Macroscopic Kinetics of Simultaneous Desulfurization and Denitrification by MgO/NaClO₂ Solution

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Keywords: Reaction kinetics, Flue gas, Simultaneous desulfurization and denitrification, MgO, NaClO₂.

Abstract. Based on the early research results of reaction characteristics of the simultaneous desulfurization and denitrification by MgO/NaClO₂ solution, the macroscopic reaction kinetics was investigated in a small-scale bubbling reactor. The effect of various factors on the reaction rate was investigated in the experiments, i.e. initial NaClO₂ concentration, solution pH and reaction temperature. The reaction rate equations and the reaction order of NO, SO₂ and NaClO₂ were also obtained by experiments and analysis. The results showed that reaction orders of NO, SO₂ and NaClO₂ during simultaneous desulfurization and denitrification were all pseudo-first-order. And the reaction equations of NO, SO₂ and NaClO₂ were \(r = 0.079C_{NO}^{0.984}\), \(r = 0.066C_{SO₂}^{0.989}\) and \(r = 0.066C_{SO₂}^{0.998}\), respectively. The reaction rate of NO, SO₂ and NaClO₂ were proportional to the NaClO₂ concentration and inversely proportional to the solution pH; the reaction rate of SO₂ was less affected by the concentration and pH of NaClO₂. When the reaction temperature was 50 °C, the reaction rate of NO and SO₂ was the largest, and the reaction temperature had little effect on the reaction rate of NaClO₂.

Introduction

Pollutants such as sulfur dioxide (SO₂) and nitrogen oxides (NOₓ) released from the combustion of a large amount of coal are the leading causes of atmospheric environmental problems such as photochemical pollution, acid rain, ozone, and regional haze\[^{[1-3]}\]. As the primary pollution sources, the SO₂ and NOₓ discharged from coal-fired power plants have been effectively controlled in recent years, and the intensification of atmospheric pollution has been alleviated. However, the atmospheric pollution in China is still severe\[^{[4-7]}\]. The reason is that other pollution sources, especially the small-sized and medium-sized industrial boilers, which are the second-largest pollution source in China, have not been adequately controlled. These industrial boilers, including the glass, steel, cement and other industries, are widely distributed, small in capacity, weak in economic capacity, unstable flue gas conditions, and complex flue gas components. Because of these features, the most popular desulfurization and denitrification technologies (such as WFGD-SCR) can’t be used effectively in the small-sized and medium-sized industrial boilers. Therefore, it has important practical significance and broad application prospects to develop an efficient, safe and economical technology to control SO₂ and NOₓ emissions from small-sized and medium-sized coal-fired industrial boilers\[^{[8-10]}\].

Over 90% of the NOₓ released from coal combustion is NO. Since NO is hardly soluble in water or solution, NOₓ cannot be directly absorbed during the desulfurization process. Among the various schemes to solve this problem, the method of oxidizing NO with an oxidant to become water-soluble nitrogen dioxide (NO₂) and then performing a liquid phase absorption reaction has become the focus of research by Chinese and foreign scholars. Sodium chlorite (NaClO₂) has
become a concerned oxidant due to its high oxidation efficiency, secure storage and transportation [11-13].

