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DG RESEARCH & INNOVATION

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Collaborative Project– GA No. 608555

High Performance Capture

Deliverable N° D7.2

Proceedings of the first technical workshop

Dissemination level	Public	
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Checked by WP7 Leader	Hanne M. Kvamsdal (SINTEF)	18.05.2015
Approved by the coordinator	Hanne M. Kvamsdal (SINTEF)	18.05.2015
Main conclusions	A workshop was arranged in Melbourne 25-26 March 2015 followed by a field trip to the Latrobe Valley for visiting the CSIRO capture pilot plant connected to a brown-coal power station	
Issue date	Date	**18.05.2015**

Executive summary

As part of the HiPerCap project, a joint EU - Australian workshop targeting Breakthrough Post Combustion Capture Technologies was held on March 25-26, 2015 in Melbourne, Victoria (Australia). The workshop was hosted by CSIRO, on the University College premises at the University of Melbourne.

The purpose of the workshop was to present not only the results of the project, but also the results from other CCS projects in Europe and Australia and to create synergies on CCS between R&D organizations and industry from Europe and Australia.

Four major themes adapted from four of the technical Work-packages in HiPerCap were covered. This means that three sessions dealt with the three major separation technologies (Absorption, adsorption and membranes) and one session dealt with methodologies for technology assessment and benchmarking. On average, there were four presentations per session, in which two presenters were Australian and two were European. There were both presentations from HiPerCap partners and from other invited presenters outside the project. One presentation per session was dedicated to HiPerCap activities. Two sessions were devoted to the discussion of recent trends for technology development within the three major types of gas separation as well as methodologies for technology evaluations.

A site visit to the Latrobe Valley to view the CSIRO capture pilot plant connected to a brown coal-fired power station was conducted 27 March. This trip was sponsored by Brown Coal Innovation Australia (BCIA), while the conference dinner was sponsored by the Global CCS Institute (GCCSI).

Information about the workshop to the public was disseminated through e-mails and the external HiPerCap web-site. Prior to the meeting, a leaflet was prepared and distributed at the GHGT-12 conference. Around 70 people attended the workshop, most of them from Australia and 13 from Europe and one from the USA. Approximately 17 (13 from Europe) participated in the field trip (see picture below).

In the present report, a summary of the workshop is given. All presentations are attached in appendix. These presentations are also uploaded on the project website http://www.sintef.no/hipercap.

Group picture taken at the AGL Loy Yang power station in Latrobe Valley, Victoria

Content

1 Introduction

1.1 Summary of the HiPerCap project

HiPerCap aims to develop high-potential novel and environmentally benign technologies and processes for post-combustion CO_2 capture leading to real breakthroughs. The project includes all main separation technologies for post-combustion CO_2 capture; absorption, adsorption and membranes. For each technology it is focused on chosen set of promising concepts (four for absorption, two for adsorption and two for membranes). We aim to achieve 25% reduction in efficiency penalty compared to a demonstrated state-of-the-art capture process in the EU project CESAR and deliver proof-of-concepts for each technology.

HiPerCap involves 17 partners, from both the public and private sectors (research, academia, and industry), from 7 different EU Member States and Associated States, and three International Cooperation Partner Countries (Russia, Canada, and Australia). The HiPerCap consortium includes all essential stakeholders in the technology supply chain for CCS: power companies, RTD providers, suppliers, manufacturers (of power plants, industrial systems, equipment, and materials), and engineering companies.

1.2 Background for the workshop

HiPerCap is one of 6 joint EU - Australian projects within the 7th framework program. Since dissemination activities are important parts of projects like HiPerCap it was planned to organize two joint workshops between Europe and Australia during the course of the project. The first one dealt with in the present proceedings was arranged in Melbourne, Victoria in Australia 25-27th March 2015, while the second one will be held in Europe in 2017. The Australian partner in HiPerCap, CSIRO was host for the workshop and the selected venue was at the University College, University of Melbourne.

1.3 The aim for the workshop

The purpose of the workshop was to present not only the results of the project, but also the results from other CCS projects in Europe and Australia and to create synergies on CCS between R&D organizations and industry from Europe and Australia. The workshop was open to all interested in CO2-capture and information on the workshop was spread by e-mails, leaflets distributed at the GHGT-12 conference and the project public web-site (www.sintef.no/hipercap).

2 Workshop program

The program for the two days of workshop is listed in Table 2.1 and 2.2, respectively. As can be seen, day 1 started with a general introduction. The Global CCS Institute (GCCSI) sponsored the workshop dinner and Clare Penrose from the GCCSI gave a presentation about the Institute and the global status of capture technologies. Then a brief overview of the Peter Cook CCS Centre was given by its representative (Geoff Stevens). Two presenters (Paul Feron from CSIRO and Adam Al-Azki from E.ON) were invited to give a presentation on CCS in Australia (in the morning of day 1) and on CCS in Europe, respectively. Finally, in the introduction session of day 1, the HiPerCap coordinator gave an overview presentation of the HiPerCap project.

Four major themes adapted from the four major Work-packages in HiPerCap were covered in the following sections. This means that three sessions dealt with the three major separation technologies (absorption, adsorption and membranes) and one session dealt with methodologies for technology assessment and benchmarking. Typically, there were four presentations per session, in which two presenters were Australian and two were European. There were both presentations from HiPerCap partners and from other invited presenters outside the project. One presentation per session was dedicated to HiPerCap activities. Two sessions (each at the end of each day) were devoted to the discussion of recent trends for technology development within the three major types of gas separation as well as methodologies for technology evaluations.

All presentations are attached in Appendix, while a summary of the discussions is given in Chapter 3.

Table 2-1: Agenda workshop 1st day – 25th March, 2015

08:30-09:00	*Registration and coffee/tea*	
09:00-09:05	**Welcome and practical information**	*CSIRO*
09:05-09:20	**Global Capture Technology**	*Clare Penrose (GCCSI)*
09:20-09:35	**Peter Cook CCS Centre**	*Geoff Stevens (Melbourne University)*
09:35-9:55	**CCS in Australia**	*Paul Feron (CSIRO)*
09:55-10:15	**HiPerCap overview**	*Hanne Kvamsdal (SINTEF)*
10:15-10:45	*Coffee Break*	
10:45-12:45	**Session 1: Absorption**	*Session chair: Peter van Os (TNO)*
10:45-11:15	**HiPerCap WP1: Absorption technologies**	*Earl Goetheer, TNO*
11:15-11:45	**Development of Reactive Chemical Absorbents at the CSIRO**	*Graeme Puxty (CSIRO)*
11:45-12:15	**Formation and destruction of NDELA in MEA and DEA**	*Hanna Knuutila (NTNU)*
12:15-12:45	**Dynamic models and control strategies for absorption-based carbon capture processes**	*Ali Abbas (Sydney University)*
12:45-14:00	Lunch	
14:00-16:00	**Session 2: Adsorption**	*Session chair: Cova Pevida (CSIC)*
14:00-14:30	**HiPerCap WP2: Adsorption technologies**	*Cova Pevida (CSIC)*
14:30-15:00	**Carbon composite adsorbents for post combustion CO_2 capture**	*Yonggang Jin (CSIRO)*
15:00-15:30	**How can MOFs save the world?**	*Richard Blom (SINTEF)*
15:30-16:00	*Coffee Break*	
16:00-16:30	**Electrical Swing Adsorption for CO_2 Capture**	Alan Chaffee (Monash University)
16:30-17:30	**Discussion_1, speakers 1st day in panel**	*Session chair: Paul Feron (CSIRO)*
	Theme: Prospects for absorption/adsorption technologies	

Table 2-2: Agenda workshop 2nd day – 26th March, 2015

08:30-09:00	*Coffee/tea*	
9:00-9:30	**CCS in Europe**	*Adam Al-Azki (E.ON)*
9:30-12:00	**Session 3: Membranes**	*Session chair: Hanna Knuutila (NTNU)*
9:30-10:00	**HiPerCap WP3: Membrane technologies**	*Marc Pfister (CNRS)*
10:00-10:30	**Control of Physical Aging in Super Glassy Polymer Membranes Without Permeability Loss**	*Cher Hon Lau (CSIRO)*
10:30-11:00	*Coffee Break*	
11:00-11:30	**Membrane contactor for CO_2 capture**	*Taek-Joong Kim (SINTEF)*
11:30-12:00	**Membranes for CO_2 capture**	*Sandra Kentish (Melbourne Uni)*
12:00-13:00	*Lunch*	
13:00-15:00	**Session 4: Technology evaluation**	*Session chair: Jock Brown (DNVGL)*
13:00-13:30	**HiPerCap WP4: Assessment of CO_2 capture technologies**	*Jock Brown (DNVGL)*
13:30-14:00	**Comparative overview of costs for capture technologies**	*Diane Wiley (UNSW)*
14:00-14:30	**Benchmarking of carbon capture technologies in development'**	*Gerben Jans (DNVGL)*
14:30-15:00	*Coffee Break*	
15:00-16:15	**Discussion_2, speakers in panel**	*Session chair: Adam Al-Azki (E.ON)*
	Theme: Industrial applications of membranes and methodologies for technology evaluations	
16:15-16:30	**Workshop wrap-up and closure**	*Hanne Kvamsdal, SINTEF*

3 Discussion sessions

3.1 Introduction

Some questions addressed in these two sessions were prepared by the HiPerCap representatives during the Technical meeting just before the workshop. Paul Feron (CSIRO) moderated the session on day 1, while Adam Al-Azki (E.ON) moderated the session on Day 2. All workshop participants were invited to be active in the discussions, however, all presenters were asked specifically to be prepared to answer the questions. During both sessions a lively one hour discussion emerged as a result of the participation of the presenters and attendants.

3.2 Discussion 1: Prospects for absorption/adsorption technologies

The questions prepared and the respective summary of answers are listed in the following:

- What is the best way of up-scaling absorption and adsorption based technologies?
  - ✓ The issue of up-scaling depends on the specific application. Focus should be on low CAPEX. 3D printing application could be an option for sorbents.
- What are the major challenges for both absorption and adsorption?
  - ✓ Major challenge for absorption is still related to the overall costs, while the adsorption application is more immature than absorption and focus is still on the sorbent capacities. In the latter it was stated that more pilot demonstrations are needed. Also the issue related to IPR protection and thus insufficient collaboration was mentioned.
- Any challenges related to emission of harmful amines and other unwanted components?
  - ✓ Regarding emissions from amine based absorption plants, some major steps for reduction of emission of harmful species have already been taken and a 1st generation mitigation approach is implemented at the Boundary Dam facility. However, more solvent loss is experienced than expected and the following question was addressed: what are the consequences if 300 applications like Boundary Dam are realized? Though some work has been done to understand the degradation mechanisms and also to establish common procedures for emission measurements and analyses, more efforts are still needed in this area. Regarding adsorption there might be an issue in case of amine functionalized sorbents, but this may be avoided dependent on the design and control of the process.
- Do the absorption and adsorption technologies have any advantages regarding operational flexibility?
  - ✓ At least for the absorption technology there are some tests conducted related to solvent storage. It was emphasized that one shall not overdesign, but try to optimize the plant size based on the operation pattern of the power plant.
- Differences and similarities between Europe and Australia and what can we learn from each other?
  - ✓ At the level of general energy supply Australia is a resource-rich country and continent with consistently high levels of coal exports and increasing levels of gas exports. Oil resources are nearing their depletion though. Europe is not a resource rich continent, being heavily reliant on imports of oil and gas and to some extent also coal as coal mines have been progressively closed over the last decades in many European countries.
  - ✓ CO2 capture is more costly in Australia for a number of reasons. Firstly, In Australia environmental controls need to be installed prior to CO2 capture to deal with acid gases other than CO2. Such environmental controls are already in place in Europe. Hence this represents a significant additional investment. Secondly, although fuel prices are lower in Australia, which is beneficial for the operating costs of a capture process, capital costs are much higher in Australia. The cost of the overall CCS-chain in Australia is dependent on the fuel type, the proximity of CO2-sources to CO2-sinks and hence the location. Nearly all

power stations in Victoria (VIC) are fuelled by brown coal and potential CO2 storage is nearby. Brown coal is not an export product because of its high moisture content. It is easily extracted in open cut mines and therefore a very low cost fuel ideal for local power generation. Black coal is used for power generation in New South Wales (NSW) and Queensland (QLD). In NSW CO2 storage locations are quite far away from the emissions sources making CCS expensive, In QLD there is better potential for CO2-storage, particularly in the Surat Basin. Australian black coal is of high quality and a commodity traded on the global market and the fuel price is higher than for black coal. Still compared to Europe or Asia, coal prices are much lower. Labor costs, on the other hand, are amongst the highest in the world, which results in high costs for installation of plant and equipment and high costs for maintenance. Despite the differences in capture cost break-down in both Australia and Europe CO2 capture costs are too high to facilitate rapid deployment of CCS technology and both continents can learn from efforts and experiences in cost reduction.

The discussion on the above questions was very lively and as a result there was no time for a discussion around the last three questions:

- Are the absorption based technologies completely developed?
- How much can you expect to reduce the heat requirement?
- Is CO_2 purity an issue for all technologies addressed?

3.3 Discussion 2: Industrial applications of membranes and methodologies for technology evaluations

3.3.1 Membranes

The questions prepared and the respective summary of answers are listed in the following:

- What is the best way of up-scaling membrane based technologies and can they really offer an improvement in plant footprint compared to amine scrubbing?
  - ✓ It was suggested that the scale up of membrane technologies for CO2-capture would be facilitated by considering how the scale-up of reverse osmosis for seawater desalination had progressed since its inception in the 1960's.
  - ✓ Based on experience at TNO with development of membrane contactors for CO2-capture from flue gas it is important to redesign the membrane module geometry for up-scaling (e.g. tubular). The advantage of the high specific surface area for membrane technologies is the potential for compact equipment and smaller footprint. As the power plant flue gases are sizeable in volumes, there is a considerable design challenge to enable these flue gases to pass through the membrane equipment at low pressure drop. Proper module design is a critical up-scaling issue. Thus it is important to establish normative equipment- as well as process design procedures.
  - ✓ The use of plastic materials in processes with acid gases has the potential to reduce the costs.
  - ✓ Low temperature membrane operation may also be considered. It has been shown that cryogenic operation at least may give an energy performance similar to amine based absorption processes.
  - ✓ Hybrid membranes combining functionalized amine groups as well as membranes combined with other technologies are present trends.
  - ✓ In order to develop equipment and processes it is important that both engineers and material scientists work together. Especially important is to have the power plant and its requirements and limitations in mind when designing the membrane module and associated capture process.
- What indication do we currently have that membranes can offer improved energy performance in comparison to amine scrubbing?

  - ✓ Rough estimates shows that there is not a big difference in the energy performance of a membrane process or an optimized amine based process.
  - ✓ The main benefit of membrane application is its simplicity, which makes it attractive for as a retrofit option with advantages in terms of operation and maintenance. Another advantage is that in the membrane process there is no use of chemicals thus avoiding emission of potential harmful species.
  - ✓ The membrane process requires electricity, which is more expensive than the steam used for the amine based absorption process. However, the membrane process is easier to integrate with the power-plant than the amine based due to the steam extraction from the power-plant in the latter case.
  - ✓ Further improvement may come from better heat-integration, but then the beneficial simplicity may be lost.
  - ✓ Benchmarking taking into account also aspects around operability and flexibility of the plants should be done. A true comparison of membrane processes with amine based technologies can be done on the basis of adequate process and equipment designs. As these are lacking a good technical starting point will be a comparison between the membrane permeability and the mass transfer coefficients for amine based absorption/desorption processes.
- ✓ What are the major challenges for membrane based capture technologies?
  - ✓ The main challenge for membranes is to demonstrate their robustness under realistic conditions, i.e. at flue gas conditions. There is a need for experimental environments, e.g. at power stations, to enable such testing.
  - ✓ Another challenge is to have scalable process designs and equipment designs and evaluate those designs at real conditions.
- ✓ Membranes in Europe vs. Australia
  - ✓ Emission controls in Australian power plant are less stringent compared to Europe. The poorer quality of the flue gases in Australia might impose additional issues for membrane technologies. This may also influence on the CO_2 purity and the strict requirement related to transport and storage. Thus flue-gas treatment may be necessary and for which multicomponent capture may be a solution. However, Australia has particulate removal installed on coal fired power plants, either ESP or bag filters so that challenges related to fly ash is not an issue.
  - ✓ At present there are no membrane manufacturing companies in Australia. This lack of technology suppliers in Australia will be a determining factor in international collaborations, as the technologies will be developed overseas rather than in Australia.

3.3.2 Technology Benchmarking

The questions prepared and the respective summary of answers are listed in the following:

- How do we account for operability and flexibility?
  - ✓ This maybe an important design criterion especially for capture plants to be connected to power plants operated at highly varying load or sources of CO_2 for which the flue gas flow-rate and/or CO2 concentration is highly fluctuating. In HiPerCap, we will consider it as part of the technology assessment, but only on a qualitative basis.
- Is CO_2 purity an issue for all technologies addressed?
  - ✓ As mentioned in connection with membranes, CO_2 purity is an issue for geological storage and transportation.
  - ✓ For pipelines, recompression is affected by impurities in the stream. Unfortunately, there is not much data in literature about specific requirements although it is a big issue. It will be dependent on the specific case so maybe that is the reason why it is not standardized. In HiPerCap we will most likely require a minimum of 95%, but check the implications for some of the technologies.
- Are there any added environmental benefits of the new technologies addressed in HiPerCap?
  - ✓ All solvent systems considered in HiPerCap are more "green" or environmental friendly than systems considered as part of the 1^{st} generation solvent system. As stated earlier, there will not

be any issue related to emission of harmful species in case of membrane applications while amine functionalized sorbents may release some of the amines dependent on operating conditions.

- Do any of the considered technologies provide reduction in CAPEX?

  ✓ It is one of the goals in HiPerCap to reduce costs, but most likely it is difficult to estimate the costs and compare all the technologies on a fair basis. It was emphasized also that the availability of the various agents at least before any extensive application is limited. Thus the novel solvents, sorbents and membrane materials may be as costly as the capture plant itself.

Finally, there was a general discussion about how to benchmark and choose the best technology.

✓ Certain technologies works better for one application, another technology maybe better for other types of applications situation.
✓ In HiPerCap we will not be able to see all the potentials of the different technologies when we are finally selecting two technologies for further studies, but we will try to be as fair as possible with the available data we will get.
✓ At the end the market will make a decision and it is important to offer alternatives.
✓ There was a remark about the lack of pilots available for demonstration of membrane based technology as a clear drawback, but it was confirmed that a membrane developed at SINTEF/NTNU has been tested at a power plant in Portugal for 6 months, in the presence of NOx and SOx. Promising results have been obtained. The same membrane was also tested in a cement plant, but less good results were obtained due to unstable cement plant operation. Presently a 10 m^2 hollow fiber pilot plant is designed and will be constructed at NTNU/SINTEF quite soon.

4 Field trip to the Latrobe Valley

Most of the European participants and some Australian (many of the participants in the workshop have already visited this site) joined the trip to the Latrobe Valley, Victoria for visiting a huge brown coal opencast mine and one of its connecting power stations. CSIRO has built and has been operating a post-combustion capture pilot plant at the power station. The tour in the mine and through the power station was kindly hosted by AGL Loy Yang.

Facts about the power station: AGL Loy Yang operates one of Australia's largest open-cut mines (2.5 by 3.5 km and 200 meters deep). The mine consists of a 10-20 meters layer of overburden. 30 Mtpa are produced for two base-load power stations with a capacity of 2.2 GW and 1.1 GW, respectively, which is 50% of Victoria's electricity need. The coal has very low ash content of about 2%, and very low sulfur levels and as such amongst the cleanest in the world. On the other hand, it contains of 62-65% moisture which dramatically affects the power stations' efficiency; ~29% HHV (34% LHV). Flue gas treatment after combustions includes cooling (heating inlet air) and electrostatic precipitation of fly-ash, which is 99.9% effective, but lack flue gas desulphurization and denitrification. As a result the flue gas is being emitted at 180 °C to prevent acid dew point from happening and the composition ranges between 10-12% CO_2, about 5% O_2, 20% H2O, 140ppm SO_2 and 180ppm NO_x. CO_2 emissions from both power plants are about 30 Mtpa. http://www.agl.com.au/about-agl/how-we-source-energy/thermal-energy/agl-loy-yang

Facts about the pilot plant: The CSIRO PCC pilot plant at AGL Loy Yang captures CO_2 from slipstream flue gas. The PCC pilot plant was commissioned in 2008 and is designed to process 50 kg/h of flue gas. The CSIRO PCC pilot plant is operated during daytime hours. The PCC pilot plant consists of a flue gas pre-treatment column, two absorber columns and one stripper column. The pre-treatment column scrubs the flue gas with sodium hydroxide to remove SO_X, NO_X (other than NO) and particulates. The liquid absorbents used to capture CO_2 in this pilot plant range from 30 % (w/w) aqueous monoethanolamine (MEA), AMP, PZ, amino acids and several proprietary blends. The absorbent inventory ranges between 150-250 L. The PCC pilot plant has been focusing on evaluation of novel amine blends and has set a base-line for emissions from long term operation of MEA (1600+ hours).

The two absorber columns are operated in series (can also be reconfigured to operate in parallel) and constructed from 200 DN stainless steel pipe. Each absorber column has an inner diameter (ID) of 211 mm, two 1.35 m packed bed sections (i.e. total packing height of 2.7 m), and the total column height is 9.4 m. The single stripper column is constructed from 150 DN stainless steel pipe with 161 mm ID. The stripper has a total column height of 6.9 m and packing height of 3.9 m. The metal random Pall ring packing used in every column has the following general specifications: (i) size/dimensions of 16 mm, (ii) specific area of 338 m^2/m^3, and (iii) packing factor of 306 m^{-1}. The steam for the stripper reboiler is generated by a 120 kW electric boiler.

Flow meters, sensors, probes and transmitters installed throughout the CSIRO pilot plant provide instantaneous measurements of flow rate, pressure and temperature. Column temperature profiles can be generated using resistance temperature detectors (RTDs) located along the height of each column. The Gasmet^{TM} FTIR gas analyzer measures gas composition online at 5 locations throughout the plant. Density meters display online density measurements of the liquid absorbent. During pilot plant operation, liquid absorbent samples are titrated onsite to determine the absorbent concentration. This is needed to monitor and maintain the water balance. Additionally, once the pilot plant reaches steady state operation, absorbent is sampled at various points in the pilot plant and sent off-site for liquid analysis.

Also the PCC related research on potassium carbonate, membranes and adsorption as carried out by the CO2CRC at the nearby Hazelwood power station was discussed by Trent Harkin of CarbonNet (previously with the CO_2CRC).

5 Acknowledgement

The HiPerCap consortium acknowledges CSIRO for hosting the event, The Global CCS Institute for sponsoring the workshop dinner, and the Brown Coal Innovation, Australia for sponsoring the field trip to the Latrobe Valley.

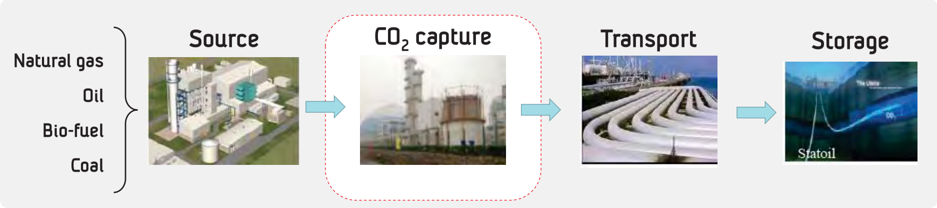
Finally, we acknowledge the HiPerCap project funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 608555. We also gratefully acknowledge the industrial partners in the consortium who financially support the project.

Appendix: Presentations from the workshop

HiPerCap - High Performance Capture

FP7 Grant agreement n° 608555

EU – Australian workshop,
Melbourne, Australia, 25th-27th March 2015



WIFI access

- Network: UC_Guests
- Network username: confgroup
- Network password: conf#11

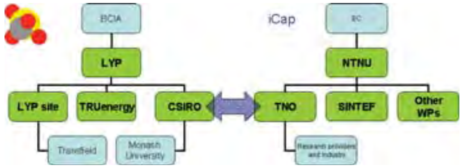
CoCAPco – collaboration (2010-2014)

iCap CO2.org
8 Research providers
6 Power companies

coCAPco
2 Research providers
2 Power companies

Objective:
Develop, test and demonstrate integrated SO_2 and CO_2 capture with stepwise regeneration.

Milestone
Demonstrate *iCap* process design with real flue gas at Loy Yang Power within *coCAPco* project



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6 EU-AU projects ~ 25 M€ (2013 – 2018)

ascent
INTERACT
M^4CO_2
MATESA
HiPerCap
GREEN

Australian twinning Organisations

- CSIRO
- CO2CRC
- University of Melbourne
- Monash University
- Australia National University
- University of Queensland
- University of Sydney

Overview

Venue: **UNIVERSITY COLLEGE**
The University of Melbourne
40 College Crescent, Parkville VIC 3052

25 March – First day of workshop
9:00 am – 5:30 pm : Presentations
6:30 am – 9:00 pm: Workshop dinner (sponsored by GCCSI)
(Il Vicolo restaurant, 50 Grattan Street, Carlton)

26 March – Second day of workshop
9:00 am – 5:00 pm: Presentations

27 March – Visit to Latrobe Valley (sponsored by BCIA)

Agenda workshop 1st day - 25 March 2015:

08:30-09:00	*Registration and coffee/tea*	
09:00-09:05	Welcome and practical information	*CSIRO*
09:05-09:20	Global Capture Technology	*Clare Penrose (GCCSI)*
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09:55-10:15	HiPerCap overview	*Hanne Kvamsdal (SINTEF)*
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16:00-16:30	Electrical Swing Adsorption for CO_2 Capture	Alan Chaffee (Monash University)
16:30-17:30	Discussion_1, speakers 1st day in panel	*Session chair: Paul Feron (CSIRO)*
	Theme: Prospects for absorption/adsorption technologies	

Agenda workshop 2nd day - 26 March 2015:

08:30-09:00	*Coffee/tea*	
9:00-9:30	CCS in Europe	*Adam Al-Azki (E.ON)*
9:30-12:00	Session 3: Membranes	*Session chair: Hanna Knuutila (NTNU)*
9:30-10:00	HiPerCap WP3: Membrane technologies	*Marc Pfister (CNRS)*
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	Theme: Industrial applications of membranes and methodologies for technology evaluations	
16:15-16:30	Workshop wrap-up and closure	*Hanne Kvamsdal, SINTEF*

Site visit to Latrobe Valley – 27 March 2015

8:00 am Departure from Melbourne (City Tempo hotel, 353 Queen Street)
11:00 am – arrival at AGL Loy Yang
1:00 pm – Lunch in Café Aura in Traralgon
2:00 pm – Departure to Melbourne
5:00 pm – Arrival in Melbourne (City Tempo hotel, 353 Queen Street)

Sponsored by BCIA

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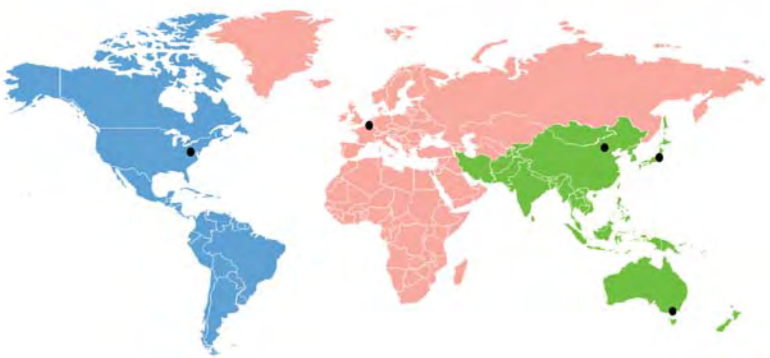
The global status of carbon capture technology

Clare Penrose, General Manager – Asia Pacific

EU-Australia Workshop, 25 March 2015, Melbourne

Global CCS Institute



- Knowledge sharing
- R&D coordination
- International collaboration
- Global networks and regional networks
- Fact-based advice and advocacy

http://www.globalccsinstitute.com/publications

http://decarboni.se/

http://co2degrees.com

CCS is critical if we are to achieve climate goals

Percentage increase in total discounted mitigation costs (2015-2100) relative to default technology assumptions – median estimate

2100 concentrations ($\text{ppm CO}_2\text{eq}$)	no CCS	nuclear phase out	limited solar/wind	limited bioenergy
450	138% 4	7% 8	6% 8	64% 8

Symbol legend – fraction of models successful in producing scenarios (numbers indicate number of successful models)

All models successful

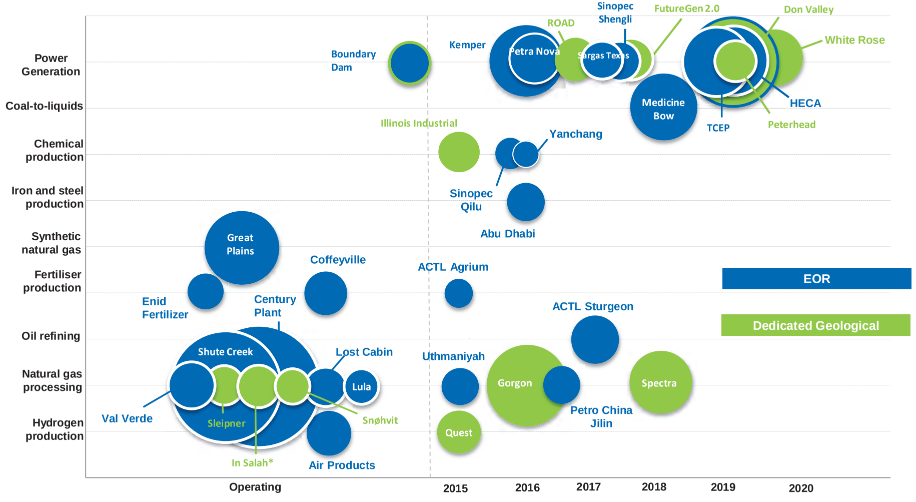
Between 80 and 100% of models successful

Between 50 and 80% of models successful

Less than 50% of models successful

Source: *IPCC Fifth Assessment Synthesis Report, November 2014.*

Actual and expected operation dates for projects in operation, construction and advanced planning



○ = 1Mtpa of CO_2 (areas of circle are proportional to capacity)

* Injection currently suspended

2014-2015 is a watershed period for CCS – it is a reality in the power sector and additional project approvals are anticipated

Power sector case study - Boundary Dam

Courtesy of SaskPower

A few highlights:

- Original capacity: 139MW Expected: 110 MW   **Actual**: 120MW
- Estimated steam consumption: ~2.5 GJ/t CO_2 (4.0GJ/t for conventional MEA)
- Utilization of concrete as materials for absorbers and amine tanks

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Key messages for capture technology development

- Capture components accounts for the majority of the cost in the CCS chain
    - For example, in power generation 70-90% of the overall cost of a large scale CCS project can be driven by capture and compression processes
- Goal is to reduce the capital and operational costs associated with CO_2 capture, particularly in new applications, such as power sector and new industrial processes
- Efforts to reduce costs include:
    - Learning by doing, through successful CCS demonstrations in power sector and additional industrial applications;
    - Continuing R&D across a range of capture technologies
    - Coordinated efforts in knowledge sharing and collaboration

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MELBOURNE

The Peter Cook Centre for CCS Research

Mission

To develop environmentally and socially acceptable, cost effective carbon capture and storage solutions for a carbon constrained world

Our Partners

- Established at the University of Melbourne
- Support from
  - CO2CRC
  - Rio Tinto
  - State Government of Victoria's Department of State Development, Business and Innovation (DSDBI)
- Australian Government's Education Infrastructure Fund provides further support for new laboratories facilities

Research and Technical Directions

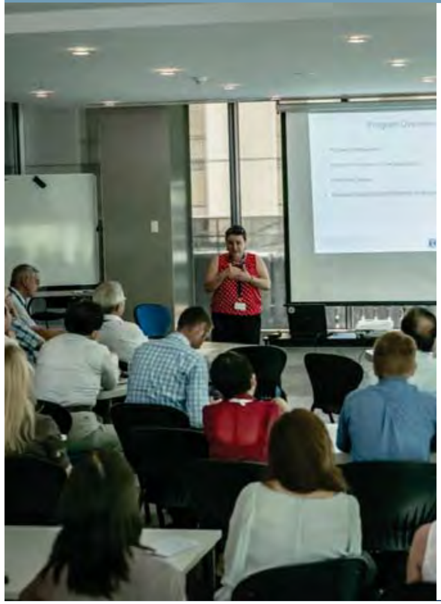
- Two research programs:

1. **Carbon Capture**
   - developing and demonstrating technologies that will significantly reduce the costs of capturing CO_2
   - minimising the environmental footprint of energy production

Research and Technical Directions

2. Carbon Storage
- developing a deeper understanding of the process of storing CO_2 in subsurface structures
- reducing the risks associated with storage
- developing appropriate monitoring and control technologies
- ensuring societal acceptance

Education and Training



- Major goal:
  - to develop the next generation of professional engineers and scientists
- Achieved by:
  - Developing short-term training and research opportunities for students and early career researchers
  - A number of research positions (PhD programs) are available

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Current Resources

- **Personnel**
  - 20 research scientists and engineers
  - 17 postgraduate students in residence
  - 3 research assistants

POSTERA CRESCAM LAUDE

THE UNIVERSITY OF MELBOURNE

CO2CRC
CRC FOR GREENHOUSE GAS TECHNOLOGIES

RioTinto

State Government Victoria

CCS in Australia

HiPerCap Workshop, Melbourne, Victoria, Australia

Paul Feron
25-26 March 2015

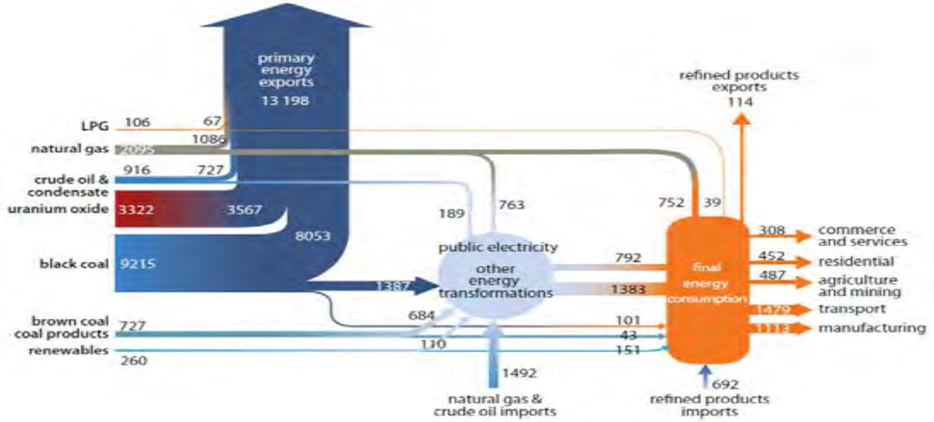
ENERGY FLAGSHIP
www.csiro.au

Overview

- ➢ Drivers for CCS in Australia
- ➢ CO_2 capture and storage in Australia
- ➢ Towards safe CO_2 storage demonstration
- ➢ CO_2 Capture Demonstration
- ➢ CCS R&D funding support
- ➢ Activities CO2CRC
- ➢ Post-combustion CO_2 Capture at CSIRO

Drivers for CCS in Australia

Australia’s energy flows: 2010-11 (petajoules)



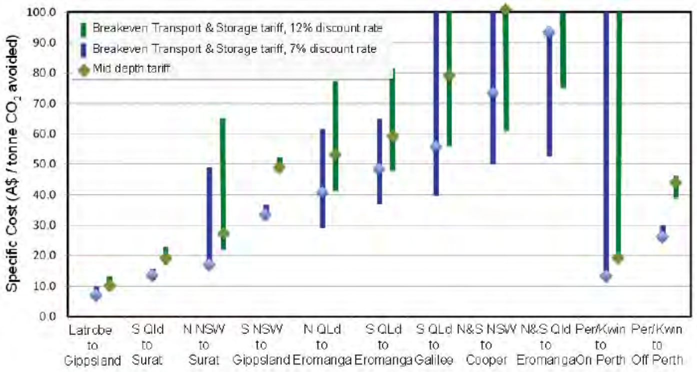
Source: BREE 2012, Australian Energy Statistics

Coal is important for Australia

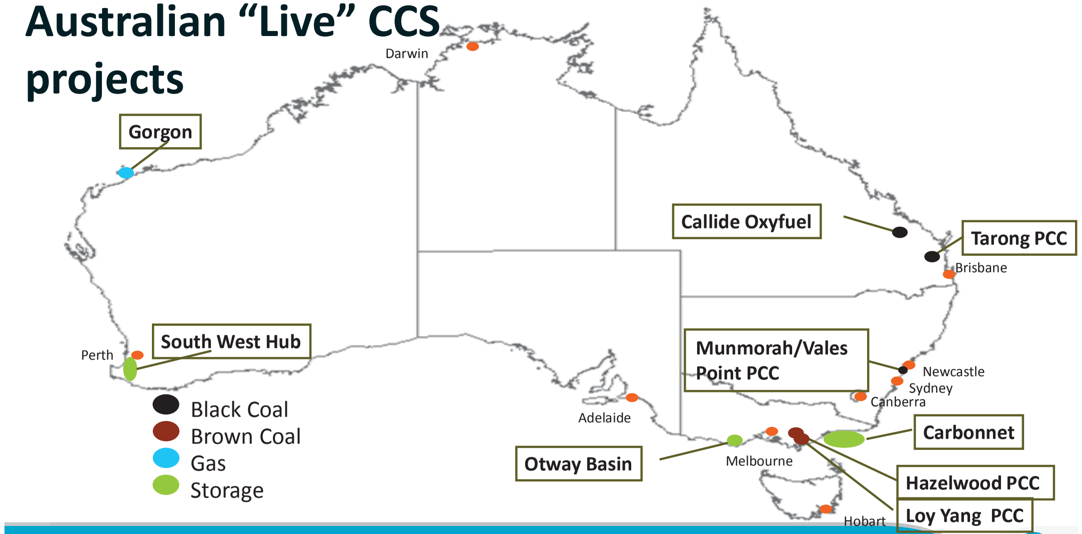
- Australia is the world’s 2nd largest coal exporter
- Coal is Australia’s 2nd largest export earner ($ 45B in 2010-11)
- Most of Australia’s electricity is produced from pulverised coal fired boilers (52% black coal, 23% brown coal in 2009-10)
  - Generation capacity ~ 28 GW
  - Electricity production ~ 170 TWh/a
  - CO_2-emissions ~ 170 Mtonne CO_2/a from ~ 60 flue gas streams

CO_2 Capture and Storage (CCS) in Australia

National Carbon Mapping and Infrastructure plan - 2009



Australian “Live” CCS projects



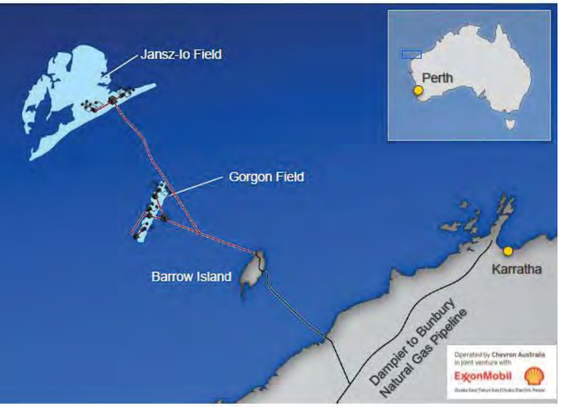
Towards safe CO_2 storage demonstration

Gorgon Project Overview

- AUD $55 billion investment
- 3 x 5.2 MTPA LNG trains
- A domestic gas plant with capacity of 300 terajoules per day
- Carbon Dioxide Injection Project

Joint Venture Participants

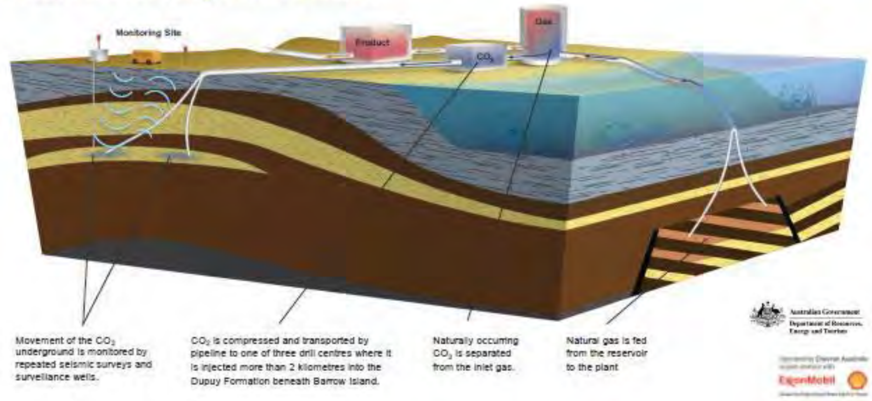
- Chevron (47.3%)
- ExxonMobil (25%)
- Shell (25%)
- Osaka Gas (1.25%)
- Tokyo Gas (1%)
- Chubu Electric Power (0.417%)



© 2014 Chevron

John Torkington, Feb 2015, Perth

Chevron-operated Gorgon Project
Carbon Dioxide (CO_2) Injection Project



Movement of the CO_2 underground is monitored by repeated seismic surveys and surveillance wells.

CO_2 is compressed and transported by pipeline to one of three drill centres where it is injected more than 2 kilometres into the Dupuy Formation beneath Barrow Island.

Naturally occurring CO_2 is separated from the inlet gas.

Natural gas is fed from the reservoir to the plant

John Torkington, Feb 2015, Perth

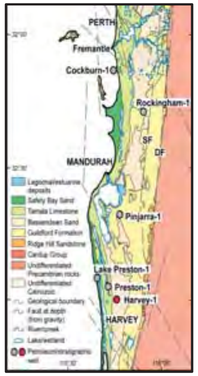
Australian CCS Flagships

1. South West Hub project, Western Australia (from June 2011)
2. CarbonNet project, Victoria (from February 2012)

- ➢ The initial focus on proving up geological storage at each of these locations
- ➢ $ 820 M investment in CCS deployment
- ➢ $100 M from Education Investment Fund

Supporting Commercial Scale Storage

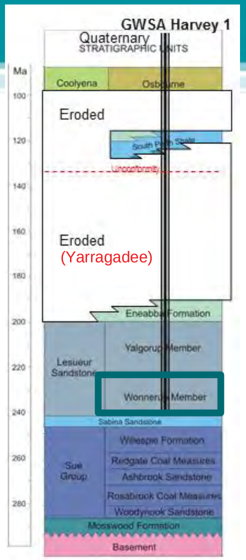
- South West Hub CCS
  - Location: 110km south of Perth, WA
  - WA DMP pre-competitive data acquisition
  - Stage gated approach
  - Greenfield site with little pre-existing data
- NGL
  - Supporting data acquisition, synthesis and interpretation for Site Characterisation
  - Deployment of dedicated equipment



Slides from Linda Stalker – Science Director NGL

SWH Site Characterisation

- Harvey-1 (2012)
  - Drilled to 2945m, 217 m cored intervals, logs etc
  - R&D Project outcomes on ANLEC R&D website
- Harvey-2, -3 & -4 drilling now (2015)
  - Shallow wells, 2 are mineral rigs, with continuous core through confining layers
- Harvey-5 (late 2015/early 2016)
  - Deeper well to characterise target injection interval in different fault block
- Seismic Activities
  - 2D survey on roads (2011); 2D shallow survey (2013); 3D survey over 115km^2 (2014); nested high resolution survey (2015)
- Future activities
  - Data integration across the area and updated models
  - Testing, testing…..!

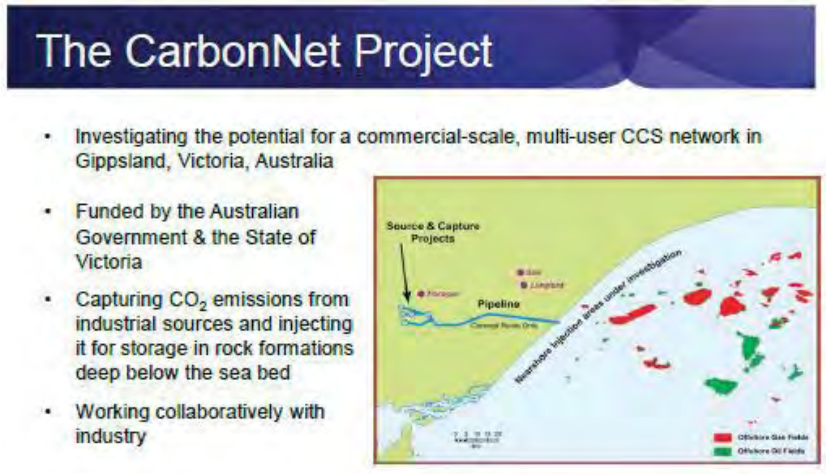


Slides from Linda Stalker – Science Director NGL

NGL Facilities

- Organic and inorganic geochemistry laboratories
- Sensors laboratory
- Rock mechanics, including petrophysics, core flooding and computer tomography
- CO$_2$ processing and sequestration laboratory (UWA)
- Mobile (containerised) geophysical and geochemical laboratories
- 3D immersive visualisation
- Surface and down-hole seismic sources
- Seismic recording and geophysical data acquisition
- Environmental (shallow groundwater, soil and atmospheric) monitoring
- Calibration and training facilities, including a 900m borehole (Curtin)
- "In situ" laboratory (SWH)

Slides from Linda Stalker – Science Director NGL



The CarbonNet Project

- Investigating the potential for a commercial-scale, multi-user CCS network in Gippsland, Victoria, Australia
- Funded by the Australian Government & the State of Victoria
- Capturing CO$_2$ emissions from industrial sources and injecting it for storage in rock formations deep below the sea bed
- Working collaboratively with industry

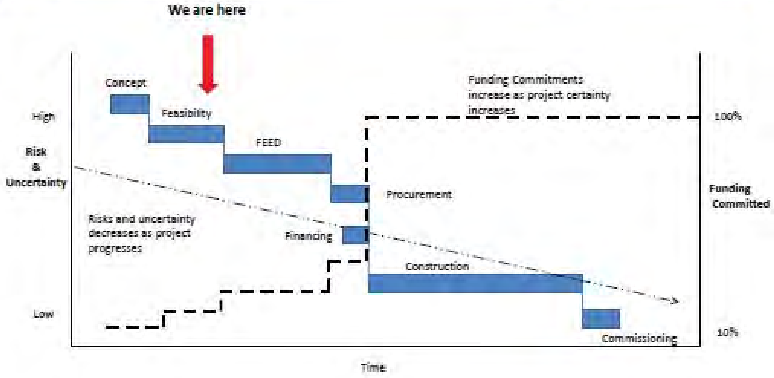
Ian Filby, Perth, Feb 2015

The CarbonNet Project

- Provide scalable infrastructure to underpin growth and development of a commercial scale CCS network
  - Foundation project: 1 to 5 mt of CO_2 pa for 25 years
  - Expansion phase: up to 20 mt of CO_2 pa
- Common user pipeline and storage infrastructure
  - Hub based concept
- Minimise conflicts with petroleum activities
  - Foundation storage sites focused on near shore zone
  - Over the longer term there is potential to use depleted oil and gas fields as production ceases

Ian Filby, Perth, Feb 2015

A gated approach



Ian Filby, Perth, Feb 2015

CTSCo's Surat Basin integrated CCS project

Surat Basin has significant potential

However, part of the Great Artesian Basin

CTSCo Carbon Transport and Storage Company

Source: Queensland Government GHG Storage Atlas 2009

- Almost 3 billion tonnes of CO2 theoretical storage potential
- Precipice Sandstone accounts for 1.3 billion tonnes of theoretical storage potential
- Identified as a key geostorage area under the 2009 National Carbon Storage Taskforce report and the Qld Govt GHG Storage Atlas
- Coal fired power stations closer to Surat Basin

1. Known geology for trial injection of CO_2 at 60 ktpa for three years to permit the option of 120ktpa injection for many years after that
2. Deploys currently available, 'industrially scalable' modular PCC technology to minimise technology risk – several choices available
3. Industry funded (ACALET) Glencore hosted project
4. Test injection on Glencore land with no overlapping CSG rights delivers lower social licence risk
5. Sensitive Social Licence environment
6. Supportive Greenhouse Gas legislation in Queensland

GLENCORE

Alan Dumee, Perth, Feb 2015

CO_2 Capture Demonstration

Callide Oxyfuel Project

- 30 MW_e Oxyfuel boiler,
- 2 x 330 TPD ASU's
- 75 TPD CO2 Capture
- CAPEX $180M; OPEX $65M

1. > 10,000 hours overall boiler operation
2. > 7,500 hours of actual oxy-firing operation
3. > 3,700 hours of CO_2 capture plant operation
4. Demonstrated sustained operation under oxy-firing conditions
5. Demonstrated boiler turn-down to 50% Load Factor
6. Demonstrated CO_2 capture rates > 85%
7. Demonstrated high purity of CO_2 product

Oxy-firing flame

Chris Spero – National CCS Conference 2014

CCS R&D funding support

R&D Funding organisations

- ANLEC R&D - $150 M
  - Accelerate the technology development cycle by making accessible the knowledge and skills that reduce the risk and/or cost of developing and deploying Low Emissions Coal Technology (LECT) in Australia.
  - 50/50 Commonwealth – Coal Industry
  - Targeted research - Alternatives/Fundamentals ($ 35 M)
- Brown Coal Innovation - $16 M R&D funding
  - Developing research, technologies and people to reduce the environmental impact - and deliver social and economic benefits - from sustainable use of brown coal
  - Membership based organisation including international members

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Activities CO_2CRC

CO2CRC: one of the world's leading CCS research organisations

- R&D across the CCS value chain
- Brings industry sectors together (coal, gas, power, etc) to provide an exceptional stakeholder base
- Brings together Commonwealth, States, local government and the community in the Otway Project
- Includes major research institutions - CSIRO, Geoscience Australia, Universities, major overseas institutions eg. LBNL(USA) , KIGAM(Korea)
- Over 150 leading researchers in CCS
- Broad international perspective and experience
- Successful track record in running major CCS facilities

Slides from Dianne Wiley/Matthias Raab

Participants

Supporting Partners

CO2CRC research portfolio

R&D Program	**Capture** • Solvents • Adsorbents • Membranes • Capture engineering	**Storage** • Finding & characterising storage • Managing storage • Subsurface MMV • Failure & mitigation	**Economics, Risk & Finance** • Capture economics • Storage economics • Network economics • Economics & policy • Risk methodologies	**Environmental Monitoring & Communities** • Marine MMV • Induced Seismic • Atmospheric monitoring • Near surface pressure effects • Community engagement • Education & training
Pilot & small demos	**Demonstration** • Solvent pilot • Adsorbent pilot • Membrane pilots • Membranes and adsorbents at Otway	**Otway** • Priority subsurface program	**Dynamic Modelling** • CCS chain dynamics	**Field Research** • Gippsland MMV • Community engagement

Slides from Dianne Wiley/Matthias Raab

CO2CRC Otway Project

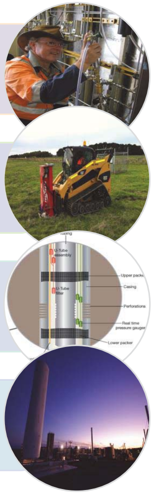
The CO2CRC Otway Project is Australia's first demonstration of the deep geological storage or geosequestration of carbon dioxide (CO_2), the most common greenhouse gas.

- Stored over 65,000 t CO_2
- World first residual trapping study

Slides from Dianne Wiley/Matthias Raab

CO2CRC Storage Research Highlights

Exceptional Datasets	•Atmospheric (continuous monitoring) •Soil Gas •Seismic •Reservoir fluids
Field Validation	•Validation of models in actual field tests •Fully permitted and operational site •Availability of CO_2 •Globally unique advantage
Developing Novel & Innovative Concepts & Technology	•Single Well Test for reservoir characterisation •Several generations of U-Tube systems deployed •Innovative well instrumentation
First of its kind experiments	•First CO_2 storage demonstration project in Australia •Reducing risk and uncertainty •Advising regulators and project proponents in Australia and world wide •A go-to project



Slides from Dianne Wiley/Matthias Raab

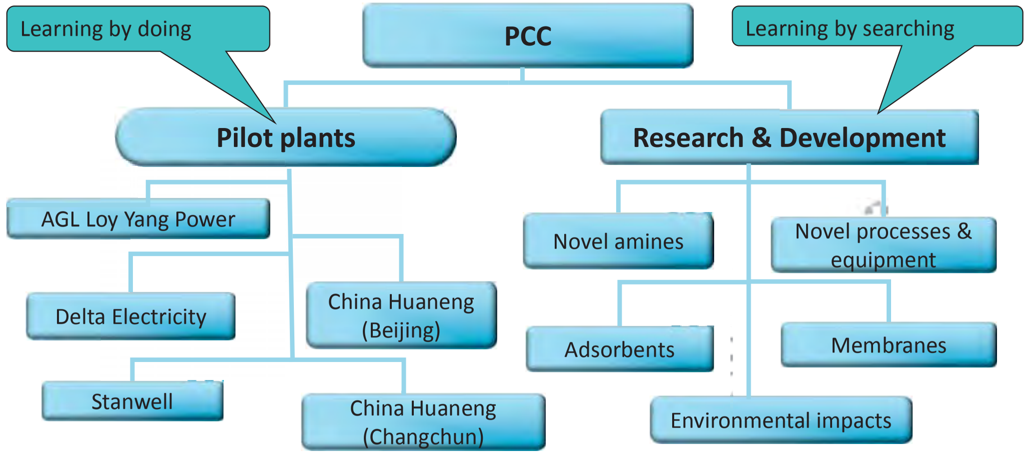
CO2CRC Capture Research Achievements

- Post-combustion field facilities for solvents, adsorbents and membranes.
- Patented potassium carbonate solvent.
- Testing of nanofiltration and electrodialysis for heat stable salt removal.
- Patented pelletization technique for PEI adsorbents.
- Identified trapdoor mechanisms of chabazite adsorbent for CH_4/CO_2 separation.
- Rapid screening and process cycle tools for adsorbents.
- Patented flat sheet CAP gas membrane fabrication process.
- Fabrication and testing of high performance hollow fibres for post-combustion capture.
- Fabrication of inorganic metal oxide silica membrane for CO_2/H_2 separation.

Slides from Dianne Wiley/Matthias Raab

Post-combustion CO_2 Capture at CSIRO

CSIRO's PCC program 2014



Learning by doing

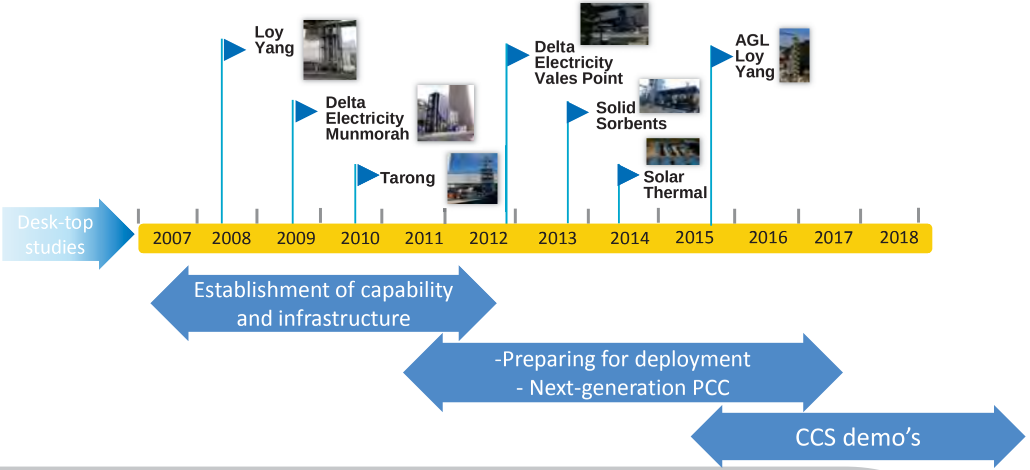
PCC

Learning by searching

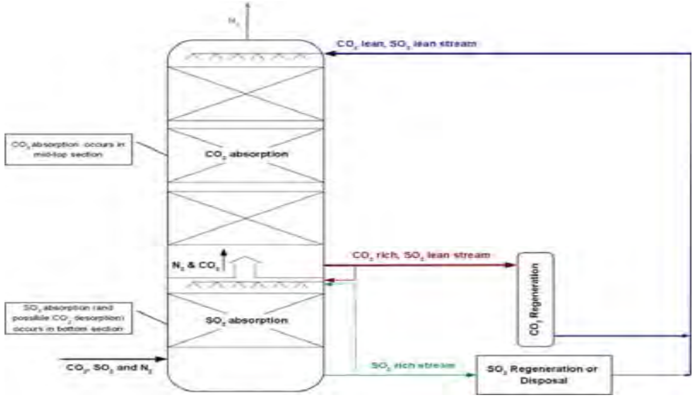
Pilot plants
- AGL Loy Yang Power
- Delta Electricity
- Stanwell
- China Huaneng (Beijing)
- China Huaneng (Changchun)

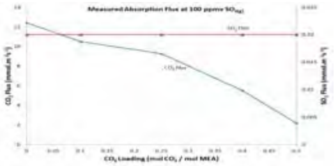
Research & Development
- Novel amines
- Novel processes & equipment
- Adsorbents
- Membranes
- Environmental impacts

Piloting PCC Technologies in Australia



Integrated Single Stream SO_2 and CO_2 Capture (Dr. Erik Meuleman)





Puxty *et al.*, 2012, WO2012_097406

Rotating Liquid Sheet contactor (Dr. Leigh Wardhaugh)

Basic principles

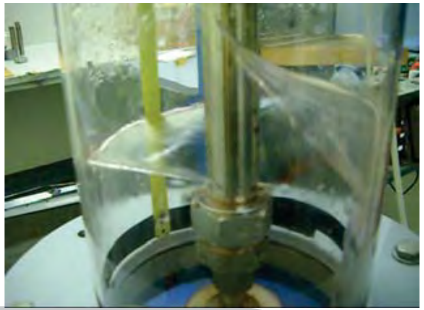
- Surface area of stabilized liquid sheet greater than that resulting droplets.
- Rotating liquid surface proven experimentally to pump gas .
- Centrifugal + liquid pumping force creates interfacial area.

