Fuel 168 (2016) 7–13

Contents lists available at ScienceDirect

Fuel

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

The effect of selenite on mercury re-emission in smelting flue gas scrubbing system

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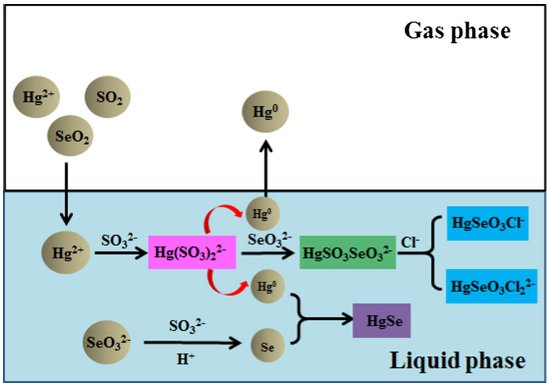
HIGHLIGHTS

- Selenite ions would have inhibition effect on mercury re-emission.
- The inhibition mechanism is different under acidic and alkaline condition.
- The inhibition is due to the formation of $HgSeO_3SO_3^{2-}$ and $Hg(SeO_3)_2^{2-}$ in alkaline condition.
- The inhibition is due to the formation of HgSe in acidic condition.
- The mercury reduction could be inhibited due to the formation of $HgSeO_3Cl^-$ and $HgSeO_3Cl_2^{2-}$.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 August 2015
Received in revised form 18 November 2015
Accepted 20 November 2015
Available online 2 December 2015

Keywords:
Hg
Mercury re-emission
Selenite ions
Smelting flue gas

ABSTRACT

Recently, the mercury re-emission from the scrubbing solution has become a hot topic in wet flue gas desulfurization process (WFGD). Selenite is one of the most important matters in the solution. It is discovered that selenite have great effect on the mercury re-emission in the WFGD process in this paper. Several important parameters, such as selenite concentration, pH value, temperature and chloride concentration, and reaction mechanisms were studied on the Hg^0 re-emission. The experimental results indicate that mercury reduction and re-emission can be effectively inhibited with high selenite and chloride concentrations, low temperature and pH value. The mechanisms for inhibition of mercury reduction and re-emission are proved to be different under acid and alkaline conditions respectively. Under acid condition, it is the formation of stable HgSe that decrease Hg^0 re-emission. However, the formation of more stable $HgSeO_3SO_3^{2-}$ or $Hg(SeO_3)_2^{2-}$ than $Hg(SO_3)_2^{2-}$ contributes to avoid the oxidized mercury reduction by sulfite ions and then the mercury re-emission under the alkaline condition. In addition, it is also found that Cl^- ions can further enhance the inhibition effect and suppress Hg^0 re-emission by the formation of stable $HgSeO_3Cl^-$ and $HgSeO_3Cl_2^{2-}$ complexes.

1. Introduction

Mercury, due to its characteristics of high toxicity, volatility and bioaccumulation, are receiving increasingly attentions [1,2]. The anthropogenic mercury emissions are primarily from combustion of fossil fuel and minerals, such as coal-fired power plants and

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http://dx.doi.org/10.1016/j.fuel.2015.11.072
0016-2361/

heavy metals smelters [3]. With ever-increasing awareness of environmental protection, many mercury control technologies, such as catalysts [4–6], sorbents [7,8] and strong oxidizer [9–12], have been developed to reduce mercury in flue gas. Generally, almost all of mercury are transferred into flue gas within three forms of mercury in flue gas, that is, oxidized mercury (Hg^{2+}), elemental mercury (Hg^0) and particulate mercury (Hg^p), in the combustion of coal or minerals [13]. Due to large solubility of Hg^{2+} in the water, it is easily captured by wet flue gas desulfurization (WFGD), by which other water-soluble pollutants, such as SO_2 and NO_2 are removed simultaneously [14]. Thus, it is fulfilling to study the effects of various facts on mercury removal efficiency.

Recently, many studies reported that Hg^{2+} would be reduced to Hg^0 by some reducible matters and then flee to atmosphere in the WFGD process [15]. Some researchers studied the mechanism of mercury re-emission and suggested that sulfite ions is the main reason because it can easily form unstable $HgSO_3$ and then decompose to Hg^0 [16–21]. Moreover, other ions in WFGD solutions, such as NO_2^- and Cl^-, could also interact with the Hg^{2+}or SO_3^{2-} to impacted the Hg^{2+} reduction process [22–27]. NO_2^- was proved to have complicate effect on Hg^{2+} reduction process: it will be benefit for Hg^0 re-emission due to the formation of more unstable $HgSO_3NO_2^-$ than $HgSO_3$ at low concentration; however, it would play an inhibiting effect on Hg^{2+} reduction because of the formation of Hg-nitrite complex $Hg(NO_2)_x^{2-x}$ at high concentration [20]. Cl^- has an effect to suppress Hg^0 re-emission through the formation of relatively stable $HgSO_3Cl^-$ or $HgSO_3Cl_2^{2-}$ [21].

