# Energy-Saving Emission Control for Glass Melting Furnace by Plasma-Chemical Hybrid Processing

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**Abstract:** The plasma hybrid exhaust gas treatment technology proposed is a method that combines it with a chemical process to clean exhaust gas. This study reports the simulation and application of glass melting furnace exhaust gas treatment as a practical result of the plasma chemical hybrid process (PCHP). From the comparison, the simulated and experimental temperature distributions and  $NO_x$  concentration were found to be in good agreement.

Keywords: Nonthermal plasma, Glass melting furnace, Plasma-chemical process, NO<sub>x</sub>

#### 1. Introduction

The recent increase in the fossil fuel combustion rate in the energy supply has changed the Japanese domestic environmental protection and energy situation. However, carbon oxides, sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), particulate matter (PM), and hydrocarbons (HCs) in the atmosphere generated by the combustion of fossil fuels pollute the environment. Of these harmful components, SO<sub>x</sub> is pre-desulfurized or treated by flue gas desulfurization, and PM is filtered using a bag filter or an electrostatic precipitator. As a result, technologies for preventing the release of SO<sub>x</sub> and PM into the atmosphere have been almost completely established.

The concentration of NO<sub>x</sub> in the exhaust gas is typically several tens to several hundred ppm. In many thermal power plants and regional waste disposal plant combustion furnaces, NO<sub>x</sub> reduction (denitration or De-NO<sub>x</sub>) is performed using the selective catalytic reduction (SCR) method. This is an effective De-NO<sub>x</sub> technology. However, the operational cost is relatively high. Moreover, an exhaust gas temperature of 300°C is required to activate the catalyst.

This study reports the application results of plasma hybrid aftertreatment technology on glass melting furnace exhaust gas treatment [1]-[3] performed. It is difficult to apply the SCR for De-NO<sub>x</sub> due to the corrosive impurities contained in the exhaust gas of the glass manufacturing system (glass melting furnace). Because the SCR cannot be applied, there was almost no effective De-NO<sub>x</sub> aftertreatment method. Osaka Prefecture University has been conducting joint research with Nihon Yamamura Glass Co., Ltd. of Japan with the intention to apply the plasma and chemical hybrid process (PCHP) that has been developed and put into practical use. Therefore, a smallscale laboratory experiment was carried out prior to the actual equipment test. Based on the results, we incorporated the technology into the actual desulfurization facility of a glass-melting furnace and conducted an experiment to demonstrate its practical use. In this study, we develop an analytical model on the scale of actual equipment to simulate the plasma oxidation of NO at different exhaust gas flow rates, to apply the model to various applications.



Fig. 1. Schematic of glass bottle manufacturing system and dry exhaust gas treatment system.

## 2. Experiment

Figure 1 shows a schematic of the glass bottle manufacturing system and the dry exhaust gas treatment process. The raw materials are melted in a glass melting furnace at approximately 1500°C using a fossil fuel such as city gas or C-heavy oil. Because of technical issues of glass melting, the furnace cannot be used for city gas firing alone. C-heavy oil is used at a ratio of approximately 1/4-1/3, which results in SO<sub>x</sub> generation. In a bottle manufacturing system, the melted glass is transformed into a bottle shape using a mold and then it is slowly cooled for distortion removal. Subsequently, it is used to develop a glass bottle product. However, the exhaust gas emitted by combustion contains air pollutants such as SO<sub>x</sub> derived from raw materials and fuels, NO<sub>x</sub> generated by hightemperature air combustion, and dust (mainly scattered materials). Therefore, exhaust gas treatment facilities are installed to reduce environmentally hazardous substances. The exhaust gas from the glass melting furnace passes through a thermal storage apparatus and is introduced into a downstream reaction tower called a stabilizer. In this reaction tower, an aqueous solution of sodium hydroxide (NaOH) is sprayed, and SO<sub>x</sub> in the exhaust gas is removed. The removed  $SO_x$  is converted to sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>), which is oxidized and recovered as Na<sub>2</sub>SO<sub>4</sub> and reused as a glass raw material. The generated fine particles of Na<sub>2</sub>SO<sub>4</sub> and dust are removed by an EP and a BF, which are located downstream and are used as a dust collector. The cleaned exhaust gas is discharged from the stack. However, because the exhaust gas contains a large amount of sticky dust produced by raw materials and highconcentration SO<sub>x</sub>, De-NO<sub>x</sub> equipment has not been able to improve. NO<sub>x</sub> regulations (NO<sub>x</sub> < 350 ppm at O<sub>2</sub> = 15%) have been complied with by the reduction of NO<sub>x</sub> due to low air ratio combustion at the source side. However, because NO<sub>x</sub> reduction in low air ratio combustion is accompanied by a deterioration in fuel efficiency, the demand for energy-saving NO<sub>x</sub> reduction technology has increased.