Advantages

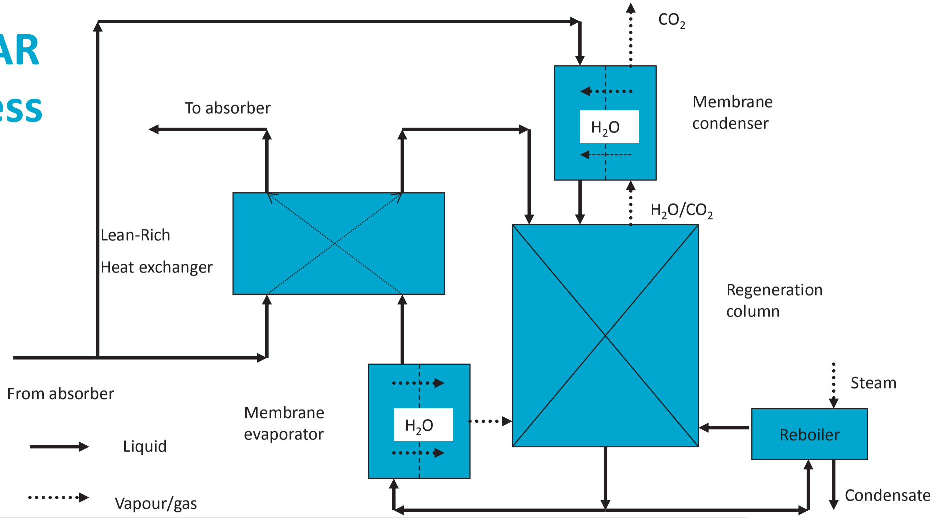
- Higher gas velocities possible.
- Liquid entrainment significantly reduced
- Suitable for viscous solvents

Challenges

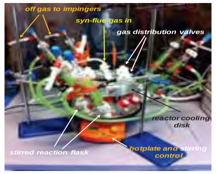
- Scale-up to commercial scale
- Liquid residence time low



MALAR Process

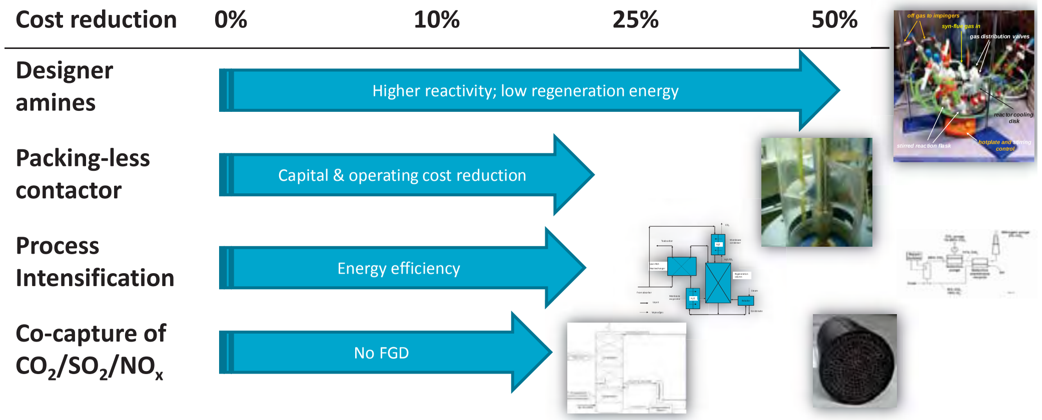


Emission issues addressed via integrated approach (Dr. Merched Azzi)



1. **Formation of potentially harmful components**
    - Absorbent degradation in absorber
    - Absorbent degradation in desorber
2. **Emission analysis**
    - Estimation of concentrations using process models
    - Actual measurements in pilot plants
3. **Dispersion**
    - Smog chamber to investigate atmospheric degradation
    - Updating dispersion models with atmospheric chemistry

Perspective on PCC cost reductions in Australia



Cost reduction	0% 10% 25% 50%
Designer amines	Higher reactivity; low regeneration energy
Packing-less contactor	Capital & operating cost reduction
Process Intensification	Energy efficiency
Co-capture of $CO_2/SO_2/NO_x$	No FGD

Key research and engagement partners in PCC

Australian Government Department of Industry
Victoria The Place To Be
NSW Government
Delta electricity
anlecr&d
Global CCS Institute
Brown Coal Innovation Australia
stanwell
IHI Realize your dreams
Energy in action AGL
EnergyAustralia
GASSNOVA
Statoil
TNO innovation for life
SINTEF
华能清洁能源研究院 HUANENG CLEAN ENERGY RESEARCH INSTITUTE
RITE Research Institute of Innovative Technology for the Earth
iCO2ap
HiPerCap
MONASH University
Newcastle
The Rochelle Lab The University of Texas at Austin CO2 Capture
Federation University Australia
清华大学 Tsinghua University
Zhejiang University

Thank you

Energy Flagship

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w http://www.csiro.au/science/Post-combustion-capture.html

CSIRO TV
http://tv.csiro.au/#v=xbz189hynwj6

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HiPerCap - **High Performance Capture**
FP7 Grant agreement n° 608555

HiPerCap Overview

Hanne Kvamsdal, Co-ordinator

Melbourne, Victoria, Australia, 25th -27th March 2015

Content

- ☐ Main facts
- ☐ Project partners
- ☐ Main objectives
- ☐ Overview work-packages
- ☐ Dissemination

Main facts

- ☐ HiPerCap is funded by EU
  - ✓ Call specifically important twinning with Australian partners and projects
  - ✓ Integrated with 5 other projects within the same call
- ☐ Budget:
  - ✓ Total: 7.7 M€
  - ✓ From EU: 4.9 M€
- ☐ Duration:
  - ✓ 4 years started January 2014
    - ➢ WP1-4: year 1-3
    - ➢ WP5: year 4

Project partners:

SINTEF
NTNU
TNO innovation for life
Ministerio de Economia y Competitividad CSIC
PROCEDE
CSIRO
TIPS RAS
MAST
DNV·GL
EDF
CNRS Centre National de la Recherche Scientifique
CO2 Solutions
Algae-Tech
e·on
ANDRITZ
gasNatural fenosa

Main objectives

1. Develop environmentally benign energy- and cost-efficient technologies for post-combustion capture
   - ✓ Absorption
   - ✓ Adsorption
   - ✓ Membranes

2. Develop a methodology for fair comparison and benchmarking of the technologies

---

Objectives - more specifically:

- Reduce the total efficiency penalty by 25% compared to state-of-the-art capture technology
  - ✓ demonstrated in the EU project CESAR
- Deliver proof-of-concepts for each technology
- Improve the process designs to reduce capital and operating costs, considering aspects such as :
  - ✓ environmental impact
  - ✓ operability and flexibility
  - ✓ size of equipment
  - ✓ choice of materials
- Assess technologies and processes for selection:
  - Two most promising breakthrough capture processes
- Establish a technological roadmap for the further development

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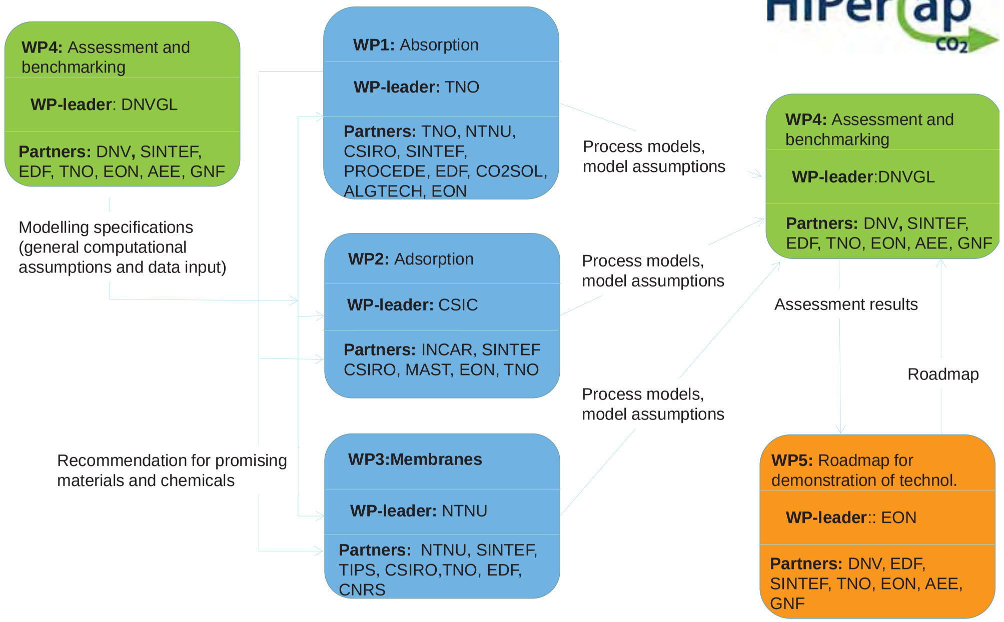


WP4: Assessment and benchmarking

WP-leader: DNVGL

Partners: DNV**,** SINTEF, EDF, TNO, EON, AEE, GNF

Modelling specifications (general computational assumptions and data input)

Recommendation for promising materials and chemicals

WP1: Absorption

WP-leader: TNO

Partners: TNO, NTNU, CSIRO, SINTEF, PROCEDE, EDF, CO2SOL, ALGTECH, EON

WP2: Adsorption

WP-leader: CSIC

Partners: INCAR, SINTEF CSIRO, MAST, EON, TNO

WP3:Membranes

WP-leader: NTNU

Partners: NTNU, SINTEF, TIPS, CSIRO,TNO, EDF, CNRS

Process models, model assumptions

Process models, model assumptions

Process models, model assumptions

WP4: Assessment and benchmarking

WP-leader:DNVGL

Partners: DNV**,** SINTEF, EDF, TNO, EON, AEE, GNF

Assessment results

Roadmap

WP5: Roadmap for demonstration of technol.

WP-leader:: EON

Partners: DNV, EDF, SINTEF, TNO, EON, AEE, GNF

WP1 Absorption based technologies (1)

(WP-leader: Peter van Os from TNO)

Task 1.1 Enzyme catalysis of CO_2 absorption

- **Idea:** Enzymes in the solvents can drastically accelerate the capture of CO_2
- **In the project:** test carbonic anhydrase and developed an optimized process
- **Challenges:** keep the enzymes stable throughout the whole process and separation of enzymes prior the desorption

Task 1.2: Precipitating solvent systems

- **Idea:** Only the CO_2 part (small stream) of the total solvent system needs regeneration and higher regeneration pressure (lower CO_2 compression work) and no harmful emission (amino acids)
- **In the project:** developed an optimized process
- **Challenge:** Control absorption and precipitation and development of large scale slurry process

WP1 Absorption based technologies (2)

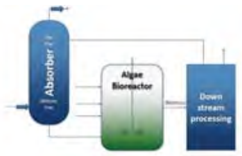
(WP-leader: Peter van Os from TNO)

Task 1.3: Strong bicarbonate forming solvents

- **Idea:** Bicarbonate forming amines with a high pKa will accelerate reactions kinetics and also allows to regenerate at lower temperatures
- **In the project:** Determine 2-3 promising candidates for detail studies
- **Challenge:** Many candidates. Potentially low absorption rates. A promoter might be required.

Task 1.4: Integration of CO_2 absorption with CO_2 utilization

- **Idea:** use the loaded solvent as "food" for the algae, which will eat the CO_2 and then produce biomass
- **In the project:** Test a combination of an absorber and a bioreactor and select a suitable algae strain
- **Challenge:** Selection of solvent which is attractive to the algae, but not eaten by the algae.



WP1 Absorption based technologies (3)

(WP-leader: Peter van Os from TNO)

Task 1.5: Study of bio-mimicking systems

- **Idea:** Fundamental study of CO_2 binding mechanisms in nature and determine processes for utilization industrially. Input to development in other tasks (1.1, 1.2, and 3.1).
- **In the project:** Reviewing and assessment of potential applicability of biological CO_2 binding processes. Some screening experiments
- **Challenges:** define possible systems
-

Task 1.6: Process modelling and simulation

- **In the project:** Model and simulate concepts from tasks 1.1, 1.2, and 1.3 as input to benchmarking in WP4
- **Challenges:** interactions with the other tasks and WP4, lack of proper data and modelling assumptions

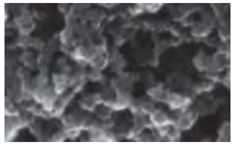
---

WP2 Adsorption based technologies

WP-leader: Cova Pevida from CSIC

Task 2.1: Sorbent development

- **Idea:**
  Development of low temperature solid sorbents:
  1. High surface area
  2. Low-cost carbon-based
- **In the project:** production and characterization
- **Challenges:** attain the performance targets



Task 2.2: Process development

- **Idea:** Two temperature swing processes:
  1. Fixed beds
  2. Moving beds
- **In the project:** Lab and semi-pilot testing
- **Challenge:** the process heat efficiency strongly depend on the selected design

---

WP2 Adsorption based technologies

WP-leader: Cova Pevida from CSIC

Task 2.3: Process modelling

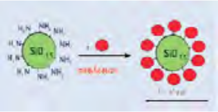
- **In the project:** Model and simulate concepts based on work in Tasks 2.1 and 2.2 as input to benchmarking in WP4
- **Challenges:** interactions with the other tasks and WP4, lack of proper data and modelling assumptions

WP3 Membrane based technologies

WP-leader: May-Britt Hägg from NTNU

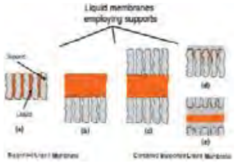
Task 3.1: Hybrid membrane development

- **Idea:** Develop a high flux mixed matrix membrane based on incorporation of nanoparticles in a polymer
- **In the project:** production and study on transport phenomena
- **Challenges:** attain the performance targets



Task 3.2: Supported ionic liquid membranes (SILMs) development

- **Idea:** Develop supported ionic liquid membranes
- **In the project:** development and preparation and performance testing
- **Challenges:** attain the performance targets



WP3 Membrane based technologies

WP-leader: May-Britt Hägg from NTNU

Task 3.3 : Process modelling and simulation

- **In the project:** Model and simulate concepts based on work in Tasks 3.1 and 3.2 as input to benchmarking in WP4
- **Challenges:** interactions with the other tasks and WP4, lack of proper data and modelling assumptions

---

WP4 Assessment of CO_2 capture technologies (1)

WP-leader: Jock Brown from DNVGL

Task 4.1: Establishment of assessment methodology

- **Idea:**
  1. Screening on basic information availability
     - ✓ Creating a minimum level of principle and conceptual knowledge of a capture process
  2. Bring the concepts and technologies to the level of a process or applications
     - ✓ The novel capture technology imbedded in an application or process
  3. Consistent way of scaling up to representative scale of application
     - ✓ Using modelling and/or engineering approaches
- **In the project:** Definition of base case(s), reference capture technology, system boundaries, modeling approaches/assumptions, comparison criteria etc.
- **Challenge:** define a methodology which is really fair for all technologies involved

---

WP4 Assessment of CO2 capture technologies (2)

WP-leader: Jock Brown from DNVGL

Task 4.2: Data collection of capture technologies studied in WP1-3

- **Idea:** Assist WP1-3 in gathering the data for showing the technical feasibility of each technology.
- **In the project:** Define how to communicate with the other WPs (i.e. questionnaire, interest group, integrated workshops) and collection of the necessary data determined in Task 4.1
- **Challenge:** Communication with WP1-3

WP4 Assessment of CO2 capture technologies (3)

WP-leader: Jock Brown from DNVGL

Task 4.3: Assessment of capture technologies studied in WP1-3

- **Idea:** 3 steps procedure
- **In the project:**
  1. Assessment of each technology
  2. Comparison and benchmarking against the reference technology
  3. Assessment and if necessary update of the chosen methodology (input to Task 4.1)
- **Challenge:** Uncertainty range for the various technologies

---

WP4 Assessment of CO2 capture technologies (4)

WP-leader: Jock Brown from DNVGL

Task 4.4: Guidelines for selection and benchmarking of the two breakthrough technologies studied in WP5

- **Idea:** Establish guidelines for selection of two promising technologies for further studies and benchmarking (selection will be supported by all partners)
- **In the project:** The guidelines will be based on the previous work in the other tasks and results from 4.3, but also discussed in the interest group and with the whole consortium
- **Challenge:** agreed guidelines supported by all partners in the consortium

---

WP5 Study of breakthrough processes for pilot testing **WP-leader: Adam Al-Azki from E.ON**

Task 5.1 Detailed study of selected capture technology 1

Task 5.2 Detailed study of selected capture technology 2

For both tasks:

- **Idea:** Establish a roadmap for demonstration of the technology
- **In the project:** Identification of any knowledge gaps and plan for demonstration at industrial pilot plant. Other activities might be additional experiments in the lab, improved models and further optimization.
- **Challenge:** Limited budget

WP and task structure

- WP6: Project Management
  - ✓ WP-leader: Hanne Kvamsdal
- WP7: Dissemination outside of the consortium
  - ✓ WP-leader: Hanne Kvamsdal
  - ✓ Arranging two workshops (Australia 2015, Europe 2017)
  - ✓ Presentations at international conferences (GHGT-12, PCCC-3 and others)
  - ✓ Web-site: www.sintef.no/hipercap
- WP8: Collaboration with an Australian partner
  - ✓ WP-leader: Paul Feron in CSIRO
  - ✓ CSIRO will be a working partner in HiPerCap and contribute to WP 1, 2, 3, and 7.

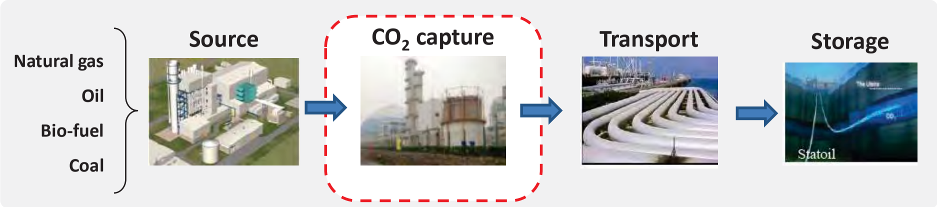
Acknowledgement:

The project receives funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 608555. We gratefully acknowledge the industrial partners who also financially support the project.

HiPerCap

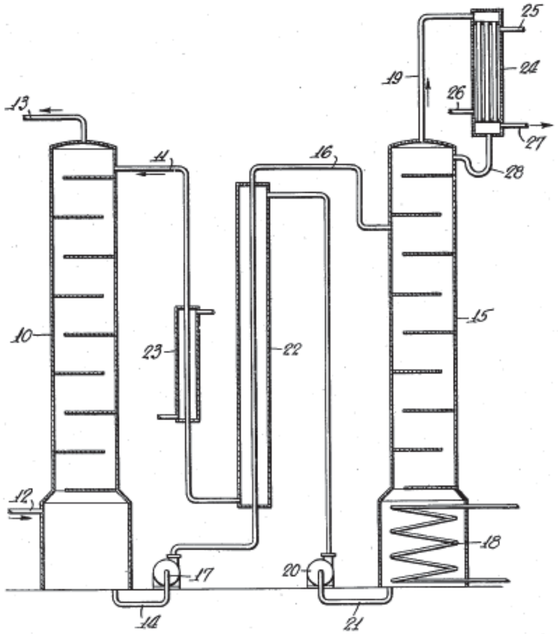
High Performance Capture

Absorption Systems

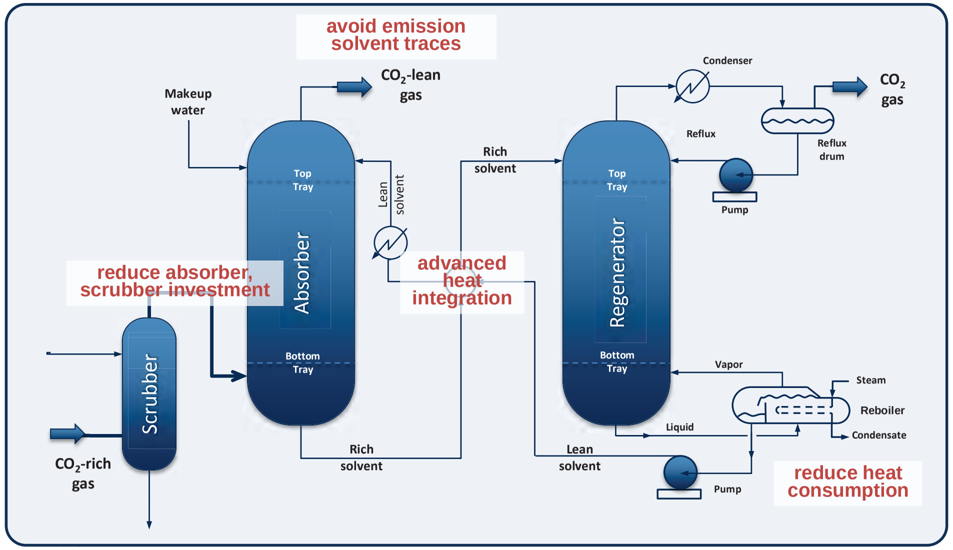


Earl Goetheer, Principal scientist at TNO

Capture in 1930



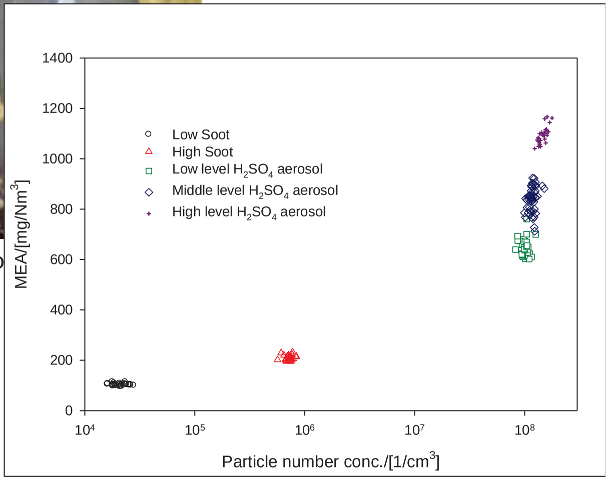
Challenges Post-combustion Capture



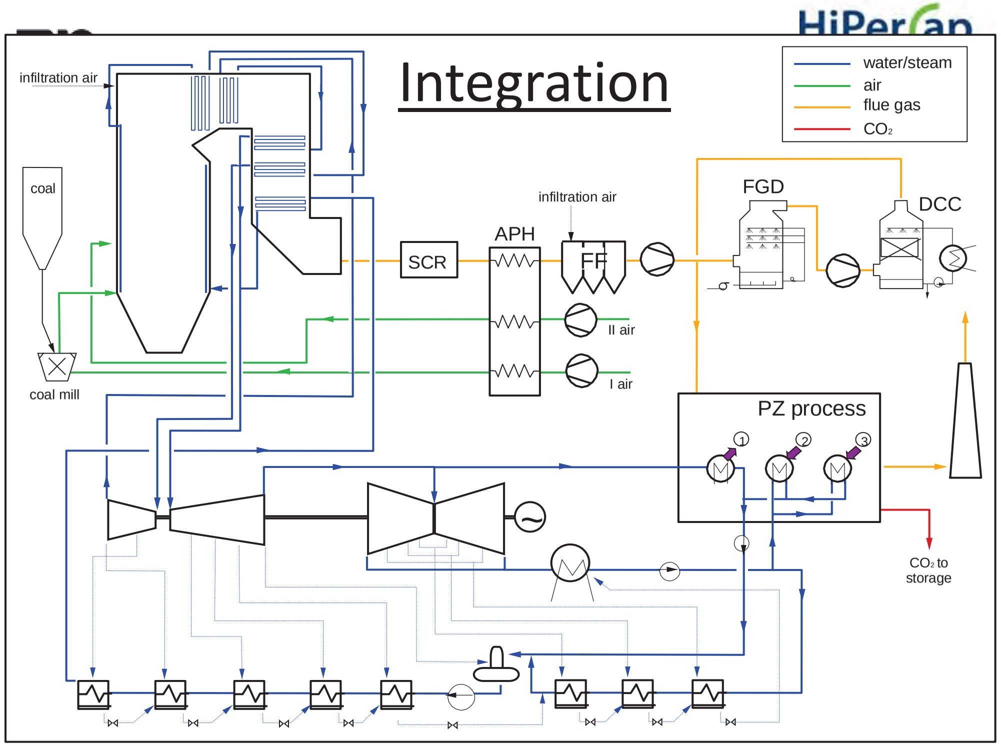
Emission


Volatile emission

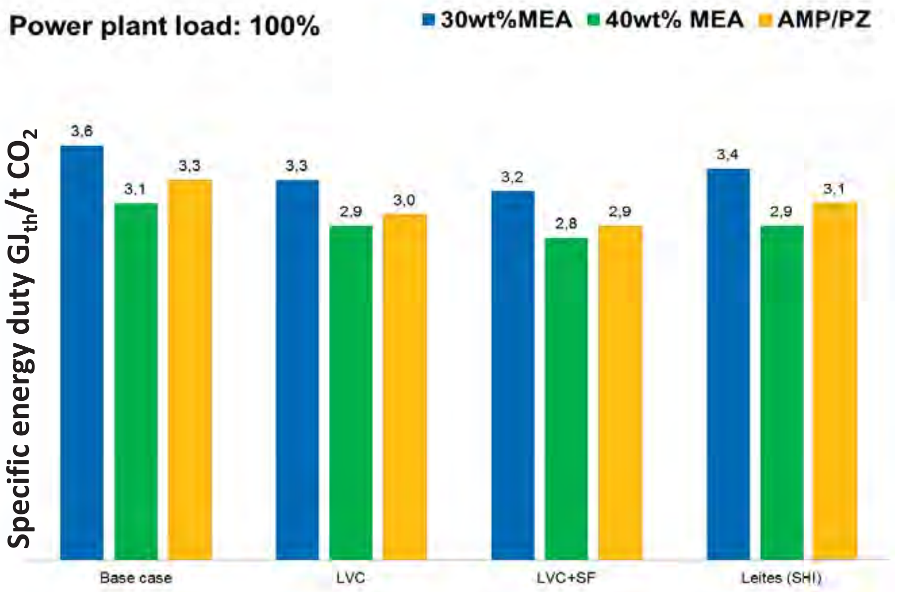
Aero



Integration



Energy Consumption



Technologies

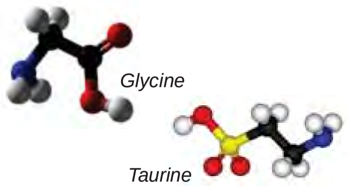
- Enzymatic catalysed CO2 capture
- Biomimicking
- Strong bicarbonate formers

- Precipitating solvent systems

- Capture integrated with algae cultivation

Precipitating solvent systems

CO_2 absorption with amino acid salts



- ✓ Resistant to oxidative degradation
- ✓ Less waste generated products
- ✓ Zero emissions of active reactant
- ✓ Potential energy savings
- Limited solubility in water

Ionic equilibria In water:

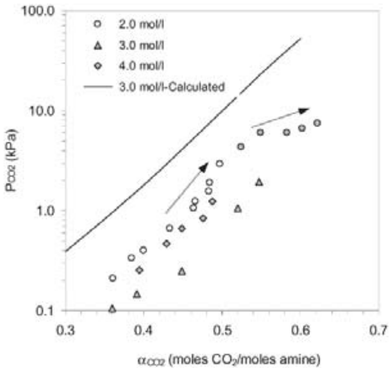
R-(NH_2)COOH → R-$(NH_3)^+COO^-$ zwitterion

R-$(NH_3)^+$ COOH $\overset{-H^+}{\leftrightarrow}$ R-$(NH_3)^+COO^-$ $\overset{-H^+}{\leftrightarrow}$ R-(NH_2)+COO^-

R-$(NH_3)^+COO^-$ + KOH → R-$(NH_2)COO^-K^+$ reactive

Effect of solid precipitation

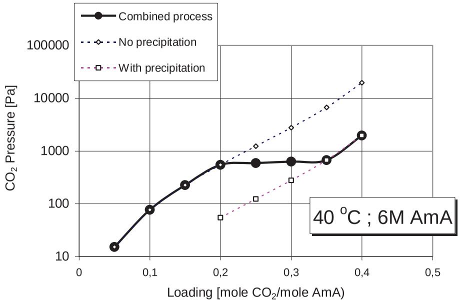
Enhanced absorption capacity: DECAB principle



Experimental: Aqueous potassium taurate.

Dark points: precipitation

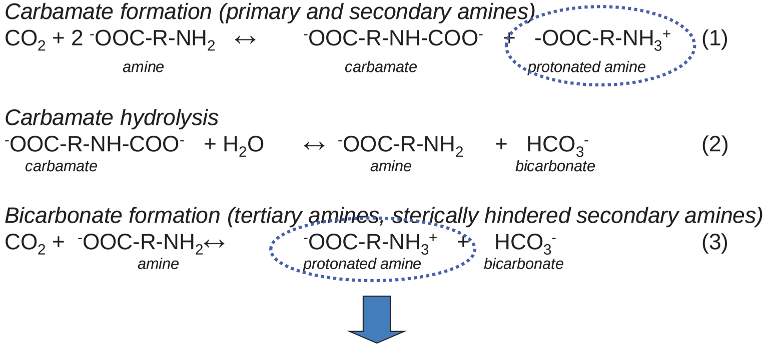
From: Kumar et al. Ind. Eng. Chem. Res. 42, 2003, 2841-2852



Schematic picture: effect of solvent precipitation

Why do you get higher capacity?

Reactions with CO_2 (similar to “normal” amine systems):



Carbamate formation (primary and secondary amines)

CO_2 + 2 $^-$OOC-R-NH_2 ↔ $^-$OOC-R-NH-COO^- + -OOC-R-NH_3^+ (1)

amine carbamate protonated amine

Carbamate hydrolysis

$^-$OOC-R-NH-COO^- + H_2O ↔ $^-$OOC-R-NH_2 + HCO_3^- (2)

carbamate amine bicarbonate

Bicarbonate formation (tertiary amines, sterically hindered secondary amines)

CO_2 + $^-$OOC-R-NH_2↔ $^-$OOC-R-NH_3^+ + HCO_3^- (3)

amine protonated amine bicarbonate

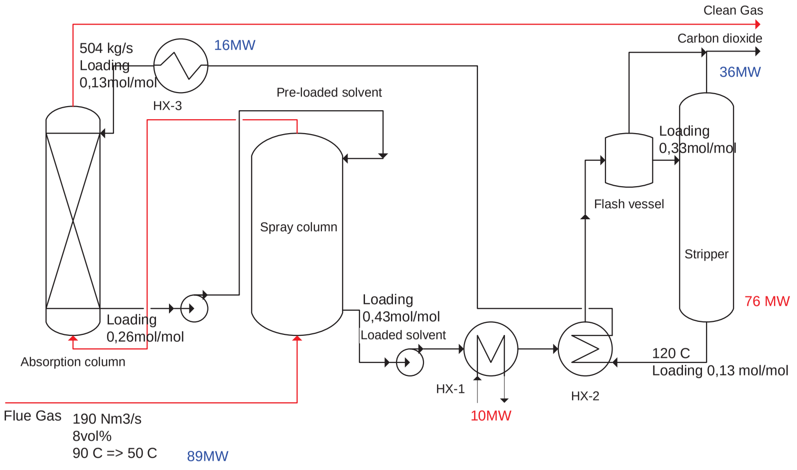
Removed by precipitation

Working with solids in the process

- Controlled precipitation of the solvent
- Solids should appear where they can be handled
- Equipment selected for solids handling
- Process complexity increased

Working with solids IF there is an economic breakthrough

DECAB Process
(Design & Modelling Results)

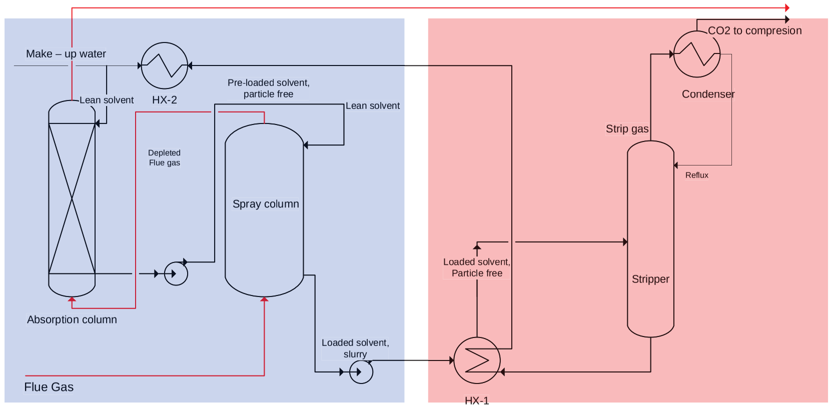


From DECAB to DECAB+

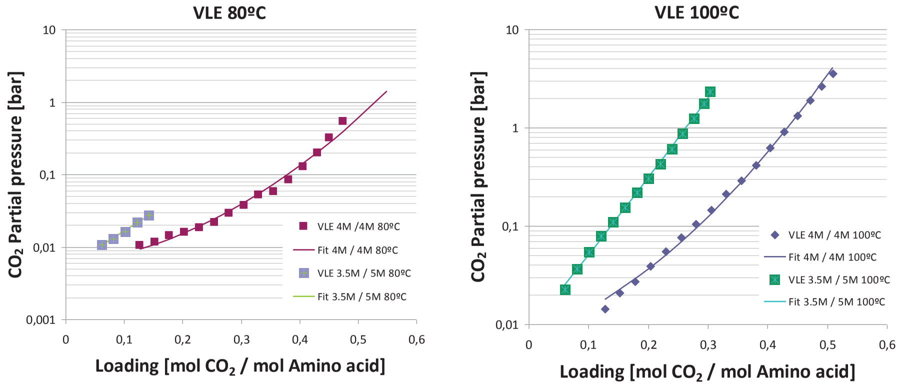
Conditions to enhance absorption and desorption

Absorption: High pH (basicity)

Desorption: Low pH (acidity)

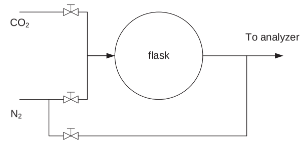


Effect of DECAB$^+$. Enhanced desorption



The pH shift increases the partial pressure of CO_2 at a given loading

Proof of principle



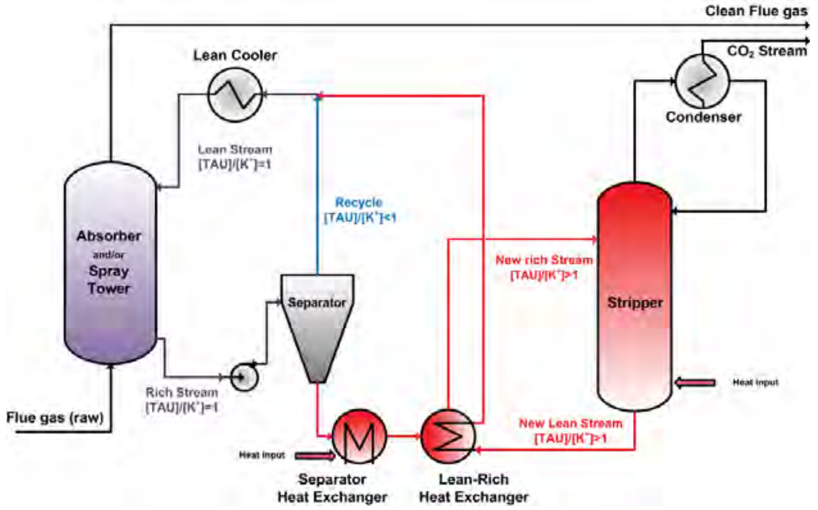
Low lean loadings are possible at relatively low temperatures

Liquid removed Vol (%)	Conc. M	T C	Rich Loading mol/mol	Lean Loading mol/mol
0%	4	74.1	0.65	0.36
21%	4.3	77.1	0.65	0.3
42%	4.9	76	0.65	0.17
0%	4	89.7	0.65	0.24
21%	4.3	95.4	0.65	0.13
42%	4.9	93.7	0.65	0.09

Key advantages of DECAB$^+$

- Low desorption temperature
  - Possibility to use low grade heat / waste heat (Ideal for the refinery case)
  - Possibility to achieve lower lean loadings without increasing reboiler temperature (Ideal for streams with low CO_2 concentrations such as flue gas from gas turbines combustion)
- High pressure desorption
  - Lower operating costs due to enhanced desorption
- All environmental advantages from amino acids

DECAB$^+$ Process Concept

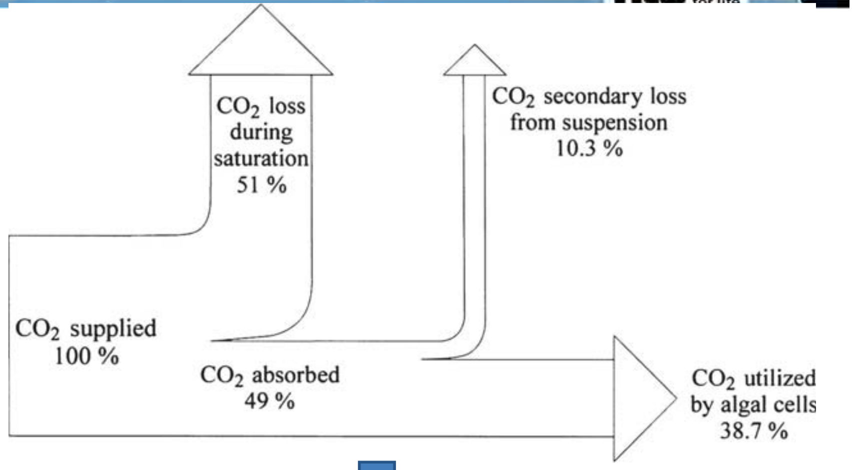


CO2 capture algae cultivation

EXAMPLES OF HIGH PRODUCTIVITY BIOMASS

Biomass community	Location	Yield (t d.w. ha^{-1} y^{-1})	Photosynthetic efficiency (%)
Hybrid poplar (Populus spp.) (C3)	Minnesota	8 -11	0.3- 0.4
Water hyacinth (Eichornia crassipes)	Mississippi	11 – 33 (>150)	0.3- 0.9
Switch grass (Panicum virgatum) (C4)	Texas	8-20	0.2- 0.6
Sweet sorghum (Sorghum bicolor) (C4)	Texas-California	22 - 47	0.6-1.0
Coniferous forest	England	34	1.8
Maize (Zea mays) (C4)	Israel	34	0.8
Tree plantation	Congo	36	1.0
Tropical forest	West Indies	60	1.6
Algae	Different locations	70	2-2.5
Sugar cane (Saccharum officinarum)	Hawaii-Java	64-87	1.8-2.6
Napier grass (Pennisetum purpureum)	Hawaii, Puerto Rico	85-106	2.2-2.8

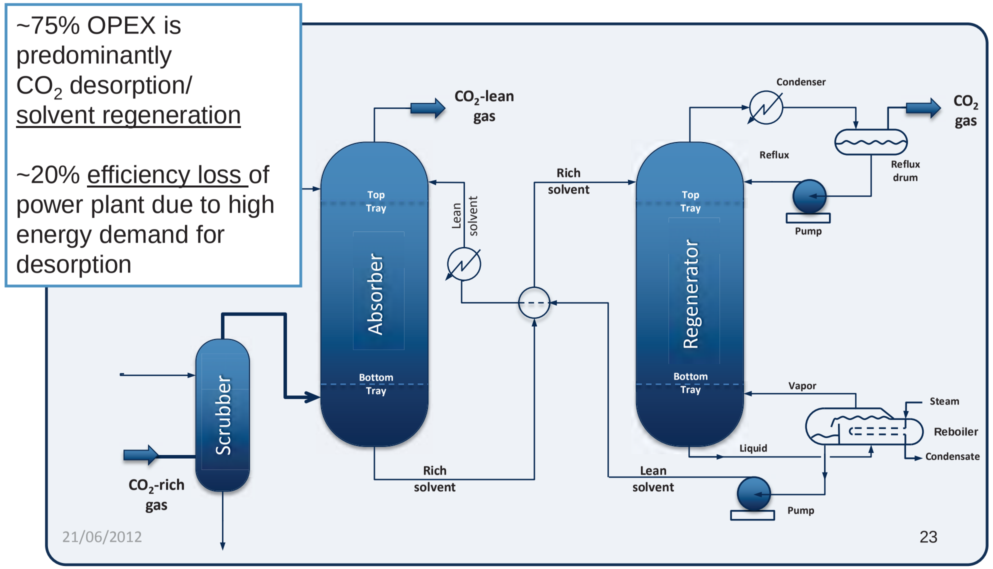
M. Tredici, Symposium " I Biocarburanti di seconda e terza generazione" Roma 14 April 2011



Per kg dry biomass ~ 4,4 kg of CO2 is needed

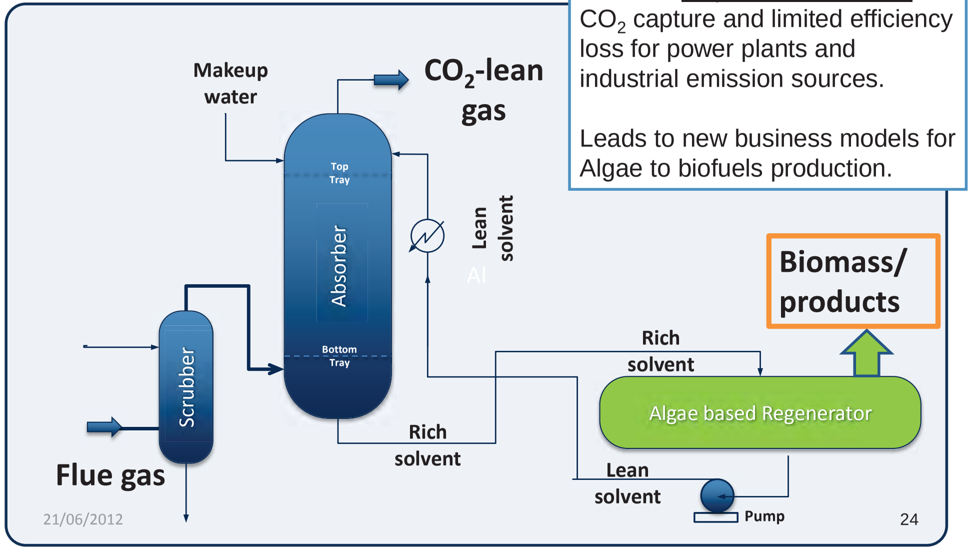
~75% OPEX is predominantly CO$_2$ desorption/ <u>solvent regeneration</u>

~20% <u>efficiency loss</u> of power plant due to high energy demand for desorption

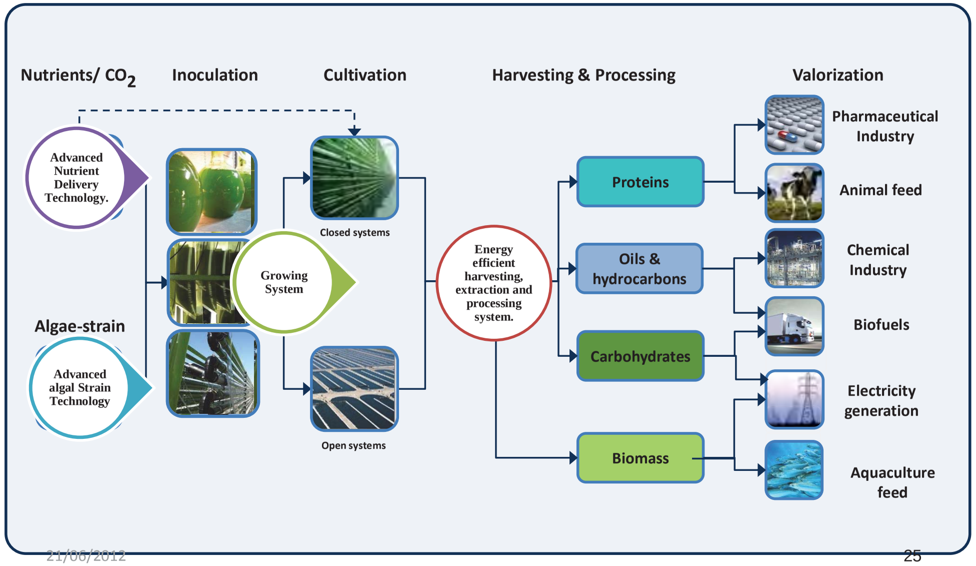


Need for <u>major cost reduction</u> of CO$_2$ capture and limited efficiency loss for power plants and industrial emission sources.

Leads to new business models for Algae to biofuels production.



From algae to products – improvement options



Nutrients/ CO_2

Inoculation

Cultivation

Harvesting & Processing

Valorization

Advanced Nutrient Delivery Technology.

Algae-strain

Advanced algal Strain Technology

Growing System

Closed systems

Open systems

Energy efficient harvesting, extraction and processing system.

Proteins

Oils & hydrocarbons

Carbohydrates

Biomass

Pharmaceutical Industry

Animal feed

Chemical Industry

Biofuels

Electricity generation

Aquaculture feed

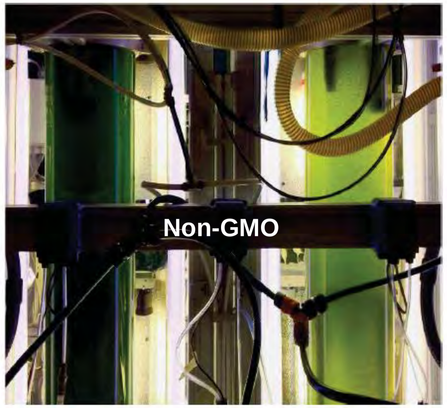
Advanced algal Strain Technology

Limitation: Mutual shading

Decreased light penetration
=
Slower growth
=
Lower biomass density

Solution: Light efficient strains
Same algal density **1,5 gr/ltr**

Wild strain Improved Strain



Max. algal cell density of **8 gr/ltr** for Light Efficient Strain

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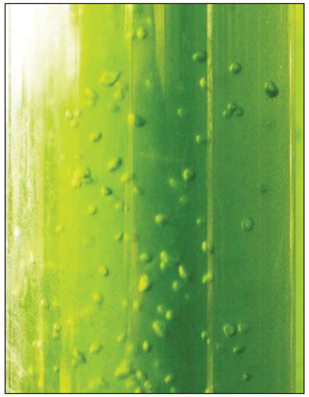
Advanced Nutrient Delivery Technology.

Efficient CO_2-nutrient feeding

Current state-of-the-art



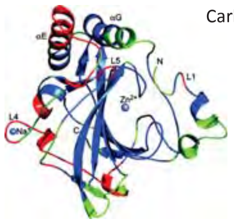
Pure CO_2 bubbling

Flue gas washing/bubbling
(diluted CO_2 stream)

Two possible routes researched at TNO

Enzyme promoted CO_2 capture

- **Carbonic Anhydrase** enhances the uptake rate of CO_2 into an absorption liquid
- **Algae** regenerate the carbonate-based absorption liquid



Carbonic Anhydrase II

(source: Premkumar *et al.* (2005) PNAS, 102 (21) p.7493-7498)

Amine based CO_2 capture

- Cultivation of algae directly on CO_2 "captured" in **amine-based solvents**
- **Algae** regenerate solvent which can be reused for CO_2 capture

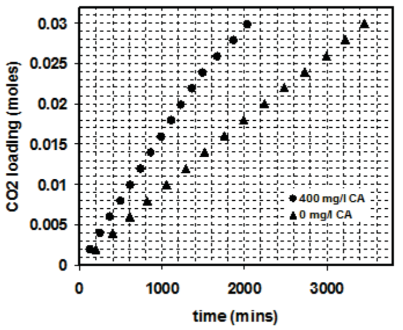
Spirulina platensis

(source http://www.energen.it/inglese/olio_da_alghe.html)

Route 1: Enzyme promoted CO_2 capture

- Carbonate solutions are **cheap** compared to other CO_2 absorption liquids, but have a **slow CO_2 uptake rate**
- Addition of **carbonic anhydrase** to sodium carbonate solution **increases** the rate of CO_2 uptake

Carbonic Anhydrase effects on CO_2 loading



Kinetic experiments showing the rate of CO_2 loading in the reference (▲, 2M sodium carbonate) and catalyzed (●, 2M sodium carbonate plus 400mg/L carbonic anhydrase) tests

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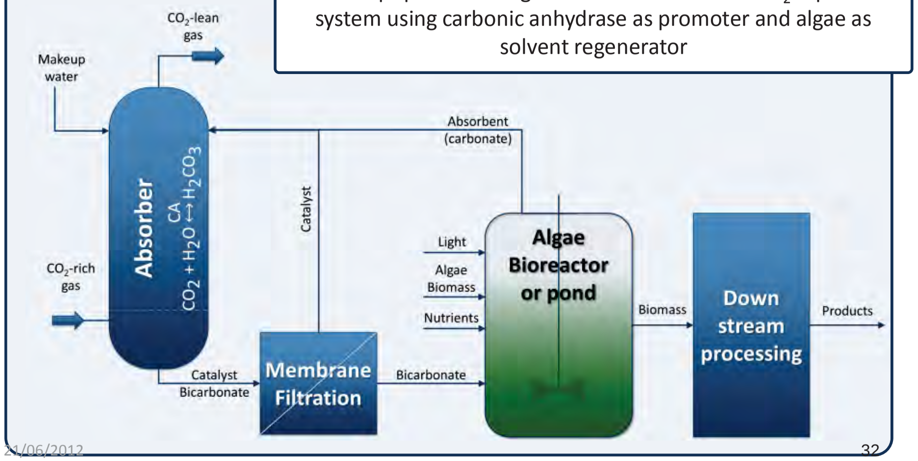
Route 1: Enzyme promoted CO_2 capture

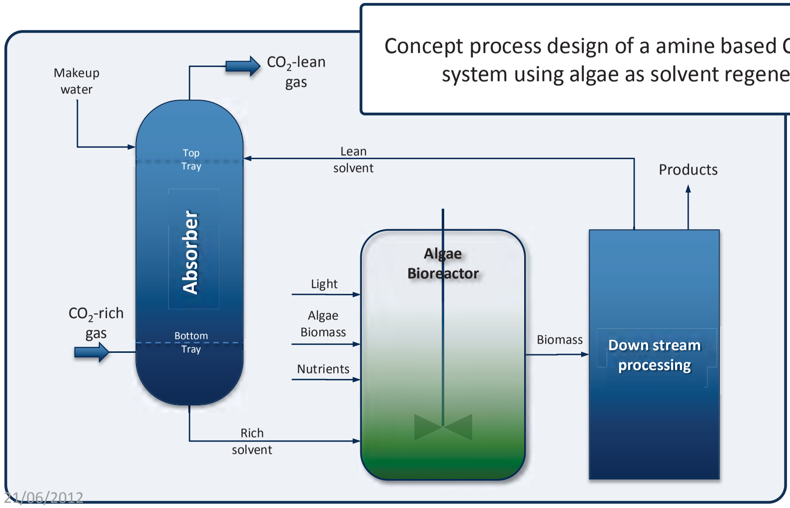
Concept process design of a carbonate based CO_2 capture system using carbonic anhydrase as promoter and algae as solvent regenerator



Route 2: Combining CO_2 capture with amine based solvents & algae cultivation

- The uptake of CO_2 by a amine-based solvent
- CO_2 stripping of solvent by consumption through algae in a solvent & medium solution
- Recycle of the solvent for new cycle of CO_2 uptake
- The algae biomass can be used for product.

Route 2: Algae-mediated CO_2 desorption from amine-based solvents



Concept process design of a amine based CO_2 capture system using algae as solvent regenerator

---

Capture solvent selection criteria

- 1. Non-toxic to algae culture
- 2. Slow biodegradable by algae culture
- 3. Cheap/abundant
- 4. Efficient capture of CO2
  (partly absorbed CO2 should be bicarbonate species)

It is of importance to note that 90% CO2 capture is **not** the objective

---

From problem to business

www.stichtingmilieunet.nl/.../sailing-algae.bmp

www.altdotenergy.com/wp-content/uploads/2009/...

Acknowledgement

Some references

US2014295531 (A1) - ENZYME PROMOTED CO2 CAPTURE INTEGRATED WITH ALGAE PRODUCTION – Goetheer et al.

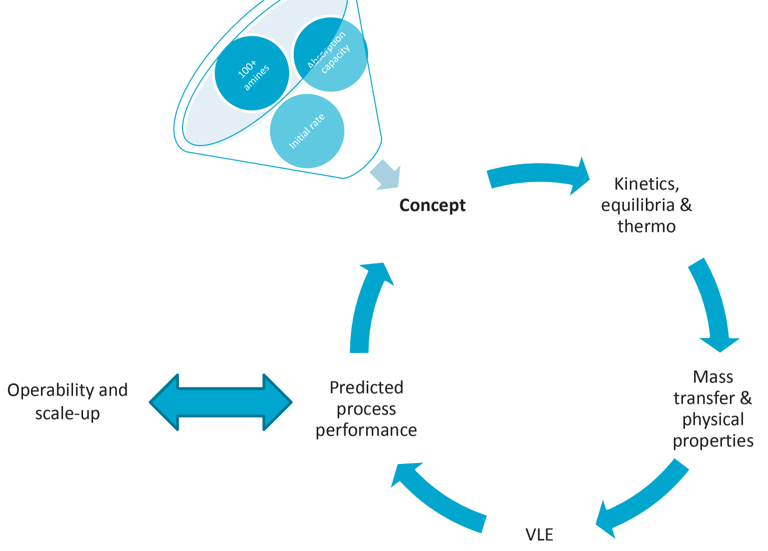
WO2013022349 (A1) - COMBINING ALGAE CULTIVATION AND CO2 CAPTURE – Goetheer et al.

Development of reactive chemical absorbents at the CSIRO

HiPerCap Workshop, March 25 2015
Graeme Puxty
Research Team Leader

CSIRO ENERGY FLAGSHIP
www.csiro.au

CSIRO's chemical absorbent research program



Concept

Kinetics, equilibria & thermo

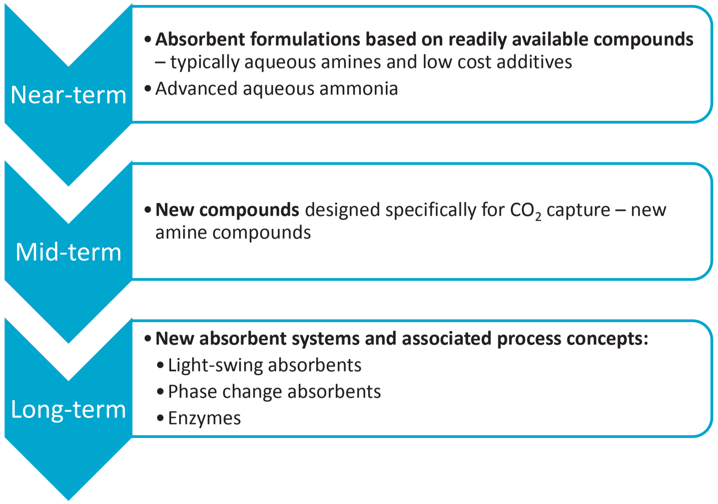
Mass transfer & physical properties

VLE

Predicted process performance

Operability and scale-up

CSIRO's chemical absorbent research program

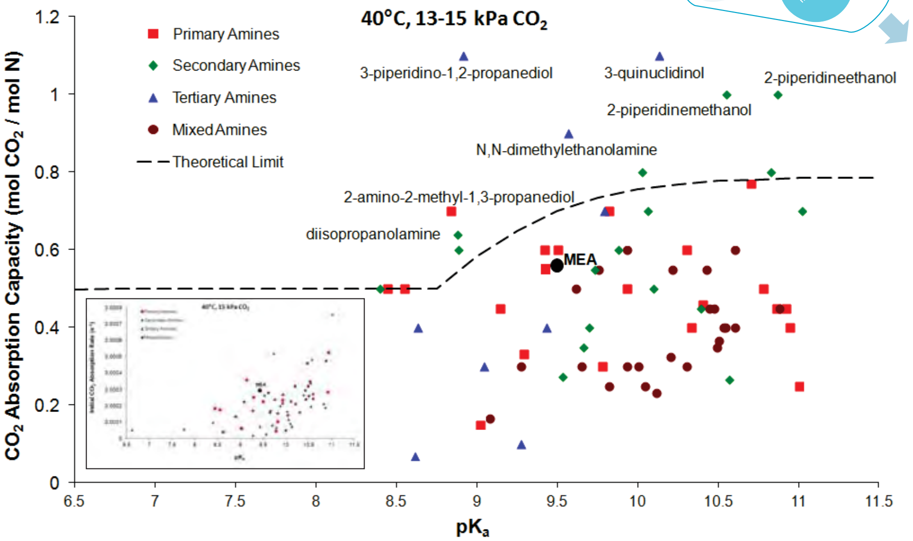


Near-term
- **Absorbent formulations based on readily available compounds** – typically aqueous amines and low cost additives
- Advanced aqueous ammonia

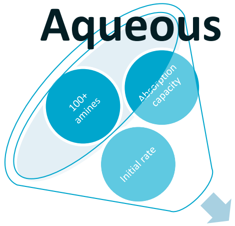
Mid-term
- **New compounds** designed specifically for CO_2 capture – new amine compounds

Long-term
- **New absorbent systems and associated process concepts:**
  - Light-swing absorbents
  - Phase change absorbents
  - Enzymes

Aqueous amine screening study



Aqueous amine screening study

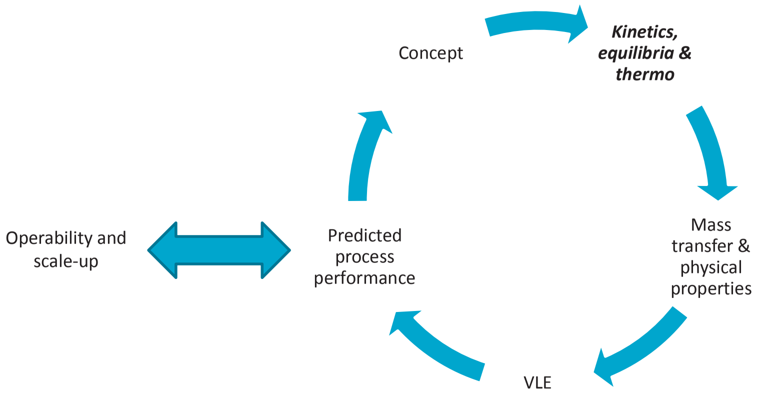


- **Over 100 amines screened** for CO_2 absorption capacity and initial absorption rate at a single set of conditions (40°C, 13-15 kPa CO_2)
- A combination of model predictions and experimental results allowed identification of **7 amines that performed better than expected**
- **Cyclic compounds** looked the most interesting
- Results have been **patented and published**:

M. I. Attalla, G. D. Puxty, A. W. Allport, M. Bown, Q. Yang and R. C. Rowland, Carbon dioxide capturing process, involves contacting carbon dioxide containing gas stream with aqueous alkanolamine solution, where alkanolamine solution is selected from group consisting of Tricine and salts. WO2009121135-A1 (2009).

G. Puxty, R. Rowland, A. Allport, M. Attalla, Q. Yang, M. Bown, R. Burns and M. Maeder, Carbon dioxide post combustion capture: a novel screening study of the carbon dioxide absorption performance of 76 amines. *Environmental Science & Technology*, 43 (2009) 6427-6433.

Understanding the chemistry



Concept

Kinetics, equilibria & thermo

Mass transfer & physical properties

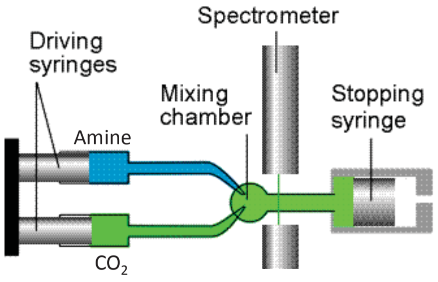
VLE

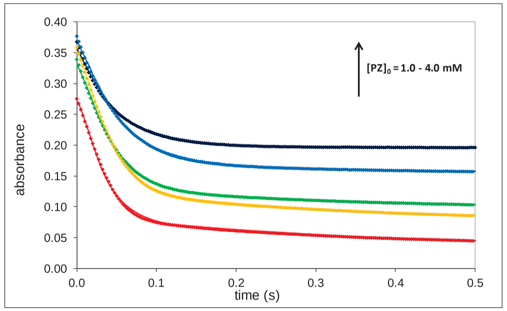
Predicted process performance

Operability and scale-up

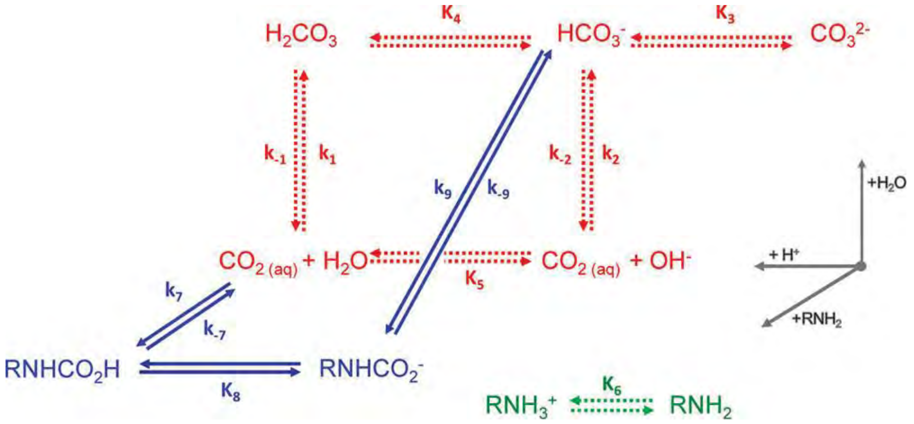
Kinetics, equilibria and thermodynamics

- Stopped-flow and UV-visible spectroscopy used to determine CO_2-amine reaction kinetics
- ^{1}H-NMR used to determine CO_2-amine reaction equilibria





What we learned – mechanistic understanding



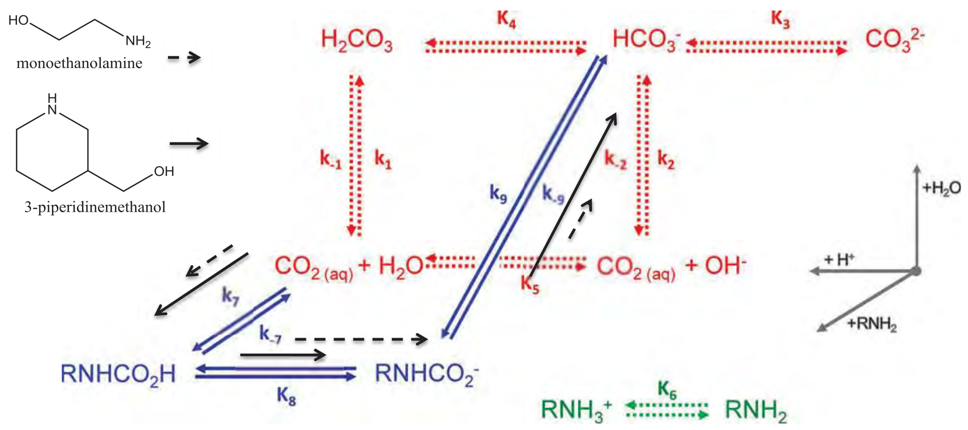
Fernandes, D., et al., *Protonation constants and thermodynamic properties of amines for post combustion capture of CO2. Journal of Chemical Thermodynamics*, 2012. ***51**: p. 97-102.*

Conway, W., et al., *Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO2(aq) and HCO3- with Monoethanolamine (MEA) in Aqueous Solution. Journal of Physical Chemistry A*, 2011. ***115(50)**: p. 14340-14349.*

McCann, N., et al., *Kinetics and Mechanism of Carbamate Formation from CO2(aq), Carbonate Species, and Monoethanolamine in Aqueous Solution. Journal of Physical Chemistry A*, 2009. ***113(17)**: p. 5022-5029.*

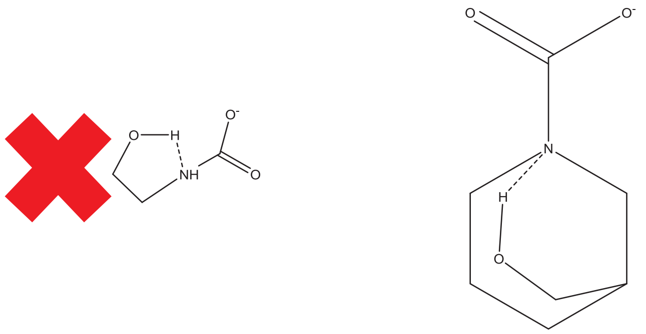
McCann, N., et al., *Molecular Interactions between Amine and Carbonate Species in Aqueous Solution - Kinetics and Thermodynamics. Greenhouse Gas Control Technologies 9*, 2009. ***1(1)**: p. 995-1002.*

What we learned – what is it about cyclic compounds?

