

## Experimental study of the influence of sodium salts as additive to NO<sub>x</sub>OUT process

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**Abstract**—An experimental study of the SNCR process with urea as reducing agent and sodium salts as additive has been carried out, and detailed analysis of the reaction mechanism has been given here. In the temperature range of 800–975 °C, NO concentration decreases at first and then increases while the concentration of N<sub>2</sub>O increases at first and then decreases with the increasing of temperature, and the turning point is 900 °C. With increasing of normalized stoichiometric ratio of reduction nitrogen to NO<sub>x</sub> (NSR), NO removal efficiency increases, while the concentration of N<sub>2</sub>O also increases, which decreases overall NO<sub>x</sub> removal efficiency. With sodium salts as additive, the concentration of N<sub>2</sub>O decreases with increasing of sodium salts addition at all temperatures, while the concentration of NO decreases at first and then increases at low-temperature side of the temperature window and increases at high-temperature side with additional increasing, whose changing extent is smaller than N<sub>2</sub>O. Since sodium salts as additive can remove N<sub>2</sub>O effectively and have no large influence on the removal of NO, the effect of sodium salts as additive is the combined effect of the production of active radicals and the removal of HNCO produced by the decomposition of urea through neutralization reactions, which is more important. To achieve the same effect under each condition, the needed addition of NaOH and CH<sub>3</sub>COONa is less than that of Na<sub>2</sub>CO<sub>3</sub>, counting as Na atom. For the decomposition of CH<sub>3</sub>COONa can produce CH<sub>3</sub>COO, its addition can promote the reduction of NO more obviously at the lower temperature than Na<sub>2</sub>CO<sub>3</sub> or NaOH. Overall NO<sub>x</sub> removal efficiency at 900 °C with NSR=1.5 had been improved from about 30% to 70.45% through the addition of sodium salts. Sodium salts as additive caused the flue gas to become alkaline gas, but it was not serious for sodium salts existing as NaNCO.

Key words: NO<sub>x</sub> OUT, Sodium Salts, N<sub>2</sub>O Removal, Overall NO<sub>x</sub> Removal Efficiency, Flue Gas Alkaline

### INTRODUCTION

Nitrogen oxide (NO<sub>x</sub>) pollution is an environmental problem worldwide. It can cause the greenhouse effect, acid rain and destruction of the ozone layer. NO<sub>x</sub> produced from combustion is made of NO mainly, and a little part of which would be NO translated into NO<sub>2</sub> when combustion gases are mixed with air and cooled quickly.

At present, several NO<sub>x</sub> removal processes have been developed, such as selective catalytic reduction (SCR) [1], selective non-catalytic reduction (SNCR), reburning [2], etc. Among them, selective non-catalytic reduction (SNCR) denitrification process is a well-known commercial process for NO<sub>x</sub> control. Besides low cost and ease of combining with other processes, it also takes up small space and has simple facilities, especially suitable for the existing power plants which will carry out renovation [3,4].

There are three most widely used reduction agents: ammonia [5, 6], urea [7,8] as well as ammonium bicarbonate [9]. Because urea exists as stable solid, it has advantages in transportation and storage. Though the main composition of NO<sub>x</sub> in flue gas achieved from combustion of industrial boilers is NO, the amount of N<sub>2</sub>O produced is large in the SNCR process with urea as reduction agent (NO<sub>x</sub>-OUT process). Zhou et al. have performed special research on the generation and emission of N<sub>2</sub>O [10]. So far, many researches have been done on urea as reduction agent [11-13], but N<sub>2</sub>O has not been

taken into consideration or given enough attention. Using additives to improve reaction characteristics of SCNR process has been studied by many scholars; the additives are usually hydrocarbons to De NO<sub>x</sub> process [14,15] and sodium salts to NO<sub>x</sub>OUT process [16-19]. Most studies on the NO<sub>x</sub>OUT process with additives did not consider the detailed effects on N<sub>2</sub>O for its low concentration or explained the effect just from the aspect of active radicals' effect. To reduce N<sub>2</sub>O emissions and enhance NO<sub>x</sub> removal efficiency, the effect of sodium salts (Na<sub>2</sub>CO<sub>3</sub>, NaOH, and CH<sub>3</sub>COONa) as additive to the NO<sub>x</sub>OUT process has been studied in this article. One N<sub>2</sub>O molecule contains two nitrogen atoms, which has a certain influence on the reflection of the total nitrogen content of NO<sub>x</sub> and the utilization rate of reduction agent. To reflect the amount of NO<sub>x</sub> more correctly, besides the concentrations of NO, NO, N<sub>2</sub>O, the concentrations of NO<sub>x1</sub> (NO+NO<sub>2</sub>+N<sub>2</sub>O) and NO<sub>x2</sub> (NO+NO<sub>2</sub>+2N<sub>2</sub>O) that have outstanding importance of N<sub>2</sub>O have been brought into analysis.

### EXPERIMENTAL EQUIPMENT AND TECHNOLOGICAL PRINCIPLES

#### 1. Experimental Equipment

Experiments were conducted in a pilot reactor, as shown in Fig. 1. The reactor is Ø610 mm flue lined with a 300 mm×25 mm corundum tube, which is covered by an aluminum silicate fiber-insulating layer (150 mm thick) and a steel protective layer (5 mm thick) as the outermost layer. The 6 m long reactor is vertically upward for 3 m, and then bends 90° presenting a horizontal trend. The simu-

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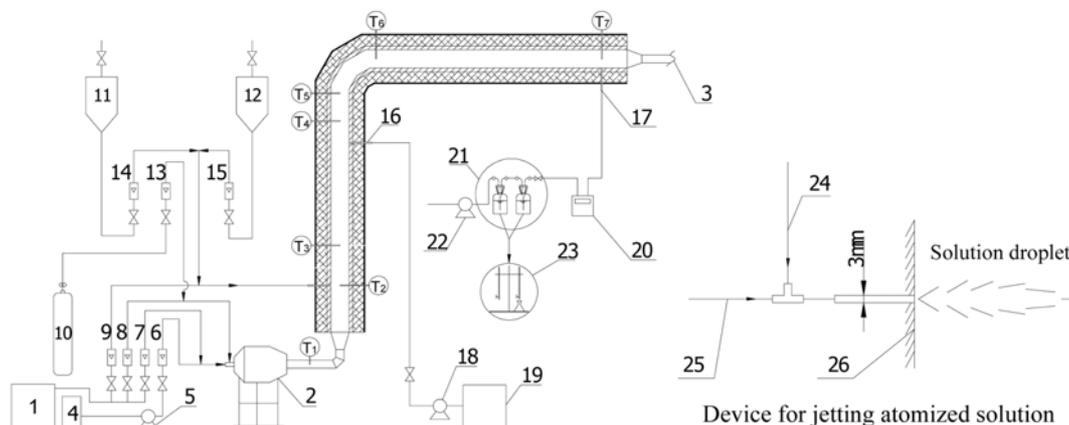


Fig. 1. Structure diagram of experimental table.

