Simultaneous desulfurization and denitrification of sintering flue gas via composite absorbent *

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Abstract Experiments on simultaneous absorption of SO₂ and NO_x from sintering flue gas via a composite absorbent NaClO₂/NaClO were carried out. The effects of various operating parameters such as NaClO₂ concentration (m_s), NaClO concentration (m_p), molar ratio of NaClO₂/NaClO (M), solution temperature (T_R), initial solution pH, gas flow (V_g) and inlet concentration of SO₂ (C_s) and NO (C_N) on the removal efficiencies of SO₂ and NO were discussed. The optimal experimental conditions were determined to be initial solution pH=6, T_R =55 °C and M =1.3 under which the average efficiencies of desulfurization and denitrification could reach 99.7% and 90.8%, respectively. Moreover, according to the analysis of reaction products, it was found that adding NaClO to NaClO₂ aqueous solution is favorable for the generation of ClO₂ and Cl₂ which have significant effect on desulfurization and denitrification. Finally, engineering experiments were performed and obtained good results demonstrated that this method is practicable and promising.

Keywords simultaneous desulfurization and denitrification, sintering flue gas, composite absorbent

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1 Introduction

Among the various processes in iron and steel industry, the emission of NO_x from the sintering process accounts for 50% of the total NO_x emission. Additionally, the SO_2 discharging from the sintering process is about 80%. These gases are the main pollutant harmful to human and other living beings, the reduction of which is an important work of the iron and steel production enterprises [1]. Along with the fact that the emission standard of NO_x and SO_2 is more and more rigorous, the development of novel technologies for simultaneous desulfurization and denitrification of sintering flue gas will be another challenging and urgent issue following the flue gas treatment of power plant [2]. At present, wet flue gas desulfurization (FGD) is a relatively mature and most widely applied technology in iron and steel industry to control the SO_2 emission. However, it is not much effective for the absorption of NO_x because NO_x from the sintering flue gas mainly exists in the form of NO which is poorly soluble in water [3]. The common technologies for denitrification used in coal-fired power plant are the selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) methods [4-6], but neither of them can be applied to sintering flue gas directly due to the special characteristics of sintering flue gas whose gas temperature is relative low (80 -160 °C), gas flow rate is too large (average $2.5 \times 10^6 \text{ m}^3 \cdot \text{h}^{-1}$), and the concentration of NO_x is low (100 – 400 $\text{mg} \cdot \text{m}^{-3}$). What is more, establishment of completely new equipment and technology to remove SO_2 and NO_x simultaneously requires too much economic budget and thus is hardly accepted by most iron and steel industries. An alternative way is to add NO removal function to the existing FGD system to reach the goal of simultaneous absorption of SO_2 and NO_x [7]. In other words, the aim of this technique is to use proper oxidize agents to react NO into NO_2 which ultimately can be absorbed by water.

Currently, commonly used oxidizing agents include ClO_2 [8, 9], O_3 [10, 11], KMnO_4 [12- 15], H_2O_2 [16-18], NaClO_2 [19-27], NaClO [28, 29] and so on. For the wet FGD, the reaction mainly occurs in the liquid phase, so ClO_2 , O_3 etc. will not be taken into consideration. KMnO_4 , H_2O_2 could be effective for simultaneous absorption of SO_2 and NO_x in alkaline conditions, and the

