

# Emission characteristics of Cl<sub>2</sub> and ClO<sub>2</sub> during simultaneous removal of SO<sub>2</sub> and NO using NaClO<sub>2</sub> solution

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**Abstract.** In this study, an experimental apparatus of oxidation + absorption columns was set up to investigate ClO<sub>2</sub> and Cl<sub>2</sub> emission characteristics when NaClO<sub>2</sub> 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<sub>2</sub> in the outlet of oxidation column increased first and then decreased while Cl<sub>2</sub> barely changed during the experiment. The concentration of Cl<sub>2</sub> was far less than ClO<sub>2</sub>, which indicated that the chlorine-containing gaseous component was mainly in the form of ClO<sub>2</sub>. 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<sup>-</sup> was detected in the absorption liquid, while no ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup> existed. As the reaction proceeded, the oxidation liquid gradually turned into light yellow, and pungent odor released.

## 1. Introduction

Sulfur dioxide (SO<sub>2</sub>) and nitric oxides (NO<sub>x</sub>, 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.<sup>[1,2]</sup>. The mature air pollution control devices for SO<sub>2</sub> 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<sub>3</sub> 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<sup>[3]</sup>. Based on the fact that the WFGD system has already obtained wide application in China, how to realize simultaneously desulfurization and denitrification in WFGD system has become one of the research hotspots in the field of air pollution control.

Recently, some oxidations including KMnO<sub>4</sub><sup>[4]</sup>, S<sub>2</sub>O<sub>8</sub><sup>2-</sup><sup>[5]</sup>, Fenton's reagent<sup>[6,7]</sup>, H<sub>2</sub>O<sub>2</sub><sup>[8]</sup>, ClO<sub>2</sub><sup>[9]</sup>, NaClO<sup>[10,11]</sup> have already been used as additives in absorption liquid of WFGD system to achieve simultaneously desulfurization and denitrification purpose. Among them, NaClO<sub>2</sub> is one of the most potential reagent can be used in the field of simultaneously SO<sub>2</sub> and NO<sub>x</sub> removal. Some research has already been done. For example, Huson et al<sup>[12]</sup> carried out an experiment of simultaneous removal of SO<sub>2</sub>, NO<sub>x</sub> and Hg from coal flue gas by using a NaClO<sub>2</sub>-enhanced wet scrubbing method, from which, a NaClO<sub>2</sub> 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<sup>[13]</sup>, NaClO+NaClO<sub>2</sub> oxidant was used to investigate simultaneous removal of SO<sub>2</sub> and NO from fuel gas, under the optimal conditions, the removal efficiency of SO<sub>2</sub> and NO reached 100% and 85% respectively. In NaClO<sub>2</sub>+NaBr oxidant oxidation



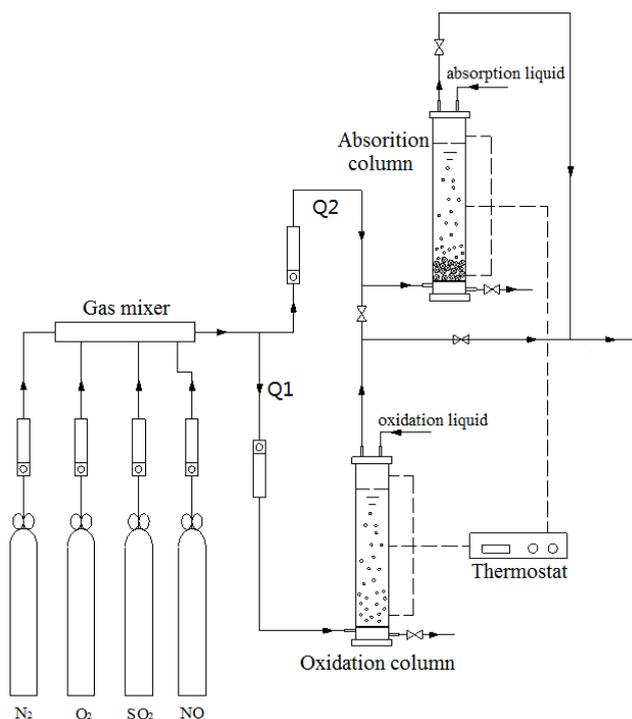
system, NO and  $\text{Hg}^0$  are first pre-oxidized and then along with  $\text{SO}_2$  absorbed by  $\text{Ca}(\text{OH})_2$ , the average simultaneous removal efficiencies of  $\text{SO}_2$ , NO and  $\text{Hg}^0$  were 91%, 100% and 93% respectively<sup>[14]</sup>. Hao et al<sup>[15]</sup> proposed a novel complex oxidant  $\text{NaClO}_2/\text{Na}_2\text{S}_2\text{O}_8$ , the system could convert NO and  $\text{SO}_2$  into  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  with the efficiency of 87.2% and 100%.

