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An improved method of removal for high concentrations of NO by electro-scrubbing process

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ABSTRACT

In the Ag(II)/Ag(I) redox mediator integrated scrubber system, NO reacts with the Ag(II) ions produced by the electrochemical oxidation of Ag(I) in an electrochemical cell present in the scrubbing solution (aqueous HNO_3 acid) to form NO_2. This NO_2 is then absorbed into the scrubbing solution and degraded to nitrate. Numerous experimental runs were carried out to evaluate the feasibility of the integrated system to treat industrial waste gases containing high NO_x levels. The results showed that the levels of NO and NO_x removal increased with increasing Ag(II) loading and contact time. Under optimized conditions, 93.5% and 73.3% of the NO and NO_x, respectively, were removed by a single stage gas scrubber with $1.62\,g\,L^{-1}$ Ag(II) operating at 25 °C and atmospheric pressure.

Keywords: NO; NO_x; Wet scrubber; Mediated electrochemical oxidation; Ag(I)/Ag(II) redox system

1. Introduction

Denitration processes involve the removal of NO_x from flue gases, and are classified according to whether NO_x is absorbed into solution or is reduced catalytically to N_2 by a reducing gas. Commercially applied technologies are based typically on selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), adsorption and wet scrubbing. Of the many technologies currently in use, wet scrubbing is considered the most economical with the added advantages of controlling other acid gases and particulates (Lee et al., 2005; Yang et al., 1996).

NO_x removal by wet scrubbing is complicated due to the many parallel and consecutive reactions that can occur in the solution phase. The two major constituents of NO_x are nitric oxide (NO) and nitrogen dioxide (NO_2). NO accounts for more than 90% of the NO_x in flue gas and its inert nature is problematic. NO is only slightly soluble in water and does not react well in aqueous solutions. Additives are generally added to wet scrubbers to convert the relatively water insoluble NO to water soluble NO_2, which is highly soluble in water. Extensive investigations have been undertaken on the chemistry and performance of additives, such as ozone (Shaw, 1976), hydrogen peroxide (Myers and Overcamp, 2002), potassium permanganate (Brogren et al., 1997), chlorine dioxide (Jin et al., 2006) and sodium chlorite (Brogren et al., 1998; Chu et al., 2001; Lee et al., 2005), in the wet scrubbing processes.

Electrochemical processes are considered potential alternatives to chemical methods because they avoid the continuous use of large quantities of chemical oxidants, and do not generate secondary waste in spent scrubbing solutions (Chen, 2004; Panizza and Cerisola, 2007). Although some studies on the direct reduction of NO_x have been carried out (Kleifges et al., 1997), mediated electrochemical oxidation (MEO) based on redox systems, such as Ce(IV)/Ce(III) (Aurousseau et al., 1994; Hoffmann et al., 1997) and Mn(III)/Mn(II) (Bringmann et al., 1997), has shown to be more suitable for NO_x removal. The oxidation of NO to NO_2 can occur via the oxygen in air as a carrier and a mediator ion with a high oxidation state generated in situ at the anode surfaces, $M^{(n+1)}$, according to Eqs. (1) and (2):

$$2NO + O_2 \rightarrow 2NO_2 \tag{1}$$

$$2NO + 5M^{(n+1)} + 3H_2O \rightarrow HNO_3 + NO_2 + 5M^{(n+)} + 5H^+ \tag{2}$$

The oxidation of NO_2 by the mediator ions generated can be described by the following reaction:

$$NO_2 + M^{(n+1)} + H_2O \rightarrow HNO_3 + M^{(n+)} + H^+ \tag{3}$$

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NO_2 oxidized in reactions (1) and (2) can also be absorbed by water or nitric acid. Indeed, MEO-based processes using redox systems, such as Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Ce(II), and Mn(III)/Mn(II), have been used to completely mineralize several organic pollutants to CO_2 and H_2O (Balaji et al., 2007a,b,c; Bringmann et al., 1995; Chandrasekara et al., 2009; Farmer et al., 1992; Galla et al., 2000; Kaba et al., 1990; Matheswaran et al., 2007a,b,c, 2008). Recently, the MEO technique has been used to oxidize and absorb NO and NO_2 (Aurousseau et al., 1994; Bringmann et al., 1997; Hoffmann et al., 1997). The MEO system, however, has low oxidation efficiency due to the low standard redox potential of the redox couples used, e.g. Ce(IV)/Ce(III), Co(III)/Ce(II) and Mn(III)/Mn(II). On the other hand, the Ag(II)/Ag(I) ($E^0 = 1.98$ V (NHE)) redox system is expected to be more effective in NO_x removal because it has the highest standard redox potential of all known MEO systems. Raju et al. (2008) recently studied the removal of NO and NO_2 from artificial flue gas using a Ag(II)/Ag(I) redox couple in a nitric acid solution, and reported that NO_x could be removed completely at ambient temperature and atmospheric pressure, even when both species were present at below 400 ppm. Although the Ag(II)/Ag(I) redox system in aqueous acid is capable of oxidizing organic pollutants and NO (Chandrasekara et al., 2009; Matheswaran et al., 2007c; Raju et al., 2008), the removal of high NO_x concentrations ($\geq$1000 ppm) from flue gas has not been reported. From an industrial perspective, conventional purification systems, such as SCR, SNCR and commercial wet scrubbing systems, cannot operate efficiently if the optimal operating conditions (concentration, temperature and NO_x gas flow) are not uniform, which can result in secondary waste problems (Chironna and Altshuler, 1999; Chui and Gao, 2010; Moon et al., 2007).

