

选择性非催化脱硝还原中NH₃漏失因素的试验研究

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Experimental Study on Effect Factors of NH₃ Slip in SNCR Process

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ABSTRACT: Influences caused by different factors on NH₃ slip was analysed in a pilot-plant of selective non-catalytic reduction experiments. The experiments were carried out on a combustion research facility (CRF) and chemical titration was used to measure the NH₃ slip of extracted gas that goes out from the rear flue. The results confirm that NH₃ slip increases with both higher ratio of NH₃ to NO ($n(\text{NH}_3)/n(\text{NO})$) and higher concentration of a reducing reagent, while it decreases with the increase of temperature. Initial NO concentration and its residence time can also affect the NH₃ slip. A higher initial NO concentration lead to higher NH₃ slip, but added residence time has the opposite effect. Among urea, ammonium carbonate and ammonia liquor, the NH₃ slip of urea is the highest and that of ammonia liquor is the lowest.

KEY WORDS: selective non-catalytic reduction; NH₃ slip; chemical titration; reducing reagent

摘要: 在选择性非催化还原过程中试验中, 研究不同因素对氨漏失含量的影响。选择性非催化还原过程试验研究是在燃烧试验装置上进行的, 在尾部烟道抽取烟气采用化学滴定法测量烟气中的NH₃漏失含量。试验结果表明: 温度越高, 漏失氨含量越低; 随氨氮物质的量比的增加, NH₃漏失含量不断增加; 还原剂质量浓度越低, NH₃漏失含量越低; NO初始浓度和停留时间对漏失氨浓度也有影响, NO初始浓度越高NH₃漏失浓度越高, 停留时间越长漏失氨浓度越低; 不同还原剂NH₃漏失浓度不同, 尿素、碳酸氨、氨水3种还原剂中, 尿素的NH₃漏失浓度最高, 氨水的NH₃漏失浓度最低。

关键词: 选择性非催化还原; 氨漏失; 化学滴定法; 还原剂

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0 INTRODUCTION

Selective Non-catalytic reduction (SNCR) is a popular technology for reducing emissions of NO_x. Among technologies of post combustion, SNCR has the advantage of low cost as well as a short period of alteration on both operated boilers and new sets [1-2]. During the SNCR process, a reducing reagent is injected into hot flue gas that contains a reducing agent (such as ammonia and urea), which reduces NO to form N₂ and H₂O [3]. The reaction mechanisms of SNCR have been studied in miniature facilities to investigate its process and the different factors that affect it, such as the influence of temperature, the ratio of NH₃ to NO ($n(\text{NH}_3)/n(\text{NO})$), mixture and adding adjunction to reducing reagent on SNCR [4-13]. In addition, the modeling of the Hybrid reburn/SNCR has been investigated [14]. Many researchers have been trying to analyze the rules of N₂O emission with the help of models in chemical kinetics and the SNCR process in CFB boilers and waste incineration plants [15-18]. SNCR in incinerators has also been studied with numerical simulation and experimental data are compared with those of the simulation [19-20].

Since not all NH₃ can be consumed by reacting with NO, the unreacted NH₃ will certainly cause secondary pollution. Therefore, NH₃ slip has greatly restricted the application of SNCR technology, and therefore it is important to develop a way to reduce NH₃ slip while keeping high NO removal efficiency. Several of the factors that can influence the SNCR

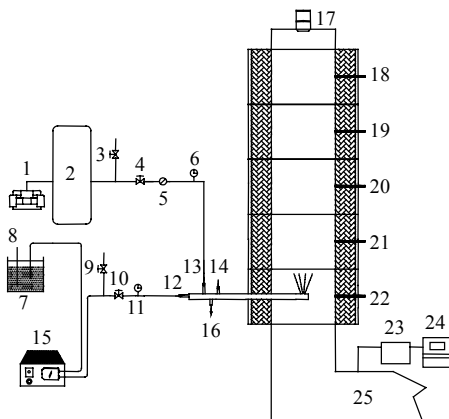
process have been analyzed in this work, including the reducing reagent concentration, $n(\text{NH}_3)/n(\text{NO})$, temperature of flue gas, initial NO concentration, residence time, different kinds of reagent and the relation between the NH_3 slip and NO removal efficiency. Temperature of furnace, gas residence time and mixture of gas and the reagent in the pilot-scale CRF are similar to those of large-scale power stations, so the research is significantly important as a reference to both the mechanism study of NH_3 slip and the engineering design of the SNCR process.

