



Reducing aerosol and ammonia emission in post-combustion CO₂ capture: Additives as key solutions

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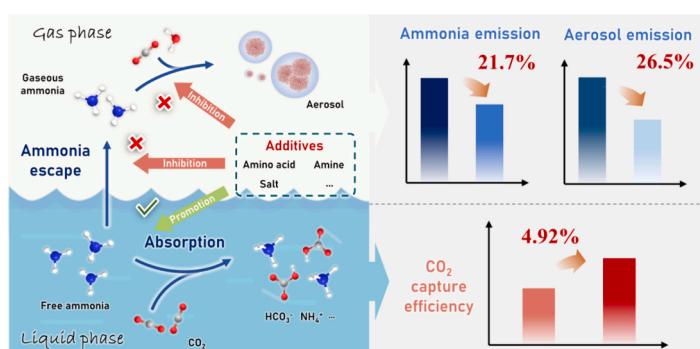
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HIGHLIGHTS

- Amino acids reduce ammonia emission of 21.7 % by protonation of free ammonia.
- Aerosol formation directly related to absorbent volatilization.
- Achieving emission reduction of 84.4 % for ammonia by combining water wash.
- Advocating ammonia reuse for desulfurization.

GRAPHICAL ABSTRACT



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ABSTRACT

Advancement of the absorbent for CO₂ capture is essential in optimizing the performance and reducing the negative environmental effects associated with this technology. Despite ammonia's promise as an absorbent, the volatility limits its practical application and creates potential environmental pollution. Therein, we assess various additives (amino acids, carbonates, and alkanolamines) for ammonia-based solvents using multi-stage circulation absorber from the viewpoints of aerosol emission, ammonia emission, and CO₂ capture efficiency. Experimental findings reveal that ammonia volatilization can be inhibited by the protonation of free ammonia by carboxyl groups and the formation of hydrogen bonding between amino/hydroxyl groups and ammonia, with ammonia emission reduced by 21.7 %, aerosol emission reduced by 26.5 %, and CO₂ capture efficiency increased to a maximum of 87.8 % under the condition of adding histidine. Moreover, the experiment highlights a positive correlation between total ammonia emission and aerosol concentration/diameter. Additionally, tests combining source abatement with water wash exhibit up to 50.5 % aerosol removal efficiency and up to 76.6 % ammonia

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removal efficiency. To further mitigate emissions, a comprehensive approach is proposed, achieving an 84.4 % reduction in ammonia emission and a 61.9 % reduction in aerosol emission. Finally, a method for recycling ammonia for desulfurization is suggested.

1. Introduction

The combustion of fossil fuels releases large quantities of greenhouse gases (GHGs), especially CO₂, into the atmosphere, causing temperatures to rise and contributing to the climate change (Ali et al., 2021; Cheng et al., 2022). Among numerous carbon capture technologies, post-combustion CO₂ capture (PCCC) by chemical absorption has been recognized as the most widely utilized and commercially viable carbon capture method due to its improved flue gas adaptability and higher capture efficiency (Orlov et al., 2021; Rochelle, 2009). Within this process, the selection of a suitable solvent plays a crucial role, as the performance of the process is strongly dependent on the properties of the solvent.

While monoethanolamine (MEA) stands as the prevalent absorbent owing to its rapid absorption and cost effectiveness, its challenges lie in its high degradation rate, corrosiveness, and substantial energy demands for regeneration, posing limitations on the technology's scalability (Amirkhani et al., 2023; Liang et al., 2016; Orlov et al., 2021). Hence, ammonia is frequently regarded as a promising absorbent due to its low price, mild corrosiveness and non-degradative properties (Darde et al., 2012; Wang et al., 2018).

Nevertheless, ammonia escape, leading to significant solvent loss, equipment clogging, and secondary environmental pollution, stands as a critical technical and economic challenge impeding the widespread commercial implementation of ammonia-based CO₂ capture technology (Zhao et al., 2012). According to the test results of PCCC plants of Alstom, CSIRO etc., the ammonia concentration escaping from the absorber outlet can reach >10,000 ppm (6953.0 mg/m³) (Han et al., 2013; Yu et al., 2011), which will far exceed the national standard in Korea (industrial exhaust gas NH₃ emission ≤50 ppm) (Li et al., 2014b) and the emission standards in China (NH₃ emission ≤3 mg/m³, HJ 2001—2018, China). Therefore, many studies have been developed to control ammonia emissions from PCCC systems. Several researches have also achieved ammonia escape suppression through process optimization, such as the chilled ammonia process developed by Alstom (Bak et al., 2015; Darde et al., 2009), which achieves <1 % ammonia loss, but also has significant energy costs associated with cooling. Our previous research also established a multi-stage circulation (MSC) absorber, which achieved solvent loss suppression for amine-based carbon capture through decoupled regulation of operating parameters, while still facing the problem of inherent volatility of solvents (Shao et al., 2023). As a result, additives have been of interest to researchers as a potential method to inhibit ammonia escape at the source.

Currently, candidates of inorganic additives, organic additives, etc. have been proposed by researchers to prevent ammonia slip, which feature different reaction mechanisms, such as complexation, hydrogen bonding, and so on. Li and Ma et al. (Li et al., 2014a; Ma et al., 2016) demonstrated that the incorporation of transition metal ion additives into solvents forms complexes with NH₃, resulting in a reduction of ammonia emissions by over 30.0 % in a bubbling reactor. However, this mechanism essentially reduces the concentration of free ammonia involved in CO₂ absorption, which can result in a decrease in capture efficiency (Li et al., 2017). Besides, the formation of hydroxides and carbonates from metal ions can cause clogging of the packing and piping, which can compromise the proper operation of the system (Li et al., 2017; Wang et al., 2018). Moreover, mixed salt solution for carbon capture, as a novel technology introduced by SRI (Jayaweera et al., 2014), realized the improvement of capture efficiency and reduction of ammonia escape by mixing ammonia and potassium carbonate solution, in which the principle of ammonia escape reduction and solvent ratio

are still worth exploring.

Organic additives are commonly employed in formulating blended solvents, playing a vital role in enhancing the performance of the primary absorbent. This enhancement stems from the significant impact of intermolecular interactions between the original absorbent and the additive on the physical-chemical properties of the blended absorbent (Ma et al., 2013a; Ma et al., 2013b; You et al., 2008). Therefore, alkanolamine, which has both hydroxyl and amino groups, has the potential to form hydrogen bonds with ammonia molecules, as well as to enhance CO₂ absorption, and was considered as the additive with potential application. Piperazine (Kang et al., 2013), 2-amino-2-methyl-1-propanol (AMP) (Jeon et al., 2013; You et al., 2008) were selected to inhibit ammonia escape, and the experimental results showed that ammonia emission could be reduced by 44.1 %. However, the ammonia emission reduction rates reported for the same additives in different literatures vary greatly, e.g., for the same 30 wt% of AMP, the ammonia emission reduction rate ranges from 27.4 % to 64 % in different studies. This may be due to the fact that the utilization of the aforementioned organic additives with NH₃ relies predominantly on weak physical intermolecular interactions, and the resulting weak bonds formed are sensitive to external variables (Wang et al., 2018), which leads to the fact that the experimental results in the bubbling reactor, wet-wall columns will be dramatically different from those in the absorber possibly. Besides, in the research on reducing ammonia escape from ammonia desulfurization, Yang et al. proposed the protonation of free ammonia through the carboxyl and phenolic groups of fulvic acid, which in turn led to a reduction in ammonia emission without affecting the absorption efficiency (Yang et al., 2016). Thus, amino acids, as additives with both amino and carboxyl groups, have been considered as a feasible method to inhibit ammonia escape and to improve absorption (Kim et al., 2022; Yang et al., 2016). For example, L-histidine, a common amino acid, has been studied for its preferable CO₂ absorption rate and cycling capacity (Hu et al., 2017), and its carboxyl group and three amino groups may be able to enhance CO₂ capture performance and reduce ammonia escape. Therefore, the selection of the appropriate additives and the verification of inhibition effect in the absorber still need to be investigated.