The research on desulfurization and denitrification by NaClO₂ started in the last century. Hsu[14] carried out a low-concentration NO kinetic study in a flat-plate gas-liquid interface stirred tank, and determined that the reaction rate constant of NaClO₂/NaOH solution absorption of NO was $6.55 \times 10^8 \text{ L}^{-2} \text{ mol}^{-2} \cdot \text{s}^{-1}$. While Brogren[15] studied the reaction kinetics of NO in packed columns, it was found that when the reaction temperature was below 20 °C and the pH was 8-11, the reaction order of NO was 1.3-1.8, and the reaction order of NaClO₂ was 0.6-0.9. Samuel O et al. [16] carried out experiments on the desulfurization and denitrification of NaClO₂ solution in a bubbling column and found that the pH of the solution was the critical factor for desulfurization and denitrification, and that SO₂ inhibited the NO absorption efficiency. And the conclusion that the buffered absorbent can weaken the escape of ClO₂ was obtained. Chien [17-18] used a spray tower to study the absorption of NO by NaClO₂ absorbing solutions with different pH. The experimental results found that the solution under acidic conditions has a significantly higher NO absorption efficiency than that under alkaline conditions. Under acidic conditions, the reaction order of NaClO₂ is 2, the reaction order of NO is 1.4, and the activation energy is 71.8 kJ/mol; under alkaline conditions, the reaction order of NaClO₂ is 2.5, the reaction order of NO is 1.6, and the activation energy is 139.6 kJ/mol. Hsin Chu et al. [19-20] carried out a desulfurization and denitrification reaction in a stirred reactor using an alkaline NaClO₂ solution. And they found that when $c(\text{NaClO}_2) > 0.2\text{ mol/L}$ and $c(\text{NaOH}) > 0.1\text{ mol/L}$, the desulfurization process is controlled by the gas film. At this time, NO had no effect on SO₂ absorption, and O₂ had no obvious effect on combined desulfurization and denitrification. Zhao Yi et al. [21-22] used a bubbling reactor at a pH of 5.5 and a reaction temperature of 25 °C to determine the SO₂ reaction order is 1 and the activation energy 21.6 kJ/mol. Furthermore the NO reaction order is 1 and the activation energy is 8.2 kJ/mol. Hao Runlong et al. [23-27] used the combined absorption solution of NaClO₂ and sodium humate to remove the flue gas pollutants, and found that under the synergistic effect of pH/temperature and pH/retention time, the yield of ClO₂ was significantly affected. The optimal pH range of NaClO₂ is 3~7. These research results have promoted the development of NaClO₂ desulfurization and denitrification technology. However, there are still problems such as high removal costs and unsuitable for desulfurization and denitrification of small-sized and medium-sized industrial boilers.

The desulfurization technology of Magnesium oxide (MgO) converts SO₂ to magnesium sulfate (MgSO₄), which has higher economic value. Therefore, it could not only control pollution but also recover by-production. Moreover, it has many other advantages, such as high desulfurization efficiency, small liquid-gas ratio, stable operation, and strong flue gas adaptability [28]. In addition, China's magnesite reserves rank first in the world. Therefore, the use of MgO desulfurization can not only take advantage of China's unique resource advantages to control SO₂ emissions, but also greatly reduce the cost of desulfurization by recycling by-product MgSO₄ [29]. In recent years, this technology has been widely used in small-sized and medium-sized industrial boilers in China. The combination of MgO desulfurization technology and the oxidation characteristics of NaClO₂ would provide a new and effective method for the simultaneous desulfurization and denitrification of small-sized and medium-sized industrial boilers. Therefore, based on MgO method in the previous research, the research team used NaClO₂ as an additive in the simultaneous desulfurization and denitrification. The reaction characteristics of simultaneous desulfurization and denitrification by MgO/NaClO₂ were determined. Under the optimal experimental conditions, the NO, NOₓ and SO₂ removal efficiencies by MgO/NaClO₂ reached 96.93%, 60.16% and 99%, respectively [30]. The method achieves the purpose of simultaneous desulfurization and denitrification without changing the structure of the desulfurization body, and only by modifying the desulfurization slurry preparation system. Although scholars have carried out many studies on the macrodynamics of NaClO₂, their research cannot directly guide the improvement and theoretical analysis of simultaneous desulfurization and denitrification by MgO/NaClO₂ due to the differences between these systems. Therefore, based on the previous research results, this paper conducted macroscopic reaction kinetics research, explored the effects of NaClO₂ concentration, reaction temperature, and
solution pH on the reaction rate of desulfurization and denitrification by MgO/NaClO₂, studied the reaction order of each reactant, and determined the reaction rate equation.

