NOx EMISSIONS UNDER OXY-COAL COMBUSTION

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1) Situation of energy and material resources

Life Period of Fossil Fuels

How long can we use the fossil fuels?

<table>
<thead>
<tr>
<th>Primary fossil fuels</th>
<th>Life period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>42 years</td>
</tr>
<tr>
<td>Natural gas</td>
<td>60 years</td>
</tr>
<tr>
<td>Coal</td>
<td>122 years</td>
</tr>
<tr>
<td>Uranium</td>
<td>? (44) years</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal</th>
<th>Life Period (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold</td>
<td>20</td>
</tr>
<tr>
<td>Silver</td>
<td>19</td>
</tr>
<tr>
<td>Copper</td>
<td>31</td>
</tr>
<tr>
<td>Diamond</td>
<td>17</td>
</tr>
<tr>
<td>Platinum</td>
<td>218</td>
</tr>
<tr>
<td>Aluminum</td>
<td>211</td>
</tr>
<tr>
<td>Iron</td>
<td>151</td>
</tr>
<tr>
<td>Nickel</td>
<td>45</td>
</tr>
<tr>
<td>Lead</td>
<td>25</td>
</tr>
<tr>
<td>Zinc</td>
<td>20</td>
</tr>
<tr>
<td>Herium</td>
<td>&gt;74</td>
</tr>
</tbody>
</table>

Jewelry?
Is Mobile phone “Treasure-trove”?]

Mobile phone: 2 million/y---Dumped in 1998
(Mass of one mobile phone = about 100 g)

1 t - Mobile phone :  
- Gold 150 g
- Silver 3,000 g

Hishikari gold mine in Kagoshima Pref. in Japan

No. 1 gold concentration in the world

1 t - ore :  
- Gold 50 g
2) Trends of primary energy

Transition of worldwide primary energy consumption

TOE (ton of oil equivalent)

Transition of Japanese primary energy consumption

- Hydro & New Energy: 6.7%
- Nuclear: 6.7%
- Natural Gas: 18.6%
- Coal: 22.8%
- Oil: 41.9%

http://www.enecho.meti.go.jp/topics/hakusho/2010energyhtml/2-1-1.html
Thailand’s primary energy supply (2012)

- Natural gas: 27.9%
- Coal: 13.9%
- Oil: 39.0%
- Bio-fuels: 18.6%
- Hydro: 0.6%
Future trend of electric power generation in Thailand
3) NOx EMISSIONS UNDER OXY-COAL COMBUSTION

BACKGROUND (1)

What is the oxy-fuel combustion?

Current combustion system

Coal

Air

Boiler

Dust removal
What is the oxy-fuel combustion?
OBJECTIVES

Emission behaviors of NOx (NO + N_2O)

Oxy-fuel (Flue gas recirculation) ↔ Air

CONTENTS

- Combustion experiments using an electrically heated drop tube furnace
- Effects of combustion atmospheres on NO_x emissions
- Effects of coal types on NO_x emissions
DROP TUBE FURNACE

**Fuel injection part**
- Continuous feeding
- Entraining gas: $\text{CO}_2+\text{O}_2$ or Air

**Reaction part**
- Temperature controlled by electric heater
- Residence time: 3s@1300mm

**Sampling part**
- Iso-kinetic sampling
- Gas analysis
- Particle analysis

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**Diagram Details**
- Primary gas
- Mass flow controller
- Secondary gas
- Heater unit
- Injector
- Water in
- Water out
- Distance (H)
- Sampling probe
- Filter
- $\text{N}_2$
- $\text{O}_2+\text{CO}_2(+\text{NO, N}_2\text{O})$ or Air

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### Coal properties

<table>
<thead>
<tr>
<th>Sample coal</th>
<th>Coal-O</th>
<th>Coal-E</th>
<th>Coal-M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis [wt%, dry]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>5.59</td>
<td>1.70</td>
<td>3.88</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>34.12</td>
<td>34.80</td>
<td>34.71</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>54.46</td>
<td>55.30</td>
<td>53.66</td>
</tr>
<tr>
<td>Ash</td>
<td>11.42</td>
<td>9.90</td>
<td>11.63</td>
</tr>
<tr>
<td><strong>Ultimate analysis [wt%, d.a.f.]</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>77.43</td>
<td>78.91</td>
<td>80.90</td>
</tr>
<tr>
<td>H</td>
<td>5.54</td>
<td>4.85</td>
<td>5.45</td>
</tr>
<tr>
<td>N</td>
<td>1.05</td>
<td>1.88</td>
<td>2.52</td>
</tr>
<tr>
<td>O</td>
<td>15.82</td>
<td>13.93</td>
<td>10.78</td>
</tr>
<tr>
<td>S</td>
<td>0.16</td>
<td>0.43</td>
<td>0.35</td>
</tr>
<tr>
<td><strong>Fuel ratio (=FC/VM)</strong></td>
<td>1.60</td>
<td>1.59</td>
<td>1.55</td>
</tr>
</tbody>
</table>