- |                          |                                   |  |                           |
|--------------------------|-----------------------------------|--|---------------------------|
| 1. Air compressor        | 8. Burning air                    | 15. Additives solution                 | 22. Vacuum pump 2         |
| 2. Burner                | 9. Carrier air for reducing agent | 16. Sampling point 1                   | 23. Titration device      |
| 3. Outlet of the reactor | 10. Ammonia tank                  | 17. Sampling point 2                   | 24. Solution              |
| 4. Oil tank              | 11. Liquid storage tank 1         | 18. Vacuum pump 1                      | 25. Carrier air           |
| 5. Oil pump              | 12. Liquid storage tank 2         | 19. Gas analyzer                       | 26. Reactor inner surface |
| 6. Oil                   | 13. Ammonia gas                   | 20. Gas meter                          |                           |
| 7. Atomizing air         | 14. Urea solution                 | 21. Alkaline matters collection device |                           |

lated flue gas was generated by an oil burner in front of the reactor with 0# diesel oil as fuel. The temperature of flue gas was controlled by regulating the amount of fuel and burning air, and measured by seven S type thermocouples arranged along the reactor. For the low nitrogen content of 0# diesel oil,  $\text{NO}_x$  concentration of the flue gas achieved from the burning of the oil was much lower than that in conventional utility boilers. To increase the concentration of  $\text{NO}_x$  in flue gas,  $\text{NH}_3$  had been mixed into the burning air to generate  $\text{NO}_x$ , whose production was regulated by the flow rate of  $\text{NH}_3$ .

In the experiments, the concentration of urea solution was 2.1 mol/L, the concentration of sodium salts solution was 2.5 mol/L, and the flow rate of flue gas through the reactor was maintained at 280  $\text{m}^3/\text{h}$ . It has been known that the effect of the process is greatly influenced by the mixing effect of the reduction agent and the main flue gas stream [20-22]. To achieve a better mixing effect, the aqueous solutions of urea and sodium salts were atomized by compressed air before being injected from the nozzle into the flue gas; the atomization effect was good when the amount of atomized air was 4.5  $\text{m}^3/\text{h}$  with the inner diameter of nozzle  $\text{Ø}3$  mm. The flow rates of solutions and compressed air were controlled by flow meters. The concentrations of  $\text{NO}_x$  and flue gas composition were measured by NGA200 type multi-component gas analyzer (Rosemount Company) on-line at sample site 1. The distance between sample site 1 and the nozzle is 2 m (gas's residence time=0.25 s). The alkaline matter in the gas was dissolved by the water in the washing bottle and measured through chemical titration with HCl as neutralization reagent; the gas sample was extracted from sample site 2, which is located 5 m away behind the nozzle.

## 2. Technological Principles of Reactions

Rota et al. [23] had put forward the detailed reaction principles of  $\text{NO}_x$  OUT process, in which the decomposition reactions of urea are as follows:



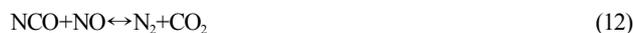
$\text{NH}_3$  and  $\text{NH}_2$  produced from the decomposition of urea reduce  $\text{NO}$  through reactions:



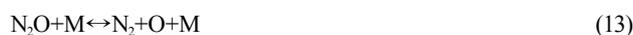
$\text{NH}_3$  will be oxidized to  $\text{NO}$  at higher temperatures:



$\text{HNCO}$  will be converted into  $\text{N}_2\text{O}$  through the following reactions:



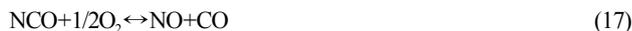
The decomposition reactions of  $\text{N}_2\text{O}$  at higher temperatures are:



From the two reactions above, it can be found that the removal of  $\text{N}_2\text{O}$  mainly depends on the decomposition under higher temperature and the existence of enough active radicals.

$\text{NCO}$  can also be oxidized to  $\text{NO}$  through the following reactions:





The technological principles with Na<sub>2</sub>CO<sub>3</sub> as additive have been explained by some scholars [16] as following reactions:



From the reactions above, they considered that the main effect of Na<sub>2</sub>CO<sub>3</sub> is to raise the concentrations of atoms and radicals, such as O, H, OH etc., which promote NO<sub>x</sub> reduction on the low-temperature side of the optimum temperature.

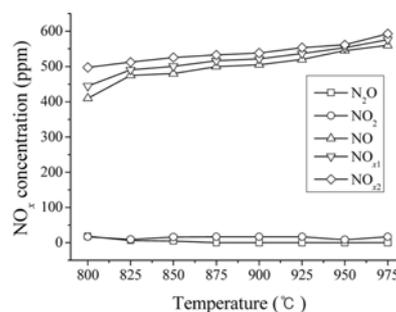
The mechanism and effect of hydrocarbons as additive to the process has a generally accepted conclusion: it extends the temperature window and shifts it towards lower temperature through promoting the production rate of active radicals, but decreases the maximum NO<sub>x</sub> removal efficiency [15].

## RESULTS AND DISCUSSION

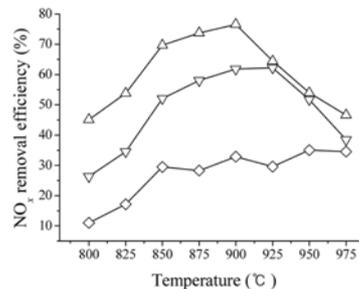
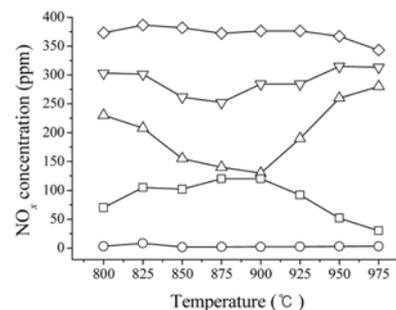
For the heat dissipation of the reactor, the temperature of the reactor declined along the reactor. So the reaction temperature was not a fixed temperature but a temperature section. Since the temperature was controlled by the flow rate of oil, the compositions of flue gas had some difference at different temperatures. The concentrations of main compositions of flue gas under different temperatures are shown in Table 1.

