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Experimental study and modified modeling on effect of SO₂ on CO₂ absorption using amine solution



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ABSTRACT

Understanding the competitive mechanism in absorption process between SO_2 and CO_2 is essential for simultaneous absorption of SO_2 and CO_2 . In this study, the effect of SO_2 on CO_2 absorption using amine solution was studied experimentally and theoretically. The CO_2 absorption rates in MEA/MMEA/MDEA solutions were determined using wetted wall column. Results showed that the reduction of flue gas temperature was beneficial for CO_2 absorption at the typical coal-fired flue gas CO_2 concentration. On this basis, the effect of SO_2 on CO_2 absorption performance was studied. Firstly, the overall CO_2 mass transfer coefficient decreased under exposure to SO_2 . Secondly, in the presence of SO_2 , pH variation of amine solution increased. In addition, the saturated CO_2 capacity largely decreased when SO_2 was continuously bubbled into the solution. Furthermore, the quantum chemical calculation showed that CO_2 had little effect on the absorption performance of SO_2 whereas SO_2 greatly weakened the interaction between CO_2 and amines. The overall CO_2 mass transfer coefficient was modified considering the effect of SO_2 . The competitive absorption factor, χ , was introduced to modify the CO_2 liquid phase diffusion coefficients. The average deviation of overall CO_2 mass transfer coefficient narrowed to 1.76 % (0.5 mol/L MEA), 1.13 % (1.0 mol/L MEA), 1.88 % (1.0 mol/L MMEA) and 1.43 % (1.0 mol/L MDEA) respectively, which agreed well with the experimental results.

1. Introduction

Carbon dioxide (CO_2) is the most dominant greenhouse gas emitted and human activities contribute the most to the current global warming [1–3]. Efficient CO_2 mitigation technologies should be implemented to prevent the adverse effects of the high atmospheric level of CO_2 . A proposed option to mitigate CO_2 , referred to as carbon capture, utilization and storage (CCUS) has been considered as a promising and necessary technology, and eventually achieve carbon neutrality that curbs climate change [4,5]. Requiring minimal retrofitting existing facilities, post-combustion carbon capture is considered as an efficient process for carbon emission mitigation. Chemical absorption or adsorption is currently one of the most widely adopted techniques within the carbon capture category involving various physical and chemical capture processes. Over the last few decades, numerous novel absorbents have been designed and applied to improve the efficiency and reduce costs of for CO_2 capture, including amino acid salts [6], ionic liquids [7], nanoparticle organic hybrid materials [8], carbonate solution [9], nanofluids [10], etc. However, as with any new materials and techniques, the biggest challenge is the transition of the technologies from laboratory conditions to the more realistic large-scale industrial conditions.

Among the emerging novel solvents or materials, amine-based solvent is widespread due to its maturity [11]. CO₂ absorption with amine solution is a well-understood and widely used technology which dates back to 1930 [12]. Researches have been carried out on the kinetics of CO₂ absorption reaction in order to evaluate the capture performance of amine-based solvents, including single amine [13], blended amine [4,14] and biphasic solvent [15,16]. As for SO₂, Schiff [17] began to study SO₂ absorption with amines in 1866. Rich researches in flue gas desulfurization (FGD) with amine solution stem from its high efficiency, high utilization of SO₂ recovery and high selectivity for SO₂ [18,19]. In most cases, the CO₂ capture unit operates independently of FGD unit,

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χ competitive absorption factor
k_{OH^-} reaction rate constant for CO ₂ hydration, s ⁻¹ Subscripts/Superscripts
Ld gas loading in amine solution, mol/mol g gas
N mass transfer rate, $mol/(m^2 \cdot s)$ in inlet
p partial pressure, Pa l liquid
<i>P</i> pressure, Pa <i>out</i> outlet
<i>Q</i> volumetric flow rate, m ³ /h * equilibrium state
R universal gas constant, 8.314 J/(mol K)

resulting in economic challenge. A potentially lower cost solution is to capture CO_2 and SO_2 simultaneously from the flue gas in a single process.

Combined capture of SO₂ and CO₂ from the flue gas has already received attention from numerous commercial and research organizations and carried out commercial scale projects. The combination of FGD unit and CO₂ capture unit offers potential capex savings, which has good practical significance [20]. Cansolv evolved amine-based regenerable technologies that capture SO₂ and CO₂ simultaneously [21]. SO₂ was absorbed from the flue gas in an initial amine absorption step, followed by CO₂ capture in a separate downstream amine absorption unit. The SO₂-loaded absorbent was thermally regenerated. Then, the regenerated SO2 was used in the production of sulfuric acid. The Netherlands Organization for Applied Scientific Research invented an integrated CO2 and SO₂ capture system named CASPER process [22]. SO₂ was absorbed at the bottom of the column in the flue gas, whereas the CO₂ level was progressively reduced as the flue gas rising through the column. Commonwealth Scientific and Industrial Research Organization (CSIRO) has developed an amine-based combined capture process, named CS-Cap [23]. An amine absorbent rich in sulfate is produced in this process that could impart significant capital savings for the overall capture process because of removing the requirement for FGD. However, the negative impacts of SO₂ on CO₂ capture in the absorbent have not been reported. In actual operation, the absorbent will be more easily degraded due to the presence of SO₂, resulting in corrosion and foaming [24]. Therefore, it is necessary to study the effect of SO₂ on CO₂ absorption performance.

