Post-combustion CO_2 capture process applied to flue gases with high CO_2 contents: micro-pilot experiments and simulations

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***Abstract*—In the context of Carbon Capture and Utilization (CCU), the present article focuses on the investigation, for the cement industry of the post-combustion CO_2 capture using amine solvents applied to the conventional combustion and to an innovative type of combustion called O_2-enriched air combustion.**

After a previous screening, the solvents selected were tested at micro-pilot scale in an absorption-regeneration device in order to determine their absorption performances and respective regeneration energies.

Simple and activated solvents were tested in such conditions, such as primary and secondary alkanolamines and compared to the conventional solvent Monoethanolamine 30 wt.% (benchmark), both in conventional and high CO_2 contents conditions.

As the experimental data, Aspen Hysys™ simulations of the micro-pilot unit proved that the solvents regeneration energies decrease for an increased CO_2 concentration in the gas to treat, which is the main advantage of the post-combustion CO_2 capture applied to partial oxy-fuel combustion.

***Index Terms*-- Cement industry; partial oxy-fuel combustion; post-combustion CO_2 capture; micro-pilot unit; simulations.**

I. INTRODUCTION

Reduction of greenhouse gases and especially CO_2 emissions is one of the major problem nowadays. CO_2 emitted from the cement industry represents 5% of the global annual emissions and 30% of the annual industrial emissions [1].

The application of Carbon Capture Storage (CCS) or Utilization (CCU) to power plants flue gases ($5\% < y_{CO2} < 15\%$) has already been considered in many studies. In this context, the objective of this work is to test the applicability of absorption in amine solvents to CO_2-rich flue gases deriving from an O_2-enriched air combustion from the cement industry. This kind of technique will produce a more CO_2-concentrated flue gas ($30\% < y_{CO2} < 60\%$) at the outlet of the cement industry compared to a conventional combustion ($20\% < y_{CO2} < 30\%$). Indeed, thanks to a more CO_2-concentrated flue gas and the choice of an adequate solvent, this process will assure a decrease of the regeneration energy [2]-[4] in the amine plant (compared to the conventional post-combustion case) as well as the reduction of the cost of O_2 production (O_2-enriched air) in the Air Separation Unit (ASU) compared to a total oxyfuel combustion (requiring pure O_2).

In this paper, the absorption performances and energy requirements of different amine solvents for conventional and partial oxy-fuel cement plant flue gases (y_{CO2} between 20% and 60%) are evaluated at micro-pilot scale. Moreover, this study will expose the concordant results of the Aspen Hysys™ simulation of this absorption-regeneration micro-pilot device.

II. MATERIALS AND METHODS

A. *Solvents tested and methodology*

As a previous step, a screening of solvents has been realized to select the best ones based on their absorption performances [5]. Tab. 1 enumerates the different types of amine solvents, mixed with water, that were selected for the comparison at micro-pilot scale by means of their absorption performances and regeneration energies.

TABLE 1. TYPES OF AMINE SOLVENTS TESTED

Amine name	Amine type	Abbreviation
Monoethanolamine	Primary alkanolamine	MEA
2-amino-2-methyl-1-propanol	Sterically hindered alkanolamine	AMP
Piperazine	Cyclical di-amine	PZ

In order to enhance the absorption performances of the amines, different amine blends (activated amines) can be advantageous by combining interesting properties, i.e. good reaction kinetics of primary or secondary amines with the high absorption capacity of tertiary or sterically hindered amines. Activated amines are obtained by blending an amine with an activator. The most commonly used are Piperazine (PZ) and Triethylenetetramine (TETRA). PZ, a cyclical diamine, was here studied.

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Besides, simulations of the micro-pilot unit were conducted for the reference solvent MEA 30 wt.% with Aspen Hysys[TM] V8.8 software and for various y_{CO2} values.

