Aspects of alkali chloride chemistry on deposit formation and high temperature corrosion in biomass and waste fired boilers

Markus Broström
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Abstract
Combustion of biomass and waste has several environmental, economical and political advantages over the use of fossil fuels for the generation of heat and electricity. However, these fuels often have a significantly different composition and the combustion is therefore associated with additional operational problems. A high content of chlorine and alkali metals (potassium and sodium) often causes problems with deposit formation and high temperature corrosion. Some different aspects of these issues are addressed in this thesis.

The overall objective of this thesis was to study and highlight different means by which operational problems related to alkali chlorides can be overcome, reduced or prevented.

The most important results of this thesis are: (1) A full description of the in-situ alkali chloride monitor, its operational principles, the calibration procedure, and an example of a full-scale application was made public in a scientific publication. (2) Efficient sulfation of gaseous alkali chlorides in a full-scale boiler was achieved by injecting ammonium sulfate in a water solution into the hot flue gas. (3) Reduced deposit growth and corrosion rates were achieved by lowering the alkali chloride concentration in the flue gas by sulfation. (4) Evidence of decreased deposit growth and chlorine content in deposits during peat co-combustion. (5) Results are presented from high temperature corrosion tests with different superheater steels in two different combustion environments. (6) Controlled KCl and NaCl condensation under simulated combustion conditions resulted in deposits which consisted of mostly pure phases, in contrast to the solid solution that would be expected under the prevailing conditions at chemical equilibrium.
Populärvetenskaplig sammanfattning

Arbetena i denna avhandling har gett resultat som är direkt eller indirekt användbara för att öka effektivitet, ekonomi och miljöprestanda vid industriell produktion av el och värme via förbränning av biomassa och avfall.

**Industriell förbränning av biobränslen och avfall**


Förbränning bör i möjligaste mån ske i industriell skala för att dels öka effektiviteten och dels nyttja möjligheten att producera el samtidigt som värme i ett så kallat kraftvärmeverk. Vid industriell förbränning är också möjligheterna till effektiv rökgasrening betydligt större och det är därför möjligt att elda avfall som i liten skala skulle släppa ut stora mängder miljö- och hälsoskadliga ämnen.

**Problem vid förbränning**


**Förutse driftsproblem**

Om driftproblemen kan förutses så kan mycket vinnas t.ex. genom att då kunna vidta lämpliga åtgärder innan problemen uppstår. I detta arbete har ett instrument för att mäta koncentrationen av de problematiska salterna beskrivits (artikel 3). Instrumentet går att använda till att upptäcka problem i bränslemix, förutse driftsproblem och även till att övervaka åtgärder för att minska salthalterna i rökgasen. I artiklarna 1 och 4 är instrumentet en del av metoden i olika undersökningar.
Ett annat angreppssätt är att med ökad kunskap om belägningarnas kemiska och fysikaliska egenskaper förutse vad som händer i olika situationer. I artikel 5 har undersökts detaljer i hur salterna kondenserar från den heta gasen. Detta ger en viktig pusselbit till förståelsen för och möjligheten att teoretiskt efterlikna vad som händer i pannan.

**Minska driftsproblem**
Problemen med kondenserande salter (natrium- och kaliumklorid) kan hanteras genom att antingen blandar ett problematiskt bränsle med ett annat som har gynnsamma kemiska effekter och förstör de problematiska salterna. Exempel på bränslen att blandad in är torv eller kol som på grund av deras innehåll av svavel och mineraler binder upp alkali (natrium och kalium) till mer oskadliga komponenter. Framgångsrik sameldning med torv ingår i artikel 4.

Ett annat alternativ är att tillsätta kemiska additiv till förbränningen. I artiklarna 1 och 4 har ammoniumsulfat (ett vanligt gödningsmedel) testats som additiv. Detta visade sej ha mycket goda egenskaper och förutom att minska beläggningsbildning och korrosion så bidrog det till att minska utsläppen av försurande kväveoxider.

**Relevans och intresse**
Arbetena i denna avhandling har kommit till i nära samarbete med flera stora industrier som hela vägen genom sina respektive engagemang visat stort intresse för resultaten och den forskning vi bedriver vid avdelningen för Energiteknik och Termisk Processkemi. Genom att resultaten (artiklarna) publiceras i erkända internationella tidskrifter så görs alla tillkomna hypoteser och resultat tillgängliga för andra intresserade. Artiklarna 1, 3 och 4 är produkter av samarbeten med Vattenfall Utveckling AB. Artikel 2 är ett samarbete med Umeå Energi AB. Artikel 5 kom till tillsammans med Metso Power OY.
Appended publications

This thesis includes the following papers, referred to in the text by their Roman numerals I-V:

I. Sulfation of corrosive alkali chlorides by ammonium sulfate in a biomass fired CFB boiler

II. High temperature corrosion in a 65 MW waste to energy plant

III. Principle, calibration and application of the in-situ alkali chloride monitor

IV. Measures to reduce chlorine in deposits: application in a large-scale circulating fluidised bed boiler firing biomass
   Håkan Kassman, Markus Broström and Lars-Erik Åmand. Submitted to *Fuel*.

V. Condensation in the KCl-NaCl system
   Markus Broström, Sonja Enestam, Rainer Backman and Kari Mäkelä. Manuscript
Additional publications, not included in this thesis due to relevance or depth:

1. **IACM – In-situ alkali chloride monitor**

2. **High temperature corrosion in a 65 MW waste to energy plant**

3. **Sulfation of corrosive alkali chlorides by ammonium sulfate in a biomass fired CFB boiler**

4. **Experimental studies on the influence of H₂S on solid oxide fuel cell performance at 800°C**

Publications 1-3 are conference proceedings, later revised and published as Papers I - III.
Author's contribution

Paper I. Sulfation of corrosive alkali chlorides by ammonium sulfate in a biomass fired CFB boiler
Broström contributed substantially to the planning of the study, carried out most of the experimental work and wrote the paper. The results were evaluated in close collaboration with the co-authors.

Paper II. High temperature corrosion in a 65 MW waste to energy plant
Broström and master’s student Persson contributed approximately equally to the planning, experimental work and writing of the paper. Persson carried out the literature review under the supervision of Broström. The results were evaluated in close collaboration with the co-authors.

Paper III. Principle, calibration and application of the in-situ alkali chloride monitor
Broström contributed substantially to the planning and did most of the experimental work. The results were evaluated in collaboration with the co-authors. Broström carried out the literature review and wrote the paper.

Paper IV. Measures to reduce chlorine in deposits: Application in a large-scale circulating fluidised bed boiler firing biomass
Broström contributed substantially to the planning and the experimental part of the study. He also contributed to evaluations and discussions. Kassman wrote most of the paper with contributions from Broström.

Paper V. Condensation in the KCl-NaCl system
Broström contributed substantially to the planning and carried out all experimental work. Broström evaluated the results and wrote the paper in collaboration with the co-authors.
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Introduction
The environmental, economical and political aspects of energy production are the driving forces in the search for a sustainable energy system based on renewable energy sources. In Sweden, as in many other countries, this has led to an increased use of biomass and waste derived fuels in heat and electricity production. In the heat and power plants, these “new” fuel assortments of different composition often give rise to severe ash related operational problems such as slagging, fouling and high temperature corrosion. Many biomass and waste derived fuels contain relatively high amounts of alkali and chlorine compared with fossil fuels. This causes the differences in the behavior of ash forming elements that change deposit characteristics and are the focus of the studies included in this thesis. Other differences such as heating value, volatility, water content, feeding properties and chemical and physical heterogeneity also contribute to challenges in the combustion of these fuels. Waste derived fuels often cause the greatest challenges in boiler operation due to a high content of some of the most troublesome components, but on the other hand, they are relatively inexpensive since land filling with combustible fractions is no longer allowed in many countries.

The overall aim of this thesis was to increase the understanding of several important aspects of ash-related operational problems in heat and power plants, and especially those associated with ashes containing alkali chlorides. All the appended articles describe different perspectives and means by which problems can be overcome, reduced or prevented.

The objectives of the different studies within this thesis were to:
I. Evaluate if ammonium sulfate injection could reduce sticky, corrosive alkali chlorides in deposits. Tests were performed in a full scale circulating fluidized bed (CFB) boiler with positive results.
II. Evaluate corrosion resistance of different superheater steels in waste combustion. The effect of increasing PVC content (chlorine) in the fuel mix was also investigated. Corrosion tests in a full-scale waste incineration plant were performed.
III. Calibrate, evaluate and provide a full description of the in-situ alkali chloride monitor (IACM) used within two of the other appended papers for measuring alkali chlorides in hot flue gas.
IV. Evaluate the positive effects of peat co-combustion and compare experimental results with those of ammonium sulfate injection. Tests were performed in a full scale circulating fluidized bed (CFB) boiler with positive results.
V. Provide detailed information about the chemistry of condensing KCl and NaCl vapors. An experimental investigation of condensing (desublimating) alkali chlorides (KCl and NaCl) on a cooled probe gave information...
necessary for correct predictive modeling of deposit formation and high temperature corrosion.

