Pulse corona induced plasma chemical process: a horizon of new plasma chemical technologies

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Abstract - A very intense corona discharge can be produced
by applying a sharp rising, narrow pulse high voltage bet-
ween corona and counter electrodes of a corona system.
Because of an extremely increased spark voltage electrons
are highly accelerated even under ordinary gas pressure,
while ions with much larger mass are not effectively accele-
rated as a result of too short pulse duration time. Hence, a
strongly non-equilibrium plasma with a high electron temper-
ature and low ion and molecular temperatures is produced. A
number of gas phase reactions, such as DeNOx, DeSOx and
control of hazardous and toxic gaseous pollutants like mer-
cury vapour from incineration plants, can be effectively
realized, where the pollutants are converted into solid
aerosol particles, with or without additive agents like
ammonia, to be easily removed in downstream precipitators.
This also opens a new way of producing ultra-fine particles
of various exhotic materials. Treatment and dry processing
of various surfaces under ordinary pressure (and also
reduced or increased pressures) are also possible.

1. INTRODUCTION

The author investigated with his co-worker a possibility of enhancing DeSOx
and DeNOx in E-beam method from a thought that copious electrons, produced
by ionizing collision of primary high energy electrons and remaining with
low energy after performing useful chemical reactions, could be regenerated
in energy by applying an electric field. The results of experiments were
very positive (1), but only under the condition that corona discharge took
place. Further more, the use of DC voltage produced a comparatively large
ionic current to cause quite a high electric loss. This suggested that a
very narrow pulse high voltage or microwave high voltage must be used for
exploitation of such effect in order to avoid energy loss due to accelera-
tion of ions. A great technical difficulty to proceed with this idea was the
lack of power supplies which must be high in efficiency, low in cost, and
durable enough to allow a long term continuous operation. The microwave was
discarded because of its too high cost and too low efficiency in power
supply. A sharp rising, very narrow pulse voltage was only one possibility
in view of its cost. The author and his co-workers succeeded to develop a
very efficient, low cost, and reliable nanosecond or submicrosecond pulse
power supply using a rotary spark gap for fast switching of a condenser in
combination with its phase-selective AC charging (2). Fig. 1 indicates its
circuit diagram, and Fig. 2 a photograph of one of the pulse power supply
which can energize 2,000 m² in terms of total counter electrode area. This
pulser can be directly connected to the load when it is small, but in the
case when load capacity is large, the use of the corona transmission line
(3) should be most effective in both plasma chemical performance and energy
efficiency. This uses a long corona wire, zig-zag formed, on which such a
narrow pulse voltage proceeds in a form of a travelling wave without losing
its original rise and duration times, thus producing its essential activity
and uniformity along the entire length of the wire.

After completing the nanosecond pulse power supply and the circuit technolo-
gies for an effective use of the pulse, the author and co-workers started
(1) DeNOx and DeSOx tests in laboratory and an incineration plant, (2) tests
of mercury vapour control at the incineration plant, and (3) ozone produc-
tion test in laboratory. Based on these test results theoretical considera-
tions were also made on the mechanism of the pulse corona induced plasma
chemical process (PPCP).

The author is convinced at this stage that PPCP could provide a number of
cost-effective means for oxidizing and other applications. In the following
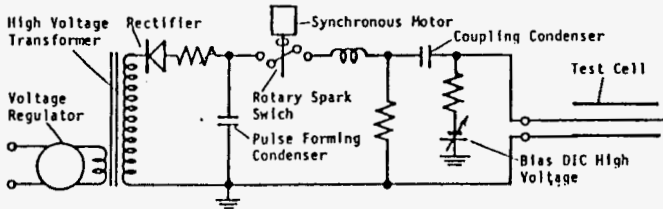our test results are presented together with the discussion on the results.

