The Sulphur Mass Balance in Oxy-Fuel Combustion of Lignite

An experimental study

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Introduction

Aims of the work

• Quantify sulphur sinks

• Are there differences in sulphur chemistry between air and oxy-fuel combustion?
Motivation of the work

- Lowered SO$_2$ emissions in literature
- Design of the flue gas cleaning
- Sulphur self-retention of the ash
- SO$_2$ concentration influences corrosion
Experiments

Chalmers 100kW oxy-fuel test unit

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Schematic of the test unit

Fuel → Oxidiser → Pre-heater → (Air) → Dry flue gas recycle → Stack

Furnace → Cyclone → Flue gas cooler → Flue gas condenser

Bottom ash → Cyclone ash → Cooler ash → Filter ash

Gas sample: SO₂, CO₂, O₂ and CO

Condenser water
Sulphur mass balance:

\[
m_{S,\text{fuel}} = m_{S,\text{ash}} + m_{S,\text{gas}} + m_{S,\text{water}}
\]

Sulphur ash mass flow:

\[
m_{S,\text{ash}} = m_{S,\text{bottom ash}} + m_{S,\text{cyclone ash}} + m_{S,\text{residual ash}}
\]
Determination of S-flows

Sulphur ash flows:

\[ m_{S,\text{bottom ash}} = Y_{S,\text{bottom ash}} \cdot m_{\text{bottom ash}} \]
\[ m_{S,\text{cyclone ash}} = Y_{S,\text{cyclone ash}} \cdot m_{\text{cyclone ash}} \]
\[ m_{S,\text{residual ash}} = Y_{S,\text{residual ash}} \cdot m_{\text{residual ash}} \]

Residual ash flow:

\[ m_{\text{residual ash}} = Y_{S} \cdot m_{\text{fuel}} - m_{\text{bottom ash}} - m_{\text{cyclone ash}} \]

Y_S... sulphur mass concentration
Determination of S-flows

**Sulphur flue gas flow:**

\[
\frac{m_{S,\text{gas}}}{m_{S,\text{fuel}}} = \frac{X_{SO_2,\text{measured}}}{X_{SO_2,\text{max}}} \cdot Y_{S,\text{fuel}} \cdot m_{\text{fuel}}
\]

Conversion of fuel-S to SO₂

**Sulphur fuel flow:**

\[
m_{S,\text{fuel}} = Y_{S,\text{fuel}} \cdot m_{\text{fuel}}
\]

**Sulphur water flow:**

\[
m_{S,\text{water}} = Y_{S,\text{water}} \cdot m_{\text{condenser water}}
\]
Test cases

- Air fired case
- Dry oxy-fuel case OF35
- Wet oxy-fuel case OF43w

In all test cases:
- Predried Lausitz lignite 13kg/h, 76kW

Roughly same max. temperatures
**Fuel analysis (Lausitz lignite)**

<table>
<thead>
<tr>
<th></th>
<th>Proximate [wt. %, as received]</th>
<th>Volatile matter [wt. %, d.a.f.]</th>
<th>Ultimate [wt. %, d.a.f.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Y_{moist.}$</td>
<td>$Y_{ash}$</td>
<td>$Y_{comb.}$</td>
</tr>
<tr>
<td><strong>Air</strong></td>
<td>10.7</td>
<td>4.38</td>
<td>84.9</td>
</tr>
<tr>
<td><strong>OF35</strong></td>
<td>10.6</td>
<td>4.56</td>
<td>84.8</td>
</tr>
<tr>
<td><strong>OF43w</strong></td>
<td>10.5</td>
<td>4.75</td>
<td>84.7</td>
</tr>
</tbody>
</table>
Results

Conversion to $\text{SO}_2 / \text{SO}_2$ concentrations

- Air: 67%
  - 550 ppm (dry)
  - 500 ppm (wet)
- OF35: 43%
  - 1870 ppm (dry)
  - 1600 ppm (wet)
- OF43w: 46%
  - 1960 ppm (dry)
  - 1300 ppm (wet)

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Ash flows / S-concentrations

