Capture in 1930
Challenges Post-combustion Capture

- **Avoid emission solvent traces**
- **Reduce absorber, scrubber investment**
- **Advanced heat integration**
- **Reduce heat consumption**

Diagram showing the flow of CO₂ lean gas and CO₂ rich gas through absorber and regenerator, with makeup water and CO₂ gas inputs and outputs.
Carbamate formation: Zwitterion mechanism

\[
\text{CO}_2 + R_1R_2NH \rightleftharpoons R_1R_2NH^+COO^- \\
R_1R_2NH^+COO^- + B \rightleftharpoons R_1R_2NCOO^- + BH^+
\]

Caplow., 1968
Bicarbonate formation

\[ R_1R_2NCOO^- + H_2O \rightleftharpoons R_1R_2NH + HCO_3^- \]

\[ CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \]
\[ CO_2(aq) + OH^- \rightleftharpoons HCO_3^- \]
\[ H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \]

Bicarbonate can again be deprotonated by a base molecule (B).

\[ HCO_3^- + B \rightleftharpoons CO_3^{2-} + B \]
Tertiary amines

\[
\text{CO}_2\text{(aq)} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \\
\text{CO}_2\text{(aq)} + \text{OH}^- \leftrightarrow \text{HCO}_3^- \\
\text{CO}_2 + R_1R_2R_3N + \text{H}_2\text{O} \leftrightarrow R_1R_2R_3N^+\text{H} + \text{HCO}_3^-
\]
Other reactions

- Ionization of water:

\[
\text{OH}^- + \text{H}_3\text{O} \leftrightarrow 2\text{H}_2\text{O}
\]

- Protonation of amine molecule:
Criteria for solvent selection

I. “basic” criteria

- vapor pressure
  - solvent losses
  → water-washing
- thermal / chemical stability
  - reclaiming or refill frequency
- corrosivity
  → stainless steel or plastics
- solubility
  - in water
  - for carbonates and/or carbamates
- viscosity
  - mass transfer
  - hydrodynamics
- selectivity \((\text{NO}_x, \text{SO}_x)\)
  - solvent consumption
  → refill frequency
- price
  - market acceptance
Criteria for solvent selection

II. “no-no” criteria

- toxicity
- ecotoxicity
- biodegradability
- availability

III. “nice-to-have” criteria

- no dual use
- foaming tendency

→ chemical weapons
Criteria for solvent selection

IV. Thermal Effectivity

- CO₂ capacity
  - molecular weight
  - equilibrium
  - pKₐ

- liquid pump around
  - column diameter
  - size of pumps & tubes
  - energy requirement

- heat of CO₂ absorption

- mass transfer
  - contact time
  - height of column

- equilibrium
  - pKₐ

- kinetics
Development lines: Strategy for solvent selection

1. Selection: Subset A1 of solvents
   • Equilibrium data $\Rightarrow$ solvent flow and regeneration energy

2. Selection: Subset A1.1 of solvents
   • Absorption kinetics $\Rightarrow$ column height

3. Selection: Subset A1.1.1 of solvents
   • Chemical stability, Corrosiveness, …

4. Selection: Subset A1.1.1.1 of solvents

Appropriate solvents for CO$_2$-capture from flue gas
Lower energy demands solvent regeneration
Conditions: Flue gas flow 5000 Nm$^3$/h, Optimal L/G, CO$_2$ removal • 90%, Stripper pressure 1.85 bara

<table>
<thead>
<tr>
<th></th>
<th>MEA</th>
<th>CESAR 1</th>
<th>CESAR 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific steam consumption (G/ton CO$_2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard</td>
<td>3.5</td>
<td>3.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Improved Hx</td>
<td>3.3</td>
<td>3.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Improved Hx+IC</td>
<td>2.5</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Improved Hx+LVR</td>
<td>2.5</td>
<td>3.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Improved Hx+IC+LVR</td>
<td>2.5</td>
<td>3.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Improvement solvent:

<table>
<thead>
<tr>
<th>Specific energy duty GJ/t CO₂</th>
<th>Thermal GJ/tCO₂</th>
<th>Electric GJ/tCO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>30wt% MEA</td>
<td>3.6</td>
<td>0.4</td>
</tr>
<tr>
<td>40wt% MEA</td>
<td>3.1</td>
<td>0.4</td>
</tr>
<tr>
<td>AMP/PZ</td>
<td>3.3</td>
<td>0.4</td>
</tr>
<tr>
<td>HP PZ</td>
<td>2.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Including compression
Improved flowsheet
Process
Absorption enhancement

InterCooled Absorber (ICA)  InterHeated Absorber (IHA)

Split Flow Arrangement (SFA)  Double Loop Absorber/Stripper (DLA)
Technology for a better society

Vacuum Operated Stripper (VOS)
Improved Economizer Arrangement (IEA)
Stripper Split Feed (SSF)
Overhead Condensate Bypass (OCB)

Heat integration

Rich Solvent Preheating (RSP)
Rich Solvent Flashing (RSF)
Multistage heated Flash Stripping (MFS)

