

## Non-thermal Plasma Process for simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub> from a Sintering Plant of Steel Works

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### <Abstract>

For the simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub> from an iron-ore sintering plant, industrial plasma experiments have been conducted with a flue gas flow rate of 5,000 Nm<sup>3</sup>/hr. The maximum 40kW power using the magnetic pulse compression (MPC) system generates a peak value of 100-150kV pulse voltage with its risetime of 200nsec and full width at half maximum (FWHM) of 500nsec, and with a frequency <300Hz. The plasma reactor module adopts a wire-plate structure with a gap of 200-400mm ID between plates. Initial concentrations of SO<sub>2</sub> and NO<sub>x</sub> were around 100-150ppm, respectively in the presence of 15% O<sub>2</sub> and <10% H<sub>2</sub>O. Various reaction parameters such as specific energy (Whr/Nm<sup>3</sup>), NH<sub>3</sub> injection with corona discharge, flow rate and injection of hydrocarbons were investigated for SO<sub>2</sub>/NO<sub>x</sub> removal characteristics. About 90/65% of SO<sub>2</sub>/NO<sub>x</sub> were simultaneously removed with a specific energy of 3.0 Whr/Nm<sup>3</sup> when both NH<sub>3</sub> and hydrocarbons were injected. Practical implications that the pilot-scale plasma results provide are further discussed.

*Key words: Plasma, corona discharge, NO<sub>x</sub>, SO<sub>2</sub>, simultaneous removal*

### 1. Introduction

The emissions of SO<sub>2</sub>/NO<sub>x</sub> from combustion sources such as power plants, steel works

and industrial boilers are enormous, and their impacts on the environment are significant, resulting in the major causes of air pollution such as acid rain, photochemical smog and even global warming. There are various

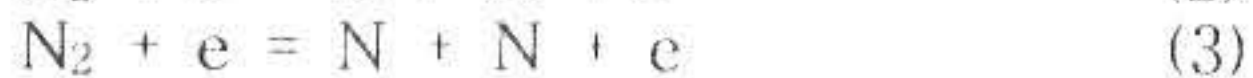
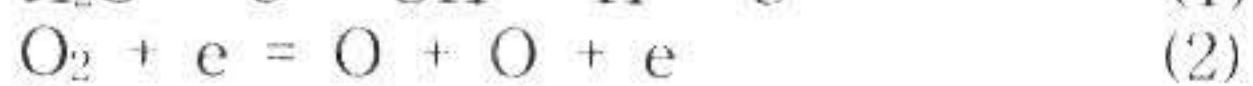
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conventional measures available including wet-limestone and SCR/SNCR processes, and commercially operated worldwide<sup>1,2,11,12</sup>.

However, these processes are not only very costly and complicated, but also include the disposal problems of byproducts.

Since 1980s, the pulsed corona discharge process (non-thermal plasma) as an alternative technology has received great attention for flue gas treatment in the aspects of simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub> pollutants<sup>3-5</sup>. The plasma process is first initiated by active radicals and species, which are produced as the energetic electrons produced by the corona discharge excite, dissociate and ionize background gas molecules as follows:



These radicals and species then react with gaseous pollutants of SO<sub>2</sub>/NO<sub>x</sub> to form aerosols (e.g. sulfuric and nitric acids), and here M represents third-body molecule. In this process, a majority of the electric energy contributes into the production of energetic electrons, rather than into gas heating. If NH<sub>3</sub> is injected into the corona reactor, it reacts with sulfuric and nitric acids to form final products such as ammonium sulfates and nitrates (e.g. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>), which can be collected by typical electrostatic precipitators. Several advantages in this process are as follows; a) low capital cost, b) easy-retrofitting, c) final products can be used as agricultural fertilizer, and d) simple, dry process. However, the main limitation is that energy consumption (Whr/Nm<sup>3</sup>) inducing corona discharge is relatively high for flue gas treatment, compared with other conventional limestone, electron-beam and SCR/SNCR processes. Civitano<sup>5</sup>) previously suggested that acceptable energy consumption would be about 5-6% of total power production, which now looks too much power consumption for commercialization, and which is roughly equivalent to 50eV per the removed NO<sub>x</sub> molecule. Up to now, it has been known that injecting chemical additives (NH<sub>3</sub> and hydrocarbons) and the efficient matching between a pulse generator and a reactor could save energy consumption<sup>6-8</sup>.

Furthermore, the fast-rising pulses and high peak voltages are crucial for enhancing plasma performance and for an industrial application<sup>4</sup>). When n-octane (HCs/NO<sub>x</sub>=4.0,

molar ratio) was injected into a gas mixture including 5% O<sub>2</sub>, 10% H<sub>2</sub>O and 900ppm NO<sub>x</sub> through a wire-cylinder type of reactor, about 45% of initial NO<sub>x</sub> was removed at an energy consumption of 28 Whr/Nm<sup>3</sup>, corresponding to 80 eV/NO<sub>x</sub>. One feature is that NH<sub>3</sub> injection significantly promotes the thermochemical reactions with SO<sub>2</sub> at the lower temperatures (50 °C) rather than at the higher temperatures (>70 °C) in the presence of water<sup>9,10</sup>. These may lead to the formation of the above neutral sulfates.

