INDUSTRIAL PLASMA EXPERIMENTS FOR SIMULTANEOUS REMOVAL OF SO₂/NOₓ FROM A COAL-FIRED POWER PLANT

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Abstract: Experimental investigations for simultaneous removal of SO₂/NOₓ were performed using the pulsed corona discharge process under coal-fired, pilot-scale flue gas conditions. A pulse voltage of 70kV, its risetime of 200 nsec and total duration of 500 nsec were generated using a thyristor-type spark gap switch. Initial concentrations of SO₂ and NOₓ were around 340 and 150 ppm in the presence of 4% O₂ and 6~8% H₂O. Various reaction parameters such as specific energy (Whr/Nm³), NH₃ injection with/without corona discharges, gas temperature and C₃H₄ injection were investigated for SO₂/NOₓ removal characteristics. SO₂ removal was rather dependent on temperature and NH₃, but the influence of energy consumpiton into the gas remained negligible. NOₓ removal efficiency increased with increasing energy consumption, but at lower energy consumption (<5 Whr/Nm³), NO to NO₂ conversion was significantly limited below 30%. However, NOₓ removal rate was sharply increased with C₃H₄ injection by which energy consumption was significantly reduced. The effects of residence time and frequency were also discussed. Consequently, about 90/65% simultaneous removal of SO₂/NOₓ was achieved at 4.7 Whr/Nm³ when both NH₃ and C₃H₄ additives were injected.

Key Words: corona discharge, flue gas, NOₓ, plasma, simultaneous removal, SO₂

INTRODUCTION

Air pollution by SO₂/NOₓ has been a growing concern for several decades because of the harmful effects on human society and global environment. In particular, the emissions from stationary sources such as large-scale power plants and industrial boilers are enormous, and various conventional measures such as wet-limestone and SCR/SNCR processes have been developed.\(^1,2,12\)

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 SO₂/NOₓ pollutants.\(^3-5\) The process works in such a manner that radicals are produced as the energetic electrons in the corona discharge excite, dissociate and ionize gas molecules, and then react with gaseous pollutants of SO₂/NOₓ to form aerosols, which can either be collected by an electrostatic precipitator or a separation process. Several advantages are as follows; a) low capital cost, b) final products can be used as agricultural fertilizer, c) easy-retrofitting and d) simple, dry
process. However, the main limitation is that energy consumption (Whr/Nm³) inducing corona discharge is relatively high for flue gas treatment, compared with other conventional limestone, electron-beam and SCR/SNCR processes. Civitano suggested that acceptable energy consumption would be about 5~6% of total power production, which is roughly equivalent to 50eV per the removed NOx molecule. Up to now, it has been known that injecting chemical additives (NH3 and hydrocarbons) and the efficient matching between a pulse generator and a reactor could save energy consumption.

Furthermore, the fast-rising pulses and high peak voltages are crucial for enhancing plasma performance and for an industrial application. When n-octane (HC/NOx=4.0 molar ratio) was injected into a gas mixture including 5% O2, 10% H2O and 900 ppm NOx through a wire-cylinder type of reactor, about 45% of initial NOx was removed at an energy consumption of 28 Whr/Nm³, corresponding to 80 eV/NOx. Other parameters may be gas temperature, initial concentrations of SO2/NOx, gas composition, residence time and reactor geometry (electrode arrangement), which will simultaneously affect the SO2/NOx removal characteristics. One feature is that NH3 injection significantly promotes the thermochemical reactions with SO2 at the lower temperatures (≈50°C) rather than at the higher temperatures (≈70°C) in the presence of water. These may lead to the formation of neutral sulfates ((NH4)2SO4) and acid sulfites (e.g. NH4HSO3), which may cause an emission of NH3 slip. Therefore, a better performance can be achieved through gas energization by keeping temperature above 70°C.

