Latest trends of membrane technologies in Norway and Europe

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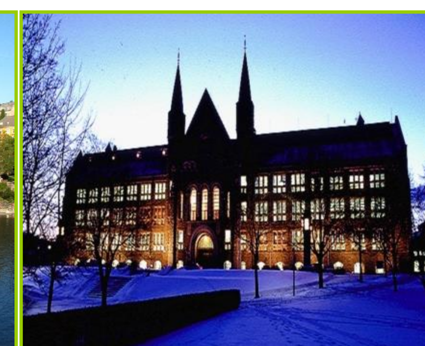
at

Symposium for Innovative CO2 Membrane Separation Technology
Tokyo February 2nd 2015

Norwegian University of Science and Technology

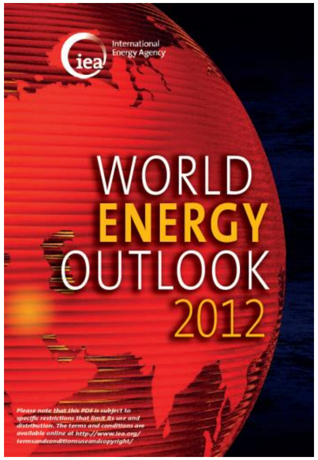


Outline

- Background - Why is CCS important?
- CO2 capture with membranes
  - General
  - Membrane research and innovation in Memfo - NTNU
- Some pilot demonstration projects
- Introducing Sintef MC – membranes – Norway
- Introducing selected institutions in Europe / membrane research
- A brief look at other capture technologies
- Summing up

WEO2012:
Important question: Do we need CCS?

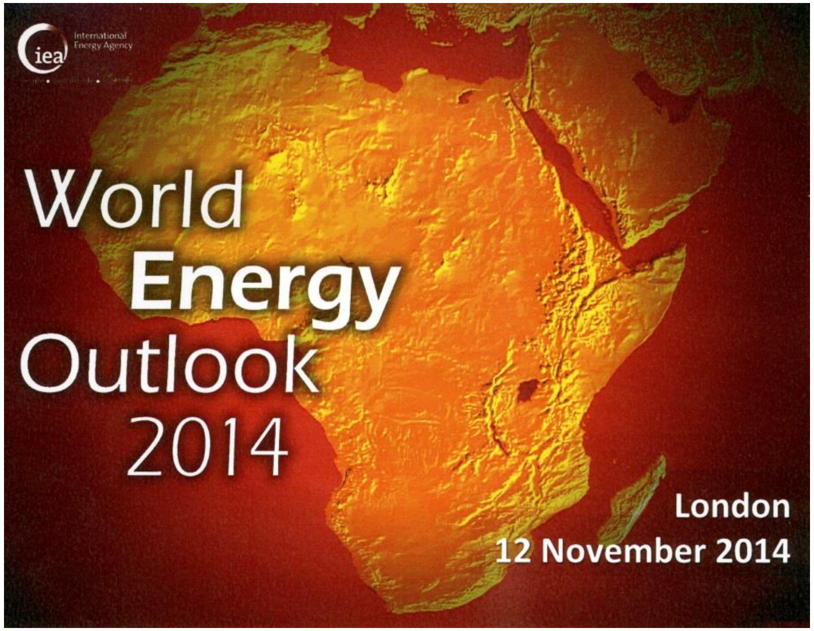


- *No more than one-third of proven reserves of fossil fuels can be consumed prior to 2050 if the world is to achieve the 2 °C goal, unless carbon capture and storage (CCS) technology is widely deployed. This finding is based on our assessment of global "carbon reserves", measured as the potential CO_2 emissions from proven fossil-fuel reserves.*

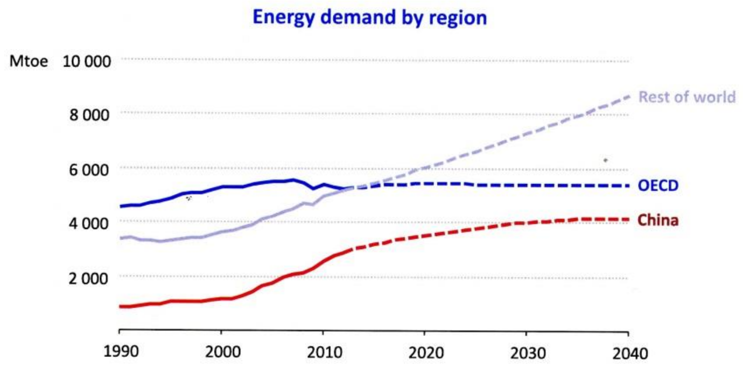
- *Almost two-thirds of these carbon reserves are related to coal, 22% to oil and 15% to gas. Geographically, two-thirds are held by North America, the Middle East, China and Russia.*

- *These findings underline the importance of CCS as a key option to mitigate CO_2 emissions, but its pace of deployment remains highly uncertain, with only a handful of commercial scale projects currently in operation."*

WEO 2014: *Underlining why CCS is important:*



- MIXED SIGNALS upfront climate summit in Paris in 2015:
  - Global CO_2 emissions are still rising
  - Increasing emphasis on energy efficiency is starting to bring results



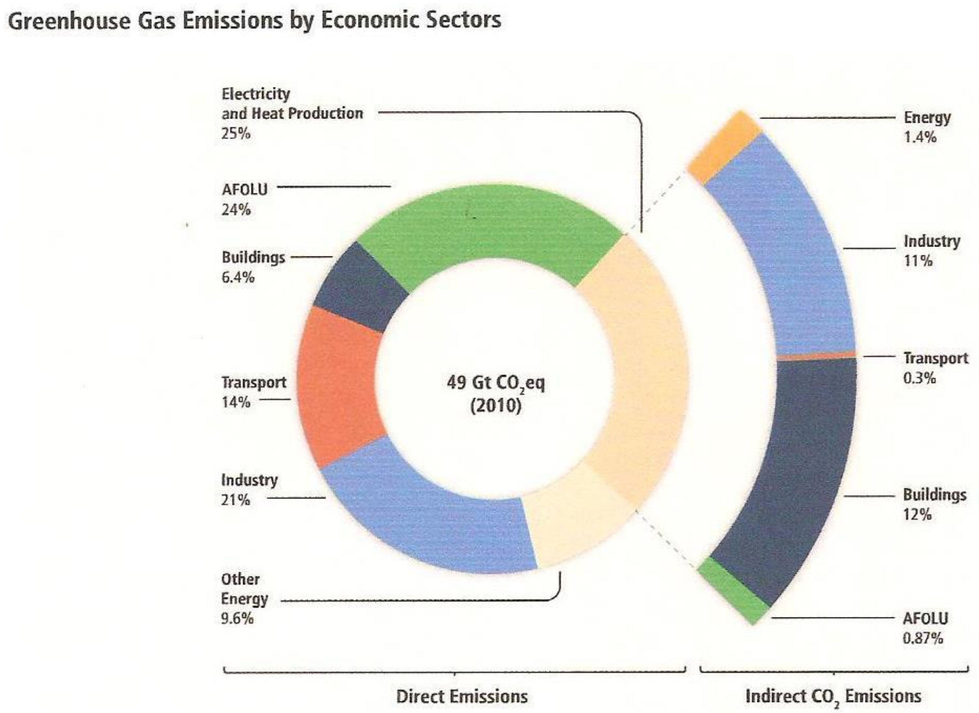
As China slows, then India, Southeast Asia, the Middle East and parts of Africa & Latin America take over as the engines of global energy demand growth.

HOWEVER:

- Without clear directions from Paris in 2015, the world is set for warming well beyong the 2°C goal – *and we will then see a dramatic change in life and environment on earth*

We need CCS!

And with MEMBRANE TECHNOLOGY we can contribute to solve this problem!



Total anthropogenic GHG emmissions (GtCO2eq/yr) by economic sectors. Inner circle shows direct GHG emission shares % of total anthropogenic GHG emissions, and show how electricity and heat production are attributed to sectors of final energy use.

Source: IPCC, 5th assessment report, Mitigation of climate change

NTNU

CCS is needed in order to reach the 2°C Goal!
Alternative CO_2 capture technologies – overview:

CO_2 Capture Technology

Post-combustion	Pre-combustion	Oxyfuel combustion	Industrial gas separation

Separation Methods

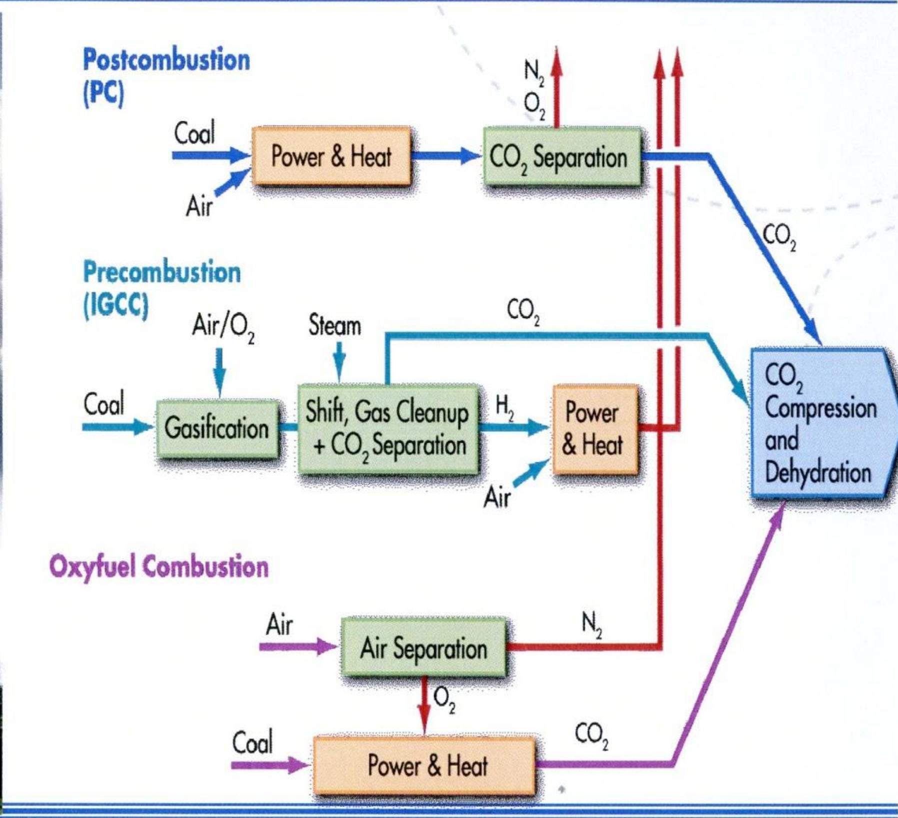
Chemical and physical absorption	Physical adsorption	Membrane	Cryogenic distillation	Chemical looping

