Simultaneous Desulfurization and Denitrification from Flue Gas by Ferrate(VI)

Simultaneous Desulfurization and Denitrification from Flue Gas by Ferrate(VI)

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ABSTRACT: An innovative semidry process has been developed to simultaneously remove NO and SO_2 from flue gas. According to the conditions of the flue gas circulating fluidized bed (CFB) system, ferrate(VI) absorbent was prepared and added to humidified water, and the effects of the various influencing factors, such as ferrate(VI) concentration, humidified water pH, inlet flue gas temperature, residence time, molar ratio of Ca/(S+N), and concentrations of SO_2 and NO on removal efficiencies of SO_2 and NO were studied experimentally. Removal efficiencies of 96.1% for SO_2 and 67.2% for NO were obtained, respectively, under the optimal experimental conditions, in which the concentration of ferrate(VI) was 0.03 M, the humidified water pH was 9.32, the inlet flue gas temperature was 130 °C, the residence time was 2.2 s, and the molar ratio of Ca/(S+N) was 1.2. In addition, the reaction mechanism of simultaneous desulfurization and denitrification using ferrate(VI) was proposed.
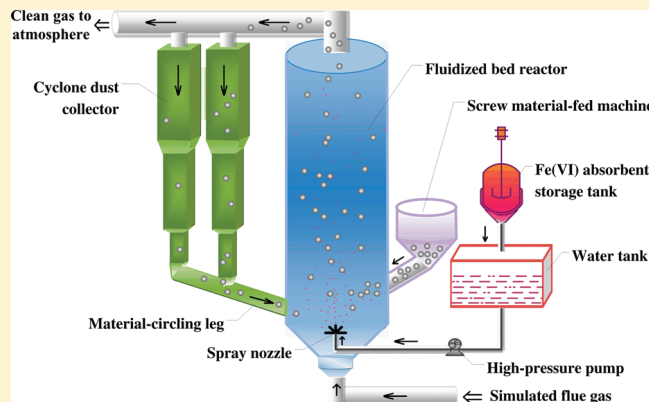
1. INTRODUCTION

Flue gas desulfurization (FGD) technology has experienced high removal efficiency of SO_2, but that is not applicable to NO_x. Typically, NO, as the chief component of NO_x, has a very low solubility in aqueous solutions, which leads to difficulty of removal by FGD. Commonly, additional denitrification equipment, such as that for selective catalytic reduction (SCR) or selective noncatalytic reduction (SNCR), has been considered for installation after the boiler. Although this stage-treatment technology succeeded in combined removal of SO_2 and NO, it has the disadvantages of large occupying area and high running cost.

In recent years, simultaneous desulfurization and denitrification has received considerable attention from both academia and industry because of simplified equipment, better operation properties, smaller occupying areas, and lower running cost.[1−3] For simultaneous desulfurization and denitrification, the key point is to oxidize NO into NO_2 rapidly in the flue gas, the latter being easily dissolved in water. There have been several reports on the rapid oxidation of NO at low temperature;[4] however, most of them have technical and economic disadvantages and cannot be developed to practicable technologies. Various oxidants such as sodium chlorite, permanganate, ozone, etc., are often used to absorb NO in flue gas.[2,3,5,6] These classical oxidants either have lower economical efficiencies or may release several hazardous byproducts that can adversely affect the environment. For example, sodium chlorite is considered as one of the most effective reagents, but it is estimated that about 1.38 pounds of

$NaClO_2$ is needed to remove 1 pound of NO_x; therefore, the cost of absorbent is prohibitive. High removal efficiencies for SO_2 and NO can also be obtained by using permanganate as an absorbent; however, its cost is also too high. Furthermore, for the removal of two chemicals, a large number of heavy metal, manganese, and chlorine species that cause secondary pollution can remain in the removal products from the process. Although ozone is an environmentally benign and effective absorbent, the energy consumption for the generation of ozone is excessive. The investigations of simultaneous desulfurization and denitrification using Fe-(II)EDTA as absorbent have been reported.[7] Nevertheless, it is too expensive for practical purposes; also, Fe(II)EDTA is known to cause secondary pollution of water. Therefore, development of high efficiency, practical, and pollution-free technologies for simultaneous desulfurization and denitrification is still necessary and urgent.

