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

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Abstract

A plant of low emission hot water or steam supplying system which consisted of a multi-fuel boiler (gas or oil fuel) and a plasma-chemical hybrid NO_x removal was demonstrated. The boiler had a steam generation rate of 2.5 t/h. Many experiments were conducted using fuel gas and oils, and the flue gas flow rate was from 550 to 2250 Nm^3/h. Operational characteristics were investigated in order to achieve stable continuous operation. Ozone injection for NO oxidation and Na_2SO_3 solution for NO_2 reduction were essential factors for the NO_x removal system. Operational indexes were obtained, such as O_3 injection method, Na_2SO_3 supply rate, and the flow rate correlation among Na_2SO_3 supply, drainage, and fresh water.

1 Introduction

Particulate, SO_x, and NO_x are emitted from boiler. Particulates are generally removed by electrostatic precipitator (ESP), and SO_x by $CaCO_3$ De-SO_x, and NO_x by selective catalytic reduction (SCR) De-NO_x apparatuses. For large boilers, such as utilities or big factories, flue gas treatment system combined with ESP, De-SO_x, and De-NO_x is applied as shown in Fig. 1 (a) to keep individual emission regulations. On the contrary the same flue gas treatment system is not applied for small boilers of hot-water and steam supply because the cost of individual apparatuses is high. The number of small boilers is increasing year by year. As a boiler fuel, compressed natural gas (CNG), and heavy oil are used. Emission regulations are being anticipated more stringent. So, flue gas treatment is needed soon. Therefore, a cost-effective system development of flue gas treatment is required to meet the regulations. Fig. 1 (b) shows a flue gas treatment system for small boiler proposed by the authors, consisting of ESP for particulate and hybrid SO_x and NO_x removal apparatuses. 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. However, because the flue gases must be treated directly, treatment of large volumes required 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 [1]-[2]. This was because only the necessary amounts of gas are treated externally at ambient temperature and pressure. The authors propose that the plasma-chemical hybrid process consists of the indirect nonthermal plasma process followed by the wet-chemical treatment. The principle of the NO_x removal is as follows:

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

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

$$2NO_2 + 4Na_2SO_3 \rightarrow N_2 + 4Na_2SO_4 \qquad (3)$$

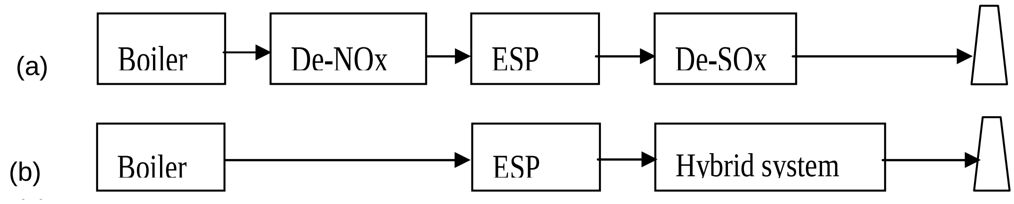

Fig. 1. Boiler flue gas treatment system (a) conventional, and (b) hybrid system (De-NOx&De-SOx)

On the basis of the 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 the first pilot-scale apparatus. The NO_x removal efficiency during the combustion of CNG exceeded 90% [3]. The further experiments were carried out using the second pilot-scale apparatus. Continuous operation for 3–5 h was successful, and the NO_x removal performance characteristics were investigated [4]-[6]. The experiment was conducted using the third demonstration plant consisted of a multi-fuel boiler and an improved chemical scrubber. There were three investigation items which were to obtain minimum NO_x emission when firing CNG, and to confirm combustion characteristics and NO_x removal performance when firing bio-oils, and to confirm the boiler system continuous operation with the NO_x removal. The results of these items are reported [7]-[8]. The further investigation item is to obtain operational characteristics of the system for industrial application. In this paper the operational characteristics are described.

