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Effect of copper ions on the mercury re-emission in a simulated wet scrubber

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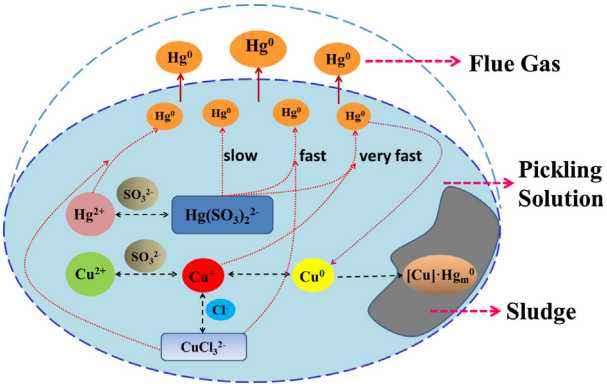
HIGHLIGHTS

- $CuCl_3^{2-}$ ions could directly reduce Hg^{2+} to insoluble Hg^0.
- $CuCl_3^{2-}$ ions play a catalytic role in the decomposition of $Hg(SO_3)_2^{2-}$.
- Low Cu^{2+} concentration could promote Hg^0 re-emission due to the generation of Cu^+.
- The Hg^0 re-emission decreased due to the formation of metal Cu which could absorb Hg^0 to form amalgam in high Cu^{2+} concentration.
- The addition of Cu ions change the electron transfer path of $Hg(SO_3)_2^{2-}$.

GRAPHICAL ABSTRACT



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ABSTRACT

In recent years, Hg re-emission from the wet scrubber has become a hot topic in the field of Hg abatement since wet scrubber has been considered as an effective way to remove Hg. In this paper, the effects of Cu ions on Hg re-emission were investigated for the first time in the presence of SO_3^{2-}. The effect of $CuCl_3^{2-}$ was proved to directly reduce Hg^{2+} to insoluble Hg^0 and to catalytically decompose $Hg(SO_3)_2^{2-}$ to Hg^0 and SO_4^{2-} in the presence of SO_3^{2-}. When adding the Cu^{2+} into solution with low concentration, Hg re-emission was increased due to the generation of Cu^+ from the reduction of Cu^{2+} by SO_3^{2-}. Further increase of Cu^{2+} concentration inhibited Hg re-emission, which was possibly owing to the formation of metal Cu which could absorb Hg^0 to form amalgam. The decomposition of $Hg(SO_3)_2^{2-}$ by $CuCl_3^{2-}$ and Cu^+ meet pseudo-first-order reaction with respect to Hg^0 and the activation energy parameters are 64.43 and 48.78 kJ/mol, respectively. Difference of electron transfer path in the decomposition of $Hg(SO_3)_2^{2-}$ with Cu^+ was proposed to be the reason of low activation energy.

1. Introduction

Mercury, due to its characteristics of high toxicity, volatility, bioaccumulation and long-distance transmission, has become an urgent environmental problem [1,2]. Due to the huge production of nonferrous metals in China, the atmospheric mercury emission of nonferrous metal industries, especially the heavy metal smelter, is regarded as one of the largest anthropogenic sources in China [3–5]. Compared with coal-fired plants, another largest source of Hg emission, the flue gases of heavy metal smelter have much higher concentrations of SO_2 and Hg because Hg is easy to be asso-

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ciated and enriched with sulfide minerals, the main raw materials of heavy metal smelter [6–8].

In the traditional processes of heavy metal smelter, few specialized facilities were installed to remove the Hg in the flue gas [9]. The main destiny of Hg were acid waste water from the smelter flue gas scrubbing and sulfuric acid from smelter acid plant, which accounts for 60–70% and 30–40% respectively [9,10]. Since high Hg concentration will deteriorate the quality of sulfuric acid product, it is very important to understand the Hg behavior in the flue gas scrubbing to reduce Hg amounts to sulfuric acid and then to the environment.

Recently, Hg re-emission from the wet scrubber has become a hot topic in the field of Hg abatement since wet scrubber has been considered as an effective way to remove Hg [11]. Many literatures have concluded that the SO_3^{2-} ions play the most important role in mercury re-emission due to the formation of unstable $HgSO_3$ [12–17] for wet flue gas desulfurization (WFGD). Furthermore, there are a large number of impurities in washing solution, such as Cl^-, SO_4^{2-}, F^-, and Fe^{2+}. These ions could interact with Hg^{2+} or SO_3^{2-} to affect the reduction behaviors of Hg^{2+} [18]. Taking Cl^- for examples, Cl^- could react with $HgSO_3$ to form $HgSO_3Cl^-$ or $HgSO_3Cl_2^{2-}$ which are more stable than $HgSO_3$ [14]. Such phenomenon was suggested to take place in smelter gas wet scrubbing (SGWS). But Hg behavior should be different since SGWC are different with WFGD in many aspects, such as high SO_2 concentration, various heavy metal ions and acidic scrubbing solution. In SGWS system, the main species of sulfite and mercury ions are HSO_3^- and $Hg(SO_3)^{2-}$ respectively and scrubbing solution contains high levels of heavy metal ions, such as Fe^{2+}, Pb^{2+}, and Cu^{2+}.

