New NOx Removal Process from Exhaust Gas in Glass Furnace ~PCHP de-NOx System~

Ryota Tsuji

Nihon Yamamura Glass Co.,Ltd.

About Glass Bottle Production of Nihon Yamamura Glass

Harima Plant

Head Office

Environmental Affairs Office

Saitama Plant

Tokyo Plant

Number of Furnace	: 9
Number of Production line	: 28
Quantity of Product	: 450,000t/year

Mission of Environmental Affairs office

Defense

Co-existence

Offense

Environmental Management

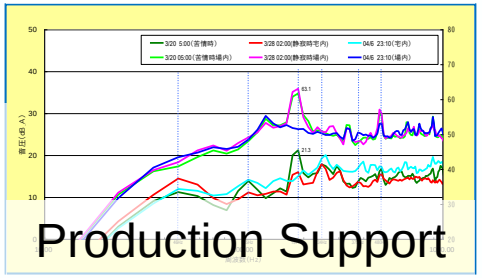
ISO14001

PCB Management

Waste Management

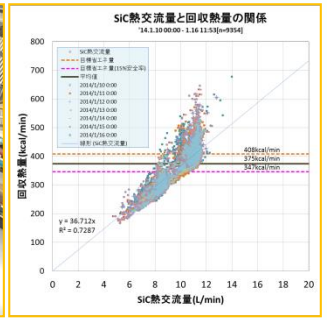
Choice of Electric Power Company

Upholding Government Regulations



Production Support

Environmental Business

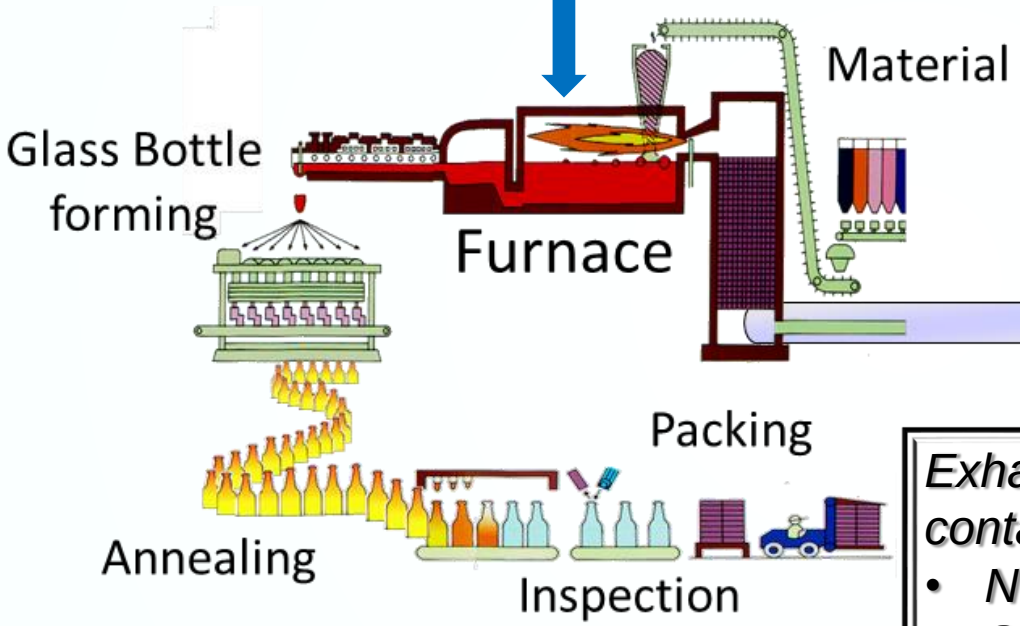


de-NOx **Exhaust Heat Utilization**

Improvement of Rare Metal Handlings **Solar Power**

Glass Bottle Production Process

Dissolved at approximately 1500°C by combustion of LNG or Heavy Oil



