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Experiment on NO_x reduction by advanced reburning in cement precalciner

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ABSTRACT

Experiment on NO_x reduction by advanced reburning in cement precalciner was performed on a laboratory-scale circulating fluidized bed reactor. In reburning zone, the order of the adsorption ability on CaO surface is $CO_2 > NO > CO$, CO_2 occupies a large fraction of the active sites to inhibits NO reduction by CO, the decrement of NO reduction rate is about 35% when CO_2 increases from 15% to 30%, and the increment of NO reduction rate is about 40% when temperature increases from 850 °C to 1050 °C. In SNCR zone, CO_2 concentration has an optimal range (25–27%) due to the competitive adsorption of CO_2 and NH_3 and the formation of $(NH_2)_2CO$ on CaO surface, the optimal temperature range becomes narrow (850–975 °C) in comparison with that in utility boiler, the optimal concentration of O_2 is in the range of 2% to 3.3%, and NO reduction rate reaches above 75% at 900–970 °C.

1. Introduction

Cement is one of the most produced materials around the world, and its production is a significant nitrogen oxides (NO_x) emission source. China is the largest cement producing and consuming country in the world, the cement industry contributes to 11% of the total NO_x emission in China [1,2].

The dry process cement kiln with preheater and precalciner is the most widespread cement production style, and the schematic diagram is provided in Fig. 1. The process has two combustion zones (i.e., rotary kiln and precalciner), and most often coal is used as a fuel. At the outlet of rotary kiln, about 40% coal is injected into rotary kiln combustion zone, the flue gas temperature is usually greater than 1700 °C, and thus thermal NO_x dominates NO_x formation in the combustion zone of a rotary kiln due to the temperature well above 1400 °C [3–5]. The secondary combustion zone is precalciner, about 60% coal is injected at the bottom of precalciner, the flue gas temperature is in the range of 870–1050 °C, and thus fuel NO_x dominates NO_x formation in the combustion zone. In the dry process cement kiln with preheater and precalciner, NO_x emission can reach 800–1300 mg/m³. Increasingly stringent standard imposed on NO_x emissions results in a greater effort to develop novel NO_x reduction approaches.

High temperature is necessary for the required clinkering reactions to take place in the cement rotary kiln, and thus NO_x control technologies are difficult to be effectively applied in the rotary kiln. Precalciner is considered as the most suitable zone for low- NO_x control technologies (e.g., staged combustion and selective non-catalytic reduction

(SNCR)) because of its appropriate configuration and temperature distribution (870–1050 $^\circ$ C) [5].

In order to effectively reduce NO_x emission in the dry process cement kiln with preheater and precalciner, when the rotary kiln exhaust gas containing large amount of NOx (about 1000 ppm) enters into the precalciner, coal can used as reburning fuel to be injected into the exhaust gas from the precalciner bottom, and this creates a reducing environment to effectively promote NO_x reduction (see Fig. 1); the hightemperature tertiary air (about 900 °C) drawn from the clinker cooler is divided into two parts, one part of tertiary air is introduced into reburning zone to promote the proper reducing environment for NO_x control, the other part of tertiary air used as over fire air (OFA) is introduced into burnout zone to complete fuel burnout (see Fig. 1); the precalciner is considered as the most suitable zone for SNCR deNO_x because of its appropriate temperature distribution (870-1050 °C) and enough residence time for mixing and reaction. SNCR process is the injection of ammonia in the form of ammonia water or urea into the flue-gas at a suitable temperature [6]. SNCR removes NO_x by a two step process, as follows:

$$4NO + NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
 (1)

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$$
 (2)

Above two equations suggest that SNCR can function best in an oxidizing atmosphere, thus ammonia can be injected above OFA (see Fig. 1).

In Fig. 1, it combines aspects of coal reburning with SNCR, and the

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Fig. 1. Principle of advanced reburning in dry process cement kiln with preheater and precalciner.

Table 1

The comparison of utility boiler and cement precalciner for advanced reburning system [3,4,7,8].