This paper presents the pilot-scale plasma experimental results performed particularly under a sintering plant of steel works, and discusses the efficient matching of electric system and simultaneous removal characteristics of SO<sub>2</sub>/NO<sub>x</sub>. Various reaction parameters are applied such as specific energy (Whr/Nm<sup>3</sup>), the injection of chemical additives and residence time. Particularly, these industrial results are presented as a model of field application prior to any potential construction of a commercial-scale process.

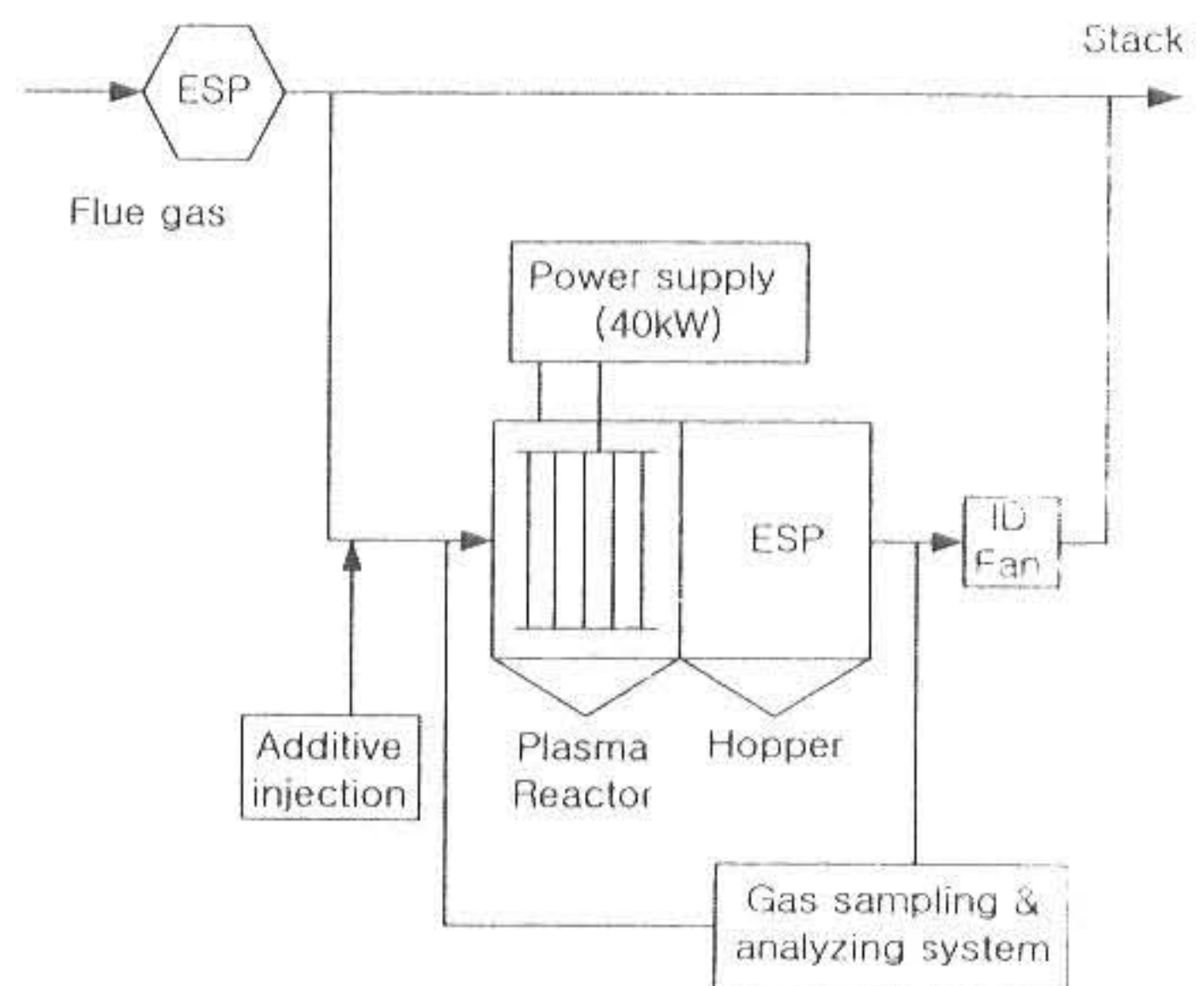


Fig. 1. A schematic of a pilot-scale plasma process.