B. Description of the micro-pilot unit

The absorption-regeneration micro-pilot unit includes two columns (respectively absorption and regeneration columns) connected via an internal heat exchanger through which the rich and lean solutions flow counter-currently. After humidification, the gaseous blend (composed of nitrogen and carbon dioxide) enters continuously the absorption column contacting counter-currently the absorption solution (fed initially in the system), the process taking place at atmospheric pressure. The CO_2 loaded solution at the outlet of the absorption column is then pumped through a preheater (maximum heating power of 1 kW) to the regeneration column where the CO_2 is recuperated at the top of the column by heating the solution up to its boiling point and the consequently regenerated solvent is pumped back to the absorption column. The water vapor produced by heating the solution is removed by a total condenser installed at the top of the regeneration column.

The main operating parameters are summarized in Tab. 2.

TABLE 2. OPERATING CONDITIONS OF THE MICRO-PILOT UNIT ABSORPTION-REGENERATION TESTS

Pressure (kPa])	101.325
T_{ABS} (°C) (inlet abs. column)	40
T_{preh} (°C) (inlet regen. column)	95
L_{rich} and L_{lean} (l/h)	7 to 19
G= Gas flow rate dry / wet (l/h)	1030 / 1110
Packing type	Glass Raschig rings (6x6 mm)
Column packing heights (m) Abs. column / regen. column	1 / 0.5
Columns diameter (mm)	56
P_{boiler} (kW)	2
C_{amine} (max) (wt.%)	35
CO_2 contents ($y_{CO2,in}$) (vol.%)	20 to 60

Like represented in the micro-pilot device P.I.D. in Fig. 1, the unit is instrumented and completely automated in order to obtain a temporal data acquisition from all the sensors (temperature, pressure, etc.) as well as from gas analyzers and from regulators (temperatures T_{ABS} and T_{preh} at the inlet of the columns (through complementary heat exchangers), liquid level in the sump of the absorption column and regeneration heat power).

C. Determination of the absorption ratio, regeneration energy and CO_2 loading of the different solvents

Thanks to temporal acquisitions from gas analyzers of the micro-pilot unit and to regular liquid samplings, gas phase analyses and liquid phase analyses were conducted for each amine solvent and for each CO_2 concentration in the gas to treat. The CO_2 absorption ratio, the regeneration energy of the solvent and the CO_2 loading of the solvent are quantified as follows.

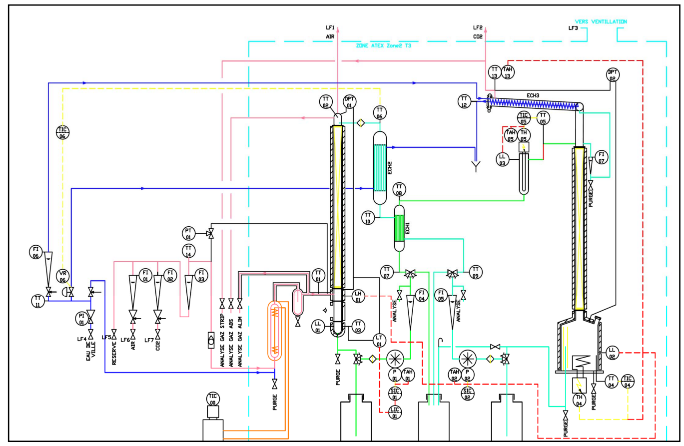


Figure 1. P.I.D. of the micro-pilot unit

- Gas phase analyses

Online CO_2 gaseous analyses at the inlet and the outlet of the absorption column (extracted and dried flow rate of 70 l/h) are performed by an infrared gas analyzer (Emerson X-STREAM X2GP) to give direct access to the temporal evolution of the absorption efficiency (or absorption ratio):

$$A=\frac{G_{CO2,abs}}{G_{CO2,in}}=\frac{G_{CO2,in}-G_{CO2,out}}{G_{CO2,in}} \quad (1)$$

where $G_{CO2,in}$ and $y_{CO2,in}$ are the CO_2 flow rate and the CO_2 volume (or molar) fraction respectively in the gas phase at the inlet of the contactor, $G_{CO2,out}$ and $y_{CO2,out}$ being equivalent parameters at the outlet of the contactor. The difference between $G_{CO2,in}$ and $G_{CO2,out}$ is equal to the amount of CO_2 captured ($G_{CO2,abs}$) in the absorption column and it corresponds to the CO_2 flow released at the outlet of the regeneration column where a CO_2 gaseous analysis is also performed in order to check the purity of the rich CO_2 gaseous flow production.

