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# Simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> from flue gas by ferrate (VI) solution



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#### ABSTRACT

Simultaneously removing SO<sub>2</sub>, NO and Hg<sup>0</sup> from flue gas was examined by ferrate (VI) solution at a bubbling reactor. The removal efficiencies of 100% for SO<sub>2</sub>, 64.8% for NO and 81.4% for Hg<sup>0</sup> were achieved respectively, under the optimum experimental conditions, in which concentration of ferrate (VI) solution was 0.25 mmol/L, solution pH was 8.0, flue gas flow rate was 1 L/min and reaction temperature was 320 K. Based on the discussions of the ferrate (VI) solution characteristics, the comparisons of the standard electrode potential ( $E_0$ ) of ferrate (VI) solution with  $E_0$  values of reactant, and the analysis of the reaction products, a mechanism of simultaneous removal was proposed. In the process of simultaneous removal, FeO<sub>4</sub><sup>2</sup> and HFeO<sub>4</sub> as the dominant species of ferrate (VI), could rapidly oxidize SO<sub>2</sub>, NO, and Hg<sup>0</sup> into SO<sub>4</sub><sup>2</sup> , NO<sub>3</sub> and Hg<sup>2+</sup>.

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## 1. Introduction

Coal burning, the primary source of China's atmosphere pollution, generates many air pollutants including sulfur dioxide (SO<sub>2</sub>), nitrogen oxides ( $NO_x$ ) and mercury (Hg) [1-3].  $SO_2$  and NO will lead to worsening local air quality as well as regional acid rain pollution and photochemical smog [4]. Mercury is considered as one of the most toxic trace element, its main consequences are realized in aqueous environment. Once mercury enters water bodies, either directly or through air deposition, inorganic mercury can be methylated biotically under anaerobic conditions, to its most toxic form, dimethyl mercury. The latter biomagnifies readily in the food chain, severely endangering ecosystems and public health [5]. Currently, the most successful and commercialized processes for removing SO<sub>2</sub>, NO<sub>x</sub> and Hg are limestone-gypsum flue gas desulfurization (FGD), selective catalytic reduction (SCR), and activated carbon adsorption [6,7]. However, the combined system of these three processes has the disadvantages of large occupying area, high running cost and low stability of flue gas system [8,9]. Therefore, simultaneous multi-pollution control technologies have been extensively researched in recent years, and many reagents, i.e. NaClO<sub>2</sub>, KMnO<sub>4</sub>/NaOH, Fe(II)EDTA, urea, O<sub>3</sub>, UV/H<sub>2</sub>O<sub>2</sub>, etc., have been introduced into aqueous solutions as absorbents to achieve simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> [10-18]. Hutson et al.

[15] carried out an experiment of simultaneous removal of SO<sub>2</sub>, NO<sub>x</sub> and Hg from coal flue gas using a NaClO2-enhanced wet scrubber, from which, a new method of the simultaneous removal of the multi-pollutant was proposed. Fang et al. [16] used urea/KMnO<sub>4</sub> as the absorbent to investigate the effects of various factors such as urea concentration, KMnO<sub>4</sub> concentration, inlet Hg<sup>0</sup> concentration, initial pH, reaction temperature, SO<sub>2</sub> concentration and NO concentration on the efficiencies of simultaneous removal of Hg<sup>0</sup>, SO<sub>2</sub> and NO, and the experimental results indicated that the removal efficiencies of NO and Hg<sup>0</sup> mainly depended on the concentration of KMnO<sub>4</sub>. Jia et al. [17] found that Hg<sup>0</sup> oxidation could be promoted by UV light and CH<sub>4</sub>, and Hg<sup>0</sup> removal efficiency of 65.5% was obtained under the 253.7 nm light. However, these classical oxidants either have lower economical efficiencies or may release several hazardous byproducts that can adversely affect the environment. Hence, researchers have focused on using efficient, practical and pollution-free absorbent for simultaneous removal of SO<sub>2</sub>, NO, and Hg from flue gas.

