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Preliminary evaluation of $NaClO_2$ powder injection method for mercury oxidation: Bench scale experiment using iron-ore sintering flue gas

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Abstract−The injection of powdered sodium chlorite ($NaClO_2$(s)) for mercury oxidation into iron-ore sintering flue gas has been evaluated by using the bench scale of tubular flow reactor, where the flow rate and temperature of flue gas stream were controlled to 250 $Nm^3\ hr^{-1}$ and 135 °C, respectively, and either 50 or 260 μg Nm^{-3} of the mercury concentration was introduced intentionally to the gas stream. We have observed that 90% of Hg^0 oxidation was obtained at 0.18 g Nm^{-3} $NaClO_2$(s) injection, indicating that the oxidized weight of Hg^0 by the loaded weight of $NaClO_2$(s) is 1026 (±333) (μg-Hg^0) (g-$NaClO_2$(s))$^{-1}$. This result leads us to suggest that the simple injection of $NaClO_2$(s) into the flue gas has the potential to achieve over 90% mercury control in practical application.

Key words: Sodium Chlorite, Mercury, Oxidation, Real Plant, ClO

INTRODUCTION

Mercury, as a highly toxic pollutant, tends to be bio-accumulate in the food chain with adverse effects on human health [1,2]. A large portion of anthropogenic mercury emissions comes from municipal waste combustors and coal-burning utilities [1]. Mercury emissions occur in association with particulate matter (Hg^p), gaseous elemental form (Hg^0), and various gaseous mercuric compounds (Hg^{2+}) [1]. Although Hg^{2+} and Hg^p can be effectively removed by conventional air pollution control devices such as electrostatic precipitation (ESP) and flue gas desulfurization (FGD), Hg^0 is harder to capture because of its high vapor pressure and low water solubility. Unfortunately, the vast majority of mercury is emitted in the form of Hg^0. Therefore, most studies are focused on the oxidation of Hg^0 to Hg^{2+} species, such as HgO and $HgCl_2$, for the effective control of mercury emission.

In our previous studies, we examined the oxidation of NO by using powdered sodium chlorite ($NaClO_2$(s)) in laboratory scale. It was found that NO oxidizes to NO_2 by $NaClO_2$(s) and in turn NO_2 reacts with $NaClO_2$(s) leading to the formation of OClO, followed by the further reaction of OClO with NO to produce ClO, Cl and Cl_2 which play an important role in the oxidation of Hg^0 [3]. On the basis of such observation, we further examined whether the oxidation of Hg^0 by using $NaClO_2$(s) proceeds well in the presence of NO_x and, eventually, we observed that the co-benefit removal of mercury by using $NaClO_2$(s) in the presence of NO_x is possible [4]. However, our previous study focused on only the detailed mechanism behind the oxidation of Hg^0 and used a packed-bed reactor containing $NaClO_2$(s) within N_2 balance, instead of the flow system of the real flue gas. $NaClO_2$(s) has a form of powder, indicating that the direct injection of $NaClO_2$(s) is more convenient way than the packed $NaClO_2$(s) when we try to control mercury contained within the real flue gas.

To evaluate the performance of $NaClO_2$(s) injection toward mercury control, it is necessary to know the oxidized weight of Hg^0 by the loaded weight of $NaClO_2$(s). Besides, the effectiveness of $NaClO_2$(s) in the real flue gas must be examined because the real flue gas contains other gas components such as H_2O, CO, CO_2, NO_x, H_2O, SO_2 and dust. Therefore, for the first time, we conducted the injection of $NaClO_2$(s) to the real flue gas containing other gas components emitted from the iron-ore sintering plant of steel making works with the following objectives: (1) to confirm the possibility of oxidizing Hg^0 by the injection of $NaClO_2$(s) into the real flue gas, and (2) to evaluate the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s).

