Study of the post-combustion CO_2 capture applied to conventional and partial oxy-fuel cement plants

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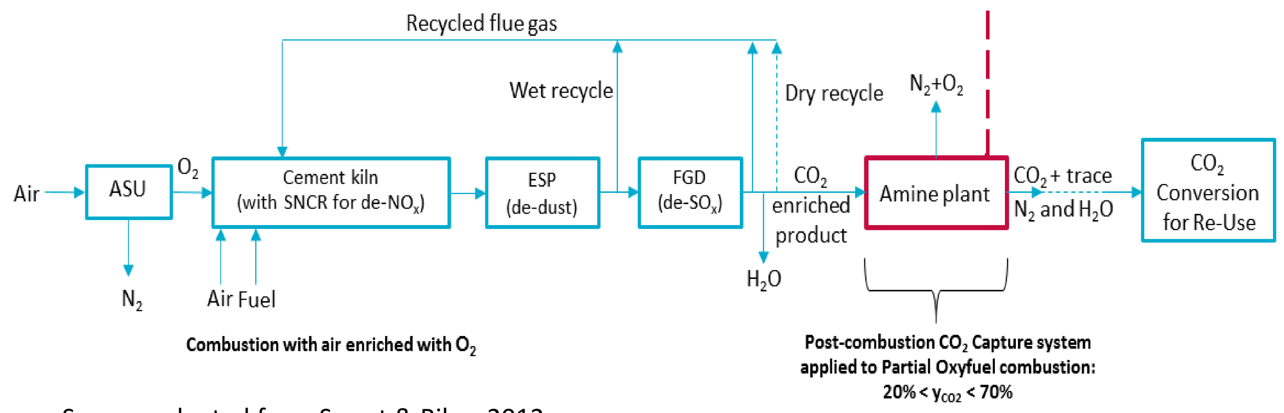
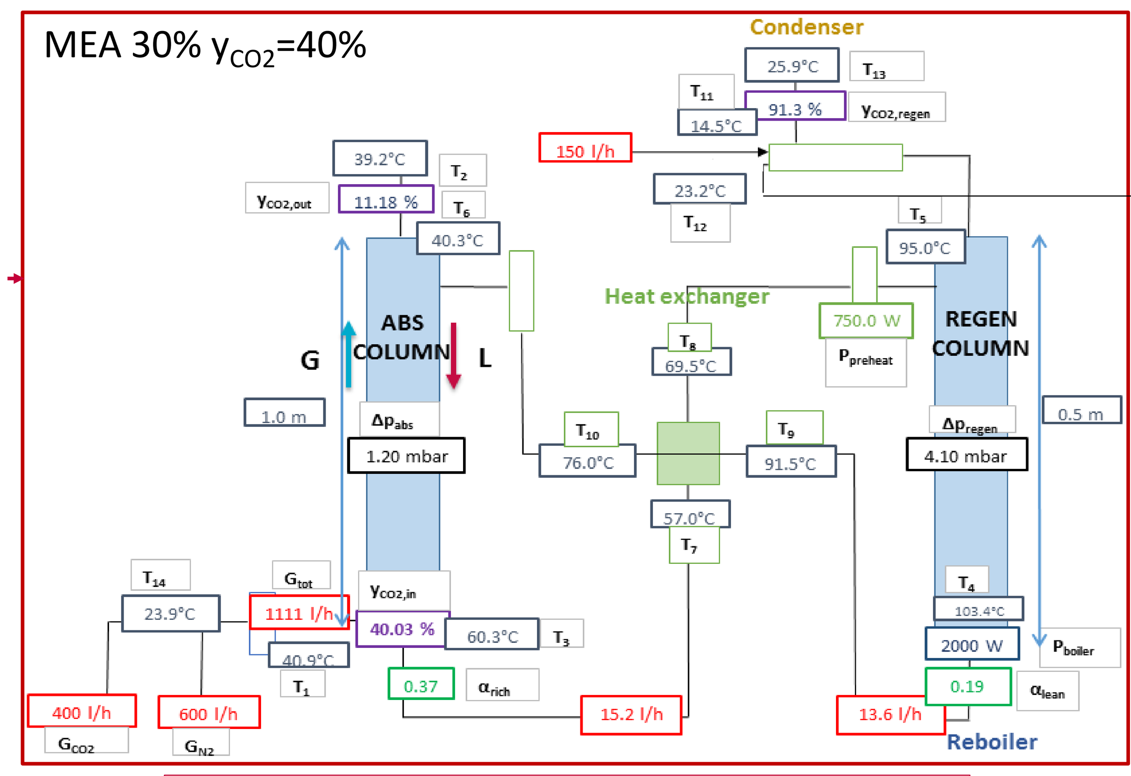
Context of the study: CCU (Carbon Capture and re-Use)

