation!**

- **Secondary and tertiary amines form stable nitrosamines (potent mammalian carcinogens)**

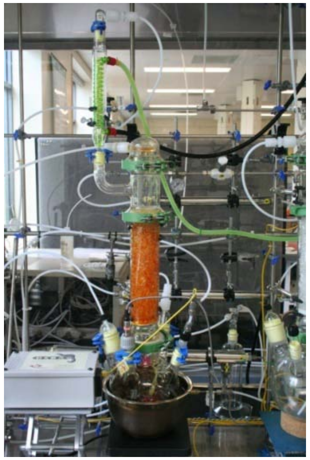
Reference: J.J. Renard *et al*. *J. Harzardous Mater.* **2004,** *B108*, 29

Key Research Program Emissions

- **Program currently being undertaken at the Energy Centre, Newcastle includes:**

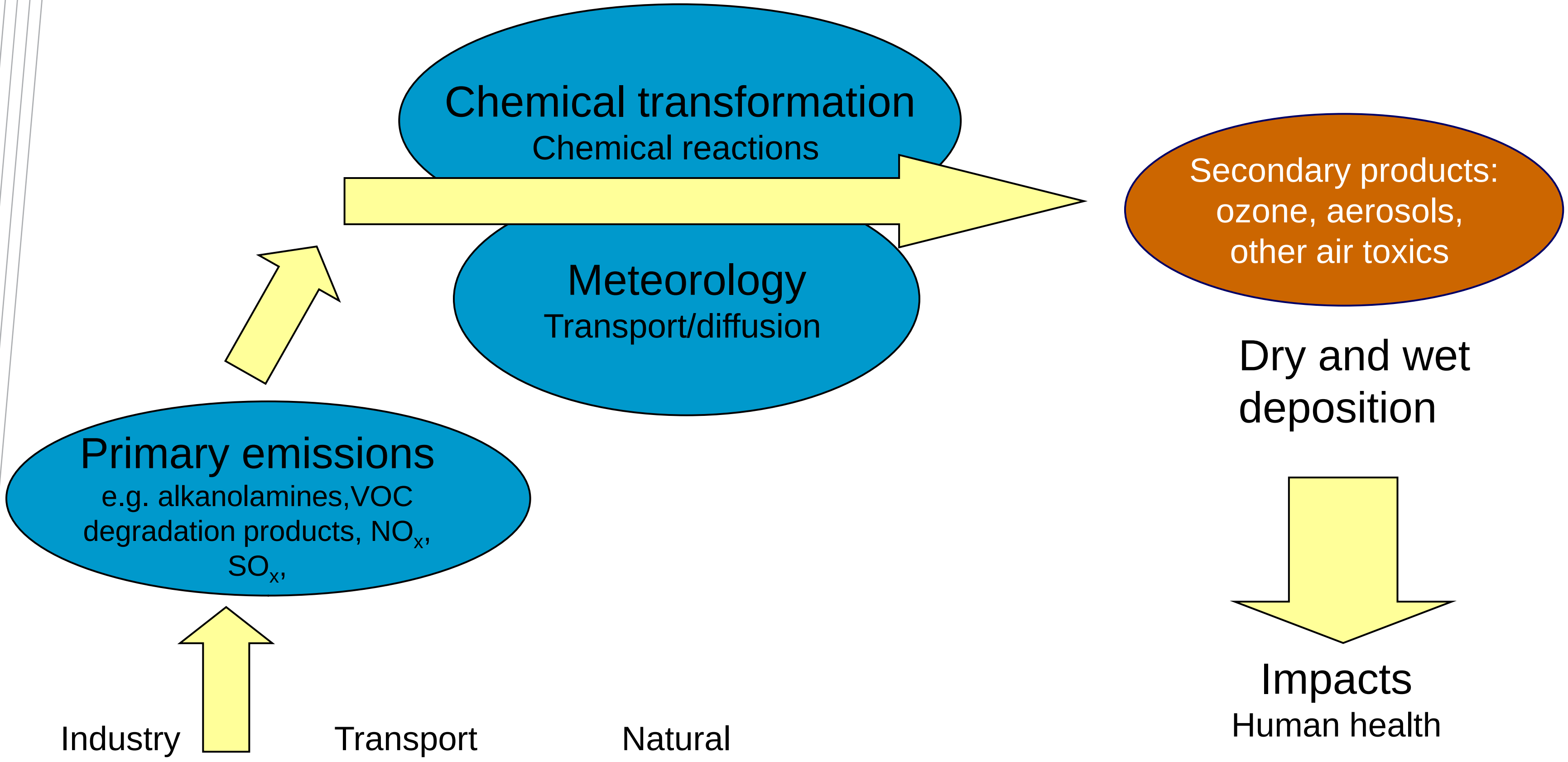


1. Oxidative/ thermal mechanisms of amine degradation *in the capture plant and under controlled realistic laboratory conditions*
2. the fate of ‘slipped’ amine and amine degradation products in the troposphere
3. Under what atmospheric conditions amine catalysed smog-inducing photochemistry and photo-oxidation.
4. whether secondary or tertiary amines form nitrosamines in the atmosphere
5. Develop new screening methods for assessing atmospheric amine impacts
6. Develop dispersive models with a clearer understanding of amine atmospheric chemistry taken into account
7. The environmental impact of amine slip



National Research FLAGSHIPS CSIRO

Fate and impacts of atmospheric amine emissions



Chemical transformation
Chemical reactions

Meteorology
Transport/diffusion

Primary emissions
e.g. alkanolamines,VOC degradation products, NO_x, SO_x,

Secondary products: ozone, aerosols, other air toxics

Dry and wet deposition

Impacts
Human health
Ecosystem health

Industry

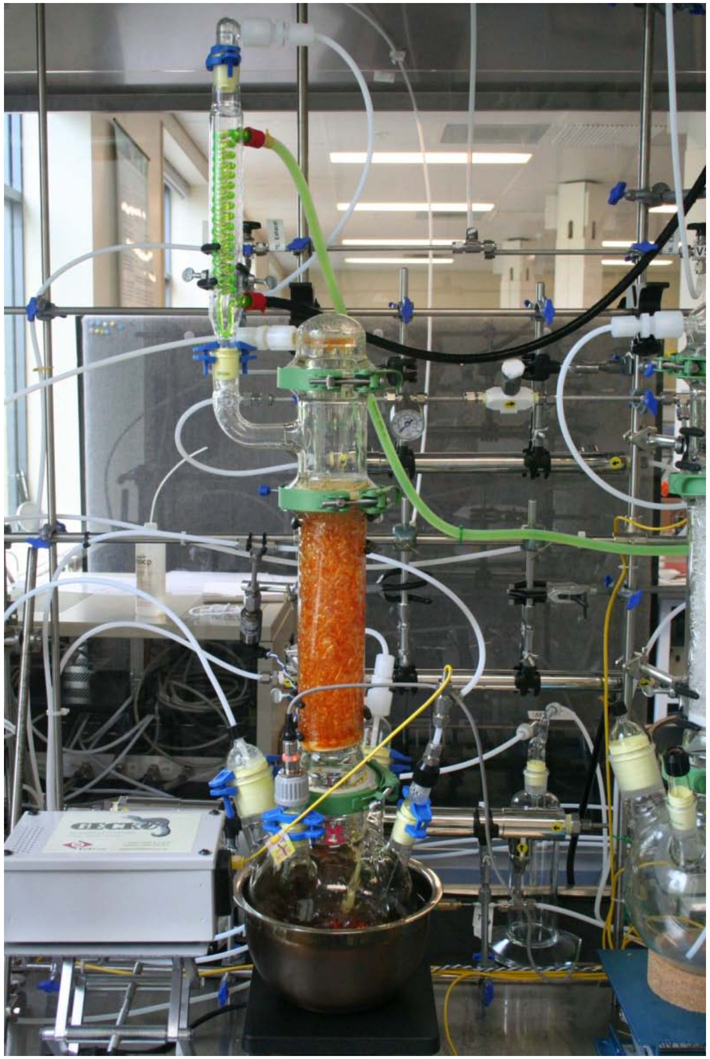
Transport

Natural

- *What would be the impact of changing emissions profiles ?*

Packed absorber column for solvent degradation studies

Attalla, Jackson, Sexton



- **Packing height = 25 cm**
  - 8 mm Rasching rings
- **Column diameter = 6 cm**
- **Absorber sump: 3-L capacity**
- **L: 1 L/min, recirculating flow**
- **G: 3.5 SLPM, once-through**
  - 10% O_2, 2% CO_2 baseline
- **T = 40^{o}C**
- **Baseline: MEA, plastic packing, metal salts**
- **Future Work:**
  - CS, SS packings (no metal salts)
  - Effects of NO_x/SO_x
  - Novel solvents

The CSIRO Smog Chamber Facility

The smog chamber is an 8 m^3 teflon lined environment with UV lamps at one end to simulate sunlight.

The chamber is filled with clean air and dosed with NOx and VOC to stimulate ozone and secondary aerosol formation in the atmosphere.

Dedicated instruments track the concentrations of;
- Ozone
- NOx
- Particles
- VOCs

National Research FLAGSHIPS CSIRO

Smog Chamber Facility

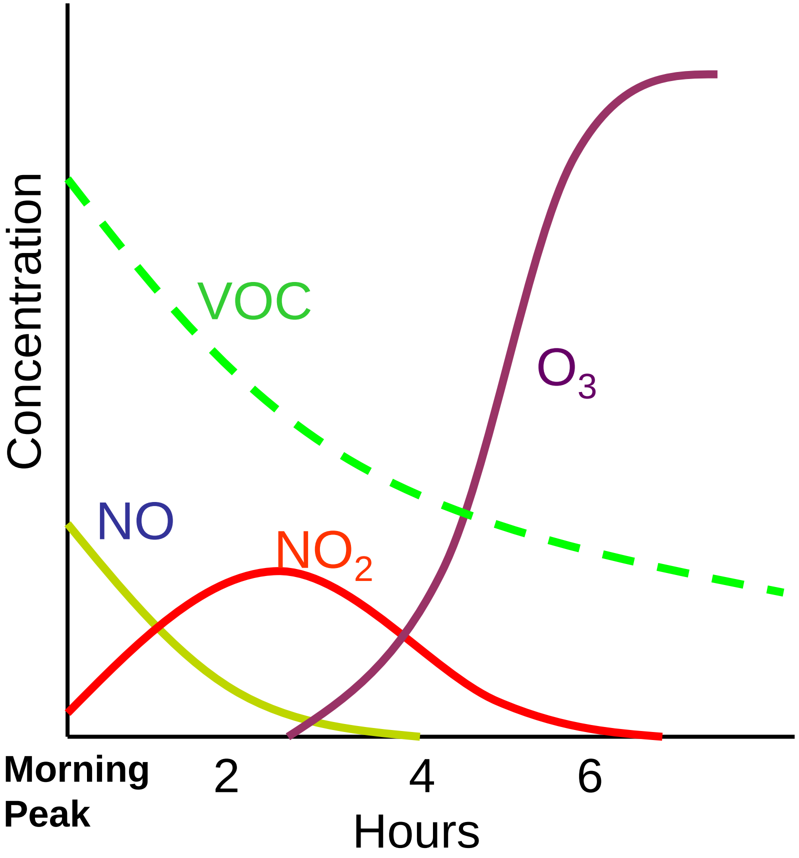
- **Study of the chemical basis for O_3, NO_2 ,aerosol and other oxidants formation**
- **Provide necessary data to develop and test chemical mechanisms for different ranges of conditions**
- **Evaluation of atmospheric impacts of using different types of scenarios on photochemical smog oxidants formation**
- **Identification of the appropriate chemical reaction paths for ozone and SOA formation using explicit mechanisms**

- ***The data obtained are used to update and develop advanced techniques that can be embedded into our air quality tools for air quality modelling and assessment.***

Mechanisms of photochemical smog formation

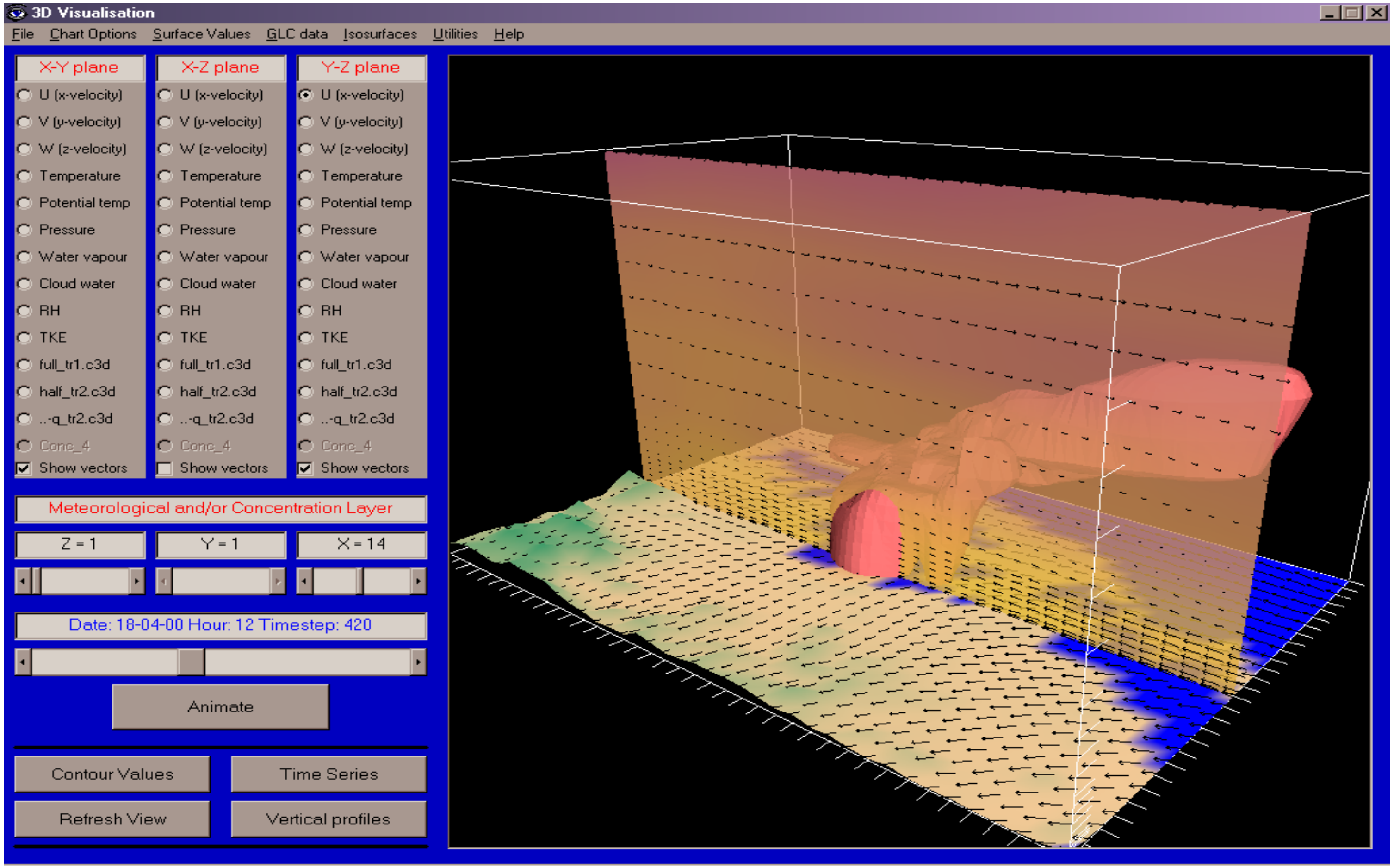
VOC + NO_x + hv ✹ O_3 + SOA + other smog products

- Chemistry is non-linear and changes in concentrations and ratios can have significant impacts on photochemistry
- Two photochemical smog regimes
- O_3 production depends on available sunlight, temperature and the concentrations of VOC and NOx and their ratio
- NO_x determines the maximum ozone potential
- Real air parcels are also subject to fresh emissions



Smog Chamber used to elucidate the detailed photochemistry

Modelling power station emissions



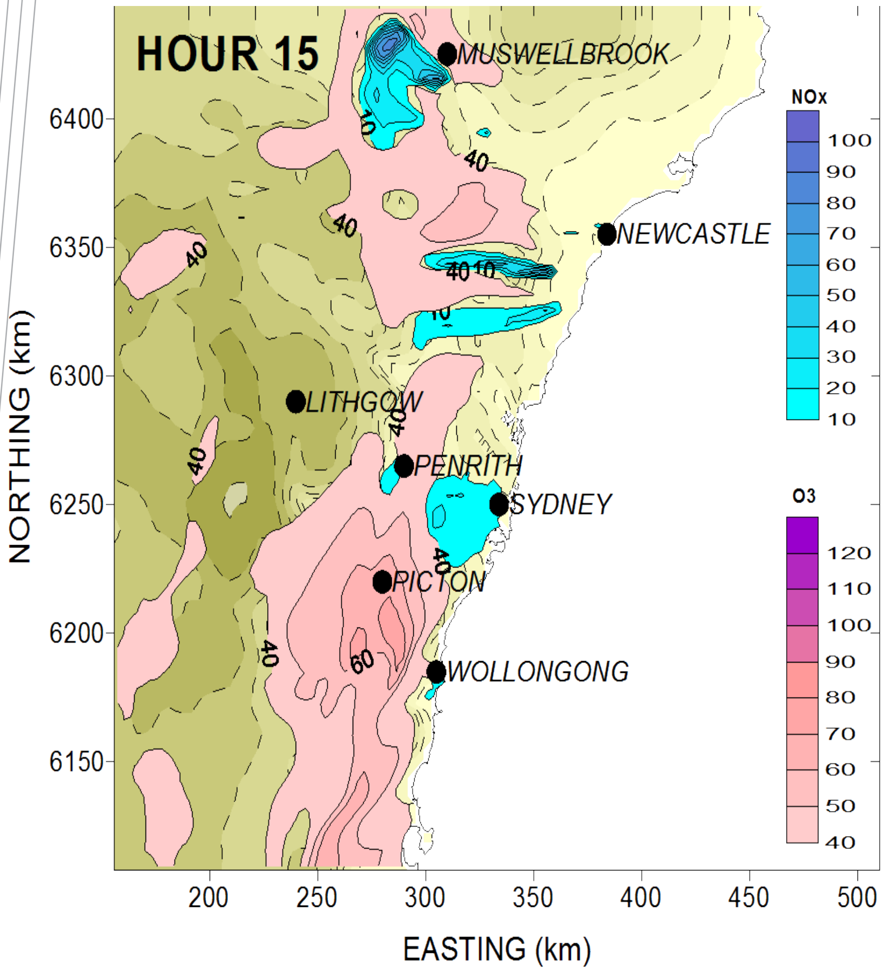
X-Y plane	X-Z plane	Y-Z plane
○ U (x-velocity)	○ U (x-velocity)	● U (x-velocity)
○ V (y-velocity)	○ V (y-velocity)	○ V (y-velocity)
○ W (z-velocity)	○ W (z-velocity)	○ W (z-velocity)
○ Temperature	○ Temperature	○ Temperature
○ Potential temp	○ Potential temp	○ Potential temp
○ Pressure	○ Pressure	○ Pressure
○ Water vapour	○ Water vapour	○ Water vapour
○ Cloud water	○ Cloud water	○ Cloud water
○ RH	○ RH	○ RH
○ TKE	○ TKE	○ TKE
○ full_tr1.c3d	○ full_tr1.c3d	○ full_tr1.c3d
○ half_tr2.c3d	○ half_tr2.c3d	○ half_tr2.c3d
○ ..-q_tr2.c3d	○ ..-q_tr2.c3d	○ ..-q_tr2.c3d
○ Conc_4	○ Conc_4	○ Conc_4
☑ Show vectors	☐ Show vectors	☑ Show vectors

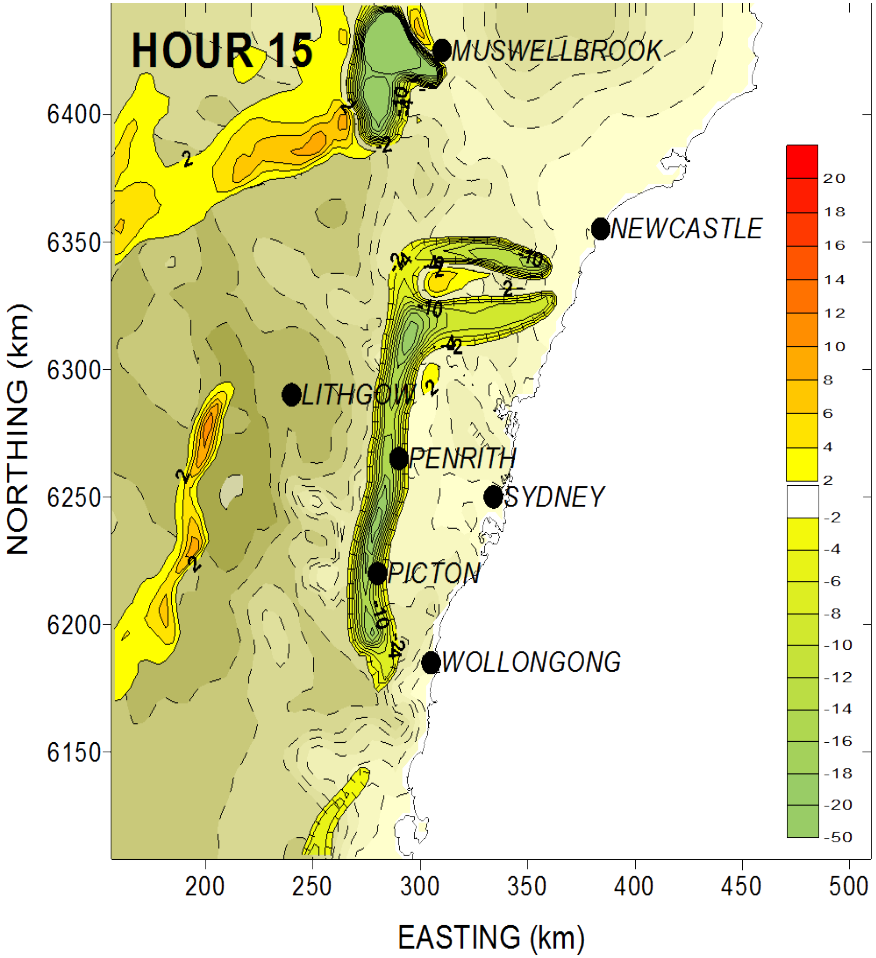
Meteorological and/or Concentration Layer

Z = 1
Y = 1
X = 14

Date: 18-04-00 Hour: 12 Timestep: 420

Inter-regional transport of pollutants





Amine emissions

- *With the exception of ammonia, the majority of alkanolamine capture solvents have boiling points > 100 °C*
- *This does not mean that amine losses will be small…..for a 1 million tonne CO_2/p.a. capture plant, this means amine losses of ~ 40-160 tonnes/p.a.**
- *Amine oxidation* ***within the capture plant*** *produces aldehydes and small organic acids (see next slide)*
- *The small organic acids react with primary or secondary capture amines to produce amides*
- *Solution-based MEA oxidation:*

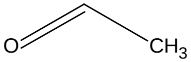
***NILU OR 77/2008**

Molecules that should be monitored close to PCC plants

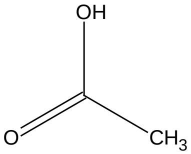
Absorber side

ammonia **1.2.3** NH_3

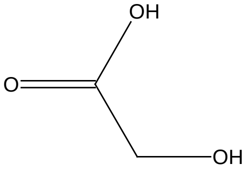
acetaldehyde **2**



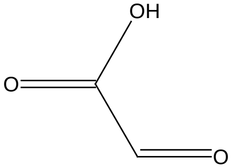
acetic acid **1.2.3**



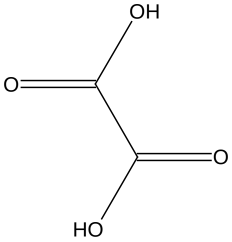
hydroxyacetic acid **1.2.3.5**

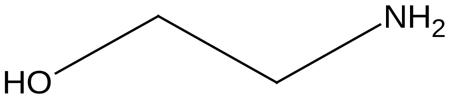


oxoacetic acid **1.2.3.5**

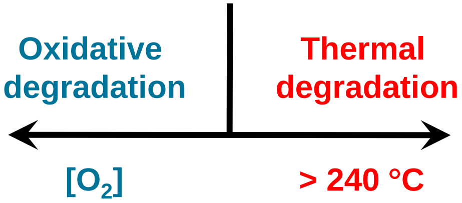


ethanedioic acid **1.2.3.5**





2-aminoethanol, MEA



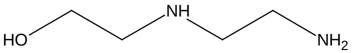
Oxidative degradation

Thermal degradation

$[O_2]$

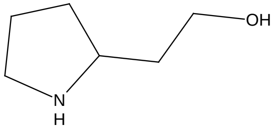
> 240 °C

1. **assists particle aggregation**
2. **undergoes photochemical reactions**
3. **undergoes acid rain forming reactions**
4. **can form nitrosamines**
5. **ultimate fate is unknown**



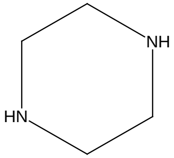
1.2.4.5

2-[(2-aminoethyl)amino]ethanol



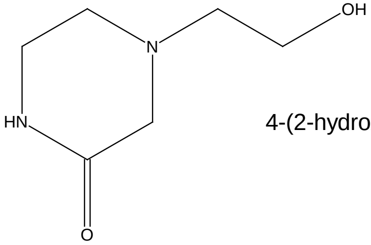
2-(pyrrolidin-2-yl)ethanol

1.2.4.5



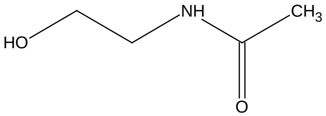
piperazine

1.2.4.5



4-(2-hydroxyethyl)piperazin-2-one

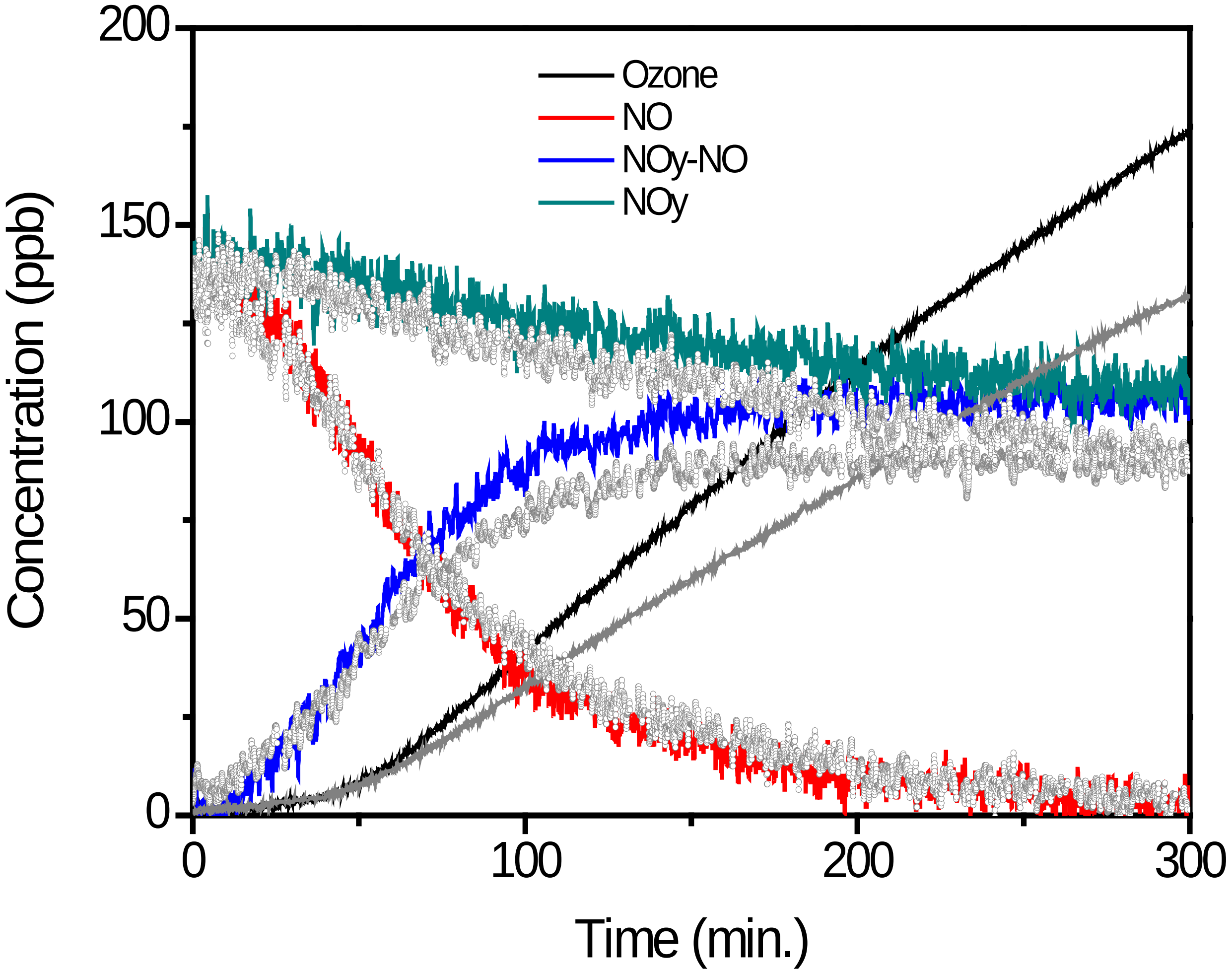
1.2.4.5



N-(2-hydroxyethyl)acetamide

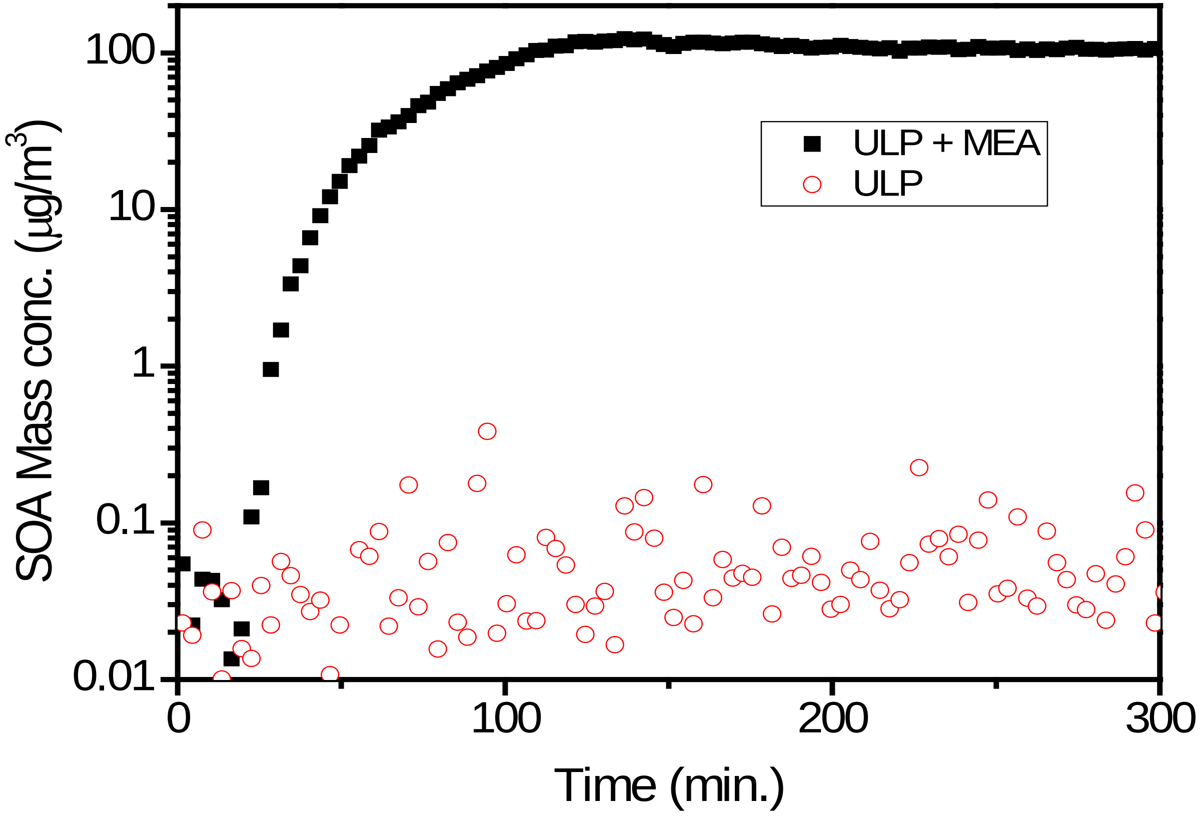
1.2.4.5

Ozone and NOx profiles for ULP (grey) and ULP+MEA (colours) experiments



National Research FLAGSHIPS
CSIRO

SOA mass conc. profiles for ULP (red) and ULP+ MEA (black) experiments



Current and future work at CSIRO

Realistic lab based data and analytical procedures:

Oxidation and thermal degradation experiments carried out under controlled conditions

Low level analytical procedures

Pilot plant samples from exhaust and liquor

Long term operational data

Smog chamber simulations will be carried out to:

Identify the major pollutants produced by the photo-decomposition of the flue gas compounds of the absorber under selected ambient conditions

Identify the major chemical reactions pathways responsible for the MEA oxidation

Develop the appropriate chemical mechanism required to simulate the oxidation of MEA

Airshed modelling to determine the potential environmental impact of using amine solution for CO_2 capture

Embedded the modified chemical mechanism into the airshed model

Simulate different atmospheric scenarios to assess the potential impact of the new CO_2 capture process

Determine the trade off between CO_2 capture and local and regional air quality

CSIRO Division of Energy Technology
Moetaz Attalla

Phone: +61 2 4960 6083
Email: moetaz.attalla@csiro.au
Web: www.csiro.au/org/ET

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

Chilled Ammonia - Pilot Testing at the We Energies Pleasant Prairie Power Plant

12th IEA Post-Combustion Meeting

Regina, Saskatchewan

Sean Black, Alstom

Richard Rhudy, EPRI

30th September 2009

EPRI | ELECTRIC POWER RESEARCH INSTITUTE

POWER | ALSTOM

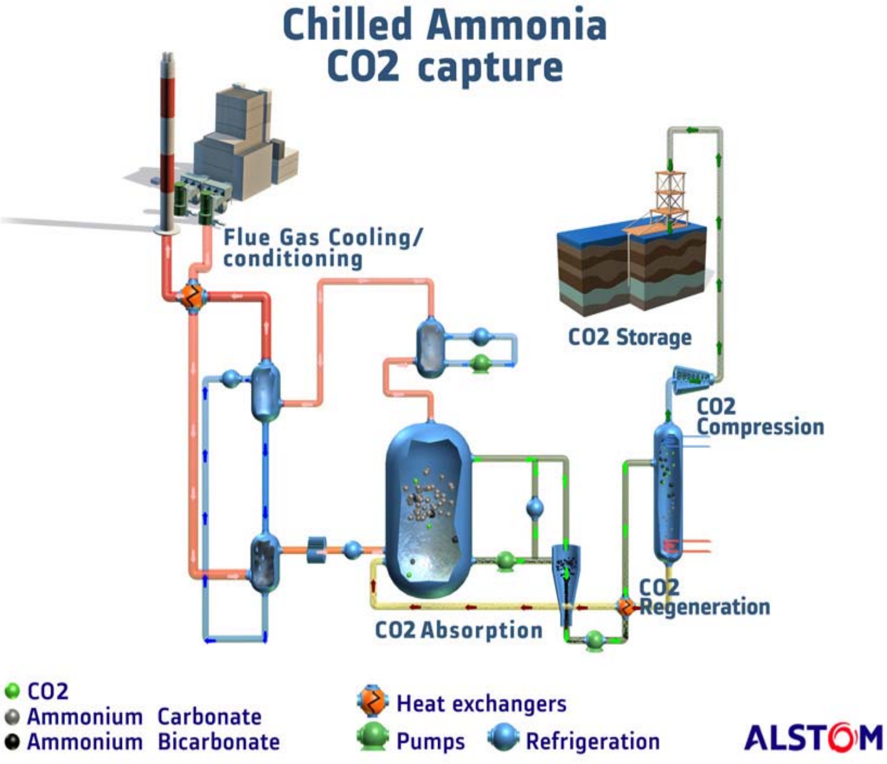
Chilled Ammonia Process

Principle

- Cooled flue gas is treated with ammonium carbonate in solution, which reacts with CO_2 to form ammonium bicarbonate
- Raising the temperatures reverses the above reactions – releasing pressurized CO_2

Advantages

- Energy-efficient capture of CO_2
- High CO_2 purity
- Tolerant to oxygen and flue gas impurities
- Stable reagent, no degradation possible, no emission of trace contaminants
- Low-cost, globally available reagent



A promising technology!

Alstom’s development program of carbon capture technologies

Running

We Energies Pleasant Prairie
USA - 5 MWth
Chilled Ammonia - Coal

Vattenfall Schwarze Pumpe
Germany - 30 MWth
Oxy - Lignite

EoN Karlshamn
Sweden - 5 MWth
Chilled Ammonia - Fuel/Gas

Total Lacq
France - 30 MWth
Oxy - Gas/Fuel

Commissioning

AEP Mountaineer
USA - 30 MWth
Chilled Ammonia - Coal

Dow Chemical Co.
USA, West Virginia
Advanced Amines

Study / Engineering

TCM Mongstad
Norway - 40 MWth
Chilled Ammonia - Gas

Transalta
Canada - >200 MWe
Chilled Ammonia - Coal

PGE Belchatow
Poland – 260 Mwe
Adv. Amines - Lignite

Vattenfall Jänschwalde
Germany - 250 MWe
Oxy - Lignite

Pre-selected for European Energy Programme for Recovery funding

A pioneer in developing Post and Oxy combustion capture technologies

Chilled Ammonia Process
Field Pilot at We Energies

Pleasant Prairie Power Plant (“P4”)

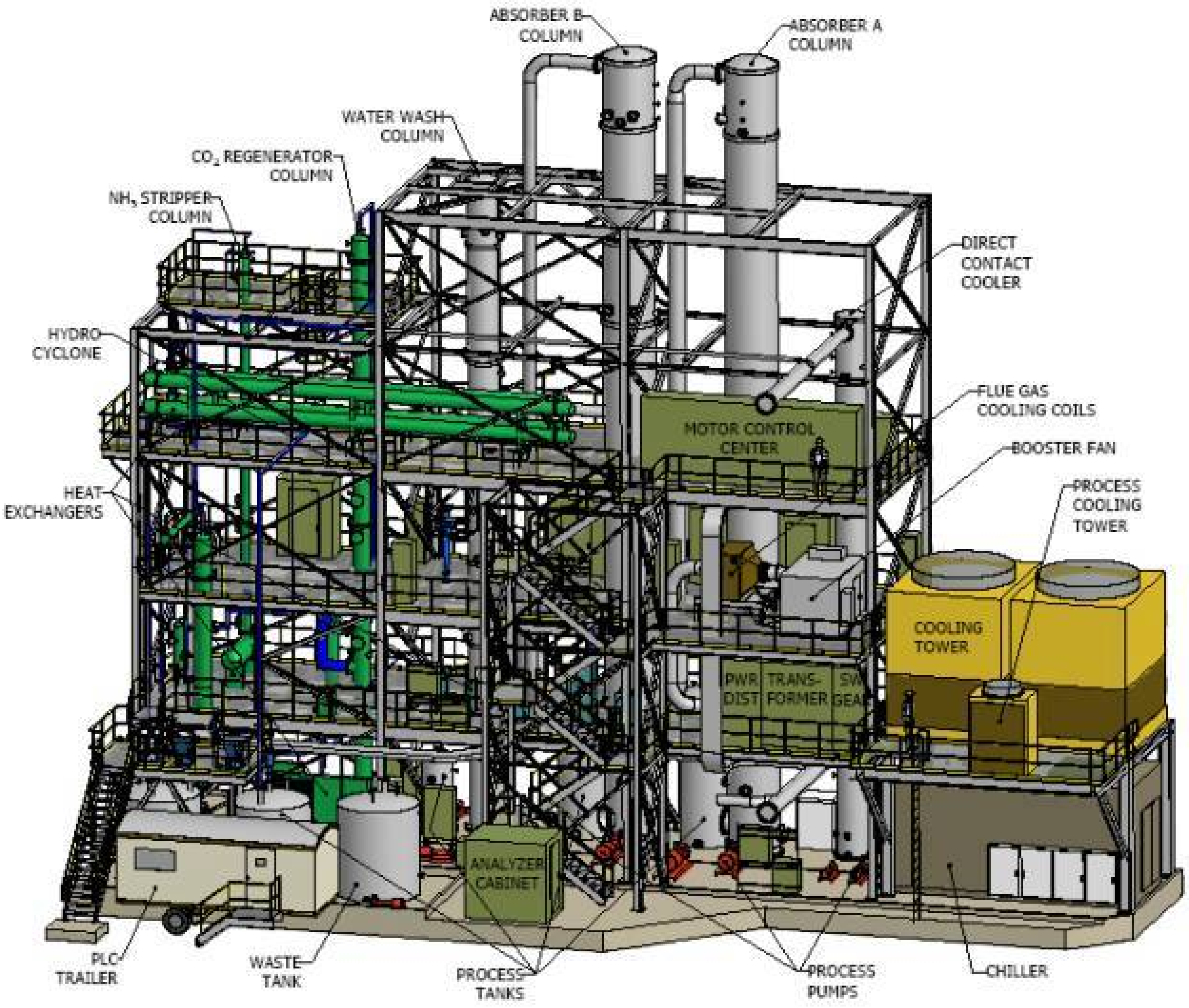
CO_2 Field Pilot at Pleasant Prairie

Validation Pilot Program

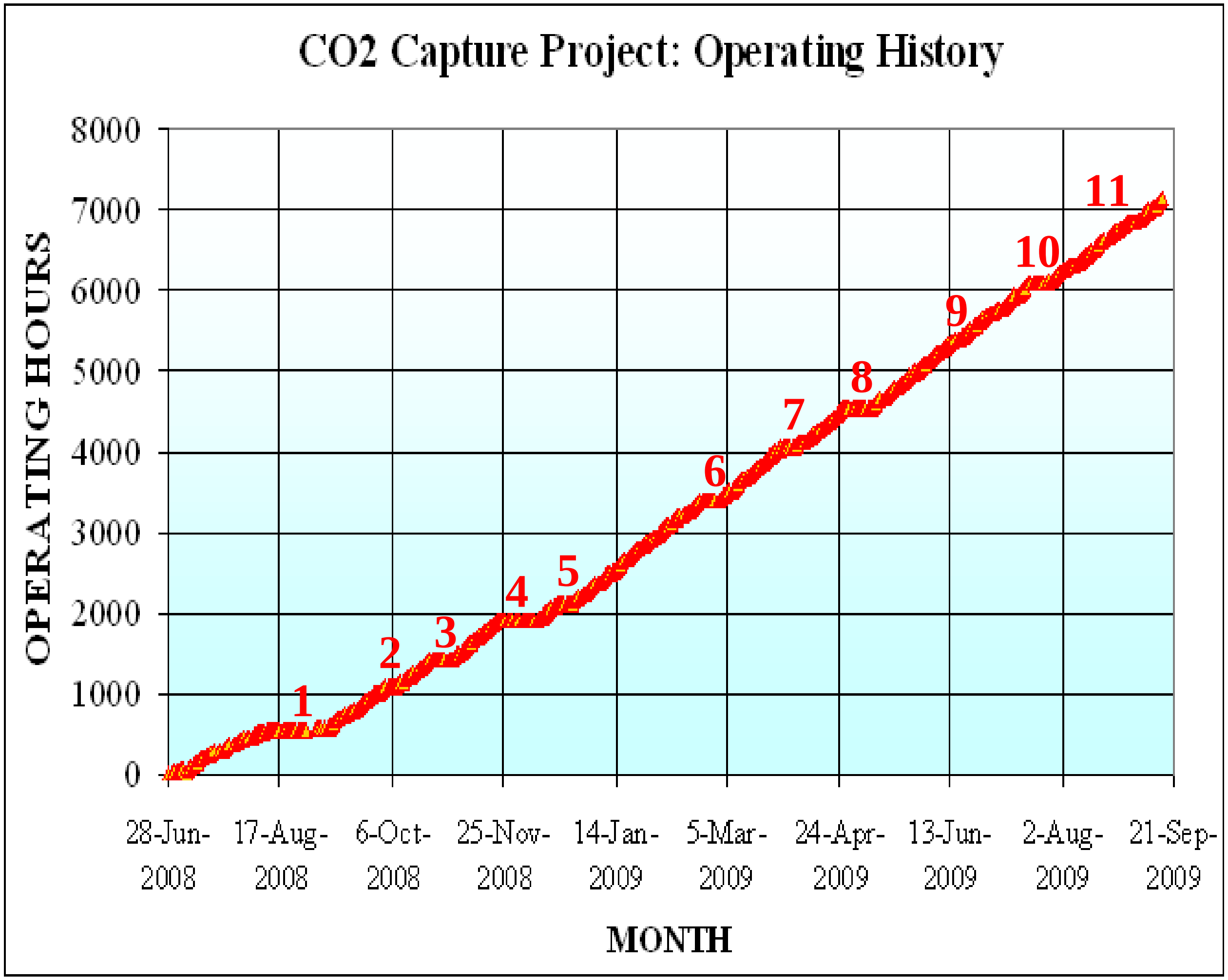
- Project participation through EPRI by 37 US and international utilities
- Designed to capture 1,600 kg CO_2/hour
- Operations commenced in June 2008
  - Over 7,000 hours operation
  - Achieved 90% capture in continuous operation at full load
  - Empirical data collected from pilot to date supports “proof of concept”
  - Initial data on steam and electrical energy consumption is consistent with expectations

A great technical success!

Validation Pilot at We Energies
3-D View of Pilot



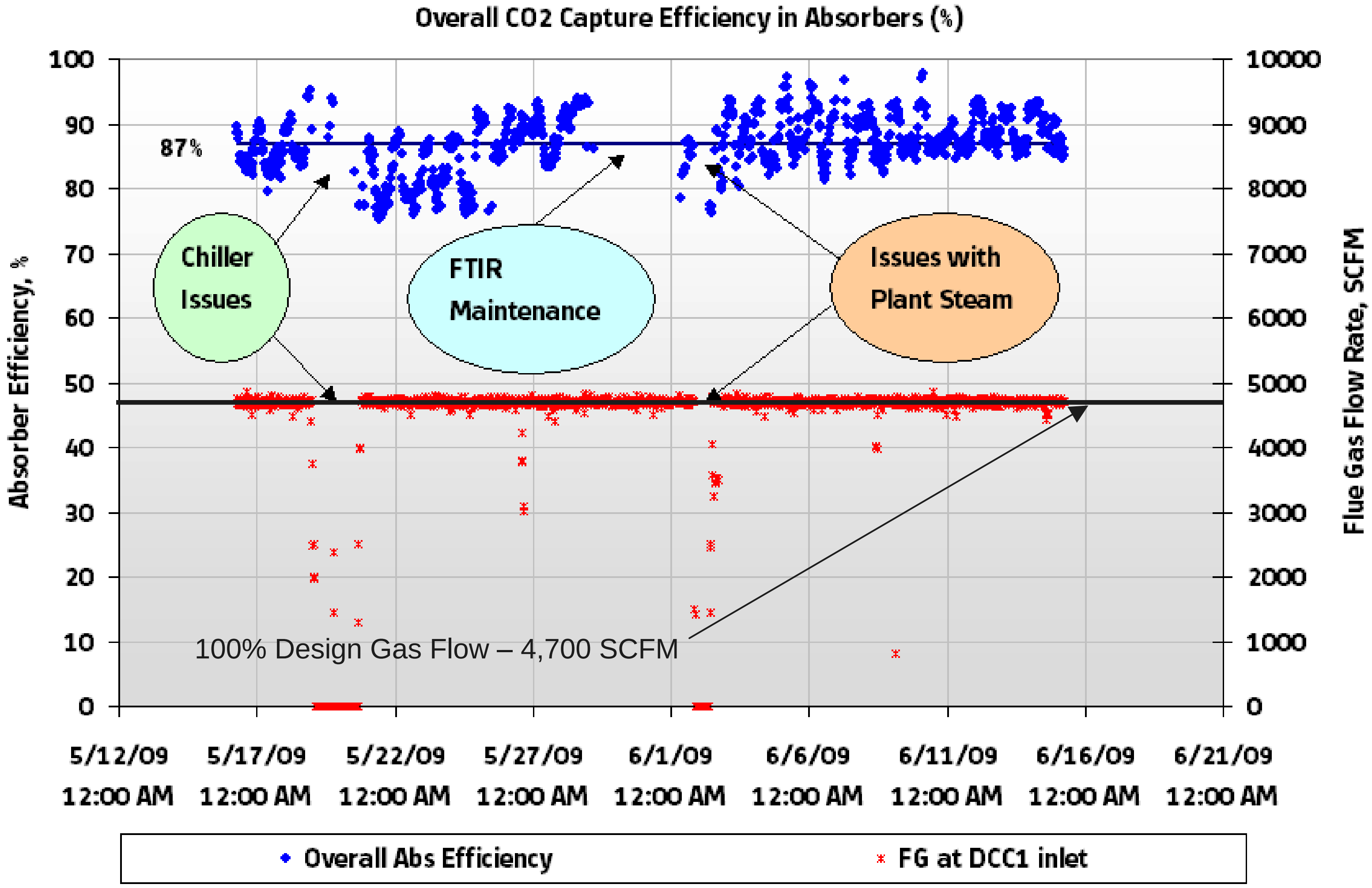
Field Pilot Activities
Operating History



1. **Planned outage to support pilot modifications**
2. **Power Plant Forced Outage**
3. **Planned outage to support pilot modifications**
4. **Thanksgiving + Planned outage to support modification**
5. **Christmas Holidays**
6. **Power Plant Forced Outage**
7. **Planned outage for pilot maintenance**
8. **Unplanned outage for pilot maintenance (chiller)**
9. **Unplanned outage for pilot maintenance (stripper)**
10. **Planned outage to support piping modifications for Hydro cyclone and Absorbers**
11. **Planned outage to install additional instrumentation**

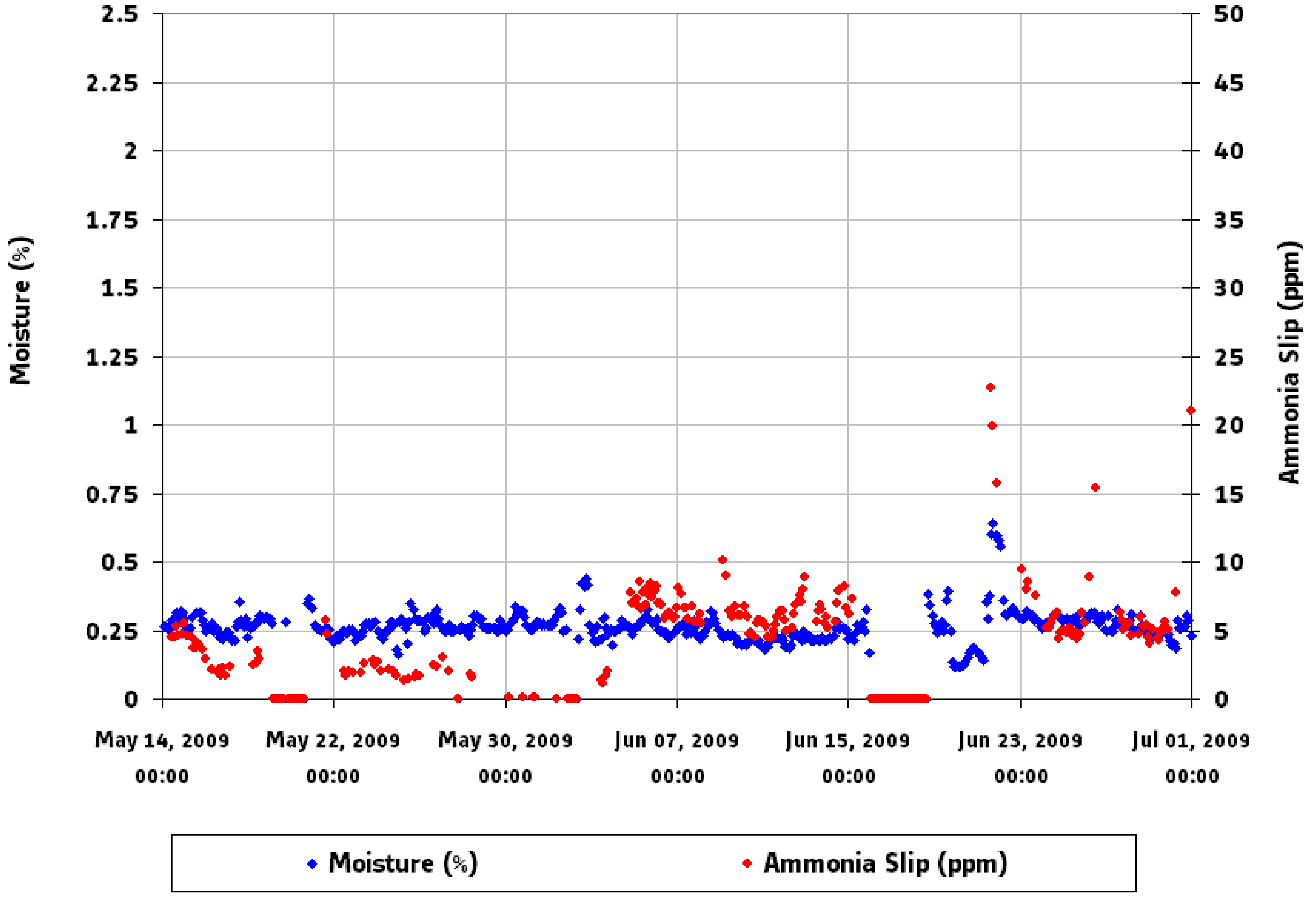
Total operating hours through Sept 16, 2009: 7,136

Validation Pilot at We Energies
CO_2 Capture Efficiency



Validation Pilot at We Energies

CO_2 Quality



EPRI Material Monitoring Approach - 2009

ELECTRIC POWER
RESEARCH INSTITUTE

- Every-day activities
  - Routinely collect and analyze liquid samples for NH_4^+, HCO_3^-, CO_3^{2-}.
  - Log FTIR gas analyzer data for CO_2, SO_2, NOx, NH_3.
  - Log other continuous data; T, P, F
- Multiple “mini-campaign” tests for material and energy balances:

Flue gas inlet	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
Flue gas outlet	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
CO_2 produced	CO_2, O_2, N_2, NH_3, H_2O, Flow, T, P
DCC blowdown	NH_3, Flow
Thermal / electrical / CW utilities	

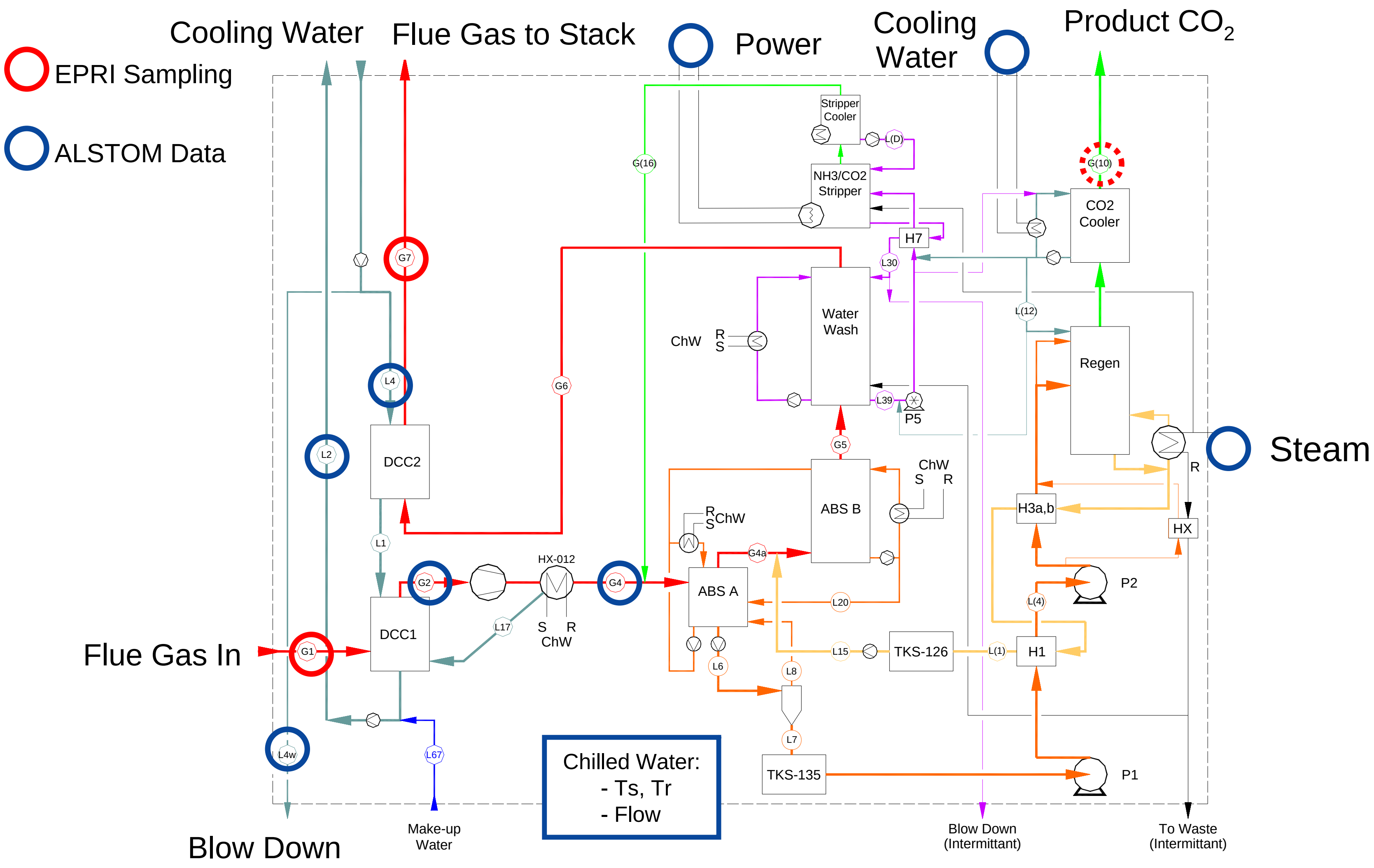
- One **campaign test** for material and energy balances around selected control volumes: (Manual) Gas, Liquids, and Solids sampling – Late Summer 2009.

EPRI Mini-Campaign Testing

Testing Objective – Accumulate high-reliability data on process performance.

- Independent Parameters:
  - Flue Gas Flow rate
  - Solution Strength
  - Process Temperatures, Pressures, Flows
- Dependent Parameters
  - CO_2 Removal, Quality
  - Utilities usage (Heat, electrical, cooling water)
  - Materials usage/disposal
    - Water CW blowdown / CW make-up
    - NH_3 loss / make-up

Mini-Campaign Sampling



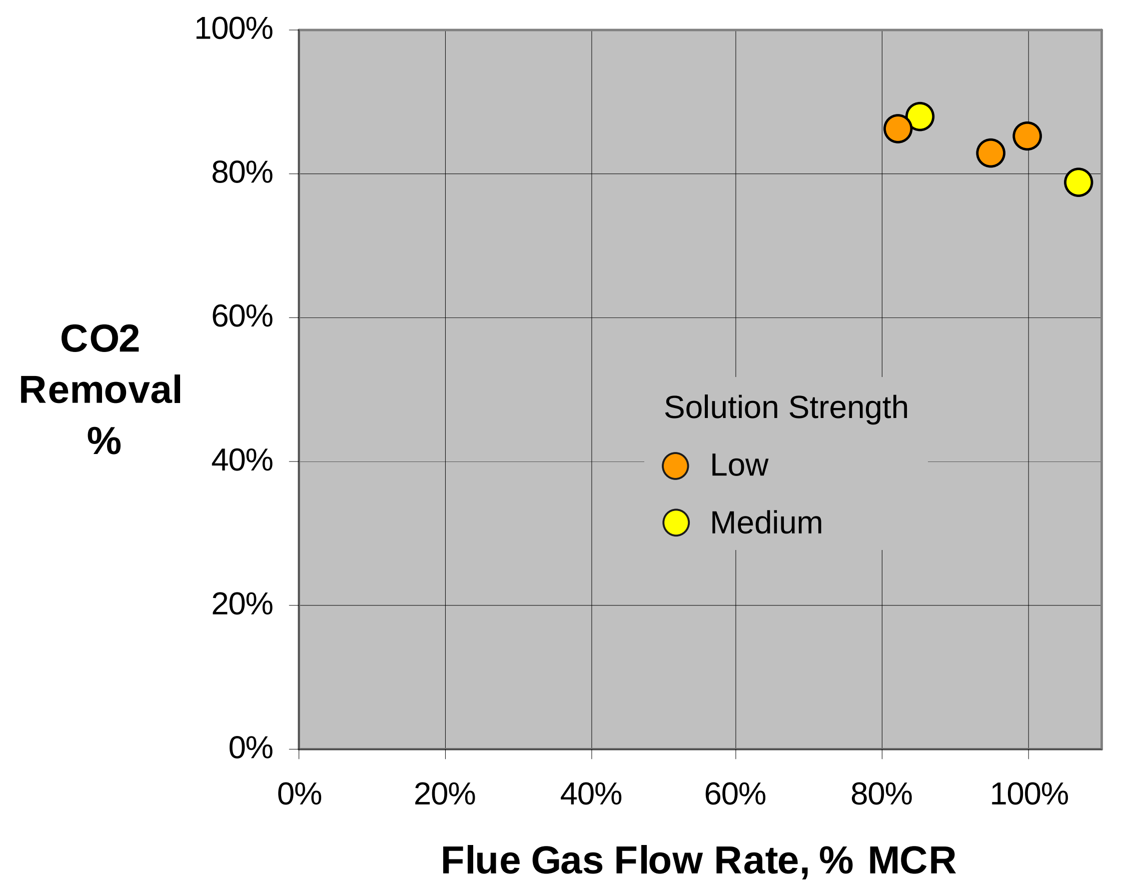
Chilled Water:
- Ts, Tr
- Flow

Mini-Campaign Test Conditions

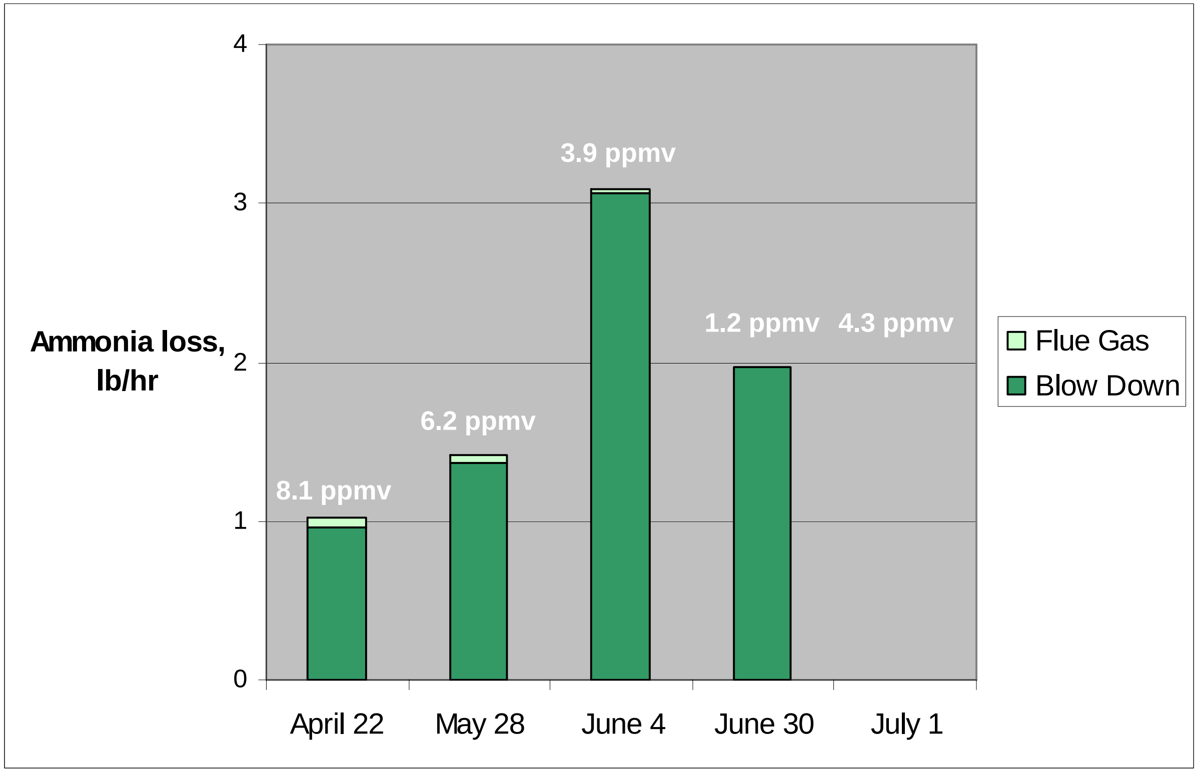
Date	Inlet Flue Gas Flow	Inlet Flue Gas Temperature	CO_2 content vol %, wet	Solution Strength
April 22	85.1%	127°F 53°C	11.9%	Low
May 28	94.8%	128°F 53°C	12.3%	Medium
June 4	100.1%	130°F 54°C	13.0%	Medium
June 30	82.4%	130°F 54°C	11.5%	Low
July 1	106.9%	132°F 55°C	12.0%	Low

Overall CO_2 Removal Performance

Date	Inlet Flue Gas Flow	CO_2 Removal
April 22	85.1%	87.9%
May 28	94.8%	82.7%
June 4	100.1%	85.0%
June 30	82.4%	86.2%
July 1	106.9%	78.5%



Ammonia Losses (Measured by EPRI)



Ammonia loss streams

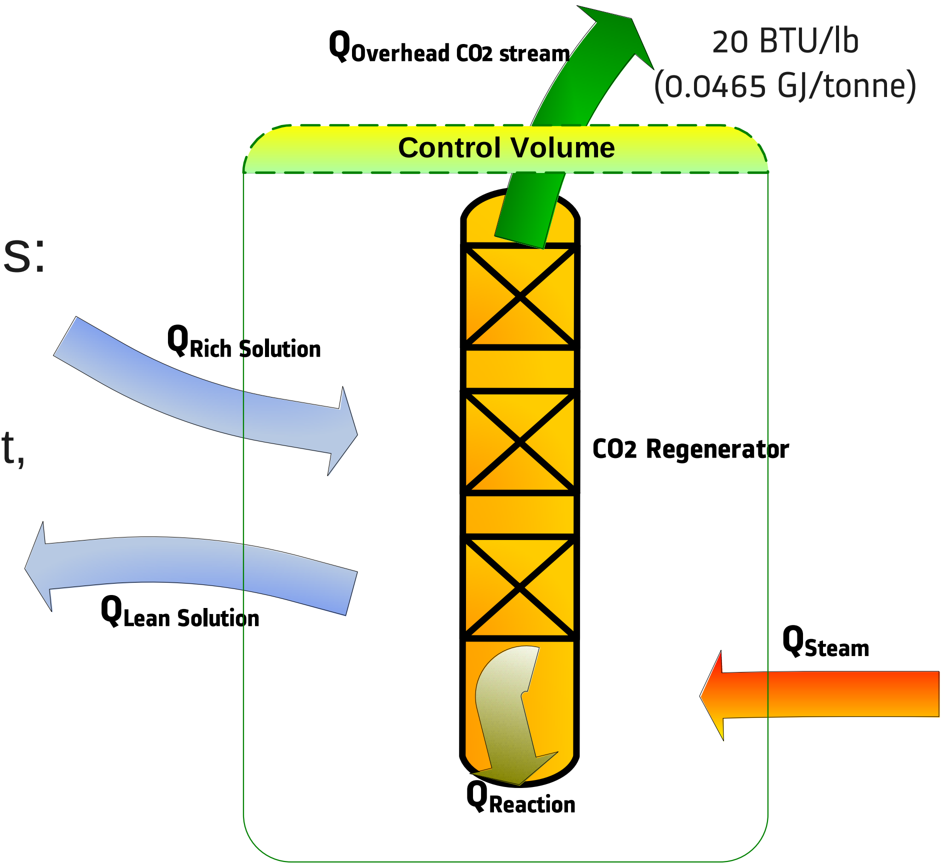
- DCC blow down
- Slip in flue gas
- Product CO_2
  much less than flue gas loss
- Cooling tower exhaust
  Insignificant when DCC cooling water pH is adequately controlled

Design blow down NH_3 loss is ~1 lb/hr.

July 1 blow down data still under review

Chilled Ammonia Process
Steam Energy Consumption

- Steam Consumption
  - Heat of Regeneration
  - $NH_3\backslash CO_2$ Stripping
- Heat of Regeneration includes:
  - Heat of reaction
    - Heat required to drive the reactions, regenerate reagent, produce pure CO_2 stream
  - Solids dissolution
  - Sensible heat requirements
  - Heat in overhead stream leaving the regenerator



$$Q_{\text{Heat of Reaction}} = Q_{\text{Heat Input (steam)}} - Q_{\text{Overhead } CO_2 \text{ stream}} - Q_{\text{Liquid Sensible Heat Losses (Lean/Rich solution)}}$$

Validation Pilot at We Energies

Summary – Thermal Energy

- Total steam energy consumption must be validated on an efficiently designed system that is demonstrated at a commercial scale and fully integrated with the power plant.
- In contrast, heat of reaction is dictated by the process chemistry and can be validated at the pilot scale.
- Heat of reaction measured at We Energies compares favorably with values determined in the laboratory setting;
  - Validates the figure used to size the validation pilots;
  - Validates the figure being used in commercial studies and FEEDs.
- The results extrapolated to a commercial scale system support Alstom's original estimate for total steam consumption

Validation Pilot at We Energies

Summary – Electrical Energy

- Chiller system is primary component
  - Electrical demand varies with ambient conditions
  - Use of cold water source can eliminate chillers
  - Free cooling to minimize electrical consumption
  - Chiller load dependant on cross exchanger performance
- Estimated energy consumption for the pumps in line with expectations
- Booster fan draft loss lower than expected
- Total electric power consumption consistent with expectations, after adjustments to reflect a commercial design
  - Pump power demand based on typical efficiency for larger pumps
  - Refrigeration Coefficient of Performance (CoP) based upon levels provided by refrigeration suppliers for a commercial design versus the unit installed at We Energies

Accomplishments

- Unit operations have been successfully integrated as a complete process
- Achieved high levels of CO_2 removal at design gas flow
- Accomplished high pressure regeneration
- Achieved low ammonia emissions
- Achieved high purity CO_2 with low concentrations of ammonia, water and other impurities.
- Steam and electrical energy consumption in line with expectations

Next Steps

- Complete parametric testing program for absorber
- Support completion of EPRI’s gas and liquid analysis test series
- Conduct long-term test at stable operating conditions
- Continue program at 10 x scale at AEP Mountaineer

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EPRI ELECTRIC POWER RESEARCH INSTITUTE

POWER ALSTOM

12th Meeting of the International Post-Combustion
CO_2 Capture Network, Canada, 29th Sep-1st Oct, 2009

Development of Amine Absorbents for Post-Combustion Capture

2009. 09. 30

Ji-Hyun Lee, Jun Han Kim, Kyung-Ryong Jang, In-Young Lee and Jae Goo Shim

KEPRI (Korea Electric Power Research Institute)

Project overview

- ***A-COS* Project** (Development of an Advanced CO_2 Capture System)
- Project Leader : KEPRI
- Research Periods : NOV, 2008 ~ OCT, 2014 (6 Years)
- Funding : 31 million $
  (Financially supported by the Korean government and Power Companies)
- Participants :
  KEPCO, 3 Power companies (KOMIPO, KOWEPO, KEWP) & KOPEC

Collaboration

- ***Co-work with 12 participants***

R&D	*Power Companies*	*Engineering Company*
KEPRI (Project Leader)	KEPCO	KOPEC
KIER	KOMIPO	
KRICT	KOWEPO	
IAE	KEWP	

University

SoongSil Univ.
Yonsei Univ.
Chungnam Univ.

