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Polymeric Membranes for CO_2-capture:

Results obtained with a small pilot-scale module at a coal-fired power plant; and further progress

Professor May-Britt Hägg et al.
Dep. Chemical Engineering

Content of presentation

- Briefly about the facilitated transport membrane
- Challenges in up-scaling – from lab to pilot
- Results from pilot scale testing – CO_2 capture
- Further progress in demonstration

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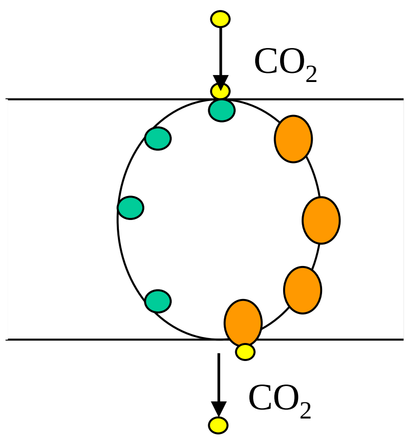
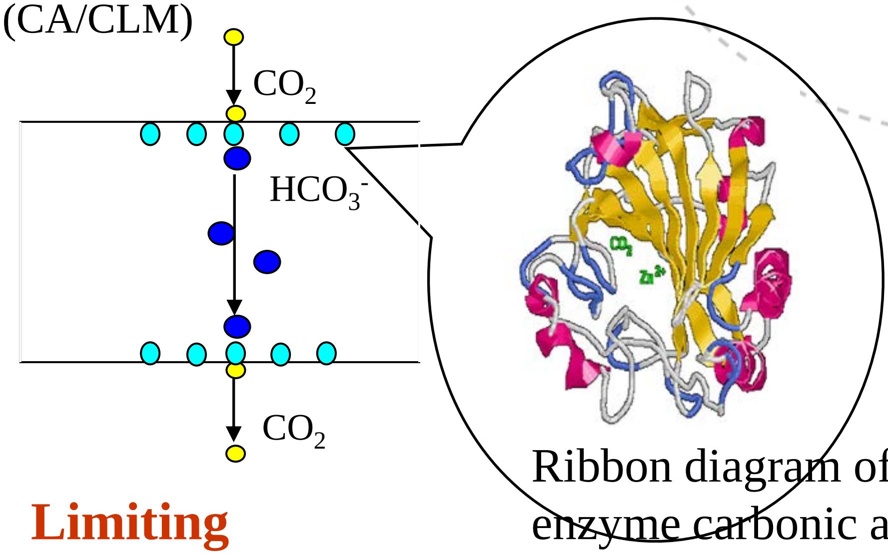
An illustration of the facilitated transport with a) Fixed-site-carrier or b) Biomimetic design

Carrier Mediated Facilitated Transport Systems



Limiting diffusion rate is that of CO_2-carrier complex

CA Catalyzed Facilitated Transport System (CA/CLM)



Limiting diffusion rate is that of HCO_3^-

Ribbon diagram of the enzyme carbonic anhydrase (CA) as in mammals

The FSC-PVAm membrane is mimicking Nature (Fixed-Site-Carrier Polyvinylamine)

- Dominating reactions:

$$CO_2 + H_2O -> H_2CO_3$$

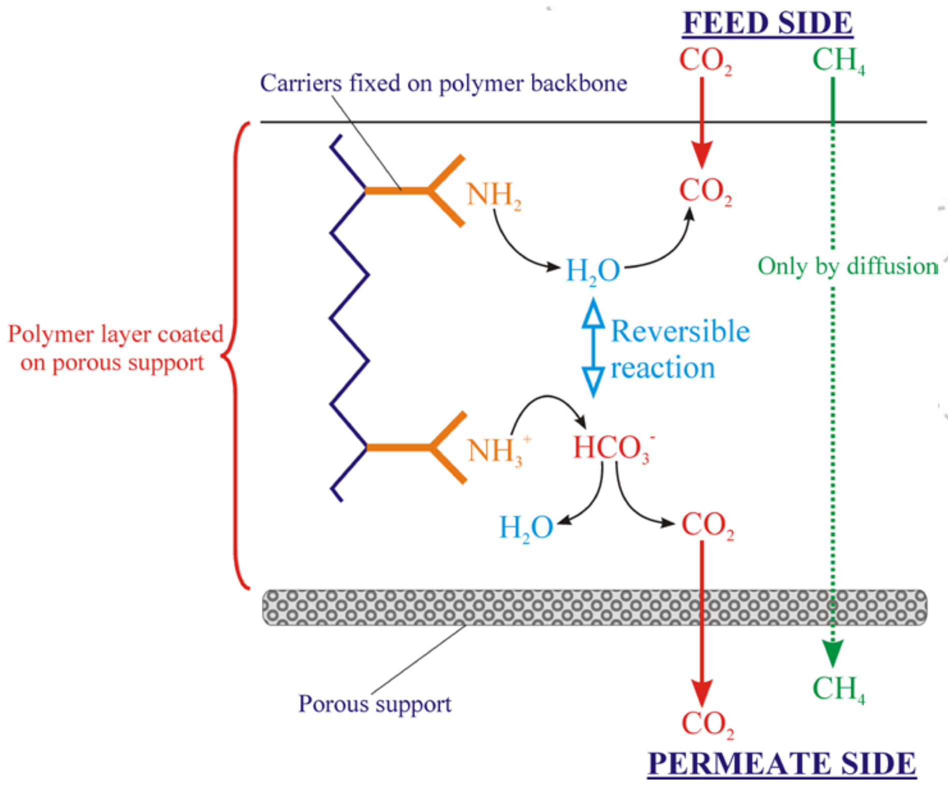
$$H_2CO_3 + NH_2 -> HCO_3^- + NH_3^+$$

$$HCO_3^- + NH_3^+ -> H_2CO_3 + NH_2$$

$$H_2CO_3 -> H_2O + CO_2$$

- Flux equation:

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



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

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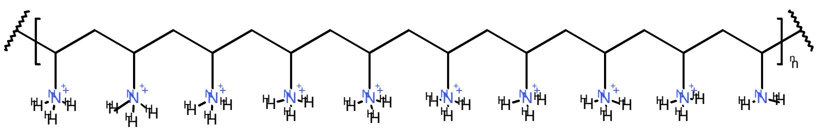
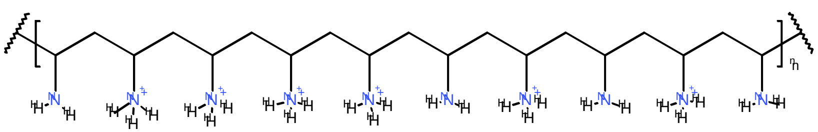
Effect of pH on PVAm structure

