



A novel pre-oxidation method for elemental mercury removal utilizing a complex vaporized absorbent

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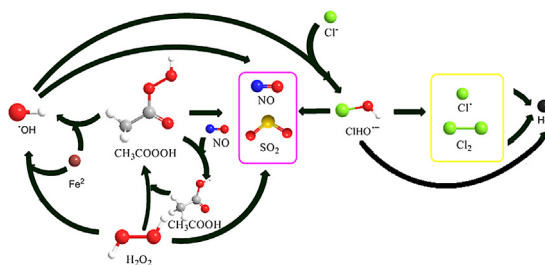
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HIGHLIGHTS

- An innovative liquid-phase complex absorbent (LCA) for Hg⁰ removal was prepared.
- A novel integrative process for Hg⁰ removal was proposed.
- The simultaneous removal efficiencies of SO₂, NO and Hg⁰ were 100%, 79.5% and 80.4%, respectively.
- The reaction mechanism of simultaneous removal of SO₂, NO and Hg⁰ was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel semi-dry integrative method for elemental mercury (Hg⁰) removal has been proposed in this paper, in which Hg⁰ was initially pre-oxidized by a vaporized liquid-phase complex absorbent (LCA) composed of a Fenton reagent, peracetic acid (CH₃COOOH) and sodium chloride (NaCl), after which Hg²⁺ was absorbed by the resultant Ca(OH)₂. The experimental results indicated that CH₃COOOH and NaCl were the best additives for Hg⁰ oxidation. Among the influencing factors, the pH of the LCA and the adding rate of the LCA significantly affected the Hg⁰ removal. The coexisting gases, SO₂ and NO, were characterized as either increasing or inhibiting in the removal process, depending on their concentrations. Under optimal reaction conditions, the efficiency for the single removal of Hg⁰ was 91%. Under identical conditions, the efficiencies of the simultaneous removal of SO₂, NO and Hg⁰ were 100%, 79.5% and 80.4%, respectively. Finally, the reaction mechanism for the simultaneous removal of SO₂, NO and Hg⁰ was proposed based on the characteristics of the removal products as determined by X-ray diffraction (XRD), atomic fluorescence spectrometry (AFS), the analysis of the electrode potentials, and through data from related research references.

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1. Introduction

Due to its high toxicity, volatility, and bioaccumulation [1], Hg⁰ emitted from coal-fired power plants has become a major concern in recent years. In 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule (CAMR) aimed at

reducing the Hg⁰ emissions from coal-fired power plants [2]. China, as the country having the greatest amount of mercury emissions in the world, has also taken many measures to control the Hg⁰ emissions from coal-fired power plants. Mercury found in coal-fired flue gases is often presented as three chemical forms: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particle bound mercury (Hg^p) [3]. The latter two can be partially removed by Wet Flue Gas Desulfurization (WFGD) systems, fabric filters (FF) or electrostatic precipitation (ESP) systems. While Hg⁰, due to its high volatility and low solubility in water, is difficult to be collected through the

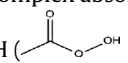
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use of existing Air Pollution Control Devices (APCDs), its removal has become an important focus of research in recent years.

In recent years, there are a lot of methods, including adsorption, homogeneous oxidation and heterogeneous oxidation, have been extensively researched to remove Hg^0 [4]. For adsorption method, fly ash [5], activated carbon, etc. [6,7], were used to effectively remove Hg^0 . The current state of the art technology for the capture of Hg^0 from flue gases utilizes activated carbon injection (ACI) [8]. However, ACI has the disadvantages of very high costs (about \$US 3,810 to \$US 166,000 per pound of Hg^0) [9] and secondary environmental problems. In addition, metallic sorbents, especially Au and Pd, are also potential alternatives for Hg adsorption as well as oxidation. Wilcox and Lim [10,11] have done a lot of works on Hg^0 removal by gold-based adsorbents, and obtained satisfactory results. And Sasmaz et al. [12] has determined the binding mechanism of Hg^0 on noble metals to well understand the surface reactivity of Hg^0 on noble metals. As for the oxidation method, the core of which is to rapidly convert the Hg^0 into soluble Hg^{2+} , the methods of Hg^0 oxidation include catalytic oxidation, liquid-phase oxidation, gas phase oxidation and light chemical oxidation. Among these methods, the catalyst used in the process of selective catalytic reduction (SCR) has the ability to oxidize Hg^0 [13], especially in the presence of halogens [14]. Fan et al., [15] carried out an experiment of $\text{CeO}_2/\text{HZSM-5}$ catalytic oxidation of Hg^0 , and found that the acidic site on the surface of the HZSM-5 exhibited a strong ability to adsorb Hg^0 , with CeO_2 as a key component. The SO_2 and NO increased the Hg^0 oxidation in the presence of O_2 , while the H_2O vapor inhibited the Hg^0 removal process. The highest removal efficiency of Hg^0 was obtained when the reaction temperature was below 300°C and the loading of CeO_2 was 6%. Hutson et al. [16] carried out an experiment on the simultaneous removal of SO_2 , NO_x and Hg^0 from coal-fired flue gas, using a NaClO_2 -enhanced wet scrubber, from which a novel method for the simultaneous removal of multi-pollutants was proposed. In addition, Fang et al., [17] adopted urea/ KMnO_4 as an absorbent to investigate the effects of various factors on the simultaneous removal of Hg^0 , SO_2 and NO. These factors included urea concentration, KMnO_4 concentration, inlet Hg^0 concentration, initial pH, reaction temperature, SO_2 concentration, and NO concentration. Their experimental results indicated that the removal of NO and Hg^0 depended primarily on the KMnO_4 concentrations. Halogen-containing compounds have been employed as gas phase oxidants to oxidize Hg^0 . Yan et al. [18,19] synthesized S_2Cl_2 , S_2Br_2 and S_2I_2 to carry out Hg^0 oxidation, and found that Hg^0 could be oxidized faster under the synergistic effect of fly ash. Jia et al. [20] found that Hg^0 oxidation could be enhanced by UV light in the presence of CH_4 , and the Hg^0 removal efficiency was 65.5% under a 253.7 nm light.