Furthermore, aerosol emission has emerged as a major form of absorbent escape with the application of equipment such as water wash device and demister, which has been reported in studies of ammonia-based desulfurization and amine-based PCCC (Huang et al., 2017; Shao et al., 2022; Yang et al., 2023). Pan and Huang et al. (Huang et al., 2020; Pan et al., 2016) investigated the aerosol formation and emission characteristics in an ammonia-based desulfurization system and indicated that non-homogeneous phase reaction of NH₃-SO₂-H₂O was the main contributor to the formation of aerosols, with the aerosol mass concentration up to the 10²–10³ mg/m³. Khakharia et al. (Khakharia et al., 2015) measured the aerosol emission from the PCCC system using MEA and found that the emission could be up to 1.7 × 10⁸ 1/cm³ in the presence of sulfuric acid aerosol, resulting in 1900 mg/m³ of amine emission. However, aerosol emission resulting from the NH₃-CO₂-H₂O system in the ammonia-based PCCC process are still lacking in studies. Besides, the above investigations on aerosol emission focused on heterogeneous condensation caused by condensation nuclei (e.g., dust, sulfuric acid aerosol, etc.) carried by the flue gas at the absorber inlet, and NH₃-induced homogeneous nucleation under ammonia emissions of over 10⁴ ppm in the ammonia-based PCCC process also needs further attention.

In this study, based on the above concept, with our unique MSC absorber, we investigated the effects of additives such as alkanolamines, amino acids and carbonates on ammonia and aerosol emissions, which

have not been investigated by others, and explored new absorbent formulations without decreasing CO₂ capture efficiency. The ammonia and aerosol removal performance in combination with water wash was also explored. This study provides new insights into the development of PCCC technology, which is significant for the decarbonization of combustion.

2. Materials and methods

2.1. Experimental system

A schematic of the MSC absorber is displayed in Fig. 1. The system consists of a pre-scrubber (0.1 m internal diameter (I.D.), spray tower), an absorber (0.1 m I.D., 2.0 m long, packed quartz glass column), and a desorption column (0.06 m I.D., packed quartz glass column). The MSC absorber comprises four stages arranged sequentially from bottom to top. Stages 1 to 3 of the MSC are dedicated to CO₂ capture, while the fourth stage functions to perform a water wash, capturing any escaping solvent. The desorption column with effective packing height of 0.9 m, is wrapped with external insulation to prevent heat loss. Metal wire gauze structured packings ($a = 700 \text{ m}^2/\text{m}^3$) are used for both the absorber and the desorption column.

The main stream of simulated flue gas is generated by an induced fan, the temperature of which is controlled by an electric heater at the inlet, and the gas flow rate is 5 m³/h in the experiments. The CO₂ concentration in the experiment is adjusted by a rotameter (accuracy of $\pm 20 \text{ mL/min}$). The solvent flow rate can be regulated by peristaltic pump (BT-600CA, Chongqing Jieheng Peristaltic Pumps Co., Ltd., China,

accuracy of $\pm 1 \text{ mL/min}$), which is used to realize the decoupled regulation of the liquid flow rate in each section.

2.2. Experimental and analytical method

2.2.1. Chemicals and materials

All chemicals utilized in the study were commercially available and employed without additional purification. Ammonium hydroxide (NH₄OH, 28 % NH₃ in H₂O, Sinopharm Chemical Reagent Co., Ltd., China) was used to prepare an aqueous solution of 3 M NH₃ with deionized water. N-methyldiethanolamine (MDEA, 98 %, Macklin Biochemical Co., Ltd., China), L-histidine (His, 99 %, Aladdin Biochemical Technology Co., Ltd., China) and Potassium carbonate (K₂CO₃, 99 %, Sinopharm Chemical Reagent Co., Ltd., China) were prepared as the absorbent additives in the experiment. High-purity CO₂ (>99 %, Linan Gas Co., Ltd., China) served as the gas source for the experimental setup.

2.2.2. Aerosol measurement

The electrical low-pressure impactor (ELPI⁺, Dekati Ltd., Finland), which has been demonstrated by many researchers to be reliable for aerosol (e.g., sulfuric acid aerosols, etc.) measurements (Fdez-Arroyabe et al., 2022; Ngohang et al., 2015; Saha and Irvin, 2017), was chosen for the purpose of measuring aerosol concentration and size distribution, with minimum detection limits of 450 1/cm³ (number concentration) and 0.05 mg/m³ (mass concentration). The impactor provided aerosol number and mass concentration data for 14 size fractions in real time. Also, to prevent the loss and growth of aerosols in the sampling line, the

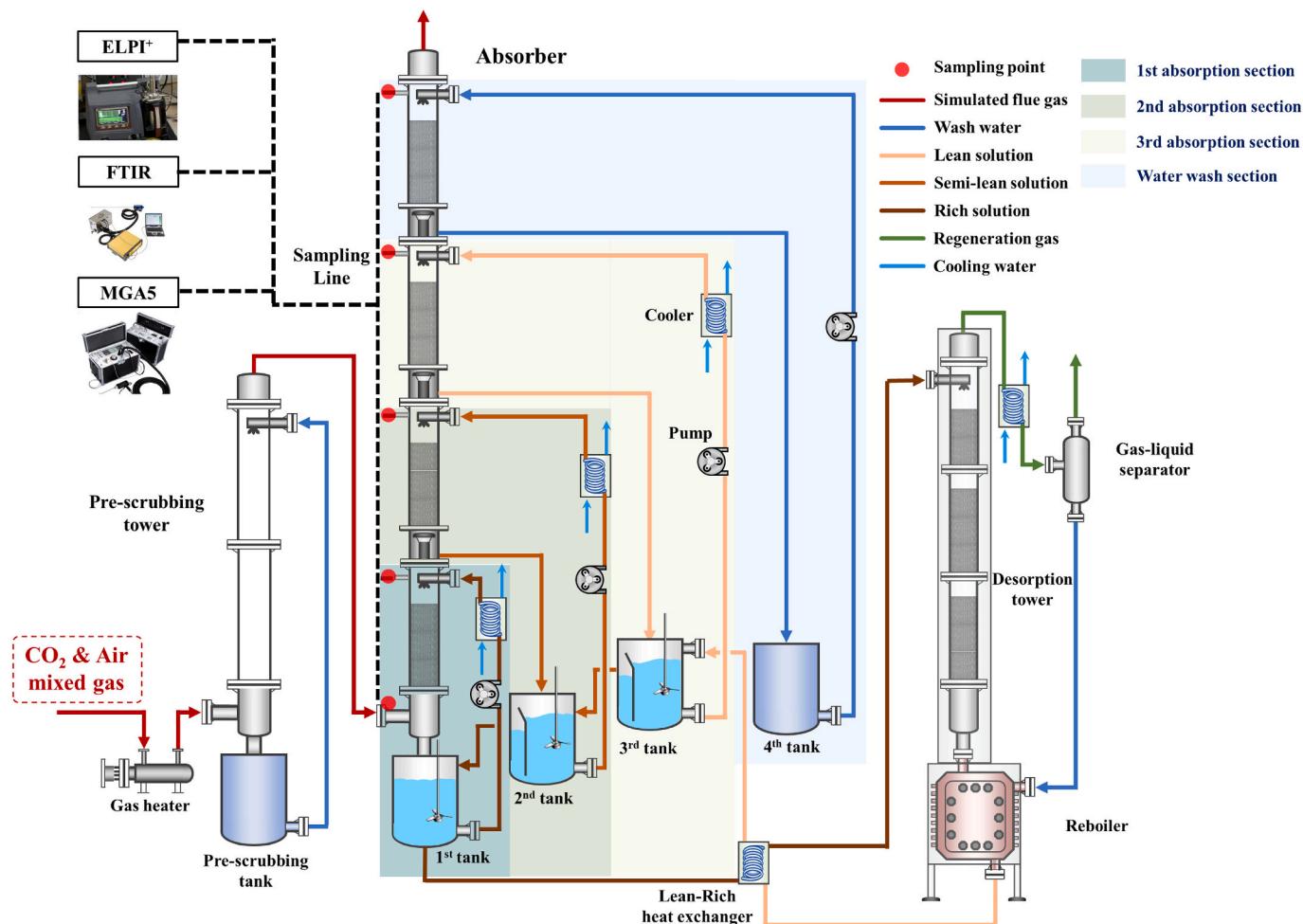


Fig. 1. Schematic diagram of the MSC absorber.

