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Absorption characteristics of elemental mercury in mercury chloride solutions

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ABSTRACT

Elemental mercury (Hg^0) in flue gases can be efficiently captured by mercury chloride ($HgCl_2$) solution. However, the absorption behaviors and the influencing effects are still poorly understood. The mechanism of Hg^0 absorption by $HgCl_2$ and the factors that control the removal were studied in this paper. It was found that when the mole ratio of Cl^- to $HgCl_2$ is 10:1, the Hg^0 removal efficiency is the highest. Among the main mercury chloride species, $HgCl_3^-$ is the most efficient ion for Hg^0 removal in the $HgCl_2$ absorption system when moderate concentrations of chloride ions exist. The Hg^0 absorption reactions in the aqueous phase were investigated computationally using Moller–Plesset perturbation theory. The calculated Gibbs free energies and energy barriers are in excellent agreement with the results obtained from experiments. In the presence of SO_3^{2-} and SO_2, Hg^{2+} reduction occurred and Hg^0 removal efficiency decreased. The reduced Hg^0 removal can be controlled through increased chloride concentration to some degree. Low pH value in $HgCl_2$ solution enhanced the Hg^0 removal efficiency, and the effect was more significant in dilute $HgCl_2$ solutions. The presence of SO_4^{2-} and NO_3^- did not affect Hg^0 removal by $HgCl_2$.

Introduction

Mercury has attracted global attention due to its high toxicity and persistence in the environment (Barbosa et al., 2001; Winfrey and Rudd, 1990). The “Minamata Convention on Mercury” was recently signed in October, 2013 in Kumamoto, Japan. It is an international treaty aimed to reduce mercury emission globally.

Among the anthropogenic sources of mercury emission, nonferrous metal production, such as the smelting of Pb and Zn sulfide ores, has been recognized as one of the primary sources (UNEP, 2010; Hylander and Herbert, 2008; Li et al., 2010). In China, over 40% of the total mercury emission is from nonferrous metal smelting (Wu et al., 2006; Wang et al., 2006; Pacyna et al., 2010). Therefore, it is urgent to look for an approach to reduce Hg emission in this industry.

As one of the main mercury species in nonferrous metal smelting flue gas, elemental mercury (Hg^0) is hard to remove because of its high volatility and insolubility (Pacyna et al., 2001; Pacyna and Pacyna, 2002). Generally, the major technique for controlling Hg^0 emission from flue gas is to convert Hg^0 to its particulate form (Hg^P) or oxidized form (Hg^{2+}) and remove them using existing air pollution control devices, such as electrostatic precipitators or wet flue gas desulfurization units (Qu et al., 2009; Yan et al., 2009; Liu et al., 2011a). However, the concentration of Hg^0 in nonferrous metal smelting flue gas ranges from several to tens of mg/m^3 (Dong, 1994; Wang et al., 2010). It is difficult to remove such high concentrations of Hg^0 in this industry. Furthermore, Hg^0 is a valuable resource in many fields such as dentistry, mercury thermometers and gold mining. Therefore, reclaiming mercury from nonferrous metal smelting flue gas is a better choice than

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just removing it by using air pollution control devices for mercury emission control. The mercury chloride absorption technique is an effective Hg^0 reclamation technology and has been applied in many nonferrous metal smelters.

According to the typical smelting process of nonferrous metal ores, the flue gas from a roasting furnace goes through an electrostatic precipitator, wet scrubber and electrostatic demister to remove particulate matter and clean the flue gas, respectively. Meanwhile, the flue gas is allowed to cool down to about 313 K. Then, the Hg^0 in the flue gas is reclaimed by mercury chloride absorption technology (Hylander and Herbert, 2008; Wang et al., 2010). The mercury chloride absorption process is based on the oxidation of Hg^0 by mercuric chloride to form insoluble calomel (Hg_2Cl_2). The main chemical reactions in the absorption process are summarized as follows (Hylander and Herbert, 2008).

$$HgCl_2 + (n{-}2)Cl^- = {HgCl_n}^{2-n} (2 \le n \le 4) \quad (1)$$

$$Hg^0 + {HgCl_n}^{2-n} = Hg_2{Cl_2}^- + (n{-}2)Cl^- (2 \le n \le 4) \quad (2)$$

Although the Hg^0 removal efficiency of the mercury chloride absorption process is about 90%, the outlet Hg^0 concentration of the mercury chloride absorption process is still very high, and cannot satisfy the discharge standard (Wang et al., 2010). Furthermore, the nonferrous metal smelting flue gas contains high concentrations of SO_2, which if absorbed by the mercury chloride absorption solution will reduce the Hg^0 removal efficiency because SO_3^{2-} reduces Hg^{2+} in the absorption solution (Liu et al., 2011b). With the emission regulation of Hg^0 in the nonferrous metal industry becoming increasingly strict, the mercury chloride absorption technology has difficulty meeting the stringent requirements of mercury emission control. Thus, it is important and necessary to improve the mercury chloride absorption technique and enhance its mercury removal performance.

However, relevant reports on the mechanism and main factors affecting mercury chloride absorption technology are lacking, thus limiting its development. This paper systematically researched the mercury chloride absorption technique and developed a method to enhance it.

