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Removal of mercury from flue gas from nonferrous metal smelting, by use of mercury chloride solution, and mechanisms of inhibition by sulfur dioxide

Yongpeng Ma · Haomiao Xu · Zan Qu · Naiqiang Yan · Wenhua Wang

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Abstract Elemental mercury (Hg^0) in flue gas can be efficiently captured by use of mercury chloride ($HgCl_2$) solution. However, the ability of $HgCl_2$ to absorb Hg^0 is severely reduced by high concentrations of sulfur dioxide (SO_2) in the flue gas. Methods used to remove Hg^0 by absorption in $HgCl_2$ solution, and mechanisms by which these methods are inhibited by SO_2, were studied in this work. Reduction of $HgCl_2$ and absorption of Hg^0 both occurred in $HgCl_2$ solution in the presence of SO_2. The reduced efficiency of Hg^0 removal was attributed to reduction of $HgCl_2$ to Hg^0 by SO_3^{2-} or HSO_3^-, formed from SO_2. Moderate concentrations of Cl^- and H_2O_2 had synergistic effects with low pH on Hg^0 removal by $HgCl_2$ solution. A new composite absorption solution containing 7.36 mmol/L $HgCl_2$ and 73.6 mmol/L Cl^- at pH 0 was suitable for treatment of flue gas containing high concentrations of both Hg^0 and SO_2, the latter of which is reclaimed by production of sulfuric acid after Hg^0 removal. Another new composite absorption solution containing 7.36 mmol/L $HgCl_2$ and 1.0 % H_2O_2 at pH 0 was suitable for treatment of flue gas containing high concentrations of Hg^0 and lower concentrations of SO_2, the latter of which is co-absorbed in the Hg^0 removal unit.

Keywords Nonferrous metal smelting · Flue gas · Mercury chloride · Sulfur dioxide · Mercury removal

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Introduction

Mercury has attracted global attention as a persistent, high-bioaccumulation, and high-toxicity pollutant [1–3]. The "Minamata Convention on Mercury", a new global treaty intended to protect human health and the environment from anthropogenic emission and release of mercury and mercury compounds, was adopted in October 2013 in Kumamoto, Japan [4, 5]. Reduction of emission of mercury is, therefore, important and urgent.

According to calculations by Pirrone et al. [6], approximately 2,320 tons of mercury is emitted annually as a result of human activity. Among anthropogenic sources of mercury emissions, smelting of nonferrous metals, for example smelting of Pb and Zn sulfide ores, is recognized as a primary source [7–9]. In China, especially, it has been estimated that over 40 % of total mercury emissions are from the flue gas of nonferrous metal smelting [10, 11]. Therefore, reduction of mercury emission by the nonferrous metal-smelting industry will have a direct effect on mercury control performance in the future.

Gaseous oxidized mercury (Hg^{2+}), particulate-bound mercury (Hg^p), and elemental mercury (Hg^0) are the main species of mercury in the flue gas of nonferrous metal smelting [12]. Hg^p can be efficiently captured by use of current air pollution-control devices (APCDs), for example, such particulate matter collection devices as electrostatic precipitators or fabric filters; it is then returned to the furnace with the bulk fly ash [13, 14]. Hg^{2+} is absorbed and lost in the wet-cooling scrubber and enters acid wastewater as a typical heavy metal pollutant. However, Hg^0 is more difficult to remove than Hg^p and Hg^{2+} because of its high volatility and insolubility [15]. Effective removal if Hg^0 is, therefore, crucial to reducing mercury emissions from nonferrous metal smelting flue gas. Furthermore, mercury concentrations in nonferrous metal smelting flue gas range from several to tens of mg/m [1, 12], and Hg^0 is a valuable resource in many fields, for example dentistry, gold mining, and mercurial thermometers. High concentrations of Hg^0 in flue gas can be captured and reclaimed by use of absorption methods [16, 17].

Mercury chloride ($HgCl_2$) absorption technology is one type of effective Hg^0 reclaim technique which has been utilized in some nonferrous metal smelters [12, 18]. The absorption process is based on oxidation of Hg^0 by $HgCl_2$ to form insoluble calomel (Hg_2Cl_2). Some of the Hg_2Cl_2 is re-chlorinated to $HgCl_2$, then added to the absorption solution to replenish the $HgCl_2$ lost. The remaining Hg_2Cl_2 is treated as calomel product. The main chemical reactions in the absorption process are summarized as follows:

$$Hg^0 + HgCl_2 = Hg_2Cl_2 \downarrow \tag{1}$$

$$Hg_2Cl_2 + Cl_2 = 2HgCl_2 \tag{2}$$

It has been reported that the efficiency of Hg^0 removal by the $HgCl_2$ absorption process is >98 %. However, outlet Hg^0 concentrations from the $HgCl_2$ absorption process still do not satisfy increasingly stringent discharge standards in China [12]. Sulfate (SO_3^{2-}) and sulfite (HSO_3^-) ions can substantially affect efficiency of Hg^0 removal

[19, 20]. Generally speaking, $SO_3{}^{2-}$ and $HSO_3{}^{-}$ in solution are generated by high concentrations of sulfur dioxide (SO_2), which often accompanies mercury in flue gas from nonferrous metal smelting [21]. The effects of SO_2 on Hg^0 removal from this flue gas should therefore be taken into account when $HgCl_2$ absorption technology is used. There is still a lack of understanding of $HgCl_2$ absorption behavior and the effects of SO_2; this is limiting the development of $HgCl_2$ absorption technology.

In the work discussed in this paper, several methods were found to inhibit the effects of SO_2 on removal of Hg^0 from flue gas from nonferrous metal smelting containing different concentrations of SO_2. The mechanisms of inhibition of Hg^0 removal by SO_2 in $HgCl_2$ absorption technology were also studied. The results reported in this paper will enable significant improvement of mercury chloride absorption technology and should popularize its application.