ELPI⁺ was set up near the sampling point and the temperature of the sampling system was kept constant with the flue gas temperature. Five replicate measurements were made under the same conditions for each experiment, with a sampling time of 60 s for each sample.

The aerosol removal efficiency computed from the aerosol mass concentration is as follows:

$$\eta_{\text{aerosol}} = \left(1 - \frac{m_{\text{outlet}}}{m_{\text{inlet}}}\right) \times 100\% \quad (1)$$

$$m(d_j) = n(d_j) \frac{\pi \rho_p}{6} d_j^3 \quad (2)$$

$$m = \sum m(d_j) \quad (3)$$

where m_{outlet} and m_{inlet} represent the aerosol-mass concentrations (mg/m^3) of the water wash section outlet and inlet measured by ELPI⁺, respectively, n is the aerosol number concentration ($1/\text{cm}^3$), d_j represents the aerosol diameter (μm) corresponding to level j , and ρ_p is the assumed-spherical aerosol density.

2.2.3. Gas analysis

In the case of CO₂ measurements, a non-dispersive infrared multi-gas analyzer (MGA 5, MRU, Germany, accuracy of $\pm 0.01 \text{ vol\%}$) was applied to measure the CO₂ concentration at each absorption section outlet as a means of identifying the CO₂ capture efficiency. During the experiments, with the aim of avoiding condensation of water/ammonia vapors in the measurement system, the probe was heated to 423 K and the sampling line was heated to 393 K. The CO₂ capture efficiency was calculated as shown in the following equation:

$$\eta_{\text{CO}_2} = \left(1 - \frac{n_{\text{CO}_2,\text{outlet}}}{n_{\text{CO}_2,\text{inlet}}}\right) \times 100\% \quad (4)$$

where $n_{\text{CO}_2,\text{outlet}}$ and $n_{\text{CO}_2,\text{inlet}}$ represent the CO₂ concentrations (vol\%) of the absorption section outlet and inlet, respectively.

In the case of ammonia measurements, a Fourier Transform Infrared gas analyzer (FTIR, DX4000, GASMET Ltd., Finland, accuracy of $\pm 0.1 \text{ ppm}$) was utilized to measure the ammonia concentration at the outlet of each stage, thus determining the variation of ammonia concentration in each absorption section and the ammonia removal efficiency by water wash. Both the sampling line and the sample gas chamber were heated to 453 K to ensure that there would be no interference from the liquid form, i.e., total ammonia emissions were defined as ammonia in the gaseous and aerosol form combined. The ammonia removal efficiency was calculated by the following equation:

$$\eta_{\text{NH}_3} = \left(1 - \frac{n_{\text{NH}_3,\text{outlet}}}{n_{\text{NH}_3,\text{inlet}}}\right) \times 100\% \quad (5)$$

where $n_{\text{NH}_3,\text{outlet}}$ and $n_{\text{NH}_3,\text{inlet}}$ represent the NH₃ concentrations (ppm) of each section outlet and inlet, respectively.

2.2.4. CO₂ loading of wash water analysis

For the measurement of CO₂ loading of the wash water, the Total Organic Carbon Analyzer (TOC-L CPN, Shimadzu corporation, Japan, accuracy of $\pm 4 \text{ }\mu\text{g/L}$) was used to measure the mass concentration of inorganic carbon (m_{IC}) and total nitrogen (m_{TN}) in the wash water to determine the CO₂ loading (α) of the wash water, which was calculated by the following equation:

$$\alpha = \frac{M_N \times m_{\text{IC}}}{M_C \times m_{\text{TN}}} \quad (6)$$

where M_N and M_C represent the molar mass of carbon atom and nitrogen atom, respectively.

3. Results and discussion

3.1. Changes in performance with the addition of additives

3.1.1. Ammonia and aerosol emission characteristics

Ammonia emissions from CO₂ absorption processes could be categorized into two main forms, gaseous and aerosol, both of which are directly related to ammonia volatilization from the solvent. As shown in Fig. 2 (a), ammonia volatilization is due to the process of diffusion of free ammonia in the solution on the surface of the liquid phase, which is transferred to the gas phase when approaching the gas-liquid interface. The volatilized gaseous ammonia is carried directly by the flue gas, such that the gaseous ammonia emission is formed. On the other hand, in a high humidity condition, ammonia molecules in the gas phase form clusters with H₂O and CO₂ molecules, resulting in homogeneous nucleation and then hygroscopic growth to form aerosols, which leads to the emission in the form of aerosols. In order to have a better understanding of this process, we explored the flow of CO₂ migration and ammonia escape at CO₂ concentration of 10.2 vol%, as shown in Fig. 2 (b) and (c). CO₂ was absorbed by the solvent counter-currently with the flue gas flow (which corresponds to process I in Fig. 2 (a)), and 87.98 % of the CO₂ was finally absorbed into the solvent. As for ammonia, the high temperature of the inlet flue gas and the absence of gaseous ammonia caused the higher mass transfer drive of free ammonia to the gas phase, and 55.73 % of the ammonia (8888 ppm, taking the ammonia concentration at the outlet of the 3rd stage as a reference) escaped to the flue gas, and then re-dissolved into the water in the water washing section, where the ammonia dissolved in the water absorbed part of the CO₂.

Through the above process, we found that in order to reduce the ammonia emission (corresponding to Process II in Fig. 2 (a)), it is crucial to solve the diffusion problem of free ammonia from the root. To this end, the reduction of the free ammonia concentration by enhancing the reaction with CO₂ or protonating the free ammonia could be the effective way, which requires the assistance of additives.

In this section, we have first tested the ammonia and aerosol emission characteristics of absorption section in the presence of various additives. Notably, in order to cover a wider range of combustion scenarios, we set the inlet CO₂ concentration to 5–30 vol% (e.g., the CO₂ concentration of the flue gas from marine diesel engine is about 5 vol%, the CO₂ concentration of the flue gas from coal-fired boiler is about 11–15 vol%, and the CO₂ concentration of the flue gas from the cement industry is about 30 vol%) (Baker et al., 2018).

As shown in Fig. 3 (a), the ammonia emission from the absorption section under the condition of 3 M NH₃ as absorbent was 10,261.3–18,899.2 ppm and decreased with the increase of CO₂ partial pressure. After adding L-histidine, a significant decrease in ammonia emission was observed. According to the molecular structure of L-histidine, the presence of the carboxyl group (-COOH) causes it to protonate free ammonia in the liquid phase to form NH₄⁺ upon the addition of ammonia solution, which reduces the ammonia emission. Interestingly, however, comparing the ammonia emission under 2 M NH₃ conditions, the emission with the addition of L-histidine was still lower than that of it, indicating that the reduction of ammonia emission is not only an effect of the carboxyl group. According to previous research, the amino group (-NH₂) also can interact with the ammonia molecule to form hydrogen bonding (Jeon et al., 2013), which becomes an influential factor in the reduction of ammonia escape, reducing the ammonia emission to 6203.9–13,195.8 ppm. Further, as shown in Fig. 3 (b), the hydrolysis of free ammonia to NH₄⁺ was inhibited by the alkaline nature of K₂CO₃ presented in the water after its addition, which in turn made the deterioration of ammonia escape, i.e., ammonia emission increased to 13,324.0–21,378.6 ppm. Moreover, hydroxyl group (-OH) has also been shown to form hydrogen bonds with ammonia in previous studies (You et al., 2008), and therefore, ammonia emission was reduced to 9720.8–17,002.1 ppm after the addition of MDEA (as shown in Fig. 3

