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## SIMULTANEOUS REMOVAL OF SO<sub>2</sub> AND NO<sub>x</sub> FROM SINTERING FLUE GAS USING AMMONIA-Fe(II)EDTA COMBINED WITH ELECTROLYTIC REGENERATION

Sulfur dioxide and nitrogen oxide are health hazardous gases, which contribute to the formation of submicron acidic particulates. To reduce SO<sub>2</sub> and NO<sub>x</sub> emission from the sintering flue gas, the combination of ammonia-Fe(II)EDTA solution scrubbing with Fe(III) electrolytic regeneration is proposed. The above method has the following advantages: direct conversion of NO<sub>x</sub> and SO<sub>2</sub> to harmless N<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, recovery of the by-product (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> emission from flue gas in the reactor. The effect of the pH, initial Fe(II)EDTA concentration, and voltage on the desulfurization and denitration efficiencies was investigated using a bench-scale reactor. The maximal desulfurization and denitration efficiencies were 98% and 52%, respectively. The optimum parameters were pH > 5.0, 2.1 V, and 0.05 mol·dm<sup>-3</sup> Fe(II)EDTA concentration. SO<sub>2</sub> and NO<sub>x</sub> removal from the sintering flue gas by ammonia-Fe(II)EDTA solution scrubbing combined with electrolytic regeneration was also demonstrated in a pilot-scale reactor.

### 1. INTRODUCTION

Sulfur dioxide and nitrogen oxide are gases hazardous to human health and contribute to the formation of submicron acidic particulates that can penetrate into the human lungs and even be absorbed in the bloodstream [1,2]. The main sources of SO<sub>2</sub> and NO<sub>x</sub> are the exhaust gas from fossil fuel combustion in industries such as coal combustion power plants, paper mills, iron and steel plants, and in waste incinerators [3]. In 2014, it was reported that the iron and steel industry in China emitted about 2.15×10<sup>6</sup> t of SO<sub>2</sub> and 1.01×10<sup>6</sup> t of NO<sub>x</sub> [4]. Moreover, SO<sub>2</sub> and NO<sub>x</sub> emitted from the sintering process

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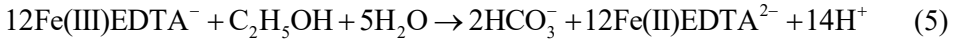
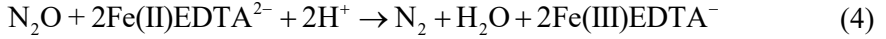
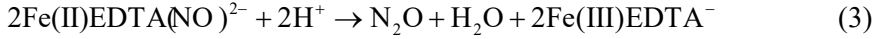
accounted for 85% and 40% of the total emissions in the iron and steel industry [5]. In order to improve the air quality, the Ministry of Environmental Protection of China issued a new emission standard for decreasing air pollutants from the sintering and pelletizing process in the iron and steel industry (GB28662-2012). This standard stipulates that the SO<sub>2</sub> and NO<sub>x</sub> concentration in the exhaust flue gas from sintering plants must be below 200 and 300 mg·Nm<sup>-3</sup>, respectively. However, the current NO<sub>x</sub> emission from most sintering plants is about 400 mg·Nm<sup>-3</sup>, which is above the emission limit [6].

At present, various desulfurization technologies such as dry desulfurization, semi-dry desulfurization, and wet desulfurization techniques have been utilized. The ammonia-based wet flue gas scrubber is regarded as one of the most reliable approaches and has been widely applied in China because of its low investment cost, high desulfurization efficiency, the lack of generation of secondary pollutants, and the production of useful by-products [7, 8]. In the ammonia-based wet flue gas scrubber system, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and small amounts of NH<sub>4</sub>HSO<sub>3</sub> coexist in the scrubbing solution without free NH<sub>3</sub>. It was reported that (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> has the capacity to absorb NO<sub>x</sub> (but is ineffective for desulfurization [9]), and 20–40% denitration efficiency could be achieved with the ammonia-based wet flue gas scrubber [10]. The reaction between NO<sub>x</sub> and (NH<sub>3</sub>)<sub>2</sub>SO<sub>3</sub> is described below



However, the NO<sub>x</sub> concentration in the sintering flue gas after passing through the ammonia-based wet flue gas scrubber is still above the emission limit. In order to further reduce NO<sub>x</sub> emission, technologies such as ammonia-based selective catalytic reduction (NH<sub>3</sub>-SCR) [11] and complex absorption [12, 13] have been developed. Although ammonia-based selective catalytic reduction (NH<sub>3</sub>-SCR) is widely used in coal-fired power plants, SCR is not suitable for sintering flue gas because the temperature (120–180 °C) of the sintering flue gas is lower than the optimal reaction temperature of the current commercial catalysts [2, 11]. Complex absorption is considered as one of the most promising approaches due to its rapid absorption rate and moderate operation cost [14, 15]. The addition of Fe(II) (EDTA) (EDTA – ethylenediaminetetraacetate) to the scrubbing solution (such as ammonia-based solutions and calcium-based solutions) could improve the solubility of NO<sub>x</sub> via formation of the Fe(II)(EDTA)(NO) complex [16, 17]. However, Fe(II)EDTA is easily oxidized to Fe(III)EDTA by oxygen in the flue gas (the sintering flue gas contains 15–18% of oxygen) and loses its capability to bind NO [18]. Hence, the challenge in the denitration process by Fe(II)EDTA solution is reducing Fe(III)EDTA. Chandrashekhara et al. [15] combined biomass from municipal sewage sludge with ethanol to reduce Fe(III)EDTA and Fe(III)NTA with the maximum reduc-

ing rates 0.0021 and 0.0026, mmol·dm<sup>-3</sup>·d<sup>-1</sup>·mg<sup>-1</sup> biomass. They proposed that the denitration reaction by Fe(II)EDTA solution and Fe(EDTA) reduction proceeded according to the following stoichiometric equations:



Guo et al. [17, 19] demonstrated that the electrochemical method employing an activated carbon catalyst was effective for reducing Fe(III)EDTA to Fe(II)EDTA, and found that 99% denitration efficiency could be achieved over 10 h. However, activated carbon and a Nepem-117 proton exchange membrane were used to accelerate the reduction process in their experiments, which resulted in higher operation costs. Notably, there was a large amount of fly ash in the sintering flue gas, which would form a slurry in the scrubber and block the membrane in the case of real sintering flue gas.

