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_2 was developed.
- The laws of fate of mercury in Stage I of the integrated process were studied and revealed.
- $HgSO_4$ was determined as a more efficient absorbent on Hg^0 removal and was introduced to Stage II of the integrated process.
- 1.0% H_2O_2 was introduced to the composite absorption solution to overcome the negative effect of SO_2 on Hg^0 removal in Stage II.

ARTICLE INFO

ABSTRACT

A new integrated process was developed for the removal and reclamation of mercury from the flue gas in the presence of SO_2, 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_2 from flue gas can be efficiently absorbed by ferric sulfate and reclaimed sulfuric acid. Meanwhile, the proportion of Hg^{2+} and Hg^0 in the flue gas can be redistributed in this stage. Then, over 95% of the Hg^0 and the residual SO_2 can be removed simultaneously with a composite absorption solution from the flue gas in Stage II, which is much more efficient for the Hg^0 reclaiming than the traditional method. The composite absorption solution in Stage II, which is composed of 0.1 g/L $HgSO_4$, 1.0% H_2O_2 and H_2SO_4, could effectively remove and reclaim Hg^0 overcoming the negative effect of SO_2 on Hg^0 absorption. Moreover, the concentrations of $HgSO_4$ and H_2O_2 were adjusted with the changes in of the concentrations of Hg^0 and SO_2 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_2.

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^p), oxidized gaseous mercury (Hg^{2+}) and elemental mercury (Hg^0) 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_2) [6]. Therefore, the removal of SO_2 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_2 is either captured with a desulfurization unit or converted to SO_3 to produce sulfuric acid, which depends on the concentration level of SO_2 in the gas [7].

Throughout the above process, Hg^p can be efficiently captured by a particulate matter collection device and returned to the furnace together with the bulk fly ash. Hg^{2+} will be absorbed and lost in the wet-cooling scrubber and enter the acid wastewater as a typical heavy metal pollutant. However, Hg^0 is more difficult
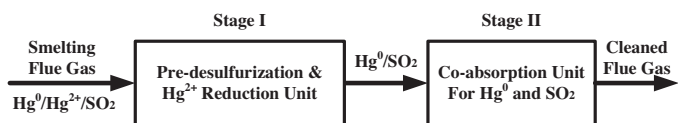
Fig. 1. The reaction scheme for enhanced mercury removal and recovery.

to remove than Hg^p and Hg^{2+} because of its high volatility and insolubility. The concentration of Hg^0 in the flue gas of nonferrous metal smelting is very high. For example, the concentration of Hg^0 in the lead and zinc smelting flue gas ranges from several to tens mg/m³ [5,8]. Furthermore, Hg^0 is a valuable resource in fields such as dentistry, mercurial thermometers and gold mining. For flue gas containing a high concentration of Hg^0, the Hg^0 can be captured and reclaimed using absorption methods [9–12], of which the Boliden–Norzink process, with $HgCl_2$ solution, was considered to be on 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^0 in flue gas can be removed by conventional processes, and almost all of the Hg^{2+} 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_2 in flue gas will reduce Hg^{2+} to Hg^0 in solution [7,13,14], and the generated Hg^0 will re-emit from mercury absorption solution which decreases the reclaiming efficiency of total mercury. Generally, SO_2 always is reclaimed by double contact double absorption process to produce sulfuric acid in the presence of high concentration of SO_2 in the flue gas. However, when the concentration of SO_2 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_2, Hg^0 and Hg^{2+} was cooled and pre-desulfurized with a ferric sulfate ($Fe_2(SO_4)_3$) solution in the same unit (noted as Stage I), where Hg^{2+} will be absorbed together with SO_2. In Stage I, maximum removal of SO_2 was attempted to enhance the reduction of the absorbed Hg^{2+} back to Hg^0 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^{2+}, when reduced back to Hg^0, could prevent pollution from the H_2SO_4 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_2 on Hg^0 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^0 and low concentration levels of SO_2 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^0, Hg^{2+}, and SO_2 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_2 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_2 and NO on Hg^0 absorption, both SO_2 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^0 concentration in the inlet gas of the absorption reactor was 1.5–2.1 mg/m³, which was controlled by adjusting the temperature of the water bath. The inlet and outlet Hg^0 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/m³. The signal was collected and recorded by a data transition and acquisition device (N2000, Zhida Ltd., China). The Hg^0 concentration in the flue gas was calibrated by a Lumex mercury analyzer (RA915, Lumex Ltd., Russia). The Hg^0 concentration in solution was measured by a Lumex mercury analyzer (RA915+/RP-91, Lumex Ltd., Russia). The SO_2 concentration was detected by a flue gas analyzer (KM900, Kane Ltd., England).

The Hg^0 removal efficiency (η) was defined according to Eq. (1):

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

where η_{Hg^0} is the Hg^0 removal efficiency, and $C_{Hg^0(in)}$ and $C_{Hg^0(out)}$ are the inlet and outlet Hg^0 concentrations of the absorption bottle, respectively.

The factors affecting Hg removal included the concentrations of SO_2, $Fe_2(SO_4)_3$, $HgSO_4$, H_2SO_4, Cl^-, SO_4^{2-}, SO_3^{2-}, NO_3^- and H_2O_2. SO_2 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^{2+}, SO_3^{2-}, Sn^{2+} and $NaBH_4$, were employed to accelerate the reduction of Hg^{2+} to Hg^0.

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^0 was 1.8 mg/m³. The amount of Hg in the initial $HgCl_2$ solution was 1.104×10^{-3} mmol. The flue gas containing Hg^0 was absorbed for 30 min and 60 min. Using the integral calculation method, the amounts of Hg^0 absorbed into the $HgSO_4$ solutions were found to be 0.238×10^{-3} mmol and 0.414×10^{-3} mmol. Next, the total amount of Hg in the $HgSO_4$ solutions detected by a Lumex mercury analyzer was 1.357×10^{-3} mmol and 1.541×10^{-3} 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_2 (99.9%) and N_2 (99.9%) were stored in cylinders and obtained from Dalian Date Gas Co., Ltd.
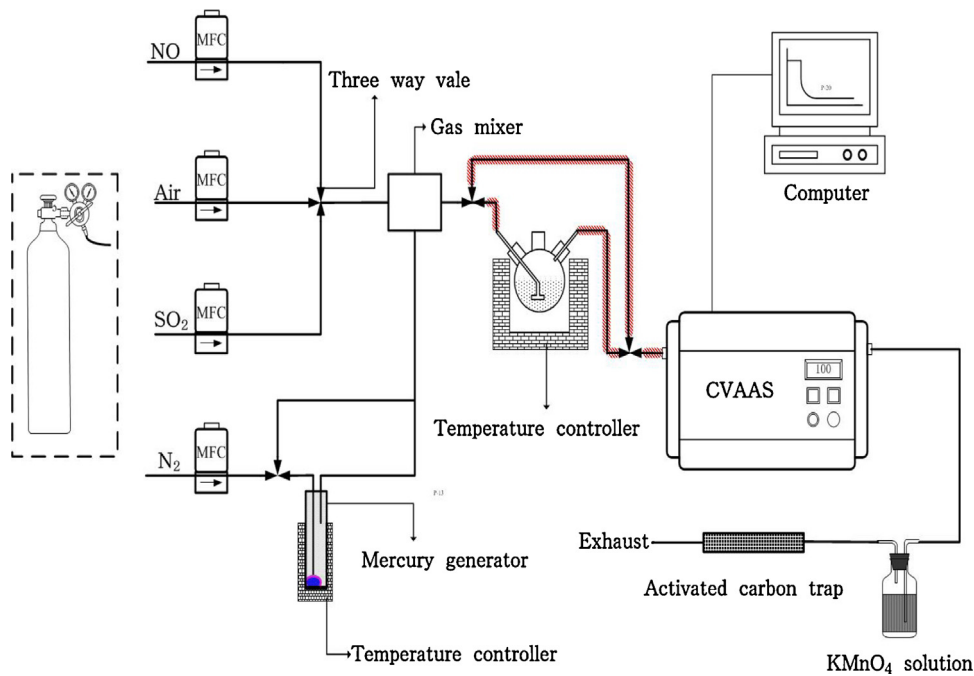
Fig. 2. The schematic diagram of the absorption experimental apparatus.

3. Results and discussion

3.1. The fate of mercury in Stage I

3.1.1. The fate of Hg^0

It is well known that transition metal ions, such as Fe^{3+} and Mn^{4+}, can act as effective catalysts for the oxidation of SO_2 by dissolved oxygen in aqueous solution, and this method is widely used for flue gas desulfurization and sulfuric acid production [15–18]. In this study, $Fe_2(SO_4)_3$ was applied to absorb and catalytically oxidize SO_2 in Stage I. The pre-experimental results show that approximately 90% of the SO_2 could be removed by the $Fe_2(SO_4)_3$ solution. Clearly, the Stage I processing steps could meet the demands of the flue gas pre-desulfurization system. However, there are a few researches on mercury removal from flue gas by $Fe_2(SO_4)_3$ solution in the presence of SO_2, which is important for evaluating the effect of the Stage I processing steps on mercury removal and recovery from flue gases containing SO_2. Therefore, the absorption performance of Hg^0 by $Fe_2(SO_4)_3$ solution was investigated in the presence of SO_2.

As shown in Fig. 3, the outlet Hg^0 concentration decreased remarkably at the beginning; then, it increased slowly when there was only N_2 and Hg^0 in the simulated flue gas. Clearly, the $Fe_2(SO_4)_3$ solution could only absorb a certain amount of Hg^0. However, the Hg^0 concentration increased quickly in the $Fe_2(SO_4)_3$ absorption solution when in the presence of SO_2. Furthermore, the outlet Hg^0 concentration is higher than the initial inlet Hg^0 concentration ($1.5\,mg/m^3$). This means that the Hg^0 absorbed at the beginning of the absorption reaction was re-emitted to the flue gas from the $Fe_2(SO_4)_3$ solution. Although the Hg^0 absorption could be enhanced with an increase in $Fe_2(SO_4)_3$ concentration, When the SO_2 and Hg^0 were simultaneously added to the simulated flue gas, the Hg^0 concentration after 50 s of treatment in Stage I was higher than the initial Hg^0 concentration, which indicates that only little of Hg^0 could be absorbed from the flue gas in the Stage I.

3.1.2. The fate of Hg^{2+}

In addition, the flue gas of nonferrous metal smelting always contains a certain amount of Hg^{2+}, which will be co-absorbed by the
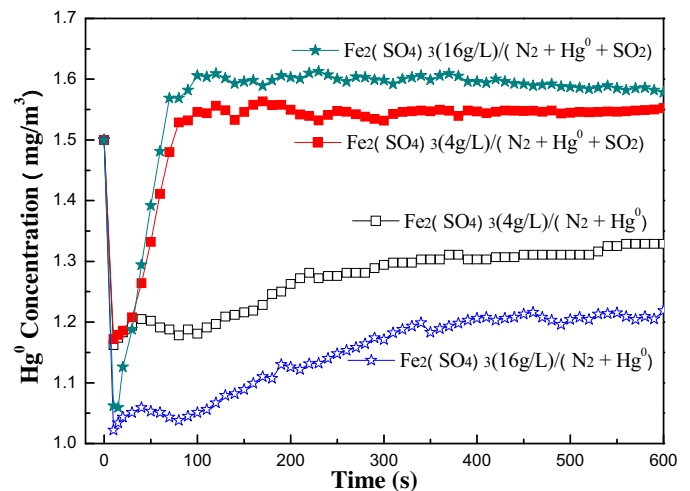

Fig. 3. Hg^0 absorption by $Fe_2(SO_4)_3$ with or without SO_2 in Stage I. The flow rate of the simulated flue gas was 1.0 L/min. The initial concentrations of Hg^0 and SO_2 in the simulated flue gas were $1.5\,mg/m^3$ and $8000\,mg/m^3$, respectively. The concentration of $Fe_2(SO_4)_3$ was 4 g/L and 16 g/L, respectively. The volume of the absorption solution was 30 mL. The temperatures of the flue gas and the absorption solution were maintained at approximately about 303 K and 298 K, respectively.

$Fe_2(SO_4)_3$ solution. To investigate the influence of absorbed Hg^{2+} on Hg^0 removal and its fate in Stage I, $HgSO_4$ was added into the $Fe_2(SO_4)_3$ solution to provide Hg^{2+}, and the behaviors of Hg^{2+} were investigated. The results are shown in Fig. 4.

