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A wet process for oxidation-absorption of nitric oxide by persulfate/calcium peroxide

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Abstract

This study develops and evaluates a novel wet method for NO removal using a \text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2 solution. The effects of these two components both and alone in solution, \text{Na}_2\text{S}_2\text{O}_8 concentration, \text{CaO}_2 concentration, initial pH, reaction temperature, and the concentrations of NO and O\textsubscript{2} on NO removal efficiency were evaluated using a bubbling reactor. The combination of \text{Na}_2\text{S}_2\text{O}_8 and \text{CaO}_2 had a synergistic effect on NO removal efficiency. NO removal was effected by \text{CaO}_2 concentration, reaction temperature and the initial solution pH, while \text{Na}_2\text{S}_2\text{O}_8 concentration and O\textsubscript{2} concentration had little effect. The NO removal efficiency decreased linearly from 94.5\% to 75.1\% when the NO concentration increased from 139 to 559 ppm. The products were characterized using XRD, XPS and IC, and \text{CaSO}_4\cdot2\text{H}_2\text{O}, \text{NaNO}_3 and

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Ca(NO$_3$)$_3$ were found to be the main products. The EPR analysis showed that free radicals of O$_2$$^-\cdot$, SO$_4$$^-\cdot$ and •OH were the key species involved in the NO removal process. Finally, the corresponding reaction mechanisms were proposed.

Keywords: NO removal; Na$_2$S$_2$O$_8$; CaO$_2$; Free radical; EPR analysis

1. Introduction

Nitric oxide (NO) accounts for more than 90% of NO$_x$ emitted from coal-fired boilers and plays a key role in the formation of photochemical smog and acid rain \[1\]. Several denitration techniques have been developed to control emissions of NO$_x$. Recently, selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) have been widely used in industrialization \[2\]. In order to meet the required standards of emission concentrations for SO$_2$ and NO$_x$ (lower than 35 and 50 mg/m$^3$, respectively), SCR or SNCR have been used before wet desulfurization in coal-fired boilers. However, this “1+1” type of approach to desulfurization and denitration has many disadvantages, including its complex system, large footprint and high operating cost \[3,4\]. These disadvantages can be addressed by simultaneous removal of NO$_x$ and SO$_2$ in the same wet scrubber.

Unlike SO$_2$, NO is an insoluble gas. Therefore, it is much more difficult to remove with conventional wet scrubbing \[5\]. To convert NO into more easily removable soluble nitrogen oxides, reagents are added that include ozone (O$_3$) \[6\], hydrogen peroxide (H$_2$O$_2$) \[7\], chlorine dioxide (ClO$_2$) \[8\], potassium permanganate (KMnO$_4$) \[9\], sodium chlorite (NaClO$_2$) \[10\], sodium hypochlorite (NaClO) \[11\], sodium persulfate (Na$_2$S$_2$O$_8$) \[12\], Fe(II)EDTA and Co(NH$_3$)$_6^{2+}$ \[13-14\]. There is much interest
in hydrogen peroxide (H$_2$O$_2$) in particular because it is relatively low cost and does not produce secondary pollution. Cooper et al. [15] studied the injection of H$_2$O$_2$ into hot flue gases for NO emission control. At the optimum temperature of 500 °C, hydrogen peroxide can be thermally activated to generate active radicals including hydroxyl radical (•OH) and hydroperoxy radical (HO$_2$•). More than 90 % of NO can be effectively converted into soluble nitrogen oxides by these radicals of •OH and HO$_2$•. However, this gas-phase oxidation method has so far only been studied in the laboratory due to the limitations imposed by the high temperatures required.

Persulfate can be stimulated by heat [16], UV light [17], ultrasonic [18] or transition metals (Fe$^{2+}$, Co$^{2+}$, Cu$^{2+}$) [19,20] to generate sulfate radical (SO$_4^{•−}$) (Eqs. 1-2), which is an oxidant with a similar function to •OH. Adewuyi et al. [5,12] studied the absorption-oxidation of NO and SO$_2$ by Na$_2$S$_2$O$_8$ aqueous solution in a bubbling reactor. Their results indicated that Na$_2$S$_2$O$_8$ can be activated to generate active SO$_4^{•−}$ radical at 50 °C, which then reacts with H$_2$O to produce •OH radical. The reaction rate was very slow ($k$[H$_2$O] < 2 × 10$^{-3}$ s$^{-1}$), and so NO and SO$_2$ were mainly removed by SO$_4^{•−}$ radical in the thermal excitation system of Na$_2$S$_2$O$_8$ aqueous solution. Block et al. [21] found that SO$_4^{•−}$ and •OH radicals coexisted in the dual oxidation (S$_2$O$_8^{2−}$/H$_2$O$_2$) system owing to the significant synergistic relationship between S$_2$O$_8^{2−}$ and H$_2$O$_2$. In our previous studies [22,23], we also showed that the combination of S$_2$O$_8^{2−}$ and H$_2$O$_2$ had a significant synergistic effect on NO removal. In addition, the NO removal efficiency under alkaline conditions was much higher than that under acidic or neutral conditions, reaching 80 % or higher for a long period of time under strongly alkaline conditions.
conditions adjusted by the addition of sodium hydroxide (NaOH). All these indicated that $S_2O_8^{2-}$ can be activated by strong alkalinity, heat and $H_2O_2$. This finding was consistent with the conclusions of Zhao et al.\textsuperscript{[24]}

