Full Length Article

Effects of operational conditions, anions, and combustion flue gas components in WFGD systems on Hg^0 removal efficiency using a H_2O_2/Fe^{3+} solution with and without $CaSO_3$

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GRAPHICAL ABSTRACT
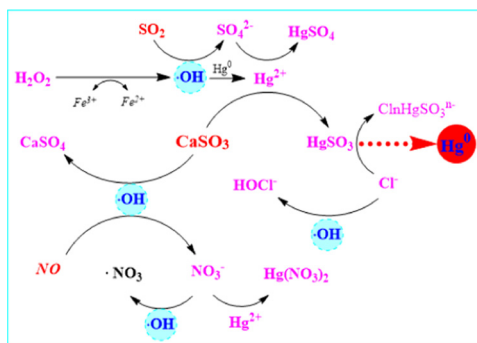
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ABSTRACT

Mercury removal in wet flue gas desulfurization (WFGD) systems has been widely known to be effective, but removal efficiency is highly susceptible to calcium sulfite ($CaSO_3$), the main byproduct of WFGD systems. Though the influence of $CaSO_3$ on Hg^0 removal from the perspective of Hg^0 re-emission has been studied, systematic studies directly devoted to removal are rare. In this study, the effects of $CaSO_3$ on Hg^0 removal efficiency were investigated using a H_2O_2/Fe^{3+} solution as an oxidizing agent. In addition, this experiment was designed to study the influence of operational conditions (temperature and pH), anions (Cl^- and NO_3^-), and combustion flue gas components (SO_2 and NO) in WFGD systems on Hg^0 removal efficiency using an H_2O_2/Fe^{3+} solution with and without $CaSO_3$. For this experiment, three groups were chosen: 1) the absence of $CaSO_3$, 2) a 0.015% $CaSO_3$ solution, and 3) a 0.075% $CaSO_3$ solution. After the investigation of Hg^0 removal efficiency with single flue gas component, the influence of co-existence gases (SO_2, NO, Hg^0) on the simultaneous removal was studied. Results indicated that $CaSO_3$ had adverse effects on Hg^0 removal. For simultaneous removal, the co-existence of SO_2 and NO was favorable for Hg^0 removal. Also, Cl^- had a desirable effect on NO removal. This study provides new insights into the simultaneous removal of SO_2, NO, and Hg^0 in WFGD systems.

1. Introduction

Mercury, increasingly known as an extremely toxic pollutant, is derived from the natural environment and human activities. Coal-fired power plants are a primary source of anthropogenic mercury discharge [1]. This has become a serious problem in China, where coal-fired power plants are common [2]. Symptoms of prolonged or acute exposure to mercury include: tremors, emotional changes, insomnia, neuromuscular changes, headaches, disturbance in sensations, changes in nerve responses and other negative symptoms [3]. In order to minimize the danger from mercury to inhabitable environment, mercury-specific environmental laws have been instituted in recent years in accordance with the Clean Air Act [4].

Mercury can be found in three forms in coal-fired flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle bound mercury (Hg^P) [5]. Oxidized mercury can be removed by wet flue gas desulfurization (WFGD) systems due to its water-solubility, and research has confirmed that the absorbing efficiency can be as high as 80–90% [6]. Particle bound mercury can be bound using an electrostatic precipitator [7]. Elemental mercury is insoluble in water and highly volatilizable, and hence, difficult to remove. Therefore, the key to Hg^0 removal from flue gas is its oxidization to Hg^{2+} that occurs when the flue gas is injected into the adsorbing solution. After that, Hg^{2+} is absorbed into wet flue gas desulfurization devices (WFGD) [8]. According to a review of the literature pertaining to elemental mercury abatement methods, there are two main methods to purify Hg^0 from flue gas: adsorption and oxidation [8,9]. Adsorbents used in the adsorption process include activated carbon [10], modified activated carbon [11], fly ash [12], modified fly ash [13], metal oxides [14], magnetic biochar [15], and calcium-based materials [16], However, the cost of purification using these materials is high [7]. In recent years, numerous oxidation technologies have been developed including catalytic oxidation [17,18], advanced oxidation [19], and traditional chemical oxidation technologies [20].

Among these methods, the Fenton reaction based methods have generally been considered to be not only highly efficient, but also cost-effective and environmentally friendly [7]. Furthermore, according to previous research, Fenton-like reactions were also used to remove Hg^0 from flue gas [21]. According to the reported results of Lu et al., the reduction of Fe^{3+} by hydrogen peroxide (H_2O_2) efficiently induces Hg^0 oxidation [22]. The reaction mechanism can be given by the following Eqs. ((1)–(4)) [9,23], where $\cdot OH$, which is highly conductive, is the key molecule necessary for the oxidation of Hg^0. In contrast, the direct reactions between Hg^0 and H_2O_2 are not the key reactions during the removal of Hg^0 from flue gas [21]. After Hg^0 is oxidized to Hg^{2+}, it can be quickly absorbed by the oxidation solution.