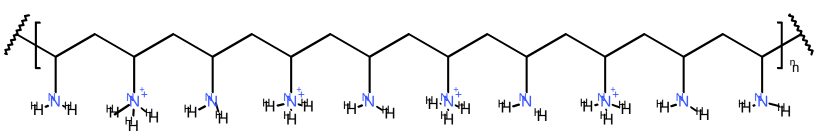
- The pH of the casting solution determins the relative amounts of free amine groups and the corresponding ammonium salts



pH=4

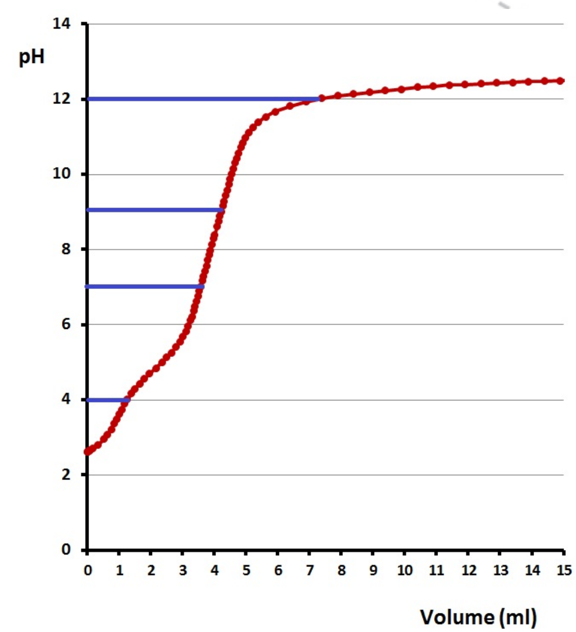


pH=6



pH=8

- At low pH most of the amino groups are protonated and converted into less reactive ammonium groups
- At high pH most amino groups are present as neutral amines



Titration curve for casting solution with varying pH

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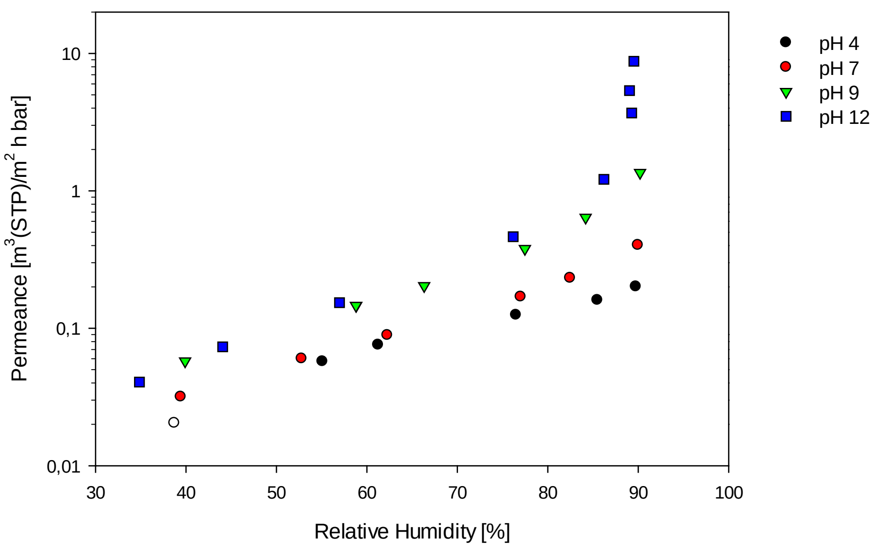
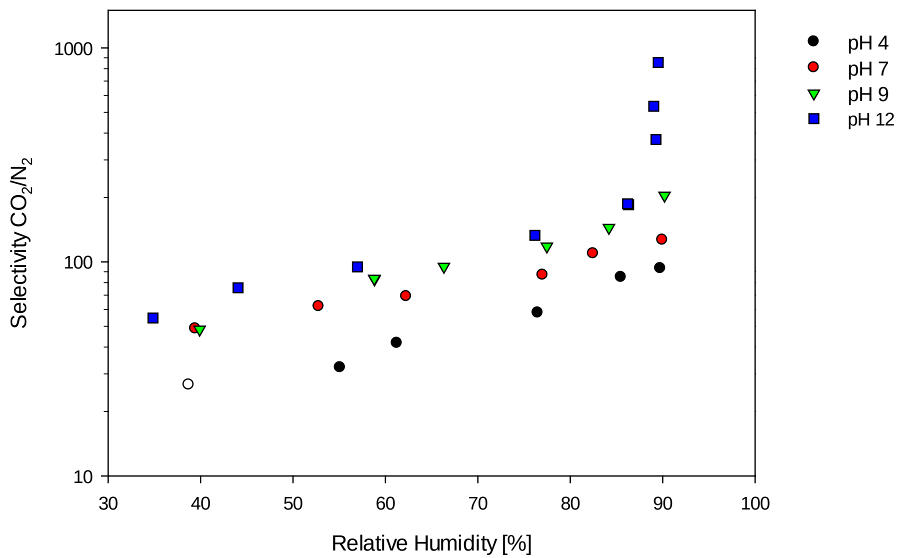
Adjusting of the pH of casting solution gave dramatic increase in performance (results from 2012)

Gas Mixture: 10%CO2 – 90% N2

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)

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..there is a big gap to cover going from lab to pilot to innovation…

- 1998→ first ideas, concept confirmed 2000
- 2001 – 2004: Basic research on the membrane material
- 2005 – 2008: KPN project with Statoil & Alstom (lab-scale)
- 2008 – 2012 BIP project with Statoil & Gassnova (~0.5 m2)
- 2007 -2012: EU project (Nanoglowa) covering part of the road towards pilot demonstation ~(~2 m2)
- 2013 – 2015: Planning a larger pilot (~10 m2) demonstration project with real flue gas with several international partners

