

Experimental study on the simultaneous desulfurization and denitrification by duct injection

ZHAO Yi*, FU Yan-chun, MA Shuang-chen, HUANG Jian-jun

(School of Environmental Science & Engineering, North China Electric Power University, Baoding 071003, China. E-mail: hgxy@sina.com)

Abstract: The highly active absorbent with oxidization based on fly ash, lime and additive was prepared. Experiments of simultaneous desulfurization and denitrification were carried out using fixture bed and duct injection. The influential factors for the absorptive capacity of the absorbent were studied. The absorptive capacities of 120.7 mg for SO₂ and 43.7 mg for NO_x were achieved at a Ca/(S + N) molar ratio 1.2, respectively, corresponding removal efficiencies of 87% and 76%, while spent absorbent appeared in the form of dry powder. The optimal temperature and humidity of flue gas treated with this process were shown to be approximately 50°C, and 5% respectively. The mechanism of removal for SO₂ and NO_x was investigated. In comparison with traditional dry FGD, this process appears to have lower cost, less complicated configuration and simpler disposal of used absorbent. The valuable references can be provided for industrial application by this process. The foreground of application will be vast in China and in the world.

Keywords: simultaneous desulfurization and denitrification; duct injection; absorptive capacity

Introduction

Fossil fuel such as coal, petroleum and natural gas has long been the major resource. It is well known that SO₂ and NO_x from flue gas emitted during combustion of fossil fuels are acid rain precursors, with NO_x also contributing to atmospheric ozone formation. Ozone is both a health hazard and a major component of photochemical smog. So, NO_x and SO₂ emissions should be regulated strictly under the current emissions standards. Development of low-cost and high efficiency simultaneous desulfurization and denitrification FGD technologies is significant and urgent at the present.

More recently, many of the technologies for combined desulfurization and denitrification FGD have been reported. Such as SNOX flue gas cleaning (Borio, 1995), SO_x-NO_x-Rox Box (SNRB) flue gas cleanup (Martinelli, 1995) and integrated dry NO_x/SO₂ emissions control system (Hunt, 1997) were demonstrated at United States. Although the objectives of these demonstration project were to achieve greater SO₂ and NO_x emissions reduction, it was also found that the stepwise removal SO₂ and NO_x would lead to waste area, higher operation cost and capital cost. Dry FGD systems are attractive in principle in terms of cost because they do not require water and reheating energy (Kiel, 1992). Nonetheless, this type of process has not yet been widely used due to the high absorbent cost, low SO₂ removal and poor absorbent utilization (Soud, 1995). Therefore, the highly active absorbent with oxidation have been exploited on the basis of previous investigation (Zhao, 2001; 2002) to avoid the disadvantages of dry FGD techniques and to carry out simultaneous desulfurization and denitrification. Current efforts described in this paper have attempted to improve uptake of SO₂ and NO by increasing the number of active sites and adding oxidative species to fly ash-based absorbent. The key assumptions for this study were that fly ash-based absorbent, modified or unmodified, will adsorb SO₂ and NO, and that modified fly ash-based absorbent having both fine pore structure and oxidizing species in the pore structure can

oxidize NO to NO₂. The capability of simultaneous denitrification and denitrification of the highly active absorbent with oxidation was verified by fixing bed and duct injection, and then, the satisfactory results were obtained.

1 Experimental

1.1 Preparation of absorbent with oxidation

The preparing method of Zhao Yi (Zhao, 2001; 2002) for highly active absorbent was referred in this study. Absorbents were prepared at the optimum conditions as follows: hydration temperature was 363 K, fly ash/Ca(OH)₂ weight ratio was 3 : 1, hydration time was 6 h. Several additives were added during preparing absorbent. At last it was found that M additive was favorable. After hydration M additive was dispersed almost to the surface of the absorbent, therefore, the abundance oxidative sites were formed.

1.2 Experimental apparatus

Bench-scale NO_x and SO₂ removal experiments were performed on myself designed fixture bed and duct injection, operation and structure details of apparatus are shown in Fig. 1 and Fig. 2.

