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Experimental study on three additives used for the removal of nitrite, a byproduct of ozone oxidation denitration technology

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ABSTRACT

Nitrogen oxides resulting from fossil fuel combustion are one of the major atmospheric pollutants. Ozone oxidation flue gas denitration technology has garnered significant attention for its benefits such as high efficiency, low temperature and simultaneous removal of multiple pollutants. However, the large amount of nitrite in the absorption products makes it prone to secondary pollution. A cost-effective and harmless treatment of the by-product nitrite will promote the ozone oxidation denitration technology. This study focused on investigating three different additives (ammonium chloride, ammonium carbonate, and urea) that can be added to react with nitrite and remove it in a harmless way. The effects of reaction temperature, initial nitrite ion concentration, reaction molar ratio, and initial pH on nitrite removal efficiency were explored. Combined with a wet spraying system, the synergistic removal of NO_x/SO_2 and by-product nitrite has also been studied. The experimental results revealed that with appropriate operating conditions and additives, the by-product nitrite can be efficiently removed while the system can achieve efficient removal of NO_x/SO_2. Among the three additives, ammonium carbonate was found to have the best overall removal effect. However, urea had an advantage over the other two additives in highly acidic and low-temperature slurry.

1. Introduction

Nitrogen oxides (NO_x) are a major type of atmospheric pollutant generated by the combustion of fossil fuels. It can result in photochemical smog, acid rain, and haze (Goldberg et al., 2019; Liu et al., 2016; Ma et al., 2012; Sun et al., 2016). In addition, NO_x can also stimulate the respiratory system, causing or aggravating respiratory diseases (Ji et al., 2020). Anthropogenic sources of NO_x mainly include fixed sources such as coal-fired power plants and industrial boiler/furnace flue gas, as well as mobile sources such as vehicle exhaust. Among these sources, fixed sources are the key object of NO_x emission control. In the face of severe environmental pressure and increasingly stringent emission standards, the control technology for single pollutant not only has a high investment cost, but also reduces the overall reliability of the system (Lin et al., 2020).

In recent years, ozone oxidation multi-pollutant synergistic removal technology has gained widespread adoption in various industrial settings, including boilers, kilns, and non-electric industries (Shao et al., 2019a; Zhang et al., 2019; Zhu et al., 2016). The innovative technology utilizes the strong oxidative properties of active molecular O_3 to convert NO in the flue gas into high valence soluble NO_2, NO_3, and N_2O_5 (Lin et al., 2016), while oxidizing Hg^0 to Hg^{2+} and VOCs to CO_2

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and H_2O (Lin et al., 2020). Combined with the wet spraying process, the integrated removal of multiple pollutants can be achieved. Compared to traditional technologies, it offers several advantages, such as broad fuel applicability, high furnace type universality, high removal efficiency, low reaction temperature (90–150 °C), and the ability to address multiple pollutants in one system (Khuntia and Mohan, 2022; Shao et al., 2019b; Wang et al., 2007). However, the denitration process may face challenges, such as the difficulty in treating a large amount of nitrite in the absorption slurry. Therefore, much attention has been given to explore methods for harmlessly treating the by-product nitrite in order to improve the environmental sustainability and economy of ozone oxidation denitration technology.

During the wet scrubbing process of ozone oxidation denitration technology, nitrite and nitrate are the primary absorption products of NO_x in flue gas (Adewuyi et al., 2018; Wu et al., 2018; Zhao et al., 2015). Nitrate has stable properties and serves as a crucial raw material in building materials, agricultural fertilizers, and phase-change materials (Guo et al., 2018; Nagano et al., 2004). However, NO_2^- is prone to the disproportionation reaction in acidic conditions (absorption slurry system is generally a slightly acidic environment), leading to the release of NO into the atmosphere, thereby causing secondary pollution (Eq. (1)) (He and Knipp, 2009; Knipp and He, 2011). Moreover, when the nitrite concentration in the absorption slurry is high, it will inhibit the absorption of NO_x and reduce NO_x removal efficiency. On the other hand, NO_2^- itself is highly toxic, and excessive emissions will cause great harm to the environment and human body (Picetti et al., 2022; Tau and Nyokong, 2007; Zhu et al., 2005). The ability to reduce the nitrite concentration with high efficiency and low cost has become critical for the widespread application of ozone oxidation flue gas denitration technology. This approach can also reduce replacement times of the slurry, effectively solving the problem of high-water consumption volume in the wet scrubbing process and improving the economy of the technology.