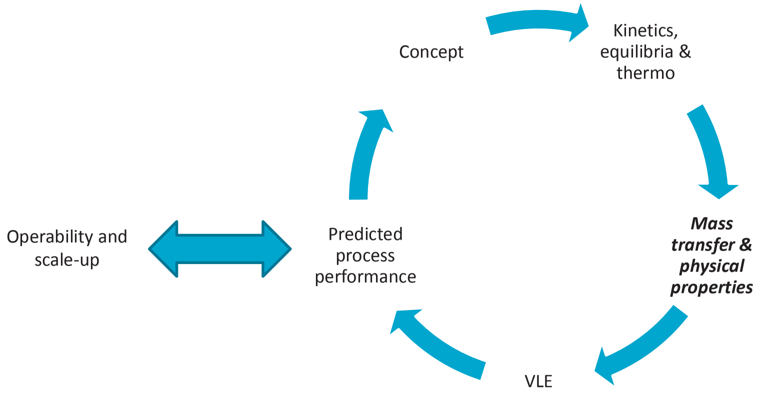


Conway, W., et al., *Toward the Understanding of Chemical Absorption Processes for Post-Combustion Capture of Carbon Dioxide: Electronic and Steric Considerations from the Kinetics of Reactions of CO2(aq) with Sterically hindered Amines. Environmental Science & Technology*, 2013. ***47(2): p. 1163-1169.***

What we learned – what is it about cyclic compounds?



Understanding absorption rates



Concept

Kinetics, equilibria & thermo

Mass transfer & physical properties

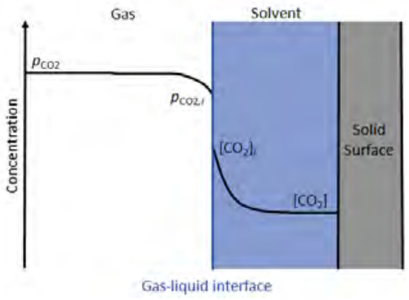
VLE

Predicted process performance

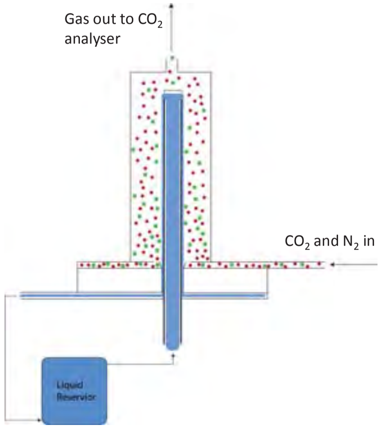
Operability and scale-up

What influences mass transfer?

- Chemical reaction kinetics
  (and equilibria as a function of CO_2 loading)
- Viscosity and surface tension
  (impacts diffusivity and flow)

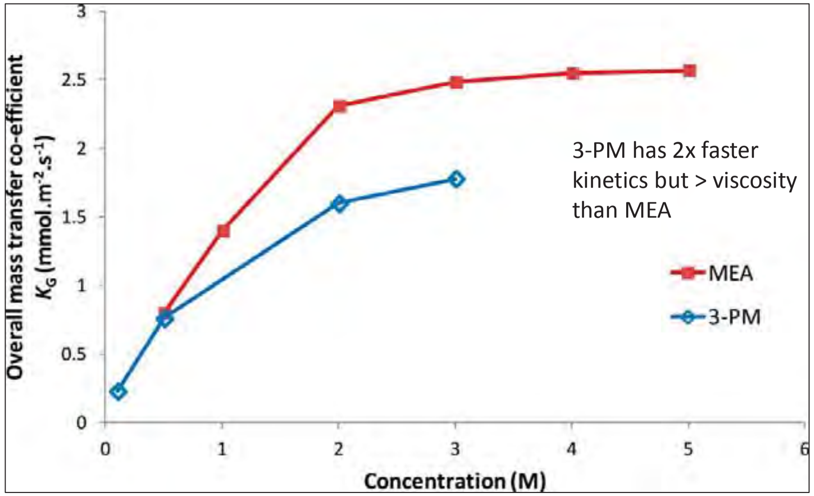


Wetted-wall reactor



The impact of viscosity

Faster kinetics ↑ ↓ Larger viscosity

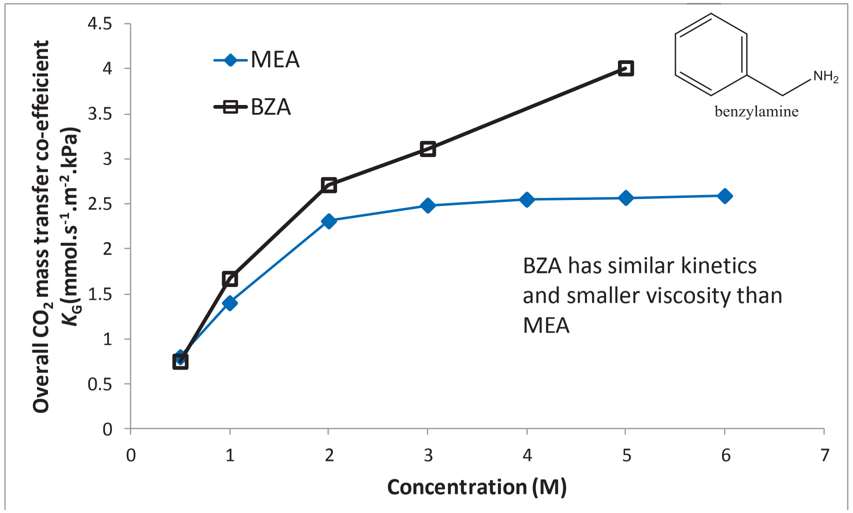


3-PM has 2x faster kinetics but > viscosity than MEA

Conway, W., et al., *CO2 Absorption into Aqueous Solutions Containing 3-Piperidinemethanol: CO2 Mass Transfer, Stopped-Flow Kinetics, H-1/C-13 NMR, and Vapor-Liquid Equilibrium Investigations. Industrial & Engineering Chemistry Research*, 2014. ***53(43): p. 16715-16724.***

The impact of viscosity

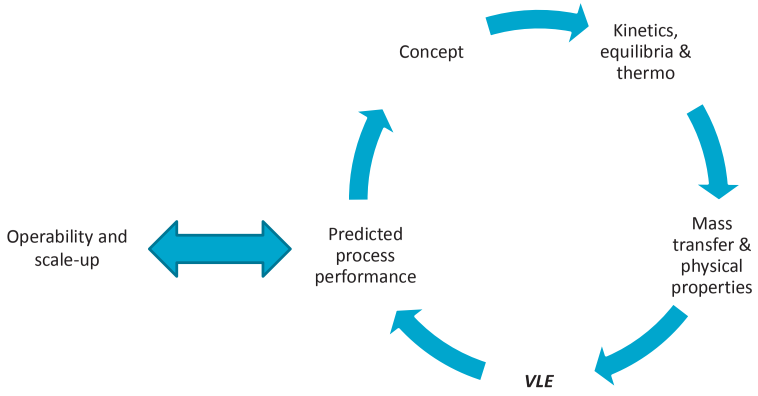
Faster kinetics ↑ ↓ Larger viscosity



BZA has similar kinetics and smaller viscosity than MEA

Conway, W., et al., *Rapid CO2 absorption into aqueous benzylamine (BZA) solutions and its formulations with monoethanolamine (MEA), and 2-amino-2-methyl-1-propanol (AMP) as components for post combustion capture processes. Chemical Engineering Jounral*, 2015. ***264: p. 954-961.***

Understanding vapour-liquid-equilibria



Concept

Kinetics, equilibria & thermo

Mass transfer & physical properties

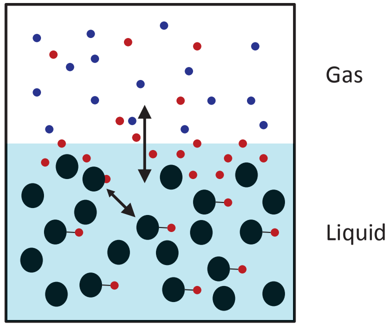
VLE

Predicted process performance

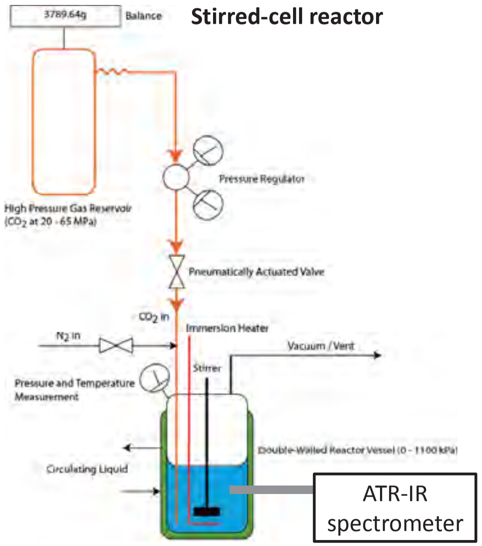
Operability and scale-up

What influences VLE?

- Chemical equilibria
- Chemical thermodynamics

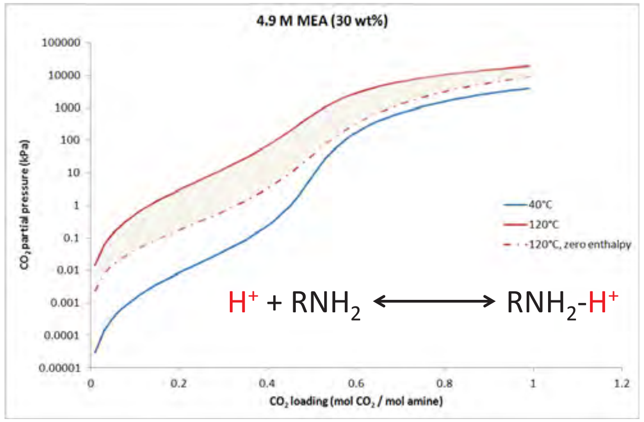


Stirred-cell reactor



What sort of VLE behaviour do we want?

- Large absorption capacity at low temperature and low CO_2 partial pressure
- Large reduction in capacity with increasing temperature



$H^+ + RNH_2 \longleftrightarrow RNH_2\text{-}H^+$

Putting it together

Fast reaction

$CO_2 + R_1R_2N\text{-}H \longleftrightarrow R_1R_2N\text{-}COO^- + H^+$

$H^+ + R_1R_2NH \longleftrightarrow R_1R_2NH\text{-}H^+$

Proton sink

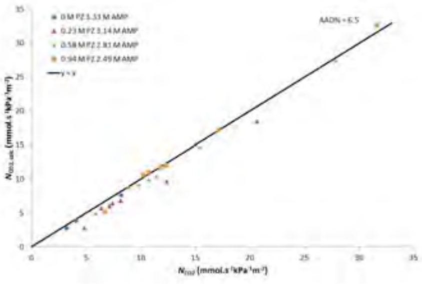
ΔH

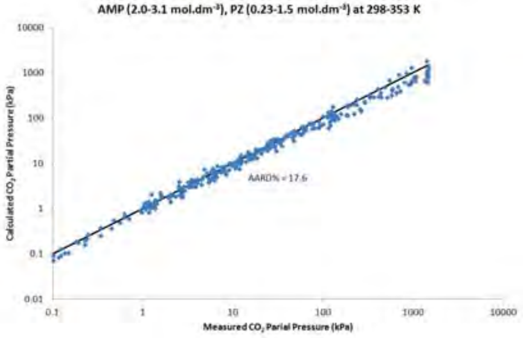
- Stable against degradation
- Non-corrosive
- Environmentally benign
- Low volatility and viscosity
- Negligible nitrosamine formation

- No single amine we investigated delivers on all these features
- Two options:
  - Amine formulations
  - New molecules

Intelligent formulation design

- Once we know the kinetics, equilibria and thermodynamics of an individual amine we can predict the behaviour of a mixture

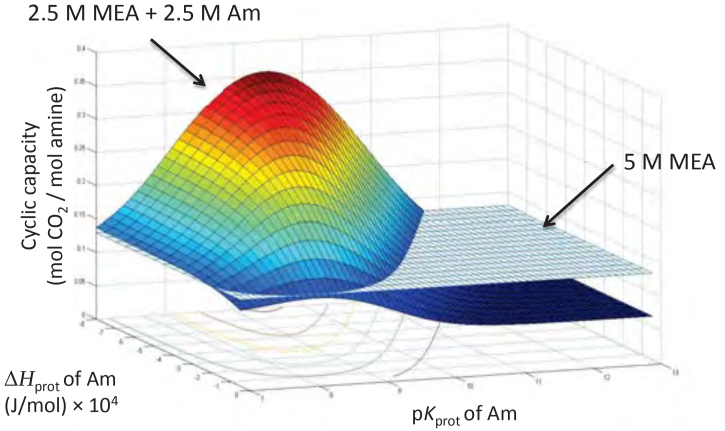




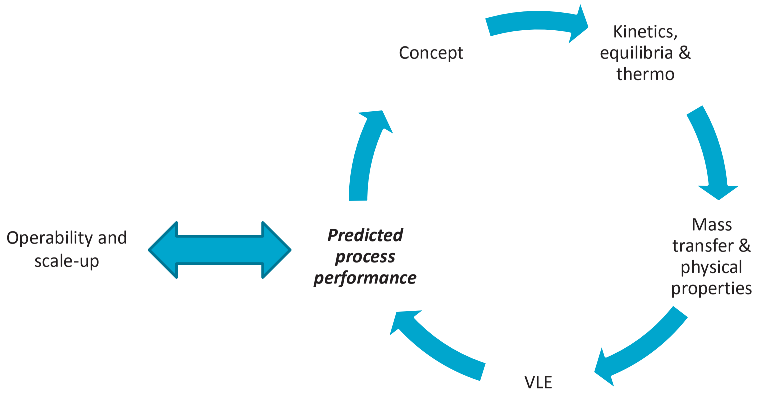
Puxty, G. and M. Maeder, *A simple chemical model to represent CO2-amine-H2O vapour-liquid-equilibria. International Journal of Greenhouse Gas Control, 2013.* ***17: p. 215-224.***
Puxty, G. and R. Rowland, *Modeling CO2 Mass Transfer in Amine Mixtures: PZ-AMP and PZ-MDEA. Environmental Science & Technology, 2011.* ***45(6): p. 2398-2405.***

Intelligent formulation design

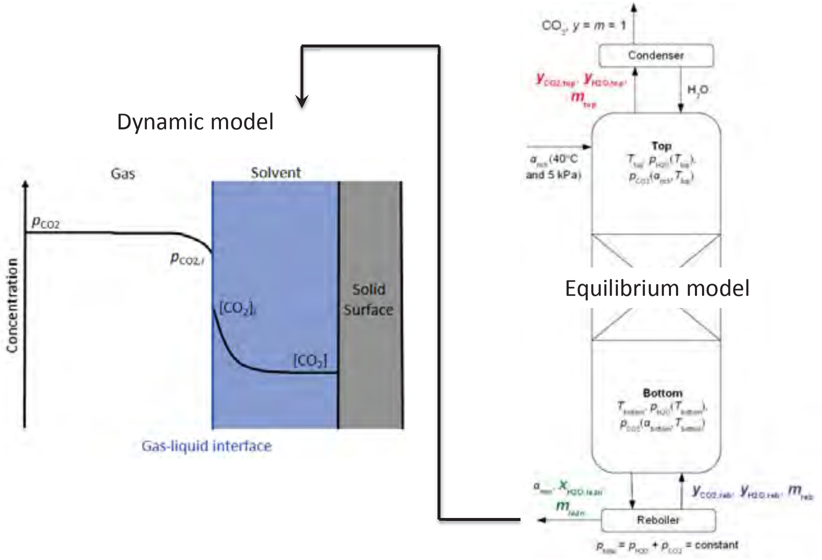
- We can vary the properties of constituent amines and investigate the impact on capture performance



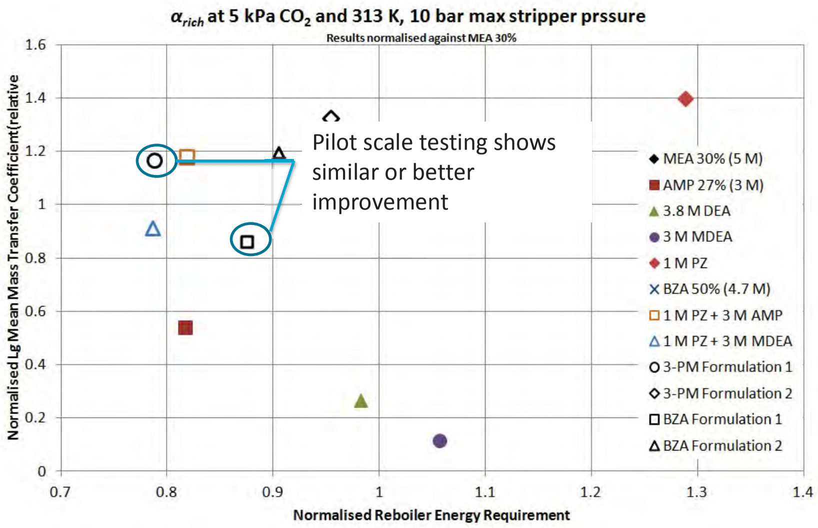
Predicting process performance



Equilibrium stripper + mass transfer prediction

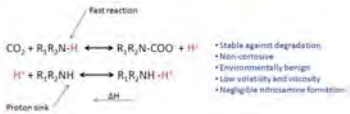


Predicted process performance - formulations



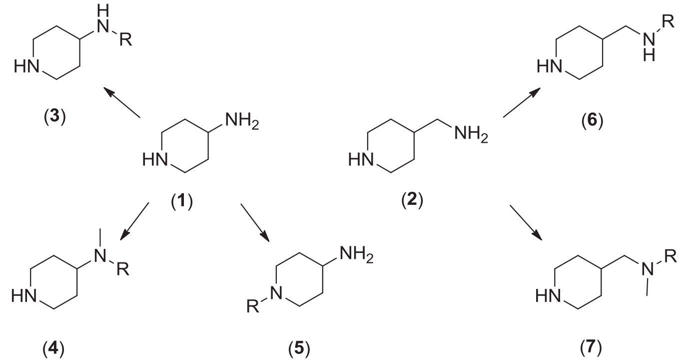
Pilot scale testing shows similar or better improvement

Intelligent molecular design



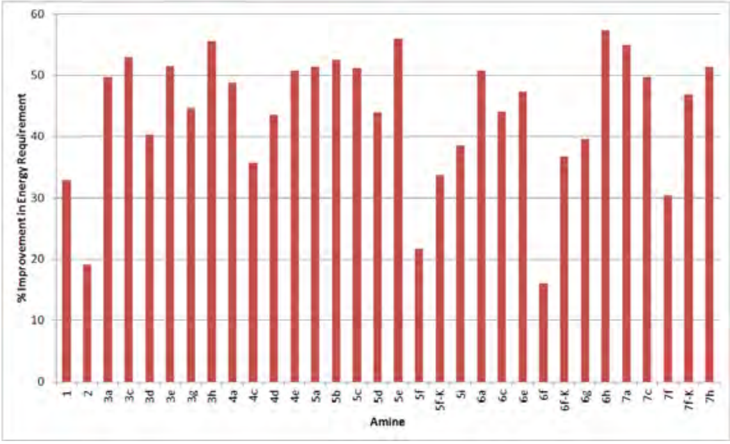
- Stable against degradation
- Non-corrosive
- Environmentally benign
- Low volatility and viscosity
- Negligible nitrosamine formation

- Design new molecules to have the properties we want



Predicted process performance – new amines

- Estimated improved energy performance (based on 2 M, measured cyclic capacity and molecular weight) relative to piperazine



Conclusions

- Still substantial scope for improvement in both formulations and new amines molecules
- Pilot scale testing revealed good performance but operational challenges to be addressed:
  - viscosity, volatility, foaming, materials compatibility
- New molecules to be synthesises at large scale for more thorough testing

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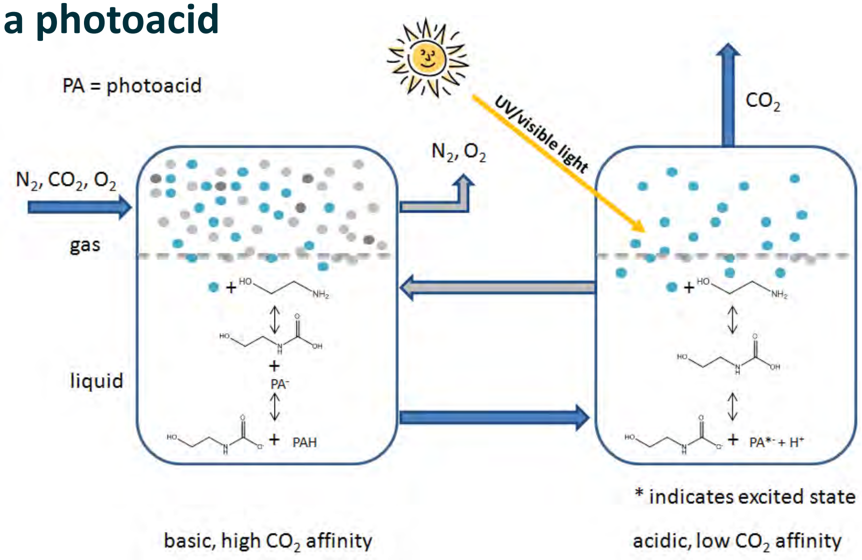
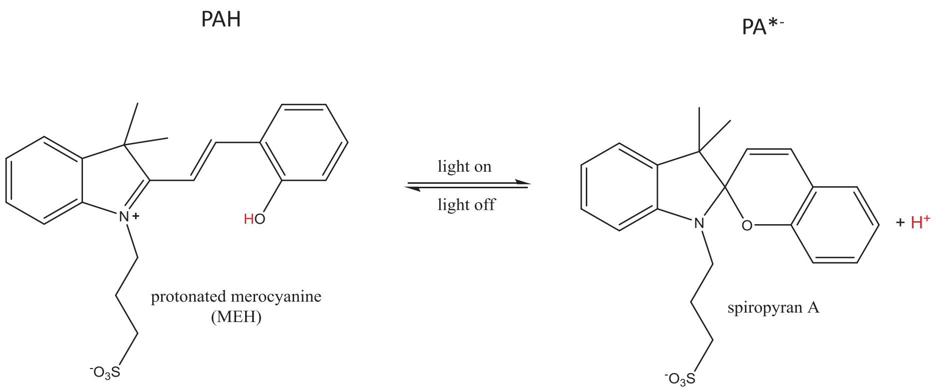
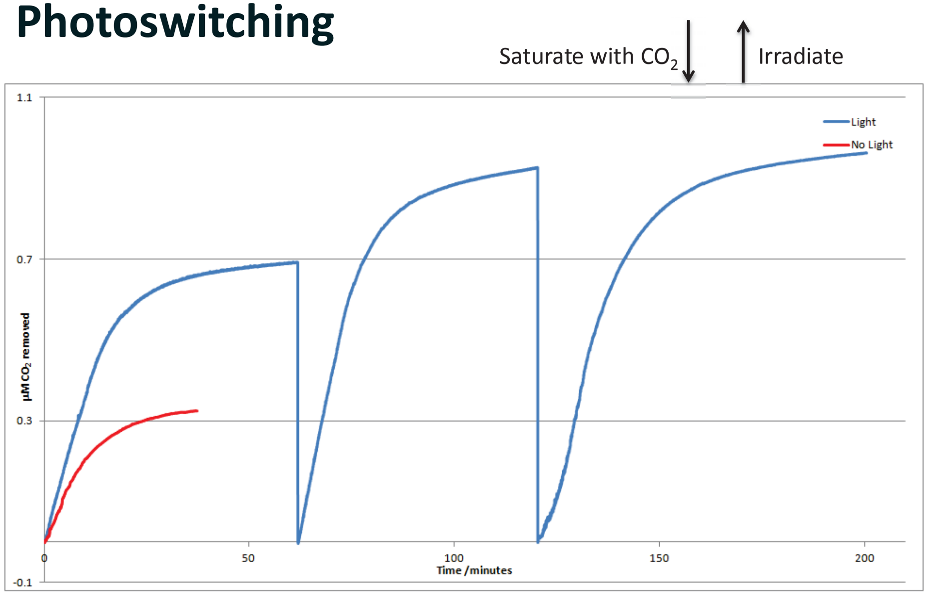
Something a bit different – photoswitching using a photoacid



Photoswitching



Photoswitching



The current team

Reactive chemical absorbents at CSIRO

Formulations/phase change	New compounds	Light-swing	Aqueous Ammonia
Will Conway Yaser Beyad Pauline Pearson	**Qi Yang** Will Conway	**Robert Bennett**	Hai Yu Kangkang Li Long Ji

The University of Newcastle
Marcel Maeder
Robert Burns
Duong Phan
Anh Nguyen
Sarah Clifford

Thank You

Dr Graeme Puxty
Research Team Leader
Energy Flagship
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CSIRO Energy Centre, 10 Murray-Dwyer Circuit, Mayfield NSW 2304
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Formation and destruction of NDELA in MEA and DEA

Hanna Knuutila, Hallvard Svendsen and Naveed Asif

NTNU- Department of Chemical Engineering
Trondheim, Norway

Content

Background

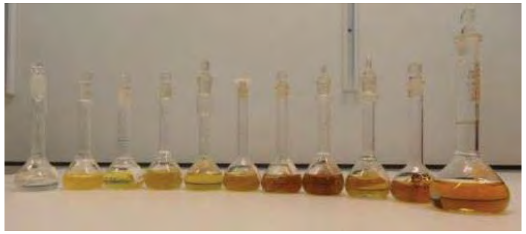
Experimental work

Results

Conclusions

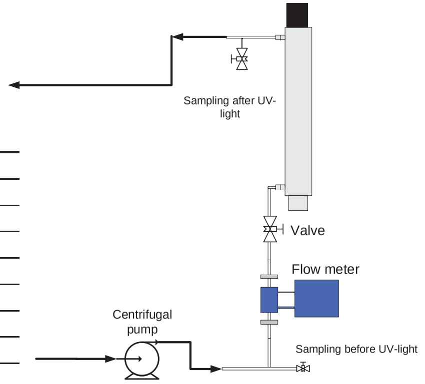
Objectives

- To study the formation of NDELA with NO and NO+NO_2 present in the gas phase
- To study the destruction of NDELA in these solutions with UV-light



UV-reactor

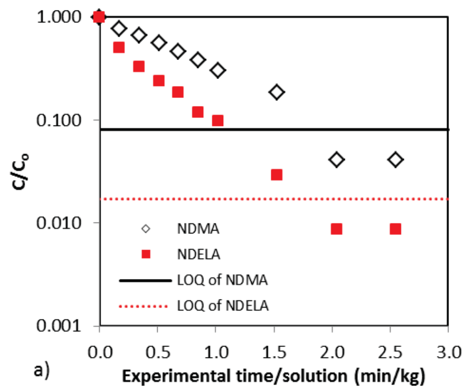
	Value
Power consumption	46 W
Lamp power	37 W
Max. flow rate	37.9 L/min
Chamber material	304 stainless steel
Chamber length	90.0 cm
Chamber diameter	6.4 cm
Lamp	Sterilume-EX model S810RL
Sleeve	Quartz Model QS-810



Background

Batch experiments

Decomposition of NDELA and NDMA in artificial water wash solution



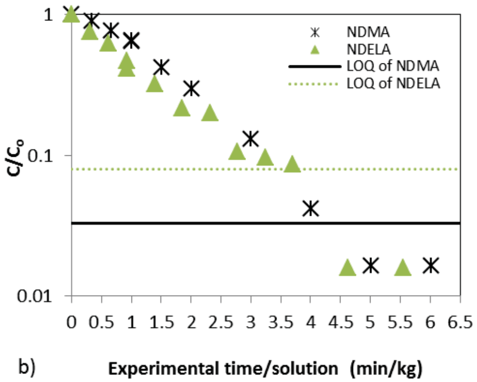
- Start concentration
  - NDMA 307 ng/ml
  - NDELA 290 ng/ml
- LOQ
  - NDMA 25 ng/ml
  - NDELA 5 ng/ml
- Concentration of NDMA and NDELA are below the LOQ after 1 hour

---

Background

Batch experiments

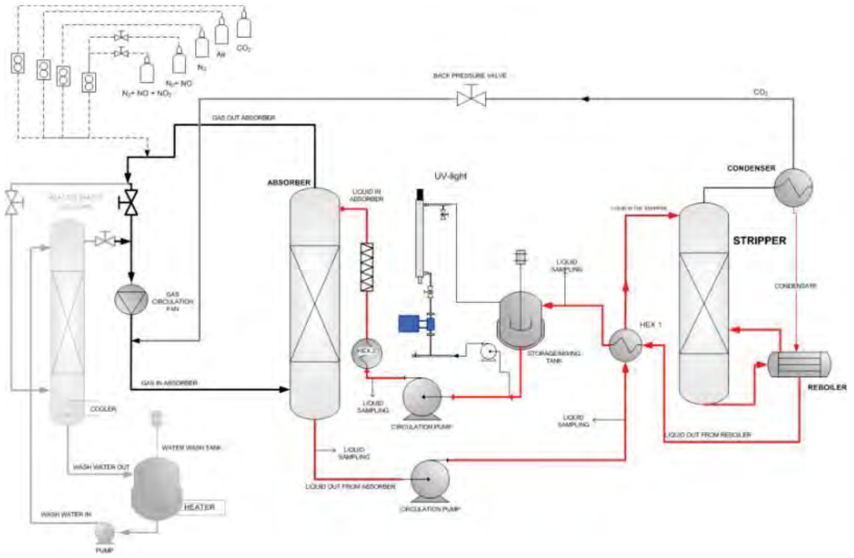
Decomposition of NDELA and NDMA in fresh 30wt% MEA



- Start concentration
  - NDMA 7620 ng/ml
  - NDELA 624 ng/ml
- LOQ
  - NDMA 250 ng/ml
  - NDELA 50 ng/ml
- Concentration of NDMA and NDELA are below the LOQ after 2.5 hours

---

Experimental setup



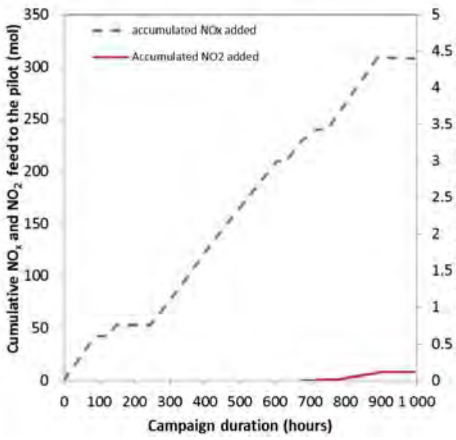
Background

Campaigns

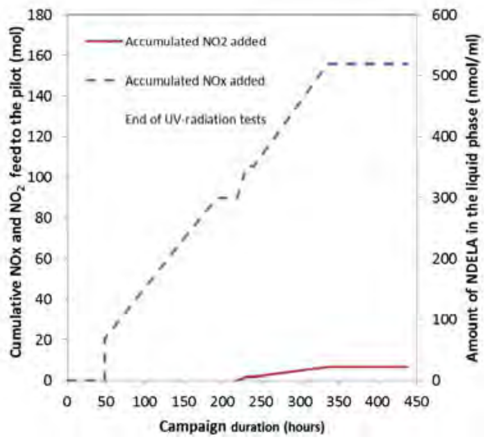
	30wt% MEA	50wt% DEA
Campaign duration	990 hours	410 hours
NO feeding hours	715 hours	250 hours
N_2O feeding hours	187 hours	100 hours
UV-light radiation in the main solvent circulation	37 hours	48 hours
UV-light radiation in the water wash circulation	-	5 hours

Results

30 wt% MEA

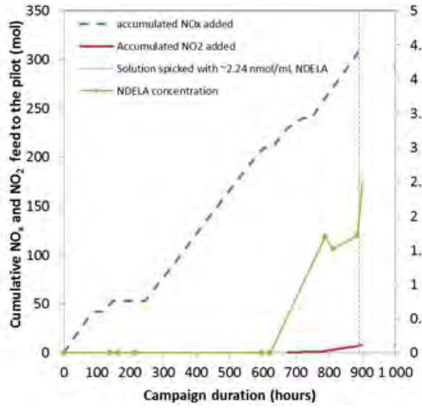


50wt% DEA

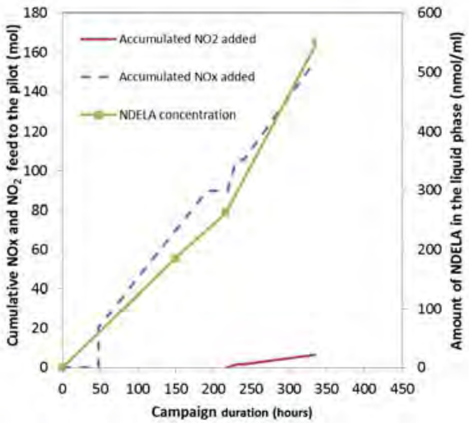


Results

30 wt% MEA

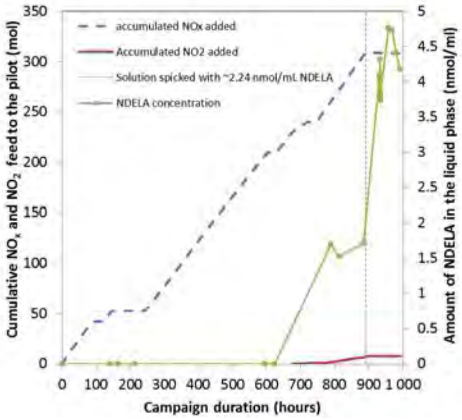


50wt% DEA

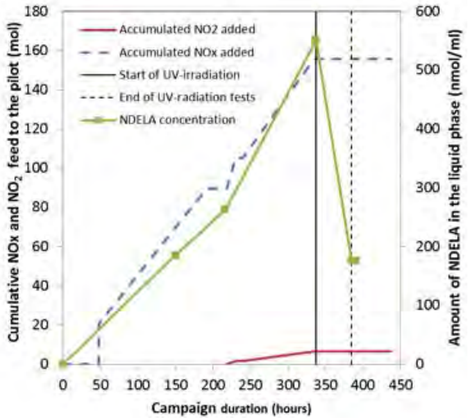


Results

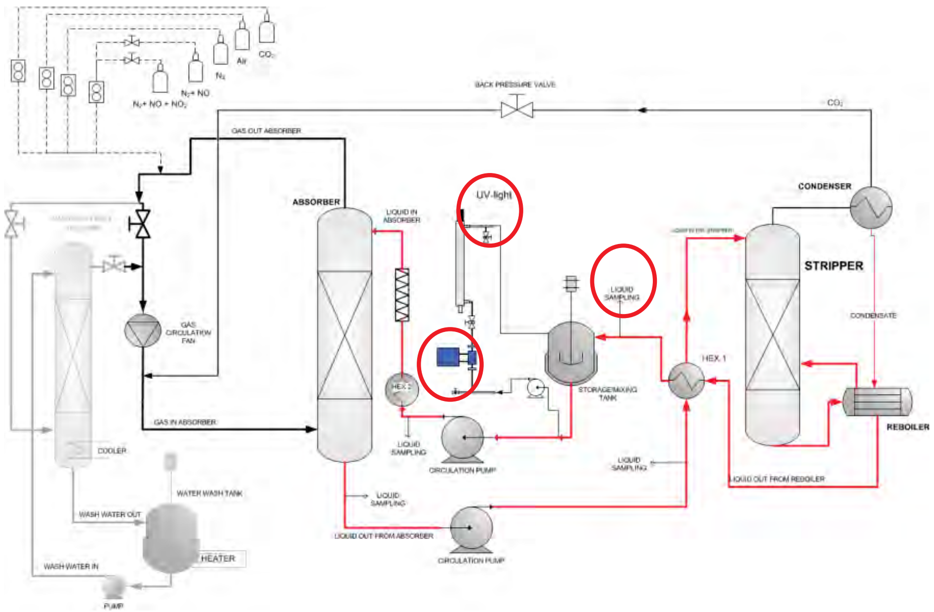
30 wt% MEA



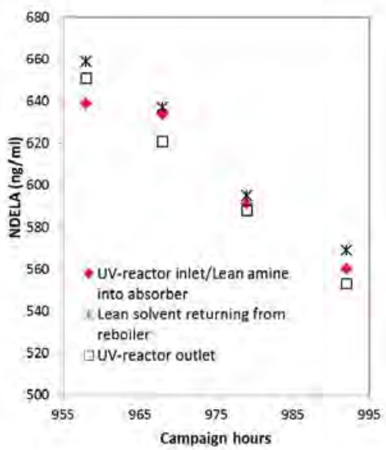
50wt% DEA



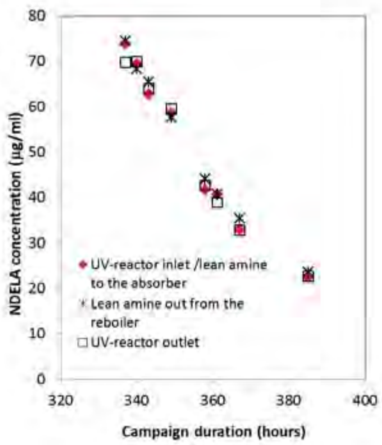
Results



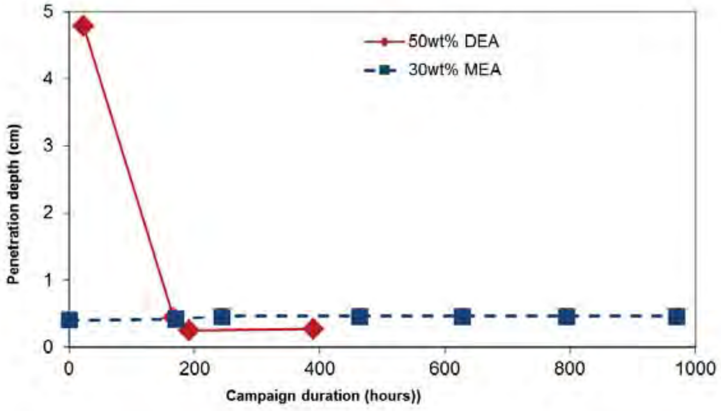
30 wt% MEA



50wt% DEA

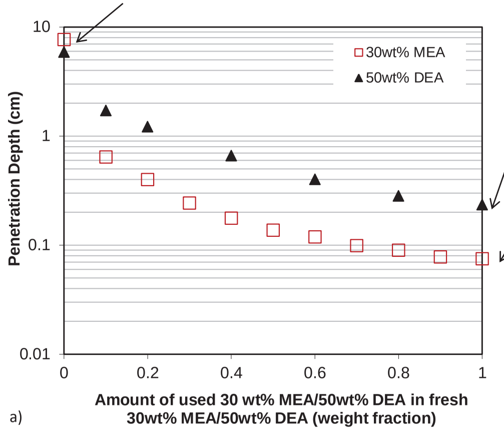


Penetration of UV-light



Effect of colour (degradation products)

Fresh amine solutions

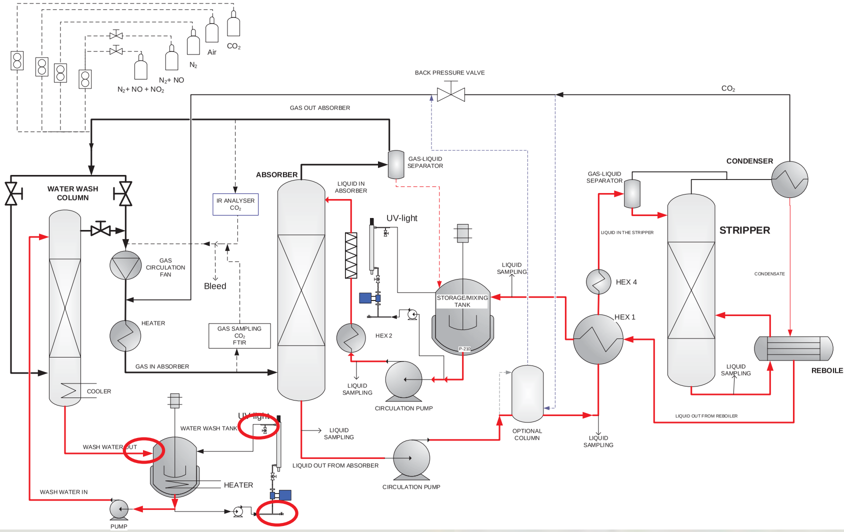


a)

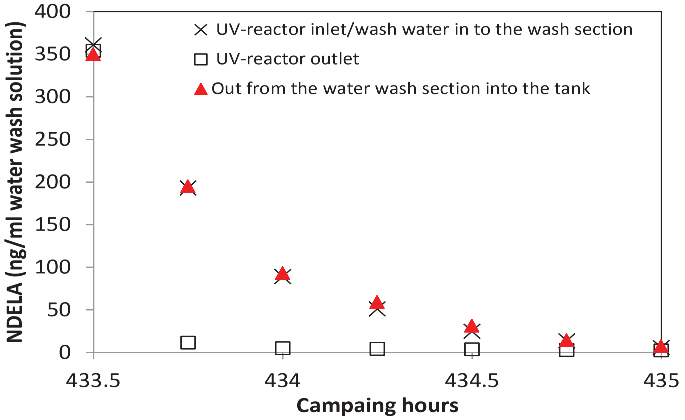
50wt% DEA used in a pilot for 410 hours.

30wt% MEA used in a pilot for 1690 hours.

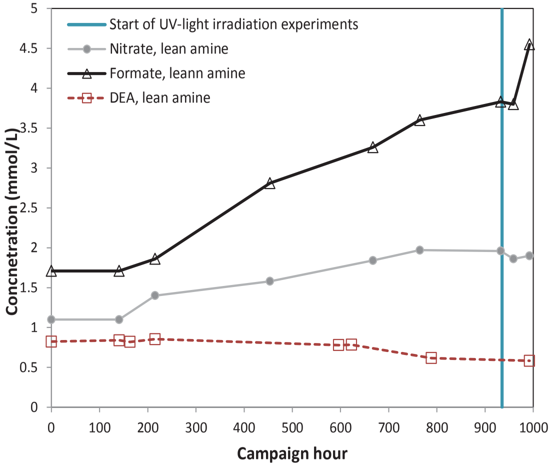
Experiment in water wash loop



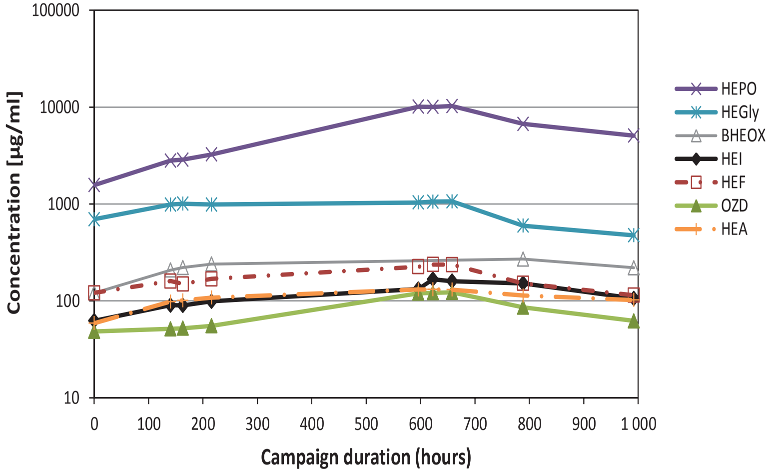
UV-light in the water wash



Degradation (30wt% MEA)



Degradation (30wt% MEA)



Conclusions

- the decomposition of NDELA decreases with increasing
  - colour of the solution
  - amine concentration

→ To use UV-light in the main solvent loop would require an optimization of the UV-light reactor.

- Open questions:
  - UV-light and amine degradation
  - Influence of temperature

Thank you!

The work is done under the RenicUV project. The project was performed under the strategic Norwegian research program CLIMIT. The authors acknowledge the partners: Det Norske Veritas AS, Fluor Enterprises, Inc., Maasvlakte CCS Project C.V. and Mitsubishi Heavy Industries, Ltd.

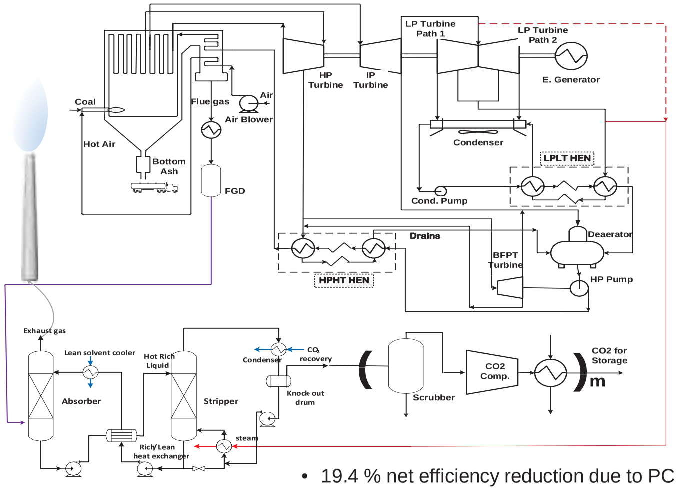
DYNAMIC MODELS AND CONTROL STRATEGIES FOR ABSORPTION-BASED CARBON CAPTURE PROCESSES

Ali Abbas
Laboratory for Multiscale Systems
School of Chemical and Biomolecular Engineering
University of Sydney

HiPerCap - High Performance Capture
EU – Australian workshop, Melbourne, Australia, 25th-27th March 2015

Content

Background



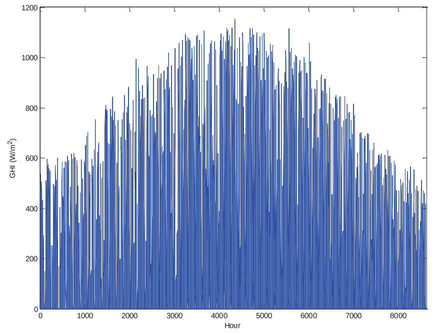
- 19.4 % net efficiency reduction due to PCC
- High capital cost
- Flexibility in operation

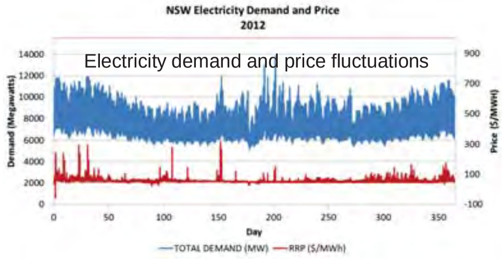
Ref. : Rajab Khalilpour and Ali Abbas, HEN optimization for efficient retrofitting of coal-fired power plants with post-combustion carbon capture. International Journal of Greenhouse Gas Control, 2011. 5(2): p. 189-199.

Motivation: A domain of operational uncertainties

- Carbon tax scheme started in July 2012, scrapped July 2014
- Variations in GHI, electricity price, electricity demand & carbon price

Hourly Global Horizontal Irradiation (GHI) in Sydney

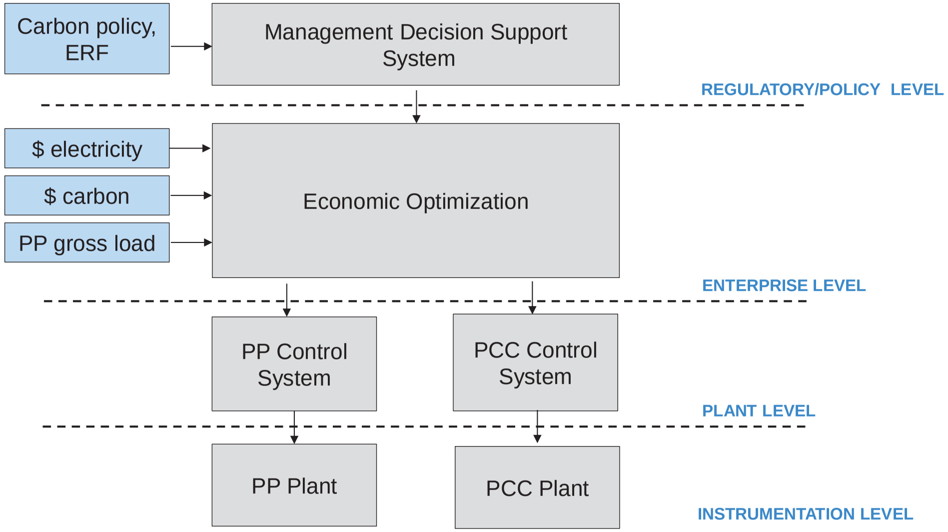




Electricity demand and price fluctuations

Carbon market dynamics of Europe

Outlook



Carbon policy, ERF

Management Decision Support System

REGULATORY/POLICY LEVEL

$ electricity

$ carbon

PP gross load

Economic Optimization

ENTERPRISE LEVEL

PP Control System

PCC Control System

PLANT LEVEL

PP Plant

PCC Plant

INSTRUMENTATION LEVEL

Significance and objective

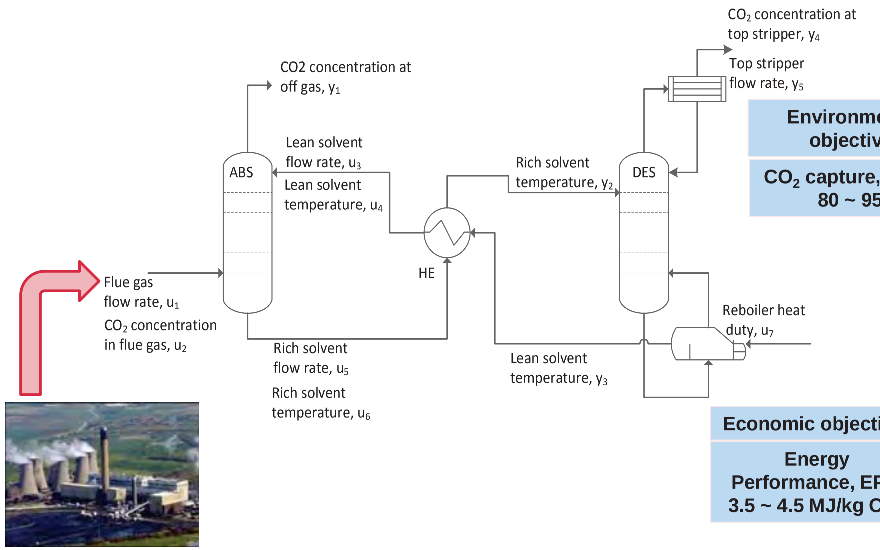
Integration of PCC into coal-fired power plant requires understanding dynamic operations.

The PCC plant must respond flexibly to three significant scenarios:

1. Power plant operations at full and partial loads,
2. Under external disturbances from power plant and auxiliary systems, and
3. Considering fluctuations in electricity and carbon prices.

The objective of this study is to develop a dynamic model and use it in simulation analysis for techno economic study includes advanced control, optimization and management decision support system.

Significance and objective



Environmental objective:

CO$_2$ capture, CC% = 80 ~ 95%

Economic objective:

Energy Performance, EP = 3.5 ~ 4.5 MJ/kg CO$_2$

Modelling Approach 1: Empirical model

Tarong power station

Tarong PCC pilot plant

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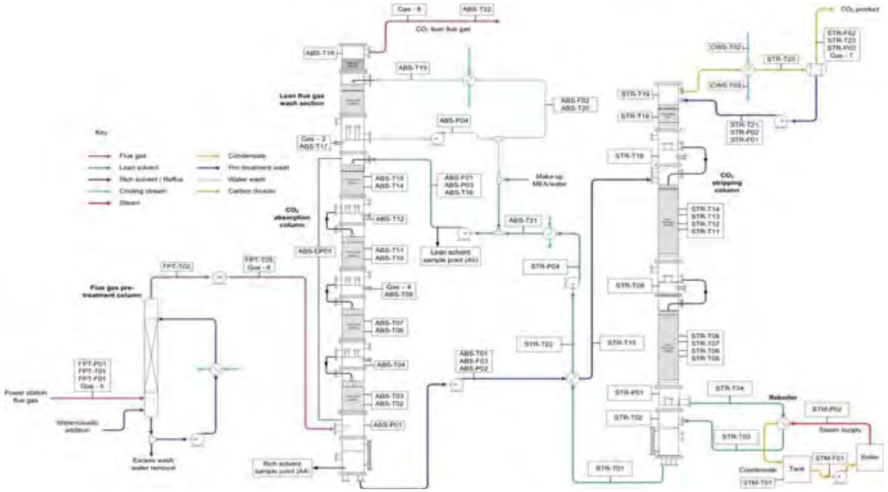
Modelling Approach 1: Empirical model

Tarong PCC pilot plant process flowsheet



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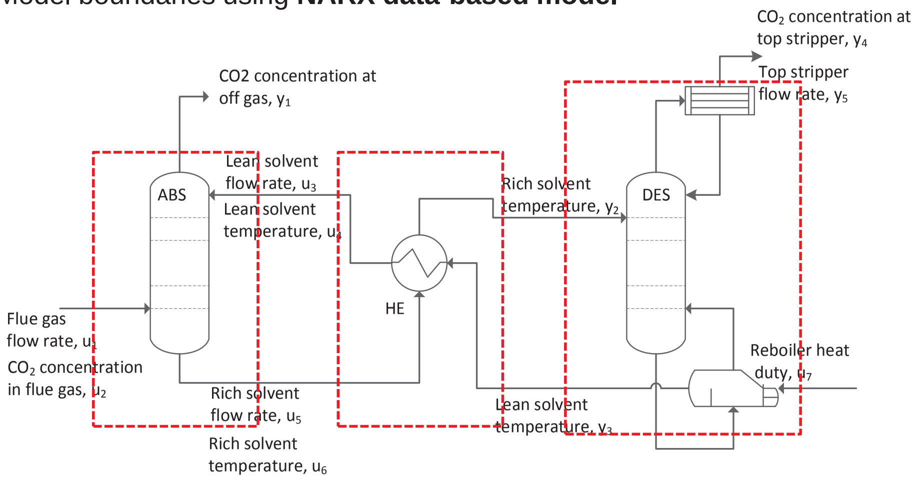
Modelling Approach 1: Empirical model

Model boundaries using **NARX data-based model**[1,2]



CO_2 concentration at top stripper, y_4

Top stripper flow rate, y_5

CO2 concentration at off gas, y_1

Lean solvent flow rate, u_3

Lean solvent temperature, u_4

Rich solvent temperature, y_2

ABS

HE

DES

Flue gas flow rate, u_1

CO_2 concentration in flue gas, u_2

Reboiler heat duty, u_7

Rich solvent flow rate, u_5

Rich solvent temperature, u_6

Lean solvent temperature, y_3

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[1] Norhuda, A. M., Ashleigh , C., Paul, F. & Ali, A. 2014. Dynamic Modelling and Simulation of Post Combustion CO2 Capture Plant. *CHEMECA 2014: Western Australia*

[2] Norhuda, A. M., Ashleigh , C., Paul, F. & Ali, A. 2014. Dynamic modelling, identification and preliminary control analysis of an amine-based post-combustion CO2 capture pilot plant. Journal of Cleaner Production (in review)

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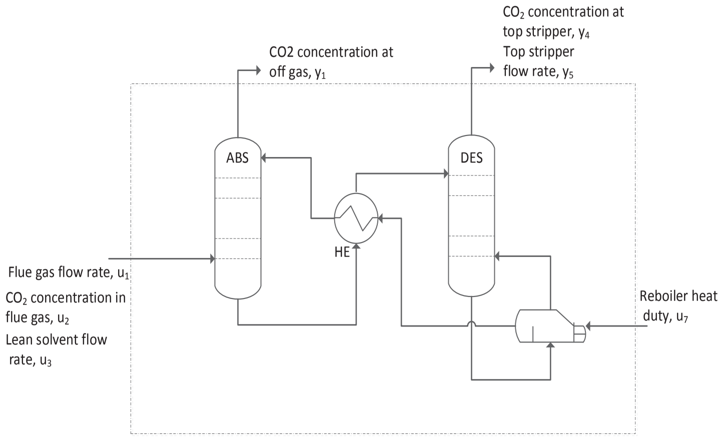
Modelling Approach 1: Empirical model

Integrated **NARX data-based model**



CO_2 concentration at top stripper, y_4

Top stripper flow rate, y_5

CO2 concentration at off gas, y_1

ABS

DES

HE

Flue gas flow rate, u_1

CO_2 concentration in flue gas, u_2

Lean solvent flow rate, u_3

Reboiler heat duty, u_7

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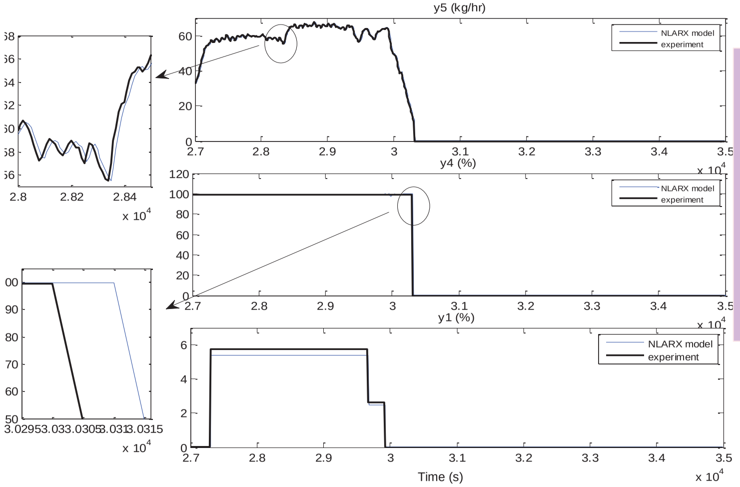
Modelling Approach 1: Empirical model

Model validation for NARX model



Pilot plant data operation : ≈ 6 hours

Sampling time: 10 sec

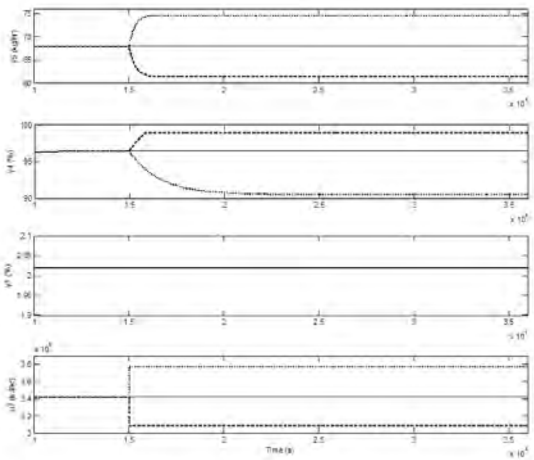
Data points: ≈ 2000

Estimate data points: ≈ 1200

Validation data points: ≈ 800

Modelling Approach 1: Open-loop dynamic analysis

Step changes in reboiler heat duty



Step changes in Reboiler heat duty (straight line: base case; dotted line: positive step change; dashed line: negative step change).

CO_2 concentration in top stripper, y_4 and top stripper flow rate, y_5 have significant open loop dynamic responses while CO_2 concentration in off gas, y_1 does not show any significant response.