1 EXPERIMENT

1.1 Experiment equipment

As shown in Fig.1, The pilot-scale experiment system for the SNCR process consists of a combustion research facility (CRF) and a reagent injecting system analyzing NH_3 slip of flue gas from the rear flue. The CRF was introduced from the Ontario hydro technologies institute (OHT) of Canada. It was designed to simulate large-scale industrial and utility boilers and its designed maximum coal feeding rate is 30 kg/h.

The furnace is 4.2 m in height and 0.4 m in diameter and the furnace contains five floors, which are coded M1, M2, M3, M4, and M5 from top to



1—Air compressor; 2—Air tank; 3,4—Control valve; 5—Gas flow meter; 6—Pressure gauge; 7—Liquid container; 8—Mixer; 9, 10—Control valve; 11—Pressure gauge; 12—Reducing reagent inlet; 13—Atomizing air; 14—Cooling water inlet; 15—Metering pump; 16—Cooling water outlet; 17—Burner; 18-22—Thermocouple of M1-M5 of furnace; 23—Filter and cooling system; 24—Flue gas analyzer; 25—Rear flue.

图1 SNCR 过程试验系统图

Fig. 1 Experiment system of SNCR process

bottom. The whole CRF contains five systems, as combusting, data collecting and control, compressed air cooling, instantaneous flue gas collecting, analyzing and coal powder producing. The flue gas analyzer (Siemens ULTRAMAT-23) can tell the instantaneous components of O_2 , CO_2 , CO , SO_2 and NO after the flue gas is filtered and cooled.

The reagent injecting system is made up of a meter pump, an injector and a liquid container. The reducing reagents are injected into the hot furnace after being atomized from the metering pump.

The NH_3 slip sampling system consists of an absorption bottle, a wet type flow meter and a sampling pump. NH_3 slip can be measured by Chemical titration after sampling.

1.2 Experiment method

Experiments were carried out after the temperature and composition of the flue gas in the furnace became steady. A reducing reagent was introduced to the location of injection through a diaphragm meter pump, so the flux could be adjusted continuously. The air in the fixed flux supplied by the air compressor was used as the atomizing medium. The reducing reagent is injected adversely to the flow of the flue gas. The experiment system is shown schematically in Fig.1.

Once the experiment became stable, the gas was sampled with a sampling pump, the flue gas sucked was measured by the wet type flow meter and the NH_3 in the flue gas could be absorbed by dilute sulfuric acid of 0.05mol/L. Absorption bottles were sealed and absorbed. The NH_3 was measured by chemical titration after the SNCR experiment. In the chemical titration, The NH_3 in the absorption bottle was substituted with an excessive strong base and measured by ammonia electrode. The system was shown in Fig.2.

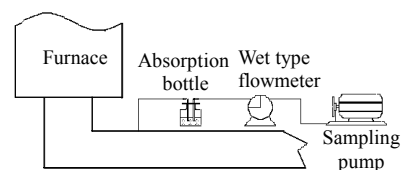


图2 漏失氨取样系统

Fig. 2 NH_3 slip sampling system

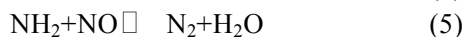
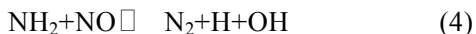
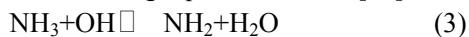
2 EXPERIMENT RESULTS AND ANALYSIS

2.1 Influences of temperature and the ratio of NH₃/NO and comparison of NO removal efficiency

A 10% urea solution was used as reducing reagent in these experiment cases. The reagent was injected from the middle of M5, M5 and M3 respectively in different cases, and the corresponding T_{inj} is 850, 900 and 1000 °C. The Urea decomposed in high temperature [21]:



NH₃ generated in the above reactions reduces NO in flue gas as the following equations shows [22]:



NH₃ could reduce NO to N₂ while NH₃ may be oxidized to form NO. SNCR is the combination of these two opposite courses. Unreacted NH₃ is left in the flue gas. It is clear in Fig.3 that change in temperature has significant influence on NH₃ slip of SNCR. NH₃ slip decreases with the rise of temperature, while the decomposition and oxidation of NH₃ become heavier with higher temperature. Consequently, NH₃ would decompose and be oxidized even while not reacting with the NO. The NH₃ slip would not be larger than 0.8 mg/m³(normal state) while temperature of the injecting location is higher than 1000 °C.

