Asian Journal of Chemistry; Vol. 26, Supplementary Issue (2014), S27-S30

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.19007

Simultaneous Removal of SO_2 and NO_X by Wet Scrubbing Using NaOH Solutions

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Published online: 24 December 2014; AJC-16432

In this paper, the study on the effect of desulfurization and denitration in a counter current packed column using NaOH solutions was introduced. The desulfurization efficiency was high and the factors of denitration were complex. The factors included NaOH solutions concentration, pH value, sulfur dioxide concentration. The mechanism of desulfurization and denitration using NaOH solutions were deduced. The desulfurization efficiency was about 100 % and the denitration efficiency was lower. In this paper, the better conditions for simultaneous desulfurization and denitration were determined. The experimental results show that the simultaneous desulfurization and denitration are available and the results can meet the increasingly stringent emissions regulations of International Maritime Organization.

Keywords: Desulfurization, Denitration, NaOH, Reaction mechanism.

INTRODUCTION

The main emission pollutants of engines are sulfur dioxide and nitrogen oxide. The marine emission regulations have become more stringent in recent years, which require the shipping industry to remove these emissions to a large extent[1]. Currently, the typical desulfurization technologies are classified into three major types depending on reaction conditions *i.e.*, wet flue gas desulfurization, semi-dry flue gas desulfurization and dry flue gas desulfurization. In order to control nitrogen oxide, SCR technology has quite mature in shipping industry[2]. Due to high reliability and high removal efficiency, those technologies have been commercially put into practice. However, applying those technologies separately to remove sulfur dioxide and nitrogen oxide in one plant will need large areas of ships, complex systems and high capital cost. So it is necessary to find effectively technologies that could remove sulfur dioxide and nitrogen oxide simultaneously with acceptable cost and appropriate areas.

In recent years, the oceanic environment is becoming the focus of attention. The oceanic environment includes sea and atmospheric environment and the oceanic atmospheric pollutants mainly come from ships exhaust emission, as well as SO_x, NO_x and particulate matter[3]. Effects of sulfur oxides on the environment are growing. The International Maritime Organization has formulated strict sulphur emission regulations. And many regions also set sulphur emission control areas. It is time for the reduction of sulphur emissions. In this paper, the sodium hydroxide ship flue gas desulphurization spray tower as research subjects, to contribute to the cause of flue gas desulfurization, to be able to develop better desulfurization equipment, desulfurization method to lay the foundation[4].

There are two basic ways to control marine exhaust SO_2 emission. One is to use low-sulfur oil and the other is exhaust washing desulfurization technology. Given the issues of the low sulphur such as lubrication and cost and emission regulations becoming more stringent, the exhaust desulfurization technology is becoming the focus of attention. The desulfurization efficiency based on sodium-alkali method is high, about up to 98 %[5,6]. But the high cost of this method limits its application on land. At this stage, considering the high cost of low-sulphur fuel for marine diesel engine and diesel retrofit costs and taking all factors into consideration, using natrium-alkali waste gas cleaning system on the ship is feasible. The operating costs can be significantly reduced and investment will be recovered during the 2-5 years[7,8]. The application prospect of ship exhaust gas scrubbing system is wide.

In this paper, the study of absorption theory and technology of desulfurization of denitration with NaOH solution is presented. Compared to nitrogen oxide, sulfur dioxide could be absorbed easily, so the nitrogen oxide absorption was more focused on by using sodium-alkali solutions[9]. Some process parameters were investigated to determine the effect of those variables on NO_x removal efficiency. The optimal conditions for simultaneous removal of SO_2 and NO_x were determined[10,11]. Meanwhile, the reaction mechanism for synergistic effect and simultaneous removal of SO_2 and NO_x based on sodium-alkali method were deduced.

EXPERIMENTAL

The desulfurization device is a king of packed tower, which is widely used in land-based power plant and other chemical industries. The device mainly includes demister, main spraying, cooling spraying, packing layer and other auxiliary devices. The device is showed in Fig. 1. The desulfurization device is a king of packed tower, which is widely used in land-based power plant and other chemical industries. The device mainly includes demister, main spraying, cooling spraying, packing layer and other auxiliary devices. The device is showed in Fig. 1.