Materials

Chemical and physical absorption	Physical adsorption	Membrane	Chemical looping
• MEA, MDEA • Selexol, Rectosil • ILs	• Microporous materials Zeolite, MOFs • PSA, TSA	• Inorganic • Polymeric • Hybrid	• Metal oxides CuO

Membrane technologies for CO2 capture

Challenges: fly ash, SOx and NOx



- *Depending on where in the process the membrane will be placed, the transport mechanisms and demands on the material will be very different*

Which possibilities do we have?

Membrane R&D in Norway

- MEMFO – membrane research group at DCE - NTNU
  - About the group
  - Membranes being researched
  - Pilot projects – the long road towards commercialization
- SINTEF Materials and Chemistry (Oslo-Trondheim)

Membrane research in MEMFO

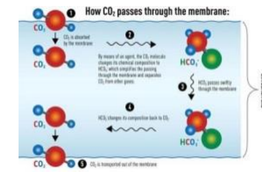
Main Fields of Research:

- Material technology – membrane development
- Membranes for (industrial) gas applications
- (eg: CO_2, CH_4, H_2, N_2, O_2, VOC, Cl_2, SF_6....)
- Membranes for renewable energy (biogas, H_2)
- Design of environmental friendly processes
- Simulation & optimization of (integrated) membrane processes
- Scaling up for pilot testing

More Recent Fields of Research:

- Membrane development for PRO processes (saline power)
- Membranes in bioprocessing; biodiesel & bioethanol
- Membrane contactors for gas-liquid (CO_2 from NG)
- Membrane contactors using ionic liquids

Material technology – membrane development



- Polymeric based materials - *examples*
  - PVAm; pure and blended (facilitated transport for CO_2 capture)
  - Matrimid /Chitosan/CMS/MOFs (mixed matrix; fundamental studies)
  - PMP/PTMSP/nanoparticles (nanocomposites; fundamental studies)

- Carbon Molecular Sieves *(basis for the company MemfoACT)*
  - CMS membranes from cellulosic precursor; tailored for CO_2 - H_2 or CO2-CH4 separation

- Glass Membranes (*first collaboration Japan 1999 – AIST and Himeji)*
  - surface modified for separation of aggressive gases; Cl_2, HCl…)

- Development of membranes on pilot scale *(three projects ongoing)*
  - hollow fibres – flat sheets

”The upper bond” with respect to driving force for polymeric membranes

➢ The upper-bond must be broken for the gas pair CO_2-N_2 if membranes are to be used in ***post-combustion***.

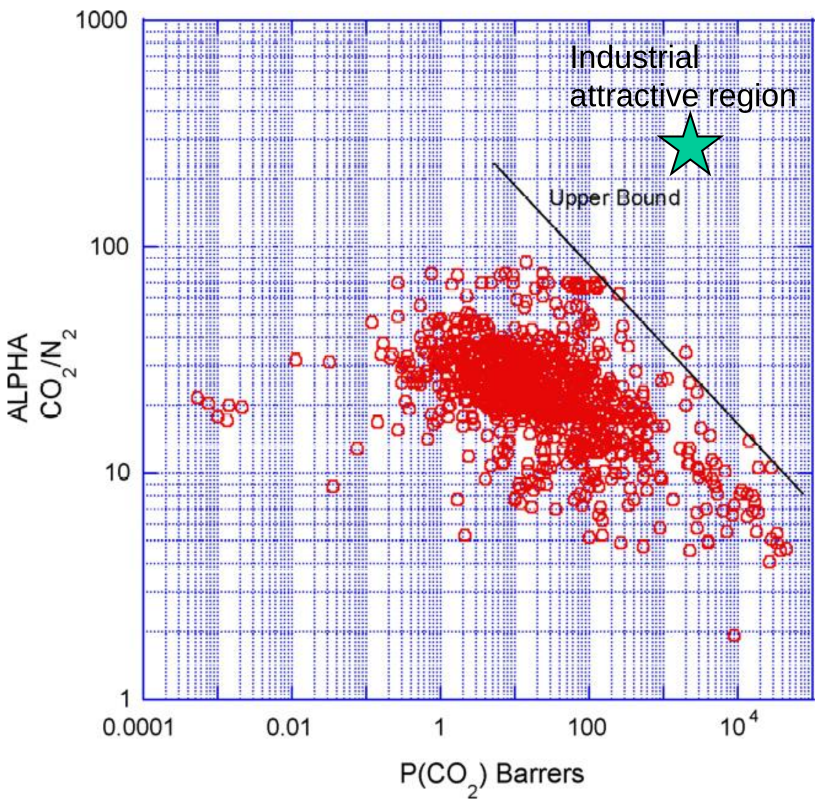
This can be done in several ways:

1) Facilitated transport membranes
2) Nanocomposite materials
3) Pore tailored inorganic membranes

Two other ways to neglect upper-bond:

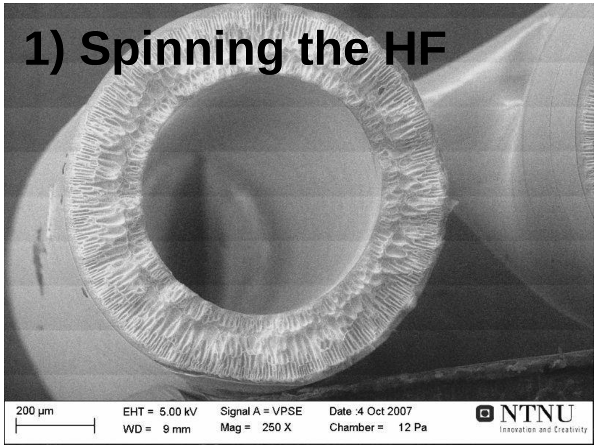
➢ Using membrane contactors
➢ Innovative process design

At NTNU we work with all these types of membranes

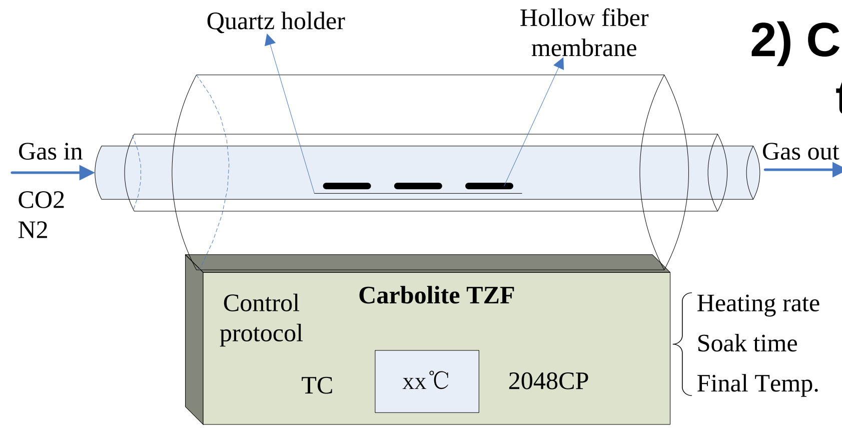


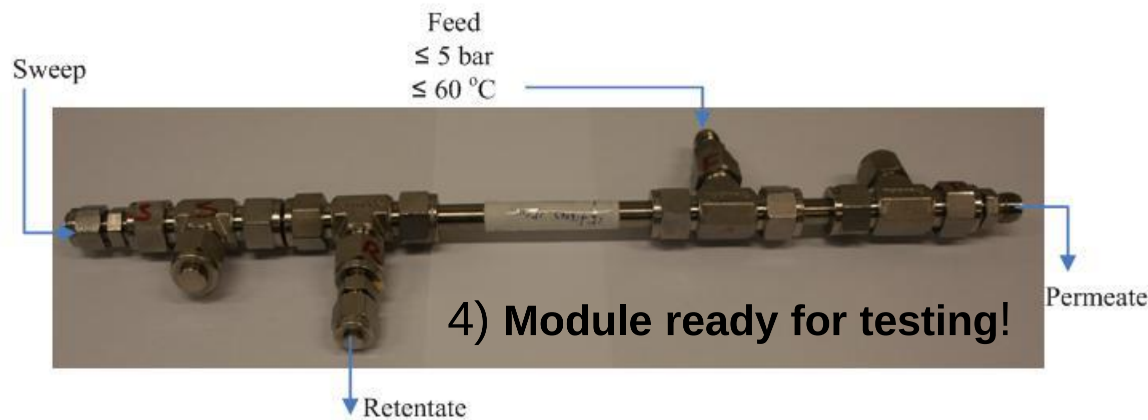
1) Carbon Molecular Sieve (CMS membranes) are pore tailored membranes and can be used up to 500°C

