« From CO₂ to Energy: Carbon Capture in Cement Production and its Re-use »

Scientific Committee Meeting in Dusseldorf

News from 13/04/16 to 19/05/17 (~13 months)

19/05/17
Content of the meeting:

- **Introduction**: M. Schneider and P. Lybaert

- **General information** (D. Thomas):
  - External communication activities & Future
  - Various informations
  - 4th annual report

- **Scientific information**
  - Framework of the ECRA Chair:
    - 4 PhD theses + works of undergraduate students
  - Finalization of the post-doc works of L. Dubois
  - PhD Thesis of S. Mouhoubi
  - PhD Thesis of S. Laribi
  - and discussions ECRA-UMONS

--- **LUNCH**

- PhD Thesis of N. Meunier
- PhD Thesis of R. Chauvy
- and discussions ECRA-UMONS

- **Final remarks – closing**

Next meeting of the Scientific Committee of the ECRA Chair
GENERAL INFORMATION
**ECRA Academic Chair Timeline**

**Phase 1 (2013-2016):**
2 PhD theses + 1 Post-doc

- **2013:**
  - PhD THESIS 1 – N. MEUNIER
- **2014:**
  - PhD THESIS 2 – S. LARIBI
- **2015**
- **2016**
  - POST-DOC – L. DUBOIS

**Phase 2 (2016-2019):**
2 PhD theses + 1 Post-doc

- **2017**
- **2018**
- **2019**

**ECRA ACADEMIC CHAIR – 3 YEARS (1)**

**ECRA ACADEMIC CHAIR – 3 YEARS (2)**

- **★ = today**
- NEW POST-DOC?

**PhD THESIS 3 – R. CHAUVY**

**PhD THESIS 4 – S. MOUHOUBI**

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24/04/13

**ECRA Chair « CO₂ to Energy » - Scientific Meeting in Dusseldorf – 19/05/2017**
External communication activities (1)

FOA 12 – Fundamentals Of Adsorption – Friedrichshafen (Germany) – 29 May - 3 June 2016

→ Dehydration of CO₂ coming from cement oxyfuel kilns by temperature swing adsorption (TSA) using zeolites 5A, 13X and silica gel
Nicolas Meunier, Lionel Dubois, Diane Thomas and Guy De Weireld

Acceptation of one abstract - Presentation of one poster

Conference "La chimie verte, une industrie d’avenir (GreenWin-GEPROC) » – Gembloux (Belgique) – May 2016

→ ECRA Academic Chair From CO₂ to Energy at the University of Mons: CO₂ Capture & Reuse in the Cement Industry
Dubois Lionel, Laribi Sinda, Mouhoubi Seloua, Meunier Nicolas, Chauvy Remi, De Weireld Guy and Thomas Diane

Poster presentation
External communication activities (2)

2nd EFCATS-CNRS European Summer School on Catalyst Preparation – Vogüé (France) – june 2016

→ CO₂ re-use from oxyfuel cement kilns: Optimization of the CO₂ catalytic conversion into methanol
Nicolas Meunier, Remi Chauvy, Lionel Dubois, Diane Thomas, Guy De Weireld

Poster presentation

ICCDU XIV – 14th International Conference on Carbon Dioxide Utilization – Sheffield (UK) - 11-15 september 2016

→ CO₂ re-use from oxyfuel cement kilns: Optimization of the CO₂ catalytic conversion into methanol
N. Meunier, R. Chauvy, L. Dubois, D. Thomas, G. De Weireld
→ CO₂ utilization from cement plant flue gas: Selection of suitable CO₂ conversion routes for the cement sector
R. Chauvy, N. Meunier, L. Dubois, D. Thomas, G. De Weireld

Acceptation of two abstracts - Presentation of two Posters
External communication activities (3)

**GEPROC PhD Day – Louvain-La-Neuve (Belgium) - October 2016**

→ *CO₂ utilization from cement plant flue gas: Methodological selection of CO₂ conversion pathways*
  Chauvy Remi, Meunier Nicolas, Dubois Lionel, Thomas Diane, De Weireld Guy
→ *Optimisation de la conversion du CO₂ provenant de fours de cimenterie « oxyfuel » en méthanol*
  Meunier Nicolas, Chauvy Remi, Dubois Lionel, Thomas Diane, De Weireld Guy
→ *Study of post-combustion CO₂ capture process using biphasic solvents applied to cement flue gases*
  Mouhoubi Seloua, Dubois Lionel, De Weireld Guy, Thomas Diane
→ *Study of the post-combustion CO₂ capture applied to conventional and partial oxy-fuel cement plants*
  Laribi Sinda, Dubois Lionel, De Weireld Guy, Thomas Diane

4 Flash and Poster presentations
GEPROC PhD Day
Best Flash and Poster presentation Award for Seloua
External communication activities (4)

GHGT-13 congress – Lausanne (Switzerland) - November 2016

→ Simulations of various configurations of the post-combustion CO₂ capture process applied to a cement plant flue gas: parametric study with different solvents  
L. Dubois and D. Thomas

→ Study of the post-combustion CO₂ capture applied to conventional and partial oxy-fuel cement plants  
L. Dubois, S. Laribi, S. Mouhoubi, G. De Weireld and D. Thomas

→ Optimization of the Sour Compression Unit (SCU) process for CO₂ purification applied to flue gases coming from oxy-combustion cement industries  
S. Laribi, L. Dubois, G. De Weireld and D. Thomas

Acceptation of three abstracts and three papers  
Presentation of  
- 2 oral presentations (LD and SL)  
- 1 poster communication
Greetings from Lausanne!
Future external communication activities (1)

**TCCS9** – 9th Trondheim Conference on CO₂ Capture, Transport and Storage - Trondheim (Norway) – 12-14 June 2017

→ *Techno-economic and environmental assessment of the conversion of CO₂ into methanol*
  N. Meunier, R. Chauvy, D. Thomas and G. De Weireld

Acceptation of the abstract for an Oral presentation

→ *Optimization of different CO₂ capture processes applied to cement flue gases*
  S. Laribi, L. Dubois, **G. De Weireld** and D. Thomas

Acceptation of the abstract for a Poster presentation
Future external communication activities (2)

**SFGP2017** – Congrès de la Société Française de Génie des Procédés – Nancy (France) - July 2017

→ *Post-combustion CO₂ capture applied to conventional and partial oxy-fuel cement plants*
S. Laribi, S. Mouhoubi, L. Dubois, G. De Weireld and D. Thomas

Acceptation of the abstract for an Oral presentation

→ *Simulation of a Sour Compression Unit (SCU) process for CO₂ purification applied to flue gases coming from oxy-combustion cement industries: parametric study*
S. Laribi, L. Dubois, G. De Weireld and D. Thomas

Acceptation of the abstract for a Poster presentation
Future external communication activities (3)

ICCDU XV - 15th International Conference on Carbon Dioxide Utilization – Shangai - July 2017

→ Techno-economic and environmental assessment of the conversion of CO₂ into methanol
N. Meunier, R. Chauvy, D. Thomas and G. De Weireld

Acceptation of the abstract for an Oral presentation

→ Electrochemical reduction of CO₂ into formic acid from cement plant flue gas: techno-economic and environmental assessment
R. Chauvy, N. Meunier, D. Thomas and G. De Weireld

Acceptation of the abstract for a Poster presentation
Future external communication activities (4)

GLS13 - 13th international conference on Gas-Liquid and Gas-Liquid-Solid Reactor Engineering – Brussel (Belgium) - August 2017

→ *Modeling of CO$_2$ post-combustion capture process using biphasic solvents*
  S. Mouhoubi, L. Dubois, G, De Weireld and D. Thomas

→ *Experiments and simulation of the post-combustion CO$_2$ capture absorption-regeneration process applied to cement flue gases with high CO2 contents*
  S. Laribi, S. Mouhoubi, L. Dubois, G. De Weireld and D. Thomas

Acceptation of the abstracts for Poster presentations

→ *Parametric study of the Sour Compression Unit (SCU) process for CO$_2$ purification applied to flue gases coming from oxy-combustion cement industries*
  S. Laribi, L. Dubois, G. De Weireld and D. Thomas

Acceptation of the abstract for an Oral presentation
Future external communication activities (5)

PCCC4 - 4th Post-Combustion Capture Conference – Alabama (USA) - September 2017

→ *Modeling of post-combustion CO$_2$ capture process by absorption-regeneration using demixing DEEA and MAPA aqueous mixtures*
S. Mouhoubi, L. Dubois, G, De Weireld and D. Thomas

Submission of 1 abstract

CIEM 2017 - 8th International Conference on Energy and Environment – Bucharest (Roumany) - October 2017

→ *Post-combustion CO$_2$ capture process applied to flue gases with high CO2 contents: micro-pilot experiments and simulations*
S. Laribi, L. Dubois, G. De Weireld and D. Thomas

Submission of 1 abstract -> accepted -> one paper will be written
Simulations of various configurations of the post-combustion CO₂ capture process applied to a cement plant flue gas: parametric study with different solvents
L. Dubois and D. Thomas
Energy Procedia, 2017
DOI: 10.1016/j.egypro.2017.03.1265

Study of the post-combustion CO₂ capture applied to conventional and partial oxy-fuel cement plants
L. Dubois, S. Laribi, S. Mouhoubi, G. De Weireld and D. Thomas
Energy Procedia, 2017
DOI: 10.1016/j.egypro.2017.03.1188

Optimization of the Sour Compression Unit (SCU) process for CO₂ purification applied to flue gases coming from oxy-combustion cement industries
S. Laribi, L. Dubois, G. De Weireld and D. Thomas
Energy Procedia, 2017
DOI: 10.1016/j.egypro.2017.03.1756
A paper was submitted to the Journal of CO₂ Utilization:

