Exhaust Gas Cleaning by Plasma Jet*

(Designing of Plasma Generator and Formation of Nitrogen Oxides in Presence of Oxygen)

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The possibility of removing the pollutants by arc plasma injection from dirty gas containing higher concentrations of NO_x , SO_x , HCl and dust emitted from a municipal refuse incinerator has been studied in this paper. A low-power arc plasma generator is designed and operated continuously on argon gas with high stability. The air is injected from a capillary into an argon plasma jet, and the formation of NO_x is measured in order to assess the generation of specific radicals in the plasma wake. The optimum injection points for generating radicals and for the stable operation of the plasma are discussed; the formation of NO_x in the presence of oxygen for a practical system is also evaluated.

Key Words: Dirty Gas, Municipal Refuse Incinerator, Gas Cleaning, Argon Plasma Jet, Radical, Nitrogen Oxides

1. Introduction

In recent years, the removal of nitrogen oxides (NO_x) in flue gas from municipal refuse incinerators has become a major concern in relation to the regulation of total NO_x emission in urban areas. To reduce the NO_x in combustion flue gas, the selective non-catalytic reduction of NO_x , flue gas recirculation and catalytic reduction of NO_x have been successfully applied to a municipal refuse incinerator by the authors^{(1)~(4)}.

In view of the public requirement to save energy, the use of high-energy radiations such as beta, alpha and electron beams have recently been investigated for flue gas cleaning. For example, an irradiation technique using a high-energy electron beam was studied in the presence of ammonia for removing of NO_x and SO_x (sulfur oxides) contained in flue gases⁽⁵⁾. Before the practical use of such techniques, however, problems remain to be solved in terms of energy consumption reduction and huge capital cost require-

ments at present, as well as the aspects of better safety control with less cautious handling. In connection with these factors, further studies on reduction of required radiation dose, determination of optimal treatment temperature and so on are included.

To find a possible solution to the energy consumption problem, the use of pulse corona discharge was tested in some works⁽⁵⁾ for the removal of NO_x , SO_x and Hg (mercury) from the flue gases of municipal refuse incinerators. They observed that, in the presence of O_2 (oxygen), NO_2 was converted into NO : without showing decomposition, and they also found it difficult to clarify the mechanism of Hg removal.

With regard to the use of plasma for the flue gas cleaning, Weinberg⁽⁹⁾, Behbahani et al.⁽¹⁰⁾ and Hilliard and Weinberg⁽¹¹⁾ studied experimentally its NO removal efficiency from a gas mixture ($\text{NO} + \text{N}_2$). They suggested that the use of N_2 (nitrogen) plasma would also reduce the NO concentration in the presence of O_2 . In view of the time since this paper was written (Oct-1988), the authors might wish to check the validity of this statement. As the flue gases of refuse incinerators actually contain a considerable amount of O_2 in general, NO formation through dissociation of O_2 and N_2 as well as its conversion into NO_2 must be studied.

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The purpose of our present work is to investigate the possibility of using a variety of chemical energetic species like free radicals, electrons, ions, excited atoms and molecules that are produced by plasma for removing the harmful substances, such as NO_x , SO_x , HCl and heavy metals, contained in the flue gases of municipal refuse incinerators. Here, we report firstly on the examination of the plasma generator and then on the investigation of NO formation under the conditions of feeding air from outside to an atmospheric argon plasma jet. Finally we discuss the formation and distribution of chemical energetic species produced in the plasma.

Nomenclature

- d : anode nozzle diameter
 h : distance from plasma axis to air feeding nozzle
 I : plasma current
 k : reaction rate constant⁽¹⁴⁾
 L : distance between electrodes
 l : distance from anode nozzle exit
 l_n : throat length of anode nozzle
 l_p : length of plasma flashing region
 P : plasma input power
 Q : argon flow rate
 Q_a : air feeding flow rate
 Q_w : cooling water flow rate
 T : temperature
 V : voltage between electrodes
 ϵ : emissivity

subscript

- st : the value under standard condition

2. Plasma Generator and Experimental Conditions

Figure 1 shows the experimental apparatus. By employing a gas heating method which makes it easy to generate plasma continuously based on the use of electrical discharge, stable operation of this apparatus through high-speed rotation of the operation fluid

(argon) around the cathode (tungsten) is ensured.