It is obvious in Figs.3 and 4 that NO removal efficiency is higher as 900 °C is in the temperature window and NH₃ slip is also higher. However, NO removal efficiency is lower because a large amount of reducing reagent is out of temperature windows at 1000 °C and NH₃ slip is lower too, which has less effect on the following facility. Therefore, the influence of temperature on NH₃ slip and NO removal should be considered during the application.

As shown in Fig.3, NH₃ slip increases with $n(NH_3)/n(NO)$. This is due to the reaction of the NO and the reagent approaches to saturation and there is more and more NH₃ left, which causes an increase in the NH₃ slip. When $n(NH_3)/n(NO)$ becomes larger

than 2.0, the NH₃ slip still increases fast although NO removal efficiency also becomes higher. Higher NH₃ slip causes more serious erosion to the following facilities. The SNCR process was controlled, to a large extent, by mixing. An aerodynamic nozzle was used in the experiment and the great surface and high velocity of the droplets which are atomized by the nozzle can improve mixing. On the other hand, because the scale of the CRF is so much smaller than the actual boiler, mixing of the reduction reagent with the flue gas become better. Injection of 900 °C and $n(NH_3)/n(NO)=1.5$ is recommended for the urea.

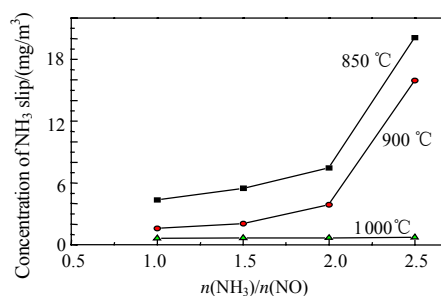


图 3 温度对NH₃漏失的影响

Fig. 3 Influence of temperature on NH₃ slip

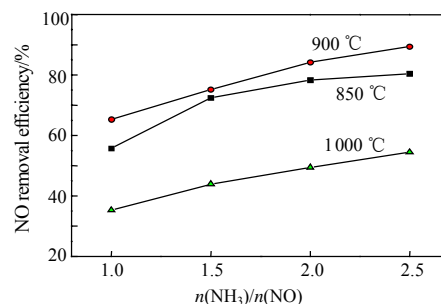


图 4 温度对 NO 脱除率的影响

Fig. 4 Influence of temperature on NO removal efficiency

2.2 Influences of reducing reagent concentration on NH₃ slip and comparison of NO removal efficiency

The temperature of the injection location is 900 °C. From Fig.5, it can be known that NH₃ slip increases with a concentration of urea solution. A lower concentration requires a larger volume of a reducing reagent and causes larger droplets to surface, which could make the mixture better and promote the reducing reaction. A more complete reaction can also decrease NH₃ slip.

As shown in Fig.6, NO removal efficiency increases with the decrease of concentration.

Consequently, a lower concentration should be selected if NH_3 slip and NO removal is to be considered together in application. Lower concentration of the solution (8%~12%) is recommended in practice.

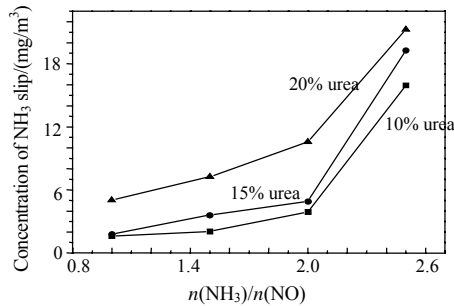


图5 还原剂浓度对 NH_3 漏失的影响

Fig. 5 Influence of concentration of reagent on NH_3 slip

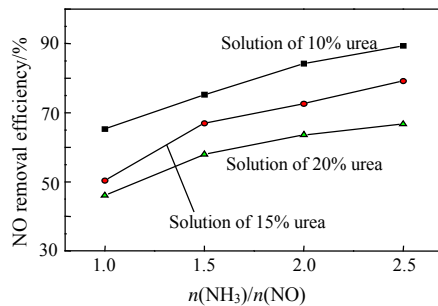


图6 还原剂浓度对NO脱除率的影响

Fig. 6 Influence of concentration of reagent on NO removal efficiency

2.3 Influences of initial NO concentration on NH_3 slip and comparison of NO removal efficiency

These experiments were carried out with an urea solution of 10%, $n(\text{NH}_3)/n(\text{NO})$ of 1.5 and a temperature at the injecting location of 850 °C. From Fig.7 it can be known that a higher initial NO concentration equals a higher amount of reducing reagent with the same $n(\text{NH}_3)/n(\text{NO})$. This can promote the mixture and increase the possibility of a reducing reaction, which can also improve the NO removal effectiveness. Meanwhile, remnants of unreacted NH_3 will increase NH_3 slip.