1. Materials and methods

1.1. *Experimental apparatus*

A typical absorption reactor was applied in this research. As shown in Fig. 1, several cylinder gases were used to provide the simulated flue gas at a flow of 1.0 L/min. Mercury vapor was generated by a mercury bottle in a water bath and was carried by N_2 gas, and the simulated flue gas passed through a three-neck flask which was filled with 30 mL $HgCl_2$ absorption solution. Meanwhile, a pulse reaction system was used to investigate the instantaneous reaction in the absorption solution. Mercury vapor was also generated by a mercury bottle in a water bath and was carried by the simulated flue gas and passed through a three-neck flask. Then, a certain amount of Na_2SO_3 solution was injected into the three-neck flask that was filled with 30 mL $HgCl_2$ solution to investigate the reduction of $HgCl_2$ by SO_3^{2-}. SO_2 was introduced into the reaction system to study the effect of SO_2 on Hg^0 removal by $HgCl_2$ solution. The average temperature of the simulated flue gas and absorption solution was about 303 and 298 K, respectively. The time for the gas mixture to pass through the absorption solution in the reactor was about 1.2 sec. The initial concentration of Hg^0 in the inlet gas of the absorption reactor was maintained at about 1.2–2.1 mg/m^3, which could be controlled by adjusting the temperature of the water bath and the flow rate of N_2. The inlet and outlet Hg^0 concentrations of the absorption reactor were monitored by a mercury analyzer (SG-921, Jiangfen Ltd., Taizhou, Jiangsu, China). The signal was collected and recorded by a data transition and acquisition device (N2000, Zhida Ltd., Hangzhou, Zhejiang, China). The concentration of Hg^0 in the flue gas was calibrated by a Lumex mercury analyzer (RA915, Lumex Ltd., St.petersburg, Russia).

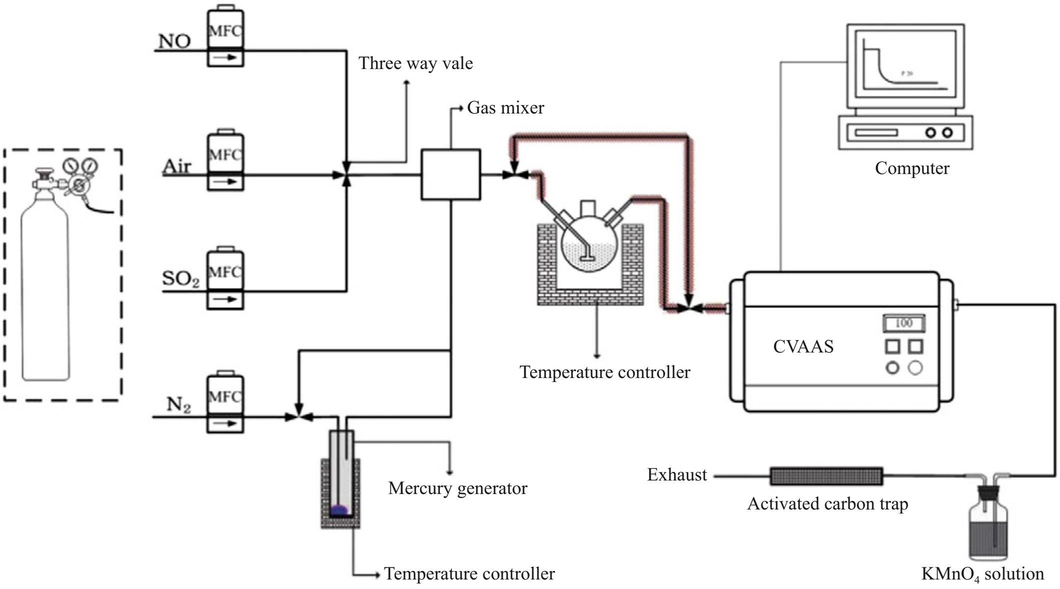

Fig. 1 – Schematic diagram of the absorption experimental apparatus.

The Hg^0 removal efficiency (η) was calculated by Eq. (3):

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

where, η^0_{Hg} is the Hg^0 Caesilia Unic Roman (True Type)removal efficiency, and $C^0_{Hg(in)}$ and $C^0_{Hg(out)}$ are the inlet and outlet Hg^0 concentrations of the absorption bottle, respectively.

1.2. *Fluorescence spectra study*

A fluorescence spectra study was carried out on a fluorescence spectrophotometer (RF-5301PC, Shimadzu Co., Ltd., Kyoto, Japan) by scanning a 1.0 cm quartz cuvette containing a prepared solution with a scan speed of 5000 nm/min. The solution was prepared by mixing $HgCl_2$ solution and sodium chloride or sodium sulfite solution with certain mole ratios.

1.3. *Computation methods*

In order to further explain the essence of the reactions between mercury chloride species and Hg^0 at the molecular level, the reaction mechanisms of $HgCl_n^{2-n} + Hg^0 \rightarrow Hg_2Cl_2 + (n-2)\ Cl^-$ (n: 2–4) in the aqueous solution were investigated using *ab initio* molecular orbital calculations. The geometry optimizations of the reactants, products, and transition states in aqueous solution were performed at the second-order Moller–Plesset perturbation theory level using the Turbomole 6.3 program (Turbomole GmbH Co. Ltd., karlsruhe, Germany) (Ahlrichs et al., 2011). The effects of the aqueous solvent on structure and energetics of all the species were studied using the conductor-like screening model (Klamt and Schüürmann, 1993). In this dielectric continuum solvent model, charges centered on surface elements, induced by the electrostatic potential of the solute, are determined self-consistently. For Hg, we adopted the def2-TZVPP effective core potential basis sets. In these basis sets, the 60 innermost-electrons for Hg atoms were replaced by the effective core potentials, which included relativistic effects known to be important for heavy transition metal atoms. The def2-TZVPP basis set was used for Cl atom (Andrae et al., 1990; Haase and Ahlrichs, 1993). Transition states were located using synchronous transit-guided quasi-Newton methods in combination with stepwise partial optimization along each pathway, with one geometric parameter fixed as constant. The harmonic vibrational frequencies of all the species were derived by following each optimization to obtain the zero point energy and to confirm all of the stationary points as either minima (the number of imaginary frequencies = 0 or the number of imaginary transition states = 1). Intrinsic reaction coordinate calculations were performed to confirm the relationship of each transition state with its reactant and product.

