Simultaneous Removal of SO₂ and Hg⁰ by Composite Oxidant NaClO/NaClO₂ in a Packed Tower

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ABSTRACT: Based on the implementation of the global Minamata Convention, developing an efficient and economical technology for mercury reduction in coal-fired flue gas becomes a hotspot in the field of air pollution control. The composite oxidant NaClO/NaClO₂ combined with limestone was used in the simultaneous removal of SO₂ and Hg⁰ in this study, and the three-factor and four-level orthogonal experiments were performed in a packed tower. The influence sequence of various factors on SO₂ and Hg⁰ removals was investigated through range analysis of the orthogonal experiments. Results showed that factors affecting desulfurization was C > A > B (liquid–gas ratio > oxidant concentration ratio > initial pH of absorption liquid), while factors affecting Hg⁰ removal was A > C > B (oxidant concentration ratio > liquid–gas ratio > initial pH of absorption liquid). Optimum conditions of simultaneous desulfurization and demercuration by NaClO/NaClO₂ were A4B1C4; that is, the oxidant concentration ratio was 10/4 (mmol/L: mmol/L), the initial pH was 5, and the liquid–gas ratio was 18 (L/m³). The simultaneous removal efficiencies of SO₂ and Hg⁰ reached 99.5 and 85.4% under these optimum conditions, respectively. Analysis of the characteristics of the solid products showed that the main products of the wet oxidation were CaSO₄ and CaSO₃. Analysis of the existing form of oxidized mercury showed that 23% of mercury was in the gypsum, while 77% was in the supernatant. Results of this research would provide a practical reference for promoting the simultaneous removal of SO₂ and Hg⁰ by NaClO/NaClO₂ with limestone in industrial application.

1. INTRODUCTION

Mercury pollution has attracted great attention all around the world.¹⁻¹° The existing form of mercury in coal-fired flue gas is mainly categorized into three types, the particulate mercury (Hg⁰), oxidized mercury (Hg²⁺), and elemental mercury (Hg⁰).¹¹ Various methods for mercury removal from flue gas have been researched, including selective adsorption¹²⁻¹⁵ and catalytic oxidation.¹⁶ The removal of mercury by wet oxidation was a technology that could make full use of the existing facilities for air pollution control.¹⁶⁻¹⁹ Hg⁰ could be removed effectively when the flue gas passed through the dust removal device,¹⁶⁻¹⁸ while Hg²⁺ could be absorbed during wet flue gas desulfurization (WFGD).¹⁴ Since Hg⁰ has the characteristics of long-distance migration and high volatility, it is the most concerning one, which is also the most difficult to remove in the coal-fired flue gas.¹⁵,¹⁶ Wet oxidation is a method to add an oxidant into the existing WFGD device to oxidize Hg⁰ to Hg²⁺ and then absorb them.¹²¹¹ The key point of the wet oxidative demercuration was to rapidly oxidize Hg⁰ to soluble Hg²⁺. Thus, the oxidizing ability of the oxidant directly determined the Hg⁰ removal efficiency. Many strong oxidants have been studied to remove Hg⁰ from flue gas, including KMnO₄,¹⁸ K₂S₂O₈,¹⁹ (Na₂S₂O₈)²⁰, K₂FeO₄,²¹ Fenton²² (Fenton-like²³,²⁴), and chlorate series.²⁵⁻²⁶ In order to find out a kind of oxidant that is both efficient and economical, composite oxidants have gradually become the hotspot in the research of Hg⁰ removal.

KMnO₄ has been widely used in the research of wet oxidation because it presents a strong oxidation ability under both acidic and alkaline conditions.²⁷ However, the secondary pollution produced by KMnO₄ limited its industrial applications. K₂S₂O₈ also had strong oxidizing properties. The addition of Fe²⁺ and Fe₃O₄ could increase the Hg⁰ removal efficiency by means of activating of K₂S₂O₈.²⁷ However, the addition of activator not only increased the cost but also caused secondary pollution easily. The complex process of K₂S₂O₈ activation was a hindrance to its industrial application.¹³ K₂FeO₄, H₂O₂, and Fenton-like all had the capability of oxidizing Hg⁰ to Hg²⁺, but their instability and harsh reaction conditions indicated that these oxidants were not appropriate for industrial promotion.²⁸⁻³¹ When NaClO