This thesis begins with a few sections describing operational problems of relevance for the heat and power industries. Next, experimental methods used in the thesis are described. After that, results from the different appended publications are summarized and placed in perspective to the relevant literature. This part of the thesis is divided into the different problem areas rather than by the different publications.
Ash related operational problems

Ash is the non-combustible part of a fuel and consists of different ash forming elements. Amount and composition of ashes varies both among and within different fuel types, and also depend on process parameters and where in a boiler the ash is deposited. Detailed knowledge about fuel composition, and especially ash forming elements, is an important parameter when trying to understand a process and prevent ash-related operational problems. Biofuels represent a very heterogeneous group including fuels with ash contents ranging from less than 0.1 % (wood) to more than 10 % (straw). Also chemical compositions vary greatly with high amounts of troublesome potassium and chlorine in straw fuels, and relatively much potassium also in woody biofuels. Peat, though, is quite low in alkali and chlorine and sometimes contains more sulfur and minerals that could be beneficial for the combustion process.

Fuel composition varies, and so do the chemical reactions taking place during and after combustion. The content of ash-forming elements determines what chemical systems should be considered when trying to understand or model for what happens. Besides the ash chemistry treated by thermodynamic equilibrium calculations, physical parameters such as boiler design and operational parameters, must also be considered as they create varying and local conditions that make global equilibrium models inappropriate. Furthermore, one must take into account that reactions of some components are kinetically restricted, and others are not fully available for reaction due to their physical form.

Deposit formation

Deposit formation on heat transferring surfaces in a boiler can be defined as either slagging or fouling. Slag is deposits in areas that “see the flame”, which means that they are subjected to radiant heat from the flames. Fouling is deposits in the convective heat transferring parts such as superheaters or economizers [1]. The build-up of deposits causes problems with heat transfer and bulky deposits can also affect fuel or flue gas flows by plugging up parts of the boiler. Deposit characteristics also have a great impact on corrosion of high temperature parts of a boiler.

Slag is formed when temperatures in the combustion zone exceeds a critical temperature where a fraction of the ash is molten and becomes sticky, gluing other particles together. If the semi molten ash remains in the fuel bed, a sticky deposit, slag, is formed. Slagging on cooled surfaces can cause a rapid build-up of troublesome solid, hard to remove, and insulating deposits.

Fouling deposits are formed by the deposition of aerosols. Either those condensed from ash components evaporated from the fuel in the combustion
zone, or larger particles carried from the fuel bed by the gas stream. Several physical mechanisms are responsible for particles attaching to the surfaces, but also chemical composition influences the process. Dew point, melting point, stickiness and increased sintering reactions of the deposited material are important for the overall deposition rate.

The first melting temperature is usually not enough for creating a gluing effect in a deposit. Instead, the temperature where approximately 15% of the ash is molten, called the sticky temperature, $T_{15}$, has been reported as critical [2]. By increasing the amount of molten components in the deposit even further, either by higher temperatures or by changing to a more low melting composition, gravitational shedding of molten ash can occur [3].

Operational problems involving deposit growth are often correlated to the melting behaviour of the ashes and can be overcome by taking control over the ash chemistry by using an intelligent fuel mix or additives. Other possible means include optimizing of operational parameters or boiler design for the specific fuels.

**High temperature corrosion**

When using heat engines for electricity production, the overall fuel-to-electricity efficiency is important for both economical and environmental reasons. On an ideal and strict thermodynamic basis, the heat-to-work efficiency is limited by the difference between the highest and the lowest temperatures in the thermal cycle of the engine. This is regardless of whether the cycle is an internal combustion engine, a gas turbine, a steam turbine, or a combined system. Other factors also influence the overall efficiency, but as the temperature difference reflects the theoretical maximum, a great deal of effort has been put into optimizing (maximizing) the difference.

The lower temperature is usually set by a heat sink available in the surroundings. A district heating system, cooling towers or sea water are all heat sinks utilized in different systems for electricity generation. For the efficiency, the only requirement is a low temperature of the working fluid entering the system. Using the excess heat in district heating systems for the heating of homes or industries, however, drastically increases the overall energy efficiency of the total system. The higher temperature of the cycle is an integrated parameter of the industrial process, and the work of increasing the temperature is technically demanding. This thesis is focused on systems for combined heat and power (CHP) generation that rely on steam turbines for generating electricity. These systems, called indirectly fired, use steam as a working fluid. The opposite would be the gas turbine cycle where the combustion gas itself is the working fluid. The much desired maximum steam temperature is set by the dimensioning of the heat exchanger in combination with the boiler design, i.e. flue gas temperatures. Limiting factors are material strength and corrosion resistance.
In CHP systems, the heat transferring parts of a boiler are usually arranged with counter current flows, i.e. the maximum temperature of the steam is reached in the superheater section closest to the combustion zone where flue gas temperatures are highest. Pre heaters are situated further back in the boiler at lower gas temperatures. This approach places high demands on the superheaters as the material is working with high temperature (and pressure) steam on the inside and hot corrosive gas and deposits on the outside. Therefore, corrosion of superheaters is a primary economic issue for a plant owner, both due to the influence on the efficiency mentioned earlier, and also due to the large maintenance costs associated with unscheduled shutdowns and the repairing or replacing of corroded superheaters.

**Experimental equipment and methods**
In this section, the experimental equipment and methods used within this thesis will be described.

**Full scale boilers**
The thesis includes tests on two different full scale boilers. In Papers I and IV, sulfation of alkali chlorides was studied in a CFB boiler in Munksund, Sweden (Figure 1). This Foster Wheeler built plant was designed for 96MWth/25MWe production. The boiler was fired mainly with bark (> 80 %), but also sawdust, woodchips, and waste (reject) from cardboard recycling. The maximum steam temperature is approximately 420°C after the second superheater and 480°C after an extra superheater, called Intrex, in the loop seal.
Figure 1. Schematic sketch of the Munksund boiler (Foster Wheeler compact CFB).

The flue gas leaves the combustion zone through a vertical flue gas exit followed by the two parallel cyclones dividing the flue gas into two streams, passing separate, parallel ducts separated by a wall (not shown in the figure) until just prior to the second superheater where they mix again. The separate flows were utilized in the present studies by adding sulfating additive at one cyclone entrance, using the other as an unaffected reference. Sampling points for low pressure impactor and corrosion probes were situated on both sides in the ducts before the gases were mixed again. IACM measurements were performed cross stack before the superheaters.

In Paper II, corrosion tests were performed in a grate fired boiler in Dåvamyran, Umeå, Sweden (Figure 2). The figure also shows the comprehensive flue gas cleaning system needed to meet the emission demands on waste combustion. The boiler built by Von Roll was designed to be fired with household and industrial waste. The plant was designed for 50MWth/15MWel production. The steam design criteria are 40 bar and 400°C. Failure cases have indicated corrosion problems at the lower part of superheater no.2. The corrosion probe was installed as close to the problematic area as possible.
Figure 2. Schematic drawing of the Dåva boiler (von Roll).

In-situ alkali chloride monitor
The in-situ alkali chloride monitor (IACM) [4-5] is an optical instrument for measuring concentrations of gaseous alkali chlorides (KCl and NaCl) in hot flue gas from the combustion of mainly biomass and waste derived fuels.

Corrosion problems related to alkali chlorides are often found on superheater tubes, and therefore the IACM is always situated closely adjacent to the tubes. Here, the temperature is also high enough for the monitored salts to be in the gaseous phase, which is a requirement for the instrument to work properly. The instrument measures UV absorption in a cross stack arrangement with the light source on one side of the flue gas channel and a spectrometer unit on the other. In Paper III, the instrument and its calibration procedure was described. In Papers I and IV, it was used in a full scale boiler for online monitoring of KCl+NaCl and also SO₂ concentrations.

Particle sampling
In Papers I and IV, measurements with a Berner type [6] low pressure impactor (LPI, Dekati, Ltd., Tampere, Finland) were performed in order to characterize the size distribution of solid particles in the flue gas. The 13 stages of the impactor collect and separate particles with respect to aerodynamic diameter. An ejection diluter was used to dilute and thereby decrease particle concentrations to allow longer sampling periods without overloading the impactor. Dilution also increased sampling gas velocity, and thereby the cooling rate of the sampling gas, which promoted a desirable homogenous nucleation of condensable gaseous species within the probe. Besides size distribution, collected samples can be analyzed with respect to elemental and phase composition.
Corrosion and deposit probes
Temperature gradient corrosion probes for sampling in full-scale boilers were used in Papers I, II and IV. The probes (Figure 3) consisted of an inner part with pipes for cooling air and for thermocouples. The outer part of the probe was the 18 corrosion rings and three extra temperature sensing rings (one in each end and one in the middle). The rings were held together with a spring load placed outside the boiler wall. Pressurized air, proportional pneumatic valves, and PID regulators were used to keep a constant temperature profile. The temperature for each ring was approximated by fitting an exponential function to the three set point temperatures.

