Study of the postcombustion CO₂ capture by absorption into amine(s) based solvents: application to cement flue gases

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Abstract

The purpose of this work was to evaluate the absorption-regeneration performances of different types of amine(s) based solvents (primary, secondary and tertiary alkanolamines, sterically hindered amines, non-cyclical tetramine and cyclical absorption activators), previously selected thanks to a methodological study and separate laboratory absorption and regeneration tests. In this work absorption-regeneration experiments were carried out using a newly developed CO₂ capture laboratory micro-pilot and applying a high gaseous CO₂ content (from 20% to 30%) representative of cement plant flue gases.

The different experiments allowed us to compare a large number of solvents (simples and blends) by weighing absorption and regeneration performances measured in our plant. The positive effect of an activator (especially the cyclical di-amine piperazine, from 5 to 10%) on the absorption-regeneration performances of the different solutions (especially on the sterically hindered amine 2-amino2-methyl-1-propanol and on the secondary amines diethanolamine and methylmonooethanolamine, 30% solutions) was clearly highlighted. The influence of other components present in industrial emissions, especially in cement plant flue gases (mainly O₂, SOₓ, and NOₓ), on the absorption-regeneration performances of the amine solvents was also studied.

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Keywords: postcombustion CO₂ capture ; amine(s) bases solvents ; absorption ; micro-pilot

1. Introduction

The reduction of concentrated carbon dioxide emissions from different industries (power plants, cement plants, etc.) is a necessity at world scale which requires the implementation of technically feasible
solutions such as Carbon Capture and Storage (CCS). Regarding more specifically the capture phase, the postcombustion technique, using the CO$_2$ absorption into amine solvents, is the technology which should be envisaged in the short term on an industrial scale. Many experimental studies have already been conducted with the aim of applying this technique to power plants flue gases (CO$_2$ contents between 5 and 15%) but there is a lack of experimental studies concerning its application in the cement industry. The innovative aspect of this work is therefore relative to higher CO$_2$ contents considered (from 20% to 30%), more representative of cement plant flue gases. Even if various technical-economic studies have already studied the implementation of CO$_2$ capture in a cement plant (as for example reported in the ECRA reports [1, 2]), there is also a lack of information concerning the effects of other components of cement plant flue gases (O$_2$, SO$_2$, NO and NO$_2$) on the absorption-regeneration performances of the solvents. This point will be also considered in the present work.

Concerning the choice of the adequate solvent, the use of an alkanolamine-based solution such as monoethanolamine (MEA) remains the preferred choice for such a gas treating technology, but new research are crucial to find alternative solvents more competitive than MEA, and taking different aspects into account such as: absorption performances and energy consumption for the solvent regeneration, solvent resistance to degradation (which can induce corrosion problems and higher solvent consumption), solvent toxicity and volatility. Among these, the two most important criteria in a solvent screening were found to be absorption and regeneration efficiencies, as discussed for example in the technical and economic studies of [3] and [4].

In this context, this work is focusing on the evaluation of the absorption-regeneration performances of different types of amine(s) based solvents (primary, secondary and tertiary alkanolamines, sterically hindered amines, non-cyclical tetramine and cyclical absorption activators), previously selected by separate laboratory absorption and regeneration tests, by carrying out absorption-regeneration experiments with a newly developed CO$_2$ capture laboratory micro-pilot. The solvents choice was also based on the results of methodological developments.

The tests were divided in two phases: firstly, the absorption-regeneration performances of the different solvents were evaluated with a reference gaseous composition (N$_2$ (80%) + CO$_2$ (20%)), and secondly, using the solvents presenting the best performances during the first phase, the absorption rates of other components present in industrial emissions, especially in cement plant flue gases (mainly O$_2$, SO$_x$, and NO$_x$), were also studied. This communication focuses mainly on the first experimental phase and gives the first trends of the second phase being still in progress.