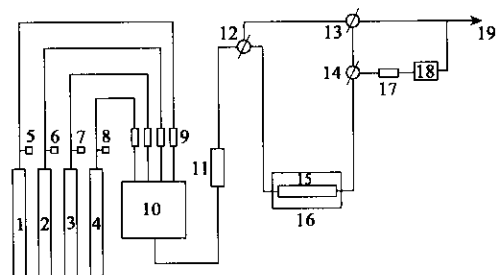


Fig. 1 The experimental apparatus of fixture bed

1. SO₂ metal flask; 2. NO metal flask; 3. N₂ and CO₂ metal flask; 4. O₂ metal flask; 5, 6, 7, 8. reducing pressure valve; 9. flux meters; 10. mixing flask; 11. gas flow meter; 12, 13, 14. valve; 15. reactor; 16. heater; 17. drying pipe; 18. MRU95/3 CD flue gas analyzer

1.3 Experimental procedures

1.3.1 Experiment of fixture bed



Fig.2 The experimental apparatus of duct injection

1. feeder; 2. simulated flue gas; 3. humidifier; 4. heater; 5. thermometer; 6. particulate removal device; 7. drier; 8. MRU95/3 CD flue gas analyzer; 9. induced draft fan

A reactor looked like glass tube being used in the experiment, 3 g of absorbent was dispersed on 1 g of glass fibre equably in the reactor to increase reaction time and to make the airflow disperse equably. The blended fully and heated simulated flue gas passed through the reactor, during the experiments, the concentrations of SO_2 and NO in discharge gas after the reactor were recorded by a flue gas analyzer hand-running. At the end of the experiments, the reactor was bypassed and the initial concentrations of SO_2 and NO were recorded again. The figure was done by relating absorptive capacities to the absorbents (Fig.3).

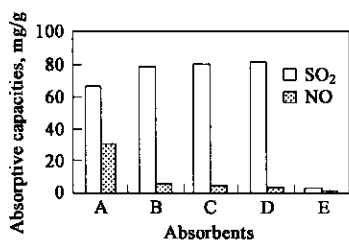


Fig.3 The effect of absorbents on the absorptive capacities

Simulated flue gas flow, $0.16 \text{ m}^3/\text{h}$; humidity of flue gas, 20%; temperature of flue gas, 50°C ; concentration of SO_2 , $2516 \text{ mg}/\text{m}^3$; concentration of NO , $1087 \text{ mg}/\text{m}^3$, $\text{Ca}/(\text{S} + \text{N}) = 1.2$

1.3.2 Experiment of duct injection

The absorbent was injected directly into flue gas pipeline and made it to distribute equably among the humidified hot flue gas. The absorbent reacted with SO_2 and NO_x in the flue gas the spent absorbent was removed by dust catcher. The length of pipeline is 20 mm and the diameter is 35 cm. The experimental driftway is shown in Fig.2.

2 Results and discussion

The absorptive capacity of the prepared absorbent is an important index for the availability of the absorbent, to evaluate the superiority or inferiority for absorbent, it is defined as the mass of SO_2 and NO_x which is absorbed by the specific mass of the absorbent, the unit is mg/g . In order to facilitate to expression of the simultaneous desulfurization and denitration, the removal efficiencies for SO_2 and NO_x are expressed as the absorptive capacity in the paper, another index, the Ca/S used in desulfurization is replaced by $\text{Ca}/(\text{S} + \text{N})$. Calculating formula of $\text{Ca}/(\text{S} + \text{N})$ as follows:

$$\text{Ca}/(\text{S} + \text{N}) = \frac{n_{\text{CaO}}}{n_{\text{SO}_2} + 1/2 n_{\text{NO}_x}}$$

2.1 Initial selection of the absorbent

Using a fixture bed to select appropriate absorbent carried out the experiments. The results are shown in Fig.3, A, B and C were highly active absorbents added different additives respectively. D was highly active absorbent no added additives, E was fly ash. It can be seen from the fig.

