Vol. 1, No. 1, pp. 52-57, December 2002

INTERNATIONAL JOURNAL OF SAFETY
www.kiis.or.kr

Decomposition of NO_2 by SPCP

Hyun Choon Kang*, Hyung Whan An[1], Han Seob Lee[2], Myung Whan Hwang[3], In sung Woo[3] and An Soo Kang[4]

Department of Environmental System Management Engineering, Jeju College of Technology, Jeju 690-714, Korea
[1]Department of Safety Engineering, Chungju National University, Chungju 380-702, Korea
[2]Department of Environmental Engineering, Yong-In University, Yongin 449-714, Korea
[3]Department of Safety Engineering, University of Incheon, Incheon 402-749, Korea
[4]Department of Chemistry Engineering, Myongji University, Yongin 449-714, Korea

(Received October 10, 2002; Accepted December 15, 2002)

Abstract: The Decomposition of NO_2 (nitrogen dioxide), one of the Hazardous Air Pollutant (HAP), was studied by utilizing the SPCP (Surface induced discharge Plasma Chemical Processing) reactor so as to obtain optimum process variables and maximum decomposition efficiencies. Experimental results showed that for the frequency of 10 kHz, the highest deco position efficiency of 84.7% for NO_2 was observed at the power consumptions of 20 W. The decomposition efficiency of NO_2 was found to be: 1) proportional to the residence times, and inversely proportional to the initial concentrations of NO_2; 2) the maximum when the electrode diameter was 3 mm; 3) influenced by the electrode material, decreasing in the order of W>Cu>Al; and 4) proportional to the CH_4 content, due to which the highest efficiency of 98% was obtained with almost all the NO_2 removed.

Key words : discharge plasma, NO_2, decomposition efficiency, power efficiency

1. Introduction

Air pollutants resulting in environmental contamination are generated from automobile, aircraft, ships, thermal power plants and chemical industry of various fields. NO_2 emissions, generated from these combustion processes, have become a significant issue in recent years because NO_2 emissions contribute to acid rain, photochemical smog and are harmful to the human body [1].

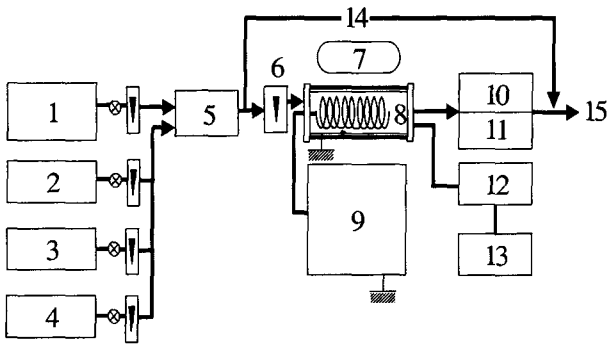
Great research efforts have been made to solve these problems, and newly-developed technologies, such as electron beam irradiation [2], silent discharge [3], pulsed corona discharge [4, 5], partial discharge in ferroelectric pellet layer [6] have proved their efficiency in removing NO_2 from flue gas. Surface induced discharge Plasma Chemical Processing represents a very attractive alternative to the above methods, as already demonstrated by several laboratory experiments [7~9].

In this paper, decomposition efficiency and power consumption of nitrogen dioxide (NO_2) were investigated by SPCP (Surface discharge induced Plasma Chemical Process) reactor to obtain optimum process variables and maximum decomposition efficiencies. Decomposition efficiency of NO_2 with various electric frequencies (5~50 kHz), flow rates (100~1,000 mL/min), initial concentrations (100~1,000 ppm), electrode materials (W, Cu, Al), electrode thickness (1, 2, 3 mm) and additive (CH_4) were measured.

