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Removal of NO_x and SO_2 from simulated ship emissions using wet scrubbing based on seawater electrolysis technology

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ABSTRACT

This paper proposed a promising method for removal of NO_x and SO_2 from simulated ship emissions by wet scrubbing using electrolyzed seawater. Several factors were investigated on removal efficiencies of NO and NO_x in a semi-continuous bubble column reactor. Results showed that NO_x removal was enhanced with the increase of active chlorine concentration, NO inlet concentration, reaction temperature, and concentrations of coexisting gases (CO_2 and O_2), but was inhibited with increasing gas flow rate. The pH of the electrolyzed seawater had a significant impact on the NO_x removal. Then, simultaneous removal of NO_x and SO_2 in both single stage and double stage reactors were studied preliminarily. Maximum removal efficiencies of NO_x and SO_2 from simulated ship emissions (NO_x 1000 ppm, O_2 15%, CO_2 5%, SO_2 751 ppm) were 92% and 100% respectively under optimum conditions. Final products (NO_2^- and NO_3^-) of the process effluent were analyzed by the ion chromatography, and reaction pathways were also discussed.

1. Introduction

With the development of world seaborne trade, the past few decades have witnessed a rapid increase in the number and size of the global fleet. The world fleet of all ships over 300 gross tons as of 1st January 2016 grew to 51,405 ships of 1146 million gross tons [1]. Although international shipping is considered as the most energy-efficient way for long-distance transportation, air pollution generated from international shipping has caused a severe impact on human health and marine ecosystem, especially in East Asia [2,3]. Huan Liu et al. [4] reported that 60% of total emissions in the studied East Asian Region happened within 20 nautical miles of shore, and 80% of emissions in the Yangtze River Delta region occurred within 60 nautical miles of coastal communities. Among all the environmental impacts of ship emissions, sulfur oxide (SO_x), nitrogen oxide (NO_x), and particulate matter (PM) have gained the most attention. Currently, stringent regulations for SO_x and NO_x emission control from ship exhaust gas have been implemented by International Maritime Organization (IMO) and environmental protection authorities around the world at international and regional levels [5,6].

To date, many denitrification technologies have been proposed and applied to meet strict regulations for ship emissions [7]. Some of these technologies have already been installed on board, including liquified natural gas (LNG), exhaust gas recirculation (EGR), and selective catalytic reduction (SCR). In fact, most of these commercially available technologies evolve from onshore flue gas purification techniques, which are used for on-road and stationary NO_x sources. Despite that they have demonstrated the good environmental performance of themselves, they also suffer from several kinds of limits in practical applications on board. For example, there are some critical issues for using LNG as an alternative marine fuel, including the infrastructure development for LNG bunkering, as well as safety operation and CH_4 leakage [8]. EGR, as one of the most effective on-engine NO_x reduction techniques, leads to an increase in specific fuel consumption and PM emissions during operation [9]. NH_3 SCR is the best-known post-treatment technology for NO_x emissions. However, high concentrations of SO_x and PM from large marine diesel engines burning low-quality fuels will deactivate the commercial catalysts in a short time [10].

Compared with dry NO_x reduction methods (e.g. SCR and EGR), NO_x removal by wet scrubbing methods has not been adopted on ships because of the low solubility of NO (accounting for more than 90% of NO_x). However, many wet scrubbing systems for SO_x removal using seawater have been successfully used on ships. As seawater can be readily accessed around ships, this situation inspires us to develop suitable oxidative additives into seawater, so that simultaneous removal of SO_x and NO_x can be achieved in one reactor. For marine diesel engines, Ilan Boscarato et al. [11] proposed an integrated system, which consisted of a monolithic Pt/Al_2O_3 oxidation catalyst and a seawater

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scrubber. They achieved a single compact device for simultaneous abatement of multi-gas pollutants. However, due to the limited sulfur resistance of the catalyst, this system could only be used with fuel sulfur content of up to 0.4%. In addition, Janusz Licki et al. [12] developed a hybrid process of electron beam irradiation plus seawater scrubbing to clean flue gas from marine diesel engines. The active species formed in the plasma reaction converted NO into NO_2, which favored seawater absorption. From the viewpoint of industrial application, this kind of integrated process for multi-gas pollutants removal will be especially suitable for ocean-going ships. It shows a great potential to reduce the equipment footprint and complexity of the system.

