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Experiments and simulation of the post-combustion CO_2 capture absorption-regeneration process applied to cement flue gases with high CO_2 contents

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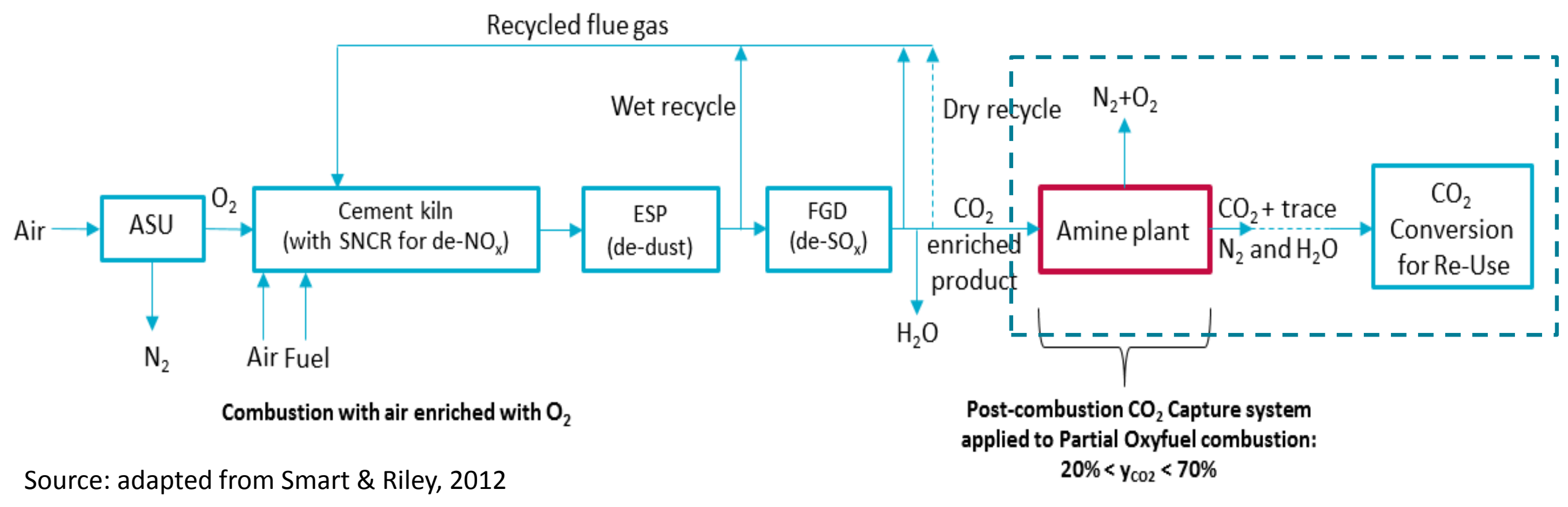
Context of the study: CCU (Carbon Capture and re-Use)

