Thesis for the Degree of Doctor of Philosophy

Ash Behavior in Fluidized-Bed Combustion and Gasification of Biomass and Waste Fuels
Experimental and Modeling Approach

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Abstract

Over the past few decades, a growing interest in the thermal conversion of alternative fuels such as biomass and waste-derived fuels has been observed among the energy-producing companies. Apart from meeting the increasing demand for sustainable heat and power production, other advantages such as reducing global warming and ameliorating landfilling issues have been identified. Among the available thermal conversion technologies, combustion in grate-fired furnaces is by far the most common mode of fuel conversion. In recent years, Fluidized-Bed (FB) technologies have grown to become one of the most suitable technologies for combustion and gasification of biomass and waste-derived fuels.

In spite of the benefits, however, some difficulties are attributed to the thermal conversion of the alternative fuels. Ash-related issues could be a potential problem, as low-grade fuels may include considerable concentrations of ash-forming elements such as K, Na, S, Ca, Mg, P, Si and Cl. These elements undergo many undesirable chemical and physical transformations during the thermal conversion, and often cause operational problems such as deposition-related issues, slag formation in furnaces, corrosion of the heat transfer surfaces, and bed agglomeration of the fluidized-beds. Ash-related problems in the utility boilers are a major concern that may result in decreased efficiency, unscheduled outages, equipment failures, increased cleaning and high maintenance costs.

This thesis investigated the ash behavior and ash-related problems in two different FB conversion systems: a Bubbling Fluidized-Bed (BFB) boiler combusting solid waste, and a Dual Fluidized-Bed (DFB) gasifier using biomass as feedstock. Full-scale measurements, chemical analysis of fuel and ash, as well as thermodynamic equilibrium modeling have been carried out for the BFB boiler (Papers I-IV), to investigate the impact of reduced-bed temperature (RBT) and also co-combustion of animal waste (AW) on the ash transformation behavior and the extent of ash-related issues in the boiler. For the DFB gasifier (Paper V), a thermodynamic equilibrium model was developed to assess the risk of bed agglomeration when forest residues are used as feedstock.

The experimental results showed that the RBT and AW co-combustion could decrease or even resolve the ash-related issues in the BFB boiler, resulting in a lower deposit-growth rate in the superheater region, eliminating agglomerates, and a less corrosive deposit (in RBT case). Thermodynamic equilibrium modeling of the BFB boiler gave a better understanding of the ash transformation behavior, and also proved to be a reliable tool for predicting the risk of bed agglomeration and fouling. The modeling of the DFB gasifier indicated a low risk of bed agglomeration using the forest residues as feedstock and olivine as bed material, which was in good agreement following the observations in a full-scale DFB gasifier.

Keywords: Fluidized-bed, combustion, gasification, waste-derived fuels, biomass, ash-related problems, deposit, fouling, slagging, bed agglomeration, thermodynamic equilibrium modeling
This thesis is based on the results presented in the following articles:


Statement of Contributions

Farzad Moradian’s contributions to the appended papers:

**Paper I:** Co-author of the paper, contributed to the full-scale measurements, and SEM-EDX analysis of the ashes.

*XRD analysis of the ashes was performed by Anita Pettersson. Standard chemical analysis of the fuel and ashes were performed by an authorized laboratory.*

**Paper II:** Principal author of the paper, contributed to the full-scale measurements, and performed the chemical fractionation and SEM-EDX analyses of the ashes.

*XRD analysis of the ashes was performed by Anita Pettersson. Standard chemical analysis of the fuel and ashes were performed by an authorized laboratory. Lab-scale bed agglomeration tests were carried out by SP.*

**Paper III:** Principal author of the paper, contributed to the full-scale measurements, and performed the chemical fractionation of the ashes, SEM-EDX analyses of the ashes, as well as the thermodynamic equilibrium modeling of the BFB boiler.

*XRD analysis of the ashes was performed by Anita Pettersson. Standard chemical analysis of the fuel and ashes were performed by an authorized laboratory. Lab-scale bed agglomeration tests were carried out by SP.*

**Paper IV:** Principal author of the paper, contributed to the full-scale measurements, and performed the chemical fractionation of fuel, as well as the thermodynamic equilibrium modeling of the BFB boiler.

*XRD analysis of the ashes was performed by Anita Pettersson. Standard chemical analysis of the fuel and ashes were performed by an authorized laboratory.*

**Paper V:** Principal author of the paper, and performed the chemical fractionation of the fuels, as well as the thermodynamic equilibrium modeling of the DFB gasifier.

*Lab-scale steam gasification of the biomass was carried out by Placid A. Tchoffor. Standard chemical analyses of the fuels were performed by an authorized laboratory.*
Licentiate Thesis and Conference Contributions

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International meeting abstract:

Living in Sweden since 2007 and carrying out my Masters and Ph.D. studies at the University of Borås have been wonderful opportunities and a challenging journey for me. As a student with an educational background in chemistry and a short but valuable practical experience in the energy industry, it was a great opportunity for me to start a Master’s program in *Energy and Resource Recovery* and then pursue my Ph.D. within the field of *Energy Engineering*. I would like to take this moment to acknowledge those who with their contribution, help, and guidance made this long journey possible.

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Borås, April 2016
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AW</td>
<td>Animal Waste</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling Fluidized-Bed</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined Heat and Power</td>
</tr>
<tr>
<td>CFB</td>
<td>Circulating Fluidized-Bed</td>
</tr>
<tr>
<td>DFB</td>
<td>Dual Fluidized-Bed</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
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<td>EU</td>
<td>European Union</td>
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<tr>
<td>EfW</td>
<td>Energy from Waste</td>
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<tr>
<td>FB</td>
<td>Fluidized-Bed</td>
</tr>
<tr>
<td>HSC</td>
<td>High-Sulfur Content</td>
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<tr>
<td>LSC</td>
<td>Low-Sulfur Content</td>
</tr>
<tr>
<td>Mtoe</td>
<td>Million tonnes of oil equivalent</td>
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<tr>
<td>MW_{th}</td>
<td>Megawatt thermal</td>
</tr>
<tr>
<td>ppm_{V}</td>
<td>parts per million by volume</td>
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<tr>
<td>RBT</td>
<td>Reduced-Bed Temperature</td>
</tr>
<tr>
<td>RES</td>
<td>Renewable Energy Sources</td>
</tr>
<tr>
<td>RF</td>
<td>Reactive Fraction</td>
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<tr>
<td>Ref</td>
<td>Reference</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<tr>
<td>SNG</td>
<td>Substitute Natural Gas</td>
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<tr>
<td>Twh</td>
<td>Terawatt hour</td>
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<tr>
<td>WtE</td>
<td>Waste-to-Energy</td>
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1 Introduction

1.1 EU energy policy

The European Union (EU) is the world’s largest energy importer. About half of the energy consumption in the EU countries comes from imports, where the majority of the member states are highly dependent on the imports of fossil fuels, especially oil and gas. Figure 1.1 illustrates the EU’s energy consumption and the percentage share of the different sources of energy in 2012. The main end-use sectors are transport, industry, and households. The challenges of the supplier countries, for instance, political and economic problems, are a source of uncertainty and risk in the EU energy supply. In addition, the volatile oil markets lead to large price differences from time to time. Therefore, the dependence on the foreign energy sources may result in increased vulnerability of national economics, and serious problems in the security of the energy supply [1, 2].

![Figure 1.1 EU-28 gross inland consumption (as % of total Mtoe), Source: Eurostat 2012 (Adapted from [1])](image)

Besides the energy crisis, the enhanced greenhouse effect, known as global warming, is a serious issue associated with the fossil fuels consumption. Carbon dioxide (CO₂) is the primary greenhouse gas that contributes to global warming. Nearly three-fourths of the emission of the greenhouse gases is related to the CO₂ emission through human activities. Utilizing the fossil fuels for electricity generation, transportation, and industry are the main
causes of the carbon dioxide being released into the atmosphere. The use of fossil fuels has generated the highest levels of CO₂ emission during the last century. Without a global agreement on the reduction of CO₂ emissions, the concentrations of atmospheric CO₂ would double over the next 50 years. Melting glaciers, rising sea and ocean levels, as well as flooding along thousands of miles of coastlines are the devastating effects of global warming. Additionally, extreme weather events such as droughts, floods, and heat waves, as well as loss of plant and animal species could also be the undesired consequences of the rise in the global temperatures [2].

1.2 Renewable energy sources

Under these conditions, renewable energy sources (RES) can play an important role as sustainable and environmentally friendly energy sources. RES are generated from the natural resources including sunlight, wind, hydro-power, biomass, tides, and geothermal heat. Given that the RES are available everywhere and have sufficient generating capacity, they are used to cover human energy requirements such as electricity, heating, cooling and transport sector. Additionally, the amount of carbon dioxide released into the atmosphere through renewable energy technologies is small or almost nonexistent. For instance, biofuels such as bioethanol, biogas, and biodiesel emit a third less CO₂ compared to gasoline and diesel used in the transport sector. Currently, different types of RES are used to generate electricity. Figure 1.2 shows the share of renewable energy, and also the share of different RES in the EU electricity generation in 2012. The renewables and nuclear power, CO₂-neutral sources, accounted for 51 % of the EU’s electricity generation in 2012, which shows an increase from less than 45 % in the 90s. While the share of RES in electricity generation is expected to grow strongly in the future, the arguments against the use of nuclear energy have been intensified because of the risks and possible devastating effects on human health and safety [1, 2].
Given the consequences of climate change and increased dependence on fossil fuels, the development of RES is one of the main objectives of the EU energy policy. According to the 2009/28/EC Directive on the promotion of the use of energy from renewable sources, the share of renewable energy in the total consumption should reach the target of 20 % by 2020. Sweden is known as one of the pioneering EU countries to use RES, and has a well-developed renewable energy sector. The country has already achieved its national 2020 RES target, which is 49 % of renewables in its gross final energy consumption. The renewables share improved to 51 % in 2012 and is now aiming for a higher goal for 2020 [1, 2].

1.3 Waste-to-Energy

It has been a long debated issue in the field of waste regulation to establish a consistent definition of ‘waste.’ In the context of Waste Framework Directive 2008/98/EC, ‘waste’ means “any substance or object which the holder discards or intends to discard or is required to discard.” However, waste is often reused when its value is recognized and it can also be considered as a ‘resource’ [3]. In a modern industrialized society, large quantities of waste are generated from agricultural, silvicultural, industrial, and urban activities. In most countries, the main final waste disposal method is controlled and uncontrolled landfills [4]. Nowadays, the drawbacks of this method are well recognized as it significantly contributes to the release of methane gas as a greenhouse gas (equalling 21 times CO₂) [5-7] and also a number of hazardous chemical compounds in the form of leachates and particulate matter [8, 9].
The current European waste management strategy imposes the following ‘waste hierarchy’ as a priority order in the waste prevention and management: prevention, preparing for reuse, recycling, other recovery (e.g., energy recovery), and disposal. Re-use and recycling of waste are aimed at effective material recovery, while the energy recovery is the path to be followed when the material recovery is not effectively applicable [10]. Thermal (thermo-chemical) and biological (bio-chemical) treatments are two routes to energy recovery. Biological treatment refers to methods such as composting and anaerobic digestion to produce biofuels from the appropriate streams. Thermal treatment of waste streams is defined as high temperature processes such as combustion (or incineration) with energy recovery and also gasification and pyrolysis, which can produce energy (fuel, heat, and power) [4, 10, 11].

The thermal treatment of waste associated with energy production is commonly addressed as waste-to-energy (WtE) or energy from waste (EfW) [10]. Nowadays, the thermal treatment of waste with energy recovery in waste-to-energy (WtE) plants has become significant. Some of the EU member states like Germany, Sweden, Netherlands, Belgium, Denmark, and Austria have significantly reduced the dependence on landfills by combining material recycling, biological treatment, and WtE technology. Figure 1.3 shows the treatment of municipal waste in Europe in 2013, and the share of landfill, thermal treatment, recycling, and biological treatment for each EU member [12]. Combustion of waste in WtE boilers is generally associated with energy recovery in the form of electricity and/or heat production. In countries with cold climates and high heat demand, WtE in the form of heat and power (CHP) can be quite efficient. In warm countries with mainly power demand, the efficiency level is reduced because corrosion on the boiler tubes limits the steam temperature. One way toward electricity production from waste, with higher efficiency is gasification in combination with combustion of product gas, where the cleaned product gas is burnt in a boiler with high steam data. The application of pyrolysis in the WtE plants is limited to a few specific waste streams, particularly pure and homogeneous waste flows [11]. Among the thermal conversion technologies available, such as grate-fired, fluidized-bed, and rotary furnaces, combustion in grate-fired furnaces is by far the most common mode of fuel conversion [11]. However, fluidized-bed technologies have grown to become one of the most suitable technologies for thermal conversion of biomass and waste-derived fuel [13, 14].
In spite of the benefits, however, some difficulties are attributed to the thermal treatment of biomass and waste derived-fuels. Ash-related issues could be a potential problem in the thermal conversion of low-grade fuels, as they may include considerable concentrations of ash-forming elements. The main ash-forming elements in biomass and waste-derived fuels are considered to be K, Na, S, Cl, Ca, Mg, Si, P, Al, and Fe. Pb and Zn are also important ash-forming elements that may present in considerable amounts in the waste-derived fuels. The ash-forming elements can release during the thermal conversion and contribute to the formation of bottom and fly ashes. The bottom and fly ashes subsequently affect the thermal process and often cause operational problems known as deposit formation and corrosion on the heat transfer surfaces, slag formation in the furnaces, as well as bed agglomeration in the fluidized-bed boilers. Deposit formation on the surface of the superheater tubes reduces the heat transfer and negatively affects the efficiency of the boiler. High concentrations of alkali and chlorine in the deposit also cause severe corrosion of the steel surfaces. Bed agglomeration in the fluidized-bed boilers, as a result of the interaction between the bed material and the fuel-derived ash, may lead to defluidization and unwanted collapse of the fluidized-bed. Great efforts have been made to reduce the above-mentioned operational issues in order to prevent unscheduled shut downs and high maintenance costs. Several methods have been suggested to improve the boiler operation such as changing the fuel mix, using additives, and modifying the boiler functions [13, 15-19].
1.4 Objectives of the thesis

Within this thesis, the ash transformation behavior and also the extent of the ash-related problems in two different fluidized-bed thermal conversion systems, a Bubbling Fluidized-Bed (BFB) boiler and a Dual Fluidized-Bed (DFB) gasifier, was investigated. The 20 MWth BFB boiler has been employed in a CHP plant owned by Borås Energi och Miljö AB (Borås, Sweden), using sorted industrial and household solid wastes, consisting mainly of wood, paper, and plastics, as ordinary feedstock. The bulk of the research work presented in this thesis (Papers I-IV) deals with ash-related problems in the BFB boiler. The last part of the thesis (Paper V) deals with the ash-related issues in a DFB gasifier, owned by Göteborg Energi (Göteborg, Sweden), which was recently constructed to produce a substitute natural gas (SNG) by gasification of the biomass (forest residues).

1.4.1 Research objectives for the BFB boiler

The research work on the BFB boiler, presented here, was initiated in the Reduced-Bed Temperature (RBT) project (Paper I) [20]. The main objective of the RBT project was to investigate whether lower bed temperatures could change the alkali and chlorine distribution in the boiler, and reduce the deposit formation and corrosion. It is known that boilers using waste are designed for low steam temperatures, to avoid severe corrosion of the superheater tubes [21]. Therefore, the RBT project investigated the possibility of capturing alkali and chlorine in the bed ash by reducing the temperature in the bed region by approximately 150 °C, through flue gas recirculation and spraying of water on the fuel.

The Animal Waste (AW) project was a continuation of the RBT project. The aim of the AW project (Paper II) [22] was to investigate the effects of a changed fuel composition without any major changes in the operating conditions, except for the decreased bed temperature similar to the previous project, but now only caused by the increased moisture in the new fuel mix. Hence, co-combustion of animal waste products with the ordinary waste fuel mix was suggested for the BFB boiler.

The experimental methods provided information about the ash chemistry, deposit-growth rate, and bed agglomeration tendency in the BFB boiler during the RBT and AW combustion scenarios. However, the ash transformation behavior was not fully understood solely by the experimental methods. Therefore, thermodynamic equilibrium modeling was carried out to better understand and fill in the gaps in knowledge regarding the bed agglomeration
(Paper III) [23] and deposit formation (fouling) (Papers IV) [24] behavior during the different combustion scenarios.

1.4.2 Research objective for the DFB gasifier

DFB gasification is one of the recently developed technologies for steam gasification of biomass. In Sweden, the GoBiGas (Gothenburg Biomass Gasification) project, a 20 MWth DFB gasifier, was recently constructed to produce SNG using biomass as feedstock. The plant has initially utilized wood pellets as feedstock, but the aim is to switch to a cheaper feedstock (e.g., forest residues) to make the SNG production economically feasible. Forest residues, however, contain a higher ash content, meaning that a higher risk of ash-related problems in the gasifier is expected. In addition, there is limited knowledge regarding the ash transformation behavior in a DFB gasification system. Hence, the research objective for the DFB gasifier was to investigate the ash transformation behavior, particularly the risk of bed agglomeration when forest residues are used as feedstock. The risk of bed agglomeration for the requested feedstock was assessed by thermodynamic equilibrium modeling of the DFB gasifier (Paper V).
2 Background

2.1 Fluidized-bed technology

Fluidized-bed (FB) combustion is a leading technology allowing for the utilization of a variety of fuels, including low-quality fuels with a high moisture content and high mineral matter. In a typical fluidized-bed combustion system, the bed consisting of fuel (or fuels) particles and inert bed material (e.g., sand) is kept suspended through the distribution of the fluidizing agent (most often air and recirculated flue gases) by a large number of specially designed nozzles distributed over the furnace floor. The high turbulence created promotes an efficient heat transfer and uniform mixing, thereby, enhancing the combustion process. The inert bed material promotes the combustion by dispersing the incoming fuel particles throughout the bed, quick heating of the fuel particles to the ignition temperature, storing a large amount of thermal energy, and also providing sufficient residence time for the combustion process. Fuel flexibility, excellent heat transfer, lower combustion temperatures, high combustion efficiency, low NOx emission, in situ control of the SO2 emissions, and good system availability are the inherent advantages of the FB combustion over the conventional grate-fired combustion systems. Despite the advantages, there are some disadvantages with the technology such as fuel preparation in some cases (e.g., size reduction of the fuel), a well-designed system needed for ash removal (for fuels with a high ash content), and increased N2O formation due to the lower combustion temperatures [4, 11, 13].

The inherent advantages of the FB technology also make it ideal for the gasification of biomass and waste-derived fuels. However, the low temperatures result in high concentrations of heavy tars in the gas, which limits the application of the gas to direct thermal applications like burning in boilers [14, 25]. Based on the fluidizing gas velocity, the FB systems can be classified into Bubbling Fluidized-Bed (BFB) or Circulating Fluidized-Bed (CFB) systems. The BFB boilers have lower fluidization velocities in order to prevent an elutriation of solids from the bed into the convective pass, while the CFB boilers apply higher velocities to promote solid elutriation. Considering the technical aspects, they have some advantages and disadvantages over each other, but in general, the BFB is the preferred choice for moderately sized boilers, while the CFB is the more attractive alternative for the larger boilers [13, 26].
2.2 Ash-related problems

Decades of research have been conducted to develop a better understanding of the ash transformation behavior and ash-related problems in the combustion of conventional and alternative fuels, e.g., [15-19, 27-79]. Low-grade fuels often contain a significant amount of alkali metals (K and Na), which are rapidly released into the gas phase during combustion and interact with other ash-forming elements. It is known that K and Na, in the presence of Cl, S, and Si, undergo many undesirable chemical and physical transformations, forming low-melting-temperature alkali silicates in the bottom ash and also alkali sulfates and chlorides in the fly ash, resulting in a deposit formation on the heat transfer surfaces of the boiler [15, 16, 18, 27, 28]. Deposits that form on the radiant section of the boiler are called “slag,” and deposits that form on the steam tubes in the convective pass are called “fouling” [16]. Ash deposition in the utility boilers is a major problem that may result in decreased efficiency, unscheduled outages, equipment failures, increased cleaning, and high maintenance costs. Therefore, assessing the extent of the ash-related problems is of critical importance in the design and operation of the combustion systems [15, 16].

An attractive aspect of FB conversion technology is the lower bed temperatures (typically between 800-900 °C), which reduce the operating problems associated with high-fouling and –slagging fuels [13]. However, care is still required because low-grade fuels may contain a significant amount of ash-forming elements, resulting in problems with fouling, slagging, and corrosion. The formation of deposit on the superheater surfaces or later in the cooler section of the boiler may deteriorate the heat transfer and disturb or even plug the flow of the flue gas through the heat-exchanger package. Fouling may also cause high-temperature corrosion of the heat-exchanger tube metal. The corrosive nature of the deposit in boilers burning low-grade fuels results in significantly lower steam temperature (to avoid problems) and reduced power production efficiency. The melting property of the fly ash is an important factor determining the stickiness and corrosiveness of the deposited ash [15]. In the FB systems, an important ash-related problem that should be assessed is the risk of bed agglomeration, which must be taken into account in the design of the system or selection of the feedstocks [13]. The interaction of the fuel-derived ash with the bed material can lead to bed agglomeration, and subsequently defluidization of the bed [18].
2.2.1 Transformation of the ash-forming matter

The physicochemical transformation of a solid fuel during combustion can be explained in the following three steps: drying, devolatilization (pyrolysis), and char oxidation. When fuel particles enter the furnace, they first rapidly heat up and dry. In the pyrolysis step, the organic volatile species release and burn. Thereafter, char oxidation takes place. The transformation of the fuel ash-forming matter during combustion (Figure 2.1) can be divided into the release mechanisms and the fate of the residual ash. The mechanisms that contribute to the release of the ash-forming matter during combustion are vaporization, thermal or chemical disintegration of the inorganic material, and convection during rapid devolatilization. The residual ash (included and excluded minerals) may undergo fragmentation, coalescence, and chemical and physical transformation. The released fraction undergoes gas phase reactions forming different inorganic gas species, which nucleate homogenously and condense heterogeneously on the surfaces of the larger particles (e.g., residual ash). The two different routes of ash formation result in a bimodal particle size distribution of the final ash product (fly ash). Sub-micrometer particles (aerosols or fine mode) are formed as a result of the homogenous condensation of the volatilized ash species, and are typically enriched in chlorides, sulfates and carbonates of alkali metals, and also zinc and lead salts (e.g., in case of demolition wood). The heterogeneous condensation of the volatilized species on the non-volatilized ash residuals results in fly ashes with a particle size of several micrometers (coarse mode) [15, 18, 27, 28].

Figure 2.1 Scheme of the ash particle formation (Reproduced with permission from [18])
2.2.2 Ash deposition

The formation of deposit on the heat transfer surfaces can be described by the following steps: (1) formation of the ash particles or ash-forming compounds, (2) transport of the ash particles to a surface, (3) adhesion to the surface, and (4) consolidation of the deposit. Inertial impaction and thermophoresis are the two most significant mechanisms that contribute to the transport of the ash particles to a surface. Inertial impaction is important in the transport of the large particles (10 µm and larger), and the bulk of the ash deposit on the surface is most often transported by this process. Thermophoresis transports the finer ash particles in a gas due to the local temperature gradient. Adhesion of the fly ash particles on the surfaces can take place by the presence of a partly molten ash (sticky ash), where the condensation mechanisms play an important role. Condensation is the mechanism by which vapors (e.g., alkali chlorides) are collected on the surfaces cooler than the local gas. The gaseous ash-forming compounds can diffuse and directly condense on the surfaces (or particles), and/or homogeneously nucleate and form fine fly ashes, and subsequently arrive on the surface by thermophoresis. The properties of the deposited ash (e.g., ash stickiness) are significantly affected by the condensed fraction. The quantity of the condensed fraction in a deposit strongly depends on the mode of occurrence of the inorganic material in the fuel, which in the case of low-rank fuels (e.g., biomass and waste-derived fuels) becomes a significant or even dominant contributor to the development of the deposit. The heterogeneous reactions of the gas phase constituents with the deposit (e.g., sulfation), complete the mechanisms by which material can be accumulated in a deposit. It should be noted that both condensation and chemical reactions are strongly temperature dependent [16, 18, 28].

2.2.3 Bed agglomeration

The terms bed agglomeration and bed sintering are used to describe the same phenomena in the fluidized bed systems, when bed particles can be held together by a molten phase. The unwanted collapse of the fluidized-bed as a result of bed agglomeration is defined as de-fluidization. Bed agglomeration in the FB combustion and gasification systems has been studied by several research groups [43, 56, 80-99]. Bed agglomeration is quite a complex phenomenon where both physical and chemical phenomena play roles. From a chemical point of view, the interaction between the bed material and the ash-forming matter of fuel may result in the formation of a molten phase on the bed material, which is usually a prerequisite for the initiation of bed agglomeration. The formation of a viscous glassy silicate melt is the
most common reason for the bed agglomeration in the FB combustion, using silica sand as the bed material [15, 18]. The formation of alkali phosphates has also been reported to be the reason for the bed agglomeration [88, 96].

The two most important routes identified for the initiation of the bed agglomeration during the FB combustion of biomass fuels are the formation of low-melting-temperature fuel-derived ash compounds, and/or formation of low-melting-temperature coating layers on the surface of the bed particles, illustrated as Figure 2.2 [18, 97]. In literature, direct adhesion of the bed particles through partly molten fuel-derived ash is defined as melt-induced agglomeration [81, 95, 98]. Coating-induced agglomeration refers to the formation of sticky coating layers on the bed particles as a result of the chemical reactions between the bed material and the gaseous or liquid phase ash (e.g., alkali-compounds), described as reactions 1 and 2 [15, 43, 81].

\[
\begin{align*}
\text{SiO}_2(s) + 2\text{KCl}(g) + \text{H}_2\text{O}(g) &\leftrightarrow \text{K}_2\text{SiO}_3(l) + 2\text{HCl}(g) \quad (1) \\
\text{SiO}_2(s) + 2\text{KOH}(g) &\leftrightarrow \text{K}_2\text{SiO}_3(l) + \text{H}_2\text{O}(g) \quad (2)
\end{align*}
\]

The different mechanisms of coating formation result in different coating growing patterns. If the coating formation occurs independent of the bed material, the coating may grow outwards onto the bed particle, and the bed particle acts as an inert carrier for the coating material. In contrast, when the ash compounds react with the bed material, the coating grows into the particle [83]. Besides silica sand (quartz), there are alternatives suggested as bed material such as olivine sand and porous alumina. Olivine, for instance, is commonly used in the FB gasifiers due to its catalytic properties with respect to tar reduction in the producer gas. Using alternative bed materials may eliminate the formation of molten and glassy silicates. However, due to the extra cost of most alternative bed materials, quartz is still the dominantly used bed material today [15, 99].
Figure 2.2 Scheme of the bed agglomeration (*Reproduced with permission from* [18]),
(1) formation of an alkali rich (e.g., K) coating, (2) integration of small fly ash particles such as 
CaSO$_4$ and Ca$_3$(PO$_4$)$_2$, (3) homogenization and sintering of the coating layer and bed particles, 
(4) direct adhesion of the bed particles through the molten ash particles

2.3 Predicting the ash behavior

It is of great importance to predict the ash transformation behavior and find methods to estimate the degree of ash-related problems for various fuels and fuel mixtures. The elemental analysis of the fuel ash content is the first step to determine the suitability of a given fuel, from the ash behavior point of view [15]. Other techniques such as fusion temperatures and fuel indices have been developed for predicting the ash behavior, initially, for pure coal firing, but recently also used for biomass and waste-derived fuels [15, 16, 44]. These techniques, however, lack the information on the association and mineralogy of the ash-forming matter [44]. The knowledge regarding the chemical forms of the ash-forming elements in the fuel matrix is important to predict their behavior during the thermal conversion. In fact, the release, reactivity, and stability of the ash-forming elements during the thermal conversion strongly depend on their mode of occurrence in the fuel matrix. For instance, K or Na in the form of organically bonded or dissolved alkali metals are readily volatilized, but alkalis in silicate minerals are generally more stable during combustion. Chemical fractionation, an advanced fuel analysis technique, was developed for determining the association of the ash-forming elements in the fuel matrix [13, 15, 16, 18, 44]. Apart from the analytical methods, thermodynamic equilibrium modeling has also become a commonly used tool to better understand and predict the ash transformation behavior and the ash-related problems. Thermodynamic equilibrium modeling has been used to predict the physical and chemical properties of the ash in various processes such as deposition, bed agglomeration, and corrosion [19].
3 Methods

3.1 Full-scale measurements of the BFB boiler

The BFB boiler is designed for a bed temperature of 870 °C and superheated steam of 405 °C and 49 bar. During the RBT and AW projects, full-scale tests were carried out in the boiler, and the performance was monitored. The experimental procedure included sampling of the fuel mix, bed material (return sand), bed and fly ashes, as well as the deposit collected in the superheater region using a deposit probe. Figure 3.1 shows the schematic view of the BFB boiler and also the ash sampling and measurement positions, including bed material, boiler ash, cyclone ash, deposit probe position, as well as HCl and SO₂ measurements in the flue gas downstream of the economizer. The structure of the furnace floor, air nozzles of the fluidized-bed, and the superheater region of the BFB boiler are shown in Figure 3.2.

![Figure 3.1](image-url)  
*Figure 3.1 Schematic view of the BFB boiler in Borås, plus the ash sampling and measurement positions: (1) bed ash, (2) boiler ash, (3) cyclone ash, (4) deposit probe upstream of the superheaters, (5) HCl and SO₂ measurement in the flue gas downstream of the economizer (with permission from Borås Energi och Miljö AB)*
Figure 3.3 shows the different samples collected during the RBT and AW projects. For sampling of the deposit collected on the surface of the superheater tubes, a deposit probe was inserted upstream of the convective pass, shown as Figure 3.4. The deposit probe represents a superheater tube and consists of an air-cooled tube for adjusting the probe’s surface temperature on the basis of the operating conditions requested. Two high-alloy rings of the same material as the original tubes were mounted on the deposit probe: one for elemental analysis and one for SEM-EDX analysis. The rings were also weighed before and after the measurements to calculate the deposit-growth rate during the different combustion cases. A 2 to 3 hour exposure time was considered, and the surface temperature of the probe was maintained at 435 °C, simulating the actual steam temperature of 405 °C in the tubes.

