Sulfur Dioxide Capture by Limestone in a Lab Scale Circulating Fluidized Bed Combustor†

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During the combustion of fossil fuel in the industry, SO_x and NO_x can be emitted. The emission of SO_x and NO_x gases during the combustion of coal or petroleum pitch in the lab scale circulating fluidized bed has been studied. The emission of SO_x can be reduced by limestone in the circulating fluidized bed combustion. N_2O emission also reduced after the introduction of limestone pulse in the beginning stage. The emission level at the Herbei coal combustion at 900 ℃ after introduction of 50 g of T limestone pulse was rapidly decreased from 1200 ppm to 10 ppm.

Key Words: Sulfur dioxide, Limestone, Circulating fluidized bed combustor, Emission, Nitric oxide.

INTRODUCTION

Unexpected environmental problems are troublesome to scientists who are devoting themselves to scientific and industrial development. The production of sulfur oxide (SO_x) or nitric oxide (NO_x) is such a problem. Sulfur oxides, called "SO_x", gases form when the coal and heavy oil are burned in the industry. SO_2 readily dissolves in water vapour and leads to the formation of acid and interacts with other gases and particles in the air to form sulfates and other products that can be harmful to people and environment[1,2]. Nitrogen oxides, so called "NO_x", are highly reactive gases that contain nitrogen and oxygen in varying molecular combinations. The major source of NO_x is the combustion of fossil fuels such as coke in electric power plants or petroleum in vehicle engines[3-5]. Both sulfur dioxide and nitrogen oxides are known to cause acid rain. One member of the NO_x family, nitrous oxide (N_2O), is a potent greenhouse gas[6]. For those reasons, SO_x and NO_x emissions should be controlled.

In the field of fluidized bed combustion with high thermal capacities, circulating fluidized bed reactors are considered to be the most efficient commercial utility which burns various solid fuels, including coals, with a minimum operation and maintenance cost[7-9]. Although the best operation parameters for the boilers could be collected from the actual experience of the commercial scale boilers[9], the information is not always intuitive since the parameters of the commercial boilers in

operation are normally interrelated. For example the change of the fuel rate is accompanied with the change of the air flow rate, simultaneously resulting in the variation of the bed temperature and pressure. It is quite difficult to understand the actual effects of specific variables on the performance of the commercial boiler in operation. On the other hand, many experimental results from previous researches were carried out with packed bed units in small scale and turned out to be impractical to be applied to the commercial circulating fluidized bed boilers[6,8-14]. To systematically investigate the emission characteristics of circulating fluidized bed, a circulating fluidized bed combustor, consisting of a riser combustor and a cyclone with a return leg connected to the riser, was in-house developed in lab scale. The emission of SO_x and NO_x gases during the combustion of coal or petroleum pitch in the circulating fluidized bed has been studied. The aim of this study is to elucidate the absorption of SO_2 by limestone through the circulating fluidized bed combustor. Emission of SO_x and NO_x in the circulating fluidized bed and reaction of them with limestone have been investigated and basic reaction kinetics of the reaction was suggested.

EXPERIMENTAL

Circulated fluidized bed: Fig. 1 shows the schematic diagram of the circulating fluidized bed combustor developed in-house with quarts tubes to prevent any possible catalytic

| TABLE-1 |
| BET SURFACE ANALYSIS OF T LIMESTONE |

Size cut (mm)	CaCO₃			CaO calcined @900 ℃ for 2 h		
	Area (m^2/g)	Volume* (cm^3/g)	Pore diameter (μm)	Area (m^2/g)	Volume* (cm^3/g)	Pore diameter (μm)
T limestone (1.4)	0.53	0.15	1.13	6.77	2.21	1.30

effect caused by ferrous materials[10,11]. The most important parts of the unit are a riser and a cyclone-return leg. The inner diameter and height of the riser are 0.025 m and 2 m, respectively. The exit of the riser is connected to the cyclone and the bottom of the cyclone is connected to a downcomer tube (the return leg) which returns collected particles to the riser combustor. The inner diameter and height of the down-comer are 0.02 m and 1.8 m, respectively. Since the heat generated from the combustion of coals was not sufficient to sustain the desired combustor temperature, multi sets of electric heaters were installed around the outer side of the test unit.