Overall objectives

- Develop post-combustion CO_2 separation technology by alkanolamine absorbents at coal-fired power station
- Develop absorbents with improved regeneration energy compared to MEA (Reduce regeneration energy more than 30% than MEA)
- CO_2 capture process design and demonstration plant construction (2 TPD CO_2 capture plant until 2010, 50 TPD until 2013)

Strategy

1st Stage : `2008~11

2nd Stage : `2012~14

3rd Stage : `2015~20

Capture Energy

< 3.2 GJ/tonCO_2

2.5~3.0 GJ/tonCO_2

< 2.5 GJ/tonCO_2

S T R A T E G Y

Test bed

2 TPD Test bed

- Develop advanced absorbent
- Reduce regeneration energy

Pilot Plant

50 TPD Pilot Plant

- Search innovative absorbent
- Process innovation

Demonstration

50~500MW

Goal

Development of an Advanced CO_2 Capture System

Location of test bed for CO_2 capture

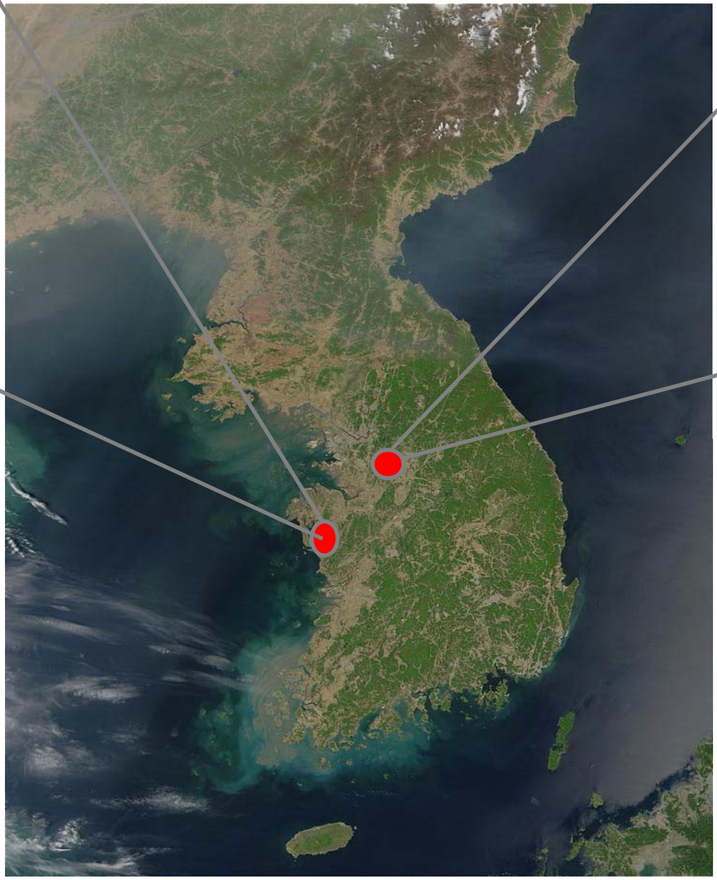
- **Boryong Power Station**

  - branch of KOMIPO

  - 5,800 MWe (Coal)

- **CO_2 Capture Test Bed (plan)**

  - 2TPD (2010), 50TPD(2013)



- **Seoul Power Plant**

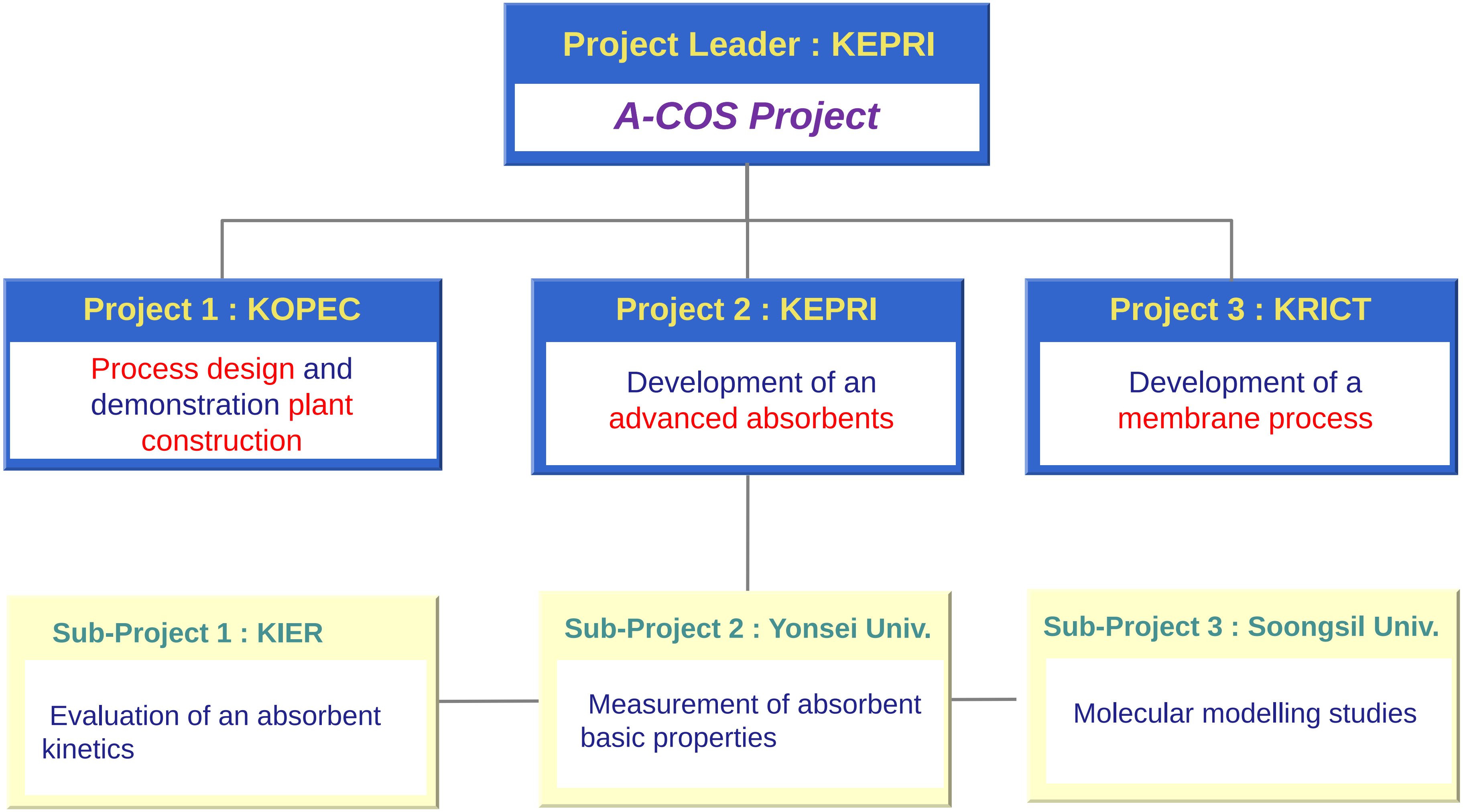
  - branch of KOMIPO

  - 387MWe(LNG)

- **CO_2 Capture Test Bed**

  - 2TPD (constructed at 2001)

Research frame



Project Leader : KEPRI

A-COS Project

Project 1 : KOPEC

Process design and demonstration plant construction

Project 2 : KEPRI

Development of an advanced absorbents

Project 3 : KRICT

Development of a membrane process

Sub-Project 1 : KIER

Evaluation of an absorbent kinetics

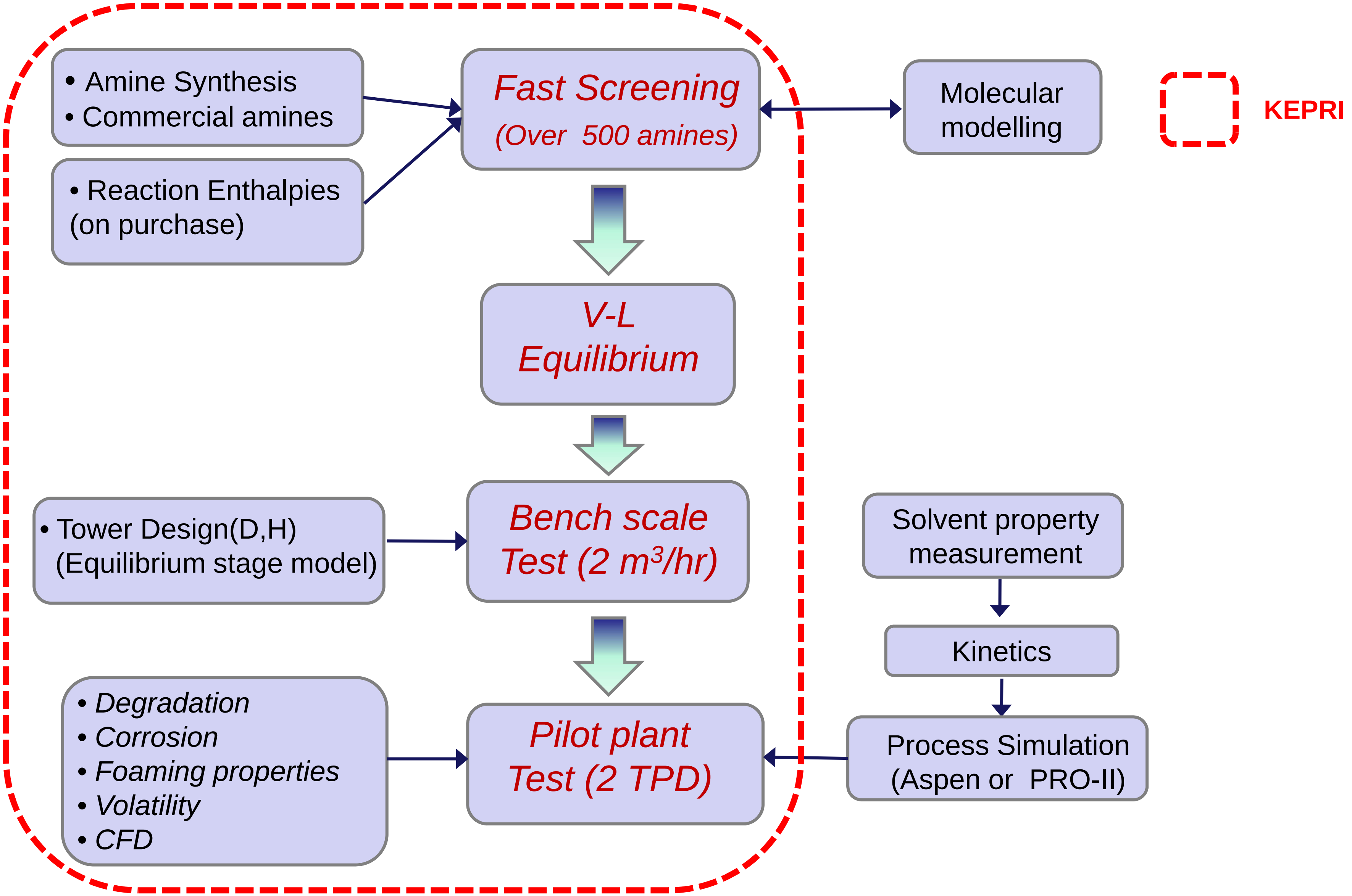
Sub-Project 2 : Yonsei Univ.

Measurement of absorbent basic properties

Sub-Project 3 : Soongsil Univ.

Molecular modelling studies

Solvent development procedures



- Amine Synthesis
- Commercial amines

- Reaction Enthalpies (on purchase)

Fast Screening

(Over 500 amines)

Molecular modelling

KEPRI

V-L Equilibrium

- Tower Design(D,H) (Equilibrium stage model)

Bench scale Test (2 m^3/hr)

Solvent property measurement

Kinetics

Process Simulation (Aspen or PRO-II)

- *Degradation*
- *Corrosion*
- *Foaming properties*
- *Volatility*
- *CFD*

Pilot plant Test (2 TPD)

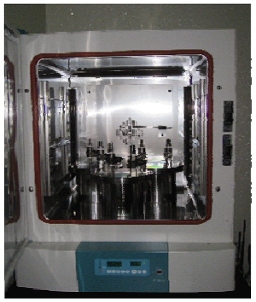
Research facilities

- *Fast Screening*

- *V-L Equilibrium*

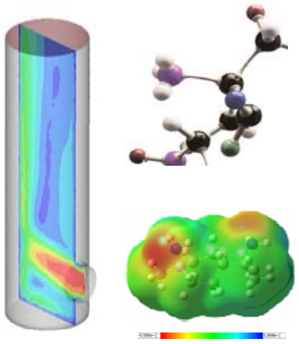
- *Degradation*

- *Corrosion*

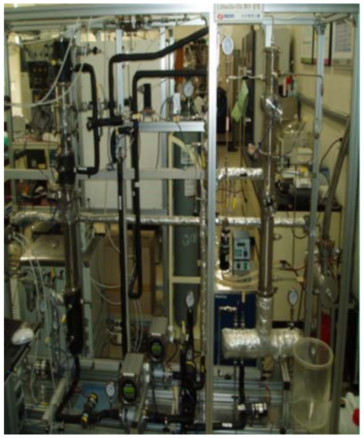


- *Reaction Calorimetry (on purchase)*

- *CFD & Molecular simulation*



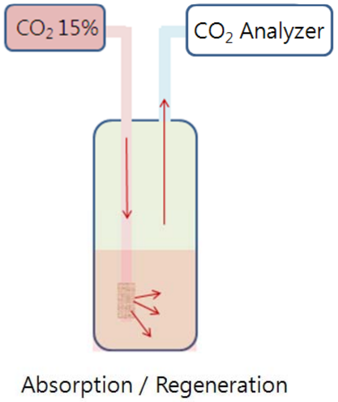
- *Bench unit*

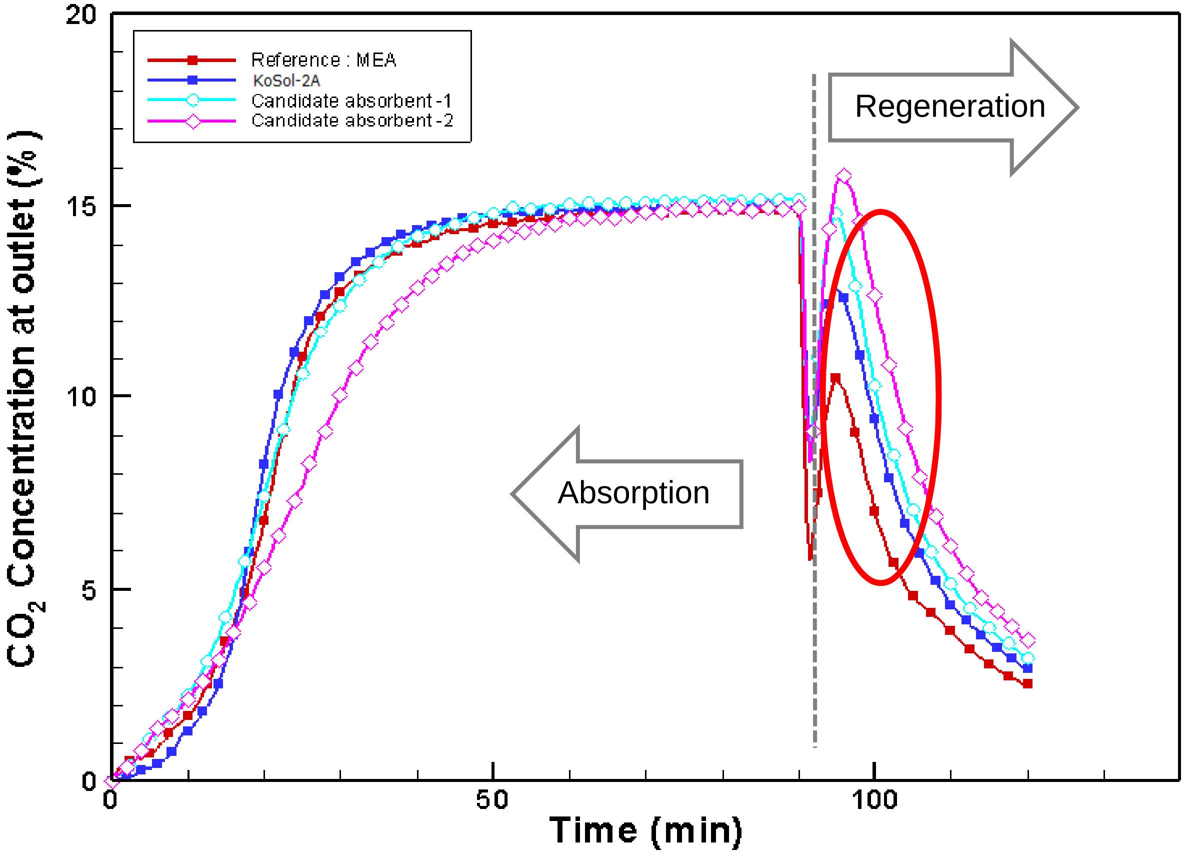


- *Pilot plant (2TPD)*

Test results : Screening test

Screening Test

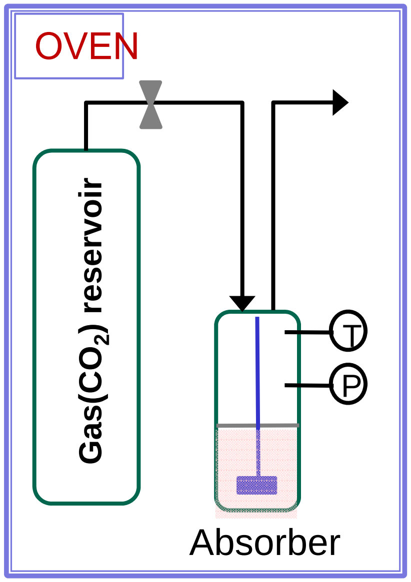


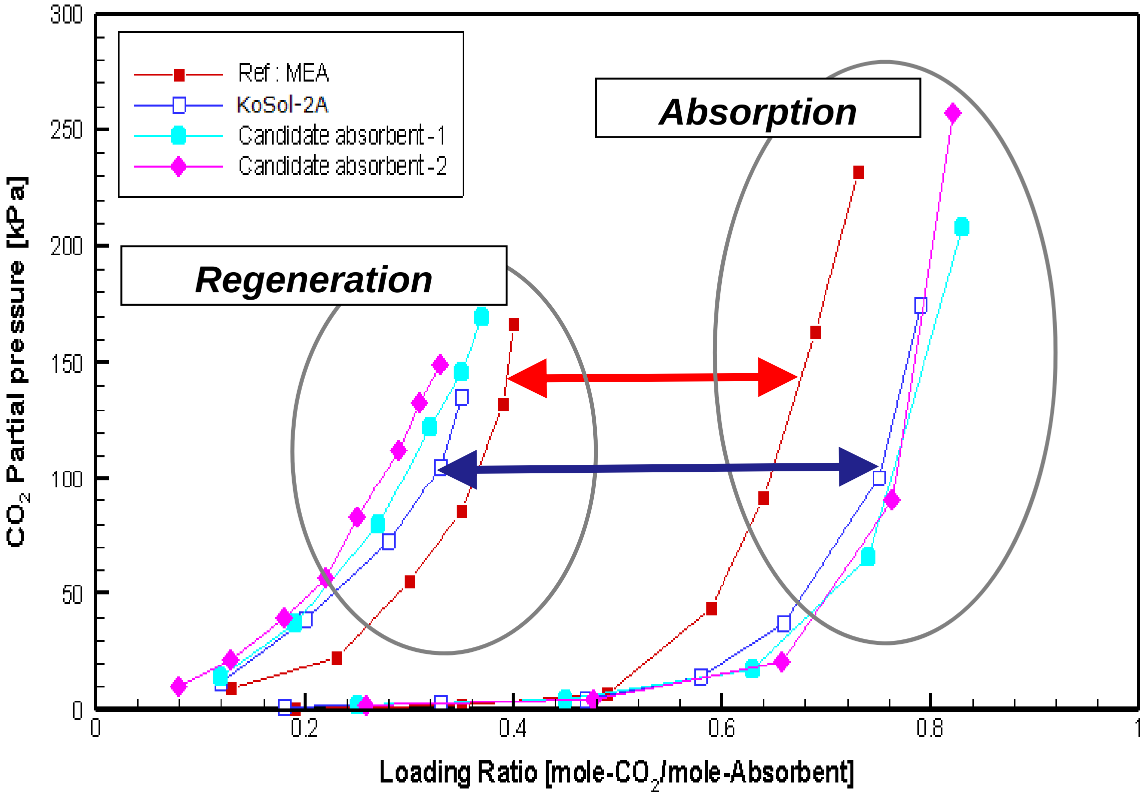


- Quantification of an absorbent capacity
- Fast screening of candidate absorbents

Test results : V-L Equilibrium

- ***Vapor-Liquid Equilibrium Test***



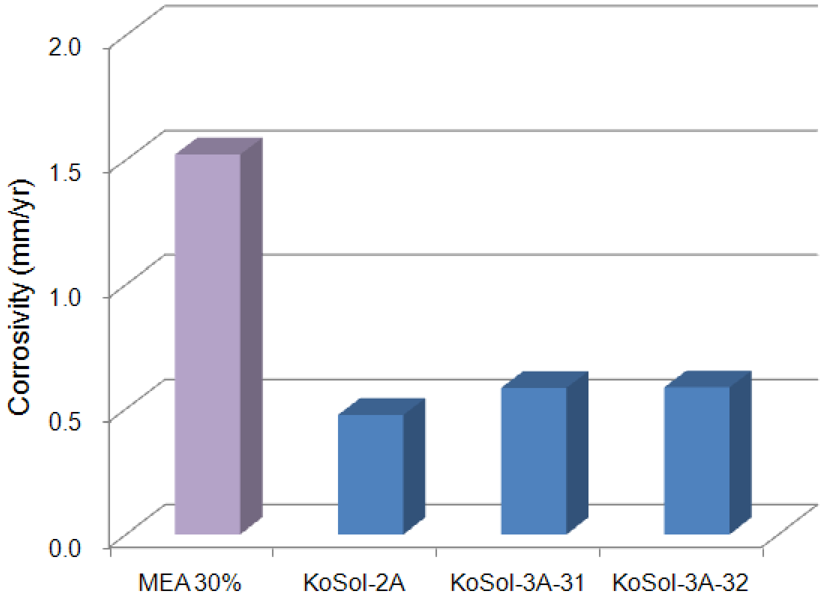


- *Verification of the fast screening test results*
- *Delta loading estimation*

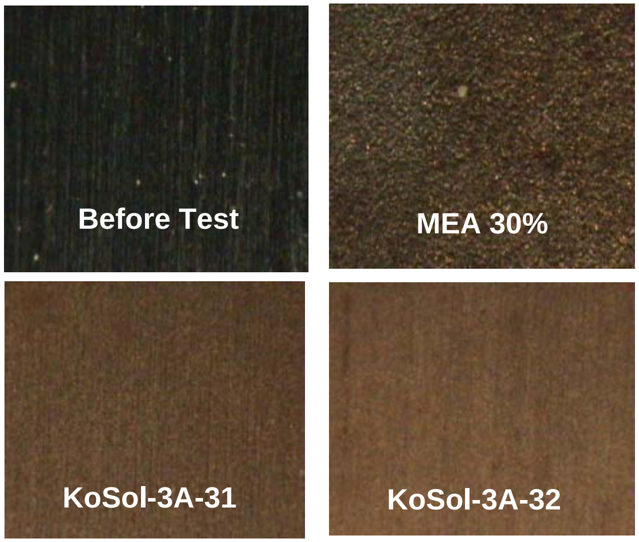
Test results : Corrosion

- **Corrosion**

Corrosion measurement



Optical analysis of the test coupons

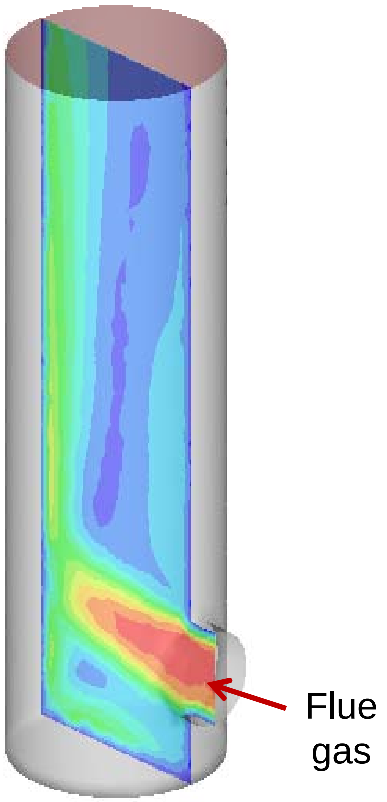


(Test coupon : carbon steel at 120℃)

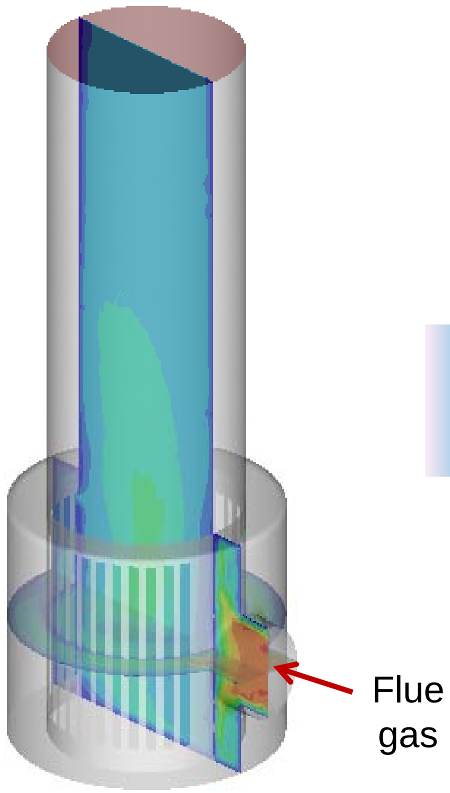
KoSol Series are less corrosive than MEA

Test results : CFD (Computational Fluid Dynamics)

- ***Gas distribution near the inlet of absorber***



[Conventional]



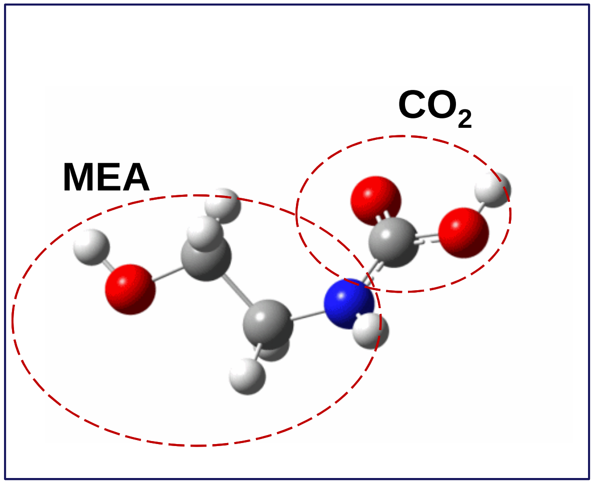
[Gas Distributor]

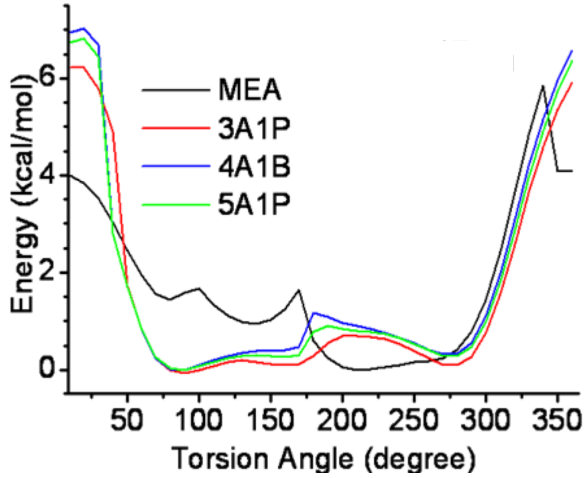
Gas distributor can enhance the distribution of the feeding gas

Test results : Quantum chemical molecular modelling

- ***Molecular Modelling***
  - *Calculation for reaction pathway of alkanolamine absorbent*
    (Zwitterion vs. Termolecular mechanism)
  - *Calculation of reaction enthalpy*
  - *Estimation of accessibility between CO_2 and alkanolamine absorbent*

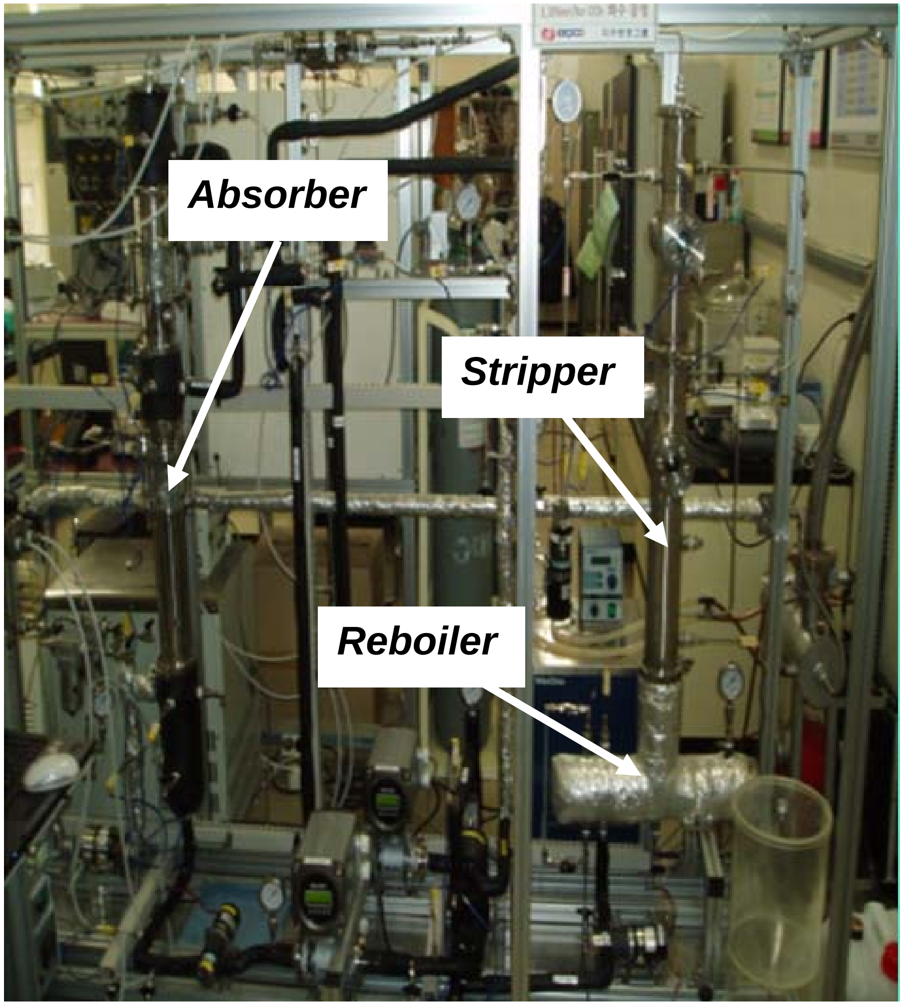
- ***Quantification of steric hindrance for alkanolamine absorbent***





Test results : Bench–scale facility

- ***Bench scale facility***

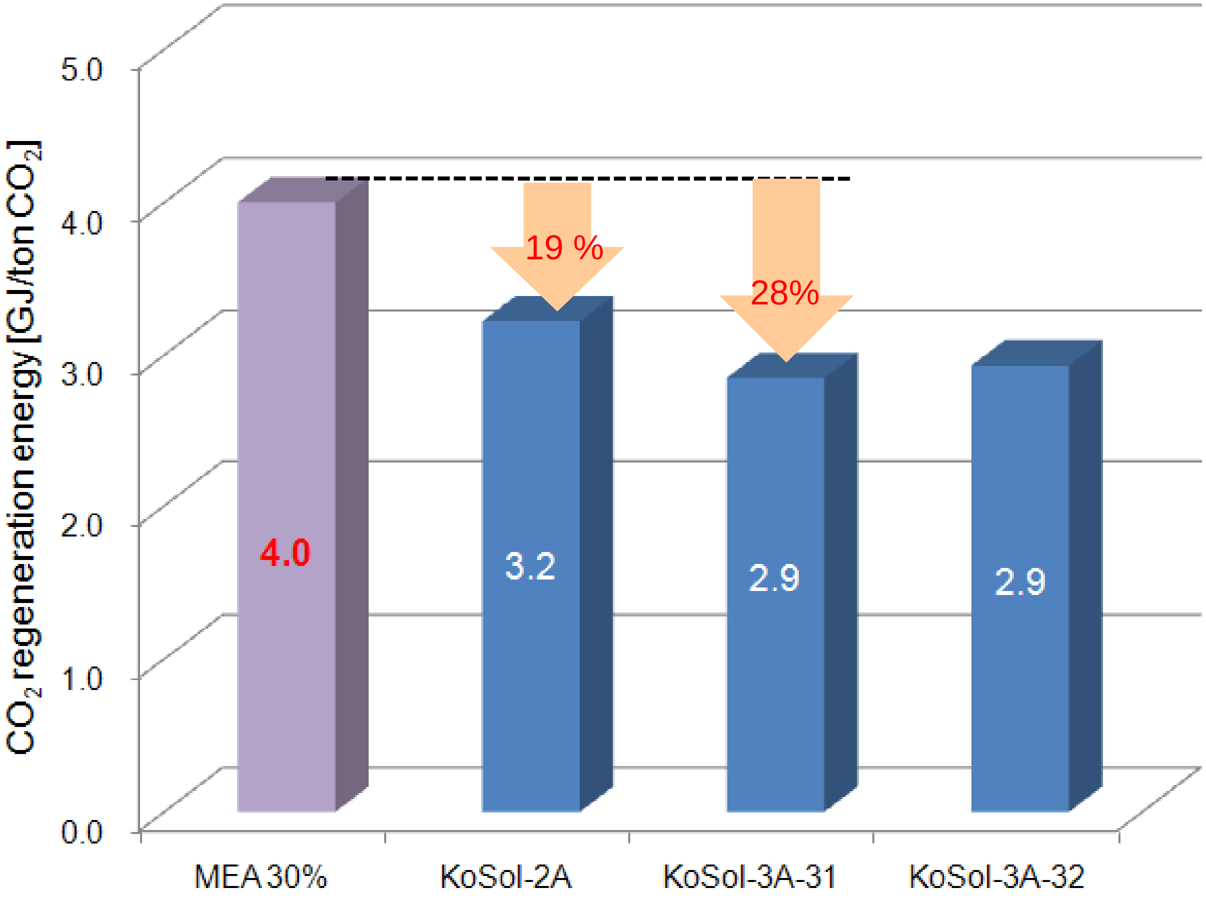


Experimental Condition

- CO_2 concentration : 11~15%
- Gas volume : 2.0 ~ 2.5 m^3/h
- Reboiler : Electric heater
- Packing : Random packing
- L/G ratio : 2.5 ~ 5.0 L/m^3

Test results : Bench–scale facility

- **CO$_2$ Regeneration Energy (Bench scale test : 2m^3/h)**



(CO$_2$ Concentration : 11~12%)

Test results : 2TPD Test bed

- ***2TPD Test bed***

Location : Seoul Power Plant, Korea

Capacity : Flue gas 600 Nm^3/hr

CO_2 Recovery 2 Ton/day

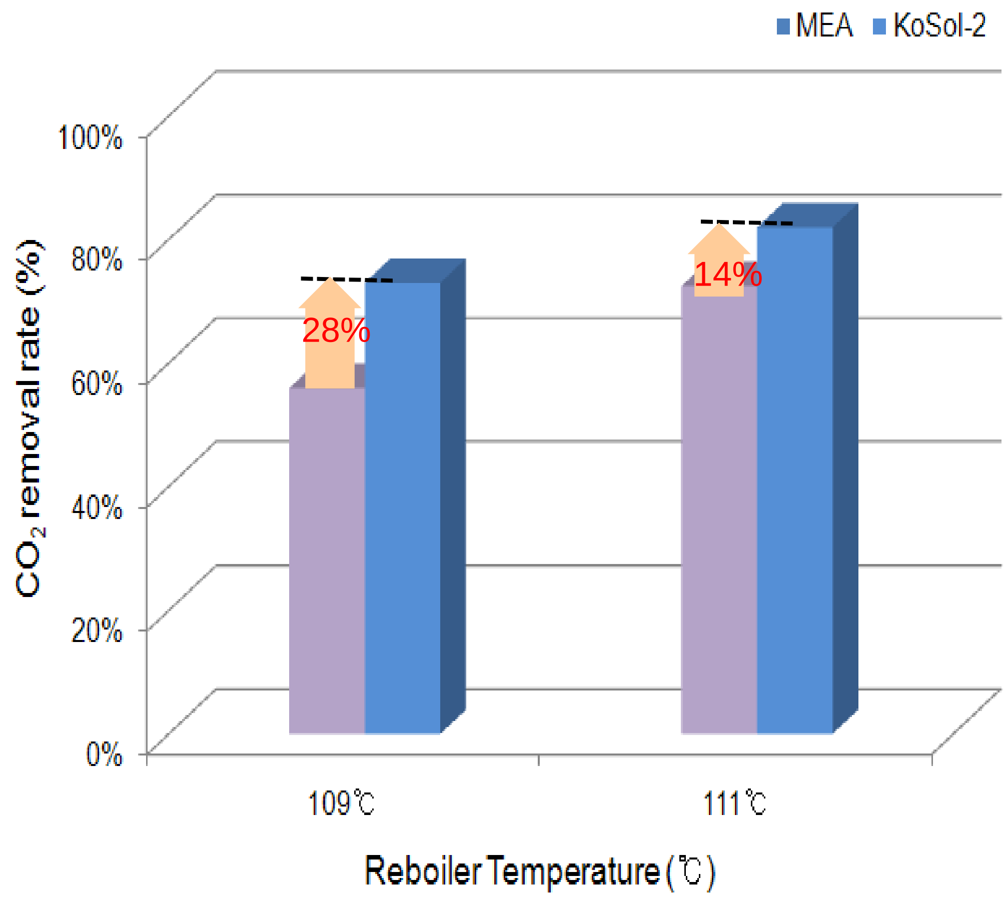
Start Up : 2002

Purpose of the Plant :

Development of advanced absorbent

Test results : 2TPD Test bed

Test Bed Data



Test Period : Jun,'07 ~ July,'07

MEA Test : Jun,'07

KoSol-2 Test : July,'07

Conclusion & Future works

Conclusion

a. Improvement with KoSol series compared to MEA

- Decreased regeneration energy (2.9 GJ/ton CO_2)

- less corrosive than MEA

b. Process Optimization

- Gas distributor can enhance the distribution of the feeding gas

Future works

a. Applying advance absorbent to 2 TPD Test bed

b. Process optimization & Innovation (Gas distributor & Pre-contactor)

THANK YOU
FOR YOUR ATTENTION

Ji-Hyun Lee (leejha@kepri.re.kr)

KRICT
Korea Research Institute of Chemical Technology

IAE 고등기술연구원
Institute for Advanced Engineering

KIER 한국에너지기술연구원
KOREA INSTITUTE OF ENERGY RESEARCH

KEPCO

충남대학교
CHUNGNAM NATIONAL UNIVERSITY

숭실대학교
Soongsil University

YONSEI UNIVERSITY

EWP KOREA EAST-WEST POWER CO.,LTD.

KOMIPO

WP KOREA WESTERN POWER CO., Ltd.

KOPEC

Hazelwood/H3 Capture Demonstration Projects

Prof. Geoff Stevens
University of Melbourne
Leader-Solvent Research
Cooperative Research Centre
for Greenhouse Gas
Technologies (CO2CRC)

IEA Capture Test Network
Regina
30th Sept 2009

Outline

- Introduction
- Latrobe Valley PCC Activities
- International Power Carbon Capture Project
  - Background
  - Timeline/Status
- CO2CRC H3 Capture Project
  - Timeline/Status
  - Technology/Results
- Heat Integration Studies
- Conclusions

Acknowledgements

- Industry Partners
  - International Power
    - ➢Australia's largest private generator of electricity. It owns and operates more than 3700MW (Gross) of renewable, gas-fired and brown coal-fired generating plants in Victoria, South Australia and Western Australia. It also operates a retail operation in Victoria and South Australia through Simply Energy.
  - The Process Group
    - ➢Process Group is a leading supplier of packaged process systems for the oil and gas industry and is at the forefront of implementation of carbon capture technologies. The company is based in Melbourne with a large facility also in the UAE.
- Victorian Government ETIS Brown Coal R&D program

CO2CRC Participants

Australian Government
Geoscience Australia

CSIRO

Curtin
University of Technology

MONASH University

THE UNIVERSITY OF ADELAIDE
AUSTRALIA

THE UNIVERSITY OF MELBOURNE

UNSW
THE UNIVERSITY OF NEW SOUTH WALES
SYDNEY • AUSTRALIA

ANGLO AMERICAN

ACARP

bhpbilliton

bp

Chevron

ConocoPhillips

NSW DEPARTMENT OF
PRIMARY INDUSTRIES

State Government Victoria
Department of Primary Industries

FOUNDATION FOR RESEARCH SCIENCE & TECHNOLOGY

Queensland Government

INPEX

한국지질자원연구원
Korea Institute of Geoscience and Mineral Resources

Mitsui & Co.
(Australia) Ltd

GNS SCIENCE
genesis ENERGY
NZ Resource Consortium

Origin energy

QER

RioTinto

sasol
reaching new frontiers

SOLID ENERGY
Coals of New Zealand

STANWELL
CORPORATION LIMITED

Schlumberger

Government of Western Australia
Department of Mines and Petroleum

woodside

xstrata
coal

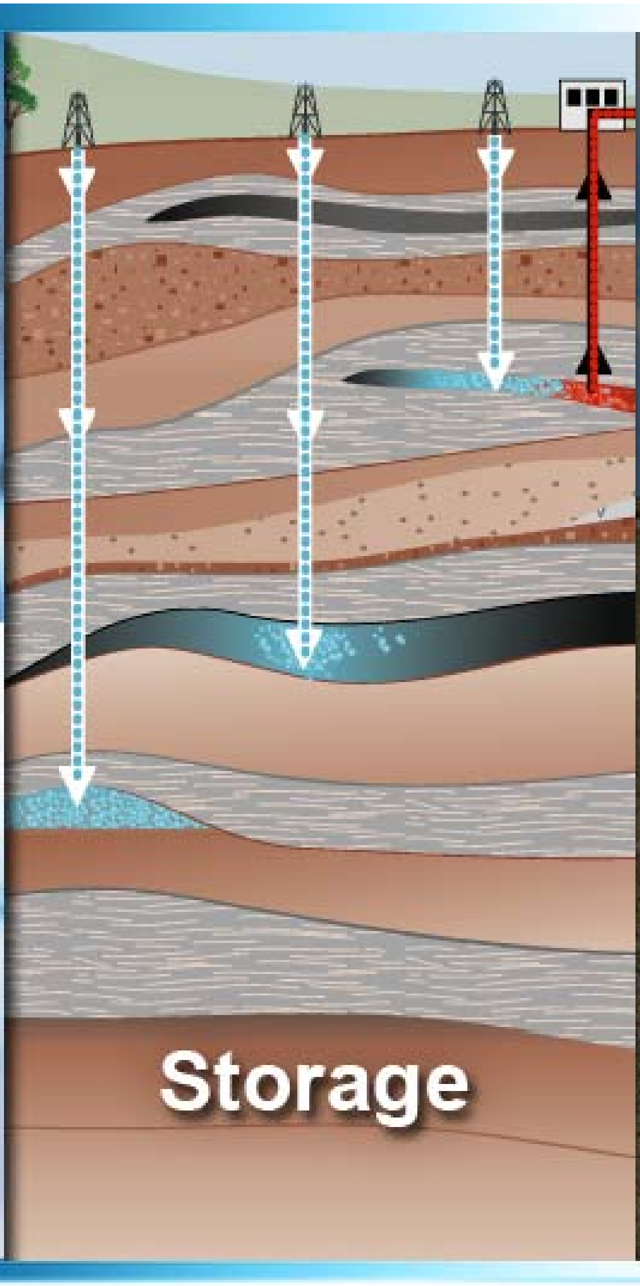
Supporting participants: **Supporting participants: Department of Resources, Energy and Tourism| CANSYD | Meiji University Process Group | University of Queensland | Newcastle University | U.S. Department of Energy | URS**

CRC

Established & supported under the Australian Government's Cooperative Research Centres Program

CO2CRC

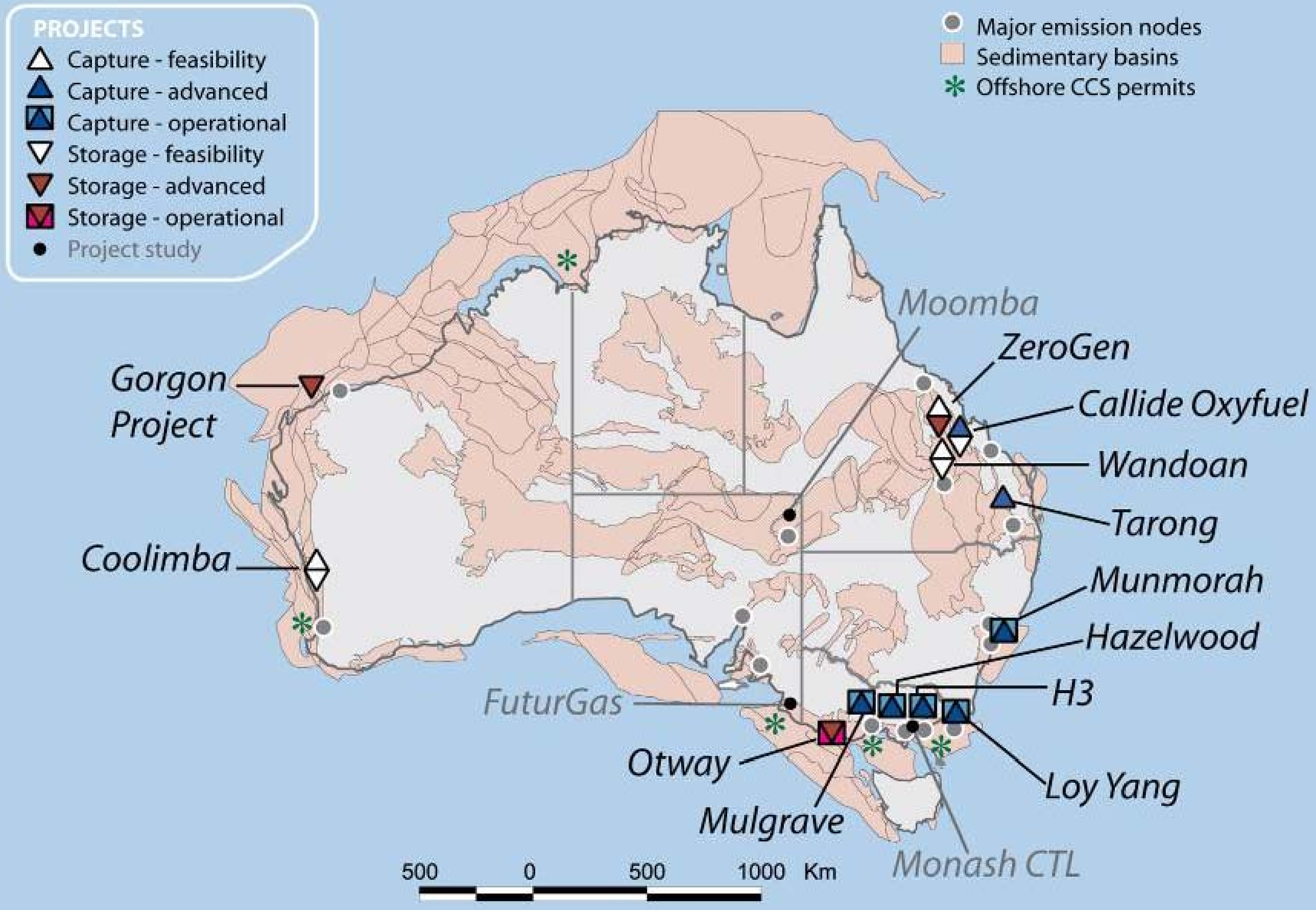
Capture



Storage

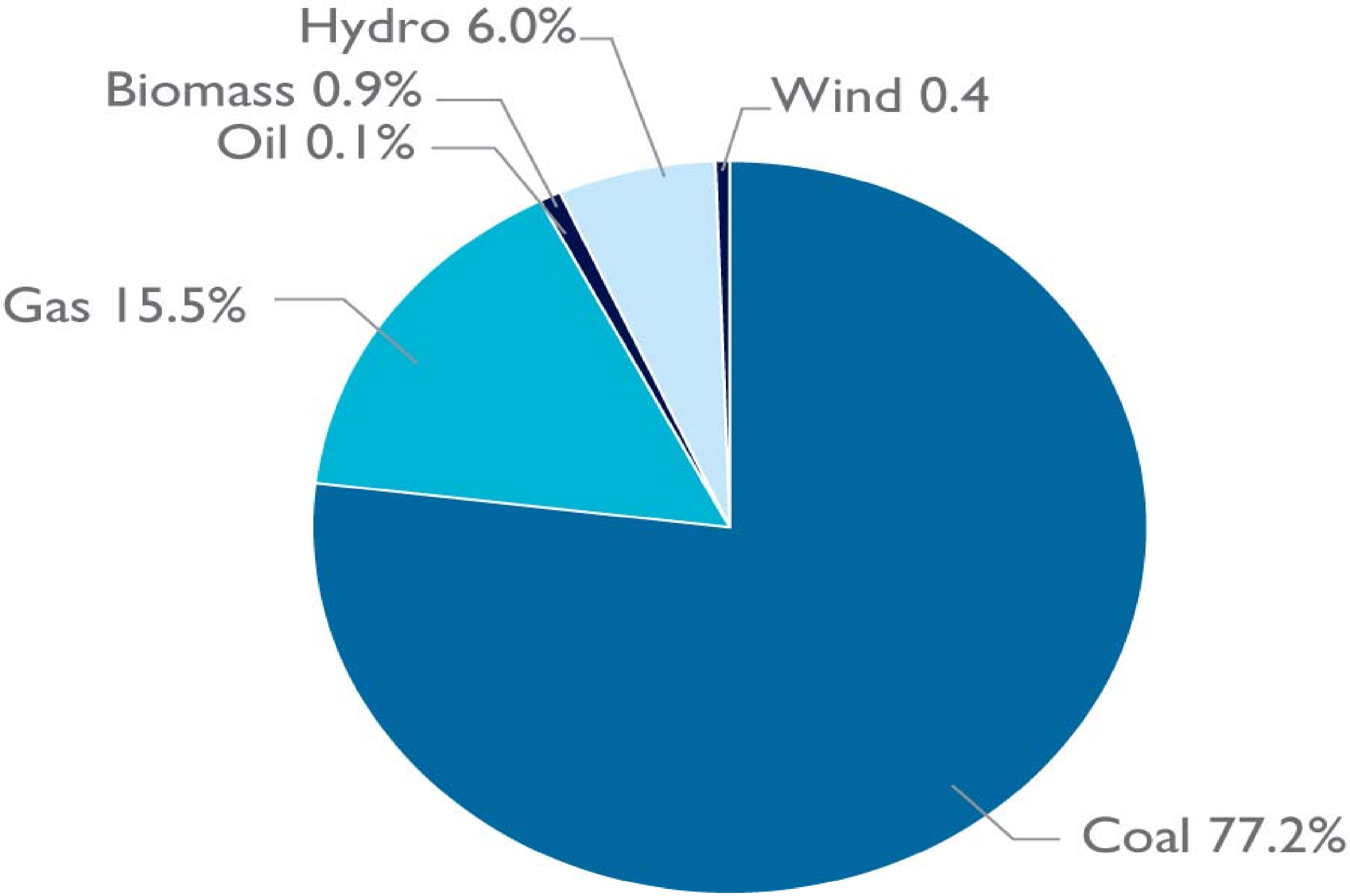
Pilot & demonstration projects

CO2CRC


PROJECTS
△ Capture - feasibility
▲ Capture - advanced
Capture - operational
▽ Storage - feasibility
▼ Storage - advanced
Storage - operational
● Project study
● Major emission nodes
Sedimentary basins
* Offshore CCS permits
Gorgon Project
Coolimba
Moomba
ZeroGen
Callide Oxyfuel
Wandoan
Tarong
Munmorah
Hazelwood
H3
FuturGas
Otway
Mulgrave
Loy Yang
Monash CTL
500
0
500
1000
Km

Electricity Supply in Australia

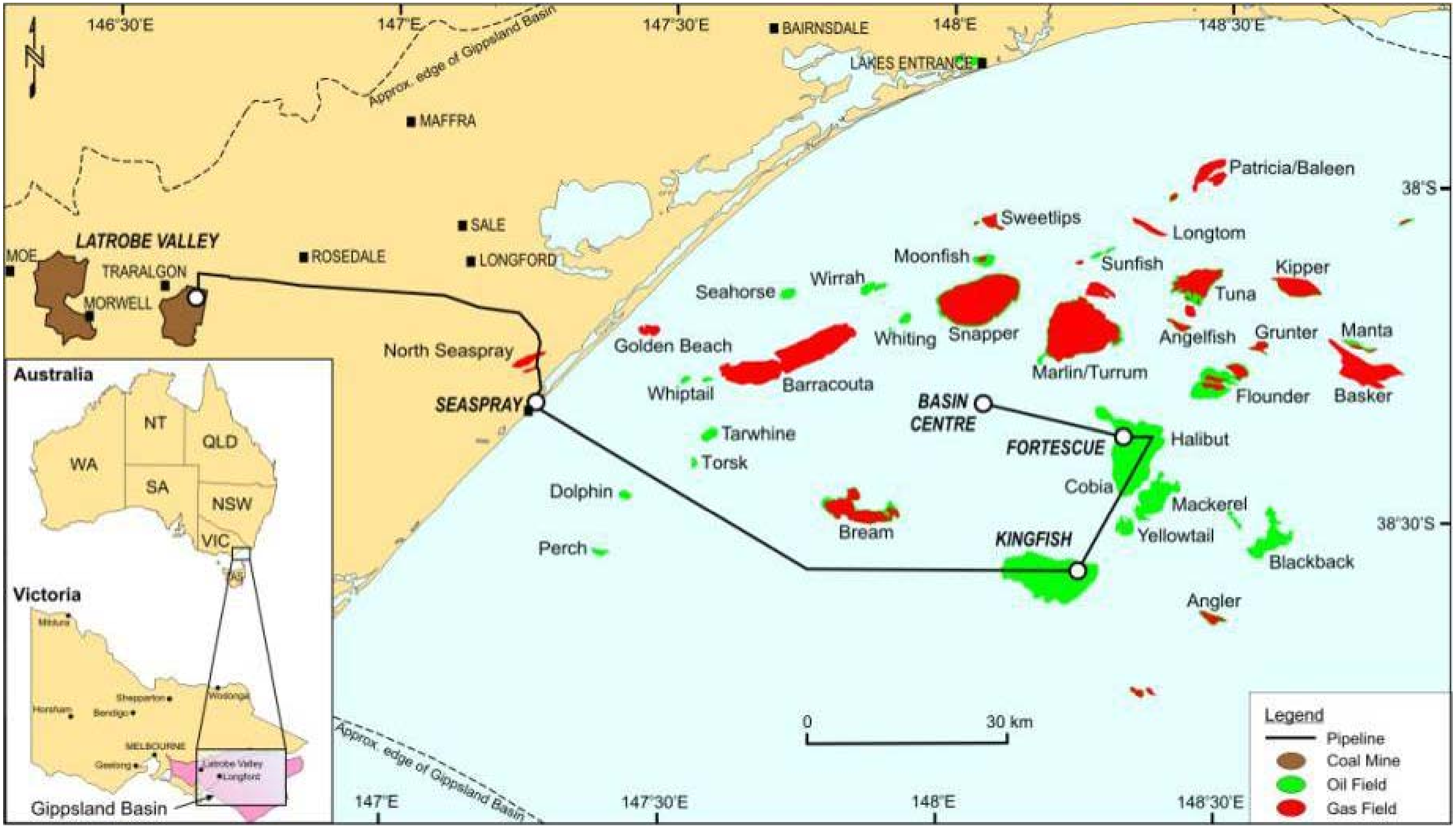
(ESAA 2007)



Latrobe Valley Background

- The Latrobe Valley, in eastern Victoria, is a major power producing region (~ 6500 MW over five sites) based on vast cheap brown coal reserves (~500 years)
- Generates the majority of electricity requirements in the state and supplies power to the national grid
- The coal has high moisture content (~ 60%) resulting in high specific emissions
- The region is close to prospective storage sites in the offshore Gippsland Basin offering excellent source-sink matching
- Victorian Government Energy Technology Innovation Strategy (ETIS) is providing support for the shift to low emission energy mix, including renewables, energy efficiency and CCS
  - CO2CRC, including Otway Project
  - Large Scale Demonstration Project
  - Onshore CCS legislation enacted
  - ETIS Brown Coal R&D
  - ETIS 2 – Large Scale Integrated demo – submissions closed Aug 31
  - ETIS 3 – R&D funding for low emissions power – guidelines to be released

Potential Storage Sites



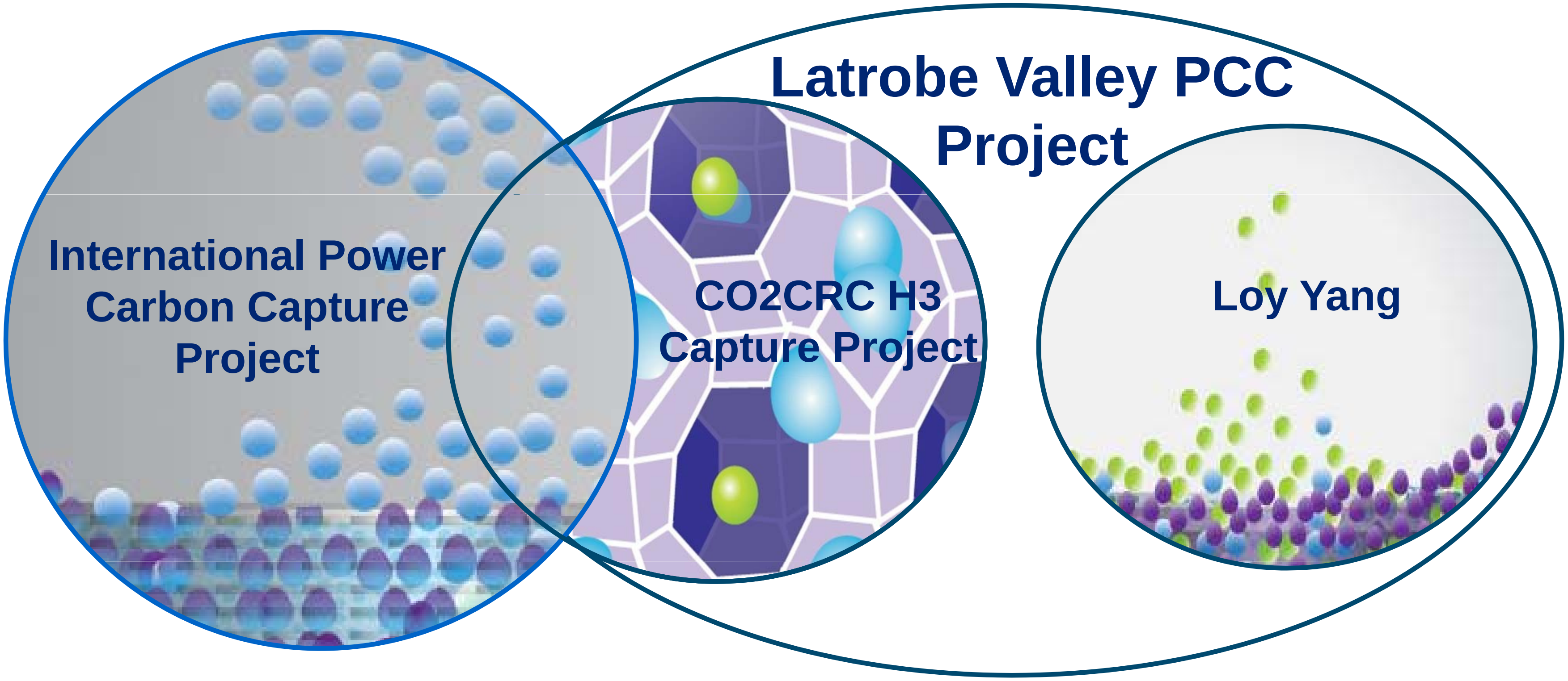
Two projects are underway at Hazelwood to demonstrate post combustion capture

International Power

process group

CO2CRC

Post-combustion capture demonstration - Victoria



Latrobe Valley PCC Project

International Power Carbon Capture Project

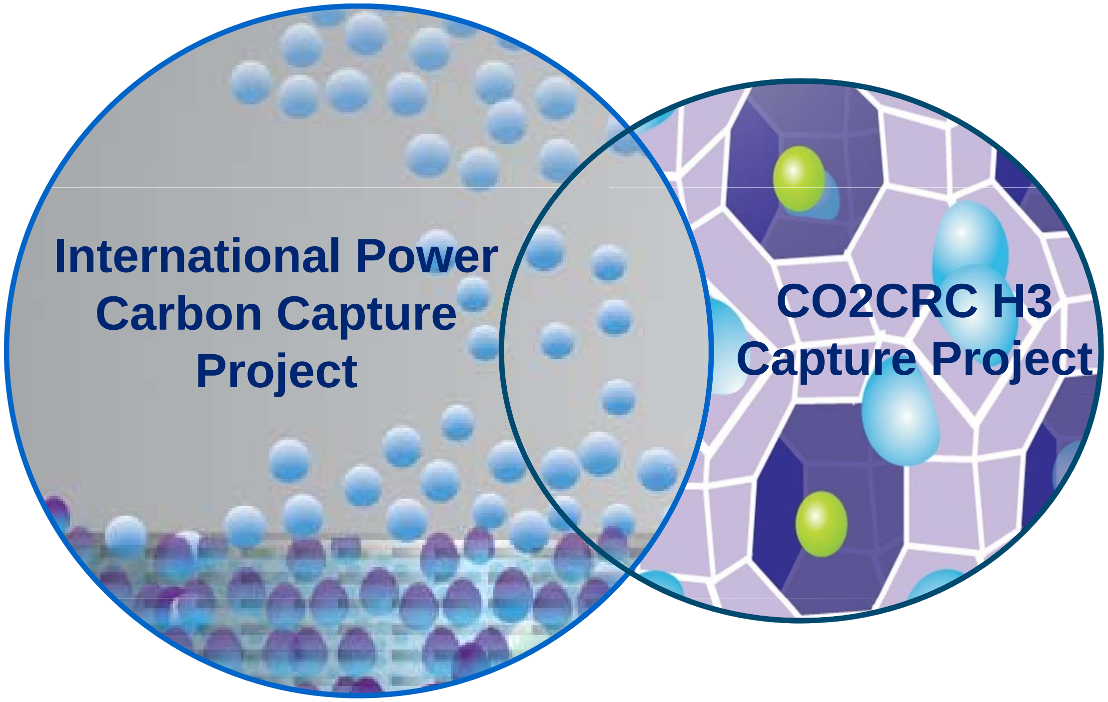
CO2CRC H3 Capture Project

Loy Yang

Issues for capture from Latrobe Valley plants

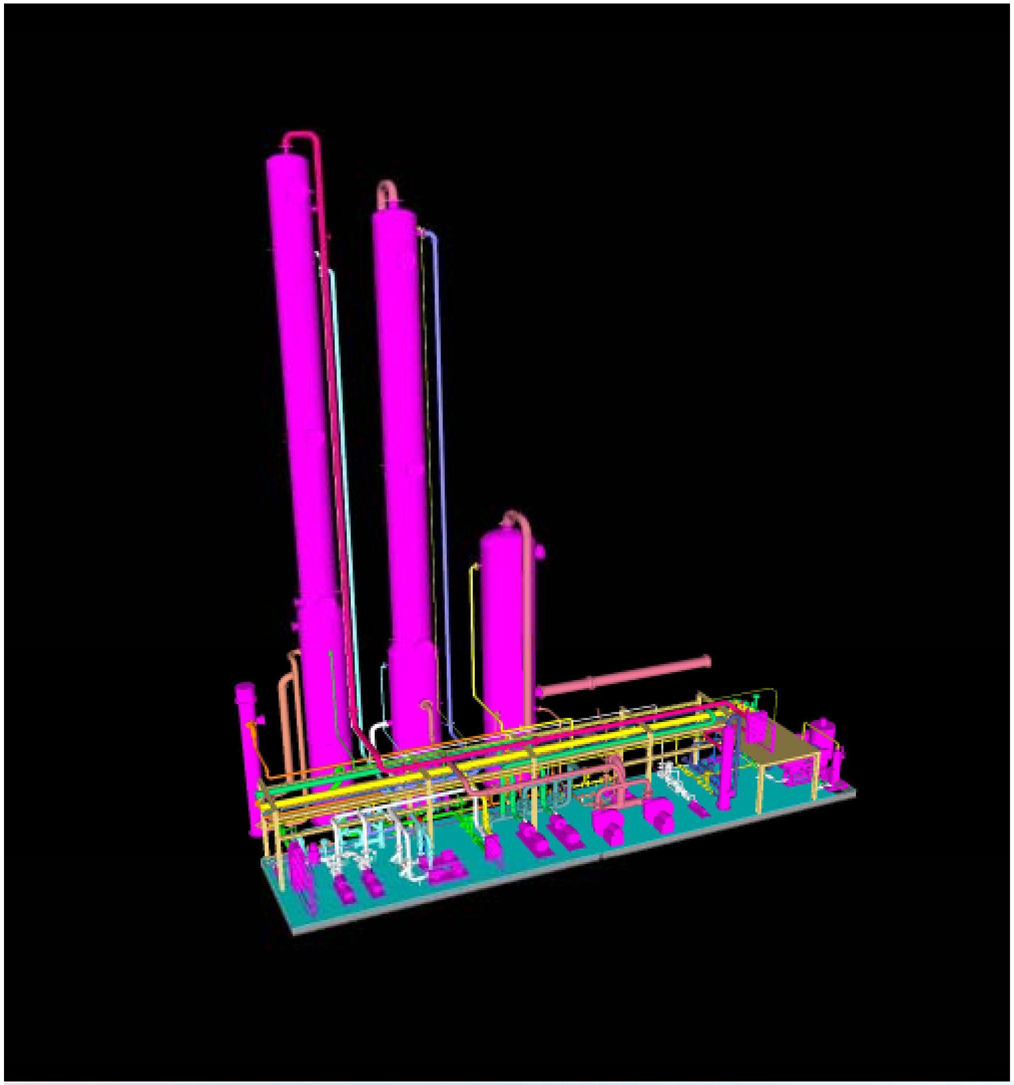
- **Gas Composition:**
  - N_2 ~ 62%
  - O_2 ~ 5%
  - CO_2 ~ 11%
  - H_2O ~ 22%
  - SO_2 ~ 200 ppm
  - NO_x ~ 150 ppm
  - Dust ~ 0.10 g/Nm3
- **Efficiency** 24-29 % HHV
- **Flue Gas Temperature** 180 -250 deg C
- **CO_2 Emission Intensity** 1.2-1.5 t CO_2/MWh sent out

Post-combustion capture demonstration - Victoria


International Power Carbon Capture Project

CO2CRC H3 Capture Project

25 tpd (expandable to 50 tpd) PCC plant



- Site erected columns
  - Prewash/DCC
  - Absorber
  - Stripper
- Offsite fabricated skids
- International Power
  - Plant owner/operator and project management
- Process Group
  - Responsible for design, fabrication, and commissioning of the CO_2 capture plant.
- Alstom
  - Responsible for the installation of the CO_2 capture plant.
- CO2CRC
  - Project assistance and capture R&D input

International Power

process group

CO2CRC

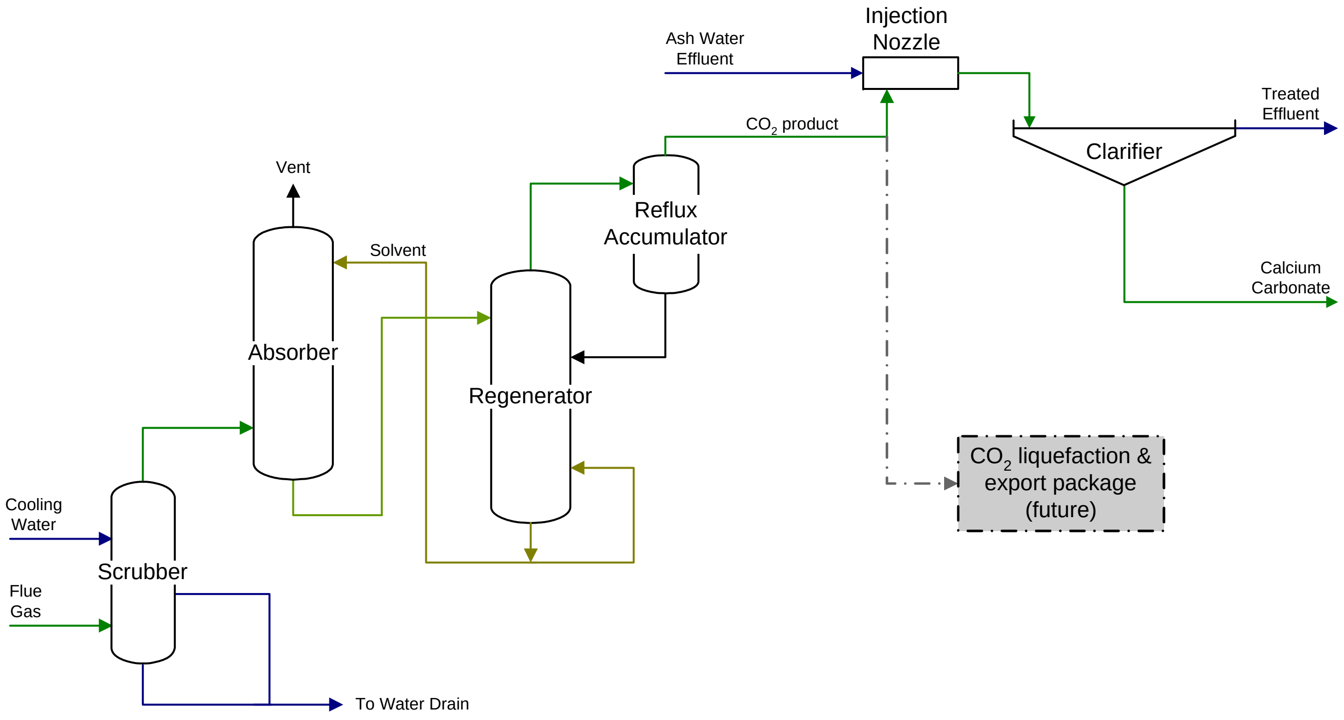
Background – International Power Carbon Capture

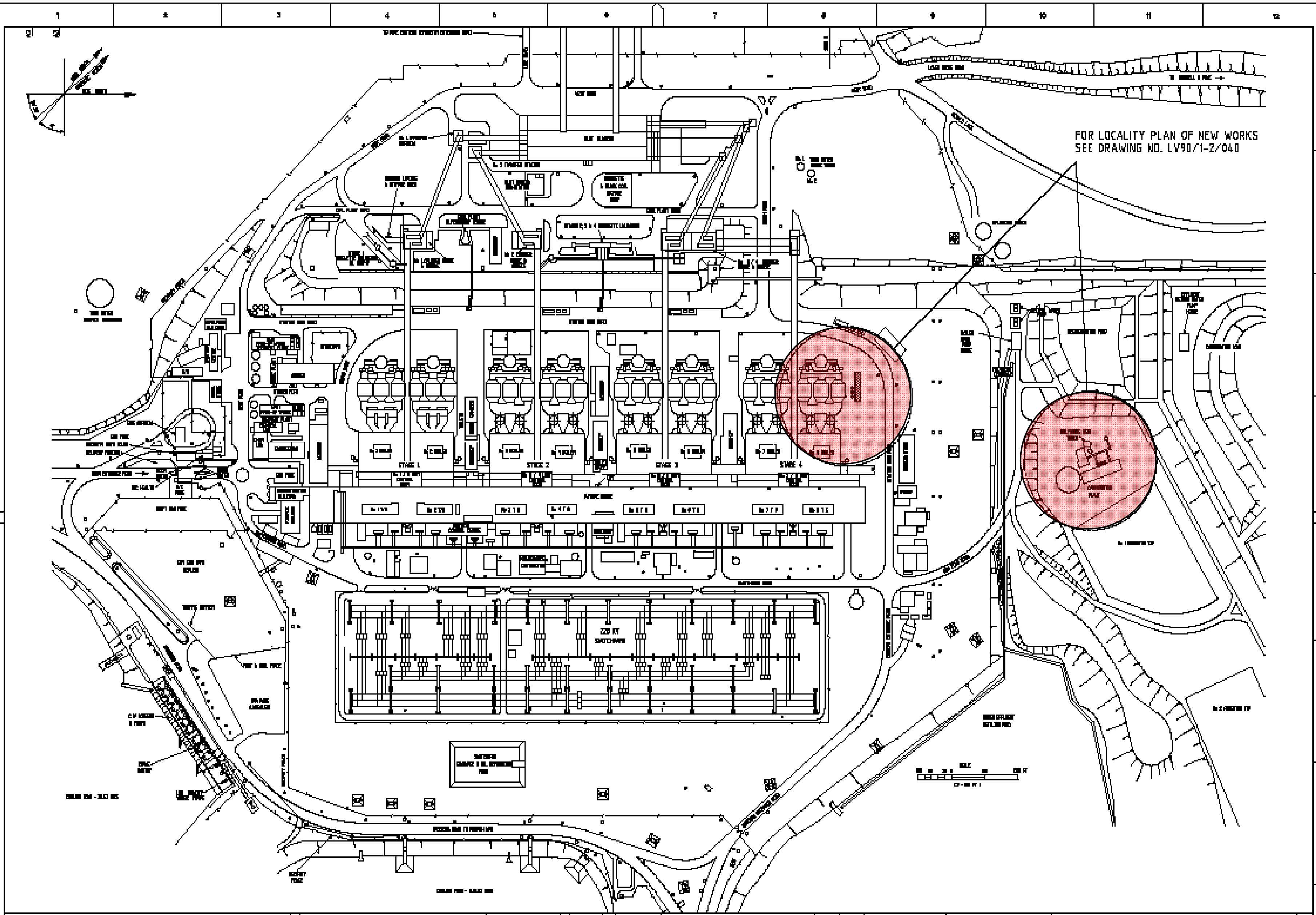
- Supported by the Federal Government’s Low Emissions Technology Development Fund (LETDF) & Victorian Government's Energy Technology Innovation Strategy (ETIS LSDP).