Figure 3. Sketch of the corrosion probes used in Papers I, II and IV. From Paper IV, reprinted with permission.

The alloys tested within the studies are listed in Table 1. They include a wide range of steels to represent different possible choices of superheater materials. Non- or low-alloy ferritic steels, a martensitic steel (X20) and two austenitic, high nickel steels (E1250, San28).
Table 1. Mass compositions (%) of alloys tested within the studies (Papers I, II and IV). Fe is balance.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST35.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>C:0.2, Si:0.4, P, S</td>
</tr>
<tr>
<td>15Mo3</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.6</td>
<td>C: 0.2, Si: 0.2</td>
</tr>
<tr>
<td>13CrMo44</td>
<td>0.9</td>
<td>-</td>
<td>0.5</td>
<td>0.7</td>
<td>C: 0.1, Si: 0.3</td>
</tr>
<tr>
<td>10CrMo910</td>
<td>2.2</td>
<td>-</td>
<td>1.0</td>
<td>0.6</td>
<td>C: 0.1, Si: 0.3</td>
</tr>
<tr>
<td>X20CrMoV12.1</td>
<td>11.2</td>
<td>0.5</td>
<td>1.0</td>
<td>0.5</td>
<td>C: 0.2, Si: 0.3, V: 0.3</td>
</tr>
<tr>
<td>Esshete 1250</td>
<td>15.0</td>
<td>9.5</td>
<td>1.0</td>
<td>6.3</td>
<td>C: 0.1, V, Nb, B</td>
</tr>
<tr>
<td>Sanicro 28</td>
<td>26.4</td>
<td>30.4</td>
<td>3.3</td>
<td>1.7</td>
<td>Cu:0.9, Si:0.4, N, C</td>
</tr>
</tbody>
</table>

Prior to the exposure, the mass of each probe ring was determined and the thickness of each ring measured with a micrometer at 18 points around the mid-circumference. After exposure, the rings were carefully dismounted. The mass change was used as a measure of deposit growth, even though corrosion products also contributed to the weight change. After exposure, the probe rings were cast in epoxy, cut in half, and the cross sections dry ground and polished with SiC grinding papers starting in range from #80 and down to #1200 or #5000 depending on the requirements set by the following analyses. An optical measuring microscope was used to measure the thickness of the remaining material of the probe rings after exposure. From the micrometer and microscope measurements, the corrosion of each ring was determined. SEM/EDS analysis gave information about morphology and chemical composition of different layers of the corrosion products and deposits.

In **Paper IV**, probes dedicated only for deposit sampling were also used. They were designed to keep six test rings pair-wise at three different temperatures. Other than that, the design was similar to that of the corrosion probes. Rings from the deposit probes were analyzed by means of wet chemical analysis.
Lab-scale equipment for studying condensation at high temperatures
This setup was designed for the purpose of answering the detailed questions addressed in Paper V regarding the condensation products of gaseous NaCl and KCl mixtures. The tests required an atmosphere containing gaseous alkali chlorides (KCl and NaCl) in separately controllable concentrations. A cooled surface with a temperature gradient was also necessary for collecting condensed matter.

An electrically heated tube furnace (Figure 4) was designed in stainless steel. Evaporation chambers flushed with nitrogen were inserted in separate inlets and evaporation temperatures were controlled by thermocouple readings and insertion depth.

![Diagram of tube furnace with salt volatilization chambers](image)

**Figure 4.** Tube furnace with salt volatilization chambers (only one shown), condensation probe and gas washing equipment. Gas through salt volatilization chamber (1), diluting gas (2), cooled condensation probe (3), gas washing bottle (4), rotameter (5), valve (6) and ejector pump (7). From Paper V.

Gas flows were controlled by mass flow controllers. Concentrations of KCl and NaCl in the gas were monitored by bubbling and dissolving the outgoing aerosol carrying gas in water and using ion selective electrodes (Orion model 720A ISE, Orion 9719BN K-electrode and Orion 8611BN Na electrode) to measure the ion concentrations of K and Na. As aerosols were also deposited on the cool walls of the exit pipe, measurements were performed every five minutes after flushing the pipe with water. Flushed water was also collected in the gas washing bottle prior to analysis. Tests were performed with two
serial bottles to capture any aerosols escaping from the first washing step, but the water from the second step did not contain significant amounts of K or Na and therefore the subsequent tests were performed with only one washing bottle.

The cooled deposit probe (Figure 5) was made from a 20 mm steel tube (Sandvik steel, 253MA) with thermocouples fitted level with the surface by using a ball nosed milling tool with the same radius as the thermocouples to ensure good thermal contact between the thermocouple and the pipe. Cooling air was supplied through an 8 mm pipe with drilled holes distributing the cooling flow in a pattern that generated a temperature profile with enough range (460–730°C) for the application. A close to linear temperature profile was desired to simplify evaluations.

**Figure 5.** Air cooled deposition probe. 1) Cooling air inlet. 2) Assembly for thermocouples (1 to 5, only one shown). 3) Cooling air outlet. From Paper V.

After exposure, the probe was withdrawn from the hot gas and rapidly cooled to room temperature. Photos were taken and samples for SEM/EDS and XRD analysis were carefully scratched off and prepared accordingly.

**Chemical analysis**

A scanning electron microscope (SEM) was used in Paper I, II, IV and V for morphology characterization and semi-quantitative compositional analyses of deposits and oxide scales. The SEM/EDS instrument was a Philips model XL30 environmental scanning electron microscope with an energy-dispersive x-ray spectrometer. To gain knowledge of the quantitative composition of the sample, information from energy dispersive x-ray spectrometry (EDS) analysis was used. The EDS detects characteristic x-ray energies emitted from different elements. By analyzing the relative peak heights of a continuous EDS spectrum, semi-quantitative information from a selected sample area was obtained.

X-ray powder diffraction (XRD) was used in Paper V to determine the phase composition of deposited salts. The instrument used was a Bruker d8Advace instrument in θ-θ mode with an optical configuration including a primary Göbel mirror and a VÅNTEC-1 detector. Bruker software with the PDF2 databank [7] and the ICSD database [8] were used for evaluation.
Both the SEM/EDS and XRD analysis were performed at Energy Technology and Thermal Process Chemistry (ETPC) research group, Umeå University.

In Paper IV, wet chemical analysis was used to characterize deposits. Samples were prepared by ultrasound treatment in de-ionized water. Filtered leachates were analyzed by means of ion chromatography for detection of Na+, K+, Cl−, and SO4− ions. The wet chemical analysis was performed at Vattenfall R&D.

Thermogravimetric analysis
Thermogravimetric analysis was used in Paper V to evaluate sintering mechanisms of KCl and NaCl, both separately and mixed together. The instrument was a Q5000IR TGA from TA instruments. Platinum sample pans were used and samples were purged with nitrogen.

Thermodynamic calculations
Thermodynamic considerations and calculations were used to predict and interpret results in the present work (mainly Paper V). Calculations were performed to determine melting temperatures, dew points, vapor pressures and phase stabilities of different chemical systems with varying temperatures. The thermodynamic software package FactSage [9] was used for thermodynamic equilibrium calculations and for generating graphics.

Results in perspective

Measuring alkali concentration in hot flue gas
Due to the strong correlation between alkali chlorides and problems with deposit formation and corrosion, there is a need for reliable measurements of these components. Several different approaches are suggested in the literature. All instruments are associated with one or several limitations such as a high detection limit, insufficient measuring range, error in measurement, long response time, expensive equipment or limitations in speciation detection. All these aspects must be considered in the choice of detection method. A survey of existing instruments is presented below:

- Lee et.al. [10] measured alkali emissions from coal combustion by using an analytical activated-bauxite sorber bed (AASB). It is an extractive method that involves leaching of the bauxite and atomic absorption analysis of the leachates. It detects alkali from ppb-levels.
- Molecular beam mass spectrometer (MBMS). The sampling equipment involves rapid quenching of chemical reactions by a vacuum driven free jet expansion followed by ionization and detection with respect to mass numbers. The main applications of this instrument are in measurements
of molecules and/or molecule fragments in hot gases. Using this instrument, it is possible to distinguish between different alkali containing compounds. Detection limits are relatively high, usually at ppm-level. Investigations using the MBMS for alkali metal speciation and release in thermal treatment of biomass were found in the literature [11-17].