*Corresponding author: hckang_env@jeju.ac.kr

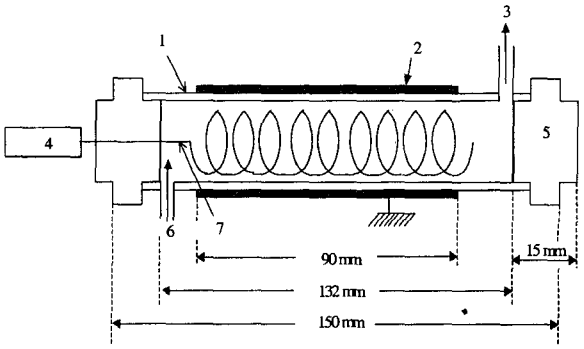
2. Experiment

Experimental set-up used in this work is shown schematically in Fig. 1. Standard sample gas used in this work is 1,500 ppm NO_2 (N_2 base 99.95%). The cylinder with N_2 (base gas) was also prepared to obtain the desired NO_2 concentration. These gases were mixed in the mixing tank before being injected to the reactor. Gas flow rate to the plasma reactor was controlled by adjusting the bypass valve and NO_2 concentration were analyzed by NOx, SOx analytical instrument (Ecom-AC, Germany). NO_2 concentration were measured at the reactor inlet and outlet before a series of measurements.



1. Sample gas
2. Air bombe
3. O_2 bombe
4. N_2 bombe
5. Mixing tank
6. Flow meter
7. Cooling fan
8. SPCP reactor
9. H. V. power supply
10. Gas analyzer
11. Gas chromatograph
12. H. V. probe
13. Oscilloscope
14. By-pass
15. Exhaust

Fig. 1. Schematic diagram of experimental apparatus.



1. Quartz(Di : 13 mm, Do : 15 mm)
2. Aluminum
3. Sample gas out
4. High voltage power supply
5. Teflon stopper
6. Sample gas in
7. Tungsten(9 mm)

Fig. 2. Schematic diagram of discharge plasma reactor.

Coil type cylindrical ceramic SPCP reactor was employed in this experiments, the outside of which is attached with cooling fan to maintain the temperature of reactor uniformly. To obtain power necessary for discharge, High Voltage Power Supply (SIS electronics co. SHP6501) with voltage output ranging from 1 to 12 kV was used and the exciting frequency of the high voltage applied between two electrode in Fig. (Figure No.) was varied among 5, 10, 20 and 50 kHz. Discharge power was monitored by an oscilloscope (Hewlett Packard model 54601A, 500 MHz). To lower the high voltage and current to 1000 : 1, attenuator (PR30 AC/DC, England) was used. Final by-product gas was analysed by FT-IR (Nicolet, Magna-IR 560) and 10 cm diameter Pyrex gas cell was used.

Fig. 2 shows the details of coil type ceramic SPCP reactor which is 13 mm in inner diameter, 15 mm in outer diameter and 132 mm in length. Quartz tube and Teflon stopper, which is thermally stable and good for discharge, was used as an insulation holder. A hand-made W-coil is used as the discharge electrode, which is attached on the inner wall of the quartz tube. The quartz tube was wrapped with a rounded aluminium foil as the ground electrode. When high frequency and high voltage is applied between the two electrodes, strong surface discharge occurs around the edge of the electrodes. The discharge starts at the contact point between the discharge electrode and the inner quartz tube wall and develops along the inner surface when the high voltage is applied between the discharge electrode and ground electrode.

3. Results and Discussion

Fig. 3 shows NO_2 decomposition efficiency as a function of discharge power at four different values of frequencies 5, 10, 20 and 50 kHz, where the inlet concentration is 300 ppm, flow rate 200 ml/min, base gas N_2 and discharge electrode W. Decomposition efficiency increases with increasing discharge power. Maximum decomposition rate of 84.7% is obtained at 10 kHz and