Experiment
Experimental Device and Method
The experimental device mainly consisted of a simulated flue gas preparation system, a reaction system, and a data acquisition and analysis system. Controlled by the mass flow meters (D08-3E, D08-4E, Beijing SevenStar Electronics Co., Ltd.), N₂ (99.999%), O₂ (99.999%), NO (0.25%) and SO₂ (0.40%) (Baoding North Special Gas Co., Ltd.) were passed into the gas distribution cabinet (QH-2, Beijing Tongsheng Leader Technology Co., Ltd.) to mix uniformly to become a simulated flue gas with a set concentration. The primary device of the system was a bubbling reactor with a volume of 1 L. The reaction temperature was controlled by a digital constant temperature water bath (DF-101S, Zhengzhou Great Wall Technology Industry and Trade Co., Ltd.) under the monitoring of a thermocouple. The desulfurization and denitrification reaction of the simulated flue gas were carried out in the reaction system. The data acquisition and analysis system were mainly composed of a Fourier infrared flue gas analyzer (ARIS IGS Analyzer, Thermo Fisher Scientific, USA, ±0.01 ppm) and a computer, which was used to monitor and record the concentration change of various components in the flue gas before and after the simulated flue gas reaction. When the concentration of SO₂ and NOₓ observed by the analyzer changes within ± 5 ppm (SO₂±13.085 mg/m³, NO±6.135 mg/m³), the reaction was considered to have reached equilibrium.

The reagents used in the experiment were all analytical grade except that the purity of NaClO₂ was 90%. Deionized water was used throughout the experiment. The absorbent solution was prepared by dissolving MgO and NaClO₂ reagents in deionized water with a predetermined quality. The pH of the solution was determined from a citric acid-sodium dihydrogen phosphate buffer solution or a sulfuric acid solution under the monitoring of a pH meter (PHS-3E, Shanghai Inesa Scientific Instrument Co., Ltd.).

![Figure 1. Main experimental apparatus for simultaneous desulfurization and denitrification by MgO/NaClO₂](image)

(1-data processing system; 2-flue gas analyzer; 3-cold trap; 4-thermostatic water bath and bubble reactor; 5-gas distribution system; 6-cylinder; 7-three-way valve).

Data Calculation and Analysis Methods
The removal efficiency of flue gas pollutants was calculated by equation (1).

\[
\eta = \frac{A_o - A_1}{A_o} \times 100\% 
\]

\(\eta\)—removal efficiency of pollutants [%];
\(A_o\)—Initial concentration of flue gas pollutants [mg/m³];
\(A_1\)—concentration of flue gas pollutants after reaction [mg/m³].

When the reaction was performed for 0, 10, 20, 30, 40, and 50 minutes, respectively, the pipette gun was used to remove 2 ml of the absorption solution accurately, and then various ions were
measured. The chloride, sulfate, sulfite, nitrate, and nitrite ions in the solution were quantitatively analyzed by an ion analyzer [31]. Chlorite ion (ClO\textsubscript{2}\textsuperscript{-}), chlorine dioxide (ClO\textsubscript{2}), and chlorine gas (Cl\textsubscript{2}) in the solution were measured by a five-step iodometric method [32].

**Experimental Results and Analysis**

**Effect of Initial NaClO\textsubscript{2} Concentration**

As an oxidant and absorbent, the concentration of NaClO\textsubscript{2} directly affects the oxidation rates of SO\textsubscript{2} and NO\textsubscript{x} in the solution. Therefore, experiments on the effect of initial NaClO\textsubscript{2} concentration on the reaction rate were carried out.

The experimental conditions were as follows: NO 613.5 mg/m\textsuperscript{3}, SO\textsubscript{2} 2093.6 mg/m\textsuperscript{3}, MgO 0.172 g/L, O\textsubscript{2} 10%, flue gas flow rate 1.0 L/min, reaction temperature 50 °C, and solution pH 5.3. The concentration of NaClO\textsubscript{2} was used as experimental variables to select as 3 mmol/L, 5 mmol/L, 7 mmol/L, 10 mmol/L, and 20 mmol/L. The experimental results are shown in Figure 2.

![Effect of NaClO\textsubscript{2} concentration on the rate of NO\textsubscript{3}- production](image)

(a) Effect of NaClO\textsubscript{2} concentration on the rate of NO\textsubscript{3}- production

![Effect of NaClO\textsubscript{2} concentration on the rate of SO\textsubscript{4}\textsuperscript{2-} production](image)

(b) Effect of NaClO\textsubscript{2} concentration on the rate of SO\textsubscript{4}\textsuperscript{2-} production

![Effect of NaClO\textsubscript{2} Concentration on the Reaction Rate of NaClO\textsubscript{2}](image)

(c) Effect of NaClO\textsubscript{2} Concentration on the Reaction Rate of NaClO\textsubscript{2}

Figure 2. Effect of NaClO\textsubscript{2} concentration on reaction rate.

