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Wet Removal of Sulfur Dioxide and Nitrogen Oxides from Simulated Flue Gas by $Ca(ClO)_2$ Solution

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To study the simultaneous removal of Sulfur Dioxide (SO_2) and Nitrogen Oxides (NO_x) from simulated flue gas by wet method, a bubbling device containing calcium hypochlorite ($Ca(ClO)_2$) solution was used in the experiments. In the first place, thermodynamic analysis was conducted to determine the depth of reaction process, and the reaction mechanism of desulfurization and denitration was proposed. After that, experimental results exhibited that SO_2 could be removed by $Ca(ClO)_2$ solution completely while the removal efficiency of NO_x was 41.2%. Moreover, on the basis of high SO_2 removal efficiency, the effects of various factors on the removal efficiency of NO_x, such as: the height of liquid layer, $Ca(ClO)_2$ concentration, reaction temperature, initial pH value, O_2 percent, SO_2 concentration, and additives were investigated, respectively. Finally, simultaneous removal of SO_2 and NO_x under the optimized conditions were investigated, SO_2 removal efficiency of 100% and NO_x removal efficiency of 85.9% were achieved. The analysis of reaction products indicated that the main anions in the liquid phase were SO_4^{2-} and NO_3^-. © 2015 American Institute of Chemical Engineers Environ Prog, 34: 1586–1595, 2015

Keywords: desulfurization, denitration, a bubbling device, thermodynamic analysis, additives

INTRODUCTION

Recently, Sulfur Dioxide (SO_2) and Nitrogen Oxides (NO_x) discharged from the flue gas, which are main components of air pollutants, have been received much attention from the government and the public. It is known that the emission of SO_2 and NO_x are primary contributors to acid rain, which is associated with acidification of lakes and streams, corrosion of buildings and monuments. Moreover, they can affect human health by irritating lungs and lowering resistance to respiratory infection (such as influenza) [1]. As the world's largest producer and consumer of coal, China has paid great attention on the emission of SO_2 and NO_x from fossil fuel combustion, while that has promoted the development of technologies to eliminate them.

Techniques for SO_2 removal were more mature than NO_x removal. Wet flue gas desulfurization, which showed high removal efficiency, was widely used in coal-fired boilers and power plants. For NO_x removal, selective catalytic reduction (SCR) [2] is the most popular one. However, the high cost, large area, and potential poisoning of catalysts have made SCR processes less attractive. The cheap catalysts and low-temperature catalytic technology is a growing tendency for further research and utilization of SCR [3]. Recently, many literatures have been published about the research on simultaneous removal of SO_2 and NO_x, the methods contained catalysis [4], photocatalysis [5], electron beam [6], nonthermal plasma [7], and wet method [1,8–10]. Among them, wet scrubbing process has gained much more concern because SO_2 is easily soluble in water and could be removed completely after scrubbing by absorbent. Additionally, it is the most economical method, and has advantages of controlling other soluble gases. Nevertheless, NO, which is the majority of NO_x in the flue gas, is insoluble; therefore, wet method is difficult for denitrification [11]. To date, lots of technologies over wet method have been developed for simultaneous removal of SO_2 and NO_x, which include reduction and oxidation. Removal of SO_2 and NO_x using urea solution was studied by Fang *et al.* [12,13], it showed that urea played the role of reductant in the reaction process and exhibited high removal efficiency after additives were added into the absorbent. Besides, many oxidations have been tested for SO_2 and NO_x removal as well, such as $KMnO_4$, $NaClO_2$, NaClO, and H_2O_2 [1,8,9,14]. Among these oxidants, $KMnO_4$ showed high removal efficiency and stable properties. However, the oxidants were difficult to be widely applied in industry due to their high cost.

Calcium hypochlorite ($Ca(ClO)_2$), which is also called bleaching powder, is a cheap and practical absorbent. As a mature chemical product with steady quality, strong oxidizing ability, and wide source, it has been widely used in waste water treatment [15–17]. However, it was rarely used in flue gas treatment, and the use for simultaneous removal of SO_2 and NO_x was much less. According to the previous investigation, when $Ca(ClO)_2$ dissolves into water, it can react with H_2O as Eq. 1 [18]. The generated HClO played the main role of oxidation during the process of eliminating

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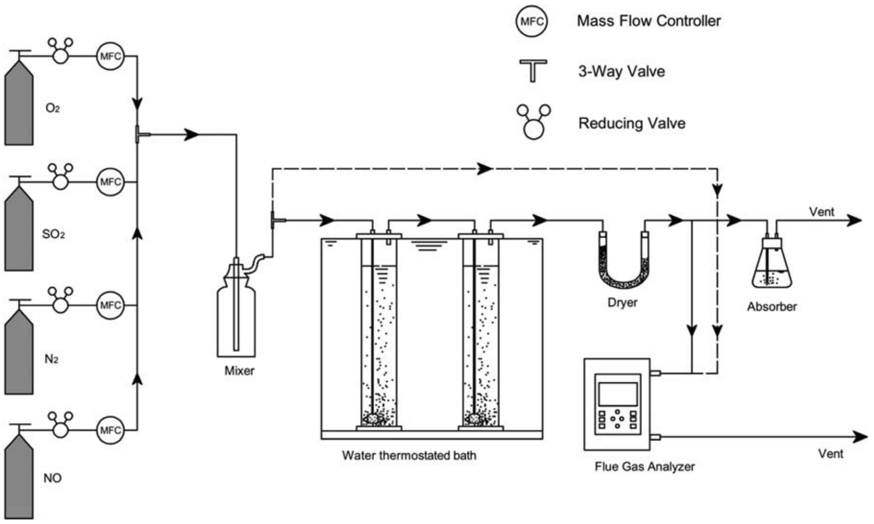

Figure 1. Schematic diagram of the experimental system.

pollutants, which can greatly improve removal efficiency of SO_2 and NO_x.

$$2ClO^- + 2H_2O \rightarrow 2OH^- + 2HClO \tag{1}$$

To improve removal efficiency of NO_x and reduce the cost of simultaneous removal of SO_2 and NO_x, $Ca(ClO)_2$ solution used as absorbent was investigated in this work while the reaction mechanisms of desulfurization and denitration were deduced, and the depth of the reaction was analyzed from thermodynamic measurement. On the basis of high SO_2 removal efficiency, some experiments were performed to explore the effect of different parameters on denitration efficiency in $Ca(ClO)_2$ solution. Finally, experiments about simultaneous removal of SO_2 and NO_x under the optimized conditions were done and the liquid reaction products were analyzed.

