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

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Nihon Yamamura Glass Co., Ltd.
About Glass Bottle Production of Nihon Yamamura Glass

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

Harima Plant
Head Office
Saitama Plant
Tokyo Plant
Environmental Affairs Office
Mission of Environmental Affairs office

**Defense**

Environmental Management

- ISO14001
- PCB Management

Waste Management

Choice of Electric Power Company

Upholding Government Regulations

Production Support

**Offense**

Environmental Business

- de-NOx
- Exhaust Heat Utilization

- Improvement of Rare Metal Handlings
- Solar Power

2015/10/21
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
- **NaOH**
- **Electrostatic Precipitator**
- **Bag Filter**
- **FAN**
- **Stack**

### Wet Type
- **Mist Eliminator**
- **Exhaust Gas Heat boiler**
- **Scrubber**
- **FAN**
- **Stack**

### Comparison Table

<table>
<thead>
<tr>
<th>Before treatment</th>
<th>After treatment</th>
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</thead>
<tbody>
<tr>
<td><strong>Semi-Dry type</strong></td>
<td><strong>Wet Type</strong></td>
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<tr>
<td>Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>SOx</td>
<td>50~500ppm or below</td>
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<tr>
<td>Dust</td>
<td>Under 10mg/Nm³</td>
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<tr>
<td>NOx</td>
<td>200~400ppm</td>
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*Both systems do not include de-NOx system.*
**NOx Emission Regulation**

<table>
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<tr>
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<td>ppm</td>
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</table>

*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.

**Selective Catalytic Reduction method (SCR)**

→ 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)

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

4NO + 4NH\textsubscript{3} + O\textsubscript{2} → 4N\textsubscript{2} + 6H\textsubscript{2}O (1)

6NO\textsubscript{2} + 8NH\textsubscript{3} → 7N\textsubscript{2} + 12H\textsubscript{2}O (2)

NO + NO\textsubscript{2} + 2NH\textsubscript{3} → 2N\textsubscript{2} + 3H\textsubscript{2}O (3)

Side Reaction
(If SO\textsubscript{2} is present)

2SO\textsubscript{2} + O\textsubscript{2} → 2SO\textsubscript{3} (4)

2NH\textsubscript{3} + SO\textsubscript{3} + H\textsubscript{2}O → (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} (5)

NH\textsubscript{3} + SO\textsubscript{3} + H\textsubscript{2}O → NH\textsubscript{4}HSO\textsubscript{4} (6)

These side reactions, including dust, develop catalyst poison and clogging problems.
SCR is difficult to use for de-NO\textsubscript{x} in glass melting furnaces.
Formation mechanism of thermal NOx

\[ \text{N}_2 + \text{O} \Leftrightarrow \text{NO} + \text{N} \]
\[ \text{O}_2 + \text{N} \Leftrightarrow \text{NO} + \text{O} \]
\[ \text{N} + \text{OH} \Leftrightarrow \text{NO} + \text{H} \]

Low air combustion can decrease NOx.

However, low air ratio combustion causes incomplete combustion.

\[ \text{C} + \text{O}_2 = \text{CO}_2 + 394\text{kJ} \]
\[ \text{C} + \frac{1}{2}\text{O}_2 = \text{CO} + 283\text{kJ} \]

Retention time 10msec

Low air combustion causes incomplete combustion.

Consequently losing heat energy

Low air ratio combustion

The most suitable Air ratio

\[ m = \left( \frac{A}{A_o} \right) \]

2015/10/21
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
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 ($2NO_2 + 4Na_2SO_3 \rightarrow N_2 + 4Na_2SO_4$

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.
PCHP Installation Requirement

Requirement with installing PCHP in glass furnace

- Temperature of exhaust gas at the entrance of the system 300~450°C.
  (The O₃ is broken down to O₂ in temperatures of more than 150°C, losing effectiveness in NO oxidation.)

- Temperature of exhaust gas should be cooled to less than 100°C
Focus of this development

To form a localized low-temperature area by spraying water before introducing the \( \text{O}_3 \).
Demonstration at the wet type system

2013.6 Harima plant (Wet Type System)

Exhaust gas
Scrubber

FAN
Electrostatic Precipitator

de-SOx Scrubber

Ozone gas
(O$_3$ = 276 g/h, 3.8 g/m$^3$N)

Ozonizer

3.6 kW × 4

Oxygen gas

O2

3.1 kW × 3

Ozonizer (with PSA)
(O$_3$ = 90 g/h, 100 g/m$^3$N, O$_2$=90 %)

Treated gas
(harmless N$_2$ with Na$_2$SO$_4$ aerosol)

NaOH solution

(1) NO+$O_3$$\rightarrow$NO$_2$$+O_2$
(2) SO$_2$+2NaOH $\rightarrow$Na$_2$SO$_3$$+H_2$$O$
(3) 2NO$_2$+4Na$_2$SO$_3$$ ightarrow$N$_2$$+4Na$_2$SO$_4$

Refine and reuse as raw material for glass

Localized low temperature area

Exhaust gas
NO+SO$_2$

O$_3$ gas with water spray into cooling zone
Demonstration Results for Wet Type System

Exhaust gas volume: 8,030 m³ N/h
Injected ozone volume: 1,443 g/h

NOx removal efficiency 34%
From 322 ppm to 211 ppm

Reaction Efficiency → 86%
from 120 ppm to more than 31 ppm

SOx > 99%

The conc. and removal efficiency of NOx by PCHP.

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.

2015/10/21
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 100°C
2. Maintain temperature of outlet exhaust gas at 200°C
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)**

<table>
<thead>
<tr>
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<th>2013.6</th>
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<tr>
<td><strong>Treatment Type</strong></td>
<td>Wet</td>
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<td>Semi-dry</td>
</tr>
<tr>
<td><strong>Reaction Efficiency</strong></td>
<td>Plasma ($\Delta$NO/injectedO$_3$)</td>
<td>86%</td>
<td>57%</td>
<td>80%</td>
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<tr>
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<td>Total ($\Delta$NOx/injectedO$_3$)</td>
<td>86%</td>
<td>5%</td>
<td>30%</td>
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</table>

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