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:

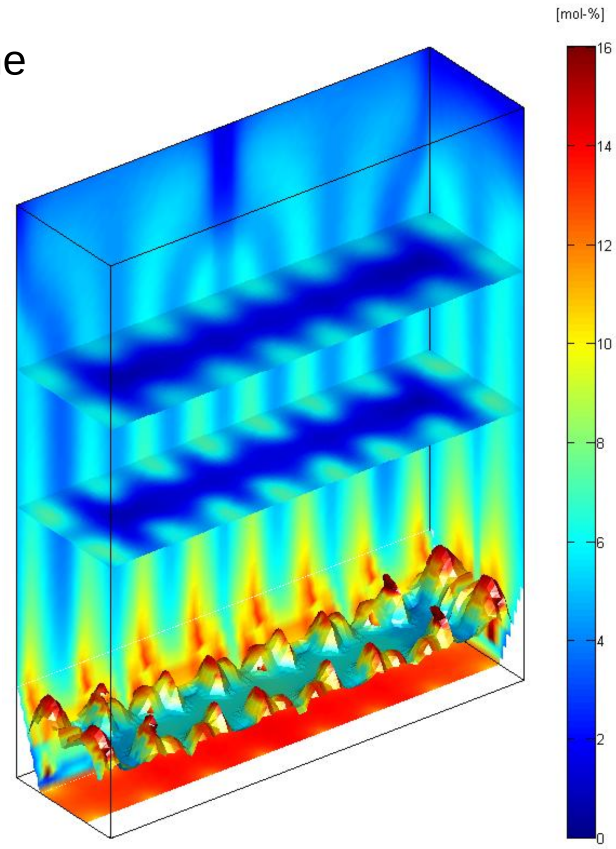
This work was carried out in the Carbon Capture and Storage Program (CCSP) research program coordinated by CLEEN Ltd. with funding from the Finnish Funding Agency for Technology and Innovation, Tekes.

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.

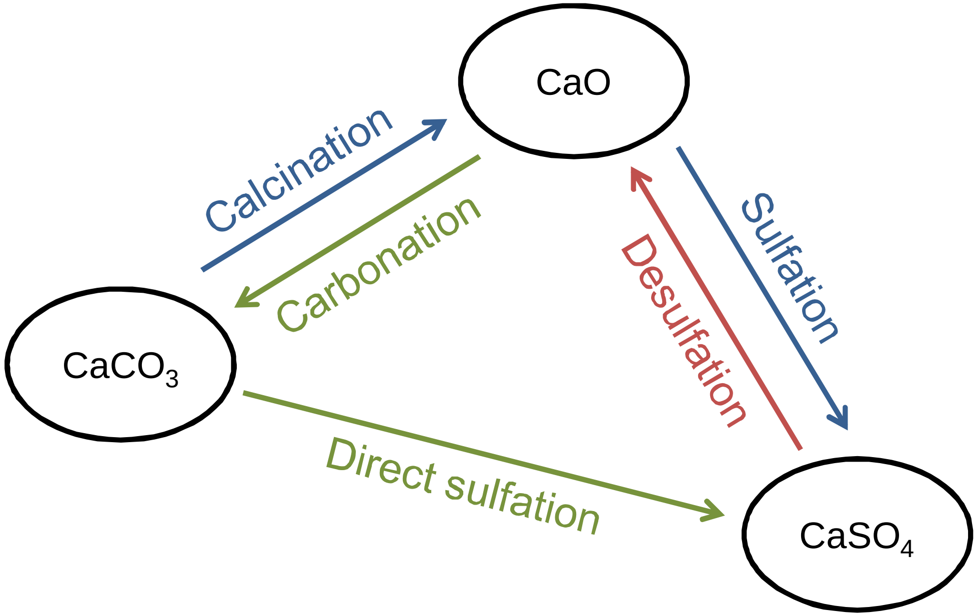
- 3D-modelling of furnace based on control volume method.

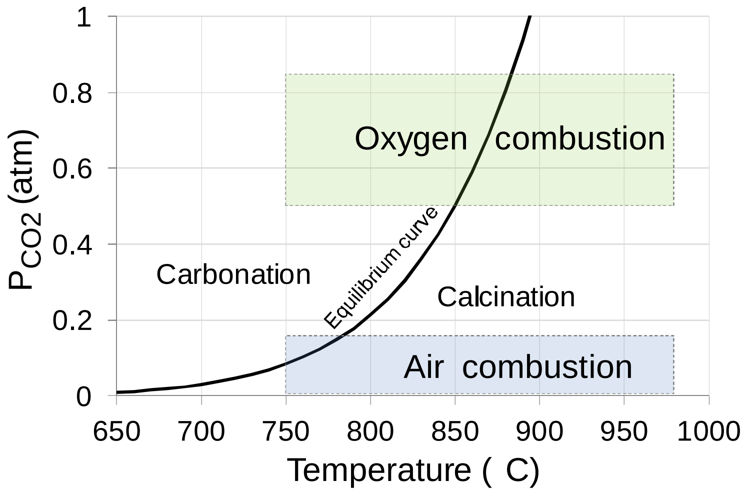
- Validation based on field tests at pilot scale and full scale units.



Modeled oxygen profile of a large scale CFB combustor

Limestone reactions in CFB combustion





Above calcination temperature:

Calcination
$CaCO_3 \rightarrow CaO + CO_2$

Sulfation
$CaO + SO_2 + ½O_2 \rightarrow CaSO_4$

Below calcination temperature:

Carbonation
$CaO + CO_2 \rightarrow CaCO_3$

Direct sulfation
$CaCO_3 + SO_2 + ½O_2 \rightarrow CaSO_4 + CO_2$

Reducing conditions:

Desulfation (decomposition of sulfate)
$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$

Simplified model equations for limestone

Empirical solid concentration fields for particle sizes i

$$\varepsilon_{sorb,i} = \left(\varepsilon_{btm} - \varepsilon_{top} e^{c_{di} H}\right) e^{-c_{tr} h} + \varepsilon_{top} e^{c_{di}(H-h)}$$

