Purification of Oxyfuel-Derived CO$_2$

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Purification of Oxyfuel-Derived CO$_2$: Outline

- Oxyfuel CO$_2$ Purification Requirements
- Theory of SO$_x$/NO$_x$/Hg removal – from GHGT7
  - Reactions and Process
- Oxycoal UK Phase 1: Oxyfuel Fundamentals
  - 160kW$_{th}$ Oxyfuel-fired coal combustion
  - Sour compression apparatus
  - Initial results
- Development plan
Oxyfuel CO$_2$ Purification

- Oxyfuel combustion of coal produces a flue gas containing:
  - CO$_2$ + H$_2$O
  - Any inerts from air in leakage or oxygen impurities
  - Oxidation products and impurities from the fuel (SO$_x$, NO$_x$, HCl, Hg, etc.)

- Purification requires:
  - Cooling to remove water
  - Compression to 30 bar
    - Integrated SO$_x$/NO$_x$/Hg removal
  - Low Temperature Purification
    - Low purity, bulk inerts removal
    - High purity, Oxygen removal
  - Compression to pipeline pressure
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NO$_x$ SO$_2$ Reactions in the CO$_2$ Compression System

- We realised that SO$_2$, NO$_x$, and Hg can be removed in the CO$_2$ compression process, in the presence of water and oxygen.

- SO$_2$ is converted to Sulphuric Acid, NO$_2$ converted to Nitric Acid:
  
  - NO + $\frac{1}{2}$ O$_2$ = NO$_2$ \hspace{1cm} (1) \text{Slow}
  - 2 NO$_2$ = N$_2$O$_4$ \hspace{1cm} (2) \text{Fast}
  - 2 NO$_2$ + H$_2$O = HNO$_2$ + HNO$_3$ \hspace{1cm} (3) \text{Slow}
  - 3 HNO$_2$ = HNO$_3$ + 2 NO + H$_2$O \hspace{1cm} (4) \text{Fast}
  - NO$_2$ + SO$_2$ = NO + SO$_3$ \hspace{1cm} (5) \text{Fast}
  - SO$_3$ + H$_2$O = H$_2$SO$_4$ \hspace{1cm} (6) \text{Fast}

- Rate increases with Pressure to the 3$^{rd}$ power
  - only feasible at elevated pressure

- Little Nitric Acid is formed until all the SO$_2$ is converted

- Pressure, reactor design and residence times, are important.
Air Products’ CO₂ Compression and Purification System: Removal of SO₂, NOₓ and Hg

- SO₂ removal: 100%
- NOₓ removal: 90-99%

1.02 bar
30°C
67% CO₂
8% H₂O
25%
Inerts
SOₓ
NOₓ

30 bar to Driers
Saturated 30°C
76% CO₂
24% Inerts

15 bar

30 bar

Dilute H₂SO₄
HNO₃
Hg

Dilute HNO₃

Water
SO$_x$/NO$_x$ Removal – Key Features

- Adiabatic compression to 15 bar:
  - No interstage water removal
  - All Water and SO$_x$ removed at one place

- NO acts as a catalyst
  - NO is oxidised to NO$_2$ and then NO$_2$ oxidises SO$_2$ to SO$_3$: The Lead Chamber Process

- Hg will also be removed, reacting with the nitric acid that is formed

- FGD and DeNO$_x$ systems are not required for emissions or CO$_2$ purity
  - SO$_x$/NO$_x$ removed in compression system
  - Low NO$_x$ burners are not required for oxyfuel combustion

- Verification was required: Oxycoal-UK Phase 1
OXYCOAL-UK : Phase 1 : BERR 404 Oxyfuel Fundamentals

- WP1: Combustion Fundamentals
- WP2: Furnace Design & Operation
- WP3: Flue Gas Clean-up / Purification
- WP4: Generic Process Issues
Doosan Babcock NO$_x$ Reduction Test Facility (NRTF)

- Heat Input: 160kW
- In-Furnace (Primary) NO$_x$ Reduction Technologies
  - Air Staging, Overfire Air (OFA) injection
  - Gas and Coal Reburn
- Post-Combustion (Secondary) NO$_x$ Reduction Technologies
  - Selective Non-Catalytic Reduction (SNCR)
  - Selective Catalytic Reduction (SCR)
- Electro Static Precipitator (ESP)
- Oxyfuel experiments carried out early 90’s with Air Products/Babcock Energy
Schematic Diagram of NRTF – Air Firing Configuration
Schematic Diagram of NRTF – Oxyfuel Firing Configuration