2 Experimental set-up

Fig. 2 shows a schematic diagram of the plant. The boiler (Takao Iron Co., Ltd.) had both an original burner for gas or/and oil and was operated by using CNG (13 A) at 157 Nm^3/h, heavy oil (Type A) at 171 L/h and bio-oils. The boiler had a steam generation rate of 2.5 t/h. One or two sets of commercial ozonizers (Ebara Jitsugyo Co., Ltd., EW-90Z) with a pressure swing adsorption (PSA) oxygen generator were employed for generation; when the O_3 gas flow rate was 0.9 Nm^3/h and the discharge power was 1.5 kW, 90 g/h of ozone was generated, and its concentration was approximately 4.7%. The ozone was injected into a flue gas duct for NO oxidation. The flue gas was then introduced into the scrubber with a height of 3.7 m to reduce NO_2. The diameters were 0.9 m at the sump part of the scrubber and 0.7 m at the packing material layer part. The scrubbing solution was pumped from the sump to the top of the scrubber and sprayed through a nozzle over the packing material. After the NO_x in the flue gas was removed in the scrubber, the cleaned flue gas was discharged in the air through the smokestack. On the other hand, the scrubbing solution passed through the packing layer into the sump was circulated by a multistage centrifugal pump operating at 1.5 kW. A small amount of scrubbing solution was continuously drained from the scrubber to keep the activity of the solution, i.e., remove the reaction product from the scrubber solution. The liquid flow rate was set to 3000 or 5000 L/h. Meters installed on a tributary line connected to the sump monitored the ORP and pH of the scrubbing solution. An aqueous solution of Na_2SO_3 and NaOH (concentrations: 200 g/L and 10 g/L) obtained from a chemical factory as a byproduct was continuously added into the sump. The flow rate of the

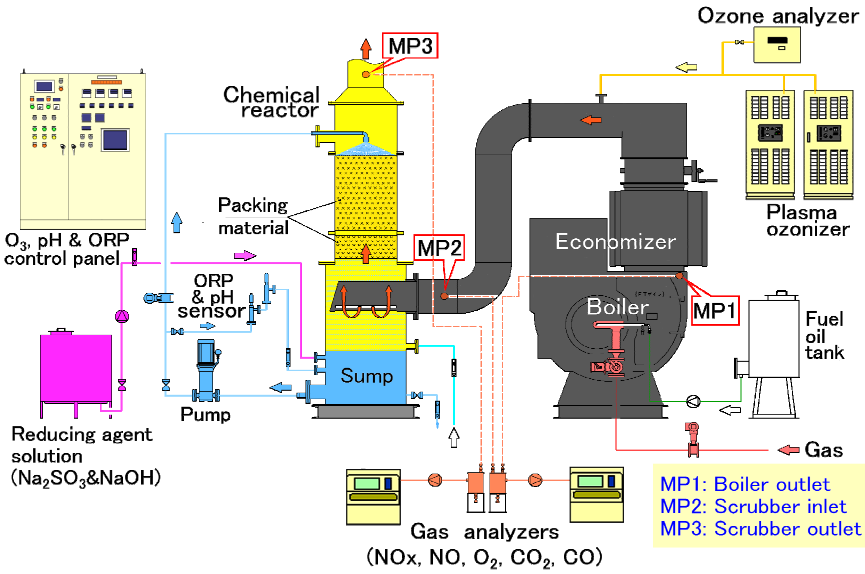

Fig. 2. Schmatic diagram of the pilot plant.

fresh aqueous solution was carefully controlled according to the pH and ORP of the scrubbing solution. The initial Na_2SO_3 concentration of the scrubbing solution in the sump was set to more than 16 g/L. The boiler was operated at 30%–100% of the boiler rated load. The concentrations of the flue gas constituents (O_2, CO_2, CO, NO_x and NO) were measured by using gas analyzers (Horiba PG-240). The temperature of the flue gas and concentrations of its constituents were measured at the following three sampling points: MP1 (boiler outlet), MP2 (scrubber inlet) and MP3 (scrubber outlet). The O_3 concentration generated was measured by using an O_3 monitor (Ebara Jitsugyo Co., Ltd., EG-550). The experiments were carried out by firing CNG, and heavy oil and bio-oils. The experiment was carried out for 120–450 min on a single day.