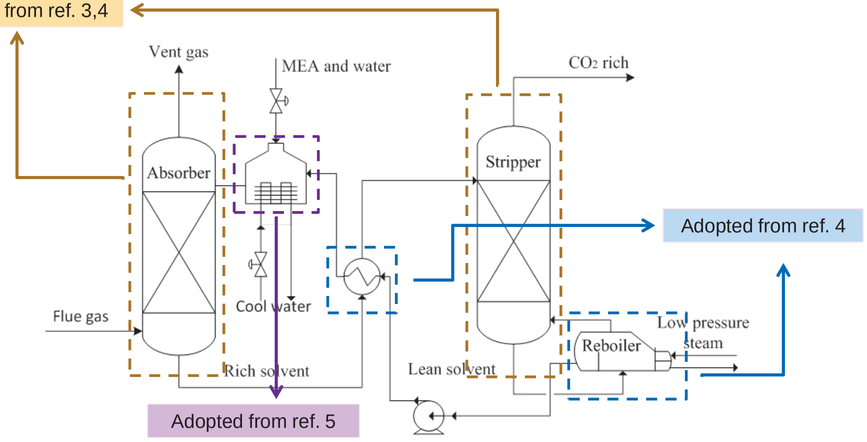
Process time constants:

1) 6 – 15 mins for the fastest dynamics (reboiler heat duty – CO_2 concentration in top stripper relationship).

2) 8 -27 mins for the slowest dynamics (reboiler heat duty – top stripper flow rate relationship).

Modelling Approach 2: Mechanistic model

Model boundaries using **mechanistic model** [3,4,5]


Modified from ref. 3,4

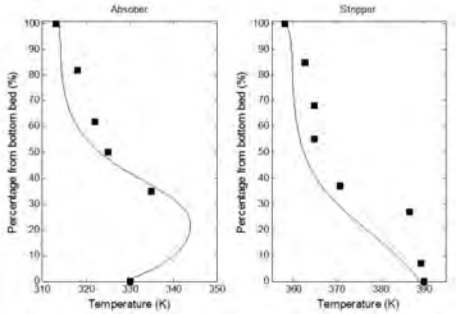
Adopted from ref. 4

Adopted from ref. 5

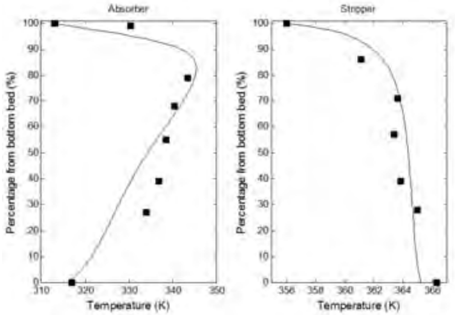
3.Kvamsdal, H. M., Jakobsen, J. P. & Hoff, K. A. 2009. Dynamic modeling and simulation of a CO2 absorber column for post-combustion CO2 capture. Chemical Engineering and Processing: Process Intensification, 48(1), pp 135-144.
4.Harun, N., Nittaya, T., Douglas, P. L., Croiset, E. & Ricardez-Sandoval, L. A. 2012. Dynamic simulation of MEA absorption process for CO2 capture from power plants. *International Journal of Greenhouse Gas Control*, 10(295-309).
5.Nittaya, T., Douglas, P. L., Croiset, E. & Ricardez-Sandoval, L. A. 2014. Dynamic modelling and control of MEA absorption processes for CO_2 capture from power plants. *Fuel*, 116(0), pp 672-691.

Modelling Approach 2: Mechanistic model

Model validation for **mechanistic model**[6]



Column temperature profiles from the simulation (line) and the pilot plant study (dot) for the pilot plant test no. 32[7].



Column temperature profiles from the simulation (line) and the pilot plant study (dot) for the pilot plant test no. 47[7].

	Flue gas		Lean solvent		Rich solvent	
Case number	32	47	32	47	32	47
Temperature (K)	320	320	314	314	358	356
Flow rate (mol/s)	4.013	9.3	31.19	26.7	31.19	26.7

---

[6] Minh Tri Luu, Norhuda Abdul Manaf, Ali Abbas. Control strategies for flexible operation of amine-based post-combustion CO_2 capture systems. Journal of Greenhouse Gas Control (accepted with revisions)

[7] Dugas, R. E. 2006. Pilot Plant Study of Carbon Dioxide Capture by Aqueous Monoethanolamine. M.S.E. Thesis, The University of Texas

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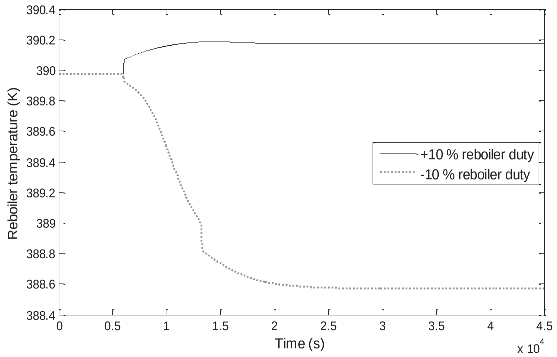
Modelling Approach 2: Open-loop dynamic analysis

Step changes in reboiler heat duty



Step changes in reboiler duty (straight line: positive step change; dashed line: negative step change).

It can be seen that a 10% reduction (increment) in the heat duty caused the temperature to reduce by 1.4°C (increased by 0.2°C).

Process time constants:

1) 3 hours for the fastest dynamics at 10% increment of heat duty

2) 4.3 hours for the slowest at 10% reduction of heat duty

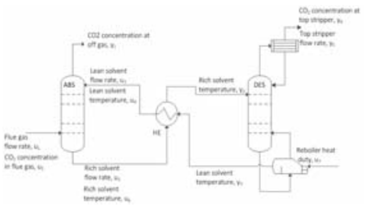
* High time constant : Due to a large amount (1.5 m^3) of holdup solvent, the reboiler temperature inherited a high time constant

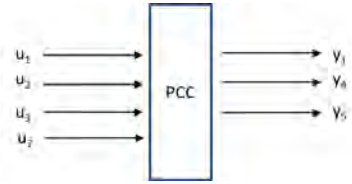
Control Approach

Identified 2 key performance metrics:

1. Carbon capture efficiency, $CC\ (\%) = \frac{(y_4/100)\ y_5}{u_1\ (u_2\ /100)}$

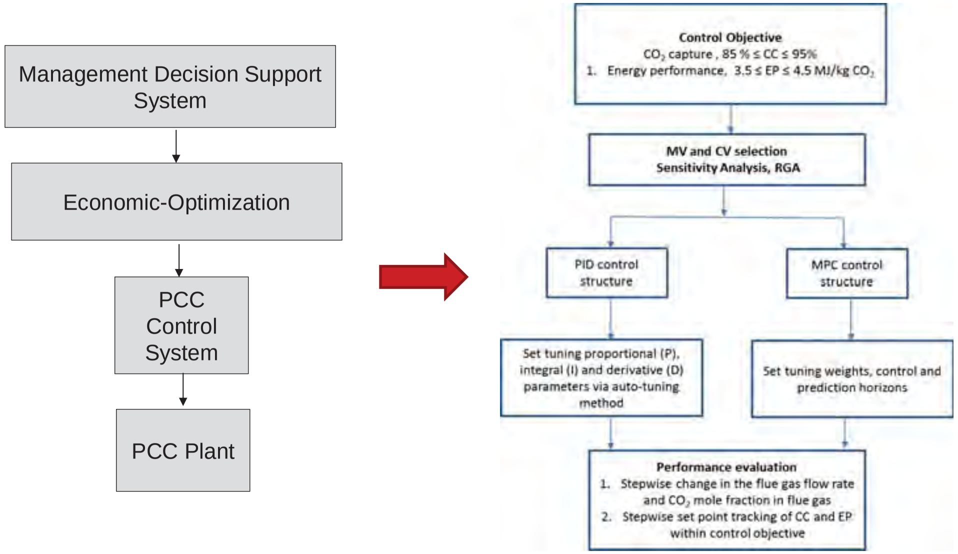
2. Energy performance, $EP\ (\text{MJ/kg}) = \frac{u_7}{(y_4/100)\ y_5}$





Simplified 4 x 3 PCC system

Control Approach



Management Decision Support System

Economic-Optimization

PCC Control System

PCC Plant

Control Objective
CO_2 capture , 85 % ≤ CC ≤ 95%
1. Energy performance, 3.5 ≤ EP ≤ 4.5 MJ/kg CO_2

MV and CV selection
Sensitivity Analysis, RGA

PID control structure

MPC control structure

Set tuning proportional (P), integral (I) and derivative (D) parameters via auto-tuning method

Set tuning weights, control and prediction horizons

Performance evaluation
1. Stepwise change in the flue gas flow rate and CO_2 mole fraction in flue gas
2. Stepwise set point tracking of CC and EP within control objective

---

Control Approach – RGA Analysis

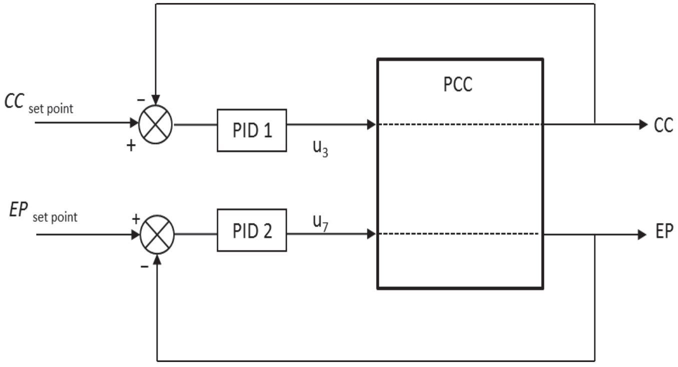
RGA results for different steady-state operating conditions

Condition	Steady state input values				Final steady state output values		RGA*
	u_1 (kg/hr)	u_2 (mass %)	u_3 (L/min)	u_7 (kJ/hr)	*CC* (%)	*EP* (MJ/kg)	
Condition 1	500	16	24	270 000	≈ 80	≈ 4	$\begin{array}{c c} & EP \quad CC \\ \begin{array}{c} u_3 \\ u_7 \end{array} & \begin{pmatrix} 0.1934 & 0.8066 \\ 0.8066 & 0.1934 \end{pmatrix} \end{array}$
Condition 2	550	16	25	288 000	≈ 70	≈ 5	$\begin{array}{c c} & EP \quad CC \\ \begin{array}{c} u_3 \\ u_7 \end{array} & \begin{pmatrix} -0.3790 & 1.3790 \\ 1.3790 & -0.3790 \end{pmatrix} \end{array}$
Condition 3	650	16	30	324 000	≈ 40	≈ 8	$\begin{array}{c c} & EP \quad CC \\ \begin{array}{c} u_3 \\ u_7 \end{array} & \begin{pmatrix} -2.9065 & 3.9065 \\ 3.9065 & -2.9065 \end{pmatrix} \end{array}$

*RGA was performed by introducing +10% perturbation in u_3 and u_7.

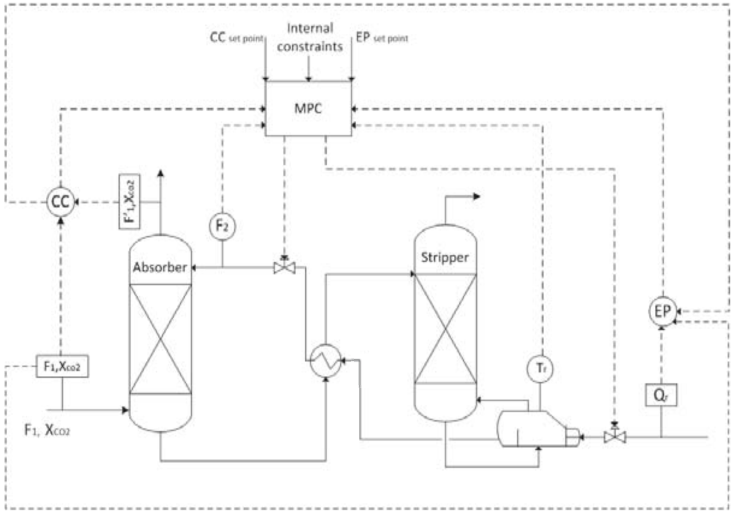
Negative pairing = The control loop is unstable

Control Approach 1 – PID Controller



PID Control Scheme

Control Approach 2 – MPC Controller

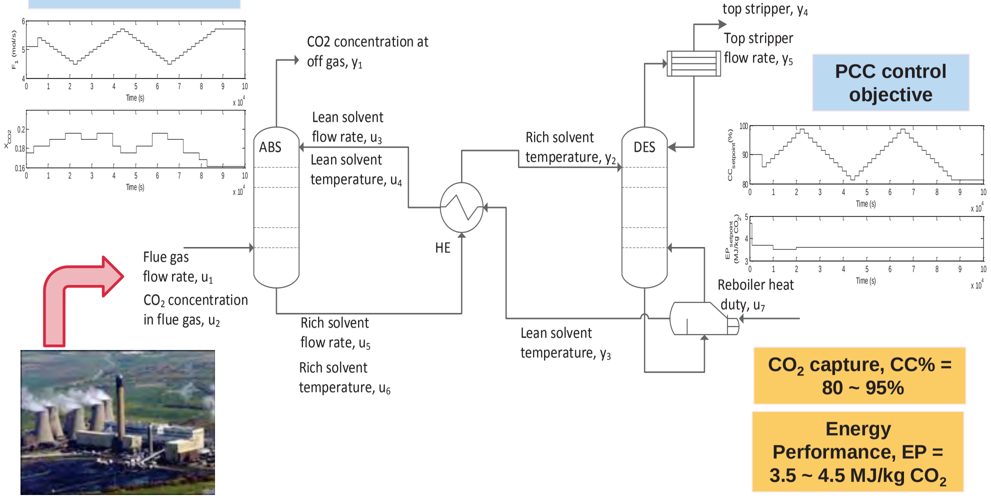


MPC Control Scheme

Control Approach – Controllability Analysis

Upstream disturbances

PCC control objective

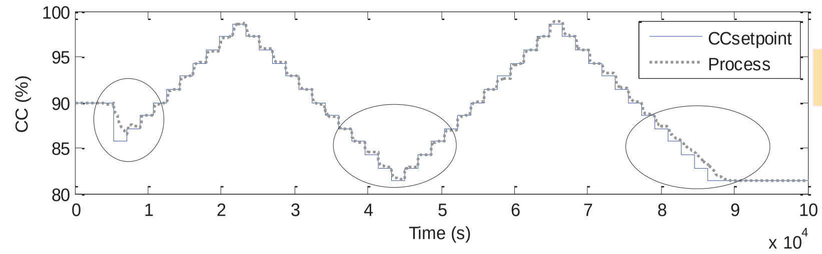


CO_2 capture, CC% = 80 ~ 95%

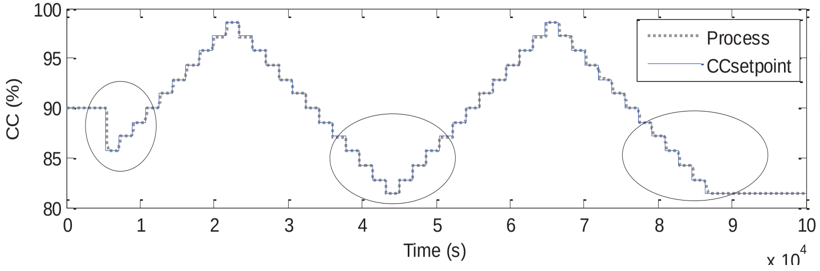
Energy Performance, EP = 3.5 ~ 4.5 MJ/kg CO_2

Control Approach – Controllability Analysis

Controllability analysis on set point changes and rejection disturbances.



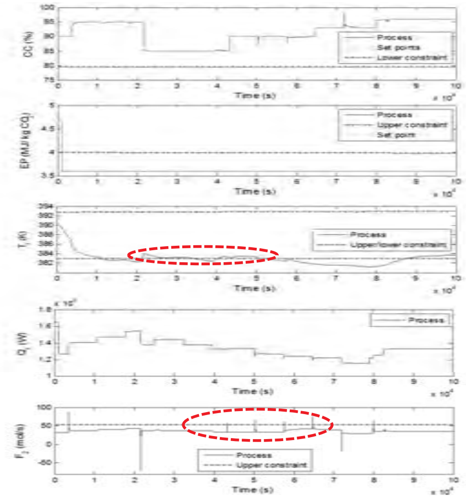
PID Controller



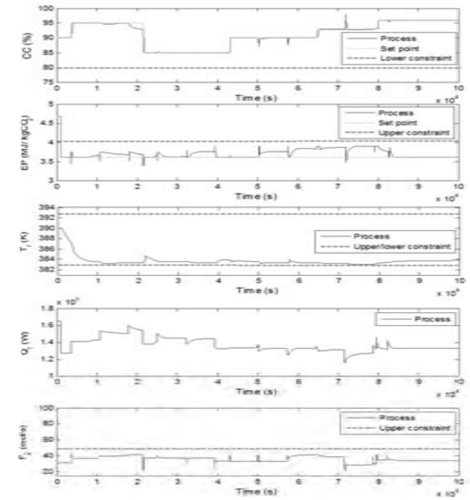
MPC Controller

Control Approach – Controllability Analysis

Control performance under process operational constraints

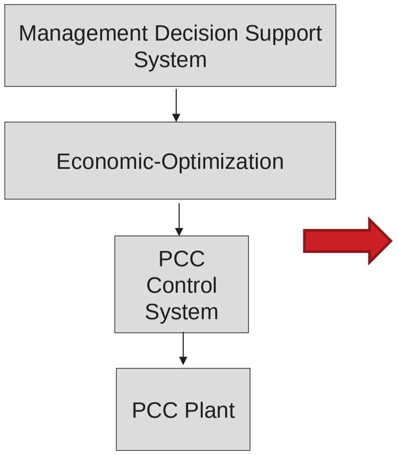


PID Controller



MPC Controller

Control-Optimization Approach

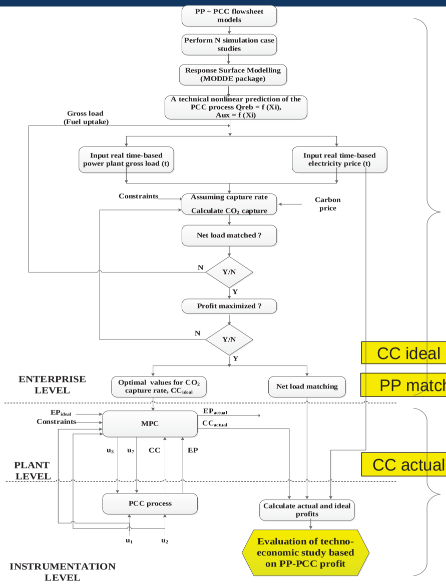


Management Decision Support System

Economic-Optimization

PCC Control System

PCC Plant



CC ideal

PP match load

CC actual

Economic study via optimization with GA based on real-time based plant/data

Technical study via NARX-MPC data-based model

Control-Optimization Approach

PP-PCC plant revenue

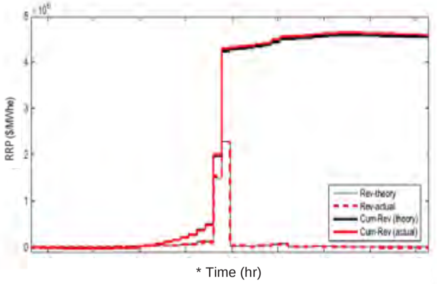
$$\text{Revenue} = \int P_e * \underbrace{(\text{Power plant net load} - \text{PCC penalty})}_{\text{Rev-PP}} * dt - $$

$$- \underbrace{\int C_t * CO_2 \text{ emitted } dt}_{A} \ - \underbrace{P_{PP}}_{B} - \underbrace{P_{PCC}}_{C}$$

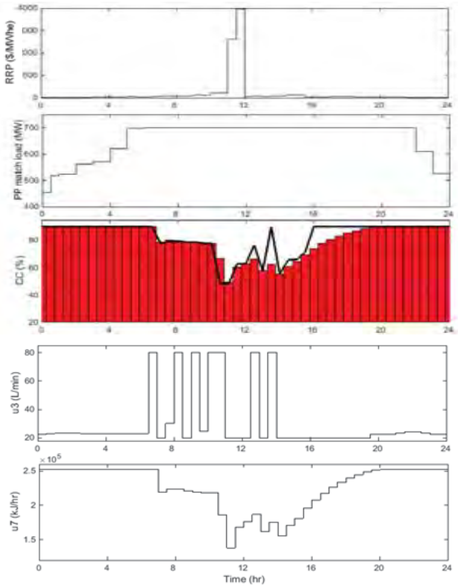
Rev-PP:	**Revenue generated through selling of electricity**
A:	**Cost of CO2 emission**
B:	**Power plant operating cost (PP-OPEX)**
C:	**PCC operating cost (PCC-OPEX)**

Techno-economic Approach – Optimization Control

Scenario:
Simulation period: 24 hrs
$ RRP : 2011
CT: $ 25/ tonne-CO$_2$



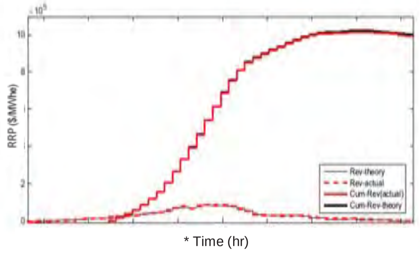
* Time (hr)



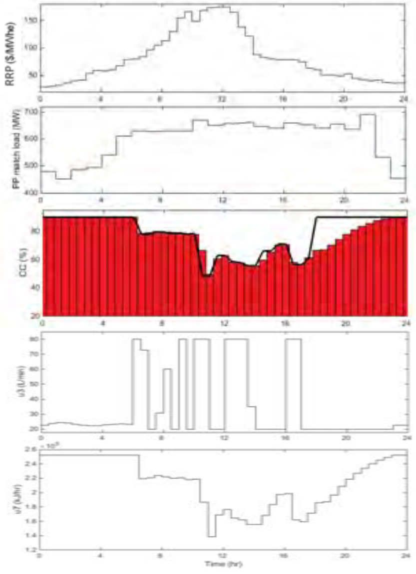
* 24 hours

Techno-economic Approach – Optimization Control

Scenario:
Simulation period: 24 hrs
$ RRP : 2020 (assuming 5% yearly increment from the base year 2008)
CT: $ 25/ tonne-CO$_2$



* Time (hr)

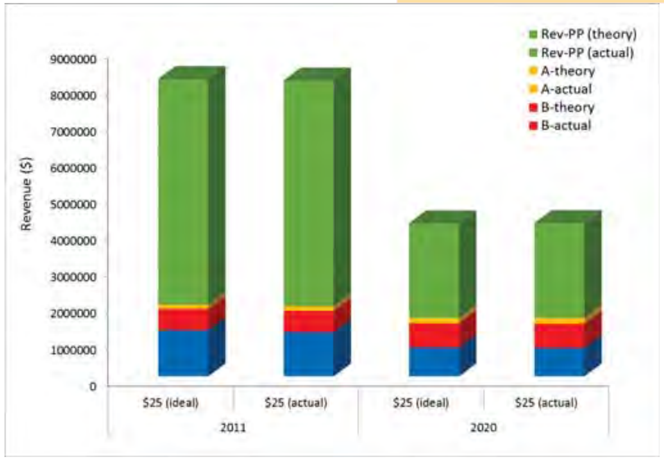


* 24 hours

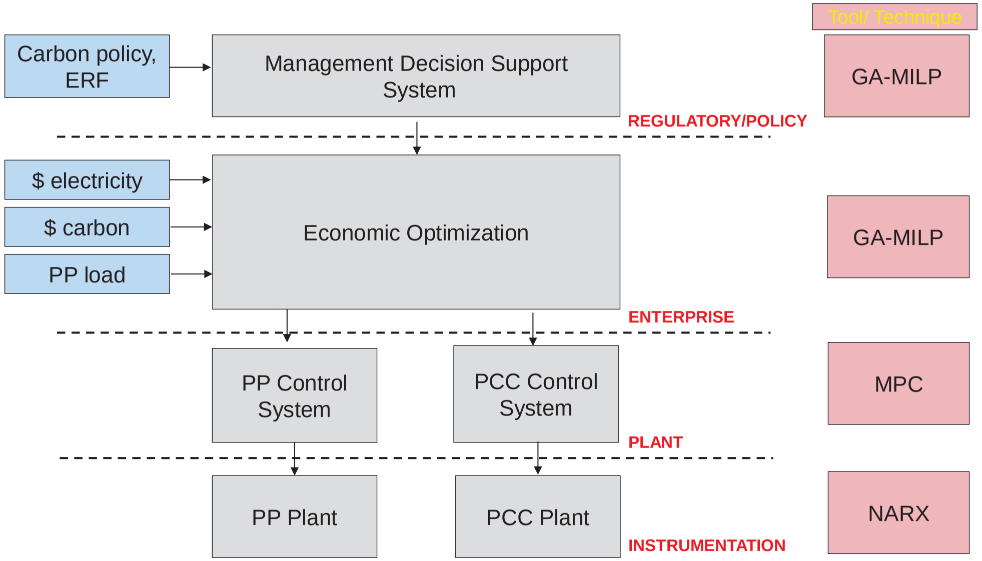
Control-Optimization Approach

Revenue Composite

Rev-PP: Revenue generated through selling of electricity
A: Cost of CO_2 emission
B: Power plant operating cost (PP-OPEX)
C: PCC operating cost (PCC-OPEX)



Opportunity



Tool/ Technique

Carbon policy, ERF

Management Decision Support System

REGULATORY/POLICY

GA-MILP

$ electricity

$ carbon

PP load

Economic Optimization

ENTERPRISE

GA-MILP

PP Control System

PCC Control System

PLANT

MPC

PP Plant

PCC Plant

INSTRUMENTATION

NARX

ACKNOWLEDGMENT

The authors wish to acknowledge partial financial assistance provided through Australian National Low Emissions Coal Research and Development (ANLEC R&D). ANLEC R&D is supported by Australian Coal Association Low Emissions Technology Limited and the Australian Government through the Clean Energy Initiative.

Norhuda Abdul Manaf

The University of Sydney

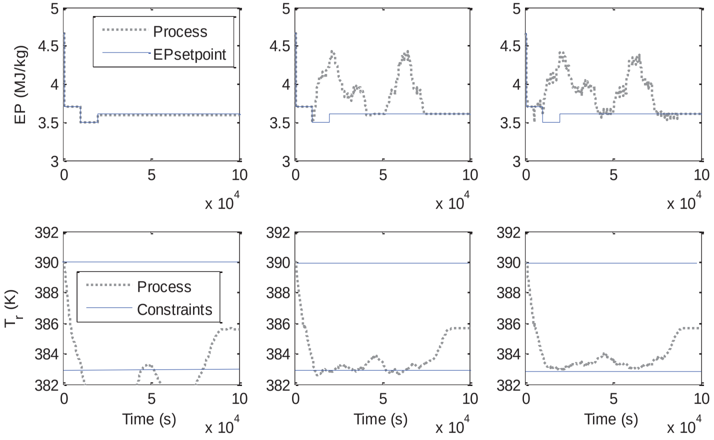
Ashleigh Cousins & Paul Feron

CSIRO

THANK YOU!

Control Approach – Controllability Analysis

Control performance of *EP* under process constraint (T_r)



PID Controller

PID-Cascade Controller

MPC Controller

The MPC-PCC did not violate the specified operational constraints for Tr and F2. However, the other two controllers were incapable to maintain respective process variables (Tr and F2) from violating its specified constraint.

Table 4.2 Operating conditions for case studies 32 and 47 (inputs to gPROMS simulations)

	Flue gas		Lean solvent		Rich solvent	
Case number	32	47	32	47	32	47
Temperature (K)	320	320	314	314	358	356
Flow rate (mol/s)	4.013	9.3	31.19	26.7	31.19	26.7
Mole fraction						
H_2O	0.025	0.032	0.86	0.846	0.846	0.828
MEA	-	-	0.11	0.12	0.104	0.1181
CO_2	0.175	0.167	0.029	0.034	0.05	0.0534
N_2	0.8	0.8	-	-	-	-
CO_2 loading	-	-	0.264	0.28	0.48	0.46
L/G ratio	-	-	6.5	4.6	-	-

HiPerCap WP2: Adsorption Technologies

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Energy Processes and Emission Reduction Group (PrEM)
Instituto Nacional del Carbón, INCAR-CSIC
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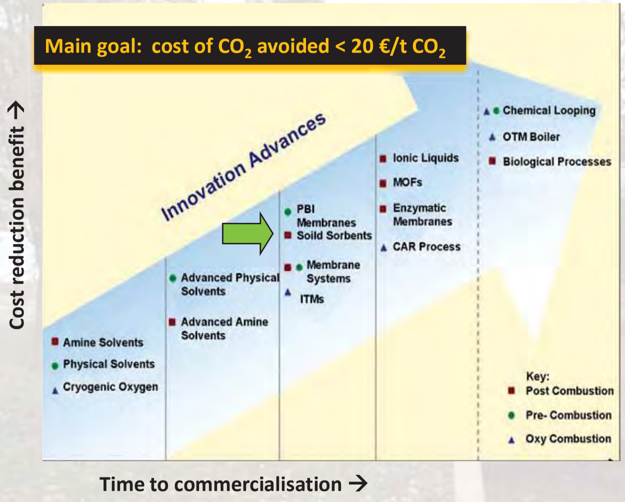
Melbourne, 25th March 2015

Alternative capture technologies



- Technologies need to demonstrate clear competitive edge
- Technologies need to overcome challenges of other acids gases, SO_x and NO_x etc
- Rapid development required
- Risk that technologies will not scale up

Source: Figueroa *et al.* Int. J. Greenhouse Gas Control 2, 9-20 (2008)

Solid sorbents: *Why?*

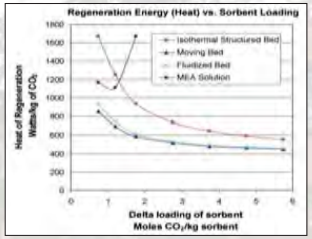
Advantages over *Absorption*

- ✓ Significantly increased contact area over solvent systems
- ✓ Reduced energy for regeneration and moving sorbent materials (if high capacity achieved)
- ✓ Elimination of liquid water (corrosion, etc.)
- ✓ Potential to reduce energy loading by 30-50%

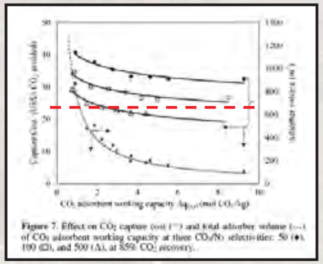
Challenges of CO_2 adsorbents

- High capacity
- High selectivity
- Adequate adsorption/desorption kinetics
- Good stability / lifetime
- Mechanical strength
- Reasonable cost

< 25 $/t CO_2 avoided



Gray *et al.* J. Greenhouse Gas Control 2, :3-8 (2008)



Ho *et al.* Ind. Eng. Chem. Res. 47, 4883-90 (2008)

Post-combustion capture application- challenges

	PC (w FGD)	NGCC	Oxyfuel
Volume flow (m^3/h)	2.2×10^6	3.8×10^6	0.5×10^6
Pressure (barg)	0.05	0.05	0.05
Temperature (°C)	70-90	70-90	170
N_2 (%)	71	75	
CO_2 (%)	12.6	3.4	62.6
Water (%)	11.1	6.9	31.5
Oxygen (%)	4.4	13.8	4.5
SO_2 (ppm)	200		
NOx (ppm)	670	25	

- ➢Very large: pressure drop
- ➢Very low: no driving force
- ➢Relatively high for adsorption
- ➢Ranges from 12 to 63% (wet basis)
- ➢High water content
- ➢SOx, NOx, ash, heavy metals, etc. present

Source: Webley, P.A. (2010). CO_2 *capture by adsorption processes: from materials to process development to practical implementation.*

Post-combustion capture applications

Power generation

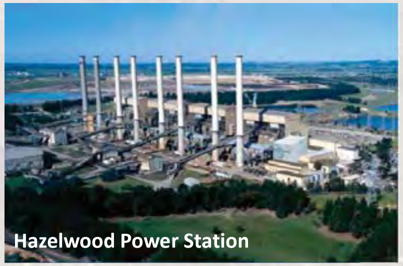
The **CO2CRC H3 Capture Project** at International Power's Hazelwood Power Station, completed in 2011, conducted research into adsorption technologies for CO_2 capture.

Goal:

- demonstrate adsorption for CO_2 capture from flue gas;
- assess adsorption process, equipment and different adsorbents under various working conditions and equipment configurations;
- assess the effect of impurities, temperature and load on the vacuum swing adsorption process;
- assess economic and engineering issues for scale-up

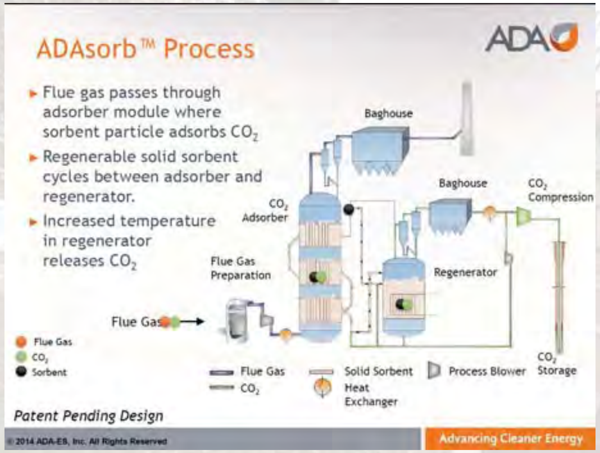
The H3 project was part of the Latrobe Valley Post-combustion Capture Project, supported by the Victorian Government, through the Energy Technology Innovation Strategy (ETIS) Brown Coal R&D funding.


CO2CRC H3 Capture Project


Hazelwood Power Station

Post-combustion capture applications

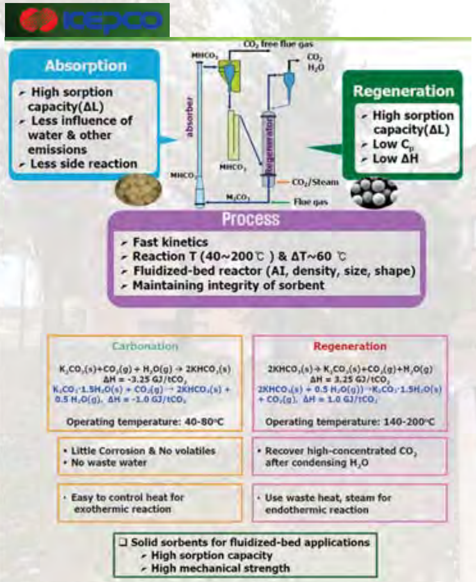
Power generation



- Over 250 potential CO_2 adsorbents have been evaluated by ADA to date (including INCAR-CSIC)
- Slipstream of flue gas from a coal-fired power plant
- A 1MWe pilot plant being designed and installed to validate performance for this novel technology. The current EPC schedule indicated the pilot should be ready for operation in early 2014

Post-combustion capture applications

Power generation



- 10 MW slipstream from 500 MW coal-fired power plant
- Location: Hadong, Korea
- 200 t CO_2/d
- Sorbent: KEP-CO2P2 or P3
- Targets:
  > 80% CO_2 capture rate
  <95% CO_2 purity
  US$ 30/t CO_2
- Start up: October 2013


10 MW Pilot Plant at KOSPO's Hadong coal-fired power plant, Unit # 8

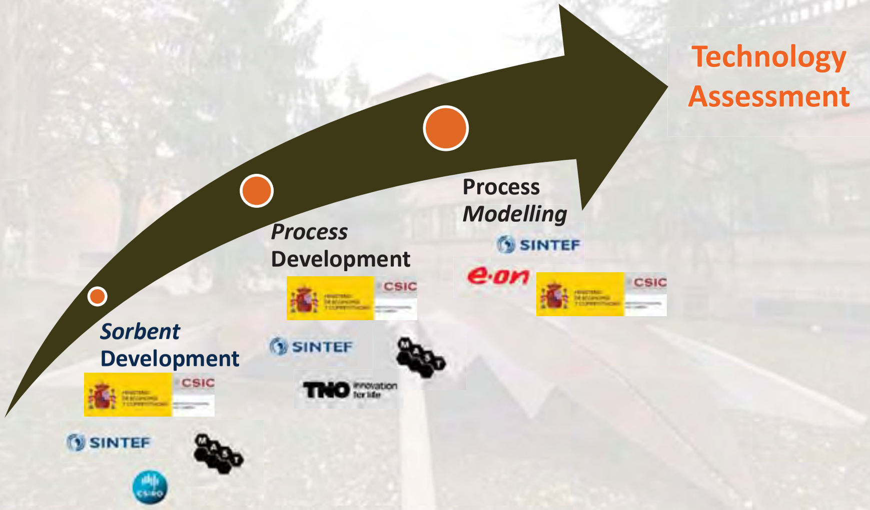
WP2 Objectives

The main objective in WP2 is to prove **adsorption** with **low-temperature solid sorbents** as a high efficiency and environmentally benign technology for post-combustion CO_2 capture by means of experimental and modelling work.

- Produce a **particulate solid adsorbent** for a moving bed reactor having suitable cyclic capacity under post-combustion conditions (e.g. >2.5 mmol/g for the high surface area sorbents) and that can withstand a 100°C temperature change within 3-4 minutes.
- Produce a structured **carbon monolith** sorbent with substantial equilibrium carbon dioxide uptake in high relative humidity environments (e.g. >1.5 mmol/g at 150 mbar CO_2 and 20°C) and with acceptable adsorption/desorption kinetics. The monoliths should also have enhanced thermal conductivity characteristics of better than 2W/mK.
- **Evaluate** and **model moving** and **fixed bed** based adsorption processes that combine low pressure drop and high thermal efficiency and determine the process performance.

Data will be generated, which allows the determination of the energy potential of the different concepts and benchmark the different concepts (WP4)

Partners/tasks in WP2



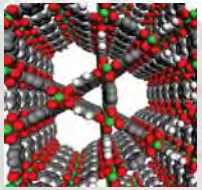
Sorbent Development

Process Development

Process Modelling

Technology Assessment

Porous solid sorbents: low temperature



Metal-Organic Frameworks(MOF)

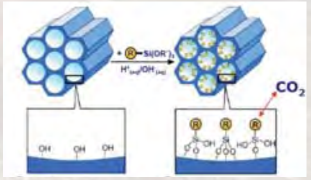
Cristaline compounds integrated by metal ions liked by organic ligands in a forming a porous network. Extremely high porosity suitable for gas storage and purification. Air/moisture sensitive.

Zeolites

Aluminosilicate molecular sieves. High capacity and selective CO_2 sorbents in the higher pressure range. Very sensitive to water.

Functionalised porous materials

- Surface (e.g. amine grafted)
- Matrix (e.g. N containing polymer)



Carbon-based

From activated carbons to carbon molecular sieves. Less sensitiveness to water, easy regeneration and lower cost. Low temperature CO_2 sorption.

Sorbent selection

Ideal adsorbent:

- ✓ Low cost
- ✓ Availability
- ✓ High capacity
- ✓ High selectivity towards CO_2
- ✓ Ease of regeneration
- ✓ High stability/durability

Carbon materials	
Cost	✓
Ease of regeneration	✓
Water tolerance	✓
Durability	✓
Availability	✓

Carbon precursors selected within HiPerCap:

- Agricultural by-products
- Phenolic resins
- Natural polymers/precursors

Sorbent & Process development

I. Sorbent Production

II. Evaluation

- ✓ Characterization
- ✓ Pure component adsorption isotherms at selected T: CO_2, N_2, H_2O

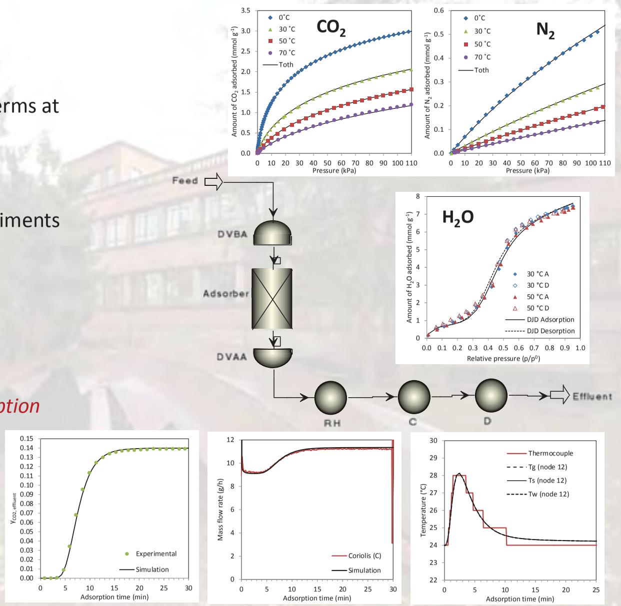
Equilibrium of adsorption

- Multicomponent adsorption experiments
  - Selectivity
  - Kinetics of adsorption
  - Evaluation of operating conditions
  - Influence of impurities
  - Validation of adsorption model

Dynamics of adsorption-desorption

III. Modelling

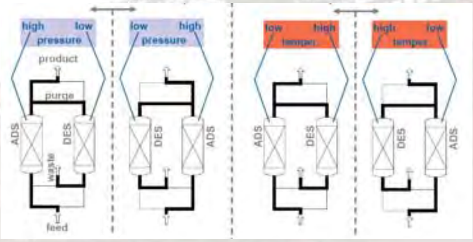
Design of adsorption-based CO_2 capture unit



Adsorbent requirements from process operation

1. Minimal compression of flue gas (vacuum operation) needs large working capacities between 0 and 1 bar
2. Regeneration of the adsorbent is where the energy is needed
3. Difference between adsorption and desorption for CO_2 compared to other gases is key
4. Large adsorption amount is not necessarily better
5. Interaction of species is important (impurities)

Pressure Swing Adsorption (PSA/VSA)



Temperature Swing Adsorption (TSA)

Process design parameters

- ***Adsorbent inventory***: scales with CO_2 working capacity
- ***Purity and recovery***: scales with CO_2 working selectivity
- Cycle should be optimized for specific feed gas-adsorbent combinations

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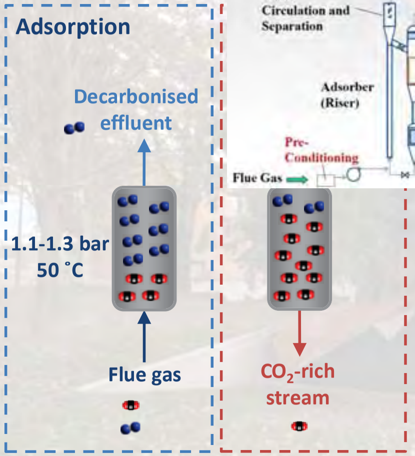
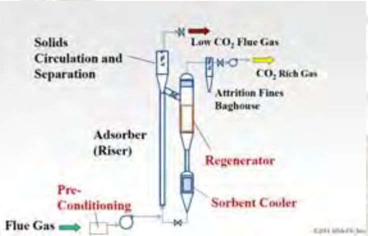
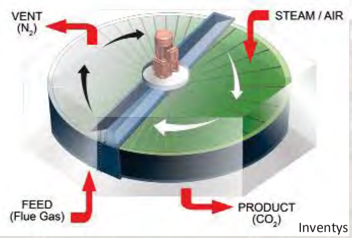
Adsorption based processes







Inventys

TSA

⊖ Longer cycles => lower productivity

=> Circulating solids (ADA-ES)

=> Rotating bed (Veloxotherm^{TM}, Inventys)

⊕ **$ 15 per tonne!**

VSA

⊕ Rapid swing cycles

Temperature Swing Adsorption based processes

Fixed –bed

Conventional heating (steam or hot gas) is lengthy

Mass transfer↔ Heat transfer

Cycle duration ↔ Productivity

How to heat and cool the adsorbent bed more rapidly and increase the productivity of a TSA process?

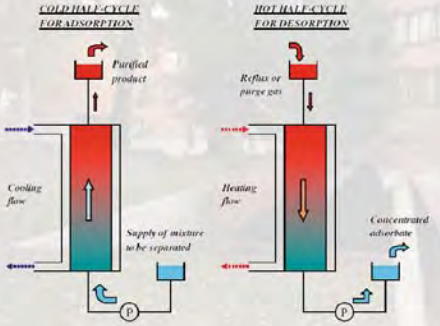
. Improve thermal conductivity: promoters

. Cycling -zone adsorption

. Circulating fluidized bed

How to heat and cool the adsorbent bed more rapidly and increase the separation efficiency of a TSA process?

. Electro-Thermal swing operation



Source: Luo, L. (2013). *Intensification of adsorption processes in porous media.* Chapter 2. Heat and mass transfer intensification and shape. A multi-scale approach.

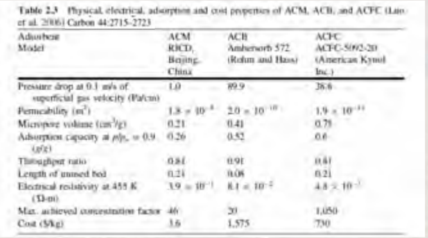


Table 2.3 Physical, electrical, adsorption and cost properties of ACM, ACB, and ACFC (Luo et al. 2006) Carbon 44:2715-2723

Adsorbent Model	ACM RICD, Beijing, China	ACB Ambersorb 572 (Rohm and Hass)	ACFC ACFC-5092-20 (American Kynol Inc.)
Pressure drop at 0.1 m/s of superficial gas velocity (Pa/cm)	1.0	89.9	26.6
Permeability (m^2)	1.8×10^{-8}	2.0×10^{-10}	1.9×10^{-11}
Micropore volume (cm^3/g)	0.21	0.41	0.75
Adsorption capacity at p/p_o = 0.9 (g/g)	0.26	0.52	0.6
Throughput ratio	0.84	0.91	0.81
Length of unused bed	0.21	0.08	0.21
Electrical resistivity at 455 K (Ω·m)	3.9×10^{-1}	8.1×10^{-2}	4.8×10^{-3}
Max. achieved concentration factor	46	20	1,050
Cost ($/kg)	3.6	1,575	730

Monolith Spherical Beads Fiber cloth

Temperature Swing Adsorption based processes

Fixed –bed: Structured adsorbents

Advantages:

- Superior mass transfer kinetics
- Effective heat transfer: uniform T distribution
- Low pressure drop

Challenges:

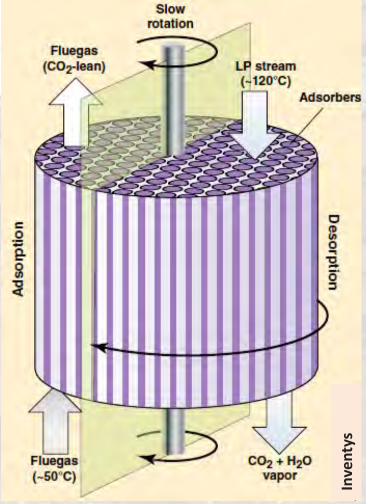
- Throughput: working capacity
- Working capacity: wall thickness and voidage

Conformations:

- Monoliths: HiPerCap focus
- Fabric structures
- Laminates

Monolith design parameters:

- Cell density: ensure high loading
- Wall thickness: mass transfer resistance (external film and pore diffusion)
- Bed length: sufficient residence time



Temperature Swing Adsorption based processes

Moving-bed: Particulates

Advantages:

- High working capacities
- Uses the heat contained in the flue gas for regeneration
- Low pressure drop

Challenges:

- Hydrodynamics: scarce data
- Velocity: limited by fluidization
- Particle residence time in the regeneration section

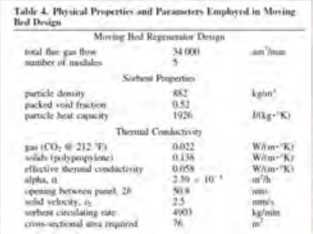
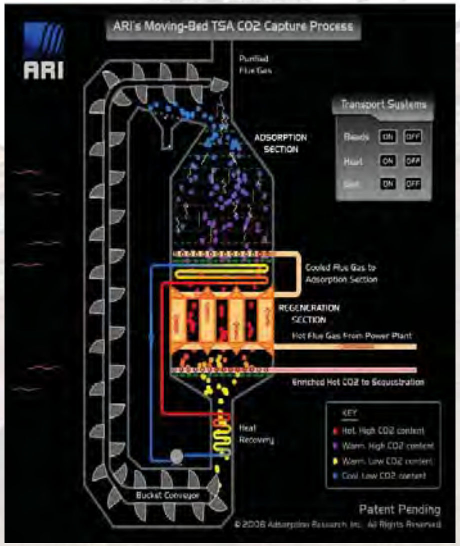


Table 4. Physical Properties and Parameters Employed in Moving Bed Design

Moving Bed Regenerator Design		
total flue gas flow	34 000	am³/min
number of modules	5	
Sorbent Properties		
particle density	882	kg/m³
packed void fraction	0.52	
particle heat capacity	1926	J/(kg·°K)
Thermal Conductivity		
gas (CO_2 @ 212 °F)	0.022	W/(m·°K)
solids (polypropylene)	0.138	W/(m·°K)
effective thermal conductivity	0.058	W/(m·°K)
alpha, α	2.39×10^{-5}	m²/h
opening between panel, 2δ	50.8	mm
solid velocity, v_s	2.5	mm/s
sorbent circulating rate	4903	kg/min
cross-sectional area required	76	m²



Source: Yang et al., Ind. Eng. Chem. Res., 2009, *48*, 341-351

HiPerCap WP2: Adsorption Technologies

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Melbourne, 25th March 2015

Energy Processes and Emission Reduction Group

Carbon Composite Adsorbents for Post Combustion CO_2 Capture

Presenter: Yonggang Jin
Research Team: Shi Su, Yonggang Jin, Ramesh Thiruvenkatachari, Jun Bae, Xinxiang Yu

HiPerCap EU-Australia workshop, Melbourne, 25-27 March 2015

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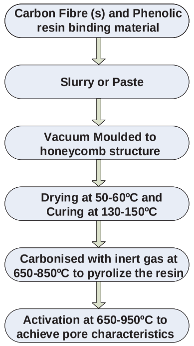
Lab Scale Study – Carbon Fibre Composites

Fabrication and Testing of Lab Size Honeycomb Carbon Fibre Composite Monoliths

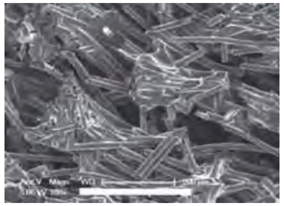

Molding equipment


3 processing furnaces


Carbon Fibre (s) and Phenolic resin binding material
Slurry or Paste
Vacuum Moulded to honeycomb structure
Drying at 50-60ºC and Curing at 130-150ºC
Carbonised with inert gas at 650-850ºC to pyrolize the resin
Activation at 650-950ºC to achieve pore characteristics

Length: 80mm, Dia: 30mm, Number of Channels: 17,


Fabricated (HMCFC)


Microscopic morphology

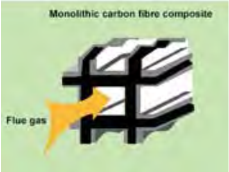
Adsorbent Testing Equipments


Adsorbent Characterisation


Breakthrough Test Rig with Lab Scale Adsorption Chamber

Solid Carbon Sorbent CO_2 Capture Technology

- Based on honeycomb carbon composite monoliths
  - ✓ Enable CO_2 capture with low pressure drop
  - ✓ Potentially low energy consumption for adsorbent regeneration
    - Lower heat capacity of solid adsorbents than liquid solvents
    - Physisorption - lower heat of CO_2 adsorption
    - Utilisation of flue gas waste heat for CO_2 desorption
  - ✓ Tolerant to moisture, SO_x and NO_x
    - Avoid flue gas pre-treatment prior to CO_2 capture; this is important as there are no FGD and SCR $DeNO_x$ facilities at coal fired power plants in Australia



Evolutionary Journey

Lab scale CO_2 capture (2006-2008)

- Proof-of-Concept
- Capture studies using simulated flue gas

Large scale CO_2 capture with regeneration (2009-2011)

- CO_2 capture combined with thermal and vacuum regeneration

CO_2 capture site trials (2011-2014)

NEXT

- To evaluate CO_2 capture and regeneration under real flue gas conditions

Lab scale studies
Development of next generation carbon composite adsorbents
(2010 – present)

Lab scale study
New regeneration process with enhanced heat transfer
(2011 – present)

Large Scale Capture-Regeneration Studies

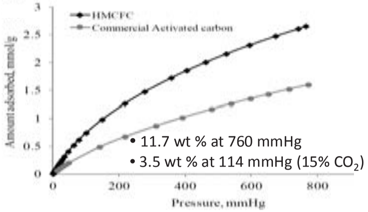
CF composites

Lab size adsorbent (Ø 30mm)

Large size adsorbent (Ø 123 mm)

Large scale moulding unit for composite fabrication

CO_2 adsorption Isotherms at 25 °C



- 11.7 wt % at 760 mmHg
- 3.5 wt % at 114 mmHg (15% CO_2)

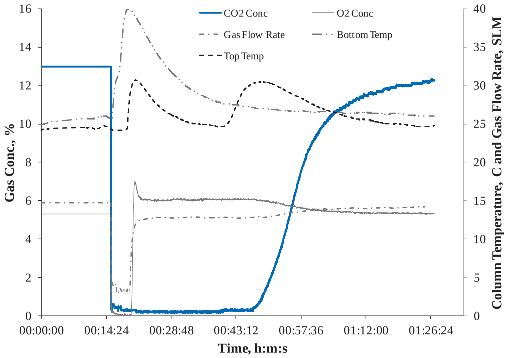
Large scale CO_2 capture-regeneration unit

- Two 2 meter long columns
- Repetitive capture & regeneration capability
- Thermal and vacuum swing regeneration

R. Thiruvenkatachari, S. Su et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

Summary of Large Scale Study Results

Adsorption Breakthrough Profile Showing CO_2 capture at Real Time

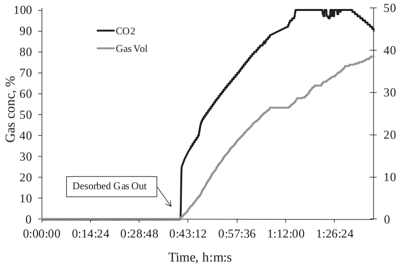


- CO_2 capture carried out at ambient temperature and pressure
- Simulated flue gas consisting of 13% CO_2, 5.5% O_2 and balance N_2
- CO_2 adsorption efficiency > 97% from adsorption breakthrough

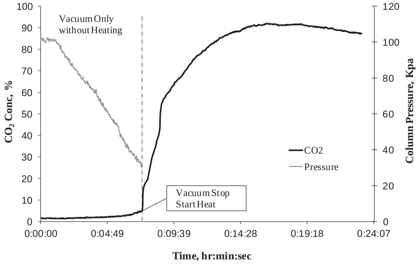
R. Thiruvenkatachari et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

Thermal and Vacuum Regeneration

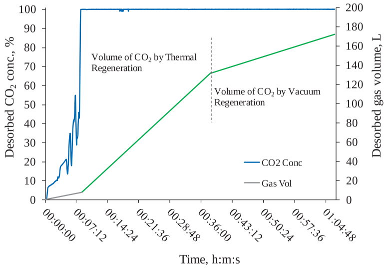
Individual Thermal Regeneration



Vacuum Regeneration



Combined Thermal and Vacuum Regeneration



- Residual CO_2 inside column after thermal regeneration
- Vacuum regeneration alone is ineffective
- Heating is essential to desorb CO_2
- Combined thermal and vacuum regeneration with pure product purge is most effective
- Very high purity of recovered CO_2
- CO_2 recovery > 95%

R. Thiruvenkatachari, S. Su et al., *International Journal of Greenhouse Gas Control*, 2013, 13, 191-200.

Site Trials of Prototype CO_2 Capture Unit

- **Objective**
  - to evaluate the stability of honeycomb CF composite monolithic adsorbents using the real flue gas at Vales Point Power Station
  - to test the effect of real flue gas characteristics on the operation and performance of the CO_2 capture unit
- **Site installation, commissioning and testing**

Opening of real flue gas to test unit for first time at Vales Point Power Station

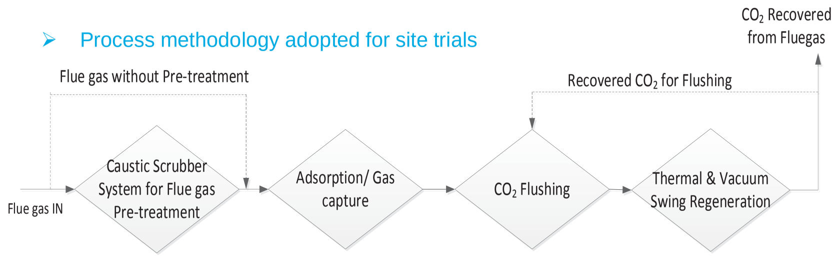
Fully commissioned solid sorbent prototype unit at Vales Point power Station

Individual sensors to measure SOx, NOx, CO and CO_2 for accurate measurement

Site Trials of Prototype CO_2 Capture Unit (continued)

- ❖ **Site trial testing involving two main scenarios**
  - – CO_2 capture performance with flue gas pre-treatment
  - – CO_2 capture performance without flue gas pre-treatment

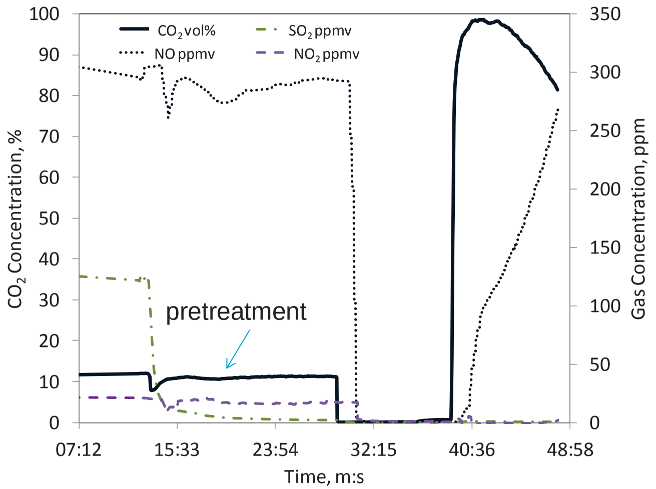
➢ Process methodology adopted for site trials


Flue gas without Pre-treatment
Flue gas IN
Caustic Scrubber System for Flue gas Pre-treatment
Adsorption/ Gas capture
CO_2 Flushing
Thermal & Vacuum Swing Regeneration
Recovered CO_2 for Flushing
CO_2 Recovered from Fluegas

- ❖ **Performance of carbon composite solid adsorbents evaluated:**
  - – Stability of adsorbents to real flue gas evaluated from over 200 tests
  - – CO_2 removal performance
  - – Solid sorbent performance to removal of other gases apart from CO_2

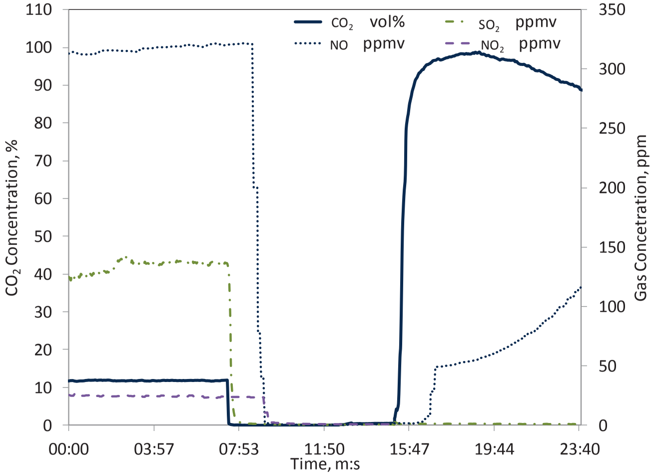
Results of Site Trials

- ❖ Adsorption & desorption: flue gas with pretreatment



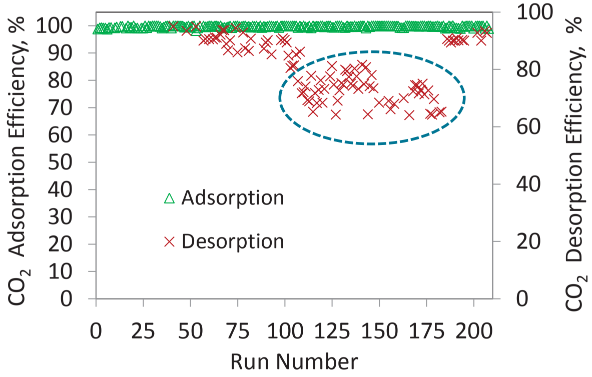
Results of Site Trials (continued)

- ❖ Adsorption & desorption: flue gas without pretreatment



Results of Site Trials (continued)

- ❖ Adsorbent stability



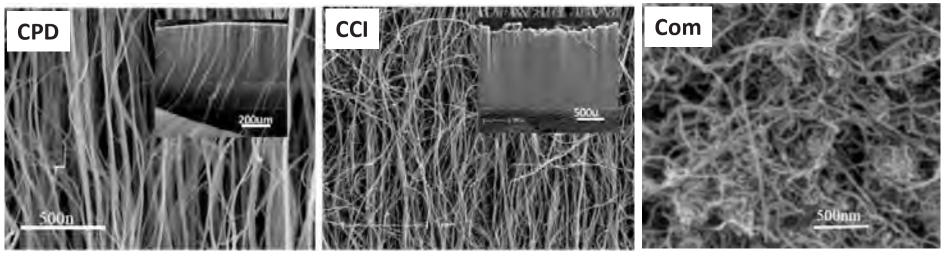
➢ **Excellent stability** to real flue gas over 200 site tests
  - – CO_2 adsorption efficiency consistently over 98%
  - – CO_2 desorption efficiency between 90-95%.

