Simultaneous Removal of SO_2 and NO_2 by Wet Scrubbing Using Aqueous Limestone Slurry

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Abstract: The simultaneous removal of SO_2/NO_2 by limestone slurry was studied in a gas-liquid bubbling reactor. Experiments were carried out to find the effect of various operating parameters such as inlet concentration of SO_2 and NO_2, reaction temperature, O_2 content in the flue gas and additive on the SO_2 and NO_2 removal efficiencies. SO_2 removal efficiency decreased with inlet NO_2 concentration, reaction temperature and O_2 content in the flue gas. Inlet SO_2 concentration had a favorable effect on NO_2 absorption while reaction temperature and O_2 content in the flue gas had an inhibition effect on it. And additives such as $MgSO_4$ and Na_2SO_4 could promote the removal of SO_2 and NO_2.

Keywords: SO_2/NO_2 simultaneous removal; limestone slurry; reaction temperature; additive

1 INTRODUCTION

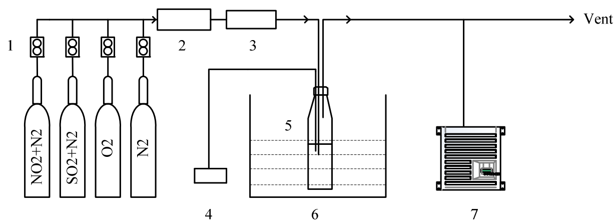
Acid rain is one of the major air pollutants at present, which is mainly caused by SO_2 and NO_x emitted from coal-fired power plants. Conventionally, each pollutant is removed with different air pollution control device at high cost and space requirements. As we all know, wet scrubbing technology is the most widely used process that can remove SO_2 with high efficiency. Makansi [1] indicated that a wet scrubbing combined SO_2/NO_x removal system is one of the best technologies.

Most of the NO_x emitted from coal-fired power plants are NO (more than 95%) and NO_2. NO_2 can be absorbed effectively by some aqueous solutions [2-4], while NO is relatively and can not be removed in this way. So removal of NO from flue gas may be achieved by its oxidation to NO_2 followed by absorption with alkaline solution such as Na_2SO_3, $NaHSO_3$ and Na_2S [5-12]. However, most chemical reagents for NO_2 absorption are effective only at high pH and uneconomic. In this work, we aimed at finding the simultaneous absorption characteristic of SO_2 and NO_2 by limestone slurry, which is the most widely used absorbent in wet flue gas desulfurization system.

2 EXPERIMENTAL

The experimental system can be divided into three parts: a flue gas simulation system, a bubbling reactor and a gas sampling and analyzing system as shown in Fig. 1. The simulated flue gas was prepared by pure N_2, 2000 ppm SO_2 (balanced with N_2) and 2000 ppm NO_2 (balanced with N_2) purchased from New Century Gas Co., China. And their flow rates were controlled by three mass flow controllers (MFC, QixingHuachuang Co., China). After mixed sufficiently in a mixing box, the simulated flue gas was then heated to predetermined temperature before entering into the bubbling reactor. Solution pH was monitored with a Mettler Delta 320 pH meter.

The reactor was a glass-made cylinder with a inner diameter of 50 mm and a height of 170 mm, which was immersed in a water bath to keep the gas phase and liquid phase all at the desired temperature. The absorbent is 0.1% (w/w) limestone slurry and 100 ml is used in one test. The limestone particle diameter varied from 38.5 μm to 43.5 μm. And the chemical components of the limestone were measured and are listed in Table 1.



1. Mass flow controller 2. Mixing box 3.Heating apparatus
4. pH meter 5. Bubbling reactor 6. Water bath
7. Gas analyzing unit

Fig. 1 A schematic diagram of lab-scale bubbling reactor for simultaneous removal of SO_2 and NO_2 from simulated flue gas

The total flow rate of the simulation flue gas was fixed to 1000 ml/min. And the initial gas concentrations used in the test were: SO_2 200 ppm–1000 ppm, NO_2 100 ppm–300 ppm, O_2 0%–10% (v/v). A continuous flue gas analyzer (Rosemount Analytical NGA2000, Emerson Process Management Co. Ltd.) was used to analyze the concentration of SO_2, NO, NO_2 and N_2O.

