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Simultaneous Removing SO_2 and NO by Ammonia-Fe^{II} EDTA Solution Coupled with Iron Regeneration

Han, J., Yao, X., Qin, L.B., Jiang, M., Xing, F. T. and Chen, W. S.*

College of Resource and Environment Engineering, Wuhan University of Science and
Technology, Wuhan 430081, China

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ABSTRACT: In this paper, the simultaneous absorption of SO_2 and NO from the simulated sintering flue gas by ammonia-Fe^{II}EDTA complex solution was investigated in a pilot scale reactor. The experiment results showed that the maximum removal efficiencies of SO_2 and NOx by ammonia-Fe^{II}EDTA complex solution scrubbing were 99% and 68.26%, respectively. However, the denitiration efficiency was gradually declined due to the oxidation of Fe^{II}EDTA into Fe^{III}EDTA. At the same time, Fe^{III}EDTA did not have the ability of binding NO. In order to keep the high denitration efficiency, Fe^{III}EDTA regeneration by iron and the surplus iron ion removal by the precipitation were proposed. Moreover, the optimum parameters of the surplus iron ion removal were also investigated, the experimental results showed that the optimum addition of ammonia carbonate was 0.4 g/L. After the regeneration and precipitation, the denitration efficiency by ammonia-Fe^{II}EDTA complex solution could be kept at 55%, and the desulfurization efficiency in the test was above 99%.

Key words: Desulfurization, Denitration, Ferrous chelate, Reduction, Iron

INTRODUCTION

SO_2 and NO_X are the main causes of acid rain, urban smog and respiratory disease, which mainly come from fossil fuel combustion such as coal fired power plants, iron and steel plants, vehicle(Xu et al., 2015). In 2015, about 246,000 tons of SO_2 and 972,000 tons of NO_X were emitted from the Iron & Steel industry in China (National Bureau of Statistics of China, 2015). In addition, it was reported that 90% SO_2 and 48% NO_X emitted by the Iron & Steel plants came from the sintering process (Han et al., 2014; Fan et al., 2015; Chen et al., 2015a). In order to improve air quality, China had issued a more stringent emission standard, which required that NOx concentration in the emitted sintering flue gas must be below 300 mg/Nm^3 since 2015. However, the currently NO_X concentration of the sintering flue gas in the most of Iron & Steel plants is about 180-400 mg/Nm^3 (Fan et al., 2015).

At present, the selective catalytic reduction (SCR) has been widely applied to remove NOx from the flue gas in the coal fired power plants (Yang et al., 2016; Sekhavatjou et al., 2011; Karbassi et al., 2008). However, the temperature of the sintering flue gas is about 120-180 ^oC, which is lower than the temperature windows of the commercial catalysts (Wang and Zhong, 2016). Hence, SCR has not been successfully applied in Iron & Steel plants. Ferrous chelates have the ability of absorbing NO because NO selectively binds to the Fe centre, as Eq.1-2.

$$NO(g) \leftrightarrow NO(aq) \tag{1}$$

$$NO(aq) + Fe^{II}EDTA \leftrightarrow Fe^{II}EDTA(NO) \tag{2}$$

Hence, the solubility limitation of NO can be improved by adding Ferrous chelate, which increases the reaction time of NO and the reducing agent, and NOx removal efficiency can be promoted. Compared to SCR, NOx adsorption and reduction by the metal chelating agents solution such as Fe^{II}EDTA (Ferrous ethylene diamine tetra acetic acid), FeNTA (Ferrous nitrilotriacetic acid) and FeDTPA(Ferrous diethylene triamine pentaacetic acid) is an alternative, environmental and effective technology (Pham and Chang, 1994; Li et al., 2016a, Zhou et al., 2012; Chandrashekhar et al., 2013; He et al., 2016; Li et al., 2016b). Chen et al. reported a maximum NO removal efficiency of 96.5% was achieved when Fe^{II}EDTA was used as the scrubbing solution(Chen et al., 2013). However, Fe^{II}EDTA is easily oxidized to Fe^{III}EDTA by O_2 in the sintering flue gas (O_2 concentration in the sintering flue gas is about 15-18%), as Eq.3.

