

Full Length Article

Aerosol emissions and mitigation of aqueous AMP/PZ solvent for postcombustion CO₂ captureLianbo Liu^a, Xiaojun Wang^b, Huanjun Wang^a, Tao Wang^{b,*}, Mengxiang Fang^b^a National Key Laboratory of High-efficiency Flexible Coal Power Generation and Carbon Capture Utilization and Storage & Beijing Key Laboratory of CO₂ Capture and Process, China Huaneng Group Clean Energy Research Institute, Beijing 102209, China^b State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

Aerosol emissions from the CO₂-capture process have a significant impact on both solvent depletion and environmental contamination. This work comprehensively investigated the emissions of AMP (2-amino-2-methyl-1-propanol)/PZ (piperazine) from a bench-scale platform and a CO₂-capture pilot plant. The concentration of nuclei in flue gas is a key factor affecting aerosol emissions, and a high nuclei concentration leads to more serious aerosol emission problems. The amine emissions after the absorber in the three different scenarios (no added nuclei, nuclei added, and pilot plant) were 273, 1051, and 1347 mg/Nm³, respectively. Increasing the lean-solvent temperature promoted aerosol emissions, and increasing the liquid/gas ratio and CO₂ loading in the lean solvent suppressed aerosol emissions. In the pilot plant, the effects of four mitigation measures were evaluated, and it was found that dry bed and acid washing had better mitigation effects than did conventional water washing; amine emissions could be reduced to as low as 21 mg/Nm³ PZ and 25 mg/Nm³ AMP. This study provides a reference for the design and optimization of carbon-dioxide-capture systems, which can help to reduce the impact on the environment.

1. Introduction

The adaptability, flexibility, and technological maturity of amine scrubbing have positioned it as the preferred technology for postcombustion carbon capture, especially for capturing carbon from coal-fired power plants. (Rochelle, 2009) However, when the amine solvent comes into direct contact with the flue gas in the absorber, the solvent and its degradation products are released into the atmosphere as vapors and aerosols, leading to secondary pollution and solvent loss (P. Khakharia et al., 2013; Li et al., 2021; Spietz et al., 2018). Amines and their degradation products, including ammonia (Buvik et al., 2021; Spietz et al., 2018) and nitrosamines (Toma et al., 2023), as well as other compounds such as aldehydes and ketones (Muchan et al., 2024), may be emitted from CO₂-capture plants.

Solvent emissions after an absorber can be divided into vapor-type and aerosol-type emissions. Many studies have shown that aerosol emissions, which are an order of magnitude greater than vapor emissions, are potentially significant. (Kamiyo et al., 2013; Khakharia et al., 2015; P. 2013; Maree et al., 2013; Mertens et al., 2014b) In general, aerosol emissions are typically produced through heterogeneous and homogeneous condensation processes. Mertens et al. (Mertens et al., 2014a) found that fine particles in the original flue gas enhanced aerosol formation and that a nuclei concentration of 10⁶ cm⁻³ was a critical value for

significant aerosol emissions. Amine emissions increase with increasing particle number concentration at the inlet of the absorber. (Dhanraj and Biswas, 2020) Khakharia et al. (Khakharia et al., 2015) measured MEA emissions in a range of 1000–2000 mg/m³ at lean-solvent temperatures of 40–80 °C through experiments conducted in a carbon-capture pilot plant. Fujita et al. (Fujita et al., 2014; K. 2013) found that only a small amount of aerosol was produced at high lean-solvent loadings and low CO₂ concentrations. The above studies have shown that aerosol formation and emissions are strongly influenced by the origin flue gas and operating parameters. Therefore, aerosol emissions during the CO₂ absorption process utilizing solvents such as monoethanolamine (MEA) can be effectively mitigated through the development of advanced manipulation techniques of operating parameters, which has not been further investigated.

To mitigate the release of amines and volatile compounds resulting from degradation, washing mechanisms, including water wash columns, acid scrubbing, and demisters, are employed. A water wash column is designed to eliminate vaporized amines after absorption, facilitating a moist, supersaturated environment that promotes particle coalescence and thus improves removal efficiency. Traditional demisters have limited efficiency in controlling particles with diameters <3 μm. Mitsubishi Heavy Industries (MHI) developed a multistage water wash system to reduce amine emissions and reduce solvent use by 25 %. (Kamiyo et al.,

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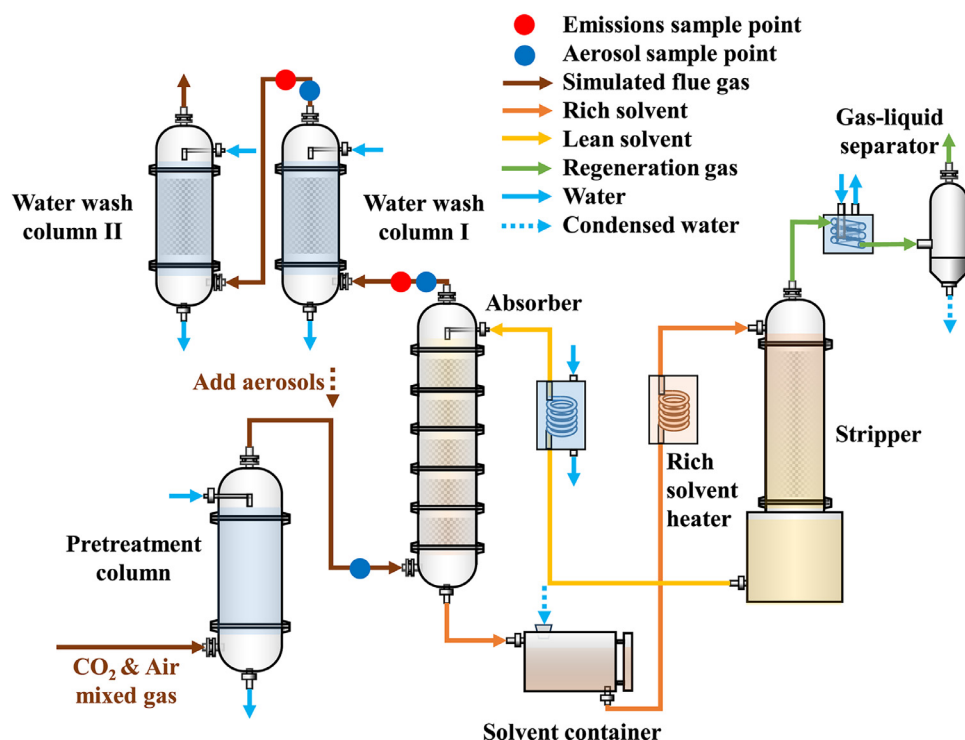


Fig. 1. Schematic diagram of the CO₂ chemical absorption test platform.

2013) Moser et al. (Moser et al., 2014) found that the dry bed at the top of the absorber column, which is minimally wetted by water washing, can significantly reduce emissions even with flue gas rich in ultrafine aerosol droplets. Aker Clean Carbon used a 10 % mass concentration of sulfuric acid solution for acid washing to reduce the pH of the wash water to 4–5, which reduced ammonia emissions from 4 ppm to 1 ppm and reduced the emissions of degradation products such as dimethylamine and methylamine. (Knudsen et al., 2013) Furthermore, intercooling processes designed for absorption enhancement may suppress the growth of aerosols. (Fulk and Rochelle, 2013; Majeed and Svendsen, 2018a) However, most studies have focused on single-stage water scrubbing, the most common configuration that has been tested in pilot plants and experimental setups, and the effect of amine emission control methods varies based on the distinct characteristics of individual plants. There remains a lack of research exploring the detailed characterization of amine aerosol emissions from facilities of different scales and the integration of diverse amine emission control methods within a single plant.