As an environmentally benign chemical, ferrate (VI) has a strong oxidizing property [19–22], and it is often used in waste-water treatment as a disinfectant and biocide for removal of inorganic contaminants, organic compounds, odor, nutrients, radionuclides, humic acids, and so on [23–31]. In addition, many heavy metals such as As<sup>3+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>3+</sup>, and Hg<sup>2+</sup> can be effectively removed using ferrate (VI) through oxidation and coagulation [32,33]. Ferrate (VI) has given a convincing result in water and wastewater treatment even as an oxidant for nitrogen and sulfur-containing pollutants [19,29]. However, by far, there is

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still no report on the application of Ferrate (VI) as oxidant for the removal of SO<sub>2</sub>, NO and Hg<sup>0</sup>.

Hence, this study is aimed at understanding the oxidation reactions with Ferrate (VI) in order to explore a new approach to simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> from flue gas in liquid phase. The developed technology can be used to coal fired flue gas cleaning of power station boiler and industrial boiler.

## 2. Materials and methods

## 2.1. Materials

All chemicals used were analytical grade and purchased from Tianjing Chemical Reagents Co., China. High purity deionized water (specific resistance  $\geq 18.25~\text{M}\Omega/\text{cm}$ ) was prepared using the Barnstead water purification system. Potassium ferrate ( $K_2\text{FeO}_4$ ) was prepared in our laboratory according to Thompson's method and its concentration was determined by a UV-3000 spectrophotometer at 510 nm [34,35]. The ferrate (VI) solution was prepared by adding a suitable amount of  $K_2\text{FeO}_4$  and a trace of sodium hypochlorite into deionized water, in which sodium hypochlorite acted as stabilizing agent for ferrate (VI) [36]. The initial solution pH value was adjusted by dilute sodium hydroxide or hydrochloric acid.

# 2.2. Experimental apparatus and procedure

Fig. 1 shows the schematic diagram of experimental equipments including a flue gas simulation system, a bubbling reactor with 250 mL of the effective volume and 15.5 cm of height in a thermostat water bath, a flue gas analysis system and a tail gas absorption system. The gas mixture containing SO<sub>2</sub>, NO, N<sub>2</sub> and Hg<sup>0</sup> was used to simulate actual flue gas, in which SO<sub>2</sub>, NO, and N<sub>2</sub> were each supplied from a compressed gas steel cylinder, while Hg<sup>0</sup> was generated from mercury osmotic tube (VICI Metronics Co., USA) in a thermostatic water bath, and carried over by N<sub>2</sub> with 1 L/min. During the experiments, the gas mixture was mixed in a buffer bottle and then introduced into the bubble reactor containing ferrate (VI) solution. The spent gases were absorbed by a tail gas absorption bottle containing 10% (v/v) H<sub>2</sub>SO<sub>4</sub>-4% (w/w) KMnO<sub>4</sub> solutions after absorption.

In our previous work [37], the mass transfer-reaction kinetics on oxidation of  $\mathrm{Hg}^0$  by  $\mathrm{NaClO}_2$  solution was studied experimentally in a bubbling reactor, and the results showed that with an increase of  $\mathrm{NaClO}_2$  concentration and the decrease of pH value, the enhancement factor (E) and ratio of KG ( $\mathrm{Hg}^0$ )/kG ( $\mathrm{Hg}^0$ ) increased, and the liquid phase mass transfer resistance decreased, which was benefit to the mass transfer adsorption reaction. An increase of reaction temperature had a promotion for factor (E) and an inhibition for the ratio of KG ( $\mathrm{Hg}^0$ )/kG ( $\mathrm{Hg}^0$ ). The latter was one of the most important factors for decreasing the removal efficacy of  $\mathrm{Hg}^0$ . The research results have an important reference value for the present work.