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



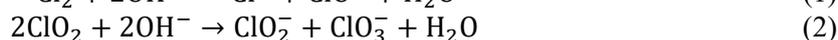
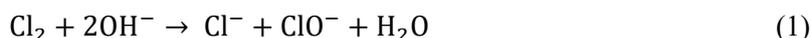
**Figure 1.** Schematic diagram of the experimental apparatus

$\text{N}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$  and NO were obtained from cylinders and metered by mass flow controllers (Beijing seven-star electronic Co., Ltd., China). The concentration of  $\text{O}_2$ ,  $\text{SO}_2$  and NO remained 6.95-7.40 vol.%, 1000-1030 ppm and 490-530 ppm, respectively.  $\text{N}_2$  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 ( $\Phi 12.5 \times 12.5$  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  $\text{NaClO}_2$  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 SO<sub>2</sub> and NO<sub>x</sub> 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 Cl<sub>2</sub> and ClO<sub>2</sub> 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 Cl<sub>2</sub> and ClO<sub>2</sub> 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 Cl<sub>2</sub> is easily converted into Cl<sup>-</sup> and ClO<sup>-</sup> with 1:1 mole ratio, and ClO<sub>2</sub> is easily converted into ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup> with 1:1 mole ratio in alkaline condition, which shown as equation (1) and equation (2). Then the concentration of Cl<sub>2</sub> and ClO<sub>2</sub> in outlet gas emitting from oxidation column can be calculated by the detecting concentration of Cl<sup>-</sup> and ClO<sub>2</sub><sup>-</sup> 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 NaClO<sub>2</sub> was used as additive for SO<sub>2</sub> and NO simultaneously removal, the oxidation liquid and absorption liquid before and after reaction were analysed by IC too.



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<sup>-</sup>, ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup>

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<sup>-</sup>, ClO<sub>2</sub><sup>-</sup> and ClO<sub>3</sub><sup>-</sup>, the spectrum and standard curves are shown in Fig.2 and Table 1.

