

Simultaneous removal of nitrogen and sulfur oxides using the NaClO₂/NaOH composite absorbent via ultrasonic atomization

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Abstract. In this study, NaClO₂ was used as an oxidant and mixed with NaOH to prepare a sodium-based composite absorbent. Simultaneous desulfurization and denitrification experiments were conducted in an ultrasonic atomization reactor and the effects of experimental parameters including pH value, NaClO₂ concentration, initial concentration of NO, reaction temperature, the addition of SO₂ and the utilization of ultrasonic atomization on desulfurization and denitrification efficiencies were investigated. Under the circumstance of the pH of 10, oxygen content of 8%, reaction temperature of 55°C, and NO concentration of 500 mg/m³, SO₂ concentration of 1400 mg/m³, 69.38% of NO and 99.95% of SO₂ can be removed using the composite absorbent composed of 0.02 mol/L NaClO₂ and 0.1mmol/L NaOH. Ultrasonic atomization increased the denitrification rate by 10.6%.

1 Introduction

The main atmospheric pollutants produced by coal combustion are SO₂ and NO₂, which are responsible for acid rain and haze formation. SO₂ and NO₂ as gaseous precursors interact with organic contaminants and are oxidized in photochemical reactions to generate fine particles that form haze. Currently, the technologies of desulfurization and denitrification of flue gas use a step-by-step disposal model that treats only one pollutant at a time. The simultaneous removal of SO₂ and NO_x is associated with many problems such as poor matching among various systems, the demand for a large area for equipment and repeated investment, a high cost of construction and operation of the system, and high energy consumption.

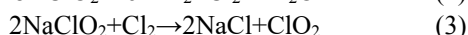
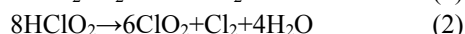
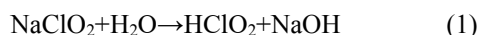
Wet flue gas desulphurization process cannot remove NO because approximately 90% of the NO_x is NO, which is insoluble in water. At 0°C, the dissolution of NO in 100 g water is 7.34 mL; at 100°C, NO is completely insoluble in water. On the contrary, NO₂ is easily soluble in water and especially easy to be absorbed by the sulfite aqueous solution. NO_x is a very complex family of air pollutants that include NO, NO₂, N₂O₃, and N₂O₄, among which, NO and NO₂ are the main components. According to the thermodynamic equilibrium under different temperature conditions, both are relatively stable at low temperatures (<200°C). When the temperature is higher than 200°C, NO₂ is very unstable and decomposes easily. After the temperature reaches 700°C, there is no NO₂ left in the NO_x system. The non-reductive denitrification technology removes NO at the high-temperature range. At low temperatures, NO is difficult to be removed; it can only be removed with an alkaline absorbent in the NO₂ form. Therefore, to achieve simultaneous wet flue gas

desulfurization and denitrification, a new absorber that can oxidize and absorb NO at low temperatures is needed.

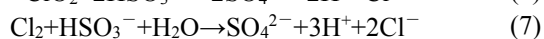
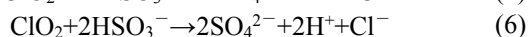
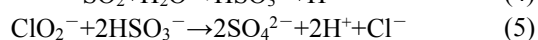
There are many types of sodium-based absorbents and some of them have strong oxidizing properties. The composite absorbent is mainly composed of an oxidizing agent and an alkaline absorbent. Sodium-based absorbents were first used in the sodium sulfite circulation process, also called the Wellman-Lord process [1]. The desulfurization rate of the technology is above 90%, the regeneration process of the removal agent is simple, and the energy consumption is low. Additionally, there is no fouling or clogging problem during operation and high concentrations of SO₂ can be recovered. The results of Teramoto, Ikeda, and Teranishi [2] showed that the absorption rate of NO was mainly affected by the concentrations of NO and NaClO₂ and high concentrations of NaOH had an inhibitory effect on the absorption reaction. The experimental results of Sada et al. [3] showed that, in the process of removal, the decomposition degree of NaClO₂ was much greater than that of independent desulfurization and ClO₂ produced by NaClO₂ oxidized NO to NO₂. The results of Yang, Shaw, and Perlmutter [4, 5] showed that the NaClO₂ solution could absorb NO quantitatively. The mixed solution formed by adding low-concentration NaOH increased the NO absorption by 7%. However, high-concentration NaOH would decrease or impede NO absorption. The results of Chan [6] and Brogren, Karlsson, and Bjerle [7] showed that the NaClO₂ oxidation method showed a high removal rate for both SO₂ and NO. The results of Hsu, Lee, and Chou [8] and Chien, Chu, and Hsueh [9] showed that the reaction temperature of desulfurization and denitrification of the NaClO₂ solution was between 20–30°C and the removal reactions were as follows:

(1) NaClO₂ is decomposed in an acid solution:

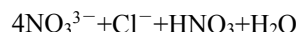
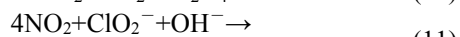
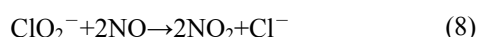
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(2) SO₂ removal reaction



(3) NO removal reaction



Sodium chlorite solution has been widely studied as an absorbent for flue gas desulfurization and denitrification. It has the advantages of high removal efficiency, simultaneous oxidation and absorption, no scaling, and low investment cost in the simultaneous desulfurization and denitrification of the liquid phase. Adewuyi et al. [10] used a buffer system of NaClO₂ to achieve optimal absorption when pH was controlled at 6-7. Deshwal et al. [11] investigated the desulfurization and denitrification performance of the NaClO₂ solution under acidic conditions. When pH was less than 4, the maximum denitrification effect was achieved (~81%). However, owing to the high price of NaClO₂, its use in practical applications is not ideal. Sodium-based absorbents have a high removal effect on both SO₂ and NO, especially on NO, which makes them increasingly popular.

Based on the previous research results, in this study, the exhaust gas from new dry cement production was used as the treatment target and the renewable NaClO₂/NaOH composite absorbent was adopted to conduct simultaneous desulfurization and denitrification experiments in an ultrasonic atomization reactor. Meanwhile, the parameters affecting the oxidation and absorption of NO were studied. The main parameters of the experiment including initial pH, NaClO₂ and NO₂ concentrations, reaction temperature, and the effect of SO₂ on denitrification efficiency were investigated. The effects of ultrasonic atomization on the desulfurization and denitrification of composite absorbents were analyzed.

2 Experimental Materials, methods and apparatus

Standard gases including zero gas and N₂ (99.995%), O₂ (99.995%), SO₂ (99.6%), and NO (99.4%) span gas were purchased from Beijing HuaYuan Gas Chemical Co. Ltd. NaOH (purity>99%), NaClO₂ (purity>87%), and Ca(OH)₂ (purity>95%) were from Beijing Chemical Works.

The experimental device is shown in Fig. 1. It mainly consists of five parts: a gas supply system, a proton flowmeter, an ultrasonic atomization reactor, a temperature control device, and a flue gas analyzer. The flue gas simulates the exhaust of a new dry process

cement plant. N₂, O₂, NO_x, and SO₂ are used to form the simulated flue gas at a prescribed ratio and are heated to the desired temperature in a constant temperature control system. The parameters of the simulated flue gas are presented in Table 1. A certain concentration of the absorbent is atomized in the dosing tank through an ultrasonic nozzle. The mixed gas is passed into the ultrasonic reactor and reacts with the atomized absorbent. After the reaction, the absorbent is collected and exported through the slots at the bottom of the ultrasonic reactor. The ultrasonic atomization device is composed of an ultrasonic nozzle and an ultrasonic atomization special controller with a size of 18 cm×18 cm×15 cm. The reaction field diameter is 10 cm and the length is 50 cm. The reactor is equipped with an ultrasonic atomization nozzle with a flow rate of 0.04 L/min. The reacted gas is passed through the flue gas analyzer (Thermo Fisher Model 42i-HL) to monitor SO₂ and NO concentrations in real time. The initial pH of the absorbent is adjusted by the absorbent concentration and the reaction temperature is adjusted by a heating device (tube furnace).