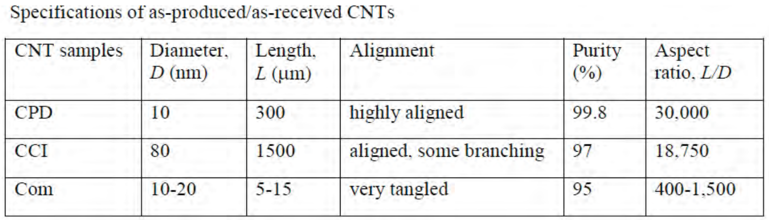
Development of New-Generation Carbon Composite Adsorbents

- **Objective**
  - ➢ Enhance CO_2 adsorption capacity (smaller footprint, lower capital and operating costs)
  - ➢ Lower the cost of adsorbents using local biomass waste and brown coals
- **New-generation carbon composite adsorbents**
  - Carbon nanotube (CNT) modified carbon composite monoliths
  - *Biomass derived carbon composites (HiPerCap WP2)*

CNT Composites - Source of CNTs

- CPD &CCI are home made, Com the commercial product

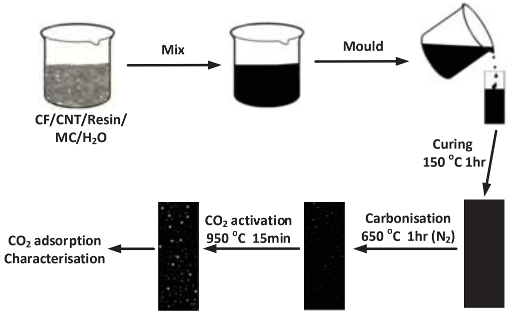




Specifications of as-produced/as-received CNTs

CNT samples	Diameter, D (nm)	Length, L (μm)	Alignment	Purity (%)	Aspect ratio, L/D
CPD	10	300	highly aligned	99.8	30,000
CCI	80	1500	aligned, some branching	97	18,750
Com	10-20	5-15	very tangled	95	400-1,500

Preparation of CNT Composite Adsorbents



Schematic of composite preparation procedures

Prepared CNT composite monolith

The current preparation method (physical activation with CO_2) is simpler and more economic than chemical activation (e.g. with KOH) and functionalisation with basic groups

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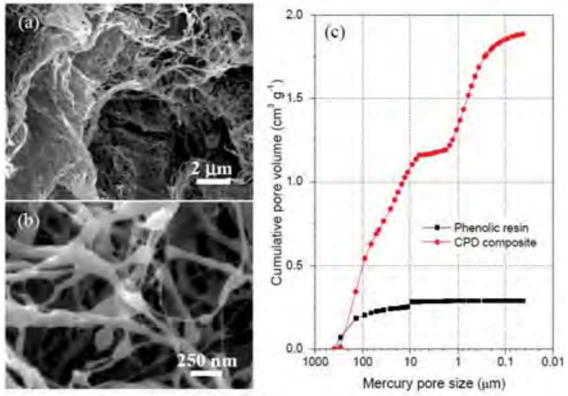
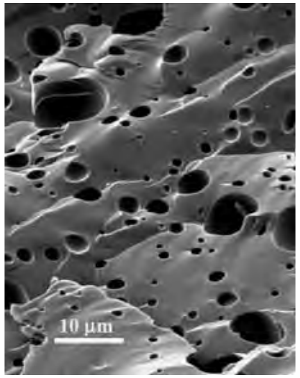
SEM Morphology



Morphology and macropore size distributions of CNT composites

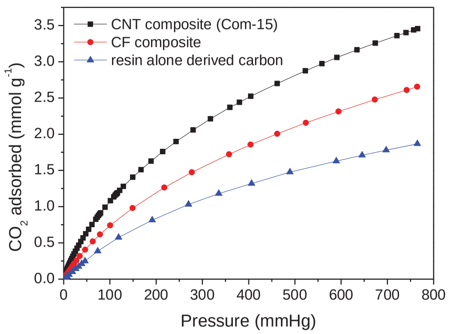


Morphology of activated phenolic resin

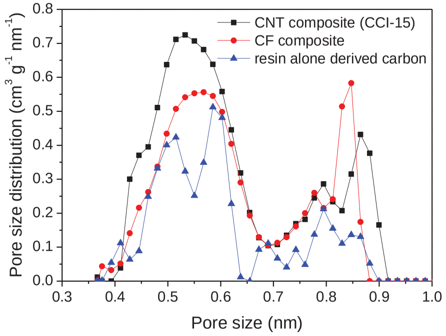
Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

Comparisons of CNT and CF composites

CO_2 uptake at 25 °C



Narrow micropore size distributions



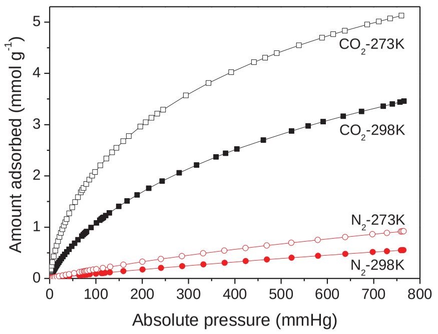
CNT composites exhibit much higher CO_2 adsorption capacities

- *CO_2 uptake: 15.9 wt% at 25 °C and 1 bar, and 5.2 wt% at 25 °C and 0.15 bar*
- *Up to 30% increase in CO_2 adsorption capacity at 25 °C and 1 bar*
- *Over 45% increase in CO_2 adsorption capacity at 25 °C and low CO_2 pressures (0.15 bar)*

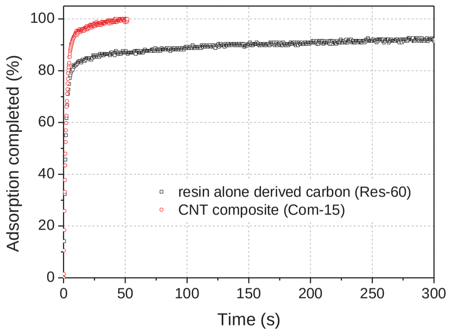
Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

Adsorption Selectivity & Kinetics

CO_2 & N_2 uptake adsorption Isotherms at 0 and 25 °C



Rates of CO_2 adsorption at 25 °C and 25 mmHg



- CO_2/N_2 selectivity: 32.6 at 273 K and 19.8 at 298 K
- Fast adsorption kinetics observed in the CNT composites

Y. Jin, S. Hawkins, C. Huynh, S. Su, *Energy Environ. Sci.*, 2013, 6, 2591-2596.

Conclusions

- Porous carbon composite monoliths show great promise in post-combustion CO_2 capture.

- Site trials demonstrate the excellent stability of the carbon composite adsorbent towards real flue gas.

- New-generation CNT carbon composite adsorbents exhibit significantly enhanced CO_2 uptake particularly under low CO_2 pressures, which is of more relevance for flue gas applications.

Acknowledgements

- Funding supports from:
  - Coal Innovation NSW for the site trials of prototype CO_2 capture unit at the Vales Point power station
  - ANLEC R&D for the development of CF/CNT composites
  - CSIRO
- Site support from Delta Electricity

Thank you

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Senior Principal Research Scientist
Team Leader

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How can MOFs save the world?

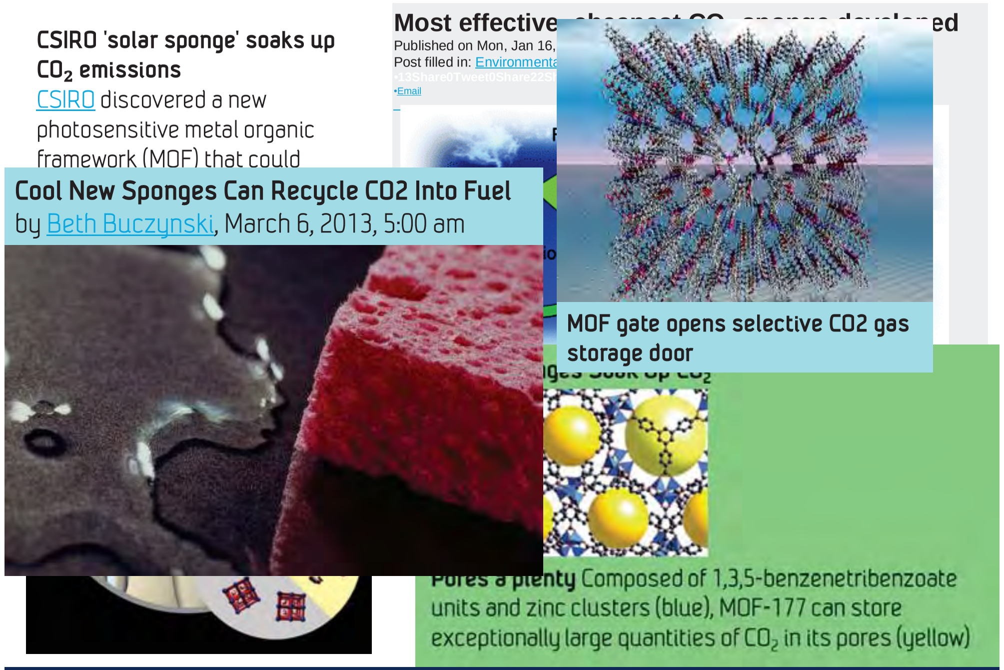
Breakthrough Post Combustion Capture Technologies workshop

March 25-26th 2015, Melbourne, Austalia

Richard Blom

SINTEF Materials and Chemistry, Norway

richard.blom@sintef.no



CSIRO 'solar sponge' soaks up CO_2 emissions

CSIRO discovered a new photosensitive metal organic framework (MOF) that could

Most effective

Published on Mon, Jan 16,

Post filled in: Environmenta

•Email

Cool New Sponges Can Recycle CO2 Into Fuel

by Beth Buczynski, March 6, 2013, 5:00 am

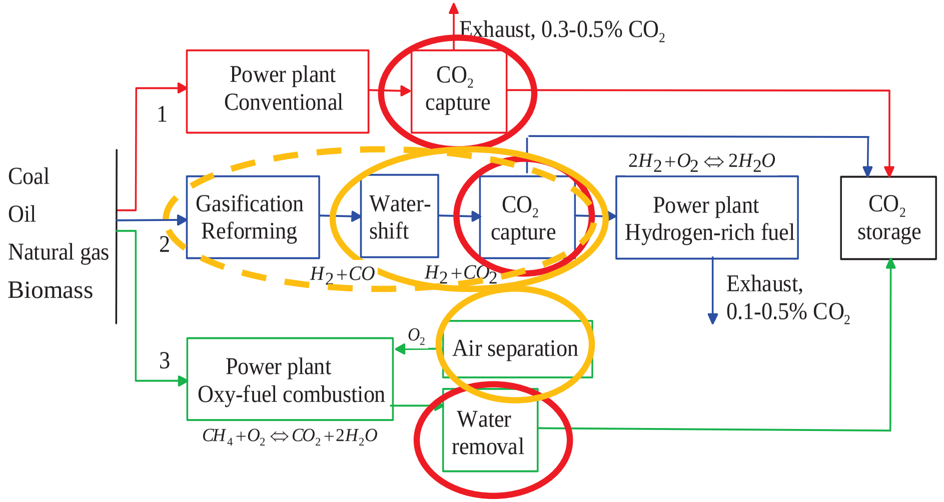
MOF gate opens selective CO2 gas storage door

Pores a plenty Composed of 1,3,5-benzenetribenzoate units and zinc clusters (blue), MOF-177 can store exceptionally large quantities of CO_2 in its pores (yellow)

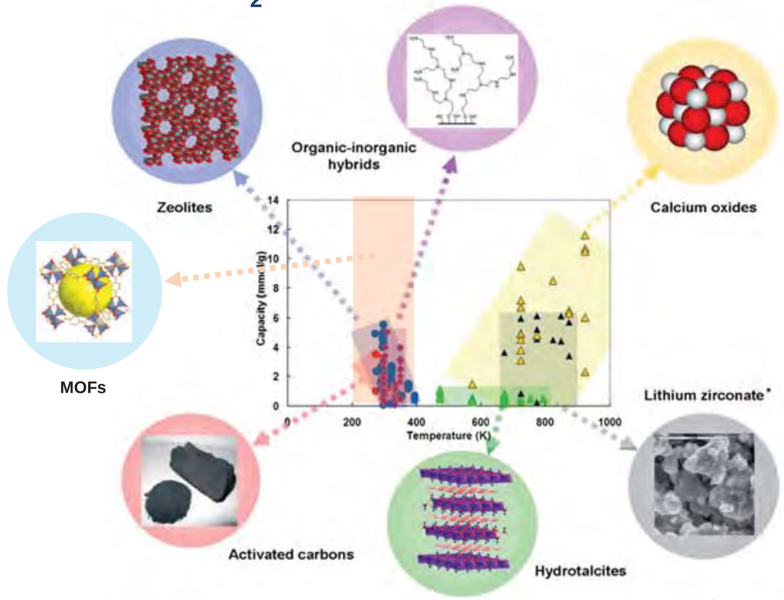
Outline

- CO_2 capture schemes
- Various sorbents - What are MOFs?
- MOFs in CO_2 capture
  - Requirements for use in CO_2 capture
    - Post-combustion adsorption
    - Pre-combustion adsorption
  - MOF formulation
- Conclusions

CO_2 capture technologies – possible use of MOF based sorbents



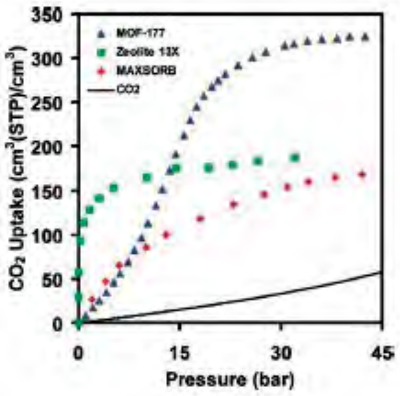
Various families of CO_2 sorbents:



Partly taken from: Choi et al, *ChemSusChem*, 2009

What determines the applicability of a certain adsorbent?

- The shape of the isotherm relative to boundary conditions of the adsorption process.
  - T, p & composition of inlet gas
  - T, p & composition demand of outlet gas(es)
  - For TSA processes you need a sorbent having large capacity difference between sorption and desorption temperatures
  - For a PVSA process you need a sorbent having large capacity different between the sorption and desorption pressures



- And kinetics!
- And certainly; selectivity is an issue…….
- And so is the physical stability of the sorbent….

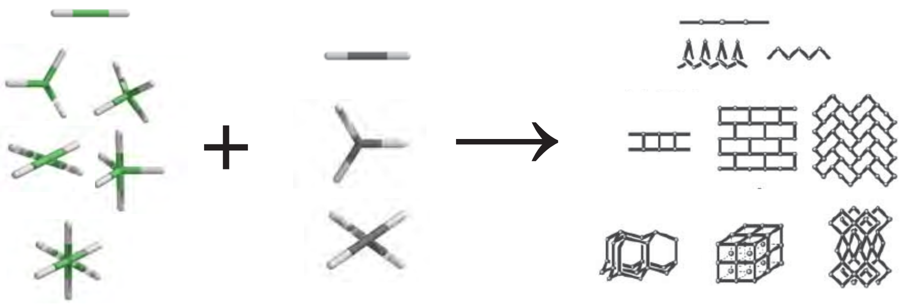
Milward & Yaghi, *J. Am. Chem. Soc*, 2005

What are MOFs?

Metal centre or cluster (inorganic part)

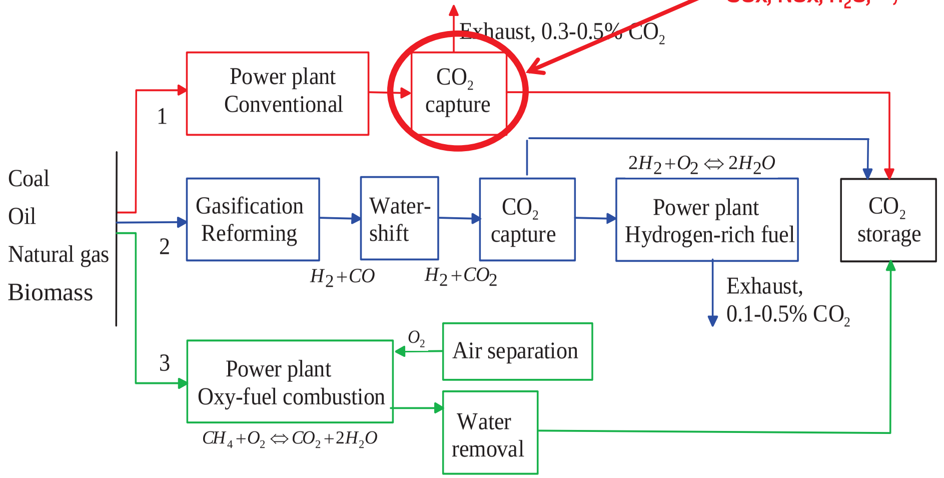
Linker (organic part)

Metal Organic Framework (coordination polymer)



- Combining the whole inorganic chemistry with the whole organic chemistry give a close to infinite number of possible diverse structures !

Post-combustion CO_2 capture – possible use of MOF based sorbents



1 atm, ambient T, 4-13% CO_2, SOx, NOx, H_2O,++)

Exhaust, 0.3-0.5% CO_2

Coal

Oil

Natural gas

Biomass

1

Power plant Conventional

CO_2 capture

2

Gasification Reforming

H_2+CO

Water-shift

H_2+CO_2

CO_2 capture

$2H_2+O_2 \Leftrightarrow 2H_2O$

Power plant Hydrogen-rich fuel

Exhaust, 0.1-0.5% CO_2

CO_2 storage

3

Power plant Oxy-fuel combustion

$CH_4+O_2 \Leftrightarrow CO_2+2H_2O$

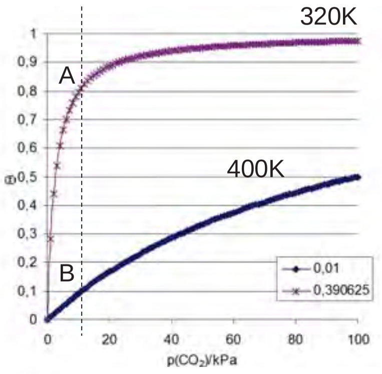
O_2

Air separation

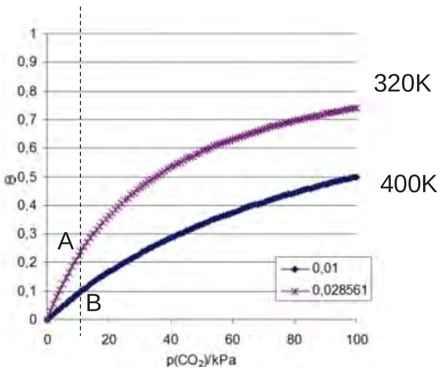
Water removal

Temperature swing adsorption (TSA):

Langmuir: $\theta = \frac{y}{y_{\max}} = \frac{bp}{1+bp}$



E_{ads} = 46 kJ/mole

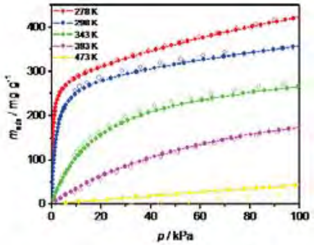


E_{ads}= 16 kJ/mole

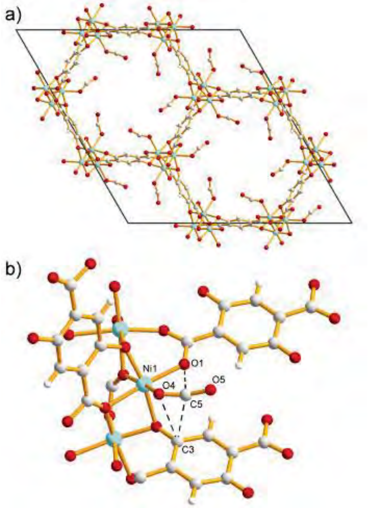
Post-combustion

The CPO-27-M family:

- Relatively high adsorption energies are needed to selectively adsorb CO_2 from dilute flue gas
- High potential cyclic CO_2 capacities
- Synthetic gas mixtures (also H_2O) seems to give stable and good results
- Ongoing work on cyclic capacity using realistic gas composition



The best adsorbent can adsorb as much as 25 wt% CO_2 at room temperatures and 10 kPa CO_2 pressure (0.1 atm)

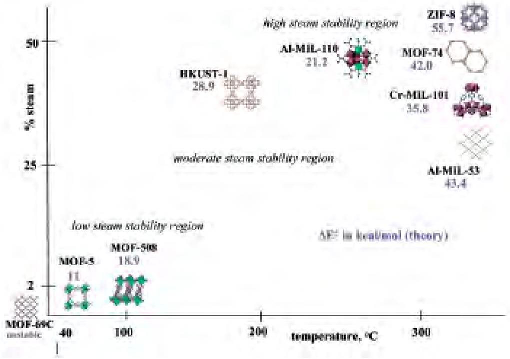


Structural analyses show that CO_2 bonds directly to the open metal center on CPO-27-Ni

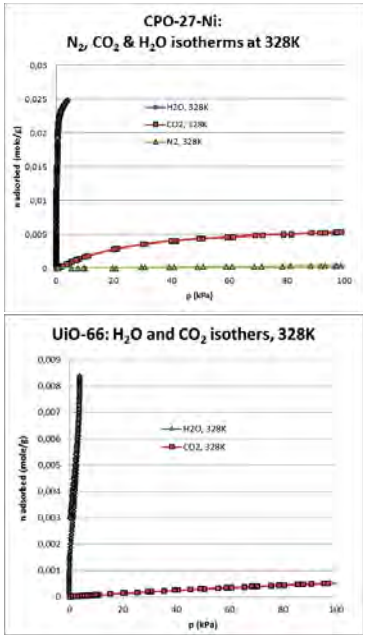
Dietzel, Johnsen, Fjellvåg, Bordiga, Groppo, Chavan & Blom, *Chem. Commun.*, 2008

MOF challenges: Water stability and selectivity….

- Hydrothermal stability……
- If stable… what is the moisture limit?
- Kinetics……



Low, Benin, Jakubczak, Abrahamiam, Faheem & Willis, *J. Am. Chem. Soc.* 2009



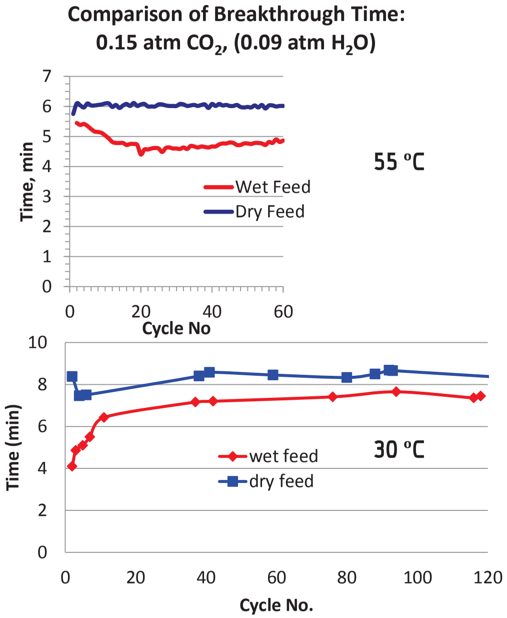
CPO-27-Ni: N_2, CO_2 & H_2O isotherms at 328K

UiO-66: H_2O and CO_2 isothers, 328K

Grande & Blom, 2013

VSA using CPO-27-Ni beads:

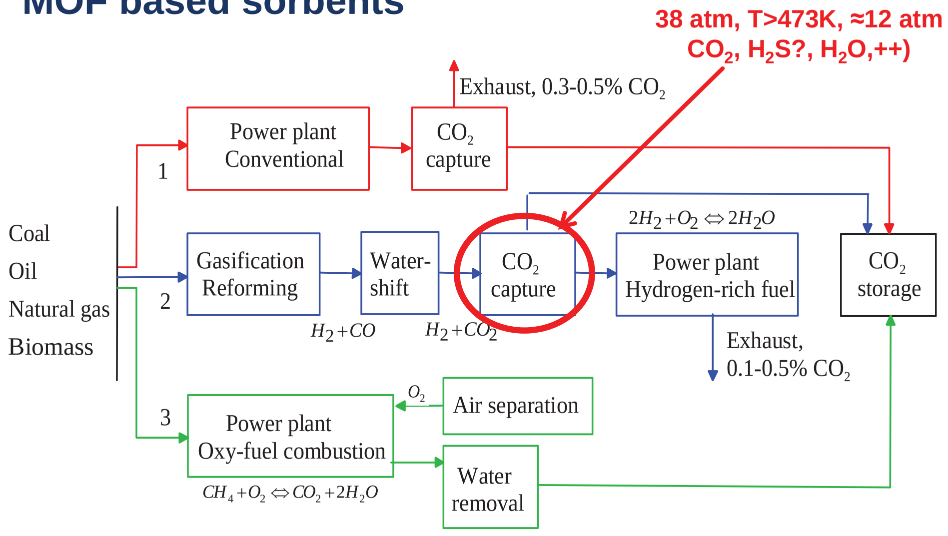
- Steady cyclic CO_2 capacity is achieved also in the presence of moisture
- At wet conditions, under counter-current regeneration, the cyclic CO_2 capacity reaches a steady state level of about 80% of the cyclic CO_2 capacity at dry conditions.



Comparison of Breakthrough Time: 0.15 atm CO_2, (0.09 atm H_2O)

Nanoti & Blom, 2014.

Pre-combustion CO_2 capture – possible use of MOF based sorbents



38 atm, T>473K, ≈12 atm CO_2, H_2S?, H_2O,++)

Coal
Oil
Natural gas
Biomass

1 Power plant Conventional → CO_2 capture → Exhaust, 0.3-0.5% CO_2

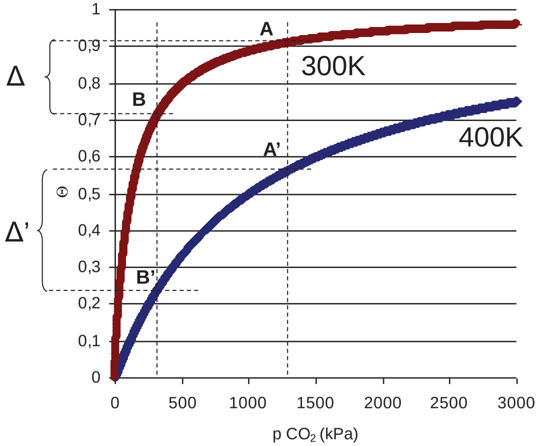
2 Gasification Reforming → H_2+CO → Water-shift → H_2+CO_2 → CO_2 capture → Power plant Hydrogen-rich fuel ($2H_2+O_2 \Leftrightarrow 2H_2O$) → Exhaust, 0.1-0.5% CO_2

3 Power plant Oxy-fuel combustion ($CH_4+O_2 \Leftrightarrow CO_2+2H_2O$) ← O_2 ← Air separation; → Water removal

CO_2 storage

Pre-combustion

Pressure/Vacuum swing adsorption (PVSA)



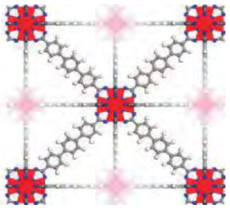
E_{ads} = 20 kJ/mol.
Vertical dotted lines at 13 and 3 atm.

Pre-combustion

Systematic increment of pore size: UiO-6X system

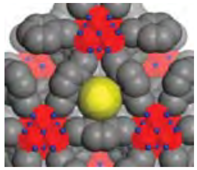
UiO-66
BET=1100-1350 m²/g

UiO-67
BET=2200-2450 m²/g

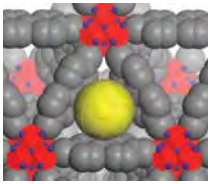


UiO-68
BET≈ 4000 m²/g

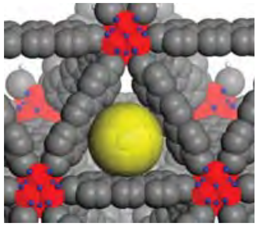
Increasing the length of the linker results in materials with lager pore size and higher surface area.



UiO-66; Probe 6 Å diameter.



UiO-67; Probe 8 Å diameter.



UiO-68; Probe 10 Å diameter.

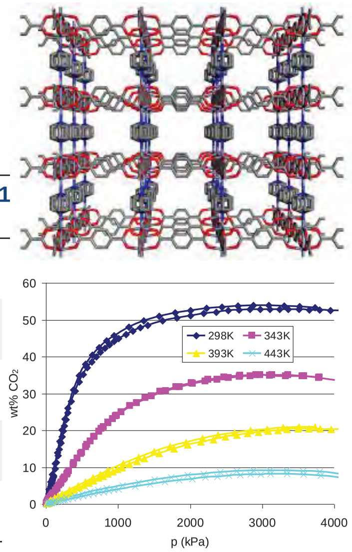
The pore openings are also increasing as a function of linker length.

Cavka, Jakobsen, Olsbye, Guillou, Lamberti, Bordiga & Lillerud, *J. Am. Chem. Soc.*, 2008

Pre-combustion

Physical properties of the different adsorbents: state-of-art vs. novel MOF adsorbents

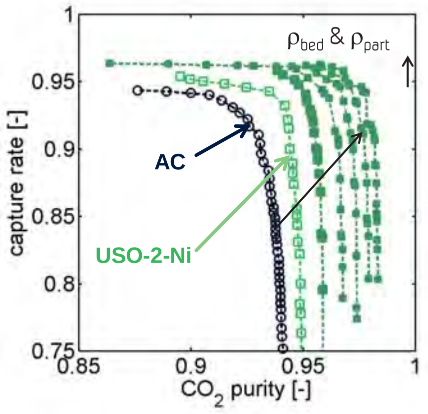
	Activated Carbon	USO-2-Ni	UiO-67/MCM-41
d_p [mm]	3	1-2	0.2-0.5
r_{mat} [kg/m3]	1970	1700	1570
r_{part} [kg/m3]	850	531	557
r_{bed} [kg/m3]	507	300	320
Cs [J/K kg]	1000	1160	1250



Structure and CO_2 isotherms of USO-2-Ni

Casas, Schell, Blom, Mazzotti, *Sep. Purif. Techn.* 2013

Comparison assuming higher densities for the MOFs
- modeling of 6-column PSA separation process based on breakthrough experiments



Density	Porosity	
original	ε_{bed}	0.435
	ε_{tot}	0.823
+ 10%	ε_{tot}	0.805
+ 20%	ε_{tot}	0.788
+ 30%	ε_{tot}	0.771
+ 40%	ε_{tot}	0.7529
+ 50%	ε_{tot}	0.735

$$\varepsilon_{bed} = 1 - \frac{\rho_{bed}}{\rho_{part}}$$

$$\varepsilon_{tot} = 1 - \frac{\rho_{bed}}{\rho_{mat}}$$

Casas, Schell, Blom, Mazzotti, *Sep. Purif. Techn.* 2013

So formulation is important !

Firstly, because a chemical engineer will never put a fluffy powder into their reactor……..

Secondly, because it really improve the process performance!

But – important to keep the properties of the virgin (nano)-powder throughout the formulation process

MOF formulation: Can a general method be developed?

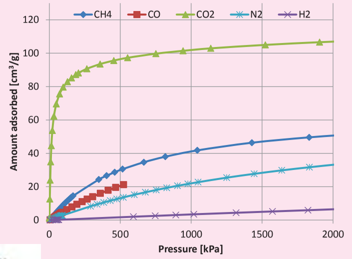
- ***Pelletizing***: The fine powder is blended with a binder (e.g. polyvinylalco (PVA), graphite or silica) and pressed at a certain pressure to give pell can be crushed and fractionized by sieving.
- ***Cake crushing***: The fine powder is mixed with a certain amount of a binder, typically PVA, dissolved in a solvent. Enough binder/solvent solution is to make a paste that is dried, then crushed and sieved into the wanted p size fraction.
- ***Mixing/extrusion/Spheronizing***: Using this method the fine powder is mixed with a binder (e.g. cellulose, PVA, etc.) and a solvent (e.g. water, alcoho to give a paste. The paste is extruded to give “spaghetti” which is then ma into spheres in a “spheronizer” (a fast circulating plate)
- ***The alginate method***: A slurry of the fine powder is made in a solution of an alginate dissolved in water. The homogeneous slurry is dropwise added water solution of Ca^{2+} ions where a spontaneous cross-binding of the al slurry droplets occur.

Formulation of metal-organic frameworks - Extrusion

Focus on utilization of organic linkers that remain in the structure but provide hardness and porosity.

UTSA-16

- Adsorbent presents low surface area loss after extrusion. High CO$_2$ loading remains.
- No significant mass transfer resistance added after extrusion.

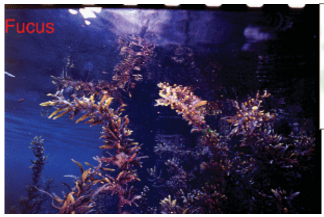


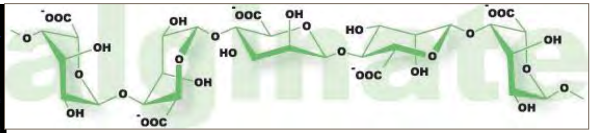
Scale

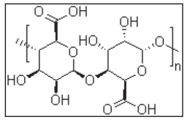
- We have obtained around 200 grams of extruded UTSA-16 with: very low surface area loss, good adsorption properties, narrow pore distribution and with density comparable to zeolite materials.

Agueda, et al. *Chem. Eng. Sci.* 2015, *124*, 159; Grande, et al, *Chem. Eng. Sci.* 2015, *124*, 154.

MOF Formulation: The alginate method





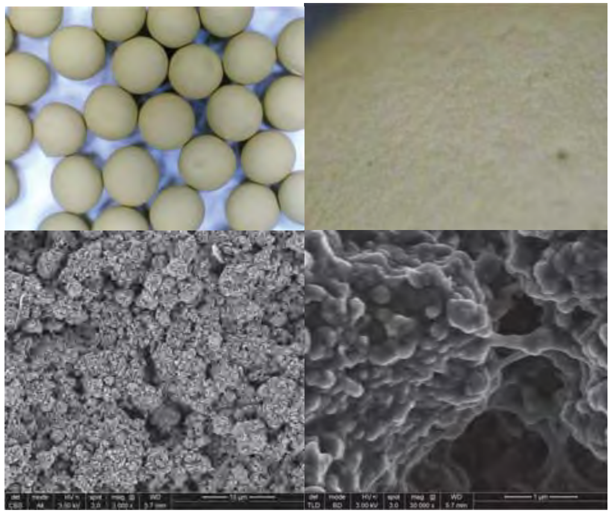


Molecular Formula: $(C_6H_8O_6)_n$

- Discovery of alginates were done by Edward Stanford in 1883
- Polymerizes into a three dimentional metal-bioorganic network in the presence of cations such as Ca^{2+}
- Used in molecular gastronomy for ages…..

MOF formulation by molecular gastronomy methods……

Looking into the spheres: CPO-27-Ni/alginate



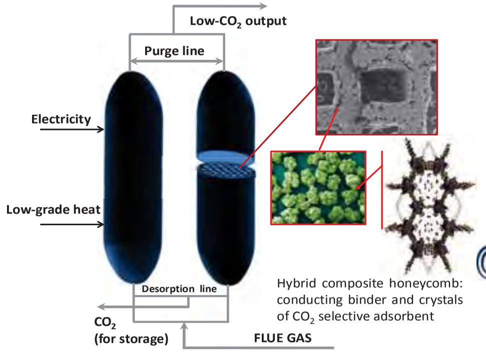
- The interior has macro-pores that give fast gas diffusion
- The alginate matrix seems evenly distributed and glue to MOF crystallites together
- Still, there is a lot to gain on increasing the particle density through optimisation of the procedure

Spjelkavik, Didriksen, Aarti, Divekar, Blom. *Chem. Eur. J.* 2014

But formulation is not only preparation of well defined particulates…..

Advanced Materials and Electric Swing Adsorption Process for CO_2 Capture (MATESA)

The objective of MATESA is to make a "**proof of concept**" of a cutting-edge adsorption technique termed Electric Swing Adsorption (ESA) as a **new-generation high-efficiency** post-combustion CO_2 capture process.



Hybrid composite honeycomb: conducting binder and crystals of CO_2 selective adsorbent

Main benefits for Europe

- Novel energy-efficient technology for CCS
- Improved hybrid materials for improved adsorption processes
- High CO_2 loading adsorbents for CCS.
- Promote R&D cooperation with Australia

→ Develop an innovative CO_2 capture technique with better environmental fingerprint.

Total budget = 5.709 K€
Total EU funding = 2.966 K€
Coordinator: Carlos A. Grande

Concluding comments:

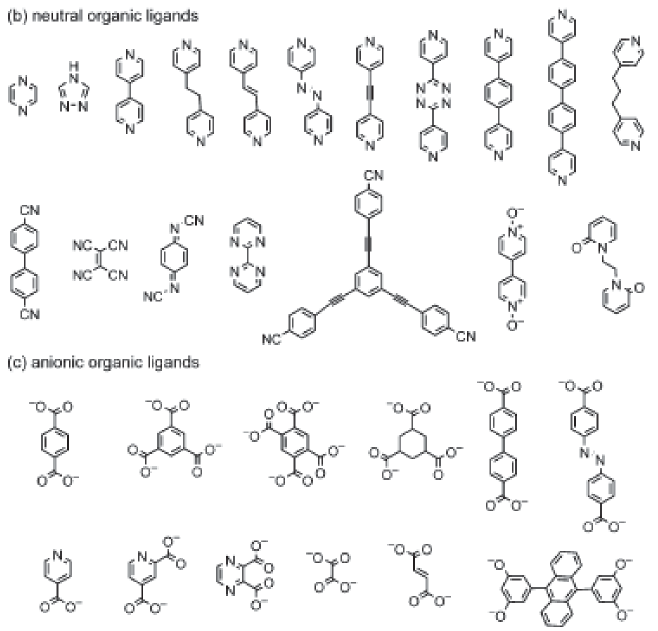
- Several MOFs have adsorption properties superior to state-of-art adsorbents like Zeolites and Activated Carbon both for post- and pre-combustion CO_2 capture.
- However, the MOF field is still in its infancy, and certain issues needs more attention:
  - Hydrothermal stability
  - Stability in the presence of contaminants (SOx, NOx, etc.)
  - Water selectivity (?)
  - Still black box synthesis (?)
  - Price (?)
- Developing good formulation techniques that maintain the good properties of the MOF at high volumetric capacities are needed before real application takes place

---

Thanks to:

- Coworkers through the last years:
  - Prof. Pascal D. C. Dietzel, UiB (NO)
  - Prof. Helmer Fjellvåg, UiO (NO)
  - Prof. Marco Mazotti, Dr. Johanna K. Schell, Dr. Natalie Casas, ETHZ (CH)
  - Dr. Anshu Nanoti, Dr. Arti, Dr. Soumen Dasgupta, Mr. Swapnil Divekar, IIP (IN)
  - Prof. Stefano Brandani, Mr. Shreenath Krishnamurthy, University fo Edinburgh
  - Dr. Jasmina Cavka, Dr. Carlos Grande, Mr. Terje Didriksen, Ms Giorgia Mondino, Ms Aud I. Spjelkavik, SINTEF (NO)
- Funding organizations:
  - Research council of Norway (through NANOMAT, CLIMIT, KOSK, RENERGI and PETROMAX programs)
  - EU FP6 and FP7 (MOFCAT and NANOMOF through NMP program, DECARBIT through the ENERGY program)
  - The Norwegian Embassy in Delhi

For your kind attention !



Electrical Swing Adsorption for CO_2 Capture

Alan Chaffee* and Paul Webley+
*School of Chemistry, Monash University
+Dept Chemical & Biomolecular Engineering, Uni of Melbourne

Electrical Swing Adsorption for CO_2 Capture

Advanced Materials and Electric Swing Adsorption Process for CO_2 Capture

EU-Australian Cooperation, 7th Framework Project, ENERGY

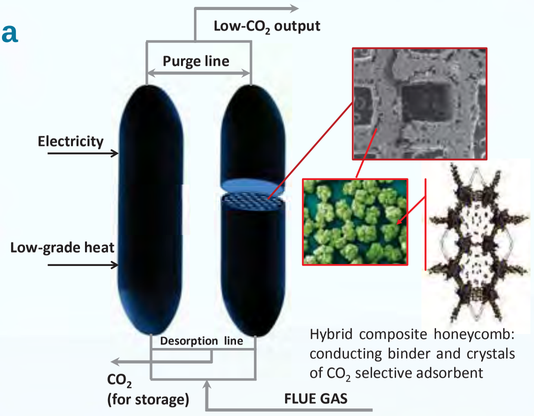
MATESA partners

- ❑ The consortium is formed by: 5 universities (2 Australian), 2 R&D institutes, 3 SMEs and 2 large industries.

- SINTEF, Norway
- University of Belgrade, Servia
- Fraunhofer Institute, Germany
- University of Torino, Italy
- Corning SAS, France
- Linde Engineering, Germany
- Politecnico di Milano, Italy
- Cycleco, France
- Biokol, Sweden
- Process Systems Enterprise, United Kingdom
- University of Melbourne
- Monash University, Australia

web-page:
www.sintef.no/projectweb/MATESA

The main idea



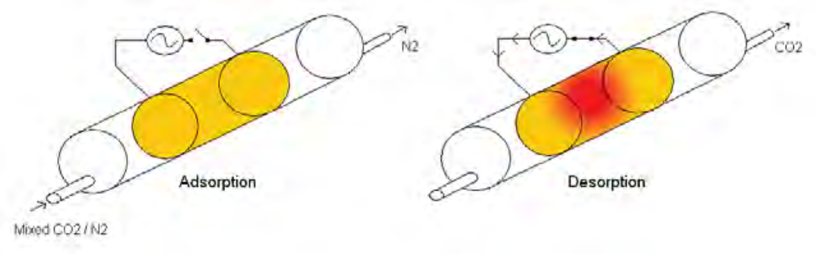
Hybrid composite honeycomb: conducting binder and crystals of CO_2 selective adsorbent

- ❑ Create a honeycomb material able to conduct electricity.
- ❑ Embed within this a material able to selectively adsorb CO_2.
- ❑ Use this material in an innovative Electric Swing Adsorption (ESA) process.
- ❑ Evaluate the integration of the ESA process into the power plant.
- ❑ Make a full life cycle assessment of the entire capture process.

ESA Concept

Electrical Swing Adsorption

- **A controlled (efficient), rapid, low cost regeneration process for conductive monolithic adsorbents**



<u>De</u>sorption is the key to an efficient <u>ad</u>sorption process

---

Objectives of Australian Study

Develop active carbon monoliths from brown coal

Embed this with a highly CO_2 selective adsorbent material

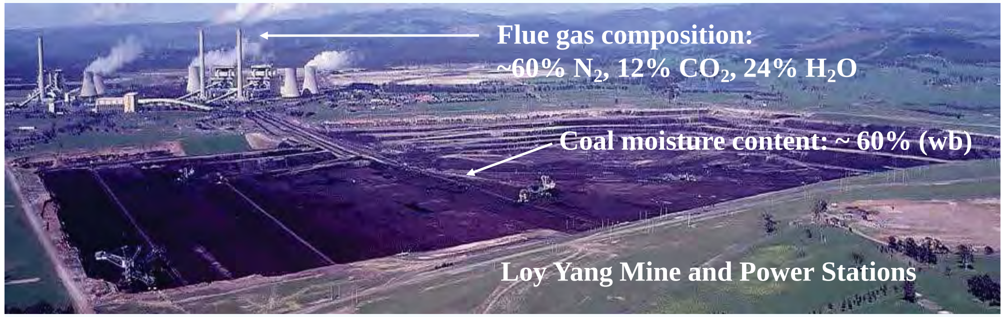
Evaluate performance at bench scale

Process modeling

Life cycle analysis

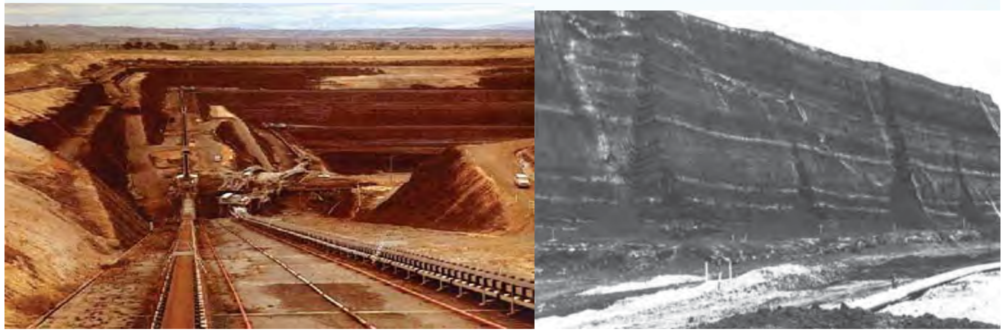
Victorian brown coal is a good carbon precursor
- it is very cheap
- it has very low inorganic content

Latrobe Valley Coal Fields


Flue gas composition:
~60% N_2, 12% CO_2, 24% H_2O

Coal moisture content: ~ 60% (wb)

Loy Yang Mine and Power Stations

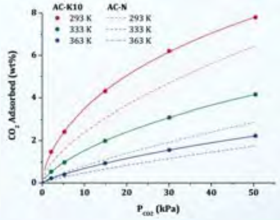


Heterogeneity of Victorian Brown Coal (VBC)

Active carbon monoliths from brown coal

Known features from work to date:

- Brown coal monoliths can be made.
- Active carbon from powdered brown coal has good reversible CO_2 capacity.
- Functionalised carbon monoliths improve CO_2 capacity.
- Active carbon monoliths prepared from polymers work for ESA.



Dewatering by Densification

Strength Development on Drying

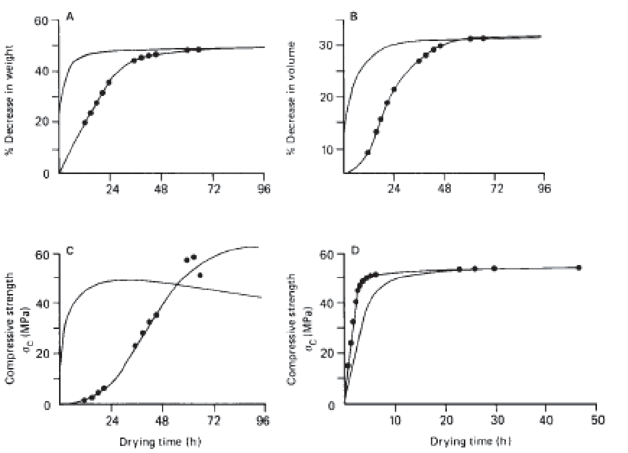
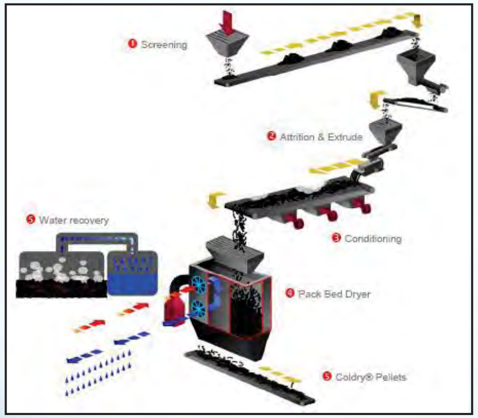


Fig. 3. Drying behaviour of densified brown coals in still (●-●) and in forced draught (—) conditions. A, B and C = Morwell coal (Narracan bore) containing 5% magnesite. D = Maddingley coal. (5 h kneading in each case, 55% relative humidity, 20 °C; forced draught of 0.5 m/s). D — = 10 mm pellets; ●-● = 3 mm pellets, both under forced draught conditions.

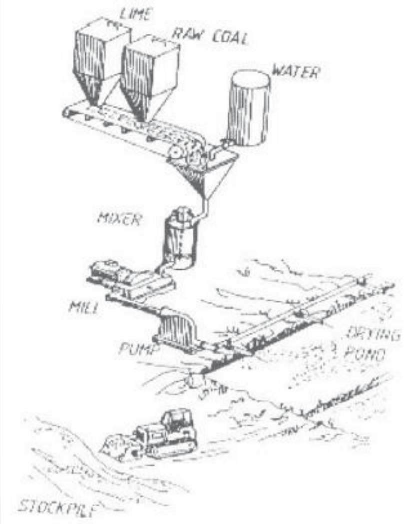
Fuel Proc Tech 21, 208 (1989)

Solar dried coal

Coldry® Process*



* Environmental Coal Technologies Ltd
See: www.ectltd.com.au/coldry/the-coldry-process



Allardice et al, Ch 3, in: Advances in the Science of Victorian Brown Coal, Ed C-Z Li, Elsevier, 2004

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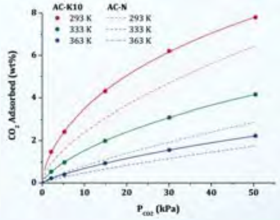
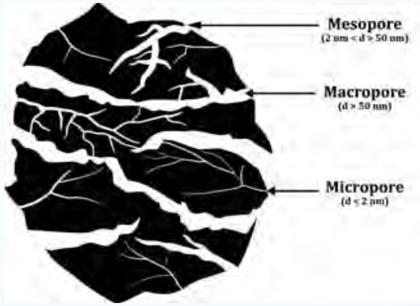


Active carbon powders from brown coal

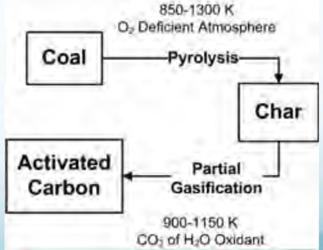
Activated Carbons (ACs)

- High Surface Area & Porosity (wide PSD)
- Water tolerant (usually)
- Precursors inexpensive & readily available
- Surface chemistry easy to tailor
- Adsorption of gases on ACs is non-selective



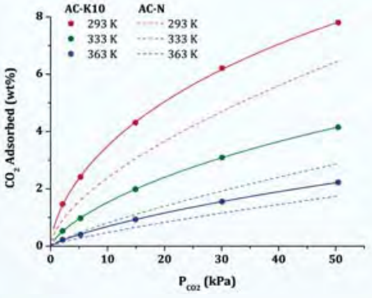
AC Production

- Prepared by one of two activation methods:
  - **Physical Activation:** Pyrolysis, followed by partial gasification.
    1. **Pyrolysis** – Volatile Matter Removal
    2. **Partial Gasification** – Pore Development
  - **Chemical Activation:** Uses catalysts in addition to pyrolysis & partial gasification.

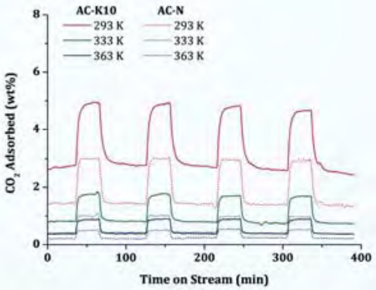


CO_2 adsorption of brown coal derived carbon

Adsorption Isotherm



Partial Pressure Swing (0.15 – 0.05 bar)



Sample Name	Yield (wt%)	Surface Area (m²/g)		Pore Volume (cm³/g)		True Density (g/cm³)
		S_{DR}	S_{BET}	V_{micro}	V_{meso}	
AC-N	-	794.3	673.9	0.276	0.094	1.48
VBC	-	179.1	-	0.001	-	1.40
AC-K10	51.2	859.7	-	0.229	-	1.38

LA Ciddor et al, Proceedings of the Int Conf on Coal Science & Technology 2013, State College PA, Sept 29-Oct 3, 2013, 8pp.

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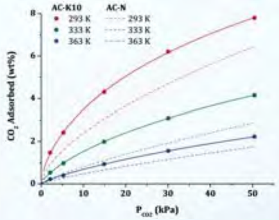
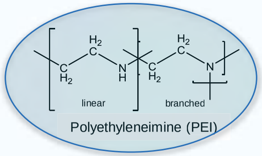
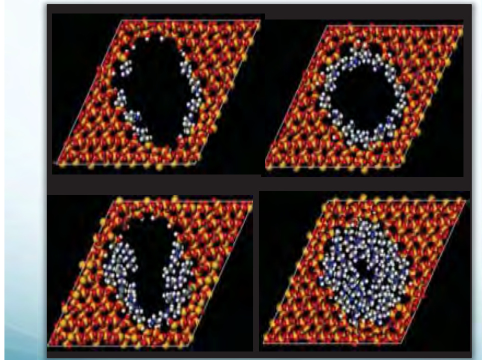
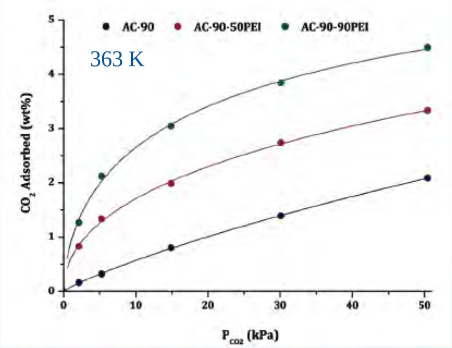


CO$_2$ adsorption on functionalised VBC carbons







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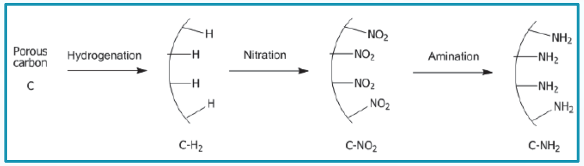
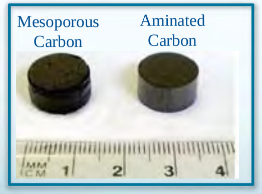
CO$_2$ adsorption on synthetic mesoporous carbons

Mesoporous Carbon Synthesis

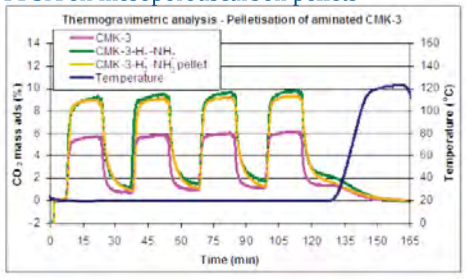
Amination procedure



Pellet products



PPSA on mesoporouscarbon pellets



S Delaney, PhD Thesis, 2009, Electrically Regenerable Carbon Adsorbents for CO$_2$ Capture

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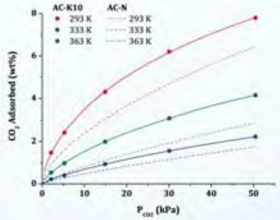
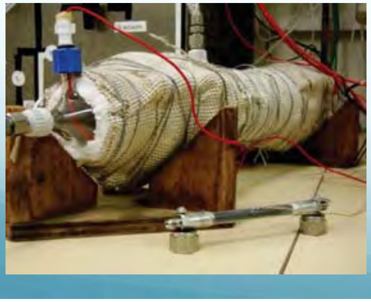


ESA Test Facilities – Mk 1



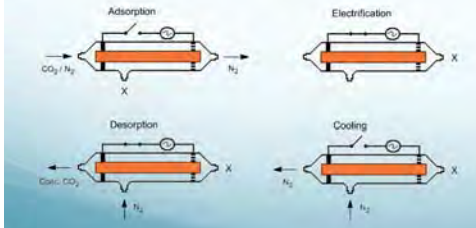
Electrically heated reactor units

- Monoliths acquired from Mast Carbon Pty Ltd, UK
- Thermocouple reading on external surface of monolith
- Sealed in glass vessel or with heat shrink wrap

ESA Investigation

Protocol

- Adsorption
  - Feed gas (15% CO_2 in N_2) at 80ml/min, ‘breakthrough’ at 35-40ml of CO_2 adsorbed
- Electrical Stimulation
  - Power requirements (10W)
  - ~65 sec to heat to 105ºC (~5V, 2A)
- Desorption
  - Thermal evolution
  - Purge flow (4 – 8 ml/min), varied durations
- Cooling
  - High purge (cool) flow rates



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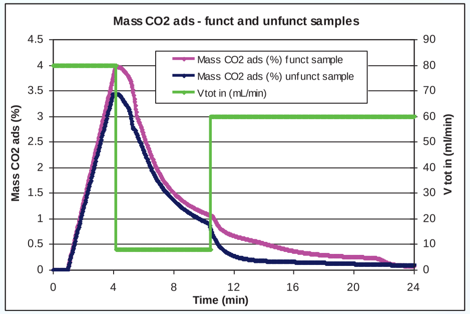

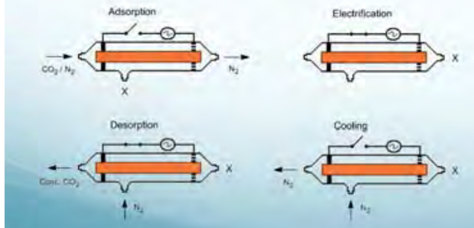

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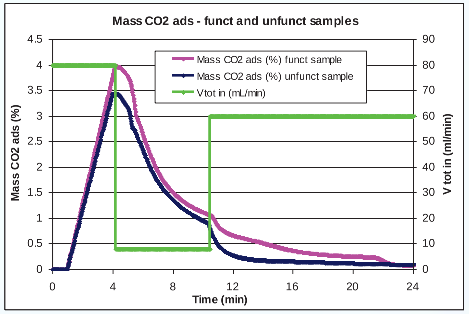
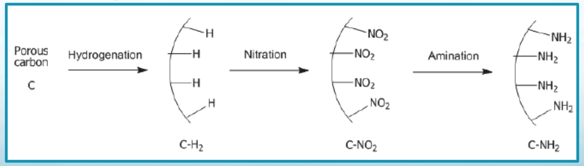


Amination procedure



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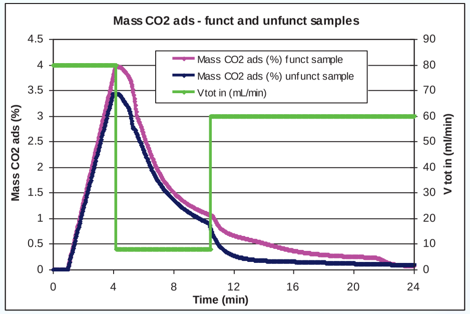
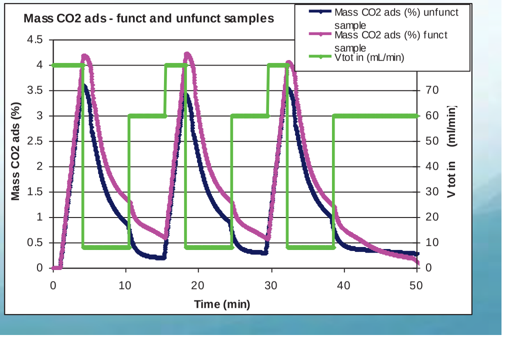


Functionalisation

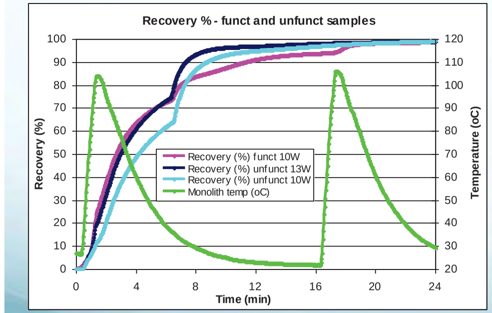
- Improved CO_2 adsorption capacity
- Slower breakthrough time
- Working capacity slightly increased for functionalised sample

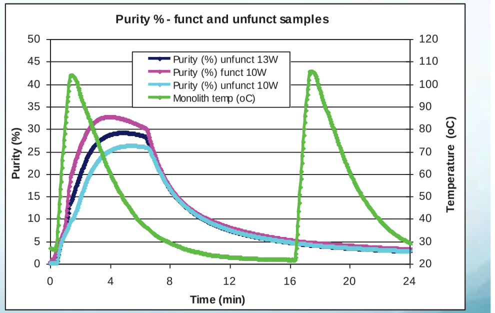


ESA test unit - Effect of functionalisation

Purity and Recovery of Desorbed CO_2

- Increased rate of recovery for functionalised sample.
- Electrical stimulation higher (~30%) to effect same temp increase
  - ~30% increase in resistivity for functionalised sample





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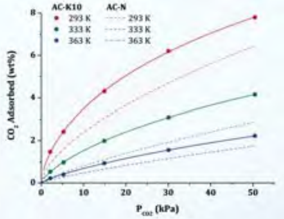
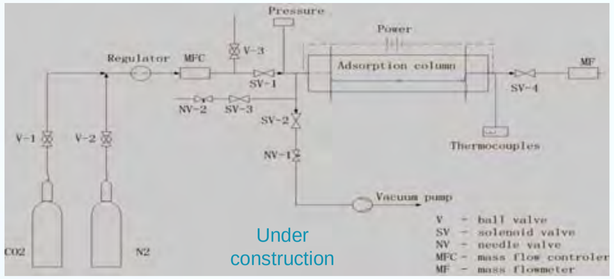


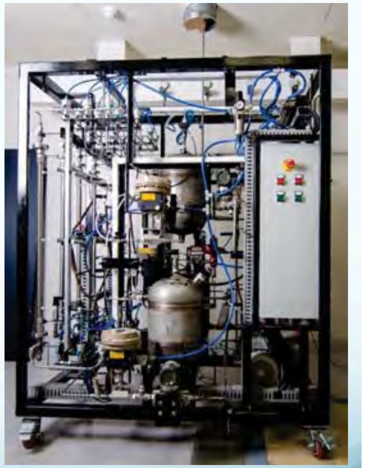
ESA Equipment – Mk 2 and 3

Bench scale testing

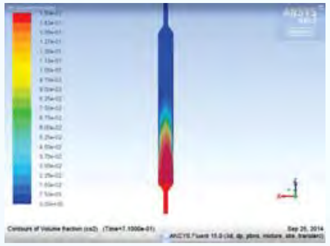
4-bed testing



Under construction

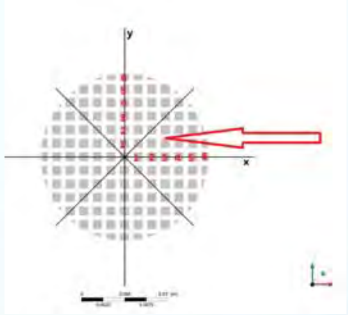


Computational Fluid Dynamics



Dimension of Monolith

Diameter: 20mm
Length: 200mm
Wall: 0.525mm
Channel: 1.05mm
CPSI: 286
Open area: 42%

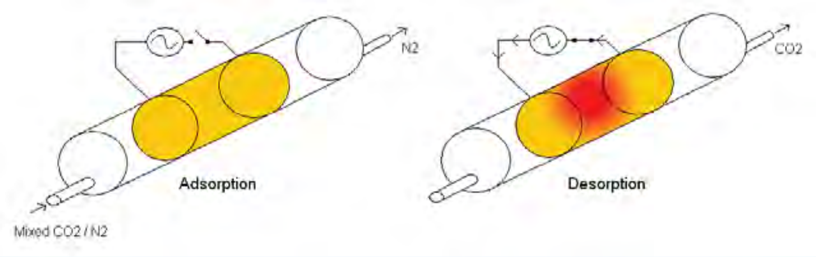


Due to symmetry, need to study the velocity of just 1/8 of monolith

ESA Concept

Electrical Swing Adsorption

- **A controlled (efficient), rapid, low cost regeneration process for conductive monolithic adsorbents**



Desorption is the key to an efficient adsorption process

Thank you!