Figure 3.2 (a) the furnace floor, (b) air nozzles of the fluidized-bed, (c) upstream of the superheaters, and (d) superheater tubes, photographed during the shutdown and overhaul of the BFB boiler (photographed by the author with permission from Borås Energi och MiljöAB)
Figure 3.3 Photos illustrating the different samples collected for the chemical analysis; (a) solid waste mix, (b) animal waste, (c) bottom ash, (d) bed material (return sand), (e) boiler ash, (f) cyclone ash (photographed by the author with permission from Borås Energi och Miljö AB)

Figure 3.4 (a) Installation of the deposit probe upstream of the convective pass, (b) deposit rings before sampling (c) deposit rings after sampling (photographed by the author with permission from Borås Energi och Miljö AB)
3.2 Standard chemical analysis

The standard chemical analysis (e.g., elemental analysis) of the solid waste fuel, animal waste, biomass, ash fractions, and also collected deposits, presented in this work, were carried out by an authorized laboratory. Detailed information regarding the standard analysis techniques and obtained results for the different samples are found in Papers I-V.

3.3 Chemical fractionation

The ash-forming matter in the solid fuel can be divided into four classes: dissolved salts, organically bound matter, included mineral matter, and excluded mineral matter, illustrated as Figure 3.5 [18, 44]. Chemical fractionation [44], a stepwise leaching method, was used to determine the chemical association of the ash-forming elements in the different fuels studied in Papers I-V (except for the animal waste). With this methodology, the water-soluble compounds in the form of dissolved salts such as alkali chlorides, sulfates, carbonates, and phosphates are extracted by de-ionized water in the first step. Ammonium acetate (NH₄Ac, 1M) is used as the second solvent to leach out the organically bound metal cations (e.g., Mg, Ca, K, and Na) by ion exchange. In the final step, 1.0 M HCl is used to dissolve most of the scarcely soluble inorganic salts such as carbonates, sulfates, and phosphates of alkaline-earth metals and other metals, at a temperature of 70 °C. The insoluble solid residue consists of silicates and other minerals. Note that elements covalently bound to the organic fuel matrix, such as S, Cl, and P may stay in the insoluble fraction [15, 44]. Figure 3.6 shows the different steps of the chemical fractionation procedure. With chemical fractionation, an indication of the ash chemistry could also be obtained, determining the association of the ash-forming elements in the bottom or fly ashes [54, 100-103].

![Figure 3.5](image_url) Association of the ash-forming matter in the fuel matrix (Adapted from [44])
Figure 3.6 The chemical fractionation procedure leaches a fuel with water, ammonium acetate, and hydrochloric acid (Adapted from [15] and [44]).

3.4 SEM-EDX

A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray spectrometer (EDX) is a powerful tool for advanced chemical characterization of a specimen. SEM provides information regarding the morphology and microstructure, and EDX identifies the chemical composition of the specimen. The basic principle of the method is scanning of the specimen surface with a focused electron beam. The interaction between the electron beam and the atoms in the sample gives information about the morphology and composition of the specimen. Secondary electrons (SE), back-scattered electrons (BSE), and characteristic X-ray are some types of signals that are emitted. The SE mode is suitable for topographic imaging, while the BSE mode is oriented toward the detection of the atomic density. X-ray identifies the composition of the sample and also the abundance of each element in the specimen [104].

The topology of the ash fractions and collected deposits during the RBT and AW projects was analyzed by an Environmental SEM (ESEM). ESEM is able to examine the susceptible and non-conducting materials without any sample damage, since there is no need for covering the
sample surface by a conducting material, thus, avoiding sample damage. The specimen was spread on a carbon adhesive, mounted in epoxy, or analyzed directly (in the case of the deposit rings). Distribution of the key elements in the samples, including both qualitative and quantitative analyses, was conducted by the ESEM, equipped with an EDX detector. In order to investigate the elemental distributions in the coating layers of the particles such as return sand and boiler ash, the particles were mounted in epoxy and polished prior to the cross-sectional SEM-EDX analysis.

3.5 XRD
The presence of crystalline compounds in the ash fractions sampled during the RBT and AW projects was investigated, using X-ray diffraction (XRD). For this purpose, a Siemens D5000 X-ray powder diffractometer, using the characteristic Cu radiation source and a scintillation detector, was employed. The JCPDS database, version 2010, was used as a standard when identifying the crystalline compounds present in the ashes. It should be noted that the major limitation in the use of XRD for the ash analysis is attributed to the presence of sand particles, giving uncertainties to the analysis results.

3.6 Laboratory-scale bed agglomeration test
In order to evaluate the bed agglomeration tendency before and after the addition of AW, a lab-scale bed agglomeration test [105] was conducted (Paper II). In this method a fluidizing gas (85 % N₂ and 15 % CO₂) at a rate of 50 L min⁻¹ was uniformly introduced through the bed of a bench-scale combustor with 68mm diameter. The bed temperature was initially stabilized at 750 °C and gradually increased from 750 °C to 1100 °C, at a rate of 3.5 °C min⁻¹, while the pressure drop was continuously monitored across the bed. The first pressure reduction gives the partial agglomeration temperature, when the sand particles start to sinter together. The total agglomeration temperature is determined when the slope of the pressure drop starts to increase, meaning that the decrease is no longer sharp. The accuracy of the method is estimated to be within ±10 °C, although the results could not be directly linked to a full-scale boiler.
3.7 Laboratory-scale FB steam gasification of the biomass

In Paper V, lab-scale BFB tests were conducted to investigate the chemical composition of the residual char after the steam gasification of virgin forest residues. It should be noted that the chemical composition of the char was needed for the modeling of the combustion reactor of the DFB gasifier. The lab-scale BFB reactor (Figure 3.7) has a diameter of 7 cm and a height of 140 cm, which is divided into upper and lower sections by a perforated ceramic plate. A bed of sand particles rests on the ceramic plate, where the sand particles had an average diameter of 0.35 mm. A wire-mesh basket containing fuel pellets was used to collect the char resulting from each experiment. The wire-mesh basket had a height of 14 cm, a diameter of 6 cm, and a mesh size of 0.8 mm, which allows sand particles to easily enter and leave the basket. The lower section of the reactor (below the ceramic plate) is a gas-preheater, where steam is generated and heated to the desired bed temperature. The reactor is heated by the surrounding heating elements, which can control the bed temperature within ±5 °C. The used fuel pellets had an average length of 15 mm and diameter of 8 mm. Before the experiments, the fuel pellets were dried in an oven at 105 °C. The experiments were performed at a bed temperature of 850 °C, and a fuel particle residence time of 2.5 min. The aforementioned operational condition simulates the steam gasification of forest residues in the gasification reactor of the DFB gasifier, before their residual char enters the combustion reactor. The residual char was analyzed to determine the elemental composition and association of the ash-forming elements using standard analysis and chemical fractionation techniques [106, 107].

[Figure 3.7 Laboratory-scale bubbling fluidized-bed reactor (Paper V)]
3.8 Thermodynamic equilibrium modeling and its limitations

Thermodynamic equilibrium modeling has become a widely used tool to better understand and predict the complicated chemical interactions of the ash-forming elements during the combustion and gasification of the biomass and waste-derived fuels [19]. This type of modeling has been extensively used to predict the ash transformation behavior, and also the physical and chemical properties of ash in various ash-related processes such as deposition-related issues, slag formation in furnaces, bed agglomeration of fluidized-beds, corrosion of heat transfer surfaces, and smelt bed behavior in the recovery boilers, e.g., [19, 37, 65, 69, 71, 81, 83, 97, 108-140]. Thermodynamic equilibrium modeling of complex (multiphase multicomponent) systems is often based on the Gibbs energy minimization techniques, which calculate the chemical equilibrium composition (the most stable composition) of the system at specified conditions, considering the included thermodynamic data from all the phases and compounds [19].

Despite the demonstrated capabilities of the thermochemical equilibrium modeling, certain limitations of the technique need to be taken into account. One of the deficiencies is the lack of comprehensive databases that contain the thermodynamic data for all the ash compounds and phases (pure compounds, solution phases, and gaseous compounds), which are likely to be formed at any given condition in a boiler or a gasifier. Furthermore, the chemical kinetics and transport phenomena are not taken into consideration by the thermodynamic equilibrium models. In other words, the equilibrium assumption implies infinite reaction times and perfect mixing in the system. In the fluidized-bed environment, due to a fairly good gas-solid contact and mixing as well as a relatively long residence time for the solids, the ash transformation reactions could approach equilibrium and the addressed issues could be resolved to a large extent. While the elemental composition of the fuel is essential for thermodynamic modeling, the reactivity of the ash-forming elements should also be taken into account. Chemical fractionation of the fuel, prior to the thermodynamic modeling, was suggested as a solution to ease the addressed issue. The reactive fraction (water and acetate soluble) of the ash-forming elements is expected to reach equilibrium during combustion, while the less-reactive fraction (acid soluble and solid residue) can be in such stable or inert forms that simply pass through the combustion process unaffected. Additionally, the variations that may occur inevitably in the real system, for instance, local temperature gradients and variations in the chemical compositions of the fuel are not considered. Sensitivity analysis can be performed in such
cases to investigate the effects of these variations on the ash chemistry [15, 19, 41, 51, 109, 110, 113].

3.8.1 Ash chemistry

The ash from the biomass and waste-derived fuels can be divided into two chemically distinct categories: oxide/silicate system and salt mixture system [37]. The silicate system forms polymeric silicate anions, which tend to have high melting points and are highly viscous in the liquid state. The silicates have low volatility and are often found in the bottom ash or furnace wall slag. The salt mixture system consists of relatively simple ionic compounds such as Cl⁻, SO₄²⁻, CO₃²⁻, O²⁻, S²⁻, and PO₄³⁻ together with different metal cations. They span a large range of melting points (e.g., ZnCl₂: 318 °C, CaO: 2597 °C), and the viscosity of the liquid phase is generally rather low. The volatility of these salt-like compounds is often higher than for the silicates, and they are often found in the fly ash. There are some exceptions regarding the silicate/salt classification, for instance, phosphates that form polymeric anions, meaning that they show some similar patterns of behavior as silicate melts like high viscosity in the liquid state [19, 37].

3.8.2 FactSage

FactSage [141], a thermochemical software and database, was employed in this work for the thermodynamic equilibrium calculations (Papers III-V). FactSage is a powerful predictive tool that was introduced in 2001 when two well-known software packages, F*A*C*T/FACT-Win and ChemSage, were combined. Today, FactSage is commonly used in metallurgical and thermochemical processes for calculations of multicomponent multiphase equilibria, as well as complex phase diagrams. The software contains extensive thermodynamic databases for different thermochemical processes, including molten salts and slags for the modeling of the ash chemistry [19, 141]. The FTsalt database included in FactSage is the most extensive thermodynamic database available for salt systems (pure salts and salt solutions) [141]. However, addition of other elements such as Ca, Pb, and Zn to the alkali salt mixtures would be of relevance in the modeling of ash chemistry, which is being implemented [19]. The FToxid database in FactSage is also possibly the most comprehensive thermodynamic database for solid and liquid silicates and oxides [19, 141, 142]. However, in predictions of the melting of the alkali-rich silicate slags, caution is needed since the addition
of Na$_2$O and K$_2$O has not been optimized over the whole compositional range in the FToxid. In addition, the available thermodynamic data for solid and liquid phosphates are deficient, and further evaluations are needed [19]. In a recently released version of the software (FactSage 7), the P-related thermodynamic data in the FToxid database has been improved. In addition, the systems containing Na$_2$O and K$_2$O in the FToxid database have recently been re-evaluated and re-optimized [143]. In general, the current databases give a relatively high accuracy in the predictions of the phase equilibria and melting properties of the alkali salt mixtures and silicate slags relevant to the ash chemistry. Lindberg et al. [19] comprehensively reviewed the state-of-the-art thermodynamic models and databases for the ashes of biomass and waste combustion.
4 Summary of the results and discussion in papers I-V

4.1 BFB boiler (Papers I-IV)

This section presents a summary of the results and discussion of the BFB boiler in the Papers I-IV, including experimental and modeling results.

4.1.1 Impact of RBT on Cl, S, and alkali distribution (Papers I and IV)

*Paper 1* investigated the impact of the reduced-bed temperature on alkali and chlorine distribution in the BFB boiler. The experimental design considered two combustion scenarios denoted as Reference (Ref) and Reduced-Bed Temperature (RBT) cases. In the Ref case, the boiler was run at a bed temperature of 870 °C (the normal bed temperature of the BFB boiler), while in the RBT case the bed temperature was reduced to approximately 720 °C. The fuel analysis of both cases showed no significant differences for the key ash-forming elements, except for the sulfur, which was found in higher concentrations in the RBT case. Note that due to the full-scale measurements and the heterogeneous nature of the fuel mix, research with exactly the same fuel composition is impossible to achieve.

Chemical analysis of the five ash streams including the bed ash, return sand, boiler ash, cyclone ash, and textile filter ashes found chlorine in higher concentrations in the three coarser ash fractions in the RBT case, where the largest increase was found in the return sand. The Cl concentrations, however, in the finer ash fractions (cyclone and filter ash) were decreased in the RBT case. The results, therefore, indicated a higher capture of Cl in the bed during the RBT case. Concerning the distribution of the alkali metals (Na and K) in the different ash fractions, no significant differences were observed between the two cases. The concentration of S in all the ash fractions of the RBT case was higher, particularly in the case of the coarser ash fractions. This was also in agreement with the results of the element balance over the boiler, which showed that the increase of S was larger in the bed ash and boiler ash. The higher amount of S found in the ash fractions of the RBT case correlated well with the higher S input flow with the fuel. The EDX element analysis on the coating layer of the return sand particles (Figure 4.1) indicated the same trend, as higher concentrations of Cl and S were observed for the RBT case compared to the Ref case. Concerning the composition of the deposit collected in the superheater region, the element analysis showed that the concentration
of Cl was reduced and that S increased on all the rings in the RBT case compared with the Ref case. This resulted in a higher S/Cl ratio in the deposit, which suggested improved environment and less corrosive deposit in the superheater region [144, 145]. The difference in the alkali concentrations was not significant; however, an increase of 0.3 to 4.3 wt% was observed on all the rings from the RBT case.

Figure 4.1 Element concentrations on the coating layer of the return sand particles in the Ref and RBT cases, measured by SEM-EDX spot analysis (Paper I)

In paper IV, the impact of the bed temperature on the transformation behavior of Cl, S, and alkali for the Ref and RBT combustion cases was further studied using thermodynamic equilibrium modeling. In the modeling results, the LSC (Low Sulfur Content) represents the composition of the fuel mix with a lower S content (the Ref case), and RBT represents the composition of the fuel mix in the RBT case. The equilibrium calculations for each combustion case were carried out considering the same bed temperature, applied during the full-scale measurements. Table 4.1 presents the distribution of Cl, S, Na, and K in the gas phase (hot flue gas leaving the furnace) and the condensed phase in the LSC and RBT cases. The condensed phase ash may remain in the bed or entrained with the flue gas leaving the furnace. The results indicate that at 870 °C (LSC), higher amounts of alkali chlorides released to the gas phase, which supports the earlier experimental findings. In addition, the higher content of S introduced to the boiler in the RBT case was predicted to mainly remain in the condensed phase ash as alkali sulfates and CaSO₄. This can explain why S was mainly
enriched in the coarser ash fractions in the RBT case. Furthermore, the modeling results can support the lower concentrations of SO\textsubscript{2} in the flue gas during the RBT case, despite the higher amount of S present in the fuel stream. Accordingly, the higher S/Cl ratio observed in the deposit of the RBT case could be explained by the modeling results, indicating lower concentrations of the alkali chlorides in the flue gas, as well as higher sulfation of the alkali chlorides.

Table 4.1 Distribution of Cl, S, Na, and K in the gas phase and condensed phase in the LSC and RBT combustion cases, calculated by thermodynamic equilibrium modeling

<table>
<thead>
<tr>
<th></th>
<th>LSC</th>
<th>RBT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase (ppm\textsubscript{V})</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl(g)</td>
<td>59</td>
<td>56</td>
</tr>
<tr>
<td>SO\textsubscript{2}(g)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>NaCl(g)</td>
<td>182</td>
<td>127</td>
</tr>
<tr>
<td>KCl(g)</td>
<td>141</td>
<td>68</td>
</tr>
<tr>
<td><strong>Condensed phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(g kg\textsuperscript{-1} fuel)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO\textsubscript{4}(s)</td>
<td>2.30</td>
<td>4.84</td>
</tr>
<tr>
<td>Na\textsubscript{2}SO\textsubscript{4}(l)</td>
<td>2.52</td>
<td>3.21</td>
</tr>
<tr>
<td>NaCl(l)</td>
<td>0.18</td>
<td>1.48</td>
</tr>
<tr>
<td>K\textsubscript{2}SO\textsubscript{4}(l)</td>
<td>0.90</td>
<td>1.07</td>
</tr>
<tr>
<td>KCl(l)</td>
<td>0.07</td>
<td>0.59</td>
</tr>
</tbody>
</table>

A sensitivity study was also carried out to examine the effect of the bed temperature on the alkali chlorides released to the gas phase, assuming a constant amount of Cl, Na, K, and S in the fuel mix. Figure 4.2 shows the predicted concentrations of the alkali chlorides in the hot flue gas as a function of the bed temperatures. Comparing the results, the higher bed temperatures results in higher concentrations of the alkali chlorides in the flue gas, meaning that at lower bed temperatures a higher amount of alkali chlorides remain in the condensed phase ash.
Figure 4.2 Impact of the bed temperature on the amount of alkali chlorides in the hot flue gas leaving the furnace, calculated by thermodynamic equilibrium modeling (Paper IV)

4.1.2 Impact of the AW co-combustion on the ash chemistry (Papers II and IV)

*Paper II* investigated the impact of animal waste co-combustion on the ash chemistry in the BFB boiler. Combustion of the AW products, such as crushed animal carcasses and slaughterhouse waste products has increased as a consequence of the mad cow disease epidemic in the 1990s. Apart from the sanitary aspects, the high fat content of the AW made it a new “opportunity fuel” for combustion in waste-to-energy boilers [146]. The elemental analysis of the ash-forming elements in the AW showed high concentrations of Ca and P, as well as notable amounts of S, Cl, Na, K, Mg, and Zn. The high concentrations of Ca and P in the AW products are mainly due to the presence of hard tissue such as crushed bone containing $Ca_{10}(PO_{4})_6(OH)_2$ and $\beta$-$Ca_3(PO_4)_2$, which are mainly non-reactive during the combustion process. Up to 99 % of the calcium content of the AW may present in the bone and teeth material, while phosphorus is still an essential component in the organic fraction and proteins derived from the soft tissue. This fraction of P is in a reactive form and can be released during the combustion, contributing to the ash transformation reactions [127, 147-149].
In the AW project, 20-30 wt % AW (secondary fuel) was added to the ordinary solid waste. As a result, the composition of the fuel mix was changed; also, due to the high moisture content of the AW, a reduction of the bed temperature was achieved, thus removing the need for flue gas recirculation and water spraying. Adding AW to the solid fuel mix reduced the bed temperature by 70-100 °C. Figure 4.3 shows the element balance over the boiler for the mono-combustion of solid waste (Ref case), and also for the co-combustion of animal waste and solid waste (AW case). Comparing the results, P is enriched in both coarse and fine ash fractions, while Ca is enriched in the bed ash and boiler ash in the case of AW co-combustion. The SEM-EDX spot analysis of the coating formed on the bed particles (return sand) indicted higher concentrations of Ca, S, Cl, and P in the coating layer of the AW case. The chemical fractionation of the bed particles revealed that the higher Ca-, P-, and S- associated compounds in the coating of the AW case are mainly acid soluble compounds such as calcium phosphate and sulfate. The enriched calcium phosphate in the bed ash as a result of the animal waste co-combustion was also reported by Hagman et al [127]. The elemental analysis of the deposit rings showed that the increased amount of Ca and P in the fuel mix is not reflected in the deposit composition. Cl and S, however, were found in lower amounts in the deposit of the AW case. Additionally, the average concentrations of the SO2 and HCl in the flue gas measured after the economizer were significantly increased in the AW case.

Figure 4.3 Element balance over the boiler: (a) Ref case and (b) AW case (X shows the total inflow of the element to the boiler by the fuel) *(Paper II)*
Thermodynamic equilibrium modeling of the two combustion cases (presented in *paper IV*) provided more information regarding the impact of the AW co-combustion on the ash transformation behavior in the boiler. Table 4.2 presents the distribution of Cl, S, Na, K and P in the gas phase (hot flue gas leaving the furnace) and condensed phase for the Ref and AW cases. The modeling results predicted higher levels of SO$_2$ and HCl in the flue gas of the AW case, which is consistent with the measurements. Higher concentrations of SO$_2$ and HCl in the flue gas during the AW co-combustion could be explained by the reaction between the released phosphorus with available CaO(s), which acts as a natural desulphuriser during combustion, described as reaction 3 [18].

\[
\text{CaO(s) + SO}_2\text{(g) +} \frac{1}{2} \text{O}_2\text{(g) → CaSO}_4\text{(s)} \quad (3)
\]

In fact, phosphorus has a high affinity for calcium during combustion and produces stable solid products in the residual ash, according to reaction 4 [41]:

\[
\text{P}_2\text{O}_5\text{(g) + 3CaO(s) ↔ Ca}_3\text{P}_2\text{O}_8\text{(s)} \quad (4)
\]

Therefore, it could be argued that the higher concentrations of reactive P in the AW case reduced the available CaO(s) in the furnace, and consequently increased the free SO$_2$ in the flue gas. Subsequently, the higher levels of SO$_2$ increased the rate of the alkali chloride sulfation, and more HCl was formed in the furnace. Reactions 5 and 6 summarize the sulfation of the alkali chlorides, where A is either K or Na [150-153]:

\[
\text{SO}_2\text{(g) +} \frac{1}{2} \text{O}_2\text{(g) → SO}_3\text{(g)} \quad (5)
\]

\[
2 \text{ACl(g) + SO}_3\text{(g) +} \text{H}_2\text{O(g) → A}_2\text{SO}_4\text{(s,l) + 2 HCl(g)} \quad (6)
\]

The modeling results also predicted a significant reduction of the gaseous alkali chlorides in the flue gas in the AW case, which could be attributed to the lower bed temperature and also the higher rate of alkali chloride sulfation in the furnace.
Table 4.2 Distribution of Cl, Na, K, S, and P in the gas phase and condensed phase in the Ref and AW combustion cases, calculated by thermodynamic equilibrium modeling

<table>
<thead>
<tr>
<th></th>
<th>Ref</th>
<th>AW</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase (ppmV)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl(g)</td>
<td>205</td>
<td>221</td>
</tr>
<tr>
<td>SO$_2$(g)</td>
<td>15</td>
<td>55</td>
</tr>
<tr>
<td>NaCl(g)</td>
<td>170</td>
<td>68</td>
</tr>
<tr>
<td>KCl(g)</td>
<td>116</td>
<td>53</td>
</tr>
<tr>
<td><strong>Condensed phase (g kg$^{-1}$ fuel)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO$_4$(s)</td>
<td>6.29</td>
<td>3.58</td>
</tr>
<tr>
<td>Ca$_3$HO$_3$P$_3$(s)</td>
<td>0.62</td>
<td>4.29</td>
</tr>
<tr>
<td>Na$_2$SO$_4$(l)</td>
<td>2.72</td>
<td>2.56</td>
</tr>
<tr>
<td>NaCl(l)</td>
<td>0.30</td>
<td>0.19</td>
</tr>
<tr>
<td>K$_2$SO$_4$(l)</td>
<td>0.93</td>
<td>1.26</td>
</tr>
<tr>
<td>KCl(l)</td>
<td>0.10</td>
<td>0.11</td>
</tr>
</tbody>
</table>

4.1.3 Bed agglomeration modeling (Paper III)

In the RBT project, agglomerates were observed in the samples of the Ref case (870 °C), but not in the RBT case (720 °C). In addition, the particles of the Ref case had a transparent and glassy coating, while the coating of the RBT case was white powder-like. In the AW project, the agglomerated particles were observed in the mono-combustion of the waste (Ref case), and they disappeared in the case of AW co-combustion, shown as Figure 4.4. Both the lower bed temperature and also the changed fuel composition were considered as possible explanations for the elimination of bed agglomerates in the AW case.

![Figure 4.4](image)

Figure 4.4 Back-scattered electron images of cross sections for bed sand particles for (a) agglomerated sands in the Ref case and (b) no agglomerates in the AW case (Paper III)
In *Paper III*, thermodynamic equilibrium modeling of the bed area was carried out to better understand and interpret the chemistry and melting behavior of the ash in the bed during the Ref and AW cases. Figure 4.5 illustrates the modeling approach of the bed area where the elemental composition of the fuel mix, together with the primary air, was considered as input into the model. The output of the equilibrium model determines the composition of the gas phase, as well as the chemical composition and melting behavior of the bed ash (condensed phase), at a specified pressure (1 atm) and bed temperature.

![Figure 4.5 Modeling approach of the bed area of BFB boiler (Paper III)](image)

The slagging tendency of the fuel mix in the Ref and AW cases as a function of the bed temperature is shown in Figure 4.6. For both the combustion cases, the model predicted formation of slag (molten oxides) at a bed temperature of approximately 815 °C. The presence of the sticky molten oxides at 870 °C can explain the formation of the agglomerates in the Ref case. At 750 °C, no slag formation was predicted, which is in a good agreement with the experimental observations, indicating no bed agglomeration in the RBT (720 °C) and AW (750 °C) cases. According to the modeling, at bed temperatures higher than 875 °C, the slagging tendency drastically increases for the Ref case fuel mix compared to the AW fuel mix. Table 4.3 shows the results of the controlled FB agglomeration tests. The results indicate that the addition of AW increases the bed agglomeration temperature by 70-100 °C. The agglomeration temperature in the lab-scale tests, however, is higher than the real boiler, meaning that this measurement is only comparative between the cases and cannot be directly used in a full-scale boiler.
The composition and melting behavior of the bed ash were also studied as ternary phase diagrams. The EDX spot analysis of the coating layer of the particles, together with the extracted phase diagrams were used to identify the oxide systems and the corresponding melting temperatures of the bed ash in the Ref and AW cases. Figure 4.7 presents the composition of the CaO-Na₂O-SiO₂ associated compounds, as well as their corresponding solidus temperatures (initial melting temperature) in the bed ash of the Ref and AW cases. Figure 4.7 shows the presence of the bed ash (in both cases) in an area with a solidus temperature as low as 834 °C, meaning that the coating in the Ref case (850 °C or higher) could have been in a more or less liquid state under combustion condition. Accordingly, from the results obtained by the equilibrium modeling and also ternary phase diagrams, the higher
bed temperature was identified as the primary cause of the agglomeration in the Ref case. Melt-induced agglomeration due to the formation of the sticky molten silicates in the bed was suggested as the mechanism for agglomeration.

**Figure 4.7** CaO–Na₂O–SiO₂ ternary phase diagram with some solidus temperatures presenting the bed ash composition for the Ref (solid triangles) and AW (solid squares) cases *(Paper III)*
4.1.4 Fouling modeling (*Paper IV*)

Over a period of two years, several measurement campaigns were carried out to evaluate the effect of the bed temperature and the different fuel mixes on the deposit-growth rate in the superheater region of the BFB boiler. Figure 4.8 shows the results of the deposit-growth rate, and corresponding elemental analysis for the different measurement campaigns, denoted as Ref, HSC, LSC, RBT, and AW. Ref represents combustion of the ordinary waste fuel mix under the normal bed temperature of the boiler (around 870 °C). HSC and LSC denote high-sulfur content and low-sulfur content fuel mixes, respectively, which were combusted under the normal bed temperature of the boiler. RBT represents combustion of the ordinary fuel mix under the reduced-bed temperature condition (around 720 °C). AW refers to animal waste co-combustion, when the fuel mix contained 20 wt % AW and the bed temperature was reduced by 70-100 °C (around 760 °C).

* Mostly oxygen, but also other elements that are not shown in the figure

**Figure 4.8** The deposit-growth rates and elemental analyses of the deposit for the different measurement campaigns (*Paper IV*)
In *Paper IV*, a three-stage thermodynamic equilibrium model was developed for fouling prediction in the BFB boiler. The model combined thermodynamic equilibrium calculations with the chemical fractionation technique to predict the composition of the hot flue gas leaving the furnace and becoming condensed on the superheater tubes. Thereafter, the fouling tendency was estimated, determining the fraction and quantity of the melt in the salt condensed (deposited) on the tubes. The modeling results were then compared with the results obtained by the measurements to estimate the accuracy and validity of the applied model. Figure 4.9 illustrates the three-stage model and the input data considered in each stage (equilibrium reactor (eq)). The high volatile content of the alternative fuels yields different temperature profile in the combustion chamber, leading to overheating of the freeboard compared to the bed zone. The model considers the combustion pattern and also the temperature profile in the BFB boiler, thus, dividing the combustion chamber into the bed zone (eq.1) and freeboard (eq.2) section. Accordingly, it was assumed that 60% of the fuel (reactive fraction (RF) according to the chemical fractionation results) is combusted in the bed zone (T=T_{bed}), and the rest of the fuel is burned in the freeboard (T=T_{freeboard}) [154]. Thereafter, the predicted composition of the flue gas was cooled down (eq.3) to determine the quantity and fraction of the melt in the condensed phase at a temperature range of 650-550 °C, where the flue gas meets the deposit probe and the first superheater tube bundle in the BFB boiler.