It can be easily demonstrated that:

$$A=\frac{y_{CO2,in}-y_{CO2,out}}{y_{CO2,in}(1-y_{CO2,out})} \quad (2)$$

The regeneration energy (E_{regen}) (GJ/t_{CO2}) is also calculated in order to characterize and compare the solvents regeneration performances:

$$E_{regen}=\frac{\Phi_{boiler}}{G_{CO2,abs}} \quad (3)$$

where Φ_{boiler} is the duty provided for regeneration taking account of the thermal losses of the regeneration column (measured and equal to ± 15% of P_{boiler})

- Liquid phase analyses

Liquid samplings are extracted in order to perform offline liquid analyses by quantifying the pH and CO_2 loading of the solution. The CO_2 loading representing the quantity of CO_2

that has been absorbed by a mole of amine is quantified and α_{CO2} (t) (mol CO_2/mol amine) can be determined at every moment of the absorption test:

$$\alpha_{CO2}(t) = \frac{C_{CO2}(t)}{C_{amine}(t=0)} \qquad (4)$$

where C_{CO2} (t) is the amount of CO_2 present in the solution at the time (t) of the absorption test, measured by the Total Organic Carbon (TOC), and C_{amine} (t=0) is the concentration of the unloaded fresh amine at the beginning of the test.

III. Experimental results of the micro-pilot unit

Thanks to gas phase analyses and liquid phase analyses, for each amine solvent and the corresponding CO_2 content in the gas to treat, temporal evolutions of the CO_2 contents in the gas phase and the solvent's pH and CO_2 loading could be drawn, as represented respectively in Fig. 2 and Fig. 3 for the blend AMP 30% + PZ 5% and for $y_{CO2,in}$ equal to 20%.

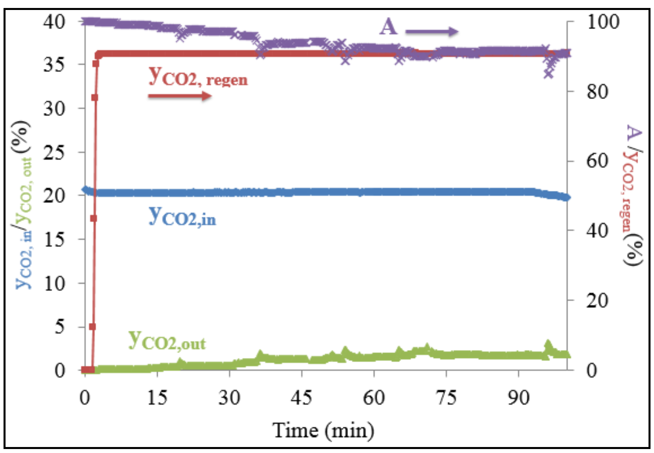


Figure 2. Temporal evolutions of $y_{CO2,in}$, $y_{CO2,out}$, $y_{CO2,regen}$ and A for AMP 30% + PZ 5% micro-pilot tests at $y_{CO2,in}$ = 20%

For a constant value of $y_{CO2,in}$ a regime is reached after 80 min when $y_{CO2,out}$ and A stabilize. The production of a rich CO_2 flow during regeneration ($y_{CO2,regen}$) appearing in Fig. 2 is also checked.

Fig. 3 shows the parallel and progressive CO_2 loading increase linked to a decrease of the pH of the solution, due to the acidity of the solubilized carbon dioxide.

It also illustrates CO_2 loadings of rich and lean solutions, which confirms the regeneration of the solvent.