Pore tailored for : H2–CO2 (precombustion), CO2–CH4 (NG and biogas)



2) Carbonizing the HF



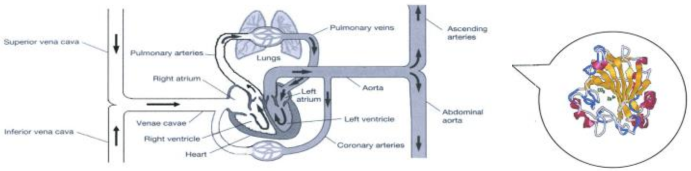


2) Several types of untraditional materials for membranes are being investigated

- Hybrid materials / Blends / Nanocomposites /Functionalized
  - *Show nice potential, only demonstrated in lab*

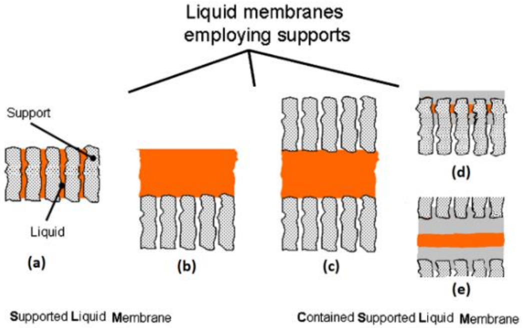
Self-organized PVAc with ZA4

- Enzymes and mobile carriers
  - *ex. in membrane contactors*

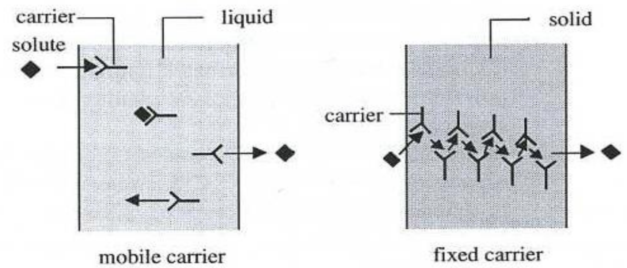


The enzyme carbonic andyhrase (CA) helps to transport CO_2 as HCO_3^-

- Supported Ionic Liquid Membranes (SILM)



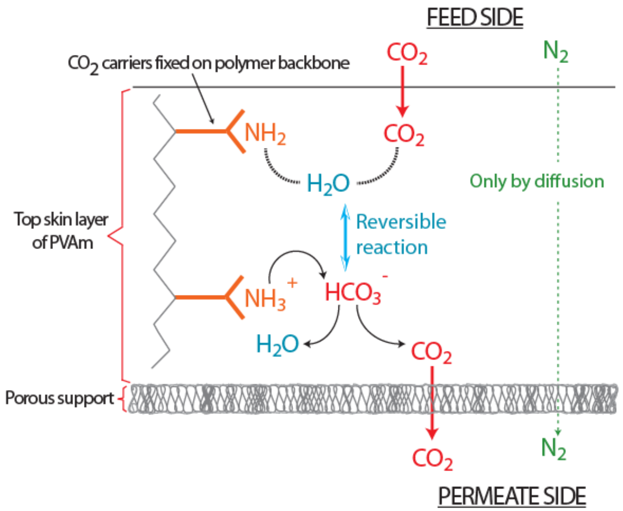
- Fixed Site Carriers (FSC) with facilitated transport



3) Facilitated transport by a "fixed-site-carrier"

- *example, PVAm as developed at NTNU, for CO2 – N2 sep.*

- *Mechanism of separation*: diffusion through a non-porous (swelled) membrane + carrier transport.



Mimicking nature: Separation by solution-diffusion and the fixed amine carrier

$$J_i = \frac{D_i}{l}\left(c_{i,0} - c_{i,l}\right) + \frac{D_{ic}}{l}\left(c_{ic,0} - c_{ic,l}\right)$$

Right hand side: 1st term: Fickian diffusion, 2nd term: facilitated transport

Facilitated transport in polyvinylamine (PVAm):

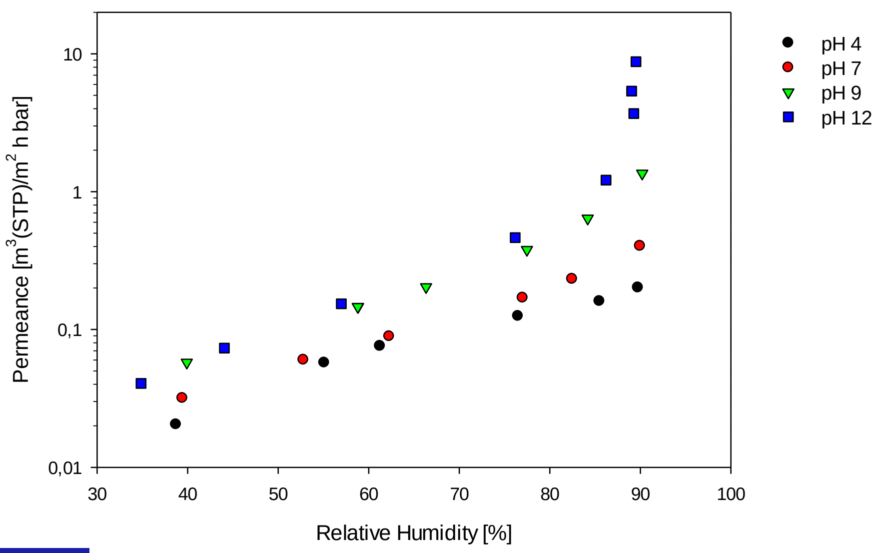
–The amino group contributes to transport of CO_2 through membrane as a bicarbonate ion (HCO_3-) in the wet membrane while N_2 is only transported by diffusion.

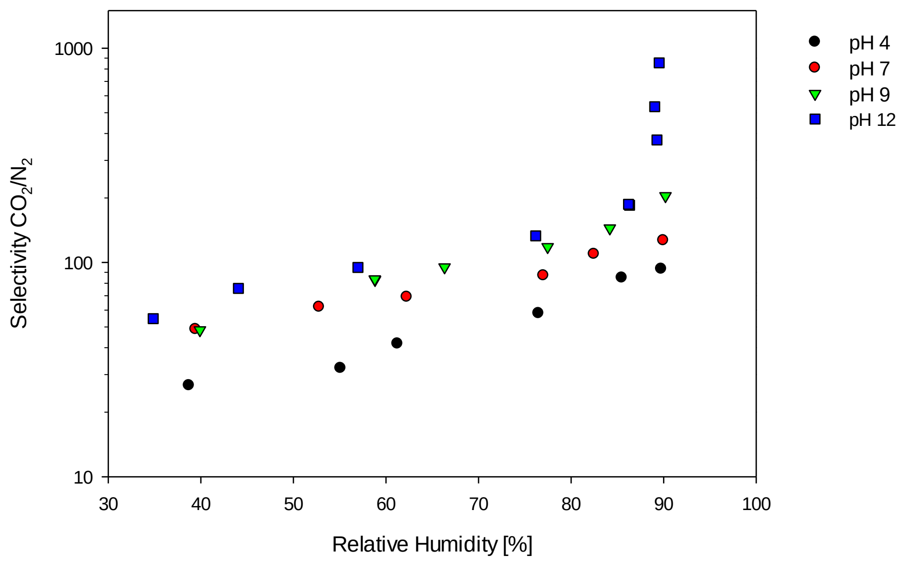
– CO_2 transport through the membrane is attributed to this carrier effect along with the Fickian diffusion.

Adjusting the pH of casting solution gave dramatic increase in performance *(below, results from 2012)*