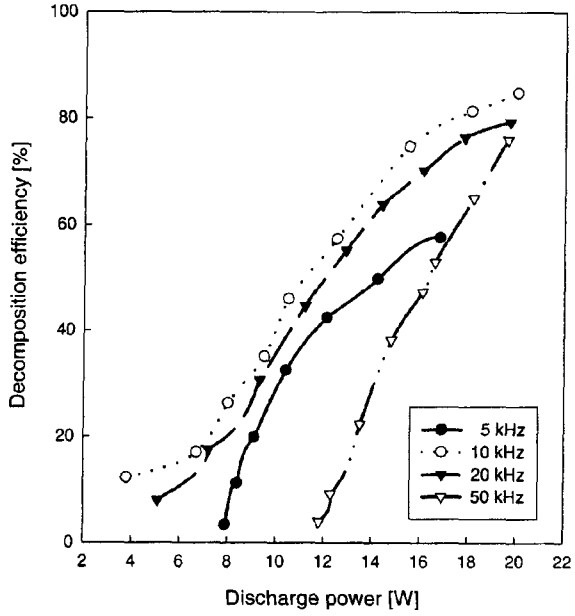


Fig. 3. Effect of electric frequency on decomposition efficiency of NO_2 ($C^0_{NO_2}$: 300 ppm, flow rate: 200 ml/min, base gas: N_2, discharge electrode: W).

20 W. Results shows that at diverging point 10 kHz, decomposition efficiency increased with decreasing frequency above 10 kHz and increased with increasing frequency below 10 kHz. As the life time of ions is more than one period at high frequency, those ions also supplies the electric energy which may be changed to heat energy causing bad energy efficiency [10]. Fig. 3 indicates that 10 kHz is the most effective decomposition frequency. In this experiment, we selected 10 kHz as a standard frequency which enables an effective decomposition efficiency within the regular range of discharge power.

Decomposition efficiency as a function of residence time, which is calculated as the reactor volume divided by the gas flow rate, at different discharge power, is shown in Fig. 4, where the inlet concentration is 300 ppm, frequency 10 kHz, base gas N_2 and discharge electrode W. In general, it is very clear that the decomposition efficiency is proportional to residence time, or discharge power consumption. As the residence time passing through the reactor increases, collision frequency with base gas increases and energy necessary for reaction becomes large. Hence, it can be considered that the rise of decomposition efficiency is due to the radical increase of reacting NO_2 gas [11~13].

The concentration dependence of NO_2 removal in this reactor is shown in Fig. 5 at 200 ml/min, 10 kHz, N_2 base gas and W electrode. The initial concentrations of NO_2 is 100, 300, 500 and 1000 ppm, respectively. Lowering NO_2 concentration enhanced the NO_2 decomposition efficiency. This is because that higher energy necessary for decomposing NO_2 can be obtained at lower concentration for a given specific power. It can

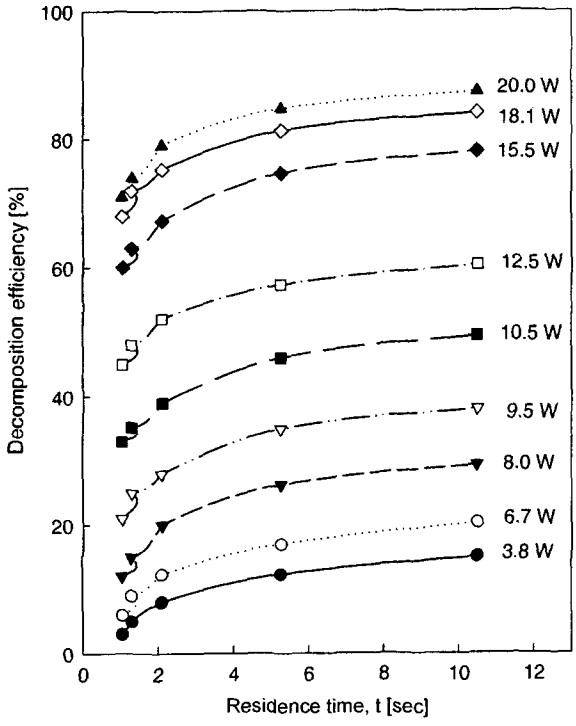


Fig. 4. Effect of residence time on decomposition efficiency of NO_2 ($C^0_{NO_2}$: 300 ppm, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

