

## PILOT-SCALE NO<sub>x</sub> AND SO<sub>x</sub> REMOVAL FROM BOILER EMISSION USING RADICAL INJECTION AND CHEMICAL HYBRID PROCESS

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### ABSTRACT

The pilot-scale NO<sub>x</sub> and SO<sub>x</sub> simultaneous removal from boiler emission was performed using radical injection and chemical hybrid process. The radical injection is often called as indirect plasma (or remote plasma) and air radicals are produced at room temperature with less than 1/10 of the flue gas flow rate. The flue gas from the boiler was in the range of 450~1,470 Nm<sup>3</sup>/hr, the gas temperature of 280°C, and NO<sub>x</sub> concentration of 30 ppm for city gas, and 70 ppm of NO<sub>x</sub> and 35 ppm of SO<sub>x</sub> for heavy oil, respectively. The radical injection was demonstrated to be extremely effective for NO oxidation especially when the flue gas temperature is in the range of 300°C where NO<sub>x</sub> is rather generated at this temperature range. The produced NO<sub>2</sub> was further reduced to N<sub>2</sub>, and nontoxic and water soluble Na<sub>2</sub>SO<sub>4</sub> by Na<sub>2</sub>SO<sub>3</sub> solution in the chemical scrubber. For the case of oil firing boiler SO<sub>2</sub> was simultaneously adsorbed by NaOH solution. The NO<sub>x</sub> removal efficiency for gas firing exceeds 90% but NO<sub>x</sub> removal efficiency for oil firing was in the range of 60% due to the lack of radicals and ozone concentration with the pulse power supply used. The removal efficiency of SO<sub>2</sub> was in the range of 85~90%. The NO<sub>x</sub> removal efficiency was evaluated by the ratio of the radical flow rate by the indirect plasma to the primary flue gas flow rate, specific energy density, and Na<sub>2</sub>SO<sub>3</sub> concentration and chemical flow rate. Scrubbing solution was chemically analyzed and it is confirmed that the waste solution can be disposed outside of the plant.

## 1. INTRODUCTION

The laboratory-scale nonthermal plasma-chemical hybrid process for simultaneous NO<sub>x</sub> and SO<sub>x</sub> removal has been investigated over the years and demonstrated to achieve a nearly complete NO<sub>x</sub> and SO<sub>x</sub> removal with negligible reaction byproducts. These results were obtained by Yamamoto et al. (1998, 2000, 2001, 2002, 2003). The operating cost was less than 1/4 of the conventional selective catalytic reduction (SCR) system. Based on the laboratory-scale experimental studies, the pilot-scale NO<sub>x</sub> and SO<sub>x</sub> removal from boiler emission was carried out using the radical injection-chemical hybrid process. The flue gas flow rate was in the range of 450~1,470 Nm<sup>3</sup>/hr, the gas temperature of 280°C, and NO<sub>x</sub> concentration of 30 ppm for city gas firing, and 70 ppm of NO<sub>x</sub> and 35 ppm of SO<sub>x</sub> for oil firing, respectively. The radical injection (often referred to as indirect plasma or remote plasma) means that air radicals are externally produced at ambient temperature and pressure, and injected into the hot flue gas. It is extremely effective for NO oxidation especially when the flue gas temperature exceeds 300°C where NO<sub>x</sub> is generated at this temperature. The produced NO<sub>2</sub> was further reduced by Na<sub>2</sub>SO<sub>3</sub> solution in the chemical scrubber to form N<sub>2</sub>, and nontoxic and water soluble Na<sub>2</sub>SO<sub>4</sub>. For the case of oil firing boiler, SO<sub>2</sub> was simultaneously adsorbed by NaOH solution.

The radical injection methods for the purpose of NO oxidation and reduction have been investigated using ozone (O<sub>3</sub>), ammonia (NH<sub>3</sub>), nitrogen (N<sub>2</sub>), and methane (CH<sub>4</sub>) and N<sub>2</sub> mixture in both laboratory-scale and pilot-scale experiments. Zhou et al. (1992) have investigated the NO<sub>x</sub> removal using NH<sub>3</sub> radical injection, which was generated by the plasma jets using NH<sub>3</sub>, CH<sub>4</sub>, H<sub>2</sub> and their mixtures. The results showed that NH<sub>3</sub> plasma-injection was more effective than direct plasma with NH<sub>3</sub> mixture in the flue gas and the maximum of 85 % NO<sub>x</sub> removal was achieved at 400 W in a small-scale laboratory combustor. Similarly, 85~90 % of NO<sub>x</sub> removal was achieved at plasma torch power of 1.5 kW in a large-scale combustor. Nishida et al. (2001) reported that NO in N<sub>2</sub> gas was removed by injecting NH<sub>3</sub> radicals, which were externally generated by NH<sub>3</sub> diluted with argon, Ar, through the dielectric barrier discharge. Similar large-scale experiments were carried out by Dinelli et al. (1990) and demonstrated a successful result. Chang et al. (1998) examined the combustion flue gas NO<sub>x</sub> removal by the corona discharge activated by CH<sub>4</sub> radical injection using the two types of corona radical injectors, hollow needle and multi-hollow types at a laboratory-scale setup. The experimental results showed that NO<sub>x</sub> removal efficiency increased with increased voltage and non-monotonically depended on CH<sub>4</sub> stoichiometry. Regarding O<sub>3</sub> injection, Sano et al. (2003) and Yoshioka et al. (2001) have evaluated NO removal from diesel vehicle exhaust gas using oxygen injection, HC addition and direct discharge. It was found that oxygen injection could remove more NO than the case without oxygen, but HC addition to the ozonizer deteriorated NO removal efficiency. Simakev et al. (1988) have carried out the ozone-ammonia injection for simultaneous SO<sub>x</sub> and NO<sub>x</sub> removal of the flue gas generated from a 200 MW coal fired-boiler. The gas flow rate was varied at 5,000, 7,000 and 10,000 m<sup>3</sup>/hr. The results showed that around 90% of SO<sub>2</sub> removal efficiency and 75% of NO<sub>x</sub> removal efficiency were achieved with optimal operating mode with flue gas-ozone contact time of 0.45 seconds and with an ozone flow rate of 0.4 g/m<sup>3</sup> when the gas flow rate was 10,000 m<sup>3</sup>/hr. Slator et al. (1980) and some other researchers investigated ozone injection for NO<sub>x</sub> removal and showed the effectiveness of the indirect plasma method.

Air radical injection and chemical hybrid process was employed to remove the NO<sub>x</sub> and SO<sub>x</sub>, which is effective NO oxidation for the gas temperature in the range of 300°C, where NO oxidation is difficult with direct plasma. The NO<sub>x</sub> removal efficiency was evaluated by the ratio of the indirect plasma flow rate to the primary flue gas flow rate, specific energy density,

and Na<sub>2</sub>SO<sub>3</sub> concentration and chemical flow rate. Finally, the quality of disposed water was investigated.

## 2. EXPERIMENTAL SETUP

Figure 1 shows a schematic diagram of the pilot plant facility of air radical injection and a chemical flue gas treatment system. Flue gas was generated from the 2.0 ton/hr of steam generation boiler with firing a city gas (13A) of 121 Nm<sup>3</sup>/hr or heavy oil of 115 kg/hr as the rated values (Takao Tekko Co.). Air radicals were generated by the pulse plasma reactor at atmospheric pressure and temperature, and then injected into 280°C flue gas right after of the boiler exit. The flue gas was cooled down with spraying water in the duct to decrease the gas temperature low enough for protection of 1.2 m high polypropylene packing materials in the 0.9 m in diameter and 5.14 m high scrubber. Na<sub>2</sub>SO<sub>3</sub> solution as reducing chemical was sprayed from the top of the scrubber to react with NO<sub>2</sub> ( $2\text{NO}_2 + 4\text{Na}_2\text{SO}_3 \rightarrow 4\text{Na}_2\text{SO}_4 + \text{N}_2$ ) and additional NaOH solution for oil firing was used for SO<sub>2</sub> absorption. Then, flue gas was discharged to the stack.

The plasma reactor consists of 14 sets of twisted wire centered in the 0.2 m in diameter and 0.5 m high stainless steel spiral coil electrode. The ambient air was induced and passed through the 10 kW pulse generator to produce active species. The thyristors were used as a high voltage switch to release the stored energy through the capacitor. The magnetic pulse compression circuit was utilized to produce the sharp rise time with extremely short pulse width. The pulse repetition frequency can be varied up to 1,000 pps (pulse per second).

The experiments were performed after the gas temperature reached steady state. The flue gas was based on 20~80% load and was set at 450, 940, and 1,470 Nm<sup>3</sup>/hr for firing gas and 660 and 1,470 Nm<sup>3</sup>/hr for firing heavy oil where the gas flow rate was determined by fuel consumption and O<sub>2</sub> concentration. The flue gas temperature was measured with thermocouples and read with the digital recorder. The concentrations of gas constituents (O<sub>2</sub>, CO, CO<sub>2</sub>, NO, and NO<sub>x</sub>) were measured with a gas analyzer (Shimadzu, NOA-7000, chemiluminescence NO<sub>x</sub> analyzer, O<sub>2</sub> for zirconia method, and CGT-7000, Infrared adsorption for CO-CO<sub>2</sub> analyzer), and by a gas analyzer (Horiba, PG-235, chemiluminescence NO analyzer). SO<sub>x</sub> was measured in accordance with JIS K 0103 turbidimetric analysis method, and the particulates concentration with JIS Z 8808 filter paper method. The air radical flow rate was varied from 50 ~ 230 Nm<sup>3</sup>/hr and measured with a float type flow meter. The O<sub>3</sub> concentration was continuously measured by O<sub>3</sub> meter (Ebara, EG-2001B). The voltage-current waveforms were measured by an oscilloscope (Tektronix, TDS380P) through the voltage divider (Tektronix, P6015A) and the current probe. The liquid samples of the scrubbing solution were extracted periodically through a valve at the bottom basin of the scrubber, and pH of the sample was measured by the pH meter (Horiba, B-211). After the experiments, the sampled scrubbing solutions were chemically analyzed to check the dissolved constituents for disposal.

## 3. RESULTS AND DISCUSSION

The pulsing peak voltage was 83 kV, the peak current 355 A, and the rising time 100 nano-seconds (ns) at the 1,000 pps. The energy was measured at every 100 pps and showed 3.28 J/pulse regardless of the pulse frequency. The electrical power was 3.28 kW at the 1,000 pps, 2.27 kW at 700 pps, and 1.32 kW at 400 pps, respectively. The pulse frequency was set at 1,000 pps during whole experiments. Air radicals such as O<sub>3</sub>, O, OH, O<sub>2</sub><sup>\*</sup>, HO<sub>2</sub>, and N were produced by the plasma generator. The O<sub>3</sub> generation increased up to 80g/h as the pulse power increased to 3.3 Wh/m<sup>3</sup>.

### 3.1 NO<sub>x</sub> Removal from City Gas Boiler

The flue gas temperatures are 250°C at the boiler outlet (i), 200°C at the scrubber inlet (ii), 170°C at the scrubber outlet (iv) without cooling water spray and 120°C at (ii) and (iv) with cooling water spray when the gas flow rate was 995 Nm<sup>3</sup>/hr. When the gas flow rate was 1,452 Nm<sup>3</sup>/hr, the flue gas temperature became 290°C at (i), 200°C at (ii), and 180°C at (iv) without water spray, and 60°C at (iv) with cooling water spray.

Figure 2 shows the NO and NO<sub>x</sub> removal efficiencies (here-in-after called,  $\eta_{\text{NO}}$  and  $\eta_{\text{NO}_x}$ ) for firing the city gas when the flow rate of the radical air,  $Q_a$ , was set at 50, 100, 151, or 238 Nm<sup>3</sup>/hr and the flow rate of flue gas,  $Q_g$ , was at either 450, 900 or 1,470 Nm<sup>3</sup>/hr. The ratio of air radical to flue gas ( $Q_a/Q_g$ ) was in the range of 3.3 to 37.5%. As can be seen from the figure that  $\eta_{\text{NO}}$  increased with increased  $Q_a/Q_g$ . When  $Q_a/Q_g=10\%$ ,  $\eta_{\text{NO}}$  was around 83 % on average, and when  $Q_a/Q_g=25\%$ ,  $\eta_{\text{NO}}$  be 90% on average where inlet NO concentration was 24 ppm. When  $Q_a/Q_g$  was at maximum of 37.5%,  $\eta_{\text{NO}}$  reaches 95%. It implies that radical injection is extremely effective even with small fraction of the gas volume. On the other hand,  $\eta_{\text{NO}_x}$  increased with increased  $Q_a/Q_g$ . The data were rather scattered as compared to  $\eta_{\text{NO}}$  because it was related to unstable chemical reaction in the scrubber. The  $\eta_{\text{NO}_x}$  increased 57%, 78% and 87% on average when  $Q_a/Q_g$  was set at 10%, 25%, and 37.5%, respectively.

The time-dependent NO, NO<sub>x</sub> and pH value of Na<sub>2</sub>SO<sub>3</sub> solution with  $Q_g=940$  m<sup>3</sup>N/hr and  $Q_a/Q_g=10.5\%$  during 260 minutes' operation of the city-gas firing was observed. The NO concentrations at the scrubber inlet (ii) and outlet (iv) did not vary but NO<sub>x</sub> concentration at the scrubber outlet (iv) increased and pH value at the scrubber bottom decreased from 9.1 to 6.8 as time elapsed. The experimental results indicated that chemicals should be continuously added to keep the effectiveness of NO<sub>2</sub> reduction because the portion of Na<sub>2</sub>SO<sub>3</sub> solution reacts with oxygen in flue gas:  $2\text{Na}_2\text{SO}_3 + \text{O}_2 \rightarrow 2\text{Na}_2\text{SO}_4$ . Thereafter, one stoichiometric amount of Na<sub>2</sub>SO<sub>3</sub> solution was continuously added to the spraying system of the scrubber.

Figures 3(a)-(b) show  $\eta_{\text{NO}}$  and  $\eta_{\text{NO}_x}$  vs. specific energy density based on flue gas,  $W_{pg}$ , for all the experiments when  $Q_g=450, 900$  and  $1,470$  Nm<sup>3</sup>/hr and  $Q_a/Q_g$  varied from 3.3% to 37.5%. The  $\eta_{\text{NO}}$  and  $\eta_{\text{NO}_x}$  increased with increase in  $W_{pg}$ , which is directly related to amount of air radicals. As shown in Fig. 5(a),  $\eta_{\text{NO}}$  were 84%, 90% and 93% on average when  $W_{pg}=0.4, 0.8$  and  $1.2$  Wh/m<sup>3</sup>. The  $\eta_{\text{NO}_x}$  were 62%, 77% and 86% at the same specific powers, respectively as was shown in Fig. 3(b). The NO reduction energy efficiency (g-NO/kWh) is expressed as the ratio of the total amount of NO removal (g-NO) to a 1 kWh of input power. All experimental data were somewhat scattered because  $Q_a/Q_g$  varied widely from 6.0% to 37.5%. The NO removal energy efficiency was around 30 g-NO/kWh with  $\eta_{\text{NO}}=90\%$  and 50 g-NO/kWh with  $\eta_{\text{NO}}=80\%$ .

The ratio of the scrubbing solution to the flue gas ( $L/G$ ) on  $\eta_{\text{NO}_x}$  was investigated when  $Q_g=450$  Nm<sup>3</sup>/hr,  $Q_a/Q_g=37.5\%$  and scrubbing solution flow rate,  $L$ , was varied 5.0, 8.0 and the maximum 11.0 m<sup>3</sup>/hr. The  $\eta_{\text{NO}_x}$  was hardly influenced by  $L/G$ . The effect of gas residence time ( $R_t$ ) through the tower packing of the scrubber on the amount of NO<sub>x</sub> removal was investigated when  $Q_g=450, 900$  and  $1,470$  Nm<sup>3</sup>/hr and  $Q_a/Q_g=6.0\% \sim 37.5\%$ . As  $R_t$  increased, the amount of NO<sub>x</sub> removal increased slightly because NO inlet concentration was in the range of 30 ppm.

### 3.2 NO<sub>x</sub> Removal for Oil Fired-Boiler

Figure 4 shows  $n_{NO}$  and  $n_{NOx}$  vs.  $Q_a/Q_g$  when  $Q_a$  was at 50, 100, 151, or 238 Nm<sup>3</sup>/hr, and  $Q_g$  was either 650 or 1,170 Nm<sup>3</sup>/hr. The  $Q_a/Q_g$  was varied in the range of 2.4% to 23.9%. When  $Q_a/Q_g$  was 10%, 15%, and 20%,  $n_{NO}$  increased to 50%, 64%, and 73% on average, respectively and increased further up to around 80% with  $Q_a/Q_g=23.9\%$ . As compared to the results of the city-gas firing,  $n_{NO}$  were 20~25% lower because NO inlet concentration was three times higher than those of the city-gas, while O<sub>3</sub> concentration was lower for the present pulse power supply. On the other hand, as  $Q_a/Q_g$  increased,  $n_{NOx}$  increased less than that of  $n_{NO}$ . This was considered to be unstable chemical reaction in the scrubber. When  $Q_a/Q_g=10\%$ , 15%, and 20%,  $n_{NOx}$  was around 37%, 47%, and 53% on average, and reached 57% with  $Q_a/Q_g=23.9\%$ .

Figures 5(a)-(b) show  $n_{NO}$  and  $n_{NOx}$  as a function of the specified power density ( $W_{pg}$ ) for  $Q_g=650$ , and 1,170 Nm<sup>3</sup>/hr and  $Q_a/Q_g=2.4\% \sim 23.9\%$ . It is clear from Fig. 5(a) that  $n_{NO}$  increased rapidly with increasing  $W_{pg}$  regardless of the gas flow rate. The  $n_{NO}$  was 60% on average at  $W_{pg}=0.4$  Wh/m<sup>3</sup>, and up to around 80% on average at 0.8 Wh/m<sup>3</sup> (equivalent to  $Q_a/Q_g=23.9\%$ ). Fig. 5(b) shows that  $n_{NOx}$  was widely scattered as compared to  $n_{NO}$ , especially in the range of more than 0.3 Wh/m<sup>3</sup>. This was again caused by the lack of O<sub>3</sub> from the present plasma reactor and unstable chemical reaction in the scrubber. The  $n_{NOx}$  was 43% on average at  $W_{pg}=0.4$  Wh/m<sup>3</sup>, and up to around 60% on average at 0.8 Wh/m<sup>3</sup>. The NO removal energy efficiency decreased significantly as  $n_{NO}$  increased. NO energy efficiency was around 90 g-NO/kWh for  $n_{NO}=60\%$  and 70 g-NO/kWh for  $n_{NO}=80\%$ , respectively, which was significantly higher for the city-gas firing.

Figure 6 compares  $n_{NO}$  vs. the ratio of air radical to gas flow rate ( $Q_a/Q_g$ ) for both fuels. As can be seen from the figure  $n_{NO}$  increased with increased  $Q_a/Q_g$ . The  $n_{NO}$  for the city-gas increased moderately with increase in  $Q_a/Q_g$ , but  $n_{NO}$  for the oil firing increased sharply. The difference of  $n_{NO}$  between both fuels depend on the difference of NO inlet concentration i.e. 30 ppm for the city-gas and 80 ppm for the oil, which was similar to the laboratory test results. The highest NO removal efficiency obtained was in the range of 89%~95% at  $Q_a/Q_g=37.5\%$  for the city-gas and 81%~84% at  $Q_a/Q_g=23.6\%$  for the oil. As a result, in order to obtain more than 80% of  $n_{NO}$ , the  $Q_a/Q_g$  over 20% was needed for both fuels using for this plasma device.

Figure 7 showed that amount of NO removal with stoichiometric O<sub>3</sub> injection was significantly higher, indicating that NO oxidation takes place more than required O<sub>3</sub> concentration. The ratio of NO removal to stoichiometric amount of O<sub>3</sub> was 1.8~2.4 for the oil and 1.2~1.8 for the city-gas. The results indicated that air radicals were not limited to O<sub>3</sub>, but included other radical species. In addition, the flue gas constituents for both fuels such as moisture and CO<sub>2</sub> were responsible for NO oxidation.

Figure 8 shows the correlation between the penetration and the specific power density (Wh/m<sup>3</sup>/ppm) in which all the experimental data using both fuels were included. The NO penetration ( $1 - n_{NO}$ ) means that the penetrated NO was not removed by the system and discharged outside. The NO penetration was 25% on average at 0.01 Wh/m<sup>3</sup>/ppm in specific power density, and 10% on average at 0.03 Wh/m<sup>3</sup>/ppm, resulting in 90% of NO removal efficiency. This means that even for the case of the oil firing, NO penetration was reduced with increase in specific power density. It is interesting to note that NO penetration of the laboratory results based on  $Q_g=0.6$  Nm<sup>3</sup>/hr,  $Q_a/Q_g=5\sim 40\%$  and NO inlet concentrations of 300, 500, and 700 ppm, were entirely higher than those of the pilot scale test results. If we compare both penetration at 0.04 Wh/m<sup>3</sup>/ppm, the NO penetration was 40% in the laboratory test, but

only 10% in the pilot test result. In other words, in order to achieve 80% NO efficiency, the specific power density of 0.013 Wh/m<sup>3</sup>/ppm is needed for the pilot test, but 0.051 Wh/m<sup>3</sup>/ppm for the laboratory test. The pilot test result was only a quarter of specific power of the laboratory test results. The similar trend was observed with other pilot-scale experiments [5].

Figure 9 shows  $n_{NOx}$  vs. the specific power density (Wh/m<sup>3</sup>/ppm) for all experimental data when  $Q_a/Q_g=3\sim37\%$  for both fuels. The laboratory test data were also plotted. The laboratory test condition was set at  $Q_g=0.3, 0.49$  and  $0.6$  Nm<sup>3</sup>/hr,  $Q_a/Q_g=10\%$  and NO inlet concentrations of 300 ppm. The laboratory data were very close to the pilot scale data. Even for the case of the heavy oil firing,  $n_{NOx}=80\%$  could be achieved with the specific power density of 0.045 Wh/m<sup>3</sup>/ppm.

### 3.3 SO<sub>x</sub> and Particulate Removal

SO<sub>x</sub> and particulate removal efficiencies were measured with  $Q_g=676$  Nm<sup>3</sup>/h,  $Q_a/Q_g=15.1\%$  for heavy oil firing of which sulfur content was 0.082%. The measured SO<sub>x</sub> concentration was 35 ppm at the boiler outlet (i), and less than 5 ppm at the scrubber outlet (iv). More than 86% of SO<sub>x</sub> removal efficiency was achieved by the system. On the other hand, particulate concentration was 11 mg/Nm<sup>3</sup> at the inlet, and 7 mg/Nm<sup>3</sup> at the outlet. Particulate removal efficiency was 36.4%, which was better than expected considering extremely fine particulates and the use of the chemical scrubber. According to these results, the air radical injection and chemical hybrid system was confirmed to remove simultaneously NO<sub>x</sub> and SO<sub>x</sub> with some particulates from the boiler emission.

### 3.4 Analytical Results of Scrubbing Solution

Table 1 shows the analytical results of the scrubbing solution extracted from the bottom of the scrubber for both fuels. The concentration of SO<sub>4</sub><sup>2-</sup> for both fuels was significantly higher than SO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>. It implies that SO<sub>2</sub> was dissolved in the solution, and Na<sub>2</sub>SO<sub>4</sub>, which Na<sub>2</sub>SO<sub>3</sub> reacted with NO<sub>2</sub> and O<sub>2</sub> in flue gas. The SO<sub>3</sub><sup>2-</sup> concentration showed high for both fuels. The NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> for the oil were detected higher than that for the city-gas due to NO concentration in fuel. For industrial application, the regulation of waste water as well as sewage water should be taken into consideration and pH, BOD, COD, SS and T-N ions are important items. The measured data were shown in Table I and the results were satisfied with the regulation except S-Fe (soluble ferrous ion), which was caused by the corrosion due to the scrubber casing made of carbon steel. This issue can be resolved by using anti-corrosion materials such as stainless steel. Therefore, the waste solution can be exposed outside of the plant as a general waste water.

## 4. SUMMARY

The pilot-scale NO<sub>x</sub> and SO<sub>x</sub> removal from boiler emission was successfully demonstrated using radical injection and chemical hybrid process. This hybrid process is extremely effective for NO oxidation and NO<sub>2</sub> reduction, resulting in the reduction of the size of the plasma reactor. The ratio of NO removal to stoichiometric O<sub>3</sub> concentration for NO oxidation was 1.2~1.8 for the city-gas and 1.8~2.4 for the oil firing. Although O<sub>3</sub> is the major NO oxidation species, air radicals were not limited to O<sub>3</sub> but other radicals. The removal efficiency of SO<sub>2</sub> was in the range of 85~90%. Scrubbing solution was chemically analyzed and it is confirmed that the waste solution can be disposed outside of the plant.

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Table 1: Analytical results of the scrubbing solution extracted from the bottom of the scrubber for both fuels

Unit	Analyzed sample		Analysis method	Sewage disposal regulation	Waste water regulation
	City-gas (8/2)	Heavy oil (8/3)			
pH (-)	7.5 (20°C)	8.5 (20°C)	JIS K0102 12.1	5.8~8.6	5.8~8.6
BOD (mg/L)	84	150	JIS K0102 14.1	300	160 (Day ave. 120)
COD (mg/L)	7	34	JIS K0102 17	-	160 (Day ave. 120)
SS (mg/L)	<1	<1	JIS K0102 21	300	200 (Day ave. 150)
S-Fe (mg/L)	46	84	JIS K0102 57.2	10	10
T-N (mg/L)	19	34	JIS K0102 45.2	240	120 (Day ave. 60)
NO <sub>2</sub> -N (mg/L)	3	17	JIS K0101 37.1.1	380	-
NO <sub>3</sub> -N (mg/L)	13	10	JIS K0101 37.2.3		-
NH <sub>4</sub> -N (mg/L)	-	-	-		-
SO <sub>3</sub> <sup>2-</sup> (mg/L)	1250	625	JIS K010240.1	-	-
SO <sub>4</sub> <sup>2-</sup> (mg/L)	16000	22000	JIS K010241.3	o	-
Remarks	1. The waste water disposal standard is based on the sewage regulation standard of Sakai city for the specified manufacturing industry of more than 50 m <sup>3</sup> /d.				

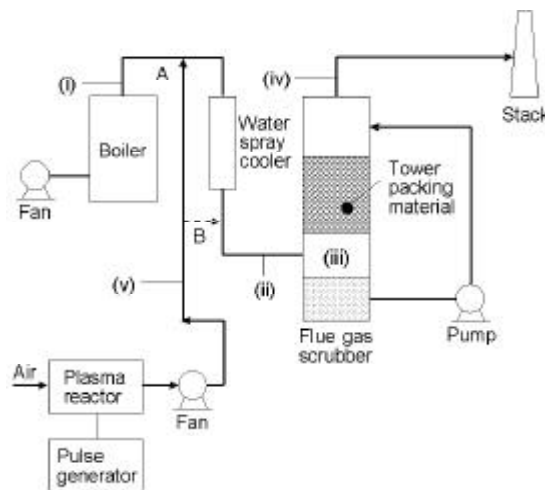


Figure 1: Schematic diagram of the pilot plant facility of air radical injection and a chemical flue gas treatment system

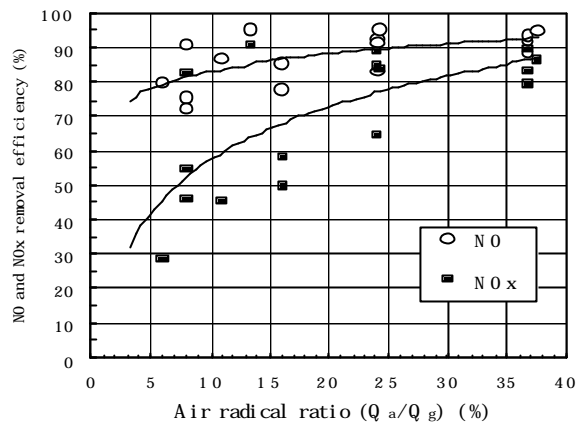
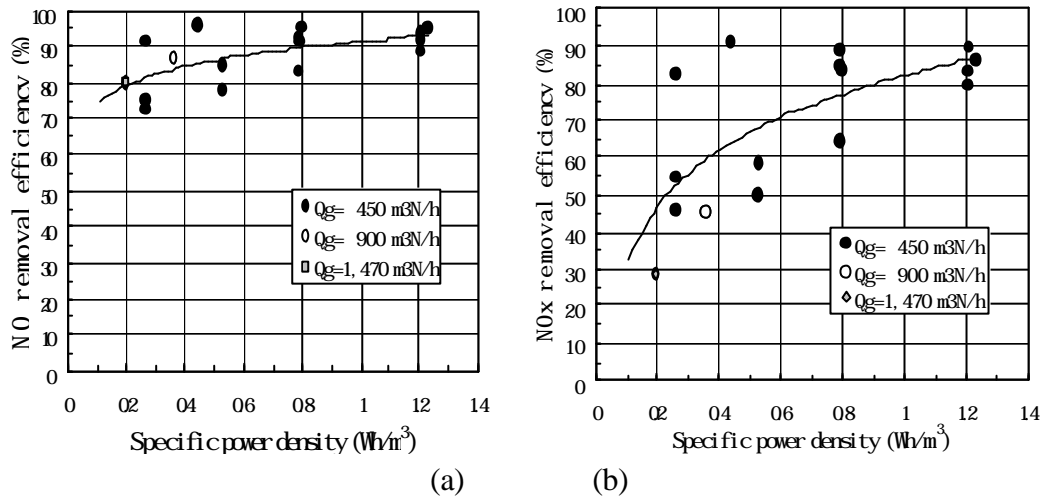


Figure 2: NO and NOx removal efficiencies vs. air radical ratio ( $Q_a/Q_g$ ) for the city-gas firing



Figures 3(a)-(b): NO and NOx removal efficiencies vs. specific power density ( $W_{pg}$ ) for the city gas

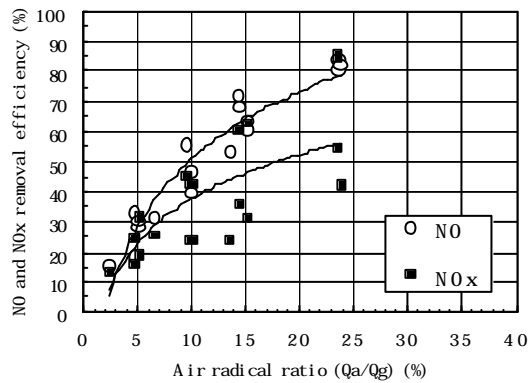
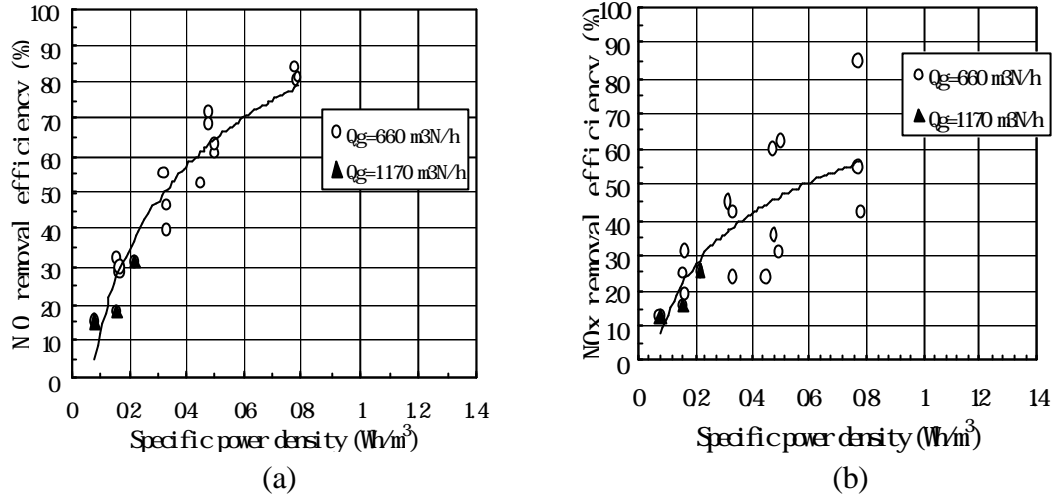


Figure 4: NO and NOx removal efficiencies vs.  $Q_a/Q_g$  for the oil-fired boiler



Figures 5(a)-(b): NO and NOx removal efficiencies vs. specific power density ( $W_{pg}$ ) for the oil-fired boiler