Potential flow equation

$$\varepsilon_{sorb,i} \rho_{sorb} \mathbf{v}_{sorb,i} = \nabla P_{fs,sorb,i}$$

Velocity fields for each particle size i

$$\mathbf{v}_{sorb,i}$$

Continuity equation for sorbent (particle size i)

$$\oint_A \varepsilon_{sorb,i} \rho_{sorb} \mathbf{v}_{sorb,i} \cdot d\mathbf{A} = \int_V \phi'''_{sorb,i} \, dV + \int_V R'''_{sorb,i} \, dV - \int_V \sum_{j,j \neq i} k_{C,sorb,ij} \varepsilon_{sorb,i} \rho_{sorb} \, dV + \int_V \sum_{j,j \neq i} k_{C,sorb,ji} \varepsilon_{sorb,j} \rho_{sorb} \, dV$$

convection | sources | reactions | comminution out | comminution in

Reactivity equations for different reactions

$$k_{calc,i} = 1.22 \, a_{calc,i} \exp\left(\frac{-4026}{T}\right)\left(p_{eq} - p_{CO_2}\right) A_{m0,CaCO_3} M_{CaCO_3}$$

$$k_{carb,i} = 0.0169 \, a_{carb,i} \exp\left(\frac{-3488}{T}\right)\left(p_{CO_2} - p_{eq}\right) A_{m0,CaO} M_{CaO}$$

$$k_{sulf,i} = 0.001 \, a_{sulf,i} \exp\left(\frac{-2400}{T}\right) \exp\left(-8 \, X_{CaSO_4,i}\right) C_{SO_2} C_{O_2} A_{m0,CaO} M_{CaO}$$

$$k_{dirs,i} = 0.01 \, a_{dirs,i} \exp\left(\frac{-3031}{T}\right) C_{SO_2}^{0.9} C_{CO_2}^{-0.75} C_{O_2}^{0.001} A_{m0,CaCO_3} M_{CaCO_3}$$

$$k_{desu,i} = 0.005 \, a_{desu,i} \exp\left(\frac{-10\,000}{T}\right) C_{CO} A_{m0,CaSO_4} M_{CaSO_4}$$

Combined reaction rates for sorbent species r

$$R'''_{r,i} = \sum k_{reac,i} \varepsilon_{r,i} \rho_r$$

Continuity equation for sorbent species
(r = $CaCO_3$, CaO, $CaSO_4$, i = particle size)

$$\oint_A w_{r,i} \varepsilon_{sorb,i} \rho_{sorb} \mathbf{v}_{sorb,i} \cdot d\mathbf{A} - \oint_A \varepsilon_{sorb,i} \rho_{sorb} D_{sorb,i} \nabla w_{r,i} \cdot d\mathbf{A}$$

$$= \int_V \phi'''_{r,i} \, dV + \int_V R'''_{r,i} \, dV$$

$$- \int_V \sum_{j,j \neq i} w_{r,i} k_{C,sorb,ij} \varepsilon_{sorb,i} \rho_{sorb} \, dV + \int_V \sum_{j,j \neq i} w_{r,j} k_{C,sorb,ji} \varepsilon_{sorb,j} \rho_{sorb} \, dV$$

Concentration fields of different species

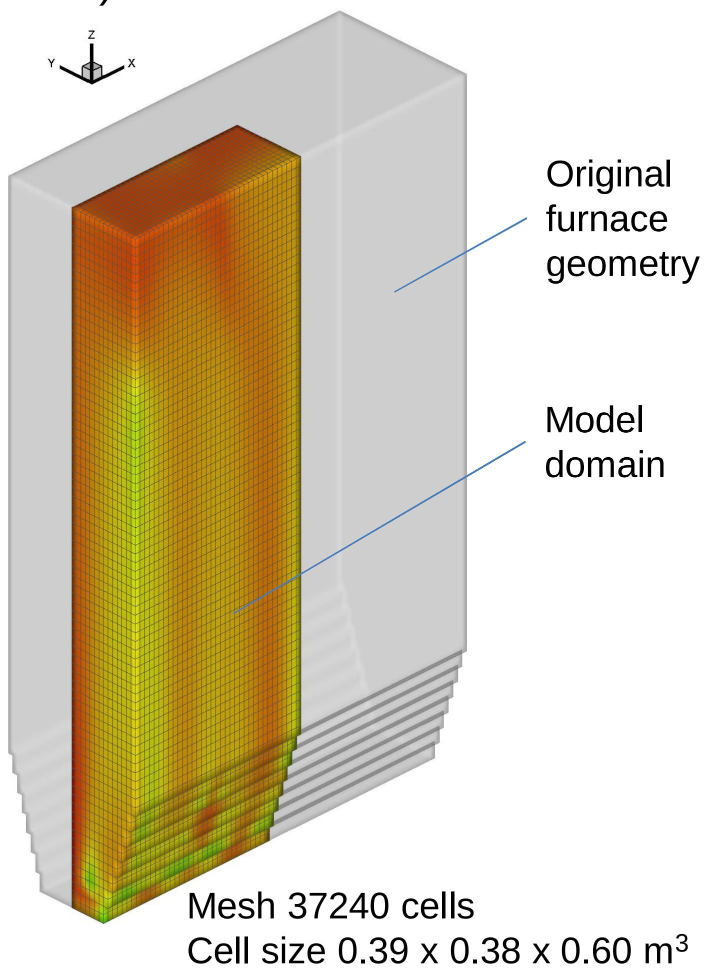
$$w_{r,i}$$

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.