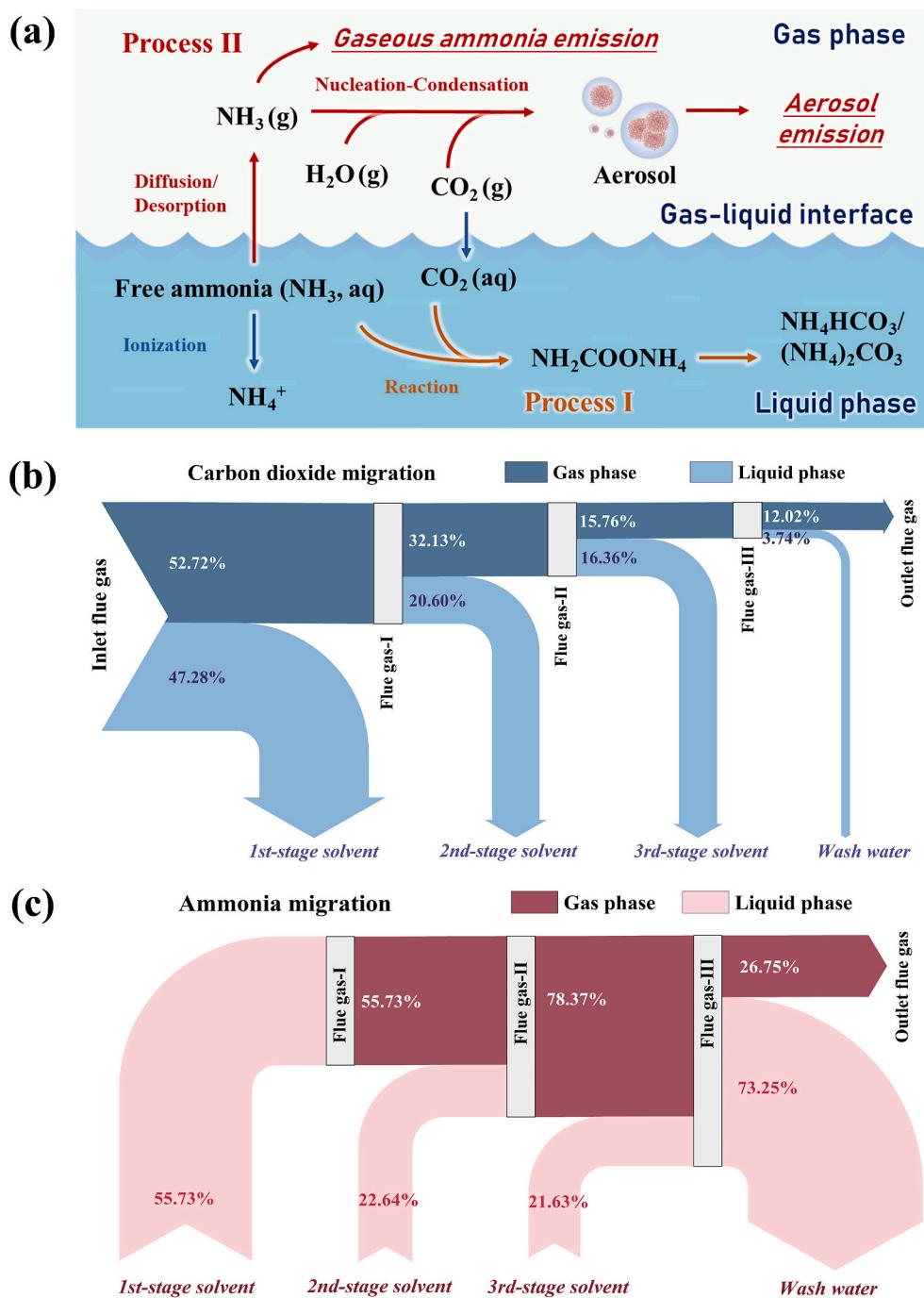


Fig. 2. (a) Schematic diagram of ammonia-escape from CO₂ capture process, (b) CO₂ migration in gas and liquid phase along the absorber, and (c) ammonia migration in gas and liquid phase along the absorber.

(c)). Furthermore, transport of CO₂ between different absorbent molecules also occurred within the mixed solvent, usually by the more reactive absorbent molecules reacting with CO₂ first, and the reaction products further reacting with less reactive absorbent molecules to achieve CO₂ transfer, i.e., the CO₂ “shuttle mechanism” (Luo et al., 2022). The reduction of ammonia emissions from MDEA also could be due to the transport of CO₂ within the solvent, which makes more free ammonia inclined to react with CO₂, thus reducing ammonia volatilization.

Meanwhile, the aerosol emission at the absorption section outlet under the effect of different additives was also explored. As shown in Fig. 3 (d), for instance, in the case of CO₂ concentration of 10.2 vol%, the number concentration of aerosols decreased after the addition of L-

histidine and MDEA, while the number concentration of aerosols above 0.1 μm decreased more significantly. After adding the K₂CO₃, the number of aerosols increased significantly, accompanied by a shift of the peak diameter to the right, and the total number concentration could reach $1.6 \times 10^5 \text{ cm}^{-3}$.

According to the test results of ammonia emission and aerosol emission, when the ammonia concentration at the absorption outlet was changed by the addition of additives, the number concentration of aerosols changed in a relatively similar pattern. Therefore, the correlation between ammonia and aerosol emissions was further explored with different additives. As illustrated in Fig. 3 (e), as the ammonia concentration at the outlet of the absorption section increased, the mass concentration of aerosols also increased, which increased to 103.2 mg/m³

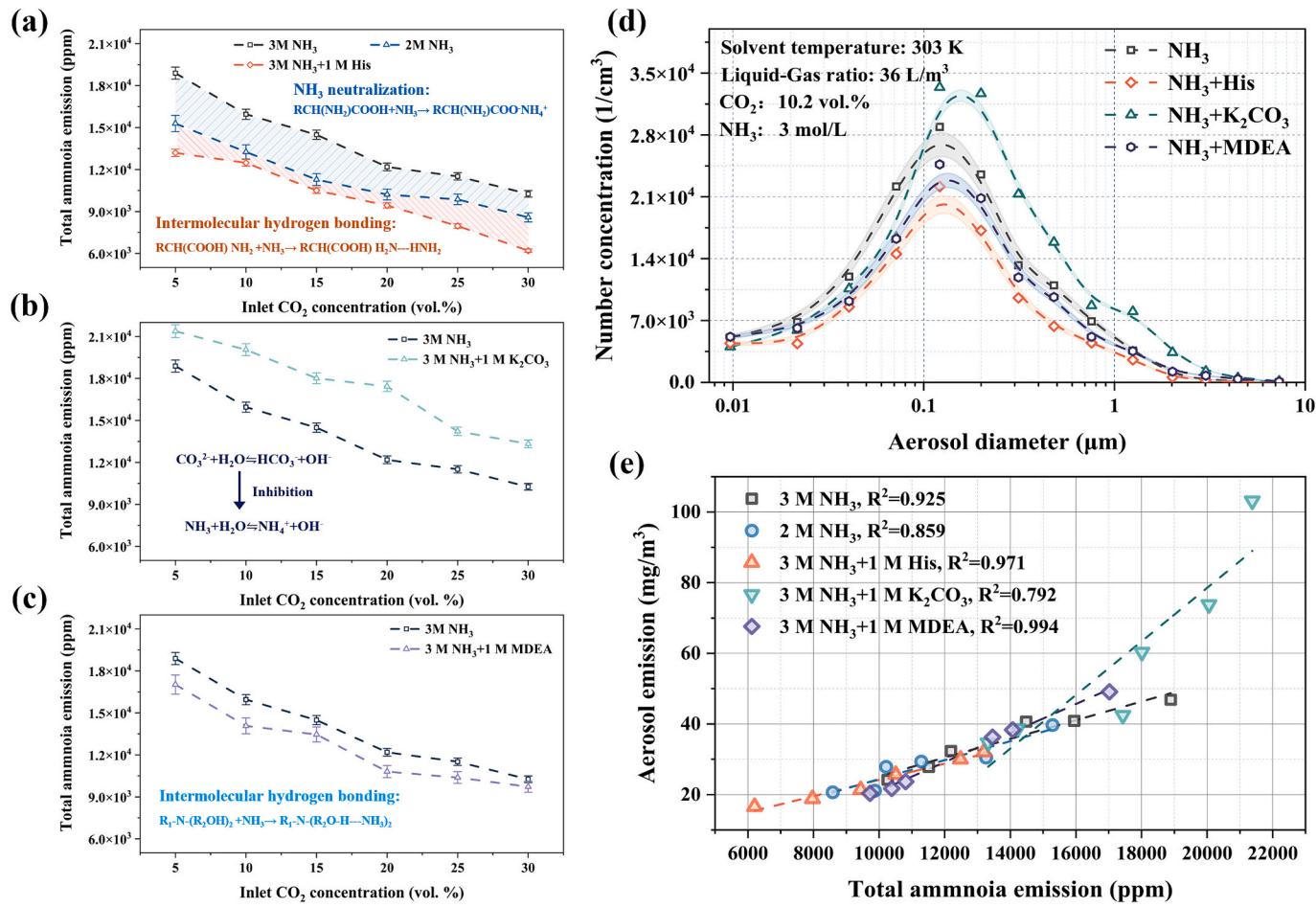


Fig. 3. (a) The impact of L-histidine addition on ammonia emission at the 3rd absorption section outlet, (b) the impact of K₂CO₃ addition on ammonia emission at the 3rd absorption section outlet, (c) the impact of MDEA addition on ammonia emission at the 3rd absorption section outlet, (d) variation in aerosol number concentration at the outlet of the third absorption section after additive addition, and (e) relations between total ammonia emissions and aerosol emissions with different additives.