In the context of Carbon Capture Storage (CCS) or Utilization (CCU), this work evaluates the application of the post-combustion CO_2 capture process by absorption-regeneration to cement plant flue gases coming from conventional and partial oxy-fuel kilns. The strategy of the study was to carry out a screening at lab scale (cables-bundle contactor) and then for the best solvents, at micro-pilot scale (absorption-regeneration micro pilot unit) of different amine(s) based solvents, especially to compare their absorption performances in a wide range of CO_2 contents into the gas phase (from 20 to 60 vol.%). Simulations were also conducted with Aspen Hysys[TM] of the application of the CO_2 capture process to highly CO_2-concentrated flue gas in order to estimate the energy savings linked to the partial oxy-fuel conditions.

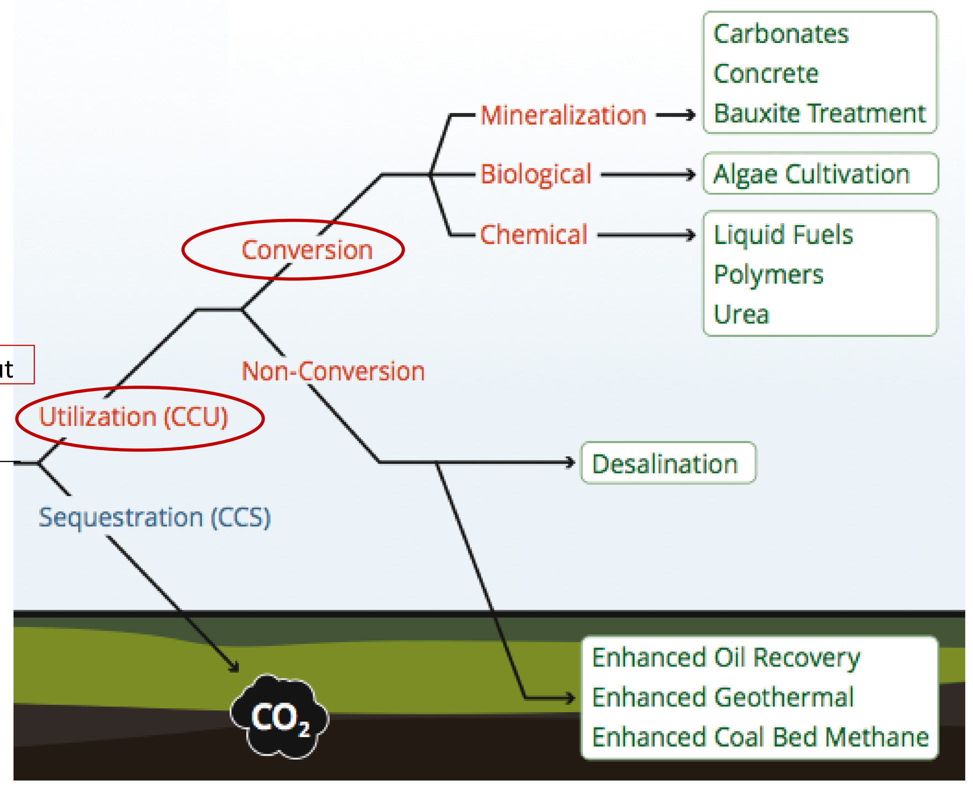


Source: adapted from Smart & Riley, 2012

PARTIAL OXYFUEL COMBUSTION CAPTURE



ABSORPTION-REGENERATION PROCESS



Source: The Pembina Institute with Integrated CO2 Network (ICO2N)

