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NO_x and SO_x Simultaneous Removal from Exhaust Gas in a Glass Melting Furnace Using a Combined Ozone Injection and Chemical Hybrid Process

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Abstract A novel technology of the simultaneous NO_x and SO_x removal from the exhaust gas in a glass manufacturing system is developed using a nonthermal plasma-chemical hybrid process (PCHP). Pilot-scale experiments are conducted in a wet-type and a semi-dry type de-SO_x reactors of the glass melting plants. The flow rate of exhaust gas is in the range of 6550–17250 m^3N/h for the both experiments. NO_x and SO_x emissions at the furnace outlet range 158–289 ppm and 122–249 ppm, respectively. Ozone generated by ozonizers is injected into the exhaust gas area cooled with water to below 150°C at the de-SO_x reactor inlet or the reactor inside in order to oxidize NO to NO_2. Almost all of the SO_2 is absorbed by a NaOH absorbent resulting in the generation of Na_2SO_3. Furthermore, reduction of the water-soluble NO_2 by Na_2SO_3 to N_2 affords Na_2SO_4, which can be reused as glass material. The averaged (highest) de-NO_x and de-SO_x efficiencies are 28 (39)% and 99%, respectively in a wet-type de-SO_x reactor. It is expected that the de-NO_x efficiency increases in accordance with the increase of de-NO efficiency if the more amount of ozone is injected. This simultaneous de-NO_x and de-SO_x technology by PCHP is highly practical and promising for exhaust gas aftertreatment in a glass manufacturing system.

Keywords: Glass furnace, Nonthermal plasma, Ozone, Na_2SO_3, NO_x treatment

1. Introduction

In glass manufacturing plants, glass bottles and dissolved raw materials are molded at ~1500°C by combustion of liquefied natural gas (LNG) and/or heavy oil in the melting furnace. The exhaust gas of this melting process contains environmental pollutants such as NO_x, SO_x, and dust. In general, SO_x is removed by a wet or a semi-dry de-SO_x apparatus using a desulfurizing agent (NaOH). Sodium sulfite (Na_2SO_3), which is the reaction product of de-SO_x, is processed together with the particle dust derived from the glass furnace and collected by a wet electrostatic precipitator (ESP), or a dry ESP and a bag filter (BF). However, the NO_x emission regulation (450 ppm at O_2 = 15% conversion) defined in the Air Pollution Control Law of Japan is lax as compared to neighboring countries. Catalyst poisons include the adhesive dust of glass derived from raw materials and high concentration SO_x composed of exhaust gas. For these reasons, the selective catalytic reduction (SCR) de-NO_x method, generally applied for coal-fired power plants, is difficult to use in glass melting furnaces. Given these circumstances, there are few instances in which the exhaust gas de-NO_x apparatus has been installed for glass melting furnaces. Attempts to suppress NO_x generation have also been carried out by using low air ratio combustion and low NO_x burners. These techniques are generally used as countermeasures to control emissions. Therefore, significant reduction of NO_x emissions is inherently difficult. However, as global environmental problems increase, NO_x emission regulation is expected to become more stringent for exhaust gas from glass melting furnaces. Consequently, the establishment of aftertreatment techniques that sufficiently decrease NO_x emissions is required. Numerous studies on plasma-based NO_x treatments are conducted. The PCHP [1-8] that combines plasma with other chemical reactions without the use of catalysts is suitable for treating the exhaust gas from glass melting furnaces. PCHP technology is easily applied to existing exhaust gas treatment apparatus for glass manufacturing systems without requiring a large amount of additional space. Furthermore, the operating cost of the apparatus may be significantly reduced.