Ferrate(VI) is an environmentally benign chemical and will not produce any harmful byproducts in the pollutant disposal process.[8] Because of its strong oxidizing power,[9] ferrate(VI) as an oxidant/disinfectant and coagulant in water and wastewater treatment has been extensively studied.[10−12] To our knowledge, there are no reports about the application of ferrate(VI) simultaneous desulfurization and denitrification of flue gas. In this

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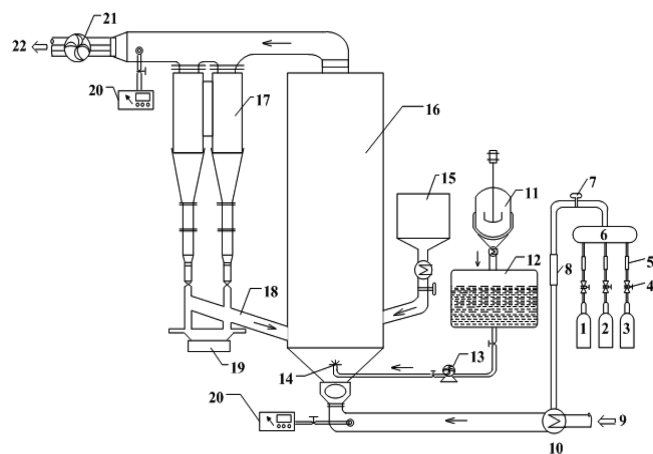
Figure 1. Schematic diagram of the experimental apparatus of the flue gas CFB system. 1: steel bottle of SO_2; 2: steel bottle of NO; 3: steel bottle of N_2; 4: relief valve unit; 5: glass-rotor flow meter; 6: buffer bottle; 7: total flow control valve; 8: summation flow indicator; 9: air inlet; 10: electric heater; 11: absorbent storage tank; 12: water tank; 13: high-pressure pump; 14: Y-type spray nozzle; 15: screw material-fed machine; 16: fluidized bed reactor; 17: cyclone dust collector; 18: material-circling leg; 19: ash hopper; 20: gas analysis instrument; 21: induced-draft fan; 22: flue gas outlet.

paper, a ferrate(VI) complex absorbent was prepared. Compared with classical chemicals, this absorbent has obvious advantages regarding the environment,[8] and as far as economy is concerned, currently, with the development of new manufacturing processes, the cost of ferrate(VI) has been decreased greatly, which implies that the price of ferrate(VI) will be able to meet the requirement of industrialized application in the near future.

Experimental investigations were conducted for the simultaneous removal of SO_2 and NO from simulated flue gas by spraying humidified water containing potassium ferrate into a flue gas CFB system. The influencing factors, such as ferrate(VI) concentration, humidified water pH, apparent residence time, molar ratio of Ca/(S+N), inlet flue gas temperature and SO_2 and NO concentrations, were investigated. Furthermore, the presumed reaction mechanism of simultaneous desulfurization and denitrification was proposed. As a new effective SO_2 and NO_x emission control strategy for flue gas cleaning, this work has great academic significance and application value.

2. EXPERIMENTAL SECTION

2.1. Experimental Apparatus and Procedure. The experiments of simultaneous desulfurization and denitrification were performed on a flue gas circulating fluidized bed (CFB) system, as shown in Figure 1. The key part of the CFB reactor is a vertical cylinder with a length of 4500 mm and an inner diameter of 250 mm, on which several temperature station points are located. The experimental system operates under negative pressure by using an induced draft fan, and the pressure drop is 800 Pa in the reactor. The gas mixture containing SO_2, NO, H_2O, and air was used to simulate actual flue gas and was heated by an electric heater. SO_2 and NO were each supplied from a compressed gas steel cylinder. The equipment to supply the humidified water was placed at the bottom of the CFB reactor. During the operation, the atomized droplets containing ferrate(VI) resulting from a high-pressure pump were sprayed into the CFB system at a spray
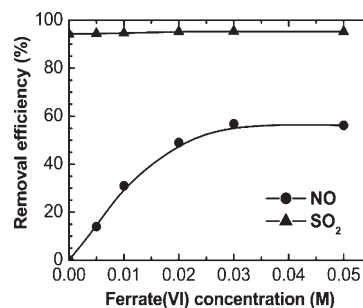
rate of 33.4 kg/h from a Y-type nozzle situated at the bottom of the fluidized bed reactor. Meanwhile, slaked lime powder was fed to the reactor by a screw feeder. Most of the solid materials discharged from the reactor were collected by a cyclone cleaner and recirculated into the reactor.