- An in-situ method for alkali detection called surface ionization (SI) is described and demonstrated in several publications [18-20]. The technique is based on in-situ partial thermal ionization of alkali containing particles followed by electrometer measurements of ion currents. It provides a quick response time (~ms) and a detection limit of approximately 1 ppb. It is disturbed by differences in particle size distribution and does not distinguish between K and Na. Neither is it possible to determine speciation of the detected alkali with the SI method.

- The particle beam mass spectrometer (PBMS) is a combined system including both surface ionization and vacuum mass spectrometry. It measures number concentrations of small alkali containing particles [21-22].

- Plasma excited alkali resonance line spectroscopy (PEARLS) [23-25] is a method based on in-situ plasma excitation of alkali atoms. The atoms are detected by emission and/or absorption resonance spectroscopy. The instrument can distinguish between the alkali metals, but not their original speciation. Loosely bound alkali in small aerosols can also be detected. The detection limit is approximately 1 ppb.

- In the fiber-optic alkali monitor (FOAM) [26], the sample gas is extracted and excited in an acetylene flame. After optical filtering, the characteristic emission wavelengths of the alkalis are detected by photodiodes. The FOAM can distinguish between the alkali metals, but not their speciation. The detection limit of the FOAM is lower than 1 ppb.

- The excimer laser induced fragmentation fluorescence (ELIF) [27-30] photodissociates alkali compounds using ArF-excimer laser light. Excited alkali atoms are detected and discriminated by their fluorescences. Performance on real flue gases is not reported, but laboratory experiments with the present setup measures KCl from 15 ppb to approximately 50 ppm.

- Photoacoustic spectroscopy (PAS) can be used to monitor KCl in hot gas. Sorvajärvi et.al. [31] report on detection limits around 15 ppb.

- The in-situ alkali chloride monitor (IACM) [4-5] is an instrument based on UV-absorption of the alkali chlorides. It measures alkali chloride concentrations (KCl+NaCl). The response time is a few seconds and the detection limit around 1 ppm.
The IACM instrument's operational principle and calibration procedure were described in Paper III. Examples from a full scale application are found in Papers I and IV.

Alkali chlorides in aerosol and deposit formation

Release of alkali and chlorine
During combustion conditions, biomass and waste derived alkali and chlorine undergo several steps of reactions and transformation before the final deposition. The volatilization of chlorine is dependent on factors such as temperature, content of other ash forming elements (reactants), fuel type (i.e. Cl-association), heating rate, and the oxygen content of the surrounding gas atmosphere. Most experiments with pyrolysis and combustion of biomass have shown chlorine release in two steps. First during heating and pyrolysis (<500°C) where Cl is released as HCl, and later during char burnout (>700°C) as evaporated KCl or NaCl [11, 32-33].

Alkali release from biomass combustion (mainly potassium) has generally been reported above 700 °C where the vapor pressure of KCl(g) is high enough for a significant evaporation and gas phase transport [33]. KOH is also a possible release form of K as a primary reaction, especially for wet fuels with low chlorine and sulfur content making KOH more prevailing [11, 34]. However, KOH reacts to chloride, sulfate or carbonate in secondary reactions if, and as soon as, equilibrium concentrations in the flue gas allow for it.

The variations in release that go beyond the generalized description above have been well summarized by van Lith et.al. [35]. There, the influences of parameters such as fuel type (composition and association of the elements) and operational parameters (stoichiometry, heating rate and time for reaction) are discussed.

Aerosol formation
In the hot combustion zone, the volatilized alkali chlorides are thermodynamically expected to be in the gaseous form while the equilibrium conditions on cooled heat exchanger parts make solid, or possibly liquid, the most stable form. The transformations in-between involve both chemical and physical steps. Mechanisms are described in the literature [36] and briefly summarized below, but as many different interacting and case specific steps are involved, their relative importance is not clear.

Condensation of alkali chlorides can occur both directly on cooled surfaces and as homogeneous or heterogeneous nucleation within cooled gas streams or in thermal boundary layers. Solid sulfates or soot particles are typically present in the flue gas and available as condensation nuclei to start
the condensation process. Homogeneous condensation is possible, but the heterogeneous process requires less supercooling, and therefore condensation on already existing surfaces is energetically favored [37].

Particle growth in the free gas stream can involve coagulation of small particles (<0.1 µm) and also further agglomeration into larger, but still sub micron particles. By physical transformations including collisions, coalescence and attrition the aggregates can grow even further.

Chemical reactions can occur within or between solid/molten aggregates and also with the surrounding gas. This includes sulfation, sintering and agglomeration.

For potassium, which is of most relevance for aerosols and deposits in the present work, the combination of all mechanisms mentioned results in a fractionation within the boiler. In the lower combustion zone (at the grate or in the fluidized bed) except for newly released gaseous KCl or KOH, potassium is found mainly in solid silicates (bottom ash). Also further up in the combustion zone potassium is found as KOH(g) or KCl(g). There may also be small gas-borne solid sulfates formed by sulfation of KOH or KCl by SO₃. Gaseous sulfate (K₂SO₄) formed directly from fuel residue particles is possible, but not likely from most processes since the sulfate requires temperatures >1100°C to generate significant vapor pressures. These general mechanisms are often valid for sodium as well, and therefore potassium and sodium are often treated together in the literature, as well as in parts of this thesis, and simply entitled “alkali”. However, there are differences between the two that can become important under specific conditions [35].

In Paper I, results from aerosol measurements by means of low pressure impactor measurements were presented. Here, samplings were carried out directly from the hot flue gas (700-750°C) prior to the superheaters of a bark fired CFB boiler. The sampled gas was rapidly cooled and diluted within the sampling equipment. Gaseous alkali chlorides were thereby nucleated, but did not grow much during the short cooling time. Therefore, they were found as fine particles in the lowest part of the LPI (0.03 and 0.05 in Figure 6a). The size distribution in the figure is displayed on a mass basis to enable a direct mass balance estimation. By adding ammonium sulfate to the flue gas and sulfating the chlorides, the fine KCl and all detectable chlorine was removed and the region typical for sulfates formed in the combustion zone increased in mass and sulfur content (<1µm in Figure 6b).

Another interesting, but not completely verified effect of ammonium sulfate injection, is that it seems that Ca is partially removed from fractions 0.1 and 0.13 when adding ammonium sulfate (marked in Figure 6). Even though Ca will be present as CaSO₄ at chemical equilibrium at many biomass and waste combustion conditions, CaO is often considered as inert to reaction since it is in solid state and thereby kinetically restricted compared to gaseous alkali components. This much Ca is usually not present in the fine
mode during biomass combustion, but as seen by Werkelin [38], much of calcium in bark is present as oxalate. The CaC$_2$O$_4$ forms small carbonate particles upon heating. CaCO$_3$ is then decomposed into CaO, probably as small and relatively reactive particles. The reduction of fine Ca containing particles (probably CaO) could then be the effect of sulfation as was also suggested as possible by Aho el.al. [39]. CaO would then be a consumer of some of the sulfurous additive and in some cases an important factor when estimating how much additive is needed to eliminate alkali chlorides. In the study by Aho, as well as in the present (Paper II and Figure 6), bark was one of the fuels tested.

However, as CaO is in the solid phase and the other reactants in the sulfation reactions are gases, the outcome, and thus the reactivity is difficult to predict. One uncertainty within the present work is that of particle bouncing, or the so called carry-over effect between the different steps of the impactor. It is possible that other changes in aerosol composition, and thereby the loading on impactor substrates, could change how many CaO particles are carried too far down the impactor between the two cases. Another factor is that of particle growth within the flue gas. It is possible that small CaO particles are involved in other secondary processes from the sulfation additive without themselves being sulfatized. This could also change the size distribution of Ca and remove the small particles from the fine mode.

![Figure 6](image_url)

**Figure 6.** Collected mass during impactor sampling firing bark at ordinary operating conditions (Ref) and with ammonium sulfate injection (Chlorout).
**Deposit formation**

When the flue gas meets with the superheaters it cools, and when KCl saturation pressure is reached, KCl condenses and deposits on cooled surfaces. This can occur either by direct vapor condensation on the surface or by the deposition of aerosols formed in the free gas stream within the thermal boundary layer close to the surface. Furthermore, condensation can occur both by homogeneous and heterogeneous mechanisms as described in the aerosol formation section above. Deposition of the small aerosols is governed by thermophoresis, diffusion or by Brownian motion. Particles too large for deposition by these mechanisms may deposit by inertial impact followed by particle capture.