## 2. Experimental

For the simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub> by the pulsed corona discharge process, the plasma pilot plant, having a capacity of 5,000 Nm<sup>3</sup>/hr, was set up downstream of the main duct of an iron-ore sintering factory at a steel works, and its schematic diagram is shown in Fig. 1. The major facilities consist of a power supply and magnetic pulse compression (MPC) system, a wire-plate type plasma reactor, gas analyzers and injection system of chemical additives. The average

40kW power is first charged on the  $C_1$  capacitor, and then stored energy is transferred to  $C_2$  and  $C_3$  by a thyatron switch (EEV, CX1525A) and compressed by magnetic switches sequentially for efficient energy delivery to the reactor (Fig. 2a). The pulse voltage was measured at positions of VD1-VD3 by an oscilloscope (LeCroy 9361) using a high voltage probe (Tektronix P6015), based on a dc division ratio of 10,000:1. The current measurement was performed at positions of CT1-CT3 using a current probe (Tektronix A6302), a current transformer (Tektronix CT-4) and an amplifier (Tektronix AM503B).

FWHM of 500nsec, and with a frequency ranging up to 300Hz. Typical pulse voltage and current waveforms are shown in Fig. 2b, as the 33kV is charged on the  $C_1$  capacitor. The plasma reactor modules, as in Fig. 1, adopt parallel plate structure, varying channel width (plate distance) from 200-400mm, as close as in an actual electrostatic precipitator at the center of which a number of emitting wires are vertically placed, having the effective wire length of 216m. The specific energy adopted for the present experiments ranged from 0.5-5.0 Whr/Nm<sup>3</sup> as discharge power. The residence time, based on the maximum flow rate reaches 8.6sec, which itself provides sufficient reaction time for SO<sub>2</sub>/NO<sub>x</sub> removal. Temperatures before the plasma reactor were usually maintained as 150°C (±10) where temperature gradients developed from the reactor inlet to the outlet were about -5°C/m ~ -10°C/m.

Flue gas is drawn through the electrostatic precipitator (ESP) into the reactor. Major gas concentrations include 100-150ppm SO<sub>2</sub>/NO<sub>x</sub>, 10,000ppm CO, 5% CO<sub>2</sub>, 10% H<sub>2</sub>O, 15% O<sub>2</sub> and around 20mg/Nm<sup>3</sup> dust, respectively where NO<sub>2</sub> emission levels were negligible. The measurements of SO<sub>2</sub>/NO<sub>x</sub> concentrations were carried out by a pulsed fluorescent SO<sub>2</sub> analyzer (Model 40, Thermo Environmental Inc.) and a chemiluminescent NO<sub>x</sub> analyzer (Model 42H) respectively, while a portable analyzer (Eurotron) was simultaneously used for the double-checks.