Experiments: Experimental devices, procedures & absorption results

Lab scale: cables-bundle contactor

Cables-bundle contactor:

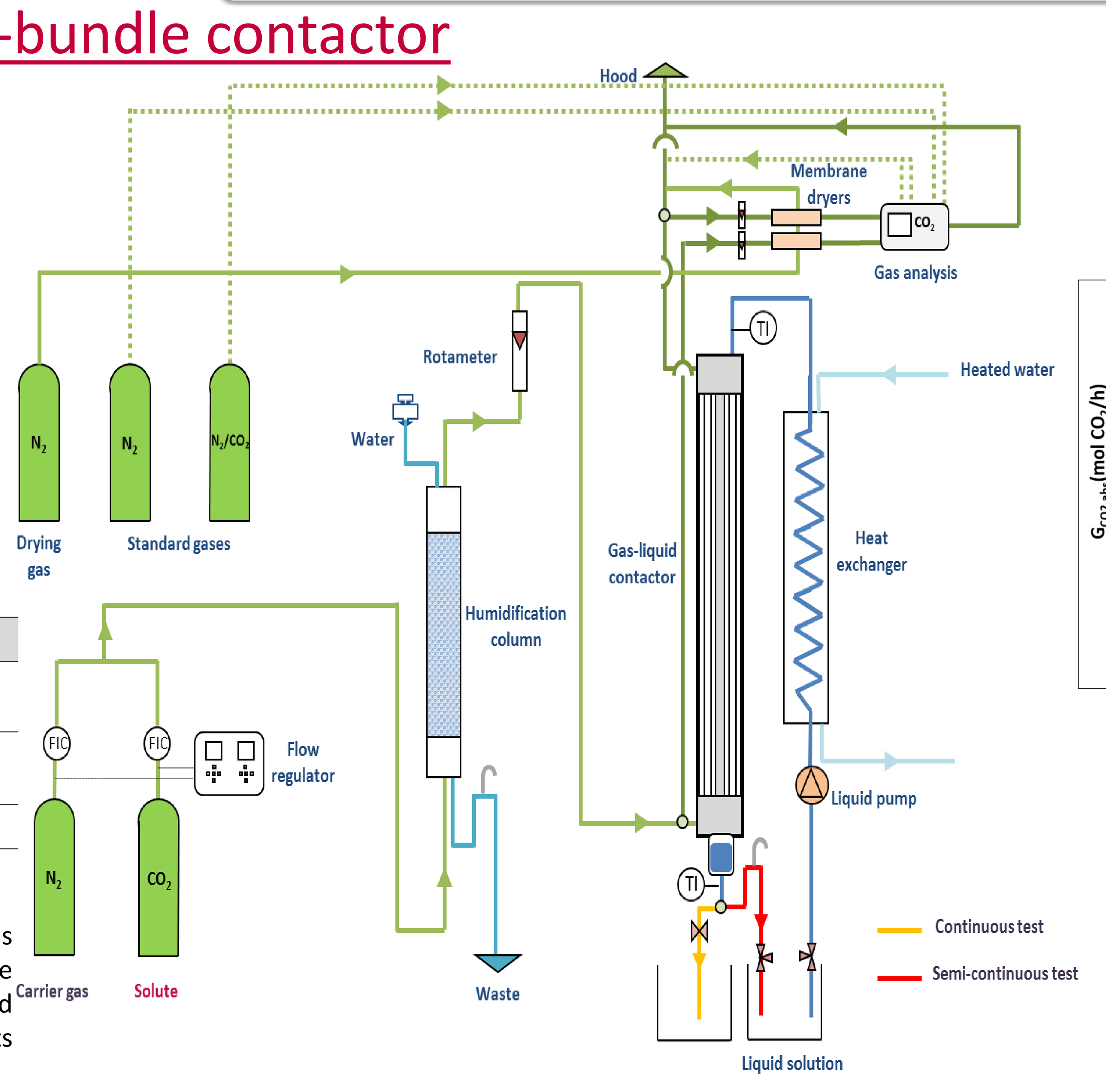
- Ring-shaped column made of a vertical glass tube
- 6 twisted polypropylene yarns of 1.7 mm diameter stretched in parallel.
- Contactor useful height: 0.54 m
- Operating parameters:

Operating conditions of the absorption tests

Operating parameter	Value
Pressure (P) Inlet liquid temperature (T)	101.325 kPa 298.15 K
Liquid flow rate (L) Gas flow rate (G)	$3.08\ 10^{-6}$ m³/s $2.15\ 10^{-4}$ Nm³/s
CO_2 contents ($y_{CO2,in}$)	10 - 60 vol.%

Two types of tests conducted:

- Continuous tests: fresh scrubbing solutions (solutions not CO_2-loaded at the inlet of the contactor) and a gas phase continuously fed in the contactor with varying CO_2 contents ($y_{CO2,in}$ from 10 to 60 vol.%)
- Semi-continuous tests: recirculation of 1.3 10^{-3} m³ of the solution fixing a CO_2 inlet content of 40 vol.% in the gas phase and allowing to follow the temporal evolution of the absorption performances together with a progressive CO_2 loading of the solvent



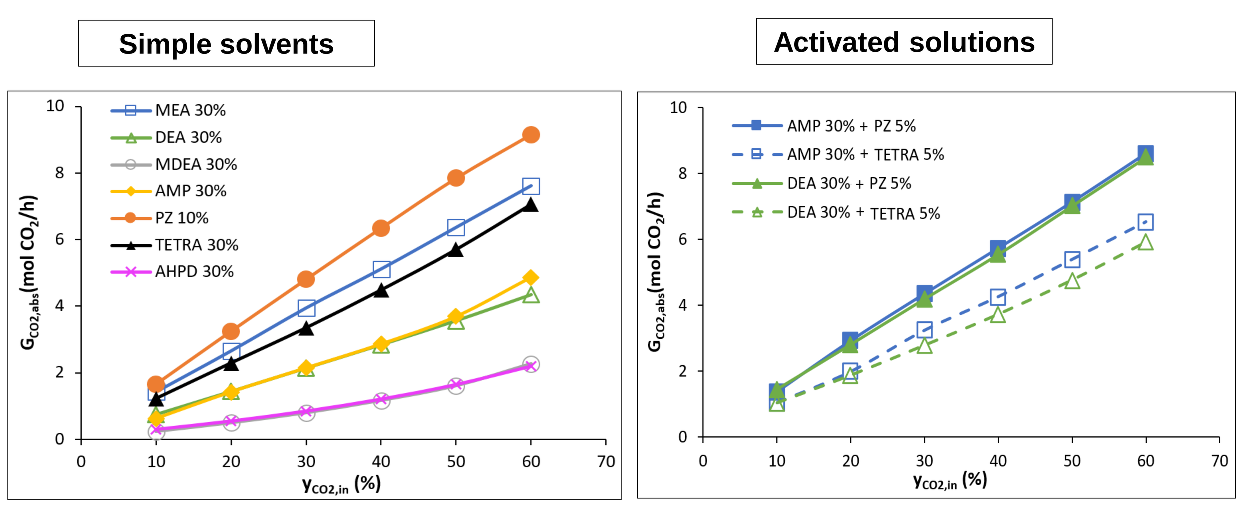
Amines investigated during the absorption tests at lab scale

Amine name	CAS number	Amine type	Abbreviation
Monoethanolamine*	141-43-5	primary alkanolamine	MEA
Diethanolamine*	111-42-2	secondary alkanolamine	DEA
N-methyldiethanolamine	105-59-9	tertiary alkanolamine	MDEA
2-amino-2-methyl-1-propanol	124-68-5	sterically hindered alkanolamine	AMP
2-amino-2-hydroxymethyl-1,3 propanediol	77-86-1	sterically hindered alkanolamine	AHPD
Triethylenetetramine	112-24-3	tetramine	TETRA
Piperazine*	110-85-0	cyclical di-amine	PZ

*Amines investigated also during the absorption-regeneration tests at micro-pilot scale.