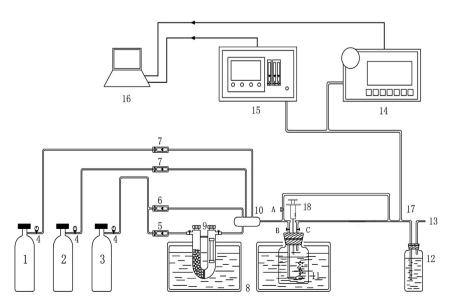
## 2.3. Analysis methods

The analysis of Hg<sup>0</sup> was carried out based on the US EPA method 101A, and the used Hg<sup>0</sup> analyzer was QM201 cold atom fluorescence mercury detector (QM201H, Suzhou, Qingan Instrument Co., China). The concentrations of SO<sub>2</sub> and NO were measured by a flue gas analyzer (MRU, VARIO, Germany). The removal efficiencies were calculated according to the concentrations of Hg<sup>0</sup>, SO<sub>2</sub> and NO before and after absorption. The reaction products of desulfurization and denitrification after oxidation reactions were characterized by an ion chromatography (792 Basic, Metrohm AG), in which  $SO_4^{2-}$ ,  $SO_3^{2-}$ ,  $NO_3^{-}$ ,  $NO_2^{-}$  were completely separated on a Metrosep A Supp 4 Anion chromatographic column with a mixture of sodium carbonate solution (1.8 mmol/L) and sodium bicarbonate solution (1.7 mmol/L) at a flow rate of 1 mL/min, and detected by an electrical conductivity detector. The detection limit was lower than 10 µg/L. The analytical instrument used for determining the concentration of Hg<sup>2+</sup> in the spent solutions was the same as that used for determining the inlet and outlet concentrations of Hg<sup>0</sup>. The detection limit was lower than 0.1 ng/m<sup>3</sup> at 253.7 nm.

# 3. Results and discussion

# 3.1. Effects of ferrate (VI) concentration on multi-pollutant removal

To obtain the optimum concentration of ferrate (VI) solution, the effect of the concentration of ferrate (VI) solution on the simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> was investigated, as shown in



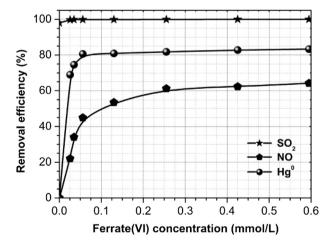
**Fig. 1.** Schematic diagram of the experimental apparatus: (1) steel bottle of SO<sub>2</sub>, (2) steel bottle of NO, (3) steel bottle of N<sub>2</sub>, (4) relief valve, (5) 60 mL flowmeter, (7) 100 mL flowmeter, (8) thermostat water bath, (9) Hg<sup>0</sup> generator, (10) buffer bottle, (11) bubble reactor, (12) tail gas absorption bottle, (13) tail gas outlet, (14) flue gas analyzer, (15) QM201H coal-fired flue gas Hg<sup>0</sup> analyzer, (16) computer, (17) sampling port, (18) 1 mL injector; A, B, C: two-way valve gate.

Fig. 2. It can be seen from Fig. 2 that desulfurization is almost unaffected when the concentration of ferrate (VI) solution is between 0 and 0.6 mmol/L. However, the removal efficiency of Hg<sup>0</sup> increases linearly from 0 to 80.0% by increasing the concentration of ferrate (VI) solution from 0 to 0.05 mmol/L. Thereafter, the removal efficiency remains basically constant. For NO removal, the efficiency increases rapidly when the concentration of ferrate (VI) solution is between 0 and 0.05 mmol/L, and slowly in the concentration of ferrate (VI) solution ranging from 0.05 to 0.25 mmol/L. After that, the removal efficiency increased very slowly. From the economy, the optimal the concentration of ferrate (VI) solution was selected as 0.25 mmol/L on simultaneous removal of SO<sub>2</sub>, NO and Hg<sup>0</sup>.

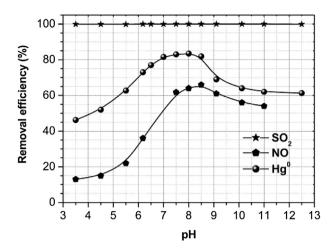
In the oxidations of NO and Hg<sup>0</sup> with ferrate (VI) solution, the competition reactions between NO and Hg<sup>0</sup> may occurred [38], NO has a priority. Apart from the direct oxidation of NO into NO<sub>2</sub>, further reactions such as the formation of NO<sub>3</sub> will consume some of the excessive ferrate (VI), which will counteract some of the Hg<sup>0</sup> oxidation.

