Formation, Sintering and Removal of Biomass Ash Deposits

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Formation, Sintering and Removal of Biomass Ash Deposits

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Preface and Acknowledgements

This dissertation is the result of three years of research, from 2014 to 2017, conducted in the Combustion and Harmful Emission Control (CHEC) research center, at the Department of Chemical & Biochemical Engineering, Technical University of Denmark (DTU), in collaboration with Energinet and Ørsted Bioenergy & Thermal Power A/S. The work is a part of the project, ‘Flexible use of Biomass on PF fired power plants’, funded by Energinet, through the ForskEL program, Ørsted and DTU. The PhD project was supervised by Senior Researcher Peter Arendt Jensen, Assistant Professor Hao Wu, Professor Peter Glarborg, Associate Professor Flemming Jappe Frandsen and Lead Process Chemistry Specialist Bo Sander.

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Above all, I would like to thank my parents, my brother Tejasvi, as well as Lana, Vikram, Pavel, Luuk, and Bart, for their continued support and understanding over the past three years.

Yashasvi Laxminarayan

January 2018
Summary

Over the last century, increasing global average temperatures have necessitated the switch from fossil fuels to renewable sources of energy. Biomass, being a CO₂ neutral fuel, can potentially replace coal for electricity and heat production. The biomass sector contributes 9.1% of the global energy consumption and has been growing by 2.5% every year since 2010, with several countries adopting biomass-firing and cofiring in power plants. However, biomass combustion in boilers may lead to several operational problems. Biomass typically contains a high amount of volatile and chemically aggressive ash species, such as K, Cl, and S, which form troublesome deposits on boiler surfaces, especially on superheater tubes. Ash deposits hinder heat transfer to the steam cycle, thereby reducing boiler efficiency, and may completely block flue gas channels in severe cases, causing unscheduled boiler shutdowns. Moreover, biomass ash deposits may cause severe corrosion of boiler surfaces. Therefore, reducing deposit formation and timely deposit removal are essential for optimal boiler operation.

The formation, sintering and removal of boiler deposits has been investigated in this PhD project, by simulating boiler conditions in laboratory-scale setups. Deposit formation was simulated in an Entrained Flow Reactor, to investigate the effect of operating conditions and ash chemistry on the rate of deposit formation. Experiments were performed using model biomass fly ash, prepared from mixtures of K₂Si₄O₉, KCl, K₂SO₄, CaO, SiO₂ and KOH, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The model fly ash particles were mixed with air, and injected into the reactor, to form deposits on an air-cooled probe. The influence of flue gas temperature (589 – 968 °C), probe surface temperature (300 – 550 °C), flue gas velocity (0.7 – 3.5 m/s), fly ash composition, fly ash flux (10000 – 40000 g/m²/h), fly ash particle size (3.5 – 90 µm) and probe residence time (up to 60 min) were investigated.

The results revealed that increasing flue gas temperature and probe surface temperature increased the sticking probability of the fly ash particles/deposit surface, thereby increasing the rate of deposit formation. However, increasing flue gas velocity resulted in a decrease in the deposit formation rate, due to increased particle rebound. Furthermore, it was observed that the deposit formation rate increased with time, fly ash flux and fly ash particle size. A mechanistic model was developed for predicting deposit formation in the reactor. Deposit formation by thermophoresis and inertial impaction was incorporated into the model, and the sticking probability of the ash particles was estimated by accounting for energy dissipation due to particle deformation. The model reasonably predicted the influence of flue gas temperature and fly ash flux on the deposit formation rate.
The deposit formation rate of the investigated species decreased in the following order: KOH > K$_2$SO$_4$ > KCl > K$_2$Si$_4$O$_9$ > SiO$_2$ > CaO, at the applied conditions. Addition of KCl to K$_2$Si$_4$O$_9$, SiO$_2$, CaO, and K$_2$SO$_4$ in the model fly ash mixture resulted in an increased deposit formation rate and induced rapid deposit sintering. Furthermore, addition of KOH to K$_2$Si$_4$O$_9$ in the model fly ash mixture resulted in a large increase in the deposit formation rate. The relative deposit formation rates of the investigated boiler fly ashes were observed to increase in the following order: wood fly ash, followed by straw + wood cofired fly ash and straw fly ash. Inertial impaction was the primary mechanism of deposit formation on the upstream side of the steel tube, when the model fly ash was present as solid or semi-molten particles. However, presence of vapor species or submicron ash particles in the flue gas resulted in the formation of deposits on both sides of the steel tube via condensation or thermophoresis.

In order to understand deposit shedding in boilers, the shear adhesion strength of biomass ash deposits was quantified by laboratory experiments. Artificial deposits were prepared using biomass fly ash from full-scale boilers, as well as from mixtures of KCl, K$_2$SO$_4$, CaO, CaSO$_4$, SiO$_2$, K$_2$CO$_3$, Fe$_2$O$_3$, K$_2$Si$_4$O$_9$, and KOH. The deposits were prepared on superheater steel tubes and sintered in an oven. Subsequently, the deposits were sheared off by an electrically controlled arm, and the corresponding adhesion strength was measured. The effects of sintering temperature (500 – 1000 °C), sintering time (0 – 24 h), deposit composition, thermal shocks on the deposit, and steel type were investigated. The results revealed that the adhesion strength of ash deposits was dependent on two factors: the ash melt fraction, and corrosion occurring at the deposit–tube interface. Adhesion strength increased with increasing sintering temperature, sharply increasing at the ash deformation temperature. However, sintering time, as well as the type of steel used, did not have a significant effect on the adhesion strength, under the investigated conditions. Addition of compounds which increased the melt fraction of the ash deposit, typically by forming a eutectic system, increased the adhesion strength, whereas addition of inert compounds with a high melting point decreased the adhesion strength. Furthermore, the study indicated that sulfation of ash deposits might lead to an increase in the adhesion strength, while cooling down the deposits after sintering decreased the adhesion strength. Finally, it was observed that adhesion strength data displayed a significant degree of scatter, following a log-normal distribution.

Additionally, the tensile adhesion strength of biomass ash deposits was investigated under the influence of a temperature gradient across the deposit. Model biomass ash deposits, containing mixtures of KCl, K$_2$SO$_4$, CaO, CaSO$_4$ and K$_2$Si$_4$O$_9$, were prepared on superheater steel tubes, and sintered in an oven. The superheater steel tube was cooled by air, incorporating a temperature gradient across the deposits. After sintering, the deposits were removed using an electrically controlled arm, and the corresponding tensile adhesion strength was measured. The effects of flue gas temperature (500 – 700 °C), steel surface temperature (500 – 650 °C) and deposit composition were investigated. The results revealed that
increasing the flue gas temperature, as well as the steel surface temperature, led to a sharp increase in the tensile adhesion strength of the model deposits. The sharp increase was typically observed near the melting temperature (or deformation temperature) of the investigated model deposits. A large temperature gradient across the deposits induced migration of molten/vapor species from the outer layer of the deposit to the deposit–tube interface, causing liquid state sintering, and thereby increasing the tensile adhesion strength. Varying the ash chemistry of the model deposits revealed that the melt fraction of the deposit was highly influential in determining deposit adhesion strength. The tensile adhesion strength data qualitatively and quantitatively agreed with the shear adhesion strength data.

Finally, heterogeneous sulfation of model biomass ash deposits was simulated in three different experimental setups. The effect of sulfation time (0 – 24 h), SO₂ concentration (0 – 600 ppm) and sintering temperature (500 – 650 °C) on the shear/tensile adhesion strength of the deposits was investigated. While increasing sulfation time resulted in a gradual increase in the adhesion strength of the deposits, varying SO₂ concentrations and sintering temperature did not significantly influence the deposit adhesion strength at the investigated conditions. A low degree of sulfation was observed in the experiments (<1 wt % S), suggesting that further investigation is required to understand the effect of heterogeneous sulfation on the adhesion strength.

Dannelsen, sintringen og fjernelsen af kedel askebelægninger er blevet undersøgt i dette ph.d. projekt ved at simulere de lokale forhold i biokedel i laboratorieopstillinger. belægningsdannelse blev simulert i en Entrained Flow Reaktor for at undersøge virkningen af driftsbedingelser og askekemi på hastigheden af belægningsopbygning. Eksperimenterne blev udført under anvendelse af model askekompromenter, fremstillet ud fra blandinger af K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}, KCl, K\textsubscript{2}SO\textsubscript{4}, CaO, SiO\textsubscript{2} og KOH, samt tre forskellige kedelflyveaske: træflyveaske, halmflyveaske og halm + træ samfyret flyveaske. Modelflyveaskepartiklerne blev indført med luft i reaktoren for at danne aflejringer på en luftkolet probe. Effekten af røggastemperatur (589 – 968 °C), probeoverfladetemperatur (300 – 550 °C), røggashastighed (0,7 – 3,5 m/s), flyveaskesammensætning, flyveaskeflux (10.000 – 40.000 g/m\textsuperscript{2}/h), flyveaskepartikelstørrelse (3,5 – 90 µm) og deponeringstid (op til 60 min) blev undersøgt.

Resultaterne viste, at stigende røggastemperatur og probeoverfladetemperatur øgede vedhæftningssandsynligheden for flyveaskepartikler og derved belægnings opbygningshastigheden. Imidlertid resulterede stigende røggashastighed i et fald i deponeringsdannelseshastigheden. Endvidere blev det observeret, at belægningsdannelseshastigheden steg med deponeringstid, flyveaskeflux og flyveaskepartikelstørrelse. Ved de undersøgte betingelser var belægningsdannelseshastigheden for modelkomponenterne faldende med følgende orden KOH > K\textsubscript{2}SO\textsubscript{4} > KCl > K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} > SiO\textsubscript{2} > CaO. Tilsætning af KCl til K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}, SiO\textsubscript{2}, CaO og K\textsubscript{2}SO\textsubscript{4} i modelflyveaskeblandinger resulterede i lignende deponeringshastigheder som for ren KCl og inducerede hurtig sintring af belægningen. Endvidere resulterede tilsætning af KOH til K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} i en stor stigning i deponeringshastigheden. Herudover var
deponeringshastigheden af flyveasken i stigende orden for træflyveask < halm + træ samfyret flyveaske < halm flyveaske under de undersøgte forhold. Inerti impaktion var den primære mekanisme for belægningsdannelse på metalrørets opstrøms side, når flyveaske forefandtes som fæste eller smeltede partikler. Tilstedeværelsen af gasfase eller submikrone partikler i flyveasken resulterede imidlertid i dannelse af aflejringer på begge sider af stålrøret via kondensering eller termophores.


med et højt smeltepunkt, såsom CaO, nedsatte trækstyrken. Desuden viste resultaterne, at korrosion forekommende ved grænsefladen påvirker trækstyrken.