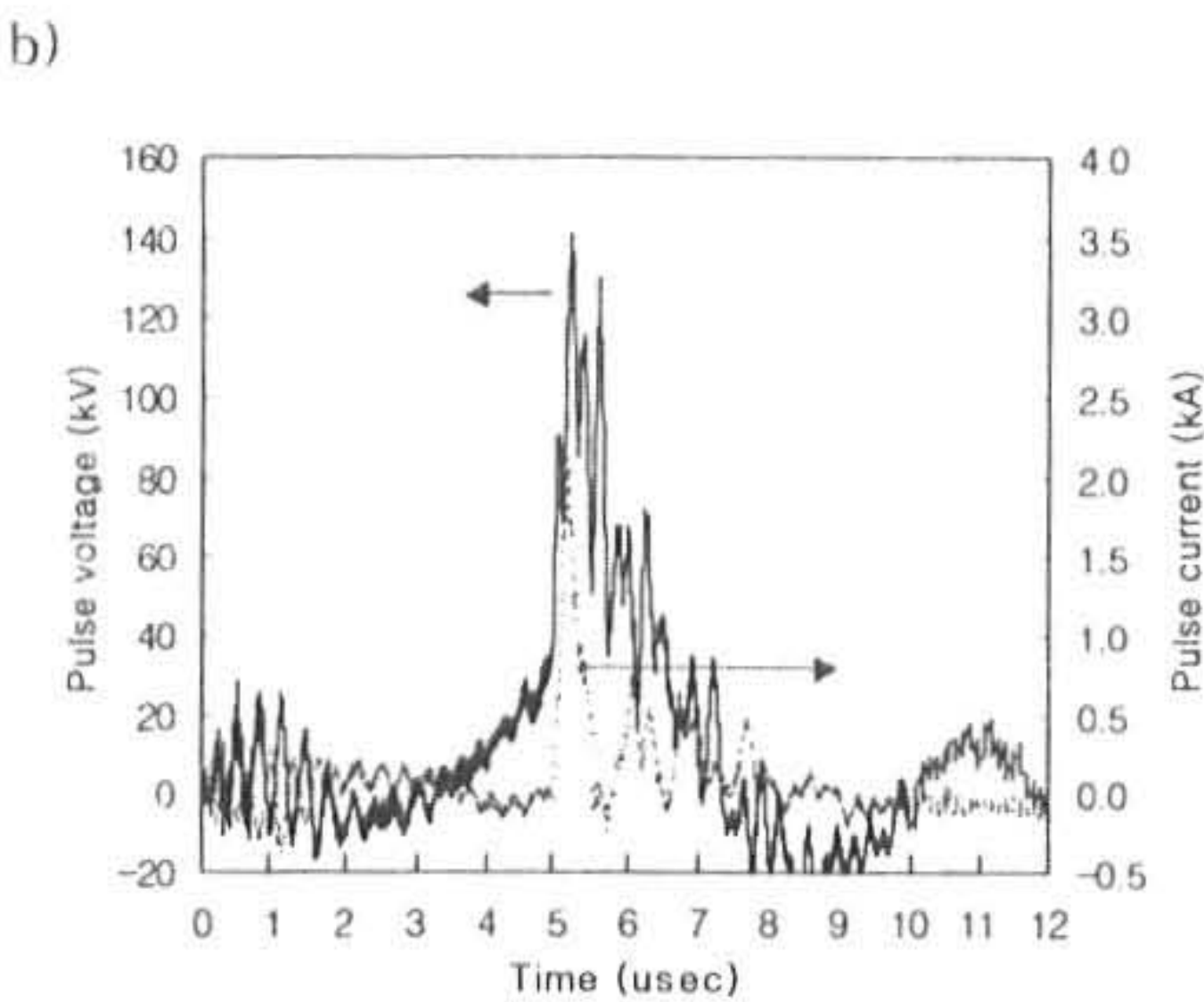
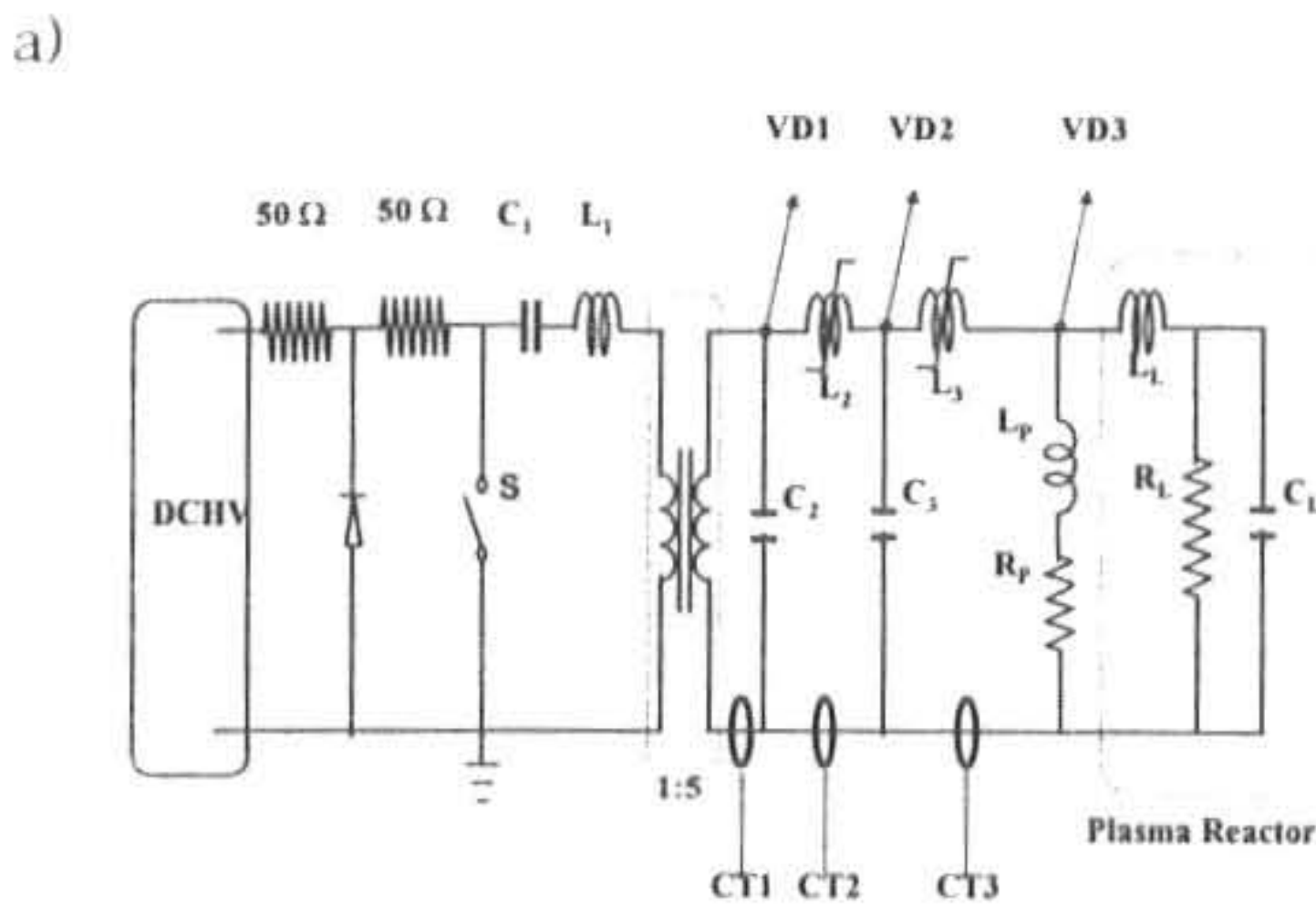


Fig. 2(a,b). Electrical circuit of a pulse power system(a), and typical waveforms of pulse voltage and current(b).