\begin{equation}
S_2O_8^{2-} + \text{heat/UV/ultrasonic} \rightarrow 2SO_4^{2-} \tag{1}
\end{equation}

\begin{equation}
S_2O_8^{2-} + \text{Me}^{n+} \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{Me}^{(n+1)+} \tag{2}
\end{equation}

The problems of $H_2O_2$ instability and extra consumption of NaOH in the dual oxidation ($S_2O_8^{2-}$/$H_2O_2$) system can be solved by dissolving the solid oxidant CaO$_2$ in water for producing $H_2O_2$ and Ca(OH)$_2$ as described in Eq. 3\textsuperscript{[25]}. As well as a source of $H_2O_2$ (liberating a maximum of 0.47 g $H_2O_2$/g CaO$_2$\textsuperscript{[25]}), CaO$_2$ is also a strong alkali oxidant. This means it can activate $S_2O_8^{2-}$ and can therefore be used as an absorbent for the alkaline absorption of NO and SO$_2$. To the best of our knowledge, no study on wet desulfurization and denitrification using the dual component of $S_2O_8^{2-}$/CaO$_2$ has yet been reported.

\begin{equation}
\text{CaO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{Ca(OH)}_2 \tag{3}
\end{equation}

This study was aimed to understand the feasibility of simultaneous absorption of NO using $S_2O_8^{2-}$/CaO$_2$. Specifically, the effects on NO removal of single and dual component methods, $S_2O_8^{2-}$ concentration, CaO$_2$ concentration, the initial pH, the reaction temperature, NO concentration, and O$_2$ concentration were investigated in a bubbling reactor. In addition, the related mechanisms of NO removal by $S_2O_8^{2-}$ and CaO$_2$ were revealed by free radical detection. The results would contribute to the knowledge of simultaneous removal of NO$_x$ and SO$_2$ in the same wet scrubber.

2. Experimental
2.1. Materials

Flue gases were simulated by mixing N₂ (99.999 %), O₂ (99.999 %), and NO mixed gas (1 %). All gases were purchased from Air Liquide Tianjin Co., Ltd. Sodium persulfate (Na₂S₂O₈, powder, 99 %), sulfuric acid (H₂SO₄, liquid, 98 %), sodium hydroxide (NaOH, pellets, 96 %) and anhydrous calcium chloride (CaCl₂, pellets, 96 %) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. All reagents used in this experiment were analytically pure. The calcium peroxide (CaO₂) powder (70 %) used was chemically pure and obtained from Shandong Western Chemical Industry Co., Ltd.

2.2. Experimental Procedure

Fig. 1 shows the experimental setup used in this study. It consisted of four parts, a simulated flue gas generation system, a bubble column reactor with an inner diameter of 75 mm and a height of 300 mm, a flue gas analysis system and a tail gas absorption system. The NO, O₂ and N₂ (Fig. 1, 1-3) had their flow rates measured by mass flowmeters (Fig. 1, 4) before being mixed in a surge flask (Fig. 1, 5). Concentrations of NO and O₂ were adjusted by diluting with N₂. The flow rate of the simulated flue gas was kept at 2 L/min.

All experiments were conducted at temperatures between 15-70 °C. The temperature was controlled by the digital thermostat water bath (Fig. 1, 9) (HWSH, ±0.1 °C, Shanghai Tian Heng Instrument co., Ltd). For a typical test, the bubble column reactor was first filled with 600 mL of water and heated to the required temperature. Sodium persulfate and calcium peroxide solutions were added into the
reactor until the total liquid volume reached 800 mL. The pH of the solution was adjusted by adding 3 mol/L H₂SO₄ or 2 mol/L NaOH solution into the reactor. When the liquid phase was ready, the simulated flue gas was passed through the bubbling reactor, the surge flask (Fig. 1, 10), the drying tube (Fig. 1, 11) containing anhydrous CaCl₂ used for the removal of moisture in the simulated flue gas, and finally through another surge flask (Fig. 1, 14) before entering the flue gas analyzer.

The direction of simulated flue gas flow was controlled by a 3-way valve (Fig. 1, 6). The inlet and outlet concentrations of NOₓ and O₂ were measured by the ecom-J2KN flue gas analyzer (German RBR Measurement Technology Co., LTD). The pH of the reaction solution was measured before and after each test with a digital pH meter (PHS-3C, E-201F of electrode assembly type, ±0.01, Shanghai Leici Co., LTD). The tail gas was further cleaned by the exhaust gas absorption unit (Fig. 1, 17) before entering the fume hood (Fig. 1, 18).