$$3NO_2^- + 2H^+ = 2NO \uparrow + NO_3^- + H_2O \tag{1}$$

Currently, the physical adsorption method is the preferred technique for removing nitrite in wastewater. Common adsorbents include activated carbon (Neşe and Ennil, 2008), reverse osmosis membrane filtration (Ahn et al., 2008; López et al., 2021), etc. However, some unfavorable factors, such as low adsorption selectivity, easy blockage of micropores, and difficulty in retrofitting the scrubber, will lead to reduce the removal efficiency and increase the cost. The common methods for wastewater treatment also include iron reduction (Hu et al., 2001; Tokazhanov et al., 2020; Vilardi and Di Palma, 2017; Zhang et al., 2010a,b), catalytic reduction (Gao et al., 2020; Marchesini et al., 2010; Martínez et al., 2017; Shih et al., 2020), γ-ray irradiation (Guo et al., 2008), ion exchange (Samatya et al., 2006), etc. Zhang et al. studied the reaction kinetics of nitrite reduction by zero-valent iron (Zhang et al., 2010b,a). However, these methods are only suitable for low-concentration NO_2^- treatment, while noble metal catalysts and expensive equipment investments make it difficult to be applied to the wet spraying process. Some chemical methods have been applied to ozone oxidation denitration technology. Zhang et al. utilized ozone to oxidize the coal-fired flue gas and added $(NH_4)_2SO_4$ to $CaSO_3$ slurry (Zhang et al., 2012). They obtained $Ca(NO_2)_2\cdot H_2O$ particles of high purity while reducing the secondary pollution of nitrite. Zhang et al. investigated the oxidation reaction of NaClO and nitrite (Zhang et al., 2015), which provided an idea for harmless treatment of denitration by-product NO_2^-. ZSM-5 zeolite is considered to be an excellent catalyst for catalytic oxidation of NO_2^-. According to the research conducted by Ikhlaq et al. ZSM-5 zeolite can effectively enhance the adsorption of oxidants, promoting the catalytic oxidation reaction (Ikhlaq et al., 2014). Ying et al. found that HZSM-5 zeolites can effectively promote the oxidation of NO_2^- in the ozone-assisted system (Ying et al., 2019). Aerobic denitrification technology (Bian et al., 2022; Hao et al., 2022) is a novel type of biological nitrogen removal technology. Under anoxic conditions, denitrifying bacteria can reduce nitrite to N_2. However, the high temperature of slurry and the running state of spraying in the ozone oxidation denitration system are not suitable for the technology.

Some novel denitrification technologies can also avoid the production of by-product nitrite like the double metal ions-double oxidants coactivation system (Liu et al., 2022) and biochar-activated peroxydisulfate oxidation technology (Wang et al., 2023). However, it is still a challenge to efficiently reduce NO_2^- concentration in the absorption slurry of ozone oxidation flue gas denitration technology. Therefore, in this study, the characteristics of three different additives (ammonium chloride, ammonium carbonate, and urea) reacting with NO_2^- have been investigated to provide an experimental basis for the harmless treatment of nitrite. The effects of reaction temperature, initial NO_2^- concentration, reaction molar ratio, and initial pH of absorbent on nitrite removal efficiency have been investigated, and the reaction characteristics of three additives with NO_2^- were compared to select the optimal additive under different conditions. At the same time, combined with a wet spraying system, the synergistic removal of NO_x/SO_2 and by-product nitrite was also studied.

2. Material and methods

2.1. Comproportionation reaction system

The comproportionation reactions of ammonium chloride, ammonium carbonate with NO_2^- are shown in Eq. (2), and the comproportionation reaction of urea with NO_2^- is shown in Eq. (3):

$$NH_4^+ + NO_2^- \triangleq N_2 \uparrow + 2H_2O \tag{2}$$

$$CO(NH_2)_2 + 2NO_2^- + 2H^+ = 2N_2 \uparrow + CO_2 \uparrow + 3H_2O \tag{3}$$

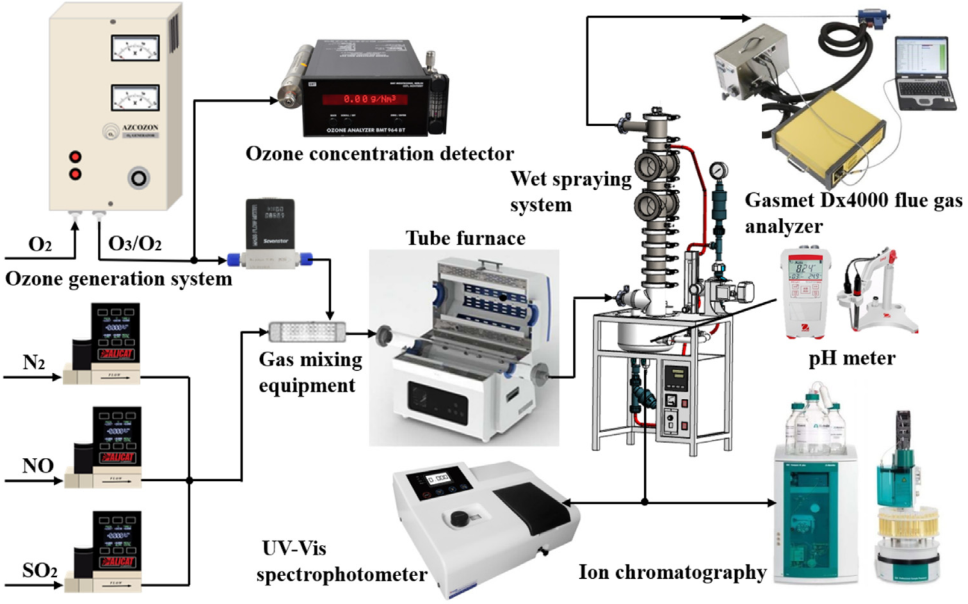


Fig. 1. Schematic diagram of ozone oxidation flue gas coupled wet spraying system.

The comproportionation reaction system is shown in Fig. S1. The system mainly included the preparation of standard reaction solution, thermostatic water bath, gas product analysis, and reaction solution composition analysis system. The effects of different experimental factors on NO_2^- removal efficiency can be investigated by changing different operating conditions. $NaNO_2$ was used as the source of by-product NO_2^- and the reaction solution was placed in a three-neck glass reactor with a capacity of 1 L. The pH value of reaction solution can be adjusted by adding NaOH solution and phosphoric acid solution, and the pH value was measured by a pH meter (OHAUS-ST3100, USA). The reaction temperature was adjusted by a thermostatic water bath (Changzhou Aohua HH-S, China). The exhaust gas from the reaction system entered the Fourier infrared flue gas analyzer (Gasmet Dx4000, Finland) after the pre-processor to measure the gas composition and content. In the experiment, the solution was continuously reacted for 180 min, and it was sampled from the three-neck glass reactor every 30 min. The samples were put into ion chromatograph (Metrohm-ECO, Switzerland) for testing.