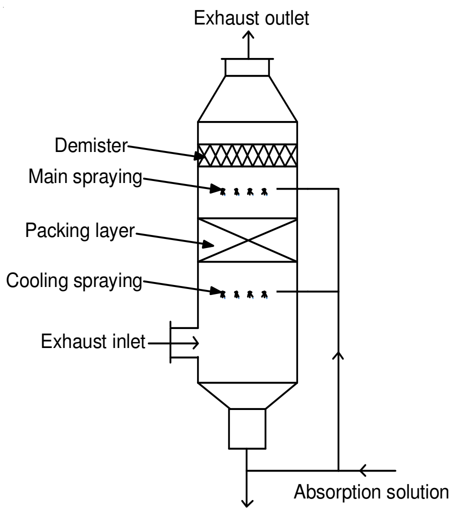

Fig. 1. Schematic chart of experimental equipment for SO_2/NO_x simultaneous removal

RESULTS AND DISCUSSION

Effect of NaOH concentration on the desulfurization efficiency: Fig. 2 is the effect of NaOH concentration on the desulfurization efficiency. SO_x was easily soluble in solutions

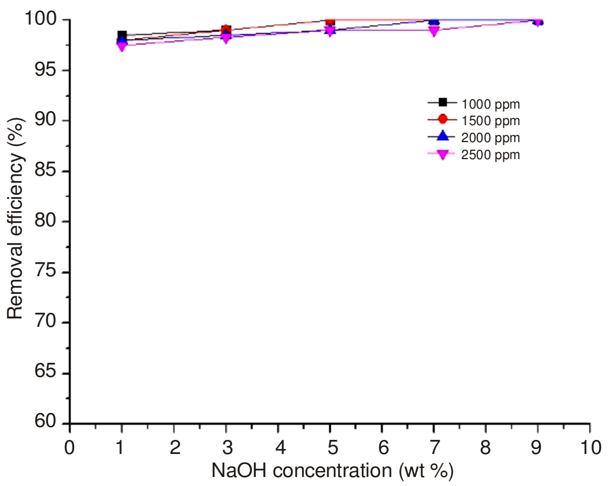

Fig. 2. Effect of NaOH concentration on SO_2 removal efficiency: flow rate = 1 L/min, flue gas temperature = 40 °C, O_2 = 14 % and pH = 7

and the Fig. 2 shows the similar results that the NaOH solution absorbs sulfur dioxide quite efficiently. The concentration of NaOH varies from 1-10 wt. % and the desulfurization efficiency is hardly affected by the concentration NaOH solutions.

All the desulfurization efficiency are up to almost 100 %. So desulfurization with NaOH solutions is efficient. Nitric oxide is difficult to be removed compared to sulfur dioxide. So the denitration efficiency in NaOH solutions was the key point.

Effect of NaOH concentration on removal efficiency of NO_x: Fig. 3 is the effect of NaOH concentration on the denitration efficiency. It can be seen from Fig. 3 that the NO_x removal efficiency kept almost 50 % and the solubility of nitrogen dioxide is higher than nitric oxide in NaOH solution. The denitration efficiency is up to 80-90 %. At NaOH concentration rising, the removal efficiency of nitric oxide is hardly changed and removal efficiency of nitrogen dioxide has a certain degree of reduction, thereby denitrationl efficiency is slightly down, standing at 60-70 %. When the concentration of NaOH is up to 5 %, the mass transfer resistance will rise due to the viscosity of solutions rising.

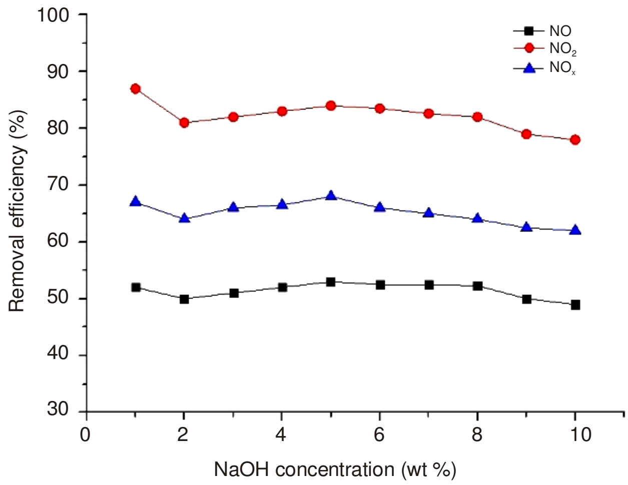

Fig. 3. Effect of NaOH concentration on NO_x removal efficiency: flow rate = 1 L/min, flue gas temperature = 40 °C, oxidation degree = 40 %, C_{NOx} = 1000 ppm and pH = 7

