3D Modelling of Limestone Reactions in Oxygen Fired CFB

Kari Myöhänen[a]1*, Sirpa Rahiala[a], Timo Hyppänen[a]

[a]*Lappeenranta University of Technology, Skinnarilankatu 34, FI-53850 Lappeenranta, Finland*

1. Introduction

The removal of sulphur oxides in a circulating fluidized bed (CFB) furnace is possible by limestone addition. In atmospheric combustion with air, the limestone, which typically consists mainly of $CaCO_3$, is first calcinated as it enters the hot furnace. The produced CaO is then sulphated in the presence of SO_2. In pressurized combustion or oxycombustion, the partial pressure of CO_2 is high, which increases the calcination temperature. If the calcination temperature is higher than the operation temperature, then the calcination is prevented and the sulphur capture can occur by direct sulphation of $CaCO_3$.

In a generic case, the local temperatures inside a CFB furnace can vary on both sides of the calcination temperature. Thus, in locations with high temperatures, the $CaCO_3$ may calcinate and in locations with low temperatures, the CaO may carbonate. Consequently, the sulphur capture can occur with different mechanisms at different locations. For optimal sulphur capture, the different mechanisms should be known. Moreover, the effect of the calcination-carbonation reactions on the fluid dynamics and thermal balance should be recognized. The following paper presents modelling results of the sorbent reactions in different operating conditions, leading to different sulphur capture mechanisms. The object of study is a commercial scale CFB and the modelling has been carried out by a three-dimensional steady-state model.
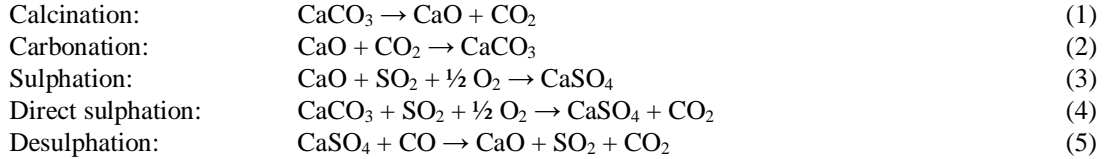
2. Modelling of Limestone Reactions in a Three-Dimensional CFB Furnace Model

The applied 3D model is a semi-empirical model for simulating the CFB furnace and it has been described in previous papers [1,2]. The model simulates the furnace process: flow dynamics of gas and solids, combustion and gasification, comminution, and heat transfer. The sorbent is handled as a mixture of main reacting species ($CaCO_3$, CaO, $CaSO_4$), inert material, and moisture. The model includes the solution of the flow and mixing of sorbent and reacting gases, comminution of the sorbent, modelling of sorbent reactions, and the thermal effects of the reactions. A more detailed description of the model is given by Myöhänen [3].

---

* Corresponding author. Tel.: +358-40-548-4482
E-mail address: kari.myohanen@lut.fi.

For modelling the limestone reactions, the following reactions are included in the model:

Calcination:	$CaCO_3 \rightarrow CaO + CO_2$	(1)
Carbonation:	$CaO + CO_2 \rightarrow CaCO_3$	(2)
Sulphation:	$CaO + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4$	(3)
Direct sulphation:	$CaCO_3 + SO_2 + \frac{1}{2} O_2 \rightarrow CaSO_4 + CO_2$	(4)
Desulphation:	$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2$	(5)

The different reaction rates are controlled by reaction rate expressions, which have been derived from literature [3]. The reactivities are specific to limestone type and the model parameters are tuned according to measured data and bench scale characterization studies.

This study was based on an earlier modelling work, which investigated conversion of an existing large scale air fired CFB unit to oxygen fired mode [2]. For this study, the furnace geometry was reduced by modelling only one quarter of the original furnace (Figure 1). The calculation mesh consisted of 37 240 hexahedral calculation cells.