Endelig blev heterogen sulfatering af biomasseaskeaflejringer simuleret i tre forskellige eksperimentelle opstillinger. Effekten af sulfateringstid (0 – 24 h), SO₂ koncentration (0 – 600 ppm) og sintringstemperatur (500 – 650 °C) på vedhæftningsstyrken af aflejringerne blev undersøgt. Undersøgelsen viste, at vedhæftningsstyrken af belægninger steg med stigende sulfateringstid, mens effekten af varierende SO₂ koncentration og sintringstemperatur ikke var signifikant. En lav grad af sulfatering var observeret i alle eksperimenter (< 1 wt % S), hvilket antyder, at yderligere forskning er nødvendig for at kunne forstå effekten af heterogen sulfatering på vedhæftningsstyrken.
# Contents

List of Figures .......................................................................................................................... i
List of Tables ............................................................................................................................. v
Abbreviations and Symbols ......................................................................................................... vii

Chapter 1  Introduction .............................................................................................................. 1
  1.1 Project objectives .................................................................................................................. 2
  1.2 Structure of this thesis .......................................................................................................... 2

Chapter 2  Background .............................................................................................................. 5
  2.1 Biomass Fuels ....................................................................................................................... 5
  2.2 Biomass firing technologies ................................................................................................. 6
  2.3 Formation of fly ash ............................................................................................................ 9
  2.4 Fly ash deposition .............................................................................................................. 11
  2.5 Deposit consolidation and maturation ............................................................................... 14
  2.6 Shedding of ash deposits ................................................................................................. 16

Chapter 3  Entrained Flow Reactor study on Biomass Fly Ash Deposition .............................. 21
  3.1 Introduction ........................................................................................................................ 22
  3.2 Experimental section ........................................................................................................ 24
  3.3 Deposit Formation Model ................................................................................................. 31
  3.4 Results and Discussion ...................................................................................................... 33
  3.5 Conclusions ....................................................................................................................... 51

Chapter 4  Shear Adhesion Strength of Biomass Ash Deposits ................................................. 53
  4.1 Introduction ........................................................................................................................ 54
  4.2 Experimental section ........................................................................................................ 55
  4.3 Results and Discussion ...................................................................................................... 59
  4.4 Conclusions ....................................................................................................................... 70

Chapter 5  Tensile Adhesion Strength of Biomass Ash Deposits ............................................. 73
  5.1 Introduction ........................................................................................................................ 74
  5.2 Experimental section ........................................................................................................ 75
  5.3 Results and Discussion ...................................................................................................... 82
List of Figures

Figure 2.1 A schematic representation of a grate-fired boiler during biomass combustion ........................................ 7
Figure 2.2 A schematic representation of fluidized bed boilers during biomass combustion ................................. 8
Figure 2.3 A schematic representation of a suspension-fired boiler during biomass combustion .................... 9
Figure 2.4 Transformation of biomass fuel to fly ash particles, aerosols and vapor species ............................ 10
Figure 2.5 Mechanisms of deposit growth ........................................................................................................ 12
Figure 2.6 Mechanisms of sintering ................................................................................................................ 15
Figure 2.7 Forces exerted by a soot-blower jet on a deposit ............................................................................. 16
Figure 3.1 Particle size distribution of the investigated K₂Si₄O₉ ........................................................................ 26
Figure 3.2 Optical Dilatometry of K₂Si₄O₉ ......................................................................................................... 27
Figure 3.3 Schematic representation of the Entrained Flow Reactor ............................................................... 28
Figure 3.4 Air-cooled deposit probe. Deposits are formed on the steel tube mounted on the probe .......... 29
Figure 3.5 Effect of flue gas temperature and probe surface temperature on the deposit formation rate .... 34
Figure 3.6 Effect of flue gas velocity on the deposit formation rate ............................................................... 37
Figure 3.7 Effect of time and fly ash flux on the deposit formation rate ........................................................ 39
Figure 3.8 Effect of fly ash particle size on the deposit formation rate .......................................................... 40
Figure 3.9 Effect of fly ash composition on the deposit formation rate .......................................................... 43
Figure 3.10 SEM image of deposit particles .................................................................................................... 48
Figure 4.1 Thermogravimetric analysis of steel used (TP347HFG), exposed to air at 600 °C ......................... 57
Figure 4.2 Experimental setup for adhesion strength measurements ............................................................. 58
Figure 4.3 Effect of sintering temperature on shear adhesion strength ......................................................... 60
Figure 4.4 Effect of varying concentration of K₂SO₄ in KCl on the shear adhesion strength ....................... 61
Figure 4.5 SEM image of the deposit–tube interface ....................................................................................... 62
Figure 4.6 Effect of composition on adhesion strength using model fly ash compounds ............................ 63
Figure 4.7 Differential Scanning Calorimetry analysis of K₂Si₄O₉ ................................................................. 65
Figure 4.8 Effect of sintering time on adhesion strength ................................................................................. 66
Figure 4.9 Effect of strength measurement temperature on adhesion strength .......................................... 67
Figure 4.10 Effect of steel type on adhesion strength ...................................................................................... 68
Figure 4.11 Log-normal distribution of adhesion strength data ................................................................. 69
Figure 5.1 Particle size distribution of the investigated straw fly ash ............................................................ 77
Figure 5.2 Teflon mold used for sample preparation ....................................................................................... 78
Figure 5.3 Experimental setup for adhesion strength measurements .......................................................... 79
Figure 5.4 Temperature gradients along the air-cooled probe ......................................................... 80
Figure 5.5 Effect of steel surface temperature on tensile adhesion strength .................................... 83
Figure 5.6 Effect of flue gas temperature on tensile adhesion strength ........................................ 86
Figure 5.7 SEM image of a KCl–K₂SO₄ (50 wt %) deposit .............................................................. 87
Figure 5.8 Effect of deposit composition on tensile adhesion strength ........................................ 90
Figure 6.1 Electrically heated horizontal quartz tube .................................................................. 97
Figure 6.2 Influence of sulfation time on shear adhesion strength, Setup 2 ................................... 98
Figure 6.3 Influence of sulfation time on shear adhesion strength, Setup 3 ................................. 101
Figure 6.4 Influence of SO₂ concentration on shear adhesion strength, Setup 1 ......................... 104
Figure 6.5 Influence of SO₂ concentration on shear adhesion strength, Setup 2 ......................... 105
Figure 6.6 Influence of SO₂ concentration on shear adhesion strength, Setup 3 ......................... 107
Figure 6.7 Influence of sintering temperature on shear adhesion strength, Setup 1 ..................... 109
Figure 6.8 Influence of sintering temperature on shear adhesion strength, Setup 3 ..................... 111
Figure A.1 Schematic representation of the Entrained Flow Reactor ............................................ 133
Figure A.2 Air-cooled deposit probe ........................................................................................... 135
Figure A.3 Variation of flue gas temperature in the bottom chamber ............................................ 136
Figure A.4 Temperature gradients along the surface of the deposit probe ................................. 137
Figure A.5 PI diagram of the air-cooled deposit probe ................................................................. 138
Figure B.1 Setup used for shear adhesion strength measurements ............................................. 141
Figure B.2 Inside view of the oven .............................................................................................. 142
Figure B.3 Experimental setup for adhesion strength measurements ......................................... 144
Figure B.4 Temperature program used during heat-up ................................................................. 144
Figure B.5 Typical force signal obtained from the load cell ......................................................... 145
Figure B.6 Gas-tight chamber for SO₂ injection ......................................................................... 146
Figure B.7 PI diagram for SO₂ injection into the oven ................................................................. 148
Figure B.8 Influence of SO₂ concentration on the corrosion layer, Setup 1 ............................... 149
Figure B.9 Influence of sintering temperature on the corrosion layer, Setup 1 ......................... 150
Figure C.1 Experimental setup used for tensile adhesion strength measurement ....................... 152
Figure C.2 Exploded view of the cooling plate heat exchanger ..................................................... 153
Figure C.3 Cross-sectional view of the mounted air-cooled probe ............................................... 154
Figure C.4 Temperatures measured on the mounted air-cooled probe .......................................... 155
Figure C.5 Temperature gradients at a flue gas temperature of 650 °C ...................................... 156
Figure C.6 Temperature gradient at a flue gas temperature of 775 °C ...................................... 156
Figure C.7 PI diagram of the Tensile Adhesion Strength Setup ................................................ 158
Figure C.8 Teflon mold used for sample preparation .................................................................. 159
Figure C.9 Experimental setup for adhesion strength measurements .......................................................... 160
Figure C.10 Influence of sulfation time on the corrosion layer, Setup 2 .................................................. 161
Figure C.11 Influence SO$_2$ concentration on the corrosion layer, Setup 2 ............................................. 162
Figure D.1 Electrically heated horizontal quartz tube ........................................................................ 163
Figure D.2 Temperature gradients along the length of the quartz tube at 650 °C .............................. 164
Figure D.3 Influence of sulfation time on the corrosion layer, Setup 3 ................................................. 166
Figure D.4 Influence of SO$_2$ concentration on the corrosion layer, Setup 3 ................................. 167
Figure D.5 Influence of sintering temperature on the corrosion layer, Setup 3 .......................... 168
List of Tables

Table 2.1 Properties and composition of coal, wood and straw ................................................................. 6
Table 2.2 Position of deposit removal, depending on the shedding mechanism ........................................ 18
Table 3.1 Composition, particle size and melting point analysis of the investigated fly ashes .................... 25
Table 3.2 Ash melting analysis of K$_2$Si$_4$O$_9$, obtained using Optical Dilatometry ................................... 27
Table 3.3 Equilibrium composition of the model fly ash compounds .......................................................... 44
Table 3.4 Deposit formation rates of model fly ash mixtures .................................................................... 46
Table 4.1 Eutectic temperature of the investigated model fly ash compounds ........................................ 56
Table 4.2 Composition of the investigated steel tubes ................................................................................ 57
Table 4.3 Adhesion strength of different types of deposits ....................................................................... 70
Table 5.1 Eutectic temperature/glass transition temperature of the investigated model deposits ............. 76
Table 5.2 Statistical analysis of data sets with varying cooling probe temperature ................................. 84
Table 5.3 Statistical analysis of data sets with varying flue gas temperature ............................................ 86
Table 5.4 Statistical analysis of data sets with varying deposit composition ............................................ 90
Table 6.1 Statistical analysis of data with varying sulfation time, Setup 2 ................................................ 98
Table 6.2 Statistical analysis of data with varying sulfation time, Setup 3 ............................................... 101
Table 6.3 Sulfur content of selected deposit samples obtained through ICP analysis ............................... 103
Table 6.4 Statistical analysis of data with varying SO$_2$ concentration, Setup 2 ....................................... 106
Table 6.5 Statistical analysis of data with varying SO$_2$ concentration, Setup 3 ....................................... 107
Table 6.6 Statistical analysis of data with varying sintering temperature, Setup 3 ................................. 111
Table 6.7 Effect of operating conditions on the mean adhesion strength ................................................ 112
Table D.1 Maximum gas flow rates ......................................................................................................... 164
Table E.1 Correlation coefficients for estimating local collision efficiency ............................................. 170
Abbreviations and Symbols

Abbreviations
SEM  Scanning Electron Microscopy
EDS  Energy-dispersive X-ray Spectroscopy
XRD  X-ray Diffraction
ICP  Inductive Coupled Plasma
TGA  Thermogravimetric Analysis
DSC  Differential Scanning Calorimetry

Symbols

Latin
\( \dot{C} \)  rate of deposit formation by condensation  kg/s
\( C_b \)  concentration of the species in the bulk gas  kg/m³
\( C_p \)  specific heat capacity  J/kgK
\( C_s \)  concentration of the species at the heat transfer surface  kg/m³
\( d \)  diameter  m
\( E \)  Young’s modulus  Pa
\( f_{dep} \)  mass fraction of impacting particles undergoing deposition  -
\( f_{melt} \)  melt fraction of particles/deposit surface  -
\( h \)  heat transfer coefficient  W/m²K
\( l \)  rate of deposit formation by inertial impaction  kg/s
\( k \)  thermal conductivity  W/mK
\( k_c \)  mass transfer coefficient  m/s
\( m \)  mass of the deposit  kg
\( N \)  sample size of the data set  -
\( p \)  p-value of Welch’s t-test  -
\( s \)  surface area of the probe/deposit  m²
\( T \)  temperature  °C/K
\( \dot{T} \)  rate of deposit formation by thermophoresis  kg/s
\( t \)  time  s
\( T \)  t-value of Welch’s t-test  -
\( u_T \)  thermophoretic velocity  m/s
\( X \) fractional conversion of KCl
\( Y_{SO_2} \) mole fraction of SO₂

Greek
\( \alpha \) significance level
\( \theta \) angular position \( \text{radians} \)
\( \Gamma \) interface energy \( \text{N/m} \)
\( \gamma \) surface tension \( \text{N/m} \)
\( \Delta T \) temperature gradient \( ^\circ \text{C} \)
\( \delta \) thickness \( \text{m} \)
\( \eta \) sticking probability of particles/deposit surface
\( \mu \) viscosity of particles/deposit surface \( \text{Pa.s} \)
\( \mu \) mean value of the data set \( \text{kPa} \)
\( \nu \) degrees of freedom
\( \rho \) density \( \text{kg/m}^3 \)
\( \sigma \) standard deviation of the data set \( \text{kPa} \)
\( \sigma \) Stefan Boltzmann constant \( \text{W/m}^2\text{K} \)

Subscripts
\( \text{crit} \) critical
\( \text{d} \) deposit
\( \text{g} \) gas
\( \text{h} \) horizontal
\( \text{p} \) particle
\( \text{ref} \) reference
\( \text{s} \) solid
\( \text{v} \) vertical
Introduction

Biomass is a renewable energy source and does not contribute to a net increase in greenhouse gas emissions, since the CO$_2$ emitted into the atmosphere during biomass combustion is equal to the CO$_2$ absorbed by the biomass during its growth, making biomass a CO$_2$-neutral fuel. Therefore, biomass would be an ideal candidate to replace coal in power plants for electricity and heat production. Denmark is planning to phase out coal from power plants by 2030, and the Danish energy company, Ørsted, has decided to replace coal with biomass in pulverized fuel-fired power plants by 2023.