Materials and methods

Apparatus

A schematic diagram of the experimental absorption apparatus is shown in Fig. 1. A three-necked flask was used as the bubbling absorption reactor in this research. Several cylinder gases and mass flowmeters were used to provide the 1.0 L/min simulated flue gas containing high concentrations of Hg^0 and SO_2. Hg^0 was generated by immersing a mercury bottle in a constant-temperature oil-bath (HH-1; Baishen Instruments, China); the concentration of Hg^0 in the simulated flue gas was controlled by adjusting the temperature of the water bath and the flow rate of the carrier gas (N_2). The simulated flue gas was passed through the three-necked flask which contained different $HgCl_2$ absorption solutions (30 mL). SO_2 was introduced into the reaction system to study its effects on Hg^0 removal by $HgCl_2$. The temperatures of the flue gas and absorption solution were maintained at approximately 303 and 298 K, respectively. The time for the simulated flue gas to pass through the absorption solution in the reactor was approximately 1.2 s. The initial concentration of Hg^0 in the inlet gas of the absorption reactor was maintained at 1.8 mg/m^3. The absorption reactor inlet and outlet Hg^0 concentrations were monitored online by use of a mercury analyzer (SG-921; Jiangfen, China). The signal was collected and recorded by use of a data transition and acquisition device (N2000; Zhida, China). The concentration of Hg^0 in the flue gas was calibrated by use of a Lumex mercury analyzer (RA915; Lumex, Russia). SO_2 concentration was determined by use of a flue gas analyzer (KM900; Kane, UK). efficiency of Hg^0 removal (η) was calculated by use of Eq. 3:

$$\eta_{Hg^0} = \frac{C_{Hg^0(in)} - C_{Hg^0(out)}}{C_{Hg^0(in)}} \times 100\,\%, \tag{3}$$

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

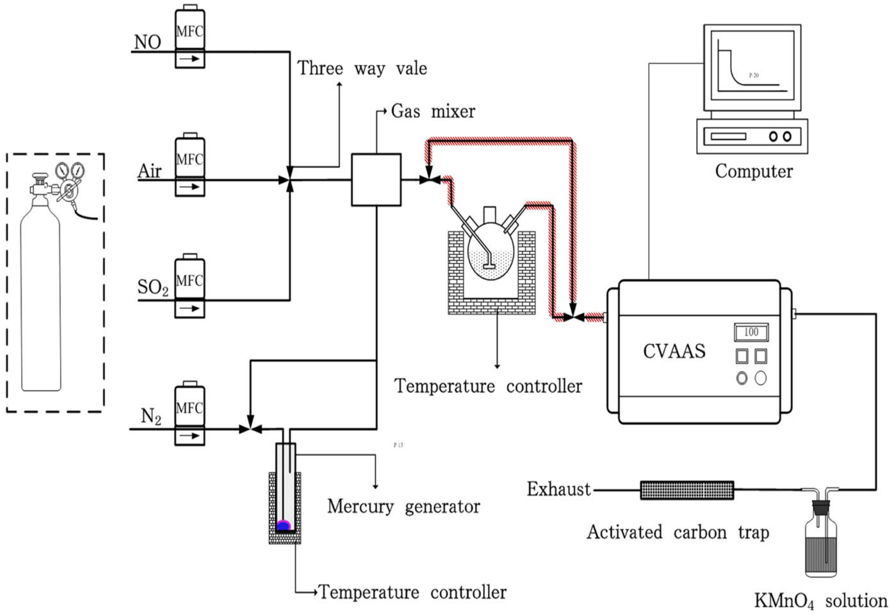

Fig. 1 Schematic diagram of the experimental absorption apparatus

Raman spectral study

Raman spectra were acquired by use of an i-Raman Plus spectrometer (B&W TEK, USA), by scanning with a laser of excitation wavelength 785 nm. The region scanned was from 200 to 500 cm^{-1}. Spectral resolution was 3 cm^{-1}. Solutions were prepared by mixing $HgCl_2$ solution and NaCl solution in different mole ratios.

Materials

The main chemicals used (mercury (99.9 %), mercuric chloride (99.5 %), sodium chloride (99.5 %), sodium sulfite (98 %), sodium hydrogen sulfite (98 %), nitric acid (69 %), sulfuric acid (98 %), hydrochloric acid (37 %), and potassium permanganate (99 %)) were from Sigma-Aldrich. SO_2 (99.9 %) and N_2 (99.9 %), stored in cylinders, were obtained from Dalian Date Gas.

Results and discussion

Effects of SO_2 on Hg^0 removal

Hg^0 can be absorbed with high efficiency by $HgCl_2$. In addition to Hg^0, however, nonferrous metal smelting flue gas contains many other components, especially high concentrations of SO_2. The effects of SO_2 on removal of Hg^0 by $HgCl_2$ solution were determined. The flow rate of the simulated flue gas was 1.0 L/min. The concentrations of SO_2 and Hg^0 in simulated flue gas were 8,000 and 1.8 mg/m^3, respectively. The concentration of $HgCl_2$ in the absorption solution was 1.84 mmol/L. The experimental results are shown in Fig. 2. It is apparent that the efficiency of Hg^0 removal is 78.6 % when the simulated flue gas contains no SO_2. When SO_2 and Hg^0 are both present in the simulated flue gas, the efficiency of Hg^0 removal is only 9 %. It is believed that $HgCl_2$ loses its ability to absorb Hg^0 in the presence of SO_2.

To investigate the mechanism of the effect of SO_2 on Hg^0 removal, other experiments were conducted. Simulated flue gas containing SO_2 and N_2, only, was used. The SO_2 concentration in simulated flue gas was 8,000 mg/m^3. The concentration of the $HgCl_2$ solution was 1.84 or 7.36 mmol/L. The results in Fig. 3 show that Hg^0 is generated in the process of simulated gas scrubbing. It is suggested that $HgCl_2$ is reduced to Hg^0 by SO_2. However, SO_2 is absorbed by the aqueous solution and SO_3^{2-}, HSO_3^-, and H_2SO_3 are generated [22]. These experiments also prove that Na_2SO_3 and $NaHSO_3$ can reduce $HgCl_2$. Therefore, S(IV) causes reduction of $HgCl_2$. The possible mechanism that can be deduced is that SO_3^{2-} or HSO_3^- formed by SO_2 react with $HgCl_2$ and generate the intermediate $HgSO_3$. However, $HgSO_3$ is so unstable it decomposes and generates Hg^0 [23, 24]. The main chemical reactions can be summarized as follows:

$$Hg^{2+} + SO_3^{2-} \rightarrow HgSO_3 \tag{4}$$

$$Hg^{2+} + HSO_3^- \rightarrow HgSO_3 + H^+ \tag{5}$$

$$HgSO_3 + H_2O \rightarrow Hg^0 + 2H^+ + SO_4^{2-} \tag{6}$$

Figure 3 also shows that when the concentration of $HgCl_2$ is low (1.84 mmol/L), the concentration of Hg^0 in the flue gas is relatively high at the start of simulated gas scrubbing, then gradually decreases to a steady concentration. When the concentration of $HgCl_2$ is increased to 7.36 mmol/L, more Hg^0 should be generated, but the concentration of Hg^0 produced by reduction of 7.36 mmol/L $HgCl_2$ solution, at the start of simulated gas scrubbing, is much lower than in 1.84 mmol/L solution. It is speculated that some of the Hg^0 produced by reduction is, initially, efficiently absorbed by the abundant $HgCl_2$ in 7.36 mmol/L $HgCl_2$ solution. With reduction of the amount of $HgCl_2$, absorption efficiency gradually decreases and the quantity of reduced Hg^0 in the simulated flue gas increases. Therefore, in the presence of SO_2, both reduction of $HgCl_2$ and absorption of Hg^0 occur in the $HgCl_2$ solution.

Methods for inhibiting the effects of SO_2 on Hg^0 removal

Increasing the concentration of $HgCl_2$

It is known that increasing the concentration of $HgCl_2$ can improve the efficiency of removal of Hg^0 from flue gas containing no SO_2. $HgCl_2$ is, therefore, believed to inhibit the effects of SO_2 on Hg^0 removal.

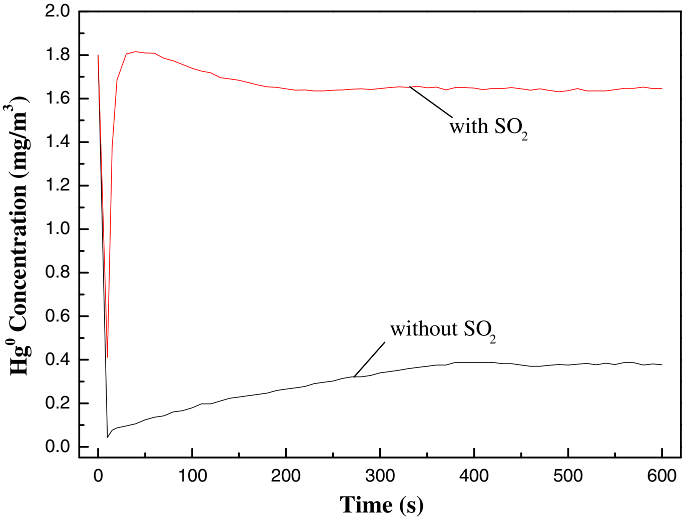

Fig. 2 Effect of SO_2 on Hg^0 concentration in treated flue gas. The flow rate of simulated flue gas was 1.0 L/min. The concentrations of SO_2 and Hg^0 in the simulated flue gas were 8,000 and 1.8 mg/m^3, respectively. The concentration of $HgCl_2$ in the absorption solution was 1.84 mmol/L and the volume of the absorption solution was 30 mL. Hg^0 removal with and without SO_2 in the simulated flue gas were compared. It is apparent that $HgCl_2$ loses its ability to absorb Hg^0 in the presence of SO_2

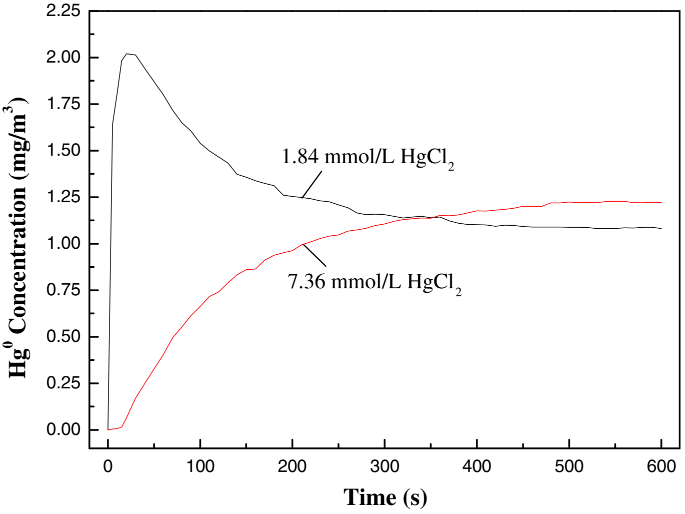

Fig. 3 Effects of SO_2 on the reduction of $HgCl_2$ solution. The flow rate of simulated flue gas was 1.0 L/min. The concentration of SO_2 in the simulated flue gas was 8,000 mg/m^3, and there is no Hg^0 in the incoming simulated flue gas. The concentration of $HgCl_2$ in the absorption solution was 1.84 or 7.36 mmol/L, and the volume of absorption solution was 30 mL. The results show that Hg^0 is generated in the process of simulated gas scrubbing. It is suggested that $HgCl_2$ is reduced to Hg^0 by SO_2, which explains the reason for the conclusion in Fig. 2

In these experiments the flow rate of the simulated flue gas was 1.0 L/min. The concentrations of SO_2 and Hg^0 in the simulated flue gas were 8,000 and 1.8 mg/m^3, respectively. The concentration of $HgCl_2$ in the absorption solution was increased from 1.84 to 7.36 mmol/L. The results are shown in Fig. 4.

Figure 4 shows that in the presence of SO_2 in the simulated flue gas the efficiency of Hg^0 removal is enhanced by increasing the concentration of $HgCl_2$. Even so, when the $HgCl_2$ concentration is 7.36 mmol/L, the efficiency of Hg^0 removal is only 55.6 % which is far below the value (98.7 %) without SO_2 in the simulated flue gas. Furthermore, mercuric chloride, a highly toxic chemical, is a potential pollutant. Increasing the consumption of $HgCl_2$ might lead to release of $HgCl_2$ into the environment. We should not, therefore, blindly rely on increasing the concentration of $HgCl_2$ to eliminate the effects of SO_2 on Hg^0 removal.

