



## Investigation on mercury removal method from flue gas in the presence of sulfur dioxide



Yongpeng Ma, Zan Qu\*, Haomiao Xu, Wenhua Wang, Naiqiang Yan

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan, Shanghai 200240, China

### HIGHLIGHTS

- A new integrated process for the mercury removal and reclaim from the flue gas in the presence of SO<sub>2</sub> was developed.
- The laws of fate of mercury in Stage I of the integrated process were studied and revealed.
- HgSO<sub>4</sub> was determined as a more efficient absorbent on Hg<sup>0</sup> removal and was introduced to Stage II of the integrated process.
- 1.0% H<sub>2</sub>O<sub>2</sub> was introduced to the composite absorption solution to overcome the negative effect of SO<sub>2</sub> on Hg<sup>0</sup> removal in Stage II.

### ARTICLE INFO

#### Article history:

Received 25 January 2014

Received in revised form 2 July 2014

Accepted 3 July 2014

Available online 17 July 2014

#### Keywords:

Nonferrous metal smelting

Flue gas

Mercury reclaim

Sulfur dioxide

Mercury sulfate

### ABSTRACT

A new integrated process was developed for the removal and reclamation of mercury from the flue gas in the presence of SO<sub>2</sub>, typically derived from nonferrous metal smelting. The new process contains a pre-desulfurization unit (Stage I) and a co-absorption unit (Stage II). In Stage I, 90% of the SO<sub>2</sub> from flue gas can be efficiently absorbed by ferric sulfate and reclaimed sulfuric acid. Meanwhile, the proportion of Hg<sup>2+</sup> and Hg<sup>0</sup> in the flue gas can be redistributed in this stage. Then, over 95% of the Hg<sup>0</sup> and the residual SO<sub>2</sub> can be removed simultaneously with a composite absorption solution from the flue gas in Stage II, which is much more efficient for the Hg<sup>0</sup> reclaiming than the traditional method. The composite absorption solution in Stage II, which is composed of 0.1 g/L HgSO<sub>4</sub>, 1.0% H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>, could effectively remove and reclaim Hg<sup>0</sup> overcoming the negative effect of SO<sub>2</sub> on Hg<sup>0</sup> absorption. Moreover, the concentrations of HgSO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> were adjusted with the changes in of the concentrations of Hg<sup>0</sup> and SO<sub>2</sub> in the flue gas. It is a potential and promising technology for the mercury removal and reclaim from the flue gas in the presence of SO<sub>2</sub>.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

The *Minamata Convention on Mercury*, a new legally binding global treaty that aims to reduce mercury emission, was signed on Oct. 10, 2013. This means that the control of mercury emissions is becoming more urgent. Nonferrous metal production plays a very important role in mercury emission [1,2]. Especially in China, it has been estimated that about 12–15% of the total mercury emission comes from the flue gas of nonferrous metal smelting in 2010 [3,4]. Therefore, it is one of the main mercury pollution sources that should be controlled.

Particulate-bound mercury (Hg<sup>p</sup>), oxidized gaseous mercury (Hg<sup>2+</sup>) and elemental mercury (Hg<sup>0</sup>) are the main forms of mercury in the flue gas derived from nonferrous metal smelting [5].

Meanwhile, in most nonferrous metal smelting flue gas, the mercury is often accompanied by a high concentration of sulfur dioxide (SO<sub>2</sub>) [6]. Therefore, the removal of SO<sub>2</sub> should be taken into account when we select the mercury removal technology for the flue gas of nonferrous metal smelting. The typical cleaning process for smelting flue gas is as follows. First, the flue gas effused from the smelter or furnace is de-dusted by particulate matter collection devices (e.g., Electrostatics precipitator or Fabric filter). Next, the flue gas is quickly cooled by water in a wet scrubber unit, whereas the unit for mercury recovery will be installed only if the mercury concentration is high enough. Finally, SO<sub>2</sub> is either captured with a desulfurization unit or converted to SO<sub>3</sub> to produce sulfuric acid, which depends on the concentration level of SO<sub>2</sub> in the gas [7].

Throughout the above process, Hg<sup>p</sup> can be efficiently captured by a particulate matter collection device and returned to the furnace together with the bulk fly ash. Hg<sup>2+</sup> will be absorbed and lost in the wet-cooling scrubber and enter the acid wastewater as a typical heavy metal pollutant. However, Hg<sup>0</sup> is more difficult

\* Corresponding author. Tel.: +86 21 54745591; fax: +86 21 54745591.  
E-mail address: [quzan@sjtu.edu.cn](mailto:quzan@sjtu.edu.cn) (Z. Qu).