The removal efficiency of NO_2^- can be calculated in terms of Eq. (4).

$$\eta\left(NO_2^-\right) = \frac{c_{initial}\left(NO_2^-\right) - c\left(NO_2^-\right)}{c_{initial}\left(NO_2^-\right)} \times 100\% \tag{4}$$

where $c_{initial}\left(NO_2^-\right)$ represents the initial NO_2^- concentration in absorbent solution (g/L), $c\left(NO_2^-\right)$ represents the NO_2^- concentration in the solution after different reaction time (g/L).

2.2. Ozone oxidation flue gas coupled wet spraying system

When using additives to remove by-product nitrite, the removal effect of pollutants cannot be reduced due to the additives, and the stability of the spray absorption system cannot be affected. In view of the above challenges, the ozone oxidation flue gas coupled wet spraying system was used to investigate the synergistic removal of NO_x/SO_2 and by-product nitrite.

Ozone oxidation flue gas coupled wet spraying system is shown in Fig. 1. The system consisted of a simulated flue gas system, a spray absorption system, and a flue gas analysis system. The simulated flue gas system included gas transmission, ozone generation, and a tube furnace (Shanghai Yifeng YFK60 × 600/10QK-G, China) for preheating. According to the practical engineering flue gas conditions, the flue gas temperature was preheated to 100 °C through the tube furnace in the experiment. In order to maintain the flue gas temperature, the gas path from the outlet of the tube furnace to the inlet of the wet spraying system was heated by electric heating belt. The total gas volume of the system was set to 5 L/min, and the initial NO concentration was set to 250 ppm. The SO_2 concentration was set to 100 ppm, the O_3/NO molar ratio was selected to 1.6, and the O_2 concentration was 6.0%. Ozone generation system included the ozone generator (AZCOZON-HTU500, Canada) and the high concentration ozone detector (BMT-964BT, Germany). Gas flow was controlled by the gas mass flow meter (ALICAT, USA).

The spray absorption system is mainly composed of a spray tower, pump, absorbent solution, and sampling/analyzing system. The inner diameter of the spray tower is 76 mm, and the height of single layer is 52 mm. The number of layers can be increased or decreased according to the spray requirements. The slurry temperature was controlled at 60 °C by an electric heating metal rod in the spray tower. Meanwhile, we have wrapped electric heating belt around the circulation pipeline to maintain the slurry temperature. The slurry pH was adjusted to 5.5. Phosphate buffer solution (Na_2HPO_4–NaH_2PO_4) was used as the absorbent. The amount of the additives was 1 g/L. In the experiment, the absorption solution was sampled from sampling port below the spray tower and placed in ion chromatograph for testing. For two working conditions with or without additives, the NO_2^- concentration in the absorption solution after reaction under the condition of simultaneous oxidation of NO/SO_2 was measured so that the removal efficiency of by-product NO_2^- can be calculated by Eq. (4). The measurement results of ion chromatography can be verified by the spectrophotometer (Shanghai Youke LG-3, China). The flue gas after spraying and absorption entered the Fourier infrared flue gas analyzer to measure its composition and content. The denitration and desulfurization efficiency of the system can be calculated, where NO_x is the sum of NO and NO_2.

The removal efficiency of NO_x can be calculated in terms of Eq. (5).

$$\eta\left(NO_x\right)=\frac{c_{inlet}\left(NO_x\right)-c_{outlet}\left(NO_x\right)}{c_{inlet}\left(NO_x\right)}\times 100\% \tag{5}$$

where c_{inlet} (NO_x) represents NO_x concentration at system inlet (mg/Nm^3), c_{outlet} (NO_x) represents NO_x concentration at system outlet (mg/Nm^3).

The removal efficiency of SO_2 can be calculated in terms of Eq. (6).

$$\eta\left(SO_2\right)=\frac{c_{inlet}\left(SO_2\right)-c_{outlet}\left(SO_2\right)}{c_{inlet}\left(SO_2\right)}\times 100\% \tag{6}$$

where c_{inlet} (SO_2) represents SO_2 concentration at system inlet (mg/Nm^3), c_{outlet} (SO_2) represents SO_2 concentration at system outlet (mg/Nm^3).

3. Results and discussion

For convenience of comparison, the reaction molar ratios of ammonium chloride, ammonium carbonate were set as NH_4^+/NO_2^- molar ratio, and the reaction molar ratio of urea was set as $CO(NH_2)_2/NO_2^-$ molar ratio ∗ 2.

3.1. Effect of reaction temperature on NO_2^- removal efficiency by three additives

Effect of reaction temperature on NO_2^- removal efficiency by three additives is shown in Fig. 2 with an initial NO_2^- concentration of 10 g/L, a reaction molar ratio of 2:1, and an initial absorbent pH of 5. The results indicate that the three additives can react with NO_2^- and efficiently reduce the concentration of denitration by-product nitrite at the appropriate reaction temperature. On the whole, the removal rate and efficiency of NO_2^- by the three additives increase with the rise in reaction temperature. According to the principle of chemical reaction equilibrium, increasing reaction temperature can accelerate the rate of the reactions shown in Eqs. (2) and (3), thus enhancing the NO_2^- removal rate. Additionally, since both Eqs. (2) and (3) are endothermic reactions, increasing the reaction temperature can promote the chemical reaction equilibrium shift to the right, which improves NO_2^- removal efficiency in the reaction system.