Figure 4.9 Schematic representation of the three-stage thermodynamic equilibrium model and input data used to predict the fouling tendency in the BFB boiler (*Paper IV*)
Figure 4.10 presents the quantity and fraction of the melt in the deposit (condensed phase), predicted for the different measurement campaigns. The fouling tendency for each combustion case was estimated based on the critical stickiness temperature of the deposit. The critical stickiness temperature was defined by Backman et al. [33] for the recovery boiler deposits, indicating the temperature by which enough melt (15-70 % on mass basis) is present to glue an ash particle to a surface. The fouling behavior in the different measurement campaigns (Figure 4.8) could be explained by the results presented in Figure 4.10. The condensed phase in the Ref and HSC cases not only has a higher amount of melt compared with LSC, RBT, and AW cases, but also a melt fraction above 15 % in the entire temperature range. This indicates a high stickiness rate of the deposit, which resulted in a high fouling tendency in the Ref and HCS cases. For the HSC, a higher amount of melt and also a higher melt fraction is observed at temperatures below 620 °C, which may explain the higher deposit-growth rate compared to the Ref case. The LSC and RBT cases are sticky (>15 %) only between 650-635 °C, and their melt quantities are significantly lower than the HSC and Ref cases. The AW case has a very low quantity of melt and also a melt fraction below 15 % in the whole temperature range. Accordingly, it was concluded that the higher deposit-growth rates in the HSC and Ref cases could be attributed to the high stickiness of the deposit, which resulted in a higher capture of the transported ash particles to the superheater tubes. In the LSC, RBT, and AW cases, the particle capture was considerably lower considering the low stickiness of the deposit, which gave a lower rate of the deposit buildup.
Figure 4.10 (a) quantity of melt in the condensed phase and (b) percentage of melt in the condensed phase, with a flue gas temperature of 650 to 550 ºC, calculated by thermodynamic equilibrium modeling (Paper IV)

The modeling results also showed that the concentrations of the vaporized alkali chlorides in the flue gas determine the amount of the condensed phase, while the levels of SO₂ in the flue gas significantly influence the melt quantity in the condensed phase at different temperatures in the boiler. In other words, the SO₂/alkali chloride ratio in the flue gas is a decisive factor in terms of the fouling tendency in the boiler. It was also found that the co-combustion of AW and lower bed temperatures decreases the rate of the deposition buildup in the superheater region, which is consistent with the results of the full-scale measurements.
4.2 DFB gasifier (*Paper V*)

A DFB gasifier (Figure 4.11) comprises of two interconnected fluidized-beds: a gasification reactor (gasifier) by which biomass is gasified with steam at 850-900 °C to produce nitrogen-free producer gas and residual char, and a combustion reactor (riser or combustor) where the heat needed for the endothermic gasification reactions is provided by the combustion of the residual char at about 950-1000 °C. The heated bed material in the riser is circulated as a heat carrier between the gasifier and the riser [14, 99, 125, 155-157]. The formation of coating on the bed particles take place primarily in the combustion reactor, considering intensive contact between the bed particles and burning char, higher diffusion rates, as well as higher oxygen concentration in the combustion reactor [157].

![Schematic drawing of a dual fluidized-bed (DFB) steam gasifier, plus the main input and output streams to the gasification and combustion (riser) reactors (Adapted from [158]) (Paper V)](image)

*Figure 4.11* Schematic drawing of a dual fluidized-bed (DFB) steam gasifier, plus the main input and output streams to the gasification and combustion (riser) reactors (*Adapted from [158]*) (*Paper V*)

In *Paper V*, a thermodynamic equilibrium model was developed to predict the risk of bed agglomeration in the DFB gasifier. The gasification and combustion reactors of the DFB gasifier were modeled as two separate equilibrium reactors. Figure 4.12 illustrates the two-stage thermodynamic equilibrium modeling of the combustion reactor. Due to the complete oxidation of the char together with the higher temperatures available in the combustor,
conditions are created that the ash transformation reactions are more likely to reach equilibrium, and also the solid-gas phase reactions are kinetically favored [41, 157]. The model combined the thermodynamic equilibrium calculations with the chemical fractionation technique, considering only the reactive fraction of the ash-forming elements in the fuel. The two-stage equilibrium modeling approach predicts the composition and melting behavior of the fuel-derived ash (Figure 4.12, Eq.1) as well as the coating layer formed on the bed particles through the solid-gas phase reactions (Figure 4.12, Eq.2). The elemental composition of the residual char, which was obtained by the lab-scale steam gasification of the virgin forest residues at 850 °C (discussed in section 3.7), was used as input fuel data into the combustion reactor. The output from Eq.1 determines the equilibrium composition of the condensed phase ash (fuel-derived ash) and also the gas phase. In Eq.2, the interaction between the gas phase and the bed material was modeled to predict the composition of the coating layer. The available CaO(s) formed in the combustor (Eq.1) was also considered for the solid-gas phase reactions, due to high reactivity of CaO(s) in the furnace conditions [44]. Olivine and quartz are widely used bed materials in the DFB gasification plants [156]. Therefore, the impact of olivine and quartz bed on the bed agglomeration tendency was investigated.

Figure 4.12 Schematic representation of the two-stage thermodynamic equilibrium model (Eq.1 and Eq.2) applied to predict the fuel-derived ash and coating layer of bed particles in the combustion reactor of the DFB gasifier (Paper V)

Figure 4.13 (a) shows the predicted composition of the fuel-derived ash in the combustor as a function of the bed temperature, when forest residues were used as feedstock. Considering 950-1000 °C as a typical operating temperature in the combustor, the formation of pure solid compounds and also a molten salt mixture (SALT(liq)) was predicted. According to the equilibrium calculations, the formed molten salt phase mainly consists of K₂CO₃ (mole fraction ≈ 0.85) and Na₂CO₃ (mole fraction ≈ 0.1). The salt mixtures generally have a rather low viscosity and are often found in the fly ash [19]. Therefore, the likelihood of direct
adhesion of the bed particles (melt-induced agglomeration) due to the formation of the molten salt phase was assumed to be low. At approximately 1020 °C, which is higher than the typical temperature in the combustor, formation of a slag phase was predicted. The slag phase is highly viscous [19], and it can initiate bed agglomeration through direct adhesion of the bed particles. Concerning the bed agglomeration due to the formation of the sticky coating layer (coating-induced agglomeration), the modeling results found significant differences between the olivine and quartz bed, shown as Figure 4.13 (b). The quantity of the viscous molten phase (slag) in the coating of the quartz bed was predicted to be an order of magnitude higher than the olivine bed, indicating a considerably higher risk of coating-induced agglomeration when quartz is used as a bed material in the DFB gasifier. Accordingly, it was concluded that when using forest residues as feedstock and olivine as bed material, the risk of bed agglomeration in the DFB gasifier is low, as long as the dominant temperature in the combustor is below 1020 °C. This finding is consistent with the observations of a full-scale DFB gasifier (Güssing, Austria), which reported no bed agglomeration during a long operation time (approximately 56000 h) running on forest residues and olivine bed [99].
Figure 4.13 The calculated equilibrium composition and melting behavior of (a) fuel-derived ash in the combustor of the DFB gasifier as a function of the bed temperature and (b) coating layer of olivine and quartz bed particles in the combustor (950 °C) of the DFB gasifier (Paper V)
5 Concluding Remarks

The main findings of this thesis are:

- The reduced-bed temperature (870 °C to 720 °C) in the BFB boiler resulted in: (1) a lower deposit-growth rate in the superheater region, (2) a higher S/Cl ratio in the deposit as well as less corrosive deposit, (3) less demand for fresh sand and reduced operating costs, due to the elimination of the bed agglomerates, and (4) less amount of fly ashes which also saves costs for the plant (Paper I).

- Co-combustion of the AW waste in the BFB boiler: (1) prevented the formation of bed agglomerates in the BFB boiler, (2) reduced the deposit-growth rate in the superheater region, and (3) enriched the calcium phosphate and sulfate in the bed ash (Paper II).

- Thermodynamic equilibrium modeling of the bed zone of the BFB boiler suggested: (1) lower bed temperatures as the primary reason for the elimination of the bed agglomerates during the AW co-combustion, (2) Melt-induced agglomeration as the mechanism for the formation of the bed agglomerates at higher bed temperatures, and (3) 815 °C as the initiation of the slag formation during the combustion of the ordinary solid waste mix (Paper III).

- The developed thermodynamic equilibrium model for the fouling prediction in the BFB boiler: (1) proved to be a reliable technique for the prediction of fouling tendency and (2) indicated the SO₂/alkali chloride ratio in the flue gas as a decisive factor, in terms of the fouling tendency in the boiler (Paper IV).

- The thermodynamic equilibrium modeling of the DFB gasifier showed: (1) a good agreement with the experimental findings regarding the ash chemistry in a full-scale DFB gasifier, (2) a low risk of bed agglomeration, using forest residues as feedstock and olivine as bed material, (3) a high risk of bed agglomeration, when using silica sand as the bed material, and (4) a better estimation of the ash chemistry that could be achieved under the oxidation conditions compared to the reducing conditions (Paper V).
The combination of chemical fractionation and thermodynamic equilibrium modeling proved to be a reliable technique for predicting the ash-related problems such as fouling, slagging, and bed agglomeration tendency in the FB combustion of biomass and waste-derived fuels. This modeling approach can be implemented as a first indication to assess the extent of the ash-related problems when different fuel (fuels) and operating conditions (e.g., temperature, and oxidizing/reducing atmosphere) are applied. In addition, the developed prediction models could be further improved for the FB boilers and gasifiers, for instance, using more experimental data regarding the ash chemistry and the release behavior of the ash-forming elements, and also upgrading the thermodynamic databases like adding Zn and Pb to the salt melt system. It should be noted that with the work in progress to further develop the thermodynamic databases relevant to the ash chemistry, even more accurate predictions could be achieved in the near future.

In the future work, the results obtained in paper IV (fouling modeling) will be used to develop a thermodynamic equilibrium model to estimate the corrosiveness of the flue gas in a CFB boiler. This will be performed by improving the applied model using the full-scale measurements focused on corrosion monitoring in the boiler through relevant techniques such as online measurement of alkali chlorides, SO$_2$, and HCl in the flue gas, deposit probe, in-situ corrosion probe, and other corrosion tests.


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Reduced bed temperature in a commercial waste to energy boiler – Impact on ash and deposit formation

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Abstract

Waste combustion for power production is associated with many problems due to the composition and inhomogeneity of the fuel stream. A reduction of alkaline and chlorine products in the superheater region should ease these problems significantly.

Ashes and deposits from different combustion tests in a commercial 20 MWth bubbling fluidised bed (BFB) boiler were characterised by XRD and SEM-EDX. The fuel combusted was a mix of sorted municipal solid waste (MSW) and industrial waste, often referred to as RDF (refuse derived duel). These waste fuels often contain more alkali and chlorine than does biomass and are therefore considered risky fuels prone to causing bed agglomeration, deposit formation, and corrosion.

The aim of this study was to investigate whether a lowered bed temperature could change alkali and chlorine distribution in the boiler to reduce corrosion and deposit formation. The boiler used was designed for a bed temperature in the range of 850–900 °C, which in this investigation was decreased by approximately 150 °C.

Data were collected through deposit measurements and solid sampling.

The lowered bed temperature resulted in reduced demand for fresh sand, decreased agglomeration, and reduced rates of deposit formation.

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1. Introduction

The combustion of different waste fractions for heat and power production is increasing all over the world. However, these fuels often contain high concentrations of alkali and chlorine compounds with both low melting and low vaporisation temperatures, which make combustion demanding [1]. Various additives with the ability to capture alkali metals, e.g. kaolin and sulphur in different compounds, are able to ease boiler operation [2–4], and fluidised bed (FB) boilers are known to be very fuel flexible, but as the combustion takes place in a sand bed, chemical reactions between sand-bed particles and inorganic compounds in the fuel may occur. These reactions often lead to the formation of eutectic melts causing bed agglomeration, and, in the worst case, total defluidisation. The bed temperature in FB boilers is typically 780 °C to 900 °C, controlled within a range of a few degrees [5].

High alkali and chlorine concentrations in the flue gas and high temperatures will cause corrosion in parts of the pressure vessels, e.g. on the superheater tubes [6]. Therefore, to avoid severe corrosion, waste combustors are designed for low steam temperatures, typically 400 °C in grate boilers and bubbling fluidized bed (BFB) boilers and up to 450 °C in circulating fluidised bed (CFB) boilers. Consequently the electrical power output is lower than from boilers burning fossil fuels. A reduction of alkali chlorides in the superheater region could enable higher steam temperatures and thus increased electrical efficiency of the boilers.

This project investigated the possibility of capturing alkali and chlorine in the bed ash by reducing the bed temperature by approximately 150 °C, thereby decreasing the tendency for bed particle agglomeration. A pilot study was conducted to confirm the possibility of reducing the temperature in the boiler without changing the equipment [7].

2. Experimental

2.1. The fuels

The fuel used was a mixture of 70% sorted industrial waste (RDF) and 30% sorted household waste (MSW). The waste was pretreated in a separate plant and sorted into combustible, compostable, and metal fractions. The combustible fraction, consisting mainly of paper, plastics, and wood, was crushed and shredded by a hammer mill into smaller pieces of approximately 10×10 cm.
2.2. The boilers

The two twin 20 MWth BFB boilers at Borås Energy and Environment AB (Borås, Sweden) were used for the combustion tests. The boilers, which are parallel but separate units sharing both fuel feed and ash transportation systems, produce superheated steam with a temperature of 405 °C and a pressure of 49 bars. Boiler no. 1 is equipped for research with measurement openings in a number of locations in the walls and sampling equipment for solid flows. Boiler number 2 is also equipped with some measurement hatches. Because of their shared fuel and ash systems, both boilers were kept at the same temperature during the combustion tests.

2.3. The tests

To avoid memory effects from previous combustion tests, the boilers were run at the required bed temperature for the tests for 3 days prior to each measurement. In the reference case (Ref), the boilers were run at the normal bed temperature of 870 °C. In the reduced bed temperature case (RBT) the temperature was reduced to approximately 720 °C by means of flue gas recirculation and water sprayed on the fuel. This resulted in an air factor of 1.64 in the Ref case and 1.52 in the RBT case.

In the combustion experiments two deposit probes with different surface temperatures (435 °C and 500 °C) were inserted in front of the convection pass to sample for depositions (no. 4 in Fig. 1A). The lower temperature probe corresponded to the actual steam data of the boilers and the higher simulated a higher steam temperature. The probes were equipped with two deposit rings each (Fig. 2), one for elemental analysis and one for SEM-EDX analysis. Each ring was carefully weighed before and after sampling. The deposit probes were exposed in the boiler for 2 h in each sampling. The samplings were repeated twice, with positions A and B reversed in the second instance, see Fig. 1B. The distance between the positions A and B was around 0.2 m. Samples of fuel, bottom ash, return sand, cyclone ash, boiler ash, and textile filter ashes were taken in the morning, afternoon, and evening during the combustion tests. The three samples of each material taken were mixed and treated as an average for the whole day. All analytic results presented here originate from these samples.

To investigate whether the decreased bed temperature affected the flue gas temperature in the convection path, a suction pyrometer was inserted in front of the superheaters (measurement hole C, Fig. 1B).

2.3.1. Flue gas analysis

The flue gas from the combustion was continuously analysed by FTIR (Fourier Transform Infra-Red spectrometry), which measures H2O, CO2, SO2, CO, NOx, HCl, NH3, and N2O. Also, HCl and SO2 in the gas phase were sampled downstream of the economiser (no 5 in Fig. 1A) by means of wet chemical analysis [8]. A measured volume of flue gas was sucked through a heated glass probe and bubbled through a solvent of 0.1 M NaOH(aq) and 0.3% H2O2 capturing HCl and SO2. Continuous sampling took place during 2 h.

2.3.2. Analytical methods

Solid samples were analysed for Ca, Al, Fe, K, Mg, Na, P, Si, S, Cl, Ba, and Ti using Inductive Coupled Plasma with an Atomic Emission Spectroscopy detector (ICP-AES) or a Mass Spectrometer detector (ICP-MS). All solid samples were totally dissolved according to Swedish standards SS028311 and SS028150-2. The minor elements were analysed according to ASTM D 3683.

2.3.3. SEM-EDX

The topology of ash particles and deposits on the deposit rings was examined by scanning electron microscopy (SEM) or environmental scanning electron microscopy (ESEM). In addition, the distribution of key elements in the sample structures was examined using Energy Dispersive X-ray fluorescence spectrometry (EDX). The fact that each element has a unique atomic structure, and they all therefore emit different energy X-rays, allows the elemental X-ray analysis of the specimens. Characteristic X-rays could provide two types of information, identifying both the composition of the sample and the abundance of each of the elements in the sample.

In this work both high-vacuum and low-vacuum (SEM and ESEM) electron microscopes were used. The advantage of using ESEM is that susceptible and non-conducting materials can be examined without damaging the sample material. The specimen is mounted in epoxy or spread on a carbon adhesive tape or, as in the case of deposit rings, analysed directly on the surface of the steel ring. A specimen mounted in epoxy is ground and polished to expose a cross section of the particles. No covering with conducting material is needed. The charge build-up on the sample surface is removed by a small injection of water vapour using the low vacuum mode in the microscope.

2.3.4. XRD

X-Ray Diffraction (XRD) was used to determine the crystalline elements in the ash fractions. We used a powder diffractometer Siemens
emissions. The concentration of SO2 decreased somewhat downstream of the economiser together with operating parameters. The bed temperature increased from 695 °C to 755 °C during the measurements in the RBT case. In addition, the FTIR measurements after the textile filter ash showed that there were no large differences in fuel composition between the two combustion tests (Table 1). The element showing the largest disparity is S, which is found in higher concentrations in the RBT case than in the Ref case. Because of the size of the boilers and the type of fuel, research with exactly the same fuel composition is impossible to achieve. The concentrations of total alkali, Cl, Al, and Ca in the fuel, which are important in deposit formation and agglomeration, were found in equal amounts during the two tests.

3.2. Flue gas composition

Table 2 shows the flue gas measurements of HCl and SO2 downstream of the economiser together with operating parameters. The HCl concentration increased with 25% in the flue gas in the RBT case. In addition, the FTIR measurements after the textile filter show an increase of HCl by 36%. Unfortunately, the bed temperature increased from 695 °C to 755 °C during the measurements in the RBT case, which could have caused a release of Cl captured in the bed. It is also possible that more Cl was added with the fuel in the RBT case because of the imperfect homogeneity of the waste fuels, although this was not shown by the fuel analysis prior to the higher HCl emissions. The concentration of SO2 decreased somewhat downstream of the economiser in the RBT case, even though more S was introduced by the fuel in this combustion case.

### 3.3. Ash composition and element distribution

Visible differences in the ash formation were found in both the bed ash and return sand. The ash particles in the RBT case had a white powder-like coating, whereas the coating on the particles in the Ref case was transparent and glassy. Agglomerates were found in the samples from the Ref case but not from the RBT case. All ash flows during the combustion tests with RBT were decreased, except for the bed ash flow, which increased. Because of the lack of agglomerates in the RBT case, more return sand was collected and returned to the boiler than in the Ref case, thus reducing the demand for fresh new bed sand. Table 3 shows that Cl was found in higher concentrations in the three coarser ash fractions in the RBT case. The largest increase in Cl was found in the RBT return sand, with 500% more Cl than in the Ref case. Both bed ash and boiler ash (160%) and boiler ash (20%) also had large increases in Cl compared with the Ref case. However, the Cl concentration in RBT decreased in the cyclone and filter ash. The Al concentrations decreased in the bed ash and return sand in the RBT case and thus increased in the other ash fractions. No significant changes were seen in the Ca, P, and Si distributions. Fe increased by 7% in the bed ash, 24% in the boiler ash, and 11% in the cyclone ash in the RBT case. The largest increase of Fe (41%) was found in the return sand. However, the RBT case had higher input concentrations of Fe from the fuel. The total alkali input from fuel was similar in both cases, although the distribution between K and Na varied. There were some variations in the composition of the ashes as well, but the differences in total alkali in the three coarser ashes were small. However, in the RBT case the concentration of both K and Na was decreased in the cyclone ash and increased in the filter ash. The concentration of S was higher in all ash fractions in the RBT case, which correlates well with the higher S input flow with the fuel in this case (Table 1). Element balances over the boiler showed that the increase of sulphur was larger in the bed ash and boiler ash than in the cyclone ash and filter ash.

Most of the trace elements did not show any clear trend in their distribution. However, the concentration of Cu was depleted in the boiler ash and enriched in all other ash fractions and Ni was found in higher concentrations in all ashes in the RBT case. Both Pb and Zn were found in lower concentrations in RBT bed ash and return sand and increased in boiler and cyclone ash.

#### 3.3.1. SEM-EDX analysis on ashes

As mentioned, differences in ash formation were visible in both bed ash and return sand. Bed ash from the RBT case contained several glass pieces which were not seen in the bed ash from the Ref case. Both the bed ash and return sand from the Ref case contained many agglomerates of different sizes with a transparent and glassy (non-crystalline) coating. SEM-EDX analyses showed that only the larger agglomerates (> 2 cm²) had a core of amorphous material (molten glass) surrounded by smaller ash and sand particles. This explains why no glass pieces were found in this ash and it also indicates that the coating had been in a more or less liquid state during combustion.

### Table 1

Fuel analysis.

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<th>Ref</th>
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</thead>
<tbody>
<tr>
<td>Moist, raw, Wt-%</td>
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<tr>
<td>Ash, dry, Wt-%</td>
<td>18</td>
<td>19</td>
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</table>

### Table 2

Measured SO2 and HCl (recalculated for 11% O2) and operational parameters during sampling.

<table>
<thead>
<tr>
<th></th>
<th>Ref Mean</th>
<th>RBT Mean</th>
</tr>
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<tbody>
<tr>
<td>Tbed °C</td>
<td>874</td>
<td>754</td>
</tr>
<tr>
<td>O2 vol.%</td>
<td>7.3</td>
<td>6.2</td>
</tr>
<tr>
<td>CO mg/Nm³, dg. 11% O2</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>H2O vol.%</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>HCl mg/Nm³, dg. 11% O2</td>
<td>13</td>
<td>16</td>
</tr>
<tr>
<td>Total air Nm³/s</td>
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<td>11</td>
</tr>
<tr>
<td>FGR Nm³/s</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

FGR = Flue Gas Recirculation.
Table 3
Analysis of the five ash streams.

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<tr>
<th>Sample</th>
<th>Bed ash</th>
<th>Return sand</th>
<th>Boiler ash</th>
<th>Cyclone</th>
<th>Textile filter</th>
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</table>

<table>
<thead>
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<th>Ref</th>
<th>RBT</th>
<th>Ref</th>
<th>RBT</th>
<th>Ref</th>
<th>RBT</th>
<th>Ref</th>
<th>RBT</th>
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<tbody>
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<td>2.4</td>
<td>1.5</td>
<td>1.8</td>
<td>22</td>
<td>20</td>
<td>170</td>
<td>142</td>
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<tr>
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<td>63</td>
<td>55</td>
<td>65</td>
<td>59</td>
<td>68</td>
<td>70</td>
<td>100</td>
<td>112</td>
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<tr>
<td>Ca</td>
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<td>59</td>
<td>70</td>
<td>86</td>
<td>53</td>
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<td>160</td>
<td>159</td>
<td>325</td>
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<tr>
<td>Fe</td>
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<td>16</td>
<td>17</td>
<td>24</td>
<td>25</td>
<td>31</td>
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<tr>
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<td>2.6</td>
<td>1.4</td>
<td>9.1</td>
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<td>6.6</td>
<td>13</td>
<td>17</td>
<td>15</td>
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<tr>
<td>Ti</td>
<td>4.5</td>
<td>2.8</td>
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<td>16</td>
<td>17</td>
<td>7</td>
<td>9.8</td>
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<th>Ref</th>
<th>RBT</th>
<th>Ref</th>
<th>RBT</th>
<th>Ref</th>
<th>RBT</th>
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<td>6</td>
<td>42</td>
<td>32</td>
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<td>11</td>
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<td>Cr</td>
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<td>5600</td>
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<td>2000</td>
<td>6100</td>
<td>4700</td>
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<td>140</td>
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<td>500</td>
<td>670</td>
<td>1000</td>
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<td>3400</td>
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<td>40</td>
<td>36</td>
<td>40</td>
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<tr>
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<td>2500</td>
<td>2700</td>
<td>2900</td>
<td>5500</td>
<td>7500</td>
<td>4600</td>
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<td>76</td>
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<td>350</td>
<td>120</td>
<td>130</td>
<td>210</td>
<td>200</td>
<td>440</td>
<td>400</td>
</tr>
</tbody>
</table>

Fig. 3. Return sand, Ref case: SEM photo (upper left) and EDX mapping on the cross section of the sample. Analyses of the elements Na, K, Si, Cl, S, Ca, Ti and Al.
The coating on the particles was most clearly seen in the return sand samples, Figs. 3 and 4.

EDX element analysis of the composition of the coating on the return sand particles showed increases in Cl (116%), S (163%), P (26%), Al (13%), Ti (13%), and Mg (44%) and decreases in Si (27%) and Ca (12%) in the RBT case compared with the Ref case (Fig. 5). The concentration of alkali, however, was nearly unchanged in the RBT case. This indicates that the coating in the RBT case contains less alkali silicate, which is known to cause low temperature melts, than the Ref case. Of course, increased temperature also increases the amount of molten phase in coatings, which leads to increased stickiness. In addition, the variation in atmosphere (reducing/oxidising) in the bed during combustion influences the ash melting. The return sand particles in both cases consisted of alkali silicates from the sand bed and alkali aluminium silicates, the latter found mostly in the RBT case. These alkali aluminium silicates are most probably derived from feldspars and glass introduced to the boiler as contaminants in the waste fuels.

The analyses of the bed ash in both cases resembled those of the return sand, except in agglomeration behaviour. Even the boiler ash correlated well with the return sand, with the difference that no agglomerates were found in either of the two boiler ashes.

The SEM-EDX analyses of the cyclone ashes showed no differences in structure or composition between the RBT case and the Ref case. In both cases Ca-Al-silicates, Ca-silicates, (K, Na)-Al-silicates, CaSO₄, and CaCl₂ were found. However, the filter ash showed some variations. The Cl concentration was 16% lower in the RBT case while the concentrations of K and P were increased by 67% and 68% respectively; increases in Na, Mg, Si, and Al concentrations were also found in the elemental analysis. As, Cd, Pb, and Sb decreased with reduced bed temperature, while Co, Ni, Cr, Cu, and Zn increased as expected. The results from the SEM-EDX supported the elemental analysis.

3.3.2. XRD analysis on ashes

Table 4 shows the XRD results for all the ashes except the bed ash. Bed ash from this boiler contains mainly glass, minerals, and metals.
from contaminants in the fuel stream that, ground to a fine powder, would not allow X-ray powder diffraction to give reliable results.

In general, the XRD analysis gave less information than expected. The difference in concentration of crystalline compounds between the two cases was very small. Return sand and boiler ash contained much SiO2 from the sand, diluting the samples to such a degree that the only differences seen in the cyclone ashes were less CaCO3 and CaSO4.

No differences in the results from the boiler ashes were found, and ash components to many K-silicates with low melting temperatures. The difference in concentration of crystalline compounds between the two cases was very small. Return sand and boiler ash contained much SiO2 from the sand, diluting the samples to such a degree that the only differences seen in the cyclone ashes were less CaCO3 and CaSO4.

In position A the deposit rate increased with increased gas flow rate was the same in all tests, indicating that it may be possible to obtain a good result by comparing the deposits from different tests on the rings collected from the same measurement hole.

### 3.4. Deposit formation

#### 3.4.1. Element analysis and deposition rate

The deposit measurements were performed twice during each combustion test for 2 h each. At each measurement two deposit probes carrying two deposit rings each were inserted in the measuring holes A and B respectively, as explained in Section 2.3. The mass gained by the rings during the two-hour measurement is recalculated as deposit formation rate in Fig. 6.

The deposition rate is clearly reduced in the RBT case compared to the Ref case. In position A the deposit rate increased with increased probe temperature as was expected, but in position B the rate decreased. No certain explanation for this was found. The differences in deposit formation rate and deposit composition were larger between the two measurement holes than between the combustion tests. This might be explained by the location of the holes just downstream of the bend of the flue gas channel (see Fig. 1A), in which the gas flow field is known to be very uneven across the duct. However, the gas flow rate was the same in all tests, indicating that it may be possible to obtain a good result by comparing the deposits from different tests on the rings collected from the same measurement hole.

#### 3.4.2. EDX analysis on deposits

The EDX analysis on the wind side (0°) showed almost the same trends as the deposit analysis, with a reduction of Cl and an increase of alkali and S in most cases (Fig. 8). However, on the lee side (180°) the results varied among the rings. The deposits on the lee side were much thinner than on the wind side, making the analyses less accurate. Because this analysis was conducted on the deposit surface and in small areas, the results may vary more than in the previous element analysis.

This method does, however, show the element distribution on the surface of the ring. In most samples no large changes in the element distribution were found, but on the wind side of the 500 °C rings in position B in both combustion cases large KCl crystals covered the surfaces (Figs. 9 and 10). However, only dispersed crystal formations were found at the surface of the 500 °C rings in position A, and no large crystals were found on the rings with deposits collected with a probe temperature of 435 °C. Deposits of CaSO4 were found on all four rings.

---

**Table 4**

Results from the XRD analysis.

<table>
<thead>
<tr>
<th></th>
<th>Return sand</th>
<th>Boiler ash</th>
<th>Cyclone ash</th>
<th>Filter ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)2</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>CaCO3</td>
<td>T</td>
<td>T</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Ca3Al2O6</td>
<td>LL</td>
<td>LL</td>
<td>LL</td>
<td>LL</td>
</tr>
<tr>
<td>CaO</td>
<td>L</td>
<td>T</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO4</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>LL</td>
<td>LL</td>
<td>LL</td>
<td>LL</td>
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<tr>
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</tr>
<tr>
<td>KAlSi3O8</td>
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<td>C</td>
<td>L/C</td>
<td>L/C</td>
</tr>
<tr>
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<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Na4Ca(SO4)3</td>
<td>T/L</td>
<td>T/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaClOH</td>
<td>C</td>
<td>C</td>
<td>C</td>
<td>C</td>
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<tr>
<td>MgO</td>
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<td>L</td>
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<td>T</td>
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<tr>
<td>Ca5(PO4)3Cl</td>
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<tr>
<td>Na4Ca(SO4)3</td>
<td>T/L</td>
<td>T/L</td>
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<tr>
<td>CaClOH</td>
<td>C</td>
<td>C</td>
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<td>L</td>
</tr>
<tr>
<td>MgO</td>
<td>L</td>
<td>L</td>
<td>T</td>
<td>T</td>
</tr>
</tbody>
</table>

C = Clear crystals, L = Less clear, T = Trace (diffractions of crystals), L/LL = less than in Ref, + more than in Ref, *Uncertain result.