Operating conditions

Process data

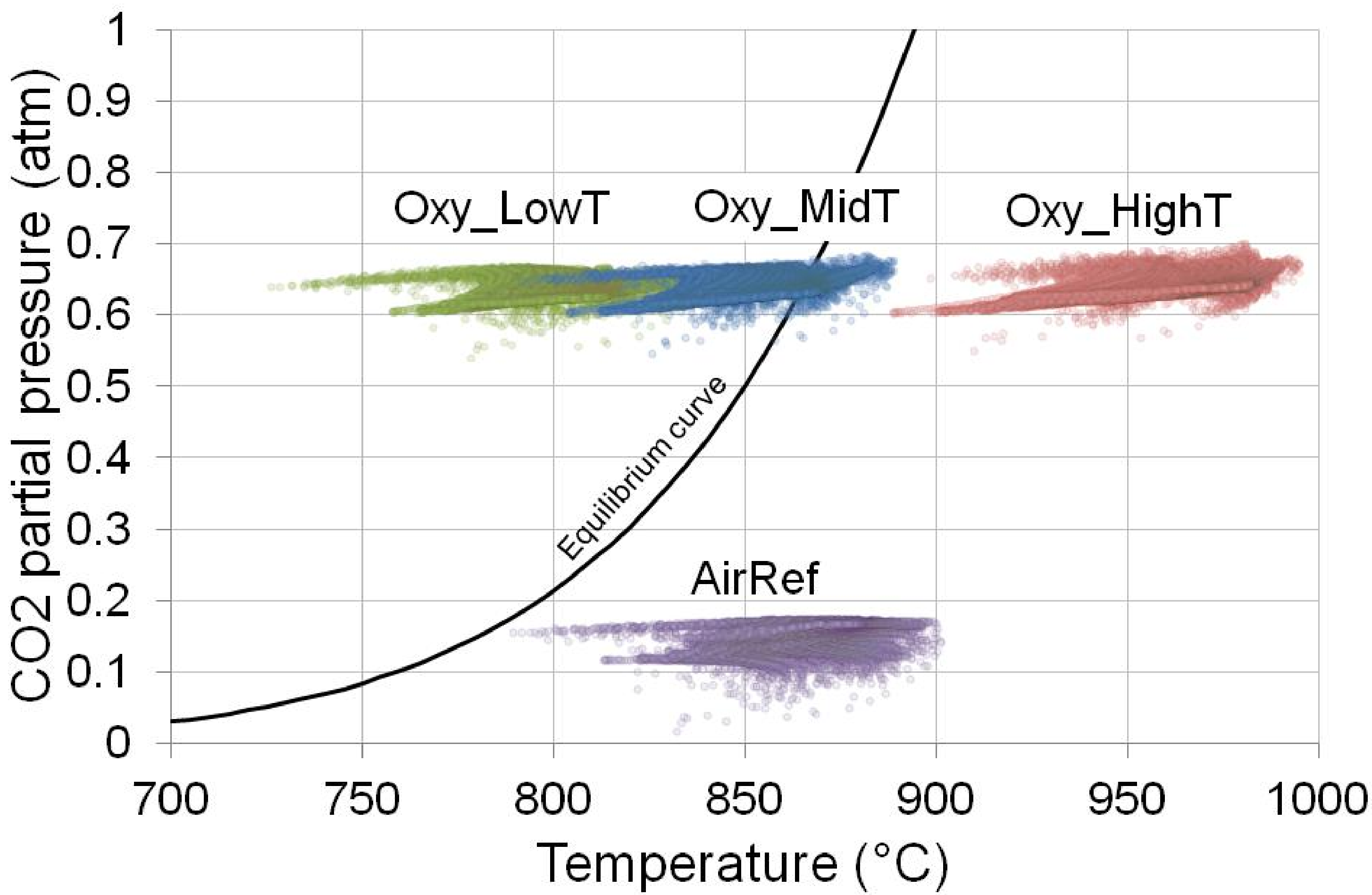
Parameter	Unit	AirRef	Oxy_HighT	Oxy_LowT	Oxy_MidT
Fuel flow rate	kg/s	13.4	13.4	13.4	13.4
Limestone flow rate	kg/s	1.6	1.6	1.6	1.6
Ca/S-ratio in feed	mol/mol	3.1	3.1	3.1	3.1
Furnace gas flow rate	kg/s	116	116	116	116
Recycle gas ratio (wet)	%	0	71	71	71
Primary oxidant O_2	%-wet	20.6	23.8	23.8	23.8
Bed temperature	°C	870	963	817	870
Furnace exit temperature	°C	855	945	791	843
Flue gas O_2	%-wet	2.3	1.9	1.9	1.9
Flue gas CO_2	%-wet	15.2	62.7	62.1	62.2
Flue gas H_2O	%-wet	9.4	32.5	33.1	33.0

Fuel analysis

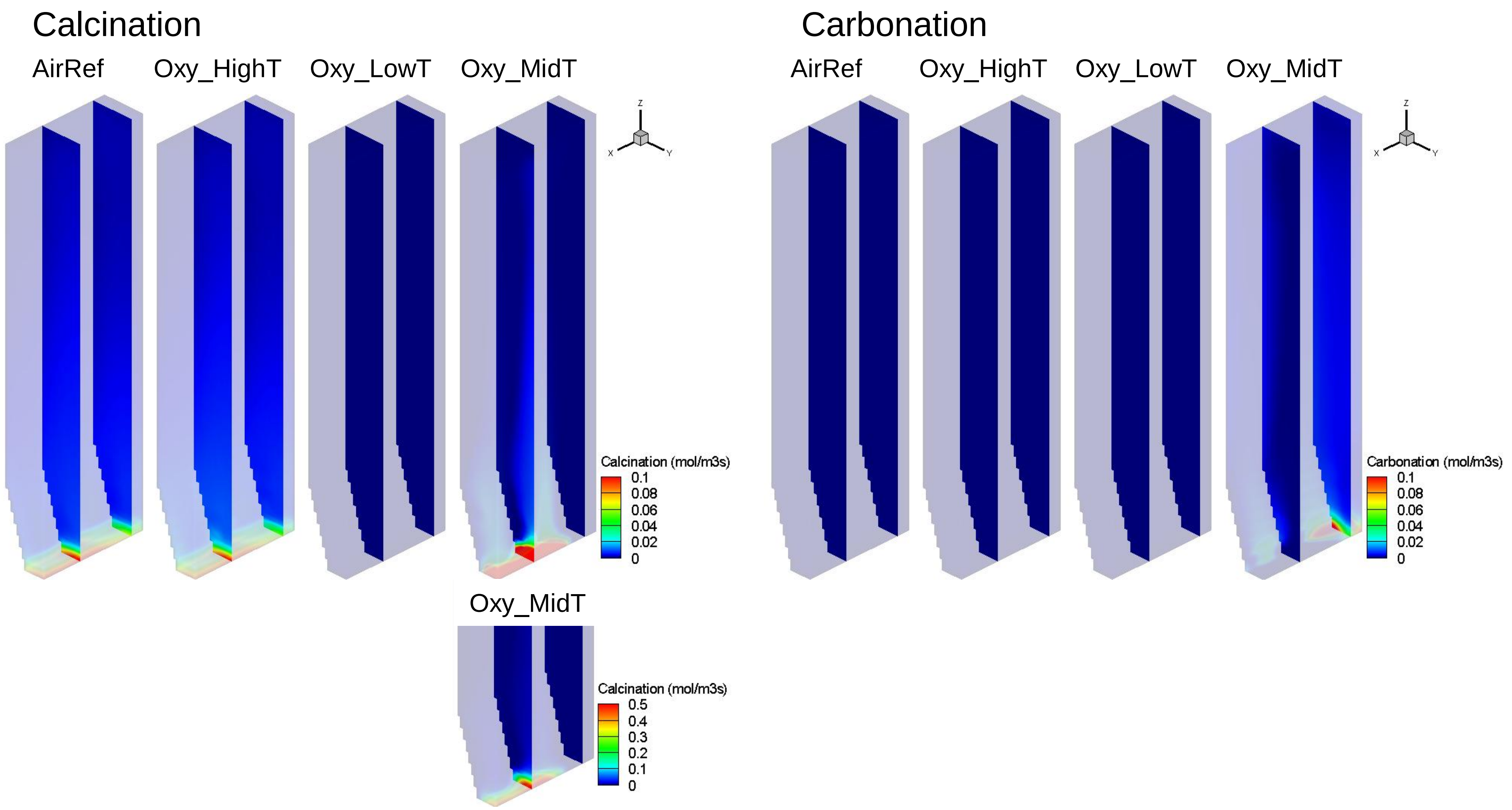
Proximate analysis	Char	Volatiles	Moisture	Ash	
(%, as fired)	41.6	23.4	12.0	23.0	
Ultimate analysis	C	H	N	S	O
(%, daf)	80.6	5.2	0.8	1.8	11.5
HHV (MJ/kg, in d.s.)	23.06				