The NO_2^- removal efficiency increased as the reaction time increased. The reaction rate was highest from 0 to 90 min and then gradually stabilized. Fig. 2(a) shows that the NO_2^- removal efficiency by NH_4Cl after 180 min of reaction is 2.0%, 12.1%, 33.8%, 63.4%, 73.8% and 82.3% from 40 °C to 90 °C (per 10 °C). Similarly, Fig. 2(b) shows that the NO_2^- removal efficiency by $(NH_4)_2CO_3$ after 180 min of reaction is 11.0%, 27.1%, 53.2%, 72.0%, 75.0% and 70.2% from 40 °C to 90 °C. When the temperature is 90 °C, the NO_2^- efficiency by $(NH_4)_2CO_3$ decreases because $(NH_4)_2CO_3$ is more prone to decomposition at higher temperature. Fig. 2(c) demonstrates that the NO_2^- removal efficiency by $CO(NH_2)_2$ after 180 min of reaction is 23.1%, 32.7%, 48.6%, 68.0%, 72.4% and 77.1% respectively. At lower temperatures, the NO_2^- removal efficiency by $CO(NH_2)_2$ is higher than that of NH_4Cl and $(NH_4)_2CO_3$. These experimental results confirm that lower reaction temperatures result in slower NO_2^- removal rates and lower NO_2^- removal efficiency. When the reaction temperature reaches 70 °C, NO_2^- removal efficiency is significantly improved compared with 60 °C. However, excessively high temperature may cause additives like $(NH_4)_2CO_3$ to decompose, thus negatively affecting NO_2^- removal efficiency. In the practical engineering, industrial settings should also take economic costs and other factors into account. Therefore, the reaction temperature should not be set too high. Long-term circulating spray of absorption slurry in the scrubbing tower makes efficient removal of NO_2^- viable.

3.2. Effect of initial NO_2^- concentration on NO_2^- removal efficiency by three additives

To investigate the effect of initial NO_2^- concentration on nitrite removal efficiency, the system was set with a reaction temperature of 70 °C, a reaction molar ratio of 2:1, and an initial absorbent pH of 5. Fig. 3 illustrates the effect of initial NO_2^- concentration on NO_2^- removal efficiency by three additives. The results indicate that the three additives are effective in reducing the concentration of denitration by-product nitrite. The removal rate and efficiency of NO_2^- by the three additives

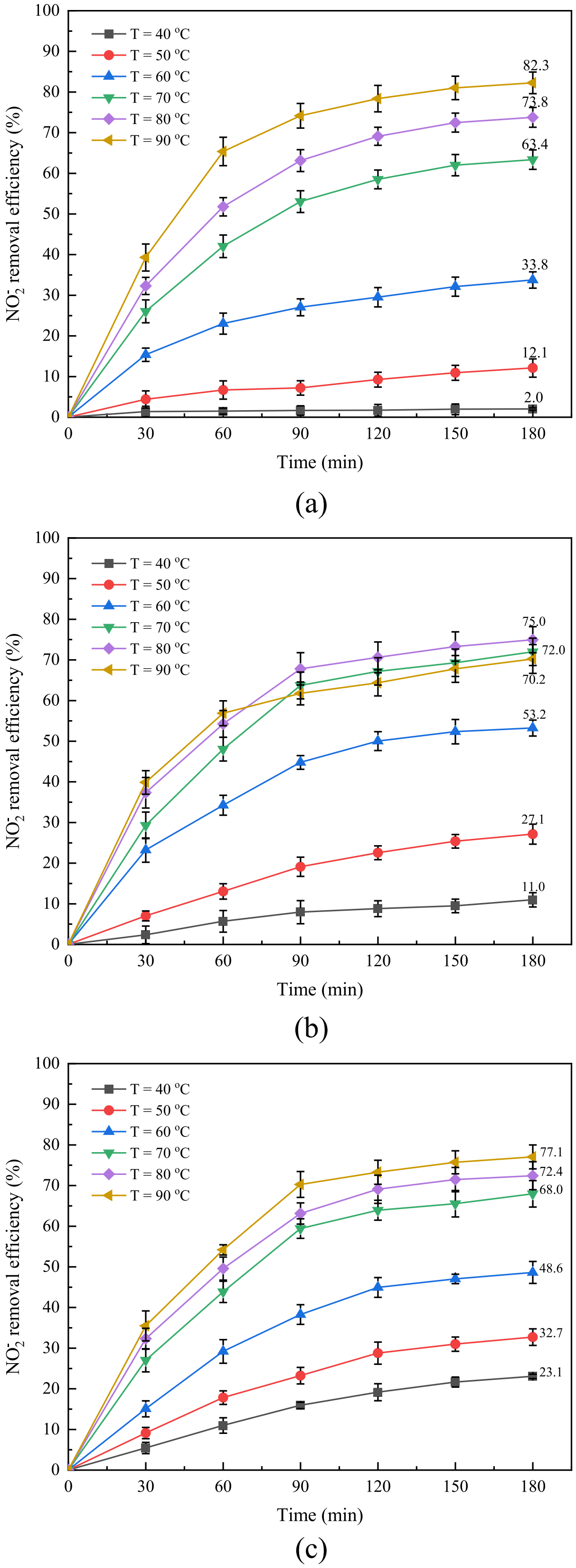
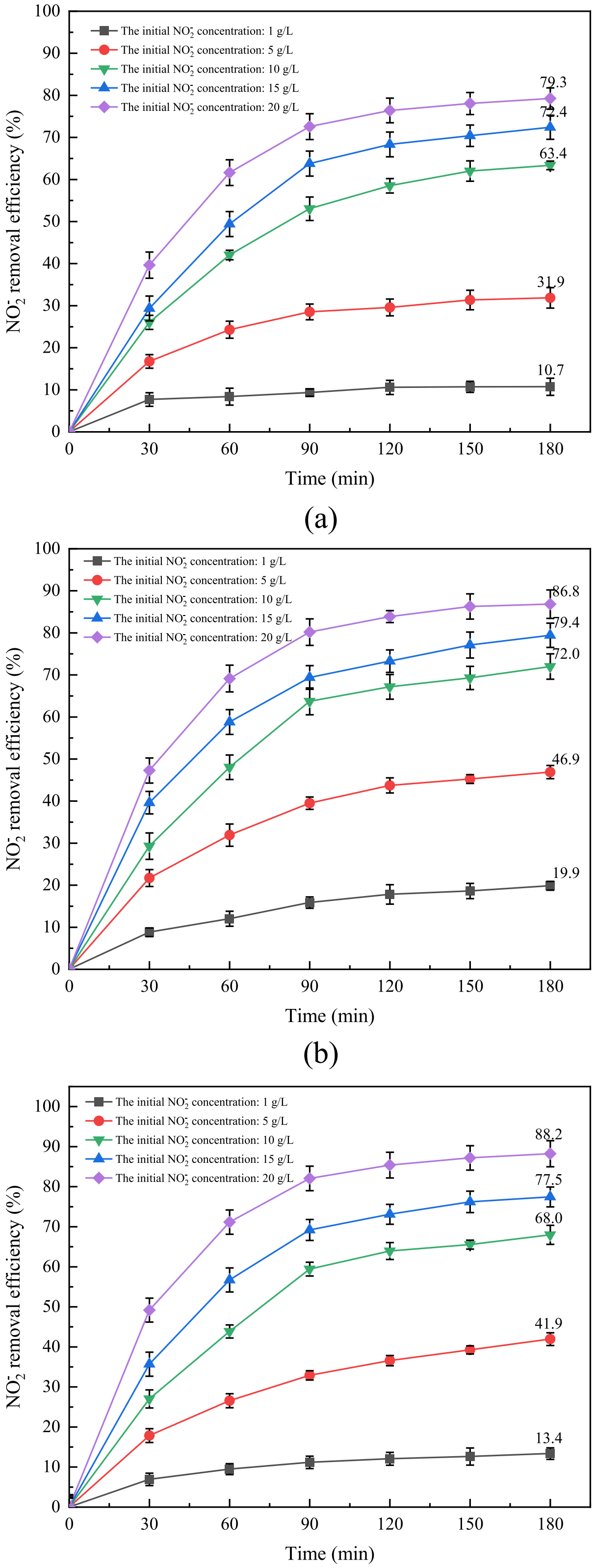