1. Riser
2. Cyclone
3. Downcomer
4. Feed hopper
5. L-valve
6. Digital flowmeter
7. Compressor/cylinder
8. Coal feeder
9. Gas analyzer
10. PC
P1, P7, P8; Pressure tap
Q1, Q2; Aeratlon air
P/A; Primary air
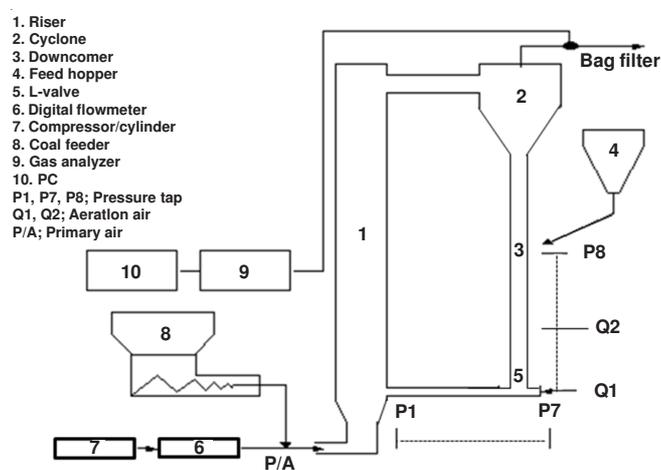
Fig. 1. Schematic diagram of laboratory scale circulating fluidized bed

Sulfur dioxide capture by limestone and analysis: Test coal samples were screened with the particle size between 0.1-0.7 mm and their mean diameter was 0.073 mm. The Herbei coal is high sulfur bituminous coal widely used in the power industries of China and the Shenhwa coal is low sulfur, high heating value coal from China. The petroleum coke is a byproduct from a Korean refinery. The combustor installed with bed materials was heated with air only to the pre specified temperature by electric heaters. As the temperature of the combustor reached the pre-set value, the coal was fed into the bottom of the riser. While the coal was burned inside of the riser, the ashes were entrained to the top of the combustor and led to the cyclone. The particles except very fine ashes were collected by the cyclone and recycled to the riser through the return leg. The particles were circulated between the riser and the return leg until the combustion is completed and the particle size is reduced enough to flow out of the cyclone to the bag filter. The effluent from the cyclone to the bag filter was analyzed by the URAS Model 14-1, 14-2 of ABB Hartman and Braun to measure the levels of SO_2, NO_x, N_2O, CO, CO_2 and O_2. Table-1 presents the BET analysis of Korean limestone from Tanyang, T limestone, utilized in the experiment. BET surface analyses obtained by a Quantachrome Autosorb 1 with the absorption of nitrogen gas at its boiling temperature.

The samples as received and calcined in nitrogen environment at 1173 K for 2 h were compared. The limestone was feeding by 50 g to circulating fluidized bed reactor. The limestone was calcined in a muffle furnace at 900 ℃ for 2 h. The surface area of $CaCO_3$ was increased from 0.53 m^2/g to 6.77 m^2/g after the calcinations to CaO at 900 ℃ for 2 h at the circulating fluidized bed combustor. Table-2 presents the elemental analysis of the coke and petroleum coke for circulating fluidized bed combustion. Three fuels such as Herbei coal, Shenhwa coal and petroleum coke are introduced to the circulating fluidized bed reactor.

| TABLE-2 |
| ANALYSIS OF COAL AND PETROLEUM COKE |

Fuel type	Herbei Coal	Shenhwa Coal	Petroleum Coke
Proximate analysis (% as received)			
Moisture	0.87	4.84	1.75
Volatiles	20.70	32.63	9.76
Ash	33.29	5.46	0.79
Fixed Carbon	45.13	52.07	87.70
Ash analysis (% dry basis)			
CaO	4.95	25.45	53.14
MgO	0.33	1.35	0.94
Elemental analysis (% dry basis)			
C	57.19	73.16	89.38
H	3.48	4.11	3.65
N	0.98	0.93	1.21
Total S	3.91	0.49	6.09
HHV [kcal/kg (meas.)]	5399	6530	8506

RESULTS AND DISCUSSION

The major parameters for the emission experiments were considered to be air/fuel ratio and reaction temperature. Since the reactor temperature was fixed for one set of experiments, only the air/fuel ratio, *i.e.*, the amount of oxygen was the controllable variable. Fig. 2 shows the effects of the aeration on the emissions of SO_2, NO_x and N_2O from the combustions of the Herbei coal, the Shenhwa coal and the petroleum coke, respectively. The emission values are recalculated at 3.5 % O_2. In the Herbei coal combustion, about 1200-1600 ppm of SO_2 emission was observed as the oxygen content increases. About 200 ppm of NO_x was steadily observed even if the oxygen feeding was increased. In the Shenwha coal combustion, the NO_x emission gradually increases from 150 ppm to 300 ppm as the oxygen feeding increases. Meanwhile, the SO_2 emission was steadily observed at about 250 ppm as the oxygen content increases. The emission profile of the petroleum coke seems quite different from others. As the oxygen flow increases to 5 %, the emission of SO_2 decreases from 4000 ppm to 2600 ppm and the emission of N_2O increases by two times.