1-Nitric oxide cylinder; 2-Oxygen cylinder; 3-Nitrogen cylinder; 4-Mass flowmeter; 5- Surge flask; 6-3-way valve; 7-Electronic thermometer; 8-Bubble column reactor;
9-Thermostat water bath; 10-Surge flask; 11-Dryer; 12,13,16-Two-way valve; 14-Surge flask; 15-Flue gas analyzer; 17- Exhaust gas absorption unit; 18-Fume hood.

Fig. 1. Schematic diagram of the experimental setup.

2.3. Data Analysis

The ions in the spent scrubbing solution were analyzed with a Dionex ICS 1000 ion chromatography system under the following chromatographic conditions: ion pac AS11-HC capillary column (4 × 250 mm), eluent (2 mmol/L NaOH), injection volume (25 μL), column temperature (303 K), flow rate (1.0 mL/min) and automatic regeneration suppression system (60 mmol H₂SO₄ and H₂O). The crystalline structure of fresh and spent solid absorbents was analyzed by X-ray diffraction (XRD, D8 ADVANCE type, BRUKER-AXS in Germany) (60 kV and 50 mA) with a Ni-Filtered Cu Kα, with a scanning 2θ range of 5° to 90° and a step size of 0.02. The fresh and spent solids were analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM Scanning ESCA Microprobe (Physical Electronics), Ulvac-Phi Inc in Japan) with a hemispherical detector operated at a constant pass energy (PE=55 eV) using Al Kα radiation (1486.6 eV). All binding energies were referenced to C 1s line at 284.8 eV. Active free radical species were detected with an electron spinresonance (EPR) spectrometer (JES-FA200) using 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) (99 %, Sigma) as a spin trap agent.

The inlet concentrations of NOₓ and O₂ were measured immediately upstream of the gas inlet. The outlet concentrations of NOₓ and O₂ from the bubble column reactor were continuously monitored and recorded. Each measurement lasted for 90 minutes,
and the mean concentration within the 90 minutes was used for the calculation of removal efficiency. When the mixed gas was bubbled through the reactor, NO reacted with the $\text{S}_2\text{O}_8^{2-/\text{CaO}_2}$ solution. The corresponding NO removal efficiency was calculated by:

$$\eta_{\text{NO}}(\%) = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100$$

where $\eta_{\text{NO}}$ is the removal efficiency of NO, $\text{NO}_{\text{inlet}}$ and $\text{NO}_{\text{outlet}}$ are the NO concentrations in the inlet and outlet gas.

3. Results and Discussions

3.1. Stability of the dual component of $\text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2$

Experiments were conducted with the pH changes of different $\text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2$ solutions over time at room temperature and atmosphere pressure to determine the stability of $\text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2$ solution. The corresponding results are shown in Fig. 2. 0.1 mol/L $\text{Na}_2\text{S}_2\text{O}_8$ solution was acidic due to the hydrolysis of $\text{Na}_2\text{S}_2\text{O}_8$ via Eq. 5 $^[5]$, and exhibited negligible change in pH over time, likely because of the very slow hydrolysis of $\text{Na}_2\text{S}_2\text{O}_8$ at room temperature and atmosphere pressure $^[26]$. 0.22 mol/L $\text{CaO}_2$ solution was strongly alkaline and exhibited a slow increase in pH over time because of the slow release of $\text{Ca(OH)}_2$ caused by the dissolution of $\text{CaO}_2$ in water via Eq. 3 $^[25, 27]$. The change in pH of different $\text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2$ solutions was not large enough to suggest instability. We therefore consider $\text{Na}_2\text{S}_2\text{O}_8/\text{CaO}_2$ solution to be stable at room temperature and atmosphere pressure.

$$2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow 4\text{HSO}_4^- + \text{O}_2$$

(5)
3.2. Effects of single and dual component on NO removal

3.2.1 Effect of CaO₂

In order to verify the synergistic effects of Na₂S₂O₈ and CaO₂, the effects of each, both alone (single component) and together (dual component) on NO removal performance were analyzed at 55.5 °C. Fig. 3 shows that NO removal efficiency was about 10 % when using CaO₂ alone. This confirmed our expectations that H₂O₂ released from CaO₂ has weak oxidation capacity due to its low oxidation reduction potential (E°(H₂O₂) =1.77 V). As shown in Fig. 3, NO removal efficiency decreased from 21 % to 6 % for the reaction time of 4000 s. One reason for the decrease of NO removal efficiency with time might be that as the reaction proceeded, the main oxidant H₂O₂ released from CaO₂ was gradually consumed to remove NO. In addition, the pH of the single CaO₂ solution increased from 10.98 to 11.54 for the reaction time of 4000 s. Zhang et al. [27] found that the generation rate of H₂O₂ from CaO₂ slowed down with the increase of pH, which may also explain the observed decline in removal efficiency. O₂ was not detected in the NO removal process when CaO₂ was
the only component. This is because the release of O$_2$ through the decomposition of H$_2$O$_2$ (See Eq. 6) and the dissolution of CaO$_2$ in water (See Eq. 7) were inhibited by the increase of alkalinity $^{[27]}$. In addition, the released O$_2$ was fully involved in the oxidation process of nitrogen oxides.