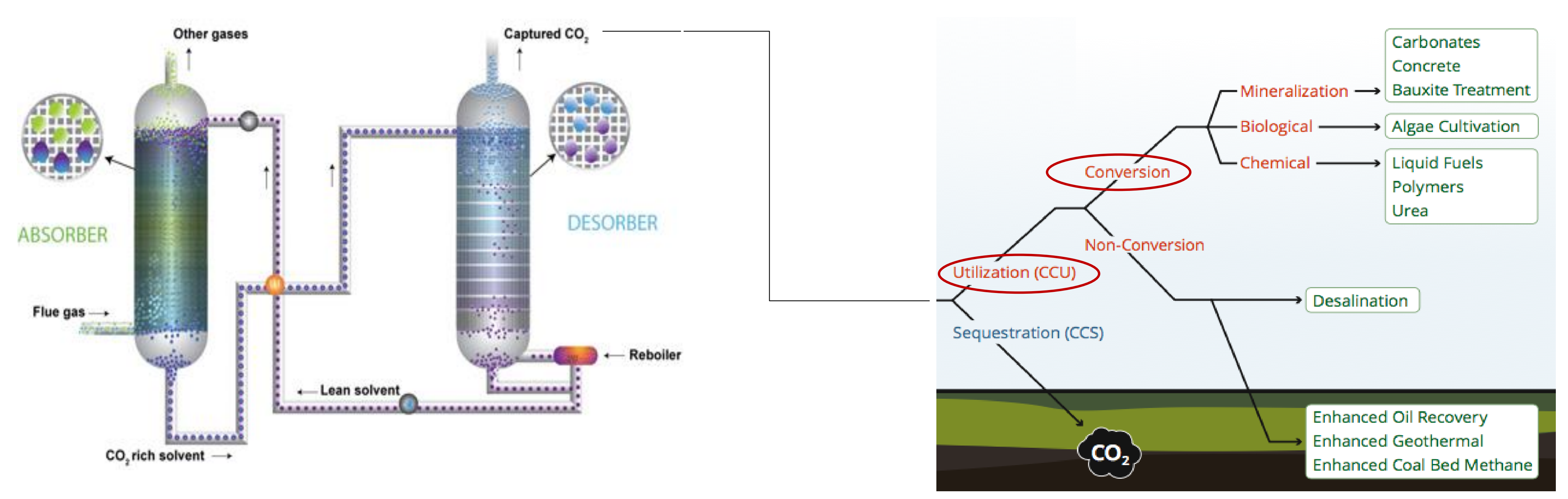
In the context of Carbon Capture Storage (CCS) or Utilization (CCU), this work evaluates the application of the post-combustion CO_2 capture process by absorption-regeneration to cement plant flue gases coming from conventional and partial oxy-fuel kilns. The strategy of the study was to carry out a **experimental 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™ 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