1.4. *Materials*

The following main chemicals were employed: mercury (99.9%), mercuric chloride (99.5%), sodium chloride (99.5%), sodium sulfate (99%), sodium sulfite (98%), sodium nitrate (99%), ferric nitrate (98%), ferric chloride (98%), nitric acid (69%), and potassium permanganate (99%) from Sigma-Aldrich Co., Shanghai, China SO_2 (99.9%) and N_2 (99.9%). The latter two chemicals were stored in cylinders and were obtained from Dalian Date Gas Co. Ltd., Dalian, China.

2. Results and discussion

2.1. *Comparisons of several absorption solutions on Hg^0 removal efficiency*

To remove a high concentration of Hg^0 and generate stable Hg_2Cl_2, which is insoluble and favorable for recycling, several chlorine compounds were screened as active constituents of the absorption liquid, such as mercury chloride, ferric chloride, copper chloride, and sodium hypochlorite. In addition, as a comparison, hydrogen peroxide was also investigated. 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. From the experimental results shown in Fig. 2, it can be seen that the Hg^0 removal efficiency of $HgCl_2$ is distinctly higher than that of other chlorides. Obviously, in mercuric chloride solution, Hg(II) is inferred as the active ingredient for absorbing Hg^0 rather than Cl^-. When the $HgCl_2$ concentration was 3.68 mmol/L, the Hg^0 removal efficiency was 93.9%, which is higher than the value of 48.3% obtained with H_2O_2. When the concentrations of ferric chloride, copper chloride and sodium hypochlorite were all 0.03 mol/L, the Hg^0 removal efficiencies were below 20%, far lower than the efficiency of mercury chloride. Therefore, mercury chloride solution was studied as an efficient absorbent in this paper.

2.2. *Effects of the concentration of the initial Hg^0 and $HgCl_2$ solution*

The effects of the initial Hg^0 and $HgCl_2$ solution concentrations on Hg^0 removal were determined. The $HgCl_2$ solution

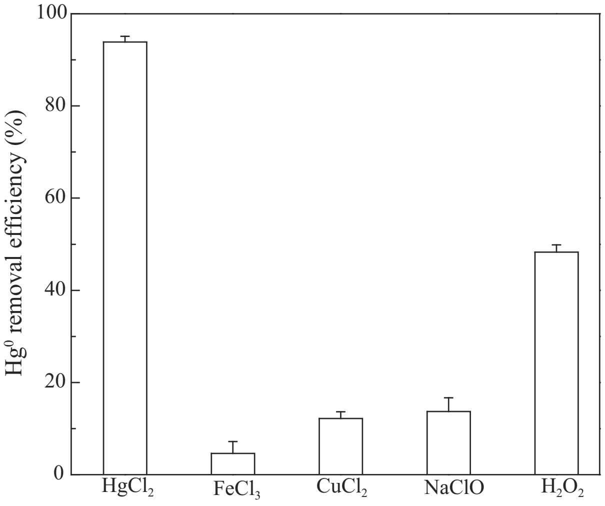

Fig. 2 – Comparison of several absorbents on Hg^0 removal. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, initial Hg^0 concentration of 1.8 mg/m^3, $HgCl_2$ concentration of 3.68 mmol/L, other chloride concentrations all of 0.03 mol/L and H_2O_2 concentration of 15%.

concentration was between 0.368 and 7.36 mmol/L, and the initial gaseous Hg^0 concentration was 1.2 to 2.1 mg/m^3. Fig. 3 shows that the Hg^0 removal efficiency declined gradually with the increase of initial gaseous Hg^0 concentration. Furthermore, the lower the $HgCl_2$ concentration, the more obvious the decline in Hg^0 removal efficiency. For example, when the $HgCl_2$ concentration was 3.68 mmol/L, the Hg^0 removal efficiency decreased from 94.6% to 92.2% when the initial Hg^0 concentration increased from 1.2 to 2.1 mg/m^3; and when the $HgCl_2$ concentration was 0.368 mmol/L, the Hg^0 removal efficiency decreased from 29.8% to 22.1%. Therefore, high initial Hg^0 concentration was unfavorable for Hg^0 removal by the $HgCl_2$ solution absorption technology.

Fig. 3 also shows that when the $HgCl_2$ concentration was lower than 1.84 mmol/L, the Hg^0 removal efficiency decreased sharply, for example the efficiency decreased from 86.3% to 27.8% when the $HgCl_2$ concentration decreased from 1.84 to 0.368 mmol/L. The removal efficiency of Hg^0 increased from 27.8% to 97.7% when the $HgCl_2$ concentration increased from 0.368 to 7.36 mmol/L when the initial Hg^0 concentration was 1.8 mg/m^3. This means that increasing the $HgCl_2$ concentration is helpful for Hg^0 removal. However, the increasing tendency of Hg^0 removal efficiency slowed down when the $HgCl_2$ concentration was higher than 7.36 mmol/L. Therefore, infinitely increasing the $HgCl_2$ concentration is not necessary for higher Hg^0 removal efficiency.

In these experiments, the mass balance of the Hg was assessed strictly. The flow rate of the simulated flue gas was 1.0 L/min and the initial concentration of Hg^0 was 1.8 mg/m^3. 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 and 60 min, respectively. Using the integral method to calculate, the amount of Hg^0 absorbed into the $HgCl_2$ solutions was 0.238×10^{-3} and 0.414×10^{-3} mmol. Then the total amount of Hg in $HgCl_2$ solutions detected by the Lumex mercury analyzer was 1.380×10^{-3} and 1.474×10^{-3} mmol, respectively. Therefore, the error of the mass balance of Hg was 2.9% and 2.7%, respectively. Thus the mass balance of the Hg was accurate during the course of the experiments.