Acknowledgement

The authors wish to acknowledge financial assistance provided by **Brown Coal Innovation Australia Limited**,

a private member-based company with funding contracts through

Australian National Low Emissions Coal Research and Development Ltd (ANLEC R&D)

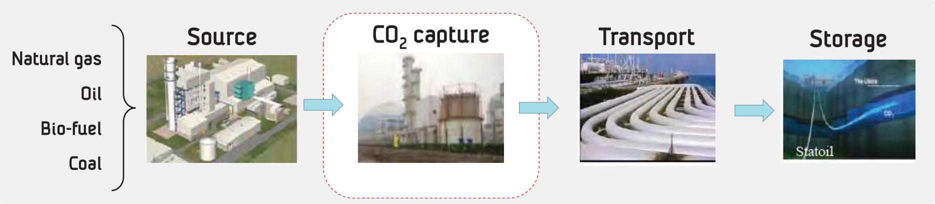
and the **Victorian State Government**.

HiPerCap - High Performance Capture

FP7 Grant agreement n° 608555

Panel discussions

Melbourne, Australia 25-26 March 2015



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1. Prospects for absorption/adsorption technologies

- What is the best way of up-scaling absorption and adsorption based technologies?
- What are the major challenges for both absorption and adsorption?
- Any challenges related to emission of harmful amines and other unwanted components?
- Do the absortion and adsorption technologies have any advantages regarding operational flexibility?
- Differences and similarities between Europe and Australia and what can we learn from each other?
- Are the absorption based techncologies completely developed?
- How much can you expect to reduce the heat requirement?
- Is CO_2 purity an issue for all technologies adressed?

---

2. Industrial applications of membranes and methodologies for technology evaluations

Membranes

- What is the best way of up-scaling membrane based technologies and can they really offer an improvement in plant footprint compared to amine scrubbing?
- What indication do we currently have that membranes can offer improved energy performance in comparison to amine scrubbing?
- What are the major challenges for membrane based capture technologies?
- Membranes in Europe vs. Australia

Technology Benchmarking

- How do we account for operability and flexibility?
- Is CO_2 purity an issue for all technologies adressed (absorption/adsorption/membranes)
- Are there any added environmental benefits of the new technologies addressed in HiPerCap?
- Do any of the considered technologies provide reduction in CAPEX?

CCS in Europe – Current Status and Future Prospects

Adam Al-Azki *E.ON Technologies (Ratcliffe) Ltd.*
26 March 2015 – Melbourne, Australia

Overview

- What has been the motivation for developing CCS technologies and projects within Europe?
- What has been the outcome of European initiatives?
- Why hasn't this led to large scale demonstration?
- …and what does the future hold for CCS in Europe

The E.ON Group: An overview

- We stand for **cleaner** & **better** energy and are a global, specialized provider of energy solutions.
- E.ON SE is one of Europe's largest energy companies with over 62,000 employees and a presence throughout Europe, North America, Russia, Brazil and Turkey.
- Global Business Units Include:
  - Exploration & Production
  - Generation
  - E.ON Technologies
  - Global Commodities
  - Renewables

As an owner and operator of coal and gas fired power plant – CCS is of direct relevance to E.ON

European Motivation – Recognising a requirement to reduce greenhouse gas (GHG) emissions

First Kyoto Period (2008-2012): Under the Kyoto Protocol the EU-15 committed to GHG emissions **reduction of 8%** below 1990 levels – 16% was achieved

Second Kyoto Period (2013-2020): Further emission reductions are required over the second Kyoto period – **20% reduction** – on track to achieve (22-27% expected)

EU2020 Growth Strategy: Emission reduction targets to achieve a 20% reduction of GHG emissions compared to 1990 levels – EU offers a conditional 30% reduction

2030 Climate and Energy Policy: 40% reduction in GHG emissions by 2030 (compared to 1990 levels)

2050 vision: Leaders have endorsed an emissions reduction target of 80-95% by 2050
This requires decarbonisation of Europe's power sector (93-99% GHG reduction)

European Motivation – Implementing CCS

Tools & Policy:
- EU Emissions Trading Scheme
- CCS Directive
- CCS Readiness

EU Funded Research:
Around 40 projects since 1998 (FP3 to FP7)

Demonstration:
- New Entrants Reserve
- European Energy Programme for Recovery

Initiatives in progressing the development of CCS in Europe

National initiatives (UK):
- Carbon price floor
- Emissions performance standard (450 g CO_2/kWh)

National initiatives (UK):
UK CCS Competition (phases 1 and 2) **<u>£1 bn for demos</u>**

National initiatives (Norway):
- Norwegian CO_2 Tax
- Gassnova established
- Gas plants CCS ready

Initiatives can work!

More than 11 million tonnes of CO_2 stored at Sleipner

e·on

European CCS Demonstrations on Power Plant

EEPR (2009):
Janschwalde (DE)
Porto-Tolle (IT)
ROAD (NL)
Belchatow (PL)
Compostilla (ES)
Don Valley (UK)

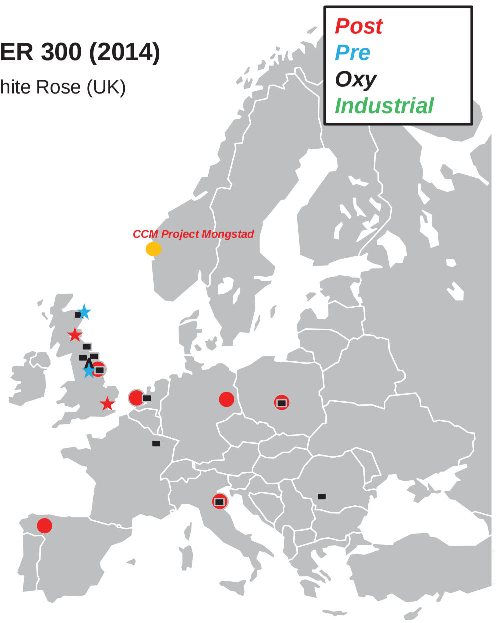
NER 300 (2012)
Don Valley (UK)
Belchatow (PL)
Green Hydrogen (NL)
Teeside CCS (UK)
UK Oxy CCS (UK)
C.Gen North Killingholme (UK)
Porto-Tolle (IT)
ULCOS-BF (FR)
Getica (RO)
Peterhead (UK)

NER 300 (2014)
White Rose (UK)

1st UK Competition
Longannet
Kingsnorth

2nd UK Competition
Peterhead
White Rose - Drax

- ● European Energy Programme for Recovery
- ■ New Entrants Reserve 300 (first call)
- ▲ New Entrants Reserve 300 (second call)
- ★ UK CCS Competition (1)
- ★ UK CCS Competition (2)



European CCS Demonstrations on Power Plant

EEPR (2009):
ROAD (NL)

NER 300 (2012)

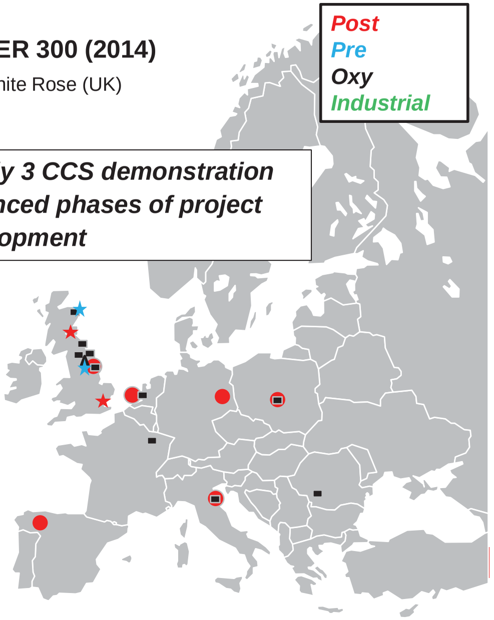
NER 300 (2014)
White Rose (UK)

***Situation in 2015:* Only 3 CCS demonstration projects in the advanced phases of project development**

1st UK Competition

2nd UK Competition
Peterhead
White Rose - Drax

- ● European Energy Programme for Recovery
- ■ New Entrants Reserve 300 (first call)
- ▲ New Entrants Reserve 300 (second call)
- ★ UK CCS Competition (1)
- ★ UK CCS Competition (2)



Why are projects failing to progress?

<u>UK CCS Competition Phase 1</u>
- Changing the rules (Killingholme)
- Economic downturn (Kingsnorth)
- Failure to agree on overall project costs and contingencies (Longannet)

<u>EEPR Funded Projects</u>
- Environmental permitting and public acceptance *Porto Tolle* and *Janschwalde*
- Funding gaps and CO_2 tax *Compostilla, Porto Tolle* and *Belchatow*

E.ON's 360 MW Killingholme Pre-Combustion CCS Project (cancelled 2007)

<u>Lessons Learnt:</u>
- Pilot capture plants have traditionally not focussed on addressing emissions (permitting challenges)
- Two-phase flow in in pipelines and within injection wells will occur
- Considerable amount of time required to appraise storage sites (5-10 yrs)
- Modifying existing storage infrastructure (e.g. platforms) can be a challenge
- Local, regional and national government support is essential to address legal challenges

Status of the Current Demos (UK Competition)

Project: Peterhead CCS Project
Location: Aberdeenshire, Scotland
Partners: Shell UK Ltd, SSE Ltd.
Process: Retrofit (gas) post combustion capture
Scale: 1 Mtpa
Storage: Offshore depleted gas field (62 miles)
Status: FEED underway, FID expected Q4 2015

Project: White Rose CCS Project
Location: North Yorkshire, England
Partners: Alstom, Drax, BOC
Process: New Build (coal) oxyfuel combustion
Scale: 2 Mtpa
Storage: Offshore saline formation (102 miles)
Status: FEED underway, FID expected Q4 2015

Secured NER300 Funding

No progress expected before 2015 UK general elections

Status of the Current Demos (EEPR)

EEPR + €150 million Dutch gov't funding

Project: Rotterdam Opslag en Afvang Demonstratieproject **(ROAD)** CCS Project
Location: Rotterdam, Netherlands
Partners: E.ON, GDF Suez
Process: Retrofit (coal) post combustion, Fluor EFG+
Scale: 1.1 Mtpa
Storage: Offshore depleted gas field (15.5 miles)
Status: FEED + flue gas tie-ins completed. Positive FID is dependent on closing funding gap

Project: Don Valley CCS
Location: South Yorkshire, England
Partners: 2Co Energy, Samsung, BOC
Process: Pre-combustion (coal), Rectisol
Scale: 5 Mtpa
Storage: Offshore saline formation (102 miles)
Status: Negotiations in 2014 to sell the project

Not likely to progress further

European Pilot Plants

Development across the innovation chain has led to the advancement of first generation systems to a point at which the technology is ready for demonstration.

This is a result of:

- R&D driven by EU or government funded initiatives
- Partnerships between utilities and technology suppliers

Research Scale:
CATO (NE)
Tiller (NO)
E.ON Oxyfuel CTF (UK)
MTU

Large Generic:

Heilbronn (post)
Brindisi (post)
Esbjerg (post)
PACT (post)
Renfrew (oxy)
Schwarze Pumpe (oxy)
Buggenum (pre)
Puertollano (pre)

Partnerships
Post-CC:
Staudinger (E.ON/Siemens)
Karlshamn (E.ON/Alstom CAP)
Wilhelmshaven (E.ON/Fluor)
Niederaussen (RWE/Linde,BASF)
Ferrybridge (SSE/Doosan, HTC)
Le Havre (EDF/Alstom AA)
Aberthaw (RWE/Cansolv)
TC Mongstad (Alstom CAP/Aker)

Oxyfuel:
Compostilla (ENDESA)
Lacq (Total)

Pre-CC:
Puertollano (ELCOGAS)
Buggenum (Nuon/Vattenfall)

European Pilot Plants in Operation

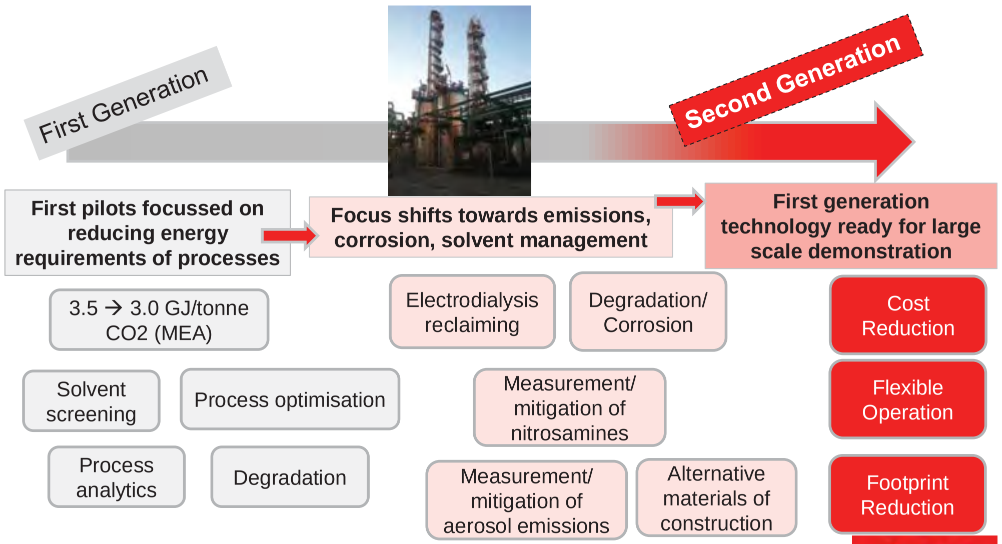
- Consists of one amine (Aker) and one chilled ammonia plant (Alstom) – 100 ktCO_2/year
- CHP and refinery cracker gas source (3-13 % CO_2)
- 30 wt.% and 40 wt.% MEA campaigns completed
- Aker Advanced Amine and Alstom CAP campaigns completed in 2014.
- Emission reduction systems tested
- Cansolv currently testing on amine unit (CHP gas)

TCM - Norway

E.ON/Fluor - Wilhelmshaven

- 70 tpd post-combustion capture pilot
- Based on Fluor's Econamine FG+ process
- 19400 m^3/h of flue gas treated from 824 MWe coal-fired unit
- Process includes intercooling and lean vapour compression
- Gained more than 5000 hours of operation
- Investigated impact of dust and SO_3 on aerosol emissions
- Evaluation of energy saving systems is underway

European Pilot Plants – Post Combustion Experience



First pilots focussed on reducing energy requirements of processes

- 3.5 → 3.0 GJ/tonne CO2 (MEA)
- Solvent screening
- Process optimisation
- Process analytics
- Degradation

Focus shifts towards emissions, corrosion, solvent management

- Electrodialysis reclaiming
- Degradation/ Corrosion
- Measurement/ mitigation of nitrosamines
- Measurement/ mitigation of aerosol emissions
- Alternative materials of construction

First generation technology ready for large scale demonstration

- Cost Reduction
- Flexible Operation
- Footprint Reduction

In summary

- Europe is aiming to decarbonise its power sector – CCS provides a means of achieving this whilst maintain economic growth and energy security.
- Public acceptance, lack of decisive government action, competing incentives and the collapse of the CO_2 price have impeded the demonstration of CCS in Europe.
- Market based mechanisms such as the Emissions Trading Scheme are best suited to achieving emission reductions at least cost – but only if they currently do not work.
- Biggest hope of demonstrating full chain CCS in Europe currently lies with the UK CCS Competition
- Large pilot plant activities in Europe are reducing– 1st generation technologies are ready for deployment.
  – but what about the next generation of pilots?

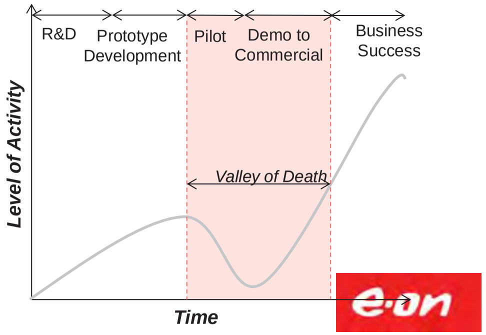
Future Prospects

- Revision of the CCS Directive within the context of 2030 and 2050 targets
- Improving the Emissions Trading Scheme
- Reconsidering a European Emissions Performance Standard
- Creation of NER300 successor, NER400, has been agreed
- National subsidies, e.g. Contracts for Differences – Feed in Tariffs

CCS is formally included in the UK Energy Act and is eligible for CfD payments anticipates 5 - 13 GW by 2030.

Fruition of the current European demos may signify that CCS in Europe is emerging from the "Valley of Death"…

…however, the correct regulatory environment and framework is required to ensure this 'rise' continues.



Thank You

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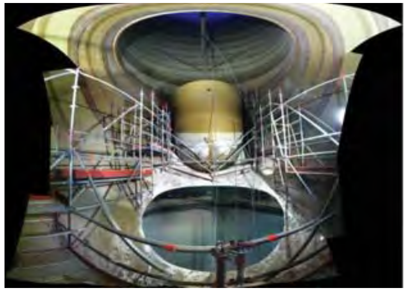
ROAD CCS: Host Power Plant (E.ON MPP3)

Output: 1070 Mwe

Efficiency: 46%

Operational: 2015

Capture Ready



Flue-gas interface construction work has already been completed

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Connecting CCS and CCUS

Rotterdam industrial area has set a target to achieve a 50% reduction in CO2 emissions by 2025 (compared to 1990).

CCS expected to contribute 60-70% of this reduction

Proposed network will link various sources of CO_2 such as the ROAD capture plant to CO_2 sinks (e.g. greenhouses)

ROAD: CO2 Storage

- Depleted natural gas field (P18-4) will be used for CO2 storage (350 → 20 bar)
- Reservoir is 3.5 km below the sea bed
- Field is 20 km offshore
- 1.1 million tonnes per year will be stored
- Capacity is 8 million tonnes of CO2 (5 years)
- Applied for storage permit in 2010 – awarded in 2013
- Ready for CO2 injection

WP3
Membrane Based Technologies

Marc Pfister & May-Britt Hägg

PhD-student CNRS Professsor NTNU

Partners:

- NTNU Norway (WP-Leader)
- Sintef M&C Norway
- TNO. The Netherlands
- TIPS, Russia
- CNRS, France
- EDF, France1
- CSIRO, Australia

Membrane based technologies

Task 3.1 Hybrid membrane development (NTNU, SINTEF, TNO) - OBJECTIVES

- Develop high flux mixed matrix membrane based on incorporation of nanoparticles in polymer.
  - ➢ Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100.
  - ➢ Membrane fabrication and study on transport phenomena.

Task 3.2 Supported ionic liquid membranes (SILM) (NTNU, TIPS) - OBJECTIVES

- Develop contained supported ionic liquid ceramic membranes (CILM)
  - ➢ Target: CO_2 permeance above 4 m^3(STP)/ m^2 h bar, selectivity CO_2/N_2 above 100
- Develop nanoporous polymer/ILs membranes
  - ➢ Target: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Task 3.3 Process modelling and simulation (CNRS, EDF, NTNU) - OBJECTIVES

- Develop membrane module simulation model for nanocomposite and SILM membranes.
  - ➢ Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

Task 3.1: Hybrid Membrane Development

Objectives

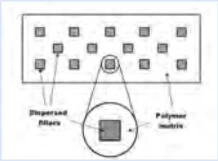
- Develop a high flux mixed matrix membrane based on incorporation of functionalized SiO-particles and nano TiO2-particles in a polymer.
  - ➢ Target: CO_2 permeance of 2.5 m^3(STP)/ m^2 h bar selectivity CO_2/N_2 above 100.
  - ➢ Membrane fabrication and study on transport phenomena.

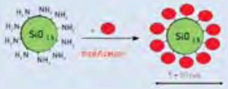
Research Activities

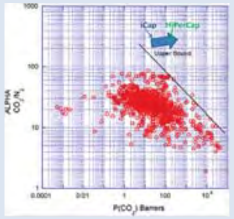
- Study of the transport mechanism and role of the nano-sized particles.
- Tailoring nanoparticles to tune the desired membrane properties such as selectivity and flux.
  - ➢ Nanosized particles prepared and characterized (SINTEF & TNO)
  - ➢ Hybrid membranes prepared and performance tested at NTNU
- Optimization in different iteration steps for the hybrid membrane.

Expected outcome

- Hybrid membranes with targeted performance
- Dedicated permeability model based on experimental flux data over a wide range of operating conditions







Task 3.1 Hybrid membrane development
Status on Work

1. **Study of the transport mechanism and role of the nano-sized particles: (report delivered)**
2. **The mechanism of gas transport in Facilitated Transport Membranes (FTM) most complicated** The total transport flux is the sum of both the Fickian diffusion and the carrier mediated diffusion.

Hence: The gas stream has to be humid for the facilitated transport to take place

→ CO_2 reacts and forms bicarbonate (fast reaction) and is released again as CO_2 on permeate side

→ The functionalized SiO-particles (HAPS) must not be protonised in order to promote facilitated transport (hence pH must be high)

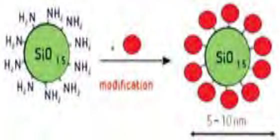
3. Two types of hybrid membranes will be tested:

HAPS embedded in PVA (facilitated transport)

TiO2 nanoparticles in PVA (Maxwell adapted transport)

(PVA is hydrophilic by nature and has good film forming properties)

$$J_A = -D_A \frac{dC_A}{dx} = \frac{D_A}{dx}(C_{A,f} - C_{A,p}) + \frac{D_{AC}}{dx}(C_{AC,f} - C_{AC,p})$$

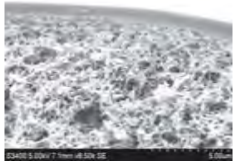


HAPS Nanoparticles

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2H^+ + CO_3^{2-}$$

$$H_2CO_3^- + NH_2 - R + H_2O \Leftrightarrow R - NH_3^+ HCO_3 + OH^-$$

$$R - NH_3^+ HCO_3 \rightarrow R - NH_2 + H_2O$$



SEM: 2%PVA on PSF Membrane support

Task 3.1 Hybrid Membrane Development
Status on Work

At NTNU-Sintef: Facilitated transport : Initial focus is on reproducing good results obtained

- New PVA-HAPS-1 membrane samples are manufactured
  - ➢ PPO-supported PVA/HAPS asymmetric membrane
  - ➢ PSf-supported PVA/HAPS asymmetric membrane

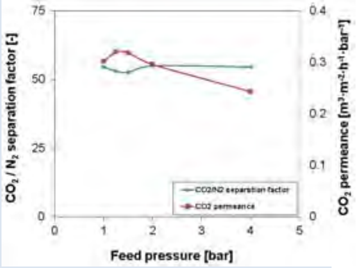
  (PPO = Hollow fibers; PSf = flat sheets)

Results to date

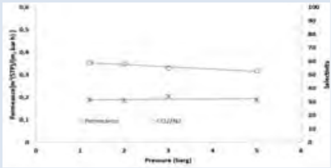
- First permeance measurements using PPO HF support, indicated CO_2 no success in facilitated transport

Conclusion

- The various parameters and variables which may influence the preparation of these membranes containing the functionalized nanoparticles are currently being systematically investigated
- Aim is to establish a reproducible manufacturing, and prepare a somewhat larger module for flux evaluation providing task 3.3 and WP4 with the required input



Performance of PVA-HAPS on PPO



Performance of 2% PVA Membrane on PSf

Task 3.1: Hybrid Membrane Development
Status on Work

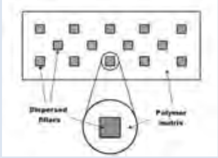
Ongoing Research Activities at TNO

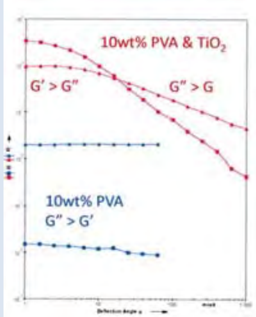
- Synthesis of Nano-TiO2 particles seams successful (first indication

  d < 20 nm)
- Well soluble/dispersible in water
- Study on interaction between PVA and nano-TiO2 to indicates physical network is formed (see figure). More solid-like behaviour at low deformation and more liquid-like behaviour at high deformation.
- Factors affecting interaction under study.

Further:

- Nanoparticles will be sent to NTNU to be prepared as hybrid membranes; embedded in PVA on PSf flat sheet support
- Performance will be measured with and without humid gas





Task 3.2 Ionic Liquid Membranes

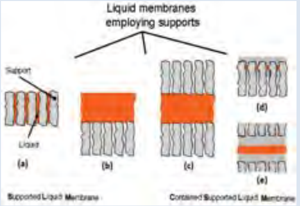
Objectives

- Develop contained supported ionic liquid membranes (CILM)
  - ➢ Target: CO_2 permeance above 4 m³(STP)/ m² h bar, selectivity CO_2/N_2 above 100
- Develop nanoporous polymer/ILs membranes
  - ➢ Target: CO_2 permeance 12-15 m³(STP)/ m² h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Research activities

- Selection, synthesis & evaluation of ILs for CO_2 facilitated transport membranes (NTNU).
- Selection and synthesis of high free volume polymers and advanced porous ceramic membranes (TIPS, NTNU).
- SILMs preparation, with focus on polymeric thin film composite support (TIPS).
- SILMs preparation, with focus on ceramic supports (NTNU).
- Separation performance testing (NTNU).

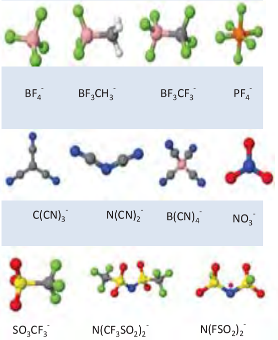
Type of SLM membranes



Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – screening; OK ☺

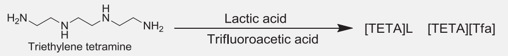
ILs	T_d °C	Types of absoption	CO_2 absorption capcity		Conditions bar/°C
			mol CO_2/IL	g CO_2/g IL	
[bmim][PF_6]	622.15	physisorption	0.295	0.0459	15.79/60
[C_8mim][PF_6]	647.15	physisorption	0.330	0.0428	17.38/60
[bmim][NO_3]	243	physisorption	0.224	0.0492	15.61/60
[bmim][Tf_2N]		physisorption	0.213	0.0224	13.64/60
[TETA]L	——	chemisorption	0.944	0.176	/110
[aP_{4443}][Ala]-SiO_2	283	chemisorption	~1.0	0.126	/25
[aP_{4443}][Gly]-SiO_2	281	chemisorption	~1.0	0.132	/25
[P_{66614}][Im]	252	chemisorption	1.0	0.0799	/23
[Li(DOBA)][Tf_2N]	319	chemisorption	0.71	0.072	/100

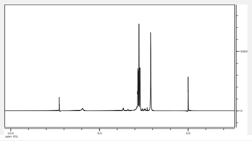
Common anions in ILs

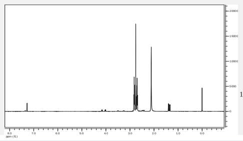


Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – synthesis and charact.; OK ☺

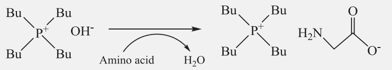
- **Polyamine-based ILs**



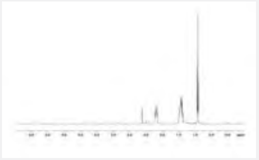

¹HNMR of [TETA]Tfa

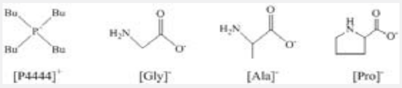

¹HNMR of [TETA]L

- **Amino acid ILs**



P4444[Gly]


¹HNMR of P444[Gly]



Structures of the cation and anions of AAILs

Task3.2 Ionic Liquid Membranes
Status on Work at NTNU – evaluation of synthesized IL; OK ☺

- **CO_2 sorption**

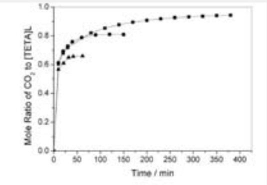
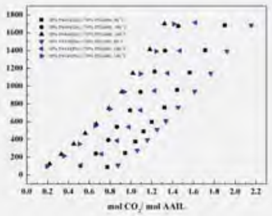
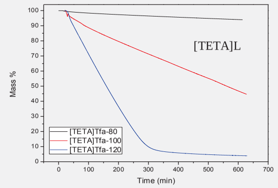


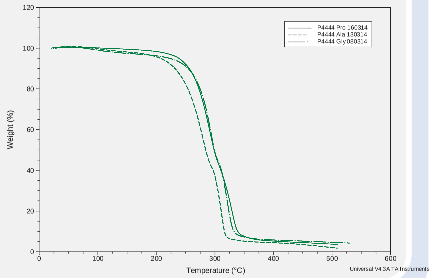
Fig. 2 Absorption of CO_2 in [TETA]L with pure CO_2 at different temperatures: ■, 110 °C; ●, 120 °C; ▲, 130 °C.

Ref: Ren, S., Y. Hou, et al. (2012). Rsc Advances **2**(6): 2504-2507



- **Thermal stability**





Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

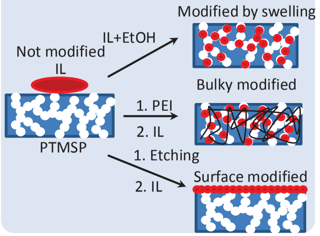
Objectives

- Develop nanoporous polymer/ILs membranes
  - ➢ Target: CO_2 permeance 12-15 m^3(STP)/ m^2 h bar, selectivity CO_2/ N_2 = 20-30
- Temperature stability >100°C.

Research activities at TIPS

- ✓ The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.
- ✓ Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity for gas pair CO_2/N_2 were selected.
- ✓ Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization by X-linked PEI and IL incorporation, surface hydrophilization by chemical etching and IL incorporation.

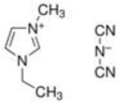
Methods of IL incorporation in PTMSP



Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS – the Concept

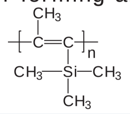
Imidazolium-based IL (EmimDCA)

- ✓ High CO_2/N_2 selectivity – 50
- ✓Low vapor pressure
- ✓ High thermal stability
- ✓ High tunability
- ✓ Relatively high CO_2 solubility



Nanoporous glassy polymers (PTMSP)

- ✓ Extra high CO_2 permeability coefficient 29000 Barrer
- ✓ High thermal stability
- ✓ High film-forming ability



$$\left[-C(CH_3)=C(Si(CH_3)_3)-\right]_n$$

Bara J. E. , et al. Guide to CO2 separations in imidazolium-based room-temperature ionic liquids *Ind. & Eng. Chem. Res.* 48.6 (2009): 2739-2751.

Robeson L. M. The upper bound revisited. J. Membr. Sci. 320.1 (2008): 390-400.

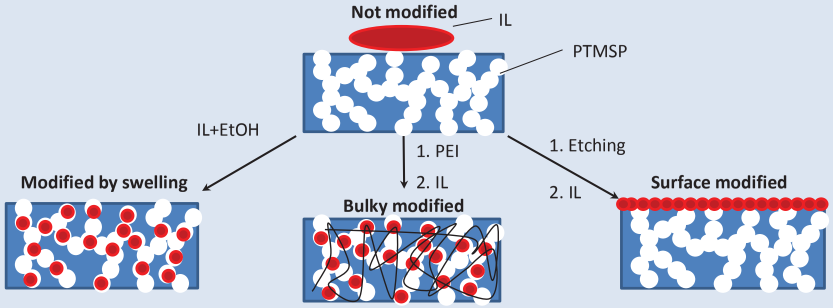
Hybrid PTMSP/EmimDCA membrane material with improved CO_2/N_2 selectivity

Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

Research activities at TIPS

- ✓ The two samples of high free volume glassy polymer - poly[1-trimethylsilyl-1-propyne] (PTMSP) were synthesized.
- ✓ Two ionic liquids (ILs) based on imidazolium cation with high solubility selectivity (50 – 80) for gas pair CO_2/N_2 were selected.
- ✓ Three methods of incorporation of selected ILs into the PTMSP dense membranes were developed: modification by swelling in IL/EtOH mixture, bulky hydrophilization and IL incorporation, surface hydrophilization and IL incorporation

Methods of membranes modification



Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

Gas permeation results

Membrane	CO_2 permeance, l(STP)/m²h bar	N_2 permeance, l(STP)/m²h bar	CO_2/N_2 selectivity	Membrane thickness, µm	Gas pressure, bar
PTMSP unmodified	2700	670	4	30	1
	2900	770	3.8		5
PTMSP / IL	6.8	0.43	16	42	1
	20.7	0.42	47		5
Bulky modified PTMSP + IL	110	8	14	25	1
	120	8	15		5
Surface modified PTMSP + IL	240	20	12	45	1
	240	18	13		5

Task3.2 Supported Ionic Liquid Membranes
Status on Work at TIPS

PTMSP modified by swelling in alcohol/IL

Membrane	Sorption, vol.%	CO_2 permeance, l(STP)/m²h bar	N_2 permeance, l(STP)/m²h bar	CO_2/N_2 selectivity
PTMSP unmodified	-	2900	770	3.8
PTMSP + (1% EmimDCA in EtOH)	0.2	2930	660	4.4
PTMSP + (5% EmimDCA in EtOH)	3.1	1060	230	4.6

- ➢ **Relatively low CO_2 permeance loss and gradual increase during incorporation of IL in PTMSP**
- ➢ **Optimization of swelling method is in progress**

Task 3.3 Process modelling and simulations

Task 3.3 Process modelling and simulation (NTNU, CNRS, EDF)

Objectives

- Develop membrane module simulation model for nanocomposite and SILM membranes.
  - ➢ Evaluate the energy requirement & membrane area for different set of operating conditions
- Develop concepts for utilizing the membranes in a post-combustion process.

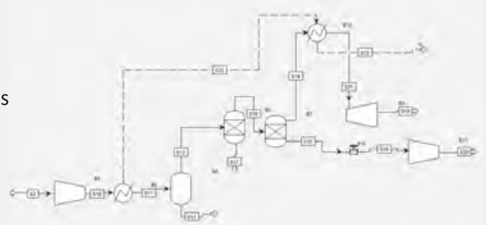
Research Activities

- Development of permeability models based on the experimental results obtained in tasks 3.1 and 3.2 :
  - ➢ Analysis of the mass transfer characteristics (constant or variable permeability, coupling phenomena, role of temperature)
  - ➢ Modelling of the mass transfer performances for the different compounds through a general permeability relationship.
- Parametric simulation study of the performances for the two types of membranes
  - ➢ Review of the different modelling approaches
  - ➢ Influence of feed mixture composition (i.e. CO2 content)
  - ➢ Parametric study for a target CO2 purity and capture ratio
  - ➢ Analysis of the energy (pressure ratio) / membrane area trade-off
- Modelling framework in a process simulation environment with energy integration aspects

Task 3.3 Process Modelling and simulations
Status on Work at CNRS

Objectives

- Develop membrane module simulation model for hybrid membranes.
  - Model mass transfer with a reaction diffusion mechanism
  - Enquire about possible disturbances of process modelling (temperature, water impact, competing reaction…)
  - Evaluate the impact of inlet conditions variations
- Develop concepts for utilizing the membranes in a post-combustion process (Aspen Plus software)

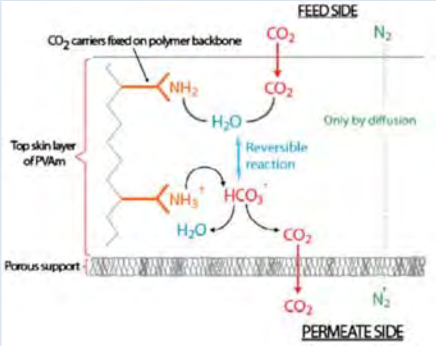


Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Two transport mechanisms:
  - Sorption diffusion for N2 compound
  - Reaction diffusion for CO2 compound
- Main reversible chemical reaction:

$$CO_2 + H_2O \overset{+NH_2}{\longleftrightarrow} HCO_3^- + H^+$$

- Water in the feed flow is a requirement
- Competing reactions between amine fixed sites and CO2 occur



Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Two Transport mechanisms but only one equation:

$$J_A = -D_A \frac{dC_A}{dx} = \boxed{\frac{D_A}{dx}(C_{A,f} - C_{A,p})} + \boxed{\frac{D_{AC}}{dx}(C_{AC,f} - C_{AC,p})}$$

🟥 Sorption diffusion mechanism

🟩 Reaction diffusion mechanism

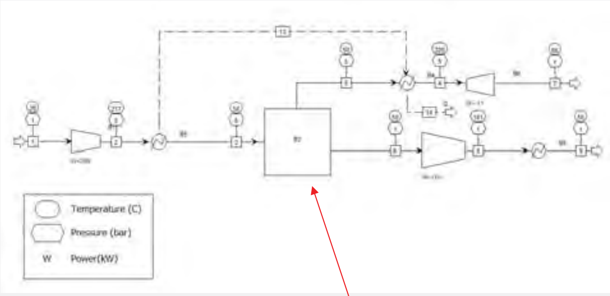
$$C_{AC,f} = \frac{KC_{A,f}C_T}{1 + KC_{Af}}$$

$$C_{AC,p} = \frac{KC_{A,p}C_T}{1 + KC_{A,p}}$$

- Important parameters :
  - K (equilibrium constant of the reaction) depends on temperature
  - C_T (Total carrier concentration) depends on nanoparticles volume fraction (5, 10, 25 wt%)
  - Carrier diffusion coefficient is considered as constant

Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Membranes in a post-combustion process:
  - Aspen Plus software



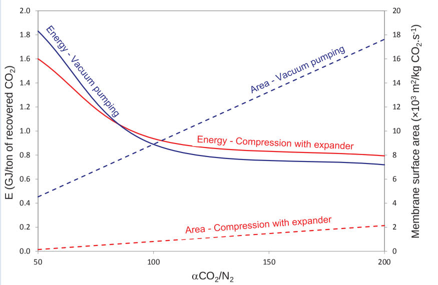
Retentate Flow

Permeate Flow

Membrane unit

Task 3.3 Process Modelling and simulations
Status on Work at CNRS

- Variation of the Input conditions:
  - Temperature
  - Pressure in the upside part of the membrane
  - Pressure in the downside part of the membrane
  - CO2 volume fraction in the feed flow
- Membrane area estimation
- Energy requirement evaluation (compressor, expender, vacuum pumping)
- Technical economical estimation (in collaboration with EDF)



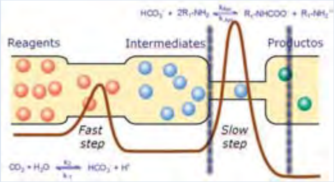
Task 3.3 Process Modeling and simulations
Status on Work at NTNU

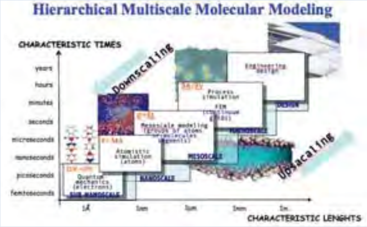
NTNU will contribute with:

- Details on the facilitated transport model for the functionalized nanocomposite hybrid membranes.
- Providing experimental data to check the model at given conditions
- Compare the simulation results with their own in-house model, and discuss the impact of inlet conditions variations

- Contribute in discussions with respect to utilizing the hybrid

membranes in a post-combustion process.





Membranes for CO_2 Capture

Sandra E. Kentish

The Peter Cook Centre for Carbon Capture & Storage Research

The Peter Cook Centre for Carbon Capture & Storage Research

Overview

- Mixed Matrix Membranes
- Membrane Gas Contactors
- Electrodialysis for Solvent Remediation
- Other Activities

The Peter Cook Centre for Carbon Capture & Storage Research

MIXED MATRIX MEMBRANES

The Peter Cook Centre for Carbon Capture & Storage Research

Mixed Matrix Membranes


Matrimid


Carbon A


Carbon B


Carbon C

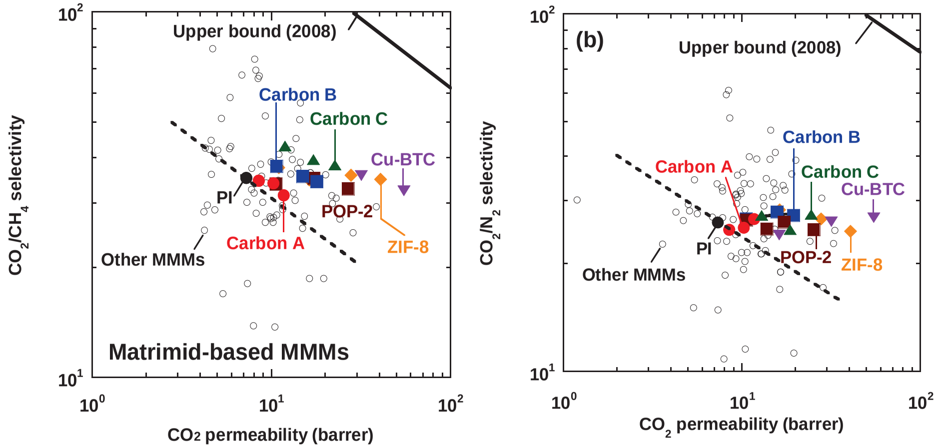

ZIF-8


Cu-BTC


PCN-2

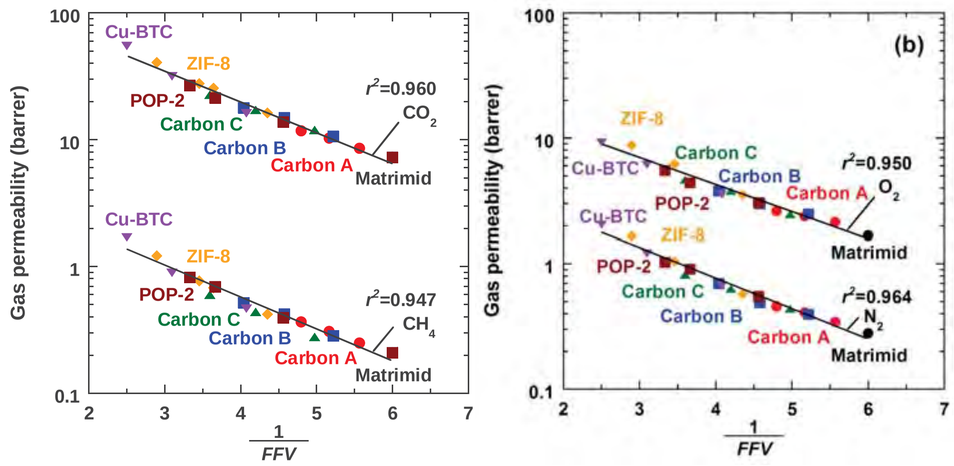

UiO-66

Mixed Matrix Membranes



Journal of Membrane Science, 482 (2015) 49-55

Mixed Matrix Membranes



$$Total\ FFV = FFV_{polymer}(\phi_{polymer}) + FFV_{filler}(\phi_{filler})$$

Journal of Membrane Science, 482 (2015) 49-55

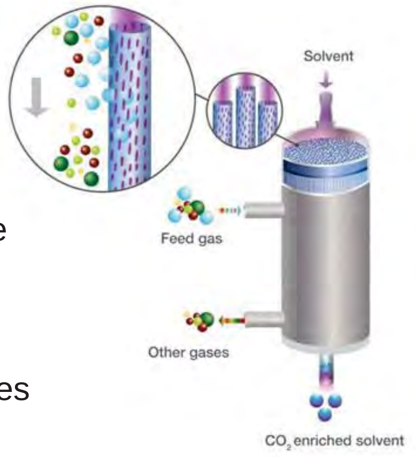
MEMBRANE GAS ABSORPTION

Gas-solvent Membrane Contactors

Take advantage of both membrane and solvent technology

Solvent – high selectivity for CO_2

Membrane – controlled flow regimes



The Peter Cook Centre for Carbon Capture & Storage Research

CO2CRC H3 Project

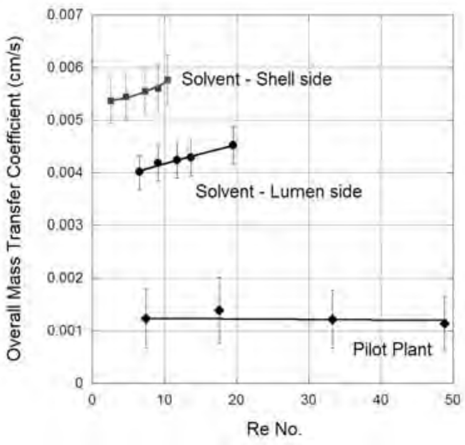
Post-combustion capture
15 tonne of CO_2 per annum
from flue gas

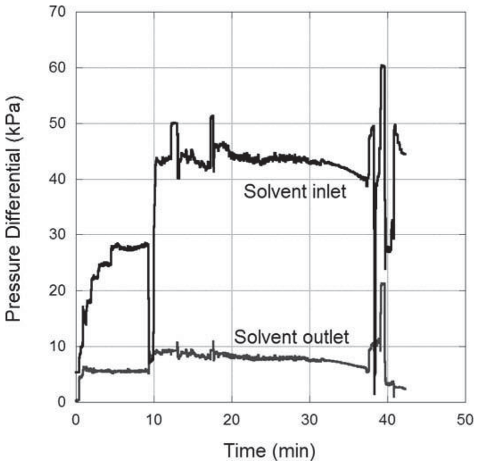
Pressure ~10 kPag
Temperature 50 ºC

Composition (mol%)	
CO_2	13.0
N_2	62.2
O_2	3.5
Water	20.5
Ar	0.8

The Peter Cook Centre for Carbon Capture & Storage Research

PTFE Contactor – PuraTreat Performance



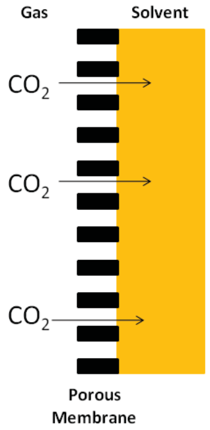


Separation Science and Technology, 49 (2014) 2449–2458

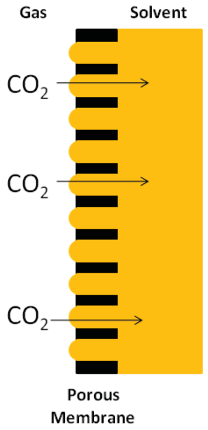
The Peter Cook Centre for Carbon Capture & Storage Research

Non-Porous Membrane Contactors

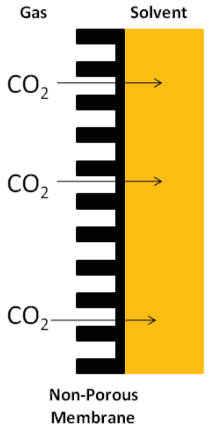
Gas filled Pores



Solvent filled Pores



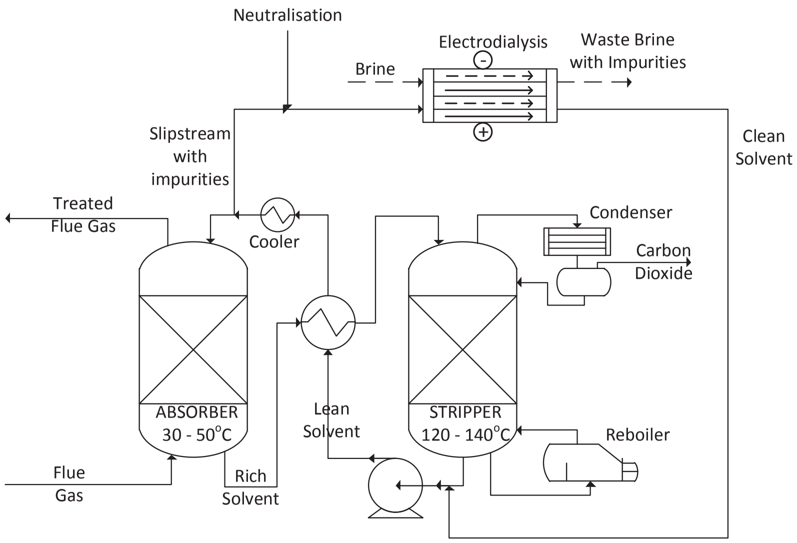
Non-Porous (Gas filled)



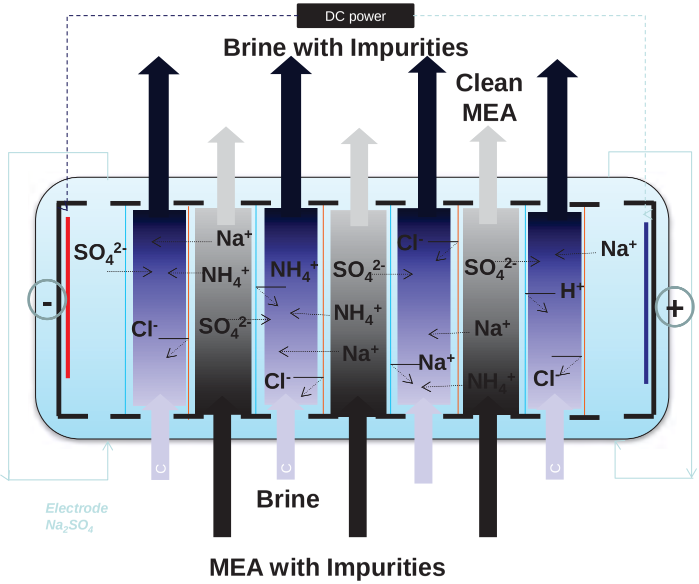
The Peter Cook Centre for Carbon Capture & Storage Research

ELECTRODIALYSIS

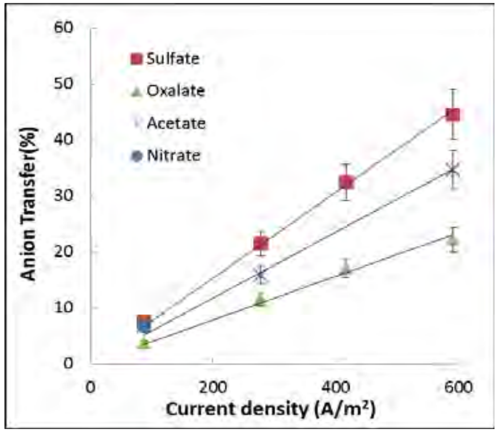
Solvent Remediation

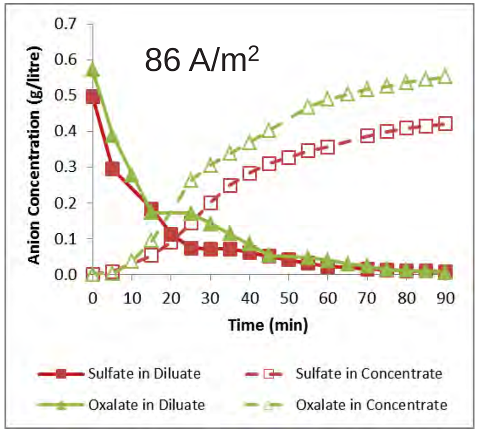


Electrodialysis Removes Charged Impurities

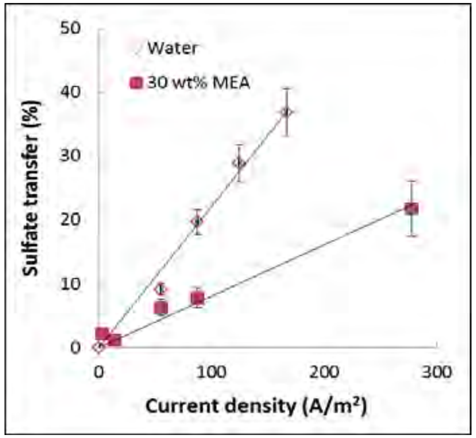


Stronger acids Transfer better when Current Density is High

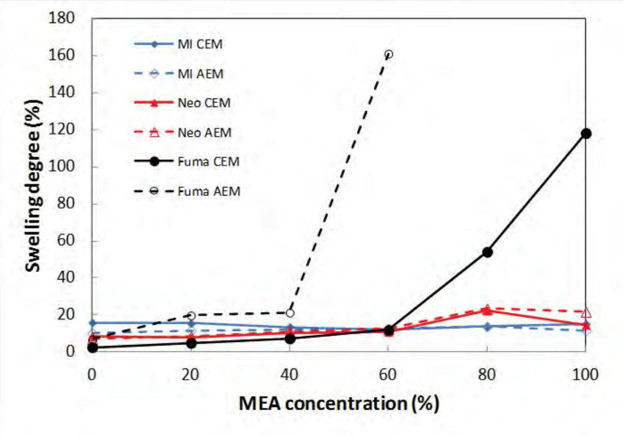




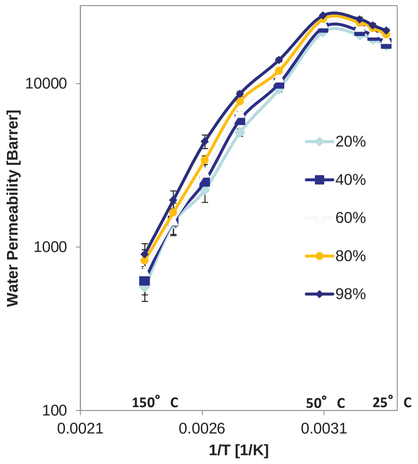
Performance falls in the MEA system



Some membranes fail in strong MEA concentrations



Membranes – Other Projects



- Impact of water and other impurities upon cellulose acetate performance
- Recovery of water vapor from hot flue gas streams
- Effective delivery of CO_2 to algal ponds
- Development of membrane process flowsheets using simulation
- Mixed matrix membranes for catalytic applications

THE UNIVERSITY OF MELBOURNE

Control of Physical Aging in Super Glassy Polymer Membranes Without Permeability Loss

MOF Mixed Matrix Membranes

Cher Hon (Sam) LAU| Research Scientist
25 March 2015

MANUFACTURING FLAGSHIP/ ADAPTIVE POROUS MATERIALS TEAM
www.csiro.au

The University of Melbourne | The University of Adelaide | Monash University | Australian National University | University of Colorado Boulder

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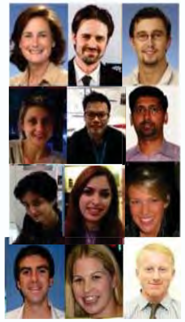
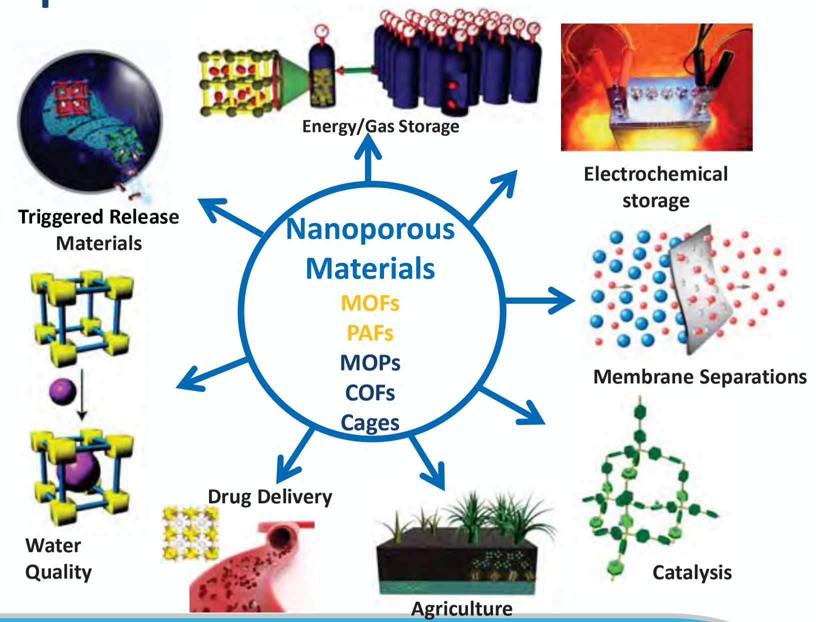
Presentation Outline

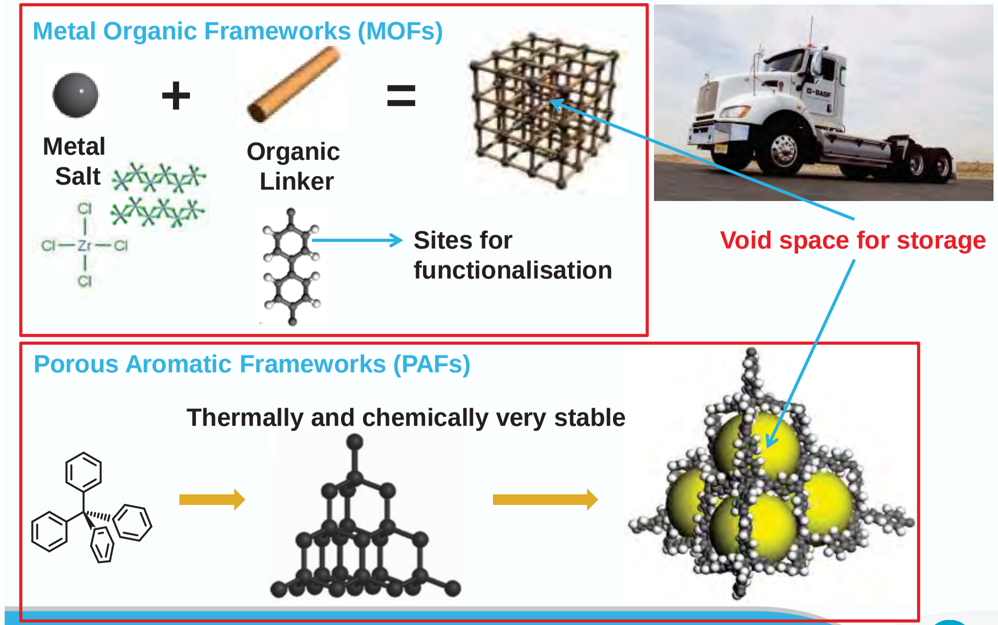
- Adaptive Porous Materials Team
- Porous Frameworks
- CSIRO's Approach
- Conclusion



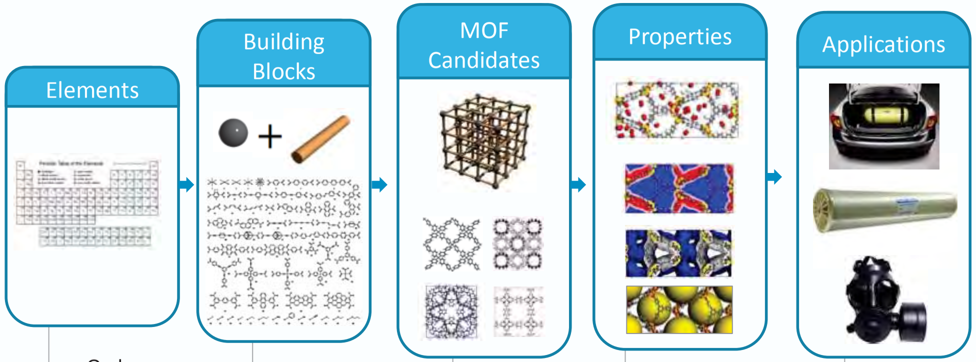
Adaptive Porous Materials Team in CSIRO



Porous Frameworks



Virtual screening of MOF candidates



Elements

Building Blocks

MOF Candidates

Properties

Applications

- Carbon
- Zinc
- Oxygen
- Hydroge n
- Nitrogen
- +

- Zn^{+2}
- Cu^{+2}
- BTB
- BDC
- DOBDC
- +

- PAFs
- ZIFs
- COFs
- POCs
- SNUs
- +

- Surface area
- Porosity
- Gas adsorption
- Gas permeation
- Water permeation
- +

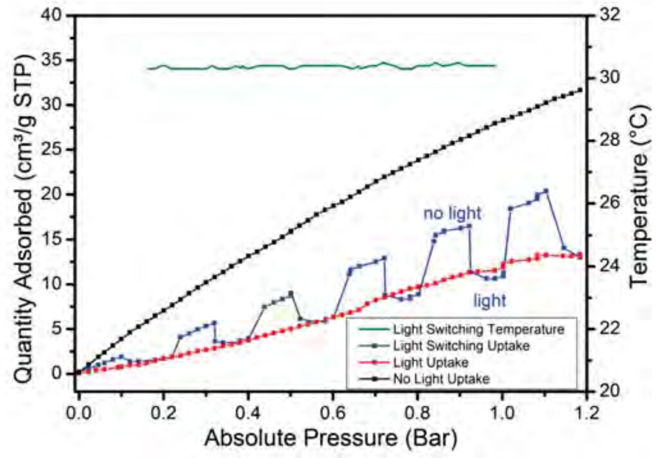
- Separation
- Storage
- Catalysis
- Sensors
- Barriers
- +

Triggered Release Materials

UV-triggered release of CO_2

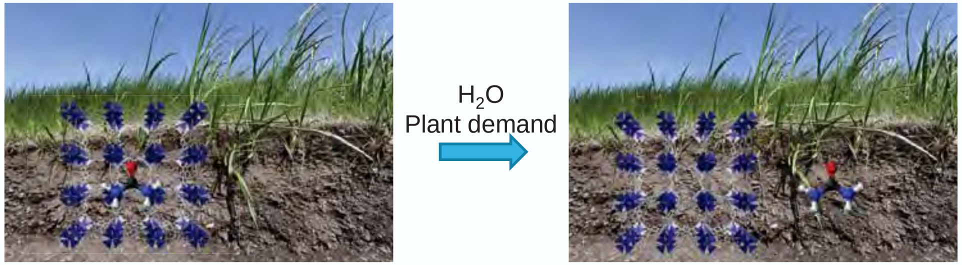
R. Lyndon, K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2013**, *52*, 3695.