- Pilot Post Combustion CO_2 Capture Plant (timing: commissioning by late 2008):
  - separate CO_2 from flue gas stream (Unit 8)
  - Amino acid based technology
  - CO_2 converted to an inert material (calcium carbonate)
  - CO_2 capture of 25 tonnes/day, expandable to 50 tonnes/day

Technology –
Carbon Capture Plant (25 tpd – 50tpd design)

- Technology adapted to Latrobe Valley flue gas conditions;
- 16 tpd sequestration through calcium carbonate production;
- Excess CO_2 potential for other commercial uses;
- Stage 1 CO_2 capture at 25tpd from Hazelwood Unit 8 (Stage 2 at 50 tpd – future option to be approved yet).





IPH STD A1

TITLE	DRAWING No
LOCALITY PLAN	LV90/1-2/040

DATE	REV	WO/FILE	AMENDMENT	CHECKED	APPROVED

DESIGN VERIFICATION No.

DRAWN
DATE
CHECKED
DATE
DESIGNED
APPROVED

INTERNATIONAL POWER HAZELWOOD, PO BOX 195, MORWELL, VICTORIA, 3840, AUSTRALIA

REV

DRG No: LV90/1-2/039

HAZELWOOD POWER STATION
UNIT 8 - CO2 CAPTURE PLANT
& CARBONATION PLANT CO2 INJECTION SYSTEM
SITE PLAN

International Power CO_2 Project Timeline/Status

▪ LETDF/ETIS Submissions	Dec 2005
▪ LETDF/ETIS Award	Oct 2006
▪ Agreements Signed	2007
▪ Solvent plant	
– Delivered	Nov 2008
– Commissioned	Q1 2009
– Operational	Q2 2009
▪ Capture Plant Cost	
& carbonation plant refurbishment	A$ 10 million (approx)


JON MONOCR

CO2 Capture Plant : Skid Section 1

process group

CO2 Capture Plant : Skid Section 2

process group

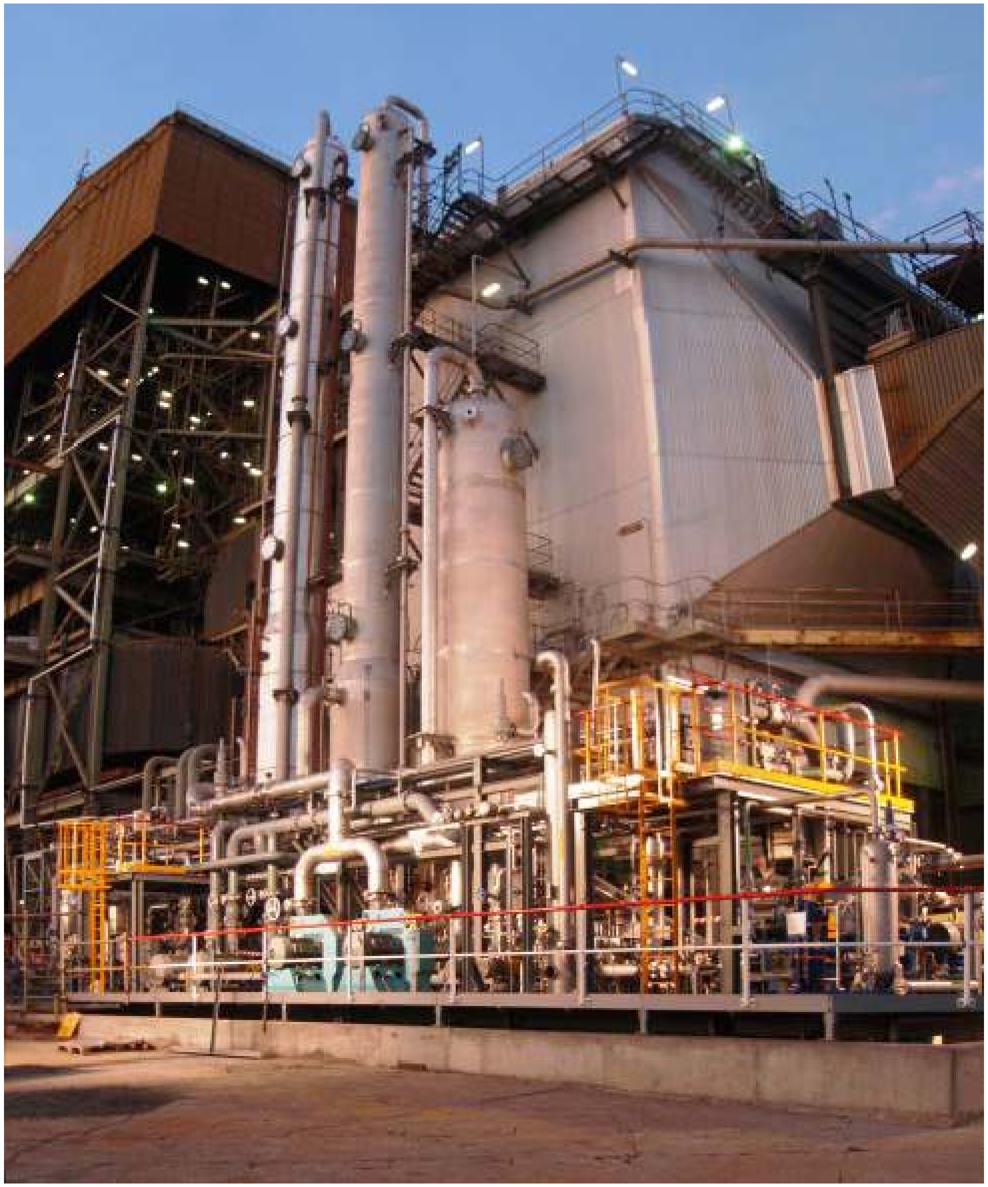
process group

Site erected columns

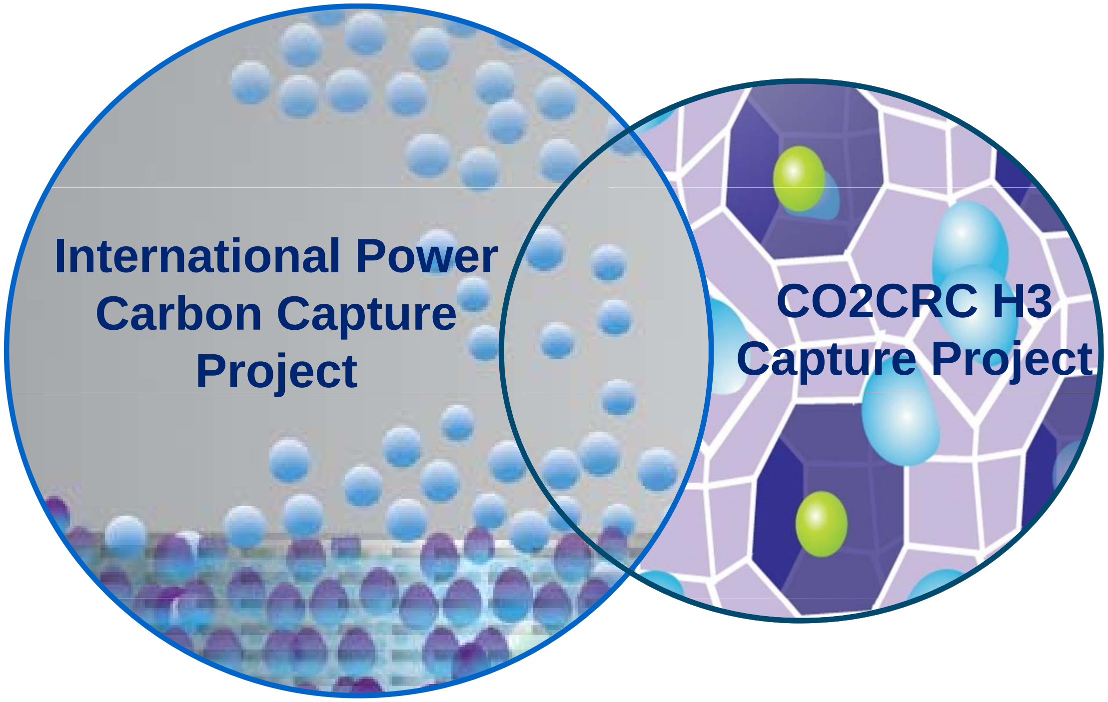
- Prewash/DCC
  (8.5m x 2.1m dia)
  Installed height 14 m
- Absorber
  (22m x 2-1.5m dia)
  Installed height 26 m
- Stripper
  (23.4m x 1.7-1.4m dia)
  Installed height 28 m

International Power CO_2 Capture Plant

process group



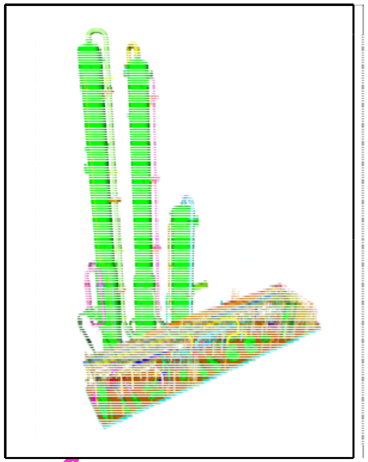
Post-combustion capture demonstration - Victoria



International Power Carbon Capture Project

CO2CRC H3 Capture Project

CO2CRC H3 Capture Project

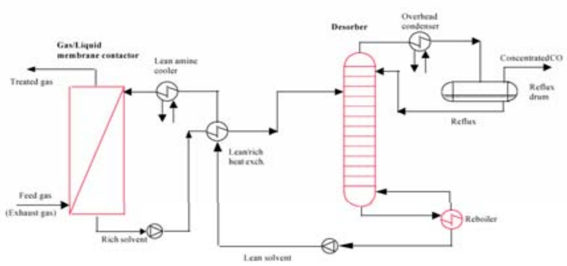


Solvent

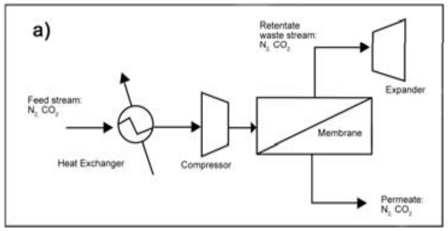
(10,000 tpa)

Image courtesy of
The Process
Group:

**Flue Gas from
Hazelwood
Power Plant**



Membranes



Adsorbent

Image courtesy of
Monash University

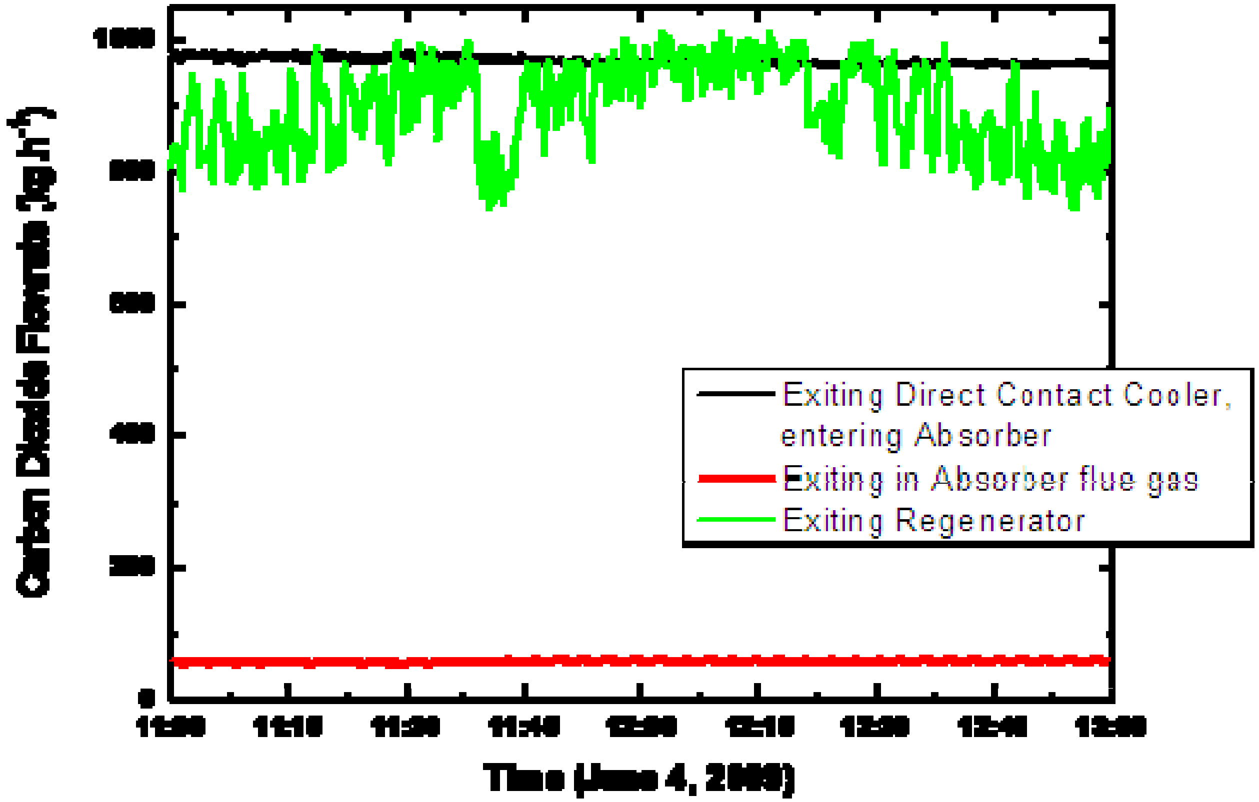
CO2CRC H3 Capture Project

- **New Solvent Development Research**
  - Laboratory research on new solvents for PCC at University of Melbourne(CO2CRC)
  - Potassium Carbonate and activators
- **Membrane Research**
  - Laboratory and field research on gas separation and gas absorption technologies by the University of Melbourne(CO2CRC) using existing and new test rigs – 15 tpa.
- **Adsorbent Research**
  - Laboratory and field research on solid adsorbents and adsorption technologies at Monash University(CO2CRC) using existing and new test rigs – 165 tpa.
- **Solvent Testing in 10,000 tpa (approx.) Demonstration Plant**
  - Testing of new and commercial solvents at IP Hazelwood site to obtain operating data and operating experience with brown coal flue gas.
  - Reviewing need for flue gas contaminant removal
  - Modified operating conditions including vacuum stripping and new materials
- **Process and Energy Integration Studies**
  - State of the art techniques to optimise heat integration
- **Technical and Economic Assessment Studies**

International Power

CO2CRC

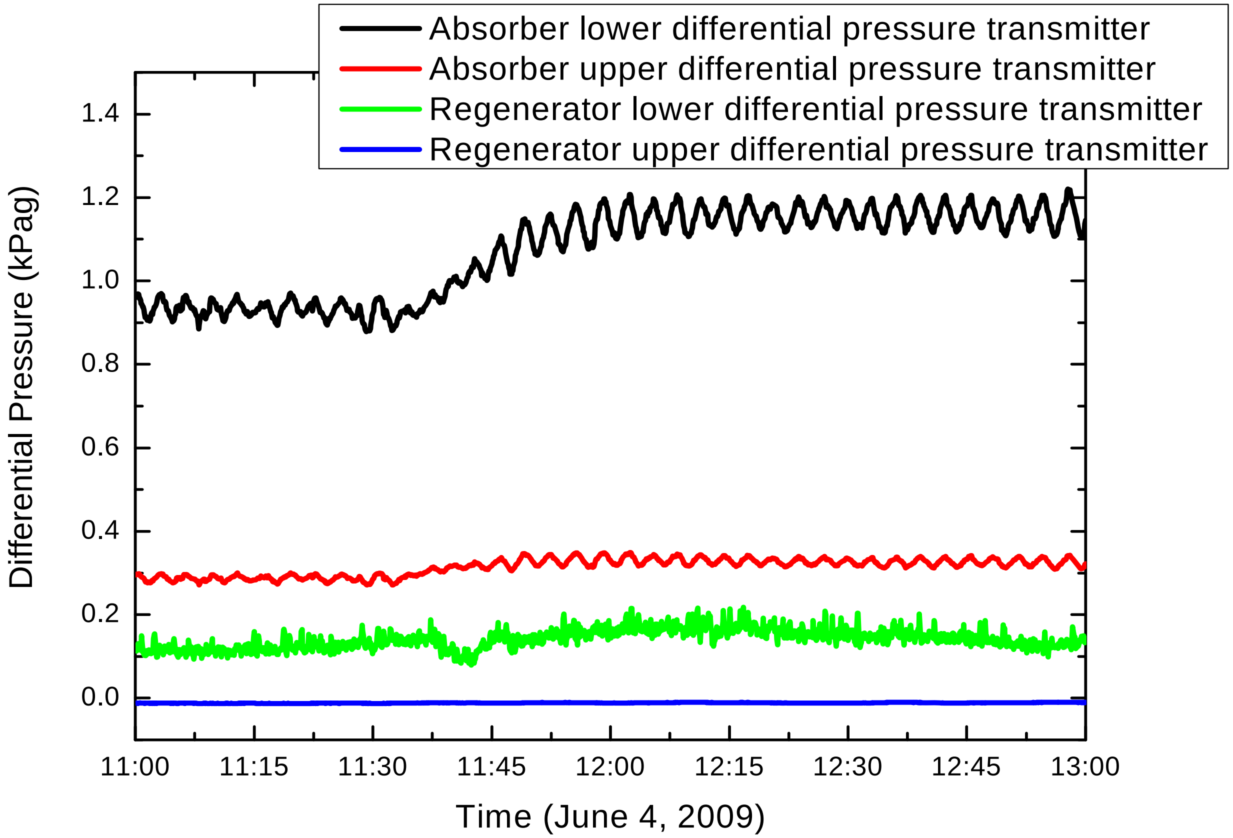
Solvent Plant Operating Data - Throughput



International Power

CO2CRC

Solvent Plant Operating Data – Pressure drop



Membranes

CO_2 can selectively pass through gas separation membranes to be extracted from the flue gas.

Membrane/solvent

A membrane separates flue gas from liquid solvent. CO_2 is absorbed by the solvent via pores in the membrane.

CO2CRC H3 Capture Project

Membrane skid

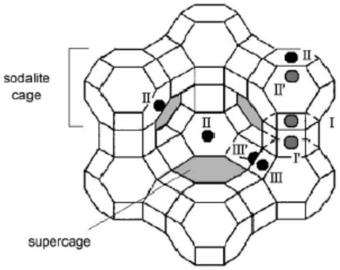
process group

CO2CRC

Initial Membrane results

- Membrane gas separation
  - Trialed a single pass hollow fibre polysulfone based module, with a laboratory CO_2/N2 selectivity of 14.3.
  - CO_2 partial pressure of 20.3 kPa across the membrane.
  - Initial operation ~25 % of the CO_2 in the feed passes through to the permeate stream.
  - Minor components in the flue gas, NOx and CO have been shown not to pass through the membrane, and are retained with N_2.
  - Insufficient initial data to determine the behaviour of SOx
- Membrane gas absorption
  - Trialed a hollow fibre polypropylene contactor with ~8 m2 surface area between the solvent and flue gas
  - Initial performance CO_2 loading into the solvent of 0.127 moles of CO_2 for every mole of solvent passing through the plant resulting in 85% of the CO_2 in the flue gas being absorbed
  - Minor components present in the feed, NOx and CO, remain with the flue gas and do not absorb into the solvent
  - Insufficient initial data to determine extent of reaction of SOx in the contactor.

2. Interaction of Adsorbent Development and Process Development – putting the picture together



Adsorbent development

Maximize: →

Working Capacity
Working Selectivity
T Tolerance
H_2O tolerance
contaminant tolerance

Process development for a given adsorbent

Optimize: →

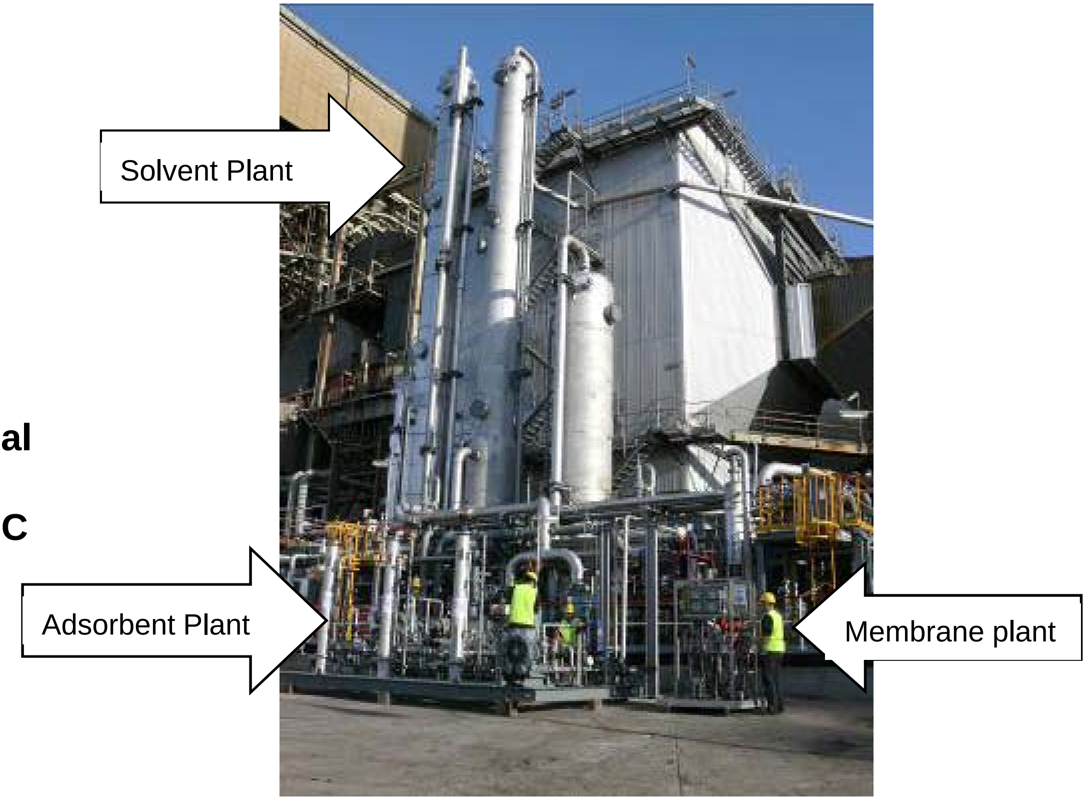
Pressure Window
Operating T
Effect of pressure drop
Cycle time
contaminant and water tolerance

CO2CRC H3 Capture Project

Adsorbent skid

International Power/CO2CRC H3 Post Combustion Capture Project

A unique Post-combustion Capture project combining Solvent, Adsorbent and Membrane Plants at International Power's Hazelwood site and featuring Australia's largest PCC plant



International Power

process group

CO2CRC

Process Design & Heat Integration: Post-combustion

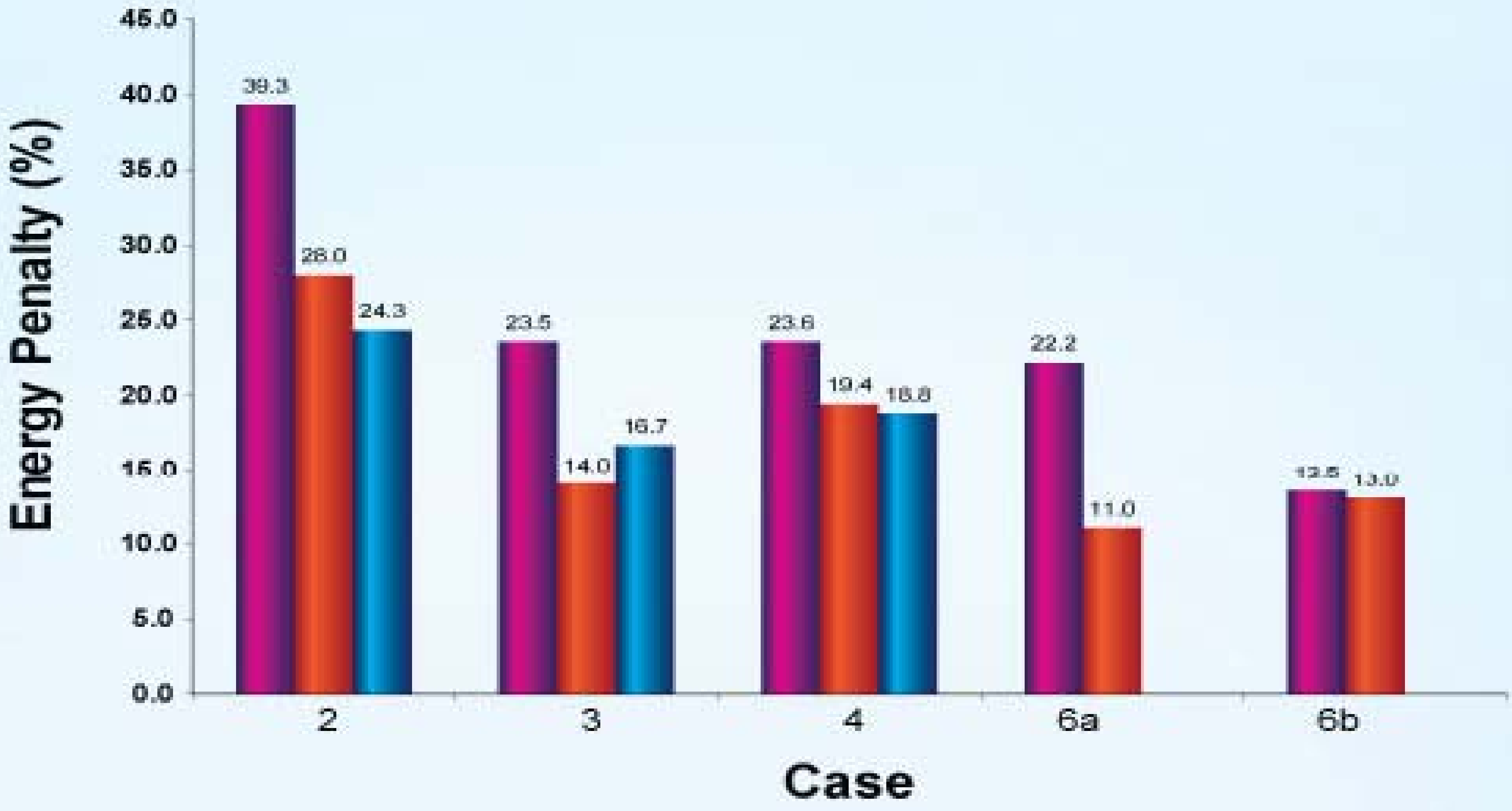
- **Comparison of the effect of power plant design on the parasitic energy loss has been studied**

- **The majority of the energy savings targeted through process integration for a retrofit that does not involve coal drying is achieved in the cold end of the power plant - downstream of the economiser for flue gas and upstream of the deaerator for the boiler feed water**

- **Optimal design configurations are continuing to be developed to reduce the energy penalty.**

- **For the solvent systems, targets for the optimal heat integration of amine solvents has been completed, carbonate solvents is in progress. Adsorbent and membrane integration work still to be completed**

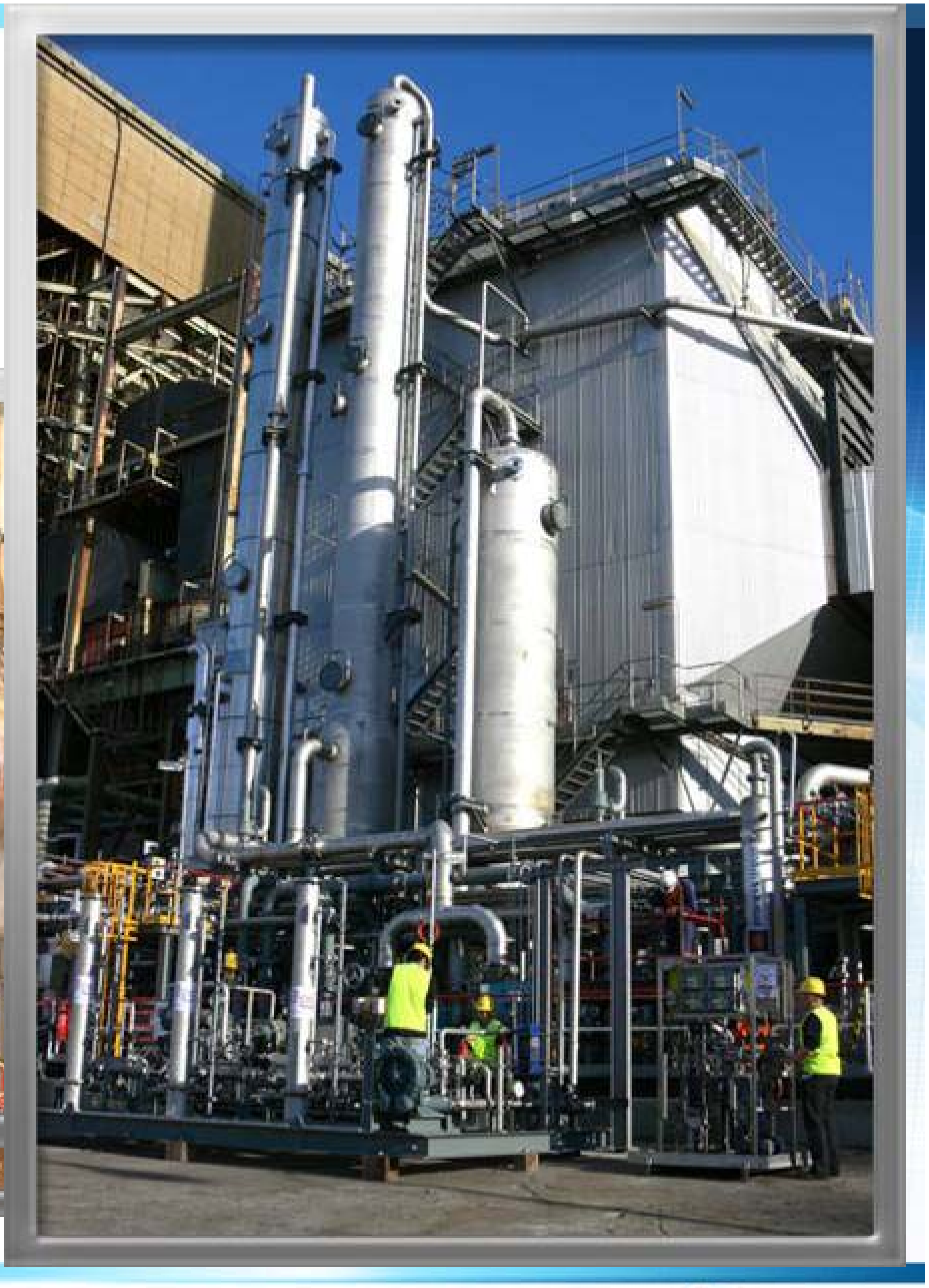
Comparisons of typical Australian power plants



Purple – Low efficiency Brown Coal
Red – Higher efficiency Brown Coal
Blue – Moderate efficiency Black Coal

CO2CRC covers nano

& cost



Conclusion

- **The International Power/CO2CRC H3 projects will provide valuable capture information for post capture from brown coal sources, and indeed, all fuel types.**
- **Unique capture RD&D capability, both in size and breadth of separation technology**
- **Post Combustion**
  - **Contribute to the knowledge of possible PCC cost reductions for all fuel types**
  - **Novel separation technologies demonstrated**
- **Overlap and integration with basic research programs**
  - **Identify those areas to continue and those to drop**
- **Extend to other demonstration projects at larger scale**
  - **It is extremely important that large scale integrated CCS demonstration projects begin post haste**
  - **Heat Integration is very important in CCS designs**

Acknowledgements

- CO2CRC H3 Capture Project team
  - CO2CRC
    - A.Qader,T.Harkin
  - Solvents
    - G.Stevens,K.Smith,K.Mumford,A.Khan,U.Ghosh,W.Tao
  - Adsorbents
    - P.Webley,A.Chaffee,T.Zhang,P.Xiao,R.Singh,K.Joshi
  - Membranes
    - S.Kentish,C.Scholes
  - Economics
    - D.Wiley,G.Allinson,M.Ho

CO2CRC Post-Combustion Capture Material:

Post-combustion capture of carbon dioxide

Membrane technologies

Post-combustion capture of carbon dioxide

Solvent absorption

Post-combustion capture of carbon dioxide

Adsorption technologies

CO2CRC H3
CAPTURE PROJE
Demonstrating CO_2 cap

RESEARCHING AND DEMONSTRATING CARBON DIOXIDE CAPTURE

http://www.co2crc.com.au/publications/brochures.html

Design Considerations of Post-Combustion CO_2 Capture Process during Part Load Operation of Coal-Fired Power Plants

Institute of
Energy Systems

Sebastian Linnenberg

Jochen Oexmann

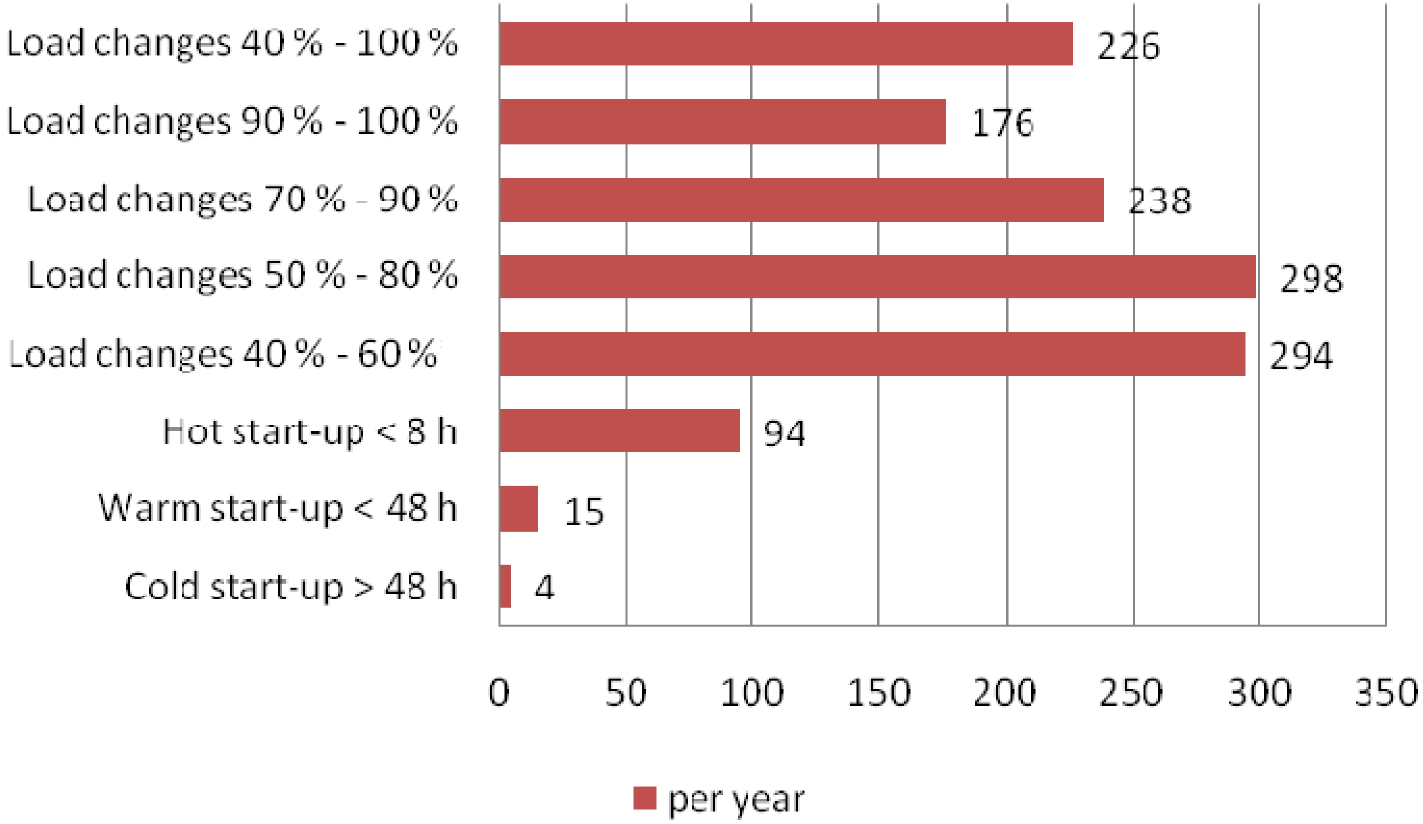
Alfons Kather

Technische Universität Hamburg-Harburg

12th International Post Combustion Capture Network Meeting

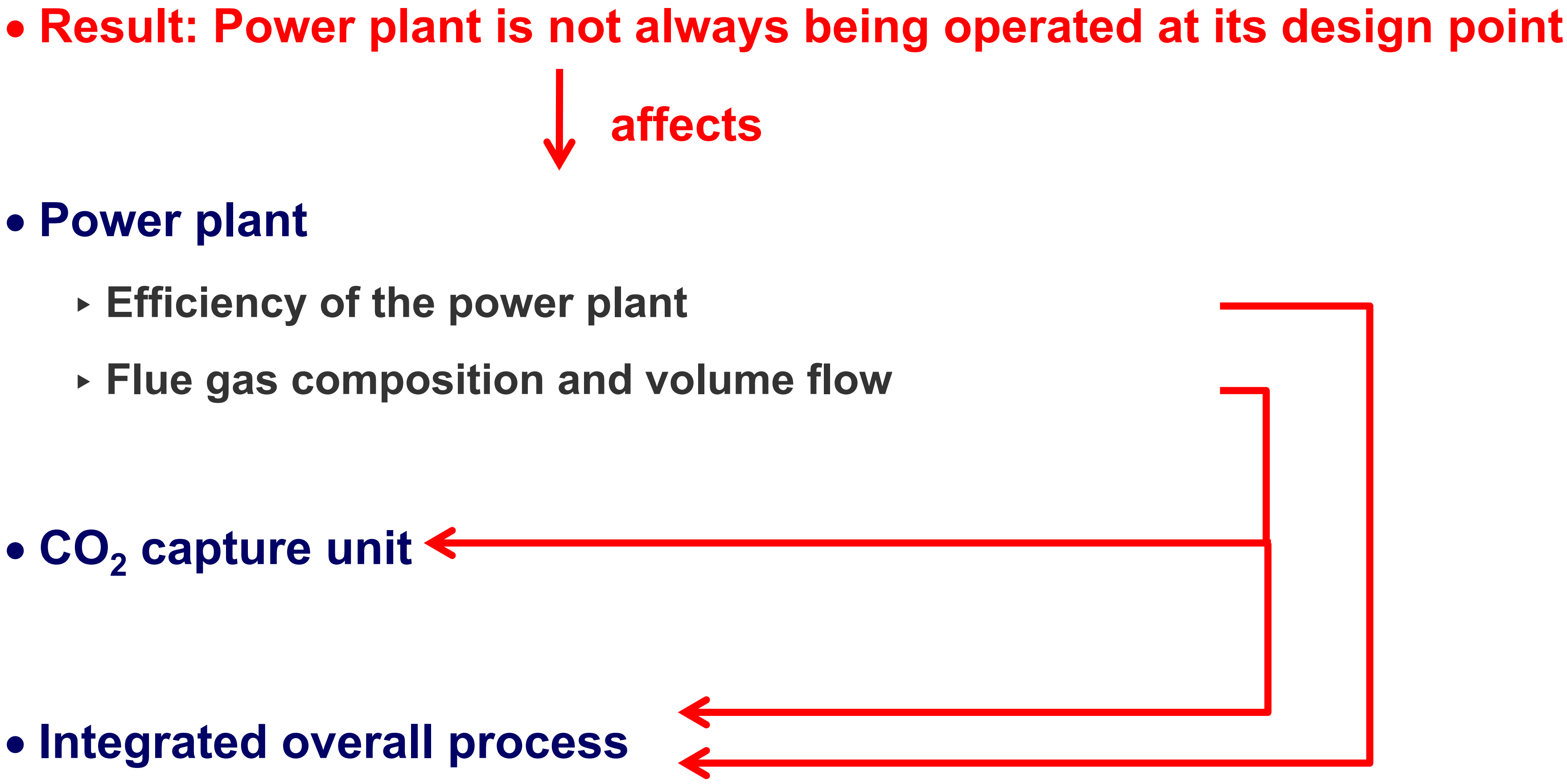
30 September 2009, Regina, Canada

- **Operation of a power plant depends on:**
    - **time of day / day of the week / season**
    - **grid feed-in of power from renewable energy systems (e.g. wind energy)**



Source: Trautmann, 2007

Introduction



- **Result: Power plant is not always being operated at its design point**

↓ **affects**

- **Power plant**
  - **Efficiency of the power plant**
  - **Flue gas composition and volume flow**
- **CO_2 capture unit**
- **Integrated overall process**

Contents

- Introduction
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  - CO_2 Capture Unit
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- Effect of part-load operation on
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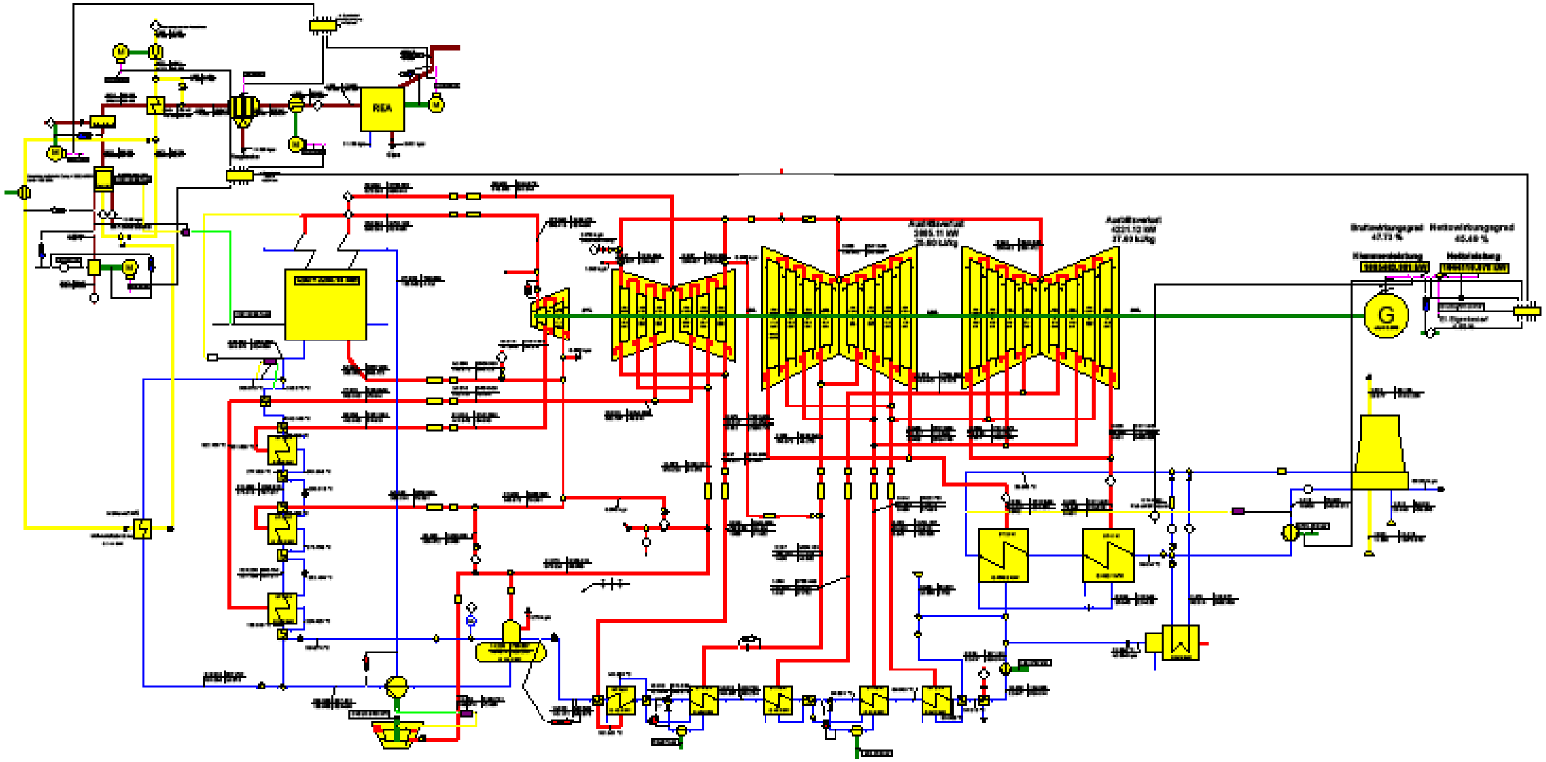
- Summary

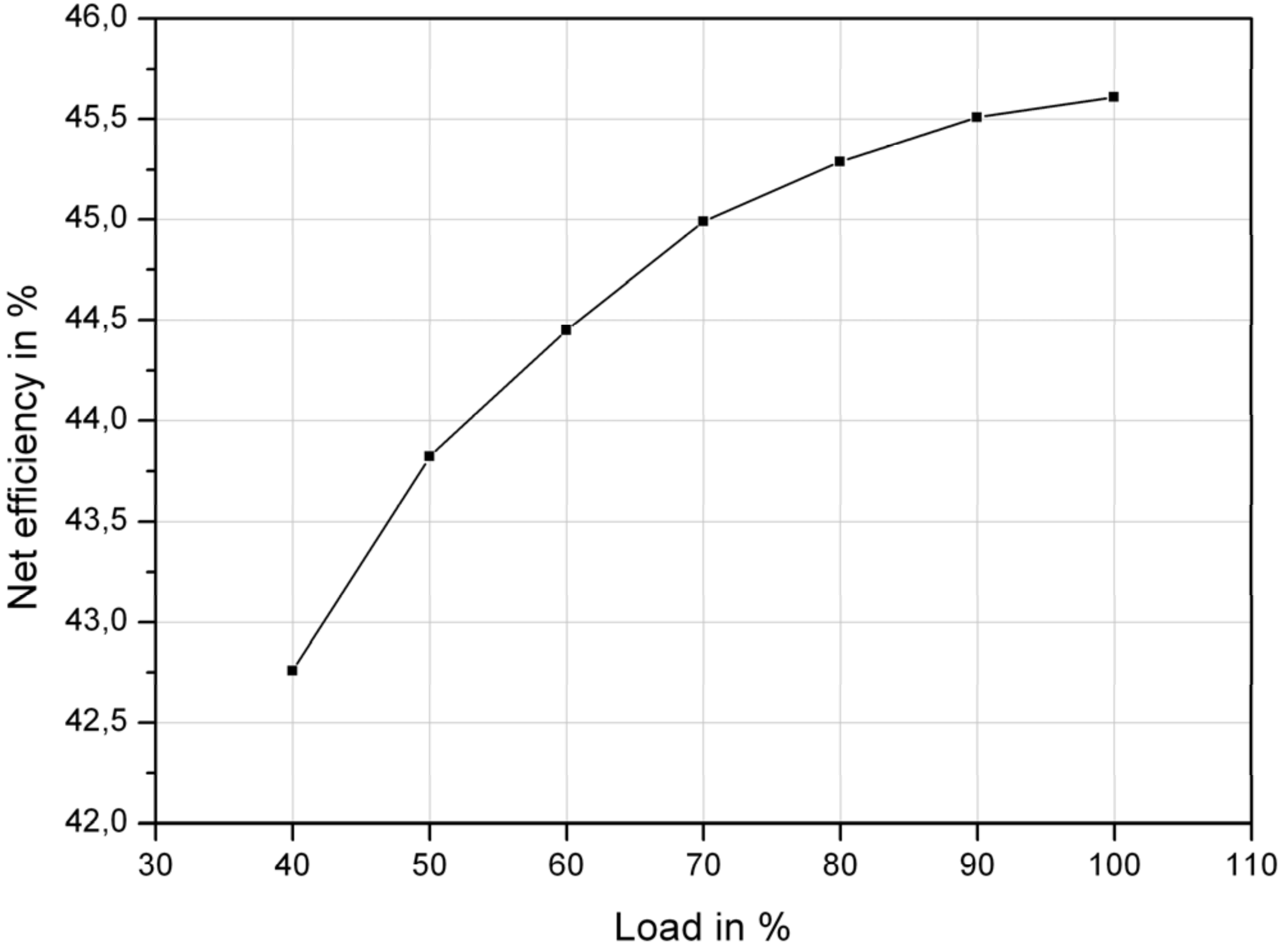
State-of-the-art Supercritical Power Plant

- **Boundary conditions for the power plant (100 % load) modelled in EBSILONProfessional®**
  - **Gross (Net) output capacity:** 1100 (1045) MW
  - **Net efficiency:** 45.6 %
  - **High steam parameters:** 280 bar, 600 °C



Part-Load Characteristics

- **(Net) efficiency loss of up to 2.8 %-pts. at minimum load**
- **It mainly depends on the part-load characteristics of:**



- **steam turbines**
- **electric consumers**

(i.e. Pumps, FGD, SCR...)

CO_2 Capture Unit

Solvent: 30-wt% MEA

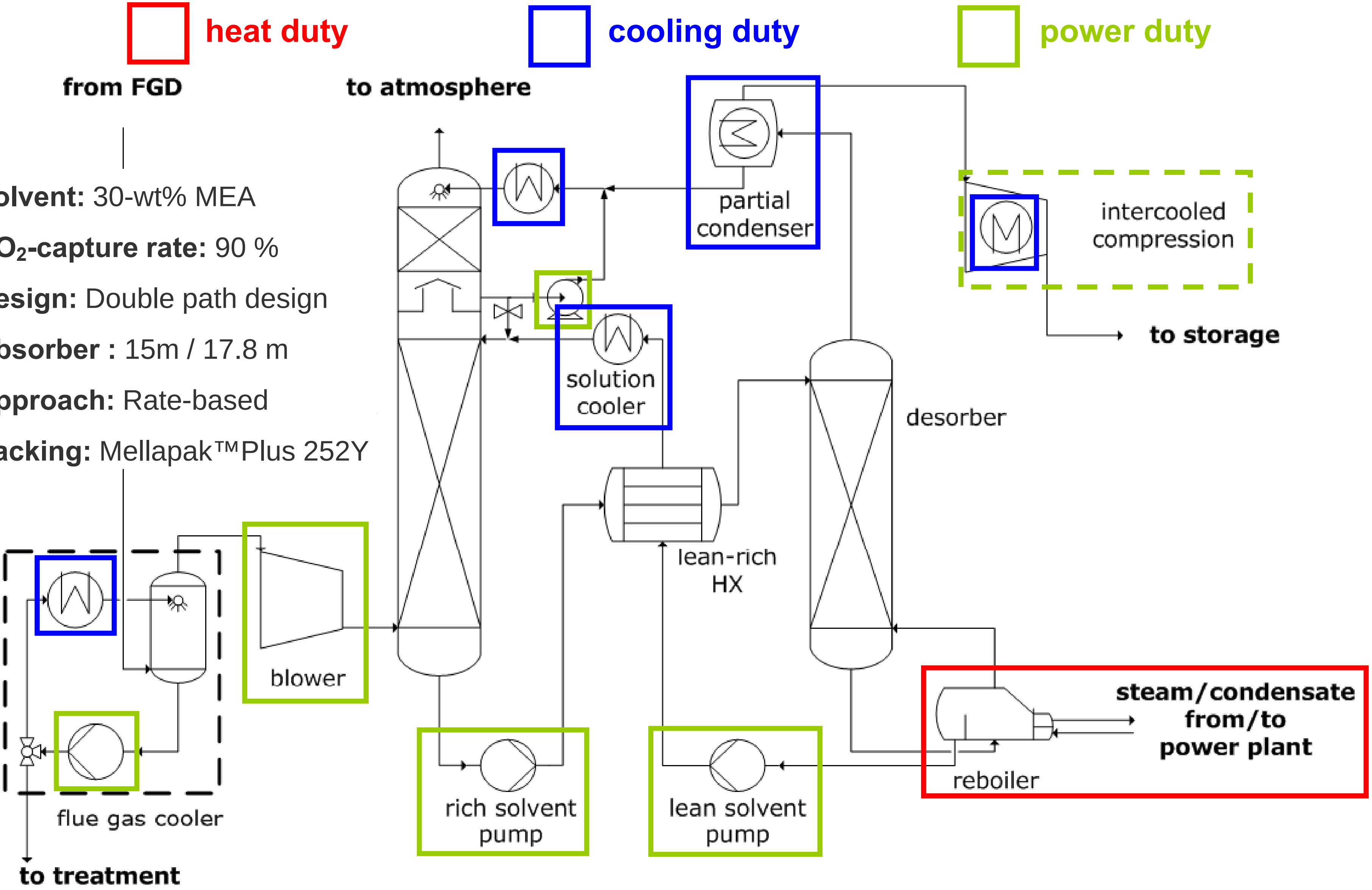
CO_2-capture rate: 90 %

Design: Double path design

Absorber : 15m / 17.8 m

Approach: Rate-based

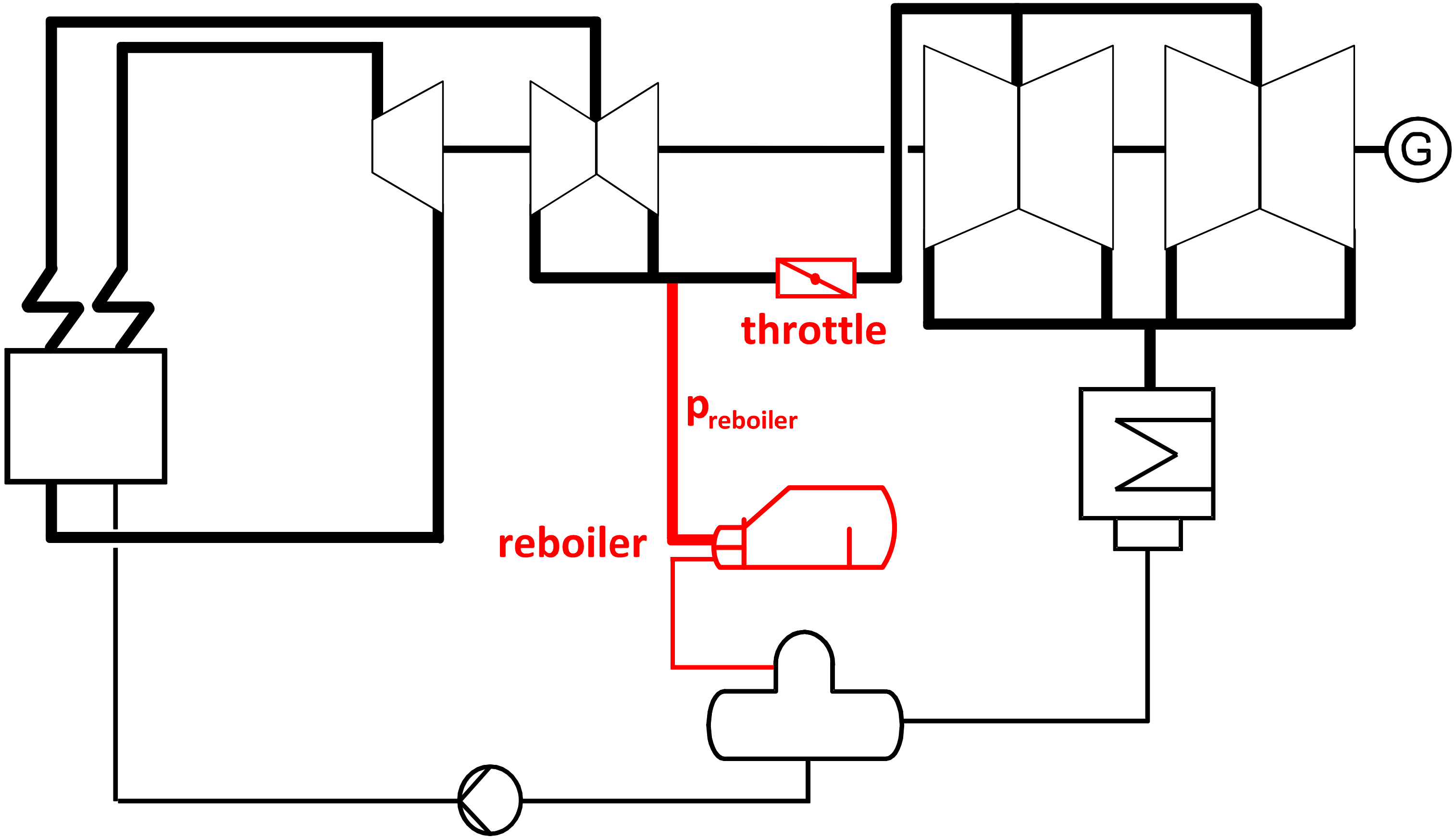
Packing: Mellapak™Plus 252Y



Integration of the Reboiler

TUHH
Technische Universität Hamburg-Harburg

- **The post-combustion CO_2 capture process is integrated as a retrofit option to the existing power plant.**



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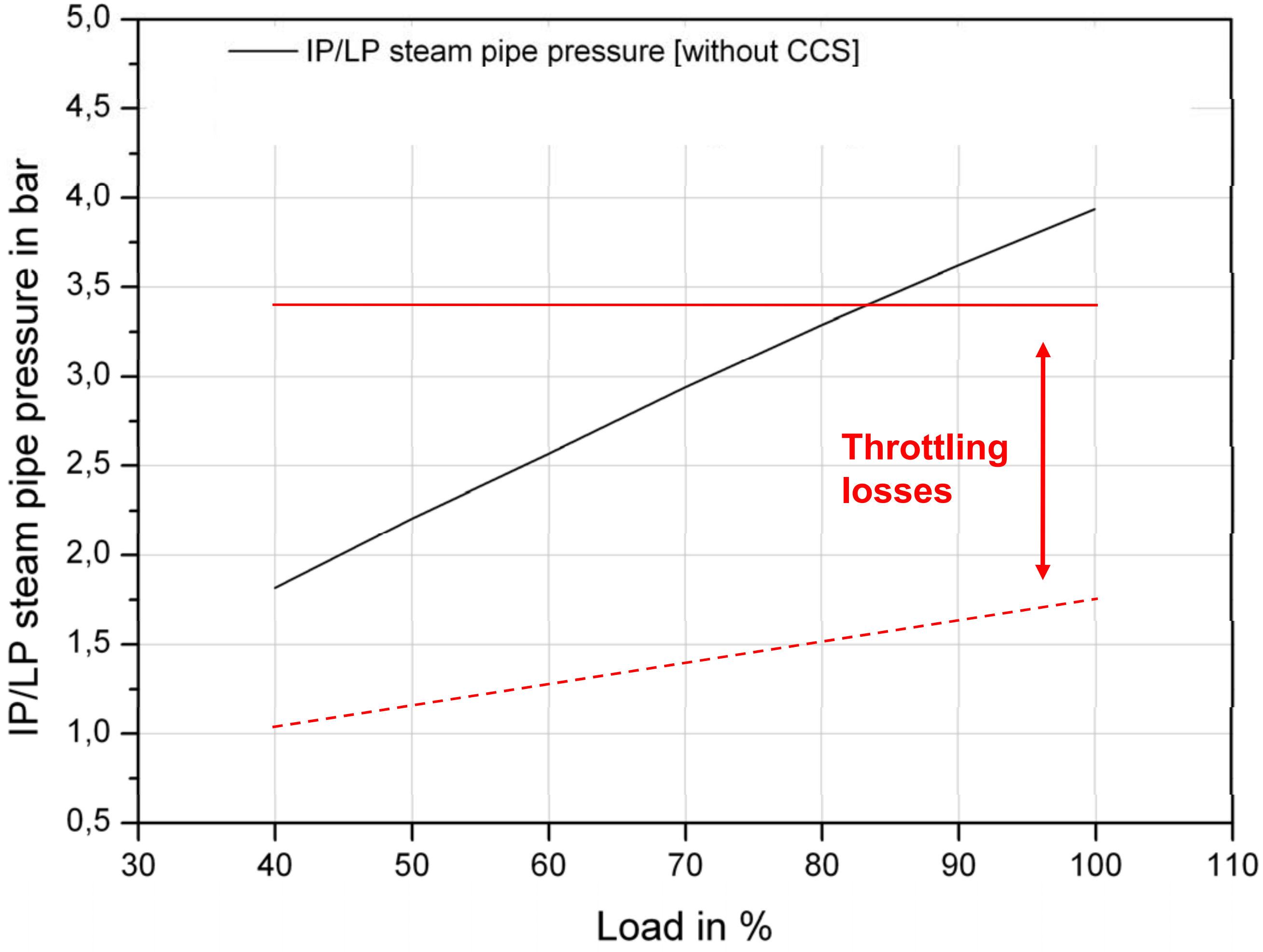
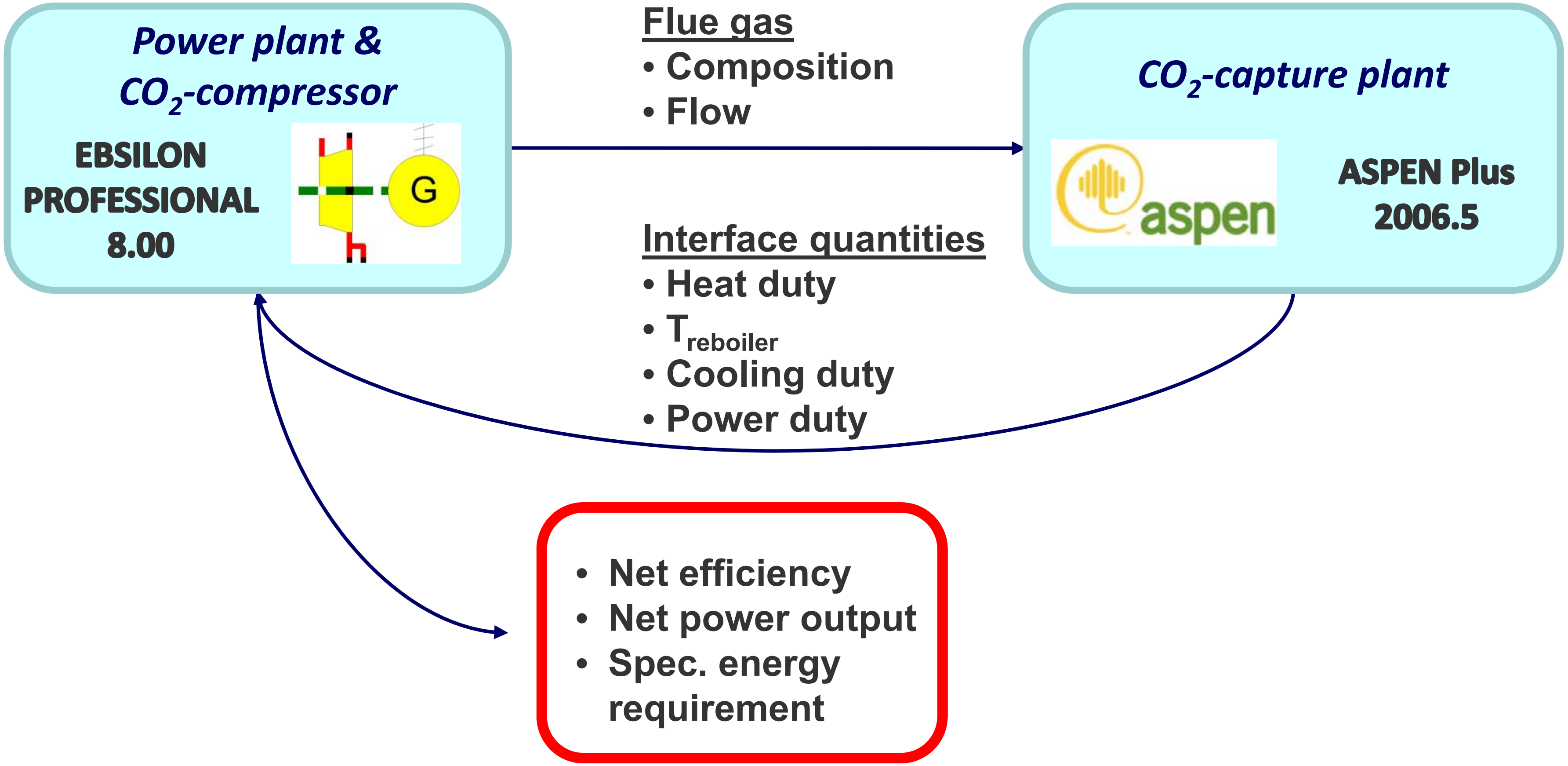


Linking of CO_2 Capture Unit and Power Plant Model

- **Link of EBSILON and ASPEN allows to use the most suitable software tool for each sub-process**



Power plant &
CO_2-compressor

EBSILON PROFESSIONAL 8.00

Flue gas
- Composition
- Flow

CO_2-capture plant

ASPEN Plus 2006.5

Interface quantities
- Heat duty
- $T_{reboiler}$
- Cooling duty
- Power duty

- Net efficiency
- Net power output
- Spec. energy requirement

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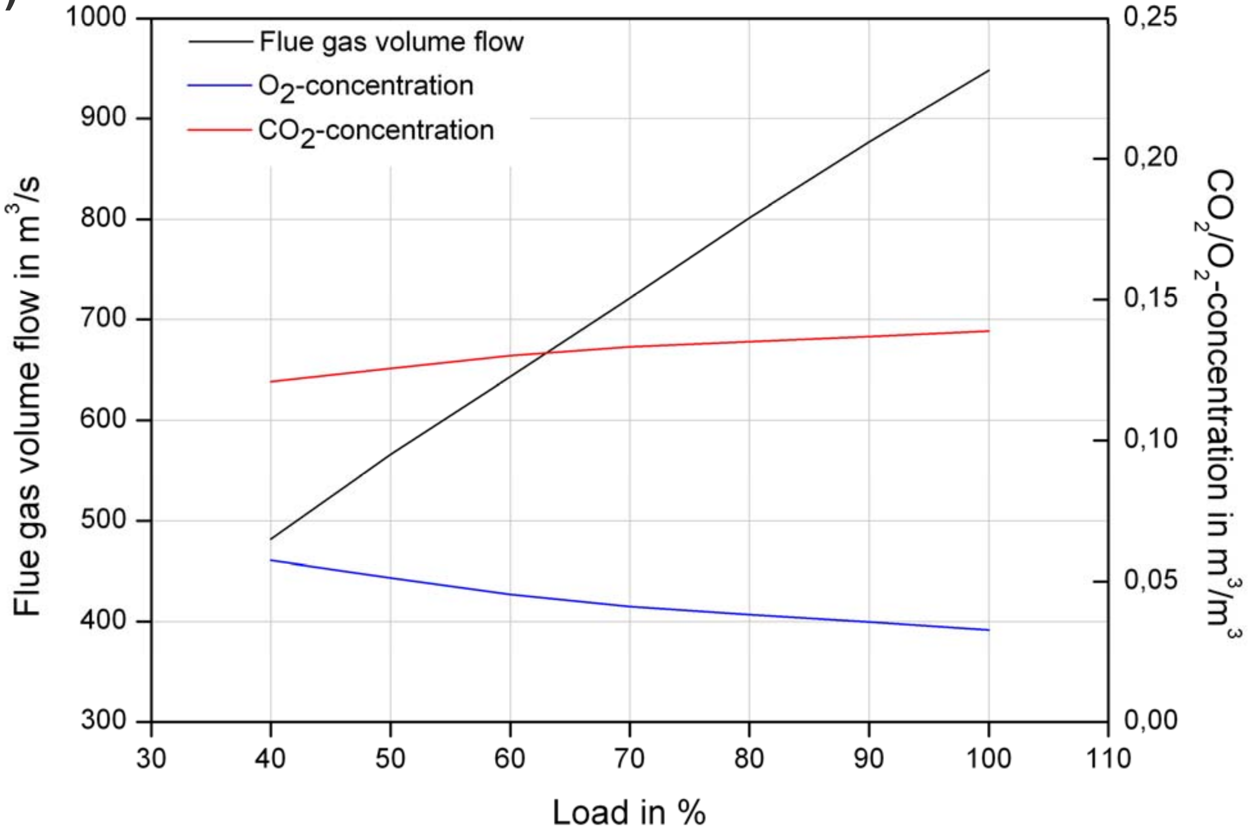
Effect of Part-Load Power Plant Operation on the Flue Gas

- **Flue gas volume flow is decreasing for lower loads**
- **The specific flue gas volume flow is increasing**
  - **The air ratio of a boiler is increased for lower loads (e.g. to support the reheater temperature)**

O_2 ↑ :
3.3 vol-%→ 5.7 vol-%

CO_2↓ :
13.9 vol-%→ 12.1 vol-%



Effect of Flue Gas Parameters on the CO$_2$ Capture Unit

- **Optimisation of the L/G to receive the minimal efficiency loss:**

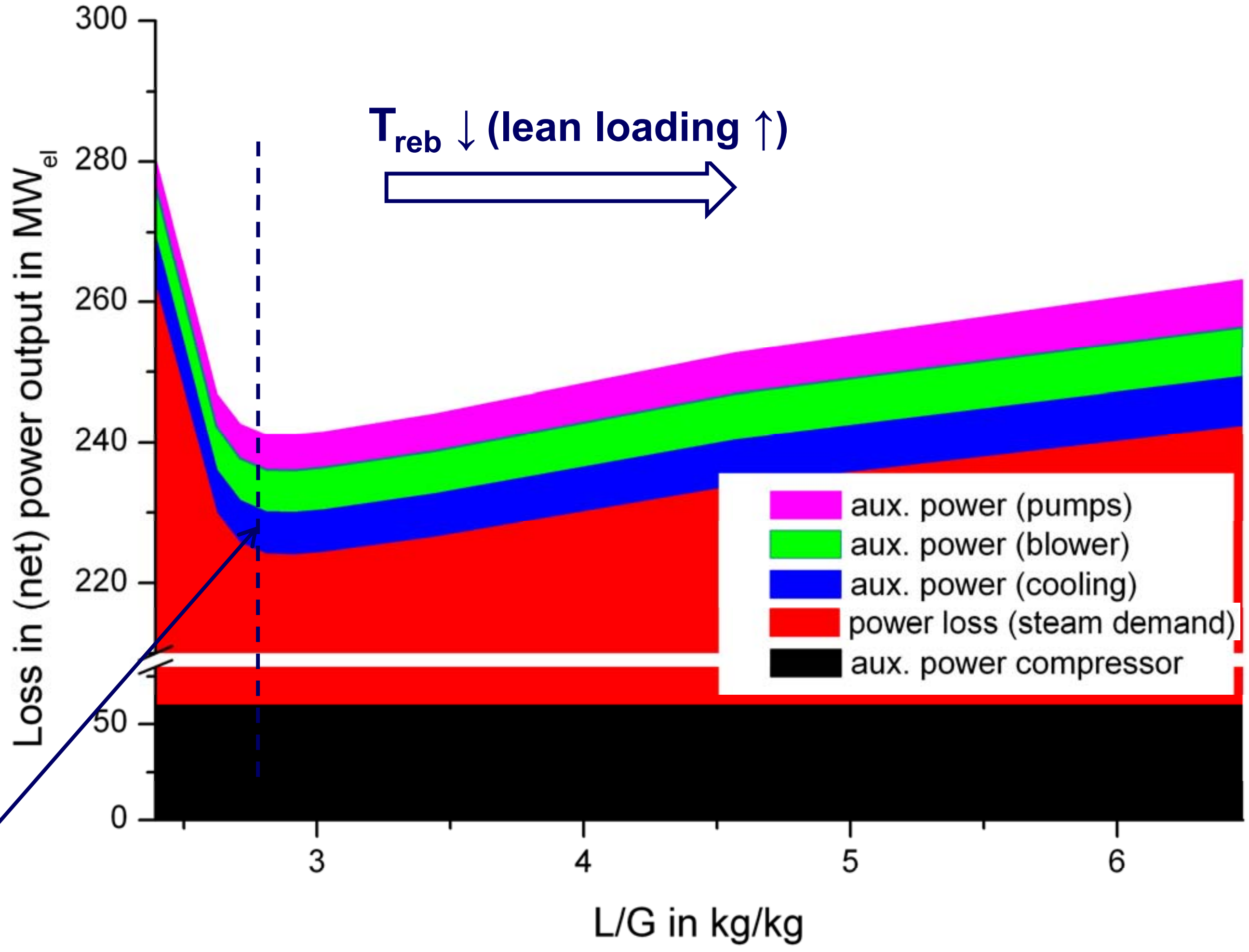
For a higher L/G

Q_{Reb} ↑

T_{Reb} ↓

W_{pumps} ↑

Q_{cool} ↑



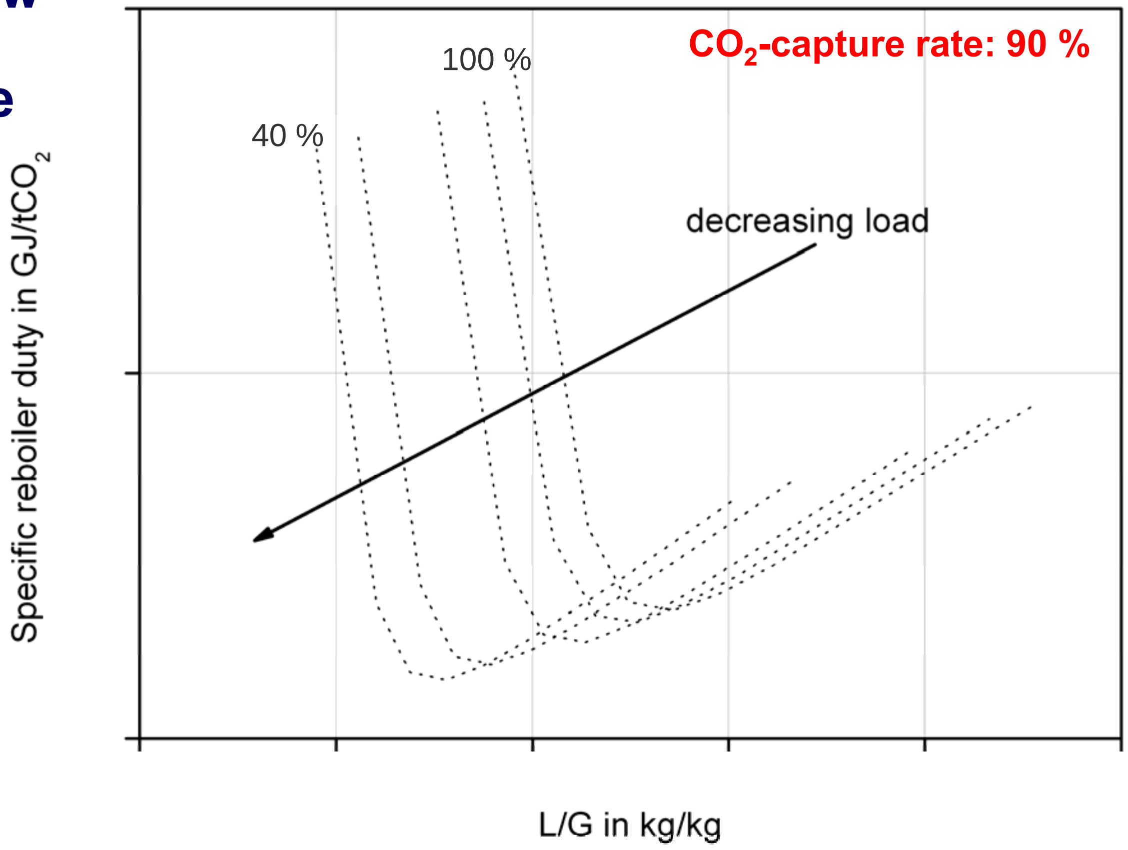
Minimum in power loss agree with minimum in steam demand!