EXPERIMENTAL SECTION

1. Description of the Iron-ore Sintering Plant in a Steel-making Company

We installed a tubular flow reactor in an iron-ore sintering plant of steel making works. The function of a sintering plant is to pro-

Table 1. Gas conditions of iron-ore sintering plant conducted the injection of $NaClO_2$(s) for the oxidation of Hg^0

Flow rate	250 $Nm^3\ hr^{-1}$
Reactor temperature	135 °C
Baseline O_2 concentration	14-16%
Baseline NO concentration	180 ppm
Baseline SO_2 concentration	175 ppm
Baseline CO_2 concentration	2.5%
Baseline CO concentration	5,850 ppm
Baseline Hg^0 concentration	<10 μg Nm^{-3}
Baseline particle concentration	10 mg Nm^{-3}
Inlet Hg^0 concentrations	50 μg Nm^{-3}, 260 μg Nm^{-3}

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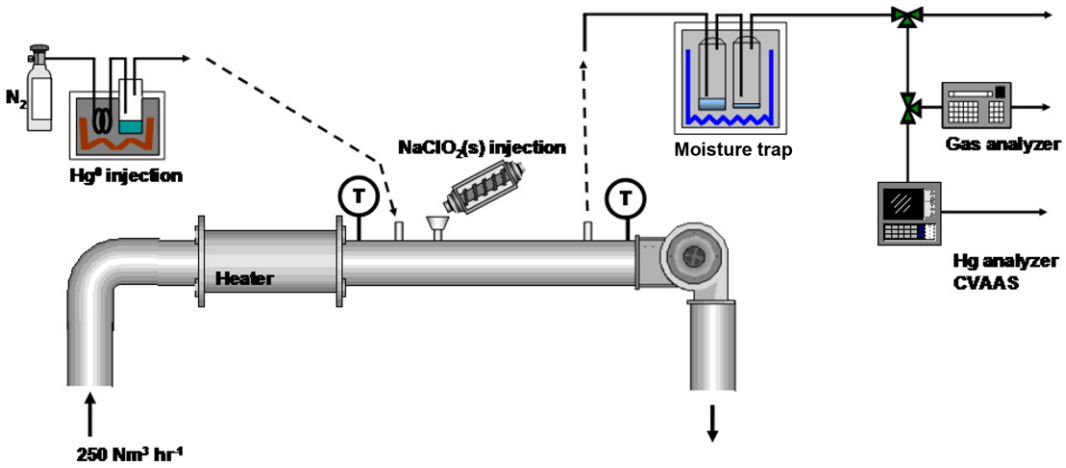

Fig. 1. Schematic diagram of the experimental system.

cess the fine grain of raw iron-ore material into coarse grained iron-ore before being charged to the blast furnace. The flow rate of flue gas emitted from the iron-ore sintering plant is about 1 million $Nm^3\ hr^{-1}$, where ESP, bag filter and selective catalytic reduction are equipped in series to control the air pollutants. We installed the tubular flow reactor in the duct between ESP and the bag filter. The experimental conditions such as gas composition, temperature and flow rate are listed in Table 1.

2. Tubular Flow Reactor and $NaClO_2$(s) Injection System

A schematic diagram of the tubular flow reactor is shown in Fig. 1. The flue gas of 250 $Nm^3\ hr^{-1}$ was taken out from the duct of the iron-ore sintering plant by using the induced blower, then introduced into the tubular flow reactor and eventually returned to the duct. The tubular flow reactor was made of steel pipe (10 cm in diameter). The linear velocity of flue gas in the tubular reactor was 885 cm s^{-1}. An electric heater was installed between the duct and the tubular flow reactor to control the gas temperature. The temperature difference between two ends of the tubular flow reactor was controlled to be within 5 °C. Hg^0 was introduced intentionally to the tubular flow reactor by evaporating liquid mercury wrapped by heating tape in which the temperature was controlled. A screw feeder was used to inject $NaClO_2$(s) into the reactor. The photograph of the experimental system used in this study is shown in Fig. 2. The screw feeder supplied $NaClO_2$(s) (density=0.667 g cm^{-3}, size=below 0.5 mm) to the reactor at a constant feeding rate, and then the released $NaClO_2$(s) was naturally squeezed into the reactor by the pressure difference between the inside and outside of the tubular flow reactor. The distance between $NaClO_2$(s) and mercury injection ports was separated to 15 cm. The gas sampling port for the analysis of gas composition was 300 cm away from the $NaClO_2$(s) injection port. The inside volume of the tubular flow reactor and the residence time of the flue gas passing between the $NaClO_2$(s) injection and the gas sampling ports were 23,550 cm^3 and 0.33 s, respectively.

