Study on the removal of NO from flue gas by wet scrubbing using NaClO₃

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Abstract: In order to remove nitric oxide (NO) from flue gas, from small coal-fired boilers, it is necessary to exploit the cost-effective wet denitration technology. The absorption of NO with sodium chlorate solution was studied. The effects of experimental conditions, such as temperature, NaClO₃ concentration, type of acid, mole ratio of NaClO₃ to hydrogen ions, on NO removal rate were investigated, and the optimal conditions were established. As the effect of temperature on denitrification was related to the type of acid used, the temperature required for sulfuric acid was high, and the temperature required for nitric acid was low. The optimal mole ratio between NaClO₃ and the two types of acids was the same. The reaction products were analyzed by ion chromatography. The reacted solution could be recycled after the removal of sodium chloride. The reaction mechanism and the total chemical reaction equation of NaClO₃ denitration were deduced. The thermodynamic derivations showed that this oxidation reaction could proceed spontaneously and the reaction was very thorough. NaClO₃ exhibited high NO removal efficiency and its denitration cost was much lower than sodium chlorite.

Keywords: nitrogen oxides; oxidation; absorption; NaClO₃; denitration.

INTRODUCTION

Air pollution caused by the burning of fossil fuels is increasingly serious, and the NOₓ emitted by the fuels can lead to atmospheric ozone depletion, acid rain⁹¹ and visibility problems, through a series of complex reactions with water and oxygen.³

Denitrification methods such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) have been extensively studied proved to be a great success in large power plants. However, due to the high cost of SCR and the low efficiency of SNCR, industrial denitrification process⁴ is still immature in

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1183
the practical application of small coal-fired boilers.\textsuperscript{5,6} In addition, the ammonia denitration efficiency is low due to the large temperature difference of flue gas from small boilers. These technologies can not be applied to the treatment of dusty flue gases in steel, ceramics and cement plants. A large amount of dust in the flue gas can easily block the catalyst channel and cause catalyst poisoning. The development of efficient denitration technology is of great significance to environmental protection in various countries.

The wet denitration technology is less affected by temperature in removing dust. It requires less investment and is suitable for coal-fired boilers in oil wells and remote areas. Therefore, it is necessary to develop economical and efficient wet denitration technology.\textsuperscript{7–11}

Wet denitration technology is one of the most popular technologies in industrial scale in recent years. The method uses a strong oxidant to oxidize NO to nitrogen dioxide (NO\textsubscript{2}),\textsuperscript{12,13} which can be absorbed by water or alkaline solution. Up to now, a variety of oxidants, such as ClO\textsubscript{2},\textsuperscript{14} K\textsubscript{2}MnO\textsubscript{4}/NaOH,\textsuperscript{15} NaClO\textsubscript{2},\textsuperscript{16–18} NaClO\textsubscript{2}/NaOH,\textsuperscript{19–21} NaClO\textsubscript{2}/(NH\textsubscript{2})\textsubscript{2}CO,\textsuperscript{22} H\textsubscript{2}O\textsubscript{2}\textsuperscript{23,24} and water-soluble ferrous-chelating agents,\textsuperscript{25} may be included. Among these oxidants, NaClO\textsubscript{2} showed better oxidation performance and the industrial application test was carried out. However, the treatment cost of the system was too high to be a practical NO\textsubscript{x} control process.

In order to reduce the denitration cost and improve the denitration efficiency, NaClO\textsubscript{3} was used to remove NO\textsubscript{x} from simulated flue gas in this paper. One molecule of NaClO\textsubscript{3} can oxidize more NO than the one of commonly used NaClO\textsubscript{2}, while the price of NaClO\textsubscript{3} is only one third of NaClO\textsubscript{2}. The reacted liquid could be reused after removing NaCl from the solution. Therefore, developing the denitration technology with NaClO\textsubscript{3} has a good prospect for the wet denitration of industrial flue gas. However, there are few basic researches on NaClO\textsubscript{3} denitration technology.

In this research, a new denitration solution made of NaClO\textsubscript{3} was used for the removal of NO in a bubble reactor. Various influencing factors on the removal efficiency of NO were measured, in order to determine the optimal experimental conditions. The reaction mechanism and the total chemical reaction equation for denitration using NaClO\textsubscript{3} were deduced. This method might be applied to an industrial scale denitration process.

