Environmental Technology & Innovation 11 (2018) 41–48

Contents lists available at ScienceDirect

Environmental Technology & Innovation

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

Wet oxidation and absorption procedure for NO_x removal

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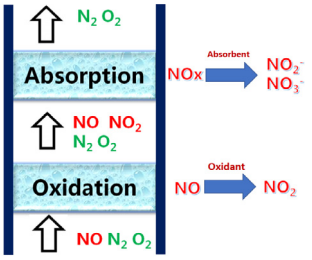
HIGHLIGHTS

- A methodology is presented to remove NO_x with low oxidation degree, low temperature and high vapor content at room temperature.
- The method is considered potential low-cost proposal and have advantage of simple equipment and low operating temperature.

GRAPHICAL ABSTRACT



An interesting and universal method to remove NOx with low oxidation degree, low temperature and high vapor content by liquid oxidation and liquid absorption at room temperature.

ARTICLE INFO

Article history:
Received 14 January 2018
Received in revised form 22 March 2018
Accepted 23 March 2018
Available online 13 April 2018

Keywords:
NO_x removal
Coal-fired boiler
Wet oxidants
Wet absorbents

ABSTRACT

The removal of NO_x with low oxidation degree, low temperature, and high vapor content from small coal-fired boiler emission through selective catalytic reduction is difficult. This study investigated liquid oxidation and absorption to remove NO_x systematically. Thermodynamic calculation showed that the equilibrium constants of the NO oxidation and NO_x absorption reaction are high; thus, NO_x treatment by liquid oxidation and absorption is feasible. Four oxidants ($NaClO_2$, NaClO, H_2O_2, and $KMnO_4$) and four absorbents ($Ca(OH)_2$, $CaCO_3$, NaOH, and Na_2CO_3) were used to study the reaction mechanism of the oxidation and absorption processes. Results show that $NaClO_2$ solution is the best oxidant, and the optimum pH value of the oxidation reaction is 5–6. The oxidation degree reaches 100% when the concentration of the $NaClO_2$ solution is 1.0%, and the oxidation degree can still reach approximately 50% when the concentration is 0.1%. $Ca(OH)_2$ slurry has the best absorption performance among the four kinds of absorbents. The NO_x removal efficiency of $Ca(OH)_2$ slurry can reach approximately 70% when the oxidation degree is 50%. The removal efficiency is up to 80% when the oxidation degree is 100%.

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https://doi.org/10.1016/j.eti.2018.03.006
2352-1864/

0. Introduction

NO_x ($NO + NO_2$) and SO_2, as the major gas-phase pollutants emitted from coal-fired boiler, raise significant environmental problems, such as acid rain and smog (Adewuyi et al., 1999). NO_x causes ozone damage and photochemical smog. Thus, numerous denitrification (de-NO_x) and desulfurization (de-SO_2) technologies have been investigated to abate NO_x and SO_2 emissions. Currently, flue gas desulfurization (FGD) technology is the most effective and widely used method for SO_2 control; however, the de-NO_x technology remains to be studied (Wang and Zhong, 2016).

For NO_x control, selective catalytic reduction (SCR) (Liu and Ihl Woo, 2006), selective non-catalytic reduction (Bae et al., 2006), wet absorption (Joshi et al., 1985), adsorption (Mok et al., 2003), and electron beam irradiation (Person and Ham, 1988) processes have been developed; among these processes, SCR is considered the best available technology (Radojevic, 1998). SCR has been widely used for its high de-NO_x efficiency, but problems, such as corrosion of NH_3, catalyst toxicity, secondary pollution, and high operation temperature (approximately 300 °C), are inevitable (Muzio et al., 2002). Thus, SCR is unsuitable in certain cases, such as low-temperature outlet gas from small coal-fired boiler. Wet absorption is a potential low-cost alternative to its simple equipment and particularly low operating temperature, reaching even below the dew point, which is suitable for low-temperature de-NO_x after the FGD process. However, NO comprises more than 90% of NO_x in the flue gas from coal-fired boiler, and the low solubility of NO in aqueous solution appreciably increases the liquid-phase resistance to mass transfer (Walker et al., 1937). Moreover, oxidants are used to first convert the relatively water-insoluble NO to reactive NO_2, which can be further removed by absorbents to increase the overall removal efficiency of NO_x.

