

Resource-Based Method for Realizing Zero Emission of Sulfur Dioxide from Flue Gas

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Abstract: A resource-based method for completely removal of SO₂ from flue gas by utilizing recycling manganese hydroxide (Mn(OH)₂) as an absorbant was proposed, which utilized catalytic oxidation of the manganese in the air on the oxidation of sulfur dioxide to soluble sulfate while removing impurities by filtration to produce high value-added products. Effects of reaction temperature and O₂ concentration on sulfite content and effects of PH value and Mn (OH)₂ content on SO₂ removal efficiency were investigated with a bubbling device to obtain the optimal experimental conditions. The method presented 100% removal efficiency with regenerated absorbent, indicating a relatively thorough desulfurization, sulfur dioxide to achieve zero emissions by recycled Mn (OH)₂ in this system. The sulfite content was very low, under 0.027%, compared with manganese sulfate 10%, which show the main component is sulfate ion, reaching to 99.7%, further for the preparation of high quality gypsum products.

Introduction

As one of the major source of haze, sulfur dioxide (SO₂), received much attention from the government and the public, being emitted into the atmosphere harmfully affected the public health by irritating lungs and lowering resistance to respiratory infection (such as influenza)[1,2]. Up to date, many methods have been adopted for the removal of sulfur dioxide, including alkali solvents such as ammonium hydroxide[3,4], calcium hydroxide and magnesium hydroxide in aqueous slurries[5,6], and oxides and mixtures of oxides such as calcium oxide, magnesium oxide, iron oxide, and manganese oxides in dry solid state or in aqueous slurries[7-13], seawater^[14], and Limestone-gypsum[15,16], as well as organic compounds such as amines[17], etc. Among them, we know that wet scrubbing process has gained much more concern due to the SO₂ is easily soluble in water and could be removed completely after scrubbing by absorbent, and manganese oxides (MnO_x) have received special emphasis as a quite effective absorbent for sulfur dioxide recovery recently[11-13]. It was known that the SO₂ in the emitted gases reacts with the manganese oxide to form manganese sulfate, and then treated to regenerate back to the manganese oxide, which is quite effective as an absorbent, but it is uneconomical to regenerate since manganese sulfate is too stable to entirely decompose at temperature about 900°C [18], resulting in relatively high costs. Meanwhile, as the dominant technology in China, and domestic large power plant widely used, the

lime/limestone process has been attracting the attention of the world due to its high efficiency and stability [19]. However, conventional methods of flue gas desulfurization (FGD) have various disadvantages, such as high capital cost, large occupation of land surface area, large consumption of fresh water, and formation of secondary pollutants [20]. In addition, with the difficulty of obtaining a grade of limestone high in calcium carbonate content, the sulfur dioxide from flue gases is absorbed by limestone under aqueous conditions to produce the low quality desulfurization gypsum requiring a large land surface area for disposal.

In this paper, the use of coupled chemical reaction to cycle desulfurization while reducing impurities to produce high quality gypsum products was proposed. According to the early studies, our research team adopted a method of removing sulfur dioxide from stack gases by using $Mn(OH)_2$ which is efficient in the removal of sulfur dioxide and readily handled and recycled to achieve resource utilization of desulfurization products. In this test, reaction temperature and O_2 content on the absorption process were considered, as well as pH values and $Mn(OH)_2$ concentrations on the influence of removal efficiency were tested to find the optimum experiment conditions, and the removal efficiency and sulfite content on different content of sulfur dioxide were studied under optimal conditions.

Experimental

Experimental Materials

All of the chemicals, such as calcium hydroxide ($\geq 95.0\%$, AR), sodium hydroxide ($\geq 99.0\%$, AR), manganese sulfate (99.0%, AR), calcium nitrate (99.0%, AR), sulfuric acid (98%, AR), nitric acid (68%, AR), iodine (99.8%, AR), Sodium thiosulfate (99.0%, AR) and deionized water, were used as received without further purification. The simulated flue gas was made up of N_2 (99.999%), O_2 (99.999%) and SO_2 (99%) (Qingdao, China).