**Table 1. Concentrations of different compositions in the flue gas**

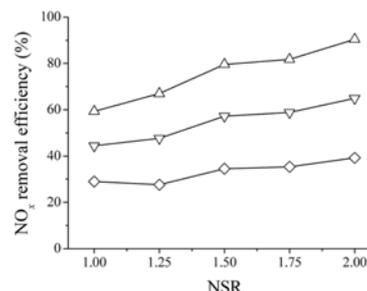
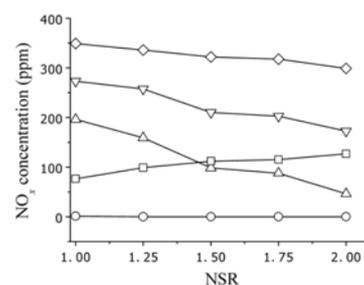
T/°C	Compositions of the flue gas/Volume percentage			
	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>
800-648	11.40	5.13	6.66	76.81
825-675	10.65	5.63	7.42	76.30
850-690	9.96	6.09	7.92	76.06
875-707	9.22	6.59	8.65	75.54
900-720	8.72	6.92	9.07	75.29
925-733	8.25	7.23	9.10	75.42
950-744	7.83	7.51	9.29	75.37
975-765	7.43	7.78	9.45	75.34



(a) Initial NO<sub>x</sub> concentrations of the flue gas



(b) NO<sub>x</sub> concentrations and removal efficiencies at different temperature with NSR=1.5



(c) NO<sub>x</sub> concentrations and removal efficiencies with different NSR at 900°C

**Fig. 2. Initial NO<sub>x</sub> concentrations of the flue gas with 230 L/h NH<sub>3</sub> mixed into burning air and process performance with NSR =1.5 and no additives. □ for N<sub>2</sub>O, ○ for NO<sub>2</sub>; △ for NO, ▽ for NO<sub>x1</sub>, and ◇ for NO<sub>x2</sub>.**

## 1. Without Additive

$\text{NH}_3$  can be oxidized to  $\text{NO}_x$  in combustion [24]. Fig. 2(a) shows the initial  $\text{NO}_x$  concentrations in the flue gas at different temperatures with 230 L/h  $\text{NH}_3$  mixed into the burning air.

As shown in the figure, the amount of  $\text{NO}_2$  and  $\text{N}_2\text{O}$  produced from the oxidization of  $\text{NH}_3$  is low, and the main component of  $\text{NO}_x$  is NO.  $\text{NO}_2$  concentrations were around 16 ppm at different temperatures, and  $\text{N}_2\text{O}$  concentration was 18 ppm at 800 °C, and then decreased to zero when temperature above 850 °C. For the production of thermal  $\text{NO}_x$ , increases with the temperature, the concentration of  $\text{NO}_x$  increases with temperature, but the extent is not significant due to the fuel  $\text{NO}_x$  being the major contributor to  $\text{NO}_x$ . After the flue gas gets out of the burner, it passes through a stainless steel tube, in which there is a mixer made of stainless steel in the tube.  $\text{NH}_3$  will decompose due to the catalytic effect of steel, so no  $\text{NH}_3$  was detected in the initial flue gas and the gas was tested weak acidic through a neutralization titration, which was caused by HNCO produced from the decomposition of urea.

Fig. 2(b) presents the concentrations and  $\text{NO}_x$  removal efficiency at different temperatures with steady normalized stoichiometric ratio of reduction nitrogen to  $\text{NO}_x$  (NSR) 1.5. At the temperature range of 800-975 °C, the amount of  $\text{NO}_2$  is low at all temperatures, and NO concentration decreases at first and then increases as temperature is increasing, while  $\text{N}_2\text{O}$  concentration increases at first and then decreases, and the turning point is 900 °C. At 875 °C and 900 °C,  $\text{N}_2\text{O}$  concentration was high to 120 ppm, which is much higher than the other scholars' research results [8,17,23]. The generation amount of  $\text{N}_2\text{O}$  is greatly affected by oxygen content, humidity and reaction temperature. There are two reasons for the high  $\text{N}_2\text{O}$  concentration: the high oxygen content of the flue gas and the high humidity in the pipe before reduction agent sprayed out. Urea had decomposed to certain extent in the pipe before being injected into the flue gas, which was caused by the high ambient temperature near the reactor, and the same problem also exists in industrial utilities.  $\text{NO}_{x1}$  concentration also shows the similar tendency as NO, while  $\text{NO}_{x2}$  concentration does not change much for the inverse changing tendency of NO and  $\text{N}_2\text{O}$ . At a temperature above 900 °C, NO concentration increases quickly for the effect of the reaction path that the reduction agent oxidized to  $\text{NO}_x$  became large.

In the temperature range of 825-950 °C, NO removal efficiencies are above 50%, and the highest is 76.56% at 900 °C with NSR=1.5. As the existence of  $\text{N}_2\text{O}$ ,  $\text{NO}_{x1}$  removal efficiencies are among 50-60% and the highest  $\text{NO}_{x2}$  removal efficiency is just about 30%. Compared with experimental results with flue gas mixed with some pure gases [17,19,23], the optimum temperature is lower; while compared with experimental results with flue gas generated from combustion [8,12], the reaction temperature is basically consistent. The experimental results of the process with  $\text{NH}_3$  as reduction agent also exist the problem that the optimum temperature with flue gas achieved from combustion is lower than that with flue gas mixed by a kind of pure gas [6,25,26]. Besides the main compositions of gases ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ), there are some trace compositions (hydrocarbon, CO,  $\text{SO}_2$  etc.) in the flue gas resulting from combustion. Just these trace compositions enhance the reaction activity and decrease the reaction temperature. That is, flue gas compositions have relatively large influence on the temperature window of process, so it is necessary to find the particular temperature window and optimal tem-

perature of the special flue gas in the industrial application of the process.  $\text{N}_2\text{O}$  concentrations are lower than 50 ppm when the reaction temperature is above 950 °C, which is also one reason for the higher  $\text{N}_2\text{O}$  concentrations than the other experimental results (whose optimum reaction temperature is higher than 950 °C).

