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Experimental study on the oxidative absorption of Hg^0 by $KMnO_4$ solution

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HIGHLIGHTS

- ▶ Theoretical and experimental results on Hg^0 removal using $KMnO_4$ solution are presented.
- ▶ The reaction mechanism of Hg^0 with $KMnO_4$ at different pH values was studied.
- ▶ SO_2 can cause Hg^0 secondary volatile problem and the mechanism of Hg^0 secondary volatile was studied.
- ▶ A method for the simultaneous removal of NO, SO_2 and Hg^0 using $CaCO_3 + KMnO_4$ solution are proposed.

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ABSTRACT

The wet FGD system is widely recognized as the co-effective removal system for oxidized Hg vapor species and SO_2. In this study, a purpose-built device was designed for this experiment and several factors potentially affecting the Hg^0 removal efficiency were systematic investigated, including different types of oxidants, pHs and concentrations of potassium permanganate, reaction temperatures, Hg^0 inlet concentrations, O_2, SO_2 and NO concentrations, and different types of absorption solutions. Results indicate that pHs and $KMnO_4$ concentrations, reaction temperatures, SO_2 and NO concentrations all have a strong influence on the removal of Hg^0, and the inlet concentrations of Hg^0 and O_2 contribute little to the removal of Hg^0. SO_2 could significantly inhibit the removal of Hg^0, the negative effect is serious especially at lower SO_2 concentration, and SO_2 could lead to the re-emission of Hg^0. Hg^0 could be removed effectively by using $CaCO_3 + KMnO_4$ solution, when the $KMnO_4$ concentration in the $CaCO_3 + KMnO_4$ solution was 1.5 mmol/L, the removal efficiencies of SO_2, NO and Hg^0 were 100%, 40.69% and 90.58%, respectively. So, considering the application to the practical engineering, adding 1.5–2 mmol/L $KMnO_4$ into limestone–gypsum flue gas desulfurization systems is necessary. This technology is a promising method for the simultaneous removal of NO, SO_2 and Hg^0.

1. Introduction

In recent years, mercury (Hg), due to its persistence, bioaccumulation and neurological toxicity, has received increasing attention as a pollutant of serious concern [1]. Worldwide mercury emissions from human activities are estimated to be 1000–6000 t/annum, which accounts for 30–55% of global atmospheric mercury emissions [2,3]. Coal combustion is considered as the largest source of anthropogenic mercury emissions [1]. In China, coal now accounts for more than 60% of the primary energy consumption and will continue to play an important role in energy uses for a long time to come [4]. Only in the power industry, the total amount of coal consumption is about 2.0 billion tons in 2011, and the number is still increasing. In China, coal contains mercury at an average concentration of around 0.22 mg/kg [5], it has been reported that large amounts of mercury from coal combustion emit into atmosphere, which leads to the increase of Hg concentration in the atmosphere in China [6,7]. Mercury contamination has become a serious problem in China, particularly concentrated in southwestern China (particularly Gui-zhou Province) [8]. Now, China is the largest mercury emitter worldwide [9], and reducing mercury pollution has been a high priority within China's environmental management and improvement program [1].

Mercury is present in the flue gas in varying percentages of three basic chemical forms: elemental mercury (Hg^0), particulate-bound mercury (Hg^P), and oxidized mercury (Hg^{2+}) (primarily mercuric chloride) [10–12]. Mercury emissions from coal-fired utility boilers vary in total amount and speciation, depending on coal types, boiler operating conditions, and configurations of air pollution control devices (APCDs) [2]. Jiang et al. considered that the main mercury forms from coal combustion in China were Hg^{2+} and Hg^P that about 61.2% of the Hg was released as Hg^{2+}, 22.5% as Hg^P, and 16.3% as Hg^0 in 2000 [13]. Generally, Hg^{2+} is

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water-soluble and can be efficiently removed in wet scrubbers, which exhibit up to 90% removal of Hg^{2+}. Most of Hg^{p} can be removed by the typical air pollution control devices (APCDs), such as fabric filter (FF) bag house, electrostatic precipitator (ESP). However, the elemental mercury is difficult to capture due to its volatility, insoluble and chemical stability [10]. So the key of control mercury emission from coal-fired boilers is to control elemental mercury emission. Many research and engineering efforts are being explored to control elemental mercury emissions from flue gas. The current suite of mercury control technologies under development employs sorbents [14–16], catalysts [17,18], scrubbing liquors [4,19], electro-catalytic oxidation [20,21], photochemical oxidation [22,23], and more. To date, activated carbon injection upstream of the ESP or FF has received a great deal of attention by the technology developers due to its high efficiency, relative simplicity, commercial availability, and successful application for the incinerator market, and it is considered as the most promise as a mercury control technology. However, the major drawback of this technology is the rather high cost of the sorbent, and activated carbon's poor utilization/selectivity for mercury. So this technology is less attractive for industrial use in China.