EXPERIMENTAL

Experimental Apparatus

Figure 1 showed the schematic diagram of experimental apparatus, it included a flue gas simulation system, an absorption reactor and a flue gas analysis system. A bubbling device with two or three reactors (height of 400 mm and volume of 1000 mL) connected in series was used as the absorption reactor and the gas sparger was made by a sand core (height of 23 mm and radius of 11 mm) with many tiny pores.

Reagents

All the reagents used in this work were analytical pure grade (AR), including: $Ca(ClO)_2$ [28–32% (available chlorine), Tianjin, China], potassium permanganate (99.5%, Changsha, China), sodium chlorite (78%, Yancheng, China), hydrogen peroxide (30.0%, Changsha, China), sodium hydroxide (96.0%, Tianjin, China), sulfuric acid (95.98%, Zhuzhou, China), and anhydrous calcium chloride (96.0%, Tianjin, China).

Experimental Methods

The basic flue gas was made up of N_2 (99.99%), O_2 (99.999%), NO (20.0%NO + 80.0%N_2), and SO_2 (20.4%SO_2 + 79.6%N_2). During the experiment, SO_2, NO, O_2, and N_2 were metered through the mass flow controllers (MFC, Beijing Sevenstar Electronics, China) and mixed in a mixer, in which SO_2 and NO were diluted by N_2 to the desired concentration, and the simulated flue gas was formed. The absorption reactions occurred when simulated flue gas was introduced into bubbling reactor. The concentrations of SO_2 and NO_x (NO and NO_2) in influent (dotted line in Figure 1) and effluent gas (full line in Figure 1) of the absorption processes were measured by flue gas analyser (KANE950, UK) to calculate the removal efficiency of SO_2 and NO_x. After the reactor, a desiccator was used to remove the water vapor in simulated flue gas and protect the flue gas analyzer. Then, the exhaust gas was eliminated by an absorber (0.5 mol L^{-1} $KMnO_4$ solution) before it was emitted into atmosphere.

In addition, the reaction temperature was regulated by digital control thermostat water bath tank (ZKSY-4 type, Gongyi Yuhua Instrument, Henan, China). The initial pH value of solution was adjusted through H_2SO_4 (0.5 mol L^{-1}) and NaOH solution (0.5 mol L^{-1}) and measured by a microcomputer pH meter (HANNA HI8424, Italy).

The removal efficiency of this study was defined as:

$$E_f(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \tag{2}$$

where E_f (%) is the removal efficiency of SO_2 and NO_x, C_{in} (mg m^{-3}), and C_{out} (mg m^{-3}) represent concentration of SO_2 and NO_x in inlet and outlet, respectively.

The experimental error is inevitable. Hence, E_f is the average of three replicates and the error bars in the figures represent the standard deviation from the mean of the series of experiments at each condition.

REACTION MECHANISM

For better understanding the process of simultaneous removal of SO_2 and NO_x using $Ca(ClO)_2$, the reaction mechanism of simultaneous desulfurization and denitration was considered in step by step pattern. In this way, the absorption process could be divided into three parts in sequence: (1) the diffusion of SO_2 and NO_x in gas phase; (2) SO_2 and NO_x transfer from gas to the liquid phase; (3) the diffusion of SO_2 and NO_x in liquid phase. In the absorption process, physical and chemical interactions were involved in every part. While the physical process would be influenced by the total flow rate, residence time, SO_2 concentration, NO concentration, and temperature, the chemical process related to some chemical reactions both in gas and liquid phase.

Desulfurization Reaction Mechanism

When the reaction took place in liquid phase, the main existence forms of sulfur were S(IV) and S(VI) species. The possible existence forms of sulfur species were SO_3, $SO_2{\cdot}H_2O$, HSO_3^-, SO_3^{2-}, HSO_4^-, and SO_4^{2-}, respectively [19]. However, as S(IV) species could be oxidized into S(VI) species by O_2 and HClO, SO_4^{2-} was the main existence form of sulfur in the solution. The mechanism of SO_2 absorption using $Ca(ClO)_2$ solution was shown in Figure 2, and the overall reaction could be written as:

$$\begin{aligned} &Ca^{2+} + 2ClO^- + 2SO_2 + 2H_2O \rightarrow CaSO_4(s) \\ &+ 4H^+ + SO_4{}^{2-} + 2Cl^- \end{aligned} \qquad (3)$$

Denitration Reaction Mechanism

The mechanism of NO_x removal by $Ca(ClO)_2$ solution could be illustrated in Figure 3. Obviously, the absorption process of NO_x in $Ca(ClO)_2$ solution was more complex than that of SO_2. Numerous chemical reactions were involved in the process. Main nitrogen oxides species in liquid and gas phases were considered as NO, NO_2, N_2O_3, N_2O_4, HNO_2, and HNO_3 [20,21]. In addition, in gas phase, the oxidation of NO to NO_2 was a limiting step for the manufacture of HNO_3 because of the very low solubility of NO. Other species such as dinitrogen trioxide (N_2O_3) and dinitrogen tetraoxide (N_2O_4) were produced rapidly. Nitrous acid was also formed in gas phase through some reversible reactions. Furthermore, in the liquid phase, high soluble compounds of N_2O_3 and N_2O_4 dissolved and reacted rapidly with water, then nitrous and nitric acids were produced [22]. So did the less soluble species NO_2. Nitric acid was stable in the liquid phase whereas aqueous nitrous acid could desorb directly or decompose into NO. But when $Ca(ClO)_2$ dissolved into water, HClO was formed in the liquid phase, and then the decomposition of HNO_2 was prevented as it was oxidized to HNO_3. This oxidation obviously improved the overall absorption rate. According to the analysis of the reaction, it could be deduced that NO_3^- was the main existence form of nitrogen in the solution. Thus, combining all equations in Figure 3, the overall reaction could be written as:

$$6ClO^- + 4NO + 2H_2O \rightarrow 4H^+ + 4NO_3{}^- + 6Cl^- \qquad (4)$$

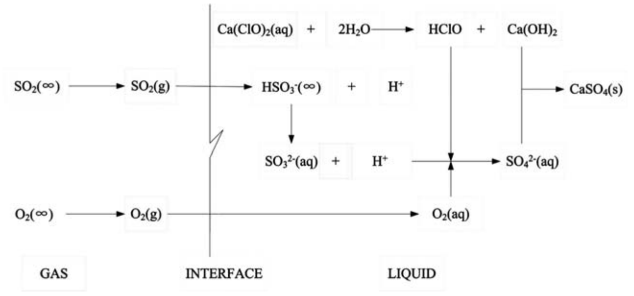

Figure 2. Reaction mechanism of SO_2 absorption in $Ca(ClO)_2$ solution.