2. Selection of the amine(s) based solvents to be tested in the absorption-regeneration micro-pilot

2.1. Methodological selection of amine(s) based solvents

In parallel of our screening tests, a systematic methodology was developed in order to evaluate the interest of the solvents based on their absorption and regeneration potentials, but also by taking into account a maximum of information published in literature concerning the other aspects that must be considered for solvent screening (solvent resistance to degradation, corrosion risk, price of the solvent, volatility of the solvent, etc.). A relative importance was given to all the aspects based on different technical and economic studies [3-5]: 70% for absorption and regeneration criteria (35% for each one), 15% for the criterion relative to degradation resistance, 10% for economical aspect (solvent cost) and finally 5% for environmental aspect (volatility and toxicity of the solvent). By ranking all the solvents for which we had enough information according to the different criteria (from 1 to 10, applying the convention that 1 = bad, 10 = very good), and by multiplying their ranking relative to each criteria by their weighting, it was possible to obtain a single indicator comparing all the solvents considered.
According to this methodology, it was found that both DEA and PZ have good potential for CO₂ capture while AMP presented an intermediary global ranking in comparison with MAPA and PE (least potential). A full description of this methodological selection will be presented in a forthcoming communication.

2.2. Screening of amine(s) based solvents

As presented in our previous papers [6-8], the purpose of the first part of our study was to determine absorption (AP) and regeneration (RP) parameters by separate absorption and regeneration tests before testing the solvents with combined absorption-regeneration tests.

An absorption parameter for different types of amine(s) based solvents was determined by achieving absorption tests with a gas-liquid contactor and deducing apparent kinetic constants. The AP being directly linked to the absorption performances of the solvent has to be maximized. Concerning the regeneration parameter it has been obtained from liquid CO₂ loading temporal profile measured in a regeneration cell at the boiling temperature of each solvent. The RP, which is related to a desorption kinetic constant, might evolve in the same way that the regeneration energy and consequently has to be minimized. By lumping both these parameters it is possible to compare the absorption-regeneration performances of all the solvents studied (Global Solvent Parameter (GSP = AP/RP) which has to be maximized), as presented on Tab. 1. Note that the AP and the RP (and therefore the GSP) can be defined differently according to each study and in particular according to the devices used.

From Tab. 1, the good potential of cyclical amines (PZ 15% for example) was confirmed with their high GSP values compared to other simple amine solutions with a particularly low GSP value for MDEA 30%, because of its poor absorption performances despite its good regeneration performances. Regarding the different activated solutions of MDEA and AMP, the best results were obtained with the addition of PZ as activator (GSP ≥ 1.4). These preliminary results were taken into account in our solvents selection.

Table 1. Comparison of the GSP values calculated for all the amine(s) based solvents [8]

<table>
<thead>
<tr>
<th>Solvent</th>
<th>GSP</th>
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<tbody>
<tr>
<td>PZ 15%</td>
<td>1.47</td>
</tr>
<tr>
<td>PIP 15%</td>
<td>1.43</td>
</tr>
<tr>
<td>MDEA 15% + PZ 15%</td>
<td>1.41</td>
</tr>
<tr>
<td>AMP 15% + PZ 15%</td>
<td>1.40</td>
</tr>
<tr>
<td>AMP 15% + PIP 15%</td>
<td>1.38</td>
</tr>
<tr>
<td>MDEA 15% + PIP 15%</td>
<td>1.37</td>
</tr>
<tr>
<td>MDEA 15% + PZEA 15%</td>
<td>1.35</td>
</tr>
<tr>
<td>MDEA 15% + MEA 15%</td>
<td>1.26</td>
</tr>
<tr>
<td>PZEA 30%</td>
<td>1.22</td>
</tr>
<tr>
<td>MEA 30%</td>
<td>1.13</td>
</tr>
<tr>
<td>AMP 30%</td>
<td>0.92</td>
</tr>
<tr>
<td>MDEA 30%</td>
<td>0.46</td>
</tr>
</tbody>
</table>

2.3. Amine(s) based solvents considered in this study

Based on the results of our preliminary screening tests and of our methodological study, ten solvents have been selected (see Fig. 1) and experimented with typical concentrations: from 15 wt.% to 40 wt.%, including 5 to 10 wt.% of activator for the amines blends.
The interest of this selection is the fact that different amines types have been investigated (primary, secondary and tertiary alkanolamines, stericly hindered amines, cyclical amines as activators and also a tetramine), the absorption-regeneration performances depending mainly on the amine type.