Effect of Flue Gas Parameters on the CO_2 Capture Unit in Part-load Operation

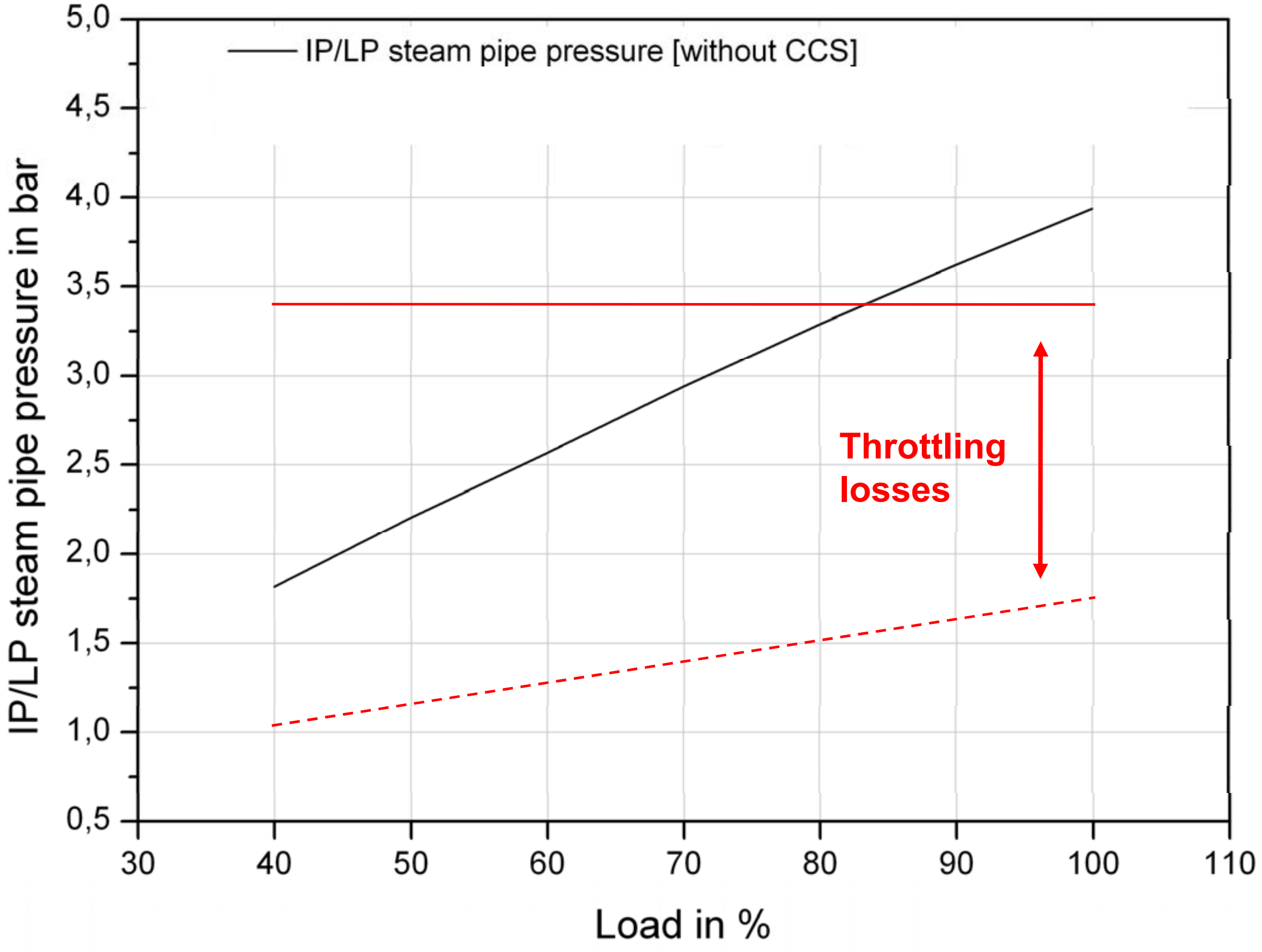
- **Optimisation of the L/G and the corresponding minimal heat demand of the reboiler for different load cases (100 % - 40 %)**

- **lower flue gas volume flow**

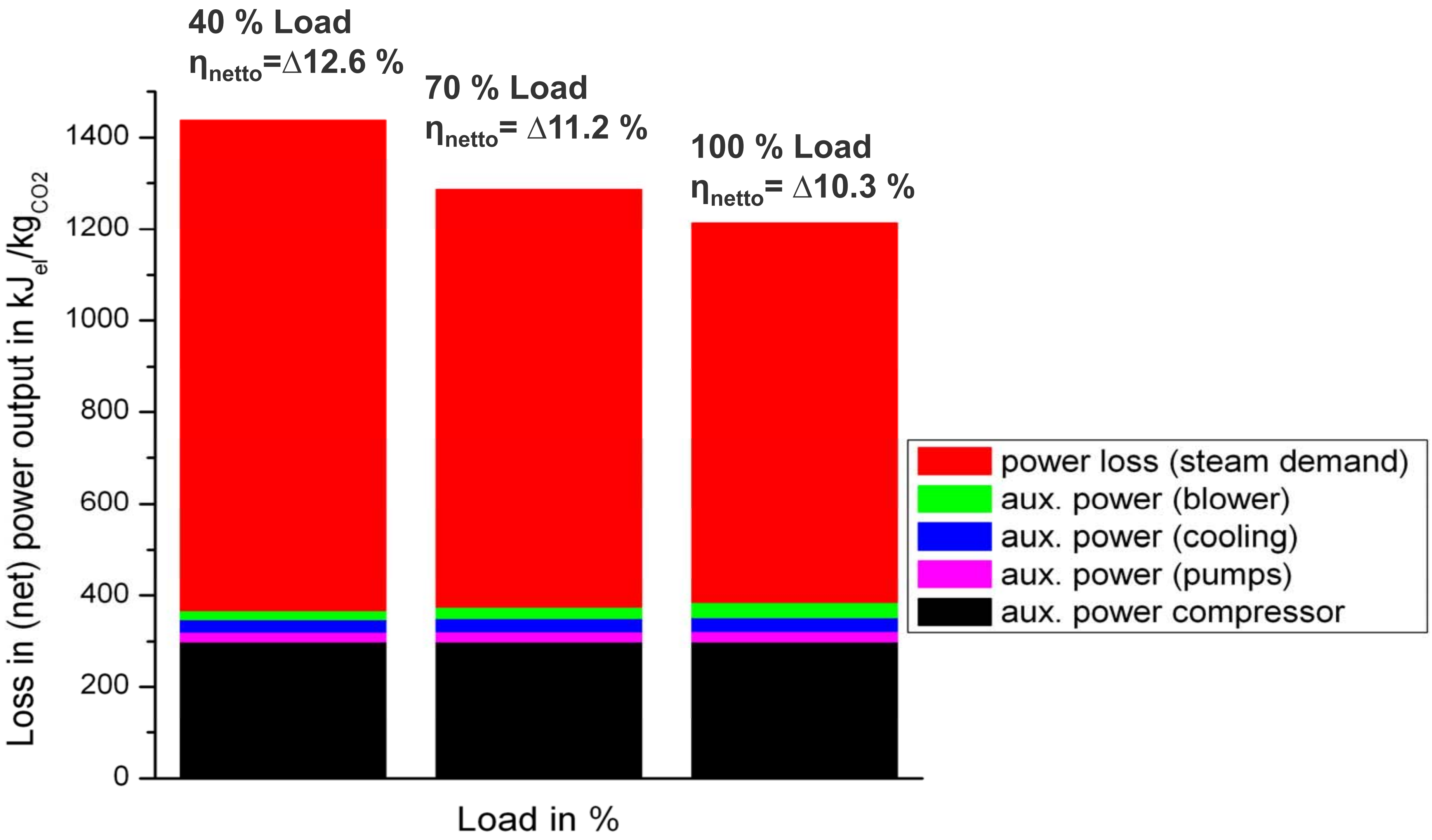
→increased residence time



- **The post-combustion CO_2 capture process is integrated as a retrofit option to the existing power plant.**



Effect on the Integrated Overall Process in Part-load Operation



Effect on the Integrated Overall Process in Part-load Operation

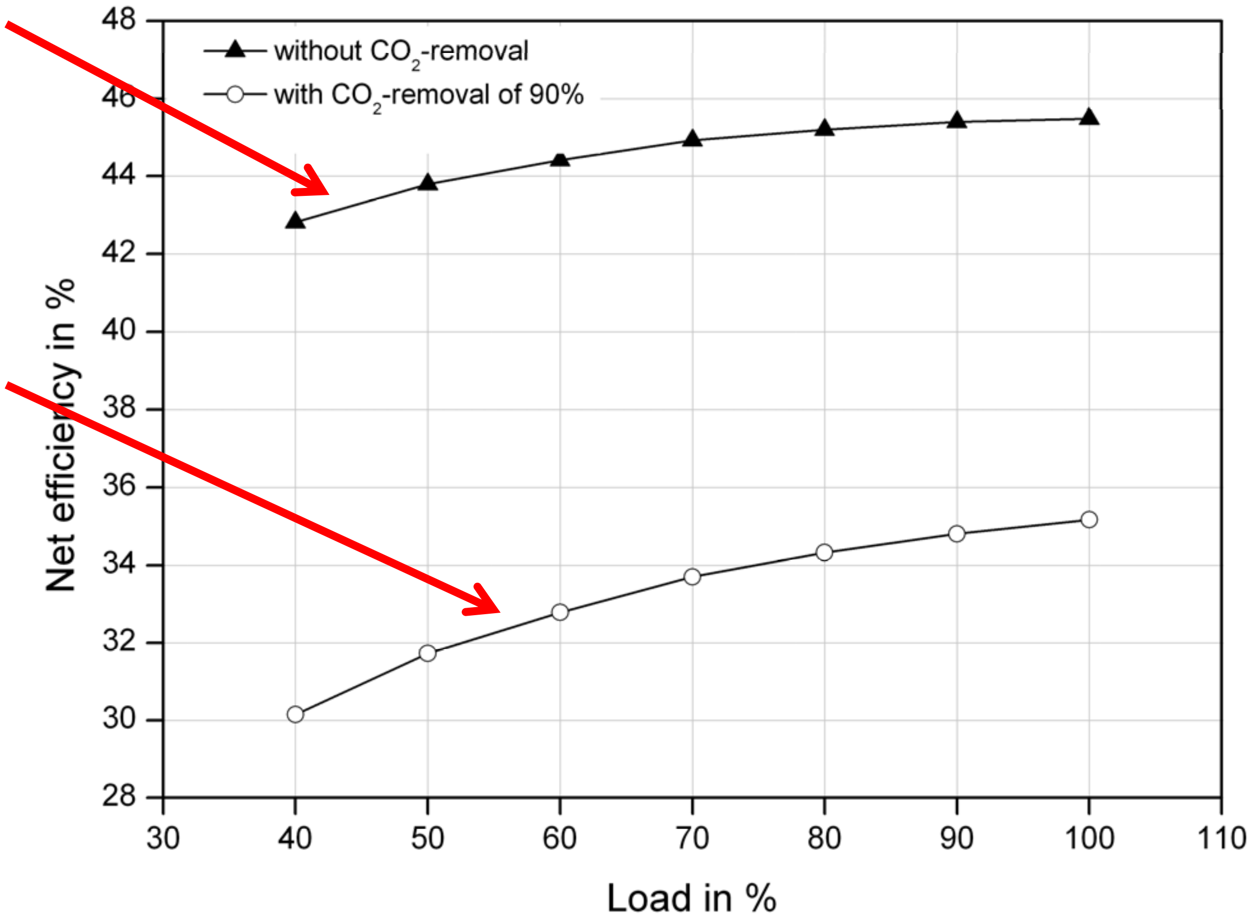
- **Net efficiency penalty of 10.3 %-pts at full load**
- **The net efficiency is decreasing for decreasing load.**
  - **reference power plant**

    45.6 % to 42.8 %

    (by 2.8 %-pts)
  - **with 90% CO_2 removal**

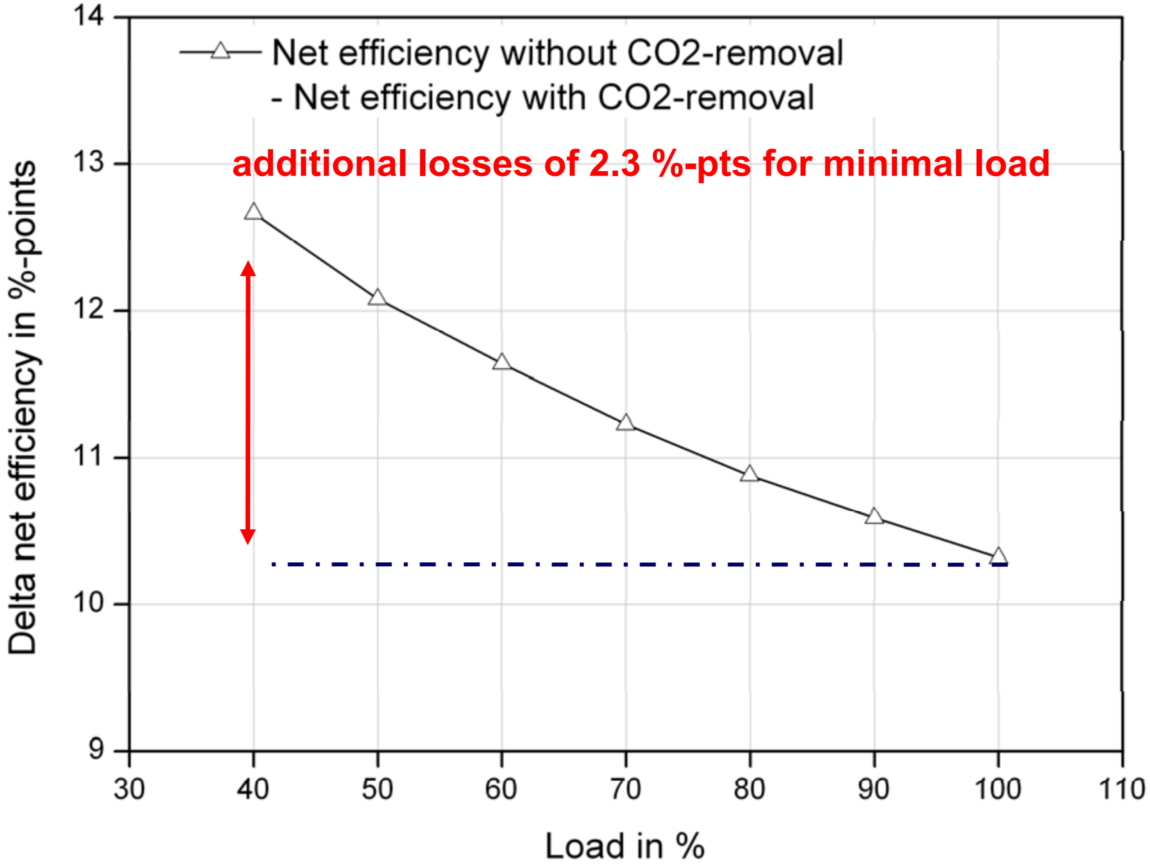
    35.3 % to 30.2

    (5.1 %-pts.)



Effect on the Integrated Overall Process in Part-load Operation

- **A decreasing load results in a loss of net efficiency of 10.3 %-pts at full load and up to 12.6 %-pts for minimum load.**
  - **Due to throttling losses!**



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Conclusions

- **The effect of different part load cases (40 % - 100 %) on the power plant, the CO_2 capture process and the integrated over all process was analysed.**
  - **the L/G has to be optimised with respect to the integrated overall process**
  - **flue gas volume flow is decreasing (specific volume flow is increasing)**
  - **flue gas composition changes (O_2 ↑ / CO_2 ↓)**
- **The net efficiency penalty of the integrated overall process is increasing for lower loads.**
  - **throttling losses due to the steam extraction increase**

Thank you for you attention!

Sebastian Linnenberg - linnenberg@tuhh.de

Institute of Energy Systems

Jochen Oexmann

Imo Pfaff

Sebastian Linnenberg

Alfons Kather

Optimized Integration of Post-Combustion CO_2 Capture Process in Greenfield Power Plants

12th International Post Combustion Capture Network Meeting

30 September 2009, Regina, Canada

TUHH

Hamburg University of Technology
Institute of Energy Systems

Prof. Dr.-Ing. A. Kather

Background

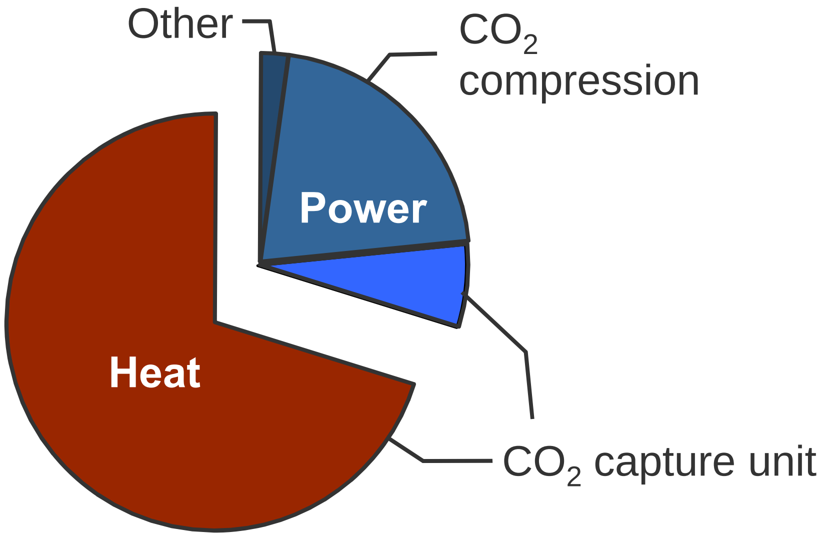
Post-combustion CO_2 capture by wet chemical absorption processes

+ Based on the conventional steam power plant process
+ Retrofittable
− Relatively high efficiency penalty

Efficiency losses due to

- CO_2 capture unit
  - Heat demand to regenerate solvent
  - Power demand
- CO_2 compression
- Further auxiliary loads (fans etc.)

Structure of efficiency losses



Focus of most studies: Retrofit integration

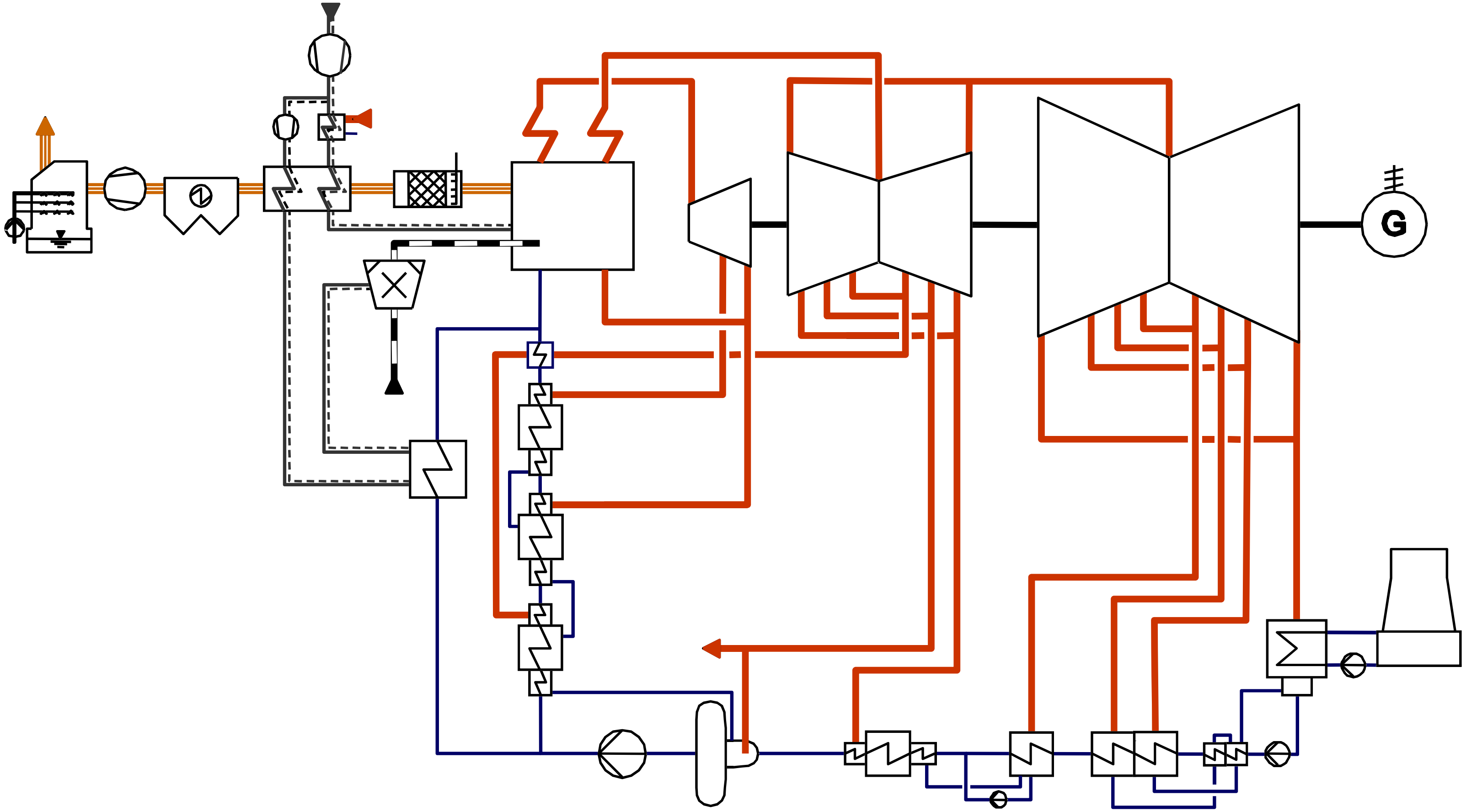
➔This study: focus on Greenfield

- Water-steam-cycle and overall power plant optimization possible

Methodology (1)

Reference power plant process (Ebsilon Professional)

- Concept study Reference Power Plant North Rhine-Westphalia (RPP-NRW) (USC, hard-coal, η_{net} = 45.6 %, 600 $MW_{el, gross}$)



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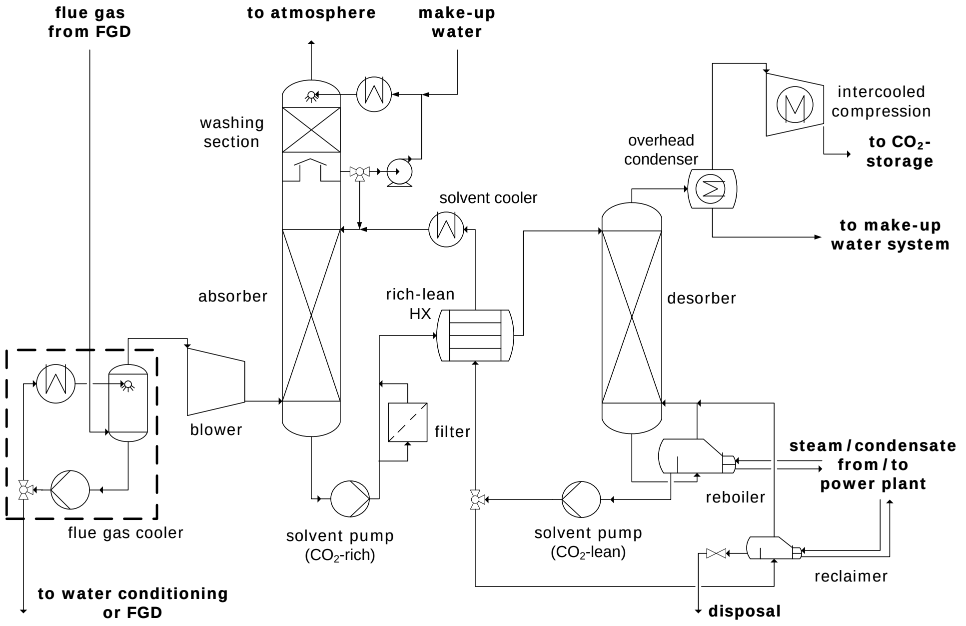
Wet chemical absorption process (Aspen Plus)

- MEA based process with optimistic performance parameters:

  3.3 GJ/t CO_2 @ 124 °C (90% capture)



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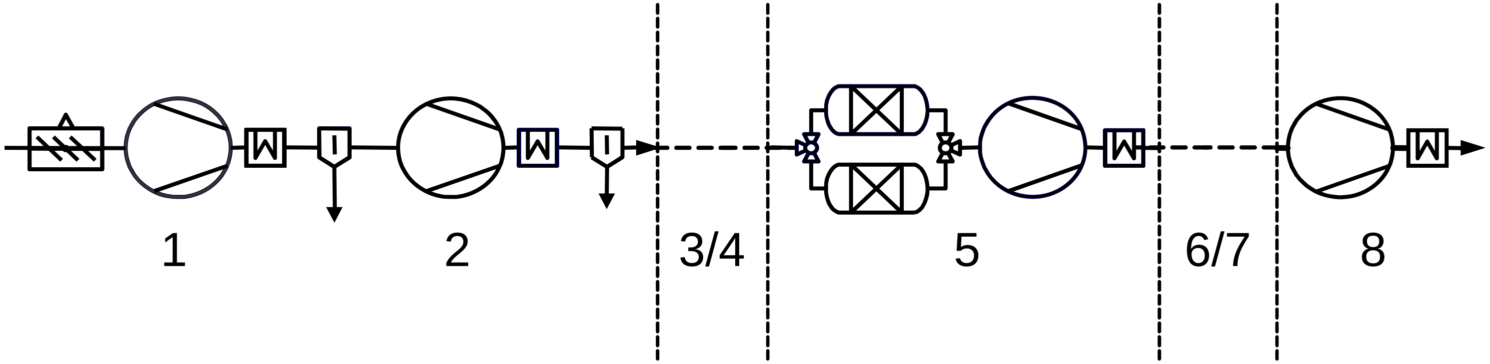
- MEA based process with optimistic performance parameters:

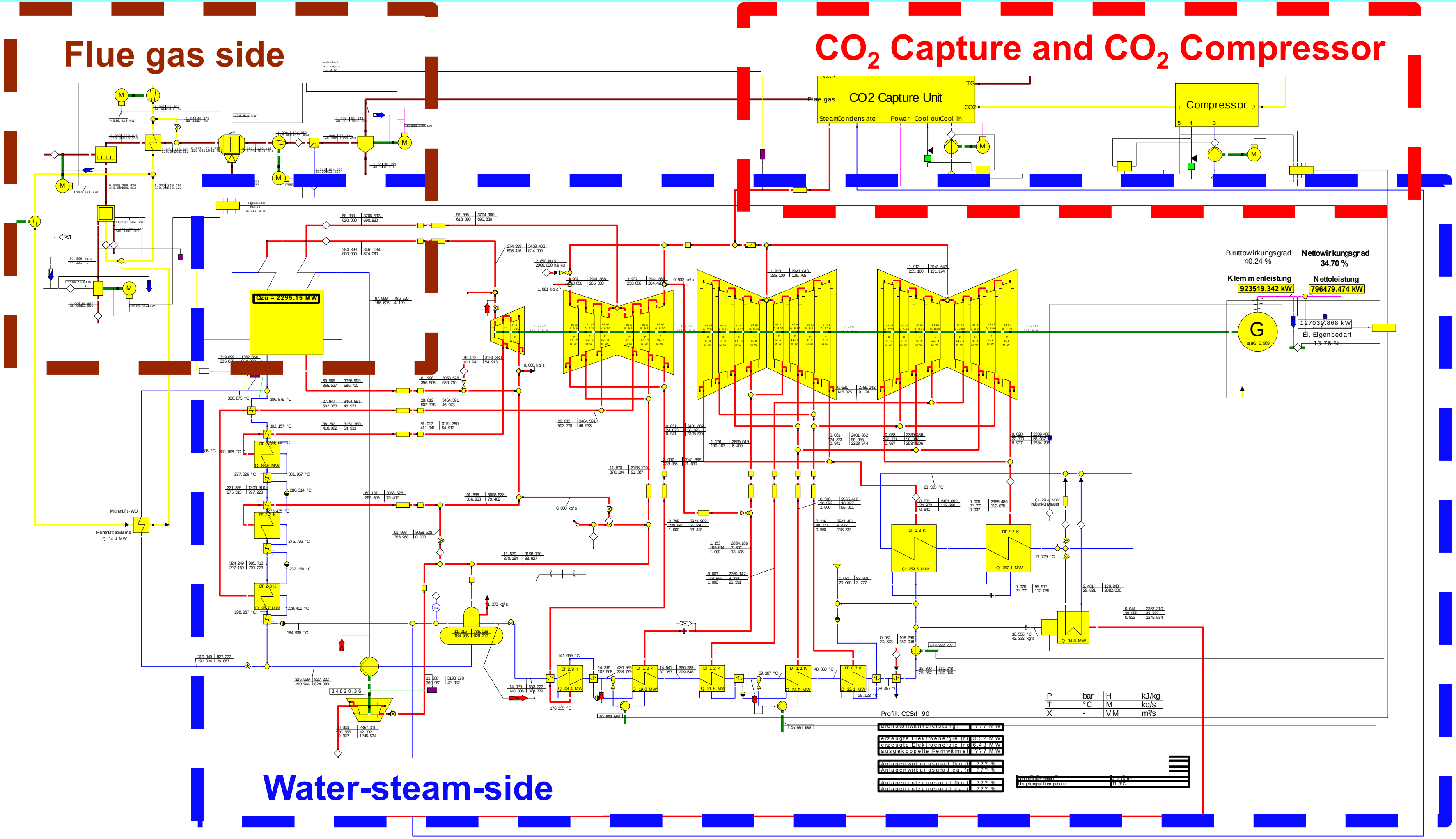
  3.3 GJ/t CO_2 @ 124 °C (90% capture)

CO_2 compression process (Ebsilon Professional)

- 8-staged compressor, each stage intercooled
- Pipeline conditions 110 bar, 40 °C

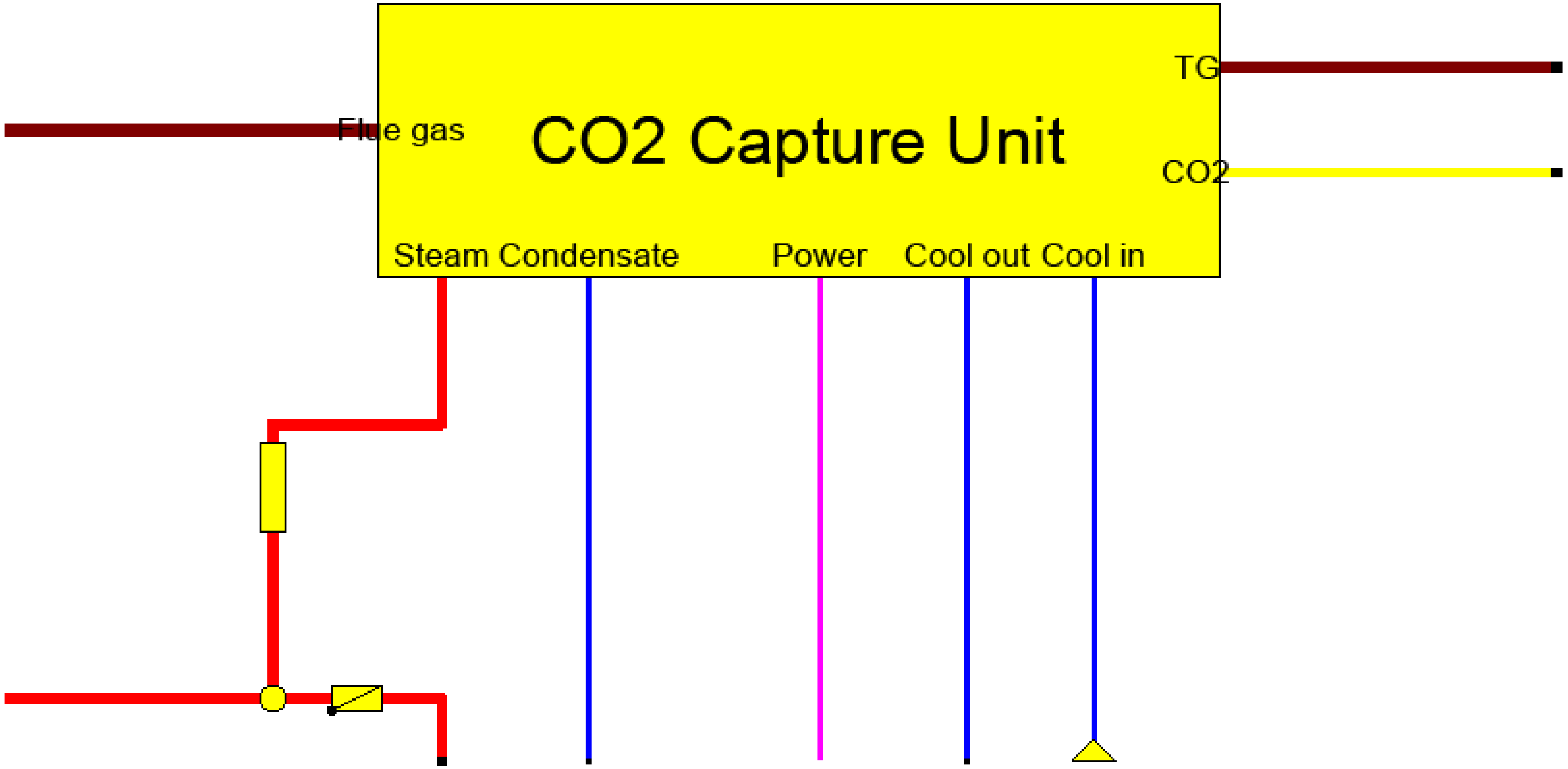


Methodology (2)



- **Integration of CO$_2$ capture unit by implementing interface characteristics in “yellow-box” within power plant simulation tool EBSILONProfessional**

Methodology (2)



- **Integration of CO_2 capture unit by implementing interface characteristics in “yellow-box” within power plant simulation tool EBSILONProfessional**

Study Approach

CCS power plant

- Design point: 100 % load with 90 % CO_2 capture
- Flow sheet layout unchanged to maintain comparability

For each design case

- Optimization of steam bleed pressures of pre-heat train
- Optimal reboiler condensate return point

Conducted analyses

1. Evaluate impact IP/LP crossover pipe pressure (basic integration)
2. Optimization by waste heat recovery

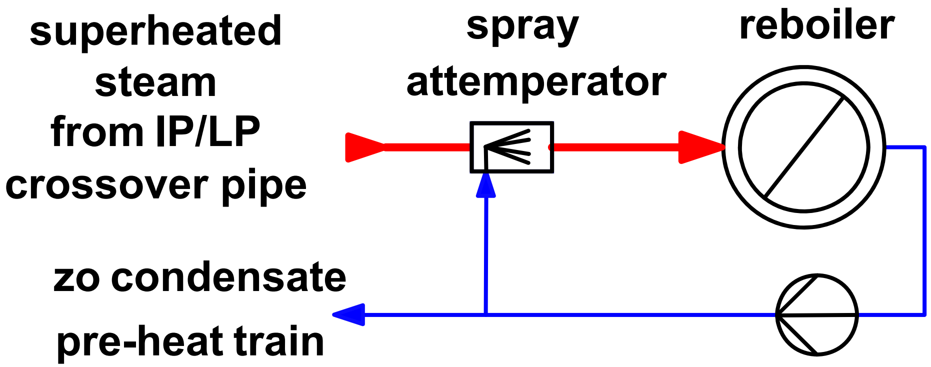
Basic Integration

Interface requirements delivered by the power plant

1. Heat for regeneration in sufficient quantity and quality
2. Power to drive the CO_2 compressor, pumps and fans
3. Cooling water to discharge waste heat

Only reasonable option to extract LP-steam: IP/LP crossover pipe

- Best suited to extract large steam <u>quantity</u> (~ 50% needed)
- To meet the required <u>quality</u> (T,p) over entire load range
  - steam attemperation



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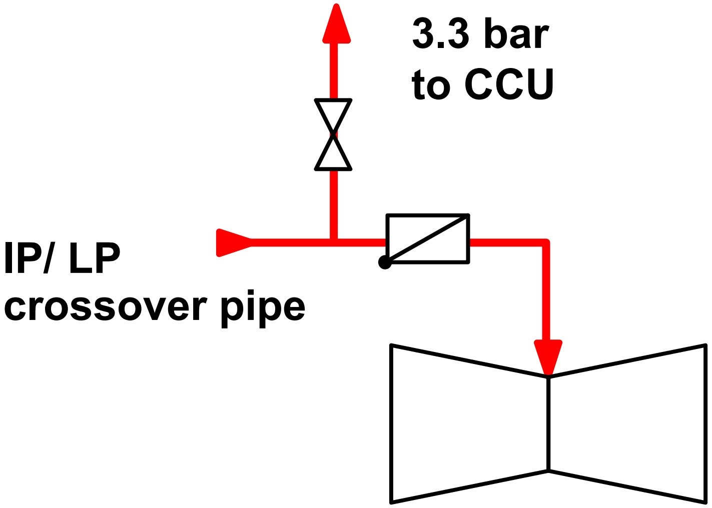
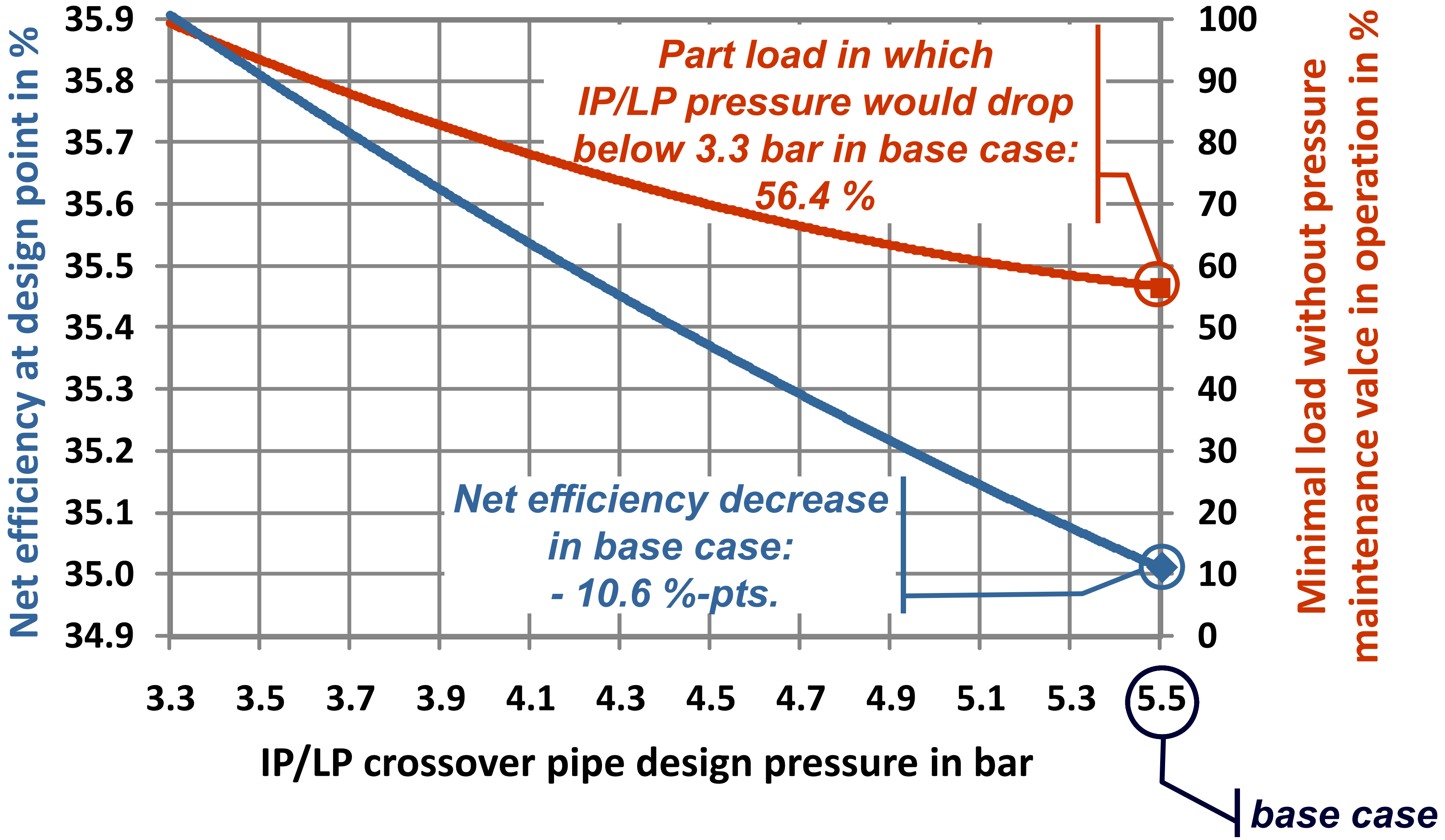
- Best suited to extract large steam quantity (~ 50% needed)
- To meet the required quality (T,p) over entire load range
  - steam attemperation
  - pressure maintenance concept:

$T_{reboiler} + \Delta T = 124 + 10 = 134$ °C
➔ steam @ 3.0 bar + 8 % press. loss: 3.3 bar



Impact of IP/LP Crossover Pipe Pressure

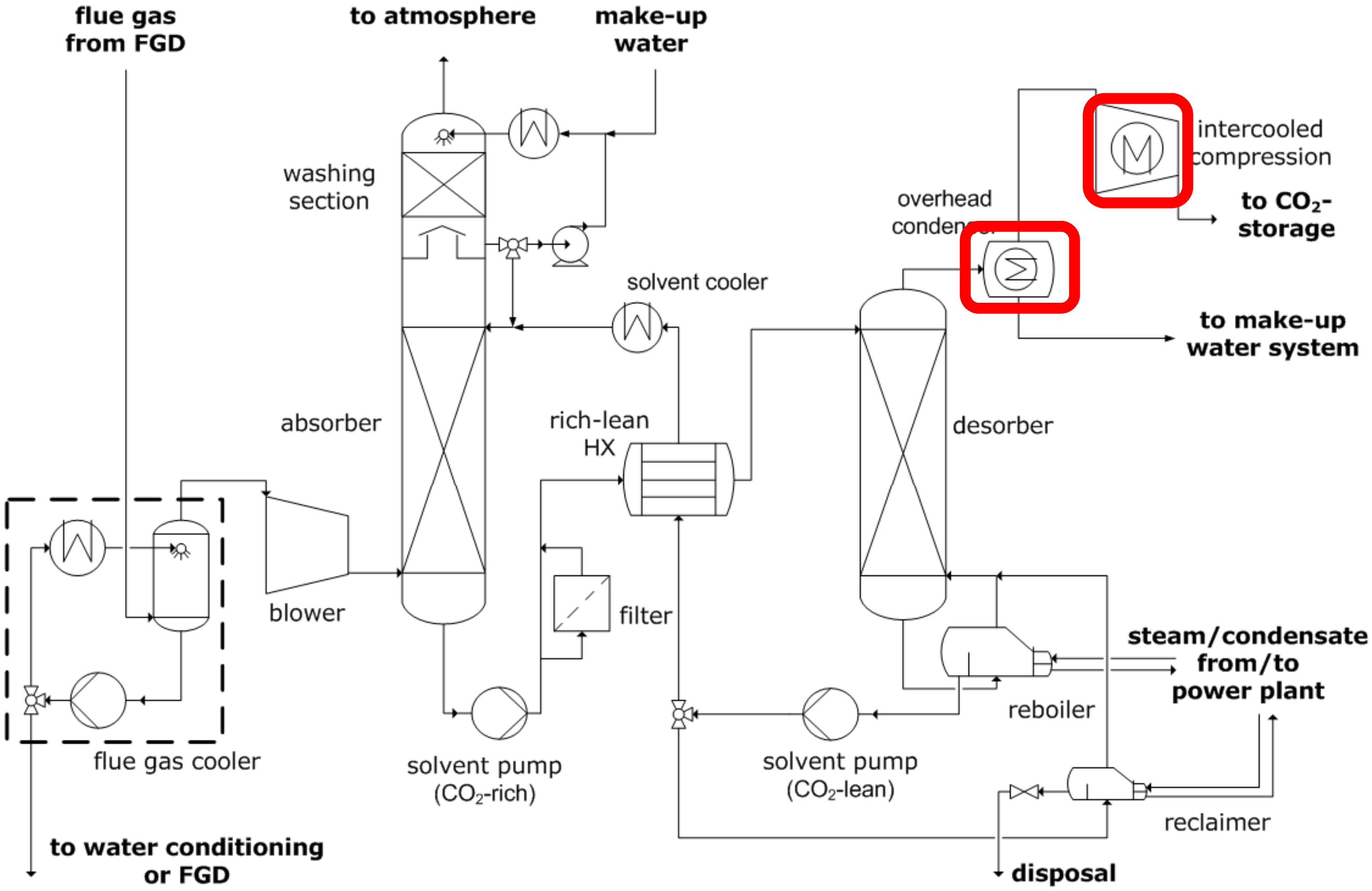
Choice of IP/LP design pressure: trade-off between design point and part-load efficiency



Optimisation by Waste Heat Recovery (I)

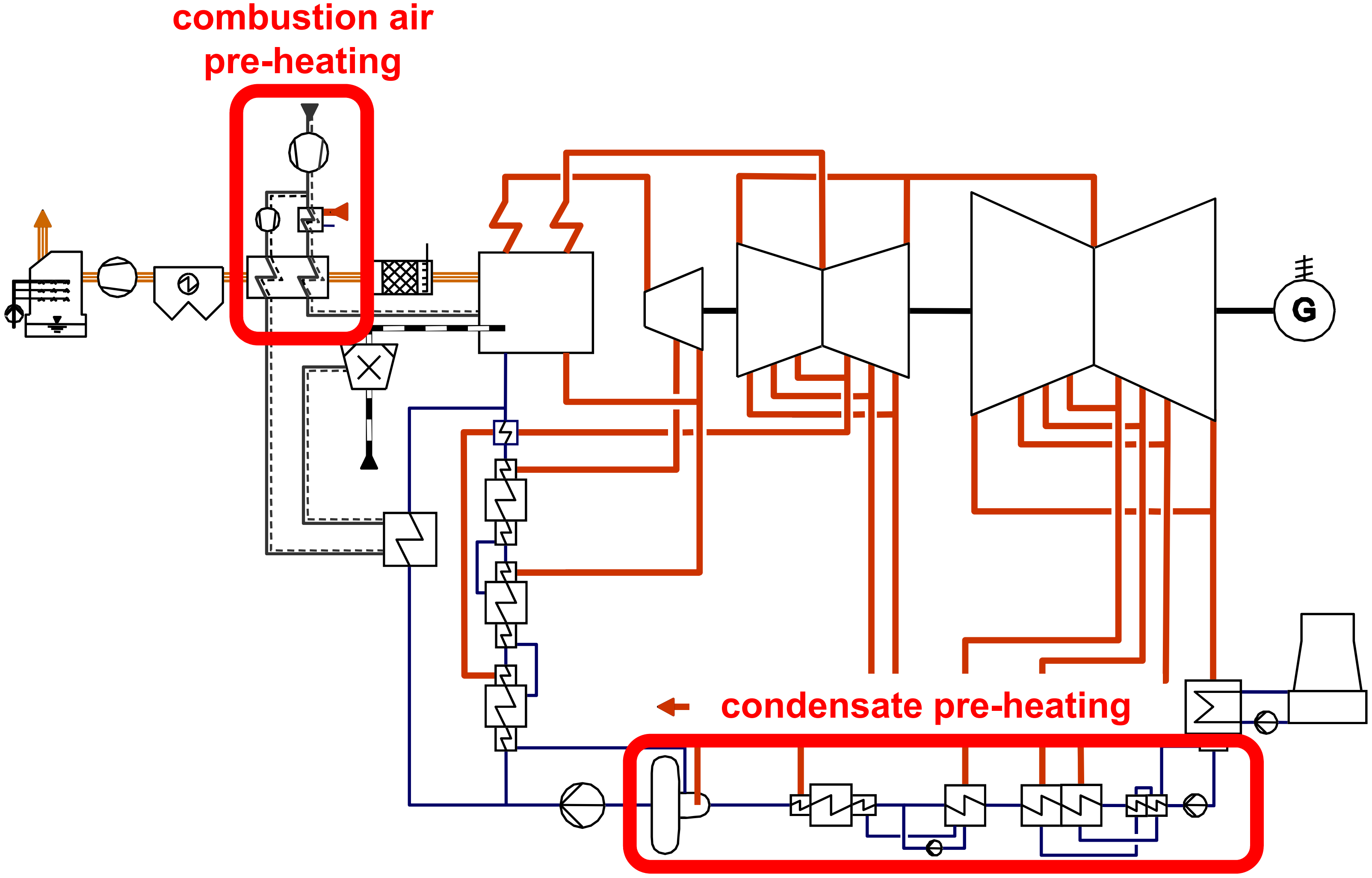
Potential sources of waste heat for recovery

- Reasonable temperature level needed



Optimisation by Waste Heat Recovery (I)

Possible heat sinks for direct integration



Optimisation by Waste Heat Recovery (I)

Potential sources of waste heat for recovery

- Reasonable temperature level needed
  - Desorber overhead condenser (OHC)
  - Intercoolers and aftercooler of CO_2 compressor

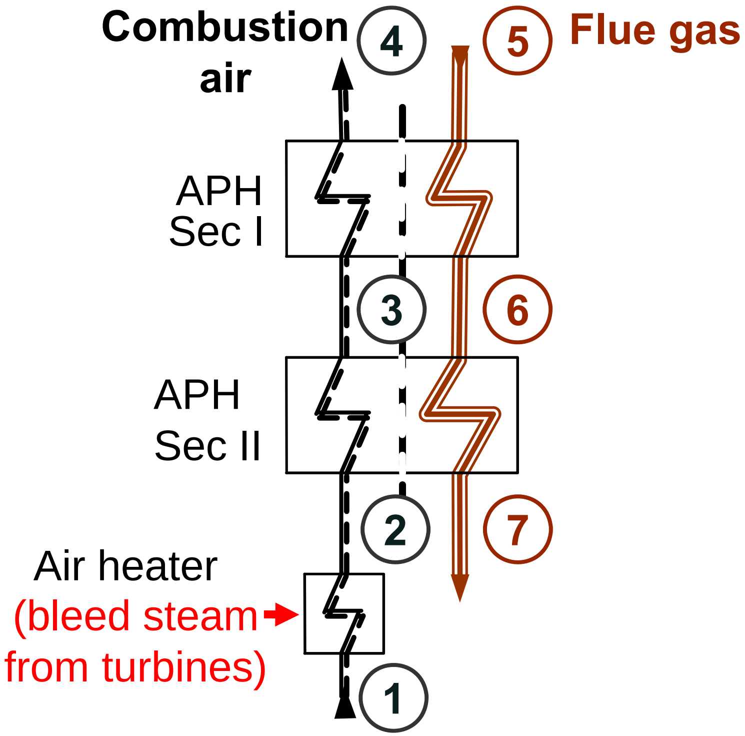
Possible heat sinks for direct integration

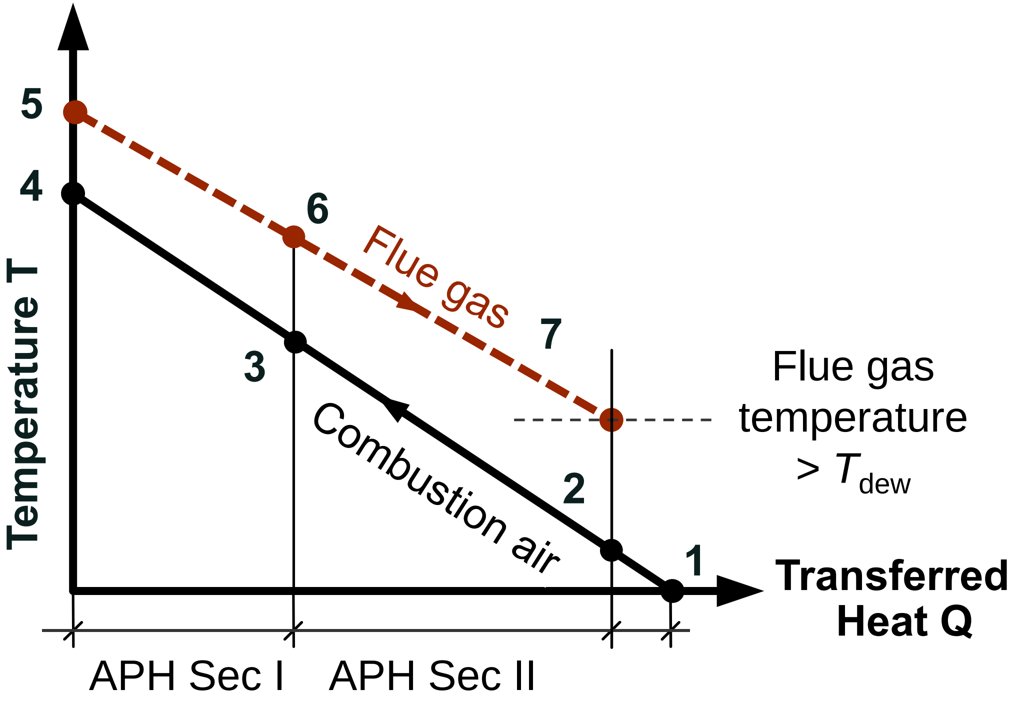
- Condensate pre-heating
- Combustion air pre-heating

Advanced heat integration ➔ improve temperature level of the waste heat

- Skipping distinct intercoolers of CO_2 compressor (heat pumping)
- Advanced combustion air pre-heat configuration (heat shifting)

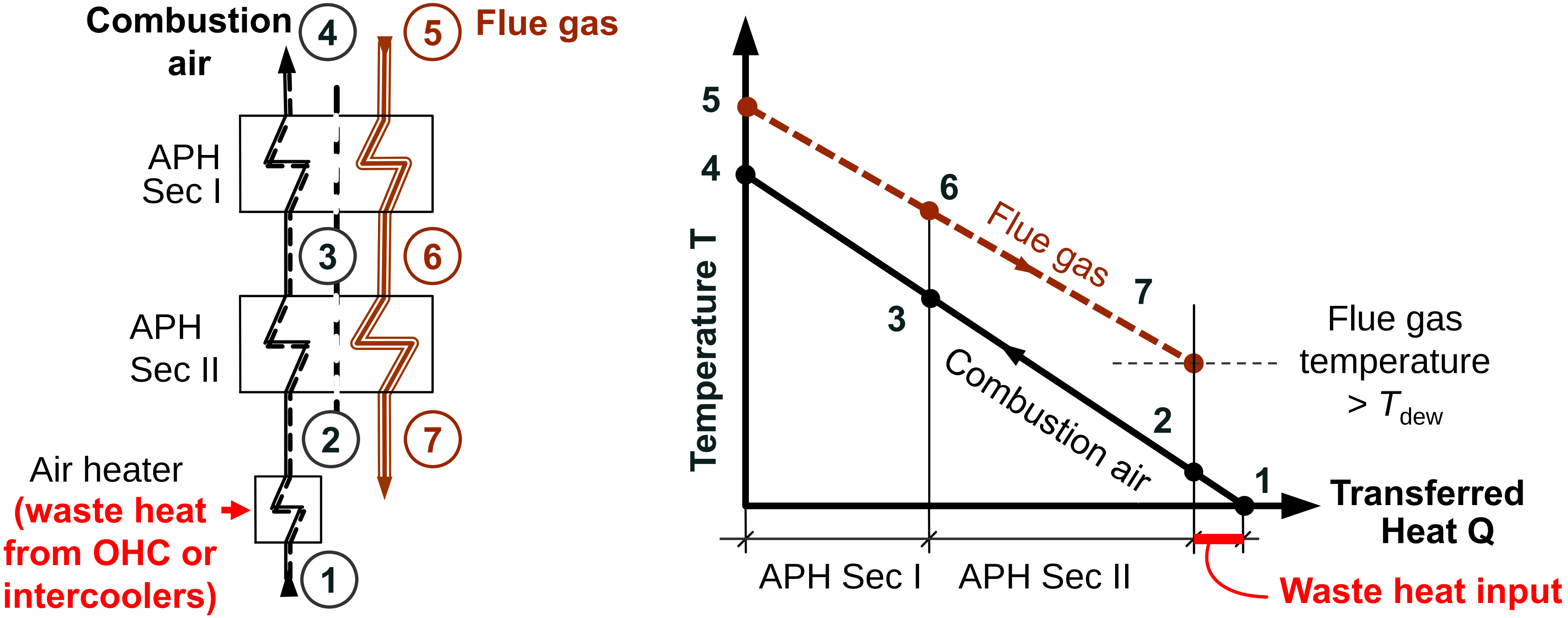
Advanced Combustion Air Pre-Heat Configuration





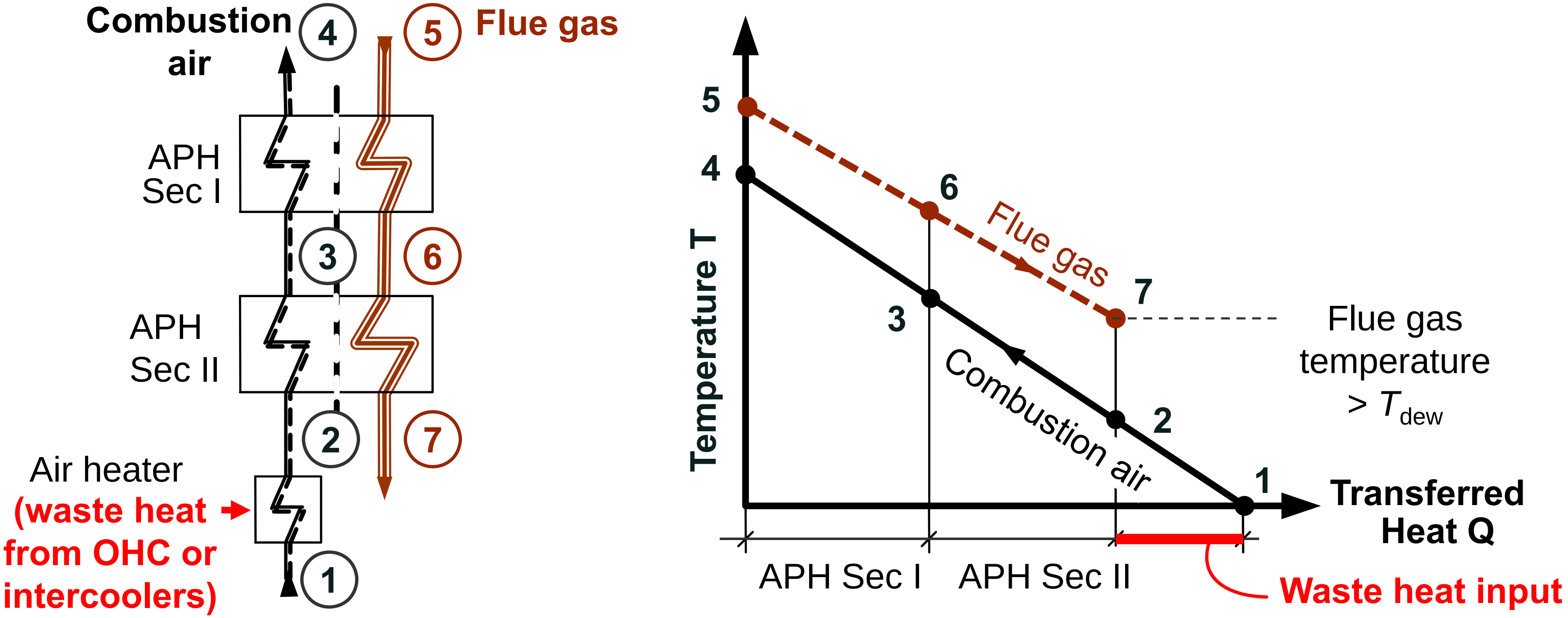
Flue gas temperature > T_{dew}

Advanced Combustion Air Pre-Heat Configuration



i. **Waste heat replaces steam bleed air heater (η_{net} +0.3 %-pts.)**

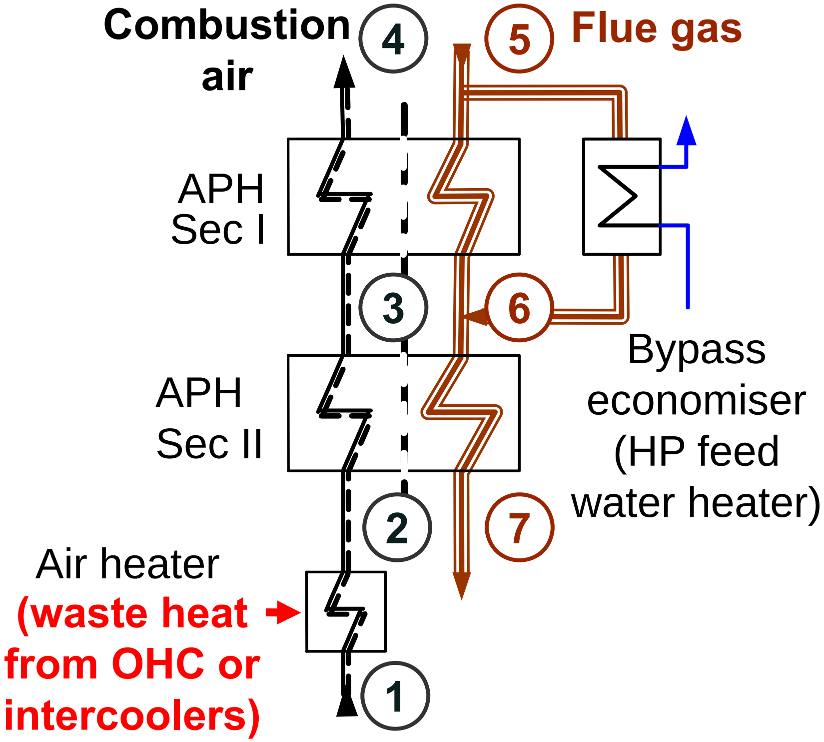
Advanced Combustion Air Pre-Heat Configuration

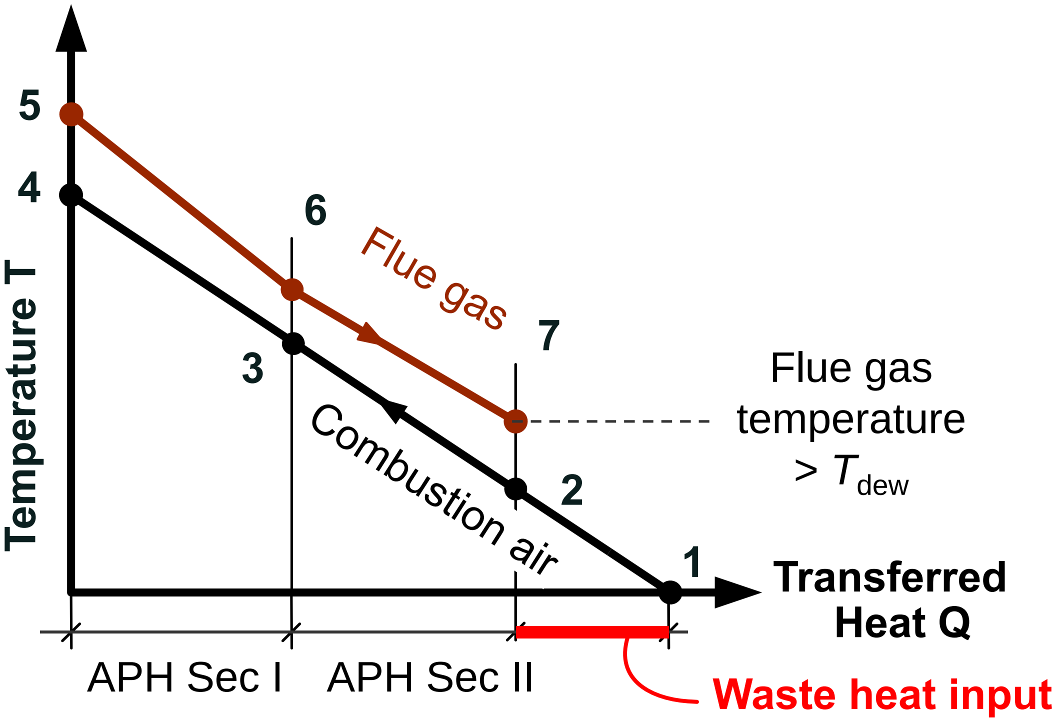


i. **Waste heat replaces steam bleed air heater (η_{net} +0.3 %-pts.)**

ii. **Increased waste heat integration leads to higher flue gas losses**

Advanced Combustion Air Pre-Heat Configuration





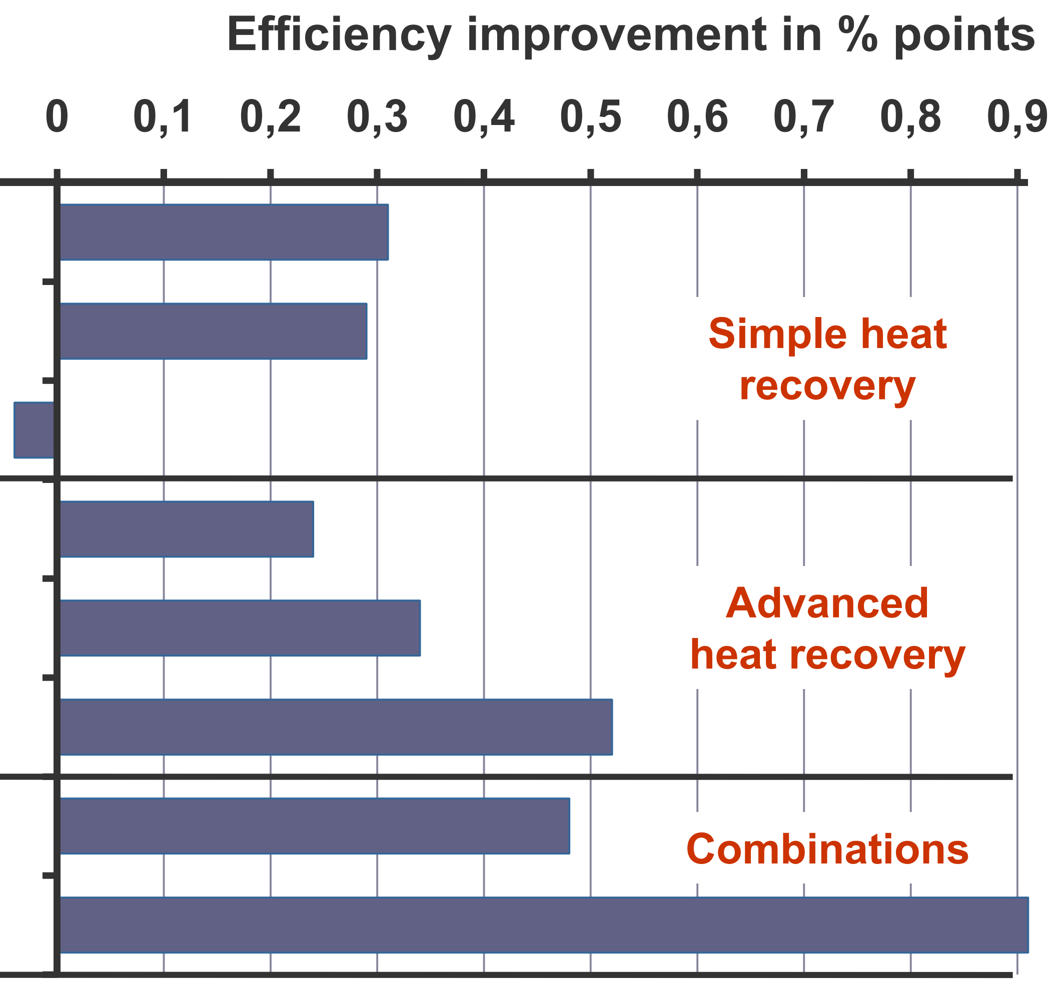
i. **Waste heat replaces steam bleed air heater (η_{net} +0.3 %-pts.)**

ii. **Increased waste heat integration leads to higher flue gas losses**

iii. **Bypass economiser to decrease flue gas outlet temperature (+0.5 %-pts. total)**
    i. **High costs of additional gas-liquid heat exchanger**
    ii. **Lower temperature difference in APH ‣ larger HX area ‣ larger costs**

Optimisation by Waste Heat Recovery (II)

No	Heat recovery measure
1	OHC ▶ Condensate
2	OHC ▶ Combustion Air
3	7 IC ▶ Condensate
4	3 IC ▶ Condensate
5	1 IC ▶ Condensate
6	OHC ▶ Advanced APH
7	Combination of 1+5
8	Combination of 1+5+6



Conclusions

Heat demand predominant reason for efficiency penalty

Design point and part-load efficiency strongly depend on IP/LP pressure

- Careful consideration of scheduled power plant operation
  - Excess of 2.2 bar decreases efficiency by 0.9 % points at design point
  - Slope of part-load efficiency improved with increased crossover pipe pressure

Optimization by waste heat recovery

- Up to 0.9 % points advancement in overall net efficiency
- Increases degree of integration ➔ potentially lowers availability / operability
- Most cost effective option has to be evaluated

Thank you for your attention!

