Towards controlling PCDD/F production in a multi-fuel fired BFB boiler using two sulfur addition strategies. Part II: Thermodynamic analysis

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HIGHLIGHTS

- We have developed a method to perform thermodynamic modeling for a 140 MW$_{th}$ BFB boiler using Excel and FactSage macros.
- We have demonstrated that the speciation of Cu is correlated to the PCDD/F production.
- We have shown that peat co-firing can aid PCDD/F abatement if Cu content in the fuel mixture is low.

ARTICLE INFO

ABSTRACT

A staged equilibrium process model was developed for a bubbling fluidized bed boiler firing SRF, bark and sludge. The model was used to study the influence of sulfur addition strategies (S-pellet additive and peat co-firing) on the behavior of copper, bromine, and alkalis. Aerosol samples collected from the backpass of the boiler were used to validate the chemistry predicted by the model. The model revealed that Cu existed as $Cu_2S_{(s3)}$ in the reducing zone, and $CuCl_{(g)}$ (for all test cases) and $CuO_{(s)}$ (during peat co-firing) in the oxidation zones. $CuBr_{3(g)}$ was also present after the introduction of tertiary air. However the model failed to predict the formation of $CuSO_4$, an important passive species of Cu necessary for PCDD/F abatement. The modes of occurrence of Cu were classified as either active or passive with respect to de novo synthesis and an active/passive species molar ratio (APR) was introduced. APR showed high correlation with the PCDD/F production levels. Sensitivity analysis revealed that excessive Cu in the fuel mixture decreased the volatility of the element due to the formation of $CuO_{(s)}$. Simulation for peat co-firing with low Cu content showed that PCDD/F concentration is decreased and is comparable to that of S-pellet addition. Sensitivity analysis revealed that increasing the energy share of sludge can likewise lower PCDD/F production.

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1. Introduction

In the first part of this study series, sulfur addition strategies influenced the production of dioxin and furan in a bubbling fluidized bed boiler firing SRF–bark–sludge (Case 1) [1]. Adding S-pellet to the fuel mixture (Case 2) decreased the PCDD/F production, while firing SRF–peat–sludge (Case 3) led to an increase. The homologue distribution pointed to a de novo mechanism as the formation pathway of these compounds. Cu is the main catalyst for this mechanism. Aerosol data showed that the volatility and speci-ation of Cu are different for the two cases. When S-pellet was added, Cu may have been sulfated to form copper sulfate and been less likely to participate in the de novo formation. During peat co-firing, Cu has limited volatility and may have remained in its active form in the fly ash. These observation help explained the differences in PCDD/F production for the sulfur addition strategies tested.

For this part of the study series, a thermodynamic equilibrium calculation and details of the de novo mechanism are used to explain the results obtained earlier. An empirical model is developed to determine if the elevated concentration of Cu had significant effect on PCDD/F formation when firing SRF–peat–sludge. In addition, a sensitivity analysis on the variation in energy share of sludge for Case 2 is tested.

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1.1. Chemical equilibrium modeling

Chemical equilibrium calculations have been used to analyze systems such as combustion [2–4], gasification [5], cement kiln chemistry [6] and several others [7]. The flexibility of the computation approach and the rapid growth in computing power enabled systematic calculation of multi-phase multi-component equilibrium systems. Equilibrium calculations give accurate results in high temperature applications because the assumptions of the calculation are met. On the other hand, the applicability of thermodynamic equilibrium modeling can be limited by local temperature gradients, physical processes such as adsorption and capillary condensation, non-ideal mixing behavior between different ash forming elements and the mode of occurrence of components in the fuel which dictates its release or retention rate [20,38]. However, clever and carefully designed methodologies can produce valuable information about overall stabilities and speciation trends [10].

In the field of combustion, applications include the study of the behavior of fuel components during combustion [8], multi-fuel combustion strategies [9,10], alkali chemistry related to combustion [11,12], bed agglomeration [13–15] and the fate of trace elements [16–19]. However in practice, the role of reaction kinetics is equally important. This makes simulations of large-scale systems challenging when using straightforward global equilibrium calculation alone.