Zamansky et al. [17] studied the variation of  $\text{N}_2\text{O}$  concentration with  $\text{Na}_2\text{CO}_3$  as additive, but the detailed law was not given out for their high temperature window and low  $\text{N}_2\text{O}$  content. At the optimum temperature, a detailed analysis on  $\text{NO}_x$  concentrations with different NSR was carried out. At 900 °C, the concentrations of NO,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_{x1}$ ,  $\text{NO}_{x2}$  in initial flue gas are 482, 9.2, 0, 491.6, and 491.6 ppm respectively. In Fig. 2(c), it shows the concentrations and removal efficiencies of  $\text{NO}_x$  at 900 °C with different NSR.

As NSR increases from 1.0 to 2.0, the removal efficiency of NO increases from 59.27% to 90.46%, while that of  $\text{NO}_{x1}$  and  $\text{NO}_{x2}$  increase from 44.43% to 64.91% and from 28.97% to 39.18% respectively. Compared with the results of Gao [11], NO and  $\text{NO}_2$  removal efficiencies are higher with the same NSR. It can be explained by the atomizing of the solution before being injected into the main flue gas leading to a better mixing. 900 °C is the optimal temperature of the process, and it also the temperature that has the largest generation amount of  $\text{N}_2\text{O}$ , which diminishes  $\text{NO}_x$  reduction performance.

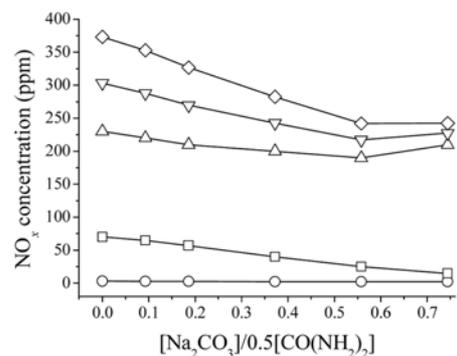
## 2. With Sodium Salts as Additive

$\text{Na}_2\text{CO}_3$ , NaOH, and  $\text{CH}_3\text{COONa}$  were used in the experiments to investigate the influence of sodium salts to the process. The additions of the sodium salts solution were fixed at 2.5 ml/min, 5 ml/min, 10 ml/min, 15 ml/min and 20 ml/min, which are  $1.34 \times 10^{-3}$ ,  $2.68 \times 10^{-3}$ ,  $5.36 \times 10^{-3}$ ,  $8.04 \times 10^{-3}$ ,  $1.07 \times 10^{-2}$  respectively, when counted as (mol/ $\text{Nm}^3$  flue gas) for the total flue gas quantity was maintained at 280  $\text{Nm}^3/\text{h}$ . In the analysis of the experimental results, the additions of sodium salts adopt different expression ways to outstanding different analysis emphases.

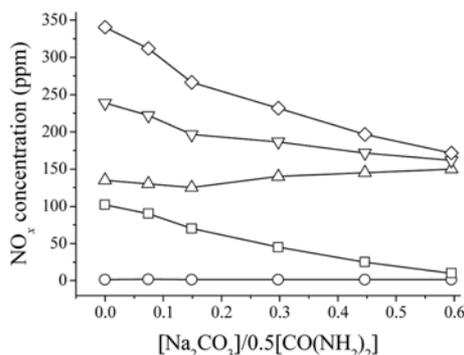
### 2-1. Influence on $\text{NO}_x$ Concentrations

Fig. 3 shows the concentrations of  $\text{NO}_x$  at four typical temperatures with different  $\text{Na}_2\text{CO}_3$  additions and NSR=1.5. The proportional relationship of  $\text{Na}_2\text{CO}_3$  and urea,  $\text{Na}_2\text{CO}_3$  addition is counted as molar ratio of  $\text{Na}_2\text{CO}_3$  to reduction nitrogen, which is  $[\text{Na}_2\text{CO}_3]/0.5[\text{CO}(\text{NH}_2)_2]$ . Because  $\text{NO}_x$  concentration at various temperatures is different as Fig. 2(a) shows,  $[\text{Na}_2\text{CO}_3]/0.5[\text{CO}(\text{NH}_2)_2]$  with same  $\text{Na}_2\text{CO}_3$  addition at different temperatures have a little difference.

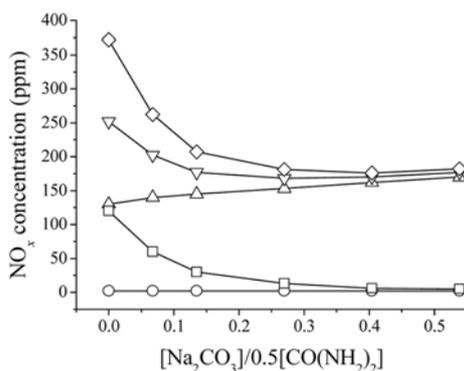
As shown in Fig. 3(a) and Fig. 3(b), NO concentration decreases at first and then increases with the increasing of  $\text{Na}_2\text{CO}_3$  addition at 800 °C and 850 °C, the turning point of addition becomes less with the increasing of temperature. While at 900 °C and 950 °C as Fig. 3(c) and Fig. 3(d) show, NO concentrations increase with the increasing of  $\text{Na}_2\text{CO}_3$  addition, which means  $\text{Na}_2\text{CO}_3$  only reduces  $\text{N}_2\text{O}$  and the active radicals produced from its decomposition reactions go against the removal of NO on the high-temperature side of the optimum temperature. Because 800 °C and 850 °C are lower than the optimum NO reduction temperature (900 °C) and the active radicals under which are not enough,  $\text{Na}_2\text{CO}_3$  as additive can promote NO reduction through increasing the active radicals' concentration before reaching the turning point. If the addition exceeds the turning point, the active radicals' concentration will be larger than NO reduction needed, which is harm to NO removal. The experimental results shown from Fig. 3 also indicate that the optimum