Exhaust Gas Treatment System

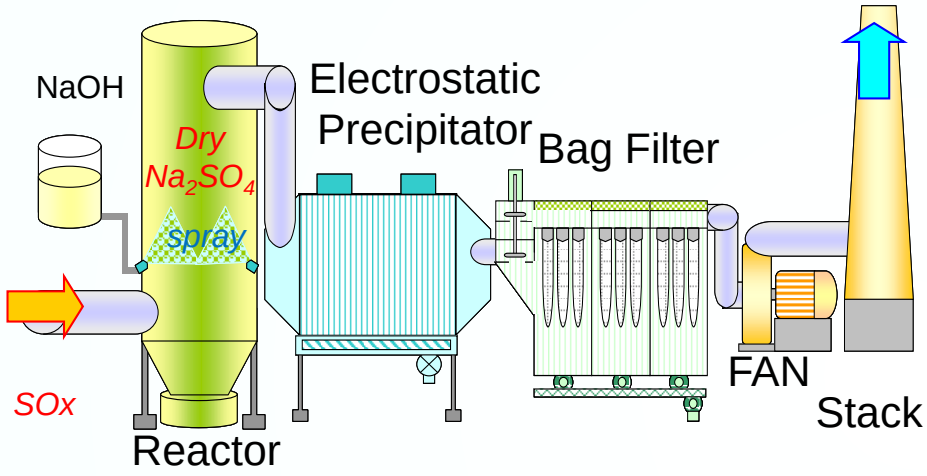
- *de-SOx equipment*
  - *Semi-dry*
  - *Wet*
- *Remove Dust*
  - *Electrostatic Precipitator*
  - *Bag Filter*

Exhaust gas contains

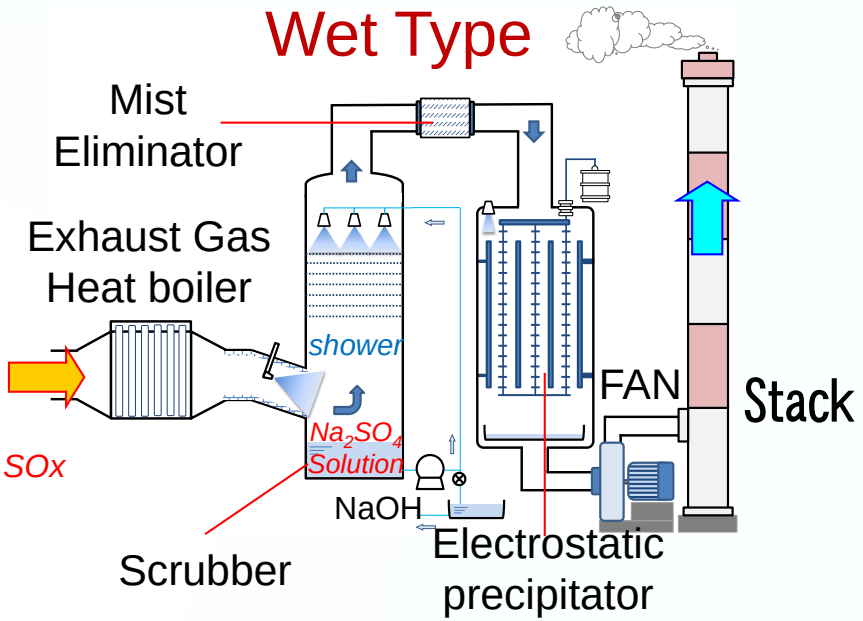
- *NOx*
- *SOx*
- *Dust*

Exhaust Gas Treatment System

Semi-Dry Type



Wet Type



	Before treatment	After treatment	
		Semi-Dry type	Wet Type
Temperature	300~450°C	200°C	60°C
SOx	100~1000ppm	50~500ppm or below	Under 10ppm
Dust	100~500mg/Nm^3	Under 10mg/Nm^3	Under 10mg/Nm^3
NOx	200~400ppm	200~400ppm	200~400ppm

*Both systems do not include de-NOx system.

About de-NOx

NOx Emission Regulation

Japan			USA	Germany	Korea	China
Country	Local (Sagamihara)	Local (Harima)	Local (California)	Country	Country	Country
450ppm	240ppm	290ppm	240ppm	121ppm	157ppm	167ppm

*For comparison purpose,
parameters used to calculate emission regulations are adjusted to match Japan regulation