removal effects improve with the increase of pH. However, the pH of actual desulfurization slurry is between 5 and 7, KMnO_4 , H_2O_2 will not be primarily considered. Moreover, the reaction products of KMnO_4 may contaminate the FGD gypsum and causing secondary pollution. And the chemical performance of H_2O_2 is unstable, so it is difficult to be transported for long distance and reserved for long time. In general, NaClO_2 is the oxidizing agents which had been researched a lot and its effect is great for simultaneous desulfurization and denitrification. For example, Sada *et al.* [19-21] used $\text{NaClO}_2/\text{NaOH}$ solution as the absorbent to study the removal efficiency of NO under various operating parameters. They found that adding NaOH to NaClO_2 would decrease the absorption rate of NO, The removal efficiency is mainly affected by the L/G ratio and the concentration of NaClO_2 in the solution. Next, Chien *et al.* [22-24] did a series of similar experiments in a bench-scale spraying scrubber system in order to investigate the absorption kinetics of SO_2 and NO and the reaction mechanism were revealed. Unlike previous research, Yang *et al.* [25,26] performed the absorption experiments of NO by nitric acid solution of NaClO_2 in a packed bed scrubber and found the color of solution turned greenish yellow due to the presence of ClO_2 , they also used bubble column and spary chamber scrubber to absorb NO in acidic NaClO or Cl_2 solution and obtained the similar results. Deshwal *et al.* [27] revealed that NaClO_2 could decomposed into ClO_2 gas in acidic solution, which was believed to participate in denitrification and determined the removal efficiency of NO. In addition, researches on NaClO are relatively rare due to the fact that the Oxidation of NaClO is weak compared with NaClO_2 . Chen *et al.* [28, 29] developed a two-stage chemical scrubbing system to removal NO, the efficiency is obvious but the process is complicated.

According to the previous studies, NaClO_2 was demonstrated to be comparatively effective among all kinds of oxidizing agents in desulfurization and denitrification, but it is still difficult to be applied extensively in industry because of the high cost. In order to solve such problems, a compound absorbent containing NaClO_2 and NaClO was used to investigate simultaneous removal of SO_2 and NO in this study, and the key point of this art is to determine the amount of oxidizing agents and the optimal experimental conditions. At last, the success of engineering test proved that this novel method has advantages of both higher efficiency and lower cost compared with the NaClO_2 oxidation absorption method.

2 Experimental set-up

The experimental device is illustrated in Fig. 1 which includes four main parts: a flue gas simulation system, an absorption reactor system, a gas sampling and analyzing system and an off-gas treatment system. The flue gas simulation system mainly consists of a pure N₂ gas cylinder (Shangyuan Gas, purity 99.9%), a pure SO₂ gas cylinder (Shangyuan Gas, purity 99.9%), a pure NO gas cylinder (Shangyuan Gas, purity 99.9%), a gas buffer tank and four mass flow controllers (MFC). The absorption reactor unit mainly includes a self-designed lab-scale bubbling reactor and a digital heating and temperature control device. Besides, the reactor is made of stainless steel with a diameter D₁ of 320 mm and a height H₁ of 240 mm. There are 4 intake-tubes with a diameter D₂ of 14 mm and 1 exhaust tube with a diameter D₃ of 80 mm. The gas sampling and analyzing system contains a sample conditioner (Juchuang, JCGH-2) and a flue gas analyzer (MRU, Germany). The off-gas treatment system is a tank saturated with aqueous alkaline solution. The grade of sodium chlorite is analytical-pure (available chlorine $\geq 80\%$, Aladdin Industrial Corporation, Shanghai, China). The grade of sodium hypochlorite is technical-pure (available chlorine $\geq 30\%$, Nanjing Chemical Reagent Co., Ltd., Nanjing, China). The grade of sodium hydroxide ($\geq 96\%$) and phosphoric acid (65-68%) are analytical-pure (BOLT Chemical Trading Co., Ltd., Tianjin, China).

Fig. 1. Schematic diagram of experimental system

During the experiment, the flow rates of N₂, SO₂ and NO were controlled through the mass flow meters and mixed into desired concentrations in a buffer tank firstly. 10L aqueous solution with a required amount of NaClO₂/NaClO in the reactor was heated and then kept in desired

temperatures by a digital heating and temperature control device. Thereafter, the simulated gas continuously flowed through the reactor with a flow rate and was absorbed by the solution. After reaction, the simulated flue gas was sampled by a sample conditioner and analyzed through a flue gas analyzer so that the concentration of NO and SO₂ would be monitored in real time. Meanwhile, the test data was recorded in every 2 minutes, so the removal efficiency of NO and SO₂ can be calculated through Eqs. (1) to (2).