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was used in the simultaneous removal of SO2, NO, and Hg0, it presented a high ability to oxidize Hg0 to Hg2+. Zhao et al. studied the oxidation of NaClO2 and found that Hg0 removal efficiency could reach up to 65% under optimal conditions. Thus, the chlorate series would be a good choice for wet oxidation of Hg0 removal from coal-fired flue gas. The simultaneous control of multipollutants from coal-fired flue gas was the trend of industrial flue gas purification. The simultaneous removal of SO2 and Hg0 could be achieved in industrial application with the development of wet oxidation technology. In this work, Hg0 oxidation by six strong oxidants was studied and the composite oxidant combined with limestone was carried out in a packed tower. Results of this study would be helpful for the wet oxidation technology of simultaneous desulfurization and demercuration.

2. EXPERIMENTAL SETUPS AND MATERIALS

2.1. Experimental Setups. SO2 and Hg0 were the typical pollutants of the coal-fired flue gas in these experiments. N2 and O2 were selected as the equilibrium gases to make up the simulated flue gas. The experimental study on simultaneous removal of SO2 and Hg0 by composite oxidant NaClO/NaClO2 combined with limestone was carried out in a packed tower, and the experimental setups are shown in Figure 1.

Figure 1. Experimental setup for the simultaneous removal of SO2 and Hg0 in a packed tower. 1 - SO2, 2 - O2, 3 - N2, 4 - water bath, 5 - pressure reducing valve, 6 - mass flow meter, 7 - U-tube, 8 - mercury permeation tube, 9 - mixing chamber, 10 - packed tower, 11 - cistern, 12 - air plate, 13 - packings, 14 - spray nozzle, 15 - silica drying tube, 16 - three-way valve, 17 - atomic absorption mercury detector, 18 - computer, 19 - flue gas analyzer, 20 - tail gas absorption bottle.

The gas flow rates of SO2 (1), O2 (2), and N2 (3) were controlled by mass flow meters (6), and they entered the mixing chamber (9) to make up the simulated flue gas with mercury vapor. N2 (3) that acted as a carrier gas blew out the mercury vapor overflowing from the mercury permeation tube (8) in the U-tube (7). The temperature in the U-tube (7) was adjusted using a water bath (4) so that different initial concentrations of Hg0 vapor could be obtained by the corresponding temperature. The simulated flue gas entered from the lower portion of the packed column (10). The oxidizing absorption liquid in the water tank (11) was lifted to the upper portion of the packed column using a mechanical diaphragm metering pump (12) and then sprayed through the nozzle (14). The addition of the filler (13) could effectively improve the contact between the absorption liquid and the flue gas so that they could fully react. After the oxidation and absorption reactions, the flue gas entered the silica drying tube (15) to remove the water vapor. Then, the dried gas was diverted through the three-way valve (16). Part of the gas entered a KANE-950 portable flue gas analyzer (19), and the SO2 concentration of the outlet was measured. Another part entered a QM-208b atomic absorption mercury detector (17), and the Hg0 concentration was measured as well. The tail gas entered the exhaust gas absorption bottle (20), which contained a mixed solution of 4% (w/w) KMnO4 + 10% (v/v) H2SO4.

2.2. Materials. The simulated flue gas was made up of SO2, Hg0, N2, and O2. The initial concentration of SO2 was set to 2000 mg/m3, and that of Hg0 was 50 μg/m3. The volume fraction of O2 was set to 8%, and N2 acted as the carrier gas. Since the standard redox potential of Hg2+/Hg0 is 0.85 V, the selected oxidants need to have a higher standard potential than that. Limestone used in the desulfurization experiments was an analytical reagent.

The removal efficiency η was used to evaluate the oxidation and absorption of SO2 and Hg0. The removal efficiency of SO2 could be calculated using eq 1

$$\eta_{SO2} = \frac{C_{SO2,\text{in}} - C_{SO2,\text{out}}}{C_{SO2,\text{in}}} \times 100$$

where ηSO2 is the removal efficiency of SO2 (%), CSO2,in is the inlet SO2 concentration (mg/m3) of the flue gas, and CSO2,out is the outlet SO2 concentration (mg/m3) of the flue gas.

The removal efficiency of Hg0 could be calculated using eq 2

$$\eta_{Hg0} = \frac{C_{Hg0,\text{in}} - C_{Hg0,\text{out}}}{C_{Hg0,\text{in}}} \times 100$$

where ηHg0 is the removal efficiency of Hg0 (%), CHg0,in is the inlet Hg0 concentration (μg/m3) of the flue gas, and CHg0,out is the outlet Hg0 concentration (μg/m3) of the flue gas.

