Membranes and Post Combustion Carbon Dioxide Capture: Challenges and Prospects

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Outline

i) Introduction: Membranes & Post combustion capture

ii) Membrane contactors

iii) Gas separation membranes

iv) Chemically reactive membranes and alternative approaches

vi) Conclusion
Introduction

Separation processes in industry at a glance

Separation agent:

I. Thermal energy

II. Auxiliary phase

III. Membrane

(Humphrey & Keller, Separation Process Technology, 2005)
Gas separation membranes and post combustion carbon capture

Membrane processes are used commercially for CO₂ removal from natural gas at high pressure and at high CO₂ concentration (see Section 3.2.2). In flue gases, the low CO₂ partial pressure difference provides a low driving force for gas separation. The removal of carbon dioxide using commercially available polymeric gas separation membranes results in higher energy penalties on the power generation efficiency compared to a standard chemical absorption process (Herzog et al., 1991, Van der Sluijs et al., 1992 and Feron, 1994). Also, the maximum percentage of CO₂ removed is lower than for a standard chemical absorption processes. Improvements can be made if more selective membranes become available, such as facilitated membranes, described below.

O. Davidson, B., Metz, Special Report on Carbon Dioxide Capture and Storage, International Panel on Climate Change, Geneva, Switzerland, 2005

Membranes for CO₂ separation from flue gases should have a minimum CO₂/N₂ selectivity of 200 (van der Sluijs, 1992). At present the best polyimid membranes attain a CO₂/N₂ selectivity of 30. Hydrogen can be


Carbon capture processes: A tentative roadmap 1/2

### Carbon capture processes: A tentative roadmap 2/2

#### Carbon capture strategy

<table>
<thead>
<tr>
<th>Carbon capture strategy</th>
<th>Target mixture</th>
<th>Conditions</th>
<th>First generation separation process</th>
<th>Possible breakthrough membrane process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxycombustion</td>
<td>O₂/N₂</td>
<td>P atmospheric T ambient</td>
<td>Cryogeny</td>
<td>Ion Transfer Membranes (ITM)</td>
</tr>
<tr>
<td>Pre-combustion</td>
<td>CO₂/H₂</td>
<td>P up to 80 Bar T 300 – 500 C</td>
<td>Gas-liquid absorption in physical solvent</td>
<td>Membrane reactor</td>
</tr>
<tr>
<td>Post-combustion</td>
<td>CO₂/N₂</td>
<td>P atmospheric T 100 – 250 C</td>
<td>Gas-liquid absorption in chemical solvent (MEA)</td>
<td>Membrane gas separation</td>
</tr>
</tbody>
</table>
Membranes and post-combustion carbon capture: Synopsis

- Intensified gas liquid absorption: Membrane contactors
- Gas permeation membranes: physical
- Gas permeation membranes: chemical
- Alternative approaches & miscellaneous

Membranes contactors for intensified CO$_2$ absorption processes
Membranes and post-combustion carbon capture: Synopsis

- Intensified gas liquid absorption: Membrane contactors
  
- Gas permeation membranes: physical
  
- Gas permeation membranes: chemical
  
- Alternative approaches, miscellaneous

Membrane contactors for intensified gas-liquid absorption: Principle

- Key issue: design a porous material and use it between the liquid solvent and the gas phase under non wetting conditions

- Advantages:
  - increased interfacial area (a)
  - no flooding or weeping limitations
  - improved liquid distribution, no sensitivity to orientation
  - limited solvent losses
  - scale-up modular and easy

- Drawbacks:
  - additional mass transfer resistance
  - no economy of scale (numbering up)
Membrane contactors: a novel intensification process for fluid mass transfer processes

Hollow fiber module
Internal fiber diameter \( \sim 0.2-5 \text{ mm} \)
Specific interfacial area \((a)\): 1000-5000 \text{ m}^{-1}

\[
K_{\text{G,INT}} = \frac{1}{k_G r_e + \frac{(r - \delta)}{k_m r_{ml}} + \frac{1}{m.E.k_L}}
\]

Membrane contactors in industry at a glance

- Numerous industrial applications (carbonated beverages, aroma recovery, oxygen stripping…)

- Dozens of publications each month on CO₂ capture at lab scale…

- Very limited feedback and limited number of actors at pilot and industrial scale (Statoil, TNO)