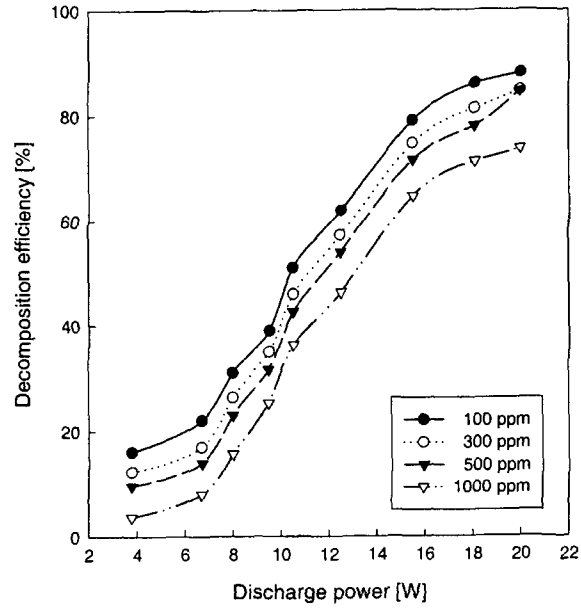


Fig. 5. Effect of initial concentration of NO_2 decomposition efficiency (flow rate: 200 ml/min, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

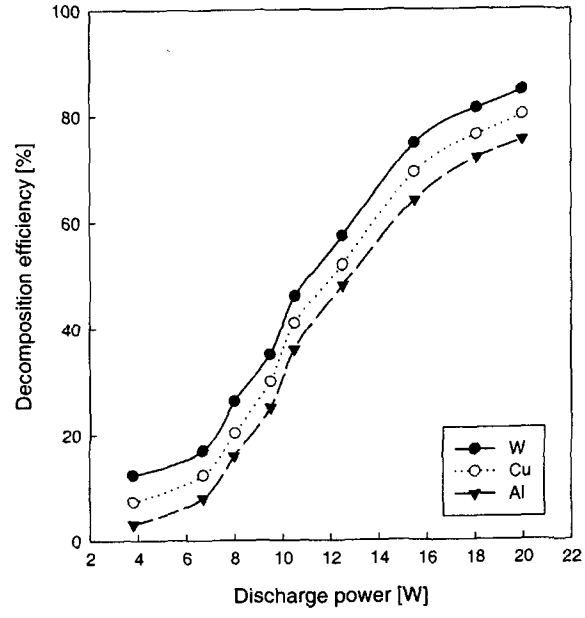


Fig. 6. Effect of electrode material on decomposition efficiency of NO_2 ($C^0_{NO_2}$: 300 ppm, flow rate: 200 ml/min, frequency: 10 kHz, base gas: N_2).

be rationalized that decomposition efficiency rise at small concentration is due to the large probabilities of N·, O· and OH· radicals colliding with base gas, or of free electrons directly reacting with NO_2.

Fig. 6 shows NO_2 decomposition efficiency as a function of discharge power at three different electrode material W, Cu and Al, where the inlet concentration is 300 ppm, flow rate 200 ml/min, frequency 10 kHz and base gas N_2. W has turned out to be the best employed wire. Melting point of electrode material W(3,407°C), Cu(1,084.9°C) and Al(660.3°C) is the key point of Fig. 6. The fact that the higher melting point material leads to higher decomposition efficiency may be due to the generation of free electrons on the surface of electrode by roughness of the electrode [14].

The next set of experiments was carried out to clarify the influence of the thickness of the electrode on NO_2 removal efficiency, where the inlet concentration is 300 ppm, flow rate 200 ml/min, frequency 10 kHz, base gas N_2 and discharge electrode W. As shown in Fig. 7, 3 mm thickness electrode has turned out to be the best employed wire. It can be seen that the thicker the electrode, the higher the decomposition efficiency because of the increase of discharge area.