Limestone: Calcitic limestone, 97% CaCO3, 3% inert

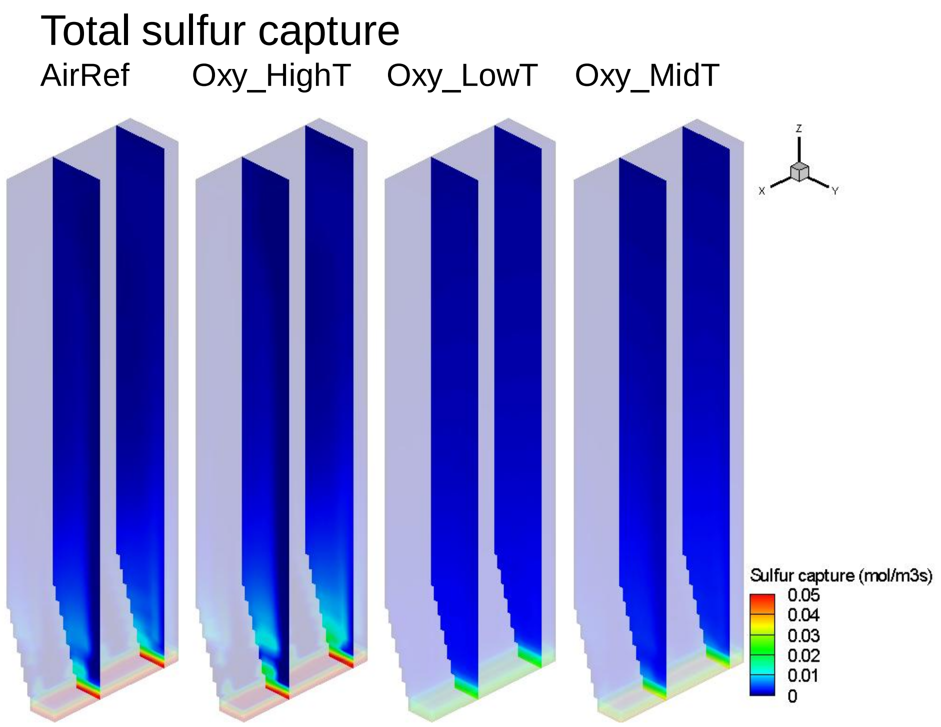
Operating conditions vs. calcination curve

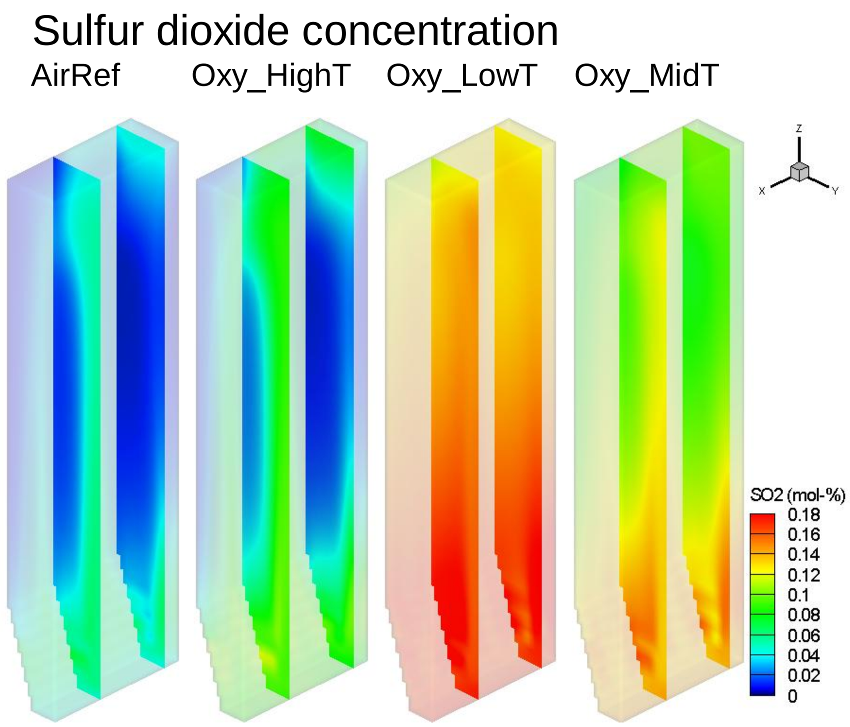


Calcination and carbonation profiles



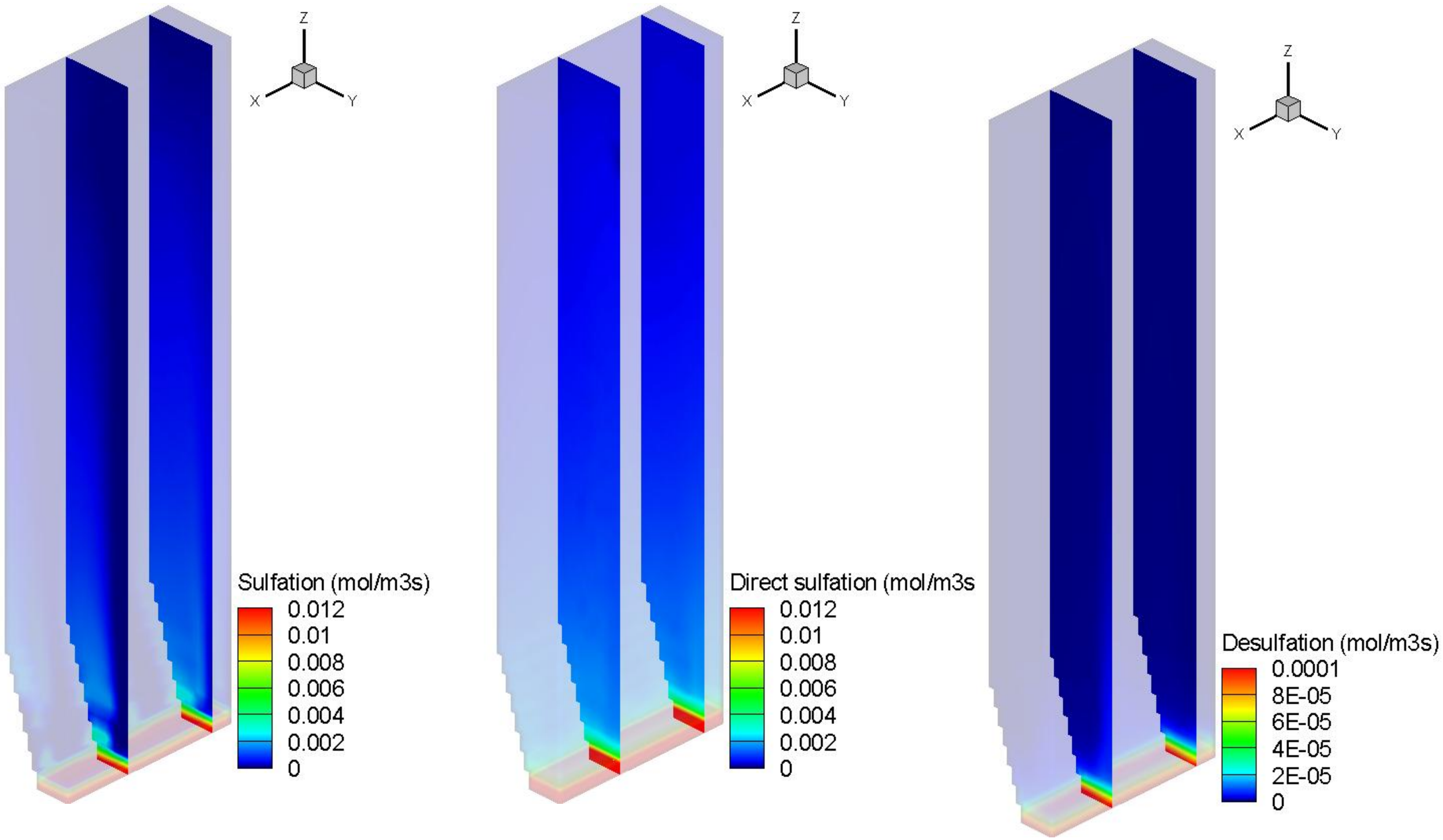
Total sulfur capture and sulfur dioxide profile