Gas Mixture: 10%CO_2 – 90% N_2

Process conditions: Feed at 1.2 bar, 35°C
Slight vacuum on permeate side

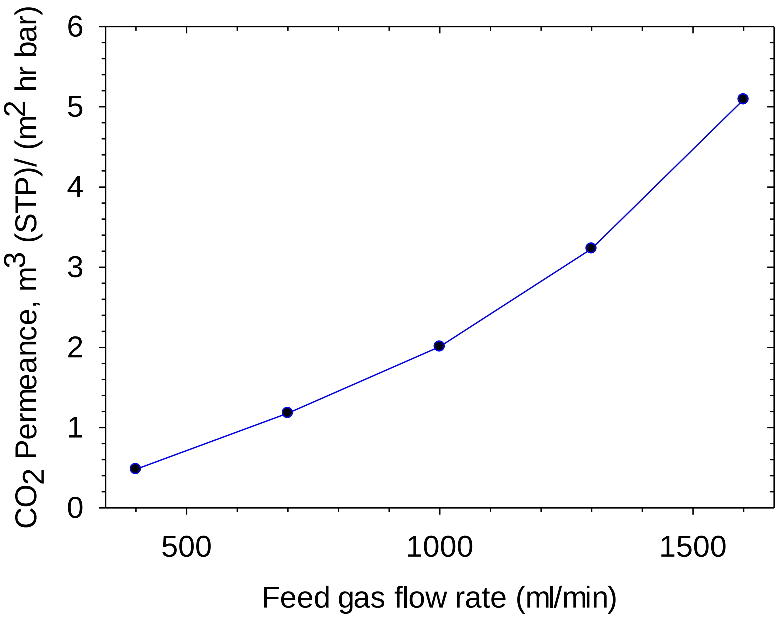


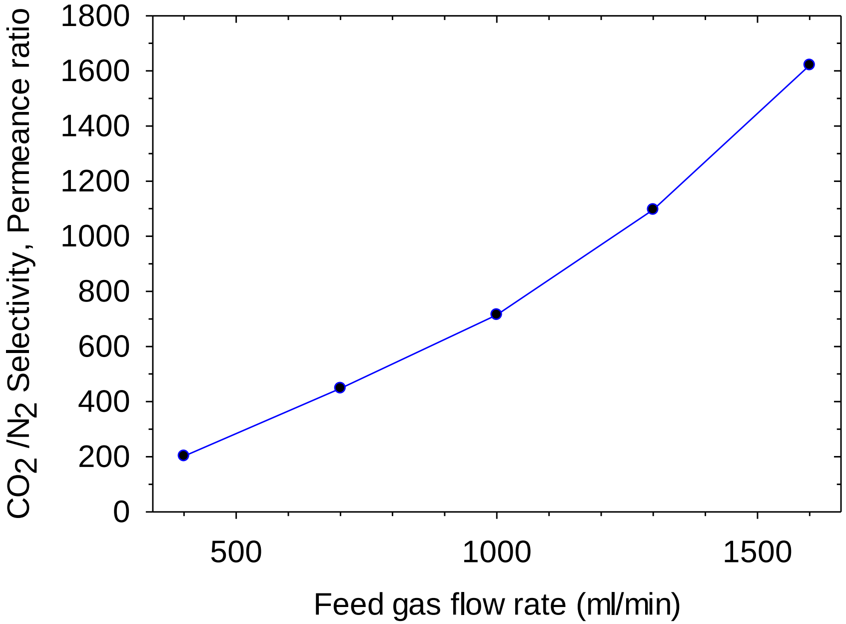


pH = 10 was set as standard for the casting solution
As documented, humidity is of major importance for the separation – flue gas is saturated with humidity.
The support material for PVAm is Polysulfone (PSf)

Process conditions are important also on larger scale -

- Results 2012 using a flat sheet small pilot, varying feed flow rate

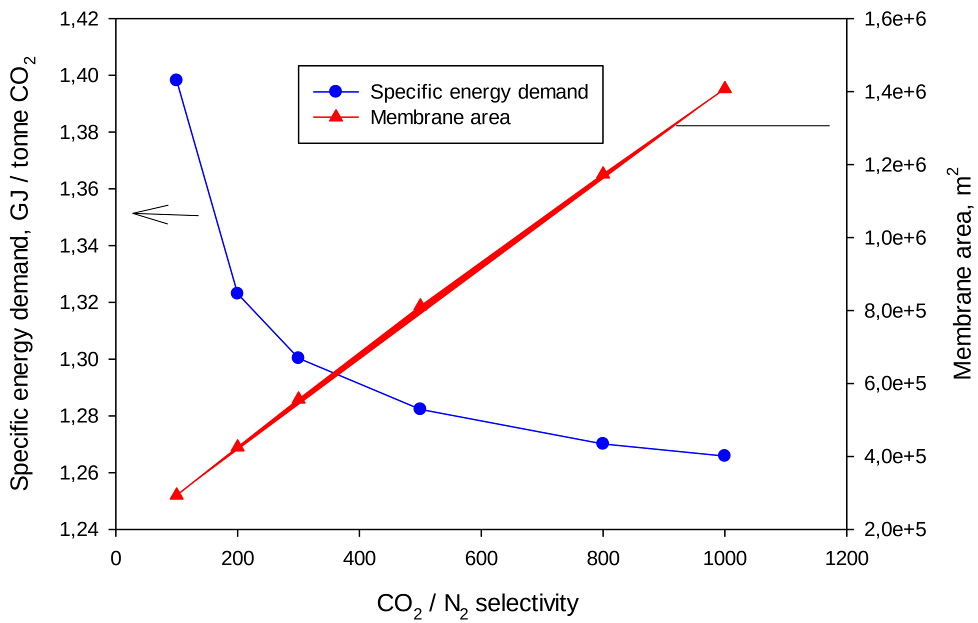




Permeance & selectivity of PVAm/PSf membrane at 1.2 bar, 35°C
Flat sheets, 30x30 cm (Feed gas: 10% CO_2+ 90% N_2 mixed gas)

Simulations help to identify the best operating conditions – *However, facilitated transport is difficult to simulate due to the combined transport mechanisms:*

$$J_A = \frac{D_A}{l}(c_{A,0} - c_{A,l}) + \frac{D_{AC}}{l}(c_{AC,0} - c_{AC,l})$$



X.He et.al, CEJ , Jan.2015

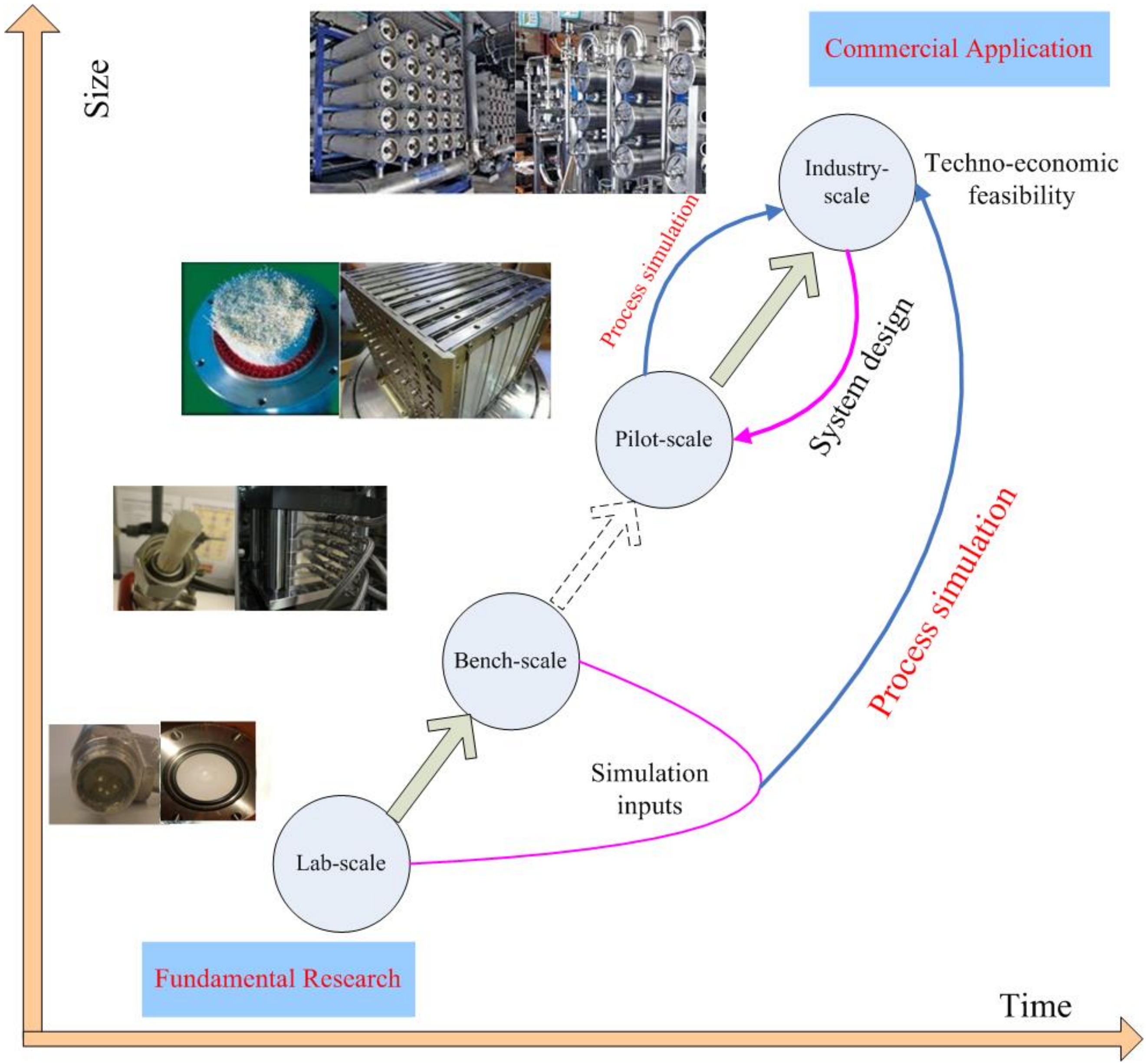
General demands, membranes for post combustion CO2 capture:

- High permeance (> 1000 GPU)
- Selectivity > 200 is preferred
- Low feed pressure (<3 bar) and vacuum on permeate side (200-300 mbar)
- Membrane module design should be hollow fibers or spiral-wound
- Process design must be optimized

Spesific demands, FSC

- Humidity level > 75%RH

The importance of process simulation



MEMFO: Sample EU-projects on CO_2 the last 10 years

- NaturalHy
  - Preparing for Hydrogen Economy by using the Natural Gas System as Catalyst (CMS-membrane)
- Nanoglowa
  - Nanomaterials against global warming (FSC-membrane)
- iCap
  - Innovative Capture of CO_2 (Hydbrid (MMM) membrane)
- Hipercap
  - High Performance CO_2 Capture
  - (SILM + nanocomposite membrane)
- ECCSEL
  - European CCS laboratory and Infrastructure (NTNU & Sintef are Host Institutions

MEMFO: Samples national projects on CO_2

On natural gas sweetening (CO2 removal):