### Experimental conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coal-O, Coal-E, Coal-M</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmosphere</strong></td>
<td>Air, CO\textsubscript{2}-O\textsubscript{2}, Oxy-fuel</td>
</tr>
<tr>
<td><strong>Coal feed rate [g/min]</strong></td>
<td>1.0</td>
</tr>
<tr>
<td><strong>Temperature [K]</strong></td>
<td>1073</td>
</tr>
<tr>
<td><strong>Stoichiometric O\textsubscript{2} ratio</strong></td>
<td>1.2</td>
</tr>
<tr>
<td><strong>Sampling points [mm]</strong></td>
<td>100 ~ 1300</td>
</tr>
</tbody>
</table>
How to simulate the flue gas recirculation

O₂-fuel ratio 1.2

CO₂-O₂ combustion experiment (i=0)

Flue gas

VM = Volatile matter
FC = Fixed Carbon

1ˢᵗ recirculation experiment (i=1)

NO

N₂O

Recirculated gas

CO₂

O₂

VM

FC

Additional O₂

O₂-fuel ratio 1.2

Ar
Result (1):
Effects of combustion atmospheres on NO\textsubscript{X} emissions
~ NO\textsubscript{X} concentrations at the reactor exit (Sampling point: 1300mm)~

- Air and CO\textsubscript{2}-O\textsubscript{2} atmospheres
  - NO : Air > CO\textsubscript{2}-O\textsubscript{2}
  - N\textsubscript{2}O : Air < CO\textsubscript{2}-O\textsubscript{2}, slightly

- CO\textsubscript{2}-O\textsubscript{2} and Oxy-fuel atmospheres
  - NO, N\textsubscript{2}O : CO\textsubscript{2}-O\textsubscript{2} < Oxy-fuel, slightly
  - Accumulations due to the flue gas recirculations
Result (1):
Effects of combustion atmospheres on NO\textsubscript{X} emissions
~ NO\textsubscript{X} concentration profiles in the reactor for Coal-E ~

- **Air**: NO $\rightarrow$ Large peak in upstream, $N_2O$ $\rightarrow$ Increase downstream
  
  NO conversion to $N_2O$ via NCO + NO $\rightarrow$ CO + $N_2O$

- **CO\textsubscript{2}-O\textsubscript{2}**: NO $\rightarrow$ Small peak in upstream, $N_2O$ $\rightarrow$ Rapidly increase
  
  High CO concentration may affect $N_2O$ generation. --- CO profile?
Result (1):
Effects of combustion atmospheres on NOₓ emissions
~ CO concentration profiles in the reactor for Coal-E ~

- CO₂-O₂ atmosphere:
  - CO ➔ Larger peak in upstream
- High N₂O conversion
  - (CO + OH ➔ CO₂ + H, N₂O + H ➔ N₂ + OH)

High concentration of CO₂ suppresses the reaction of “CO + 1/2O₂ → CO₂”.

In upstream region, CO: CO₂-O₂ > Air
Result (1):
Effects of combustion atmospheres on NO\textsubscript{X} emissions
~ NO\textsubscript{X} concentration profiles in the reactor for Coal-E ~

- **Oxy-fuel atmosphere**
  - N\textsubscript{2}O at the exit: a little increase in spite of large recirculated N\textsubscript{2}O
  - N\textsubscript{2}O will be decomposed by char particles during combustion,
Result (2): Effects of coal types on NOX emissions

~ NOX concentrations at the reactor exit (1300mm) and NCR ~

\[ \text{NCR: Nitrogen Conversion Ratio} \]

\[ \text{NCR} = \frac{N(\text{Fluegas}_\text{-NO}) \text{ or } N(\text{Fluegas}_\text{-N}_2\text{O})}{N(\text{Fuel}) + N(\text{Recycle}_\text{-NO}) + (\text{Recycle}_\text{-N}_2\text{O})} \times 100 \]

- N2O: proportional to N contents
- NCR does not correlate with N contents.
Result (2):
Effects of coal types on NO\textsubscript{X} emissions

~ Residual fractions of N in char to N in original coal, and their relationship with NCR~

