Simultaneous Absorption of SO₂ and CO₂ from Conventional and Partial Oxy-fuel Cement Plant Flue Gases

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In the context of Carbon Capture Utilisation or Storage (CCUS) applied to the cement industry to reduce its CO₂ emissions, the current study was performed considering a CO₂ capture technique likely to lower the energy costs of such process, namely the post-combustion CO₂ capture by absorption-regeneration process applied to flue gases derived from an O₂-enriched air combustion cement plant. Moreover, the present work is related to the effect of the presence of SO₂ in the gas to treat on the CO₂ absorption performances for several types of amine solvents (simple and blended solutions of MEA, MMEA, MDEA, AMP and PZ) considering a CO₂ content in the flue gas between 20% and 60%. Absorption tests were performed in a laboratory gas-liquid contactor considering both CO₂-loaded and unloaded solutions. It was shown that the presence of SO₂ in the gas to treat lowers the CO₂ absorption performances of the amine based solvents, contrarily to the SO₂ absorption performances, staying quite high during the tests and confirming that this component is absorbed selectively relatively to CO₂. Regarding the novel aspects deriving from the solvents screening, it was highlighted that PZ 10% leads to both high CO₂ and SO₂ absorption performances even in considerably CO₂ loaded solution, while AMP 30% seems a good candidate to selectively absorb SO₂ in the presence of CO₂.

1. Introduction

Lowering the anthropogenic carbon dioxide emissions is a necessity at world scale in different sectors including the cement industry and Carbon Capture Storage or Utilization is envisaged for this purpose. Focusing on the CO₂ capture step, two technologies are currently under development for the application in cement plants, namely the post-combustion capture applied to conventional cement flue gases (CO₂ content between 20% and 30%) and the full oxy-fuel combustion capture, where the combustion is performed with pure oxygen instead of air leading to highly CO₂ concentrated (with more than 70%) flue gases that require further purification processes (de-SOₓ, de-NOₓ, etc.) prior to storage or conversion. These two techniques requiring disadvantageously large amounts of energy, this work was performed considering the implementation in the cement industry of an innovative capture technique called partial oxy-fuel combustion capture (see Figure 1).

Figure 1: Post-combustion CO₂ capture applied to conventional or O₂-enriched air combustions

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This technology combines an O₂-enriched air combustion involving a more CO₂-concentrated flue gas (between 20 and 70 %) compared to a conventional combustion and allowing the application of a post-combustion CO₂ capture using amine based solvents (e.g. aqueous MEA 30 wt.) in an absorption-regeneration process. In the case of power plants, this capture technique has been proven to lower the regeneration energy of the amine based solvent comparatively to a conventional combustion due to the high CO₂ concentration in the gas to treat (e.g. in (Vega et al., 2016)). The main objective of the present work is related to another gaseous component of cement flue gases and leading to solvent degradation in an absorption-regeneration process, namely the sulfur dioxide. Indeed, in addition to CO₂, formation and emissions of SO₂ (together with NOx, HCl, heavy metals, VOC and dust) in the exhaust gases are inevitable. As SO₂ is also an acid gas as CO₂, the purpose of the current work is to investigate the possibility to capture both SO₂ and CO₂ (present in the flue gases at very different concentrations) in an unique process using amine based solvents. The CO₂ and SO₂ absorption performances of different solvents (simple and activated solutions) were therefore compared thanks to absorption tests in a gas-liquid contactor in order to identify the impact of the co-absorption of these two species.

2. CO₂ and SO₂ absorption into amine(s) based solvents

2.1 CO₂ and SO₂ reactions with amines

The most commonly accepted reaction mechanism regarding the CO₂ reaction with primary amines or secondary amines (Da Silva and Svendsen, 2007) takes place as follows:

\[
2 \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 \leftrightarrow \text{R}_1\text{R}_2\text{NCOO}^- + \text{R}_1\text{R}_2\text{NH}_2^+ \tag{1}
\]

the stoichiometry of this overall reaction showing that 0.5 mol CO₂/mol of amine is the maximum loading that the primary and secondary amines could achieve.

The CO₂ reaction with tertiary amines (Donaldson and Nguyen, 1980) can be characterized as follows:

\[
\text{R}_1\text{R}_2\text{R}_3\text{N} + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ \tag{2}
\]

the stoichiometry of this overall reaction indicating that the theoretical CO₂ absorption capacity of this type of amine is 1 mol CO₂/mol amine.