\section*{EXPERIMENTAL}

\subsection*{Materials}

The analytical grade reagents used in experiment were H\textsubscript{2}SO\textsubscript{4} (95–98 wt. \%) and HNO\textsubscript{3} (65–68 wt. \%), obtained from Laiyang Chemical Reagent Factory, China. NaClO\textsubscript{3} (purity > 99 wt. \%) was obtained from Tianjin Chemical Reagent Factory, China. Standard gases, N\textsubscript{2} (99 \%) and NO/N\textsubscript{2} (2.02 vol. \% NO) span gas, were obtained from Oxygen Co., Ltd., China. Reverse osmosis water was applied to prepare the solutions.
**Experimental setup**

The experimental system of this research consists of three parts: a flue gas simulation section, a bubble reactor and a nitrogen oxide analyzer. A schematic diagram of the experimental device is shown in Fig. 1.

![Schematic diagram of the experimental setup.](image)

Nitrogen and NO/N$_2$ were obtained from cylinders and metered through mass flow controllers. The total flow of blended gas was kept at 160 mL/min. The simulated flue gas was then introduced into the mixer and NO was diluted to 800 ppm. The absorption experiments were performed in a bubbling reactor. The temperature of the absorbing liquid (solution volume = 500 mL; liquid height = 12 cm) was controlled by a water bath. The solution was stirred magnetically and the simulated flue gas entered the bubbling reactor. The concentration of NO$_x$ was continuously recorded by flue gas analyzer.

In order to protect the flue gas analyzer, the gas coming from the reactor passed through a drying tube containing anhydrous calcium chloride and a scrubber with phosphoric acid.

**Data analysis**

When the simulated flue gas flowed through the aqueous solutions of NaClO$_3$, NO reacted with the oxidant and was removed. The removal efficiency of NO in % was defined as:

$$E_r = 100 \frac{C_{NO_{in}} - C_{NO_{out}}}{C_{NO_{in}}}$$

where $E_r$ is the efficiency of NO removal, $C_{NO_{in}}$ and $C_{NO_{out}}$ represent the inlet and outlet gas concentrations, respectively. The denitration rate was calculated by the integral method.

**RESULTS AND DISCUSSION**

**Contrast study in different systems**

NaClO$_3$ was used to remove NO in a bubble reactor and a series of comparative experiments were carried out under different conditions. The result is shown in Fig. 2. NO removal efficiency was 29.11 % in water, 28.82 % in H$_2$SO$_4$ solution and 29.63 % in HNO$_3$ solution. The removal efficiency of NO was only 29.52 % by NaClO$_3$ solution without the presence of acid, which was just similar to water. However, the removal efficiency of NO achieved 84.40 % by the com-
bination of 0.50 % NaClO₃ and 0.60 mol/L HNO₃. Similarly, the removal efficiency of NO in the mixed solution of NaClO₃ and H₂SO₄ reached 86.17 %. The results showed that NaClO₃ combined with acid significantly promoted the removal of NO.

**Effect of temperature**

The reaction temperature was an important factor affecting the denitration effect. Experiments were carried out under the condition of room temperature to 80 °C. It could be seen from Fig. 3a that the concentration of outlet NOx gradually decreased when the temperature rose from 30 to 80 °C in NaClO₃/H₂SO₄ system. Considering the accelerating evaporation of water with the increase of temperature, the optimal temperature in practical application was chosen to be 80 °C.

However, for NaClO₃/HNO₃ system, the denitration efficiency decreased rapidly from 85.14 to 54.83 % with the temperature from 40 to 80 °C (Fig. 3b), which was contrary to the NaClO₃/H₂SO₄ system. Therefore, 40 °C was selected as the optimal temperature for NaClO₃/HNO₃ system. The optimal temperature
was close to the operating temperature of wet flue gas desulfurization (WFGD), which was very conducive to the joint operation of desulfurization and denitration process.