Table 1 Chemical components of limestone (wt%)

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	Ignition loss
53.90	0.25	2.96	0.44	0.25	41.26

3 CHEMICAL REACTIONS

The simultaneous absorption of SO_2 and NO_2 by limestone slurry is a very complex process. During this process of SO_2 absorption, the following reversible parallel reactions may take place:

$$CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-} \quad (1)$$

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \quad (2)$$

$$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^- \quad (3)$$

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

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad (5)$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^{2-} \quad (6)$$

When NO_2 is absorbed into the aqueous sulfite solution, the irreversible parallel reactions may occur in the boundary layer and promote the absorption of NO_2 [3,13,14]:

$$2NO_2(aq) + H_2O \rightarrow HNO_2(aq) + NO_3^- + H^+ \quad (7)$$

$$2NO_2(aq) + HSO_3^- + H_2O \rightarrow 2NO_2^- + SO_4^{2-} + 3H^+ \quad (8)$$

$$2NO_2(aq) + 2HSO_3^- \rightarrow 2NO_2^- + S_2O_6^{2-} + 2H^+ \quad (9)$$

$$2NO_2(aq) + 2HSO_3^- \rightarrow 2NO_2^- + HON(SO_3)_2^{2-} + \frac{1}{2}O_2 + H^+ \quad (10)$$

The importance of these reactions on the absorption of NO_2 depends on the concentration of the components, the temperature and the pH value of the solution [15].

4 RESULTS AND DISCUSSION

4.1 Effect of Inlet NO_2 Concentration on SO_2 Removal

Effect of inlet NO_2 concentration on SO_2 removal was investigated at 55 □ and inlet SO_2 concentration of 1000 ppm. Fig. 2 shows the SO_2 removal efficiency at various inlet NO_2 concentrations. It was found that SO_2 removal efficiency decreased when NO_2 concentration was increased from 100 ppm to 300 ppm. The results are just on the contrary to that of Siddiqi et al [15], they found that the increasing of inlet NO_2 concentration was favorable to SO_2 absorption. It may be attributed to the fact that the solution pH value drop caused by the absorption of NO_2 would inhibit the absorption of SO_2 while the absorption of NO_2 could promote it, but the two factors have different influence degree on SO_2 absorption in different test apparatus because of their different hydrodynamic conditions.

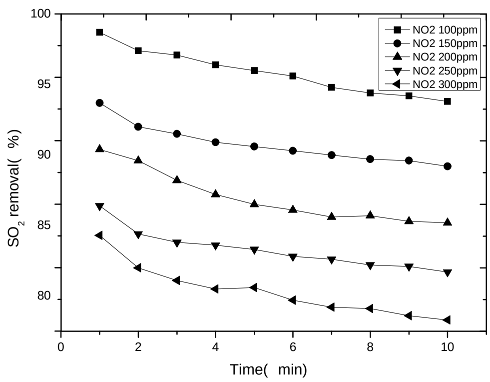


Fig. 2 Effect of inlet NO_2 concentration on SO_2 removal, at 55 □, inlet SO_2 concentration of 1000 ppm

4.2 Effect of Inlet SO_2 Concentration on NO_2 Removal

Experiments were also carried out at 55 □ and inlet NO_2 concentration 200 ppm to investigate the effect of inlet SO_2 concentration on NO_2 removal. As can be seen in Fig. 3, when inlet SO_2 concentration was increased from 200 ppm to 1000 ppm, NO_2 removal efficiency increased from about 33 to about 57%. This is due to the reaction of HSO_3^- and SO_3^{2-} with NO_2 (aq) plays an important role during the absorption of NO_2 [16].