In this study, the emissions of AMP (2-amino-2-methyl-1propanol)/PZ (piperazine) were measured and compared between the bench-scale platform and the pilot plant using batch analytical methods. A preliminary examination of aerosol concentrations and evolutionary patterns in the bench platform was conducted by comparing emissions with and without the addition of nuclei. Through comparative analyses, the effects of original nuclei concentration, solvent temperature, liquid/gas ratio, and lean solvent CO₂ loading on aerosol growth and removal were evaluated, which provides a basis for optimizing amine emission control strategies. The effectiveness of the conventional water washing method, dry-bed method and acid washing method, employed individually or in combination, for solvent emission control in the pilot plant was discussed and compared. This research is crucial to the advancement of CO₂-capture systems and pollutant control technologies.

2. Experiments and methods

2.1. Experimental system

The bench-scale system simulated the entire CO₂ chemical absorption-desorption cycle and the process of purifying exhaust gas

with a pretreatment column, an absorber, a stripper, and two water wash columns. A process flow diagram of the platform is shown in Fig. 1. The absorber was divided into five sections, each packed with 0.24 m of high-specific surface area (950 m²/m³) packing (Φ6×6 Dixon ring). Compared with the same-scale experimental platform, this absorber had a longer gas residence time (~5 s) and a higher CO₂-capture rate (85–90 %). All columns were made of stainless steel, except for the top section of the absorber, which was made of plexiglass. Therefore, the contact of the scrubbing solvent with the flue gas could be directly observed. The two water wash columns were designed to capture and contain the escaping solvents. It is worth noting that no demister was installed at the top of the absorber or the water wash column, which differed from the pilot plant. A mixture of CO₂, air and aerosols was used to simulate real flue gas, and a pretreatment column was used to heat and humidify the flue gas. High-concentration aerosols were generated by a Laskin nozzle aerosol generator.

Fig. 2 depicts the process flow of the CO₂-capture pilot plant, which was employed for continuous monitoring of amine emissions and testing various control strategies, including a complete chemical absorption-desorption cycle. An oil-fired boiler was used to generate postcombustion flue gas. The absorber was divided into two sections, each equipped with structured packing, and an in-and-out intercooler was arranged between Absorber I and Absorber II. After countercurrent contact with the lean solvent in the absorber, the flue gas entered the amine emission control section, and different measures (water wash, dry bed, acid wash and demister) were applied individually or in combination to minimize amine emissions, capture aerosols and droplets, and recover escaping solvents from the treated flue gas.

2.2. Operation parameters

The solvent used in this test was 2.6 M AMP (2-amino-2-methylpropan-1-ol)/1.3 M PZ (piperazine). AMP (95 %, 5 % water) and PZ anhydrous (≥99.5 %) were obtained from Baiju Technology Limited Co., Nanjing, China, and were used without further purification. The piperazine fragments were dissolved in preheated water and then mixed with AMP. The final concentration of the solvent was analyzed using cation ion chromatography (Thermo Scientific, Dionex Aquion,

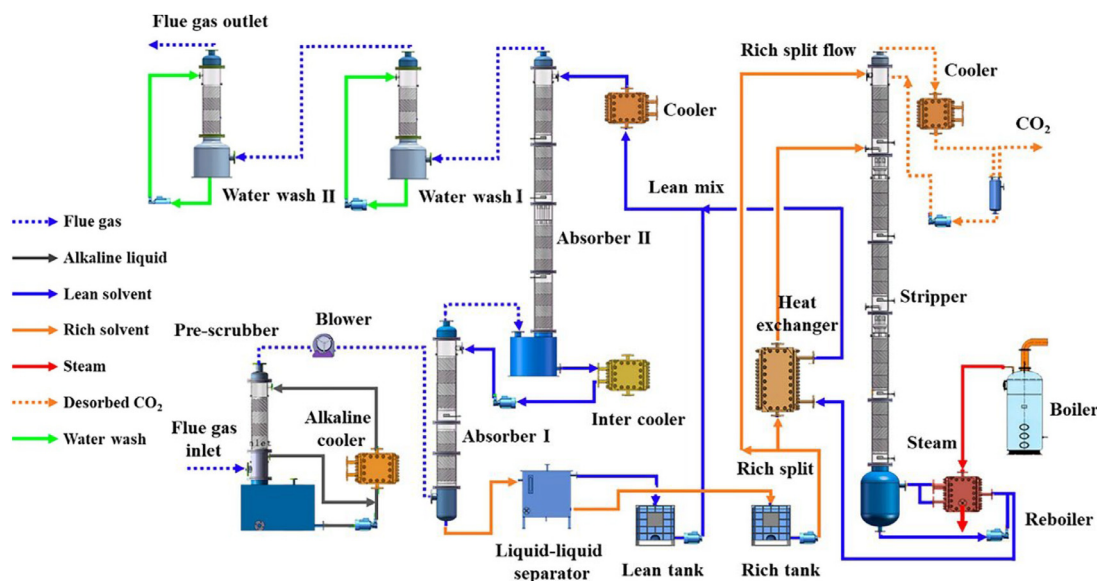
Fig. 2. Process flow diagram of CO₂ capture pilot plant.

Table 1
Summary of operating parameters under basic conditions.

Parameter	Bench-scale platform	Pilot plant
Amine concentration (mol/L)	2.6 M AMP /1.3 M PZ	2.6 M AMP /1.3 M PZ
Flue gas rate (m ³ /h)	3.6	280–290
Gas inlet temperature (°C)	40	42
CO ₂ in flue gas (%)	12.0 (dry basis)	11.6 (dry basis)
Lean solvent flow rate (m ³ /h)	0.036	0.8
Lean solvent temperature (°C)	40	40
Lean solvent loading (mol CO ₂ /mol amines)	0.25	0.29
Water wash flow rate (m ³ /h)	0.036	0.9
Water wash temperature (°C)	40	38–40
Absorber temperature (°C)	41–48	56–65
Stripper temperature (°C)	100–102	87–100
CO ₂ removal efficiency (%)	85–90	88–93
Intercooling temperature (°C)	–	40

ICS-5000). CO₂ (>99 %, Jingong Gas Co., Ltd., Hangzhou, China) was applied as the gas supply for the bench-scale system. The aerosols were generated by a Laskin nozzle aerosol generator (Huifen 3321 plus, China) with a 5.0 wt.% NaCl solution at a pressure of 0.10 MPa.

For the bench-scale platform, the flue gas CO₂ concentration was controlled by a gas mass flowmeter with an accuracy of ± 20 mL/min. The lean-solvent flow rate and water wash flow rate were adjusted by peristaltic pumps with an accuracy of ± 10 mL/min. For the pilot plant, the flue gas rate was measured using a V cone flow meter with an accuracy of ± 0.1 % (full scale). The amine solvent flow rate was measured using an electromagnetic flow meter with an accuracy of ± 0.5 % (full scale).

