3rd Oxyfuel Combustion Conference
Ponferrada, Spain, 9th - 13th September 2013

3D Modelling of Limestone Reactions in Oxygen Fired CFB

Presented by: Sirpa Rahiala
Co-authors: Kari Myöhänen, Timo Hyppänen

Lappeenranta University of Technology
Presentation outline

- 3D CFB furnace model.
- Limestone reactions in air-fired and oxygen-fired CFB combustion.
- Modelling results at different furnace temperatures.
- Utilization of steady-state model results for transient particle model.
- Modelling results of Oxy-CFB-300 project.
- Discussion and conclusions.

Acknowledgements:
This work was carried out in the Carbon Capture and Storage Program (CCSP) research program coordinated by CLEEN Ltd. with funding from the Finnish Funding Agency for Technology and Innovation, Tekes.
Three-dimensional model

- A steady-state, semi-empirical model, which describes the CFB furnace process (Myöhänen and Hyppänen, 2009).
  - Linked with sub models for separators and external heat exchangers.

- 3D-modelling of furnace based on control volume method.

- Validation based on field tests at pilot scale and full scale units.
Limestone reactions in CFB combustion

Above calcination temperature:
Calcination
\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
Sulfation
\[ \text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 \]

Below calcination temperature:
Carbonation
\[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \]
Direct sulfation
\[ \text{CaCO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \]

Reducing conditions:
Desulfation (decomposition of sulfate)
\[ \text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \]
**Simplified model equations for limestone**

**Empirical solid concentration fields for particle sizes**

\[ \varepsilon_{\text{sorb},i} = (\varepsilon_{\text{btm}} - \varepsilon_{\text{top}})e^{-\varepsilon_{\text{tr}}H} + \varepsilon_{\text{top}}e^{\varepsilon_{\text{tr}}(H-H)} \]

**Continuity equation for sorbent (particle size )**

\[ \oint_A \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} \mathbf{v}_{\text{sorb},i} \cdot dA = \oint_V \phi^{''''}_{\text{sorb},i} dV + \oint_V R^{''''}_{\text{sorb},i} dV - \oint_V \sum_{j,j \neq i} k_{C,\text{sorb},ji} \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} dV + \oint_V \sum_{j,j \neq i} k_{C,\text{sorb},ji} \varepsilon_{\text{sorb},j} \rho_{\text{sorb}} dV \]

- **Convection**
- **Sources**
- **Reactions**
- **Comminution out**
- **Comminution in**

**Potential flow equation**

\[ \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} \mathbf{v}_{\text{sorb},i} = \nabla P_{\text{f,s,sorb},i} \]

**Velocity fields for each particle size**

**Reactivity equations for different reactions**

\[ k_{\text{calc},i} = 1.22 a_{\text{calc},i} \exp\left(\frac{-4026}{T}\right)(p_{eq} - p_{CO_2})A_{m,0,Co_3,MaCO_3} \]

\[ k_{\text{carb},i} = 0.0169 a_{\text{carb},i} \exp\left(\frac{-3488}{T}\right)(p_{CO_2} - p_{eq})A_{m,0,Co_0,MaO} \]

\[ k_{\text{sulf},i} = 0.001 a_{\text{sulf},i} \exp\left(\frac{-2400}{T}\right)\exp(-8 X_{\text{CaSO_3,j}})C_{SO_2}C_{CO_2}A_{m,0,CoM,MaO} \]

\[ k_{\text{dirs},i} = 0.01 a_{\text{dirs},i} \exp\left(\frac{-3031}{T}\right)C_{SO_2}C_{CO_2}^{0.75}C_{O_2}^{0.01}A_{m,0,Co_3,MaCO_3} \]

\[ k_{\text{desul}} = 0.005 a_{\text{desul},i} \exp\left(\frac{-10000}{T}\right)C_{CO_2}A_{m,0,CoO_4,MaSO_4} \]

**Combined reaction rates for sorbent species**

\[ R_{r,i}'' = \sum_{r} k_{r,\text{react},i} \varepsilon_{r,i} \rho_{r} \]

**Continuity equation for sorbent species**

\[ \oint_A w_{r,i} \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} \mathbf{v}_{\text{sorb},i} \cdot dA - \oint_V \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} D_{\text{sorb},i} \nabla w_{r,i} \cdot dA = \oint_V \phi_{r,i}'' dV + \oint_V R_{r,i}'' dV \]

- \[ \sum_{j,j \neq i} w_{r,i} k_{C,\text{sorb},ji} \varepsilon_{\text{sorb},i} \rho_{\text{sorb}} dV + \oint_V \sum_{j,j \neq i} w_{r,j} k_{C,\text{sorb},ji} \varepsilon_{\text{sorb},j} \rho_{\text{sorb}} dV \]

**Concentration fields of different species**

**Lappeenranta University of Technology**
Modelling the effect of furnace temperature on sulfur capture

- The model cases were based on earlier study, which investigated conversion of Lagisza CFB to oxygen fired mode (Myöhänen, et al., 2009).