As shown in Fig. 4, Hg^{2+} enhanced the absorption of Hg^0 significantly in the $Fe_2(SO_4)_3$ solution when there was only N_2 and Hg^0 in the simulated flue gas. If SO_2 is introduced into the simulated flue gas, the outlet Hg^0 concentration is much higher than the initial Hg^0 concentration ($1.5\,mg/m^3$), which means that Hg^{2+} could be reduced to Hg^0 and re-emitted from the absorption solution quickly. The Hg^0 absorption was enhanced slightly by increasing the $HgSO_4$ concentration from 0.01 g/L to 0.10 g/L without SO_2 in flue gas. However, more of the Hg^{2+} was converted to Hg^0 and re-emitted with a higher Hg^{2+} concentration in the presence of SO_2.
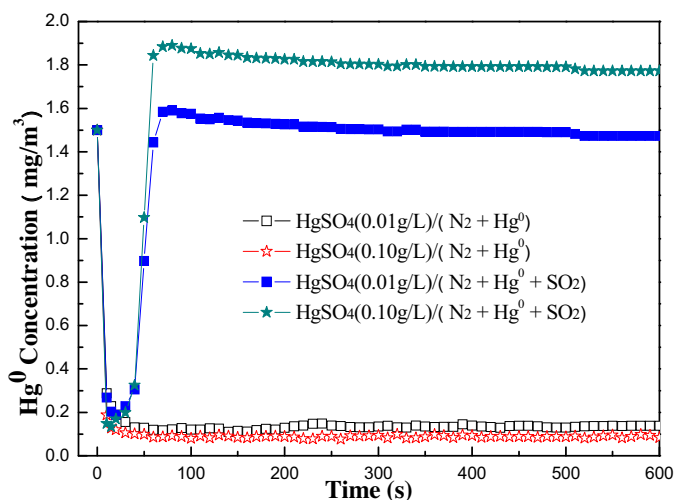
Fig. 4. *The transformation of the Hg²⁺ species in Stage I.* The flow rate of the simulated flue gas was 1.0 L/min. The initial concentrations of Hg^0 and SO_2 in the simulated flue gas were 1.5 mg/m³ and 8000 mg/m³, respectively. The concentration of $HgSO_4$ was 0.01 g/L and 0.10 g/L, respectively. The volume of absorption solution was 30 mL. The temperatures of the flue gas and the absorption solution were maintained at approximately 303 K and 298 K, respectively.
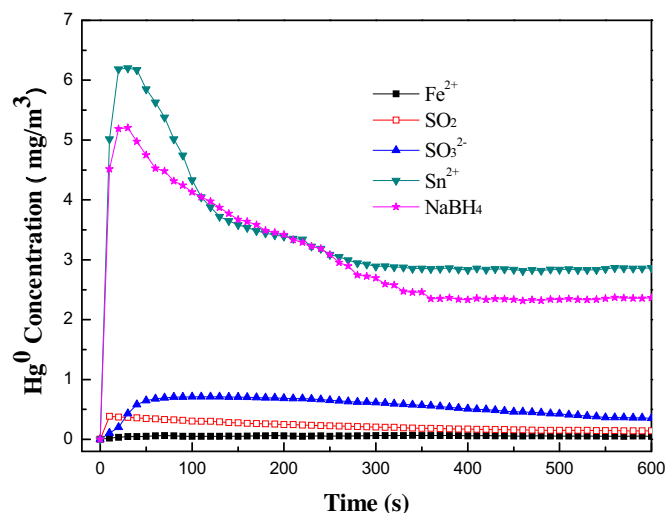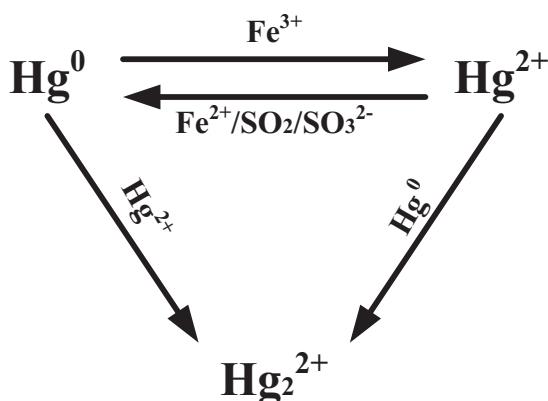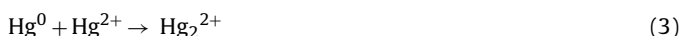

Fig. 5. The transformations of mercury species in Stage I.

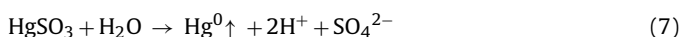The reaction involved in Stage I is shown in Fig. 5.

In fact, the nature of the conception can be ascribed to several parallel or interaction reactions among Hg^0, Hg^{2+}, and SO_2 in the pre-desulfurization system (Stage I) and the co-absorption system (Stage II). In Stage I, Hg^0 could be absorbed and converted to Hg^{2+} by $Fe_2(SO_4)_3$. Moreover, the absorption of Hg^0 could be improved by the Hg^{2+} generated from the flue gas in this stage. Meanwhile, the Hg^{2+} absorbed by the $Fe_2(SO_4)_3$ solution could be converted to Hg^0 and re-emitted to the flue gas by SO_2.

