Energy 67 (2014) 652–658

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Simultaneous removal of SO_2, NO and Hg^0 from flue gas by ferrate (VI) solution

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ARTICLE INFO

Article history:
Received 1 October 2013
Received in revised form
4 December 2013
Accepted 22 January 2014
Available online 18 February 2014

Keywords:
Ferrate (VI) solution
Simultaneous removal of SO_2, NO and Hg^0
Oxidation reaction

ABSTRACT

Simultaneously removing SO_2, NO and Hg^0 from flue gas was examined by ferrate (VI) solution at a bubbling reactor. The removal efficiencies of 100% for SO_2, 64.8% for NO and 81.4% for Hg^0 were achieved respectively, under the optimum experimental conditions, in which concentration of ferrate (VI) solution was 0.25 mmol/L, solution pH was 8.0, flue gas flow rate was 1 L/min and reaction temperature was 320 K. Based on the discussions of the ferrate (VI) solution characteristics, the comparisons of the standard electrode potential (E_0) of ferrate (VI) solution with E_0 values of reactant, and the analysis of the reaction products, a mechanism of simultaneous removal was proposed. In the process of simultaneous removal, FeO_4^{2-} and $HFeO_4^-$ as the dominant species of ferrate (VI), could rapidly oxidize SO_2, NO, and Hg^0 into SO_4^{2-}, NO_3^- and Hg^{2+}.

1. Introduction

Coal burning, the primary source of China's atmosphere pollution, generates many air pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x) and mercury (Hg) [1–3]. SO_2 and NO will lead to worsening local air quality as well as regional acid rain pollution and photochemical smog [4]. Mercury is considered as one of the most toxic trace element, its main consequences are realized in aqueous environment. Once mercury enters water bodies, either directly or through air deposition, inorganic mercury can be methylated biotically under anaerobic conditions, to its most toxic form, dimethyl mercury. The latter biomagnifies readily in the food chain, severely endangering ecosystems and public health [5]. Currently, the most successful and commercialized processes for removing SO_2, NO_x and Hg are limestone–gypsum flue gas desulfurization (FGD), selective catalytic reduction (SCR), and activated carbon adsorption [6,7]. However, the combined system of these three processes has the disadvantages of large occupying area, high running cost and low stability of flue gas system [8,9]. Therefore, simultaneous multi-pollution control technologies have been extensively researched in recent years, and many reagents, i.e. $NaClO_2$, $KMnO_4$/NaOH, Fe(II)EDTA, urea, O_3, UV/H_2O_2, etc., have been introduced into aqueous solutions as absorbents to achieve simultaneous removal of SO_2, NO and Hg^0 [10–18]. Hutson et al. [15] carried out an experiment of simultaneous removal of SO_2, NO_x and Hg from coal flue gas using a $NaClO_2$-enhanced wet scrubber, from which, a new method of the simultaneous removal of the multi-pollutant was proposed. Fang et al. [16] used urea/$KMnO_4$ as the absorbent to investigate the effects of various factors such as urea concentration, $KMnO_4$ concentration, inlet Hg^0 concentration, initial pH, reaction temperature, SO_2 concentration and NO concentration on the efficiencies of simultaneous removal of Hg^0, SO_2 and NO, and the experimental results indicated that the removal efficiencies of NO and Hg^0 mainly depended on the concentration of $KMnO_4$. Jia et al. [17] found that Hg^0 oxidation could be promoted by UV light and CH_4, and Hg^0 removal efficiency of 65.5% was obtained under the 253.7 nm light. However, these classical oxidants either have lower economical efficiencies or may release several hazardous byproducts that can adversely affect the environment. Hence, researchers have focused on using efficient, practical and pollution-free absorbent for simultaneous removal of SO_2, NO, and Hg from flue gas.

As an environmentally benign chemical, ferrate (VI) has a strong oxidizing property [19–22], and it is often used in waste-water treatment as a disinfectant and biocide for removal of inorganic contaminants, organic compounds, odor, nutrients, radionuclides, humic acids, and so on [23–31]. In addition, many heavy metals such as As^{3+}, Mn^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Cr^{3+}, and Hg^{2+} can be effectively removed using ferrate (VI) through oxidation and coagulation [32,33]. Ferrate (VI) has given a convincing result in water and wastewater treatment even as an oxidant for nitrogen and sulfur-containing pollutants [19,29]. However, by far, there is

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http://dx.doi.org/10.1016/j.energy.2014.01.081

still no report on the application of Ferrate (VI) as oxidant for the removal of SO_2, NO and Hg^0.

Hence, this study is aimed at understanding the oxidation reactions with Ferrate (VI) in order to explore a new approach to simultaneous removal of SO_2, NO and Hg^0 from flue gas in liquid phase. The developed technology can be used to coal fired flue gas cleaning of power station boiler and industrial boiler.

2. Materials and methods

2.1. Materials

All chemicals used were analytical grade and purchased from Tianjing Chemical Reagents Co., China. High purity deionized water (specific resistance $\geq$ 18.25 MΩ/cm) was prepared using the Barnstead water purification system. Potassium ferrate (K_2FeO_4) was prepared in our laboratory according to Thompson's method and its concentration was determined by a UV-3000 spectrophotometer at 510 nm [34,35]. The ferrate (VI) solution was prepared by adding a suitable amount of K_2FeO_4 and a trace of sodium hypochlorite into deionized water, in which sodium hypochlorite acted as stabilizing agent for ferrate (VI) [36]. The initial solution pH value was adjusted by dilute sodium hydroxide or hydrochloric acid.