Therefore, we developed PCHP technology for a glass melting furnace that performs  $De-NO_x$  by injecting ozone gas generated by the plasma ozonizer into the reaction tower while cooling the gas with water. The  $De-NO_x$  reactions are given as reactions (1)–(3).

$$\begin{array}{ll} O_3 \rightarrow O_2 + O & (1) \\ NO + O \rightarrow NO_2 & (2) \end{array}$$

$$2NO_2 + 4Na_2SO_3 \rightarrow N_2 + 4Na_2SO_4 \tag{3}$$

Ozone is injected into the flue gas. According to reaction (1), ozone is thermally decomposed to form the O radical. In reaction (2), the NO in the exhaust gas is oxidized to NO<sub>2</sub>. In reaction (3), NO<sub>2</sub> reacts with Na<sub>2</sub>SO<sub>3</sub> to produce Na<sub>2</sub>SO<sub>4</sub>; These reactions help in achieving complete purification. Furthermore, Na<sub>2</sub>SO<sub>4</sub> can be reused as a glass raw material in the furnace. In reaction (4), Na<sub>2</sub>SO<sub>3</sub> is obtained as a reducing agent between NaOH in the stabilizer and SO<sub>2</sub> in the exhaust gas.

 $SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$  (4)

Two sets of plasma-type ozonizers (ozone yields of 4 and 6 kg/h) are used simultaneously in the pilot scale demonstration test. Both are dielectric barrier discharge ozonizers, which use an oxygen tank as the oxygen supply source. Each unit has 300-400 nonthermal plasma reactors. In this demonstration test, two sets of ozonizers are used simultaneously to inject ozone into the reactor. The maximum concentration of ozone generated is 7.0% (= 150 g/Nm<sup>3</sup>) and the mass flow rate is 10.0 kg/h at a maximum power consumption of 28 + 48 = 76 kW. The thermal input for the furnace is 10 MW, whereas the input power to the plasma ozonizer is 76 kW, which is a small portion of 0.8% of the thermal input, because the plasma ozonizer acts efficiently and is only used for the oxidation of NO to NO<sub>2</sub>. NO<sub>2</sub> reduction to N<sub>2</sub> is performed using the chemical process in the PCHP. The structure of a single nonthermal plasma reactor uses the dielectric barrier type shown in Figure 2. It consists of a glass dielectric, a centered electrode covered with dielectric material, and a grounded electrode cooled with cooling water. The total flow rate of oxygen is 26.7 and 40.0 Nm<sup>3</sup>/h for the 4.0 and 6.0 kg/h ozonizers, respectively.



Fig. 2. Structure of a single nonthermal plasma reactor in the ozonizers.

#### **3.Numerical model**

A numerical design was used for the prediction of the system. Numerical simulation was carried out inside the two-phase chemical reaction flow of the stabilizer.  $O_3$  is injected before the gas passes through the stabilizer.

**Figure 3** shows the analysis model. The simulated exhaust gas flows from the pipe (z = 0 mm) connected to the reactor (stabilizer). Water is then sprayed from a three-fluid nozzle installed at a position of z = 2050 mm and a two-fluid nozzle installed at a position of z = 4050 mm to form a local cooling area in the reactor. Further, ozone is ejected from the three-fluid nozzle to oxidize NO in the simulated exhaust gas. The treated simulated exhaust gas flows out through the pipe (z = 14900 mm) connected to the upper part of the reactor. Heat dissipation and non-slip conditions at wall boundaries are used as boundary conditions. A steady three-dimensional simulation is performed using the finite volume method. CFD-ACE+ (CFD-ACE-GUI version 2020.5.0, ESI Group) was used as the simulation software.