→ Selecting CO₂ utilization pathways for deployment to the cement sector
R. Chauvy, N. Meunier, D. Thomas and G. De Weireld

A paper was submitted to the International Journal of Greenhouse Gas Control:

→ Comparison of various configurations of the absorption-regeneration process for the post-combustion CO₂ capture applied to cement flue gases
L. Dubois and D. Thomas
Total of communication activities (May 2016-April 2017)

- Intern. Congress - POSTER
- Intern. Congress - ORAL
- National - POSTER
- National - ORAL
- accepted internat. publications
- submitted internat. Publications
- Submissions to Intern. Conf.
- Future Intern. Comm. - POSTER
- Future Intern. Comm. - ORAL
PhD thesis committees

Annual meetings of PhD theses committees with internal (UMONS) and external members:

- For R. Chauvy:
  → took place on 10-10-2016
  → was validated

- For S. Mouhoubi:
  → took place on 20-03-2017
  → was validated

(reports available)
4th Annual report 2016-2017

- for the period May 2016 – April 2017
- sent in May 2017

Remarks ?? Approval ??
ECRA Chair Website

- with a section including all the documents of the Chair
- Password to access the “Documents section”: ecra2013chairum
Second ECRA Chair scientific event

Day I
9 November 2016
Mons
Second ECRA Chair scientific event

Day II
10 November 2016
Lixhe
SCIENTIFIC INFORMATION
General framework of the ECRA Chair – PhD Theses

**CO₂ Capture & Purification**

- **Oxy-fuel**
  - CO₂ capture
  - \( Y_{CO₂} > 70\% \)

- **Partial oxy-fuel**
  - CO₂ capture
  - \( 35 < Y_{CO₂} < 70\% \)

- **Post-combustion**
  - CO₂ capture
  - \( Y_{CO₂} < 35\% \)

**Air Products CO₂ Purification Unit (CPU)**

- **Sour Compress. Unit**
- **Dehydration Unit**
- **Cryogenic Unit**

**Modeling and Optimization**

- Pressure Swing Adsorption (PSA)
  - Adsorption Process

**Modeling and Experiments**

- (materials screening)
  - **Absorption-Regeneration Process: conventional solvents**

- (solvents screening)
  - **Absorption-Regeneration Process: demixing solvents**

- **Absorption-Regeneration Process: other configurations**

**CO₂ Conversion**

- CO₂ Catalytic Conversion into methanol
  - Modeling and Experiments (effect of impurities on catalytic process)

- Other CO₂ Conversion routes
  - Modeling and Technico-economic analysis

= Sinda Laribi’s PhD Thesis
= Nicolas Meunier’s PhD Thesis
= Remi Chauvy’s PhD Thesis
= Seloua Mouhoubi’s PhD Thesis
= Lionel Dubois’s Post-Doc
= Other works
Works of undergraduate students in the framework of the ECRA Chair

- Oxy-fuel CO₂ capture $\gamma_{\text{CO₂}} > 70\%$
- Partial oxy-fuel CO₂ capture $35 < \gamma_{\text{CO₂}} < 70\%$
- Post-combustion CO₂ capture $\gamma_{\text{CO₂}} < 35\%$

Air Products CO₂ Purification Unit (CPU)

- Sour Compress. Unit
- Dehydration Unit
- Cryogenic Unit

Modeling and Optimization
- Pressure Swing Adsorption (PSA)
- Adsorption Process
- Modeling and Experiments (materials screening)

Absorption-Regeneration Process: conventional

Absorption-Regeneration Process: demixing solvents

Absorption-Regeneration Process: other configuration

MAB1 Project M, Didier 2016-2017

BAB3 Project Richoux/Bruneau 2016-2017

Modeling and Experiments (solvents screening)

Modeling and Experiments (effect of impurities on catalytic process)

Modeling and Technico-economic analysis

- Master Thesis L. Le Martelot 2015-2016
- Master Thesis T. Bryans 2016-2017
- MAB1 Project L. Brousmiche 2016-2017

CO₂ Catalytic Conversion into methanol

Other CO₂ Conversion routes

Absorption-Regeneration Process: other configurations

Modeling and Technico-economic analysis

- = Sinda Laribi’s PhD Thesis
- = Nicolas Meunier’s PhD Thesis
- = Remi Chauvy’s PhD Thesis
- = Seloua Mouhoubi’s PhD Thesis
- = Lionel Dubois’s Post-Doc
- = Other works

Cement industry

Works of undergraduate students in the framework of the ECRA Chair

ECRA Chair « CO₂ to Energy » - Scientific Meeting in Dusseldorf – 19/05/2017
Works of undergraduate students (1)

→ « Modeling and optimization of PSA processes for the treatment of gaseous effluents rich in CO₂»

Nicolas DEBAISIEUX (UMONS)

Master thesis achieved in the Thermodynamics Department, between February and June 2016 - Report written in French

ECRA Chair Award
Works of undergraduate students (2)

→ « Technical, economical and environmental evaluations of CO₂ capture techniques »

Lucas LE MARTELOT (ECOLE SUPERIEURE DE CHIMIE ORGANIQUE ET MINERALE (ESCOM), Compiègne (France))

Master thesis, between March and August 2016 - Report written in English, in two parts:

1°) Part I: in the Chemical and Biochemical Process Engineering Departement Working with Sinda

2°) Part II: in the Thermodynamics Department Working with Remi
Works of undergraduate students (3)

-> « Study of the aqueous amines solutions performances for the absorption of SO₂ present in a gaseous phase containing CO₂ »

Olivia RICHOUX and Valentin BRUNEAU (UMONS)

BAB3 Project, between February and May 2017
Report (in French)
Working with Sinda
Works of undergraduate students (4)

→ « Post-combustion CO₂ capture by absorption-regeneration in amine solvents: process optimization for the cement industry »

Maxime DIDIER (UMONS)

**MAB1 Project**, between October and May 2017
Report and Poster
Working with Lionel and Diane

→ « Formic acid production by electrochemical reduction and from CO₂ »

Lola BROUSMICHE (UMONS)

**MAB1 Project**, between February and May 2017
Report (in French) and Poster
Working with Remi and Nicolas
Works of undergraduate students (5)

→ « CO₂ catalytic conversion into methanol »

Timothée BRYANS (UMONS)

Master Thesis, between February and May 2017
Report (in French)
Working with Nicolas and Guy

-> « Study of conventional and alternative ways of methanol production »

Raphael VREUX (UMONS)

Master Thesis, since February 2017
Report (in French)
Working with Remi and Guy

- Concluded his post-doctoral researches on the 31-03-2017
- New Post-doc recruitment under progress

3 main post-doctoral subjects in addition to the support tasks for the ECRA Chair:

- Membrane technology for the post-combustion CO₂ capture in cement industry
- Bibliographic study on the CO₂ mineralization processes
- Simulation of the post-combustion CO₂ capture process by chemical absorption applied to the Brevik cement plant flue gases

These tasks were mainly defined and carried out in the framework of the collaboration with HeidelbergCement (co-funding of the post-doctoral position during 2014 and 2015).
ECRA Chair support tasks

- **Membrane technology for the post-combustion CO₂ capture in cement industry:**
  Part 1: General overview on membrane technology for CO₂ capture
  (Part 2: Specific aspects related to the application to cement flue gases)
  Part 3: Technological monitoring on hybrid technology combining membrane and conventional amine process

  **REPORT 1** (April 2014)

- **Bibliographic study on the CO₂ mineralization processes:**
  Part 1: General overview on CO₂ mineralization into olivine derived compounds
  Part 2: Complementary information on pH-swing CO₂ mineralization process

  **REPORT 2** (April 2015)

- **Simulation of the post-combustion CO₂ capture process by chemical absorption applied to the Brevik cement plant flue gases:**
  Part 1: General model development for the CO₂ capture simulation (MEA 30%)
  Part 2: Sensibility study of different operating parameters (optimization) (MEA 30%)
  Part 3: Study of the **different configurations** for CO₂ capture process (MEA 30%)

  **REPORT 3** (November 2015)

  Part 4: Comparison between MEA 30% and **other solvents** (PZ and MDEA+PZ)


Post-doc specific tasks

- ECRA Chair « CO₂ to Energy » - Scientific Meeting Düsseldorf – 19/05/2017
Global comparison of the simulation results

Brevik cement plant flue gas ($y_{CO2,in} \approx 20\%$)
CASTOR/CESAR Project Design

Lower $E_{regen}$ with MDEA 10 wt.% + PZ 30 wt.%

LVC and RVC configurations leading to the minimum of $E_{regen}$
(heat recovery process modifications)
Comparison with Aker’s Mobile Test Unit (MTU)

Generic flow sheet of Aker Solutions ACC™ process

Possible to reduce from 2.8 to 2.4 GJ/t\(\text{CO}_2\)
News of the ECRA Chair PhD Theses

- PhD Thesis of S. Mouhoubi
- PhD Thesis of S. Laribi

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- PhD Thesis of N. Meunier
- PhD Thesis of R. Chauvy
Modeling and simulation of post-combustion CO₂ capture process using demixing solvents applied to cement flue gases
General framework of the ECRA Chair

CO₂ Capture & Purification

**Oxy-fuel**
CO₂ capture
\( y_{CO₂} > 70\% \)

**Partial oxy-fuel**
CO₂ capture
35 < \( y_{CO₂} < 70\% \)

**Post-combustion**
CO₂ capture
\( y_{CO₂} < 35\% \)

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**CO₂ Conversion**

**CO₂ Catalytic Conversion into methanol**

**Other CO₂ Conversion routes**

**Modeling and Experiments**
- (effect of impurities on catalytic process)
- Modeling and Technico-economic analysis

**Absorption-Regeneration Process: conventional solvents**

**Absorption-Regeneration Process: demixing solvents**

**Absorption-Regeneration Process: other configurations**

**Air Products CO₂ Purification Unit (CPU)**

- Sour Compress. Unit
- Dehydration Unit
- Cryogenic Unit

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\( \text{CO₂ Capture & Purification} \)