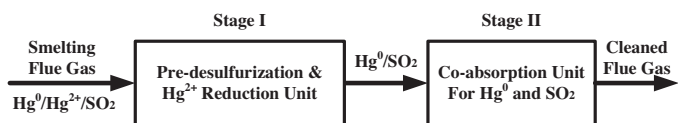


Fig. 1. The reaction scheme for enhanced mercury removal and recovery.

to remove than Hg<sup>p</sup> and Hg<sup>2+</sup> because of its high volatility and insolubility. The concentration of Hg<sup>0</sup> in the flue gas of nonferrous metal smelting is very high. For example, the concentration of Hg<sup>0</sup> in the lead and zinc smelting flue gas ranges from several to tens mg/m<sup>3</sup> [5,8]. Furthermore, Hg<sup>0</sup> is a valuable resource in fields such as dentistry, mercurial thermometers and gold mining. For flue gas containing a high concentration of Hg<sup>0</sup>, the Hg<sup>0</sup> can be captured and reclaimed using absorption methods [9–12], of which the Boliden–Norzink process, with HgCl<sub>2</sub> solution, was considered to be one of the most common processes. However, even after treatment in a Boliden–Norzink unit, the mercury concentration in flue gas often remains too high to meet the strict emission limitations [5]. Meanwhile, only the Hg<sup>0</sup> in flue gas can be removed by conventional processes, and almost all of the Hg<sup>2+</sup> in flue gas will be pre-absorbed in the upstream wet-cooling units, thus becoming one of the main pollutants in the cooling water (acid wastewater). This will reduce the reclamation efficiency of total mercury because once the mercury enters the wastewater, it is hard to be reclaimed. Therefore, reclaiming this part of mercury is an essential factor for increasing the recovery of all mercury and minimizing its pollution in waste acid water. In addition, the high concentration of SO<sub>2</sub> in flue gas will reduce Hg<sup>2+</sup> to Hg<sup>0</sup> in solution [7,13,14], and the generated Hg<sup>0</sup> will re-emit from mercury absorption solution which decreases the reclaiming efficiency of total mercury. Generally, SO<sub>2</sub> always is reclaimed by double contact double absorption process to produce sulfuric acid in the presence of high concentration of SO<sub>2</sub> in the flue gas. However, when the concentration of SO<sub>2</sub> is not suitable for the double contact double absorption process, the liquid-phase catalytic desulfurization technology will be a good choice as desulfurization process.

Based on the above consideration, a new conception is proposed for obtaining a higher level of mercury recovery (Fig. 1). First, the de-dusted flue gas with SO<sub>2</sub>, Hg<sup>0</sup> and Hg<sup>2+</sup> was cooled and pre-desulfurized with a ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) solution in the same unit (noted as Stage I), where Hg<sup>2+</sup> will be absorbed together with SO<sub>2</sub>. In Stage I, maximum removal of SO<sub>2</sub> was attempted to enhance the reduction of the absorbed Hg<sup>2+</sup> back to Hg<sup>0</sup> and to minimize the loss of mercury from the flue gas. The function of Stage I had three aspects: the first one was that the Hg<sup>2+</sup>, when reduced back to Hg<sup>0</sup>, could prevent pollution from the H<sub>2</sub>SO<sub>4</sub> products derived from mercury; the second one was that the reclaiming efficiency of total mercury could be enhanced; and the third one was that the effects of SO<sub>2</sub> on Hg<sup>0</sup> removal in Stage II could be weakened. Next, the method for fully reclaiming mercury and deeply desulfurizing the downstream unit in the presence of Hg<sup>0</sup> and low concentration levels of SO<sub>2</sub> is discussed in the subsequent section (noted as Stage II). However, there is still a lack of basic understanding regarding the interaction reactions among Hg<sup>0</sup>, Hg<sup>2+</sup>, and SO<sub>2</sub> in Stage I and Stage II, which is critical for the application and development of a new composite process. To clarify such queries, a series of experiments and theoretical analyses are reported in this paper.

