UTCCS-3
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POLYTECH MONS
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« Study of the post-combustion CO_2 capture applied to cement plant flue gases with high CO_2 contents »

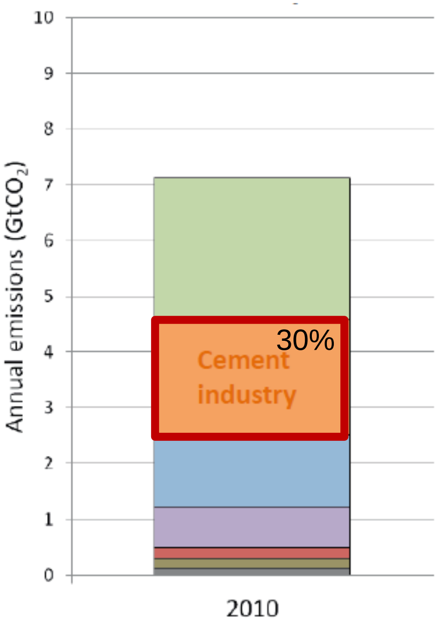
Ir Sinda Laribi, Dr Lionel Dubois, Prof. Guy De Weireld and Prof. Diane Thomas

Ir Sinda Laribi
PhD Student – ECRA Academic Chair
Chemical and Biochemical Engineering Department
Faculty of Engineering - University of Mons (Belgium)
sinda.laribi@umons.ac.be

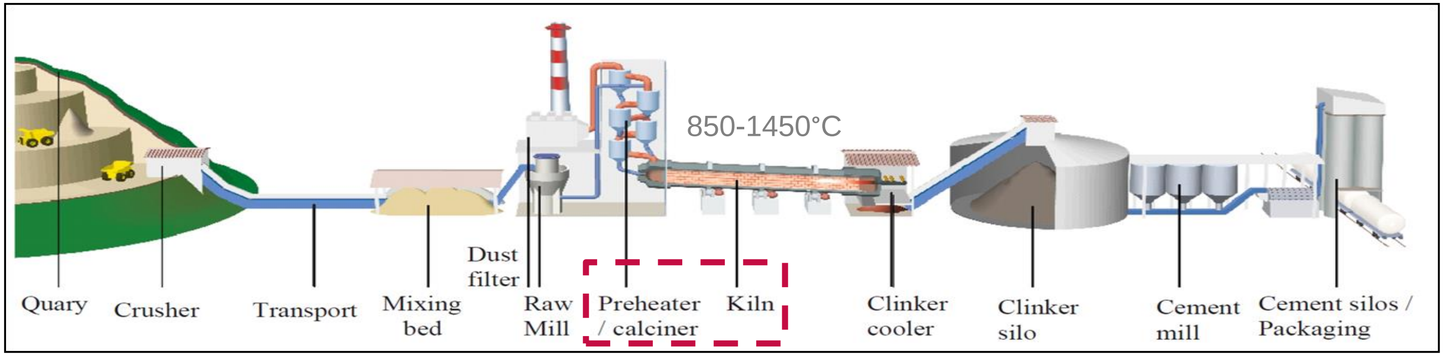
Partners: HEIDELBERGCEMENT Global Environmental Sustainability — NORCEM HEIDELBERGCEMENT Group — ecra european cement research academy

Context of this work

- Cement plants → 30% of the industrial CO_2



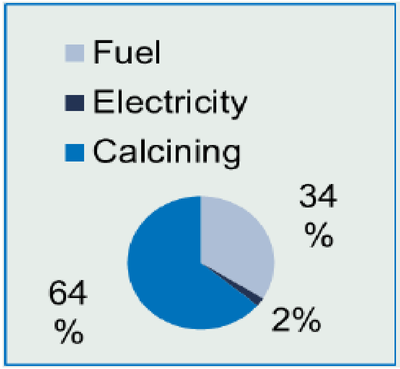
Source: IEA(2013b), «Global Action to Advance Carbon Capture and Storage: a Focus on Industrial Applications»



$CaCO3 + heat^* \rightarrow CaO + \uparrow CO_2$

*Between 3200 and 4200 kJ/tonne of clinker

Pre-combustion not applied to cement industry



<u>CO_2 concentrations in industrial flue gases</u>

5-15% for conventional power plants

25-30% for conventional cement kilns

70-90% for oxyfuel cement kilns

What is a hybrid technology?

= Combination of two (or more) different technologies allowing to increase individual performances or reduce the overall energy consumption in comparison with the use of the technologies separately.

Examples in the context of CO_2 capture:

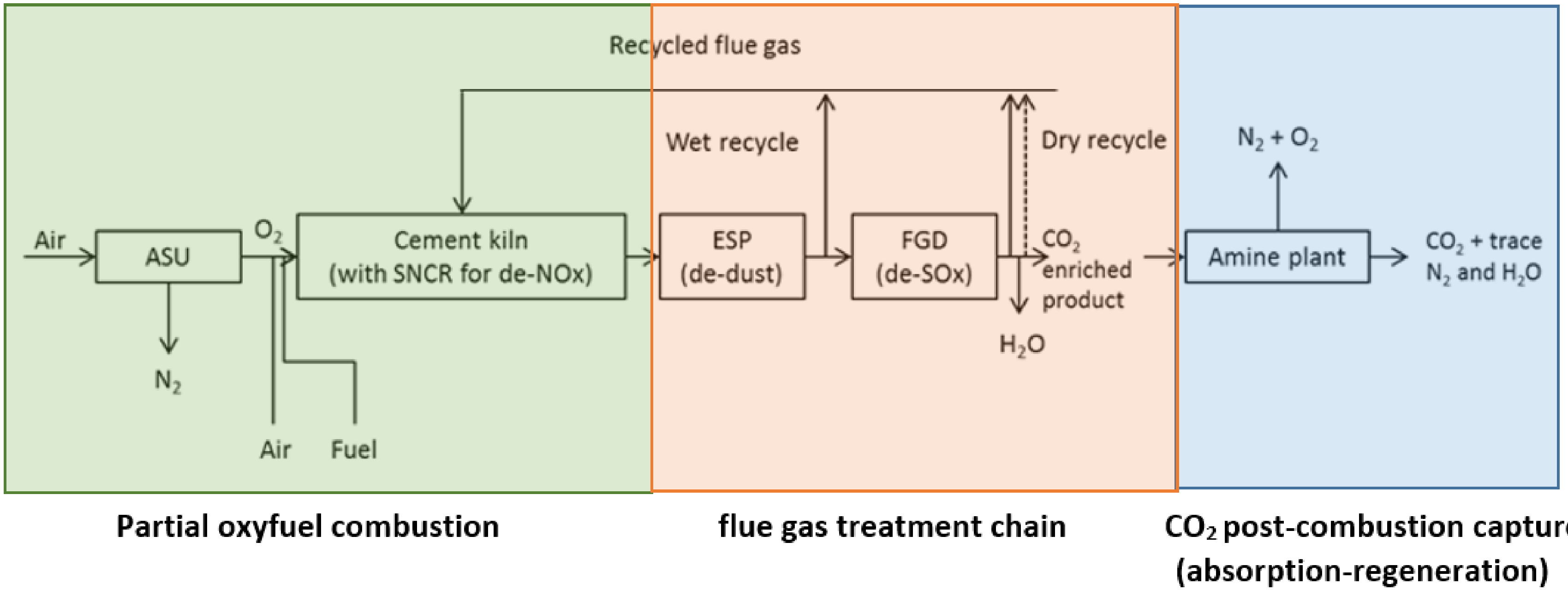
- Combination of membranes gas separation and absorption technologies ;
- Combination of membranes gas separation and cryogenic CO_2 capture technologies ;
- …

In this work:

- **Combination of partial oxy-fuel combustion plant with an amine post-combustion technology = Post combustion capture applied to O_2-enriched air combustion (= partial oxy-fuel combustion) ;**
- **Combination of chemical and physical solvents in a post-combustion CO_2 capture plant = hybrid solvents.**

Purpose & Innovative aspects of this work

➢ Partial oxy-fuel combustion technology: Post-combustion capture applied to O_2-enriched air combustion.



→ allows increasing the CO_2 content of the flue gas.