3 Experimental results and discussions

NO_x emission depending on O_2 concentration in flue gas was investigated in firing heavy oil. Fig. 3 shows that the relation between NO_x emission and different O_2 concentartions at MP1 while boiler was operated at low load, middle load, and high load, equivalent to fuel flow rates of 67, 126, and 157 L/h, respectively. O_2 concentration was varied within 2.4% to 7.8%. Measured data indicated that as O_2 concentration decreased from 6% to 2.4%, NO_x emission decreased from 100 ppm to 80 ppm at low load, and from 100 ppm to 90 ppm at high load, respectively.

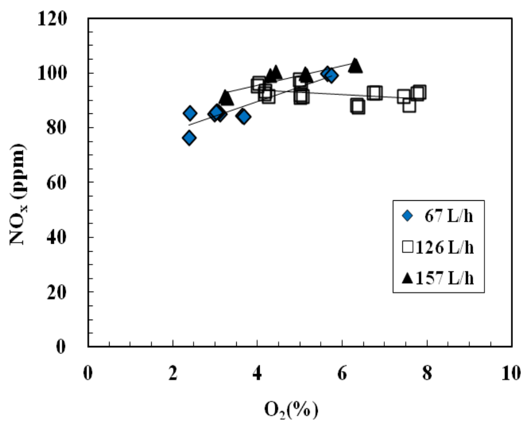

Fig. 3. Relation between NO_x emission and O_2 concentrations at MP1 at low load, middle load, and high load operations.

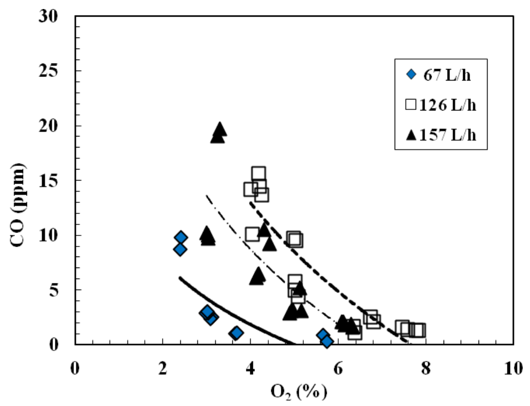

Fig. 4. CO concentrations as a function of O_2 concentrations at three loads as Fig. 4.1.

Table 1. Effect of O_3 flow direction on NO removal to flue gas flow; a) along gas flow, b) right-angled gas flow, c) against gas flow

O_3 flow direction	a)	b)	c)
⊿NO (ppm)	47.8	48.1	48.5
De-NO (%)	87.1	87.3	86.8

However, at middle load NO_x emission slightly increased within 90-95 ppm. The result indicated that it is desiable to operate boiler at lower O_2 concentaration because NO_x emission decreased less. On the other hand CO emission at MP1 was quite dependent on O_2 concentration in flue gas. Fig. 4 shows CO concentration as a function of O_2 concentrations at the same boiler operation conditions. It is clear that CO increased definitely as O_2 decreased. In order to keep CO emission less than 10 ppm, O_2 concentration should be more than 5% in firing heavy oil.

According to the equation (1), NO is oxidized to NO_2 by O_3. O_3 injection is an important operational factor in the system. The point was which direction to inject O_3 to the flue gas flow. O_3 was injected at 9.6 m/s into flue gas while flue gas velocity was 5.6 m/s in gas duct. Table 1 shows the effect on NO removal depending on the three O_3 directions (along, right-angled, and agaist flue gas flow). There was no difference of NO removal effect at any direction. In result O_3 was injected against gas flow. Furthermore, effects of velocity variety of both O_3 and flue gas on NO removal was investigated. However, the effect was not detected while both O_3 and flue gas velocities were within 2.6-5.6 m/s and 7.3-9.6 m/s, respectively. It is clarified that the amount of NO removed (⊿NO) was nearly the same as the amount of O_3 required to oxidize NO to NO_2 (almost 1:1 or a stoichiometric ratio) [8]. Fig. 5 shows

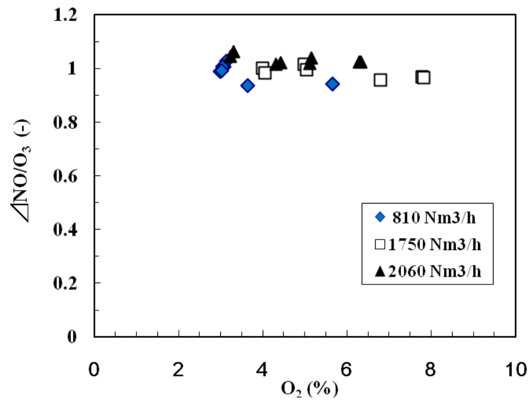

Fig. 5. Ratio (⊿NO/O_3) as a function of O_2 concentration at MP1.