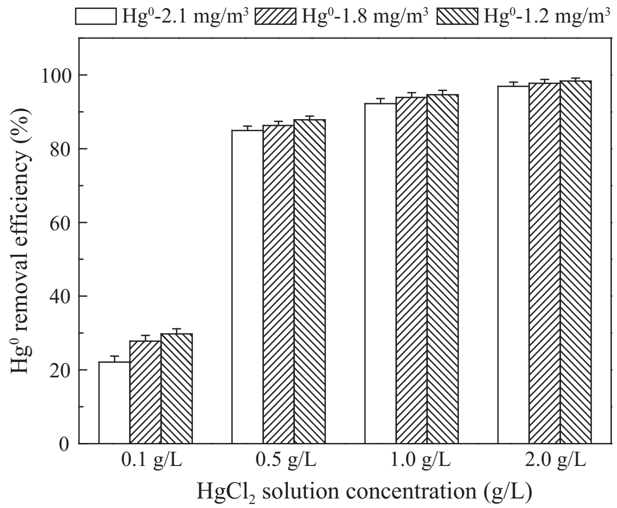

Fig. 3 – Effects of the initial Hg^0 and $HgCl_2$ solution concentrations on Hg^0 removal. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, initial Hg^0 concentration of 1.2–2.1 mg/m^3, $HgCl_2$ concentration of 0.368–7.36 mmol/L.

2.3. Effects of the pH value in $HgCl_2$ solution

The pH of the absorption solution is a key factor in air pollutant washing technology. The influence of pH on mercury absorption by $HgCl_2$ solution was also considered. 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. The concentration of $HgCl_2$ was 0.243, 0.736, and 3.68 mmol/L, respectively. In this paper, nitric acid was employed to adjust the pH and the background pH of the 0.736 mmol/L $HgCl_2$ solution was about 4.5.

The results in Fig. 4 show that lower pH was beneficial to the Hg^0 removal efficiency, and it is clearly seen that the pH was more important to the Hg^0 removal efficiency in low concentration of $HgCl_2$. For example, when the pH value is decreased from 4.5 to 0 in 0.243 mmol/L $HgCl_2$ solution, the Hg^0 removal efficiency increased from 11.1% to 55.6%. But for the same change in pH in 3.68 mmol/L $HgCl_2$ solution, the Hg^0 removal efficiency only increased from 93.9% to 95.8%. The mechanism of the pH effects may be that H^+ is helpful for promoting the ionization of molecular $HgCl_2$, and Hg^{2+} or $HgCl^+$ generated by ionization of molecular $HgCl_2$ is more effective in absorbing Hg^0 for its removal. Furthermore, this ionization is more significant in dilute $HgCl_2$ solution.

2.4. Effects of SO_3^{2-}, SO_4^{2-} and NO_3^- anions in $HgCl_2$ solution

The components of the nonferrous metal smelting flue gas are complicated. The SO_2 and NOx of the flue gas are absorbed by the $HgCl_2$ solution and form anions such as SO_3^{2-}, SO_4^{2-} and NO_3^-, which may affect Hg^0 removal by $HgCl_2$. To investigate the influence of these anions on the Hg^0 removal efficiency, 3.68 mmol/L Na_2SO_3, Na_2SO_4 and $NaNO_3$ was added into the $HgCl_2$ solution, respectively. The results are shown in Fig. 5.

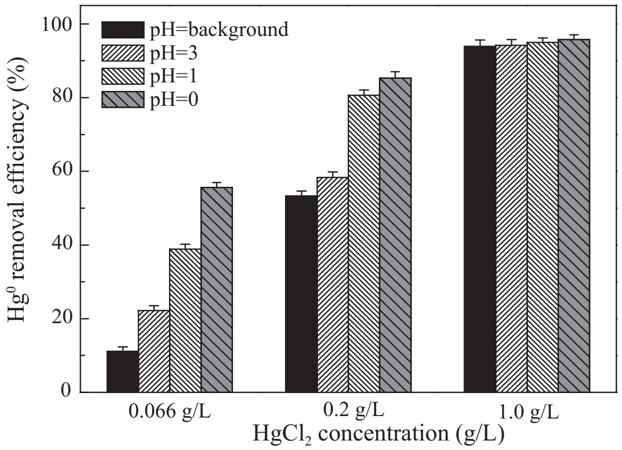

Fig. 4 – Effects of pH in $HgCl_2$ solution on Hg^0 removal. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, initial Hg^0 concentration of 1.8 mg/m^3, $HgCl_2$ concentration of 0.243, 0.736, and 3.68 mmol/L, respectively, and solutions pH of 4.5, 3, 1, and 0 and nitric acid used for pH.

Fig. 5 shows that the efficiency of the Hg^0 removal is completely consistent with pure $HgCl_2$ solution when Na_2SO_4 or $NaNO_3$ is added into the $HgCl_2$ solution. This means that SO_4^{2-} and NO_3^- do not affect the Hg^0 removal efficiency in the $HgCl_2$ solution. However, with 3.68 mmol/L Na_2SO_3 in the $HgCl_2$ solution, the Hg^0 concentration in the simulated flue gas increased from 0.9 to 1.6 mg/m^3 in 5 sec and then dropped to 0.9 mg/m^3 in 100 sec. The presence of SO_3^{2-} has adverse effects on Hg^0 removal by the $HgCl_2$ solution.