In order to simultaneously remove NO<sub>x</sub> and SO<sub>2</sub>, ammonia-Fe(II)EDTA scrubbing combined with electrochemical regeneration is proposed herein. Fe(II)EDTA is added to the ammonia-based solution to increase the solubility of NO by forming the Fe(II)(EDTA)(NO) complex. The Fe(II)(EDTA)(NO) complex is then reduced electrochemically, assisted by (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> in the ammonia-based solution. The final products are N<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. When the amount of (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> in the ammonia-based solution is insufficient, Fe(II)(EDTA)(NO) can also be reduced to N<sub>2</sub> directly by the electrochemical process. This method has several advantages such as (i) direct conversion of NO<sub>x</sub> and SO<sub>2</sub> to harmless N<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>, (ii) recovery of the by-product (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and (iii) simultaneous removal of NO<sub>x</sub> and SO<sub>2</sub> in the reactor. Moreover, the influence of the operation parameters such as the Fe(II)EDTA concentration, pH, and electrolysis voltage on the denitration and desulfurization efficiency is also investigated to determine the optimum parameters using a bench-scale reactor and a pilot-scale reactor.

## 2. EXPERIMENTAL

*Bench-scale reactor.* The bench-scale reactor consisted of a simulated flue gas supply system, spray reactor, and electrochemical regeneration system (Fig. 1). In the simulated flue gas system, NO was used as it is the major component of NO<sub>x</sub> (90–95%) and can reasonably represent NO<sub>x</sub>. SO<sub>2</sub> and NO were supplied from separate cylinders and the flow rates of SO<sub>2</sub> and NO were controlled by mass flow controllers (CS200D, Sevenstar Electronics Co., Ltd., Beijing). Air provided by a fan was used as the balance gas

and the flow rate of air was controlled by a rotameter. The simulated flue gas was mixed in a tank to improve the distribution uniformity before entering the spray reactor.

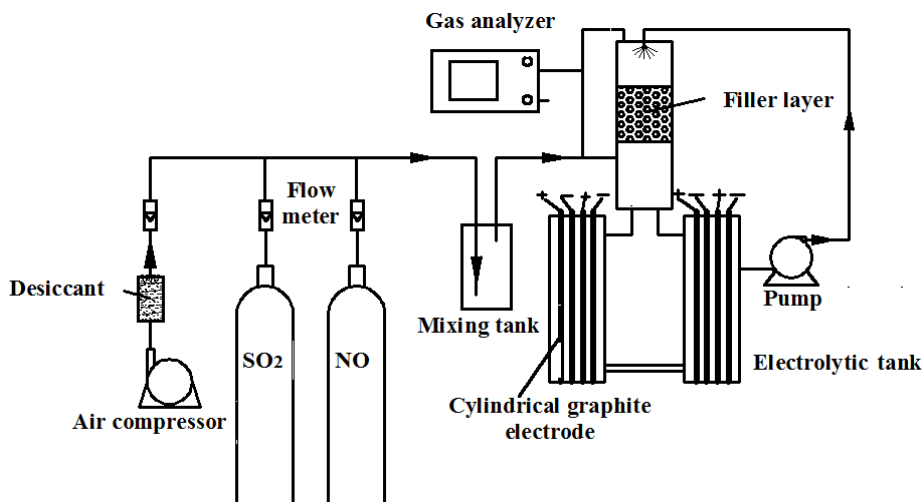


Fig. 1. Schematic diagram of the bench-scale reactor desiccant

The spray reactor was made of polyvinyl chloride (PVC) 100 mm in diameter and 1200 mm high. In order to optimize the time for reaction between the solution and the simulated flue gas, a pall ring filler 150 mm high was packed into the spray reactor. The electrochemical regeneration system was also made of two PVC cylindrical reactors 600 mm high, 100 mm in diameter. Six graphite electrodes 10 mm in diameter and 600 mm high were used as the anodes and another six graphite electrodes were used as cathodes. The total effective surface area of the electrodes was 0.2 m<sup>2</sup>. The voltage was provided by using DC regulated power (Shanghai Liyou Electrification Co., Ltd., 0–10 V). A vertical view of the cylindrical graphite electrodes is shown in Fig. 2.

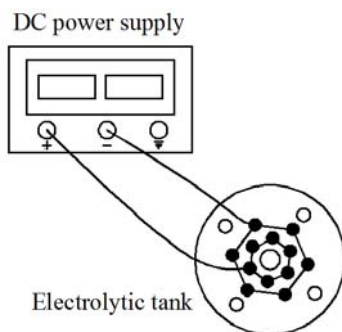


Fig. 2. Vertical view of the cylindrical graphite electrode

Before the experiment, Fe(II)EDTA was prepared from Na<sub>2</sub>EDTA and FeSO<sub>4</sub>·7H<sub>2</sub>O. In order to simulate the scrubbing solution in the ammonia-desulfurization system, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added to the solution and a 1.5 mol·dm<sup>-3</sup> (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution was prepared. The pH of the solution was adjusted with ammonia and sulfuric acid. The concentrations of SO<sub>2</sub> and NO were 1400 mg·m<sup>-3</sup> and 400 mg·m<sup>-3</sup>, respectively. The flow rate of the simulated flue gas was 7.9 m<sup>3</sup>·h<sup>-1</sup>, which was recorded by a flowmeter, and the reaction time of the liquid and the flue gas was about 3.5 s. In order to maintain a liquid to gas ratio of 12 dm<sup>3</sup>·m<sup>-3</sup>, the amount of spray solution was about 100 dm<sup>3</sup>·h<sup>-1</sup>. The operation parameters for the bench-scale experiment are summarized in Table 1 (from run 1 to run 4).