We have proposed a de-NO_x technology using PCHP, as described in the following formula:

$$O_3 \rightarrow O_2 + O \qquad (1)$$

$$NO + O \rightarrow NO_2 \qquad (2)$$

$$SO_2 + 2\ NaOH \rightarrow Na_2SO_3 + H_2O \qquad (3)$$

$$2\ NO_2 + 4\ Na_2SO_3 \rightarrow N_2 + 4\ Na_2SO_4 \qquad (4)$$

First, NO in the exhaust gas is oxidized to water-soluble NO_2 by injecting plasma-induced ozone gas into the exhaust gas duct (reactions (1)–(2)). Na_2SO_3 is then produced as a byproduct of the de-SO_x process using NaOH solution (3), after which NO_2 is reduced to N_2 gas by a chemical process producing sodium sulfate (Na_2SO_4) as the byproduct (4). We set up a laboratory-scale model of the equipment that implemented the proposed technology, and conducted experiments to obtain the basic characteristics of the technique when applied to the treatment of exhaust gas from a glass melting furnace [8]. In succession, we have carried out pilot-scale simultaneous removal experiments of NO_x and SO_x using ozone injection and chemical hybrid process for exhaust gas in glass melting furnace.

2. Experimental apparatus and method

Figure 1 (a) and (b) show schematic diagrams of a wet-type and a semi-dry type exhaust gas aftertreatment systems for the bottle glass melting furnaces in Japan. The wet-type aftertreatment system consists of a wet-type de-SO_X apparatus and a wet ESP for exhaust gas from glass melting furnace followed by a waste heat boiler (WHB). The furnace can process 215 t/d of raw glass material by the combustion of LNG. A set of combustion burners is installed inside the furnace. The burners are located on the east and west sides of the factory building and their use alternates with a period of 20 min for heat exchange with the regenerative furnace. The average total exhaust gas flow rate is 21 500 m^3N/h, and the total heat input of the burners is 6.3 MW. For this experiment, the exhaust gas stream is divided into two and is approximately one third of the total exhaust gas flow rate (6990 m^3N/h). Then, the divided exhaust gas is introduced into the WHB (1.5 t/h steam) and the gas temperature decreases from 400°C to less than 250°C. A three-fluid spray O_3 injection nozzle is mounted on the duct at 1.6 m upstream from a wet-type de-SO_x reactor, where O_3 is injected into gas flow. NO in the exhaust gas is oxidized to NO_2. After passing the injection nozzle, the exhaust gas is then introduced into the reactor. The reactor is a cylindrical one (12.3 m h × 2.3 m i.d.) made of three-layer fiber reinforced plastics (FRP) containing with seven spray nozzles and seven-stage perforated plates for an efficient absorption. The absorbent aqueous solution (main component: NaOH) is circulated by a pump (72 m^3/h). The pH of the absorbent solution is maintained at approximately 8 by a continuous supply of NaOH solution (24% mass). The chemical reactions (3)–(4) occur in the reactor. Reaction of SO_2 in the exhaust gas with NaOH produces SO_3^{2-} in the solution. In addition, the NO_2 generated by O_3 injection reacts with SO_3^{2-} and is converted to N_2 and a solution containing SO_4^{2-}(Na_2SO_4 solution). The absorbent solution containing SO_4^{2-} is introduced into a crystallization device through oxidation and filtration processes to crystallize Na_2SO_4. The Na_2SO_4 crystals are then reused as part of the glass raw material. Downstream of the reactor, dust and mist are collected by a wet ESP. The highly purified exhaust gas is released from the FRP stack into the atmosphere.