Previous studies showed that only NO\textsubscript{3}- was detected in the simultaneous desulfurization and denitrification solution, and NO\textsubscript{2} was not observed. Therefore, it can be considered that the NO removed in the reaction was completely converted into NO\textsubscript{3}-. The rate of NO\textsubscript{3}- production in solution was directly proportional to the rate of NO removal. It can be seen from Figure 2 (a) that the NO\textsubscript{3}- formation rate increased with the increase of NaClO\textsubscript{2} concentration. When the NaClO\textsubscript{2} concentration increased from 3 mmol/L to 20 mmol/L, the rate of NO\textsubscript{3}- production increased from 0.7738 mg/(L·min) to 0.9301 mg/(L·min). It can be seen from the above figure that the reaction rate of NO\textsubscript{3}- accelerated with the increase of the concentration of NaClO\textsubscript{2}. However, when the NaClO\textsubscript{2} concentration was higher than 10 mmol/L, the increase rate of NO\textsubscript{3}- generation decreased with the increase of the NaClO\textsubscript{2} concentration. This is because the reaction of MgO/NaClO\textsubscript{2} with NO is a
gas-liquid phase reaction with chemical reactions. The reaction rate was determined by the gas-liquid mass transfer rate and the chemical reaction rate. An increase of the NaClO₂ concentration can enhance the chemical reaction rate and reduce the concentration of NO in the liquid phase, thereby further improving the gas-liquid mass transfer rate. However, NO is a poorly soluble gas. When the concentration of NaClO₂ increased to a certain extent, the rate of increase of the chemical reaction rate with the NaClO₂ concentration was limited. At this time, the total reaction rate was mainly controlled by the resistance of gas-phase mass transfer, which means that increasing the NaClO₂ concentration cannot significantly promote the total reaction rate.

There was only SO₄²⁻ but no SO₃²⁻ in the simultaneous desulfurization and denitriﬁcation solution. Therefore, similar to the relationship between NO₃⁻ and NO, it can be considered that all the removed SO₂ was converted into SO₄²⁻. The higher the rate of SO₄²⁻ formation, the more the SO₂ removed. It can be seen from Figure 2 (b) that the NaClO₂ concentration did not change regularly to the reaction rate of SO₂. When the NaClO₂ concentration in the solution was 3-20 mmol, the rate of SO₄²⁻ generation fluctuated between 4.5462-4.8805 mg/(L·min). The fluctuation was consistent with the experimental phenomenon of the inﬂuencing factors in the earlier period. In the experimental range, the removal efficiency of SO₂ remained above 99.6%. The high SO₂ removal efficiency is mainly because the solubility of SO₂ is significant, and its reaction rate with MgO and NaClO₂ was very fast, so even a smaller NaClO₂ concentration can obtain a higher desulfurization efficiency.

It can be seen from Figure 2 (c) that the initial NaClO₂ concentration had a signiﬁcant effect on the reaction rate of NaClO₂ when other reaction conditions were unchanged. It can be seen from 2.4.3 that the reaction order of NaClO₂ was 0.998. Therefore, the larger the initial NaClO₂ concentration, the faster the decline rate of the NaClO₂ concentration in the solution. After dimensionless treatment of the reaction rate of NaClO₂, it can be found that when the initial concentration of NaClO₂ increased from 3 mmol/L to 20 mmol/L, the corresponding reaction rate rised from 3.4570 to 11.2107.

Influence of Solution PH

The effect of solution pH on the oxidation ability of NaClO₂ is signiﬁcant. Therefore, the solution pH was set to 3.0, 4.0, 5.3, 6.2, and 7.0, respectively. Other conditions were NO of 613.5 mg/m³, SO₂ of 2093.6 mg/m³, MgO of 0.172 g/L, O₂ of 10%, flue gas flow rate of 1.0 L/min, reaction temperature of 50 ℃, and NaClO₂ concentration of 5 mmol/L. The experiments on the effect of the solution pH on the reaction rates of NO, SO₂ and NaClO₂ were carried out. The experimental results were shown in Figure 3.