The equations for calculating the removal rate of SO₂ and NO_x are as follows:

$$\eta_{\text{SO}_2} = \frac{c_{\text{inSO}_2} - c_{\text{outSO}_2}}{c_{\text{inSO}_2}} \times 100\% \quad (12)$$

$$\eta_{\text{NO}_x} = \frac{c_{\text{inNO}_x} - c_{\text{outNO}_x}}{c_{\text{inNO}_x}} \times 100\% \quad (13)$$

3 Results and discussion

3.1 Effect of initial pH value on denitrification rate

The NaClO₂ oxidant was used in the alkaline desulfurization and denitrification system. The pH value is an important parameter affecting the denitrification reaction. Therefore, this section focuses on the effect of pH on the denitrification rate.

Under different NO concentrations, the influence of initial pH on the NO removal rate was basically the same (Fig. 2). The pH range examined here was 7-12. The NO removal rate began to decrease slowly with increasing pH and the NO absorption rate declined sharply when the pH was higher than 10 because the oxidizing ability of NaClO₂ was inversely proportional to pH and generated more ClO₂ under acidic conditions [12]. However, the increase in pH was beneficial to the absorption of NO₂ in the follow-up reaction. Furthermore, the composite solution should contain a sufficient amount of NaOH. Based on the study of Sada et al. [13, 14], when the NaOH concentration changed within the range of less than 0.5 mol/L, the NO absorption rate ($k=3.8\exp(-3.73C_{\text{NaOH}})$) decreased exponentially with increasing NaOH concentrations; thus, the experimental pH value was assumed to be 10.

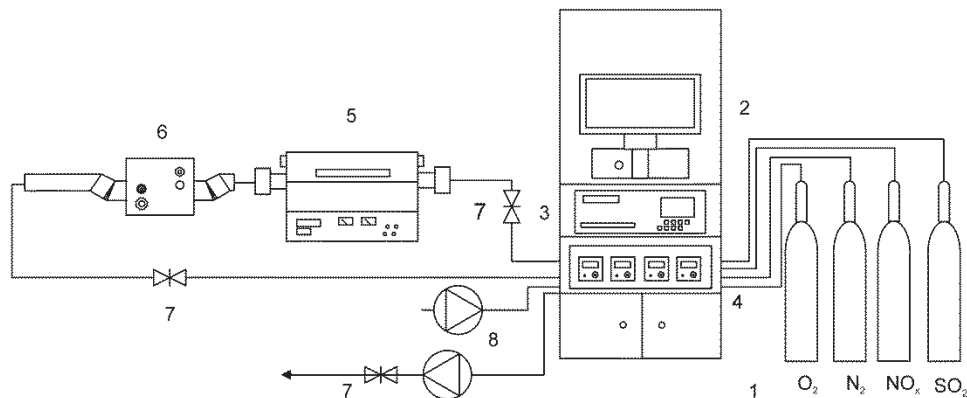


Fig. 1. Experimental device

Table 1. The parameters of the simulated flue gas

Simulation parameters	Parameter value	Unit
Flue gas flow	0.3	m ³ /h
SO ₂ inlet concentration	800~1500	mg/m ³
NO inlet concentration	200~1000	mg/m ³
Oxygen content	8	%
Temperature	20~100	°C