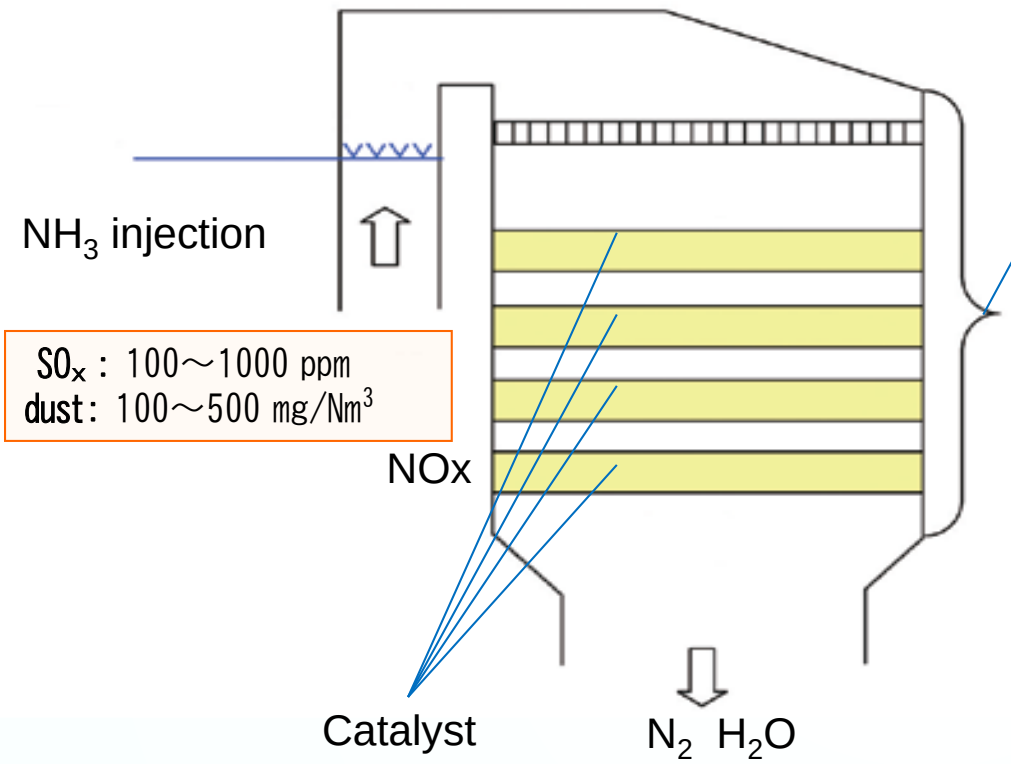
As global environmental problems increase, NOx emission regulation is expected to become more stringent for exhaust gas from glass melting furnace.

SCR — **S**elective **C**atalytic **R**eduction method
→ **Generally used for exhaust gas treatment in coal-fired power plants.**

Low Air Combustion → **Generally used in various fields.**

NOx Removal Method (SCR)

Selective Catalytic Reduction Method(SCR)



Reactor

Main Reaction
(Between 250°C and 450°C)

$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O$ (1)

$6NO_2+8NH_3 \rightarrow 7N_2+12H_2O$ (2)

$NO+NO_2+2NH_3 \rightarrow 2N_2+3H_2O$ (3)

Side Reaction
(If SO_2 is present)

$2SO_2+O_2 \rightarrow 2SO_3$ (4)

$2NH_3+SO_3+H_2O \rightarrow (NH_4)_2SO_4$ (5)

$NH_3+SO_3+H_2O \rightarrow NH_4HSO_4$ (6)

SCR

These side reaction, including dust develops catalyst poison and clogging problems.

→ SCR is difficult to use for de-NO_x in glass melting furnaces.

NOx Removal Method (Low Air Combstion)

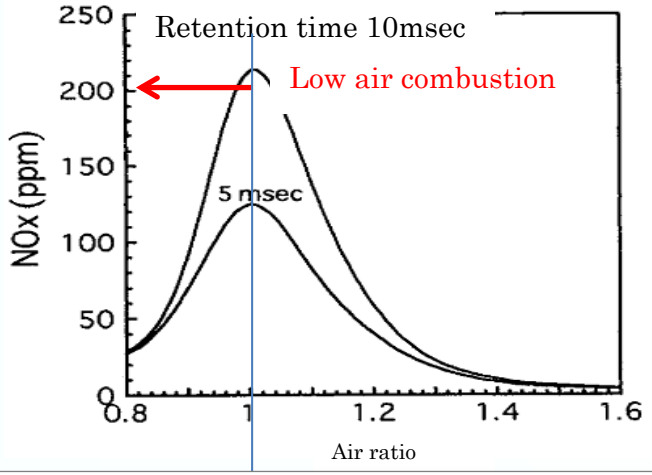
Formation mechanism of thermal NOx

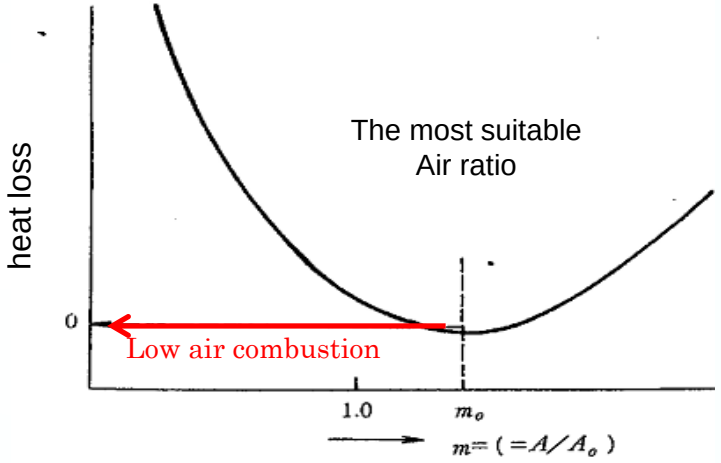
$N_2 + O \Leftrightarrow NO + N$
$O_2 + N \Leftrightarrow NO + O$
$N + OH \Leftrightarrow NO + H$

→ Low air combustion can decrease NOx.