3. Experimental set up and procedure

The absorption-regeneration micro-pilot (tailor made by Pignat company, see Fig. 2), based on the CO₂ capture industrial process, includes two one meter high stainless steel columns (diameter of 56 mm and easily adjustable height of 0.5 m or 1m) packed with glass Raschig rings (6x6 mm), and other equipments (heat exchangers, boiler with a maximum heating power of 2 kW, condenser, etc.) which makes it quite representative of an industrial pilot.
The pilot is also completely computerized in order to obtain a temporal data acquisition from all the sensors (temperature, pressure, etc.) as well as from gas analyzers (CO₂, O₂, SO₂, NO and NO₂) and from regulators (liquid level in the sump of the absorption column, temperatures at the inlet of the columns and regeneration heat power).

The gaseous blend entering the absorption column, composed in a first step of nitrogen and carbon dioxide, is humidified by bubbling. A counter-current contact between this gas mixture and the absorption solution is achieved in this column at atmospheric pressure.

The CO₂ loaded solution (“rich 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, by heating the solution up to its boiling point, the CO₂ is liberated from the solution (the solution after this step is called “lean 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. Head losses in the two columns are measured with differential pressure transmitters. Different heat exchangers are also judiciously placed 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, as observed in the industrial process. By means of temperature measurements and heat flux calculations, the heat balance of the whole process can be checked. The operating conditions imposed for the absorption-regeneration tests are summarized in Tab.2.

Table 2. Operating conditions for the absorption-regeneration tests

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>T_{abs}: 40°C</td>
<td>H_{G}: 0.5 and 1 m</td>
<td>L_{rich} - L_{lean}: 14 l/h</td>
<td>y_{CO₂,in}: from 10 to 30 vol.%</td>
</tr>
<tr>
<td>T_{preh}: 95°C</td>
<td>P_{boiler}: 2 kW</td>
<td>G: 2700 l/h</td>
<td>C_{Amine (max)}: 40 wt.%</td>
</tr>
</tbody>
</table>

During the absorption-regeneration tests, online CO₂ gaseous analyses (of dried samples) at the inlet and the outlet of the absorption column, performed by an infrared gas analyzer (Emerson X-STREAM X2GP with three analysis channels in the range 0-100 vol.%), give direct access to the temporal evolution of the absorption efficiency:

\[ A = \frac{G_{CO₂,in} - G_{CO₂,out}}{G_{CO₂,in}} = \frac{y_{CO₂,in} - y_{CO₂,out}}{(y_{CO₂,in} (1 - y_{CO₂.out}))} \]  

where \( G_{in} \) and \( y_{CO₂,in} \) are respectively the gas flow rate and the CO₂ volume fraction in the gas phase at the inlet of the contactor, \( G_{out} \) and \( y_{CO₂,out} \) being the gas flow rate and the CO₂ volume fraction in the gas phase at the outlet of the contactor.

CO₂ gaseous analysis at the outlet of the regeneration column is also performed in order to check the purity of the rich CO₂ gaseous flow production. Offline liquid analyses in terms of pH (measured with a pH meter Mettler Toledo, model: FiveGo FG2-Basic, electrode LE438 in polypropylene) and CO₂ loading (using a Shimadzu TOC-VCSH analyzer with NDIR detector and OCT-1 auto-sampler, calibrated in the range 0-1000 mg C/l with a standardized solution of potassium hydrogen phthalate) are also achieved during the tests especially to check the CO₂ balance between gas and liquid phases, and also to calculate the regeneration efficiency of the solvent:

\[ \eta_{regen} = \frac{\alpha_{CO₂,rich} - \alpha_{CO₂,lean}}{\alpha_{CO₂,rich}} \]
where $\alpha_{CO2,\text{rich}}$ and $\alpha_{CO2,\text{lean}}$ are respectively the CO₂ loadings of the rich and lean amine solutions. The regime value of $\eta_{\text{regen}}$ can be used to calculate the Regeneration Parameter (RP) characterizing and comparing the solvents regeneration performances:

$$RP \ (\text{kW}) = \Phi_{\text{boiler}} \ (\text{kW}) / \eta_{\text{regen}}$$ (3)

where $\Phi_{\text{boiler}} \ (\text{kW})$ is the energy provided for regeneration taking account of the thermal losses of the regeneration column (measured and equal to $\pm \ 15\%$ of $P_{\text{boiler}}$).