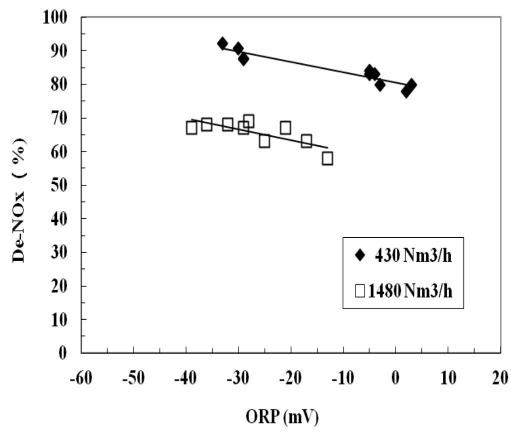

Fig. 6. Relationship between NO_x removal and ORP at low load and high load operations.

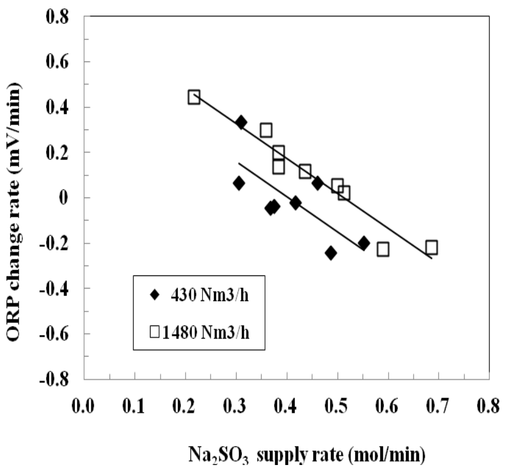

Fig. 7. Effect of Na_2SO_3 supply rate on the ORP change rate at 430 and 1480 Nm^3/h.

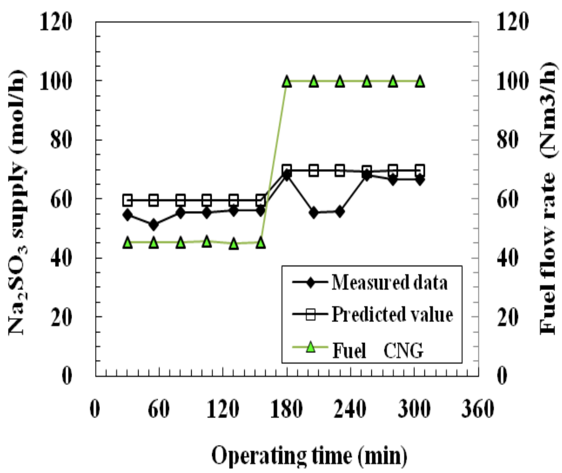

Fig. 8. Time-dependent Na_2SO_3 supply rate together with measured rate when fuel flow rate of CNG were set to 45 and 100 Nm^3/h.

the ratio (◢NO)/O_3) as a function of O_2 concentration at MP1 while flue gas flow rates were in the range of 810-2060 Nm^3/h in firing heavy oil. It is clear that the ratio (◢NO/O_3) was almost 1.0 (stoichimetric ratio) at any O_2 concentration in flue gas and at any load operation.