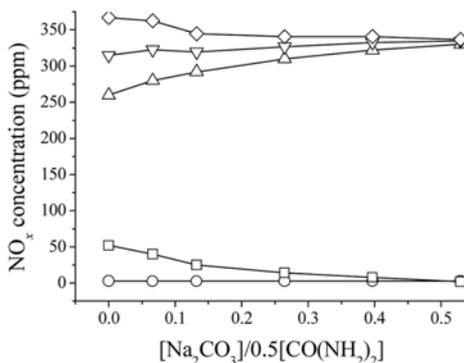
(a) 800 °C



(b) 850 °C



(c) 900 °C

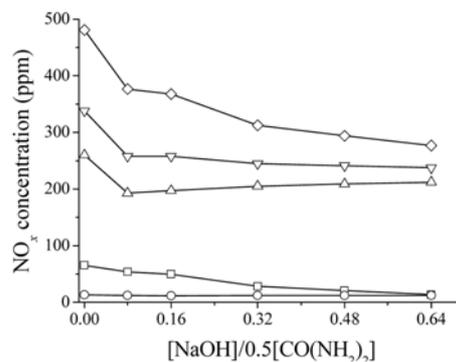


(d) 950 °C

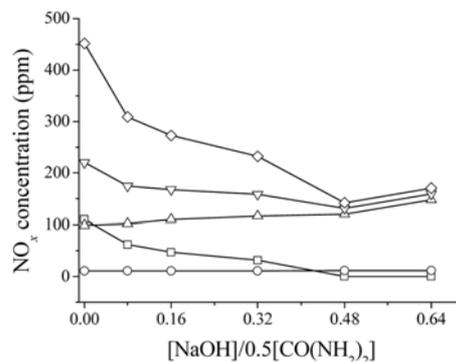
**Fig. 3.** Variation of NO<sub>x</sub> concentrations with different Na<sub>2</sub>CO<sub>3</sub> additions at four typical temperatures with NSR=1.5. Na<sub>2</sub>CO<sub>3</sub> addition is counted as molar ratio of Na<sub>2</sub>CO<sub>3</sub> to reduction nitrogen, □ for N<sub>2</sub>O, ○ for NO<sub>2</sub>; △ for NO, ▽ for NO<sub>x1</sub>, and ◇ for NO<sub>x2</sub>.

temperature for NO reduction is about 900 °C, under which the active radicals to initiate and maintain NO reduction reactions are just enough with no additions.

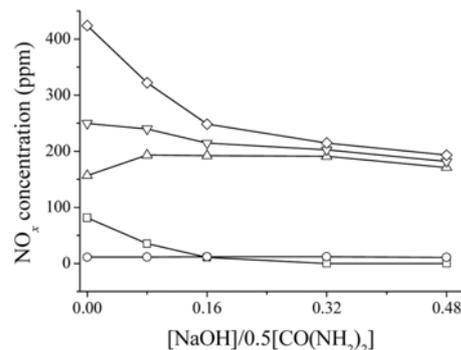
N<sub>2</sub>O concentration decreases as Na<sub>2</sub>CO<sub>3</sub> addition increases and can be decreased to zero if the addition of Na<sub>2</sub>CO<sub>3</sub> is large enough at all temperatures. If we just explain the phenomenon from the production of active radicals, the changing extent of NO is much smaller than that of N<sub>2</sub>O especially under the temperature 850 °C and 900 °C. If the amount of active radicals can cause the decomposition of large amount of N<sub>2</sub>O, it will also affect NO reduction significantly inevitably. So alkaline material, Na<sub>2</sub>CO<sub>3</sub> and radicals produced from its decomposition have taken place neutralization reactions with HNCO



(a) 820 °C

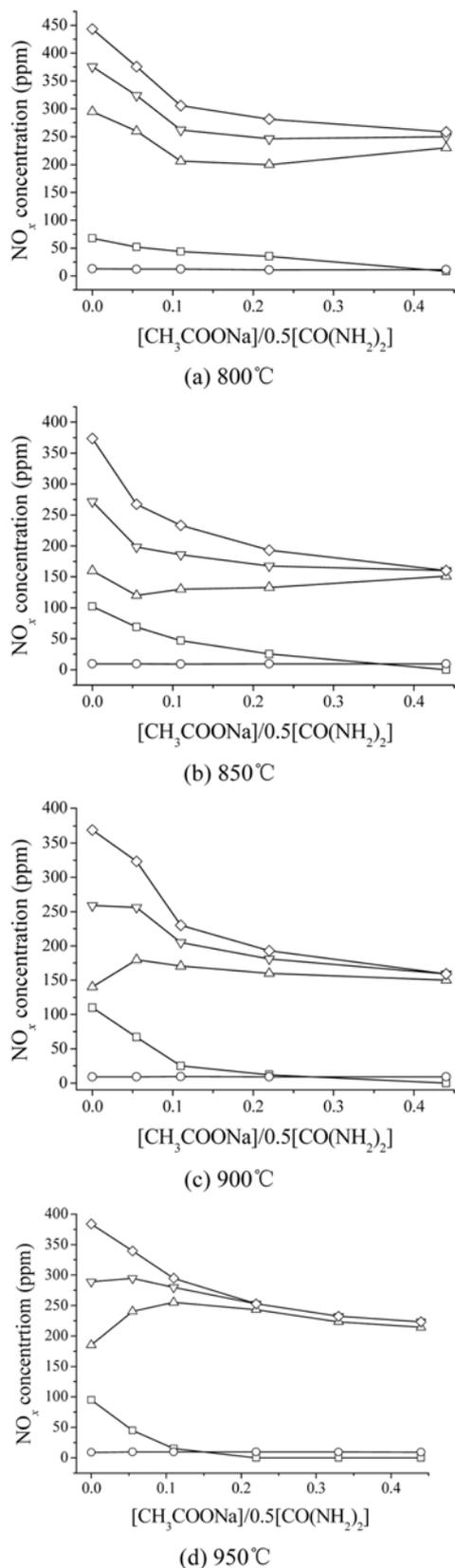


(b) 900 °C



(c) 960 °C

**Fig. 4.** Variation of NO<sub>x</sub> concentrations with different NaOH additions at three typical temperatures with NSR=1.5. NaOH addition is counted as molar ratio of NaOH to reduction nitrogen, □ for N<sub>2</sub>O, ○ for NO<sub>2</sub>; △ for NO, ▽ for NO<sub>x1</sub>, and ◇ for NO<sub>x2</sub>.