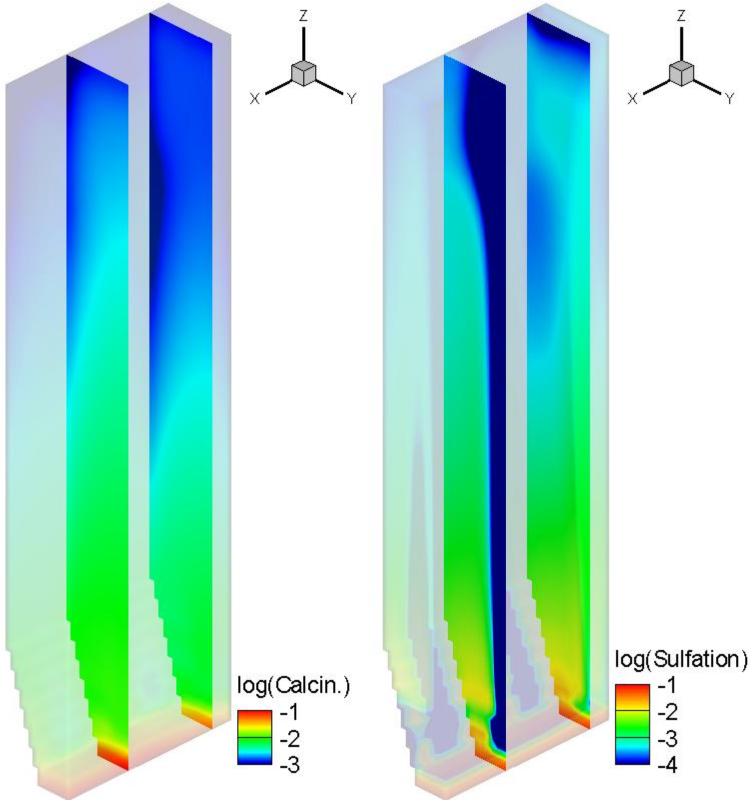
Sulfur capture = sulfation + direct sulfation – desulfation

Indirect and direct sulfation and desulfation in Oxy_MidT



Sorbent reactions at lower vs. upper furnace (Oxy_HighT)