3. RESULTS AND DISCUSSION

3.1. Selection of Oxidants for Hg0 Removal. Experiments of oxidant selection for Hg0 removal were performed in the bubble scaled reactor. Typical strong oxidants in these experiments were KMnO4, H2O2, NaClO2, NaClO2, K2S2O8, and K2FeO4. The redox potentials of these oxidants were all higher than 0.85 V, which is the standard redox potential of Hg2+/Hg0. The results of Hg0 removal by these oxidants are shown in Figure 2.

It could be seen from Figure 2 that the removal efficiency of Hg0 increased with rising concentration of the oxidants, which indicated that the Hg0 removal efficiency was positively correlated with the concentrations of the oxidants. When the concentration increased from 2 to 4 mmol/L, the Hg0 removal efficiency increased significantly. Hg0 removal efficiency by KMnO4 increased from 85 to 89%, NaClO2 increased from 54 to 58%, NaClO2 increased from 54 to 62%, K2S2O8 increased from 51 to 57%, K2FeO4 increased from 59 to 68%, and H2O2 increased from 38 to 48%. As the concentration of oxidants exceeded 4 mmol/L, the growth rate of Hg0 removal efficiency was obviously slowed down with rising concentration of the oxidant. When the oxidant concentration was 10 mmol/L, the Hg0 removal efficiencies of KMnO4, NaClO2, NaClO2, K2S2O8, K2FeO4, and H2O2 reached 95, 63, 68, 59, 73, and 51%, respectively. Hg0 removal efficiencies by these six oxidants...
were significantly different. KMnO₄ presented a Hg⁰ removal efficiency of more than 90%; the oxidative removal efficiencies of Hg⁰ by NaClO₃ and NaClO₃ absorption were both about 70%; Hg⁰ removal efficiencies by K₂S₂O₈ and K₂FeO₄ absorption liquid were about 60%; H₂O₂ showed the lowest removal efficiency of all these six oxidants, which was only around 50%.

The standard redox potential of Hg²⁺/Hg⁰ is 0.85 V. Theoretically, the oxidant whose redox potential is greater than 0.85 V would have the capacity to oxidize Hg⁰ to Hg²⁺. Although KMnO₄ had the highest oxidative removal efficiency of Hg⁰ among all the six strong oxidants, it was still not suitable for the wet oxidation in actual industrial coal-fired flue gas due to its high price and secondary pollution. K₂S₂O₈ needed complex activation to enhance its oxidation. K₂FeO₄ was unstable under acidic and high temperature conditions. The stability of H₂O₂ was also very poor, and Hg⁰ removal efficiency by H₂O₂ was relatively low. Since NaClO₃ was widely used in disinfection of water supply and oxidation treatment of wastewater as a disinfectant and bleaching agent, it had the characteristics of relatively strong oxidation and low price. Meanwhile, the oxidative removal of Hg⁰ by NaClO₃ was higher than that by the other oxidants except KMnO₄. Since KMnO₄ would not be a good choice in the treatment of wastewater, the NaClO₃ was selected to form a kind of composite oxidant to oxidize Hg⁰ in the simulated flue gas. The NaClO₃/NaClO₃ composite oxidant combined with limestone was used in the simultaneous removal of SO₂ and Hg⁰ in a packed tower.

3.2. Thermodynamic Analysis of Wet Oxidation of Mercury Removal. The reaction temperature is an important factor that affects the oxidative removal efficiencies of SO₂ and Hg⁰. The effect of reaction temperature on Hg⁰ removal by the NaClO₃/NaClO₂ composite oxidant was investigated. The absorption liquid was sprayed from the top of the packed tower through the nozzle. The reaction temperature was set from 20 to 80 °C uniformly in seven temperature gradients. The results of Hg⁰ removal efficiency by the composite oxidant NaClO₃/NaClO₂ are shown in Figure 3.