4. Experimental results

4.1. Absorption-regeneration tests with MEA 30%

The first tests were performed with MEA 30% solutions in order to validate the absorption-regeneration micro-pilot for experiments combining absorption and regeneration phases with different types of amine(s) based solvents. In Fig. 3 (a) it can be noticed, on the one hand, the constancy of the $y_{CO2,\text{in}}$ value ($\approx 20\%$) during the whole test and, on the other hand, that a regime is reached after about 90 minutes when $y_{CO2,\text{out}}$ stabilizes at 11%, leading to a steady absorption efficiency ($A$) value of 45%. The production of an almost pure CO₂ flow during regeneration ($y_{CO2,\text{regen}}$ $\approx 100\%$ on Fig. 3 (a)) is also checked. Fig. 3 (b) shows CO₂ loading and pH temporal evolutions of rich and lean solutions, which confirm the regeneration of the solvent.

![Fig. 3. MEA 30% micro-pilot tests, temporal evolutions of: (a) $y_{CO2,\text{in}}, y_{CO2,\text{regen}}, y_{CO2,\text{out}}, A$; (b) $\alpha_{CO2,\text{rich}}, pH_{\text{rich}}, \alpha_{CO2,\text{lean}}, pH_{\text{lean}}$](image)

Table 3. Effect of inlet gas CO₂ content on the absorption and regeneration results of MEA 30% solution

<table>
<thead>
<tr>
<th>$y_{CO2,\text{in}}$ (%)</th>
<th>$A_{\text{str}}$ (AP) (%)</th>
<th>$\alpha_{CO2,\text{rich}}$ (mol/mol)</th>
<th>$\alpha_{CO2,\text{lean}}$ (mol/mol)</th>
<th>RP (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>71.00</td>
<td>0.32</td>
<td>0.19</td>
<td>4.09</td>
</tr>
<tr>
<td>20.1</td>
<td>50.76</td>
<td>0.43</td>
<td>0.28</td>
<td>4.44</td>
</tr>
<tr>
<td>30.1</td>
<td>41.96</td>
<td>0.47</td>
<td>0.29</td>
<td>4.59</td>
</tr>
</tbody>
</table>

The effect of $y_{CO2,\text{in}}$ on the absorption-regeneration performances of MEA 30% was also studied and can be analyzed from Tab. 3. When $y_{CO2,\text{in}}$ is higher, the CO₂ loadings of the rich and lean solutions are higher, which lead to a decrease in the absorption efficiency regime value (AP) but also to an increase in the RP value, meaning a higher energy consumption for solvent regeneration.
4.2. Comparison of the absorption-regeneration performances of the solvents

The absorption-regeneration performances of all the solvents tested (with $y_{\text{CO}_2,\text{in}}$ equal to 20%) are compared on Fig. 4 with respect to reference solvents MEA 30% (see (8) on Fig. 4) and MDEA 30% (see (16) on Fig. 4).

Fig. 4. Global comparison of the absorption-regeneration performances of the solvents for $y_{\text{CO}_2,\text{in}}$ equal to 20%

Concerning the absorption performances (AP to be maximized), the best results were obtained with AMP 30% + PZ 10% and MMEA 30% + PZ 8.6%, while the absorption results of different solutions (DEA 30% + PZ 5%, MMEA 30% and AMP 30% + PZ 5%) were equivalent to those obtained with MEA 30%. On the other hand, the AP of MDEA 30% and AHPD 30% solutions are very low, which can be linked to the slower CO$_2$-amine kinetics of tertiary alkanolamines and sterically hindered amines.

Regarding the regeneration performances (RP to be minimized), as expected, the RP of MDEA 30% solution (between 1 and 2 kW) is clearly lower than those calculated for the other solvents (mainly between 2.5 and 5 kW). The worst regeneration performances were obtained with AMP 30% + PIP 5% and with TETRA 30% solutions. Except for MDEA 30%, the best RP were obtained with AMP 30% and PZ 13.5% (lower than 3 kW).