when the ammonia concentration reached 21,378.6 ppm, i.e., there was a positive correlation between these two variables. And this phenomenon was not apparently related to the type of additives. This may be due to the ammonia-induced nucleation and accelerated mass transfer of ammonia to the aerosol phase, which led to an increase in the number of aerosols as well as the aerosol growth, which in turn led to an increase in the aerosol mass concentration. Besides, at further increase in ammonia concentration (3 M NH₃ + 1 M K₂CO₃), a noticeable lift in aerosol concentration occurred with increasing ammonia concentration.

3.1.2. CO₂ capture performance

In addition to the inhibition of ammonia escape, additives should be added with due consideration of the impact on CO₂ absorption. In general, the additives should not lead to a significant decrease in CO₂ capture efficiency, which would deviate from the initial purpose of post-combustion CO₂ capture. Hence, in this work, the CO₂ absorption performance of the additives was fully considered in the selection of additives to ensure that the capture efficiency would not be degraded.

Fig. 4 presents the variation of CO₂ capture efficiency under the effect of different additives. In the case of no additive (Fig. 4 (a)), the CO₂ capture efficiency of 3 M NH₃ was 76.0–86.9 %, and the capture efficiency decreased with the rise of CO₂ concentration. With the addition of L-histidine, although the presence of -COOH reduced the concentration of free ammonia that reacted with CO₂, the amino and imidazole groups inherent in L-histidine also participated in the CO₂ absorption, which improved the CO₂ capture efficiency to 78.8 %–87.8 % (Fig. 4

(b)). In the meantime, although K₂CO₃ increased the ammonia emission, the alkalinity of the solution would be increased, and more CO₂ would be reacted to HCO₃⁻, in which case the CO₂ capture efficiency would be increased to 79.0 %–90.4 %, indicating a more significant enhancement of the capture efficiency (Fig. 4 (c)). In addition, MDEA did not directly participate in the reaction with CO₂ absorption, but catalyzed the hydrolysis of CO₂ to HCO₃⁻, thus did not affect the reaction between ammonia and CO₂, just a linear superposition of two independent reactions, thereby increasing the CO₂ capture efficiency to 80.0 %–88.4 % after the addition of MDEA (Fig. 4 (d)).

According to the above-mentioned test results of ammonia escape and CO₂ capture under the effect of different additives, the enhanced performance of various additives compared with 3 M NH₃ was summarized in Fig. 5. The results show that the addition of amino acids or alkanolamines to the solvent could realize the reduction of ammonia escape and enhance the CO₂ capture efficiency, especially in the presence of L-histidine, the ammonia escape could be reduced by 21.7 % and the aerosol emission could be reduced by 26.5 %. Whereas simply reducing the ammonia concentration in solution could reduce ammonia emissions, the decrease in capture efficiency and the possible increase in regeneration energy consumption indicated that this method was not suitable.

Incidentally, although the addition of K₂CO₃ increased ammonia escape (25.8 % increase in ammonia emission and 80.6 % increase in aerosol emission), the enhancement of CO₂ capture efficiency was also noticeable, which made it possible to reduce the ammonia proportion in

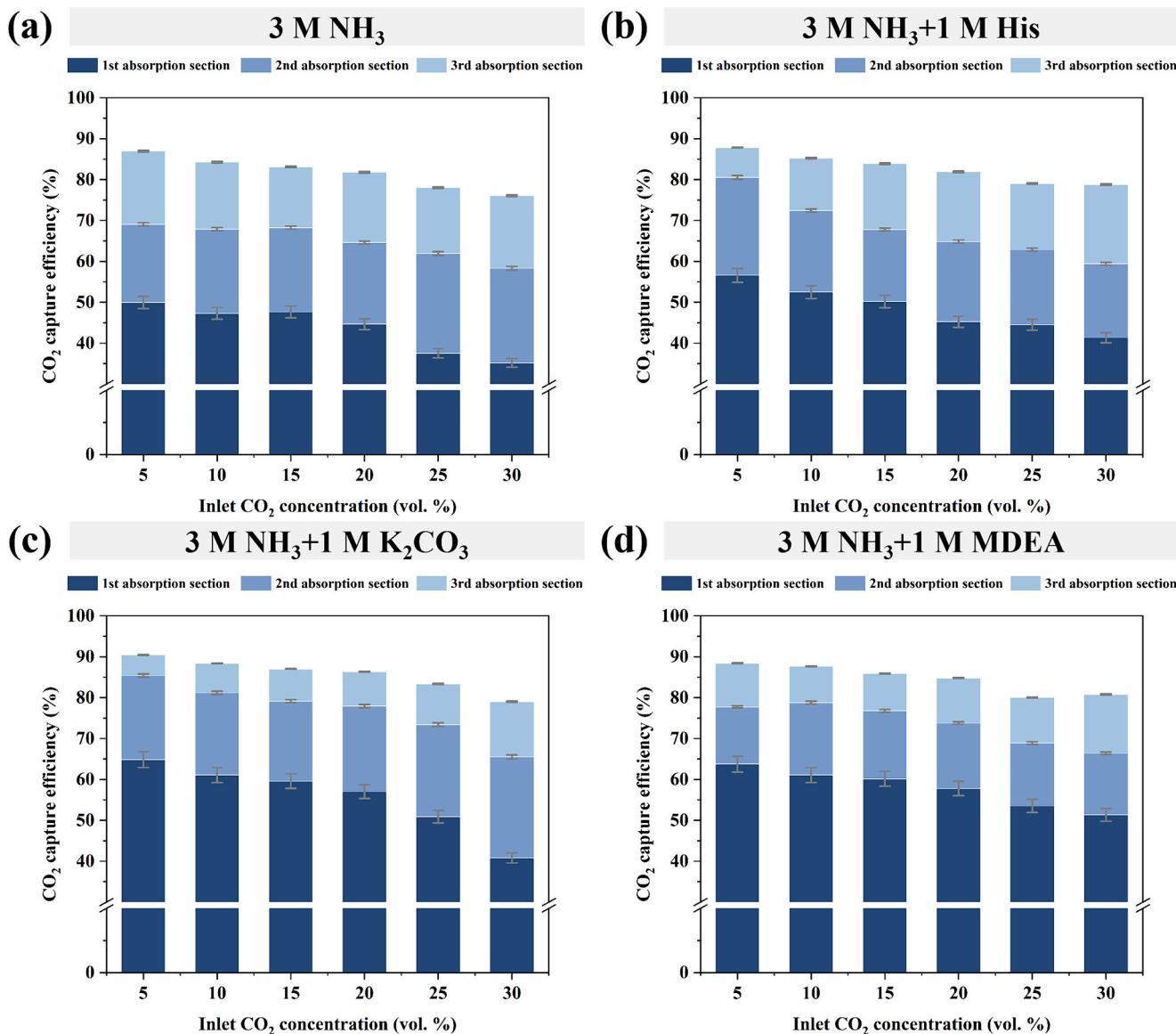


Fig. 4. (a) CO₂ capture efficiency of absorber with 3 M NH₃ only, (b) change in CO₂ capture efficiency after adding 1 M L-histidine, (c) change in CO₂ capture efficiency after adding 1 M K₂CO₃, and (d) change in CO₂ capture efficiency after adding 1 M MDEA.

the solvent with the addition of K₂CO₃. Meanwhile, K₂CO₃ does not have the oxidative and thermal degradation problems associated with organic additives. As a result, “NH₃+K₂CO₃” is a potential absorbent formulation if flue gas treatment can be utilized to effectively control ammonia escape.