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

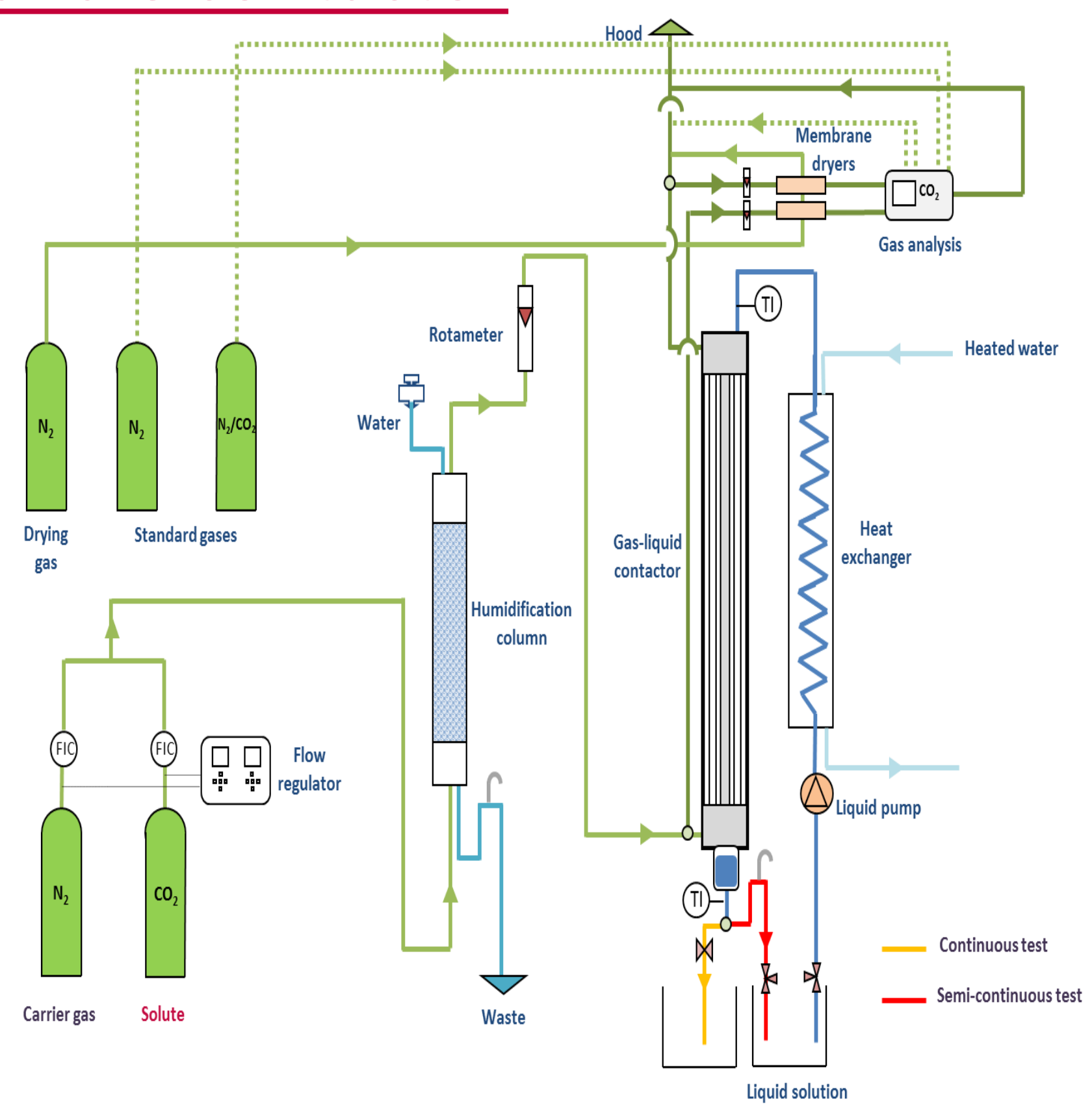
ABSORPTION-REGENERATION PROCESS

Experiments: Experimental devices, procedures & absorption results

Lab scale: cables-bundle contactor

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:

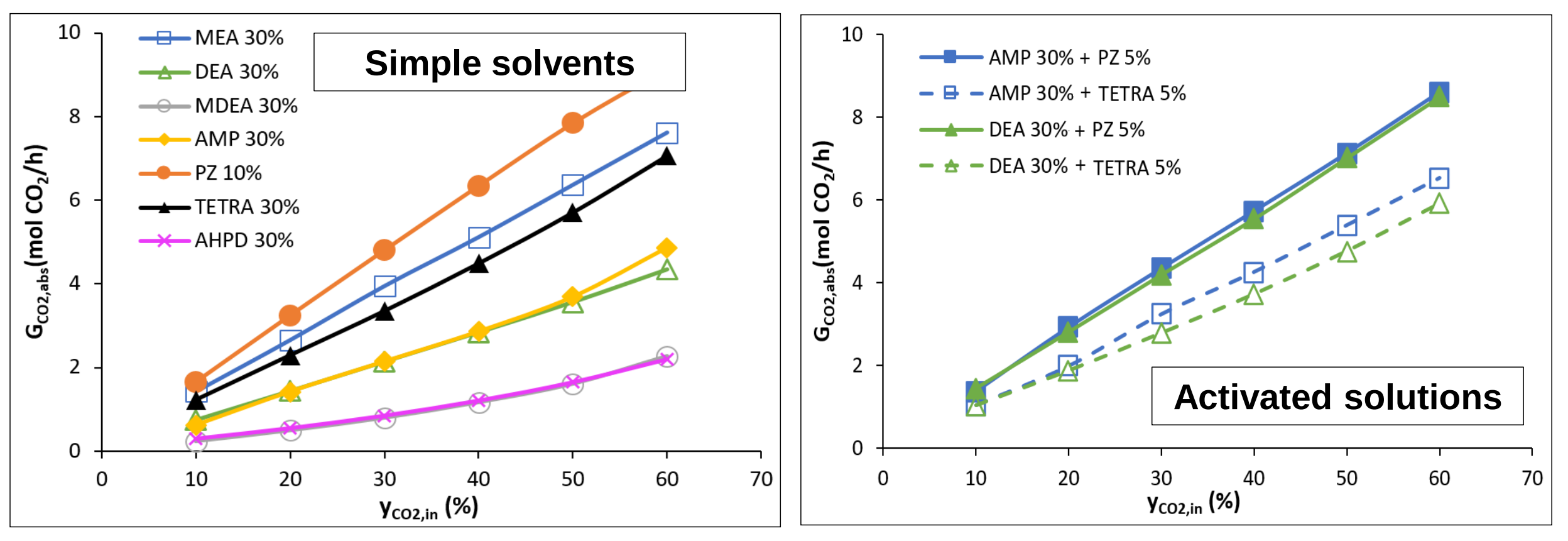
- ☐ Continuous tests: fresh scrubbing solutions (not CO_2-loaded solutions at the inlet of the contactor) and a gas phase continuously fed in the contactor with varying CO_2 contents ($y_{CO2,in}$ from 10 to 60 vol.%).
- ☐ Semi-continuous tests: recirculation of $1.3\ 10^{-3}$ m³ of the solution fixing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