The reaction temperature had a significant effect on the removal of Hg⁰ by the composite oxidant as shown in Figure 3, and the Hg⁰ removal efficiency first increased and then decreased with rising reaction temperature. When the reaction temperature increased from 20 to 40 °C, Hg⁰ removal efficiency by NaClO₃/NaClO₂ began to decrease, dropping to 81 and 75%, respectively. Therefore, the reaction temperature of absorption liquid directly affected the oxidative removal of Hg⁰ by the composite oxidant NaClO₃/NaClO₂. In order to find out the reason why the reaction temperature affected the removal efficiency of Hg⁰, a thermodynamic analysis of the reaction of oxidative demercuration was carried out. The oxidative demercuration was conducted at a solution of pH = 5, where chlorine mainly exists as HOCl and ClO₂ rather than ClO⁻ and ClO₃⁻ under this condition. As the oxidation of Hg⁰ kept consuming ClO⁻ and ClO₃⁻ in the solution as shown in eq 3, HOCl and ClO₂ would proceed to the reaction direction of generating ClO⁻ and ClO₃⁻ so that ClO⁻ and ClO₃⁻ could be supplemented in the solution.

\[
\text{ClO}^- + \text{ClO}_2^- + 6\text{H}^+ + 3\text{Hg}^0 \\
\rightarrow 3\text{Hg}^{2+} + 2\text{Cl}^- + 3\text{H}_2\text{O} \tag{3}
\]

The standard molar formation enthalpy and Gibbs functions of reactants and products in eq 3 under a temperature of 298.15 K and an atmospheric pressure of 100 kPa are shown in Table 1. The standard molar formation Gibbs functions of reactants and products in this study were obtained by querying the Lange’s Handbook of Chemistry. The formation enthalpy and Gibbs function of a chemical reaction could be calculated using eqs 4 and 5.

\[
\Delta_fH_m^\circ(298.15 \text{ K}) = \sum B \nu B \Delta_fH_m^\circ(B, 298.15 \text{ K}) \tag{4}
\]
The reaction could be performed completely. The 

\[ \Delta H_m^o = 3 \Delta H_m^{o}(\text{Hg}^{2+}, \text{ao}) + 2 \Delta H_m^{o}(\text{Cl}^{-}, \text{ao}) + 3 \Delta H_m^{o}(\text{H}_2\text{O}, \text{l}) - \Delta H_m^{o}(\text{ClO}_2^{-}, \text{ao}) \]

\[ - \Delta H_m^{o}(\text{ClO}_2^{-}, \text{ao}) - 6 \Delta H_m^{o}(\text{H}^{+}, \text{ao}) - 3 \Delta H_m^{o}(\text{H}_2\text{O}, \text{g}) \]

\[ = 3 \times 171.1 + 2 \times (-167.159) + 3 \times (-285.8) - (-107.1) - (-66.5) - 3 \times 61.3 \]

\[ = -688.8 \text{ (kJ mol}^{-1}\text{)} \]

The equilibrium constant of eq 3 could be calculated using eq 8.

\[ \ln K^\theta = -\frac{-556.503 \times 10^3}{8.314 \times 298.15} = 224.5 \rightarrow K^\theta = e^{224.5} \]

It could be concluded from the calculation results that \( \Delta H_m^{o}(\text{Hg}^{2+}, \text{ao}) \) of eq 3 was less than zero, which meant that it was an exothermic reaction. An increase in reaction temperature was not conducive to the forward progress of the reaction in an exothermic reaction. However, the rising temperature could increase the reaction speed by strengthening the Brownian motion between molecules. As was calculated using eq 7, \( \Delta G_m^{o} \) of the reaction was less than zero, which meant that Gibbs free energy decreased after the oxidation of Hg\(^0\). Thus, the chemical reaction of Hg\(^0\) oxidation by NaClO/NaClO\(_2\) was spontaneous. Meanwhile, the value of the equilibrium constant in eq 3 was very large, which indicated that the chemical reaction could be performed completely.

### 3.3. Simultaneous Removal of SO\(_2\) and Hg\(^0\) in a Packed Tower.

Based on the results of Hg\(^0\) removal by NaClO/NaClO\(_2\), the limestone was added to carry out the experiment of simultaneous desulfurization and demercuration in a packed tower. The orthogonal experiment was used to select the optimal parameters, which was designed as a three-factor and four-level experiment as shown in Table 2. The effects of the oxidant concentration ratio, initial pH, and liquid–gas ratio on the simultaneous removal of SO\(_2\) and Hg\(^0\) were investigated. In the design of the orthogonal experiment, Hg\(^0\) removal efficiency and SO\(_2\) removal efficiency were selected as the two evaluation indexes. A three-factor and four-level orthogonal experiment with double evaluation indexes was performed. The results of desulfurization and demercuration efficiency in the orthogonal experiment are shown in Figure 4, and the data of the orthogonal experiment are shown in Table 3.

