Emission characteristics of Cl\textsubscript{2} and ClO\textsubscript{2} during simultaneous removal of SO\textsubscript{2} and NO using NaClO\textsubscript{2} solution

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Abstract. In this study, an experimental apparatus of oxidation + absorption columns was set up to investigated ClO\textsubscript{2} and Cl\textsubscript{2} emission characteristics when NaClO\textsubscript{2} was used as oxidant. Two sets of experiments were designed and compared, one was sampled every 15 min for 2 h and the other one was continuous sampling for 2 h. The results show that the concentration of ClO\textsubscript{2} in the outlet of oxidation column increased first and then decreased while Cl\textsubscript{2} barely changed during the experiment. The concentration of Cl\textsubscript{2} was far less than ClO\textsubscript{2}, which indicated that the chlorine-containing gaseous component was mainly in the form of ClO\textsubscript{2}. After 2 h reaction, the chlorine-containing ions in oxidation liquid before and after reaction were in good consistence with the theoretical calculation. High concentration of Cl\textsuperscript{-} was detected in the absorption liquid, while no ClO\textsubscript{2-} and ClO\textsubscript{3-} existed. As the reaction proceeded, the oxidation liquid gradually turned into light yellow, and pungent odor released.

1. Introduction
Sulfur dioxide (SO\textsubscript{2}) and nitric oxides (NO\textsubscript{x}, 90%-95% in the form of NO) are the most concerned air pollutant in China, which mainly emit from coal-fired power stations and industrial boilers have resulted in photo chemical smog, acid rain, etc.\textsuperscript{[12]}. The mature air pollution control devices for SO\textsubscript{2} and NO in coal-powered stations and industrial boilers are wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) systems. Although the combination of WFGD and SCR can meet the national pollutants emission standards, the high running cost, complicated system and NH\textsubscript{3} escape are the unavoidable problems for industrial applications. Under this background, simultaneous wet flue gas technology might be a valuable option, considered its high efficiency and low investment\textsuperscript{[3]}. Based on the fact that the WFGD system has already obtained wide application in China, how to realize simultaneously desulfurization and denitrification in WEGD system has become one of the research hotspots in the field of air pollution control.

Recently, some oxidations including KMnO\textsubscript{4}\textsuperscript{[4]}, S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-}\textsuperscript{[5]}, Fenton’s reagent\textsuperscript{[6,7]}, H\textsubscript{2}O\textsubscript{2}\textsuperscript{[8]}, ClO\textsubscript{2}\textsuperscript{[9]}, NaClO\textsubscript{2}\textsuperscript{[10,11]} have already been used as additives in absorption liquid of WFGD system to achieve simultaneously desulfurization and denitrification purpose. Among them, NaClO\textsubscript{2} is one of the most potential reagent can be used in the field of simultaneously SO\textsubscript{2} and NO\textsubscript{x} removal. Some research has already been done. For example, Huson et al\textsuperscript{[12]} carried out an experiment of simultaneous removal of SO\textsubscript{2}, NO\textsubscript{x} and Hg from coal flue gas by using a NaClO\textsubscript{2}-enhanced wet scrubbing method, from which, a NaClO\textsubscript{2} began to be used as an additive of simultaneous removal of multi-pollutant of fuel gas was proposed. In the research of Zhao et al\textsuperscript{[13]}, NaClO\textsubscript{2}+NaClO\textsubscript{2} oxidant was used to investigated simultaneous removal of SO\textsubscript{2} and NO from fuel gas, under the optimal conditions, the removal efficiency of SO\textsubscript{2} and NO reached 100% and 85% respectively. In NaClO\textsubscript{2}+NaBr oxidant oxidation
system, NO and Hg$^0$ are first pre-oxidized and then along with SO$_2$ absorbed by Ca(OH)$_2$, the average simultaneous removal efficiencies of SO$_2$, NO and Hg$^0$ were 91%, 100% and 93% respectively$^{[14]}$. Hao et al$^{[15]}$ proposed a novel complex oxidant NaClO$_2$/Na$_2$S$_2$O$_8$, the system could convert NO and SO$_2$ into NO$_2^-$, NO$_3^-$ and SO$_4^{2-}$ with the efficiency of 87.2% and 100%.