3.2. Ammonia escape reduction by combining with water wash

On the basis of the test results of ammonia emission and aerosol emission in the absorber section, the ammonia emission was still over 6000 ppm even with the additives, which is considerably more than the emission limit requirement. Consequently, flue gas treatment after the absorber is essential. In this section, the ammonia escapes from the system after combination with water wash under the condition of applying different additives was explored and evaluated in terms of aerosol emission and ammonia emission, respectively.

3.2.1. Aerosol removal

Fig. 6 depicted the changes in aerosol emissions after the wash section in effect of different additives. With only 3 M NH₃, the aerosol mass

concentration after the water wash section was in the range of 14.2–25.4 mg/m³ (Fig. 6 (a)). Upon addition of L-histidine, the aerosol concentration at the absorber outlet decreased, which in turn caused the aerosol concentration at the outlet of the water wash section to decrease to 14.2–19.0 mg/m³ (Fig. 6 (b)), indicating that the addition of additives can reduce the aerosol mass concentration to a certain extent by combining with the water wash. Simultaneously, even though the mass concentration of aerosol at the outlet of the absorption section was greatly increased by K₂CO₃, the concentration of aerosol at the outlet of the water wash section was only increased to 19.4–51.0 mg/m³ (Fig. 6 (c)). Besides, the change of the aerosol concentration by the addition of MDEA was similar to that by the addition of L-histidine, while the decrease of the aerosol concentration in the water wash section was limited to 14.3–28.0 mg/m³ (Fig. 6 (d)). The above results showed that there was a limit to the aerosol removal performance by water wash. The results indicated that there is a limit to the aerosol removal performance by water wash, which can only reduce the aerosol mass concentration to 14 mg/m³ at most, and it is still necessary to consider a more efficient aerosol removal technology.

Given that the aerosol mass concentration at the water wash stage

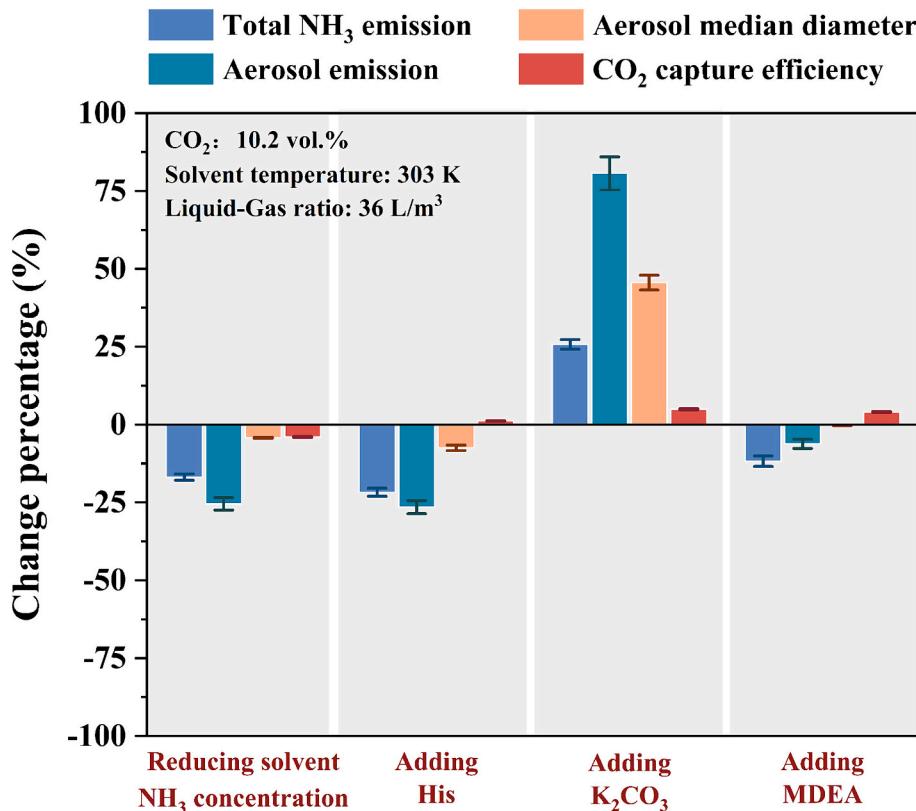
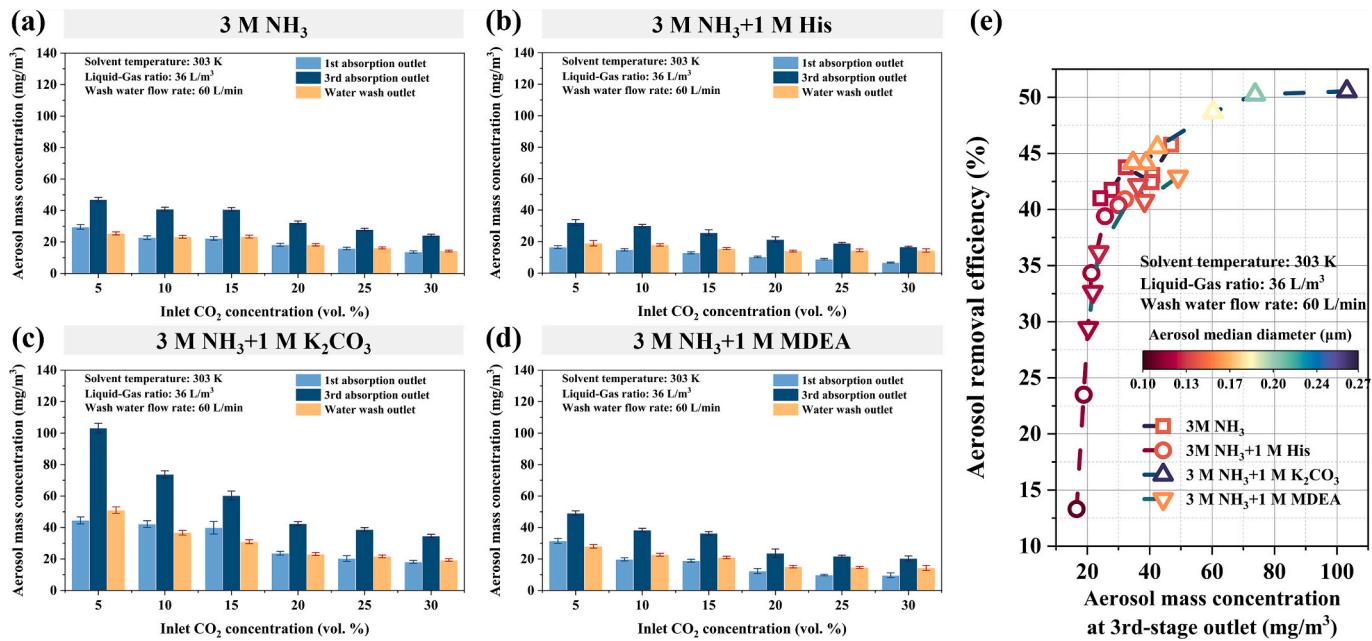


Fig. 5. Alterations in performance resulting from additive addition.

Fig. 6. (a) Aerosol removal performance with 3 M NH₃ only, (b) change in aerosol removal performance after adding 1 M L-histidine, (c) change in aerosol removal performance after adding 1 M K₂CO₃, (d) change in aerosol removal performance after adding 1 M MDEA, and (e) correlation of aerosol removal performance with aerosol concentration and size.

outlet was maintained above 14 mg/m³ for different additive additions, the relationship between the aerosol concentration, median diameter at the outlet of the absorption stage and the removal efficiency of the aerosol at the water wash stage was further explored. For the purpose of analyzing the correlation between aerosol size and removal efficiency,

the median aerosol size was obtained from the number concentration distribution of aerosols based on the arithmetic mean, which was calculated as follows:

$$\bar{d} = \frac{\sum n_j d_j}{n} \quad (7)$$

where n is the aerosol number concentration ($1/\text{cm}^3$), d_j represents the aerosol diameter (μm) corresponding to level j , and n_j represents the aerosol number concentration corresponding to level j .