1. RECCO2 → two nice high pressure rigs were built
2. NaGaMa → further development of membrane

On CO2 from flue gas:

1. CEPEME → early development of FSC-membrane
2. FSC Phase 1 → further development, small pilot
3. FSC Phase 2 → larger demonstration pilot
4. NORCEM (cement plant) – ECRA →Gassnova demonstration pilot, cement plant in South Norway

5. BIGCCS → multiple industries (Center of Excellence)

-

The Research Council of Norway

Statoil

PETROBRAS

Statoil

Statoil

SINTEF

Statoil

AIR PRODUCTS

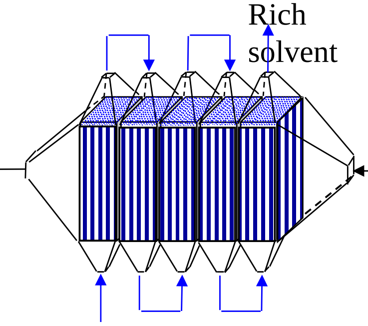
Statoil

Alberta Innovates Technology Futures

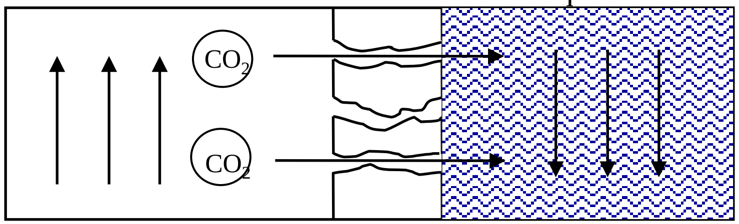
BIGCCS International CCS Research Centre

The Research Council of Norway

..and some national projects for Membrane Contactors



- A Green Sea → *nanocomposite membrane* development for contactor – *natural gas sweetening* (CO_2 removal)
- MCIL-CO_2 →membrane contactor using *ionic liquids for precombustion* CO_2 – H_2 separation
- MC-Enzyme →membrane contactor using *mimic carbonic anhydrase for postcombustion* CO_2 capture from flue gas
- 3GMC → membrane contactor using *3rd generation solvents* – *postcombustion* CO_2 capture from flue gas



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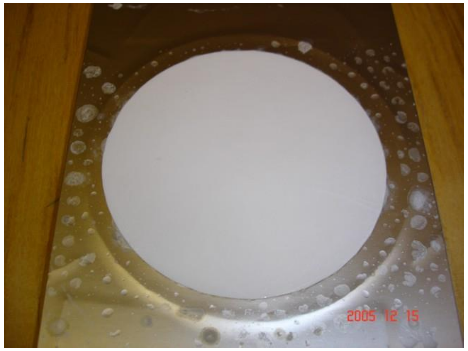
..The long road towards commercialization

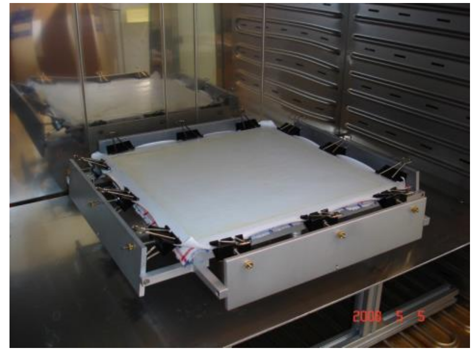
From lab to pilot testing

Some examples and lessons learnd

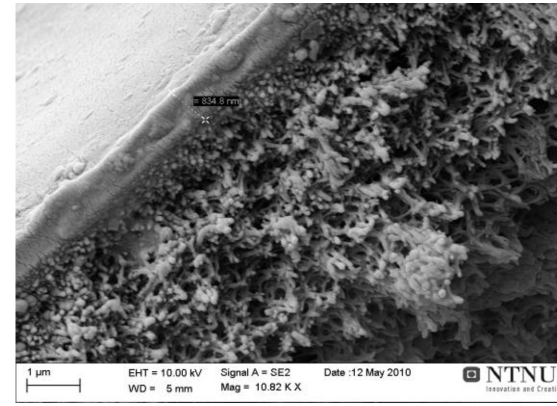
There is a long way from lab to pilot demonstration…….
1) small membrane pieces 2) large sheets, 3) spinning & coating fibers



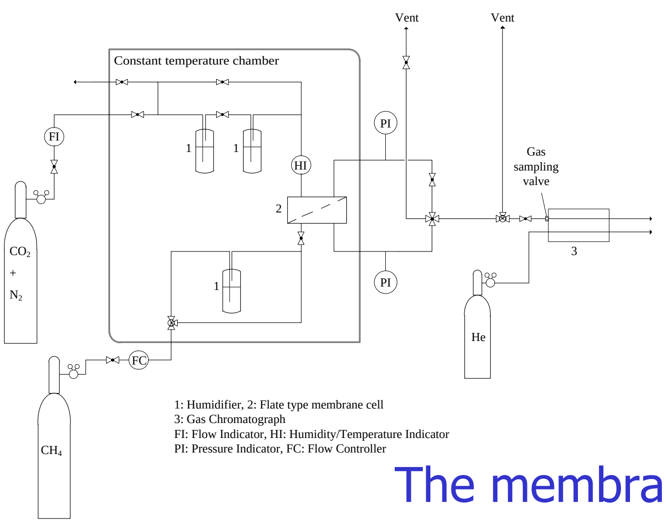
✓<u>1st step (→2008)</u>:
Lab, diameter 5-7 cm

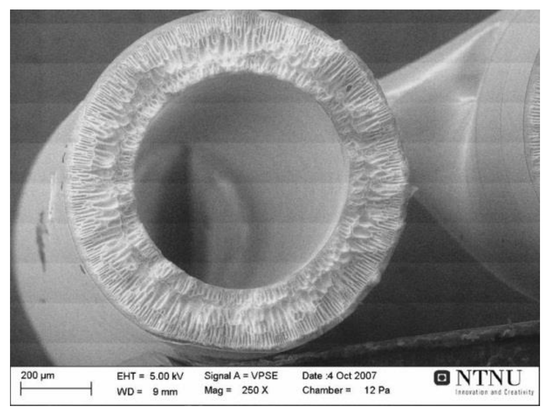


✓<u>2nd step (→2012)</u>:
Small bench-pilot,
Flat sheets,0.5 – 2m^2



…with durability testing and studies…





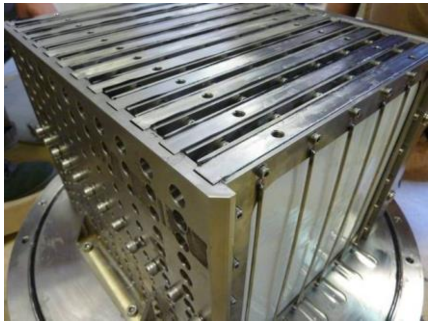
<u>3rd step (→ 2015)</u>:
Demonstration pilot with hollow fibres 8 - 10m^2

The membrane is PVAm on polysulfone support – both as flat sheets and hollow fibers – 3 patents

Memfo's FSC-PVAm membrane in pilot tests:

1. EDP, Sines, Portugal, the FSC-membrane; flat sheets (ended)

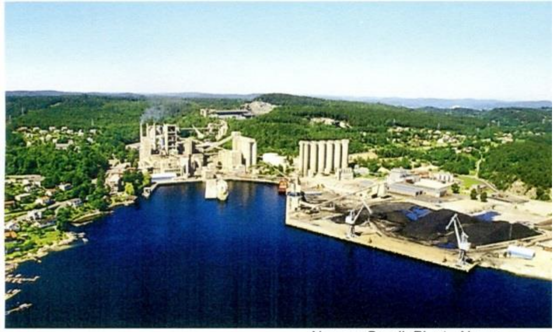
2012→



Flat sheets, ~2m2, - durability demonstrated towards SOx and Nox In flue gas: ~13% CO2 Tested in Nanoglowa

2. NORCEM Cement plant at Brevik, Norway; the same membrane module as above; tested for flue gas with 20% CO2 (ongoing)

2014→



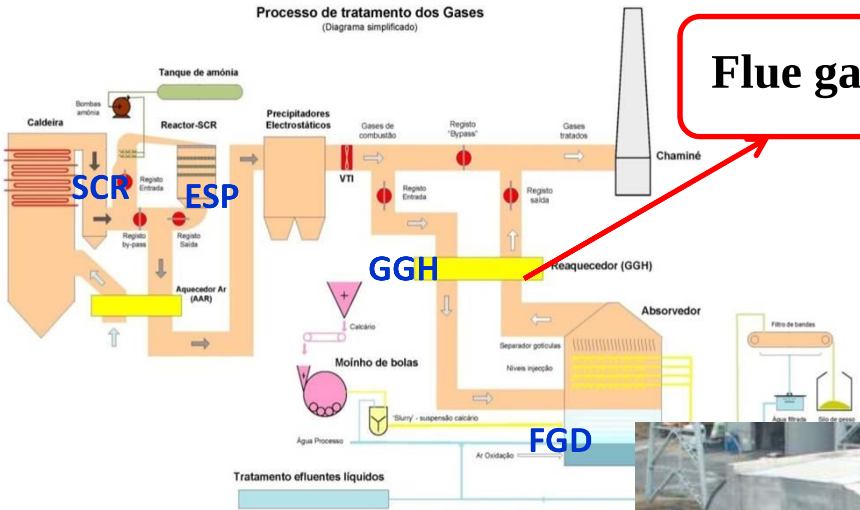
Norcem Brevik Plant - Norway

This cement-plant has been chosen as the official CO2 capture test site for the cement industry in Europe (ECRA) Cement industry are emitting 5% of total CO2 emmissions