Amine	Category	Kinetic constant at 25°C k_2 (m³/kmol.s)	Reference
PZ	Cyclical diamine	76000	(Derks et al., 2006)
MMEA	Secondary amine	7940	(Patil et al., 2012)
MEA	Primary amine	5938	(Versteeg & Swaaij, 1988)
DEA	Secondary amine	3240	(Versteeg et al., 1990)
TERA	Non-cyclical tetramine	1252	(Amann and Bouallou, 2009)
AMP	Sterically hindered amine	810	(Xu et al., 1998)
AHPD	Sterically hindered amine	285	(Bougie and Iliuta, 2009)
MDEA	Tertiary amine	12	(Versteeg et al., 1996)

Different types of amines
CO_2-amines kinetic constants

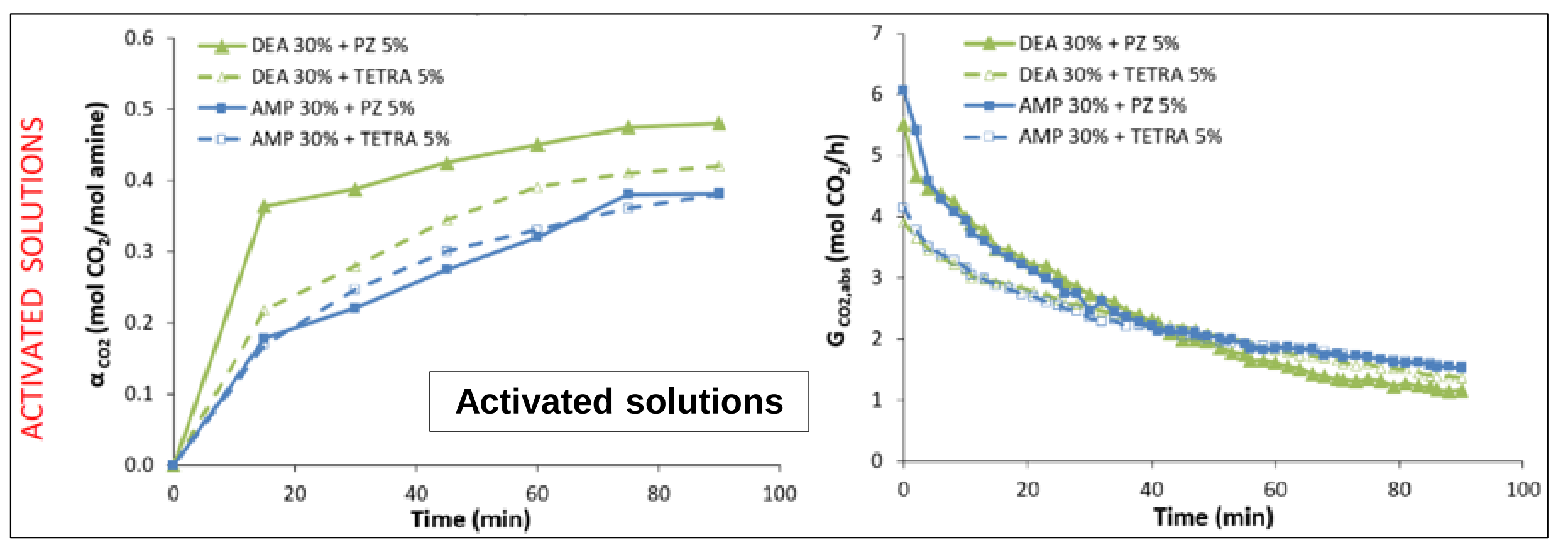
Results of the *continuous* absorption tests:

Comparison of the absorption performances of the solvents at different CO_2 contents into the gas phase



Results of the semi-*continuous* absorption tests:

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



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

- ☐ **Gas analyses:** CO_2 (IR)
  The absorption efficiency A (%) of the solvent is calculated by:
  $$A\ (\%) = \frac{G_{CO2,in} - G_{CO2,out}}{G_{CO2,in}} * 100$$
  The results can be explained in terms of the CO_2 molar absorption flow rate:
  $$G_{CO2\ abs}\left(\frac{mol\ CO2}{h}\right) = A * y_{CO2,in} * G_{in,\ dyr}$$
- ☐ **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:
  $$\alpha_{CO2}(t) = \frac{C_{CO2}(t)}{C_{amine}(t=0)}$$

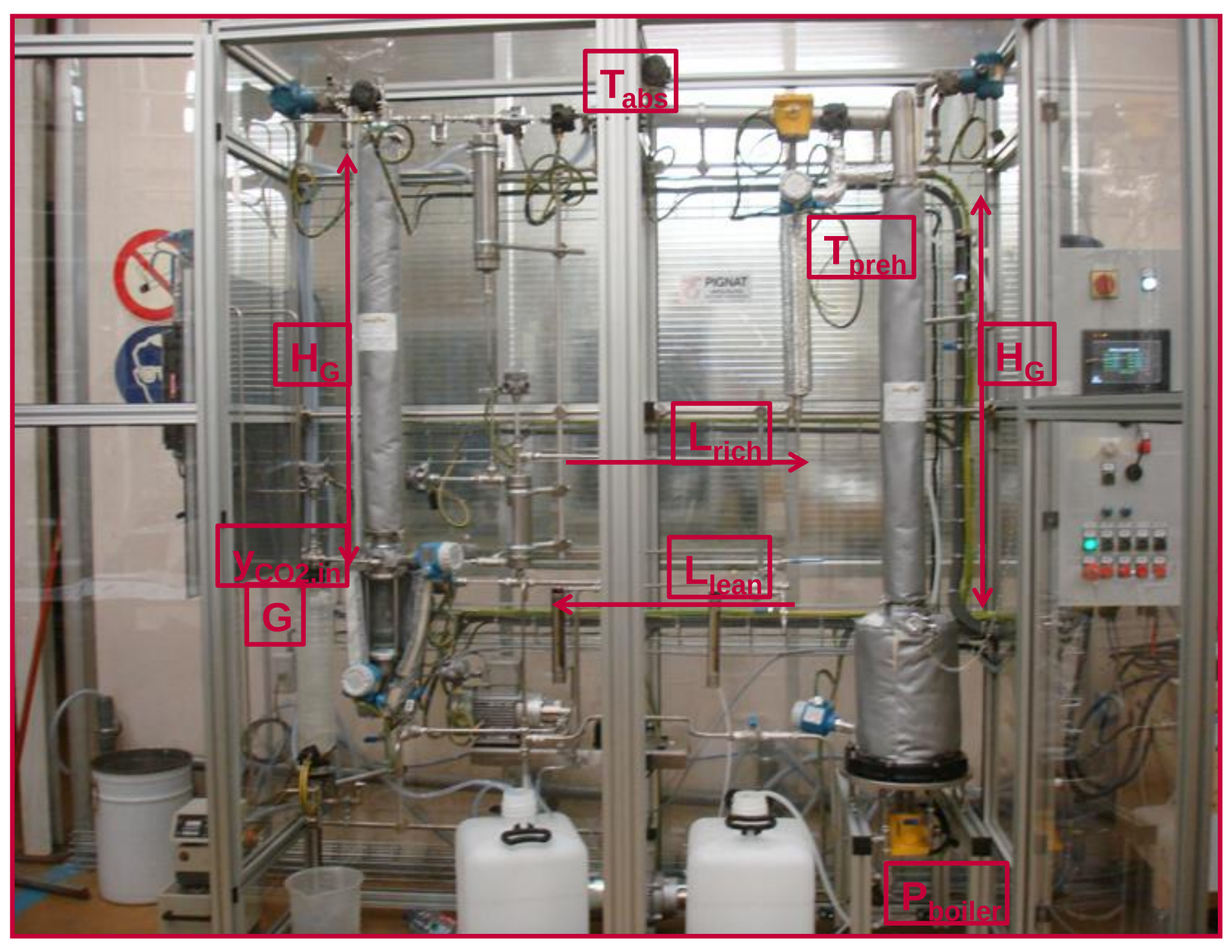
Interpretation of experimental results :