The argon, which flows into the torch unit through the gas cylinder, the reducing valve and the float meter, circulates around the cathode at a high speed, is ionized and transformed into the plasma state in the discharge unit and is ejected from the anode nozzle (copper). Inside the vacuum chamber, the argon reverts to its original gaseous state as it flows in the downstream direction and is then exhausted by a vacuum pump.

Both electrodes are water-cooled, and the clearance between the electrodes is controlled by a feed screw. The flowing condition of the plasma jet can be observed from the observation windows on the right and left sides of the measuring room. As to the copper anode nozzle, five different types were prepared with varying diameter d and throat length l_n (Fig. 2) to determine the effect of nozzle shape on plasma characteristics.

A variable DC power supply of 3.6 kW maximum output (100 A, 36 V) is used as a power supply. The power supply of the plasma jet generator must have the drooping characteristic. In this experimental apparatus, the circuit obtains this characteristic by connecting a series of resistors. After carrying out a

Fig. 2 Anode nozzle

Fig. 1 Schematic diagram of the DC arc plasma jet

number of experiments with different resistance values, the value was set to $R=0.135 \text{ ohm}^{(12)}$ in view of the stable operation of plasma. The contact method was used in ejecting the plasma.

The experiment was carried out at plasma currents ranging from 35 to 100 amperes, 11 to 23 volts of plasma potential between electrodes, 6 to 20 l/min argon flow rate, 2.5 l/min cooled water flow rate, and 0 to 8 mm distance between the electrodes. The thermal efficiency of the plasma generator was 60 to 65 %.

3. Characteristics of Plasma Jet and Anode Nozzle

Figure 3 shows the results of distance L and voltage V between the electrodes, current density I and length l_p of the flashing region of plasma flow. The relation between V and I is shown in Fig. 4. Here l_p is defined as the length of the white-colored part of the plasma in photos (Figs. 5(a) to (c), left) taken with an exposure time of 1/1 000 sec, representing the

Fig. 3 Fundamental characteristics of plasma jet (Voltage, current, distance between electrodes and jet length)

length of the very high temperature region in the plasma jet. From Fig. 3, it is obvious that nozzles A and B have a wider range of L as well as a wider range of I than nozzles C and D to generate plasma. For nozzle E, which is easier to manufacture, those ranges of plasma generation were found to be narrow. Figure 4 shows the drooping characteristics of voltage V with increase in electric current I .

The temperature of the plasma jet, which was

Fig. 4 Relation between voltage and current of plasma flow

Fig. 5 Plasma and plasma thermogram (18 V, 1.3 kW)

expected to have the greatest effect on the formation of energetic species like radicals, could not be measured directly at the flashing inner part of the plasma because of the lack of optical measurement equipment. Therefore, the temperature condition was visualized by use of a thermogram obtained by means of a radiation pyrometer subjected to the exposure of mean radiant energy in the depth direction of the plasma jet flow. The emissivity ϵ of the gas was unknown and assumed to be $\epsilon=0.3$ because such a value allowed easier comparison of thermograms.

The results of the nozzles used are shown on the right-hand side of Figs. 5(a) to (c). With reference to the measurements taken by a tungsten-rhenium (W-Re) thermocouple for high-temperature measurement, the thermograms indicate temperatures corresponding to about 1600 K for the outer shell of the plasma jet and to over 5000 K at its center. It can be seen that nozzle A produced the highest temperature plasma among the nozzles used. Figure 6 shows the temperature on the axis of the plasma jet flow measured by a thermocouple, whereby nozzles A and C were used. From these results, it was concluded that the use of nozzle A, showing the highest convergence of plasma, gave the highest energy density to correspondingly produce the highest temperature plasma flow which would be able to promote a high level of formation of energetic species. Nozzle A was therefore used in the following experiments. It was also confirmed from Fig. 5 that the length of the white-colored part of the plasma in the photograph, corresponded to that of the high-temperature region in the thermogram, and this region corresponded to the plasma recombination region. The formation of chemically energetic species must also be possible in the

wake flow after recombination because the temperature observed there was sufficiently high.