Fig.1 Circuit Diagram of Nanosecond
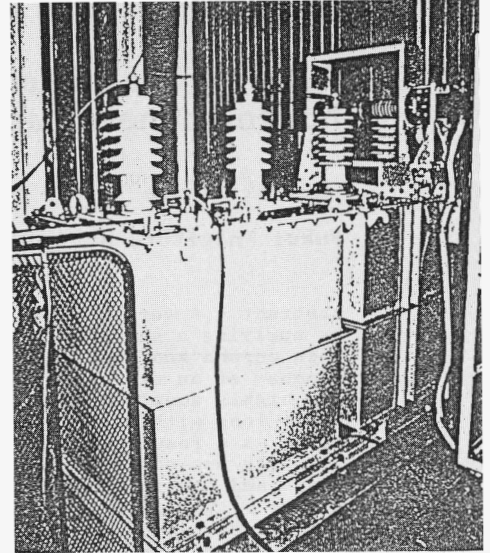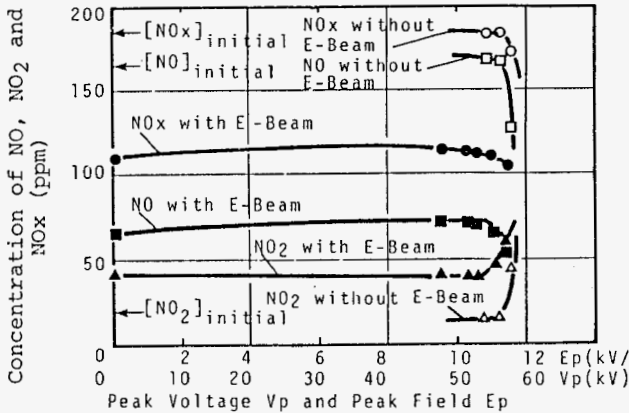Pulser with Rotary Spark Gap

wire(12mm dia)-to-cylinder(100mm dia)
dry air-NO-Ammonia(180ppm)
E-Beam(50uA;1.5MV;30Hz scan.)
Pulse(50ns rise; 300ns half tail;50Hz)

Fig.3 Correlation between E-Beam and
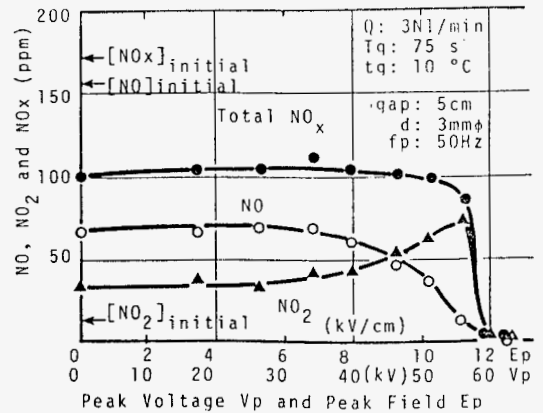PPCP (Negative Polarity)

Fig.5 Effect of Humidity (Positive)

Fig.2 Industrial Nanosecond Pulser
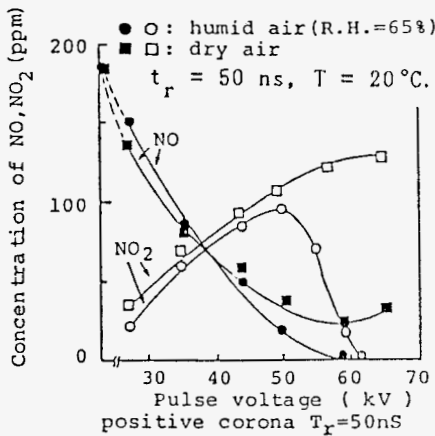

Fig.4 Effect of Pulse Field Intensity
(conditions: see Fig.3)

2. TEST RESULTS

2.1 Correlation between E-beam and PPCP (pulse corona induced plasma chemical process)

At first tests were made to clarify if a cross-correlation exists, as expected before, in the overall effect of reactions between E-Beam and PPCP, or if they are independent in their effects. Fig. 3 indicates a typical result which were obtained for NO gas in dry air with negative pulse corona, where ammonia was added. The curves with E-Beam only do not indicate any change up to 11 kV/cm, where sharp changes occur in both NO and NO₂ concentrations. However, these changes are exactly those which happen with PPCP without the aid of E-Beam. Hence, it can be concluded that no cross-correlation exists between E-Beam and PPCP. Hence E-Beam process and PPCP must be considered separately.