Reducing the concentration of SO_2

Because SO_2 is the main cause of the decrease in the efficiency of removal of Hg^0 by $HgCl_2$ solution, the effects of different SO_2 concentrations in the simulated flue gas should be investigated. In this work, three concentrations of SO_2 were selected—8,000, 4,000 and 1,000 mg/m^3. The concentration of Hg^0 in simulated flue gas was 1.8 mg/m^3 and the concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L. Figure 5 shows that efficiency of Hg^0 removal was 55.6, 77.8, and 85.8 % for SO_2 concentrations of 8,000, 4,000 and 1,000 mg/m^3, respectively. This means the effect of SO_2 on Hg^0 removal gradually decreases with decreasing SO_2 concentration in the simulated flue gas. This may because reduction of $HgCl_2$ by SO_3^{2-} or HSO_3^-, which are generated by SO_2 in the absorption solution, is weakened. Therefore, to ensure high Hg^0-removal efficiency, pre-desulfurization is a good choice when SO_2 and Hg^0 are present simultaneously in the simulated flue gas.

Changing the pH of the $HgCl_2$ solution

Absorption solution pH is a crucial aspect of air pollutant scrubbing technology. In this work the pH of the $HgCl_2$ solution was adjusted to determine whether this altered the effect of SO_2 on Hg^0 removal by $HgCl_2$ solutions. The flow rate of the simulated flue gas was 1.0 L/min. The initial concentration of Hg^0 was 1.8 mg/m^3 and the concentration of SO_2 in the simulated flue gas was 8,000 mg/m^3. The concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L. Nitric acid (HNO_3), sulfuric acid (H_2SO_4), or hydrochloric acid (HCl) was used to adjust the pH. The background pH of 7.36 mmol/L aqueous $HgCl_2$ solution was approximately 4. The results are shown in Fig. 6.

Figure 6a shows that pH has an obvious effect on the efficiency of Hg^0 removal. It is apparent that the efficiency of Hg^0 removal increases with decreasing pH when HNO_3 and H_2SO_4 are used, and that the tendencies are consistent for use of HNO_3 and H_2SO_4. For example, when the pH is adjusted from 4 to 0 with HNO_3 in 7.36 mmol/L $HgCl_2$ solution, efficiency of Hg^0 removal increases from 55.6 to 98.2 %. When the pH is adjusted from 4 to 0 with H_2SO_4, efficiency of Hg^0 removal increases from 55.6 to 95.7 %.

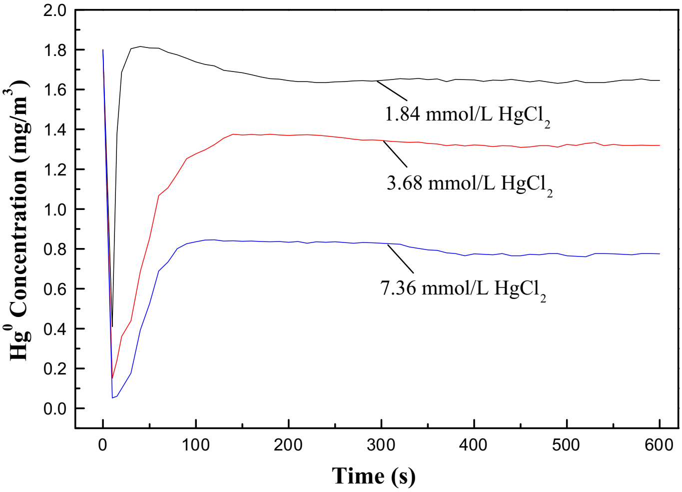

Fig. 4 Effects of increasing $HgCl_2$ concentration on Hg^0 concentration in flue gas containing SO_2. The flow rate of simulated flue gas was 1.0 L/min. The concentrations of SO_2 and Hg^0 in the simulated flue gas were 8,000 and 1.8 mg/m^3, respectively. The concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L, and the volume of absorption solution was 30 mL. In the presence of SO_2 in the simulated flue gas the efficiency of Hg^0 removal was enhanced by increasing the concentration of $HgCl_2$

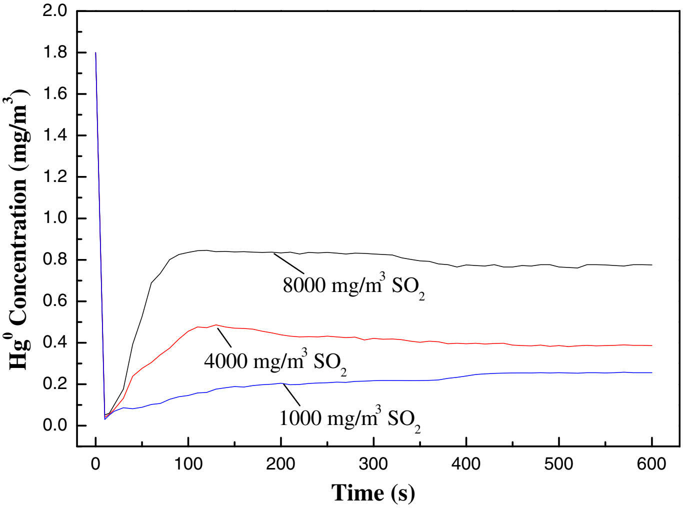

Fig. 5 Effect of decreasing SO_2 concentration on Hg^0 concentration in flue gas. The flow rate of the simulated flue gas was 1.0 L/min. The initial concentration of Hg^0 in the simulated flue gas was 1.8 mg/m^3 and the concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L. The concentration of SO_2 was 8,000, 4,000, or 1,000 mg/m^3. The volume of absorption solution was 30 mL. The effect of SO_2 on Hg^0 removal is gradually weakened by reducing the concentration of SO_2 in the simulated flue gas

Possible mechanisms of inhibition of the effect of SO_2 by pH could be: first, the solubility of SO_2 decreases with reduction of pH. As shown in Fig. 6b, the amount of SO_2 absorbed is smaller at lower pH; and, second, SO_2 is absorbed by aqueous