Triggered Release Materials



R. Lyndon, K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2013**, *52*, 3695.

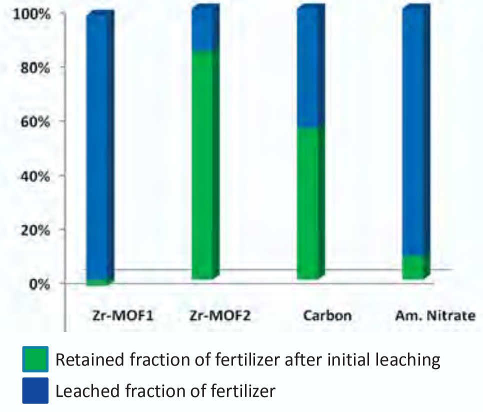
Intelligent Fertilizers



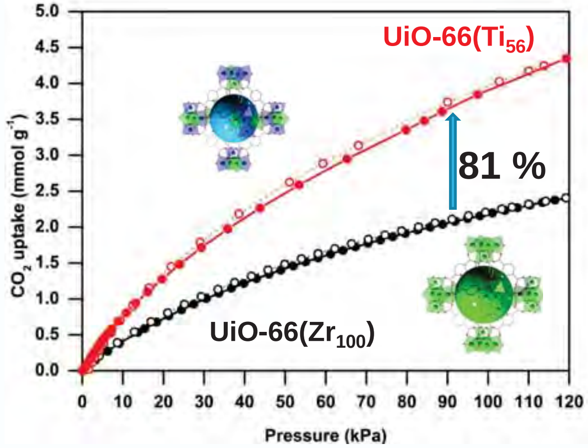
***Requirements*:**

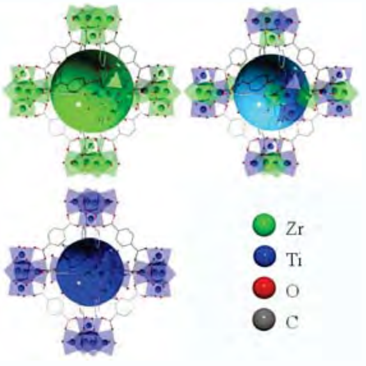
- *High pore volume*
- *Low cost*
- *Water stable*
- *Eco-friendly*

Intelligent Fertilizers



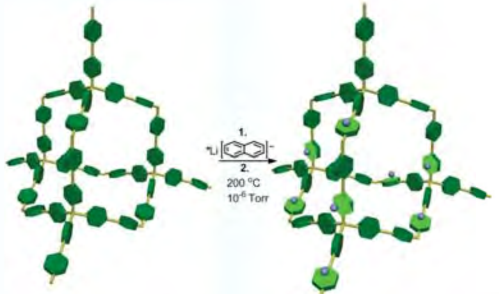
Carbon Capture



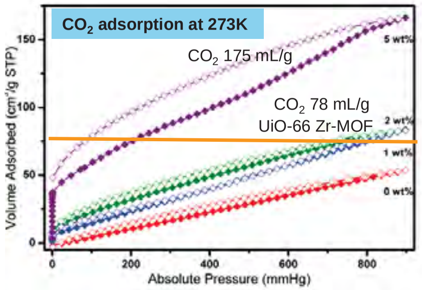


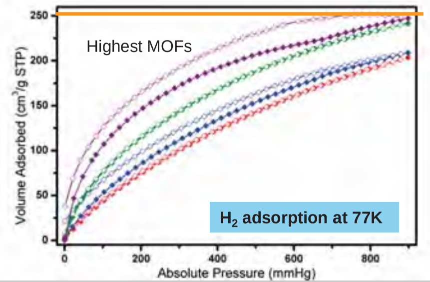
Lau, C. H.; Babarao, R.; Hill, M. R., *Chem. Commun.* 2013, 49 (35), 3634

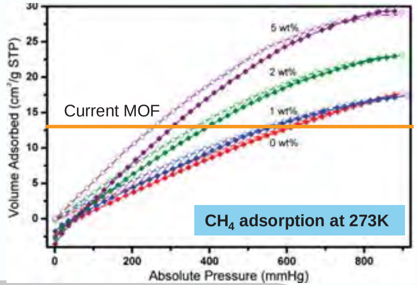
Energy & Gas Storage



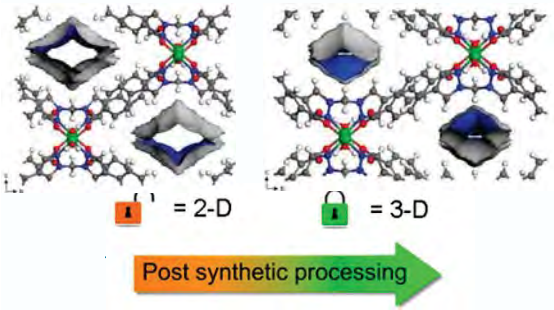
K. Konstas, M. R. Hill; *Angew. Chem. Int. Ed.*, **2012**, *51*, 6639-6642.

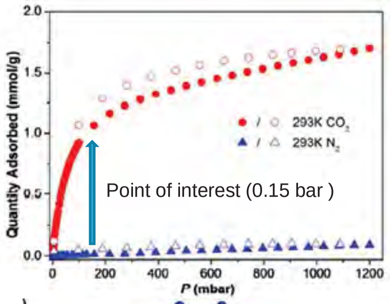


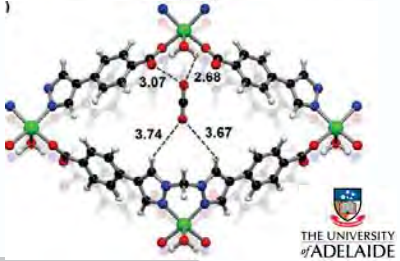




Energy & Gas Storage







- ❑ Predicted selectivity for CO_2/N_2 (15/85 wt %) mixture) of 590 at 293 K and 1 atm
- ❑ Flue gas composition CO_2 (15%), N_2 (75%), O_2 (4 - 5 %), H_2O (5 - 8 %) and SOx and Nox
- ❑ Predict mixed gas isotherms (difficult to obtain experimentally)

Witold, MB; **Babarao, R**; Hill, MR; Doonan, CJ; Sumby, CJ, ***J. Am. Chem. Soc.***, 135, 2013

Porous Frameworks

As adsorbents for CO_2 capture

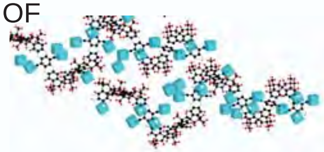
600 MW coal-fired power plant
Flue gas 13 % CO_2 (460 tonnes/hr)[a]

MOF CO_2 Capacity [b]

146 tonne MOF = **$2.9 billion** (based on BASF prices)

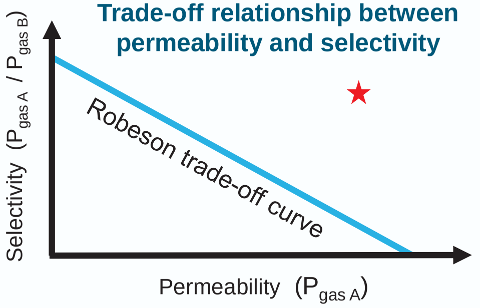
MOF Mixed Matrix Membrane
a, b

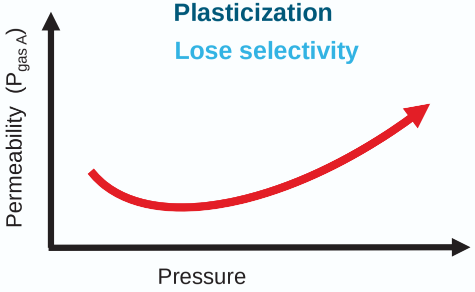
0.17 million m^2 – 2.46 million m^2
0.15 - 2.1 tonne MOF

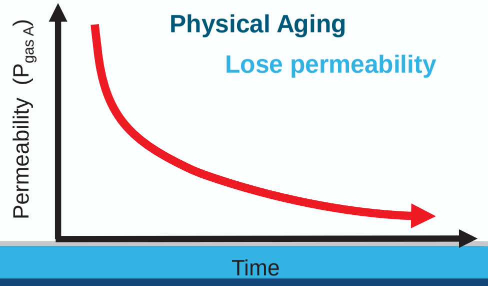


a) T. C. Merkel∗, H. Lin, X. Wei, R. Baker; J. Membr. Sci., 359 (2010) 126–139
b) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu; Chem. Soc. Rev, 2012,41, 2308–2322
c) L. M. Robeson, J. Membr. Sci., 2008, 320, 390-400

What we aim to achieve with CSIRO's MOF Membranes?

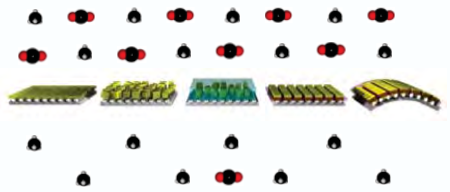




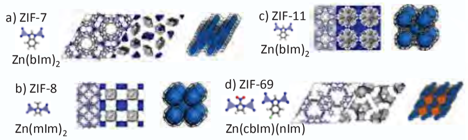


Example: Screening for membrane materials

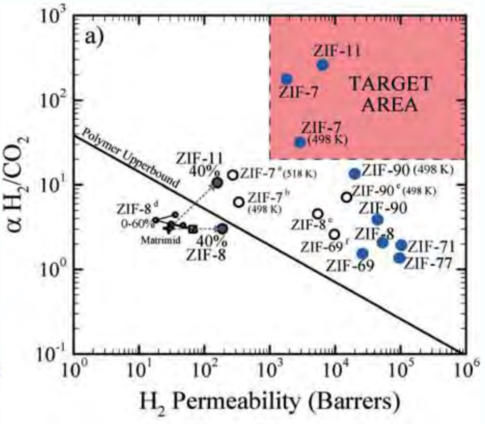
Application: CO_2 capture and H_2 generation



Candidate Materials: Zeolitic Imidazolate Frameworks



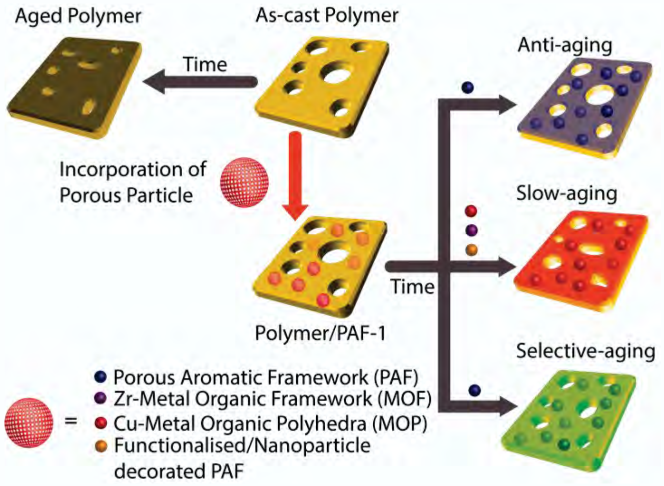
Industrial Feasibility Criteria
Intergovernmental Panel on Climate Change (IPCC)



Thornton et al. "Feasibility of Zeolitic Imidazolate Framework membranes for clean energy applications" Energy & Environmental Science 2012

CSIRO's Approach

Mixed Matrix Membranes with Porous Frameworks



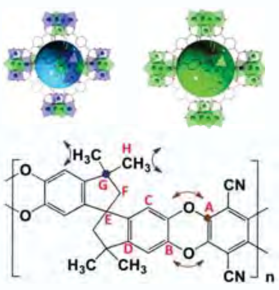
- Porous Aromatic Framework (PAF)
- Zr-Metal Organic Framework (MOF)
- Cu-Metal Organic Polyhedra (MOP)
- Functionalised/Nanoparticle decorated PAF

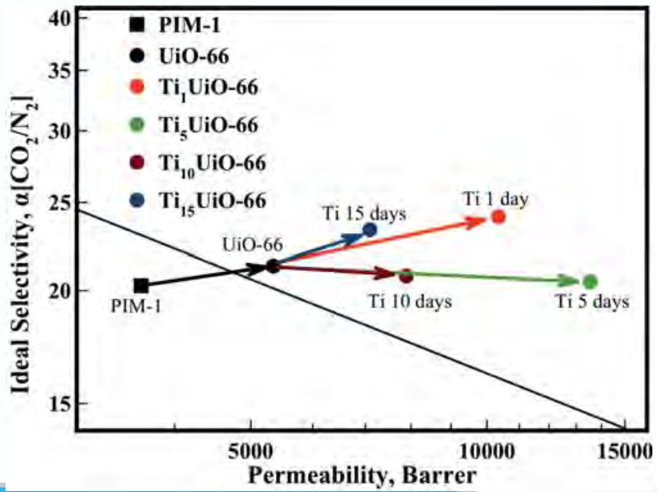
CSIRO's Membranes

Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF, Ti-UiO-66

Polymer: PIM-1



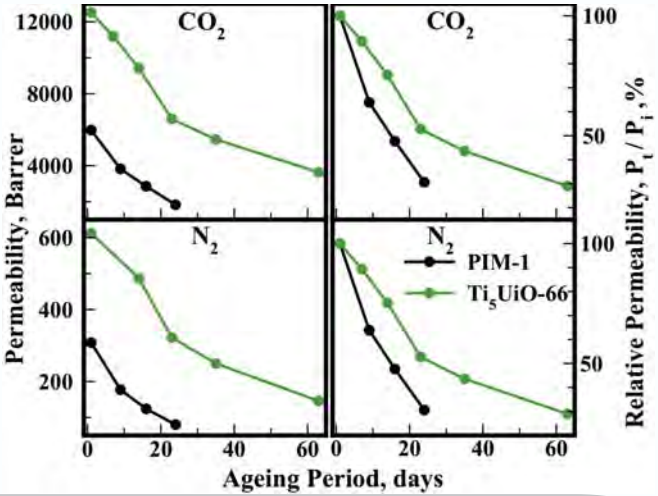


Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823

CSIRO's Membranes

Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF

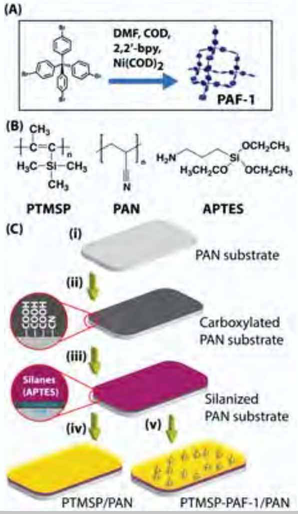


Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823

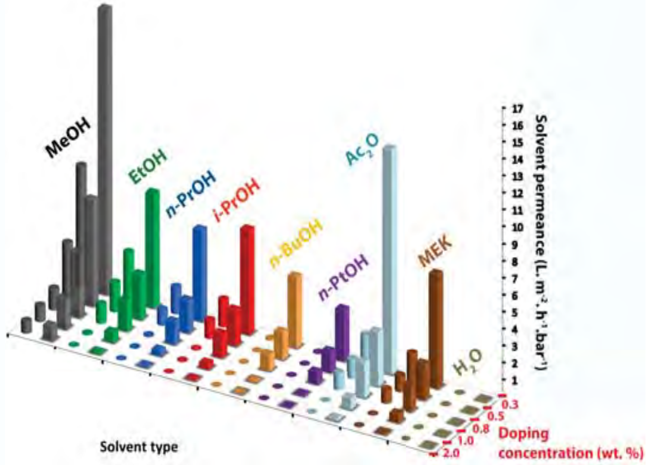
CSIRO's Membranes

Slow Aging Membranes – Organic Solvent Nanofiltration

Additive: PAF-1



Water-Hydrocarbon Separations

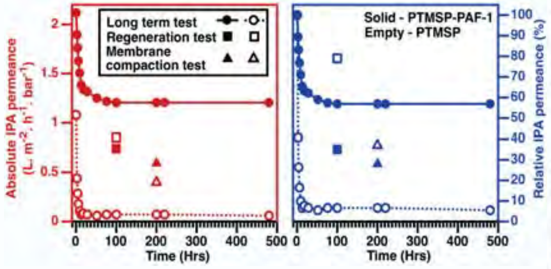


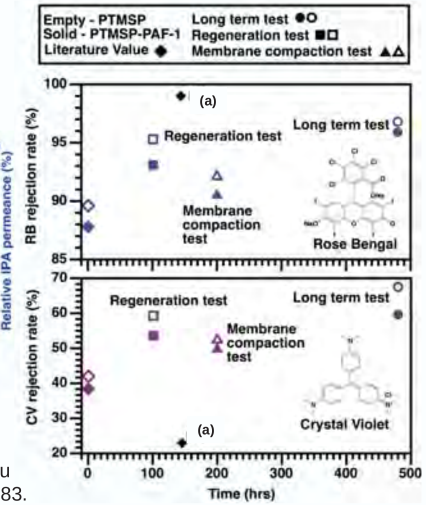
CSIRO's Membranes

Slow Aging Membranes – Organic Solvent Nanofiltration

Additive: PAF-1

Hydrocarbon-Dye Separations

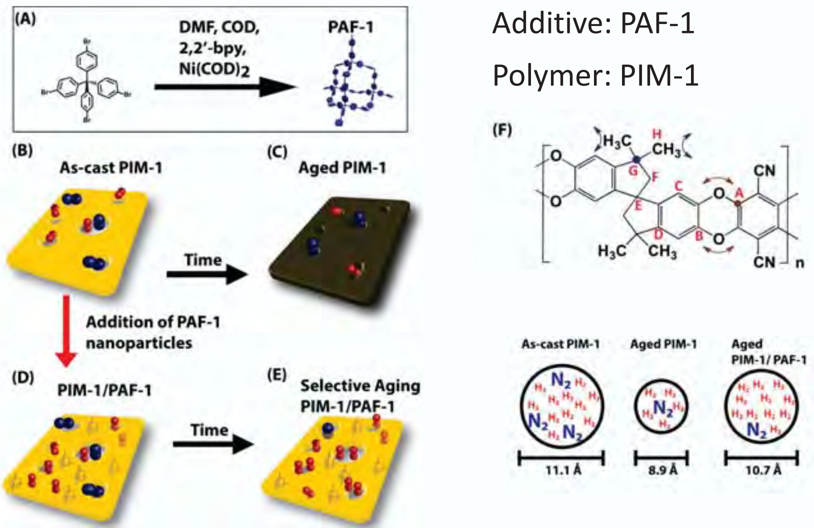




(a) Li, X.; De Feyter, S.; Chen, D.; Aldea, S.; Vandezande, P.; Du Prez, F.; Vankelecom, I. F. J. *Chem. Mater.* **2008**, 20, 3876 – 3883.

CSIRO's Membranes

Selective Aging Membranes – Hydrogen Purification



Additive: PAF-1

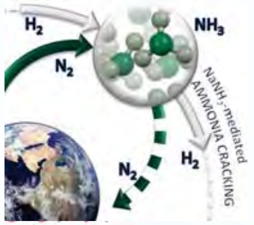
Polymer: PIM-1

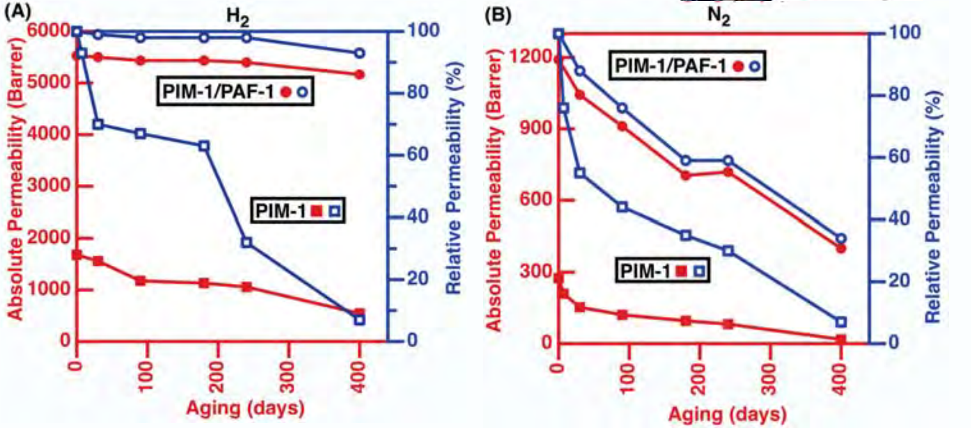
C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

CSIRO's Membranes

Selective Aging Membranes – Hydrogen Purification

David *et al.*; *J. Am. Chem. Soc.* **2014**, *136*, 13082.

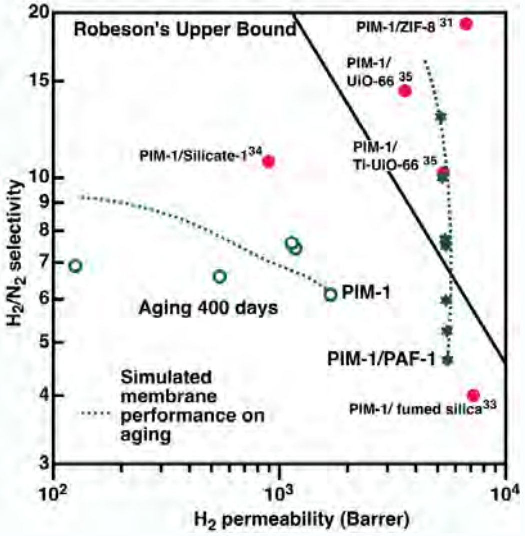


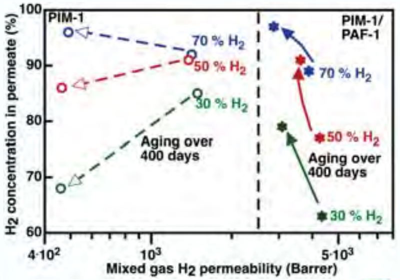


C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

CSIRO's Membranes

Selective Aging Membranes – Hydrogen Purification





Simulated membrane performance on aging

○ PIM-1

✱ PIM-1/PAF-1

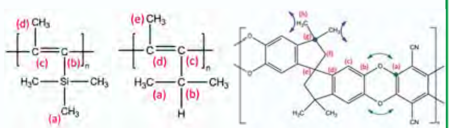
C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

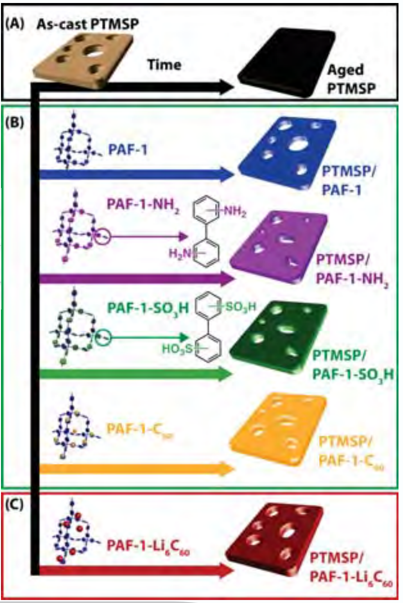
CSIRO's Membranes

Anti-Aging Membranes – Carbon Capture

Additive: PAF-1

Polymer: PTMSP, PMP, PIM-1





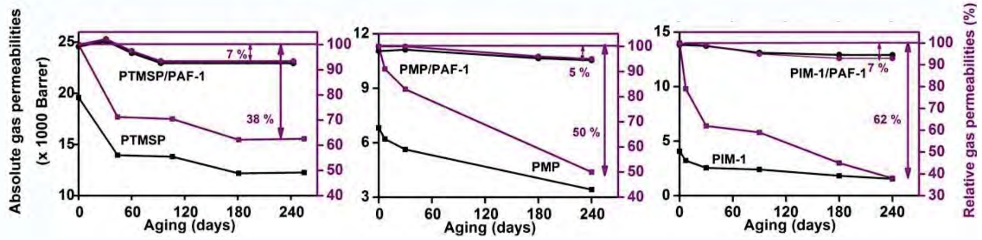
C. H. Lau, M. R. Hill *et al. Angew. Chem.* 2014, 53, 5322 - 5326

CSIRO's Membranes

Anti-Aging Membranes – Carbon Capture

Additive: PAF-1

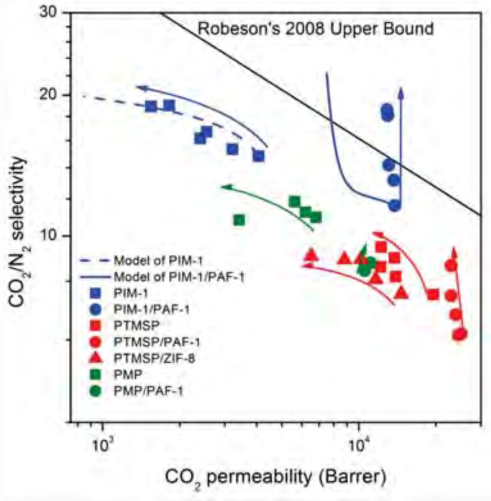
Polymer: PTMSP, PMP, PIM-1

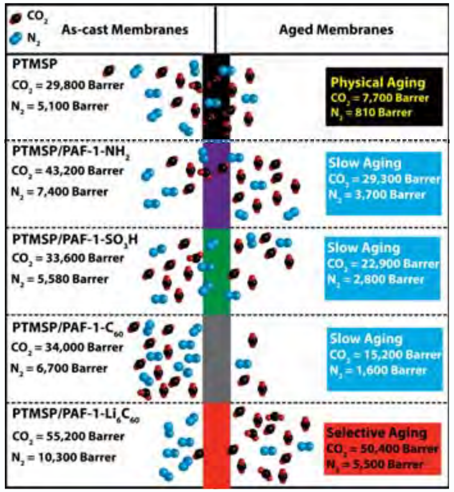


C. H. Lau, M. R. Hill *et al. Angew. Chem.* 2014, 53, 5322 - 5326

CSIRO's Membranes

Anti-Aging Membranes – Carbon Capture



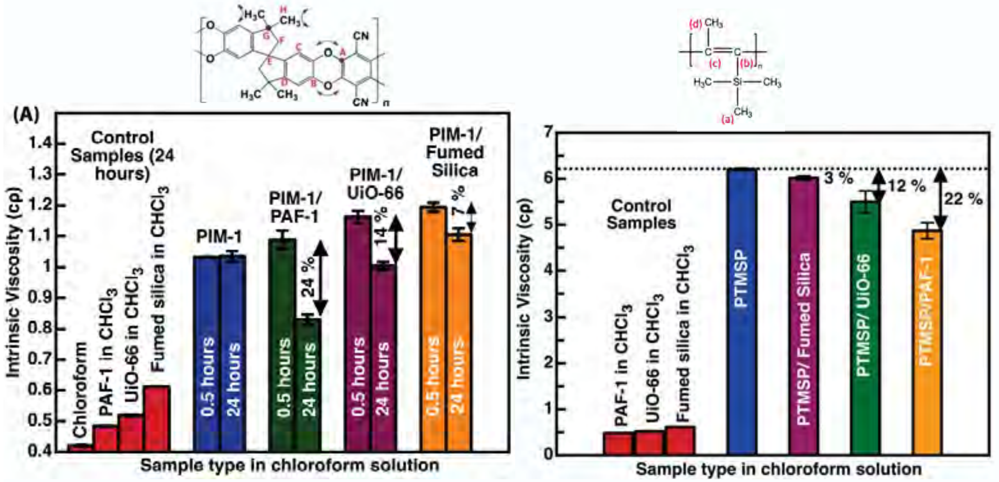


C. H. Lau, M. R. Hill *et al. Angew. Chem.* 2014, 53, 5322 - 5326

CSIRO's Membranes

How does it work?

1. Intimate interaction between porous additives and polymers

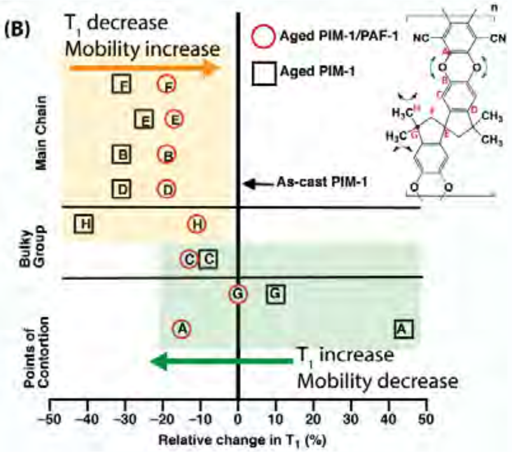


C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

CSIRO's Membranes

How does it work?

2. Freezing mobility in carbon atoms of bulky groups in polymer

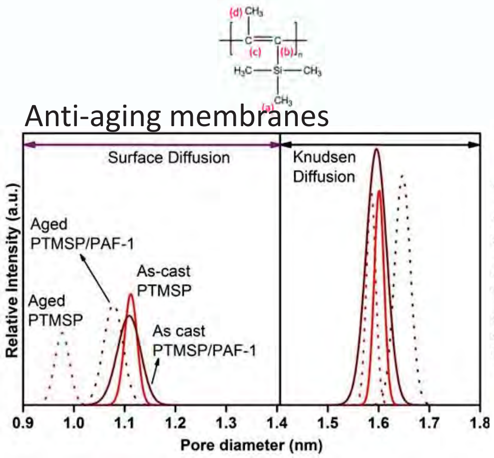


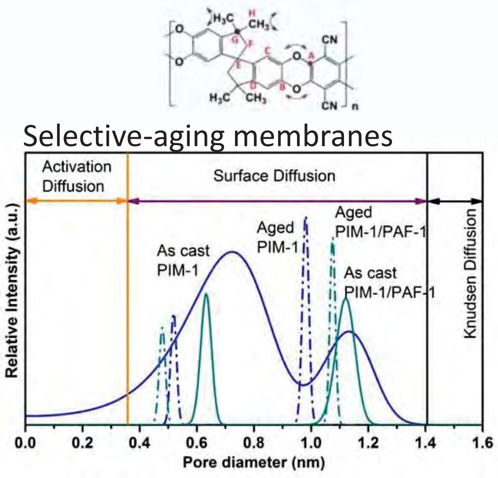
C. H. Lau, K. Konstas, A. W. Thornton, A. C. Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill, M. R. Hill, *Angew. Chem. Int. Ed.* 2015, 54, 2669 – 2673

CSIRO's Membranes

How does it work?

3. Unchanged pore sizes over time





C. H. Lau, M. R. Hill *et al. Angew. Chem.* 2014, 53, 5322 - 5326

Scale-Up Production

Membranes & MOFs

Membranes

Hollow Fiber Spinning Line

MOFs

Flow Chemistry

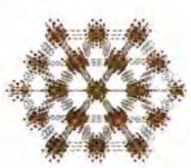
M. Rubio-Martinez, M. P. Batten, A. Polyzos, K.-C. Carey, J. I. Mardel, K.-S. Lim, M. R. Hill, *Sci. Rep.* 2014, *4: 5443*

Scale Up Production

MOFs

Proof-of-concept

HKUST-1



UiO-66

NOTT-400

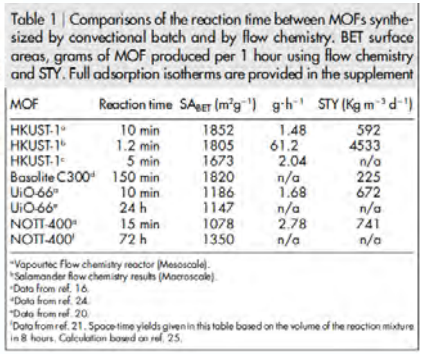
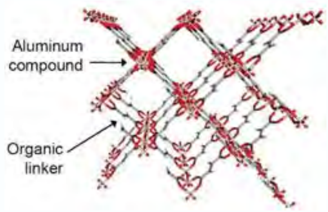


Table 1 | Comparisons of the reaction time between MOFs synthesized by convectional batch and by flow chemistry. BET surface areas, grams of MOF produced per 1 hour using flow chemistry and STY. Full adsorption isotherms are provided in the supplement

MOF	Reaction time	SA_{BET} (m^2g^{-1})	$g \cdot h^{-1}$	STY ($Kg\ m^{-3}\ d^{-1}$)
HKUST-1[a]	10 min	1852	1.48	592
HKUST-1[b]	1.2 min	1805	61.2	4533
HKUST-1[c]	5 min	1673	2.04	n/a
Basolite C300[d]	150 min	1820	n/a	225
UiO-66[a]	10 min	1186	1.68	672
UiO-66[e]	24 h	1147	n/a	n/a
NOTT-400[a]	15 min	1078	2.78	741
NOTT-400[f]	72 h	1350	n/a	n/a

[a] Vapourtec Flow chemistry reactor (Mesoscale).
[b] Salamander flow chemistry results (Macroscale).
[c] Data from ref. 16.
[d] Data from ref. 24.
[e] Data from ref. 20.
[f] Data from ref. 21. Space-time yields given in this table based on the volume of the reaction mixture in 8 hours. Calculation based on ref. 25.

Proof-of-scalability



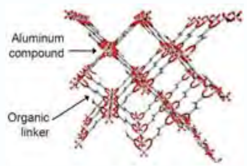
Al fumarate

M. Rubio-Martinez, M. P. Batten, A. Polyzos, K.-C. Carey, J. I. Mardel, K.-S. Lim, M. R. Hill, *Sci. Rep.* 2014, *4: 5443*

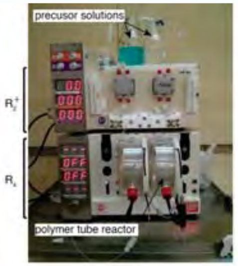
Scale-Up Production

MOFs

Al fumarate



Proof-of-concept: 40 g/h



Reactor: 2,5,10mL
T: 0-150C
Diameter tube: 1mm
Flow rate: 0.10-10 mL/min
(up to 10 bar)

Proof-of-scalability: 400 g/h

Reactor: 100mL
T: 0-150C
Diameter tube: 6mm
Flow rate: 1-45mL/min

Scale-up: 10 kg/h

Reactor: 2000mL
T: 0-150C
Diameter tube: 12mm
Flow rate: 1000mL/min

Conclusions

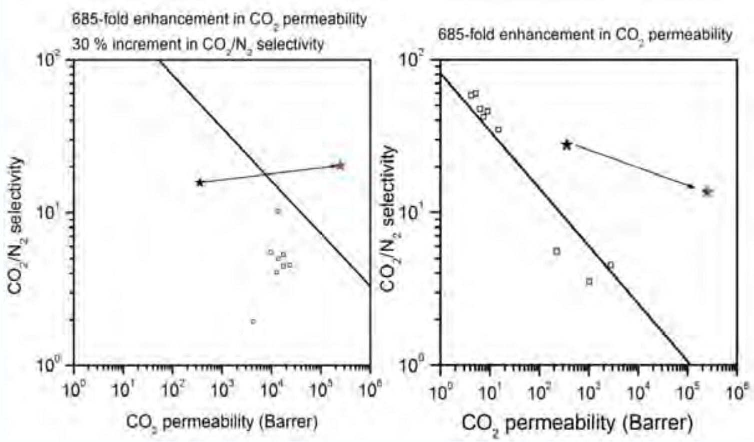
Capable of scale up productions of porous additives required to:

1) **Enhance** gas permeability by up to 300 %
2) **Maintain** enhanced gas permeability beyond 1 year
3) **Tailor** aging mechanism in membranes according to application
4) Fabricate **multi-functional** membranes for carbon capture, solvent purification, and dye sequestration.

Thank you

Manufacturing Flagship/Adaptive Porous Materials Team
Cher Hon (Sam) Lau
Research Scientist

t +61 3 9545 2943
e cherhon.lau@csiro.au

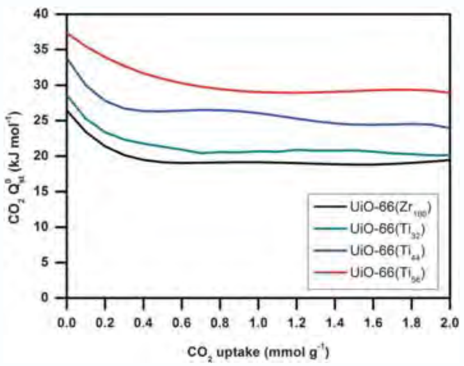


CSIRO's Membranes

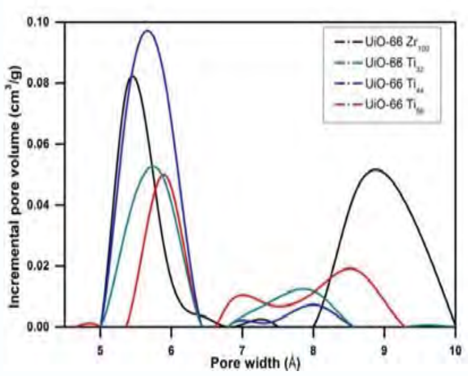
Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF

Enthalpy of Adsorption



Pore Size

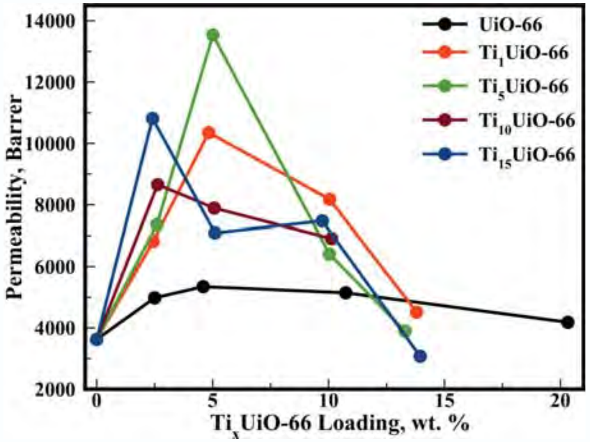


Lau, C. H.; Babarao, R.; Hill, M. R., *Chem. Commun.* 2013, 49 (35), 3634

CSIRO’s Membranes

Slow Aging Membranes – Carbon Capture

Additive: UiO-66 MOF



Smith, S. J. D.; Ladewig, B. P.; Hill, A. J.; Lau, C. H.; Hill, M. R., *Sci. Rep.* 2015, 5, 7823

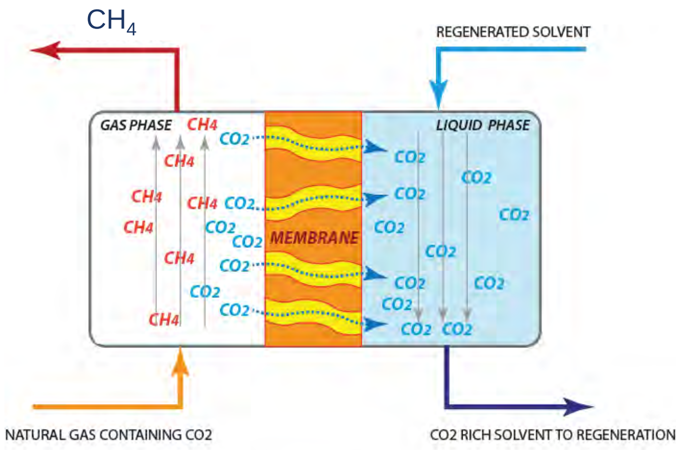
Membrane contactor for CO_2 capture

Taek-Joong Kim
Department of CO_2 Capture Process Technology
Sustainable energy technology Sector
SINTEF Materials and Chemistry

Overview

- What is membrane contactor?
- Advantages
- Mass transfer resistance
- High pressure
- Wetting
- Materials
- Long-term stability
- Actual operation window
- Counter-current
- Microporous
- Concluding remarks

What is membrane contactor?



Basic Concept of Membrane Gas-Liquid Contactor for Natural Gas Sweetening
(the original figure at thegreenasia.com (Advantages of Membrane Gas Absorption Method) posted by Asela De Silva on Feb 21, 2010)

http://www.co2crc.com.au/aboutccs/cap_membranes.html

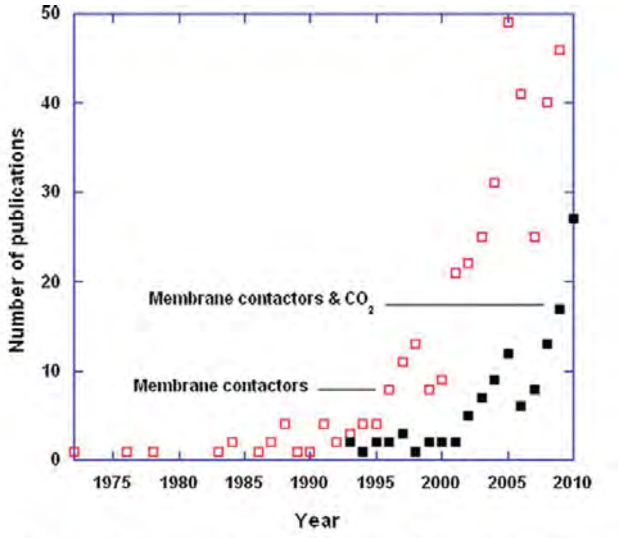


Fig. 1. Evolution of the number of publications per year in scientific journals which include the keywords "membrane contactors" (closed squares) and "membrane contactors + CO_2" (open squares).

ISI Web of Science, December 2011.

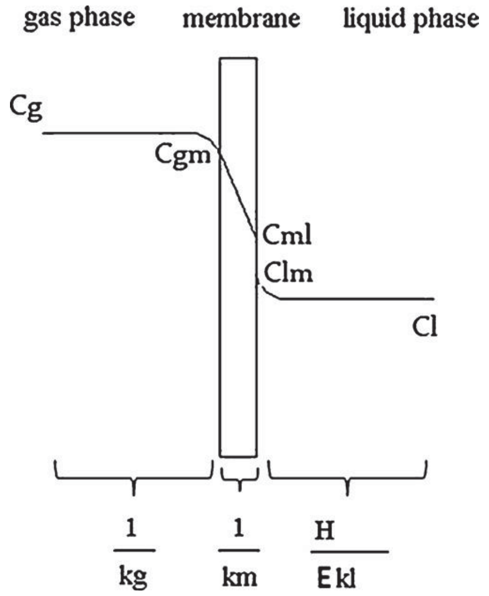
Favre and Svendsen / Journal of Membrane Science 407–408 (2012) 1–7

Advantages of Membrane Contactor

- High surface area per unit contactor volume
- Independent control of gas and liquid flow rates
- Free of entrainment and flooding
- Modularity and easy scale up or down
- Process intensification

Bougie et al. / Chemical Engineering Science 123 (2015) 255–264

Added resistance?



P.T. Nguyen et al. / Journal of Membrane Science 377 (2011) 261– 272

High pressure?

High pressure
High temperature
- Swelling
- Compression
- Wetting

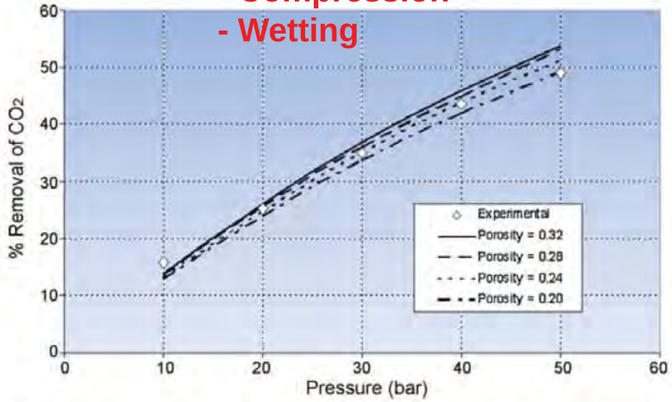


Fig. 6. Effect of porosity on the physical absorption of CO_2 using pseudo-wetting (0.5%), gas flow rate = 800 (ml min^{-1}), liquid flow rate = 100 (ml min^{-1}), tortuosity = 3.

Faiz et al./ Journal of Membrane Science 365 (2010) 232–241

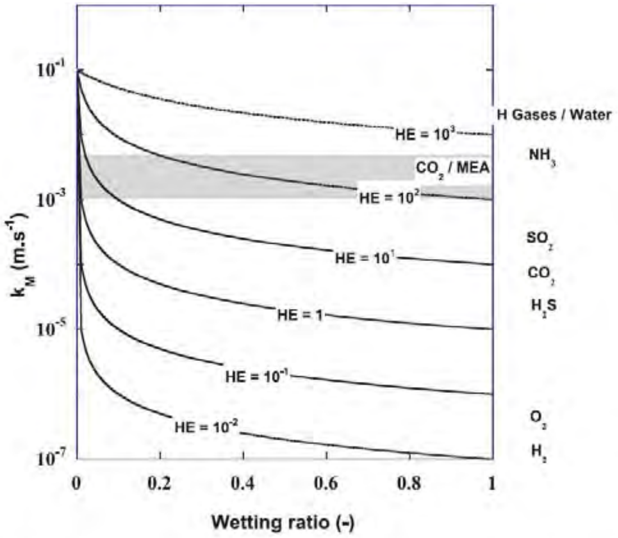
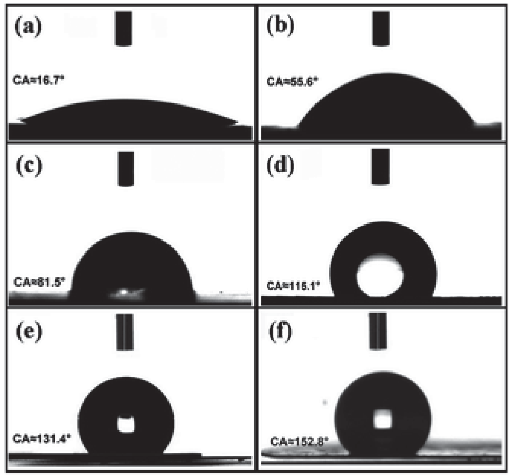


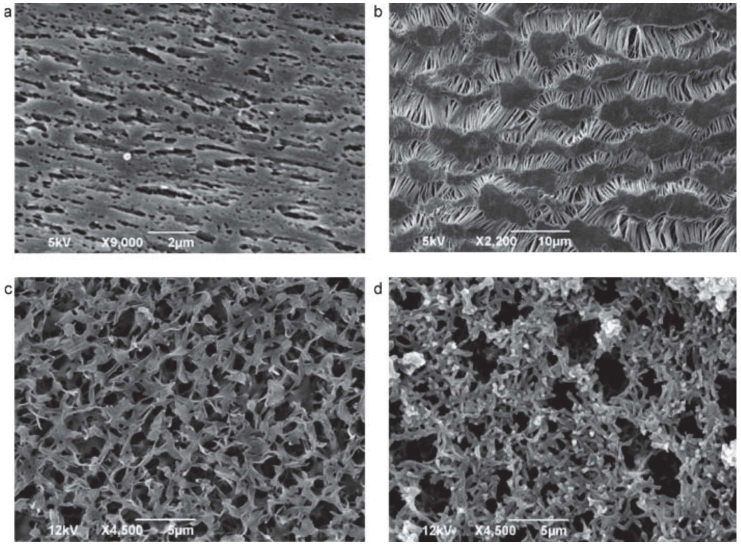
Fig. 4. Influence of wetting on the effective membrane mass transfer coefficient (k_m) based on resistance in series approach. The diffusion coefficients in the gas and liquid phases are assumed to be 10^{-5} and 10^{-9} m^2 s^{-1}, respectively. The different curves correspond to different values of H.E, where H is the gas–liquid Henry coefficient and E the enhancement factor. For CO_2 absorption in MEA, H.E usually ranges between 100 and 300.

Favre and Svendsen / Journal of Membrane Science 407–408 (2012) 1–7



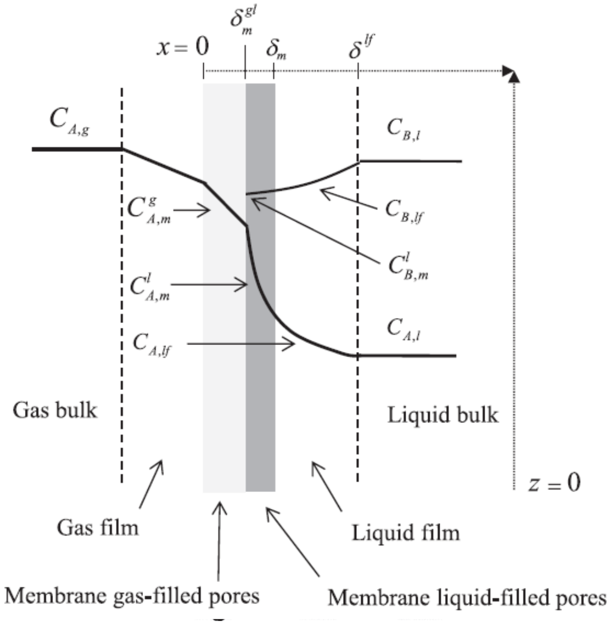
$$\Delta P_c = -\frac{2\gamma_L \cos\theta}{r_p}$$

Tang et al. / J. Mater. Chem., 2006,16, 1741-1745



Porous structures for membrane contactor applications showing the differences in pore size distribution, pore geometry and material structure:
(a) PP, (b) PTFE, (c) PVDF, (d) PES.

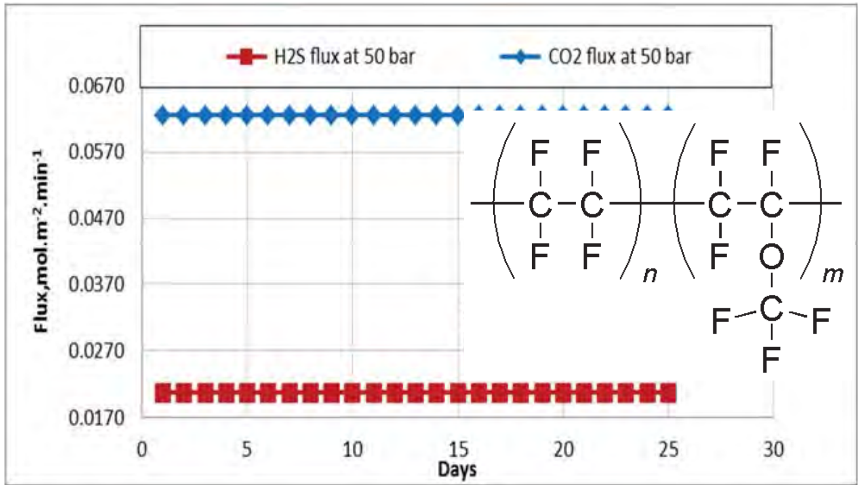
Favre and Svendsen / Journal of Membrane Science 407–408 (2012) 1–7



F. Bougie et al. / Chemical Engineering Science 123 (2015) 255–264

Materials?

Long-term stability?



i) Feed gas composition: ETHANE 6.9%m, PROPANE 3.6%m, METHANE 81.64%m, CARBON DIOXIDE 4.2%m, HYDROGEN SULFIDE 1.4%m, ISOBUTANE 0.3%m, NITROGEN 1.4% m and NBUTANE 0.56%m).
ii) The solvent composition: 30wt% K2CO3 + 1wt% DEA solution,
iii) Feed gas temperature: 50 oC; Solvent temperature: 100 oC,
vi. Feed gas pressure: 50 bar

Al-Marzouqi et al. / https://www.jccp.or.jp/international/conference/docs/1-2UAEU.pdf

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Actual operation window?

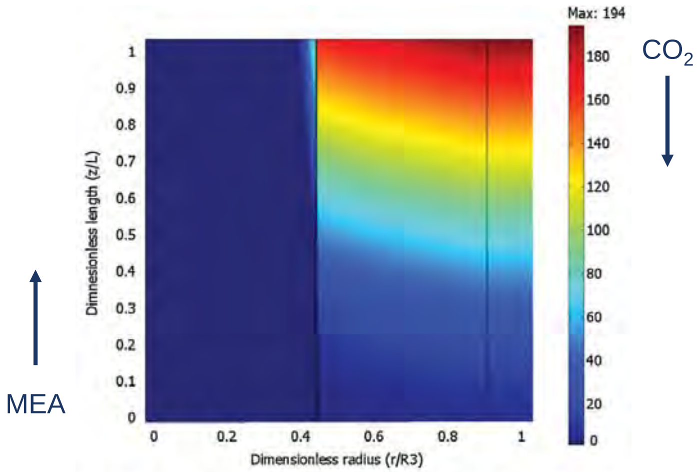
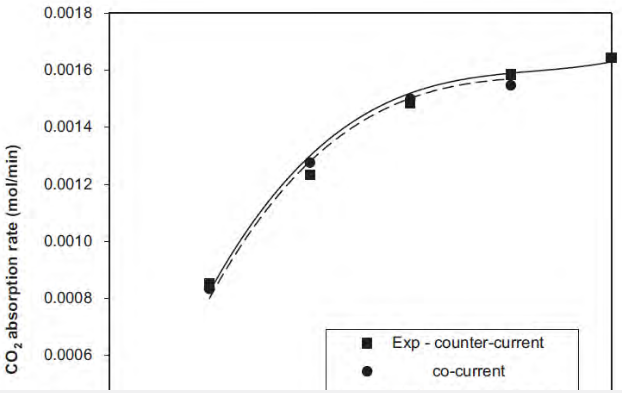


Fig. 14. Model solution and the concentration gradient of CO_2 ($mol\,m^{-3}$) at 50 bar using 0.5 M MEA as the absorbent solvent while considering partial-wetting (1%).

Faiz et al. / Journal of Membrane Science 365 (2010) 232-241

Counter-current?

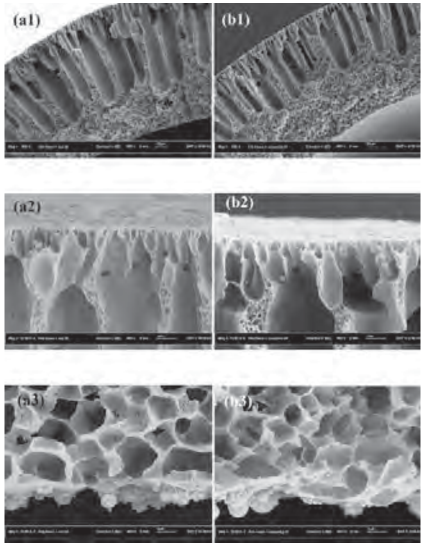


….. Small pressure difference can provide enough CO2 capture rate, the little higher pressure induced by counter-current flow is less important than increasing operation flexibility in real plant.…

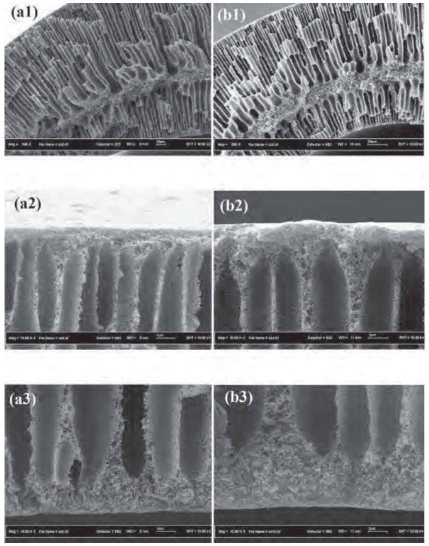
Fig. 11. Predicted versus experimental CO_2 absorption rate in a 3-FSMC (PTFE) – CO_2/AHPD-Pz system (gas flow rate of 100 ml/min; liquid flow rate of 20 ml/min).

Bougie et al. / Chemical Engineering Science 123 (2015) 255–264

Microporous?



The structure of PVDF hollow fiber membranes for (a) plain and (b) with PEG (1) cross section, (2) shell side, and (3) lumen side.



The structure of PEI hollow fiber membranes (a) plain and (b) with PEG (1) cross section, (2) shell side, and (3) lumen side.

Naim et al. / Chemical engineering research and design 9 2 (2 0 1 4) 1391–1398

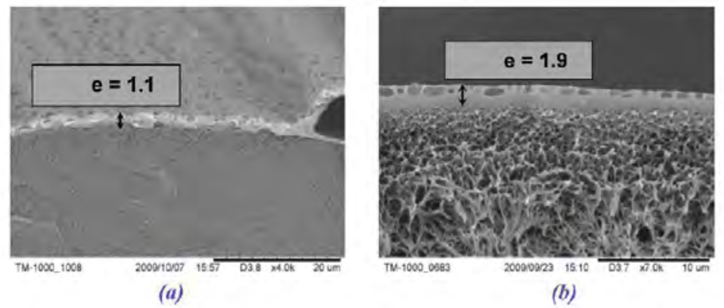


Fig. 7. SEM pictures (cross section) of the two different types of composite hollow fibers prepared and tested in this study. (a) Teflon AF 2400 average coating thickness 1.1 µm (Oxyphan_TF). (b) PTMSP average coating thickness 1.9 µm (Oxyphan_PTMSP).

Mechanically stronger top layer?

Nguyen et al. / Journal of Membrane Science 377 (2011) 261– 272

Concluding remarks

How to prevent the membrane from wetting in the long term operation?

- Hydrophobic membranes
- Surface modification of membranes
  (hydrophobicity, chemical resistance)

- Composite membranes
- Selection of denser membranes

- Selection of liquids with suitable surface tension

- Optimization of operation conditions/technique

How to increase operation flexibility?

- How to increase allowable transmembrane pressure (liquid & gas break-through pressure)?

- Reducing operation cost
- Reducing installation cost
- Reducing expected process complexity

(subtle control of transmembrane pressure over hundreds of large modules, ready for break-through of liquid and gas)

Thank you!