However, low air ratio combustion causes incomplete combustion.

$C + O_2 = CO_2 + 394kJ$
$C + 1/2O_2 = CO + 283kJ$





Low Air Ratio Combustion

Low air ratio combustion causes incomplete combustion

→Consequently losing heat energy

Background of the development

NYG developed a new technology.

Plasma and Chemical Hybrid Process ~PCHP Process~

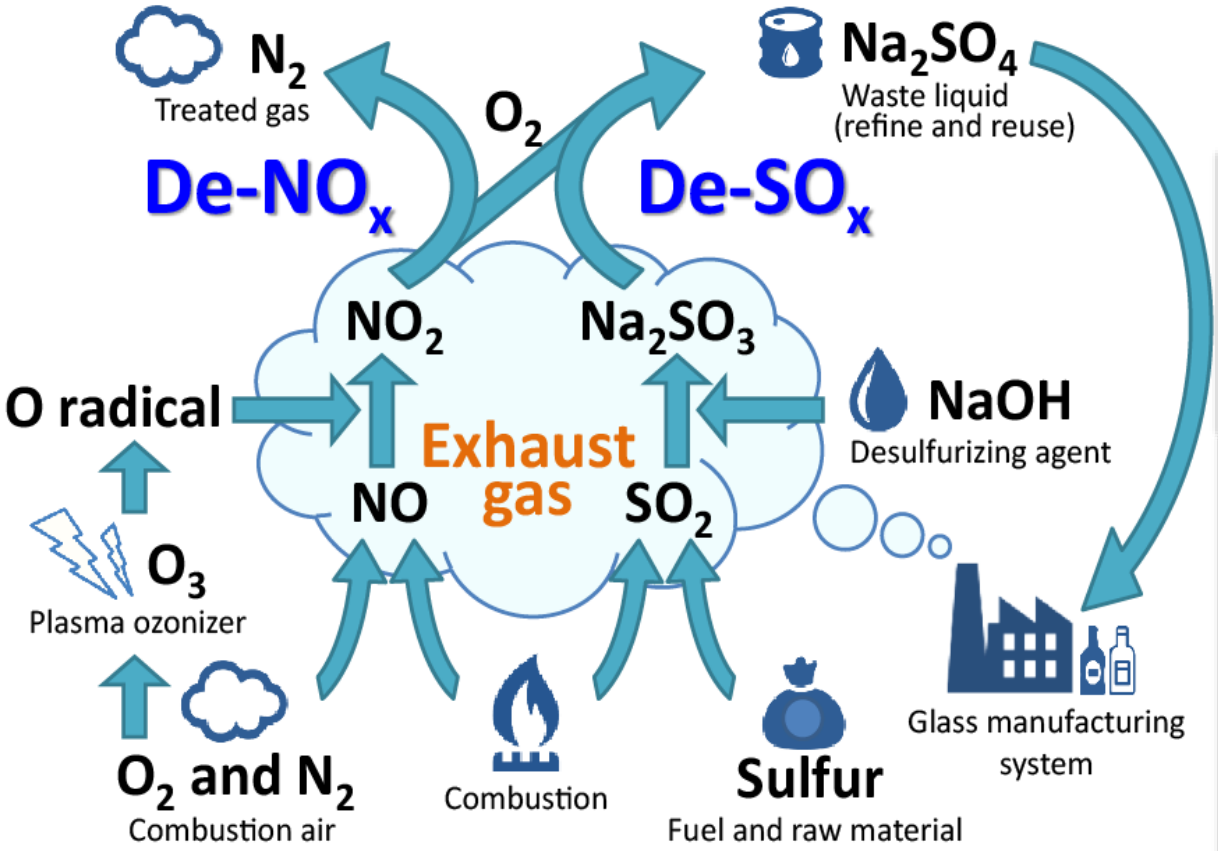
- **Simultaneous de-SOx, de-NOx technology**
- **De-NO_x technology** without the use of catalysts.