However, biomass combustion in boilers may lead to several operational problems. Biomass typically contains a high amount of volatile and chemically aggressive ash species, such as K, Cl, and S, which form troublesome deposits on boiler surfaces, especially on superheater tubes. Ash deposits hinder heat transfer to the steam cycle, thereby reducing boiler efficiency, and may completely block flue gas channels in severe cases, causing unscheduled boiler shutdowns. Moreover, biomass ash deposits may cause severe corrosion of boiler surfaces. Therefore, understanding deposition of biomass ash on boiler surfaces is essential in order to alleviate such problems.

Upon formation, ash deposits undergo sintering in boilers. Sintering decreases the porosity of the deposits and may cause the deposits to be strongly adherent to boiler surfaces. During sintering, KCl present in the deposits may react with SO$_2$ in the flue gas to form K$_2$SO$_4$. Heterogeneous sulfation of KCl may influence corrosion and adhesion strength of the deposits to boiler surfaces.

Ash deposits in boilers require regular and effective removal for optimal boiler operation. Soot-blowing is the most commonly used technique for deposit removal in boilers, where a jet of steam is blown onto the deposits. Thermal and mechanical stresses induced by the soot-blower jet may cause the deposit to fall off. However, soot-blowing causes abrasion and erosion of superheater tubes, and consumes a large amount of high-pressure steam, which may otherwise be used in the steam cycle. Therefore, an insight into the adhesion strength of ash deposits to superheater tubes may aid soot-blower optimization.
1.1 Project objectives

Aiming to improve the understanding of formation, sintering and removal of biomass ash deposits in boilers, this PhD project conducted studies simulating the aforementioned processes in laboratory-scale experimental setups.

Specifically, the PhD project had the following objectives:

- *Deposit formation*: Simulate deposit formation in biomass-fired boilers in an Entrained Flow Reactor, to understand the effect of operating conditions and ash chemistry on the rate of deposit formation.
- *Deposit removal*: Quantify the shear, as well as the tensile adhesion strength of biomass ash deposits to superheater tubes, to understand the effect of operating conditions and deposit composition.
- *Deposit sintering*: Understand the effect of heterogeneous sulfation of biomass ash deposits on deposit adhesion strength.

1.2 Structure of this thesis

Including the introduction, the thesis is divided into 7 chapters.

Chapter 2: Background

This chapter provides an overview of biomass combustion in boilers. The formation, deposition, sintering, and shedding of fly ash in biomass-fired boilers has been described.

Chapter 3: Entrained Flow Reactor study on Biomass Fly Ash Deposition

This chapter presents the results of an investigation quantifying the effect of operating conditions and fly ash chemistry on the rate of deposit formation. Deposit formation experiments were performed in a laboratory-scale Entrained Flow Reactor, using model biomass fly ash, prepared from mixtures of $K_2Si_4O_9$, KCl, $K_2SO_4$, CaO, SiO$_2$ and KOH, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The model fly ash particles were mixed with air, and injected into a 2 m long electrically heated furnace, to form deposits on an air-cooled probe at the outlet of the furnace. The effects of flue gas temperature (589 – 968 °C), probe surface temperature (300 – 550 °C), flue gas velocity (0.7 – 3.5 m/s), fly ash composition, fly ash flux (10000 – 40000 g/m$^2$/h), fly ash particle size (3.5
1.2 Structure of this thesis

- 90 µm) and probe residence time (up to 60 min) were investigated. Furthermore, a mechanistic model was developed for predicting deposit formation in the reactor.

Chapter 4: Shear Adhesion Strength of Biomass Ash Deposits

This chapter describes an experimental study on the shear adhesion strength of biomass ash deposits in a laboratory oven. The deposits were prepared using biomass ash from full-scale boilers, as well as from mixtures of KCl, K₂SO₄, CaO, CaSO₄, SiO₂, K₂CO₃, Fe₂O₃, K₂Si₄O₉, and KOH. The deposits were prepared on superheater tubes and sintered in the oven. The effect of sintering temperature (500 – 1000 °C), sintering time (0 – 24 h), deposit composition, thermal shocks on the deposit, and steel type was investigated.

Chapter 5: Tensile Adhesion Strength of Biomass Ash Deposits

This chapter presents the results of an experimental study, quantifying the tensile adhesion strength of model biomass ash deposits. An experimental setup to investigate the tensile adhesion strength of biomass ash deposits was designed and constructed during this PhD project. The setup incorporated a temperature gradient across the deposit layer, allowing superior replication of boiler conditions. Model biomass ash deposits were prepared on superheater steel tubes, from mixtures of KCl, K₂SO₄, CaO, CaSO₄ and K₂Si₄O₉, and sintered in the setup. The effects of flue gas temperature (500 – 700 °C), steel surface temperature (500 – 650 °C) and deposit composition were investigated.

Chapter 6: Heterogeneous Sulfation of Biomass Ash Deposits

This chapter presents the results of an experimental campaign understanding the heterogeneous sulfation of biomass ash deposits. Heterogeneous sulfation of biomass ash deposits was investigated in three different experimental setups. The setup used for shear adhesion strength measurements was modified to allow sulfation of the deposits. Furthermore, SO₂ was injected into the setup used for tensile adhesion strength measurements. Additionally, sulfation experiments were carried out in an electrically heated horizontal quartz tube. Model biomass ash deposits were prepared on superheater steel tubes using KCl and sintered in the experimental setups. The effect of sulfation time (0 – 24 h), SO₂ concentration (0 – 600 ppm) and sintering temperature (500 – 650 °C) on the shear/tensile adhesion strength of the deposits was investigated.

Chapter 7: Concluding Remarks

This chapter summarizes the main conclusions of this thesis and provides suggestions for future work.
This chapter provides an overview of biomass combustion in boilers. Specifically, this chapter focusses on the life cycle of fly ash in boilers, including formation of fly ash, deposition of fly ash on boiler surfaces, sintering and shedding of boiler deposits. A more detailed literature review of deposit formation, deposit sulfation and deposit adhesion strength is provided in the other relevant chapters.

### 2.1 Biomass Fuels

Biomass is a complex heterogeneous mixture of organic matter and inorganic matter. The organic matter is predominantly present as cellulose, hemicellulose and lignin, whereas the inorganic matter can be present as water soluble minerals, organically bound species and amorphous solids. During combustion, the organic matter is primarily converted into CO\textsubscript{2} and water, whereas the inorganic matter is either released into the gas phase, or converted to residual ash.

As a solid fuel resource, biomass can be classified into several categories:

1. Woody biomass, e.g., wood, sawdust
2. Herbaceous and agricultural biomass, e.g., straw, grass
3. Aquatic biomass, e.g., algae
4. Animal and human biomass wastes, e.g., bones, chicken litter
5. Industrial biomass wastes, e.g., municipal solid waste, refuse-derived fuel

Wood and straw are the most commonly used fuels in boilers for heat and electricity production. The typical composition of wood, straw and coal is provided in Table 2.1.

Typically, coals have a higher ash content, when compared to biomass fuels. However, biomass ash typically contains a higher fraction of volatile and chemically aggressive species, such as K, Cl, S, which may cause problems related to ash deposition and corrosion. Furthermore, biomass fuels are characterized by lower heating values.
Table 2.1 Properties and composition of coal, wood and straw. Data compiled from multiple sources.\textsuperscript{1,10,11}

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Wood</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Variation</td>
<td>Typical</td>
</tr>
<tr>
<td>Moisture (wt %)</td>
<td>3</td>
<td>2.1–14</td>
<td>45</td>
</tr>
<tr>
<td>LHV, water and ash free (MJ/kg)</td>
<td>30</td>
<td>29–32</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Chemical composition, wt % on dry basis

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Wood</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Typical</td>
<td>Variation</td>
<td>Typical</td>
</tr>
<tr>
<td>Ash</td>
<td>10</td>
<td>4–11</td>
<td>1</td>
</tr>
<tr>
<td>Volatiles</td>
<td>30</td>
<td>5–35</td>
<td>81</td>
</tr>
<tr>
<td>Hydrogen, H</td>
<td>5</td>
<td>3–6</td>
<td>5.8</td>
</tr>
<tr>
<td>Carbon, C</td>
<td>88</td>
<td>69–93</td>
<td>50</td>
</tr>
<tr>
<td>Nitrogen, N</td>
<td>1.5</td>
<td>1–1.8</td>
<td>0.3</td>
</tr>
<tr>
<td>Sulfur, S</td>
<td>1</td>
<td>0.9–5.0</td>
<td>0.05</td>
</tr>
<tr>
<td>Chlorine, Cl</td>
<td>–</td>
<td>0.04–0.17</td>
<td>0.02</td>
</tr>
<tr>
<td>Silicon, Si</td>
<td>2.1</td>
<td>–</td>
<td>0.1</td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>0.28</td>
<td>–</td>
<td>0.015</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>–</td>
<td>0.08–0.74</td>
<td>0.015</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>–</td>
<td>0.62–0.95</td>
<td>0.2</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>–</td>
<td>0.57–0.78</td>
<td>0.04</td>
</tr>
<tr>
<td>Sodium, Na</td>
<td>–</td>
<td>1.52–1.86</td>
<td>0.015</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>–</td>
<td>0.02–0.03</td>
<td>0.1</td>
</tr>
<tr>
<td>Phosphorus, P</td>
<td>–</td>
<td>–</td>
<td>0.02</td>
</tr>
</tbody>
</table>

2.2 Biomass firing technologies

The most commonly used systems for large-scale biomass combustion are grate-fired boilers, fluidized bed boilers, and suspension-fired boilers.

In grate-fired boilers, solid fuel is combusted on a grate, using primary air injected upwards through the grate. Combustion is completed in the secondary combustion zone above the grate, using secondary air. A schematic representation of a grate-fired boiler is provided in Figure 2.1.
2.2 Biomass firing technologies

Figure 2.1 A schematic representation of a grate-fired boiler during biomass combustion.\(^1\)

The grate can be present in different configurations, including a fixed flat grate, a fixed sloping grate, a vibrating grate, and a chain grate. Grate-fired boilers are suitable for several types of fuels, such as coal, wood, straw, waste fuels and peat. The mass fraction of ash entrained is low, ranging from 5 – 30\(^\circ\).\(^1\) However, the final steam temperatures (480 – 520 °C) and the electrical efficiency (25 – 30\%) of typical grate boilers is relatively low, compared to fluidized-bed boilers and suspension-fired boilers.\(^1,11\)

In fluidized bed boilers, the fuel particles are suspended in a fluidizing stream of air and inert bed material. The two main types of fluidized bed boilers are Bubbling Fluidized Bed (BFB) boilers (10 – 30 MW\(_{th}\)), and Circulating Fluidized Bed (CFB) boilers (>30 MW\(_{th}\)).\(^12\) A schematic representation of CFB and BFB boilers is provided in Figure 2.2. In BFB boilers, the fluidized bed material is retained in the combustion chamber, with the combustion air entering from the bottom, and leaving from the top of the combustion chamber. However, in CFB boilers, the bed material is entrained with the flue gas, separated using hot cyclones or a U-beam separator, and fed back into the combustion. Compared to BFB boilers and grate-fired boilers, CFB boilers are characterized by higher electrical efficiencies, and higher steam temperatures (550 – 600 °C). However, CFB boilers have higher investment, operational and maintenance costs.\(^12\)
The intense heat transfer and mixing in fluidized bed boilers provides good conditions for complete combustion, with low excess air demand. However, the high content of alkali salts in biomass fuels may cause fouling, slagging, and bed agglomeration.\textsuperscript{13} Furthermore, fluidized bed boilers require a low fuel particle size (<40 mm for CFB and <80 mm for BFB), compared to grate-fired boilers, and a long start-up time (8 – 15 hours).\textsuperscript{13}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2}
\caption{A schematic representation of a (a) circulating fluidized bed boiler, and (b) bubbling fluidized bed boiler during biomass combustion.\textsuperscript{14}}
\end{figure}

In suspension fired boilers, the biomass fuel, typically present as pellets, is pulverized and mixed with air. Subsequently, the air-fuel mixture is injected into the boiler through burners, where combustion takes place. A schematic representation of a suspension-fired boiler is provided in Figure 2.3. Compared to grate-fired boilers, suspension-fired boilers can be operated at higher steam temperatures (580 – 630 °C), resulting in higher electrical efficiencies (43 – 48%). Furthermore, the mass fraction of ash entrained in the flue gas is considerably high (80 – 95%).