- 2 main membrane materials: PP and PTFE

Membrane phase contactor unit for stripping of oxygen from water. (Provided by Hoechst Celanese Corporation).
Membrane contactors for CO₂ capture: Materials challenge

\[ k_m = \frac{D_m \cdot \varepsilon}{\tau \cdot \delta} \]

- \( D \): diffusion coefficient (bulk – Knudsen)
- \( \varepsilon \): Porosity
- \( \delta \): Membrane thickness
- \( \tau \): Tortuosity

Trade-off between permeability and breakthrough pressure

Porous hydrophobic membrane materials:
Examples of different structures

Polypropylene (PP)
Polyvinylfluoridilène (PVDF)
Polytetrafluoroethylene (PTFE)
Nylon
Membrane contactors and CO\textsubscript{2} absorption in 30% MEA: A parametric study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference case: Packed column</th>
<th>Membrane contactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet solvent (MEA) loading ((\alpha_{\text{IN}}))</td>
<td>0.24 (Abu-Zahra et al., 2007)</td>
<td>Variable (usually 0)</td>
</tr>
<tr>
<td>Outlet solvent (MEA) loading ((\alpha_{\text{OUT}}))</td>
<td>0.48 (Abu-Zahra et al., 2007)</td>
<td>Variable</td>
</tr>
<tr>
<td>Gas phase pressure drop ((\Delta P_{\text{G}}))</td>
<td>5000 – 7000 Pa (NETL, 2007)</td>
<td>Usually not mentioned</td>
</tr>
<tr>
<td>Gas-liquid interfacial area ((a))</td>
<td>200-500 m(^{-1}) (Tobiesen et al., 2007)</td>
<td>1000 – 5000 m(^{-1}) (Gabelman &amp; Hwang, 1999)</td>
</tr>
<tr>
<td>Overall mass transfer coefficient (K)</td>
<td>4x10(^{-3}) – 10(^{-2}) m.s(^{-1}) (Tobiesen et al., 2007)</td>
<td>3x10(^{-3}) – 10(^{-3}) m.s(^{-1}) (Feron et al., 2002)</td>
</tr>
<tr>
<td>Overall volumetric CO\textsubscript{2} absorption capacity (C)</td>
<td>1 mol CO\textsubscript{2}.m(^{-3}).s(^{-1}) (Tobiesen et al., 2007; NETL, 2007; Mangalapally et al., 2010)</td>
<td>0.7 - 10 mol CO\textsubscript{2}.m(^{-3}).s(^{-1}) (Nishikawa et al., 1995; Feron and Jansen, 2002; Yeon et al., 2003; Hoff et al., 2004; deMontigny et al., 2005)</td>
</tr>
</tbody>
</table>
Parametric study: Targets and framework

1. Compute, through a number of simulations, the volumetric absorption capacity of different membrane contactors (isothermal conditions, plug flow on gas side, liquid in, counter current mode, 30% MEA, 15% CO₂ in feed mixture, capture ratio 0.9)

2. Select the set of data with a maximal gas pressure drop of 50 mBar and liquid pressure drop of 1 Bar

3. Identify the requirements in terms of membrane permeance, fiber geometry and module packing fraction which enable intensification to be achieved

Lab scale tests and simulations with membrane contactors

A typical lab scale set-up for membrane contactors testing

Prediction performances of simulations with 30% MEA
**Parametric sensitivity: variables and range of variation**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Variation range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_e$ hollow fiber external radius</td>
<td>$10^{-4} - 3.10^{-3}$</td>
<td>[m]</td>
</tr>
<tr>
<td>$\delta$ membrane thickness</td>
<td>$5.10^{-5} - 10^{-4}$</td>
<td>[m]</td>
</tr>
<tr>
<td>$\varphi$ module packing fraction</td>
<td>0.1 - 0.6</td>
<td>[-]</td>
</tr>
<tr>
<td>$u_G$ interstitial gas velocity</td>
<td>0.1 - 5</td>
<td>[m.s^{-1}]</td>
</tr>
<tr>
<td>$k_m$ membrane effective mass transfer coefficient</td>
<td>$10^{-2} - 10^{-5}$</td>
<td>[m.s^{-1}]</td>
</tr>
</tbody>
</table>

**Parametric study: summary of results**

Approximately 11,000 simulations performed

An intensification factor larger than 1 is obtained within the $\Delta P$ limits for ca 300 cases, with module length between 0.1 and 2m

A maximal intensification factor of 8.5 seems to be attainable for a very limited number of cases

An intensification larger than 1 requires: $k_m > 7x10^{-4} \text{ m/s}$

$\delta < 80 \mu m$ and $r_e < 400 \mu m$

A packing fraction of 0.5-0.6 is required for an intensification factor larger than 8
Membrane contactors and CO₂ capture: one step forward....