\( \text{CO₂ Conversion} \)

- Modeling and Optimization
- Pressure Swing Adsorption (PSA) Adsorption Process
- Modeling and Experiments (materials screening)
- Absorption-Regeneration Process: conventional solvents
- Modeling and Experiments (solvents screening)
- Absorption-Regeneration Process: demixing solvents
- Modeling and Experiments
- Absorption-Regeneration Process: other configurations
- Modeling and Technico-economic analysis

- Other works

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= Sinda Laribi’s PhD Thesis

= Nicolas Meunier’s PhD Thesis

= Remi Chauvy’s PhD Thesis

= Seloua Mouhoubi’s PhD Thesis

= Lionel Dubois’s Post-Doc

= Other works

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Ir. MOUHOUBI Seloua | ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017

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Presentation outline

I. Thesis context

II. Bibliographic review on biphasic solvents

III. Evaluation of DEEA-MAPA system

IV. Modeling of DEEA-MAPA system

V. Conclusion and future works
I. Thesis context

- Conventional monoethanolamine (MEA 30 wt.% ) process

\[ \alpha_{\text{CO}_2} \approx 0.50 \text{ (mol CO}_2\text{/mol MEA)} \]

\[ \alpha_{\text{CO}_2} \approx 0.25 \text{ (mol CO}_2\text{/mol MEA)} \]

\[ P \approx 2 \text{ bars} \]

\[ T \approx 40 \, ^\circ \text{C} \]

\[ T \approx 120 \, ^\circ \text{C} \]

\[ E_{\text{reg}} \approx 3.3 \text{ to } 3.8 \text{ GJ/tCO}_2 \]

L/G_v: [0.003-0.008]
IFP Energies Nouvelles DMX™ process

α_{CO2} (rich) >> α_{CO2} (lean)

- lowering the circulation rate
- it can increase the CO₂ pressure in the desorber

E_{reg} ≈ 2.1 GJ/tCO₂

≈ 40% decrease of the regeneration energy comparing to MEA 30 wt%
II. Bibliographic review on biphasic solvents

DMX solvents

Blend of amines

Self-concentrating solvents

Amine + alcohol

DEEA-BDA blend

DEEA-MAPA blend

DEEA-TETA blend

Demixing solvents

Thermomorphic biphasic solvents

MCA, DMCA, ...

MCA  N-methylcyclohexylamines
DMCA  N,N-dimethylcyclohexylamine
BDA  1,4-Butanediamine
TETA  Triethylentetramine
MAPA  3-Methylaminopropylamine
DEEA  2-Diethylaminoethanol
II. Bibliographic review on biphasic solvents

- solvent showing liquid-liquid separation;
- good absorption-regeneration performances;
- validation of the solvent performances at pilot scale;
- maximum data availability for Aspen Plus process simulation.

Main selection criteria

Chemical structures of DEEA and MAPA
Biphasic behavior depending on blend composition

One phase, two liquid phases formation and solid precipitation phenomena were observed.

III. Evaluation of DEEA-MAPA system

D = DEEA  
M = MAPA

Source: Ciftja et al 2015

Cyclic capacity

\((a_{\text{rich}} - a_{\text{lean}})\)
III. Evaluation of DEEA-MAPA system

⇒ CO$_2$ bubbling test

Experimental conditions

5M DEEA+2M MAPA **demixing** mixture

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>40°C</td>
</tr>
<tr>
<td>CO$_2$ flowrate</td>
<td>120 l/min</td>
</tr>
<tr>
<td>Solution volume</td>
<td>250 ml</td>
</tr>
<tr>
<td>Bubbling</td>
<td>3, 6 and 9 min for the demixing mixture</td>
</tr>
<tr>
<td>Bubbling</td>
<td>9 min for the non demixing mixture</td>
</tr>
</tbody>
</table>

Results

- t = 0 min
- t = 3 min
- t = 6 and 9 min
III. Evaluation of DEEA-MAPA system

➢ CO₂ absorption performances

Experimental device
CO$_2$ absorption performances

Experimental conditions

3M DEEA+2M MAPA **non-demixing** mixture

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>25</td>
</tr>
<tr>
<td>Liquid stirring speed ($N_L$)</td>
<td>rpm</td>
<td>35</td>
</tr>
<tr>
<td>Gas stirring speed ($N_G$)</td>
<td>rpm</td>
<td>500</td>
</tr>
<tr>
<td>Gas flow rate ($G_{sec}$)</td>
<td>l/min</td>
<td>5</td>
</tr>
<tr>
<td>Liquid volume ($V$)</td>
<td>l</td>
<td>1</td>
</tr>
<tr>
<td>Inlet gas composition</td>
<td>Volume percent</td>
<td>10, 20, 30 %</td>
</tr>
<tr>
<td>Concentrations</td>
<td>mol/l</td>
<td>5M MEA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3M DEEA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2M MAPA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2M MAPA+3M DEEA</td>
</tr>
</tbody>
</table>

Our device and experimental conditions were **not well adapted** to test demixing solutions. **Another device will be developed.**
Results

Absorption performances of 2M MAPA, 3M DEEA and their mixture compared to the benchmark MEA 5M

MAPA+DEEA aqueous non-demixing mixture can be particularly promising for CO₂ capture

\[
A(\%) = \frac{G_{\text{in}CO_2,\text{in}} - G_{\text{out}CO_2,\text{out}}}{G_{\text{in}CO_2,\text{in}}} \times 100
\]
IV. Modeling of DEEA-MAPA system

- Initiation to Aspen simulation with MEA 30 wt.%

- Gas composition from Brevik cement plant reference -> ECRA reference
- Process design from CASTOR/CESAR Europen project -> All data available
IV. Modeling of DEEA-MAPA system

➢ Schematic description of the simulation

Reactions
Kinetics

Properties
Models

Chemistry

Aspen process modelling

Results
IV. Modeling of DEEA-MAPA system

DEEA-MAPA solution preliminary kinetic study

Reaction mechanism

Termolecular mechanism

Zwitterion mechanism

One-step mechanism

Two-step mechanism

\[ CO_2 + R_1R_2NH \leftrightarrow R_1R_2N^+HCOO^- + BH^+ \]

B is a base which can be H₂O, OH⁻, or amine
**IV. Modeling of DEEA-MAPA system**

➢ **DEEA-MAPA solution preliminary thermodynamic study**

The main products identified are: primary/secondary carbamate, dicarbamate and carbonate-bicarbonate.

I-Reactons involved in CO₂-water system:

Dissociation of water: \[ 2H_2O \leftrightarrow H_3O^+ + OH^- \]

Hydration of CO₂: \[ 2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^- \]

Dissociation of bicarbonate: \[ HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \]

II-CO₂ reaction in tertiary amines such DEEA:

\[ DEEA + CO_2 + H_2O \leftrightarrow DEEAH^+ + HCO_3^- \]

*Based on: Ciftja et al 2013*
II-CO$_2$ reactions in primary/secondary amines such as MAPA:

Dissociation of protonated MAPA:

\[
MAPAH^+ + H_2O \leftrightarrow MAPA + H_3O^+
\]
\[
H^+MAPAH^+ + H_2O \leftrightarrow MAPAH^+ + H_3O^+
\]

Formation of MAPA carbamates:

\[
MAPA + CO_2 + H_2O \leftrightarrow MAPACOOO_P^- + H_3O^+
\]
\[
MAPA + CO_2 + H_2O \leftrightarrow MAPACOOO_S^- + H_3O^+
\]

Dissociation of protonated carbamates:

\[
H^+MAPACOOO_P^- + H_2O \leftrightarrow MAPACOOO_P^- + H_3O^+
\]
\[
H^+MAPACOOO_S^- + H_2O \leftrightarrow MAPACOOO_S^- + H_3O^+
\]

Dicarbamate formation:

\[
MAPACOOO_P^- + CO_2 + H_2O \leftrightarrow MAPA(CO_2^-)_2 + H_3O^+
\]
\[
MAPACOOO_S^- + CO_2 + H_2O \leftrightarrow MAPA(CO_2^-)_2 + H_3O^+
\]

Based on: Ciftja et al 2013
According to Arshad et al 2016, these two assumptions might be made for the modeling:

- formation of secondary carbamate and dicarbamate is very small
- the primary carbamate of MAPA is the dominating carbamate species present in the aqueous phase.
II-CO$_2$ reactions in primary/secondary amines such as MAPA:

Dissociation of protonated MAPA:

\[
MAPAH^+ + H_2O \leftrightarrow MAPA + H_3O^+ \\
H^+MAPAH^+ + H_2O \leftrightarrow MAPAH^+ + H_3O^+
\]

Formation of MAPA carbamates:

\[
MAPA + CO_2 + H_2O \leftrightarrow MAPACOOO_P^- + H_3O^+ \\
MAPA + CO_2 + H_2O \leftrightarrow MAPACOOO_S^- + H_3O^+
\]

Dissociation of protonated carbamates:

\[
H^+MAPACOOO_P^- + H_2O \leftrightarrow MAPACOOO_P^- + H_3O^+ \\
H^+MAPACOOO_S^- + H_2O \leftrightarrow MAPACOOO_S^- + H_3O^+
\]

Dicarbamate formation:

\[
MAPACOOO_P^- + CO_2 + H_2O \leftrightarrow MAPA(CO_2^-)_2 + H_3O^+ \\
MAPACOOO_S^- + CO_2 + H_2O \leftrightarrow MAPA(CO_2^-)_2 + H_3O^+
\]

*Based on: Ciftja et al. 2013*
IV. Modeling of DEEA-MAPA system

Thermodynamic modeling

Models used for thermodynamic modeling of electrolyte systems containing $\text{H}_2\text{O}$-amine-acid gas are:

- **Electrolyte NRTL**
  - Available in Aspen plus

- **Extended UNIQUAC**
  - Not available in Aspen plus

Use of experimental data from the literature for regressing parameters in Aspen Plus:

- **DEEA-$\text{H}_2\text{O}$-$\text{CO}_2$ system**
- **MAPA-$\text{H}_2\text{O}$-$\text{CO}_2$ system**
- **DEEA-MAPA-$\text{H}_2\text{O}$-$\text{CO}_2$ systems**

Availability of Extended UNIQUAC parameters in the literature for **DEEA-MAPA-$\text{H}_2\text{O}$-$\text{CO}_2$ system**.