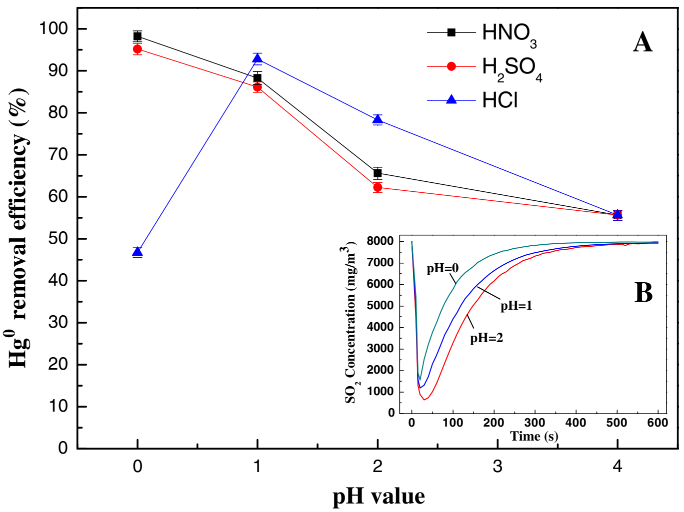

Fig. 6 Effects of pH on efficiency of Hg^0 removal and SO_2 absorption. The flow rate of simulated flue gas was 1.0 L/min. The initial concentration of Hg^0 was 1.8 mg/m^3 and the concentration of SO_2 in the simulated flue gas was 8,000 mg/m^3. The concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L and the volume of absorption solution was 30 mL. HNO_3, H_2SO_4, or HCl was used to adjust the pH. The background pH of 7.36 mmol/L $HgCl_2$ aqueous solution was approximately 4. **a** Effects of absorption solution pH on efficiency of Hg^0 removal, and the effects of using three different acids. **b** Effect of pH on the concentration of SO_2 in flue gas, indicative of the mechanism of inhibition of the effect of SO_2 by pH in **a**

solution generating H_2SO_3 and part of the H_2SO_3 ionizes and generate HSO_3^- and SO_3^{2-}, so three species are present when SO_2 dissolves in water [22]:

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{7}$$

$$H_2SO_3 \leftrightarrow H^+ + HSO_3^- \tag{8}$$

$$HSO_3^- \leftrightarrow H^+ + SO_3^- \tag{9}$$

When HNO_3 and H_2SO_4 are added to the $HgCl_2$ solutions, the increase of H^+ would inhibit the reactions depicted by Eqs. 8 and 9, so the lower the pH, the greater the amount of H_2SO_3 [25]. However, $HgCl_2$ is reduced solely by SO_3^{2-} or HSO_3^-; molecular H_2SO_3 cannot reduce $HgCl_2$ in the absorption solution.

Figure 6a also shows that pH adjusted with HCl has a significant effect on the efficiency of removal of Hg^0, although the trend for use of HCl is not the same as for use of HNO_3 and H_2SO_4. It can be seen that when the pH of $HgCl_2$ solution is adjusted from 4 to 1 with HCl, efficiency of Hg^0 removal increases from 55.6 to 92.8 %. The mechanism of the increase is the same as for use of HNO_3 and H_2SO_4, discussed above.

However, there are two queries. The first is why, when the pH is adjusted from 4 to 1 with HCl, is the efficiency of removal of Hg^0 higher than when HNO_3 or H_2SO_4 is used? The second is why, when the pH is adjusted from 1 to 0 with HCl, does the efficiency of removal of Hg^0 decline sharply to 46.7 % rather than continue to increase?

HCl contains only hydrogen ion and chloride ion. To answer these queries, chloride ions were introduced to $HgCl_2$ absorption solutions.

Effects of adding Cl^- to $HgCl_2$ solutions

To investigate the effect of chloride ion, sodium chloride was added to the $HgCl_2$ solution. In the first group of experiments, the simulated flue gas contained SO_2 and N_2 only. The concentration of SO_2 in the simulated flue gas was 8,000 mg/m^3. The concentration of $HgCl_2$ was 7.36 mmol/L and the mole ratio of Cl^- to $HgCl_2$ was 0:1, 5:1, 10:1, 20:1, or 50:1. The results are shown in Fig. 7. It is apparent that when Cl^- is added into $HgCl_2$ solutions, reduction of $HgCl_2$ by SO_2 is substantially reduced, and the reduction does not depend on Cl^- concentration.

In the second group of experiments, the concentrations of Hg^0 and SO_2 in simulated flue gas were 1.8 and 8,000 mg/m^3, respectively. The concentration of $HgCl_2$ in the absorption solution was 7.36 mmol/L. efficiency of Hg^0 removal for different mole ratios of Cl^- to $HgCl_2$ are shown in Fig. 8. It is apparent that efficiency of Hg^0 removal increases when the mole ratio of Cl^- to $HgCl_2$ is increased from 0 to 10:1 then declines gradually as the Cl^- to $HgCl_2$ mole ratio is increased further. Taking 7.36 mmol/L $HgCl_2$ absorption solutions as examples, efficiency of Hg^0 removal increases from 55.6 to 85.6 % when the mole ratio of Cl^- to $HgCl_2$ is increased from 0 to 10:1. efficiency of Hg^0 removal then decreases substantially to 41.1 % when the mole ratio is 100:1.

The results in Figs. 7 and 8 explain the two queries in Fig. 6a. First, when the pH is adjusted to 2 with HCl, the amount of Cl^- added is twice the amount already present as $HgCl_2$; when the pH is 1, the amount of Cl^- added is fourteen times the amount already present as $HgCl_2$. Owing to inhibition of the reduction of $HgCl_2$ by SO_2 by both hydrogen ions and chloride ions and enhancement of efficiency of Hg^0 removal when the appropriate amount of HCl are added into $HgCl_2$ solution, efficiency of Hg^0 removal is higher than the corresponding efficiency after use of HNO_3 and H_2SO_4. Second, when the pH is adjusted to 0 with HCl, the amount of Cl^- added is 135 times the amount already present as $HgCl_2$. efficiency of Hg^0 removal decreases substantially when the ratio is 135:1 (Fig. 8).