Fig. 8 shows NO_2 decomposition efficiency as a function of discharge power, among which the concentration of CH_4 additive is varied. At this time, the inlet concentration is 300 ppm, flow rate 200 ml/min, frequency 10 kHz, base gas N_2 and discharge electrode W. In this case tested, increasing the concentration of CH_4 enhanced the decomposition efficiency, hence the highest decomposition efficiency of 98% at 20 W can be obtained and NO_2 was almost completely decomposed. In contrast of Fig. 3, decomposition efficiency has considerably increased. From this experiment, it is clearly seen that the combination of discharge plasma with CH_4

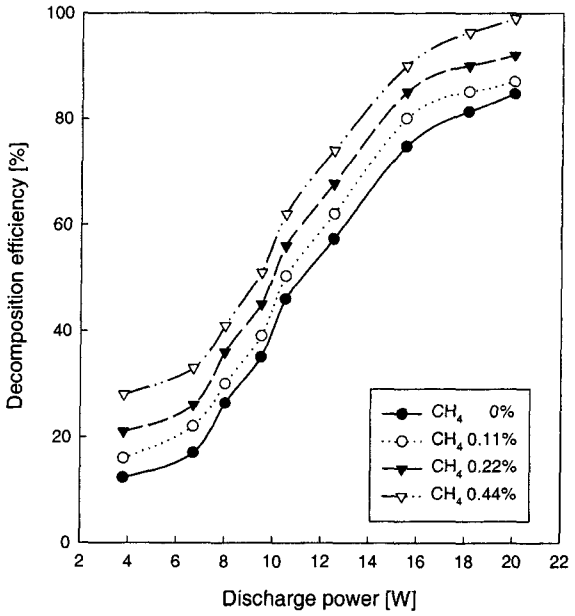


Fig. 8. Effect of additive CH_4 on decomposition efficiency of NO_2 ($C^0_{NO_2}$: 300 ppm, flow rate: 200 ml/min, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

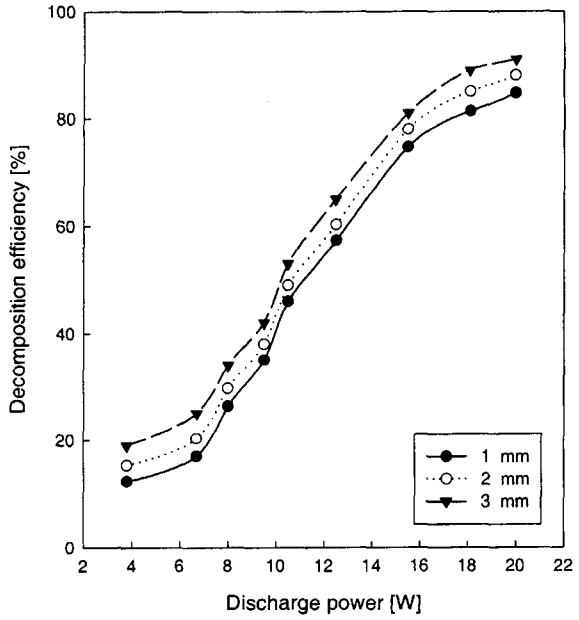


Fig. 7. Effect of thickness of electrode on decomposition efficiency of NO_2 ($C^0_{NO_2}$: 1000 ppm, flow rate: 200 ml/min, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

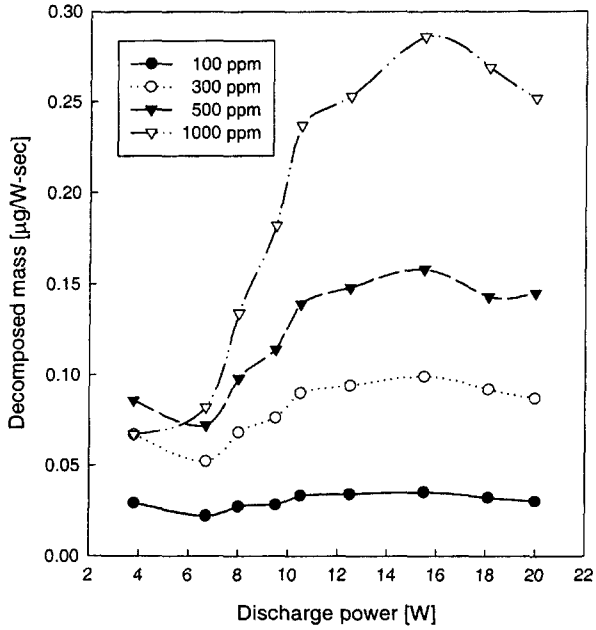


Fig. 9. Decomposed mass of NO_4 per unit power and sec (flow rate: 200 ml/min, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