$$2H_2O_2 \rightarrow 2H_2O + O_2$$  \hspace{1cm} (6)

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2$$  \hspace{1cm} (7)

3.2.2 Effect of Na$_2$S$_2$O$_8$

Fig. 3 shows that the NO removal efficiency reached approximately 20 % when Na$_2$S$_2$O$_8$ was the only component. Na$_2$S$_2$O$_8$ can be thermally decomposed into SO$_4$$^{2-}$ at 55.5 °C (See Eq. 8). Water can consume SO$_4$$^{2-}$ at all pH levels to produce •OH as described in Eq. 9, but the rate of this reaction is very slow ($k[H_2O] < 2 \times 10^{-3} \text{ s}^{-1}$) $^{[5]}$. SO$_4$$^{2-}$ was the main oxidant due to its high oxidation reduction potential of $E^\circ$(SO$_4$$^{2-}$) =2.60 V. NO removal efficiency decreased from 30 % to 13 % once the reaction time reached 4000 s because Na$_2$S$_2$O$_8$ was constantly consumed during the reaction, leading to a decrease in the generation of SO$_4$$^{2-}$. O$_2$ concentrations in the outlet flue gas remained at 0 % with the reaction time of 4000 s in the NO removal process with single Na$_2$S$_2$O$_8$. This could be because the O$_2$ released from hydrolysis of Na$_2$S$_2$O$_8$ (See Eq. 5) was fully involved in the oxidation process of nitrogen oxides.

$$S_2O_8^{2-} \xrightarrow{\text{heat}} 2SO_4^{2-}$$  \hspace{1cm} (8)

$$SO_4^{2-} + H_2O \rightarrow \bullet OH + SO_4^{2-} + H^+$$  \hspace{1cm} (9)

3.2.3 Effect of dual components

Fig. 3 also shows that the denitrification performance of the combined dual
component Na$_2$S$_2$O$_8$/CaO$_2$ solution were much better than that of systems with Na$_2$S$_2$O$_8$ or CaO$_2$ only. The NO removal efficiency could remain at 70 % or higher when both Na$_2$S$_2$O$_8$ and CaO$_2$ were present. These results indicate that the combination of Na$_2$S$_2$O$_8$ and CaO$_2$ has great synergistic effects on the removal of NO.

As seen in Fig. 3, the NO removal efficiency curve for the reaction time of 6300 s first dropped, then rose, and finally remained stable. This is because Na$_2$S$_2$O$_8$ reacted with H$_2$O$_2$ to generate SO$_4$$^{2-}$ and HO$_2$. via Eqs. 10-11 \[23, 26\]. HO$_2$ quickly reacted with OH$^-$ to produce O$_2$$^{-}$ (See Eq. 12) \[28\]. Na$_2$S$_2$O$_8$ was activated by OH$^-$ to generate SO$_4$$^{2-}$ and O$_2$$^{-}$ (See Eqs. 13-14) \[29\]. NO removal efficiency decreased once the reaction time reached 3000 s because of the constant consumption of these reactive radicals by NO. The pH of the dual component Na$_2$S$_2$O$_8$/CaO$_2$ increased from 10.26 to 11.72 once the reaction time reached 6300 s. The resulting alkaline conditions caused the formation of \( \cdot \)OH radicals via Eq. 15 \[29\]. These are more reactive than SO$_4$$^{2-}$ and O$_2$$^{-}$. As a result, NO removal efficiency increased and finally remained stable after the reaction time passed 3000 s. The O$_2$ concentration first fell, then rose, and then decreased to 0 at 6300 s. The propagation and scavenging reactions among the excess SO$_4$$^{-}$, \( \cdot \)OH and O$_2$$^{-}$ (See Eqs. 16-17) \[29\] increased the O$_2$ concentration for the time from 3000s to 4000s. The constant consumption of O$_2$ released from chemical reactions between Na$_2$S$_2$O$_8$ and CaO$_2$ during the oxidation process of nitrogen oxides reduced the O$_2$ concentration after 6300 s.

\[
\text{S}_2\text{O}_8^{2-} \xrightleftharpoons{\text{heat}} \text{2SO}_4^{\cdot^-} \\
\text{SO}_4^{\cdot^-} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{SO}_4^{2^-} + \text{HO}_2 \cdot
\]

\[\text{(10)}\]
\[\text{(11)}\]
Fig. 3. Effects of single and dual component on NO removal (Reaction temperature=55.5 °C; total gas flow= 2 L/min; NO concentration= 345 ppm; O₂ concentration=0 %) (Full symbol — NO removal efficiency; Void symbol — O₂ concentration).

