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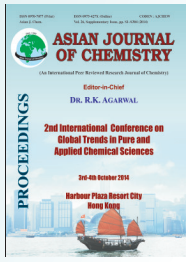

Enhancement Mechanism on Removal of NO in Shipping Desulphurization System Using NaOH Solution

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The NO removal characteristic of sodium-alkali solutions was studied in a counter current packed column in continuous flow mode. The effect mechanism of pH, S(IV), H_2O and UV oxidation was discussed in the paper. When S(IV) did not exist in the absorbent, pH was not effect on removal of NO. When there was S(IV) in the absorbent, the NO removal was high and pH was also effect on NO removal. The essence of reaction was that the high pH value could increase the concentration of S(IV) and the redox reactions of NO were stronger than hydrolysis reactions. The mechanism of UV oxidation on NO removal was also deduced. The active molecules such as O_3 derived from UV-photocatalytic were the main ingredient enhancing the conversion of NO to NO_2 and the oxidation ratio was associated with the oxygen content in exhaust. The presence of H_2O in exhaust could enhance NO removal, but the presence of SO_2 could reduce this enhancement on NO removal. The reaction showed that SO_2 could react with the OH radical and it could reduce the NO oxidation ratio. The experimental results show that the NO_x removal in desulfurization process is available under proper operation conditions and the NO_x removal efficiency can satisfy the stringent emissions regulations of International Maritime Organization.

Keywords: NO_x, SO_2, Sodium-alkali, Removal efficiency, Enhancement mechanism.

INTRODUCTION

Nitrogen oxides and sulfur dioxide emitted from marine diesel engine have a direct negative effect on human health. Generally, sulfur dioxide is absorbed by wet scrubbing technology and nitrogen oxides is always controlled by selective catalytic reduction or selective non-catalytic reduction. Those technologies have the high removal efficiency but can usually only be used for one particular pollutant treatment. Because the exhaust of marine diesel engine contains nitrogen oxides and sulfur dioxide[1]. The simultaneous removal nitrogen oxides and sulfur dioxide technology with low investment and working cost has attracted considerable attention[2]. Some simultaneous removal technologies had been investigated, such NTP and new types of wet scrubbing. For the wet scrubbing technology, oxidants such as chlorine dioxide, sodium chlorite, hydrogen peroxide, ozone and others are used. The key aim is to oxidize NO, which has low solubility in subsequent absorbing processes. Among these oxidants, ozone is promising because its life time is long enough under usual exhaust gas temperature of marine diesel engine.

The simultaneous removal of nitrogen oxides and sulfur dioxide by a two-step process. The ozone lead to the rapid oxidation of NO to NO_2 and subsequent absorption using NaOH achieved the simultaneous removal of nitrogen oxide and sulfur dioxide[3]. A similar two-step process claimed the injection of ozone could simultaneously capture NO and SO_2 in packed device. It indicated that a higher oxidation state of nitrogen oxides was beneficial to the absorption capacity and N_2O_5 has the highest solubility among the common nitrogen oxides[4]. Sulfur dioxide might be oxidized by O_3 to form sulfur trioxide, which is more corrosive than SO_2 to the scrubbing facility[5,6].

This paper focus on investigation of reactions among O_3, NO and SO_2. The effect of pH, S(IV) and SO_2 on NO_2 absorption by wet scrubbing using NaOH solution.

EXPERIMENTAL

Fig. 1 is a schematic diagram of the experimental system including a flue gas simulation system and an absorption reactor and a flue gas analysis system. This is a counter current packed column in continuous flow mode and diesel engine

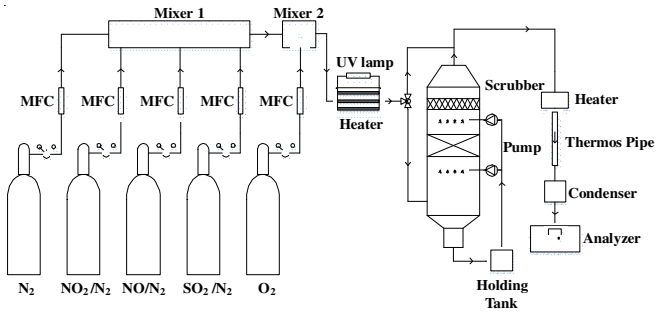

Fig. 1. Schematic chart of experimental equipment

emission gas was simulated (Paiva, 1998). The flow rate was 0.5 L/min. All gases are provided by compressed gas cylinders and metered through mass flow controllers (MSF). There were two mixer pipes. SO_2 and NO are diluted with N_2 in mixer 1, then they mixed with oxygen in mixer 2. That can avoid NO over oxidized to NO_2. NO_2 was only used to enhance the oxidation degree (OD) of NO_x. The temperature of the flue gas after the other equipment emitted from marine diesel engine should be close to 150 °C. The simulated flue gas was heated to the required temperature by heater. Then the simulated flue gas flowed into the scrubber. The cooling spray layer was at the bottom of the packing and it could control the reaction temperature by adjusting the pump. The main spray layer was above the packing and it played a major role on the removal of SO_2 and NO_x. The concentration of SO_2 and NO_x was measured by flue gas analyzer (PG-300, HORIBA, Ltd., Japan). The flue gas analyzing module included heater, thermos pipe, condenser and analyzer. The analyzing temperature of the flue gas should be heated to 180 °C.