In Table 3, A is the oxidant concentration ratio, mmol/L:mmol/L; B is the initial pH of the absorption liquid; C is the liquid–gas ratio, L/m\(^3\); \( \eta_f \) is the Hg\(^0\) removal efficiency, \%; \( \eta_{fl} \) is the SO\(_2\) removal efficiency, %. \( K_{ij} \) is the average value of \( K_{ij} \) that is, \( K_{ij} = K_{ij}/n \), where \( n \) is the number of occurrences on the j column. \( R_j \) is the range analysis of the factor j, which reflects the fluctuation level of the experimental results on the j column. \( R_j = \max(k_{ij}) - \min(k_{ij}) \). From the perspective of index \( \eta_f \), the larger the value of Hg\(^0\) removal efficiency was, the better the Hg\(^0\) oxidation performance would be. Thus, the maximum level among k\(_{1p}\), k\(_{2p}\), k\(_{3p}\), and k\(_{4p}\) would be selected in this experiment. It could be seen from Table 3 that the three factors of A, B, and C in four levels were compared as follows: k\(_{1A} > k_{3A} > k_{2A} > k_{1A} > k_{2B} > k_{1B} > k_{2B} > k_{3B} \) and k\(_{4C} > k_{3C} > k_{1C} > k_{4C} \). Therefore, A2, B2, and C4 were the optimal levels of A, B, and C, respectively, and the optimal combination was A2B2C4. That is, the ratio of oxidant concentration, initial pH, and liquid–gas ratio on the simultaneous removal of SO\(_2\) and Hg\(^0\) was 10/4/4 (mmol/L:mmol/L), the initial pH was 6, and the liquid–gas ratio was 1. Since the result of the range analysis was \( R_A > R_C > R_B \), the influence of these three factors on index \( \eta_f \) was A > C > B. That is, the oxidant concentration ratio was the main factor, the liquid–gas ratio was the secondary factor, and the initial pH of the absorption liquid was the third factor. From the perspective of index \( \eta_{fl} \), it showed similar characteristics. The larger the value of SO\(_2\) removal efficiency was, the better the SO\(_2\) absorption performance would be. As could be seen from Table 3, the three factors A, B, and C in four levels were compared as follows: k\(_{2A} > k_{4A} > k_{3A} > k_{1A} > k_{2B} > k_{1B} > k_{2B} > k_{3B} \) and k\(_{4C} > k_{3C} \). Therefore, A2, B1, and C4 were the optimal levels of A, B, and C, respectively, and the optimal combination was A2B1C4. That is, the ratio of oxidant concentration, initial pH, and liquid–gas ratio on the simultaneous removal of SO\(_2\) and Hg\(^0\) was 10/4/8 (mmol/L:mmol/L), the initial pH was 6, and the liquid–gas ratio was 1. Since the result of the range analysis was \( R_A > R_C > R_B \), the influence of these three factors on index \( \eta_{fl} \) was A > C > B. That is, the oxidant concentration ratio was the main factor, the liquid–gas ratio was the secondary factor, and the initial pH of the absorption liquid was the third factor.
concentration NaClO/NaClO₂ was 6/4 (mmol/L: mmol/L), the initial pH was 5, and the liquid–gas ratio was 18. Since the result of the range analysis was $R_c > R_A > R_B$, the influence of these three factors on index $\eta_1$ was $C > A > B$. That is, the liquid–gas ratio was the main factor, and the oxidant concentration ratio was the secondary factor, and the initial pH of the absorption liquid was the third factor.