$$\eta_N = \frac{C_{\text{NO},\text{in}} - C_{\text{NO},\text{out}}}{C_{\text{NO},\text{in}}} \times 100\% \quad (1)$$

$$\eta_S = \frac{C_{\text{SO}_2,\text{in}} - C_{\text{SO}_2,\text{out}}}{C_{\text{SO}_2,\text{in}}} \times 100\% \quad (2)$$

In addition, the initial pH of absorption solution in the bubbling reactor could be adjusted by adding acid or alkaline solution (H₃PO₄ and NaOH) and detected by the LEICI pH meter. Continuous stirring was provided by a mechanical agitator. The operating conditions are shown in Table 1. Finally, the simulated flue gas before released into atmosphere would be post-processed by the off-gas treatment system.

Table 1. Operating conditions

Variables	Range
NaClO ₂ concentration (m_s) /mmol·L ⁻¹	1 - 6
NaClO concentration (m_p) /mmol·L ⁻¹	1 - 6
Solution temperature (T_R) / °C	20 - 80
Initial solution pH	2 - 8
Gas flow rate (V_g) / L·h ⁻¹	20 - 100
NO inlet concentration (C_N) / mg·m ⁻³	200 - 400
SO ₂ inlet concentration (C_S) / mg·m ⁻³	800 - 1200

3 Results and Discussion

3.1 Effect of the concentration of NaClO₂ (m_s) and NaClO (m_p)

Figure 2 depicts the variation in NO and SO₂ removal efficiencies with the concentration of absorbent, it can be seen that the removal efficiency of NO increases at first and then slow down with m_s and the SO₂ removal efficiency almost remains constant. When m_s increases from 1 to 3 mmol·L⁻¹, the removal efficiency of NO is sharply improved by 11%. While m_s changes from 4 to

6 mmol·L⁻¹, the removal efficiency increases by 4% only. If m_s is constant, the removal efficiency of NO in $m_p=3$ mmol·L⁻¹ is higher than $m_p=0$ mmol·L⁻¹. It means that adding NaClO to NaClO₂ aqueous solution has obvious promotion on denitrification but the effect would be weakened if excess quantities of NaClO were used.

Figure 2 Effect of the concentration of NaClO₂/NaClO on the removal efficiencies ($T_R=25$ °C, pH=6, $V_g=30$ L·h⁻¹, $C_N=350$ mg·m⁻³, $C_S=1000$ mg·m⁻³)

Moreover, considering that the oxidation properties of the solution may be different under different molar ratios of NaClO₂/NaClO (M) which is calculated by using Eq. (3), experiments were carried out in different molar ratios of NaClO₂/NaClO to check the oxidization of the solution. Due to the fact that the removal efficiency of SO₂ is less affected by the concentration of oxidizing agent, we focus on the removal efficiency of NO here.

$$M = \frac{m_s}{m_p} \quad (3)$$

As shown in Fig. 3, the removal efficiency of NO shows an upward trend with the increase of M . When M is above 1.3, the removal efficiency of NO begins to be stable. These results indicate that NaClO₂ plays an important role in the process of oxidative absorption, slight change of its concentration can lead to significant increase of the removal efficiency of NO. From the aspect of economy that the price of NaClO₂ is much higher than NaClO, the cost of oxidizing agent can be reduced by decreasing NaClO₂ concentration while increasing NaClO concentration. In this study, based on the efficiency and the cost consideration, the optimal M was chosen as 1.3.