SO₂ is considered as an impurity to impede the performance and chemical stability of CO₂ absorbents [7,8,25–28], such as absorption rate, mass transfer coefficient, absorption capacity, etc. Li et al. [29] investigated the effect of SO₂ on CO₂ capture using chilled aqueous ammonia. Experimental results showed that the CO₂ mass transfer decreased with the increase concentration of SO₂ in the gas phase. Li et al. [30] studied the effects of the presence of SO₂ with low concentration to CO₂ absorption behavior in ionic liquid 1-ethyl-3-methylimidazolium acetate [C₂mim][OAc] through experimental method and theoretical method. Results showed that the CO₂ absorption capacity was decreased by 25 % under exposure to SO₂. Alexander et al. [27] found that CO₂ capture capacity of the primary-amine based polymeric CO₂ sorbent decreased as a result of exposure to 431 ppm SO₂ in simulated flue gas. Due to an irreversible reaction between SO₂ and the amine, the sorbent was difficult to fully regenerated. Existing studies described only the effects of SO₂ on CO₂ in terms of apparent phenomena, which cannot reveal the essence of competitive mechanism between SO₂ and CO₂. A simple but accurate modified method is still not available to quantify the SO₂ effect on CO₂ absorption performance of amine solutions.

Though the multi-component absorption of SO₂ and CO₂ has been appeared in several researches and applications, a comprehensive evaluation of the adverse effect of SO₂ on CO₂ absorption performance of amine solution has not yet been reported, not to mention an accurate correction method. Hence, the present study focused on the effects of SO₂ on CO₂ absorption using amine solution. Firstly, experimental investigation was carried out on CO2 absorption rate of Ethanolamine (MEA), 2-(Methylamino)ethanol (MMEA) and N-Methyldiethanolamine (MDEA) solution using wetted wall column (WWC). On this basis, the effect of SO₂ on CO₂ absorption performance was studied from overall mass transfer coefficient, pH variation of amine solution, absorption capacity and the interaction between CO₂/SO₂ and amine through experiments and quantum chemical calculations. Finally, the overall CO₂ mass transfer coefficient was modified considering the effect of SO₂, which is practical enough to be used in multi-component absorption scenarios, such as simultaneous absorption of SO₂ and CO₂.

2. Experiments and methods

2.1. Materials

The reagents used in the experiment, MEA (99 %, mass fraction), MMEA (99 %, mass fraction) and MDEA (99 %, mass fraction), were purchased from Shanghai Macklin Biochemical Co., ltd., China. CO_2 (99.9 %, volume fraction), N_2 (99.999 %, volume fraction), and SO_2 (99.999 %, volume fraction) were supplied by Hangzhou Linan Gas Co., Ltd., China. All chemicals were commercially available and directly used without further purification. For preparing aqueous solvent deionized water was used.

2.2. Experimental methods and apparatus

The WWC was fabricated to study the reaction kinetics of CO2/SO2

absorption. Fig. 1 presents a schematic of the apparatus. Within the WWC, the stainless-steel hollow tube had an outer diameter of 12 mm, a height of 10.0 cm and a contact area of the gas liquid reaction of 37.70 cm². During the experiments, the amine solution was continuously pumped into the hollow tube and formed a layer of liquid film on its outer surface. CO_2/SO_2 was mixed with nitrogen to the desired concentration. The simulated flue gas flow rate was controlled through a mass flow controller with a constant flow rate of 2 L/min. The simulated flue gas, controlled at 30 to 65 °C, entered from the bottom of WWC and was in countercurrent contact with the liquid film on the surface of the hollow tube.

The simulated gas was discharged from the top of the WWC and passed through the drying tube, after which the non-dispersive infrared (NDIR) multi-gas analyzer (MGA 5) was used to measure the CO_2/SO_2 concentration at the exit of the drying tube. The amine solution was preheated in a constant temperature water bath. The amine solution flow rate was controlled at 50 ml/min using a peristaltic pump. It was then returned from the bottom of the WWC to the water bath, forming a liquid circuit circulation. The WWC was surrounded by water bath to ensure constant temperature in the reaction space. The reactor was equipped with temperature probes with an uncertainty of 0.1 °C. The measured values were recorded automatically and continuously in the computer. Because the reaction time was less than one hour throughout the gas–liquid reaction process and the total amount of the absorbent was much higher than that of the absorbed gas, the absorbed CO_2/SO_2 had little effect on the loading comparing to long-term absorption.

