Simultaneous NO_x/SO_2 removal by ammonia gas excited by atmosphere plasma
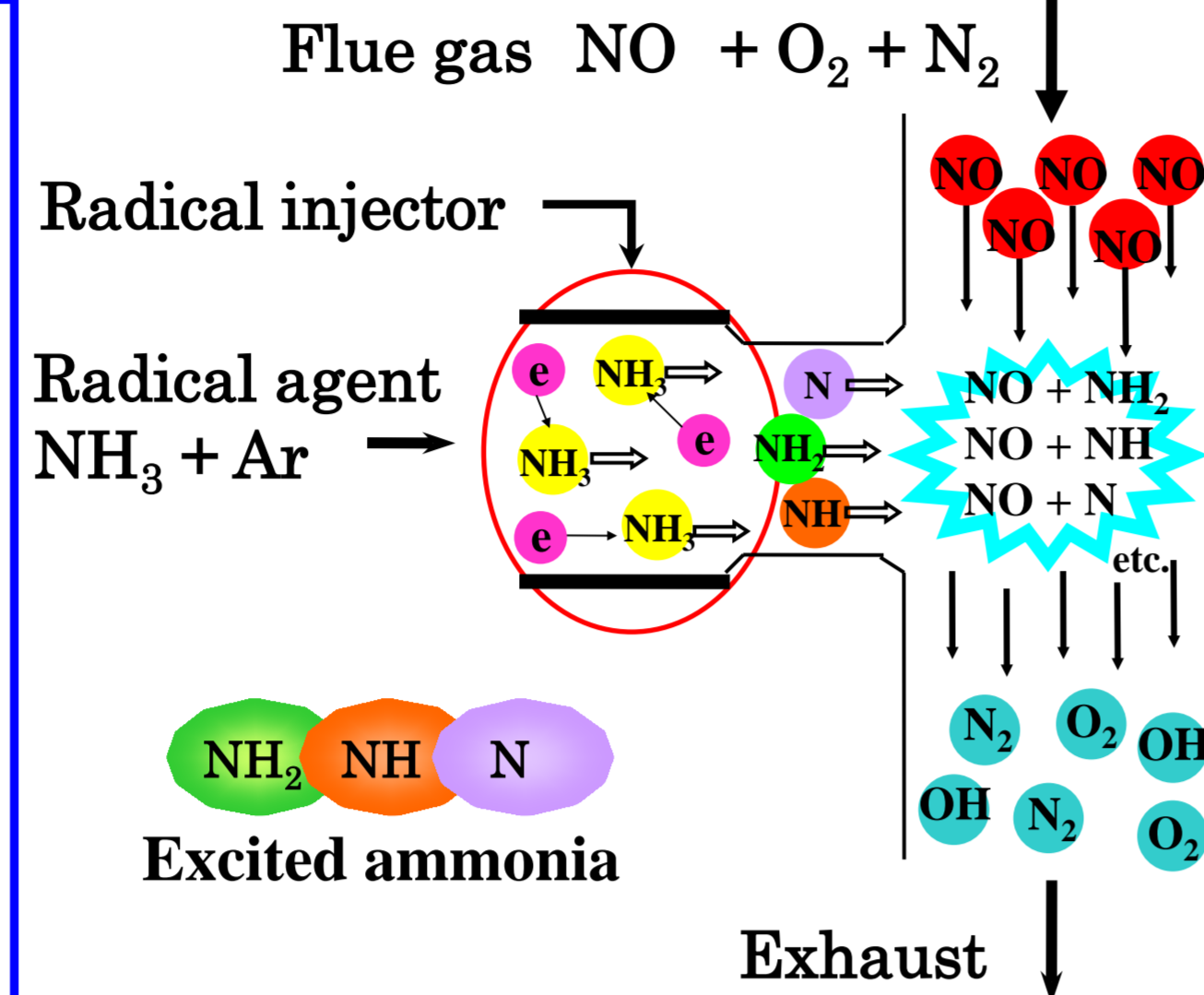
S. Kambara, Y. Hayakawa, M. Masui, K. Kumabe, H. Moritomi

GIFU UNIVERSITY

Introduction

In Japan, effluent control of NO_x and SO_x becomes severe. The combustion facilities of small and medium-size scale must meet the effluent control, too. But, the SCR method which is an existing technique can't introduced to all combustion facilities from the point of cost and setting area. Therefore, new processing system that meet requirement of small size, dry process, cheap craves.

Flue gas NO + O_2 + N_2

Radical injector

Radical agent
NH_3 + Ar

$NO + NH_2$
$NO + NH$
$NO + N$
etc.