As shown in Fig. 6 (e), the removal efficiency increased up to 50.5 % with the rise of aerosol mass concentration at the outlet of the 3rd stage. Moreover, there was a positive correlation between the removal efficiency of aerosols and their median diameter, i.e., the increase in aerosol mass concentration was strongly associated with the ammonia-induced aerosol growth, and the larger diameter made the aerosols more likely to be trapped under the effect of inertial interception. As a consequence, appropriate elevation of ammonia emissions will also facilitate ammonia recovery.

3.2.2. Total ammonia removal

Owing to the highly solubility of ammonia in water, water wash has been the most commonly applied treatment technique for the exhaust gas of the ammonia PCCC system. The ammonia removal performance of water wash with different additives was exhibited in Fig. 7. Results showed that in the absence of additives, the ammonia concentration after water wash was reduced from 10,261.3–18,889.2 ppm to 2868.0–4985.2 ppm, where ammonia removal efficiency was maintained at about 73 % (Fig. 7 (a)). In contrast, after the addition of L-histidine (Fig. 7 (b)) and MDEA (Fig. 7 (d)), the reduction of ammonia emission at the absorption section outlet did not lead to a noticeable improvement in the system's terminal ammonia emission, which was reduced to 1750.4–3519.0 ppm at most, and there still remained ammonia emission of the order of 10^3 magnitudes. For this reason,

extending the wash section or coupling with wet electrostatic precipitator would be necessary.

Additionally, although the addition of K_2CO_3 led to an increase in the ammonia concentration at the absorption section outlet, it was kept at a similar level to the other conditions with ammonia concentrations ranging from 3973.9 to 5000.6 ppm after the water wash (Fig. 7 (c)), which was attributed to an increase in the partial pressure of ammonia in the gas phase in the water wash section, causing an increase in ammonia dissolved in water, thereby improving the removal efficiency (up to 76.6 %).

Eventually, a comprehensive ammonia escape control method that combines from the source to the flue gas treatment was proposed. As shown in Fig. 8, the addition of amino acid additives reduced the ammonia emission by 21.7 % and aerosol emission by 26.5 %, and further combined with the unique decoupling regulation of multi-segment parameters of the MSC absorber (Shao et al., 2023) (lowering the liquid/gas ratio of the 3rd absorption section to 9.6 L/m^3 , increasing the liquid/gas ratio of the 1st absorption section to 14.4 L/m^3 , and keeping the total liquid/gas ratio constant), the ammonia emission could be lowered to 8652.8 ppm. Finally, by incorporating the water wash section, the ammonia emission of the system was decreased by 84.4 % and the aerosol emission was decreased by 61.9 %.

Notably, shown in Fig. 9, the wash water achieves a pH range of 9.1–9.12 after 300 min of system operation, accompanied by an increase in CO_2 loading to $0.45 \text{ mol CO}_2/\text{mol ammonia}$, which demonstrated the uptake of escaped ammonia and CO_2 by the wash water during operation. By monitoring the changes in pH and CO_2 loading during

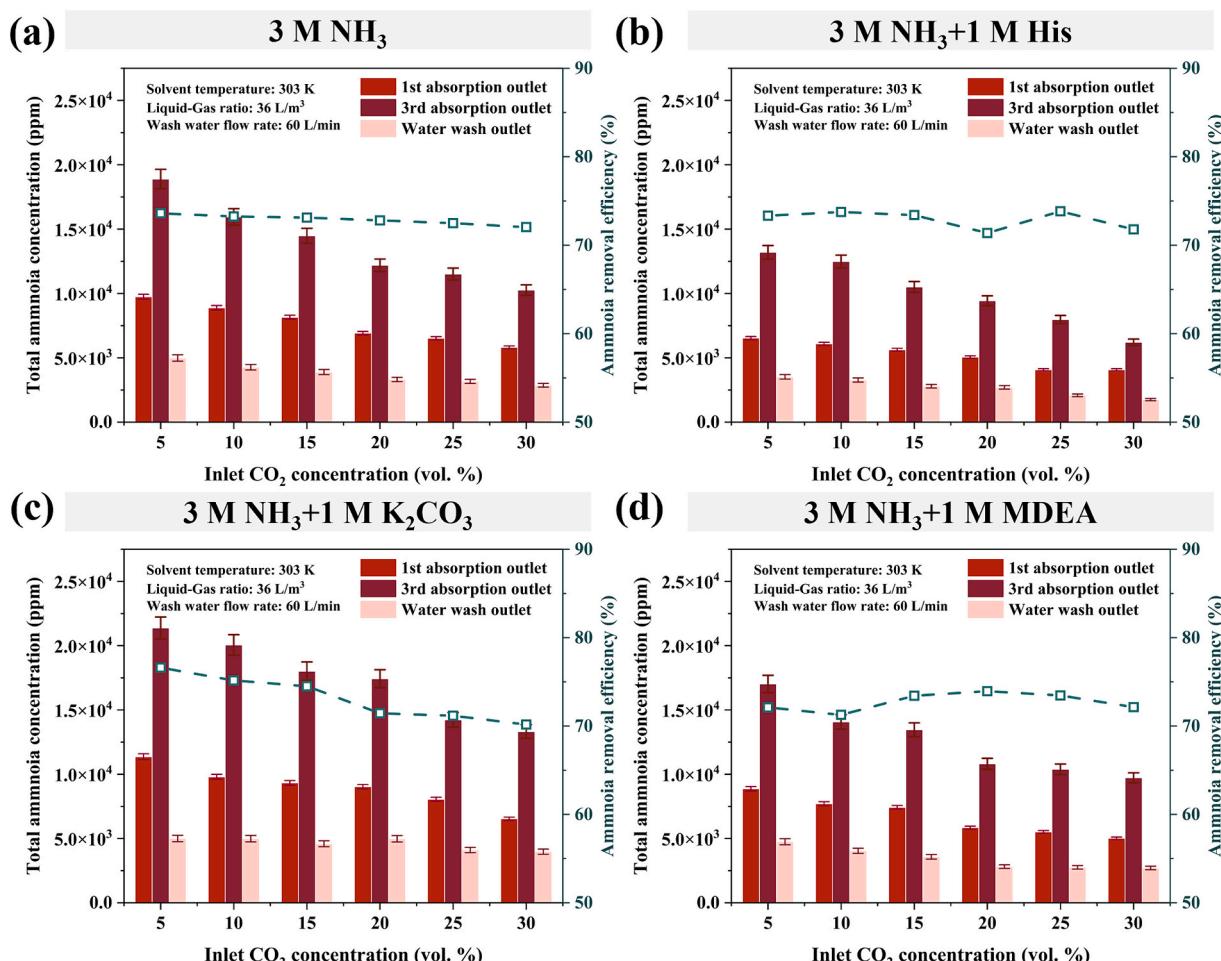


Fig. 7. (a) Ammonia removal performance with 3 M NH_3 only, (b) change in ammonia removal performance after adding 1 M L-histidine, (c) change in ammonia removal performance after adding 1 M K_2CO_3 , and (d) change in ammonia removal performance after adding 1 M MDEA.