Chemical reactions between different components of the deposit and the surrounding gas may change the conditions for deposit formation. This includes sulfation and parts of the mechanisms of sintering and agglomeration.

Stickiness of the ashes caused by partial melting is an important factor influencing deposit growth. It is possible to estimate the melting behavior of ashes by considering chemical composition and the existing thermodynamic data [2, 40]. Alkali chlorides generally contribute to lowering the melting temperatures of ashes and thereby deposits generally grow faster as solid particles stick more easily to the surface by gluing from the semi molten components.

In deposit formation, as well as in aerosol formation, many different case specific, contemporary, and interacting mechanisms contribute to the process and their relative importance must be considered in order to create valid predictive models. The mechanisms mentioned have been described in detail and placed in perspective by Baxter [41].

In Paper V, some specific aspects of condensing alkali chlorides were investigated. Alkali chlorides are known to increase deposit-related operational problems due to their melting properties. The basic thermodynamic differences between KCl and NaCl are rather clear since available data are well determined. Practical non-equilibrium interactions between the two salts are, however, not completely covered in the literature. The binary phase diagram (Figure 7) shows complete solubility of the two components in solid state below the solidus curve. This region is of interest when it comes to alkali chlorides depositing on cooled surfaces as a solid solution has a different melting point and dew points compared with the pure salts. The outcome of rapid condensation is hard to predict theoretically and therefore experiments were designed in order to gain the lacking mechanistic knowledge.
Figure 7. Binary phase diagram of KCl and NaCl. “Liq” is a molten solution. “ACl ss” is a solid solution. “ACl ss1 and ACl ss2” are two compositionally different solid solutions. Calculated and drawn using FactSage [9] with data from FACT-SALT and FACT-ACl.

The experiments included deposition from 60 ppm KCl, NaCl or KCl+NaCl in nitrogen at 850°C. Deposits were collected on a cooled probe. At these low concentrations, liquid phase is not expected to form. Instead the condensation takes place as gas to solid desublimation.

An interesting observation provided conclusions about particle and vapor deposition mechanisms. Different deposit morphologies were formed on the probe and are shown in Figure 8. At lower temperatures (≤500°C) fractal like dendrites were formed, indicating homogeneous nucleation and particle transport within the thermal boundary layer. Above that temperature the deposits from the pure salts (Figure 8 a and b) consisted entirely of elongate crystals. These were probably cooled by thermal conduction from the probe and thereby grew outwards by direct condensation from vapors. At even higher temperatures the crystals had rounded edges and an increasingly fused structure. The fused appearance was suggested to be due to evaporation and re-deposition by direct condensation. Liquid phase was not thermodynamically expected in the case of deposition as separate phases since the dew point was considerably lower than the melting point at the conditions chosen for this study. On the other hand, if solid solution was formed, a liquid could be present at the hot part from 657°C to the solution dew point at 690°C.
Figure 8. Schematic sketch of deposit morphology. Deposits formed on the cooled probes at different temperatures: a) 60 ppm KCl, b) 60 ppm NaCl, c) 30 ppm KCl + 30 ppm NaCl. From Paper V.

The resulting phase composition was not unambiguous, but clearly indicated the possibility that condensing gases can form separate phases (pure NaCl (halite) and KCl (sylvite)) upon rapid cooling, and that they do so to a great extent under the prevailing experimental conditions. Condensation from the mixed gas (Figure 8, c) showed that desublimated particles from a gas mixture of 60 ppm KCl+NaCl (30 ppm of each) consisted mostly of pure phases according to XRD analysis, but also approximately 10% of a mixed NaCl:KCl phase in 90:10% proportions. This was seen as a peak broadening in the XRD diffractogram with only one peak separated from that of NaCl. Also, traces (approximately 1%) of a 50:50 and a 60:40 mixed salts were found.

Another interesting finding was that the morphology of the deposited salts mixture (Figure 8c) had a gravel-like, strikingly different appearance compared to that of deposited pure salts. This was probably connected to the phase compositions, but the exact mechanism of formation or reformation was not established. Sintering was suggested as a plausible explanation, and complementary thermogravimetric tests were carried out to clarify the relevance of the suggested mechanism. A simple, but new approach was used where ground salts (KCl and NaCl) were melted at 10°C/min, separately, and mixed together. The analysis of the TGA/DTG curves gave clear evidence that rapid sintering of KCl and NaCl particles took place with simultaneous
melting above the melting point expected from a solution, even though the starting particles were as pure phases. It was also seen from the analysis that volatilization at lower temperatures was higher when the solid particles were mixed together, which indicated that slow solid phase sintering also took place, even during this relatively short period of time.

These results are of relevance when making models for aerosol and deposit formation. At higher gas concentrations where a liquid phase might be involved, the solid solution will probably appear upon cooling according to the phase diagram (Figure 7), but this case was not included in the present experiments.

Eliminating alkali chlorides
Alkali and chlorine in the fuel are hard to get rid of. Experiments have shown that alkali in straw fuels (high ash, alkali and chlorine contents) can be partially leached by washing in water [19] or by spring harvesting [42], i.e. natural washing by rain and snow. For woody biomass there is no realistic pre-treatment or leaching technique available. Once in the boiler, there are two principally different approaches discussed in the literature when trying to overcome the deposit and/or corrosion problems associated with alkali chlorides in the flue gas. Either alkali can be reacted with minerals and retained in bottom ash or the alkali chlorides can be eliminated by selective sulfation reactions in the flue gas forming less troublesome sulfates. Both reaction paths are relevant to the present study and will be discussed in the following sections.

Reducing alkali chloride concentration by sulfation

Gas phase sulfation
Publications from several previous studies report on investigations aiming at reducing the amount of sticky and corrosive alkali chlorides (KCl(g) or NaCl(g)) in flue gas by sulfation [43-54]. Gaseous alkali chlorides are converted into less harmful alkali sulfates by different sulfur containing additives. A simplified overall sulfation reaction of alkali chlorides has been supported by experimental work [46, 55] and is summarized as reaction 1 below where A is either K or Na:

\[
2 \text{ACl}(g) + \text{SO}_2(g) + \text{H}_2\text{O}(g) + 1/2 \text{O}_2(g) \rightarrow \text{A}_2\text{SO}_4(s, l) + 2\text{HCl}(g) \quad (1)
\]

Sulfation of gaseous alkali chlorides in the gas phase is typically fast, and according to Iisa et.al. [44] the oxidation of SO₂ to SO₃ in the reaction mechanism is rate limiting for the sulfation reaction. By adding this sulfur oxidation step the reactions, still simplified, would look accordingly:
\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \tag{2}
\]

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

Glarborg and Marshall [45] have formulated a detailed reaction mechanism, still uncontradicted, involving intermediate steps (Figure 9) in addition to the reactants and products mentioned above. The most apparent intermediate, H\textsubscript{2}SO\textsubscript{4} is rejected due to low thermal stability in high temperatures. Instead, thermodynamic data for KSO\textsubscript{3}Cl and KHSO\textsubscript{4} are estimated by Gaussian 3 ab initio calculations and also fitted into the overall sulfation reaction. They agree that SO\textsubscript{3} formation is the rate-limiting step and they also suggest an additional possible reaction path with intermediate steps also for the SO\textsubscript{2} to SO\textsubscript{3} oxidation. The intermediates discussed have not been experimentally identified.

**Figure 9. Sulfation mechanisms, adapted from Glarborg and Marshall [45]. Reprinted with permission.**

The availability of sulfur for sulfation reactions is important for deposition and corrosion rates. An empiric relation has been formulated by Salmenoja and Mäkelä [56] that is based on the ratio between sulfur and chlorine (Figure 10). Experiences from industrial biomass and coal combustion provided the conclusion that with S/Cl > 4 in the fuel, chlorine-related corrosion problems were seldom seen, whereas S/Cl < 2 often led to problems (Figure 10). This ratio can be useful as a guideline, but more factors of the ash chemistry must be taken into account for making better
predictions. For example reactive CaO or high concentrations of KOH may consume sulfur by sulfating reactions and thereby increasing the amount (ratio) needed for sulfation of KCl. Salmenoja and Mäkelä [56] also exclude and make a reservation for black liquor combustion where sulfates and chlorides, both at high concentrations co-exist, making the S/Cl ratio less useful for predicting corrosion problems.

![Figure 10. Sulfur and chlorine content of some different fuels correlated to corrosivity of the flue gas. After Salmenoja and Mäkelä [56].](image)

**Ammonium sulfate injection**

Adding ammonium sulfate to the combustion is a potential solution to operational problems associated to alkali chlorides. A concept involving ammonium sulfate injection has been patented by Vattenfall AB and is called ChlorOut [57]. It was tested within this study (Papers I and IV) and also in a couple of other publications [50-51, 53-54, 58].