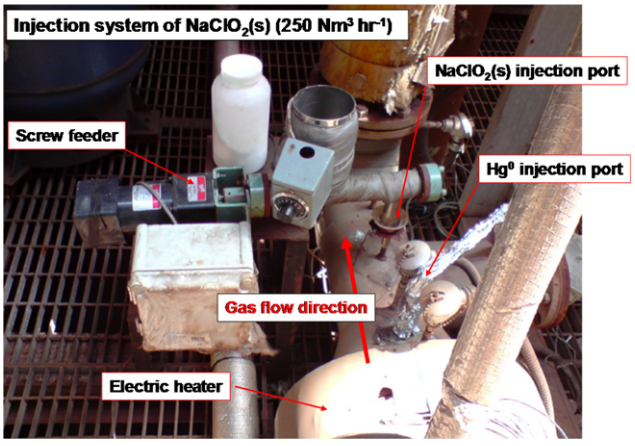

Fig. 2. Photograph of the experimental system.

3. Gas Analysis and Hg^0 Calibration Procedure

A gas sample of 10 L min^{-1} for the analysis of gas composition was taken from the sampling port by using a peristaltic pump. The mercury concentration was determined by using cold vapor atomic absorption spectrometry (CVAAS) having two absorption cells [5]. The concentrations of gas components were monitored with a non-dispersive infrared type of gas analyzer (ZKJ, Fuji Electric Systems Co.). Before the concentrations of gas components were analyzed, the water cooling section for the gas stream was positioned to remove water entering the analyzer.

The mercury analyzer was calibrated with the calibration equipment (Fig. 3). The concentration of Hg^0 was controlled both by N_2 flow and by the temperature of the mercury condensation vessels. Hg^0 was vaporized within a mercury evaporation vessel and swept out by using N_2 gas passing through the vessel. The Hg^0 laden N_2 then entered a saturation vessel within a finely controlled temperature

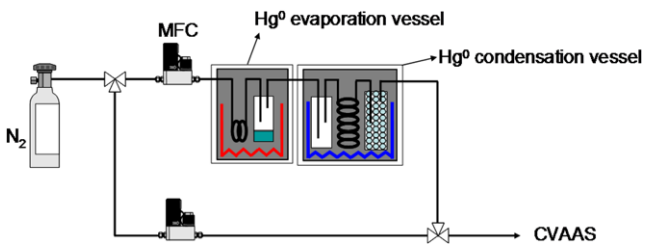

Fig. 3. Schematic diagram of the calibration system for Hg^0 analyzer. MFC: Mass flow controller.

bath. The gas residence time and surface of condensation materials within the saturation vessel ensured that the gas stream of Hg^0 in N_2 was saturated with Hg^0 vapor at the controlled temperature of the saturation vessel. The temperature of Hg^0 evaporation vessel was set to ensure that the mercury content of the gas stream leaving the evaporation vessel was greater than that of the saturation concentration corresponding to the value of the saturation vessel temperature. The stream of N_2 and Hg^0 exiting the saturation vessel was diluted prior to entering to the CVAAS. In such a way, we obtained the signal of the Hg^0 concentration by using CVAAS.

RESULTS AND DISCUSSION

We injected $NaClO_2$(s) into the tubular flow reactor containing 50 μg Nm^{-3} of Hg^0, where the feeding rate of $NaClO_2$(s) was set to 0.06 g Nm^{-3} (Fig. 4). As soon as $NaClO_2$(s) was introduced into the tubular flow reactor, Hg^0 was decreased suddenly to 10 μg Nm^{-3}. In our previous study, we observed that the introduced NO reacts with $NaClO_2$(s) to produce NO_2 through the following reaction:

$$2NaClO_2(s)+NO \rightarrow NO_2+NaClO_3(s)+NaCl(s) \quad (1)$$

The generated NO_2 further reacts with $NaClO_2$(s) to produce OClO through the reaction (2):