In suspension-fired boilers, the fuel requires a considerable amount of pre-treatment (drying, milling, pelletizing, etc.), due to which the investment and operational costs are high. Ideally, the fuel should have a moisture content below 15% and a particle size below 1.5 mm.\textsuperscript{11}
2.3 Formation of fly ash

During combustion, the inorganic content in biomass undergoes several chemical and physical transformations, as shown in Figure 2.4. The volatile compounds are released into the gas phase (forming released ash), whereas the non-volatile residual ash particles may be entrained into the flue gas channel, forming fly ash. Since the flue gas cools down as it flows through the boiler, the inorganic released ash species (in vapor phase) may become supersaturated, resulting in homogeneous condensation (nucleation), forming submicron aerosol particles. Furthermore, the vapor species may undergo heterogeneous condensation on fly ash particles or existing aerosols. The formed aerosol particles may undergo coagulation, forming chain agglomerates, or be scavenged in-flight by the larger fly ash particles, effectively increasing the particle size of the fly ash/aerosol particles.
Therefore, the inorganic content in the flue gas may exist as vapor species, submicron aerosol particles, and larger fly ash particles.

**Figure 2.4** Transformation of biomass fuel to fly ash particles, aerosols and vapor species.

Compared to coal, the formation of aerosols in the flue gas is significantly higher when biomass fuels, especially straw, are fired, because of the relatively higher content of K and Cl in straw. The concentration of aerosols in the flue gas, predominantly consisting of KCl and K₂SO₄, may vary from 75 – 2000 mg/Nm³ in grate-fired boilers, firing straw, while measurements in suspension-fired boilers, cofiring coal and
stra, have revealed aerosol concentrations of 30 – 110 mg/Nm\(^3\).\(^{19,20}\) The formation of aerosols is initiated by homogeneous condensation of K\(_2\)SO\(_4\), occurring when the flue gas cools down to 900 °C.\(^{19,20}\) Thereafter, the aerosols grow in size by coagulation and heterogeneous condensation of K\(_2\)SO\(_4\) and KCl.

Potassium and Calcium species, such as KCl and CaO, present as released or residual fly ash, may react with SO\(_2\) in the flue gas.\(^{21-25}\) Sulfation of alkali chlorides may strongly influence ash deposition, corrosion and shedding in boilers.\(^{26}\) A few studies indicate that sulfation of KCl may reduce overall deposit growth in boilers.\(^{26}\) Investigations cofiring biomass with coal,\(^{27-29}\) elemental sulfur,\(^{30}\) ammonium sulfate,\(^{30-32}\) ferric sulfate,\(^{33,34}\) aluminum sulfate\(^{34,35}\) and ferrous sulfide\(^{36}\) have indicated that sulfation of KCl prior to deposit formation may reduce corrosion in boilers. However, heterogeneous sulfation of KCl in the deposit, resulting in the liberation of HCl or Cl\(_2\) may increase corrosion of superheater tubes.\(^{37}\) Furthermore, sulfation of KCl, in the presence of water vapor, leads to the formation of HCl, increasing emission of acidic species from the boiler. Further information on sulfation mechanisms, and the effect of sulfation of deposit formation, corrosion and shedding is provided in Chapter 6.

### 2.4 Fly ash deposition

The vaporized ash species and residual fly ash may form deposits on boiler surfaces via several different mechanisms, as illustrated in Figure 2.5. The vapor ash species may diffuse through the thermal boundary layer and condense heterogeneously on heat transfer surfaces through the thermal boundary layer. Deposition of submicron aerosol particles may occur via thermophoresis, Brownian motion or eddy diffusion.\(^{9,38,39}\) Deposition of larger fly ash particles primarily occurs via inertial impaction.

#### 2.4.1 Diffusion and condensation of vapors

When the ash vapor species in the flue gas approach the thermal boundary layer of a heat transfer surface, the vapors may heterogeneously condense on the heat transfer surface. The rate of deposit formation by condensation may be described by the following equation,\(^{9}\)

\[
\dot{C} = k_c (C_b - C_s) s
\]

where \(\dot{C}\) is the rate of deposit formation by condensation (kg/s), \(k_c\) is the mass transfer coefficient (m/s), \(s\) is the surface area of the probe (m\(^2\)), \(C_b\) and \(C_s\) are the concentration of the species in the bulk gas and at the heat transfer surface respectively (kg/m\(^3\)).

Deposits formed by condensation are usually observed on both the upstream and the downstream side of superheater steel tubes, and are typically formed during the initial stages of the deposit formation process,
when the temperature gradient in the thermal boundary layer is relatively large. Furthermore, deposits formed by condensation are characterized by a low porosity, forming strongly adherent deposits.

![Mechanisms of deposit growth](image)

**Figure 2.5 Mechanisms of deposit growth.**

### 2.4.2 Thermophoresis

Thermophoresis is a process by which particles are transported through a gas medium due to the presence of a temperature gradient. In the vicinity of a relatively cold heat transfer surface, a small ash aerosol particle is exposed to a temperature gradient. The particle experiences collisions from hot flue gas molecules with a greater kinetic energy, when compared to cold flue gas molecules, thereby inducing a net force and movement of particles towards the cold heat transfer surface.

The vaporized ash species in the flue gas may undergo homogeneous/heterogeneous condensation in the thermal boundary layer of the steel tube, resulting in the formation of submicron aerosol particles, followed by thermophoretic deposition. Similar to condensation, deposits formed by thermophoresis may be formed throughout the circumference of the tube. Thermophoretic models have indicated that deposit formation by thermophoresis is significant only for submicron particles, as the thermophoretic velocity sharply decreases with increasing particle size.
2.4 Fly ash deposition

2.4.3 Brownian motion and Eddy diffusion

Brownian motion is described as the random motion of particles in the gas phase, whereas eddy diffusion refers to diffusion occurring in turbulent systems due to the formation of eddies. However, models have indicated that the contribution of Brownian motion and Eddy diffusion towards overall deposit formation is small in most cases.

2.4.4 Inertial impaction

Deposition of larger fly ash particles (>10 µm) typically occurs by inertial impaction. Larger fly ash particles are unable to follow the flue gas streamlines around superheater tubes, detaching from the flow, and thereby impacting the deposit surface. Deposition of larger fly ash particles primarily occurs via inertial impaction, which is dependent on the concentration of fly ash in the flue gas, the flue gas and fly ash particle velocities, the impaction efficiency and the sticking probability of the fly ash particles to the boiler surface. The impaction efficiency can be described using models describing the flow of entrained particles around an obstacle.

The sticking probability of fly ash particles has been described by several models in literature. For ashes rich in Si, which behave as glasses, the sticking probability has been correlated with the viscosity of the ash, such that decreasing viscosity results in an increased sticking probability. However, for ashes rich in alkali salts, the melt fraction of the ash may be used to estimate the particle sticking probability, where increasing melt fraction results in an increased sticking probability. In the low temperature region of the boilers, where the ash predominantly exists as solid particles, deposition can be described using detailed models incorporating the viscoelastic behavior of ash particles, the particle size and velocity. A detailed description of the different sticking probability models in literature is provided in Chapter 3.

Inertial impaction has been identified to be the dominant mechanism of deposit formation in boilers. Furthermore, impaction deposits are coarse-grained and are predominantly formed on the upstream side of the tubes.

2.4.5 Slagging and fouling deposits

The deposits formed in boilers may broadly be classified as slagging or fouling deposits.

Slagging

Slagging deposits are primarily found in the combustion or furnace zone of the boiler, where the temperatures are relatively high and radiant heat transfer is dominant. As the deposit grows in size, the temperature at the outer surface of the deposit gradually increases. If the outer surface temperature of the
deposit reaches the melting temperature of the deposit, slagging deposits are formed.\textsuperscript{1} The molten layer is typically dominated by silicate or alkali species.\textsuperscript{1}

**Fouling**

Fouling deposits are often formed in the convective pass of the boiler. Fouling deposits formed in biomass boilers typically contain a dense inner layer, rich in alkali salts, and a porous outer layer containing larger fly ash particles. Fouling may lead to several operational problems in boilers, including erosion and corrosion of tube surfaces. In severe cases, fouling may completely block flue gas channels, causing expensive, unscheduled boiler shutdowns.

**2.5 Deposit consolidation and maturation**

The deposits in boilers may undergo sintering over time. Furthermore, chemical reactions may occur in the deposit, influencing deposit properties. The deposits may also induce corrosion at the deposit–tube interface.

**2.5.1 Sintering**

Sintering is a process by which particles in the deposit agglomerate, resulting in increased contact between deposit particles, and thereby a decrease in deposit porosity. The driving force for sintering is the lowering of the surface energy of the particles.\textsuperscript{1} Sintering increases the density and thermal conductivity of the deposits,\textsuperscript{48} thereby influencing heat transfer to the steam cycle. Sintering may occur through several mechanisms, as illustrated in Figure 2.6.

- **Liquid state sintering**: Liquid state sintering causes densification of deposits, due to the formation of a melt, which may form a neck between adjacent particles. If the deposit particles are viscoelastic (e.g., when the deposit is rich in silicates), liquid state sintering is typically referred to as viscous flow sintering.\textsuperscript{1,49}
- **Sintering by condensation**: In systems rich in alkali salts, vaporization and condensation of volatile species within the deposit may cause sintering. Material transfer may occur due to difference in surface curvature, and thereby a difference in vapor pressure.\textsuperscript{50} Material may be transferred from the surface of a particle (with a positive curvature, and thereby a higher vapor pressure) to the neck region connecting two adjacent particles (with a negative curvature, and thereby a lower vapor pressure).
2.5 Deposit consolidation and maturation

- **Chemical reaction sintering**: Chemical reaction sintering may occur when adjacent solid particles undergo a chemical reaction, resulting in the formation of a third component, which forms a neck between the particles.\(^1\) Furthermore, chemical reactions occurring between the particles and the components present in the flue gas (e.g., \(\text{SO}_2\)), may induce sintering of the deposits. In boilers, the K and Ca species in the deposit may undergo heterogeneous sulfation, which may cause sintering and corrosion.\(^{21,51}\) A detailed description and literature review of heterogeneous sulfation of boiler deposits is provided in Chapter 6.

- **Solid state sintering**: Solid state sintering occurs if material is transported to the neck area via diffusion along the particle surface, or diffusion through the bulk of the particle.\(^{1,50}\) Consequent changes in particle shape may result in densification.

![Mechanisms of sintering](image)

**Figure 2.6 Mechanisms of sintering.**\(^{1,52}\)

Sintering of deposits may result in the formation of strongly adherent deposits to the steel tube.\(^5\) Furthermore, sintering influences the thermal properties of the deposit, thereby influencing heat transfer across the deposit surface.\(^{48}\) Sintering increases the density and thermal conductivity of the deposits.\(^{48}\)

### 2.5.2 Corrosion

If the deposits contain chemically aggressive species, especially alkali salts, such as \(\text{KCl}\) and \(\text{K}_2\text{SO}_4\), the steel tubes may undergo severe corrosion. Potassium may react with the iron and chromium present in the steel tube to form \(\text{Fe}/\text{Cr}\) chlorides, oxides, chromates, sulfates, etc.\(^{4,53–56}\) Furthermore, heterogeneous
sulfation of boiler deposits may cause corrosion of steel tubes. In order to prevent corrosion, boilers are operated at lower steam temperatures, hindering the electrical efficiencies.

2.6 Shedding of ash deposits

Ash deposits hinder heat transfer to the steam cycle, and may block flue gas channels in severe cases, causing boiler shutdowns. Therefore, regular deposit removal is essential for optimal boiler operation.

Shedding of ash deposits may occur naturally during normal boiler operation, or it may be induced artificially, using techniques such as soot-blowing, cleaning by ultrasound, detonation waves, shot cleaning and rapping gears. Soot-blowing is the most commonly used technique for deposit shedding in coal, biomass and kraft recovery boilers. In soot-blowing, a jet containing steam, water or pressurized air is injected onto a deposit, inducing mechanical drag (in the direction of flow) and lift (perpendicular to the direction of flow) forces on the deposit, as well as thermal stresses on the deposit, as shown in Figure 2.7. As a result, the deposit may fall off, leaving a clean tube. However, soot-blowing may cause abrasion and erosion of boiler tubes, and consumes a large amount of high-pressure steam, which may otherwise be used in the steam cycle.

![Diagram of forces exerted by a soot-blower jet on a deposit](image)

**Figure 2.7** Forces exerted by a soot-blower jet on a deposit. $F_D$ and $F_L$ correspond to the drag and lift forces acting on the deposit.
2.6 Shedding of ash deposits

2.6.1 Mechanisms of deposit shedding

Deposit shedding may occur through several mechanisms, as described below.

