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The effects of Cu(II) ion as an additive on NH_3 loss and CO_2 absorption in ammonia-based CO_2 capture processes

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HIGHLIGHTS

- ▶ The effect of Cu(II) ion in ammonia-based CO_2 capture processes is investigated.
- ▶ Cu(II) ion mitigates ammonia loss and increases CO_2 absorption capacity.
- ▶ Cu(II) ion can reduce economic cost of the ammonia-based processes.

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ABSTRACT

Chemical CO_2 absorption is one of the most cost- and energy-intensive processes in carbon capture and storage (CCS) technology. Among various absorption processes, ammonia-based processes attract much attention, due to many benefits: high CO_2 absorption rate and low energy consumption for ammonia regeneration. Ammonia-based processes, however, have a problem to be solved for practical implementation due to the high vapor pressure of ammonia, which incurs ammonia loss during regeneration. In this study, the effect of Cu(II) ion as an additive on NH_3 loss and CO_2 absorption was investigated to examine the potential of Cu(II) ion to enhance the economic performance of ammonia-based processes. Continuous operations were conducted with and without the addition of Cu(II) ion. The results showed that the addition of Cu(II) ion noticeably decreased NH_3 loss in the regeneration process due to the complexation of copper and ammonium ions, i.e., $[Cu(NH_3)_4]^{2+}$. The Cu(II) addition also increased the CO_2 absorption capacity in the absorption process because ammonia concentration remained higher. In conclusion, Cu(II) ion can be used to reduce ammonia make-up cost and to enhance CO_2 absorption performance in ammonia-based CO_2 capture processes.

1. Introduction

Since climate change has become one of the world's serious problems, CO_2 capture technologies have started getting attention. To sequestrate CO_2 from combustion processes in industrial plants, three types of technology are being developed: (i) pre-combustion, (ii) oxyfuel combustion, and (iii) post-combustion. Among the post-combustion processes, absorption process using chemical absorbents is one of the most effective ways to remove CO_2 from flue gas [1]. As most effective absorbents, MEAs (monoethanolamines) have been used to develop commercial processes [2]. MEA-based processes, however, have a drawback, due to high temperature (i.e., 120–140 °C) required to regenerate MEA. In other words, MEA leads to high energy consumption and cost [3]. Thus, recent studies have focused on ammonia as an alternative absorbent [1,2,4,5].

Ammonia-based absorption CO_2 process has a high capacity to capture CO_2. The absorption capacity is higher than 1.0 kg CO_2/kg aqueous ammonia [1]. Compared to MEA, ammonia has higher absorption capacity based on the volume of the absorption reactor (i.e., for ammonia, 0.025 mol CO_2/mL (1.20 kg CO_2/kg or 0.46 mol CO_2/mol); and for MEA, 0.008 mol CO_2/mL (0.36 kg CO_2/kg or 0.50 mol CO_2/mol)). Moreover, ammonia-based process is more cost- and energy-effective than MEA-based process due to lower regeneration temperature (i.e., 80–85 °C) and lower cost of ammonia. Ammonia absorbent has, however, a limitation in practical application because of its high vapor pressure, which incurs high loss of ammonia in regeneration process. This leads to considerable loss of ammonia and requires high cost to make up ammonia in practical implementation. Therefore, appropriate measures should

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Table 1
Solubility product constants (K_{sp}) of copper and zinc carbonates.

Literature	$CuCO_3$	$ZnCO_3$
Verma et al. [10], Patnaik [11]	1.4×10^{-10}	1.4×10^{-11}
Sincero and Sincero [12]	1.37×10^{-10}	6×10^{-11}
Kelter et al. [13], Zumdahl [14]	2.5×10^{-10}	2×10^{-10}
Dean [15]	1.4×10^{-10}	1.46×10^{-10}

be taken to mitigate ammonia loss and, accordingly, enhance economic performance.

Several studies have been performed to reduce ammonia loss in the processes. As a way, process and operating conditions have been improved to recover volatilized ammonia. For example, Zhuang et al. have added washing steps after absorption and regeneration processes [6]. Dave et al. have used the ASPEN^{TM} simulator to find optimum operating conditions [2]. Another way is to apply additives to ammonia absorbent. For examples, Pellegrini et al. have developed a hydro-alcoholic solvent by adding ethanol into aqueous ammonia [7]. You et al. have used sterically hindered amines [8]. As an inorganic additive, Mani et al. have found that Zn(II) ion is effective to reduce ammonia loss and to increase CO_2 absorption capacity, because Zn(II) ion forms complex ion with ammonia to prevent the volatilization of ammonia [9]. It should be mentioned that, despite these advantages, Zn(II) ion generates zinc carbonate and consequently causes scaling on packing materials in the absorption reactor. This eventually decreases absorption efficiency and increases pressure drop.