In order to investigate the reactions between $HgCl_2$ and Na_2SO_3, different concentrations of Na_2SO_3 were injected into $HgCl_2$ solution, and N_2 was used as carrier gas. In these absorption solutions, the $HgCl_2$ concentration was 0.368 mmol/L, and the mol ratio of SO_3^{2-} was $HgCl_2$ was 0.5:1, 1:1, 2:1, 5:1, and 20:1, respectively. The flow rate of N_2 was 1.0 L/min. The results are shown in Fig. 6. When the mole ratio of Na_2SO_3 to $HgCl_2$ was 0.5:1, the Hg^0 concentration brought out by the carrier gas was relatively lower. This is because the insufficient amount of SO_3^{2-} only reduced a part of the $HgCl_2$. The Hg^0 concentration rose with the increase of SO_3^{2-} added to the $HgCl_2$ solution and reached a maximum (about 0.9 mg/m^3) when the mole ratio of Na_2SO_3 to $HgCl_2$ was 1:1. Then, with continuing increase in the mole ratio, the Hg^0 concentration brought out by the carrier gas declined gradually. When the mole ratio of Na_2SO_3 to $HgCl_2$ was 20:1, the Hg^0 concentration decreased to 0.03 mg/m^3. The possible mechanism can be deduced as follows: first, the Na_2SO_3 reacted with $HgCl_2$ and generated the intermediate $HgSO_3$ (Eq. (4)).

$$HgCl_2 + Na_2SO_3 \rightarrow HgSO_3 + 2NaCl \tag{4}$$

However, $HgSO_3$ is so unstable that it decomposes and generates Hg^0 (Liu et al., 2011A; Chang and Ghorishi, 2003; Wu et al., 2010).

$$HgSO_3 + H_2O \rightarrow Hg^0 + H_2SO_4 \tag{5}$$

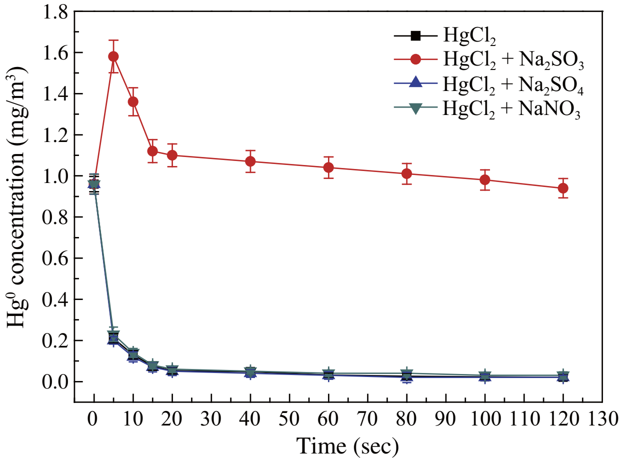

Fig. 5 – The influence of SO_3^{2-}, SO_4^{2-} and NO_3^- on Hg^0 removal. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, initial Hg^0 concentration of 0.9 mg/m^3, $HgCl_2$ concentration of 0.184 mmol/L, and Na_2SO_3, Na_2SO_4 and $NaNO_3$ concentration of 1.84 mmol/L.

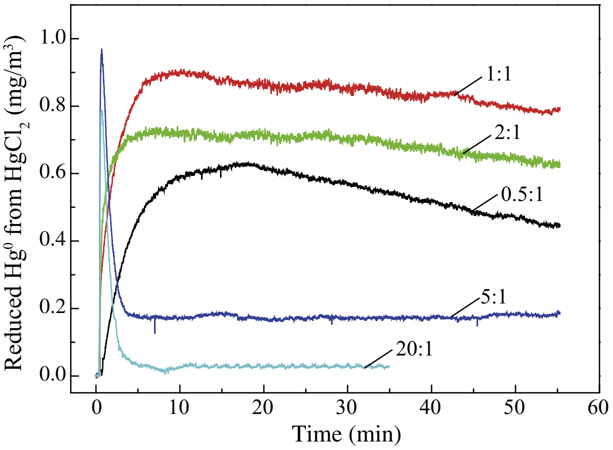

Fig. 6 – The influences of different concentrations of SO_3^{2-} on $HgCl_2$ solution. Experimental conditions: flow rate of the N_2 of 1.0 L/min, absorption solutions of 30 mL, $HgCl_2$ concentration of 0.368 mmol/L, and the mol ratio of SO_3^{2-} to $HgCl_2$ of 0.5:1, 1:1, 2:1, 5:1, and 20:1, respectively.

When the mole ratio of Na_2SO_3 to $HgCl_2$ is higher than 1:1, the excess SO_3^{2-} ions react with the intermediate $HgSO_3$ and form $[Hg(SO_3)_2]^{2-}$ complex anions, which are more stable in solution (Lu et al., 2011; Wo et al., 2009).

$$HgSO_3 + SO_3^{2-} \rightarrow [Hg(SO_3)_2]^{2-} \tag{6}$$

In order to verify the hypothesis, $HgCl_2$ solutions with different concentrations of Na_2SO_3 were measured by fluorescence spectrometry, and the results are shown in Fig. 7. There was only one peak at approximately 511 nm in the 1.84 mmol/L $HgCl_2$ solution. When the mole ratio of Na_2SO_3 to $HgCl_2$ was 1:1 in the $HgCl_2$ solution, the peak at 511 nm decreased, and new peaks appeared at approximately 367 nm and 468 nm. This is consistent with Eqs. (4) and (5), and the