Since 2011, started Collaborative investigation with Osaka Prefecture University

Out line of Plasma Chemical Hybrid Process

『Simultaneous de-SOx, de-NOx technology』

- Plasma Process ($O_2+O \rightarrow O_3$, $NO+O_3 \rightarrow NO_2+O_2$)
- De-SOx Process ($SO_2+2NaOH \rightarrow Na_2SO_3+H_2O$)
- Chemical Process ($2NO_2+4Na_2SO_3 \rightarrow N2+4Na_2SO_4$)



PCHP

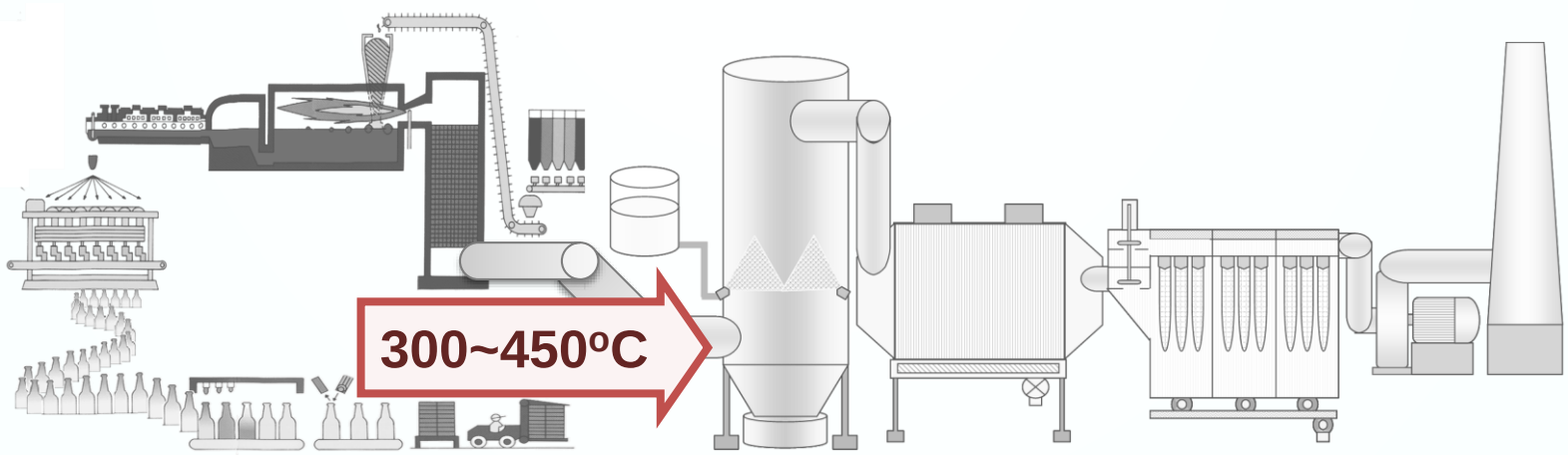
High concentration of SOx and existence of adhesive dust do not affect.

Low maintenance. Applied easily into existing exhaust gas treatment equipment.
→ Reducing initial and running cost compared to installing SCR.

Requirement with installing PCHP in glass furnace

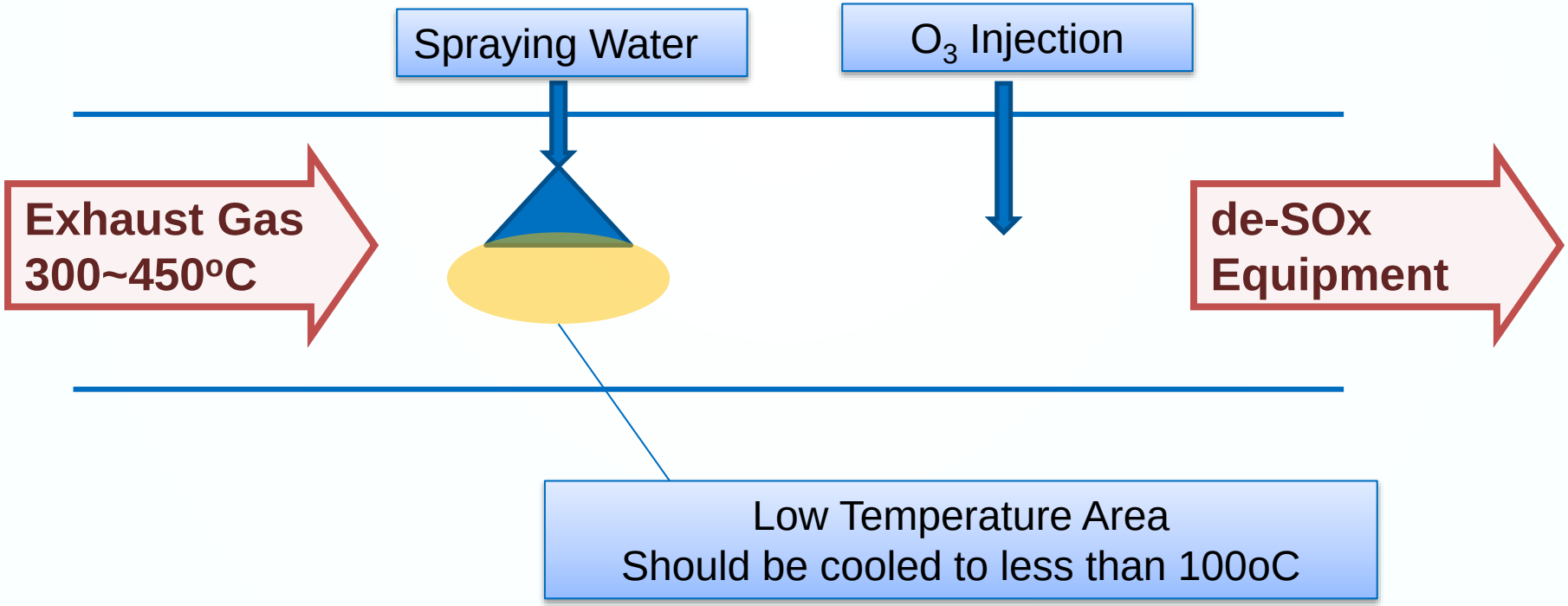
- Temperature of exhaust gas at the entrance of the system 300~450^{o}C.
  (The O_3 is broken down to O_2 in temperatures of more than 150^{o}C, losing effectiveness in NO oxidation.)