**Effect of NaClO₃ concentration**

The effect of NaClO₃ concentration on NO absorption efficiency was carried out to ascertain the optimal NaClO₃ concentration and the results were shown in Fig. 4. The removal efficiency of NO in NaClO₃/H₂SO₄ system increased sharply with an increment of NaClO₃ concentration at first, and then grew slowly. When the concentration of NaClO₃ was 0.50 %, the NO removal efficiency reached 83.53 %. This can be explained from two aspects: chemical reaction and physical properties. The chemical reaction can improve the removal efficiency of NO, but the viscosity of denitrification liquid increases with the increment of NaClO₃ concentration, therefore, the liquid diffusion coefficient and solubility of NO decrease.

![Fig. 4. Effect of NaClO₃ concentration on NO removal efficiency: H₂SO₄ concentration, 0.30 mol/L, HNO₃ concentration, 0.60 mol/L.](image)

The effect of NaClO₃ concentration on NO absorption efficiency in NaClO₃/HNO₃ system indicated that NO absorption efficiency increased sharply from 35.48 to 91.65 % with NaClO₃ concentration rising from 0.05 to 0.50 %. But the change was not obvious when NaClO₃ concentration exceeded 0.50 %. So the optimal NaClO₃ concentration was chosen to be 0.50 %.

**Effect of NaClO₃ to H⁺ mole ratio and type of acid**

The influence of NaClO₃ to H⁺ mole ratio on the removal efficiency of NO was studied, and the result was shown in Fig. 5. A significant increment of the NO removal efficiency from 53.30 to about 87.32 % was observed when the mole ratio of NaClO₃ to H⁺ varied from 1:2.13 to 1:8.50. When the mole ratio of NaClO₃ to H⁺ was 1:12.76, the maximum absorption efficiency of NO was about 91.68 %. This indicated that the oxidizing ability of NaClO₃ gradually increased with the increase of acid intensity. With the further increase of molar ratio, the removal efficiency of NO did not change much.
The type of acid was also a factor affecting NO absorption. It could be seen from Fig. 5 that the absorption efficiency of NO by H2SO4 was slightly higher than by HNO3 at the same molar ratio.

**Analysis of products in solution**

In order to deduce the reaction mechanism, the results of ion chromatography (IC) analysis of the products are given in Table I. Nitrites were not found, while the main anions in the absorbent solution were nitrates and chlorides. This indicates that the NOx directly oxidize to nitrates. The Cl\(^-\) comes from the reduced chlorate.

<table>
<thead>
<tr>
<th>Medium</th>
<th>C(_{NO_3^-}) / mg L(^{-1})</th>
<th>C(_{Cl^-}) / mg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>85.03</td>
<td>24.24</td>
</tr>
<tr>
<td>A2</td>
<td>80.12</td>
<td>21.205</td>
</tr>
<tr>
<td>A3</td>
<td>–</td>
<td>24.240</td>
</tr>
<tr>
<td>A4</td>
<td>–</td>
<td>22.066</td>
</tr>
</tbody>
</table>

**Denitration reaction mechanism**

It was worth pointing out that the solution remained clear and transparent rather than yellow-green during the denitration process using NaClO3 solution, indicating that no chlorine dioxide (ClO2) was generated. This was different from the phenomenon of removing NOx from simulated flue gas by acidic NaClO2 solution.28,29 ClO2 is a very harsh gas and even very small amount of ClO2 can be detected. In a mass concentration of 0.025 % NaClO2 and 0.12 % H\(_2\)SO\(_4\) solution, it could be observed clearly that the solution was yellow-green. However, the solution of a mass concentration of 0.40 % NaClO3 and 2.55 % H\(_2\)SO\(_4\) remained colourless, proving that no ClO2 existed. The process involved numerous
chemical reactions. The mechanism of NO absorption by NaClO₃ may be as follows:

\[
\begin{align*}
\text{NaClO}_3 + H^+ & \leftrightarrow \text{Na}^+ + \text{HClO}_3 \quad \text{(2)} \\
13\text{NO} + 6\text{HClO}_3 + 5\text{H}_2\text{O} & \rightarrow 6\text{HCl} + 3\text{NO}_2 + 10\text{HNO}_3 \quad \text{(3)} \\
3\text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{NO} \quad \text{(4)} \\
2\text{NO} + \text{H}_2\text{O} + \text{HClO}_3 & \rightarrow \text{HCl} + 2\text{HNO}_3 \quad \text{(5)} \\
2\text{NO} + \text{H}_2\text{O} + \text{NaClO}_3 + \text{H}^+ & \rightarrow \text{Na}^+ + \text{HCl} + 2\text{HNO}_3 \quad \text{(6)} \\
\text{NaClO}_3 + 2\text{NO} + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{NaCl} \quad \text{(7)}
\end{align*}
\]