Figure 3 Effect of the molar ratio of $\text{NaClO}_2/\text{NaClO}$ on the removal efficiencies
 $(T_R=25\text{ }^\circ\text{C}, \text{pH}=6, V_g=30\text{ L}\cdot\text{h}^{-1}, C_N=350\text{ mg}\cdot\text{m}^{-3}, C_S=1000\text{ mg}\cdot\text{m}^{-3})$

3.2 Effect of solution temperature (T_R)

For the gas-liquid two phase chemical reaction, the temperature plays dual role. On one hand, the increase of temperature is beneficial to ion diffusion in solution which accelerates the rate of reaction and promotes the removal of SO_2 and NO . On the other hand, the increase of temperature lowers the solubility of SO_2 and NO in solution which increases the mass transfer resistance between gas and liquid and restrains the oxidation and absorption of SO_2 and NO . Therefore, the rise of temperature has effects of promoting and inhibiting on the experiment. Theoretically, the reaction exists optimal reaction temperature. As shown in Fig. 4, when T_R is between $30\text{ }^\circ\text{C}$ and $50\text{ }^\circ\text{C}$, the removal efficiency of NO increases with the increase of T_R , which indicates that the positive effect of temperature is greater than its inhibition on the reaction. When the temperature is above $50\text{ }^\circ\text{C}$, the removal efficiency of NO remains almost unchanged with further increasing T_R , which indicates that the promotion and inhibition of temperature on the reaction are in an equilibrium state. In the actual projects, the reaction temperature is between 50 to $70\text{ }^\circ\text{C}$, so the optimal T_R was selected as $55\text{ }^\circ\text{C}$.

Figure 4. Effect of solution temperature on the removal efficiencies
($\text{pH}=6$, $V_g=30 \text{ L}\cdot\text{h}^{-1}$, $m_s=4 \text{ mmol}\cdot\text{L}^{-1}$, $m_p=3 \text{ mmol}\cdot\text{L}^{-1}$, $C_N=350 \text{ mg}\cdot\text{m}^{-3}$, $C_S=1000 \text{ mg}\cdot\text{m}^{-3}$)

3.3 Effect of initial solution pH

Previous study shows that the removal efficiencies of NO and SO_2 were greatly affected by the initial solution pH [27], because the variation of pH would influence the oxidative absorption characteristics of solution and lead to the change of the removal efficiencies of SO_2 and NO. As shown in Fig. 5, the removal efficiency of SO_2 is slightly affected and the removal efficiency of NO decreases with increasing the initial solution pH. The main reasons are as follows: SO_2 is easily soluble in water to produce HSO_3^{2-} and H^+ . When the solution pH increases, the equilibrium reaction takes place in the positive direction which promotes the absorption of SO_2 . Furthermore, when the solution pH decreases, ClO_2 and Cl_2 are generated by the aqueous solution of $\text{NaClO}_2/\text{NaClO}$ in acidic condition, and both of the gases are beneficial to increase the removal efficiencies of NO and SO_2 . Therefore, the solution pH has slight effect on desulfurization, but its decrease can dramatically improve the removal efficiency of NO. Moreover, NO is insoluble in water which means that the absorption of NO can only rely on oxidizing agent. Therefore, the removal of efficiency of NO drops continuously when pH of the solution increases. Above analysis indicates that the lower the initial pH of the solution is, the higher removal efficiency of NO will be obtained. By considering that strong acid condition could cause severe corrosion on the experimental equipment, optimal solution pH was usually taken as 6.

Fig. 5. Effect of initial solution pH on the removal efficiencies

($T_R=25\text{ }^{\circ}\text{C}$, $V_g=30\text{ L}\cdot\text{h}^{-1}$, $m_s=4\text{ mmol}\cdot\text{L}^{-1}$, $m_p=3\text{ mmol}\cdot\text{L}^{-1}$, $C_N=350\text{ mg}\cdot\text{m}^{-3}$, $C_S=1000\text{ mg}\cdot\text{m}^{-3}$)

3.4 Effect of gas flow rate (V_g)

For a specific experiment device, V_g determines the staying time of gas in water, influences the gas-liquid mass transfer process, and changes the removal efficiencies of NO and SO₂, so it is necessary to take V_g into consideration. From Fig. 6, it can be seen that the removal efficiency of SO₂ decreased slightly but NO drops almost linearly as V_g increases. The high removal efficiency of SO₂ is due to the SO₂ dissolved in water. While NO is not soluble in water, it must be oxidized firstly by composite absorbent, and then absorbed by water. When V_g is large, the time of NO touching oxidizing agent will be reduced, consequently, there is not enough time for NO to be oxidized and absorbed thoroughly. The results indicate that V_g is lower, the removal efficiency of NO is higher. Considering about V_g is constant in actual projects, we just discuss the effect of it, and the optimal V_g will not be given.

Fig. 6. Effect of gas flow rate on the removal efficiencies
($T_R=25\text{ }^{\circ}\text{C}$, $\text{pH}=6$, $m_s=4\text{ mmol}\cdot\text{L}^{-1}$, $m_p=3\text{ mmol}\cdot\text{L}^{-1}$, $C_N=350\text{ mg}\cdot\text{m}^{-3}$, $C_S=1000\text{ mg}\cdot\text{m}^{-3}$)

3.5 Effect of the inlet concentration of SO_2 (C_S) and NO (C_N)

In the practical engineering process, the content of nitrogen and sulfur is different in various types of coal, which will change C_S and C_N from the sintering flue gas and affect the concentration driving force between gas and liquid phases. Therefore, the removal efficiencies of SO_2 and NO will also change. As shown in Fig. 7, the removal efficiency of SO_2 remains 100% and the removal efficiency of NO presents a slight upward trend with the increase of C_S . The phenomenon may be attributed to the hydrolysis of SO_2 , resulting in decreasing the solution pH and improving the oxidation of the absorbent. As seen from Figure 8, the removal efficiency of SO_2 remains stable and the removal efficiency of NO increases slightly with increasing C_N . The reason might be that the increase of C_N makes the pressure of NO in the gas phase rise and accelerates the gas-liquid mass transfer, which leads to the increase of removal efficiency of NO .

Fig. 7. Effect of SO_2 concentration on the removal efficiencies
($T_R=25\text{ }^{\circ}\text{C}$, $\text{pH}=6$, $V_g=30\text{ L}\cdot\text{h}^{-1}$, $m_s=4\text{ mmol}\cdot\text{L}^{-1}$, $m_p=3\text{ mmol}\cdot\text{L}^{-1}$, $C_N=350\text{ mg}\cdot\text{m}^{-3}$)

Fig. 8. Effect of NO concentration on the removal efficiencies

($T_R=25$ °C, pH=6, $V_g=30$ L·h⁻¹, $m_s=4$ mmol·L⁻¹, $m_p=3$ mmol·L⁻¹, $C_S=1000$ mg·m⁻³)

3.6 Parallel tests

In order to check the stability and accuracy of experiment, parallel tests were carried out under the optimal conditions in which $m_s=4$ mmol·L⁻¹, $m_p=3$ mmol·L⁻¹, $T_R=55$ °C, the initial solution pH=6, $V_g=30$ L·h⁻¹, and $C_S=1000$ mg·m⁻³, $C_N=350$ mg·m⁻³. From Table 2, it can be seen that the average removal efficiencies of SO₂ and NO are 99.5% and 90.8%, respectively, and the standard deviation of removal efficiencies are 0.5 and 0.795, respectively. It indicates that the reproducibility of experiment date is good, and the performance of experiment apparatus is stable.

Table 2. Results of parallel experiments

	NO.				Average	Standard deviation
	1	2	3	4		
η_N	100	99	99	100	99.5	0.5
η_S	91.7	89.8	91.4	90.2	90.8	0.795

4 Reaction Mechanism

For revealing the reaction mechanism and the process of simultaneous removal of SO₂ and NO by the aqueous solution of NaClO₂/NaClO, products of desulfurization and denitrification were qualitatively and quantitatively analyzed. As we know, the possible existence of ion are ClO₂⁻, ClO⁻, ClO₃⁻, Cl⁻, NO₂⁻, NO₃⁻, SO₃²⁻, SO₄²⁻ and some intermediate products ClO₂ or Cl₂ [7]. Based on the chemical properties of different ions, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻ were tested by the hydronium chromatography method and ClO₂⁻, ClO₂, ClO₃⁻ were detected by the electric potential

titrimetric method.