Densities of the amine solutions were measured by pycnometer method. The kinematic viscosities of the amine solutions were measured by the Ubbelohde viscometer according to ASTM D445 and ISO 3104. Both of them were calibrated with deionized water at the temperatures of 30–65 °C. A thermostatically controlled and well-stirred water bath were prepared for the measurement, which was controlled below \pm 0.01 K. The pycnometer and viscometer filled with liquid were kept in the water bath for at least 30 min. Each experimental value was an average of five measurements.

2.3. Mass transfer and reaction mechanism

The essence of CO_2 and SO_2 absorption in amine solution is acid-base neutralization reaction, in which acid gas reacts with weak base to form soluble salt. In a weak alkaline aqueous environment, H_2O and OH^- still react with CO_2 simultaneously. So, the following reactions may occur in the aqueous solution:

$$CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+$$
(1)

$$CO_2(aq) + OH^- \rightleftharpoons HCO_3^-$$
 (2)

 CO_2 absorption by amines can be explained by the zwitterion mechanism and base-catalyzed hydration mechanism. Typical primary and secondary amines, represented as R_1NH_2/R_1R_2NH , is often depicted by zwitterion mechanism when react with CO_2 . Firstly, CO_2 reacts with amine to form a zwitterion intermediate [31]:

$$\mathbf{R}_{1}\mathbf{N}\mathbf{H}_{2} + \mathbf{CO}_{2}(\mathbf{aq}) \rightleftharpoons \mathbf{R}_{1}\mathbf{N}\mathbf{H}_{2}^{+}\mathbf{COO}^{-}$$
(3)

Then, the zwitterion is subsequently deprotonated:

$$R_1 N H_2^+ COO^- + B \rightleftharpoons R_1 N H COO^- + B H^+$$
(4)

Where, B represents the bases including the amine as well as $\rm H_2O$ and $\rm OH^-.$

Based on base-catalyzed hydration mechanism, tertiary amine, which can be represented as $R_1R_2R_3N$, cannot react directly with CO_2 . In aqueous solution, besides reaction (1) and (2), the following reaction will occur:

$$R_1R_2R_3N + CO_2(aq) + H_2O \rightleftharpoons R_1R_2R_3NH^+ + HCO_3^-$$
 (5)

As acid gas, SO_2 combines with free amine reducing the amine concentration. The reactions of SO_2 with amines are similar to that of CO_2 with tertiary amines. In aqueous solution, the reversible hydration and ionization of SO_2 take place as shown in reactions (6) and (7):

$$SO_2(aq) + H_2O \Rightarrow HSO_3^- + H^+$$
 (6)

$$HSO_3^- \rightleftharpoons SO_3^- + H^+ \tag{7}$$

$$R_1R_2R_3N + SO_2(aq) + H_2O = R_1R_2R_3NH^+ + HSO_3^-$$
 (8)

With the addition of amines capturing H^+ , the equilibrium of reactions (6) and (7) lies to the right, which increases the solubility of SO_2 and facilitates the reaction (8). When O_2 is present reacting with sulfite, amine degradation might occur through oxidation to form heat stable salts (HSS), resulting in corrosion, extra energy requirements and reduced capture efficiency [32].

The absorption rate of CO_2 and SO_2 in amine solution is controlled by diffusion limitation and reaction rate. Generally speaking, it is a mass transfer process between the gas and liquid phases in steady state which



Fig. 1. Schematic of the apparatus. (1) N₂; (2) CO₂; (3) SO₂; (4) mass flowmeters; (5) mixing tank; (6) wetted wall column; (7) thermometer; (8) pressure meter; (9) water bath kettle; (10) drying tube; (11) gas analyzer; (12) exhaust gas treatment; (13) peristaltic pump.

is not only related to the driving force, but also affected by the resistance in and between phases.

The overall mass transfer coefficient K_g is obtained by the mass transfer flux and the driving force, as shown in Eq. (6) to (9):

$$K_g = \frac{N_{CO_2}}{\left(p_{CO_2} - p_{CO_2}^*\right)}$$
(9)

$$N_{CO_2} = \frac{(\varphi_{CO_2,in} - \varphi_{CO_2,out})Q_g}{V_M \cdot A}$$
(10)

$$p_{CO_2} = \frac{p_{CO_2,in} - p_{CO_2,out}}{In \frac{p_{CO_2,in}}{p_{CO_2,out}}}$$
(11)

$$p_{CO_2}^* = H_{CO_2} c_{CO_2}^* \tag{12}$$

The total resistance to mass transfer can be described as Eq. (13) based on the two-film theory, which yields a series resistance relationship between the mass transfer coefficients.

$$\frac{1}{K_g} = \frac{1}{k_g} + \frac{1}{k_l} = \frac{1}{k_g} + \frac{H_{CO_2,amine}}{k_l^0 \cdot E_{CO_2}}$$
(13)