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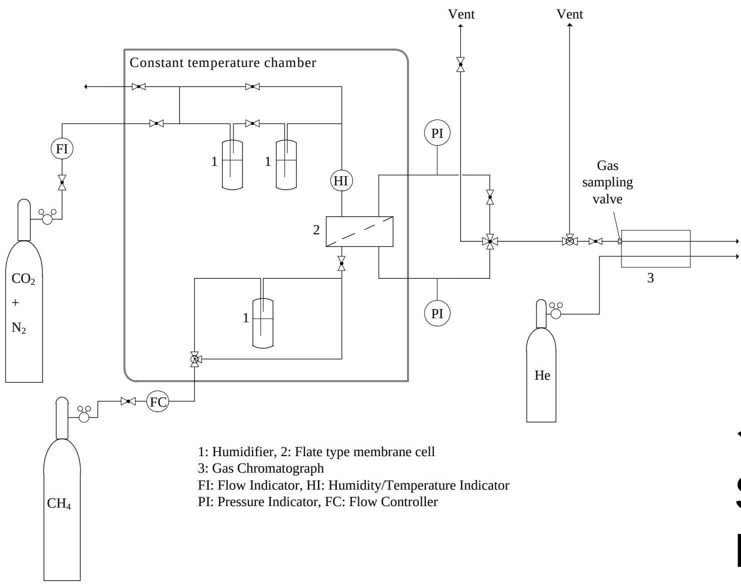
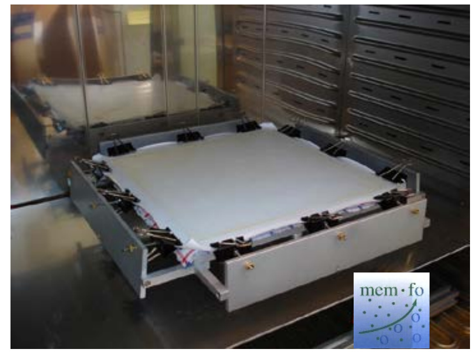
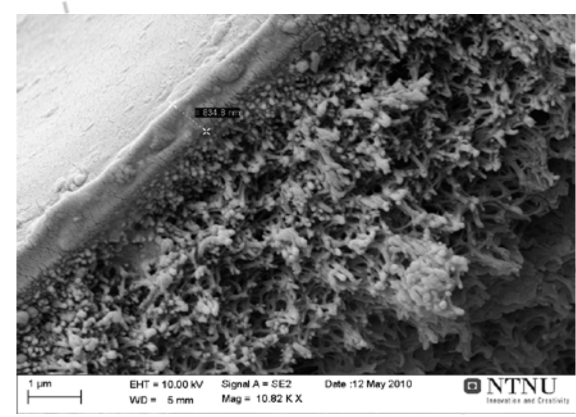
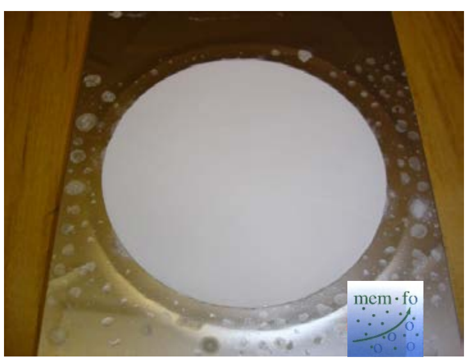
Measurements are done both on small and larger sheets

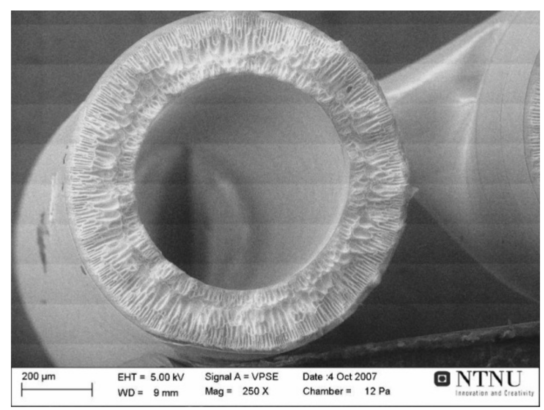






✓2nd step (→2011):
Small bench-pilot,
Flat sheets,0.5 – 2m²





3rd step (→ 2015):
Demonstration pilot with
1) hollow fibres 8 - 10m²
2) Flat sheets

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

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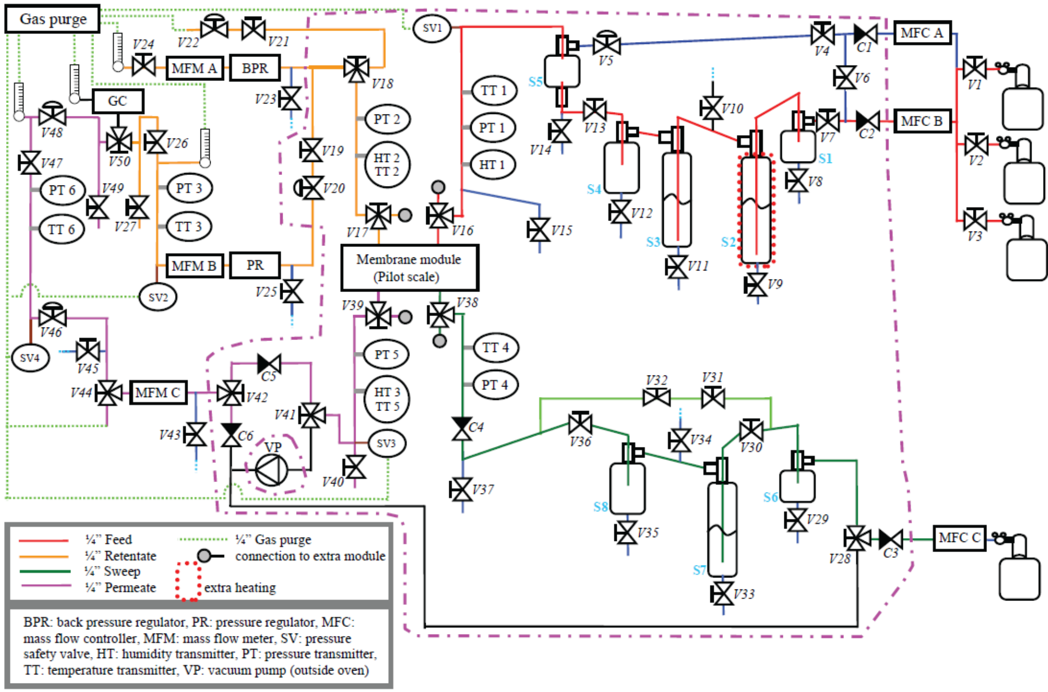
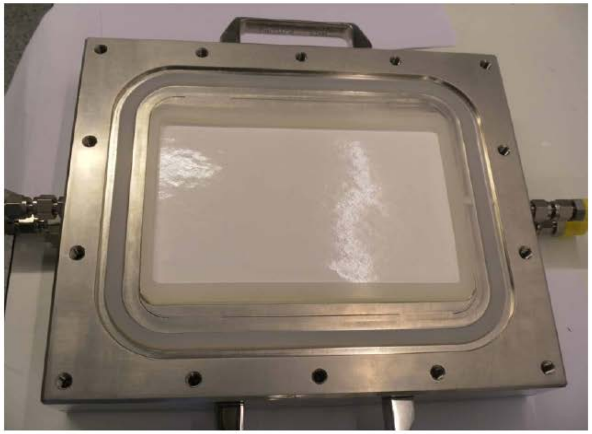
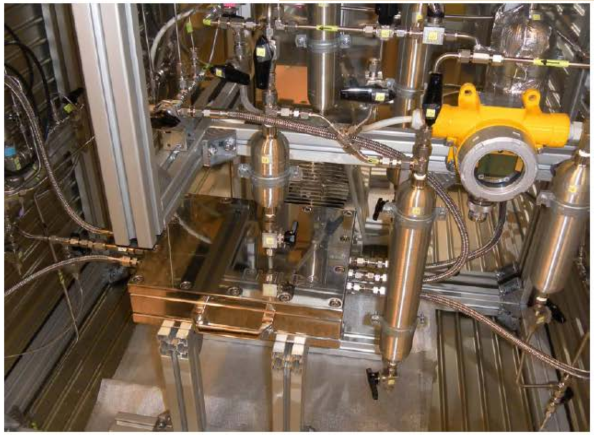
The small pilot rig is very advanced and fully automized