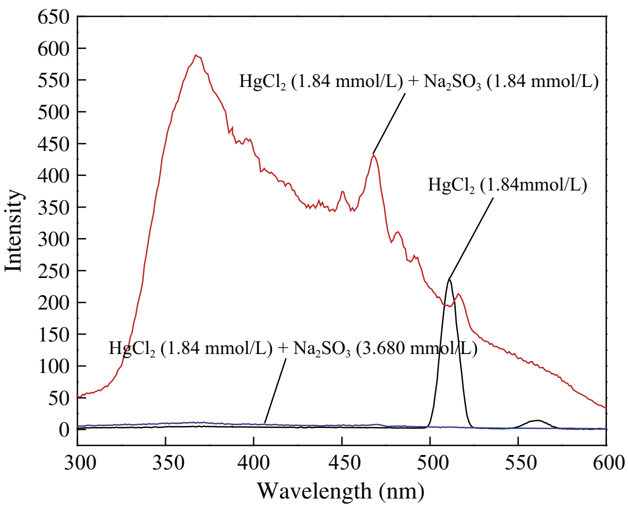

Fig. 7 – The fluorescence spectrums of the $HgCl_2$ and Na_2SO_3 solutions. Experimental conditions: $HgCl_2$ concentration of 0.184 mmol/L and the mol ratio of Na_2SO_3 to $HgCl_2$ of 0:1, 1:1, and 2:1, respectively.

two new peaks may belong to the solid Hg_2Cl_2 generated by Hg^0 (Eq. (5)) and $HgCl_2$. When the mole ratio of Na_2SO_3 to $HgCl_2$ was 2:1 in the $HgCl_2$ solution, there were no $HgCl_2$ or Hg_2Cl_2 peaks in the fluorescence spectrum. This may confirm Eq. (6). Because the $[Hg(SO_3)_2]^{2-}$ complex anions cannot be detected by molecule fluorescence spectrometry, there was no peak in the fluorescence spectrum.

It is known that $HgCl_2$ can be reduced by SO_3^{2-}, which can not only decrease the effectiveness of $HgCl_2$ in Hg^0 removal, but also increase the Hg^0 concentration of the flue gas. Thus, methods to restrain reduction by SO_3^{2-} should be considered. Some ions were added into $HgCl_2$ solutions, such as SO_4^{2-}, NO_3^- and Cl^-, but only Cl^- was found to be effective. It can be clearly seen from Fig. 8 that the Hg^0 concentration due to reduction by SO_3^{2-} declines gradually with increasing Cl^- added into the $HgCl_2$ solution. When the mole ratio between Cl^- and $HgCl_2$ was 10:1, the Hg^0 concentration due to reduction was at nearly the minimum value (about 0.045 mg/m^3). When the mole ratio of Cl^- to $HgCl_2$ was more than 10:1, the inhibition by Cl^- did not continue to strengthen. The possible mechanism can be deduced as follows: first, the Na_2SO_3 reacts with $HgCl_2$ and generates the intermediate $HgSO_3$ (Eq. (4)). Then, the additional Cl^- added combines with $HgSO_3$ and generates intermediates including $[ClHgSO_3]^-$ and $[Cl_2HgSO_3]^{2-}$ complex anions, which are so stable that it is difficult for SO_3^{2-} to reduce them in solution (Eq. (7) and Eq. (8)) (Lu et al., 2011; Wo et al., 2009).

$$HgSO_3 + Cl^- \rightarrow [ClHgSO_3]^- \tag{7}$$

$$[ClHgSO_3]^- + Cl^- \rightarrow [Cl_2HgSO_3]^{2-} \tag{8}$$

Moreover, the additional Cl^- added also can combine with $HgCl_2$ and generate $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ complex anions, which are hard for SO_3^{2-} to reduce in solution (Tang et al., 2010). The higher the concentration of Cl^- added is, the more complexes are formed.

Therefore, it will be helpful to add a proper amount of chloride additives into $HgCl_2$ solution to restrain reduction by SO_3^{2-}.

2.5. Effects of Cl^- anions on Hg^0 removal

As known from previous studies, additional Cl^- added into $HgCl_2$ solution could restrain reduction by SO_3^{2-}. However, what are the effects of Cl^- ions on Hg^0 removal efficiency? To answer this question, chloride additives such as sodium chloride, potassium chloride and hydrochloric acid were added to the $HgCl_2$ solution to investigate the influence of Cl^- anions on Hg^0 removal. The Hg^0 removal efficiency under different chloride additives is shown in Fig. 9.

Fig. 9 shows that the Hg^0 removal efficiency increased from 86.3% to 91.0% when the mole ratio of NaCl to $HgCl_2$ increased from 0:1 to 10:1. However, the Hg^0 removal efficiency decreased quickly to 55.7% when the mole ratio of NaCl to $HgCl_2$ increased to 200:1. Similar results were acquired when different chloride additives, such as HCl or KCl, were added into the $HgCl_2$ solution. Clearly, Cl^- anions are important for Hg^0 removal by the $HgCl_2$ solution, but the cations do not affect Hg^0 removal (except H^+, which changes the pH).