An aqueous solution of ammonium sulfate is sprayed into the hot zone prior to the superheaters aiming at the sulfation of corrosive gaseous alkali chlorides in the flue gas. The process can be described with the three simplified reactions below (reactions 4-6) for potassium, which is the most relevant alkali metal in biomass combustion, but the reactions are valid for sodium as well. Ammonium sulfate decomposes into NH$_3$ and SO$_3$ (reaction 4). The formation of SO$_3$ is favored by oxidizing conditions. Alkali chlorides are converted into less harmful sulfates in the simplified sulfating reaction (reaction 4). The ammonium sulfate also reduces NO$_x$ by selective non-catalytic reduction (SNCR, reaction 6) [50-51]. Other sulfates (Al, Fe) have
been tested and found to be successful as well [54], but without the NO\textsubscript{x} reducing ability of ammonium sulfate.

\[(\text{NH}_4)_2\text{SO}_4(aq) \rightarrow 2\text{NH}_3(g) + \text{SO}_3(g) + \text{H}_2\text{O}(g)\]  \hspace{1cm} (4)

\[2\text{ACl}(g) + \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{A}_2\text{SO}_4(s) + 2\text{HCl}(g)\]  \hspace{1cm} (5)

\[4\text{NH}_3(g) + 4\text{NO}(g) + \text{O}_2(g) \rightarrow 4\text{N}_2(g) + 6\text{H}_2\text{O}(g)\]  \hspace{1cm} (6)

Factors possibly influencing the efficiency of alkali chloride reduction include:

a) Amount of ammonium sulfate added (stoichiometry).
b) Oxygen partial pressure high enough to limit SO\textsubscript{3} decomposition.
c) Turbulence at the injection points for maximum contact between ACl and the newly formed SO\textsubscript{3}.
d) Moisture content of the gas for the sulfate formation, reaction (5).
e) Temperatures favoring the sulfation reactions.

Also, flue gas components such as KOH or reactive particles of CaO can possibly consume SO\textsubscript{3} and thereby decrease the efficiency of the additive for alkali chloride sulfation [54].

A thermochemical evaluation of alkali sulfation by ammonium sulfate shows that the optimal temperature range for sulfation of gaseous KCl is at 750-850°C and 800-900°C for NaCl. A theoretical conversion of more than 80% of the chlorides (somewhat higher for NaCl than for KCl) is achieved at stoichiometric conditions [59].

Sulfation of gaseous alkali chlorides in hot flue gas by the injection of ammonium sulfate was tested in the study presented in Paper I, and the results from that campaign also form part of the method evaluation in Paper IV. Under standard operational conditions, 15-20 ppm KCl (+NaCl) was found in the hot flue gas, as measured by the IACM. The levels were considered high and possibly a cause for the high corrosion rates observed on the superheaters. Therefore, tests with ammonium sulfate injection (ChlorOut) were performed in order to reduce the alkali chloride concentrations. Measurements with corrosion probes, IACM and a low pressure impactor enabled evaluation of the effects of the additive. IACM showed that KCl+NaCl concentration was decreased from more than 15 ppm to approximately 2 ppm by the additive. The addition of ammonium sulfate also had a positive effect on deposit formation and initial corrosion rates which both decreased by approximately 70%. The deposits contained much
less chlorides with the additive, which made them less sticky and fast growing, and also less corrosive to the steel. The method was concluded to be efficient in the sulfation of corrosive alkali chlorides (see Figure 11).

![Figure 11. Deposits on the corrosion probe rings after four weeks of exposure: normal fuel mix without (a) and with (b) ammonium sulfate injection. From Paper I, reprinted with permission.](image)

In **Paper III**, adding PVC to the fuel mix was tested. This can be seen as the opposite to a sulfur containing additive as the S/Cl ratio of the flue gas is hereby decreased. The flue gas cleaning system threshold value for HCl limited the amount of PVC that could be added, but increased corrosion rates were observed by only minor additions, and interpreted as an effect of the increased Cl content of the flue gas.

**Solid phase sulfation**
At the lower temperatures where solid chlorides are found, the oxidation reactions of SO$_2$ are believed to be too slow for efficient sulfation [48, 60]. Even though solid phase KCl sulfation is faster than that of NaCl, it is probably not fast enough to account for the sulfates found in fly ashes [44]. However, solid state sulfation is possibly significant in deposits, but over longer periods of time. It is probably one of the mechanisms involved in aging of deposits. Aging begins as soon as deposit starts to form. Changes in crystal and chemical composition over time, depending on temperature and gas concentrations, can create gradients by reformation, accumulation or depletion within the different parts of the deposit. The aging process is important for the long term properties of a deposit. Details on solid phase sulfation are further discussed in **Paper IV**.
Reducing operational problems by co-combustion with peat

Cofiring of peat together with more troublesome biofuels can have positive effects on fouling and high temperature corrosion [61-65]. Peat is used as a “clean” fuel, which means that its addition improves the operational characteristics of operationally troublesome ashes. The mechanisms behind the positive effects can vary depending on fuel and peat type. Theis et.al.[64] found a decreased deposition rate and increased S/Cl ratio in the deposits when cofiring bark with peat, which was explained by sulfation reducing alkali chloride content due to a higher sulfur content in the added peat. In the same study, a mixture of straw and peat behaved rather differently. Deposition rates remained rather low even at lower S/Cl ratios. Suggested explanations were either the formation of A-Si compounds capturing potassium, or increased erosion by the peat ash particles. The different results from the study are typical for peat fuels, i.e. different mechanisms can be expected for different fuel mixes and peats. Pommer et.al. [62] suggested several possible mechanisms and also pointed at higher concentrations of calcium, iron and aluminum in peat ash as potentially positive parameters for increasing the bed agglomeration temperature.

The importance of clay minerals in alkali capture is well known from coal co-combustion [49, 66-68]. Peats, similar to coals, can decrease chlorine deposition by mineral interactions depending on the composition and type of the peat. The effect of mineral inclusion of potassium has also been demonstrated by adding minerals to the combustion. Kaolin, especially, has proven efficient in capturing alkali (potassium) and thereby preventing chlorine in deposits [39, 69], bed agglomeration [70] and sintering [71].

In Paper IV, peat co-combustion was tested as a method for reducing chlorine in deposits and thereby decreasing deposit growth and the high temperature corrosion of superheaters. Peat was added to a fuel mix, originally containing bark and a minor part consisting of cardboard reject with a high chlorine content. Gaseous alkali chlorides were monitored by IACM and deposits were collected for analysis. Only a minor reduction of KCl+NaCl was found in the gas analysis. This was also supported by LPI measurements. On the other hand, chlorine content of the deposits and also deposit growth were greatly reduced and sulfur was increased, both according to wet chemical analysis. Taken together, this led to the conclusion that gas phase sulfation was not important in the observed positive effect of peat co-combustion in this case. Instead, in-deposit reactions or possibly the eroding effect of peat ash described by others [64, 72], were suggested.

One of the possibilities was the slow process of solid phase sulfation. This would agree with the higher content of sulfur in deposits under peat co-combustion. The gas measurements indicated only slightly more SO₂ in the co-combustion case compared with the reference. Therefore, the increased sulfur content and decreased chlorine content in the deposit must correlate
to the availability of sulfur and KCl for reaction if in-deposit sulfation was the explanation. It could be that KCl is less embedded in the deposits due to different mechanical properties of the peat ash, and therefore more available for sulfation. It is also possible that the, for sulfation, important formation of SO$_3$ is catalyzed by in-deposit Fe$_2$O$_3$ originating from peat ash.

In Paper IV, it is also suggested that mineral inclusion of potassium could act as a sink for KCl. Tran et.al. [73] report on the efficient conversion of KCl by kaolinite between 750 and 950°C with a somewhat higher efficiency at a lower temperature. Glazer [74] did similar tests in controlled TGA measurements at 800 and 850°C and reported on no obvious temperature to efficiency correlation. The focus in both studies was on retention in the combustion bed and extending to lower temperatures of relevance for superheater deposits was not discussed. Since low temperature mineral inclusion of potassium (and sodium) has not been fully investigated, it is not possible to draw any general conclusions at this point. If mineral inclusion would explain the KCl depletion, the high sulfur content of the deposits would remain to be explained.

**Corrosion of different alloys in biomass and waste combustion gases.**

Based on chemical equilibrium at combustion conditions, the elements Fe, Cr, Ni and any alloys containing these elements are not stable in metallic form in the oxidizing environment at the prevailing high temperatures and would thus form oxides. On the other hand, the oxides that are formed are protective against oxygen penetration and further oxidation and thereby the oxidation process is ultimately ceased. Under real industrial combustion conditions, the harsh chemical and physical environment makes the final outcome of the oxidation process more difficult to predict as protective oxides are affected by many factors.