Cu ions, as a typical heavy metal ion, extensively exist in various flue gas scrubbing solutions since the cupric oxide and chloride can dissolve in flue gas scrubbing solutions. In some scrubbing solutions of copper smelter [19], the copper ions content reach over as large as 1 g L^{-1}. Although some researches have been conducted to prove cupric ions would play a positive role in promoting Hg^0 re-emission [20], no report has been found to clarify the effect of Cu for SGWS, especially with SO_3^{2-}, the very common and important anion in both SGWS and WFGD. For SGWS, Cu may have a complicated influence on Hg^0 re-emission since it has catalytic effect in many fields. The relationship of Cu and SO_3^{2-}, leading to different valence of Cu, would play an important role in Hg^0 re-emission. Therefore, it is meaningful to evaluate the effect of copper on Hg^0 re-emission.

In this paper, the effect of cuprous ions and copper ions on the Hg reduction and Hg^0 re-emission were first performed in a self-built absorption device. The mechanism and kinetics of Hg^0 re-emission under different conditions were then proposed.

2. Experimental

2.1. Experimental apparatus and method

A typical lab-scale reactor was applied in this study to investigate the reactions involved in the Hg^0 re-emission. As shown in Fig. 1, the high purity nitrogen gas was used as a carrier gas at a flow of 1.0 L/min to take the re-emission Hg^0. The carrier gas (N_2) was bubbled into reaction equipment which was a 500 mL, 3-neck, round bottom flask and contained a carry gas inlet, an outlet and a placement of electrode in order to measure Eh and pH. At the beginning of every test, the simulate solutions which contained certain cuprous ions or copper ions were put into flask firstly. Then heated up to setting temperature and adjusted pH. Thereafter, the solutions with certain concentration of Hg^{2+} and SO_3^{2-} were injected fast. In the course of experiment, the total solution volume was 300 mL. Throughout the experiment, the airtightness need to be ensured and the pipelines were made from Teflon to prevent the condensation of Hg^0. 30% (w/v) NaOH was required to avoid the corrosion of SO_2 gas. A S220-Basic Seven Compact Mettler Toledo apparatus was used for pH and Eh measurement. After mercury test, the tail gas required to be dealt with by the solution containing 5% (w/v) $KMnO_4$ and coconut shell activated carbon to ensure the security of the tail gas emission.

2.2. Experimental materials

Sodium sulfite anhydrous, sodium chloride and potassium permanganate were obtained from Sinopharm Chemical Reagent Co., Ltd. Perchloric acid (70%), copper nitrate, cuprous oxide, sulfuric acid, hydrochloric acid and nitric acid were purchased form Kemiou Chemical Reagent Co., Ltd. Sodium chloride, perchloric acid, nitric acid and cuprous oxide were guarantee reagent while others were analytical grade. Mercury nitrate ($Hg(NO_3)_2$) and mercuric oxide (HgO) as the source of divalent mercury were analytical grade and the purity was higher than 99.9%.

2.3. Analytical method

2.3.1. Hg^0 measurement

A Lumex Zeeman RA-915M Mercury Spectrometer could directly measure re-emission Hg^0 in flue gas. Mercury Spectrometer needed to be calibrated by pure nitrogen before taking measurement. Liquid samples were diluted to a suitable concentration and then measured by atomic fluorescence spectrometry (AFS).

2.3.2. UV-vis spectra characterization

To identify the mechanism in the mixed solution, the UV-visible spectrum of solution was employed in this research. The solution containing mercury was prepared by dissolving HgO in concentrated perchloric acid ($HClO_4$) and then diluted to the required concentration. The cuprous solution was prepared by dissolving Cu_2O in dilute hydrochloric acid (HCl). Other solutions were made up by dissolving sodium sulfite (Na_2SO_3), copper nitrate ($Cu(NO_3)_2$) or sodium chloride (NaCl) in a ultrapure water respectively. The pH of scanning solution was adjusted by the addition of NaOH and $HClO_4$ solutions. The prepared solutions were placed in quartz cuvettes with the volume of 3 mL. Before each measurement, the baseline spectrum of a solution with ultrapure water was collected. And the baseline spectrum would be subtracted from the spectrum of sample solution to ensure the correctness of detector response.

3. Result and discussion

3.1. Mercury re-emission in the presence of cuprous ions (Cu (I))

Usually, single cuprous ion in the water is instable. Thus, a certain concentration of chloride ions is added to stabilize cuprous ions due to the existence of Cl^- in smelter acidic wastewater. According to the thermodynamic constants for Cu (I) chloro-complexes and Hg (II) chloro-complexes (see Table S1 of Supporting Information), $CuCl_3^{2-}$ and $HgCl_4^{2-}$ dominate the speciation of Cu (I) and Hg (II) ions due to the existence of Cl^- in smelter acidic wastewater, which is also proved from these studies [21,22]. For the sake of studying the effect of $CuCl_3^{2-}$ on the reduction of bivalent mercury, a set of tests were carried out under different content of $CuCl_3^{2-}$ ranging from 0 to 0.12 mM. All the solutions in experiment contain constant chloride ions to avoid interference. Results in Fig. 2 show that Hg^0 re-emission increases with $CuCl_3^{2-}$ concentration. The cuprous ion is a reduction agent, which may deoxidize bivalent mercury ions into Hg^0. During the experiments, the redox