\( \text{NCR: Nitrogen Conversion Ratio} \)

\[
\text{NCR} = \frac{N(\text{Fluegas}_\text{NO}) \text{ or } N(\text{Fluegas}_\text{N}_2\text{O})}{N(\text{Fuel}) + N(\text{Recycle}_\text{NO}) + (\text{Recycle}_\text{N}_2\text{O})} \times 100
\]

- Total NCRs (NO & N\textsubscript{2}O) are governed by char-N/fuel-N.
- Relationship between NO\textsubscript{x} generation and char-N
Summary of oxy-fuel combustion

1. Comparing between Air and CO$_2$-O$_2$ atmospheres,
   • NO : Air > CO$_2$-O$_2$
   • N$_2$O : Air < CO$_2$-O$_2$, slightly
     In CO$_2$-O$_2$ combustion atmosphere,
     high concentration of CO promotes the reaction,
     “2NO + CO → N$_2$O + CO$_2$”, resulting in large N$_2$O generations.

2. In Oxy-fuel, N$_2$O accumulation happens due to the recirculated N$_2$O at the inlet, but its contribution is small.

3. Investigating effects of coal types on NO$_x$ emission,
   • N$_2$O concentration is almost proportional to N content in original coal
   • Total NCRs (NO & N$_2$O) are governed by char-N/fuel-N.
   • NO concentration is high when char combustibility is high.
4) What do we have to do in the near future?
The Earth Calendar

The Earth was born before 4.6 billion years
Time when the Earth was born: at 0:00 on January 1st
Present: at 24:00 on December 31st

Middle of February: Life was born
End of June: O₂ was produced (Photosynthesis)
November 23rd: Plants & Insects were appeared on the ground.
December 14th: Dinosaurs were born.
December 26th: End of Dinosaurs period.
Evening in December 26th: Primates were born.

Evening in December 30th: Original of human was born.
December 31st
  23:59  Chinese Civilization
  23:59:40  Egyptian Civilization
Result (2): Effects of coal types on NOX emissions

~ CO concentration and carbon conversion profiles in the reactor ~

**Char combustibility:**
Coal-O > Coal-E = Coal-M

Coal-O: Low CO (and char), resulting in low reducing ability in the reactor

Small NO reduction in upstream

**CO: Coal-O < Coal-E = Coal-M**
### DARS素反応式

#### NO生成反応

<table>
<thead>
<tr>
<th>反応式</th>
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</tr>
</thead>
<tbody>
<tr>
<td>( N + O_2 \Leftrightarrow NO + O )</td>
<td>( N + NO \Leftrightarrow N_2 + O )</td>
</tr>
<tr>
<td>( N + OH \Leftrightarrow NO + H )</td>
<td>( HO_2 \Leftrightarrow NO \Leftrightarrow NO_2 + OH )</td>
</tr>
<tr>
<td>( N_2 O + O \Leftrightarrow 2NO )</td>
<td>( NO + O + M \Leftrightarrow NO_2 + M )</td>
</tr>
<tr>
<td>( NO_2 + O \Leftrightarrow NO + O_2 )</td>
<td>( NH + NO \Leftrightarrow N_2 + OH )</td>
</tr>
<tr>
<td>( NO_2 + H \Leftrightarrow NO + OH )</td>
<td>( NH + O \Leftrightarrow NO + H )</td>
</tr>
<tr>
<td>( NH + O_2 \Leftrightarrow NO + OH )</td>
<td>( H + NO + M \Leftrightarrow HNO + M )</td>
</tr>
<tr>
<td>( NNH + O \Leftrightarrow NH + NO )</td>
<td>( NCO + NO \Leftrightarrow N_2 O + CO )</td>
</tr>
<tr>
<td>( HNO + O \Leftrightarrow NO + OH )</td>
<td>( NCO + NO \Leftrightarrow N_2 + CO_2 )</td>
</tr>
<tr>
<td>( HNO + OH \Leftrightarrow NO + H_2 O )</td>
<td>( C + NO \Leftrightarrow CN + O )</td>
</tr>
<tr>
<td>( HNO + O_2 \Leftrightarrow HO_2 + NO )</td>
<td>( CH + NO \Leftrightarrow HCN + O )</td>
</tr>
<tr>
<td>( NCO + O \Leftrightarrow NO + CO )</td>
<td>( CH + NO \Leftrightarrow H + NCO )</td>
</tr>
<tr>
<td>( NCO + OH \Leftrightarrow NO + H + CO )</td>
<td>( CH + NO \Leftrightarrow H + NO )</td>
</tr>
<tr>
<td>( NCO + O_2 \Leftrightarrow NO + CO_2 )</td>
<td>( CH_2 + NO \Leftrightarrow H + HNCO )</td>
</tr>
<tr>
<td>( HCNN + O \Leftrightarrow HCN + NO )</td>
<td>( CH_2 + NO \Leftrightarrow OH + HCN )</td>
</tr>
<tr>
<td>( CN + NO_2 \Leftrightarrow NCO + NO )</td>
<td>( CH_2 + NO \Leftrightarrow OH + HCN_2 )</td>
</tr>
<tr>
<td>( N + CO_2 \Leftrightarrow NO + CO )</td>
<td>( CH_2(S) + NO \Leftrightarrow H + HNCO )</td>
</tr>
</tbody>
</table>