4.1 Interaction mechanism of $\text{NaClO}_2/\text{NaClO}$

By monitoring the color and smell of absorption solution and analyzing the reaction products, we can find that the oxidizability of $\text{NaClO}_2/\text{NaClO}$ may be different under various initial solution pH. As shown in Fig. 9, Samples 1 and 2 are the aqueous solution containing NaClO_2 and NaClO , respectively. Sample 3 is the aqueous solution of $\text{NaClO}_2/\text{NaClO}$ whose pH is 9.8 without adding acid or alkaline solution to adjust, the solution is almost colorless and a little pungent odor could be smelled. Sample 4 is the solution whose initial pH is adjusted to 6 on the basis of Sample 3, the color of it turns yellowish green, pungent odor becomes more intense. The phenomenon is attributed to products from the reaction of $\text{NaClO}_2/\text{NaClO}$ in acidic condition. From a survey of previous literatures [30-32], we can speculate that the products may be ClO_2 and Cl_2 which have positive effect on desulfurization and denitrification. In order to further understand the interaction mechanism of $\text{NaClO}_2/\text{NaClO}$, ions concentration of a single absorbents and its mixture were determined. The results are shown in Table 3.

Fig. 9. The color contrast of absorbents in different experiments process

Table 3. The changes of ions concentration in absorbing liquid ($\text{mg} \cdot \text{L}^{-1}$)

NO.	Sample	ClO_2^-	ClO^-	ClO_3^-	Cl^-
1	NaClO_2	217.252	-	4.537	22.669
2	NaClO	-	109.186	-	26.638
3	$\text{NaClO}_2 + \text{NaClO}$ (pH=9.8)	181.047	96.252	12.464	34.226
4	$\text{NaClO}_2 + \text{NaClO}$ (pH=6)	67.623	10.334	7.672	70.883

The possible reactions between ClO_2 and Cl_2 in alkaline solution are listed as follows:

So the existence of ClO_2 and Cl_2 can be confirmed by checking the variation of ClO_3^- and Cl^- concentration. Comparing Sample 1 to 3, we can find that Samples 1 and 2 both contain Cl^- , but ClO_3^- only exists in Sample 1. It can be considered that the properties of single oxidant had changed under acid condition, the reaction equations are presumed as follows [32, 33]:

The concentration of ClO_3^- and Cl^- in Sample 3 is higher than in Samples 1 and 2, indicating that ClO_2 and Cl_2 are produced. In addition, by comparing Samples 3 and 4, we can find that the concentration of ClO_2^- and ClO^- decreases, while the concentration of ClO_3^- and Cl^- increases, stating that a lower pH of the solution makes it more favorable for the generation of ClO_2 . According to the analysis of the reaction products and the reaction mechanism presumed above, the overall reaction equation of $\text{NaClO}_2/\text{NaClO}$ acid solution can be considered as follow:

4.2 Reaction mechanism of simultaneous desulfurization and denitrification

In order to explore reaction mechanism of simultaneous absorption of NO and SO_2 , experiments were carried out under the optimal conditions and the reaction products were detected. The results of products analysis are listed in Table 4.

Table 4. Products analysis of simultaneous desulfurization and denitrification using $\text{NaClO}_2/\text{NaClO}$ complex absorbent ($\text{mg} \cdot \text{L}^{-1}$)

Sample	ClO_2^-	ClO_3^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
5	67.621	7.637	70.881	-	-	-
6	10.253	3.345	113.41	5.453	13.132	45.348
7	-	0.576	218.560	2.148	35.25	207.746

Sample 5 is the initial solution containing NaClO₂/NaClO which is not involved in the reaction of simultaneous removal of NO and SO₂, Sample 6 is NaClO₂/NaClO aqueous solution which has been in reaction for 10 min, and Sample 7 is the solution whose oxidizability has been in failure for 5 min. As shown in Table 4, both the concentration of ClO₂⁻ and ClO₃⁻ decreases, and meanwhile Cl⁻, NO₃⁻, SO₄²⁻ and NO₂⁻ are produced continuously by comparing Sample 5 and 6. It indicates that composite absorbent can oxidize SO₂ and NO to the highest state in acidic condition. After the failure of oxidizing agent, the concentration of Cl⁻, NO₃⁻ and SO₄²⁻ is still rising while NO₂⁻ concentration begins to decline, so NO₂⁻ is speculated as an intermediate product.