For both the bench-scale platform and pilot plant, data on the flue gas rate, amine solvent rate, temperature, and pressure were acquired in the control system. An infrared gas analyzer (GHX-3010E1, Beijing Huayun Company, China) was used to measure the CO₂ concentration of the absorber gas outlet with an accuracy of ± 2 % (full scale). Table 1 provides information on the test parameters (basic configuration). CO₂ loading in the amine solvent was determined using an acid-base titration method.

2.3. Measurement methods

Batch analytical methods were used to measure the concentrations of amines in the flue gas. The sample points were set at the gas outlet of the

absorber and the outlet of the two water wash columns. The sampling gas from the isokinetic sampling probe was heated to 120 °C to vaporize droplet-state amines and water. There were two bubblers filled with 1 mol/L H₂SO₄ solution in an ice-cooled water bath. When the heated gas passed through the bubblers, most amines were condensed and reacted with the sulfuric acid solution to form salts. The solution samples in the bubblers were weighed and analyzed by a Dionex Aquinon IC with a Dionex IonPac CS17 analytical column (4 × 250 mm). The analysis results showed that the amine concentration of the second bubbler was <1 % of that of the first bubbler, indicating that the bubbler has very high efficiency in collecting amine.

An ELPI+ (Dekati, Finland) was used to measure the nuclei distribution in the flue gas. The impactor provided real time (10 Hz) data on aerosol number and mass concentration with 14 size fractions. The sample gas was directly measured without dilution to avoid droplet shrinkage. The accuracy of the measurement was evaluated prior to the normal investigation. In the high-nuclei scenario, the particle density was still in the range of the ELPI+. The measurement time was controlled within 5 min. Five replicate measurements were conducted under identical conditions, each with a sampling duration of 60 s. Furthermore, the sample line and ELPI+ were kept at the same level as the flue gas temperature with a heating cover to ensure the accuracy of the aerosol measurements.

In this research, the aerosol size and mass distribution are expressed as $D_p - dN/d \log D_p$ and $D_p - dM/d \log D_p$, which can be expressed by

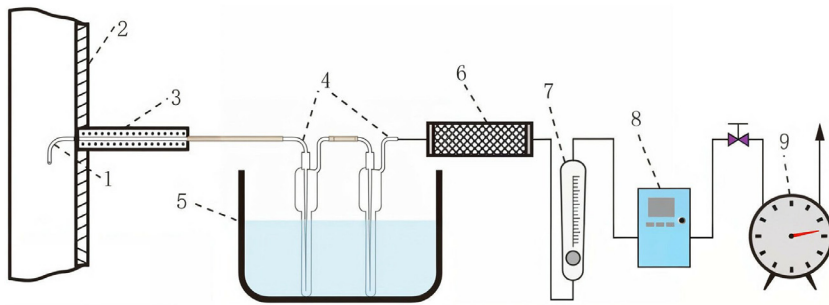


Fig. 3. Amine emission measurements (1: sample point, 2: gas channel, 3: heated line, 4: bubbling absorber, 5: ice-water bath, 6: silica gel drying tube, 7: rotor flow meter, 8: gas sample pump, 9: cumulative gas flow meter).

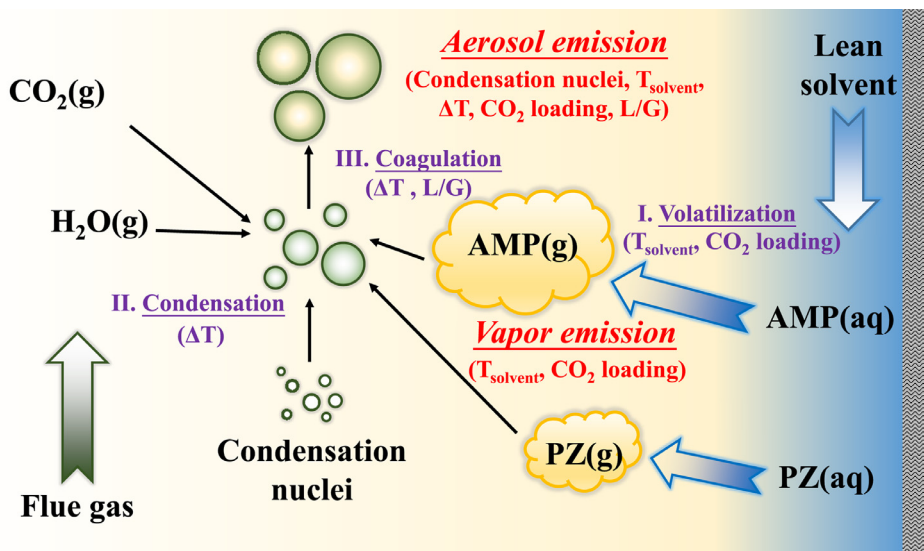


Fig. 4. Schematic of aerosol emission formation in the absorber and its potential influences.

the following equations

$$\frac{dN}{d \log D_p} = \frac{\Delta N}{\log D_{i,up} - \log D_{i,low}} \quad (1)$$

$$\frac{dM}{d \log D_p} = \frac{\Delta M}{\log D_{i,up} - \log D_{i,low}} \quad (2)$$

where N is the aerosol number concentration ($1/\text{cm}^3$), M is the aerosol mass concentration (mg/m^3), D_p is the aerosol diameter (μm), and $D_{i,up}$ and $D_{i,low}$ represent the upper and lower diameters (μm) for a certain size range, respectively Fig. 3.

3. Results and discussion

3.1. Aerosol emission characteristics under basic conditions

Sulfuric acid, soot and other condensation nuclei in the flue gas provide the core of the condensate transfer process of the condensable gases in the absorber, which may lead to high aerosol emissions. As shown in Fig. 4, the process of CO_2 absorption entails the volatilization of the amine from the liquid phase to the gaseous phase, which is influenced by factors such as the volatility of the amine, solvent temperature and CO_2 loading. Subsequently, gaseous amines, CO_2 , and water vapor migrate towards the surface of the condensation nuclei, primarily driven by the temperature difference between the gas and liquid phase. As amines and CO_2 continue to accumulate in the aerosol, the salt concentration in the aerosol particles rises and water vapor is transferred from the gas to the aerosol to reach the water balance. This phenomenon of salt accumulation and water replenishment results in continuous aerosol growth. Meanwhile, collision and coagulation also occur among aerosols, resulting in the formation of high aerosol emissions. In the water washing

section, fully grown aerosols are captured by droplet collisions and inertial interception, while the rest will be discharged.

Based on the above analysis, in this work, as shown in Fig. 5a, b, the amine emissions with and without added condensation nuclei were compared and discussed. The amount of amine emissions in the flue gas increased as follows: no nuclei added (bench-scale) < nuclei added (bench-scale) < pilot plant. The absence of nuclei in the flue gas resulted in a negligible quantity of nuclei, and the total amine emissions were closely approximated by vapor emissions. The amounts of PZ and AMP in the emissions were 47 and 226 mg/Nm^3 , respectively, after the absorber and both were 8 mg/Nm^3 after the water wash column. After adding nuclei, the amine emissions increased rapidly both before (from 273 to 1051 mg/Nm^3) and after the water wash column (from 16 to 97 mg/Nm^3), which indicated that aerosol-based emissions were generated.

