

Pilot-Scale NO_x Removal from Boiler Emission Using Plasma-Chemical Process

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Abstract— NO_x removal from an actual boiler flue gas was investigated using a commercial ozonizer for indirect NO oxidation and a scrubber using Na₂SO₃. The flue gas was in the range of 470~1,480 Nm³/h, the gas temperature of 327°C, and NO_x concentration of 40 ppm. Approximately 80% of NO_x removal efficiency was achieved during 180 min of system operation by maintaining pH of 8 and oxidation reduction potential of -50~0 mV and an additional Na₂SO₃ and NaOH solutions were injected into the scrubber to sustain the condition.

I. INTRODUCTION

The laboratory-scale nonthermal plasma chemical hybrid processes for NO_x removal from stationary source emission such as a boiler, a power generator and an incinerator have been investigated over the years and demonstrated to achieve a nearly complete NO_x removal with negligible reaction byproducts [1-6]. However, it was not effective to oxidize NO using nonthermal plasma directly when the flue gas temperature exceeds 300°C. In addition, the gas volume is large, which requires the large plasma reactor. As an alternative methods for the purpose of NO oxidation and reduction, the radical injection has been investigated using ozone (O₃), ammonia (NH₃), nitrogen (N₂), and methane (CH₄) and N₂ mixture which are generated by the indirect plasma (or often referred to as remote plasma) in both laboratory-scale and pilot-scale experiments [9-18]. The indirect plasma has advantage that radicals can be externally produced at ambient temperature and pressure, and injected into the hot flue gas stream. It is extremely effective for NO oxidation especially when the flue gas temperature exceeds 300°C where NO_x is rather generated with direct plasma at this temperature.

Based on the laboratory-scale experimental studies, both NO_x and SO_x removal from the boiler emission was first demonstrated using the pilot-scale apparatus using indirect

plasma combined with a chemical hybrid process [7]. As a result, NO_x removal efficiency for the gas firing exceeds 90% but NO_x removal efficiency for the oil firing was in the range of 60% due to the lack of ozone concentration from the power supply used for the plasma reactor. The removal efficiency of SO₂ was in the range of 85~90%. The quality of disposed water was proved to be disposable [7].

In this paper, the results based on the second generation of the pilot scale (commercial scale) apparatus were reported. The volume of the scrubber was reduced to approximately 1/3 of the first apparatus by optimizing the system operation. The flue gas flow rate was in the range of 470~1,480 Nm³/h, the gas temperature of 327°C, and NO_x concentration of 40 ppm throughout the experiments. The ozone injection using the ozonizer was demonstrated to be extremely effective for NO oxidation. The produced NO₂ was further reduced to N₂ and Na₂SO₄ using Na₂SO₃ solution in the chemical scrubber. In order to perform NO_x removal effectively, the scrubber was operated by controlling pH and oxidation reduction potential (ORP), and an additional Na₂SO₃ and NaOH aqueous solution were injected into the sump of the scrubber when required.