The third type of amine regularly used in CO₂ capture applications is the sterically hindered amine (SHA), the following global mechanism (Sartori and Savage, 1983) occurring with such amine:

\[
\text{RNH}_2 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{RNH}_3^+ + \text{HCO}_3^- \tag{3}
\]

SHA having the same theoretical absorption capacity as tertiary amines, namely 1 mol CO₂/mol amine.

Regarding the reactions between SO₂ and amine, Lv et al. (2012) described the chemical reactions between SO₂ and the amines as a result of a combination of SO₂ reactions occurring into water and aqueous alkali solution. The SO₂ reaction with primary or secondary amines comprises the aqueous dissociation of SO₂:

\[
\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{H}^+ + \text{SO}_3^{2-} \tag{4}
\]

\[
\text{H}_2\text{SO}_3 + 2 \text{R}_1\text{R}_2\text{NH} \rightarrow (\text{R}_1\text{R}_2\text{NH}_2)_2\text{SO}_3 \tag{5}
\]

leading to the overall reaction system as follows:

\[
\text{SO}_2 + 2 \text{R}_1\text{R}_2\text{NH} + \text{H}_2\text{O} \rightarrow 2 \text{R}_1\text{R}_2\text{NH}_2^+ + \text{SO}_3^{2-} \tag{6}
\]

Concerning the tertiary amines and the SHA, the overall reactions with SO₂ can be described respectively as:

\[
\text{SO}_2 + 2 \text{R}_1\text{R}_2\text{R}_3\text{N} + \text{H}_2\text{O} \rightarrow 2 \text{R}_1\text{R}_2\text{R}_3\text{NH}^+ + \text{SO}_3^{2-} \tag{7}
\]

\[
\text{RNH}_2 + \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{RNH}_3^+ + \text{HSO}_3^- \tag{8}
\]

These different reaction mechanisms occur depending on the amine(s) used and on the process configuration implemented (separate or simultaneous co-absorption of SO₂ and CO₂).

2.2 CO₂ and SO₂ absorption processes

Mainly two different configurations of the CO₂ and SO₂ absorption-regeneration process are possible (see Figure 2) and considered in the present work, namely: a single-absorption column configuration (Puxty et al., 2014) and a two-absorption columns configuration (Stéphenne, 2014). In the single-column configuration (see Figure 2 (a)), the CO₂ and SO₂ lean solvent enters the top of the contactor, where it flows counter-currently with the gas to treat.
Figure 2: Schematization of the simultaneous SO2 and CO2 absorption-regeneration processes: one-column (a) and two-columns (b) absorption configurations

The CO2 absorption occurs in mid-top section of the column and consequently the solvent captures CO2 without the presence of SO2 in the gas. Afterwards, a part of the CO2 rich and SO2 lean solvent is extracted for solvent heat regeneration (CO2) and the other part continues to flow down to the bottom section of the absorber where the SO2 absorption (and possible CO2) desorption takes place. However, the absorbent regeneration of the SO2 rich stream is achieved using a sulfur recovery process (thermal reclaiming) appropriate for a concentrated SO2 stream use with aqueous amines. This process exploits the differences in physical solubility, absorption rate and acidity of CO2 and SO2. A potential solvent to be used in this process must present high CO2 absorption performances in absence of SO2 and high SO2 absorption performances even in CO2-loaded solutions. According to (Puxty et al., 2014), SO2 is likely to be absorbed by the amine based solvents preferentially to CO2 since it represents a stronger acid resulting in an irreversible reduction in CO2 absorption capacity and rate due to solvent neutralisation and the formation of heat stable salts.

Moreover, thanks to a larger reaction rate constants and greater solubility for SO2, it would be expected that SO2 mass transfer is favoured over CO2, leading to a highly selectivity of the absorption process towards SO2. Regarding the two-absorption column process (see Figure 2 (b)), it is composed of two absorbers and their respective strippers. The flue gas from pre-conditioning containing SO2 and CO2 enters the bottom of the first absorber where the SO2 absorption takes place. Indeed, the required solvent in this step is a solvent with high SO2 absorption performances and low CO2 absorption performances, thus presenting a selective absorption towards SO2. Afterwards, the SO2 rich solvent is regenerated in the SO2 stripper and the SO2-purified gas flows to the second absorber where the CO2 absorption takes place in another amine based solvent by means of the traditional absorption-regeneration process. An adequate solvent for the last absorption process is likely to present good absorption performances for CO2 in absence of SO2. An industrial example of such process is currently in operation in the Boundary Dam CCS plant (Saskatchewan, Canada) where a combined SO2-CO2 capture process is provided by Shell Cansolv technology, showing 100% and 90% SO2 and CO2 absorption efficiency respectively, the captured SO2 being converted to sulfuric acid before commercialization.