Туре	Utility boiler	Precalciner kilns system
Reburning rate	10–28% of the total heat input	About 60% of the total heat input
CO ₂ concentration	About 15%	15-30%
CaO concentration	Negligible	1 kg (CaO)/m ³ (flue gas)
Temperature	1200–1600 °C	870–1050 °C
OFA temperature	20–200 °C	About 900 °C

method of NO_x reduction is advanced reburning (AR) [7]. The Energy and Environmental Research Corporation demonstrated that advanced reburning could potentially provide up to 85–90% NO_x reduction and was suitable for retrofit applications in coal-fired utility boiler [7,8]. However, the advanced reburning of the precalciner kilns system is different from that of utility boiler, and the differences are shown in Table 1.

As known from Table 1, the concentrations of CaO particle and CO_2 in the cement precalciner can be as high as 1 kg (CaO)/m³(flue gas) and 20–30%, respectively [9,10]. Some researchers found that CO_2 inhibited NO reduction by CO/CH₄ in the absence of O_2 over CaO catalyst [11,12]. Although many researchers investigated the effects of CO_2 and CaO on NO_x reduction in coal-fired fluidized bed [13–17], the temperature and the concentrations of CO_2 and CaO in the cement precalciner are greater than those in coal-fired fluidized bed, and few researchers have investigated SNCR deNO_x in cement precalciner [18]. The efficiency of SNCR deNO_x in cement precalciner ranged from 15% to 80% [5], which indicates that SNCR deNO_x process used cement precalciner is more complex and different from those used in the utility boilers. Thus, the advanced reburning of cement precalciner needs further study.

The objective of the present study is to investigate the influences of high concentrations of CO_2 and CaO on NO_x reduction by advanced reburning and to optimize the operating parameters of cement precalciner.

2. Experimental

The advanced reburning in cement precalciner for NO_x reduction was evaluated with a laboratory-scale circulating fluidized bed reactor. The experimental system schematic is shown in Fig. 2. The reactor was made of quartz tube with inner diameter of 5.3 cm and height of 4.3 m, and it was inserted into the constant-temperature zone of an electric furnace. The particle size of CaO varied from 125 µm to 150 µm with the mean diameter of 137 µm, its concentration was 1 kg (CaO)/m³ (flue gas), CaO particles suspended in the quartz tube, the simulated



Fig. 2. Schematic of fluidized bed experimental system.

flue gas (NH₃, NO, O₂, CO and CO₂) was supplied by gas cylinders, and the flow rate of flue gas was 6L/min. Gas concentrations were adjusted by mass-flow controllers, and gases were mixed in a gas mixer. The gas mixture went through liquid H₂O contained in a bottle, the relative humidity and temperature of gas mixture at the outlet was 84% and 32 °C, respectively. The gas was analyzed with a portable FTIR gas analyzer (GasmetTM DX4000), the portable sampling unit was equipped with a ZrO₂ sensor for accurate measurement of oxygen, and the maximum relative error for the measured species was 5%. In cement kiln, the largest fraction of nitrogen oxides is NO, it accounts for 95% [5]. In the experiment, NO₂ emission is less than 5 ppm, thus it is not considered in the study. NO reduction efficiency was calculated:

$$\eta_{\rm NO} = \frac{C_{\rm NO,in} - C_{\rm NO,out}}{C_{\rm NO,in}} \times 100\%$$
 (3)

where η_{NO} was the NO reduction rate, $C_{\text{NO,in}}$ and $C_{\text{NO,out}}$ (ppm)were the inlet and outlet concentrations of NO, respectively.

3. Results and discussion

3.1. NO reduction by CO in fuel reburning zone

In the reburning zone of cement precalciner, coal releases the reducing gases (e. g., CH_4 , CO and H_2) from volatile to reduce NO_x produced in the primary combustion zone (see Fig. 1). However, CH_4 cannot reduce NO_x at about 900 °C [11], and H_2 is very active and rapidly oxidized at the bottom of precalciner due to 2–3% O_2 in the rotary kiln exhaust gas. It was found that CO had high NO_x reduction rate, and the reduction rate increased from 38 to 81% with the increase of temperature from 800 °Cto 1100 °C [19]. In coal reburning zone, CO concentration can reach about 5%. At 870–1050 °C of the reburning zone, the reducing capacity of char and hydrocarbon gas is much lower than CO. Thus, in the study, only CO is considered to reduce NO in the reburning zone of cement precalciner with high concentrations of CaO and CO_2 .