Chemical Thermodynamics

To estimate reaction depth of the two chemical reactions (Eqs. 3 and 4), thermodynamic calculations of the two equations were performed. Enthalpy change of reaction $[\Delta_r H_m(T)]$, entropy change $[\Delta_r S_m(T)]$, and Gibbs function of reaction $[\Delta_r G_m(\mathrm{T})]$ were calculated, respectively. Thermodynamics parameters including, standard formation enthalpy, standard entropy, and standard formation Gibbs function of substances [23] were given in Table 1.

Enthalpy change, entropy change, and Gibbs function of the reactions (Eqs. 3 and 4) adjusted at 298.15 K were obtained by Eqs. 5–7, respectively [12,24]:

$$\Delta_r H_m{}^{\Theta} = \sum \gamma\ \Delta_f H_m{}^{\Theta}(\text{products}) - \sum \gamma\ \Delta_f H_m{}^{\Theta}(\text{reactants}) \qquad (5)$$

$$\Delta_r S_m{}^{\Theta} = \sum \gamma\ \Delta_f S_m{}^{\Theta}(\text{products}) - \sum \gamma\ \Delta_f S_m{}^{\Theta}(\text{reactants}) \qquad (6)$$

$$\Delta_r G_m{}^{\Theta} = \sum \gamma\ \Delta_f G_m{}^{\Theta}(\text{products}) - \sum \gamma\ \Delta_f G_m{}^{\Theta}(\text{reactants}) \qquad (7)$$

The chemical reaction equilibrium constants (K^{Θ}) of Eqs. 2 and 3 were given as follows [24]:

$$\Delta G^{\Theta} = -RT\ \ln K^{\Theta} \qquad (8)$$

Thermodynamic calculation results were shown in Table 2 The results stated that $\Delta_r H_m^{\Theta}$ values of the two chemical reactions are negative, which was conformed to the exothermic nature of the process [25,26]. Therefore, increasing the reaction temperature was unfavorable for the two reactions from the thermodynamic point of view. $\Delta_r S_m^{\Theta} < 0$ KJ mol^{-1} indicated that entropy of the reaction was reducing in the process, which implied that the amount of gas molecule

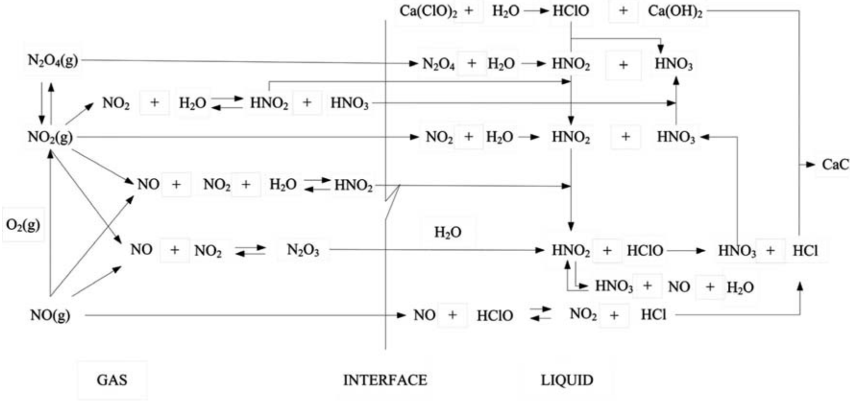

Figure 3. Reaction mechanism of NO_x absorption in $Ca(ClO)_2$ solution.

continuously decreased during the reaction [27]. Besides, the values of K^Θ in the two chemical reactions were $>10^5$, so the reactions could completely took place under the experimental conditions [12].

For the reaction with constant temperature, pressure and only work of volume expansion is done, Gibbs energy was indicative of process spontaneity [28]. The Gibbs function of the reaction could be written as follows [26] (ignoring the impact of temperature on thermodynamic parameters):

$$\Delta_r G_m = \Delta_r H_m{}^\Theta - T\ \Delta_r S_m{}^\Theta \qquad (9)$$

$\Delta_r G_m$ at different temperatures were calculated through Eq. 9, the results were listed in Table 3. The negative values of $\Delta_r G_m$ indicated that two reactions happened spontaneously, the reaction depth was greater [24].

RESULTS AND DISCUSSION

A sequence of experiments for simultaneous removal of SO_2 and NO_x were conducted. According to the experiments, the discussion was divided into four parts: $(SO_2 + NO_x)$-$Ca(ClO)_2$ experiment, NO_x-$Ca(ClO)_2$ experiment, liquid reaction products and comparison of the results of this study with some published works.

$(So_2 + NO_x)$-$Ca(ClO)_2$ Experiment

SO_2 and NO_x were removed simultaneously by $Ca(ClO)_2$ solution as shown in Figure 4. It could be observed that SO_2 was cleaned up by $Ca(ClO)_2$ solution with the removal efficiency of 100%. As SO_2 was a soluble gas, SO_2 could rapidly react with water to form HSO_3^- and SO_3^{2-} in liquid phase according to the equations listed in Figure 2. Once contact with water, the SO_2 gas would be absorbed by the solution. So the main limiting step of SO_2 absorption was the diffusion rate in gas phase, then it could be deduced that the gas-liquid reaction between SO_2 and $Ca(ClO)_2$ solution was completely gas-film controlled. What's more, the results also demonstrated that desulfurization using the $Ca(ClO)_2$ solution was feasible and efficient. However, due to the solubility of SO_2 in water was 20 times more than that of NO [11], the experimental results of NO_x removal (the NO_x removal efficiency was 42.2%) were dissatisfactory compared with that of SO_2. As a result, SO_2 could be removed easily by $Ca(ClO)_2$ solution, but not NO_x, and improving NO_x removal was the key point in the following experiments.