2.2 Effect of pulse peak field intensity

The effect of PPCP begins to appear only after corona onset as shown in Fig. 4 in which the corona starts at E_p=5 kV/cm (E_p: peak voltage V_p/(gap)). This figure also includes the effect of E-Beam which produced initial drops of NO and NOx. With increasing field NO indicates a gradual drop to become zero at E_p=12 kV/cm, while NO_2 rises concurrently, as a result of NO oxidation, up to 11.5 kV/cm, beyond which it suddenly drops. In other words, the dominant active species producing NO_2 removal is different from those for NO oxidation, and the formers are produced beyond a much higher threshold value of E_p. It is anticipated from Fig. 5 indicating the effect of humidity (4), and Fig. 6 indicating the effect of oxygen (5), that O and O_3 are likely to be dominant for NO oxidation while OH radical is likely to be essential for NO_2 removal.

2.3 Effect of polarity of pulse voltage

This is very complicated, as shown in Figs. 7 and 8. At room temperature positive pulse always produces much better performance than negative one, although energy based efficiencies are the same (5). However, with the
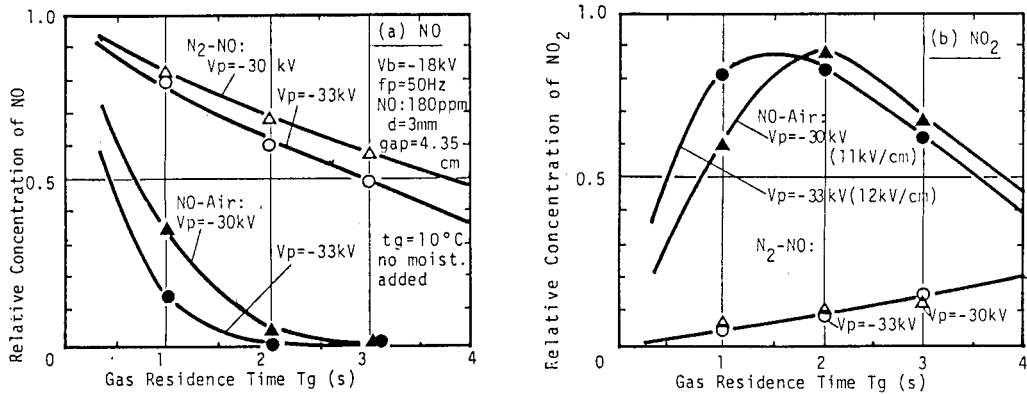

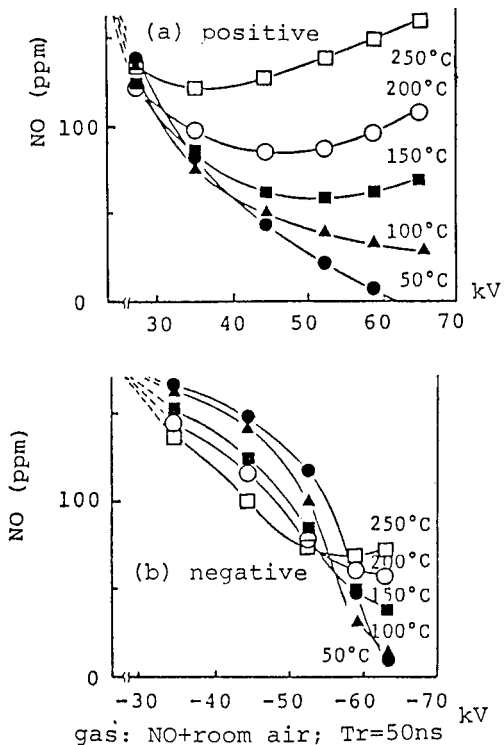Fig.6 Effect of Oxygen (Negative; Dry)
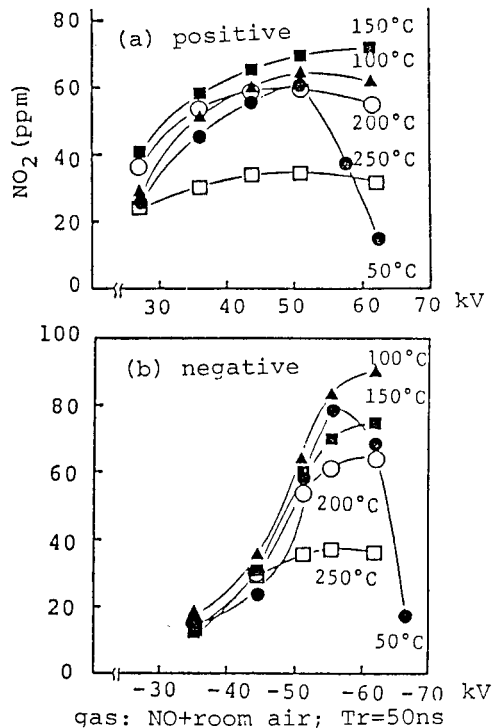