Flow sheet for FSC-pilot plant (STATOIL-Gassnova-NTNU), Drawing version 2010 12 01, Project # 40112000





The module design does not, however, give correct Info on flow patterns - a scaled-up module based on HF is proposed

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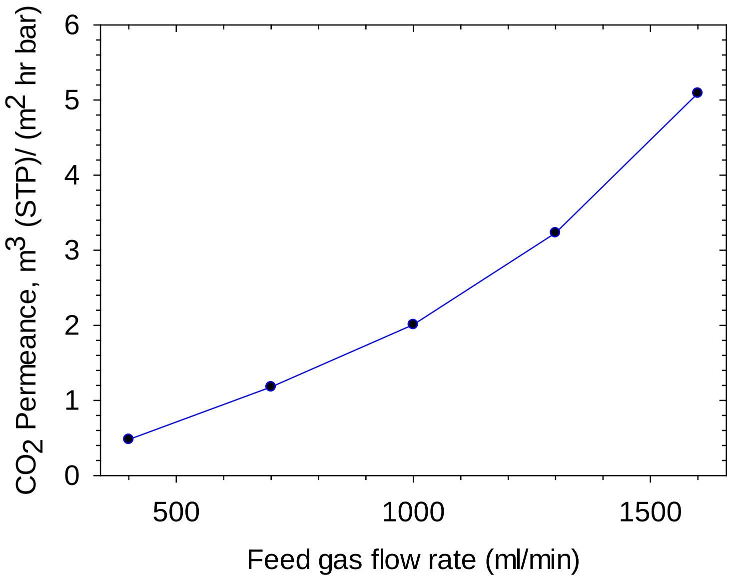
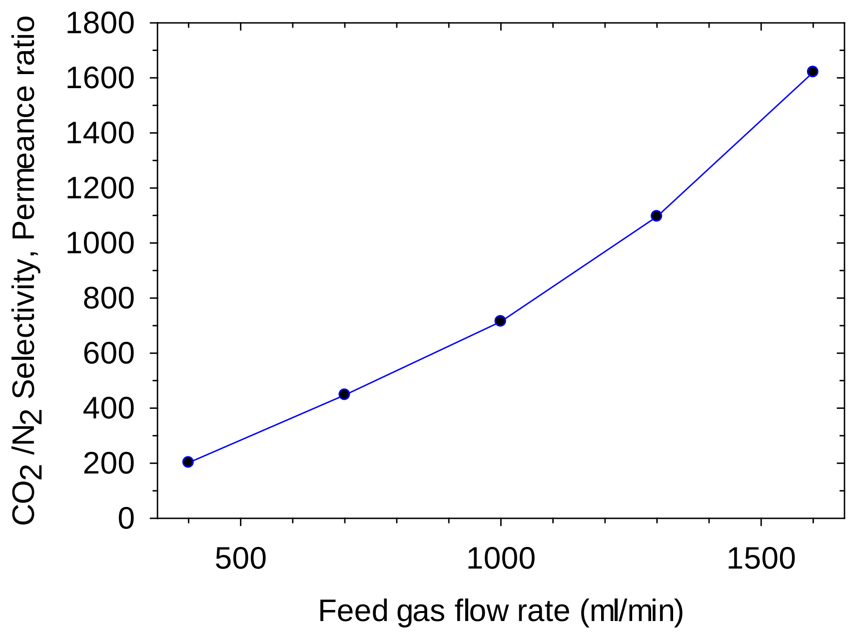
Sample results 2012; optimized process conditions FSC Membrane; Mixed Gas Tests CO_2 – N_2