3.1.1. The effects of CO_2 concentration and temperature on NO reduction

Fig. 3 shows the effects of CO_2 concentration and temperature on NO reduction by CO in the presence/absence of CaO at 4% CO, 0% O_2 and 1000 ppm NO. In the absence of CaO, NO reduction rate slightly decreases with the increase of CO_2 concentration at a given temperature, and the maximal decrement occurs at 1050 °C, where the decrement is only 8.6% when CO_2 increases from 15% to 30%. However, temperature has notable influence on NO reduction rate, and the increment of NO reduction rate is more than 50% when temperature increases from 850°Cto 1050 °C.

In the presence of CaO, both CO_2 concentration and temperature have notable influences on NO reduction rate, the decrement of NO reduction rate is about 35% when CO_2 increases from 15% to 30%, and the increment of NO reduction rate is about 40% when temperature



Fig. 3. The effects of CO₂ concentration and temperature on NO reduction by CO.

increases from 850°Cto 1050°C. As known from the comparison between Fig. 3(a) and (b), CaO significantly catalyses NO reduction by CO, particularly when CO₂ concentration is low. NO reduction rate can reaches 94.3% at 1050°C and 15% CO₂. However, increasing CO₂ concentration apparently weakens CaO catalysis of NO reduction by CO, and the catalysis is inhibited by CO₂. In the presence of CaO, the influence of temperature on NO reduction rate is similar to that in the absence of CaO (see Fig. 3).

In order to analyze CaO catalysis of NO reduction by CO, based on periodic density functional theory (DFT), the adsorption energies of CO₂, CO and NO on the most stable sites of CaO (1 0 0) surface are calculated using the program package Cambridge Sequential Total Energy Package (CASTEP) with a plane wave basis set in the Materials Studio software [20,21], and the computation results are provided in Table 2, where a negative value of adsorption energy indicates an exothermic chemisorption process [21,22]. As known from Table 2, the species of CO₂, CO and NO easily adsorb on CaO surface, the order of the adsorption ability on CaO (1 0 0) surface is CO₂ > NO > CO. Dam-Johansen proposed the catalytic reaction mechanism of NO reduction by CO over CaO surface [12]:

$$NO + * \rightleftharpoons NO_{ads}$$
 (R1)

 $NO_{ads} + CO \rightleftharpoons NO \cdot CO_{ads}$ (R2)

$$NO \cdot CO_{ads} \approx CO_2 + N_{ads}$$
 (R3)

$$N_{ads} \rightarrow N_2 + 2*$$
 (R4)

where * represents active sites on CaO surface. The adsorption energy of CO over clean CaO surface is -0.465 ev, but the energy adsorption over CaO surface adsorbing NO is -1.14 ev. This means that NO adsorption over CaO surface can enhance CO adsorption to promote NO reduction by CO through (R1)–(R4). However, compared to CO and NO, CO₂ easily adsorbs on CaO surface to occupy a large fraction of the active sites, and thus increasing CO₂ concentration accelerates CaO deactivation and significantly weakens CaO catalysis of NO reduction by CO (see Fig. 3(b)).

Table 2						
Computed adsorption	energies on	the most	stable sit	tes on C	CaO (1 0	0) surface.

Species	Bond length(Å)	Adsorption energies (ev)
CO ₂	1.394	- 1.79
CO	1.371	- 0.465
NO	1.443	- 0.78



Fig. 4. The effect CO concentration on NO reduction.

3.1.2. The effect of CO concentration on NO reduction

Fig. 4 shows the effect of CO concentration on NO reduction rate in the presence CaO. NO reduction rate increases from 3.6% to 47.5%when CO concentration increases from 1% to 5%. Dam-Johansen found that, when CO₂ was absent, NO reduction rate was almost independent of CO concentration between 2 and 6 vol% [12]. In Dam-Johansen's experiment, NO reduction reaction lasted for 300 s, NO had enough time to react with CO, and thus the effect of CO concentration on NO reduction was negligible in his experiment. However, in practice the residence time in the reburning zone of cement precalciner is less than 1 s, the reaction rate of NO reduction by CO is definite, CO concentration has significant influence on NO reduction rate for the limited reaction time. Li found that NO reduction depended on the combined effects of H and CO, increasing CO concentration could excite the formation of free-radical H to enhance NO reduction [19]:

$$OH + CO = CO_2 + H \tag{R5}$$

$$3NO + H + CO + NH = CO_2 + 2N_2 + 2OH$$
 (R6)

Therefore, NO reduction greatly depends on CO concentration in the reburning zone of cement precalciner.