# 3.2. Effects of solution pH on multi-pollutant removal

The redox potential and aqueous stability of ferrate (VI) solution. and the reactivity of dissociating compounds, are known to be pH dependent [39], which will affect the aqueous reactions of SO<sub>2</sub>, NO, and Hg<sup>0</sup> with ferrate (VI). Hence, the removal experiments for SO<sub>2</sub>, NO and Hg<sup>0</sup> at different solution pH ranging from 3.5 to 12.5 were performed. As shown in Fig. 3, the solution pH has a weak effect on desulfurization, and a remarkable effect on denitrification and mercury removal, in which the removal efficiencies of Hg<sup>0</sup> and NO increase rapidly when solution pH is varied from 3.5 to 8.0, and decrease gradually in solution pH ranging from 8.0 to 12.5. It can be predicted that the oxidation reactions of NO and Hg<sup>0</sup> will be promoted at lower solution pH based the fact that the redox potential of Fe(VI) solution rises as the solution pH decreasing [20]. However, the removal efficiencies of NO and Hg<sup>0</sup> increase as the solution pH varying from acidic to alkaline in the pH range of 3.5 and 8.0, as shown in Fig. 3, which may mainly be because the stability of ferrate (VI) solution decreases as an increase of solution pH. although Fe(VI) solution has the higher redox potential at lower solution pH. indicating that the effect of the stability of ferrate (VI) solution on the oxidation reactions of  $\mathrm{Hg}^0$  and NO is larger than that of redox potential of ferrate (VI) solution. It was reported [40] that the



**Fig. 2.** SO<sub>2</sub>, NO, and Hg<sup>0</sup> removal vs. ferrate (VI) concentration. The reaction temperature is 320 K, the solution pH is 8.0, flue gas flow rate was 1 L/min and the concentrations of SO<sub>2</sub>, NO and Hg<sup>0</sup> are 3085 mg/m<sup>3</sup>, 1075 mg/m<sup>3</sup> and 20  $\mu$ g/m<sup>3</sup>, respectively.

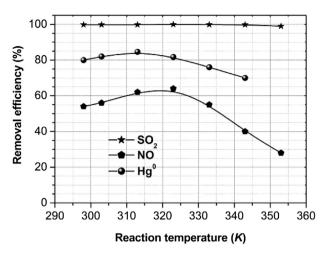


**Fig. 3.** SO<sub>2</sub>, NO, and Hg<sup>0</sup> removal vs. solution pH. Ferrate (VI) concentration is 0.25 mmol/L, the reaction temperature is 320 K, flue gas flow rate was 1 L/min and the concentrations of SO<sub>2</sub>, NO and Hg<sup>0</sup> are 3035 mg/m<sup>3</sup>, 1025 mg/m<sup>3</sup> and 20  $\mu$ g/m<sup>3</sup>, respectively.

stability of the ferrate was highly pH-dependent and there appeared to be an optimal performance in alkaline medium as an oxidizing agent. This result is consistent with previously established conclusion, i.e. the ferrate is much more chemically stable and persists much longer in alkaline solution. From the downward trend of the removal efficiencies of Hg<sup>0</sup> and NO in the solution pH range of 8.0 and 12.5, it can be estimated that the reaction rates of oxidation reactions of NO and Hg<sup>0</sup> are dropped due the decrease of redox potential of ferrate (VI) solution [20]. In that case, the effect of the redox potential on the oxidation reactions of NO and Hg<sup>0</sup> was predominant. Based on the experimental results, the optimal solution pH was selected as 8.0. Sulfuric and nitric acids resulting from the oxidations of SO<sub>2</sub> and NO will acidify aqueous solutions and may have a significantly impact on the stability and effectiveness of ferrate (VI). To maintain a stable solution pH, a buffer solution should be added in ferrate (VI) solution. For a practical and scalable removal process, the solution pH can be kept at 8.0 by continuously adding the complex absorbent of alkaline chemical combined with ferrate (VI) solution in a spray scrubber, which is similar to the process of limestone-gypsum flue gas desulfurization.

## 3.3. Effects of reaction temperature on multi-pollutant removal

The dependence of the simultaneous removal efficiencies on reaction temperature is shown in Fig. 4. It can be seen that the reaction temperature has a slight effect on desulfurization but an obvious effect on denitrification and mercury removal. The removal efficiencies of Hg<sup>0</sup> and NO increase at first and then drop with an increase of reaction temperature ranging from 298 to 353 K, the highest removal efficiencies of Hg<sup>0</sup> and NO are achieved at 313 and 320 K, respectively. After the peak values, removal efficiencies decrease sharply. In fact, removal of SO<sub>2</sub>, NO and Hg<sup>0</sup> by ferrate (VI) solution is a gas-liquid reaction process, in which the diffusion, absorption, and desorption of SO<sub>2</sub>, NO and Hg<sup>0</sup> on the interface of gas-liquid are affected greatly by reaction temperature. The diffusion and absorption of Hg<sup>0</sup> and NO in ferrate (VI) solution are improved by increasing reaction temperature when the temperatures are in the range of 298-313 K for Hg<sup>0</sup> removal and 298-320 K for NO removal. At the same time, the desorption of Hg<sup>0</sup> and NO is enhanced owing to an increase of the mass transfer resistance of gas molecules on the interface of gas-liquid [38] when the