Fig.7 Effect of Polarity on NO Removal

Fig.8 Effect of Polarity on NO_2 Removal

increase in temperature the tendency reverses, as shown in the above figures
(4), at least in clean gas (room air + NO) conditions. However, in a combus-
tion gas from an incinerator boiler plant these differences between positive
and negative polarities in the performance disappears, while energy effi-
ciency is always better in positive pulsing PPCP (6). The difference in gas
lies in much higher concentrations of water (17 %), CO_2 (10 %), CO (300
ppm), and HCl (350 ppm) and existence of fine particulate in combustion gas.
The superiority of using negative pulsing for PPCP may open a way to ap-
plying PPCP inside an electrostatic precipitator, where both particulates
and gaseous pollutants (NOx, SOx, mercury vapour, etc.) could be simulta-
neously removed. All these results tell that a careful preliminary test must
be made on a case by case basis to avoid a risk due to a drastic change in
PPCP characteristics caused by a small change in gas composition.

2.4 SO$_x$ removal

The laboratory tests indicate that SO_2 can only removed after NO and NO_2
have been removed by PPCP. In the practical combustion gases, however, SO_2
is the first to be removed, followed by NO and NO_2 removal. It is antici-
pated that, in combustion gas which includes particulate, SO_3 converted from
SO_2 will be rapidly absorbed on the particulate surface to avoid its reverse
decomposition into SO_2. This scavenging effect of SO_3 is likely to be an
essential factor which enhanced SOx removal by PPCP in combustion gases. The
active species dominant for DeSOx by PPCP is likely to be OH radical.

2.5 Effect of corona power, pulse frequency and gas residence time

The PPCP effect is determined by a parameter $(P/Q)/T_g^{1/2}$, where P = corona
power, Q = gas flow rate, and T_g = gas residence time (Fig. 9) (5). At room
temperature the PPCP effect is a linear function of pulse frequency, as
shown in Fig. 10, while at an elevated temperature a deviation occurs from
the straight line. A number of test data indicate that the pollutant con-
centration shows an exponential decay with the gas residence time and pulse
frequency (Fig. 11) (4).

2.6 Effect of ammonia

Addition of ammonia produces a substantial improvement in the removal of
NO_2, while it has a much less effect on NO removal. NO_2 fast indicates a
rise owing to NO oxidation, arriving at peak, and drops. This peak value is
reduced to the half of that without ammonia addition at room temperature
(5). However, at an elevated temperature this advantage of ammonia is lost,
and the performance becomes deteriorated by ammonia addition in DeNOx. Its
effect on DeSOx at an elevated temperature is not yet clear.