Fig. 2. Effect of reaction temperature on NO_2^- removal efficiency (a) NH_4Cl, (b) $(NH_4)_2CO_3$, (c) $CO(NH_2)_2$.



(a)

(b)

(c)

Fig. 3. Effect of initial NO$_2^-$ concentration on NO$_2^-$ removal efficiency (a) NH$_4$Cl, (b) (NH$_4$)$_2$CO$_3$, (c) CO(NH$_2$)$_2$.

increase with an increase in its initial concentration. In accordance with the principle of chemical reaction equilibrium, increasing the initial NO_2^- concentration can accelerate the reaction rates of Eqs. (2) and (3), thus promoting the reactions and improving the removal rate and efficiency of NO_2^- in the reaction system. With an increase in reaction time, the NO_2^- removal efficiency at various initial concentrations increased. The reaction was faster from 0 to 90 min and then tended to be stable gradually.

Fig. 3(a) illustrates that NH_4Cl-mediated removal efficiency of NO_2^- after 180 min of reaction is 10.7%, 31.9%, 63.4%, 72.4% and 79.3%, with initial concentration ranging from 1 g/L to 20 g/L. Similarly, Fig. 3(b) demonstrates that the NO_2^- removal efficiency by $(NH_4)_2CO_3$ after 180 min of reaction is 19.9%, 46.9%, 72.0%, 79.4% and 86.8% respectively. At various initial concentrations, the NO_2^- removal efficiency by $CO(NH_2)_2$ after 180 min of reaction is shown in Fig. 3(c), which is 13.4%, 41.9%, 68.0%, 77.5%, and 88.2%. The experimental results reveal that the NO_2^- removal efficiency by three additives all enhanced as the initial concentration increased from 1 g/L to 20 g/L. In practical industrial settings, the concentration of denitration by-product nitrite is constantly accumulated and is not set artificially. In this experiment, when the initial NO_2^- concentration was increased to 10 g/L, the removal rate and efficiency of NO_2^- significantly increased compared with 1 g/L and 5 g/L. Thus, in other experimental conditions, the initial NO_2^- concentration was set to 10 g/L to ensure significant experimental effects.

3.3. Effect of reaction molar ratio on NO_2^- removal efficiency by three additives

When the system reaction temperature was set to 70 °C, the initial NO_2^- concentration was set to 10 g/L, and the initial absorbent pH was 5, effect of reaction molar ratio on NO_2^- removal efficiency by three additives is shown in Fig. S2. The results indicate that the removal rate and efficiency of NO_2^- by the three additives increase with an increase in the reaction molar ratio. Based on the principle of chemical reaction equilibrium, increasing the reaction molar ratio equates to increasing the initial concentration of NH_4^+ or $CO(NH_2)_2$ in the reaction system, which can not only accelerate the reaction rate, but also promote the chemical reaction equilibrium of Eqs. (2) and (3) moving to the right, thus improving the removal rate and efficiency of NO_2^-. Furthermore, the NO_2^- removal efficiency at various reaction molar ratios increased with an increase in reaction time. The reaction gradually stabilizes after 90 min.