---

**Fig. 6.** Measured deposit growths upstream of the superheaters.

**Fig. 7.** Elemental analysis of the deposit removed from the rings, oxygen excluded. The samples are marked by temperature, measurement hole, and combustion case.
4. Discussion

Although this research was performed on a full scale waste-to-energy boiler, the input data for the different combustion cases were kept at comparable levels. The fuel mix used for the different combustion tests had equal compositions of Cl, Na, K, Ca, and Al, which are all important elements in combustion-related problems. Only the concentration of S differed between the two test days (Table 1), however, the difference in S concentration was well within the range of normal fluctuation in the fuel stream to the boiler. A pre-study was conducted to investigate the possibility of decreasing the bed temperature to around 720 °C without reconstructing the boiler and to test whether the predicted results might be obtained [7]. The increased amount of S introduced to the boiler in the RBT case may be the main reason why the S concentrations were higher in all ash fractions, but it does not explain the decrease in the SO2 concentration in the flue gas. One probable explanation could be the alkali sulphate and calcium sulphate formation capturing SO2 and releasing HCl [4,9,10], but then alkali and calcium also would have to have increased in the ash, and that was not the case here. However, according to Pedersen et al. [11] the sulphur release to the gas phase is both fuel specific and temperature dependent. Their study showed that the S release in the temperature range of 500 °C to 750 °C was dependent on the original association of S in the fuel and increased only slightly with temperature, but from 750 °C to 1000 °C the release increased considerably. These results support our finding of higher S release in the Ref case with a bed temperature of 870 °C than in the RBT case with a bed temperature of 720 °C.

Coatings were found on all ash particles in the three coarse ashes in both cases. However, visible differences in the surface structure were discerned. The coating on the particles from the Ref case was amorphous and transparent and agglomerates were plentiful in the bed ash and return sand. The coating in the RBT case was crystalline and powdery and no agglomerates were found in any of these ashes. In addition, calcium–aluminium-silicates were found by XRD in both cases, but more often in the decreased bed temperature case and in presence of calcium-silicate. Both alkali–aluminium-silicates and calcium-silicates have relatively high melting temperatures and research has showed that adding kaolinite/kaolin [2,3] and Ca

Fig. 8. EDX analysis of the deposit rings, oxygen excluded. The samples are marked by temperature, measurement hole, and combustion case.

Fig. 9. Deposit ring, Ref case, wind side, 500 °C, Position B: SEM photo (upper left) and EDX mapping on the surface of the ring. Analyses of the element Si, Al, Na, K, Cl, Ca, S, and Mg.
[12,13] under the right conditions prevents agglomeration. Ca can both prevent and promote agglomeration [12,2] depending on Na concentration in the material. The increase of Al and Mg in the coatings from the RBT case could also help to prevent agglomeration [13]. The increase of Cl in the RBT case was found not only in the flue gas but also in the three coarse ashes: bed ash, return sand, and boiler ash. The concentration of Cl was six times as high in the return sand from the RBT case than in the Ref case, which means a capture of Cl in the bed of the boiler, which also was predicted. As a result the concentration of Cl was decreased in the two fly ashes – cyclone ash and filter ash – and also in the collected deposits. The alkali distribution pattern of the ashes did not follow that of either Cl or S, but the alkali concentration was decreased in the cyclone ash and increased in the filter ash in the RBT case, which suggests that it is found in smaller particles (sub micron).

The lack of agglomerates in the RBT case resulted in a decreased demand for fresh sand to the bed, which in turn resulted in a reduction of all ash flows, except the bed ash flow which increased. Both the reduced demand for fresh sand and the shift in ash flow result in saved costs, because it is generally more costly for boiler owners to deposit fly ash than bed ash.

In the RBT case, the rate of deposit formation was decreased by approximately 20% and less Cl was found in the deposits. In addition, both S and alkali increased, probably as a result of alkali sulphation. The gain of S in the deposits and the increased S/Cl ratio helps diminish the corrosion rate of the superheaters [14,15]. This suggests that the capture of Cl in the bed ash and return sand improved the deposit environment in the superheater in the RBT case, however differences in sulphur concentrations in fuel mixes in the two combustion test may have influenced the results to some extent.

5. Conclusions

When the bed temperature was reduced from approximately 870 °C to 720 °C all agglomerates in the bed ash and return sand disappeared. This resulted in a reduced demand for fresh sand to the bed, which in turn reduces operating costs. In addition, more ash was collected as bed ash, and the flow of boiler ash, cyclone ash, and filter ash was decreased, which also saves costs for deposition.

The decreased bed temperature allowed chlorine to be captured in the coating of the bed material (bed ash and return sand), thus raising the concentration of Cl in the bed. The concentration of chlorine was also decreased in the cyclone ash, the filter ash, and the deposits, and the fly ash flow was reduced. The deposit formation rate was decreased by 20% and the sulphur concentration in the deposits increased, resulting in a higher S/Cl ratio. These results suggest a means for creating an improved environment in the superheater region, decreasing corrosion problems. However, the effects of differences in sulphur concentrations in fuel mixes require further study.

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References


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Abstract: Co-combustion of animal waste, in waste-to-energy boilers, is considered a method to produce both heat and power and to dispose of possibly infected animal wastes. This research conducted full-scale combustion tests to identify the impact of changed fuel composition on a fluidized-bed boiler. The impact was characterized by analyzing the deposit formation rate, deposit composition, ash composition, and emissions. Two combustion tests, denoted the reference case and animal waste case, were performed based on different fuel mixes. In the reference case, a normal solid waste fuel mix was combusted in the boiler, containing sorted industry and household waste. In the animal waste case, 20 wt% animal waste was added to the reference fuel mix. The collected samples, comprising sampling probe deposits, fuel mixes, bed ash, return sand, boiler ash, cyclone ash and filter ash, were analyzed using chemical fractionation, SEM-EDX and XRD. The results indicate decreased deposit formation due to animal waste co-combustion. SEM-EDX and chemical fractionation identified higher concentrations of P, Ca, S, and Cl in the bed materials in the animal waste case. Moreover, the risk of bed agglomeration was lower in the animal waste case and also a decreased rate of NOx and SO2 emissions were observed.

Keywords: bubbling fluidized bed (BFB) boiler; animal waste; MSW; deposit; ash
1. Introduction

Increasing demand for sustainable heat and power production, as well as problems landfilling wastes, has prompted heat and power plants to replace fossil fuels with alternatives such as combustible municipal solid wastes (MSW) or refuse-derived fuels (RDF) [1,2]. Combustion of MSW and RDF, however, can lead to serious fouling and corrosion problems, due to their physical and chemical properties. The major difficulties with thermally processing waste fuels are attributed to their heterogeneity, high concentrations of alkali and chlorine, and high content of inorganic incombustible materials [3]. Fluidized-bed boilers, with their inherent fuel flexibility, have been developed to resolve problems concerning fuel heterogeneity and high ash content [4]. High concentrations of alkali and chlorine compounds could cause severe corrosion of steel surfaces, particularly at temperatures above 450 °C. Potassium, sodium, and chlorine are known to be the main causes of severe high-temperature corrosion [5]. In addition, interaction between alkali species and silica sand leads to the formation of low-temperature eutectics, which could cause the agglomeration/defluidization of fluidized-bed boilers [6]. Formation of bed and fly ashes, which may contain large amounts of potentially toxic metal compounds, is also a problem when waste fuels are combusted. These ashes, which could harm the environment, are classified as hazardous materials and need special treatment and storage when landfilled [7].

Regardless of these problems, the combustion of waste fuels is still an interesting option, considering their often high energy content, their abundance, and the economic aspects of combusting them. Improved boiler operation has been investigated by either modifying the boiler function or changing the fuel mix. For example, a previous full-scale project, the Reduced-Bed Temperature (RBT) project [8], reduced the bed temperature by recirculating flue gas and spraying water on the fuel to modify the boiler function. The outcome was positive in terms of deposit formation rate, fly ash flow rate, reduced risk of bed agglomeration and some capture of chlorine in the bed [8]. Co-combustion and additive use have also proved useful in alleviating the addressed problems. Co-combustion of secondary waste fuels, such as sewage sludge and animal waste, has previously shown benefits in some projects [9–11]. Animal waste, a new fuel type, has proved beneficial when co-fired with wood chips, sorted MSW, and peat in commercial boilers [11].

The present research investigated co-combustion of animal waste with a mix of sorted industrial and sorted household waste, in a full-scale bubbling fluidized bed (BFB) boiler. The paper investigates the impact of the new fuel composition on the boiler operation. Especially the effects on operational issues, such as deposition growth rate in the heat transfer area, bed agglomeration and flue gas emissions, were followed. The distribution of major ash forming elements such as Ca, S, Cl, Na, K and P in the bed and fly ashes were examined. It was particularly significant to find out how the high concentrations of calcium phosphate compounds in the animal waste and its high moisture content [11] affected the ash transformation behavior in the bed area. Analysis of the formed deposit on the deposit rings was also performed to determine the amount of corrosive elements such as Cl and alkalis. A series of complementary lab-scale tests were also conducted to determine the effect of animal waste co-combustion on bed agglomeration temperature. The emissions of NOx in the flue gas were measured, to identify whether high nitrogen content of animal waste [11] may change NOx emissions in positive or negative way.
2. Experimental

2.1. The Fuel

Since the 2000s, the incineration of animal wastes classed at high risk of being infectious, such as animal carcasses and slaughterhouse waste products, has been regulated by the EU Commission, due to the bovine spongiform encephalopathy (BSE) crisis in the European beef industry [11,12]. Apart from sanitary considerations, the acceptable heating value of animal waste, approximately 7–8 MJ·kg\(^{-1}\), make it an interesting co-fuel for waste-to-energy boilers [11]. The animal waste is crushed and grinded into a slurry (Figure 1) in a separate plant, and transported to a receiving tank at the combustion plant. From the receiving tank, the slurry is pumped into the boiler through a closed pipe system [11]. The slurry which was injected to the boiler consists of two fractions; hard tissue (bone) and soft tissue (fat and protein) which have high concentrations of calcium phosphate compounds.

![Figure 1. Crushed and ground animal waste prepared for combustion.](image)

Two tests were performed with fuels of different compositions, referred to as the reference (Ref) and the animal waste (AW) cases. The fuel used in the Ref case was the ordinary waste fuel mix usually used in this boiler, consisting of 70 wt% sorted and pretreated industrial waste (RDF) and 30 wt% sorted and pretreated household waste (MSW). The waste fuel mix (MSW and RDF) consists mainly of paper, plastic, and wood and has a moisture content of approximately 35%, which is below what the boiler was designed to handle. In the AW case, 20–30 wt% of AW, representing approximately 20% of the total energy content of the fuel mix, was added as secondary fuel to the ordinary waste fuel mix. All fuels were grinded to a particle size <100 mm, which is the designed fuel size for this boiler.

2.2. The Boiler

Full-scale tests were conducted in a 20 MWth BFB boiler designed for waste combustion (Figure 2) owned by Borås Energy and Environment AB. The plant launched the co-combustion of AW with the ordinary waste fuel mix in the autumn of 2010. The tests were carried out in boiler No. 1 of the two twin boilers, which is equipped with measurement openings in the walls and equipment for fuel and ash sampling. Boiler No. 1 operates parallel to boiler No. 2, both of which use the same fuel feeding and ash transportation system. These boilers produce superheated steam of 405 °C and 49 bar, used for power and heat production. The boilers are designed for a bed temperature of 870 °C, but due to decreased bed agglomeration and lower deposition growth rate in the RBT project [8], the goal is a bed temperature of 750 °C.
2.3. The Tests

The full-scale co-combustion tests were carried out with typical operation conditions for a BF-boiler. Also bed sand, fuel size, moisture in with fuel and fluidization of the boiler corresponded to normal conditions. The experimental procedure entails sampling the return sand, bed and fly ashes, and deposits collected on a deposit probe, in addition to analyzing the flue gases emitted for two fuel compositions: the Ref and AW cases. Before each test, the boilers were operated with the desired fuel mixture for at least three days to eliminate any memory effects of the previous fuel. In deposit sampling, a deposit probe, simulating the super-heater tubes, was inserted upstream of the superheaters (No. 4 in Figure 2) where the flue gas has temperature of approximately 630 °C. The deposition analysis was repeated twice, once in the morning and once in the afternoon. The surface of the deposit probe was maintained at a temperature of 435 °C in all tests, representing a steam temperature of 405 °C, corresponding to normal boiler performance. The probe was equipped with two high-alloyed steel rings, one for elemental analysis and one for SEM-EDX analysis of the collected material. The exposure time for each sampling was three hours.

Bed materials, return sand, and fly ashes were sampled continuously during the combustion tests, to examine the effects of the two fuel compositions on bed agglomeration and ash chemistry. The bed material consists of both coarse and fine fractions. The coarse fraction of the bed material is discharged as bed ash (No. 1 in Figure 2), while the fine fraction, comprising mostly bed sand, is recycled to the boiler after sieving (return sand). In addition, the level of bed material is maintained by continuously injecting fresh sand into the bed area. The fly ashes, i.e., boiler ash, cyclone ash, and filter ash, were collected from the empty pass, cyclone, and textile filter, respectively. For each ash fraction and each fuel blend, sampling was repeated four times, at two hour intervals for each sampling. To obtain a mean value, a mixture of the four samples of each fraction was sent to the laboratory [13]. The emission rates of $\text{H}_2\text{O}$, $\text{CO}_2$, $\text{SO}_2$, $\text{CO}$, $\text{NO}_x$, $\text{HCl}$, $\text{NH}_3$, and $\text{N}_2\text{O}$ in the flue gas were continuously analyzed using Fourier Transform Infra-Red (FTIR) spectrometry (ABB Bomem Inc., Quebec, Canada).
2.4. The Analysis

2.4.1. SEM-EDX

A scanning electron microscope (FEI Quanta 200 ESEM FEG) (Oxford instruments Inc., Abingdon, UK) equipped with Oxford Inca Energy Dispersive X-ray (EDX) (Oxford instruments Inc., Abingdon, UK) was used for elemental analysis of ash particles. In particular, the topography was examined using SEM, while the distribution of key elements, including both qualitative and quantitative analysis, was performed using EDX. As surface preparation, ashes were mounted in epoxy and polished before the cross-sectional SEM-EDX analysis.

2.4.2. Chemical Fractionation

Chemical fractionation, a progressive leaching method using various solvents, has proven useful to estimate whether compounds in the fuel are reactive or inert during combustion [14]. With this method, an indication of the ash chemistry could be obtained; it could also be applied to determine the compound composition of ashes as a complementary method to SEM-EDX analysis [15]. The method was used for analyzing boiler and cyclone ashes in addition to the coating layer on return sand particles.

In the first step of chemical fractionation, deionized water is used to extract water-soluble compounds such as alkali sulfates, carbonates and chlorides. Recent studies indicate that some phosphates can also be extracted [16]. In the second step, carbonates, as well as sulfates, which are not easily dissolved by water, are leached out using ammonium acetate, NH₄Ac [15]. The fractions that are insoluble in water or ammonium acetate are considered less reactive during combustion. In the last step of the fractionation, other phosphates, carbonates and sulfates are extracted using 1.0 M HCl at 70 °C. The remaining solid residue, an insoluble fraction, consists of silicates and other compounds such as oxides, sulfides and minerals [15,16].

An inductive coupled plasma with atomic emission spectroscopy (ICP–AES) detector and an inductive coupled plasma with mass spectrometry (ICP–MS) detector were employed to analyze Ca, Al, Fe, K, Mg, Na, P, Si, S, Cl, and Ti in the leachates and solid samples. All solid samples were entirely dissolved according to Swedish standards SS028311 and SS028150-2 [17] before analysis.

2.4.3. Bed Agglomeration Test

To compare the bed agglomeration behavior, a series of complementary lab-scale tests was conducted. The return sands collected from the full-scale tests were put in a lab-scale fluidized-bed combustor to assess the consequences of AW co-combustion on bed agglomeration. The combustor was initially stabilized at 750 °C and fluidizing gas (85% N₂ and 15% CO₂) was uniformly introduced through the bed, 68 mm in diameter, at a rate of 50 L min⁻¹. The temperature was gradually increased from 750 °C to 1100 °C at a rate of 3.5 °C min⁻¹, while the pressure was continuously monitored across the bed. The first pressure drop gives the initial point when sand particles start to sinter together, which is called the partial agglomeration temperature. The total agglomeration temperature occurs when the slope of the pressure drop starts to increase; i.e., the decrease is no longer sharp. The method
is estimated to be accurate to within ±10 °C. This measurement, however, is comparative between the cases and cannot be directly used in a full-scale boiler [18].

2.4.4. XRD

X-ray diffraction (XRD) was used to determine the chemical composition of the crystalline compounds found in the ash fractions. The XRD data presented were obtained from a Siemens D5000 X-ray powder diffractometer (Siemens AG Inc., Munich, Germany) using the characteristic Cu radiation, and a scintillation detector. The JCPDS database, version 2010 (ICDD, Pennsylvania, USA), was used as a standard when identifying the crystalline compounds present in the ashes.

3. Results and Discussion

3.1. Fuel Analysis

The results of the fuel analyses are presented in Table 1. The ash content of the AW is almost half that of the ordinary MSW, making the ash content slightly lower in the resulting fuel mix. The calorific value of the fuel mix, however, decreased from 10.9 MJ kg\(^{-1}\) to 9.4 MJ kg\(^{-1}\) with the addition of wet AW.

<table>
<thead>
<tr>
<th>Table 1. Fuel analysis.</th>
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<tr>
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<tr>
<td>C</td>
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<tr>
<td>H</td>
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<tr>
<td>N</td>
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<tr>
<td>O</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>LHV, raw, MJ kg(^{-1})</td>
</tr>
<tr>
<td>HHV, raw, MJ kg(^{-1})</td>
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<tr>
<td>K</td>
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<tr>
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<td>Mn</td>
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<td>P</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Zn</td>
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<tr>
<td>Pb</td>
</tr>
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</table>
Table 1 also shows that the concentration of N is much higher in AW compared to the ordinary waste mix. The elemental analysis presented in Figure 3 indicates significantly more P, and Ca and less S, Cl, Na, and K in AW than in the ordinary waste mix. The resulting fuel mix of ordinary waste fuel and AW contains a four times higher phosphorus concentration than does the ordinary waste mix. Note that, due to the characteristics of waste fuels, the composition of this fuel changes over time and was not exactly the same for all tests.

3.2. Deposit Formation

The deposits formed on the surface of the rings during the various combustion tests are illustrated in Figure 4. In addition, Figure 5 shows the deposition growth rate and corresponding elemental analysis for the sampled deposit for each combustion test. The results indicate a reduction in the rate of deposit formation during AW co-combustion by three times.
Regarding the elemental distribution on the rings, the Cl concentration (11 wt%) in the deposit was higher in the AW case than the 7 wt% in the Ref case. However, the total amount was lower in the AW case than in the Ref case. The total alkali concentration rose from 6 wt% in the Ref case to approximately 14 wt% for the AW case. Moreover, the increased amount of Ca and P in the fuel (Figure 3) is not reflected in the deposit composition. The Ca concentration was 30 wt% lower and P was at the same level in the deposits formed during the AW case versus the Ref case. In addition Si and Al were found in lower concentrations in the deposits in the AW case. The concentration of S, however, increased by 33.5 wt% in the AW case.

Even though the deposit rings indicate a reduction in the amount of deposit formed in the AW case, a higher risk of corrosion might be expected due to the increased concentration of alkali and chlorine. However, visual inspection of the boiler tubes after almost one year of co-combustion with AW, did not reveal any increased corrosion.

3.3. SEM-EDX Analysis on Ashes

SEM-EDX was employed to perform elemental analysis of the coating layers formed during combustion on the particles of sampled return sand and boiler ash. The analyses presented here focus mainly on the return sand, though the coating on the boiler ash was similar in nature. Two types of sand particles are present in the boiler, consisting of silicon oxides or feldspar. Therefore, it was important to determine whether their original composition could have affected the compounds bonding to their surface during combustion. The results, however, showed no indications of differences between the particles and, in contrast to previous findings, no signs could be found of alkali silicate melt on the inner surface of the silica sand particles [6,19,20].

Figures 6a,b shows cross-sectional SEM-EDX spot analyses of the entire coating from its outer layer to the surface of the sand particles, for two return sands from the Ref and AW cases. The corresponding elemental distributions of Cl, S, Ca, Na, P, Al and Si are presented in Figure 6c,d. Comparison of the two cases indicates that the concentrations of Ca, S, Cl and P are higher in the
coating layer on return sand from the AW case. Si and Al, however, are found to be slightly lower in this case. The higher concentrations of Na, Si, and Al at point No. 8 in both cases reflect the original compositions of the feldspars in the sand particles.

**Figure 6.** Cross-sectional SEM-EDX spot analysis of the coated return sands: (a) and (c) for the Ref case; (b) and (d) for the AW case.

To achieve an average coating composition, three of the analyzed sand particles were picked from each combustion test. The results presented in Figure 7 confirm the higher concentrations of Ca, Cl, P, and S (which increased by 4.3, 1.3, 2.4 and 1.8 wt%, respectively) in the coating of the return sand particles in the AW case compared to the Ref case. The same coating composition was also found on the bed ash material and on the boiler ash particles. Higher capture of Ca, S, Cl and P compounds in the bed area could be connected to the lower rate of deposit formation in the super heater area. The results for alkali (Na, K), however, did not indicate any notable differences between the two cases, suggesting that the changed boiler conditions did not significantly affect the alkali capture in the bed.

**Figure 7.** Average element concentrations in the coating surrounding the sand particles.
3.4. Chemical Fractionation Results for Return Sand and Cyclone Ash

The chemical fractionation results for the particles more or less support the results obtained using SEM-EDX. As Figure 8 shows, higher concentrations of Ca, S, and P could be observed in the coating of the sand particles in the AW case, while the difference between the concentrations of Na and K are small. Note also that the largest part of the alkali found in the non-soluble fraction originates from the feldspar particles in the sand.

Figure 8. Results of chemical fractionation analysis of return sands with coatings: (a) Ref; (b) AW.

Comparing the two cases, the major differences in the concentrations of Ca, S, and P are found in the acid-soluble fractions. The water-and acetate-soluble fractions, in addition to the insoluble portions of Ca, P, and S are almost the same in both cases. All of the extra Ca, S, and P is found in acid-soluble forms in the AW case. This was partly explained by the fact that AW is rich in crushed bone containing Ca_{10}(PO_{4})_{6}(OH)_{2} and β-Ca_{3}(PO_{4})_{2} \cite{11,12,21}, which is soluble in acid. But in addition, parts of the P introduced with the AW fuel derive from proteins in the soft tissue of the animals and are reactive during combustion \cite{22}. This reactive part of P dominates over Si in the competition for Ca^{2+} to form calcium-phosphate, which is a stable compound \cite{23}.

The results of chemical fractionation of cyclone ash are presented in Figure 9. In addition, the concentration of acid-soluble Ca and P apparently increased in the AW case. The solubility of S changed drastically when adding AW. In the Ref case, the largest part of S occurred as acetate-soluble compounds, but in the AW case most S was found as acid-soluble compounds. The results do not indicate in which form this S is found in the ash. For the boiler ash, the results are almost similar to the cyclone ash.
3.5. XRD

The XRD results for boiler ash, cyclone ash, filter ash and fresh sand are presented in Table 2. The differences between the three cases are very small, probably due to the original composition of the fresh sand. The ordinary composition of Swedish sands, which contain feldspars, make it difficult to distinguish, analytically, between the sands and ashes. Quartz (SiO₂), albite (NaAlSi₃O₈), microklin (KAlSi₃O₈) and klinoklor ((Mg,Al)₆(Si,Al)₄O₁₀(OH)₈) are compounds found in the fresh sand. Several of these compounds were also found in the ash, for example, quartz, albite and microklin in the boiler ash.

Despite the limitations of the analysis, one can conclude that no large changes occurred in the crystalline part of the ashes. The cyclone ash in all cases had a high NaCl content, but only the Ref case contained KCl. Regarding the fact that high concentrations of small NaCl crystals in the cyclone ash can impede good analytical results, the samples were washed with deionized water, dried, and then reanalyzed. However, the washing had only a small impact on the results in these cases. Calcium aluminum oxide, calcium aluminum silicate and quartz were the dominant compounds in all cases, and only one phosphate was detected in one case, that of AW.

3.6. Chemical Analysis of Ashes

Five ash fractions were analyzed (see Figure 10). The comparison indicates increasing concentrations of S, Cl, and Ca when following the system from bed ash—the first fraction sampled—to filter ash. However, for Al, Si, and alkali the reverse is the case, with the lowest concentrations being found in the filter ash. This could be explained by the smaller amount of sand particles, consisting mostly of Si, Al, K, and Na, in the filter ash.

Once more, higher concentrations of Ca, P, S, and Cl could be observed in the ashes in the AW case. For S and Cl, this is more noteworthy given that S and Cl concentrations in the fuel in both the Ref and AW cases were fairly similar (Figure 3). This may be linked to the lower bed temperature because the results are close to those from the RBT case, in which the lower bed temperature led to higher capture of S and Cl in the bed material coating [8]. Ca and P, mainly introduced as bone tissue
with the AW, seem to be enriched in the bed ashes. The results for K and Na in Table 3 reconfirm that no major differences of the alkali concentration could be seen between the two cases.

Table 2. XRD results from the Ref and AW cases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiler ash</th>
<th>Cyclone ash</th>
<th>Filter ash</th>
<th>Fresh Sand</th>
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<tr>
<td></td>
<td>Ref</td>
<td>AW</td>
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<tr>
<td>Ca(OH)₂</td>
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<td>L</td>
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<td>CaCO₃</td>
<td>-</td>
<td>-</td>
<td>L</td>
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<tr>
<td>(Mg,Al)₆(Si,Al)₄O₁₀(OH)₈ Clinochlore</td>
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</table>

Notes: M = Much; L = Little; T = Trece.

Figure 10. Elemental analysis of bed ash, return sand, boiler ash, cyclone ash, and filter ash, for the Ref and AW cases.
Table 3. Elemental analysis of ashes \([\text{g (kg ash)}^{-1}]\).

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<td>79</td>
<td>105</td>
<td>196</td>
<td>206</td>
<td>365</td>
<td>373</td>
</tr>
<tr>
<td>K</td>
<td>16</td>
<td>15</td>
<td>24</td>
<td>20</td>
<td>21</td>
<td>20</td>
<td>12</td>
<td>12</td>
<td>7.4</td>
<td>11</td>
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<tr>
<td>Na</td>
<td>48</td>
<td>42</td>
<td>31</td>
<td>30</td>
<td>28</td>
<td>30</td>
<td>19</td>
<td>19</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>Cu</td>
<td>4.6</td>
<td>7.0</td>
<td>3.0</td>
<td>1.4</td>
<td>6.6</td>
<td>5.3</td>
<td>4.1</td>
<td>3.5</td>
<td>5.3</td>
<td>4.8</td>
</tr>
<tr>
<td>Pb</td>
<td>0.7</td>
<td>0.4</td>
<td>0.7</td>
<td>0.3</td>
<td>0.6</td>
<td>0.4</td>
<td>0.9</td>
<td>0.7</td>
<td>3.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Zn</td>
<td>2.5</td>
<td>1.9</td>
<td>3.0</td>
<td>2.1</td>
<td>3.8</td>
<td>2.5</td>
<td>7.0</td>
<td>5.8</td>
<td>5.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe</td>
<td>33</td>
<td>23</td>
<td>31</td>
<td>29</td>
<td>29</td>
<td>28</td>
<td>26</td>
<td>24</td>
<td>3.4</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Figure 11 presents the elemental balances over the boiler for the various fractions. The results were calculated using the measured ash and fuel flows, in addition to the chemical compositions of both fuels and ashes. The fractions entering the system are fuel and lime and the fractions coming out are the ash fractions. The element balances agree very well, considering the size of the boiler.

Figure 11. Element balances over the boiler: (a) Ref case; (b) AW case. X = The total inflow of the element to the boiler (fuel and lime) compared to the outflow (ash flows).

Table 4 presents more detailed information about the proportion of elements in different ash fractions. As a result of AW co-combustion, the proportion of total P increased from 15% to 23% in the bed ash but decreased from 46% to 40% in the cyclone ash. The Ca concentration increased by 2.7 and 3.6 percentage points in the bed ash and boiler ash, respectively, but decreased by 6.6 percentage points in the filter ash. The S concentrations rose by approximately 8 percentage points in the bed ash and boiler ash, but declined by 1 percentage points in the cyclone ash and 20 percentage points in the filter ash. The total alkali decreased by 13 percentage points in the bed ash, but increased in the boiler, cyclone and filter ashes. The greatest reduction in Cl concentration was observed in cyclone ash, in which it decreased by over 20 percentage points, while it increased by 1.5 percentage points in the bed ash.
### Table 4. Elemental analysis balance of the ashes (wt-% distribution).

<table>
<thead>
<tr>
<th>%Proportion in Ash</th>
<th>Bed Ash</th>
<th>Boiler Ash</th>
<th>Cyclone Ash</th>
<th>Filter Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref</td>
<td>AW</td>
<td>Ref</td>
<td>AW</td>
</tr>
<tr>
<td>P</td>
<td>13.6</td>
<td>23.3</td>
<td>25.7</td>
<td>24.8</td>
</tr>
<tr>
<td>Ca</td>
<td>7.5</td>
<td>11.4</td>
<td>12.1</td>
<td>15.9</td>
</tr>
<tr>
<td>S</td>
<td>4.1</td>
<td>11.4</td>
<td>12.1</td>
<td>20.0</td>
</tr>
<tr>
<td>K</td>
<td>27.9</td>
<td>25.8</td>
<td>38.2</td>
<td>36.3</td>
</tr>
<tr>
<td>Na</td>
<td>44.3</td>
<td>39.3</td>
<td>27.2</td>
<td>31.0</td>
</tr>
<tr>
<td>Cl</td>
<td>0.9</td>
<td>2.2</td>
<td>1.3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

### 3.7. Bed and Agglomeration Temperature

Adding AW to the fuel mix, reduced the bed temperature by 70 °C relative to that of the Ref case. The positive effects of AW co-combustion on the bed agglomeration are shown in Figure 12a,b, in which visual inspection of the bed ashes for both cases shows considerably less amount of agglomerated particles in the AW case than do those from the Ref case. This difference could be explained by the change in temperature, the changed chemistry or both [8].