II. EXPERIMENTAL SETUP

Fig. 1 shows the overview of the commercial-scale indirect plasma and chemical hybrid system. Fig. 2 shows a schematic diagram of this system. The flue gas was generated from the 2.0 t/h of steam generation boiler (Takao Steel Co., Ltd.) with firing a city gas (13 A) of the rated values of 121 Nm³/h. The flue gas was cooled down using an economizer in order to decrease the flue gas temperature low enough for the protection of the polypropylene packing materials in the scrubber. A commercial ozonizer (Ebara Jitsugyo Co, Ltd, EW-90Z, 90 g/h at 3.1 kW) with a pressure swing adsorption (PSA) oxygen generator was employed for ozone generation, and ozone was injected into an exhaust duct upstream of the scrubber for NO oxidation ($\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$). Then, the flue gas enters the 0.6 m in diameter and 3.7 m high scrubber. In the scrubber, Na₂SO₃ and NaOH solutions were used for NO₂ reduction ($2\text{NO}_2 + 4\text{Na}_2\text{SO}_3 \rightarrow \text{N}_2 + 4\text{Na}_2\text{SO}_4$) and pH control, respectively. The aqueous solution of Na₂SO₃ was sprayed from the nozzle, which was located on the top of the scrubber. Two types of packing materials were used for effective gas-liquid interfacial area. One was S-II Type Tellerette made of polypropylene (specific surface of 150m²/m³ and void fraction of 92%). The other type was RSR No. 1 Type Raschig Super-Ring made of SUS304 (specific surface of 163 m²/m³ and void fraction of 98%) and was packed beneath the Tellerette Packing in the scrubber. The height of Tellerette and Raschig Super-Ring layer were 0.8 and 0.4 m, respectively. After the treatment by the scrubber, the flue gas was discharged to the stack. The aqueous solution was recirculated through the scrubber using the circulation pump. The flow rate was set at 4.5 m³/h by the valve of the circulation pump. The pH and the oxidation reduction potential (ORP) were measured at the tributary line, which returned to the sump. In order to perform NO_x removal effectively, it was essential to maintain pH of more than 7 and ORP of less than 0 mV, respectively. Therefore, the scrubber was carefully operated by controlling pH and ORP, and additional Na₂SO₃ and NaOH aqueous solutions were injected into the sump of the scrubber when required. The initial concentration of Na₂SO₃ in the sump was set at 15.8 g/L.

The experiments were performed after the flue gas temperature reached steady state.

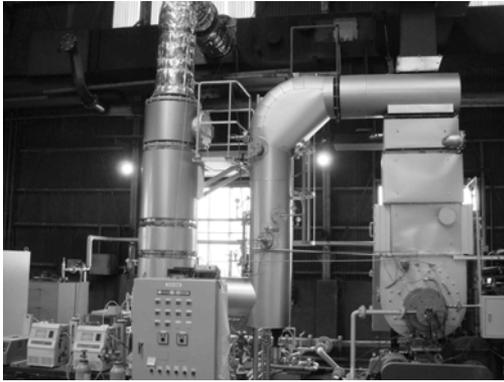


Fig. 1 Overview of the commercial scale indirect plasma and chemical hybrid system (Scrubber height ~ 3.7 m)

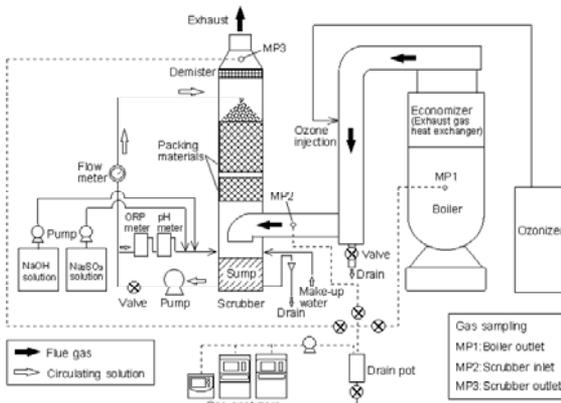


Fig. 2 Schematic diagram of the commercial-scale indirect plasma and chemical hybrid system

The flue gas was based on 20~80% load and was set at $470 \text{ Nm}^3/\text{h}$ with a low load, $1,020 \text{ Nm}^3/\text{h}$ with a medium load, and $1,430 \text{ Nm}^3/\text{h}$ with a high load operation, where the gas flow rate was determined by the fuel consumption and O_2 concentration. The flue gas temperature was measured with thermocouples. The concentrations of gas constituents (O_2 , CO , CO_2 , NO , and NO_x) were measured with a gas analyzer (Shimadzu, NOA-7000, chemiluminescence NO_x analyzer, O_2 for zirconia method, and CGT-7000, Infrared adsorption for CO-CO_2 analyzer), and by a gas analyzer (Horiba, PG-240,

chemiluminescence NO analyzer). The gas temperature and concentrations of the flue gas constituents were measured at SP1 (the boiler outlet), SP2 (the scrubber inlet) and SP3 (the scrubber outlet).