According to the previous analysis of interaction mechanism of NaClO₂/NaClO, it was found that there exists a small quantity of ClO₂ and Cl₂ in the complex absorbent solution, and there might be a part of ClO₂ and Cl₂ from the liquid phase to the gas phase because their partial pressures in gas phase are smaller than the gas-liquid equilibrium partial pressures. Considering that SO₂ is soluble in water, the absorption of SO₂ mainly happens in the liquid phase. However, NO is poorly soluble in water, and the mass transfer resistance from liquid phase to gas phase is large, so the oxidation of NO mainly through touching with ClO₂ and Cl₂ in the interface between gas and liquid phases, then the reaction products can be absorption in the liquid phase, so the absorption of NO might happen in the gas and liquid phases at the same time.

On the basis of analysis above and the results of previous research [31-33], the possible reaction equations of simultaneous desulfurization and denitrification by NaClO₂/NaClO acid solution are listed as follows:

(1) Hydrolytic reactions of SO₂

(2) Oxidation reactions of HSO₃⁻

(3) Oxidation and Absorption of NO

In conclusion, the process of simultaneous removal of SO₂ and NO using NaClO₂/NaClO aqueous solution is relatively complex, the overall reaction equations can be summarized as follows:

5 Engineering Experiments

In order to verify the availability of above experimental results and provide a solid technical support on the large-scale industrial application in the future, engineering experiments were carried out in a 2×220 m² sintering flue gas desulfurization tower at Nanjing Iron & Steel Co. The system of the wet FGD is shown in Fig. 10. The experimental conditions are as follow: the flow rate of inlet gas ranges from 1.36×10⁶ to 2.51×10⁶ m³·h⁻¹, the inlet gas temperature increases from 125.1 to 166.63 °C, the desulfurization slurry temperature in absorber is between 50 to 70°C, the SO₂ concentration of inlet gas changes from 517.24 to 1128.06 mg·m⁻³, the NO_x concentration of inlet gas ranges from 249.75 to 340.05 mg·m⁻³ and the molar ratio of NaClO₂/NaClO is about 1.3. The variation of NO and SO₂ mass flux was monitored through the Pollution Source On-line Monitoring system of Nanjing City, then the removal efficiencies of NO_x and SO₂ can be evaluated by Eqs. (26) to (27), respectively.

$$\eta_N = \frac{Q_{NO_X, in} - Q_{NO_X, out}}{Q_{NO_X, in}} \times 100\% \quad (26)$$

$$\eta_S = \frac{Q_{SO_2, in} - Q_{SO_2, out}}{Q_{SO_2, in}} \times 100\% \quad (27)$$

Fig. 10 The system of wet FGD: (a) Appearance of bubbling gas absorbing tower; (b) The technological progress of sintering flue gas desulfurization

As shown in Fig. 11 and Fig. 12, during the experimental period, Q_s decreases from 9.8 to 6.9 $\text{kg} \cdot \text{min}^{-1}$, the removal efficiency of NO_X increases around 20% compared with ordinary times and the removal efficiency of SO_2 remains stable above 94%. The results meet national environmental standards and demonstrate the capability of the technology for simultaneous desulfurization and denitration. However, it can be seen in Fig. 12 that the increase of NO_X removal efficiency is limit. It is speculated that when NO was oxidized to NO_2 which cannot be absorbed completely, because the treated flue gas with a little reddish brown color (The original flue gas color is white) and the color is similar to NO_2 during engineering experiment.