Fig. 5c, d illustrates the variation in the aerosol particle size distribution and mass distribution in the absorber and water-washing columns. When no additional nuclei were added, condensation nuclei were formed from the water vapor in the flue gas by homogeneous condensation following pretreatment. These nuclei were concentrated in a diameter range of 0.01–1 μm , with a concentration of $1.6 \times 10^5 \text{ cm}^{-3}$. Upon entering the absorber, the coagulation and condensation of these condensation nuclei resulted in a notable reduction in the number of small aerosols (<1 μm), and the number of larger aerosol size segments (> 1 μm) increased. This suggests considerable growth of aerosols, which became more apparent with the addition of additional nuclei. In the scenario involving nuclei, the initial nuclei concentration at the inlet ($4.8 \times 10^6 \text{ cm}^{-3}$) was similar to that of the pilot plant ($4.1 \times 10^6 \text{ cm}^{-3}$), as evidenced by the comparable levels of amine emissions at the outlet of the absorber. After the absorber, the aerosol peak size shifted from approximately 0.06 μm to the right to approxi-

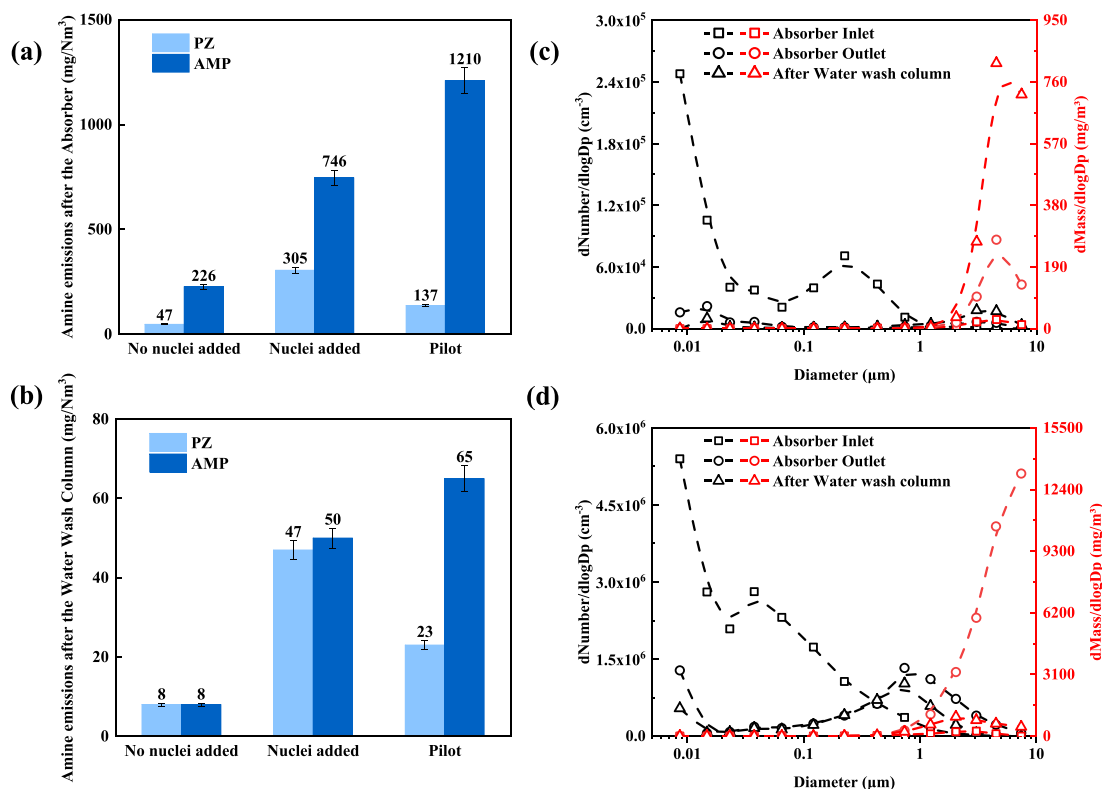


Fig. 5. (a) Amine emissions under three scenarios: basic conditions after the absorber, (b) basic conditions after the water wash column, (c) change in the aerosol number and mass distribution in the case of no added nuclei (bench-scale platform), and (d) change in the aerosol number and mass distribution with the involvement of additional nuclei (bench-scale platform).

mately 1 μm. Fujita (Fujita et al., 2017) also noted that the peak diameter of aerosol particles transitioned from the range of 60 to 100 nm to 1.5–3.5 μm as the flue gas was processed through an absorber and two water wash columns. In the water wash column, without the involvement of additional nuclei, the aerosols grew further, and the proportion of large aerosols increased. The opposite was observed with the addition of extra nuclei, where the aerosols grew large enough to be intercepted and the number concentration decreased significantly. The results of mass concentration tests were the same as those of number concentration tests. In the absence of added nuclei, the aerosol mass gradually increased after the initial simulated flue gas (14 mg/Nm³) passed through the absorber (103 mg/Nm³) and water-wash columns (382 mg/Nm³). However, once the original flue gas carried nuclei, a surge in aerosol mass occurred after the absorber (from 155 to 7211 mg/Nm³). The interception and capture of large droplets by the water wash contributed to the reduction in the aerosol mass concentration, which was 735 mg/Nm³ at the outlet of the water-wash column.

In the absence of added nuclei, after pre-scrubbing, a limited number of condensation nuclei were formed by homogeneous condensation of water vapor in the flue gas due to gas cooling. However, the quantity of these nuclei was insufficient to generate aerosol emissions. In other words, in the scenario with only homogeneous nucleation, the aerosols lacked significant growth in absorber and water wash column. In the scenario involving additional nuclei, compared to amine emissions, the increase in aerosol mass is significantly faster. This indicated that coagulation was the primary process in the absorber, rather than condensation, which increased the aerosol mass concentration through non-homogeneous phase coagulation and mass transfer. Although aerosols continued to grow during the water-washing process, they tended to be intercepted after reaching a sufficiently large size. Comparing the emissions with and without the addition of nuclei, it is obvious that reducing aerosols in flue gas is the most direct way to control amine

emissions after an absorber and water wash column. The ideal existing coal-fired power plant to retrofit with amine scrubbing will be a plant having established means of flue gas purification to reduce aerosols to a minimum.

The difference in emissions between AMP and PZ in the bench-scale platform and pilot plant may have been due to the variations in the intensity of chemical reactions and the ambient environmental conditions. As shown in Fig. 6, in the pilot plant, the duration of gas scrubbing was extended, and more intense chemical reactions and higher overall absorber temperatures resulted in high volatility of AMP dominating the emissions. Due to the CO₂ capture pilot test being conducted in summer when the ambient temperature was above 35 °C, and limited by the ambient temperature as well as the cooling water flow rate in the lean cooler and intercooler, further reduction of the absorber temperature was constrained. However, emission differences narrowed after the water wash column, probably due to the effect of the volatility of the amine and its proportion in the solvent on the distribution in the aerosol. The removal rate of AMP was found to be greater than that of PZ, and one might posit that gaseous AMP was more readily removed from the water wash. In the pilot plant, a demister-equipped water wash column showed improved aerosol removal efficiency.

The above study presents a preliminary investigation of aerosol concentrations and evolutionary patterns in a bench-scale platform. In general, the concentration of nuclei in the flue gas of coal-fired power plants is as high as 10⁷–10⁸ cm⁻³ prior to pretreatment. After the application of ultralow emission technology, including desulfurization, denitrification and dedusting (PM<5 mg/Nm³), the concentration of condensation nuclei remains within a range of 10⁵–10⁷ cm⁻³ (Harsha et al., 2019; Zhang, 2019). One of the most effective strategies for reducing solvent loss and amine emissions is to impede the further growth of aerosols in the absorber. Thus, it is necessary to understand the processes involved in aerosol formation and the factors that influence this process.