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>OF35</th>
<th>OF43w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual ash</td>
<td>49g/h</td>
<td>72g/h</td>
<td>112g/h</td>
</tr>
<tr>
<td></td>
<td>9-15% S</td>
<td>8-17% S</td>
<td>10-18% S</td>
</tr>
<tr>
<td>Cyclone ash</td>
<td>412g/h</td>
<td>385g/h</td>
<td>378g/h</td>
</tr>
<tr>
<td></td>
<td>3.0% S</td>
<td>3.6% S</td>
<td>3.7% S</td>
</tr>
<tr>
<td>Bottom ash</td>
<td>109g/h</td>
<td>136g/h</td>
<td>128g/h</td>
</tr>
<tr>
<td></td>
<td>6.6% S</td>
<td>6.5% S</td>
<td>6.8% S</td>
</tr>
</tbody>
</table>

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Sulphur flow in ash

- **Residual ash**: 4 - 7g/h
- **Cyclone ash**: 12g/h
- **Bottom ash**: 7g/h

Air: 12g/h

OF35: 14g/h

OF43w: 14g/h

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### Sulphur mass balance

#### Air

- **S in water**: 0.5%
- **S in flue gas**: 67%
- **S in ash**: 24 - 27%
- **Difference**: 6 - 9%

#### OF35

- **S in water**: 1.2%
- **S in flue gas**: 43%
- **S in ash**: 29 - 35%
- **Difference**: 21 - 27%

#### OF43w

- **S in water**: 1.7%
- **S in flue gas**: 46%
- **S in ash**: 35 - 44%
- **Difference**: 8 - 17%

Sulphur mass flow in the fuel is set to 100%
Conclusions

- Lowered emission of SO₂ by unit energy in oxy-fuel combustion compared to air firing
- More than 3 times higher SO₂ concentrations in the flue gas from oxy-fuel combustion
- Sulphur mass flow in the ash is higher in oxy-fuel compared to air firing
- Sulphur mass flow in condenser water is low
Ongoing work and future work

- Clarify the gap in the mass balance
- Parameter study SO$_2$ emissions
- Limestone + lignite
- SO$_3$ measurements
- Particle sampling from the combustion zone
Vattenfall AB is acknowledged for financial support

Thank you for your attention!
**Sulphur balance**

- **SO₂**
  - Reactions with ash to **Na₂SO₄, K₂SO₄, CaSO₄, MgSO₄**
- **SO₃**
- **H₂SO₄**
- **Conden-sation**

**Sulphur in fuel**
- Sulphides (FeS₂) sulphates
- Organic compounds

**SO₂ and 0.1...5% SO₃**

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Fate of sulphur during coal combustion weiss nicht ob das mit soll/kann

- **Sulphur in coal:**
  - Pyrite (FeS₂), organically bound sulphur,...

- **Combustion**
  - Gases: SO₂, SO₃, H₂S,...
  - Sulphur in ash:
    - Not converted
    - Captured (sulphates)
Sulphur release, laboratory conditions

- **Y-axis:** Release of lignite-S to SO$_2$ in % ts from coal
- **X-axis:** Combustion temperature [°C]

The graph shows the release of sulphur (as % of total sample weight) from lignite as a function of combustion temperature. Different markers represent different samples, indicating variations in sulphur release with temperature.
Discussion

• Lower conversion of fuel-S to SO₂
  → Higher sulphur ash mass flows

Possible reason:
SO₂ concentration affect the ash self retention

• However a higher difference in oxy-fuel
  → Difficult at do sulphur mass balance
  Difficult to get residual ash samples
Sulphur release, laboratory conditions

Release of lignite-S to SO\textsubscript{2}

\textit{in \% ts from coal}

Combustion temperature [\degree C]
Sulphur mass balance

- $\text{SO}_2$ with NDIR instrument (NGA 2000)

- Ash amount
  - Bottom and cyclone ash were weighed
  - Residual ash by difference

- Sulphur in ash and fuel
  - Standard method SS 187177

- Sulphur in condenser water
  - Solubilize with nitric acid ICP-OES inductively coupled plasma - optical emission spectrometer

Durch diese Sachen schnell durchgehen.

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Sulphur release from ashes, laboratory conditions

![Graph showing sulphur release from ashes at different temperatures for Cyclone ash, Filter ash, and Bottom ash. The x-axis represents temperature in °C, ranging from 400 to 1400. The y-axis represents sulphur release from ashes, ranging from 0% to 100%. The data points indicate higher sulphur release at higher temperatures.]