- **Erosion:** Erosion occurs when non-sticky, relatively large and sharp edges fly ash particles collide with non-sticky regions of the deposit. If the deposits are ductile, they may undergo deformation, and if the deposits are brittle, they may experience cuts. Erosion is commonly found when the fly ash is rich in SiO$_2$, and occurs at the deposit surface.$^{149}$

- **Gravity shedding:** Gravity shedding occurs when the weight of the deposit exceeds the adhesion strength of the deposit to a boiler surface. Furthermore, if the weight of the deposit exceeds the cohesive forces keeping the deposit together, fractures may occur within the deposit. As a result, the deposit or a part of the deposit falls off.

- **Melting:** If the temperature at the deposit surface exceeds the melting temperature of the deposit, a molten slag may be formed, which flows off the deposit. Full-scale investigations have shown that melting is an important deposit shedding mechanism in straw-fired grate boilers.$^{159}$

- **Thermal shocks:** Deposit shedding may be induced through thermal fluctuations induced by soot-blowing or sudden cooling of superheater tubes caused by load changes. This may be attributed to differences in thermal expansion coefficients between the superheater tube, the deposit and the corrosion layer. If the oxide layer is not able to absorb rapid changes in the size of the deposit and the superheater tube, the deposit may fall off.

- **Mechanical shocks:** Mechanical fluctuations, typically induced by vibrations and momentum transfer during soot-blowing, may cause deposit shedding. A break may occur within the deposit or at the deposit–tube interface.

2.6.2 Position of deposit removal

Deposit removal may occur at the deposit–tube interface, within the deposit or at the surface of the deposit. An overview of the part of deposit where the deposit shedding takes place, with respect to the different shedding mechanisms is provided in Table 2.2. Full-scale investigations in suspension-fired boilers have revealed that the most commonly observed position of deposit removal is at the deposit–tube interface.$^{60}$ The process of deposit removal at the deposit–tube interface is known as debonding.
Table 2.2 Position of deposit removal, depending on the shedding mechanism.$^{1,64}$

<table>
<thead>
<tr>
<th>Position of deposit removal</th>
<th>Deposit–tube interface</th>
<th>Within the deposit</th>
<th>Deposit surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erosion</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Gravity shedding</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Melting</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Thermal shocks</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Mechanical shocks</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

2.6.3 Overview of lab-scale adhesion and compression strength investigations

Coal fly ash deposits

Previous lab-scale studies by Moza and Austin,$^{62,63}$ investigating the adhesion strength of coal ash deposits to steel surfaces, have indicated that the adhesion strength increased with increasing temperature (25 – 700 °C) of the steel surface. Furthermore, a sticking temperature was identified, where a sharp increase in adhesion strength was observed, suggesting that melting of the coal ash was essential for substantial adhesion. An increase in adhesion strength with increasing Ca content and decreasing Fe content in the coal ash was reported. Moreover, deposits formed on stainless steels (Cr = 18%, Ni = 8%) were weaker than deposits formed on mild steels (C = 0.2%, Mn = 0.5%), suggesting that the increased corrosion observed on mild steels increases adhesion strength.

Investigations by Raask$^{64}$ had indicated that the adhesion strength of coal ash deposits increased with time (0 – 25 days). Furthermore, the study reported an increased adhesion strength of coal ash to austenitic steels (Cr = 18%, Ni = 13%), when compared to ferritic steels (Cr = 9%). Several studies have investigated the compression strength of coal fly ash pellets,$^{65-68}$ concluding that increasing sintering temperatures (700 – 1100 °C) and increasing alkali content of the fly ash led to increased compression strengths.

Deposits from kraft recovery boilers

The adhesion strength of deposits in kraft recovery boilers has been investigated by Kaliazine et al.$^{58}$ The study reported that the adhesion strength of deposits increased with increasing surface temperature (250 – 425 °C), until the formation of a molten phase, after which the adhesion strength decreased (425 – 600 °C).
2.6  Shedding of ash deposits

°C). Furthermore, it was observed that the adhesion strength data roughly followed a lognormal distribution. Studies investigating the bend strength of pellets made from fireside deposits of kraft recovery boilers reported a similar observation, where the bend strength increased until the first melting temperature of ash, followed by a subsequent decrease in bend strength. Moreover, increasing sintering time (0 – 240 min) of the deposits led to a decrease in porosity and an increase in bend strength. Investigations simulating soot-blowing in kraft recovery boilers have suggested that the soot-blower jet drills through the impacting side of the deposit, inducing cracks, which propagate through the deposit.

**Biomass fly ash deposits**

The compression strength of pellets prepared from fly ash from a suspension boiler, co-fired with coal and straw, was investigated by Hansen et al. The study reported an increase in compression strength with increasing temperatures (850 – 1150 °C), with a sharp increase in compression strength at approximately 1000 °C. Furthermore, the compression strength increased with sintering time (0 – 12 hours), as well as melt fraction of the ash (0 – 30%). The increase in compression strength was attributed to liquid state sintering. A similar study, investigating the compression strength of pellets prepared from straw fly ash obtained from grate- and suspension-fired boilers, at temperatures from 25 – 900 °C, reported a higher compression strength for fly ash from the suspension-fired boiler, when compared to the fly ash from the grate-fired boiler.

Additional information on deposit adhesion strength can be found in Chapter 4 and Chapter 5.

**2.6.4 Overview of full-scale investigations of deposit shedding**

Bashir et al. investigated ash deposit shedding in a suspension-fired boiler, firing straw and wood. The study reported that natural deposit shedding, as well as deposit shedding induced by plant soot-blowing, increased with increasing flue gas temperatures (600 – 1050 °C). Investigations using an artificial soot-blowing probe indicated that the adhesion strength of deposits increased with increasing probe surface temperature (500 – 600 °C). Furthermore, the study identified that deposit shedding primarily occurred through debonding.

Investigations in straw grate-fired boilers, with a flue gas temperature of approximately 750 °C, have reported that increasing probe surface temperatures (400 – 550 °C) lead to strongly adherent deposits, requiring high soot-blowing peak impact pressures for removal. Debonding was identified as the primary mechanism of deposit shedding. However, investigations in grate-fired boilers, firing straw, have indicated that surface melting was the primary mechanism of deposit shedding from the superheaters, at temperatures greater than 1100 °C.
This chapter has been written in a manuscript format. A compressed version of this chapter, showing selected results, has been submitted to the peer-reviewed journal, *Proceedings of the Combustion Institute*. The remaining results will be published in the peer-reviewed journal, *Fuel*.

**Abstract**

Fly ash deposition on boiler surfaces is a major operational problem encountered in biomass-fired boilers. Reducing deposit formation is essential for maximizing boiler efficiency and availability. This study investigated deposit formation of biomass fly ash on steel tubes, in a lab-scale Entrained Flow Reactor. Experiments were conducted using model biomass fly ash, prepared from mixtures of $\text{K}_2\text{Si}_4\text{O}_9$, $\text{KCl}$, $\text{K}_2\text{SO}_4$, $\text{CaO}$, $\text{SiO}_2$ and $\text{KOH}$, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The fly ashes were injected into the reactor, to form deposits on an air-cooled deposit probe, simulating deposit formation on superheater tubes in boilers. The influence of flue gas temperature ($589 – 968 ^\circ\text{C}$), probe surface temperature ($300 – 550 ^\circ\text{C}$), flue gas velocity ($0.7 – 3.5 \text{ m/s}$), fly ash composition, fly ash flux ($10000 – 40000 \text{ g/m}^2/\text{h}$), fly ash particle size ($3.5 – 90 \text{ µm}$) and probe residence time (up to 60 min) was investigated. The results revealed that increasing flue gas temperature and probe surface temperature increased the sticking probability of the fly ash particles/deposit surface, thereby increasing the rate of deposit formation. However, increasing flue gas velocity resulted in a decrease in the deposit formation rate, due to increased particle rebound. Furthermore, the deposit formation rate increased with time, fly ash flux and fly ash particle size. A mechanistic model was developed for predicting deposit formation in the reactor. Deposit formation by thermophoresis and inertial impaction was incorporated into the model, and the sticking probability of the ash particles was estimated by accounting for energy dissipation due to particle deformation. The model reasonably predicted the influence of flue gas temperature and fly ash flux on the deposit formation rate. Inertial impaction was the primary mechanism of deposit formation, when pure $\text{K}_2\text{Si}_4\text{O}_9$, $\text{SiO}_2$ or $\text{CaO}$ was injected into the reactor, forming deposits only on the upstream side of the steel tube. However, feeding $\text{KCl}$, $\text{K}_2\text{SO}_4$ or $\text{KOH}$ into the reactor resulted in deposit formation on both sides of the steel tube, via condensation, thermophoresis, and inertial impaction. Addition of $\text{KCl}$ to $\text{K}_2\text{Si}_4\text{O}_9$, $\text{SiO}_2$, and $\text{CaO}$ resulted in an increased deposit formation rate, when compared to their respective weighted average deposit...
form. Moreover, addition of 10 wt % KOH to K$_2$Si$_4$O$_9$ in the model fly ash mixture resulted in a significant increase in the deposit formation rate. A low rate of deposit formation was observed for the wood fly ash, whereas a high rate of deposit formation was observed for the straw fly ash. Analysis of deposits obtained using a model fly ash containing KCl and K$_2$Si$_4$O$_9$ (50 wt %), using a Scanning Electron Microscope, revealed the presence of tiny KCl nuclei on K$_2$Si$_4$O$_9$ particles. Furthermore, the K$_2$Si$_4$O$_9$ particles in the deposit were glued together by molten KCl.

3.1 Introduction

Combustion of biomass for electricity and heat production is a promising solution for reducing net CO$_2$ emissions. Denmark is planning to phase out coal by 2030, with intentions to replace coal with biomass in pulverized fuel-fired power plants.\(^2\) However, the inorganic content in biomass causes several operational problems, including increased deposition of chemically aggressive ash species (such as KCl and KOH) on boiler surfaces. Ash deposits hinder heat transfer to steam cycle, thereby reducing boiler efficiency, and may completely block flue gas channels in severe cases, causing unscheduled boiler shutdowns.\(^1,3\) Moreover, ash deposition may cause severe corrosion of boiler surfaces.\(^4\) Therefore, reducing deposit formation is essential for maximizing boiler efficiency and availability.

During combustion, the inorganic content in solid fuels undergoes several chemical and physical transformations. The volatile compounds are released into the gas phase, whereas the non-volatile residual ash particles may be entrained into the flue gas channel, forming fly ash.\(^1,15\) Since the flue gas cools down as it flows through the boiler, it may become supersaturated with vapor species, resulting in either homogeneous condensation of vapors, forming submicron aerosol particles, or heterogeneous condensation of vapors on fly ash particles.\(^1,73\) The formation of aerosols is typically initiated by homogeneous condensation of K$_2$SO$_4$, followed by coagulation and heterogeneous condensation of K$_2$SO$_4$ and KCl.\(^19,20\) Therefore, the inorganic content in the flue gas may exist as vapor species, submicron aerosol particles, and larger (>10 µm) fly ash particles, which may subsequently form deposits on boiler surfaces.

The vapor species may undergo diffusion and heterogeneous condensation on heat transfer surfaces through the thermal boundary layer. Deposition of submicron aerosol particles may occur via thermophoresis, Brownian motion or eddy diffusion.\(^9,38,39\) Thermophoresis occurs when the ash particles experience collisions from the hot flue gas molecules with a greater kinetic energy, when compared to cold flue gas molecules, thereby inducing a net force and movement of particles towards the cold heat transfer surface. Furthermore, vapors in the flue gas may undergo homogeneous condensation in the thermal boundary layer, forming aerosol particles, which may undergo thermophoretic deposition.\(^39\)
Deposition of larger fly ash particles primarily occurs via inertial impaction, which is dependent on the concentration of fly ash in the flue gas (fly ash flux), the flue gas and fly ash particle velocities, the impaction efficiency and the sticking probability of the fly ash particles to the boiler surface. While detailed impaction efficiency models describing the flow of entrained particles around an obstacle exist in literature, quantification of the sticking probability has been a challenge. Simple sticking models correlate the sticking probability, $\eta(T)$, with the viscosity of the particles and the surface of the deposit, where decreasing particle/deposit surface viscosity results in an increased sticking probability, as shown below,

$$\eta(T) = \begin{cases} \frac{\mu_{\text{ref}}}{\mu} & \mu > \mu_{\text{ref}} \\ 1 & \mu \leq \mu_{\text{ref}} \end{cases}$$

(3.1)

where $\mu$ is the viscosity of the particle/deposit surface, and $\mu_{\text{ref}}$ is a reference viscosity, such that particles (or deposit surface) with viscosities lower than the reference viscosity are perfectly sticky. The net mass fraction of the impacting particles undergoing deposition, $f_{\text{dep}}$, is a function of the sticking probability of the ash particles, and the deposit surface, as shown below,

$$f_{\text{dep}} = p(T_g) + p(T_s)[1 - p(T_g)]$$

(3.2)

where $T_g$ and $T_s$ are the gas and deposit surface temperatures, and the gas temperature is assumed to be equal to the particle temperature.

Viscosity based models are unable to accurately predict the sticking probability when the ash composition is dominated by alkali salts. Alkali salts may form a melt and alter the ash sticking behavior. In such cases, the sticking probability may be empirically expressed as a function of the melt fraction of the particle/deposit surface ($f_{\text{melt}}$), where the sticking probability increases with increasing melt fraction, as shown below,

$$\eta(T) = \begin{cases} 0 & 0 \leq f_{\text{melt}} < 0.1 \\ 1.67 \cdot f_{\text{melt}} - 0.167 & 0.1 < f_{\text{melt}} < 0.7 \\ 1 & 0.7 < f_{\text{melt}} \leq 1 \end{cases}$$

(3.3)

In the low temperature region of the boilers, where the ash predominantly exists as solid particles, deposition can be described using detailed models incorporating the viscoelastic behavior of ash particles, the particle size and velocity. When viscoelastic particles collide with the deposit, they deform and dissipate energy. If the kinetic energy of the impacting particles is greater than the energy dissipated, the particles rebound from the deposit surface. Such models define a critical velocity of the incoming particle ($u_{p,\text{crit}}$) as a function of the diameter ($d_p$), density ($\rho_p$), interface energy (surface tension) ($\Gamma$)
and Young’s modulus ($E$) of the particles, such that deposition occurs if the particle velocity is lower than the critical velocity.

$$u_{p,\text{crit}} = \left(\frac{2\gamma}{\rho_p} \right)^{5/6} \left(\frac{\rho_p^2 E^2}{\nu P_{\text{f}}}\right)^{1/6}$$  \hspace{1cm} (3.4)

Several experimental investigations quantifying deposit formation in full-scale grate-fired\textsuperscript{59,75} and suspension-fired\textsuperscript{47,76–78} boilers, have been identified in literature. However, owing to the fluctuating conditions in full-scale boilers, the experimental data cannot be used to quantify the effect of operating conditions and ash chemistry on particle/deposit sticking probability, or to accurately validate deposit build-up models. Furthermore, pilot-scale and lab-scale investigations\textsuperscript{29,79–88} understanding deposit formation in biomass and kraft recovery boilers exist in literature. However, most of the investigations involve combustion of a fuel prior to deposit formation, introducing uncertainties in ash chemistry and particle size. The literature lacks fundamental and comprehensive investigations quantifying the effect of different operating conditions and ash chemistry on deposit build-up at conditions relevant for biomass-fired boilers.

The present study quantifies ash deposition on steel tubes in an Entrained Flow Reactor, at conditions simulating full-scale biomass-fired boilers. Experiments were conducted using model biomass fly ash, prepared from mixtures of $K_2Si_4O_9$, KCl, $K_2SO_4$, CaO, SiO\textsubscript{2} and KOH, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The fly ashes were injected into the reactor, to form deposits on an air-cooled deposit probe. The influence of flue gas temperature, probe surface temperature, flue gas velocity, fly ash composition, fly ash flux, fly ash particle size and probe residence time was investigated. Furthermore, selected deposit samples were analyzed using a Scanning Electron Microscope.

3.2 Experimental section

3.2.1 Materials

Simulating the composition of typical biomass fly ash, experiments were carried out with model fly ash, prepared using mixtures of $K_2Si_4O_9$ (Alfa Aesar, CAS number: 1312-76-1), KCl (Sigma Aldrich, CAS number: 7447-40-7), $K_2SO_4$ (Sigma Aldrich, CAS number: 7778-80-5), CaO (Sigma Aldrich, CAS number: 1305-78-8), SiO\textsubscript{2} (Sigma Aldrich, CAS number: 60676-86-0) and KOH (Sigma Aldrich, CAS number: 1310-58-3). Furthermore, experiments were carried out using straw fly ash from a grate-fired boiler (Avedøreværket unit 2, 100 MW\textsubscript{th}), a wood fly ash from a suspension-fired boiler (Avedøreværket unit 2, 800 MW\textsubscript{th}), and
a straw + wood cofired fly ash from a suspension-fired boiler (Amagerværket unit 1, 350 MWth, straw share in feed ≈ 10%). The fly ashes were obtained from the electrostatic precipitator or bag filter of the boilers. The fly ash properties are provided in Table 3.1. The median particle sizes were measured using a wet dispersion in a Malvern Mastersizer 3000. The straw fly ash was dominated by agglomerated KCl and K2SO4, whereas the main elements in the straw + wood cofired fly ash were Ca, Si and K. Compared to the straw + wood cofired fly ash, the wood fly ash had a lower content of K and a higher content of Si.

Table 3.1 Composition, particle size and melting point analysis of the investigated fly ashes.

<table>
<thead>
<tr>
<th>Elemental composition (wt %, dry basis)</th>
<th>straw fly ash, grate-fired</th>
<th>straw + wood cofired fly ash, suspension-fired</th>
<th>wood fly ash, suspension-fired</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>–</td>
<td>2</td>
<td>2.13</td>
</tr>
<tr>
<td>Ca</td>
<td>1.3</td>
<td>20</td>
<td>20.8</td>
</tr>
<tr>
<td>Cl</td>
<td>19</td>
<td>1.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.044</td>
<td>1.4</td>
<td>1.73</td>
</tr>
<tr>
<td>K</td>
<td>43</td>
<td>9.1</td>
<td>6.26</td>
</tr>
<tr>
<td>Mg</td>
<td>0.12</td>
<td>3.3</td>
<td>3.22</td>
</tr>
<tr>
<td>Na</td>
<td>0.9</td>
<td>0.9</td>
<td>0.43</td>
</tr>
<tr>
<td>P</td>
<td>–</td>
<td>1.4</td>
<td>1.09</td>
</tr>
<tr>
<td>S</td>
<td>7.9</td>
<td>1.5</td>
<td>1.08</td>
</tr>
<tr>
<td>Si</td>
<td>1.1</td>
<td>12</td>
<td>17.7</td>
</tr>
<tr>
<td>Ti</td>
<td>–</td>
<td>0.14</td>
<td>–</td>
</tr>
<tr>
<td>Mn</td>
<td>0.059</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Deformation temperature89 (°C)</td>
<td>640</td>
<td>1240</td>
<td>1220</td>
</tr>
<tr>
<td>Hemispherical temperature89 (°C)</td>
<td>640</td>
<td>1250</td>
<td>1230</td>
</tr>
<tr>
<td>Fluid temperature89 (°C)</td>
<td>760</td>
<td>1260</td>
<td>1240</td>
</tr>
<tr>
<td>Median particle size (μm)</td>
<td>51.7</td>
<td>44.5</td>
<td>34.7</td>
</tr>
</tbody>
</table>

K2Si4O9 particle size measurements were performed using a Malvern Mastersizer 3000, and the measurements were performed on wet and dry dispersions of the particles. Wet measurements, where the
particles are dispersed in water, break down agglomerates, resulting in true particle size measurements. However, dry measurements retain particle agglomerates, revealing cluster diameters. The particle size distribution of $K_2Si_4O_9$ is provided in Figure 3.1. The volume-median particle diameter ($D_{50}$) of the wet dispersion was 13.2 µm ($D_{10} = 3.47$ µm, $D_{90} = 29.7$ µm), whereas the volume-median particle diameter ($D_{50}$) of the dry dispersion was 62.3 µm ($D_{10} = 7.31$ µm, $D_{90} = 272$ µm). KCl, $K_2SO_4$, CaO, SiO$_2$ and KOH were milled and sieved individually to obtain particle sizes lower than 32 µm. The sieving process was subjected to rigorous shaking, in the presence of magnetic balls for negating static charges, and thereby breaking down agglomerates. However, it should be noted that fly ash in boilers typically forms a bimodal particle size distribution, containing submicron particles, as well as larger particles with sizes up to 200 µm.$^{38,90}$

![Particle size distribution of the investigated $K_2Si_4O_9$, obtained using Malvern Mastersizer 3000.](image)

**Figure 3.1** Particle size distribution of the investigated $K_2Si_4O_9$, obtained using Malvern Mastersizer 3000. *Wet dispersion: $D_{10} = 3.47$ µm, $D_{50} = 13.2$ µm, $D_{90} = 29.7$ µm. Dry dispersion: $D_{10} = 7.31$ µm, $D_{50} = 62.3$ µm, $D_{90} = 272$ µm.*

$K_2Si_4O_9$ was subjected to Differential Scanning Calorimetry (DSC), revealing that $K_2Si_4O_9$ forms a glass phase at 650 °C, after which the viscosity of $K_2Si_4O_9$ decreases with increasing temperature.$^{91}$ Additionally, Optical Dilatometry was carried out on cylindrical $K_2Si_4O_9$ pellets. The variation of normalized projected area and height of the pellet with temperature is provided in Figure 3.2a. The ash melting analysis of $K_2Si_4O_9$, quantifying the shrinkage starting temperature, maximum shrinkage temperature, deformation
temperature, hemispherical temperature and flow temperature is provided in Table 3.2. It was observed that the pellet started shrinking above 520 °C, while retaining its cylindrical shape (see Figure 3.2c, 3.2d). However, at 710 °C, the pellet began to deform, resulting in a spherical shape, while maintaining an obtuse contact angle with the ceramic surface (see Figure 3.2e, 3.2f). Eventually, the pellet spread out over the supporting tile, with a flow temperature corresponding to 1142 °C (see Figure 3.2g).

![Figure 3.2](image)

**Figure 3.2** Optical Dilatometry of $K_2Si_4O_9$. (a) Variation of normalized projected area and height with temperature. Images of pellet at (b) room temperature, (c) shrinkage starting temperature, (d) maximum shrinkage temperature, (e) deformation temperature, (f) hemispherical temperature and (g) flow temperature. Analysis performed using cylindrical pellets with a height of 10.9 mm, diameter of 8 mm, mass of 0.9161 g, at a heating rate of 5 K/min.

**Table 3.2** Ash melting analysis of $K_2Si_4O_9$, obtained using Optical Dilatometry.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrinkage starting temperature</td>
<td>520</td>
</tr>
<tr>
<td>Maximum shrinkage temperature</td>
<td>633</td>
</tr>
<tr>
<td>Deformation temperature</td>
<td>710</td>
</tr>
<tr>
<td>Hemispherical temperature</td>
<td>852</td>
</tr>
<tr>
<td>Flow temperature</td>
<td>1142</td>
</tr>
</tbody>
</table>
XRD analysis was performed on $K_2Si_4O_9$, revealing that the investigated $K_2Si_4O_9$ was completely amorphous. The majority of biomass fly ashes and deposits contain significant quantities of amorphous materials, including silicates, characterized by their viscoelastic behavior, justifying the use of $K_2Si_4O_9$ for experimental analysis.

### 3.2.2 Experimental Setup

Simulating the deposit formation process in biomass-fired boilers, experiments were carried out in an Entrained Flow Reactor (EFR). The setup consisted of a gas supply system, a screw feeder for injecting solids, a gas preheater, a 2 m long electrically heated furnace, and a fly ash deposition system comprising of an air-cooled deposit probe. A schematic representation of the setup is shown in Figure 3.3. A detailed description of the EFR may be found in previously published literature.

![Figure 3.3 Schematic representation of the Entrained Flow Reactor.](image-url)
The model fly ash was mixed with a primary air stream (15 NL/min), and fed into the furnace using the screw feeder. Subsequently, the inlet stream was mixed with preheated secondary air, with a maximum flow rate of 200 NL/min. The secondary air could be preheated up to 1100 °C, while the walls of the furnace could be heated up to 1450 °C. Furthermore, a purge air stream (5 NL/min) was injected into the furnace through the heating element chambers, in order to protect the heating elements from corrosion.