2.2. Preparation of the Ferrate(VI) Absorbent. All reagents used were analytical grade and purchased from Beijing Chemical Reagents Company. Potassium ferrate(K_2FeO_4) was prepared by the method described by Thompson et al.[13] and characterized with an X-ray diffractometer (XRD, Bruker D8 ADVANCE). The spectrogram of K_2FeO_4 powder matches that of JCPDS file No. 75−2468 and is in good agreement with the previously measured powder X-ray diffraction spectra by Hoppe et al.[14] The ferrate(VI) solutions were prepared by adding a suitable amount of K_2FeO_4 and additives to $Na_2HPO_4/Na_2B_4O_7 \cdot 10H_2O$ buffer solution, in which additives and phosphate/borate act as stabilizing agents for ferrate(VI) salt and complexing agents for Fe(III) produced, respectively.[15]

2.3. Analysis Methods. In the experiments, the inlet and outlet concentrations of SO_2 and NO were measured by a flue gas analyzer (MRU95/3 CD flue gas analyzer, made in Germany), from which the removal efficiencies were calculated. The analytical data of the removal products were derived from an X-ray diffractometer (Bruker D8 ADVANCE). The contents of sulfate, sulfite, nitrate, and nitrite in the spent absorbent were determined using the methods of chemical analysis.

3. RESULTS AND DISCUSSION

3.1. Effect of Ferrate(VI) Concentration and Additives on Simultaneous Removal Efficiencies. Experiments were performed to search out the optimum concentration of ferrate(VI) for the humidified water. SO_2 and NO removal efficiencies as functions of ferrate(VI) concentrations are shown in Figure 2. Desulfurization is almost unaffected by increasing ferrate(VI) concentration from 0 to 0.05 M, while denitrification is affected greatly. The removal efficiency for NO is enhanced rapidly with the increase in ferrate(VI) concentration, especially within the range from 0 to 0.03 M. When ferrate(VI) concentration continues to increase, the removal efficiencies remain constant, possibly because of saturation of the "oxidizing-points" on the gas−liquid interface of absorbent with an increase in ferrate(VI) concentration. Hence, the optimal ferrate(VI) concentration was set at 0.03 M.

Figure 2. Effect of ferrate(VI) concentration on simultaneous removal efficiencies. The inlet flue gas temperature is 130 °C, the residence time is 2.2 s, the flow rate is 320 m^3/h, Ca/(S+N) ratio is 1.2, and the concentrations of SO_2 and NO are 3135 mg/m^3 and 1177 mg/m^3, respectively.
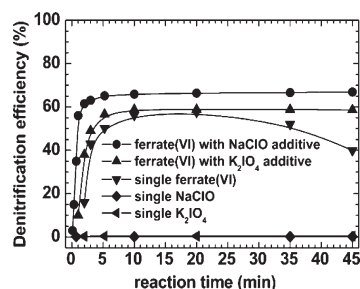
Figure 3. Effects of different additives for removal efficiency of NO. Ferrate(VI) concentration is 0.03 M, pH is 9.32, the inlet flue gas temperature is 130 °C, the residence time is 2.2s, the flow rate is 320 m^3/h, and the concentration of NO is 1000 mg/m^3.
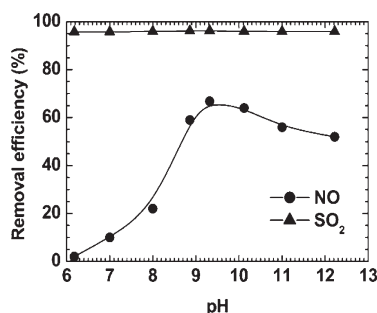

Figure 4. Effect of humidified water pH on simultaneous removal efficiencies. The inlet flue gas temperature is 130 °C, the residence time is 2.2 s, the flow rate is 320 m^3/h, Ca/(S+N) is 1.2, the ferrate(VI) concentration of humidified water is 0.03 M, the additive is hypochlorite, and the concentrations of SO$_2$ and NO are 3095 mg/m^3 and 1068 mg/m^3, respectively.