## 2. Experimental materials and methods

### 2.1. Experimental methods

A schematic diagram of the absorption experimental apparatus is shown in Fig. 2. A three-neck flask was used as the absorption

reactor in this research. Several cylinder gases were used to simulate the 1.0 L/min high concentration of mercury and sulfur dioxide flue gas. Mercury vapor was generated using a mercury bottle in a water bath that was carried by N<sub>2</sub> gas. The simulated flue gas passed through the reactor. A certain amount of mercury absorption solution was injected into the reactor to investigate the instantaneous and continuous mercury absorption reaction. To study the effect of SO<sub>2</sub> and NO on Hg<sup>0</sup> absorption, both SO<sub>2</sub> and NO were introduced into the simulated flue gas. The temperatures of the flue gas and the absorption solution were maintained at approximately 303 K and 298 K, respectively. The residence time of the simulated flue gas in the absorption solution was approximately 1.2 s. The initial Hg<sup>0</sup> concentration in the inlet gas of the absorption reactor was 1.5–2.1 mg/m<sup>3</sup>, which was controlled by adjusting the temperature of the water bath. The inlet and outlet Hg<sup>0</sup> concentrations of the absorption reactor were detected by a mercury analyzer (SG-921, Jiangfen Ltd., China), whereas the detection limit of the mercury analyzer was 6.8 mg/m<sup>3</sup>. The signal was collected and recorded by a data transition and acquisition device (N2000, Zhida Ltd., China). The Hg<sup>0</sup> concentration in the flue gas was calibrated by a Lumex mercury analyzer (RA915, Lumex Ltd., Russia). The Hg<sup>0</sup> concentration in solution was measured by a Lumex mercury analyzer (RA915+/RP-91, Lumex Ltd., Russia). The SO<sub>2</sub> concentration was detected by a flue gas analyzer (KM900, Kane Ltd., England).

The Hg<sup>0</sup> removal efficiency ( $\eta$ ) was defined according to Eq. (1):

$$\eta_{\text{Hg}^0} = \frac{C_{\text{Hg}^0(\text{in})} - C_{\text{Hg}^0(\text{out})}}{C_{\text{Hg}^0(\text{in})}} \times 100\% \quad (1)$$

where  $\eta_{\text{Hg}^0}$  is the Hg<sup>0</sup> removal efficiency, and  $C_{\text{Hg}^0(\text{in})}$  and  $C_{\text{Hg}^0(\text{out})}$  are the inlet and outlet Hg<sup>0</sup> concentrations of the absorption bottle, respectively.

The factors affecting Hg removal included the concentrations of SO<sub>2</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, HgSO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub>. SO<sub>2</sub> was introduced into the simulated flue gas by one of the cylinder gases, and the other factors were introduced into the solutions. In Stage I, some reductants, such as Fe<sup>2+</sup>, SO<sub>3</sub><sup>2-</sup>, Sn<sup>2+</sup> and NaBH<sub>4</sub>, were employed to accelerate the reduction of Hg<sup>2+</sup> to Hg<sup>0</sup>.

The mass balance of the Hg during the course of the experiment had been assessed strictly. For example, the flow rate of the simulated flue gas was 1.0 L/min and the initial concentration of Hg<sup>0</sup> was 1.8 mg/m<sup>3</sup>. The amount of Hg in the initial HgCl<sub>2</sub> solution was 1.104 × 10<sup>-3</sup> mmol. The flue gas containing Hg<sup>0</sup> was absorbed for 30 min and 60 min. Using the integral calculation method, the amounts of Hg<sup>0</sup> absorbed into the HgSO<sub>4</sub> solutions were found to be 0.238 × 10<sup>-3</sup> mmol and 0.414 × 10<sup>-3</sup> mmol. Next, the total amount of Hg in the HgSO<sub>4</sub> solutions detected by a Lumex mercury analyzer was 1.357 × 10<sup>-3</sup> mmol and 1.541 × 10<sup>-3</sup> mmol. Therefore, the mass balance error of Hg was 1.1% and 1.5%. Thus, the mass balance of the Hg was accurate during the course of the experiment.

### 2.2. Materials

The following main chemicals were employed: mercury (99.9%), mercuric chloride (99.5%), mercury sulfate (99.5%), hydrogen peroxide (30%), sodium chloride (99.5%), hydrogen chloride (36%), sodium sulfate (99%), sodium sulfite (98%), sodium nitrate (99%), sodium hypochlorite (99%), ferric nitrate (98%), ferric chloride (98%), ferric sulfate (98%), copper dichloride (99%), nitric acid (69%), and potassium permanganate (99%) from Sigma-Aldrich Co., Ltd. The SO<sub>2</sub> (99.9%) and N<sub>2</sub> (99.9%) were stored in cylinders and obtained from Dalian Date Gas Co., Ltd.

Download English Version:

<https://daneshyari.com/en/article/576609>

Download Persian Version:

<https://daneshyari.com/article/576609>

[Daneshyari.com](https://daneshyari.com)