Thus, fast-rising and narrow pulse voltages and currents are generated, where a peak value of pulse voltage reaches 100-150kV with a risetime of 200nsec and

### 3. Results and Discussion

#### 3.1 Energy transfer efficiency

One of the main problems in a plasma process is that relatively higher energy input into the reactor load is required for optimum corona discharge and higher SO<sub>2</sub>/NO<sub>x</sub> removal, and thus the energy loss throughout electrical circuits should be minimized for industrial application. The energy transfer efficiency in this work can be defined as the ratio of the energy delivered to the reactor ( $E_p$ ) to the energy stored on the  $C_1$  capacitor ( $E_s$ ). The  $E_s$  can be expressed as follows;

$$E_s = \frac{1}{2} \cdot C_1 \cdot V_c^2 \quad (5)$$

where  $V_c$  represents the charging voltage, while  $E_p$  is equal to the time integral of the product of the measured voltage and current. Fig. 3 shows the energy transfer efficiency

from the C<sub>1</sub> capacitor to the plasma reactor by charging 30kV as a function of plate distance. As the plate distance varies from 200 to 300mm, almost little difference is observed, indicating about 64% energy transfer efficiency, which however decreases up to 40% with 400mm channel width. With the 30kV on C<sub>1</sub> capacitor, the peak voltage similarly reached around 110kV between 200 and 300mm. Hence, the mean electric field intensity ranges from 7.3–11 kV/cm, which must be the suitable conditions for optimum corona discharge, depending on the geometric capacitance and wire length. This value is compared with so called, stability field, 5kV/cm, in air with positive polarity propagating corona streamers energetically stable<sup>11</sup>. Mok<sup>8)</sup> previously reported in his laboratory experiments using spark-gap switch that maximum energy transfer (71%) could be achieved as the ratio of C<sub>p</sub>/C<sub>R0</sub> approaches 3–5, where C<sub>p</sub> and C<sub>R0</sub> are the pulse-forming and reactor geometric capacitance.

