Fuel 90 (2011) 2501–2507

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

A mechanism study of chloride and sulfate effects on Hg^{2+} reduction in sulfite solution

Yue Liu [a], Yuejun Wang [a], Zhongbiao Wu [a,b,*], Siyao Zhou [a], Haiqiang Wang [a]

[a] *Department of Environmental Engineering, Zhejiang University, Hangzhou 310027, PR China*
[b] *Zhejiang Provincial Engineering Research Center of Industrial Boiler & Furnace Flue Gas Pollution Control, Hangzhou 310027, PR China*

ARTICLE INFO

Article history:
Received 12 November 2010
Received in revised form 22 January 2011
Accepted 10 February 2011
Available online 6 March 2011

Keywords:
Hg
Mercury removal
Reduction
SO_4^{2-}
Cl^-

ABSTRACT

This paper studied the effects of sulfate and chloride ions on bivalent mercury (Hg^{2+}) absorption and reduction behaviors in a simulated WFGD system. The aqueous mercuric ion-sulfite system reduction behaviors were monitored and investigated using a UV–visible spectrum. Thereafter, the mechanism of Hg^{2+} reduction in the presence of sulfate and chloride ions was proposed. Experimental results revealed that both sulfate and chloride ions had inhibition effects on aqueous Hg^{2+} reduction to Hg^0. The inhibition was assumed due to the formation of $HgSO_3SO_4^{2-}$ (in the presence of SO_4^{2-}) and $ClHgSO_3^-/Cl_2HgSO_3^{2-}$ (in the presence of Cl^-). And it was found that $Cl_2HgSO_3^{2-}$ complex was more stable than $ClHgSO_3^-$ in excess of Cl^-. The formation of the above-mentioned complexes in the presence of SO_4^{2-} and Cl^- would damp the formation of $HgSO_3$, whose decomposition was assumed to be the key step of Hg^{2+} reduction.

1. Introduction

Mercury, due to its persistence, bio-accumulation and neurological toxicity, has received tremendous attentions [1]. Although nature emission was recognized as the main source in atmospheric mercury cycle, anthropogenic mercury emission, particularly from coal combustion, still accounted a great proportion [2]. Many mercury control technologies were currently developed, including sorbents [3–5], catalysts [6–8], and ultraviolet radiation [9–11]. Elemental mercury is insoluble in water, whereas compounds such as mercuric chloride are soluble. One strategy that is being explored is the use of a catalyst to oxidize elemental mercury upstream of a wet FGD. Previous report had indicated that oxidized mercury in coal-fired flue gas could be effectively captured by wet flue gas desulfurization (WFGD) system [12], which provides a co-effective, economic option for mercury control. However, since a portion of absorbed oxidized mercury will be reduced to elemental mercury (Hg^0) in WFGD system and eventually release into flue gas [13–15], the total mercury removal efficiency was significantly limited. As such, to improve the efficiency, a detail study on Hg^0 re-emission process is highly desirable.

The Hg^0 re-emission phenomenon was first reported by Broset [16] and then further studied by Loon et al. [17,18], who had indicated that the reduction process presumably occurred via aqueous-reduction of Hg^{2+} by sulfite ions. The process was initiated by the formation of unstable intermediate, $HgSO_3$, which immediately decomposed to aqueous Hg^0 and eventually re-emitted to gas-phase. The authors also proposed a pseudo-first order reaction model and argued a two-electron transfer of $HgSO_3$ as the most possible way to form Hg^0, i.e. sulfite would directly transfer two electrons to Hg^{2+} and release the Hg^0. However, Munthe et al. [17] had proposed a one-electron transfer model, indicating that the initial step of mercury re-emission process was the reduction of Hg^{2+} to Hg^+, following by a rapid dimerization of Hg^+ to Hg^0. Nerveless, both one or two electrons transfer was considered as the possible way for the reduction of aqueous Hg^{2+} [19]. As the reduction process is very complex and it is really difficult to verify these proposed models.