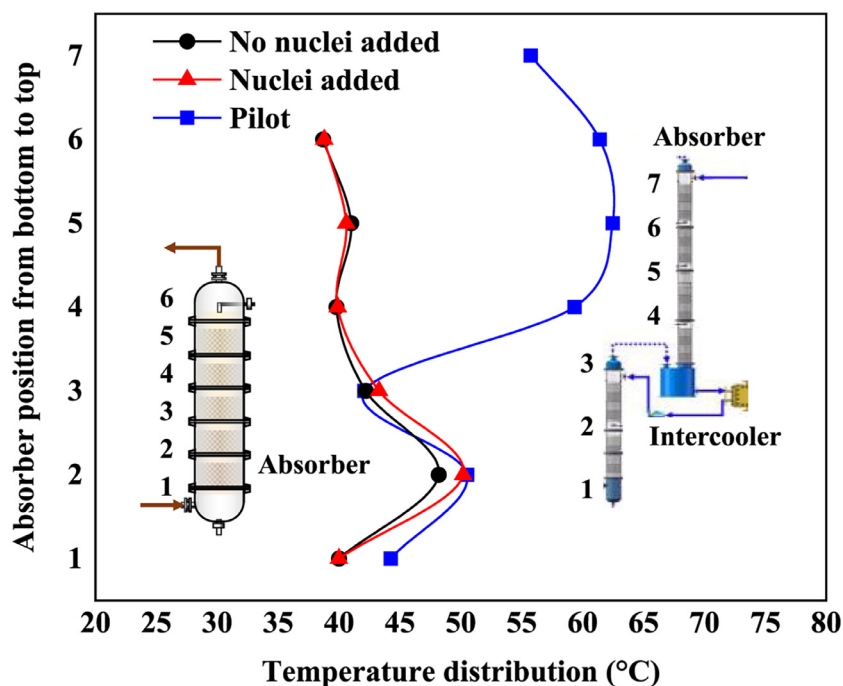


Fig. 6. Temperature distribution along absorber under three scenarios: basic conditions.

3.2. Effect of operating parameters on reducing aerosol emissions

3.2.1. Effect of the lean-solvent temperature

The lean-solvent inlet temperature of the absorber significantly affected the temperature distribution of the whole absorber and the volatility of the amine. The flue gas outlet temperature was similar to that of the lean solvent due to their common location at the top of the absorber. Consequently, an increase in the lean-solvent temperature inevitably led to higher vapor emissions, which served as the driving force for aerosol emissions. Kang et al. (Zhang et al., 2017). and Majeed and Svendsen (Majeed and Svendsen, 2018b) both showed that a higher lean-solvent temperature provided a greater amine driving force, resulting in higher amine emissions. As shown in Fig. 7a, b, the experimental investigation of the lean-solvent temperature ranged from 30 °C to 50 °C (35–45 °C for the pilot plant due to the heat exchange efficiency). The rest of the operating parameters were virtually the same as the basic conditions. After the absorber, both vapor and aerosol emissions increased sharply as the temperature of the lean solvent increased. For the bench-scale platform, vapor amine emissions increased by 500 % from 30 °C to 50 °C, while amine emissions nearly doubled in the scenario involving nuclei. In the pilot plant, amine emissions after the absorber grew even faster due to differences in heat dissipation, resulting in higher temperatures throughout the column. The overall temperature of the absorber on the bench-scale platform was approximately 8–17 °C lower than that of our pilot plant (shown in Fig. 6). The temperature decrease resulting from heat loss influenced aerosol growth and amine emissions, a factor that is inherent in small-scale test systems and impossible to completely avoid. Aerosol emissions following the water wash column exhibited a slight initial increase followed by a subsequent decrease.

In general, a water wash column exerts significantly less control over aerosol emissions than over vapor emissions. The change in amine emissions before and after the water washing section allows a rough quantitative analyze. As shown in Fig. 8a, interestingly, while a reasonable increase in solvent temperature may increase aerosol emissions after the absorber, emissions after the water-wash column may be reduced. A high temperature at the top of the absorber, typically achieved by not using a lean solvent cooler, will induce greater growth of the aerosol, which facilitates its collection in the water wash. (Rochelle, 2024) Therefore, a reasonable increase in solvent temperature with the config-

uration of the water washing section is beneficial for reducing aerosol emissions, but more accumulation of amines in the water should also be considered. This emission mitigation measure necessitates better solvent management to avoid high amine accumulation in the water-wash column resulting in lower removal efficiency.

3.2.2. Effect of the liquid–gas ratio

The liquid–gas (L/G) ratio is a critical parameter in the operation of carbon-capture systems, influencing both the decarbonization efficiency and the partial pressure of solvents. In this section, the effect of varying the total liquid–gas ratio on aerosol emissions from 5 to 10 L/m³ (2.1–3.6 L/m³ in the pilot plant) was investigated. As shown in Fig. 7c, amine emissions after the absorber on the bench platform increased when the liquid–gas ratio was too low (5 L/m³) because at low lean-solvent flow rates, the same reaction heat was concentrated in less liquid, and the absorber temperature was significantly higher than that at high flow rates, resulting in higher vapor emissions. The L/G ratio was negatively correlated with aerosol-based emissions after water washing, as depicted in Fig. 7d, while vapor-based emissions remained almost constant. Furthermore, the experimental results revealed that the aerosol emissions of PZ intensified with an increasing liquid–gas ratio following the water-washing stage (from 40 to 47 mg/Nm³ in the case of the addition of nuclei and from 20 to 25 mg/Nm³ in the pilot plant), while the aerosol emissions of AMP decreased (from 56 to 50 mg/Nm³ in the case of the addition of nuclei and from 70 to 59 mg/Nm³ in the pilot plant).

The effect of changing L/G on aerosol emissions was insignificant compared to that of other conditions, as depicted in Fig. 8b. Increasing the liquid–gas ratio reduced the temperature bulge within the absorber column and caused the bulge to migrate to a lower position within the column. The reduction of the temperature profile along the gas column leads to lower gas phase supersaturation and thus lower aerosol emissions. (Khakharia et al., 2015) Meanwhile, due to the increase in liquid retention, the absorption of CO₂ was enhanced, which in turn reduced the concentration of free amines in the liquid phase, thereby reducing amine volatilization and inhibiting aerosol formation. A lower ratio of AMP:PZ indicates that relatively more PZ is present than AMP in the aerosol droplets. Therefore, an appropriate increase in the solvent content is beneficial for reducing aerosol emissions.