Institute of Energy Systems

Jochen Oexmann - oexmann@tuhh.de

This work has been submitted for publication in “Energy”.

Imperial College
London

12th Meeting of the International
Post-Combustion CO_2 Capture Network

Retrofitting Post Combustion Capture to Existing Power Plant

Jon Gibbins, Mathieu Lucquiaud, Jia Li and Hannah Chalmers
Imperial College Centre for Carbon Capture and Storage
www.imperial.ac.uk/ccs

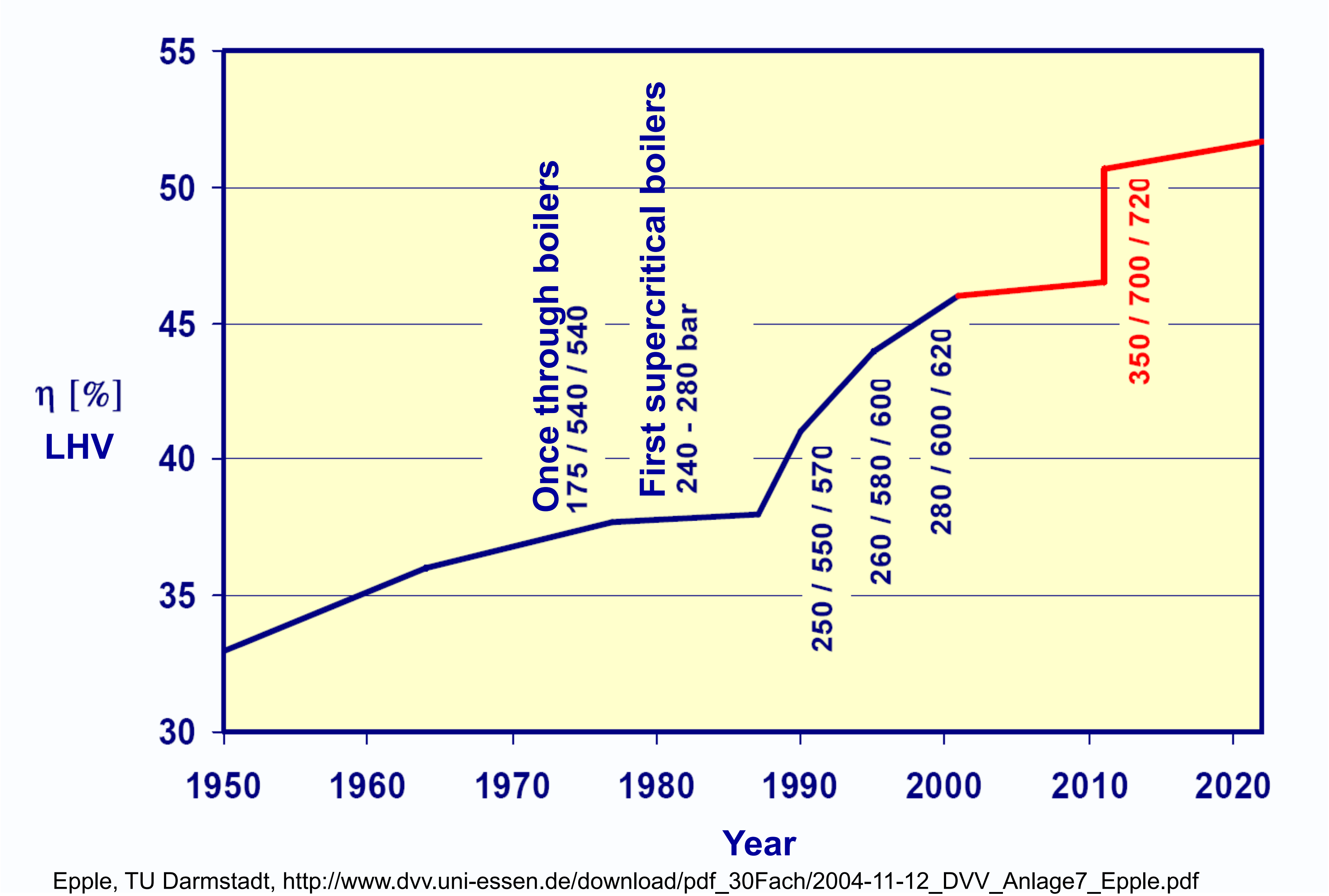
Acknowledgements: DECC, RCUK, IEA GHG

Imperial College London

Outline

- Retrofit economics - does the power plant efficiency matter?
- Options for efficient, flexible and upgradable retrofits

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

Penalties and benefits for retrofitting CCS to an existing plant

It can be assumed that fuel, capital payments and operating costs for the base plant remain unchanged, but less electricity is available for sale and the capture equipment incurs additional capital and non-fuel operating costs.

Penalties for implementing CCS

- **Less electricity (and no premium for low C electricity)**
- **Extra CAPEX and OPEX for capture plant, including storage costs**
- **(Increased risks)**

Benefits for implementing CCS

- **No emission allowance purchase / carbon tax per tonne CO_2 stored**

Cost of carbon is the cost of the lost electricity per unit carbon emissions avoided

$$COC = \frac{\delta.POE}{\eta.e.c} + \frac{fcc}{N} + vcc$$

plus the capital and operating costs of the capture plant

Cost of carbon is the cost of the lost electricity per unit carbon emissions avoided

$$COC = \frac{\delta.POE}{\eta.e.c} + \frac{fcc}{N} + vcc$$

plus the capital and operating costs of the capture plant

plant efficiency x kgCO$_2$/kWhe   η.e = f   kgCO$_2$/kWh in fuel

$$COC = \frac{\delta}{f.c}.POE + \frac{fcc}{N} + vcc$$

Power plant efficiency does not matter
Just the efficiency penalty and costs for the capture unit
It costs more to run a less efficient unit with capture
But you capture more CO$_2$

A sub-critical plant gets a lower net revenue after paying carbon charges (or CCS costs) than a supercritical plant, an entirely predictable result given its higher specific carbon emissions.

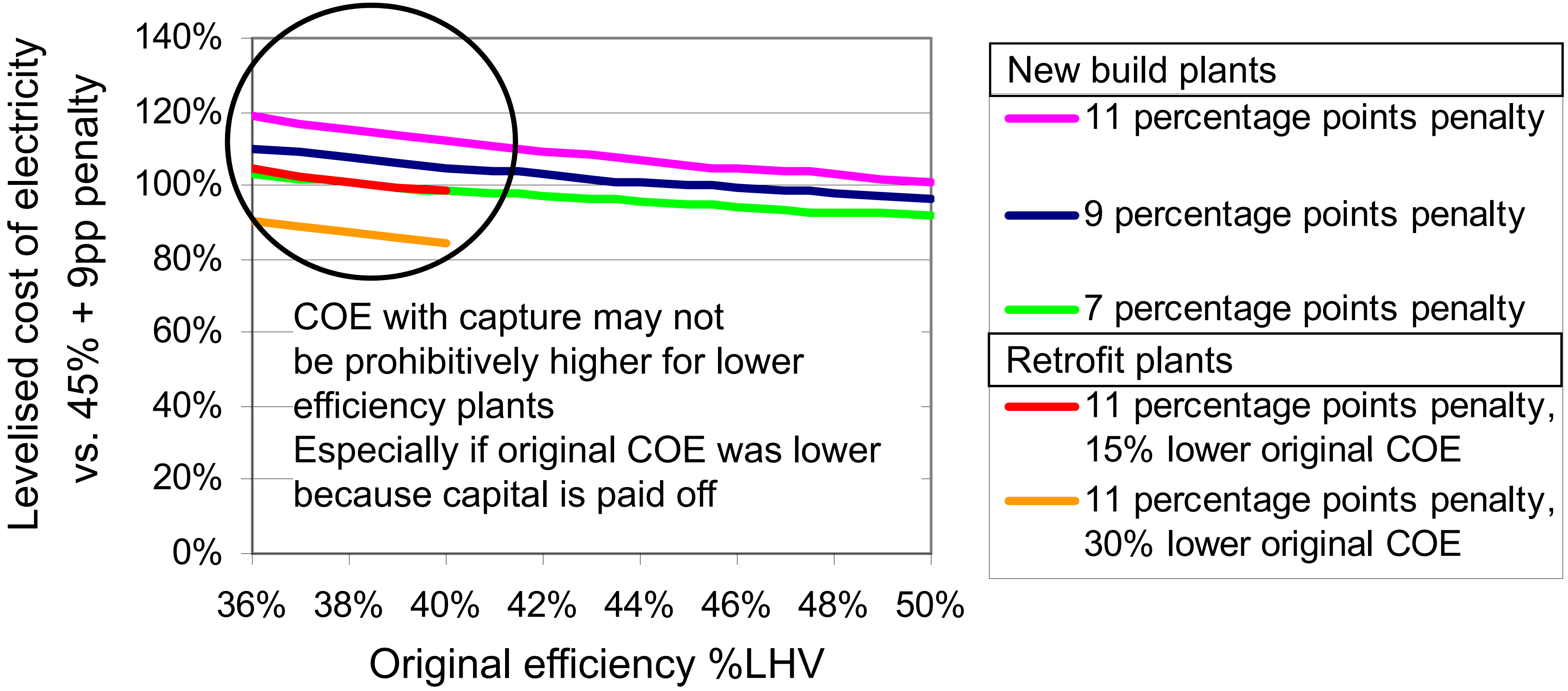
It is, however, unlikely that the relatively small difference would alone be sufficient to justify the construction of a <u>new</u> supercritical plant to replace the sub-critical plant.

The new plant would have somewhat lower fuel, carbon and other operating costs but would also have to recover its capital costs.

For an existing plant that would otherwise have to be closed down capital charges are effectively zero.

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

All new-build plants are assumed to have the same load factor, before and after capture, and same original COE, efficiency penalty, capture equipment capital costs (allowing for throughput) and same economic lifetime after retrofit. Retrofit plants have lower original COE but are pessimistically assumed to have 11 percentage points penalty to allow for less efficient integration being possible for a retrofit.

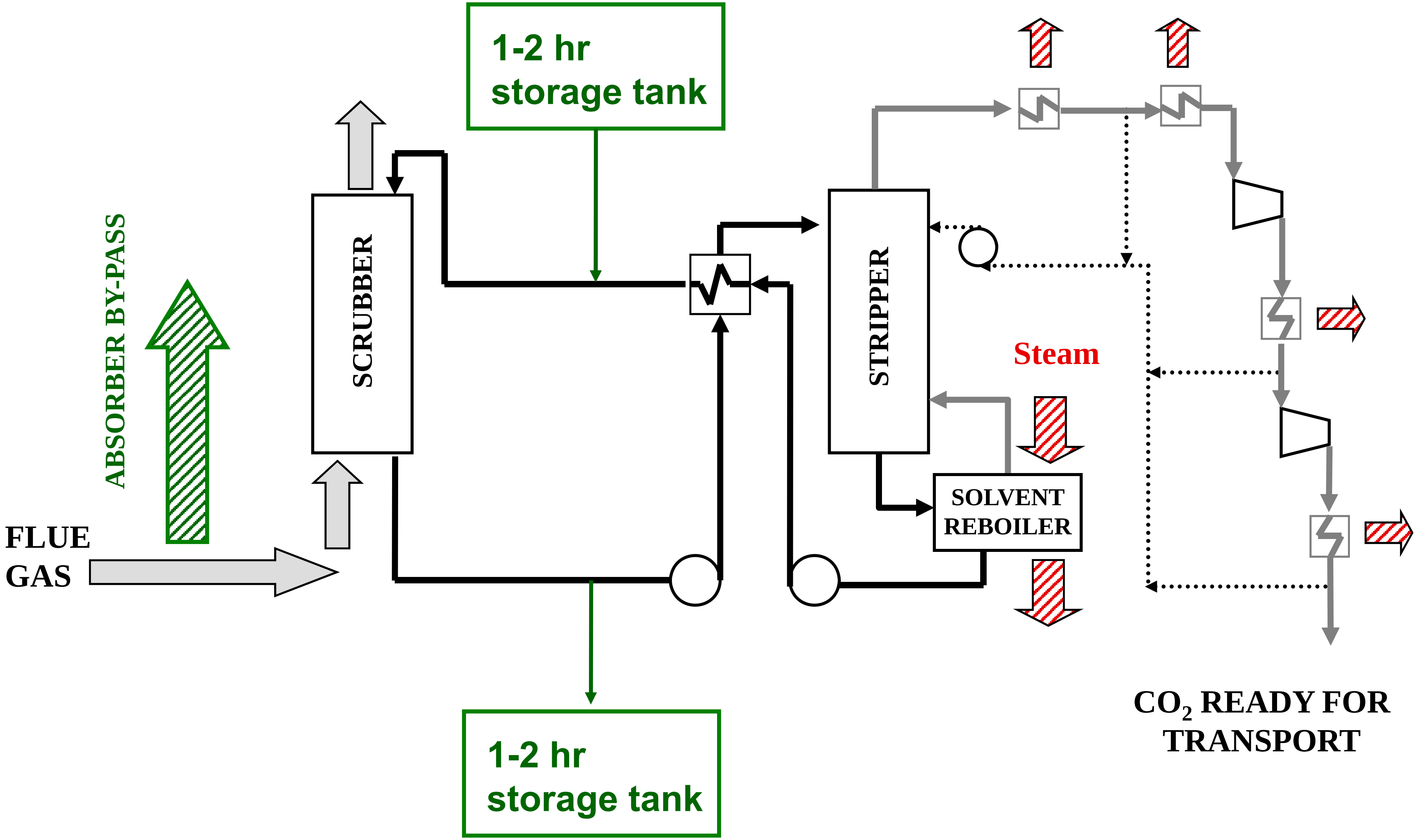


COE with capture may not be prohibitively higher for lower efficiency plants
Especially if original COE was lower because capital is paid off

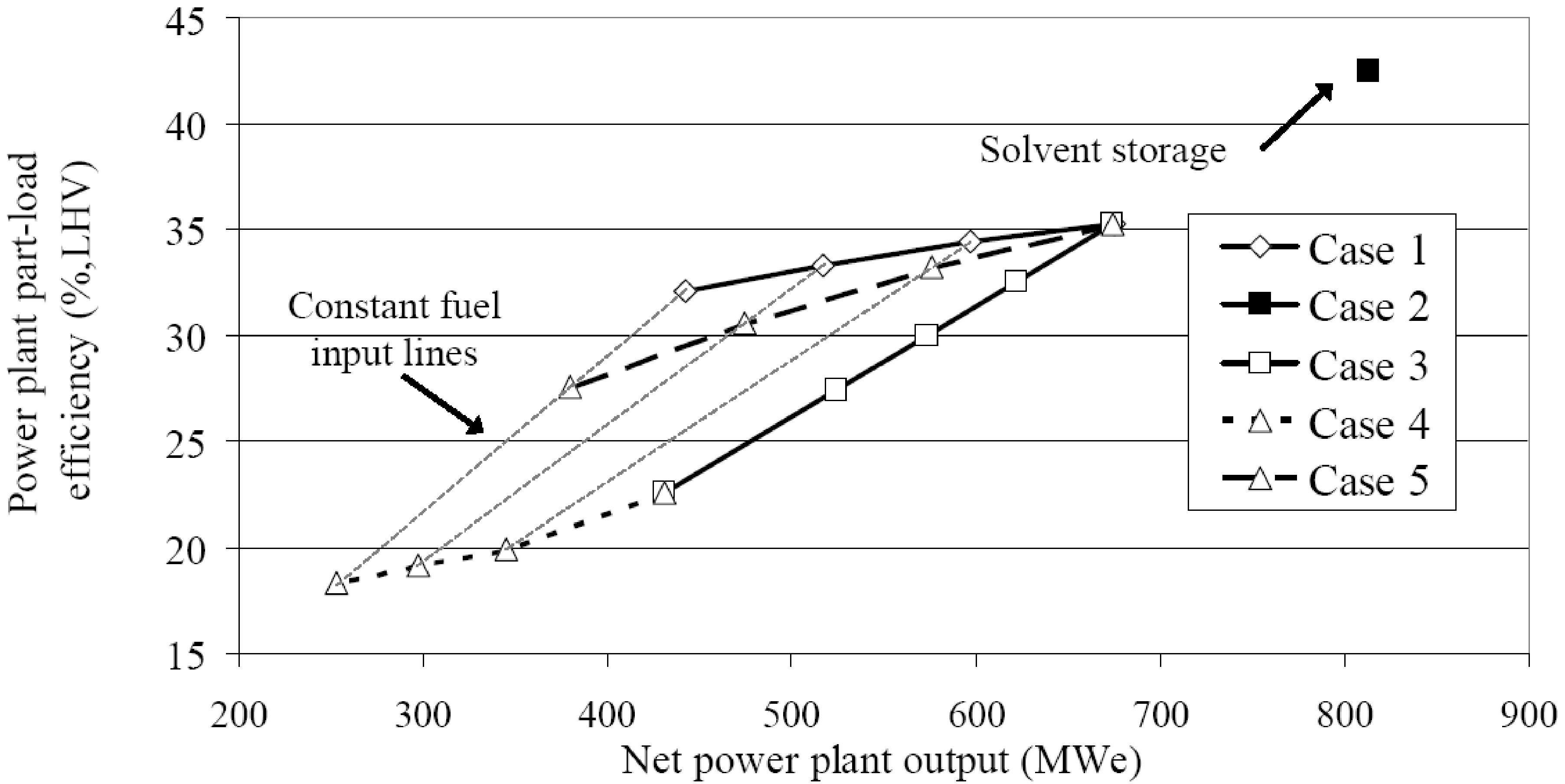
Outline

- Retrofit economics - does the power plant efficiency matter?
- Options for efficient **flexible** and upgradable retrofits

Operational Flexibility



Operational flex - solvent storage and part-load



Case 1 - immediate regeneration of rich solvent.

Case 2 - rich solvent from storage, no regeneration.

Case 3 - full firing rate, 0-100% additional solvent regeneration.

Case 4 - maximum regeneration set by minimum flow in LP turbine.

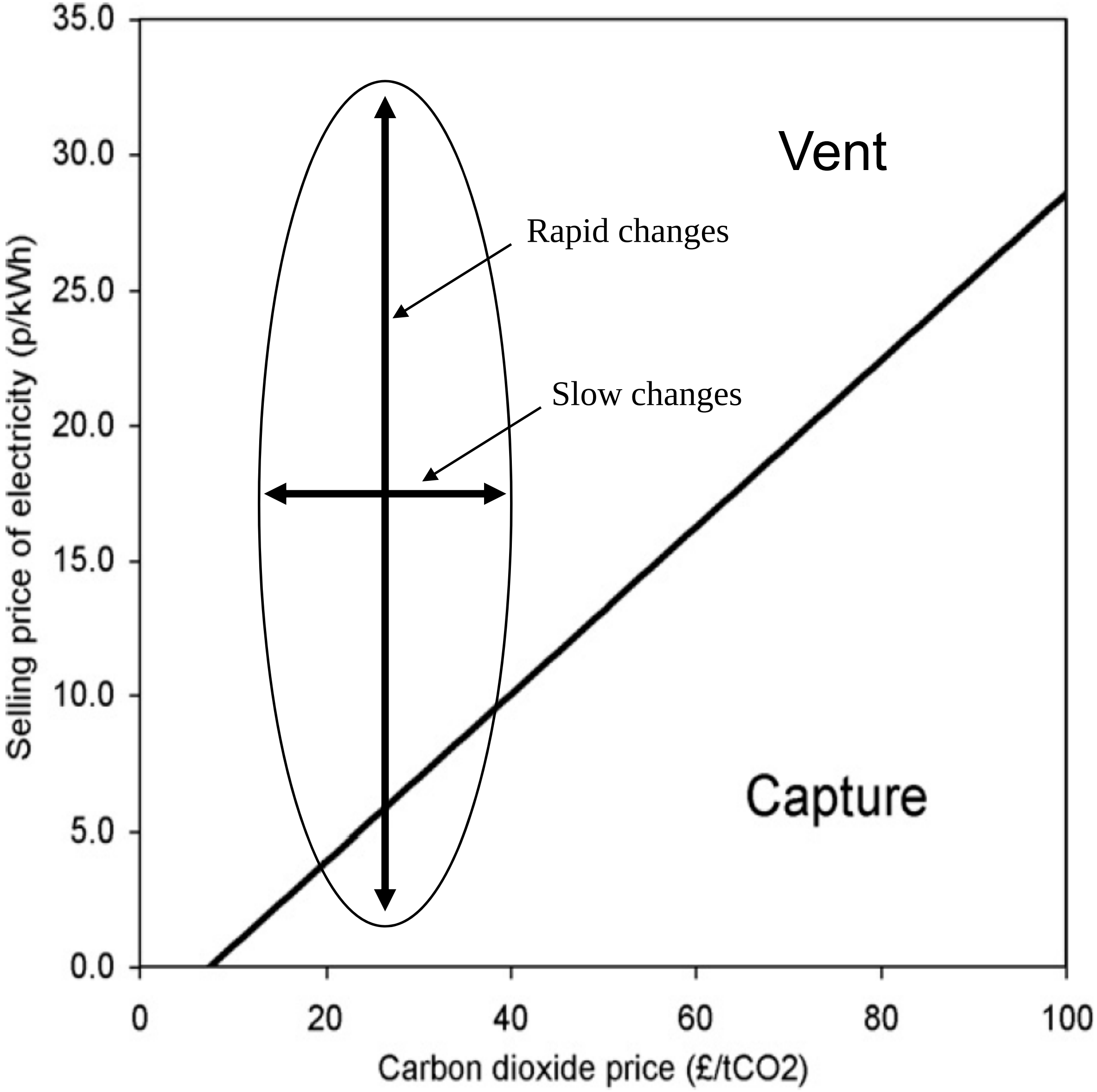
Case 5 - part load, but regeneration of some stored solvent to give 100% load CO_2 to storage.

Lucquiaud M, Chalmers H and Gibbins J, Potential for flexible operation of pulverised coal power plants with CO_2 capture, Energy Materials 2008 2(3), 177-183

Operational Flexibility

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)

Retrofit considerations

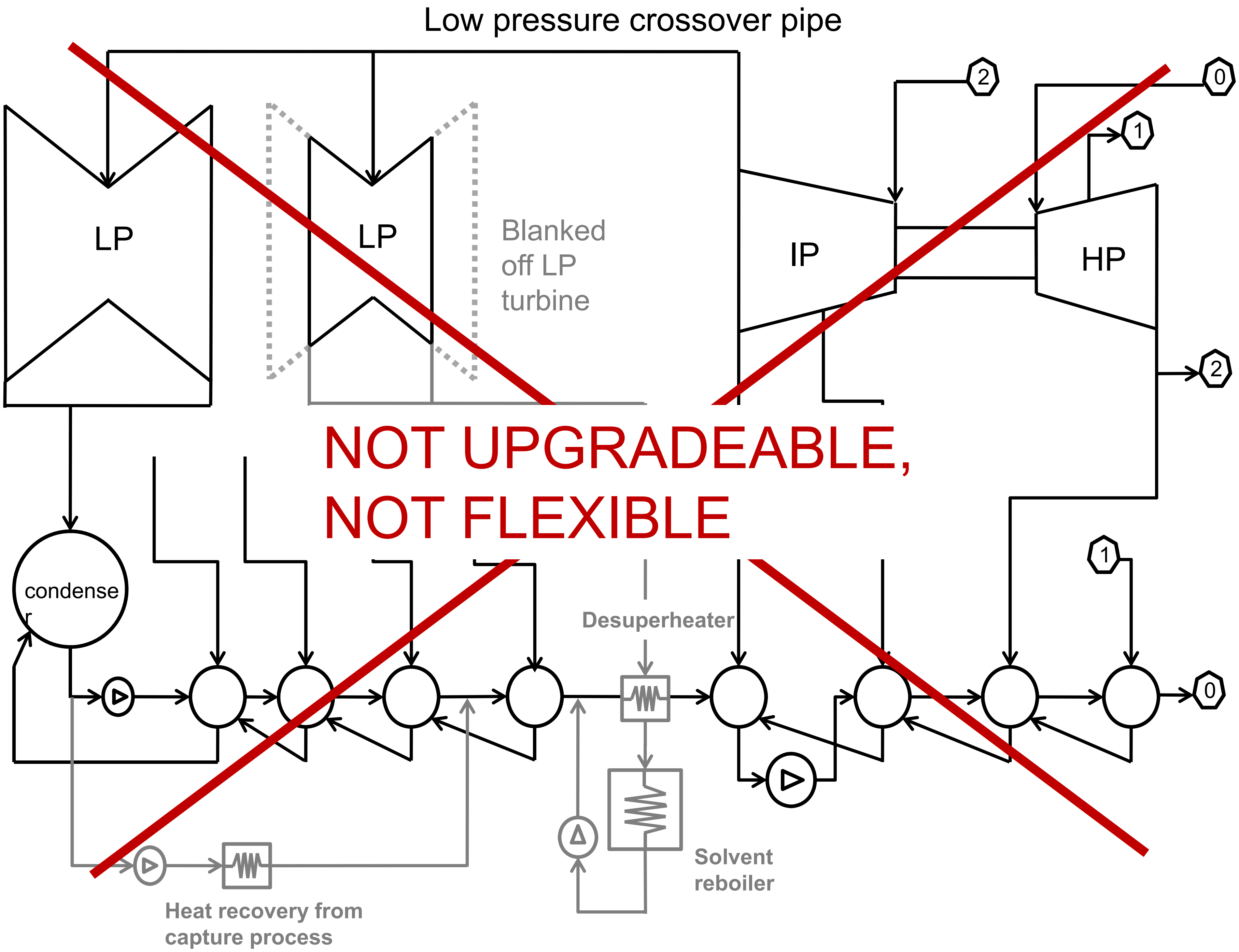
- Flexibility matters
- 1st generation of plants needs to be upgradeable with better solvent to avoid stranded plant asset
  - => requires appropriate absorber design
  - => appropriate regeneration system
  - => appropriate steam turbine design

Retrofit considerations

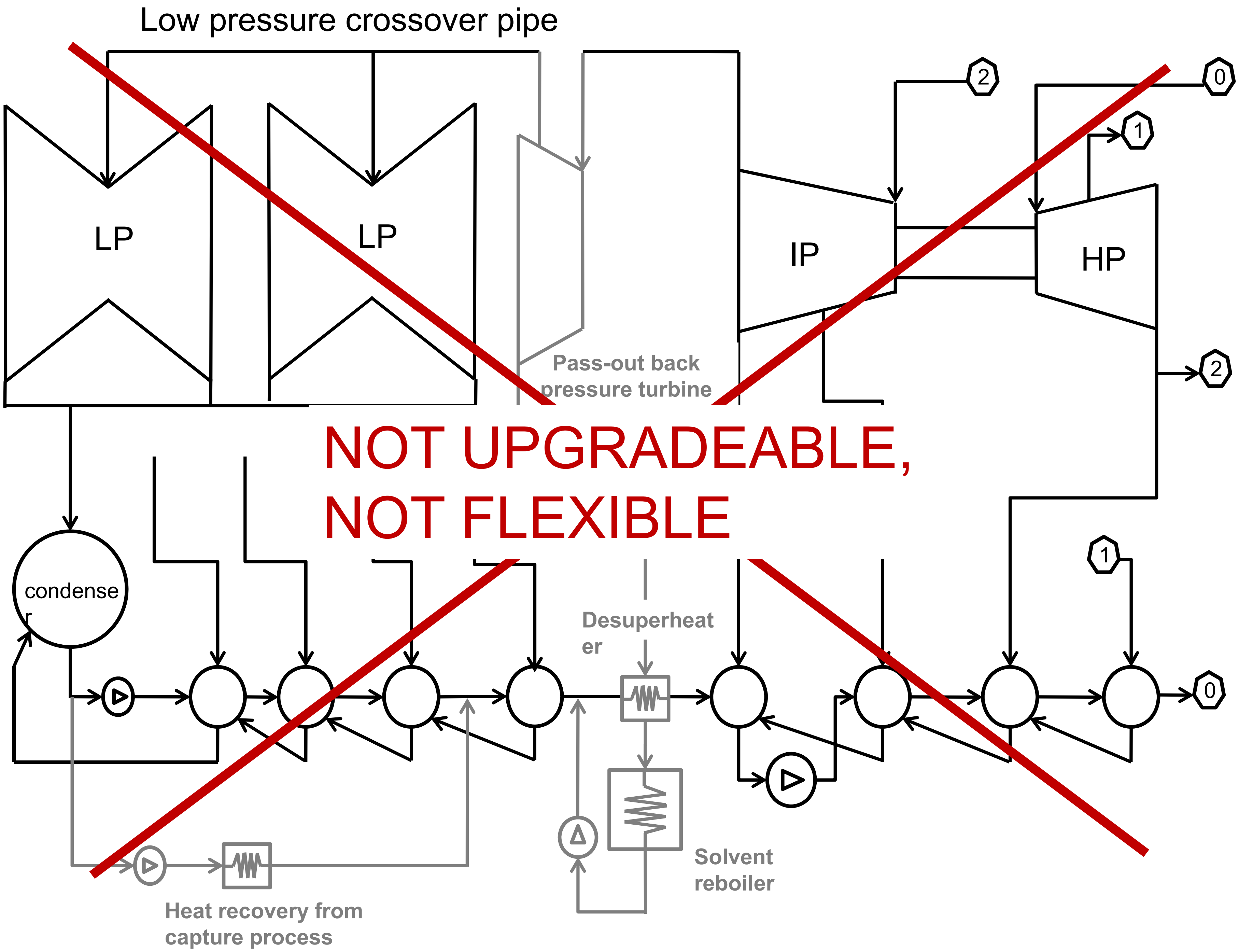
- Trade-off between
    - Base-load efficiency
    - Part-load operation
    - Flexibility
    - Upgradability

- For retrofits oversized LP turbine, generators etc => Flexibility and upgradability comes for free IF the steam turbines are retrofitted with that objective

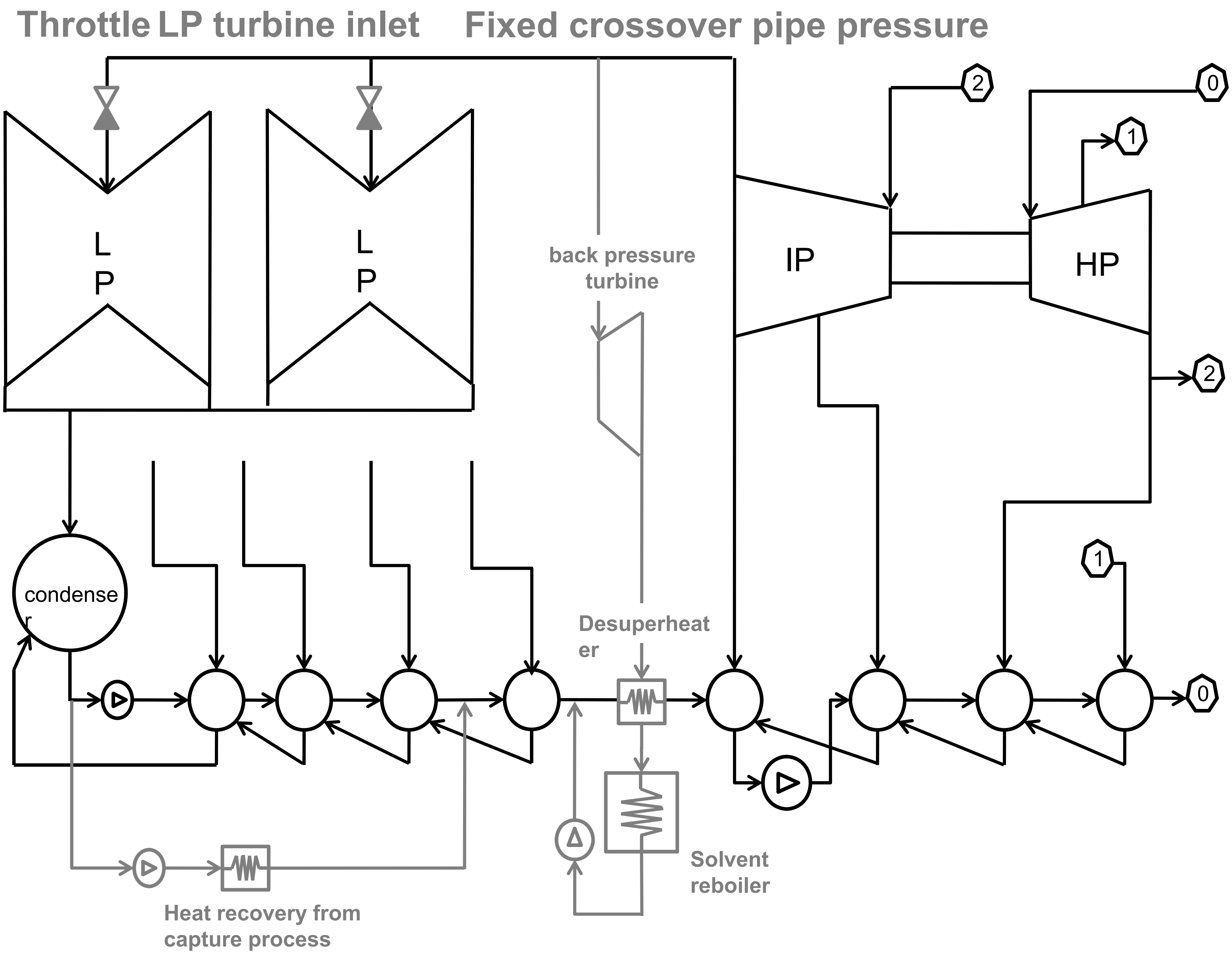
- Maintain LP turbine steam swallowing capacity and <u>focus on IP turbine</u>

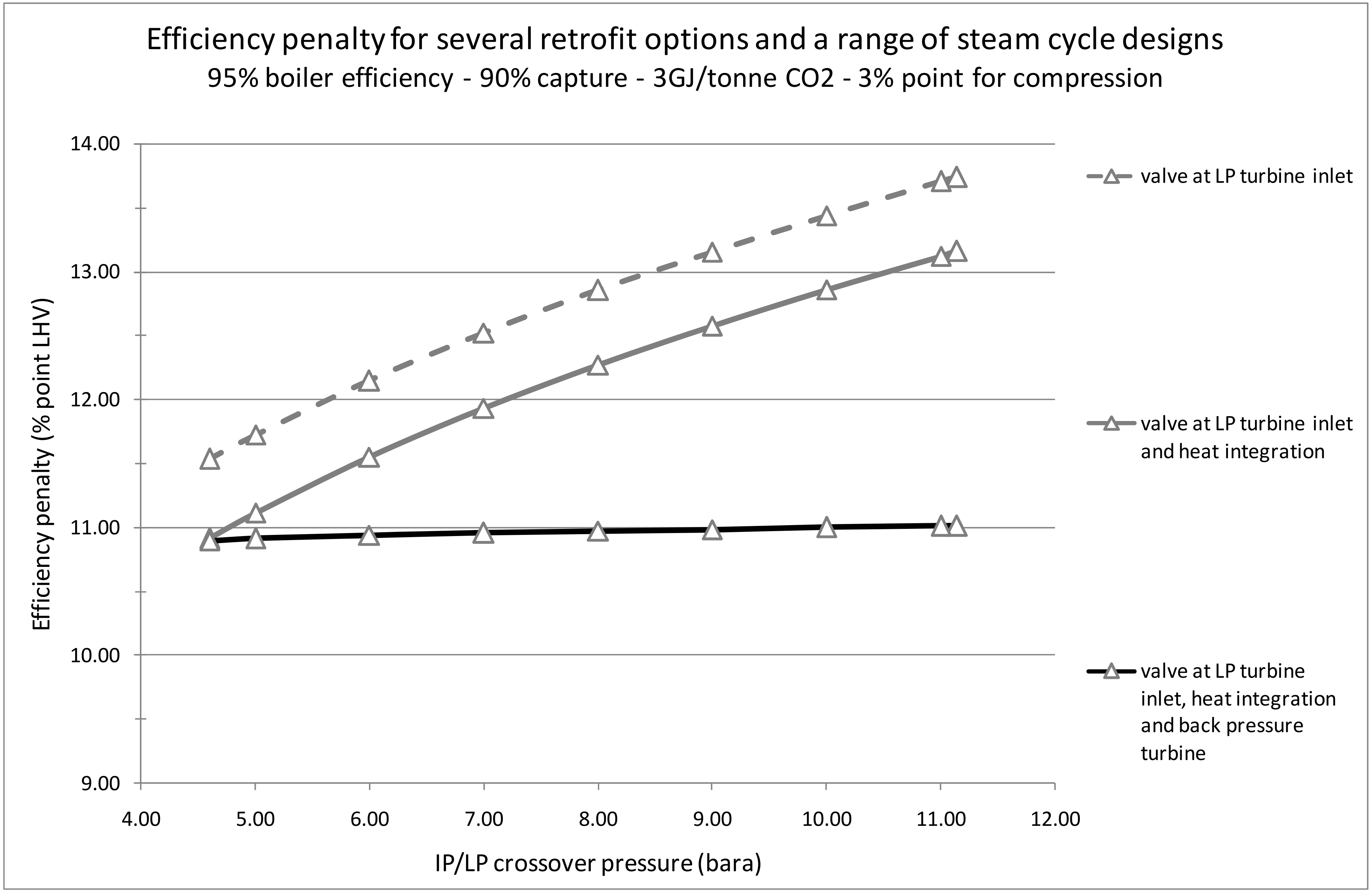


NOT UPGRADEABLE,
NOT FLEXIBLE



NOT UPGRADEABLE,
NOT FLEXIBLE

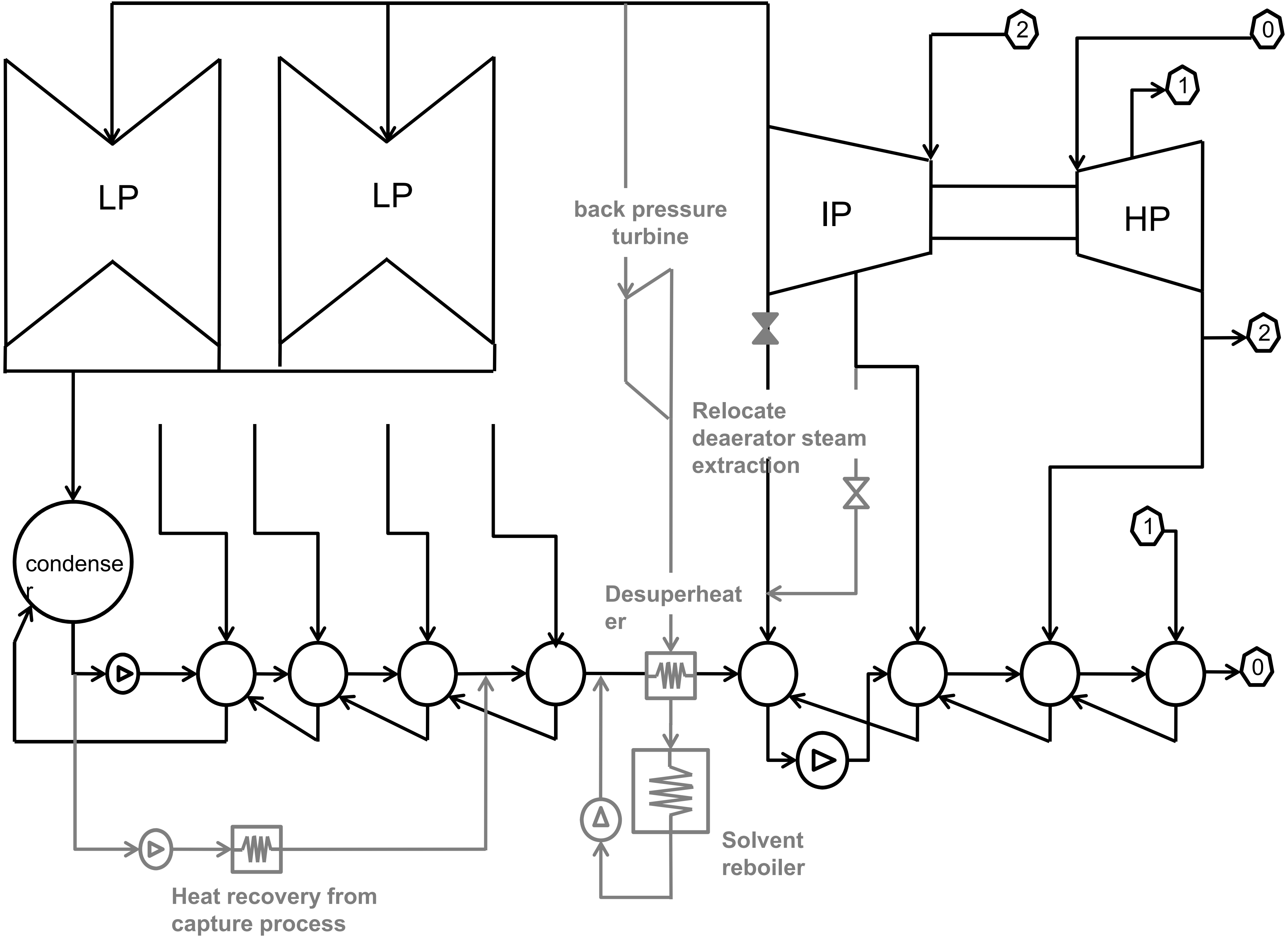

Throttle LP turbine inlet
Fixed crossover pipe pressure
LP
LP
back pressure turbine
IP
HP
2
0
1
2
condenser
1
0
Desuperheater
Solvent reboiler
Heat recovery from capture process

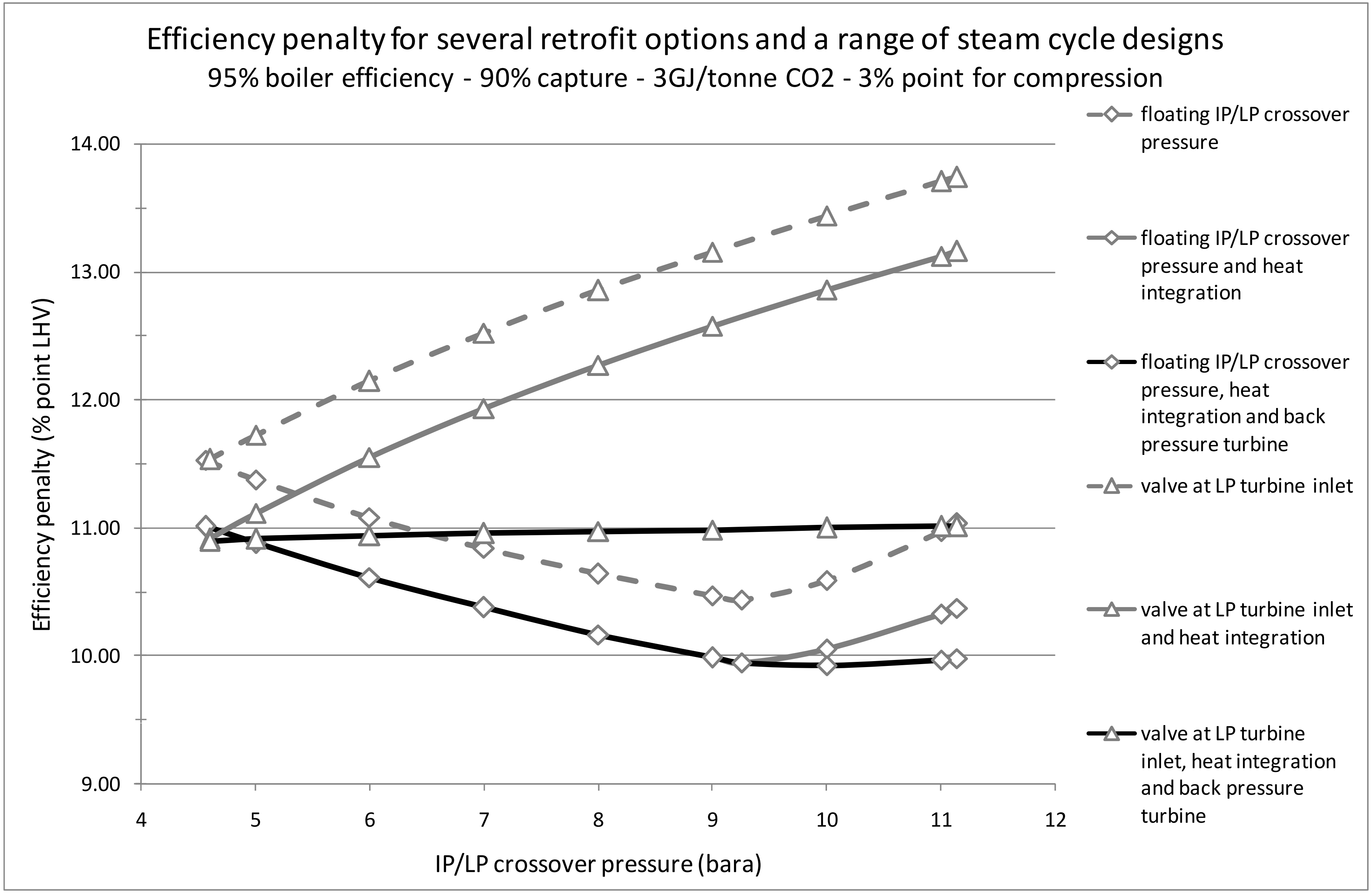


Efficiency penalty for several retrofit options and a range of steam cycle designs

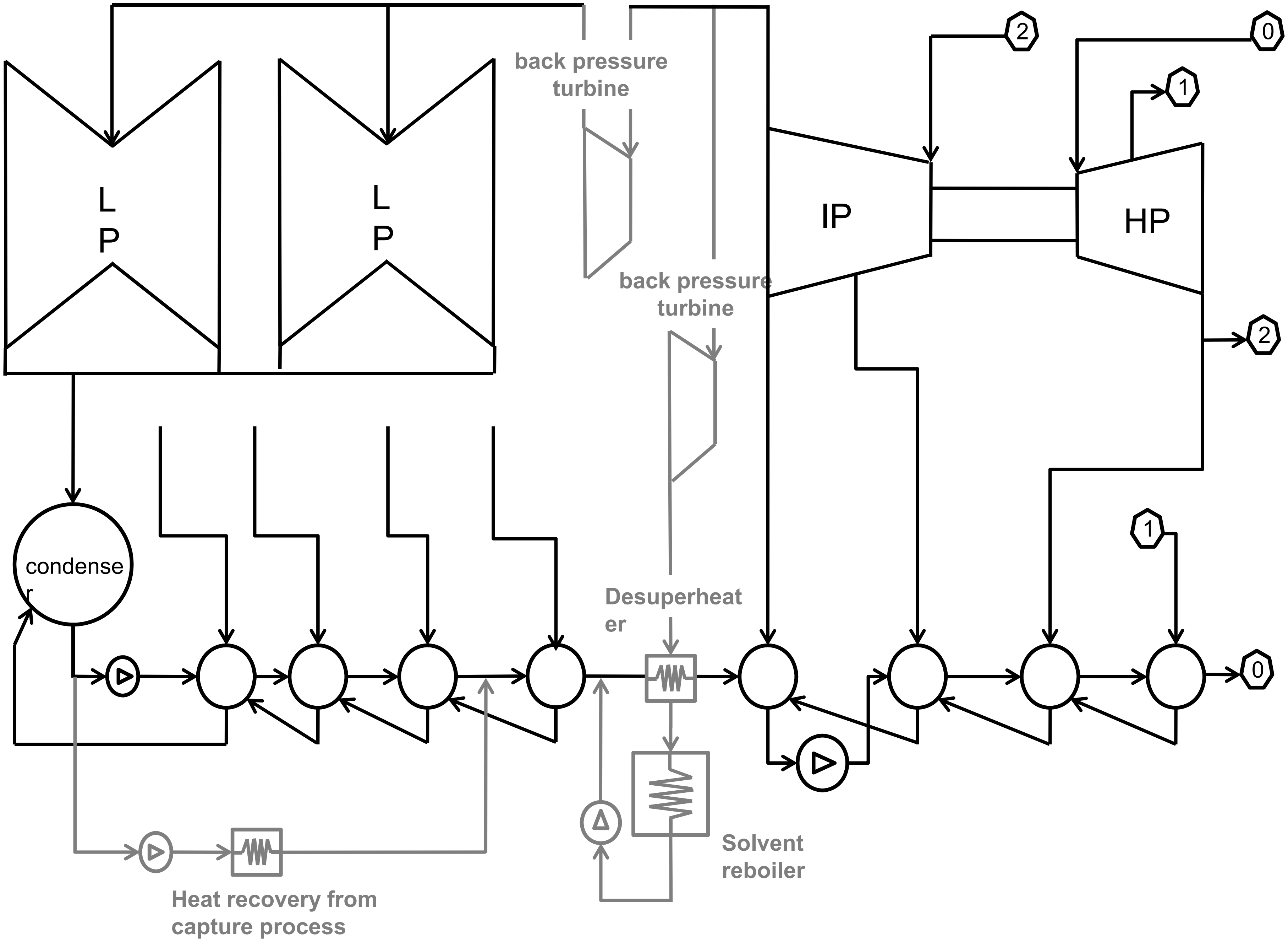
95% boiler efficiency - 90% capture - 3GJ/tonne CO2 - 3% point for compression

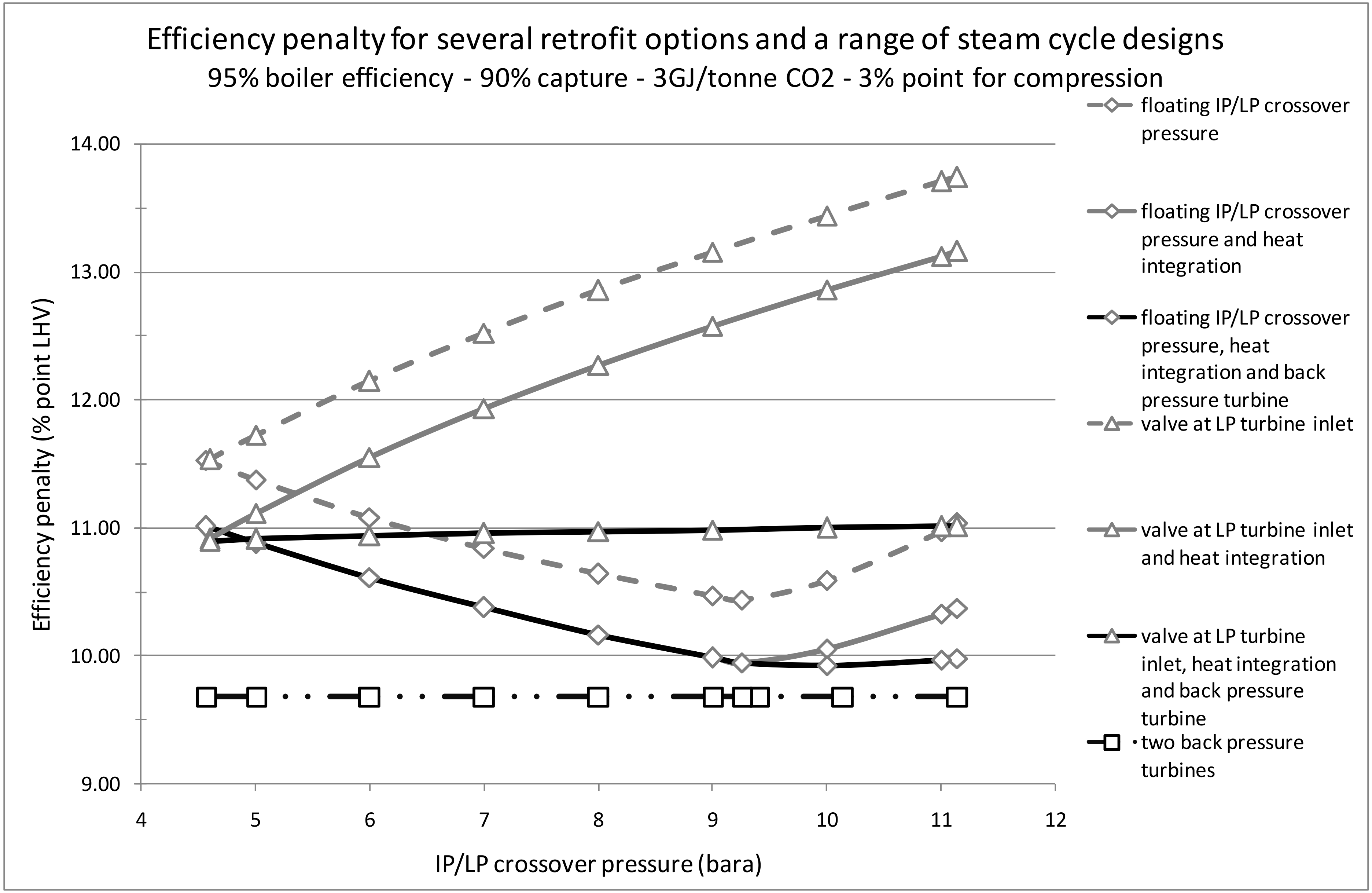
Floating pressure – no valve at LP inlet at base load




Efficiency penalty for several retrofit options and a range of steam cycle designs
95% boiler efficiency - 90% capture - 3GJ/tonne CO2 - 3% point for compression
Efficiency penalty (% point LHV)
14.00
13.00
12.00
11.00
10.00
9.00
4
5
6
7
8
9
10
11
12
IP/LP crossover pressure (bara)
floating IP/LP crossover pressure
floating IP/LP crossover pressure and heat integration
floating IP/LP crossover pressure, heat integration and back pressure turbine
valve at LP turbine inlet
valve at LP turbine inlet and heat integration
valve at LP turbine inlet, heat integration and back pressure turbine

Dual back pressure turbine




Efficiency penalty for several retrofit options and a range of steam cycle designs
95% boiler efficiency - 90% capture - 3GJ/tonne CO2 - 3% point for compression
Efficiency penalty (% point LHV)
14.00
13.00
12.00
11.00
10.00
9.00
4
5
6
7
8
9
10
11
12
IP/LP crossover pressure (bara)
floating IP/LP crossover pressure
floating IP/LP crossover pressure and heat integration
floating IP/LP crossover pressure, heat integration and back pressure turbine
valve at LP turbine inlet
valve at LP turbine inlet and heat integration
valve at LP turbine inlet, heat integration and back pressure turbine
two back pressure turbines

Floating pressure trade-offs

1. Imbalance of IP turbine since end thrust increases with pressure ratio

$\Rightarrow$ Reinforce balancing pistons of turbine if single flow IP turbine

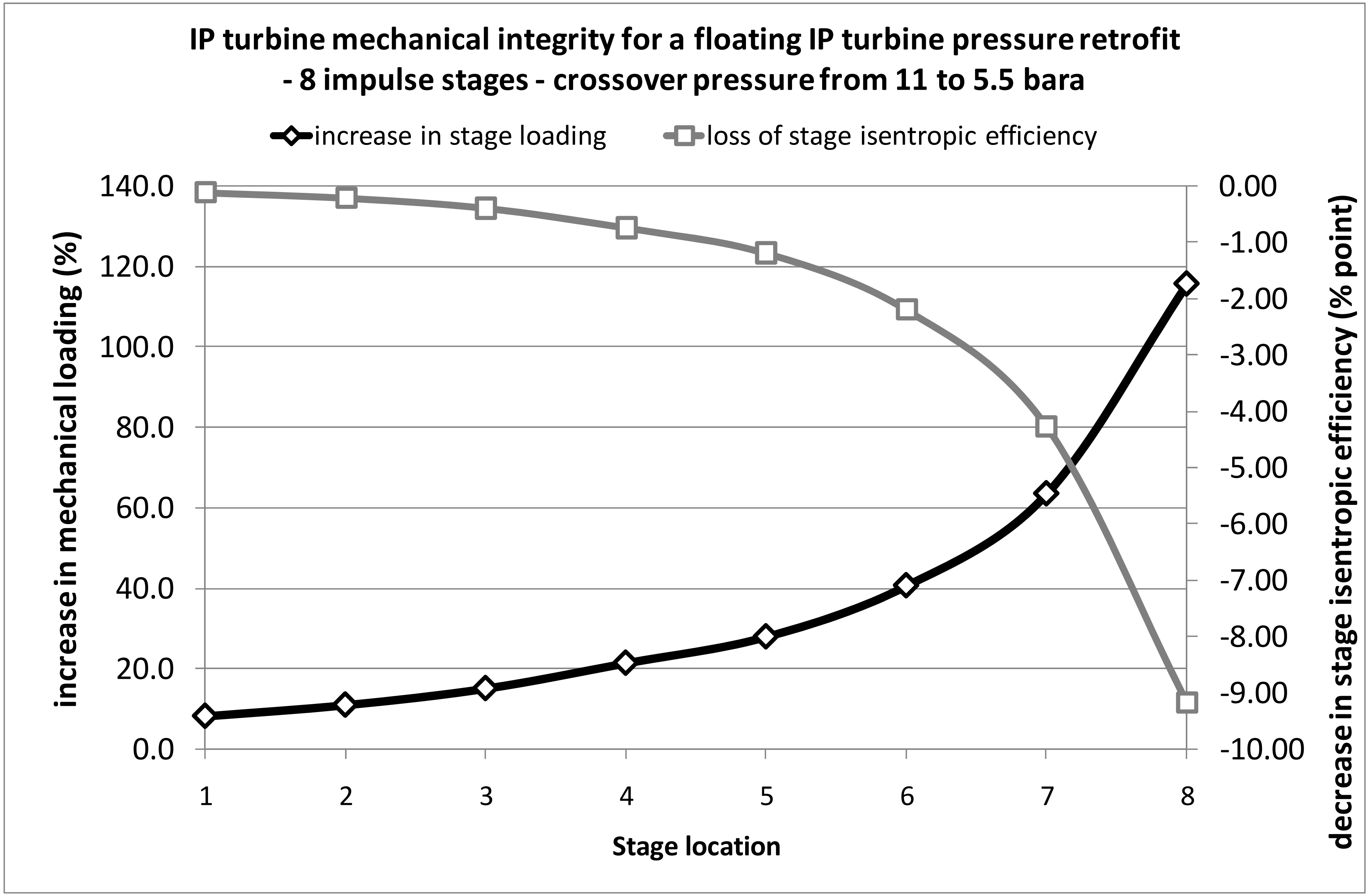
$\Rightarrow$ End thrust balances out for double flow IP turbine when outlet pressure changes

Floating pressure trade-offs

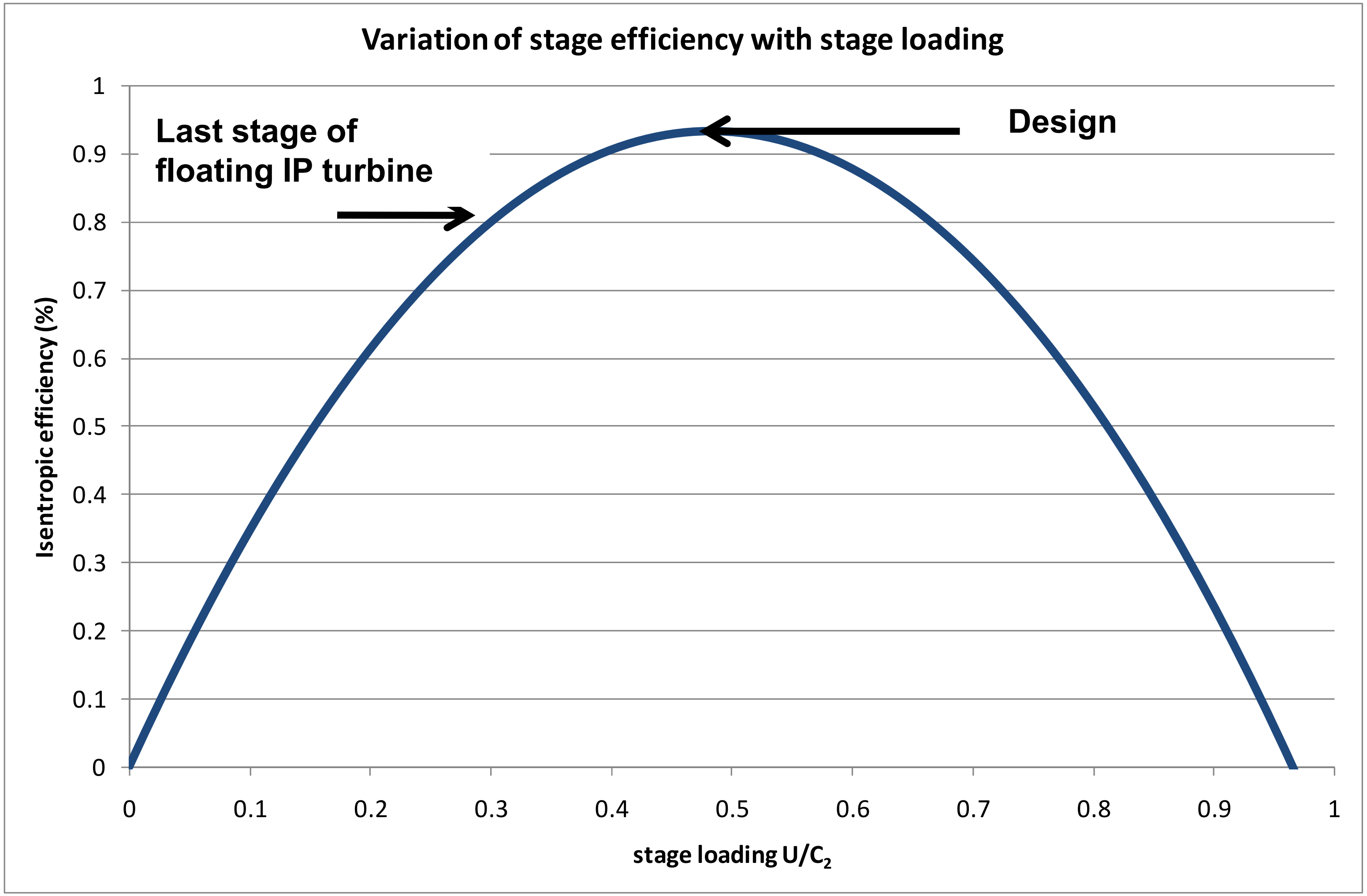
2. Mechanical integrity of IP turbine

   Lower outlet pressure increases the enthalpy drop of the last stages

   - Change of velocity ratio affects the stage efficiency
   - Increased steam bending moment on the blade
   - Recirculation losses

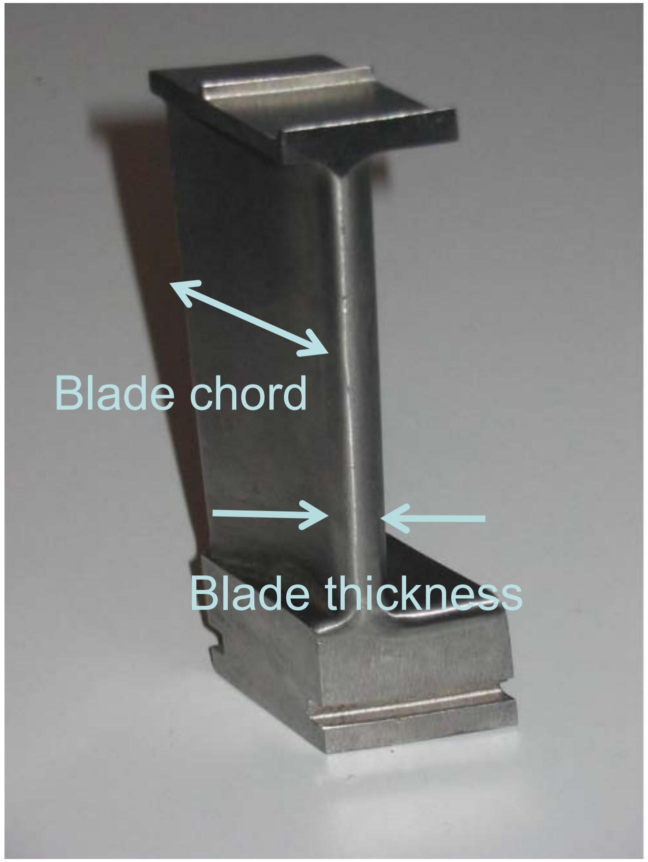


Overall drop of turbine isentropic efficiency: -2.2% point


Variation of stage efficiency with stage loading
Last stage of floating IP turbine
Design
Isentropic efficiency (%)
stage loading U/C2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