2.7 Effect of pulse rise time

The pulse rise time has a substantial effect on the performance of PPCP.
Shorter the rise time the more the intensive and elongated are the pulsed
streamers, and better is the PPCP performance. In the application of PPCP in
a very large plant having a very large inter-electrode capacity, it is
difficult to reduce the rise time below 500 - 1000 ns, even if the high
frequency oscillation part of the pulse leading edge be used. The only way
of overcoming this difficulty is to use the travelling wave mode, as
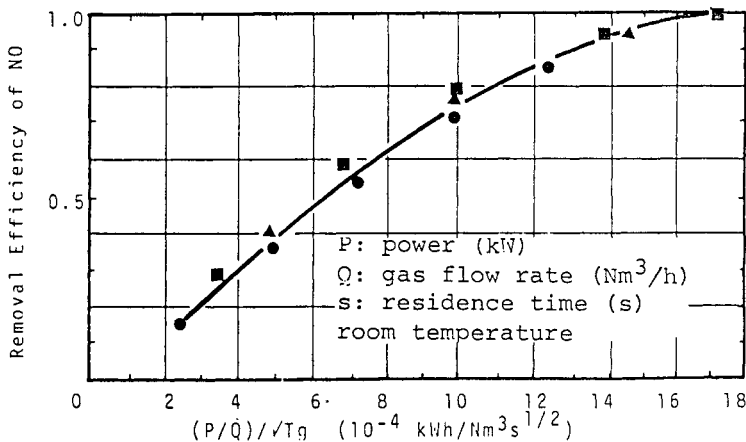described above.

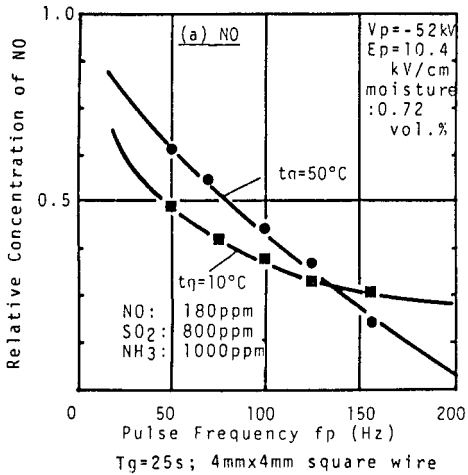Fig.9 Effect of Power
(negative; dry)
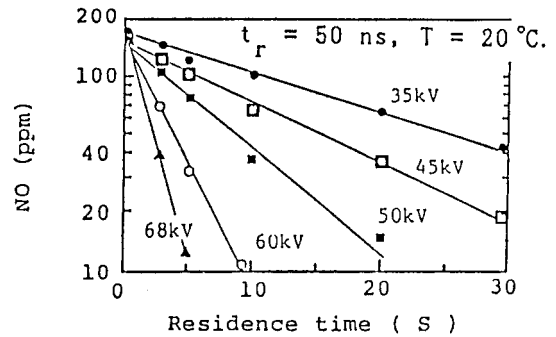
Fig.10 Effect of Frequency (Negative)

Fig.11 Effect of Residence Time
(positive polarity)

2.8 Control of mercury vapour in combustion gas

The test made at an incineration plant for PPCP removal of Hg vapour from
combustion gas indicated a drastic result (6). Within 2 seconds gas residen-
ce time mercury vapour with 0.5 mg/Nm³ (0.06 ppm) could be 100 % converted
into solid particulates (oxides and chlorides) in a wide range of gas tem-
perature (30 - 300 deg.C) with a pulse frequency of 50 Hz. The mercury
removal was enhanced by the addition of HCl or Cl_2. The larger residence
time did not produce a substantial improve (at a reduced voltage), while
lowering of residence time caused a substantial drop in performance. This
tells that a certain quantity of radicals must be produced to fully oxidize
Hg vapour, while beyond this quantity no improvement occurs. In other words,
the reaction speed is likely to be very high.

3. FUNDAMENTAL MECHANISM OF PPCP

The mechanism is divided into electrical one and chemical one. The elec-
trical one id that PPCp enables a highly non-equilibrium plasma with a high
electron temperature and low ionic and molecular temperatures to occur under
normal pressure, as described previously. This is a unique feature resulted
by a sharp rising, narrow pulse high voltage applied to a corona system
which has a strong electron source (corona electrode). The chemical mecha-
nism is not yet fully understood, although a number of analysis have been
presented (7, 8). It is certain that electrons having an adequately high
energy (upper tail of Dryvestin distribution) would produce copious active
species: O, O_2^*, N, O_2^-, OH^- radical, etc. Some of the theoretical calcula-
tions indicate reasonably good approximations of the test results, while
others very different results.

4. CONCLUSION

The unique feature of PPCP for various applications under ordinary gas
pressure is indicated with many examples. It is expected that PPCP would
provide a new area of plasma chemical process in many applications.

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