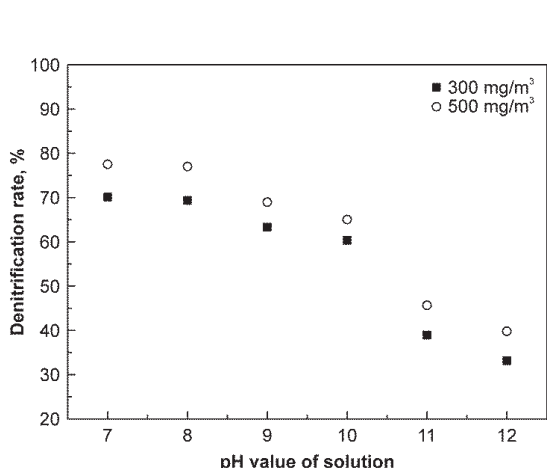


Fig. 2. The effect of initial pH on NO removal rate

3.2 Effect of NaClO₂ concentration on denitrification rate

The NaClO₂ oxidant was used in the alkaline desulfurization and denitrification system. The pH value is an important parameter affecting the denitrification reaction. Therefore, this section focuses on the effect of pH on the denitrification rate. In general, NO is insoluble in water and NO₂ is easily soluble in water and in the alkaline solution. Therefore, the concentration of NaClO₂ plays a key role in the oxidation and absorption of NO. A new alkaline absorbent was prepared by mixing the NaClO₂ solution with a concentration of 0.005–0.030 mol/L and NaOH solution with a concentration of 0.1mmol/L. The denitrification results of the new alkaline absorbent are shown in Fig. 3.

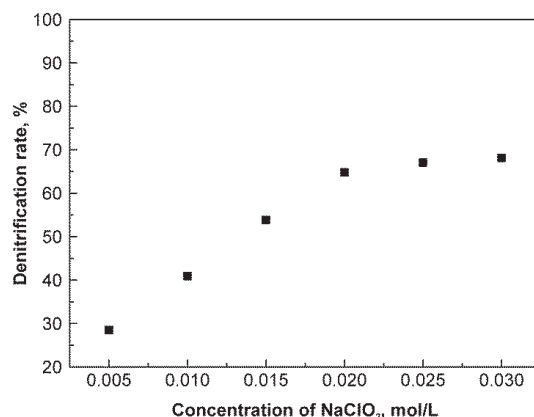


Fig. 3. Effect of NaClO₂ concentration on denitrification rate

Figure 3 shows the relationship between NaClO₂ concentrations and the NO removal rate. The removal rate of NO increased significantly with the increase in NaClO₂ concentrations. When the NaClO₂ concentration increased from 0.005 to 0.020 mol/L, the NO removal rate almost increased linearly from 28.51% to 63.78% because with the increase in the NaClO₂ concentration, the concentration of effective chlorine in the absorbent increased and this was beneficial for more NO to be oxidized and absorbed. Therefore, the removal efficiency was greatly improved.

When the NaClO₂ concentration reached 0.02 mol/L, the increase in the NO removal rate slowed down and it was finally maintained at 68.11%. The mass transfer equation of the chemical absorption in the liquid phase [15] is:

$$N = K_L(C_i - C_L)(1 + \gamma S) \quad (14)$$

where N is the mass transfer rate through the gas-liquid interface, kmol/(m²·s); C_i is the concentration at the phase interface, kmol/m³; C_L is the liquid phase concentration, kmol/m³; K_L is a liquid film mass transfer coefficient driven by the concentration difference, m/s; is

the enhancement coefficient (E); γ is the diffusion coefficient ratio, which is usually approximately 1; and S is the ratio of the measured concentration, which mainly reflects the influence of the chemical reaction on the mass transfer rate N (CBL is the NaClO₂ concentration in the absorbent).

As CBL increases, E and N also increase accordingly. Therefore, the decrease in the NO concentration in the gas phase is accelerated and the absorption rate of NO_x increases. The CL increases with the increase in CBL. However, when the concentration of the absorbent increases continuously and reaches or approaches a critical value, the promotion of the mass transfer rate N is no longer obvious. Therefore, the effect on NO removal rate is not significant. Considering the effect on denitrification, the optimal concentration of NaClO₂ was determined to be 0.02 mol/L.