N_2, O_2, OH, N_2, O_2

Excited ammonia

Exhaust

Development of radical injection method (RI method)

The advantage of the radical injection method
- The device is a simple configuration.
- A coolant and a catalyst are unnecessary.
- A reduction agent (NH_3) only is activated.
  → **NHi radical is generated by smaller energy**

NO_x and SO_x are reduced with high efficiency and low cost

Objectives of this study

SO_2 is usually included in combustion flue gas, it is likely that the DeNOx properties using the radical injection is affected by reaction of SO_2 and NH_3.
↓
This study clarifies a radical injection DeNOx characteristic under the condition of the SO_2 exist

Experimental

Post heater : 500-800℃

NH_3 Scrubber

NOx/O_2 Analyzer

Sampling pump

N_2O Analyzer

SO_2 Analyzer

Radical injector L = 490

Injection gas

Denitration gas was prepared

HV

Mixing chamber

NH_3 was excited by Ar plasma

Ground electrode L = 360

Gas blender 1

Ar NH_3

Pre-heater : 500℃

Pre-heater (Gold furnace)

Ground

NO O_2 N_2 SO_2

Quartz tube $\phi = 46$

Gas blender 2

Simulated gas was prepared

Model gas
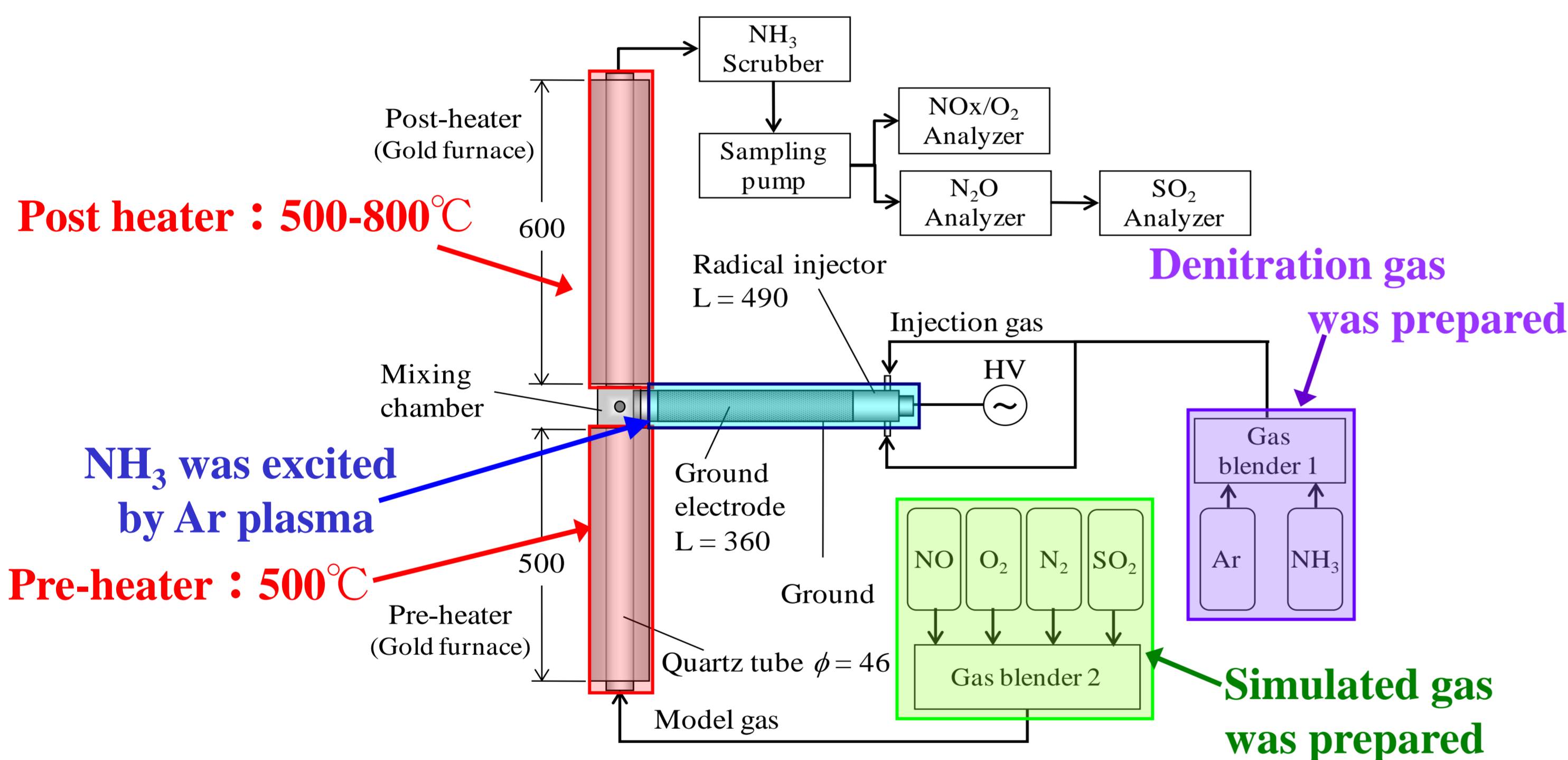
Post-heater (Gold furnace)

Fig.1   Schematic diagrams of experimental apparatus.