III. EXPERIMENTS

A. Flue gas temperature, constituent concentrations and ozonizer performance

Fig. 3 shows the flue gas temperature at MP1, MP2 and MP3 when the flue gas flow rates were 470, 1,020 and 1,430 Nm³/h, respectively. The flue gas temperature at MP1 reached 327°C when the gas flow rate was 1,430 Nm³/h. However, the gas temperature decreased to 145 °C at MP2 when the economizer was used. The gas temperature at MP3 was approximately 60°C in all conditions. In the previous study, when the water spray was employed for gas cooling, corrosion problem was encountered at the bottom of the duct, where the solution was identified to contain acids owing to water spray in the duct. However, the water spray was unnecessary for the present system.

Fig. 4 shows the NO, NO_x, CO, CO₂ and O₂ concentrations at MP1 when the flue gas flow rates were 470, 1,020 and 1,430 Nm³/h, respectively. NO and NO_x concentrations slightly increased as the gas flow rate increased, indicating that the load of boiler was increased. The CO₂ concentration was almost unchanged with the flow rate. Although CO was generated at 470 Nm³/h, the CO generation increased dramatically as the flow rate increased, and reached 80ppm at 1,430 Nm³/h. As far as oxygen was concerned, lower O₂ concentration was preferable because O₂ reacts with Na₂SO₃. However, O₂ concentration was in the range of 4.0~4.5 % because CO and particulate matter (PM) were generated when O₂ concentration was less than 4%.

Fig. 5 shows the ozonizer performance as a function of input power when the ozone gas flow rate was 0.9 Nm³/h. The PSA consumed 1.6 kW in the input power, and the remainder of the power was used as the discharge power for the ozone generation. The amount of

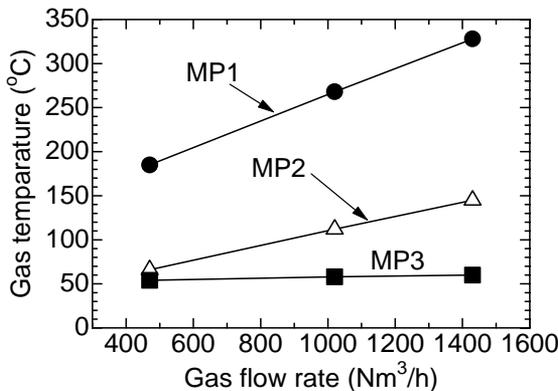
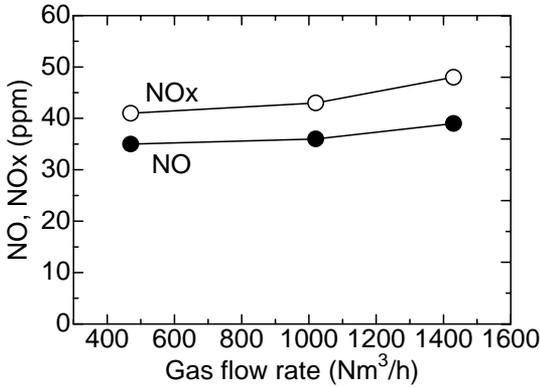


Fig. 3 Flue gas temperature at MP1, MP2 and MP3 as a parameter of gas flow rate



(a) NO and NOx

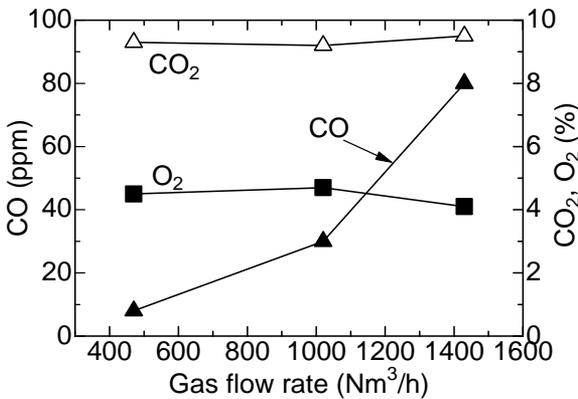
(b) CO, CO₂ and O₂

Fig. 4 Gas concentrations as a parameter of the gas flow rate: (a) NO and NOx, (b) CO, CO₂ and O₂