3.3 Effect of initial concentration of NO on denitrification rate

Figure 4 shows the influence of NO inlet concentrations on the denitrification rate when other reaction conditions were unchanged. When NO concentrations were 200, 500, 800, and 1000 mg/m³, the denitrification rate increased first and then decreased with the increasing import concentration. When the NO concentration was 500 mg/m³, the absorption rate was 64.55%, higher than the 55.53% when the NO concentration was 200 mg/m³ because the increase in the NO concentration enhanced the conversion of NO. When NO was within a certain concentration range (200-800 mg/m³) [16], the absorption process was controlled by kinetics. Increasing the NO concentration can increase the gas-liquid mass transfer kinetics to some extent. When the NO inlet concentrations were 800 mg/m³ and 1000 mg/m³, the corresponding NO absorbance rates were 60.32% and 61.82%, respectively. At a certain amount of composite absorbent, with the increase in NO concentration, a part of NO could not be oxidized to NO₂; therefore, the amount of NO_x decreased. At the same time, a part of NO₂ was further oxidized to nitrate and the rest was released as NO. Thus, the absorption rate of NO was slightly decreased by the composite absorbent.

3.4 Effect of reaction temperature on denitrification rate

The effects of reaction temperature on the absorptivity of NO were studied at 40, 50, 60, 70, and 80°C and the results are shown in Fig. 5.

As the reaction temperature increased, the denitrification rate also increased. When the reaction temperature was over 60°C, the denitrification rate decreased slightly. The increase in the reaction temperature can effectively increase the activation energy of gas molecules, the number of collisions between molecules per unit time, and thus the reaction rate. The appropriate temperature increase can improve the oxidation ability of NaClO₂, but excessive temperatures may also lead to the decomposition of NaClO₂ and thus

the loss of its oxidation ability. The solubility of NO decreased at higher temperatures, but the reaction rate increased with increasing temperature. Ultimately, these two effects canceled each other out; the temperature continued to rise but the changes in the overall NO_x absorption rate were not obvious. When temperature was further increased, the reduction in NO dissolution was evident; thus, the denitrification rate decreased. Therefore, the reaction temperature suitable for the absorption of NO_x was determined as 50-60°C and the optimum reaction temperature was 55°C.

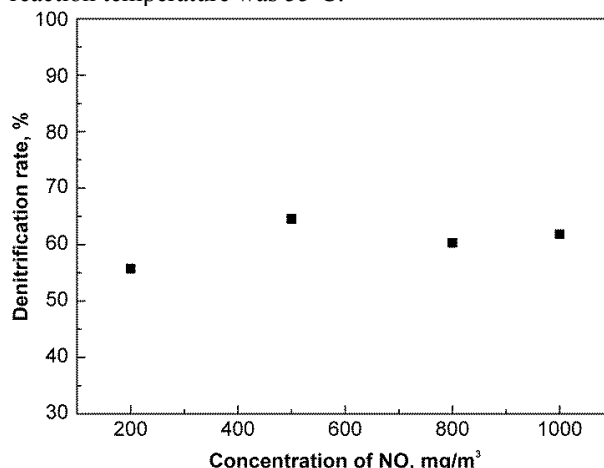


Fig. 4. Effect of initial concentration of NO on denitrification rate

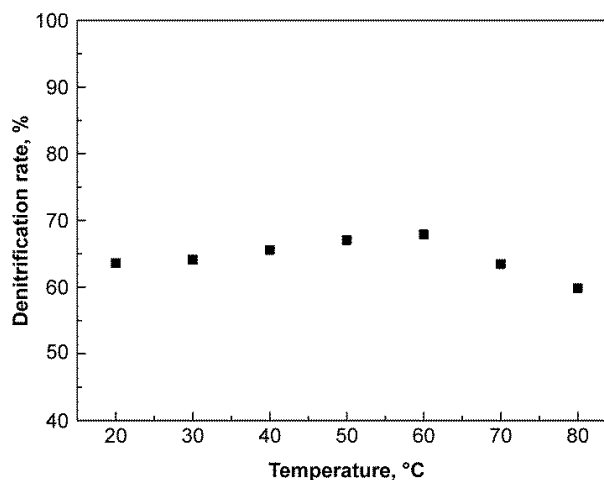


Fig. 5. Effect of reaction temperature on denitrification rate

3.4 Effect of reaction temperature on denitrification rate

The effects of reaction temperature on the absorptivity of NO were studied at 40, 50, 60, 70, and 80°C and the results are shown in Fig. 5.