3 that the capabilities of desulfurization of the former 4 kinds of absorbent were better, the absorptive capacities had been achieved 65—80 mg/g . The denitrification capability of A was better, the absorptive capacity had been achieved 35 mg/g , while the denitrification capabilities of B, C and D were worse. The desulfurization and denitrification capability of E were both bad. Finally, A was selected as the useable absorbent.

2.2 Finally selection of the absorbent

The experiments were done in duct injection system based on the experimental results of Fig.3 and the experimental parameters were magnified, the results are shown in Fig.4. The capabilities of desulfurization and denitrification of absorbents were consistent basically with the results of experiments of fixture bed. At the same time, though the experimental condition was magnified several hundred times (for example, the flue gas flow was magnified from $0.16 \text{ m}^3/\text{h}$ to $60 \text{ m}^3/\text{h}$), the absorptive capacities of absorbents increased greatly by analyzing absorptive capacities of above 5 different absorbents and combining with the experimental results of fixture bed, it is thought that A is the highest synthetically valuable in use.

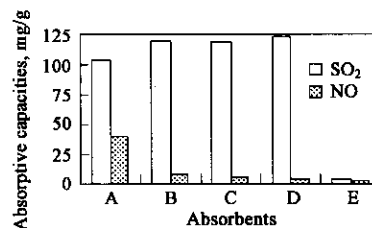


Fig.4 The effect of absorbent on the absorptive capacity at duct injection

Flue gas flow: $60 \text{ m}^3/\text{h}$; humidity of flue gas: 5%; temperature of flue gas: 50°C ; concentration of SO_2 : $2619 \text{ mg}/\text{m}^3$; concentration of NO : $984 \text{ mg}/\text{m}^3$; $\text{Ca}/(\text{S} + \text{N}) = 1.2$

2.3 Investigation of experimental conditions for desulfurization and denitrification based on duct injection

2.3.1 Comparison of desulfurization and denitrification with different content of additive

A is excellent for desulfurization and denitrification based on the experimental results of Fig.3 and Fig.4. It was a highly active absorbent with M additive. In order to get the optimal additive quantity of M, the comparing experiment of desulfurization and denitrification with different content of M was carried out. The experimental results are shown in Fig.5.

The content of additive has no obvious effect on desulfurization, this phenomenon is basically consistent with the results of Fig.3 and Fig.4, but have an obviously effect on the removal of NO . The efficiencies of denitrification increased as the content of A increased at lower content of A. When the content of A reached at 1.6%, the turning point appeared and the efficiencies of denitrification increased slowly as the content of A increased. The reason is that A is high dispersed on the surface of active absorbent during the course of assimilation which made it contain abundant "oxidation point". The reaction was primarily on the control of transformation from NO to NO_2 at lower content of A. With the increase of the content, "oxidation point" and transformation from NO to NO_2 also increased greatly, then

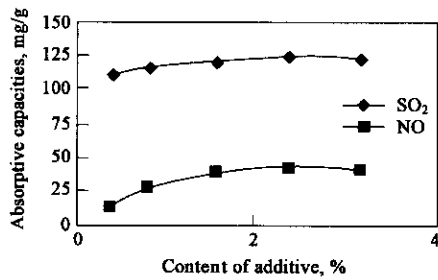


Fig. 5 The comparison of desulfurization and denitrification on different content of additive

Flue gas flow: $60 \text{ m}^3/\text{h}$; humidity of flue gas: 5%; temperature of flue gas: 50°C ; concentration of SO_2 : $2516 \text{ mg}/\text{m}^3$; concentration of NO : $992 \text{ mg}/\text{m}^3$; $\text{Ca}/(\text{S} + \text{N}) = 1.2$

the efficiencies of denitrification were improved obviously. The "oxidation point" on the surface of active absorbent tended to "saturation" when the content of A reached 1.6%. Finally the content of A was selected as 1.6%.