The mechanism of the effect of Cl^- on efficiency of Hg^0 removal can be deduced as follows. It is well known that the degree of ionization of $HgCl_2$ is very small, so the concentration of Hg^{2+} or $HgCl^+$ in $HgCl_2$ solution is also very low. Therefore, the main mercury species in the $HgCl_2$–NaCl mixed solution are $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ [26]. Equilibria between $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$, and Cl^- are present in mixed solutions. The distribution of the three mercury chloride species is related to the mole ratio of Cl^- to $HgCl_2$ in absorption solutions [27]. As reported, the $HgCl_3^-$ and $HgCl_4^{2-}$ concentrations increase with increasing concentration of Cl^-. The proportion of $HgCl_3^-$ was close to its highest value, and the amount $HgCl_4^{2-}$ was still small, when the mole ratio of Cl^- to $HgCl_2$ was 10:1. When the mole ratio of Cl^- to $HgCl_2$ was beyond 20:1, $HgCl_3^-$ concentrations decreased gradually, whereas the $HgCl_4^{2-}$ concentration increased substantially. When the

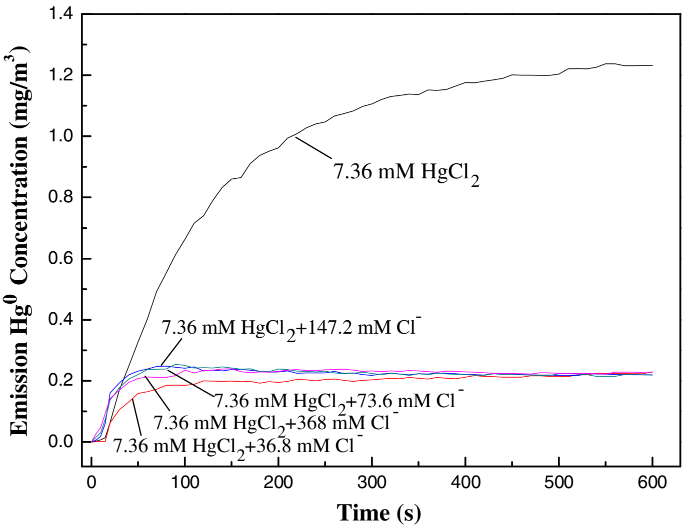

Fig. 7 Effect of Cl^- anions on reduction of $HgCl_2$ by SO_2 in flue gas. The flow rate of the simulated flue gas was 1.0 L/min. The SO_2 concentration in the simulated flue gas was 8,000 mg/m^3. The concentration of $HgCl_2$ was 7.36 mmol/L and the mole ratio of Cl^- to $HgCl_2$ was 0:1, 5:1, 10:1, 20:1, or 50:1. The volume of absorption solution was 30 mL. When Cl^- is added into $HgCl_2$ solutions, reduction of $HgCl_2$ by SO_2 is substantially reduced, and the reduction does not depend on Cl^- concentration

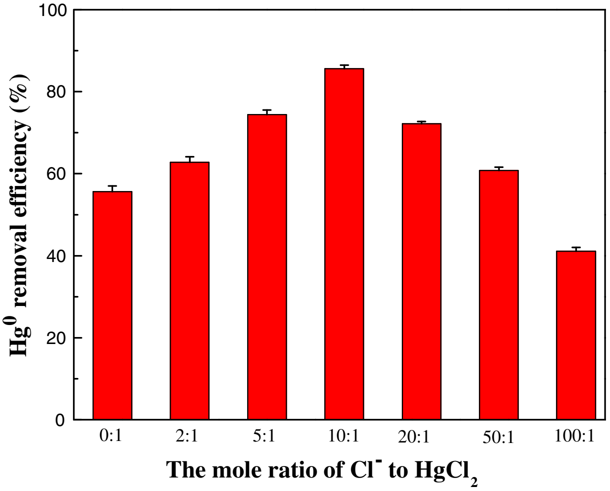

Fig. 8 Effect of the Cl^- anions on efficiency of Hg^0 removal. The flow rate of the simulated flue gas was 1.0 L/min. The concentrations of Hg^0 and SO_2 in the simulated flue gas were 1.8 and 8,000 mg/m^3, respectively. The concentration of $HgCl_2$ was 7.36 mmol/L and the mole ratio of Cl^- to $HgCl_2$ was 0:1, 2:1, 5:1, 10:1, 20:1, 50:1, or 100:1. The volume of absorption solution was 30 mL. The figure shows efficiency of Hg^0 removal for different Cl^- to $HgCl_2$ mole ratios. It apparent that efficiency of Hg^0 removal increases when the Cl^- to $HgCl_2$ mole ratio is increased from 0 to 10:1 then decreases substantially when the mole ratio of Cl^- to $HgCl_2$ is increased further

mole ratio of Cl^- to $HgCl_2$ was 100:1, the proportion of $HgCl_4^{2-}$ in the mixed $HgCl_2$–Cl^- solution was >80 %. Therefore, it is deduced that the increase of efficiency of Hg^0 removal is caused by the increase of $HgCl_3^-$ concentration when the mole ratios of Cl^- to $HgCl_2$ are increased from 0 to 10:1. The decline of efficiency of Hg^0 removal may be caused by both the increase of $HgCl_4^{2-}$ concentration and the decrease of $HgCl_3^-$ and $HgCl_2$ concentrations.

The symmetric stretching frequencies of $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ are 320, 290, and 269 cm^{-1}, respectively [26]. To verify the conclusions deduced above, Raman spectra of mixed solutions containing different mole ratios of NaCl to $HgCl_2$ were acquired; the results are shown in Fig. 9. In Fig. 9a there is one peak only, at 320 cm^{-1}, which represents $HgCl_2$, when the mole ratio of Cl^- to $HgCl_2$ is 0:1. When the mole ratio of Cl^- to $HgCl_2$ is 100:1, there is a major peak at 269 cm^{-1} which represents $HgCl_4^{2-}$. When the mole ratio of Cl^- to $HgCl_2$ was 10:1, several peaks were present in the Raman spectrum. This spectrum was investigated by peak fitting; the results are shown in Fig. 9b. Peak separation reveals three peaks at 320, 290, and 269 cm^{-1}, so $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ are the major mercury chloride species present in this mixed solution. Because the efficiency of removal of mercury increases with increasing $HgCl_3^-$ concentration in $HgCl_2$ solution, it can be deduced that $HgCl_3^-$ is more efficient than $HgCl_2$ and $HgCl_4^{2-}$ at removal of mercury by $HgCl_2$ solution. The efficiency of removal of mercury when the mole ratio of Cl^- to $HgCl_2$ is 100:1 is lower than when it is 0:1, which proves the efficiency of $HgCl_4^{2-}$ is the lowest.