Fig. S2(a) illustrates that the NO_2^- removal efficiency by NH_4Cl after 180 min of reaction is 39.3%, 63.4%, 69.9%, 79.3% and 87.3% at various reaction molar ratios from 1:1 to 5:1. Fig. S2(b) shows that the NO_2^- removal efficiency by $(NH_4)_2CO_3$ after 180 min of reaction is 48.1%, 72.0%, 78.0%, 85.4% and 92.8% at various reaction molar ratios. Similarly, Fig. S2(c) shows that the NO_2^- removal efficiency by $CO(NH_2)_2$ is 43.8%, 68.0%, 74.9%, 81.6% and 88.9% respectively. The experimental results indicate that increasing the reaction molar ratio from 1:1 to 5:1 enhances the NO_2^- removal efficiency by three additives. When other conditions are appropriate, ensuring sufficient additives can efficiently remove NO_2^- in the absorbent. Moreover, when the reaction molar ratio is higher than 2:1, the removal rate and efficiency of NO_2^- are significantly improved compared to lower molar ratio.

3.4. Effect of absorbent pH on NO_2^- removal efficiency by three additives

To investigate the effect of absorption slurry pH on nitrite removal efficiency, the system reaction temperature was set to 70 °C, the initial NO_2^- concentration was set to 10 g/L, and the reaction molar ratio was set to 2:1. Effect of absorbent pH on NO_2^- removal efficiency by three additives is shown in Fig. S3. The results indicate that the removal efficiency of NO_2^- by the three additives decreases with an increase in initial pH. According to the principle of chemical reaction equilibrium, high slurry pH inhibits the reactions of Eqs. (2) and (3), which is not conducive to the removal of NO_2^-. Reducing the initial pH can promote the chemical reaction equilibrium of Eqs. (2) and (3) moving to the right, thus improving the NO_2^- removal efficiency. With the increase of reaction time, the NO_2^- removal efficiency at various pH all increased. Fig. S3(a) shows that the NO_2^- removal efficiency by NH_4Cl after 180 min of reaction is 70.1%, 63.4%, 54.4%, 38.0%, 18.0% and 4.1%, with initial pH ranging from 4 to 9. Fig. S3(b) shows that the NO_2^- removal efficiency by $(NH_4)_2CO_3$ after 180 min of reaction is 72.6%, 72.0%, 59.2%, 41.9%, 20.4% and 9.2% at various initial pH. After 180 min of reaction, the NO_2^- removal efficiency by $CO(NH_2)_2$ is 93.0%, 68.0%, 51.4%, 17.9%, 1.4%, and 1.1% respectively, as shown in Fig. S3(c). $CO(NH_2)_2$ exhibits higher reactivity with NO_2^- than NH_4Cl and $(NH_4)_2CO_3$ when the slurry pH is low. During the experiment, absorbent solution pH changed with increasing reaction time. After 180 min of reaction, the solution pH under various initial pH conditions was concentrated in the range of 5–6.

The experimental results reveal that increasing the initial slurry pH reduces the NO_2^- removal efficiency by NH_4Cl and $(NH_4)_2CO_3$. This is because in an alkaline environment, a part of NH_4^+ and OH^- in the reaction system are combined into $NH_3{\cdot}H_2O$, which is heated and escapes as NH_3 (Eq. (7)). The escaping NH_3 not only reduces the NH_4^+ concentration in the reaction system, making it unable to meet the requirements of the reaction shown in Eq. (2) and thus affecting the NO_2^- removal efficiency, but also causes additional aerosol pollution. Furthermore, since Eq. (3) must be reacted under acidic conditions, the NO_2^- removal efficiency by $CO(NH_2)_2$ when pH > 7 is nearly zero. In fact, a low pH value is also not recommended as it could affect the absorption efficiency in the spray tower, thus impacting the removal efficiency of flue gas pollutants. Moreover, it will cause the decomposition of NO_2^- and generate harmful gases (Eq. (1)).