Source: Arshad et al 2016, Denmark university

These two models will be used depending on the data availability and accuracy.
V. Conclusion and future works

Bibliographic review

- Study of different phase change CO₂ capture processes
- Focus on liquid biphasic solvents

Identification of the promising biphasic solvent: **DEEA+MAPA mixture**

- Fixing the reactions set and their respective kinetic constant
- Identification of thermodynamic properties and parameters

Modeling and simulation

**eNRTL without demixing**

- Aspen Plus simulation of **MEA-H₂O-CO₂ system**
- Aspen Plus simulation of:
  - **DEEA-H₂O-CO₂ system**
  - **MAPA-H₂O-CO₂ system**
  - **DEEA-MAPA-H₂O-CO₂ system**

**Extended UNIQUAC with demixing**

- Separate vapor liquid-liquid equilibrium modeling of **DEEA-MAPA-H₂O-CO₂**
UMONS micro pilot

Experimental section
- DEEA+MAPA aqueous mixture CO$_2$ bubbling test
- Absorption performances tests for DEEA-MAPA systems
- Regeneration tests for DEEA-MAPA systems
- Absorption-regeneration tests in UMONS micro pilot for the mixture without demixing phenomenon

Adaptation of the micro pilot for the demixing mixtures

Global technico-economic evaluation of the technology

Ir. MOUHOUBI Seloua  |  ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017
Thank you for your attention

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Chemical & Biochemical Process Engineering Unit
seloua.mouhoubi@umons.ac.be
Annexes
Demixing phenomenon

- Biphasic even without CO$_2$

- Biphasic only in presence of CO$_2$

At appropriate temperature

Blend of amines

CO$_2$ absorption

CO$_2$ critical loading

Phase separation

CO$_2$ lean phase

CO$_2$ rich phase
DEEA-MAPA lower and upper phase CO₂ composition

CO₂ content in the lower and upper phases as function of CO₂ partial pressure

Source: Pinto et al 2014
DEEA-MAPA innovative simulation in Aspen Plus

- use of Extended UNIQUAC thermodynamic parameters for demixing calculation
- use of eNRTL thermodynamic parameters for the remaining calculations
Table 5.4: $u_{ij}^T = u_{ij}^P$ parameters for calculating UNIQUAC interaction energy parameters ($u_{ij} = u_{ij}^P + u_{ij}^T (T - 298.15)$). Bold values are determined in this work.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>DEEA</th>
<th>MAPA</th>
<th>CO$_2$</th>
<th>H$^+$</th>
<th>DEEAH$^+$</th>
<th>MAPAH$^+$</th>
<th>CO$_3^-$</th>
<th>HCO$_3^-$</th>
<th>OH$^-$</th>
<th>MAPACOO$^-$</th>
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<td>$H_2O$</td>
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<tr>
<td>CO$_2$</td>
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<td>1.822</td>
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<td>H$^+$</td>
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<tr>
<td>DEEAH$^+$</td>
<td>0.1918</td>
<td>1.816</td>
<td>-1.132</td>
<td>3.745</td>
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<td>MAPAH$^+$</td>
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<td>HCO$_3^-$</td>
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<td>MAPACOO$^-$</td>
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</table>

*Thomsen and Rasmussen

*The value is corrected from the previous value (2.5176, an editing mistake) as reported in Thomsen and Rasmussen

Table 5.3: $u_{ij}^P = u_{ij}^P$ parameters for calculating UNIQUAC interaction energy parameters ($u_{ij} = u_{ij}^P + u_{ij}^T (T - 298.15)$). Bold values are determined in this work.

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>DEEA</th>
<th>MAPA</th>
<th>CO$_2$</th>
<th>H$^+$</th>
<th>DEEAH$^+$</th>
<th>MAPAH$^+$</th>
<th>CO$_3^-$</th>
<th>HCO$_3^-$</th>
<th>OH$^-$</th>
<th>MAPACOO$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
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</tr>
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<td>H$^+$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td></td>
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<td>DEEAH$^+$</td>
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<tr>
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<td>-13.017</td>
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<tr>
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<td>10$^{10}$</td>
<td>10$^{10}$</td>
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<td>OH$^-$</td>
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<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
<td>10$^{10}$</td>
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<tr>
<td>MAPACOO$^-$</td>
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<td>10$^{10}$</td>
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<td>1121.9</td>
<td>342.24</td>
<td>592.19</td>
</tr>
</tbody>
</table>

*Thomsen and Rasmussen

*The value is corrected from the previous value (2.5176, an editing mistake) as reported in Thomsen and Rasmussen
| Amine                                      | Abbreviation | Cas number | Toxicity                                                                 
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Monoethanolamine</td>
<td>MEA</td>
<td>141-43-5</td>
<td>Oral: LD50= 1515 mg/kg (rat) Inhilation: LC50&gt;1.3 mg.l⁻¹/6h (rat) Dermal: LD50= 1025 mg/kg (rabbit)</td>
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<tr>
<td>Diethylaminoethanol</td>
<td>DEEA</td>
<td>100-37-8</td>
<td>Oral: LD50=1300 mg/kg (rat) Inhilation: Dermal: LD50=1124 mg/kg (rabbit)</td>
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<tr>
<td>N-Methyl-1,3-Propanediamine</td>
<td>MAPA</td>
<td>6291-84-5</td>
<td>Oral: LD50=951 mg/kg (rat) Inhilation: LC50=&gt;0.189 mg.l⁻¹/6h (rat) Dermal:</td>
</tr>
</tbody>
</table>

According to Pinto et al 2014, thermal degradation of MAPA loaded with CO₂ is slightly lower than MEA while for DEEA it is significantly lower than for MEA.
Capture and purification processes applied to CO$_2$ derived from cement industry

Ir Sinda LARIBI
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General framework of the ECRA Chair

**CO₂ Capture & Purification**

- **Oxy-fuel**
  - CO₂ capture
  - \( Y_{CO₂} > 70\% \)

- **Partial oxy-fuel**
  - CO₂ capture
  - \( 35 < Y_{CO₂} < 70\% \)

- **Post-combustion**
  - CO₂ capture
  - \( Y_{CO₂} < 35\% \)

**Air Products CO₂ Purification Unit (CPU)**

- **Sour Compress. Unit**
- **Dehydration Unit**
- **Cryogenic Unit**

**Modeling and Optimization**

- Pressure Swing Adsorption (PSA)
- Adsorption Process

**Modeling and Experiments**

- Absorption-Regeneration Process: *conventional solvents*
- (materials screening)

- Absorption-Regeneration Process: *demixing solvents*
- (solvents screening)

- Absorption-Regeneration Process: *other configurations*
- (materials screening)

**CO₂ Conversion**

- CO₂ Catalytic Conversion into methanol
  - Modeling and Experiments (effect of impurities on catalytic process)

- Other CO₂ Conversion routes
  - Modeling and Technico-economic analysis

Legend:

- \( \Box \) = Sinda Laribi’s PhD Thesis
- \( \square \) = Nicolas Meunier’s PhD Thesis
- \( \bigcirc \) = Remi Chauvy’s PhD Thesis
- \( \triangleleft \) = Seloua Mouhoubi’s PhD Thesis
- \( \bigtriangledown \) = Lionel Dubois’s Post-Doc
- \( \ldots \) = Other works

University of Mons  |  Ir. LARIBI Sinda  |  ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017
PART 1: CO$_2$ purification process (de-SO$_x$ & de-NO$_x$) applied to full oxy-fuel combustion
Considered combustion technology

Cement production using conventional combustion

\[ \gamma_{\text{CO}_2, \text{out}} = 20 - 30\% \]

Full oxyfuel combustion

\[ 70\% < \gamma_{\text{CO}_2, \text{out}} < 90\% \]

Adapted from Carrasco-Maldonado et al., 2016.
Flowsheet of the Sour-compression Unit (SCU)

Temperature and pressure conditioning

First absorber $P = 15$ bar

Second absorber $P = 30$ bar

T=50°C

P= 1 bar

Flue gas in (FULL OXYFUEL):

$\gamma_{CO_2,\text{in}} = 83\%$

$\gamma_{NO,\text{in}} = 861$ ppm

$\gamma_{NO_2,\text{in}} = 96$ ppm

$\gamma_{SO_2,\text{in}} = 156$ ppm

Flowsheet of the Sour-compression Unit (SCU)

Modelling characteristics:

- Aspen Plus V8.8
- ELEC-NRTL model for electrolyte systems
- Rate-based calculations in the contactors
- Flue gas compositions from ECRA oxyfuel combustion simulations.
New chemical mechanism considered

**pH influence:** Reactions selected for $1 \leq \text{pH} \leq 4$

**Gas**
- $\text{SO}_2$
- $\text{SO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{SO}_3$
- $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{HNO}_2$
- $\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$
- $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$
- $2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$
- $\text{CO}_2$