$20\% < Y_{CO2} < 70\%$

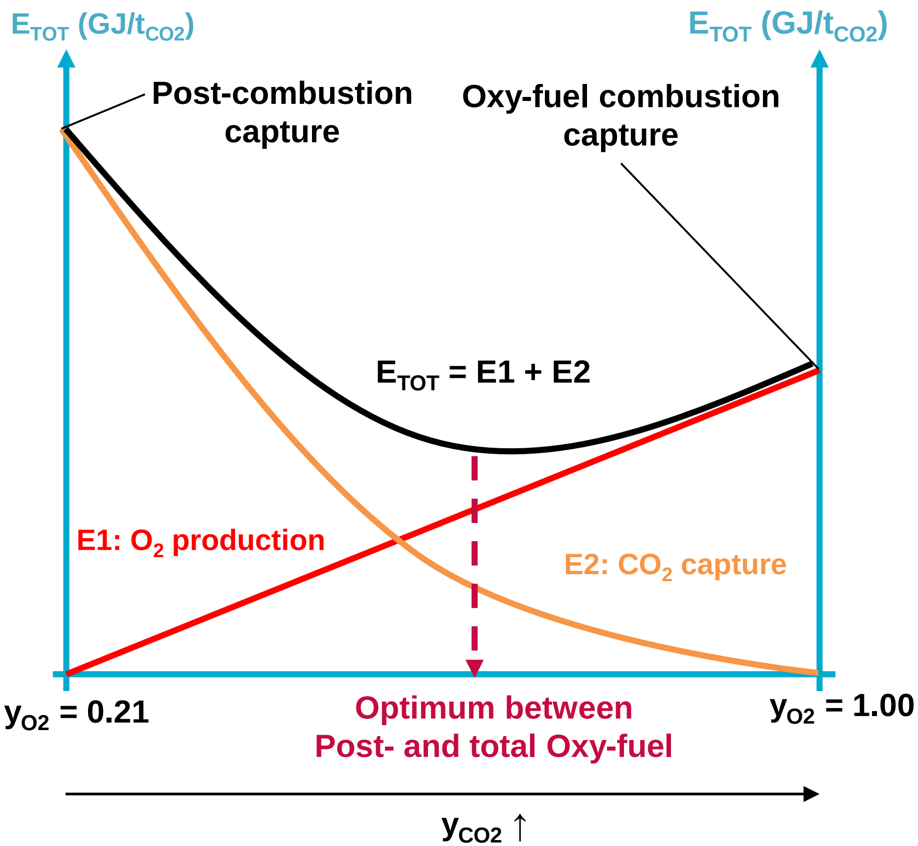
Adapted from Smart J P and Riley G S, "Use of oxygen enriched air combustion to enhance combined effectiveness of oxyfuel combustion and post-combustion flue gas cleanup", 2012

✓ **Applicability** of this technology for **power plants** proved : European Project ECO SCRUB.

http://cordis.europa.eu/project/rcn/87195_en.htm
Main reference articles available in: http://www.maneyonline.com/
& http://iasks.org/

Purpose & Innovative aspects of this work

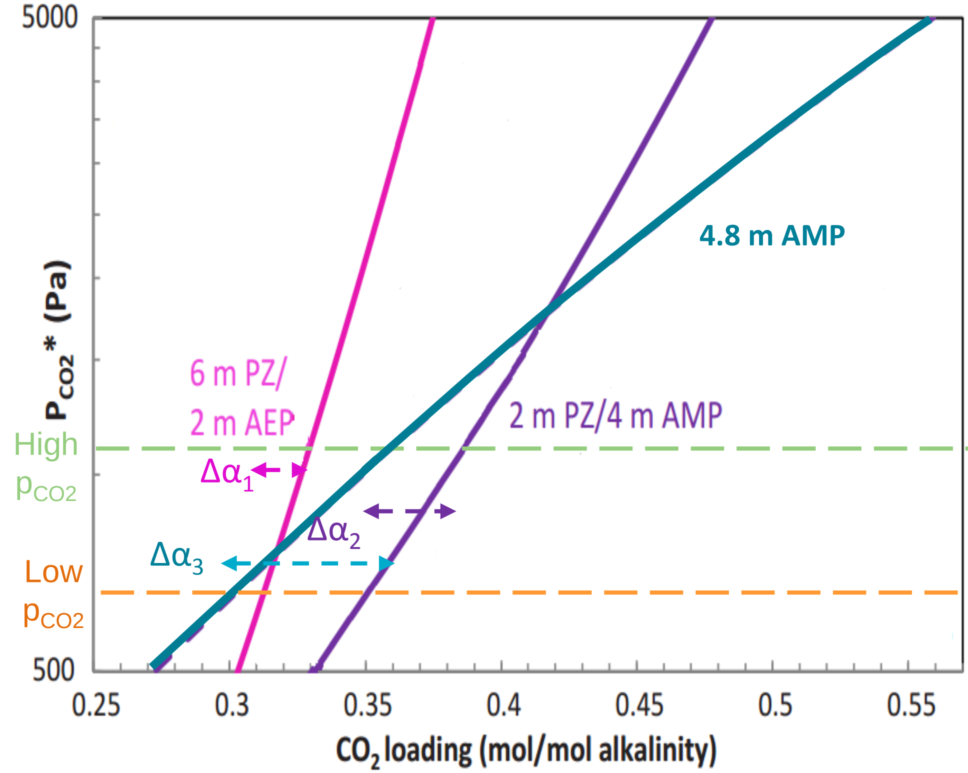
Energetic effect



Adapted from Favre E., Bounaceur R., Roizard D., Vol 68, Issue 1, pp. 30–36, 30 June 2009

Chemical effect

Testing and screening of solvents for CO_2 content $\mathbf{Y_{CO2,in}}$ **= 10-60 %** under partial oxy-fuel conditions.



Example taken from literature:
Le Li et al./Energy Procedia 37 (2013) 370-385
CO_2 solubility at 40°C (P_{CO2} * 0.5-5 kPa)

Advantages :

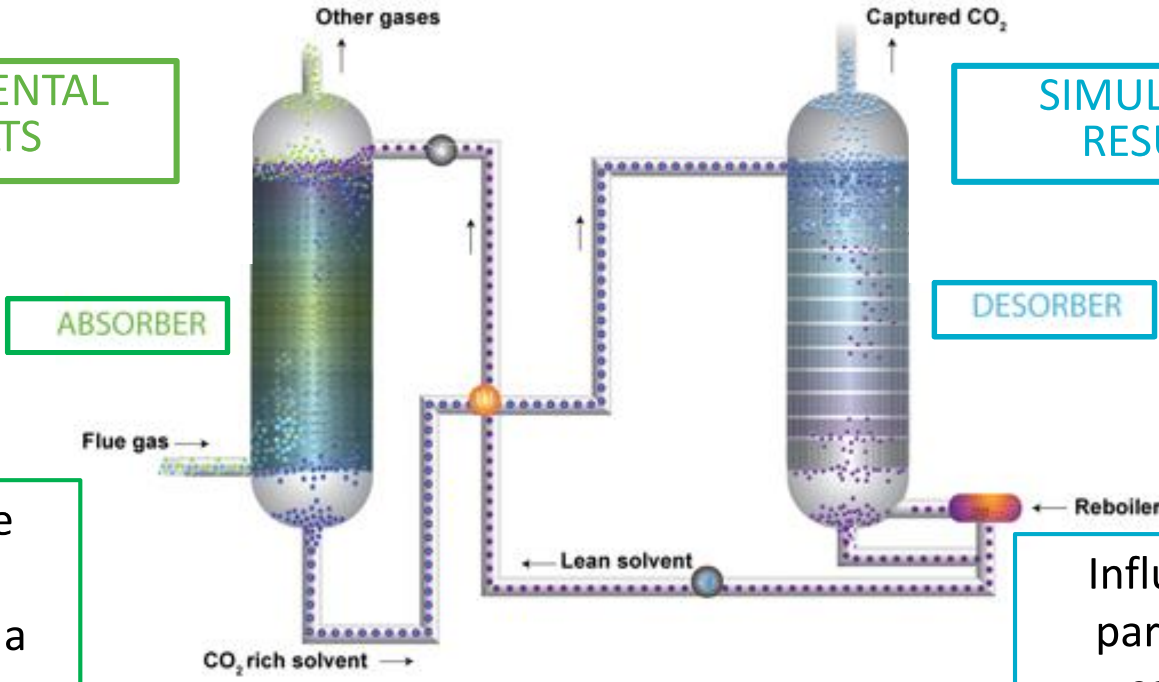
- **Less cost for the ASU** (less O_2 needed in comparison with total oxy-fuel).
- **Less regeneration energy** in the amine plant thanks to a more CO_2-concentrated flue gas.