Table 1

Operation parameters

Parameter	Run 1	Run 2	Run 3	Run 4	Run 5
Temperature, °C	25	25	25	25	25
pH	5–6	4–8	5–6	5–6	5–6
SO <sub>2</sub> concentration, mg·m <sup>-3</sup>	1400	1400	1400	1400	473
NO <sub>x</sub> concentration, mg·m <sup>-3</sup>	400	400	400	400	792
Oxygen concentration, %	20	20	20	20	16
Fe(II)EDTA concentration, mol·dm <sup>-3</sup>	0.05	0.05	0.01–0.07	0.05	0.05
Flue gas, m <sup>3</sup> ·h <sup>-1</sup>	7.9	7.9	7.9	7.9	79.2
Spray solution, dm <sup>3</sup> ·h <sup>-1</sup>	100	100	100	100	1000
Voltage, V	2.0	2.0	2.0	1.5–2.4	2.1
Current, A	15	15	15	10.8–15.4	62

*Pilot-scale reactor.* The pilot-scale reactor (Fig. 3) also consisted of a flue gas supply system, absorption reactor, and an electrochemical regeneration system. A photograph of the pilot-scale reactor is presented in Fig. 4. In the flue gas supply system, the flue gas comes from a bypass in a sintering plant and the flow rate is controlled by a valve and a flowmeter. The concentrations of NO<sub>x</sub> and SO<sub>2</sub> in the sintering flue gas were monitored online by gas analyzers (Horiba Corp., PG-250, Japan); the concentrations of NO<sub>x</sub> and SO<sub>2</sub> were 473 mg·m<sup>-3</sup> and 792 mg·m<sup>-3</sup>, respectively. The absorption reactor 2465 mm high and 200 mm in diameter was made of stainless steel. A pall ring filler 900 mm and three nozzles for the spray solution were installed in the absorption reactor. The spray solution was separately provided by pumps and controlled by flowmeters. In addition, the pH of the solution was recorded online by pH meters (PHG-6201, Shanghai Jingmi Instrument Co., Ltd.) and was adjusted by adding ammonia. In the electrochemical regeneration system, the voltage was provided by using four DC regulated power supplies (Shanghai Liyou Electrification Co., Ltd., 0–10 V).

The cathode and anode were made of graphite plates, fifteen plates each, arranged in parallel. Their dimensions were 500×400×5 mm. The distance between the cathode

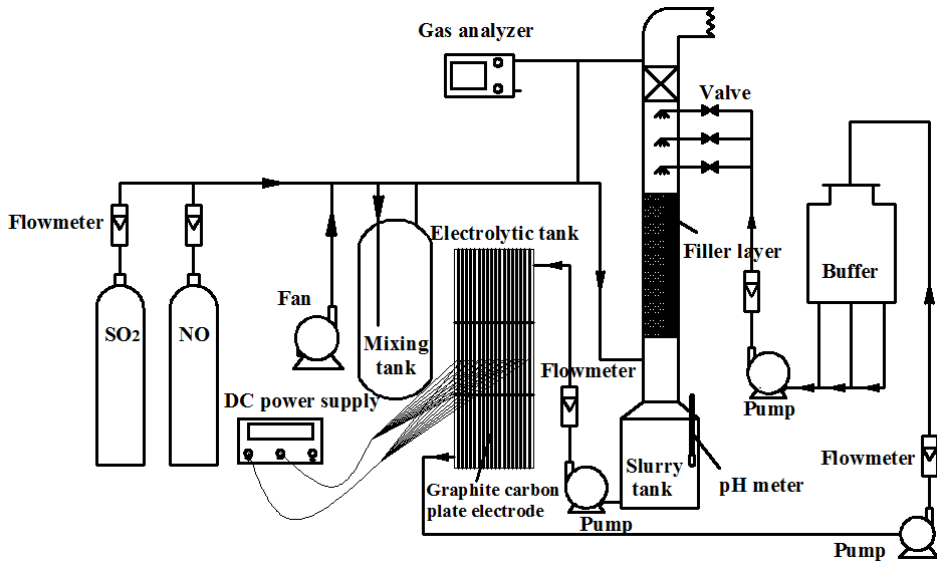


Fig. 3. Schematic diagram of the pilot-scale reactor



Fig. 4. Photograph of the pilot-scale reactor

and anode was 10 mm. The total effective surface area of the graphite electrodes was 9.0 m<sup>2</sup>. A side-view of the graphite plate electrodes is shown in Fig. 5.

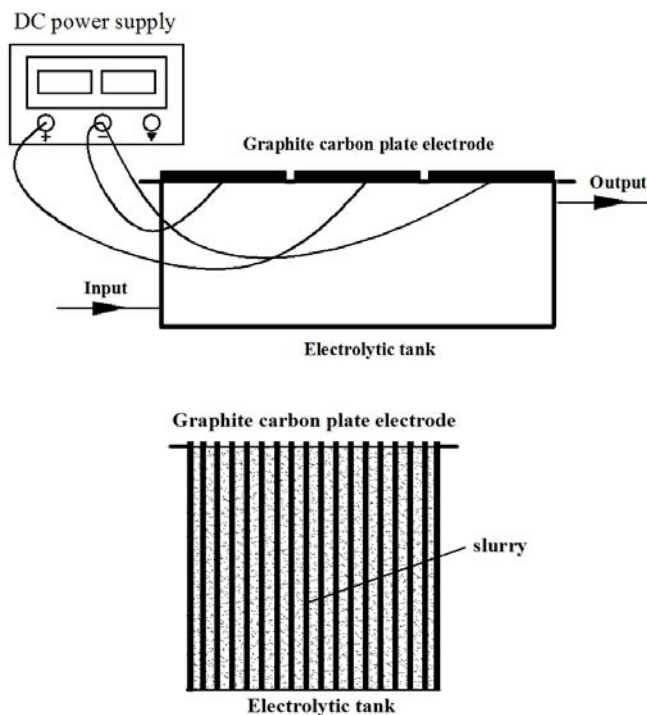


Fig. 5. Side-view of the graphite plate electrodes

Before the experiment, 200 dm<sup>3</sup> of scrubbing solution was obtained from the ammonia-based desulfurization tower in the sintering plant. Fe(II)EDTA was prepared from Na<sub>2</sub>EDTA and FeSO<sub>4</sub>·7H<sub>2</sub>O, and the concentration of Fe(II)EDTA in the solution was 0.05 mol·dm<sup>-3</sup>. The concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was about 1.5 mol·dm<sup>-3</sup>. The flow rate of the flue gas was 79.2 m<sup>3</sup>·h<sup>-1</sup>, the amount of spray solution was 1000 dm<sup>3</sup>·h<sup>-1</sup>. The liquid/gas ratio was similar to that in the bench-scale reactor. The operation parameters for the pilot-scale experiment are also summarized in Table 1 (run 5).