3.3. Effects of CaO₂ and Na₂S₂O₈ concentration on NO removal

The effects of CaO₂ concentration on NO removal efficiency were analyzed (Fig. 4). With an increase of CaO₂ concentration from 0.005 mol/L to 0.215 mol/L, the NO removal efficiency increased from 18.3 % to 82.6 %. When CaO₂ concentration doubled from 0.215 mol/L to 0.413 mol/L, the efficiency increased by only 3 %. The increase of CaO₂ concentration improved the yields of SO₄⁻, O₂⁻ and •OH free radicals (See Eqs. 10-15), thereby enhancing the efficiency of NO removal. However,
the scavenging reactions of excess free radicals generated by excess CaO\textsubscript{2} competed with the reactions among free radicals with NO (See Eqs. 16-20). The changes of NO removal efficiency curves over time for low CaO\textsubscript{2} concentrations (i.e. 0.005 and 0.014 mol/L) were different from those for higher CaO\textsubscript{2} concentrations (from 0.073 to 0.430 mol/L). The pH of 0.005 mol/L CaO\textsubscript{2} concentration decreased from 3.0 to 2.51 after the reaction had been in progress for 4980 s, while that of 0.014 mol/L CaO\textsubscript{2} concentration decreased from 8.6 to 8.41 after the reaction had been in progress for 5520 s. The presence of SO\textsubscript{4}\textsuperscript{2–} radical generated by the thermal activation of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} was attributed to the release of small amounts of H\textsubscript{2}O\textsubscript{2} and Ca(OH)\textsubscript{2} from CaO\textsubscript{2} at low concentration. At higher CaO\textsubscript{2} concentrations (from 0.073 to 0.430 mol/L), the changes of NO removal efficiency curve over time were almost similar attributing for the similar changes of pH of dual component of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CaO\textsubscript{2} from 10.01 to 11.35, from 10.80 to 11.80 and from 10.87 to 11.83 with the reaction times of 5400 s, 6300 s and 6420 s respectively, when the corresponding CaO\textsubscript{2} concentrations were 0.073, 0.215 and 0.430 mol/L respectively.

\[ \cdot \text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \] \hspace{1cm} (18)
\[ \text{SO}_4^{2–} + \text{SO}_4^{2–} \rightarrow \text{S}_2\text{O}_8^{2–} \] \hspace{1cm} (19)
\[ \text{SO}_4^{2–} + \cdot \text{OH} \rightarrow \text{HSO}_5^{–} \] \hspace{1cm} (20)
Fig. 4. Effects of CaO$_2$ concentration on NO removal efficiency (Reaction temperature = 55.5 °C; total gas flow = 2 L/min; NO concentration= 345 ppm; O$_2$ concentration= 0 %; Na$_2$S$_2$O$_8$ concentration= 0.1 mol/L).

The effects of Na$_2$S$_2$O$_8$ concentration on NO removal efficiency are shown in Fig. 5. NO removal efficiency clearly increased when Na$_2$S$_2$O$_8$ concentration increased from 0.03 mol/L to 0.05 mol/L, and increased slightly when Na$_2$S$_2$O$_8$ concentration changed from 0.05 mol/L to 0.14 mol/L. The increase in Na$_2$S$_2$O$_8$ concentration improved the yields of SO$_4$$^{2-}$, O$_2$$^{\cdot-}$ or •OH free radicals (See Eqs. 10-15), and consequently enhanced the removal efficiency of NO. However, the scavenging reactions of excess free radicals generated by the excess Na$_2$S$_2$O$_8$ would compete for the free radicals which react with NO (See Eqs. 16-20). NO removal efficiency for the Na$_2$S$_2$O$_8$ concentration of 0.03 mol/L declined constantly until 5400s. This was because there was too little SO$_4$$^{2-}$ produced from Na$_2$S$_2$O$_8$ to generate O$_2$$^{\cdot-}$ and •OH. Therefore, SO$_4$$^{2-}$ was fully involved in the oxidation of NO. The changes in NO removal efficiency over time followed a similar trend at higher Na$_2$S$_2$O$_8$
concentrations (from 0.05 to 0.14 mol/L). The pH of dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solutions changed from 10.98 to 11.88, from 10.80 to 11.78, from 10.76 to 11.80 and from 10.0 to 11.72 for the reaction times of 6240 s, 6000 s, 6000 s and 5820 s at higher Na$_2$S$_2$O$_8$ concentrations of 0.05, 0.08, 0.10 and 0.14 mol/L, respectively.

Na$_2$S$_2$O$_8$ concentration had relatively little effect on NO removal efficiency when compared with CaO$_2$ concentration. Considering the costs and denitration performances, CaO$_2$ concentration of 0.215 mol/L and Na$_2$S$_2$O$_8$ concentration of 0.10 mol/L were recommended as the optimal concentration.

Fig. 5. Effects of Na$_2$S$_2$O$_8$ concentration on NO removal (reaction temperature= 55.5 °C; total gas flow= 2 L/min; NO concentration= 345 ppm; O$_2$ concentration= 0 %; CaO$_2$ concentration= 0.215 mol/L).