3. Experimental procedure

Several amine based solvents (primary, secondary and tertiary alkanolamines, SHA and cyclical diamine, see Table 1) were screened at lab scale considering a CO2 molar fraction in the inlet gas (yCO2,in) corresponding to both conventional and O2-enriched air conditions (20%<yCO2,in<60%). The purpose of the screening was to identify the most efficient solvents for each absorption-regeneration process configuration. The CO2 and SO2 co-capture was investigated to highlight the consequence on the CO2 and SO2 absorption performances of an increased SO2 content in the inlet gas, but also to see the effect on these performances of an increased CO2 loading of the solvent. As it is an important factor regarding more specifically the CO2 absorption performances, the second order CO2-amine kinetic constants at the experimental temperature (25°C) are also provided in Table 1. Globally, the choice of the selected solvents was also based on other important factors such as: chemical stability, degradation resistance, cost, industrial availability, volatility, toxicity, biodegradability, etc. The experimental device used for the tests, and its dimensional parameters together with the experimental operating conditions, are provided in Figure 3 and Table 2 respectively. This test rig was completely described in (Liémans and Thomas, 2013). It consists of a cables-bundle contactor where the gas-liquid contact takes place around the six cables. This device is well suited for such studies as its specific surface was well characterized in our previous works and it has a low sensitivity to the liquid flow rate and to the viscosity.
Table 1: Types of amines tested (simples or blended), with the corresponding kinetic constant ($k_{2,CO2-amine}$)

<table>
<thead>
<tr>
<th>Simple amines</th>
<th>Concentration (wt.%)</th>
<th>CAS number</th>
<th>Amine type</th>
<th>$k_{2,CO2-amine}$ at 25°C (m³/kmol.s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA)</td>
<td>30</td>
<td>141-43-5</td>
<td>primary alkanolamine</td>
<td>5938</td>
<td>(Versteeg and Swaaij, 1988)</td>
</tr>
<tr>
<td>Monomethylethanolamine (MMEA)</td>
<td>30</td>
<td>109-83-1</td>
<td>secondary alkanolamine</td>
<td>7940</td>
<td>(Patil et al., 2012)</td>
</tr>
<tr>
<td>N-methyldiethanolamine (MDEA)</td>
<td>30</td>
<td>105-59-9</td>
<td>tertiary alkanolamine</td>
<td>12</td>
<td>(Versteeg et al., 1996)</td>
</tr>
<tr>
<td>2-amino-2-methyl-1-propanol (AMP)</td>
<td>30</td>
<td>124-68-5</td>
<td>sterically hindered alkanolamine</td>
<td>810</td>
<td>(Xu et al., 1998)</td>
</tr>
<tr>
<td>Piperazine (PZ)</td>
<td>5-10*</td>
<td>110-85-0</td>
<td>cyclical di-amine</td>
<td>76000</td>
<td>(Derks et al., 2006)</td>
</tr>
</tbody>
</table>

*Limitation for avoiding any excess above the solubility limit.

Table 2: Dimensional characteristics, operating parameters and inlet gas compositions of the lab scale experiments

<table>
<thead>
<tr>
<th>Dimensional parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column height (m)</td>
<td>0.700</td>
</tr>
<tr>
<td>Effective packing height (m)</td>
<td>0.540</td>
</tr>
<tr>
<td>Column diameter (m)</td>
<td>0.045</td>
</tr>
<tr>
<td>Diameter of the central rod (m)</td>
<td>0.020</td>
</tr>
<tr>
<td>Packing type</td>
<td>6 propylene cables</td>
</tr>
<tr>
<td>Cable diameter (m)</td>
<td>1.600 $10^{-3}$</td>
</tr>
<tr>
<td>Void section of the contactor (m²)</td>
<td>1.600 $10^{-3}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flowrate (Nl/min)</td>
<td>16</td>
</tr>
<tr>
<td>Liquid flowrate (ml/min)</td>
<td>190</td>
</tr>
<tr>
<td>Gas analysis flowrate (Nl/min)</td>
<td>1.170</td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>101.325</td>
</tr>
<tr>
<td>Inlet liquid temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>inlet gas compositions (carrier gas: N₂)</td>
<td></td>
</tr>
<tr>
<td>$y_{CO2,in}$ (mol.%)</td>
<td>20-40-60</td>
</tr>
<tr>
<td>$y_{SO2,in}$ (ppmv)</td>
<td>0-1500</td>
</tr>
</tbody>
</table>