According to the equation (2), NO_2 is reduced to N_2 by Na_2SO_3 solution. It is a key of stable operation of the system to set optimally Na_2SO_3 supply rate. Fig. 6 shows the relationship between NO_x removal and ORP at low load and high load operations which were carried out at the second plant (2.0 t/h steam generation). All measured data indicated that the NO_x removal increased as the ORP decreased. In the high-load operation, the gas flow rate was to 1480 Nm^3/h, and the Na_2SO_3 solution was in the range of 0.38-0.69 mol/min, with 0.04 mol/min of NaOH. The NO_x removal was more than 60% when the ORP was –15 mV, and increased around 70% at –40 mV. The trend of the correlation between the NO_xremoval and the ORP proved to be similar in any load operation. As a result, it is clear that the NO_x removal is definitely influenced by the ORP in the liquid, and the less ORP, the more NO_x removal. The ORP, however, fluctuated from time to time. As Na_2SO_3 increased, the ORP decreased inversely. An attention was paid to the ORP change rate depending on the Na_2SO_3 supply rate, which was an index for the stable plant operation. Fig. 7 shows the effect of Na_2SO_3 supply rate on the ORP at 430 and 1480 Nm^3/h. If the ORP change rate became negative value, the ORP decreased as operating time went on, which means the NO_x removal would be stable or increased. It is important that the ORP change rate should be less than zero (0 mV/min) in order to keep the NO_x removal performance stable. So, it is essential to predict properly Na_2SO_3 supply rate for boiler operation conditions. The supply rate of Na_2SO_3 (mol/h) depends mainly on three factors of fuel flow rate (Nm^3/h for gas fuel or L/h for liquid fuel), NO_x concentration (ppm) at MP1, and that at MP3. Furthermore, for oil fuel, calorific value (J/g) is introduced as another factor, considering a variety of oil fuel. The empirical formula of Na_2SO_3 supply rate is determined using the multiple variables regression analysis method from accumulated measured data on both gas and oil fuels. Na_2SO_3 supply rate can be predicted from the empirical equation, based on fuel flow rate and NO_x concentrations expected at MP1 and that at

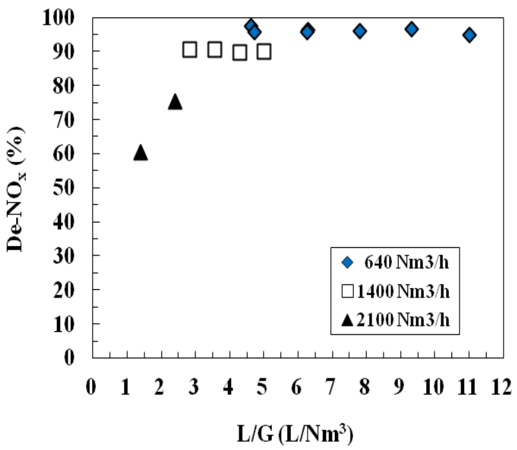

Fig. 9. Effect of Liquid-to gas (L/G) on NO_x removal efficiency when the flue gas flow rate was set to 640, 1400, and 2100 Nm^3/h in firing CNG.

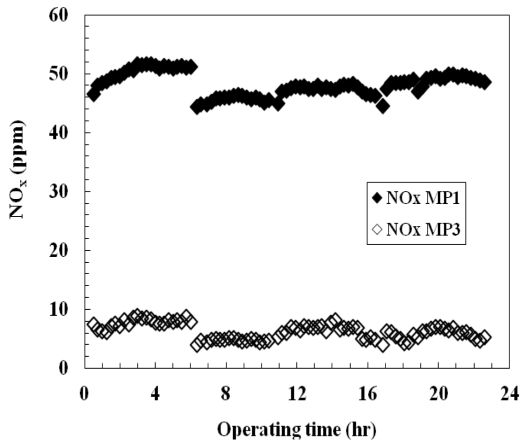

Fig. 10. Time dependent NO_x concentrations at MP1 and those at MP3.

MP3. Fig. 8 shows an example of predicted Na_2SO_3 supply rate together with measured rate, based on that fuel flow rates of CNG were set to 45 and 100 Nm^3/h, and NO_x concentrations expected at MP1 and MP3 were 50 ppm and less than 7 ppm. The predicted rate coincides with the measured rate during the operation.

Effect of liquid rate on NO_x removal was investigated. The liquid flow rate was varied 3000, 4000, 5000, 6000, and 7000 L/h while flue gas flow rate was set to 640, 1400, and 2100 Nm^3/h, respectively in firing CNG. Thus, the liquid-to-gas ratio (L/G) was obtained in the range of 1.4-11.0 L/Nm^3. The result of the actual measurements performed during the experiments are shown in Fig. 9. The data indicated that the scrubbing effectiveness of NO_x removal was not depended on L/G in the range of 3-11 L/Nm^3 when flue gas rates were 640 and 1400 Nm^3/h, but was depended when 2100 Nm^3/h. This result shows that L/G should be set to more than 2.5 in this experimental set-up. It proved that scrubbing effectiveness was very moderate as compared to that of SO_2 removal scrubber.

