

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

Sinda Laribi, Lionel Dubois, Guy De Weireld, Diane Thomas

Chemical & Biochemical Process Engineering and Thermodynamics Units, Faculty of Engineering, University of Mons, 20 Place du Parc, 7000 Mons, Belgium
Diane.Thomas@umons.ac.be

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-SO_x, de-NO_x, 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).

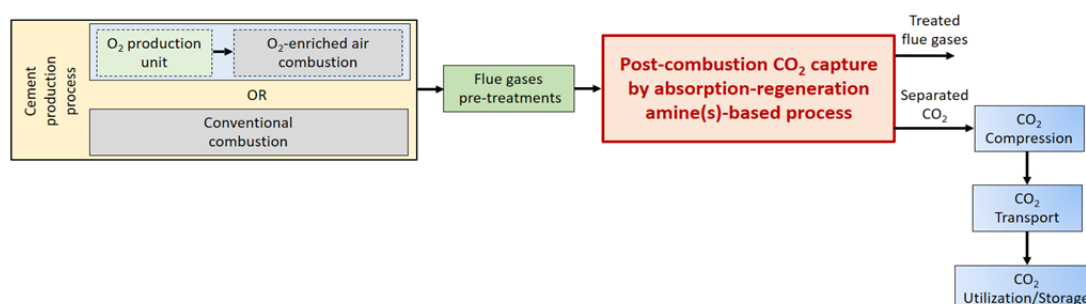


Figure 1: Post-combustion CO₂ capture applied to conventional or O₂-enriched air combustions

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 NO_x, 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:



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:



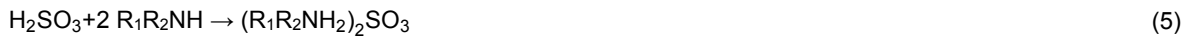
the stoichiometry of this overall reaction indicating that the theoretical CO₂ absorption capacity of this type of amine is 1 mol CO₂/mol amine.

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:



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:



leading to the overall reaction system as follows:



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



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.

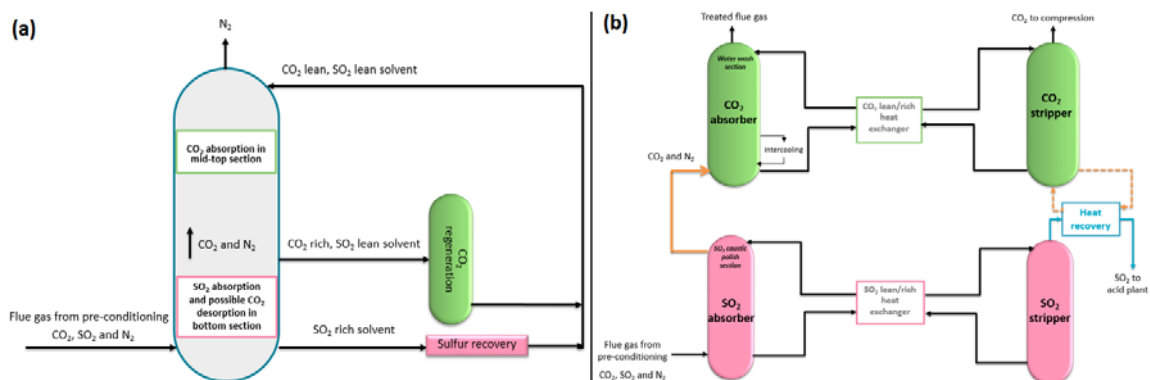


Figure 2: Schematization of the simultaneous SO_2 and CO_2 absorption-regeneration processes: one-column (a) and two-columns (b) absorption configurations