Experimental Apparatus and Procedure

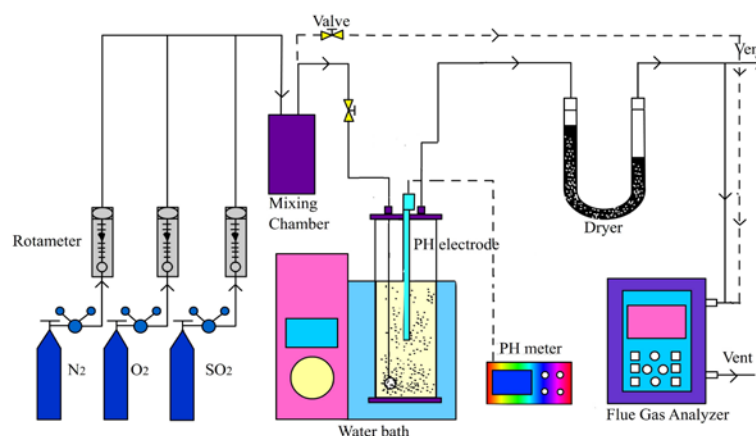
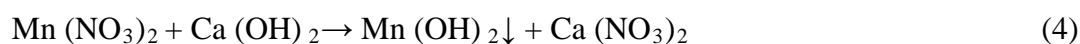
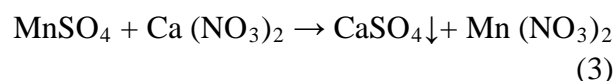
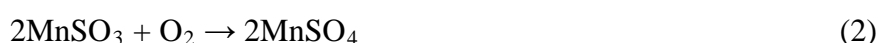


Fig. 1 Schematic diagram of the experimental apparatus for desulfurization

The experimental system of flue gas desulfurization includes a simulated flue gas system, a photochemical reactor and an analytical system. The experimental apparatus for desulfurization is shown in Fig. 1 that N_2 and SO_2 were supplied from the cylinders and mixed with oxygen completely in a mixing chamber before being fed to the reactor. The reactor was a bubbling device

with a volume of 500 mL (60 mm in diameter and 160 mm in height). The gas flow rates were measured by gas rotameters which was 2L/min. The reactor was immersed in a water bath for stable temperature. The pH value of the solution was adjusted with sodium hydroxide and was detected with a MP511 pH meter. SO₂ and O₂ concentrations at the inlet and outlet were measured continuously using British Kane KM950 flue gas analyzer. After the reactor, a desiccator was used to remove the water vapor in simulated flue gas to protect the flue gas analyzer. The manganese sulfate after desulfurization thereby produced can be used for regeneration of Mn (OH)₂. The particle size was measured by Zetasizer Nano ZS90 nano-particle size analyzer.

The cycle absorption process only needs to add one material which is calcium hydroxide. The main reactions occurring in the experimental procedure may be stated as follows:



Data Process

The removal efficiency of SO₂ with Mn (OH)₂ was defined by the following formula:

$$E_f (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (5)$$

Where E_f (%) is the removal efficiency of SO₂, C_{in} (mg/m³), and C_{out} (mg/m³) represent concentration of SO₂ at inlet and outlet, respectively.

The method of iodimetry is used to analyze the content of sulfite. The calcium content in the regenerated manganese hydroxide was determined by EDTA titration.

Results and Discussions

Sample Analysis

The sample of Mn (OH)₂ was regenerated under optimized conditions, and the contents of Mn (OH)₂ and CaO were analyzed. The main components of the absorbant are Mn (OH)₂ which show greater than 94%, compared with CaO less than 0.6%. The particle size distribution is relatively concentrated, with an average particle size of about 350nm, easy to separate. The regenerated Mn (OH)₂ is easy to agglomerate and form larger particles, which leads to its good filtration performance. Easy to agglomerate to have larger specific surface area, the surface adsorption force is large, in order to ensure the regeneration of manganese hydroxide in flue gas desulfurization process can achieve the desired effect.

Effects of Reaction Temperature and O₂ Concentration on the Absorption Process

The sulfite content in the absorption liquid was investigated when the accumulation of manganese sulfate reached 10% with the content of Mn (OH)₂ was 1.0wt% at different reaction temperature and O₂ concentration which were shown in Fig. 2.