Though NaClO$_2$ can be used as an oxidant in SO$_2$ and NOx simultaneous removal reaction, Cl$_2$ and ClO$_2$ are produced as reaction byproducts of NaClO$_2$, which consume NaClO$_2$ and may affect the removal efficiency of SO$_2$ and NOx. So in this study, a two-column (oxidation column + absorption column) experimental apparatus was set up for simultaneous removal of SO$_2$ and NO using NaClO$_2$ solution, Cl$_2$ and ClO$_2$ emitting from the oxidation column were sampled and detected by ion chromatography.

2. Materials and methods

2.1. Experimental apparatus

Fig.1 shows the schematic diagram of the experimental apparatus of simultaneous removal of SO$_2$ and NOx by wet scrubbing using NaClO$_2$ solution. This experimental apparatus included a flue gas simulation system, an oxidation column and an absorption column. The pipeline was made of Teflon to avoid erosion and the temperature of oxidation column and absorption column both remain constant by using a thermostat.

N$_2$, O$_2$, SO$_2$ and NO were obtained from cylinders and metered by mass flow controllers (Beijing seven-star electronic Co., Ltd., China). The concentration of O$_2$, SO$_2$ and NO remained 6.95-7.40 vol.%, 1000-1030 ppm and 490-530 ppm, respectively. N$_2$ was used as dilution gas, and the total gas flow was 2 L/min. The experiments were performed in a two-column reactor, both columns were made of borosilicate glass (10 cm in diameter and 25 cm in length). Different from oxidation column, about 10 cm height of ceramic rashing rings (Φ 12.5 × 12.5 mm) was packed in the absorption column. The ratio of flue gas diversion Q1:Q2 was 1:1.4. Both oxidation liquid and absorption liquid volume were 1 L. The initial concentration of NaClO$_2$ in oxidation column was 0.1 wt.%, the concentration of NaOH in absorption column was 5 wt.%. Throughout the experiment, the oxidation liquid and
absorption liquid remained 50 °C. The removal efficiency of SO₂ and NOx can maintain at 99% and 80% after purifying by oxidation-absorption column system.

2.2. Experiment procedure and analysis method
In order to determine the emission characteristics of Cl₂ and ClO₂ during the 2 h reaction process, two sets of experiments were designed and compared. The first one was periodical experiment, in which every 15 min the Cl₂ and ClO₂ in the outlet of oxidation column were sampled with the velocity of 0.5 L/min. 10 ml 1 mol/L NaOH was used as absorption solution with a smoke sampler (Qingdao Laoshang, YQ-2). The second experiment was simply continuous sampling for 2 h. Because Cl₂ is easily converted into Cl⁻ and ClO⁻ with 1:1 mole ratio, and ClO₂ is easily converted into ClO₂⁻ and ClO₃⁻ with 1:1 mole ratio in alkaline condition, which shown as equation (1) and equation (2). Then the concentration of Cl₂ and ClO₂ in outlet gas emitting from oxidation column can be calculated by the detecting concentration of Cl⁻ and ClO₂⁻ in the NaOH absorption solution by ion chromatography (IC, Thermo Fisher Scientific, ICS-1100). To have a better understanding of chlorine-containing components in both gaseous and ionic forms when NaClO₂ was used as additive for SO₂ and NO simultaneously removal, the oxidation liquid and absorption liquid before and after reaction were analysed by IC too.

\[
\begin{align*}
\text{Cl}_2 + 2\text{OH}^- & \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O} \\
2\text{ClO}_2 + 2\text{OH}^- & \rightarrow \text{ClO}_2^- + \text{ClO}_3^- + \text{H}_2\text{O}
\end{align*}
\]

IC conditions: anion separation column AS19, suppressor ASRA-4mm, quantitative ring volume 25 μL, eluent type hydroxyl(KOH), elution concentration 10.0 mmol isocratic elution, flow rate 1 ml/min.