Long time scale results are required for material selection

Experimental results at a large scale, on real flue gases are of primarly importance

Non isothermal conditions, water evaporation, gas and liquid dispersion effects should be added in simulation packages

Desorption thanks to temperature resistant MC should be more systematically explored

Dense skin membrane contactors in order to prevent liquid wetting problems

Post combustion capture by gas separation membranes
Membranes and post-combustion carbon capture: Synopsis

- Intensified gas liquid absorption: Membrane contactors
- Gas permeation membranes: physical
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- Alternative approaches, miscellaneous

Dense membrane permeation

Permeability of A \( \equiv P_A = D_A S_A \)
where \( D_A = \) diffusion coefficient
\( S_A = \) solubility coefficient

Selectivity
\[
\alpha_{A/B} = \left( \frac{P_A}{P_B} \right) = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right)
\]

(1) Sorption on upstream side
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side
Membrane Gas Separation: Applications & Market

Market size: 150 MUS$/y (Baker, 2002)

Trade-off curves predictions for physical process

[Graph showing trade-off curves]
Step 1: Selectivity challenge

\[ \text{Feed composition } x \]
\[ \text{Capture ratio } R \]
\[ \text{Purity } y \]
\[ \frac{\text{Selectivity challenge } \alpha}{g68} \]

Capture Cost

Gas permeation module design: single stage case

\[ P': \text{ Upstream pressure} \]
\[ P_{in}: \text{ Feed pressure} \]
\[ Q_{in}: \text{ Flowrate} \]
\[ x_{in}: \text{ CO}_2 \text{ mole fraction} \]
\[ P'': \text{ Downstream pressure} \]
\[ Q_p: \text{ Flowrate} \]
\[ y: \text{ CO}_2 \text{ mole fraction} \]

Key variables

Selectivity
\[ \alpha^* = \frac{\Pi_{\text{CO}_2}}{\Pi_{N_2}} \]

Pressure ratio
\[ \psi = \frac{P''}{P'} \]

Stage cut
\[ \theta = \frac{Q_p}{Q_{in}} \]

Separation performances:

\[ R: \text{ Recovery } = \text{ Capture ratio} \]
\[ y: \text{ Permeate content } \text{CO}_2 \]
**Permeation module simulation: Cross plug flow case**

\[
\frac{dQ^*}{ds} = \left\{ x - \psi y_p + x \frac{dQ^*}{ds} \right\}
\]

\[
\frac{dQ^*}{ds} = \left\{ x - \psi y_p + \frac{1}{\alpha} \left( 1 - x - \psi (1 - y_p) \right) \right\}
\]

\[
y_p = \alpha \left( \frac{x - \psi y_p}{1 - x - \psi (1 - y_p)} \right)
\]

**ODE system resolution : DASSL (M3Pro© software)**


**Gas permeation module master / curves**

10% CO\(_2\) in flue gas:

Impossible to achieve 

\( R > 0.8 \) and \( y > 0.8 \)

unless \( \alpha > 200 \)
Step 2: Energy challenge

\[ \text{Feed composition } x \]
\[ \text{Capture ratio } R \]
\[ \text{Purity } y \]
\[ \Rightarrow \text{Selectivity challenge } \alpha \]

\[ \text{Operating Conditions } \Psi, \theta \]
\[ \Rightarrow \text{Energy Challenge } E < 2 \text{ GJ}_\text{th}/\text{ton} \]
\[ \Rightarrow \text{Energy cost} \]
\[ \Rightarrow \text{OPEX} \]
\[ \Rightarrow \text{Capture Cost} \]
Energy requirement computation: Feed compression

\[ E_1 = \frac{Q_{\text{In}} \cdot \gamma RT}{\eta} \left[ \left( \frac{P_{\text{max}}}{P_{\text{min}}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \]

Parametric study results: Feed compression

1. High parametric sensitivity: \( E \) strongly influenced by \( x_{\text{in}} \)
2. For a 10% \( \text{CO}_2 \) content the energy requirement and the minimal membrane selectivity are too high
Energy requirement computation: Vacuum pumping

\[ E_1 = \frac{Q_p}{\eta'} \cdot \frac{\gamma \cdot RT}{\gamma - 1} \left( \frac{P_{\max}}{P_{\min}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \]

