Sulphur Impacts in Coal Fired Oxy-fuel Combustion with CCS

(Impacts and Control Options)

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Outline

- General sulphur impacts
- Pilot Work
- Sulphur Thermodynamics
- Control and Mitigation
The Oxy-fuel Process

Combustion

ASU

Coal Handling

O₂

H₂SO₄ corrosion

Recycle

Slagging & Fouling

Higher H₂S & COS

SCR – SO₃ formation

SNCR – (NH₄)₂SO₄

CO₂ purity

Compression

Transport (Pipeline, Truck, Ship)

Sequestration Site

Deep Geological Storage

CO₂ purity

Recycle

Enhanced – SO₃ coating

H₂SO₄ corrosion

Cooling - H₂SO₄

pH & porosity

Deep Geological Storage

HEX – acid dew point

Cooling - H₂SO₄
Pilot Work

- IHI Test facility
- Callide Oxy-fuel Project
- 3 coals
- Air & Oxy-fuel
- Each test ~ 3 hours
- Some work previously reported
IHI Pilot Plant

Oxy-fuel combustion flowchart

Ash Deposits

SO₂/ SO₃

PAF

Electrical heater

Furnace

Gas cooler

Air heater

Gas cooler

Bag filter

IDF

Stack

Fly Ash

Bottom Ash

Pulverized coal

PAF

Pulverized coal

IDF

Electrical heater

Steam gas heater

Water spray tower

Air

FDF/GRF

O₂
Pilot SO$_2$ Results

Oxy-fuel concentration higher but produces LESS total SO$_2$

Higher concentration acts as driver for secondary products
Pilot SO3 Results

- **SO3, ppm (dry)**
  - Measured Oxy Fired
  - Measured Air Fired

- **Acid Dew Point, °C**
  - Oxy Fired
  - Air Fired

Graphs showing the relationship between fuel sulfur content (% Fuel-S) and SO3 ppm, as well as acid dew point for Oxy and Air Fired conditions.
Pilot Ash Results

No SO3 in Bottom Ash and Radiative Deposits for other coals
Mass Balance & Thermodynamics
Theoretical Mass Balance

SO$_2$, ppm (dry)

- Measured Air
- Measured Oxy

From Mass Balance

Difference due to the formation of secondary sulphur products

Fuel-S, %
Theoretical Mass Balance

- Oxy - hot recycle
- Oxy - recycle after NOx, SOx, H2O removed
- Air Fired

Effect of Recycle

Effect of Lower Flow Rate

Theoretical SO2, ppm

Fuel-S, %
In-flame Sulphur Products

(Coal A Thermodynamics at 1500°C)

ONCE THROUGH

(O₂/CO₂ vs O₂/N₂)

WITH RECYCLE

(~69% recycle, 28% O₂ IN, 5% O₂ OUT)
SO$_2$ Conversion to SO$_3$

<table>
<thead>
<tr>
<th>SO$_3$</th>
<th>Fuel-S %, db</th>
<th>Air ppm</th>
<th>Oxy ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal A</td>
<td>0.24</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Coal B</td>
<td>0.57</td>
<td>9</td>
<td>18</td>
</tr>
<tr>
<td>Coal C</td>
<td>0.88</td>
<td>3</td>
<td>11</td>
</tr>
</tbody>
</table>

1000°C used to estimate SO$_3$ conversion for acid dew point (Okkes, Verhoff & Banchero methods)
Mitigation Options

- Air Separation Unit
- O₂
- Soot Blowing
- Low S Coal
- Coal Handling
- Limestone
- Condenser/Cooler
- Recycled Flue Gas
- Sulphur Scrubber
- ESP
- Sulphur Scrubber
- Sequestration Site
- CO₂ compression
- Transport (pipeline, truck, etc)
- Sulphur removal in compression circuit
- Deep Geological Storage

- N₂

- CO₂ compression
- Site Transport
- Site Handling
- Limestone Scrubber
- Condenser/Cooler
- Sulphur Scrubber
- Sequestration Site
- Deep Geological Storage
Control Strategies

- **SO2 limited** - low sulphur coals
- **SO2 removed** - FGD (85-98% capture)
  - Limestone addition (<50% capture)
  - High calcium coals (5-10% capture)
  - Cooling/Caustic wash (Air Liquide)
  - In compression (Air Products)
  - In purification
- **Soot-blowers**
- **Flue Gas above acid dew point**
- **Corrosion resistant materials**
Conclusion – Pilot Sulphur

- Higher SO2 in Oxy-fuel
- Higher SO3 & acid dew point
- Fly Ash & Bottom Ash unaffected
- Oxy-fuel Deposits higher in S
Conclusion- Sulphur Impacts

- Sulphur Impacts throughout oxy-fuel CCS
- Oxy-fuel SO$_2$ - higher conc, lower output
- SO$_2$ Concentration driver for S products
- Furnace Products different with recycle
- SO$_3$ conversion ~thermodynamics 1000°C
Thank you for your attention
## Sulphur Impacts

<table>
<thead>
<tr>
<th>Component</th>
<th>Impact Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>corrosion, slagging</td>
</tr>
<tr>
<td>Convective Pass</td>
<td>corrosion, fouling</td>
</tr>
<tr>
<td>SCR</td>
<td>fouling, catalytic formation- SO$_3$</td>
</tr>
<tr>
<td>ESP</td>
<td>higher performance</td>
</tr>
<tr>
<td>Heat Exchange</td>
<td>acid dew point</td>
</tr>
<tr>
<td>Compression</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>CO$_2$ Purity</td>
<td>SO$_2$</td>
</tr>
<tr>
<td>Transport</td>
<td>corrosion, H$_2$SO$_4$</td>
</tr>
<tr>
<td>Storage</td>
<td>Corrosion, injection (pH zone)</td>
</tr>
</tbody>
</table>
In-flame Sulphur Products

(Thermodynamics at 1500°C)

ONCE THROUGH

(O₂/CO₂ vs O₂/N₂)

WITH RECYCLE

(~69% recycle, 28% O₂ IN, 5% O₂ OUT)
SO$_2$ in Compression

- High H$_2$O Scenario: 500 ppm
- Low H$_2$O Scenario: 50 ppm

For Aquifer Storage:
- 3% O$_2$, 100 ppm SO$_2$, 50 ppm H$_2$O, CO$_2$ balance

For EOR Storage:
- 100 ppm O$_2$, 100 ppm SO$_2$, 500 ppm H$_2$O, CO$_2$ balance

(Dynamis Project recommendations for Pre-combustion capture)
IVD - Stuttgart

AIR-BLOWN COMBUSTION_LAUSITZ

OF27_3000 COMBUSTION_LAUSITZ

Distance from Burner [m]
Sulphur Products & Effects

Acid dew point
Corrosion in compression
Convective Fouling
In-flame reduction products

Equilibrium

Temperature, °C

H₂SO₄
SO₃
SO₂
Limestone Addition

* Assumes max Ca/S = 2
Limestone Addition

* Assumes max Ca/S = 2