The simulated flue gas included N_2 (> 99.99 %), O_2 (> 99.99 %), NO_2/N_2 (2.43 % NO_2, v/v), NO/N_2 (1.98 % NO, v/v), SO_2/N_2 (1.98 % SO_2, v/v) span gas. All of them were the products of the Gas Co., Ltd. Of Tong Da, Harbin, China. Sodium hydroxide was a product of Harbin Chemical Reagent Factory, China (> 98.00 %). Sulfuric acid (96-98 wt.%, Harbin Chemical Reagent Factory, China), sodium sulfite (80.00 wt.%, Ya Xing Chemical Engineering Co., Ltd., China), ammonia sulfite (78.00 wt.%, Ya Xing Chemical Engineering Co., Ltd., China), sodium hyposulfite (99.00 wt. %, Fu chen Chemical Reagent Factory, Tianjin, China), sodium sulfide (98.00 wt.%, Fu chen Chemical Reagent Factory, Tianjin, China) were the analytical grade reagents used in this experiment.

RESULTS AND DISCUSSION

The key step of simultaneous removal of nitrogen oxides and sulfur oxide is to oxidize NO to the soluble NO_x of high state. When the molar weights of O_3 and NO are equal, NO_2 is the main nitrogen oxide. With the injection of NO_2 increasing, NO_3 and N_2O_5 are formed. Compared to sulfur dioxide, the characteristic of soluble NO_x is different. The solubility coefficient of NO_2 is lower than SO_2. NO_2 has the oxidation and can react with the reducing agents of solutions such as SO_3^{2-} and HSO_3^-. The redox reaction can increase the absorption rate. N_2O_5 is the anhydride of nitric acid and can tract with H_2O to form nitric acid rapidly.

When the molar weights of O_3 and NO are equal, NO_2 is the main composition of nitrogen oxides and the dosage of O_3 and the consumption of electricity are less. So the paper studies the removal SO_2 and NO_2 by wet scrubbing using NaOH solution.

Effect of pH on NO_2 absorption: With preparing the absorption liquid with different concentration of hydrogen ions, the liquid contains the inert anion and cation, H^+ and OH^-. Then the effect liquid factor of NO_x absorption is only the pH value. The experimental results are shown in Fig. 2.

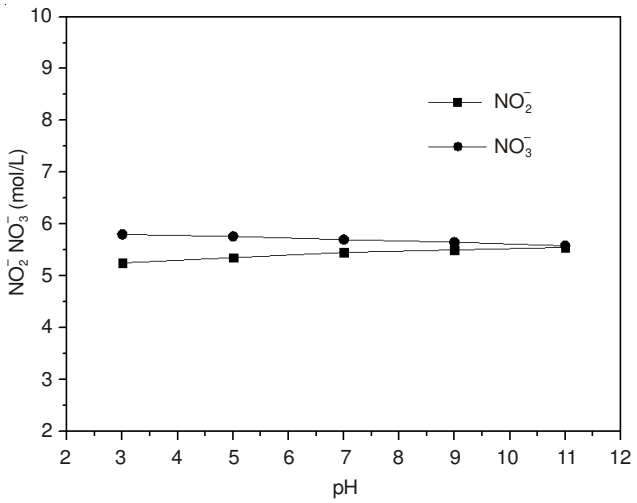

Fig. 2. Concentration of NO_2^- and NO_3^- in different pH value

The detection of NO_x absorption product is show in Fig. 2. The liquid contains NO_2^- and NO_3^-. The mole ratio of NO_2^- and NO_3^- are the same and with pH value rising, the concentrations of them are close. When pH value is lower, the concentration of NO_3^- is higher. This is because the ionization reaction of hydrolysate HNO_2 happens and the rest of HNO_2 react according to the reaction.

Effect of S(IV) on NO_2 absorption: The desulfurization efficiency will be high on condition of alkaline pH value in the desulfurization tower, but the pH value is kept at 6-8 due to saving materials and reducing corrosion. So the effect of pH on NO_2 removal is studied in the presence of S(IV).