In this paper, pilot-scale plasma experimental results are reported on the simultaneous removal characteristics of SO2/NOx, based on various reaction parameters such as specific energy, NH3 injection with/without corona discharges, gas temperature before the reactor, frequency, residence time and hydrocarbon additives. In addition, the implications of the results, obtained from the field application, as well as the understanding of important plasma chemistry are discussed.

**EXPERIMENTAL**

Experimental investigations for simultaneous removal of SO2/NOx were performed using the pulsed corona discharge process under coal-fired, pilot-scale flue gas conditions (3,000 Nm³/hr).

The plasma pilot plant was set up at the Boryung thermal power plant (unit #3, 500MW), west-coast of Korea, and its schematic diagram is shown in Figure 1. The major facilities consist of power supply and pulse generator (PG) system, a cylinder-type reactor, gas analyzers and injection system of chemical additives. The power supply system generates peak values of 70kV pulse voltage and 360A current, using a base voltage of 30kV and a thyristor-type spark gap switch. The rising time of 200 nsec, full width at half maximum (FWHM) of 250 nsec and frequency range of voltage pulses were measured as in Table 1. The pulse voltage was measured by an oscilloscope (Tektronix TDS 304A) using a high-voltage probe (EP-100K), based on a dc division ratio of 5000:1, and for current measurement, a current probe (Tektronix A6303XL) and an amplifier (Tektronix AM503B) were used. The frequency of the pulses was determined by the frequency of the power supply. The specific power (wall plug basis) adopted for the present experiments ranged from 3~16 Whr/Nm³. The reactor consists of six cylinders connected in parallel where each, hav-

![Figure 1. Schematic diagram of pilot-scale plasma process.](image-url)
Table 1. Pulse and gas composition specifications adopted for experiments

<table>
<thead>
<tr>
<th>Items</th>
<th>Range</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Base voltage</td>
<td>30 kV</td>
<td></td>
</tr>
<tr>
<td>Peak voltage</td>
<td>70 kV (360 A)</td>
<td>Flow rate: 800~3000 Nm/hr</td>
</tr>
<tr>
<td>Frequency</td>
<td>0.68~1.33 kHz</td>
<td></td>
</tr>
<tr>
<td>Rising time</td>
<td>200 nsec</td>
<td></td>
</tr>
<tr>
<td>FWHM</td>
<td>250 nsec</td>
<td></td>
</tr>
<tr>
<td>Gas composition</td>
<td></td>
<td>Gas temp.: 65~120°C</td>
</tr>
<tr>
<td>SO₂</td>
<td>300~400 ppm</td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>100~250 ppm</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>3~4%</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>6~8%</td>
<td></td>
</tr>
<tr>
<td>Dust</td>
<td>5 mg/Nm³</td>
<td></td>
</tr>
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</table>

ing 250 mm ID and 2 m length, can treat a capacity of 500 Nm³/hr flue gas and the positive corona discharge occurs through the circled-spiky pin electrode (90 mm OD). Temperature gradients developed from the reactor inlet to the outlet are about -3.7~5°C/m. Hereafter, gas temperatures represent temperatures at the reactor inlet, and a temperature range of 60~120°C was selected for the experiments.

Flue gas is drawn through the electrostatic precipitator (ESP) into the reactor, and includes major gas components such as SO₂, NOₓ, O₂, H₂O and fine particulate matters where NO₂ emission levels were negligible (Table 1). The measurements of gas concentrations were carried out by gas analyzer system (Multigas 2000 Series). Before introducing the sampled gas into the detector, the gas was led into an ammonia scrubber to avoid interference with SO₂ where concentrated phosphoric acid was used as a trapping solution. The portable analyzer (rbr-com-KD) was simultaneously used for double-checks. More details for the above contents were previously described elsewhere.¹⁰,¹¹

RESULTS AND DISCUSSION

The plasma experiments for the simultaneous removal of SO₂/NOₓ have largely been conducted following parameter investigations such as the influence of gas energization (Whr/Nm³), temperature, residence time and the injection of chemical additives (NH₃ and C₂H₄), etc. The injection of ammonia is normalized as a molar ratio of ammonia to nitrogen and sulphur oxides (α = NH₃/(2SO₂+NOₓ)), while C₂H₄ is injected according to the NOₓ amount (β = C₂H₄/NOₓ).