The optimal combinations of $A4B2C4$ and $A2B1C4$ could be obtained by evaluation of the two indexes $Hg^0$ removal efficiency $\eta_1$ and SO$_2$ removal efficiency $\eta_2$. If factor A took level 4, the average value $k_{A4,Hg}$ of $Hg^0$ removal efficiency $\eta_1$ was 83.0, and the average value $k_{1A,SO2}$ of SO$_2$ removal efficiency $\eta_2$ was 96.8. If factor A took level 2, the average value $k_{2A,Hg}$ of $Hg^0$ removal efficiency $\eta_1$ was 77.5, and the average value $k_{2A,SO2}$ of SO$_2$ removal efficiency $\eta_2$ was 97.1. The change rate of $Hg^0$ removal efficiency $\eta_1$ was $\frac{83.0 - 77.5}{83.0} \times 100 = 6.6\%$, while the change rate of SO$_2$ removal efficiency $\eta_2$ was $\frac{96.8 - 97.1}{96.8} \times 100 = 0.31\%$. This indicated that the change between level 2 and level 4 showed a more significant effect on $Hg^0$ removal efficiency $\eta_1$ than on SO$_2$ removal efficiency $\eta_2$. Thus, level 2 of factor A was the optimal condition. Similarly, if factor B took level 2, the average value $k_{1B,Hg}$ of $Hg^0$ removal efficiency $\eta_1$ was 74.4, and the average value $k_{1B,SO2}$ of SO$_2$ removal efficiency $\eta_2$ was 96.6. If factor B took level 1, the average value $k_{2B,Hg}$ of $Hg^0$ removal efficiency $\eta_1$ was 74.4, and the average value $k_{2B,SO2}$ of SO$_2$ removal efficiency $\eta_2$ was 96.7. The change rate of $Hg^0$ removal efficiency $\eta_1$ was $\frac{74.8 - 74.4}{74.8} \times 100 = 0.53\%$, while the change rate of SO$_2$ removal efficiency $\eta_2$ was $\frac{96.6 - 96.7}{96.6} \times 100 = 0.1\%$. This indicated that the change between level 2 and level 4 showed a larger effect on $Hg^0$ removal efficiency $\eta_1$ than that of SO$_2$ removal efficiency $\eta_2$, but the difference between these two was not much. Thus, level 1 and level 2 of factor B were both the optimal conditions.

Two optimal combinations of $A4B1C4$ and $A2B2C4$ were obtained by the analysis of the results of the orthogonal experiment. They were as follows: the oxidant concentration ratio was 10/4, the initial pH of absorption liquid was 5, and the liquid–gas ratio was 18 ($A4B1C4$); the oxidant concentration ratio was 10/4, the initial pH of absorption liquid was 6, and the liquid–gas ratio was 18 ($A4B2C4$). In order to verify the correctness of the optimal parameters, the simultaneous desulfurization and demercuration experiments were carried out under both the two optimal conditions. $Hg^0$ removal efficiency $\eta_1$ and SO$_2$ removal efficiency $\eta_2$ reached 85.4 and 99.5% under the condition of $A4B1C4$ as shown in Table 3, while $\eta_1$ and $\eta_2$ were 84.7 and 98.8% under the condition of $A4B2C4$ in the supplementary experiment, respectively. Therefore, the optimal combination of the orthogonal experiment was an oxidant concentration ratio of 10/4, an initial pH of absorption liquid of 5, and a liquid–gas ratio of 18 ($A4B1C4$).

### 3.4. Mechanism Analysis of Simultaneous Removal of SO$_2$ and Hg$^0$

In order to analyze the content of mercury and its existing form in the absorption liquid and the by-product gypsum, the absorption liquid after the experiment of simultaneous desulfurization and demercuration by NaClO/NaClO$_2$ combined with limestone was collected. Solid products of oxidation and absorption reactions were collected as well. After the separated gypsum solids were dried and milled, the samples were characterized by SEM. The results are shown in Figure 5.

Figure 5a shows the morphological features of Ca(OH)$_2$ as the blank sample, Figure 5b shows the morphological features of the solid sample after Ca(OH)$_2$ absorbed SO$_2$, and Figure 5c shows the morphology features of the solid sample after...
oxidation and absorption of SO\(_2\) and Hg\(^0\) by NaClO/NaClO\(_2\) composite oxidants combined with limestone. As could be seen from Figure 5, the surface of the blank sample Ca(OH)\(_2\) (sample a) was rough, the surface of sample b was full, and the surface of sample c was relatively smooth. The rough surface of Ca(OH)\(_2\) became full after absorbing SO\(_2\). The full surface of the solid sample became relatively smooth after the oxidation product that was produced from SO\(_2\) and Hg\(^0\) oxidation adhered to the surface of Ca(OH)\(_2\). To further explore the main components of these solid samples, XRD characterization analysis of them was carried out, and the results are shown in Figure 6.