ozone generation reached 110 g/h and the energy efficiency of ozone generation was 37.3 g/kWh when the input power was 2.95 kW.

Fig. 6 shows the relationship between the concentration of NO removed and the ozone concentration estimated at the duct of ozone injection. The gas flow rates were at 970 Nm³/h with a medium load and 1,480 Nm³/h with a high load operation, respectively. It is clear that the amount of NO removed was almost the same as the amount of corresponding O₃ concentration to oxidize NO (1:1 stoichiometric ratio). As a result, the energy efficiency for NO oxidation can be estimated at 4.9~35.7 g(NO₂)/kWh.

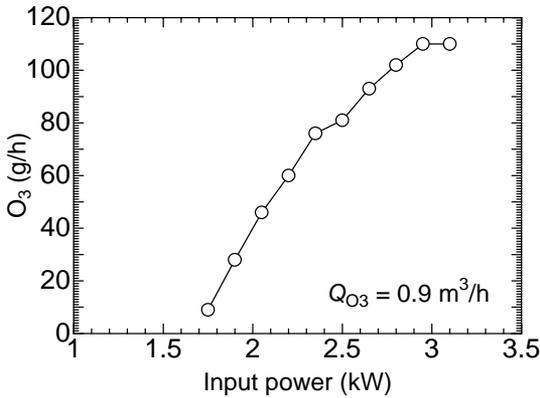


Fig. 5 Ozonizer performance as a function of the input power

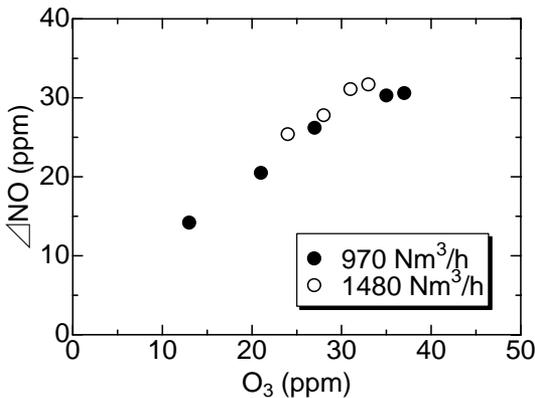


Fig. 6 Relationship between the concentration of NO removed and the ozone concentration estimated at the injection point

B. Effect of ORP and pH on NO_x removal efficiency

Fig. 7 shows the relationship between NO_x removal efficiency and ORP when the gas flow rate was set at 470 Nm³/h with low load operation. The solution of Na₂SO₃ was supplied in the range of 1.7 to 4.2 kg/h. The amount of NaOH supply was fixed at 0.1 kg/h. The NO_x removal efficiency reached more than 80% (less than 8ppm) when ORP was lower than 0 mV. As ORP increased, NO_x removal efficiency decreased proportionally and deteriorated to 45% at 70 mV. To maintain 80% of NO_x removal efficiency with low load operation, a 4.2 kg/h of Na₂SO₃ was needed to supply continuously.