Corrosion mechanisms with relevance for the high temperature parts (metals or refractory lining) of biomass or waste fired CHP plants involve oxidizing reactions with the formation of metallic oxides. Other mechanisms such as sulfidation, carbonation or nitridation can occur at specific local conditions, but do generally not cause the problems that are focus of this thesis. High temperature corrosion problems in biomass and waste fired boilers are often associated with the relatively high chlorine content in these fuels. Chlorine present as gaseous chlorides (KCl, NaCl, PbCl$_2$, ZnCl$_2$) condensing on cooled surfaces in the boiler, such as waterwalls and superheaters, tend to aggravate corrosion rates in many cases [75-76]. Recent research has shown that not only the increased amount of chloride containing melt in a deposit, but also small amounts of chlorine in dry deposits increase corrosion rates at typical superheater temperatures [77].
Although much effort has been put into the understanding of the mechanisms involved in chloride associated corrosion, they are still not fully understood today. A mechanism called *active oxidation* or *chlorine induced corrosion* is described \[78\], refined \[79\] and often referred to in literature dealing with high temperature corrosion issues in combustion of chlorine containing fuels. A vapor pressure of gaseous chlorine containing species \((\text{Cl}_2(g) \text{ or Cl}(g))\) close to the metal and high enough for the formation of \(\text{FeCl}_2(s)\) is the starting point of a series of reactions causing loss of iron from the metal surface. The vapor pressure of \(\text{FeCl}_2(g)\) causes diffusion outwards through the oxide layer until it reaches oxygen partial pressures high enough for oxides to be the thermodynamically favored forms of \(\text{Fe}\) (see stability diagram, Figure 14). Parts of the chlorine released in the oxidation can return to the metal and thereby take part again in the continued corrosion. The evaporation and outward diffusion of \(\text{FeCl}_2(g)\) is believed to be rate limiting for the process \[79-80\]. The chlorine hereby catalyzes the oxidation process. Also \(\text{CrCl}_2(s)\) is a possible component in the chloride layer and evaporation process.

The inward transport of chlorine to the corrosion front has been discussed in many studies. Gaseous \(\text{HCl or Cl}_2\) in hot flue gas are known to accelerate corrosion \[81-83\], but only in areas of high temperature, high chlorine concentrations and reducing conditions. Corrosion by chlorine containing gases \((\text{HCl, Cl}_2)\) at normal conditions is generally not as troublesome as that associated with alkali chlorides, and therefore \(\text{HCl}(g)\) or \(\text{Cl}_2(g)\) are often preferred forms of chlorine in the flue gas bulk flow. Instead, it seems that deposited alkali chlorides are an important part of the chlorine enrichment and transport. Three principally different mechanisms for transport of chlorine to the corrosion front have been found in the literature (Numbers 1-3 in the list below and in Figure 12).
Figure 12. The mechanisms of active oxidation and molten salt induced corrosion. Different transport ways for chlorine to reach the metal surface (1-3).

1. **In deposit sulfation of alkali chlorides.**
   Solid phase sulfation is believed to be slow and probably concentrated to the surface of the deposits [48, 79]. However, it is possible that solid phase sulfation increases the activity of the gaseous Cl species in the deposit enough for an inward transport that initiates and maintains active corrosion [84].

2. **Formation of alkali ferrites or chromates.**
   Reactions between KCl or NaCl and Fe₂O₃ or Cr₂O₃ in the oxide scale forming K₂Fe₂O₄, K₂CrO₄, Na₂Fe₂O₄ or Na₂CrO₄ could be able to liberate corrosive gaseous chlorine in the oxide scale [79]. K₂CrO₄ has been reported as a product from corrosion by KCl causing both breakdown of protective chromia layers and is possibly also a supplier of chlorine to the corrosion front at the metal/oxide boundary layer [85-86].

3. **Diffusion**
   Grain boundary diffusion, solid state diffusion or diffusion of chlorine containing species through cracks and pores are all possible, but probably too slow to account for the accelerated corrosion rates observed in Cl-containing gases according to calculations by Grabke et.al. [79].

When moving from the combustion of biomass to waste, problems of deposit formation, slagging and corrosion increase even further. Even though waste derived fuels represent a very heterogeneous group, they generally contain higher concentrations of the most troublesome elements such as sodium, chlorine, zinc, lead [79] and, in the case of electronic waste, also bromine from brominated plastics and flame retardants [87-89].
Waste fired boilers usually operate at somewhat lower steam temperatures, and therefore the vapor pressure of FeCl$_2$ is probably too low for the FeCl$_2$ outward diffusion in the active oxidation to be a predominant corrosion mechanism [76]. However, there are problems with chlorine related high temperature corrosion. In these cases, molten chloride mixtures are suggested to cause what has been called molten salt induced corrosion [76, 90–92]. Low melting mixtures of chlorides of K, Na, Zn or Pb, fluxes oxide scales and form melts on the metal surface, providing an electrolyte with fast ionic and electronic transport for the corrosion process. Iron from the metal surface is dissolved as FeCl$_2$(diss), or possibly also FeCl$_3$(diss) and is transported within the melt to the melt/gas interface where it is oxidized (Figure 12). The oxides formed by this process are typically porous and badly adherent and they therefore offer bad protection against further corrosion. The chlorine released at oxidation can participate in the melt formation again and thereby catalyze corrosion in a similar manner as in the case of active oxidation earlier described.

In (Paper II), corrosion probe measurements were performed between 320 and 460°C during combustion of household waste. An important result from the measuring campaign was that corrosion did not vary much with temperature within this range. In Figure 13 (from Paper I), on the other hand, the temperatures are higher and corrosion is also much more temperature dependent. This agrees with the hypothesis of a threshold temperature for chlorine activated corrosion at about 460°C [76, 93], increasing corrosion rates with increased vapor pressure of the chlorinated metals and referring corrosion at lower temperatures to other mechanisms. However, the probe rings from both campaigns showed evidence of a layer of Fe, Cl and sometimes Cr close to the metal surface even at low temperatures. The components suggested to lower melting temperatures of a melt (KCl, NaCl, ZnCl$_2$ or PbCl$_2$), and leading to molten salt induced corrosion, were not found at significant amounts, which left the high corrosion rates on the cooler probe rings partially unexplained. However, even though the low vapor pressures from Fe/Cr-chlorides are expected to limit chlorine induced corrosion, SEM images of the cross sections from samples at lower temperatures (low-alloy steels from both Papers I and II) indicated both the previously mentioned Fe/Cr chloride layer close to the metal and also outwards growing oxide layers in the deposit indicating an outward transport of volatilized iron. For detailed information, see Figure 3 in Paper II. The conclusions from these observations are that the metal chloride and its vapor pressure do play a role in the corrosion process also at lower temperatures. However, this is during initial deposit and oxide build-up and it is possible that this corrosion will decrease when protective oxide layer form. Also, the relative importance for the chloride vaporization for the overall corrosion is not clear. Similar observations with chloride vaporization
at lower temperatures were made by Bankiewicz et.al. [94] in a laboratory study with ZnCl₂ and KCl in synthetic ash mixtures.

![Graph](image.png)

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</table>

Figure 13. Average corrosion rates of different steels at 18 different temperatures based on four-weeks of exposure. From Paper I, reprinted with permission.

At higher temperatures with alkali chlorides present in the flue gas (reference in Figure 13 and Paper I) oxides appeared more porous and badly adherent, which would suggest that active oxidation was the dominating mechanism. No, or very little alkali was found in the oxide layer and the chlorine transport discussed above remains unclear. Layers of Fe, Cr and Cl on the metal surface were found on all specimens, but to different extents. Even the less corroded E1250 had the characteristic layer, but much thinner (a few micrometers) than the worst case X20 where layers of more than 100 micrometers (Figure 16a) could be found.

Steels used for superheaters in biomass or waste fired units have traditionally been low-alloy iron-based materials. Demands for higher efficiency, i.e. higher steam temperature and pressure, call for other alloys to also resist the increasingly corrosive environment in the boiler. Construction and heat transferring materials must endure a harsh chemical environment with high and fluctuating temperatures. Also factors such as thermal stress, cracking and spalling of protective oxide scales must be considered. In fluidized bed combustion, erosion resistance is also an important factor for material durability.

Chromium (Cr) is a common alloying element in iron-based superheater materials. Chromium is added to the alloy with the aim of forming chromia (Cr₂O₃) or chromium containing mixed spinels more protective than the iron
oxides. The corrosion behavior of the steel in a pure oxidizing atmosphere is to some extent correlated to how much chromium is added and Chromium content of more than 15% generally performs well at the high temperatures of a superheater. However, Fe-based alloys with Chromium as the only alloying element do not offer good protection in hot atmospheres containing alkali chlorides [76, 95]. High corrosion rates on high chrome ferritic and martensitic steels have been found in KCl containing environments also by others, while austenitic steels with high contents of both nickel and chrome offer better corrosion resistance [47, 83-84, 96]. This agrees well with the findings reported in appended Papers I and II where no positive effect on corrosion resistance was seen from only increasing chromium content in ferritic or martensitic alloys.