This research demonstrates the ability of an MEO process based on the Ag(II)/Ag(I) redox system in an aqueous acid solution to treat gases containing high levels of NO concentration. The principal independent variables in these parametric experiments were in the initial NO concentration, Ag(II) loading and temperature in the scrubbing solutions.

2. Experimental setup and method

The Ag(II)/Ag(I) redox system in nitric acid was used to remove high concentrations of NO using a wet scrubbing technique. The experimental unit was composed of an electrochemical Ag(II) ion production stage and a gas treatment stage. Fig. 1 presents a schematic diagram of the experimental setup.

The electrochemical cell used was a plate and frame type with a narrow gap flow cell configuration. The cell consisted of a mesh type Pt/Ti anode and a mesh type Ti cathode (Wesco Co. Ltd., Korea), each with a working area of 1.12 dm^2 and separated by a Nafion 324 membrane (DuPont, USA). The electrochemical cell was operated galvanostatically by applying a constant current of 10 A. 10.79 $g\,L^{-1}$ of $AgNO_3$ (Daesung Metal Co. Ltd., Korea) was mixed with 6 $mol\,L^{-1}$ of HNO_3 (Sam Chun Chemicals, Korea) in a 7 L glass anolyte storage tank. 3 $mol\,L^{-1}$ H_2SO_4 (DC Chemicals Co. Ltd., Korea) was placed in a separate catholyte glass tank equipped with a heating jacket to maintain the temperature to within ±2 °C of the stated temperature. Both electrolyte solutions were circulated continuously through the respective partitions of the electrochemical cell at 0.12 $m^3\,h^{-1}$ using magnetic pumps (Pan World Co., Ltd., Taiwan). The concentration of electrogenerated Ag(II) in the anolyte was determined by titration against a standard Fe(II) solution using a potentiometric method, as described previously (Raju et al., 2008).

The scrubber-related units included a scrubber column made of glass, which was placed on the anolyte storage tank, as shown in Fig. 1. A magnetic pump was connected between the anolyte storage tank and the top of the scrubber column. The scrubber column was 1.2 m long with an inner diameter of 0.05 m, and 0.8 m of the column was packed with Raschig glass rings (0.01 m) to give an approximate internal working column volume of 2.4 L.

The flue gas simulation system was composed of a pure NO cylinder (99.5%), an air compressor (model: AC-B15PA2, Kyungwon Airboy Co. Ltd., Korea), two mass flow controllers (model: 1179A13CS1BK-S, MKS Co. Ltd., USA), and a custom-made gas mixer. Flow rates of air and pure NO were controlled by two mass flow controllers. NO had to be diluted by compressed air in a plug flow mixer to the desired concentrations. Undesired NO_2 formed by oxidation of NO by O_2 in the air as Eq. (1), was always 10–15% of the initial concentration of NO gas feed, fed to the scrubber with desired concentration and flow rate of NO/air gas mixtures.

Before starting the gas removal experiments, the electrochemical cell was run until the required level of Ag(II) formation had been achieved. Subsequently, the anolyte solution was pumped to the scrubber at a flow rate of 0.24 $m^3\,h^{-1}$. A simulated gas composed of 400–1200 ppm NO at a flow rate of 0.60–1.80 $m^3\,h^{-1}$ was fed with the anolyte (6 $mol\,L^{-1}$ nitric acid containing 0.16–1.62 $g\,L^{-1}$ of Ag(II)) to the top of the scrubber in a co-current flow pattern. The outlet solution from the scrubber column, which contained Ag(I), was re-circulated through the electrochemical cell to regenerate Ag(II). The pressure drop across the scrubber, which was calculated using the equation derived by Mitchell and Perona (1979), was 38 mmAq at the highest gas flow rate (1.80 $m^3\,h^{-1}$) that did not disrupt the NO elimination process.

The NO and NO_2 concentrations in the gas–air mixture before and after the reaction were monitored continuously online using a NO_x-Teledyne gas analyzer (model No. 9110, USA). The removal efficiencies (expressed as η) of NO and NO_x were calculated from the inlet and outlet gas concentrations, and the NO_x concentration is defined as the sum of the NO and NO_2 concentrations measured in the system at given time.

3. Results and discussion

3.1. *The effects of temperature on NO removal*

Temperature is one of the most important process parameters in the MEO procedure because it has a direct effect on the formation of Ag(II) at the electrode surface, which can in turn affect the NO removal efficiency. Therefore, the formation of Ag(II) in an electrochemical cell was investigated at various temperatures (15–45 °C). Fig. 2 shows the results at a fixed Ag(I) concentration, liquid flow rate, HNO_3 concentration and applying current of 10.79 $g\,L^{-1}$, 0.12 $m^3\,h^{-1}$, 6 $mol\,L^{-1}$ and 10 A, respectively. The level of Ag(II) formation decreased significantly with increasing temperature. The concentration of Ag(II) at 15 °C (1.73 $g\,L^{-1}$) decreased to 1.07 $g\,L^{-1}$ at 45 °C due to the lower stability of the $[Ag(II)NO_3]^+$ complex at higher temperatures.

The effect of temperature on the removal efficiency of NO was examined by performing a series of experiments from 15 to 45 °C at a fixed NO feed concentration of 800 ppm, and