Figure 3: Laboratory experimental device: cables-bundle contactor

The solvent flowing from top to bottom on the cables contacts counter-currently the gas that flows in the void space of the contactor. This device is suitable for gas absorption with very variable kinetics of the chemical reactions involved. Gas flowmeters allows to fix partial and total flowrates, together with gas phase contents ($y_{CO2}$ and $y_{SO2}$, measured by IR and NDUV analysers respectively, at the inlet and outlet of the contactor). Before adding SO₂, the gas is saturated in water in a humidification column to avoid water exchange between solvent, and prior to analyses, the gas is dried in a membrane dryer. The online gas analysers give direct access to the absorption efficiency (or ratio) values, defined as the difference between the inlet and outlet CO₂ or SO₂ gas flow rates relatively to the inlet flow rate. Offline liquid analyses in terms of pH and CO₂ loading ($α_{CO2}$ (mol CO₂/mol amine), measured by a TOC analyzer) are also achieved during the tests.

Two series of experiments were carried out, namely: (1) continuous absorption tests with fresh scrubbing solutions ($α_{CO2} = 0$), without and with SO₂ ($y_{SO2} = 1500$ ppmv) in the gas to treat (the purpose being to evaluate the effect of $y_{CO2,in}$ (between 20% and 60%) on the CO₂ and SO₂ absorption performances by the solvents); (2) continuous absorption tests with various progressively CO₂ loaded solutions ($α_{CO2} ≠ 0$, beforehand loaded thanks to pure CO₂ bubbling) with 1500 ppmv of SO₂ in the gas to treat (the objective was, for fixed $y_{CO2,in}$ (40%) and SO₂ content (1500 ppmv), to compare the CO₂ and SO₂ absorption performances by the solvents).

4. Experimental results

The comparison of the CO₂ absorption performances by the CO₂-unloaded solvents is shown in Figure 4 for $y_{SO2,in} = 0$ ppmv, (a) and $y_{SO2,in} = 1500$ ppmv, (b), and for three values of $y_{CO2,in}$. The effect of the presence of SO₂ in the gas to treat is demonstrated here for fresh solutions. Clearly, $A_{CO2}$ of each solvent decreases when...
considering SO\(_2\) in the gas to treat, no significant influence of y\(_{\text{CO}_2,\text{in}}\) being observed.

These observations highlight the selectivity towards SO\(_2\) absorption matching the ones of (Puxty et al., 2014) and the reaction competition with CO\(_2\) like pointed out by (Lv et al., 2012). Indeed, during the simultaneous desulphurization and decarbonization, the SO\(_2\) competes with CO\(_2\) and consumes a part of amine solvent disfavoring CO\(_2\) absorption. Moreover, it is shown that when A\(_{\text{CO}_2}\) (without SO\(_2\)) is higher, the effect of SO\(_2\) regarding the CO\(_2\) absorption is less pronounced. Consequently, the SO\(_2\) being absorbed preferentially to CO\(_2\) as a stronger acid, this can explain the decrease of the A\(_{\text{CO}_2}\) when adding SO\(_2\). Contrary to A\(_{\text{CO}_2}\), A\(_{\text{SO}_2}\) is relatively high for all the amine-based solvents tested (see Table 3). As also stated by (Qu et al., 2016), these observations can be justified by the instantaneous reaction between SO\(_2\) and the amine which leads to a negligible liquid-side mass transfer resistance in the case of SO\(_2\) while being more significant for CO\(_2\).