The operating parameters (solvent, $y_{CO2,in}$, volumic liquid flow rates) taken for our different absorption-regeneration tests are the ones described in Tab. 3.

The main results of the micro-pilot unit tests with simple (MEA, PZ) and activated (AMP + PZ) solvents are shown in Tab. 3, Fig. 4 and Fig. 5.

The basis of our comparison between the different solvents is equal values of the liquid flow rate (L_{lean}) imposed at the different $y_{CO2,in}$.

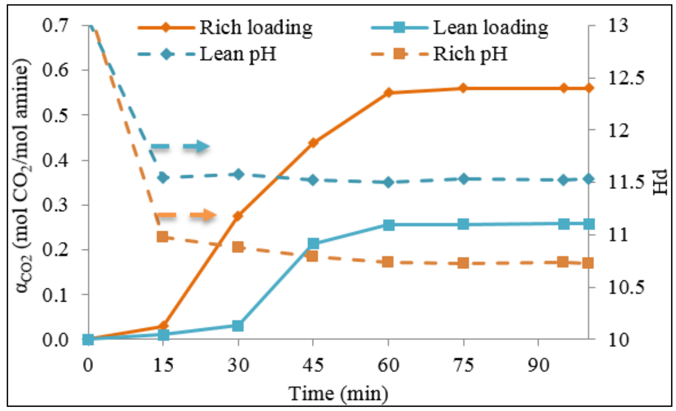


Figure 3. Temporal evolutions of $\alpha_{CO2,rich}$, pH_{rich} and $\alpha_{CO2,lean}$, pH_{lean} for AMP 30% + PZ 5% micro-pilot tests at $y_{CO2,in}$ = 20%

Table 3: Main results of the absorption-regeneration test
Note: Values of α given in mol CO_2/mol amine

Solvents	$y_{CO2, in}$ (%)	L_{lean} (L/h)	L_{rich} (L/h)	$y_{CO2,regen}$ (%)	α_{rich}	α_{lean}
MEA 30%	20	7.76	9.5	90.7	0.37	0.12
	30	10.68	12.35	90.6	0.4	0.23
	40	13.59	15.2	91.3	0.4	0.22
	50	15.53	17.1	91.28	0.33	0.15
	60	18.44	19.95	92.15	0.4	0.23
PZ 10%	20	7.76	9.5	90.33	0.643	0.126
	40	13.59	15.2	92.46	1.2	0.731
	60	18.44	19.95	92.7	0.994	0.412
AMP 30% + PZ 5%	20	7.76	9.5	91.4	0.518	0.255
	40	13.59	15.2	90.12	0.493	0.263
	60	18.44	19.95	90.72	0.392	0.179

It has to be noted that since MEA 30% is the reference solvent, complementary absorption-regeneration tests were conducted for this solvent at $y_{CO2,in}$ = 30% and $y_{CO2,in}$= 50% as shown in Fig 4. and Fig 5.

Fig. 4 represents for the different amine solvents and for $y_{CO2,in}$ between 20% and 60%, the absorption ratios calculated from the gas phase analyses at micro-pilot scale. Interesting performances were shown in both cases for PZ 10% and the activated solution AMP 30% + PZ 5% compared to the reference solvent MEA 30 wt.%.