The optimum $HgCl_2$ solution conditions

Use of $HgCl_2$ solution of moderate Cl^- concentration and low pH can inhibit the effects of SO_2 and improve the efficiency of Hg^0 removal, but the two mechanisms are different. To discover the optimum conditions, the synergistic effect of Cl^- and pH was examined. In these experiments, the concentrations of Hg^0 and SO_2 in the simulated flue gas were 1.8 and 8,000 mg/m^3, respectively. The $HgCl_2$ concentration was 7.36 mmol/L. The mole ratio of Cl^- to $HgCl_2$ was 10:1. efficiency of Hg^0 removal at different pH is shown in Fig. 10.

It is apparent that when the pH of $HgCl_2$ solution is adjusted from 4 to 0 with HNO_3, efficiency of Hg^0 removal increases gradually from 85.6 to 98.6 %. Study of the effect of Cl^- in $HgCl_2$ solution at low pH reveals that the efficiency of Hg^0 removal is highest at low pH when the mole ratio of Cl^- to $HgCl_2$ is 10:1. This shows that Cl^- and pH have synergistic effect on Hg^0 removal by $HgCl_2$ solution. Therefore, the optimum conditions for Hg^0 removal by $HgCl_2$ solution are confirmed as: 7.36 mmol/L $HgCl_2$, 73.6 mmol/L Cl^-, and pH 0. Under these conditions, loss of SO_2 from the flue gas is small and the efficiency of Hg^0 removal is high. These optimum conditions are suitable for flue gas containing high concentrations of both Hg^0 and SO_2, the latter of which is reclaimed by production of H_2SO_4 after Hg^0 removal.

Effects of adding H_2O_2 on Hg^0 removal by $HgCl_2$ solution

It is reported that hydrogen peroxide (H_2O_2) is both a stronger oxidizing agent and most stable in low pH solution, and that SO_2 can be absorbed effectively by H_2O_2

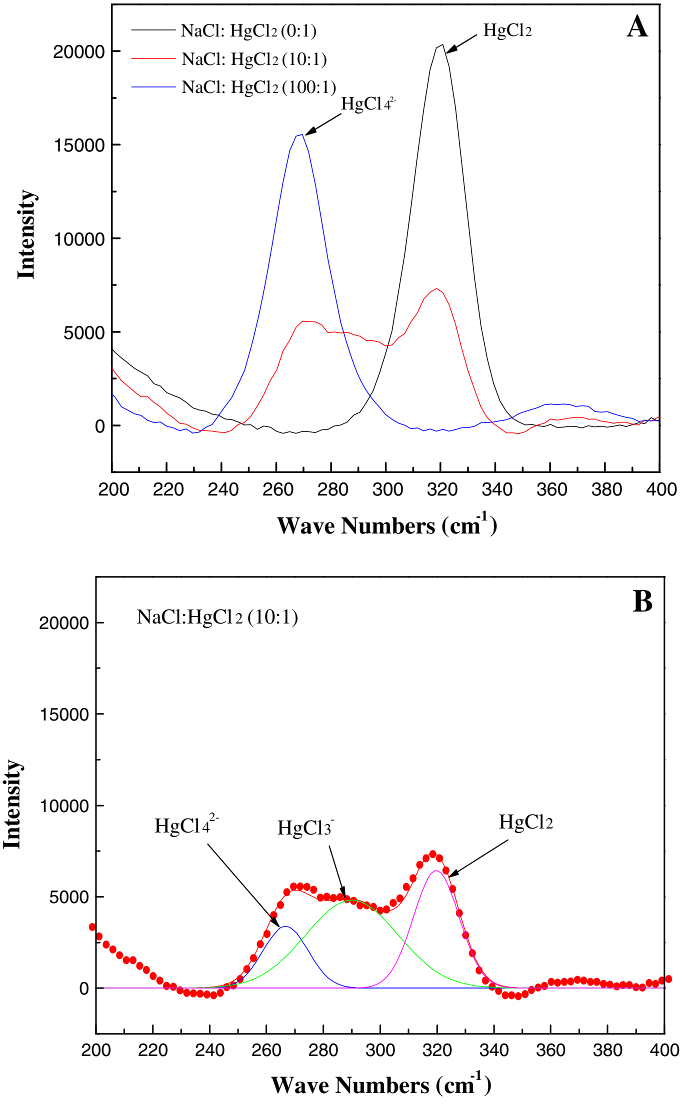

Fig. 9 Raman spectra of mixed $HgCl_2$–NaCl solutions. The solutions contain 0.172 mol/L $HgCl_2$, 1.59 mol/L $HClO_4$, and different concentrations of NaCl. Raman spectra were excited by use of a laser of wavelength 785 nm. The region scanned was from 200 to 500 cm^{-1}. The spectral resolution was 3 cm^{-1}. The solutions were prepared by mixing NaCl and $HgCl_2$ in the mole ratios 0:1, 10:1, and 100:1. **a** Shows the Raman spectra of mixed solutions of NaCl and $HgCl_2$ in different mole ratios. It is apparent there is only one peak, at 320 cm^{-1}, which represents $HgCl_2$, when the mole ratio of Cl^- to $HgCl_2$ is 0:1. When the mole ratio of Cl^- to $HgCl_2$ is 100:1, there is one major peak at 269 cm^{-1}, which represents $HgCl_4^{2-}$. **b** Shows the Raman spectrum (for mole ratio is 10:1) investigated by peak fitting. After separation of the peaks it is apparent there are three peaks at 320, 290, and 269 cm^{-1}, which are indicative of the presence of $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$ in this mixed solution

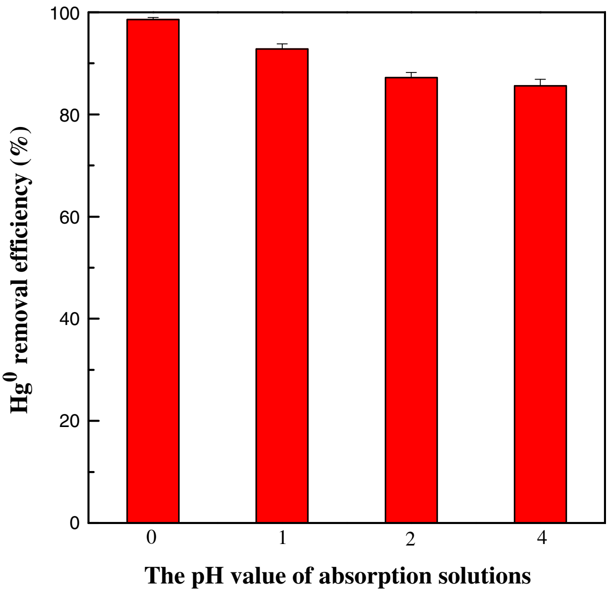

Fig. 10 Effect of pH on efficiency of Hg^0 removal by $HgCl_2$ solution for which the mole ratio of Cl^- to $HgCl_2$ was 10:1. The flow rate of simulated flue gas was 1.0 L/min. The concentrations of Hg^0 and SO_2 in the simulated flue gas were 1.8 and 8,000 mg/m^3, respectively. The concentration of $HgCl_2$ in solution was 7.36 mmol/L. The pH was adjusted from 4 to 0 with HNO_3. The volume of absorption solution was 30 mL

[28]. Therefore, H_2O_2 was added to the Hg^0 absorption system to prevent inhibition of Hg^0 removal by SO_2. The results are shown in Fig. 11.