**Figure 12.** Bed ash samples: (a) Ref case, (b) AW case.

The results of the lab-scale bed agglomeration test are presented in Table 5. These results confirm that co-combustion of AW, with the normal waste fuel, increases the sintering temperature by 70–100 °C. However, the sintering temperatures in the tests are higher than the bed temperature in the full scale boiler.
Table 5. Agglomeration temperatures for return sand.

<table>
<thead>
<tr>
<th>State</th>
<th>Unit</th>
<th>Ref</th>
<th>AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial agglomeration</td>
<td>°C</td>
<td>953</td>
<td>981</td>
</tr>
<tr>
<td>Total agglomeration</td>
<td>°C</td>
<td>993</td>
<td>1079</td>
</tr>
</tbody>
</table>

3.8. Emission

Co-combustion of AW with MSW raises concern about higher NO\textsubscript{x} emissions, regarding high concentration of nitrogen in the fuel. However, flue gas analysis indicated a reduction in NO\textsubscript{x} emissions of approximately 50% when AW was added to the fuel mix, as seen in Figure 13. The NO\textsubscript{x}-reduction effect of AW co-combustion has been reported previously [11]. The decrease in NO\textsubscript{x} concentration in the flue gas, despite the much higher nitrogen content of the AW, could be explained by the release of nitrogen as ammonia (NH\textsubscript{3}) during combustion. In the AW, nitrogen is found as amino acids, which are decomposed during thermal treatment, releasing the amino-group. However, the lower bed temperature and lower primary air flow are other possible explanations. Adding AW also resulted in a 50% lower demand for ammonia injection into the boiler, to reduce NO\textsubscript{x} emission. In addition, SO\textsubscript{2} emissions also declined from 11 to under 1 mg per normal cubic meter of flue gas in the case of AW addition (Table 6). This might be due to a higher concentration of Ca and a lower concentration of S in the AW case fuel mix, leading to the capture of S as CaSO\textsubscript{4} [24].

Figure 13. Emissions of N\textsubscript{2}O, NO\textsubscript{x}, and NH\textsubscript{3} together with ammonia addition to boiler No. 1 in the Ref and AW cases: (a) Ref; (b) AW.

Table 6. Flue gas emissions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit</th>
<th>Ref</th>
<th>AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x}</td>
<td>mg/Nm\textsuperscript{3} 11% O\textsubscript{2}</td>
<td>95.5</td>
<td>53.0</td>
</tr>
<tr>
<td>N\textsubscript{2}O</td>
<td>mg/Nm\textsuperscript{3} 11% O\textsubscript{2}</td>
<td>1.4</td>
<td>3.0</td>
</tr>
<tr>
<td>NH\textsubscript{3}</td>
<td>mg/Nm\textsuperscript{3} 11% O\textsubscript{2}</td>
<td>6.3</td>
<td>4.2</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>mg/Nm\textsuperscript{3} 11% O\textsubscript{2}</td>
<td>11</td>
<td>0.5</td>
</tr>
<tr>
<td>HCl</td>
<td>mg/Nm\textsuperscript{3} 11% O\textsubscript{2}</td>
<td>8.1</td>
<td>8.0</td>
</tr>
</tbody>
</table>
4. Conclusions

Adding 20–30 wt% AW to the ordinary waste fuel mix reduced the bed temperature by 70–100 °C and effectively reduced the deposition growth rate in the super heater area. Despite higher concentrations of Cl, alkali and S for the deposits formed in the AW case, there were no indications of higher corrosion. Inspection of the boiler after almost one year of operation also revealed no signs of increased corrosion damage.

SEM-EDX analysis of the coatings formed on return sand and bed ash particles indicated higher concentrations of P, Ca, S, and Cl in the bed material in the AW case; this was confirmed by the chemical fractionation analysis. In addition, chemical fractionation indicated that more acid-soluble compounds of P, Ca, and S were formed in the AW case. The increased amount of Ca and P, in the form of bone tissue, and P from the soft tissue introduced into the boiler by the AW did not affect the combustion, but appeared as calcium phosphates in the ashes. Positive effects of AW co-combustion were also observed in the bed, where agglomerates were found in the Ref case but not in the AW case.

The emission data indicated lower NO\textsubscript{x} emissions in the AW case, despite a higher concentration of nitrogen in the AW fuel mix; this consequently reduced the rate of ammonia addition by 50%, relative to the Ref case. Later analyses indicated that the NO\textsubscript{x} emissions from the boiler decreased to minimum levels and that ammonia addition could be completely stopped when adding 15–20 wt% of AW. Furthermore, SO\textsubscript{2} emissions declined during the co-combustion of AW, resulting in a decreased demand for added lime to capture sulfur.

Acknowledgments

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References


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University of Borås, School of Engineering, SE-501 90 Borås, Sweden

ABSTRACT: Full-scale waste combustion tests showed that adding animal waste (AW) to municipal solid waste (MSW) prevented bed agglomeration, and the reason for this finding was not fully understood. This study uses thermodynamic modeling to investigate the composition of equilibrium products for two combustion scenarios: monocombustion of MSW (the reference case) and cocombustion of AW with MSW (the AW case). The modeling was performed using FactSage, and experimental data obtained during the full-scale combustion tests were used as input data for the calculations. The results of equilibrium modeling, together with information extracted from ternary phase diagrams, suggest higher bed temperature as the primary cause for formation of bed agglomerates in the reference case. In addition, melt-induced agglomeration is suggested as the bed agglomeration mechanism in this case. In the AW case, however, reduced bed temperature, as well as enriched calcium phosphate and sulfate in the bottom ashes are considered to significantly decrease the slagging tendency.

1. INTRODUCTION
As a consequence of the mad-cow-disease epidemic in the late 1990s, combustion of animal waste products such as crushed animal carcasses and slaughterhouse waste products were thought to prevent the risk of infectious waste.1,2 The acceptable heating value of the waste, approximately 7–8 MJ/kg, made it an interesting choice for cocombustion.2 In previous work3 cocombustion of a slurry of crushed and ground animal carcasses and slaughterhouse waste products, that is, animal waste (AW), and municipal solid waste (MSW), in a 20 MWth bubbling fluidized-bed (BFB) boiler, showed improvements concerning operational conditions. Adding 20–30 wt % AW to the MSW prevented agglomeration in the bed and also considerably reduced the deposition growth rate. Moreover, NOx and SO2 emissions were reduced.

The reduced bed temperature due to the high water content of AW and also the changed chemistry are considered as two possible explanations for the elimination of bed agglomerates. An earlier study4 also found that a reduction of the bed temperature from 870 to 720 °C, combusting only MSW, eliminates virtually all agglomerates in the bed ash. In terms of the chemistry of the fuel, cocombustion of AW was shown to enrich Ca, P, and S in the bed ashes.3

A full understanding of the bed agglomeration mechanisms solely by experimental methods is not simply attainable. Hence, combined theoretical and experimental methods are performed, providing greater understanding of the ash transformation behavior and the related melting temperature. In this study, thermodynamic equilibrium calculations, using FactSage 6.4, were compared with the results of the previous experiments. Data obtained from the full-scale BFB boiler were used as input parameters to simulate both combustion scenarios and predict the equilibrium products in the bed. This strategy aims to provide an estimation of the compounds that would be formed in the bed at real conditions, which could help to interpret the combustion chemistry when different fuels are used. In addition, SEM-EDX (FEI Quanta 200 ESEM FEG) analysis data for the bed ashes3 together with the calculated phase diagrams were used to estimate ash compositions and first melting temperatures.

2. FULL-SCALE EXPERIMENTS
In the previous study,3 cocombustion of AW with MSW was suggested to identify the impact of changed fuel composition on operational problems, such as bed agglomeration, deposit formation, corrosion, and emission. Full-scale tests were carried out in a 20 MWth BFB boiler (Figure 1), which combusts

Figure 1. Schematic view of the 20 MWth bubbling fluidized-bed boiler, showing the locations of air system and feeding system.

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MSW as ordinary waste fuel. The MSW is a mix of presorted combustible industrial and household waste. The boiler is designed for a bed temperature of 870 °C. Two combustion tests were executed on the basis of different fuel mixes, denoted as the reference (ref) case and the animal waste (AW) case. The waste fuel in the ref case was the ordinary MSW. In the AW case, the fuel mix composition was changed, adding 20 wt % animal waste to the ref fuel mix. As a result of the high moisture content of AW, the bed temperature was reduced by 70−100 °C.3

A visual inspection of the bed materials and return sands showed formation of agglomerates in the ref case, whereas no agglomerates were observed for the AW case (Figure 2).3 Chemical fractionation and SEM-EDX were used to determine the composition and element distribution of the bed ashes.3 Chemical fractionation, a stepwise leaching method, was applied to quantify the associated inorganic compounds in the bed ashes and sand-coating layers.3 SEM-EDX was employed to perform elemental analysis on the coating layers formed on the bed particles during combustion. The combined chemical fractionation and SEM-EDX methods revealed significant information concerning the chemistry of the bed ashes and the sand-coating layers.3

3. THERMODYNAMIC MODELING OF THE ASH-FORMING ELEMENTS

Thermodynamic equilibrium modeling, coupled with experimental methods, has become commonly used for better prediction of ash formation behavior during combustion of biomasses and waste-derived fuels.6−10 Neither experimental work nor thermodynamic calculation is able to provide accurate information about combustion chemistry on its own in a complex and multicomponent system such as a waste boiler. However, advanced fuel and ash analysis methods along with thermodynamic calculations seem to give a better prediction of the ash transformation process.11

FactSage thermochemical software and databases,12 as one of the most powerful predictive tools, has been extensively used in waste combustion research for calculating multicomponent, multiphase equilibria, and complex phase diagrams, as functions of temperature, composition, and atmospheric conditions.10 The program is based on Gibbs energy minimization and consists of extensive databases for oxide/silicate and salt mixture systems. The databases cover both pure compounds and solution phases. The pure compound databases contain the properties of stoichiometric substances, whereas solution databases contain the optimized parameters for solution phases (e.g., oxides, salts, and metals).12 Lindberg et al.10 comprehensively reviewed the methods used to develop thermodynamic databases.

The most important ash-forming elements in the waste-derived fuels are Si, Ca, Mg, S, Na, K, Cl, Al, Fe, P, Pb, and Zn with C, H, and O.10 These elements can contribute to the formation of oxide/silicate and salt mixture systems. Silicates, which are often found in the bed ashes and on furnace walls, form polymeric silicate anions with a high melting temperature, except for alkali silicates, which are known to have low melting temperatures.4,10 These silicates are highly viscous in the liquid state. The salt mixtures are simple ionic compounds and consist of anions, such as Cl−, SO42−, CO32−, O2−, S2−, and PO43−, with different metal cations. These salts are often present in fly ash, and their melting temperature differs widely, from very low (ZnCl2: 318 °C) to very high (CaO: 2,597 °C) temperatures. They also have lower viscosity than silicates in the liquid phase. There are some exceptions for the two simplified categories mentioned, such as phosphates in the form of polymeric anions and ZnCl2 as polymeric species.10 The release pattern of the above elements and their subsequent chemical reactions during combustion depend on several factors such as association of

Figure 2. Bed material samples: (a) ref case, magnified picture shows more agglomerated particles; (b) AW case, magnified picture shows no agglomerated particles.
elements and combustion conditions. The chemical equilibrium program does not discriminate the mode of occurrence of the element in the fuel, and calculations may vary considerably from the combustion of the real fuel.\(^{10}\) Zevenhoven et al.\(^{11}\) applied the chemical fractionation method, prior to thermodynamic modeling, to make an accurate prediction of fly ash and bottom ash reactions.

The major limitation attributed to thermodynamic modeling of the combustion process is the lack of comprehensive databases. Despite recent developments, consistent and accurate thermodynamic data are not accessible even now for all compounds that might form in the furnace and bed area. For example, the lack of thermodynamic data for solid and liquid phosphates makes an accurate assessment of the behavior of P-related compounds difficult. In spite of limits for some elements, the current databases give a relatively high accuracy in predictions on the phase equilibria and melting properties for alkali salt mixtures and silicate slag systems (with low alkali content).\(^{10}\)

### 4. MODELING STRATEGY

In the experimental data,\(^{3}\) it became apparent that addition of AW to MSW positively changed the combustion chemistry, indicating no bed agglomeration. Despite the obtained information regarding the distribution of elements in the bed ashes, the reason behind the elimination of bed agglomerates remained unanswered.

In order to explain the possible agglomeration mechanisms, a deeper understanding of combustion products was required. Therefore, the strategy was to predict the equilibrium products in the system. For this purpose, computational modeling was performed for the ref and AW combustion scenarios. The software’s equilibrium module was employed to predict the formation of combustion products in each combustion case. Subsequently, the equilibrium products were used, together with experimental data to fill in the gaps in knowledge regarding AW co-combustion effects on the boiler.

#### 4.1. Global Equilibrium Modeling over the Bed

The system studied is part of a bubbling fluidized-bed boiler (Figure 1), and consists of a fluidized-bed, an air distribution system, and a feeding system. The air system distributes air to the system in two steps: First, primary air is introduced through the bottom nozzles and reacts with the fuel in the bed’s temperature range. Next, secondary air is blown into the system in the upper part of the bed (below the nose) and reacts with the produced gases and unburned fuels. In order to predict the equilibrium products in the bed area in this study, a global equilibrium model (Figure 3) with specified temperature and pressure was considered. In the model, the fuel and primary air (\(O_2\) and \(N_2\)) represent the input material into the equilibrium reactor, and the bed ashes and equilibrium gases correspond to the output products from the reactor.

#### 4.2. Input Parameters, Selected Databases, and Assumptions

In order to have an accurate thermodynamic model that represents the condition in a real system, parameters such as fuel composition, bed temperature, and pressure should be carefully characterized, and the model inputs have to reflect the inputs into the boiler. In this case, all input data were based on the experimental data and recorded operational data from each combustion case (ref and AW cases). A large number of elemental components in the fuel were considered for the modeling. They were selected for their role in combustion and related issues, including bulk elements, alkali metals, alkali earth metals, some heavy metals, and chlorine.\(^{10}\) In total, 19 species were considered: C, H, O, N, S, Cl, K, Na, Ca, Mg, Si, Al, Fe, P, Pb, Zn, Ti, Mn, and Ba. Other trace and ultratrace elements were excluded in the calculations, due to computational constraints and also because they do not affect the bulk properties or overall behavior of ash particles.\(^{7,10}\)

The selection of databases was based on the formation of possible compounds for the given conditions regarding input elements, temperature, and pressure. The included databases were FactPS, FToxide, and FTsalt for prediction of the pure solid, liquid, and gas products. Additional databases for possible solid and liquid (molten) solution phases were also included, such as FToxide-SLAGA, FTsalt-CSOB, and FTsalt-SALTF. FToxide-SLAGA covers all oxide components in a liquid solution containing dilute sulfides, whereas FTsalt-CSOB contains solid alkali sulfate/carbonate solutions and FT salt-SALTF includes molten alkali salt solutions.

The chosen parameters for calculations are shown in Tables 1 and 2. The data presented in Table 1 are a typical composition of 1 kg MSW before and after addition of AW (20% AW + 80% MSW). It should be noted that the total concentrations of alkali metals (Na and K) in the calculations were considered as Na, considering the similar functions and roles of Na and K in the ash transformation reactions.\(^{13}\) The
Note also that during the actual combustion tests, considerable temperature and pressure were neglected during this study. However, inhomogeneity of the waste stream and also instability of the operational conditions give rise to variability in the residence time in the bed ($\tau_{res}$) by the inflow of the particles into the bed ($M_n$) and represents the average residence time for a perfectly mixed fluidized bed:

$$\tau_{res} = m_i/M_n \rightarrow \tau_{res} = \frac{5000\text{kg}}{289\text{kg/h}} \rightarrow \tau_{res} \approx 17h$$

It is concluded that the residence time for each sand particle in the bed is approximately 17 h, and this time is long enough to justify the assumption of equilibrium in the bed solids.

Second, fluctuations of operational parameters such as temperature and pressure were neglected during this study. Note also that during the actual combustion tests, considerable efforts were made to stabilize the bed temperature and pressure within a narrow range.

5. RESULTS

5.1. Equilibrium Products. The output format of the thermodynamic calculations shows the distribution of given elements among the possible solid, liquid, and gas compounds, as well as solid and liquid solution phases. FactSage predicts the equilibrium products, from input elements with respect to pressure and temperature. The calculations determine both condensed and vaporized phases. The condensed phase consists of pure solid and liquid compounds and also solution (solid and liquid) phases, which are mostly found in the bed as bottom ash. The vaporized phase consists of pure equilibrium gases, which release to the furnace and also contribute to the bed reactions. Tables 3 and 4 present the predicted pure solid

| Table 2. Input Parameters for Operational Conditions in the Ref and AW Case |
|-----------------|-------------|-------------|
| operational parameters | ref case | AW case |
| av bed temperature ($^\circ$C) | 850 | 750 |
| av bed pressure (atm) | 0.995 | 0.995 |
| kgO$_2$ (primary air) kg$^{-1}$ fuel | 0.862 | 0.813 |
| kgN$_2$ (primary air) kg$^{-1}$ fuel | 2.800 | 2.640 |

Table 3. Results of Chemical Equilibrium Model Calculations for the Pure Solid Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>(g kg$^{-1}$ fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref case</td>
</tr>
<tr>
<td>CaSiO$_3$(s)</td>
<td>35.54</td>
</tr>
<tr>
<td>NaAlSiO$_4$(s)</td>
<td>31.04</td>
</tr>
<tr>
<td>Ca$_2$SiO$_4$(s)</td>
<td>15.16</td>
</tr>
<tr>
<td>Na$_2$SiO$_3$(s)</td>
<td>11.45</td>
</tr>
<tr>
<td>Ca$_2$H$_2$PO$_4$(s)</td>
<td>3.22</td>
</tr>
<tr>
<td>Na$_2$Ca$_2$Si$_5$O$_9$(s)</td>
<td>3.42</td>
</tr>
<tr>
<td>Fe$_3$SiO$_4$(s)</td>
<td>1.22</td>
</tr>
<tr>
<td>(FeO)$_2$(TiO$_2$)$_2$(s)</td>
<td>4.67</td>
</tr>
<tr>
<td>(BaO)$_2$(SiO$_2$)$_3$(s)</td>
<td>0.27</td>
</tr>
<tr>
<td>Ca$_2$Fe$_3$Si$<em>5$O$</em>{12}$</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca$_5$TiO$_3$(s)</td>
<td>0.00</td>
</tr>
<tr>
<td>ZnS(s)</td>
<td>0.00</td>
</tr>
<tr>
<td>Mn$_2$SiO$_4$(s)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4. Results of Chemical Equilibrium Model Calculations for the Gas Compounds

<table>
<thead>
<tr>
<th>compd</th>
<th>(g kg$^{-1}$ fuel)</th>
<th>wt % of total gas phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref case</td>
<td>AW case</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>637.9</td>
<td>722.0</td>
</tr>
<tr>
<td>N$_2$(g)</td>
<td>2807</td>
<td>2650</td>
</tr>
<tr>
<td>CO(g)</td>
<td>944.8</td>
<td>914.0</td>
</tr>
<tr>
<td>H$_2$(g)</td>
<td>9.046</td>
<td>1.975</td>
</tr>
<tr>
<td>CO(g)</td>
<td>82.17</td>
<td>10.75</td>
</tr>
<tr>
<td>H$_2$S(g)</td>
<td>2.877</td>
<td>2.142</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>4.050</td>
<td>2.825</td>
</tr>
<tr>
<td>SO$_2$(g)</td>
<td>0.015</td>
<td>0.130</td>
</tr>
<tr>
<td>NaCl(g)</td>
<td>0.209</td>
<td>0.013</td>
</tr>
<tr>
<td>ZnCl$_2$(g)</td>
<td>0.063</td>
<td>0.018</td>
</tr>
<tr>
<td>PbCl$_2$(g)</td>
<td>0.128</td>
<td>0.037</td>
</tr>
</tbody>
</table>

Energy & Fuels
matrix, as is predicted in Table 3. These silicate compounds are in crystalline forms and mostly have high melting temperatures at FB conditions. For the gas phase, higher concentration of H\textsubscript{2}O(g) is observed in the AW case, which could be connected to higher water content of the animal waste. In this case, a higher concentration of SO\textsubscript{2} is formed in the bed as well. The equilibrium calculations did not predict formation of any solution phase in the AW case. For the ref case, however, considerable amounts of molten oxides are predicted at the investigated temperature. Figure 4 shows slagging tendency versus temperature for the fuels in the ref and AW cases. Considering the theoretical results, 815 °C is estimated as a temperature in which molten oxides start to

<table>
<thead>
<tr>
<th>compd</th>
<th>(g kg\textsuperscript{-1} fuel)</th>
<th>wt % of total solution phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}(l)</td>
<td>0.946</td>
<td>47.02</td>
</tr>
<tr>
<td>NaAlO\textsubscript{2}(l)</td>
<td>0.522</td>
<td>25.96</td>
</tr>
<tr>
<td>MnO(l)</td>
<td>0.178</td>
<td>8.873</td>
</tr>
<tr>
<td>CaO(l)</td>
<td>0.107</td>
<td>5.349</td>
</tr>
<tr>
<td>FeO(l)</td>
<td>0.148</td>
<td>7.364</td>
</tr>
<tr>
<td>MgO(l)</td>
<td>0.019</td>
<td>0.940</td>
</tr>
<tr>
<td>ZnO(l)</td>
<td>0.047</td>
<td>2.368</td>
</tr>
<tr>
<td>Na\textsubscript{2}O(l)</td>
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<td>0.550</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}(l)</td>
<td>0.019</td>
<td>0.948</td>
</tr>
<tr>
<td>TiO\textsubscript{2}(l)</td>
<td>0.003</td>
<td>0.146</td>
</tr>
</tbody>
</table>

5.2. Experimental and Theoretical Results for the Coating Layer. Figure 5 shows cross-sectional back-scattered electron images for sampled sand particles in the ref and AW cases. In the ref case, formation of agglomerated sand particles are observed, whereas coated sands in the AW are not glued together. The results from the experimental part\textsuperscript{3} showed differences in the composition of the coating layer in the two cases. The SEM-EDX results showed a higher concentration of Ca\textsubscript{2x}, P\textsubscript{y}, and S-associated compounds in the coating in the AW case, whereas the concentration of Si- and Al-related compounds was decreased. In addition, slightly higher Cl was found in the coating in the AW case, whereas Na and K did not show any significant differences between the cases.\textsuperscript{3} Chemical fractionation of the return sands\textsuperscript{3} not only supported the results obtained by SEM-EDX but also gave complementary information concerning the chemical composition and solubility of the compounds present in the coating layer (Figure 6). Comparing the two cases, concentrations of acid soluble fractions of Ca, S, and P were significantly increased in the AW case, indicating enrichment of coating layer by compounds such as calcium phosphate and sulfate. Hagman et al.\textsuperscript{15} reported that calcium phosphates occurred in significant amounts in bottom ash as a result of animal waste cocombustion. Concentrations of Na, K, and Cl do not show significant differences between two cases, as SEM-EDX results indicated.\textsuperscript{3} Note also that the major part of the nonsoluble alkali in Figure 6 (marked as rest) originates from the feldspar portion of the bed sands.

The equilibrium calculations on the bed ashes are in good agreement with the experimental data. As Table 3 clearly shows, the formation of hydroxyapatite considerably increased with the AW cocombustion. Boström et al.\textsuperscript{16} stated that during combustion of P-rich fuels, phosphorus dominates silicon in the competition for base cations such as Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, and K\textsuperscript{+} (Na\textsuperscript{+}). This finding is confirmed in chemical fractionation analysis as well (Figure 6), where elevated levels of Ca and P are attributed to the presence of acid-soluble compounds.\textsuperscript{3} It should be noted that according to previous research\textsuperscript{15,17,18} the additional P in the ashes of the AW case is attributed to two main sources in the animal waste: hard and soft tissue. Hard tissue refers to crushed bones that contain Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH\textsubscript{2}) and β-

Figure 4. Slagging tendency versus temperature for the fuels in the ref and AW cases.

Figure 5. Back-scattered electron images of bed sand particle cross sections for (a) agglomerated sands in the ref case and (b) no agglomerates in the AW case.
Ca₃(PO₄)₂. This portion of calcium phosphates is mainly nonreactive during combustion and remains in its original state at the investigated temperature.15 The soft tissue, containing more reactive P and Ca in organic and ionic forms, transform to different phosphates during combustion. Supposing that all the Ca and P in the animal waste react to form apatite and whitlockite, there will be still some excess P available to react with other elements of the fuel mix.15

Apart from Ca and P, an increase of acid-soluble S was observed as a result of the addition of AW to the MSW. This increase might be linked to the higher formation of CaSO₄ according to reaction 1:14

\[
\text{CaO(s) + SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(s)
\]

As equilibrium calculations state (Table 4), a higher concentration of SO₂ is available in the bed during AW cocombustion. Reaction 1 is considered as one of the most important reactions for calcium, which has a great impact to the rest of the flue gas chemistry. Removing free SO₂ in the flue gas by CaO will reduce the rate of other competing reactions such as sulphation of alkali chlorides.14

5.3. Phase Diagram Information. Prior studies have shown that the chemical composition and melting behavior of the coating layer on the bed materials is a significant factor regarding bed agglomeration.8,9,19 Hence, in this study, phase
diagrams were utilized to evaluate the composition and melting behavior of the formed compounds in the coating during combustion. The ternary phase diagrams, which are presented in this section, were calculated for the range of investigated temperature in this study (750−850 °C) and 1 atm bed pressure.

Figure 8. CaO−Al₂O₃−SiO₂ ternary phase diagram with some solidus temperatures (extracted from FactSage) presenting bed ash composition for ref (solid triangles) and AW (solid squares) cases.

Figure 9. Al₂O₃−Na₂O−SiO₂ ternary phase diagram with some solidus temperatures (extracted from FactSage) presenting bed ash composition for ref (solid triangles) and AW (solid squares) cases.

The EDX spot analysis of the coatings and extracted phase diagrams for the oxide systems were used to identify the possible compounds in the coating and corresponding melting temperature. The SEM-EDX spot analysis results for each element (as oxides) are summarized in Figure 7. Six spots were chosen to investigate the composition of the elements in the
coating layer, not the sand itself. Each bar represents the weight % of the oxide for the related element in the coating, and each spot represents a different position in the layer covering the sands. Additionally, the results in Figure 7 imply that coating layers covering return sands are more inhomogeneous when combusting only MSW, although with the addition of AW to the MSW, more uniform layers are formed.

Figure 7 indicates that CaO, SiO$_2$, and Al$_2$O$_3$ are dominant oxides surrounding the coating in the ref case. Almost 80% of the composition of the coated layer comprises different phases of the ternary CaO–SiO$_2$–Al$_2$O$_3$ system. In the AW case, however, the overall compositional distribution showed CaO and SiO$_2$ as predominant oxides, whereas the concentration of Al$_2$O$_3$ oxide decreased when the composition of the coatings was altered to higher amounts of P and S oxides. Figure 8 presents the predicted compounds in the coating layer and corresponding solidus (initial melting) temperatures for the ternary CaO–Al$_2$O$_3$–SiO$_2$ system. Among the predicted products in the marked area (solid triangles and squares) formation of CaSiO$_3$(s) is also predicted by equilibrium calculations (Table 3). Despite no formation of Ca–Al silicates among the equilibrium products, our XRD results confirmed the presence of Ca$_2$Al$_2$SiO$_7$ in the bed ash. According to the phase diagram, all predicted compounds were expected to be present as solids in the ref and AW combustion conditions.

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In contrast to Figures 8 and 9, which show the presence of high-melting-point minerals in the coating layer, the CaO–Na$_2$O–SiO$_2$ ternary system (Figure 10) indicates formation of partly molten ash in the ref case. Here again, the phase diagram information are in fairly good agreement with the theoretical results obtained for the solid phase in the equilibrium section, where formation of alkali–calcium silicates in the coating layer are predicted for the ref and AW cases. Considering the average bed temperatures in the ref and AW case, 850 and 750 °C respectively, and also locations of the bed ashes in the ternary phase diagram, the formed alkali-calcium silicates in the ref case could be partly molten under combustion condition. This is particularly notable for the outer layers of the coating, which
are located close to the area with the first melting temperature of 834.75 °C. Assuming the presence of alkali–calcium silicates in the bed ashes for the AW case and due to the average bed temperature of 750 °C, these minerals are considered to be in the solid form.

5.4. MSW Bottom Ash Minerals Identified by XRD. The sand particles which are used in the investigated BFB boiler are typical Swedish sand, consisting of silicon oxides and feldspar. The high concentration of quartz (SiO2), albite (NaAlSi3O8), and microclin (KAlSi3O8) found in the fresh sand makes it difficult to distinguish, analytically, between sands and ashes, particularly in the case of bottom ash. Despite limitations, the XRD results obtained during our experimental study and other studies using MSW and animal waste as fuels are in good agreement with the thermodynamic results obtained for solid minerals in this study. Presence of minerals such as CaSiO3, NaAlSiO4, CaMgSi2O6, SiO2 and Fe2O3 in the bottom ash were observed in our previous studies. However, a major portion of SiO2 and feldspar in the bottom ash could be originated from the fresh sand, not ash. In addition, other studies using MSW as fuel confirmed the presence of the mentioned minerals in the bottom ash. Another study, which used MSW in a grate-firing boiler with a bed temperature of 850–950 °C, also identified formation of alkali–calcium silicates in the ash fraction. With regard to the contribution of animal waste in the bottom ash, our XRD results showed enriched calcium phosphates in the cyclone ash for the AW case. In the bottom ash, however, due to high concentrations of other minerals such as silica sand, feldspar, and glass contaminants, calcium phosphates were not detected. A study that used animal waste as a cofuel supported the presence of calcium phosphates in a significant amount in both fly and bottom ash.

5.5. O2 Variation. In order to evaluate the effect of atmosphere (reducing/oxidizing) on the composition of pure solid compounds and also solution phase in the bed, equilibrium products were calculated for the fuel in the ref case (MSW) with the same bed temperature and pressure, but with different amounts of O2 in the primary air. In total, four concentration levels were considered. The first represents the used O2 concentration in the AW case (0.813 kg O2 kg−1 fuel) based on a mix of air and recirculated flue gas. The second is the ref case (0.862 kg O2 kg−1 fuel), where only air was used. The third O2 concentration was the calculated theoretical oxygen demand (0.942 kg O2 kg−1 fuel) for a complete combustion of the fuel, and in the last case, 20% excess air was added (1.130 kg O2 kg−1 fuel).