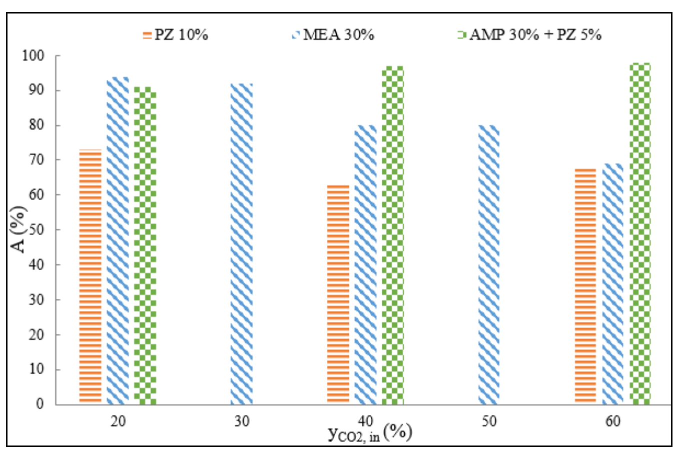
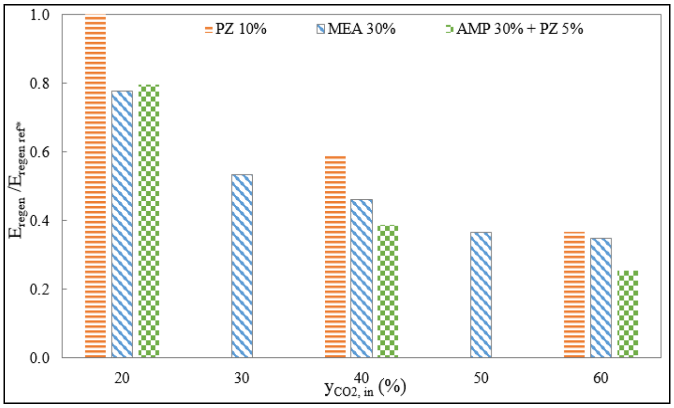


Figure 4. Absorption ratios of the solvents tested at micro-pilot scale

Fig. 5 represents the evolution of the regeneration energies of the solvents tested relatively to PZ 10% at $y_{CO2,in}$=20%, which is the solvent requiring the highest regeneration energy.



ref : PZ 10% at $y_{CO2,in}$=20%

Figure 5: Evolution of the regeneration energies for the different solvents tested

The effect of the CO_2 content in the gas to treat on the energy of regeneration of the solvents is clearly shown in Fig.5: when increasing $y_{CO2,in}$, the regeneration energy decreases. Besides, we can see clearly the interest of the activated amine solution AMP 30% + PZ 5%, which presents the highest absorption ratios (Fig. 4) and the lowest regeneration energies (Fig. 5) at micro-pilot scale.

IV. SIMULATION RESULTS OF THE MICRO-PILOT UNIT

The micro-pilot absorption-regeneration unit has been simulated in Aspen Hysys™ in order to compare the regeneration energies obtained during the experimental tests with the values obtained with the modelling.

The solvent tested in this case is the MEA 30 wt.% which is commonly taken as a reference for the absorption-regeneration tests.

The modeling was developed in Aspen Hysys™ V.8.8 software using the Acid Gas Package and the "Efficiency calculation mode". The package includes the physicochemical properties of acid gases, water and amines, and it takes into account thermodynamic [6] and rate-based calculation models. More specifically, Electrolyte Non-Random Two-Liquid (eNRTL) activity coefficient model is used for electrolyte thermodynamics in liquid phase [7] and the Peng-Robinson equation of state for the vapor phase.

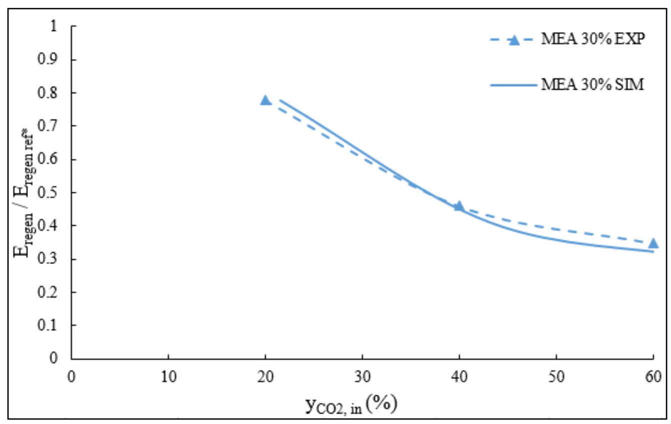
The reactions included in the Acid Gas Package for this solvent are listed in Tab. 4.