Fixed conditions
- Power-supply unit ... pulsed power supply by SAWAFUJI
- Power supply frequency, R_R ... 10 [kHz]
- Total flow rate of simulated exhaust, F_0 ... 3.0 [L/min]
- Pre-heater temperature ... 500 [℃]

Parameter
- Composition of simulated exhaust
  - NO conc.   0, 497 [ppm]
  - SO_2 conc.   0, 251 [ppm]
  - O_2 conc.   2.1-8.3 [%]
- Post-heater temperature, T_1 ... 500-800 [℃]
- Molar ratio (NH_3/NO+SO_2), M_R ... 1-1.5 [-]
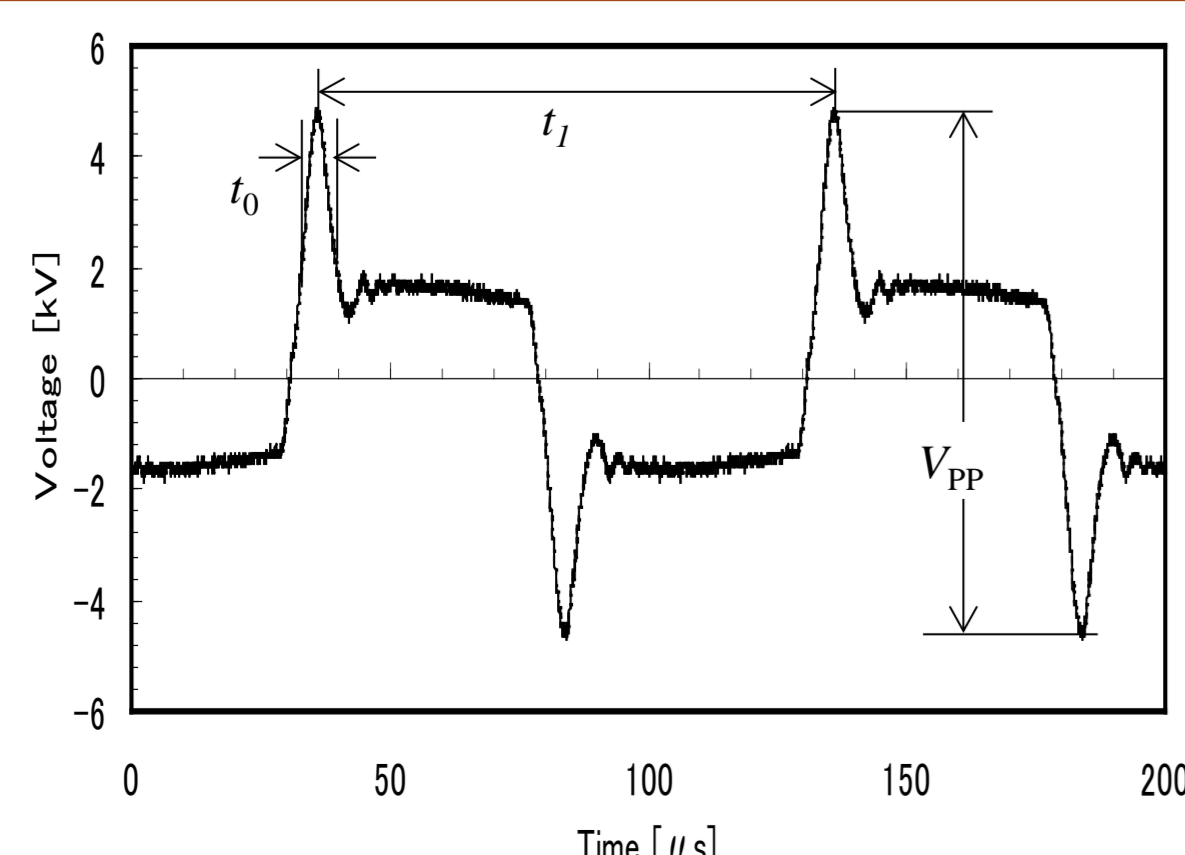- Applied voltage, V_{PP} ... 0-15 [kV]

t_1 : Pulse interval
t_0 : Wave pattern retention time
V_{PP} : Voltage between plus and minus peaks
R_R : 1 / T_1 (frequency)

Fig.2 Waveform of the applied voltage.