The reactions for the absorption of Hg^0 and the reduction of Hg^{2+} are as follows [19–21]:

Absorption reactions:

$$Hg^0 + 2Fe^{3+} \rightarrow Hg^{2+} + 2Fe^{2+} \tag{2}$$

$$Hg^0 + Hg^{2+} \rightarrow Hg_2^{2+} \tag{3}$$

Reduction reactions:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+ \tag{4}$$

$$HSO_3^- \rightarrow SO_3^{2-} + H^+ \tag{5}$$

$$Hg^{2+} + SO_3^{2-} \rightarrow HgSO_3 \tag{6}$$

$$HgSO_3 + H_2O \rightarrow Hg^0\uparrow + 2H^+ + SO_4^{2-} \tag{7}$$

Fig. 6. *The reduction effect of Hg²⁺ by strengthening regulations.* The flow rate of the simulated flue gas was 1.0 L/min. The initial concentration of SO_2 was 8000 mg/m³ in the simulated flue gas. The concentration of $HgSO_4$ was 0.00182 g/L, and the volume of the absorption solution was 30 mL. The concentration of reductants, such as Fe^{2+}, SO_3^{2-}, Sn^{2+} and $NaBH_4$, were 10%. The temperatures of the flue gas and the absorption solution were maintained at approximately 303 K and 298 K, respectively.

$$Hg^{2+} + 2Fe^{2+} \rightarrow Hg^0\uparrow + 2Fe^{3+} \tag{8}$$

According to the experimental results, most of the SO_2 could be removed from the flue gas without losing much Hg^0 in Stage I. Furthermore, the absorbed Hg^{2+} could be converted to the Hg^0 and re-emitted to the flue gas and the proportion of Hg^{2+} and Hg^0 in the flue gas was redistributed in this stage. According to the typical flue gas treatment progression of the Boliden–Norzink process, most of the Hg^{2+} in smelting flue gas is removed by a wet scrubber and enters the wastewater from which it is hard to be reclaimed and requires continuous treatment. In this research, the Hg^{2+} could be converted to Hg^0 and re-emitted into the flue gas. The outlet Hg^0 concentration generated during Stage I is much higher than the inlet Hg^0 concentration, which is favorable for promoting the total recovery of mercury by a subsequent mercury absorption unit. Meanwhile, no significant effects of the NO on the reduction of Hg^{2+} were observed in Stage I, and the absorptions of SO_2 and Hg^0 were also not affected. Therefore, the effects of SO_2 on the reduction of Hg^{2+} and the absorption of Hg^0 were investigated.

3.1.3. The enhancement methods of the reduction of Hg²⁺

Because the reduction rate of Hg^{2+} by SO_2 is rather slow, reductants such as Fe^{2+}, SO_3^{2-}, Sn^{2+} and $NaBH_4$ were introduced to accelerate the reduction of Hg^{2+} to Hg^0.

Based on the time course plot in Fig. 6, it is clear that the effect of Fe^{2+} on the reduction of Hg^{2+} is very weak. The reduction of Hg^{2+} by SO_3^{2-} is much better than gaseous SO_2. However, both SO_2 and SO_3^{2-} can only reduce approximately 20–30% of the total Hg^{2+} in the solution. Among all of these reductants, Sn^{2+} exhibited the best effect on Hg^{2+}. According to the integral calculation result, nearly 100% of the Hg^{2+} could be reduced by Sn^{2+}. Therefore, the optional additive to fully drive away the accumulated Hg^{2+} from wastewater in Stage I is either Sn^{2+} or $NaBH_4$.

3.2. The Hg⁰ absorption and enhancement method in Stage II

3.2.1. Selection of the absorbents for Hg⁰ removal

To select a more efficient absorbent for Hg^0 absorption, several chlorides and mercury compounds were tested. Based on the data exhibited in Fig. 7, it can be observed that mercury compounds achieve a higher mercury removal efficiency than the other
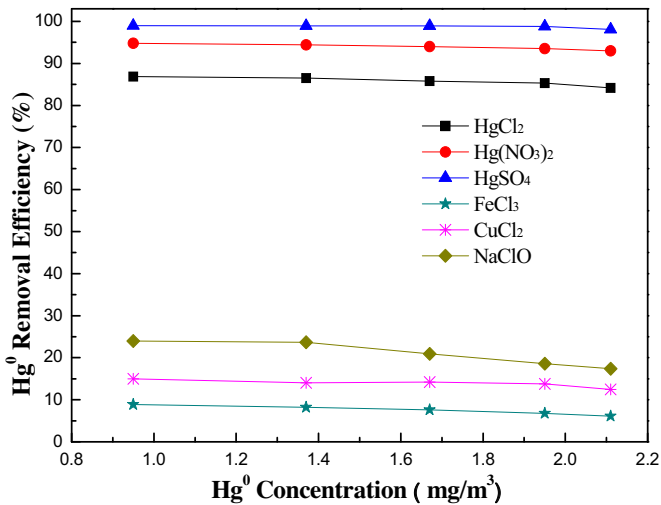
Fig. 7. *The selection of absorbents on Hg⁰ removal.* The flow rate of simulated flue gas was 1.0 L/min. The initial concentration of Hg⁰ was 2.1 mg/m³ in the simulated flue gas. The concentrations of absorbents were 0.5 g/L and the volumes of absorption solution were 30 mL. The temperature of the flue gas and absorption solution was maintained at about 303 K and 298 K, respectively.
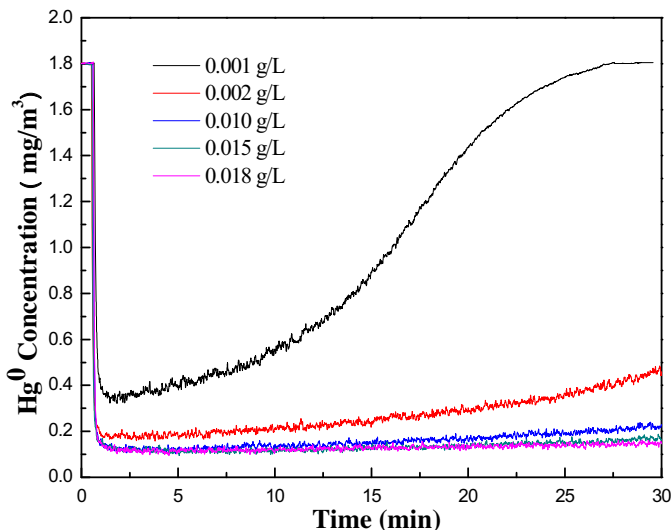