The model fly ash may undergo physical and chemical transformations in the furnace. It should be noted that the particle and gas temperatures in the furnace might be slightly lower than the temperature of the furnace walls. Furthermore, it was assumed that the particles in the furnace were perfectly entrained in the gas flow, resulting in equal particle and gas velocities. The terminal velocity of the $\text{K}_2\text{Si}_3\text{O}_9$ particles was estimated to be 0.38 % of the gas velocity, using the Wen and Yu drag model, justifying the aforementioned assumption.

![Diagram of air-cooled deposit probe](image)

**Figure 3.4** Air-cooled deposit probe. Deposits are formed on the steel tube mounted on the probe.

After the furnace, the entrained flow entered a bottom chamber, where the model fly ash formed deposits on a steel tube (type 316), simulating deposit formation on the first row of platen superheater tubes in boilers. Type 316 steel is commonly used in heat transfer surfaces in boilers, with its high Cr and Ni content providing superior corrosion resistance. For each experiment, the steel deposit tubes were used as received, without any pre-oxidization. The steel tube, with an outer diameter of 10 mm, a thickness of 1 mm, and a length of 140 mm, was mounted on a retractable annular cooled probe (diameter of 8 mm), as
shown in Figure 3.4. The probe was cooled using air preheated to 200 °C. Thermocouples were mounted on the outer surface of the deposit probe (and thereby, in contact with the inner surface of the steel tube), and the temperature at the axial centerline of the reactor (referred to as probe surface temperature, see Figure 3.4) was controlled electronically. The cooling probe surface temperature is analogous to steam temperature in boilers. It should be noted that the temperature at the external surface of the steel tube would be slightly higher than the cooling probe surface temperature. The difference between steel surface temperature and steam temperature in full-scale boilers is approximately 20 – 50 °C.5,100

It should be noted that a horizontal temperature gradient was present across the deposit probe. The temperature on the deposit probe 40 mm away from either side of the axial centerline of the reactor (ΔT, see Figure 3.4) was typically 50 °C lower than the (central) probe surface temperature.

The bottom chamber of the EFR was water-cooled, resulting in a decrease in the flue gas temperature. Therefore, the flue gas temperature in the bottom chamber was measured by replacing the deposit probe with a suction pyrometer. It should be noted that the fly ash particles might not cool down as rapidly as the flue gas, possibly resulting in higher particle temperatures, when compared to the measured flue gas temperature in the bottom chamber.

The fly ash deposition process was recorded by a high-speed camera, mounted on a port in the bottom chamber (see Figure 3.3). After deposit formation for a specified duration, the deposit probe was retracted out, and the deposit was removed and weighed.

### 3.2.3 Experimental Conditions

Baseline experiments were performed at a furnace temperature of 1100 °C, resulting a flue gas temperature of 781 °C, a probe surface temperature of 475 °C, a flue gas velocity of 1 m/s, a fly ash feeding rate of 100 g/h, corresponding to a fly ash concentration of 26.57 g/Nm³ and an ash flux of 20412 g/m²/h, using pure K₂Si₄O₉ for 15 min. In other experiments, the flue gas temperature was varied from 589 to 968 °C, the probe surface temperature was varied from 300 to 550 °C, the flue gas velocity was varied from 0.7 to 3.5 m/s, and the fly ash flux was varied from 10000 to 40000 g/m²/h. Fly ash particles with sizes from 3.5 to 90 µm were investigated up to a deposition time of 60 min.

Typical superheater steam temperatures in biomass-fired boilers range from 440 – 580 °C, while the flue gas temperatures in the superheater/tube bank region range from 580 – 1300 °C.76,92,100,101 The velocity of flue gas in full-scale boilers ranges from 4 – 8 m/s. 38,76 However, since the diameter of the steel tube (10 mm) in the experiments was smaller than the typical diameter of superheater tubes in full-scale boilers (around 40 mm), lower gas velocities were adopted during the experiments in order to maintain a similar degree of Stokes number. The typical fly ash flux in biomass boilers varies from 10000 to 60000 g/m²/h.92
with the higher values observed during coal ash addition. In order to maintain a similar degree of fly ash flux in the experimental setup, higher fly ash concentrations were adopted in the experiments (13 – 53 g/Nm$^3$), compared to typical fly ash concentrations in full-scale biomass-fired boilers (1 – 6 g/Nm$^3$).

### 3.3 Deposit Formation Model

A mechanistic deposit formation model was developed to simulate deposit formation of K$_2$Si$_4$O$_9$ in the reactor. The model incorporated deposit formation by thermophoresis and inertial impaction of K$_2$Si$_4$O$_9$ particles, while deposit formation by condensation was neglected due to the absence of vapor species in the gas phase.

\[
\frac{dm(t, \theta)}{dt} = \dot{T}(t, \theta) + \dot{I}(t, \theta)
\]  
(3.5)

where $m$ is the mass of the deposit (kg), $t$ is the time (sec), and $\theta$ is the angular position (radians).

The rate of deposit formation by thermophoresis ($\dot{T}(t, \theta)$) was described using Equation 3.6$^{102}$

\[
\dot{T}(t, \theta) = u_r(\theta) \cdot C \cdot s(\theta)
\]  
(3.6)

where $u_r$ is the thermophoretic velocity (m/s), dependent on the particle size, Knudsen’s number, temperature gradient, and gas/particle thermal conductivities, $C$ is the concentration of K$_2$Si$_4$O$_9$ (kg/m$^3$), and $s$ is the surface area of the deposit (m$^2$).

The rate of deposit formation by inertial impaction $\dot{I}(t, \theta)$ was described using Equation 3.7$^{103}$

\[
\dot{I} = u_g \cdot C \cdot \eta_t(\theta) \cdot \eta_s(\theta) \cdot s(\theta)
\]  
(3.7)

where $u_g$ is the gas velocity (m/s), $\eta_t$ is the local collision efficiency of each particle, and $\eta_s$ is the sticking probability of the ash particles. Since the K$_2$Si$_4$O$_9$ particles are viscoelastic in nature, the sticking probability of ash particles was estimated by accounting for energy dissipation due to particle deformation. The critical velocity of the incoming particles ($u_{p,crit}$) was calculated$^{104}$ such that

\[
\eta_s = \begin{cases} 
0 & u_p \cdot \sin(\alpha_{\text{impact}}) > u_{p,crit} \\
1 & u_p \cdot \sin(\alpha_{\text{impact}}) \leq u_{p,crit}
\end{cases}
\]  
(3.8)

where $u_p$ is the particle velocity (m/s) and $\alpha_{\text{impact}}$ is the angle of impaction (radians).
The critical velocity of the incoming particle is a function of the particle diameter \(d_p\), particle density \(\rho_p\), interface energy (surface tension) \(\Gamma\) and equivalent Young’s modulus \(E\).\(^{105}\)

\[
u_{p,exit} = \left(\frac{2\Gamma}{d_p}\right)^{\frac{5}{6}} \left(\rho_p E^2\right)^{\frac{1}{6}}
\]

\[
\frac{1}{E} = \frac{1-\nu^2}{E_{\text{particle}}} + \frac{1-\nu^2}{E_{\text{deposit}}}
\]

where \(\nu\) is the Poisson’s ratio. The Young’s modulus was estimated as \(E = A \cdot \exp(-BT)\), where \(A = 5 \cdot 10^{13}\) and \(B = 0.01208\) are empirical constants obtained from literature.\(^{106}\)

Furthermore, the model incorporated heat transfer across the deposit layer and the steel tube, as described by Equation 3.11.

\[
\frac{k_{\text{tube}}}{\delta_{\text{tube}}} (T_{\text{tube}} - T_{\text{probe}}) = \frac{k_{\text{deposit}}}{\delta_{\text{deposit}}} (T_{\text{deposit}} - T_{\text{tube}}) = h_{\text{gd}} (T_{\text{gas}} - T_{\text{deposit}}) + \varepsilon \sigma \left(T_{\text{gas}}^4 - T_{\text{deposit}}^4\right)
\]

\(T_{\text{gas}}\) is the gas temperature, whereas \(T_{\text{deposit}}\), \(T_{\text{tube}}\), and \(T_{\text{probe}}\) are the temperatures at the surface of the deposit, steel tube and probe (K). \(k\), \(\delta\), \(h\), \(\varepsilon\), and \(\sigma\) refer to the thermal conductivity (W/mK), thickness (m), heat transfer coefficient (W/m\(^2\)K), emissivity, and Stefan Boltzmann constant (W/m\(^2\)K).

The particles were assumed to be isothermal, with the corresponding heat transfer equation described in Equation 3.12.

\[
\rho_p \left(\frac{\pi}{6} d_p^3\right) C_p \frac{dT_{\text{particle}}}{dt} = h_{\text{gd}} \left(\pi d_p^2\right) (T_{\text{gas}} - T_{\text{particle}}) + \varepsilon \sigma \left(\pi d_p^2\right) \left(T_{\text{gas}}^4 - T_{\text{particle}}^4\right)
\]

\(\rho_p\), \(C_p\), \(d_p\), and \(T_{\text{particle}}\) refer to the particle density (kg/m\(^3\)), specific heat capacity (J/kgK), diameter (m), and temperature (K).

It was assumed that the particles in the furnace were perfectly entrained in the gas flow, resulting in equal particle and gas velocities. The terminal velocity of the K\(_2\)Si\(_4\)O\(_9\) particles was estimated to be 2% of the gas velocity, using the Wen and Yu drag model,\(^{96}\) justifying the aforementioned assumption. The particle
3.4 Results and Discussion

3.4.1 Effect of Flue Gas Temperature

The effect of flue gas temperature on $K_2Si_4O_9$ deposit formation rate is shown in Figure 3.5. It was observed that the deposit formation rate increased with increasing flue gas temperature at the investigated conditions. Visual observations of the formed deposits (see Figure 3.5) revealed that deposits were formed only on the upstream side of the steel tube, suggesting that $K_2Si_4O_9$ deposition occurred primarily via inertial impaction, under the investigated conditions. Studies on deposit formation in full-scale boilers have also identified inertial impaction as the primary mechanism of deposit formation.\textsuperscript{5,38,74} Increasing the flue gas temperature decreased the viscosity/Young's modulus of the $K_2Si_4O_9$ particles, thereby resulting in stickier particles, and increasing deposit formation via inertial impaction. The results were reproducible with a relative standard error of 4\%, based on 5 repetitions of the baseline experiments.

The experimental results agree with full-scale investigations,\textsuperscript{76} where increasing flue gas temperatures led to increased deposit formation. Furthermore, it was observed that increasing the flue gas temperature in the experiments resulted in increased adhesion strength of the deposits to the steel tube, corroborated by subsequent adhesion strength investigations (see Chapter 4 and Chapter 5).\textsuperscript{91}

The deposit formation model was able to predict the influence of flue gas temperature on the observed deposit formation rates with an accuracy ($R^2$) of 94\% (see Figure 3.5), suggesting a fairly accurate representation of the sticking probability of the fly ash particles.
Figure 3.5 Effect of flue gas temperature and probe surface temperature on the deposit formation rate. Experiments performed with K$_2$Si$_4$O$_9$ with a median particle size of 13.2 µm, flue gas velocity of 1 m/s, fly ash flux of 20412 g/m²/h for 15 min. Flue gas temperature at the deposit probe during variation of probe surface temperature = 781 °C. Probe surface temperature during variation of flue gas temperature = 475 °C. Images captured at the end of the experiments.
3.4 Results and Discussion

3.4.2 Effect of Probe Surface Temperature

Figure 3.5 shows the effect of probe surface temperature on the deposit formation rate. It was observed that increasing the probe surface temperature from 300 °C to 450 °C increased the deposit formation rate at the investigated conditions. Further increase in probe surface temperature up to 550 °C did not influence the rate of deposit formation significantly.

Increasing the probe surface temperature led to increased temperatures at the surface of the deposit, thereby decreasing the corresponding viscosity/Young’s modulus. This resulted in an increased sticking probability of the deposit surface, causing increased deposit formation. However, it appears that increasing the probe surface temperature from 450 – 550 °C did not influence the sticking probability of the deposit surface at the investigated experimental conditions. Quantification of the temperature at the surface of the deposit is essential for understanding of the effect of probe surface temperature on the rate of deposit formation.

The results suggest that increasing steam temperatures in boilers might increase deposit formation. However, after a certain steam temperature, determined by the thermal properties of the deposits, a further increase in the steam temperatures might not influence the rate of deposit formation. The results concur with a previous investigation in literature, where varying probe surface temperatures from 475 – 650 °C had a negligible effect on deposition rate of peat and straw. Nevertheless, it should be noted that high steam temperatures might lead to severe corrosion of the superheater tubes in boilers.