$$3NaClO_2(s)+NO_2 \rightarrow NaClO_3(s)+NaCl(s)+NaNO_3(s)+OClO \quad (2)$$

OClO also can react with NO to give rise to the formation of ClO, Cl and Cl_2 via the reaction channels of (3), (4) and (5) [6],

$$OClO+NO \rightarrow NO_2+ClO \quad (3)$$

$$ClO+NO \rightarrow NO_2+Cl \quad (4)$$

$$Cl+Cl \rightarrow Cl_2 \quad (5)$$

These chlorine-containing species of ClO, Cl and Cl_2 can significantly oxidize Hg^0 to $HgCl_2$ and HgO. However, we did not confirm whether the removed Hg^0 by injecting $NaClO_2$(s) was exactly 40 μg Nm^{-3} as shown in Fig. 4. When SO_2 presents with Hg^0 in flue gas, it can interfere with the detection of Hg^0, because it also absorbs the light of 253.7 nm used in CVAAS [7]. Typically, solutions containing NaOH or Na_2CO_3 have been used to remove SO_2 [8]. Solid NaOH granules also have been used [9]. Although the flue gas of an iron-ore sintering plant contains about 175 ppm of SO_2 as listed in Table 1, we did not employ such a system to remove acidic gas of SO_2, because $NaClO_2$(s) and Cl_2 can be dissolved in solutions to result in oxidizing Hg^0. The solid NaOH granules can also absorb Hg^0. Therefore, the Hg^0 concentration of about 10 μg Nm^{-3} shown in Fig. 4 originates from the signal of SO_2 contained in the flue gas. Since we cannot overcome such an interference of SO_2 at the present stage, we have planned to utilize a gold amalgamation method equipped with cold vapor atomic fluorescence spectrometry.

It is difficult to obtain the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s) in these experimental conditions containing just 50 μg Nm^{-3}, because Hg^0 is oxidized completely, which indicates that the injected amount of $NaClO_2$(s) is too much as compared to that of Hg^0 in flue. Under the present experimental conditions, there are two possible methods to obtain the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s). One is to increase the concentration of Hg^0 and the other is to decrease the feeding rate of $NaClO_2$(s). The minimum feeding rate of $NaClO_2$(s) is 0.05 g Nm^{-3} in our screw feeder, implying that decreasing the feeding

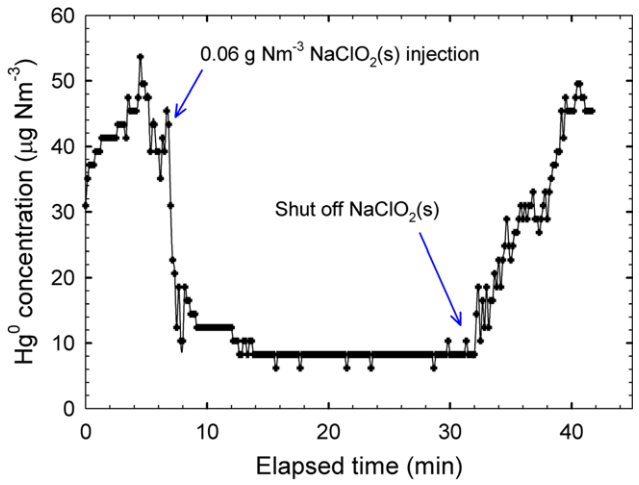

Fig. 4. Temporal profile of Hg^0 concentration obtained by the injection of $NaClO_2$(s) at 50 μg Nm^{-3} of Hg^0.