**Liquid**
- $\text{SO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_3^-$
- $\text{HSO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_3^{2-}$
- $\text{SO}_3 + 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-$
- $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$
- $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-$
- $2 \text{HNO} \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O}$
- $\text{ONSO}_3^- + \text{H}_2\text{O} \rightarrow \text{HNO} + \text{HSO}_4^-$
- $\text{HNO}_2 + \text{HSO}_3^- \rightarrow \text{ONSO}_3^- + \text{H}_2\text{O}$
- $\text{HONO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{H}_3\text{O}^+$
- $\text{ONSO}_3^- + \text{HSO}_3^- \rightarrow \text{HONO}(\text{SO}_3^2^-)^2^- + 2 \text{H}_3\text{O}^+$
- $\text{HONO}(\text{SO}_3^2^-)^2^- + 2 \text{H}_2\text{O} \rightleftharpoons \text{HONO}(\text{SO}_3^-)^2^- + 2 \text{H}_3\text{O}^+$
- $\text{HONO}(\text{SO}_3^-)^2^- + 2 \text{H}_2\text{O} \rightleftharpoons \text{HONO}(\text{SO}_3^2^-)^2^- + 2 \text{H}_3\text{O}^+$
- $\text{HONO}(\text{SO}_3^-)^2^- + \text{H}_2\text{O} \rightleftharpoons \text{HONO}(\text{SO}_3^2^-)^2^- + \text{H}_3\text{O}^+$
- $\text{HONO}_3 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{H}_3\text{O}^+$
- $3 \text{HNO}_2 \rightarrow \text{H}_2\text{O} + 2 \text{NO} + \text{HNO}_3$

Without SOx/NOx interactions

With all the SOx/NOx interactions

Ir. LARIBI Sinda | ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017
Parametric study of the SCU

- Influence of the column packing height
- Influence of the column operating pressure
- Influence of the total liquid flowrate
- Influence of the recycle ratio
PART 2.a.: Post-combustion CO$_2$ capture process applied to conventional and partial oxy-fuel combustion
Considered combustion technology

Cement production using conventional combustion

\[ Y_{CO_2,\ out} = 20-30\% \]

Partial oxyfuel combustion

\[ 30\% < Y_{CO_2,\ out} < 70\% \]

Adapted from Carrasco-Maldonado et. al, 2016.
Absorption-regeneration process

- Post-combustion capture: absorption-regeneration in amine based solvents

EXPERIMENTAL RESULTS

- Lab scale first screening of solvents
  (Master thesis Guillaume Pierrot, 2015)

- Micro-pilot tests for the best solvents screened
  (Master thesis Lucas Lemartelot, 2016)

SIMULATION RESULTS

Aspen Hysys™ simulations ($E_{\text{regen}}$):
- of the micro-pilot unit
- of an industrial unit
Micro-pilot tests of the best solvents screened

- Absorption-regeneration tests for the best solvents screened at lab scale

![Absorption-regeneration tests for the best solvents screened at lab scale](image)

<table>
<thead>
<tr>
<th>Y_{CO_2, in} (%)</th>
<th>L (l/h)</th>
<th>G (l/h dry)</th>
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</thead>
<tbody>
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<td>7.76</td>
<td>1030</td>
</tr>
<tr>
<td>30</td>
<td>10.68</td>
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<tr>
<td>40</td>
<td>13.59</td>
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<td>50</td>
<td>15.53</td>
<td>1030</td>
</tr>
<tr>
<td>60</td>
<td>18.44</td>
<td>1030</td>
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</tbody>
</table>

Abs-regen micro-pilot unit
Micro-pilot tests: experimental results

- Evolution of the solvents absorption performances and regeneration energy ($E_{\text{regen}}$) with increased CO$_2$ content in the gas to treat

$$ A(\%) = \frac{G_{\text{in}} y_{\text{CO}_2,\text{in}} - G_{\text{out}} y_{\text{CO}_2,\text{out}}}{G_{\text{in}} y_{\text{CO}_2,\text{in}}} \times 100 $$

$$ E_{\text{regen}}(\frac{MJ}{kg CO_2}) = \frac{Q_{\text{reboiler}}(\frac{MJ}{h})}{G_{CO_2,\text{regen}}(kg CO_2/h)} $$

Best performances for MMEA 30% and activated solutions

When $y_{\text{CO}_2,\text{in}}$ increases, $E_{\text{regen}}$ decreases

*Eregen reference=Eregen EXP of PZ 10% at $y_{\text{CO}_2,\text{in}}=20\%$
## Two scales of simulations

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>Micro-pilot scale</th>
<th>Industrial scale</th>
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<tbody>
<tr>
<td></td>
<td>$G_{\text{in, wet}} = 1111 \text{ l/h}$</td>
<td>CASTOR/CESAR pilot= reference European projects</td>
</tr>
<tr>
<td></td>
<td>$L_{\text{in}} = 7.76 - 18.44 \text{ l/h}$</td>
<td>$G_{\text{in}} = 4000 \text{ m}^3/\text{h}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$L_{\text{in}} = 21 \text{ m}^3/\text{h}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{\text{CO}_2, \text{regen}} = 1.5 \text{ t CO}_2/\text{h}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO$_2$ contents in the gas to treat</th>
<th>Micro-pilot scale</th>
<th>Industrial scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_{\text{CO}_2, \text{in}} = 20% - 40% - 60%$</td>
<td></td>
<td>Base case: flue gas from Brevik ($Y_{\text{CO}_2, \text{in}} = 20.4 \text{ mol.}%$)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Other cases: simulations of partial oxyfuel combustion for high $Y_{\text{CO}_2}$ (compositions provided by ECRA).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvents tested</th>
<th>Micro-pilot scale</th>
<th>Industrial scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 30% and PZ 10%</td>
<td></td>
<td>MEA 30%</td>
</tr>
</tbody>
</table>
Flowsheet of the simulations

Aspen Hysys™ V8.8

\[ E_{\text{regen}} = \frac{P_{\text{boiler}}}{G_{\text{CO}_2,\text{regen}}} \]
Micro-pilot simulations results: $E_{\text{regen}} = f(y_{\text{CO}_2, \text{in}})$

*E_{\text{regen}}$ reference = $E_{\text{regen}}$ EXP of PZ 10% at $y_{\text{CO}_2, \text{in}} = 20$

Comparison $E_{\text{regen}}$ EXP/SIM

When $y_{\text{CO}_2, \text{in}}$ increases, $E_{\text{regen}}$ decreases
Industrial simulations results: $E_{\text{regen}} = f(y_{\text{CO}_2,\text{in}})$

- Results for the tested cases:

<table>
<thead>
<tr>
<th></th>
<th>Base case</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_{\text{CO}_2,\text{in}}$ (%)</td>
<td>20.4</td>
<td>31</td>
<td>44.1</td>
<td>51.44</td>
<td>62.03</td>
</tr>
<tr>
<td>$E_{\text{regen}}$ (GJ/ t $\text{CO}_2$)</td>
<td>3.39</td>
<td>2.96</td>
<td>2.56</td>
<td>2.48</td>
<td>2.30</td>
</tr>
<tr>
<td>$E_{\text{regen}}$ saving / base case</td>
<td>12.61%</td>
<td>24.31%</td>
<td>26.79%</td>
<td>31.99%</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{\text{CO}_2,\text{rich}}$</td>
<td>0.508</td>
<td>0.536</td>
<td>0.562</td>
<td>0.557</td>
<td>0.590</td>
</tr>
<tr>
<td>$\alpha_{\text{CO}_2,\text{lean}}$</td>
<td>0.198</td>
<td>0.232</td>
<td>0.264</td>
<td>0.259</td>
<td>0.285</td>
</tr>
</tbody>
</table>

- If $y_{\text{CO}_2,\text{in}}$ for $\text{CO}_2$ from 20 to 44%:
  - $E_{\text{regen}}$ saving = 24% 
  - Costs for $\text{O}_2$ production

PART 2.b.: Simultaneous absorption of SO$_2$ and CO$_2$ from conventional and partial oxyfuel cement plant flue gases

(Bachelor Project, Olivia Richoux & Valentin Bruneau, 2017)
SO\textsubscript{2} and CO\textsubscript{2} absorption: one-column configuration

SO₂ and CO₂ absorption: Lab scale absorption tests results

- Results of the tests with fresh amine solvents (simple and activated)

**CO₂ without SO₂**

**CO₂ + 1500 ppm SO₂**

- SO₂ absorbed preferentially to CO₂ → stronger acid

- Best solvent for CO₂ capture: MMEA 30% → two-column configuration for CO₂ absorption
SO₂ and CO₂ absorption: Lab scale absorption tests results

Results of the tests with CO₂ loaded amine solvents (simple and activated)

\[ \text{CO}_2 + 1500 \text{ ppm SO}_2 \]

Best solvent for SO₂ abs + low CO₂ abs performances (selectivity): AMP 30%
→ two-column configuration for SO₂ absorption

Best solvent for CO₂ absorption and simultaneously SO₂ absorption: PZ 10%
→ one-column configuration for CO₂ and SO₂ absorption
## Conclusions

### FLUE GAS TREATMENT TECHNOLOGIES

#### CO₂ absorption

- Interesting solvents screened in lab and micro-pilot scales.
- Determination of $E_{\text{regen}}$ (EXP and SIM values):
  - when $\gamma_{\text{CO}_2,\text{in}} < E_{\text{regen}}$
  - => Interest of post-combustion capture applied to partial oxyfuel combustion.

#### CO₂ + SO₂ absorption

- Interesting solvents screened in lab scale for CO₂ and SO₂ absorption
- one-column process: PZ 10%
- two-column process: AMP 30% for SO₂ MMEA 30% for CO₂.