Results Ⅰ : NO removal by RI (Radical Injection)

NO = 497 ppm
SO_2 = 0 ppm
[NH_3]/[NO] = 1.5
O_2 conc. = 8.3%
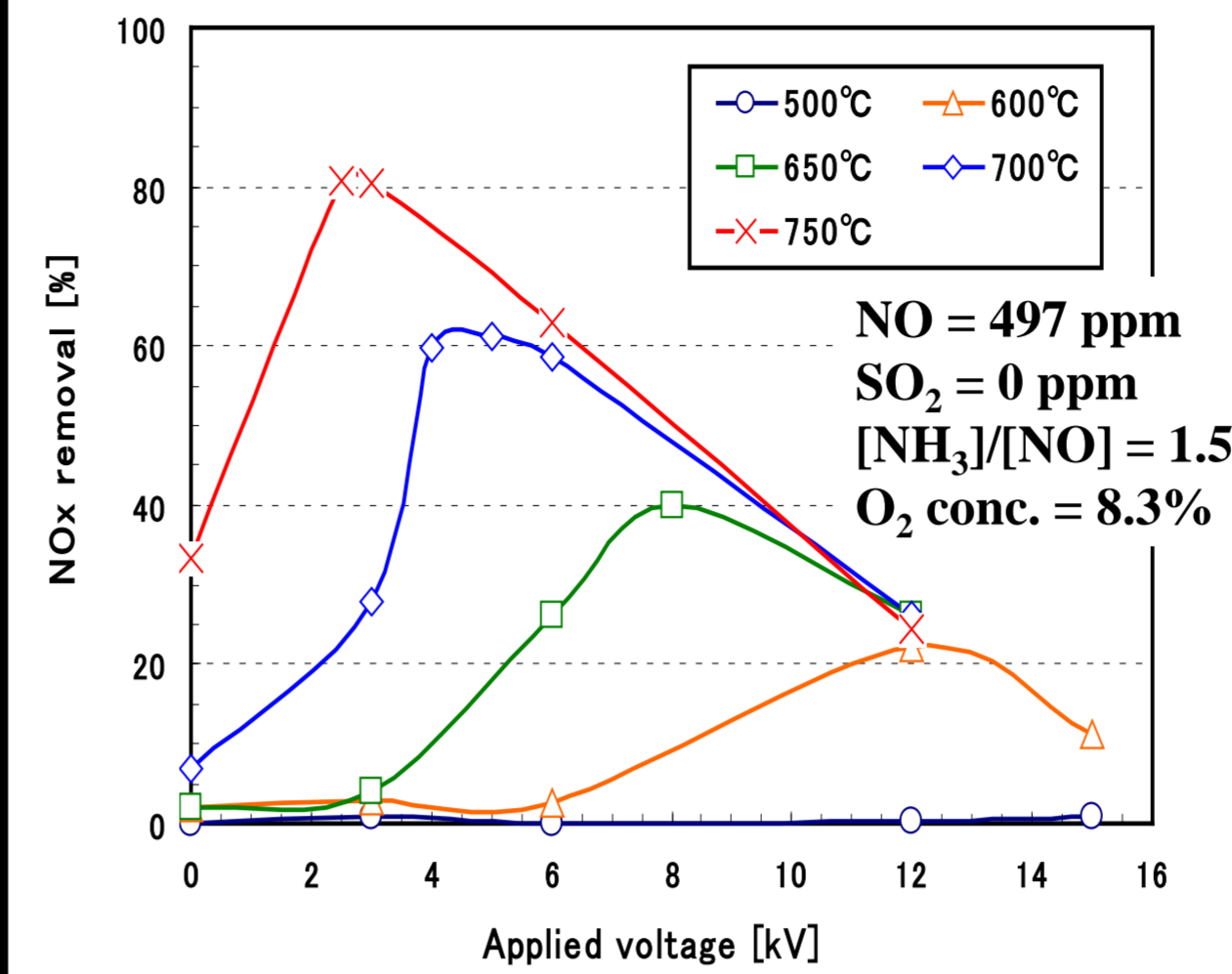
Fig.3 Characteristics of NO removal by RI

NO = 497 ppm
SO_2 = 0 ppm
[NH_3]/[NO] = 1.5
O_2 conc. = 8.3%
V_{PP} = optimum

Radical Injection + Thermal DeNOx

Thermal DeNOx

Fig.4 Comparison of NO_x removal characteristics between RI and thermal DeNOx

Figure 3 shows variation in NO removal at various applied voltage and reaction temperatures ranged from 500 to 750 ℃. NO removal was observed to suddenly increase at a boundary of the applied voltage, and gradually decrease for progressively greater applied voltages after a maximum level. A higher percentage of NO removal was observed at the lowest applied voltage and the highest reaction temperature.