**Fig. 5.** Variation of  $\text{NO}_x$  concentrations with different  $\text{CH}_3\text{COONa}$  additions at four typical temperatures with  $\text{NSR}=1.5$ .  $\text{CH}_3\text{COONa}$  addition is counted as molar ratio of  $\text{CH}_3\text{COONa}$  to reduction nitrogen,  $\square$  for  $\text{N}_2\text{O}$ ,  $\circ$  for  $\text{NO}_2$ ,  $\triangle$  for  $\text{NO}$ ,  $\nabla$  for  $\text{NO}_{x1}$ , and  $\diamond$  for  $\text{NO}_{x2}$ .

produced from decomposition of urea as reaction Eq. (30) to Eq. (32) show, which avoids the generation of  $\text{N}_2\text{O}$ .



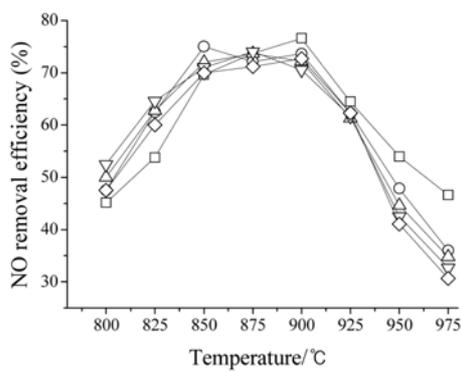
The reaction above is the main path for  $\text{N}_2\text{O}$  removal. According to the reactions as Eq. (11) and Eq. (12) show, the avoiding of one molecular  $\text{N}_2\text{O}$ 's generation will cause one molecular  $\text{NO}$  can't be removed. So the variation of  $\text{NO}$  concentration is the combined effect of active radicals and the removal of  $\text{HNCO}$  through neutralization reactions, which caused the little change of  $\text{NO}$  concentration under  $850^\circ\text{C}$  and  $900^\circ\text{C}$ . It also can explain that  $\text{NO}$  concentration increases when the addition of  $\text{Na}_2\text{CO}_3$  is too large, which is caused by the removal of large amount of  $\text{HNCO}$  at  $800^\circ\text{C}$  and  $850^\circ\text{C}$ . At  $950^\circ\text{C}$ , the increasing extent of  $\text{NO}$  is larger than the decreasing extent of  $\text{N}_2\text{O}$ , so the function of the active radicals is larger enough to have an adverse effect on  $\text{NO}$  reduction. As shown from the concentration of  $\text{NO}_{x1}$  and  $\text{NO}_{x2}$  at  $800^\circ\text{C}$  and  $900^\circ\text{C}$ , the optimal additions of  $\text{Na}_2\text{CO}_3$  are, respectively, 0.55 and 0.40, while it doesn't reach the optimal additions at  $850^\circ\text{C}$  and  $950^\circ\text{C}$ .

Fig. 4 shows the concentrations of  $\text{NO}_x$  at three typical temperatures with different  $\text{NaOH}$  additions and  $\text{NSR}=1.5$ . The effect of  $\text{NaOH}$  is similar to  $\text{Na}_2\text{CO}_3$ , and the addition counted as  $\text{Na}$  atom was much fewer with the same effect. According to the mechanism introduced above,  $\text{NaOH}$  has participated in the reactions as  $\text{Na}_2\text{CO}_3$  except Eq. (18). In contrast to  $\text{Na}_2\text{CO}_3$ , the participation of  $\text{NaOH}$  in the reaction system is more direct and does not have the problem of decomposition equilibrium, so its needed addition counted as  $\text{Na}$  atoms is fewer to get the same effect.

Fig. 5 shows the concentrations' variation of  $\text{NO}_x$  at four typical temperatures with different  $\text{CH}_3\text{COONa}$  additions and  $\text{NSR}=1.5$ . Besides smaller addition than  $\text{Na}_2\text{CO}_3$ , there is a significant difference from the two other sodium salts that the enhancement to  $\text{NO}$  reduction at lower temperature was more obvious (especially at  $800^\circ\text{C}$ ). The decomposition of  $\text{CH}_3\text{COONa}$  at high temperature will produce  $\text{CH}_3\text{COO}$ , which also has participated in the reactions as a hydrocarbon. Hydrocarbon as additive can produce active radicals to improve  $\text{NO}$  reduction on the low-temperature side of the optimum temperature, but it does not influence the removal of  $\text{N}_2\text{O}$  significantly, which verifies the point that  $\text{N}_2\text{O}$  was not mainly removed through its decomposition but the removal of  $\text{HNCO}$ .

## 2-2. Influence on $\text{NO}_x$ Removal Efficiency

Fig. 6 shows  $\text{NO}_x$  removal efficiency at different temperatures with different  $\text{Na}_2\text{CO}_3$  additions and  $\text{NSR}=1.5$ .  $\text{Na}_2\text{CO}_3$  addition is counted as mole value  $\text{Na}_2\text{CO}_3$  per  $\text{Nm}^3$  flue gas. From Fig. 6(a), it can be found that  $\text{Na}_2\text{CO}_3$  as additive increases  $\text{NO}$  removal efficiency at lower temperature and decreases it at higher temperature, but the effect is not very obvious and the variation of  $\text{Na}_2\text{CO}_3$  addition also has little influence. As shown in Fig. 6(b), adding  $\text{Na}_2\text{CO}_3$  can enhance the removal of  $\text{NO}_{x1}$  obviously, and  $\text{NO}_{x1}$  removal efficiency increases as  $\text{Na}_2\text{CO}_3$  addition is increased. As shown in Fig. 6(c), adding  $\text{Na}_2\text{CO}_3$  raises  $\text{NO}_{x2}$  removal efficiency significantly and  $\text{NO}_{x2}$  removal efficiency increases obviously with the increasing of  $\text{Na}_2\text{CO}_3$  addition. In all, the main function of  $\text{Na}_2\text{CO}_3$  as additive is that of reducing  $\text{N}_2\text{O}$  emission and having a little effect on  $\text{NO}$  re-



