Performance Characteristics of Pilot-Scale NO_x Removal from Boiler Emission Using Plasma-chemical Process

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Abstract: NO_x removal from a smoke tube boiler flue gas was investigated using a commercial ozonizer for indirect NO oxidation and a Na_2SO_3 chemical scrubber. The flue gas flow rate was in the range of 410 Nm^3/h-1480 Nm^3/h, the gas temperature of 185 ℃-325 ℃, and NO_x concentration of around 40 ppm in city gas firing. Operational and performance data were obtained. The NO_x removal efficiency was clearly dependent on the ORP, and increased inversely as the oxidation reduction potential (ORP) in the liquid decreased. To keep the specified NO_x removal performance, it is essential to maintain the ORP properly by controlling additional Na_2SO_3 and NaOH solution injection. NO_x emission of less than 4 ppm was attained at 410 Nm3/h for a 300 minutes system continuous operation by maintaining ORP of -30 mV and pH of more than 7.8.

Keywords: NO_x removal, nonthermal plasma, indirect plasma, oxidation reduction potential, Na_2SO_3

1 INTRODUCTION

The laboratory-scale nonthermal plasma chemical hybrid processes for NO_x removal from stationary source emissions, such as a boiler, a diesel power generator and a refuse incinerator, have been investigated over the years and demonstrated to achieve a nearly complete NO_x removal with negligible reaction byproducts [1-7]. However, it was not effective to oxidize NO using nonthermal plasma directly when the flue gas temperature exceeds 300 ℃. In addition, gas volume is large, which requires a large plasma reactor. As an alternative method for the purpose of NO oxidation and reduction, the radical injection has been investigated, using ozone (O_3), ammonia (NH_3), nitrogen (N_2), and methane (CH_4) and N_2 mixture which are generated by the indirect plasma (or often referred to as remote plasma), in both laboratory-scale and pilot-scale experiments [8-17]. The indirect plasma has advantage that radicals can be externally produced at ambient temperature and pressure, and injected into flue gas stream. It is extremely effective for NO oxidation, especially when the flue gas temperature exceeds 300 ℃ at which NO_x is rather generated with direct plasma. Based on the laboratory-scale experimental studies, both NO_x and SO_x removal from boiler emission was first demonstrated using the pilot-scale apparatus combined with indirect plasma and chemical hybrid process [18]. As a result, the NO_x removal efficiency for city gas firing exceeded 90%, but it was in the range of 60% for oil firing, because of lack of ozone supplied from plasma reactor. The SO_2 removal efficiency was in the range of 85%-90%. The quality of waste water was proved to be disposable [18]. The preliminary test result was reported, based on the second generation of the pilot scale (commercial scale) apparatus of which the scrubber volume was reduced to approximately 1/3 of the first apparatus by optimizing the system operation [19]. In this paper the further detail test result regarding the performance characteristics of NO_x removal was reported. The flue gas flow rate was in the range of 410 Nm^3/h-1,480 Nm^3/h, the gas temperature of 185℃-325℃, and the NO_x concentration of around 40 ppm in firing a city gas (13A) throughout the experiments.

Operational and performance data were obtained. The ozone injection using the ozonizer was demonstrated to be extremely effective for NO oxidation. The produced NO_2 was further reduced to N_2 and Na_2SO_4 by the Na_2SO_3 solution in the chemical scrubber. In order to perform the NO_x removal effectively, the scrubber was operated by controlling ORP and pH, and additional Na_2SO_3 and NaOH aqueous solution were injected into the sump of the scrubber. The NO_x removal performance characteristic was obtained. Furthermore, the NO_x removal was confirmed for a 300 minutes continuous operation and NO_x emission of less than 4 ppm was attained throughout the experiment.

1.1 Experimental Setup

Fig. 1 shows a schematic diagram of the pilot-scale indirect plasma and chemical hybrid system. The flue gas was generated from the 2.0 t/h of steam generation boiler (Takao Iron Co., Ltd.) with firing a city-gas (13 A) of the rated values of 121 Nm^3/h. The flue gas was cooled down using an economizer (exhaust gas heat-exchanger) in order to decrease 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 the ozone was injected into a flue gas duct, upstream the scrubber, for NO oxidation ($NO + O_3 \rightarrow NO_2 + O_2$). Then, the flue gas was introduced into the 0.6 m in diameter and 3.7 m in height scrubber. In the scrubber, Na_2SO_3 and NaOH solutions were used for NO_2 reduction ($2NO_2 + 4Na_2SO_3 \rightarrow N_2 + 4Na_2SO_4$) and pH control, respectively. The aqueous solution of Na_2SO_3 and NaOH was sprayed from a nozzle located on the top of the scrubber. Two types of packing materials were used for effective gas-liquid interfacial area. The one was S-II Type Tellerette made of polypropylene (specific surface of $150 m^2/m^3$ and void fraction of 92%). The other was No. 1 Type Raschig Super-Ring (RSR) made of SUS304 (specific surface of $163 m^2/m^3$ and void fraction of 98%) and was packed beneath the Tellerette Packing in the scrubber. The heights of Tellerette and RSR layer were 0.9 m and 0.3 m, respectively. After NO_x removal in the scrubber, the cleaned flue gas was discharged through the stack. The aqueous solution was circulated through the scrubber by a circulating pump. The liquid flow rate was set at $3.0 m^3/h$-$4.5 m^3/h$ by controlling the valve of the circulating pump. The Na_2SO_3 concentration and pH of the scrubbing solutions were monitored by the oxidation reduction potential (ORP) and pH meters installed at the tributary line which was connected 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, while Na_2SO_3 and NaOH aqueous solutions were added to the sump of the scrubber. The initial concentration of Na_2SO_3 in the liquid of the sump was set at 15.8 g/L. The experiments were performed after the flue gas temperature reached in a steady state. The flue gas was based on 25%-85% of boiler load and was set at 440 Nm^3/h as a low load, 980 Nm^3/h as a medium load, and 1,480 Nm^3/h as a high load operation, where the gas flow rate was determined by the fuel consumption and O_2 concentration of flue gas. The flue gas temperature was measured with thermocouples. The concentrations of gas constituents (O_2, CO, CO_2, NO_x and NO) were measured by 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 the sampling points, MP1 (the boiler outlet), MP2 (the scrubber inlet) and MP3 (the scrubber outlet) as shown in Fig. 1.

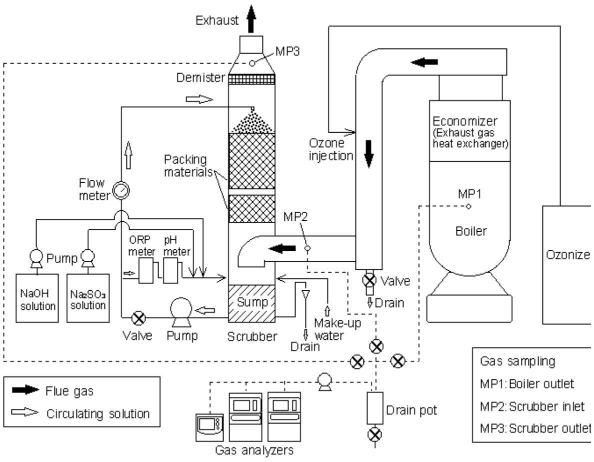


Fig. 1 Schematic diagram of the pilot scale indirect plasma and chemical hybrid system

1.2 Experimental Results

Flue gas properties and ozone performance

Fig. 2 shows the flue gas temperature at MP1, MP2 and MP3 when the flue gas flow rates were 440, 980 Nm^3/h and 1,480 Nm^3/h, respectively. The flue gas temperature at MP1 reached 325 ℃ when the gas flow rate was 1,480 Nm^3/h. However, the gas temperature decreased to 132 ℃ at MP2 when the economizer was in service. The gas temperatures at MP3 were approximately 60 ℃ in all conditions. Fig. 3 shows the NO, NO_x, CO, CO_2 and O_2 concentrations at MP1 when the flue gas flow rates were 440, 980 Nm^3/h and 1,480 Nm^3/h, respectively. The NO_x concentration slightly increased from 37 ppm to 41 ppm as the gas flow rate increased. The CO_2 concentration was almost unchanged, but the CO concentration increased, up to 70 ppm at 1,480 Nm^3/h, with the gas flow rate. On the other hand the O_2 concentration was kept in the range of 4.0%-4.9% to prevent from both CO and particulate matter (PM) generation in the case of less than O_2 of 4%. Regarding the ozonizer performance, a 1.6 kW of the ozonizer input power was consumed by the PSA and the rest was for the ozone (O_3) generation as the discharge power. The ozonizer produced 110 g/h of O_3 at 2.95 kW when O_3 gas flow rate was 0.9 Nm^3/h. Fig. 4 shows the relationship between the NO concentration removed and the O_3 concentration estimated in the flue gas duct where the ozone was injected. The gas flow rates were at 970 and 1,480 Nm^3/h, respectively. It is clear that the amount of NO removed from NO to NO_2 was almost the same as the amount of corresponding O_3 concentration to oxidize NO (1:1 stoichimetric ratio) of flue gas.

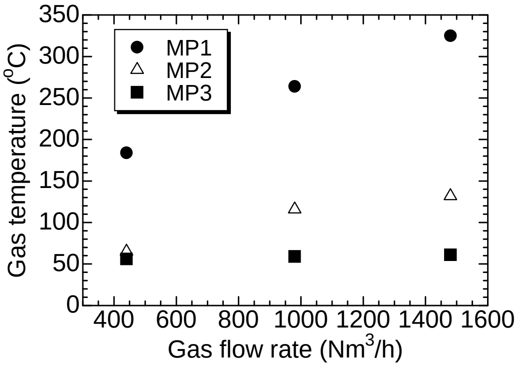
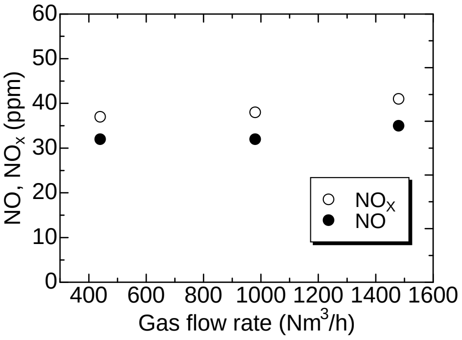
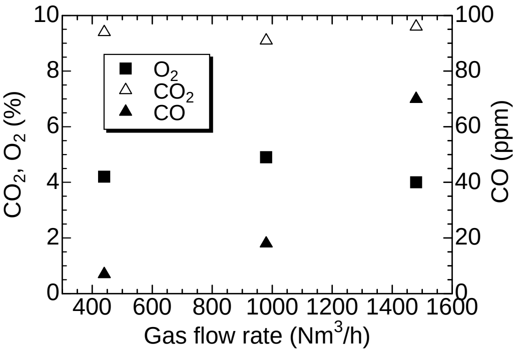


Fig. 2 Flue gas temperature at MP1, MP2 and MP3 vs. gas flow rate



(a) NO and NO_2



(b) O_2, CO_2 and CO

Fig. 3 Gas concentration vs. gas flow rate:(a) NO and NO_2, (b) O_2, CO_2 and CO

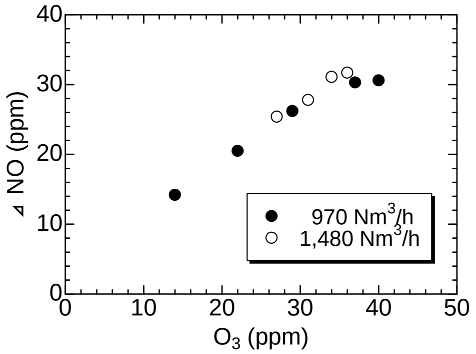


Fig. 4 Relation between the concentration of NO removed and the ozone concentration estimated in the duct where the ozone was injected

Effect of ORP and pH on NO_x removal efficiency

Fig. 5 shows the time-dependent NO_x removal efficiency and the ORP in the liquid. The gas flow rate was set at 995 Nm^3/h, the Na_2SO_3 injection rate was in the range of 2.6 kg/h -4.6 kg/h, and the NaOH was 0.1kg/h. The NO_x removal initially showed 83% when the ORP was -20 mV, but it decreased to 68%, as the ORP increased to 4 mV due to the Na_2SO_3 injection rate change from 3.7 kg/h to 2.6 kg/h. In order to improve the NO_x removal, the Na_2SO_3 injection rate was increased from 2.6 kg/h to 3.9 kg/h, and then to 4.6 kg/h. The ORP again decreased to -12 mV, and the NO_x removal increased up to 75%. So that, it is clear that the NO_x removal and the ORP correlated closely to each other.

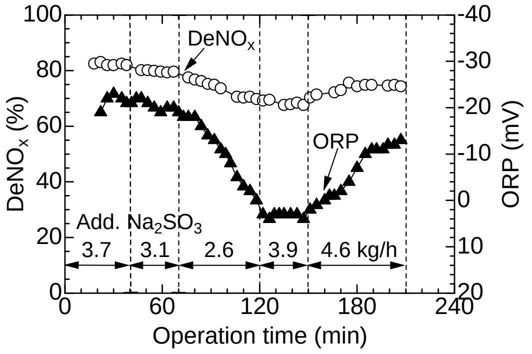


Fig. 5 Time dependent NO_x removal and oxidation reduction potential

Fig. 6 shows the relationship between NO_x removal and ORP at low load, medium load and high load operations. All measured data indicated that the NO_x removal increased as the ORP decreased. In the case of the low load operation, the gas flow rate was set at 440 Nm^3/h, and the solution of Na_2SO_3 was injected in the range of 2.3 kg/h-3.9 kg/h, together with the fixed amount of NaOH supply, 0.1 kg/h, The NO_x removal was ranged from 80% to 90%, while the ORP varied from around 0 mV to –30mV. The negative ORP indicates that sulfite is a reducing agent and its concentration is only proportional value. In the medium load operation, the gas flow rate was at 980 Nm^3/h, and the Na_2SO_3 solution was in the range of 2.7 kg/h-4.7 kg/h, with 0.1 kg/h of NaOH. The NO_x removal was ranged from 70% to 80%, while the OPR varied from around 0mV to -30 mV. In the high-load operation, the gas flow rate was at 1, 480 Nm^3/h, and the Na_2SO_3 solution was in the range of 2.9 kg/h-5.2 kg/h, with 0.1 kg/h of NaOH. The NO_x removal was more than 60% when the ORP was -15 mV, and increased around 70% at -40 mV. The trend of the correlation between the NO_x removal and the ORP proved to be similar in any load operation. As a result, it is clear that the NO_x removal is definitely influenced by the ORP in the liquid, and the less ORP, the more NO_x removal.

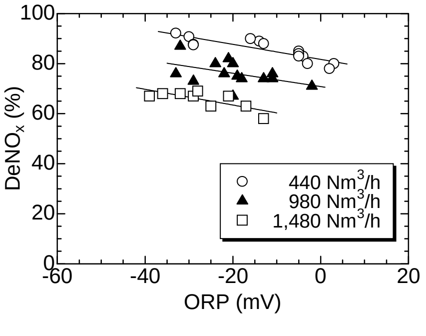


Fig. 6 NO_x removal efficiency vs. oxidation reduction potential (ORP)

The ORP, however, fluctuated from time to time. As Na_2SO_3 increased, the ORP decreased inversely. An attention was paid to the ORP change rate (mV/min) depending on the Na_2SO_3 injection rate, which was an index for the stable plant operation. Fig. 7 shows the effect of Na_2SO_3 injection rate on the ORP at 440, 980 Nm^3/h and 1,480 Nm^3/h. If the ORP change rate became negative value, the ORP decreased as operation time went on, which means the NO_x removal would be stable or increased. It is essential that the ORP change rate should be less than zero (0 mV/min) in order to keep the NO_x removal performance stable, in other words, Na_2SO_3 should be added at least more than 55 g/min (3.3 kg/h) at low load condition, and more than 70 g/min (4.2 kg/h) at medium load and high load conditions.