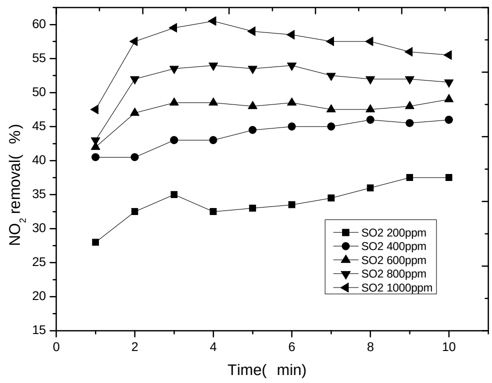


Fig. 3 Effect of inlet SO_2 concentration on NO_2 removal, at 55 □, inlet NO_2 concentration of 200 ppm

4.3 Effect of Temperature on SO_2 and NO_2 Removal

A series of experiments were performed to investigate the effect of reaction temperature on SO_2/NO_2 removal, the inlet SO_2 and NO_2 concentration were 1000 and 200 ppm, respectively. As is shown in Fig.4 and Fig.5, when reaction temperature was increased from 25 □to 55 □, both the removal efficiency of SO_2 and NO_2 decreased about 10%. Such an effect may be attributed to the decreased solubility of SO_2 and NO_2 in the liquid at higher temperature. In addition, lower temperature is favorable to the formation of N_2O_4, the dimer of NO_2, which is of higher solubility than NO_2 at lower temperature [3].As can be seen from Fig.5, at the beginning of the experiment, NO_2 removal efficiency increased, after 2 minutes, it decreased gradually. At the beginning, the absorption of SO_2 increased the concentration of HSO_3^- and SO_3^{2-} in the solution, which is favorable to the absorption of NO_2. With the whole reaction carried through, the pH value of the solution decreased, thus the absorption of NO_2 was inhibited.

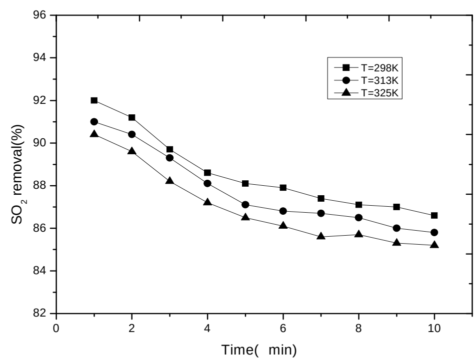


Fig. 4 Effect of Temperature on SO_2 removal, inlet SO_2 and NO_2 concentration of 1000 ppm and 200 ppm, respectively

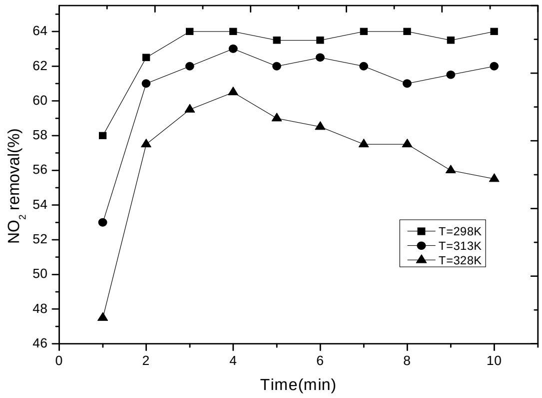


Fig. 5 Effect of temperature on NO_2 removal, inlet SO_2 and NO_2 concentration of 1000 and 200 ppm,respectively

4.4 Effect of O_2 Content on SO_2 and NO_2 Removal

To find the effects of O_2 content in the flue gas on SO_2 and NO_2 removal, some experiments were carried for the simulated flue gas with 5%–10% O_2 and the results are shown in Figs.6 and 7. Fig. 6 indicates that SO_2 removal efficiency increases with increasing O_2 content. This may result from the quick oxidation of HSO_3^- and SO_3^{2-} with higher O_2 content. Fig.7 reveals that NO_2 removal efficiency decreases with increasing O_2 content and the effect is quite significant. Takeuchi et al. [3] also observed that the absorption rate of NO_2 into Na_2SO_3 solution was about 40% lower in air rather than nitrogen. This may due to the quick depletion of sulfite in the gas-liquid mass transfer boundary layer caused by the sulfite oxidation in a chain mechanism, which is initiated by the free radicals produced by NO_2 reaction with SO_3^{2-} and HSO_3^- [3,13,16].