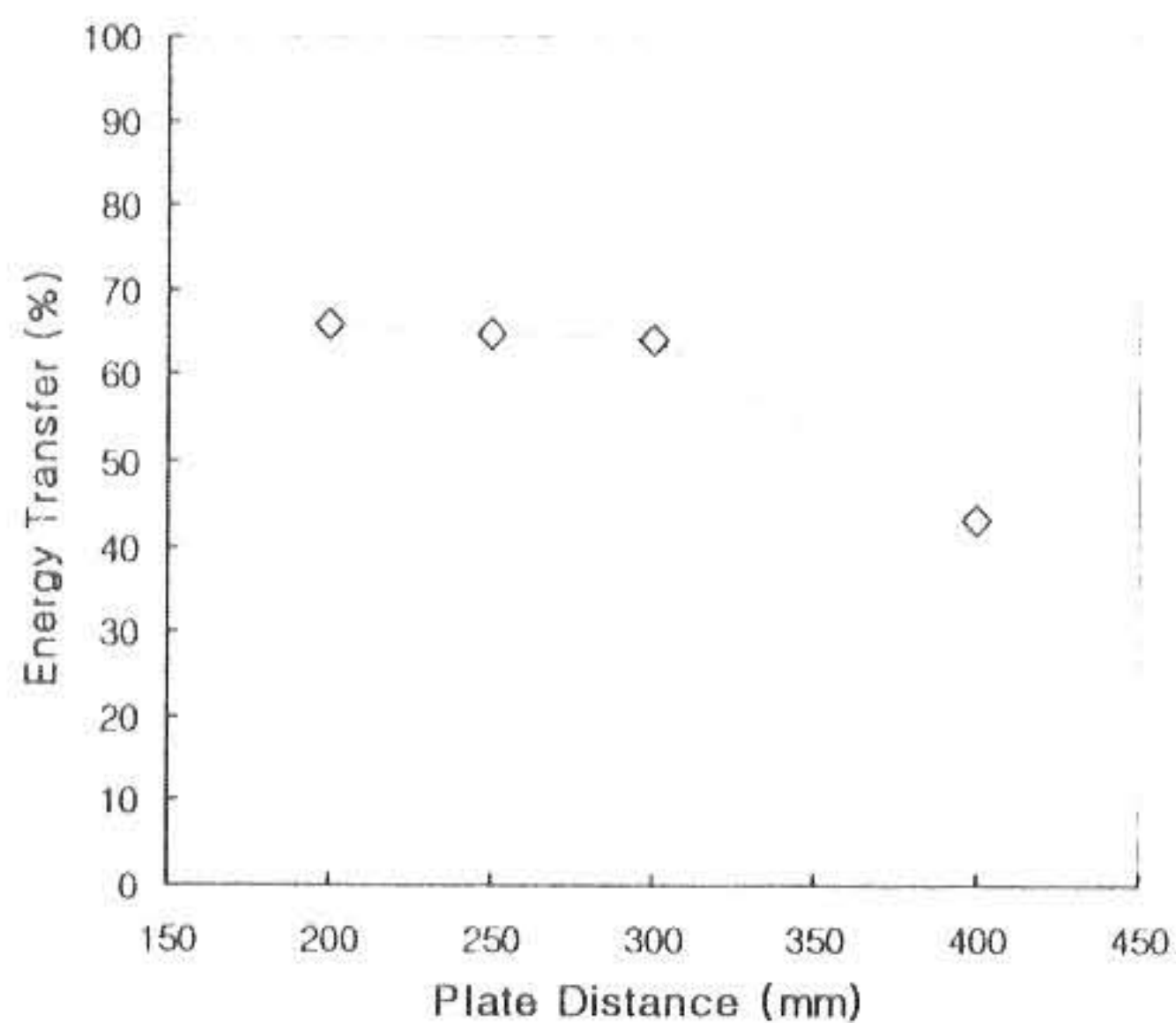


Fig. 3. Energy transfer efficiency with a charging voltage of 30kV on C<sub>1</sub> capacitor as a function of plate distance.

The present MPC modulator using a thyatron switch, whose methods were more discussed by Odom et al<sup>14)</sup>, is recognized adopting the slightly lower value of C<sub>p</sub>/C<sub>R0</sub> (~2). As the plate gap becomes more distant, the electric field intensity (kV/d) becomes less, and thus flue gas electric resistance becomes larger to hinder as much current flow as possible. Despite the fact that the plate gap of typical electrostatic precipitators is mostly around 400mm, the plasma experiments in this work have been therefore conducted with the optimum gap of

300mm because of higher energy transfer efficiency.

### 3.2 Simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub>

It is relatively well agreed that the effect of pure corona discharge on the removal of SO<sub>2</sub>/NO<sub>x</sub> remains less significant particularly at lower energy consumption (<5 Whr/Nm<sup>3</sup>, wall-plug basis), limited below 20–30% removals. These lower energy levels are preferable for a scale-up process, as previously discussed by other investigators<sup>5,13)</sup>. However, NO<sub>x</sub> removal increases proportionally with increasing energy consumption further up to e.g. 20 Whr/Nm<sup>3</sup>. For the aspects of reducing energy consumption and increasing SO<sub>2</sub>/NO<sub>x</sub> removal potential, hydrocarbon additives such as C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> have been injected together with NH<sub>3</sub>. The amount of NH<sub>3</sub> injected is usually normalized as a molar ratio of ammonia to nitrogen and sulfur oxides ( $\alpha = \text{NH}_3 / (2\text{SO}_2 + \text{NO}_x)$ ), while C<sub>3</sub>H<sub>6</sub> for example is injected according to the NO<sub>x</sub> amount ( $\beta = \text{C}_3\text{H}_6 / \text{NO}_x$ ). Mostly, less than a molar ratio was injected for less emission of unreacted byproducts. Fig. 4 shows the effect of corona discharge and chemical additives (NH<sub>3</sub> and C<sub>3</sub>H<sub>6</sub>) on the simultaneous removal of SO<sub>2</sub>/NO<sub>x</sub> as a function of specific energy (Whr/Nm<sup>3</sup>). About 95% SO<sub>2</sub> removal efficiencies are achieved with NH<sub>3</sub> injection ( $\alpha = 0.8$ ), apparently indicating negligible effects of the energy consumption. It clearly shows that NH<sub>3</sub> plays an important role in SO<sub>2</sub> removal, as in literature<sup>13)</sup>.