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*Corresponding author E-mail: chenwangsheng@wust.edu.cn

$$4Fe^{II}EDTA^{2-} + O_2 + 4H^+ \rightarrow 4Fe^{III}EDTA^- + 2H_2O \tag{3}$$

At the same time, Fe^{II}EDTA is not capable of binding NO. As a result, the denitration efficiency by the Fe$^{a!}$EDTA solution scrubbing decrease with the reaction time (Mi et al., 2009). Many attempts have been made to reduce Fe$^{\Pi}$EDTA to Fe EDTA by $Na_2S_2O_8$(Adewuyi and Khan, 2015), bio-reduction(Xia et al., 2013; Chen et al., 2015b), activated carbon(Yang et al., 2013) and iron(Ma et al., 2004). Fe^{II}EDTA reduction by $Na_2S_2O_8$ and activated carbon were not widely applied due to their high operation cost, and the main challenge of biological reduction was the low reduction rate.

At present, ammonia was widely used to remove SO_2 from the sintering flue gas in China. Especially, ammonia method had the ability of removing 20-30% NOx from the flue gas (Resnik et al., 2004; Gao et al., 2010). In this paper, the ammonia-Fe^{II} EDTA solution was investigated to remove SO_2 and NOx in a pilot scale reactor. Fe^{III}EDTA regenerated by iron and the surplus ferric ion removal by the precipitation were proposed to keep the high denitration efficiency.

MATERIALS & METHODS

The denitration and desulfurization reactor was consisted with the gas supply system, absorption system, regeneration system, iron removal system and gas analysis system, as shown in Fig. 1. The simulated flue gas were prepared by SO_2, NO and air. The air was provided by fan, besides SO_2 and NO came from the cylinder bottles. The concentrations of NOx and SO_2 and the flow rate of the simulated gas were controlled by the mass flowmeters. After the blend in a buffer tank, the simulated flue gas was fed to the absorption reactor. The absorption reactor was made of the stainless steel with a height of 2465 mm and a diameter of 200 mm. In the absorption reactor, there was 900 mm height of pall ring filler and three nozzles for spraying solution. The spraying solution was separately provided by pumps and controlled by the flowmeters. In addition, pH of the solution was online recorded by a pH meters and adjusted by adding the ammonia solution.

Before entering the absorption tower, the scrubbing solution was regenerated in a regeneration tower. The regeneration tower was made of PVC with a height of 1600 mm and a diameter of 100 mm, respectively. Iron scrap blended with pall ring with a height of 1000 mm was packed in the tower. In these experiments, the weight of iron scrap was 3.66 kg. In order to keep Fe(III)EDTA regenerated rate, the surplus Ferric ion in the solution must be removed by the precipitation. The solution was firstly fed into a 50 L PVC tank, then ammonium carbonate or sodium carbonate was added to adjust pH at 7.0. After the precipitation, the centrifugal machine was applied to remove $Fe(OH)_3$ and the liquid was recycled. In this experiment, NOx, SO_2 and O_2 concentration at the inlet and outlet of the reactor were recorded by the gas analyzers (PG 250, Horiba Corp, Japan). The repeatability and the linear for CO, CO_2, SO_2, NOx and O_2 are ≤ 1% full scan and ≤ 2% full scan, respectively. The variation of Fe^{II}EDTA concentration was detected at the absorbance of 450 nm by UV/Visible spectrophotometer. Ferrous ion and total iron were determined colorimetrically after filtration (0.22 lm) using a modified 1,10-phenanthroline colorimetric method at 512 nm, which was detailedly described in the previous paper (Dong et al. 2013).

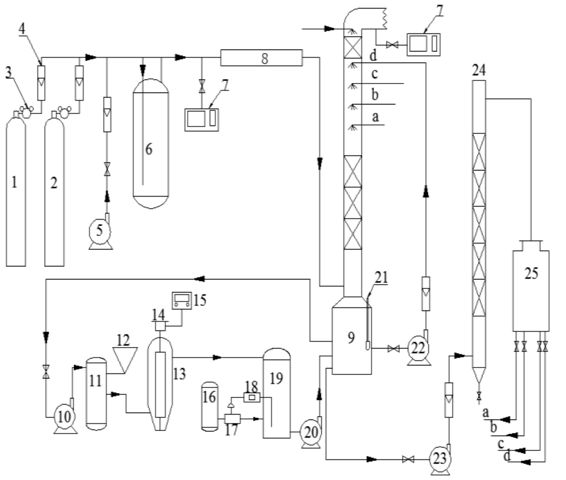

Fig.1. Diagram of the pilot scale reactor of removing SO_2 and NO

1.NO cylinder 2.SO_2 cylinder 3.Valve 4. flowmeter 5.turbine fan 6.Buffer tank 7.gas analyzer 8.heater 9.absorption tower 10.Pump 11.mixing tank 12.feeder 13.centrifuge 14.shaft 15.speed meter 16.sulfuric acid tank 17.sulfuric acid pump 18.pH meter 19.adjusting tank 20.slurry pump 21.pH meter 22.circulating pump 23.regeneration pump 24. regeneration tower 25.buffer slot