4. Formation and Distribution of Radicals in Plasma Jet

In view of the purpose of our present work, to investigate the possibility of the removal of harmful substances contained in flue gases by means of chemical reaction with using energetic species like free radicals, it was important to study the formation and distribution of energetic species in a plasma flow.

The formation of NO_x was experimentally studied by feeding air through a fine tube into the plasma flow, assuming that the formation of NO_x directly corresponds to the formation of energetic species. In addition to the effect of the position of air inlet, the effect of parameters on the formation of NO_x such as argon flow rate, airflow rate, voltage and current density of plasma was investigated. Determination of the formation of NO_x by varying the air feeding rate was expected to contribute to the understanding of the effect of O_2 contained in a flue gas on the formation of NO_x in the case of feeding in an actual flue gas.

In the case where air is fed to the plasma flow, NO will be formed according to the mechanism proposed by Zeldovich⁽¹³⁾:

Weinberg⁽⁹⁾ Behbahani et al.⁽¹⁰⁾ and Hilliard and Weinberg⁽¹¹⁾ proposed that the following reaction mechanism, whereby atomic N formed in the plasma was fed to a gas mixture of NO and N_2 predominantly occurred:

They suggested that NO could also be removed in the presence of O_2 because the reaction rate constant k_3 ⁽¹⁴⁾ was found to be higher in Eq. (3) than k_1 , k_2 in Eq. (1). Figure 7 which shows the reaction rate constants for Eqs. (1) to (3) as a function of temperature, however, suggests that the formation of NO can occur at a higher level than the removal of NO in the higher temperature range where the value for k_1 becomes larger than that for k_3 .

In our present work, air was fed to the plasma flow, and thus the reaction was assumed to occur in the following way, such that atomic oxygen and nitrogen produced through dissociation react with O_2 and N_2 radicals to form NO according to Eqs. (1) and (2), and then a part of NO thus formed reacts further with atomic O to form NO_2 .

Samples of gas were analyzed continuously for O_2 by the magnetic induction method, and for NO_x by chemiluminescence reaction analysis. The airflow rate was measured with a float-type meter.

Fig. 6 Temperature distribution at plasma wake

5. Experimental Results and Consideration

Figure 8 shows the relation between the NO_x concentration in the exhaust gas and the position of the air inlet nozzle, whereby the oxygen concentration is represented by $\text{O}_2 = Q_a \times 0.21 / (Q + Q_a) \%$, which is proportional to the air feeding rate. It is obvious from Fig. 8 that the air inlet placed nearer the nozzle exit gave the higher concentration of NO_x formed, which is roughly consistent with the result of Weinberg⁽⁹⁾ showing the higher level removal of NO for the region nearer to the nozzle. From these, it is suggested that a higher formation of energetic species could be obtained for the air inlet placed nearer to the nozzle. It was observed, however, that the air inlet placement near the nozzle resulted in unstable plasma generation accompanied by unstable voltage between the electrodes. For this reason, the air inlet in the following experiments was placed at the end region of plasma recombination (point A in Fig. 8). In the present experiment, NO_2 was found at the level of 3 to 8 % to total NO_x .

Figure 9 shows the effects of the distance h between the position of air inlet and the axis of

Fig. 7 Temperature dependences of rates constants

Fig. 8 Relation between NO_x and l/d

plasma jet on the NO_x formation. NO_x concentration shows a slight decrease with increasing of h , which is thought to have resulted from the fact that the air feeding velocity as high as over 100 m/s showed a slight damping in the distance h as short as in this experiment. This result can be supported by the experimental result that the use of a tube of inner diameter 2 mm showed a damping in air velocity with increasing h and resulted in a slightly higher level of NO_x concentration than use of a tube of inner diameter 1.2 mm.

Figure 5(d) shows the thermograms with and without feeding of air. It is seen that the temperature condition was nearly the same in the flashing region of plasma jet, but different in the region after that, showing a smaller high-temperature region for the case of feeding air.