As shown in Fig. 11, the efficiency of Hg^0 removal clearly increased with increasing H_2O_2 concentration. The efficiency of Hg^0 removal is approximately 90.8 % when the H_2O_2 concentration is 1.0 %. According to the previous experimental results, the effect of only 1.0 % H_2O_2 solution on Hg^0 removal is very weak. Therefore, the enhancement of Hg^0 removal by H_2O_2 is because it reduces the negative effect of SO_2 by oxidizing SO_3^{2-}, HSO_3^-, and H_2SO_3 to SO_4^{2-}. When the pH is 0 and the H_2O_2 concentration is 1.0 % in $HgCl_2$ solution, the efficiency of Hg^0 removal is increased to 98.7 %. This shows that H_2O_2 and pH also have synergistic effects on Hg^0 removal by $HgCl_2$ solution. In addition, when the concentration of SO_2 is low, the effect of H_2O_2 is stronger.

Because 1.0 % H_2O_2 alone has little effect on absorption efficiency, the mechanism of Hg^0 removal by the composite absorption solution may be that S(IV), for example SO_3^{2-}, HSO_3^-, and H_2SO_3 [22], are immediately oxidized to SO_4^{2-}, so SO_2 is almost removed from the simulated flue gas [29] and, thus, does not affect absorption of Hg^0 by $HgCl_2$.

These studies have led to formulation of a new composite solution (7.36 mmol/L $HgCl_2$, 1.0 % H_2O_2, pH 0) for removal of Hg^0. The concentrations of $HgCl_2$ and H_2O_2 can be adjusted in accordance with changes of the concentrations of Hg^0 and SO_2 in the flue gas. This new composite absorption solution is suitable for flue gas

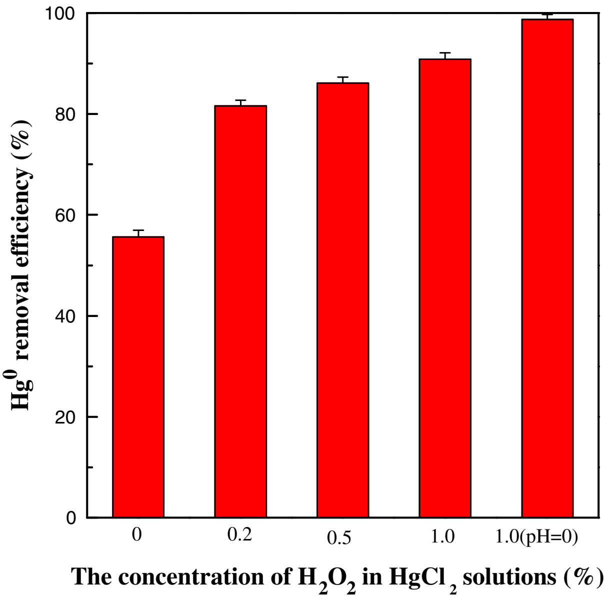

Fig. 11 Effects of H_2O_2 concentration on the efficiency of removal of Hg^0 by $HgCl_2$ solution. The flow rate of the simulated flue gas was 1.0 L/min. The concentrations of Hg^0 and SO_2 in the simulated flue gas were 1.8 and 8,000 mg/m^3, respectively. The concentration of $HgCl_2$ in solution was 7.36 mmol/L. The concentrations of H_2O_2 were from 0 to 1 %. The pH was adjusted to 0 with HNO_3. The volume of absorption solution was 30 mL. This shows that H_2O_2 effectively removes the effect of SO_2 on Hg^0 removal. efficiency of Hg^0 removal clearly increased with increasing H_2O_2 concentration

containing high concentrations of Hg^0 and comparatively lower concentrations of SO_2, which is co-absorbed in the Hg^0-removal unit.

Conclusions

The methods used to remove Hg^0 from nonferrous metal smelting flue gas by absorption in $HgCl_2$ solution, and mechanisms by which these are inhibited by SO_2, were studied in this work. According to the experimental results, in the presence of SO_2, both reduction of $HgCl_2$ and absorption of Hg^0 occur in $HgCl_2$ solution. The decrease in the efficiency of Hg^0 removal was attributed to reduction of $HgCl_2$ to Hg^0 by SO_3^{2-} or HSO_3^- formed by SO_2. Although increasing the concentration of $HgCl_2$ and reducing the concentration of SO_2 could, to some extent, both improve the efficiency of Hg^0 removal, results were still unsatisfactory. Moderate Cl^- and low pH both inhibited the effects of SO_2 on the $HgCl_2$ solution and had a synergistic effect on improving the efficiency of Hg^0 removal. In this research, the efficiency of Hg^0 removal was the highest at low pH when the mole ratio of Cl^- to $HgCl_2$ was 10:1. The results also showed that H_2O_2 and pH had synergistic effect on Hg^0 removal by $HgCl_2$ solution. To conclude, a new composite $HgCl_2$ absorption solution containing 7.36 mmol/L $HgCl_2$ and 73.6 mmol/L Cl^- at pH 0 is suitable for flue gas containing high concentrations of Hg^0 and high concentrations of SO_2, the latter of which is reclaimed by production of H_2SO_4 after the process of Hg^0 removal. Another new composite $HgCl_2$ absorption solution containing 7.36 mmol/L $HgCl_2$ and 1.0 % H_2O_2 at pH 0, is suitable for flue gas containing high concentrations of Hg^0 and comparatively lower concentrations of SO_2 which is co-absorbed in the Hg^0 removal unit.

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