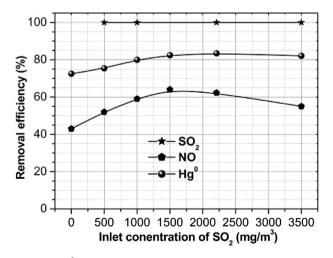
**Fig. 4.** SO<sub>2</sub>, NO, and Hg<sup>0</sup> removal vs. reaction temperature. Ferrate (VI) concentration is 0.25 mmol/L, the solution pH is 8.0, flue gas flow rate was 1 L/min and the concentrations of SO<sub>2</sub>, NO and Hg<sup>0</sup> are 3055 mg/m<sup>3</sup>, 1015 mg/m<sup>3</sup> and 20 μg/m<sup>3</sup>, respectively.

temperatures are higher than 313 K and 320 K. 313 K for  $Hg^0$  removal and 320 K for NO removal are the turning point. Because  $Hg^0$  and NO are difficult to dissolve in aqueous solution, Henry's law can be used to explain the experimental phenomena, where  $k_{\rm H}$ , Henry's law constant may vary with different factors such as temperature and salinity and is often decreased with increased temperature and salt concentration [41], which will lead to the decrease of the solubility of the gas. In addition, the oxidizing power of ferrate (VI) solution will be reduced because of its decomposition at higher temperature [42–44], which may be another factor resulting in the decrease in the removal efficiencies.

In consideration of adaptability to typical FGD process, the optimum reaction temperature was determined as 320 K accordingly. In order to meet the reaction temperature in practical applications, the flue gas needs to be cooled off by a spray scrubber before the flue gas passes the reactor.

#### 3.4. Effect of SO<sub>2</sub> and NO concentration on multi-pollutant removal

Experiments were carried out to evaluate the effects of  $SO_2$  and NO concentrations on  $Hg^0$  removal, as shown in Fig. 5. The removal



**Fig. 5.** NO and Hg<sup>0</sup> removal vs. SO<sub>2</sub> concentration. The reaction temperature is 320 K, the solution pH is 8.0, ferrate (VI) concentration is 0.25 mmol/L, flue gas flow rate was 1 L/min and the concentrations of NO and Hg<sup>0</sup> are 1000 mg/m<sup>3</sup> and 20  $\mu$ g/m<sup>3</sup>, respectively.

efficiencies are enhanced to about 83.0% for  $Hg^0$  and about 63.0% for NO, respectively when  $SO_2$  concentration increases from 0 to 1500 mg/m³, Compared with the simulated flue gas without  $SO_2$ , the removal efficiencies are improved by 11.0% for  $Hg^0$  and 21.0% for NO, respectively. It means that about 1500 mg/m³ of  $SO_2$  in flue gas is to the benefit of removing  $Hg^0$  and NO. However, from the downtrend of the removal efficiencies of NO in  $SO_2$  concentration ranging from 1500 to 3000 mg/m³, the higher concentration  $SO_2$  seems to go against NO removal, which may be due to the competing reaction between  $SO_2$  and NO. The promoting action of  $SO_2$  on  $Hg^0$  removal may be attribute to the complex of  $Hg \cdot S(IV)$  [43]. In Eqs. (1) and (2), the removal product,  $Hg^{2+}$  reacted with  $SO_3^{2-}$  to form  $HgSO_3$ , and then sequentially reacted with  $SO_3^{2-}$  to form  $Hg(SO_3)_2^{2-}$  which was more stable than  $HgSO_3$ . Therefore, the removal efficiency of  $Hg^0$  could be improved by an increase of  $SO_2$  concentration.