It can be seen from Figure 3 (a) that the NO₃⁻ formation rate in the solution gradually decreased with the increase of the solution pH. When the solution pH was 7.0, the NO₃⁻ formation rate was 0.1349 mg/(L·min). When the pH decreased to 3, the NO₃⁻ production rate increased to 0.7767 mg/(L·min). When the pH value decreased from 6.2 to 5.3, the NO₃⁻ production rate increased obviously; when the pH value was less than 5.3, the increasing tendency of the rate with the pH value decreases was slowed. The reason is the lowering of the pH value of the solution increased the oxidizing power of the solution. At this time, the rate of NO and NO₂⁻ being oxidized to NO₃⁻ and NO₃⁻ increased, thereby reducing the gas-liquid mass transfer resistance and increasing the rate of a chemical reaction.

Figure 3 (b) showed that when the solution pH was between 3 and 6.2, there was no signiﬁcant change in the SO₄²⁻ formation rate. This was because MgO was hydrolyzed in water to form magnesium hydroxide (Mg(OH)₂). According to the calculation of the chemical equilibrium constant in the Mg(OH)₂-SO₂-H₂O system, it can be known that there was scarcely any SO₂ molecule in the solution at the pH value of 3.0 ~ 9.5 [26]. In other words, the Mg(OH)₂ solution can achieve high-efficiency desulfurization.

It can be seen from Figure 3(c) that the reaction rate of NaClO₂ increased with the increase of pH. Because the lower the pH value of the solution was, the stronger the oxidation of NaClO₂ was, and the faster the reaction rate with other substances was. When the pH was lower than 4, ClO₂⁻ reacted with H + through disproportionation reaction [23].
\[ 8H^+ + 8ClO_2^- \rightarrow 6ClO_2 + Cl_2 + 4H_2O \]

ClO₂ and Cl₂ with stronger oxidizing capacity were generated, and these substances rapidly reacted with NO and SO₂ and consumed by NO and SO₂, which promoted the reaction, thereby increasing the reaction rate of NaClO₂.

![Graph](image1)

(a) Effect of pH value of the solution on NO₃⁻ production

![Graph](image2)

(b) Effect of solution pH on the rate of SO₄²⁻ rate formation

![Graph](image3)

(c) Effect of solution pH on the reaction rate of NaClO₂

Figure 3. Effect of pH on Reaction Rate.

**Influence of Solution Temperature**

The effect of solution temperature on gas-liquid reaction is complicated, which mainly manifests in two aspects. On the one hand, an increase in the temperature of the solution increases the mass transfer resistance of the gas from the gas film to the liquid film, reduces the solubility of the gas in the liquid phase, further reduces the reaction rate. On the other hand, an increase in temperature promotes an increase in the rate of chemical reactions. Therefore, when experimentally studying the effect of solution temperature on the reaction rate, the temperatures were selected as 25 °C, 40 °C, 50 °C, 60 °C, and 70 °C, respectively. Other conditions were NO of 613.6 mg/m³, SO₂ of 2093.6 mg/m³, MgO of 0.172 g/L, O₂ of 10%, flue gas flow rate of 1.0 L/min, solution pH value of 5.3, NaClO₂ concentration of 5 mmol/L condition. The experimental results were shown in Figure 4.

![Graph](image4)

(a) Effect of the temperature of the absorbing solution on the rate of NO₃⁻ production

![Graph](image5)

(b) Effect of solution temperature on SO₄²⁻ production rate
Effect of solution reaction temperature on NaClO₂ reaction rate

As shown in Figure 4 (a), the effect of reaction temperature on the NO₃⁻ production rate did not change monotonously. When the solution temperature was between 40 °C and 60 °C, the rate of NO₃⁻ production increased with the increasing temperature. At 60 °C, the NO₃⁻ production rate reached a maximum of 0.8493 mg/(L·min). After that, as the temperature continued to increase, the NO₃⁻ production rate showed a downward trend. Because before the reaction temperature reached 60 °C, the promotion effect of the increased chemical reaction due to the increase of the reaction temperature was greater than the inhibition effect caused by the increase of the gas-phase mass transfer resistance. The overall system showed an increase in both temperature and the rate of NO₃⁻ production (NO removal efficiency). However, when the temperature exceeded 60 °C, the inhibitory effect due to the increase in the resistance of gas phase mass transfer was dominant, so that the NO₃⁻ production rate (NO removal efficiency) decreased with the further increase of the reaction temperature.