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





Results using a Small Pilot

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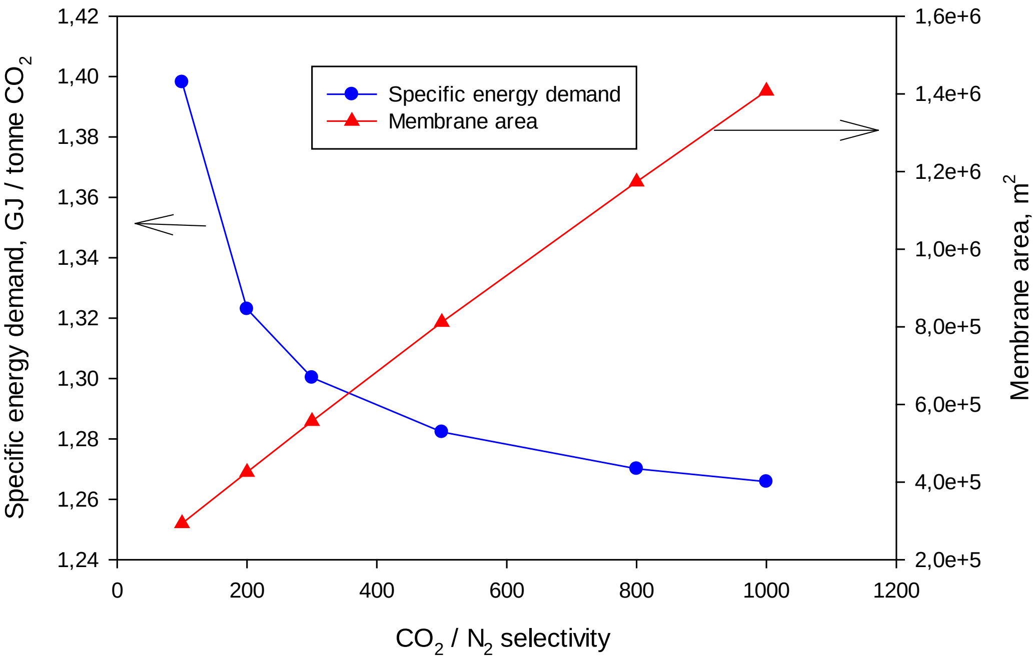
Simulations can help to identify best conditions – however, the facilitated transport is difficult to simulate



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

General demands, membranes:

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

Spesific demands, FSC

- Humidity level > 75%RH

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Back to: the EU-*NanoGloWa project, 2007 - 2011*

- Nanoglowa = Nanomaterials against Global Warming
- 24 partners, R&D inst., engineering, power producers

Main Goals:

- Membrane up-scaling, pilot testing at a power plant
- CO_2 separation from flue gas at coal fired power plants using membrane technology
- Documenting durability of the membrane material over time when exposed to components such as SO_2 and NOx

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In parallel to the upscaling, durability tests were performed at NTNU; preparing for flue gas tests at a coal fired power plant

Experimental procedure

- ❑ 6 membranes exposed each to SO_2 (500ppm), NO_2 (200ppm), NO (200ppm) for 168 h, at 25^0C and 50^0C, 2 bar, maximum relative humidity.
- ❑ The contamination gas composition: 17%CO_2-78%N_2-5%O_2 + 1 contaminant
- ❑ Mixed gas permeation, IR, NMR, SEM tests before and after exposure
- ❑No change in performance could be detected

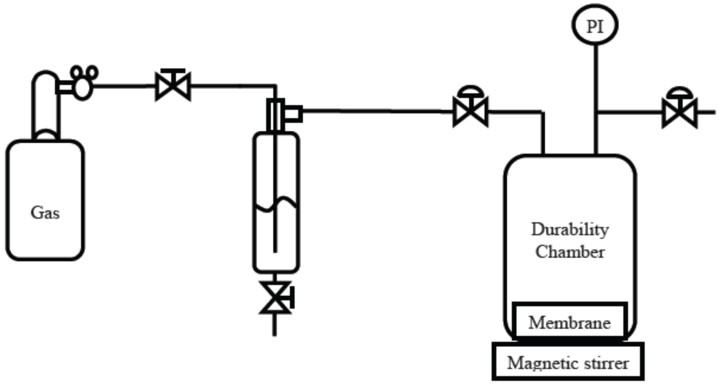

Figure 1: Experimental set-up of static durability tests

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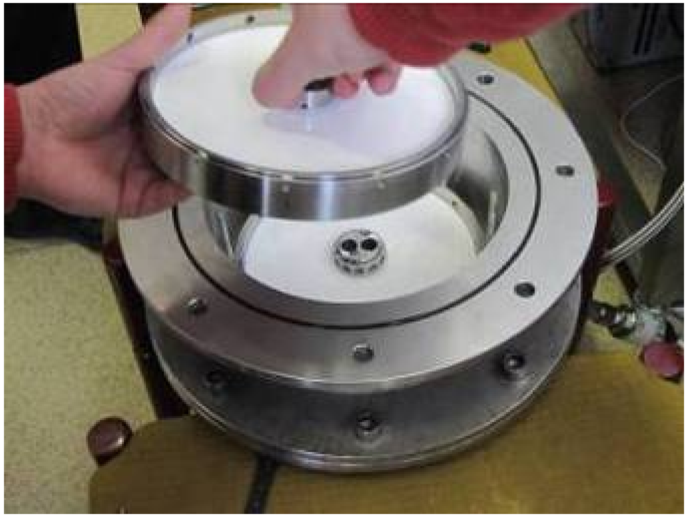
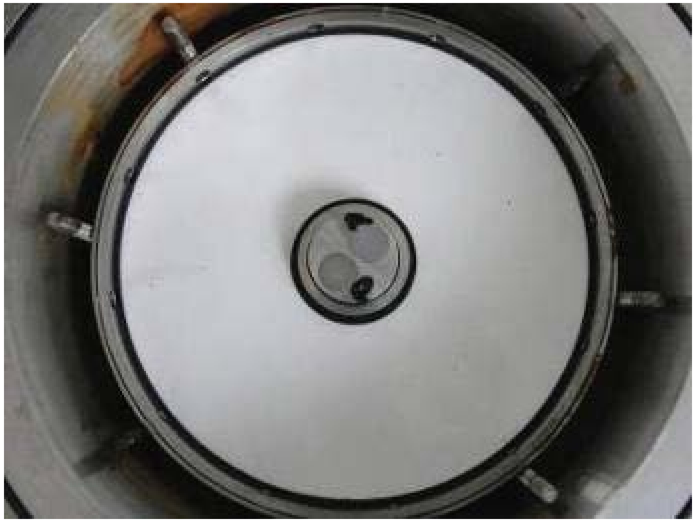
Next step in the project: Continuous durability using synthetic and real flue gas

Testing (March 2010- December 2010) at ICHP Poland, Warsaw

Before



After exposure



- ❑ 4 months continuous operation including 3 weeks synthetic and 2 weeks **real flue gas at** Borselle power plant, The Netherlands
- ❑ Gas permeation, IR, NMR spectroscopy and SEM pictures were used to identify the effect of contaminants
- ❑Main challenge: the module - sealing, leakage, flow pattern
- ❑Total membrane area installed: 435 cm^2

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Continuous durability using synthetic flue gas

Test parameters and results obtained at IChP Poland (~4 months)

Test parameters:

- Temperature 30°C and 50°C, feed flow 44 - 565 l/h,
- Feed pressure 1.05 bar (fan), feed humidity RH 94 - 100%,
- Feed gas composition (18% CO_2, 5% O_2 rest N_2)

Permeate flow rate

250 mbar vacuum: 11-16 l/(m^2 h)

100 mbar vacuum: 17-35 l/(m^2 h)

Permeate purity - CO_2 % in permeate

250 mbar vacuum: 57-65 %

100 mbar vacuum: 72-80 %

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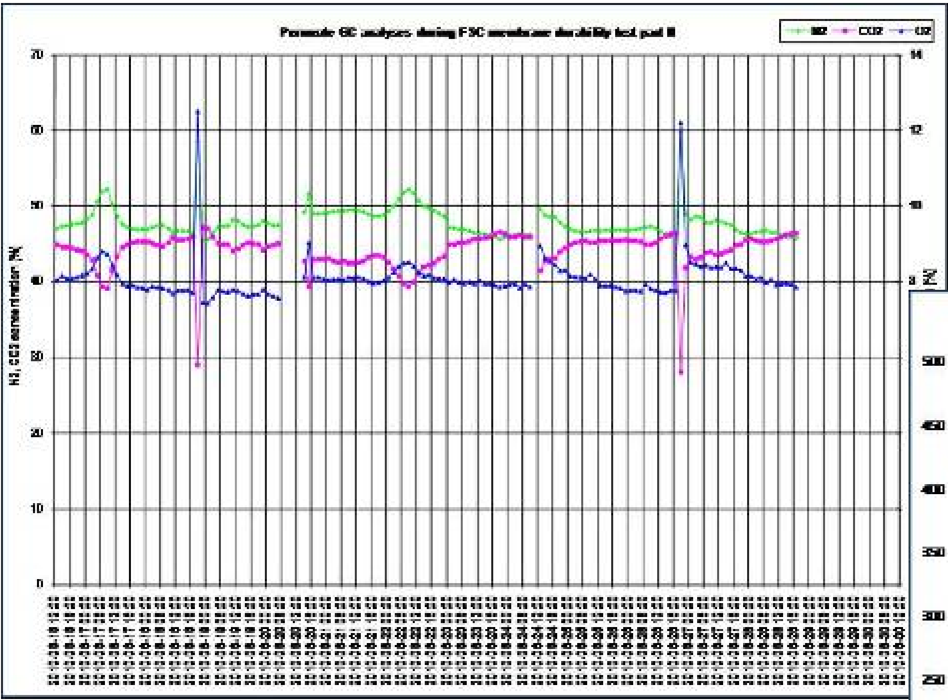
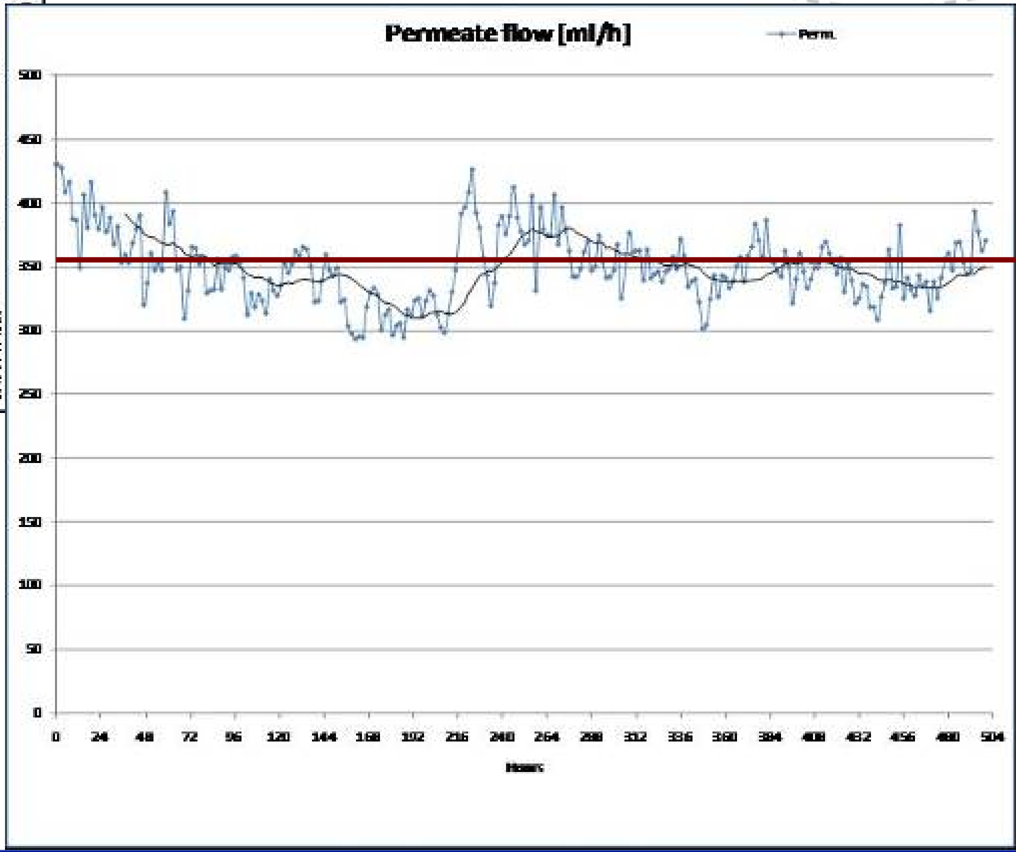
Continuous durability using synthetic and real flue gas

Results: raw data synthetic flue gas – 500 hours



- exposure to SO_2 and NOx (200 mg/m^3 each), synthetic flue gas



Conclusion:

Real flue gas contaminants (SO_2, NOx, particulates) have no effect on membrane separation performance

Next step: Pilot scale long term testing; real flue gas

Membrane testing at EDP power plant Sines, Portugal

Main goals

- **Demonstration in 2011**
  - **Longer time: 6 months**
  - Larger: membrane area, flows
  - Durability: checking any performance degradation

Secondary goals

- **Performance charting**
  - Behaviour in real flue gas (a first!)
  - Finding optimal conditions / settings
- **Membrane module** validation
- **Membrane installation** validation / optimisation
- (Recovery optimisation of CO_2 was not focused on)