(a) NO

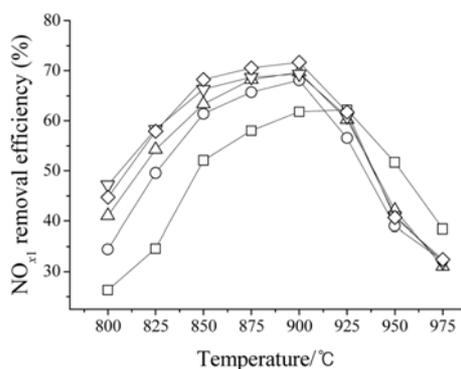
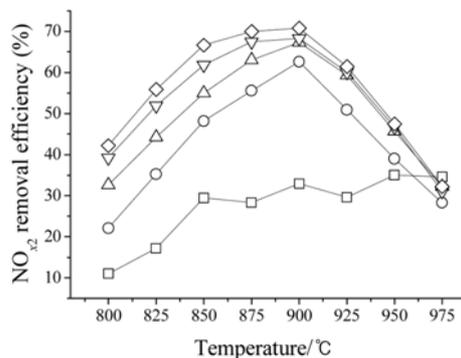
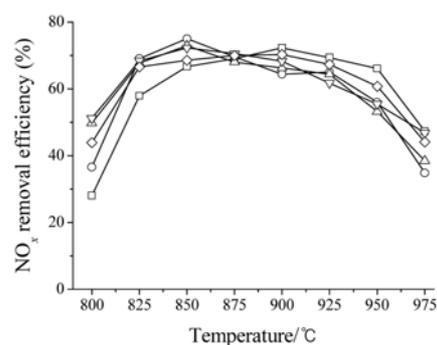
(b) NO<sub>x1</sub>(c) NO<sub>x2</sub>

Fig. 6. NO<sub>x</sub> removal efficiencies with different Na<sub>2</sub>CO<sub>3</sub> addition at different temperatures and with NSR=1.5. Na<sub>2</sub>CO<sub>3</sub> addition is counted as mole per Nm<sup>3</sup> flue gas, □ for 0, for ○ for 2.68 × 10<sup>-3</sup>, △ for 5.36 × 10<sup>-3</sup>, ▽ for 8.04 × 10<sup>-3</sup>, and ◇ for 1.07 × 10<sup>-2</sup>.

duction, but it greatly promotes the overall NO<sub>x</sub> removal.

Fig. 7 shows NO<sub>x</sub> removal efficiency at different temperatures with different CH<sub>3</sub>COONa addition and NSR=1.5. In contrast to Na<sub>2</sub>CO<sub>3</sub> as additives, the improvement to NO removal efficiency at lower temperatures is much larger as Fig. 7(a) shows. With enough, NO<sub>x2</sub> removal efficiencies are maintained above 60% under the temperature of 825 °C-950 °C with CH<sub>3</sub>COONa addition 1.07 × 10<sup>-2</sup> mol/Nm<sup>3</sup>. It can be concluded that the effect of hydrocarbon is larger than sodium salts on the aspect of producing active radicals, while sodium salts can enhance overall NO<sub>x</sub> removal efficiency significantly through the removal of N<sub>2</sub>O.



(a) NO

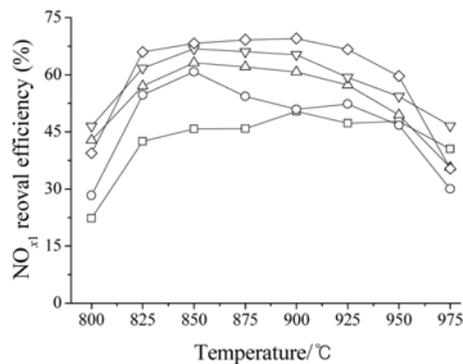
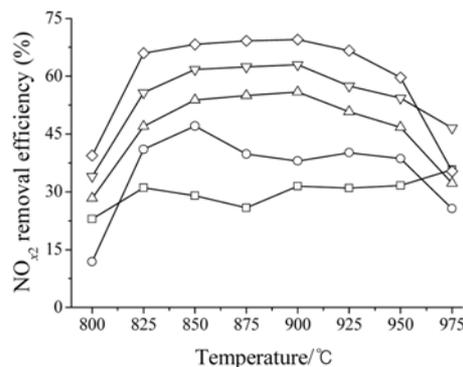
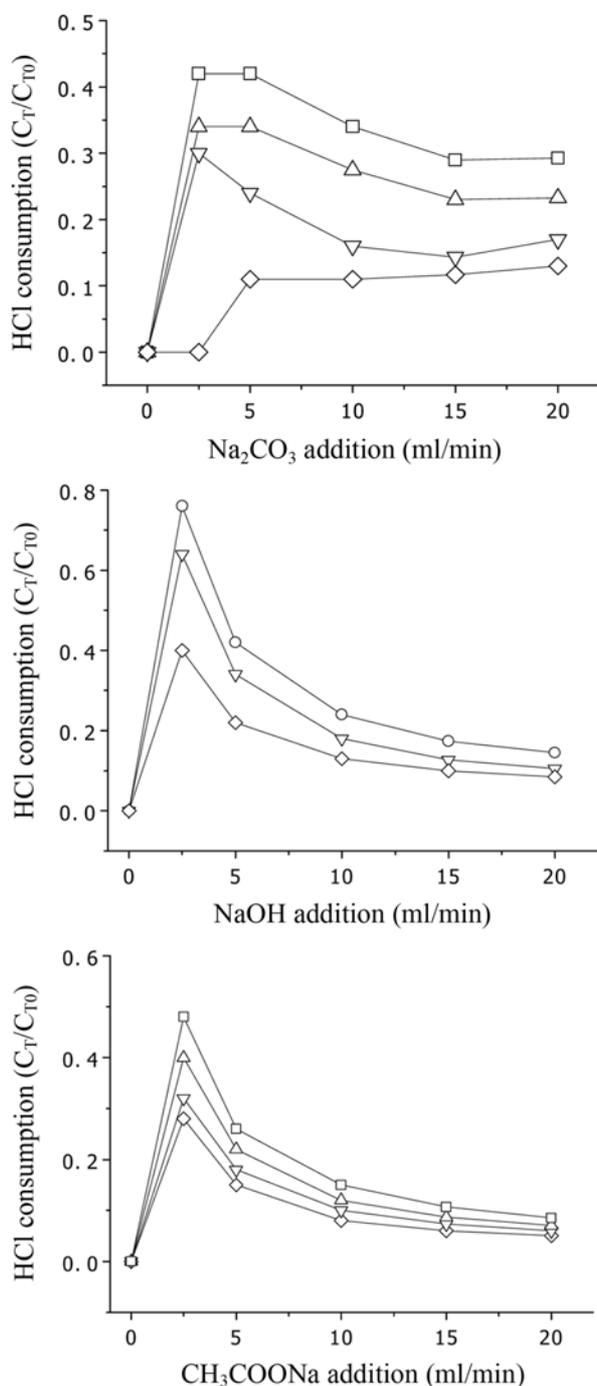
(b) NO<sub>x1</sub>(c) NO<sub>x2</sub>

Fig. 7. NO<sub>x</sub> removal efficiencies with different CH<sub>3</sub>COONa addition at different temperatures and with NSR=1.5. CH<sub>3</sub>COONa addition is counted as mole value per Nm<sup>3</sup> flue gas, □ for 0, ○ for 2.68 × 10<sup>-3</sup>, △ for 5.36 × 10<sup>-3</sup>, ▽ for 8.04 × 10<sup>-3</sup>, and ◇ for 1.07 × 10<sup>-2</sup>.