TABLE 4 : REACTIONS INCLUDED IN THE ACID GAS PACKAGE FOR MEA ($HO(CH_2)_2NH_2$)

Reaction	Type
$2\,H_2O \leftrightarrow H_3O^+ + OH^-$	E
$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-}$	E
$CO_2 + OH^- \rightarrow HCO_3^-$	K
$HCO_3^- \rightarrow CO_2 + OH^-$	K
$HO(CH_2)_2H^+NH_2 + H_2O \leftrightarrow HO(CH_2)_2NH_2 + H_3O^+$	E
$HO(CH_2)_2NH_2 + H_2O + CO_2 \rightarrow HO(CH_2)_2NHCOO^- + H_3O^+$	K
$HO(CH_2)_2NHCOO^- + H_3O^+ \rightarrow HO(CH_2)_2NH_2 + H_2O + CO_2$	K

Note: E= Equilibrium and K= Kinetic

The flowsheet developed in Aspen Hysys™ is illustrated in Fig. 6. The design and operating conditions used for the simulations are described in Tab. 2 and Tab. 3.



ref : PZ 10% at $y_{CO2,in}$=20%

Figure 7: Comparison of regeneration energies for MEA 30 wt.%, obtained with experimental tests and simulation tests of the micro-pilot unit.

Fig. 7 represents the comparison of the regeneration

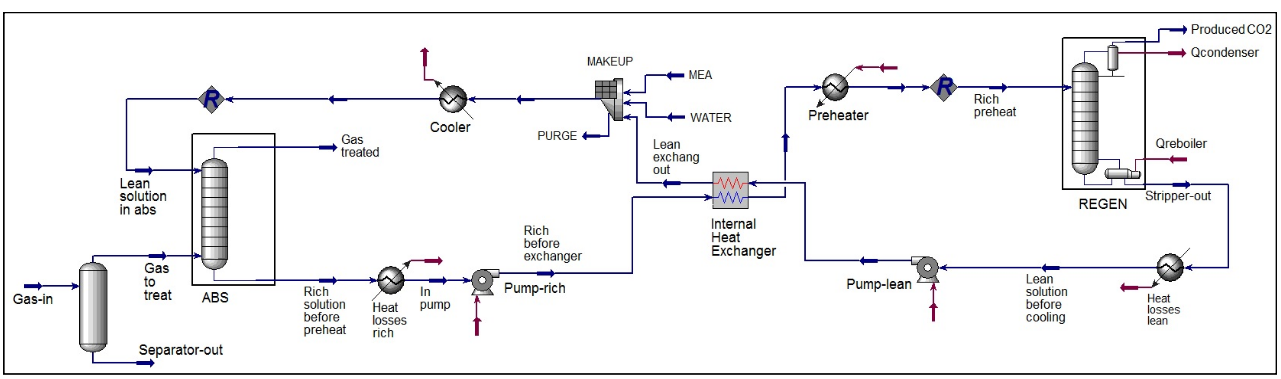


Figure 6 : Aspen Hysys™ simulation flowsheet of the micro-pilot unit for the conventional MEA process configuration

energy of MEA 30 wt.% for $y_{CO2, in}$= 20%, 40% and 60%, obtained with the experimental tests and with the simulation tests of the absorption-regeneration micro-pilot unit.

We can see clearly from Fig. 7 that for the conventional MEA 30 wt.% system the regeneration energies obtained with the experimental tests are very similar to the ones obtained with Aspen Hysys^{TM} simulations of the absorption-regeneration micro-pilot unit, concluding that the model is adequate for this application. Consequently, the same important conclusion as the one from the experimental results (Fig. 5) could be drawn from these simulations in Aspen Hysys^{TM}: when increasing the CO_2 content in the gas to treat, the regeneration energy of the solvent decreases.