Table 3. Results and Analysis of the Orthogonal Experiment

| experiment no. | factors | results | | |
|---------------|---------|---------|---|---|
|               | A       | B       | C   | \(\eta_1\) | \(\eta_2\) |
| 1             | 1       | 1       | 1   | 220.5 | 95.4 |
| 2             | 1       | 2       | 2   | 297.6 | 91.2 |
| 3             | 1       | 3       | 3   | 290.8 | 93.6 |
| 4             | 1       | 4       | 4   | 309.9 | 94.8 |
| 5             | 2       | 1       | 2   | 322.7 | 57.5 |
| 6             | 2       | 2       | 1   | 332   | 75.4 |
| 7             | 2       | 3       | 4   | 77.5  | 77.8 |
| 8             | 2       | 4       | 3   | 80.7  | 78.6 |
| 9             | 3       | 1       | 3   | 83.0  | 81.4 |
| 10            | 3       | 2       | 4   | 83.5  | 83.1 |
| 11            | 3       | 3       | 1   | 78.3  | 92.5 |
| 12            | 3       | 4       | 2   | 79.5  | 96.3 |
| 13            | 4       | 1       | 4   | 55.1  | 85.4 |
| 14            | 4       | 2       | 3   | 77.5  | 84.7 |
| 15            | 4       | 3       | 2   | 80.7  | 82.6 |
| 16            | 4       | 4       | 1   | 83.0  | 79.3 |

\(\eta_1\) (Hg\(^0\) removal efficiency)

- \(K_{i1}\) = 220.5, \(K_{i2}\) = 297.6, \(K_{i3}\) = 290.8
- range analysis \(R_1\): 27.9, order A > C > B
- optimal level: A4 B2 C4
- optimal condition: A4B2C4

\(\eta_2\) (SO\(_2\) removal efficiency)

- \(K_{j1}\) = 375.7, \(K_{j2}\) = 386.7, \(K_{j3}\) = 371.2
- range analysis \(R_2\): 3.2, order C > A > B
- optimal level: A2 B1 C4
- optimal condition: A2B1C4

Figure 6a shows the XRD of Ca(OH)\(_2\) as the blank sample, and Figure 6b shows the XRD of the solid sample after Ca(OH)\(_2\) absorbed SO\(_2\), and Figure 6c shows the XRD of the solid sample after oxidation and absorption of SO\(_2\) and Hg\(^0\) by NaClO/NaClO\(_2\) composite oxidants combined with limestone. The main crystal structure of sample a was Ca(OH)\(_2\), the main crystal structure of sample b was CaSO\(_3\), and the main crystal structure of sample c was CaSO\(_4\). CaSO\(_4\) was produced by the process of Ca(OH)\(_2\) and the composite oxidant NaClO/NaClO\(_2\) oxidizing and absorbing SO\(_2\) and Hg\(^0\), which indicated that SO\(_2\) was also oxidized while Hg\(^0\) was being oxidized. Thus,
the simultaneous desulfurization and demercuration by composite oxidant NaClO/NaClO2 combined with limestone were beneficial to SO2 removal. According to the XRD characterization results of the solid samples, the mechanism of Ca(OH)2 and composite oxidant NaClO/NaClO2 oxidizing and absorbing SO2 could be obtained as follows:

$$\text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$$  \hspace{1cm} (9)

$$2\text{Ca}^{2+} + 2\text{SO}_2 + \text{ClO}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{CaSO}_4 + \text{Cl}^- + 4\text{H}^+$$  \hspace{1cm} (10)

$$\text{Ca}^{2+} + \text{SO}_2 + \text{ClO}^- + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 + \text{Cl}^- + 2\text{H}^+$$  \hspace{1cm} (11)

The mercury content in the process of simultaneous desulfurization and demercuration oxidized by composite oxidants NaClO/NaClO2 was measured, which included the mercury content both in the gypsum solid sample and in the supernatant. The results are shown in Table 4.

