



# Experimental studies and rate-based simulations of CO<sub>2</sub> absorption with aqueous ammonia and piperazine blended solutions



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## ABSTRACT

Piperazine (PZ) is a potential promoter for CO<sub>2</sub> absorption with aqueous ammonia (NH<sub>3</sub>) solutions. Here, we focus on the performance of a blended NH<sub>3</sub>/PZ solution for CO<sub>2</sub> capture using a laboratory-scale packed column to analyse the effects of key operating parameters, including NH<sub>3</sub> and PZ concentration, absorption temperature and solution flow rate. A rigorous, rate-based model was developed in Aspen Plus and validated against the experimental results. Using the model, we predicted the CO<sub>2</sub> capture process under experimental conditions to gain insight into CO<sub>2</sub> absorption with NH<sub>3</sub>/PZ blended solutions. The addition of PZ to aqueous NH<sub>3</sub> markedly increased CO<sub>2</sub> absorption, achieving a CO<sub>2</sub> removal efficiency comparable to that of monoethanolamine-based capture processes. However, the presence of PZ also increased the temperature along the column and the concentration of free NH<sub>3</sub> in the solution, leading to a high NH<sub>3</sub> loss from the absorber.

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## 1. Introduction

Post-combustion capture of CO<sub>2</sub> via chemical absorption is one of the leading technologies for significantly reducing greenhouse gas emissions from coal-fired power plants (Figueroa et al., 2008; Rochelle, 2009; Wang et al., 2011; Goto et al., 2013). An effective, economic absorbent for CO<sub>2</sub> absorption is aqueous ammonia, which is low cost, has high CO<sub>2</sub> absorption capacity and low regeneration energy, resists degradation and can capture multiple acid gases from the flue gas (Bai and Yeh, 1997; Yeh et al., 2005; Zhuang et al., 2011; Han et al., 2013). Several processes of CO<sub>2</sub> capture with aqueous ammonia solution have been proposed by research groups including Alstom, Powerspan, Commonwealth Scientific and Industrial Research Organization, Korea Institute of Energy Research and Research Institute of Industrial Science & Technology (You et al., 2007; McLarnon and Duncan, 2009; Darde et al., 2010; Yu et al., 2011; Rhee et al., 2011). Pilot plant trials have proven the feasibility of aqueous ammonia as the absorbent of CO<sub>2</sub>. However, two important issues must be addressed for NH<sub>3</sub>-based CO<sub>2</sub> capture process. First, the reaction rate of CO<sub>2</sub> with aqueous ammonia is relatively low compared with

that of monoethanolamine (MEA). This low reaction rate requires an absorber with larger geometric dimensions or larger circulation flow rate of solution than the MEA-based CO<sub>2</sub> capture process. Second, the high volatility of NH<sub>3</sub> causes massive NH<sub>3</sub> loss during the absorption process, requiring further treatment and extra energy consumption for NH<sub>3</sub> abatement and recovery processes to avoid a health, safety and environment (HSE) issue. To minimise NH<sub>3</sub> loss, a low temperature and concentration of NH<sub>3</sub> is usually adopted for the lean solution, further reducing its CO<sub>2</sub> absorption rate.

Many chemicals, including alkanolamines, amino acids and inorganic bases, have been proposed as promoters for CO<sub>2</sub> absorption using aqueous ammonia solution (You et al., 2008; Rowland et al., 2011; Yu et al., 2012, 2013; Li et al., 2014). From the perspective of mass transfer, piperazine (PZ) is thought to be the best among these chemicals, and it can significantly increase the CO<sub>2</sub> absorption rate (Liu et al., 2011a,b; Rowland et al., 2011; Yu et al., 2012). The fast reaction rate of PZ with CO<sub>2</sub> is believed to be one of the reasons for this. Concentrated PZ is able to provide a CO<sub>2</sub> absorption rate and capacity that is almost double that of MEA and its performance for CO<sub>2</sub> capture has been evaluated in The University of Texas at Austin (Freeman et al., 2010; Plaze and Rochelle, 2011). Aqueous PZ has also been blended with K<sub>2</sub>CO<sub>3</sub> and MDEA to enhance the CO<sub>2</sub> absorption and good performances have been achieved (Zhang et al., 2001; Oexmann et al., 2008).

Alstom patented a PZ-promoted, chilled ammonia process and claimed that the addition of 0.4–1.0 mol/L PZ into aqueous ammo-

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nia solution significantly increased CO<sub>2</sub> absorption, and that PZ was stable at low temperatures for absorption, and under high pressures and temperatures for regeneration (Alstom, 2009). However, detailed information about this work was rarely disclosed. The fundamental properties of NH<sub>3</sub>/PZ blended solutions, including vapour–liquid equilibrium, mass transfer and heat of reaction, have been studied. The addition of PZ can increase NH<sub>3</sub> partial pressure in the NH<sub>3</sub>–PZ–H<sub>2</sub>O system, enhance the mass transfer and has no significant effect on the heat of reaction with CO<sub>2</sub> (Liu et al., 2011a,b, 2012a,b). However, CO<sub>2</sub> absorption processes using NH<sub>3</sub>/PZ blended solution in industrially applicable absorbers have not yet been reported in open publications.

In this work, we investigated the CO<sub>2</sub> absorption process in a laboratory-scale packed column using NH<sub>3</sub>/PZ blended solution. The effects of operating parameters on the absorption process were analysed and a reliable model to predict the CO<sub>2</sub> capture process was developed.