Furthermore, there are a great amount of other substances compared to mercury in the flue gas, e.g. SO_2 (800–2000 ppm), HCl (around 100 ppm), SO_3 (10–40 ppm), etc. [8–11,20,21]. These species after absorption into FGD system can impact the absorbent chemistry, thereby affecting the Hg reduction and re-emission. Some literatures [22,23] had yet concluded that the Cl^- had inhibition effect on the reduction of Hg^{2+}, where the formation of $ClHgSO_3^-$ was suggested as the main cause for this inhibition [19] and our previous study had found that the presence of SO_4^{2-} (coming from the absorption of SO_2 or SO_3) could also have negative effect on the reduction of Hg^{2+} in Ca-based WFGD system [24]. However, the investigations on their inhibition effects are still rare. The Hg^{2+} reduction in Dual-Alkali WFGD system, which has been widely applied in China, was observed less than Ca-based WFGD

---

* Corresponding author at: Department of Environmental Engineering, Zhejiang University, Hangzhou 310027, PR China . Tel./fax: +86 571 87953088.
E-mail address: zbwu@zju.edu.cn (Z. Wu).

0016-2361/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2011.02.036

system [25]. But the reduction mechanism was not discussed in detail compared with Ca-based WFGD system.

Therefore, the study on the effects of the chloride and sulfate on gas-phase bivalent mercury removal was firstly performed in a self-built absorption device. Secondly, the UV–visible spectra analysis was carried out to determine the changes of Hg reduction intermediates in the absorption solution under different conditions. Finally, the Hg reduction mechanism in the presence of chloride and sulfate ions was then proposed.

2. Materials and methods

2.1. Absorption experimental apparatus

A purpose-built absorption device reported in our previous work [24] was used to investigate the Hg^{2+} absorption and reduction process in sulfite solution. This device was composed of three parts: Hg^{2+} generation oven, gas mixing oven and bubbling absorbing reactor. At the beginning of each experiment, 300 ml of the $NaSO_3$ solution was firstly placed inside the Hg^{2+} bubbling reactor and then heated up to a predetermined temperature. 2 L/min of simulated flue gas containing 80 μg/m³ Hg^{2+} balanced with N_2 was introduced into the bubbling reactor to initiate the absorbing experiment. The exhaust gas was decontaminated by passing through two washing-bottles and one adsorbent column. The Hg^{2+} and Hg^0 concentration were determined through the Ontario Hydro method. The testing samples were analyzed using cold–atomic fluorescence spectroscopy (AFS-230E, Beijing Kechuanghaiguang Instrument Co., Ltd.). The uncertainty of the test data was 5.5% in the experiment.

2.2. UV–visible spectra study

UV–visible spectra study was carried out on a UV–visible spectrophotometer (UV–vis DRS: TU-1901, China) by scanning a 1 cm square quartz cuvette containing a prepared solution at 0.5 nm resolution with a scan speed of 300 nm/min. The solution was prepared by mixing sulfite solution and mercuric ion solution with a certain molar ratio. The mercuric ions solution was prepared by dissolving HgO in concentrated perchloric acid ($HClO_4$) and then diluted with ultrapure water to produce a stock solution of 6 mM bivalent mercury in 20 mM $HClO_4$. Sulfite solution was prepared by dissolving sodium sulfite anhydrous ($NaSO_3$) in the N_2-saturated ultrapure water for 12 h before experiment.

2.3. Materials

Sulfuric acid, nitric acid, sodium chloride, potassium chloride and potassium dichromate were supplied by Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid was obtained from Hangzhou Chemical Reagent Co., Ltd. The perchloric acid (70%) was bought from Shanghai Jinlu Chemical Co., Ltd. Sodium sulfite anhydrous and sodium sulfate anhydrous were supplied by Shanghai No. 4 Reagent & H.V. Chemical Co., Ltd. All the chemicals above were of analytical grade. $HgCl_2$ and HgO were bought from Shanghai Shenbo Chemical Co., Ltd. and the purity was higher than 99.9%.