Four cases were calculated: air fired case as a reference (AirRef) and three oxygen fired cases (Oxy1, Oxy2, Oxy3). In the oxygen fired cases, the operating temperature was adjusted by modifying the heat transfer surfaces inside the furnace and in the return leg system. The oxygen content in the inlet gas stream was 23.9 vol% in Oxy1 and Oxy2 and 29.6 vol% in Oxy3, similar to original study [2].

Figure 2 presents the modelled operating conditions compared with the equilibrium curve for calcination. The data points show carbon dioxide vs. temperature calculated for cross-sectional averages in the 3D-model. In AirRef and Oxy1 cases, the operation temperature is above the calcination temperature, which will result to indirect sulphation. In Oxy2, the calcination does not occur and the sulphur capture occurs by direct sulphation. In Oxy3, both sulphur capture mechanisms are possible as the conditions vary on both sides of the equilibrium curve.
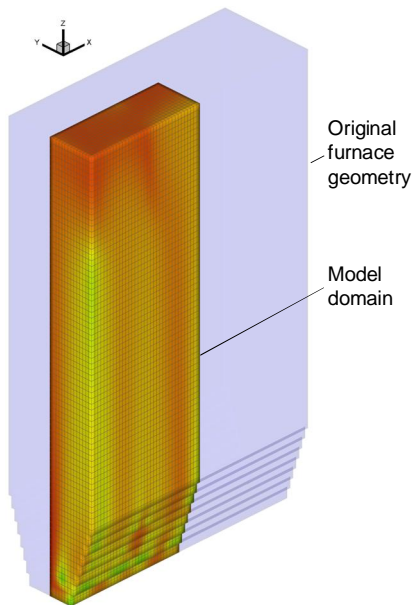

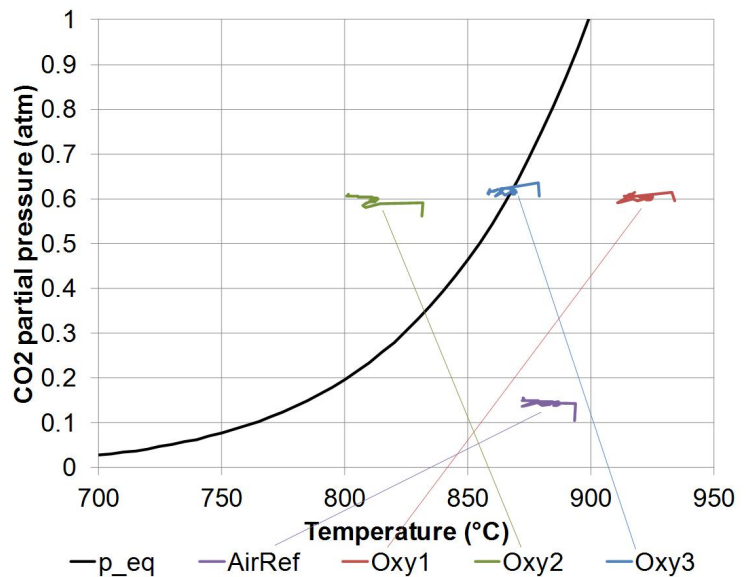Figure 1. Model geometry and mesh (coloured by CO_2 field of Oxy1).

Figure 2. Modelled CO_2 vs. temperature in the 3D-model compared with the equilibrium curve p_eq.