According to previous study [33], the correlation of gas phase mass transfer coefficient, k_g , can be obtained by Eq. (14) to (17):

$$k_g = \frac{Sh \cdot D_{CO_2,g}}{RTd}$$
(14)

$$Sh = 1.075 (Re \cdot Sc \cdot d/h)^{0.85}$$
 (15)

$$Sc = \frac{\mu_g}{\rho_g \cdot D_{CO_2,g}} \tag{16}$$

$$Re = \frac{d \cdot u \cdot \rho_g}{\mu_e} \tag{17}$$

The physical liquid film mass transfer coefficient, k_l , reflects the rate of mass transfer in liquid phase without chemical reactions. In terms of the WWC, the correlation can be expressed as Eq. (18) [34].

$$k_l^0 = \left(\frac{3^{1/3} \cdot 2^{1/2}}{\pi^{1/2}}\right) \left(\frac{Q_l^{1/3} \cdot h^{1/2} \cdot W^{2/3}}{A}\right) \left(\frac{g \cdot \rho_l}{\mu_l}\right)^{1/6} D_{CO_2,amine}^{1/2}$$
(18)

Analogical method was applied to obtain the Henry's law constant of CO₂, $H_{CO_2,amine}$ [35], expressed as Eq. (19) to (21), because the ratio of N₂O and CO₂ solubilities remained constant for various amine solutions. It is inaccurate to measure CO₂ solubility in amine solutions directly since CO₂ will react with the amine [36].

$$H_{CO_2,amine} = H_{N_2O,amine}\left(\frac{H_{CO_2,water}}{H_{N_2O,water}}\right)$$
(19)

$$H_{N_2O,water} = [8.552 \times 10^6 \exp(-2284/T)]^{-1}$$
(20)

$$H_{CO_2,water} = [2.82 \times 10^6 \exp(-2044/T)]^{-1}$$
(21)

According to the regression equation from Hartono [37], N_2O solubility in amine solution can be expressed as Eq. (22).

$$H_{N_2O,amine} = \exp\left[\left(8.3194 + 4.52 \times 10^{-3} w_{amine} - 4.78 \times 10^{-2} L d_{CO_2} + 4.56 \times 10^{-2} w_{amine} \cdot L d_{CO_2}\right) - 1905 \left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$$
(22)

Using the same method as the Henry's law constant, the diffusion coefficients of CO_2 can be estimated as follows:

$$D_{CO_2,amine} = D_{N_2O,amine} \left(\frac{D_{CO_2,water}}{D_{N_2O,water}} \right)$$
(23)

$$D_{N_2O,water} = 2.397 \times 10^{-2} \exp(-2122.2/T)$$
(24)

$$D_{CO_2,water} = 4.041 \times 10^{-2} \exp(-2288.4/T)$$
⁽²⁵⁾

Taking the temperature and viscosity into account, the correlation of N_2O diffusion coefficient in amine solution was given by Pacheco [38].

$$D_{N_2O,amine} = 5.533 \times 10^{-12} \exp(T/\mu_l^{0.545})$$
(26)

Because of the presence of SO₂, the absorption of CO₂ is negatively affected. CO₂ and SO₂ diffuse to gas–liquid interface simultaneously. Chiefly, SO₂ reacts instantaneously with amine diffused from liquid film and reduces the concentration of amine in the region significantly. Meanwhile, the selective absorption of SO₂ inhibits the CO₂ mass transfer. Then, the CO₂ diffuses through the low-amine-concentration region and reacts rapidly with the amine where the amine concentration is slightly lower than that in the liquid bulk.

The reaction of CO_2 with amines can be simplified as the pseudo first order reaction [39], which implies that the amine is not considerably depleted at the gas–liquid interface. The zwitterion mechanism applies to the carbamate formation [40] and the rate of absorption can therefore be given by Eq. (27).

$$r_{CO_2,amine} = k_2 c_{CO_2} c_{amine} \tag{27}$$

The expression of the enhancement factor for a pseudo first order regime can be given in by Eq. (28).

$$E = \frac{\sqrt{(k_2 c_{amine} + k_{OH^-} c_{OH^-}) \cdot D_{CO_2, amine}}}{k_l^0}$$
(28)

Hikita [41] obtained a good fit of the experimental data while calculating the kinetic rate constant k_2 as a function of the temperature, as shown by Eq. (29).

$$k_2 = 9.77 \times 10^7 \exp(-4955/T) \tag{29}$$

The expression of the reaction rate constant for CO₂ hydration, k_{OH^-} , has been put forward by Pinsent [42].

$$lg(k_{OH^-}) = 13.635 - \frac{2895}{T}$$
(30)

 SO_2 absorption can be considered as instantaneous reaction. The diffusion of amines to the reaction interface dominates the process. High driving forces weaken the effect of kinetics and bring the diffusion resistance to the fore.

2.4. Quantum chemical calculation

To get a deep insight into the interaction between amines and CO_2/SO_2 , the Gaussian 09 program was applied to simulate the absorption into amine solutions based on density functional theory (DFT) [43]. The interactions between the amines and CO_2/SO_2 were calculated according to corresponding reaction mechanisms. Geometry optimization and vibrational frequency calculation were carried out at the B3LYP-GD3/6-31G(d) basis set [44]. The calculations were performed on the universal solvation model (SMD) in consideration of the solvent effects [45]. The interaction energies were obtained after basis set superposition error (BSSE) and zero-point energy (ZPE) correction [46].