The reported denitration mechanism with NaClO₂ is shown in Eqs. (8)–(12), in which ClO₂ is produced in the reaction process, which possesses a potential hazard for the actual use:

\[
\begin{align*}
8\text{NaClO}_2 + 8\text{H}^+ & \rightarrow 6\text{ClO}_2 + \text{Cl}_2 + 4\text{H}_2\text{O} + 8\text{Na} \quad \text{(8)} \\
5\text{NO} + 2\text{ClO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HCl} + 5\text{NO}_2 \quad \text{(9)} \\
5\text{NO} + \text{ClO}_2 + 3\text{H}_2\text{O} & \rightarrow \text{HCl} + 5\text{HNO}_3 \quad \text{(10)} \\
5\text{NO} + 3\text{ClO}_2 + 4\text{H}_2\text{O} & \rightarrow 3\text{HCl} + 5\text{HNO}_3 \quad \text{(11)} \\
3\text{NaClO}_2 + 4\text{NO} + 2\text{H}_2\text{O} & \rightarrow 4\text{HNO}_3 + 3\text{NaCl} \quad \text{(12)}
\end{align*}
\]

Reacting 1.00 kg of NO requires 2.26 kg NaClO₂, but only 1.77 kg NaClO₃ calculated with Eqs. (7) and (12). In addition, the price of NaClO₃ is one third of NaClO₂. In other words, the cost of NaClO₃ process is about a quarter of the current cost of NaClO₂ wet denitration technology. Due to the high rate of denitration and low cost, the denitration technology with NaClO₃ has a good industrial application prospect for the wet denitration of industrial flue gas.

**Chemical thermodynamics**

The thermodynamic data of chemical reactions are important for assessing the extent of the reaction (Eq. (7)). Data calculations of the thermodynamic parameters were conducted and the enthalpy change of reaction (\(\Delta_r H_m(T)\)), Gibbs energy change of reaction (\(\Delta_r G_m(T)\)) and chemical reaction equilibrium constant (\(K^{\ominus}\)) of Eq. (7) were obtained. The thermodynamic data of related substances in this research were given in Table II.³⁰

**TABLE II.** Standard formation enthalpy, standard formation Gibbs function, standard entropy and calorific capacity

<table>
<thead>
<tr>
<th>Substance</th>
<th>(\Delta_r H_m^{\ominus} / \text{kJ mol}^{-1})</th>
<th>(\Delta_r G_m^{\ominus} / \text{kJ mol}^{-1})</th>
<th>(S_m^{\ominus} / \text{J mol}^{-1} \text{K}^{-1})</th>
<th>(C_p^{\ominus} / \text{J mol}^{-1} \text{K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ (aq)</td>
<td>−207.36</td>
<td>−111.34</td>
<td>146.4</td>
<td>−86.6</td>
</tr>
<tr>
<td>NaClO₃ (aq)</td>
<td>−344.09</td>
<td>−269.91</td>
<td>221.3</td>
<td>111.3</td>
</tr>
<tr>
<td>NaCl (aq)</td>
<td>−407.27</td>
<td>−393.17</td>
<td>115.5</td>
<td>−90.0</td>
</tr>
<tr>
<td>NO (g)</td>
<td>91.29</td>
<td>87.60</td>
<td>210.76</td>
<td>29.85</td>
</tr>
<tr>
<td>H₂O (l)</td>
<td>−285.83</td>
<td>−237.14</td>
<td>69.95</td>
<td>75.35</td>
</tr>
</tbody>
</table>
\[ \Delta r H_m(T) \] at different temperatures have been calculated based on the Eqs. (13) and (14):

\[
\Delta r H_m(T) = \sum \Delta r H_m^G(\text{products}) - \sum \gamma \Delta r H_m^G(\text{reactants}) \tag{13}
\]

\[
\Delta r H_m(T) = \Delta r H_m^G + \int_{289.15}^{T} \Delta r C_{p,m}dT \tag{14}
\]

\[
\Delta r C_{p,m} = \sum \gamma C_{p,m}^G(\text{products}) - \sum \gamma C_{p,m}^G(\text{reactants}) \tag{15}
\]