Effect of pH on the removal efficiency of NO_x : Fig. 4 is the effect of pH on the denitration efficiency. The pH of the absorption solution was adjusted to the required value by adding sulfuric acid. The pH varies from 3-11. It can be seen from Fig. 4 that the higher denitration efficiency is achieved at pH = 5-9, the denitration efficiency varies from 80 to 85 %. When the pH drops from 5 to 3, a sharp decreace happens. The reason is that when the acidic conditions are strong, it can make nitrous acid to decompose puickly and inhibit the absorption of nitrogen oxide. When the pH is higher, greater than 9, the denitration efficiency is hardly affected by the pH value.

Effect of SO_2 concentration on denitration efficiency: Fig. 5 showed that the desulfurization efficiency is about 100 % with the change of sulfur dioxide concentration and the result is the same to the study. The denitration efficiency has a trend of increasing when the sulfur dioxide concentration is lower

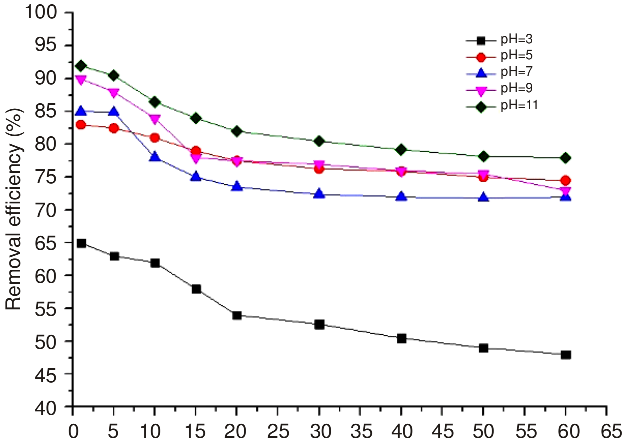

Fig. 4. Effect of pH on NO_x removal efficiency: flow rate = 1 L/min, flue gas temperature = 40 °C, C_{NaOH} = 5 wt. %, oxidation degree = 40 % and C_{NOx} = 1000 ppm

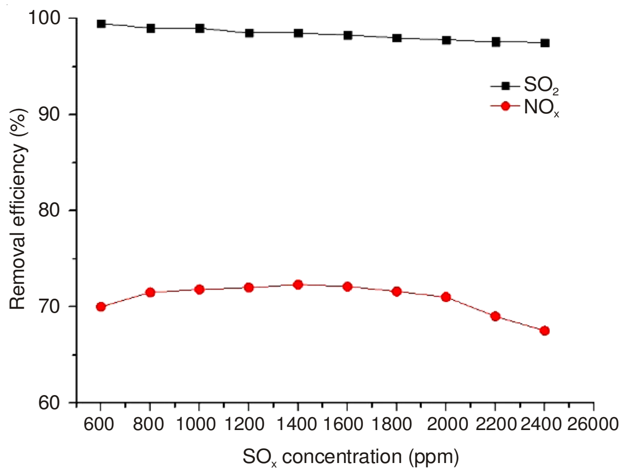

Fig. 5. Effect of SO_2 concentration on NO_x removal efficiency: flow rate = 1 L/min, flue gas temperature = 60 °C, C_{NaOH} = 5 wt. %, oxidation degree = 40 %, C_{NOx} = 1000 ppm, pH = 7

than about 800 ppm. Then the denitration efficiency begins to drop with the sulfur dioxide concentration increasing. In the process of desulfurization, the nitric oxide oxidation can be promoted. When the concentration of sulfur dioxide is high, the pH will be low and the strong acidic condition could inhibit the absorption of nitrogen oxide. The concentration of sulfur dioxide in maring diesel engine is about 500 ppm, so NO_x removal efficiancy can be promoted when sulfur dioxide and nitrogen oxide simultaneously being removed with NaOH solutions.

