7. CO$_2$ Membrane Separation

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Present Cost of CCS (coal fired power plant)

recovery amount: 1Mt-CO$_2$/yr, distance: 20km, pressure: 7MPa
injection method: ERD, injection amount: 0.1Mt-CO$_2$/yr/well

Power loss for extraction steam from low pressure turbine: 0.05kWh/MJ

New plant
- coal fired plant to aquifer

Existing plant
- Existing coal fired plant to aquifer

Upgrading desulfurization facilities & Auxiliary coal fired boiler

Avoided cost JPY/t-CO$_2$

Capture cost 4,200 JPY/t-CO$_2$

NET storage = 670/1000

NET storage = 502/1000

CCS total cost 7,300 JPY/t-CO$_2$
CO₂ capture methods for various Sources

1. CO₂ Sources

- Fossil Fuel
- Bio-Mass

Power plant (Combustion)

Blast-furnace

Gasification

2. CO₂ Capture (Chemical Research Group)

Absorption

Absorber

CO₂ < 2%

HEX

Absorbent

Novel process

Waste heat utilization

Regenerator

CO₂ > 99%

Membrane

Absorber

CO₂ < 2%

Regenerator

CO₂ > 95%

Absorber

CO₂ > 97%

Absorber

CO₂ < 2%

Absorptive materials:
- Polymer
- Zeolite
- Carbon
- Nano composite material

Absorption pilot Plant (COURSE50: NEDO Project)
Source: Nippon Steel Eng. HP.

3. Storage (CO₂ Storage Group)

Geological

Utilization

Ocean

Plant analysis for the decreasing energy and cost
Schematic of IGCC with CO₂ Capture

Coal → O₂ → Gasifier → Steam → After WGS H₂, CO₂ → Heat Exchanger → CO₂ → Product H₂

Advantage in Membrane Separation

-2 to 4 MPa
-ca 40% CO₂
-CO₂/H₂ Separation

Insufficient Selectivity
Prospect for CO₂ Separation Cost of Membrane Separation

<table>
<thead>
<tr>
<th>CO₂ Source</th>
<th>Gas Pres.</th>
<th>Gas Comp.</th>
<th>Membrane Performance (Target)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ Prod. Plant</td>
<td>4MPa</td>
<td>CO₂:40% H₂, H₂O</td>
<td>αCO₂/H₂: 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO₂ Permeance: 1x10⁻⁹ (m³ m⁻² s⁻¹ Pa⁻¹)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ref. Absorption</th>
<th>Amine solution (MDEA-Flash)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine solution (KS solution)</td>
<td></td>
</tr>
</tbody>
</table>

Out put: 300MW
Membrane Area: 100,000 m²

* Duration period: Facility: 15 years Membrane: 5 years
Membrane Skid Cost: 50,000 JPY/m²
**CO₂ Molecular Gate for CO₂/H₂ Separation**

Feed

High Pressure Difference

Low Permeate

CO₂

0.33 nm

H₂

0.29 nm

Membrane

Excellent CO₂ selectivity

Conventional Polymeric Membrane:

CO₂ / H₂ Selectivity: <1
Possible Model of H₂ Perm. Blockage

Carbamate Formation

Pseudo-cross-linkage

H₂ permeation blockage
Dendrimer Membrane for CO$_2$ Capture from Pressurized Gas Stream

O-OH-PAMAM dendrimer

+ 

PEGDMA

+ 

TMPTMA

UV Curing
Dendrimer membrane for CO$_2$ capture from a pressurized gas stream

PAMAM/PEGDMA/TMPTMA = 50/37.5/12.5, Feed : 100 mL/min, Sweep : 20 ml/min, $T = 313$ K, R.H. = 80%
Temperature and Performance

- Temperature readings: 25°C, 40°C, 55°C
- CO$_2$/H$_2$ Selectivity
- CO$_2$/H$_2$ Permeance / m$^3$(STP)/(m$^2$ s Pa)
- PAMAM/PEGDMA/TMPTMA = 50/37.5/12.5
- Thickness: 500µm
CO$_2$/H$_2$ Separation Properties of Dendrimer Membranes at High Pressure

CO$_2$/H$_2$ Selectivity (-)

CO$_2$ Permeance / m$^3$(STP)/(m$^2$ s Pa)

Separation of CO$_2$/CH$_4$ using molecular gate membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CO$_2$ conc. in Feed</th>
<th>CO$_2$ conc. in Permeate</th>
<th>Permeance, Q$_{CO2}$</th>
<th>Separation factor, $\alpha_{CO2/CH4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>79.6</td>
<td>99.2</td>
<td>$7.6 \times 10^{-12}$</td>
<td>30</td>
</tr>
<tr>
<td>B</td>
<td>74.5</td>
<td>99.9</td>
<td>$1.2 \times 10^{-11}$</td>
<td>260</td>
</tr>
</tbody>
</table>

Temperature: 40 °C, Total pressure in feed gas: 0.1 MPa, Relative humidity in Feed gas: 80%, He sweep gas at permeate side.

Molecular gate membranes possess high potential for separation of CO$_2$/CH$_4$ mixed gas
Dendrimer Composite Membrane

Substrate of UF Membrane (commercial)

Selective Layer
0OH Dendrimer/
Polymeric Matrix

Porous Substrate

300 nm

For CO$_2$ separation from ambient pressure gas stream (1$^{st}$ Term)
Dendrimer Composite Membrane Module

<table>
<thead>
<tr>
<th>Module #</th>
<th>Membrane Area $cm^2$</th>
<th>$CO_2/N_2$ Selectivity $\alpha_{CO_2/N_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
<td>290</td>
</tr>
<tr>
<td>2</td>
<td>180</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>4000</td>
<td>150</td>
</tr>
</tbody>
</table>

Dendrimer: conventional PAMAM dendrimer (0OH), Temperature: 25 °C

For $CO_2$ separation from ambient pressure gas stream ($1^{st}$ Term)
Feed gas mixture: CO$_2$/N$_2$ (32/68 v/v%) containing unknown amount of water vapor
Measured temperature: 14-25°C, Pressure difference between feed and permeate: 0.1MPa

Long-term Stability

CO$_2$ Permeance $Q$(CO$_2$) $\times 10^{10}$ [m$^3$ (STP) m$^{-2}$ s$^{-1}$ Pa$^{-1}$]

Separation Factor, $\alpha$ CO$_2$/N$_2$ [-]

CO$_2$ Conc. in Permeate [%]

Test period [h] 800mm-3/8inch module

average 95%
minimum 90%
Membrane modules

Hollow-fiber module:

Merits:
・Well-studied structure for gas separation
・Large membrane area per unit volume

Issues:
・Pressure durability up to 4MPa
・Coating method for hollow-fibers

Spiral-wound Module (flat-sheet membranes):

Merits:
・Pressure durability up to 10MPa (water)
・Easy to coat flat-sheet membranes

Issue:
・Membrane area per unit volume
Cooperation with private companies (Development of Membrane module)

Cooperation with
Four membrane companies (Kuraray, Daicel, Toray, Nitto-Denko)
Engineering company (Nippon Steel Engineering)
Membrane module test using syngas

Testing apparatus at ECOPRO Gasifier, Nippon Steel Corporation (Yawata plant), Nippon Steel Engineering Co., Ltd.

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Thank you for your attention!

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