3.5 Effect of SO₂ input on denitrification rate

Figure 6 shows that the absorption of SO₂ promotes the absorption of NO_x, but the denitrification rate decreases slightly with the increase in the reaction time because SO₂ preferentially reacts with NaOH in the composite

absorption and generates SO_3^{2-} [17]. The rapid reaction of free radical exchange between SO_3^{2-} and NO_2 promoted the absorption of NO_x and the denitrification rate increased from 63.15% to 69.38%. The presence of SO_2 also consumed some of the NaClO_2 in the composite absorbent. Therefore, the absorption rate of NO_x decreased slightly in the later period. The absorption rate of the composite absorbent for SO_2 was 99.95%; the removal rate was close to 100% and it did not change with the increase in the reaction time.

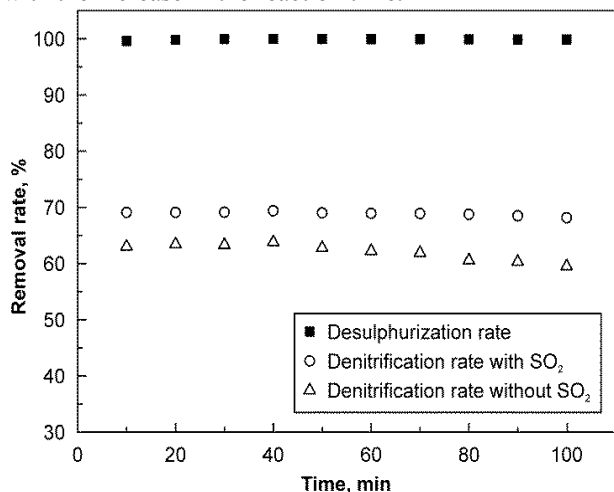
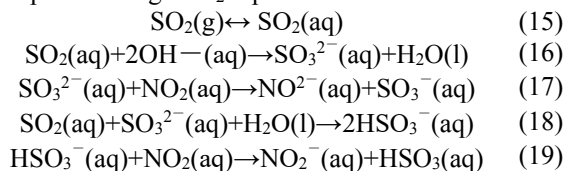


Fig. 6. Effect of SO_2 input on denitrification rate

The reaction mechanisms that promoted NO_x absorption through SO_2 input were as follows:



3.6 Effect of ultrasonic atomization on simultaneous desulfurization and denitrification

Ultrasound refers to sound waves with frequencies of 20 kHz to 50 MHz. Their high frequency and short wavelength give them the properties of high energy density, good directionality, and strong penetration. Ultrasound application to chemical reactions can speed up the reaction process and improve the reaction yield. The mechanism of ultrasonic atomization process originates from the phenomenon of "acoustic cavitation" [18].

Figure 7 shows the high desulfurization rate observed in two reaction devices. The highest desulfurization rates of the ultrasonic atomization device and the bubbling reaction device were 99.95% and 99.00%, respectively, suggesting that ultrasonic atomization had a slight increase in desulfurization rate. The highest denitrification rate in the ultrasonic atomizing device was 69.38% and average denitrification rate was 68.89%. The highest denitrification rate in the bubbling reaction device was 59.49% and average denitrification rate was 58.29%. The denitrification rate of the ultrasonic atomizing reactor was 10.6% higher than that of the bubbling reaction device. The ultrasonic atomization greatly improved the

denitrification of the new alkaline absorbent and the high denitrification rate could be maintained for a long time in the ultrasonic atomization device.