As it is well known that the ionization degree of $HgCl_2$ is very small, the concentration of Hg^{2+} or $HgCl^+$ in $HgCl_2$ solution is also very low accordingly. Therefore, the main mercury chloride species in $HgCl_2$ and NaCl mixed solutions are $HgCl_2$, $HgCl_3^-$ and $HgCl_4^{2-}$, respectively (Patrice et al., 1985). There is an equilibrium between $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$ and Cl^- in $HgCl_2$ and NaCl mixed solutions. The distribution of these three mercury chloride species is related to the mole ratio between Cl^- and $HgCl_2$ in the mercury chloride absorption solution (Belevantsev et al., 2004). As observed in the literature, the $HgCl_3^-$ and $HgCl_4^{2-}$ concentration increases with the increase of the Cl^- concentration. When the Cl^- to $HgCl_2$

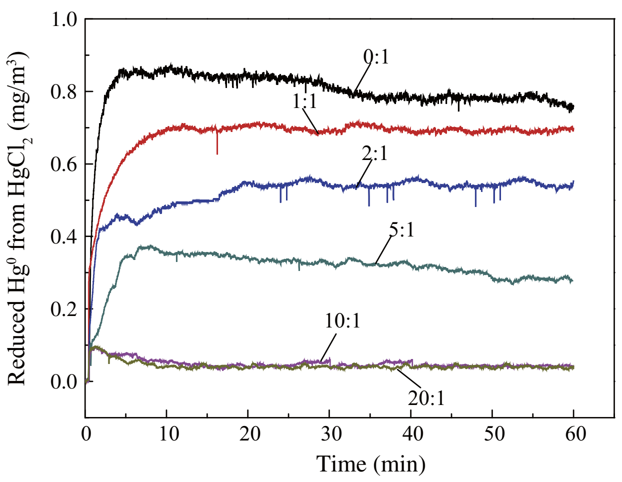

Fig. 8 – The effects of Cl^- on restraining the reduction of SO_3^{2-} in $HgCl_2$ solution. Experimental conditions: flow rate of the N_2 of 1.0 L/min, absorption solutions of 30 mL, $HgCl_2$ concentration of 0.368 mmol/L, the mol ratio of SO_3^{2-} to $HgCl_2$ of 1:1, and the mol ratio of Cl^- to $HgCl_2$ of 0:1,1:1, 2:1, 5:1, 10:1, and 20:1, respectively.

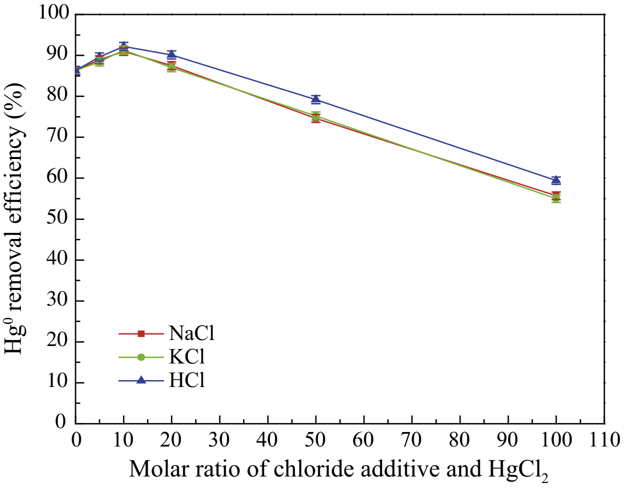

Fig. 9 – The influence of Cl^- on Hg^0 removal. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, $HgCl_2$ concentration of 0.184 mmol/L, the mol ratio of Cl^- to $HgCl_2$ of 0:1, 5:1, 10:1, 20:1, 50:1, and 100:1, respectively, and Cl^- from NaCl, KCl, and HCl.

mole ratio is higher than 20:1, the $HgCl_3^-$ concentration decreases gradually, while the $HgCl_4^{2-}$ concentration increases quickly. When the Cl^- to $HgCl_2$ mole ratio is 100:1, the proportion of $HgCl_4^{2-}$ in the mixture solution is more than 80%. Since the mercury removal efficiency increases with the increase of the $HgCl_3^-$ concentration in $HgCl_2$ solution, the mercury removal efficiency is lower when a high proportion of $HgCl_4^{2-}$ exists in $HgCl_2$ solution. Therefore, it can be deduced that the $HgCl_3^-$ is more efficient than $HgCl_2$ and $HgCl_4^{2-}$ in mercury removal in the mercury chloride absorption system.

In order to further explain the essence of the deduction, the reaction mechanisms of $HgCl_n^{2-n}$ (n: 2–4) + Hg^0 → Hg_2Cl_2 + (n − 2) Cl^- in the solvent (=water) were modeled using Moller–Plesset many-body perturbation theory. The Gibbs free energies and enthalpies of various reactions were computed. The absorption reaction between $HgCl_2$ and Hg^0 produced Hg_2Cl_2 *via* the transition state TS1 (80 i cm^{-1}) with a 26.82 kcal/mol barrier and only released approximately 0.23 kcal/mol of heat. Hg^0 was directly inserted in one Hg–Cl bond, and Cl was removed as a result. This Hg^0 absorbing reaction, $HgCl_2 + Hg^0 \rightarrow TS1 \rightarrow Hg_2Cl_2$, had difficulty occurring because of the high barrier, although the calculated Δ_rG_m (298 K) was −6.70 kcal/mol. For the absorption reaction between $HgCl_3^-$ and Hg^0, the reaction produced one intermediate $Hg_2Cl_3^-$ *via* the transition state TS2 (28 i cm^{-1}) with a 6.69 kcal/mol barrier, and the intermediate $Hg_2Cl_3^-$ decomposed to Hg_2Cl_2 and Cl^-. This Hg^0 absorption reaction easily occurred because of the low barrier, and the Δ_rG_m (298 K) of $HgCl_3^- + Hg \rightarrow Hg_2Cl_3^-$ was −2.95 kcal/mol. Although the calculated Δ_rG_m (298 K) of $Hg_2Cl_3^- \rightarrow Hg_2Cl_2 + Cl^-$ was 8.85 kcal/mol, this reaction would be driven by the insolubility of Hg_2Cl_2. The absorption of Hg^0 by $HgCl_4^{2-}$ was a thermodynamically disadvantageous reaction due to the very positive Gibbs free energy of reaction (Δ_rG_m (298 K)) of 17.87 kcal/mol. Furthermore, a transition state could not be found. Therefore, the case predicted by the MP2/def2-TZVPP level shows excellent agreement with the results obtained by our experiments.