In order to promote the stabilization and oxidation of ferrate(VI), the experiments on denitrification were carried out by using ferrate(VI) with different additives including Na$_3$PO$_4$, NaClO, Na$_2$SO$_3$, Na$_2$SiO$_3$, Na$_2$S$_8$O$_2$, K$_2$S$_2$O$_8$, KClO$_3$, K$_2$IO$_4$, (NH$_4$)$_2$S$_2$O$_8$, Ca(ClO)$_2$, K$_2$CO$_3$, C$_6$H$_5$Na$_3$O$_7$, CH$_3$COONa, and some ions such as Fe^{3+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Ba^{2+}, and Ca^{2+}. The results showed that most of the additives do not promote ferrate(VI) stability and oxidation except for K$_2$IO$_4$ and NaClO. Subsequently, the effects of the humidified water containing ferrate(VI) with periodate, the humidified water containing ferrate(VI) with hypochlorite, the ferrate(VI) humidified water containing ferrate(VI), the humidified water containing hypochlorite, and the humidified water containing periodate upon removal of NO were investigated (Figure 3). In part of the reaction time, maximum removal efficiency is obtained by using the humidified water containing ferrate(VI) with hypochlorite, and that of the humidified water containing ferrate(VI) with periodate ranks second. When the reaction time is beyond 20 min, the denitrification efficiency of the humidified water containing ferrate(VI) obviously decreases, which suggests that ferrate(VI) might be decomposed. In addition, hypochlorite has obvious economic advantages over costly periodate, because it is a cheap byproduct of industrial production and it is always used for preparing ferrate(VI) by wet oxidation methods under highly alkaline conditions.[16] Therefore, residual hypochlorite is more appropriate for serving as the stabilizing agent of ferrate(VI). For flue gas desulfurization and denitrification, the complicated purification process of ferrate(VI) would be avoided.[17] In
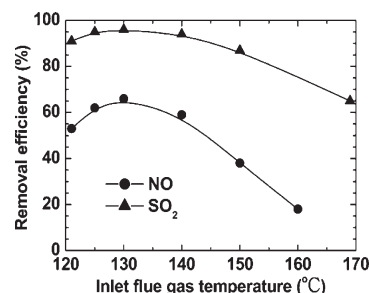

Figure 5. Effect of the inlet flue gas temperature on simultaneous removal efficiencies. The ferrate(VI) concentration of humidified water is 0.03 M, the additive is hypochlorite, the residence time is 2.2 s; the humidified water pH is 9.32, the flow rate is 320 m^3/h, Ca/(S+N) is 1.2, and the concentrations of SO$_2$ and NO are 3125 mg/m^3 and 1000 mg/m^3, respectively.

this case, the humidified water containing ferrate(VI) and hypochlorite is preferable in terms of its practical use for simultaneous desulfurization and denitrification of flue gas.

3.2. Effect of Humidified Water pH on Simultaneous Removal Efficiencies. pH is a crucial parameter in the removal process of SO$_2$ and NO using the humidified water containing ferrate(VI) and hypochlorite, because the oxidation potential and aqueous stability of ferrate(VI) ion are known to be pH dependent, for instance, its oxidation potential is high but instable at low pH,[9] mainly because ferrate(VI) has a reduction potential of 2.2 V in acidic solution and the spontaneous decomposition of ferrate(VI) is accelerated in acidic solution; thus, it is necessary to investigate the effect of pH on the simultaneous removal of SO$_2$ and NO. During the experiments, the spray rate of humidified water was maintained at 33.4 kg/h to provide the desired content of ferrate(VI) and to adjust the reactivity. Figure 4 shows that, although pH has a weak effect on desulfurization, it has a significant effect on denitrification. The removal efficiency is enhanced rapidly when the pH is between 6 and 9.32. However, as pH rises above 9.32, denitrification efficiency decreases gradually, possibly because of the decrease in oxidation potential of ferrate(VI).[9]