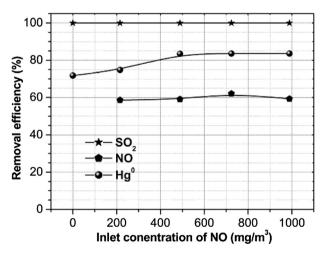
$$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3 \tag{1}$$

$$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$$
 (2)

Fig. 6 shows the effect of NO concentration on  $\mathrm{Hg^0}$  removal. The removal efficiencies of  $\mathrm{Hg^0}$  increase from about 72.0% to about 84.0% when NO concentration increases from 0 to about 500 mg/m³. Thereafter, the removal efficiencies remain constant, which indicate that the lower concentration of NO in flue gas has a promoting effect on  $\mathrm{Hg^0}$  remove. The improvement for  $\mathrm{Hg^0}$  removal can be explained by that, in the absence of buffer solution, with an increase of NO concentration, the solution pH raised because the oxidation of NO by ferrate (VI) solution was a reaction of releasing  $\mathrm{OH^-}$  [45], which was helpful to increase the ferrate (VI) solution stability and to promote the removal efficiency. Additionally, in the presence of  $\mathrm{HNO_3}$  resulting from the oxidation of NO, the produced  $\mathrm{Hg^{2+}}$  seemed to slightly catalyze  $\mathrm{Hg^0}$  absorption in the aqueous solutions. Zhao and Rochelle [12] calculated that in the 0.8 mol L $^{-1}$  HNO $_3$ , the reactions were first order for  $\mathrm{Hg^0}$  and  $\mathrm{Hg^{2+}}$ , respectively.

# 3.5. Parallel test

Five parallel experiments of simultaneous removing  $SO_2$ , NO and  $Hg^0$  were carried out under the optimal conditions in which reaction temperature was 320 K, ferrate (VI) concentration was



**Fig. 6.** SO<sub>2</sub> and Hg<sup>0</sup> removal vs. NO concentration. The reaction temperature is 320 K, the solution pH is 8.0, ferrate (VI) concentration is 0.25 mmol/L, flue gas flow rate was 1 L/min and the concentrations of SO<sub>2</sub> and Hg<sup>0</sup> are 3045 mg/m<sup>3</sup> and 20  $\mu$ g/m<sup>3</sup>, respectively.

0.25 mmol/L, flue gas flow rate was 1 L/min and solution pH was 8.0. Average removal efficiencies of 100% for SO<sub>2</sub>, 64.8% for NO and 81.4 for Hg<sup>0</sup> were obtained, respectively when the concentrations of SO<sub>2</sub>, NO and Hg<sup>0</sup> were 2000 mg/m³, 700 mg/m³ and 20  $\mu$ g/m³, respectively. And the efficiencies were stable in 50 min of the operation time without replenishing the ferrate (IV) solution. The experimental results also showed that the standard deviations of five experiments for removing SO<sub>2</sub>, NO and Hg<sup>0</sup> were 0.01, 0.08 and 0.09, respectively. In addition, it can be seen from Figs. 6 and 7 that the removal efficiencies of SO<sub>2</sub> and NO vary slightly in the range of 1000–3500 mg/m³ for SO<sub>2</sub>, in the range of 400–1000 mg/m³ for NO, and in the concentration of 20  $\mu$ g/m³ for Hg<sup>0</sup>, respectively. The results showed that the proposed process was preferably adapted to different types of coal and combustion conditions.

In order to verify the ability to close mass balances on  $SO_2$ , NO and  $Hg^0$  for the reactor,  $Hg^0$  removal was chosen as an example, a mass balance calculation was carried out.  $3.34~\mu g/L$  of  $Hg^{2+}$  in the spent solution was calculated in 50 min of the operation time under the optimal conditions when the concentration  $Hg^0$  was  $20~\mu g/m^3$  and the removal efficiency was 83.6%, compared with 3.46  $\mu g/L$  in sample 1 of Table 1, The calculation result was basically consistent to the measured value. Hence the availability and reliability of the reactor was verified.