2.2. Experimental apparatus and procedure

Fig. 1 shows the schematic diagram of experimental equipments including a flue gas simulation system, a bubbling reactor with 250 mL of the effective volume and 15.5 cm of height in a thermostat water bath, a flue gas analysis system and a tail gas absorption system. The gas mixture containing SO_2, NO, N_2 and Hg^0 was used to simulate actual flue gas, in which SO_2, NO, and N_2 were each supplied from a compressed gas steel cylinder, while Hg^0 was generated from mercury osmotic tube (VICI Metronics Co., USA) in a thermostatic water bath, and carried over by N_2 with 1 L/min. During the experiments, the gas mixture was mixed in a buffer bottle and then introduced into the bubble reactor containing ferrate (VI) solution. The spent gases were absorbed by a tail gas absorption bottle containing 10% (v/v) H_2SO_4–4% (w/w) $KMnO_4$ solutions after absorption.

In our previous work [37], the mass transfer-reaction kinetics on oxidation of Hg^0 by $NaClO_2$ solution was studied experimentally in a bubbling reactor, and the results showed that with an increase of $NaClO_2$ concentration and the decrease of pH value, the enhancement factor (E) and ratio of KG (Hg^0)/kG (Hg^0) increased, and the liquid phase mass transfer resistance decreased, which was benefit to the mass transfer adsorption reaction. An increase of reaction temperature had a promotion for factor (E) and an inhibition for the ratio of KG (Hg^0)/kG (Hg^0). The latter was one of the most important factors for decreasing the removal efficacy of Hg^0. The research results have an important reference value for the present work.

2.3. Analysis methods

The analysis of Hg^0 was carried out based on the US EPA method 101A, and the used Hg^0 analyzer was QM201 cold atom fluorescence mercury detector (QM201H, Suzhou, Qingan Instrument Co., China). The concentrations of SO_2 and NO were measured by a flue gas analyzer (MRU, VARIO, Germany). The removal efficiencies were calculated according to the concentrations of Hg^0, SO_2 and NO before and after absorption. The reaction products of desulfurization and denitrification after oxidation reactions were characterized by an ion chromatography (792 Basic, Metrohm AG), in which SO_4^{2-}, SO_3^{2-}, NO_3^-, NO_2^- were completely separated on a Metrosep A Supp 4 Anion chromatographic column with a mixture of sodium carbonate solution (1.8 mmol/L) and sodium bicarbonate solution (1.7 mmol/L) at a flow rate of 1 mL/min, and detected by an electrical conductivity detector. The detection limit was lower than 10 μg/L. The analytical instrument used for determining the concentration of Hg^{2+} in the spent solutions was the same as that used for determining the inlet and outlet concentrations of Hg^0. The detection limit was lower than 0.1 ng/m^3 at 253.7 nm.

3. Results and discussion

3.1. Effects of ferrate (VI) concentration on multi-pollutant removal

To obtain the optimum concentration of ferrate (VI) solution, the effect of the concentration of ferrate (VI) solution on the simultaneous removal of SO_2, NO and Hg^0 was investigated, as shown in

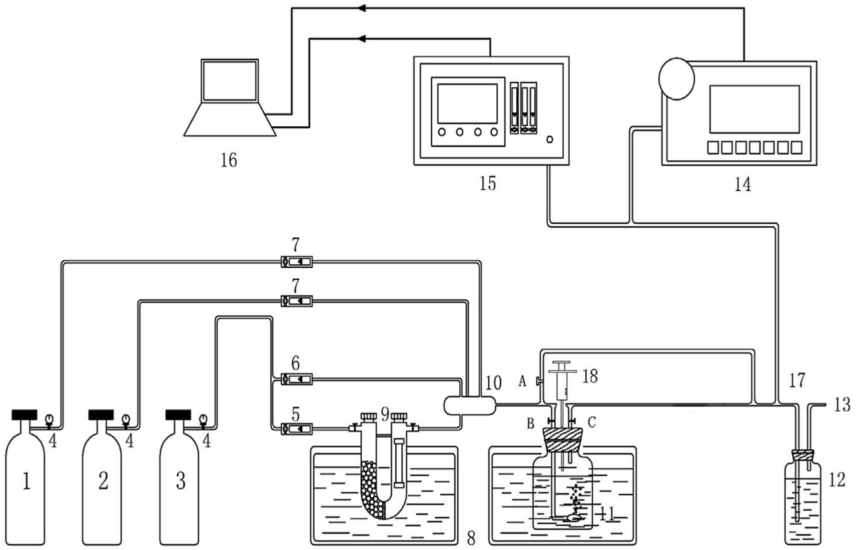

Fig. 1. Schematic diagram of the experimental apparatus: (1) steel bottle of SO_2, (2) steel bottle of NO, (3) steel bottle of N_2, (4) relief valve, (5) 60 mL flowmeter, (6) 1 L flowmeter, (7) 100 mL flowmeter, (8) thermostat water bath, (9) Hg^0 generator, (10) buffer bottle, (11) bubble reactor, (12) tail gas absorption bottle, (13) tail gas outlet, (14) flue gas analyzer, (15) QM201H coal-fired flue gas Hg^0 analyzer, (16) computer, (17) sampling port, (18) 1 mL injector; A, B, C: two-way valve gate.