*Analysis and detection instruments.* The components of the flue gas (NO<sub>x</sub>, SO<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and O<sub>2</sub>) in the inlet and outlet flue gas were recorded online by gas analyzers (Horiba Corp., PG-250, Japan). pH was measured with a pH/ORH meter (PHG-6201, Shanghai Jingmi Instrument Co., Limited). The concentration of Fe(II)EDTA was determined from the absorbance at 420 nm using a UV/visible spectrophotometer (UNICO (Shanghai) Instruments Co., Limited). The ferrous iron and total iron were determined colorimetrically at 510 nm after filtration (0.22 μm) by using a modified 1,10-phenanthroline colorimetric method. Meanwhile, gas chromatography coupled with a TCD

detector (Agilent Corp., 7820A, USA) was used to analyze  $N_2$  and  $H_2$ .  $NO_3^-$  and  $NO_2^-$  in the liquid phase were determined using ion chromatography (Dionex Corp., ICS-90, USA).

### 3. RESULTS AND DISCUSSION

#### 3.1. REMOVAL OF $SO_2$ AND $NO_x$ WITH AMMONIA-Fe(II)EDTA SOLUTION

Figure 6 shows that 99% desulfurization efficiency could be achieved with the ammonia-Fe(II)EDTA scrubbing solution in the bench-scale reactor.

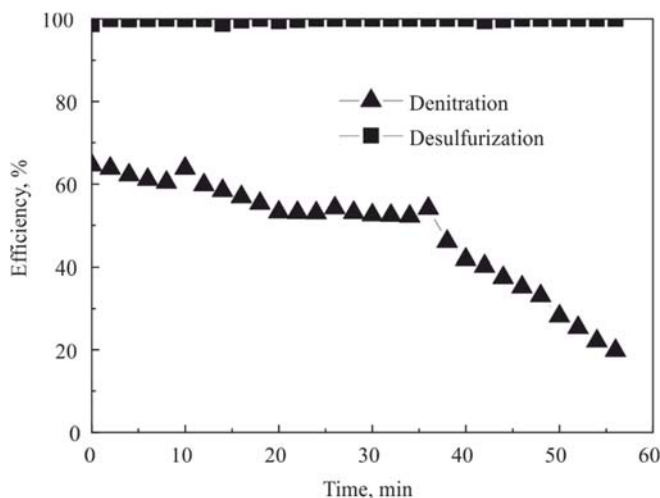


Fig. 6. Simultaneous removal of  $SO_2$  and  $NO_x$  with ammonia-Fe(II)EDTA (25 °C, pH 5–6, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>,  $NO_x$  – 400 mg·m<sup>-3</sup>,  $SO_2$  – 1400 mg·m<sup>-3</sup>,  $O_2$  – 20%)

The operation parameters are listed in Table 1 (run 1). Figure 6 shows that the initial denitration efficiency was 62%. However, the denitration efficiency decreased to 21% after 60 min. The variation of the concentration of Fe(II) and Fe(III) in the ammonia-Fe(II)EDTA solution with the reaction time is shown in Fig. 7. The concentration of Fe(III) in the scrubbing solution initially increased dramatically from 0 to 0.020 mol·dm<sup>-3</sup> as the reaction time increased from 0 to 25 min, after which, the Fe(III) concentration increased slightly from 0.020 to 0.026 mol·dm<sup>-3</sup> as the reaction time further increased from 25 min to 60 min. In contrast, the concentration of Fe(II) in the scrubbing solution decreased dramatically from 0.050 to 0.030 mol·dm<sup>-3</sup>, followed by another slight decrease to 0.024 mol·dm<sup>-3</sup> when the reaction time was increased from 0 to 60 min.



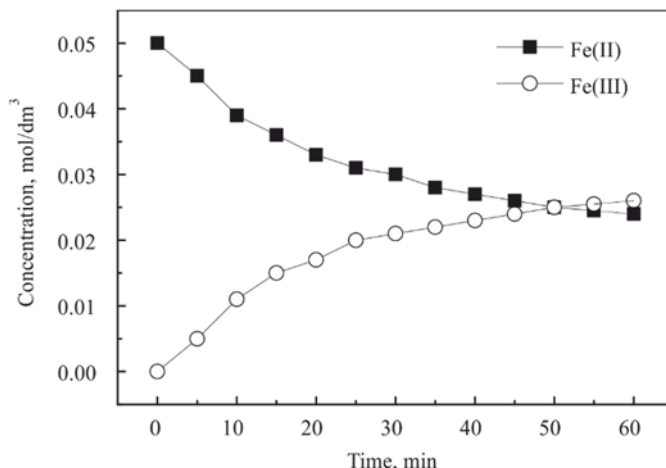
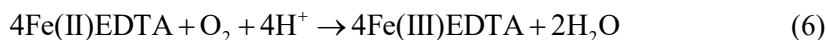


Fig. 7. Effect of reaction time on F(II) and Fe(III) concentrations in ammonia-Fe(II)EDTA (25 °C, pH 5–6, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, NO<sub>x</sub> – 400 mg·m<sup>-3</sup>, SO<sub>2</sub> – 1400 mg·m<sup>-3</sup>, O<sub>2</sub> – 20%)

Fe(II)EDTA was oxidized to Fe(III)EDTA in the presence of O<sub>2</sub> and lost its binding capacity for NO:



Hence, the scrubbing solution must be regenerated to maintain the denitration efficiency.

### 3.2. DENITRATION AND DESULFURIZATION WITH AMMONIA-Fe(II)EDTA SOLUTION COMBINED WITH ELECTROCHEMICAL REGENERATION

In order to investigate the pH effect, pH was varied from 4.0 to 8.0, while other parameters were kept constant (run 2 in Table 1, Fig. 8). Before the experiment, Fe(III) in the scrubbing solution was reduced electrolytically, and then oxidized with pure oxygen from a cylinder. When the denitration efficiency was 20%, reduction or oxidation of the scrubbing solution was stopped; the concentration of Fe(II) in the scrubbing solution was about 0.021 mol·dm<sup>-3</sup>. pH was adjusted to the pre-determined value by adding ammonia or sulfuric acid. The experiment was then initiated. The results demonstrated that the denitration efficiency increased during the electrochemical regeneration process. After 60 min, the denitration efficiency increased from 20% to 52.6% at pH 6.0. Figure 9 demonstrates that the concentration of Fe(III) in the scrubbing solution first decreased dramatically from 0.03 to 0.009 mol·dm<sup>-3</sup> as the regeneration time increased from 0 to 60 min and then remained constant as the regeneration time increased from 60 to 100 min.