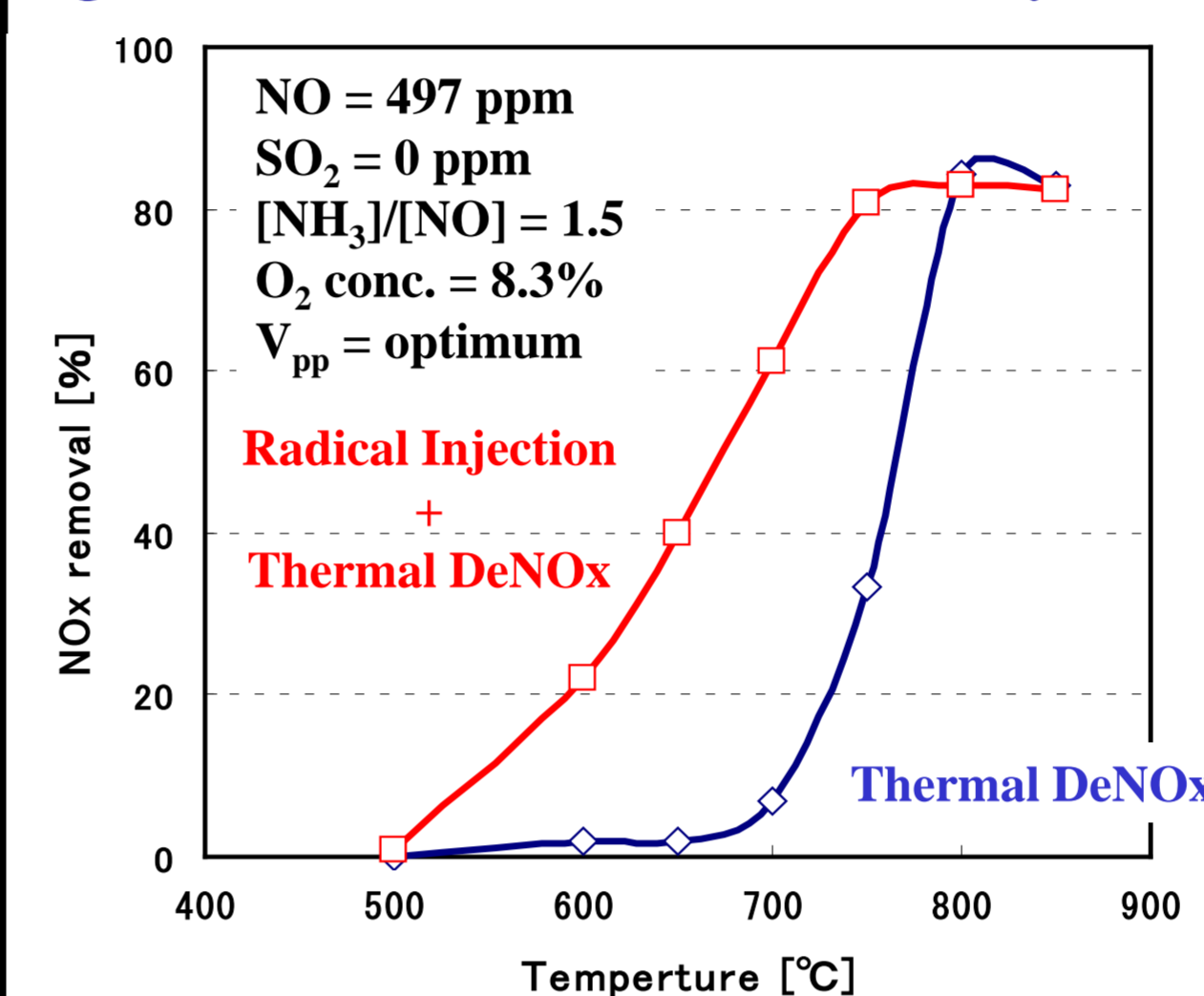**Most effective radical for DeNOx (NH_2 radical) was formed at the low applied voltage.**

The maximum values of NO removal by the radical injection method at each temperature in Fig.3 were compared with NO removal by thermal $DeNO_x$ in **Figure 4**. In the RI method, an increase of NO_x removal observed above 600℃: it clearly indicates that the radical injection broadened the temperature window and lowered its starting temperature (in comparison to thermal $DeNO_x$). The reaction temperature shift was 150℃ at an NO removal of 20 %.