The results showed that the O2 variation mainly affected the composition of the solid phase in the case of excess air. As Table 6 shows, formation of some sulfates (CaSO4(s) and BaSO4(s)) are predicted for this case, in contrast to the other cases. In addition, formation of CaSiO3(s) and NaAlSiO4(s) was decreased, whereas a higher amount of NaAlSiO3 was formed. In addition, no formation of any solution phases were detected in this case (Table 7).

For the other cases, however, the composition of the equilibrium products did not show any significant dependence on atmosphere. Comparing the effects of O2 variation for case 1 to case 3, indicated no notable changes for the composition of the pure solid compounds, although small changes were predicted for the composition of the solution phase. As Table 7 shows, formation of SiO2(l), NaAlO2(l), CaO(l), FeO(l), and MgO(l) is important for the MSW combustion. However, the formation of these compounds is not significant in the case of bottom ash, as indicated no notable changes for the composition of the solution phase.

5.6. Effect of Excess SiO2 on Slagging Tendency. The silicon found in the coating on the bed particles could originate both from the fuel and bed particles. However, silicon which is present as silica (SiO2) sand is relatively inert under combustion conditions. Zevenhoven et al. explained that layer formation on sand particles could be formed by inward growth, outward growth, or a combination of both. In the case of inward growth, the layers grow inward into the bed particle as a result of reaction between sand particles and ash reactive compounds. During outward growth, however, bed particles are inert, and all the elements in the layer originate from the fuel. In the present study, the sand particles seem to be inert during combustion, which is proved by the following: (1) The coating layers are grown outward onto the bed particles, as is shown in Figure 7. (2) In the case of inward growth, the innermost layer is rich in alkali oxides, but the concentration of alkali oxides in the coating layer (Figure 7) is much lower, which confirms this hypothesis.
In order to investigate the effect of reactive silica sands on the composition of the molten phase, equilibrium calculations, with excess SiO₂ and different bed temperatures, were performed. The calculations were carried out with the input data of the fuel mix with higher phosphorus content (AW case fuel), comparing the effect of increased SiO₂ (0.25 mol) on the amount of produced molten ash. As Figure 11 shows, up to the temperature of 850 °C, a similar trend could be observed for both cases, meaning that excess SiO₂ does not participate in the molten phase but remains in the solid phase. At higher temperatures, however, SiO₂ can affect the amount of the oxide melt with a sharp increase at temperatures higher than 875 °C. Therefore, the slagging tendency, for the investigated temperature in this study, probably would not be affected in the presence of reactive silica sand, introduced to the system as excess SiO₂.  

**6. DISCUSSION**

Bed agglomeration may be initiated by direct attack of gaseous alkali compounds on silica sand causing formation of sticky layers on the bed material, and/or by melt-induced mechanism, when bed materials are glued together by molten ash particles. The molten phase could consist of a viscous glassy silicate melt and/or a nonviscous melt. During the first mechanism, the coating grows inward into the bed sands, assuming bed materials react with reactive compounds such as KCl(g), KOH(g), and NaCl(g) and form rich alkali layers. In the present study, however, the SEM-EDX analysis do not show any evidence of bed sands attacked by alkali gases. In this case, though, the coating layers were grown outward onto the particles (Figure 7), and it seems like the bed particles act as inert carriers of the coating layer. Therefore, the second mechanism (melt-induced agglomeration) could be considered as an explanation for why the coating in the ref case led to agglomeration, when more molten ash particles were available to glue the bed particles together. Equilibrium calculations predicted that considerable amounts of molten oxides were formed in the ref case (Table 5), whereas no molten phase was predicted in the AW case. The results obtained by ternary phase diagrams also indicate the presence of partly molten ashes of alkali—calcium silicates in the coating layer for the ref case. In the literature, formation of alkali—calcium silicates are explained as a first reaction between silicon and alkali (Na and K), forming alkali silicates with a first melting point as low as some 750 °C. This reaction may form the first layer on the bed particles. This sticky layer catches other small particles, as calcium phosphates, sulfates, and oxides, which are released from the fuel. The high thermodynamic affinity of silicate melt for earth alkali metal oxides supports formation of alkali—calcium silicates, as secondary ash-forming reaction described as reaction 2:13

\[
K₂SiO₃(l) + CaO(s) \leftrightarrow K - Ca - silicate(l)
\]  

Dissolving earth alkali oxides in the alkali silicate melt led to the alkali being driven out by Ca and Mg, increasing the first melting point of the silicates which could be studied as ternary phase diagrams. Reaction 2 is a rather slow reaction, highly dependent upon the dispersion of the fuel and reactant particles.13

Another mechanism considered for coating formation is the reaction between silicon and calcium forming calcium silicates with a first melting point above 1500 °C.14 Because of the high first melting temperature, this formed calcium silicate layer is considered unlikely to cause agglomeration. Partanen et al.25 also suggested that formation of CaCl₂ during the combustion process may contribute to formation of calcium-rich layers, described as reaction 3. CaCl₂ may react with SiO₂ in the fluidized bed and intensify the formation of the coating on the bed particles.

\[
\begin{align*}
\text{Step 1} & \quad \text{CaO(s)} + 2\text{HCl(g)} \rightarrow \text{CaCl}_2(s, l) + \text{H}_2\text{O(g)} \\
\text{Step 2} & \quad \text{CaCl}_2(l) + \text{SiO}_2(s) + \text{H}_2\text{O(g)} \\
& \quad \rightarrow \text{CaSiO}_3(s) + 2\text{HCl(g)} \\
\text{or} & \quad \text{Step 2} \quad \text{CaCl}_2(l) + \text{SiO}_2(s) + \frac{1}{2}\text{O}_2(g) \\
& \quad \rightarrow \text{CaSiO}_3(s) + \text{Cl}_2(g)
\end{align*}
\]  

The nature of the coating layer for the bed sands in the ref and AW cases seems to be different (Figure 7). In the AW case, thick layers of deposited ash with no agglomerates are formed on the sand particles. A clear difference between the particle core and deposited ash can be observed. This may be explained by coating formation as a result of physical processes rather than chemical reactions.26 The coating layers of the sands in the ref case are predicted to be partly in liquid state during combustion. Pettersson et al.3 stated that during combustion of MSW, in the same boiler employed in this work with different bed-temperatures, the coating layers formed at the temperature of 870 °C are transparent and glassy (noncrystalline), although with the bed temperature of 720 °C, a white powder-like coating was formed (crystalline).

Regarding the bed agglomeration, bed temperature seems to play the main role in the present work. As already suggested in our earlier research, the lower bed temperature considerably prevented bed agglomeration, even without changing the fuel composition. According to the equilibrium calculations, molten oxides start to form at 815 °C. This temperature is higher than the prevailing bed temperature in the AW case and lower for the ref case, explaining why agglomerates were formed in the ref case but not in the AW case. Regardless of bed temperature, the composition of the fuel may be the second factor that affects the slagging tendency, albeit at higher temperatures than the temperatures investigated in this work (Figure 4). The enriched bottom ash with high-melting-point compounds such as calcium phosphate (melting point = 1670 °C) and calcium sulfate (melting point = 1460 °C) may decrease the bed agglomeration tendency.2 This is supported by lab-scale
agglomeration tests for the sand particles, showing an increase in the agglomeration temperature of around 90 °C in the AW case compared with the ref case.

7. CONCLUSION
As a result of AW addition to the MSW, the bed temperature was reduced by 70–100 °C. The results of equilibrium modeling together with information extracted from the ternary phase diagrams suggest reduced bed temperature as the main reason preventing bed agglomeration in the AW case. The bed temperature is shown to significantly affect the slagging tendency in the fluidized bed. In the absence of any evidence of alkali gases attacking sand particles, melt-induced agglomeration is suggested as the mechanism causing the formation of sticky layers on the bed particles in the ref case. The molten phase in this case may be formed by oxide solution phase and/or partly molten viscous silicates. Cocombustion of AW with MSW could also enrich the bottom ash with high-melting-point compounds such as calcium phosphate and sulfate, which may decrease the bed agglomeration tendency at higher temperatures.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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■ ABBREVIATIONS
MSW = municipal solid waste.
AW = animal waste.
BFB boiler = bubbling fluidized-bed boiler.
SEM-EDX = scanning electron microscopy-energy dispersive X-ray.

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Thermodynamic Equilibrium Model Applied To Predict the Fouling Tendency in a Commercial Fluidized-Bed Boiler, Combusting Solid Waste

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ABSTRACT: A thermodynamic equilibrium model, combined with an advanced fuel analysis, was applied to predict the fouling tendency in a commercial bubbling fluidized-bed (BFB) boiler, combusting a mixture of solid waste. In order to enhance the performance of the model, further modifications were made, considering the combustion pattern in the fluidized-bed system and also the temperature profile in the combustion zone. The modeling was performed using Factsage, and experimental data obtained during the full-scale measurements were used as input for the model, simulating the deposit formation in the real boiler. The simulation results were then compared with the results obtained during the full-scale combustion tests to estimate the accuracy and validity of the applied model. The thermodynamic equilibrium modeling proved to be a reliable tool for predicting the fouling in the BFB boiler, thus determining the fraction of the melt in the deposited salts formed on the heat transfer surfaces during the flue gas condensation. The calculations showed that the ratio of the SO₂ to alkali chloride concentration in the flue gas was the decisive factor that affected the rate of the deposit formation in the boiler. Both the simulation and the experimental results indicated that lower bed temperatures and cocombustion of P-rich fuels decrease the deposition buildup in the boiler.

1. INTRODUCTION

Over the past few decades, the combustion of Municipal Solid Waste (MSW) and Industrial solid Waste (IW) has increased, owing to the substantial heating value of the waste and also as a way to reduce the amount of waste going to the landfills. Landfilling of waste significantly contributes to the release of methane gas and also a number of hazardous compounds. Utilizing the energy value of the solid waste for heat and electricity, the fluidized-bed combustion technology is increasingly applied, taking into consideration the flexibility of the technology for efficient combustion of heterogeneous, high moisture, and high ash content fuel. MSW and IW contain a high concentration of the following ash-forming elements: Ca, S, Cl, Na, K, Mg, Si, Al, Fe, and P, and also minor quantities of Zn and Pb. The formation of bottom and fly ashes, as a result of the interaction of the ash-forming elements during the combustion, may result in serious operating issues in the fluidized-bed boilers, such as bed agglomeration, fouling, and corrosion. It is known that alkali metals (K and Na), in the presence of Cl, S, and Si, undergo many undesirable reactions, forming low melting-temperature alkali silicates in the bottom ash and also alkali sulfates and chlorides in the fly ash, resulting in bed agglomeration and deposit formation on heat transfer surfaces of the boiler. Fly ash deposition on the heat transfer surfaces reduces the energy efficiency of the plant and also leads to shutdowns and increased maintenance costs for the boiler. A large number of studies have been performed to identify the interactions between the ash-forming elements during the combustion, leading to the deposit formation. Thermodynamic equilibrium modeling, coupled with experimental methods, has been used to achieve a better understanding of the ash transformation mechanisms during the combustion of biomass and waste-derived fuels.

In a previous study, a thermodynamic equilibrium model was applied to assess the composition of the bottom ash in a commercial bubbling fluidized-bed (BFB) boiler, combusting a waste mixture of 20% MSW and 80% IW, referred herein as Solid Waste (SW). Data obtained from the full-scale tests were used as input for the equilibrium model, to evaluate the agglomeration tendency based on the different fuel composition, bed temperature, and air/fuel ratio. The objective of the present study is to apply and validate a thermodynamic equilibrium model to predict the fouling tendency in a BFB boiler. The applied model used advanced thermodynamic equilibrium calculations, coupled with an advanced fuel analysis technique, to estimate the composition of the flue gas leaving the furnace and consequently becoming condensed on the heat transfer surfaces. Here, the advanced fuel analysis refers to the chemical fractionation methods to determine how ash-forming elements are bound in the fuel. In addition, the advanced thermodynamic equilibrium calculation predicts complicated chemical interactions of the ash-forming elements during combustion. This type of approach has previously been used to predict the composition and melting properties of the different fly ash fractions. In this study, further modifications were made to enhance the performance of the model for fouling prediction, considering the combustion pattern in the fluidized-bed system and the temperature profile in the combustion zone. Chemical composition of the sampled fuels, as well as recorded operating data such as temperature, pressure, and air/fuel ratio were used as input for the model, simulating the conditions in the real BFB boiler. The theoretical
results were then compared with the measurements to estimate the accuracy and validity of the applied model.

1.1. Deposit Formation. The steps involved in the formation of the deposit on the heat transfer surfaces can be described as (a) formation of an ash particle or an ash-forming compound, (b) transport of the ash particle to a surface, (c) adhesion to the surface, and (d) consolidation of the deposit.16 The processes that contribute to the deposit formation are inertial impaction, thermophoresis, condensation, and heterogeneous reactions.7,11 The bulk of the ash deposit is most often transported by inertial impaction, which is most important for large particles (10 μm and larger). In thermophoresis, the finer particles are transported in a gas due to the local temperature gradients. Adhesion of fly ash particles on the surfaces can take place by a molten phase, where the condensation mechanisms play an important role in forming the molten or partially melted components.19 Condensation is defined as a mechanism by which vapors (like alkali chlorides) are collected on the surfaces cooler than the local gas. In the boiler, the ash-forming gases can diffuse and directly condense on the surfaces (or particles), or homogeneously nucleate and form fine fly ashes. The amount of the condensed fraction of the deposit strongly depends on the mode of occurrence of the inorganic material in the fuel, which in the case of low rank fuels, such as biomass and waste-derived fuels, is a significant or an even dominant contributor to the development of the deposit. Furthermore, the deposit properties are significantly affected by this condensed fraction. Finally, the heterogeneous reactions of the gas phase constituents with the materials in the deposit, like sulfation, complete the mass accumulation mechanisms in a deposit.16,18

1.2. Fouling Thermodynamic Modeling and Its Limitations. Advanced thermodynamic modeling is a powerful and stand-alone tool in predicting the ash-related problems in a multicomponent/multiphase system such as biomass and waste combustors. Application of the chemical equilibrium models to predict the fouling tendency has shown to be useful, calculating the condensed phase and the melted salts formed along the convective zone of a combustion system.7,10,11,15,20 It is known that completely or partly molten ash particles can act as a form of glue between the particles and the surface, leading to the growth of ash deposits. The term critical stickiness temperature was defined for the recovery boiler deposits by Backman et al., indicating the temperature by which enough melt is present to glue an ash particle to a surface. It was experimentally shown21 that the ash particles (or outer surface of the deposit) should have a melt fraction between 15–70% (on mass basis) to be sticky and contribute to the deposit formation. At a lower melt fraction (<15%), almost no deposition was observed; at a higher melt fraction (>70%), the deposit started to flow and no longer grow in thickness. It is notable that the criterion is only valid for alkali salt and partly valid for alkaline earth salt mixtures (chlorides, sulfates, and carbonates); however, for deposit containing silicon, leading to viscous melts, the limits are not applicable.16,22 The only relatively simple method to determine the fraction of the melt in the salt mixtures is multicomponent phase equilibrium modeling.7 Based on the T1 and T2 concepts, Zevenhoven et al.11 applied a model that combined the advanced fuel analysis with the advanced thermodynamic equilibrium calculations to predict the fouling tendency in a fluidized-bed boiler, combusting different solid fuels. The advanced fuel analysis (chemical fractionation) makes it possible to evaluate the chemical association of the elements in the fuel and consequently allow for a distinction between the reactive and less-reactive fractions of the fuel. It is particularly important when predicting the deposit formation, where only the reactive (volatile) fraction of the fuel is used as an input for the model. In the case of bed agglomeration modeling, however, all of the ash forming elements present in the fuel should be taken into account.16 The approach, combining chemical fractionation and thermodynamic equilibrium modeling, has been used in several studies to estimate the deposition behavior of the solid fuels in fluidized-bed combustion.10,14,15

Despite the demonstrated capabilities of the thermodynamic equilibrium modeling applied in the combustion systems, there are some limitations generally encountered with the technique. First, there is a lack of consistent and accurate thermodynamic databases for all the possible species that may form under different furnace and boiler conditions. A typical example is the lack of comprehensive thermodynamic databases for complex liquid and solid solution phases, such as molten salts and silicate slags. Nevertheless, the current databases, for instance FTsalt, can predict the phase equilibria and the melting properties of the alkali salt mixtures relevant to the ash chemistry with high accuracy,7 although the inclusion of the other elements such as Ca, Pb, and Zn to the system is still needed. Second, it must be emphasized that thermodynamic models only take chemical reactions into consideration, not physical processes such as nucleation and particles elutriation, which are significant phenomena in a fluidized-bed boiler. Furthermore, not all reactions reach equilibrium at the same rate during combustion, depending on the degree of mixing of reactants, residence time, and the kinetics of the reactions. Therefore, the assumption that all reactants reach equilibrium during combustion is a rough approximation.15

2. EXPERIMENTAL SECTION

2.1. Boiler. A schematic view of the 20 MWth bubbling fluidized-bed boiler is shown in Figure 1. The boiler is employed in a heat and power plant for combusting the SW as ordinary waste fuel mix. The pretreated fuel is injected into the

![Figure 1. Sketch of the BFB boiler: (1) combustion chamber, (2) fuel feed chute, (3) primary air, (4) secondary and tertiary air, (5) empty pass, (6) superheaters followed by an evaporator, (7) cyclone (average particle size = 70 μm), and (8) economizer.](image-url)
boiler through a fuel feed chute (position 2), located over the bed. The air system distributes air to the boiler as primary, secondary, and tertiary air (positions 3 and 4). The boiler is designed for a bed temperature of around 870 °C, and flue gas recirculation is used to control the bed temperature. The flue gas temperature at the top of the combustion chamber is normally between 900–950 °C, and the temperature is around 630 °C after the empty pass and before the superheater. The temperature is then decreased to around 350 °C prior to the economizer and is cooled down to about 150 °C afterward.5,23

2.2. Deposit Sampling. Prior to this study, a series of full-scale combustion tests were conducted in the BFB boiler to evaluate the effects of fuel composition and bed temperature on the deposit formation in the convective zone of the boiler.6,23,24 In order to sample the super heater deposits, a deposit probe, simulating a super heater tube, was inserted upstream into the superheater section (A in Figure 1). The probe was 2 m long with a diameter of 38 mm and equipped with two high alloy steel rings at the top. The surface temperature of the probe was maintained at 435 °C, representing a steam temperature of 405 °C, which corresponds to the normal performance of this boiler. The exposure time for each test was 2–3 h. Each ring was weighed before and after the sampling, and the mass gained by the rings was recalculated as the deposition-growth rate. The deposits were dissolved in an acid solution and analyzed, using the Inductive Coupled Plasma with Atomic Emission Spectroscopy detector (ICP-AES) or the Mass Spectrometer detector (ICP-MS), for ash-forming matter, according to the Swedish standards SS028311 and SS028150-2, and for trace elements according to ASTM D 3683.

2.3. Fuel and Particle Sampling. Fuel and ash particles were also sampled continuously during each measurement. The SW is the ordinary fuel mix used in the boiler, consisting of presorted combustible industrial and household waste. In addition, animal waste (AW), a slurry of crushed carcasses and slaughter house waste, was used as a secondary fuel during some measurements.24 Samples of the SW were extracted right before the fuel feed chute, a few times daily during the measurements, and subsequently analyzed to determine the fuel elemental composition. Chemical fractionation was performed to quantify the reactive and less-reactive fractions of the SW. Samples of the fly ash particles were withdrawn, before and after the convective pass, to identify the ash chemistry under various combustion conditions. The sampled ashes were further analyzed with X-ray powder diffraction (XRD) to identify and quantify the crystalline phases present in the ash. Detailed information regarding the fuel and fly ash sampling and related analytical methods, in addition to the obtained results, are found in our previous studies.6,24

3. MODELING STRATEGY

3.1. Fluidized-Bed Combustion of Waste. In order to create an accurate thermodynamic equilibrium model that represents the condition in a real boiler, detailed knowledge about the combustion process, the temperature profile, and the thermal behavior of the fuel is required. The reason for this is that the results from the chemical equilibrium calculations are very sensitive to the input data such as elemental composition of the fuel, temperature, pressure, as well as the air/fuel ratio.

From a practical point of view, the waste combustion in a BFB boiler can be simplified by the following steps: (1) fuel particles fall partly into the bed and are partly entrained to the freeboard by the fluidizing air (primary air), (2) the primary air, which is introduced through the bottom nozzles, combusts a fraction of the fuel in the suspended bed of sand, (3) the unburned fuel and the produced gases react with the secondary air, which is introduced at the top of the bed (splash zone) and also with the tertiary air in the freeboard, see Figure 1.4,25 Theoretically, however, the combustion process of the fuel is more complicated. The physicochemical transformation of a solid fuel in a fluidized-bed combustion system is explained as the following three steps: drying, devolatilization (pyrolysis), and char oxidation. When a fuel particle is injected into a hot fluidized bed, first the moisture content is evaporated, and subsequently the organic volatile species are released. The released gases are then burned homogeneously, partly inside and partly above the bed. Thereafter, the remaining char, composed of carbon and ash, is burnt.25 Accordingly, both the practical and theoretical mechanisms indicate that a percentage of the fuel is oxidized in the bed, and the rest of it is oxidized above the bed. For a full-scale BFB boiler, combusting refuse-derived fuel, the percentage of the fuel burning in the bed is about 60%.25

A high volatile content of the alternative fuels, such as the waste-derived fuels and biomass, yields different temperature profiles in the bed zone and above the bed, compared to the conventional fuels. In fact, in case of fuels with high volatile content, a large fraction burns in the splashing region, above the bed, leading to overheating in this zone.15,26 In our measurements, the temperature above the bed was 100 to 150 °C higher than the bed temperature. Therefore, considering the fact that part of the fuel is combusted above the bed and also that the elements reactivity is dependent on the temperature, this temperature difference must be considered when modeling BFB combustion.

The release pattern of the inherent inorganic material of solid fuels is influenced by its volatility as well as the organic fraction of the fuel. While some inorganic compounds of the fuel are inherently volatile at the combustion temperature, the organic matter leaving the fuel in the pyrolysis stage can carry some ash-forming elements out of the fuel by convection. The released inorganic fraction of the fuel, the reactive fraction, tends to produce vapors and small particulates (less than 0.1 μm). The residual ash, the less-reactive fraction, tends to produce larger ash particles as a result of fragmentation, coalescence, and chemical or physical transformation.6,17 Based on this, the knowledge regarding the concentrations and speciation of the elements that are considered reactive in the fuel is essential to predict the prevailing reactions during the combustion. This approach also minimizes the limitation regarding the reactivity of the elements based on the residence time of the gases inside the boiler, which is usually lower than 3–6 s.3,25 Hence, chemical fractionation, as an advanced analytical methodology, was applied to determine the reactivity of the inorganic elements by their chemical association in the fuel matrix.

3.2. Modeling Approach. In this study, a thermodynamic equilibrium model has been created aiming to predict the fouling tendency in a BFB boiler, taking into consideration the fuel composition, temperature in the combustion zone, pressure, and air/fuel ratio. The reliability of the model was then compared with the experimental data obtained during the full-scale measurements. In order to minimize the limitations attributed to the equilibrium modeling tools, and also create a model that represents the real system as much as possible, the facts discussed earlier were taken into consideration: (1) Only,
the reactive fraction (RF) of the fuel, which is usually related to fouling problems, was used for calculations; (2) It was assumed that 60% of the waste is combusted in the bed with the primary air, and the rest reacts with the secondary and tertiary air above the bed and the freeboard; and (3) The temperature profile in the combustion zone was carefully determined, taking into consideration the high volatile content of the fuel and the importance of temperature on the elements reactivity. Accordingly, a three-stage equilibrium model was created, as shown in Figure 2.

In the first step, 60% of the fuel (RF) was reacted with primary air, at atmospheric pressure, and specified bed temperature. Then, the predicted equilibrium gas phase together with the unburned fuel (40%) was transferred in the second step, while the equilibrium condensed phase was assumed to remain in the bed or entrained with the flue gas, regardless of the solid–gas phase reactions. The applied temperature in the second step was higher than the bed temperature, while the pressure was constant. Again, the condensed phase was withdrawn from the system. The output equilibrium gas phase determines the composition of the hot flue gas leaving furnace to the convection zone. Step three included the evaluation of the changes in the chemical composition and the physical state of the flue gas as the temperature decreased. The maximum temperature that the flue gas reaches in the furnace (1000 °C) down to the gas temperature prior to the economizer (350 °C) was considered, including the temperatures in the empty pass, deposit probe location, superheaters, and cyclone. The main emphasis was to predict the condensation behavior of the flue gas in the superheater section. Therefore, calculating the amount of the melt present in the condensed phase, where the flue gases meet the superheater steel tubes (650–550 °C), making it possible to evaluate the fouling tendency.

3.3. Equilibrium Tool, Input Data, and Databases.

The thermodynamic program package Factsage 6.4 was employed for the thermodynamic equilibrium modeling. Thermodynamic equilibrium modeling is based on the Gibbs energy minimization technique. The Equilib module of Factsage calculates the phase assemblage and phase composition of a multicomponent and multiphase system at the lowest Gibbs energy, based on the specified conditions and included thermodynamic databases.

All input data in the equilibrium model are based on experimental data and operational data obtained during the full-scale measurements. Therefore, it is possible to compare the experimental findings with the theoretical calculations and thus evaluate the accuracy of the thermodynamic model for the fouling prediction. The input elements were selected on the basis of their importance in terms of fouling and their role during combustion. Only the reactive fraction of each element present was considered in the calculations. In total, 16 elements were considered: C, H, O, N, S, Cl, Na, K, Ca, Mg, P, Si, Al, Ti, Zn, and Pb. Other elements present in the typical waste fuels were excluded, owing to their less-reactive nature or very low concentrations. The water content of the fuel was specified separately by the fuel hydrogen and oxygen content.

The selection of the used database is one of the most critical factors for the reliability of the thermodynamic equilibrium calculations. This determines which chemical species and, particularly, which phases are to be considered. In the present work, three FACT databases: FactPS, FToxide, and FTSalt were selected for the calculation of the stoichiometric gas and the condensed phases. The solution phases of relevance included the following: a liquid solution for molten salts containing Na+, K+ // Cl−, SO4 2−, CO3 2−, NO3 −, OH− (SALTF); an alkali chloride solid solution, (Na,K)Cl(ss); two alkali sulfate-carbonate solid solutions, (Na,K)2(SO4,CO3)(ss); and non-stoichiometric K2Na(SO4)2(ss).

4. RESULTS AND DISCUSSION

4.1. Fuel Analysis.

The heterogeneous nature of the SW produces variations in the chemical composition of the fuel from time to time, particularly in terms of the ash-forming species and the trace elements. The chemical composition of the SW used in this study was obtained by performing a repeated sampling over a long period of time. Table 1 presents the chemical composition of 1 kg SW, showing average values from 12 samples obtained during a period of one year. The composition of the fuel mix when 20 wt % AW was added to the SW is also shown in the table. In order to determine the reactive and less-reactive fraction of a single element in the fuel, the chemical fractionation and existing data from the literature were used. Chemical fractionation, a stepwise leaching method, is used to evaluate the chemical association of the ash-forming elements in the fuel. The leaching method uses water first and then ammonium acetate to leach out the reactive ash-forming elements, in the form of ionic salts and organically associated elements, respectively. These fractions are assumed to be volatilized during combustion and form fine ash particles or condense on cool surfaces. The fraction which remains insoluble is assumed to be less-reactive and forms coarse ash.

Figure 2. Schematic representation of the three-stage thermodynamic equilibrium model and input data used to predict the fouling tendency in the BFB boiler.
SW are released during the combustion, which was taken into consideration for this study. Almost the whole amounts of Fe and Cu were shown to remain in the bottom ash. Therefore, these elements were excluded in this study. The studies also indicated that about 60% of the elements Zn and Pb are released during the combustion of the SW. This is due to the release pattern of Zn and Pb, which is more temperature-dependent than fuel-specific, particularly Pb.31,32

Due to the lack of chemical fractionation data for animal waste, the reactive fraction is estimated based on the existing information in the literature.33 Our elemental analysis of the animal waste showed a notable amount of the ash forming elements: S, Cl, Na, K, Mg, and Zn and a high level of P and Ca. Moreover, it is known that a major fraction of P and Ca in the animal waste is attributed to the bone fraction (hard tissue), mainly as a mixture of Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} and other calcium phosphates.33,34 This portion of calcium phosphate is mainly nonreactive during the combustion.34 While up to 99% of the calcium content of the AW is found in the bone and the teeth material, phosphorus is still an essential component of the organic fraction. Approximately 35% of the P content of the AW is in the reactive form.35 It was also assumed that the S, Cl, Na, K, Mg, and Zn contents of the animal waste are in organic form and are reactive during the combustion. Accordingly, the reactive fraction of the ash-forming elements is recalculated for the fuel mix consisting of the SW, and 80 wt % SW and 20 wt % AW, presented in Table 3.

### Table 2. Chemical Fractionation Results for the SW

<table>
<thead>
<tr>
<th>element</th>
<th>water leachable (%)</th>
<th>acetate leachable (%)</th>
<th>acid leachable and residual (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>60</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>S</td>
<td>70</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Na</td>
<td>40</td>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>K</td>
<td>48</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td>Ca</td>
<td>12</td>
<td>18</td>
<td>70</td>
</tr>
<tr>
<td>Mg</td>
<td>15</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>Si</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>Pb</td>
<td>0</td>
<td>1</td>
<td>99</td>
</tr>
</tbody>
</table>

“Oxygen is calculated as a percentage difference.”