$$Hg^0 + H_2O_2 = HgO + H_2O \tag{1}$$

$$2Fe^{3+} + H_2O_2 = 2Fe^{2+} + O_2 + 2H^+ \tag{2}$$

$$Fe^{2+} + H_2O_2 = Fe^{3+} + \cdot OH + OH^- \tag{3}$$

$$Hg^0 + 2 \cdot OH = HgO + H_2O \tag{4}$$
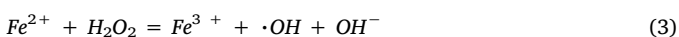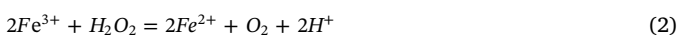
Wet Flue Gas Desulfurization (WFGD), is the most commonly used in coal-fired power plants worldwide for high sulfur dioxide (SO_2) control [24]. As this kind of process uses limestone or lime slurry [25], calcium sulfite ($CaSO_3$) is generated as an inevitable byproduct. Some research results have shown that $CaSO_3$ solids with high BET surface areas are favorable for Hg retention [6]. However, $CaSO_3$ can react with Hg^{2+} to form $HgSO_3$, which is unstable and results in the re-emission of Hg^0 [1,6]. However, when the amount of $CaSO_3$ is large enough, Hg $(SO_3)_2^{2-}$ will be formed, which is much more stable and Hg^0 can then be captured [1,6]. Liu et al. studied the simultaneous removal of Hg^0, NO and SO_2 from flue gas using Fenton-like reagents (H_2O_2/Fe^{3+}). These investigators also performed preliminarily studies of the effects of

several parameters, such as H_2O_2 concentration, Fe^{3+} concentration, reaction temperature, solution pH, NO concentration and SO_2 concentration [26]. However, in WFGD, the effect of $CaSO_3$ on Hg^0 removal and the role that NO, and SO_2 play while using Fenton-like reagents (H_2O_2/Fe^{3+}) has not been studied and clarified yet. Therefore, the role that $CaSO_3$ and other parameters play during the purification of Hg^0 requires further exploration.

This was the first study to investigate and discuss Hg^0 removal efficiency in WFGD systems using a H_2O_2/Fe^{3+} solution with and without $CaSO_3$. The influence of operational conditions (temperature and pH), anions (Cl^- and NO_3^-), and combustion flue gas components (SO_2 and NO) on Hg^0 removal efficiency in WFGD systems was also studied in the case of no $CaSO_3$, a 0.015% $CaSO_3$ solution, and a 0.075% $CaSO_3$ solution.

2. Experimental apparatus and methods

2.1. Chemical reagents

Reagents used in this research were all analytical reagents. Reagents including H_2O_2 (30%, AR), $CaSO_3$ (98%, AR), hydrogen chloride (HCl) (36.0%-38.0%, AR), sodium hydroxide (NaOH) (99.5%, AR), sodium chloride (NaCl) (99.5%, AR), sodium nitrate ($NaNO_3$) (99.5%, AR), potassium chloride (KCl) (> 99.5%, AR), potassium permanganate ($KMnO_4$) (> 99.5%, AR) and sulfuric acid (H_2SO_4) (95–98%, AR) were all purchased from Beijing Chemical Co.. Ferric chloride ($FeCl_3 \cdot 6H_2O$) (99.0%, AR) was purchased from Jinke Fine Chemical Research Institute of Tianjin.

2.2. Experimental apparatus

As shown in Fig. 1, the experimental facility can be divided into six parts: simulated flue gas generation system, mercury generator, gas distribution system, reaction system, gas analyzer and tail gas treatment. N_2, SO_2 and NO were provided from cylinders (1–3) (PQ-07QPP, China). An elemental mercury permeation tube (5) ($40 \mu g/m^3$, VICI Metronics Co., USA) was heated in a thermostatic water bath (4) (HH-ZK2, Yuhua Instrumental Company, Gongyi, China) to generate Hg^0 vapor with 0.4 L/min of N_2 as the carrier gas. N_2, SO_2 and NO were mixed with Hg^0 in a Gas distribution system (6) (PQ-07QPP, China). The reaction occurred in a 0.6 L three necked flasks (8) (VICI Metronics Co., USA) surrounded by water at 60 °C in a thermostatic water bath (4) (HH-ZK2, Yuhua Instrumental Company, Gongyi). The outlet gas were dried through silica gel (9) (HH-ZK2, Yuhua Instrumental Company, Gongyi, China) before entering the mercury analyzer (10) (VM-3000, Germany) and the flue gas analyzer (12) (MRU-NOVA plus RCU, Germany), for the purpose of protecting the equipment and obtaining more accuracy for $Hg^0/SO_2/NO$ detection.

2.3. Experimental procedure

N_2, SO_2 and NO were metered through mass flow controllers (15–18) and mixed with Hg^0 in a gas distribution system (6) at a total flow rate of 0.7 L/min. The simulated flue gas was with concentration ranges of 99.85%-100% for N_2, 200–1200 ppm for SO_2 (if there was), and 50–300 ppm for NO (if there was). Before initiating the experiment, 50 mL slurry solution containing $CaSO_3$ was freshly prepared and fed into the reactor with a continued stirring. The reaction started when the absorption solution of H_2O_2/Fe^{3+} was injected into the flask (8). The gas was bubbled through the aqueous solution with a gas distributor, a porous glass frit attached at the end of the gas supply line in flask (8). The generated gas bubble was about 2 mm and the average residence time of gas bubbles in the absorption solution was 2 s. NaCl and $NaNO_3$ were used to provide Cl^- and NO_3^- to study the corresponding influence, respectively. The pH value of the solution was adjusted by HCl and NaOH, and it was obtained by a pH meter (7). The computer (11)