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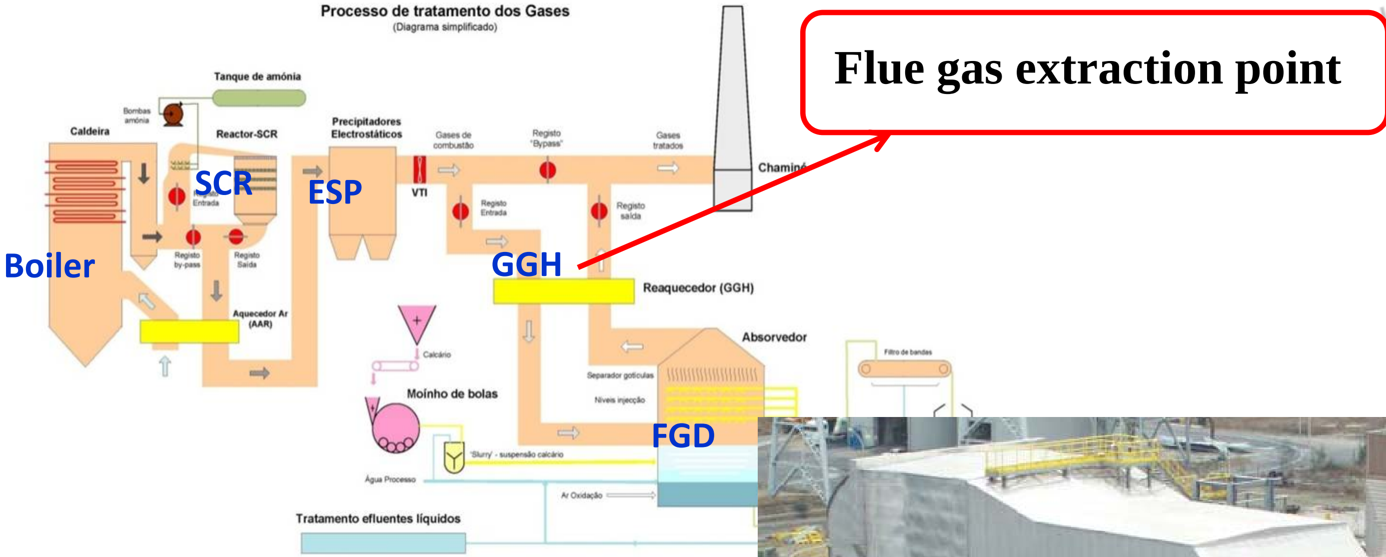
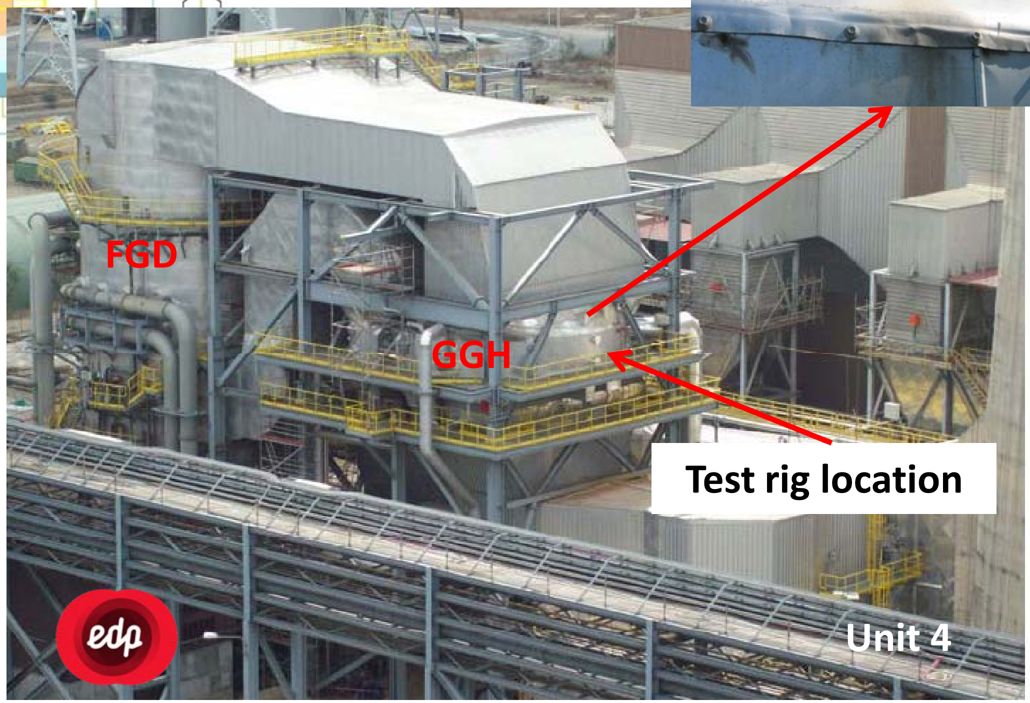
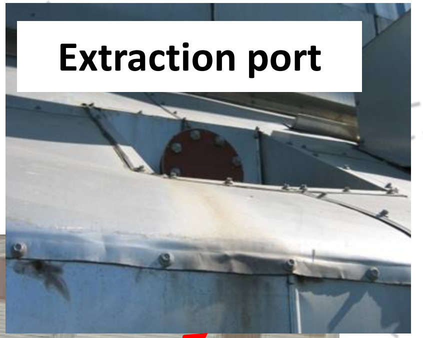
Pilot scale long term testing with real flue gas; EDP in Portugal

Flue gas extraction point and test rig location







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

Compliments of EDP

Pilot scale long term testing with real flue gas 2011

Test parameters: feed flow: 6-24 m^3/h, permeate vacuum 100-200 mbar

	From 23rd May until mid July	From 17th August to December
Type of membranes (from NTNU)	**FSC (Fixed-Site Carrier) flat sheet**	
Membrane area in use	**~ 0,25 m^2**	**~ 1,5 - 2m^2**
Membranes module (from Yodfat)	**With 2 out of 12 elements (4 membranes)**	**With 12 elements (24 membranes)**
Sines Power plant Unit 4	**314 MWe, pulverised bituminous coal, flue gas cleaning (ESP, Wet FGD limestone-gypsum, SCR from mid August)**	
Flue gas main composition:	**Saturated gases at ~ 50 °C (~ 13% H_2O)** **Feed flow**: 6-24 m^3/h, **vacuum** 100-200 mbar	
• **SO_2**	**< 200 mg/Nm^3, 6%O_2, dry gas**	
• **NOx**	**500-600 mg/Nm^3, dry gas (SCR out of service)**	**< 200 mg/Nm^3, dry gas (SCR in service)**
• **Dust (fly ashes)**	**< 20 mg/Nm^3, 6% O_2, dry gas**	
• **CO_2**	**~ 12% vol. at MCR (lower at boiler low loads)**	
• **O_2**	**~ 6% vol. at MCR (higher at boiler low loads)**	