In the experimental process, the flow rate of the simulated flue gas was about 40 m^3/h. At the same time, the initial concentration of SO_2, NO and O_2 were 1200, 400 mg/m^3 and 21%, respectively. The flow rate of the scrubbing solution was about 900 L/h. Before the experiment, 150 L scrubbing solution was prepared by Na_2EDTA, $FeSO_4 \cdot 7H_2O$, $(NH_4)_2SO_4$ and ammonia solution, the concentration of Fe^{II} EDTA and $(NH_4)_2SO_4$ were 0.5 and 1.5 mol/L, respectively. pH of the solution in the absorption tower was controlled at 5.2-5.6.

RESULTS & DISCUSSION

Ammonia/ Fe^{II}EDTA desulfurization and denitration: Fig. 2 shows the denitration and desulphurization efficiency as a function of the reaction time. In the startup stage, the desulphurization efficiency was only 95%. As the absorption reaction continuing, the desulphurization efficiency was increased, and reached 99%. The desulphurization reaction can be described by Eq.4-6.

$$SO_2(g) \rightarrow SO_2(aq) \quad (4)$$

$$SO_2 + H_2O + 2NH_3 \rightarrow (NH_4)_2SO_3 \quad (5)$$

$$SO_2 + H_2O + (NH_4)_2SO_3 \rightarrow 2NH_4HSO_4 \quad (6)$$

In the startup stage, there was no $(NH_4)_2SO_3$ in the scrubbing solution, and the desulphurization reaction was depended on Eq. 5. After the solution absorbing SO_2, the concentration of $(NH_4)_2SO_3$ in the solution was increased and Eq. 6 became more important. Wei reported that the reaction rate of Eq. 6 was higher than that of Eq. 5 (Wei, 2008). Especially, $(NH_4)_2SO_3$ has the ability of reducing Fe^{III} to Fe^{II}, as Eq. 7 (Zhu et al., 2013).

$$2Fe^{III} + SO_3^{2-} + H_2O \rightarrow 2Fe^{II} + 2H^+ + SO_4^{2-} \quad (7)$$

Fig. 2 also presents that 60% denitration efficiency can be obtained at the initial stage. However, the denitration efficiency was sharply decreased due to the oxidation of Fe^{II}EDTA. After 55 minutes, the denitration efficiency was decreased to 21%. Ma et al. reported the reaction rate of Eq.3 was 1.09×10^4 exp(-2.33×10^4/RT)(Ma et al., 2004). Thus, most of Fe^{II}EDTA in the scrubbing solution was oxidized to Fe^{II} EDTA. As described above, Fe^{II}EDTA has not the ability of binding NO. Hence, the denitration efficiency was decreased.

Ammonia/ Fe^{II} EDTA desulfurization and denitration with iron regeneration: In order to keep the denitration efficiency, Fe^{II}EDTA in the scrubbing solution must be reduced. In this experiment, the iron scrap with a width of 15 mm and a thickness of 1mm was used as the reducing agent. The total weight of the iron scrap was 3.66 kg. In the regeneration process, the iron scrap would react with Fe^{III}EDTA and form Fe^{II}EDTA, as showed in Eq.8-9.

$$2\,Fe^{III}EDTA + Fe \rightarrow 2Fe^{II}EDTA + Fe^{II} \quad (8)$$

$$2Fe^{II}EDTA(NO) + Fe + 8H^+ \rightarrow 2Fe^{II}EDTA + Fe^{II}(OH)_2 + 2NH_3 \quad (9)$$

In the comparison of Fig. 2 and Fig. 3, it was found that the regeneration by iron had a significant influence on the denitration efficiency. In the case of no regeneration, the denitration efficiency would decrease to 21% at 55 minutes. However, the denitration efficiency would keep above 42% after 100 minutes. Moreover, it was also found that the regeneration had no negative effect on the desulfurization efficiency, and the desulfurization was kept at above 99% in this run.