It can be seen from Fig. 2 that the sulfite content decreases from 0.096 to 0.0197 while the SO₂ removal efficiency was 100% when the temperature increases from 25 °C to 65 °C under other

conditions being equal, indicating the reaction temperature favors the conversion of sulfite to sulfate. It was known that the reaction temperature could influence the diffusion behavior, dissolution, and reaction characteristics of molecules or ions in liquid phase [20]. Therefore, the conversion rate of sulfite could be improved with increasing temperature. In addition, combined with the operating temperature for further denitration, the reaction temperature in this experiment to be determined was 55 °C. As shown in Fig. 2, the sulfite content decreases as the O₂ concentration increases from 4.0% to 6.8%, and then the sulfite content varies little in the range from 6.8% to 9.5% with other conditions unchanged. We know that the reaction of the Mn(OH)₂ and SO₂ to manganese sulfate consumes oxygen, and for this reason, there should be a sufficient supply of oxygen to the absorbant slurry to support the conversion of sulfite to sulfate. Therefore, the results show that the absorption of SO₂ could be improved with increasing O₂ concentration and the 6.8% is sufficient in this slurry system.

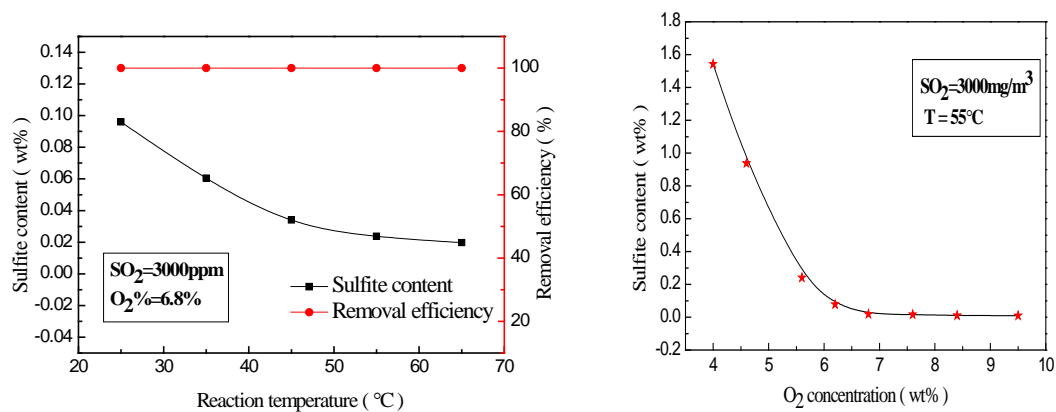


Fig. 2 Effects of reaction temperature and O₂ concentration on the absorption process

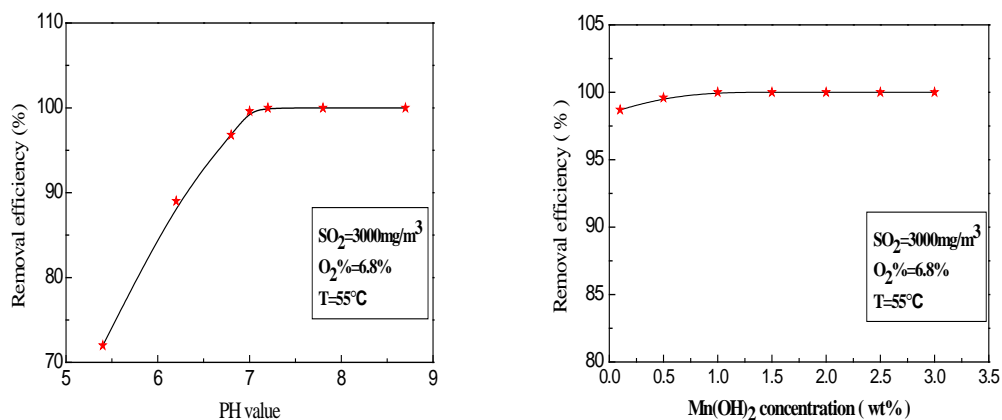


Fig. 3 Effects of PH value and Mn (OH)₂ content on SO₂ removal efficiency

Effects of PH Value and Mn (OH)₂ Content on SO₂ Removal Efficiency

Fig. 3 shows the SO₂ removal efficiency with various slurry pH values and different Mn(OH)₂ content at the temperature 55 °C, SO₂ 3000 mg/m³, and O₂ 6.8%. It is obvious that the removal efficiency rapidly increases as the slurry pH value increases from 5.4 to 6.8, gets to the 100% at 7.2 and remains unchanged from 7.2 to 8.7. The effect of Mn (OH)₂ concentration varies little as the slurry range from 0.1 to 5.0 percent by weight (wt %). The results show that the content of 1.0wt% is sufficient in this slurry system. Generally, higher values of Mn (OH)₂ being used in the

experiment, the higher amounts slurry will be employed, which should be a higher efficiency.