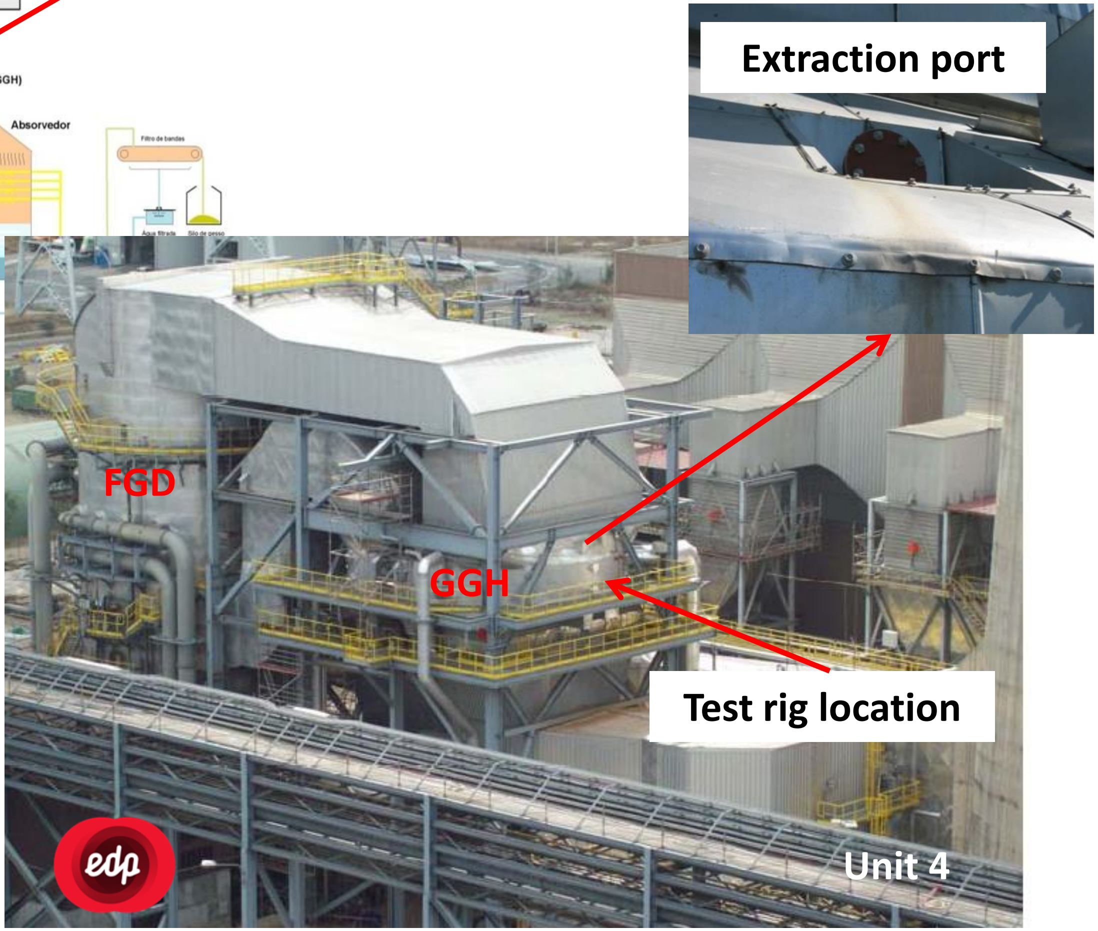
3. Tiller test site, Trondheim – Norway *(to be tested 2015-2016)* Scaling up to 10 m2 – coating the FSC-membrane on PSf hollow fibers (started - details on the project next slide)

1) Pilot scale long term testing real flue gas; EDP in Portugal

Flue gas extraction point and test rig location



Flue gas extraction point



- ❑ Sines Power Plant Unit 4 (314 MWe)
- ❑ On the gas-gas heater inlet hood (cold gases)

Compliments of EDP – Nanoglowa EU-project

Flue gas from coal fired power plants

FACTS

1. CO_2 concentration is ~13-16%, delivered at atmospheric pressure – huge gas streams
2. The PVAm membrane needs water for the facilitated transport
3. FDG unit is needed to keep the SOx concentration fairly low
4. There are fly ashes in the flue gas – filters must be installed upfront the membrane process

CHALLENGES

1. Driving force must be created by using permeate vacuum to have an economic viable process – pressure drop must be low
2. If temperature is not well controlled, too much water may condense (at low temperature) – this may create problems in the process system and equipment
3. Too high SOx and NOx content may ruin the membrane over time
4. The membrane process must be able to handle outages of the power plant and minor amounts of dusts

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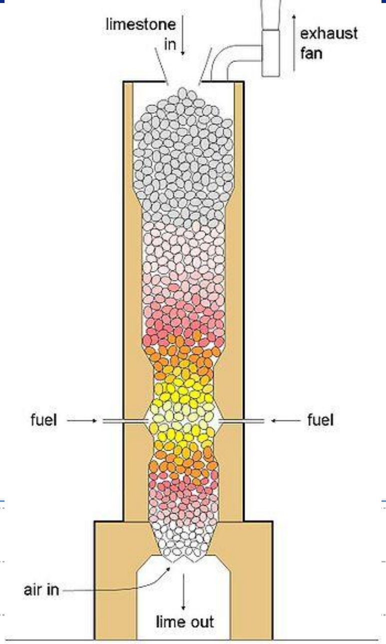
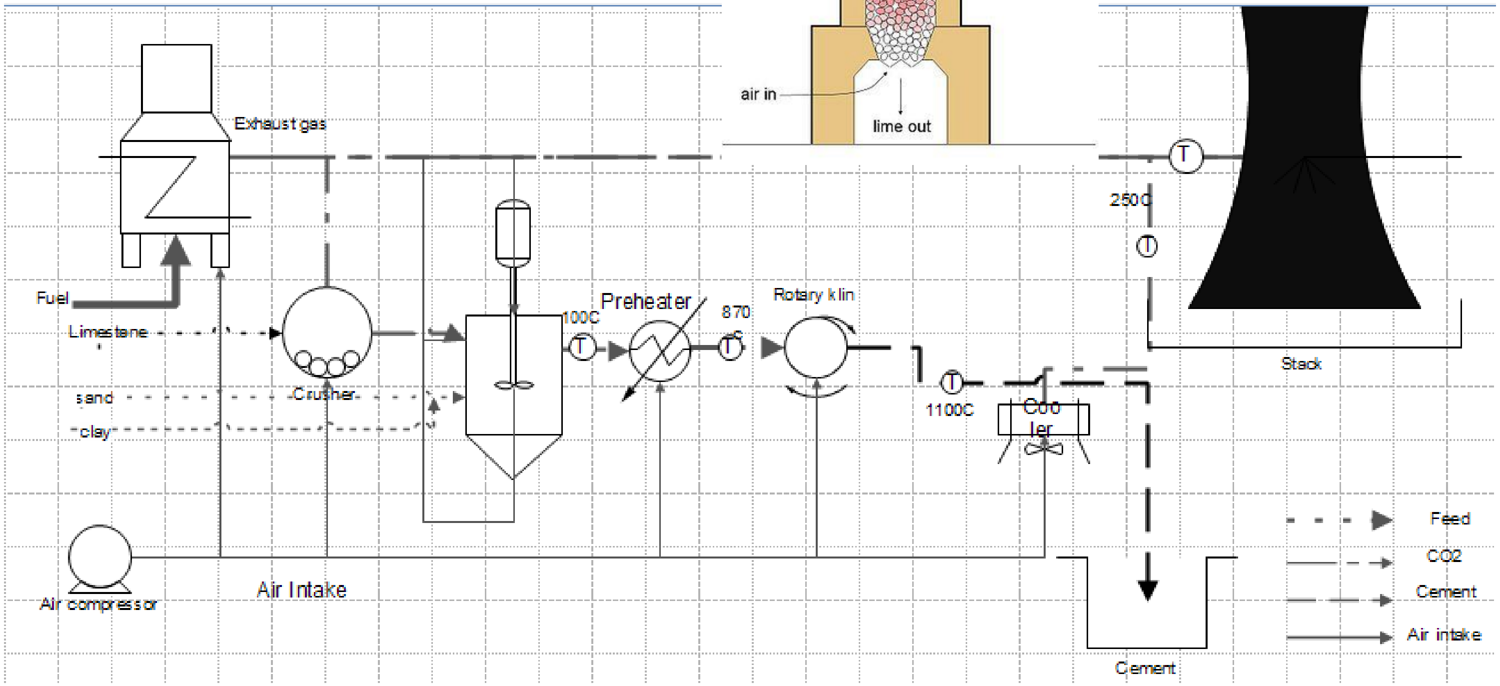
Pilot scale testing
Cement Plant , NORCEM

$CaCO_{3(s)} \rightarrow CaO + CO_2$



Simple process Flow Diagram



Flue gas from cement industry

FACTS

1. CO2 concentration ~20% - gas volumes smaller than power plants – both facts give advantages
2. Depending on raw material, flue gas temperature may vary 85°C-180°C (with or without FDG)
3. Can be high SOx and NOx content –FGD is needed
4. There are ashes and dust in the flue gas (quite often a lot) filters must be installed
5. Cement factories are often old plants – deposits from scaling and rust may follow the flue gas