V. Conclusions and prospects

Besides the conventional techniques of reducing carbon dioxide industrial emissions, CCS or CCU is a complementary solution allowing to reduce the CO_2 emissions deriving from the cement industry. The present work was focused on the study, for the cement industry, of an innovative capture technique called the post-combustion capture applied to a partial oxyfuel combustion (O_2-enriched air combustion) involving a more CO_2-concentrated flue gas ($20\% < y_{CO2} < 60\%$). Regarding more specifically the CO_2 capture step, the absorption-regeneration process using amine(s) based solvents is the one investigated in this work.

Indeed, in order to check the applicability of this technology to the cement industry, mainly three aspects were investigated: in our previous studies, the performances of several solvents were evaluated thanks to absorption tests carried out at lab scale considering high CO_2 contents ($y_{CO2,in}$ = 20-60 vol.%). Simple and activated solvents were compared in such conditions and screened.

Based on the results obtained, tests at the micro-pilot scale were conducted for the best solvents selected: for the simple solvents, the system PZ 10% presents interesting absorption performances and the use of the activated solution of AMP 30% with PZ 5 wt.% leads particularly to high absorption performances both in conventional and high CO_2 contents conditions, the performances becoming even better than with the conventional reference solvent MEA 30 wt.%.

Simulation tests of the micro-pilot unit carried out with the conventional reference solvent MEA 30 wt.% using Aspen Hysys^{TM} software V8.8 confirmed the performances obtained during the experimental tests. The experimental and simulation results for the solvents tested showed the same relevant conclusion: the regeneration energy decreases when increasing the CO_2 content in the gas to treat, which proves the interest of applying a post-combustion capture to a partial oxyfuel combustion.

As prospects, a larger study will apply the global solvents screening methodology in partial oxyfuel conditions, at lab scale firstly and at micro-pilot scale in a second step. Moreover simulations of an industrial pilot (for example the CASTOR/CESAR pilot unit whose all the design and operating parameters are available in literature) will be achieved testing solvents like MEA and PZ, both present in the database of Aspen Hysys^{TM}, in order to enlarge the application.

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References

[1] IEA (International Energy Agency), "Technology Roadmap Carbon Capture and Storage.", 2013.

[2] J. P. P. Smart, and G. S. S. Riley, "Use of oxygen enriched air combustion to enhance combined effectiveness of oxyfuel combustion and post-combustion flue gas cleanup Part 1 - combustion," *J. Energy Inst.*, vol. 85, no. 3, pp. 123–130, 2012.

[3] E. Favre, R. Bounaceur and D. Roizard, "A hybrid process combining oxygen enriched air combustion and membrane separation for post-combustion carbon dioxide capture," *Sep. Purif. Technol.*, vol. 68, no. 1, pp. 30–36, 2009.

[4] G. Riley, G. Sakellaropoulos, S. Kaldis, J.A. Gimeno, L. Fryda, M. Houkema, P. Grammelis, P. Klimantos, E. Kakaras, M. Pourkashanian, W. Nimmo, B. Gibbs, C. Papapavlou, T. Liese and S. Schmidt, *Enhanced capture with oxygen scrubbing of CO_2 (ECO-Scrub)*, vol. 2, 2013.

[5] L. Dubois, S. Laribi, S. Mouhoubi, G. De Weireld and D. Thomas, "Study of the post-combustion CO_2 capture applied to conventional and partial oxy-fuel cement plants", *Energy procedia*, DOI 10.1016/j.egypro.2017.03.1756, 2017.

[6] Y. Zhang, H. Chen, C. C. Chen, J.M. Plaza, R. Dugas and G.T. Rochelle, "Rate-based process modeling study of CO_2 Capture with aqueous monoethanolamine solution," *Ind. Eng. Chem. Res.*, vol. 48, no. 20, pp. 9233–9246, 2009.

[7] Y. Song and C.C. Chen, "Symmetric electrolyte nonrandom two-liquid activity coefficient model," *Ind. Eng. Chem. Res.*, vol. 48, no. 16, pp. 7788–7797, 2009.