# 4. Reaction mechanism analysis

As we all know, ferrate (VI) occurs in four forms  $(H_3FeO_4^+, H_2FeO_4, HFeO_4^-, and FeO_4^2^-)$  that depend on the solution pH. In general, HFeO\_4^- predominates in mildly acidic conditions, while  $FeO_4^{2^-}$  is the dominant species in alkaline conditions and is instable in acidic conditions [46]. The previous work [42] showed that the ratio of  $FeO_4^{2^-}$  was about 80% and that of  $HFeO_4^-$  was about 20% when the solution pH was 8.0, from which, it could be estimated that  $FeO_4^{2^-}$  was main reaction species with  $SO_2$ , NO and  $SO_2$ 0 and  $SO_2$ 1 was second in the optimal conditions.

Because the redox potential of ferrate (VI) varies from 2.2 V to 0.72 V throughout the entire pH range [20,25,27–29], the oxidizability of ferrate (VI) will be a significant difference at different pH values. In order to verify the feasibility of oxidation reactions among Fe(VI), SO<sub>2</sub>, NO, and Hg<sup>0</sup>, -113.8 mV/pH unit of the linear response slope of ferrate (VI) solution was calculated by virtue of the Lange's handbook of chemistry, from which, the values of standard electrode potential at various pH were estimated, and the standard electrode potential ( $E_0$ ) values of 2.2 V, 1.4 V, 1.29 V and 1.17 V for pH at 1.0, 8.0, 9.0 and 10.0 were obtained, respectively. Obviously, under our optimal experimental conditions (the solution pH was 8.0),  $E_0$  of FeO<sub>2</sub><sup>2</sup>/Fe<sup>3+</sup> (1.4 V) was obviously higher than

**Table 1** Concentration of  $Hg^{2+}$  in the spent absorption solution  $(\mu g/L)$ .<sup>a</sup>

Numbers	1	2	3	4	5	Average
Scan blank	0	0	0	0	0	0
Sample 1	3.42	3.51	3.47	3.44	3.48	3.46
Sample 2	0	0	0	0	0	0
Sample 3	3.89	3.75	3.95	3.82	3.88	3.86

<sup>&</sup>lt;sup>a</sup> In 50 min of the operation time.

those of  $\rm Hg^{2+}/\rm Hg_2^{2+}$  (0.911 V),  $\rm Hg^{2+}/\rm Hg^0$  (0.796 V),  $\rm NO_2/\rm NO$  (1.049 V),  $\rm NO^{3-}/\rm NO$  (0.957 V),  $\rm NO^{3-}/\rm NO^{2-}$  (0.835 V),  $\rm SO_4^{2-}/\rm H_2SO_3$  (0.172 V), which meant that  $\rm SO_2$ ,  $\rm NO$ , and  $\rm Hg^0$  could be oxidized by ferrate (VI) solution.

Four samples taken from the bubble reactor, in which, scan blank was the fresh ferrate (VI) solution, sample 1 was the spent ferrate (VI) solution after absorption of  $Hg^0$ , sample 2 was the spent ferrate (VI) solution after absorption of  $Hg^0$ , and  $Hg^0$  was the spent ferrate (VI) solution after absorption of  $Hg^0$ , and  $Hg^0$  were analyzed by a coal-fired flue gas mercury analyzer to reveal the removal mechanism of  $Hg^0$ , as shown in Table 1. There is no  $Hg^{2+}$  in scan blank and sample 2, while  $Hg^{2+}$  is found in samples 1 and 3, which demonstrates that  $Hg^0$  can be oxidized as  $Hg^{2+}$  by ferrate (VI) solution.

It can be seen from Fig. 7 that  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$  appear in the spent ferrate (VI) solution after absorbing  $SO_2$  and NO. For these ions,  $Cl^-$  may be resulting from the conditioning agent of pH (chlorhydric acid) and the stabilizing agent (sodium hypochlorite) for ferrate (VI), and  $SO_4^{2-}$  and  $NO_3^-$  are the reaction products of  $SO_2$  and NO. The analysis results of ion chromatography demonstrate that  $SO_2$  and NO are oxidized completely by ferrate (VI) solution because  $SO_3^{2-}$  and  $NO_2^{-}$  are not found in ion chromatogram.