Removal of SO₂

Figure 2 shows SO₂ removal characteristics using pure corona discharge at various flue gas temperatures (65, 90 and 120°C). Only 20~30% of SO₂ was removed over a wide range of energy consumption (4~16 Whr/Nm³) at temperatures of 90 and 120°C where increasing energy consumption remained of little use for SO₂ removal. However, SO₂ removal efficiency gradually increased with decreasing flue gas temperatures (<65°C). Without ammonia injection, the removal efficiencies were maintained relatively low because of slightly high gas temperatures investigated.

The effects of gas energization and NH₃ injection on SO₂ removal are shown in Figure 3. When NH₃ injection system (α = 0.8) and the PG were switched on, SO₂ removal efficiencies were sharply increased under the specific conditions, and reached more than 90% with quick response, but suddenly dropped when they

Figure 2. SO₂ removal characteristics as a function of specific energy at various flue gas temperatures (300 ppm SO₂, 150 ppm NO, 1500~2000 Nm³/hr and 1.3 kHz).
Figure 3. SO$_2$/NO$_x$ removal characteristics as functions of gas energization and NH$_3$ injection as additive (346 ppm SO$_2$, 150 ppm NO, 0.975 kHz, 1530 Nm$^3$/hr, 90°C and $\alpha=0.8$, 4.7 Whr/Nm$^3$).

were switched off. It clearly shows that NH$_3$ plays an important role in SO$_2$ removal. Furthermore, gas energization is indispensable to achieve sufficient SO$_2$ removal when flue gas temperatures are slightly high (>90°C) since NH$_3$ injection without corona discharge developed only about 50% SO$_2$ removal at the same conditions.\textsuperscript{11)

Simultaneous Removal of SO$_2$/NO$_x$

NO$_x$ removal efficiency is shown in Figure 4 without additive injection as functions of the specific energy transferred into the gas and temperature. NO$_x$ removal steadily increased with increasing energy transfer into the gas at all temperatures investigated. About 50–70% removal efficiencies were achieved at 8–16 Whr/Nm$^3$, while 20–40% at 3–7 Whr/Nm$^3$. Moreover, higher temperatures (90, 120°C) seem to be better conditions than the lower temperature (<65°C) for NO$_x$ removal. These phenomena such as energy and temperature dependence obtained from field application well agree with other small-scale results.\textsuperscript{4–6,13) However, without additive injections, NO to NO$_2$ conversion was significantly limited below 30% especially at lower energy consumptions (<5 Whr/Nm$^3$), which is the key factor, and eventually leads to lower NO$_x$ removal.

For the aspects of reducing energy consumption and enhancing NO to NO$_2$ conversion,
energy consumption of 3.7 Whr/Nm³. As expected, more than 90% SO₂ removal was maintained by ammonia at three flue gas temperatures where gas energization enhanced reaction performance, but ethylene effects were minimal for SO₂ reaction environments. In contrast, NOₓ removal efficiencies steadily increased with increasing C₂H₄, but tend to reach a maximum value above β = 0.5 at each temperature. About 60% NOₓ removal was achieved with a gas temperature of 90°C at β = 0.6. According to previous results (1000 Nm³/hr) by Dinelli et al.⁴, similar SO₂ removal efficiencies (75 ~ 90%) were achieved by ammonia injection, but without hydrocarbon injections only 20 ~ 30% NOₓ removal was obtained by 3 ~ 6 Whr/Nm³, which well support the present work (Figure 3). However, the effects of the present high frequency range (0.68 ~ 1.33 kHz) were not significant on SO₂/NOₓ removal characteristics.¹¹

Rough calculation of energy consumption for NOₓ removal in case of with/without additive is shown in Table 2, based on the conditions of 90°C and 150 ppm initial NOₓ. Using pure corona discharge process (without additives, Figure 4), energy consumption ranged from 80 ~ 112 eV/NOₓ, but it was greatly reduced to 34 ~ 56 eV/NOₓ through C₂H₄ injection (β = 0.9, Figure 5). In particular, 70% NOₓ reduction with 4.7 Whr/Nm³ (34 eV/NOₓ) is very encouraging because that energy consumption is only less than 2.5% of total power production (500MW).