3. Results and Discussions

3.1. Standard curves of Cl⁻, ClO₂⁻ and ClO₃⁻
According to the experimental procedure and analysis method, the chlorine-containing ions in the NaOH solution, oxidation liquid and absorption liquid were speculated to be Cl⁻, ClO₂⁻ and ClO₃⁻, the spectrum and standard curves are shown in Fig.2 and Table 1.

![Figure 2. Spectrum of chlorine-containing ions](image-url)
Table 1. Standard curves of chlorine-containing ions

| Concentration (mg/L) | 01 | 02 | 03 | 04 | 05 | Standard curve | RSD | R²  |
|----------------------|----|----|----|----|----|----------------|-----|-----|
| ClO₂⁻                | 2.000 | 5.000 | 10.00 | 15.000 | 20.000 | y=0.0887x | 4.2422 | 0.99968 |
| Cl⁻                  | 0.264 | 0.660 | 1.320 | 1.980 | 2.640 | y=0.2078x | 3.6364 | 0.99937 |
| ClO₃⁻                | 2.000 | 5.000 | 10.000 | 15.000 | 20.000 | y=0.0778x | 4.9652 | 0.99924 |

3.2. Concentrations of Cl₂ and ClO₂

According to the experimental method, Cl₂ and ClO₂ in the outlet of oxidation column were sampled and analysed, the results are shown in Table 2.

Table 2. Concentration of Cl₂ and ClO₂ in the flue gas of oxidation column outlet

| Sampling volume (L) | ClO₂ (mg/m³) | Cl₂ (mg/m³) | Sampling mode       |
|---------------------|--------------|-------------|---------------------|
| 1st set             |              |             |                     |
| 6.750               | 0.19037      | 0.42944     | Sampling time 0-15min, 15min |
| 6.090               | 19.70772     | 0.46285     | Sampling time 30-45min, 15min |
| 6.730               | 19.21991     | 0.37816     | Sampling time 60-75min, 15min |
| 5.940               | 12.50547     | 0.52462     | Sampling time 90-105min, 15min |
| 2nd set             |              |             |                     |
| 53.19               | 10.66559     | 0.53064     | Contaneous sampling, 120min |

It can be found in the first set of experimental data, the concentration of ClO₂ in the flue gas increased first and then decreased with the same sampling time as the experiment proceeding. The reason can be explained as that NaClO₂ is hard to decompose in the alkaline environment at the beginning of the reaction, as the reaction proceeded, the pH value of the absorption liquid decreased gradually, then NaClO₂ decomposed in acidic conditions, at this time ClO₂ and Cl₂ produced (the main product was ClO₂, which shown in equation (3) to equation (5)). ClO₂ began to release when the pH value was less than 7. While with the reaction continued, despite the fact that the pH value decreased further, the production of ClO₂ decreased because NaClO₂ consumed and the remaining NaClO₂ in the absorption liquid was low. Throughout the whole reaction process, the concentration of Cl₂ barely changed, and far less than that of ClO₂, which indicated that the chlorine containing gaseous component emitted from the oxidation column was mainly in the form of ClO₂.

\[
\begin{align*}
\text{ClO}_2^- + H^+ & \rightarrow HClO_2 \quad (3) \\
8\text{HClO}_2 & \rightarrow 6\text{Cl}_2 + \text{Cl}_2O + 4\text{H}_2O \quad (4) \\
2\text{NaClO}_2 + \text{Cl}_2 & \rightarrow 2\text{Cl}_2O_2 + 2\text{NaCl} \quad (5)
\end{align*}
\]

From the second set of experimental data in Table 2, it can be estimated that the amount of Cl₂ and ClO₂ discharged in the flue gas from the oxidation column during the whole reaction process was 0.057 mg and 1.152 mg respectively.

3.3. Analysis of chlorine-containing ionic composition of absorption liquid

The concentrations of chlorine-containing ionic components of oxidation liquid and absorption liquid before and after 2 hours reaction were detected, and the results are shown in Table 3.