Logarithmic scales

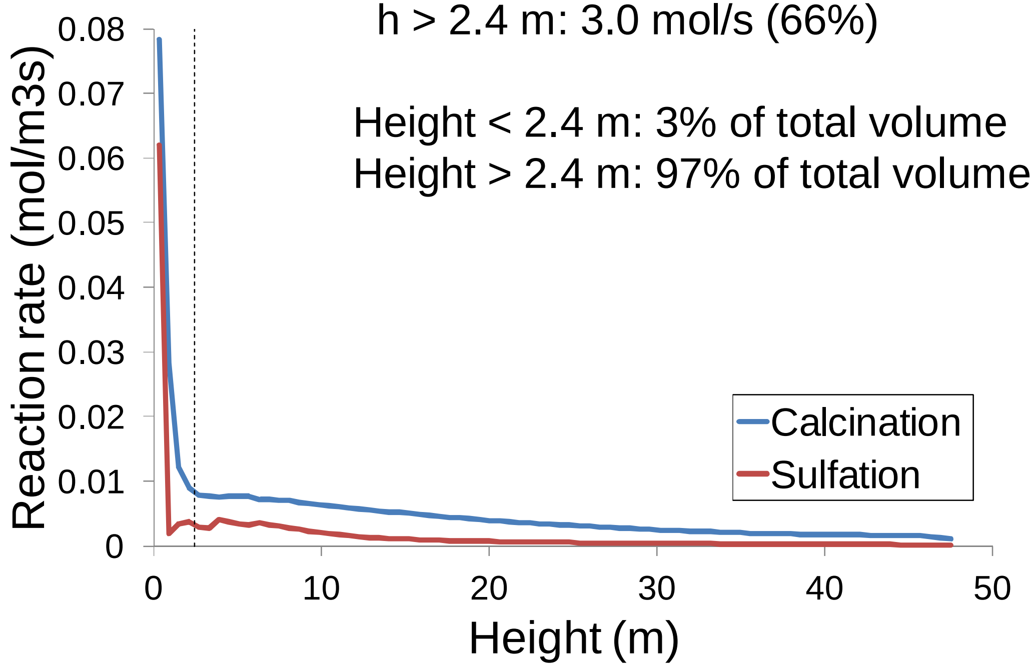


Integrated reaction rates

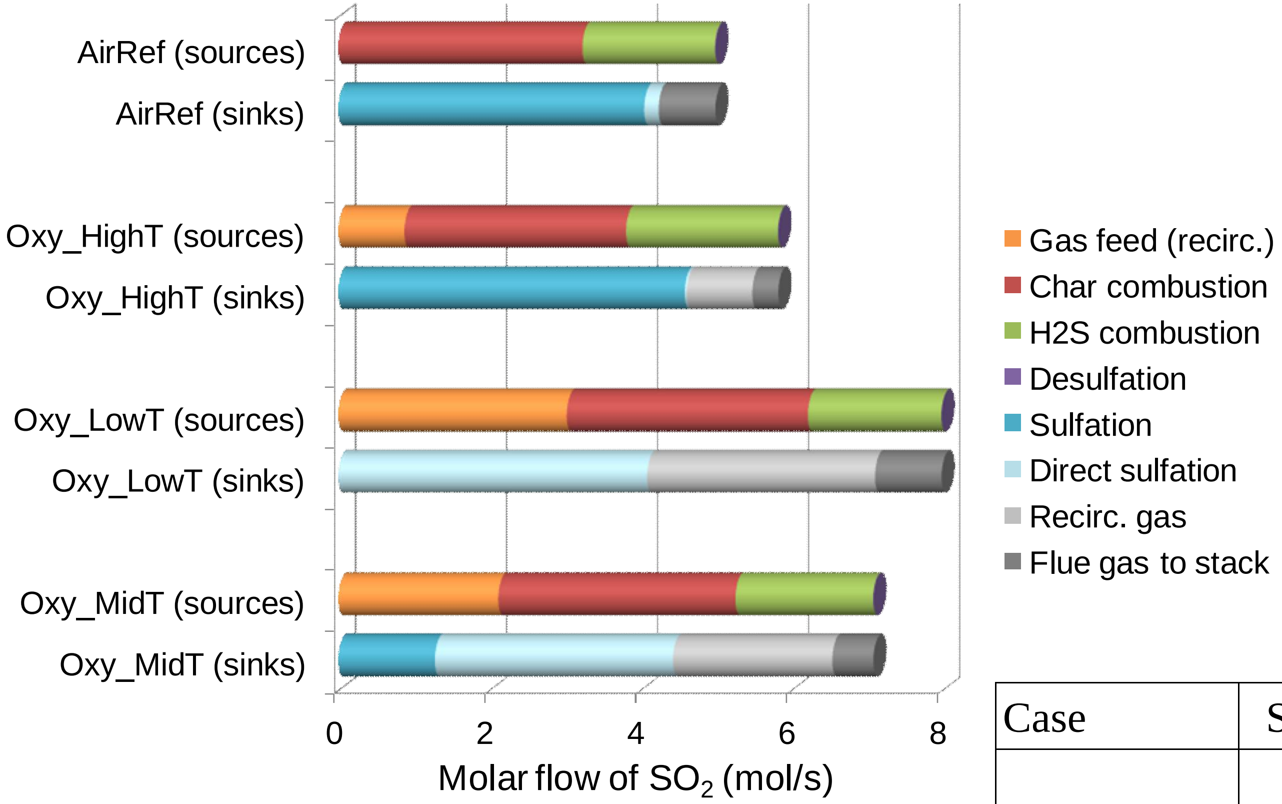
Calcination
h < 2.4 m: 2.9 mol/s (20%)
h > 2.4 m: 11.8 mol/s (80%)

Sulfation
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

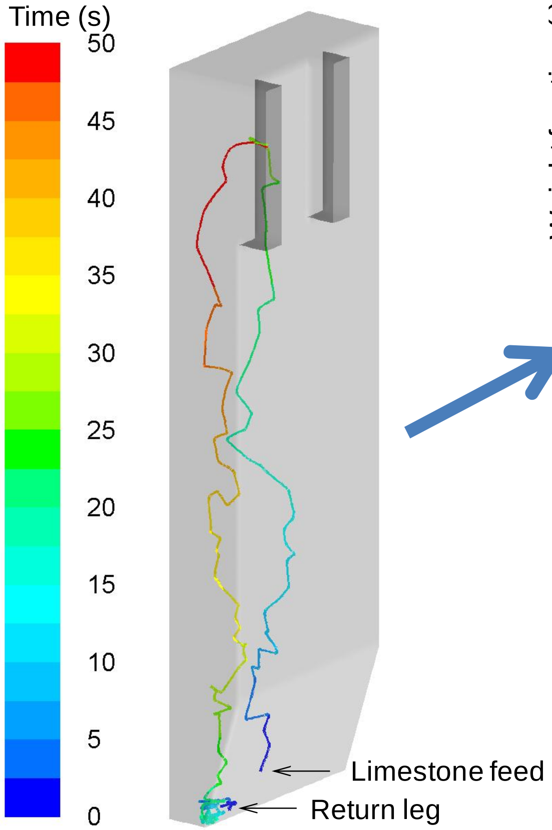


Molar balance of sulfur dioxide

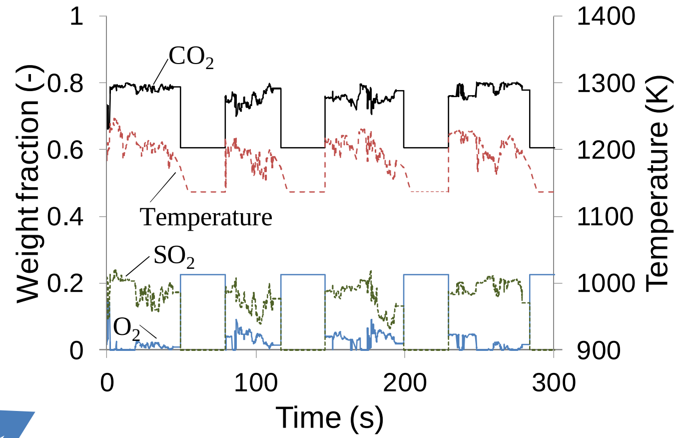


Case	S-retention (%-mol)	Flue gas SO2 (ppm-wet)
AirRef	84.9	195
Oxy_HighT	93.0	368
Oxy_LowT	82.2	1286
Oxy_MidT	89.1	898

Utilization of the steady-state 3D-data for a transient single particle model for limestone

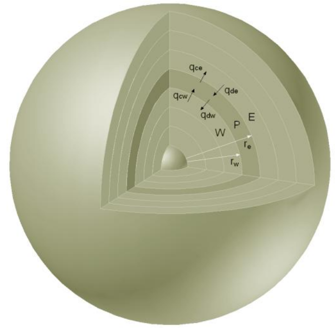


Solved particle tracks in steady-state 3D-model

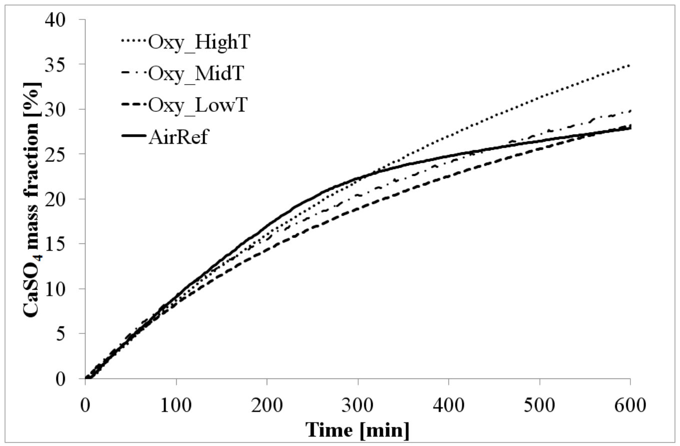


Recorded process data during first 300 s of particle history

Environment data
T, CO_2, O_2, SO_2, ...