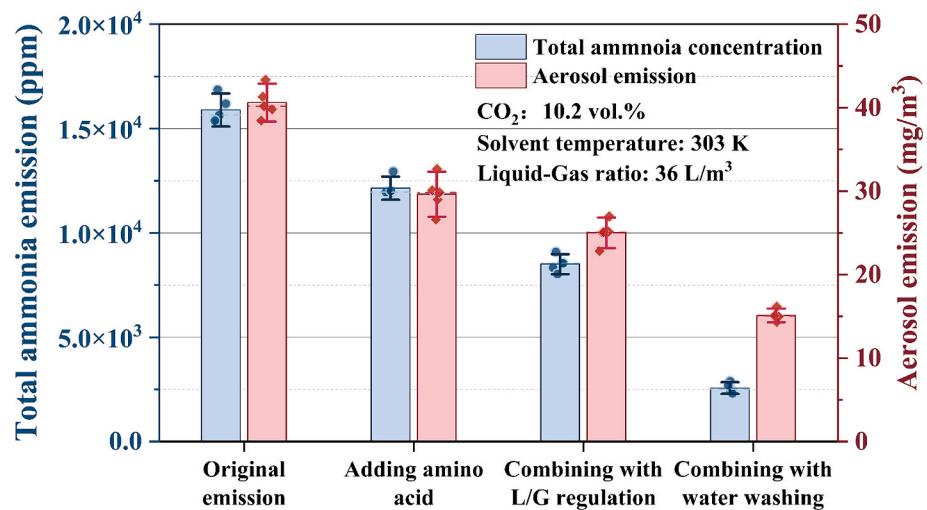
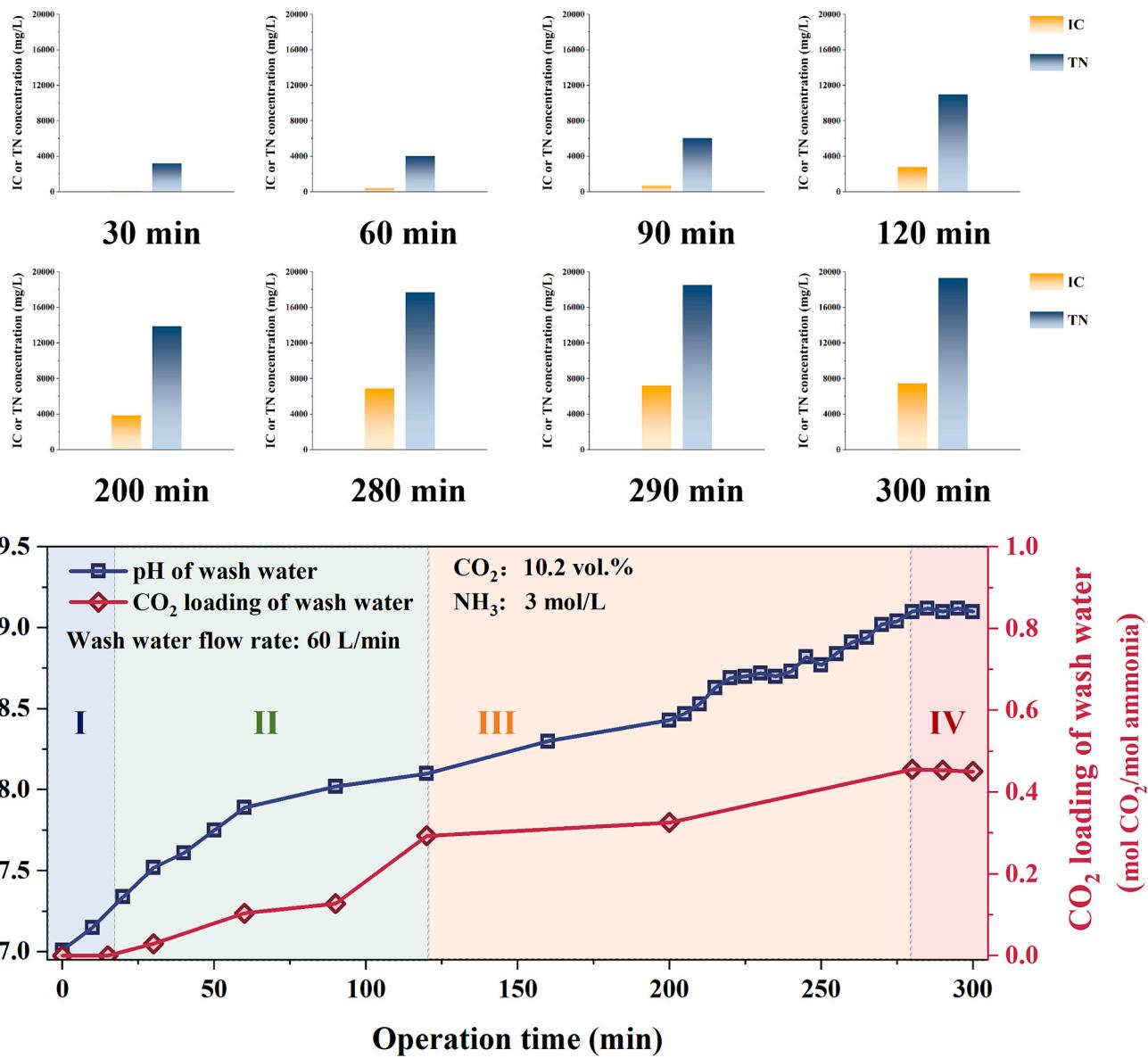


Fig. 8. Comprehensive emission control of ammonia and aerosols.

Fig. 9. Change in pH and CO_2 loading of the wash water.

operation, we identified four stages to stabilize the pH of the arrival water wash water. Firstly, the wash water first captured the ammonia escaping from the absorption process, resulting in an increase in pH without a significant change in CO₂ loading (Stage I). When the pH reached a certain value, CO₂ rapidly accumulated in the wash water, resulting in a rapid increase in CO₂ loading (Stage II). Subsequently, due to the low partial pressure of CO₂ in the flue gas after the absorption section, the CO₂ absorption capacity of the wash water would be limited, causing the accumulation of ammonia and CO₂ to reach a relatively steady state, with the pH still increasing and the CO₂ loading relatively stable (Stage III). Eventually, the pH and CO₂ loading of the wash water reached stable values (Stage IV).

Moreover, higher pH of washing water indicated a substantial ammonia content available for recycling. This solvent displays significant potential for desulfurization, as the required pH for desulfurization ranges from 5.0 to 7.0. Also, the stronger acidity of SO₂ would break down the HCO₃⁻ in solution, making some of the ammonia that had reacted with CO₂ potentially available. Consequently, a prospective avenue for advancing PCCC technology involves establishing a CO₂ and SO₂ co-removal system by utilizing recovered ammonia for desulfurization. This innovative approach aims to circumvent augmenting the current flue gas treatment process in coal-fired power stations, thereby reducing equipment and space costs for modifications. Additionally, it leverages existing equipment like wet electrostatic precipitators to recover escaped solvents, further curbing secondary pollutant emissions from the system. The findings of this study serve as a foundational step towards enhancing and proliferating PCCC technology.

4. Conclusions

Solving the ammonia solvent loss issue is vital to drive the development of environmentally friendly CO₂ capture technology. In this study, based on the established MSC absorber, the characterization of ammonia and aerosol emissions in the effect of different additives (amino acids, carbonates, alkanolamines, etc.) for ammonia solvents was investigated, and the main results are as follows:

1. L-histidine performed better in reducing ammonia emission and enhancing CO₂ capture efficiency in a comprehensive sense, reducing ammonia and aerosol emission by 21.7 % and 26.5 % respectively, through ammonia protonation and amino group provision. Conversely, potassium carbonate addition increased ammonia emission.
2. Aerosol emission positively correlated with ammonia emission, indicating volatile absorbents as the primary aerosol formation source in carbon capture systems, crucial for cluster formation.
3. Incorporating additives and post-absorber water wash reduced ammonia emission by up to 84.4 %. However, controlling aerosol emissions remains challenging, necessitating additional measures like wet electrostatic precipitation.
4. Wash water, exhibiting high ammonia concentration (>1 mol/L) and low CO₂ loading with a pH of 9.12, shows promise as a desulfurizer for future novel flue gas treatment system.

CRediT authorship contribution statement

Lingyu Shao: Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **Feng Xu:** Investigation, Methodology. **Zhicheng Wu:** Methodology, Visualization. **Chang Liu:** Conceptualization, Investigation. **Chengjin Pan:** Investigation, Methodology. **Yifan Wang:** Investigation, Visualization. **Zhengda Yang:** Conceptualization, Visualization. **Tao Wang:** Conceptualization, Writing – review & editing. **Longchao Yao:** Visualization, Writing – review & editing. **Chenghang Zheng:** Conceptualization, Funding acquisition, Writing – review & editing. **Xiang Gao:** Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Data availability

Data will be made available on request.

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