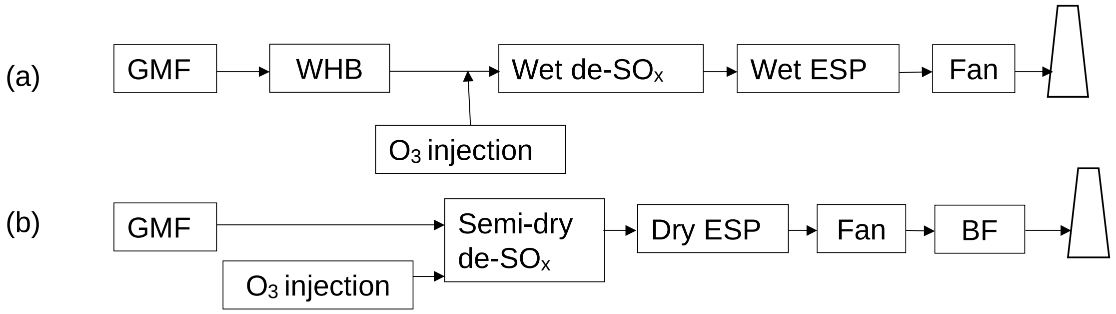


Figure 1. Exhaust gas aftertreatment system for glass melting furnace (a) wet-type, (b) semi-dry type (GMF: Glass melting furnace, WHB: Waste heat boiler, ESP: Electrostatic precipitator, BF: Bag filter)

Table 1 Ozonizer specifications

(a) Ozonizer A	
Raw material gas	More than 90% O_2 gas from PSA
O_3 generation	Air-cooled silent discharge plasma
O_3 mass flow rate	0–90 g/h
O_3 concentration	0–100 g/m^3N = 0–4.7%
O_3 volume flow rate	0.9 m^3N/h
Power consumption	1.6 kW (PSA), 1.5 kW (Discharge)
Dimension (W × D × H)	740 mm × 925 mm × 1840 mm

(b) Ozonizer B	
Raw material gas	O_2 gas from cylinders
O_3 generation	Air-cooled surface discharge plasma
O_3 mass flow rate	276 g/h
O_3 concentration	38 g/m^3N = 1.8%
O_3 volume flow rate	7.2 m^3N/h
Power consumption	3.6 kW
Dimension (W × D × H)	1000 mm × 1600 mm × 700 mm

The semi-dry aftertreatment system consists of a semi-dry type de-SO_x apparatus, a dry ESP and a BF. The exhaust gas flow rate for this experiment is 12700 m^3N/h, and the total heat input of the burners is 6.9 MW. The exhaust gas downstream of the furnace is then introduced into the semi-dry de-SO_x reactor. The reactor is a cylindrical one (10 m h × 3.5 m i.d.) containing with seven two-fluid spray nozzles for gas cooling and desulfurization. The desulfurization aqueous solution (NaOH: 1.6% mass) is sprayed by a pump (5 m^3/h). The nozzles are mounted at 2.9 m downstream from the reactor inlet. Ozone is injected into the gas cooling area formed by NaOH solution spray where NO in the exhaust gas is oxidized to NO_2. The NO_2 generated reacts with SO_3^{2-} and is converted to N_2 and a solution containing SO_4^{2-} (Na_2SO_4 solution). The solution containing SO_4^{2-} is dried to a dust of Na_2SO_4 particles. Downstream of the reactor, the dried Na_2SO_4 particles are collected by the dry ESP. The collected Na_2SO_4 particles are then reused as part of the glass raw material. Further downstream of the dry ESP, dust is removed by the BF for highly purified exhaust gas. The injection pipe of neutralizing agent (composition: $NaHCO_3$) is mounted on the duct at 2 m upstream from the BF. The $NaHCO_3$ is injected at the dry ESP outlet (BF inlet). The function of the neutralizing agent is to neutralize the NO_2 as the $NaHCO_3$ decomposes into Na_2CO_3 by the heat of exhaust gas. Then, the exhaust gas purified by the BF is dischareged from the stack into the atmosphere.

The followings are described for the both aftertreatment systems. The gas temperature is measured at the five points in each system. The concentrations of the exhaust gas components such as O_2, SO_2, and NO_x are measured at the inlet and outlet measurement points of the reactor using the SO_2 and NO_x analyzers. In addition, the O_2 concentration is measured using an Orsat gas analyzer according to JIS K 0301. The absorbent aqueous solution is sampled before and after the test. The SO_3^{2-} concentration in the solution is measured with a visible light spectrophotometer using a color developing reagent. Furthermore, ORP and pH are measured using a pH, and ORP meters. The concentrations of NO_3^- and NO_2^- in the absorbent solution are measured using absorption spectrophotometry according to JIS K 0102.