Fig. 8. *Effects of the concentration of mercury sulfate on Hg⁰ removal.* The initial Hg⁰ concentration of the simulated flue gas was 1.8 mg/m³, and the flow rate of simulated flue gas was 1.0 L/min. The HgSO₄ concentrations were 0.001 g/L, 0.002 g/L, 0.01 g/L, 0.015 g/L and 0.018 g/L. The sulfuric acid concentration in the HgSO₄ absorption solution was 0.02 mol/L. The temperatures of the flue gas and the absorption solution were maintained at approximately 303 K and 298 K, respectively.

chlorides. Clearly, Hg(II) is the key ingredient to absorb Hg⁰ rather than Cl⁻. Among these mercury compounds, mercury sulfate is better than mercury nitrate and mercury chloride on mercury absorption. The Hg⁰ removal efficiency is approximately 98.5% when the initial Hg⁰ concentration and mercury sulfate are 2.1 mg/m³ and 0.5 g/L, respectively. Therefore, the mercury sulfate solution was considered to be a new, efficient absorbent in this research.

The influence of the HgSO₄ concentration on Hg⁰ removal was also investigated. The sulfuric acid concentration of the HgSO₄ absorption solution was found to be 0.02 mol/L. The HgSO₄ concentrations for the samples tested were 0.001 g/L, 0.002 g/L, 0.01 g/L, 0.015 g/L and 0.018 g/L. The initial Hg⁰ concentration of the simulated flue gas was 1.8 mg/m³, and the flow rate of the simulated flue gas was 1.0 L/min. As shown in Fig. 8, increasing the HgSO₄
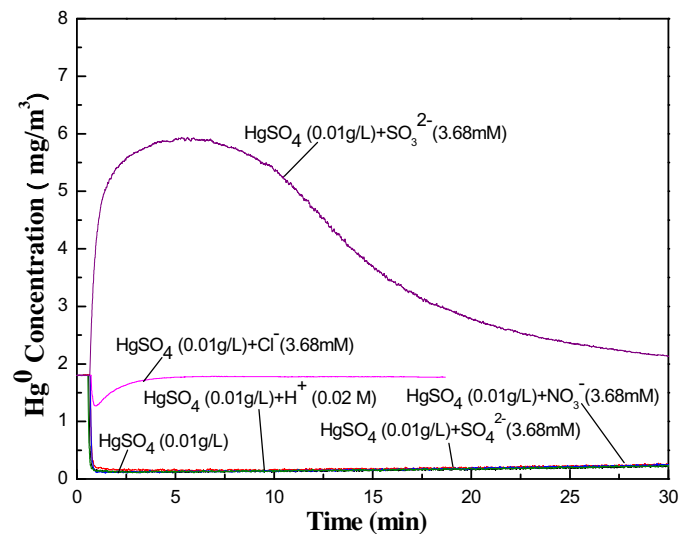

Fig. 9. *Effects of ions on Hg⁰ removal in HgSO₄ solution.* The initial Hg⁰ concentration of the simulated flue gas was 1.8 mg/m³, and the flow rate of the simulated flue gas was 1.0 L/min. The concentration of HgSO₄ was 0.01 g/L. The sulfuric acid concentration in the HgSO₄ absorption solution was 0.02 mol/L. The mol ratios between various ions and HgSO₄ were 100:1. The temperatures of the flue gas and the absorption solution were maintained at approximately 303 K and 298 K, respectively.

concentration is beneficial for removal of Hg⁰. The Hg⁰ removal efficiency was approximately 95% when the HgSO₄ concentration was 0.01 g/L. However, the Hg⁰ removal efficiency tends to be reduced when the HgSO₄ concentration increased beyond 0.01 g/L. The absorbent (HgCl₂) concentration in the Boliden–Norzink process occurs from 1.0 g/L to 3.0 g/L [8], which is much higher than the HgSO₄ concentration in this research. Thus, it will save a huge amount of absorbent if HgSO₄ was applied as the mercury absorbent, which means that the cost of this process may be lower than the conventional process.