Table 1. Standard formation enthalpy, standard entropy, and standard formation Gibbs function.

Substance	$\Delta_f H_m^\Theta$ $(KJ \cdot mol^{-1})$	$\Delta_f S_m^\Theta$ $J \cdot (mol \cdot K)^{-1}$	$\Delta_f G_m^\Theta$ $(kJ \cdot mol^{-1})$
$Ca(ClO)_2(aq)$	−757.20	27.40	−627.14
$SO_2(g)$	−296.81	248.22	−300.13
$H_2O(l)$	−285.83	69.95	−237.14
$CaSO_4(s)$	−1425.2	108.40	−1309.10
$H_2SO_4(aq)$	−909.27	20.10	−744.63
$HCl(aq)$	−167.15	56.50	−131.25
$NO(g)$	91.29	210.76	87.60
$HNO_3(aq)$	−207.36	146.40	−111.34
$CaCl_2(aq)$	−877.13	59.80	−816.05

NO_x-$Ca(ClO)_2$ Experiment

Effect of the Liquid Layer Height

The effect of the liquid layer height was evaluated through changing the liquid layer height of bubbling reactors. As shown in Figure 5, the removal efficiency of NO_x was significantly affected by the height of liquid layer, and it sharply increased from 19.5 to 75.9% when the height of liquid layer increased from 40 to 120 cm. As a matter of fact, with the augment of the liquid layer height, the residence time of NO_x in the reactor increases, then the pollutants have an adequate reaction time. Thus, the NO removal efficiency was significantly promoted. This was in accord with the research of Liu [29,30]. However, as the extent of the reaction between NO_x and $Ca(ClO)_2$ solution was very deep and the reaction rate was very fast [31], enhancing the mass transfer rate may become more effective than further lengthening the residence time (increasing the height of liquid layer). Therefore, the effect of $Ca(ClO)_2$ concentration, a main factor to the mass transfer process, would be investigated in next experiments.

Effect of $Ca(ClO)_2$ Concentration

Effect of $Ca(ClO)_2$ concentration on NO_x removal efficiency was shown in Figure 6. As seen in Figure 6, the more $Ca(ClO)_2$ in the solution, the higher denitration efficiency. The result indicated that the efficiency of NO_x removal increased quickly as the $Ca(ClO)_2$ concentration increased from 0 to 0.1 wt %. But when the $Ca(ClO)_2$ concentration exceeded 0.1 wt %, NO_x removal efficiency increased slowly. The two-film theory holds that when the chemical reaction rate is far bigger than the mass-transfer rate, the mass-transfer process may be the controlling step. A higher $Ca(ClO)_2$ concentration could supply more HClO to react with NO_x according to the Eq. 1. The mass transfer would be more rapid and it would accelerate the reaction rate, which was mainly responsible for the absorption process. The results also stated that the reaction was controlled simultaneously by the gas-film and the liquid-film when the $Ca(ClO)_2$ concentration lower than 0.1 wt %, but mainly controlled by the gas-film as the $Ca(ClO)_2$ concentration increased above 0.1 wt %.

Table 2. Enthalpy change, entropy change, Gibbs function, and equilibrium constant of reactions.

Reaction	$\Delta_r H_m^\Theta$ $(KJ \cdot mol^{-1})$	$\Delta_r S_m^\Theta$ $J \cdot (mol \cdot K)^{-1}$	$\Delta_r G_m^\Theta$ $(kJ \cdot mol^{-1})$	K^Θ (298.15 K)
Equation 2	−749.26	−0.422	−614.55	$e^{247.92}$
Equation 3	−982.73	−0.300	−888.21	$e^{358.32}$

Table 3. Change of Gibbs function of reactions in different temperatures.

Reaction temperature (K)		313	323	333	343	353
ΔG_m $(kJ \cdot mol^{-1})$	Equation 2	−614.20	−609.98	−605.76	−601.54	−597.32
	Equation 3	−888.83	−885.83	−882.83	−879.83	−876.83

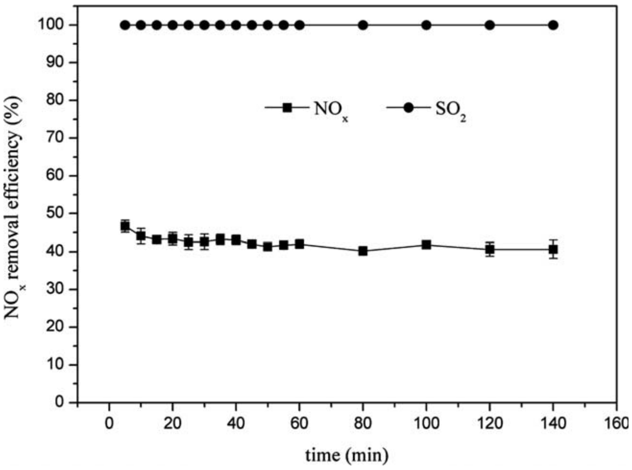

Figure 4. Simultaneous removal of SO_2 and NO_x using $Ca(ClO)_2$ solution. (Reaction condition: Q (Gas flow rate)-= 500 mL min^{-1}; $\rho(NO)_{inlet} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(Ca(ClO)_2) = 0.1$ wt %; $T = 60$°C; Initial pH value = 12; $[O_2](v/v) = 8\%$; $\rho(SO_2) = 1200$ mg m^{-3}).

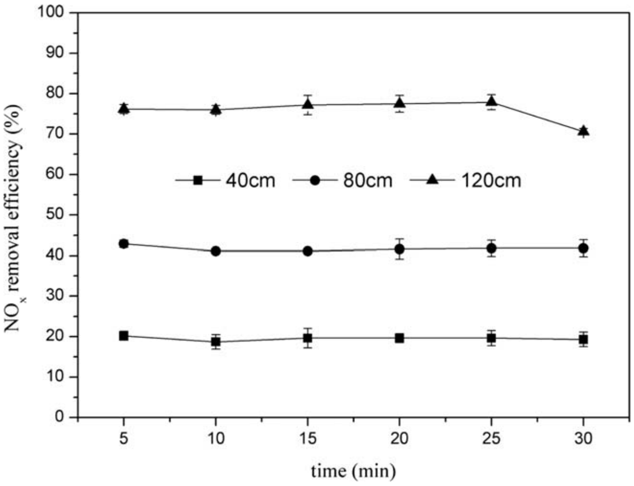

Figure 5. Effect of the height of liquid layer on NO_x removal efficiency. (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(NO)_{inlet} = 800$ mg m^{-3}; $\omega(Ca(ClO)_2) = 0.1$ wt %; $T = 60$°C; Initial pH value = 12; $[O_2](v/v) = 8\%$).