3.3. Effect of Inlet Flue Gas Temperature on Simultaneous Removal Efficiencies. Because temperature has an effect both on physical diffusion and on chemical absorption, the effect of inlet flue gas temperature on efficiencies of denitrification and desulfurization was investigated, as shown in Figure 5. Satisfactory efficiencies were obtained at an inlet flue gas temperature of 130 °C. However, when the temperature was higher than 130 °C, the removal efficiencies decreased sharply as temperature increased. The optimal inlet flue gas temperature was selected at 130 °C accordingly. In fact, removal of SO$_2$ and NO is a gas—liquid reaction process, in which the diffusion, absorption, and desorption of SO$_2$ and NO on the interface of absorbent are affected greatly by the flue gas temperature. When the temperature was lower than 130 °C, the diffusion and absorption were predominant and the efficiencies increased with the temperature. However, when the temperature was higher than 130 °C, the desorption of gas molecules on the interface of the absorbent was enhanced, causing a decrease of equilibrium absorptive capacity of the gas. Therefore, the removal efficiencies evidently decreased with the temperature. In addition, the oxidizing power of ferrate(VI) would be reduced because of its decomposition at higher temperature, resulting in a decrease in the removal
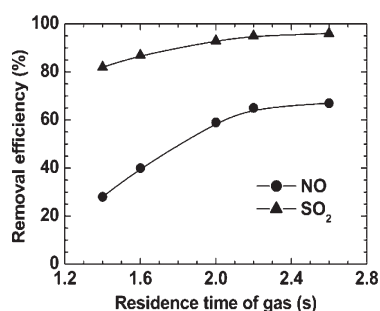
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Figure 6. Effect of the residence time on the simultaneous removal efficiencies. The ferrate(VI) concentration of humidified solution is 0.03 M, the additive is hypochlorite, the humidified water pH is 9.32, the inlet flue gas temperature is 130 °C, Ca/(S+N) ratio is 1.2, and the concentrations of SO_2 and NO are 3125 mg/m^3 and 1000 mg/m^3, respectively.

Figure 8. Effect of concentration of SO_2 and NO_x on the simultaneous efficiencies. The inlet flue gas temperature is 130 °C, the ferrate(VI) concentration of humidified water is 0.03 M, the additive is hypochlorite, the humidified water pH is 9.32, the flow rate is 320 m^3/h, the residence time is 2.2 s, and Ca/(S+N) ratio is 1.2.
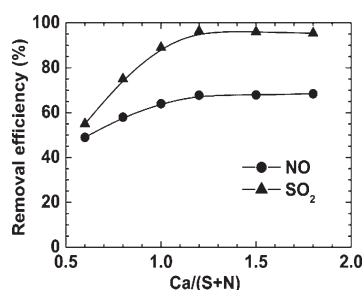

Figure 7. Effect of Ca/(S+N) on the simultaneous removal efficiencies. The inlet flue gas temperature is 130 °C, the ferrate(VI) concentration of humidified water is 0.03 M, the additive is hypochlorite, the humidified water pH is 9.32, the flow rate is 320 m^3/h, the residence time is 2.2 s, and the concentrations of SO_2 and NO are 3125 mg/m^3 and 1000 mg/m^3, respectively.

Figure 9. Variation of ferrate(VI) species with pH.

efficiency. Obviously, 130 °C is a turning point for the diffusion, absorption, and desorption of SO_2 and NO, and for the decomposition of ferrate(VI), which is close to the flue gas temperature in coal-fired power plants after dust removal.[18,19] Therefore, this optimal temperature, as a feasible operation parameter, is very suitable for simultaneous desulfurization and denitrification of flue gas in industry. Under the optimal experimental conditions, 121.8 °C of dew point was calculated by the method described by A. G. Okkes.[20] This data is below 130°C, indicating that the corrosion of the equipment will much less.

3.4. Effect of Residence Time of Flue Gas on Simultaneous Removal Efficiencies. Figure 6 shows that efficiencies of desulfurization and denitrification increase with the residence time in the flue gas CFB, especially for denitrification. This result could be due to the fact that the contact of flue gas with absorbents is as important as an increase in the residence time, which leads to the rise of removal efficiencies. For the removal of NO, because of the low water solubility, it can hardly be absorbed by the absorbent. Therefore, the oxidation of NO to NO_2 is necessary, which can be carried out by an increase in the residence time of the flue gas. However, excessive residence time of the flue gas would increase the volume capacity of the reactor and the running cost. The optimal residence time of flue gas was determined to be 2.2 s in the experiments.