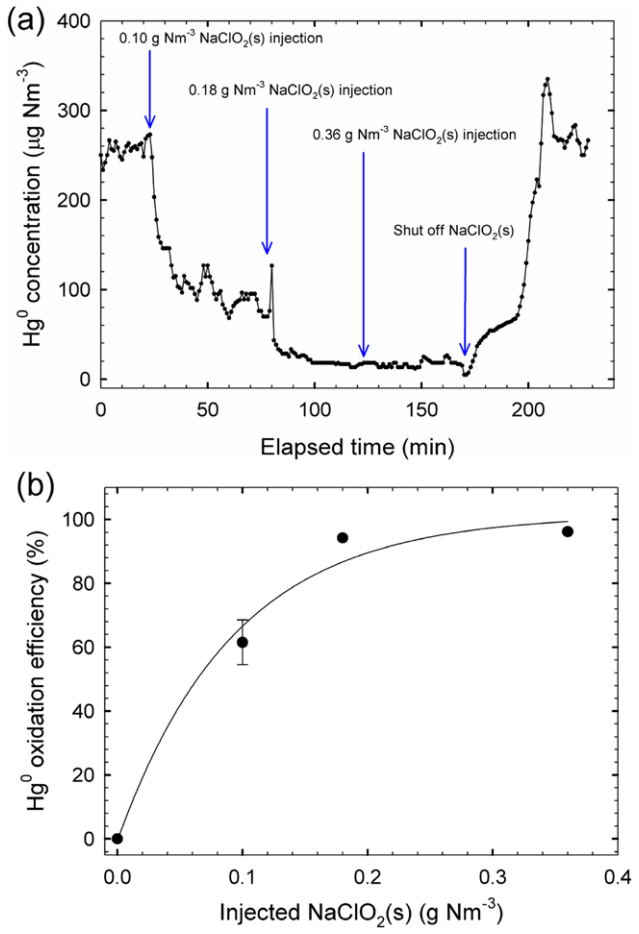

Fig. 5. Oxidation of Hg^0 by $NaClO_2$(s) injection. (a) Temporal profile of Hg^0 concentration. (b) Hg^0 oxidation efficiency as a function of weight of injected $NaClO_2$(s). Error bars represent the standard deviation of Fig. 5(a) for the measurement duration of about 50 min.

rate is difficult. Therefore, we increased the concentration of Hg^0 to 260 μg Nm^{-3} (Fig. 5). At first, 0.1 g Nm^{-3} of $NaClO_2$(s) was introduced into the tubular flow reactor. The Hg^0 concentration began to drop suddenly and reached 100 μg Nm^{-3} (Fig. 5(a)). As the injection weight of $NaClO_2$(s) was increased to 0.18 g Nm^{-3}, about 90% of Hg^0 oxidation efficiency was achieved. When the injection weight of $NaClO_2$(s) was further increased to 0.36 g Nm^{-3}, the oxidation efficiency of Hg^0 was achieved to be over 92% (Fig. 5(b)). Based on these experimental results, we obtained the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s), i.e., 1026 (±333) (μg-Hg^0) (g-$NaClO_2$(s))$^{-1}$.

The amount of $NaClO_2$(s), for example, used in 1 million Nm^3 hr^{-1} is calculated to be about 936 kg day^{-1} (1,403 L day^{-1}) for 40 μg Nm^{-3} of Hg^0 oxidation, which was estimated from the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s). Based on this observation, we concluded that the simple injection of powdered $NaClO_2$ (s) into the flue gas has a potential to achieve over 90% Hg^0 oxidation in practical application.

The iron-ore sintering flue gas contains many other gas components which can influence the oxidation of Hg^0. Therefore, we investigated their effect on the oxidation of Hg^0 by using a laboratory scale of the experimental system. Since the overall experimental system of laboratory scale was described in detail elsewhere [3], only a general outline of the scheme was inset in Fig. 6. Initially, the effect of SO_2 on the Hg^0 oxidation was investigated in this study. 1.2 g of $NaClO_2$(s) was packed within the packed-bed reactor for which the temperature was set to 130 °C and then only Hg^0 (260 μg Nm^{-3}) in 2.6 L min^{-1} N_2 balance was introduced to the reactor. As shown in Fig. 6, no oxidation of Hg^0 occurred. As soon as 15 ppm SO_2 was introduced into the packed-bed reactor, Hg^0 oxidation occurred suddenly to give about 70% of the oxidation efficiency. With further increase of the addition of SO_2 to 35 ppm, the complete oxidation of Hg^0 was obtained. Although the insight into the oxidation mechanisms cannot be verified well presently, this result