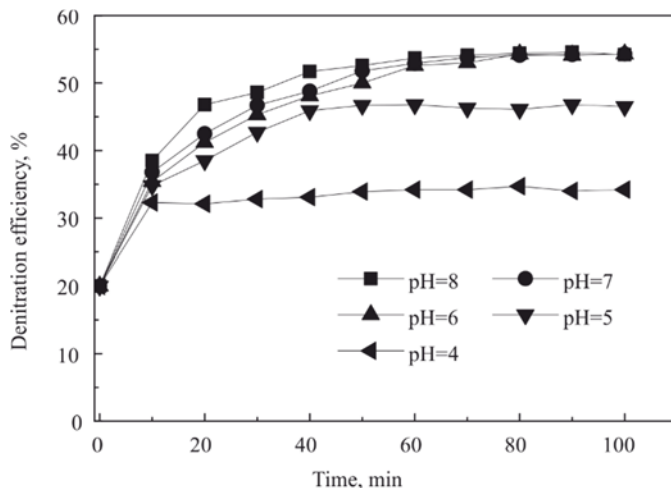


Fig. 8. Effect of pH on  $\text{NO}_x$  removal efficiency (25 °C, concentrations of:  $\text{Fe(II)EDTA} - 0.05 \text{ mol} \cdot \text{dm}^{-3}$ ,  $\text{NO}_x - 400 \text{ mg} \cdot \text{m}^{-3}$ ,  $\text{SO}_2 - 1400 \text{ mg} \cdot \text{m}^{-3}$ ,  $\text{O}_2 - 20\%$ , 2.0 V, 15 A)

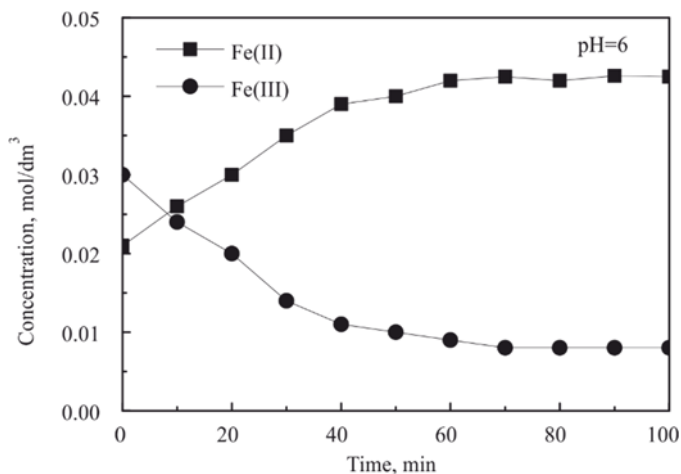
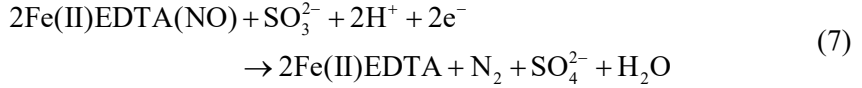


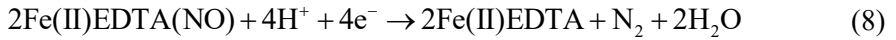
Fig. 9.  $\text{Fe(II)}$  and  $\text{Fe(III)}$  concentrations in ammonia- $\text{Fe(II)EDTA}$  solution during electrochemical regeneration (25 °C, pH 6, concentrations of:  $\text{Fe(II)EDTA} - 0.05 \text{ mol} \cdot \text{dm}^{-3}$ ,  $\text{NO}_x - 400 \text{ mg} \cdot \text{m}^{-3}$ ,  $\text{SO}_2 - 1400 \text{ mg} \cdot \text{m}^{-3}$ ,  $\text{O}_2 - 20\%$ , 2.0 V, 15 A)

In contrast, the concentration of  $\text{Fe(II)}$  in the scrubbing solution increased dramatically from  $0.021$  to  $0.042 \text{ mol} \cdot \text{dm}^{-3}$  and remained constant when the regeneration time exceeded 60 min. Hence, the regeneration rate of  $\text{Fe(III)}$  in the scrubbing solution was about  $0.021 \text{ mol} \cdot \text{dm}^{-3} \cdot \text{h}^{-1}$  when the operation parameters were pH 6.0,  $0.05 \text{ mol} \cdot \text{dm}^{-3}$   $\text{Fe(II)EDTA}$ , and 2.1 V.

The mechanism of electrochemical regeneration can be described as follows [17, 9, 21]. Fe(II)(EDTA)(NO) complex was electrochemically reduced with the participation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> in the ammonia-based solution. The final products were N<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>



In the initial stage, no SO<sub>3</sub><sup>2-</sup> ions were present in the solution or the amount of SO<sub>2</sub> in the flue gas was insufficient; Fe(II)(EDTA)(NO) could also be directly reduced to generate N<sub>2</sub> by the electrochemical reaction



Meanwhile, Fe(III)(EDTA) was also regenerated electrochemically



Figure 4 also shows that pH had a significant influence on the denitration efficiency. At pH 4, the denitration efficiency was only 33% after 100 min. At pH 8.0, the final denitration efficiency was as high as 54.6%. Though the half-cell reduction potential of Fe<sup>3+</sup>/Fe<sup>2+</sup> (0.771 V) is much higher than that of H<sup>+</sup>/H<sub>2</sub> (0.0 V), H<sup>+</sup> ions still competed with Fe<sup>3+</sup> ions when the concentration of H<sup>+</sup> ions was high enough. Thus, the rate of Fe<sup>3+</sup> reduction decreased below pH 5. Figure 10 presents the effect of pH on the desulfurization efficiency. Below pH 5, the desulfurization efficiency would be low due to the lower concentration of OH<sup>-</sup> in the ammonia-based solution. However, the desulfurization efficiency could reach 99% at pH > 6.

The effect of the Fe(II)EDTA concentration on the denitration and desulfurization efficiency was also studied (Fig. 11). The operation parameters for this run are summarized in Table 1 (run 3). The initial Fe(II)EDTA concentration was 0.01–0.07 mol·dm<sup>-3</sup>. After reduction and oxidation of the solution, the initial denitration efficiency was also fixed at 20% before the experiment.