It can be seen from Figure 4 (b) that the change in solution temperature had a small effect on the rate of SO₄²⁻ formation, and its lowest value reached 4.4723. This was in line with the experimental phenomenon found in previous studies that the SO₂ removal efficiency can reach more than 99.6% at various temperatures. It is worth noting that the highest value occurred at a reaction temperature of 50 °C. Beyond this temperature, the increase in the reaction temperature decreased the SO₄²⁻ production rate slightly. This may be related to increasing temperature and decreasing SO₂ solubility.

As can be seen from Figure 4 (c), the reaction speed of NaClO₂ was directly proportional to the reaction temperature. As the temperature increased, the reaction rate of NaClO₂ increased. However, there was no phenomenon as shown in the Arrhenius formula: under the same conditions, the chemical reaction rate increased by 2 to 3 times for every 10 °C increase in the reaction temperature. This was because the simultaneous desulfurization and denitrification reactions need to go through a gas-liquid mass transfer process before starting the chemical reaction. An increase of the reaction temperature reduced the solubility of SO₂ and NO in water and it further raised the mass transfer resistance between gas and liquid phase, thereby inhibiting the removal of SO₂ and NO by the absorption liquid. At the same time, the simultaneous desulfurization and denitrification reactions with MgO/NaClO₂ were complex. The increase of temperature promoted the main reaction rate and the side reaction rate. With the superposition of the two effects mentioned above, there was an inflection point of desulfurization and denitrification efficiencies with increasing temperature. In a conclusion, 50 °C was selected as the optimal temperature for simultaneous desulfurization and denitrification by MgO/NaClO₂.

Determination of Reaction Order

Determination of NO Reaction Order. The experimental conditions were SO₂ of 2093.6 mg/m³, oxygen content of 10%, NaClO₂ of 5 mmol/L, flue gas flow rate of 1.0 L/min, reaction temperature of 50 °C, and pH of 5.3. The initial NO concentrations were 153.38 mg/m³, 317.50 mg/m³, 613.50 mg/m³, 920.25 mg/m³, and 1227.00 mg/m³, respectively. The experimental results were shown in Figure 5.
It can be seen from Figure 5 that the change in NO outlet concentration with time was divided into two regions. The first part was the fast reaction zone with time ranging from 0s to 15s; then, it entered the slow reaction zone. As the initial concentration of NO increased, the removal efficiency of NO showed an increasing trend. The main reason was that the initial concentration of NO changes and the partial pressure of NO gas increased, which accelerated the gas-liquid mass transfer rate.

Since the time for the gas to be delivered to the gas analyzer and stabilized was about 4 seconds, the 4th second after the gas was passed in was used as the reaction start time. At the same time, in the fast reaction zone, the initial reaction rate was calculated using the initial concentration method, and the data of rate was dimensionless.

![Figure 5. NO concentration changes over time and order of NO reaction in the fast reaction zone.](image)

The number of classifications obtained from the rate of NO in the fast reaction zone was 0.984≈1, which was a pseudo-first order reaction. The K value was 0.079 by fitting the longitudinal intercept of the equation \( \lg K = -1.1043 \). In the slow reaction zone, it can be seen from Figure 5 that the NO concentration decreased approximately linearly with time, which was consistent with the characteristics of a zero-order reaction. It can be considered that the number of NO reaction stages in the slow reaction zone was zero. When the reaction temperature was 50 °C, the expression of the macro reaction rate in the fast reaction zone was shown in formula (2):

\[
\dot{r} = 0.079C_{NO}^{0.984}\text{mg/(L} \cdot \text{min)}
\]

**Determination of SO\(_{2}\) Reaction Order.** The experimental conditions were NO of 613.5 mg/m\(^3\), oxygen content of 10%, NaClO\(_2\) of 5 mmol/L, flue gas flow rate of 1.0 L/min, reaction temperature of 50 °C, and pH of 5.3. The initial SO\(_{2}\) concentrations were 523.4 mg/m\(^3\), 1046.8 mg/m\(^3\), 2093.6 mg/m\(^3\), 3140.4 mg/m\(^3\), and 4187.2 mg/m\(^3\).