3.2. NO reduction by NH_3 in SNCR zone

3.2.1. The influence of O_2 on NO reduction by NH_3

Fig. 5 shows the influences of O_2 concentration and temperature on NO reduction rate in SNCR system at 25% CO₂, 1000 ppm NO and NH₃/NO molar ratio = 1. As known from Fig. 5(a), in the absence of CaO, the influence of O_2 concentration on NO reduction rate predominates over that of temperature in the experiment, O_2 has complex effect on



Fig. 5. The effects of O_2 concentration and temperature on NO reduction by NH_{32}

NO reduction, and there are two competitive reactions between reducing NO and oxidizing NH₃:

 $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (R7)

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{R8}$$

At a given temperature, when O_2 concentration is low, increasing O_2 concentration is conducive to NO reduction reaction by reaction (R7), but too high O_2 concentration promotes NO formation by R8. Therefore, in the absence of CaO, there is optimal range of O_2 concentration ($O_2 = 1-2\%$), where NO reduction rate reaches 93–97% at 900–970 °C.

Since temperature and the concentrations of O_2 and CO_2 have complex effects on NO_x reduction in SNCR system of cement precalciner, in order to optimize the operating conditions for NO_x reduction, variable intervals of O_2 and CO_2 concentrations and temperature were 0.2% and 20 °C, respectively. The experimental data on NO_x reduction rate were discrete to draw the contour (see Figs. 5 and 6).

Compared to Fig. 5(a) in the absence of CaO, in the presence of CaO, CaO has the inhibition effect on NO reduction in SNCR system (see Fig. 5(b) and (c)) when O_2 concentration is greater than 0.4%, the maximal NO reduction rate only reaches about 75%, and the optimal O_2 concentration is 2–3.2% at 900–970 °C.

The main mechanism of CaO catalysis in the SNCR $deNO_x$ process is summarized as follows [18,23]:

 $NH_{3(g)} \rightarrow NH_{3(ad)}$ (R9)

 $NH_{3(ad)} \rightarrow NH_{2(ad)} + H$ (R10)

 $4NH_{3(ad)} + O_{2(ad)} \rightarrow 4NH_{2(ad)} + 2H_2O$ (R11)

 $NH_{2(ad)} + NO_{(ad)} \rightarrow N_2 + H_2O$ (R12)

 $NH_{2(ad)} + O_{2(ad)} \rightarrow NO + H_2O$ (R13)

In above reaction mechanism, the first step is NH_3 adsorption on the CaO surface by R9. Afterwards, NH_3 dissociates to NH_2 by hydrogen removal reaction of R10. In the presence of O_2 , the adsorbed O_2 greatly promotes the dissociation of NH_3 to NH_2 on CaO by reaction R11. R12 and R13 are competitive reactions. When O_2 concentration is less than 0.4%, NO reduction of R12 predominate over NH_2 oxidization of R13, thus CaO has the catalytic effect of NO reduction on its surface (see Fig. 5(c)); with further increase of O_2 concentration, R13 gradually strengthens, NH_2 oxidization predominates over NO reduction, the inhibition effect of NO reduction is most noticeable when O_2 concentration is 0.7–1.7%; when O_2 concentration is greater than 1.8%, gaseous phase reaction rate of R7 increases, the catalytic effect of CaO on NH_3 oxidization is weakened (see Fig. 5(c)).

Although CaO inhibits NO reduction in SNCR system at $O_2 > 0.4\%$, the gaseous reduction reactions is dominant, and NO is finally reduced in SNCR system of cement precalciner (see Fig. 5(b)). In the presence of CaO, due to the heterogeneous-phase competitive catalytic reactions (R12) and (R13) and the gaseous-phase competitive reactions (R7) and (R8) for reducing NO and oxidizing NH₃, there is an optimal O₂ concentration range (O₂ = 2 ~ 3.3%), where NO reduction rate reaches above 75% at 900–970 °C.