**Table 4. Concentration of Hg in the Absorbing Solution and Solid Products**

| experiment no. | concentration of Hg in absorbing solution (µg/L) | concentration of Hg in solid products (ng/g) |
|----------------|-----------------------------------------------|--------------------------------------------|
|                | blank (limestone) solid products               |                                            |
| 1              | 4.37                                          | 13.27                                      | 1269.6                                    |
| 2              | 4.41                                          | 13.74                                      | 1136.7                                    |
| 3              | 4.28                                          | 13.40                                      | 1185.6                                    |
| average        | 4.35                                          | 13.47                                      | 1197.3                                    |

It could be seen from Table 4 that the concentration of mercury in the solid product of the composite oxidant combined with limestone after simultaneous removal of SO2 and Hg0 was about 1197.3 ng/g, which was much higher than the mercury content of the blank sample of 13.47 ng/g. It indicated that the solid product contains a certain amount of mercury, and this part of mercury might be combined with anions such as SO4^{2-}, SO3^{2-}, OH^-, and Cl^- in the absorption liquid. The average concentration of mercury in the three supernatant samples was 4.35 µg/L. Combined with the detection results of mercury in gypsum solid samples, it indicated that 23% of the mercury was in the gypsum as a mercury compound, and 77% of the mercury was in the supernatant as mercury ions. Normally, the solid products formed by the dehydration of CaSO4 sludge would not be considered as hazardous wastes in China. The dry CaSO4 sludge that came from the product of WFGD has been widely used in the field of building materials.39

Since the experiment of NaClO/NaClO2 composite oxidant on mercury removal was greater than that of a single oxidant, the mechanism of Hg0 oxidation by the NaClO/NaClO2 composite oxidant was studied. The chemical properties of NaClO and NaClO2 showed that the NaClO/NaClO2 composite oxidant dissociated into ClO^- and ClO2^- in solution. However, the ClO^- and ClO2^- ions were not stable in solution. When factors such as pH and temperature in the absorbing liquid changed, a series of decomposition reactions occurred. Based on the experimental results from Zhao et al.'s and Fabian et al.'s studies,30,41 the ionic components in the NaClO/NaClO2 solution were mainly ClO_3^-, ClO_2^-, ClO^-, and Cl-. Under acidic conditions, the redox potentials of ClO^-/Cl-, ClO2^-/Cl-, and ClO^-/Cl^- were 1.48, 1.57, and 1.45 V, respectively. They were all higher than 0.85 V redox potential needed to oxidize Hg0 to Hg^2+. The mechanism of NaClO/NaClO2 oxidizing Hg0 could be obtained as shown in eqs 12–14, and the mechanism diagram of SO2 and Hg0 oxidized by NaClO/NaClO2 with limestone is shown in Figure 7.

$$\text{ClO}_3^- + 2\text{H}^+ + \text{Hg}^0 \rightarrow \text{Hg}^{2+} + \text{ClO}_2^- + \text{H}_2\text{O}$$  \hspace{1cm} (12)

$$\text{ClO}_2^- + 2\text{H}^+ + \text{Hg}^0 \rightarrow \text{Hg}^{2+} + \text{ClO}^- + \text{H}_2\text{O}$$  \hspace{1cm} (13)

$$\text{ClO}^- + 2\text{H}^+ + \text{Hg}^0 \rightarrow \text{Hg}^{2+} + \text{Cl}^- + \text{H}_2\text{O}$$  \hspace{1cm} (14)

4. CONCLUSIONS

Experimental research on the removal of SO2 and Hg0 by composite oxidant NaClO/NaClO2 was carried out in a packed tower in this study, and conclusions could be drawn as follows: (1) oxidative removal of Hg0 by six oxidants such as KMnO4, NaClO2, NaClO, K2S2O8, K2FeO4, and H2O2 was investigated through a static experiment in a bubble reactor. Considering the factors of Hg0 removal efficiency, secondary pollution, and economic cost, the composite oxidant NaClO/NaClO2 was finally selected to carry out the three-factor and four-level orthogonal experiments of simultaneous removal of SO2 and Hg0 in a packed tower. (2) Results of thermodynamic analysis of Hg0 removal showed that Hg0 oxidation by NaClO/NaClO2 could react completely. Meanwhile, the orthogonal experiments showed that the optimum combination of NaClO/NaClO2 combined with limestone was A4B1C4; that is, the concentration ratio of NaClO/NaClO2 was 10/4, initial
pH was 5, and the liquid–gas ratio was 18 (L/m³). The removal efficiencies of SO₂ and Hg⁰ under these optimal conditions reached up to 99.5 and 85.4%, respectively. (3) It was found out through the characteristic analysis of the solid products that CaSO₄ was the main solid product during the wet oxidation process. 23% of the oxidized mercury was in the solid products as mercury compounds, and 77% was in the supernatant as mercury ions.

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**Notes**

The authors declare no competing financial interest.

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