Chemical Engineering Journal 341 (2018) 157–163

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

The role and mechanism of triethanolamine in simultaneous absorption of NO_x and SO_2 by magnesia slurry combined with ozone gas-phase oxidation

Qiong Wu[a,b], Chenglang Sun[a,b], Haiqiang Wang[a,b,*], Ting Wang[a,b], Yuejun Wang[b], Zhongbiao Wu[a,b]

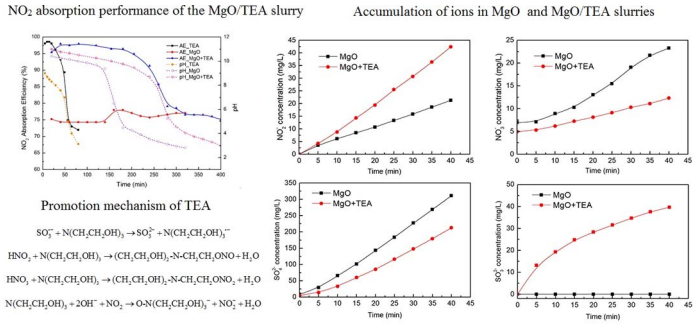
[a] Key Laboratory of Environment Remediation and Ecological Health, Ministry of Education, College of Environmental & Resources Science, Zhejiang University, Hangzhou 310058, PR China

[b] Zhejiang Provincial Engineering Research Center of Industrial Boiler & Furnace Flue Gas Pollution Control, No. 866 Yuhangtang Road, Hangzhou 310058, PR China

HIGHLIGHTS

- A novel process of simultaneous removal of SO_2 and NO_x by MgO slurry with a triethanolamine (TEA) additive was investigated.
- The addition of TEA to alkaline MgO slurry increased the NO_2 absorption efficiency significantly.
- The absorption promotion was attributed to the termination of excessive oxidation of sulfite by TEA, as a radical scavenger.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Triethanolamine
Nitrogen oxides
Sulfur oxides
Magnesia slurry

ABSTRACT

A novel absorption method was developed and used for the simultaneous removal of SO_2 and NO_x, whereby triethanolamine (TEA)-modified magnesia was utilized as an absorption slurry and combined with gas-phase oxidation by ozone. TEA was first used as the additive to magnesia slurry to facilitating the aqueous absorption of NO_x and SO_2. The injection of O_3 increased the solubility of NO_x considerably. Furthermore, the addition of TEA facilitated the absorption of NO_x in wet combined desulfurization and denitrification processes. In addition, experiments on operating factors included initial pH, TEA concentration, and the effect of SO_2 were performed in this study. The results show that after the addition of TEA to a magnesium-based slurry, the absorption efficiency of NO_2 improved to almost 100% under alkaline conditions. However, the improvement effect of TEA was less evident in acidic conditions. Based on studies of operating factors and product analysis, the reaction mechanism of TEA-assisted magnesia slurry absorption was proposed. Under alkaline conditions, TEA served as the radical scavenger, terminated the excessive oxidation of sulfite, and then strongly promoted the reaction between NO_2^- and SO_3^{2-}. Furthermore, TEA could react with NO_2 and SO_2 directly, and its alkalinity was beneficial for the absorption of NO_2 and SO_2. In acidic conditions, TEA reacted with H^+ and formed $^+$H-N(CH_2CH_2OH)$_3$, and the antioxidant capability of TEA would be lost.

* Corresponding author at: B215, Nongshenghuan Building, Zijinggang Campus, Zhejiang University, No. 866, Yuhangtang Road, Hangzhou 310058, PR China.
E-mail address: haiqiangwang@zju.edu.cn (H. Wang).

https://doi.org/10.1016/j.cej.2018.01.150
Received 7 November 2017; Received in revised form 28 January 2018; Accepted 30 January 2018
Available online 01 February 2018
1385-8947/

1. Introduction

During fossil fuel combustion, sulfur dioxide (SO_2) and nitrogen oxides (NO_x) are the main air pollutants inevitably emitted into the surrounding atmosphere. The emission of SO_2 and NO_x causes direct negative influences on the ecosystem and human health [1,2]. To date, various technologies have been applied to control the emission of SO_2 and NO_x in China, including low-NO_x burners combined with wet flue gas desulfurization (WFGD) technology, selective non-catalytic reduction (SNCR) in conjunction with WFGD technology, and selective catalytic reduction (SCR) combined with WFGD technology. However, the disadvantages of these technologies, such as large area requirements, high operational costs, system complexity, and potential poisoning of catalysts have motivated people to develop more compact and economical combined absorption technology for the removal of SO_2 and NO_x [3].

At present, magnesium-based WFGD technology has attracted considerable interest in China because of its low investment costs, less land occupied, compact flow sheet, reliable operation capability and reusable absorbent [4]. Magnesium-based WFGD has demonstrated high SO_2 removal efficiency, but it is inefficient for NO_x removal because of the low solubility of NO, which generally comprises about 95% of NO_x in flue gas. Our previous studies have shown that using O_3 as a gaseous oxidant to oxidize NO into higher-order nitrogen species (NO_2, NO_3 and N_2O_5) can facilitate greater removal of NO_x by MgO slurry [5,6]. Nevertheless, the optimal NO_2 removal efficiency in this process is only 75%, which is insufficient to meet stringent emission requirements in China. Therefore, there is an incentive to improve this magnesium-based WFGD technology by enhancing the absorption efficiency of NO_2.