#### CO₂ De-SOx & De-NOx

- SCU Chemical mechanism completed considering SOx/NOx interactions under $1 \leq \text{pH} \leq 4$ and implemented in Aspen Plus™
- Parametric study realised of the SCU for different parameters: P, Hcol, Rec ratio and Total Liq flowrate.

### Objectives:

Design and optimize CO₂ capture and purification processes for re-use & $E_{\text{tot}}$ of the global process.
**Objectives:**

Design and optimize CO₂ capture and purification processes for re-use & minimizing \( E_{\text{tot}} \) of the global process.

- **CO₂ absorption**
  - PZ 10% industrial simulation
  - Evaluation of \( E_{\text{tot}} \) for CO₂ capture under partial oxyfuel conditions for more complete conditions considering the oxygen production cost, \( E_{\text{ASU}} \).

- **CO₂ + SO₂ absorption**
  - Micro-pilot scale tests for the best solvents screened at lab scale.

- **CO₂ De-SOx & De-NOx**
  - Scale-up to industrial design
  - SCU (energetic, economic and environmental) optimization by a Design Of Experiments (DOE).
Thank you for your attention
Annexes
Complexity of implementation in Aspen Plus

- Comparison of different sources from literature for kinetic parameters determination + implementation in the required form in Aspen Plus.

- Implementation of the reactions in a defined order in Aspen Plus.

- Influence of the convergence tolerance factors studied.

- New complex species not included in Aspen Plus™ databanks! & Thermodynamic properties not available in the literature and could not be estimated by the software for ions.

  - Group contribution method (Joback) included in Aspen Plus
  - $\text{HSO}_3^-$ and $\text{SO}_3^{2-}$ properties taken as approximations for ions.
Interaction effect on the simulation results

Liquid phase composition analysis: $1 \leq \text{pH} \leq 4$

Gas phase composition analysis:

- Interaction effect: $\text{SO}_2$ abatement ratio
- Same NOx abatement ratio for the mechanisms with and without interactions.
Partial oxyfuel conditions: energetic aspects

**Principles**

Advantages:
- **Less cost for the ASU** (less $\text{O}_2$ needed in comparison with total oxy-fuel).
- **Less regeneration energy** in the amine plant thanks to a more $\text{CO}_2$-concentrated flue gas ($Q_{\text{reboiler}}$).

**ECRA calculation sheet for $E_{\text{ASU}}$ determination**

Recirculated flue gas

### Calculation of the composition of the extracted flue gas to post-combustion

$Y_{\text{vol}}$: $\text{CO}_2 \quad \text{O}_2 \quad \text{N}_2 \quad \text{Ar} \quad \text{H}_2\text{O}$

### For an $\text{O}_2$ input demand **fixed to 0.15 m$^3$ stp/kg clinker**

### ECRA calculation sheet for $E_{\text{ASU}}$ determination

- Post-combustion Capture (membrane)
- Oxy-fuel combustion capture

$$E_{\text{TOT}} = E_1 + E_2$$

$E_{\text{TOT}}$ (GJ/t$\text{CO}_2$)

1. **Post-combustion Capture (membrane)**
2. **Oxy-fuel combustion capture**

$E_1$: $\text{O}_2$ production

$E_2$: $\text{CO}_2$ capture

- $Y_{\text{O}_2} = 0.21$
- $Y_{\text{O}_2} = 1.00$

$\text{Y}_{\text{O}_2} \uparrow$

**Optimum between Post- and total Oxy-fuel**

Adapted from Favre E., Bounaceur R., Roizard D., Vol 68, Issue 1, pp. 30–36, 30 June 2009
Partial oxyfuel conditions: energetic aspects

**Principles**

E_{TOT} = E1 + E2

**Total energy required for partial oxycombustion**

For an O₂ input demand fixed to 0.15 m³ stp/kg clinker and a G_{CO₂,regen} fixed to 1500 t_{CO₂}/h.

- Interest of partial oxy-fuel combustion conditions is confirmed (ECO-Scrub project).
- Optimum conditions have to be investigated for the cement industry → completing this graph with the full and partial oxyfuel parameters (O₂ input and Recycle).

Adapted from Favre E., Bounaceur R., Roizard D., Vol 68, Issue 1, pp. 30–36, 30 June 2009
Lab scale tests of the solvents absorption performances.

- MMEA 30% presents the best absorption capacity among the unloaded solvents without necessity of using an activator (+ PZ 5%)
- PZ 5% is the best activator (compared to tetra)
- TETRA 30% has the best absorption performances among CO₂ loaded simple solvents
- DEA 30% + PZ 5% and AMP 30% + PZ 5% present good absorption performances at the beginning of the test and significant CO₂ loadings

**Master thesis G. Pierrot, 2015.**
Micro-pilot tests of the best solvents screened

- **Micro-pilot tests** → Absorption-regeneration tests using the micro-pilot unit for the best solvents screened.

- Temporal data acquisition from all the sensors (temperature, pressure, gas and liquid flowrates, etc).

- Liquid phase analysis:
  - **Total Organic Carbon (TOC)** analyzer in terms of Total and Inorganic Carbons (TC and IC) to measure the CO$_2$ loading of the solution.
  - **pH measurements** of the liquid solution.

- Gas phase analysis:
  - **IR analysers** to quantify the absorption ratio and CO$_2$ absorbed flow rate.

### Liquid Phase Analysis

- **Total Organic Carbon (TOC)**
  - Using **pH measurements** to measure the CO$_2$ loading of the solution.

### Gas Phase Analysis

- **IR analysers** to quantify the absorption ratio and CO$_2$ absorbed flow rate.

---

**Diagram Description**

- **Condenser**
  - Temperature: 150 l/h
  - Conditions: 25.9°C, 14.5°C

- **Absorption Column**
  - Temperature: 39.2°C
  - Y$_{CO_2,out}$: 11.18%

- **Heat Exchanger**
  - Temperature: 69.5°C

- **Reboiler**
  - Temperature: 103.4°C
  - Conditions: 2000 W, 0.19 mbar

- **MEAs 30% , $Y_{CO_2,in}$ = 40%**

---

**Liquid Phase**

- **Liquid phase** analysis involves using TOC analyzers and pH measurements to assess the CO$_2$ loading of the solution.

**Gas Phase**

- **Gas phase** analysis uses IR analysers to determine the absorption ratio and CO$_2$ absorbed flow rate.
Micro-pilot tests: experimental results

- Temporal evolutions of $y_{\text{CO}_2,\text{in}}$, $y_{\text{CO}_2,\text{out}}$, $y_{\text{CO}_2,\text{regen}}$ and $A$ for MEA 30% at $y_{\text{CO}_2,\text{in}} = 40\%$

$$A (\%) = \frac{G_{\text{in}} y_{\text{CO}_2,\text{in}} - G_{\text{out}} y_{\text{CO}_2,\text{out}}}{G_{\text{in}} y_{\text{CO}_2,\text{in}}} \times 100$$

CO$_2$ production from the solvent regeneration remains stable

Regime phase

<table>
<thead>
<tr>
<th>$y_{\text{CO}_2,\text{in}}$ (%)</th>
<th>$L$ (l/h)</th>
<th>$G$ (l/h dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>14</td>
<td>1030</td>
</tr>
</tbody>
</table>

Internship L. Le Martelot, 2016.
Micro-pilot tests: experimental results

- Temporal data acquisition from all the sensors (temperature, pressure, gas and liquid flowrates, etc).

- Gas phase analysis: **IR analysers** to quantify the absorption ratio and CO\textsubscript{2} absorbed flow rate.

- Liquid phase analysis: **TC and IC measurements** $\rightarrow$ CO\textsubscript{2} loading of the solution. **pH measurements**.

Temporal evolutions of $\nu_{\text{CO}_2,\text{in}}$, $\nu_{\text{CO}_2,\text{out}}$, $\nu_{\text{CO}_2,\text{regen}}$ and $A$ for DEA 30% + PZ 5% at $\nu_{\text{CO}_2,\text{in}} = 20\%$

Temporal evolutions of $\alpha_{\text{CO}_2,\text{rich}}$, $pH_{\text{rich}}$ and $\alpha_{\text{CO}_2,\text{lean}}$, $pH_{\text{lean}}$ for DEA 30% + PZ 5% at $\nu_{\text{CO}_2,\text{in}} = 20\%$
General principles of the simulations

Brevik cement plant = ECRA reference
First European project for testing CO₂ capture from cement industry

CASTOR/CESAR pilot

CASTOR/CESAR pilot= reference
European projects
All data available

Gₘᵢᵢ = 4000 m³/h
yₜₜₕ₁ = 20.4 mol.%

A = 90 mol.%
Produced CO₂ purity=98 mol.%

Modelling Characteristics:
• Aspen Hysys V8.6
• Acid gas package
• Thermodynamic models: Peng-Robinson (gas) and e-NRTL (liquid)
• Solvent: MEA 30%
• Reactions sets included in the package (validated by literature)

Simulations for different CO₂ contents in the gas to treat:
• Base case: flue gas from Brevik (yₜₜₕ₁ = 20.4 mol.%)
• Other cases: simulations of partial oxyfuel combustion for high yₜₜₕ₁ (compositions provided by ECRA).
Flowsheet of the simulations

**Absorber**

- \( H = 17 \text{ m} \)
- \( D = 1.1 \text{ m} \)
- Random packing IMTP 50

**Makeup unit**

- Solvent = MEA 30 wt.%

**Stripper**

- Purity = 98 mol.%

- \( H = 10 \text{ m} \)
- \( D = 1.1 \text{ m} \)
- Random packing IMTP 50

- \( \alpha_{\text{CO}_2,\text{rich}} \)

**Flue gas conditioning**

- \( L = 21 \text{ m}^3/\text{h} \)

- \( G_{\text{in}} = 4000 \text{ m}^3/\text{h} \)