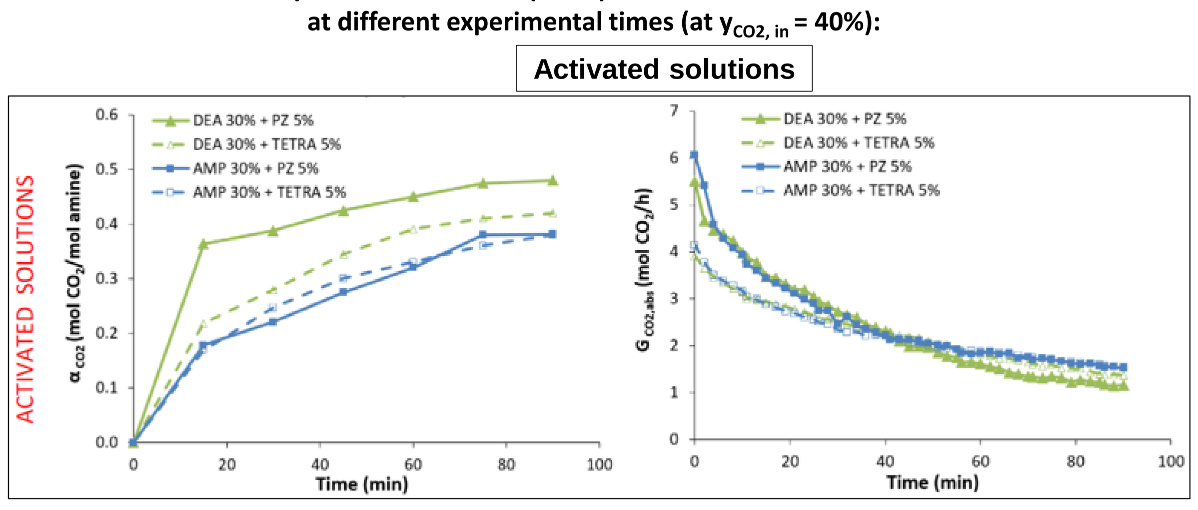
Results of the *continuous* absorption tests:

Comparison of the absorption performances of the solvents at different CO_2 contents into the gas phase (unloaded solutions):



Results of the semi-*continuous* absorption tests:

Comparison of the absorption performances of the solvents at different experimental times (at $y_{CO2,in}$ = 40%):



Analyses conducted and calculated parameters for the cables-bundle contactor and the micro-pilot unit:

- **Gas analyses:** CO_2 (IR)
- **Liquid analyses:** Total Organic Carbon (TOC) analyser: TC, IC, TOC + pH measurements
- The CO_2 loading $\alpha_{CO2}(t)$ [mol CO_2/mol amine] can be determined at every moment of the absorption test:

$$\alpha_{CO2}(t) = \frac{C_{CO2}(t)}{C_{amine}(t=0)}$$

- The absorption efficiency (A (%)) of the solvent is calculated by: $A\ (\%) = \frac{G_{CO2,in} - G_{CO2,out}}{G_{CO2,in}}$
- Based on A(%), the results can be explained in terms of the CO_2 molar absorption flow rate:

$$G_{CO2\ abs}\left(mol\ CO2/h\right) = (A) * y_{CO2,in} * G_{in,\ dyr}$$

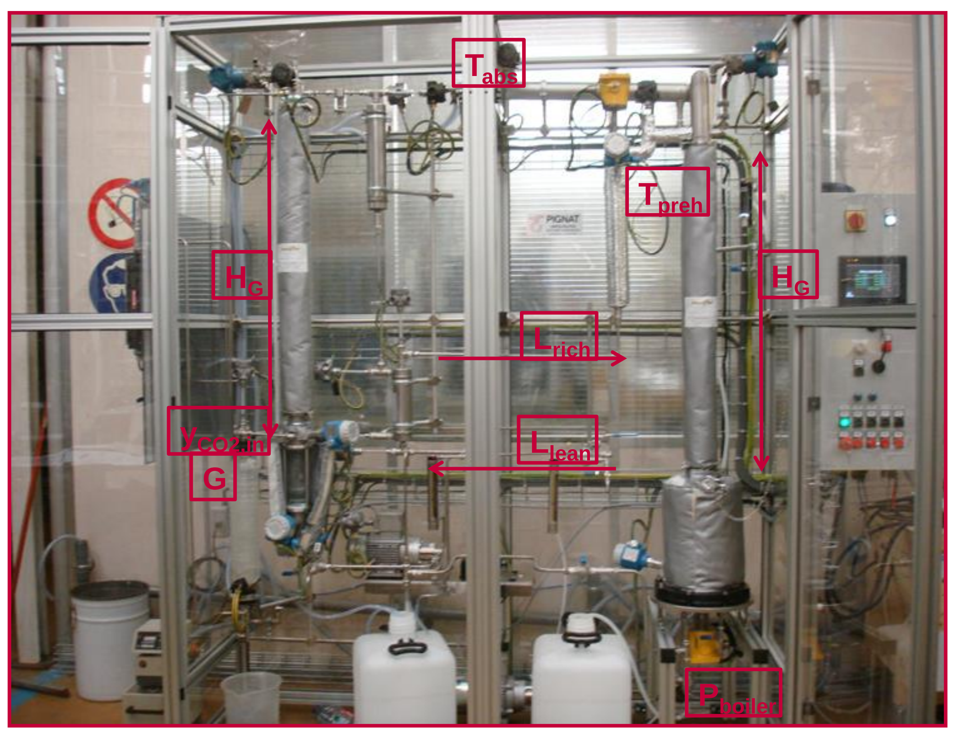
Interpretation of experimental results :

The continuous tests with simple solvents showed that the best absorption performances at both low and high $y_{CO2,in}$ were measured with PZ 10% and MEA 30% ($G_{CO2,abs}$ > 6 mol CO_2/h at $y_{CO2,in}$ = 60 %vol.), the absorption results with TETRA 30% being also clearly higher than with the other solvents (AMP, DEA and AHPD 30%).

The continuous tests with activated solvents showed that both for AMP 30% and DEA 30% solutions, the activation effect is much more significant with PZ 5% than with TETRA 5%.

On the other side, **the semi-continuous tests** revealed that the PZ activated solutions, and especially AMP 30% + PZ 5%, presents good absorption performances at the beginning of the test and also after 90 min with a significant CO_2 loading.

Micro-pilot scale: Absorption-regeneration micro-pilot unit



Micro-pilot Unit (Pignat):

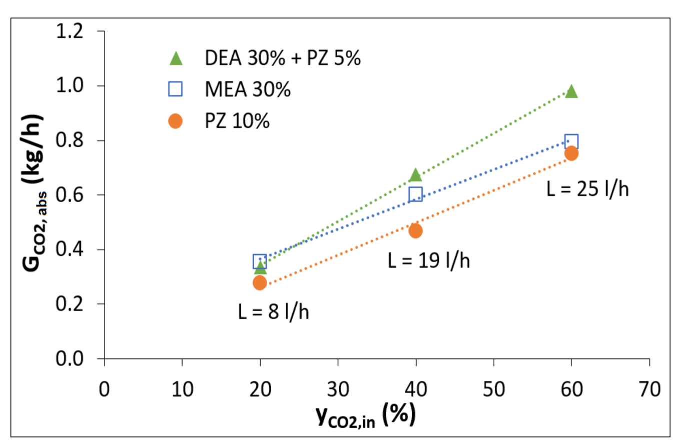
- Two stainless steel columns (height of 1 m, diameter of 56 mm)
  packing height (H_P) of 0.5 m or 1m
  packing type: glass Raschig rings (6x6 mm)
- Experimental procedure: after humidification, the gaseous blend (composed of nitrogen and carbon dioxide) enters the absorption column where a counter-current contact between this gas mixture and the absorption solution is achieved at atmospheric pressure. The CO_2 loaded solution at the outlet of the absorption column is then preheated (maximum heating power of 2 kW) to the regeneration column where, by heating the solution up to its boiling point, the CO_2 is liberated from the solution, regenerating the solvent which is pumped back to the absorption column.
- A total condenser is installed at the top of the regeneration column in order to remove the water vapor produced consequently to the solution heating.
- Gaseous and liquid flow rates are fixed and measured with the use of rotameters and the pressure drops in the two columns are measured with differential pressure transmitters.
- The unit includes different heat exchangers in order to control the solution temperature during the absorption and regeneration phases, including an "internal heat exchanger" positioned between the two columns through which the rich and lean solutions flow counter-currently.