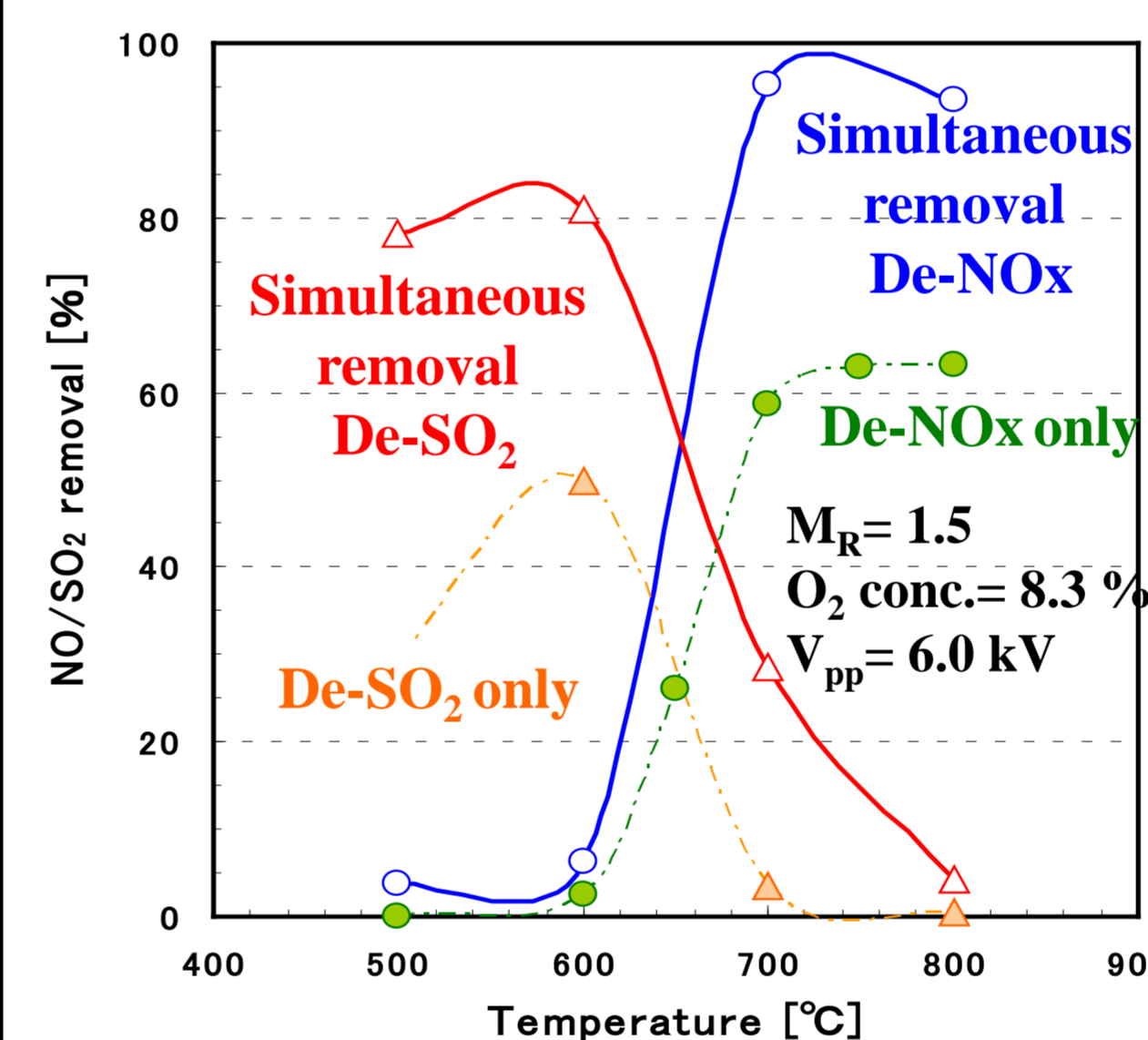## Results Ⅱ : Simultaneous NO/SO_2 removal by RI

Simultaneous removal De-NOx

Simultaneous removal De-SO_2

De-NOx only

De-SO_2 only

M_R = 1.5
O_2 conc. = 8.3 %
V_{PP} = 6.0 kV

Fig.5 Promoting effects of simultaneous NO_x/SO_2 removal by ammonia radical injection.