CHALLENGES

1. Driving force must be created by using permeate vacuum to have an economic viable process – pressure drop must be low
2. If temperature is not well controlled, too much water may condense out (at lower temperature) containing deposits – likewise if too high, this may harm the membrane (>70°C)
3. Too high SOx and NOx content may ruin the membrane over time
4. The membranes must be protected from particles and easily recover performance after outages of the plant

3) New Pilot Project started in 2014:

The FSC-PVAm on Hollow Fiber PSf membranes:

small commercial modules being prepared (~10 m2)

Two types of flue gas to be tested:

- 13 vol% CO2 (like from Mongstad cracker)
- 8 vol% CO2 (OTSG; on request from oil sand producers)

Partners on the team in the project together with NTNU:

- Air Products, Alberta Funders (oil sand companies for OTSG-gas), Statoil, DNV GL, Sintef MC
- Main funding partner: GASSNOVA/Norway

Partner: Air Products deliver the HF and modules,

NTNU/Sintef are coating them with PVAm membrane

Other partners: GASSNOVA, Alberta Funders, Statoil

Illustration: Air Products Prism Separators

Synthetic flue gas at Tiller - Trondheim

FACTS

1. Test two concentrations of CO_2: 8% and 13% - relatively low gas flows

2. Temperature and feed / permeate pressure will be easily controlled

3. Small commercial HF module (10m2) (AP)

4. Current modules have not been coated with PVAm earlier – new methods

CHALLENGES EXPECTED

1. Membrane may not be so efficient for lowest concentration (8%)

2. No challenges expected with water condensation

3. Using low feed pressure put high demands on good feed flow distribution in module

4. Fibers are being coated *in-situ* of membrane module – currently being investigated

SINTEF Materials and Chemistry – NORWAY
CO_2 capture membrane technology

<u>Main contact: Dr. Rune Bredesen</u>

<u>In Oslo:</u>

- Main focus is on membranes for precombustion (CO2-H2), but also on development of nanoparticles for mixed matrix membranes (collaboration NTNU)

<u>In Trondheim:</u>

- Mainly collaboration on polymeric membranes with Memfo (NTNU), also some work on contactors

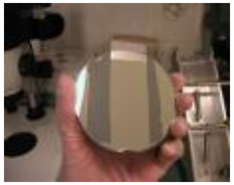
SINTEF MC:
H2 separation; thin Pd-alloy membranes – now for pilot scale

Solly H_2 permeable

- **H_2 with high purity**
- Temperature, 350-600 C
- **Application**
  - Power generation with CO2 capture
  - Low pressure H2 production for heaters & boilers
  - H2 production for H2 filling stations
  - H2 recovery and purification
  - Hydrogenation/dehydrogenation processes
  - Catalytic

- **Membrane Performance**
  - **High flux and selectivity**
  - Flux @ 26 bar: 2.5 NL/cm2/min
  - Permselectivity @ dP = 25 bar: 2800
- **Stable performance for 350 days**
  - A membrane life time of 2-3 years

  (T ≤ 400 °C) is assessed



Pd-23%Ag alloy film on silicon wafer

SINTEF two-step composite membrane preparation Solely H_2 permeable

1. **Membrane preparation on Si support by magnetron sputtering**
2. **Membrane pull-off from Si support and composite membrane preparation**

Flexibility to produce thin film binary, ternary alloys

<u>Main activities :</u>
- Up-scaling
- H_2S exposure stability testing
- Pd-alloy development
- Fabrication and long-term testing in:

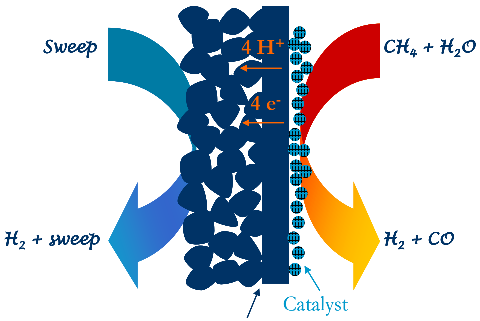
  H2/N2 or H2/CH4/CO2/CO mixtures, and H2S, As a Function of pressure & concentration

32

SINTEF MC:
High temperature ceramic membranes

- **Hydrogen transport membranes (HTMs)**

  Application areas:
  - Pre-combustion CO_2 capture
  - Steam methane reforming
  - Syngas production
  - Chemicals and hydrogen production (CMR)

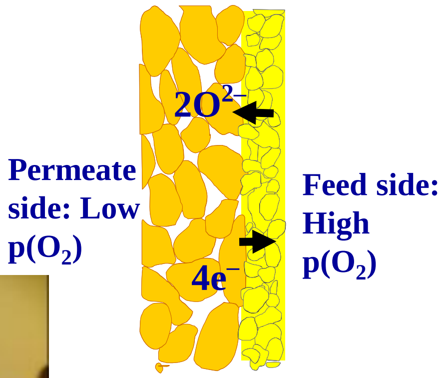


Main activities

- **New materials development;** preparation, characterization and testing
- **Development of fabrication routes and testing** ; Paste formulation, extrusion, calendaring, sintering, and sealing
- **Scaling up** of tubular $H_2 – O_2$ ceramic asymmetric membranes up to 30 cm, aiming for 1m long
- **Scaling up** of membranes support up to 1m
- Single and multi tube **reactor module design**

- **Oxygen transport membra**

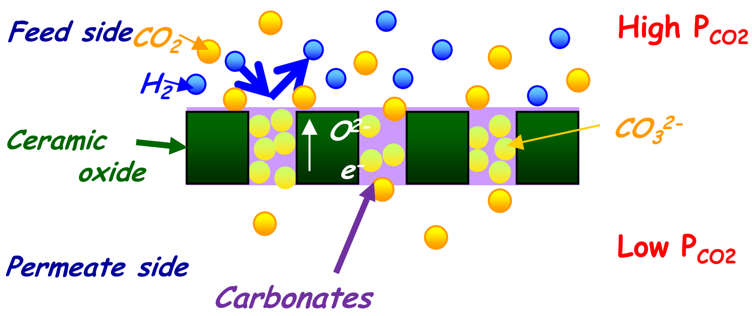
  Application areas:
  - Oxygen production
    - CTL : Coal To Liquid
    - CTG : Coal To Gas
    - GTL : Gas To Liquid
    - Oxycombustion
    - IGCC : Integrated Gasification Combined Cycle
  - Catalytic membrane reactors (OCM, ODH…)
  - Small pure O_2 production: prototype exists
    - Niche market : aerospace, healthcare,…



Asymmetric membrane = Porous support + thin dense film

33

SINTEF MC:
CO_2 selective membranes: novel dual phase membranes

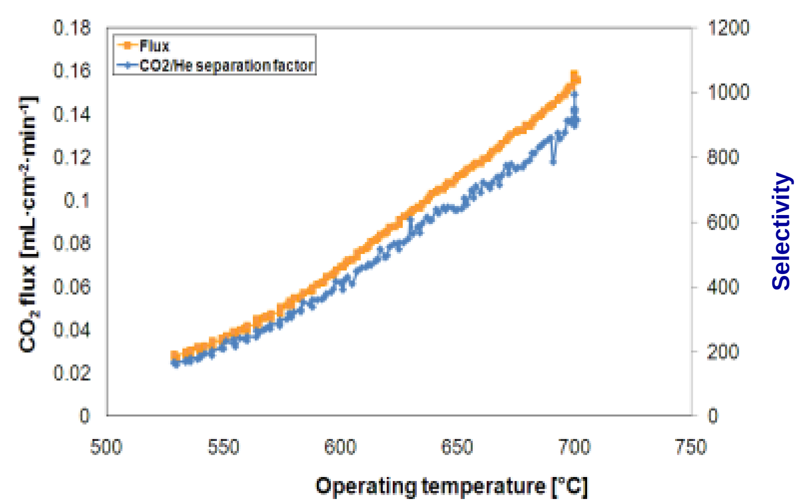


Ceramic matrix infiltrated with molten carbonates

Main Activities

- Membrane fabrication on lab scale (flat and tubular
- Characterization and testing
- Transport mechanism

- Novel membrane concept
  - Early stage of development World wide
- CO_2 separation at 400-700 C
- High flux and selectivity measured



34

EU-project: HiPerCap – WP3
Membrane based technologies

Leader:	**NTNU**					
Partner:	**SINTEF**	TIPS	CSIRO	TNO	EDF	CNRS

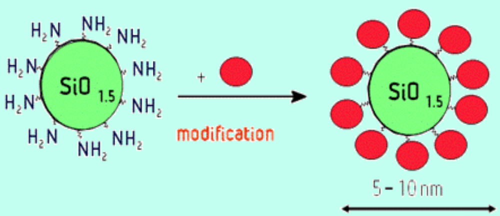
Task 3.1 Hybrid membrane development (NTNU, SINTEF,

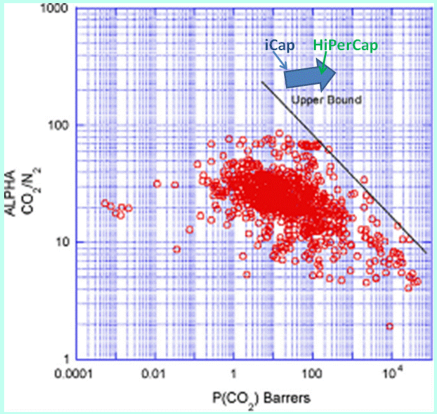
Objectives

- **Develop a high flux mixed matrix membrane based on incorporation of nanoparticles 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 in the hybrid membranes.
- 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.