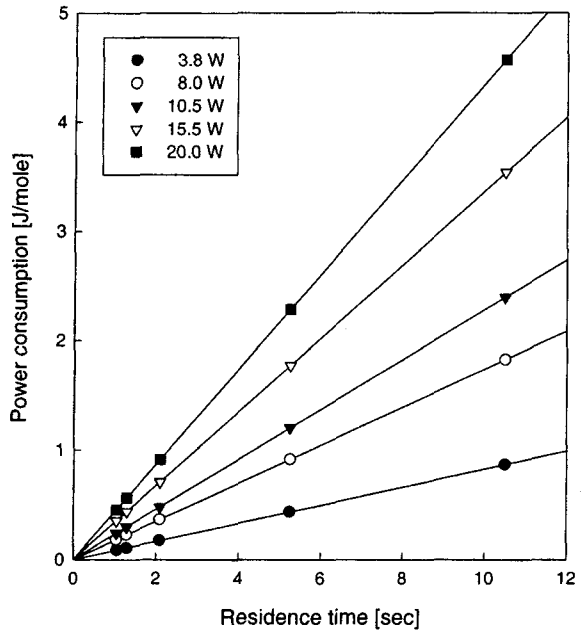


Fig. 10. Power consumption necessary to decomposed NO_2 ($C^0_{NO_2}$: 300 ppm, frequency: 10 kHz, base gas: N_2, discharge electrode: W).

additive is very effective in NO_2 decomposition.

Decomposed mass (μg) of NO_2 per unit power (W) and second(sec) are plotted against discharge power at four different concentration 100, 300, 500 and 1000 ppm. As shown in Fig. 9, decomposed mass (μg) of NO_2 increased to a maximum when discharge power was raised to 15.5 W in all case of NO_2 concentration. Decomposition efficiency was the best in this case. The decomposed mass of NO_2 slightly decreased as the discharge power was raised further. The left portion of the maximum point can be considered as the region which sufficient energetic electron necessary to decompose cannot be generated, and the right portion of the maximum point can be considered as the region that power is much consumed unnecessarily because of exceedingly supplied discharge power.

Power efficiency, that is, necessary power required to decompose one mole NO_2 is also shown in Fig. 10, where the residence time is the horizontal axis. It is very clear that the necessary energy to decompose one mole NO_2 is small (high efficiency) for short residence time and increases with residence time in any case for NO_2.

4. Conclusions

For hazardous air pollutants (HAP), NO_2 (nitrogen dioxide), decomposition efficiency, power consumption, and applied voltage were investigated by SPCP (surface induced discharge plasma chemical processing) reactor to obtain optimum process variables and maximum decomposition efficiencies.

Experimental results showed that for the frequency of 10 kHz, the highest decomposition efficiency of 84.7% for NO_2 were observed at the power consumptions of 20 W. Decomposition efficiency per unit power of NO_2 was 4.24%/W and was enhanced with increasing residence times and with decreasing initial concentration of pollutants. Decomposition efficiency was enhanced with increasing thickness of discharge electrode and the highest decomposition efficiency was obtained for the electrode thickness of 3 mm in this experiment. The decomposition efficiency was influenced by the electrode material, decreasing in the order of W>Cu>Al. Hence, W turns out to be the employed wire. The decomposition efficiency is proportional to the CH_4 content, due to which the highest efficiency of 98% was obtained with almost all the NO_2 removed. It has been found that methane (CH_4) was an effective additive in this experiment. Optimum power with the maximum decomposition efficiency were 15.5 W at all concentration range of NO_2 and power efficiency was the best in this case.

References

[1] A. T. McQueen, S. J. Bortz, M. S. Hatch, and R. L. Leonard, "Cement Kiln NOx Control", IEEE Trans. Ind. Appl., Vol. 31, No. 1, pp. 36~44, 1995.