Figure 11 shows that the denitration efficiency increased with the Fe(II)EDTA concentration. At the Fe(II)EDTA concentration of 0.07 mol·dm<sup>-3</sup>, the denitration efficiency was maintained at 68% after two hours. However, the denitration efficiency was only 30% for 0.01 mol·dm<sup>-3</sup> Fe(II)EDTA. The above phenomena can be explained in that NO<sub>x</sub> was complexed with Fe(II)(EDTA) and formed Fe(II)(EDTA)(NO); more Fe(II)EDTA can bind more NO, which resulted in the high denitration efficiency. Considering the operation cost and the denitration efficiency, it is suggested that the optimum Fe(II)EDTA concentration is 0.05 mol·dm<sup>-3</sup>.

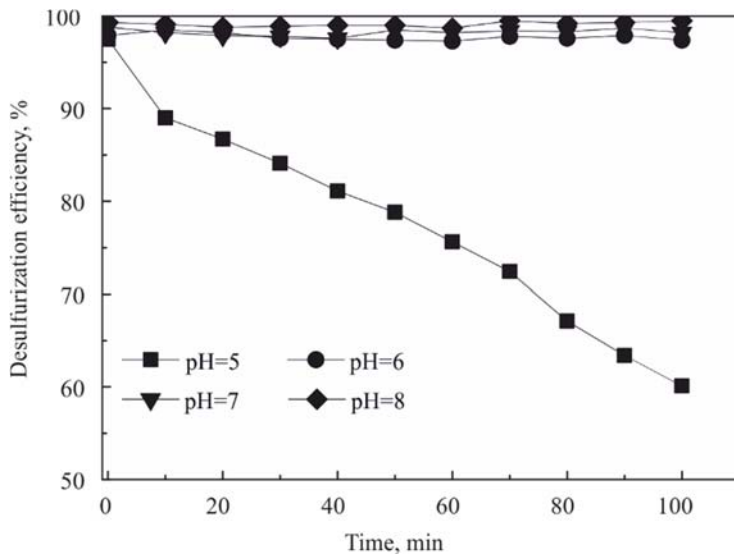


Fig. 10. Effect of pH on SO<sub>2</sub> removal efficiency (25 °C, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, NO<sub>x</sub> – 400 mg·m<sup>-3</sup>, SO<sub>2</sub> – 1400 mg·m<sup>-3</sup>, O<sub>2</sub> – 20%, 2.0 V, 15 A)

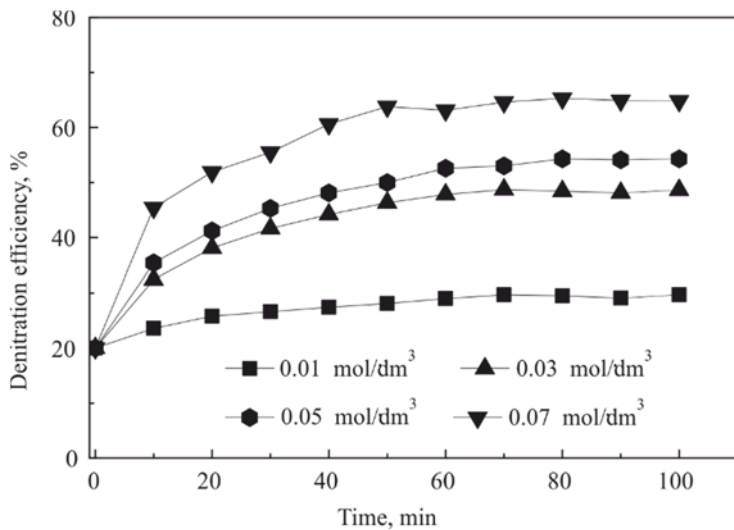


Fig. 11. Effect of Fe(II)EDTA concentration on NO<sub>x</sub> removal efficiency (25 °C, concentrations of: pH 5–6, NO<sub>x</sub> – 400 mg·m<sup>-3</sup>, SO<sub>2</sub> – 1400 mg·m<sup>-3</sup>, O<sub>2</sub> – 20%, 2.0 V, 15 A)

It was well known that the desulfurization efficiency depends on pH. Figure 12 also demonstrates that the desulfurization efficiency is not directly related to the Fe(II)EDTA concentration, and the desulfurization efficiency was above 99% in this run.

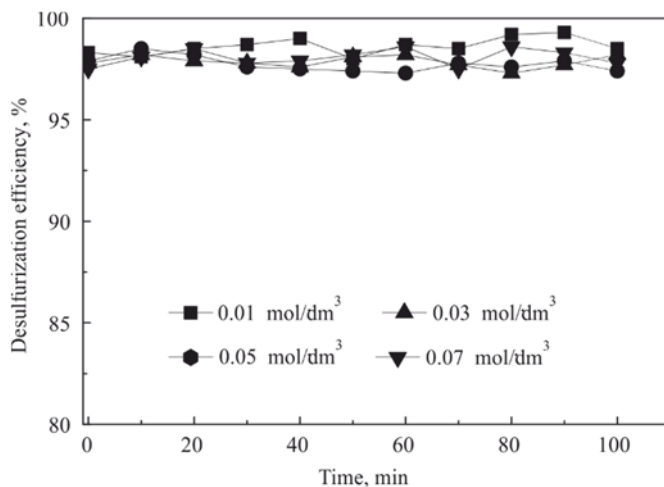


Fig. 12. Effect of Fe(II)EDTA concentration on SO<sub>2</sub> removal efficiency (25 °C, concentrations of: pH 5–6, NO<sub>x</sub> – 400 mg·m<sup>-3</sup>, SO<sub>2</sub> – 1400 mg·m<sup>-3</sup>, O<sub>2</sub> – 20%, 2.0 V, 15 A)