Fig. 8 shows the relationship between NO_x removal efficiency and ORP when the gas flow rate was at 1,020 Nm³/h with medium load operation. The Na₂SO₃ solution was

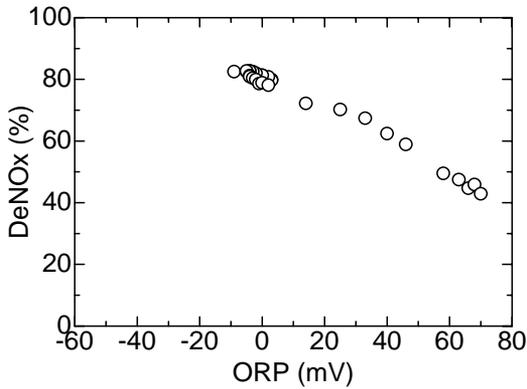


Fig. 7 Relationship between NO_x removal efficiency and ORP for 470 Nm³/h with a low load operation

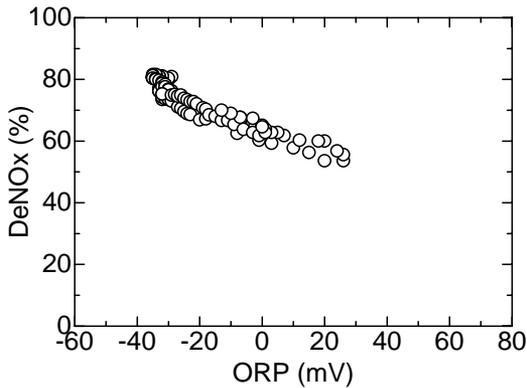


Fig. 8 Relationship between NO_x removal efficiency and ORP for 1,020 Nm³/h with a medium load operation

supplied in the range of 2.7 to 4.9 kg/h. The amount of NaOH supply was fixed at 0.1 kg/h. The NO_x removal efficiency reached more than 80% when OPR was less than -30 mV. The tendency of NO_x removal efficiency with ORP was similar to that of the low load operation and NO_x removal efficiency decreased to 55% at 25 mV. A 4.9 kg/h of Na₂SO₃ was essential to achieve 80% of the NO_x removal for boiler emission with medium load.

Fig. 9 shows the relationship between NO_x removal efficiency and ORP when the gas flow rate was at 1,430 Nm³/h with high load operation. The Na₂SO₃ solution was supplied in the range of 1.7 to 6.8 kg/h. The amount of NaOH supply was sustained at 0.1 kg/h. It is shown that ORP to obtain 80% of NO_x removal efficiency became lower in comparison

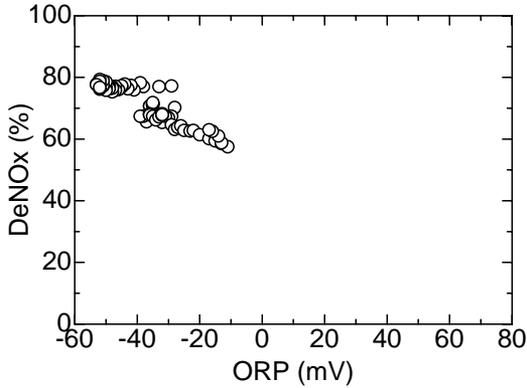


Fig. 9 Relation between NOx removal efficiency and ORP for 1,430 Nm³/h (a high load operation)

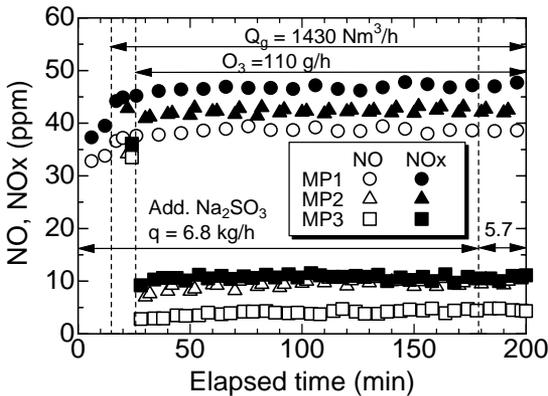


Fig. 10 NOx concentration at MP1, MP2 and MP3 as a function of the elapsed time

with that of the medium load and ORP needed to sustain at -50 mV. The NOx removal efficiency decreased with increased ORP and deteriorated up to 58% at -11 mV. The 6.8 kg/h of Na₂SO₃ was required to realize 80% of NOx removal efficiency for boiler emission with a high load operation.