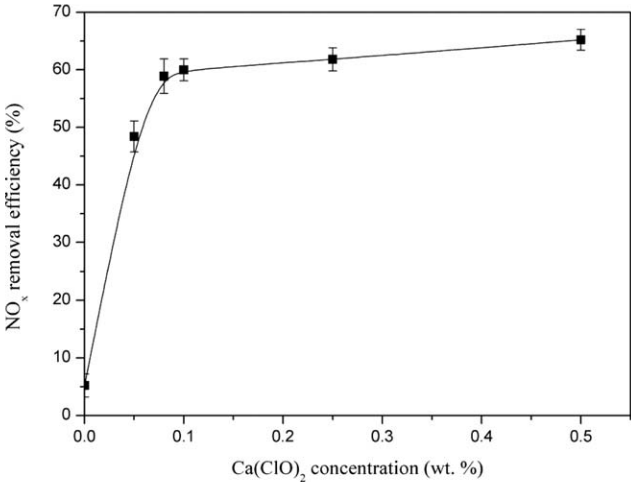

Figure 6. Effect of $Ca(ClO)_2$ concentration on NOx removal efficiency. (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(NO)_{inlet} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $T = 60$°C; Initial pH value = 12; $[O_2](v/v) = 8\%$).

Effect of Reaction Temperature

Reaction temperature could greatly influence the diffusion behavior, dissolution, and reaction characteristics of molecules or ions in liquid phase. Experiments were conducted to investigate its effect on removal efficiency of NO_x. From Figure 7, it can be seen that removal efficiency of NO_x initially increased and then reached maximum and finally decreased with increase in temperature. The highest removal efficiency of NO_x achieved at 60°C. The temperature dependence of reaction rate constant was assumed to follow the Arrhenius Model [32]. According to the Arrhenius expression of the reaction rate constant, the increasing temperature could improve the reaction rate and enhance the mass transfer of NO_x from gas to the absorbent. The increase of both the ionization of $Ca(ClO)_2$ and diffusion of NO would increase the removal efficiency at early stage of absorption. Nevertheless, as aforementioned, increasing the reaction temperature was unfavorable to the two reactions (Eqs. 2 and 3) from the thermodynamic point of view. Additionally, a higher temperature would enhance the Henry's Law constant [33], thereby reducing the solubility of NO_x in the absorbent solution. The observation is also due to the lower equilibrium concentration of N_2O_4 and N_2O_3 in the gas phase at higher temperature. Meanwhile, elevated temperature can accelerate the decomposition of nitrous acid, which leads to reduce nitrogen oxides removal [12]. Then the absorption of NO_x was inhibited consequently. Thus, as the temperature increased beyond a certain value, the increase in Henry's Law constant overshadows the enhancement in mass transfer, resulting in low removal efficiency of NO_x.

Effect of Initial pH Value

To study the effect of pH on NO_x removal efficiency, experiments were conducted at different pH in the range of 4–12, while other experimental parameters remained unchanged. The results are exhibited in Figure 8. It stated clearly that the NO_x removal efficiency declined as the initial pH of solution changing from 4 to 10, but enhanced when pH value was above 10. The results seem unexpected as strong acidic conditions are not beneficial to the absorption of NO [13]. Whereas, according to the research of Su [32], this phenomenon could be explained as: acid catalyzed decomposition pathway for $Ca(ClO)_2$ was observed at a substantially lower pH lever. It means that acidic condition was conducive to the decomposition of $Ca(ClO)_2$. Therefore, more HClO could be produced to oxidize insoluble NO to soluble NO_2 as follows [19]:

$$HClO + NO \rightarrow NO_2 + HCl \tag{10}$$

$$HClO + Cl^- + H^+ \leftrightarrow Cl_2 + H_2O \tag{11}$$

In the next stage, HClO can reacte with generated HCl to form Cl_2, which is a strong oxidizing gas [19]. Chlorine is capable of oxidizing NO into NO_2 and nitrate. The stoichiometry of reaction between chlorine with NO can be expressed as formulas (12-13) below [34]. The research of TW Chien and Chu [35] got similar results, it proved that NO is oxidized by Cl_2 under acidic conditions, and NO_2 is formed. Therefore, the removal efficiency was higher at lower initial pH of the solution.

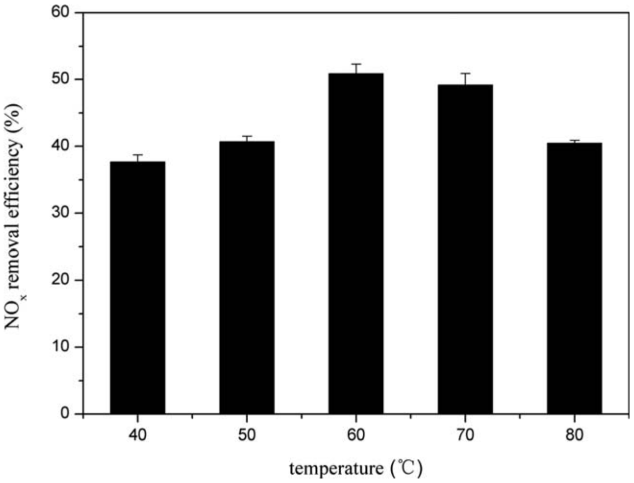

Figure 7. Effect of reaction temperature on NO$_x$ removal efficiency. (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(\text{NO})_{\text{inlet}} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(\text{Ca(ClO)}_2) = 0.1$ wt %; Initial pH value = 12; $[O_2](v/v) = 8\%$).