## 2. Experimental

Fig. 1 shows a schematic diagram of the experimental system. The CO<sub>2</sub> in the simulated flue gas was absorbed into the NH<sub>3</sub>/PZ blended solution along the column. The temperature of the simulated flue gas and the blended solution were controlled with water baths and measured at the inlet of the column. The column, randomly packed with 2.5 mm Dixon rings, has a diameter of 0.06 m and height of 1 m. The temperature distribution along the column was measured with five thermocouples equally distributed along the packing section, with their temperature profiles marked as T<sub>1</sub> to T<sub>5</sub> from top to bottom in Table 1. The column was covered with heat-shielding materials to minimise heat transfer between the column and the environment. A Fourier-transform infrared analyser (Thermo Antaris IGS, operating at 180 °C) was used for online measurement of CO<sub>2</sub> and NH<sub>3</sub> concentrations in the outlet gas. The solutions were prepared with analytical grade chemicals and deionised water, and an automatic titrator was used to determine their composition. Gas-phase NH<sub>3</sub> was removed with dilute phosphoric acid before the simulated flue gas was released to the atmosphere.

The experiment was initiated with pumping CO<sub>2</sub> loaded blended solution into the top of the column continuously at the desired flow rate. The liquid level at the bottom was kept constant by adjusting the flow rate of outlet solution. The N<sub>2</sub> and CO<sub>2</sub> were mixed to generate the simulated flue gas and then introduced into the Fourier-transform infrared analyser from the bypass to measure the concentration of CO<sub>2</sub>. The absorption process began with the simulated flue gas introduced into the bottom of the column after the concentration of CO<sub>2</sub> stabilized. Thereafter, the concentration of CO<sub>2</sub> and NH<sub>3</sub> in the outlet gas and the temperatures along the column were continuously measured to determine whether a steady state was achieved. The experiment continued for 30 min after the steady state was reached and average values of CO<sub>2</sub> and NH<sub>3</sub> concentration in the outlet gas and temperatures during the stable operation were calculated and listed in Table 1. The liquid sample was taken at the end of the experiment.

In total, 16 different cases were investigated. Table 1 lists the detailed operating conditions and results of each case. The concentration of PZ and NH<sub>3</sub> in the solution, the flow rate and temperature of the solution were varied. CO<sub>2</sub> and NH<sub>3</sub> concentrations in the outlet gas and temperature profiles along the column were recorded as shown in Table 1. Note that the CO<sub>2</sub> loading was held constant at 0.2 mol CO<sub>2</sub>/mol NH<sub>3</sub>, indicating that the PZ was treated as a substitute for water in the solution.

**Table 1**  
Summary of experiments using piperazine (PZ) and ammonia (NH<sub>3</sub>) blended solutions under a variety of operating conditions.

Operating conditions	Case no.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
NH <sub>3</sub> conc. (wt%)	4.78	4.82	4.9	4.85	2.87	7.02	8.76	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9	4.9
PZ conc. (wt%)	0	2.94	4.97	6.96	5.08	4.97	5.02	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97	4.97
CO <sub>2</sub> loading (mol CO <sub>2</sub> /mol NH <sub>3</sub> )	0.199	0.201	0.201	0.2	0.2	0.198	0.201	0.201	0.201	0.201	0.201	0.201	0.201	0.201	0.201	0.201
Liquid flow rate (L/h)	4	4	4	4	4	4	4	3	2	4.4	4	4	4	4	4	4
Liquid temp. (°C)	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.3	14.3	14.7	10.2	19.7	24.8	14.5	14.5	14.5
Gas flow rate (L/min)	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15	19.15
Gas temp. (°C)	24.6	24.8	25	25.4	25.4	25.2	25.2	24.8	24.6	25	25.1	25.1	25	25	25	25
CO <sub>2</sub> conc. in flue gas (%)	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04	10.04
CO <sub>2</sub> conc. in outlet gas (%)	5.20	4.00	1.90	1.30	2.80	1.94	1.76	4.50	5.60	1.70	2.02	2.30	3.20	4.20	7.10	4.00
NH <sub>3</sub> conc. in outlet gas (%)	1.24	2.51	4.49	6.75	1.68	8.26	8.77	4.28	3.65	4.82	3.29	6.21	6.43	2.27	0.57	3.75
Calculated CO <sub>2</sub> out (kg/h)	0.104	0.080	0.038	0.026	0.056	0.039	0.035	0.090	0.112	0.034	0.041	0.046	0.064	0.084	0.142	0.080
Calculated CO <sub>2</sub> removal efficiency (%)	48.9	60.7	81.3	87.2	72.5	80.9	82.7	55.8	44.9	83.3	80.1	77.4	68.5	58.7	30.2	60.7
T <sub>1</sub> (°C)	18.5	25.4	30.1	36.2	32.8	27.3	28.8	32.1	29.4	29.5	26.2	33.5	37.3	19.3	19.1	20.4
T <sub>2</sub> (°C)	21.2	26.3	35.7	42.5	37.2	31.8	29.2	31.7	31.7	37.1	31.8	39.3	39.7	21.1	21.4	22.7
T <sub>3</sub> (°C)	23.8	28.7	36.9	42.1	38.9	31.7	27.6	34.2	29.0	37.8	35.7	38.2	38.1	24.2	22.7	27.2
T <sub>4</sub> (°C)	24.5	30.4	35.4	38.7	36.7	30.5	29.4	31.5	27.4	36.2	32.1	37.7	34.7	24.5	21.5	28.4
T <sub>5</sub> (°C)	24.9	29.8	31.4	38.6	34.2	28.7	24.7	29.8	25.8	32.7	31.3	33.2	32.9	24.9	23.6	28.8

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