As the results, in order to obtain more than 80% of NOx removal efficiency, it is essential to set the optimum ORP corresponding to the load of the boiler operation, that is, ORP needed to be lower than 0 mV with a low load operation, -30 mV with a medium load operation and -50 mV with a high load operation, respectively.

On the other hand, the value of pH should be maintained in the range of 7.7~8.2

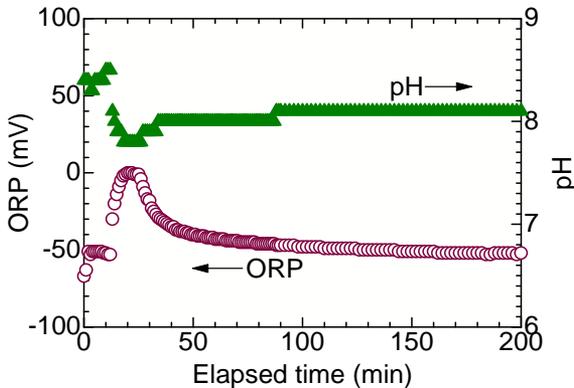


Fig. 11 The relationship between ORP and pH as a function of the elapsed time

throughout the experiments. Chen et al. reported that the high NO_2 removal efficiency using the simulated gas can be obtained by keeping pH of 11 by supplying NaOH [19]. However, it was difficult to sustain the pH of above 9 because actual exhaust gas contains approximately 9% of CO_2 in this experimental study. In addition, NaOH solution was consumed by CO_2 absorption in exhaust gas.

C. Continuous operation of the plasma chemical hybrid system

The continuous operation of the plasma chemical hybrid system for boiler emission with a high load operation was carried out to confirm the long-term operation of this system. Fig. 10 shows NO and NO_x concentrations at MP1, MP2 and MP3 as a function of the elapsed time. The flue gas flow rate was $1,430 \text{ Nm}^3/\text{h}$. The injected O_3 was 110 g/h with $0.9 \text{ Nm}^3/\text{h}$, where q in the figure was the flow rate of additional Na_2SO_3 . The flow rate of additional NaOH was 0.1 kg/h . Fig. 11 shows the time-dependent ORP and pH. The initial values of pH and ORP were 8.4 and -67 mV , respectively. The pH and ORP change greatly at the beginning of the experiments and then reached the constant values. Approximately 80% of NO_x removal efficiency was achieved for 180 min operation time by maintaining pH of 8 and ORP of negative value of $-50 \sim 0 \text{ mV}$.

IV. CONCLUSION

The commercial scale plasma-chemical hybrid system of the smoke-tube boiler emission was investigated. The NO was almost completely oxidized to NO_2 using the commercial ozonizer and one stoichiometric ratio of O_3 was required to oxidize NO . Therefore, the energy efficiency for NO oxidation was in the range of 4.9 to $35.7 \text{ g}(\text{NO}_2)/\text{kWh}$. Regarding NO_2 removal efficiency using the scrubber, approximately 80% of NO_x removal (8ppm NO_x outlet) was obtained by controlling ORP corresponding to the load of the boiler operation, namely maintaining less than 0 mV with a low load, -30 mV

with a medium load and -50 mV with a high load operation, respectively. It was demonstrated that approximately 80% of NO_x removal efficiency (8ppm of NO_x) was achieved during a 180 min operation by maintaining pH of 8 and ORP of negative value (-50 ~ 0 mV) for the boiler emission with a high load operation.

ACKNOWLEDGMENT

Authors greatly thank Mr. Tanaka from Takao Iron Steel CO., Ltd., Mr. Fukumoto, Mr. Yamamoto and Mr. Yoshioka from the students at the Osaka Prefecture University for carrying out experiments. This work was supported by the Regional R&D Foundation Program in the JST Innovation Plaza Osaka.

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