Nickel (Ni) as an alloying element is used together with chromium in austenitic stainless steels. Metallic nickel is more stable than iron and chromium in oxidizing atmospheres (horizontal axis in Figure 14) and therefore nickel oxide (NiO) is formed at the metal surface after iron and chromium have been depleted. Nickel is also more stable in chlorine containing atmospheres (vertical axis in Figure 14) which is why chlorinated and volatile nickel components are not found at combustion conditions. The positive effect of nickel explains why alloys with high nickel content (high Ni austenitic steels or Ni-base alloys) are, despite high prices, sometimes used in very corrosive alkali chloride containing environments such as the superheaters in waste incinerator plants [97].

![Figure 14. Phase stability diagram of oxides and chlorides of Fe, Cr and Ni at 500°C. Calculated and drawn using FactSage [9].](image-url)
The addition of molybdenum, silicone or aluminum have all proven efficient in reducing corrosion rates of a Fe-(15-25)Cr alloy in chlorine containing environments [76]. Also, other elements such as manganese, vanadium, copper, niobium or titanium are alloying elements used in different alloys to either stabilize oxides, prevent grain boundary diffusion or improve mechanical properties of the steel.

**Papers I and II** include corrosion probe measurements where several different alloys were tested in different environments. The tests included exposure of the different alloys to a CFB boiler fired mainly with bark (*Papers I and IV*) and a waste fired grate boiler (*Paper II*). Despite the rather different environments (thermal and chemical), similar trends of increasing corrosion resistance by increasing the content of alloying elements were found in both studies. The high-alloy austenitic steels Esshete 1250 and Sanicro28 showed comparable and low corrosion rates during the tests.

The only exception was the high chrome X20CrMoV12.1 steel (X20) that corroded equally (Figure 15) or more (Figure 13) than the low-alloy steels. X20 has been used for a long time as an alternative to low-alloy ferritic steels in fossil fired power plants due to its very high creep rupture properties, even at elevated temperatures. The sensitivity of X20 to corrosion in hot chlorine containing gas agrees well with the findings of Salmenoja et.al. [83-84]. The explanation is probably mechanisms associated with the chlorinating environment in combination with the relatively low content of stabilizing nickel in X20.
Figure 15. Average corrosion loss of different steels with and without addition of extra chlorine (PVC). Based on 10 days exposure. The error bars represent local maxima (pits). Temperatures between 350 and 460°C. After Paper II.

In Figure 16a, a SEM image shows a thick chlorine containing layer on the metal surface of X20 (ref 12 in Figure 13). The darker (richer in chromium) needle like areas spread in the chloride layer look like crystallization products from a melt, but this is not plausible since there is no known eutectic between FeCl₂ and CrCl₂ and the minimum melting temperature is that of FeCl₂ (676°C) which is well above the surface temperature of the probe ring (app. 540°C). Therefore, the layer is not likely to have existed as molten phase. The pattern also resembles the lens shapes of the original martensite indicating that it could be the remnants of a not fully dissolved metal structure. This agrees with the semi quantitative analysis by SEM/EDS that showed 10/20/70 relationship between Cl/Cr/Fe in the layer, indicating that its content of metals was only partially dissolved as FeCl₂(s) and/or CrCl₂(s).

Another interesting discovery in the corrosion products of the X20 steel was a layer of FeS (Figure 16b) situated where the original metal surface is indicated in Figure 16a. This indicates that, at least initially, not only chlorine, but also sulfur plays a role in the process. FeS could be a product
from corrosion of iron by potassium pyrosulfate or bisulfate as suggested by Vaughan and Krause [98]. The importance of the FeS formation for the overall corrosion process is not clear.

Figure 16. Oxidized area of steel X20CrMoV12 1. a) Oxide layer with metal chlorides beneath. b) FeS at the original metal surface.
Conclusions

Problems with high temperature corrosion on superheaters of biomass or waste-fired boilers are often associated with alkali chlorides in flue gas and deposits. An instrument for measuring alkali chloride concentrations in hot flue gas is described within this thesis. Measurements at a full scale industrial boiler were carried out in order to understand and minimize problems with chlorine related high temperature corrosion in biomass fired boilers. Peat co-combustion and an additive were tested to reduce alkali chloride concentrations in the flue gas and in deposits. Corrosion probes with different alloys were used in order to evaluate corrosion problems. Corrosion tests with different steels were also performed in a waste-fired boiler, where the effect of adding extra chlorine to the fuel was evaluated together with that of the different alloys. To increase the fundamental understanding of deposit formation, a laboratory study was performed with the focus on resulting phase composition upon condensation of mixtures of potassium and sodium chlorides. Important results are summarized below:

- Successful tests aiming at sulfation of gaseous alkali chlorides were performed in a full-scale boiler by the addition of ammonium sulfate. Drastic reductions of both deposit growth and corrosion rates were found when alkali chloride concentrations in the flue gas were lowered.
- Co-combustion tests with peat resulted in reduced deposit growth and chlorine content in deposit samples. Alkali chloride concentrations in the hot flue gas remained at normal levels, which indicated other mechanisms than gas phase sulfation contributed to the positive effect.
- High corrosion rates of non- or low-alloy steels were found in chlorinating environments. No positive effect on corrosion resistance was seen from only increasing chromium content in low-alloy steels. Also the high chrome, martensitic steel X20 showed high corrosion rates related to alkali chlorides in deposits. High-alloy, austenitic steels containing also nickel, corroded much less during the test periods.
- The calibration procedure of the in-situ alkali chloride monitor (IACM) was described. A detailed description of the instrument and its operational principle was provided together with examples from full-scale applications.
- Experiments on condensation of NaCl and KCl on a cooled surface indicated that even though the two salts were mixed in the gas phase and expected to be in solid solution at equilibrium surface temperatures, most of the deposited salt was present as separate phases. This result is of relevance for modeling of deposit formation and high temperature corrosion since dew points and melting points in the KCl-NaCl system will change depending on phase composition.
Suggested future work

Reflecting upon the findings in the present thesis, some suggestions for future work within different fields were identified.

Eliminating alkali chlorides

The understanding of the reaction mechanisms of sulfation could be improved by systematic investigations varying operational parameters such as temperatures, residence time, water content, form of sulfur and excess air. Tests could be conducted both in lab-scale reactors with synthetic flue gas, and in bench-scale combustion under well-controlled conditions.

Sulfation of solid CaO is an interesting subject indicated in the results from Paper II. Investigations aiming at determining the relative reactivity of CaO for sulfation, preferably in different size classes, compared to that of gaseous KCl, NaCl, KOH, NaOH would yield valuable information for combustion modelling.

In-deposit mineral inclusion of alkali is an interesting subject not yet fully evaluated. Some well-designed experiments at moderate temperatures are needed to supplement the existing knowledge from higher temperatures.

Heterogeneous (solid phase) sulfation in the deposit could eliminate alkali chlorides, but it is also a possible supplier of chlorine to the corrosion front. This should be investigated together with more details on the aging of deposits. The possibilities for increasing the in-deposit sulfation by catalytic additives for the SO₂ oxidation could also be considered.

The positive effects from peat combustion seen in Paper IV, as well as in different forms in the literature, remains partly unexplained and great deal of work remains to be done to complete the picture. More systematic investigations are needed to distinguish and evaluate all the possible mechanisms.

Alkali chloride monitoring

The calibration of the IACM can be considered accomplished when it comes to KCl and NaCl at temperatures between 650 and 1300°C. The instrument was developed for flue gas measurements in biomass and waste fired boilers, but the possibility of measuring alkali chloride concentrations in fuel gas could also be evaluated.

Other UV absorbing gas components are theoretically possible to monitor, but revision of evaluation algorithms and possibly also the optics of the instrument are parts of the development. If successful, this would, for example, enable the monitoring of hydroxide concentrations or to better distinguish between potassium and sodium components which would increase the amount of usable information from the instrument.
**Condensation of alkali chlorides**

The result from the present study (Paper V) describes condensation mechanisms under specific conditions. For a general understanding applicable under all possible conditions, complementary tests are needed. Higher gas concentrations would likely form liquid droplets at some point, which would possibly change phase composition. Changed phase composition upon aging of the deposit should be investigated. The effect of condensation nuclei is relevant for combustion applications and could be experimentally evaluated. More accurate determination of dew points are possible.
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