The continuous tests with simple solvents: best absorption performances for PZ 10% and MEA 30%, the absorption results with TETRA 30% being also clearly higher than with the other solvents (AMP, DEA and AHPD 30%) – results linked to k_2

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

The semi-continuous tests: 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 *(Pignat)*



Micro-pilot unit experimental procedure

After humidification, the gaseous blend (N_2 + CO_2) enters the absorption column where a counter-current contact between this gas mixture and the absorption solution is achieved.

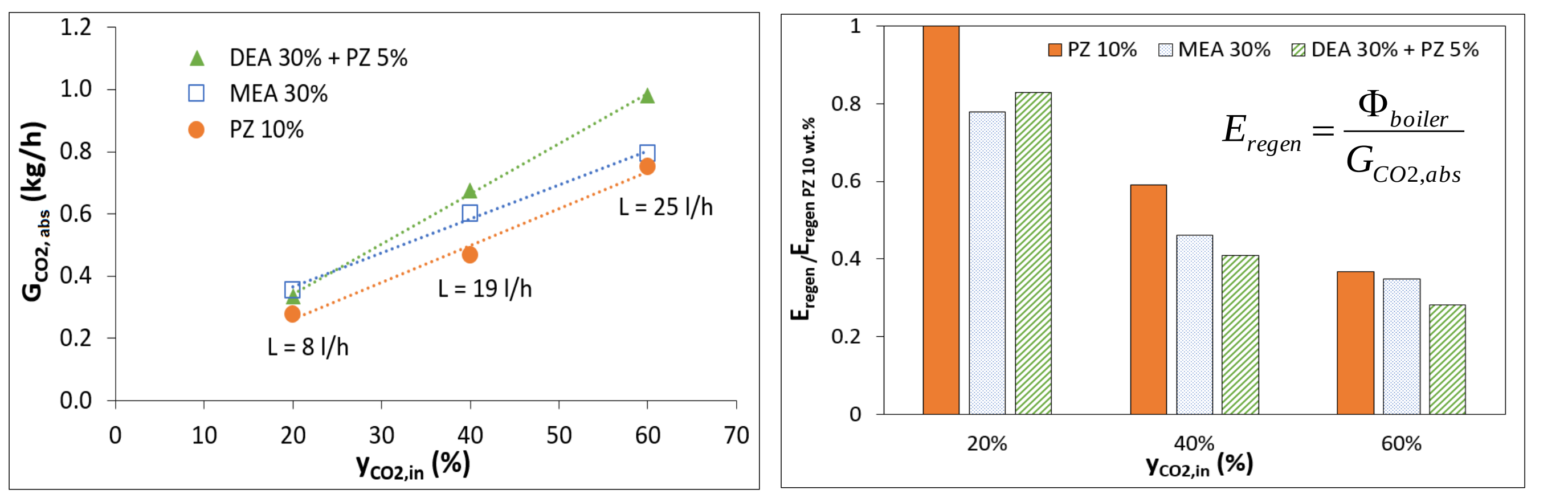
The CO_2 loaded solution at the outlet of the absorption column is then preheated ("internal heat exchanger" positioned between the two columns through which the rich and lean solutions flow counter-currently) to the regeneration column where, by heating the solution up to its boiling point (maximum heating power of 2 kW), the CO_2 is liberated from the solution, regenerating the solvent which is pumped back to the absorption column.