According above, the optimum experiment conditions were selected, and the experimental results of desulfurization in the suitable conditions are shown in Fig. 4. It could be observed that SO_2 of different content from 1800 mg/m^3 to 3000 mg/m^3 were cleaned up by $\text{Mn}(\text{OH})_2$ with the removal efficiency of 100%. It also can be seen that the sulfite content varies little from 1800 mg/m^3 to 3000 mg/m^3 , compared with manganese sulfate 10% which show the main component is sulfate ion, reaching to 99.7%. We know that SO_2 was a soluble gas, and could rapidly react with water to form weakly acid, it is theorized that the somewhat basic property of $\text{Mn}(\text{OH})_2$ is utilized in the process through the mechanism of a standard acid-base reaction to facilitate SO_2 removal. The reaction between the $\text{Mn}(\text{OH})_2$ and the SO_2 was very fast with the advantage being taken of the known catalytic effect of the manganese compounds on the oxidation of sulfur dioxide in an aqueous system. In addition, it should be a sufficient supply of oxygen to the conversion of the $\text{Mn}(\text{OH})_2$ and SO_2 to soluble manganese sulfate, facilitating absorption.

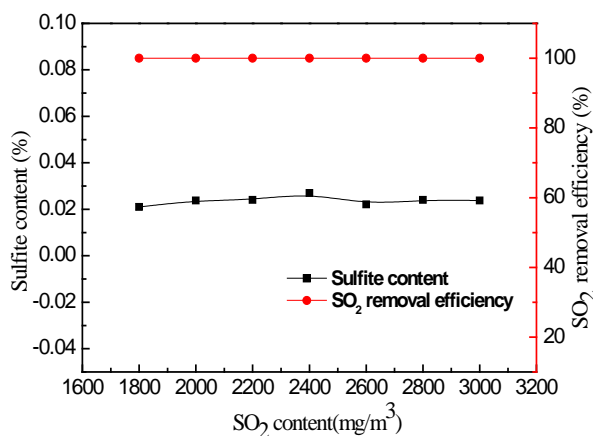


Fig. 4 Experimental results of simulated flue gas on SO_2 removal ($T=55^\circ\text{C}$; $\text{O}_2=6.8\%$; Gas flow rate= $2\text{L}/\text{min}$; $\text{Mn}(\text{OH})_2=1.0\text{wt}\%$)

Conclusions

A resource-based method for completely removal of SO_2 from flue gas by using recycling manganese hydroxide ($\text{Mn}(\text{OH})_2$) as an absorbant was proposed. The effects of reaction temperature and O_2 concentration on absorption process and the effects of PH value and $\text{Mn}(\text{OH})_2$ content on SO_2 removal efficiency were considered to achieve the optimal experimental conditions which were $T=55^\circ\text{C}$, $\text{O}_2=6.8\%$, $\text{Mn}(\text{OH})_2=1.0\text{wt}\%$, and $\text{PH}\geq 7.2$. Under the optimal conditions with a bubbling device, SO_2 of different content from 1800 mg/m^3 to 3000 mg/m^3 in the experiment could achieve 100% removal efficiency, indicating that desulfurization by the recycled manganese hydroxide was thorough. The sulfite content in the absorbing liquid was relatively low, under 0.027%, compared with manganese sulfate 10%, which show the main component is sulfate ion, reaching to 99.7%, suitable for the preparation of high quality gypsum products and the regeneration of $\text{Mn}(\text{OH})_2$.