3.5. Effect of Ca/(S+N) Molar Ratio on Simultaneous Removal Efficiencies. As an important index of flue gas
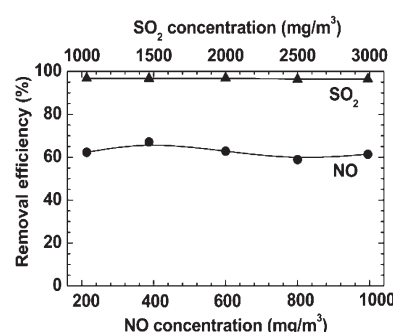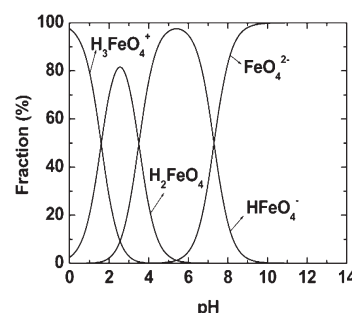
desulfurization technology, Ca/S is usually used to evaluate the utilization of absorbent and to determine the addition of absorbent. In the simultaneous desulfurization and denitrification of flue gas, Ca/(S+N) is used instead of Ca/S and calculated by the method as described by Zhao et al.[18] Different Ca/(S+N) ratios ranging from 0.6 to 1.8 were examined. Figure 7 shows the dependence of the removal efficiencies on the Ca/(S+N) molar ratio. As shown in Figure 7, the removal efficiency is enhanced rapidly, especially for desulfurization when the ratio is between 0.6 and 1.2. Thereafter, the removal efficiencies remain constant until 1.8. Hence, the optimal Ca/(S+N) ratio was set to 1.2. The experimental results also showed that desulfurization reached 96%, while denitrification was zero in the absence of ferrate-(VI) in the humidified water, indicating that ferrate(VI) is essential to denitrification, consistent with the results presented in section 3.1.

3.6. Effect of SO_2 and NO Concentration on Simultaneous Removal Efficiencies. The experiments of simultaneous desulfurization and denitrification were carried out to examine the adaptability of this process for coal species and combustion conditions of the boiler (Figure 8). The removal efficiencies vary slightly in the range 1000–3000 mg/m^3 for SO_2 and in the range 200–1000 mg/m^3 for NO, respectively, indicating that the flue gas CFB technology adapts well to different types of coal and combustion conditions. It was reported that the coexistence of SO_2 and NO can promote removal of each other;[4] this phenomenon was also observed in our experiments, but it was not obviously due to the presence of ferrate(VI).

3.7. Parallel Test. Five parallel experiments of simultaneous desulfurization and denitrification in flue gas CFB were carried
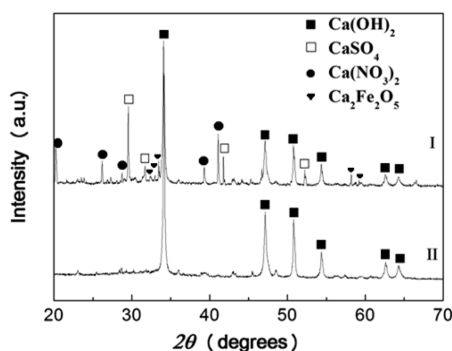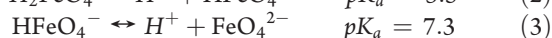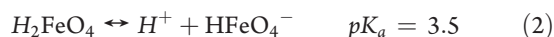
Figure 10. XRD patterns of solid products and fresh slaked lime. (■) $Ca(OH)_2$; (□) $Ca(SO)_4$; (●) $Ca(NO_3)_2$; (▼) $Ca_2Fe_2O_5$.

Table 1. Contents of Sulfur and Nitrogen Species in the Fresh Absorbent and the Spent Absorbent (mmol/g)

| samples	contents of sulfur/nitrogen species			
	$[SO_4^{2-}]$	$[SO_3^{2-}]$	$[NO_3^-]$	$[NO_2^-]$
fresh absorbent	0.001	0	0	0
spent absorbent	0.991	0.199	0.584	0.197

out under the optimal experimental conditions, as follows: the inlet flue gas temperature is 130 °C, the ferrate(VI) concentration of humidified water is 0.03 M, the additive is hypochlorite, the humidified water pH is 9.32, the flow rate is 320 m^3/h, the residence time is 2.2 s, and the Ca/(S+N) ratio is 1.2. Average removal efficiencies of 96.1% for SO_2 and 67.2% for NO were obtained, respectively.