### 2-3. Influence on Acidity and Alkalinity of Flue Gas

Although adding sodium salts can reduce N<sub>2</sub>O concentration to a great extent, adding alkaline material will also make the flue gas alkaline. Flue gas alkaline is caused by leaked NH<sub>3</sub> [27] and sodium salts contained. To survey the alkaline matters, 20 L flue gas was extracted from sample site 2 and washed by the subsequent washing bottle to dissolve the alkaline matters under different experimental conditions. Then the washing liquid was neutralized with 0.001 mol/L hydrochloride, whose consumption (C<sub>T</sub>) was used to reflect the content of the alkaline matter in 20 L flue gas. It is known by calculation that the theoretical consumptions (C<sub>T0</sub>) of hydrochloride to convert the sodium salts contained in 20 L flue gas into NaCl



**Fig. 8.** The ratio of HCl consumption at typical temperatures with different sodium salts additions to the theoretical HCl consumption of sodium salts fed to the flue gas.  $C_T$ : the consumption of HCl to neutralize alkaline matter contained in 20 L flue gas under certain reaction conditions;  $C_{T0}$ : the theoretical consumption of HCl to convert the sodium salts contained in 20 L flue gas into NaCl completely under certain reaction conditions. The concentration of hydrochloric acid solution is 0.001 mol/L; NSR=1.5; and  $\square$  for 800 °C;  $\circ$  for 820 °C;  $\triangle$  for 850 °C;  $\nabla$  for 900 °C;  $\diamond$  for 950 °C.

completely are two times of Na<sub>2</sub>CO<sub>3</sub> addition and equal to NaOH and CH<sub>3</sub>COONa addition in values when their addition is counted

as ml/min. So the addition of the sodium salts is counted as ml/min in the analysis of the consumption of HCl. Fig. 8 shows the ratio of  $C_T$  to  $C_{T0}$  at certain temperatures with different sodium additions.

As shown above, the consumptions of HCl are all lower than the calculated value, which suggests that part of sodium salts exists as NaNCO in the treated flue gas. This is because one molecule of Na<sub>2</sub>CO<sub>3</sub> contains two molecule Na atoms, whose  $C_T/C_{T0}$  value is much less than the two others under the same conditions. The reason for the much larger consumption of HCl for Na<sub>2</sub>CO<sub>3</sub> as additive than the two others is that it has low decomposition rate at high temperatures. Since hydrocarbon as additive can significantly decrease NH<sub>3</sub> slips, the  $C_T/C_{T0}$  value with CH<sub>3</sub>COONa as additive is less than that with NaOH as additive obviously, though they all have one Na atom per molecule.

Except that Na<sub>2</sub>CO<sub>3</sub>' addition is larger than 15 ml/min or under reaction temperature 950 °C, the  $C_T/C_{T0}$  values decrease with the increasing of all the sodium salts additions under the same temperature. When the additive's concentration is increased with other conditions unchanged, the amount participating in the reaction system increases while the ratio participating in the reaction system decreases, which caused the main changing trend of  $C_T/C_{T0}$  with additives' addition. When Na<sub>2</sub>CO<sub>3</sub>' addition is larger than 15ml/min or under reaction temperature 950, the amount of new added Na<sub>2</sub>CO<sub>3</sub> reacts with NCO or HNCO to produce stable NaNCO becoming less for NCO and HNCO that has been absorbed basically already or their production becoming less for too high temperature.

With same sodium salts' addition, the consumption of HCl and the value of  $C_T/C_{T0}$  decreases with increasing of the temperature, which is caused by more full reactions between the reactants for the higher reaction rate under higher temperature.

## CONCLUSION

Through the experimental study of SNCR process with urea as reduction agent and sodium salts as additive on a pilot experimental rig, some characteristics of the process and its theoretical explanations have been given.

At the temperature range of 800-975 °C without additives, NO concentration decreases first and then increases, while N<sub>2</sub>O concentration increases at first and then decreases as temperature increases with the same NSR; the turning point is 900 °C. With the increasing of NSR, NO removal efficiency increases, and the amount of N<sub>2</sub>O produced also increases at a certain temperature. Without additive, NO removal efficiency is high to 90.46% with NSR=2.0 at the optimum reaction temperature of 900 °C, but overall NO<sub>x</sub> removal efficiencies are much lower for the production of large amount of N<sub>2</sub>O. Because the flue gas used in the experiments results from the combustion of 0# diesel oil instead of a mixer of some pure gases, the results are close to industrial application.

With sodium salts as additive, NO concentrations decrease at first and then increase at low-temperature side of the temperature window, and increase all the time at high-temperature side of the temperature window with increasing of salts' addition. N<sub>2</sub>O concentrations keep decreasing with increasing of salts' addition in the temperature window. Counted as Na atoms, the addition of NaOH and CH<sub>3</sub>COONa needed to get the same effect on the removal of N<sub>2</sub>O is much fewer than Na<sub>2</sub>CO<sub>3</sub>. In contrast to Na<sub>2</sub>CO<sub>3</sub> and NaOH, CH<sub>3</sub>

COONa can extend the temperatures through improving NO<sub>x</sub> removal efficiency at lower temperature obviously, which is caused by CH<sub>3</sub>COO it contains. Totally, addition of sodium salts has much larger effect on the removal of N<sub>2</sub>O than NO. So besides the increasing of the active radicals' production rate, the neutralization reaction between sodium salts and HNCO produced from the decomposition of urea has an important effect on the removal of N<sub>2</sub>O. Through the addition of sodium salts, overall NO<sub>x</sub> removal efficiencies achieved in the temperature range of 825 °C to 950 °C are above 50% and the highest at optimum temperature is above 70%.

Sodium salts as additive increased the alkalinity of flue gas, but it's not serious for sodium salts existing as NaNCO.

#### ACKNOWLEDGEMENTS

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