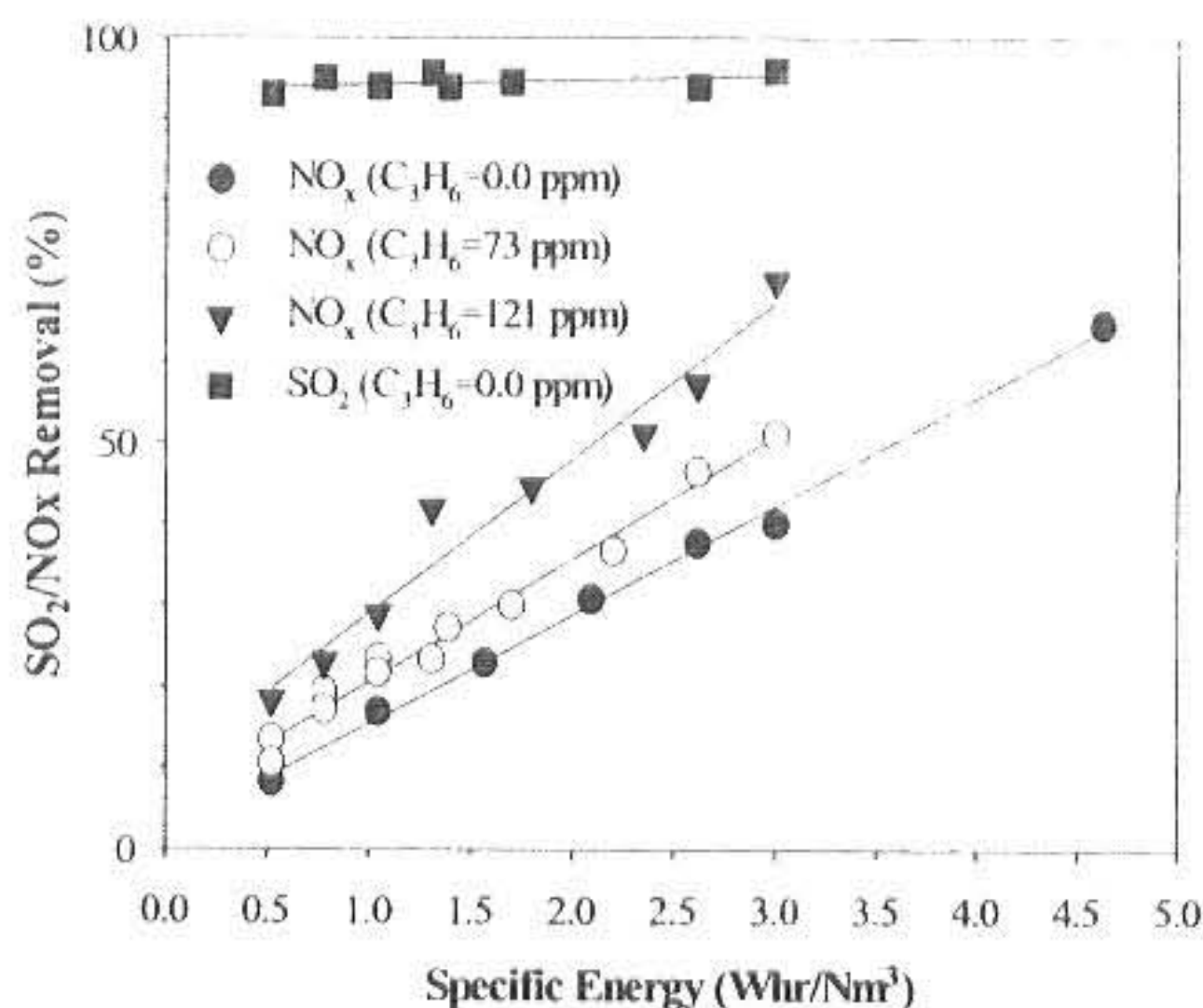
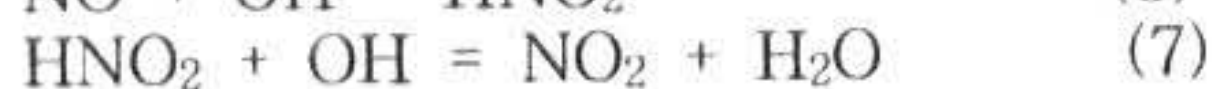
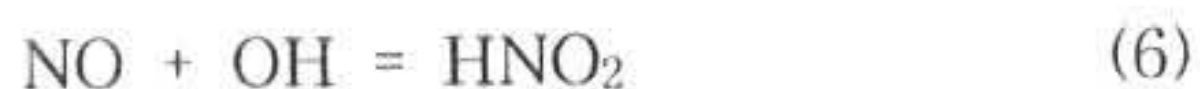
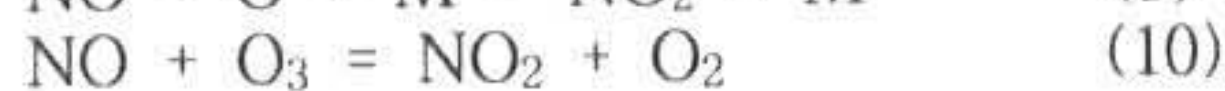
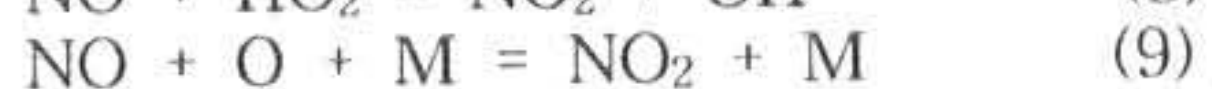
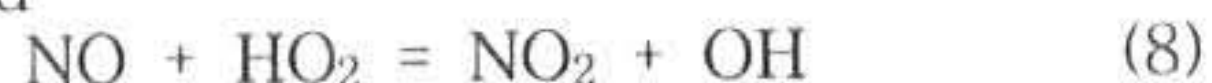


Fig. 4. Simultaneous removal characteristics of SO<sub>2</sub>/NO<sub>x</sub> as functions of specific energy and injection of chemical additives (3,000Nm<sup>3</sup>/hr,  $\alpha = 0.8$ )<sup>7)</sup>.