2.3.2 Effect of the gas temperature on the absorptive capacity

On the invariable condition of humidity and $\text{Ca}/(\text{S} + \text{N})$ ratio, the absorptive capacities of the absorbent under different reaction temperature were measured. The experimental result is shown in Fig. 6. Desulfurization and denitrification by highly active absorbent is a reaction between porous solid and gas, three parameters of the reaction would be affected by temperature (Bhatia, 1981), which are reactive velocity constant K , hole diffusivity D_e and product layer diffusivity D_p . It was known that the reactive velocity increased as the reactive temperature increased, the reason is that the increase of temperature would be make to an increase of K , D_e and D_p . At the initial stage of reaction, high absorptivity was obtained by the increase of reactive velocity, at the same time, abundant reactive products were gathered on the surface of absorbent, the parts of the hole of absorbent would be blocked, the thickness of layers for reactive product on the reactive interface increased and the surface area of reactive particles decreased, which restrained the reactive velocity and decreased the absorptive capacities (Gao, 1999a).

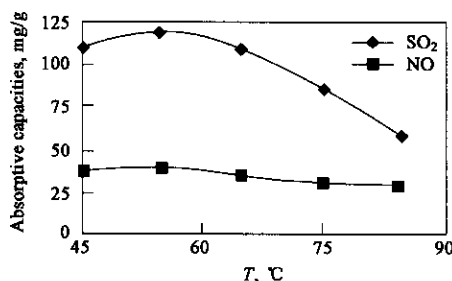


Fig. 6 Effect of the gas temperature on the absorptive capacity

Flue gas flow: $60 \text{ m}^3/\text{h}$; humidity of flue gas: 5%; concentration of SO_2 : $2675 \text{ mg}/\text{m}^3$; concentration of NO : $1080 \text{ mg}/\text{m}^3$; $\text{Ca}/(\text{S} + \text{N}) = 1.2$

The reactive velocity will increase as the temperature increased when the reactive temperature was lower than the critical temperature T_c . Nevertheless, the reactive velocity will decrease as temperature increased when the temperature was above T_c . It concerned in dissolution and desorption of

reactive gas molecule. When the temperature increased, the dissolution of reactive gas molecule should be declined and desorption of will increased (Gao, 1999b). The optimal reaction temperature was selected at 55°C .

2.3.3 Effect of the gas humidity on the absorptive capacity

The effect of the gas humidity on desulfurization and denitrification was studied. Experiments of desulfurization and denitrification on the conditions of different gas humidity were made by duct injection. The experimental result is shown in Fig. 7. From Fig. 7, the absorptive capacities had been affected significantly by gas humidity. They increased obviously as the humidity increased when the absorptive capacities were below 5%, it is primarily reason that the dissolving ratios of SO_2 and NO_x increased as the humidity increased, and the reactions between the resolved SO_2 and NO_x and absorbent are fast reaction. The reactions were controlled by the dissolving velocity of SO_2 and NO_x when the absorptive capacities were above 5%. Furthermore, when the gas humidity was above a certain value, the particle diameter increased because of the viscosity of water, then the specific surface, surface energy and activity of the absorbent decreased. An increase of the absorptive capacities were not significant. The gas humidity was chosen as 5%.

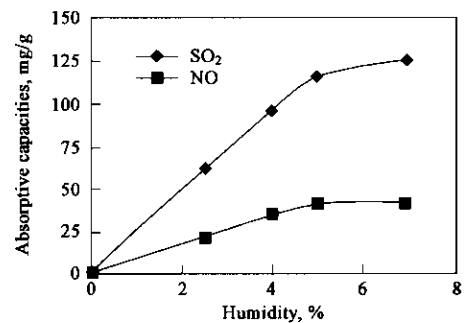


Fig. 7 Effect of the gas humidity on the absorptive capacity

Flue gas flow: $60 \text{ m}^3/\text{h}$; temperature of flue gas: 50°C ; concentration of SO_2 : $2587 \text{ mg}/\text{m}^3$; concentration of NO : $1075 \text{ mg}/\text{m}^3$; $\text{Ca}/(\text{S} + \text{N}) = 1.2$