$$NH_4^+ + OH^- \triangleq NH_3 \uparrow + H_2O \tag{7}$$

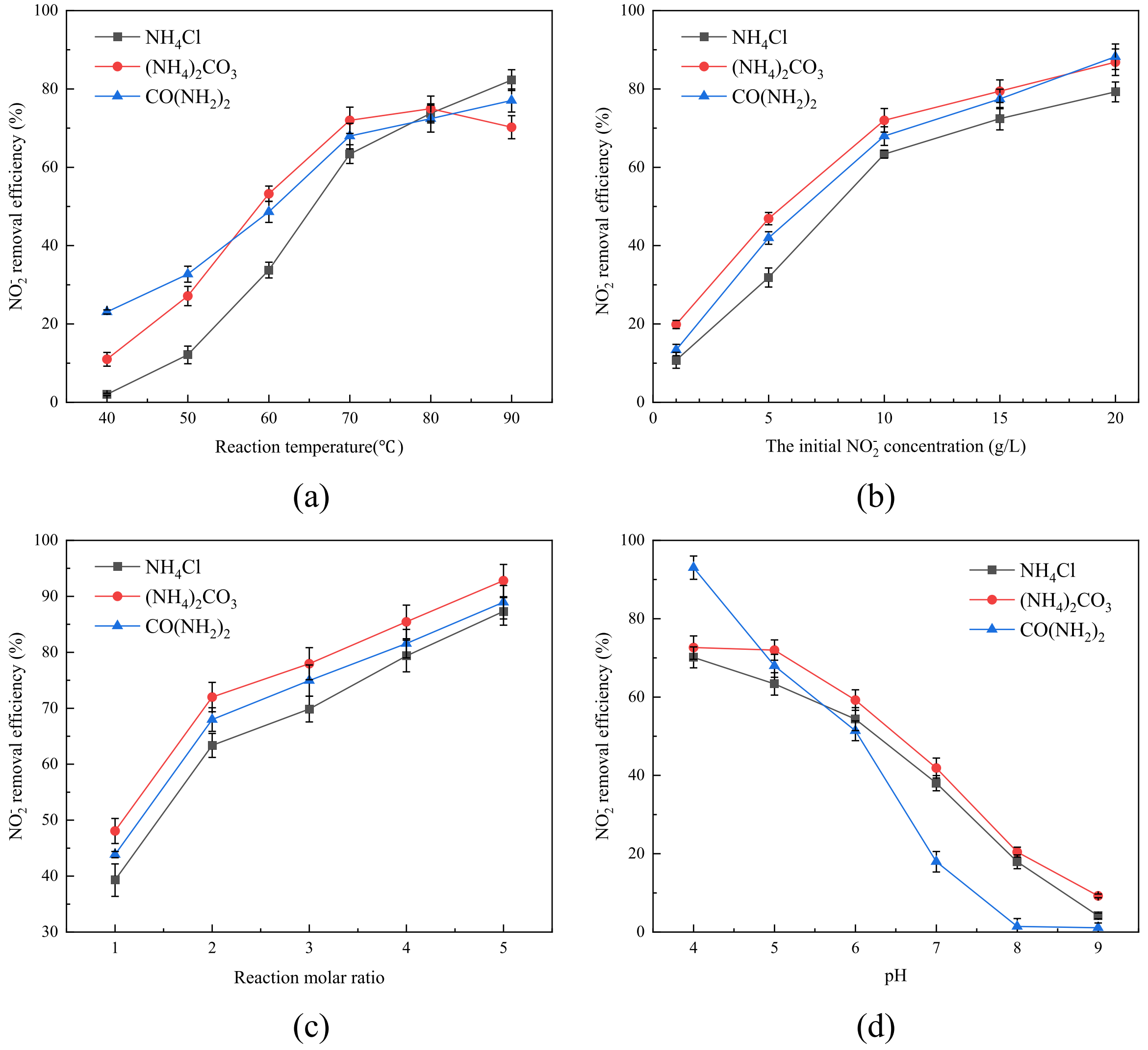


Fig. 4. Comparison of reaction characteristics of three additives with NO_2^- (a) reaction temperature, (b) initial NO_2^- concentration, (c) reaction molar ratio, (d) absorbent pH.

Considering the above conditions, the initial slurry pH is selected in the range of 5–5.5, which is consistent with the pH of the spray tower absorption slurry in practical industry.

3.5. Comparison of the reaction characteristics of three additives with NO_2^-

In the previous sections, the effects of reaction temperature, initial NO_2^- concentration, reaction molar ratio, and the initial pH on nitrite removal efficiency by three additives have been analyzed. In this section, the reaction characteristics of three additives (NH_4Cl, $(NH_4)_2CO_3$, and $CO(NH_2)_2$) with NO_2^- will be further studied and compared to select the most optimal additive for different conditions.

Comparison of the reaction characteristics of three additives with NO_2^- is shown in Fig. 4. In general, NO_2^- removal efficiency by the three additives increases with the increase of reaction temperature, NO_2^- initial concentration and reaction molar ratio, and decreases with increasing the initial absorbent pH. At common temperature, the influence law and trend of initial NO_2^- concentration and reaction molar ratio on NO_2^- removal efficiency by three additives are similar, and the overall removal effect is $(NH_4)_2CO_3 > CO(NH_2)_2 > NH_4Cl$. Under the reaction conditions of temperature = 70 °C, NO_2^- initial concentration = 10 g/L, reaction molar ratio = 2 and initial absorbent pH = 5, the NO_2^- removal efficiency by $(NH_4)_2CO_3$ reached 72.0% after 180 min of reaction. And because the absorption solution system is generally in a slightly acidic environment, CO_3^{2-} can generate CO_2, which helps to avoid introducing new impurity ions. Therefore, $(NH_4)_2CO_3$ is the best choice among the three additives. However, at lower temperatures (<50 °C), the reactivity of $CO(NH_2)_2$ with

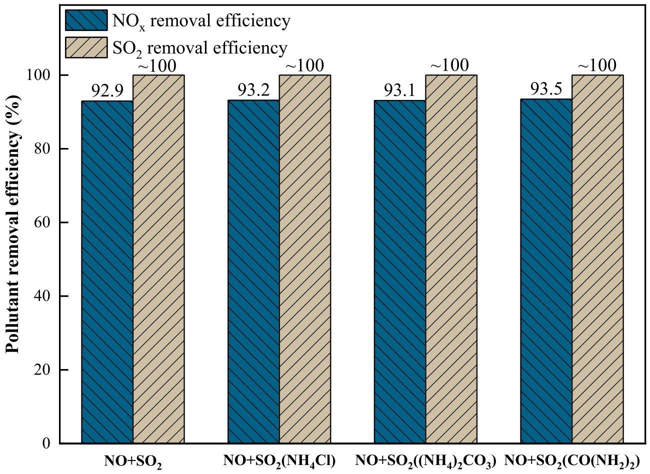


Fig. 5. Effect of three additives on NO_x/SO_2 removal efficiency.

NO_2^- is better. Under alkaline conditions, $CO(NH_2)_2$ and NO_2^- hardly react. As a result, $CO(NH_2)_2$ has more advantages than the other two additives in high acidity and low-temperature slurry.

3.6. Effect of additives on NO_x/SO_2 removal efficiency

We used the ozone oxidation flue gas coupled wet spraying system to investigate the synergistic removal of NO_x/SO_2 and by-product nitrite. Effect of three additives on the removal efficiency of flue gas pollutants is shown in Fig. 5. The experimental results reveal that the ozone oxidation flue gas coupled wet spraying system can simultaneously remove NO_x and SO_2 efficiently. The removal efficiency of NO_x under all working conditions was more than 90.0%, while the removal efficiency of SO_2 approached almost 100% after washing. Under the condition of simultaneous oxidation of NO/SO_2, the NO_x removal efficiency was 92.9% without any additive added to the absorption slurry. Under the same condition, the NO_x removal efficiency became 93.2%, 93.1% and 93.5% respectively after adding three additives (NH_4Cl, $(NH_4)_2CO_3$, and $CO(NH_2)_2$) to the absorption slurry. This indicates that the three additives have little impact on the removal efficiency of NO_x and SO_2, and will not affect the stable operation of the wet spraying system.