To Sour Comresssion Apparatus
Oxyfuel Installation

Secondary Flue Gas Recycle Fan

Secondary Flue Gas Recycle

Oxygen Injection Into Secondary Flue Gas Recycle
Sour Compression Apparatus

From NRTF

Flue Gas Cooler

Condensate Separator

Compressor & Receiver

Reactor

MFC
The effect of Pressure on SO$_2$ and NO Conversion (1 sl/min, 7 and 14 barg)

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<th></th>
<th>14 bar g</th>
<th>7 bar g</th>
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<td>ppm SO2</td>
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<tr>
<td>Conversion</td>
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<td>84%</td>
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<tr>
<td>ppm NOx</td>
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<tr>
<td>Conversion</td>
<td>90%</td>
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The effect of Pressure on SO$_2$ and NO Conversion (4 sl/min, 3 and 5 barg)

<table>
<thead>
<tr>
<th></th>
<th>3 bar g</th>
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<th>5 bar g</th>
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<tr>
<td></td>
<td>Inlet</td>
<td>After</td>
<td>Inlet</td>
<td>After</td>
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<tr>
<td></td>
<td></td>
<td>Compressor &amp;</td>
<td></td>
<td>Compressor &amp;</td>
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<tr>
<td></td>
<td>(Point A)</td>
<td>Receiver</td>
<td>(Point A)</td>
<td>Receiver</td>
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<tr>
<td>ppm SO$_2$</td>
<td>980</td>
<td>350</td>
<td>970</td>
<td>240</td>
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<tr>
<td>ppm NO$_x$</td>
<td>360</td>
<td>187</td>
<td>420</td>
<td>130</td>
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<td>Conversion</td>
<td>64%</td>
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<td></td>
<td>48%</td>
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<td>70%</td>
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<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>After Reactor</td>
<td>Conversion</td>
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<td></td>
<td>(Point A)</td>
<td>(Point D)</td>
<td></td>
<td>(Point A)</td>
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<tr>
<td>ppm SO$_2$</td>
<td>980</td>
<td>5</td>
<td>~100 %</td>
<td>970</td>
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<tr>
<td>ppm NO$_x$</td>
<td>360</td>
<td>139</td>
<td>61%</td>
<td>420</td>
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Effect of flowrate on SO$_2$ and NO$_x$ conversion after the compressor and receiver (Point C)

5 barg
SO$_2$ in 970 ppm
NO$_x$ in 420 ppm

![Graphs showing the effect of flowrate on SO$_2$ and NO$_x$ conversion.](image-url)
Effect of SO$_2$/NO$_x$ ratio in SO$_2$ conversion

- During the second week of experiments, SCR elements were introduced into the NRTF to allow the NO$_x$ concentration in the feed gas to the sour compression apparatus to be varied.
- This allowed the effect of varying the SO$_2$/NO$_x$ ratio on conversion of SO$_2$ to be studied.
- Here the effect of SO$_2$/NO$_x$ ratio show SO$_2$ conversion decreased as SO$_2$/NO$_x$ ratio increases
- This agrees with the theory that NO$_x$ acts as a catalyst
Gas phase mercury analysis was carried out on the NRTF but it was not possible to confirm gas phase composition after the sour compression rig.

Liquid phase analysis was carried out on the condensate from the sour compression rig. The results showed negligible Hg content in the liquid collected in the Receiver and the Reactor.

The liquid collected in the condensate separator has a Hg content one order of magnitude higher, indicating that any Hg present is removed from the gas phase with the first acidic condensate stream.
Discussion

- It is clear that:
  - $\text{SO}_x$ and $\text{NO}_x$ is removed by compression and contact with water.
  - The fact that further reaction happens in the Reactor indicates that residence time and vapour/liquid contacting are important to maximise conversion.

- Pressure and residence time have been shown to be important but we still have to separate the effect of increased residence time from the effect of higher pressure.

- The assumption of the fast rate of the Lead Chamber reaction compared to the nitric acid reactions needs to be reassessed, and this will be the focus of future work.
Conclusions

- This work supports the previous assertion that \( \text{SO}_x \) and \( \text{NO}_x \) components can be removed during compression of raw Oxyfuel-derived \( \text{CO}_2 \) given sufficient pressure, holdup and vapour/liquid contacting time.

- Therefore, for emissions control and \( \text{CO}_2 \) product purity, traditional FGD and de\( \text{NO}_x \) systems should not be required in an oxyfuel-fired coal power plant.
Plan for Development of Air Products’ Oxyfuel CO₂ Purification and Compression System

- Step 1: Lab results from Imperial College
- Step 2: Testing with real flue gas from Doosan Babcock’s NRTF
- Step 3: Rig being taken back to Imperial College where further experiments can be performed using synthetic flue gas
  - aim of gaining more understanding of the reaction mechanism and developing a kinetic model
- Step 4: Pilot technology in 2009/2010
- Step 5: Ready for bid on first 200-300 MW demonstration scale project
Thank you
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