- \( \gamma_{\text{CO}_2,\text{in}} \text{ from 20 to 60 mol.\%} \)

- \( T = 40^\circ \text{C} \)

- \( P = 120 \text{ kPa} \)

- Flue gas

- Gas to treat

- Rich solution before preheat

- Gas treated

- Gas to treat

- Lean solution in abs

- Lean solution before preheat

- Rich before exchanger

- Produced CO2

- Qcondenser

- Rich preheat

- Lean exchanger out

- Lean solution before cooling

- \( \alpha_{\text{CO}_2,\text{lean}} \)

- \( t_{\text{CO}_2}/\text{h} \)

- \( F_{\text{regen}} = \frac{P_{\text{boiler}}}{G_{\text{CO}_2,\text{regen}}} \) [GJ/h]
CO₂ Conversion:
Application to methanol and formic acid

Ir Remi CHAUVY
Ir Nicolas MEUNIER
PhD Students
Thermodynamics Unit
remi.chauvy@umons.ac.be
nicolas.meunier@umons.ac.be
General framework of the ECRA Chair

**CO₂ Capture & Purification**

Air Products CO₂ Purification Unit (CPU)

- **Oxy-fuel**
  - CO₂ capture
  - \( y_{CO₂} > 70\% \)

- **Partial oxy-fuel**
  - CO₂ capture
  - \( 35 < y_{CO₂} < 70\% \)

- **Post-combustion**
  - CO₂ capture
  - \( y_{CO₂} < 35\% \)

**Modeling and Optimization**

- Pressure Swing Adsorption (PSA)
- Adsorption Process

**Absorption-Regeneration Process**

- Conventional solvents
- Demixing solvents
- Other configurations

**Modeling and Experiments**

- Solvents screening
- Materials screening

**CO₂ Conversion**

- Catalytic Conversion into methanol
- Other CO₂ Conversion routes

**CO₂ Capture & Purification**

- Sinda Laribi’s PhD Thesis
- Nicolas Meunier’s PhD Thesis
- Remi Chauvy’s PhD Thesis
- Seloua Mouhoubi’s PhD Thesis
- Lionel Dubois’s Post-Doc
- Other works

Ir. CHAUVY R. & MEUNIER N. | ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017
## Selecting CO₂ conversion pathways

### Multicriteria assessment: Results

### Ranking of CO₂ conversion options for the cement industry

<table>
<thead>
<tr>
<th>CO₂-based product</th>
<th>Conversion process</th>
<th>TRL</th>
<th>Timeframe</th>
<th>Size of CO₂ utilization</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium carbonates</td>
<td>Mineral carbonation</td>
<td>TRL 7</td>
<td>Timeframe to deployment 5 to 10 years</td>
<td>Market: 113.9 Mt (2013) CO₂ avoidance potential: 50.08 Mt</td>
<td>**</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Microbial process</td>
<td>TRL 7</td>
<td>Timeframe to deployment 5 to 10 years</td>
<td>Huge market Competition with other bioethanol etc.</td>
<td>*</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Electrolysis reduction</td>
<td>TRL 6</td>
<td>Timeframe to deployment 5 to 10 years</td>
<td>Market: 0.6 Mt (2013) CO₂ avoidance potential: 0.57 Mt</td>
<td>**</td>
</tr>
<tr>
<td>Methane</td>
<td>Catalytic hydrogenation</td>
<td>TRL 7/8</td>
<td>Timeframe to deployment &lt; 5 years</td>
<td>Huge market Competition with biogas/natural gas</td>
<td>****</td>
</tr>
<tr>
<td>Methanol</td>
<td>Catalytic hydrogenation</td>
<td>TRL 8/9</td>
<td>Timeframe to deployment &lt; 5 years</td>
<td>Market: 50 Mt (2013) CO₂ avoidance potential: 68.65 Mt</td>
<td>*****</td>
</tr>
<tr>
<td>Microalgae</td>
<td>Biological process</td>
<td>TRL 7</td>
<td>Timeframe to deployment 5 to 10 years</td>
<td>Important market But limited application</td>
<td>***</td>
</tr>
<tr>
<td>Sodium carbonates</td>
<td>Mineral carbonation</td>
<td>TRL 6</td>
<td>Timeframe to deployment 5 years</td>
<td>Market: &gt; 62 Mt (2013) CO₂ avoidance potential: 25.73 Mt</td>
<td>**</td>
</tr>
</tbody>
</table>

- **Methanol via catalytic hydrogenation**
- **Formic acid via electrochemical reduction**
- Both calcium & sodium carbonates via mineral carbonation
CO₂ Conversion: 
*The Methanol Case*
1. Experimental Section
   • Catalysts Shaping
   • Micro-pilot Installation

2. Process Section
   • 1st Upgraded Process (2016)
   • 2nd Upgraded Process (2017)
   • Updated CAPEX & OPEX Estimations
   • A complete Business Case

3. Perspectives
Special Acknowledgments

Special acknowledgments to T. Bryans (Master 2 Student)

« Catalytic Conversion of CO₂ into Methanol »

✓ The quality of his Master Thesis Report
✓ The highly contributive performances during his whole Master Thesis!
Catalysts Shaping: Why?

✓ Collaboration with the European School for Catalysts, Polymers and Materials of Strasbourg (ECPM)

✓ Elaboration of new generation catalysts
  (ex: CuO/ZnO/ZrO$_2$)

❖ Innovative catalysts are synthetized:
  • In powder
  • In small quantities (< 100g)

  Shaping (pellets) required
  Long & expensive synthesis
  No 2$^{nd}$ chance!

A methodological and reproductive shaping method is required!
Catalysts Shaping: How?

The « Extrusion technique » has been chosen:

• For convenience
• The most common technique for industrial catalyst shaping
Catalysts Shaping: *With?*

**Parameters to consider:**

- **Catalyst Powder:** COMMERCIAL CATALYST
- **Solvant:** WATER
- **Organic Binder:** METHYL CELLULOSE
- **Inorganic Binder:** ALUMINA or BENTONITE

---

**Design of Experiments**

- Inadequate composition
- Adequate composition
- Potential extrudates
Micro-pilot Installation

Schematic Flowsheet of the Micro-pilot Installation

Inlet Gas

Booster Pump

Furnace

Reactor

Back Pressure Controller

Gas Analysis Bypass

Pure Hydrogen
High Temperatures (300°C)
High Pressures (80 bar)

Hot Trap Cold Trap

Outlet Gas

MS Bypass

Outlet Gas
Methanol Process Section
1st Upgraded Process (2016)

Methanol Conversion Process

Adiabatic first reactor
- 80 bar – 230°C
- $\eta \approx 21\%$

Isotherm second reactor
- 80 bar – 230°C
- $\eta \geq 99\%$

Catalytic Block

Simulations with Aspen Plus & Economics v8.4.

19,000 Nm³/h CO₂
H₂/CO₂ ratio of 3

Flare
- CH₃OH

Purge
- H₂O

1 bar
$T_{reb} \approx 99°C$
Updated CAPEX and OPEX Estimations

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX (M€)</td>
<td>21.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAPEX SAVINGS (%)</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPEX (M€/YEAR)</td>
<td>9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPEX SAVINGS (%)</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Evolution of OPEX and CAPEX estimations
Updated CAPEX and OPEX Estimations

CAPEX estimations:
• 35% of the CO₂ emissions coming from a 3,000 tpd clinker cement plant
• Global CAPEX of 19,000 k€
  ✓ Reduction of the CAPEX by 14%!

OPEX estimations:
• Estimated to reach 11 €/ton CO₂ converted (i.e. 15 €/ton CH₃OH produced)
  ✓ Reduction of the OPEX by 66%!

OPEX estimations

<table>
<thead>
<tr>
<th></th>
<th>k€/year</th>
<th>€/ton CO₂</th>
<th>€/ton CH₃OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st Compr.</td>
<td>930</td>
<td>5.4</td>
<td>7.3</td>
</tr>
<tr>
<td>2nd Compr.</td>
<td>620</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>1400</td>
<td>4.9</td>
<td>6.6</td>
</tr>
<tr>
<td>Depreciation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>187</td>
<td>0.6</td>
<td>0.9</td>
</tr>
</tbody>
</table>
A complete Business Case: The Hydrogen Drama

- Hydrogen is produced from *water electrolysis*
- Requires **54 kWh/kg** ➔ **3800 €/tonne H\(_2\)**

![Table]

<table>
<thead>
<tr>
<th></th>
<th>M€/year</th>
<th>€/tonne MeOH</th>
<th>€/tonne CO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX([1])</td>
<td>1.9</td>
<td>8.9</td>
<td>6.5</td>
</tr>
<tr>
<td>OPEX</td>
<td>3.2</td>
<td>15.0</td>
<td>10.9</td>
</tr>
<tr>
<td>H(_2) Production</td>
<td>162.4</td>
<td>762.3</td>
<td>554.4</td>
</tr>
<tr>
<td>CO(_2) Capture</td>
<td>11.4</td>
<td>53.4</td>
<td>38.9</td>
</tr>
<tr>
<td>MeOH Selling</td>
<td>95.9</td>
<td>450.0</td>
<td>327.3</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>- 83.0</strong></td>
<td><strong>- 389.6</strong></td>
<td><strong>- 283.3</strong></td>
</tr>
</tbody>
</table>

**Methanol Business Cases**

« *The Hydrogen Economy: H\(_2\) as Energetic Vector for the Future!* »
*Master Thesis in collaboration with the Faculty of Economy and Management of Mons*

\([1]\) Payback Period of 10 years for amortised CAPEX
Perspectives

- Investigation of **catalyst shaping recipes** to improve **mechanical performances** of **pelletized catalysts**
- Experiments on several **CuO/ZnO shaped** catalysts with **CO$_2$/H$_2$** mixtures on our homemade semi-pilot installation
- **Check** and **Update** of the **kinetic** data related to catalysts