3.4. Effects of temperature and pH on NO removal

Temperature affects the mass transfer rate of the chemicals of concern [30], while pH has obvious effects on the forms and oxidation-absorption potentials of the active
species in the solution \cite{31}. The effects of temperature on NO removal efficiency are shown in Fig. 6. NO removal efficiency increased from 15.9 % to 82.6 % when the temperature increased from 18.0 °C to 55.5 °C. The increase leveled off when the temperature changed from 55.5 °C to 65.5 °C. These results were similar to those for dual oxidant (Na$_2$S$_2$O$_8$/H$_2$O$_2$) system in our previous studies \cite{23}. The production of SO$_4^{2−}$ increased with the increase of temperature. Liu et al. \cite{32} also showed that the yields of SO$_4^{2−}$ increased as the activation temperature increased from 25 to 75 °C. In addition, the solubility of NO decreased with the increase of temperature. The change of NO removal efficiency at 18.0 °C over time was different from those at higher temperatures in the range of 35.5-65.5 °C. Na$_2$S$_2$O$_8$ can not be thermally activated at 18.0 °C to produce SO$_4^{2−}$ and O$_2^{−}$, and so NO was removed mainly by the Na$_2$S$_2$O$_8$ and H$_2$O$_2$ released by CaO$_2$ at 18.0 °C.

![Fig. 6. Effects of temperature on NO removal (total gas flow= 2 L/min; NO concentration= 345 ppm; O$_2$ concentration= 0 %; CaO$_2$ concentration= 0.215 mol/L; Na$_2$S$_2$O$_8$ concentration= 0.1 mol/L; pH= 10.80).]
The effects of pH on NO removal efficiency are shown in Fig. 7. NO removal efficiency increased from 7.8 % to 83.0 % when pH increased from 2.25 to 9.05, but there was little effect on the NO removal efficiency at pH levels higher than 9.05. The yields of H$_2$O$_2$ from CaO$_2$ increased with the addition of a small amount of H$_2$SO$_4$, thereby increasing the yields of SO$_4^{2−}$, O$_2^{−}$ and •OH free radicals (See Eqs. 10-15). Northup et al. [25] also verified that the yields of H$_2$O$_2$ and the dissolution rate of CaO$_2$ increased with the decrease of pH. However, the generation of white turbid CaSO$_4$ from the consumption of CaO$_2$ by H$_2$SO$_4$ (via Eq. 21) increased as the amount of H$_2$SO$_4$ increased. It can be seen from Fig. 8 that the white turbid CaSO$_4$ mainly existed in the dual component Na$_2$S$_2$O$_8$/CaO$_2$ solution at pH 2.25, which had little effect on the oxidation and absorption of NO. When pH increased from 10.80 to 12.34 with the addition of NaOH solution, NO removal efficiency decreased from 82.6 % to 75.5 %. The dissolution rate of CaO$_2$ was inhibited with the addition of NaOH solution, thereby decreasing the yields of SO$_4^{2−}$, O$_2^{−}$ and •OH free radicals (See Eqs. 10-15) due to the decrease of H$_2$O$_2$ produced from CaO$_2$. The existence of SO$_2$ in flue gas would therefore be beneficial to the removal of NO in the dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution.

\[ H_2SO_4 + CaO_2 \rightarrow CaSO_4 + H_2O \]  \hspace{1cm} (21)
Fig. 7. Effects of pH on NO removal (total gas flow= 2 L/min; NO concentration= 345 ppm; O₂ concentration= 0 %; CaO₂ concentration= 0.215 mol/L; Na₂S₂O₈ concentration= 0.1 mol/L; temperature= 55.5 °C).

3.5. Effects of NO and O₂ concentrations on NO removal

For coal-fired boilers, the emissions of NOₓ and O₂ depend on the properties of the coal used and the combustion conditions in the furnace. As shown in Fig. 8, NO removal efficiency almost linearly decreased from 94.5 % to 75.1 % as the NO concentration increased from 139 ppm to 559 ppm. At a lower NO concentration (139 ppm), the yields of SO₄⁻, O₂⁻ and •OH free radicals (Eqs. 10-15) were adequate to sustain an NO removal efficiency level of 90 % or higher for the reaction time of 5940 s. At higher NO concentrations (205, 279, 345, 415 and 559 ppm), NO removal efficiency decreased with the increase of NO concentration, perhaps because of the decrease of the ratio of reactive radicals to NO. However, the changes of NO removal efficiencies at all NO concentrations over time followed similar trends.