Dividing large processes into simpler subsystems or stages may add value to the calculation. Sandelin and Backman used this approach to analyze the behavior of trace elements in a coal-fired power plant [20]. They concluded that their modeling results agree with full scale measurements and the overall chemistry was predicted with satisfaction. Similarly Erikson and Hack used this approach to study production of metallurgical-grade silicon in an electric arc furnace. They reasoned that because the flows of two reacting substances are countercurrent, the local mass balances need not be identical to the overall mass balances. Also, the temperatures at different levels in the furnace are not controlled from the outside, but mainly determined by the heat exchange and the reactions taking place inside [21].

Staged equilibrium calculation can be done on several platforms. For example, ChemSheet combines MS Excel with the multi-phase multi-component calculation capability of FactSage [22]. Aspen Plus is also available and has been widely used in the field of chemical engineering [23,24].

This work uses the macro processing module of FactSage. Since the macros are already available in the FactSage distribution, additional software is no longer required. Macro commands enable the user to run the subprogram *Equilib* in the background and execute commands stored in a macro [25]. Although macros are advanced features of FactSage, little programming background is required.

The main motivation for the use of this platform is to take advantage of the integrated database and computing facility in FactSage, and to develop an Excel-based user interface as a process model for the boiler used in this study.

In a bubbling fluidized bed boiler (BFB) several key zones can be identified, each with unique local prevailing conditions (Fig. 1). The first is the zone above the bed (the splash zone). The atmosphere is reducing because the air to fuel ratio (λ) is less than unity. The fuel is gasified and volatile fractions are released. Non-volatile fragments can be retained in the bed and leave the boiler as bottom ash.

Then, secondary air is injected several meters above the splash zone. The reason for the staging of air is to minimize excessively hot zones where NO_x formation may occur. At this zone, the atmosphere is oxidizing with λ around the range 1.1–1.3. The temperature is highest and majority of the fuels are combusted.

Next, tertiary air is introduced below the bullnose for complete oxidation. Further downstream, the flue gas transfers heat in the superheaters resulting in a decrease in flue gas temperature. The flue gas becomes supersaturated with aerosol-forming elements, such as Na, K, Cl, leading to condensation and deposition. Then the flue gas travels to the colder post combustion zones, where other heat exchange devices cool it to around 200 °C.

This illustrates that the mass, prevailing conditions and flue gas composition are changing at the zones mentioned. These features can be incorporated to the thermodynamic model using staged equilibrium calculation.

1.2. Copper – the de novo catalyst

Copper is the most important catalyst responsible for the synthesis of PCDD/F in incineration systems [26–29]. In the BFB, Cu undergoes several chemical transformations such as sulfidation in the splash zone, oxidation in the O_2-rich stages, and chlorination in the cold zones of the boiler. The non-volatile fraction of Cu in the fuel leaves the boiler as part of the bottom ash, mostly as Cu^0, Cu^I or Cu^{II} [30]. The rest of the Cu is volatilized or entrained in flue gas and, depending on speciation, Cu can be a catalyst for the *de novo* reaction.

Using in situ X-ray absorption techniques, Takaoka and coworker observed the transformation of Cu from 200 °C to 400 °C
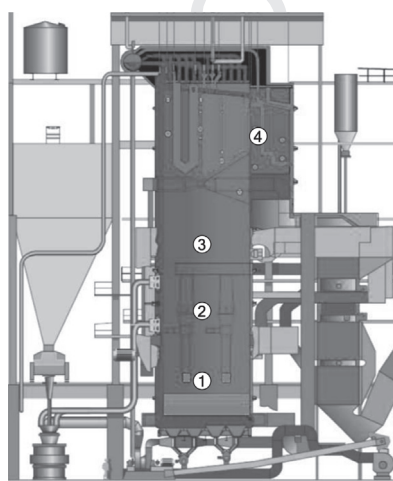
Location	Description	T_{gas}, [°C]	λ	Code
1	Just above the bed, splash zone	846 ± 4	0.600	846Rd
2	Downstream from the secondary air to just before the tertiary air.	906 ± 14	1.300	906Ox
3	Downstream from the tertiary to just below the bullnose	852 ± 4	1.379	852Ox
4	Back Pass	510 ± 9	1.379	510BP

Fig. 1. Key locations in the boiler used for the modeling and the local conditions at these locations. Aerosol sampling was made in the backpass or 4.