Figures 3 and 4 present the indirect and direct sulphation rates. In Oxy1, the total sulphation rate is about 4% higher than in AirRef, although AirRef operates closer to the optimal temperature for sulphur capture. The better sulphur capture in Oxy1 is explained by the higher SO_2 concentration inside the furnace due to lack of atmospheric nitrogen in oxycombustion.
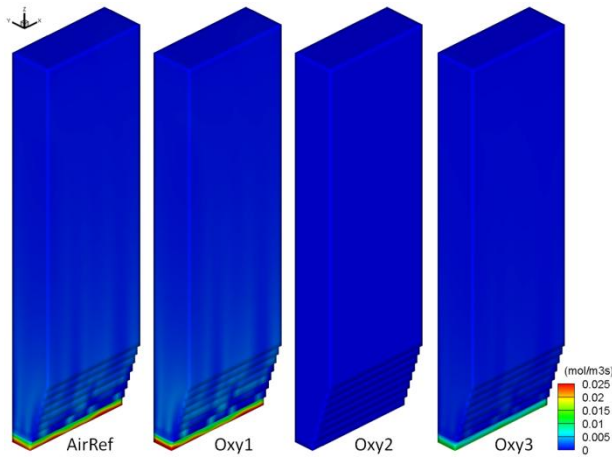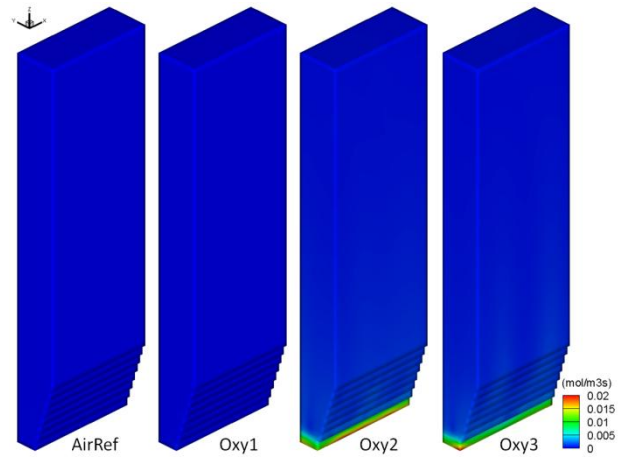
Figure 3. Modelled indirect sulphation rate.

Figure 4. Modelled direct sulphation rate.

In Oxy2, the sulphur capture occurs by direct sulphation. The total sulphur capture in Oxy2 is about the same as in AirRef. In Oxy3, the sulphur capture occurs by both sulphation mechanisms and the total sulphur capture is 13% better than in AirRef. In this case, the SO_2 concentration inside the furnace is higher than in other oxygen fired cases due to lower recirculation gas rate (higher inlet oxygen concentration). This increases the sulphation rate.

In all cases, the sulphur capture reactions are highest at the bottom of the furnace, where the amount of SO_2 is high due to combustion of char and the concentration of CaO and/or $CaCO_3$ is high due to solid concentration profile in a CFB.

Although the operation near the equilibrium curve would appear to improve the sulphur capture, this is not necessarily the optimal operating range for oxycombustion. The cycling calcination and carbonation reactions may cause control problems as large quantities of bed material are reacting and affecting the fluid dynamics and thermal balance.

The sorbent reactions will be further investigated by a separate transient particle model, which simulates the reactions inside a limestone particle as it travels through the CFB furnace in different operating conditions.

3. Conclusions

The limestone reactions in a circulating fluidized bed under different operating conditions were modelled by a steady-state semi-empirical three-dimensional model. Based on the modelled results, the sulphur capture in oxycombustion can be as good as or better than in air fired combustion. This is mainly due to higher SO_2 concentration in the furnace in oxycombustion mode. The highest sulphur capture was achieved by operating near the calcination curve, when both indirect and direct sulphation mechanisms were possible. However, this operating mode includes risks due to cycling calcination and carbonation reactions and their effects to process control.

Acknowledgements

References

[1] Myöhänen, K. and Hyppänen, T. A three-dimensional model frame for modelling combustion and gasification in circulating fluidized bed furnaces. International Journal of Chemical Reactor Engineering, 2011.
[2] Myöhänen, K. et al. Chemical Engineering & Technology, 32, pp. 355-363, 2009.
[3] Myöhänen, K. Modelling of combustion and sorbent reactions in three-dimensional flow environment of a circulating fluidized bed furnace. Dissertation, Lappeenranta University of Technology, 2011.