The effect of voltage, electric current and input power on the formation of NO_x is shown in Fig. 10. NO_x concentration increased with the increase in voltage or electric current, which suggests that the increase in these parameters gave an increase in the degree of ionization, resulting in an increased plasma temperature and consequently in the increased formation of atomic N and O as well as free radicals. Comparison of the slopes of the NO_x formation curves in Fig. 10 indicates that the effect of voltage was greater than that of electric current under our experimental conditions, which further suggests that a higher formation of energetic species will be achieved by increasing the voltage rather than by increasing the electric current for the same input power, because voltage relates directly to ionization.

From Fig. 11, which shows the effect of the argon flow rate, it is seen that when the same level of voltage and electric current was used, the degree of ionization increased with decreasing argon flow rate, resulting in a higher level of NO_x concentration with a higher degree of radical formation. The plotting of the quan-

Fig. 9 Relation between NO_x and h/d

tity of NO_x formed vs argon flow rate, however, shows a peak at a certain argon flow rate and suggests a correspondent peak of radical formation. The appearance of such a peak in the quantity of NO_x formed could be explained as follows: decreasing argon flow rate gave an increased degree of ionization and consequently increased NO_x formation, but a further decrease in the argon flow rate resulted in unstable plasma generation leading to the decrease in NO_x formation.

Figure 11 also shows the NO_x conversion ratio as a function of the argon flow rate, whereby the conversion ratio is defined as the ratio of the observed quantity of NO_x formed to the theoretical quantity of NO to be formed from O_2 contained in air strictly in accordance with the mechanism $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$.

The effect of the air feeding tube diameter is also shown in Fig. 11 for inner diameters of 1.2 mm ($\circ$ and $\square$) and 2.0 mm ($\bullet$ and $\blacksquare$). The behavior of NO_x concentration curves was found to be nearly the same for both diameters, with a slightly higher level of concentration for the 2.0 mm diameter. In addition, as shown in Fig. 11, when the argon flow rate varied, plasma generator appeared to become less stable as the flow rate decreased, and the plasma was finally

extinguished. This range of argon flow rate is represented by a broken line in Fig. 11.

Figure 12 shows the effect of the air feeding rate on NO_x formation as a function of O_2 . Under our experimental conditions, a peak of NO_x concentration was observed at the point of nearly 6% O_2 . This peak could be caused by a reduced formation of atomic O and N leading to a reduced NO_x formation at an O_2 level below 6% and by a higher air feeding rate, leading to greater dilution of NO_x formed at O_2 levels above 6%.

From our present work, as mentioned above, it can be concluded that NO_x is formed by argon plasma in the presence of O_2 and N_2 contained in combustion flue gas. Therefore, the possibility of the removal of NO_x and SO_x by the use of plasma should be studied in the future with the addition of ammonia to the flue

Fig. 10 Relation between NO_x and power

Fig. 11 Relation between NO_x and argon flow rate

Fig. 12 Relation between NO_x and O₂

gas in much the same way as in the electron beam method⁽⁵⁾, for the purpose of removing pollutants contained in combustion flue gases.

6. Conclusions

The use of chemically energetic species produced by plasma flow was investigated for the purpose of finding a solution to the problem of flue gas cleaning. A plasma generator was prepared and its basic characteristics examined. Within this generator, an atmospheric argon plasma jet was studied in terms of NO_x formation under the condition of feeding outside air to the plasma jet; on this basis, the generation and distribution of energetic species were discussed. The formation of NO_x in the presence of O₂ was also discussed, and the following basic data were obtained for future experiments on the feeding of combustion flue gases.

(1) The position of the flue gas inlet should be at the end region of plasma recombination to achieve stable plasma generation and consequently a high level of formation of the energetic species. With regard to the distance between the inlet position and the axis of plasma jet, an increase in the distance resulted in a slightly increased level of formation of energetic species.

(2) The formation of energetic species increased with increasing input power, whereby the effect of voltage was found to be greater than that of electric current under our experimental conditions.

(3) When a constant input power was applied, the degree of ionization varied with the argon flow rate and the quantity of energetic species produced reached a peak at a certain level of argon flow rate.

From our result that the feeding of flue gas containing O₂, N₂ into argon plasma jet will produce NO_x, the addition of ammonia to flue gas should be considered when studying the removal of NO_x and SO_x from combustion flue gases.

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