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%.



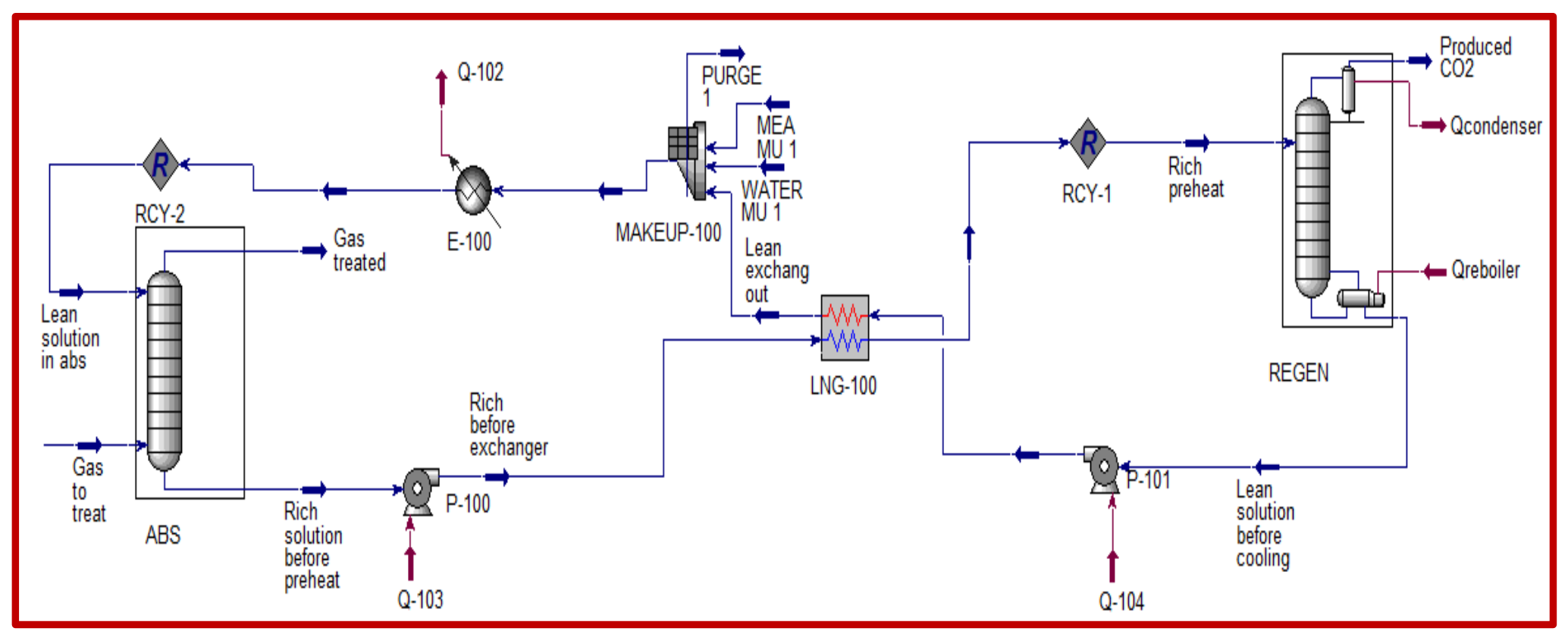
Interpretation of the absorption results for the micro-pilot tests:

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% , $G_{CO2,abs}$ of DEA 30% + PZ 5% at $y_{CO2,in}$ of 60% is higher than the one measured with the other solvents at the same $y_{CO2,in}$ (better absorption performances).

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%.