InterHeated Stripper (IHS)
Heat Integrated Stripper (HIS)
Multi Effect Stripper (MES)
Capture plant: Base Case

<table>
<thead>
<tr>
<th>Reboiler duty</th>
<th>Heat Exchangers (HEX)</th>
<th>HEX total specific UA</th>
<th>Cooling duty</th>
</tr>
</thead>
<tbody>
<tr>
<td>[GJ\textsubscript{th}/ton CO\textsubscript{2}]</td>
<td>[number]</td>
<td>[(GJ\textsubscript{th}/K)/ton CO\textsubscript{2}]</td>
<td>[GJ\textsubscript{th}/ton CO\textsubscript{2}]</td>
</tr>
<tr>
<td>3.54</td>
<td>1</td>
<td>0.62</td>
<td>4.57</td>
</tr>
</tbody>
</table>

Electricity use

<table>
<thead>
<tr>
<th>Capture</th>
<th>Compression</th>
<th>Total</th>
<th>Total including reboiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>[GJ\textsubscript{e}/ton CO\textsubscript{2}]</td>
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<td>[GJ\textsubscript{e}/ton CO\textsubscript{2}]</td>
</tr>
<tr>
<td>0.09</td>
<td>0.32</td>
<td>0.41</td>
<td>1.29</td>
</tr>
</tbody>
</table>

\textsuperscript{a} U is the overall heat transfer coefficient; A is the contact area in the heat exchanger. If U is considered constant, UA is proportional to the contact area. 
\textsuperscript{b} Assuming 1 GJ\textsubscript{e} = 4 GJ\textsubscript{th}
Split flow

Split flow: 8wt%

<table>
<thead>
<tr>
<th>Reboiler duty [GJ\text{th}/ton CO\text{2}]</th>
<th>Heat Exchangers (HEX) [number]</th>
<th>HEX total specific UA \text{^a} [(GJ\text{th}/K)/ton CO\text{2}]</th>
<th>Cooling duty [GJ\text{th}/ton CO\text{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.40</td>
<td>1</td>
<td>0.95</td>
<td>4.44</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<td>Capture [GJ\text{e}/ton CO\text{2}]</td>
</tr>
<tr>
<td>0.09</td>
</tr>
</tbody>
</table>

\textsuperscript{a} U is the overall heat transfer coefficient; A is the contact area in the heat exchanger. If U is considered constant, UA is proportional to the contact area.

\textsuperscript{b} Assuming 1 GJ\text{e} = 4 GJ\text{th}
Lean vapour compression (LVC)

Reboiler duty

<table>
<thead>
<tr>
<th>[GJ$_{th}$/ton CO$_2$]</th>
<th>[GJ$_{e}$/ton CO$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.07</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Heat Exchangers (HEX)

<table>
<thead>
<tr>
<th>[number]</th>
<th>[(GJ$_{th}$/K)/ton CO$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.53</td>
</tr>
</tbody>
</table>

HEX total specific UA $^a$

<table>
<thead>
<tr>
<th>[(GJ$_{th}$/ton CO$_2$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.96</td>
</tr>
</tbody>
</table>

Cooling duty

<table>
<thead>
<tr>
<th>[GJ$_{th}$/ton CO$_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.96</td>
</tr>
</tbody>
</table>

Electricity use

<table>
<thead>
<tr>
<th>Capture $^b$</th>
<th>Compression</th>
<th>Total</th>
<th>Total including reboiler $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[GJ$_{e}$/ton CO$_2$]</td>
<td>[GJ$_{e}$/ton CO$_2$]</td>
<td>[GJ$_{e}$/ton CO$_2$]</td>
<td>[GJ$_{e}$/ton CO$_2$]</td>
</tr>
<tr>
<td>0.13</td>
<td>0.32</td>
<td>0.45</td>
<td>1.21</td>
</tr>
</tbody>
</table>

$^a$ U is the overall heat transfer coefficient; A is the contact area in the heat exchanger. If U is considered constant, UA is proportional to the contact area.

$^b$ For this case, the electricity use for capture also includes the LVC compressor.

$^c$ Assuming 1 GJ$_e$ = 4 GJ$_{th}$
Lean vapour compression and split flow

Split flow: 8wt%
Flash pressure: 1.2

---

<table>
<thead>
<tr>
<th>Reboiler duty [GJ_{th}/ton CO_{2}]</th>
<th>Heat Exchangers (HEX) [number]</th>
<th>HEX total specific UA ( a ) [(GJ_{th}/K)/ton CO_{2}]</th>
<th>Cooling duty [GJ_{th}/ton CO_{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.94</td>
<td>1</td>
<td>0.74</td>
<td>4.16</td>
</tr>
</tbody>
</table>

**Electricity use**

<table>
<thead>
<tr>
<th>Capture ( b ) [GJ_{e}/ton CO_{2}]</th>
<th>Compression [GJ_{e}/ton CO_{2}]</th>
<th>Total [GJ_{e}/ton CO_{2}]</th>
<th>Total including reboiler ( c ) [GJ_{e}/ton CO_{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.13</td>
<td>0.32</td>
<td>0.45</td>
<td>1.18</td>
</tr>
</tbody>
</table>

---

\( a \) U is the overall heat transfer coefficient; A is the contact area in the heat exchanger. If U is considered constant, UA is proportional to the contact area.