Nevertheless, these methods cannot be applied in industrial engineering applications, due to various defects such as low removal efficiency, the possibility of secondary environmental problems, and the excessive costs. To address these drawbacks, this work has studied a Fenton-Reagent based, liquid-phase complex absorbent (LCA) designed to remove Hg^0 . It has been recognized that H_2O_2 was a promising reagent for flue gas purification due to its superior environmental friendliness, and its lower price. However, prior attempts at Hg^0 removal with H_2O_2 have been unsatisfactory [21]. A similar phenomenon was also observed in the Hg^0 oxidation by hydroxyl radicals derived from H_2O_2 [22]. In order to improve the performance of the Fenton methodology for Hg^0 removal, in this paper's research, a vaporized liquid-phase complex absorbent

(LCA) composed of a Fenton reagent, CH_3COOOH () [23] and NaCl [18,19] was prepared to effectively oxidize the Hg^0 . In addition, in order to make it possible that the low pH LCA can work together with the WFGD or CFB-FGD systems, we designed a two-stage-treatment process of the preoxidation combined with

the absorption to remove Hg^0 , in which, the vaporized LCA initially oxidized Hg^0 in a preoxidation device, and then the Hg^{2+} was absorbed by the followed alkaline industrial $\text{Ca}(\text{OH})_2$ in CFB-FGD system or CaCO_3 slurry in the WFGD system. To the authors' knowledge, there have been no reports in the field of Hg^0 removal, on this type of application of the LCA, as well as the novel flue gas stage-treatment. For the development of this novel method, the optimal preparation conditions of the LCA and the best reaction conditions, were established based on investigations of the effects on the Hg^0 removal efficiency: the different halogen additives, the pH of the LCA solution, the adding rate of the LCA, the reaction temperatures, and the initial concentrations of Hg^0 , O_2 , NO and SO_2 . The experimental results indicated that the proposed methodology exhibited a satisfactory performance on the Hg^0 removal, and on the simultaneous removal of SO_2 , NO and Hg^0 , as far as this application was concerned. Therefore, these research results have achieved not only substantial academic significance, but also offer important value for real-world applications.

2. Experimentation

2.1. Experimental apparatus

The experiments were conducted on a fixed-bed system that was made up of simulated flue gas generation, LCA vaporization, integration of pre-oxidation and absorption, and tail gas detection, as shown in Fig. 1. Compressed gas cylinders (Fig. 1, 1–5) (North Special Gas Company, Baoding, China) generated simulated flue gas of N_2 , SO_2 , NO, O_2 and CO_2 , and the Hg^0 was generated by a mercury osmotic tube (20 ng/min, VICI Metronics Co., USA) (Fig. 1, 8) heated in a thermostatic water bath (Fig. 1, 10) (HH-ZK2, Yuhua Instrumental Company, Gongyi, China) with 1 l/min of N_2 as the carrier gas. Because the Hg^0 concentrations in actual flue gas emitted from typical coal-fired power plants in China are mainly distributed about $20\ \mu\text{g}/\text{m}^3$ [24], thus Hg^0 concentration used in our experiments was determined as $20\ \mu\text{g}/\text{m}^3$. A peristaltic pump, number BT100-1F from Longerpump in Baoding, China (Fig. 1, 17), was used to add the LCA into a custom-designed vaporization device (Fig. 1, 11) that was heated by a thermally controlled electric heater (Fig. 1, 12) (ZDHW, Zhongxingweiye Company, Beijing, China). In order to avoid Hg^0 adsorption or oxidation across surfaces, the reactor was a cylindrical quartz tube (Fig. 1, 14) with a length of 30 cm and an inner diameter of 3.2 cm, heated by a tube-type resistance furnace (Fig. 1, 15) (DC-RB, Duchuang Technology Company, Beijing, China), the pipe lines used in the reaction system were made by Teflon and heated by heater bands. The tail gas was detected by a flue gas analyzer (Fig. 1, 21) (ECOM-J2KN, RBR Company, Germany) and an Atomic Fluorescence Mercury Detector (Fig. 1, 22) (QM201, SuzhouQingan Company, Suzhou, China). Internal temperatures of the vaporization device (Fig. 1, 11) and the reactor (Fig. 1, 14) were measured over time, by three digital regulators and three thermocouples (Fig. 1, 13) (XMTD, Baoding, China).

2.2. Reagents and LCA vaporization

All reagents used were analytical reagents from the Kermel Company of Tianjin, China. The LCA was prepared with H_2O_2 of 30.0% (w/w), PAA of 16.0% (w/w), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ of 99–101% (w/w), HCl of 1.0 mol/l, NaCl of 99.5% (w/w), NaBr of 99.0% (w/w) and NaClO of 10% (w/w). The absorbent was $\text{Ca}(\text{OH})_2$, and the dryer was anhydrous CaCl_2 . The method used for mercury sampling was OHM method recommended by the US EPA, in which, the oxidized mercury that escaped from reactor was absorbed by 1 mol/l of KCl solution, the mercury in tail gas was treated by 10% (v/v) H_2SO_4 –4% (w/w) KMnO_4 before being discharged to atmosphere.

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