Parametric study results: Vacuum pumping

1. \( E \) below 0.5 GJ per ton can be achieved
2. For a 20% CO\(_2\) content, the required membrane selectivity for \( E = 0.5 \) GJ per ton is around 60, i.e. a realistic figure
The ultimate (and largely unexplored) challenge: energy, productivity, cost

Feed composition $x$
Capture ratio $R$
Purity $y$

Selectivity challenge $\alpha$

Operating Conditions $\Psi, \theta$

Energy Challenge $E < 2 \, \text{GJ}_\text{th/ton}$

Feed flow rate
Permeability
Thickness

Productivity Challenge
Maximal flux

Energy cost

OPEX

Capture Cost

CAPEX

Membrane cost ($\text{€/m}^2$)

Tackling the energy (pressure ratio) / capacity trade off

15% CO$_2$ in feed mixture 90% purity at permeate
Reducing the Cost of CO₂ Capture from Flue Gases Using Membrane Technology

Minh T. Ho, Guy W. Allinson, and Dinanne E. Wiley

Main conclusion:

Best solution: single stage with vacuum

Selectivity: \( \alpha > 40 \) required (but \( y \) will be limited to 0.6)

\[ \text{Figure 8. Capture cost as a function of CO}_2/\text{N}_2 \text{ selectivity for the high-pressure feed SMS system (---) and for different vacuum membrane systems (---); SMS (○) and TCMS (■).} \]


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Reducing the Cost of CO₂ Capture from Flue Gases Using Membrane Technology

Minh T. Ho, Guy W. Allinson, and Dinanne E. Wiley

Main conclusion (ctd):

High permeability required (500 Barrer with \( z \) 0.125 \( \mu \)m)

\[ \text{Figure 6. Effect of CO}_2 \text{ permeability on the CO}_2 \text{ capture cost (U.S. $/tonne CO}_2 \text{ avoided) for different vacuum membrane systems; SMS (○), TCMS (■), and TCMS-RR (○).} \]

Reducing the Cost of CO₂ Capture from Flue Gases Using Membrane Technology

Minh T. Ho, Guy W. Alhinson, and Dinna E. Wiley

Main conclusion (ctd):
Low membrane cost required (< 50 $/sqm)

Selectivity challenge: "Physical" separation membranes

**Option 1: Single stage membrane system**

Reducing the Cost of CO₂ Capture from Flue Gases Using Membrane Technology

Minh T. Ha, Guy W. Allinson, and Dianne E. Wiley

The only way to overcome the energy challenge seems to apply vacuum, nevertheless, this option may show major limitations:
- energy efficiency can be low compared to compressors ($\eta \sim 0.85$)
- vacuum pump foot print is large and leaks can be problematic

**Option 2: Multi-stage membrane systems**

One of the earliest membrane flowsheet for post-combustion CCS application

$\text{CO}_2$ recovery 80%, $\text{CO}_2$ purity 90%
Energy requirement 50-75 % of combustion energy of coal
(MEA 47-79 %)

Challenges & unsolved issues: Water

Cellulose acetate films for moist N₂ / CO₂ mixed gas at 0.7 MPa (100 psi).

3: Depression of CO₂ permeability in Kapton caused by water vapor.

Challenges & unsolved issues: Oxygen and “minor species”

Rejection increases
Membranes and post-combustion carbon capture: Synopsis

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CAPEX + OPEX
Looking for improved performances: Chemically reactive membranes with fixed sites

- Polyelectrolyte membranes (PVBTAF) with water saturated mixture permeation: $\alpha = 900$ (Quinn, 1977)

- Plasma grafted polyacrylic acid membrane with amine carrier (Matsumya, 1994) $\alpha = 4700$, $P = 10^6$ Barrer!!

- Polyvinylamine (Hagg, 2005) $\alpha = 150-250$

- PAMAM (Duan, 2006), $\alpha = 260$

Looking for improved performances: Liquid membranes

- Numerous studies for a long time!