Figure 5 shows change of NO and SO_2 removal in various reaction temperatures in independent and simultaneous removal by the RI method. It found that NO removal was promoted under the simultaneous removal condition: above 90% NO removal was attained at 700 ℃. On the other hand, maximum levels of SO_2 removal was observed at 600℃, and SO_2 removal was decreased with an increase of reaction temperature. SO_2 removal in simultaneous removal tests was increased in compared to independent tests.
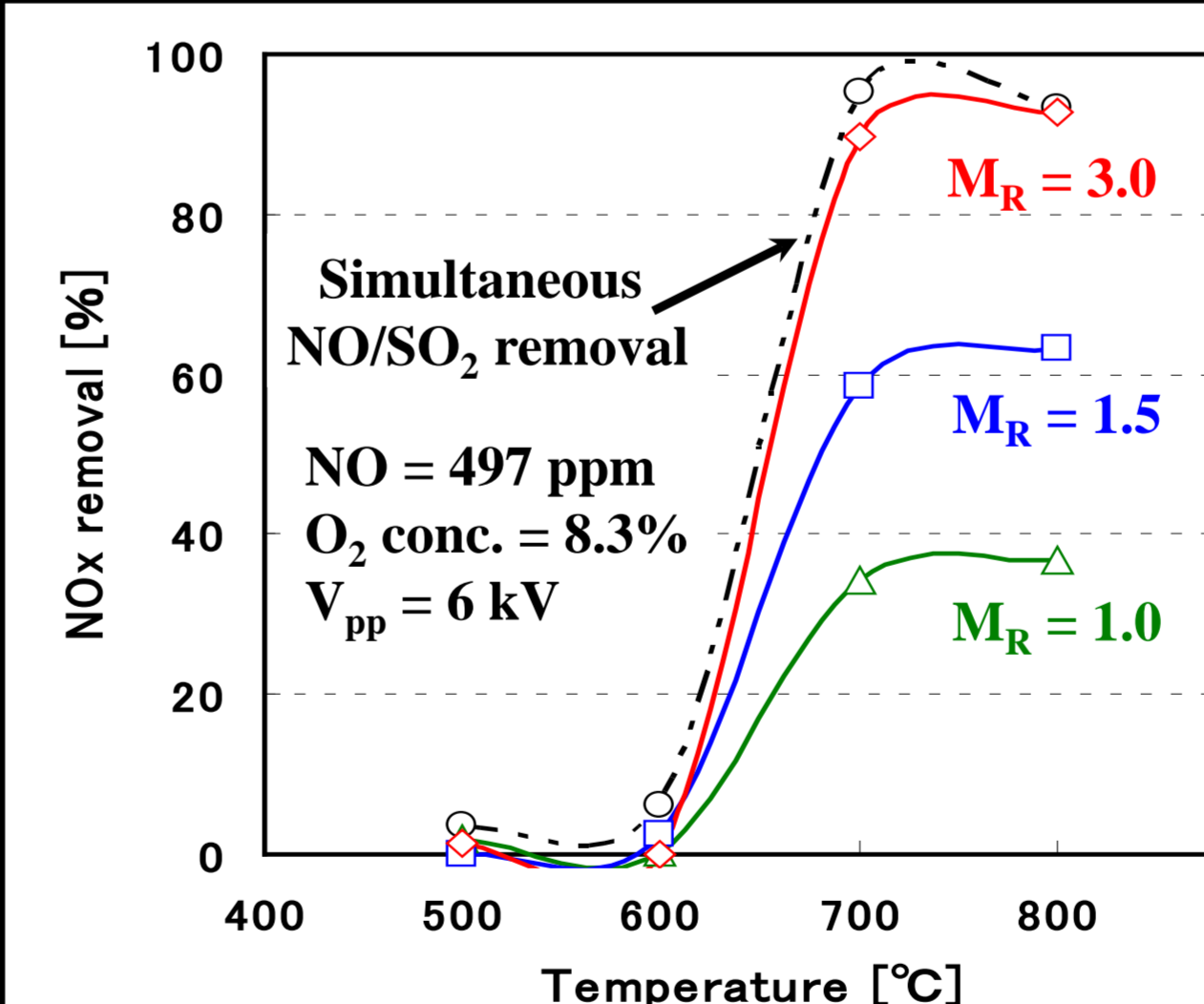
Results Ⅲ : Effects of SO_2

M_R = 3.0
M_R = 1.5
M_R = 1.0

Simultaneous NO/SO_2 removal

NO = 497 ppm
O_2 conc. = 8.3%
V_{pp} = 6 kV

Fig.6 Effect of molar ratio on NO_x removal.

M_R = 2.0
M_R = 1.5
M_R = 1.0

Simultaneous NO/SO_2 removal

SO_2 = 251 ppm
O_2 conc. = 8.3%
V_{pp} = 6 kV

Fig.7 Effect of molar ratio on SO_2 removal.

Most important factor is the deference of reactivity between NO-NH_3 system and SO_2-NH_3 system. The reaction rate of NO removal is faster than that of SO_2 removal, therefore injected NH_3 works to remove NO at the early stage of the reaction.

A condition of M_R = [NH_3]/[NO+SO_2] = 1.5 is equivalent in M_R = [NH_3]/[NO] = 3.0. **Figure 6** shows NO removal at [NH_3]/[NO] = 3.0 in NO/O_2/N_2 system and [NH_3]/[NO+SO_2] = 1.5 in NO/SO_2/O_2/N_2 system. Both characteristics of NO removal showed good agreement. Injected NH_3 and NHi radicals are selectively reacted with NO.