2.4. Removal efficiency calculation

In this article, the Hg^{2+} removal efficiency ($\eta_{Hg^{2+}}$), the Hg^{2+} reduction ratio (η_{Hg^0}) and the total mercury removal efficiency ($\eta_{Hg(tot)}$) were calculated by the equations listed as follows:

$$\eta_{Hg^{2+}} = \left(1 - \frac{c_{Hg^{2+}out}}{c_{Hg^{2+}in}}\right) \times 100\% \tag{1}$$

$$\eta_{Hg^0} = \frac{c_{Hg^0out}}{c_{Hg^{2+}in}} \times 100\% \tag{2}$$

$$\eta_{Hg(tot)} = \left(1 - \frac{c_{Hg^0out}}{c_{Hg^{2+}in}} - \frac{c_{Hg^{2+}out}}{c_{Hg^{2+}in}}\right) \times 100\% \tag{3}$$

where $\eta_{Hg^{2+}}$, $\eta_{Hg(tot)}$ are the Hg^{2+} and total mercury removal efficiencies; η_{Hg^0} is the Hg^{2+} reduction ratio; $c_{Hg^{2+}out}$, $c_{Hg^{2+}in}$ are outlet and inlet Hg^{2+}concentrations; c_{Hg^0out} is the outlet Hg^0 concentration.

3. Results and discussions

3.1. Hg^{2+} reactions in a bubbler containing sulfite

3.1.1. Effects of SO_4^{2-} ions

In the Dual-Alkali flue gas desulfurization system, sodium sulfite was considered as the main active absorbent, which was also considered as the main Hg^{2+} reduction agent in the previous study [24]. As flue gas contained about 3–5% O_2, a large portion of SO_3^{2-} in absorbent solution would be oxidized into SO_4^{2-}, which might have effect on the mercury removal. Thus, SO_4^{2-} concentration effects were firstly studied in the solution. As shown in Fig. 1, the increase of SO_4^{2-} concentration had a negative effect on bivalent mercury absorption. While SO_4^{2-} concentration increased from 0 to 0.32 mol/L, the Hg^{2+} absorption efficiency decreased from 90% to 80%. However, an inhibition of Hg^{2+} reduction was observed with the increase of SO_4^{2-} concentration. The reduction ratio decreased by 10% when SO_4^{2-} concentration reached 0.32 mol/L. Only less than 20% of the inlet Hg^{2+} was converted to elemental form and released to gas phase.

3.1.2. Effect of Cl^- ions

Also, the Cl^- ions in the actual Wet FGD absorbent solution coming from the absorption of gas-phase HCl in flue gas were normally very high. Its content depended on the inlet gas-phase chloride concentration and the recycle ratio, even exceeded 20,000 ppm. Therefore, our experiment then studied the effects of Cl^- ions in the solution on Hg^{2+} absorption. As shown in Fig. 2, it could be found that the chloride ions not only enhanced the Hg^{2+} absorption, but also greatly inhibited the aqueous Hg^{2+} reduction. Under the experimental conditions, the Hg^{2+} absorption efficiency exceeded 93% when the chloride ion concentration exceeded 1000 ppm. When

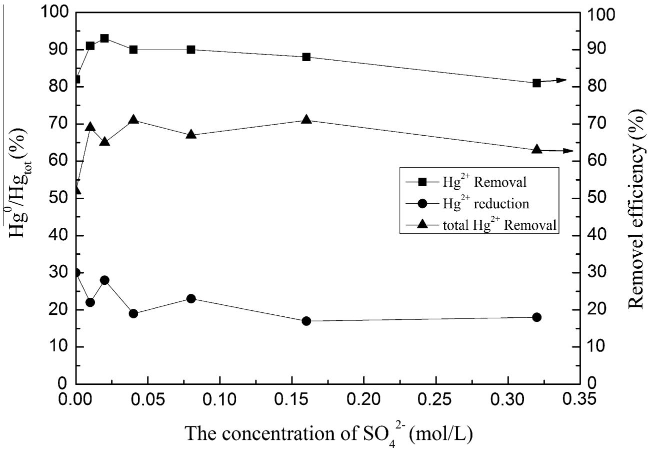

Fig. 1. Effects of SO_4^{2-} on Hg^{2+} absorption and reduction by $NaSO_3$ absorption solution. Experimental conditions: gas flow rate = 2 L/min; $[Hg^{2+}]$ = 80 μg/m³; balanced gas = N_2; solution volume = 300 ml; initial pH value = 5.51; $[SO_3^{2-}]$ = 0.4 mol/L; flue gas temperature = 110 °C; solution temperature = 40 °C.