An operation of four successive days was carried out in firing CNG. Boiler started and stopped every 6 hours a day. However, the scrubbing solution was not replaced with fresh solution when boiler stopped, but used as it was, throughout the exepriment. NO_x removal performance and relative dendity of scrubbing solution were investigated. The average flow rate of CNG fuel was 52 Nm^3/h, and that of flue gas was 718 Nm^3/h.The average both rates of O_3 injection and Na_2SO_3 supply were 86 g/h and 63 mol/h, respectively.

Fig. 10 shows time dependent NO_x concentrations at MP1 and those at MP3. NO_x concentrations at MP1 were 45-50 ppm, different each day due that O_2 concentrations at MP1 ranged between 3.3% and 4.0%. NO_x concentrations at MP3 were within 5-8 ppm, equivalent to NO_x removal efficiency of more than 85% during the experiment, which was a satisfactory result. Relative density of drainage was manually every 10 min measured by a hydrometer. Fig. 11 shows time dependent relative density of scrubbing solution together with the predicted density. The relative density increased gardually as time went on because of Na_2SO_4 generated as a byproduct. Then, density became stable, aproximately 1.08 by adjusting flow rates of Na_2SO_3, drainage, and make-up water to the scrubber. Scrubber liquid is warmed up

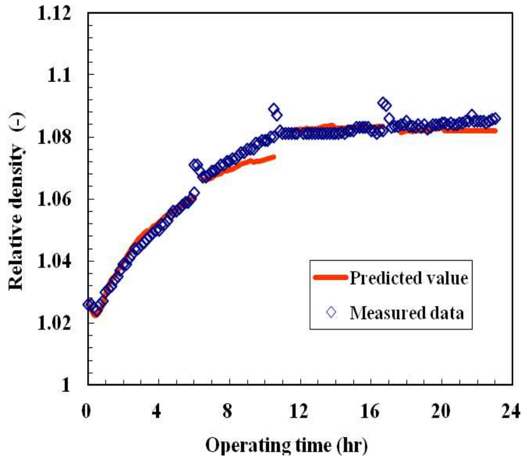

Fig. 11. Measured density together with the predicted density as a function of operating time in firing CNG.

and cooled down because boiler daily starts and stops. Care must be taken lest the byproduct is crystallized in the scrubber sump during boiler stoppage. The relative density of 1.08 is an allowable value as a control index. The predicted density was calculated from an empirical equation consisted of Na_2SO_4 generated and Na_2SO_3 unreacted, and solution temperature. The predicted density coincided with the measured throughout the experiment as shown in Fig. 11. Then, the correlation among the rates of Na_2SO_3, drainage, and make-up water in the scrubber sump was invesitgated under the condition that Na_2SO_3 concentration of scrubbing solution was kept more than 25 g/L and relative density was less than 1.08. The predicted correlation was obtained as a function of flue gas flow rate, which was an optimal operation index of the scrubber. The following is one example of predicted correlation when flue gas flow rate is 670 Nm^3/h in firing CNG; Na_2SO_3 supply rate 68 L/h, make-up water 42 L/h, and drainage 100 L/h.

The efficiency of removing SO_2 was in the 85% at the first pilot-scale apparatus using heavy oil (Type A) of which sulfer concentration was less tha 0.1%. Further investigation is planned using heavy oil (Type C) with middle sulfer content. Hybrid NO_x and SO_x removal apparatus is tested soon.

4 Conclusions

Low-emission multi-fuel boiler system with plasma-chemical hybrid NO_x was examined. Ozone injection for NO oxidation and Na_2SO_3 solution for NO_2 reduction are essential factors in the system. Operational indexes were obtained for industrial application, such as O_3 injection method (flow direction, quantity, etc.), L/G, Na_2SO_3 supply rate, and the flow rate correlation among Na_2SO_3 supply, drainage, and fresh water to the scrubber.

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