- Cases:
  - AirRef: Air-fired reference
  - Oxy_HighT: Oxygen-fired high temperature
  - Oxy_LowT: Oxygen-fired low temperature
  - Oxy_MidT: Oxygen fired middle temperature

- The model cases in this presentation differ from the cases presented in the abstract:
  - Same gas recycle ratio in each oxygen-fired case.
  - No external heat transfer units.
  - Updated reactivity correlations.

Original furnace geometry
Model domain
Mesh 37240 cells
Cell size 0.39 x 0.38 x 0.60 m³
## Operating conditions

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Operating conditions vs. calcination curve

![Graph showing Operating conditions vs. calcination curve](image)

- **Oxy_LowT**
- **Oxy_MidT**
- **Oxy_HighT**

**Axes:**
- Y-axis: CO2 partial pressure (atm)
- X-axis: Temperature (°C)

**Equilibrium curve** and **AirRef** are indicated on the graph.

Lappeenranta University of Technology
Calcination and carbonation profiles

Calcination

AirRef  Oxy_HighT  Oxy_LowT  Oxy_MidT

Carbonation

AirRef  Oxy_HighT  Oxy_LowT  Oxy_MidT
Total sulfur capture and sulfur dioxide profile

Total sulfur capture
- Sulfur capture = sulfation + direct sulfation - desulfation

<table>
<thead>
<tr>
<th>Sulfur capture (mol/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
</tr>
<tr>
<td>0.04</td>
</tr>
<tr>
<td>0.03</td>
</tr>
<tr>
<td>0.02</td>
</tr>
<tr>
<td>0.01</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>

Sulfur dioxide concentration

Sulfur capture = sulfation + direct sulfation - desulfation
Indirect and direct sulfation and desulfation in Oxy_MidT
Sorbent reactions at lower vs. upper furnace (Oxy_HighT)

Logarithmic scales
Calcination  Sulfation

h < 2.4 m: 2.9 mol/s (20%)
h > 2.4 m: 11.8 mol/s (80%)

h < 2.4 m: 1.6 mol/s (34%)
h > 2.4 m: 3.0 mol/s (66%)

Height < 2.4 m: 3% of total volume
Height > 2.4 m: 97% of total volume
Molar balance of sulfur dioxide

AirRef (sources)
AirRef (sinks)
Oxy_HighT (sources)
Oxy_HighT (sinks)
Oxy_LowT (sources)
Oxy_LowT (sinks)
Oxy_MidT (sources)
Oxy_MidT (sinks)

- Gas feed (recirc.)
- Char combustion
- H2S combustion
- Desulfation
- Sulfation
- Direct sulfation
- Recirc. gas
- Flue gas to stack

Molar flow of SO₂ (mol/s)
Utilization of the steady-state 3D-data for a transient single particle model for limestone

Recorded process data during first 300 s of particle history

Environment data T, CO₂, O₂, SO₂, ...

Sulfur capture solved by particle model (Rahiala et al., 2013)
Calculation of Oxy-CFB-300 Compostilla

- Calculation cases:
  - Oxy100  Oxygen-fired 100% load
  - Oxy40   Oxygen-fired 40% load
  - Air90   Air-fired maximum (90% load)
  - Air40   Air-fired 40% load

- Modelled operating conditions:
Sulfur dioxide and total sulfur capture in Oxy-CFB-300

Sulfur dioxide

Total sulfur capture (= sulfation + direct sulfation – desulfation)

Note scale
Molar balance of sulfur dioxide

- Oxy100 (sources)
- Oxy100 (sinks)
- Air90 (sources)
- Air90 (sinks)
- Oxy40 (sources)
- Oxy40 (sinks)
- Air40 (sources)
- Air40 (sinks)

Molar flow of SO₂ (mol/s)

Legend:
- Gas feed (recirc.)
- Char combustion
- H₂S combustion
- Desulfation
- Sulfation
- Direct sulfation
- Recirc. gas
- Flue gas to stack
Discussion and conclusions

− Limestone reactions and sulfur capture in air-fired and oxygen-fired CFB have been studied by three-dimensional modeling of the furnace.

− Based on the model results, the sulfur capture in oxygen-fired mode is highest when the operating temperature is above calcination temperature and the sulfur capture is by indirect sulfation.

− The sulfur retention is better in oxygen-fired than air-fired conditions, because of higher SO$_2$ concentration inside the furnace.

− At low load operation, the furnace temperature drops below the calcination temperature and the sulfur capture occurs by direct sulfation and the sulfur retention is smaller. This leads to higher SO$_2$ concentration, which compensates the decrease.

− The sorbent reaction rates are fastest at the bottom of the furnace, where the sorbent concentration is high. The volume share of this region is very small however, thus the largest proportion of the integrated reactions are occurring in the upper furnace, above the dense bed region.
References