As shown in Fig. 9, the NO removal efficiency decreased a little and then
increased as the O$_2$ concentration increased from 0 % to 8 %. While the free radicals might be captured by O$_2$\cite{33}, the oxidation and absorption of NO was also promoted by O$_2$ (See Eqs. 22-23). The effect of O$_2$ concentration on NO removal efficiency was less obvious. In addition, the changes in NO removal efficiency at all O$_2$ concentrations over time were similar to each other.

$$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2 \quad \text{(22)}$$

$$\text{NO} + \text{NO}_2 + \text{O}_2 \rightarrow \text{HNO}_3 \quad \text{(23)}$$

**Fig. 8.** Effects of NO concentration on NO removal efficiency (total gas flow= 2 L/min; O$_2$ concentration= 0 %; CaO$_2$ concentration= 0.215 mol/L; Na$_2$S$_2$O$_8$ concentration= 0.1 mol/L; temperature= 55.5 °C; pH= 10.80).
Fig. 9. Effects of O₂ concentration on NO removal efficiency (total gas flow= 2 L/min; NO concentration= 345 ppm; CaO₂ concentration= 0.215 mol/L; Na₂S₂O₈ concentration= 0.1 mol/L; temperature= 55.5 °C; pH= 10.80).

3.6. Reliability and replicability of the experiments

In order to verify the reliability and replicability of the experimental results, five parallel experiments were carried out under the determined optimal conditions. The Na₂S₂O₈ concentration was 0.1 mol/L, CaO₂ concentration 0.215 mol/l, solution pH 10.80, reaction temperature 55.5 °C, O₂ concentration 0 %, total gas flow 2 L/min and NO concentration 345 ppm. The results are shown in Fig. 10 and Table 1. The standard error of 2.66 % indicated a good degree of repeatability. Thus the experimental results were deemed to be reliable and to provide useful information for future industrial application.
Fig. 10. Five parallel tests for NO removal with dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution.

**Table 1** The results of five parallel tests for NO removal with dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution

<table>
<thead>
<tr>
<th>Test</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>Average</th>
<th>Standard error</th>
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</thead>
<tbody>
<tr>
<td>NO removal efficiency (%)</td>
<td>84.7</td>
<td>82.6</td>
<td>82.2</td>
<td>84.1</td>
<td>77.9</td>
<td>82.3</td>
<td>2.66</td>
</tr>
</tbody>
</table>

3.7. Reaction mechanisms

The XRD analysis for fresh CaO$_2$ and spent absorbents were conducted and the results are shown in Fig. 11. CaO$_2$ was identified as the main chemical component of the fresh 70 % CaO$_2$ powder, with possible Ca(OH)$_2$ and CaCO$_3$. CaSO$_4$·2H$_2$O was the main solid phase product throughout the oxidation and absorption of NO by Na$_2$S$_2$O$_8$/CaO$_2$. Unreacted Ca(OH)$_2$ was the main solid phase product generated by the hydrolysis of CaO$_2$, along with unreacted CaO$_2$. There were no obvious spectra
indicating presence of NaNO$_3$, NaNO$_2$, Na$_2$SO$_4$ and Ca(NO$_3$)$_2$. This might be because these molecules existed in the liquid phase.

![XRD analysis results for the fresh CaO$_2$ and spent Na$_2$S$_2$O$_8$/CaO$_2$ absorbents.](image)

**Fig. 11.** XRD analysis results for the fresh CaO$_2$ and spent Na$_2$S$_2$O$_8$/CaO$_2$ absorbents.

XPS analysis of the solid Na$_2$S$_2$O$_8$/CaO$_2$ absorbent and IC analysis of liquid phase ion products were carried out to determine the elemental oxidation states of the generated species in solid and liquid phases. The results shown in Fig. 12 and Fig. 13 showed the photoelectron peak of O 1s appeared at the binding energy of 531.7 eV. This can be divided into four individual peaks at 530.7, 531.6, 532.1 and 532.4 eV corresponding to different oxygen-containing species, such as 530.7 eV for CO$_3^{2-}$, 531.6 eV for OH$^-$, 532.1 eV for SO$_4^{2-}$, and 532.4 eV for O$_2^{2-}$. The photoelectron peak of S 2p appeared at the binding energy of 168.6 eV, indicating the formation of SO$_4^{2-}$, which was consistent with the XPS results of O 1s. The spectrum of C 1s can be considered as two peaks at 285.1 and 289.2 eV, indicating the formation of C-C bonds and CO$_3^{2-}$, respectively. This was consistent with the XPS results of O 1s. There was no photoelectron peak at N 1s, indicating that there were no N-containing species in
the solid phase of the spent CaO₂ absorbents, although it did exist in the liquid phase.

This observation was consistent with the XRD results. As shown in Fig. 13, NO₃⁻, SO₄²⁻, and NO₂⁻ were detected in the NO removal system with the dual component of Na₂S₂O₈/CaO₂, but the amount of NO₂⁻ was negligible compared with that of NO₃⁻. SO₃²⁻ was not detected in the NO removal system with the dual component of Na₂S₂O₈/CaO₂.