3.2.2. Influence of ions on Hg⁰ removal in HgSO₄ solution

The components of flue gas derived from nonferrous metal smelting are complicated. The flue gas components co-absorbed by the mercury absorption solution will generate a large concentration of anions. To investigate the influence of anions on Hg⁰ removal, equal amounts of H₂SO₄, NaNO₃, NaCl and Na₂SO₃ were added to the HgSO₄ solution. As shown in Fig. 9, there is no obvious change in the Hg⁰ removal when NO₃⁻ and H₂SO₄ were added to the HgSO₄ solution. The application of additional levels of H₂SO₄ and NO₃⁻ additives will affect the Hg⁰ removal in the following experiments (Supplementary material, Figs. S1 and S2). These results indicate that the H⁺, NO₃⁻ and SO₄²⁻ do not affect the Hg⁰ removal. However, the Hg⁰ removal was inhibited when Cl⁻ was added to the HgSO₄ solution. Meanwhile, increased levels of Cl⁻ additives in the HgSO₄ absorption solution lead to more Hg⁰ removal inhibition (Supplementary material, Fig. S3). This may be because the HgCl₂ was generated when Cl⁻ was added to the HgSO₄ solution, which is not as effective as HgSO₄ with respect to Hg⁰ absorption. Furthermore, the outlet Hg⁰ concentration was higher than the initial Hg⁰ concentration when H₂SO₃ was added to the HgSO₄ solution. Clearly, this occurs because the Hg²⁺ was reduced to Hg⁰ primarily by SO₃²⁻ [20,22,23].

It is very interesting that approximately 30% HgSO₄ can absorb Hg⁰ according to the absorption experiments conducted. We also found that only 30% of the Hg²⁺ in the HgSO₄ solutions could be reduced to Hg⁰ when excessive SO₃²⁻ was introduced into the absorption system (Fig. 9). Meanwhile, the HgSO₄ solution did not easily absorb Hg⁰ after the 30% HgSO₄ was reduced by SO₃²⁻.
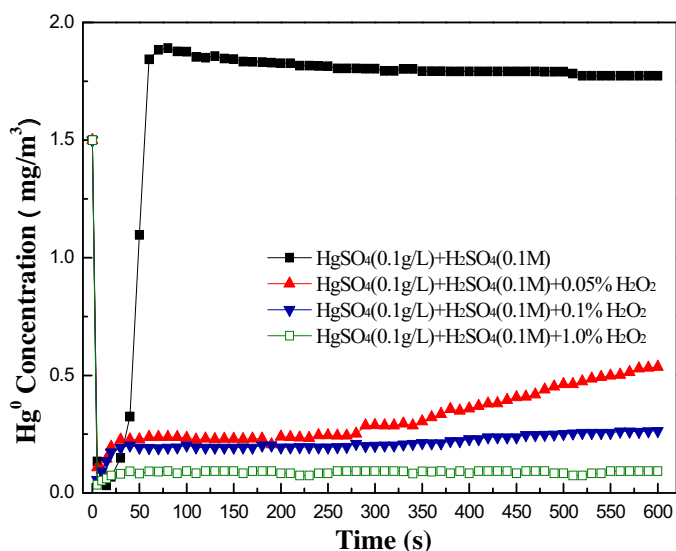
Fig. 10. *Effects of H_2O_2 on Hg^0 removal in $HgSO_4$ solution.* The initial Hg^0 concentration of the simulated flue gas was 1.5 mg/m^3 and the flow rate of simulated flue gas was 1.0 L/min. The initial concentration of SO_2 was 1000 mg/m^3. The concentration of $HgSO_4$ and H_2SO_4 was 0.1 g/L and 0.l mol/L, respectively. The concentration of H_2O_2 was 0.05%, 0.1% and 1.0%, respectively. The volume of absorption solution was 30 mL. The temperature of the flue gas and absorption solution was maintained at about 303 K and 298 K, respectively.