The ozone gas is generated by the plasma ozonizers A and B, and their specifications are shown in Table 1. Ozonizer A (EW-90Z, Ebara Jitsugyo Co., Ltd.) has a pressure swing adsorption (PSA) O_2 generator, and ozonizer B (HCII-OC70 × 12, Masuda Research Inc.,) is supplied with O_2 gas from O_2 cylinders (7 m^3). For the both pilot-scale experiments, three A and four B ozonizers are temporarily installed at site and used. The total amount of ozone generated is 1.59 kg/h (= 33.1 mol/h) with an ozone gas concentration of 2.1% (= 44 g/m^3N), and a maximum power consumption is 22 kW.

3. Experimental results of the wet-type system

Table 2 lists the averaged experimental conditions of T1 to T8 tests periods with O_3 injections at the reactor inlet in the wet-type aftertreatment system (Fig.1 (a)). The flow rate of the exhaust gas varies from 6550 to 17 250 m^3N/h. Gas temperature of the reactor inlet is in the range of 151–247°C. The O_2 concentration is 11.4–15.6%.

Table 2 Exhaust gas and test conditions at wet-type de-SO_x reactor inlet

Test number	Exhaust gas flow rate	Gas temp. (average)	O_2 (average)	NO (average)	NO_x (average)	SO_2 (average)	Injected O_3 mass flow rate
	m^3N/h	℃	%	ppm	ppm	ppm	kg/h
T1	6990	156	15.4	264	284	129	1.26
T2	6990	151	15.6	262	289	130	1.44
T3	6550	183	13.7	245	274	124	1.59
T4	12000	199	13.0	216	234	162	1.49
T5	15000	238	11.5	213	229	154	1.49
T6	17250	247	11.4	218	235	123	1.54
T7	9860	202	13.1	208	227	136	1.54
T8	8190	162	14.4	200	221	155	1.53

Figure 2 shows the NO, NO_x and SO_2 concentrations at the reactor inlet and outlet. The NO and NO_x during T4-T8 tests are almost stable, 210 ppm and 230 ppm on average, respectively, but those during T1-T3 tests increase to 260 ppm and 280 ppm respectively, due to high O_2. Further the SO_2 varies between 123 ppm and 162 ppm. Hereafter, NO, NO_x and SO_x concentrations are expressed as the converted values based on 15% O_2 concentration. Ozone gas is injected with water at the front of the reactor inlet where gas is cooled down below 150°C for effective NO oxidation by ozone. Ozone mass flow rates are 1.26–1.59 kg/h (26.1–33.0 mol/h) during these periods. Figure 3 shows the averaged gas temperature at the five points; 470°C at the furnace outlet, 342°C at the WHB inlet, 170°C at the WHB outlet, 153°C at the de-SO_x reactor inlet, and 52°C at the reactor outlet. Figures 4 (a) and (b) show the detailed time-dependent NO and NO_x concentrations at the reactor inlet and outlet during T2 test period of 80 min as a representative example. The NO and NO_x concentrations fluctuate because the east and west side burners are alternately switched on every 20 min. The averaged NO and NO_x concentrations at the reactor inlet are 262 ppm and 289 ppm, respectively. The ratio of NO to NO_x is almost more than 90%. It is clear that NO concentration at the reactor outlet decreases during O_3 injection. So does NO_x. The averaged NO and NO_x concentrations at the reactor outlet decrease to 181 ppm and 208 ppm, respectively. The averaged de-NO and de-NO_x efficiencies between the reactor inlet and outlet are obtained 31% and 28%, respectively, for T2 condition, which are the highest results throughout T1–T8 tests. In this test the molar ratio of the injected ozone of 29.9 mol/h (1.44 kg/h) to NO emission of 81.7 mol/h in the exhaust gas (= O_3/NO) is set to 0.37, which is not enough for practical use. However, this result means the de-NO efficiency increases with increasing the O_3/NO. Thereby, it is expected that the de-NO_x efficiency increases as well.