Fig. 3 shows the emission level of Herbei coal combustion at 900 ℃ after introduction of 50 g of T limestone pulse.
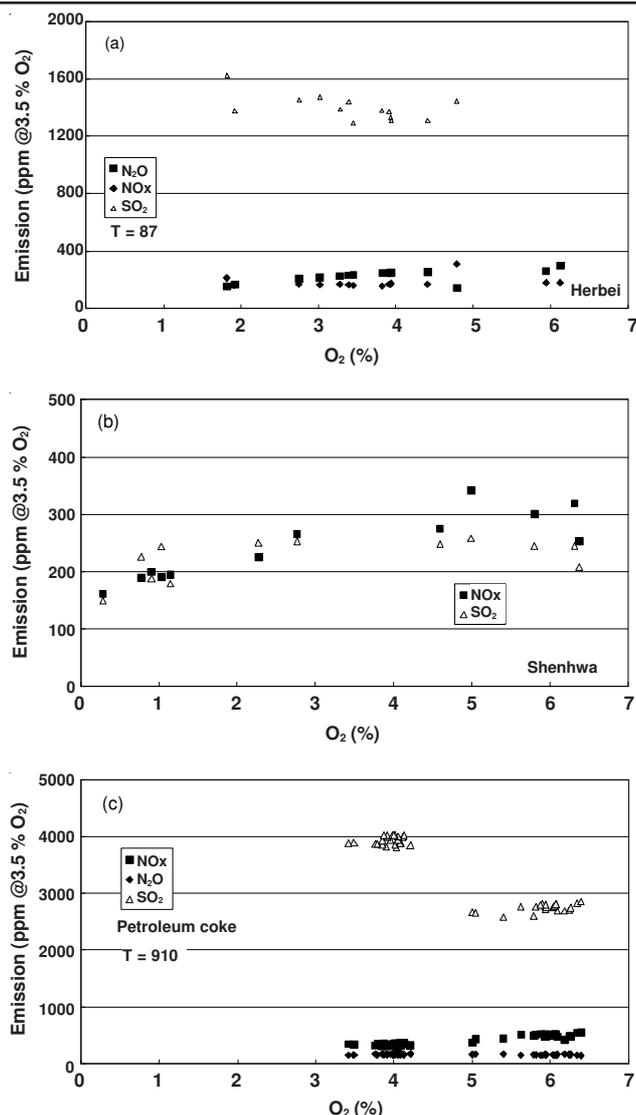
Fig. 2.   Emission of pollutants from the combustion of (a) Herbei Coal, (b) Shenhwa Coal and (c) Petroleum Coke as O_2 increases
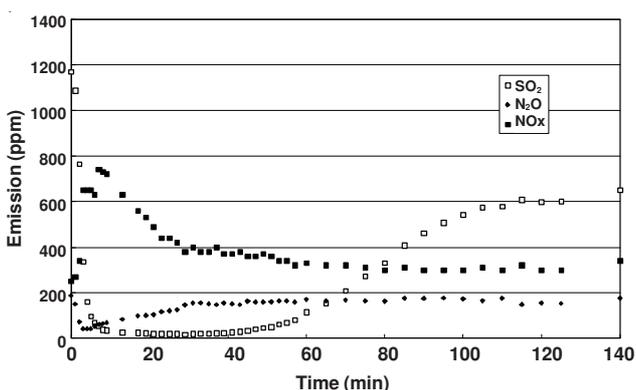
Fig. 3. Variation of emissions level by time after a pulse injection of limestone

After the injection the limestone started calcinations in the combustor for a few minutes then it starts to absorb SO_2. The initial emission of SO_2 of 1200 ppm was rapidly reduced to 10 ppm in about 10 minutes after the injection. The emission level was slowly increased and reached to the half of the initial level after 100 min. The break through point of SO_2 adsorption onto limestone was observed at 50 min and the absorption power of the limestone sustained for over 2 h. During the reaction of SO_2 and limestone, the level of NO_x emission rather increased from 300 ppm to more than two times and N_2O emission reduces from 200 ppm to 30 ppm which suggest that N_2O can be reduced by limestone as we early discussed[10,11]. The catalytic effect of CaO of N_2O emission gradually disappeared after 30 min later that can be explained by the formation of $CaSO_4$ after the reaction of CaO with SO_2[15,16].

Conclusion

SO₂, NOₓ, N₂O emission at the coal and petroleum coke combustion was monitored in a lab scale circulating fluidized bed reactor made of quarts. In the Herbei Chinese coal combustion, about 1200-1600 ppm of SO_2 emission was observed as the oxygen content increases. About 200 ppm of NO_x was steadily observed even if the oxygen feeding was increased. In the Shenwha Chinese coal combustion, the NO_x emission gradually increases from 150 ppm to 300 ppm as the oxygen feeding increases. Meanwhile, the SO_2 emission was steadily observed at about 250 ppm as the oxygen content increases. As the oxygen flow increases to 5 %, the emission of SO_2 decreases from 4000 ppm to 2600 ppm. And the emission of N_2O increases by two times when petroleum coke was used as fuel. The emission level of SO_2, NOx and N_2O at the Herbei coal combustion at 900 ºC was conducted. The initial emission of SO_2 of 1200 ppm was rapidly reduced to 10 ppm in about 10 min after the injection of limestone pulse.

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