The generation of by-product NO_2^- in absorption slurry is shown in Fig. 6. Under the conditions of simultaneous oxidation of NO/SO_2 and 180-min reaction, the NO_2^- concentration was 3.63 mg/L before adding NH_4Cl. Under the same conditions, the NO_2^- concentration dropped to 0.44 mg/L when adding 1 g/L NH_4Cl, achieving an 87.9% removal efficiency of the by-product nitrite. Similarly, in the second group of experiments, the NO_2^- concentration was 3.59 mg/L before adding $(NH_4)_2CO_3$. Under the same conditions, the NO_2^- concentration dropped to 0.38 mg/L when 1 g/L $(NH_4)_2CO_3$ was added, and the removal efficiency of by-product nitrite reached 89.4%. In the third group, the NO_2^- concentration before adding $CO(NH_2)_2$ was 3.65 mg/L. When adding $CO(NH_2)_2$, the NO_2^- concentration was 0.43 mg/L after 180 min of reaction and the nitrite removal efficiency reached 88.2%. The experimental results show that the three additives can efficiently reduce the concentration of by-product NO_2^- in the absorption slurry under the condition of ensuring the removal efficiency of NO_x/SO_2.

4. The practical applications and future research prospects

The removal of NO_x is a crucial area of research. Ozone oxidation flue gas denitration technology is widely used due to its advantage of broad fuel applicability, high furnace type universality, high removal efficiency, low reaction temperature (90–150 °C), and ability to remove multiple pollutants in one system. The ability to reduce the nitrite concentration in the absorption slurry with high efficiency and low cost has become critical for the widespread application of this technology. In this study, three different additives (NH_4Cl, $(NH_4)_2CO_3$, and $CO(NH_2)_2$) were added to react with NO_2^- to realize the harmless removal of the denitration by-product nitrite, which can improve the environmental sustainability and economy of the technology. Three additives have been proven to be effective in removing nitrite and do not affect the removal efficiency of NO_x and SO_2 in flue gas. The scheme can be coupled with existing ozone oxidation denitration technology. In practical engineering, long-term circulating spray of absorption slurry in scrubbing towers makes efficient removal of nitrite viable. Future research can focus on exploring various types of additives and absorbents.

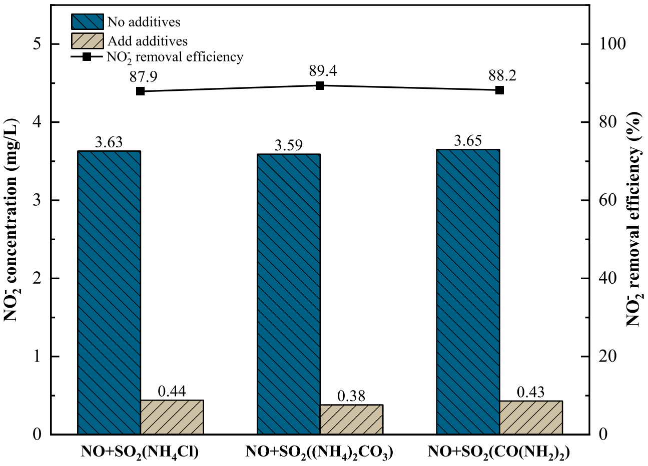


Fig. 6. Generation of by-product NO_2^- in absorption slurry.

5. Conclusions

This study investigated the use of three different additives (NH_4Cl, $(NH_4)_2CO_3$, and $CO(NH_2)_2$) to achieve the harmless removal of the denitration by-product nitrite. The experimental results revealed that all three additives were able to efficiently reduce the NO_2^- concentration. In general, NO_2^- removal efficiency by the three additives increased with the increase of reaction temperature, NO_2^- initial concentration and reaction molar ratio, but decreased with the increase of initial absorbent pH. Under the conditions of temperature = 70 °C, initial NO concentration = 10 g/L, reaction molar ratio = 2 and initial pH = 5, the NO_2^- removal efficiency by the three additives reached 63.4%, 72.0% and 68.0% respectively after 180 min of reaction. Overall, $(NH_4)_2CO_3$ had the highest removal effect under common slurry temperature and slightly acidic conditions, followed by $CO(NH_2)_2$ and NH_4Cl. However, $CO(NH_2)_2$ outperformed the other two additives in high acidity and low-temperature slurry. Furthermore, the ozone oxidation flue gas coupled wet spraying system can simultaneously remove NO_x and SO_2 efficiently. With initial NO concentration = 250 ppm, SO_2 concentration = 100 ppm, and the O_3/NO molar ratio = 1.6, the NO_x removal efficiency was 92.9% when no additive was added. The NO_x removal efficiency increased to 93.2%, 93.1% and 93.5% respectively after adding NH_4Cl, $(NH_4)_2CO_3$, and $CO(NH_2)_2$ to the absorption slurry. SO_2 was nearly 100% removed within all studied process parameters. The results indicated that the three additives had little effect on the removal efficiency of NO_x/SO_2, and would not affect the stable operation of wet spraying system. Under the same conditions, the nitrite removal efficiency by three additives reached 87.9%, 89.4% and 88.2% respectively.

CRediT authorship contribution statement

Yiwei Zhang: Experiment, Data curation, Investigation, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Zhihua Wang:** Investigation, Methodology, Formal analysis, Writing – review & editing, Supervision. **Yong He:** Methodology, Formal analysis, Writing – review & editing. **Yanqun Zhu:** Experimental apparatus, Writing – review & editing. **Jianzhong Liu:** Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.eti.2023.103236.

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