The speciation of Hg–Cl can be described as follows (Eqs. (9) and (10)).

$$HgCl_2 + Cl^- = HgCl_3{}^- \tag{9}$$

$$HgCl_2 + 2Cl^- = HgCl_4{}^{2-} \tag{10}$$

Then, the Hg^0 was absorbed by Hg–Cl complexes as follows (Eq. (11) and Eq. (12)).

$$HgCl_2 + Hg^0 = Hg_2Cl_2 \tag{11}$$

$$HgCl_3{}^- + Hg^0 \rightarrow Hg_2Cl_3{}^- \rightarrow Hg_2Cl_2 + Cl^- \tag{12}$$

2.6. Effects of SO_2 on Hg^0 removal

The nonferrous metal smelting flue gas always contains a high concentration of SO_2. According to the above research, SO_2 will be absorbed by $HgCl_2$ and generate SO_3^{2-}, which may promote the reduction of Hg^{2+} in the $HgCl_2$ solution. This study tried to adjust the pH value and Cl^- anion of the $HgCl_2$ solution to reduce SO_2 absorption and Hg^{2+} reduction. In this study, there was only SO_2 and air in the simulated flue gas. The SO_2 concentration in simulated flue gas was 8000 mg/m^3. HNO_3 and HCl were added to the $HgCl_2$ solution to investigate the influence of the pH value on Hg^{2+} reduction, respectively. The SO_2 and Hg^0 concentrations of the simulated flue gas were detected after it passed through the $HgCl_2$ solution. The experimental results are shown in Fig. 10.

Fig. 10 shows that the Hg^0 concentration increased from 0 to 3.7 mg/m^3, whereas the SO_2 concentration dropped from 8000 to 3000 mg/m^3 when the pH of the absorption solution was 4.5. Clearly, SO_2 was absorbed by the $HgCl_2$ solution, and the mercury in the $HgCl_2$ solution was reduced from Hg^{2+} to Hg^0 by the action of SO_3^{2-} (Eq. (5) and Eq. (6)). The SO_2 removal efficiency did not show any remarkable change with decreasing pH. However, the Hg^0 concentration decreased significantly with decreasing pH. Furthermore, HCl was more effective than HNO_3 in inhibiting Hg^{2+} reduction. That may be because the Cl^- anions react with $HgCl_2$ and produce $HgCl_3^-$ and $HgCl_4^{2-}$ (Eq. (1)), while $HgCl_3^-$ and $HgCl_4^{2-}$ are very stable and will not react with SO_3^{2-}, so that the reduction of Hg^{2+} is consequently inhibited.

3. Conclusions

The mechanism and main factors of mercury removal by mercury chloride absorption technology were systematically studied in this paper. According to the experimental results, when the mole ratio of Cl^- to $HgCl_2$ is 10:1, the Hg^0 removal efficiency is the highest. Additional chloride ions added can promote the generation of $[HgCl_3]^-$ and $[HgCl_4]^{2-}$ complex anions. An important conclusion is that the reaction between $[HgCl_3]^-$ and Hg^0 takes place more easily than with $HgCl_2$ or $[HgCl_4]^{2-}$. The mechanisms of the Hg^0 absorption reaction in water were investigated using Moller–Plesset many-body perturbation theory. The calculation results of reaction Gibbs free energies and energy barriers were in excellent agreement with the results obtained by experiments. Meanwhile, both SO_3^{2-} and SO_2 could promote the reduction of Hg^{2+} and decrease the Hg^0 removal efficiency, but additional chloride ions added into the $HgCl_2$ solution could restrain the negative influence to some degree. Therefore, it will be helpful to add a proper amount of chloride additives into the $HgCl_2$ solution for Hg^0 removal. A low pH value in the $HgCl_2$ solution can enhance the Hg^0 removal efficiency, and this effect is more significant in dilute $HgCl_2$ solution. In addition, SO_4^{2-} and NO_3^- do not affect Hg^0 removal by $HgCl_2$.

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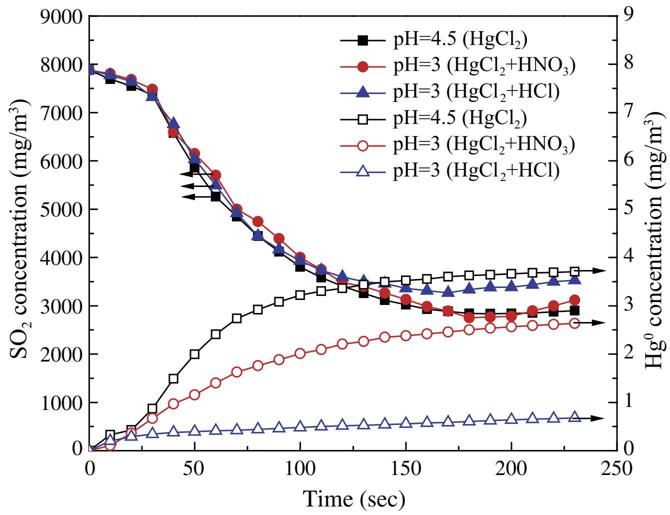

Fig. 10 – Influence of the pH value and Cl$^-$ on SO$_2$ absorption and Hg^{2+} reduction. Experimental conditions: flow rate of the simulated flue gas of 1.0 L/min, absorption solutions of 30 mL, HgCl$_2$ concentration of 0.184 mmol/L, SO$_2$ concentration of 8000 mg/m^3, solution pH of 4.5 and 3, respectively, nitric acid and hydrochloric acid used for pH.

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