Except for the traditional pollutants such as SO_2, NO_x, there are a large amount of volatile oxides in high temperature flue gas, like selenium dioxide (SeO_2), especially in the flue gas of heavy metal smelt [28]. Such oxide was changed to solid state matter due to cooling of tunnel before entering scrubbing system. In the scrubbing system, SeO_2 particles can be removed from the gas and then dissolve into the solutions in the forms of H_2SeO_3, $HSeO_3^-$ or SeO_3^{2-}. As a matter of fact, elemental selenium, similar to sulfur, obviously could be used to remove Hg^0 by the formation of HgSe [29,30]. However, for SeO_3^{2-}, it may have a complicated influence on the Hg^{2+} reduction behavior. On the one hand, SeO_3^{2-} may play the same role as SO_3^{2-} to improve Hg^0 re-emission on account of homology between Se and S. On the other hand, SeO_3^{2-} may combine Hg^{2+} to form stable complexes, thus it leads to the reduction of Hg^0 re-emission. To the best of our knowledge, few literature has studied the impact of selenite on Hg^0 re-emission in solutions. Therefore, it is meaningful to evaluate the effect of selenite on Hg^0 re-emission.

In our present research, the effects of selenite on mercury reduction and Hg^0 re-emission were investigated systematically. What's more, the reaction intermediates under different conditions was evaluated by UV–visible spectra analysis and the reaction mechanism has also been proposed.

2. Materials and methods

2.1. Experimental apparatus

A typical lab-scale apparatus was set up in this study to investigate the reactions involved in the Hg^0 re-emission. There are three systems in our device including chemical reaction system, mercury test system and tail gas treatment system. As shown in Fig. 1, in order to take the re-emission Hg^0 out, the high purity nitrogen gas was used as a carrier gas at a flow of 1.0 L/min. The main reaction equipment is a 3-neck round bottom flask of 500 mL, which has a carrier gas inlet, outlet and a neck for placement calomel electrode. The round-bottom flask was placed in a water bath. At the beginning of each test, the simulated solution was put into the flask and the magnetic stirring system was turned on. And then heated up to the set temperature and adjusted pH value by diluted nitric acid or sodium hydroxide. The pH value was determined by a pH instrument (Mettler-S220). Thereafter, the solution with certain concentration of bivalent mercury was injected quickly. At the same time, the concentration of mercury in the carrying gas N_2 began to be tested. Before the measurement of mercury, the gas flow after flask should pass through the 30% (w/v) NaOH solution to absorb the acid gases such as SO_2 gas which was produced in experiment. A RA-915 M Lumex Zeeman portable mercury spectrometer was applied to measure the content of Hg^0. The solution containing 5% (w/v) $KMnO_4$ and coconut shell activated carbon were employed to adsorb Hg^0 vapor in the tail gas. Finally, the cleaned tail gas was released into outdoor environment safely.

2.2. Materials

Sodium chloride, sodium sulfite anhydrous, potassium permanganate were bought from Sinopharm Chemical Reagent Co., Ltd. Sodium selenite pentahydrate, perchloric acid (70%), sulfuric acid, hydrochloric acid and nitric acid were purchased form Kemiou Chemical Reagent Co., Ltd. Sodium chloride and perchloric acid are guarantee reagent while others are analytical grade. Mercury sulfate ($HgSO_4$) and mercuric oxide (HgO) as the source of divalent mercury is analytical grade and the purity is higher than 99.9%.

2.3. UV–visible spectra analysis

To analyze the intermediate species which were formed by oxidized mercury and anions in the mercury reduction process, the UV–visible spectra of solutions were carried out with scanning speed of 300 nm/min on a UV–visible spectrophotometer (UV–vis DRS: UV2450, China). The mercury solution was prepared by dissolving HgO in concentrated $HClO_4$ and then it was diluted to required concentration. The reaction solutions including sulfite-containing, selenite-containing and chloride-containing solutions were made up by dissolving sodium sulfite (Na_2SO_3), sodium selenite (Na_2SeO_3) or sodium chloride (NaCl) in a ultrapure water respectively. The pH of scanning solution was adjusted by the addition of NaOH and $HClO_4$ solutions.

3. Result and discussion

3.1. Effect of SeO_3^{2-} concentration on mercury re-emission

Usually, SeO_2 is washed into solutions and dissolved selenite species. For the sake of testing the effects of SeO_3^{2-} content on the mercury reduction and re-emission, a series of experiments were carried out with the results showed in Fig. 2. Two stages were discovered for Hg^0 concentration, which were named as non-equilibrium stage and equilibrium. In non-equilibrium stage, due to high local Hg^{2+} content at the beginning of reaction, the Hg^0 concentration increases greatly and then drops sharply, and the outlet Hg^0 concentration of mercury re-emission decreases slowly in the following equilibrium stage. From Fig. 2, it can be seen obviously that the presence of SeO_3^{2-} has a favorable effect on inhibition of mercury reduction and re-emission. It is strongly associated with the concentration of SeO_3^{2-}.

It is widely recognized that SeO_3^{2-} could be combined with many heavy metal ions to form stable complex. Many literatures have shown that selenite ions have a certain antagonistic impact on mercury toxicity by chemical reaction between selenite and bivalent mercury ions [31]. Meanwhile, selenite ions could react with Hg^{2+} to form coordination compound as follows: