Total Emission Control for Multi-Fuel Boiler System with Plasma-Chemical Aftertreatment

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Abstract—A low-emission boiler system that consists of a multi-fuel boiler for hot water or steam supply and a plasma–chemical hybrid NOx removal apparatus is demonstrated. The boiler has a 2.5 t/h steam generation rate. Many experiments are conducted using fuel gas and oils at flue gas flow rates between 550 to 2250 Nm$^3$/h (N: 0°C, one pressure). Operational characteristics are investigated in order to achieve stable continuous system operation. Ozone injection for NO oxidation and a Na$_2$SO$_3$ solution for NO$_2$ reduction are essential factors of the hybrid NO$_x$ removal system. The effect of operational parameters on NO$_x$ removal characteristics are obtained, such as O$_3$ injection method, Na$_2$SO$_3$ supply rate, and the flow rate correlation between the Na$_2$SO$_3$ solution, fresh water, and drainage. An operation of four successive days is satisfactorily carried out, maintaining a stable NO$_x$ removal efficiency of more than 85%. This low-emission boiler system can be used in industry.

Keywords—Nonthermal plasma, chemical process, multi-fuel boiler, NO$_x$ and SO$_x$ treatment, ozone, Na$_2$SO$_3$.

1. INTRODUCTION

Particulates, SO$_x$, and NO$_x$ are emitted from boilers when fossil fuels such as coal, oil, and so on are combusted. Particulates are generally removed by electrostatic precipitator (ESP), SO$_x$ by wet limestone gypsum desulfurization (De-SO$_x$), and NO$_x$ by selective catalytic reduction (SCR) denitrification (De-NO$_x$). The flue gas treatment system combined with ESP, De-SO$_x$, and De-NO$_x$, as shown in Fig. 1 (a), has been applied for large boilers of utility power stations or big factories to achieve individual emission regulations. However, for small boilers for hot water, steam, and co-generation the same treatment system is not applied because SCR De-NO$_x$ is not cost-effective and it has a noxious NH$_3$ gas slip problem into the air. The number of small boilers using city natural gas (CNG), heavy oil, and waste oils has been increasing year by year in Japan, and more stringent regulations for NO$_x$ emission are being anticipated in order to reduce environmental NO$_x$ concentration. A suitable flue gas treatment system for small boilers will be required soon. Fig. 1 (b) shows a total emission control system for small boilers proposed by the authors, consisting of an ESP for particulates if necessary and a hybrid (NO$_x$ and SO$_x$ removal) apparatus.

In the present study, we focus on the NO$_x$ treatment apparatus. Several studies have been conducted on laboratory-scale nonthermal plasma–chemical hybrid processes for the removal of NO$_x$ from gases emitted from various stationary sources [1–7]. However, because the flue gases must be treated directly, treatment of large volume requires both a large plasma reactor and a large amount of power. An alternative process has been developed that involves the injection of O$_3$ or radicals generated from O$_2$, NH$_3$, N$_2$, and CH$_4$ by using plasma. This process has been found to be extremely effective for NO$_x$ removal [8–18] because only the necessary amounts of gas are treated externally at ambient temperature and pressure. The authors propose a plasma–chemical hybrid process consisting of an indirect nonthermal plasma process and wet-chemical treatment. The principle of NO$_x$ removal is as follows:

$$\text{O}_3 \rightarrow \text{O}_2 + \text{O} \quad (1)$$
$$\text{NO} + \text{O} \rightarrow \text{NO}_2 \quad (2)$$
$$2\text{NO}_2 + 4\text{Na}_2\text{SO}_3 \rightarrow \text{N}_2 + 4\text{Na}_2\text{SO}_4 \quad (3)$$

On the basis of laboratory-scale experimental studies, tests on the removal of both NO$_x$ and SO$_x$ from the gas emitted from a boiler were carried out using an initial pilot-scale apparatus [19]. The NO$_x$ removal efficiency during the combustion of CNG exceeded 90%. Further experiments were carried out using a second pilot-scale apparatus [20–22]. Continuous operation for 3–5 h was successful, and the NO$_x$ removal performance characteristics were investigated. A third experiment was conducted using a demonstration plant consisting of a multi-fuel boiler and an improved chemical scrubber [23–24]. The goal of the study is to apply the boiler system for practical industrial use. To achieve this, there are four targets to be investigated. The first is to determine the dependency of NO removal on the O$_3$ concentration at elevated flue gas temperatures. The second is to examine the performance of NO$_x$ removal...
when bio-oils mixed with heavy oil are combusted at the boiler. The third is to achieve ultralow or nearly zero NO\textsubscript{x} emission with city gas fuel. The fourth is to confirm that the system can be operated continuously for several hours with city gas fuel. The results of these investigations have already been reported. A further area of investigation is to obtain the basic operational characteristics of the small boiler system with plasma-chemical aftertreatment for industrial application. The results of the investigation of these operational characteristics are described in this paper in order to finalize the study with the present system.

II. EXPERIMENTAL SETUP

Fig. 2 shows a schematic diagram of the plant. The flue tube boiler (Takao Iron Works Co., Ltd.) has both an original rotary burner and a low-NO\textsubscript{x} burner for gas and/or oil and is operated by using CNG (13A, Osaka Gas Co. Ltd.) at 157 Nm\textsuperscript{3}/h and A-type heavy oil at 171 L/h. The boiler has a steam generation rate of 2.5 t/h. The boiler has an air damper and a combustion air blower with a motor used in a variable frequency drive system, by which flow rate of combustion air to the boiler is controlled. Two sets of commercial ozonizers (EW-90Z, Ebara Jitsugyo Co., Ltd.) equipped with a pressure swing adsorption (PSA) oxygen generator from ambient air are employed to generate O\textsubscript{3}. High-concentration O\textsubscript{3} (4.7\% in maximum) gas is injected into the duct and diluted in order to oxidize almost all the NO to NO\textsubscript{2} according to reactions (1)–(2). The O\textsubscript{3} concentration in the duct is measured using an O\textsubscript{3} analyzer (EG-550, Ebara Jitsugyo Co., Ltd.).

The flue gas is then introduced into the scrubber at a height of 3.7 m in order to reduce NO\textsubscript{2} to N\textsubscript{2} according to reaction (3). The diameters of the scrubber are 0.9 m at the sump part and 0.7 m at the packing material layer part. An aqueous solution of Na\textsubscript{2}SO\textsubscript{3} and NaOH (concentrations: 1.0 mol/L and 0.15 mol/L, respectively) obtained from a chemical factory as a by-product is continuously added into the sump at a flow rate of 0.04–0.12 m\textsuperscript{3}/h from the solution tank. The initial Na\textsubscript{2}SO\textsubscript{3} concentration of the scrubbing solution in the sump is set to more than 0.13 mol/L. Using a centrifugal pump (CRN5-B, 2.2 kW, Grundfos Pumps Co. Ltd.), the scrubbing solution is pumped at a flow rate of 3 or 5 m\textsuperscript{3}/h from the sump to the top of the scrubber and sprayed through a nozzle over the packing material layer (height: 1.2 m). Na\textsubscript{2}SO\textsubscript{4}, which is a non-toxic, water-soluble compound, is produced in the scrubbing solution as a by-product. A small amount of scrubbing solution is continuously drained from the scrubber in order to maintain the activity of the solution and to dispose of the by-product outside the plant. It is important to maintain proper Na\textsubscript{2}SO\textsubscript{3} concentration for continuous stable NO\textsubscript{2} reduction. Therefore, oxidation reduction potential (ORP) and pH sensors are installed on a tributary line connected to the sump and the values are monitored. After the treatment, the cleaned flue gas is discharged from the stack into the air. The load of the boiler is varied at 30–100\% of the rated load. The flue gas flow rate is calculated based on the fuel flow rate and O\textsubscript{2} concentration of the flue gas at the boiler outlet. The flue gas constituents (O\textsubscript{2}, CO\textsubscript{2}, CO, NO\textsubscript{x}, and NO) are measured by using two gas analyzers (PG-240, Horiba). The temperature of the flue gas and the concentrations of its constituents are measured using gas analyzers at the
following three sampling points: MP1 (boiler outlet), MP2 (scrubber inlet), and MP3 (scrubber outlet). The experiments are carried out by firing CNG and heavy oil continuously for 120–450 min on a single day [24].

Fig. 3 shows the structure of the discharge section of the plasma reactor in the ozonizer. A coaxial nonthermal plasma (NTP) reactor or silent discharge-type reactor is used. O₃ gas is generated after O₂ gas by PSA passes through the 30 discharge elements inside the ozonizer and then injected into a flue gas duct for NO oxidation. The O₃ gas flow rate is constant, 0.9 Nm³/h. When the discharge power is 1.5 kW and the PSA power is 1.6 kW, 90 g/h of O₃ is generated in maximum with a concentration of 4.7% and the energy efficiency of 29 g/kWh.

Throughout this paper, the NOₓ concentration is defined as the converted value at 5% or 4% O₂ concentration in the case of the fuel gas or oil, respectively. The NOₓ removal efficiency (η_NOₓ) is calculated using the equation:

$$\eta_{NO_x} = (1 - \frac{NO_x_{MP1}}{NO_x_{MP3}}) \times 100\%$$

where NOₓ_{MP1} and NOₓ_{MP3} represent the NOₓ concentrations at MP1 and MP3, respectively. The NO removal efficiency (η_NO) is also defined as

$$\eta_{NO} = (1 - \frac{NO_{MP1}}{NO_{MP3}}) \times 100\%$$

III. RESULTS AND DISCUSSION

A. Flue Gas Constituents

First, NOₓ emission as a function of O₂ concentration in the flue gas is investigated when firing heavy oil. The O₂ concentration at MP1 is set stepwise to 3, 4, 5, 6, and 7% by adjusting flow rate of combustion air. Fig. 4 shows the relation between NOₓ and O₂ concentrations at MP1 when the boiler is operated at low, middle, and high load conditions, which are equivalent to fuel flow rates of 67, 126, and 157 L/h, respectively. The O₂ concentration is actually 2.4–7.8%. The average flow rates of the flue gas at the three load conditions are 830, 1750, and 2060 Nm³/h, respectively. The measured data indicate that as the O₂ concentration decreases from 6% to 2.4%, NOₓ emission decreases from 100 ppm to 80 ppm at the low load and from 100 ppm to 90 ppm at the high load, respectively. However, at the middle load, NOₓ slightly increases to 90–95 ppm. This result means that it is desirable to operate the boiler at the lower O₂ concentration of 3–7% because that is the concentration at which NOₓ decreases.

Fig. 5 shows CO concentration as a function of O₂ concentrations at the same operations of Fig. 4. In results the O₂ concentration at MP1 should therefore be set to 3–5% in order to reduce NOₓ emission, taking less CO emission into consideration.
B. Ozone Injection

According to reactions (1)–(2), NO is oxidized to NO$_2$ by O$_3$. O$_3$ injection is an important operational factor of the system. The direction at which O$_3$ is injected into the duct is also an important operational factor.

Table I shows the effect of the O$_3$ flow direction on NO removal (De-NO). The O$_3$ injection velocity is 9.6 m/s at three different directions in relation to the flue gas flow, i.e., with, across, and against the flow, with the flue gas velocity set to 5.6 m/s in the gas duct. The amount of NO removed ($\Delta$NO) between MP1 and MP3 and the De-NO efficiency are almost the same at 48 ppm and 87%, respectively, at any direction. As a result, O$_3$ flow is set to be against the flow.

Furthermore, the effect of velocity changes on NO removal is investigated. However, no effect is detected when the O$_3$ and flue gas velocities are within 2.6–5.6 m/s and 7.3–9.6 m/s, respectively. These results prove that all injected O$_3$ is immediately consumed for oxidizing NO to NO$_2$ in the duct. It is clarified that $\Delta$NO is nearly the same as the amount of O$_3$ required to oxidize NO to NO$_2$ (almost 1:1, or a stoichiometric ratio) [21]. Fig. 6 shows the ratio $\Delta$NO/O$_3$ as a function of O$_2$ concentration at MP1 with flue gas flow rates in the range of 830–2060 Nm$^3$/h in firing heavy oil. It is clear that the ratio is almost 1.0 (stoichiometric ratio) regardless of the O$_2$ concentration in the flue gas or the boiler load. For industrial use, the proper O$_3$ mass flow rate is a very important operational factor [24].

C. Na$_2$SO$_3$ Supply Rate

According to reaction (3), NO$_2$ is reduced to N$_2$ by the Na$_2$SO$_3$ solution in the scrubber. It is essential to the stable operation of the system to set the Na$_2$SO$_3$ supply rate optimally.

Fig. 7 shows the relationship between the amount of NO$_x$ removed ($\Delta$NO$_x$) and the ORP under both low-load and high-load operations carried out at the second plant (2.0 t/h steam generation plant) [21]. The measured data indicate that $\Delta$NO$_x$ increases as the ORP decreases. In the low-load operation, the gas flow rate is set to 430 Nm$^3$/h and the Na$_2$SO$_3$ solution is in the range of 0.20–0.55 mol/min, with 0.04 mol/min of NaOH. $\Delta$NO$_x$ is 32 ppm when the ORP is 0 mV and it increases to approximately 36 ppm at −35 mV. The correlation between the NO$_x$ removal and the ORP is almost the same at 1480 Nm$^3$/h in the high-load operation. These results prove that the NO$_x$ removal is influenced by the ORP in the scrubbing solution. On the other hand, the ORP varies from time to time; as Na$_2$SO$_3$ increases, the ORP decreases. The ORP change rate as a function of the Na$_2$SO$_3$ supply rate, which is an operational parameter for the plant, is investigated.

Fig. 8 shows the effect of the Na$_2$SO$_3$ supply rate on the ORP under the same load operations as Fig. 7. If the ORP change rate becomes negative, the ORP decreases as the operating time elapses, which means the NO$_x$ removal performance would be stable or increase. Therefore, the ORP change rate should be maintained at less than zero (0 mV/min) in order to keep the NO$_x$ removal performance stable. In order to obtain this stability of NO$_x$ removal performance, it is essential to predict the Na$_2$SO$_3$ supply rate properly for boiler operation conditions. The supply rate of Na$_2$SO$_3$ (mol/h) depends mainly on three factors: fuel flow rate (Nm$^3$/h for gas fuel or L/h for oil fuel), NO$_x$ concentration (ppm) at MP1, and NO$_x$ concentration at MP3. Furthermore, for oil fuel, the calorific value (J/g) is introduced as another

<table>
<thead>
<tr>
<th>O$_2$ flow direction</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<tr>
<td>$\Delta$NO ppm</td>
<td>47.8</td>
<td>48.1</td>
<td>48.5</td>
</tr>
<tr>
<td>De-NO %</td>
<td>87.1</td>
<td>87.3</td>
<td>86.8</td>
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Table I

EFFECT OF O$_3$ FLOW DIRECTION ON NO REMOVAL TO FLUE GAS FLOW: (A) WITH THE FLOW, (B) ACROSS THE FLOW, AND (C) AGAINST THE FLOW

Fig. 6. Ratio ($\Delta$NO/O$_3$) as a function of O$_2$ concentration at MP1 when flow rate of flue gas is set to 830, 1750, and 2060 Nm$^3$/h in firing heavy oil.

Fig. 7. Relationship between amount of NO$_x$ removed and the ORP when the flow rates of flue gas are set to 430 and 1480 Nm$^3$/h.

Therefore, the ORP change rate should be maintained at less than zero (0 mV/min) in order to keep the NO$_x$ removal performance stable. In order to obtain this stability of NO$_x$ removal performance, it is essential to predict the Na$_2$SO$_3$ supply rate properly for boiler operation conditions. The supply rate of Na$_2$SO$_3$ (mol/h) depends mainly on three factors: fuel flow rate (Nm$^3$/h for gas fuel or L/h for oil fuel), NO$_x$ concentration (ppm) at MP1, and NO$_x$ concentration at MP3. Furthermore, for oil fuel, the calorific value (J/g) is introduced as another
factor, which depends on the variety of oil. The empirical formula for the Na$_2$SO$_3$ supply rate reported in [24] is determined using the multiple variables regression analysis method from the accumulated measured data on the gas and oil fuels.

Fig. 9 shows an example of the predicted Na$_2$SO$_3$ supply rate together with measured rate when fuel flow rate of CNG is set to 47, 100, and 150 Nm$^3$/h.

D. Liquid-to-gas Ratio

Fig. 10 shows the effect of the scrubber liquid flow rate on NO$_x$ removal efficiency. The liquid flow rate is varied at 3, 4, 5, 6, and 7 t/h with flue gas flow rates of 640, 1400, and 2100 Nm$^3$/h in firing CNG. Thus, a liquid-to-gas ratio (L/G) is obtained in the range of 1.4–11.0 L/Nm$^3$. The data indicate that NO$_x$ removal efficiency does not depend on L/G in the range of 3–11 L/Nm$^3$ when the flue gas rates are 640 and 1400 Nm$^3$/h, but it does depend on L/G of less than 2.5 at 2100 Nm$^3$/h. This result shows that L/G should be set to more than 2.5 in the scrubber. It also proves that the scrubbing effectiveness of NO$_x$ removal is very moderate as compared to that of the SO$_2$ removal scrubber.

E. Four-successive-day Operation

For industrial use, it is essential to confirm the proper operation of the system. Operations of four and two successive days are carried out when firing CNG, and A-type heavy oil, respectively. The boiler starts and stops every 6 h. However, the scrubbing solution is not replaced with a fresh chemical solution when the boiler stops; instead, the solution is reused throughout the
experiment. NO\textsubscript{x} removal performance is investigated for four days.

Fig. 11 shows NO\textsubscript{x} concentrations at MP1 and MP3 as a function of successive operating time. The average flow rate of CNG is 52 Nm\textsuperscript{3}/h and that of flue gas is 718 Nm\textsuperscript{3}/h at an O\textsubscript{2} concentration of 3.3–4.0%. The average rates of O\textsubscript{3} injection and Na\textsubscript{2}SO\textsubscript{3} supply are 86 g/h and 63 mol/h, respectively. NO\textsubscript{x} concentrations at MP1 are within 45–50 ppm. This small difference of NO\textsubscript{x} each day is due to the difference in the O\textsubscript{2} concentrations at MP1 between 3.3% and 4.0%. The NO\textsubscript{x} concentrations at MP3 are within 5–8 ppm, which are equivalent to a NO\textsubscript{x} removal efficiency of more than 85% over an operating time of 23 h. The NO\textsubscript{x} removal performance achieved is satisfactory and stable. The specific gravity of the scrubbing solution is maintained to more than 0.19 mol/L and the solution rate is set to 3 m\textsuperscript{3}/h from the scrubber sump. The specific gravity is measured by a hydrometer manually every 10 min throughout the experiment. The specific gravity increases as the operating time elapses because Na\textsubscript{2}SO\textsubscript{4} is generated as a by-product in the scrubbing solution. The specific gravity increases gradually and saturates to approximately 1.08 as the target value. Because of the fact that the boiler starts and stops daily, the scrubber liquid is warmed up and cooled down daily. For continuous system operation, care must be taken lest the by-product becomes crystalized in the scrubber sump during boiler stoppage.