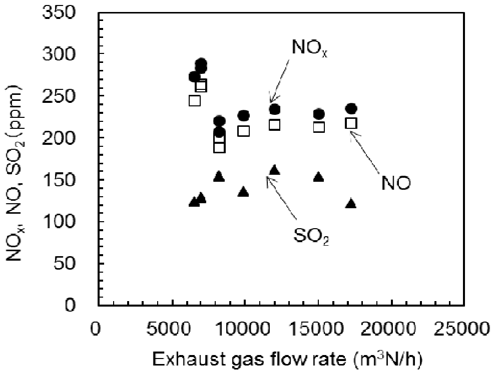
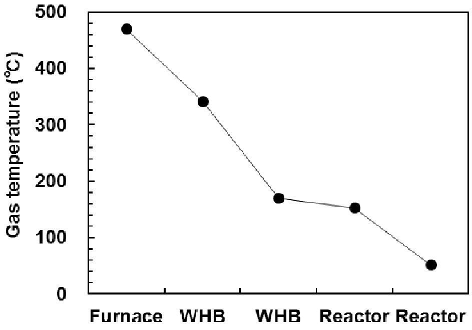


Figure 2. Exhaust gas properties at wet-type de-SOx reactor inlet



[7]. In this experiment, it is confirmed that the ⊿ NO/O_3 efficiency decreases from 84% at 151°C to 39% at 238°C. This result indicates that the gas temperature of the ozone injection point should be cooled to less than 150°C for efficient NO oxidation.

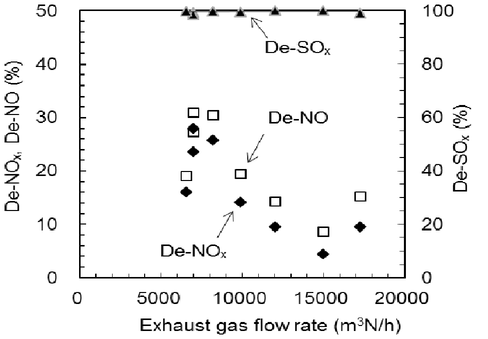


Figure 5. De-NO_x, de-NO, and de-SO_x as a function of exhaust gas flow rate in the wet-type system

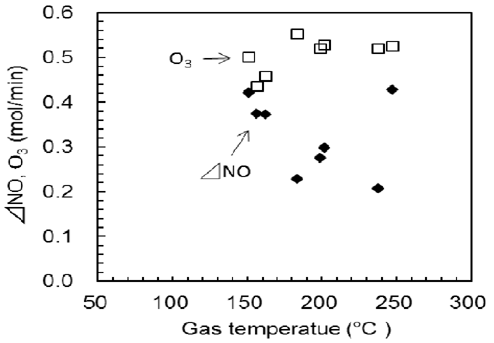


Figure 6. NO removed and O_3 as a function of gas temperature at wet-type de-SO_x reactor inlet

4. Experimental results of the semi-dry-type system

The experiments of the semi-dry type aftertreatment system are conducted under the five different test conditions, as shown in Table 3. The exhaust gas flow rate is constant, 12700 m^3N/h throughout TS1–TS5. Figure 7 shows the averaged gas temperature at the five points; 358°C at the de-SO_x reactor inlet, 67°C at the reactor inside cooling area where O_3 and NaOH solution are injected, 206°C at the reactor outlet, 180°C at the dry ESP outlet, and 176°C at the BF outlet. The gas temperature at the reactor inlet fluctuates in the range of 321–408°C because the north and south side burners are alternately switched on every 20 min. The O_2 concentration at the reactor inlet is 11.1–11.4%. The NO, NO_x and SO_2 concentrations are in the range of 159–164 ppm, 158–162 ppm and 133–141 ppm, respectively. The O_3 mass flow rates are 1.2 kg/h (25.4 mol/h) during TS1–TS2, 0 kg/h during TS3–TS4, and 1.0 kg/h (21.9 mol/h) during TS5, and the O_3/NO is within 0.28. The powdered $NaHCO_3$ is injected into the BF inlet with mass flow rates of 0 or 30 kg/h. Further, in order to check the influence on the de-NO_x and de-SO_x performance, the gas temperatures of the reactor gas cooling area varies from 67°C during TS1 to 141°C during TS2.