The CO_2 absorption occurs in mid-top section of the column and consequently the solvent captures CO_2 without the presence of SO_2 in the gas. Afterwards, a part of the CO_2 rich and SO_2 lean solvent is extracted for solvent heat regeneration (CO_2) and the other part continues to flow down to the bottom section of the absorber where the SO_2 absorption (and possible CO_2) desorption takes place. However, the absorbent regeneration of the SO_2 rich stream is achieved using a sulfur recovery process (thermal reclaiming) appropriate for a concentrated SO_2 stream use with aqueous amines. This process exploits the differences in physical solubility, absorption rate and acidity of CO_2 and SO_2 . A potential solvent to be used in this process must present high CO_2 absorption performances in absence of SO_2 and high SO_2 absorption performances even in CO_2 -loaded solutions. According to (Puxty et al., 2014), SO_2 is likely to be absorbed by the amine based solvents preferentially to CO_2 since it represents a stronger acid resulting in an irreversible reduction in CO_2 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 SO_2 , it would be expected that SO_2 mass transfer is favoured over CO_2 , leading to a highly selectivity of the absorption process towards SO_2 . 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 SO_2 and CO_2 enters the bottom of the first absorber where the SO_2 absorption takes place. Indeed, the required solvent in this step is a solvent with high SO_2 absorption performances and low CO_2 absorption performances, thus presenting a selective absorption towards SO_2 . Afterwards, the SO_2 rich solvent is regenerated in the SO_2 stripper and the SO_2 -purified gas flows to the second absorber where the CO_2 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 CO_2 in absence of SO_2 . An industrial example of such process is currently in operation in the Boundary Dam CCS plant (Saskatchewan, Canada) where a combined SO_2 - CO_2 capture process is provided by Shell Cansolv technology, showing 100% and 90% SO_2 and CO_2 absorption efficiency respectively, the captured SO_2 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 CO_2 molar fraction in the inlet gas ($y_{\text{CO}_2,\text{in}}$) corresponding to both conventional and O_2 -enriched air conditions ($20\% < y_{\text{CO}_2,\text{in}} < 60\%$). The purpose of the screening was to identify the most efficient solvents for each absorption-regeneration process configuration. The CO_2 and SO_2 co-capture was investigated to highlight the consequence on the CO_2 and SO_2 absorption performances of an increased SO_2 content in the inlet gas, but also to see the effect on these performances of an increased CO_2 loading of the solvent. As it is an important factor regarding more specifically the CO_2 absorption performances, the second order CO_2 -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 ($k_{2,CO_2\text{-amine}}$)

Simple amines	Concentration (wt.%)	CAS number	Amine type	$k_{2,CO_2\text{-amine}}$ at 25°C (m ³ /kmol.s)	Reference
Monoethanolamine (MEA)	30	141-43-5	primary alkanolamine	5938	(Versteeg and Swaaij, 1988)
Monomethylethanolamine (MMEA)	30	109-83-1	secondary alkanolamine	7940	(Patil et al., 2012)
N-methyldiethanolamine (MDEA)	30	105-59-9	tertiary alkanolamine	12	(Versteeg et al., 1996)
2-amino-2-methyl-1-propanol (AMP)	30	124-68-5	sterically hindered alkanolamine	810	(Xu et al., 1998)
Piperazine (PZ)	5-10*	110-85-0	cyclical di-amine	76000	(Derks et al., 2006)

*Limitation for avoiding any excess above the solubility limit.