![Figure 6. SO\(_{2}\) concentration changes over time and order of SO\(_{2}\) reaction in the fast reaction zone.](image)

Similar to the measurement of the NO reaction order, the initial time of the reaction for the determination of the SO\(_{2}\) reaction order started from the fourth second. The initial concentration method was used to calculate the reaction rate at the initial moment. The rate data was dimensionless. The experimental results were shown in Figure 6.
It can be seen from Figure 6 that the reaction order of SO\textsubscript{2} in the rapid reaction zone was 0.990 \approx 1, which was a pseudo-first order reaction. The K value was 0.066 by fitting the longitudinal intercept of the equation \(\lg K = -1.1828\). In the slow reaction zone, it can be seen from Figure 6 that the SO\textsubscript{2} concentration decreases linearly with time, which was consistent with the characteristics of a zero-order reaction. It can be considered that the number of reaction stages of SO\textsubscript{2} in the slow reaction zone was zero. It was experimentally measured that when the reaction temperature was 50 °C, the expression of the reaction rate in the fast reaction zone was shown in formula (3):

\[
r = 0.066C_{\text{SO}_2}^{0.990} \text{mg}/(L \cdot \text{min})
\]

(3)

**Determination of the Reaction Order of NaClO\textsubscript{2}** As shown in Figure 2 (c), the experimental conditions were NO of 613.5 mg/m\textsuperscript{3}, SO\textsubscript{2} of 2093.6 mg/m\textsuperscript{3}, oxygen content of 10\%, NaClO\textsubscript{2} of 5 mmol/L, flue gas flow rate of 1.0 L/min, reaction temperature of 50 °C, and pH of 5.3. The NaClO\textsubscript{2} concentrations were 3 mmol/L, 5 mmol/L, 6 mmol/L, 7 mmol/L and 10 mmol/L. The results were shown in Figure 7.

As can be seen from Figure 7, the reaction order of NaClO\textsubscript{2} was 0.998, which was approximately 1. From the vertical intercept of the fitted straight line equation, \(\lg K = 0.2283\), then \(K = 1.692\). The reaction rate of NaClO\textsubscript{2} was as follows:

\[
r = 1.692C_{\text{NaClO}_2}^{0.998} \text{mg}/(L \cdot \text{min})
\]

(4)

The reaction of NaClO\textsubscript{2} to oxidize SO\textsubscript{2} and NO\textsubscript{x} was a pseudo-first order.

**Conclusion**

In this study, macroscopic reaction kinetics was used to perform experiments and calculations on the number of fractions of SO\textsubscript{2}, NO, and NaClO\textsubscript{2}, respectively. The effects of different experimental conditions on the reaction rates of NO, SO\textsubscript{2} and NaClO\textsubscript{2} were explored. The following conclusions were reached.

1. The number of reaction grades for NO was a pseudo-first order. The reaction rate equation was \(r = 0.079C_{\text{NO}}^{0.984}\). The rate of NO\textsubscript{3}\textsuperscript{-} production was directly proportional to the concentration of NaClO\textsubscript{2}, but the change was small. The formation rate of NO\textsubscript{3}\textsuperscript{-} was inversely proportional to the pH value of the solution. Considering that a low pH value caused corrosion to the equipment, it was recommended that the pH value of the absorption solution be selected to be about 5. The effect of temperature on the formation rate of NO\textsubscript{3}\textsuperscript{-} had a maximum value between 50 °C ~ 60 °C, and the maximum value was 0.8493 mol/(L⋅min).

2. The reaction order of SO\textsubscript{2} was a pseudo-first order. The reaction rate equation is \(r = 0.066C_{\text{SO}_2}^{0.990}\). According to experimental observations, the NaClO\textsubscript{2} concentration and pH of the solution had no significant effect on the reaction rate of SO\textsubscript{2}. When the solution temperature was 50 °C, the reaction rate of SO\textsubscript{2} had a maximum value of 5.0959 mol/(L⋅min).

3. The reaction order of NaClO\textsubscript{2} was a pseudo-first order. The reaction rate equation was \(r =
The experimental observation showed that the reaction rate of NaClO₂ was directly proportional to the NaClO₂ concentration and inversely proportional to the pH of the solution. The reaction rate was not significantly affected by temperature.

Acknowledgment

We thank the State Key Research Program (2016YFC0204102) and the National Natural Science Foundation of China (51508188) for supporting this study.

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