Figure 11. The mass flux change of NO_X/SO_2 during experimental period

Fig. 12. The change of removal efficiencies during experimental period

In terms of the present running situation of Nanjing Iron & Steel Co, the annual costs of the composite absorbent is about 5.43 million, the fee for pollutant discharge can be saved about 1.19 million a year. If the reagents are purchased in large quantities, the price could be reduced by 30%-40%. Compared with other simultaneous desulfurization and denitrification technologies, using $\text{NaClO}_2/\text{NaClO}$ as the absorbent has certain advantages in the aspect of environmental protection and economy.

6 Conclusions

A composite absorbent containing NaClO_2 and NaClO was used to simultaneous desulfurization and denitrification from flue gas. The effects of various operating parameters on the experiment were considered and the reaction products were analyzed. According to the results of discussion, following conclusions can be made:

1. Under the optimal experimental conditions, the removal efficiencies of SO_2 and NO reach 99.5% and 90.8%, respectively. These results indicate that the oxidizing agent, which is made of NaClO_2 and NaClO , has good promotion prospects in simultaneous removal of NO and SO_2 .
2. The removal efficiency of SO_2 is slightly affected by different operating parameters in the experiment and holds steady above 98%.
3. In acidic condition, high removal efficiencies of SO_2 and NO owe to the fact that ClO_2 and Cl_2 are produced by the reaction between NaClO_2 and NaClO .

4. The initial solution pH and the gas flow rate are the main factors affecting simultaneous desulfurization and denitrification.

Nomenclature

$C_{\text{NO},\text{in}}$	the inlet concentration of NO, $\text{mg}\cdot\text{m}^{-3}$
$C_{\text{SO}_2,\text{in}}$	the inlet concentration of SO ₂ , $\text{mg}\cdot\text{m}^{-3}$
$C_{\text{NO},\text{out}}$	the outlet concentration of NO, $\text{mg}\cdot\text{m}^{-3}$
$C_{\text{SO}_2,\text{out}}$	the outlet concentration of SO ₂ , $\text{mg}\cdot\text{m}^{-3}$
C_{N}	initial NO inlet concentration, $\text{mg}\cdot\text{m}^{-3}$
C_{S}	initial SO ₂ inlet concentration, $\text{mg}\cdot\text{m}^{-3}$
M	the molar ratio of NaClO ₂ /NaClO, –
m_{p}	NaClO concentration, $\text{mmol}\cdot\text{L}^{-1}$
m_{s}	NaClO ₂ concentration, $\text{mmol}\cdot\text{L}^{-1}$
$Q_{\text{NO}_x,\text{in}}$	the inlet mass flux of NO _x , $\text{kg}\cdot\text{min}^{-1}$
$Q_{\text{NO}_x,\text{out}}$	the outlet mass flux of NO _x , $\text{kg}\cdot\text{min}^{-1}$
$Q_{\text{SO}_2,\text{in}}$	the inlet mass flux of SO ₂ , $\text{kg}\cdot\text{min}^{-1}$
$Q_{\text{SO}_2,\text{out}}$	the outlet mass flux of SO ₂ , $\text{kg}\cdot\text{min}^{-1}$
T_{R}	solution temperature, °C
V_{g}	gas flow rate, $\text{L}\cdot\text{h}^{-1}$
η	the removal efficiency, –
η_{N}	removal efficiency of NO, –
η_{S}	removal efficiency of SO ₂ , –

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Graphic abstract

In this study, experiments on simultaneous absorption of SO_2 and NO_x from sintering flue gas via a composite absorbent $\text{NaClO}_2/\text{NaClO}$ were carried out. The effects of various operating parameters such as NaClO_2 concentration (m_s), NaClO concentration (m_p), molar ratio of $\text{NaClO}_2/\text{NaClO}$ (M), solution temperature (T_R), initial solution pH, gas flow (V_g) and inlet concentration of SO_2 (C_s) and NO (C_N) on the removal efficiencies of SO_2 and NO were discussed. Moreover, reaction products were analyzed, the interaction mechanism of $\text{NaClO}_2/\text{NaClO}$ and the removal reaction mechanism were revealed with the main reaction equations summarized. Finally, engineering experiments were carried out to verify the practicability of the technology.