- Temperature of exhaust gas should be cooled to less than 100^{o}C



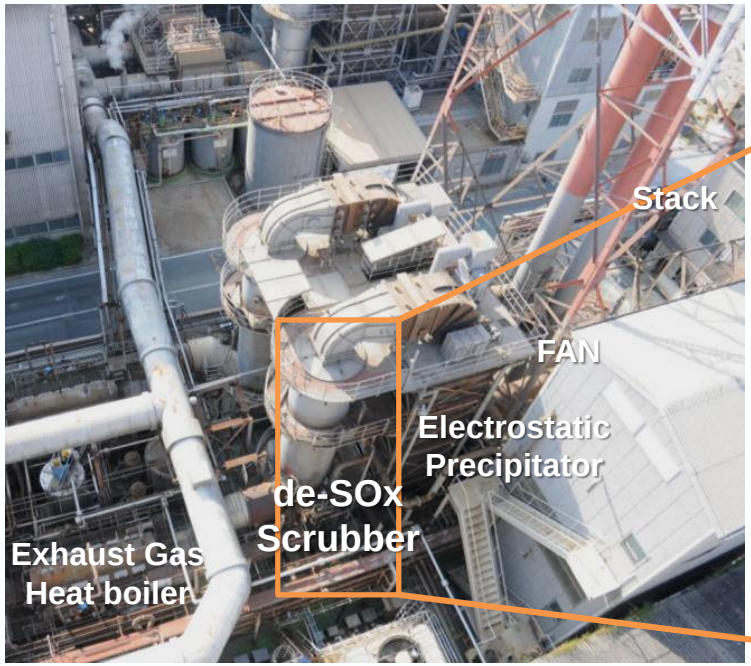
Focus of this development

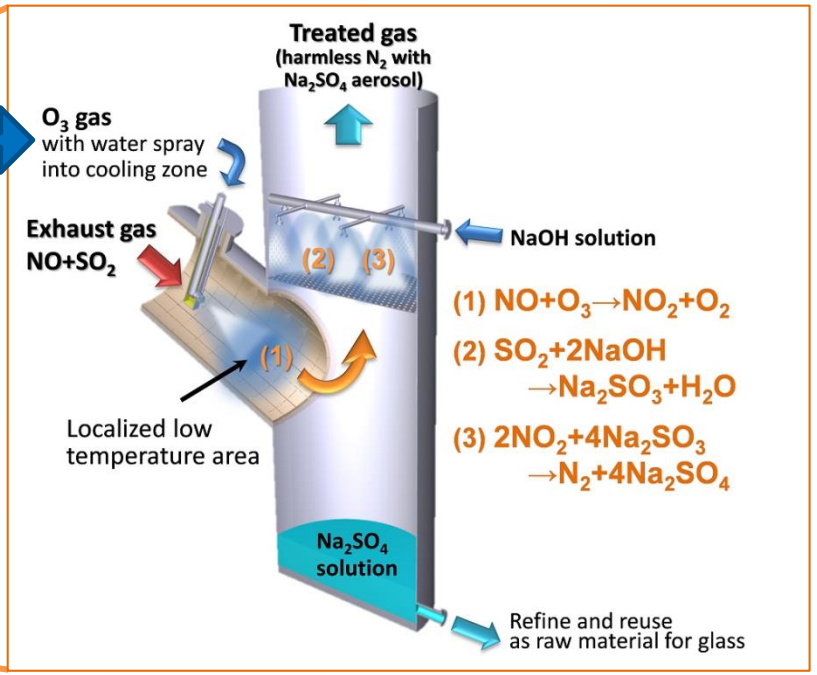
- To form a localized low-temperature area by spraying water before introducing the O_3.