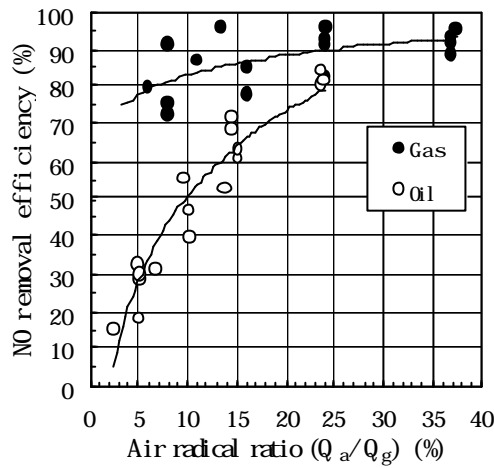


Figure 6: NO removal efficiency vs. radical ratio ( $Q_a/Q_g$ ) for both fuels

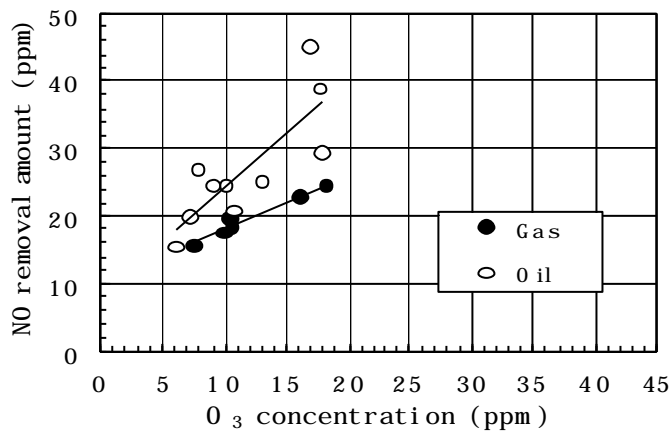


Figure 7: Amount of NO removal vs.  $O_3$  concentration when  $Q_a/Q_g = 6 \sim 10\%$  for both fuels

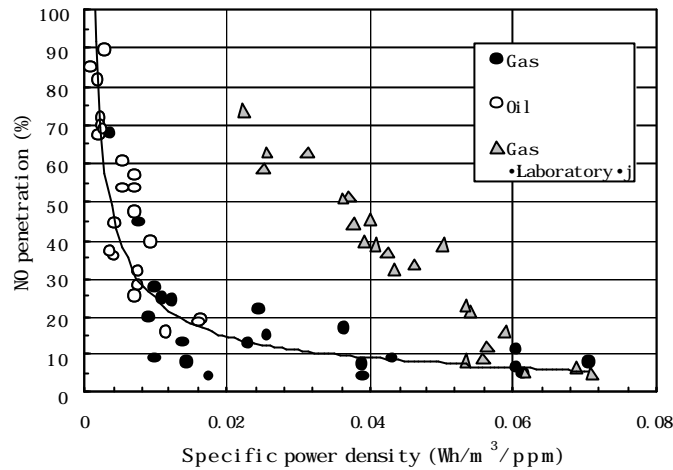


Figure 8: NO penetration rate vs. specific power density when  $Q_g=450\sim 1,470\text{ m}^3\text{N/hr}$  and  $Q_a/Q_g=3\sim 37\%$  for both fuels, including the laboratory test results when  $Q_g=0.6\text{ m}^3\text{N/hr}$ ,  $O_a/O_o=5\sim 40\%$ , and NO inlet concentration of 300~700 ppm

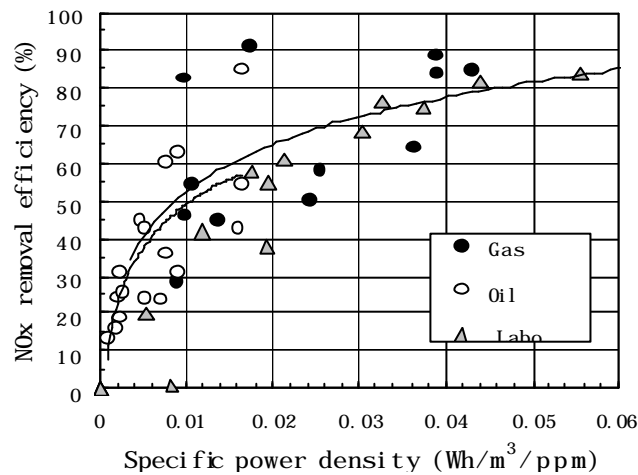


Figure 9: NOx removal efficiency vs. specific power density for both fuels when  $Q_g=450\sim 1,470\text{ m}^3\text{N/hr}$ , and  $Q_a/Q_g=3\sim 37\%$ , including the laboratory test results when  $Q_g=0.3, 0.49$  and  $0.6\text{ m}^3\text{N/hr}$ ,  $Q_a/Q_g=10\%$ , and NO inlet concentration of 300 ppm