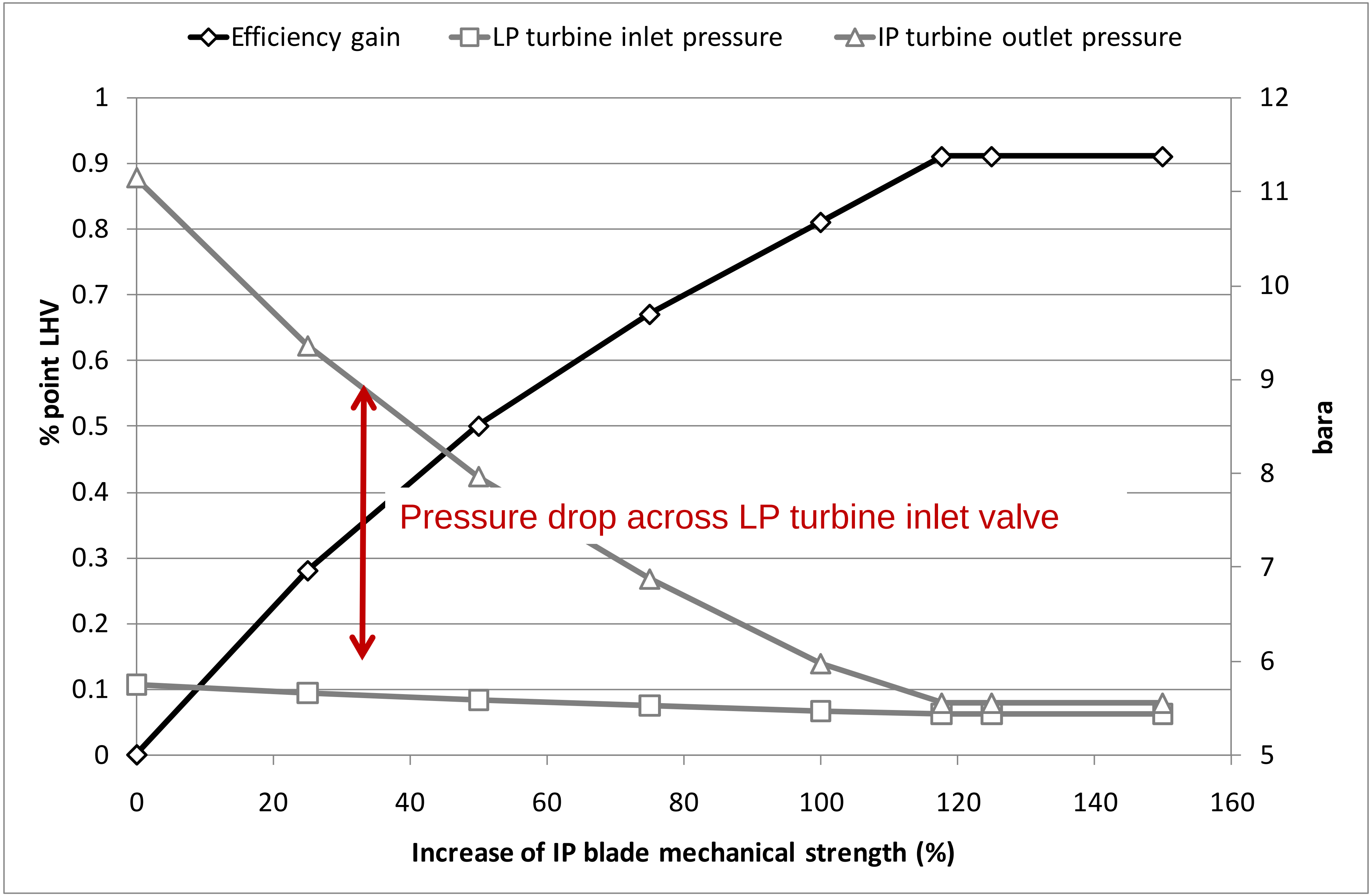
Floating pressure retrofit trade-offs

1. Reinforce very last blades of IP turbine
   - Upgrade materials with higher tensile strength - 10% gain by using LP last stage alloy for IP last stage
2. Blade design
   - Lengthen blade chord
   - Increase bending modulus with thicker blades


Blade chord
Blade thickness

Efficiency gain of a floating pressure retrofit as a function of the mechanical strength of the last IP turbine blade

Initial IP/LP crossover pressure 11 bar down to 5.5 bar



Conclusions

- **Power plant efficiency does not affect capture costs**
- **Capture plant efficiency and cost does**
- **The steam turbine is part of the capture plant**
- **Flexibility in operation and for upgrade matters**
- **Options for most retrofit situations**
- **An issue with actually fitting the equipment**
- **But NOT intrinsically an efficiency issue**
- **Look for good retrofit sites on other criteria**

Using fundamental advanced thermodynamics to model CO_2 capture using aqueous ammonia

30/09/2009

Victor Darde, Kaj Thomsen, Willy van Well, Erling H Stenby

12th meeting of the international post-combustion capture network

Regina, Canada

Outline

- Description of the process
- Description of the thermodynamic model
  - Speciation
  - VLE
  - SLE
  - Enthalpy change
- Description of the results
  - Equilibrium
  - Heat requirement
- Future work

CO_2 capture using aqueous ammonia: introduction

- Post combustion process: use of MEA
  - Degradation of solvent and corrosion
  - High energy consumption

→ Search for new alternatives

- Post combustion process
- Process can be found in 2 variants:
  - Absorption at ambient temperature
  - Absorption at low temperature (chilled ammonia process), patented process (2006), developped by Alstom
- Few publications and results
- Similarities with MEA process <u>but:</u>
  - Low temperature of absorption to prevent ammonia vaporization
  - No degradation or corrosion issues
  - High pressure of the pure CO_2 stream
  - Decrease of the heat consumption

The thermodynamic model

- Need for a fundamental thermodynamic model to evaluate the process
- Original model: Thomsen and Rasmussen (1999) (“Modeling of Vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems”, Chemical Engineering Science 54(1999)1787-1802)
  - Valid for CO_2-NH_3-H_2O mixtures
  - Use of extended UNIQUAC
  - Up to 110°C
  - About 2000 experimental data points on this system (Binary VLE, Ternary VLE, SLE, enthalpy…)

Speciation
Vapor-liquid equilibrium

- The following reactions are considered:
  - $NH_3\ (aq) + H^+ \Leftrightarrow NH_4^+$
  - $CO_2\ (aq) + H_2O\ (l) \Leftrightarrow HCO_3^- + H^+$
  - $HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$
  - $NH_3\ (aq) + HCO_3^- \Leftrightarrow NH_2COO^- + H_2O\ (l)$
- The distribution of species in the liquid phase (speciation) is calculated with Extended UNIQUAC

- Gas phase components:
  - $CO_2\ (g) \Leftrightarrow CO_2\ (aq)$
  - $NH_3\ (g) \Leftrightarrow NH_3\ (aq)$
  - $H_2O\ (g) \Leftrightarrow H_2O\ (l)$
- Chemical potentials calculated:
  - SRK for the gas phase
  - Extended UNIQUAC for the liquid phase

Solid-liquid equilibrium
Enthalpy change

- The following solids are considered

NH_2COONH_4	Ammonium carbamate
NH_4HCO_3	Ammonium bicarbonate
$(NH_4)_2CO_3 \cdot H_2O$	Ammonium carbonate
$(NH_4)_2CO_3 \cdot 2NH_4HCO_3$	Sesquicarbonate
Ice	Solid water

- SLE is handled by Extended UNIQUAC

- A large amount of heat is developed when CO_2 is dissolved in aqueous ammonia
  - Heat of reaction from speciation reactions
  - Excess enthalpy of the ionic solution
- Both terms are calculated with the Extended UNIQUAC model

Upgrading of the thermodynamic model: Description of the work

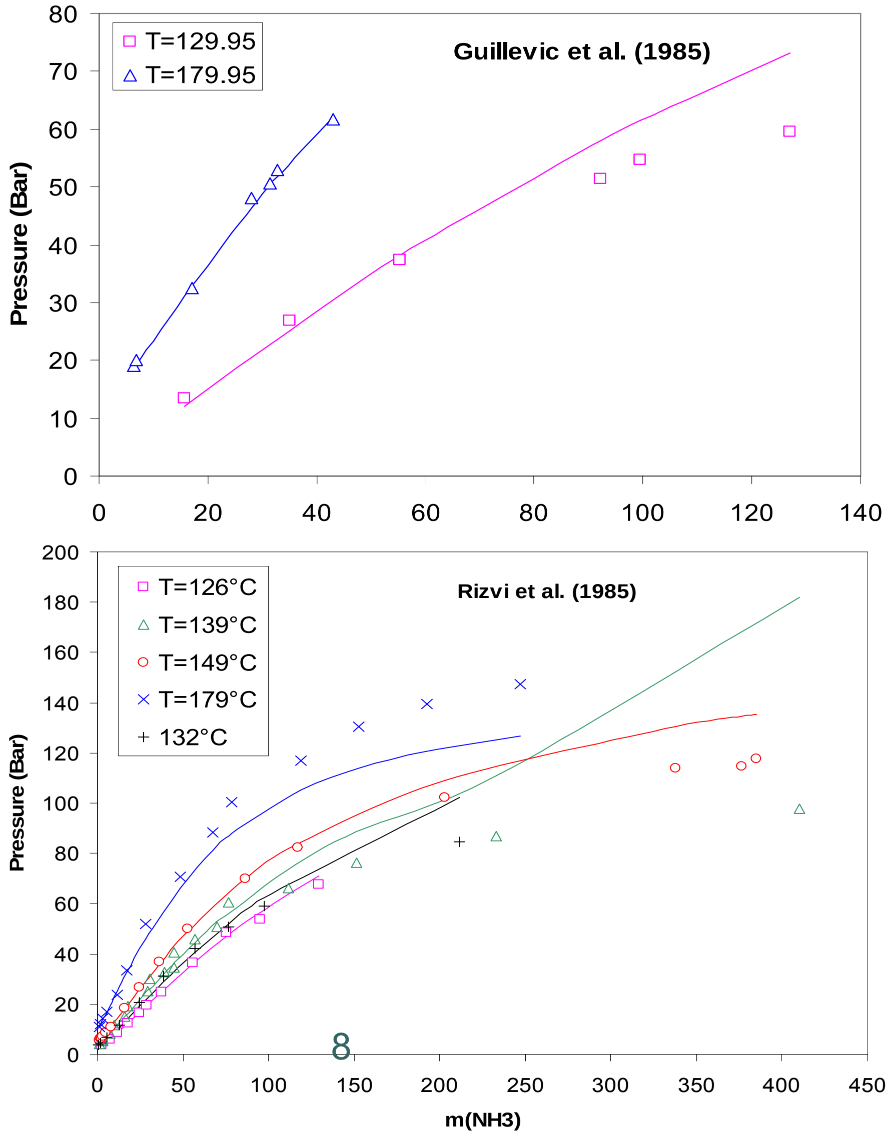
- Upgrading of the model:
  - Temperature correlation for the Henry constants for NH_3 and CO_2
  - Calculation of the residual enthalpy of the gas phase with SRK
- New data added:
  - VLE at higher temperature
  - Enthalpy data from Rumpf B and Maurer G: partial evaporation of CO_2-NH_3-H_2O mixtures
  - Speciation data from Lichtfers et al. (2000)
  - Heat capacity data
- All together: 4500 data points to refit the parameters, but some should not be trusted

  → 3800 data selected
- Parameters
  - Refitting of 60 parameters
  - Several optimization routines
  - Choice of the weight of the data

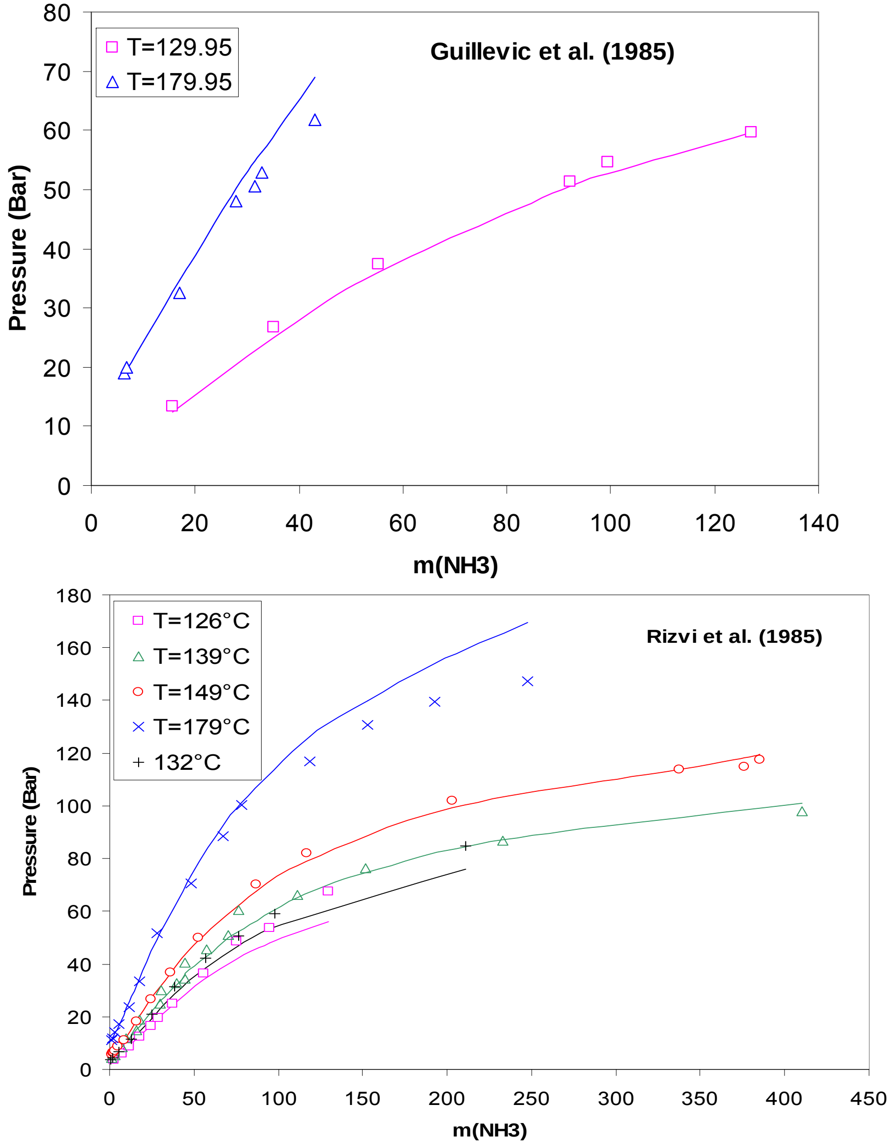
→ New set of parameters

Binary NH_3-H_2O at high temperature and m(NH_3)

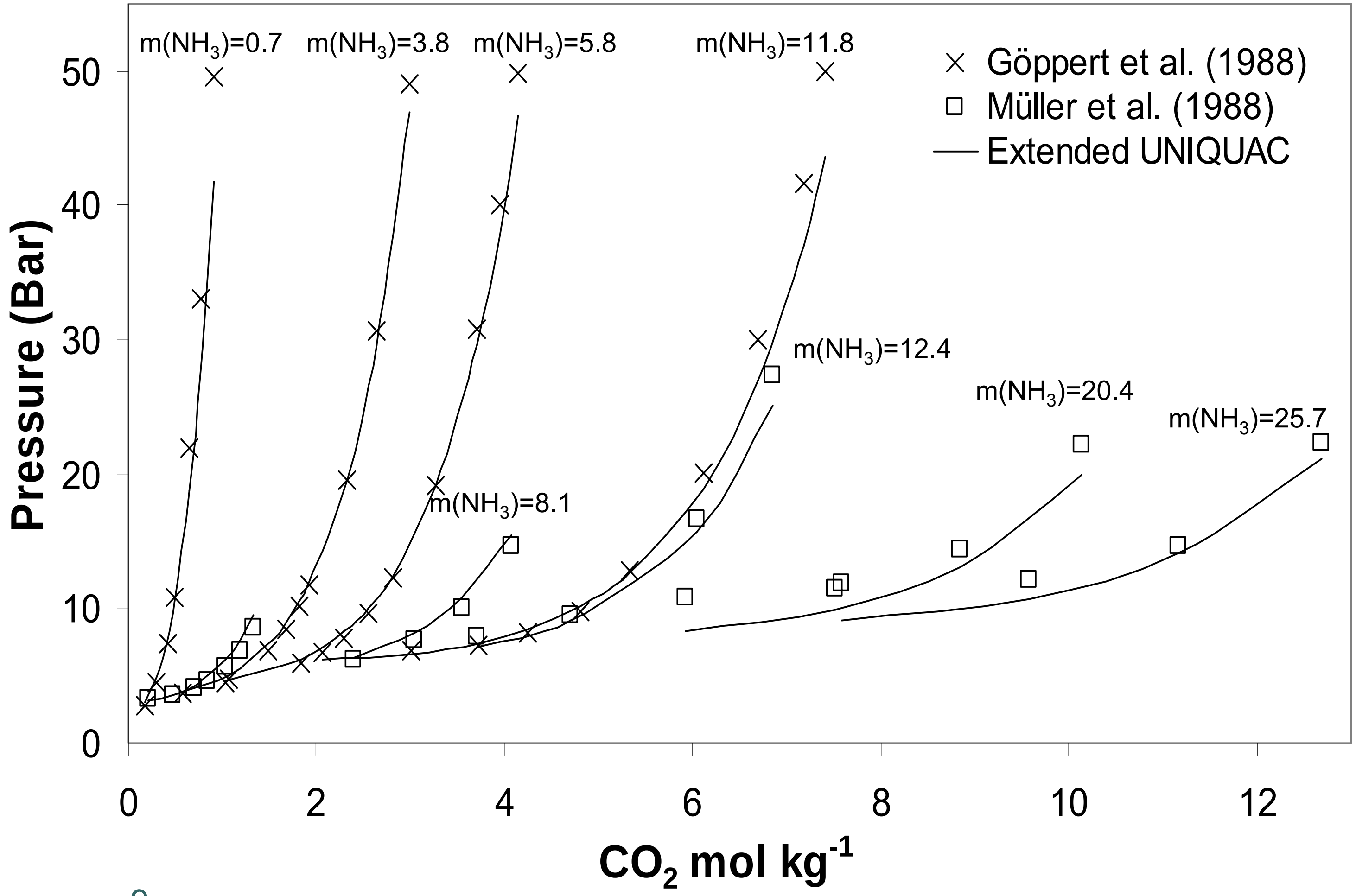
Original Parameters



New Parameters

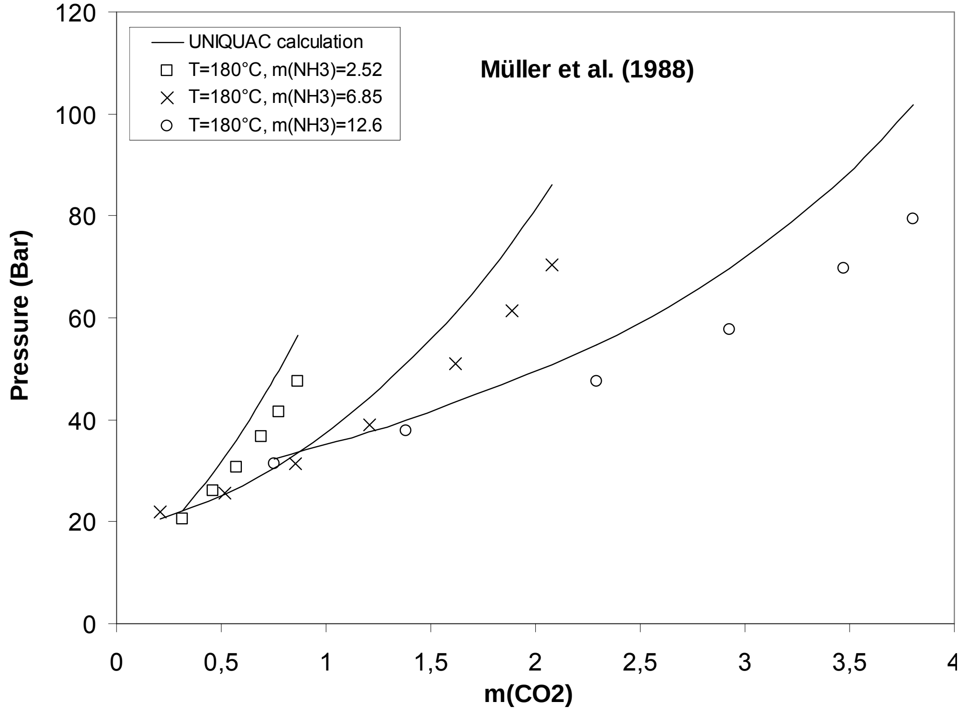


Ternary data at 120°C

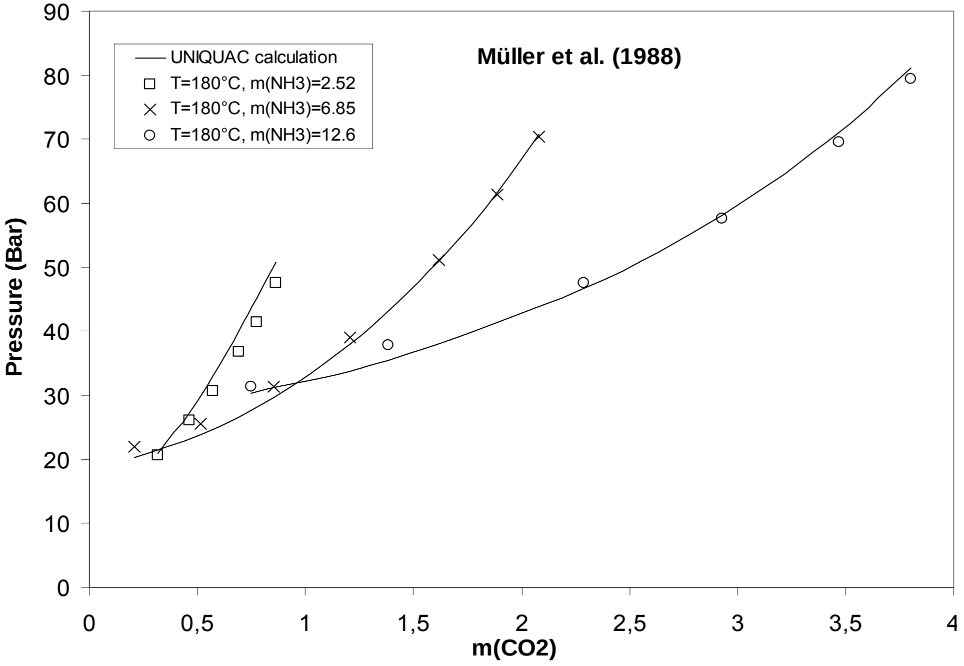


Ternary 180°C

- Original parameters

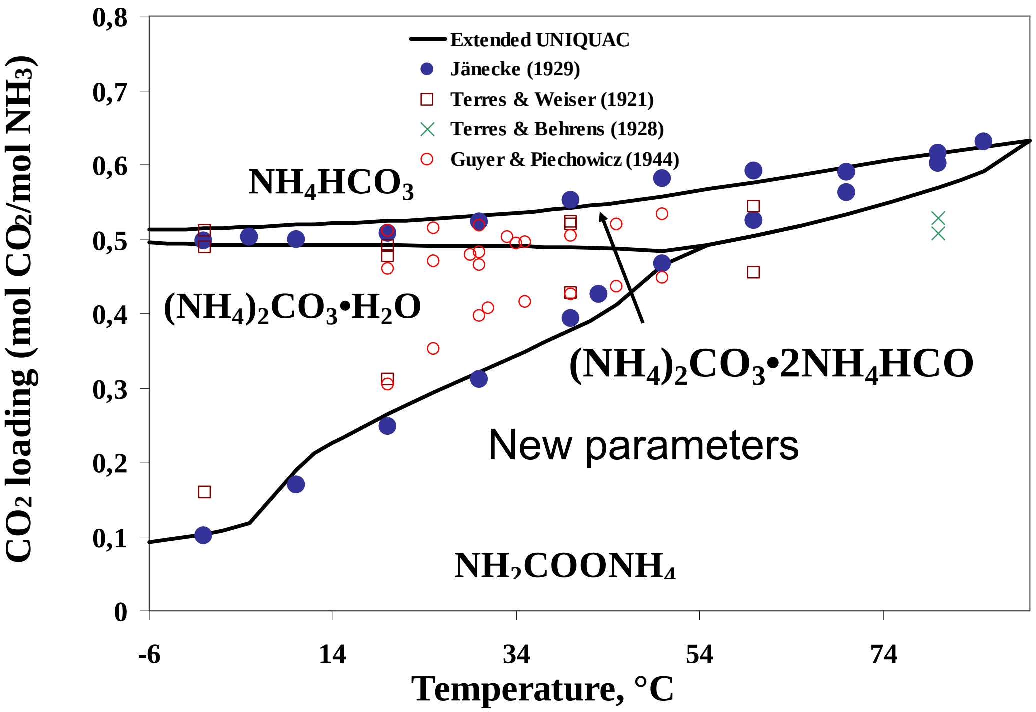


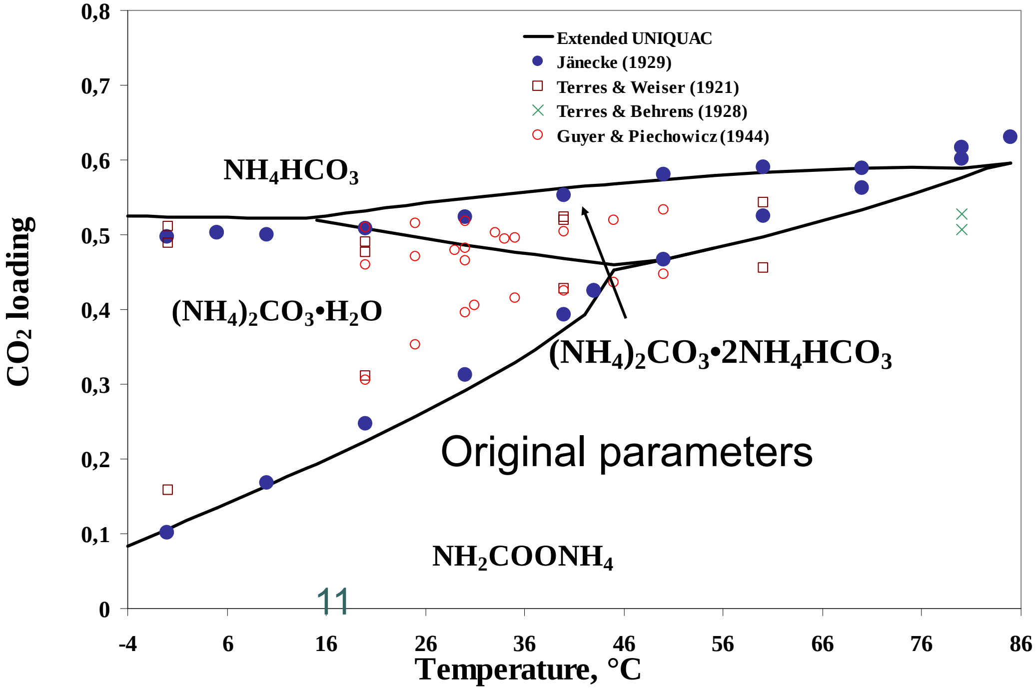
- New parameters



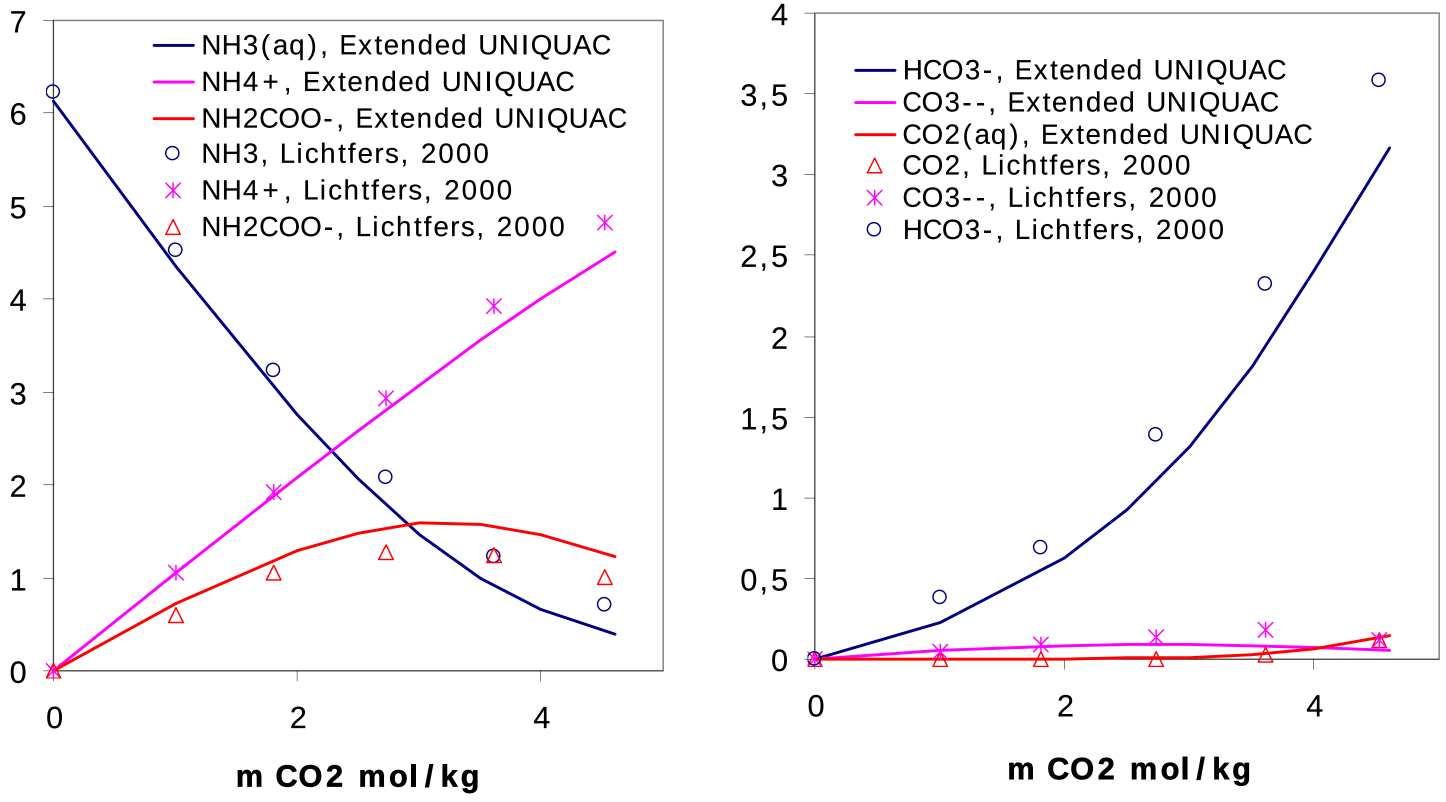
SLE results

Use of Jänecke data only (1929) for parameter estimation



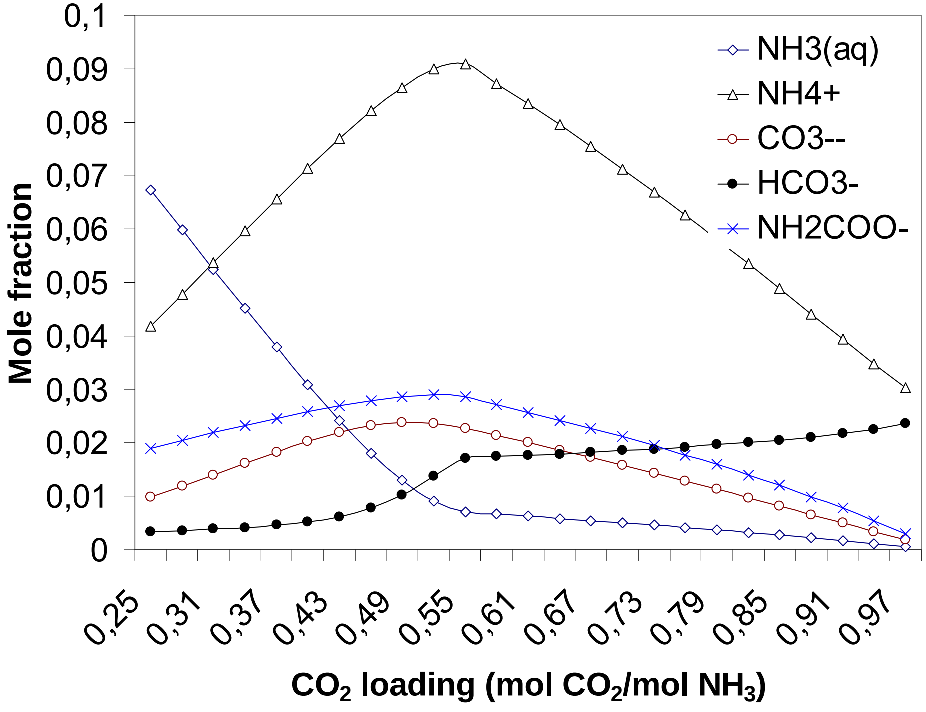


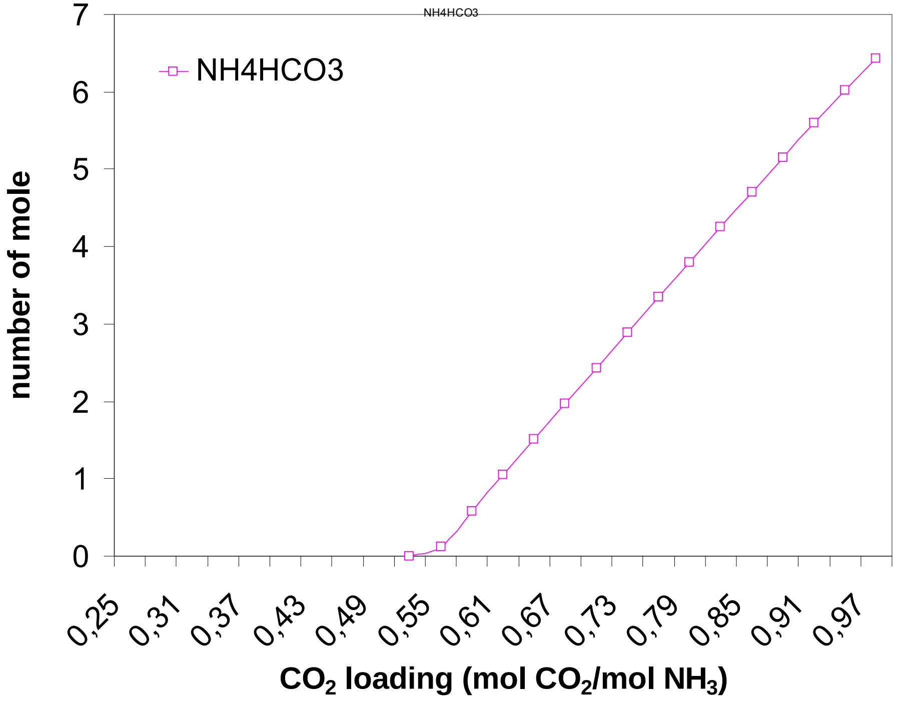
Speciation data (Lichtfers, 2000) T=80°C, m(NH_3)=6.1



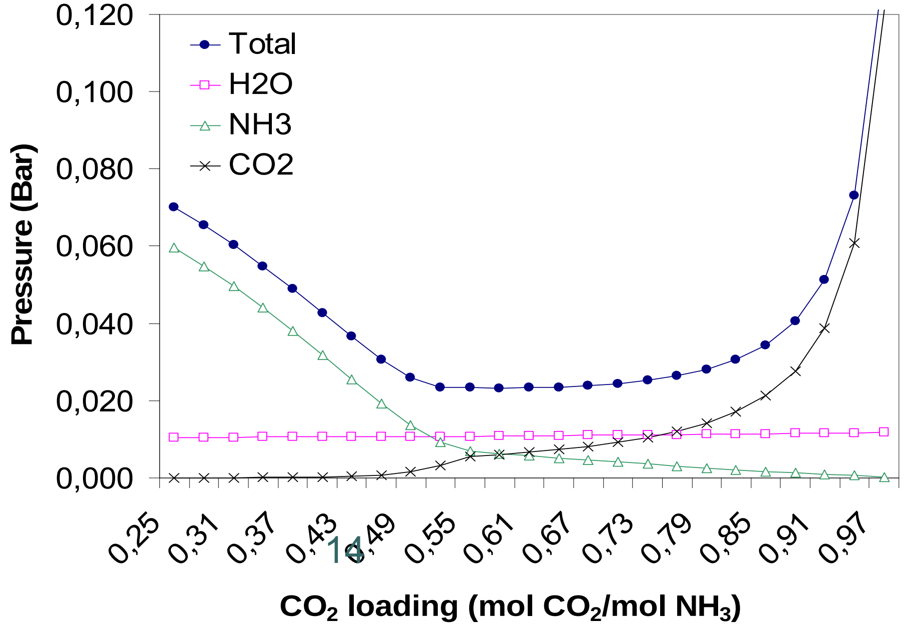
Modelling: Conclusion

- Upgrade of the model
- Extension of the validity of the temperature range
- Use of new kind of experimental data for parameter estimation
- Model can accurately describe the thermodynamic properties of NH_3-CO_2-H_2O





Formation of ammonium bicarbonate



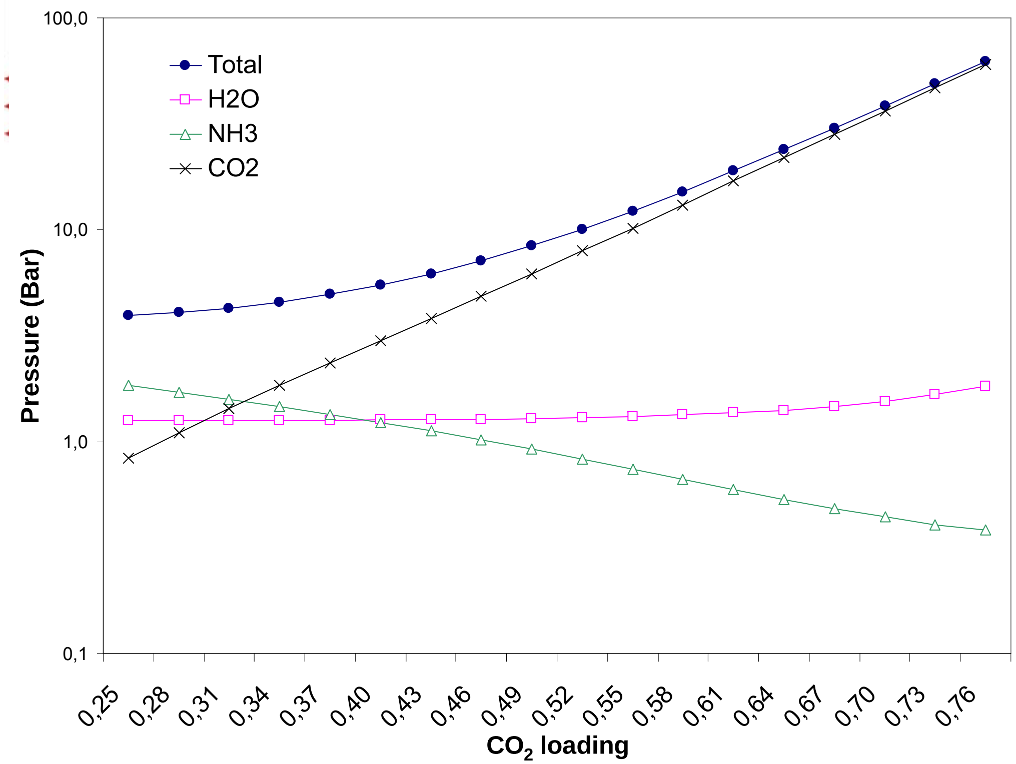
High pressure of NH_3 at low loading

Results

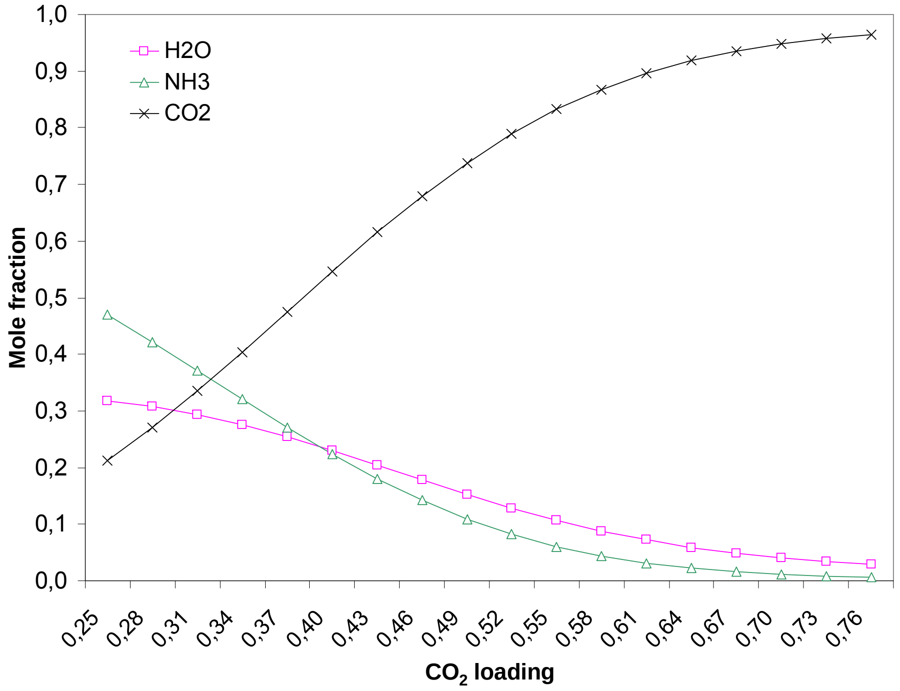
Future work

Heat requirement

10°C for



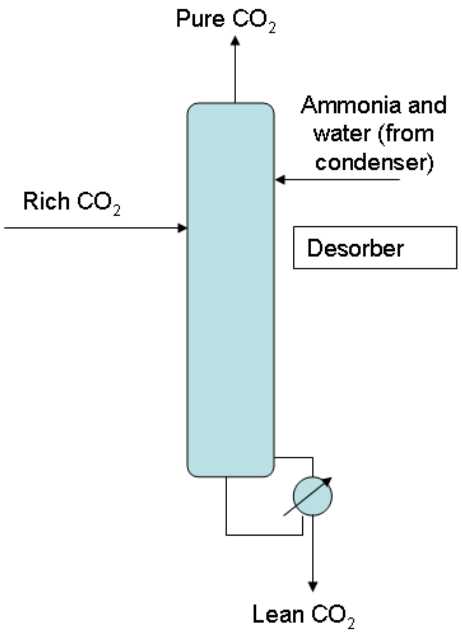
High CO_2 pressure for high loading



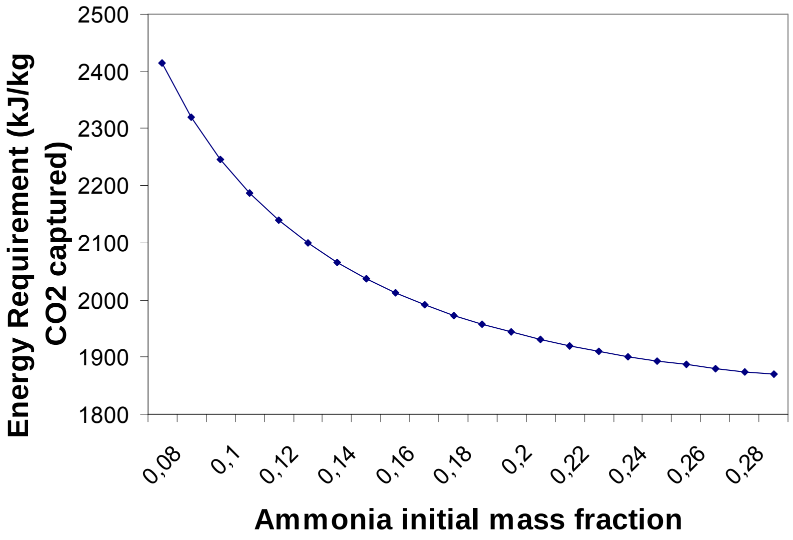
Heat requirement in the desorber

- Reference Configuration

Ammonia initial mass fraction	T CO_2 Lean stream	T CO_2 Rich stream	T Water and Ammonia from condenser	Lean CO_2 loading	Rich CO_2 loading
12%	110°C	100°C	25°C	0.33	0.67



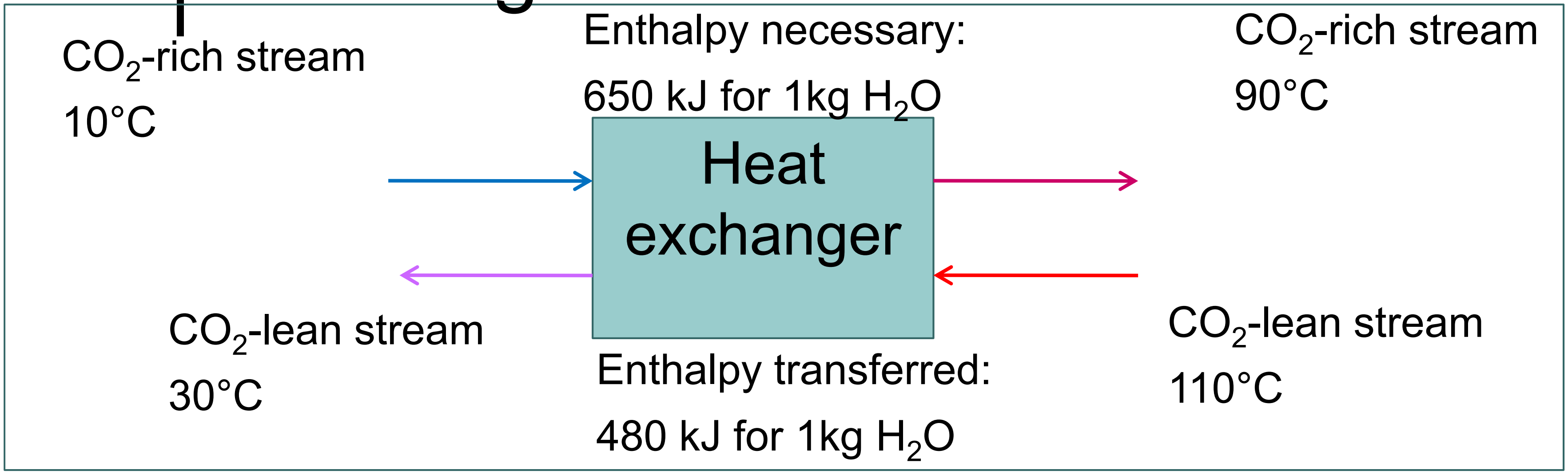
- Influence of 5 variables on the enthalpy balance



Heat requirement desorber MEA: 3700kJ/kg CO_2 captured (CASTOR project)

→ significant decrease of the heat consumption

Heat requirement in the heat exchanger



CO_2-rich stream
10°C

Enthalpy necessary:
650 kJ for 1kg H_2O

CO_2-rich stream
90°C

Heat exchanger

CO_2-lean stream
30°C

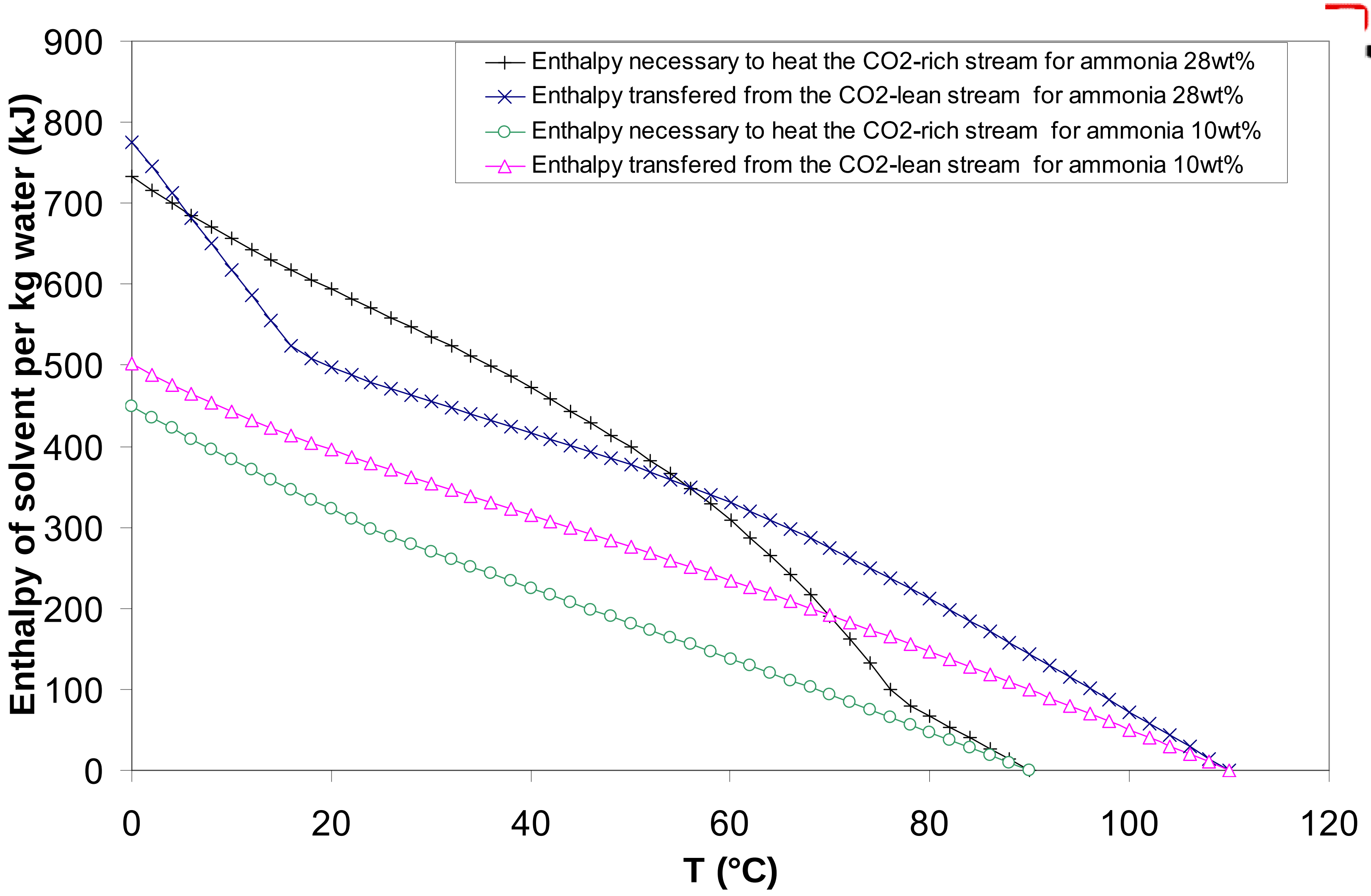
Enthalpy transferred:
480 kJ for 1kg H_2O

CO_2-lean stream
110°C

NH_3=28wt%
Reference configuration
$\Delta T_{\text{heat exchanger}} = 20°C$

A maximum of 74% of the CO_2-rich stream can be heated, because of the presence of solid

→ significant need for extra heat (645kJ/kg CO_2 captured)



- Need for additional energy to heat the CO_2-rich stream and dissolve the solid phase for a high NH_3 concentration
- Possibility to use low quality heat available at the power plant
- Limited in the case of a low NH_3 concentration

Heat requirement: Conclusion

- Heat requirement desorber chilled ammonia lower than 2000kJ/kg CO_2 captured

→ Significant reduction of the heat consumption in the desorber

- Optimization of the configuration of the process to minimize the heat consumption
- Additional energy savings during compression
- But:
  - Additional heat requirement to heat the CO_2-rich stream
  - Cooling duty for the chilling of the flue gas and solvent
  - Heat requirement to recover the vaporized ammonia

Future work

- Thermodynamic model by itself is not sufficient to perform a thorough evaluation of the process:
  - Implementation on the thermodynamic model on ASPEN
  - Test of different configurations
  - Optimization of the capture process
- Study of the integration of the process in the power plant technology
- Experimental measurement of the kinetic rate of absorption of carbon dioxide by ammonia solvent:
  - Design and manufacturing of a wetted wall column
  - First tests performed

- Thank you for your attention

vid@kt.dtu.dk

MODELING OF RELATIONSHIPS AMONG KEY PARAMETERS IN CO_2 CAPTURE PROCESS

Christine Chan, Qing Zhou, Yuxiang Wu
Energy Informatics Laboratory
Faculty of Engineering
University of Regina
Regina, SASK S4S 2V2
Canada

Outline

- Motivation and research objectives
- CO_2 capture problem domain
- 2 Approaches:
    - Statistical regression modeling
    - Artificial neural networks and sensitivity analysis
- Summary & Comparison of 2 approaches
- Conclusion
- Future works

Motivation

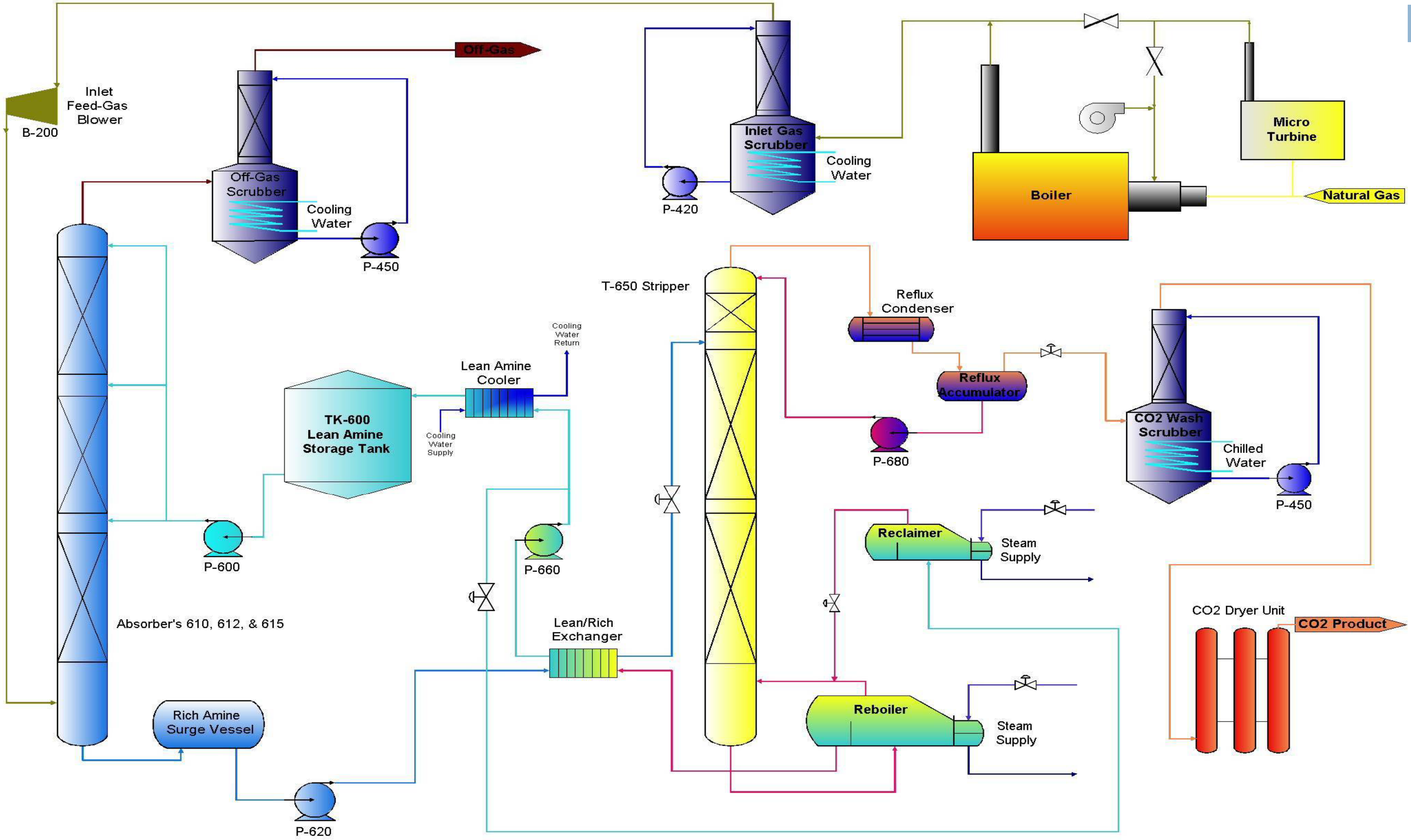
- To obtain explicit models of the CO_2 capture process for developing systems that support automated control, monitoring, and future optimization of the process

- To better understand process of CO_2 capture

Research Objectives

- To study the nature of relationships among key parameters of the CO_2 capture process
- Focus on parameters that affect CO_2 production rate

CO$_2$ Capture


Inlet Feed-Gas Blower
B-200
Off-Gas
Off-Gas Scrubber
Cooling Water
P-450
Inlet Gas Scrubber
Cooling Water
P-420
Micro Turbine
Boiler
Natural Gas
T-650 Stripper
Reflux Condenser
Reflux Accumulator
P-680
CO2 Wash Scrubber
Chilled Water
P-450
Cooling Water Return
Lean Amine Cooler
TK-600 Lean Amine Storage Tank
Cooling Water Supply
P-600
P-660
Reclaimer
Steam Supply
Absorber's 610, 612, & 615
Lean/Rich Exchanger
CO2 Dryer Unit
CO2 Product
Rich Amine Surge Vessel
Reboiler
Steam Supply
P-620

Approaches

- Data source: operational data from CO_2 capture process at International Test Center of CO_2 capture (ITC) 2003-2006
-
- Modeling approaches

(1) Statistical regression

(2) Artificial Neural Networks & Sensitivity Analysis

Approach #1

- Linear and non-linear statistical regression modeling

Statistical Analysis

- **Why statistical analysis:**

 - We have quantitative historical data

 - Supports both linear and non-linear modeling

- **Tool used: SPSS software (trademark of SPSS, Inc., USA)**

 - provide linear function model

 - provide 10 curve functions for non-linear models, such as logarithmic model, exponential model, etc.

Regression Analysis

- **Procedures:**

  - **Correlation Analysis:** To verify the correlation between parameters, and how significant they are

  - **Regression Analysis:** To create regression model and determine regression coefficients

  - **Assessment of Regression Model:** To verify the model developed is reliable and acceptable

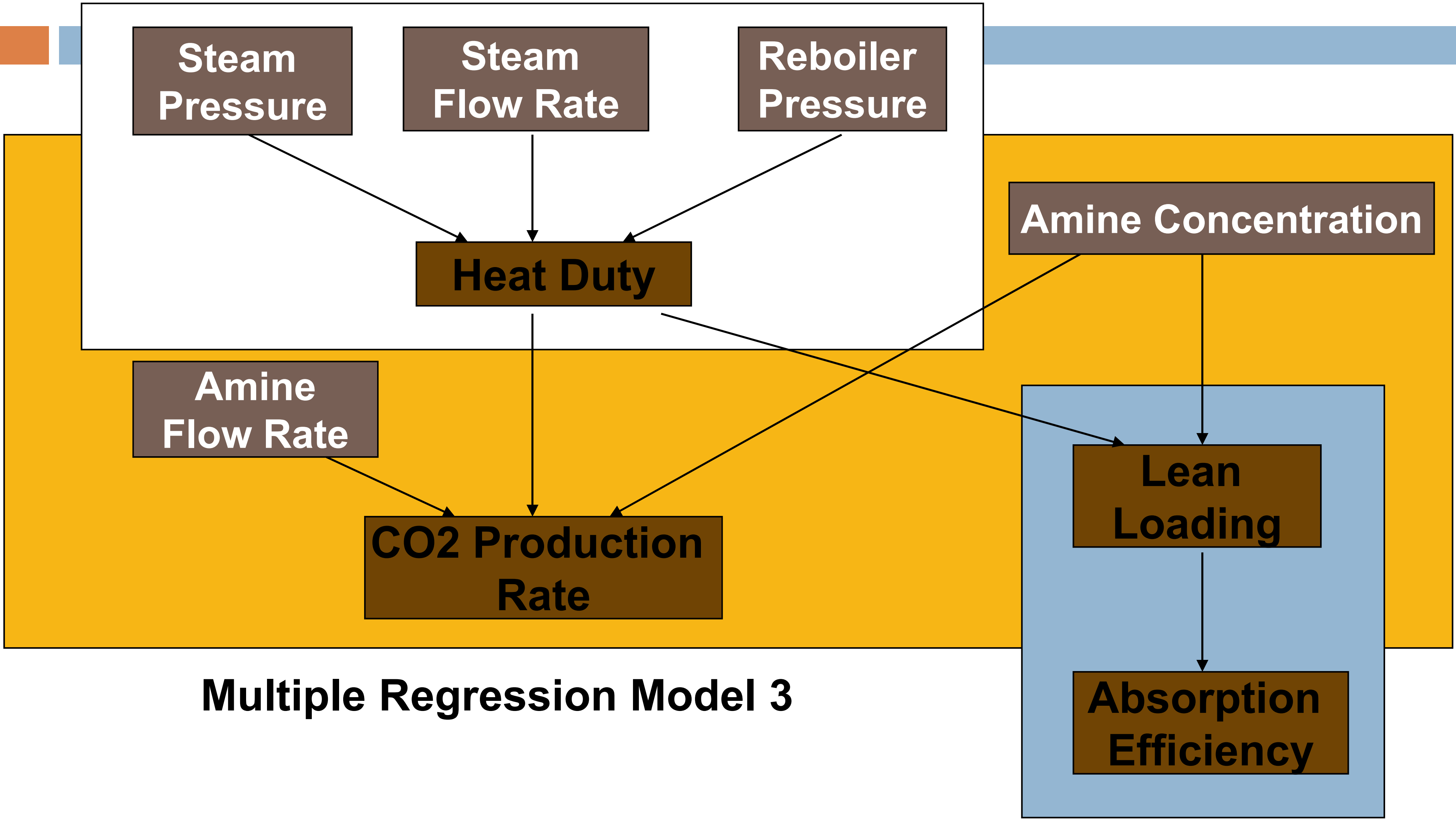
- **Results:**

  - Multiple regression model

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_n X_n + \varepsilon_i$$

  - Curve Estimation: non-linear function

Modeling Processes



Steam Pressure

Steam Flow Rate

Reboiler Pressure

Amine Concentration

Heat Duty

Amine Flow Rate

Lean Loading

CO2 Production Rate

Absorption Efficiency

Multiple Regression Model 3

Cubic Power Function

Regression Models

- **Linear Model 1:** $R^2 = 0.824$

  Heat Duty $=\alpha_1 *$ (Steam flow rate) $+\alpha_2 *$ (Steam pressure) $+\alpha_3$

- **Linear Model 2:** $R^2 = 0.771$

  Lean Loading $= -\beta_1 *$(Heat duty) $- \beta_2 *$(Amine concentration) $+ \beta_3$

- **Linear Model 3:** $R^2 = 0.718$

  CO_2 Production Rate $= \theta_1 *$ (Heat Duty) $+ \theta_2 *$ (Amine Concentration) $+ \theta_3 *$ (Amine flow rate) $+ \theta_4$

- **Cubic Function:** $R^2 = 0.882$

  Absorption Efficiency $= -\gamma_1 *$ (Lean Loading) $+ \gamma_2 *$ (Lean Loading)^2 $-\gamma_3 *$ (Lean Loading)^3 $+\gamma_4$

Observation from Model Developed

- The ***direction*** of the relations:

  - Positive α**,** β, θ, γ values → Consequent parameter increases as conditional parameter increases

  - Negative α**,** β, θ, γ values → Consequent parameter decreases as conditional parameter increases

- The ***strength*** of the relationships:

  - The values of α**,** β, θ, γ each indicate how much the consequent parameter will be influenced by a change in the corresponding conditional parameter

Assessment of Regression Model

- The models are based on four assumptions:

1. There is no multicollinearity between the predictor variables.→ **Collinearity Diagnostic**

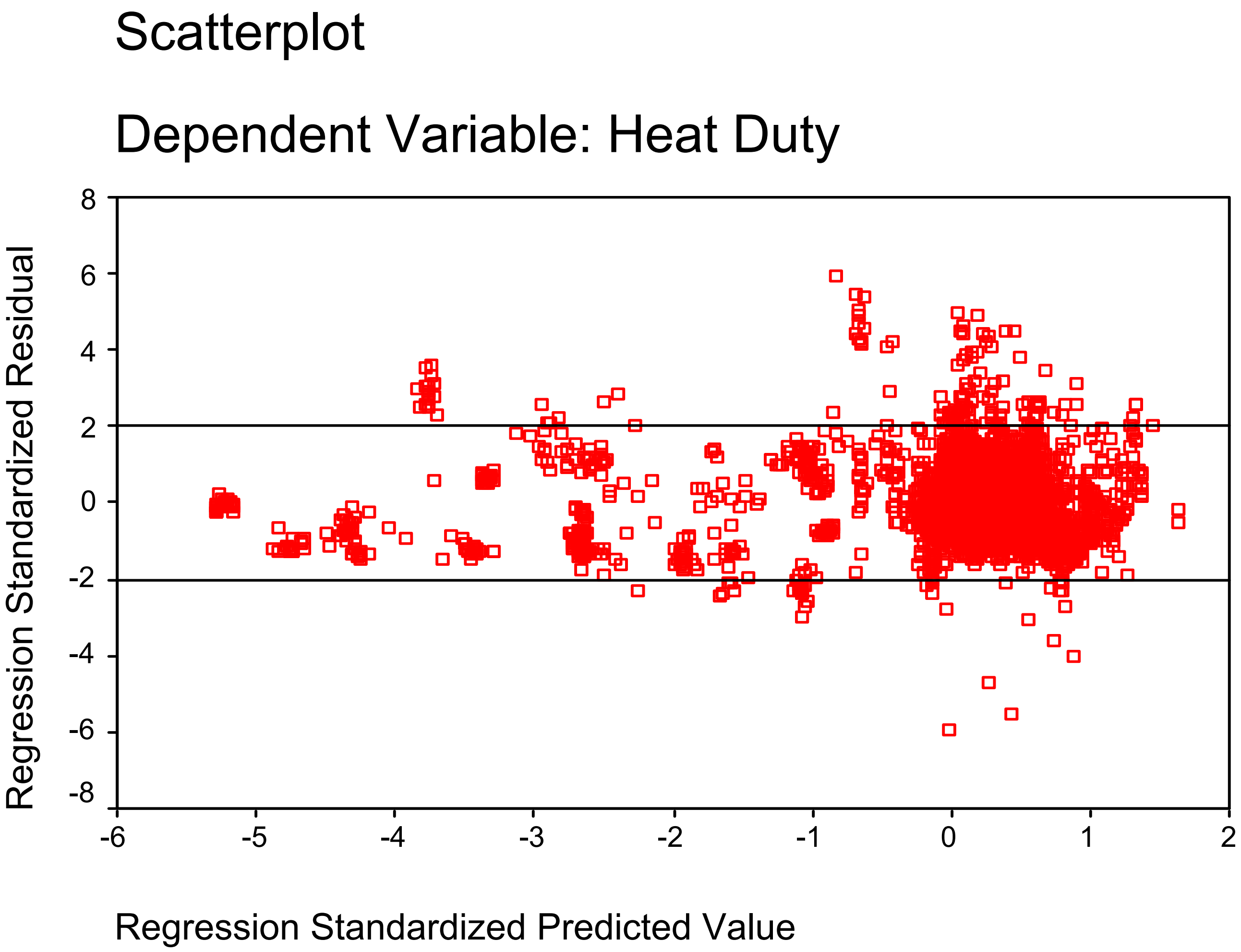
There should be no linear relationship between any two predictor variables in one model.