3.2.2. The influence of CO_2 on NO reduction by NH_3

Fig. 6 shows the influences of CO₂ and temperature on NO reduction in SNCR system at 850–1050 °C, 3% O₂, 1000 ppm NO and NH₃/NO molar ratio = 1. In the presence of CaO, CO₂ has an optimal concentration range (CO₂ = 25–27%) for NO reduction, the optimal temperature range becomes narrow (T = T = 850–975 °C) in comparison



Fig. 6. The effects of CO2 concentration and temperature on NO reduction by NH3.

with that in the absence of CaO, and CaO inhibits NO reduction.

In the absence of CaO, NO reduction rate decreases with the increase of CO₂ concentration (see Fig. 6(a)), and this indicates that CO₂ has inhibition effect on NO reduction in the gaseous phase reaction of SNCR system. At T > 875 °C and CO₂ > 18%, CO₂ concentration and temperature significantly influence on NO reduction rate, NO reduction rate rapidly decreases from 88% to 36% when CO₂ concentration increases from 18% to 30% at 850 °C, and the rate rapidly increases from 36% to 74% when temperature increases from 850 °C to 875 °C at 30% CO₂ (see Fig. 6(a)). However, at T > 875 °C, NO reduction rate slightly decreases with the increase of CO₂ concentration.

In the presence of CaO, the acidic gas of CO_2 influences the catalytic activity of CaO by competing for the adsorbed NH_3 over Lewis acid sites against NO [24], and this inhibits NH_3 dehydrogenation and NH_3 oxidization on CaO surface:

$$\mathrm{NH}_{3(\mathrm{ad})} \to \mathrm{NH}_{2(\mathrm{ad})} + \mathrm{H}^{+} \tag{R14}$$

Thus, when CO_2 concentration is low, increasing CO_2 concentration reduces NO formation by inhibiting NH₃ oxidization on CaO surface, and this is conducive to NO reduction by gaseous reaction R7 (see Fig. 6(b)). However, when CO_2 concentration is too high, Shimizu found that (NH₂)₂CO was formed through NH₃ decomposition on CaO surface [25]:

$$CaO \cdot CO_2 + 2NH_3 \rightarrow CaO + (NH_2)_2 CO + H_2 O$$
(R15)

Thus, increasing CO_2 concentration promotes $(NH_2)_2CO$ formation, which results in large amount consumption of NH_3 on CaO surface and inhibits NO reduction in SNCR system.

Based on above discussion, in the presence of CaO, the competitive absorption of CO₂ and NH₃ on CaO surface promotes NO reduction at low CO₂ concentration, but the competitive reactions of forming (NH₂)₂CO and reducing NO by NH₃ inhibits NO reduction at high CO₂ concentration. Therefore, there is an optimal CO₂ concentration range (CO₂ = 25–27%), where NO reduction rate reaches above 78% at 900–940 °C (see Fig. 6(b)). At the meantime, above complex competitive reactions on CaO surface make the optimal range of temperature become narrow (T = 850–975 °C, see Fig. 6(b)) in comparison with that in the absence of CaO.

4. Conclusions

Experiment on NO_x reduction by advanced reburning in cement precalciner was performed on a laboratory-scale circulating fluidized bed reactor. At high concentrations of CaO and CO₂, the influences of CO₂, CaO and temperature on NO reduction by CO in reburning zone was investigated, and the concentrations of CO₂ and O₂ and temperature were optimized for NO reduction in SNCR zone.

In reburning zone, CaO significantly catalyses NO reduction by CO at low CO₂ concentration, and NO reduction rate can reaches 94.3% at 1050 °C and 15% CO₂. The order of the adsorption ability on CaO surface is $CO_2 > NO > CO$, and the decrement of NO reduction rate is about 35% when CO_2 increases from 15% to 30%. The increment of NO reduction rate is about 40% when temperature increases from 850 °C to 1050 °C.

In SNCR zone, There is an optimal range of CO₂ concentration (CO₂ = 25–27%), where NO reduction rate reaches above 78% at 900–940 °C, and the optimal range of temperature becomes narrow (T = 850–975 °C) in comparison with that in utility boiler. The optimal concentration of O₂ is in the range of 2% to 3.3%, and NO reduction rate reaches above 75% at 900–970 °C. The overall NO_x reduction rate for the advanced reburning with NO reburning by CO and SNCR by NH₃ in the cement precalciner is about 67% in the optimal operating conditions.

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