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Integrated electrochemical-aerating oxidation in recovery system of seawater flue gas desulfurization

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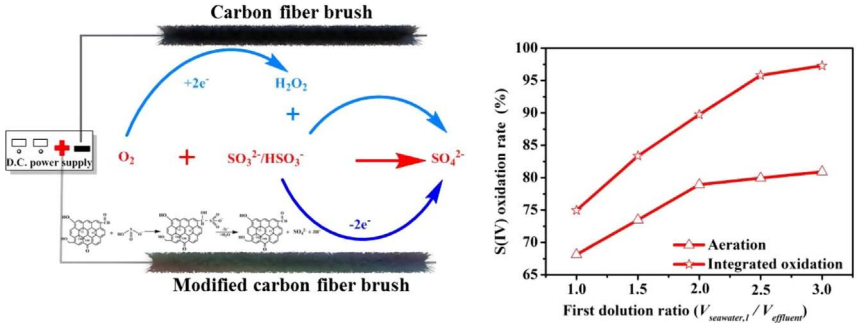
HIGHLIGHTS

- Introduction of electrochemical method into aerating process.
- Promising modified and unmodified polyacrylonitrile-based carbon fiber brush electrodes.
- Chemical-electrochemical mechanism by O-containing groups on anode surface.
- Chemical oxidation by H_2O_2 generated from cathodic oxygen reduction reaction.
- Advantages of increased energy efficiency and low seawater usage.

GRAPHICAL ABSTRACT



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ABSTRACT

In recovery system of seawater flue gas desulfurization (SWFGD) process, a novel integrated electrochemical-aerating oxidation method is developed. The influences of process factors such as anode-cathode brush assembly, applied current and dilution ratio on S(IV) oxidation performance are investigated, in connection with S(IV) oxidation rate, the anodic potential range of S(IV) oxidation, energy consumption and total amount of seawater. Compared with the conventional aerating process, the integrated oxidation is confirmed as an energy-efficient and seawater-saving improvement for existing SWFGD recovery system. Based on these experiment results, the reaction mechanism is also proposed. The electrochemical reactions on modified polyacrylonitrile-based carbon fiber (MPAN-CF) brush anode and polyacrylonitrile-based carbon fiber (PAN-CF) brush cathode, together with aerating process, synergistically accelerate the S(IV) oxidation. Therefore, integrated electrochemical-aerating oxidation method using MPAN-CF&PAN-CF anode–cathode brushes is promising for industrial application and is expected for the treatment of high sulfur flue gas in future.

1. Introduction

Since the first commercial seawater flue gas desulfurization (SWFGD) system was erected in 1968, nowadays it has been developed into a mature technology used in power plants with an installed gross capacity of up to 20 GW worldwide statistically [1]. By taking advantage of inherent alkalinity of seawater (pH 8.1–8.3), it can achieve > 90% sulfur removal efficiency and transform S(IV) into S(VI), a natural component of seawater for direct discharge. SWFGD process includes a scrubbing of SO_2 from the flue gas into seawater in

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absorption tower and the following seawater quality regulation of acidic effluent in recovery system, where the dilution and aeration are the main procedures [2]. However there are some drawbacks still remaining, for example, the huge demand of seawater and air needs a large aeration basin and high power consumption [3–5]; the slow oxidation reaction of S(IV) to S(VI) theoretically requires a long residence time which inevitably decreases the SWFGD efficiency [6]; before discharging, some seawater parameters may change back, even out of discharge criteria, due to a progressive air-oxidation of too much residual S(IV). Therefore until now, SWFGD is mainly used for the treatment of low sulfur flue gas, and how to increase the S(IV) oxidation rate becomes an essential solution to these problems.

The relationship between absorbed S(IV) by seawater and pH in the packed tower with polytetrafluoroethylene (PTFE) filler was studied, and the saturated concentration of SO_2 could reach 4.8–5.4 mmol/L and about 25% of S(IV) was oxidized to S(VI) by oxygen in seawater [7]. Moreover, some researchers tried to use catalysts, such as metal cation [8,9], metal oxide [10], activated carbon [3], organic acid [11], natural clinoptilolite [12], to preliminarily raise the S(IV) oxidation rate of acidic effluent in absorption tower; however, the extra catalyst separation and regeneration processes are needed, otherwise the inactive catalysts may become pollutants in seawater [3]. In addition, some improvements on absorption technics, such as the membrane contactor coupled with seawater absorption, could obtain higher mass transfer coefficient than conventional packed tower [13].

Vidal and Ollero [14] studied the oxidation kinetics of S(IV) by air in seawater, and they explained the necessity of dilution before aeration due to the highest efficiency at pH 6. Alternatively, other process less affected by pH is proposed to directly oxidize acidic effluent, such as plasma-induced oxidation [5,15,16]; nevertheless it requires high energy consumption from a voltage of 10–40 kV, and has difficulty in engineering scale-up. In addition, by taking advantage of good electrical conductivity of seawater and efficient electrocatalysis of electrode, some electrochemical methods are also used. Our research group electrolyzed acidic seawater to produce chlorine for SO_3^{2-} oxidization using IrO_2-SnO_2 electrode [17], whereas there are shortages of high electrode cost and small electrode area, leading to a limited effect on S(IV) oxidation. And then, we consider to introduce the electrochemical method into traditional seawater recovery system using a cheap polyacrylonitrile-based carbon fiber (PAN-CF) brush electrode to oxidize the S(IV). Here an integrated electrochemical-aerating oxidation process using PAN-CF brush electrodes is set up, and the influence of several process factors on S(IV) oxidation performance are discussed. Based on experimental results, the reaction mechanism is proposed, to provide the design basis for industrial application in SWFGD recovery system.