Demonstration at the wet type system

2013.6 Harima plant (Wet Type System)





O3

O2

Oxygen gas

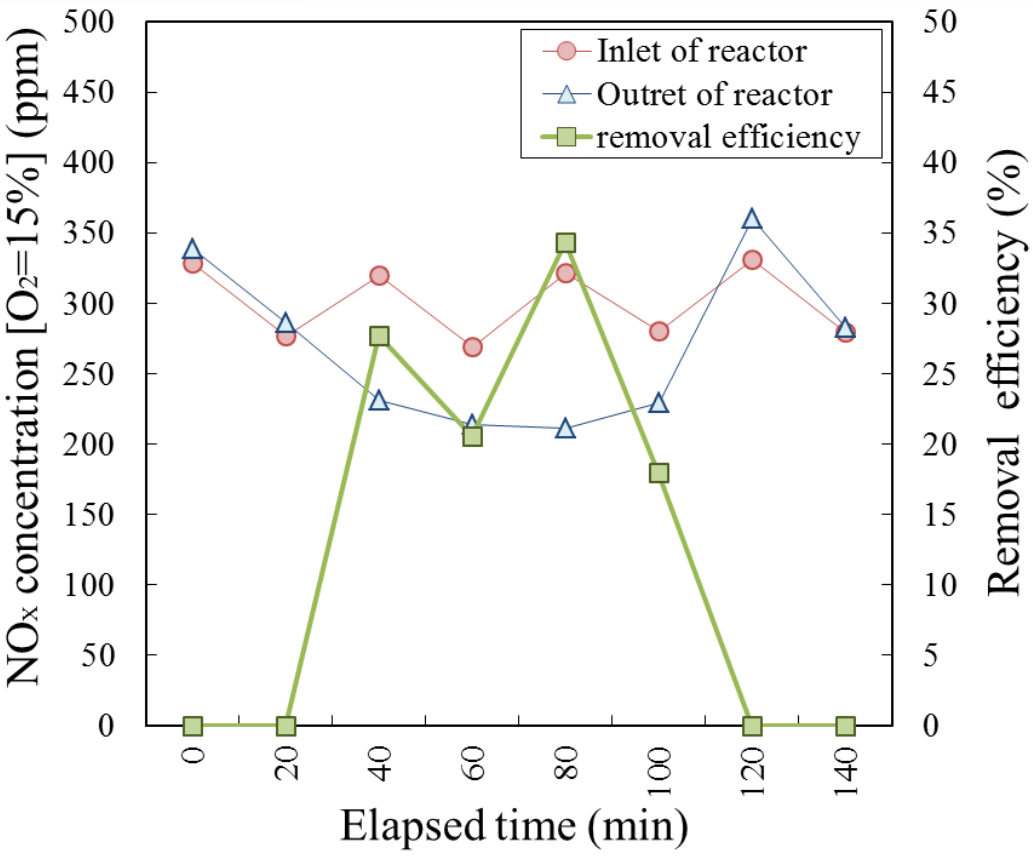
3.6 kW × 4

Ozonizer
(O_3 = 276 g/h, 3.8 g/m^{3}N)

3.1 kW × 3

Ozonizer（with PSA）
(O_3 = 90 g/h, 100 g/m^{3}N, O_2=90 %)

Demonstration Results for Wet Type System



The conc. and removal efficiency of NO_x by PCHP.

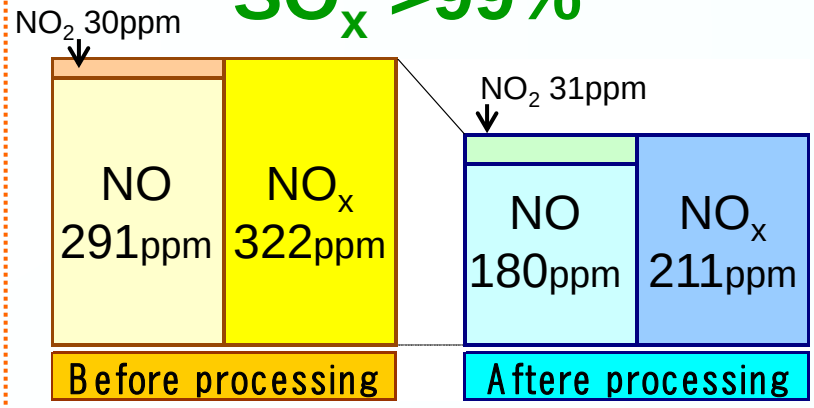
Exhaust gas volume : 8,030 m^3N/h
Injected ozone volume : 1,443 g/h