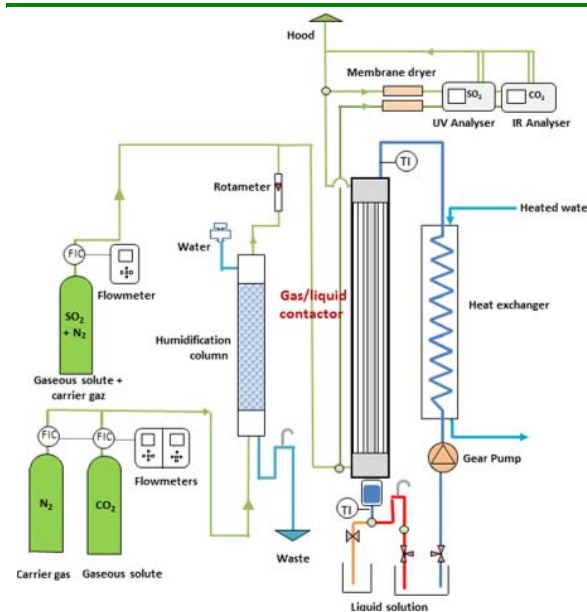


Figure 3: Laboratory experimental device: cables-bundle contactor

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_{CO_2} and y_{SO_2} , measured by IR and NDUV analysers respectively, at the inlet and outlet of the contactor). Before adding SO_2 , 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 CO_2 or SO_2 gas flow rates relatively to the inlet flow rate. Offline liquid analyses in terms of pH and CO_2 loading (α_{CO_2} (mol CO_2 /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 ($\alpha_{CO_2} = 0$), without and with SO_2 ($y_{SO_2} = 1500$ ppm_v) in the gas to treat (the purpose being to evaluate the effect of $y_{CO_2,in}$ (between 20% and 60%) on the CO_2 and SO_2 absorption performances by the solvents); (2) continuous absorption tests with various progressively CO_2 loaded solutions ($\alpha_{CO_2} \neq 0$, beforehand loaded thanks to pure CO_2 bubbling) with 1500 ppm_v of SO_2 in the gas to treat (the objective was, for fixed $y_{CO_2,in}$ (40%) and SO_2 content (1500 ppm_v), to compare the CO_2 and SO_2 absorption performances by the solvents).

4. Experimental results

The comparison of the CO_2 absorption performances by the CO_2 -unloaded solvents is shown in Figure 4 for $y_{SO_2,in} = 0$ ppm_v (a) and $y_{SO_2,in} = 1500$ ppm_v (b), and for three values of $y_{CO_2,in}$. The effect of the presence of SO_2 in the gas to treat is demonstrated here for fresh solutions. Clearly, A_{CO_2} of each solvent decreases when

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

Dimensional parameters	
Column height (m)	0.700
Effective packing height (m)	0.540
Column diameter (m)	0.045
Diameter of the central rod (m)	0.020
Packing type	6 propylene cables
Cable diameter (m)	$1.600 \cdot 10^{-3}$
Void section of the contactor (m ²)	$1.276 \cdot 10^{-3}$
Operating parameters	
Gas flowrate (NI/min)	16
Liquid flowrate (ml/min)	190
Gas analysis flowrate (NI/min)	1.170
Pressure (kPa)	101.325
Inlet liquid temperature (°C)	25
Inlet gas compositions (carrier gas: N ₂)	
$y_{CO_2,in}$ (mol.%)	20-40-60
$y_{SO_2,in}$ (ppm _v)	0-1500

considering SO₂ in the gas to treat, no significant influence of $y_{CO_2,in}$ being observed.

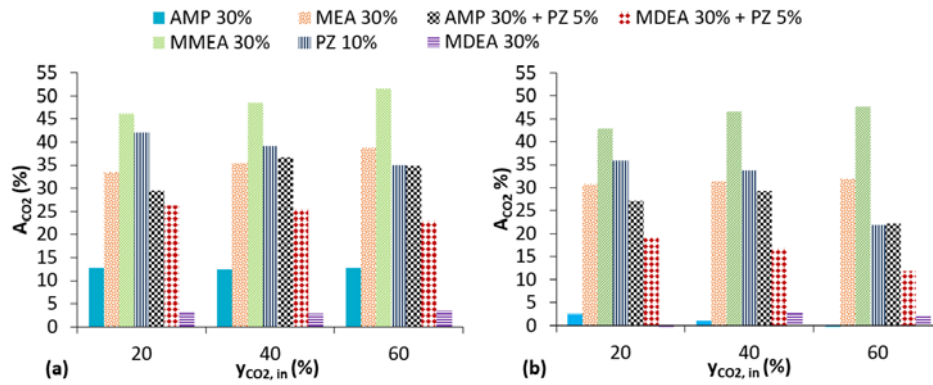


Figure 4: CO₂ absorption ratios (A) for different $y_{CO_2,in}$ values: (a) $y_{SO_2,in} = 0 \text{ ppm}_v$ and (b) $y_{SO_2,in} = 1500 \text{ ppm}_v$