Now, multi-pollutant gas cleaning systems are considered a valuable option in terms of efficiency and low investment, and the WFGD units installed in power plants for SO_2 capture are considered an optimized method for the co-capture of pollutants other than sulfur, including some mercury species [24]. Nowadays, in the field of flue gas treatment the wet FGD system has already obtained wide application in China. The practice shows that the WFGD can remove Hg^{2+} quite efficiently, but Hg^0 is insoluble and it is difficult to be removed by the WFGD. The high removal efficiencies of Hg^{2+} indicate that oxidation of Hg^0 greatly facilitates its capture in the wet scrubbers and hence is a promising method for the removal of mercury. So, most of researches have focused on the oxidation technology of Hg^0 to Hg^{2+}, and wish to efficiently remove Hg^0, SO_2 and NO simultaneously in the WFGD. The most commonly used oxidants include $K_2S_2O_8$ [4], Fenton [25], NaClO [26], $NaClO_2$ [27], O_3 [28], H_2O_2 [29] and so on. However, there is limited information on the possible process and mechanism of the reaction between Hg^0 and $KMnO_4$ in the literature. In this study, a sequence of experiments was carried out in order to evaluate the influence of different operational parameters on Hg^0 removal efficiency in a bubble column reactor, and the optimal experimental conditions were established. Meanwhile, the mechanism of the reaction between Hg^0 and $KMnO_4$ in the process was also hypothesized.

2. Experimental setup

2.1. Materials

Standard gases included N_2 (99.999%), O_2 (99.999%), SO_2/N_2 (1.96%SO_2, v/v) span gas, and NO/N_2 (1.98% NO, v/v) span gas. All of them were the products of the Gas Co., Ltd. of Zhuo Zheng, Guangzhou, China. Sodium hydroxide (96.00 wt.%, Fu chen Chemical Reagent Factory, Tianjin, China), nitric acid (65.00–68.00 wt.%, Guangzhou Chemical Reagent Factory, China), sodium chlorite (>78.00 wt.%, Yaou Chemical Engineering Co., Ltd., China), hydrogen peroxide (30.00 wt.%, Guangzhou Chemical Reagent Factory, China), potassium permanganate ($\geqslant$99.50 wt.%, Guangzhou Chemical Reagent Factory, China), potassium persulfate ($\geqslant$99.50 wt.%, Guangzhou Chemical Reagent Factory, China), sodium hypochlorite (available chlorine $\geqslant$7.50 wt.%, Guangzhou Chemical Reagent Factory, China) were the analytical grade reagents used in the present study. Reverse osmosis water was applied to prepare the solutions.

2.2. Experimental setup

Fig. 1 shows the schematic diagram of the experimental apparatus including a flue gas simulation system, mercury generation, an absorption reactor and online gas analysis system. Except the reactor, Teflon was used to avoid erosion and mercury deposition on the tube surface. The pipeline was heated up to 120 °C with a temperature-controlled heating belt as shown in Fig. 1, to avoid absorption of mercury and condensation of moisture on the surface.

Nitrogen, oxygen, nitric oxide/nitrogen, and sulfur dioxide/nitrogen were obtained from cylinders and metered through mass flow controllers (Beijing Seven-Star Electronics Co., Ltd., China). The outlet valve of cylinder could be closed when a gas was not used. O_2, NO, SO_2 were diluted with N_2 in a pipe mixer1 to form gas mixture A, meanwhile part of the purge N_2 was sent to pass through a home-made mercury generator to carry out pre-calibrated elementary mercury to form gas mixture B, then the gas mixture A and B mixed in a pipe mixer2 to form the simulated flue gas. The total flow of blended gas (Q_{gas}) was always kept at 1000 mL/min. The elemental mercury was generated from mercury osmotic tube (S56-HE-SR, VICI Metronics Co., USA) inside a glass U-tube, heated in a thermostatic water bath (T_{Hg}) with 200 mL/min N_2 as carrier gas. The concentration of Hg^0 was changed by altering the temperature of permeation (T_{Hg}) and the flux of mercury-carrying gas.

The absorption experiments were performed in a bubble column reactor made of borosilicate glass (10 cm in diameter and 25 cm in length). The column was packed with ceramic Raschig rings (12.5 mm in diameter and 12.5 mm in length), packed height was 5 cm. In each typical experiment, the temperature of water baths was adjusted to the constant values, and then 1 L solution was put into the reactor being immersed in the other water bath ($T_{reaction}$). The gas mixture continuously flowed through the system, and the concentrations of O_2, NO and SO_2 were measured by flue gas analyzer (Testo350XL, Testo Instruments International Trade Co., Ltd., Germany) before and after absorption to calculate the removal efficiencies of SO_2 and NO, and RA-915 M mercury online analyzer (Lumex Ltd. company, Russia) was used to measure the concentration of Hg^0 in flue gas to calculate the removal efficiency of Hg^0. In order to protect the flue gas analyzer and mercury online analyzer, a dryer was used to remove the moisture content in simulated flue gas. Finally, the vent gas was scrubbed by acidic $KMnO_4$ solution.

In addition, the temperature of the heating belt was regulated by the Al-518P artificial intelligence temperature controller (Electrical automation technology Co., Ltd. Xiamen Yu, China). A pH-electrode (PHS-3C, INESA Scientific instrument Co., Ltd. Shang Hai, China) was immersed into the liquid to measure the pH value.

The percent of NO, SO_2, and Hg^0 removal efficiency was determined by the following equation:

$$P(\%) = 100 \times \frac{A_{inlet} - B_{outlet}}{A_{inlet}} \qquad (1)$$

where P is the Hg^0, NO and SO_2 removal efficiency, A_{inlet} is the Hg^0, NO and SO_2 concentration in the inlet gas, B_{outlet} is the Hg^0, NO and SO_2 concentration in the outlet gas.

3. Results and discussion

3.1. Choice of oxidant

In order to validate the performance of oxidants in mercury oxidation, only Hg^0 and N_2 appeared in the gas stream during the experiment. In this study, several common oxidant solutions such