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

Aspen Hysys™ flow sheet for the conventional MEA 30% process configuration:

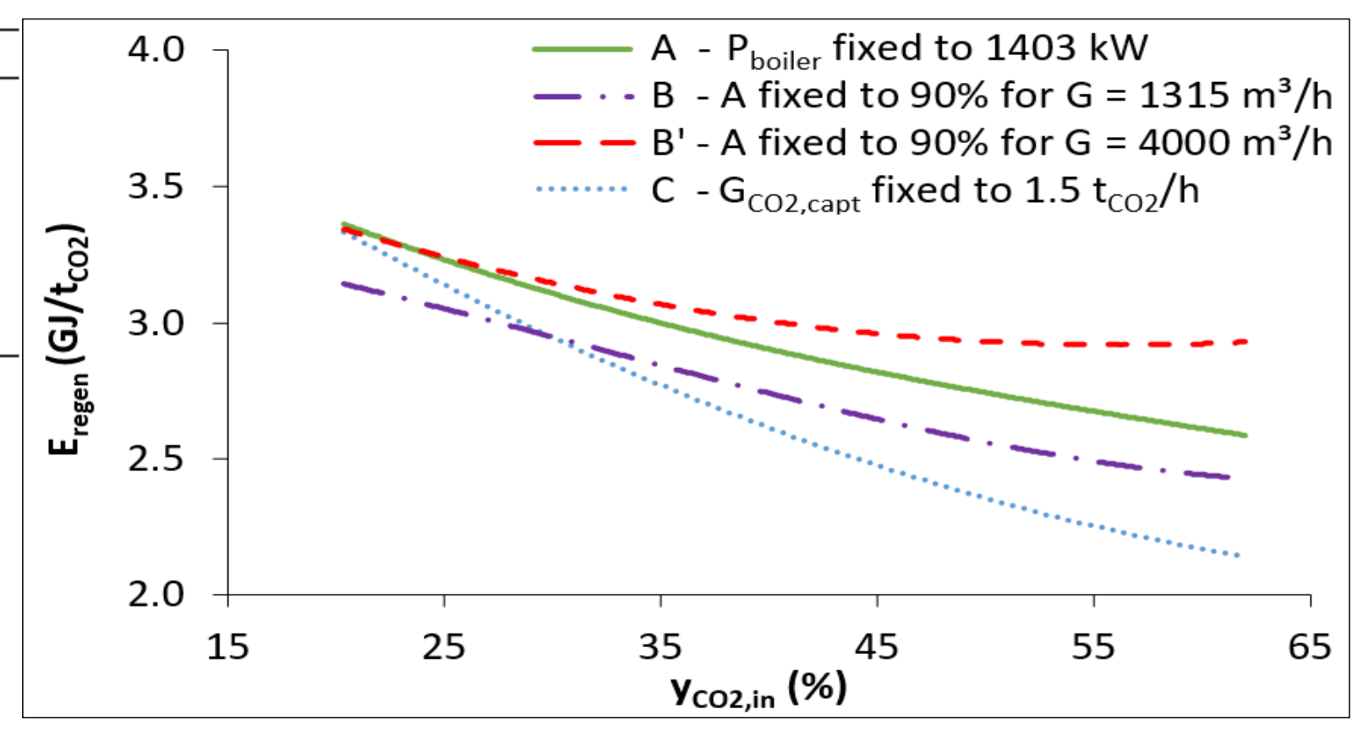


Operating parameters (CASTOR/CESAR pilot unit):
G= 4000 Nm³/h, L= 22 m³/h

	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

Flue gas composition:

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



Aspen Hysys™ 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/t_{CO2}).**

Conclusions & prospects

Screening at lab scale of different amine solvents in highly CO_2-concentrated flue gases: comparison of absorption performances. ✓
Experiments in micro-pilot unit: increasing the CO_2 content in the gas to treat allows a significant decrease of the solvent regeneration energy. ✓
Simulations with MEA 30 wt.%: increasing $y_{CO2,in}$ from 20% to 44% leads to a decrease of 26% of the regeneration energy (37% when $y_{CO2,in}$ is increased up to 60%). ✓
Application of partial oxy-fuel combustion in a cement plant= good option that will be more deeply investigated (considering the oxygen production costs). ✓
Future works: screening of solvents (both separate and combined screening experiments) with other simple and blended solutions with the associated simulations of the micro-pilot unit.

Acknowledgements

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