Assessment of Regression Model

- Assumption #2:

  The residuals are randomly distributed.
  → **Residual Plot**

Assessment of Regression Model

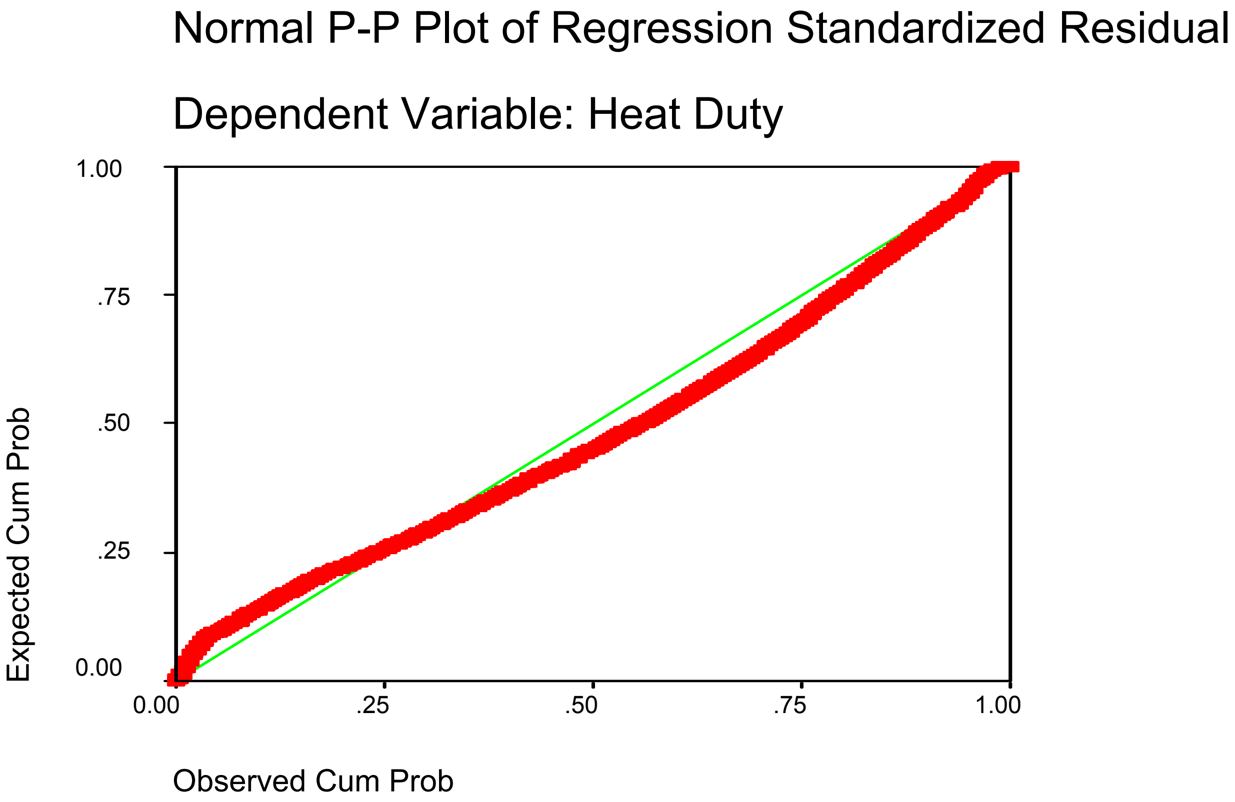


Assessment of Regression Model

- Assumption #3:

  The residuals are from a normal distribution.
  → **Normality Probability Plot**

Assessment of Regression Model



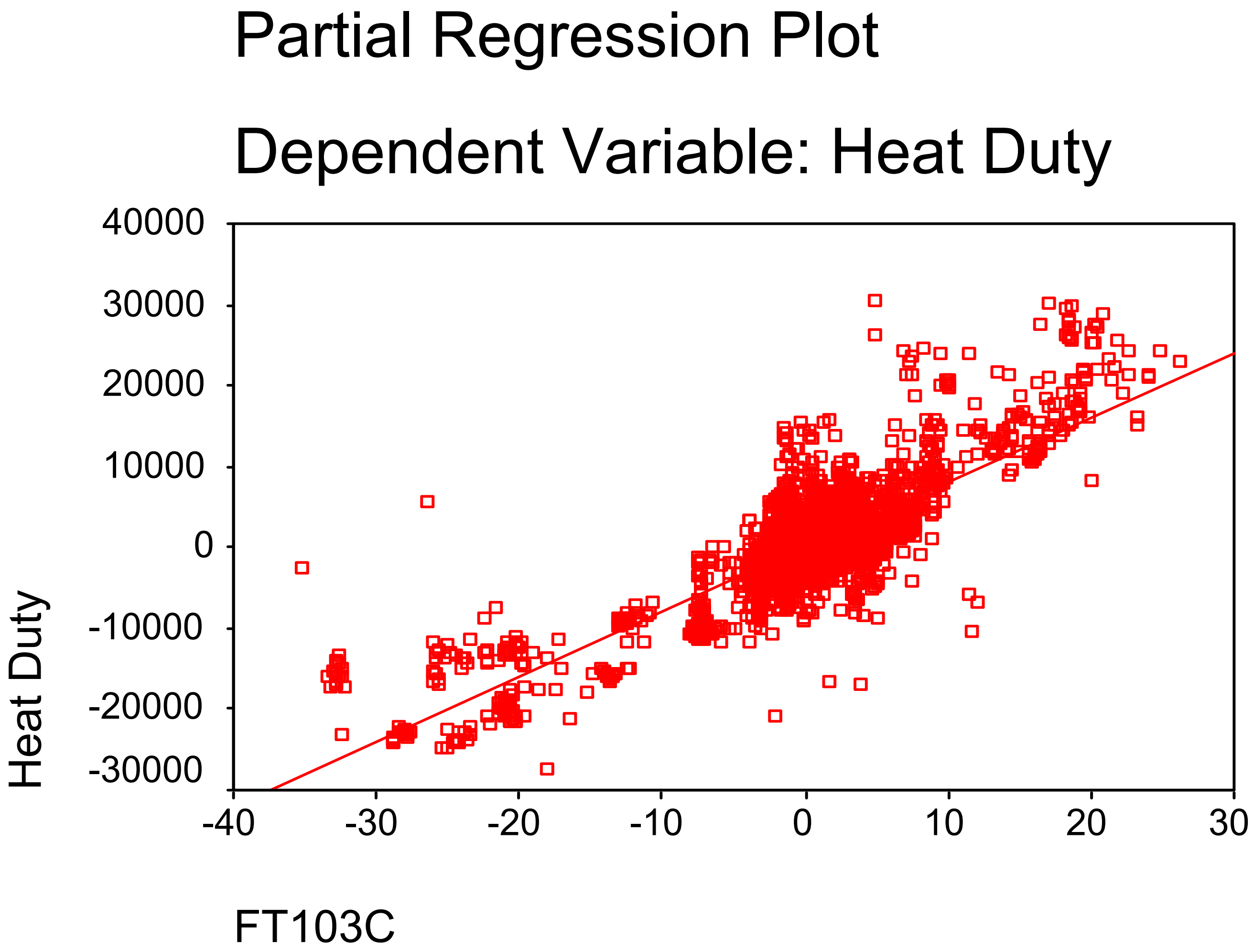
Assessment of Regression Model

- Assumption #4:

The relation between each conditional variable and the consequent variable is linear.

→ **Partial Regression Plot**

Partial Regression Plot



Statistical Study: Results

- 4 assumptions are satisfied
- 3 linear models and 1 non-linear model developed to explicate relationships among input and output parameters
- R statistic on a model shows prediction accuracy of the model

Statistical Study: R statistic

Models	Correlation-coefficient (R)
CO_2 production rate	0.847
Heat duty	0.907
Lean loading	0.878
Absorption efficiency	0.939

Statistical Study: Result

- **R statistic** shows results acceptable (range between 84% to 93%), but there is room for improvement

- **Advantage of statistical approach**

  Relationships among the parameters are revealed by the coefficient values

- **Weakness**

  - Possible irregular non-linear relationships cannot be modeled

  - Accuracy is acceptable but can be improved

Approach #2

- Combine artificial neural networks (ANN), sensitivity analysis, and expert validation

ANN: Independent or Input Parameters

- Absorber in gas actual flow (FI200ACT)
- Input absorber fluid CO_2 gas (AIT-203)
- Absorber TK440 off gas flow (FI901)
- Lean amine to absorber flow rate (FT600)
- Reboiler pressure (PT660)
- Pressure of steam entered reboiler (PT103A)
- Steam from reboiler flow rate (FT103C)
- Amine concentration (molarity)

ANN: Dependent or Output Parameters

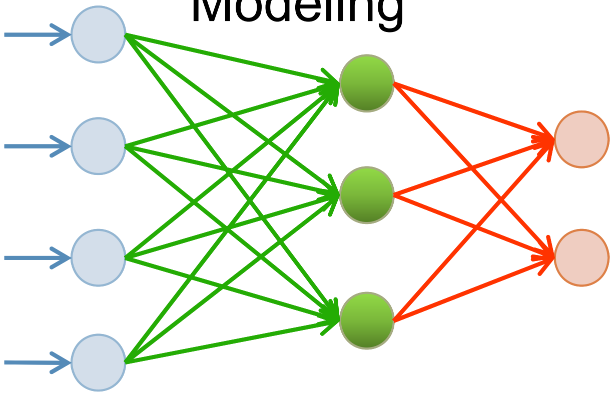
- CO_2 production rate
- Heat Duty
- Absorption Efficiency
- Lean Loading

ANN: Modeling Procedure

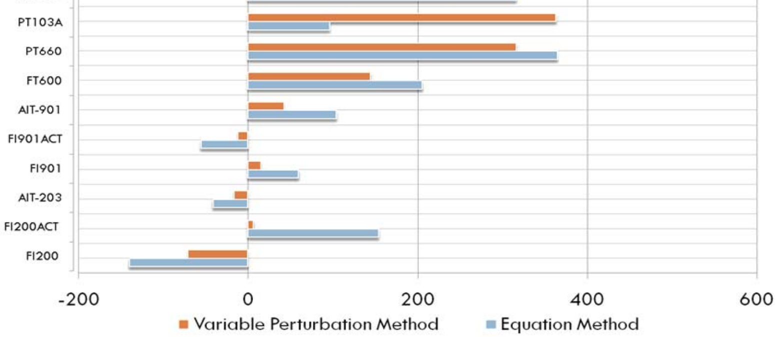
- Construct the artificial neural network models;
- Conduct sensitivity analysis on the modeling results;
- Validate with experts;
- Reformulate the neural network model.

ANN & SA: Modeling Procedure

Neural Network Modeling



Sensitivity Analysis

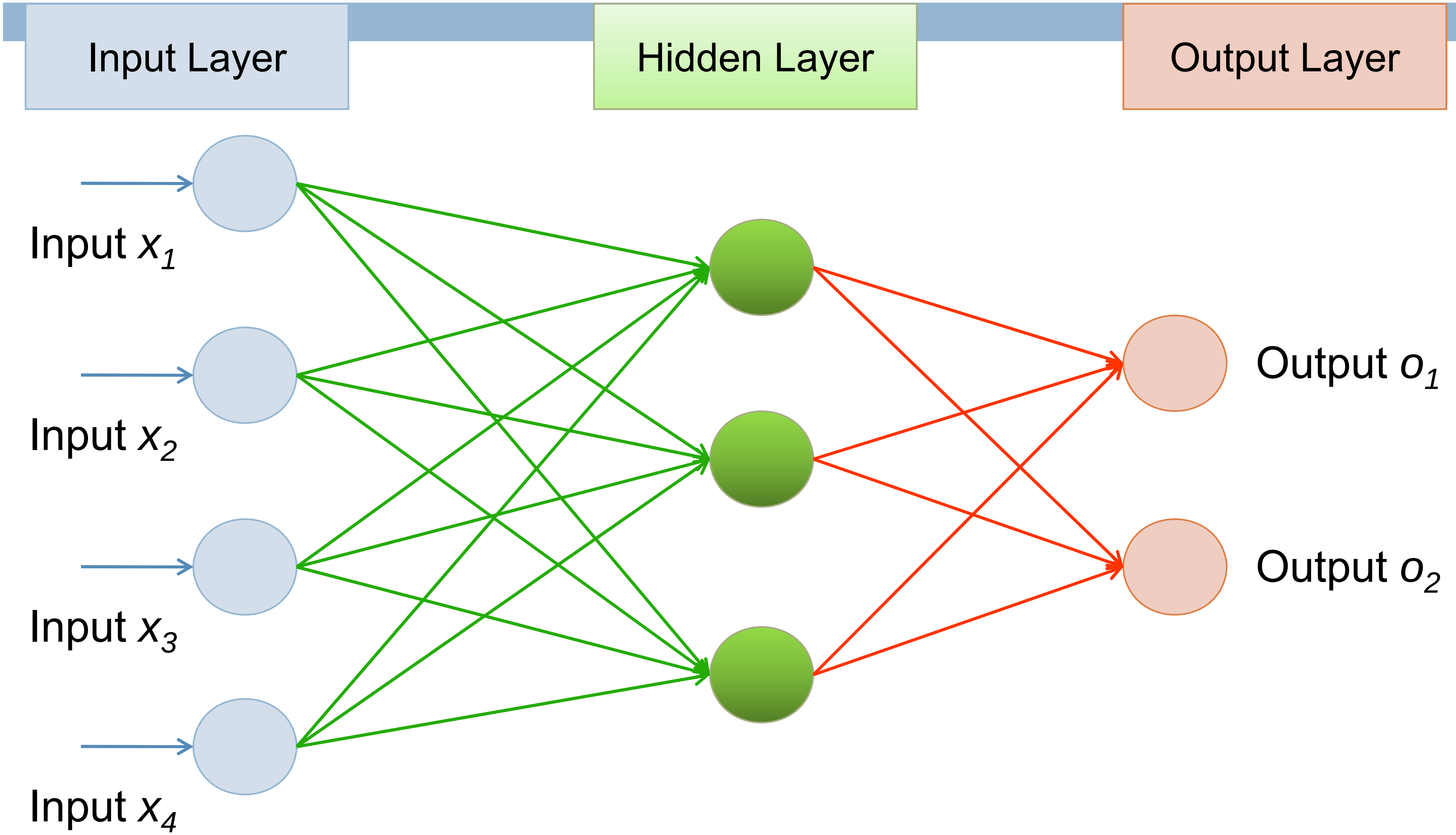


Expert Validation

Artificial Neural Network

- A learning system made up of a set of neurons configured in a highly interconnected network.
- It learns from examples and can generalize beyond the training data
- For a feed forward multilayer neural network, the neurons are grouped into three layers: input layer, hidden layer and output layer.

Artificial Neural Network



Input Layer

Hidden Layer

Output Layer

Input x_1

Input x_2

Input x_3

Input x_4

Output o_1

Output o_2

ANN Modeling Results

Production Rate	
Correlation coefficient	0.999
Root mean squared error	0.0215
Root relative squared error	40.81%
Total Number of Instances	4067

Heat duty	
Correlation coefficient	2655.6
Root mean squared error	0.0215
Root relative squared error	36.97%
Total Number of Instances	4067

Absorption efficiency	
Correlation coefficient	0.948
Root mean squared error	1.611
Root relative squared error	31.86%
Total Number of Instances	4067

Lean loading	
Correlation coefficient	0.884
Root mean squared error	0.0243
Root relative squared error	47.62%
Total Number of Instances	4067

Sensitivity Analysis (SA)

- SA shows influences of input parameters to the outputs when input parameter values change
- In the process, the modeler can study the uncertainties associated with the model parameters, and thereby,
- better understand behavior of the modeled system

Sensitivity Calculation Method #1

- Equation Method

$$I_i = \sum_k O(1-O) w_{k1}^2 v_k^2 (1 - v_k^2) w_{ik}^1$$

$O :$ the value of the output node;

$w_{k1}^2 :$ the outgoing weight of the *k*th in the second layer;

$w_{k1}^2 :$ the output value of the *k*th node in the second layer;

$w_{k1}^2 :$ the connection weights between the *i*th node of the first layer and the *k*th node in the hidden layer.

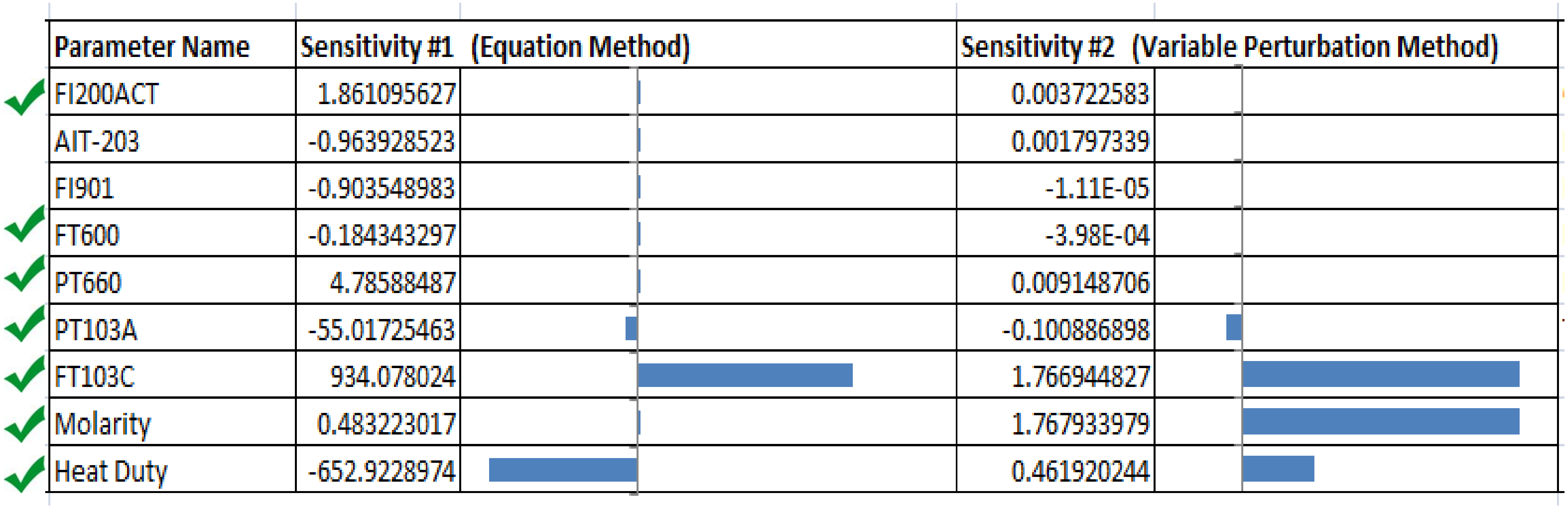
Sensitivity Calculation Method #2

- Variable Perturbation Method
  - This method adjusts the input values of one variable while keeping all the other variables untouched. These changes could take the form of

$$I_n \Rightarrow I_n + \delta$$

Sensitivity Analysis Result

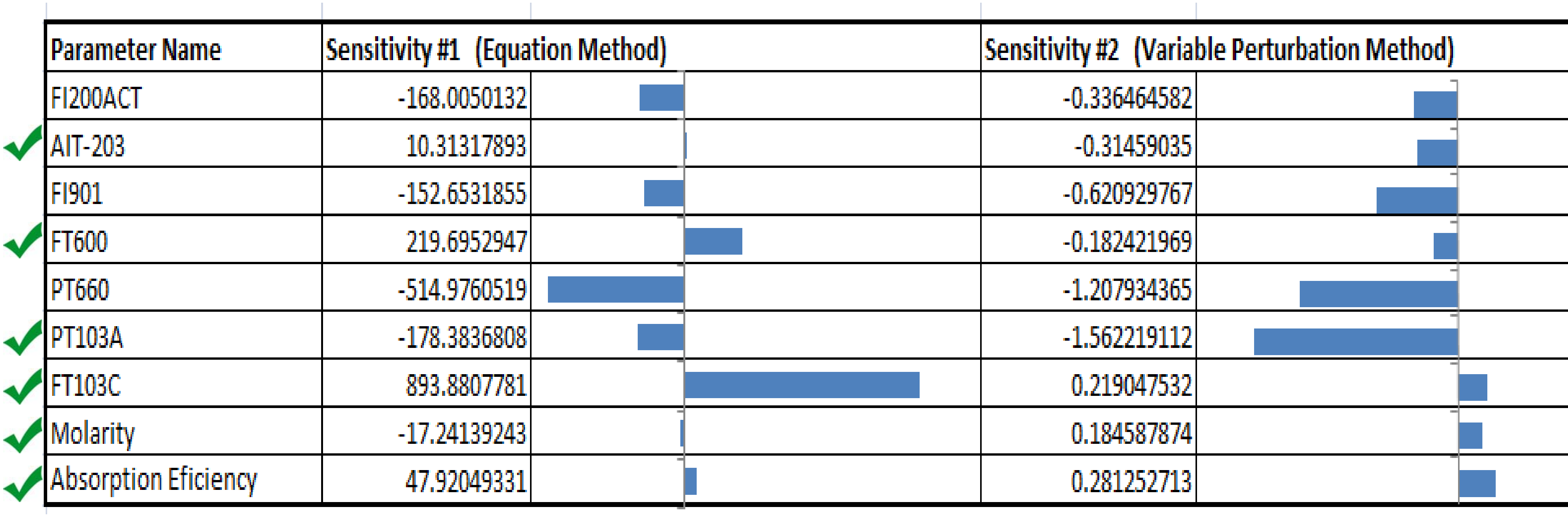
CO$_2$ Production Rate



	Parameter Name	Sensitivity #1	(Equation Method)	Sensitivity #2	(Variable Perturbation Method)
✓	FI200ACT	1.861095627		0.003722583	
	AIT-203	-0.963928523		0.001797339	
	FI901	-0.903548983		-1.11E-05	
✓	FT600	-0.184343297		-3.98E-04	
✓	PT660	4.78588487		0.009148706	
✓	PT103A	-55.01725463		-0.100886898	
✓	FT103C	934.078024		1.766944827	
✓	Molarity	0.483223017		1.767933979	
✓	Heat Duty	-652.9228974		0.461920244	

Sensitivity Analysis Result

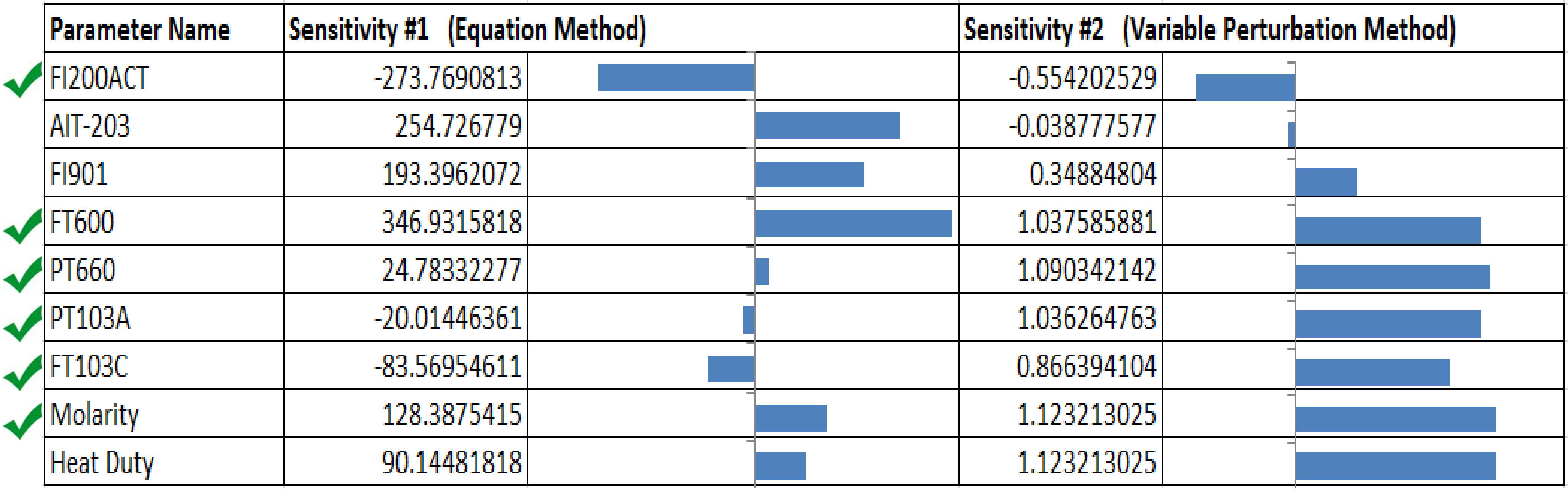
Heat Duty



	Parameter Name	Sensitivity #1 (Equation Method)	Sensitivity #2 (Variable Perturbation Method)
	FI200ACT	-168.0050132	-0.336464582
✓	AIT-203	10.31317893	-0.31459035
	FI901	-152.6531855	-0.620929767
✓	FT600	219.6952947	-0.182421969
	PT660	-514.9760519	-1.207934365
✓	PT103A	-178.3836808	-1.562219112
✓	FT103C	893.8807781	0.219047532
✓	Molarity	-17.24139243	0.184587874
✓	Absorption Eficiency	47.92049331	0.281252713

Sensitivity Analysis Result

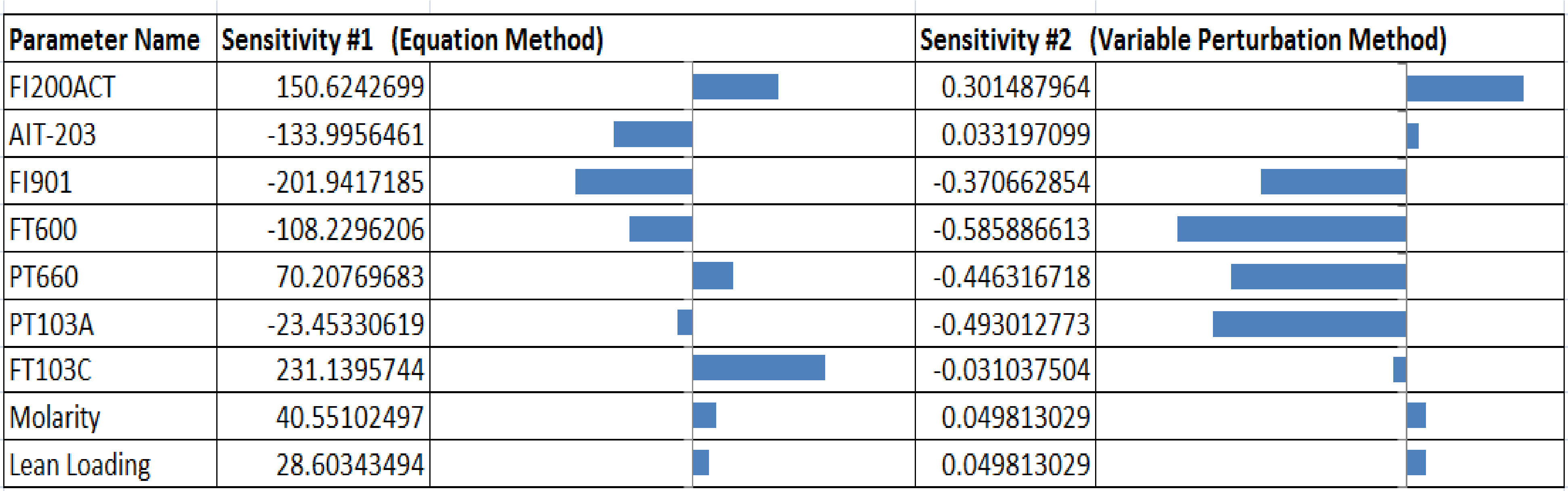
Lean loading



	Parameter Name	Sensitivity #1 (Equation Method)		Sensitivity #2 (Variable Perturbation Method)	
✓	FI200ACT	-273.7690813		-0.554202529	
	AIT-203	254.726779		-0.038777577	
	FI901	193.3962072		0.34884804	
✓	FT600	346.9315818		1.037585881	
✓	PT660	24.78332277		1.090342142	
✓	PT103A	-20.01446361		1.036264763	
✓	FT103C	-83.56954611		0.866394104	
✓	Molarity	128.3875415		1.123213025	
	Heat Duty	90.14481818		1.123213025	

Sensitivity Analysis Result

Absorption efficiency



	Parameter Name	Sensitivity #1 (Equation Method)		Sensitivity #2 (Variable Perturbation Method)	
✓	FI200ACT	150.6242699		0.301487964	
✓	AIT-203	-133.9956461		0.033197099	
✓	FI901	-201.9417185		-0.370662854	
✓	FT600	-108.2296206		-0.585886613	
✓	PT660	70.20769683		-0.446316718	
✓	PT103A	-23.45330619		-0.493012773	
✓	FT103C	231.1395744		-0.031037504	
✓	Molarity	40.55102497		0.049813029	
	Lean Loading	28.60343494		0.049813029	

Expert Validation and Model Reformulation

- Experts validated SA results
- Four models were refined and some input parameters removed from the models

Reformulated Model

CO_2 Production Rate

	ANN (All data)	Refined ANN model
Absorber in gas actual flow factored for concentration	X	X
Flow rate of flue gas into absorber	X	
CO2 concentration of flue gas into absorber	X	
Amine solvent circulation rate	X	X
Pressure of reboiler	X	X
Pressure of inlet steam of reboiler	X	X
Flow rate of outlet steam of reboiler	X	X
Amine concentration	X	X
Heat Duty	X	X
Correlation coefficient (R)	0.999	0.999

Reformulated Model

Heat duty

	ANN (All data)	Refined ANN model.
Absorber in gas actual flow factored for concentration	X	
CO2 concentration of flue gas into absorber	X	X
Off gas flow rate	X	
Amine solvent circulation rate	X	X
Reboiler pressure	X	
Pressure of inlet steam of reboiler	X	X
Flow rate of outlet steam of reboiler	X	X
Amine concentration	X	X
Absorption efficiency	X	X
Correlation coefficient (R)	0.929	0.9018

Reformulated Model

Lean loading

	ANN (All data)	Refined ANN model
Absorber in gas actual flow factored for concentration	X	X
CO2 concentration of flue gas into absorber	X	
Off gas flow rate	X	
Amine solvent circulation rate	X	X
Reboiler pressure	X	X
Pressure of inlet steam of reboiler	X	X
Flow rate of outlet steam of reboiler	X	X
Amine concentration	X	X
Heat duty	X	
Correlation coefficient (R)	0.884	0.851

Reformulated Model

Absorption efficiency

	ANN (All data)	Refined ANN model
Absorber in gas actual flow factored for concentration	X	X
CO2 concentration of flue gas into absorber	X	X
Off gas flow rate	X	X
Amine solvent circulation rate	X	X
Reboiler pressure	X	X
Pressure of inlet steam of reboiler	X	X
Flow rate of outlet steam of reboiler	X	X
Amine concentration	X	X
Lean loading	X	
Correlation coefficient (R)	0.9475	0.9233

Observation on reformulated models

- The approximate R values for the reformulated models are within 3% of those for the original models
- Refined models can still predict the target outputs with relatively high accuracy (85 – 99%) with fewer input parameters

Summary: statistical study

- Result: 3 linear and 1 non-linear models developed
- Coefficient values in the models reveal relationships among the parameters
- Predictive accuracy of model is acceptable
- Irregular non-linear relationships among parameters are not adequately modeled

Summary: ANN & Sensitivity Analysis

Result

- Four ANN models are developed
- Significance of each input parameter to the output parameter is revealed using SA

Advantage

- Irregular non-linear relationships among the parameters can be modeled

Weakness

- Black box, nature of the relationships among the parameters are not explicated

Comparison of R between two approaches

- **Result**

Models	R from Statistical Study	R from ANN modeling
CO_2 production rate	0.847	0.999
Heat duty	0.907	0.9018
Lean loading	0.878	0.8510
Absorption efficiency	0.939	0.9233

Conclusion

- Substantial improvement in prediction of CO_2 production rate from 84 to 99% using ANN+SA approach
- Statistical approach is good in capturing linear relationships among parameters but weak in describing non-linear relationships

Conlusion

- ANN and sensitivity analysis gives satisfactory modeling results as indicated by the R value, however, ANN is a black box and cannot explicate the relationships among parameters
- We believe the procedure of conducting ANN modeling, sensitivity analysis, then expert validation is generalizable for modeling other industrial processes

Future Works

- Other approaches?
- Applying neuro-fuzzy approach to modeling the data

Acknowledgments

- Generous support of the Canada Research Chair Program and Natural Sciences and Engineering Research Council of Canada (NSERC)

- Insightful discussions with Dr. R. Idem, Dr. P. Tontiwachwuthikul, Don Gelowitz of ITC

Thank you!

IMPACTS OF CARBON CAPTURE ON POWER PLANT EMISSIONS

By
Harvey Wen and Ram Narula
Bechtel Power Corp.
Frederick, MD, USA

For Presentation at the
12th Meeting of the
International Post-Combustion Capture Network
September 28-October 1, 2009
Regina, Canada

Outline

- Introduction
- Carbon Capture Processes
- Oxidation and Degradation of Amines
- Solid Wastes
- Liquid Wastes
- Air Emissions
- Conclusions

Introduction

- US emits about 6 billion tons of CO_2 per year. One third of that is emitted from power plants
- US is moving toward enacting carbon legislation to limit carbon dioxide emissions
- Controlling emissions from large sources (power plants) is more cost effective than automobiles
- Recent studies are focused on amine and ammonia scrubbers for carbon capture. The overall impact of CO_2 capture on total emissions is not well understood by utility industry and requires appropriate planning

Near Commercial Processes

- **The Amine process**
  - Generic MEA
  - MEA mixture with other amines
- **The Ammonia Process**
  - Chilled
  - Non-chilled

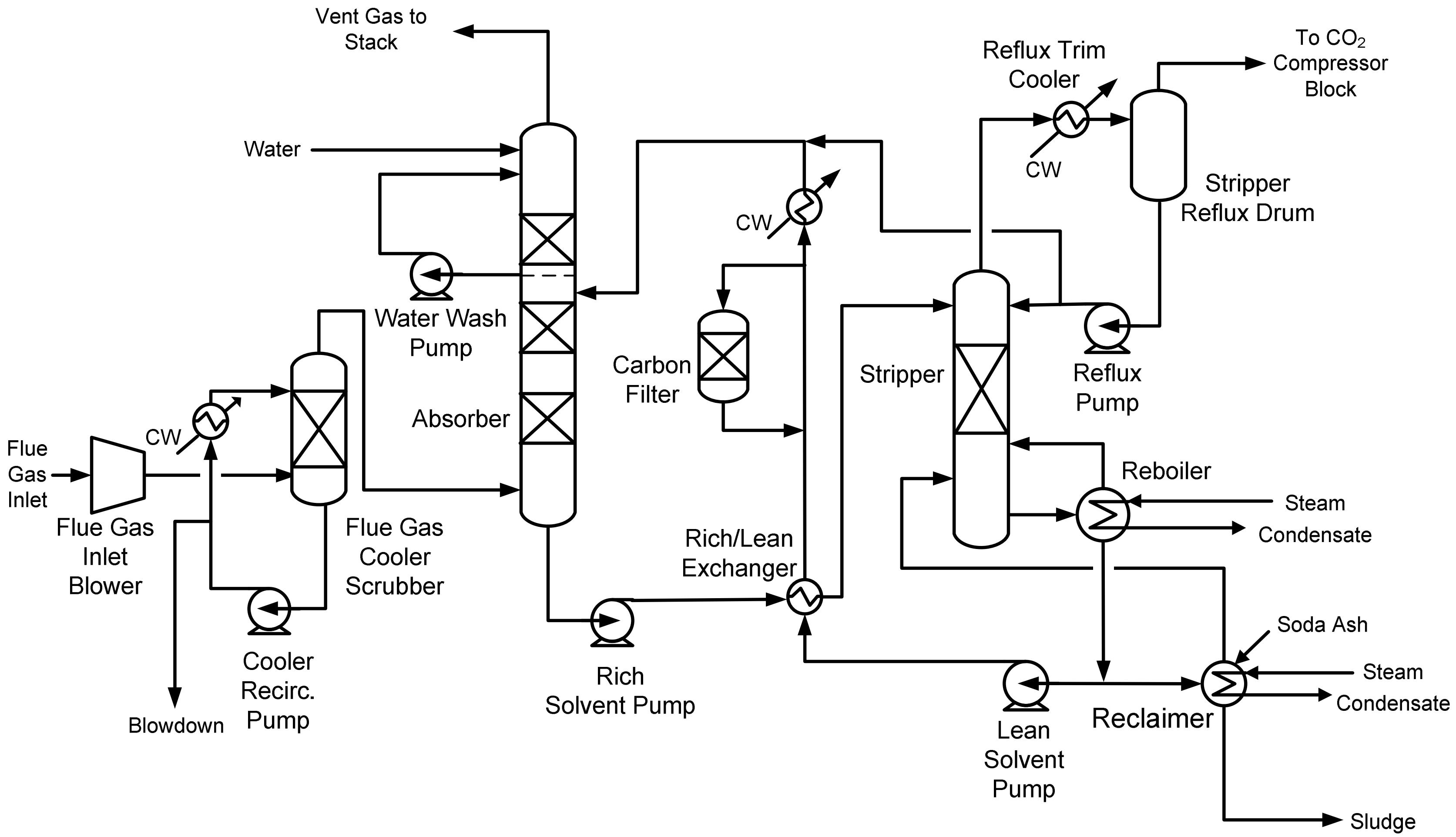
The Amine Processes

- MEA and its variations is the most commonly used amine today for industrial applications
- Most industrial MEA plants have capacities at 200-500 tpd. The largest unit in operation is about 900 tpd
- For a 750 MWe coal fired power plant, its CO_2 emission is about 17,000 tpd depending on the type of coal used. The scale-up factor is 20:1
- For a typical 400 MWe natural gas fired combined cycle unit, its CO_2 emission is about 4,000 tpd.

The Ammonia Process

- Ammonia is technically the lowest form of amine. It reacts with CO_2 to form ammonium bicarbonate and carbonate
- In the 60's, ammonia was used to react with CO_2 to make ammonium bicarbonate in China as a fertilizer
- The heat of reaction between ammonia and CO_2 is lower than that of amine absorption
- The regenerator is operated at a higher pressure than that of amine process. This reduces CO_2 compressor horsepower.

Typical Flue Gas Amine Process



Flue Gas Contaminants

- The flue gas from a gas turbine contains about 15% O2, and has fewer other impurities. Amine degradation by oxidation is more severe in gas turbine flue gas CO_2 capture project
- Coal fired boiler flue gas has about 4% O_2, but it contains a multitude of impurities including SOx, NOx, Hg, chlorides, particulates, and heavy metals.

Some Chemical Reactions Between Amine and O2 /SO2

- O2/MEA reactions
  - Acetic Acid ($C_2H_4O_2$)

    $O_2 + 2C_2H_7NO \rightarrow 2C_2H_4O_2 + 2NH_3$
  - Formic Acid (CH_2O_2)

    $1.5\ O_2 + C_2H_7NO \rightarrow 2CH_2O_2 + NH_3$
  - Oxalic Acid

    $2O_2 + C_2H_7NO \rightarrow C_2H_2O_4 + NH_3 + H_2O$
- SO2/MEA reactions:
  - Thiovanic Acid

    $SO_2 + C_2H_7NO \rightarrow C_2H_4O_2S + NH_3 + ½\ O_2$

Other MEA degradation reactions

- Thermally decomposes in reboiler hot spots to ammonia and hydrocarbon
- Reacts with CO2 to form HEED (hydroxyethylethylenediamine) which is a corrosive product
- Forms various heat stable salts in amine reclaimer where caustic or soda ash is added.

Solid Wastes

- Reclaimer sludge – sludge is produced and is handled as a hazardous material requiring off-site disposal
- Spent carbon filter
- Spent cartridge filter

Liquid Streams and Wastes

- **Process condensate sources:**
  - Reflux cooler blowdown, compressor intercoolers, tanks
- **Process condensate recycle users:**
  - Quench cooler, water wash cooler
- **Waste Streams:**
  - Excess process condensate available from coal fired flue gas wet FGD effluent gas cooling
  - Return the excess waste water back to FGD as a makeup water
  - If ion exchange reclaimer is used, more waste water may exist.

Air Emissions

- SOx emission is reduced due to sulfur capture by amine. SOx includes both SO_2 and SO_3
- NOx emission reduction is negligible.
- Amine vapor emissions are classified as VOC which is regulated
- Ammonia vapor emissions produced by decomposition of amines are additional.

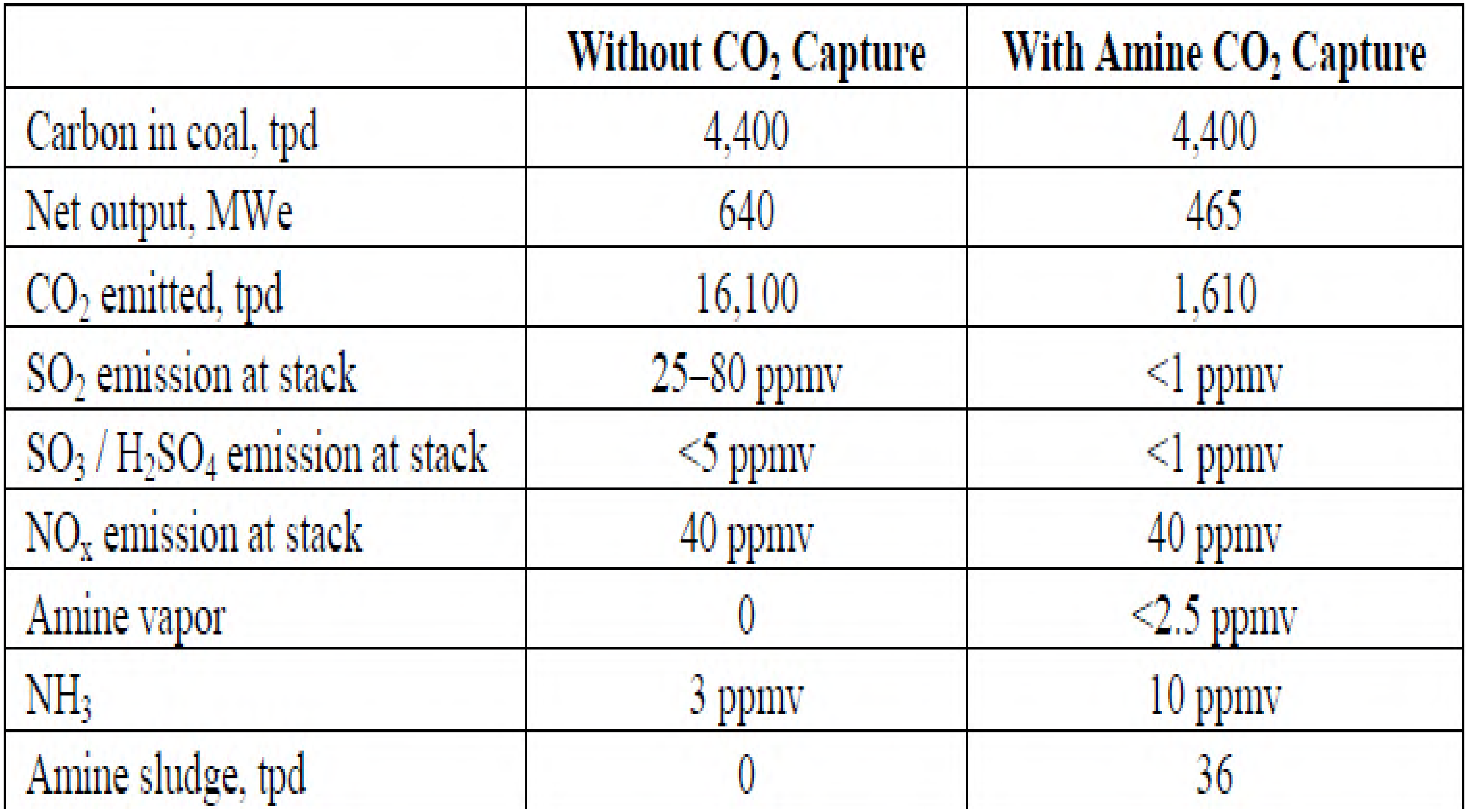
Amine Emissions

- Amine mist controlled by water wash and mist eliminators
- A water wash bed is installed above the absorber beds. The circulation water may be cooled to reduce amine vapor emission, but cooling reduces flue gas temperature and its buoyancy.
- Vapor amine emissions can be calculated by amine software, but entrainment is mainly estimated.

Impacts of Flue Gas Temp on Amine Vapor

Absorber Feed Gas Temp.	Stack Gas Temp	Amine Vapor in Stack Gas, ppmv
107.4 F	147.6 F	1.28
117.4 F	152.8 F	2.03
122.2 F	155.1 F	2.50

Emission Comparison



	Without CO_2 Capture	With Amine CO_2 Capture
Carbon in coal, tpd	4,400	4,400
Net output, MWe	640	465
CO_2 emitted, tpd	16,100	1,610
SO_2 emission at stack	25–80 ppmv	<1 ppmv
SO_3 / H_2SO_4 emission at stack	<5 ppmv	<1 ppmv
NO_x emission at stack	40 ppmv	40 ppmv
Amine vapor	0	<2.5 ppmv
NH_3	3 ppmv	10 ppmv
Amine sludge, tpd	0	36

Conclusions

- Adding CO_2 capture plant improves overall power plant sulfur capture. Residual SO_x is captured by solvent (amine or ammonia)
- Negligible NOx reduction with CO_2 capture. SCR will still be needed in most cases
- Added ammonia emission from thermal, oxygen, and chemical degradation of amine solvents
- Added VOC emissions due to entrained and vaporized amines.
- High ammonia emissions have been experienced at a demo plant

Conclusions (continued)

- Carbon capture plant may achieve water balance with little waste water or makeup
- Any waste water can be exported to wet FGD as a makeup to the FGD system
- Making stack gas hotter to vaporize excess water, if any.
- Reclaimer sludge is considered a hazardous waste and requires offsite disposal
- Power plant permits must take into account the additional wastes and emissions created by CCS

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Pilot Plant Approach for Scale Up of CO2 Capture Process Using Amine Solvents

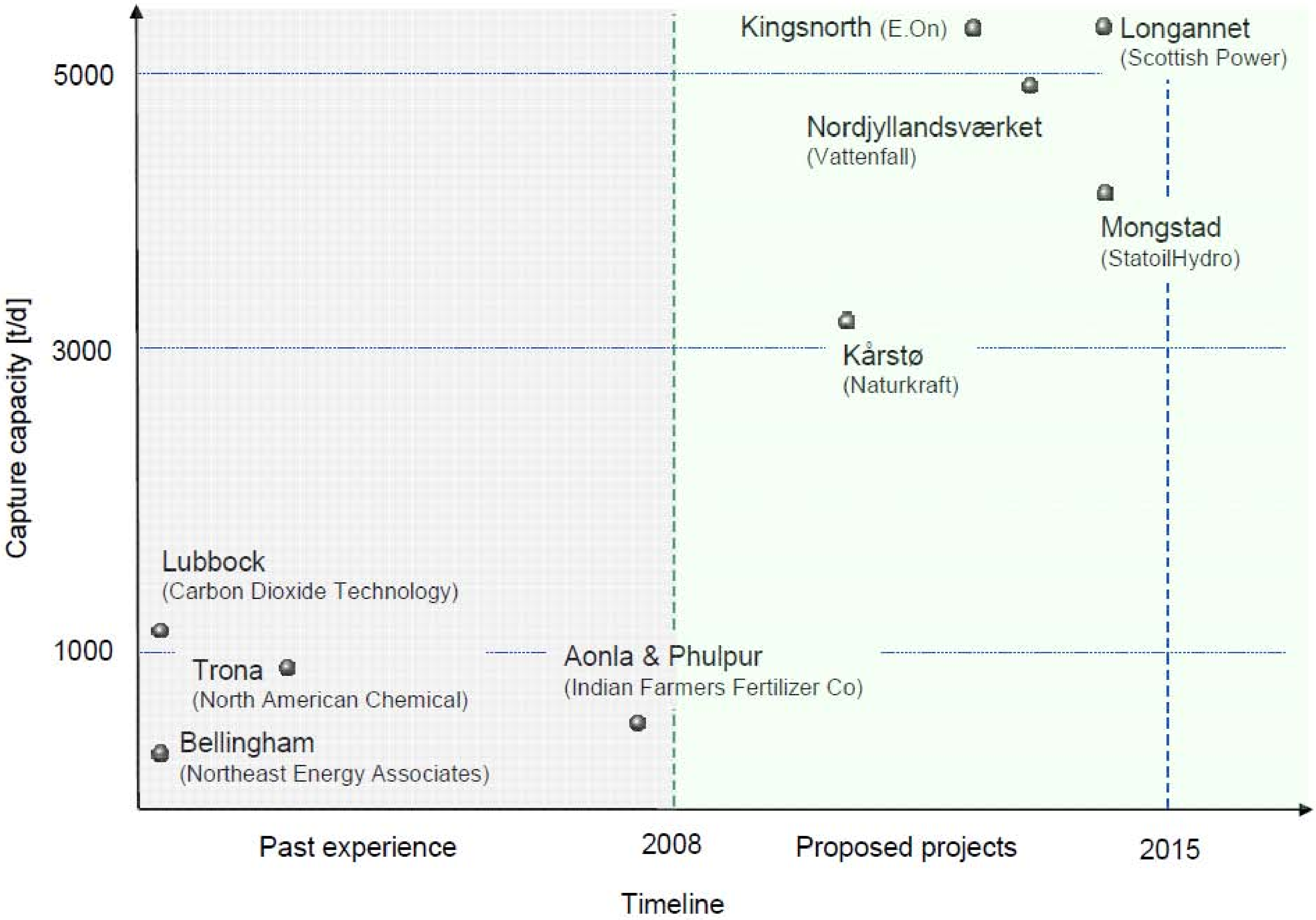
Ahmed Aboudheir & Mohamed Elgarni
Paitoon Tontiwachwuthikul, Raphael Idem

12th Meeting
of the
International Post – Combustion CO_2 Capture Network

29th September – 1st October 2009, Regina, Canada

IEA GREENHOUSE GAS R&D PROGRAMME

Commercial post-combustion CO_2 Capture Plants; experienced & proposed



Source (Kim Johnsen ea al., Energy Procedia 1, 2009, P163)

Scale up ratios

$$\text{Scale up ratio} = \frac{\text{commercial production rate}}{\text{pilot production rate}}$$

- From bench scale (laboratory) to pilot plant: 500 - 1000
- Pilot plant to commercial units: 200 - 500
- Scale-up rations proposed projects to existing: 3 - 8

Methods available to scale up

- Brute force
- Rate based modeling
- Technology qualification
  - Combines measurement, mathematical modeling, piloting and demonstration experiences

Brute Force vs. Rate Modeling

Commercial scale	Impact on Performance & Operation	Brute force	Pilot plant + models, HTC Approach
Feed quality		Same	Same
Diameter	Avoid flooding & achieve excellent distribution	Smaller	Smaller
Height	Separation efficiency	Same	Smaller
Packing size	Separation efficiency & pressure drop	Same	Smaller
Packing type	Separation efficiency & effective surface area not geometric area should be the same, Pressure drop	same	same
velocities	Related to flow rates & diameter	Same	Smaller
Gas & liquid flow rates	Good packing wetting & avoid flooding	Smaller	Smaller
Fluid entrance locations		Same	Same as model
Gas & liquid distribution	Vital in securing absorber performance by providing enough contact between gas & solvent	Good – avoid wall Flow/Channeling – maintain required packing wetting	Good – avoid wall Flow - Channeling
Pressure drop	Energy consumption – influence flooding phenomenon	Same	Smaller provided packed bed density comparable – no impact

HTC Modeling and Scale up Approach

- Scaling up strategy is based on building comprehensive rate based models

- In-house developed rigorous computer models

- Creating models using commercially available software`s, but modified to account for sound thermodynamics, kinetics and hydraulic models

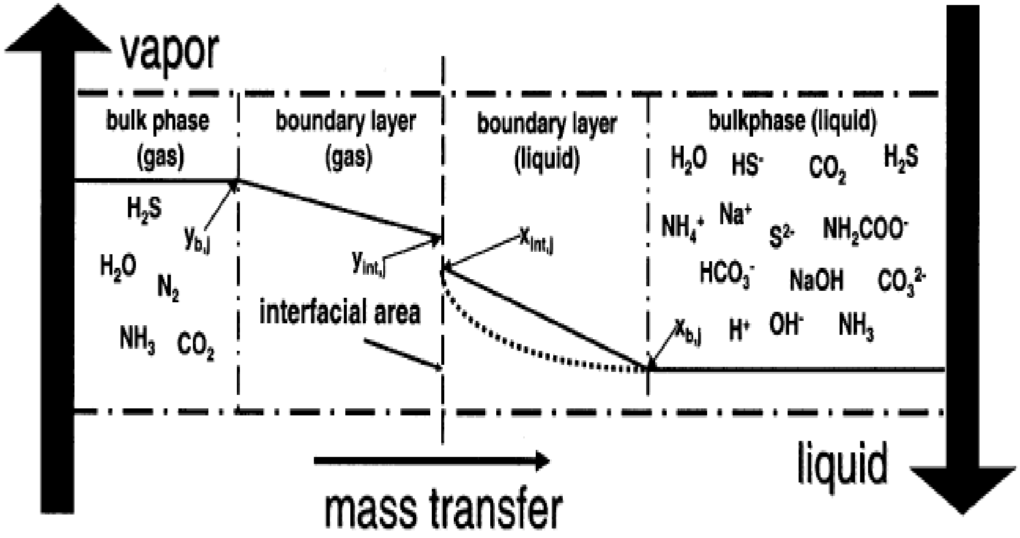
- These rate models are validated using laboratory, pilot plant and commercial plant scales

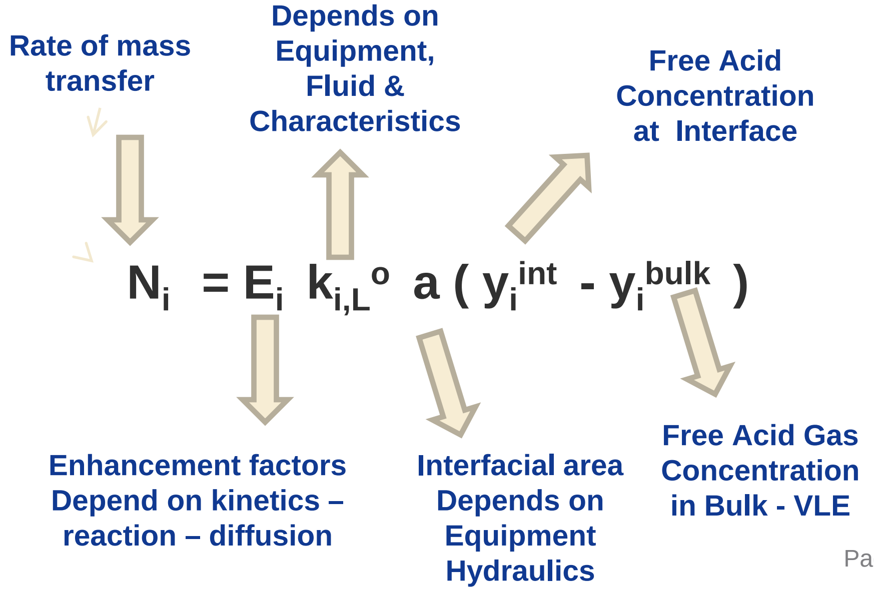
Absorption Column Design

- Column Design
  - Hydrodynamics (a)
  - Mass transfer coefficients
  - Physical & Chemical Equilibria
  - Enhancement by reaction Kinetics

- High prediction accuracy based on fundamentals and empirically generated correlations for (a, k_L, k_g, enhancement and kinetics)

- Reactive absorption is inherently operating under non-equilibrium conditions and hence – rate based model is a must





Rate of mass transfer

Depends on Equipment, Fluid & Characteristics

Free Acid Concentration at Interface

$$N_i = E_i \, k_{i,L}^o \, a \, (y_i^{int} - y_i^{bulk})$$

Enhancement factors Depend on kinetics – reaction – diffusion

Interfacial area Depends on Equipment Hydraulics

Free Acid Gas Concentration in Bulk - VLE

Plant Design & Numerical Modeling, PDEs

$$\frac{\partial C_i}{\partial t} + v_z \frac{\partial C_i}{\partial z} = D\left(\frac{\partial^2 C_i}{\partial r^2} + \frac{1}{r}\frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial z^2}\right) + \rho_B r_j$$

$$\rho_g C_P\left(\frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z}\right) = \lambda\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2}\right) + \rho_B\left[\sum -\Delta H_j r_j\right]$$

$$\rho_g\left(\frac{\partial v_z}{\partial t} + v_z \frac{\partial v_z}{\partial z}\right) = -\frac{\partial P}{\partial z} + \mu\left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2}\right] + \rho_g g_z$$

$$-\frac{dP}{dz} = \frac{\rho_g v_Z^2}{d_p}\frac{1-\varepsilon}{\varepsilon^3}\left[1.75 + \frac{150(1-\varepsilon)}{\mathrm{Re}}\right]$$

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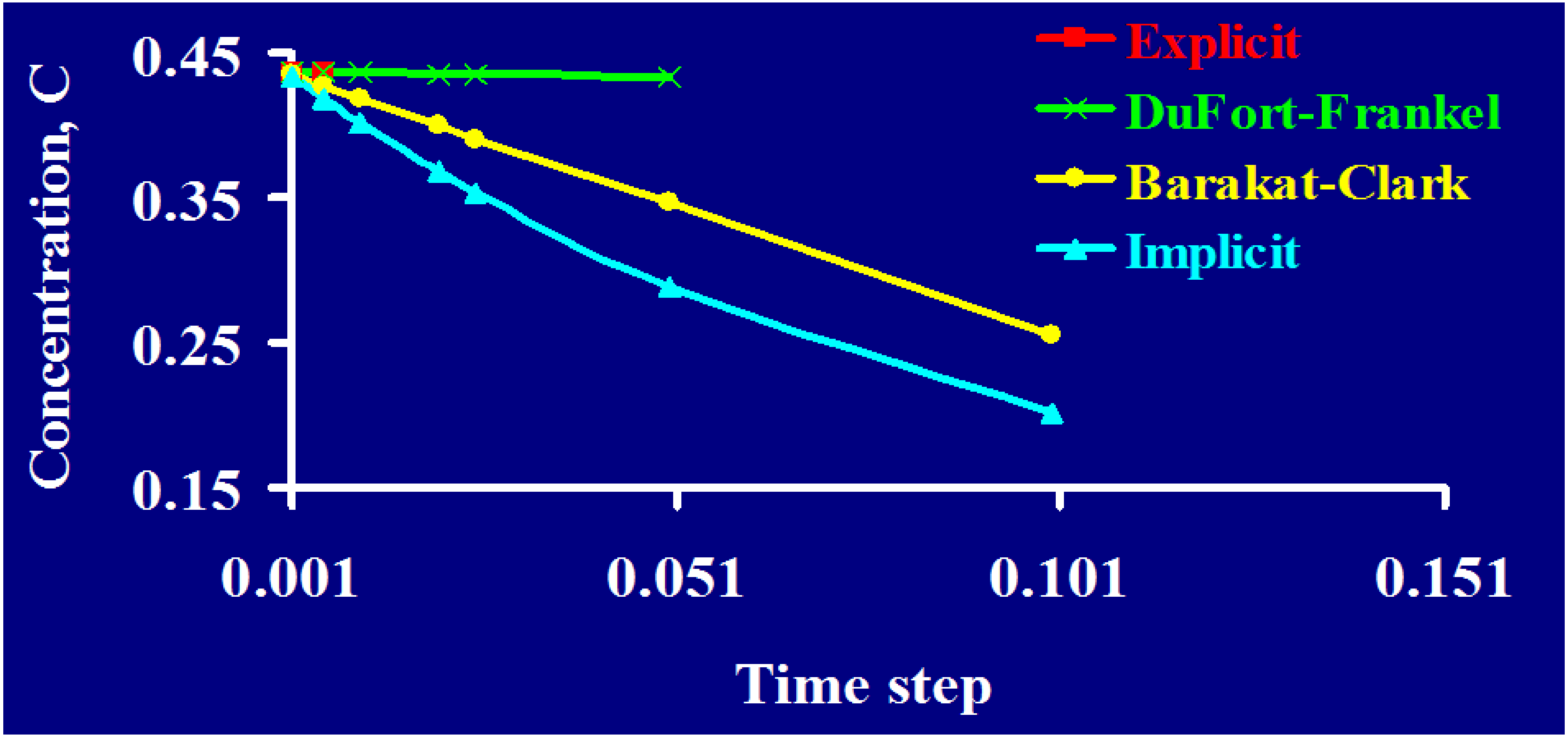
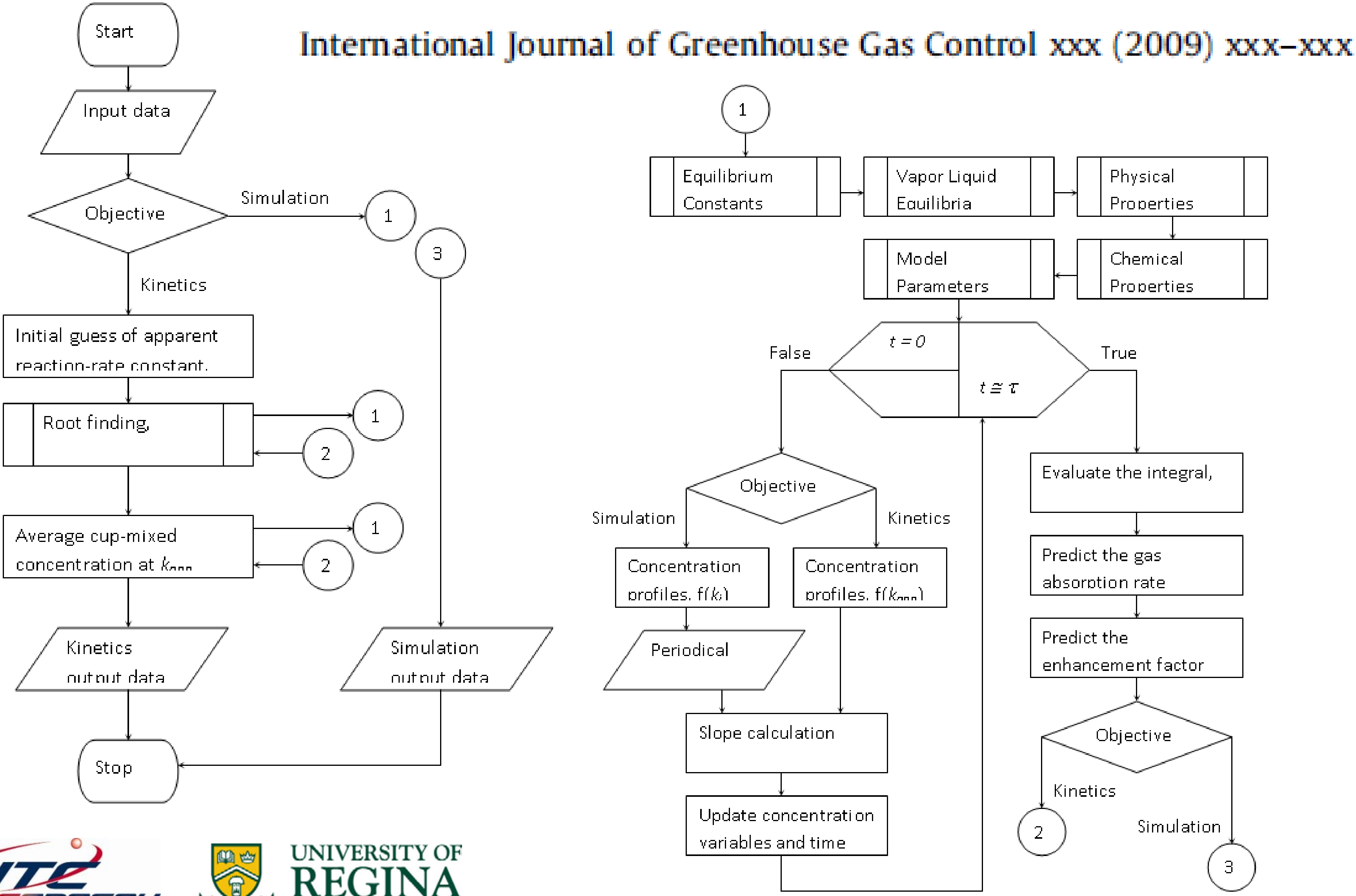
Finite-difference Methods for solving PDEs

Effect of time step on concentration profiles at time = 1 and grid interval = 0.1



Flowchart for absorption rate, enhancement factor, and kinetics models; single & mixed amines


International Journal of Greenhouse Gas Control xxx (2009) xxx–xxx

Plant Design & Numerical Modeling, ODEs

Ind. Eng. Chem. Res. **2006,** 45, 2553−2557

- Concentration gradients

$$\frac{dY_A}{dZ} = \frac{-k_{GA}a_e P\left(y_A - y_{Ai}\right)}{G_B} \qquad \frac{dY_S}{dZ} = \frac{-k_{GS}a_e P\left(y_S - y_{Si}\right)}{G_B}$$

- Temperature gradients

$$\frac{dT_G}{dZ} = \frac{-h_G a_e\left(T_G - T_L\right)}{G_B\left(C_{PB} + Y_A C_{PA} + Y_S C_{PS}\right)}$$

$$\frac{dT_L}{dZ} = \frac{\left(G_B\left(C_{PB} + Y_A C_{PA} + Y_S C_{PS}\right)\frac{dT_G}{dZ} + G_B\left(C_{PS}\left(T_G - T_0\right) + \lambda_S\right)\frac{dY_S}{dZ} + G_B\left(C_{PA}\left(T_G - T_0\right) - \Delta H_R\left(T_0, P\right)\right)\right)}{L_M C_{PL}}$$

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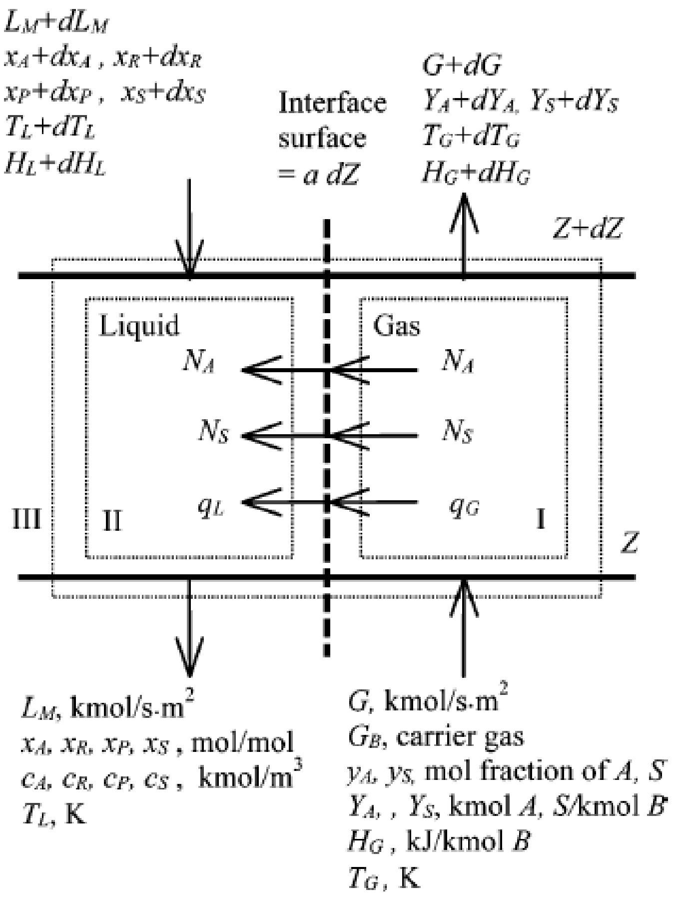
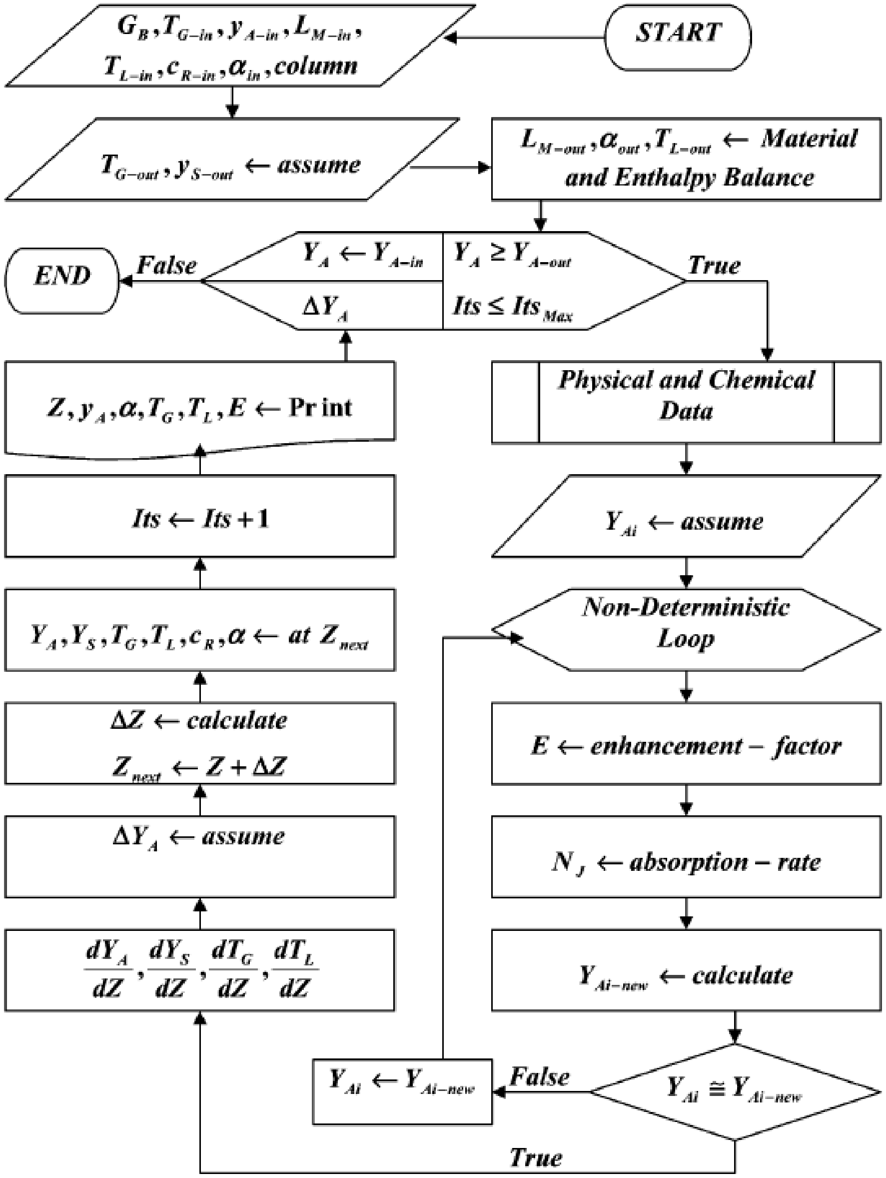
Flowchart for the CO2-amine simulation model based on shooting method of solution.