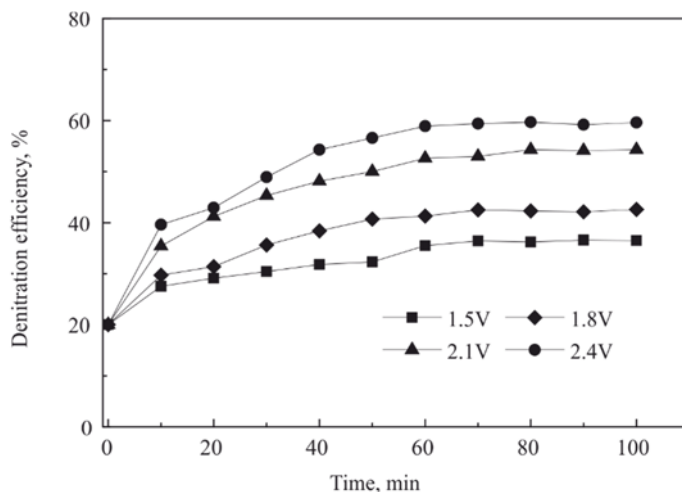


Fig. 13. Effect of voltage on NO<sub>x</sub> removal efficiency (25 °C, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, pH 5–6, NO<sub>x</sub> – 400 mg·m<sup>-3</sup>, SO<sub>2</sub> – 1400 mg·m<sup>-3</sup>, O<sub>2</sub> – 20%)

The voltage or current are the most important parameters in the process of electrolysis, and determines the reduction or oxidation rate. However, it was reported that EDTA is easily degraded in the electrolysis process at voltages above 4.0 V [17, 18, 21]. Before the experiment, the influence of the voltage on EDTA degradation was studied. It was found that EDTA decomposed when the voltage exceeded 3.5 V. Moreover, a large amount of H<sub>2</sub> and O<sub>2</sub> was produced during the electrolysis at 3.0 V. Based on the Fe<sup>3+</sup>/Fe<sup>2+</sup> (0.771 V) couple, the voltage in run 4 was predetermined as 1.5–2.4 V, and

the corresponding current was 10.8–15.4 A. After reduction and oxidation of the solution, the initial denitration efficiency was also fixed at 20%, and the corresponding Fe(II) concentration in the scrubbing solution was  $0.021 \text{ mol}\cdot\text{dm}^{-3}$ . Figure 13 shows that increasing the electrolytic voltage had a positive effect on the denitration efficiency, and the denitration efficiency was stabilized when the regeneration time exceeded 60 min.

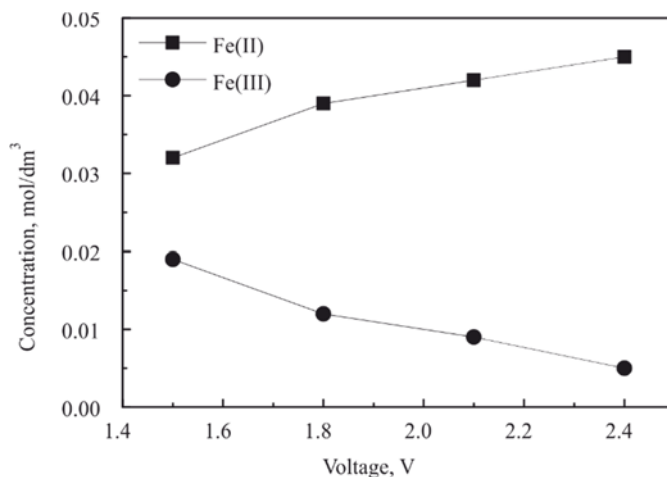


Fig. 14. Effect of voltage on Fe(II) and Fe(III) concentrations in ammonia-Fe(II)EDTA solution (25 °C, concentrations of: Fe(II)EDTA –  $0.05 \text{ mol}\cdot\text{dm}^{-3}$ , pH 5–6,  $\text{NO}_x$  –  $400 \text{ mg}\cdot\text{m}^{-3}$ ,  $\text{SO}_2$  –  $1400 \text{ mg}\cdot\text{m}^{-3}$ ,  $\text{O}_2$  – 20%)

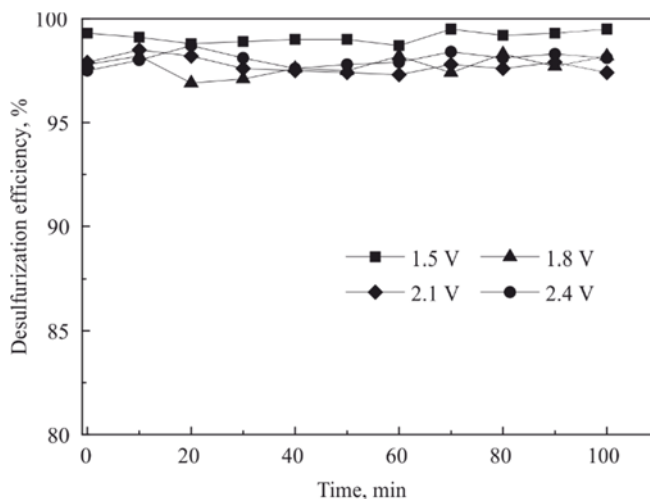


Fig. 15. Effect of voltage on  $\text{SO}_2$  removal efficiency (25 °C, concentrations of: Fe(II)EDTA –  $0.05 \text{ mol}\cdot\text{dm}^{-3}$ , pH 5–6,  $\text{NO}_x$  –  $400 \text{ mg}\cdot\text{m}^{-3}$ ,  $\text{SO}_2$  –  $1400 \text{ mg}\cdot\text{m}^{-3}$ ,  $\text{O}_2$  – 20%)

The denitration efficiency established at 31% at 1.5 V, and increased to 58% at 2.4 V. Under the voltage of 2.1 V, the denitration efficiency was 52%. Considering the operation cost and the denitration efficiency, 2.1 V is regarded as the optimum voltage. Figure 14 demonstrates that the Fe(II) concentrations in the ammonia-based solution were 0.032, 0.039, 0.042, and 0.045 mol·dm<sup>-3</sup> with application of 1.5, 1.8, 2.1, and 2.4 V, and the corresponding Fe(III) regeneration rates in the scrubbing solution were 0.011, 0.018, 0.021, and 0.024 mol·dm<sup>-3</sup>·h<sup>-1</sup>, respectively. The voltage also had a slight influence on the desulfurization efficiency. The desulfurization efficiencies in this run were above 96%, as shown in Fig. 15.

