Simultaneous Removal of SO₂ and NO by Using Piperazine-urea-triethylene Diamine Ternary System

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Abstract. Performance of simultaneous removal of SO₂ and NO from the simulated thermal power plants gas using piperazine-urea-triethylene diamine ternary system absorbent was investigated in this paper. Furthermore, the influences of the concentration of triethylene diamine, pH value, the absorption temperature and the total inlet flow rate of the simulated gas on simultaneous absorption behavior were discussed by means of the removal efficiency of SO₂ and NO. A better simultaneous desulfurization and denitration behavior could be obtained under the absorption condition of triethylene diamine concentration of 0.3 mol/L, pH value of 6, inlet simulated gas flow rate of 500 ml/min, and the absorption temperature of 40 ºC. Under the above absorption condition, the simultaneous NO removal efficiency of 70.28% and SO₂ removal efficiency of 99.30% could be obtained.

1. Introduction
It is widely known that the emission standards of SO₂ and NOₓ are becoming worse with the development of chemical industrialization in the world[1-3]. In response, more efforts have been put forward to develop new cleaner technologies to reduce the emissions of SO₂ and NOₓ. Various advanced methods have been extensively studied, including non-thermal plasma, catalysis oxidation and advanced wet scrubber technologies[4-5]. Among the above methods, simultaneous desulfurization and denitration by chemical method is regarded as one of the typical process technologies. In order to improve the desulfurization and denitration efficiency, some researchers proposed ammonia, piperazine (PZ), urea, N-(2-hydroxyethyl) piperazine and triethylene diamine (TEDA) can be used as absorbents or additives[6-9]. In this paper, the absorption performance of simultaneous desulfurization and denitration from a thermal power plant simulated flue gas by using PZ-urea-TEDA ternary system was investigated experimentally, and the influences of the absorption condition, such as TEDA concentration, pH value, the absorption temperature and the inlet simulated gas flow rate, were discussed in detail.

2. Experimental
2.1. Materials
Analytical reagent urea was obtained from Hunan Xiangzhong Institute of Geological Experiment, piperazine was provided by Wuhan Organic Industrial Co., Ltd., TEDA was supplied by Beijing Iark Technology Co., Ltd.. SO₂ (99.90%) and NO (99.90%) were obtained from Shanghai Weichuang Standard Gas Analytical Technology Co., Ltd., and N₂ (99.99%) was obtained from Wuhan Iron and Steel Co..
2.2. Simultaneous desulfurization and denitration experiment

Figure 1. Schematic diagram of simultaneous desulfurization and denitration experiment.

Figure 1 showed a schematic diagram of absorption experimental setup. The simulated flue gas was composed of N$_2$, SO$_2$ and NO with the ratio of 300:1:0.5. In every experiment, under atmosphere pressure, 50 ml absorbent solution, which was composed of 3 mol/L urea solution, 0.1 mol/L PZ solution and 0~0.7 mol/L TEDA solution, was taken into an absorption tube filled with glass beads, and then N$_2$-SO$_2$-NO simulated flue gas was introduced via rotameter at the bottom of the absorption tube and reacted with absorbent. After that, the tail gas, which was main N$_2$ and NO and SO$_2$, was led in the bottles filled with KMnO$_4$ solution and NaOH solution in turn. The inlet and outlet gas were collected and analyzed. HJ479-2009 standard naphthylethylenediamine hydrochloride colorimetric method was adopted for the determination of NO, and iodometry method was used for the determination of SO$_2$.

According to the analysis results, the removal efficiency of NO and SO$_2$ were calculated with the following formula:

$$\eta = \frac{c_{in} - c_{out}}{c_{in}} \times 100\%$$

(1)

Where $\eta$ was the NO/SO$_2$ removal efficiency, $c_{in}$ and $c_{out}$ were the inlet and outlet of NO/SO$_2$ concentrations, mg/m$^3$.

3. Results and discussion

3.1. Absorption mechanism of desulfurization and denitration

It is well known that the mechanism of the simultaneous desulfurization and denitration by using urea is that urea reacts with NO and SO$_2$ at the same moments represented as Equations (2)-(3)[10], while the mechanism for diamine, such as PZ and TEDA, is that diamine complexes with H$_2$SO$_3$ to form HSO$_3^-$ firstly and then an increment of the concentration of SO$_3^{2-}$ can be obtained shown as Equations (4)-(7), which leads to a promotion of the removal efficiency of NO[11].

$$\text{SO}_2 + \text{CO(NH}_2)_2 + \frac{1}{2} \text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow (\text{NH}_4)_2\text{SO}_4 + \text{CO}_2$$  (2)

$$6\text{NO} + 2\text{CO(NH}_2)_2 \leftrightarrow 5\text{N}_2 + 2\text{CO}_2 + 4\text{H}_2\text{O}$$  (3)

$$\text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_3$$  (4)

$$\text{H}_2\text{SO}_3 + \text{R}_1\text{NH}^+\text{R}_2\text{NR}_3 \leftrightarrow \text{R}_1\text{NH}^+\text{R}_2\text{NH}^+\text{R}_3 + \text{HSO}_3^-$$  (5)

$$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$$  (6)

$$2\text{SO}_3^{2-} + 2\text{NO} \leftrightarrow 2\text{SO}_4^{2-} + \text{N}_2$$  (7)

3.2. Effect of TEDA concentration on simultaneous absorption performance

Under the absorption condition of inlet simulated gas flow rate of 500 ml/min, absorption temperature of 40 °C, pH value of 6, the experimental results of simultaneous removal SO$_2$ and NO by using PZ-
urea-TEDA ternary system was shown in Figure 2.