Table 3. Chlorine-containing ions of oxidation liquid and absorption liquid

|                | Cl⁻ | ClO₂⁻ | ClO₃⁻ |
|----------------|-----|-------|-------|
| Oxidation      |     |       |       |
| Column before  | 112.43 | 640.79 | —     |
| Column after   | 308.33 | 199.97 | 72.42 |
| Absorption     |     |       |       |
| Column before  | —   | —     | —     |
| Column after   | 67.94 | —     | —     |
It can be seen in Table 3 that there were a large amount of ClO$_2^-$ and a certain amount of Cl$^-$ in the oxidation solution at the beginning, which had no big difference from the theoretical calculation (the purity of NaClO$_2$ was about 80%). Based on the theoretical calculation, when the NaClO$_2$ was 0.1 wt.%, the concentration of Cl$^-$ and ClO$_2^-$ in oxidation liquid were 78.75 and 596.55 mg/L respectively. When the experiment finished, the concentration of Cl$^-$ increased substantially while ClO$_2^-$ decreased dramatically in the oxidation liquid. The reason can be explained as that the SO$_2$ and NO in the initial reaction gas were oxidized into SO$_4^{2-}$ and NO$_3^-$ after reacted with NaClO$_2$. Besides, at the end of the reaction, a certain amount of ClO$_3^-$ existed, which attributed to the hydrolysis disproportionation of ClO$_2$. The equations of reactions in the oxidation column are shown as below.

\[ 2\text{ClO}_2 + 2\text{NaOH} + 2\text{NaClO}_2 \rightarrow 3\text{NaClO}_3 + \text{NaCl} + \text{H}_2\text{O} \quad (6) \]

\[ 2\text{ClO}_2 + \text{H}_2\text{O} + 5\text{NaClO}_2 \rightarrow 5\text{NaClO}_3 + 2\text{HCl} \quad (7) \]

At the end of reaction, high concentration of Cl$^-$ was detected in the absorption liquid, while no ClO$_2^-$ and ClO$_3^-$ existed. The existence of Cl$^-$ in the absorption liquid was mainly attributed to two aspects: one was presumably carried by the flue gas, in which some liquid in oxidation column was transferred into absorption column, the other anther one was that Cl$_2$ and ClO$_2$ generated in the oxidation column was absorbed by the absorption liquid. According to the concentration of Cl$^-$ in absorption liquid after reaction, the first one was the main reason.

3.4. The colour and odor change of oxidation liquids

The color of the oxidation liquid changed obviously as the reaction proceeding. The initial absorption liquid was colorless and transparent and gradually turned into pale yellow, finally the color darkened and turned into light yellow. Besides, pungent odor released during the experiment, and the odor gradually became thicker. The main reason was that as the reaction began, the absorption fluid gradually turned into acid from alkaline, and NaClO$_2$ can easily decomposed into Cl$_2$ and ClO$_2$ under acidic condition. With Cl$_2$ and ClO$_2$ dissolved into water, the absorption liquid turned into yellow, pungent odor began to release. The more gaseous product produced, the deeper color was. At the same time, ClO$_2$ is easy to volatilize from the solution under acidic condition. The greater amount of ClO$_2$ volatilized, the stronger the pungent odor was.

4. Conclusion

- The concentration of ClO$_2$ in outlet of oxidation column increased first and then decreased. The concentration of Cl$_2$ barely changed during the experiment, and far less than that of ClO$_2$, which indicated that the chlorine-containing gaseous components were mainly in the form of ClO$_2$.
- After 2 h reaction, the chlorine-containing ions in the oxidation liquid before and after reaction were in good consistence with the theoretical calculation. High concentration of Cl$^-$ was detected in the absorption liquid, while no ClO$_2^-$ and ClO$_3^-$ existed.
- The initial oxidation liquid was colourless and transparent, then gradually turned into pale yellow, and finally the color darkened and turned into light yellow. During the reaction, pungent odor released. The greater amount of ClO$_2$ volatilized, the stronger the pungent odor was.
- Considerable amount of Cl$_2$ and ClO$_2$ released from the oxidation column, while with the combination of absorption column, almost all of chlorine-containing components are in the form of ions.

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