Table 3. Exhaust gas and test conditions at semi-dry type de-SO_x reactor inlet

Test number	Gas flow rate	Gas temp (1).	NO_x (ave)	SO_2 (ave).	O_3 flow rate	$NaHCO_3$ flow rate
	m^3N/h	℃	ppm	ppm	kg/h	kg/h
TS1	12700	75	160	135	1.2	0
TS2	12700	141	158	133	1.2	0
TS3	12700	65	162	141	0.0	0
TS4	12700	67	161	142	0.0	30
TS5	12700	67	162	140	1.0	30

Note: (1) means gas temperature in cooled aera inside reactor.

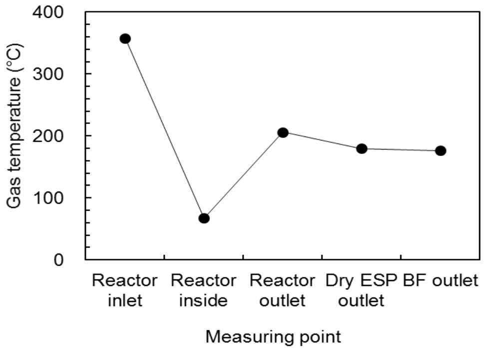


Figure 7. Exhaust gas temperature at semi-dry type aftertreatment system

Figure 8 shows the time-dependent NO concentrations at the reactor inlet and outlet measured at every 10 min. The NO concentration at the reactor inlet is 160 ppm on average. When ozone is injected, the averaged NO concentrations at the outlet decrease to 114 ppm during TS1, 119 ppm during TS2, and 132 ppm during TS5, respectively. The de-NO efficiencies between the reactor inlet and outlet are 28% during TS1, 25% during TS2, and 19% during TS5, respectivey. Further, the NO oxidation efficiencies are within 64–75% for TS1 and TS2. Figure 9 shows the time-dependent NO_x concentrations at the three points: the reactor inlet, the reactor outlet, and the BF outlet measured every 10 min.

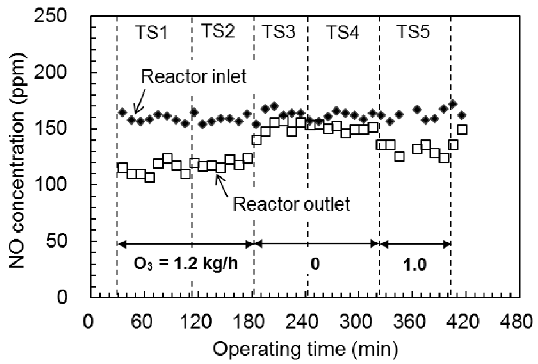


Figure 8. Time-dependent NO concentration at semi-dry type de-SO_x reactor inlet and outlet

The de-NO_x efficiencies between the reactor inlet and outlet are very low, 4–6%. As shown in Figure 8, the NO removal is effective. However, the de-NO_x efficiency is not improved. It is considered that the NO_2 reduction is not enough processed due to insufficient gas retention time in the reactor. Because the ozone and the NaOH solution are injected at the same height of the reactor, it seems that the oxidation-reduction area is locally limited and small. Therefore, the SO_3^{2-} solution has dried to a dust before the oxidized NO_2 is reduced completely. Attention on the de-NO_x in BF is paid, based on the NO oxidation in the de-SO_x reactor together with the injection of the powdered $NaHCO_3$ at the BF inlet. The NO_x concentration at the BF outlet is 130 ppm when O_3 is not injected during TS3, but that decreases to 105 ppm when O_3 is injected during TS1. So, NO_x of 25 ppm is removed by O_3 injection. Furthermore, using both injections of O_3 and the $NaHCO_3$ at the BF inlet, NO_x concentration at BF outlet decreases to 89 ppm during TS5. It is remarkable that the total de-NO_x efficiency between the reactor inlet and BF outlet increases up to 45% due to the synergistic effect of ozone and $NaHCO_3$.