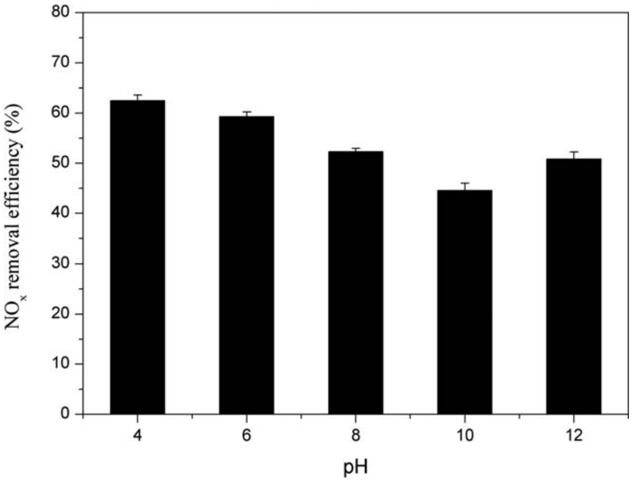

Figure 8. Effect of initial pH value on NO$_x$ removal efficiency. (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(\text{NO})_{\text{inlet}} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(\text{Ca(ClO)}_2) = 0.1$ wt %; $T = 60°C$; $[O_2](v/v) = 8\%$).

$$NO + Cl_2 + H_2O \rightarrow NO_2 + 2HCl \quad (12)$$

$$2NO + 3Cl_2 + 4H_2O \rightarrow 2HNO_3 + HCl \quad (13)$$

However, acidic conditions were not beneficial to the absorption of NO, and it would lead to accelerate the decomposition of nitrous acid. Weak alkalinity was beneficial to the NO removal [36]. In the weak alkaline environment, NO is prone to react as the formula (14). Generated HNO$_2$ and weak neutralization reacted to improving the water solubility of the NO, thereby improving the removal efficiency. For this reason, the NO$_x$ removal efficiency slightly improved as the pH over 10. Considering the practicability and economy of industrial application, the optimal pH of the Ca(ClO)$_2$ solution would be chosen at 12.

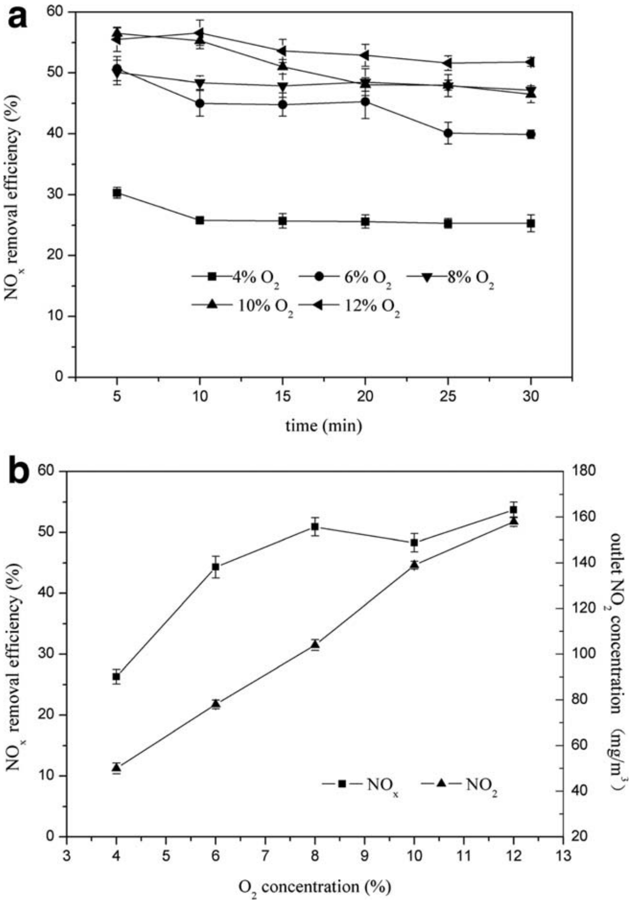

Figure 9. (**a**) Effect of O$_2$ percent on NO$_x$ removal efficiency. (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(\text{NO})_{\text{inlet}} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(\text{Ca(ClO)}_2) = 0.1$ wt %; $T = 60°C$; Initial pH value = 12). (**b**) Effect of O$_2$ percent on NO$_x$ removal efficiency and outlet NO$_2$ concentration (Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(\text{NO})_{\text{inlet}} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(\text{Ca(ClO)}_2) = 0.1$ wt %; $T = 60°C$; Initial pH value = 12).

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 \quad (14)$$

Effect of O$_2$ Concentration

To promote the dissolution of nitrogen oxides, O$_2$ was added to oxidize NO into soluble NO$_2$ in gas phase. Some tests were carried out to find the effect of O$_2$ concentration on NO$_x$ removal efficiency. The results were shown in Figure 9a, when the O$_2$ concentration in the flue gas increased from 4 to 12%, the NO$_x$ removal efficiency raised from 38.5 to 53.7%. It demonstrated that higher O$_2$ concentration was beneficial to NO$_x$ removal, for the reason that the oxidation degree of nitrogen oxides [12], which was an imperative factor for the reduction of NO$_x$, could be promoted by O$_2$. With the raise of oxygen concentration, the result is that mass-transfer driving force increases, and species in gas phase reacted violently with each other. Then lots of NO turned into NO$_2$ and passed into liquid layer, NO was removed as following pathways:

$$NO \xrightarrow{O_2} NO_2 \xrightarrow{H_2O} HNO_2 \quad (15)$$

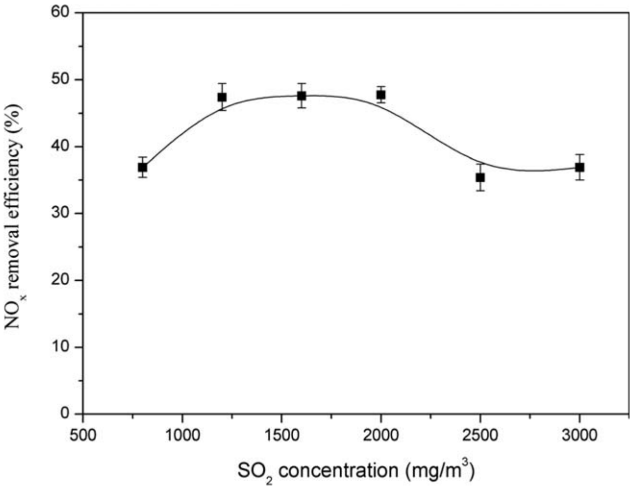

Figure 10. Effect of inlet SO_2 concentration on NO_x removal efficiency. [Reaction condition: Q (Gas flow rate) = 500 mL min^{-1}; $\rho(NO)_{inlet} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(Ca(ClO)_2) = 0.1$ wt %; $T = 60°C$; Initial pH value = 12; $[O_2] = 8\%$ (v/v)].