Better experimental conditions and results: Fig. 6 is desulfurization and denitration efficiencies by using 5 wt. % NaOH solutions. The concentration of sulfur dioxide and nitrogen oxide was 500 and 1000 ppm. Then that the desulfurization efficiency is about 100 % and the denitration efficiency is about 90 %.

Reaction mechanism

Reaction mechanism for absorption of NO_x: The mechanism for absorption of nitrogen oxide is complex compared to the desulfurization process. Fig. 7 is the reaction mechanism for absorption of nitrogen oxide in NaOH solution.

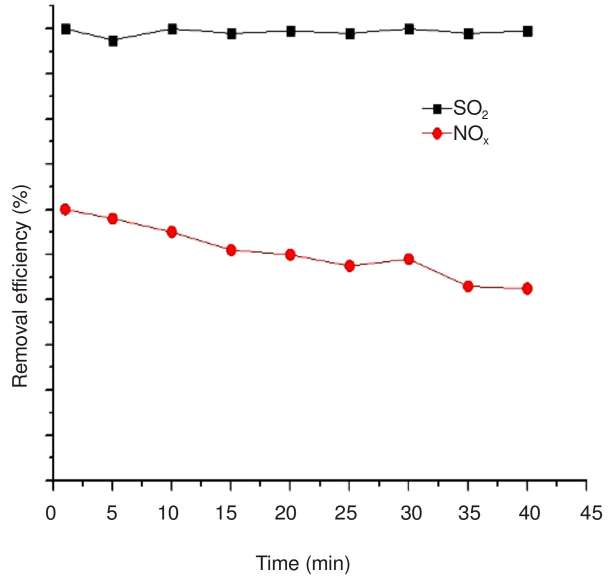

Fig. 6. Simultaneous absorption of SO_2 and NO_x: flow rate = 1 L/min, flue gas temperature = 60 °C, C_{NaOH} = 5 wt. %, 1, oxidation degree = 60 %, C_{NOx} = 1000 ppm and pH = 7

Gas	Liquid
$2NO + O_2 \rightarrow 2NO_2$	$2NO + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$
$2NO_2 \rightleftharpoons N_2O_4$	$N_2O_4 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$
$NO + NO_2 \rightleftharpoons N_2O_3$	$N_2O_3 + 2NaOH \rightarrow 2NaNO_2 + H_2O$
$NO + NO_2 + H_2O \rightleftharpoons 2HNO_2$	$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O$
$2NO_2 + H_2O \rightleftharpoons HNO_3 + HNO_2$	$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

Gas Interface Liquid

Fig. 7. Mechanism for absorption of NO_x in NaOH solution

The main nitrogen oxides forms in the process are NO, NO_2, N_2O_3, N_2O_4, HNO_2 and HNO_3. Nitric oxide is almost insoluble in water, thereby the necessary first step is the oxidation of nitric oxide to nitrogen dioxide or reaction with nitrogen dioxide. Nitrogen dioxide could react with nitric oxide to form dinitrogen trioxide based on gas-phase equilibria and also enhance nitric oxide to react with hydroxide radical in the liquid film. dinitrogen tetrioxide is also the production in the gas phase.

In the liquid phase dinitrogen trioxide and dinitrogen tetraoxide could quickly react with NaOH to form $NaNO_2$ and $NaNO_3$. The gas phase HNO_2 and HNO_3 could also rapidly dissolve in the solution and react with NaOH. Then nitric oxide can react with NaOH to form $NaNO_2$ and $NaNO_3$ under the effcet of nitrogen dioxide.

Conclusions

Through the analysis of the desulfurization device based on sodium-alkali method flow characteristic can be obtained:

(1) Installing packed layer can optimize the overall flow field and prevent the escape of exhaust gas effectively.

(2) The cooling spraying layer can make exhaust gas temperature low, achieving the best absorption temperature. The two layers spraying can improve the desulfurization efficiency.

(3) The desulfurization and denitration device based on sodium-alkali method can effectively remove SO_x and NO_x simultaneously and satisfy the limitation of IMO regulations.

ACKNOWLEDGEMENTS

This study is founded by project of Study on the Key Technology of Ship Exhaust Gas Cleaning Desulfurization Equipment and System Design Based on Sodium-Alkali Method.

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