2. Experimental

2.1. Experimental setup

Experimental apparatus is shown in Fig. 1. To minimize the transport of seawater to experiment, the seawater is recycled to simulate the overflow drain in plant. Acidic or first-diluted effluent is enclosed in a storage tank to avoid the interference of auto-oxidation from air, and it is pumped to a polymethyl methacrylate (PMMA) cylindrical oxidation tank. The lateral surface of oxidation tank is punched for recycling of effluent and the insertion of reference electrode, the top for air outlet and the insertion of anode and cathode, and the bottom for air inlet. In all aeration experiments, air flow rate is kept at 2.0 L/min, gas-to-liquid (G/L) ratio is kept at 2.67 Nm^3/m^3, the aeration time is controlled in 2 min. In electrochemical experiments, a ZF-9 D.C. power supply (Shanghai Zhengfang Electric Appliance Co., Ltd.) provides the constant current, and the anodic potential with respect to a saturated calomel electrode (SCE), as well as the cell voltage are monitored by a multifunction multimeter (UNI-T Technology Co., Ltd., UT58A). All potentials reported here are referred to SCE. DO is tested by a dissolved oxygen meter (Shanghai Leici, JPSJ-605) and pH is measured with a pH meter (Shanghai Leici, PHS-25). This set-up can be used to simulate the aeration process, electrochemical oxidation and integrated electrochemical-aerating oxidation, respectively.

2.2. Electrode preparation

Together with titanium wire (TA2) of 1.2 mm diameter used as a current collector, 12 K PAN-CF wire beam (SYT45, Zhongfu Shenying Carbon Fiber Co., Ltd.) with 7 μm fiber diameter is made into a brush electrode with 18 cm length and 3 cm diameter. And then the PAN-CF brush electrode is modified in 2 mol/L H_2SO_4 by recurrent galvanic pulse method, cycling 6 times from an anodic current of 3 A for 300 s to a cathodic current of −3 A for 300 s, and a modified polyacrylonitrile-based carbon fiber (MPAN-CF) brush electrode is obtained [18].

2.3. Effluent preparation and dilution

Acidic effluent is prepared by dissolving Na_2SO_3 (Sinopharm Chemical Reagent Co., Ltd.) in seawater (Jiaozhou Bay of Qingdao, pH 8.2, DO of 6.5–7.5 mg/L, COD of 1.2 mg/L), and the concentration of S(IV) is 0.2 g/L. The pH of acidic effluent is adjusted to 3.0 by HCl (37 wt %, Sinopharm Chemical Reagent Co., Ltd.).

The acidic effluent is diluted with fresh seawater to obtain the first-diluted effluent, and the first dilution ratio DR_1 (a volume ratio defined

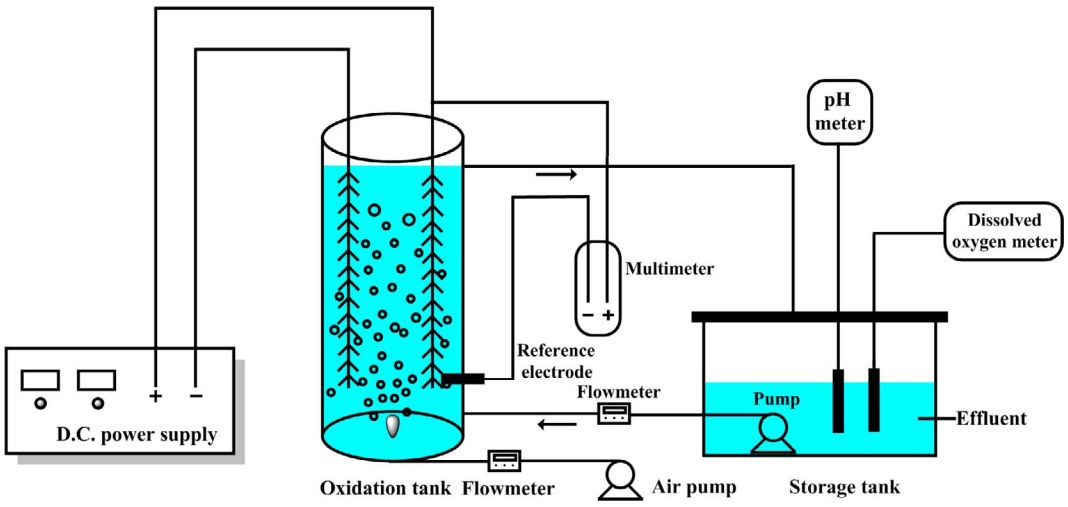

Fig. 1. Device of seawater desulfurization recovery system by aeration and electrochemical oxidation.