Cu(II) ion has the potential to overcome the limit of Zn(II) ion. Since Cu(II) ion is divalent ion of the transition metal, it can form complex ion with ammonia. Relative to Zn(II) ion, Cu(II) ion hardly forms scale because of high solubility: although literature presents the different values for the solubility product constants (K_{sp}) of copper and zinc carbonates (see Table 1) [10–15], the copper carbonate is similar or an order of magnitude higher than the zinc carbonate. Furthermore, Cu(II) ion can more stably form complex ion with ammonia than Zn(II) ion: the complex formation constant (K_f) of Cu(II) for ammonia (i.e., 1.0×10^{13}) is five orders of magnitude higher than for Zn(II) (i.e., 4.1×10^{8}) [16].

Thus, the objective of this study is to investigate the effects of Cu(II) ion as an additive on ammonia loss and CO_2 absorption to enhance the economic performance of ammonia-based processes. Continuous tests for absorption and regeneration are conducted with and without the addition of Cu(II) ion. The concentrations of ammonia, CO_3^{2-}, HCO_3^-, and NH_2COO^- are analyzed to examine the effects of Cu(II) ion on ammonia loss and CO_2 absorption capacity. Also, the scale generated in the system is analyzed to examine whether Cu(II) forms scale. This study can contribute to reducing economic costs of ammonia-based processes.

2. Process chemistry

2.1. CO_2 in aqueous ammonia

The CO_2 capture system consists of absorption and regeneration processes. For the absorption process, the overall reaction of CO_2 absorption by aqueous ammonia is as follows [1,17,18]:

$$NH_3(aq) + CO_2(g) + H_2O(l) \leftrightarrow NH_4HCO_3(aq) \quad (1)$$

With respect to more detailed reaction mechanism, CO_2 combines with ammonia, forming ammonium salts such as NH_4HCO_3 (ammonium bicarbonate), $(NH_4)_2CO_3$ (ammonium carbonate) and NH_2COONH_4 (ammonium carbamate) as follows:

$$CO_2(g) + 2NH_3(aq) \rightarrow NH_2COONH_4(aq) \quad (2)$$

$$NH_2COONH_4(s) + H_2O(l) \leftrightarrow NH_4HCO_3(aq) + NH_3 \quad (3)$$

$$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq) \quad (4)$$

$$NH_4HCO_3(aq) + NH_4^+(aq) + OH^-(aq) \leftrightarrow (NH_4)_2CO_3(aq) + H_2O(l) \quad (5)$$

$$(NH_4)_2CO_3(aq) + CO_2(g) + H_2O(l) \leftrightarrow 2NH_4HCO_3(aq) \quad (6)$$

These equilibriums have significant effects on the absorption and regeneration performance of ammonia-based processes. The high concentration of ammonia increases CO_2 absorption capacity [19]. The concentrations of ammonia and CO_2 have effect on the proportions of the ammonium salts generated in the solution: the low ratio of ammonia to CO_2 leads to an increase in the concentration of HCO_3^- [20].

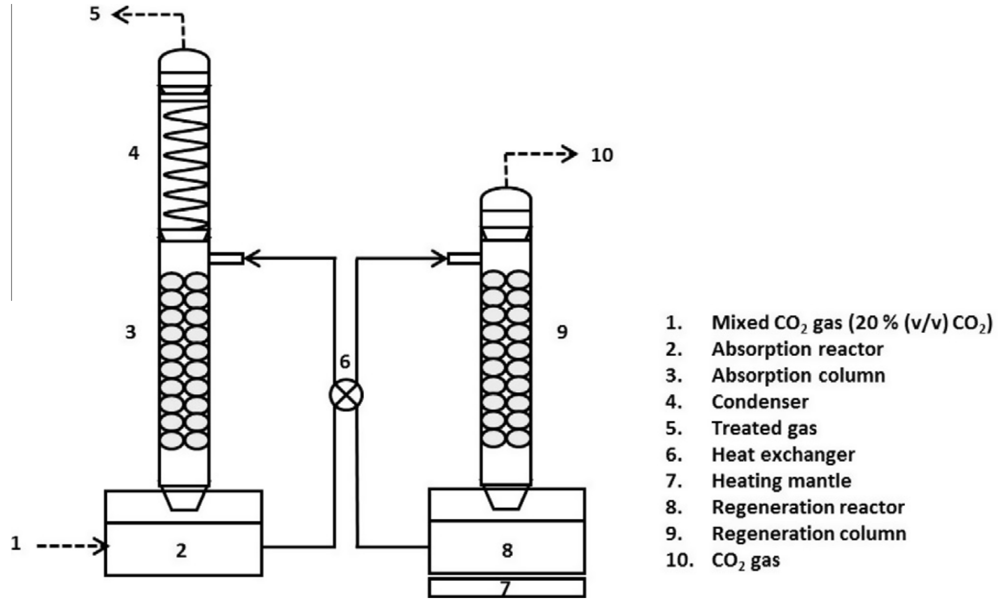

Fig. 1. Schematic diagram of the continuous CO_2 absorption process.