In absorption-based methods, knowledge on the process variables and their influence on oxidation and absorption capacities is required to maximize NO_x removal efficiency by pre-decided oxidants and absorbents. This study aims to establish test data for the design and operation of the de-NO_x absorption system.

1. Thermodynamic calculation for NO oxidation and absorption

NO oxidants can be divided into liquid- and gas-based oxidants by reaction place. Gas-based oxidants include ozone (Lin et al., 2016) and chlorine dioxide (Hoigné and Bader, 1994). The drawbacks of gas-based oxidants (O_3 and ClO_2) include leaking and high prices; however, liquid oxidants can avoid these problems. Commonly used liquid oxidants include sodium hypochlorite (Chen et al., 2005), sodium chlorite (Chien et al., 2003; Deshwal et al., 2008; Guo et al., 2013), hydrogen peroxide (Thomas and Vanderschuren, 1996; Liémans and Thomas, 2013; Bhanarkar et al., 2014), and potassium permanganate (Brogren et al., 1997; Chu et al., 1998, 2001).

NO in the flue gas is oxidized to NO_2 by the following reactions (Deshwal et al., 2008).

$$NO + ClO^- = NO_2 + Cl^- \tag{1}$$

$$2NO + ClO_2^- = 2NO_2 + Cl^- \tag{2}$$

$$NO + H_2O_2 = NO_2 + H_2O \tag{3}$$

$$NO + MnO_4^- = NO_3^- + MnO_2. \tag{4}$$

The thermodynamic calculation of Eqs. (1)–(4) is as follows. **Table S1** (Supporting information) displays the thermodynamic data of related substances (Dean, 1979).

$$\Delta_r H_m\,(T) = \Delta_r H_m^\theta\,(298.15\ \mathrm{K}) + \int_{298.15\ \mathrm{K}}^{T} \Delta_r C_{p,m} dT \tag{5}$$

$$\Delta_r G_m\,(T) = \Delta_r H_m\,(T) - T\Delta_r S_m\,(T) = \Delta_r H_m^\theta\,(298.15\ \mathrm{K}) - T\Delta_r S_m^\theta\,(298.15\ \mathrm{K}) + \int_{298.15\ \mathrm{K}}^{T} \Delta_r C_{p,m} dT - T\int_{298.15\ \mathrm{K}}^{T} \frac{\Delta_r C_{p,m}}{T} dT. \tag{6}$$

The last two items can be ignored in approximate calculation, that is,

$$\Delta_r G_m\,(T) = \Delta_r H_m^\theta\,(298.15\ \mathrm{K}) - T\Delta_r S_m^\theta\,(298.15\ \mathrm{K}) \tag{7}$$

$$\ln K\,(T) = -\frac{\Delta_r G_m\,(T)}{RT} \tag{8}$$

where $\Delta_r H_m^\theta$ (kJ mol^{-1}) is the standard enthalpy change, $\Delta_r G_m^\theta$ (kJ mol^{-1}) is the standard Gibbs free energy change, $\Delta_r S_m^\theta$ (kJ mol^{-1} K^{-1}) is the standard entropy change, $\Delta_r C_{p,m}$ (J K^{-1} mol^{-1}) is the molar heat capacity at constant pressure, R is the gas constant, and K is the equilibrium constant.

The enthalpy change, Gibbs free energy change, and equilibrium constant at 298.15 K of reactions (1)–(4) were calculated according to Eqs. (5), (7), and (8), respectively. Table 1a summarizes the results.

In Table 1a, the standard enthalpy change of reactions (1)–(4) is negative, indicating that the four reactions are exothermic reactions, and increasing reaction temperature is unfavorable to product formation. The equilibrium constant of the four reactions is large, thereby indicating that these reactions show a trend.