2.3.4 the mechanisms of highly active absorbent for SO_2 and NO_x removal

The selected absorbent was made from fly ash, lime and additive by hydration. The fly ash was primarily composed of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO , looked upon as a kind of volcanic ash because it contained abundant uncrystalline SiO_2 and Al_2O_3 . Abundant silicic and aluminous oxides contained in vitreous body of fly ash were gradually activated by alkaline. When $\text{Ca}(\text{OH})_2$ reached the surface of global vitreous body of fly ash by diffusion, adsorption and erosion occurred, vitreous body was dissolved and the network of silicic oxide and aluminous oxide was destroyed, released active SiO_2 and Al_2O_3 was to react with $\text{Ca}(\text{OH})_2$ and the reaction of volcanic ash reaction was brought about. It is seen from SEM Fig. 8 and Fig. 9 that the obvious change of microstructure of particle surface occurred after hydration.

As shown in Fig. 8 that unactivated fly ash has obvious sphere and the surface of the vitreous body is polish and light, the primary crystal should be SiO_2 and Al_2O_3 (Zhao, 1993). However, it is shown in Fig. 9 that the surface of fly ash after hydration is coarse and damaged badly. The

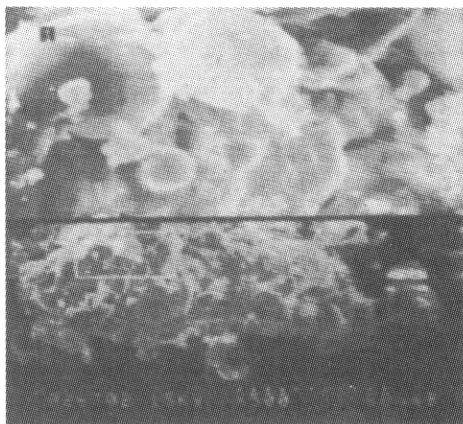


Fig.8 The SEM picture of fly ash

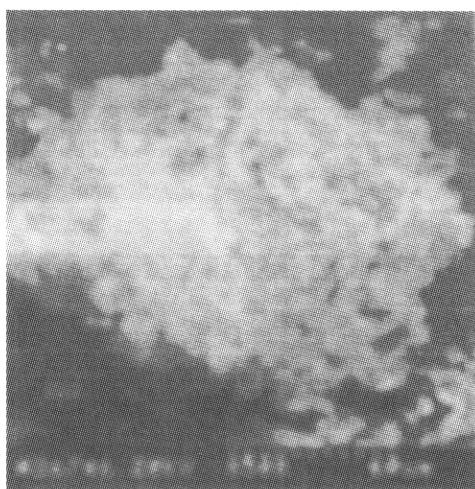


Fig.9 The SEM picture of digest fly ash

colloidal and formless substances were produced and abundant interstices were formed on the surface of fly ash, it is explained from microstructure of absorbent that the highly active absorbent has high specific surface and activity.

Nitrogen oxides in flue gas existed mostly in form of NO, whose solubility in the water was rather lower than NO₂. Although NO can be oxidized to NO₂ on the condition of nature, the residence time was too short (1—2 s) for NO to being oxidized before it left the reactor. So it is the key to oxidate NO to NO₂ in flue gas before removal. Hori M. (Hori, 1992) brought forward that NO can first be oxidated to NO₂ by adding hydroxy free radical into pipeline, before adding alkaline absorbent to desulfurization and denitrification. NO to NO₂ can be oxidated rapidly by prepared highly active absorbent in this study. It can be seen from Fig. 3 and Fig. 4 that the absorptive capacities for denitrification of absorbent A was obviously higher than the others because of additives. The absorbent D hardly had any denitrification capacity because there was no additive in it. Ferrous or manganic and other metallic oxide, transition metallic ion and parts of trace element contained in fly ash, had promotive effect on desulfurization and denitrification. S. Behrooz Ghorishi *et al.* had done relative experiments (Behrooz, 2002).