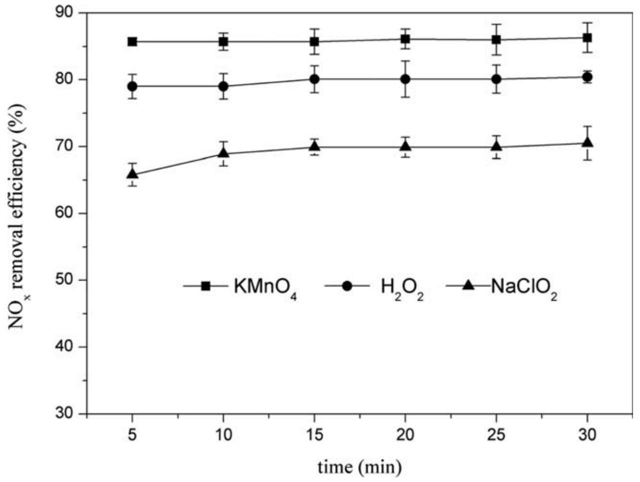

Figure 11. Effect of additive on NO_x removal efficiency. [Reaction condition: Q (Gas flow rate) =500 mL min^{-1}; $\rho(NO)_{inlet} = 800$ mg m^{-3}; The height of liquid layer = 80 cm; $\omega(Ca(ClO)_2) = 0.1$ wt %; $T = 60°C$; Initial pH value = 12; $[O_2] = 8\%$ (v/v); $\omega(KMnO_4/NaClO_2/H_2O_2) = 0.02\%$].

$$NO \xrightarrow{O_2} NO_2 \rightarrow N_2O_3/N_2O_4 \xrightarrow{H_2O} HNO_2 \qquad (16)$$

The concentration of outlet NO_2 was also measured, the results were shown in Figure 9b. It depicted that concentration of outlet NO_2 raised as O_2 percent in the simulated flue gas increased, and the NO_x removal efficiency grew, sequentially. This demonstrated that the production of NO_2 was a very important factor for NO_x removal.

Effect of So_2 Concentration

The coexistence of SO_2 and NO_x in the flue gas is bound to affect the absorption of each other. Experiments have been performed to verify the effect of SO_2 concentration on NO_x removal efficiency. The SO_2 concentration ranged from 800 to 3000 mg m^{-3} while the inlet NO concentration kept at 800 mg m^{-3}. The results were shown in Figure 10. It indicated that the NO_x removal efficiency first increased when the SO_2 concentration increased from 800 to 2000 mg m^{-3}, and then came down with the further increase of SO_2 concentration to 2500 mg m^{-3}. The reason may result from the hydrolysis of SO_2, in which the products such as HSO_3^- and SO_3^{2-} catalyzed the NO_x absorption as following equations [37–40]:

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (17)$$

$$H_2SO_3 \rightarrow HSO_3{}^- + H^+ \qquad (18)$$

$$2NO_2 + SO_3{}^{2-} + H_2O \rightarrow 2H^+ + 2NO_2{}^- + SO_4{}^{2-} \qquad (19)$$

$$2NO + HSO_3{}^- + H_2O \rightarrow 3H^+ + 2NO_2{}^- + SO_4{}^{2-} \qquad (20)$$

However, with the further increase of SO_2 concentration, more $Ca(ClO)_2$ was needed to form HClO and react with SO_2. Thus, SO_2 could be a competitor of NO_x to react with HClO, and the NO_x removal efficiency gradually declined for the limited HClO concentration. It is interesting that NO_x removal efficiency showed little growth again in the last stage with the increase of SO_2 concentration. This may be due to the fact that almost all $Ca(ClO)_2$ was consumed in the liquid, and SO_2 was no longer the competitor of NO_x for HClO. Literature [41] showed that the NO_2 would be removed by generated $CaSO_3$ under the presence of water vapor. This may be the reason of the rise in NO_x removal again.

Effect of Additives

Some oxidants including $KMnO_4$, H_2O_2, $NaClO_2$, have been proved to have good properties on NO_x removal [8,14,22]. However, it was not property to be used as absorbents in industry on account of economic efficiency. Thus, these oxidants as additives were added into absorbent to get a better NO_x removal efficiency in this work. The results were shown in Figure 11. It suggested that the removal efficiency of NO_x was greatly improved after the addition of additives into the absorbent. The additives in the absorbent could produce MnO_4^-, OH, ClO_2^-, respectively. These radicals owned strong oxidability and could react with NO as Eqs. (21–23) [8,14,22], thus the outcome products could be cleaned more easily by absorbent.

$$NO + 2MnO_4{}^- + 2{\cdot}OH^- \rightarrow NO_2{}^- + 2MnO_4{}^{2-} \qquad (21)$$

$$NO + {\cdot}OH^- \rightarrow H^+ + NO_2{}^- \qquad (22)$$

$$2NO + ClO_2{}^- \rightarrow 2NO_2 + Cl^- \qquad (23)$$

Here, the capacity on NO_x removal efficiency of additives was $KMnO_4 > H_2O_2 > NaClO_2$. The NO_x removal efficiencies reached 86.3, 80.4, and 70.5%, respectively. Therefore, $KMnO_4$ showed better performance for the promotion of NO_x removal efficiency. Figure 12 showed the SO_2 and NO_x removal efficiency under the best conditions: Q (Gas flow rate) = 500 mL min^{-1}; The height of liquid layer = 80 cm; $\omega(Ca(ClO)_2) = 0.1$ wt %; $T = 60°C$; Initial pH value = 12; $[O_2] = 8\%$ (v/v); $\rho(NO)_{inlet} = 800$ mg m^{-3}; $\rho(SO_2) = 2000$ mg m^{-3}. It could be seen from Figure 12 that the SO_2 removal efficiency retained 100% value, and the NO_x removal efficiency was about 85.9%.

Liquid Reaction Products

To confirm the composition of reaction products, the anions in solution were determined using ion chromatography (Dionex ISC-900). Ion chromatographic analysis of spent scrubbing liquor and reagent blank was depicted in Figure 13. The results indicated that SO_4^{2-} and NO_3^- were the major anion products in the solution after the absorption reactions; hence SO_2 and NO_x were mainly removed by oxidation.