Fig. 3 also demonstrates that the denitration efficiency is still slightly decreased with the reaction

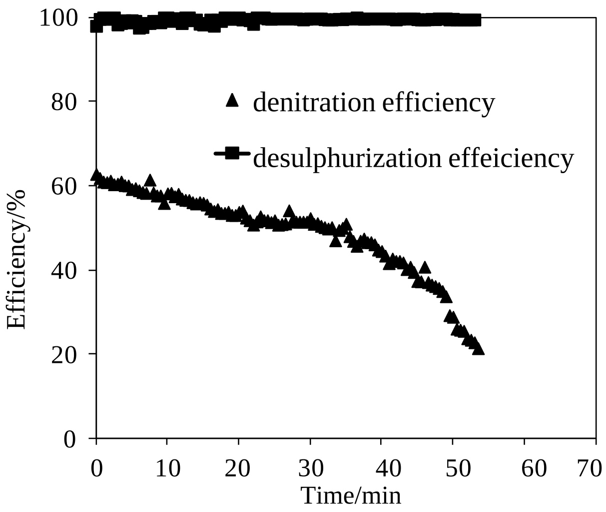

Fig.2. Ammonia/ Fe^{II} EDTA desulfurization and denitration without regeneration

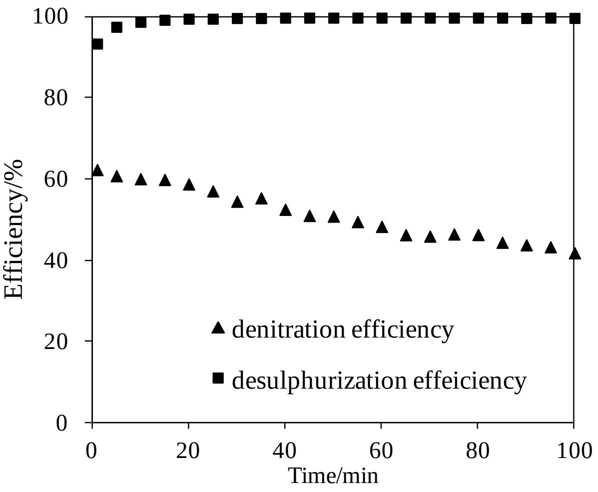

Fig. 3. Ammonia/ Fe^{II} EDTA desulfurization and denitration with regeneration

time. The above phenomenon may be attributed to the reason that Fe^{III} regeneration rate by iron is lower than $Fe^{a!}$ oxidation rate. Eq. 8 shows that a Fe^{III} is reduced into two Fe^{II}, then Fe^{II} is also oxidized by oxygen. Thus, Fe^{III} in the scrubbing solution will increase. Fig. 4 presents the variation of ferric ion in the scrubbing solution. The initial iron ion concentration was 0.05 mol/L, which was increased to 0.058 mol/L after 160 minutes. However, the weight of iron scrap in the regeneration system would decrease due Eq. 8-9, which mean the regeneration rate would decrease. When the regeneration rate was lower than the oxidization rate, the denitration efficiency would decreased.

Ammonia/Fe^{II} EDTA desulfurization and denitration with surplus iron ion and iron regeneration: In order to keep Fe^{II}concentration in the scrubbing solution, the surplus ferric ion must be removed. In this run, 10 L scrubbing solution was fed into a precipitation tank, and 0.3-0.7 g ammonia carbonate was added to adjust pH. After 10 minutes precipitation, the solid ($Fe(OH)_3$) was separated from the liquid phase by the centrifugal machine, then pH of the liquid was adjusted to 5.2-5.6 by adding sulfur acid and fed into the absorption reactor. In order to find the optimum ammonia carbonate/solution ratio, the dependence of the amount of ammonia carbonate on the ferric ion removal efficiency was also investigated, as shown in Fig. 5.

On the basis of the experimental results, it was found that the iron removal efficiency increased with the increase of ammonia carbonate addition. The further increase of ammonia carbonate addition, iron