### 3.3. DENITRATION AND DESULFURIZATION IN A PILOT-SCALE REACTOR

In order to verify the feasibility of removing SO<sub>2</sub> and NO<sub>x</sub> from the sintering flue gas by using ammonia-Fe(II)EDTA solution combined with electrolytic regeneration, the denitration and desulfurization experiment was also carried out in a pilot-scale reactor. The flue gas was transported from the sintering plant via a bypass pipe. In order to compare the experimental results obtained with the pilot-scale and bench-scale reactor, similar liquid to gas ratios and reaction times were used. In this run (run 5), the flow rate of the flue gas was 79.2 m<sup>3</sup>·h<sup>-1</sup> and the amount of spray solution was 1000 dm<sup>3</sup>·h<sup>-1</sup>. The voltage was 2.1 V and the current was 62 A; NO<sub>x</sub> and SO<sub>2</sub> concentration were 473 and 792 mg·m<sup>-3</sup>, respectively. The other parameters are summarized in Table 1 (run 5).

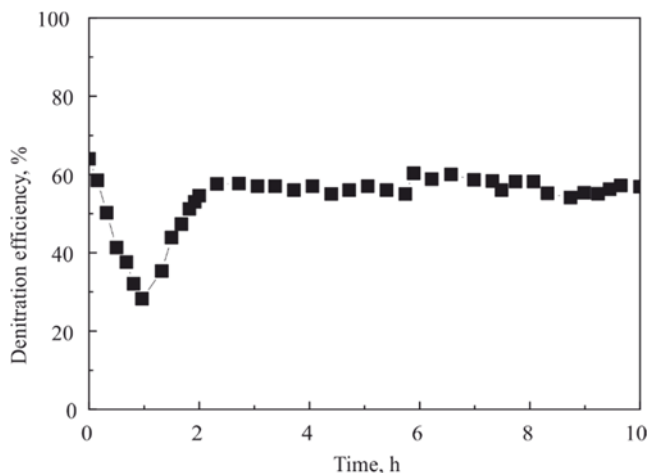


Fig. 16. Denitration efficiency in a pilot-scale reactor  
(25 °C, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, pH 5–6,  
O<sub>2</sub> – 18%, 2.1 V, 62 A)

Figure 16 demonstrates that the denitration efficiency decreased from 64% to 28.3% after 60 min without electrolytic regeneration, followed by an increase to 54.6% when

electrolysis was sustained for 60 min; the denitration efficiency remained stable at 52–63% due to the processes in Eqs. (6)–(9).

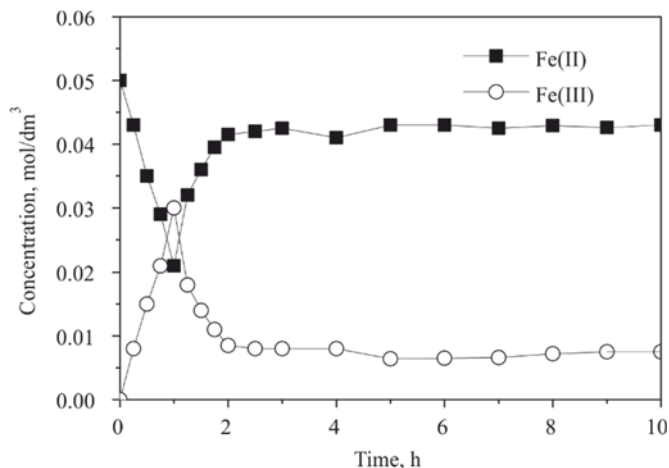


Fig. 17. Fe(II) and Fe(III) concentrations in ammonia-Fe(II)EDTA solution during electrochemical regeneration process (25 °C, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, O<sub>2</sub> – 18%, 2.1 V, 62 A)

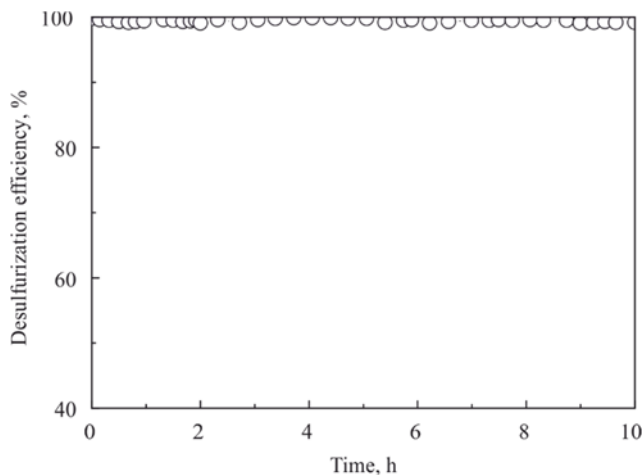


Fig. 18. Desulfurization efficiency in a pilot-scale reactor (25 °C, concentrations of: Fe(II)EDTA – 0.05 mol·dm<sup>-3</sup>, pH 5–6, O<sub>2</sub> – 18%, 2.1 V, 62 A)

The concentration of Fe(II) in the ammonia-based solution first decreased, then increased to stabilize at 0.0435 mol·dm<sup>-3</sup> (Fig. 17). The rate of Fe(III) regeneration by electrolysis was 0.0225 mol·dm<sup>-3</sup>·h<sup>-1</sup>. Comparison of Figs. 16 and 13 shows that the denitration efficiency in the pilot-scale reactor was 10% higher than that in the bench-scale reactor. Han et al. [5] reported that the sintering flue gas contained about 10–15%



NO<sub>2</sub>, which was easily captured by water. Hence, the denitration efficiency in the pilot-scale reactor was higher than that in the bench-scale reactor. The desulfurization efficiency in the pilot-scale reactor is presented in Fig. 18. It exceeded 99%.

#### 4. CONCLUSIONS

Simultaneous denitration and desulfurization of sintering flue gas via ammonia-Fe(II)EDTA solution scrubbing combined with electrolytic regeneration was demonstrated using a bench-scale reactor and a pilot-scale reactor. The experimental results showed that scrubbing with ammonia-Fe(II)EDTA solution could effectively remove NO<sub>x</sub> and SO<sub>2</sub> from the sintering flue gas. However, the solution quickly loses its de-NO<sub>x</sub> ability due to the oxidation of Fe(II)EDTA.

The experiment in the bench-scale reactor showed that Fe(III)EDTA could be effectively regenerated by electrolysis and a denitration efficiency of 52% could be maintained. The optimum parameters were also determined to be pH 5.0, 0.05 mol·dm<sup>-3</sup> Fe(II)EDTA, and 2.1 V.

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