Fig. 12 shows the measured time-dependent specific gravity of the scrubbing solution and the predicted one. The flow rate of the scrubbing solution is set to 3 m\textsuperscript{3}/h and the L/G ratio is maintained at 7.0 L/Nm\textsuperscript{3}. The flow rates of the Na\textsubscript{2}SO\textsubscript{3} solution and fresh water into the scrubber and that of the drainage discharge from the scrubber are set to 60 L/h, 47 L/h, and 90 L/h, respectively. The specific gravity is measured by a hydrometer manually every 10 min throughout the experiment. The specific gravity increases as the operating time elapses because Na\textsubscript{2}SO\textsubscript{4} is generated as a by-product in the scrubbing solution. The specific gravity increases gradually and saturates to approximately 1.08 as the target value. Because of the fact that the boiler starts and stops daily, the scrubber liquid is warmed up and cooled down daily. For continuous system operation, care must be taken lest the by-product becomes crystalized in the scrubber sump during boiler stoppage. The specific gravity of 1.08 is an allowable value as a control index. The predicted value is calculated from an empirical equation that takes into account the amount of Na\textsubscript{2}SO\textsubscript{4} generated, that of unreacted Na\textsubscript{2}SO\textsubscript{3}, and the solution temperature in the scrubber sump. The predicted rate coincides well with the measured rate throughout the experiment. Then, the correlation between the flow rates of the Na\textsubscript{2}SO\textsubscript{3} solution, fresh water, and drainage in the scrubber sump is investigated from the accumulated measured data on both gas and oil fuels under the condition that the Na\textsubscript{2}SO\textsubscript{3} concentration of the scrubbing solution is maintained to more than 0.19 mol/L and the specific gravity is 1.08. The predicted correlation is obtained depending on flue gas flow rate, which indicates reasonable operational parameters of the scrubber. An example of the predicted correlation is when the flue gas flow rate is set to 1400 Nm\textsuperscript{3}/h in firing CNG, the Na\textsubscript{2}SO\textsubscript{3} solution flow rate to 80 L/h, the fresh water rate to 68 L/h, and the drainage rate to 118 L/h. As a result, the operational indices of the scrubber such as the Na\textsubscript{2}SO\textsubscript{3} supply and solution rate, fresh water, and drainage, etc., are clarified as the operational procedures of the system.

F. SO\textsubscript{2} Removal Efficiency

A SO\textsubscript{2} removal efficiency of 85% was obtained with the first pilot-scale apparatus using A-type heavy oil in which the sulfur concentration is low, less than 0.1%. The SO\textsubscript{2} concentration at the boiler outlet was 35 ppm. Further investigation is planned using C-type heavy oil with a medium sulfur concentration. A hybrid NO\textsubscript{x} and SO\textsubscript{2} removal apparatus will be tested soon.

IV. CONCLUSION

The operational characteristics of a low-emission boiler system for a hot water or steam supply are investigated. It is found that an O\textsubscript{2} concentration at MP1 of 3–5% would reduce NO\textsubscript{x} emission. The ΔNO/O\textsubscript{3} ratio is almost 1.0 (stoichiometric ratio), regardless of O\textsubscript{2} concentration in the flue gas and the boiler load, and O\textsubscript{3} flow is set to be against the flow. Considering the ORP and the ORP change rate of the scrubbing solution, the Na\textsubscript{2}SO\textsubscript{3} supply rate must be set to a proper value, which is predicted from the empirical equation. It is confirmed that the predicted supply rate coincides well with the measured one. An operation over four successive days is satisfactorily carried out, maintaining a stable NO\textsubscript{x} removal efficiency of more than 85%. The operation indices of the scrubber, such as the Na\textsubscript{2}SO\textsubscript{3} supply and solution rates, drainage, fresh water, and so on are clarified as the operational procedures of the system. This boiler system is developed for flue tube boiler, of which the steam generation rate ranges from 2 to 30 t/h, equivalent to flow rate of flue gas, approximately from 2000 to 30000 Nm\textsuperscript{3}/h. The basic operational characteristics obtained in the study are applied for this range of the boiler capacity. It is thus confirmed that the low-emission multi-fuel boiler system with plasma-chemical hybrid NO\textsubscript{x} after-treatment is applicable for industrial use.
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