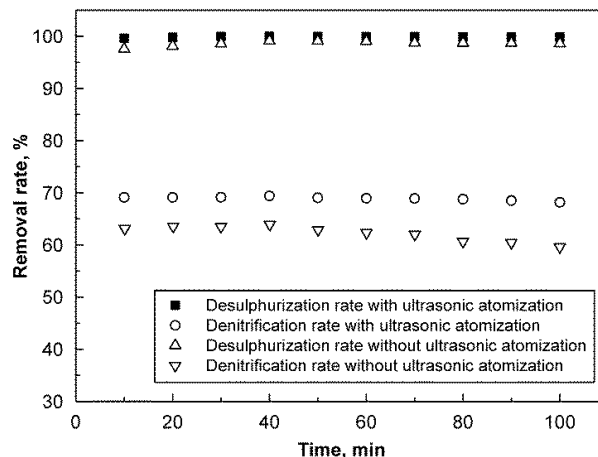


Fig. 7. Effect of ultrasonic atomization on desulfurization and denitrification rate

Ultrasound can atomize the absorbent solution to reduce the mass transfer resistance at two-phase contact sites, thereby improving the mass transfer efficiency [18]. Its promotion is reflected in both physical and chemical aspects. From the physical reaction perspective, the effect of "acoustic cavitation" can atomize the solution containing the absorbent into droplets with diameters of 5–15 μm . Atomization can increase the contact area between the flue gas and the absorbent, strengthen the gas-liquid mass transfer, improve the mass transfer efficiency, and further improve the reaction efficiency. At the same time, the vibration of the sound wave, the shock wave, and the microjet produced by "acoustic cavitation" will increase the disturbance of the droplets and the flue gas and increase the contact area between them so that the droplets and the flue gas are dispersed uniformly. From the chemical reaction perspective, the "acoustic cavitation" produces localized high-temperature and high-pressure conditions, which are suitable for desulfurization reactions; increases the reaction rate; and enables the reactions that are difficult to proceed under normal temperature and pressure conditions. In addition, under the action of "ultrasonic cavitation", hydroxyl radicals with strong oxidative properties are generated in the liquid and act as oxidants to promote desulfurization reactions and accelerate the reaction process.

3.7 Effect of ultrasonic atomization on simultaneous desulfurization and denitrification

To explore the flow field properties of the ultrasonic spray gun, a three-dimensional model was established and the numerical simulation was performed using Fluent, which is a computational fluid dynamics (CFD) analysis software.

The boundary conditions for setting the CFD numerical simulation are as follows. The exhaust gas from a 5500 t/d new dry cement production line was used as the treatment target and the exhaust gas volume is 700,000 m^3/t and 550,000 m^3/t . The spray nozzle flow is

0.13 L/min, flow velocity is 17 m/s, exhaust gas composition is SO₂, NO_x, O₂, dust, and a small amount of chloride ion. SO₂ concentration is 1500~2000 mg/Nm³ and NO_x is 850 mg/Nm³. The gas density is 1.35 based on the general density of coal-fired flue gas and the exhaust gas temperature is 90~120°C. The size of the reaction device is 2000 x 2000 mm. The nozzles are divided into four zones. Each gun has six branches and each gun branch has three nozzles. The flow velocity is 3.08 m/s and nozzle flow velocity is 17 m/s. After inputting these parameters, the flow field simulation diagram of ultrasonic atomization device was obtained.

Figure 8 shows that after atomization by the ultrasonic nozzle, small droplets form a relatively regular circle with the nozzle as the centre of a relatively dense reaction environment. This environment was beneficial to the uniform dispersion of the absorbent. It was not easy to reduce the local concentration of the absorbent because liquid drops were too loose, which affected the removal reaction.