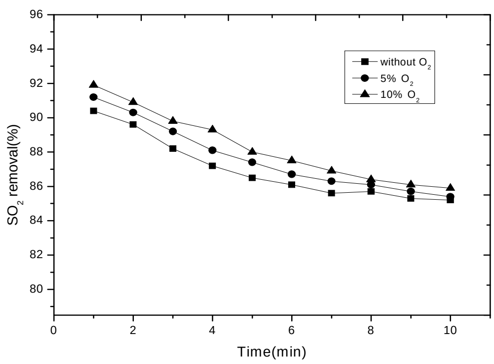


Fig. 6 Effect of O_2 content on SO_2 removal at 55 ℃, inlet SO_2 and NO_2 concentration of 1000 and 200 ppm, respectively

4.5 Effect of Additives on SO_2 and NO_2 Removal

Figs. 8 and 9 show the effect of additives on SO_2 and NO_2 removal. It seems that both $MgSO_4$ and Na_2SO_4 can enhance SO_2 and NO_2 absorption, but $MgSO_4$ is more effective. When $MgSO_4$ is added into the solution, Mg^{2+} and SO_4^{2-} come into being by its ionization. On the one hand, the formation of ion pair $MgSO_3^0$ by Mg^{2+} and SO_3^{2-}, can buffer the pH value of the solution [17], on the other hand, the formation of HSO_4^- by H^+ and SO_4^{2-}, provides an additional means of diffusing acidity to the limestone surface, thus can enhance the dissolution of limestone[18]. They are all favorable to the absorption of SO_2. With the increasing of HSO_3^- and SO_3^{2-} concentration, more NO_2 is absorbed too.

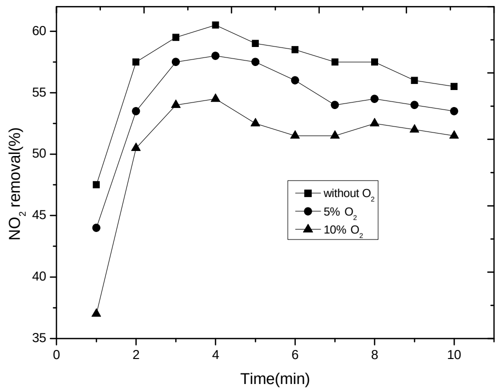


Fig. 7 Effect of O_2 content on NO_2 removal at 55 ℃, inlet SO_2 and NO_2 concentration of 1000 and 200 ppm, respectively

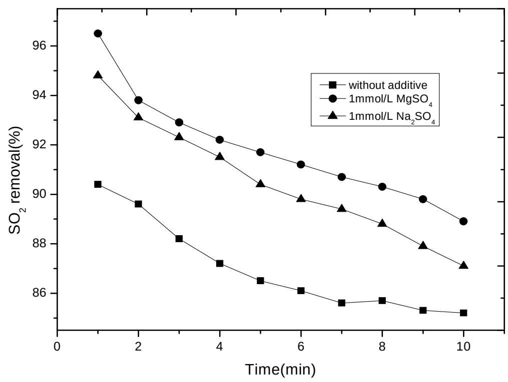


Fig. 8 Effect of additives on SO_2 removal at 55 ℃, inlet SO_2 and NO_2 concentration of 1000 and 200 ppm, respectively

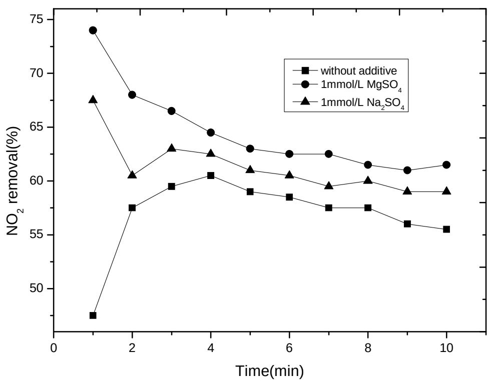


Fig. 9 Effect of additives on NO_2 removal at 55 ℃, inlet SO_2 and NO_2 concentration of 1000 and 200 ppm, respectively

5 CONCLUSIONS

For the combined SO_2/NO_2 removal process in this study, the maximum removal efficiencies of SO_2 and NO_2 vary in the range of 90%–96% and 55%–75%, respectively. These results indicate that simultaneous removal of SO_2 and NO_x with the exiting scrubbers for desulfurization has a good prospect. Further work needs to be done on the kinetics of absorption of lean SO_2 and NO_2 in limestone slurry.

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