[2] S. Pekar, J. Rosenkranz, and H. Lonekova, "Generation of Electron Beam for Technological Processes" Non-Thermal Plasma Techniques for Pollution Control Part A, Springer-Verlag Pub. Co., pp. 345~389, Heidelberg 1993.

[3] Y. Nomoto, T. Ohkubo, S. Kanazawa, and T. Adachi, "Improvement of Ozone Yied by a Silent-Surface Hybrid Discharge Ozonizer", IEEE Trans. Ind. Appl., Vol. 31, No. 6, pp. 1458~1462, 1995.

[4] S. Masuda and M. Nakao, "Control of NOx by Positive and Negative Pulsed Corona Discharges", Proc. of IEEE-IAS Ann. Meeting, pp. 1173~1182, 1986.

[5] S. Masuda, S. Hosogawa, I. Tochizawa, K. Alcutsu, K. Kuwano, and A. Iwata, "Surface Treatment of Plastic Material by Pulse Corona Induced Plasma Chemical Process-PPCP", IEEE Trans. Ind. App., Vol. 30, No. 2, pp. 377~380, 1994.

[6] A. Mizuno, Y. Yamazaki, H. Ito, and H. Yoshida, "ac Energized Ferroelectric Pellet Bed Gas Cleaner", IEEE

Trans. Ind. App., Vol. 28, No. 3, pp. 535~540, 1992.

[7] S. Masuda, S. Hosogawa, X. L. Yu, K. Sakakibara, S. Katoh and S. Sakai, "Destruction of Gaseous Pollutants by Surface-Induced Plasma Chemical Process(SPCP)", IEEE Trans. Ind. Appl., Vol. 29, No. 4, pp. 781~786, 1993.

[8] S. Masuda, S. Hosogawa, X. Tu, and Z. Wang, "Novel plasma chemical technologies-PPCP and SPCP for control of gaseous pollutants and air toxics" J. Electrostatics., Vol. 34, pp. 415~438, 1994.

[9] T. Oda, K. Tanaka, T. Kato, T. Takahashi, and S. Masuda, "Decompositon of Dilute Organic Chloride in Air by High Frequency Surface Discharge Induced Plasma Chemical Processing", Proceedings of the Institute of Electrolics(Japan), 25p, Vol. B6, pp. 275~278, 1990.

[10] T. Oda, T. Takahashi, R. Yamashita, and T. Ohno, "Non-Thermal Plasma for VOCs Decomposition and NO Removal in Flue Gas", Proc. of NEDO Symp. on Non-Thermal Discharge Plasma Technology for Air Pollution Control, pp. 1~14, 1996.

[11] T. Oda, T. Takahashi, R. Watanabe, and S. Kohzuma, "Decomposition of Dilute Trichloroethylene by Non-Thermal Plasma-Frequncy Dependence and Environmental Effect", Proc. of NEDO Symp. on Non-Thermal Discharge Plasma Technology for Air Pollution Control, pp. 49~57, 1997.

[12] T. Oda, T. Takahashi, R. Yamashita, and T. Ohno, "Non-Thermal Plasma for VOCs Decomposition and NOx Removal in Flue Gas", Proc. of NEDO Symp. on Non-Thermal Discharge Plasma Technology for Air Pollution Control, pp. 1~14, 1996.

[13] T. Oda, T. Takahashi, N. Hiroshi, and S. Masuda, "Decomposition of Fluorocarbon Gaseous Contaminants by Surface Discharge Induced Plasma Chemical Processing (SPCP) by Using Cylindrical Ceramic Reactor", Proceedings of the Institute of Electrolics(Japan), Vol. 29a, C1, pp. 1~4, 1991.

[14] R. Gasparik, M. Gasparikova, S. Ihara, S. Satoh, and C. Yamabe, "Comparison of Tungsten, Copper, Stainless and Molybdenum Used as HV Electrodes in Wire-to-Plane System Designed for NOx Treatment", Proc. of NEDO Symp. on Non-Thermal Discharge Plasma Technology for Air Pollution Control, pp. 143~154. 1997.