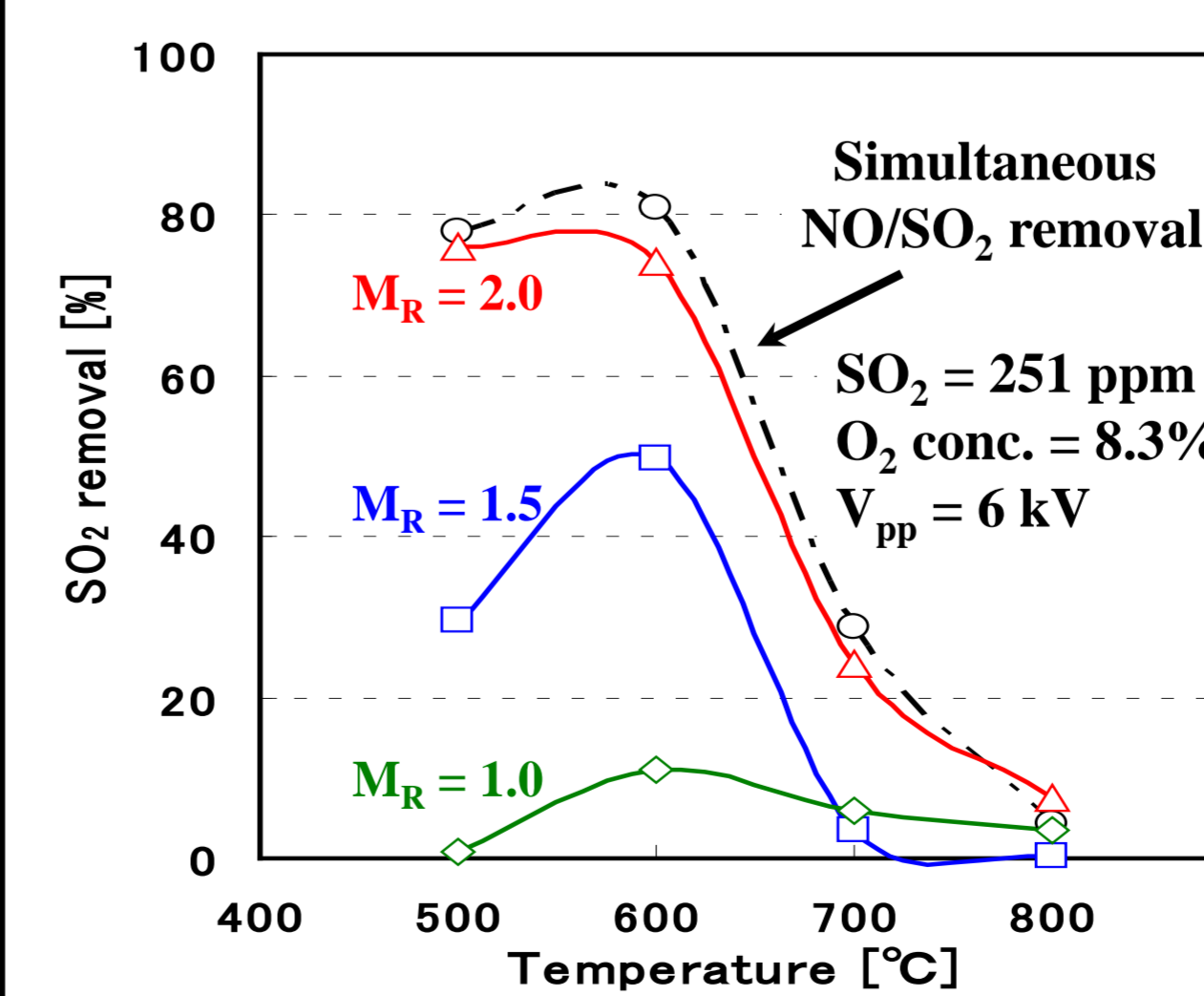**Figure 7** shows SO_2 removal at [NH_3]/[SO_2] = 2.0 in SO_2/O_2/N_2 system and [NH_3]/[NO+SO_2] = 1.5 in NO/SO_2/O_2/N_2 system. The reaction of SO_2 removal occurs after the reaction of NO removal, therefore the condition of M_R = [NH_3]/[NO+SO_2] = 1.5 is equivalent in M_R = [NH_3]/[SO_2] = 2.0, because a part of NH_3 is consumed by NO removal. In fact, SO_2 removal in NO/SO_2/O_2/N_2 system at M_R = 1.5 was similar to that in NO/O_2/N_2 at M_R = 2.0.

Conclusions

In simultaneous removal tests, NO removal was promoted under the simultaneous removal condition: above 90% NO removal was attained at 700℃. Besides SO_2 removal was increased in NO/SO_2/O_2/N_2 system. Effectiveness of NO and SO_2 removal acceleration was explained by the deference of reaction rate between NO-NH_3 system and SO_2-NH_3 system.