Advantage :

- ΔCO_2 loading capacity increases with increasing P_{CO2} → Industrial application.

Presentation schedule

- Different capture methods including absorption/regeneration using amine(s) based solvents.



From http://www.co2crc.com.au/

EXPERIMENTAL RESULTS

Evaluation of the absorption performances of a wide range of solvents in high CO_2 content conditions → **Experimental screening of solvents**

SIMULATION RESULTS

Influence of the partial oxy-fuel combustion conditions on the regeneration energy → **Aspen Hysys^{TM} simulations**

Categories of selected chemical solvents:

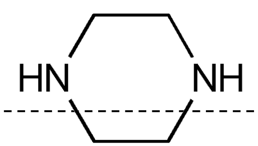
- Methodology of choice: various criteria (from Dubois PhD Thesis, 2013)

Primary amine | Se amine | Tertiary amine

MEA
(Monoethanolamine)

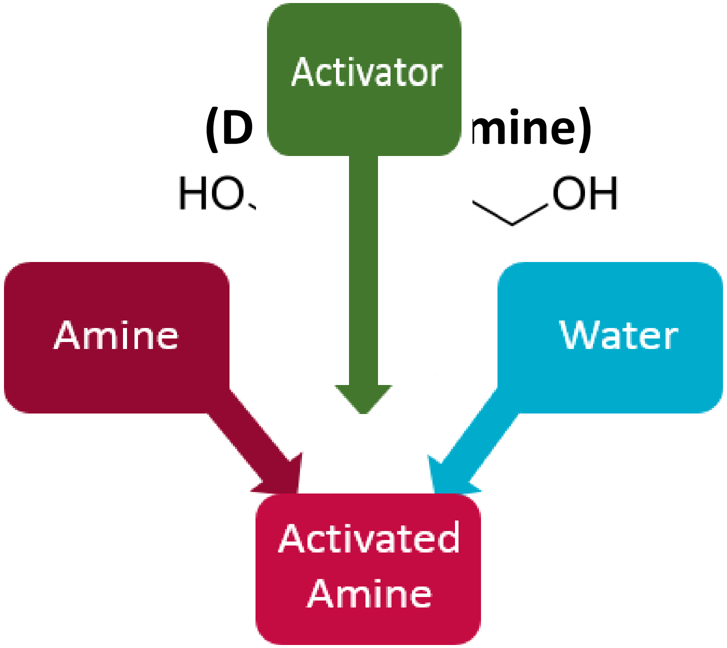
Cyclical di-amine

PZ
Piperazine



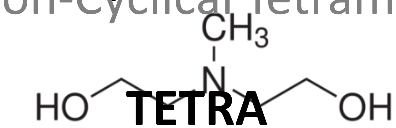
(D mine)

HO OH

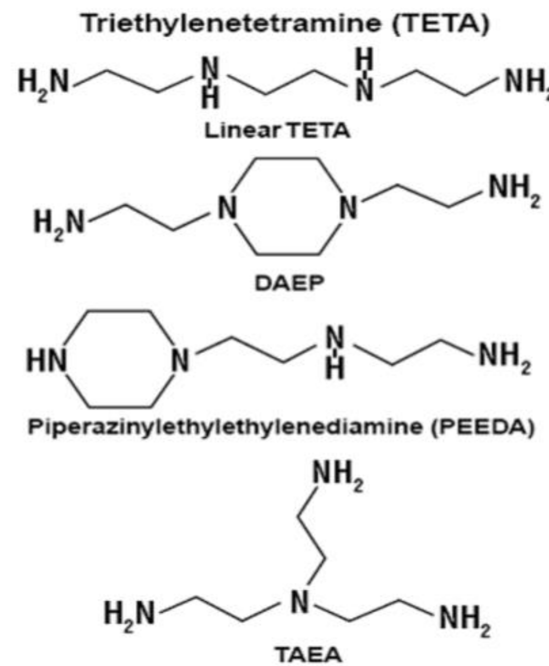


MDEA
(N-methyldiethanolamine)

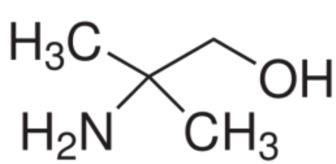
Non-Cyclical Tetramine



TETRA
(Triethylenetetramine)



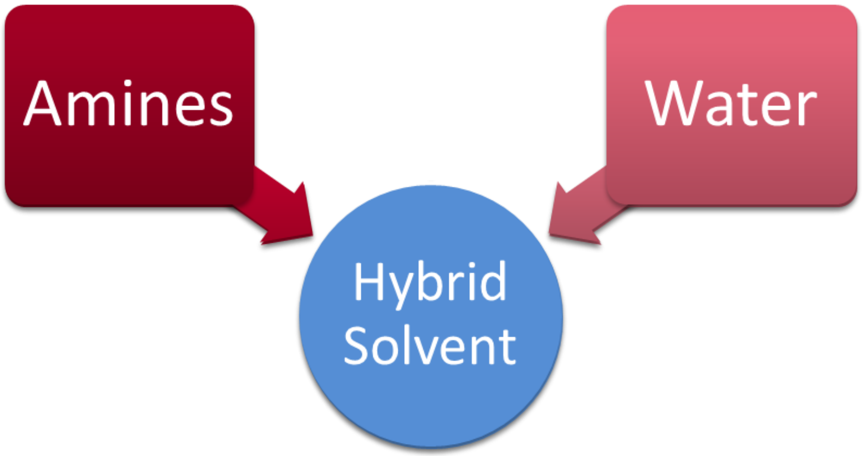
AMP
(2-amino-2-methyl-1-propanol)

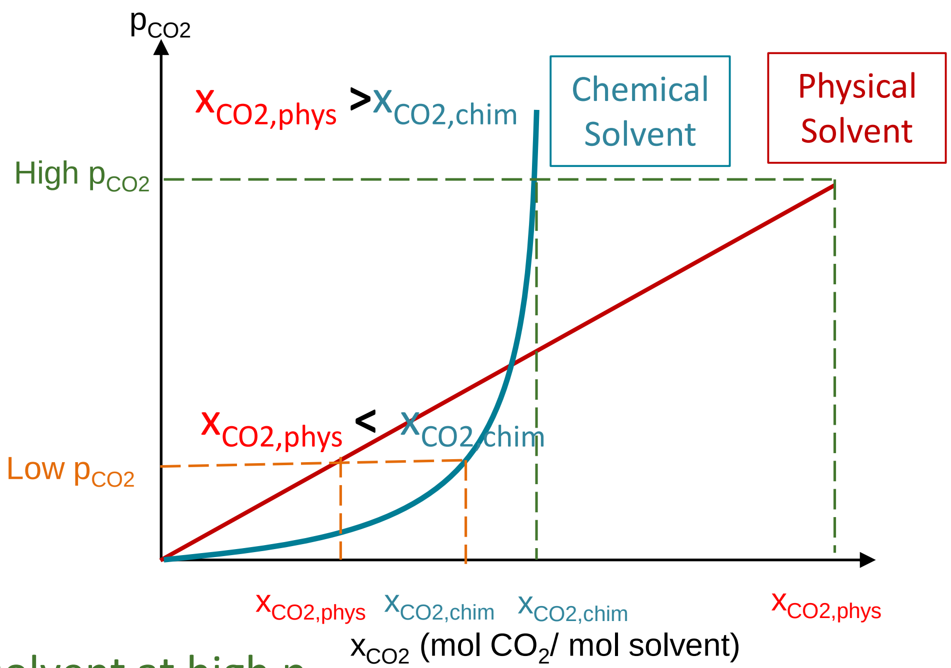


(2-amino-2–hydr l)

H

Hybrid solvent studied





Adapted from Bailey et al., 2005

Advantages of hybrid solvents:

- High absorption capacity of the physical solvent at high p_{CO2}
- Better absorption capacity of the chemical solvent at low p_{CO2}
- Lower energy consumption for the regeneration process
- High absorption kinetics due to the chemical reaction with CO_2