#### NO分解反応

<table>
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</tr>
<tr>
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<td>( NO + O + M \Leftrightarrow NO_2 + M )</td>
</tr>
<tr>
<td>( NO_2 + O \Leftrightarrow NO + O_2 )</td>
<td>( NH + NO \Leftrightarrow N_2 + OH )</td>
</tr>
<tr>
<td>( NO_2 + H \Leftrightarrow NO + OH )</td>
<td>( NH + O \Leftrightarrow NO + H )</td>
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<tr>
<td>( NH + O_2 \Leftrightarrow NO + OH )</td>
<td>( H + NO + M \Leftrightarrow HNO + M )</td>
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<td>( NNH + O \Leftrightarrow NH + NO )</td>
<td>( NCO + NO \Leftrightarrow N_2 O + CO )</td>
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<tr>
<td>( HNO + O \Leftrightarrow NO + OH )</td>
<td>( NCO + NO \Leftrightarrow N_2 + CO_2 )</td>
</tr>
<tr>
<td>( HNO + OH \Leftrightarrow NO + H_2 O )</td>
<td>( C + NO \Leftrightarrow CN + O )</td>
</tr>
<tr>
<td>( HNO + O_2 \Leftrightarrow HO_2 + NO )</td>
<td>( CH + NO \Leftrightarrow HCN + O )</td>
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<td>( CH + NO \Leftrightarrow H + NCO )</td>
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<td>( CH_2 + NO \Leftrightarrow H + HNCO )</td>
</tr>
<tr>
<td>( HCNN + O \Leftrightarrow HCN + NO )</td>
<td>( CH_2 + NO \Leftrightarrow OH + HCN )</td>
</tr>
<tr>
<td>( CN + NO_2 \Leftrightarrow NCO + NO )</td>
<td>( CH_2 + NO \Leftrightarrow OH + HCN_2 )</td>
</tr>
<tr>
<td>( N + CO_2 \Leftrightarrow NO + CO )</td>
<td>( CH_2(S) + NO \Leftrightarrow H + HNCO )</td>
</tr>
</tbody>
</table>

\( N \) 気相反応～
DARS素反応式
〜N₂O気相反応〜

N₂O生成反応

NH+NO<=>N₂O+H
colored_box
NCO+NO<=>N₂O+CO
colored_box
NCO+NO₂<=>N₂O+CO₂

colored_box

N₂O分解反応

N₂O+O<=>2NO
colored_box
N₂O+H<=>N₂+OH
colored_box
N₂O+OH<=>N₂+HO₂
colored_box
N₂O(+M)<=>N₂+O(+M)
colored_box

〜N₂O生成反応〜

〜N₂O分解反応〜
Solid carbon oxidation and gasification reactions
C(Solid) + O → CO(Solid)
C(Solid) + O₂ → CO(Solid) + O
C(Solid) + OH → CO(Solid) + H
C(Solid) + CO₂ → CO(Solid) + CO
C(Solid) + H₂O → CO(Solid) + 2H
CO(Solid) → CO

Surface site CN(Solid) related reactions
CN(Solid) + O₂ → NCO(Solid) + O
CN(Solid) + OH → NCO(Solid) + H
CN(Solid) + NO → NCO(Solid) + N
C(Solid) + N → NCO(Solid)

Char / NO reduction reactions
C(Solid) + NO → CN(Solid) + O
C(Solid) + N₂ → CN(Solid) + N

Surface site NCO(Solid) related reactions and N₂O formation
DARS解析結果

Air-CO2O2

図に示すのは、燃焼変換率（Air）と（CO₂-O₂）の時間変化を示しています。
DARS解析結果

NH₃, HCN変更

![Graph showing NO concentration over time for different NH₃:HCN ratios.](image)
DARS解析結果

Air-CO2O2

Air_反応経路

CO₂-O₂_反応経路