\( b \) For this case, the electricity use for capture also includes the LVC compressor.

\( c \) Assuming 1 GJ_{e} = 4 GJ_{th}
Intermediate heat exchanger - Stripper

Reboiler duty
[\text{GJ}_\text{th}/\text{ton CO}_2]  
3.18

Heat Exchangers (HEX)
[number]  
2

HEX total specific UA \text{a}
[\text{GJ}_\text{th}/(\text{K})/\text{ton CO}_2]  
0.66

Cooling duty
[\text{GJ}_\text{th}/\text{ton CO}_2]  
4.22

Electricity use

Capture \text{b}
[\text{GJ}_e/\text{ton CO}_2]  
0.10

Compression
[\text{GJ}_e/\text{ton CO}_2]  
0.32

Total
[\text{GJ}_e/\text{ton CO}_2]  
0.41

Total including reboiler \text{c}
[\text{GJ}_e/\text{ton CO}_2]  
1.21

\text{a} \ U \text{ is the overall heat transfer coefficient; A is the contact area in the heat exchanger. If } U \text{ is considered constant, UA is proportional to the contact area. The UA is the sum of the two HEX used.}

\text{b} \ For this case, the electricity use for capture also includes the extra semi-lean pump.

\text{c} \ Assuming 1 \text{GJ}_e = 4 \text{GJ}_\text{th}
Overview Capture Plant (2)

Electricity incl. reboiler [GJ\textsubscript{th}/ton CO\textsubscript{2}]

- Base case
- Reference improved HEX
- Stripper 2 bar, lean loading 0.33
- Split flow 10%, intermediate flash
- Stripper 2.3 bar, improved HEX
- Split flow 8%
- 2 strippers, intermediate HEX
- Stripper 2.3 bar, improved HEX
- LVC 1.2 bar
- Split flow 8% + LVC

Electricity incl. reboiler [relative to reference]
Improvement Process:

Power plant load: 100%

<table>
<thead>
<tr>
<th>Process</th>
<th>30wt% MEA</th>
<th>40wt% MEA</th>
<th>AMP/PZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base case</td>
<td>3.6</td>
<td>3.1</td>
<td>3.3</td>
</tr>
<tr>
<td>LVC</td>
<td>3.3</td>
<td>2.9</td>
<td>3.0</td>
</tr>
<tr>
<td>LVC + SF</td>
<td>3.2</td>
<td>2.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Leites (SHI)</td>
<td>3.4</td>
<td>2.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Specific energy duty $G_{\text{th}}$ / t CO$_2$
250 MW

Bar chart showing the following scenarios:
1. Power plant w/o Capture: 46.3
2. Base case MEA no integration: 43.9
3. Base case MEA low integration: 44.1
4. Base case MEA high integration: 44.1
5. MEA LVC no integration: 44.0
6. MEA LVC low integration: 44.1
7. MEA LVC+split no integration: 44.1
8. MEA LVC+split low integration: 44.2
9. MEA intermediate HEX no integration: 44.0
10. MEA intermediate HEX low integration: 44.2
Challenges Post-combustion Capture

- **Avoid emission solvent traces**
- **Reduce absorber, scrubber investment**
- **Advanced heat integration**
- **Reduce heat consumption**

Diagram:

- **CO₂-rich gas**
- **CO₂-lean gas**
- **Makeup water**
- **Absorber**
  - Top Tray
  - Bottom Tray
  - Rich solvent
  - Lean solvent
- **Regenerator**
  - Top Tray
  - Bottom Tray
  - Rich solvent
  - Lean solvent
- **Scrubber**
- **Pump**
- **Condenser**
- **Reflux drum**
- **Steam**
- **Reboiler**
- **Condensate**
Carbon capture:

from dream

via demonstration

to realization
Demonstration activities within OCTAVIUS

- TNO pilot plant / 0.25 tCO₂/h (Maasvlakte - NL)
- EnBW pilot plant / 0.3 tCO₂/h (Heilbronn - G)
- ENEL pilot plant / 2.25tCO₂/h (Brindisi - I)
Demonstrations

ROAD is an initiative focused towards capture and storage of 1.1 million tonnes of CO$_2$ per year from a new power plant in The Netherlands.

Mongstad (Consultancy) An International CO$_2$ Technology test center network to facilitate international carbon test facilities to share knowledge to accelerate the commercialization of technology.

One million tonnes of CO$_2$ per year: world’s first and largest commercial scale coal-fired CCS project ($1.24 billion)
Acknowledgement

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www.sintef.no/cemcap
Twitter: @CEMCAP_CO2