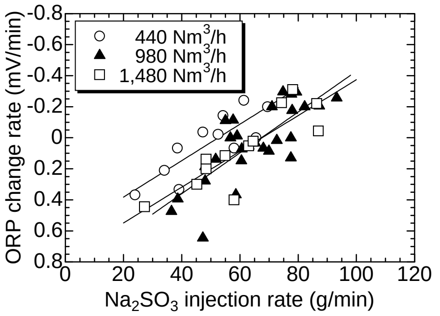


Fig.7 The effect of Na_2SO_3 injection rate on oxidation reduction potential (ORP)

On the other hand, the pH in the liquid was maintained in the range of 7.7-8.1 throughout the experiments, which was satisfactory to keep the proper NO_x removal. Chen et al. reported that the high NO_2 removal using the simulated gas can be obtained, keeping pH of 11 by the NaOH injection [20]. However, it was difficult to keep the pH of above 9 because actual flue gas contained approximately 9% of CO_2 in this experimental study. In addition, NaOH solution was consumed by CO_2 absorption in flue gas.

Effect of gas and liquid mass flow rates on NO_x removal

NO_x removal is influenced by gas and liquid flow rates. Both flow rates are converted to mass rates by dividing with the scrubber sectional area. Fig. 8 showed the relation between NO_x removal and gas mass flow rate. The gas mass flow rate was varied at 1,960, 4,380 kg/m^2h and 6,600 kg/m^2h, where the ORP was in the range of -10 mV~-40 mV.

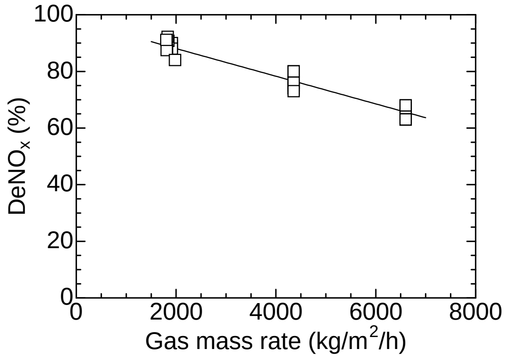


Fig. 8 The effect of gas mass flow rate on NO_x removal efficiency

The NO_x removal decreased as the gas mass rate increased. The NO_x removal on the approximate performance line was 90%, 77% and 68% corresponding to the above-described gas mass flow rates. The gas velocities were 0.5 m/s, 1.2 m/s and 1.7 m/s, respectively. A velocity of 0.5 m/s represents a 2.4 second contact time between NO_x and SO_{3-2} in the scrubber. It is considered that NO_x removal of more than 80% would require operation at gas velocities less than 1.0 m/s, equivalent to more than 1.2 second, while the ORP is in the range of -10 mV~ -40 mV.

Effect of liquid rate on NO_x removal was investigated as well. The liquid mass flow rate was maintained at 10,620 kg/m^2h and the gas mass flow rate was varied 1,920 kg/m^2h, 4,360 kg/m^2h and 6,600 kg/m^2h, while the ORP was in the range of -10 mV ~ -20 mV. Thus, the practical range of 1.6 to 5.5 liquid to gas mass ratio (L/G) was studied. The actual measurements from experiments are plotted in Fig. 9. The data indicated that the scrubbing effectiveness of NO_x removal increased with the L/G, and for the NO_x removal of 90% is required an L/G of more than 5.5. The scrubbing effectiveness was rather moderate, as compared with the test results that an L/G of more than 3 is required for high NO_2 absorption, such as 90%[20]. The difference of the effectiveness might be due to the difference of the ORP. Thus, the results showed the effect of liquid rate on the NO_x removal is smaller than that of gas rate.