Table 3: SO\(_2\) absorption performances in presence of CO\(_2\) for all the solvents tested at lab scale

<table>
<thead>
<tr>
<th>Solvents / A(_{\text{SO}_2}) (%)</th>
<th>y(_{\text{CO}_2,\text{in}}) ≈ 20%</th>
<th>y(_{\text{CO}_2,\text{in}}) ≈ 40%</th>
<th>y(_{\text{CO}_2,\text{in}}) ≈ 60%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA 30 wt.%</td>
<td>87.7</td>
<td>89.0</td>
<td>90.5</td>
</tr>
<tr>
<td>MMEA 30 wt.%</td>
<td>89.7</td>
<td>85.4</td>
<td>88.0</td>
</tr>
<tr>
<td>MDEA 30 wt.%</td>
<td>80.7</td>
<td>80.1</td>
<td>83.0</td>
</tr>
<tr>
<td>AMP 30 wt.%</td>
<td>91.0</td>
<td>90.5</td>
<td>89.0</td>
</tr>
<tr>
<td>PZ 10 wt.%</td>
<td>94.1</td>
<td>93.0</td>
<td>92.9</td>
</tr>
<tr>
<td>AMP 30 wt.% + PZ 5 wt.%</td>
<td>90.3</td>
<td>92.9</td>
<td>92.5</td>
</tr>
<tr>
<td>MDEA 30 wt.% + PZ 5 wt.%</td>
<td>93.2</td>
<td>92.6</td>
<td>91.6</td>
</tr>
</tbody>
</table>

Globally, it can be highlighted that the best solvent screened for CO\(_2\) capture is MMEA 30 wt.% (in absence of SO\(_2\)), which makes it a good candidate for the CO\(_2\) capture step in a two-columns process configuration, while AMP 30 wt.% is the solvent showing the best combination: low A\(_{\text{CO}_2}\) and high A\(_{\text{SO}_2}\), which is ideal for the SO\(_2\) capture step. The experimental results regarding the continuous absorption tests performed with a progressively increasing CO\(_2\) loading of the solutions are given in Figures 5.
It can be observed that, on the contrary to $A_{CO_2}$, $A_{SO_2}$ does not decrease when the solution is CO$_2$-loaded. Actually, all the solvents present important $A_{SO_2}$ ($A_{SO_2,minimum} = 80\%$ for MDEA 30$\%$) and keep almost the same absorption performances in the different tests with an increasing $\alpha_{CO_2}$, with a maximum decrease of 7$\%$ of $A_{SO_2}$ for MMEA 30$\%$. Indeed, as highlighted by (Puxty et al., 2014), unlike the CO$_2$ absorption flow which decreases when $\alpha_{CO_2}$ increases, SO$_2$ absorption is unaffected. These observations join our conclusions indicating that the absorption process is highly selective for SO$_2$. Moreover, it can be confirmed that the less performant solvent for CO$_2$ absorption and the best solvent for SO$_2$ absorption while CO$_2$-loaded, consequently allowing selectivity towards SO$_2$, is AMP 30$\%$ (confirming its candidature for SO$_2$ absorption in the two-columns process) while CO$_2$ can be absorbed quite conventionally by MMEA 30$\%$. Globally, the best solvent for simultaneous CO$_2$ and SO$_2$ absorptions is PZ 10$\%$, making it as good candidate for a single-column process configuration.

5. Conclusions

Considering cement plants leading to different CO$_2$ contents (between 20$\%$ and 60$\%$) in the flue gases, the present work was focused on the investigation of both CO$_2$ and SO$_2$ absorption performances by different types of amine(s) based solvents, studying two potential process configurations of the post-combustion absorption-regeneration CO$_2$ capture process (one or two absorption columns). The main conclusions arising from this study are: (1) a potential solvent for the single-column configuration is PZ 10$\%$ since it has high CO$_2$ absorption performances without the presence of SO$_2$ and at the same time absorbs well SO$_2$ even in considerably CO$_2$ loaded solutions; (2) in the two-column configuration, the solvent that could be performant for the de-SOx absorber thanks to its ability to absorb well SO$_2$ in presence of CO$_2$ is the AMP 30$\%$ and the one for the second column absorbing CO$_2$ from an SO$_2$-purified gas is MMEA 30$\%$. As a future validation of our observations and as prospect to this work, absorption-regeneration tests with flue gases simulating O$_2$-enriched air conditions (containing SO$_2$ and high CO$_2$ concentrations) will be envisaged at micro-pilot scale.

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References