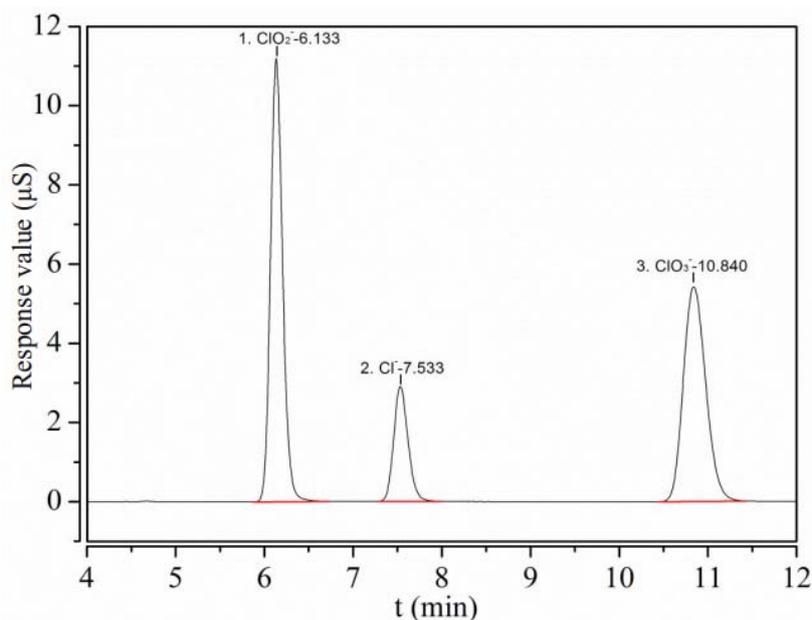


Figure 2. Spectrum of chlorine-containing ions

**Table 1.** Standard curves of chlorine-containing ions

Concentration (mg/L)	01	02	03	04	05	Standard curve	RSD	R <sup>2</sup>
ClO <sub>2</sub> <sup>-</sup>	2.000	5.000	10.00	15.000	20.000	y=0.0887x	4.2422	0.99968
Cl <sup>-</sup>	0.264	0.660	1.320	1.980	2.640	y=0.2078x	3.6364	0.99937
ClO <sub>3</sub> <sup>-</sup>	2.000	5.000	10.000	15.000	20.000	y=0.0778x	4.9652	0.99924

### 3.2. Concentrations of Cl<sub>2</sub> and ClO<sub>2</sub>

According to the experimental method, Cl<sub>2</sub> and ClO<sub>2</sub> in the outlet of oxidation column were sampled and analysed, the results are shown in Table 2.

**Table 2.** Concentration of Cl<sub>2</sub> and ClO<sub>2</sub> in the flue gas of oxidation column outlet

	Sampling volume (L)	ClO <sub>2</sub> (mg/m <sup>3</sup> )	Cl <sub>2</sub> (mg/m <sup>3</sup> )	Sampling mode
1 <sup>st</sup> 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
2 <sup>nd</sup> set	53.19	10.66559	0.53064	Contaneous sampling, 120min

It can be found in the first set of experimental data, the concentration of ClO<sub>2</sub> 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 NaClO<sub>2</sub> 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 NaClO<sub>2</sub> decomposed in acidic conditions, at this time ClO<sub>2</sub> and Cl<sub>2</sub> produced (the main product was ClO<sub>2</sub>, which shown in equation(3) to equation(5)). ClO<sub>2</sub> 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 ClO<sub>2</sub> decreased because NaClO<sub>2</sub> consumed and the remaining NaClO<sub>2</sub> in the absorption liquid was low. Throughout the whole reaction process, the concentration of Cl<sub>2</sub> barely changed, and far less than that of ClO<sub>2</sub>, which indicated that the chlorine containing gaseous component emitted from the oxidation column was mainly in the form of ClO<sub>2</sub>.



From the second set of experimental data in Table 2, it can be estimated that the amount of Cl<sub>2</sub> and ClO<sub>2</sub> 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 <sup>-</sup>	ClO <sub>2</sub> <sup>-</sup>	ClO <sub>3</sub> <sup>-</sup>
Oxidation Column	before	112.43	640.79	—
	after	308.33	199.97	72.42
Absorption Column	before	—	—	—
	after	67.94	—	—

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



At the end of reaction, high concentration of  $\text{Cl}^-$  was detected in the absorption liquid, while no  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  existed. The existence of  $\text{Cl}^-$  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 the another one was that  $\text{Cl}_2$  and  $\text{ClO}_2$  generated in the oxidation column was absorbed by the absorption liquid. According to the concentration of  $\text{Cl}^-$  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  $\text{NaClO}_2$  can easily decomposed into  $\text{Cl}_2$  and  $\text{ClO}_2$  under acidic condition. With  $\text{Cl}_2$  and  $\text{ClO}_2$  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,  $\text{ClO}_2$  is easy to volatilize from the solution under acidic condition. The greater amount of  $\text{ClO}_2$  volatilized, the stronger the pungent odor was.

#### 4. Conclusion

- The concentration of  $\text{ClO}_2$  in outlet of oxidation column increased first and then decreased. The concentration of  $\text{Cl}_2$  barely changed during the experiment, and far less than that of  $\text{ClO}_2$ , which indicated that the chlorine-containing gaseous components were mainly in the form of  $\text{ClO}_2$ .
- 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  $\text{Cl}^-$  was detected in the absorption liquid, while no  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  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  $\text{ClO}_2$  volatilized, the stronger the pungent odor was.
- Considerable amount of  $\text{Cl}_2$  and  $\text{ClO}_2$  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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