One feasible approach to improve denitrification performance is utilizing an organic amine additive [7–10], such as monoethanolamine, ethylenediamine, which have been used as absorbents for desulfuration [11–14] and simultaneous desulfuration and denitration [15]. Triethanolamine (TEA), a typical organic amine compound, is also used for the absorption of atmospheric NO_2 [16]. Levaggi et al. [17] investigated the separation of NO from NO_x using TEA as a NO_2 absorbent, and deduced the reaction mechanism of NO_2 absorption by TEA. Aoyama et al. [18] observed the absorption characteristics of NO_2 using TEA and found that the main aqueous product of the reaction was N-nitrosodiethylamine (NDEA), whereas no NO_3^- or NO_2^- was formed during the reaction. However, Glasius et al. [19,20] pointed out that the absorption of NO_2 by TEA would form equimolar NO_2^-, and that ionic OH^- was also involved in this reaction. Furthermore, Wei et al. [21] found the NO_2 absorption in TEA solution would form NO_3^- and NO_2^- in equal concentrations. However, these studies were all focused on the absorption behaviors of low-concentration NO_2 in an atmospheric environment. The absorption capability of high-concentration NO_2 in flue gases by TEA, or by TEA-assisted absorbents such as magnesium oxides, has not been thoroughly investigated.

Based on previous research, we have investigated a novel process of simultaneous removal of SO_2 and NO_x by a MgO slurry with a TEA additive. For this process, O_3 was injected into simulated gas to increase the initial solubility of NO_x. This study was focused on NO_2 absorption behavior with the addition of TEA, and on the composition of products of the simultaneous removal of SO_2 and NO_x with addition of TEA. The effects of operational parameters on the removal efficiency of both NO_x and SO_2 were investigated, and the reaction mechanism and products during the absorption process were evaluated.

2. Experimental

2.1. Gases and chemicals

Standard gases including N_2 (99.99%), O_2 (99%), SO_2 span gas (99.99%), and NO span gas (99%) were supplied by Jingong Mixed Gas Co., Hangzhou, China. MgO, $(NH_4)_2SO_4$, and TEA were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All of these chemicals were analytical reagent grade. Reverse osmosis water was used for the preparation of aqueous solutions.

2.2. Experimental system

The experimental system included a flue gas simulation system, an absorption reactor, and a flue gas analysis system, as reported in our previous research [22]. The simulated flue gas was prepared with cylinder gases, the flow rates of which were controlled by mass flow controllers (MFCs). Ozone was produced using an ozone generator (VMUS-DG, AZCO Co., Canada). The molar ratio of O_3:NO was maintained at 1:1, which was sufficient to oxidize all NO to NO_2.

All experiments for NO_2 and SO_2 absorption were carried out in a packed column with a packing layer height of 450 mm and an internal diameter of 100 mm. Stainless steel rings of 3.5 mm × 10 mm were randomly placed inside the polymethyl methacrylate column. The simulated fuel gas flowed continuously through the system, while the absorption slurry was fed by a slurry pump.

The variations of NO_2 and SO_2 concentrations at the inlet and outlet were quantitatively analyzed with an infrared gas analyzer (Photon II, Madur Co., Austria). The output of O_3 was monitored with an ozone analyzer (In 2000, USA Co., USA). NO_2^-, NO_3^-, SO_3^{2-} and SO_4^{2-} concentrations in the slurry were determined using an ion-chromatographic analyzer (Metrohm 883, Metrohm Co., Switzerland).

2.3. Removal efficiency

The absorption efficiency was calculated based on the following formula:

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%, \quad (1)$$

where η is the SO_2/NO_2 absorption efficiency, and C_{in} and C_{out} are the inlet and outlet SO_2/NO_2 concentrations.

3. Results and discussion

3.1. Effect of TEA additive on NO_2 absorption efficiency

The NO_2 removal efficiency in MgO slurry, TEA aqueous solution and MgO/TEA slurry is shown in Fig. 1. The MgO slurry was a stable absorbent for the removal of NO_2, and the removal efficiency was maintained at about 75%, whereas the pH value of MgO varied from

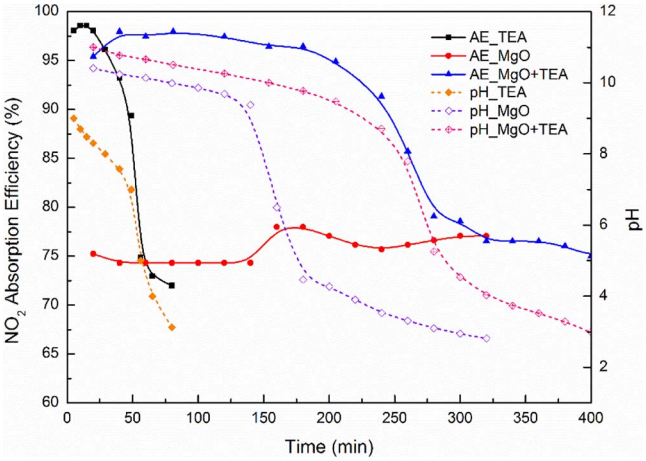


Fig. 1. Effect of the TEA additive on NO_2 absorption efficiency and pH value (O_3 concentration, 200 ppm; NO concentration, 200 ppm; SO_2 concentration, 500 ppm; N_2 gas flow, 7.6 L/min; O_2 gas flow, 0.4 L/min; MgO concentration, 0.025 mol/L; TEA concentration, 0.01 mol/L; 90 °C).