- Ward & Robb (1966) $\alpha > 4600$

- Sirkar, Ho, Noble…
Chemically reactive membranes: Performances

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Material and/or carrier</th>
<th>CO₂/N₂ selectivity</th>
<th>CO₂ permeability (Barrer) or permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas separation membrane (dense polymers)</td>
<td>PEO-PBT</td>
<td>70</td>
<td>120 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEG/Peax©</td>
<td>47</td>
<td>151 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEG-DME/ Peax©</td>
<td>43</td>
<td>600 Barrer</td>
</tr>
<tr>
<td></td>
<td>PEGDA/PEGMEA</td>
<td>41</td>
<td>570 Barrer</td>
</tr>
<tr>
<td></td>
<td>Polaris™</td>
<td>50</td>
<td>1000 GPU</td>
</tr>
<tr>
<td>Fixed Site Carrier Membrane (FSCM)</td>
<td>PAAM-PVA / PS</td>
<td>80</td>
<td>24 GPU</td>
</tr>
<tr>
<td></td>
<td>PVAm/PVA</td>
<td>145</td>
<td>212 GPU</td>
</tr>
<tr>
<td></td>
<td>PEI / PVA</td>
<td>230</td>
<td>1 GPU</td>
</tr>
<tr>
<td></td>
<td>PDMA/PS</td>
<td>53</td>
<td>30 GPU</td>
</tr>
<tr>
<td></td>
<td>PDMAMA</td>
<td>80</td>
<td>5 GPU</td>
</tr>
<tr>
<td>Liquid Membrane (LM)</td>
<td>PVAm-PVA/PS</td>
<td>90</td>
<td>22 GPU</td>
</tr>
<tr>
<td></td>
<td>PVAm/PVA</td>
<td>90</td>
<td>15 GPU</td>
</tr>
<tr>
<td></td>
<td>Amines/PVA</td>
<td>500</td>
<td>250 GPU</td>
</tr>
<tr>
<td></td>
<td>Carbonic anhydrase</td>
<td>250</td>
<td>80 GPU</td>
</tr>
<tr>
<td></td>
<td>Amines / PVA</td>
<td>493</td>
<td>693 Barrer</td>
</tr>
</tbody>
</table>

Liquid membrane processes

Carrier
K₂CO₃ aqueous solution
Assymetric PVTMS membrane
selective layer thickness 0.2 μm

Selectivity challenge: "Chemical" separation membranes

Fixed site carrier membranes:
Selectivity 80-250
Water required

Liquid membranes:
Selectivity up to 4500
Water required

Key issues:
Productivity (l ~5-7 µm)
Driving force (sweep)
Stability

Carbonic anhydrase LM: Carbozyme concept
Membranes processes for CO$_2$ capture:
Alternative approaches

Looking for alternative emission sources...

\[
W_{\text{min}} = -RT \left[ \frac{x \ln(x) + (1 - x) \ln(1 - x)}{x} + \frac{y \ln(y) + (1 - y) \ln(1 - y)}{y} \right]
\]
Towards breakthrough membrane materials?

Zeolite membranes performances. Predictions based on MD simulations (J. Memb. Sci., in press)

Unconventional approach: Reverse selective membranes

CO₂ selective membrane  N₂ selective membrane

Hybrid processes

\[ W_{\text{min}}' = -R.T \frac{x \ln(x) + (1-x) \ln(1-x)}{x} \]

\[ W_{\text{min}}'' = -R.T \left[ \frac{x \ln(x) + (1-x) \ln(1-x)}{x} \right] + R.T \frac{y \ln(y) + (1-y) \ln(1-y)}{y} \]

Hybrid process: Rationale

Cryogeny  Combustion  Flue gas drying  Gas permeation membrane module
Hybrid process: Principle

\[ E = E_1 + E_2 = \frac{E_{O_2}}{R} \cdot \frac{3n + 1}{2n} + \frac{\gamma}{\gamma - 1} \cdot \frac{9RT}{\eta'} \left[ \left( \frac{P'}{P''} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] \cdot \frac{10^{-3}}{R \cdot x' \cdot 44} \]

Hybrid process: Simulation results

Natural gas \((n = 1)\)

Most challenging!

Single module

Feed compression

\( R = 0.9 \)

\( y = 0.9 \)

\( \% 50-60\% \) oxygen in feed air seems to be the best compromise

Carbon dioxide capture by a membrane unit from biogas combustion unit: simulation results

\[ \begin{align*}
R &= 0.9 \\
y &= 0.9 \\
\alpha &= 50
\end{align*} \]

\[ y \quad \text{Oxygen mole fraction in enriched air} \]

\[ E \quad \text{[GJ/ton CO2]} \]

Methane mole fraction in biogas

- \( X_{\text{CH4}} = 0.95 \)
- \( X_{\text{CH4}} = 0.90 \)
- \( X_{\text{CH4}} = 0.80 \)
- \( X_{\text{CH4}} = 0.70 \)
- \( X_{\text{CH4}} = 0.50 \)


Miscellaneous….