Pilot scale long term testing with real flue gas

Membrane performance May-Aug. 2011 (200 mg/m^3 SO_2, 500 mg/m^3 NOx)

Inspection after 2.5 months continuous operation

- ❑ Little performance reduction
  - ❑ No fouling
  - ❑ No damage detected / visible (leaks)
  - ❑ Some slight discolouration → supports

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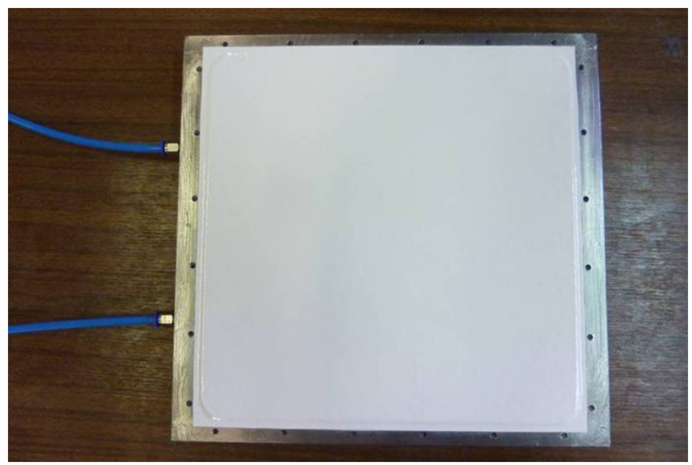
Pilot scale long term testing with real flue gas – Sines, Portugal

Photos: rig, module, membrane, extraction point



Pilot scale long term testing with real flue gas → Dec.2011

Technical issues which needed to be solved

(in bold are the factors affecting the most the membrane performances)

- **High NO_x levels**: lack of SCR
- Vacuum pump/system **leakage: module, sealing, pipes**
- Water condensation: module, tubing, sensors
- System inertia: slow equilibration
- Filter saturation
- **Vacuum pump (power) inadequate**
- **Trace heating too high** – RH effect on permeance and selectivity
- RH measurements near saturation
- Rig operating and membrane conditioning: lack of experience (operators)
- Instruments calibration
- **FREQUENT OUTAGES OF THE POWER PLANT**
- ***But the membrane survived and showed steady performance!***

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Conclusions for the membrane pilot testing in Portugal

- Constant separation perfomances over six months in real flue gas (Good durability!)
- Maximum CO_2 % in permeate measured was ~75 % («once through» one stage)
- Maximum permeate flow rate 21 l/h (525 l/day) for an area of aprox. ~1.5 m^2
- During periods of constant and normal power plant operation: the CO_2 permeance and selectivity were similar to the values obtained in the laboratory (repeatable!)

- Challenges experienced were:
  - Vacuum pump operation
  - Re-heating of the flue gas: strong effect on feed RH%, separation
  - Frequent power plant outage(s): strong effect on feed RH%, separation
  - Unaccounted internal leakages (23 linear meters of sealing)
  - Water condensation in the rig
  - Measurement of feed humidity inside module
  - Gas flow pattern in the flat sheet module is not optimal

  - ***These are important lessons learned when we now go into next phase of testing for different gas mixtures and scaling up***

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The road now towards a larger pilot

Status 2013: *We have*

- Confirmed excellent separation performance and durability of the membrane material

We do not have

- A good simulation tool for the facilitated transport membrane, but the one we have works fairly good at low feed pressures
- Experimental results from a larger, Hollow Fiber module where flow patterns will guide the process design to be chosen.

Where do we want to go → next 2 years:

- Scale up to a HF module of ~10 m2 / collaboration with international membrane producer (Air Products)
- Test at realistic process conditions (guided by end users)
- Design a Demo process based on obtained results, and better simulation tool → next level, TRL3 (2016→)

We have two new demo projects; 2013 →

- One with ECRA (European Cement Industry
- One with Oil & Gas Companies

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1) Flat sheet module (-> potential of spiral-wound) CO_2 capture membrane testing at Norcem's Brevik plant; CO2 content ~20%

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HEIDELBERGCEMENT Group

KEMA DNV

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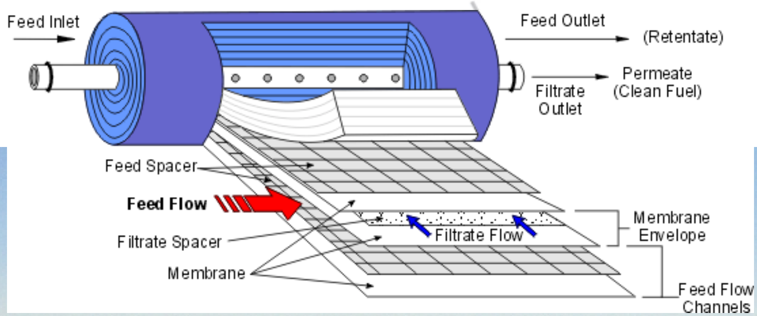

2) Hollow Fiber membranes: small commercial module (~10 m2)

Two types of flue gas:

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

Partners on the team with NTNU:

- Air Products, Alberta Funders (oil sand companies for OTSG-gas), Statoil, DNV KEMA, Sintef MC
- Additional funding partner: GASSNOVA

Air Products will deliver the HF and module,

NTNU/Sintef will coat them with PVAm membrane

Illustration: Air Products Prism Separators

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Summary

- PostCombustion Capture membranes are a promising alternative
  - Unique advantages over some other capture processes
  - (no chemicals, no waste streams, compact solutions)
- Fixed Site Carrier membranes (or facilitated transport membranes)
  - Are the only viable option for post combustion unless an innovative process solution is possible (ref. MTR)
- Rapid R&D developments
  - Durability is a key issue – this has been documented in flue gas from coal fired power plant for the FSC-membrane (ref. Nanoglowa)
  - High purity (95% CO2) / recovery (80%) potential with right choice of process solution
  - Energy usage – no thermal heating
- Higher CO_2 concentration usually means high potential
  - due to high driving force for capture

Membranes are ENVIRONMENTAL FRIENDLY solution!

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Acknowledgements to our project partners so far:

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Thank you for your attention!

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