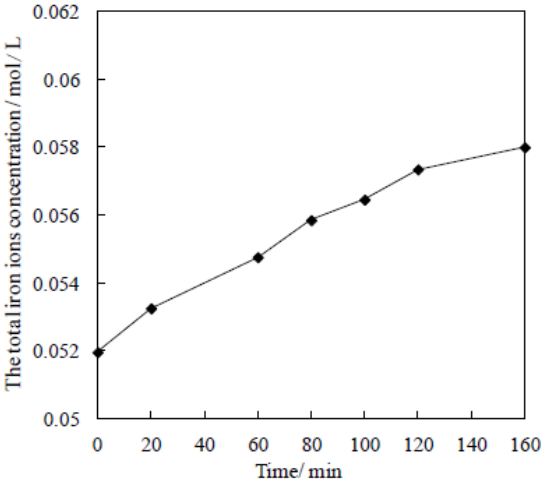

Fig. 4 .Variation of the total iron ion in the scrubbing solution

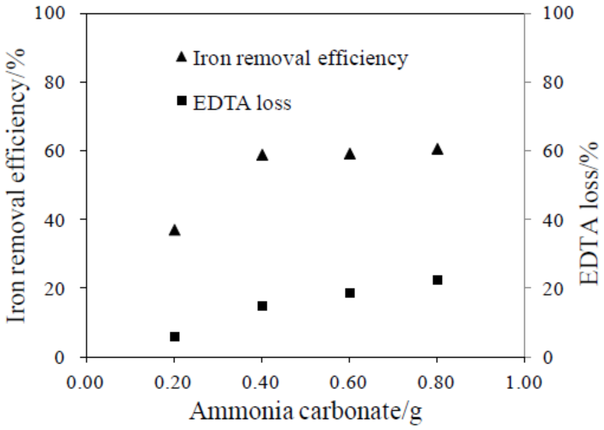

Fig. 5. Effect of the amount of ammonia carbonate on ferric ion removal efficiency

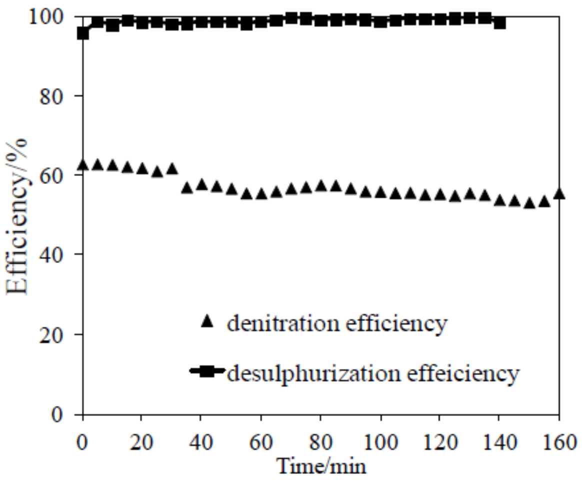

Fig. 6. Ammonia/ Fe^{II} EDTA desulfurization and denitration with regeneration and iron removal

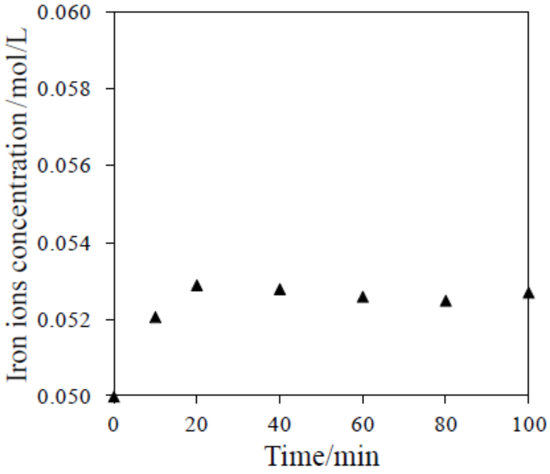

Fig. 7. Variation of the total iron ion in the scrubbing solution after iron regeneration and precipitation

removal efficiency was not significantly improved. At the same time, EDTA was also deposited and lost during the precipitation and centrifugation process. Hence, the optimum addition of ammonia carbonate was 0.4 g/L. When the ammonia carbonated addition was 0.4 g/L, the iron removal efficiency was 58.95%, as shown in Fig. 6. Fig 7 also proves that the precipitation is a feasible method of removing ferric ion, and iron ion concentration in the scrubbing solution was kept at 0.05-0.053 mol/L.

CONCLUSIONS

In this paper, the ammonia-Fe^{II} EDTA complex solution was used to simultaneously remove NO and SO_2 from the sintering flue gas. At the same time, the waste solution was regenerated by iron and surplus iron in the absorption solution was removed by the precipitation. The experiment results in a pilot scale reactor demonstrated 99% desulfurization efficiency and 55% denitation efficiency was obtained. Meanwhile, the regeneration by iron and the surplus iron ion removal by the precipitation were effective on keeping Fe^{II} concentration in the scrubbing solution.

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