Fig.12. XPS spectra of spent Na₂S₂O₈/CaO₂ absorbents.
Electron spin resonance (EPR) spectroscopy combined with DMPO was used to identify the reactive species involved in the reactions of the dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution at different times. The results are shown in Fig. 14. These hyperfine splitting constants of radical adducts ($A_N$=14.41 and $A_H$=9.94) were consistent with the data in literature $^{29, 34, 35}$. The EPR peaks of O$_2$•⁻ radical were evident for the reaction times of 1 min, 5 min and 60 min at 55.5 °C, while the EPR peak intensity of superoxide radical was lower at shorter reaction times. This was consistent with the trend of NO removal efficiency over time in the dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution at 55.5 °C. It was difficult to determine the presence of SO$_4$⁻ and •OH radicals because the fluxes of SO$_4$⁻ and •OH radicals were low in the dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution, or because the EPR peaks of SO$_4$⁻ and •OH radicals were overlapped with that of O$_2$•⁻ radical $^{36}$. The EPR peaks of SO$_4$⁻ and •OH radicals were determined in the Na$_2$S$_2$O$_8$ solution at 55.5 °C.

**Fig. 13.** IC patterns of mixed standard solution and spent Na$_2$S$_2$O$_8$/CaO$_2$ solution.

**Fig. 14.** EPR spectra of radical adducts in Na$_2$S$_2$O$_8$ solution and dual component of...
Na$_2$S$_2$O$_8$/CaO$_2$ solution at 55.5 °C.

The reaction mechanisms of NO removal by the dual component of Na$_2$S$_2$O$_8$/CaO$_2$ solution at 55.5 °C can be described as follows. In the single CaO$_2$ solution system, NO was mainly oxidized and absorbed by H$_2$O$_2$ and the Ca(OH)$_2$ released by CaO$_2$ (See Eqs. 7 and 24-27).

$$\text{NO} + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_2 + \text{H}_2\text{O} \quad (24)$$

$$\text{HNO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} \quad (25)$$

$$2\text{HNO}_2 + \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{NO}_2^- + 2\text{H}_2\text{O} \quad (26)$$

$$2\text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{NO}_3^- + 2\text{H}_2\text{O} \quad (27)$$

In the Na$_2$S$_2$O$_8$ solution system, NO was mainly oxidized and absorbed by SO$_4^{2-}$ produced by the thermal activation of Na$_2$S$_2$O$_8$ (See Eqs. 8-9 and 28-29).

$$\text{SO}_4^{2-} + \text{NO} + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} + \text{NO}_2^- \quad (28)$$

$$\text{SO}_4^{2-} + \text{NO}_2^- + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} + \text{NO}_3^- \quad (29)$$

In the dual component Na$_2$S$_2$O$_8$/CaO$_2$ solution, NO was mainly oxidized and absorbed by O$_2^{•-}$, SO$_4^{2-}$ and •OH radicals generated thermally, activation of Na$_2$S$_2$O$_8$ by H$_2$O$_2$ and OH$^-$ (See Eqs. 10-15 and 28-34) and Ca(OH)$_2$ released by CaO$_2$ (See Eqs 26-27, 35).

$$\text{OH} • + \text{NO} \rightarrow \text{H}^+ + \text{NO}_2^- \quad (30)$$

$$\text{NO}_2^- + \text{OH} • \rightarrow \text{OH}^- + \text{NO}_2 \quad (31)$$

$$\text{NO}_2 + \text{OH} • \rightarrow \text{H} + \text{NO}_3^- \quad (32)$$

$$2\text{O}_2^{•-} + 2\text{NO} \rightarrow \text{O}_2 + 2\text{NO}_2^- \quad (33)$$

$$2\text{O}_2^{•-} + 2\text{NO} \rightarrow 2\text{NO}_3^- \quad (34)$$
4. Conclusions

We studied a wet NO\textsubscript{x} removal technology using a Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CaO\textsubscript{2} solution. The performance of the dual component Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CaO\textsubscript{2} was stable at room temperature and atmosphere pressure. Comparative performance studies showed that the combination of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} and CaO\textsubscript{2} had significant synergistic effects on NO removal. With an increase of CaO\textsubscript{2} concentration and reaction temperature, NO removal efficiency first rapidly increased and then slowed down. With the increase of initial pH, NO removal efficiency first increased and then decreased. NO removal efficiency did not show a significant relationship with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} concentration or O\textsubscript{2} concentration. NO removal efficiency decreased almost linearly from 94.5 % to 75.1 % with the increase in NO concentration from 139 to 559 ppm. According to the EPR analysis, free radicals of O\textsubscript{2}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{−} and \textsuperscript{•}OH played a key role in the NO removal in the dual component of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CaO\textsubscript{2} solution. This will contribute to a better understanding of the reaction mechanisms of NO removal with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/CaO\textsubscript{2}.

Acknowledgements

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HIGHLIGHTS

- A novel wet method for NO removal with Na$_2$S$_2$O$_8$/CaO$_2$ as oxidants.
- Free radicals of O$_2$•−, SO$_4$•− and •OH as the key species were identified by EPR.
- A better understanding of the reaction mechanisms of NO removal with Na$_2$S$_2$O$_8$/CaO$_2$. 