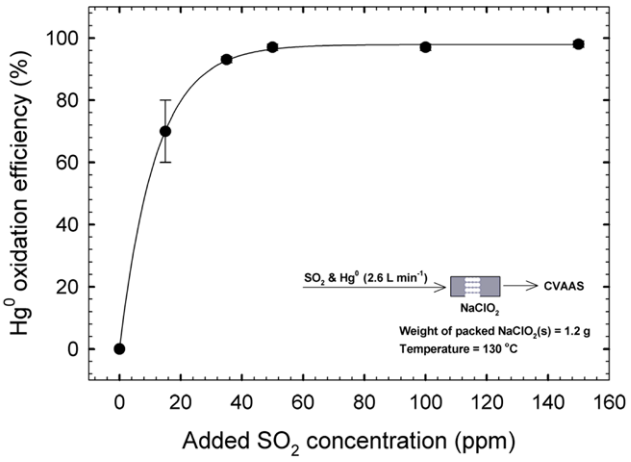

Fig. 6. Effect of SO_2 on Hg^0 oxidation by $NaClO_2$(s). These data were obtained at the laboratory-scale experiment using packed bed reactor. The inset describes the experiment setup. More detailed experimental system is described in our previous studies [3]. Experimental conditions: total flow rate= 2.6 L min^{-1}, temperature=130 °C, weight of packed $NaClO_2$ (s)=1.2 g, N_2 balance.

demonstrated that SO_2 can enhance greatly the oxidation of Hg^0. We also investigated the effect of H_2O, CO, CO_2 and O_2 on the Hg^0 oxidation and observed little enhancement of Hg^0 oxidation within experimental errors; the concentration of each gas component was increased from 0 to 200 ppm with five loading steps. Upon the basis of these results, we concluded that the most important species influencing the oxidation of Hg^0 is SO_2, rather than H_2O, CO, CO_2 and O_2.

As can be seen in Figs. 4 and 5(a), the concentration of Hg^0 was increased when the injection of $NaClO_2$(s) was stopped. However, the time for the Hg^0 concentration to reach the initial value of Hg^0 concentration took about 30 min. Considering the residence time of the flue gas passing the reactor (0.33 s), the accumulated $NaClO_2$(s) on the inner surface of the reactor has caused the slow increase of Hg^0 concentration. Although we did not use the particulate control equipment in the present stage, it must be used in the case of a larger system than the present one to prevent the release of the $NaClO_2$(s) into the atmosphere. A bag house as a particulate control equipment can provide better interaction between gas and $NaClO_2$(s) due to the accumulation of the $NaClO_2$(s) on the surface of the bag house. If so, installing a bag house gives rise to reducing the amount of $NaClO_2$(s), which is necessary to oxide Hg^0. Therefore, we feel that further studies by employing a bag house are essential to extract the required weight of $NaClO_2$(s) in a practical application.

CONCLUSIONS

Effects of the $NaClO_2$(s) injection on the oxidation of Hg^0 were evaluated experimentally in a bench scale tubular flow reactor where the flue gas emitted from iron-ore sintering plant of steel making works is used. This study demonstrated that the direct injection of $NaClO_2$(s) within flue gas can be applicable for Hg^0 emission control for a practical application. In addition, we feel that, as a next step, a long-term reliable test of this process using a bag house at a low Hg^0 concentration (below 50 μg Nm^{-3}) is necessary. The following conclusions were obtained by this study:

(1) Hg^0 oxidation efficiency of 90% was obtained at the feeding rate of 0.18 g Nm^{-3} $NaClO_2$(s), which corresponds to the oxidized weight of Hg^0 related to the loaded weight of $NaClO_2$(s) being 1026 (±333) (μg-Hg^0) (g-$NaClO_2$(s))$^{-1}$;

(2) SO_2 species contained in flue gas accelerated the oxidation of Hg^0, whereas CO, CO_2, H_2O and O_2 had little effect on the Hg^0 oxidation;

(3) The accumulated $NaClO_2$(s) inside the tubular reactor enhanced the oxidation of Hg^0, implying that installing a bag house will reduce the required amount of the $NaClO_2$(s) injection for Hg^0 oxidation.

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