Acknowledgements

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References

- [1] M. K. Mondal, V. R. Chelluboyana, New experimental results of combined SO₂ and NO removal from simulated gas stream by NaClO as low-cost absorbent, *J. Chem. Energy*. 217(2013) 48-53.
- [2] E. H. Duan, P. Zhang, K. Yang, W. Z. Liang, M. T. Yu, S. Wang, J. R. Niu, Effect of alkyl and halide moieties on the absorption and stratification of SO₂ in tetrabutylammonium halide aqueous solutions, *J. RSC Adv.* 6(2016) 55401.
- [3] X.Gao, H. L. Ding, Z. Du, L. Wu, M. X. Fang, Z. Y. Luo, K. F. Cen, Gas-liquid absorption reaction between (NH₄)₂SO₃ solution and SO₂ for ammonia-based wet flue gas desulfurization, *J. Appl. Energy*. 87 (2010) 2647.
- [4] J. B.Gao, S. J. Wang, J.Wang, L. D. Gao, S. W. Tang, Y. Xia, Effect of SO₂ on the amine-based CO₂ capture solvent and improvement using ion exchange resins, *J. Int. J. Greenh. Gas Control*. 37 (2015) 38-45.
- [5] C. F. Liu, S. M. Shih, R. B. Lin, Kinetics of the reaction of Ca (OH) ₂ /fly ash sorbent with SO₂ at low temperatures, *J. Chem. Energy. Sci.* 57(2002) 93.
- [6] Z. G. Shen, M. J. Ni, S. P., Guo, X., Chen, M. Tong, J. Lu, Kinetics of Oxidation Inhibition of Sodium Sulphite in Wet Flue Gas Desulphurization Process, *J. Asian. J. Chem.* 25(2013) 6727
- [7] S. M. Shih, J. C. Lai, C. H. Yang, Kinetics of the reaction of dense cao particles with SO₂, *J. Ind. Eng. Chem. Res.* 50(2011) 12409.
- [8] R. D. Valle-Zermeño, J. Formosa, J. A. Aparicio, M. Guembe, J. M. Chimenos, Transposition of wet flue gas desulfurization using MgO by-products: From laboratory discontinuous batch reactor to pilot scrubber, *J. Fuel. Process Technol.* 138(2015) 30.
- [9] J. Przepiórski, A. Czyżewski, J. Kapica, D. Moszyński, B. Grzmił, B. Tryba, S. Mozia, A. W. Morawski, Low temperature removal of SO₂ traces from air by MgO-loaded porous carbons, *J. Chem. Eng.* 191(2012) 147.
- [10] Y. Yang, S. T. Tong, Progress of study on iron oxide desulfurizer at ambient temperature, *J. Gas Heat*, (2002).
- [11] Y. Liu, J. Sun, X. X. Hu, Shu, S. J, Ding, S. L, Yu, Z. L., Study on flue gas desulfurization with rhodochrosite and pyrolusite pulp, *J. China's Manganese Ind.* 26(2008) 19.
- [12] Y. W. Qi, Y. J. Li, L. Kong, M. M. Ren, Q. Han, Feasibility of flue-gas desulfurization by manganese oxides, *J. Soc. Ch.* 23(2013) 3089.
- [13] Y. Osaka, T. Kito, N. Kobayashi, S. Kurahara, H. Y. Huang, H. R. Yuan, Z. H., He, Removal of sulfur dioxide from diesel exhaust gases by using dry desulfurization MnO₂ filter, *J. Sep. Purif. Technol.* 150(2015) 80.
- [14] S. Darake, M. S. Hatamipour, A. Rahimi, P. Hamzeloui, SO₂ removal by seawater in a spray tower: Experimental study and mathematical modeling, *J. Chem. Eng. Res. Des.* 109(2016) 180.
- [15] D. Lei, Energy-efficient investigation of flue gas desulfurization by limestone-gypsum method. *J. Technol. Development. Chem. Ind.* 2011.
- [16] C. Chen, S. Liu, G. Yang, Y. Liu, Investigation on mercury reemission from limestone-gypsum wet flue gas desulfurization slurry, *J. Sci. World.* 1(2014) 171.

- [17]Y. Q. Guo, Application of organic amine process in flue gas desulfurization of sintering machine, *J. Ch. Environ. Protection Ind.* 2013.
- [18]R. Ben-Slimane, M. T. Hepworth, Desulfurization of hot coal-derived fuel gases with manganese-based regenerable sorbent. 2. Regeneration and multicycle tests, *J. Energy Fuels.* 8(1994) 1175.
- [19]Z. Yan, L. Liu, Y. Zhang, J. Liang, J. Wang, Z. Zhang, X. Wang, Activated semi-coke in SO₂ removal from flue gas: selection of activation methodology and desulfurization mechanism study, *J. Energy Fuels.* 27(2013) 3080.
- [20]Y. Liu, T. M. Bisson, H. Yang, Z., Xu, Recent developments in novel sorbents for flue gas clean up, *J. Fuel Process. Technol.* 91(2010) 1175.