Acetals

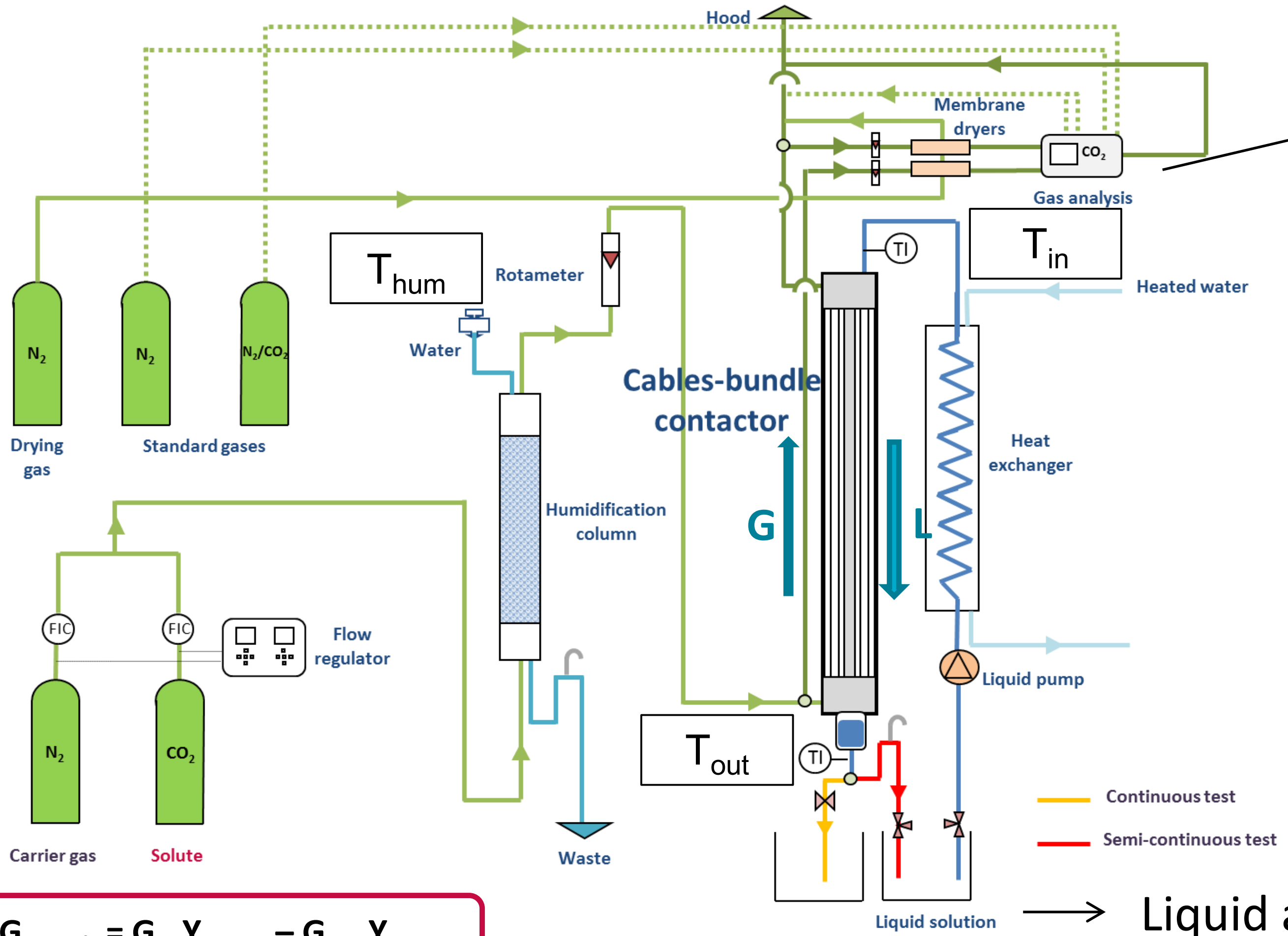
TOU (2,5,7,10-Tetraoxaundecane)

Lambiotte &Cie

Experimental schedule

Category	N°	Solvent tested
Preliminary tests with MEA	1	MEA 30% (Reference)
	2	MEA 30% (Repeatability)
	3	MEA 20% (Effect of C_{amine})
	4	MEA 10% (Effect of C_{amine})
Other conventional solvents	5	DEA 30%
	6	MDEA 30%
	7	AMP 30%
	8	PZ 10%
Other simple solvents	9	MMEA 30% (Repeatability)
	10	TETRA 30%
	11	AHPD 30%
Activated solutions: Comparison of PZ and TETRA as absorption activator	12	AMP 30% + PZ 5% (Activated SHA with PZ)
	13	AMP 30% + TETRA 5% (Activated SHA with TETRA)
	14	DEA 30% + PZ 5% (Activated secondary amine with PZ)
	15	DEA 30% + TETRA 5% (Activated secondary amine with PZ)
	16	MMEA 30% + PZ 5% (Activated SHA with PZ)
	17	MMEA 30% + TETRA 5% (Activated SHA with TETRA)
Hybrid solvents	18	MEA 30% + TOU 35%
	19	DEA 30% + PZ 5% + TOU 35%
	20	AMP 30% + PZ 5% + TOU 35%

Experimental device



$y_{CO_2,in}$
$y_{CO_2,out}$ (IR)

Pressure	101325 Pa
L	0,185 l/min
$G_{tot, dry}$	12,9 Nl/min
T_{hum}	16 to 18°C
T_{in}	25°C

$$G_{CO2,abs} = G_{in}\, Y_{CO2,in} - G_{out}\, Y_{CO2,out}$$

→ Liquid analyses (TC, IC, pH)

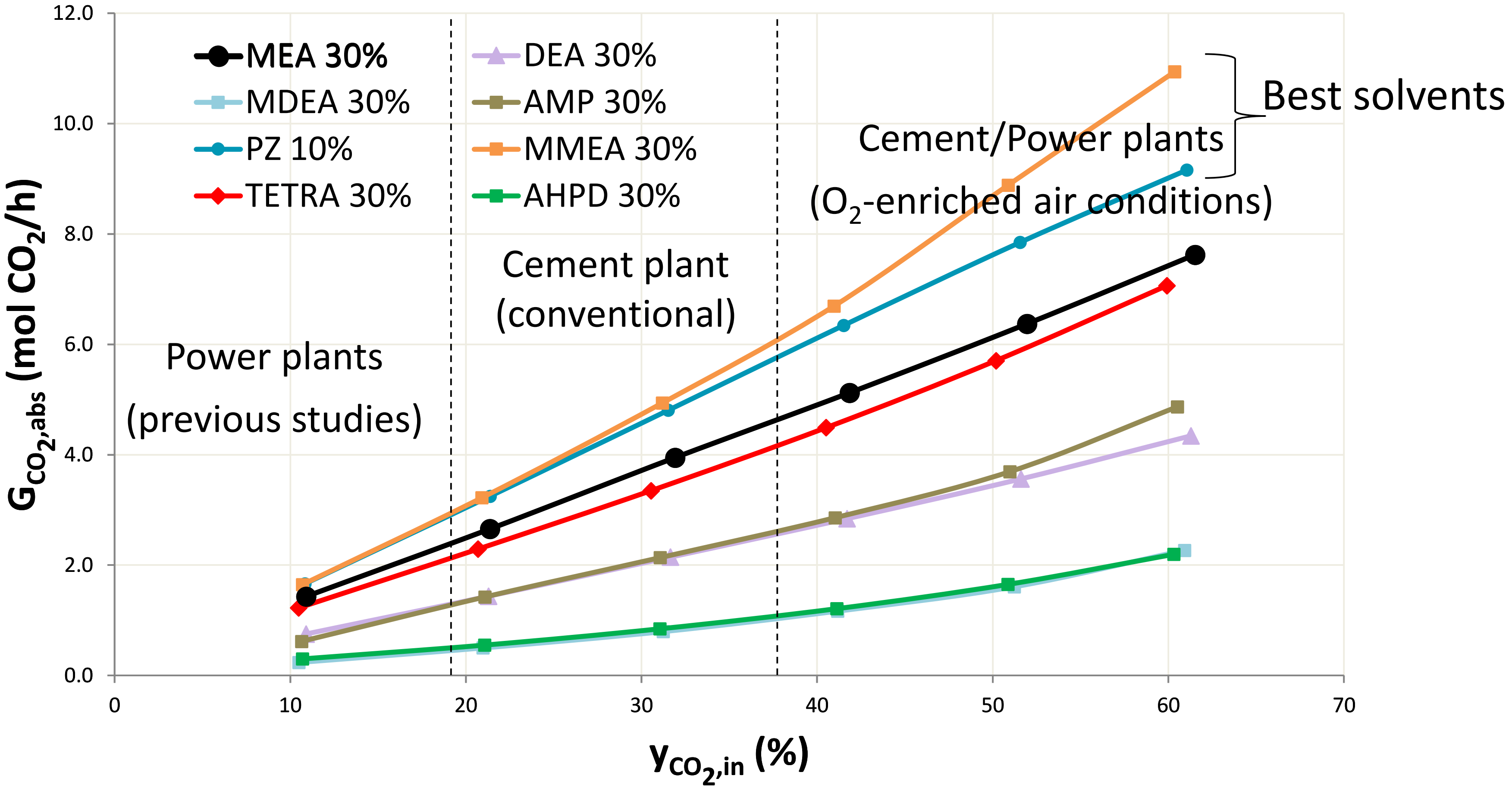
For industrial applications
CO_2 loadings of the solvents $\alpha_{CO_2} \neq 0$:

$$\alpha_{CO_2} = \frac{C_{CO_2}}{C_{amine}}$$

- **Continuous tests:** $\alpha_{CO2}=0$, $y_{CO2,\,in}$ = 10 to 60% vol.
- **Semi-continuous tests:** $\alpha_{CO2}\neq0$, $y_{CO2,\,in}$ = 40% vol.

Continuous tests with simple solvents

$\alpha_{CO2}=0$, ≠ $y_{CO2,\ in}$



➢ MMEA 30% and PZ 10% give the best absorption performances.

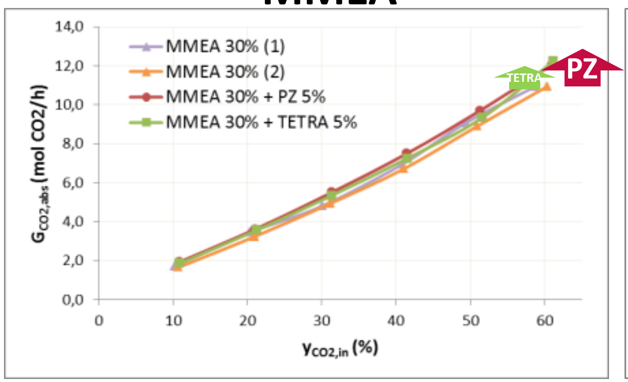
Continuous tests with activated solvents