A simulation that combines the thermal fluid flow of gasphase including chemical reactions with the thermal motion of water droplets considering evaporation is performed. The governing equations for a threedimensional compressible steady-state gas-phase problem are continuity, momentum, and energy, considering mass change, volumetric force, and heat exchange by water droplets. The transport equation of chemical species is used for the simulation of the chemical reaction. For the calculation of the thermal motion of spraying water droplets, the discrete particle method is simulated in the computational domain by solving the Lagrange equation. For the evaporation model, a water droplet is considered spherical and the temperature distribution inside the droplet is considered uniform without considering the circulation inside the droplet.



Fig. 3. 3D analysis model for the stabilizer.

#### 4. Results and discussion

For a glass melting furnace, a semi-dry De-SO<sub>x</sub> apparatus is used more frequently as an exhaust gas treatment device than the wet type, especially in the developing countries. The plant was built in Nihon Yamamura Glass Co., Ltd. Tokyo factory, and simultaneous dry De-SO<sub>x</sub> and De-NO<sub>x</sub> testing are performed with an exhaust gas volume (~18450 Nm<sup>3</sup>/h). Moreover, in this glass melting furnace, the combustion is performed by switching a pair of regenerators and burners at fixed time intervals. In this case, Na<sub>2</sub>SO<sub>3</sub> produced by the process of reaction (4) in the reaction tower or  $Na_2SO_4$ by air oxidation becomes particulate and is collected by the downstream EP. It is necessary to maintain the temperature of the exhaust gas at the outlet of the reaction tower in the range of 200 to 250°C to prevent a decrease in dust collection efficiency in a wet state. Therefore, it is necessary to maintain the spray amount of the NaOH aqueous solution low.

Previous studies showed that when the exhaust gas temperature exceeds  $150^{\circ}$ C, the NO oxidation performance due to O<sub>3</sub> injection decreases. Hence, there is a need for the reduction of NO oxidation even for averaged high-temperature exhaust gas exceeding  $150^{\circ}$ C. For this reason, it is important to efficiently supply ozone to the local cooling area containing spray droplets formed by water spray below  $150^{\circ}$ C, and the ozone spray nozzle should be directed towards the center of the cooling area. It was confirmed that the outlet temperature of the reaction tower could be maintained at 200°C or higher while the local cooling area was kept cooled to approximately 70 °C with NaOH aqueous solution.

Exhaust gas discharged from the glass melting furnace is first introduced into a semi-dry desulfurization unit (reaction tower). The reactor is a cylindrical De-SO<sub>x</sub> tower having a diameter of 3.5 m and a height of 21.5 m. Air, cooling water, and ozone gas are simultaneously sprayed by a three-fluid nozzle (manufactured by H. IKEUCHI & Co., Ltd.) installed 2.05 m above the inlet of the reaction tower to oxidize NO. Next, a two-fluid nozzle (manufactured by H. IKEUCHI & Co., Ltd.) is installed 4.05 m above the inlet of the reaction tower, and NO<sub>x</sub> and SO<sub>x</sub> were simultaneously treated by spraying NaOH solution. The exhaust gas from the outlet of the reaction tower then passes through an EP and a BF to remove PM and then is discharged into the atmosphere.

**Figures 4 and 5** show the NO and NO<sub>x</sub> measurement results. In the figures, O<sub>2</sub> = 15% equivalent values are shown for NO and NO<sub>x</sub>.  $\Delta$ NO and  $\Delta$ NO<sub>x</sub> are NO and NO<sub>x</sub> removals, respectively. Experiments are performed under three conditions. In T1, the ozone injection rate is 0 kg/h; in T2, the ozone injection rate is 11.0 kg/h; in T3, the ozone injection rate is 10.8 kg/h. The experiment is performed for 5 hrs. In the experiment, a higher air ratio ( $\lambda = 1.0$ ) with PCHP aftertreatment is used, resulting in energy-saving operation while satisfying the regulation requirements. The average value at the reaction tower temperature measurement point of z = 2.85 m above the reaction tower



Fig. 4. Time-dependent NO measurement result.