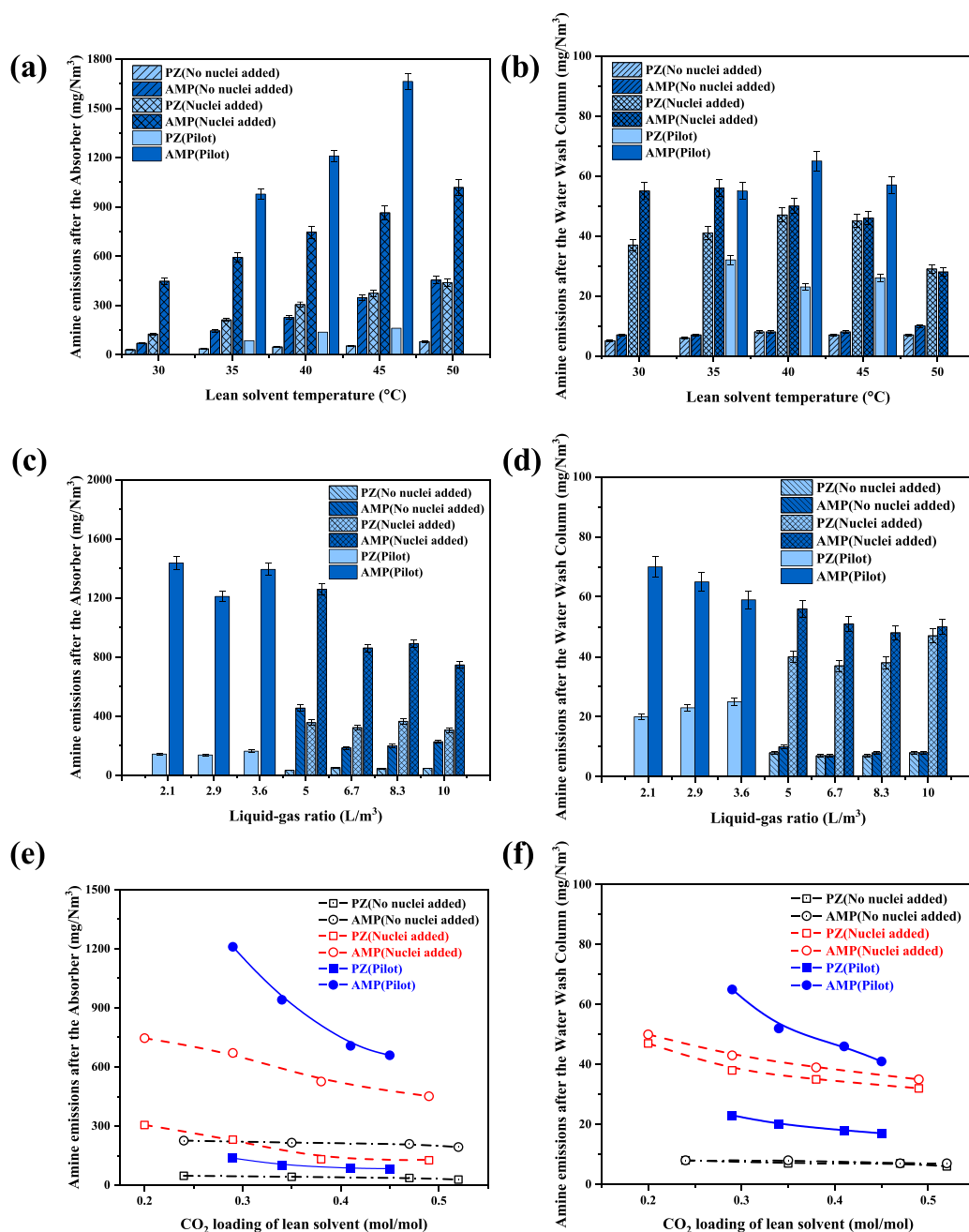


Fig. 7. Amine emissions under different parameters (a) lean solvent temperature after the absorber, (b) lean solvent temperature after the water wash column, (c) liquid-gas ratio after the absorber, (d) liquid-gas ratio after the water wash column, (e) CO₂ loading of lean solvent after the absorber and (f) CO₂ loading of lean solvent after the water wash column.

3.2.3. Effect of the lean-solvent CO₂ loading

The bench platform varied the CO₂ loading by varying the reboiler heating power, while the pilot plant changed the flow rate of steam generated by the oil-fired boiler, which heated the reboiler. The lean solvent was sampled in the middle of the amine emission measurement to test its CO₂ loading. The impact of the lean-solvent CO₂ loading on aerosol emissions was much more noticeable than that of the previous two operating parameters mentioned. A solvent with a high CO₂ loading typically exhibits lower volatility and reactivity of amines, which retards the transfer of amines and heat evolution from the reaction. As shown in Fig. 7e, F, there was a steep decline in aerosol-based emissions as the lean-solvent CO₂ loading increased both after the absorber and after the water-wash column. However, the CO₂-capture rate also

decreased due to the decrease in the absorption ability of the solvent. Low volatility due to the high CO₂ content in the solvent had a more immediate effect on AMP, in which emissions decreased by 50 % with an increase in the lean-solvent CO₂ loading from 0.29 to 0.45 mol mol⁻¹ in the pilot plant. It should be noted that the overall temperature distribution of the absorber changed during the lean-solvent CO₂ loading experiment. The temperature increased from the CO₂ chemical absorption reaction decreased with increasing CO₂ loading, which also affected the volatilization of amines.

Under the premise of ensuring the efficiency of CO₂ capture, strategically increasing the lean-solvent CO₂ loading could emerge as a viable and efficient approach to mitigate amine emissions as shown in Fig. 8. This is mainly through influencing the supersaturation and the reactivity