$\alpha_{CO_2}=0$, $\neq y_{CO_2, in}$

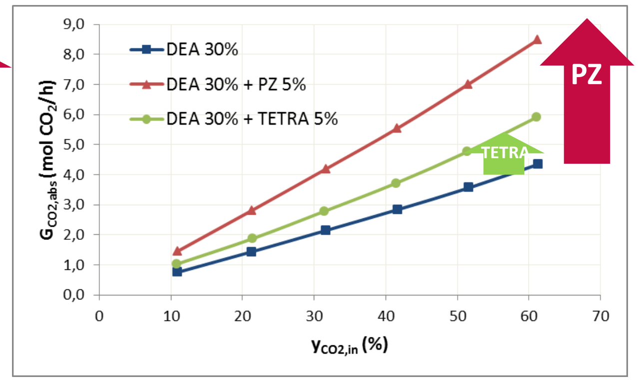
- Activation (Amine + PZ/TETRA) : YES

More significant activation effect

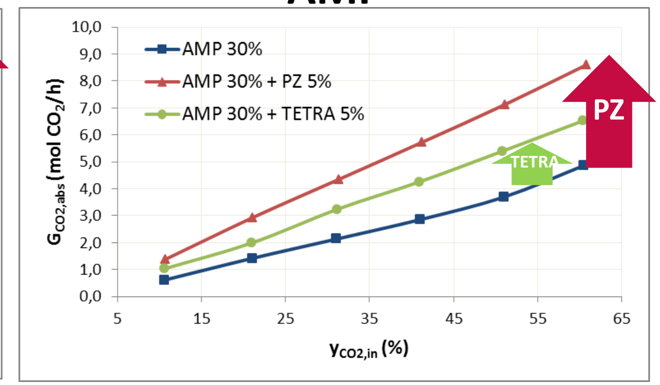
MMEA



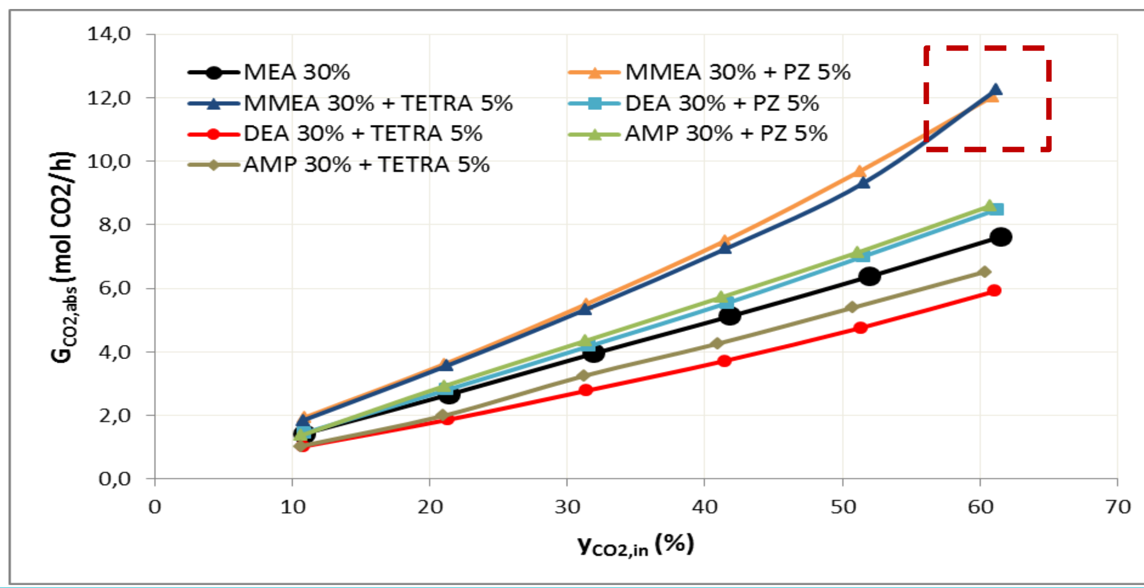
DEA



AMP

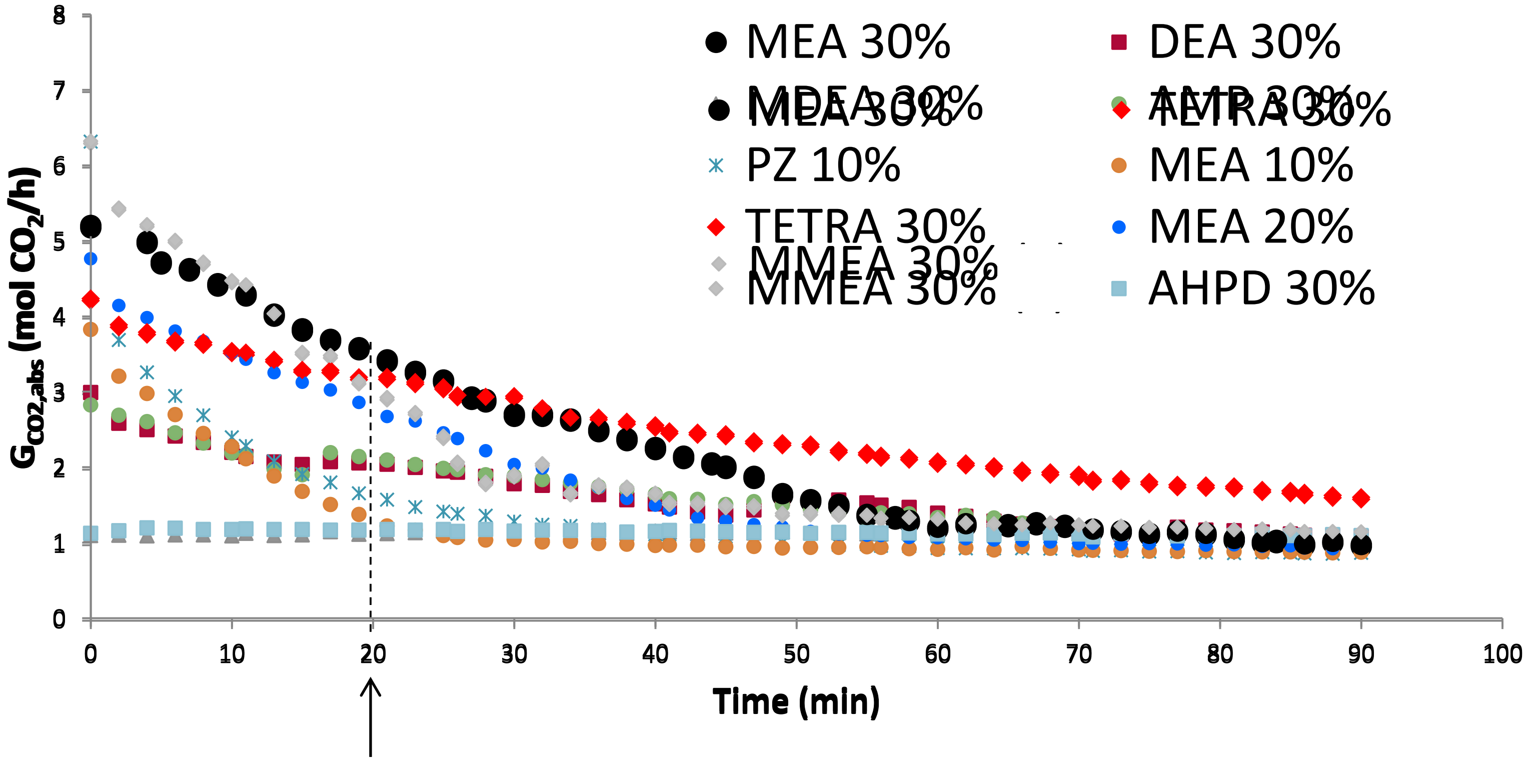


- PZ best activator.
- Activated amines: better results than the MEA (reference).
- Best results for MMEA 30% with or without activator.



Semi-continuous tests with simple solvents

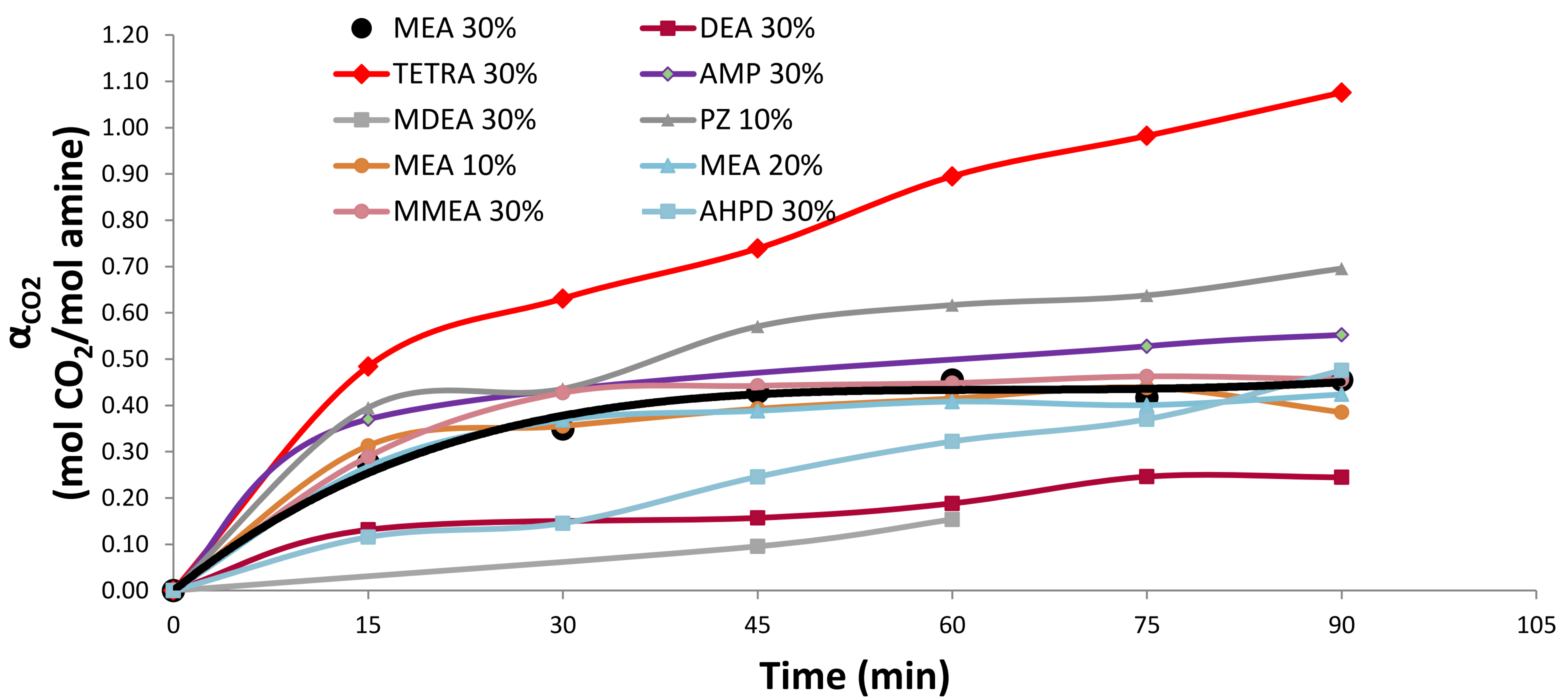
$\alpha_{CO2} \neq 0$, $y_{CO2, in}$ = 40%



- After 20 minutes of recirculation, TETRA is more performant than MMEA 30% and MEA 30%.
- G_{CO2} ↘ α_{CO2} ↗

Semi-continuous tests with simple solvents

$\alpha_{CO2} \neq 0$, $y_{CO2, in}$ = 40%

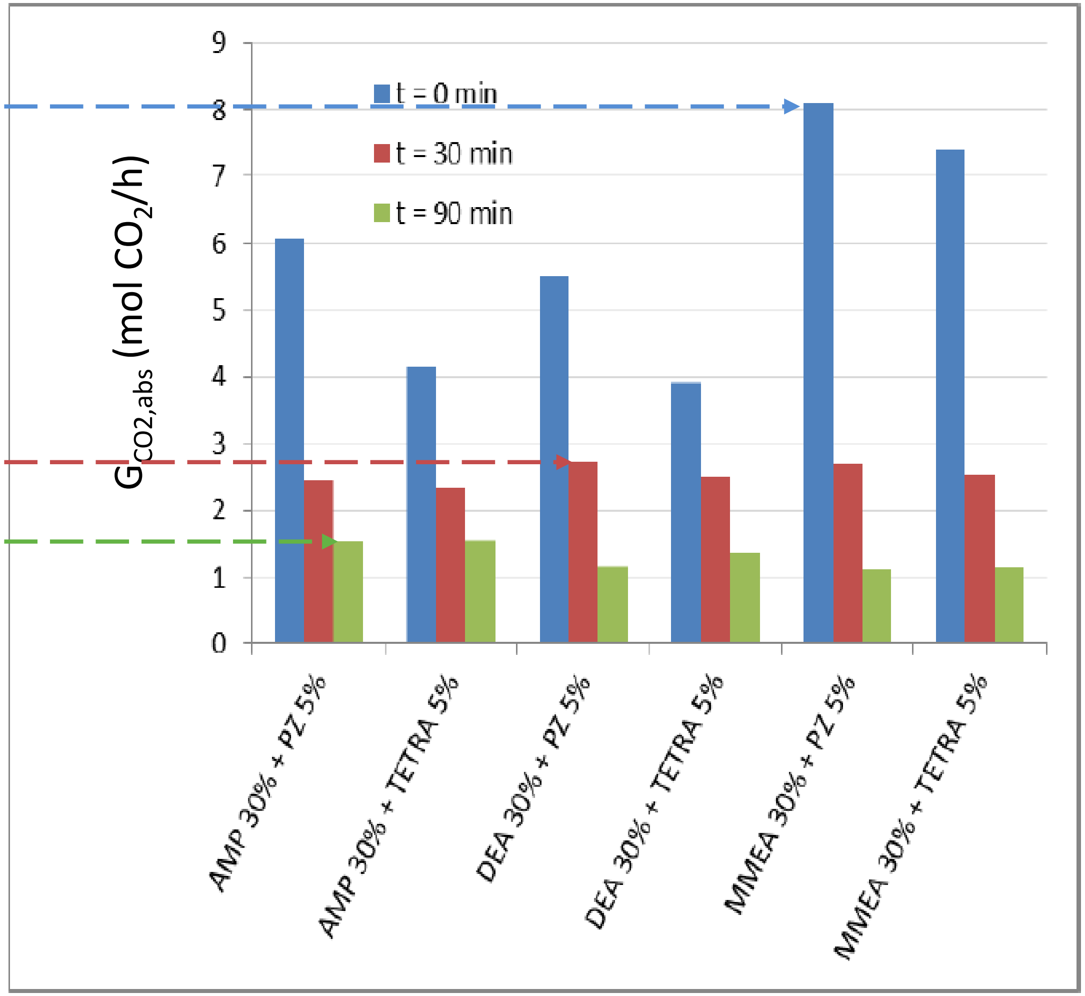


- Absorption performances of CO_2 loaded solutions (recirculation tests to measure absorption capacity) → TETRA allows absorbing more CO_2.