In the past few years, various chemical oxidants have been introduced in wet scrubbing technology for NO_x removal [13]. These oxidants achieved satisfying removal efficiencies in lab-scale and pilot-scale experiments, including $Na_2S_2O_8$, H_2O_2, $NaClO_2$, $KMnO_4$, NaOCl, O_3, and Fenton-like reagents. Nevertheless, most of these experiments used freshwater as the solvent, in which the influence of complex ions in natural seawater was neglected. High concentrations of Cl^- and HCO_3^- in seawater would likely to weaken the oxidizing ability of reagents (e.g.·H_2O_2 and $Na_2S_2O_8$) via their scavenging effects [14,15]. In addition, some other critical issues also restrict these chemical oxidants to be used on ships, such as safety of transportation and storage of hazardous chemical agents, disposal of process effluent, and availability of sufficient supply. Therefore, active chlorine (mainly includes Cl_2, HOCl, and OCl^-), which can be onsite generated by seawater electrolysis in an undivided cell, promises to be an appropriate oxidant with relatively strong oxidizing ability. So far, although there are several reports about wet scrubbing using NaOCl freshwater solution, only a few studies have been conducted on NO_x removal by electrolyzed seawater. For example, Sukheon An and Osami Nishida [16,17] performed early experiments of marine air pollution control by seawater electrolysis in a two-stage wet scrubber system. They used acidic seawater (mainly includes Cl_2) and alkaline seawater (mainly includes NaOH) to clean flue gas. The electrolyzed seawater (mainly includes Cl_2 and NaOH) was produced in a divided cell. In such case, the high concentration of total dissolved solids in seawater would result in a short lifetime of ionic membranes. Tae-Woo Kim [18] only investigated the NO oxidation characteristic by electrolyzed seawater in a bubbling reactor. Their results showed that NO conversion rate increased with increasing available chlorine concentration (ACC) and temperature. Furthermore, Ecospec, a Singapore company, invented a unique flue gas cleaning system using ultra low-frequency wave electrolysis technology [19]. This company finished a pilot test on a cruise ship in 2009. Nevertheless, there was no more information about the principle of this method, as well as further installations on more ships.

Therefore, one of the main objectives of this experimental work was to develop and investigate NO_x removal characteristics by electrolyzed seawater. Effects of ACC, pH value, NO inlet concentration, reaction temperature, gas flow rate, and concentrations of coexisting gases (CO_2 and O_2) on removal efficiencies of NO and NO_x have been studied separately. In addition, the simultaneous removal of NO_x and SO_2 from simulated ship emissions by electrolyzed seawater was further studied.

2. Experimental section

2.1. Experimental apparatus

The schematic diagram of our experimental system (Fig. 1) consisted of a simulated flue gas blending unit, a bubble column reactor unit, and a flue gas analysis system. The bubble column reactor unit included a constant temperature water bath (17), two gas distributors (18), two bubble column reactors (19) with two plastic rubber plugs (20), and a thermometer (26). Each bubble column reactor (19) (high 600 mm, inner diameter 50 mm) was custom made of perspex tube. The gas distributor (18) (ISO 4793 P4, pore size 10–15 μm, disc diameter 38 mm) was installed at the bottom of the bubble column (19), which was used to distribute the simulated flue gas. Both NO.I and NO.II bubble column reactors were placed in the constant temperature water bath (17) (Julabo F34–ED Refrigerated/Heating Circulator, Germany). The liquid was poured into the bubble column (19) by opening the rubber plug (20). The water bath temperature during experiments was measured by the thermometer (26). The flue gas analysis system included an electronic condenser (27), an infrared multi-gas analyzer (28) (MRU MGA5, Germany), and a tail gas absorber (29). To mitigate the acid corrosion to the gas analyzer (28), the electronic condenser (27) was used to cool the flue gas and remove moisture. The gas analyzer (28) was used to continuously measure the concentrations of multi-gas pollutants, including NO, NO_2, NO_x, SO_2, CO_2, and O_2. The tail gas absorber (29) filled with 5% HNO_3 and 10% H_2O_2 was used to absorb the possibly remained gas pollutants.