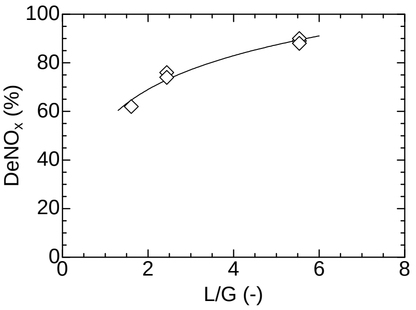


Fig. 9 The effect of liquid-gas ratio (L/G) on NO_x removal efficiency

Continuous operation of the plasma chemical hybrid system

For industrial application, it is important to check the long-term operation of the plasma chemical hybrid system for boiler emission. A continuous operation of the system was carried under the following conditions. The flue gas flow rate was set at 410 Nm^3/h. The injected O_3 was 38 g/h with 0.9 Nm^3/h. The liquid mass flow rate was maintained at 10,620 kg/m^2h by keeping Na_2SO_3 solution of 3.3 kg/h on the average and NaOH solution of 0.1 kg/h throughout the experiment. Fig. 10 shows the time-dependent NO_x and NO concentrations at MP1 and MP3, respectively, for a 300 minutes operation period. NO_x emission at boiler outlet was a low figure, 32 ppm, because that O_2 concentration was set at 4.5%, instead of 4.0% in usual operation. Fig. 11 shows the time-dependent ORP and pH in the liquid. The initial figures of ORP and pH were 0 mV and 7.7, respectively, but then, reached the constant figures. The NO_x removal ranged 88%-92% was attained and kept for a 300 minutes operation by maintaining ORP of around -30 mV and pH of 7.8. Thus, the NO_x emission was kept less than 4 ppm throughout the experiment.

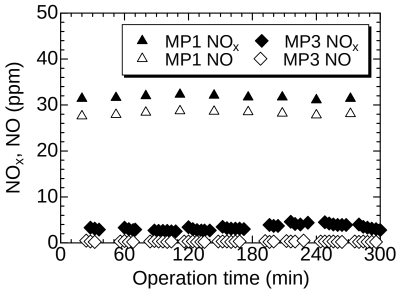


Fig.10 NO_x and NO concentration at boiler outlet and scrubber outlet as a function of the operation time

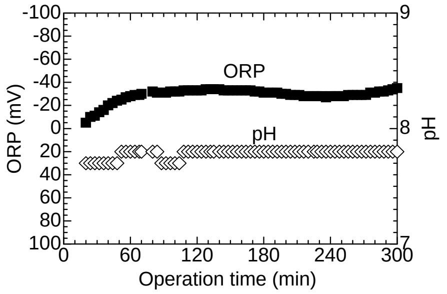


Fig. 11 The relation between oxidation reduction potential and pH as a function of the operation time

2 SUMMARY

The pilot scale plasma-chemical hybrid system was investigated and demonstrated for the NO_x removal for a smoke-tube boiler. The NO_x removal was clearly dependent on the ORP in the liquid, and increased inversely as the ORP decreased. To attain the specified NO_x removal, the ORP should be kept below 0 mV, as less as possible. However, the ORP fluctuated from time to time. It is essential that to keep NO_x removal performance effectively, the ORP change rate should be less than zero (0 mV/min) by maintaining proper Na_2SO_3 injection. The Na_2SO_3 injection rate should be at least more than 55 g/min (3.3 kg/h) at low load operation, and more than 70 g/min (4.2 kg/h) at medium and high load operations, which are so-called an index figure of Na_2SO_3 injection rate for continuous and stable operation. The NO_x removal increased from 65% to 90% as the gas mass rate decreased. it is considered that NO_x removal of more than 80% would require operation at gas velocities less than 1.0 m/s, while the ORP in the range of -10 mV ~ -40 mV. The scrubbing effectiveness of NO_x removal increased with the liquid to gas mass ratio (L/G), but was considerably moderate. The effect of liquid rate on the NO_x removal was smaller than that of gas rate.

It was demonstrated and confirmed that approximately 90 % of NO_x removal (less than 4 ppm) was attained during a 300 minutes continuous operation by maintaining ORP of around –30 mV and pH of 7.8.

ACKNOWLEDGEMENTS

Authors greatly thank Mr. Tanaka of Takao Iron Steel CO., Ltd., and Mr. Ito, and Mr. Yoshioka of the students of 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, Japan.

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