### Table 3. Reactive Fraction of Ash-Forming Elements for Fuel Mix of SW and 80 wt % SW+ 20 wt % AW

<table>
<thead>
<tr>
<th>element</th>
<th>SW reactive fraction (%)</th>
<th>SW + AW reactive fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>S</td>
<td>80</td>
<td>82</td>
</tr>
<tr>
<td>Na</td>
<td>45</td>
<td>51</td>
</tr>
<tr>
<td>K</td>
<td>60</td>
<td>64</td>
</tr>
<tr>
<td>Ca</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>Mg</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>Si</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Al</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Ti</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>P</td>
<td>20</td>
<td>33</td>
</tr>
<tr>
<td>Zn</td>
<td>60</td>
<td>79</td>
</tr>
<tr>
<td>Pb</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>

### 4.2. Fouling Measurements.

Over a period of two years, several measurement campaigns were carried out aiming to evaluate the effect of bed temperature and the SW chemical composition on deposition-growth rate in the superheater section of the BFB boiler. Deposit samples were collected, as discussed in section 2.2, for monocombustion of the SW and also cocombustion of the animal waste with the SW. The obtained results indicated that variations in the bed temperature and the waste chemical composition impact both the amount and the composition of the accumulated deposits in the convective pass of the BFB boiler.5,24 Figure 3 shows the deposit formed on the windward surface of the high-alloy steel rings and the deposition-growth rate obtained for the different measurement campaigns, denoted as ref, HSC, LSC, RBT, and AW. The ref (reference) represents the case of the ordinary waste fuel mix (SW) combustion at normal (designed) bed temperature range. The results of the normal bed temperature combustion of the SW with considerably different sulfur...
content in the SW than the ordinary waste are presented as HSC (high sulfur content) and LSC (low sulfur content) cases. RBT stands for reduced bed temperature, showing the rate of deposition buildup when combusting ordinary SW at a temperature 100 to 160 °C lower than the temperature of which the boiler is designed. The AW (animal waste) refers to the case of the animal waste cocombustion with the SW, when the composition of the fuel mix was changed to 80 wt % SW and 20 wt % AW. It should be noted that during the AW case, the composition of the fuel mix was changed to 80 wt % SW the case of the animal waste cocombustion with the SW, when the boiler is designed. The AW (animal waste) refers to elements S, Cl, Na, and K on fouling, data were taken from Table 1. Due to the significant impact of the elements S, Cl, Na, and K on fouling, data were taken from Table 4, which represents the average concentration of these elements in the sampled waste during the day of measurement. For the AW case, the elemental composition and the moisture content were recalculated for a fuel mix consisting of 80 wt % SW + 20 wt % AW, see Table 1. The reactive (volatile) fraction of the ash-forming elements was considered as input, based on the data provided in Table 3. The total concentration of the elements C, H, O, and N are considered to be reactive.

For each calculation, the average bed temperature corresponding to each full-scale measurement was used as an equilibrium temperature in the first stage, and the average of the recorded temperatures above the bed were used for the second stage, see Table 4. All calculations were performed at atmospheric pressure. The amount of air (O₂ and N₂) added was based on the recorded data in Table 4.

Tables 5 and 6 present the predicted chemical composition of the flue gas leaving the furnace and also the composition of the condensed phase for each combustion case. According to the equilibrium calculations, the concentrations of SO₂ and HCl in the flue gas vary considerably between the different cases, indicating a similar trend as found in the measurements. Table 7 shows the average measured SO₂ and HCl concentrations in the flue gas (after economizer) and also the equilibrium concentrations of SO₂ and HCl in the gas phase for the HSC and AW cases compared to the ref case, whereas the LSC and RBT cases have a lower concentration. Apart from the amount of S and Cl introduced by the fuel in each combustion case, there are also other factors governing the SO₂ and HCl quantity. It is noteworthy that even though a fairly good agreement was found between the measured and the equilibrium concentrations of the SO₂ and HCl for the different combustion cases, differences can be inevitable. The differences can be explained by variations in the fuel composition and the operational parameters during the measurements and also by the fact that the equilibrium model assumes that all the reactants reach equilibrium during the combustion.

### Table 4. Recorded Operational Data and S, Cl, Na, and K Content of the Sampled Fuel Mix for Each Measurement

<table>
<thead>
<tr>
<th>element (wt % dry basis)</th>
<th>ref</th>
<th>HSC</th>
<th>LSC</th>
<th>RBT</th>
<th>AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.46</td>
<td>0.83</td>
<td>0.25</td>
<td>0.40</td>
<td>0.45</td>
</tr>
<tr>
<td>Cl</td>
<td>0.66</td>
<td>0.63</td>
<td>0.50</td>
<td>0.49</td>
<td>0.50</td>
</tr>
<tr>
<td>Na</td>
<td>0.65</td>
<td>0.73</td>
<td>0.64</td>
<td>0.75</td>
<td>0.50</td>
</tr>
<tr>
<td>K</td>
<td>0.39</td>
<td>0.37</td>
<td>0.44</td>
<td>0.36</td>
<td>0.30</td>
</tr>
</tbody>
</table>

### Table 5. Equilibrium Flue Gas Composition for Different Measurement Campaigns

<table>
<thead>
<tr>
<th>species</th>
<th>ref</th>
<th>HSC</th>
<th>LSC</th>
<th>RBT</th>
<th>AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>vol %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>66</td>
<td>66</td>
<td>66</td>
<td>66</td>
<td>64</td>
</tr>
<tr>
<td>H₂O</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>CO₂</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>O₂</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5</td>
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<tr>
<td>ppm, HCl</td>
<td>205</td>
<td>290</td>
<td>59</td>
<td>56</td>
<td>221</td>
</tr>
<tr>
<td>SO₂</td>
<td>15</td>
<td>71</td>
<td>2</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>NaCl</td>
<td>170</td>
<td>108</td>
<td>182</td>
<td>127</td>
<td>68</td>
</tr>
<tr>
<td>KCl</td>
<td>116</td>
<td>83</td>
<td>141</td>
<td>68</td>
<td>53</td>
</tr>
<tr>
<td>(NaCl)₂</td>
<td>2.46</td>
<td>0.98</td>
<td>2.39</td>
<td>1.90</td>
<td>0.46</td>
</tr>
<tr>
<td>(KCl)₂</td>
<td>0.76</td>
<td>0.40</td>
<td>0.99</td>
<td>0.36</td>
<td>0.15</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>2.18</td>
<td>5.41</td>
<td>0.26</td>
<td>0.22</td>
<td>3.00</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>0.37</td>
<td>0.75</td>
<td>0.05</td>
<td>0.08</td>
<td>1.45</td>
</tr>
<tr>
<td>PbO</td>
<td>1.24</td>
<td>0.87</td>
<td>1.60</td>
<td>1.57</td>
<td>2.70</td>
</tr>
<tr>
<td>OH</td>
<td>3.90</td>
<td>3.90</td>
<td>4.44</td>
<td>2.99</td>
<td>3.67</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.73</td>
<td>3.52</td>
<td>0.07</td>
<td>0.05</td>
<td>2.98</td>
</tr>
</tbody>
</table>

4.3. Equilibrium Products. The thermodynamic equilibrium model was used to predict the composition of the flue gas and the condensed phase of the full-scale combustion tests. Equilibrium calculations were performed for 1 kg of fuel mix for each combustion case. The elemental composition of the SW is taken from Table 1. Due to the significant impact of the elements S, Cl, Na, and K on fouling, data were taken from
Table 6. Equilibrium Composition of the Condensed Phase (Steps 1 and 2) for Different Measurement Campaigns

<table>
<thead>
<tr>
<th>solid phase</th>
<th>(g kg⁻¹ fuel)</th>
<th>(g kg⁻¹ fuel)</th>
<th>(g kg⁻¹ fuel)</th>
<th>(g kg⁻¹ fuel)</th>
<th>(g kg⁻¹ fuel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ref HSC LSC RBT AW</td>
<td>ref HSC LSC RBT AW</td>
<td>ref HSC LSC RBT AW</td>
<td>ref HSC LSC RBT AW</td>
<td>ref HSC LSC RBT AW</td>
</tr>
<tr>
<td>Ca₃Al₂SiO₇</td>
<td>3.28 0.04 0.00 2.46 0.00</td>
<td>5.05 3.15 2.88 4.36 4.00</td>
<td>6.29 11.67 2.30 4.84 3.58</td>
<td>0.00 2.77 0.00 0.00 0.92</td>
<td>0.62 0.62 0.62 0.62 4.29</td>
</tr>
<tr>
<td>Ca₃MgSi₂O₆ x O</td>
<td>0.42 0.42 0.00 0.00 0.34</td>
<td>0.18 0.09 0.24 0.24 0.59</td>
<td>0.28 0.52 0.00 0.00 0.69</td>
<td>0.00 0.36 0.00 0.00 0.27</td>
<td>0.00 0.18 0.00 0.00 0.24</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>2.95 3.15 2.88 4.36 4.00</td>
<td>6.29 11.67 2.30 4.84 3.58</td>
<td>3.28 0.04 0.00 2.46 0.00</td>
<td>0.00 2.77 0.00 0.00 0.92</td>
<td>0.62 0.62 0.62 0.62 4.29</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.00 0.00 2.77 0.00 0.92</td>
<td>0.00 0.00 2.77 0.00 0.92</td>
<td>0.00 0.00 2.77 0.00 0.92</td>
<td>0.00 0.00 2.77 0.00 0.92</td>
<td>0.00 0.00 2.77 0.00 0.92</td>
</tr>
<tr>
<td>Ca₂ZnSi₂O₇</td>
<td>0.00 0.00 2.96 1.10 0.00</td>
<td>0.00 0.00 2.96 1.10 0.00</td>
<td>0.00 0.00 2.96 1.10 0.00</td>
<td>0.00 0.00 2.96 1.10 0.00</td>
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</tr>
<tr>
<td>Ca₂SiO₄</td>
<td>0.00 0.00 4.33 1.23 0.00</td>
<td>0.00 0.00 4.33 1.23 0.00</td>
<td>0.00 0.00 4.33 1.23 0.00</td>
<td>0.00 0.00 4.33 1.23 0.00</td>
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</tr>
<tr>
<td>NaCl(l)</td>
<td>0.30 0.16 0.18 1.48 0.19</td>
<td>0.30 0.16 0.18 1.48 0.19</td>
<td>0.30 0.16 0.18 1.48 0.19</td>
<td>0.30 0.16 0.18 1.48 0.19</td>
<td>0.30 0.16 0.18 1.48 0.19</td>
</tr>
<tr>
<td>KCl(l)</td>
<td>0.93 1.47 0.90 1.07 1.26</td>
<td>0.93 1.47 0.90 1.07 1.26</td>
<td>0.93 1.47 0.90 1.07 1.26</td>
<td>0.93 1.47 0.90 1.07 1.26</td>
<td>0.93 1.47 0.90 1.07 1.26</td>
</tr>
<tr>
<td>Na₂Cl(l)</td>
<td>0.10 0.07 0.07 0.59 0.11</td>
<td>0.10 0.07 0.07 0.59 0.11</td>
<td>0.10 0.07 0.07 0.59 0.11</td>
<td>0.10 0.07 0.07 0.59 0.11</td>
<td>0.10 0.07 0.07 0.59 0.11</td>
</tr>
</tbody>
</table>

Table 7. Measured (average) and equilibrium concentrations (calculated) of SO₂ and HCl in the flue gas for different measurement campaigns

<table>
<thead>
<tr>
<th></th>
<th>SO₂ (mg/Nm³ 11% O2 dry gas)</th>
<th>HCl (mg/Nm³ 11% O2 dry gas)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured calcd</td>
<td>measured calcd</td>
</tr>
<tr>
<td>ref</td>
<td>45 36</td>
<td>75 257</td>
</tr>
<tr>
<td>HSC</td>
<td>294 171</td>
<td>245 376</td>
</tr>
<tr>
<td>LSC</td>
<td>11 4</td>
<td>53 76</td>
</tr>
<tr>
<td>RBT</td>
<td>11 2</td>
<td>66 72</td>
</tr>
<tr>
<td>AW</td>
<td>108 131</td>
<td>420 295</td>
</tr>
</tbody>
</table>

Figure 4. Phase equilibrium of the flue gas during gas cooling between 1000–350 °C for the ref case.

According to the equilibrium calculations, a molten phase containing alkali chlorides and alkali sulfates was present in the flue gas, in the temperature range of 950–515 °C. This means that the condensed phase was expected to be sticky in the empty pass and the high-temperature sections of the superheaters. At temperatures between 950–800 °C, the molten phase was mainly composed of alkali sulfates, while as the temperature was decreased, the alkali chlorides became the main fraction in the liquid phase. At a temperature around 660 °C, the amount of alkali chlorides in the molten salt phase reached its maximum, and a further temperature decrease initiated the formation of a solid solution phase containing NaCl and KCl. Below 515 °C, no molten salts were predicted, which indicated a nonsticky condensed phase and a lower fouling tendency in this part of the boiler. There is a strong correlation between the deposit buildup and the flue gas temperature in a real boiler. The temperature of the flue gas is the major parameter controlling the rate of the deposit buildup on the boiler heat exchangers, while the tube surface temperature has an effect on the deposit hardness and strength.

4.5. Fouling Tendency: Thermodynamic Equilibrium Results versus Experimental Data. The thermodynamic equilibrium model was used to simulate the fouling tendency in the real BFB boiler in all including measuring campaigns. In order to evaluate the fouling tendency, the quantity of the melt

CaCO₃, CaO, CaClOH, and alkali-calcium-sulfates were not predicted. For instance, calcium in the form of CaCO₃ and CaO were both detected in the fly ashes. Formation of CaCO₃ in the boiler is thermodynamically favorable when the flue gas temperature is between 800–600 °C meaning that reaction 1 most likely occurs in the convective section of the boiler rather than in the furnace zone.

\[
\text{CaO(s) + CO}_2(g) \rightarrow \text{CaCO}_3(s)
\] (1)

The equilibrium model, however, did not predict any CaCO₃ due to the fact that all of the available CaO in the furnace is already in an equilibrium state like the other minerals (Table 6). In reality, however, all of the CaO does not reach equilibrium in the furnace, considering the reactant mixture degree, residence time, and reaction kinetics limitations, and it is instead transferred to the convective section where it may react further.

4.4. Cooling of the Flue Gas. The condensation behavior of the generated flue gas in the ref case was studied in the temperature range of 1000–350 °C and illustrated in Figure 4.
in the condensed phase was estimated. The study was focused in the temperature range of 650−550 °C, which is the approximate temperature where the flue gas meets the deposition probe and the first superheater tube bundle in the studied BFB boiler. Figure 5 presents the phase equilibrium of the condensed phase for the different combustion cases, when the flue gas is cooled down from 1000 °C down to 350 °C. Comparing the flue gas condensation behavior of the studied cases, it was found that the amount of the condensed phase was directly related to the concentration of the vaporized alkali chlorides in the flue gas, while the melting temperature of the condensed salt phase was significantly affected by the level of SO2. In other words, the ratio between the SO2 and the alkali chloride concentrations in the flue gas determines the melting behavior of the salt mixture at different temperatures.

In the ref, LSC, and RBT cases, all of which have a considerably higher level of alkali chlorides than SO2 in the flue gas (Table 5), a relatively similar trend for the condensed phase could be observed. The amount of melt at the high-temperature section, above 750 °C, was not significant, meaning that the alkali chlorides predominantly stay in the gas phase. The melt fraction reached its maximum value between 700−650 °C, and afterward, they rapidly decreased, where instead an alkali chloride solid phase was formed. In the temperature range between 650−550 °C, which is important in terms of fouling for the BFB boiler, the level of SO2 determines the amount of melt in the condensed phase. In the LSC and RBT cases, with a low amount of SO2, the amount of melt was decreased to a very low amount, whereas in the ref case, with a higher amount of SO2, the condensed phase contained a significantly higher amount of melt.

In the HSC and AW cases, a considerable amount of SO2 was released in the gas phase, which led to a higher SO2/alkali chloride (SO2/ACl) ratio and a different condensation pattern, compared to the ref, LSC, and RBT cases. Sulfation of the vapor alkali chlorides produced a notable amount of melt in the high-temperature section, at approximately 950−800 °C. At lower temperatures, the sulfation of alkali chlorides affected the melting behavior of the condensed phase depending on the SO2/ACl ratio in the flue gas. At around 800 °C, the formation of a high-melting-point alkali sulfate solid phase was predicted in both the HSC and the AW cases. In the HSC case, with a considerably higher amount of alkali chlorides in the flue gas than in the AW case, the solid alkali sulfate phase constitutes

![Figure 5. Phase equilibrium of the condensed phase during the flue gas cooling between 1000−350 °C for different combustion cases. Salt-liq in the legend refers to the molten salt phase.](image-url)
only a minor fraction of the condensed phase, and the molten phase was the major fraction. In the AW case, however, because of the low concentration of the vaporized alkali chlorides, the solid alkali sulfate becomes the major fraction of the condensed phase, which increased the melting temperature.

The amount and fraction of the melt in the condensed phase of the different cases, in the temperature range 650–550 °C, are presented in Figure 6. Considering the quantity of the melt and the fraction of the melt in the condensed phase, the different deposition-growth rates obtained during the measurements (Figure 3) could be explained. The ref and HSC cases had not only a higher amount of melt but also a melt fraction above 15 wt %, indicating a high stickiness rate of the deposited salt. At temperatures below 620 °C, the condensed deposit in the HSC case had a higher amount of melt and also a higher melt fraction in the condensed phase. This may explain the higher deposition rate in the HSC case, compared to the ref case. The LSC and RBT cases had a melt fraction that was higher than 15 wt %, between 650–635 °C. At lower temperatures, however, the deposit was not considered to be sticky. The LSC case also showed a slightly higher quantity of melt than the RBT case; however, in comparison with the ref and HSC cases, the amount of melt was much lower. The AW case showed a melt fraction below 15 wt % in the whole temperature range and also very low quantities of melt, indicating nonstickiness of the condensed phase in this case.

The elemental analysis of the collected deposits (Figure 3) shows a high amount of Ca, Si, Al, and a low amount of Ti and Mg associated particles in the deposits of the HSC and ref cases. These particles were predicted to form as solid fly ashes (Table 6) and are most likely enriched in the deposit by the elutriation process, considering the high stickiness of the condensed phase. Other combustion cases, however, did not show a considerable amount of elutriated particles in the deposit. Therefore, it was concluded that the condensed phase in the ref and HSC cases was sticky enough to capture larger particles transported by the inertial impaction and thermophoresis, and consequently led to a fast deposition-growth rate. In the LSC, RBT, and AW cases, the condensation seems to be the main process contributing to the deposit formation; the particle capture was considerably decreased due to the low stickiness of the condensed phase, which gave a lower rate of the deposit formation. In the BFB boiler, the flue gas temperature is approximately 630 °C, before it enters the superheater section. The calculations suggest that in order to avoid troublesome deposit formation on the superheater tubes, it is necessary to keep the flue gas temperature below 630 °C, although this temperature may be exceeded from time to time due to the deposit formation in the empty pass section.

4.6. Sensitivity Study. The results of the equilibrium modeling showed that the SO2/ACl ratio is important to determine the rate of the deposit buildup in the boiler. The amount of released alkali chlorides and SO2 in the flue gas is dependent on the chemical composition of the fuel, as the source of alkali and sulfur. In terms of the boiler performance, the applied temperature was shown to be a critical factor affecting the level of released alkali chlorides in the flue gas. In order to examine the effect of the temperature on the amount of released alkali chlorides, a sensitivity study was carried out. The SW elemental composition was taken from Table 1, and Cl, Na, K, and S concentrations were assumed to be constant for all of the calculations. The recorded bed and freeboard temperatures (Table 4) were used as the variable parameter. Figure 7a shows the effect of the increased bed temperature on the amount of released alkali chlorides into the flue gas. A
higher bed temperature showed a significant increase of the amount of alkali chloride in the gas phase, while at lower temperatures more alkali chlorides were captured in the condensed phase.

Figure 7b presents the impact of SO2/ACl ratio on the amount of melt present in the condensed phase at the temperature range 650 to 500 °C. The concentration of the alkali chlorides in the flue gas was assumed to be constant, while the level of the SO2 was changed stepwise. At a SO2/ACl ratio of 0.01 (and lower), the amount of melt in the flue gas is rather low, particularly below 600 °C. As the SO2 concentration was increased, the amount of melt also increased until a SO2/ACl ratio of approximately 0.3, where the highest amount of melt was reached. Above an SO2/ACl ratio of 0.3, a reverse effect of SO2 concentration on the quantity of the molten phase was observed, owing to the formation of the solid alkali sulfate phase. At a SO2/ACl ratio of 0.4, the amount of melt was significantly reduced, and at a ratio of 0.5, the solid alkali sulfate constitutes the major fraction of the condensed phase, and a very low amount of melt was calculated.

4.7. Effects of the Bed Temperature, S, and P on the Deposition Growth Rate. An earlier study on the BFB boiler has demonstrated that reducing the bed temperature from 870 to 720 °C decreased the deposit formation in the convective section by 20%.6 It was also shown that the lower bed temperature captures a higher amount of chlorine in the bed, resulting in a lower concentration of chlorine in the fly ash. These results are in agreement with the equilibrium calculations, which showed more alkali chlorides captured in the condensed phase during the RBT case, see Table 6. As a result, the amount of released alkali chlorides in the flue gas decreased; consequently, the rate of fouling was reduced.

The results obtained from the measurements revealed that there is an inverse relationship between the concentration of chlorine in the collected deposits and the SO2 level in the flue gas. The higher the SO2 concentration, the lower the amount of chlorine that was detected in the deposit. The depletion of chlorine in the deposit and the enrichment of sulfur could be explained by an alkali chloride sulfation mechanism. Sulfation of alkali chlorides is summarized in reactions 2 and 3 below, where A is either K or Na:

\[
SO_2(g) + 1/2O_2(g) \rightarrow SO(g) (g) \quad (2)
\]

\[
2\text{ACl}(g) + \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{A}_2\text{SO}_4(s, l) + 2\text{HCl}(g) \quad (3)
\]

Gas-phase sulfation of alkali chlorides is typically fast, and the oxidation of SO2 to SO3 in the reaction mechanism is the rate-limiting step for the sulfation reaction.41 The sulfation proceeds also directly with SO2 and O2, but at a slower rate.40 The availability of sulfur for the sulfation reaction is important in terms of the deposit formation. Several studies42–44 reported gas-phase sulfation of alkali chlorides during the biomass combustion, aiming to reduce the amount of sticky alkali chlorides in the flue gas. On the other hand, the formation of low-melting-point acidic alkali sulfates, such as K2SO3 and KH2SO4, were also reported when the SOx concentrations in the flue gas were high.45,46 In this case, the deposited alkali sulfates (such as K2SO4 and Na2SO4) are further sulfated with the presence of SO3 and lead to the formation of low-melting-point alkali pyrosulfates (Na2S2O5 with mp 389 °C, and K2S2O7 with mp 404 °C).46 However, the solid-state sulfation of alkali chlorides is believed to be slow and is only important in the deposits and not in the fly ashes.47 In our measurements, it was found that the SO2 concentrations have different effects on the rate of fouling (Table 7 and Figure 3). The equilibrium calculations suggest that the SO2 level affects the deposition-growth rate, depending on the alkali chlorides concentration in the flue gas.

Co-combustion of the animal waste with the SW changed both the composition of the fuel mix and the bed temperature. In terms of fuel composition, the addition of animal waste to the SW considerably increased the amount of reactive phosphorus in the fuel mix, thereby increasing the levels of SO2 and HCl in the flue gas. The equilibrium calculation also predicted high levels of SO2 and HCl in the AW case. Higher levels of SO2 and HCl in the flue gas has also been reported, when phosphoric acid (H3PO4) was used as an additive during the fluidized-bed combustion of biomass.48 This could be explained as an impact of phosphorus on the available CaO(s) for the rest of the combustion reactions. CaO(s) acts as a natural desulphuriser, removing the free SO2 in the flue gas, according to reaction 4.46

\[
\text{CaO}(s) + \text{SO}_2(g) + 1/2\text{O}_2(g) \rightarrow \text{CaSO}_4(s) (4)
\]

On the other hand, phosphorus has a high affinity for calcium, producing stable solid products in the residual ash through a medium fast reaction, described as reaction 5.49

\[
\text{P}_2\text{O}_5(g) + 3\text{CaO}(s) \leftrightarrow 2\text{Ca}_3\text{P}_2\text{O}_8(s) (5)
\]

Therefore, it is arguable whether the co-combustion of the animal waste was in fact reducing the available CaO(s) in the furnace and, consequently, increasing the free SO2 in the flue gas. Subsequently, the rate of alkali chloride sulfation increased, and more HCl was released in the flue gas. Grimm et al.48 showed that the addition of phosphorus to biomass changed the system from being dominated by amorphous alkali-silicate ash fractions and fine particulate alkali chlorides to a system dominated by crystalline coarse ash of alkali-Ca/Mg-phosphates and fine particulates of alkali sulfates.

In terms of operational condition, the bed temperature was reduced due to a high moisture content of the animal waste. The equilibrium calculations predicted a significant reduction of volatile alkali chloride in the AW case, owing to a lower bed temperature, as well as a higher rate of alkali chloride sulfation in the furnace. These findings are consistent with the deposition probe tests, showing a low rate of deposit buildup in the AW case.

5. CONCLUSION

Advanced thermodynamic equilibrium calculations, combined with an advanced fuel analysis, were shown to be a reliable technique for deposit formation simulation in a fluidized-bed boiler. The approach used in the combustion model, considering the combustion pattern in the fluidized-bed system and also the temperature profile in the combustion zone, allowed us to establish a reasonable correlation between the theoretical and experimental data. Comparing the results of the deposit measurements in the real BFB boiler with the modeling results, it was concluded that the applied model is able to predict the fouling tendency on the basis of the condensation behavior of the flue gas system. The main observed discrepancies between the experimental and the calculated results were due to a lack of comprehensive thermodynamic databases, as well as dynamics of the real combustion processes,
such as the physical processes, kinetics of the reactions, and solid–gas phase reactions, which could not be handled by the thermodynamic equilibrium model. Further developments of the thermodynamic databases (e.g., phosphorus-related compounds and also the addition of Ca, Zn, and Pb in the salt mixture) are needed to improve the accuracy of the equilibrium model.

Both the theoretical and the practical results showed that lower bed temperatures and also co-combustion of P-rich fuels decrease the rate of deposition buildup in the BFB boiler. According to the equilibrium calculations, the SO2/ACl ratio in the flue gas is important in terms of the fouling tendency in the boiler. It was found that the amount of condensed phase is directly related to the concentrations of alkali chlorides in the flue gas, while the level of the SO2 could significantly affect the amount of melt in the deposited salt phase at different temperatures in the boiler.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**References**


Thermodynamic Equilibrium Prediction of Bed Agglomeration Tendency in Dual Fluidized-Bed Gasification of Biomass

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Abstract

Dual fluidized-bed (DFB) gasification is one of the recently developed technologies for production of heat, power, transportation fuels and synthetic chemicals through steam gasification of biomass. Bed agglomeration is a serious ash-related problem that should be taken into account when biomass-based fuels are selected for fluidized-bed gasification and combustion. This study developed a thermodynamic equilibrium model to assess the risk of bed agglomeration in gasification and combustion reactors of a DFB gasifier using biomass (forest residues) as feedstock. The modelling approach combined thermodynamic equilibrium calculations with chemical fractionation technique to predict the composition and melting behaviour of the fuel-derived ash as well as bed particles coating layer in the gasification and combustion reactors. FactSage was employed for the thermodynamic equilibrium calculations. The modelling results were then compared with experimental data obtained from a full-scale DFB gasifier to estimate the reliability and validity of the predictive model. In general, a good agreement was found between the modelling results and experimental observations. For the forest residues as feedstock and olivine as bed material, the modelling results indicate a low risk of bed agglomeration in the DFB gasifier, as long as the dominant temperature in the combustion zone is below 1020 °C. In contrast, quartz as bed material in the DFB gasifier was shown to significantly increase the risk of bed agglomeration through coating-induced agglomeration mechanism.
1. Introduction

Global warming and climate change problems associated with fossil fuels consumption have led to substantial research and development on heat and power production from alternative sources of energy. Reduction of greenhouse gas emissions, and also replacement of non-renewable resources through biomass energy utilisation has gained particular interest in recent years. Less environmental impacts and widespread availability of biomass make it an interesting option for future energy supply and demand. The conversion of biomass to bio-energy can be achieved using either biological or thermochemical processes. Combustion, gasification, and pyrolysis are the main thermochemical conversion technologies, where gasification is considered as one of the most efficient ways of converting the energy stored in biomass. Gasification is the thermal conversion of the organic fraction of solid fuels to synthesis-gas in the presence of an oxidant whose amount is lower than that required for stoichiometric combustion. Synthesis-gas (also called ‘Syngas’ or ‘Producer gas’) contains primarily carbon monoxide, hydrogen and lower amounts of methane, which can be used to power gas engines and gas turbines or as a chemical feedstock for the production of liquid fuels.\textsuperscript{1-3} Fixed or moving bed, fluidized-bed and entrained flow are three types of gasifiers. Fluidized-bed (FB) technologies have grown to become one of the most suitable technologies for combustion and gasification of biomass. Fluidized-bed systems have a number of process advantages such as high fuel flexibility, low process temperature, emission control, high reaction rates, good gas-solid contact and mixing, and are also suitable for large-scale capacities.\textsuperscript{3-5}

Ash-related problems could be a potential problem during thermochemical conversion of biomass-based fuels. The release and transformation of inorganic species during the thermochemical processes may lead to problems, such as fouling and corrosion of heat transfer surfaces, slag formation in furnaces, as well as bed agglomeration in fluidized-bed systems. Agglomeration of bed particles in fluidized-bed systems is a highly unwanted property of some biomass fuels.\textsuperscript{3,4,6} While higher bed temperatures would enhance carbon conversion and increase tar cracking in a gasifier, the fluidized-bed temperature must be kept below the ash-fusion temperature of the biomass ash to prevent bed particle agglomeration.\textsuperscript{3} For instance, a bubbling fluidized-bed gasifier generally operates at temperatures below 900 °C to avoid bed defluidization, or even far below 900 °C for a problematic feedstock such as straw.\textsuperscript{4}
Dual fluidized-bed (DFB) gasification is one of the recently developed technologies for steam gasification of biomass. DFB steam gasification of biomass has been successfully demonstrated at the biomass power plant in Güssing, Austria (8 MWth fuel power), since late 2001. Currently, there are other plants in operation using DFB gasification technology, such as Oberwart, Austria (8.5 MWth), and Ulm, Germany (15 MWth). In Sweden, in the GoBiGas (Gothenburg Biomass Gasification) project, a DFB gasifier was recently being constructed to produce substitute natural gas (SNG) using biomass as feedstock. The plant currently operates with wood pellets, but the aim is to switch to a cheaper feedstock (e.g. forest residues) to make the SNG production economically feasible. Forest residues, however, contain higher ash content, meaning that a greater risk of ash-related problems is expected (e.g. bed agglomeration) in the DFB gasifier. There is very limited knowledge regarding the risk of bed agglomeration in DFB gasification of forest residues. This study aims to assess the risk of bed agglomeration during DFB gasification of forest residues using thermodynamic equilibrium modelling as a predictive tool.