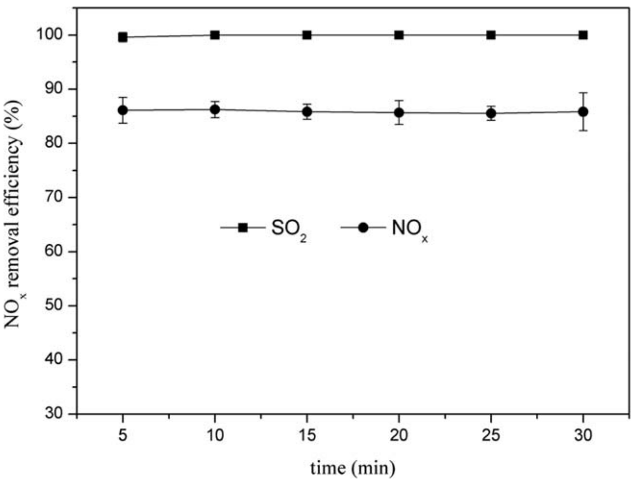

Figure 12. Simultaneous removal of SO_2 and NO_x under best conditions.

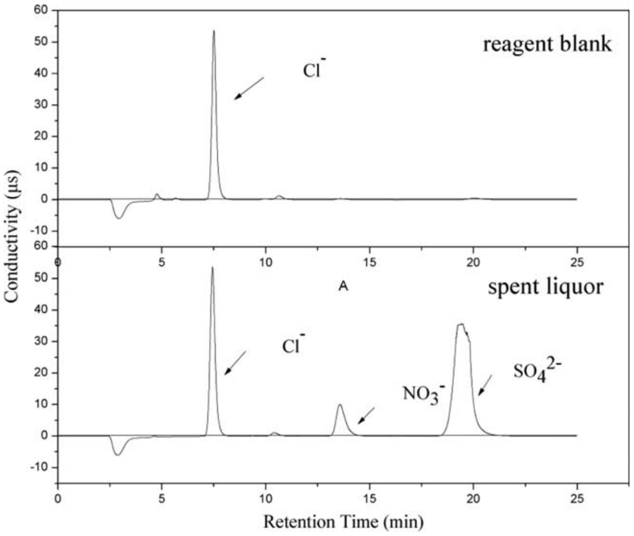

Figure 13. Ion chromatograms of absorbent solution.

Intermediate products such as SO_3^{2-}, HSO_3^-, and NO_2^- were oxidized to SO_4^{2-} and NO_3^- as follows:

$$SO_3^{2-} + ClO^- \rightarrow Cl^- + SO_4^{2-} \tag{24}$$

$$HSO_3^- + ClO^- \rightarrow H^+ + Cl^- + SO_4^{2-} \tag{25}$$

$$NO_2^- + ClO^- \rightarrow Cl^- + NO_3^- \tag{26}$$

In summary, on the basis of the results, although several other side reactions might also possibly occur in solution, the major pathways for SO_2 and NO_x removal using $Ca(ClO)_2$ solution could be concluded as: (a) the ClO^- oxidized NO into NO_2; (b) NO_2 and SO_2 was dissolved into water to form NO_2^- and SO_3^{2-}; (c) the terminal absorption of NO_x and SO_2 by turning NO_2^- and SO_3^{2-} into NO_3^- and SO_4^{2-} through ClO^- oxidation.

Comparison of the Results of This Study with Some Published Works

The results of this study were compared with some published literatures regarding removal of SO_2 and NO_x. The latest prices of the absorbents were inquired from the website of China Chemical Market Weekly. As shown in Table 4, SO_2 can be almost removed by wet method. It can also be knew that $Ca(ClO)_2$ solution is not the most efficiency one for NO_x removal, but it is a promising one due to its low cost, easy storage, and transportation. According to the Twelfth Five-year Plan of China, which have set the target of the reducing emission of total amount of major pollutants, the removal efficiency achieved in this work would be sufficient for most small medium sized enterprises to meet the stringent emission standard. Moreover, studies showed that $Ca(ClO)_2$ solution has potention of mercury removal [9]. Therefore, the research about $Ca(ClO)_2$ solution will provide reference for simultaneous removal of various pollutants from flue gas.

CONCLUSIONS

In this work, the reaction mechanism and total chemical reaction equations were investigated. Thermodynamic analysis showed that desulfurization and denitration using $Ca(ClO)_2$ solution were feasible. Experiments for simultaneous removal of SO_2 and NO_x exhibited high SO_2 removal efficiency (100%) and limited NO_x removal efficiency (42.4%). Thereafter, some important factors on denitration were investigated and it was concluded that: (1) The factors including the height of liquid layer, the concentration of $Ca(ClO)_2$, temperature and the solution pH could influence the NO_x removal efficiency to some extent; (2) As the component of the flue gas, O_2 played a important role in denitration, while SO_2 only enhanced the NO_x removal efficiency at a limited concentration section; (3) Additives in the solution

Table 4. Comparison of the results of this study with some published works.

S. No.	Absorbent	Price (RMB Yuan·t^{-1})	Removal efficiency (%)		Remark	Reference
			SO_2	NO_x		
1	NaClO	13,000	100	92	/	[1]
2	H_2O_2	570 (aqueous)	100	70	With UV lamp	[8]
3	Urea	1570–1750	100	92.65	With additive	[12]
4	$KMnO_4$	18,500	98.78	53.5	/	[13]
5	$Ca(ClO)_2$	1600	100	85.9	With additive	This study
6	ClO_2	15,000	100	66–72	/	[34]
7	$NaClO_2$	14,100	100	71.9	/	[35]
8	$Ca(OH)_2$	780	/	25–60	/	[41]
9	NaOH	2750	100	77	/	[42]

could promote denitration efficiency. At last, simultaneous removal of SO_2 and NO_x under optimized conditions were studied, the SO_2 and NO_x removal efficiencies reached 100 and 85.9%, respectively. The liquid reaction products were analyzed, and the major anion products in the solution after the absorption reactions were SO_4^{2-} and NO_3^-. Comparison of the results of this study with some published works showed that $Ca(ClO)_2$ solution is a promising absorbent in removing various pollutants from flue gas.

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