- Pursuit of the collaboration with the **European School for Catalysts, Polymers and Materials of Strasbourg** for the investigation of catalyst **modifiers** to improve **catalyst performances** and stability

- **New study** regarding the **hydrogen economy** and the influence of the **cost of electricity**

- **Life Cycle Analysis** (LCA) of the methanol conversion process (with **Remi Chauvy**)

- Propose an **environmentally friendly**, **integrated** and **optimized** **CO$_2$ conversion** process applied to the **cement sector**
Environmental assessment

- **Functional unit**: Conversion of 1 ton of CO₂ into methanol via catalytic hydrogenation
- **System boundaries**:

  ![Diagram showing the process]

  - **Cement plant**: Including the capture unit & purification unit
  - **Methanol synthesis**: 90% CO₂ captured
  - **Production of hydrogen**: 90% CO₂ captured

  - **Raw materials**: Energy, Electricity, Steam
  - **Clinker**: Raw materials
  - **Methanol**: Energy, Electricity, Steam

  - **System boundaries**:
    - Ir. CHAUVY R. & MEUNIER N. | ECRA Chair Scientific Meeting – Düsseldorf – 19/05/2017
Environmental assessment

Comparison between the 1\textsuperscript{st} upgraded (2016) and the 2\textsuperscript{nd} upgraded (2017) process

Climate change:
kg CO\textsubscript{2} eq / ton CO\textsubscript{2} converted
- Process 1\textsuperscript{st} upgraded: 331
- Process 2\textsuperscript{nd} upgraded: 227

- Simulations with SimaPro
- Method of characterization: ReCiPe Midpoint (H) V1.12 / Europe Recipe H
- Database: EcoInvent database v3.2

Environmental assessment: Comparison between the 1\textsuperscript{st} upgraded (2016) and the 2\textsuperscript{nd} upgraded (2017) process

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- Simulations with SimaPro
- Method of characterization: ReCiPe Midpoint (H) V1.12 / Europe Recipe H
- Database: EcoInvent database v3.2
Environmental assessment

• **Up to date:** no straight conclusion can be drawn

• **Need to implement:**
  
  • Construction and decommissioning of the infrastructures and equipment;
  
  • The use of the catalyst;
  
  • The environmental impact of the downstream process, i.e. linked to the capture and purification of the carbon dioxide from a cement plant.

• These first results tend to demonstrate that this process may have an environmental benefit regarding the global warming
CO₂ Conversion: 
The Formic acid Case
Formic acid Utility & Applications

Key points:

- Liquid at ambient condition (ease of storage)
- Efficient hydrogen storage molecule
- Global demand of 1 million tons/year in 2016
- Commercially available in solutions of various concentrations (85 - 99 wt%)
- Generates 600 millions €/year

Applications:

- Energy storage (hydrogen storage molecule)
- Chemicals (C\textsubscript{1} building block)
- Pharmaceuticals (preservative and antibacterial agent)
- Textiles (leather and tanning industries, etc.)
Electro-reduction of CO₂ into formic acid

Description of the process

$$\text{Mixture: CO}_2, \text{H}_2\text{O}, \text{HCOOH}, \text{H}_2$$

Electrochemical reactor

H₂O recycled

Separation unit

Formic acid 85 wt%
Electro-reduction of CO₂ into formic acid

Description of the process

**Acidic conditions**

**Cathode reactions**

\[ \text{CO}_2 \text{(aq)} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{HCOOH} \]
\[ 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2 \text{(g)} \]

**Anode reactions**

\[ 2\text{H}_2\text{O} \leftrightarrow + \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]

**Basic conditions**

**Cathode reactions**

\[ \text{CO}_2 \text{(aq)} + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{HCOO}^- + \text{OH}^- \]
\[ 2\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{H}_2 \text{(g)} + 2\text{OH}^- \]

**Anode reaction**

\[ 4\text{OH}^- \leftrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \]

**Total**

\[ \text{H}_2\text{O}(l) + \text{CO}_2(g) \leftrightarrow \text{HCOOH}(l) + 0.5 \text{O}_2(g) \] (main reaction)
\[ \text{H}_2\text{O}(l) \leftrightarrow 0.5 \text{O}_2(g) + \text{H}_2(g) \] (side reaction)
Electro-reduction of CO$_2$ into formic acid

Description of the process

- CO$_2$ recycled
- H$_2$ recycled
- Mixture: CO$_2$, H$_2$O, HCOOH, H$_2$
- Formic acid 85 wt%

Process of Electro-reduction of CO$_2$
Electro-reduction of CO\textsubscript{2} into formic acid

Water-formic acid mixture: Formation of an azeotrope

Requires special methods to facilitate their separation

Equilibrium curve: ideal case

Water-formic acid equilibrium curve at 1 bar
Electro-reduction of CO$_2$ into formic acid
Simulation under Aspen Plus

Absence of several units on the database of Aspen Plus

1) **Electrochemical reactor unit**: conversion reactor together with a split separation
   Efficiency: 15% $^{(1)}$

1) **Membrane process**: split unit
   H$_2$/CO$_2$ separation efficiency: 85% $^{(1)}$

Separation of the water-formic acid mixture:
- Pressure Swing Distillation;
- Vacuum distillation;
- High-pressure separation;
- Rectification adding a third component.

Electro-reduction of CO₂ into formic acid
Option 1: Pressure Swing Distillation

Two-column system operated by different pressures

“Shift” of the azeotrope point

Effect of the pressure on the azeotrope

Pressure Swing Distillation principle
Electro-reduction of CO$_2$ into formic acid

Option 1: Pressure Swing Distillation

Flowsheet: Conversion of 35% of CO$_2$ emissions of 1 BAT cement plant (same conditions as Nicolas Meunier)

- Simulations with Aspen Plus v. 8.6
- UNIFAC Dortmund
Electro-reduction of CO₂ into formic acid
Option 1: Pressure Swing Distillation

Formic acid business case

<table>
<thead>
<tr>
<th>INPUT</th>
<th>Unit: tpd</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>866</td>
</tr>
<tr>
<td>H₂O (REACT)</td>
<td>356</td>
</tr>
<tr>
<td>H₂O (SUP)</td>
<td>163</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OUTPUT</th>
<th>Unit: tpd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>896</td>
</tr>
<tr>
<td>O₂</td>
<td>323.5</td>
</tr>
<tr>
<td>H₂</td>
<td>1.53</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Energy requirements (per ton formic acid produced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity (without elect. reactor)</td>
</tr>
<tr>
<td>Electricity (electrochemical reactor)</td>
</tr>
<tr>
<td>Steam</td>
</tr>
<tr>
<td>Cooling water</td>
</tr>
</tbody>
</table>

Ref.: (²) A. Domingues-Ramos et al., 2015, *Global warming footprint of the electrochemical reduction of carbon dioxide to formate.*
**Electro-reduction of CO₂ into formic acid**

**Option 1: Pressure Swing Distillation**

<table>
<thead>
<tr>
<th>INPUT</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>600 €/ton</td>
</tr>
<tr>
<td>Electricity</td>
<td>7.8 c€/kWh</td>
</tr>
<tr>
<td>Steam</td>
<td>18 €/ton</td>
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<tr>
<td>CO₂ capture cost</td>
<td>40 €/ton</td>
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</table>

<table>
<thead>
<tr>
<th>UNIT COST (1)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CAPEX</td>
<td>52.5 M€</td>
</tr>
<tr>
<td>OPEX</td>
<td>202.2 M€/year</td>
</tr>
<tr>
<td>Capture cost</td>
<td>11.4 M€/year</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INCOME</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>177.4 M€/year</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TOTAL BALANCE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-41.5 M€/year</td>
</tr>
</tbody>
</table>

1) Electrodes, electrolytes etc. not taken into account

2) Process still not integrated (heat integration etc.)

3) From an electricity price at 6 c€/kWh (1), the unit is **economically viable** (total balance = 0)

→ Need further investigations

(1) Preliminary results: have to be seen with caution
Electro-reduction of CO₂ into formic acid

Option 2: Vacuum distillation

Equilibrium curves at different pressures
Electro-reduction of CO₂ into formic acid

Option 2: Vacuum distillation

at **0.06 bar**: removal of the azeotrope point

Liquid and Vapor phase diagram for the water-formic acid mixture at 0.06 bar.

- **Only 1 column**
- High CAPEX
- High OPEX

Need further investigations.
Electro-reduction of CO$_2$ into formic acid
Option 3: Rectification adding a third component

“Shift” of the azeotrope point

Rectification adding a third component
Electro-reduction of CO₂ into formic acid
Option 3: Rectification adding a third component

Effect of the entrainer (sulfolan, C₄H₈O₂S) on Txy water-formic acid mixture at 1 bar

→ at 1 bar, 50wt% sulfolan: removal of the azeotrope point

The quantity of sulfolan to add depends on the pressure:
Need for further investigations!
Perspectives

- Further investigation regarding the water-formic acid separation process in order to select the most performant option between:
  - Pressure Swing Distillation;
  - Vacuum distillation;
  - High-pressure separation;
  - Rectification adding a third component.

- **Technico-economic evaluation** of the different options and **optimization** of the overall process

- **Environmental assessment** of the different options

- Propose an **environmentally friendly, integrated and optimized CO₂ conversion** process applied to the **cement sector**!
Special Acknowledgments

Special acknowledgments to L. Brousmiche (Master 1 Student)

« Electro-reduction of CO₂ into formic acid »
Thank you for your attention

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Next meeting of the Scientific Committee of the ECRA Chair

• In Mons
• In November 2017?
Thanks very much!

For the ECRA Chair@UMONS:

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Chemical and Biochemical Process Engineering Unit - UMONS