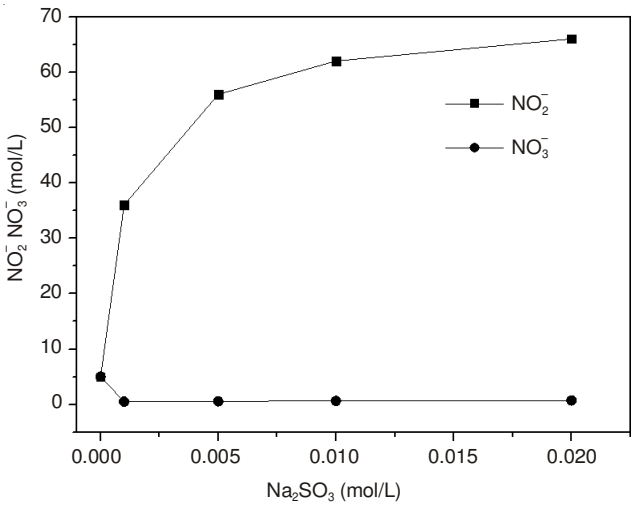

Fig. 3. Concentration of NO_2^- and NO_3^- in different S(IV)

Fig. 3 shows that the hydrolysis reaction is only reaction of NO_2 and the concentrations of NO_2^- and NO_3^- are the same

with S(IV) of 0.0 %. When S(IV) appears, the concentration of NO_2^- increases rapidly and the concentration of NO_3^- is close to 0.0 %.

Remaining the concentration of S(IV) unchanged 0.01 mol/L and adjusting pH value, the results are shown in Fig. 4. With the pH value rising, removal efficiency of NO_2 has a significant increase.

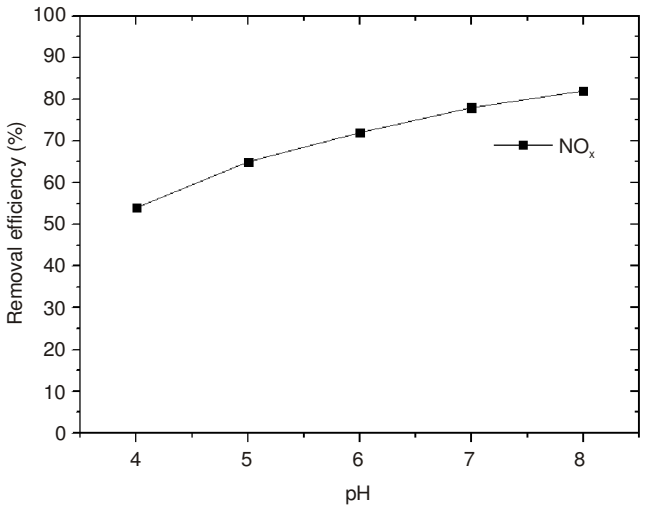

Fig. 4. Effect of pH on removal efficiency of NO_x in the presence of S(IV)

Effect of UV on oxidation of NO: The concentration of O_2 can affect the oxidation of NO. The experimental results is shown in Fig. 5. NO_x contains NO and NO_2 and NO_2 is the standard of NO oxidation.

With the concentration of O_2 increasing, NO oxidation degree becomes higher and the concentration of NO_2 increase. And the concentrations of NO_2 and O_3 are the same. It is said that the oxidants are mainly the O_3 and active oxygen atoms. The experimental results show that the NO_x removal in desulfurization process is available under proper operation conditions

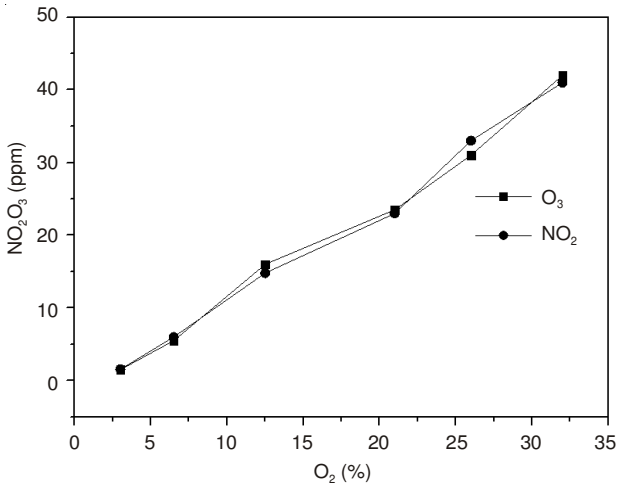

Fig. 5. Effect of O_2 on the concentration of NO_2 and O_3

and the NO_x removal efficiency can satisfy the stringent emissions regulations of International Maritime Organization.

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