3. Results and discussion

3.1. Absorption performance of CO_2

The CO_2 absorption rate with amines is an essential engineering parameter for the design of absorption towers and process optimization. For a given application scenario, the driving forces are basically the same and higher mass transfer rate generally corresponds with faster reaction. Therefore, mass transfer rate is the best measure available to compare CO₂ reaction rates in various amine systems.

In this study, the CO2 mass transfer rates of MEA/MMEA/MDEA solutions at temperatures ranging from 30 to 65 °C were experimentally measured using Eq. (7) at different CO₂ partial pressure in WWC. The CO₂ mass transfer rate of 0.5 mol/L MEA solution are illustrated in Fig. 2 (a). The mass transfer rate increased as the inlet CO₂ concentration increased, which not necessarily correspond with higher overall mass transfer coefficient. At high inlet CO₂ concentration, the rate decreased with the increase of temperature, whereas the rate did not vary monotonously with temperature at lower inlet CO₂ concentration. The gas solubility coefficient and reaction rate constant, the main factors affecting the absorption rate, are functions of temperature. The reaction rate constant was positively correlated with temperature, whereas the gas solubility coefficient showed an inverse trend. As a result, there was an optimum temperature range for CO₂ mass transfer rate at the inlet CO2 concentration of 5 % and 10 %. Fig. 2 (b) to (d) show the mass transfer rate of 1.0 mol/L MEA/MMEA/MDEA solution. It can be seen that the CO₂ mass transfer rate of MMEA solution was the highest while the lowest of MDEA solution in the same conditions. At the inlet CO₂ concentration of 5 %, the mass transfer rates varied little with the temperature. At higher inlet CO₂ concentration, the results also showed that when the temperature reached a certain range, the mass transfer rate reached the highest and gradually decreased with the increase of the temperature. The CO₂ concentration of typical coal flue gas is about 15 %. It can be seen from the figure that when the temperature was above 40°C, lower temperature meant higher mass transfer rate. The results fully proved that the reduction of flue gas temperature was beneficial to the absorption of CO₂. Studies on using intercoolers in the post-combustion CO_2 capture process have been carried out [47–49].

3.2. Effects of SO₂ on absorption performance of CO₂

3.2.1. Mass transfer coefficient

The effect of SO₂ on CO₂ mass transfer coefficient at different SO₂ concentrations and temperatures of 0.5 mol/L MEA solution at CO₂ concentration of 10 % is shown in Fig. 3 (a). It can be seen that the overall mass transfer coefficient of CO₂ without the presence of SO₂ reached 6.697 × 10⁻⁷ mol/(Pa·s·m²)) at 35 °C. The SO₂ concentration varied from 1800–3000 ppm representative of different application scenarios. The overall SO₂ mass transfer coefficient decreased with temperature and SO₂ concentration. It was obvious that the overall mass transfer coefficient of CO₂ under exposure to SO₂ largely decreased to

4.489–4.811 \times 10^{-7} mol/(Pa·s·m^2)) with the reduction by 25.6 %- 29.8 %.

Fig. 3 (b) shows the effect of SO₂ on CO₂ mass transfer coefficient of 1.0 mol/L MEA solution. The results showed that the overall CO₂ mass transfer coefficient without the presence of SO₂ increased gradually with temperature and reached $8.903 \times 10^{-7} \text{ mol}/(\text{Pa}\cdot\text{s}\cdot\text{m}^2)$) at 50 °C, which was consistent with the trend in the presence of SO₂. The mass transfer coefficient of SO₂ decreased when the SO₂ concentration increased from 1800 ppm to 3000 ppm and the temperature increased from 30 °C to 50 °C. Obviously, the overall CO₂ mass transfer coefficient under exposure to SO₂ largely decreased to $6.501-7.393 \times 10^{-7} \text{ mol}/(\text{Pa}\cdot\text{s}\cdot\text{m}^2)$) with the reduction by 17.0 % – 23.6 %.

It indicated that the overall CO₂ mass transfer coefficient of 1.0 mol/ L MMEA solution without the presence of SO₂ reached 14.054 × 10⁻⁷ mol/(Pa·s·m²)) at 35 °C (Fig. 3 (c)). When the SO₂ concentration increased from 1800 ppm to 3000 ppm and the temperature increased from 30 °C to 50 °C, the SO₂ mass transfer coefficient decreased. It was obvious that the overall mass transfer coefficient of CO₂ under exposure to SO₂ largely decreased to 8.998–10.765 × 10⁻⁷ mol/(Pa·s·m²)) with the reduction by 22.7 % – 31.3 %.