The results of Eq. (14) were \( \Delta r H_m^G = -374.65 \text{ kJ/mol} \), \( \Delta r H_m (313.15 \text{ K}) = -382.29 \text{ kJ/mol} \) and \( \Delta r H_m (353.15 \text{ K}) = -402.68 \text{ kJ/mol} \).

The results show that \( \Delta r H_m^G \), \( \Delta r H_m (313.15 \text{ K}) \) and \( \Delta r H_m (353.15 \text{ K}) \) values of the chemical reaction are negative, which indicates that the reaction between NO and NaClO3 is exothermic. Therefore, the chemical equilibrium for this reaction is unfavourable at high temperatures from the thermodynamics point of view. However, the reaction rate is generally affected by the temperature, and the reaction rate increases at high temperatures. The effect of temperature on the removal efficiency of NO showed there was an optimal reaction temperature at which NO could be removed quickly. This was the result of a combination of chemical thermodynamics and kinetics. \( \Delta r G_m(T) \) at 298.15, 313.15 and 353.15 K was calculated by Eqs. (16) and (17):

\[
\Delta r G_m^G = \sum \gamma \Delta r G_m^G(\text{products}) - \sum \gamma \Delta r G_m^G(\text{reactants}) \tag{16}
\]

\[
\Delta r G_m(T) = \Delta r G_m^G - T \Delta r S_m^G(T)\tag{17}
\]

\[
= \Delta r H_m^G - T \Delta r S_m^G(T) + \int_{298.15}^{T} \frac{\Delta r C_{p,m}}{T}dT
\]

The results of Eq. (17) were \( \Delta r G_m^G = -284 \text{ kJ/mol} \), \( \Delta r G_m (313.15 \text{ K}) = -279.33 \text{ kJ/mol} \) and \( \Delta r G_m (353.15 \text{ K}) = -267.21 \text{ kJ/mol} \).

The chemical reaction equilibrium constant \( K^{G} \) of Eq. (7) was given as follows:

\[
\Delta G^{G} = -RT \ln K^{G} \tag{18}
\]

The results of Eq. (18) for \( K^{G} \) are \( 10^{49.78} \), \( 10^{56.60} \) and \( 10^{39.52} \).

The results showed that \( \Delta r G_m^G \), \( \Delta r G_m (313.15 \text{ K}) \) and \( \Delta r G_m (353.15 \text{ K}) \) of the chemical reaction were high negative values, compared to \(-40 \text{ kJ/mol}\), and \( K^{G} \) values calculated were far greater than \( 10^{31} \). From these thermodynamic derivations, we can suggest that this oxidation reaction can proceed spontaneously and the reaction is very thorough. In the actual operation, the reason why the denitrification rate did not reach 100% should be that the residence time was short, resulting in insufficient reaction.
CONCLUSIONS

NaClO₃ is a promising absorbent for the removal of NO from flue gas. The denitrification efficiency increased with temperature from 30 to 80 °C in NaClO₃/H₂SO₄ system. However, for NaClO₃/HNO₃ system, the denitrification efficiency decreased with temperature from 40 to 80 °C. The NO removal efficiency increased with NaClO₃ and acid concentrations. The optimal mole ratio of NaClO₃ to H⁺ was 1:12.76. The NO removal efficiency was 91.86 %. The cost of NaClO₃ process was about a quarter of the NaClO₂ wet denitrification technology. The reaction product was NaCl and could be recovered. Therefore, NaClO₃ method may be an alternative way to solving the problem of denitrification of dusty flue gas small boilers produced intermittently.

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