HiPerCap Project: Assessment of CO2 Capture Technologies

Melbourne Workshop

Jock Brown
26.03.2015

SAFER, SMARTER, GREENER

Global reach – local competence

150 years

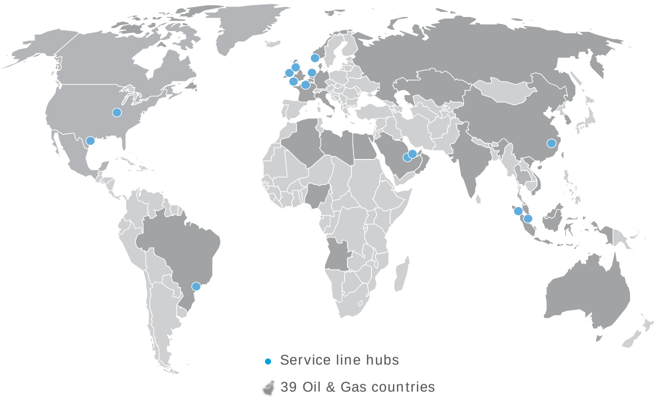
400 offices

100 countries

16,000 employees

DNV GL Oil and Gas

- 5,500 exceptional people who care about making the industry safer, smarter and greener
- Combining industry and domain knowledge with project and operational expertise
- A global network of experts, working together to solve local customer challenges.



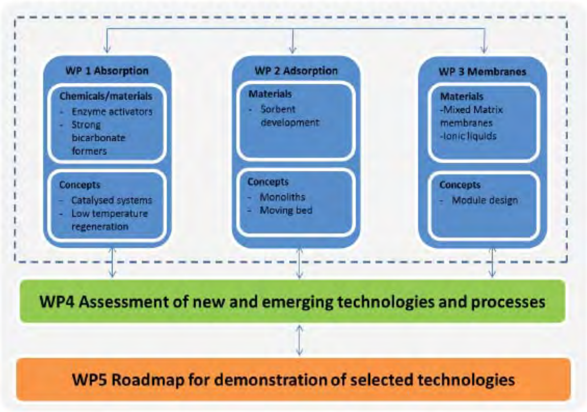
● Service line hubs

39 Oil & Gas countries

HiPerCap Objectives

1. To develop high-potential novel and environmentally benign technologies and processes for post-combustion CO_2 capture leading to real breakthroughs.
2. To achieve 25% reduction in efficiency penalty compared to a demonstrated state-of-the-art capture process
3. Deliver proof of concept for technologies
4. Develop a fair methodology for comparing capture technologies
5. Develop technology roadmaps for the two most promising technologies

HiPerCap Project



WP4 Overview

- Activities:
  - Task 4.1 – Establishment of Methodology (**DNV GL**, SINTEF, EDF, EON, AEE, GNF)
  - Task 4.2 - Data collection of capture technologies studied in WP1-3 (**SINTEF**, DNV GL, EON)
  - Task 4.3 - Assessment of capture technologies studied in WP1-3 (**DNV GL**, SINTEF, EDF, EON, AEE, GNF) – Not started
  - Task 4.4 - Guidelines for selection and benchmarking of two breakthrough technologies to be studied in WP5 (**EDF**, DNV, SINTEF, TNO, EON, AEE, GNF) – Not started

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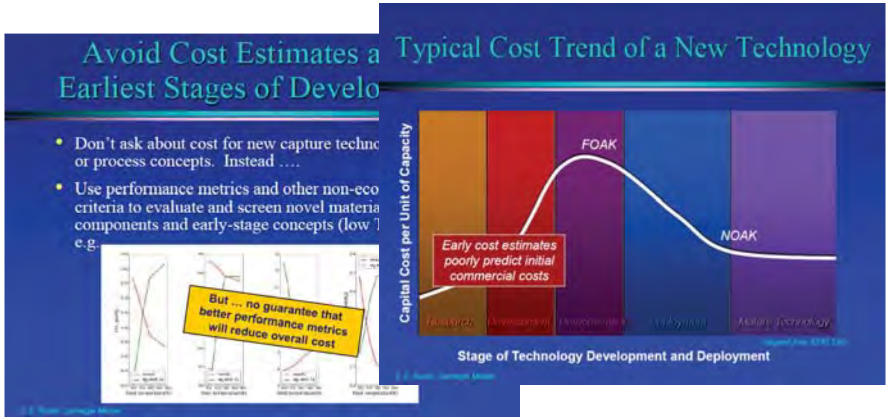
Assessment Methodology

The Final Assessment

- Ultimately the impact of CCS on the COST of the product produced will be how future CCS investment decisions are made



Avoid Cost Estimates a
Earliest Stages of Develo

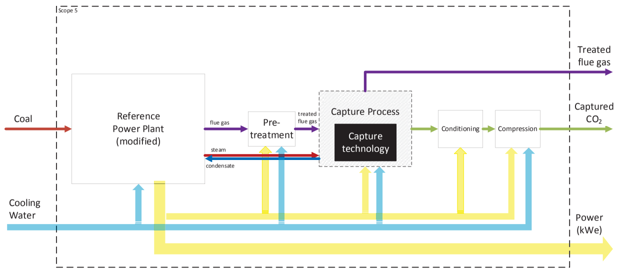
- Don't ask about cost for new capture technc or process concepts. Instead ….
- Use performance metrics and other non-eco criteria to evaluate and screen novel materia components and early-stage concepts (low T e.g.

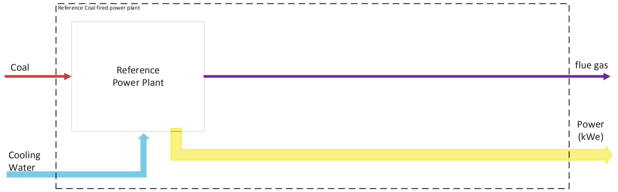
But … no guarantee that better performance metrics will reduce overall cost

Typical Cost Trend of a New Technology

Early cost estimates poorly predict initial commercial costs

Scope of the assessment





Overall comparison

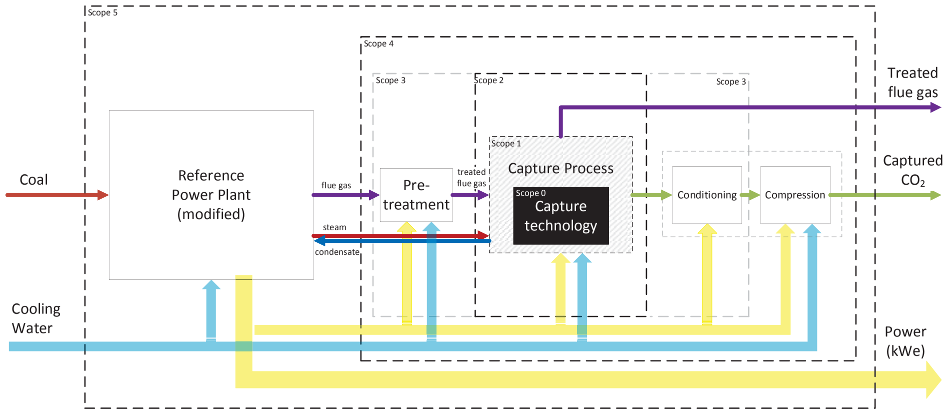
On level of key indicators the following performance can be determined:

Indicator Energy

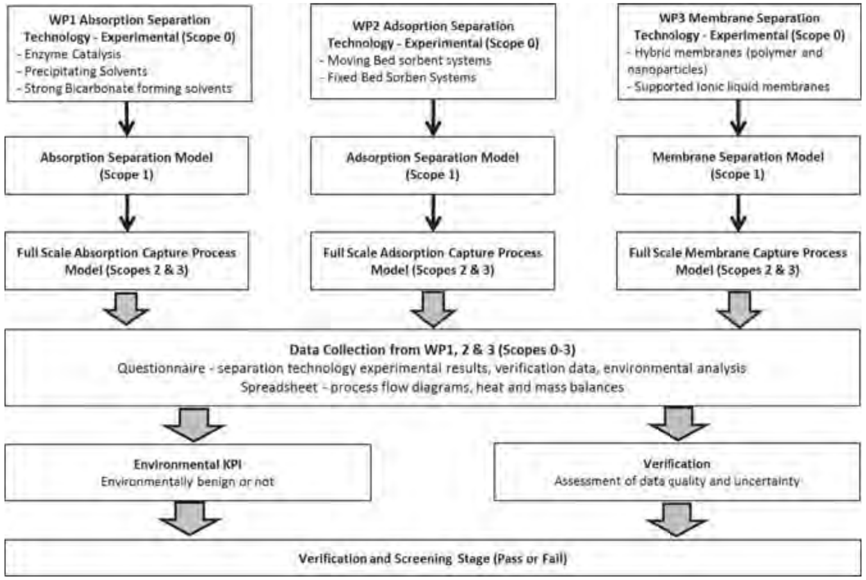
Indicator Environmental

Indicator Cost

WP4 Approach and Workflow



WP4 Approach and Workflow



WP1 Absorption Separation Technology - Experimental (Scope 0)
- Enzyme Catalysis
- Precipitating Solvents
- Strong Bicarbonate forming solvents

WP2 Adsoprtion Separation Technology - Experimental (Scope 0)
- Moving Bed sorbent systems
- Fixed Bed Sorben Systems

WP3 Membrane Separation Technology - Experimental (Scope 0)
- Hybrid membranes (polymer and nanoparticles)
- Supported Ionic liquid membranes

Absorption Separation Model (Scope 1)

Adsorption Separation Model (Scope 1)

Membrane Separation Model (Scope 1)

Full Scale Absorption Capture Process Model (Scopes 2 & 3)

Full Scale Adsorption Capture Process Model (Scopes 2 & 3)

Full Scale Membrane Capture Process Model (Scopes 2 & 3)

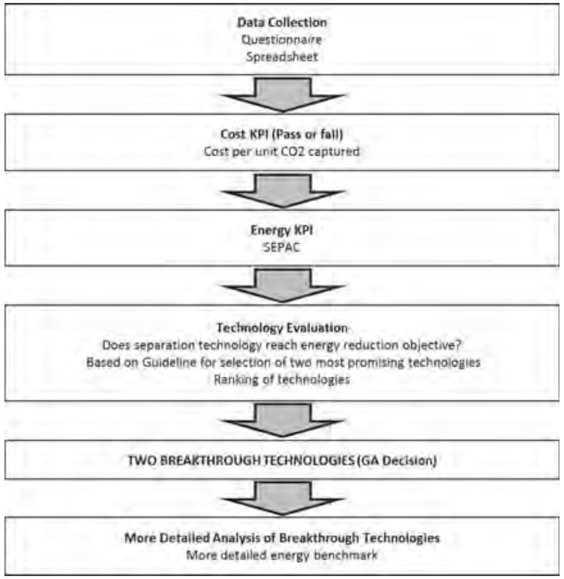
Data Collection from WP1, 2 & 3 (Scopes 0-3)
Questionnaire - separation technology experimental results, verification data, environmental analysis
Spreadsheet - process flow diagrams, heat and mass balances

Environmental KPI
Environmentally benign or not

Verification
Assessment of data quality and uncertainty

Verification and Screening Stage (Pass or Fail)

WP4 Approach and Workflow



Data Collection
Questionnaire
Spreadsheet

Cost KPI (Pass or fail)
Cost per unit CO2 captured

Energy KPI
SEPAC

Technology Evaluation
Does separation technology reach energy reduction objective?
Based on Guideline for selection of two most promising technologies
Ranking of technologies

TWO BREAKTHROUGH TECHNOLOGIES (GA Decision)

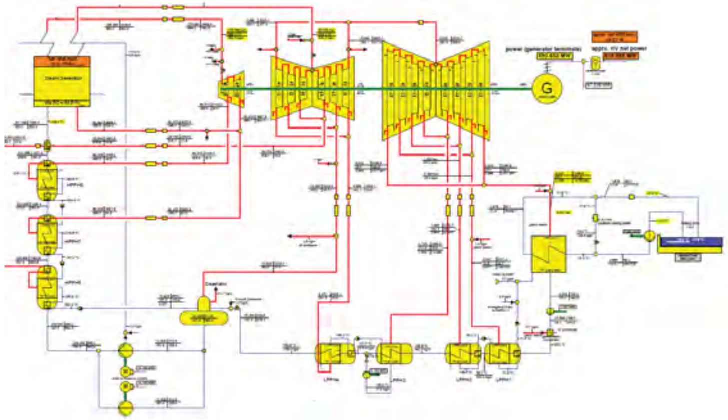
More Detailed Analysis of Breakthrough Technologies
More detailed energy benchmark

Reference Coal Fired Power Plant and State of the Art Capture

---

Reference Coal fired Power Plant

- Updated EBTF Case
- 820MW Advanced supercritical (ASC) pulverised coal (approx. 600 °C/280 bar)



State of the Art Capture Technology

- Criteria
  - Technology needs to be installed on coal power plant
  - Full set of data and details need to be publicly available
  - The largest available reference should be used
  - CESAR 1 case

Environmental

Approach

- Objective: To show that given the best available information, the capture technology is environmentally benign.
- Pass or Fail assessment
- Traffic Light Assessment for each polluting component:

Categories

- Air Pollution and Other Emissions
  - Eg. SOx, NOx, PM, metals, acid and organic chemicals
- Water
  - Eg. Water consumed and produced, nutrients and organic pollutants in water
- Materials of construction and consumed by process
  - Eg. Metals for construction, sorbent materials, minerals, membranes, solvents
- Wastes
  - Eg. Soild and liquid waste such as reclaimer waste

Energy KPI

Background

- Objective:
  - Show that capture processes have reached goal of a reduction in energy penalty by 25% compared to current state of the art technology.

- Boundary conditions
  - Minimal capture rate 85%

- What to benchmark
  - Impact of capture processes on the reference power plant output

Preferred energy KPI

Specific energy penalty of avoided CO_2 (SEPAC) [MJ_e/kg CO_2]

- $\boldsymbol{SEPAC} = \frac{P_{ref} - P}{\phi_{CO_2,ref} - \phi_{CO_2}}$
  - P = net electric output of the power plant in MW_e
  - Φ_{CO2} = the emitted flow of CO_2 in kg_{CO_2}/s

Cost

Approach

- Objective: To show new technology is cost competitive with existing technologies and costs have not been sacrificed in pursuit of a reduction in energy consumption.
- Pass or Fail assessment
- Estimate CAPEX and OPEX (excluding Energy)

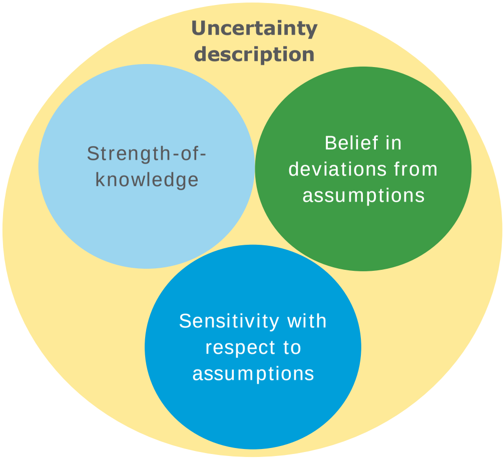
Uncertainty and Data Quality

Uncertainty

- Two types of uncertainty:

- Parameter Uncertainty
  - Uncertainty in experimental measurements made
- Model Uncertainty
  - Uncertainty related to assumptions in model and physics behind the models
  - Want to understand which assumptions the model is most sensitive to
  - Aim to reduce the influence of assumptions made

Summary of Uncertainty Drivers



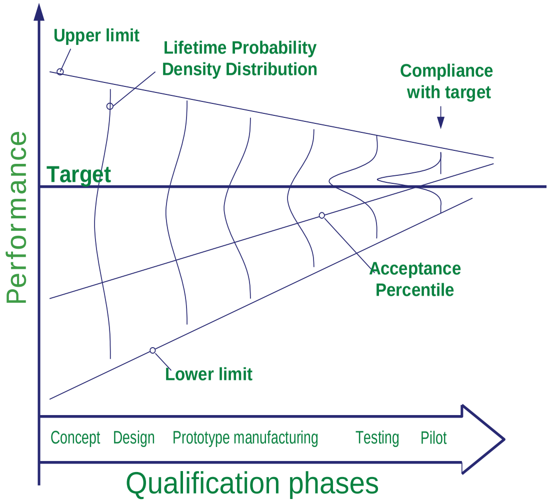
Uncertainty description

Strength-of-knowledge

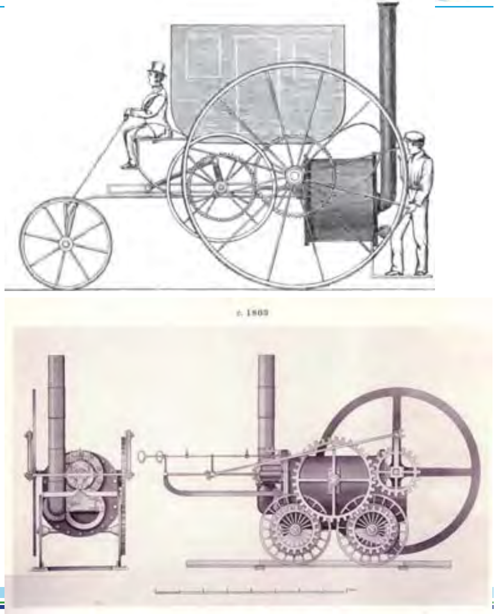
Belief in deviations from assumptions

Sensitivity with respect to assumptions

Uncertainty – A double edged sword



Seeing the Potential of Novel Technologies



Thanks very much

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SAFER, SMARTER, GREENER

Comparative Overview of Costs for Capture Technologies

Prof. Dianne Wiley
Program Manager (Capture)
Cooperative Research Centre
for Greenhouse Gas Technologies
(CO2CRC)

Breakthrough Post Combustion Capture Technologies
HiPerCap Workshop, Melbourne
March 25-27, 2015

The role of CCS economics

- **Economics is one of the four elements of quadruple bottom line business decision making**
- **Decisions also need to ensure sustainable management of risk and reliability**
- **Technology assessments used to support decisions on technology selection, capital investments, marketing strategies, R&D priorities, and related activities.**
  - Understand where and what the cost drivers are to enable development of novel and creative ways to reduce cost.

Measures of CCS economics

- **Indirect**
  - Energy penalty
  - CO_2 avoided/emission intensity
- **Direct**
  - Cost/Present Value (PV, $)
  - Cost of CO_2 avoided/captured/injected (($/t $CO_{2\ avoided/captured}$)
  - Production cost (eg. LCOE $/MWh, $/ton steel etc.)

Techno-economic assessments

- **Compare costs of alternative options.**
- **Differences reflect different configurations and operating alternatives.**
  - Relativities just as important as absolute values.
- **Rely on “technology-levelling” assumptions.**
  - Process assumptions e.g. plant size, fuel type, capacity factor, reference plant.
  - Economic assumptions e.g. cost of capital, cost year, discount rate, energy/fuel costs, nominal vs. real costs, project life.
- **Require appropriate technology benchmark.**

Reducing capture costs

Reduce!

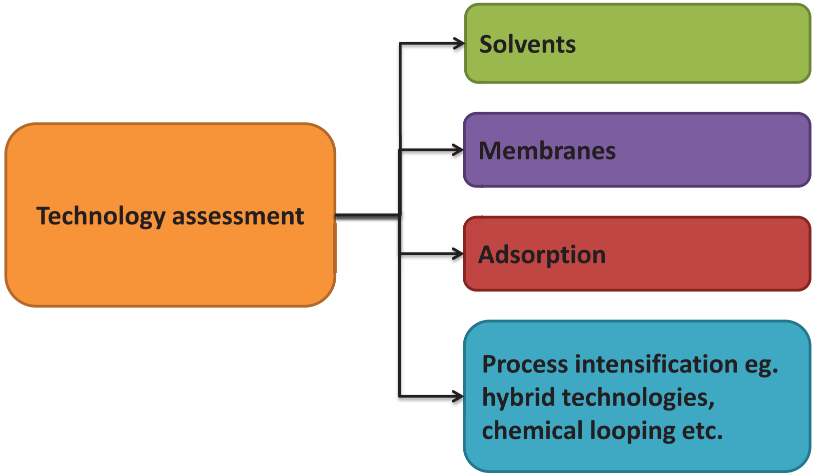
$$\frac{\$}{tonne\ CO_2\ avoided} = \frac{PV_{AllCosts}}{PV_{CO_2\ avoided}}$$

Reduce!

Increase!

- **Reduce Capital costs**
  - cheaper equipment
  - more efficient (smaller) equipment
- **Reduce Operating costs**
  - more efficient equipment
  - less energy demand
- **Reduce energy penalty**
  - use improved technologies
  - heat and process integration
- **Increase CO_2 captured**
  - improve capture efficiency
  - improve capture rate
- **Reduce CO_2 emitted**
  - improve process efficiency
  - change fuel
- **Increase energy efficiency**
  - heat and process integration

Capture economics



Technology assessment

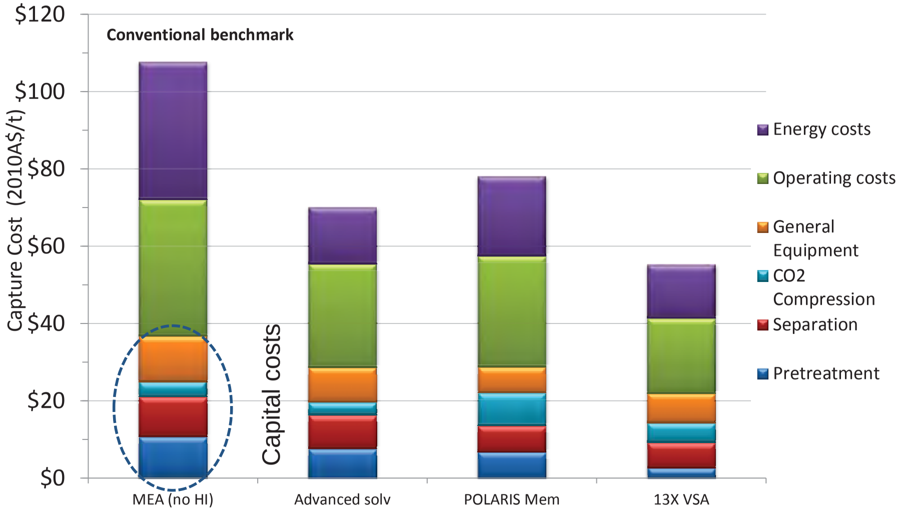
Solvents

Membranes

Adsorption

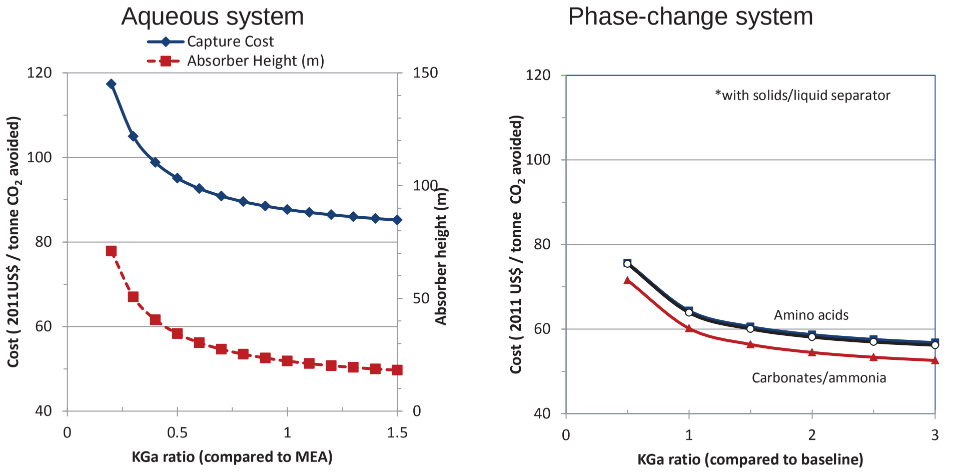
Process intensification eg. hybrid technologies, chemical looping etc.

Technology comparison (500 MW black Australian coal power plant)



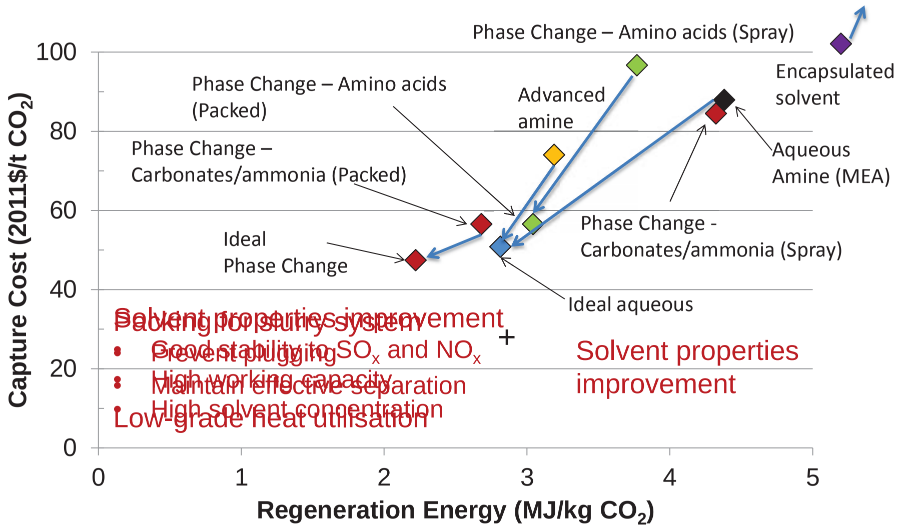
Adapted from: Stevens et al. Post-combustion Carbon Dioxide Capture Technologies for Brown Coal Power Generation - Final report for Brown Coal Innovation Australia (Condensed Version).CO2CRC Publication Number RPT11-2962

Solvent improvement: size and capital costs

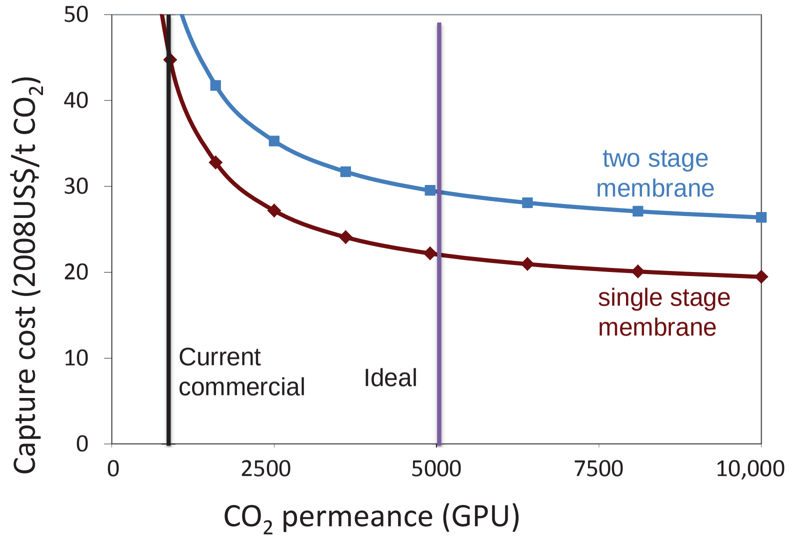


Adapted from: Raksajati et al (2013) 'Reducing the cost of capture from flue gas using aqueous chemical absorption' IECR 52 16887

Solvent improvement: reducing energy

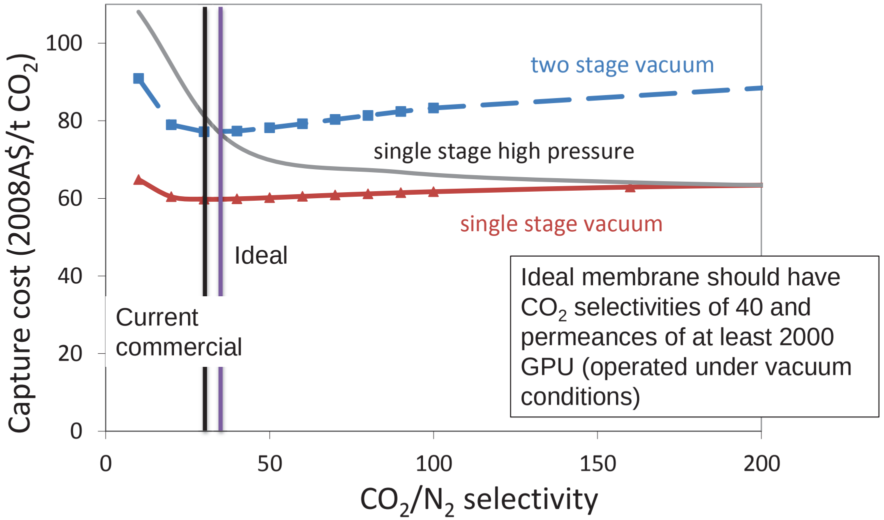


Membrane improvement: size and cost



Adapted from: Ho et al (2008) 'Reducing the cost of capture from flue gas using membrane technology' IECR 47 1562-1568

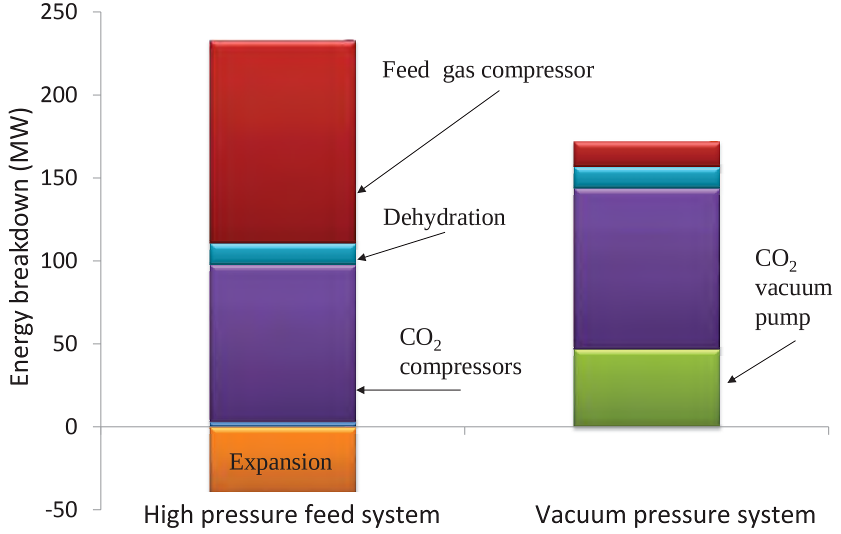
Membrane improvement: compression energy



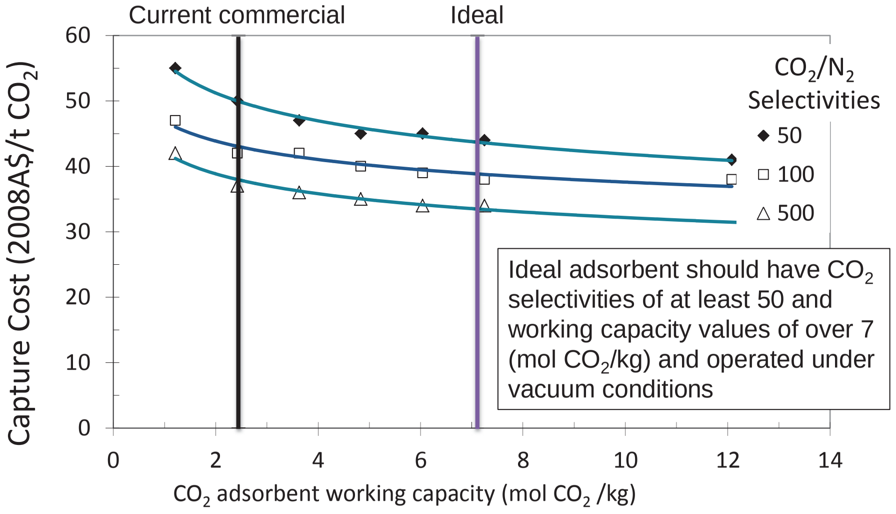
Ideal membrane should have CO$_2$ selectivities of 40 and permeances of at least 2000 GPU (operated under vacuum conditions)

Adapted from: Ho et al (2008) 'Reducing the cost of capture from flue gas using membrane technology' IECR 47 1562-1568

Adsorption development: compression energy



Adsorption improvement: size, energy, cost

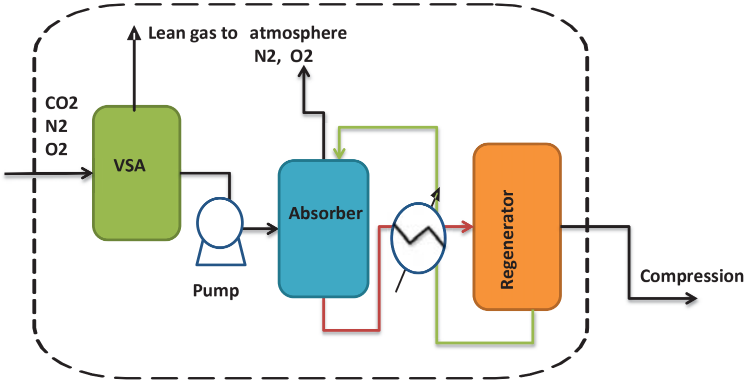


Ideal adsorbent should have CO$_2$ selectivities of at least 50 and working capacity values of over 7 (mol CO$_2$/kg) and operated under vacuum conditions

Adapted from: Ho et al (2008) 'Reducing the cost of capture from flue gas using pressure swing adsorption' IECR 47 4883-4890

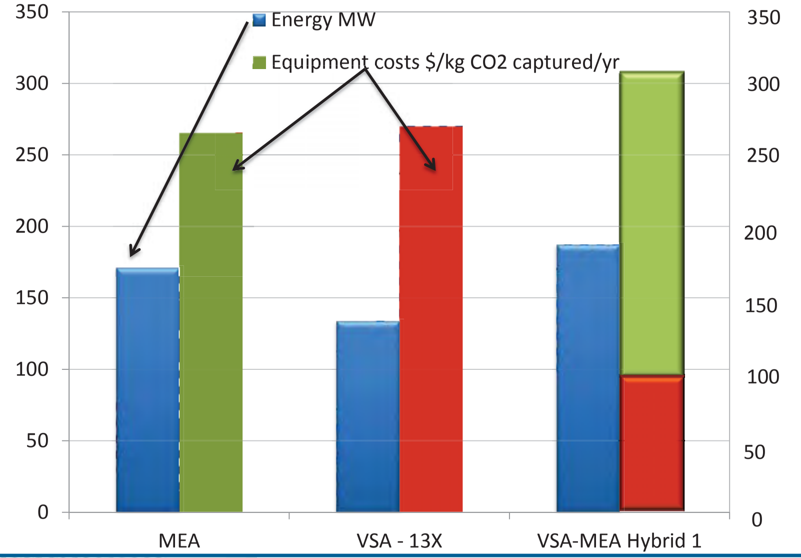
Process intensification: Hybrid capture

- Combination of adsorption and solvent technologies, membrane and solvent, adsorption and cryogenic etc.

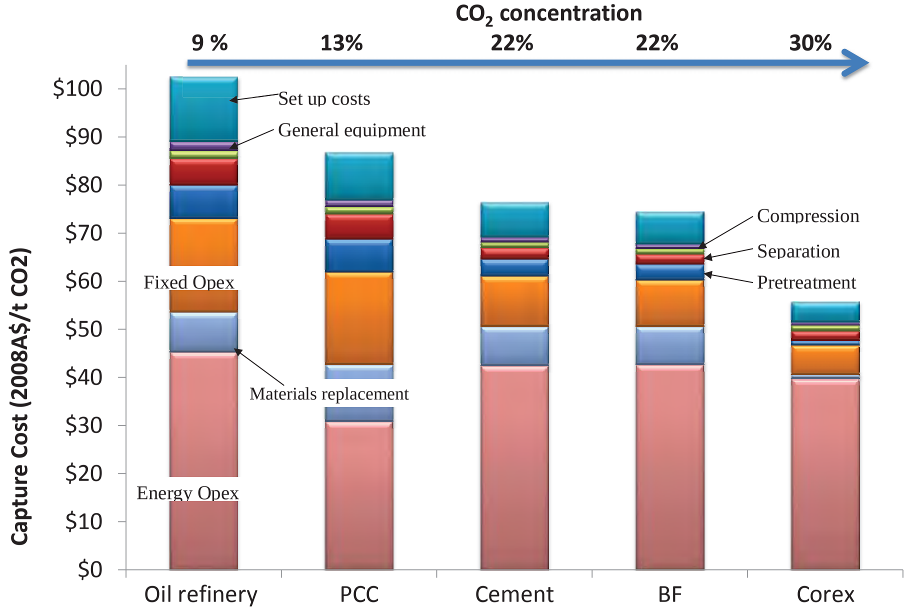


Adsorption + Solvent Hybrid Separation

Energy and costs of VSA-solvent hybrid



Effects of emission source on costs



Adapted from: Ho et al (2010) Comparison of MEA capture cost for low CO2 emissions sources in Australia, IJGGC 5(1):49-60.

Comparison of capture development options

Parameter	Solvents	Membranes	Adsorption
Capital cost	🟥	🟥	🟨

Other factors to consider

- Tolerance to impurities (SO_x, NO_x, water)
- Process configuration design and optimisation
- Optimising operating conditions
- Heat integration
- Load following and process flexibility

Conclusions from comparative costing

- **Technology improvement driven by reductions in:**
  - Energy usage
  - Capital costs (size of equipment, level of pretreatment)
  - Operating costs (materials replacement)
- **Application dependent**
  - No silver bullet
  - Technology specific intensification and integration
- **Relies on consistent benchmarks and assumptions**

CO2CRC Participants

Supporting Partners: The Global CCS Institute | The University of Queensland | Process Group | Lawrence Berkeley National Laboratory
CANSYD Australia | Government of South Australia | Charles Darwin University | Simon Fraser University

ENERGY

Benchmarking

Novel carbon capture technologies

Gerben Jans, Gerard Stienstra and Bert Heesink
26 MARCH 2015

Key elements of this presentation

- Benchmarking:
  - Why?
  - How?
- Benchmarking of technologies in early stage of development
- Experiences of DNV GL at the Carbon Capture Mongstad project

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DNV GL Energy

- An Energy Powerhouse uniting the strength of well-known brands: **DNV GL - Energy** combines the strengths and rich heritage of a couple well-known brands in energy, **DNV KEMA, GL Garrad Hassan** and **GL Renewables Certification**.

- In energy, our **3,000 experts** help customers throughout the electrical power industry realize efficient, reliable and clean energy, for today and the future.

DNV GL Energy - A Comprehensive Portfolio of Services

- Power testing, inspections and certification
- Renewables advisory services
- Renewables certification
- Electricity transmission and distribution
- Electricity production
- Smart grids and smart cities
- Energy market and policy design
- Energy management and operations services
- Energy efficiency services
- Software

Benchmarking is part of our Energy Business Decision Support-services

- Benchmarking
- Due Diligence
- Technical Consultancy
- Electricity Market Regulation Consultancy
- Roadmaps Future Energy Systems
- Technology (Development) Assessments
- Electricity Master Planning
- Market Analysis & Modelling Services

Definition Benchmarking *(European Benchmarking code of conduct):*
"Benchmarking is about the process of identifying and learning from best practices in other organizations"

What is benchmarking?

One of the first Benchmarks

The origin of the term **bench mark**, or **benchmark**,

- Chiselled horizontal marks made by surveyors in stone structures,
- Used to place an angle-iron in to form a "bench" for a levelling rod
- So this levelling rod could be replaced on the exact same level

Source: Wikipedia

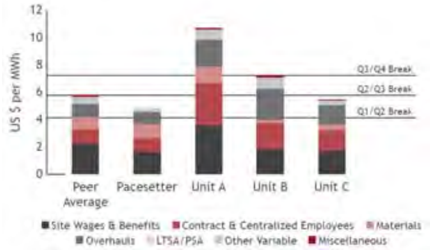
Source: http://www.waymarking.com

Goal of benchmarking

Two types of goals

1. Metrics Benchmarking
   (to determine (relative)
   position in own sector)

Learn *were you are, compared to others*



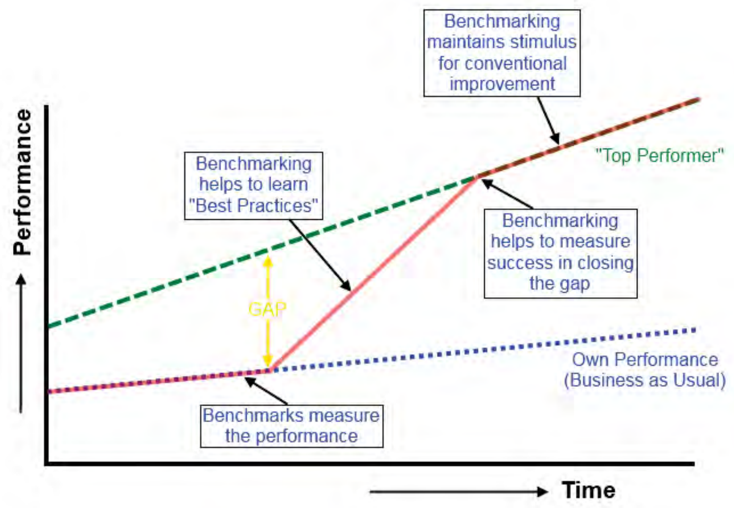
Source: http://www.solomononline.com

2. Activity Benchmarking (find & implement 'Best Practices')

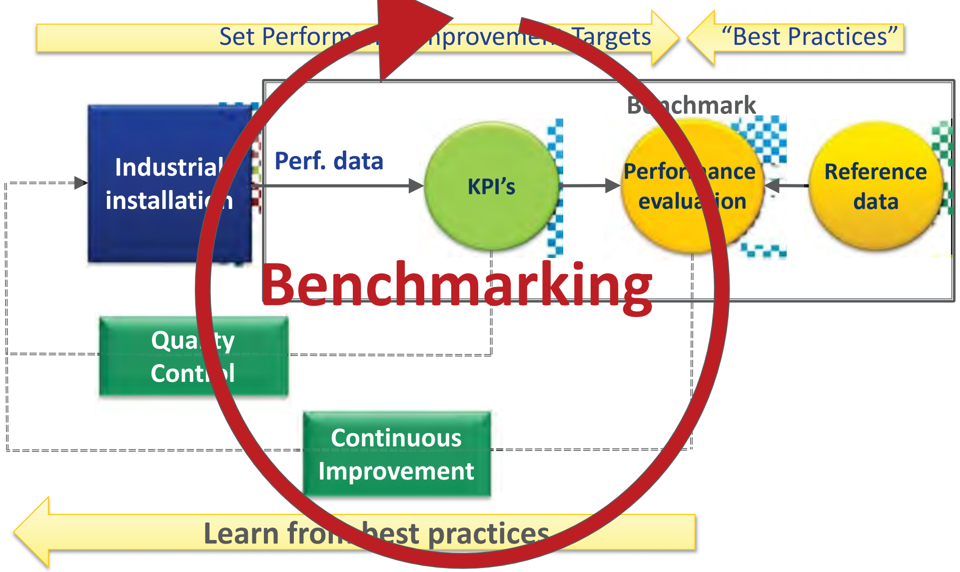
According to the European Benchmarking Code of conduct "Benchmarking is about the process of identifying and ***learning*** *from best practices in other organizations "*

Benchmarking is about learning

Goal of activity benchmarking

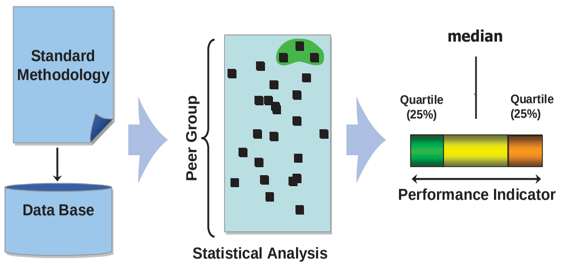


Benchmarking cycle

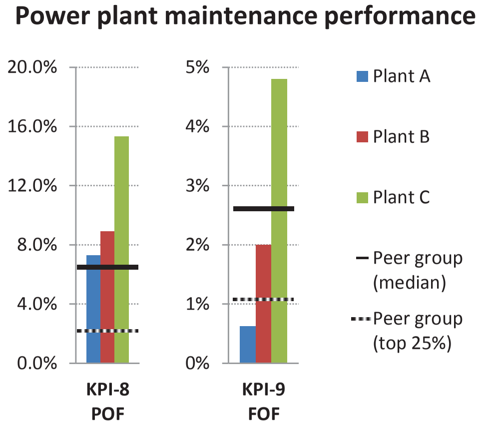


KPI's and reference data explained

- A KPI is
  - a performance measurement
  - defined by a set of values used to measure against
  - based on math that is the same for all situations
  - used to evaluate the success of a particular activity in which it is engaged
- Preferred reference data is obtained from a **peer group**



Example results

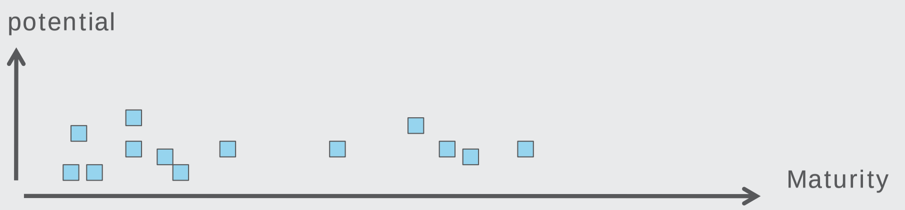


POF = Planned Outage Factor

FOF = Forced Outage Factor

Benchmarking of technologies in early stage of development

Novel Technologies



Different technologies, different potential, different maturity

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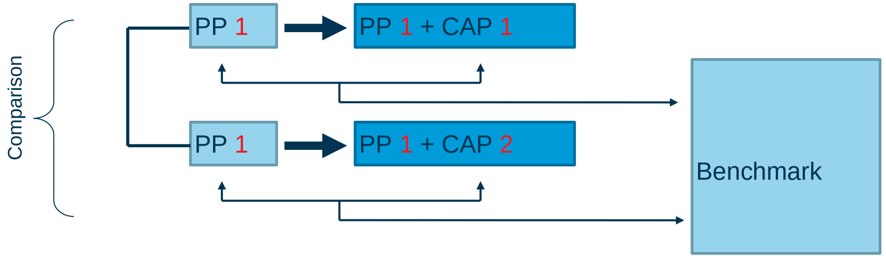
Issues for the benchmarking model

- No reference performance data available -> no peer group
  - Other reference needed?
- Not the same level of maturity (model ≠ pilot ≠ demo ≠ full scale)
  - How to scale for comparison across maturity?
- Scaling means uncertainty
  - What to do with uncertainty?

How to deal with these issues?

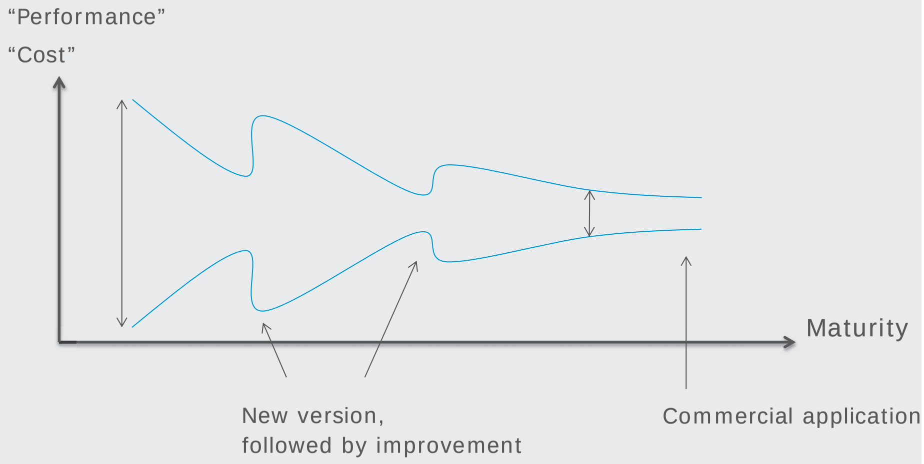
Reference

- When a peer group doesn't exist one could use a well defined reference plant.

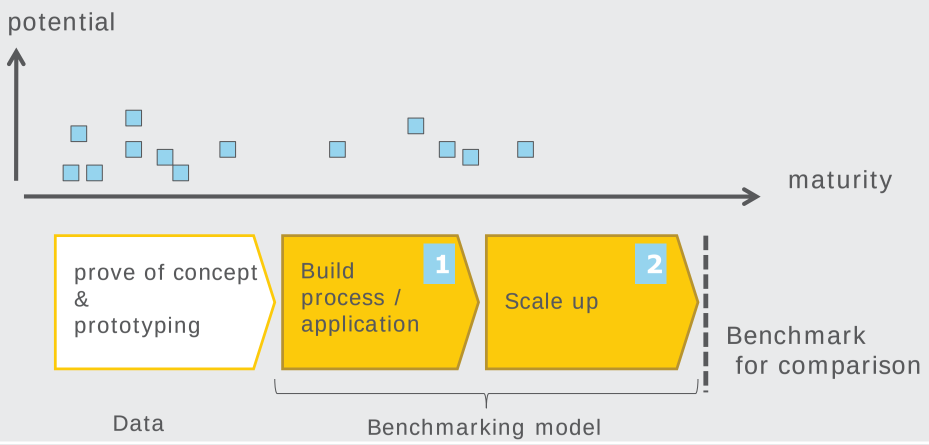


1. Reference plant
2. Plant to be benchmarked

Uncertainty



Benchmarking model



Concept of benchmarking: bringing performance indicators to one (artificial) level for comparison, generally executed by an independent 3rd party

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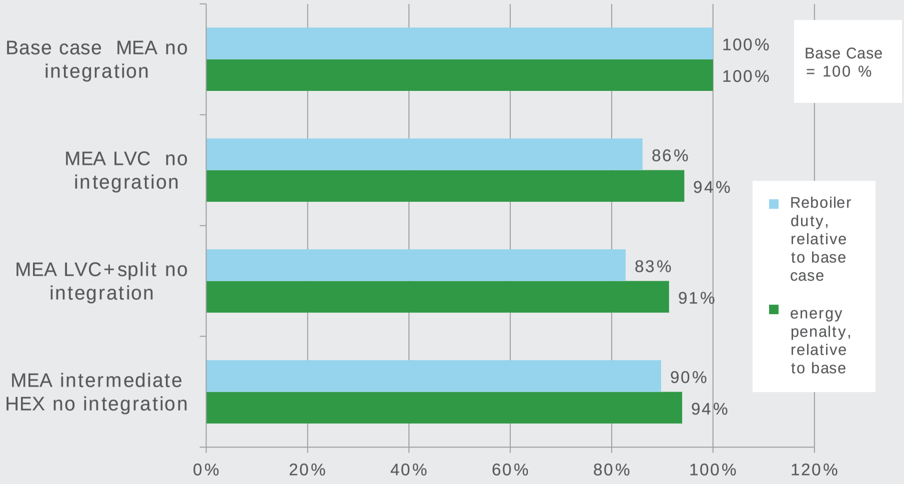
Example results: ROAD 250 MW$_e$ DEMO - design alternatives



Net Electrical output and reboiler duty compared: illustrative of the need to have a model to bring all inputs to the same level of comparison. source: de Miguel Mercader et al, IJGGC, 2013

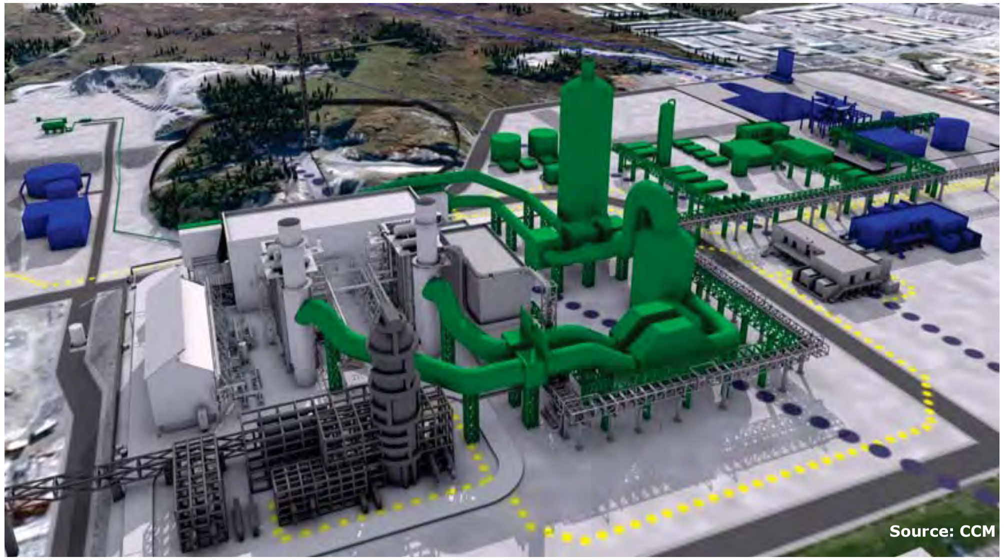
Let’s take a side-step -
Example use of TRL
Carbon Capture Mongstad (CCM)

New gas fired CHP plant at Mongstad Refinery (2010)

CCM Agreement

- CHP plant may be operated on the condition that CO_2 is captured and stored
- Max. capacity 1.3 Mton/yr
- Start-up foreseen in 2020
- Only amine based and ammonium carbonate based technologies considered

Typical post-combustion CO_2 capture plant



Source: CCM

Participating Technology Vendors

1. Huaneng CERI Powerspan
   – Proprietary amine based ECO_2 solvent
2. Siemens
   – Proprietary amino acid salt based AAS solvent
3. Aker Clean Carbon (ACC)
   – Proprietary amine based S-21 solvent
4. Mitsubishi Heavy Industries (MHI)
   – Proprietary amine based KS-1 solvent
5. Alstom
   – Ammonium carbonate solvent

POWERSPAN Clean Energy Technology

中国华能集团公司 CHINA HUANENG GROUP

SIEMENS

AkerSolutions

MITSUBISHI HEAVY INDUSTRIES, LTD.

ALSTOM

Technology qualification process

Qualification Basis

Technology Assessment

Threat Assessment

Qualification Plan

Execution of plan

Performance Assessment

Technology Deployment

Executed by Statoil + Technology Vendors

Our main task “*follow-up, verification and evaluation of all technology qualification activities*”

Goals:

- **Prove capture plant is TRL 4***
- Energy performance meet minimum requirements
- Emissions meet minimum requirements

*According to Statoil WR-1622

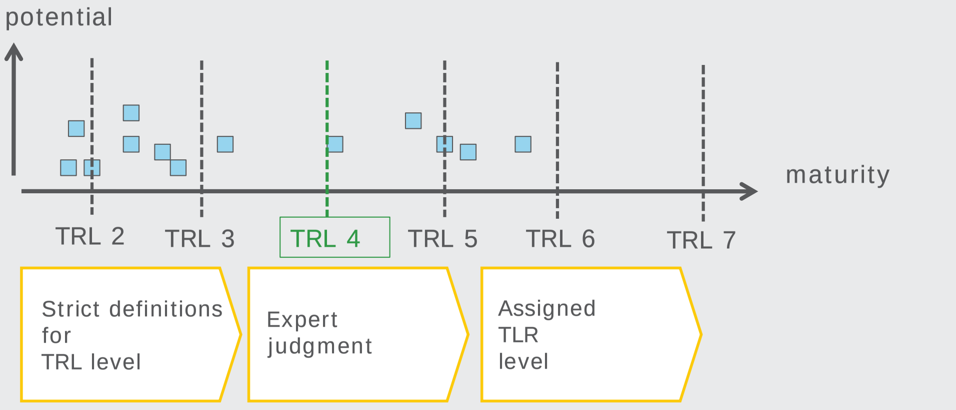
Technology Readiness Level goal

TRL 4: Representative of full scale prototype (or production unit) built and put through a qualification test program in (simulated or actual) intended environment

Technology Readiness Level (Statoil WR-1622)

Level	Development stage
TRL 0	Unproven Idea
TRL 1	Analytically Proven Concept
TRL 2	Physically Proven Concept
TRL 3	Prototype Tested
TRL 4	**Environment Tested**
TRL 5	System Integration Tested
TRL 6	System Installed
TRL 7	Proven Technology

Technology Readiness Levels



Technology qualification process

Executed by Statoil + Technology Vendors

Our main task "*follow-up, verification and evaluation of all technology qualification activities*"

Goals:

- **Prove capture plant is TRL 4***
- Energy performance meet minimum requirements
- Emissions meet minimum requirements

*According to Statoil WR-1622

Main development risks identified

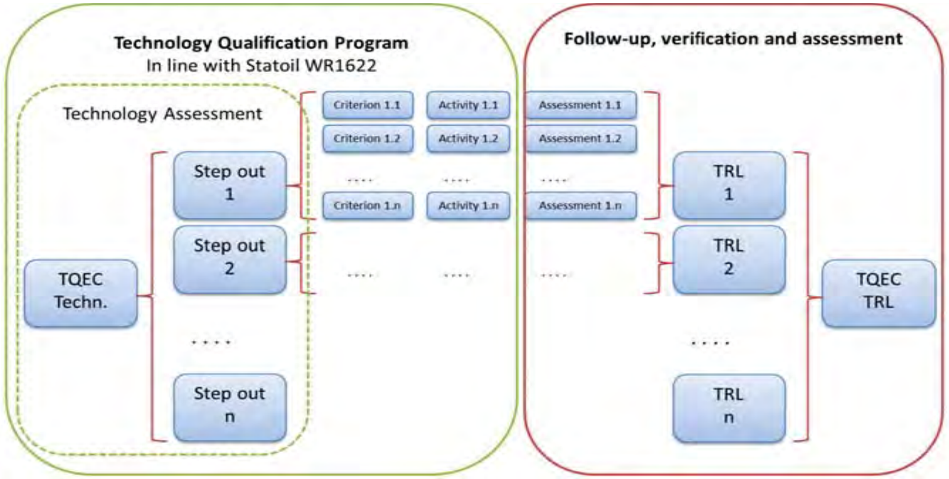
- Scale-up of absorber (and stripper)

(Diameter 0.5 m) (Diameter ~20 m)

- Severe solvent degradation
  - O_2 and NO_x in flue gas
- H&E aspects
  - Carcinogenic nitrosamines and nitramines
  - Amines and other degradation products
  - Waste (water)
  - NH_3

TRL assessed per technology step out category

- Example step out A: (design and scale-up of) Absorber



Technology Qualification Program
In line with Statoil WR1622

Technology Assessment

TQEC Techn.

Step out 1

Step out 2

. . . .

Step out n

Criterion 1.1
Criterion 1.2
. . . .
Criterion 1.n

Activity 1.1
Activity 1.2
. . . .
Activity 1.n

Follow-up, verification and assessment

Assessment 1.1
Assessment 1.2
. . . .
Assessment 1.n

TRL 1

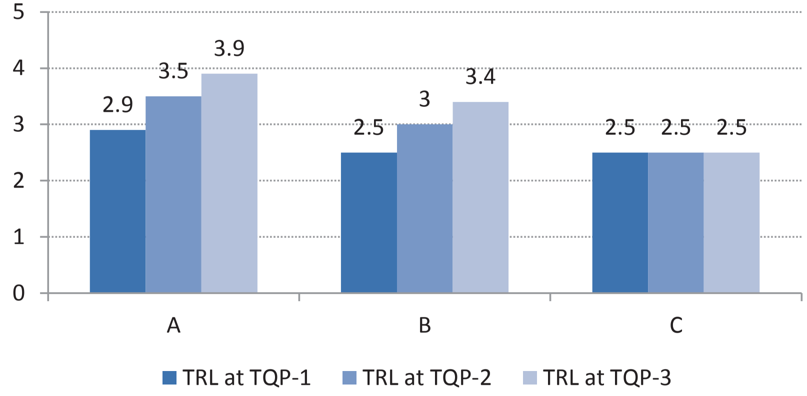
TRL 2

. . . .

TRL n

TQEC TRL

TRL assessment of technology vendors on three project phases



Because of confidentiality reasons, these numbers are not corresponding to the actual outcome of the CCM project

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Technology Center Mongstad
source: http://www.gassnova.no

TRL 4 ?

Thanks

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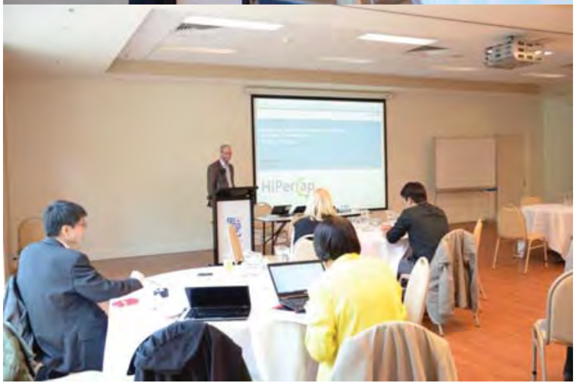
SAFER, SMARTER, GREENER

Various pictures from the workshop




HiPerCap


BACKGROUND
OBJECTIVE
DYNAMIC MODELS
CONTROL STRATEGIES
UNIVERSITY COLLEGE