2.3.5 Experiments of removal for SO₂ and NO_x by duct injection

On the basis of experimental results from fixture bed and duct injection, the process conditions by duct injection were primarily selected as follows: flue gas flow, 60 m³/h; temperature of flue gas, 50°C; humidity of flue gas, 5%; concentration of SO₂, 2500 mg/m³; concentration of NO, 1000 mg/m³; Ca/(S + N) = 1.2. 5 times parallel experiments were carried out in duct injection, the results showed that the variance, S of absorptive capacities were less, the data appeared greater reproductively. The desulfurization efficiency was 87% and that of denitrification was 76%, basic data and practical experience can be provided for the industrialized application.

3 Conclusions

The mechanisms of desulfurization and denitrification by highly active absorbent were analyzed. It is considered that the unique particular surface characteristic for absorbent after hydration is the main reason resulting in high activity of absorbent. The prepared rich-oxidation absorbent can be used to realize desulfurization and denitrification by duct injection technology.

As a result of experiments we came to a conclusion that absorption is the main process for desulfurization and denitrification, flue gas temperature and humidity are the main influential factors for the efficiencies of desulfurization and denitrification.

From parallel experiments one came to realize that the duct injection technology used prepared rich-oxidation absorbent is simple, stable and reliable.

References:

- Behrooz S G, Carl F S, Wojciech S J *et al.*, 2002. Simultaneous control of Hg⁰, SO₂, and NO_x novel oxidized calcium-based sorbents [J]. *Air & Waste Manage Assoc*, 52(5): 273—278.
- Bhatia S K, Perlmutter D D, 1981. A random pore model for fluid-solid reaction diffusion and transport [J]. *AIChEJ*, 27(2): 247—254.
- Borio D C, 1995. Status of the SNOX technology and demonstration [C]. Fourth Annual Clean Coal Technology Conference. Denver CO.
- Gao X, Luo Z Y, Chen Y F *et al.*, 1999a. Modeling the reactivity of aqueous Ca (OH)₂ particle [J]. *Journal of Environmental Sciences*, 19(4): 351—356.
- Gao X, Luo Z Y, Chen Y F, 1999b. Effect of water content on desulfurization characteristic of calcium-based sorbent [J]. *Journal of Combustion Science and Technology*, 5(1): 39—45.
- Hori M, Matsunga N, Malte P C *et al.*, 1992. Twenty-four symposium (international) on combustion [C]. Australia: The Combustion Institute Sydney. 909—916.
- Hunt T, Muzio L J, Smith R *et al.*, 1997. Integrated dry NO_x/SO₂ emissions control system performance [C]. Tampa FL: Fifth Annual Clean Coal Technology Conference.
- Kiel J H A, Prins W, van Swaaij W P M, 1992. Performance of silica-supported copper oxide sorbents for SO_x/NO_x removal from flue gas [J]. *Appl Catal, B (Environ)*: 1: 13—39.
- Martinelli R, Doyle J B, Redinger K E, 1995. SO_x-NO_x-Rox Box technology review and global commercial opportunities [C]. Fourth Annual Clean Coal Technology Conference. Denver CO.
- Soud H, 1995. Suppliers of FGD and NO_x control systems [M]. London: IEA Coal Research, United Kingdom. 18—27.
- Zhao Y, Ma S C, Li Y Z *et al.*, 2002. The experimental investigation of desulfurization and denitration from flue gas by absorbent based on fly ash [J]. *Proceedings of the Chinese Society for Electrical Engineering*, 22(3): 108.
- Zhao Y, Ma S C, Zhao J H *et al.*, 2001. Experimental study on highly reactive sorbents for SO₂ removal [J]. *Journal of North China Electric Power University*, 28(1): 72—75.
- Zhao P G, 1993. Synthetical utilization of fly ash [M]. Shenyang: Liaoning Science & Technology Publishing House. 68—99.