Fig. 3 (d) shows that the overall mass transfer coefficient of CO₂ without the presence of SO₂ increased gradually with temperature and reached $1.687 \times 10^{-7} \text{ mol/(Pa}\cdot\text{s}\cdot\text{m}^2)$) at 40 °C and then decreased, which was consistent with the trend in the presence of SO₂. The mass transfer coefficient of SO₂ decreased when the temperature increased from 30 °C to 50 °C but was not sensitive to concentration change. Obviously, the overall CO₂ mass transfer coefficient under exposure to SO₂ largely decreased to 0.853–1.247 $\times 10^{-7} \text{ mol/(Pa}\cdot\text{s}\cdot\text{m}^2)$) with the reduction by 22.4 % - 41.7 %.

Accordingly, the mass transfer resistance of CO_2 increased in the presence of SO_2 , which inhibited the CO_2 diffusion in liquid phase. However, the increase of SO_2 concentration seemed to have little effect on the reduction of CO_2 mass transfer coefficient. In summary, the presence of SO_2 reduced the overall CO_2 mass transfer coefficient. The limited sorption active sites of amines, some of its occupation by SO_2 resulted in lower CO_2 mass transfer coefficient.

3.2.2. pH variation of amine solution

pH is one of the most important parameters for the absorption performance of amine solution. Fig. 4 shows the pH variation of amine solutions with temperature. Under normal operating conditions without SO_2 this variation may be relatively small but can be quite dramatic



Fig. 2. Effect of temperature on CO_2 mass transfer rate of (a) 0.5 mol/L MEA solution; (b) 1.0 mol/L MEA solution; (c) 1.0 mol/L MMEA solution; (d) 1.0 mol/L MDEA solution. The tinted areas are error bars representing one standard deviation based on five independent samples measured.



Fig. 3. Effect of SO_2 on the overall mass transfer coefficient of (a) 0.5 mol/L MEA solution; (b) 1.0 mol/L MEA solution; (c) 1.0 mol/L MMEA solution; (d) 1.0 mol/L MDEA solution. Each experimental value was an average of five independent measurements.



Fig. 4. pH variation of amine solution in the absence/presence of 2400 ppm SO₂ of (a) 0.5 mol/L MEA solution; (b) 1.0 mol/L MEA solution; (c) 1.0 mol/L MMEA solution; (d) 1.0 mol/L MDEA solution.

under exposure to SO₂.

Fig. 4 (a) shows the pH variation of 0.5 mol/L fresh MEA solution. The average pH decrease after absorbing for 12 min was 0.33 in the

absence of SO₂. As a contrast, the experiment with 2400 ppm SO₂ had a large average pH decrease of 0.50 with an increase of 51.5 % because of the combination of SO₂ with amine.



Fig. 5. Saturation capacity (mole CO2/mole amine) of (a) MEA;(b) MMEA and (c) MDEA at various molar concentrations at 40°C.

As for 1.0 mol/L MEA and 1.0 mol/L MDEA, the pH variation of solution increased from 0.44 to 0.59 with an increase of 34.1 % (Fig. 4 (b)). Similarly, the pH variation of solution increased from 0.51 to 0.31 with an increase of 64.5 % (Fig. 4 (d)). However, for 1.0 mol/L MMEA with the largest mass transfer coefficient, the presence of SO₂ had the least influence on pH variation. The pH variation of solution increased from 0.55 to 0.58 with a minor increase (Fig. 4 (c)). The results showed that the smaller the CO₂ absorption rate, the more significant the effect of SO₂ on the absorption performance of amine solution. The CO₂ absorption rate remained stable at high pH. Due to the presence of SO₂, the pH of the amine solvent was relatively low, resulting in a decrease in the absorption capacity of CO₂.

3.2.3. Absorption capacity

In Fig. 5 (a), the absorption capacity at different MEA concentrations is given at 40°C. Based on reaction (3) and (4), two primary or secondary amine molecules react with one CO₂ molecule (in the case of B representing amine) with the maximum CO₂ loading of 0.5 mol CO₂/mole amine. While one tertiary amine molecule reacts with one CO₂ molecule with a theoretically loading of 1.0 mol CO_2 /mol amine (reaction (5)). However, both the capacity of CO₂ and the capacity of CO₂ & SO₂ in amine solution exceeded the theoretical capacity. This was due to a considerable amount of acid gas was absorbed by aqueous solvent. As the amine concentration increased, CO₂ capacity without SO₂ in amine solution slightly decreased at the same condition. The reason was that the lower concentration of amine solution had more water to absorb CO2 (reaction (1) and (2)). Under the same conditions, SO₂ was bubbled into the solution to reached saturation and it was obvious that the CO₂ capacity largely decreased from 0.807 to 0.180 mol CO₂/mol amine with the reduction of 77.7 %. The continuous absorption of SO₂ caused CO₂ to escape from the solution. However, with the increase of amine concentration, the proportion of CO₂ escaping decreased. The absorption capacity of MMEA solution is shown in Fig. 5 (b). The average CO_2 capacity reached 0.907 mol CO₂/mol amine. Obviously, the CO₂ capacity largely decreased to 0.189 mol CO2/mol amine of 0.5 mol/L MMEA solution when SO_2 was also saturated. Fig. 5 (c) shows the absorption capacity of MDEA solution. As a tertiary amine, the average CO₂ capacity was 1.093 mol CO₂/mol amine. It was obvious that the CO₂ capacity largely decreased to 0.159 mol CO2/mol amine of 0.5 mol/L MDEA solution when the amine solution reached SO₂ saturation.