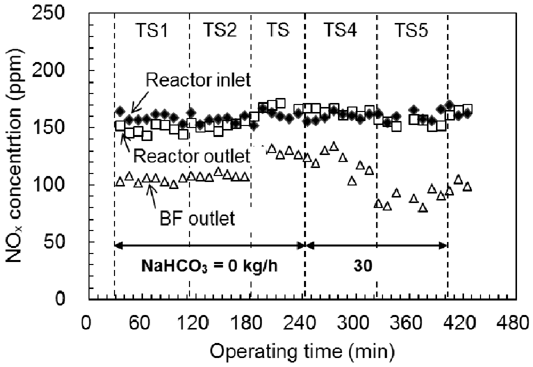


Figure 9. Time-dependent NOx concentration at semi-dry type de-SOx reactor inlet, outlet and BF outlet

Figure 10 shows the time-dependent SO_2 concentrations at the reactor inlet and the outlet. The SO_2 concentrations at the reactor inlet are in the range of 113–151 ppm. The averaged SO_2 at the reactor outlet is within 51–65 ppm, but during TS2 it is 81 ppm.

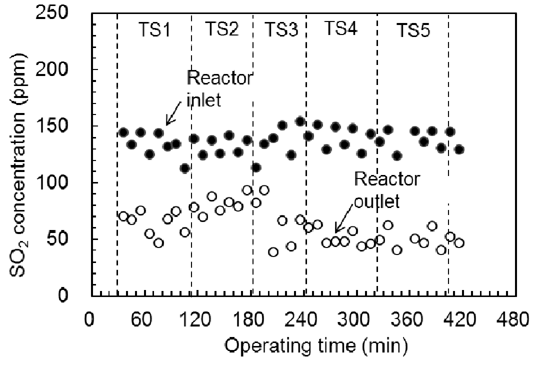


Figure 10. Time-dependent SO_x concentration at semi-dry type de-SO_x reactor inlet and outlet

The average de-SO_2 efficiencies between the reactor inlet and outlet are more than 50% except TS2, and 64% is a maximum. The de-SO_2 efficiency depends on the amount of NaOH solution. Because the amount of NaOH solution during TS2 is 0.5 m^3/h, which is 45% less than those of the other conditions, the de-SO_2 efficiency decreases to 39%. Therefore, this result indicates that the de-SO_2 efficiency is not dependent on O_3 injected.

5. Conclusions

A new technology of simultaneous NO_x and SO_x removal for exhaust gas in glass manufacturing system is examined using PCHP. Pilot-scale experiments are conducted for the wet and semi-dry type after-treatment systems. The results are summarized as follows: (1) Ozone injected oxidizes NO effectively regardless of wet or semi-dry type de-SO_x process. Ozone should be injected in the exhaust gas area cooled below 150°C. It is confirmed that the more amount of O_3 injected leads to the more NO removed, and the NO oxidation efficiency ($\varDelta NO/O_3$) decreases with increasing gas temperature. The averaged de-NO efficiency of 31% is the highest during T2 in the wet-type after-treatment system (O_3/NO=0.37). (2) In the wet-type de-SO_x reactor the averaged de-NO_x efficiency of 28% is the highest during T2. The de-NO_x efficiency increases if the ratio of the O_3/NO increases by applying bigger capacity of the ozonizers. The de-NO_x efficiency in the semi-dry type reactor is only 4% in spite of the de-NO efficiency of 28%. This is due that the NO_2 reduction is not enough processed due to insufficient gas retention time in the reactor. However, the total de-NO_x efficiency between the reactor inlet and BF outlet increases up to 45% due to the synergistic effect of ozone and $NaHCO_3$. (3) The de-SO_x efficiency is more than 99% in the wet-type reactor, and more than 60% in the semi-dry-type reactor. These efficiencies are expected. It can be said that ozone injected does not influence de-SO_x performance. (4) The experiment results prove that the simultaneous NO_x and SO_x treatment using PCHP is highly effective and practical for exhaust gas in the glass manufacturing system.

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