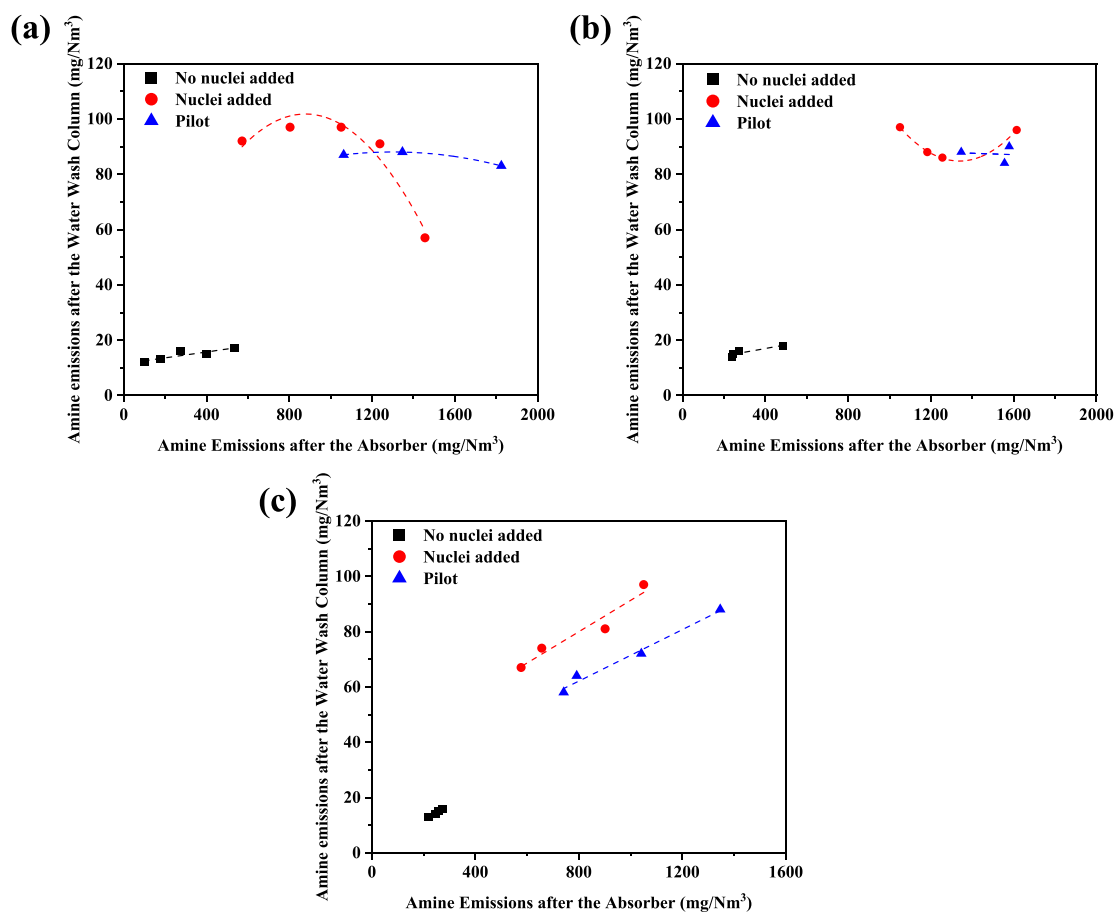


Fig. 8. Total amine emissions after the water wash column varies with that after the absorber: (a) lean solvent temperature, (b) liquid-gas ratio and (c) lean-solvent CO₂ loading.

of the amine. At a high lean-solvent CO₂ loading, the emissions following the water-wash column (17 mg/Nm³ PZ and 41 mg/Nm³ AMP) were nearly equivalent to those achieved through the other advanced control measures, which are detailed later. The impact of this strategy was further modulated by the volatility of the amine, with less volatile amines such as PZ showing reduced sensitivity to changes in CO₂ loading.

3.3. Continuous monitoring of amine emissions and control strategy test

Compared to the bench-scale platform, the pilot plant used packing and tower internals that were closer to actual industrial installations; therefore, the emission data were much more representative. In this section, the changes in amine emissions were monitored with the application of various mitigation methods. To exclude the influence of other operating parameters, the absorption-regeneration cycle was maintained at the basic operating conditions before the test started. Steady-state operation was achieved when the CO₂-capture rate, CO₂ loading, lean-solvent flow rate, and temperature remained stable for 30 min. Four different process configurations used to mitigate emissions and their interactions were evaluated, and their respective locations within the system are depicted in Fig. 9a. The first water-wash column could be used as a dry bed, while the second was fitted with a container for the preparation of an acidic solution, where CO₂ from regeneration gas was dissolved in water. The outlet of each stage of the water-wash column was equipped with a demister to intercept large aerosols.

As shown in Fig. 9b, amine emissions were sampled at 20-minute intervals after the absorber and after the control. The CO₂-capture rate, amine concentration and CO₂ loading were tested hourly and carefully maintained at 90 %, 4 mol/L and 0.25 mol mol⁻¹, respectively, as shown

in Fig. 10a, b, c. After each control was tested, fresh recirculated water was added to the water-wash column to eliminate interference from amines that had accumulated in the wash water, and the pH of the wash water was measured every 20 min (Fig. 10d). Although the plant was in a steady state, the amine emissions still seemed to fluctuate. After control measures, this variation was generally found to be within an acceptable range. Droplet growth was substantially inhibited when an intercooling system was employed, even in the scenario with a high concentration of nuclei (10⁷ cm⁻³) (Majeed and Svendsen, 2018a). With the activation of intercooling, a reduction in total amine emissions was observed both before and after the control measures. Water-wash systems are mainly intended to control gaseous emissions from absorption columns and to cause aerosol particles to grow significantly by moisture condensation, thus facilitating their removal in mist eliminators (Majeed and Svendsen, 2018b). Therefore, the temperature of the water-wash section affected the aerosol removal efficiency, and a cooler was set at the water-wash temperature to maintain the temperature of the circulating washing water at approximately 40 °C.

Due to the higher flue gas outlet temperature and the utilization of the demister, the amine removal efficiency of single water washing in the pilot plants (93.5 %) was better than that in the small-scale platform (90.8 %, nuclei scenario). Despite the almost complete control of the escaping gaseous amine in the first stage, the aerosol was able to grow larger in the second stage and be captured by the demister when using a two-stage water wash, resulting in reduced amine emissions. The dry bed was only partially wetted with circulating water at a flow rate much lower than the flow rate for water scrubbing. The slight cooling of flue gases, particles and droplets through the dry bed may help to reduce emissions because water instead of organic compounds condenses

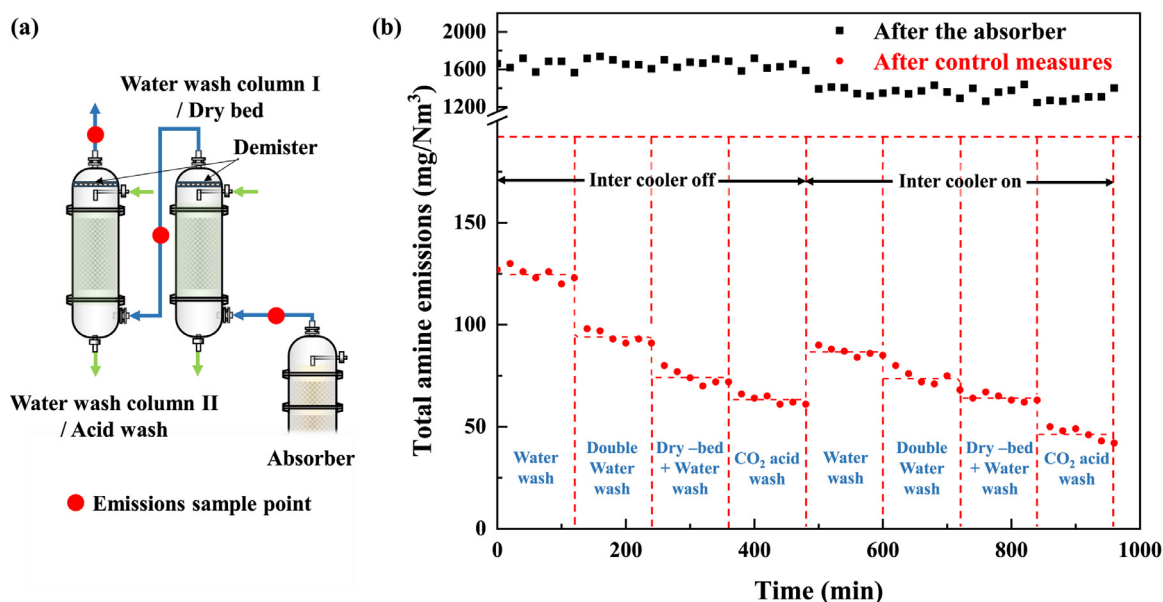


Fig. 9. (a) Process configurations to mitigate emissions in the pilot plant, (b) effect of the control measure on the emissions.