A higher initial NO concentration brings on higher NO removal efficiency and causes a higher NH_3 slip with the same $n(\text{NH}_3)/n(\text{NO})$ as compared in Figs.7 and 8. Hence, lower $n(\text{NH}_3)/n(\text{NO})$ should be preferred to avoid a higher NH_3 slip while the initial NO concentration is high. The advisable ratio is always less than 1.5.

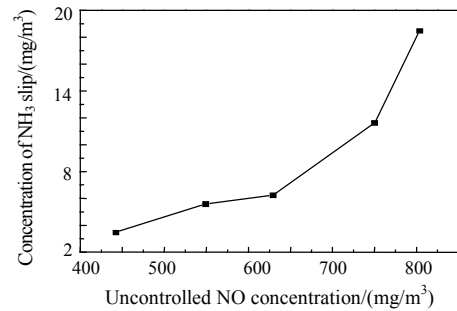


图7 NO初始浓度对 NH_3 漏失的影响

Fig. 7 Influence of initial NO concentration on NH_3 slip

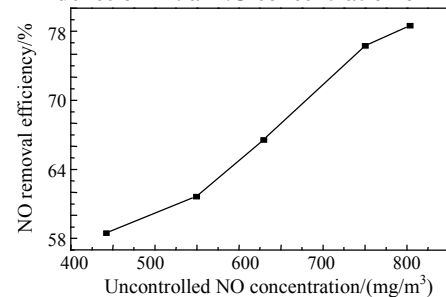


图8 NO初始浓度对NO脱除率的影响

Fig. 8 Influence of initial NO concentration on NO removal efficiency

2.4 Influences of residence time on NH_3 slip and comparison of NO removal efficiency

These experiments were carried out with an urea solution of 10%, $n(\text{NH}_3)/n(\text{NO})$ of 1.5 and a temperature at the injecting location of 820 °C. The SNCR process was so fast that it can be regarded as controlled by the mixture of NO and the reagent [4]. Comparing Figs.9 and 10, the mixture and possibility of reaction both increase with the residence time. Therefore, NO removal efficiency increases and NH_3 slip become lower. The improvement of NO removal effectiveness and decrease of NH_3 slip are evident when prolonging the residence time at first. It is because the residence time is too short to complete reaction at the beginning. However, after 533 ms, the improvement of NO removal efficiency and decrease

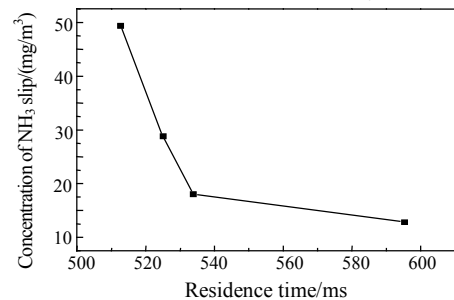


图9 停留时间对 NH_3 漏失的影响

Fig. 9 Influence of residence time on NH_3 slip

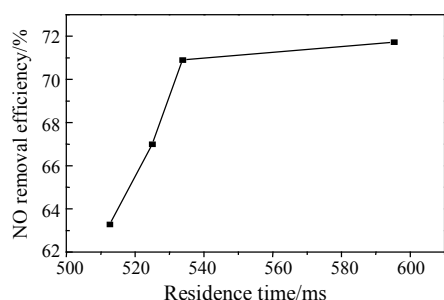


图 10 停留时间对 NO 脱除率的影响

Fig. 10 Influence of residence time on NH_3 slip

of NH_3 slip gets gentle, which means the mixture is enough for the SNCR process. However, when installing the SNCR on a real power station, especially on that already in use, we can not be sure whether or not the residence time can be long enough due to their space limitation.

2.5 Comparisons between of NH_3 slip and NO removal efficiency with different reducing reagents

Different temperatures of urea, ammonia liquor and ammonium carbonate were used, as 900, 850 and 900 °C groups respectively.

