

## **Review of the dissertation**

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**Title:** Desulphurization during oxyfuel combustion in a fluidized bed

The Ph.D. thesis (dissertation) of Pavel Skopec, Faculty of Mechanical Engineering, Czech Technical University in Prague, is a very good work containing a lot of useful, valuable experimental data on “in-situ” desulfurization by limestone under conditions of oxy-fuel fluidized bed combustion of coal and comparison with air combustion under similar hydrodynamic and thermal conditions.

The goals set for the Ph.D. thesis (dissertation), i.e. direct additive flue gas desulfurization by limestone in fluidized bed combustion under oxy-fuel conditions, effects of Ca/S ratio, temperature and oxygen concentration and comparison with air combustion, have been achieved. Further also set-up and verification of a theoretical balance model of the oxy-fuel combustion process with flue gas recirculation, effects of scale-up of experimental apparatus on process and efficiency of flue gas desulfurization in a fluidized bed (FB) have been accomplished. The main factors (effects) studied in the submitted Ph.D. thesis: effects of limestone stoichiometric excess (Ca/S) on desulfurization efficiency and degree of limestone utilization, effects of temperature and oxygen concentration in flue gas on desulfurization efficiency and CO concentration and comparison of the desulfurization process under oxy-fuel and air combustion conditions. Oxy-fuel combustion conditions (and this is very valuable) have been achieved by means of real flue gas recirculation (both wet flue gas and flue gas with partial water vapour condensation).

The literature survey (the state of the art) part explaining the process of oxy-fuel combustion, clarifying SO<sub>x</sub> emissions, their interactions in flue gas and possibilities of reduction of final emissions, is adequate (appropriate). The theoretical analysis part (chapter 5) explains and compares fundamentals of oxy-fuel fluidized bed combustion with classic air combustion and explains also „shift“ in meanings of some combustion parameters (e.g. „excess of air“) or disappearing meaning of some important combustion parameters at transition to oxy-fuel combustion. More complicated comparison of air and oxy-fuel FB combustion regimes in terms of thermodynamic heat generation and simultaneously hydrodynamic parameters with necessity of accepting some compromise in regimes is correctly and properly explained.

Similarly, direct comparison of SO<sub>2</sub> emission values (in mg SO<sub>2</sub>/Nm<sup>3</sup>) is not possible for such different methods of combustion. Therefore, it is necessary to compare rather SO<sub>2</sub> emissions related to amount of burnt coal, related to generated heat (e.g. mg SO<sub>2</sub> emissions/MJ) or compare efficiency of flue gas desulfurization by means of definition equations for SO<sub>2</sub> removal efficiency under otherwise similar conditions. Recirculation of flue gas in oxy-fuel combustion causes elevation of SO<sub>2</sub> concentration (and similarly of other pollutants). This is the reason why removal of pollutants and their capturing on sorbents is more effective, with better limestone sorbent utilization in fluidized beds.

The methods used in solution and comparison of SO<sub>2</sub> emissions are adequate, on professional level. It is obvious that candidate for Ph.D. is well-oriented in given problematics and takes advantage of broader knowledge gained from scientific/technical literature and from consultations about status of power generation, problematics in the field of mitigation of emissions and modern methods for carbon capture, sequestration and utilization (CCS and CCU).

Formal side of the Ph.D. thesis is on a relatively high level.

Presentation of Ph.D. thesis in English is highly valuable. Quality of English is relatively good, although some inaccuracies and misleading terms sometimes occur. E.g. misleading name for CaSO<sub>4</sub> (it should be calcium sulphate). On some places (e.g. page 37, 39, 71, etc.) the term calcium sulphide (= CaS) is used. Some other small errors in English text: calcium sulphate dehydrate instead of calcium sulphate dihydrate (page 28), complete instead of compete (page 31). Instead of bounded it should be bound (e.g. page 40). Instead of stabile it should be used rather the term stable. Some figures (e.g. Figs. 8-1 and 8-2) should have in figure captions more complete characterization of the experimental conditions (temperature, oxygen concentration, etc.). In bibliography (literature references) some items are incomplete (e.g. ref. No 9 and No 72).

Some other comments (on inaccuracies, omissions or incomplete data/explanations):

In my view, at least in one or two characteristic cases of oxy-fuel combustion also NO<sub>x</sub> emissions values should be mentioned. Air staging or staging of gas in oxyfuel combustion is mentioned and also stated in Fig. 6-1, scheme of Minifluid combustion facility, but further in combustion experiments is not mentioned.

There is no analysis or statement about amount and character of dust behind cyclone (i.e. small particles approx. below 5 μm). Such dust, however, can affect function of the

ventilator for flue gas recirculation and can be present also (together with SO<sub>2</sub>) in water condensate from recirculated flue gas (influence on mass balances).

Another significant question is real value of dew point temperature of H<sub>2</sub>SO<sub>4</sub> vapours in recirculated flue gas. It is important for corrosion of metallic materials.

For particles of calcined limestone at temperatures over approx. 900 °C, sintering of CaO grains is important factor decreasing reactivity and conversion of CaO to CaSO<sub>4</sub> in flue gas desulfurization. Also possible influence of acidic reactive solid components in limestone L2 (like SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) on decrease of decomposition temperature of both CaCO<sub>3</sub>, and CaSO<sub>4</sub> could be mentioned. Not only elevated CO concentrations in gas are responsible for lower degree of desulfurization in flue gas at temperatures above 900 °C. Changes in molar volumes of calcium compounds during calcination and desulfurization could be mentioned and used for explanation of incomplete conversion of CaO to CaSO<sub>4</sub>.

Reaction (3-30 on page 42) is rather unlikely in systems with two orders of magnitude higher oxygen concentration than SO<sub>2</sub> concentration.

Page 85: speculations about influence of reactions of Ca(OH)<sub>2</sub> with SO<sub>2</sub> are rather outside reality. At temperature above 800 °C, at atmospheric pressure and concentrations of water vapour in gas below approx. 50 kPa, there is no Ca(OH)<sub>2</sub> present in flue gas.

**Questions:**

1. Did you measure also emissions in oxy-fuel fluidized bed combustion with staged introduction of oxidizing gas?
2. Did you estimate/measure amount of small dust particles behind cyclone in some experiments with air or oxy-fuel combustion?
3. Do you have at least estimate of dew point temperature of H<sub>2</sub>SO<sub>4</sub> vapors for some typical case of oxy-fuel combustion of coal?
4. Do you have some plausible explanation for somewhat strange trends in CO emissions on pages 75, 76, Tables 8-4 and 8-5 (e.g. CO emissions increasing/fluctuating with increasing temperature of flue gas under the same oxygen concentration in gas)?
5. Do you have some estimates (page 105, acceptable concentrations of SO<sub>2</sub>) whether concentrations of SO<sub>2</sub> in flue gas below 250 mg/m<sup>3</sup> or somewhere between 150 a 200 mg/m<sup>3</sup> in oxy-fuel combustion are sufficiently low for further processing of CO<sub>2</sub>-rich gas (compression or/and cleaning of the gas with high CO<sub>2</sub> concentration)?

**Conclusion:**

The reviewed Ph.D. thesis by Pavel Skopec is on a very good level, complies with the requirements of Czech Ministry of Education and, is recommended for defence.

In Prague 22. 3. 2019

Assoc. Prof. Michael Pohořelý, Ph.D.