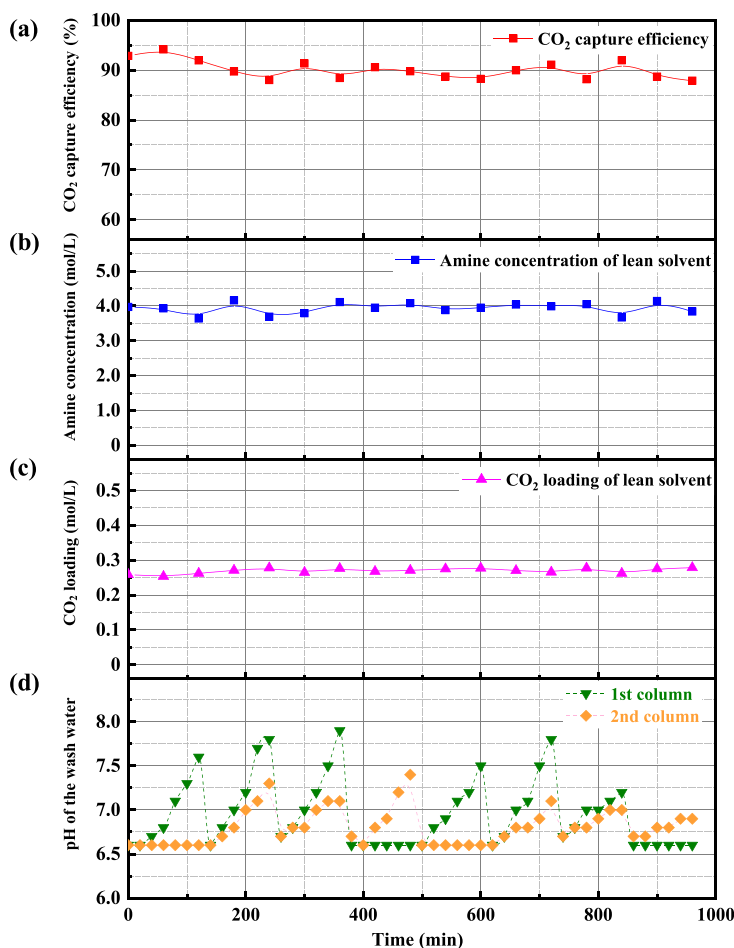


Fig. 10. Change in (a) CO₂ capture efficiency (b) amine concentration of lean solvent (c) CO₂ loading of lean solvent (d) pH of the wash water under long-term operation.

on particles and droplets in the downstream wash section (Moser et al., 2021). By activating the acid wash, emissions could be reduced to a lower level than in the dry-bed configuration. Moreover, as shown in Fig. 10d, the pH of the wash water gradually increased due to the enrichment of the escaping solvent. With a dry bed or acid wash configuration, amines accumulated relatively slowly in the wash water, with a

pH of only 7 after two hours, which was beneficial for maintaining the water balance of the system.

A comparison of AMP and PZ emission results after absorber and mitigation measures is shown in Fig. 11. The amine removal efficiency of water washing for AMP was significantly greater than that for PZ. Akinpelumi et al. (Akinpelumi et al., 2019) suggested that small PZ

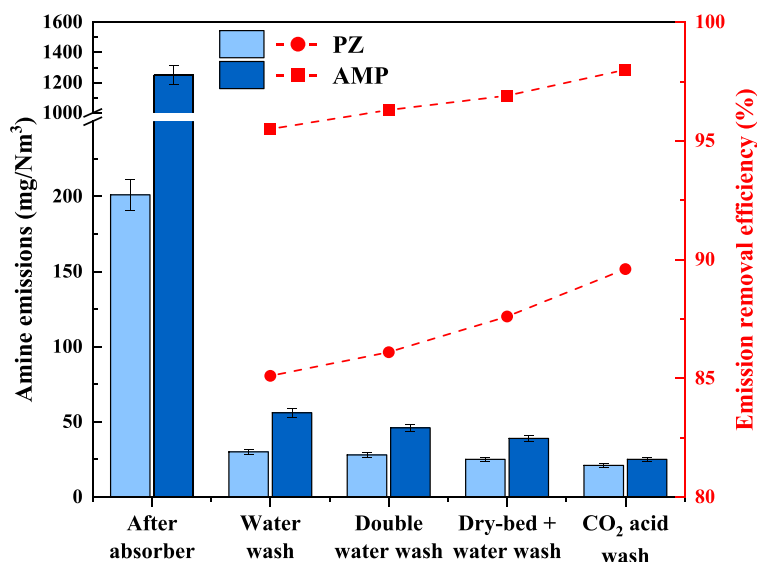


Fig. 11. Impact of different control measures on AMP/PZ, respectively (with intercooling).

aerosols are not condensable in single or multiple water-wash sections. The “dry bed + water washing” process and acid washing reduced amine emissions to 25 mg/Nm³ PZ and 39 mg/Nm³ AMP and 21 mg/Nm³ PZ and 25 mg/Nm³ AMP on average, respectively. The low-amine-concentration liquid film, created through cooling and condensation in the dry-bed section, engaged in gas–liquid equilibrium mass transfer with the flue gas, effectively recovering most of the amines in the gas phase. To assess the efficacy of the acid wash, CO₂ was introduced to the recirculation flow in the second water-wash column. The acidic solution facilitated the conversion of the amine to a carbamate or protonated amine, which resulted in a notable reduction in the vapor pressure of the amine in the liquid phase and a corresponding reduction in the amount of the amine released into the gas phase. The activation of the dry bed and acid washing had a significant effect on emissions by reducing the AMP concentration but had a negligible effect on the piperazine concentration. One possible explanation for this is that due to the lower vapor pressure of piperazine, the mass transfer rate from the gas phase to the aerosol nuclei/droplets in the absorber was reduced, and more piperazine was collected by the aerosol nuclei compared to AMP. The demisters are not as effective in intercepting aerosols of small particles <3 μm, which poses a challenge for further treatment. Thus, manipulating the aerosol formation process through the regulation of operating parameters and integrating these adjustments with control methods can effectively mitigate aerosol emissions and solvent loss, which is an important research direction in the future.

4. Conclusions

Aerosol emissions in the CO₂ capture system result in solvent loss and contribute significantly to environmental pollution. Therefore, particular attention must be devoted to the design of prospective CO₂ capture units to minimize aerosol emissions during the CO₂ capture process, thereby attaining reduced carbon emissions without causing environmental pollution. In this study, a preliminary investigation of aerosol concentrations and evolutionary patterns, as well as the impact of operating parameters on the reduction of aerosol emissions, was carried out on a bench-scale platform. Reducing aerosols in flue gas is the most direct way to control amine emissions, but even with the application of ultralow emission control equipment, nuclei in the flue gas remain at high levels. Aerosol growth in the absorber is one of the main reasons for high-quality aerosol emissions. A higher solvent temperature leads to an increase in aerosol emissions after the absorber, but emissions after water washing may be reduced. Employing appropriate high solvent-gas

ratios and lean solvent CO₂ loading has been demonstrated to result in a reduction in aerosol emissions.

The performances of several amine emission mitigation methods were evaluated in a pilot plant. Dry bed and acid washing have advantages over conventional water washing in terms of emission reduction and amine accumulation in water. The results indicate that current emission reduction strategies can be effective in controlling aerosol and vapor emissions; however, the specific impacts of these strategies, both individually and in combination, on vapor and aerosol emissions require further detailed investigation. The removal of amines with low volatility (such as piperazine) may be more of a concern for outlet decarbonized flue gas.

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.

CRediT authorship contribution statement

Lianbo Liu: Investigation, Funding acquisition. **Xiaojun Wang:** Writing – original draft, Methodology, Investigation, Conceptualization. **Huanjun Wang:** Funding acquisition. **Tao Wang:** Writing – review & editing, Supervision. **Mengxiang Fang:** Writing – review & editing.

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