Table 2. Comparison of energy consumption (eV/NOₓ) for NOₓ removal in case of with/without additives, based on Figure 4 and 5

<table>
<thead>
<tr>
<th>Specific energy (Whr/Nm³)</th>
<th>Without additives</th>
<th>With additives</th>
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<tbody>
<tr>
<td>NOₓ removed (ppm)</td>
<td>Energy consumption (eV/NOₓ)</td>
<td>NOₓ removed (ppm)</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>4.7</td>
<td>~ 80</td>
<td>105</td>
</tr>
<tr>
<td>8.3</td>
<td>~ 112</td>
<td>113</td>
</tr>
<tr>
<td>14</td>
<td>~ 112</td>
<td>-</td>
</tr>
</tbody>
</table>

- : not available

varying injection amount of C₂H₄ at temperature of 90°C and α = 0.8. As the residence time increased, NOₓ removal efficiencies were largely increased where about 30% difference in NOₓ removal occurred between 0.81 and 1.85 sec at β = 0.5. Mizuno et al.¹³ reported similar results through the small-scale, plasma reactor (Pₑ = 30W, initial NO = 425 ppm) in which NOₓ reduction increased with increasing the residence time (80% at 5sec), but decreased to 50% at 2.3 sec.

Figure 7 shows the effects of both additives (NH₃ and C₂H₄) on simultaneous SO₂/NOₓ removal with varying gas temperatures at low
reacts with sulphuric and nitric acids to form final products such as ammonium sulphates and nitrates (e.g. NH$_4$NO$_3$). As a consequence, injections of NH$_3$ and C$_2$H$_4$ not only lead to the great increases in SO$_2$/NO$_x$ removal performance, but also significantly reduced energy consumption to applicable values of 4~5 Whr/Nm$^3$ for commercialization.

**CONCLUSIONS**

Industrial experiments for simultaneous removal of SO$_2$/NO$_x$ from coal-fired flue gas have been conducted using the pilot-scale, pulsed corona discharge process. The long-term tests are ongoing for further demonstration. Fundamental SO$_2$/NO$_x$ removal characteristics obtained from large-scale, actual conditions are observed as follows:

1. SO$_2$ removal is rather dependent on temperature, but the influence of energy consumption into the gas remained negligible. When NH$_3$ is injected into the reactor, SO$_2$ is sharply removed by thermochemical reactions (50% removal), which is however more enhanced by the corona discharges at the present high temperatures (>90%).

2. NO$_x$ removal tends to be proportional to energy increase into the gas, but within 3~7 Whr/Nm$^3$ only 20~30% of NO$_x$ was removed because of less radical production. C$_2$H$_4$ injection ($\beta=0.6$) significantly promoted NO to NO$_2$ conversion, which enhanced NO$_x$ removal up to 65% at a low energy consumption of 4.7 Whr/Nm$^3$ (34eV/NO$_x$).

3. As the residence time (0.81~1.85 sec) increased, NO$_x$ removal was increased accordingly. The effects of the present high frequency range were not evident on SO$_2$/NO$_x$ removal characteristics. However, further practical investigations are recommended using sufficient residence times (>5 sec) and a wide range of frequency.

4. When both NH$_3$ and C$_2$H$_4$ additives were simultaneously injected, about 90/65% simultaneous removal of SO$_2$/NO$_x$ was achieved at
4.7 Whr/Nm³. Basically, the achievement of high performance and the significant reduction of energy consumption, obtained from field experiments, is helpful for future commercialization.

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