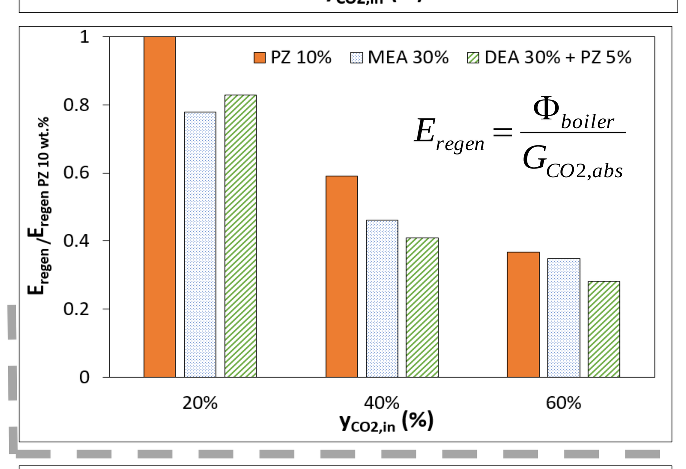
Operating conditions:

Pressure [kPa]	101.325
T_{ABS} [°C]	40
T_{preh} [°C]	95
L_{rich} and L_{lean} [l/h]	7 to 24
G [Nl/h]	960
$H_{P,ABS}$ [m]	1
$H_{P,REG}$ [m]	0.5
P_{boiler} [kW]	2
C_{amine} (max) [wt.%]	35
CO_2 contents ($y_{CO2,in}$) [vol.%]	20 to 60

Results of the micro-pilot absorption tests:

For the three selected solvents, the liquid flow rate was fixed at the beginning of the test leading to a steady absorption efficiency (A) value of around 90%.





$$E_{regen} = \frac{\Phi_{boiler}}{G_{CO2,abs}}$$

Interpretation of the absorption results for the micro-pilot tests:

The effect of increasing $y_{CO2,in}$ on the absorption-regeneration performances in terms of captured CO_2 amount ($G_{CO2,abs}$): when $y_{CO2,in}$ is increased, the same conclusion can be observed for $G_{CO2,abs}$, even if the absorption performances of the three solvents are quite similar at $y_{CO2,in}$ equal to 20% ($G_{CO2,abs}$ around 0.3 kg/h), $G_{CO2,abs}$ of DEA 30% + PZ 5% at $y_{CO2,in}$ of 60% (around 0.98 kg/h) is particularly higher than the one measured with the other solvents at the same $y_{CO2,in}$ (< 0.80 kg/h) presenting better absorption performances at high $y_{CO2,in}$.

The effect of increasing $y_{CO2,in}$ on the absorption-regeneration performances in terms of regeneration energy (E_{regen}): relatively to PZ 10 wt.% ($E_{regen}/E_{regen,\ PZ\ 10\ wt.\%\ at\ yCO2,in\ =\ 20\%}$) which is the solvent leading to the highest E_{regen} value at $y_{CO2,in}$ equal to 20%, increasing $y_{CO2,in}$ leads to a significant decrease of the solvent regeneration energy, especially for DEA 30% + PZ 5% even if the same observation can be done for the three solvents tested in the micro-pilot unit.

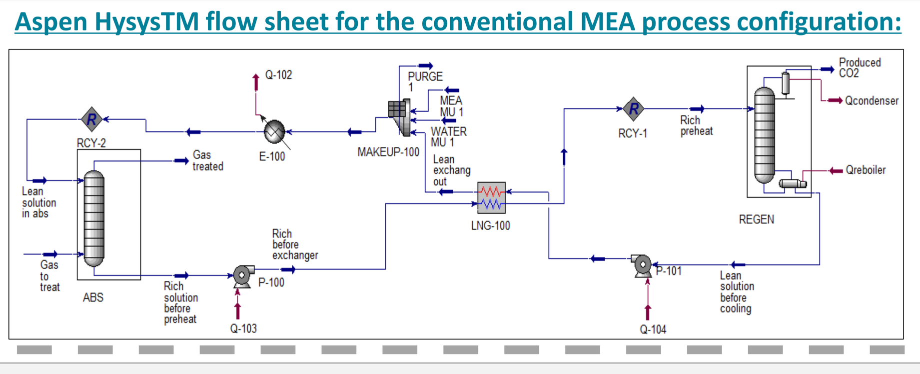
Simulations: Aspen Hysys[TM] simulations of the absorption-regeneration CO_2 capture process