4. REACTION MECHANISM ANALYSIS

The protonated forms of ferrate(VI) in aqueous solution vary in pH and buffer concentration used, which can be expressed in eqs 1−3, and the various species of ferrate(VI) as a function of pH are shown in Figure 9.[9,21]

$$H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \qquad pK_a = 1.6 \qquad (1)$$

$$H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \qquad pK_a = 3.5 \qquad (2)$$
$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \qquad pK_a = 7.3 \qquad (3)$$

In eqs 1−3 the possible forms of ferrate(VI) species are $H_3FeO_4^+$, H_2FeO_4, $HFeO_4^-$, and FeO_4^{2-}, respectively. According to the experimental results in this paper, under the optimum solution pH (at 9.32), the dominant species of ferrate(VI) in the humidified water should be FeO_4^{2-} (99.05%), with minor $HFeO_4^-$ (0.94%), an amount so small that it can be negligible relative to the total concentration. It is reported that the oxidation state of FeO_4^{2-} can be changed from +6 to +3, as shown below:[22]

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$$
$$E^0 = 2.2 \text{ V} \qquad (4)$$
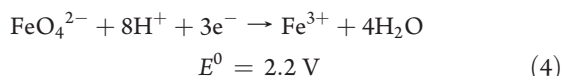
Obviously, the standard electrode potential of FeO_4^{2-}/Fe^{3+} (2.2 V) is significantly higher than SO_4^{2-}/H_2SO_3 (0.172 V), NO_2/NO (1.049 V), NO^{3-}/NO (0.957 V), and NO^{3-}/NO^{2-} (0.835 V), indicating that the oxidation reactions of SO_2 and NO may occur on the liquid film of humidified water adsorbed on $Ca(OH)_2$.

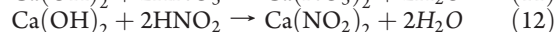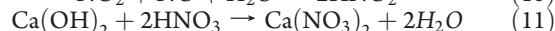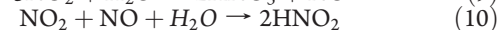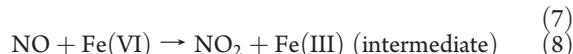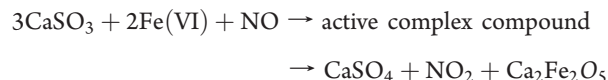In order to reveal the mechanism of simultaneous desulfurization and denitrification, the spent absorbent and fresh absorbent were analyzed with XRD (Figure 10). By contrast, it can be found that many new species which may be $Ca(SO)_4$ (JCPDS file no. 87-0674), $Ca(NO_3)_2$ (JCPDS file no. 07-0204), and $Ca_2Fe_2O_5$ (JCPDS file no. 71-2108) appear in the surface of the spent absorbent, demonstrating that chemical reactions occur among SO_2, NO_2, and absorbents. To further verify the components of the removal products, the contents of sulfur and nitrogen species

for the fresh absorbent and the spent absorbent were analyzed by chemical analysis methods, as shown in Table 1. With regard to fresh absorbent, a small quantity of sulfate was detected, which might come from $Ca(OH)_2$. Sulfite, nitrate, and nitrite were not detected in fresh absorbent. Moreover, it is clear that the molar ratio of sulfate and sulfite in the spent absorbent was 4.98, and that of nitrate and nitrite was 2.96. The combined results from XRD analysis and chemical analysis show that the principal components of the removal products are $CaSO_4$, $Ca(NO_3)_2$, $CaSO_3$, $Ca(NO_2)_2$, and $Ca_2Fe_2O_5$. Among them, $CaSO_4$ is the main desulfurization product, and $Ca(NO_3)_2$ is the main denitrification product. These dry, mixed removal products can be used directly to build roads and reconstruct highway embankments,[23] and after suitable treatment, can be used as the main materials for panel walls and steam bricks.

According to the experimental results of XRD and the chemical analysis, the possible reaction mechanism in flue gas CFB can be inferred as follows:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (5)$$

$$Ca(OH)_2 + H_2SO_3 \rightarrow CaSO_3 + 2H_2O \qquad (6)$$

$$3CaSO_3 + 2Fe(VI) + NO \rightarrow \text{active complex compound}$$

$$\rightarrow CaSO_4 + NO_2 + Ca_2Fe_2O_5$$
$$(7)$$
$$NO + Fe(VI) \rightarrow NO_2 + Fe(III) \text{ (intermediate)} \qquad (8)$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad (9)$$
$$NO_2 + NO + H_2O \rightarrow 2HNO_2 \qquad (10)$$
$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O \qquad (11)$$
$$Ca(OH)_2 + 2HNO_2 \rightarrow Ca(NO_2)_2 + 2H_2O \qquad (12)$$
$$3Ca(NO_2)_2 + 2Fe(VI) \rightarrow Ca(NO_3)_2 + Ca_2Fe_2O_5 \qquad (13)$$

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