However, gas energization is indispensable to achieve sufficient SO<sub>2</sub> removal particularly at higher flue gas temperatures (>90 °C). This is because the thermochemical reaction of NH<sub>3</sub> with SO<sub>2</sub> remains below 50% under the present high flue gas temperatures without corona discharge. As expected, NOx removals however linearly increase with increasing energy consumption with/without hydrocarbons where the NH<sub>3</sub> effects also remained low. With no hydrocarbon additive, about 40% NOx removal is achieved at 3.0 Whr/Nm<sup>3</sup>, and further 65% at 4.6 Whr/Nm<sup>3</sup>. This result proves that without hydrocarbon injection, the NO to NO<sub>2</sub> conversion is limited because of less radical production particularly at <2.5 Whr/Nm<sup>3</sup> and practical conditions. The injection of C<sub>3</sub>H<sub>6</sub> significantly increases NOx removal efficiencies in which 50-70% of NOx are removed with the injection of C<sub>3</sub>H<sub>6</sub> (73 and 121ppm, β=0.5 and 0.8) at 3.0 Whr/Nm<sup>3</sup>, respectively. It is very interesting provided that the rough energy consumption (eV/NOx) is calculated at 3.0 Whr/Nm<sup>3</sup>, based on initial concentration of 146ppm NOx and 110°C. With no hydrocarbons, the energy consumption reached about 58eV/NOx, but it was significantly reduced to about 30eV/NOx with C<sub>3</sub>H<sub>6</sub> injection (β=0.8), which is an encouraging energy consumption, and compared with other literature values. Therefore, about 90/65% simultaneous removals of SO<sub>2</sub>/NOx are possible when both NH<sub>3</sub> and C<sub>3</sub>H<sub>6</sub> are injected together with the aid of the corona discharge. These results are in good agreement with those reported by Nam et al.<sup>13)</sup> under coal-fired power plant conditions using the NH<sub>3</sub> and C<sub>2</sub>H<sub>4</sub> injection, and qualitatively with Dinellis data<sup>4)</sup>. Unlike the SO<sub>2</sub> removal, NH<sub>3</sub> injection does not significantly contribute to NOx removal particularly at lower energy consumption because of less production of radicals and species, which promote the NO to NO<sub>2</sub> conversion mainly by the following important reactions:



and



The OH radical is the main species for NO removal rate by reactions (6) and (7)<sup>12,15)</sup>. With the present work, C<sub>3</sub>H<sub>6</sub> injection must have particularly promoted peroxides of hydrocarbon and HO<sub>2</sub> formation, which resulted

in more NO<sub>2</sub> formation by reaction (8), as discussed by Nelson and Haynes<sup>18)</sup>. Other investigations<sup>7,15-17)</sup> also revealed that O<sub>3</sub> species is very effective for NO oxidation by reaction (10) under low temperature and dry conditions, but in practical combustion flue gases, the role of the above active radicals is dominant in the pulsed corona discharge process. Once NO<sub>2</sub> is formed, it easily reacts with NH<sub>3</sub> in the presence of water vapor to form neutral salts, leading to higher NOx removals. The present higher O<sub>2</sub> concentration (15%) and some amount of dust from a sintering plant are also believed to have contributed to higher SO<sub>2</sub>/NOx removals in this process under wet gas mixtures, which has been discussed by Amirov et al.<sup>15)</sup> and recently by Tsukamoto et al.<sup>19)</sup>. The present results are very encouraging for the above several aspects and provide valuable data for future commercialization, even though detailed information is not reported here. These pilot studies using the pulsed corona discharge process provide significant practical implications in the field of flue gas treatment worldwide.

#### 4. Conclusions

The application of a large-scale plasma process has been performed for simultaneous removal of SO<sub>2</sub>/NOx from an iron-ore sintering plant. The present system provided the high energy transfer efficiency (64%) for high-voltage pulsed corona discharge as the ratio of C<sub>3</sub>/C<sub>R0</sub>=2, regardless of the charging voltage from 25 to 40kV. Fundamental characteristics of SO<sub>2</sub>/NOx removal obtained from actual flue gas conditions are mostly consistent with those from the laboratories. More than 90% SO<sub>2</sub> removal was easily maintained by NH<sub>3</sub> injection, where gas energization was indispensable for higher performance, despite apparently negligible dependence. However, NOx removal was strongly dependent on the energy consumption in which about 20-40% removals were achieved at 1.0-3.0 Whr/Nm<sup>3</sup> in the absence of hydrocarbons. Some amounts of C<sub>3</sub>H<sub>6</sub> injection significantly improved the NOx removal rate up to 70%, which is due to the promotion of NO to NO<sub>2</sub> conversion. Therefore, about 90/65% simultaneous removals of SO<sub>2</sub>/NOx are possible at a specific energy of 3.0 Whr/Nm<sup>3</sup> when both NH<sub>3</sub> and C<sub>3</sub>H<sub>6</sub> are injected. The practical implications of these pilot tests are enormous in the aspects of process commercialization.

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