Operating parameters (CASTOR/CESAR pilot unit):

G= 4000 Nm³/h, L= 22 m³/h

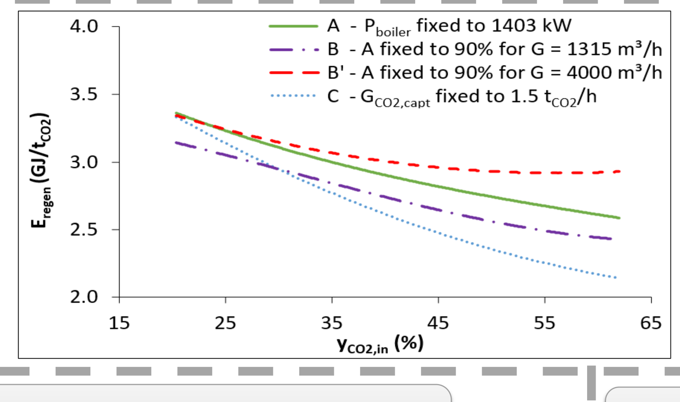
	Absorber	Stripper
Column Diameter [m]	1.1	1.1
Packing height [m]	17 (17 x 1 m)	10 (10 x 1 m)
Packing type	Random packing IMTP 50	Random packing IMTP 50
Inlet liquid temperature [°C]	40	110
Bottom pressure [kPa]	120	200
Linear pressure drop [kPa/m]	0.5	0.5

Aspen HysysTM flow sheet for the conventional MEA process configuration:



Flue gas compositions:

Component (mol. fract.)	Base case (Brevik)	ECRA simulations			
N_2	0.647	0.575	0.488	0.399	0.281
CO_2	0.204	0.310	0.441	0.514	0.620
H_2O	0.062	0.062	0.048	0.056	0.062
O_2	0.086	0.053	0.023	0.031	0.037
CO	$1.33\ 10^{-3}$	-	-	-	-
SO_2	$1.11\ 10^{-4}$	-	-	-	-
NO	$4.74\ 10^{-4}$	-	-	-	-
NO_2	$1.77\ 10^{-6}$	-	-	-	-



Aspen Hysys[TM] simulation results for different $y_{CO2,in}$ values with MEA 30 wt.%:

An increase of $y_{CO2,in}$ leads to a significant decrease of the solvent regeneration energy.

For the most favorable case (C) it can be seen that an increase of $y_{CO2,in}$ from 20% to 44% leads to a **decrease of 26% of the MEA 30 wt.% regeneration energy (from 3.36 to 2.48 GJ/tCO2).**

Conclusions & prospects:

- In this study, a screening at lab scale (cables-bundle contactor) of different amine(s) based solvents is realized to compare their absorption performances in highly CO_2-concentrated flue gases.
- Thanks to the experiments in a micro-pilot unit (aiming an absorption ratio of around 90% in this case) it was shown that increasing the CO_2 content in the gas to treat allows a significant decrease of the solvent regeneration energy.
- Besides, simulations with MEA 30 wt.% (fixing a $G_{CO2,abs}$ = 1.5 t_{CO2}/h in this case) revealed that increasing $y_{CO2,in}$ from 20% to 44% leads to a decrease of 26% of the regeneration energy. This decrease was equal to 37% when $y_{CO2,in}$ is increased up to 60%.
- The application of partial oxy-fuel combustion in a cement plant seems a good option that will be more deeply investigated, especially to take into account the oxygen production costs associated to each $y_{CO2,in}$ value.
- As future works, the screening of solvents (both separate and combined screening experiments) will be continued with other simple and blended solutions with the associated simulations of the micro-pilot unit.

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