NH_3 slip with different reducing reagents are compared in Fig.11. The NH_3 slip of urea is higher while that of the ammonia and ammonium carbonate is much lower. NH_3 slip increases slowly with $n(\text{NH}_3)/n(\text{NO})$. The urea is decomposed following the Eqs.(1) and (2) to generate NH_3 , which then reacts with the NO as described in Eqs.(3), (4) and (5) to form N_2 and H_2O . Unreacted NH_3 will decompose and get oxidized very quickly in ammonia liquor while in urea solution, due to the urea's ease of penetration and dispersion, it will slowly decompose and get oxidized. Hence, NH_3 slip in ammonia liquor is much lower than that of urea solution. Just like urea, ammonium carbonate will also decompose to form NH_3 , CO_2 and H_2O before reducing NO. The penetration and dispersion property of ammonium carbonate is more remarkable than ammonia liquor but less remarkable than urea because ammonium carbonate decomposes more easily than urea. Hence, NH_3 slip of ammonium carbonate is higher than ammonia liquor and lower than ammonium carbonate.

As in Figs.11 and 12, NO removal efficiency and NH_3 slip is higher than those of ammonia liquor and

ammonium carbonate. Urea can get an acceptable NH_3 slip and high NO removal efficiency with lower molar ratio of NH_3/NO . Furthermore, urea is convenient for transport and storage. Consequently, urea will be used more widely than ammonia liquor and ammonium carbonate.

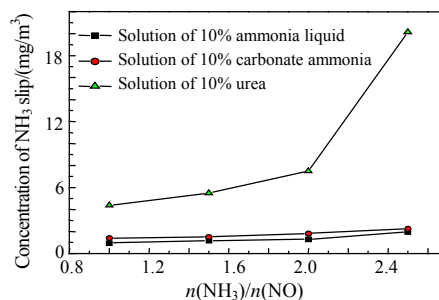
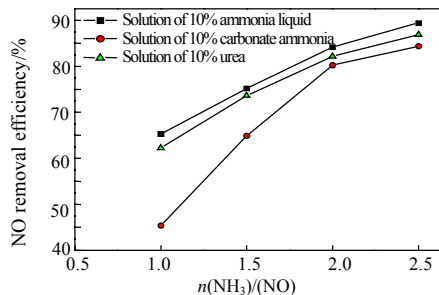
图 11 不同还原剂对 NH_3 漏失的影响Fig. 11 Comparisons of NH_3 slip with different reducing reagents

图 12 不同还原剂对 NO 脱除率的影响

Fig. 12 Comparisons of NO removal efficiency with different reducing reagents

3 CONCLUSIONS

Influences on NH_3 slip and comparisons of NO removal efficiency with different reagents have been studied in pilot-scale SNCR and the following conclusions can be obtained:

(1) The highest NO removal efficiency is obtained with an injecting temperature of 900 °C while NH_3 slip is lower than 0.8 mg/m^3 with an injecting temperature of 1 000 °C. NH_3 slip increases with $n(\text{NH}_3)/n(\text{NO})$. NH_3 slip increases fast when $n(\text{NH}_3)/n(\text{NO})$ is larger than 2.0. Higher NO removal efficiency and lower NH_3 slip can be achieved with lower concentration of the reducing reagent.

(2) Both the NO removal efficiency and the NH_3 slip increase with the initial NO concentration.

(3) NO removal efficiency increases while NH_3 slip decreases with the prolonging of residence time.

(4) Among the three reducing agents (urea,

ammonia liquor and ammonium carbonate), urea leads to the highest NH_3 slip, while that of ammonia liquor leads to the lowest. NO removal efficiency of urea is the highest of all three reagents.