NOx removal efficiency 34%
From 322ppm to 211ppm

Reaction Efficiency
➡86%

from 120ppm to more than

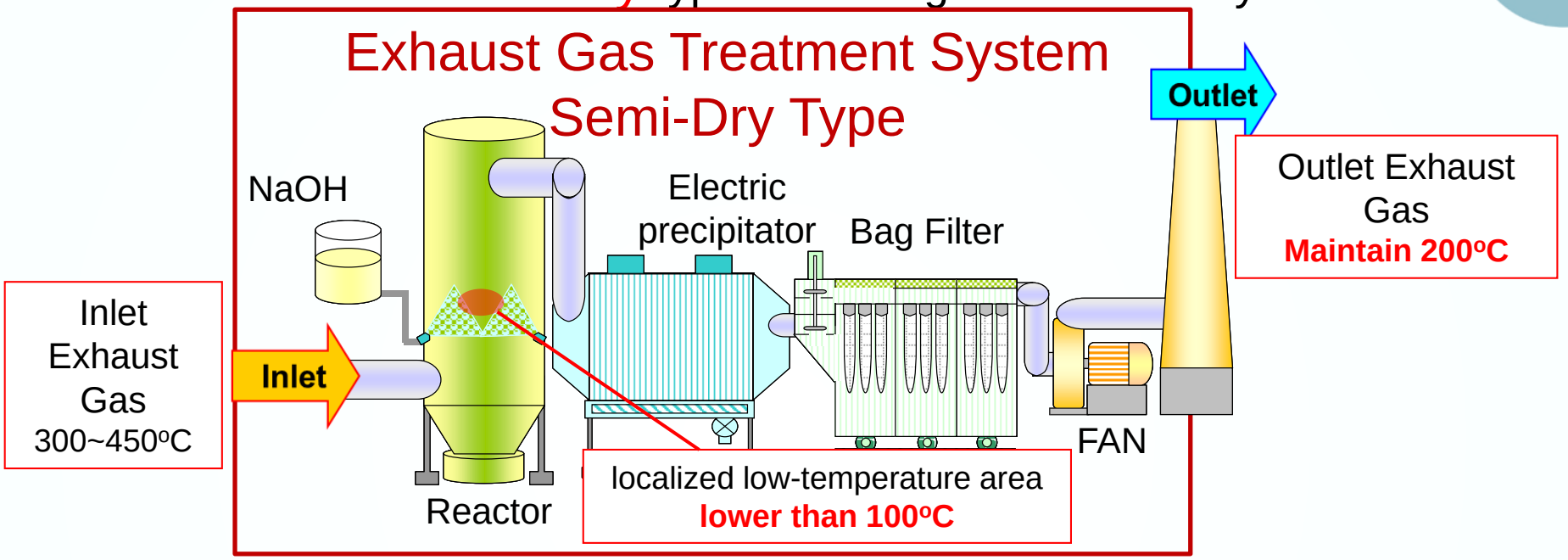
SO_x >99%



In wet type exhaust gas treatment system, it was concluded that application of the PCHP to an actual exhaust gas of glass furnace is highly effective.

Current development status

Demonstration at the Semi-Dry type exhaust gas treatment system



To succeed demonstration of the semi-dry type system

NYG has to achieve two items concurrently.

(1) Formation of localized low-temperature area lower than 100ºC

(2) Maintain temperature of outlet exhaust gas at 200ºC

Conclusion

2011 Collaborative investigation started with Osaka Prefecture University

2012 Laboratory experiment

2013 Demonstration at the Wet Type system (Success)

2014 Demonstration at the Semi-dry type system (Trial 1)

Conclusion

2015 Demonstration at the semi-dry type system (Trial 2)

		2013.6	2014.8	2015.8	2015.12
Plant		Harima	Tokyo	Tokyo	Tokyo
Treatment Type		Wet	Semi-dry	Semi-dry	Semi-dry
Reaction Efficiency	**Plasma ($\Delta NO/injected O_3$)**	**86%**	**57%**	**80%**	**Trial 3**
	Total ($\Delta NOx/injected O_3$)	**86%**	**5%**	**30%**	**Trial 3**

→ The results show that there is still room for improvements

2015 Demonstration at the semi-dry type system (Trial 3)

20XX NYG will push forward with the commercialization of the de-NOx equipment for Semi-dry Type Exhaust Gas Treatment System.


Thank you very much!
Acknowledgement
Osaka Prefecture University
Clear Blue Sky