3.2.4. Interaction of amine solution with CO_2

The absorption performance of amines is affected by the molecular structure. Studies on the interaction between amines and CO₂/SO₂ through quantum chemical calculation revealed the competitive mechanism between CO₂ and SO₂. The lowest-energy geometries of the complex, along with their N-C/N-S bond lengths and thermochemical parameters are shown in Fig. 6. The N atom in MEA showed strong interaction with the C atom in CO₂ with the distance of 1.631 Å (Fig. 6 (a)). Compared with an isolated CO_2 molecule, the strong complexation led to a largely bent CO₂ configuration. And the optimized structure of MEA-SO₂ showed the average distance of 2.168 Å between the N atom and the S atom in SO₂. When MEA interacted with one CO₂ and one SO₂ molecule, the bond length of N - S was similar to that in MEA-SO₂, which could explain remained large solubility of SO₂ in saturated CO₂ solution in Fig. 5. However, the bond length between the C atom in CO₂ and the N atom in MEA significantly extended to 3.693 Å, indicating that the interaction was weakened due to the presence of SO₂. As a result, CO2 rarely affected the absorption performance of SO2 whereas SO2 greatly weakened the interaction between amine and CO₂. Compared to CO₂ molecule, SO₂ has high molecular polarity and dipole moment, which leads to strong affinity with the amines. The thermochemical parameters including interaction energy, absorption enthalpy and Gibbs free energy also reflected the competitive effect between CO₂ and SO₂. In comparison with the interaction energy, absorption enthalpy and Gibbs free energy between the Amine-CO₂ and Amine-SO₂ complexes,



Fig. 6. Optimized structure and thermochemical parameters between CO_2 & SO_2 and (a) MEA; (b) MMEA; (c) MDEA.

all the thermodynamic parameters of Amine-SO₂ were significantly higher than that of Amine-CO₂. More importantly, the thermochemical parameters of Amine-SO₂ were closer to those of Amine-CO₂-SO₂, indicating that SO₂ had more advantages in the competition. Unfortunately, the stronger interaction between SO₂ and amines had a negative effect on the regeneration of amine solution. In the case of single component absorption of MMEA as presented in Fig. 6 (b), N—C and N—S bond length were 3.682 Å and 2.167 Å. In the case of simultaneous absorption, the N—C bond length increased to 3.947 Å while the N—S bond length was essentially unchanged. Similarly, it can be seen that the presence of SO₂ greatly changed the thermochemical parameters of CO₂ absorption reaction. The optimized structure of MDEA-CO₂ and MDEA-SO₂ showed the average distance of 4.128 Å and 2.216 Å (Fig. 6 (c)). When MDEA interacted with one CO₂ and one SO₂ molecule, the bond length between the C atom in CO₂ and the N atom was significantly extended to 5.017 Å while the N—S bond length had minor change·H₂O was considered in the calculation based on base-catalyzed hydration mechanism (reaction (5)).

3.3. Modification of CO_2 mass transfer coefficient for the influence of SO_2

The comparison of the gas phase overall mass transfer coefficient K_g between experimental and calculated results from Eq. (13) are shown in Fig. 7. Under single-component absorption condition in the absence SO₂, the deviations between the calculated results and the experimental results were 1.27 % (0.5 mol/L MEA), 1.38 % (1.0 mol/L MEA), 1.71 % (1.0 mol/L MMEA) and 1.88 % (1.0 mol/L MDEA) respectively. The good agreement between the experimental measurements and calculated results showed that the overall mass transfer coefficient was determined with sufficient accuracy. However, the single-component absorption model was no longer accurate in the presence of SO₂ as expected (the elliptical area). The average deviation of overall CO₂ mass transfer coefficient reached 38.7 % (0.5 mol/L MEA), 24.8 % (1.0 mol/L MDEA) respectively. The single-component absorption model was no longer

suitable for multi-component absorption scenarios.

The above experimental results have verified that SO_2 had a negative effect on the absorption performance of amine solutions. Meanwhile, SO_2 absorption process greatly weakened the CO_2 absorption process but basically not affected by CO_2 according to quantum chemistry calculations.

As the partial pressure of SO₂ in flue gas was much less than that of CO₂, SO₂ had minor effect on gas phase diffusion coefficient. Essentially, the negative effect of SO2 on CO2 mass transfer was reflected on the liquid phase diffusion coefficients. Molecular diffusion described the relative motion of individual molecules in a mixture arisen from concentration gradients. The resulting net diffusion flux was down the potential gradient until uniformity of the system was reached. However, when SO₂ was present, SO₂ molecules was abundant in the liquid phase due to the much smaller Henry's law coefficient than CO₂. More SO₂ reacting with amines led to the reducing of CO₂ diffusion capacity in liquid phase. Even at low SO₂ concentrations, the CO₂ liquid phase diffusion coefficient decreased. Small deviations in the prediction of diffusion coefficients might result in prediction errors for the mass transfer coefficients. The large inaccuracies in the calculated mass transfer coefficients were, therefore, to be expected for nonideal systems.