Semi-continuous tests with activated solvents

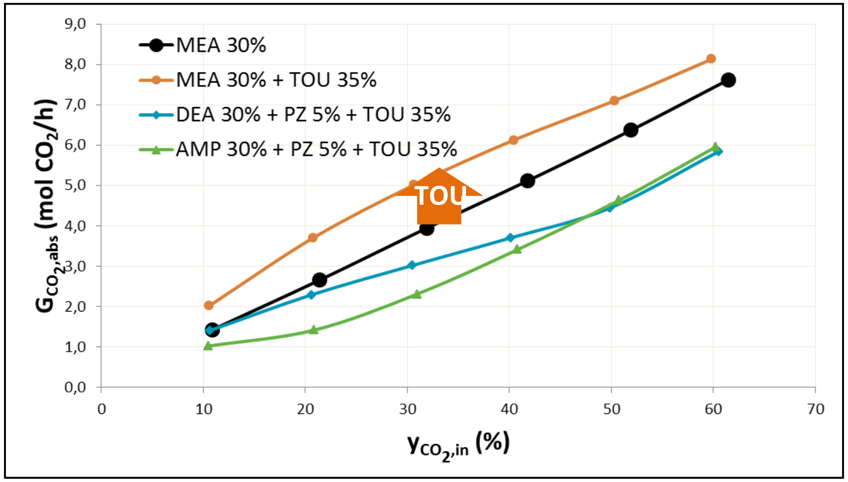
$\alpha_{CO2} \neq 0$, $y_{CO2, in}$ = 40%

- **MMEA 30% + PZ 5%** presents the best absorption capacity at t=0 min (without any CO_2 loading)
- **DEA 30% + PZ 5%** has the more important absorption capacity at t=30 min
- PZ activated solutions, and especially **AMP 30% + PZ 5%**, present good absorption performances at the beginning of the test and also after 90 min with a significant CO_2 loading.

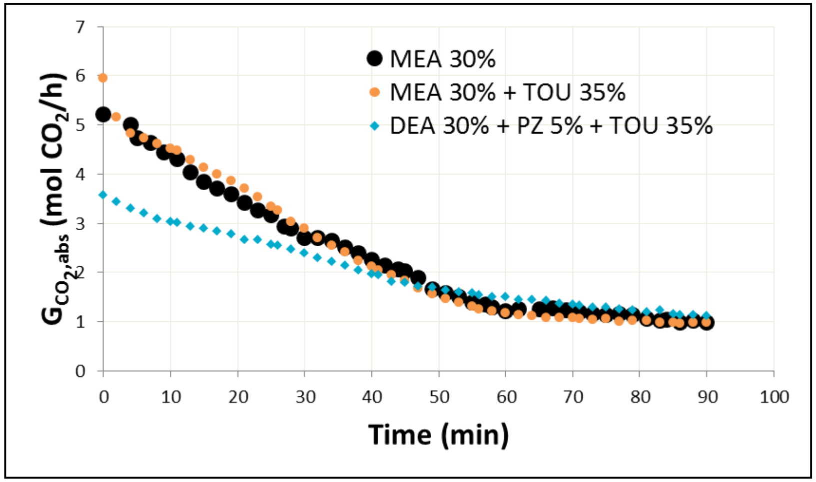


Hybrid solvents

Continuous tests



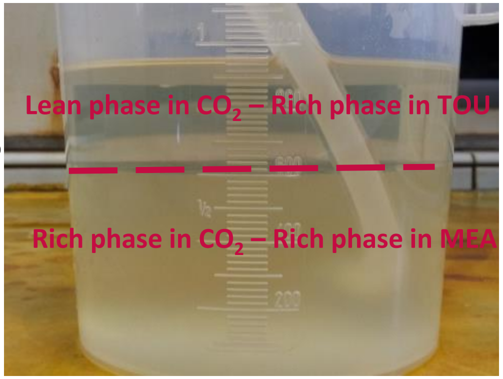
Semi-continuous tests



Phase change solvents:
Energy savings!

Demixing solvents

MEA 30% + TOU 35%
DEA 30% + PZ 5% + TOU 35%



MEA 30% + TOU 35%
(after 45 minutes)

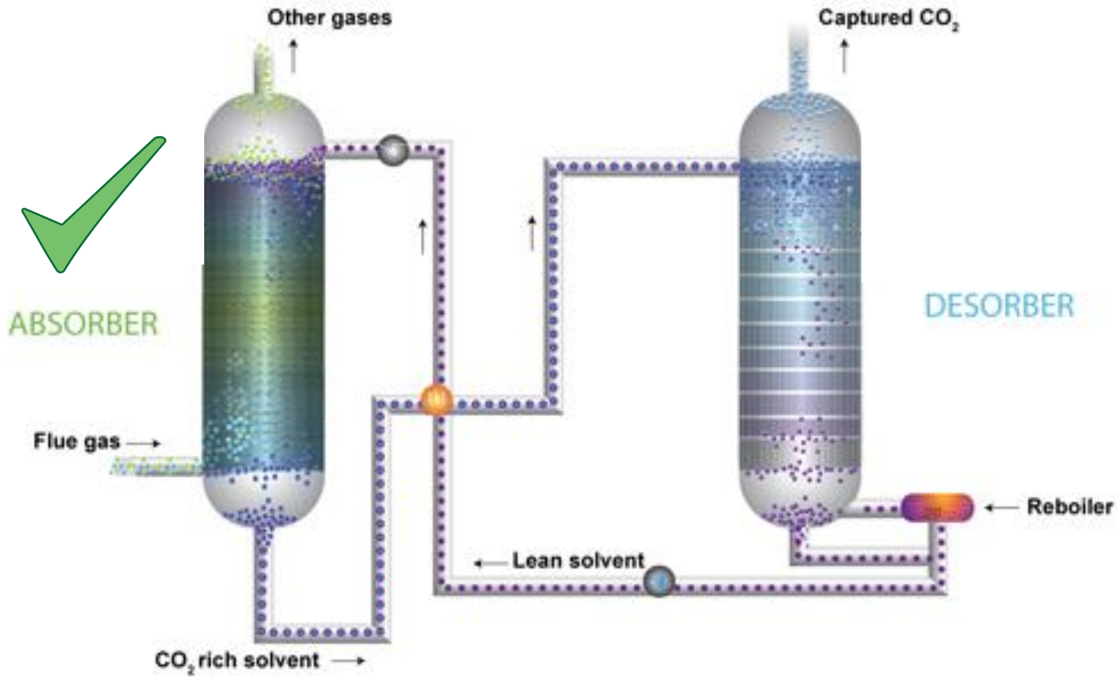
Precipitating solvent

AMP 30% + PZ 5% + TOU 35%

- **Demixing phenomenon:** use of hybrid solvent → Great potential for reducing the energy regeneration by regenerating only the CO_2-rich phase.