Likewise, it was difficult to reduce the Hg^{2+} in the $HgSO_4$ solution using SO_3^{2-} after the 30% $HgSO_4$ absorbed Hg^0. Therefore, it is believed that there is some activated mercury species in the $HgSO_4$ solution. Only these activated mercury species could absorb Hg^0 and be reduced by SO_3^{2-}. It is reported that there are four major mercury species existing in $HgSO_4$ solution: $HgSO_4$, $HgSO_4 \cdot H_2O$, $HgSO_4 \cdot 2HgO$ and $2HgSO_4 \cdot HgO \cdot 2H_2O$ [24]. Unfortunately, there is a lack of direct evidence to identify the activated mercury species and the proportional distribution of the four compounds referenced, which deserve further research. This is because mercury absorption is based on the reaction between Hg^0 and $HgSO_4$ according to Eq. (9).

$$Hg^0 + HgSO_4 = Hg_2SO_4 \downarrow \tag{9}$$

Based on the experimental results, it is difficult to reduce Hg_2SO_4 with SO_3^{2-}. The Hg^0 was absorbed from the flue gas by $HgSO_4$, generating Hg_2SO_4. The Hg_2SO_4 was first separated as a precipitate. Then, the Hg_2SO_4 could be sold as products or decomposed and reclaimed for Hg^0 by photolysis technology.

3.2.3. The enhancement method of Hg^0 removal in the presence of SO_2

To reduce the negative effect of SO_2 on Hg^0 removal, H_2SO_4 was added to the $HgSO_4$ absorption solution to decrease the co-absorption of SO_2 by adjusting the pH value of the absorption solution (Supplementary material, Fig. S4). The results show that the inhibition of SO_2 on Hg^0 removal was reduced by adding H_2SO_4 to the $HgSO_4$ absorption solution. However, the enhancement efficiency of adjusting the pH value for Hg^0 removal is not satisfied, although the lower pH value could effectively reduce the co-absorption of SO_2. It has been reported that hydrogen peroxide (H_2O_2) has stronger oxidizability and stability in low pH solutions and that SO_2 can be absorbed effectively by H_2O_2 [25,26]. Therefore, H_2O_2 was introduced into the Hg^0 absorption system to prevent the inhibition of Hg^0 removal by SO_2. The results are shown in Fig. 10.

As shown in Fig. 10, the Hg^0 removal efficiency increased significantly with the increase in H_2O_2 concentration in the presence of SO_2. The Hg^0 removal efficiency is approximately 95% when

the H_2O_2 concentration is 1.0%. According to the pre-experimental results, the effect of 1.0% H_2O_2 on Hg^0 removal is very weak. Therefore, the H_2O_2 enhancement on Hg^0 removal occurs because it reduces the negative effect of SO_2 by oxidizing the SO_3^{2-}, HSO_3^-, and H_2SO_3 to SO_4^{2-}.

Due to the lack of absorption efficiency by 1.0% H_2O_2, the mechanism of Hg^0 removal by the composite absorption solution may be that of tetravalent sulfur, such as SO_3^{2-}, HSO_3^-, and H_2SO_3 [27], which are immediately oxidized to SO_4^{2-}, and the SO_2 in the simulated flue gas is almost exhausted [28,29]. Meanwhile, the Hg^0 is absorbed by $HgSO_4$.

Based on the above studies, the composite absorption solution for Hg^0 removal was determined to contain 0.368 mmol/L $HgSO_4$ and 1.0% H_2O_2, and the concentrations of $HgSO_4$ and H_2O_2 were adjusted according to the changes in the concentrations of Hg^0 and SO_2 in the flue gas.

4. Conclusion

A new, two stage composite process for the simultaneous removal of SO_2 and mercury from flue gas may have potential applications in the nonferrous metal smelting industry. In Stage I, the liquid-phase catalytic desulfurization technology was applied to remove and reclaim high concentrations of SO_2 from flue gas. Then, Hg^0 and the residual SO_2 in the flue gas could be absorbed by the $HgSO_4$ and H_2O_2 composite absorption solution. $HgSO_4$ plays a major role in the absorption of Hg^0 from the flue gas. H_2O_2 was added to oxidize S(IV) to S(VI) in order to inhibit the reduction of Hg^{2+} ($HgSO_4$) by S(IV), which could enhance the removal of SO_2 and Hg^0. This composite process can effectively remove and reclaim SO_2 and Hg^0 from nonferrous smelting flue gas. The SO_2 and Hg^0 removal and reclamation efficiency is over 95%. Meanwhile, the amount of $HgSO_4$ used in this composite technology is much less than that of $HgCl_2$ in the Boliden–Norzink process. This method represents a promising technology for the removal and reclamation of Hg^0 from the flue gas of nonferrous metal smelting or other mercury and SO_2 containing flue gases.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.07.012.

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