CO_2 capture with membranes – Introducing selected universitites and institutes in Europe

University of Twente – Membrane Science and Technology

Prof. Kitty Nijmeijer

Prof. Nijmeijer is heading the membrane group

New activities in the field of CCS seems to be MMM with MOFs – previously very active on PEBAX and SPEEK

- EMI – European Membrane Institute – works mostly with industry and public organizations, short-term R&D projects is carried out.
- EMI works complementary to the Membrane group at the UT – pilot studies.
- Pilot Projects: Nanoglowa & CapWa

Diffusion Transport Membranes (DTM) developed by Univ. Twente (Nanoglowa project) was demonstrated at EON, power plant, Scholven (Germany),

HF curtain (above)
Parker module (below)

University of Aachen / Prof. M. Wessling Chair: Chemical Process Engineering

- Membrane research is much focused on water and water purification
- Simulations / process intensification
- New interesting materials are:
  CarboMembran:Mixed matrix membranes with CNT incorporated – both for drinking water and for CO_2 separation from flue gas
- Ceramic membranes for high temperature applications – oxyfuel combustion

Four other highly recognized institutions within membrane research - Europe

1) Universite de Lorraine; Nancy, France

Prof. Eric Favre – chemistry and molecular physics

Modelling, simulations, Basic membrane material research

- *Pilot scale (10m2) HF PTFE membrane contactor tested and modelled*

2) ITM – The Institute of Membrane Techn, Calabria – Italy

Large research institute – all membrane areas

Prof. E. Drioli; mostly on water and process intensification

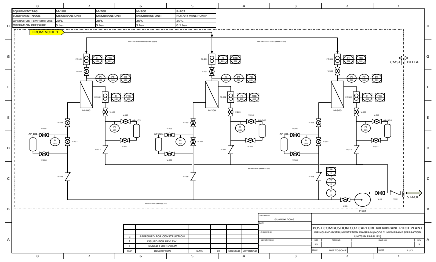
Dr. Giuseppe Barbieri – membranes for gas – characterization – catalytic materials – synthesis of new membranes

3) Helmholtz-Zentrum Geesthacht (previously GKSS)
Germany Institute of polymer research – simulations / modeling

4) TIPS-RAS : Topkiev Inst. of Petrochem. Synthesis – Russian Acad.Sci.
V. Teplyakov, V. Volkov: Polymer synthesis, membranes, m. contactors

There are a few membrane demonstration pilots around the world – two examples are:

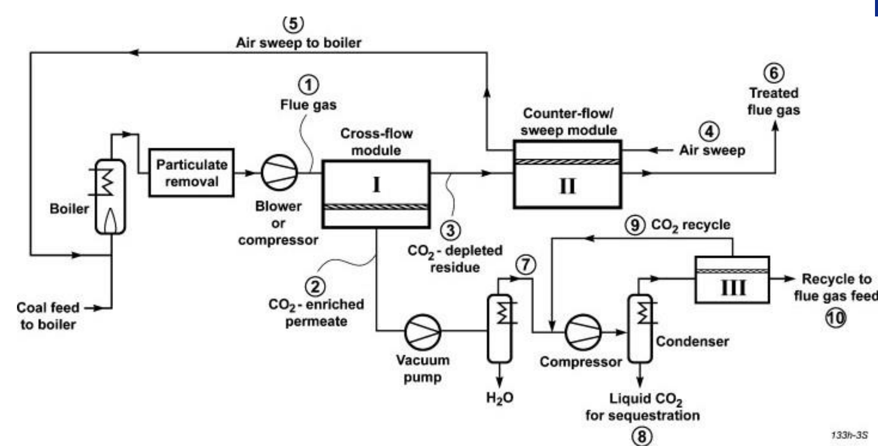
- Vales point power station (Australia), hollow fibers, 20 l/min



Compliments Dr.Guangxi Dong, UNSW

- MTR, Menlo Park, at National CC Center Wilsonville, Alabama, their Polaris membrane demonstrated on pilot scale for 1 MWe flue gas – *smart process solution!*

(ref. Merkel et al. 2010)



A brief look at other CO_2 capture technologies at the stage of large pilots in Norway

SINTEF at TILLER, Trondheim 150 kW CLC hot rig installed

Solid looping technologies – in BIGCCS

Objectives

- Bring chemical looping combustion (CLC) closer to commercialization

- Develop new and optimized oxygen carriers and production methods

- Validate performance and operability of the 150 kW CLC rig by 600 hours of operation

Spray granulated Colormax

150 kW CLC test rig

Aker Clean Carbon testing at Mongstad - Norway

Started May 2012, *proprietary solvent* comparison with MEA

Run on gas from CHP or RCC –
5 or 13% CO_2

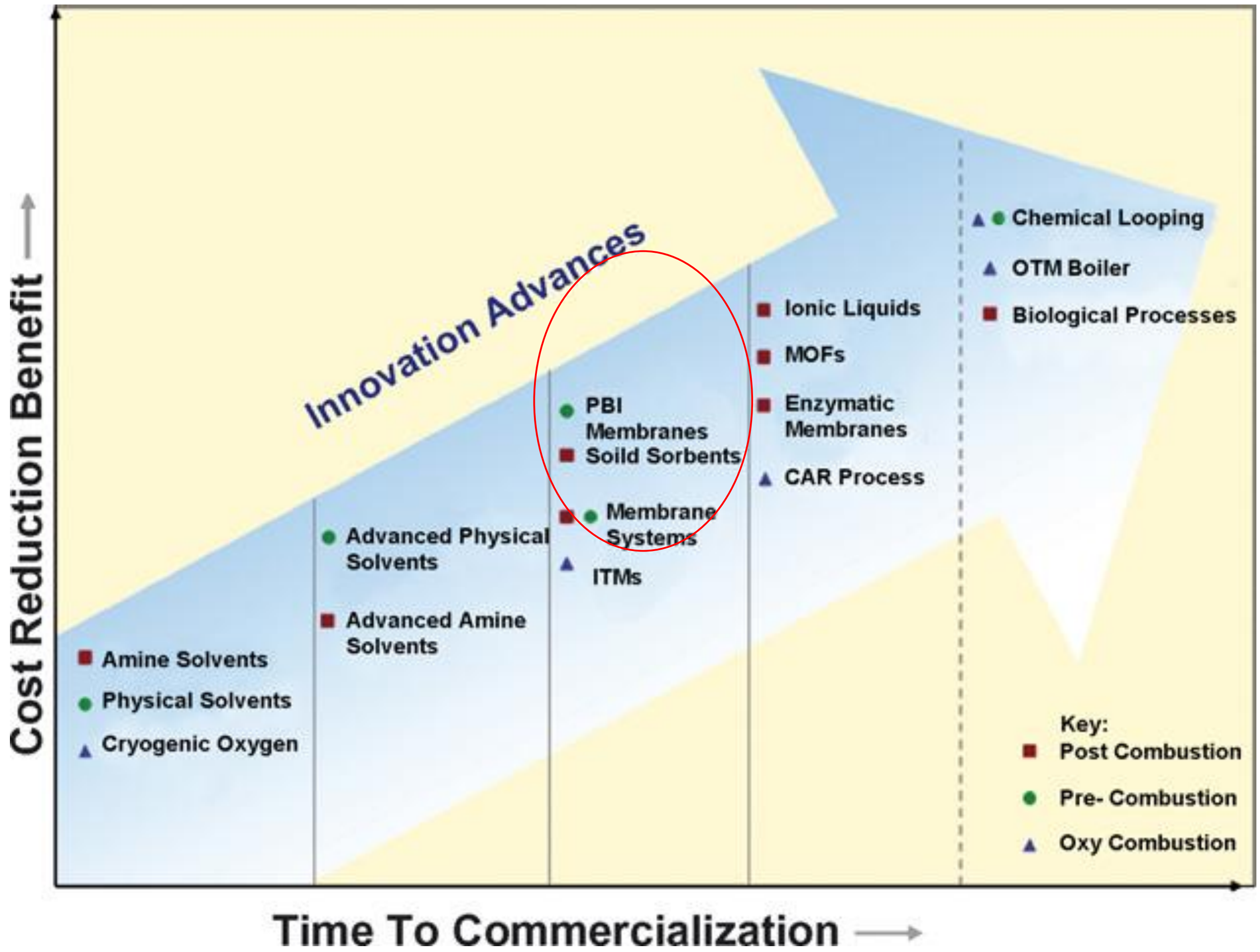
Capacity about 28/75 kt/a CO_2 depending on gas

Alstom Chilled Ammonia at Mongstad - Norway

Operation started November 2012

Run on gas from CHP or RCC

Summing up: where are membranes foreseen in the CCS chain of innovation?



Figueroa JD, et al. IJGGC. 2008;2(1):9-20.
D'Alessandro DM, et al. Angewandte Chemie International Edition. 2010;49(35):6058-82.

<u>However</u>; the «Winner of the game» for CO_2 Capture in general

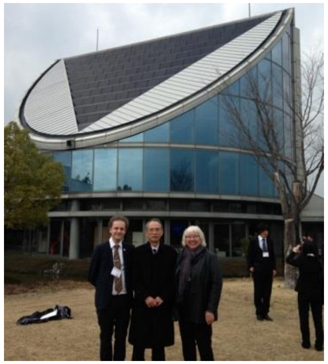
Must be the winner on:

- Energy
- Environment
- Size
- Cost

Good luck to us all!

And remember, there is not only one answer

NTNU



Visit at RITE 2014

Thank you for your attention and for the invitation!

<u>Acknowledgement</u> goes to our academic and industrial partners and the Norwegian Research Council for the financial (and moral) support in our membrane research over the years