These observations highlight the selectivity towards SO₂ absorption matching the ones of (Puxty et al., 2014) and the reaction competition with CO₂ like pointed out by (Lv et al., 2012). Indeed, during the simultaneous desulphurization and decarbonization, the SO₂ competes with CO₂ and consumes a part of amine solvent disfavoring CO₂ absorption. Moreover, it is shown that when A_{CO_2} (without SO₂) is higher, the effect of SO₂ regarding the CO₂ absorption is less pronounced. Consequently, the SO₂ being absorbed preferentially to CO₂ as a stronger acid, this can explain the decrease of the A_{CO_2} when adding SO₂. Contrary to A_{CO_2} , A_{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 SO₂ and the amine which leads to a negligible liquid-side mass transfer resistance in the case of SO₂ while being more significant for CO₂.

Table 3: SO₂ absorption performances in presence of CO₂ for all the solvents tested at lab scale

Solvents / A_{SO_2} (%)	$y_{CO_2,in} \approx 20\%$	$y_{CO_2,in} \approx 40\%$	$y_{CO_2,in} \approx 60\%$
MEA 30 wt. %	87.7	89.0	90.5
MMEA 30 wt. %	89.7	85.4	88.0
MDEA 30 wt. %	80.7	80.1	83.0
AMP 30 wt. %	91.0	90.5	89.0
PZ 10 wt. %	94.1	93.0	92.9
AMP 30 wt. % + PZ 5 wt. %	90.3	92.9	92.5
MDEA 30 wt. % + PZ 5 wt. %	93.2	92.6	91.6

Globally, it can be highlighted that the best solvent screened for CO₂ capture is MMEA 30 wt. % (in absence of SO₂), which makes it a good candidate for the CO₂ capture step in a two-columns process configuration, while AMP 30 wt. % is the solvent showing the best combination: low A_{CO_2} and high A_{SO_2} , which is ideal for the SO₂ capture step. The experimental results regarding the continuous absorption tests performed with a progressively increasing CO₂ loading of the solutions are given in Figures 5.

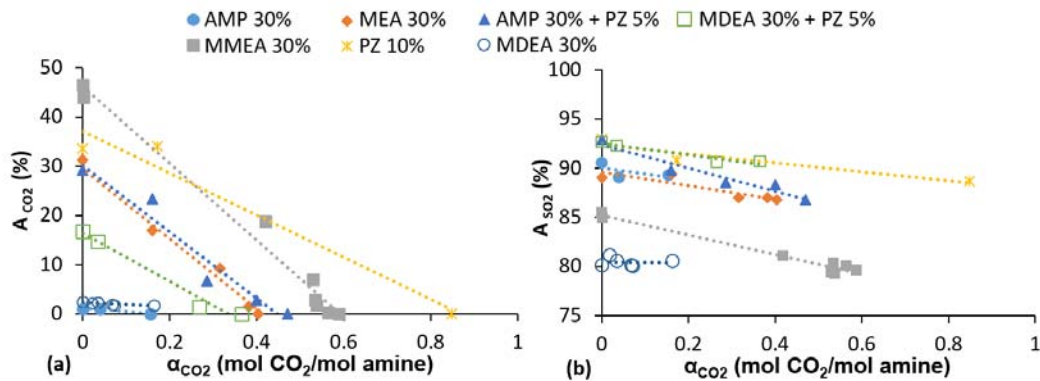


Figure 5: Evolution of the A_{CO_2} (a) and A_{SO_2} (b) for increasing α_{CO_2} values ($y_{CO_2,in}=40\%$ and $y_{SO_2,in}=1500 \text{ ppm}_v$)

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 α_{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 α_{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- SO_x 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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