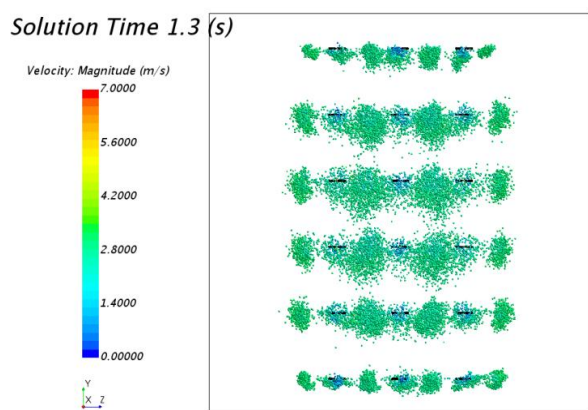


Fig. 8. Elevation view of atomized particles in ultrasonic nozzles

Figure 9 shows the trajectory of the tiny droplets produced by ultrasonic atomization in the horizontal direction. The ultrasonic nozzle can fully atomize the absorbent. The droplets formed can not only improve the mass transfer efficiency between the gas and liquid phases but also increase the viscosity of the fluid and reduce the viscous flow, further improving the mass transfer efficiency [19].

Figure 10 shows that the ultrasonic atomized tiny droplets formed an ultrasonic mist cluster, which fully filled the reaction zone and had an excellent barrier flushing effect on the over-flow fumes and achieved the best contact reaction state through full mixing.

4 Conclusion

NaClO₂ is feasible for use in denitrification under alkaline conditions. At pH 10, the oxidation and denitrification properties of NaClO₂ reached their optimal values. Wet desulfurization and denitrification experiments were conducted in an ultrasonic atomization device using the NaClO₂/NaOH composite absorbent. The optimum working conditions were as follows. The concentrations

of NO, SO₂, NaClO₂ and NaOH were 500 mg/m³, 1400 mg/m³, 0.02 mol/L, and 0.1 mmol/L, respectively. The pH value of the solution was 10, the reaction temperature was 55°C, and the oxygen content was 8%. The desulfurization rate and denitrification rates were 99.95% and 69.38%, respectively. The ultrasonic atomization can increase the denitrification rate by 10.6% while maintaining the high efficiency and stability of the desulfurization and denitrification rates.

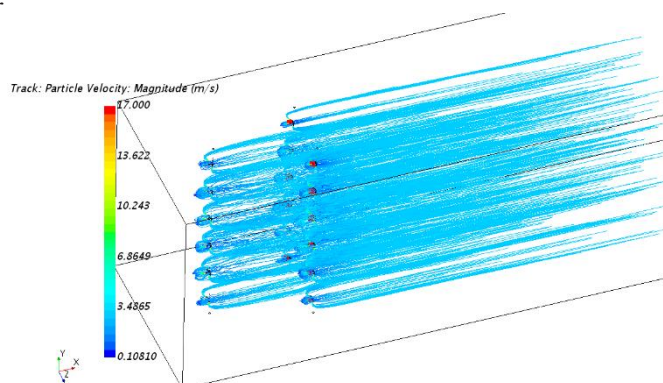


Fig. 9. Particle trajectories of atomization of ultrasonic nozzles

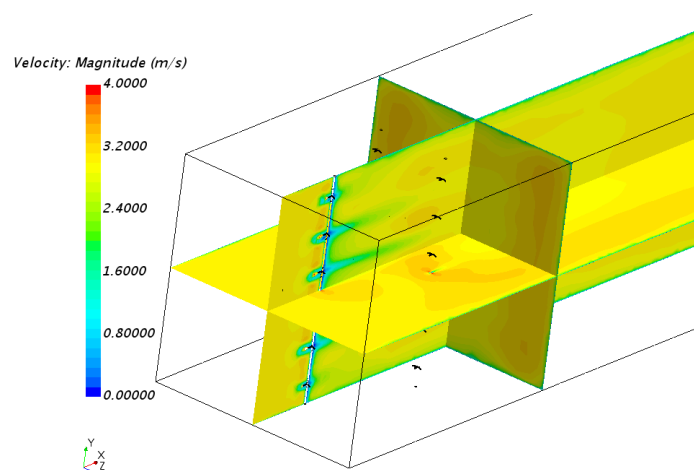


Fig. 10. Cross section velocity distribution view of ultrasonic atomization flow field

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