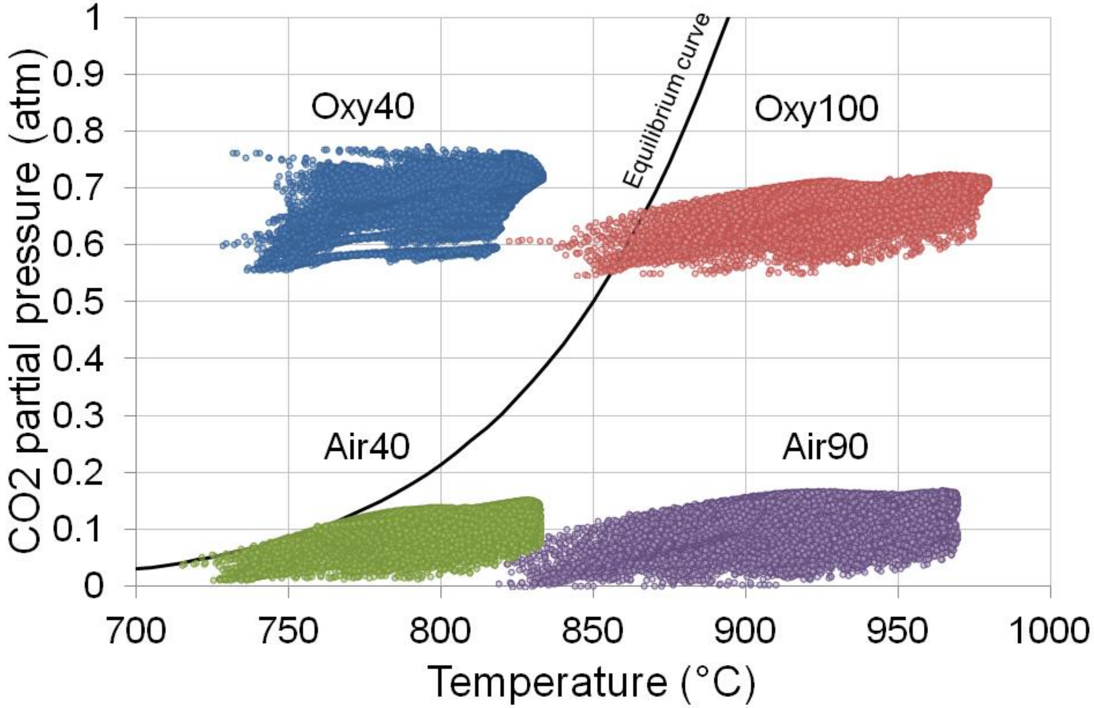
Transient particle model

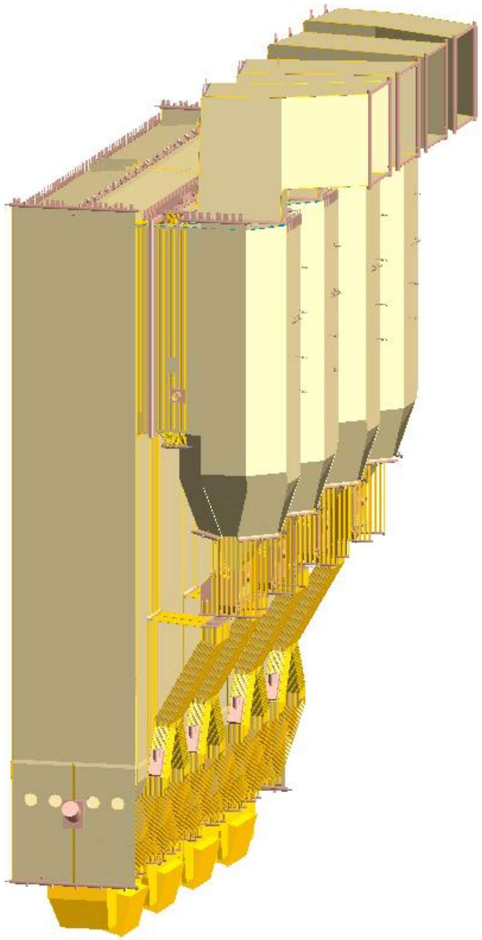


Sulfur capture solved by particle model (Rahiala et al., 2013)

Calculation of Oxy-CFB-300 Compostilla

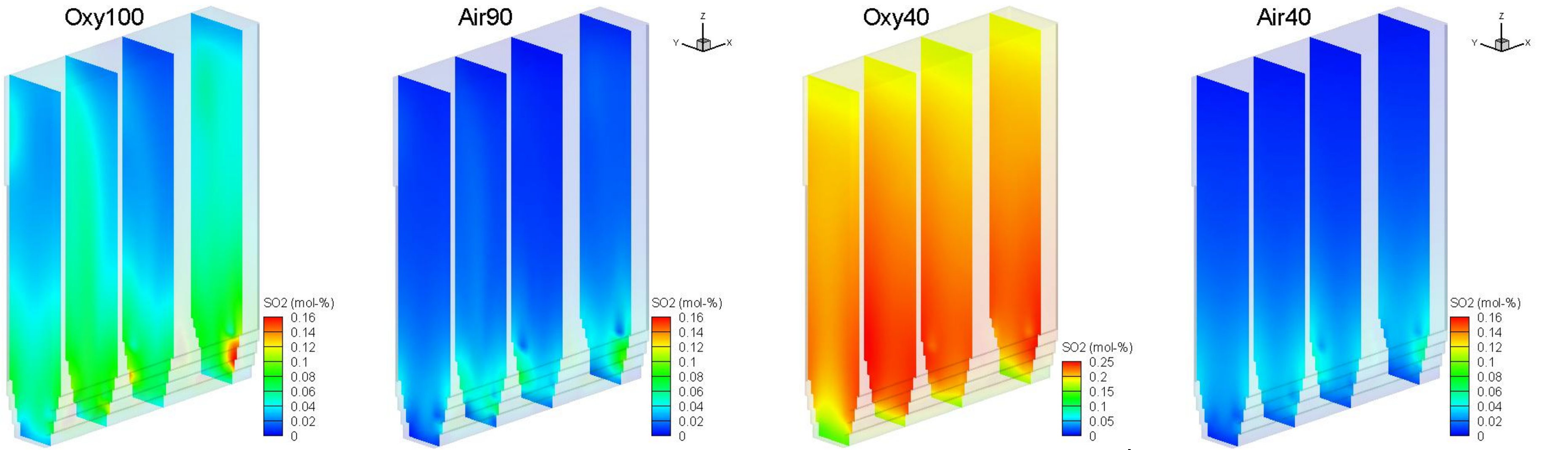
- Calculation cases:
  - Oxy100 Oxygen-fired 100% load
  - Oxy40 Oxygen-fired 40% load
  - Air90 Air-fired maximum (90% load)
  - Air40 Air-fired 40% load
- Modelled operating conditions:





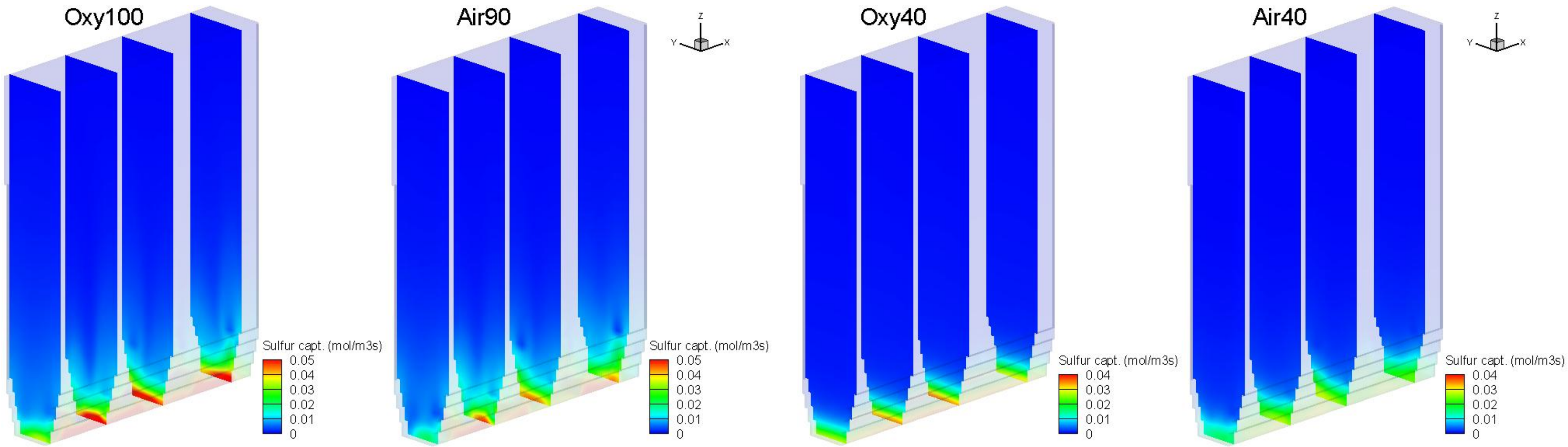
Sulfur dioxide and total sulfur capture in Oxy-CFB-300

Sulfur dioxide

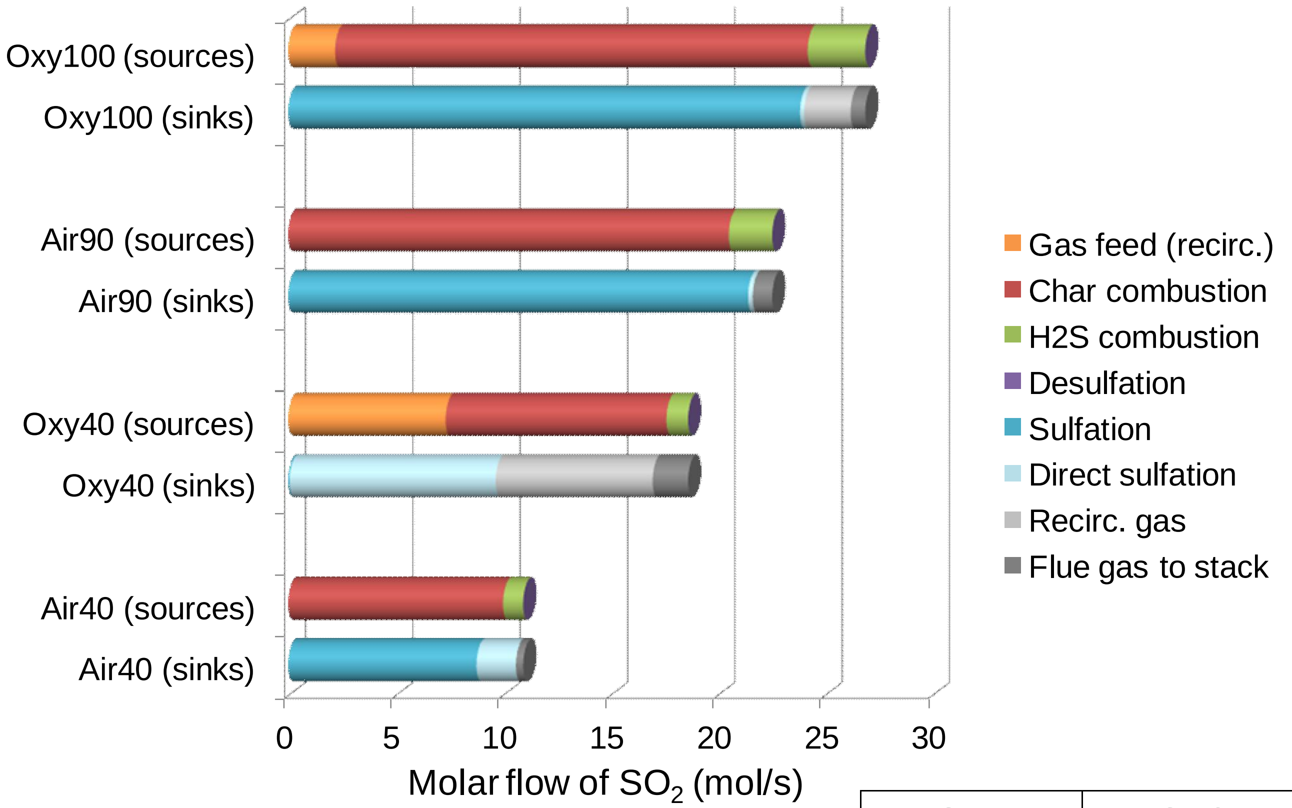


Note scale

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



Molar balance of sulfur dioxide



Case	Ca/S	S-retention	Flue gas SO_2
	(mol/mol)	(%-mol)	(ppm-wet)
Oxy100	2.7	97.2	327
Air90	3.1	96.0	97
Oxy40	3.1	85.4	1966
Air40	3.0	96.9	64

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

Myöhänen, K. and Hyppänen, T. (2011). A three-dimensional model frame for modelling combustion and gasification in circulating fluidized bed furnaces. *International Journal of Chemical Reactor Engineering*, 9. Article A25.

Myöhänen, K., Hyppänen, T., Pikkkarainen, T., Eriksson, T., and Hotta, A. (2009). Near zero CO2 emissions in coal firing with oxy-fuel CFB boiler. Chemical Engineering & Technology, 32(3), pp. 355-363.

Rahiala, S., Myöhänen ,K., and Hyppänen, T. (2013). Modeling the behavior of limestone particles in oxy-fuel CFB processes. *Fuel*. Article in press.