Finally, all the solvents can be compared by calculating their Global Solvent Parameter (GSP = AP/RP) which has to be maximized (see legend in Fig. 4) while presenting sufficient absorption performances (AP at least equivalent to the MEA 30% one) and requiring the least amount of energy for their regeneration (RP lower than the MEA 30% one). The objective of our research is represented as "Target Zone" in Fig. 4. Seven solvents present a higher GSP than MEA but only three solvents present an AP equivalent to MEA (DEA 30% + PZ 5%, MMEA 30% and AMP 30% + PZ 5%), the AP of PZ 13.5% being slightly lower than MEA. We can also note that the GSP of AMP 30% + TETRA 5% (11.25) is very close to the MEA one (11.44), the GSP of all other solvents being lower than 10.
4.3. First experimental results with other gaseous components and MEA 30%

In order to evaluate the impact of other gaseous components on the MEA 30% absorption-regeneration performances, O₂ (5%), SO₂ (1100 ppm), NO (1025 ppm) and NO₂ (75 ppm) have been added in the inlet gas composed of 20% CO₂ and 75% of N₂.

Due to our experimental procedure, since the test time (120 min) is limited, no decrease of absorption-regeneration performances can be brought out, the absorption rates of O₂ and NO being very low. On the contrary, as illustrated on Fig. 5 (a), no SO₂ is remaining at the outlet of the absorption column indicating the total absorption of this component into MEA 30% solution. Regarding NO₂ (see Fig. 5 (b)), its concentration is lower at the outlet of the column (relative decrease around 80%). This effect can be interpreted in terms of oxidation ratio (OR) defined as \( \frac{y_{NO2}}{y_{NO}+y_{NO2}} \). Indeed, the OR of the gas decreases from 6% (inlet of the absorption column) to 1.5% (outlet of the absorption column) indicating the presence of complex reactions which modify the NOx repartition in the gas. This observation requires further experimental investigation.

![Fig. 5. Absorption-regeneration tests with MEA 30%: (a) SO₂ contents at the inlet (\( y_{SO2,in} \)) and the outlet (\( y_{SO2,out} \)) of the absorption column; (b) NO₂ contents and oxidation ratios at the inlet (\( y_{NO2,in}, OR_{in} \)) and the outlet (\( y_{NO2,out}, OR_{out} \)) of the absorption column](image)

These tests are still in progress with the best solvents previously screened (especially MMEA 30%, PZ 13.5%, DEA 30% + PZ 5% and AMP 30% + PZ 5%) in order to check if the same observations can be drawn with other solvents than MEA.

5. Conclusions and perspectives

The CO₂ absorption process using amine based solvents is the CO₂ capture technology which could be commercialized rather quickly at an industrial level. In such a technology, the two most important aspects to consider in the choice of an adequate solvent are: the high CO₂ absorption performances and the low regeneration energy of the solvent. The purpose of this work was therefore to carry out combined absorption and regeneration tests with a newly developed CO₂ capture laboratory micro-pilot in order to evaluate globally the absorption-regeneration performances of different types of amine(s) based solvents previously selected by separate laboratory absorption and regeneration tests and by applying a methodological discrimination. One of the innovative aspects of this work is the high gaseous CO₂ content considered (from 20% to 30%), representative of cement plant flue gases.

The different experiments allowed us to compare a large number of solvents (simple and blends) by weighing absorption and regeneration performances measured in our plant. The positive effect of an activator (especially the cyclical di-amine piperazine, from 5 to 10%) on the absorption-regeneration
performances of the different solutions (especially on the sterically hindered amine 2-amino-2-methyl-1-propanol and on the secondary amines diethanolamine and methylmonoethanolamine, 30% solutions) were clearly highlighted. The tests are still in progress in order to optimize the solvents composition, and also to study more precisely the impact of other components present in industrial emissions (mainly O₂, SOₓ and NOₓ), on the absorption-regeneration performances of the amine solvents. Once the hydrodynamic and mass transfer characteristics determined, the absorption-regeneration results will be simulated using measured values and/or adequately selected literature data for physico-chemical properties (densities, viscosities, diffusivities, Henry’s coefficients) and kinetic characteristics (kinetic constants) relative to the CO₂-amines systems.

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References