1.1 DFB gasification

Dual fluidized-bed gasifier is a combination of a bubbling fluidized-bed (BFB) gasifier and a circulating fluidized-bed (CFB) combustor, where steam is used as gasifying agent in the BFB reactor, and air is the fluidizing and oxidising medium in the CFB reactor. Figure 1 shows a schematic view of a DFB steam gasification process. The biomass is fluidized with steam in the gasifier at bed temperature of about 850–900 °C to produce the producer gas and residual char. Average fuel particle residence times ranging from 60-160 s, in the gasification zone of DFB gasifiers, have been reported. Thereafter, the residual char is transported together with the bed material into a fast fluidized combustor (riser) via a chute, where the heat needed for endothermic gasification reactions is provided by combustion of the char at about 950–1000 °C. The hot bed materials are circulated as heat carrier between the two FBs, maintaining the required gasifier temperature. Olivine and quartz are commonly used bed materials in DFB gasification plants, where olivine is most frequently used due to its catalytic properties which have shown to significantly influence the gasification properties through tar reduction in the product gas. The embedded cyclone separates the bed materials from the flue gas, and the heated bed materials are transported to the gasifier via a loop seal. In order to prevent gas leakage
between the gasification and combustion zones, and also maintain high solid throughput, the loop seal and chute are fluidized with steam. The lower temperature difference between the gasification and combustion reactors can be achieved by higher solid circulation rate, which also conveys more char to the combustor, reducing the required amount of additional fuel.\textsuperscript{4, 7, 8, 10-15}

![Schematic drawing of a dual fluidized-bed steam gasifier](image)

**Figure 1. Schematic drawing of a dual fluidized-bed steam gasifier**

### 1.2 Bed agglomeration

Bed agglomeration is a serious ash-related problem in FB systems that should be taken into account when fuels are selected for FB gasification or combustion. Temperatures higher than the softening temperature of the fuel ash may result in agglomeration of bed particles and subsequently defluidization of the bed. The temperature at which the first sticky molten phases appear that are able to glue bed particles together into agglomerates is defined as initial agglomeration temperature.\textsuperscript{16} In a gasifier, high temperatures (above 1000 °C) can enhance tar cracking into lighter species. Such temperatures, however, are incompatible with the typical operational temperature of FB gasifiers, due to the increased risk of bed agglomeration particularly in the case of feedstock with high alkali concentrations.\textsuperscript{4}
Formation of low-melting-point fuel-derived ash and/or low-melting-point coating layers on the surface of bed particles have been suggested as the most important routes for the initiation of bed agglomeration.\textsuperscript{17-21} Partly molten fuel-derived ash can lead to direct adhesion of bed particles. This is referred to in literature as “melt-induced agglomeration”.\textsuperscript{22-24} “Coating-induced agglomeration” refers to the formation of sticky coating layers as a result of solid-gas chemical reactions between the bed particles and gaseous species, e.g. K-compounds.\textsuperscript{17, 24} In melt-induced agglomeration the formation of partly molten ash is primarily dependent on the fuel characteristics, whereas in coating-induced agglomeration both the fuel characteristics and bed material are involved.\textsuperscript{24} The possible bed agglomeration mechanisms during FB combustion of biomass can be either melt-induced or coating-induced, depending on the chemical composition and association of ash-forming elements in the fuel. Direct adhesion of bed particles typically takes place for fuels with ash rich in K and organically bound Si (formation of partly molten ash-derived K-silicates), and also for biomass rich in P, K and Ca/Mg (formation of partly molten ash-derived K-Ca/Mg-phosphates). For biomass with ash rich in Ca, K and relatively low amounts of Si and P, layer formation on bed particles (typical for quartz bed) can be initiated by K-silicate melt, accompanied by diffusion or dissolving of Ca into the melt, leading to viscous-flow sintering and agglomeration. Bed agglomeration as a result of direct reactions of K-compounds in gaseous or aerosol phase with quartz bed particles was suggested to be typical for biomass with high alkali content and relatively low Si and P content.\textsuperscript{18-21, 25}

### 1.3 Predicting ash behaviour

For a given fuel, the elemental analysis of ash-forming matter using standard analysis methods is the starting point to determine the suitability of the fuel from the ash behaviour point of view. The standard methods, however, are not able to give information about the chemical forms of ash-forming elements in the fuel. The reactivity of ash-forming elements during the thermal processes is influenced by their chemical associations in the fuel matrix. Chemical fractionation, an advanced fuel analysis technique, can provide valuable information about the chemical association of ash-forming elements in the fuel matrix. Chemical fractionation technique can distinguish ash-forming elements into reactive (volatile species) and less-reactive (non-volatile species) fractions.\textsuperscript{6, 26}
Thermodynamic equilibrium modelling has also become a widely used tool to predict the ash-related problems in combustion and gasification of alternative fuels. Thermodynamic equilibrium modelling is based on Gibbs energy minimisation techniques, which calculate the chemical equilibrium composition of a multicomponent and multiphase system at specified conditions, considering the included thermodynamic data of all phases and compounds. In order to obtain reliable results from thermodynamic equilibrium modelling, the limitations of the technique must be taken into account. While the elemental composition of the fuel is essential for thermodynamic modelling, the reactivity of ash-forming elements is also crucial. Combination of thermodynamic equilibrium calculations with chemical fractionation technique minimises the limitation regarding the reactivity of ash-forming elements in the modelling of real systems. The reactive fraction (water and acetate soluble) of ash-forming elements is expected to reach equilibrium during combustion, while the less-reactive fraction (acid soluble and solid residue) can be in such stable or inert forms that do not react further. In bed agglomeration, the reactive fraction can form molten ash and/or sticky coating layers on the bed material, whereas the less-reactive fraction could become trapped in the molten ash and sticky coating. In addition, kinetics of the reactions, and transport phenomena are not considered in the results of thermodynamic equilibrium modelling. In fluidized-bed environment due to good gas-solid contact and mixing, as well as relatively long residence time, conditions are created where the ash transformation reactions could approach equilibrium.

In the present work, thermodynamic equilibrium modelling combined with chemical fractionation technique to develop a predictive model to assess the risk of bed agglomeration in DFB gasification of biomass (forest residues). The modelling approach considered the gasification and combustion reactors of the DFB gasifier as two separate equilibrium reactors. The elemental composition of virgin forest residues and residual char were considered as input fuel in the gasification and combustion reactors, respectively. The chemical composition of residual char entering the combustor was obtained by laboratory-scale steam gasification of virgin forest residues at 850 °C. Only reactive fraction of ash-forming elements, determined by chemical fractionation, was considered for the modelling. The risk of bed agglomeration in each reactor was assessed based on the predicted composition and melting behaviour of fuel-derived ash and coating layer of bed particles. The reliability of the predictive model was evaluated by comparing with experimental observations of a full-scale DFB gasifier, using forest residues as feedstock.
2. Experimental Section

2.1 Experiments

Biomass ash composition depends on the species (e.g. wood-derived fuels or agricultural residues), used fertilizer, harvesting technique and the time of harvesting.\textsuperscript{34} Forest residues belong to the category of wood-derived fuels, which are often contaminated with sand from forest floor.\textsuperscript{26} Standard fuel analysis was carried out to determine the elemental composition of the forest residues. The amount of dry matter was determined at 105 °C, and the amount of ash content was determined by ashing at 550 °C until constant mass was achieved. Carbon, hydrogen, and nitrogen analysis was performed according to SS-EN 15104. The analysis technique for Cl was SS-EN 15289 A (ion chromatography) and SS-EN 15289 for S (sulphur analyser). Standard method ASTM D 3682 was used to quantify the main ash forming elements K, Na, Al, Si, Fe, Mg, Ca and P.

Chemical fractionation,\textsuperscript{26} a stepwise leaching method, was carried out to determine the association of ash-forming elements in the forest residues. The method implies that ash-forming matter in the solid fuel can be divided into four classes: dissolved salts, organically bound matter, included mineral matter, and excluded mineral matter. With this methodology, the fuel is leached in water solutions of increasing aggressiveness. First, the water-soluble compounds in the form of dissolved salts such as alkali chlorides, sulphates, carbonates and phosphates were leached out by deionized water. Then, 1 M ammonium acetate (NH₄Ac) was used in the second step for leaching the ion exchangeable organically bound metal cations (e.g. Mg, Ca, K and Na). Thereafter, 1 M hydrochloric acid (HCl) was used for the final step to leach out most of the scarcely soluble inorganic salts such as carbonates, sulphates, and phosphates of alkaline-earth metals and other metals. The insoluble residue mainly includes silicates and other minerals. Note that the elements that are bound to the organic fuel matrix with covalent bonds such as S and Cl may stay in the insoluble fraction.\textsuperscript{26, 35}

In order to obtain the ash composition of the char to be applied in the modelling of combustion reactor, virgin forest residues were gasified in a laboratory-scale BFB reactor at 850 °C. The forest residues were milled, homogenised, and pelletised to obtain 8 mm pellets. The pellets were dried at 105 °C in an oven to constant mass. The experimental set-up applied consisted, among
other things, of a laboratory-scale BFB reactor (see Figure 2). A description of the experimental set up is available elsewhere.36 Prior to each gasification experiment, 600 g of sand was placed in the reactor. The reactor was heated to the desired temperature after which nitrogen gas was introduced to render the atmosphere in the reactor inert. Thereafter, the fluidization gas was switched from nitrogen gas to a mixture of nitrogen gas and steam consisting of 83 % steam by volume. When the desired conditions in the reactor were achieved, 15 g of forest residues were placed in a wire-mesh basket (having openings with 0.8mm size) and introduced into the reactor. After 2.5 minutes, the basket containing the solid residue (char) was removed from the reactor and rapidly cooled in a stream of nitrogen gas. The char fines that left the openings of the basket into the bed of the reactor was quantified as described elsewhere.36 The char samples collected were then chemically analysed to ascertain the concentrations of the ash-forming elements in them. Chemical fractionation analysis was also carried out on the char samples to determine the association of ash-forming elements in them.

Figure 2. Laboratory-scale bubbling fluidized-bed reactor used in this work
2.2 Fuel characteristics

Table 1 shows the elemental composition and reactive fraction of ash-forming elements for the virgin forest residues and char sample. The char sample is the residual char obtained when virgin forest residues were exposed to steam at 850 °C for 2.5 min in the BFB reactor. Under the aforementioned operational conditions, 15 % of the char resulting from devolatilisation of the virgin forest residues was gasified. The reactive fraction (water and acetate soluble) of ash-forming elements was calculated based on the chemical fractionation results, shown as Figure 3. The results indicate that the main ash-forming elements of the forest residues are Ca, K, Si, Mg, P, Al, S, Fe, Na and Cl, where the Ca, K and Si have the highest concentrations. According to the chemical fractionation results for the forest residues, more than 80 % of the Si was insoluble (rest) in the chemical fractionation analysis. This fraction of Si in biomass is mainly present as silica (SiO₂) or other silicate minerals, which are relatively inert under FB combustion and do not cause slagging, fouling, sintering, or corrosion. This fraction, though, may affect the chemistry of other ash-forming elements K, Na and Ca through secondary reactions. 16, 26 Only less than 10 % of the Si is in the reactive form, which is mainly distributed in the fuel organic matrix (NH₄Ac soluble). Calcium was mainly found as organically bound and also in the acid-soluble fraction of the leaching test. The acid-soluble fraction of Ca is present as crystalline salts, mostly different forms of calcium oxalate. 16, 26 The major fraction of K (94 %) was found in the water and acetate soluble fractions. Potassium is the most important ash-forming element and also the main cause of bed agglomeration, fouling and corrosion in biomass-based fuels. The water and acetate soluble fractions of K in biomass are in the form of ionic salts and organically bound K ions, respectively. These forms of K in biomass can be released during thermal conversion and contribute in further reactions. 16, 26 The chemistry of Na in biomass is very similar to that of K, but its concentration is typically an order of magnitude lower than that of K. 26 The same is true for Mg, which is chemically similar to Ca. Chlorine in biomass fuels is present mainly as chloride salts, which are water-soluble. During thermal processes, the chloride salts can vaporise (KCl(g), NaCl(g)) or decompose and release the Cl to the gas phase. 26 The major fraction (roughly three-quarters) of S in woody biomass is organically bound, and the rest is in the form of soluble alkali sulphates. 26, 37 Therefore, the insoluble fraction of S (Figure 3) is most likely in organic forms involving covalent bonds, which are not capable of undergoing ion exchange in ammonium acetate. 26 The organic fraction of S can be fully released during the thermal processes, while S in
the salt form may remain connected to the alkali sulphate or decompose and release to the gas phase. Almost 60 % of P in the forest residues was leached out by water and acetate. The water-soluble fraction of P can be in the form of soluble phosphate salts (e.g. K₃PO₄), and the acetate-soluble fraction is comprised of P-organic molecules (e.g. phytic acids). Only trace amounts of Al and Fe were found in water and acetate soluble fractions of the leaching test. This is consistent with the non-volatile nature of these elements in the biomass. In furnace processes, Al and Fe related compounds would form Al₂O₃ and Fe₂O₃ which do not participate significantly in the ash chemistry and can be regarded as inert compounds.

<table>
<thead>
<tr>
<th>element</th>
<th>virgin forest residues</th>
<th>residual char</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt % (dry basis)</td>
<td>reactive fraction (%)</td>
</tr>
<tr>
<td>C</td>
<td>50.3</td>
<td>83.2</td>
</tr>
<tr>
<td>H</td>
<td>6.1</td>
<td>0.5</td>
</tr>
<tr>
<td>N</td>
<td>0.5</td>
<td>0.96</td>
</tr>
<tr>
<td>O*</td>
<td>41</td>
<td>4.2</td>
</tr>
<tr>
<td>S</td>
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<td>100</td>
</tr>
<tr>
<td>Cl</td>
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</tr>
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<tr>
<td>Ca</td>
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</tr>
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<td>Mg</td>
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</tr>
<tr>
<td>Si</td>
<td>0.12</td>
<td>10</td>
</tr>
<tr>
<td>P</td>
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<tr>
<td>Fe</td>
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<td>2</td>
</tr>
<tr>
<td>Al</td>
<td>0.021</td>
<td>2</td>
</tr>
</tbody>
</table>

* Oxygen is calculated as percentage difference.
3. Modelling Section

3.1 Modelling approach

Thermal conversion of biomass in a DFB gasifier involves a sequence of thermochemical transformation steps including drying, devolatilisation (pyrolysis), char gasification, and char oxidation.\textsuperscript{36, 38} The first three steps of thermal conversion take place in the gasifier, and char oxidation occurs in the riser (combustor). In addition, the atmosphere in each reactor is different. Steam is the fluidization agent in the gasifier, while air is the fluidization agent in the combustor. Hence, the gasification and combustion reactors were modelled as two separate equilibrium reactors. Accordingly, for each reactor, a two-stage equilibrium model was developed to predict
the composition and melting behaviour of fuel-derived ash and coating layer of bed particles, as illustrated in Figure 4. The elemental composition of the virgin forest residues (reactive fraction) and steam (H₂O) was used as input for the gasification reactor, while the elemental composition of the char (reactive fraction), and air (O₂ and N₂) was considered as input for the combustion reactor. As mentioned earlier (section 2), the chemical composition of the char applied in the modelling of the combustion reactor was obtained from the chemical analysis of the residual char from the laboratory-scale test. Calculations were carried out under atmospheric pressure and in the temperature range of 700–1200 °C in steps of 20 °C. This temperature range allows for investigating the thermal behaviour of ash at temperatures higher than the fluidized-bed that may locally occur in the combustion zone. The model output, for each reactor, determines the chemical composition and melting behaviour of the condensed phase ash (fuel-derived ash), as well as the chemical composition of the gas phase. Subsequently, the composition of the gas phase was used to simulate the interaction between the gas phase and bed material (solid-gas phase reactions).

Figure 4. Schematic representation of the two-stage thermodynamic equilibrium model applied for prediction of the fuel-derived ash and coating layer in the (a) gasification and (b) combustion reactors of the DFB gasifier
3.2 Thermodynamic equilibrium calculations

FactSage 7, the thermochemical software and databases,\textsuperscript{39} was employed for the thermodynamic equilibrium calculations. The input elements were selected on the basis of the elemental composition of the virgin forest residues and char, considering only the reactive fraction of ash-forming elements (see Table 1). In total, 12 elements were selected: C, H, O, N, S, Cl, K, Na, Ca, Mg, P and Si. Al and Fe were excluded due to the low concentrations of the reactive fraction. The total concentrations of C, H, O and N were assumed to be reactive. Steam-to-biomass ratio of 0.8 was applied for the gasification step, which is in the optimal range (0.6-0.85) for biomass gasification plants.\textsuperscript{40} For the combustion step, complete oxidation of the char with air (O\textsubscript{2}, N\textsubscript{2}) was considered, resulting in approximately 6 vol % excess O\textsubscript{2} in the flue gas. Thermodynamic databases FactPS, FToxid, FTsalt and FTpulp were employed for prediction of the gaseous compounds, pure solids, as well as possible solid and liquid (molten) solution phases. The database FTsalt-SALTF was selected for the calculation of molten salt phase under oxidation atmosphere, while FTpulp-MELTA was selected for the reducing atmosphere. The selection of the SALTF and MELTA assumes that calcium is not present in the molten salt phase. Table 2 presents the solution databases selected for the thermodynamic equilibrium calculations.

<table>
<thead>
<tr>
<th>database</th>
<th>solution phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>FToxid</td>
<td>SLAGA (molten oxide of K\textsubscript{2}O, Na\textsubscript{2}O, SiO\textsubscript{2}, CaO, MgO, P\textsubscript{2}O\textsubscript{5} + dilute sulphides)</td>
</tr>
<tr>
<td>FToxid</td>
<td>OlivA (solid solution: Mg, Ca//SiO\textsubscript{4})</td>
</tr>
<tr>
<td>FTsalt</td>
<td>SALTF( molten salt: Na\textsuperscript{+},K\textsuperscript{+}//Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−},CO\textsubscript{3}\textsuperscript{2−},NO\textsubscript{3}\textsuperscript{−},OH\textsuperscript{−})</td>
</tr>
<tr>
<td>FTpulp</td>
<td>MELTA(molten salt: Na\textsuperscript{+},K\textsuperscript{+}//Cl\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−},CO\textsubscript{3}\textsuperscript{2−},OH\textsuperscript{−},S\textsuperscript{2−})</td>
</tr>
</tbody>
</table>

The interaction between the gas phase and bed material (secondary reactions) was simulated as the second stage (Eq.2 in Figure 4) of the thermodynamic equilibrium modelling. The equilibrium composition of the gas phase in the gasifier (at 850 °C) and combustor (at 950 °C) was used for the calculations. Olivine and quartz, as widely used bed material in DFB gasification plants, were considered for the calculations.\textsuperscript{13} Forsterite (Mg\textsubscript{2}SiO\textsubscript{4}) and silicon...
dioxide (SiO$_2$) were applied for the calculations representing the chemical composition of the olivine and quartz bed, respectively.\textsuperscript{7} The amount of circulated bed material in a full-scale DFB gasifier (approximately 50 kg/kg dry biomass) was taken from the data present in the literature.\textsuperscript{13} The bed particles were assumed to be spherical and have an average diameter of 200 µm. Calculations were performed taking into account only the surface of the bed particles, corresponding to an average thickness of 5 µm (Figure 5), participating in the solid-gas phase reactions.

![Figure 5. The reactive surface of bed particles taken into account in the modelling](image)

4. Results and Discussion

4.1 Fuel-derived ash

Figure 6 shows the equilibrium composition of the condensed phase ash in the gasifier and combustor as a function of temperature. Considering 850-900 °C and 950-1000 °C as average temperature ranges in the gasifier and combustor, respectively, MgO(s), CaO(s), Ca$_2$SiO$_4$(s), Ca$_3$MgSi$_2$O$_8$(s) and Ca$_3$H$_2$O$_{13}$P$_3$(s) are the predicted pure solid compounds. Earlier studies\textsuperscript{7, 14} performed in the DFB steam gasification plant in Güssing Austria confirmed formation of some of the predicted solid compounds. The plant operates with forestry residues, where a gasification atmosphere of 850 °C and a combustion atmosphere of 970 °C are available.\textsuperscript{7} According to Kirnbauer et al.,\textsuperscript{7} the X-ray diffraction (XRD) analysis of used bed material (olivine) showed
significant amounts of Ca-Mg-silicates, Ca$_2$SiO$_4$ and MgO crystal phases, which were not observed for the unused olivine. The thermodynamic modelling also predicted formation of molten salt mixtures (SALT(liq)) in the gasification and combustion reactors. According to the modelling results, the formed molten salt phase in both reducing and oxidising conditions mainly consisted of K$_2$CO$_3$ (mole fraction $\approx 0.85$) and Na$_2$CO$_3$ (mole fraction $\approx 0.1$), together with trace amounts of other alkali chlorides, sulphates, hydroxides and sulphides. The salt mixtures have generally rather low viscosity and are often found in the fly ash.\textsuperscript{27} Formation of slag in the gasifier was not predicted by the model for the entire temperature range. In the combustor, however, formation of a slag phase was predicted at temperatures around 1020 °C, meaning that the first melting temperature of the silicate ash is fairly high compared to the average temperature range in the combustor. Slag or molten silicates consist of highly polymerised silicate networks which make them highly viscous. Silicates, either in the form of slag (liquid state) or high-melting point solid compounds, have low volatility and are often found in the bottom ash and furnace wall slag.\textsuperscript{27}
Figure 6. The calculated equilibrium composition and melting behaviour of the fuel-derived ash at different temperatures in the (a) gasification and (b) combustion reactors of the DFB gasifier.
4.2 Solid-gas phase reactions

According to the modelling results, KOH (157 ppmV), H₂S (76 ppmV), KCl (22 ppmV) and K (20 ppmV) were predicted as the main gaseous ash-forming compounds in the gasification atmosphere. In the combustion atmosphere, KOH (170 ppmV), KCl (10 ppmV) and NaOH (1 ppmV) were the dominant gaseous ash-forming compounds. In addition, the formation of CaO(s) in the gasifier and combustor (see Figure 6a and b) was predicted. The formed CaO(s) is a reactive compound and participates in further reactions in the furnace and flue gas.²⁶, ³³ Therefore, in the modelling of the coating layer in the gasifier and combustor, the available CaO(s) in each reactor was also considered for the solid-gas phase reactions.

Figure 7 shows the predicted composition of coating layer of olivine and quartz particles in the gasification (G) and combustion (C) reactors. Thus, the composition of coating layer was calculated using the equilibrium composition of the gas phase in the gasification and combustion reactors, assuming that the reactive fraction of ash-forming elements attained equilibrium. Nevertheless, the chemical fractionation results of the residual char (Figure 3d) revealed that a significant amount of the organically bound ash-forming elements remained untreated after the steam gasification of the virgin forest residues. This phenomenon could be explained by the fact that only 15% of the char was converted (gasified) during the steam gasification. According to literature³⁶, ash-forming elements that are bound to the organic fraction in the fuel matrix are released when the organic matter is converted. This complicates a quantitative estimation of the gas phase in the gasification reactor, meaning that the concentrations of the K-compounds in the gas phase are overestimated. In the combustor, however, as the char is burning out, the organic matrix collapses, and ash particles successively approach each other with increased opportunities for contact.³³ Furthermore, an earlier investigation showed that higher diffusion rates of calcium into the olivine structure takes place in the combustion reactor,¹⁴ which is in accordance with kinetic considerations. Accordingly, in the combustor due to complete oxidation of the char together with higher temperatures available, conditions are created such that it is not only the reactive fraction of ash-forming elements that is more likely to reach equilibrium, but also the solid-gas phase reactions are kinetically favoured. This means that the predicted composition of the gas phase, and consequently the predicted composition of the coating layer are more realistic.
in the combustion reactor. Thus, the focus will remain on the predicted composition of the coating layer in the combustor.

![Diagram of coating layer composition](image)

Figure 7. The calculated equilibrium composition of the bed particles coating layer in the gasification (850 °C) and combustion (950 °C) reactors of the DFB gasifier

The predicted composition of the coating layer of olivine and quartz bed in the combustor was in good agreement with the experimental results found in previous studies.7, 14, 21 Kirnbauer et al.7, 14 indicated that long-term interaction of olivine with biomass ash in the Güssing plant led to formation of two different calcium-rich layers on the bed particles. The inner layer was homogeneous resulting from the diffusion of calcium into the olivine structure, while the outer layer had a similar composition to the biomass ash. Their EDX analysis results on the inner coating layer showed Ca (46.5 wt %), Si (17.3 wt %) and Mg (12.9 wt %) as the dominant elements, while K (2.6 wt %) had low concentrations in the inner coating layer. The modelling results in Figure 7 show that the CaO(s) introduced to the system is incorporated into the crystal structure of the olivine, forming CaMgSiO₄(s). It should be noted that at temperatures higher than 800 °C, the different forms of calcium oxalate, which was found mainly in the acid-soluble
fraction of Ca, may also release to the system as small CaO(s) particles, according to multistep calcination reactions:

\[
\text{CaC}_2\text{O}_4\cdot x\text{H}_2\text{O}(s) \rightarrow \text{CaC}_2\text{O}_4(s) \rightarrow \text{CaCO}_3(s) \rightarrow \text{CaO}(s)
\]

The calcination of the calcium oxalate could increase the available CaO(s) in the system, particularly in the combustion zone, which can contribute to further reactions, including the layer formation on the olivine particles. The equilibrium calculations also showed low chemical driving force for K to be retained by the olivine bed, leading to lower amount of molten K-silicates (SLAG) in comparison with quartz bed. This finding was confirmed by the bed agglomeration tests of woody biomass carried out by Grimm et al. showing considerable capture of K by quartz particles compared with olivine bed. The authors also showed that FB combustion of woody biomass resulted in an inner reaction layer dominated by Si, K and Ca for the quartz bed, and Mg, Si and Ca with trace amounts of K for the olivine bed.

**4.3 Bed agglomeration tendency in the DFB gasifier**

The modelling results of the fuel-derived ash (section 4.1) showed low slagging tendency for the forest residues in the DFB gasifier. This indicates that the risk of bed agglomeration as a result of direct adhesion of bed particles (melt-induced agglomeration) through partly molten silicates is rather low, as long as the dominant temperature in the combustion zone is below 1020 °C. In addition, the likelihood of direct adhesion of bed particles through the molten salt phase was assumed to be low, considering the low viscosity of the molten salt particles/droplets. The assumption above could be justified by the EDX analysis performed on the bed material of the Güssing plant, showing low concentrations of potassium (3.2 wt%) in the outer coating layer. The low risk of melt-induced agglomeration is consistent with the earlier mentioned mechanisms (section 1.2), indicating that direct adhesion of bed particles takes place in case of biomass rich in K and organically bound Si (e.g. straw fuels) or biomass rich in P, K and Ca/Mg (e.g. agricultural residues). The chemical fractionation results for the forest residues showed that only less than 10 % of the Si is in the reactive form, meaning that the amount of reactive silicon entering the system is insufficient to produce high quantity of slag in the DFB gasifier. Furthermore, the influence of phosphorus on melt-induced agglomeration through formation of low-melting
phosphates was considered to be low because of the relatively low concentration of the P in the fuel. It is noteworthy that the phosphate liquids have polymeric structure and are highly viscous, showing similar patterns of behaviour as the silicate melts.

Concerning coating-induced agglomeration, the thermodynamic equilibrium calculations (section 4.2) showed significant differences between the agglomeration tendency of the olivine and quartz bed. The quantity of the molten K-silicates (SLAG) for the quartz coating layer in the combustor (see Figure 7) was an order of magnitude higher than the olivine, indicating considerably higher agglomeration tendency when quartz was considered as bed material in the DFB gasifier. The bed agglomeration tests of woody biomass were also found to be significantly different between the agglomeration tendency of the olivine and quartz bed, where the inner reaction layer was found to be responsible for the initiation of the agglomeration process in the quartz bed. In general, for the forest residues as feedstock and olivine as bed material, the calculations indicated a low risk of bed agglomeration in the DFB gasifier, as long as the unit operates at normal temperature range (950-1000 °C in the riser). This finding is consistent with the observations in the Güssing plant, which reported no bed agglomeration in the DFB gasifier during a long operation time (approximately 56,000 h). According to the modelling results (Figure 6b), at temperatures higher than 1020 °C slag starts to form in the combustor which can initiate bed agglomeration through melt-induced agglomeration. Kirnbauer et al. reported that temperatures higher than 1036 °C may locally occur around burning char particles in the combustor, which is higher than in the rest of the fluidized-bed. The authors, therefore, concluded that formation of melt in the burning char particles promote layer formation through the intensive contact with the olivine particles in the combustor. This could be explained by the melting behaviour of the fuel-derived ash in the combustor, where temperatures higher than 1020 °C make the condensed phase ash sticky due to the formation of slag. Temperatures higher than the fluidized-bed temperature that may locally occur in the combustion zone can also contribute to the formation of slag on the furnace walls.
5. Conclusion

Thermodynamic equilibrium modelling of the DFB gasifier, using forest residues as feedstock and olivine as bed material, indicated a low risk of bed agglomeration as long as the dominant temperature in the riser is below 1020 °C. Using quartz bed in the DFB gasifier, it was shown to significantly increase the risk of bed agglomeration through coating-induced agglomeration mechanism. Additionally, the modelling results indicated that the burning char particles with temperatures higher than 1020 °C become sticky due to the formation of viscous molten oxides. The sticky char particles can promote the layer formation in the combustor through the intensive contact with olivine particles, and may contribute to the formation of slag on the furnace walls.

The two-stage modelling approach applied to predict the composition of the fuel-derived ash as well as the bed material coating layer in the gasification and combustion reactors of the DFB gasifier, allowed us to establish a reasonable correlation between the modelling results and the experimental data of other studies. It is noteworthy that by using the applied model, the quantity of the condensed and gas phase ash might be estimated more accurately under the oxidation atmosphere (combustor) compared to the reduction atmosphere (gasifier). The reason for this is the better conditions created for the ash-forming elements to attain equilibrium after the complete oxidation of the organic matrix of the fuel.

Acknowledgment

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References