REFERAENCES

- [1] Zabetta E C, Hupa M, Saviharju K. Reducing NO_x emissions using fuel staging, air staging, and selective noncatalytic reduction in synergy [J]. *Ind. Eng. Chem. Res.*, 2005, 44(13): 4552-4561.
- [2] Javed M T, Irfan N, Gibbs B M. Control of combustion-generated nitrogen oxides by selective non-catalytic reduction[J]. *Environmental management*, 2007, 83(3): 251-289.
- [3] 王智化, 周俊虎, 周昊, 等. 炉内高温喷射氨水脱除 NO_x 机理及其影响因素的研究[J]. *浙江大学学报(工学版)*, 2004, 38(4): 495-500. Wang Zhihua, Zhou Junhu, Zhou Hao, et al. Experimental and modeling study on the mechanism and sensitive parameters of thermal DeNO_x [J]. *Journal of Zhejiang University(Engineering Science)*, 2004, 38(4): 495-500(in Chinese).
- [4] Oliva M, Alzueta M U, Millera A, et al. Theoretical Study of the influence of mixing in the SNCR process Comparison with pilot scale date[J]. *Chemical Engineering Science*, 2000, 55(22): 5321-5332
- [5] Østberg M, Dam-Johansen K, Johnsson J E. Influence of mixing on SNCR process[J]. *Chemical Engineering Science*, 1997, 52(15): 2511-2525.
- [6] Røjel H, Jensen A, Glarborg P, et al. Mixing effects in the selective noncatalytic reduction of NO[J]. *Ind. Eng. Chem. Res.* 2000, 39(9): 3221-3232.
- [7] Rota R, Antos D, Zanoelo E F, et al. Experiment and modeling analysis of the NO_x OUT process[J]. *Chemical Engineering Science*, 2002, 57(1): 27-38.
- [8] Alzueta M U, Bilbao R, Millera A, et al. Interaction between nitric oxide and urea under flow reactor condition[J]. *Energy and Fuels*, 1998, 12(5): 1001-1007.
- [9] Zamansky Vladimir M, Lissianski Vitali V, Maly Peter M, et al. Reaction of sodium species in the promoted SNCR process [J]. *Combustion and Flame*, 1999, 117(4): 821-831.
- [10] Rota R, Zanoelo E F, Antos D, et al. Analysis of the thermal DeNO_x process at high partial pressure of reactants[J]. *Chemical Engineering Science*, 2000, 55(6): 1041-1051.
- [11] Bae S W, Roh S A, Kim S D. NO removal by reducing agents and addibives in the selective non-catalytic reduction(SNCR) process [J]. *Chemosphere*, 2006, 65(1): 170-175.
- [12] Lee S, Park K, Park J W, et al. Characteristics of reduction NO using urea and alkaline additives[J]. *Combustion and Flame*, 2005, 141(3): 200-203.
- [13] Nimmo W, Patsias A A, Hampartsoumian E, et al. Calcium magnesium acetate and urea advanced reburning for NO control with simultaneous SO_2 reduction[J]. *Fuel*, 2004, 83(9): 1143-1150.
- [14] Han X H, Wei X L, Schnell U, et al. Detailed modeling of hybrid reburn/SNCR processes for NO_x reduction in coal-fired furnaces [J]. *Combustion and Flame*, 2003, 132(3): 374-386.
- [15] 周俊虎, 杨卫娟, 周志军, 等. 选择非催化还原过程中的 N_2O 生成与排放[J]. *中国电机工程学报*, 2005, 25(13): 91-95. Zhou Junhu, Yang Weijuan, Zhou Zhijun, et al. Nitrous oxide formation and emission in selective non-catalytic reduction process [J]. *Proceedings of the CSEE*, 2005, 25(13): 91-95(in Chinese).
- [16] Zandaryaa S, Gavasci R, Lombardi F, et al. Nitrogen oxides from waste incineration: control by selective non-catalytic reduction[J]. *Chemosphere*, 2001, 42(5-7): 491-497.
- [17] Richie D, Pickens. Add-on control techniques for nitrogen oxide emissions during municipal waste combustion[J]. *Journal of Hazardous Materials*, 1996, 47(1-3): 195-204.
- [18] Ljungdahl B, Larfeldt J. Optimised NH_3 injection in CFB boilers [J]. *Power Technology*, 2001, 120(1-2): 55-62.
- [19] Kim H S, Shim M S, Jang D S, et al. Numerical study of SNCR application to a full-scale stoker incinerator at Daejon 4th industrial complex[J]. *Applied Thermal Engineering*, 2004, 24(14-15): 2117-2129.
- [20] Shin M S, Kim H S, Jang D S. Numerical study on the SNCR application of space-limited industrial boiler[J]. *Applied Thermal Engineering*, 2007, 27(17-18): 2850-2857.
- [21] Alzueta M U, Bilbao R, Millera A, et al. Impact of new finding concerning urea thermal decomposition on the modeling of the urea-SNCR process[J]. *Energy&Fuels*, 2000, 14(2): 509-510.
- [22] Alzueta M U, Røjel H, Kristensen P G, et al. Laboratory study of the $\text{CO}/\text{NH}_3/\text{NO}/\text{O}_2$ system: Implications for hybrid reburn/ SNCR strategies[J]. *Energy & Fuels*, 1997, 11(3): 716-723.

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