To make the model more readily accurate for industrial applications, e.g. a process for simultaneous capture system of CO₂ and SO₂, a simplified equation for estimating the SO₂ effects on CO₂ mass transfer in the amine solution was developed by fitting the numerical solutions. The competitive absorption factor, χ , was introduced to modify the CO₂ liquid phase diffusion coefficients. Table 1 shows the competitive absorption factor of MEA, MMEA and MDEA.



Fig. 7. Comparisons between the calculated and experimental results of overall CO_2 mass transfer coefficient of (a) 0.5 mol/L MEA solution; (b) 1.0 mol/L MEA solution; (c) 1.0 mol/L MDEA solution.

Table 1

Competitive absorption facto	r for $D_{CO_2,amine}$	of MEA,	MMEA an	d MDEA.
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	Competitive absorption factor
MEA	$\chi = 1-0.705 \times \exp(-0.5 \ C_{amine}-2 \times 10^{-3} T) \times (1-\exp(0.05 \ p_{SO_2}))$
MMEA	$\chi = 1-0.943 \times \exp(-0.5 \ C_{amine} - 2 \times 10^{-3} T) \times (1-\exp(0.02 \ p_{SO_2}))$
MDEA	$\chi = 1-0.952 \times \exp(-0.5 C_{amine} - 2 \times 10^{-3} T) \times (1-\exp(0.01 p_{SO_2}))$

 $C_{amine},$ molar concentration of a mines; T, temperature of solution; $p_{SO_2},$ SO_2 partial pressure.

$$D'_{CO_2,amine} = \chi D_{CO_2,amine} \tag{31}$$

Fig. 8 shows relatively small deviations between the numerical and experimental results of overall CO₂ mass transfer coefficient in the presence of SO₂ after the modification of $D_{CO_2,amine}$. The average deviation of overall CO₂ mass transfer coefficient narrowed to 1.76 % (0.5 mol/L MEA), 1.13 % (1.0 mol/L MEA), 1.88 % (1.0 mol/L MMEA) and 1.43 % (1.0 mol/L MDEA) respectively. Therefore, the modified overall CO₂ mass transfer coefficient agreed well with the multi-component absorption process.

The most pressing researches needs in CO_2 mitigation are reducing the costs and simultaneously pollutant emission reduction. The number of studies on lowering energy consumption continues to increase, achieving satisfactory results but still has great potential in efficient desorption and absorbent reclaiming. Future work should be aimed at development of new absorbents and simultaneous absorption of various pollutants (SO₂, NO_x, H₂S, et al.) and CO₂, which will make positive contributions to the coordinated governance of pollution reduction and carbon emissions reduction.

4. Conclusions

In this paper, the absorption performance of CO_2 of MEA/MMEA/ MDEA solution under the exposure to SO_2 was investigated through experimental method and quantum chemical calculation. The overall CO_2 mass transfer coefficient was modified considering the effect of SO_2 .

The CO₂ absorption rates in 0.5 mol/L MEA solution and 1.0 mol/L MEA/MMEA/MDEA solution were determined at different temperatures and inlet CO₂ concentrations using WWC. The mass transfer rate increased as the inlet CO₂ concentration increased. When the temperature is above 40°C, lower temperature meant higher mass transfer rate at the CO₂ concentration of typical coal-fired flue gas (15 %). In this application scenario, the reduction of flue gas temperature was beneficial to the absorption of CO₂.

The effects of SO₂ on CO₂ absorption performance were studied from four aspects. Firstly, the overall CO₂ mass transfer coefficient decreased under exposure to SO₂. The limited sorption active sites of amines were occupied by SO₂. Secondly, in the presence of SO₂, pH variation of amine solution increased. In addition, the saturated CO₂ capacity largely decreased when SO₂ was continuously bubbled into the solution. Furthermore, the interaction between amines and CO₂/SO₂ through quantum chemical calculation revealed the competitive mechanism between CO₂ and SO₂. The results showed that CO₂ rarely affected the absorption performance of SO₂ whereas SO₂ greatly weakened the interaction between CO₂ and amine.

The competitive absorption factor, χ , was introduced to modify the CO₂ liquid phase diffusion coefficients considering the effect of SO₂. The average deviation of overall CO₂ mass transfer coefficient narrowed to 1.76 % (0.5 mol/L MEA), 1.13 % (1.0 mol/L MEA), 1.88 % (1.0 mol/L MDEA) respectively, which agreed well



Fig. 8. Comparisons between the corrected and experimental results of overall mass transfer coefficient of CO₂ in the presence of SO₂.

with the experimental results.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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