Purpose of simulations

EXPERIMENTAL RESULTS



SIMULATION RESULTS:
Influence of the partial oxy-fuel combustion conditions on the regeneration energy
→ **Aspen Hysys^{TM} simulations**

General principles of the simulations

NORCEM
HEIDELBERGCEMENTGroup
Brevik Cement plant

Brevik cement plant = ECRA reference
Single European project for testing CO_2 capture from cement industry

CASTOR/CESAR pilot

CASTOR/CESAR pilot
= reference
European projects
All data available

CO_2 recovery flow
$G_{CO_2,regen}$ = 1.5 t CO_2/h
G_{in} = 4000 m^3/h
$y_{CO_2,in}$ = 20.4 mol.%
A = 90 mol.%
Produced CO_2 purity
= 98 mol.%

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

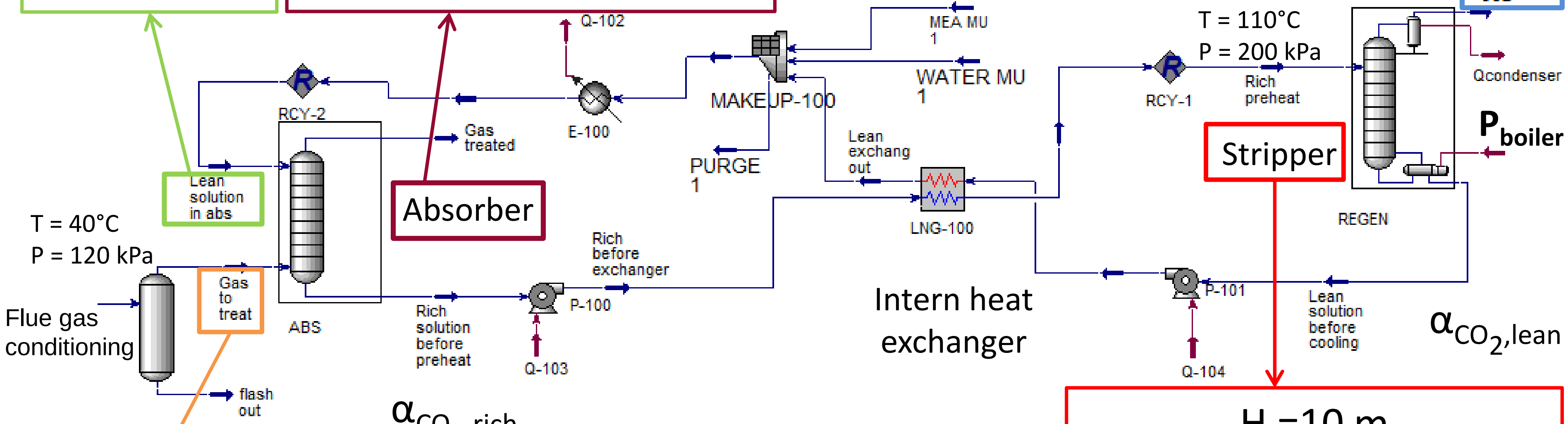
Simulations for different CO_2 contents in the gas to treat:
- Base case: flue gas from Brevik
- Other cases: simulations of partial oxyfuel combustion for high Y_{CO2} (compositions provided by ECRA).

General principles of the simulations

L = 21 m³/h

H =17 m
D = 1,1m
Random packing IMTP 50

Purity = 98 mol.%



Solvent = MEA 30 wt.%

$T_{boiling}$ = 120°C

H =10 m
D = 1,1 m
Random packing IMTP 50

G_{in} = 4000 m³/h
$y_{CO_2,in}$ from 20 to 60 mol.%

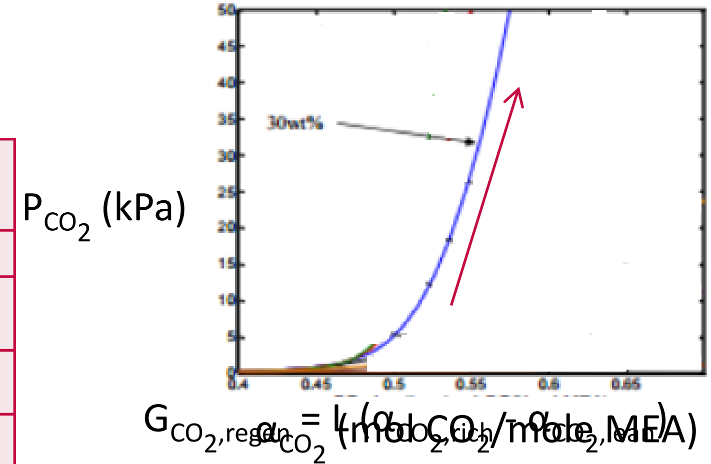
Determined → $$E_{regen} = \frac{P_{boiler}}{G_{CO_2,regen}}$$ → [kJ/h] / [kg CO_2/h]

Fixed
$G_{CO_2,regen}$ = 1500 k CO_2/h

$E_{regen} = f(y_{CO_2,in})$

Results for the tested cases:

	Base case	Intermediate case	Hybrid 1	Hybrid 2	Hybrid 3
$y_{CO2,in}$ (%)	20.4	31	44.1	51.44	62.03
E_{regen} (GJ/ t CO_2)	3.39	2.96	2.56	2.48	2.30
E_{regen} saving / base case		**12.61%**	**24.31%**	**26.79%**	**31.99%**
$\alpha_{CO_2,rich}$	0.508	0.536	0.562	0.557	0.590
$\alpha_{CO_2,lean}$	0.198	0.232	0.264	0.259	0.285



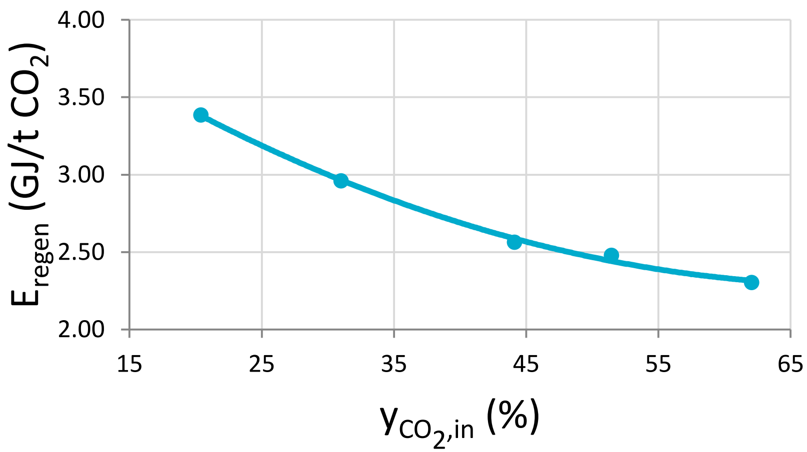
From Svendsen et al,., "Equilibrium in the H2O-MEA-CO2 system: new data and modeling", 2011

$G_{CO_2,regen} = f(\alpha_{CO_2,rich} - \alpha_{CO_2,lean})$

Fixed — Fixed — $= f(P_{CO_2})$

If p_{CO2} increases, the CO_2 absorption capacity also increases

$\alpha_{CO_2,lean}$ ↗ $\alpha_{CO_2,rich}$ ↗



If $y_{CO_2,in}$ ↗

- Costs for O_2 production ↗
- E_{regen} ↘ for $y_{CO_2,in}$ from 20 to 44%

E_{saving} = 24%

→ Optimum ?

Interest of partial oxy-fuel combustion conditions is confirmed (ECO-Scrub project)

Conclusions

Hybrid process: Post combustion CO_2 capture applied to O_2-enriched air combustion conditions leading to **high CO_2 content** (up to 60 vol.%).

- Screening of solvents:

  - Continuous tests (unloaded solutions):

  MMEA: best absorption performances, no necessity of activator

  PZ: best activation effect.

  - Semi-continuous tests (loaded solutions):

  TETRA: best absorption capacity.

  Activated AMP and DEA interesting absorption capacities.

- Energy regeneration: When $y_{CO_2,in}$ ↗ E_{regen} ↘

Prospects

- Evaluation of the impact of partial oxy-fuel combustion conditions on the global chain (from O_2 production to CO_2 conversion).

- Absorption-regeneration tests using the micro-pilot unit for the best solvents screened: internship starting in March 2016 .

- Micro-pilot unit for investigations to test demixing solvents (addition of a decanter): new PhD thesis of the ECRA CHAIR started in February 2016.

UTCCS-3

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Austin, Texas

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Thank you for your attention.

Questions?

Ir Sinda Laribi

PhD Student – ECRA Academic Chair

Chemical and Biochemical Engineering Department

Faculty of Engineering - University of Mons (Belgium)

sinda.laribi@umons.ac.be

Partners: HEIDELBERGCEMENT Global Environmental Sustainability — NORCEM HEIDELBERGCEMENTGroup — ecra european cement research academy