In Figure 2, compared with the experimental result by using PZ-urea binary system, the simultaneous removal efficiency of SO\textsubscript{2} and NO was increased by adding TEDA in PZ-urea binary system absorbent. Compared with the molecular structures of PZ and urea, the steric-hinerance effect in the molecular structure of TEDA can have an enhanced alkaline property and H\textsuperscript{+} have strong bombing ability\cite{11}, which can provide a higher removal efficiency of SO\textsubscript{2} and NO. As a result, PZ-urea-TEDA ternary system can give a better absorption of simultaneous removal efficiency of SO\textsubscript{2} and NO than that of PZ-urea binary system.

In addition, with increasing concentration of TEDA, the removal efficiency of SO\textsubscript{2} increased firstly and then maintained a constant value of about 99.30\%, and the removal efficiency of NO increased firstly and then decreased. Furthermore, a higher removal efficiency of SO\textsubscript{2} and NO could be obtained at TEDA concentration of 0.3 mol/L. When the concentration of TEDA was less than 0.3mol/L, due to the steric-hinerance effect in the structure of TEDA, the addition of TEDA was beneficial to the removal of SO\textsubscript{2} and NO. After that, on the one hand, there was a competition between the formation of HSO\textsubscript{3}\textsuperscript{-} and the reaction of SO\textsubscript{3}\textsuperscript{2-} and NO, on the other hand, a lower solubility of NO could be caused by a higher viscosity absorbent solution with a higher concentration of TEDA. As a consequence, the removal efficiency of NO was decreased while the removal efficiency of SO\textsubscript{2} was also kept in a constant value.

3.3. Effect of pH value on simultaneous absorption performance

Figure 3 showed the experimental result of simultaneous desulfurization and denitration in PZ-urea-TEDA ternary system under the condition of the inlet simulated gas flow rate of 500 ml/min, the absorption temperature of 40 °C, TEDA concentration of 0.3 mol/L. The solution pH value affects the existence forms and the oxidation potentials of oxidants. In Figure 3, along with increasing of pH value, it could be shown the removal efficiency of SO\textsubscript{2} increased firstly and then maintained a constant value of 99.30\%, and the removal efficiency of NO increased firstly and then decreased. It is because that SO\textsubscript{2} is a kind of acidic gas which is easily absorbed in the alkaline solution, then the removal efficiency of SO\textsubscript{2} was in a higher level. For the absorption of NO, it is a disadvantage factor for urea hydrolysis in the solution with a higher pH value, especially pH value between 7 and 8. Therefore, pH value of about 6 could give a better simultaneous desulfurization and denitration in PZ-urea-TEDA ternary system.

3.4. Effect of absorption temperature on simultaneous absorption performance

The simultaneous desulfurization and denitration in PZ-urea-TEDA ternary system was conducted under the condition of inlet simulated gas flow rate of 500 ml/min, the pH value of 6, TEDA concentration of 0.3 mol/L, and the experimental result was shown in Figure 4. In Figure 4, the
removal efficiency of SO2 showed a relatively stable value of 99.30%, while the removal efficiency of NO increased firstly and then decreased along with increasing of the absorption temperature. Due to the existing of diamine, such as PZ and TEDA, SO2 was easy to react with absorbent to a higher removal efficiency of SO2. Therefore, the absorption temperature had little effect on desulfurization behavior. For absorption of NO, along with the increasing of absorption temperature, on one hand, the absorption temperature had a significant influence on the gas solubility, gas-liquid mass transfer, reaction rate and diffusion rate, which was beneficial to the absorption of NO, on the other hand, the solubility of NO in absorbent decreased in a higher absorption temperature. On average, the removal efficiency of NO presented an increasing trend firstly and then a decreasing trend. In terms of comprehensive, absorption temperature of 40 °C was an appropriate value for simultaneous desulfurization and denitration by using the ternary system.

3.5. Effect of inlet simulated gas flow rate on simultaneous absorption performance

The absorption experiment was conducted under the pH value of 6, TEDA concentration of 0.3 mol/L and the absorption temperature of 40 °C, and the results were shown in Figure 5. In Figure 5, the removal efficiency of SO2 and NO showed a downward trend with the increase of inlet simulated gas flow rate. We all know, a higher flow rate of simulated gas means a shorter contact time between the simulated gas and the absorbent solution, which provides a poor state of the mass transfer. Because the solubility of SO2 in solution was higher than that of NO, the removal efficiency of SO2 was more than that of NO when the flow rate of simulated gas was in a higher value. Hence, a appropriate simulated gas flow rate could be in a lower value. However, considering the cost and capacity of industrial production, the simulated gas flow rate of 500 ml/min could give a better simultaneous desulfurization and denitration behavior.

4. Conclusion

The influences of the experimental conditions, such as TEDA concentration, the pH value, the inlet simulated gas flow rate and the absorption temperature, were discussed in detail. The experiment was carried out using absorbent which was composed of urea, PZ and TEDA. According to a relatively very high solubility of SO2 in solution, it was found that the above-mentioned influence factors had slight effect on the removal efficiency of SO2. As for the absorption of NO, the removal efficiency of NO exhibited different results under various experimental conditions. A better simultaneous removal of SO2 and NO performance could be obtained under the pH value of 6, TEDA concentration of 0.3mol/L, total inlet flow rate of simulated gas of 500 mL/min and the absorption temperature of 40 °C. As a result, the simultaneous removal efficiency of SO2 and NO was 99.30% and 70.28%, respectively.
Acknowledgement
This work were financially supported by the Wuhan Science and Technology Project (2015061701011597) and Jianghan University Student Academic Science and Technology Project (NO.2017zd045).

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