For the application of this process in limestone—gypsum flue gas desulfurization system to simultaneously removal of  $NO_x$  and Hg,  $SO_4^{2-}$  can be used as a building material because it easily reacts with  $Ca^{2+}$  to form  $CaSO_4$ , and  $NO_3^-$  and  $Hg^{2+}$  contained the desulfurization wastewater can be treated by desulfurization wastewater treatment system, in which,  $Hg^{2+}$  is effectively removed, and  $NO_3^-$  may be separated from the wastewater to produce chemical products. For the reaction product of ferrate (VI) solution,  $Fe(OH)_3$  will be regenerated by a new method in the future and used as a flocculant in desulfurization wastewater treatment system.

Based on the discussions of the ferrate (VI) solution characteristics, the comparisons of ferrate (VI) solution  $E_0$  value with  $E_0$  values of SO<sub>2</sub>, NO and Hg<sup>0</sup>, the analysis results of the reaction products and the previous works [20,25,27–29], it can be inferred that in the removal reactions, SO<sub>2</sub>, NO and Hg<sup>0</sup> were oxidized by

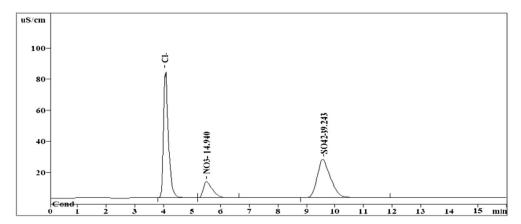


Fig. 7. Ion chromatogram of the spent ferrate (VI) solution.

about 80% of FeO $_4^{2-}$  and about 20% of HFeO $_4^{-}$  to SO $_4^{2-}$ , NO $_3^{-}$  and Hg $^{2+}$  at pH 8.0. The reaction equations are described as follows:

$$HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \quad pK_a = 7.3 \tag{3}$$

$$SO_2 + 3FeO_4^{2-} + 5H_2O \leftrightarrow SO_4^{2-} + 3Fe(OH)_3 + OH^- + 5/2O_2$$
 (4)

$$SO_2 + 3HFeO_4^{2-} + 7/2H_2O \leftrightarrow SO_4^{2-} + 3Fe(OH)_3 + OH^- + 7/4O_2$$
(5)

$$NO + 3FeO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_3 + NO_3^- + 2OH^- + 3/2O_2$$
 (6)

$$NO + 2HFeO_4^{2-} + 3H_2O \rightarrow 2Fe(OH)_3 + NO_3^- + 2OH^- + 1/2O_2$$
(7)

$$Hg^{0} + 2FeO_{4}^{2-} + 4H_{2}O \leftrightarrow Hg^{2+} + 2Fe(OH)_{3} + 2OH^{-} + 2O_{2}$$
 (8)

$$Hg^{0} + 2HFeO_{4}^{2-} + 5H_{2}O \leftrightarrow Hg^{2+} + 2Fe(OH)_{3} + 6OH^{-} + 1/2O_{2}$$
(9)

# 5. Conclusions

- (1) Compared with classical chemicals, prepared ferrate (VI) solution has obvious advantages regarding the environment, and as far as economy is concerned, it is estimated that the total price of simultaneous removing SO<sub>2</sub>, NO<sub>x</sub> and Hg<sup>0</sup> by this process is lower than that of the combined system of three processes, such as limestone—gypsum flue gas desulfurization, selective catalytic reduction and activated carbon adsorption, although the cost of lime (\$115/ton) is lower than that of ferrate (VI) (\$2131/ton). In addition, with the development of new manufacturing processes, the cost of ferrate (VI) has been decreased greatly, which implies that ferrate (VI) will be able to meet the requirement of industrialized application in the near future.
- (2) On the basis of ferrate (VI) solution, a new process was developed for simultaneously removing SO<sub>2</sub>, NO and Hg<sup>0</sup> in liquid phase. Under the optimal conditions, the removal efficiencies of 100% for SO<sub>2</sub>, 64.8% for NO and 81.4% for Hg<sup>0</sup> were obtained, respectively.
- (3) According to the discussions of the ferrate (VI) solution characteristics, the comparisons of ferrate (VI) solution  $E_0$  value with  $E_0$  values of SO<sub>2</sub>, NO and Hg<sup>0</sup>, the analysis results of the reaction products and the previous works, the reaction mechanism was deduced, namely, SO<sub>2</sub>, NO and Hg<sup>0</sup> were oxidized by FeO<sub>4</sub><sup>2-</sup> and HFeO<sub>4</sub><sup>-</sup> to SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Hg<sup>2+</sup> respectively.

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