2.2. Experimental procedures

The flue gas emitted from ships was simulated by blending five different gas species: NO (10% NO with N_2 as the balance gas), SO_2 (10% SO_2 with N_2 as the balance gas), CO_2 (99.99%), O_2 (99.99%), and N_2 (99.99%). Mass flow controllers (11–15) (MFC, Beijing Sevenstar Electronics Co., Ltd) were used to control the flow rate of each gas species from separate air bottles. All pipes, valves, regulators, and fittings were made up of either stainless steel 316 grade or Teflon.

The electrolyzed seawater used in our experiments was generated in an undivided cell as described previously [20]. The undivided cell was built with two plate electrodes (10 × 10 × 0.2 cm), which were placed vertically with an inter-electrode gap of 2 cm. The anode material and cathode material were IrO_2-RuO_2/Ti and Ti, respectively. The electrolysis was performed using a DC power supply (GuDeng Electric GD-80 V-25 A, China) with a constant current control mode. Artificial seawater (salinity of 30.0 psu, pH 8.2) was prepared according to the ASTM D1141 standard [21]. All chemicals were analytical reagent grade. The deionized water (15 MΩ·cm) was prepared in a two-stage ELGA PURELAB Option R15 purification system. To reduce the deterioration of electrogenerated chlorine (less than 2% in 12 h), the electrolyzed seawater was stored in a water bath (20 °C) shielded from light. For each run, bubbling liquid (750 mL per reactor) was prepared by freshly mixing the electrogenerated chlorine (initial ACC of about 3000 mg/L [Cl_2]) with artificial seawater. The ACC of the bubbling liquid was determined by N,N-diethyl-p-phenylenediamine (DPD) colorimetric method (ASTM 4500 G), using a spectrophotometer (Shimadzu UV1800, Japan) at a wavelength of 515 nm. The initial pH value of the bubbling liquid was adjusted to the desired value by adding HCl solution (1 mol/L) or NaOH solution (1 mol/L). The pH values of the bubbling liquid were measured by a pH meter (Mettler-Toledo S210, Switzerland). The temperature of bubbling liquid was adjusted to the designed value by the constant temperature water bath (17).

Both single stage and double stage experiments were performed using the experimental system shown in Fig. 1. The NO_x removal characteristics by electrolyzed seawater were systematically investigated using a single stage bubbling reactor. Then the simultaneous removal performance of NO_x and SO_2 by electrolyzed seawater was further studied using both single stage and double stage reactors.

For single stage experiments, the absorbent was poured into NO.I bubble column, while deionized water was added into NO.II bubble column. Two bubble column reactors were connected in parallel. Before experiments, the simulated flue gas was introduced into the NO. II bubble column by opening valve 22 with valves 21, 23–25 closed. Inlet concentrations of gas pollutants were measured by the gas analyzer (28). When the inlet concentrations of gaseous pollutants and solution temperature reached desired values and remained stable, the simulated flue gas was introduced into NO.I bubble column reactor by opening valves 21 and 24 with valves 22, 23 and 25 closed. Target gas pollutants reacted with the absorbent under atmospheric pressure. Outlet concentrations of gas pollutants were online monitored using the gas