Ind. Eng. Chem. Res. **2006,** *45,* 2553−2557

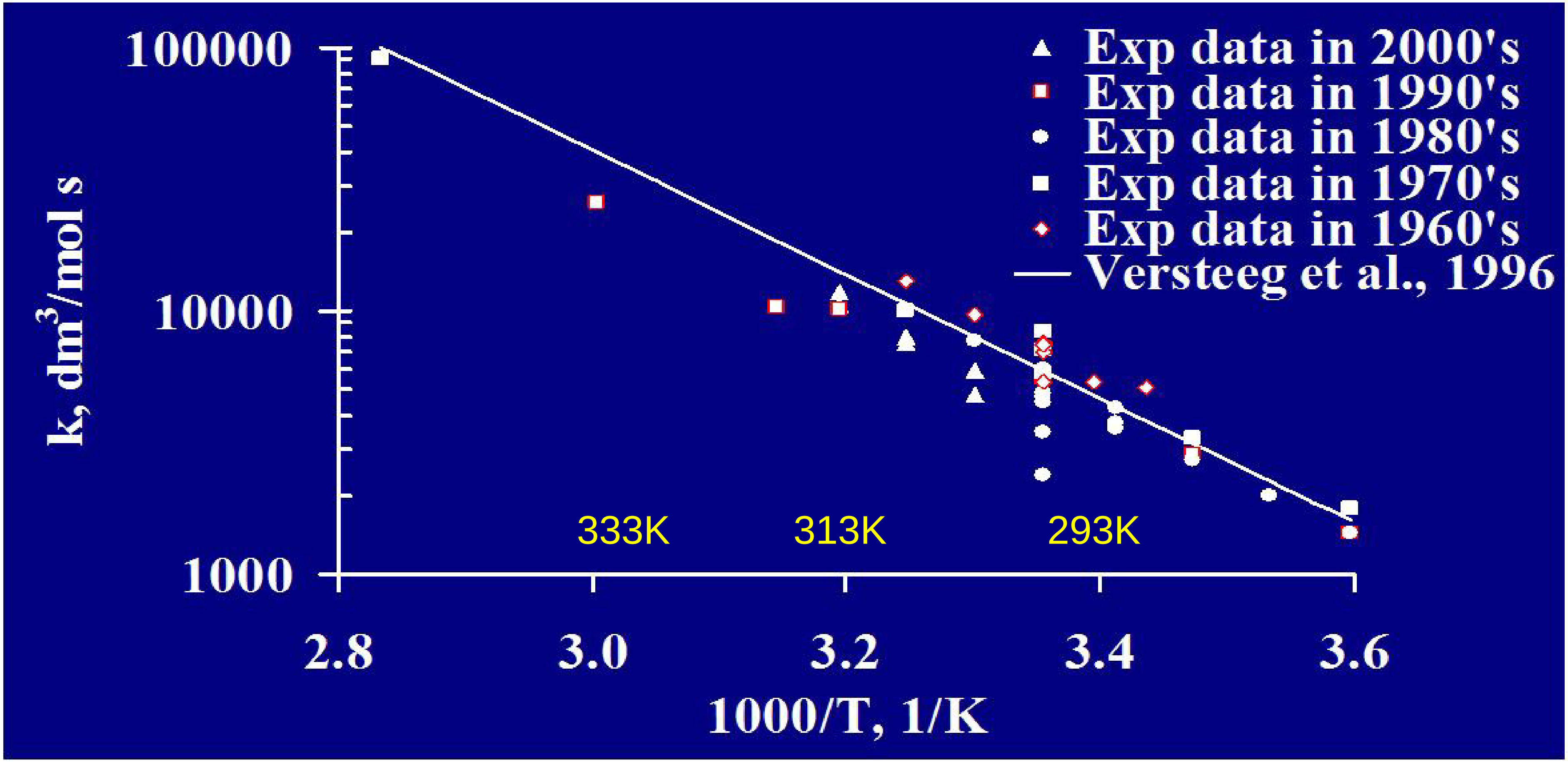




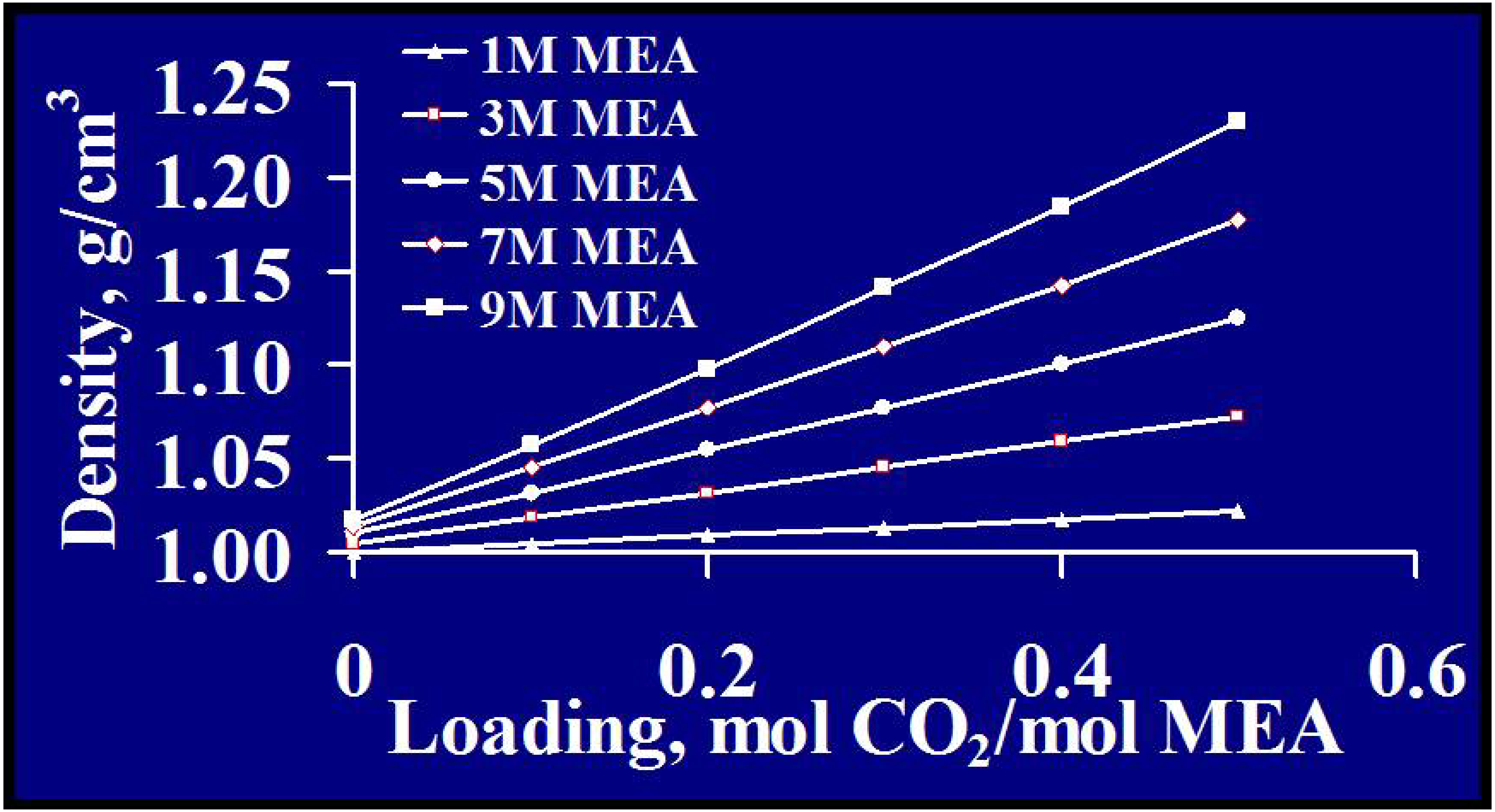
Key data for design and simulation of CO_2 Capture Process

- Physical properties
  - –Density, Viscosity, Solubility, Diffusivity, Surface Tension, etc
- Chemical Properties
  - –VLE data, Reaction Rate, Heat of reaction & mixing, etc
- Operation Conditions
  - –Temperature, pressure, flow rates, Concentration, etc
- Boundary Conditions of the Process
  - –Inlet, outlet, geometry, etc

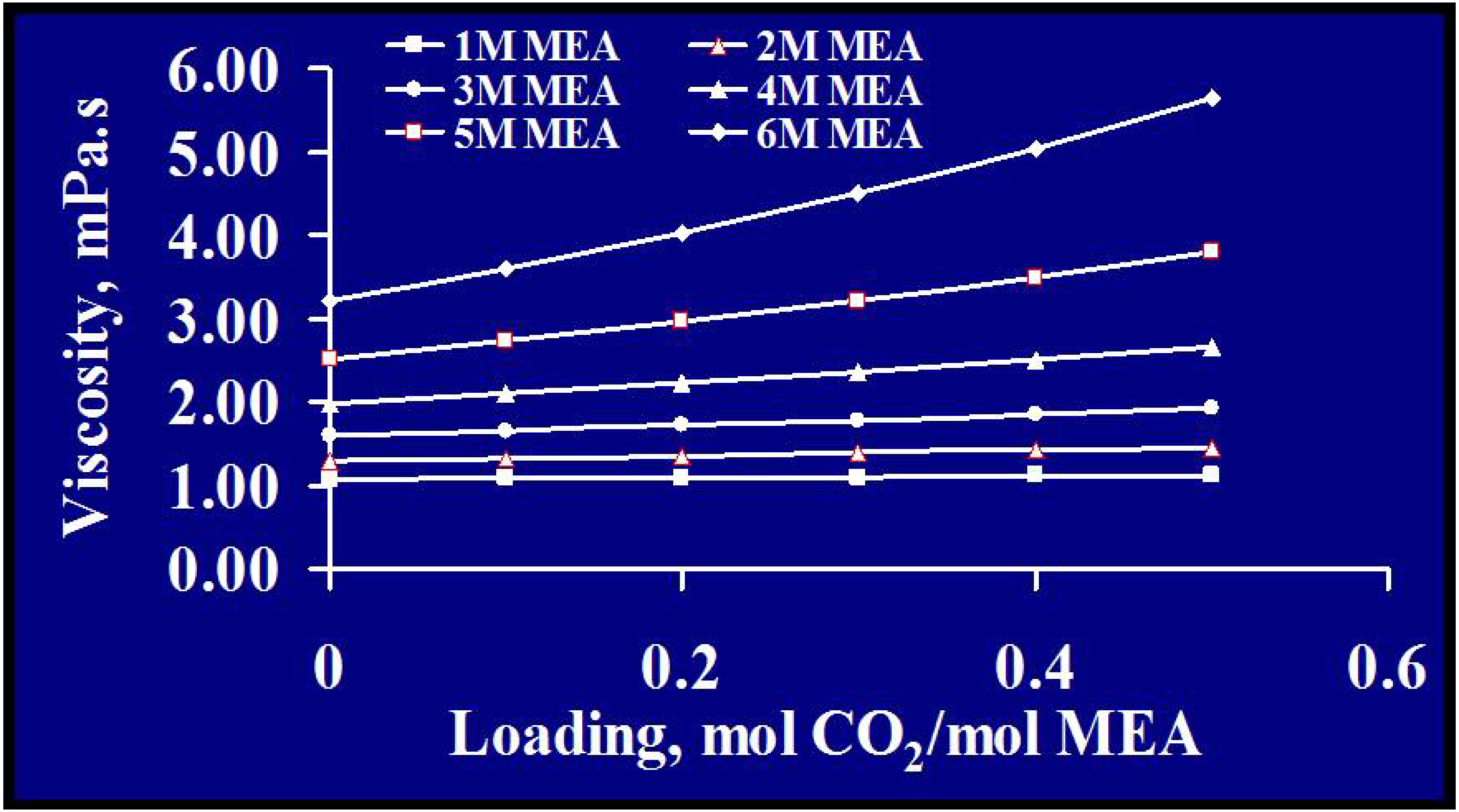
Arrhenius plot for the reaction between CO_2 and MEA solution



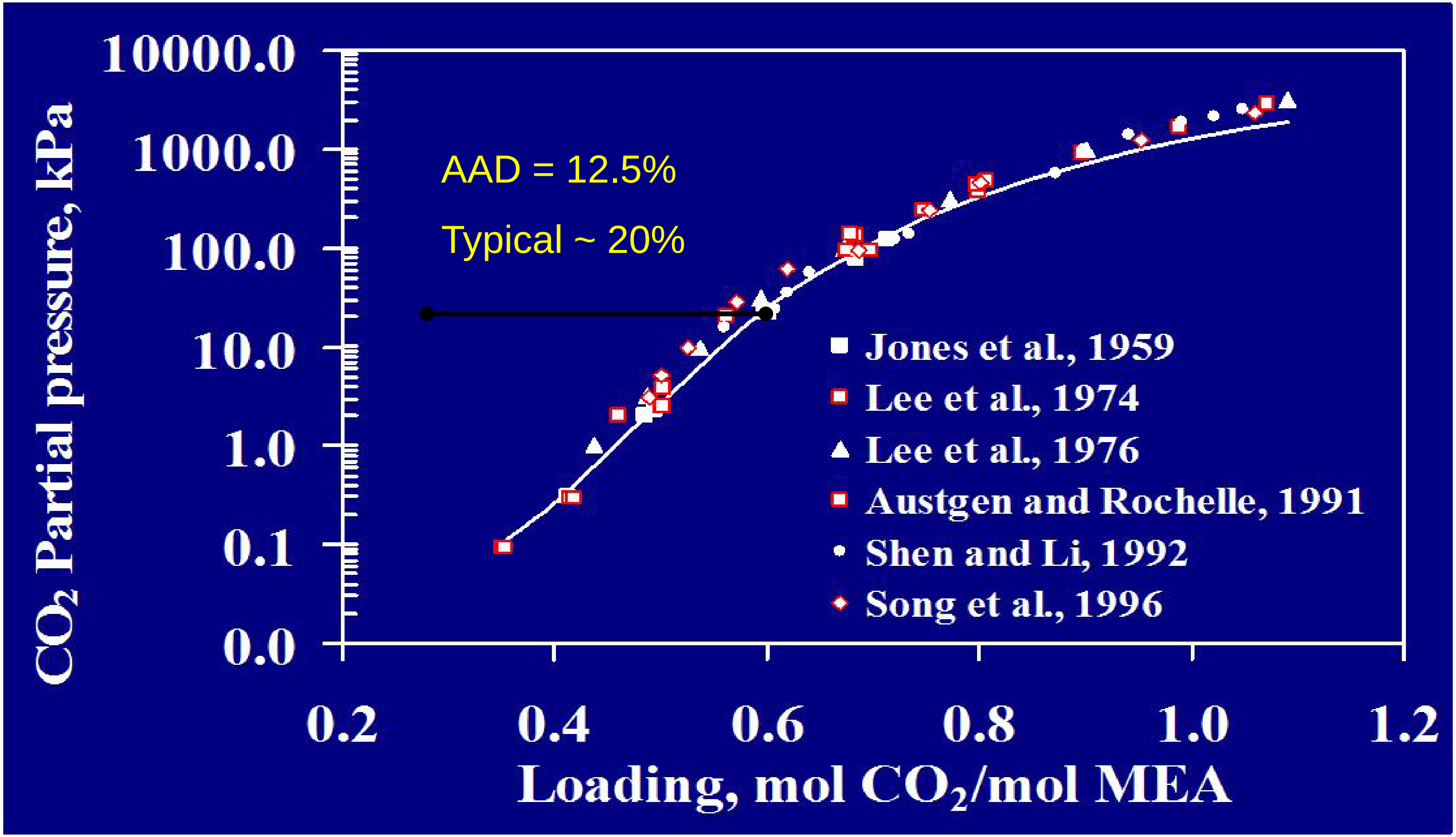
Density at 298 K



Viscosity at 298 K



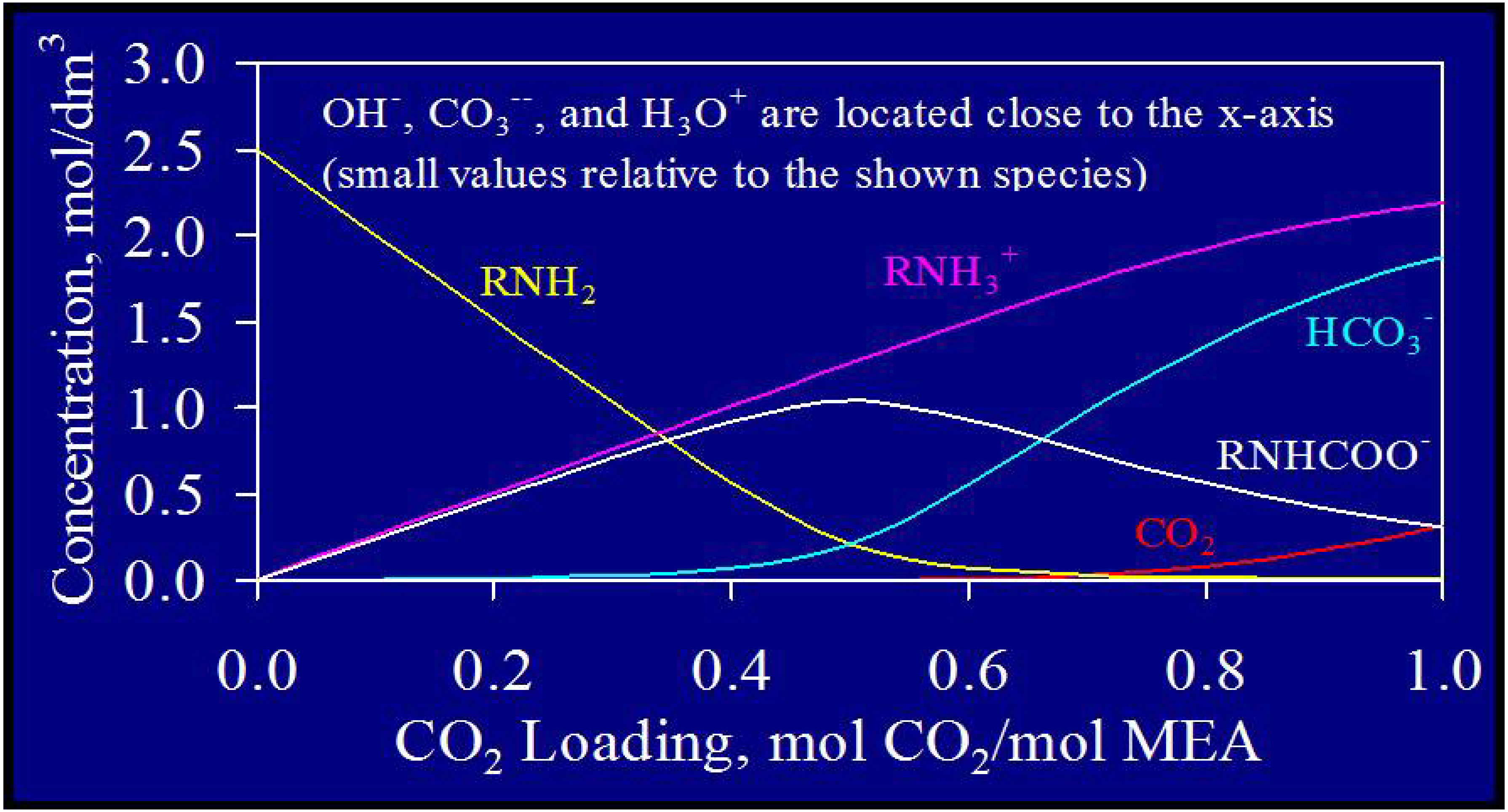
VLE model results: P_{CO2}



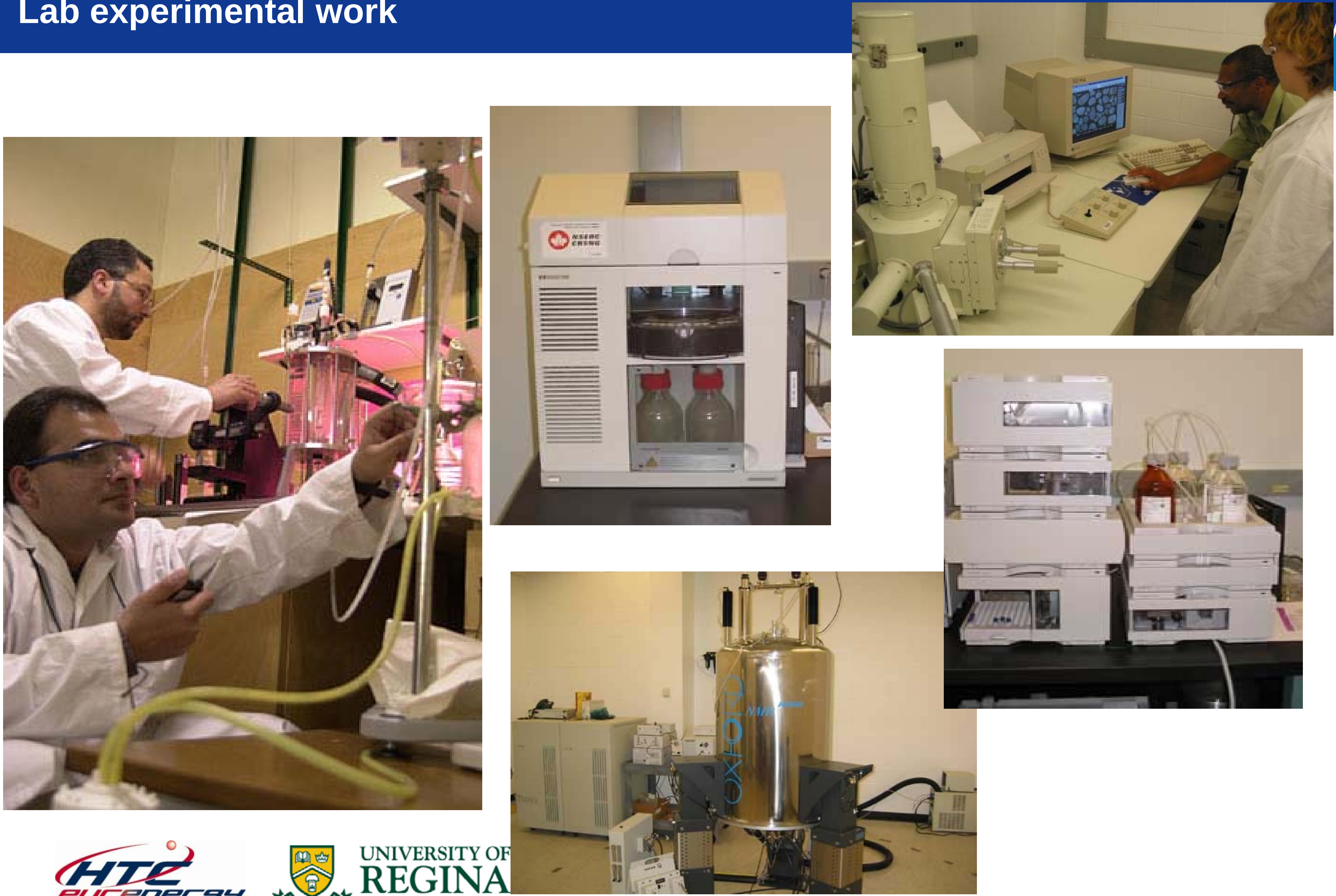
AAD = 12.5%

Typical ~ 20%

VLE model results: Composition



Lab experimental work



HTC Purenergy

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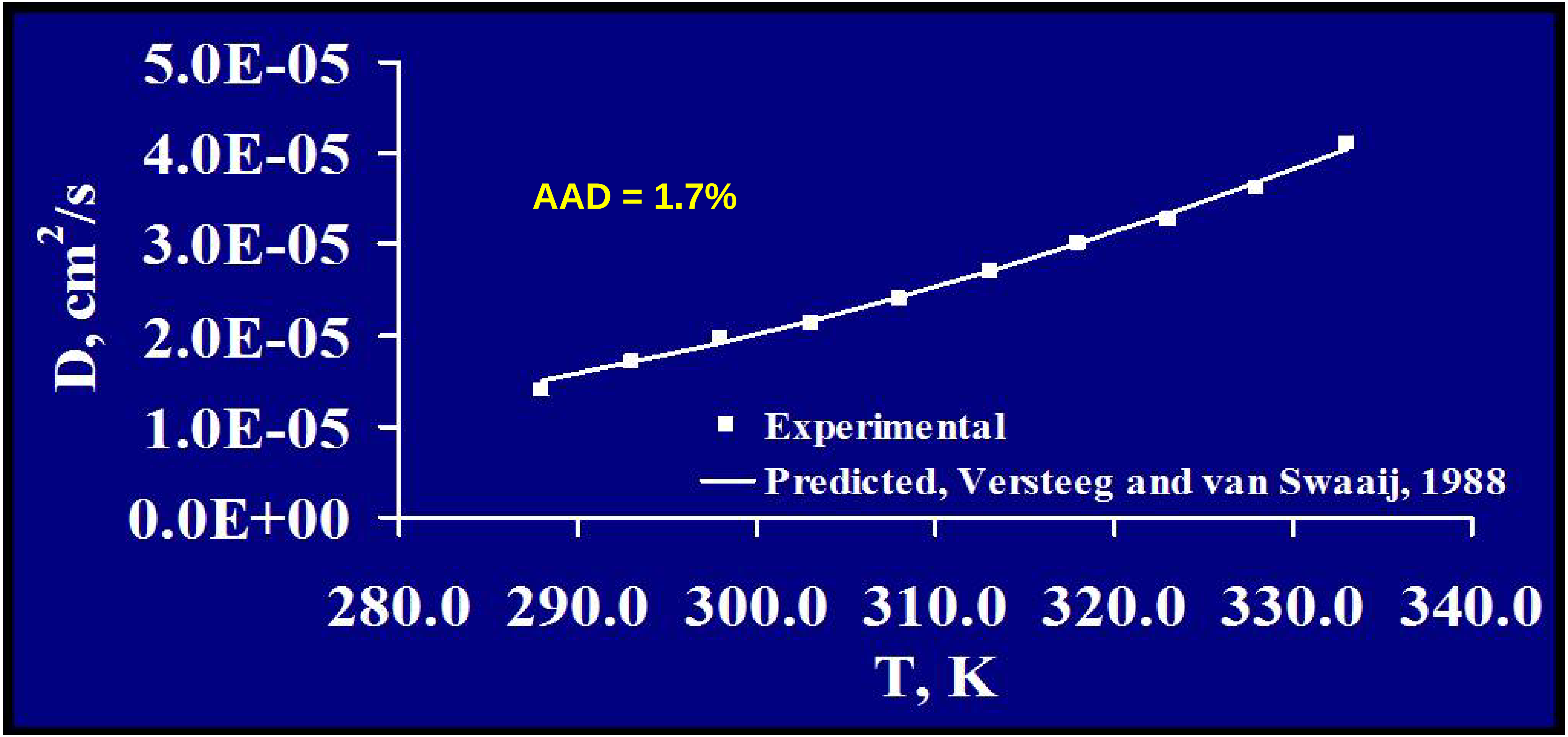
Diffusivity of CO_2 in water as a function of temperature



HTC Purenergy CARBON CLEAR SOLUTIONS

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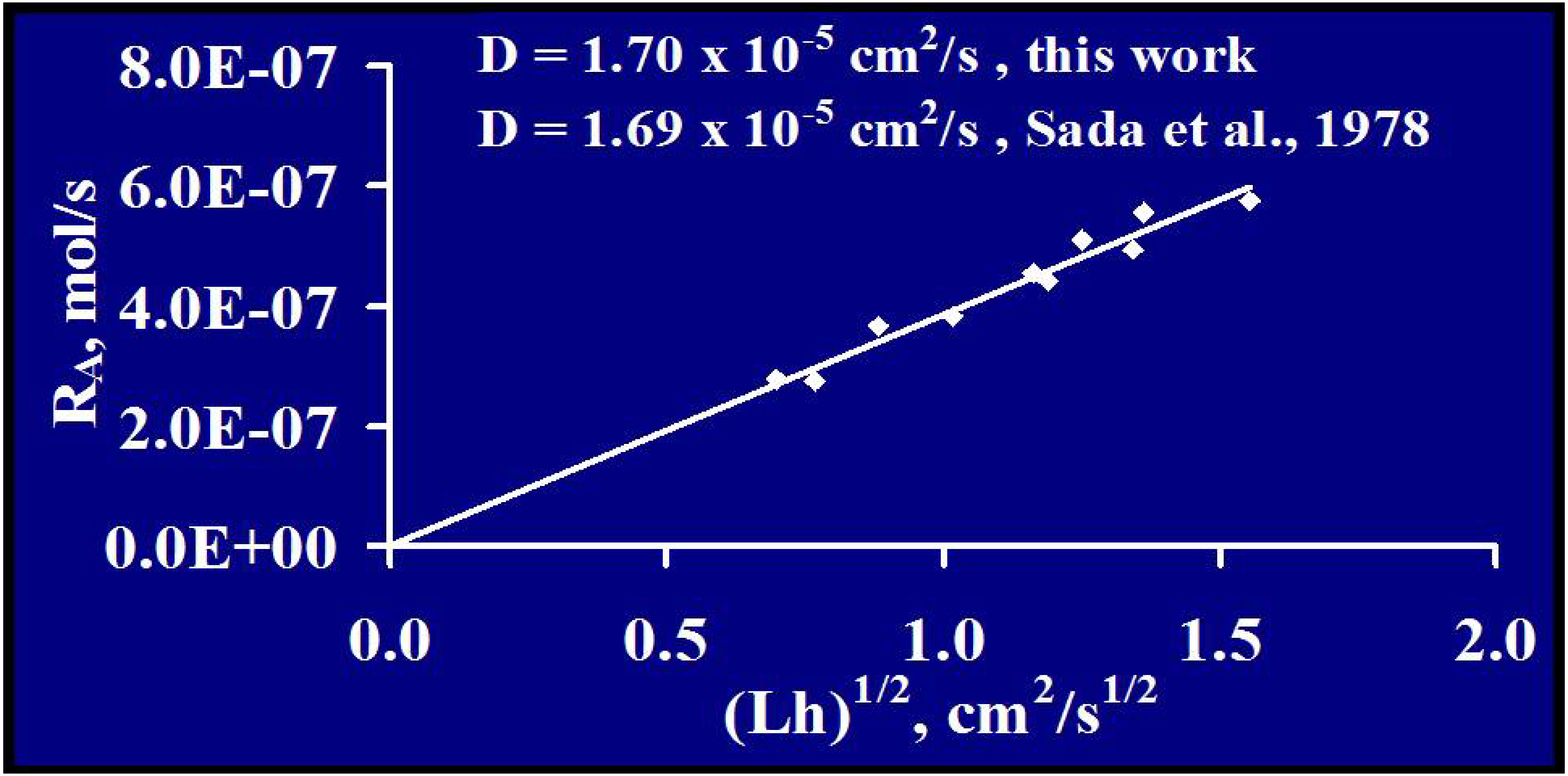
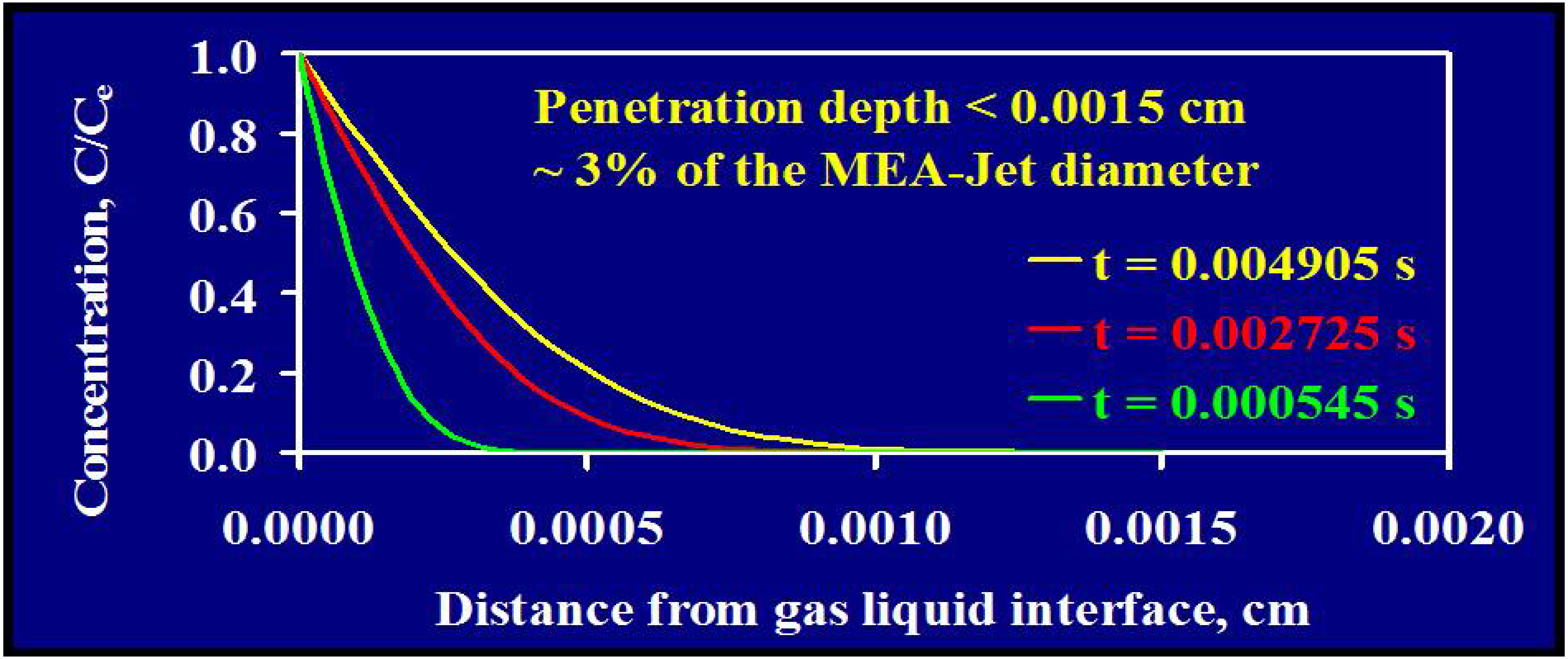
Diffusivity of N_2O in 1M-MEA at 298K



$D = 1.70 \times 10^{-5}$ cm^2/s, this work

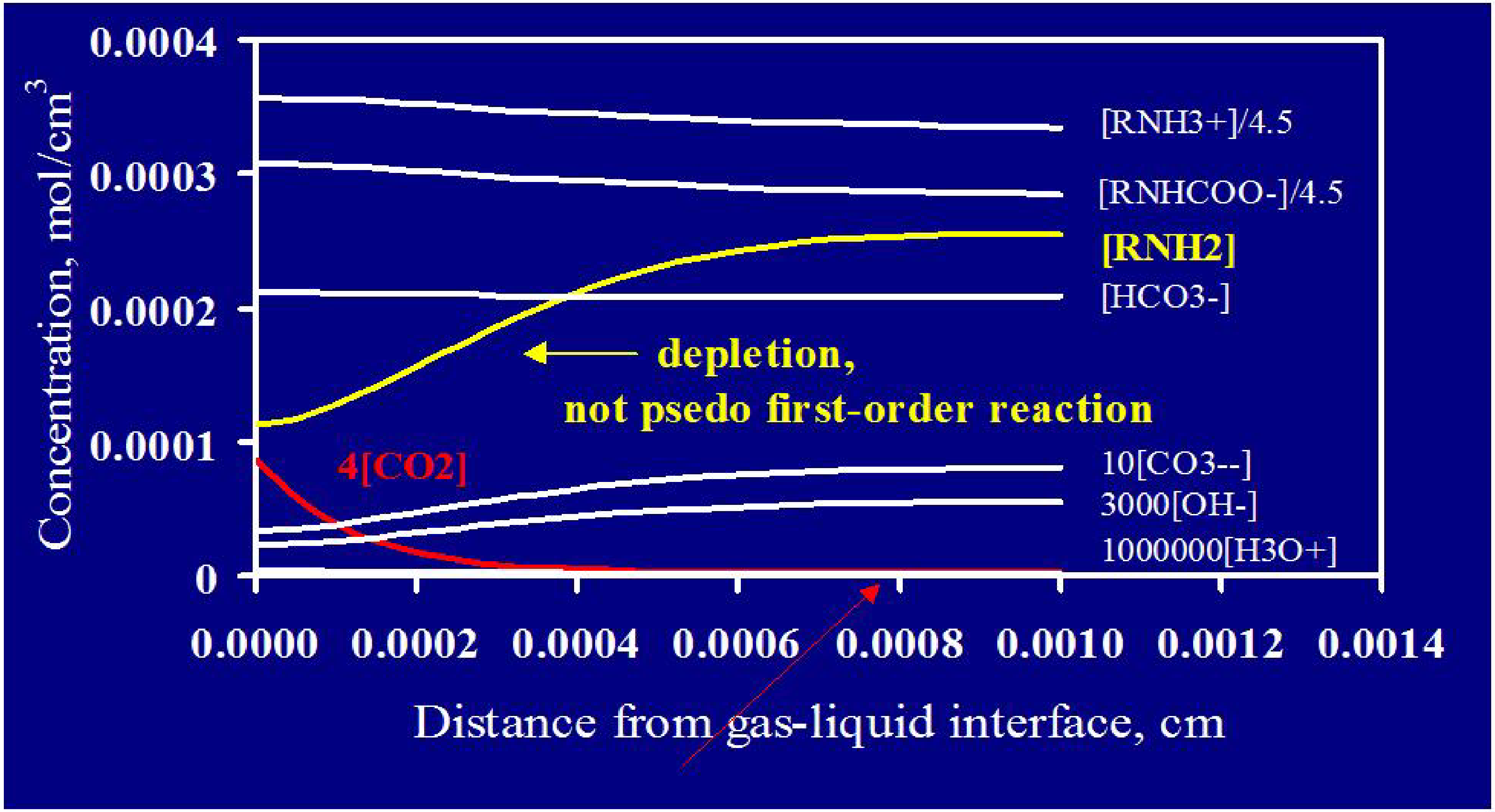
$D = 1.69 \times 10^{-5}$ cm^2/s, Sada et al., 1978

N_2O absorption into 1M-MEA-jet at 298K



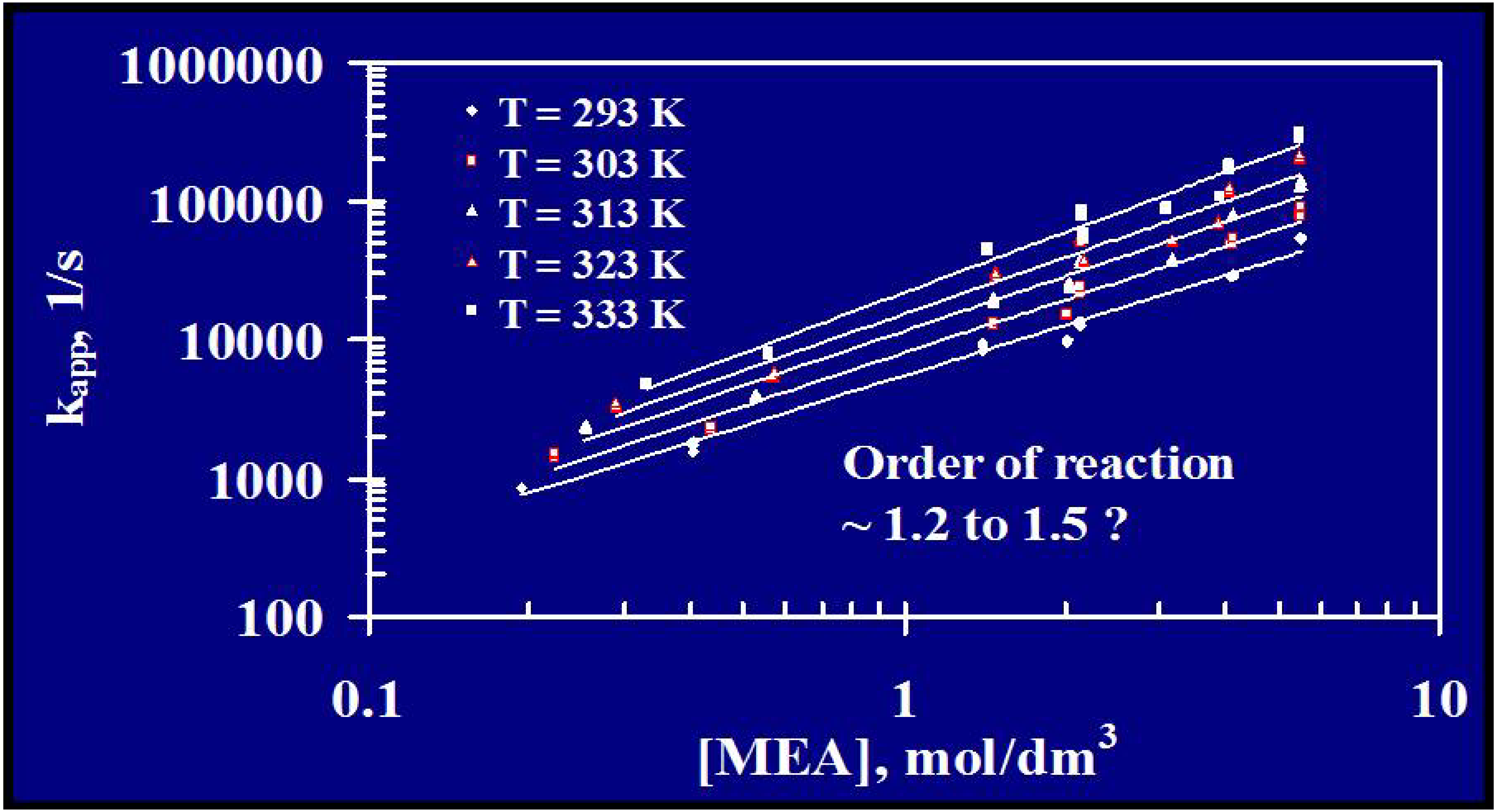
Concentration Profiles: CO_2-MEA

3M-MEA, Loading=0.49, P_{CO2}=88kPa, t=0.0097s, T=313K



Penetration depth < 0.0008 cm
< 1.5% of the MEA-Jet diameter

Kinetics Data for CO_2 Reaction with MEA Solutions



A New Termolecular-Kinetics Model

Chemical Engineering Science 58 (2003) 5195–5210

$$r = -\left(k_{RNH_2}[RNH_2] + k_{H_2O}[H_2O]\right)\left([RNH_2][CO_2] + \frac{1}{K_{RNH_2}}[RNHCOO^-][H_3O^+]\right)$$

$$k_{RNH_2} = 4.61 \times 10^9 \exp\left(\frac{-4412}{T}\right)$$

$$k_{H_2O} = 4.55 \times 10^6 \exp\left(\frac{-3287}{T}\right)$$

Application range:

- T = 293 to 333K
- Loading = 0.007 to 0.49 mol /mol
- MEA = 3.0 to 9.0 M

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University of Regina Pilot Plant

• Column height	2.4 m
• Column Diameter	0.101 m
• Packing	
– Column -1	IMTP # 15
– Column-2	Pall Rings-16mm
– Column-3	A4-structured
• Solvent	MEA, 3 to 9 M
• Loading	0.08 to 0.36 mol/mol
• CO2 Concentration	5 to 20 %

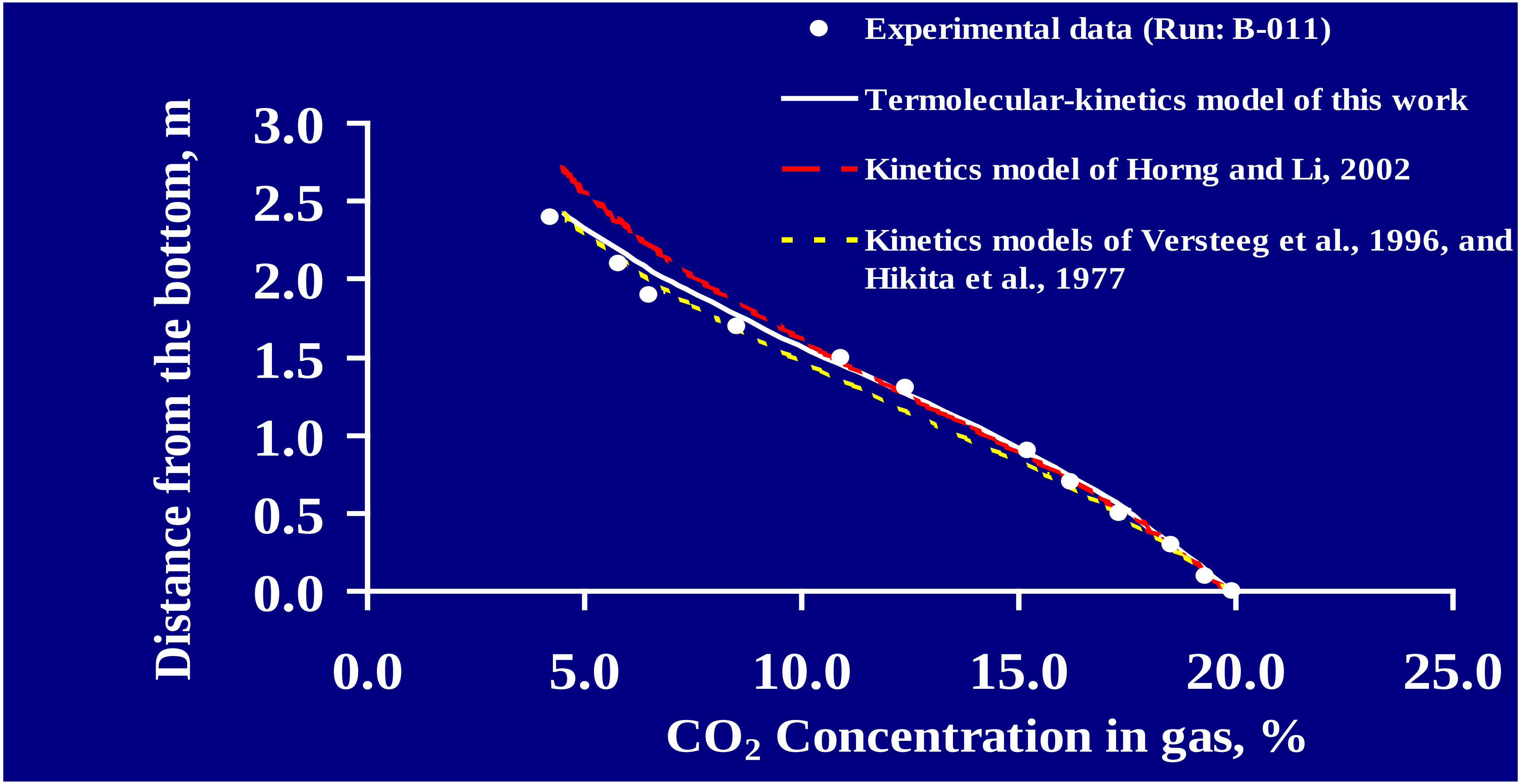
Detailed operation conditions can be found in:

1998 SPE Gas Technology Symposium.

Calgary, Alberta, Canada, 14-18 March 1998

Measured and Predicted Profiles using Various Kinetics Models

CHEMINDIX 2007
CCU/09



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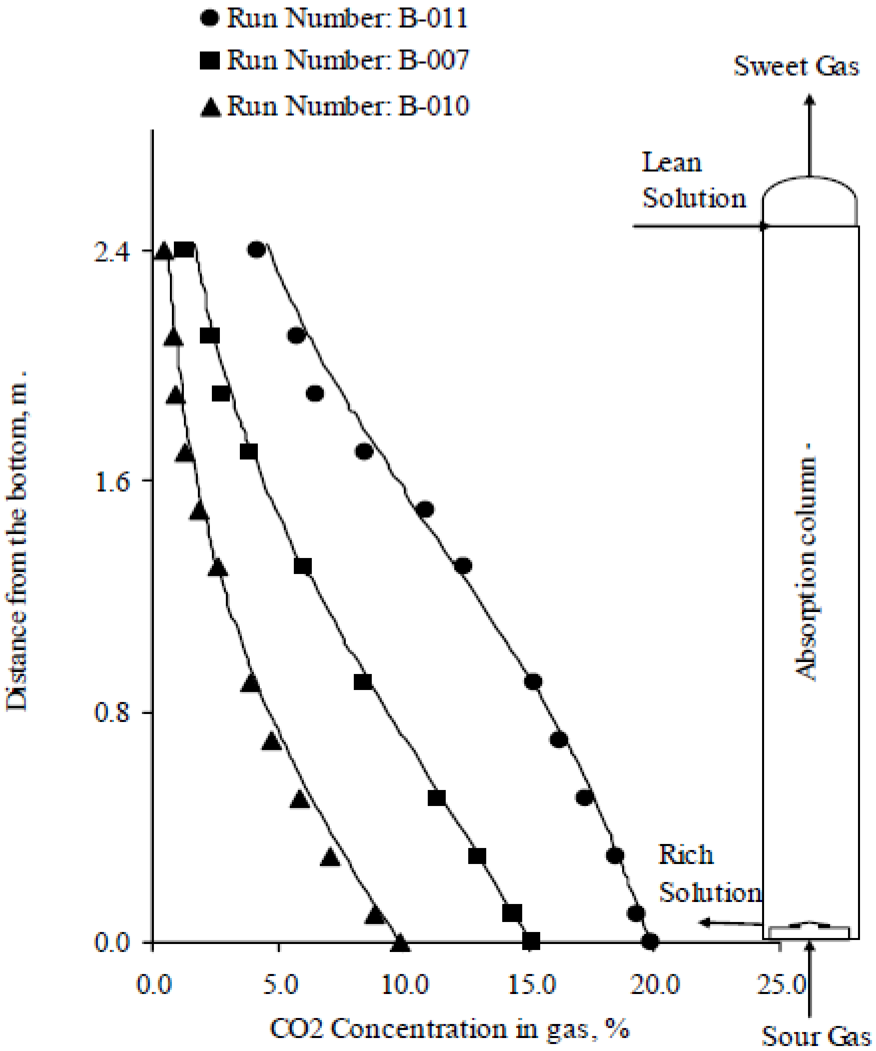
Measured and predicted CO2 concentration profiles along the packed column at various operating conditions



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Modelling the Performance of a CO2 Absorber; Structured Packing

Ind. Eng. Chem. Res. **2006,** *45,* 2594−2600

$$k_G = 0.0338\left(\frac{D_G}{d_h}\right)\left(\frac{\rho_G u_G d_h}{\mu_G \cos 45°}\right)^{0.8}\left(\frac{\mu_G}{\rho_G D_G}\right)^{0.33}$$

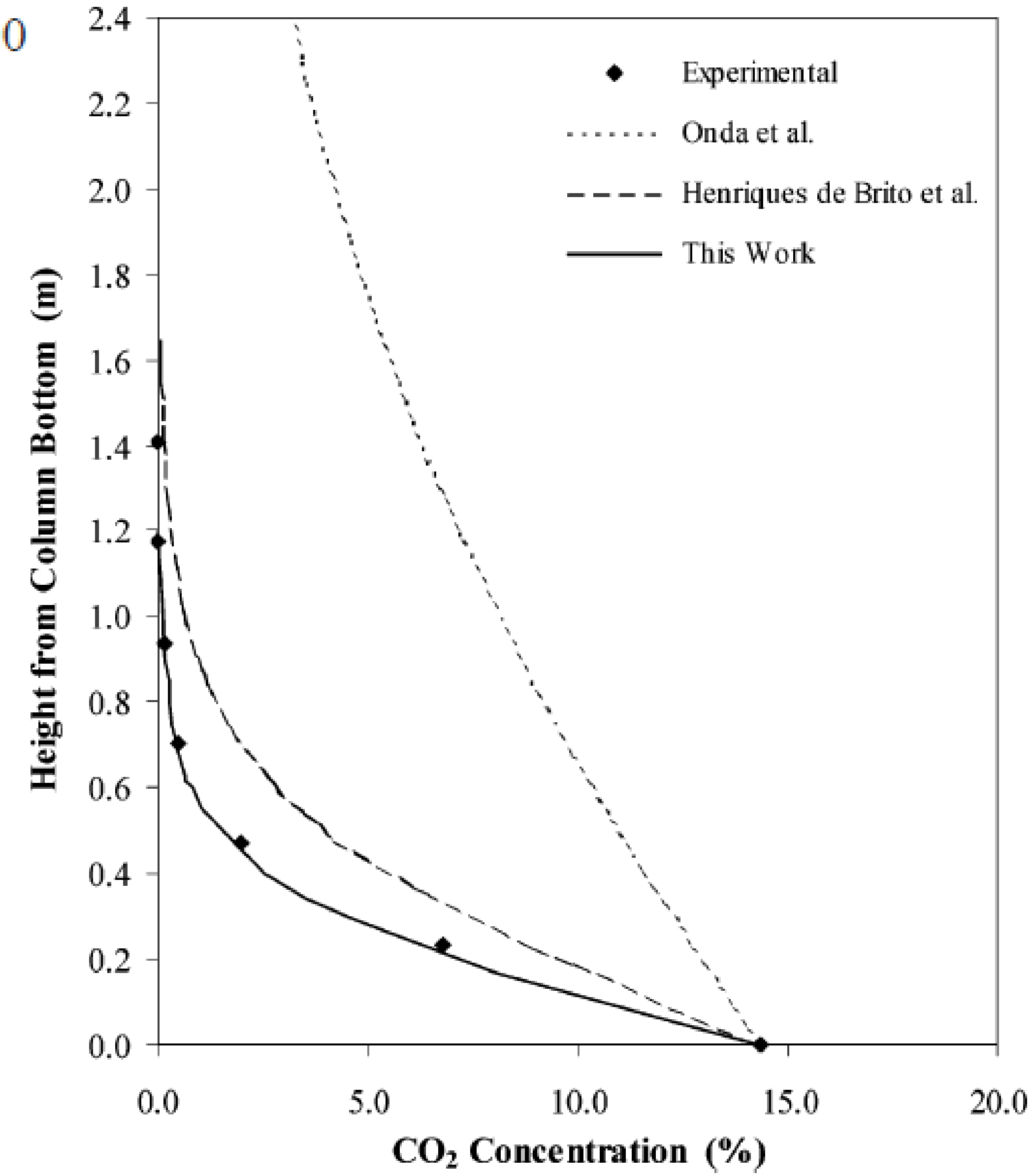
$$k_L = \frac{(D_L k_2 C_{A,L})^{0.5}}{Ha}$$

original Henriques de Brito: $$\frac{A_e}{A_T} = 0.465\left(\frac{\rho_L u_L}{A_T \mu_L}\right)^{0.3}$$

(Sulzer Mellapak)

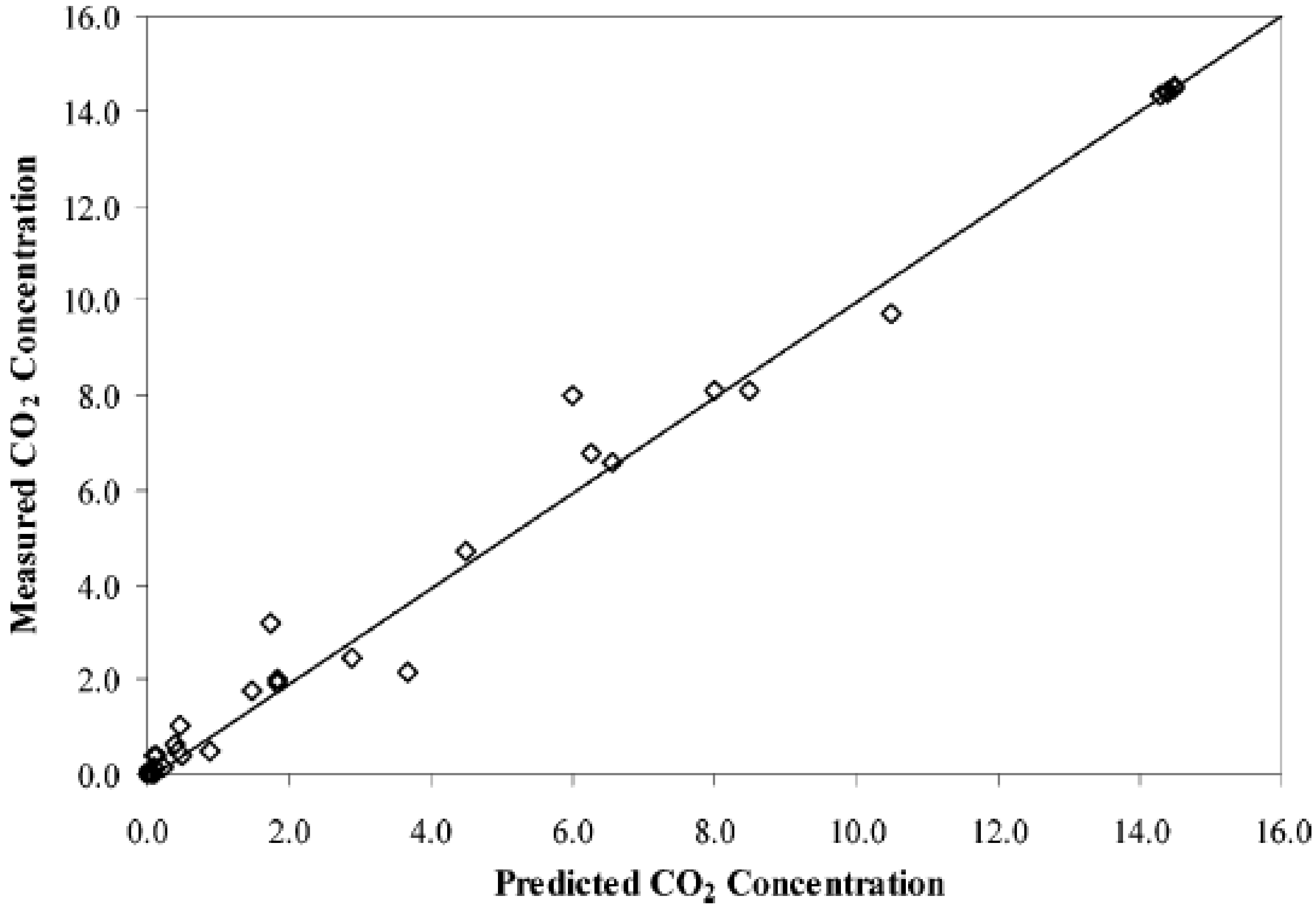
modified Henriques de Brito: $$\frac{A_e}{A_T} = 0.759\left(\frac{\rho_L u_L}{A_T \mu_L}\right)^{0.254}$$

(Sulzer DX)



Parity plot for 6 packed column runs at different operating conditions

Ind. Eng. Chem. Res. **2006,** *45,* 2594−2600

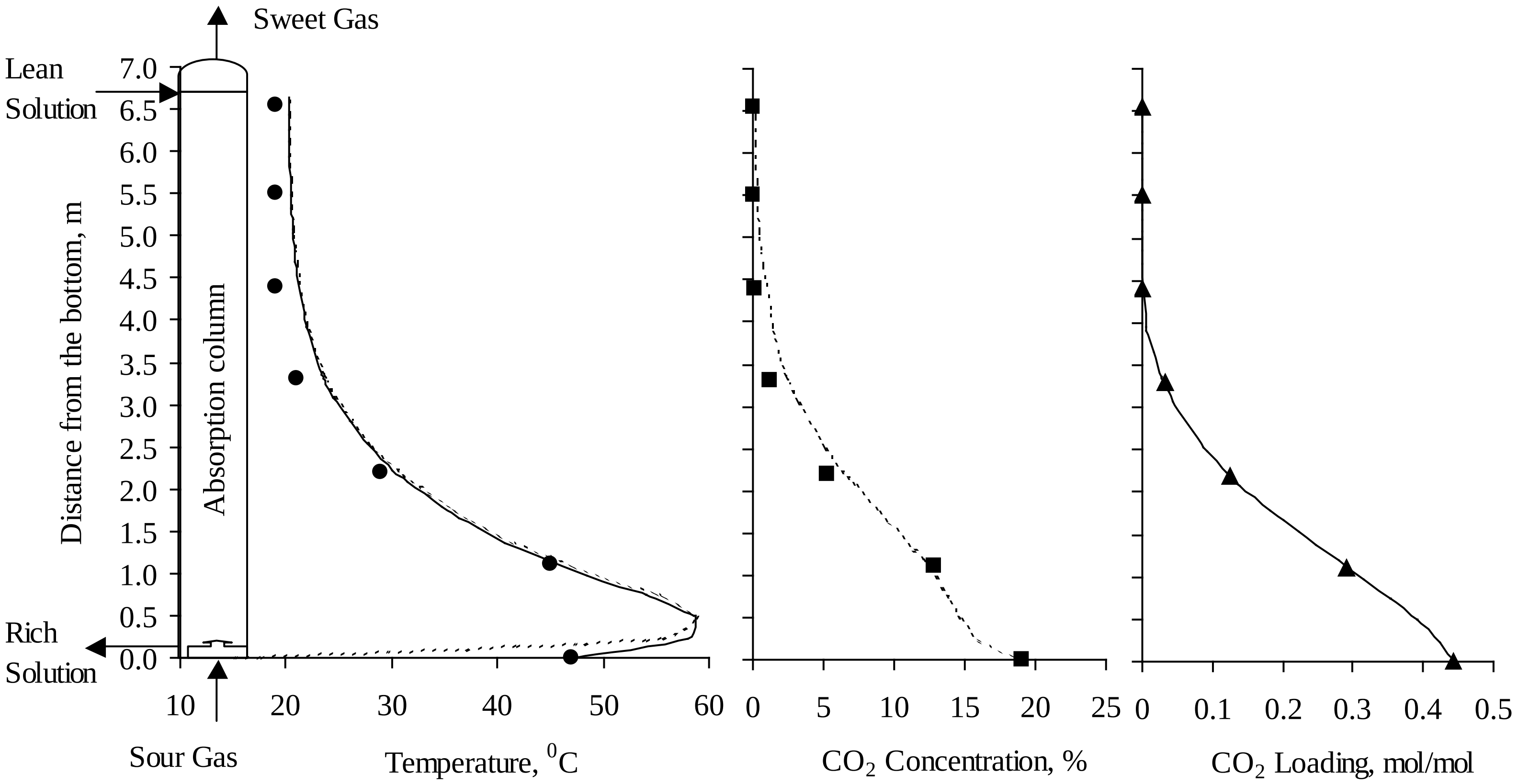


University of British Columbia (UBC) Pilot Plant

• Bed height	six sections each 1.2 m
• Column Diameter	0.1 m
• Packing	12.7-mm ceramic Berl Saddles
• Solvent	MEA, 3 M
• Simulated flue gas flow rate	14.8 mol/m2. s
• Inlet gas temperature	288 K
• Liquid flow rate	9.5 m3/m2. h
• Inlet liquid temperature	292 K
• Pressure	101.3 kPa
• Inlet gas composition	19.1% CO2

CO2-MEA, UBC Pilot Plant

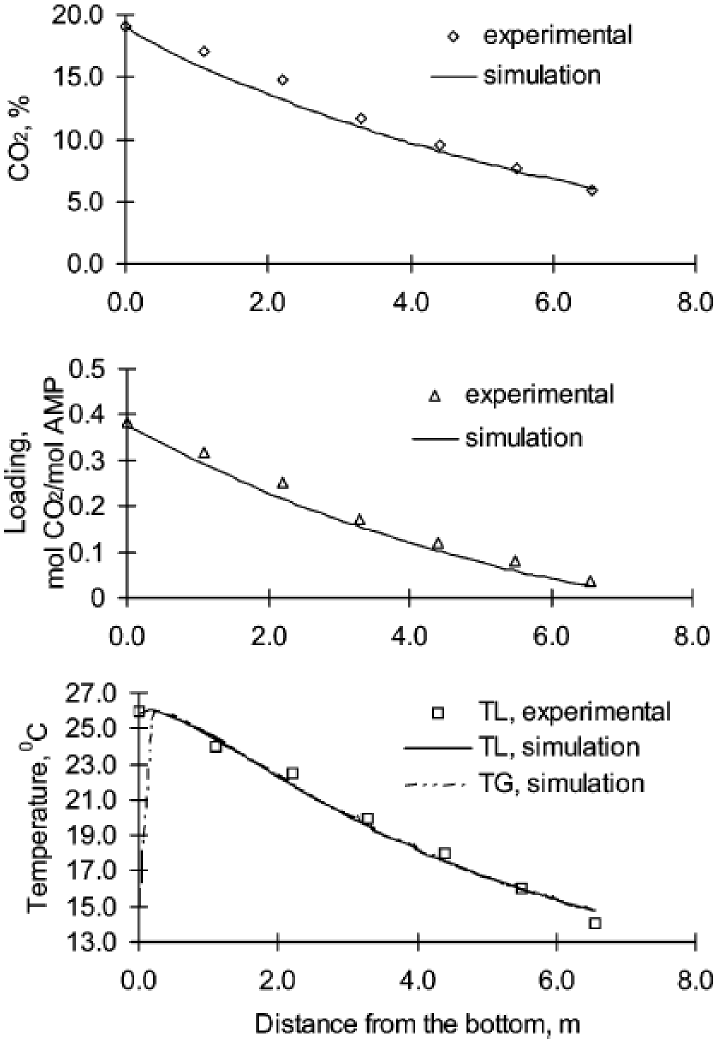
Ind. Eng. Chem. Res. **2006,** *45,* 2553−2557



CO2-AMP, UBC Pilot Plant

Ind. Eng. Chem. Res. **2006**, *45*, 2553−2557

parameter	UBC
simulated flue gas flow rate, mol/m^2•s	14.8
inlet gas temp, K	288
liquid flow rate, m^3/m^2•h	13.5
inlet liquid temp, K	287
AMP concentration, kmol/m^3	2.0
pressure, kPa	101.3
inlet gas composition, % CO_2	19.0
CO_2 removal, %	73.0



Process Configuration Optimization with 5M MEA & RS2

University of Regina, ITC: Experimental and modeling Results

Solvent		Heat Duty Btu/lbmol	Lean Loading mol/mol	Rich Loading mol /mol	CO_2 production tonne/day	Steam kg/kg CO_2
5M MEA	**Simulation**	**55590**	**0.2504**	**0.4837**	**0.57**	**1.3**
	Experiments	**43733± 5436**	**0.2279**	**0.5024**	**0.58**	**1.21±.14**
RS2	**Simulation**	**43733**	**0,2321**	**0.4222**	**0.53**	**1.04**
	Experiments	**39231± 5117**	**0.1835**	**0.4252**	**0.58**	**0.98±.17**

Euro Castor Pilot Plant Project Case, Design data

- Internal diameter 1.1 m
- Four packed beds each 4.255 meter – total of 17 meters
- IMTP 50 Packing
- Solvent Type: 30 % wt MEA
- Flue gas composition: Flue Gas from Coal based power Plant
- Design flue gas conditions:
  - ~47°C saturated,
  - <10 ppm SO2,
  - <65 ppm NOx,
  - <10 g/Nm3 dust

Euro Castor Pilot Plant Project Case; Ross Dugas, et al., Energy Procedia 1,2009, P103

Absorber Solvent Conditions for Campaign 2 of the Castor Pilot Plant (24t/d CO_2)

Run	Temp °C	Flow rate Kg/hr Solvent	MEA wt% , unloaded	Lean Loading mol CO_2/mol MEA	Plant Rich Loading mol CO_2/mol MEA	Project Model Rich Loading mol CO_2/mol MEA	HTC Model Rich Loading mol CO_2/mol MEA
1A	40	24361	32.3	0.275	0.465	0.454	0.475
2C	40	16371	31.5	0.270	0.486	0.502	0.499
3D	40	19894	30.2	0.241	0.458	0.448	0.468

Euro Castor Pilot Plant Project Case; Ross Dugas, et al., Energy Procedia 1,2009, P103

Flue Gas Conditions for Campaign 2 of the Castor Pilot Plant

Run	Temp °C	Pressure barg	Flow rate Kmol/hr Gas	Inlet CO_2 Dry mol%	Plant Outlet CO_2 Dry mol%	Project Model Outlet CO_2 Dry mol%	HTC Model Outlet CO_2 Dry mol%
1A	47.8	-0.02	219	13.2	1.5	2.4	1.47
2C	46.9	-0.04	224	13.2	4.9	4.2	4.98
3D	47.0	-0.03	217	11.4	1.0	1.5	1.26

Absorption Column Design – Main input data

- Lean Amine:

– Concentration	18 wt %
– Loading	0.08 mol/mol
– Temp	51 C
– Pressure	1.18 bara
– Flow rate	454 m3/h

- Inlet gas

– CO2 Concentration	10.7 mol%
– Temp	51 C
– Pressure	1.18 bara
– Flow rate	129,389 kg/h

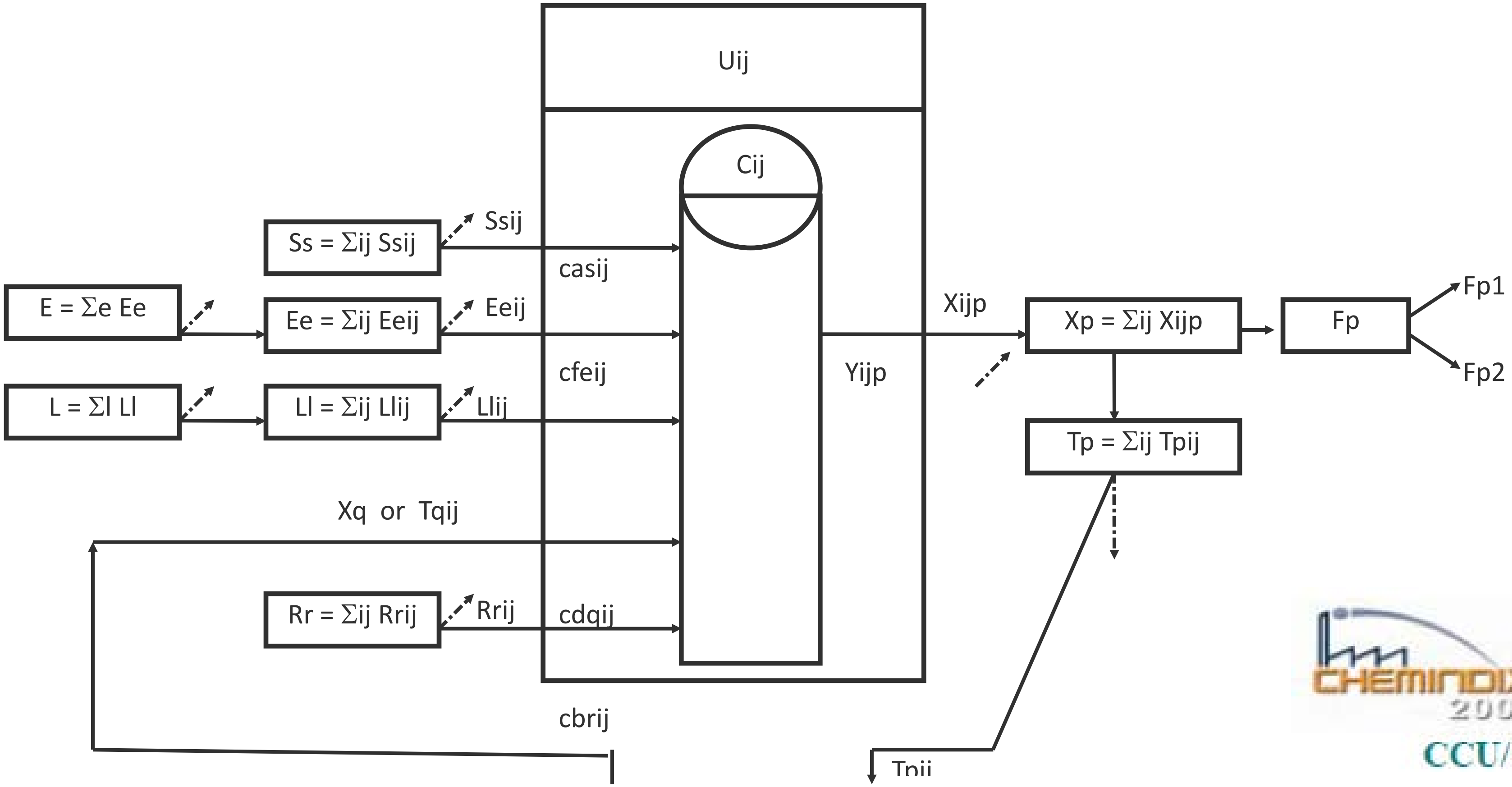
- Column data

– Packing	50 mm Rauschert, hi-flow heat stabilized rings
– Column diameter	4.42 m

Absorption Column Design – Output data, Comparison with Actual Column

- CO2 clean up target
  - Actual: 3 mol%
  - Modeling: 2.98 mol%
- Rich Amine loading
  - Actual 0.31 mol/mol
  - Modeling: 0.35 mol/mol
- Bed height two sections
  - Actual per section: 7 m, 2 sections: 14 m
  - Actual per section: 6.9 m, 2 sections: 13.8 m

HTC Optimization Approach



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DESIGN AND ENGINEERING FACTORS AFFECTING CO_2 CAPTURE AND EOR APPLICATIONS

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AS ONE WHO SERVES

Thank you …..