Fig. 5. Time-dependent NO<sub>x</sub> measurement result.

inlet (NO oxidation area) is approximately  $230^{\circ}$ C, and a sufficient local cooling area is formed. The average NO<sub>x</sub> removal efficiency is 0% for T1, 33% for T2, and 39% for T3. The average NO<sub>x</sub> removal efficiency is the highest under the condition of T3. When the spray flow rate of NaOH solution increases, the NO<sub>x</sub> removal rate tended to increase. From the above-mentioned experiments that were conducted at a real machine scale, we succeeded in securing a sufficient cooling area by increasing the spray amount. As a result, satisfactory De-NO<sub>x</sub> is obtained.

Figure 6 shows the temperature distribution. It is found that the simulated exhaust gas flows in at 488°C, is cooled by water spray from the three-fluid nozzle and the twofluid nozzle, and flows out of the outlet at 236°C. The exhaust gas flows out in a dry state due to the high temperature of 260°C. At a position of z = 2050 mm (where the three fluid nozzles are mounted), a local cooling area is formed, and the simulated exhaust gas is cooled to a minimum temperature of 120°C. Even at the spray position of z = 4050 mm (where the two-fluid nozzles are mounted), a local cooling area is still formed, and the gas is cooled to a minimum temperature of 77°C. It is also found that the simulated exhaust gas density increases with the decrease in the temperature so that a cooling region extends to the upstream (z = 1000 mm) from the spray position of the first stage.

Figure 7 shows the NO<sub>2</sub> distribution. In the figures, O<sub>2</sub> = 15% equivalent values are shown for NO and NO<sub>2</sub>. NO<sub>2</sub> is generated near the outlet of the three-fluid nozzle and reaches a local concentration of around 150 ppm at the exit of the stabilizer. The concentration of NO<sub>2</sub> agrees well with the measurement results in Fig. 4. After NO<sub>2</sub> is generated near the nozzle, it flows to the lower region (z = 800 mm)



Fig. 6. Temperature distributions of gaseous phase, (a) x-z cross-section (b) y-z cross-section.



Fig. 7. NO<sub>2</sub> concentrations, (a) x-z cross-section (b) y-z cross-section.

of the three-fluid nozzle and then disperses downstream. The region where the  $NO_2$  is generated and dispersed agrees well with the cooling region.

The results of this study thus far demonstrate that semidry PCHP can remove  $NO_x$  and  $SO_x$  with high efficiency and energy savings. Therefore, the introduction of PCHP makes it possible to treat  $NO_x$ , which enables combustion at a higher air ratio in the furnace, thereby reducing fuel consumption. **Figure 8** shows the relationship between crude oil equivalent energy consumption and air ratio with and without  $NO_x$  treatment by PCHP. Each plot is representative of data for each period during the continuous operation period. Although the air ratio may vary depending on the glass production volume, the PCHP treatment can increase the air ratio by approximately 0.5, saving an average of 3.0 kL/day of energy consumption.

#### 5. Conclusion

In this study, as an application example for plasma chemical hybrid exhaust gas treatment technology, we elaborated on the current status of glass melting furnace exhaust gas treatment, and the results obtained in actual machine tests. Furthermore, a numerical design was presented for the technology. PCHP can be considered as the most suitable method for exhaust gas treatment in glass melting furnaces because it can maintain the degree of De-NO<sub>x</sub> and De-SO<sub>x</sub> of exhaust gas while reusing SO<sub>x</sub> in the exhaust gas as a glass material using reaction (3). The company and the university jointly plan to continue further research to improve De-NO<sub>x</sub> efficiency in dry processes. Ultimately, we hope to expand the application of this exhaust gas treatment method to glass melting furnaces around the world.

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## 7. References

- [1] H. Yamamoto et. al., Mechanical Engineering Journal, 3, 15-00549 (2016)
- [2] H. Yamamoto et. al., IEEE Trans. Ind. Appl., 55, 6295 (2019)
- [3] H. Yamasaki et. al., Plasma Chem. Plasma Process., 42, 51 (2021).



Fig. 8. Energy consumption volume in crude oil equivalent against air ratio.