- **Flue gas drying**
- **Compressor purge**
- **Alternate driving forces: temperature, water vapor sweep**
- **Pressurised combustion (e.g. Combicap concept)**
- **Integrated approach (S, N, C removal)**
- **High temperature permeation**
02.04.2009 - Air Products announced it will play a key role in the world’s first full demonstration of oxyfuel carbon capture and sequestration with the signing of an agreement with Vattenfall AB. Air Products will install its proprietary carbon dioxide (CO2) capture, purification and compression system at Vattenfall’s research and development facility in Schwarze Pumpe, Germany, which is viewed globally as the preeminent CO2 oxyfuel project. Air Products will focus specifically on the purification and compression of oxyfuel combustion flue gas. The two companies also executed a joint research and development agreement related to the project. Air Products’ pilot plant is to be operational at Schwarze Pumpe in December 2010.

“This is the world’s first full demonstration of oxyfuel CO2 capture and sequestration, and our unique CO2 purification and compression technology will be validated at pilot scale through this work,” said David J. Taylor, vice president - Energy Businesses at Air Products.

At the Schwarze Pumpe facility, Air Products will take flue gas directly off Vattenfall’s 30 megawatt (MW) wall-fired boiler at the oxyfuel pilot plant. It will purify and compress the carbon dioxide, a portion of which will ultimately be transported for sequestration. Air Products’ proprietary sour compression technology uses a staged compression process to optimize pressure, hold-up, and residence time to allow removal of impurities during the compression process. This allows cost savings in the oxyfuel combustion process and minimizes the concentration of additive components, important in preventing corrosion during the CO2 sequestration process. This pilot will demonstrate the efficient purification of CO2, and remove inert gases, in particular oxygen. In addition, it will incorporate novel membrane technology, targeting carbon capture rates as high as 98 percent.

www.chemie.de/news/06130/
• Membranes processes offer a large variety of potential applications in a CCS framework (intensification, separation, concentration)

• For the capture step, the purity and recovery specifications play a key role (strong parametric sensitivity, strong flexibility)

• Material science & process engineering collaboration is crucial!

• Pilot studies & technico-economical analyses are needed!

• Post combustion CCS is a complex, multivariable landscape: no silver bullet!

• Gas separation membranes missed (as usual) the first generation

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Questions?

Further information?

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<table>
<thead>
<tr>
<th>Target</th>
<th>Membrane process</th>
<th>Main characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensified gas liquid absorption</strong></td>
<td>Membrane contactor (hydrophobic porous membrane)</td>
<td>Membrane stability (non wetting conditions) has to be ensured for long time operation. Regeneration step non achievable. Effective intensification factor remains to be clearly evaluated.</td>
</tr>
<tr>
<td><strong>Carbon dioxide capture</strong></td>
<td>1. Gas separation membranes: physical (GS) (usually a dense polymer)</td>
<td>Numerous materials investigated, few technico-economical studies, almost no pilot scale process on real flue gas. Water in flue gas could be a problem. Require multistage processes in order to achieve purity target.</td>
</tr>
<tr>
<td></td>
<td>2. Chemically reactive membranes (FSCM)</td>
<td>Require water, on both sides of the membrane, to be effective. May be applicable through a single stage process if a high selectivity is attained. Industrial feedback on real flue gas still not achieved.</td>
</tr>
<tr>
<td></td>
<td>3. Liquid membranes (LM)</td>
<td>Very high selectivity can be achieved. Require water, on both sides of the membrane, to be effective. Solvent losses due to volatility can be a problem, possibly solved by ionic liquids. Effective driving force, stability and effective permeability in a real post-combustion situation remain to be.</td>
</tr>
</tbody>
</table>

**$N_2$ purity**

<table>
<thead>
<tr>
<th>Flowrate ($Nm^3.h^{-1}$)</th>
<th>Liquid nitrogen</th>
<th>Adsorption</th>
<th>Cryogeny</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>5000</td>
<td></td>
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<tr>
<td>99.9</td>
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<td></td>
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Source:
Greenhouse Issues (2006), 84, 12