The model was unable to accurately predict the influence of probe surface temperature (see Figure 3.5), especially from 300 – 400 °C, suggesting that the sticking probability of the deposit surface requires a more accurate representation in the model. Furthermore, the deviations may have emanated from the heat transfer equations in the model, which do not account for the decrease in local gas temperatures induced by the cooling probe, especially when the probe surface temperature is maintained at 300 °C. CFD simulations of the deposit formation process in the EFR may provide more accurate model predictions. The model predicts a decrease in the deposit formation rate with increasing probe surface temperature, due to a decrease in the estimated thermophoretic deposition with reducing temperature gradients in the thermal boundary layer.

3.4.3 Effect of Flue Gas Velocity

Figure 3.6 shows the effect of flue gas velocity on the deposit formation rate for flue gas temperatures of 781 and 968 °C. At a flue gas temperature of 781 °C, it was observed that increasing the flue gas velocity from 0.7 – 3 m/s gradually decreased the deposit formation rate, with a relatively sharp decrease observed between 1 – 1.6 m/s. However, at a flue gas temperature of 968 °C, the deposit formation rate remained
relatively constant from 1 – 3 m/s, and decreased in value from 3 – 3.5 m/s. Furthermore, it was observed that the thickness of the formed deposits decreased with increasing mean flue gas velocity (see Figure 3.6). At a mean gas velocity of 3.5 m/s and a flue gas temperature of 968 °C, it was observed that the parabolic flow profile of the flue gas was seemingly projected on the deposit surface. The flow in the furnace was laminar in nature, with Reynolds numbers ranging from 435 to 1863 under the investigated conditions. However, the Reynolds number in the bottom chamber may be larger, because of the corresponding expansion geometry.

Increasing the flue gas velocity, and thereby the particle velocity, increases the kinetic energy of the impacting particles. If the particle velocity exceeds the critical velocity of impaction, the particle is unable to dissipate its kinetic energy, and rebounds from the deposit after impaction.

The experimental observations suggest that the critical velocity of the K₂Si₄O₉ particles at a flue gas temperature of 968 °C was greater than the critical velocity at 781 °C, indicating that the critical velocity increased with increasing temperature at the investigated conditions. Since the Young’s modulus is a function of viscosity, decreasing in value with increasing temperature, the critical velocity should typically increase with increasing temperature.

The model predicted a gradual decrease in the deposit formation rate with increasing flue gas velocity (see Figure 3.6), with an accuracy (R²) of 38%. However, the model was unable to predict the sharp decrease in deposit formation rate at 1 m/s and 781 °C, and at 3 m/s and 968°C, probably because the model assumed a uniform plug flow in the furnace. Furthermore, agglomeration of particles in the furnace/screw feeder have not been accounted for in the model.

For particle diameters from 10 – 100 µm, at baseline conditions, the model predicted critical velocity varied from 1.4 – 0.23 m/s. These values agree with previous experimental investigations (1.2 – 0.1 m/s) in literature. 44,109–112
3.4 Results and Discussion

Figure 3.6 Effect of flue gas velocity on the deposit formation rate. Experiments performed with $K_2Si_4O_9$ with a median particle size of 13.2 µm, probe surface temperature of 475 °C, fly ash flux of 20412 g/m²/h for 15 min. Images captured at the end of the experiments.
3.4.4 Effect of Probe Residence Time

The effect of probe residence time on deposit formation rate can be seen in Figure 3.7. The deposit formation rate increased with time up to 30 min, at the investigated conditions. However, further increase in time did not significantly influence the deposit formation rate.

As the deposit grew in size, the temperature at the surface of the deposit increased. This resulted in a corresponding decrease in the viscosity/Young’s modulus at the surface of the deposit, thereby increasing the sticking probability of the deposit surface. Therefore, the fraction of impacting particles undergoing deposition increased over time. However, the growth rate of the deposit remained constant after 30 min of deposition. Further investigation, quantifying the temperature history of the deposit surface, is required to better understand the deposit formation process. Nevertheless, the results highlight the importance of a sticky surface for deposit build-up via inertial impaction, suggesting that the rate of deposit formation on superheater tubes progressively increases as initial deposits are formed. The results are consistent with the experiments in Section 3.4.2, suggesting that the deposit formation rate may not further increase above a certain temperature at the surface of the deposit.

The model predicted a relatively linear increase in the deposit formation rate with time (see Figure 3.7), with an accuracy ($R^2$) of 39%. However, the model is not able to predict the saturation in deposit formation rate after 30 min, probably due to an inaccurate representation of the sticking probability of the deposit surface and/or the heat transfer model.

Due to high temperatures at the deposit surface, sintered deposits could be observed for experiments performed longer than 30 min. Furthermore, natural shedding events were observed when experiments longer than 60 min were conducted. The large deposits were unstable, breaking away from the steel tube at the deposit–tube interface. A video of deposit formation and shedding on the steel tube at the baseline conditions can be accessed via this link: [youtu.be/gLSHd8fAZo0](youtu.be/gLSHd8fAZo0) The results concur with previous investigations, establishing debonding as the dominant mechanism of deposit shedding in boilers.
Figure 3.7 Effect of time and fly ash flux on the deposit formation rate. Experiments performed with $K_2Si_4O_9$ with a median particle size of 13.2 µm, flue gas temperature of 781 °C, probe surface temperature of 475 °C, and gas velocity of 1 m/s. Fly ash flux during variation of time = 20412 g/m²/h. Time during variation of fly ash flux = 15 min. Images captured at the end of the experiments.
3.4.5 Effect of Fly Ash Flux

The effect of fly ash flux on deposit formation rate can be seen in Figure 3.7. The deposit formation rate increased linearly with increasing fly ash flux at the investigated conditions. Increasing fly ash flux increased the total number of particles impacting the steel tube, thereby resulting in a corresponding increase in the deposit formation rate. The results agree with deposit formation models in literature, as well as full-scale investigations, which predict a linear increase in the rate of deposit formation via inertial impaction with increasing ash flux.

The model was able to predict the increase in deposit formation rate with increasing ash flux, with an accuracy (R²) of 86%.

3.4.6 Effect of Fly Ash Particle Size

In order to understand the effect of fly ash particle size, experiments were conducted with K₂Si₄O₉ with a volume-median particle diameter (D₅₀) of 13.2 µm (D₁₀ = 3.47 µm, D₉₀ = 29.7 µm, wet dispersion, particle size distribution in Figure 3.1), and compared with K₂Si₄O₉ with a particle size distribution bounded by 32 and 90 µm. The larger particles were obtained by heating K₂Si₄O₉ to 800 °C to form a glass phase, which was subsequently cooled down, milled and sieved, to obtain particle sizes between 32 and 90 µm.

![Figure 3.8](image.png)

**Figure 3.8** Effect of fly ash particle size on the deposit formation rate. Experiments performed with K₂Si₄O₉ with a flue gas temperature of 968 °C, probe surface temperature of 475 °C, gas velocity of 1 m/s, fly ash flux of 20412 g/m²/h for 15 min. Images captured at the end of the experiments.
3.4 Results and Discussion

It was observed that increasing the particle size caused increased deposit formation at the investigated conditions, as seen in Figure 3.8. Increasing the particle size resulted in an increase in the Stokes number, as a result of which more ash particles impacted the steel tube. Larger particles are less likely to follow the gas streamlines around the steel tube, detaching from the flow, and thereby impacting the deposit surface. This effectively increased the total mass of impacting particles, thereby increasing the rate of deposit formation.

It should be noted that increasing the particle size induced a reduction in the total number of particles injected into the furnace per unit time, since the ash flux was maintained at 20412 g/m²/h for the experiments. Furthermore, the effect of submicron particles in the fly ash has not been investigated in this study.

Possible agglomeration of particles in the screw feeder and the furnace was not accounted for in this study. As shown in Figure 3.1, agglomeration may significantly increase the effective particle size. Furthermore, the particle size measurement techniques for the smaller (3.4 – 29.7 µm) and larger (32 – 90 µm) particle size groups were different (Malvern Mastersizer vs sieves). The particle size distribution of the larger particle size group was not measured using the Malvern Mastersizer. Therefore, model predictions for the larger particle size group could not be obtained. Further investigation is required to completely understand the effect of particle size on deposit formation.

3.4.7 Effect of Fly Ash Composition

Model fly ash from pure compounds

The effect of fly ash composition on deposit formation is shown in Figure 3.9. It was observed that fly ash containing pure KCl had a greater rate of deposit formation, compared to K₂Si₄O₉ at the investigated conditions. Visual observations of the KCl deposit (see Figure 3.9) revealed deposition on both the upstream and the downstream side of the steel tube, suggesting that deposit formation had occurred by inertial impaction, as well as by condensation/thermophoresis/eddy diffusion. This is contrary to the deposits formed using K₂Si₄O₉, where no deposition on the downstream side was observed.

The flue gas temperature in the bottom chamber during the experiments was 968 °C. Thermochemical equilibrium calculations using Factsage suggest that KCl predominantly exists in vapor phase at 968 °C (see Table 3.3), with 0.4 mol % of KCl dissociating into KOH and HCl (see Equation 3.13). However, owing to a relatively short residence time in the furnace, phase equilibria may not have been completely established, possibly leading to the presence of liquid phase KCl, or even solid KCl particles, in the bottom chamber. While the KCl vapors may have condensed directly on both sides of the steel tube, molten KCl droplets/solid KCl particles formed deposits on the upstream side of the steel tube through inertial
impaction. Furthermore, while the flue gas cooled down from 1450 °C to 968 °C as it entered the bottom chamber, supersaturation of KCl vapors might have induced the formation of submicron aerosol particles, especially in the vicinity of the steel tube, possibly leading to thermophoretic deposition on the steel tube.

\[ \text{KCl} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{HCl} \]  

(3.13)

Instead of feeding solid KCl particles into the EFR, liquid injection of a KCl–water slurry may reduce mass transfer limitations and aid faster establishment of phase equilibrium in the furnace. This may improve the understanding of KCl deposition phenomena in the EFR.

Experiments performed using CaO resulted in a low rate of deposit formation, with deposits formed only on the upstream side of the steel tube. The low rate of deposit formation can probably be attributed to the relatively high melting point of CaO (2572 °C), resulting in non-sticky particles at the investigated conditions.

However, experiments performed with SiO\(_2\) resulted in a similar rate of deposit formation as K\(_2\)Si\(_4\)O\(_9\), which is rather surprising, since SiO\(_2\) existed in solid phase throughout the experiments (see Table 3.3), with a melting point of 1710 °C. Deposits were formed only on the upstream side of the steel tube via inertial impaction. Furthermore, XRD analysis of the deposit did not suggest any phase change or contamination. The relatively higher deposit formation rate of SiO\(_2\) may possibly due to differences in Young’s modulus, surface tension, particle hardness, etc.

However, experiments using KOH revealed a high rate of deposit formation. Observations made using the camera indicated the formation of a molten film on the steel tube. Although KOH has a melting point of 360 °C and a boiling point of 1327 °C, equilibrium calculations indicate that KOH exists in vapor phase at 968 °C and 1450 °C (see Table 3.3). Furthermore, at 475 °C, KOH may react with atmospheric air and form KNO\(_3\) and K\(_2\)CO\(_3\) at equilibrium conditions. XRD analysis of the obtained deposit indicated the presence of K\(_2\)CO\(_3\)·1.5H\(_2\)O, whereas the presence of KNO\(_3\) was not identified in the deposit. Further equilibrium calculations confirmed the eventual conversion of KNO\(_3\) to K\(_2\)CO\(_3\) in air. It should be noted that equilibrium conditions might not have been attained in the furnace, as a result of which KNO\(_3\) droplets may not have been formed at all. Deposit formation may have occurred due to impaction of KOH/K\(_2\)CO\(_3\)/KNO\(_3\) droplets. Furthermore, as the flue gas cooled down from 1450 °C to 968 °C in the bottom chamber, aerosols may have been formed, which possibly underwent thermophoretic deposition on the steel tube. Moreover, KOH vapors might have heterogeneously condensed on the deposit surface.
Results and Discussion

Figure 3.9 Effect of fly ash composition on the deposit formation rate. Experiments performed with a furnace temperature of 1450 °C, a flue gas temperature of 968 °C, probe surface temperature of 475 °C, gas velocity of 1 m/s, fly ash flux of 20412 g/m²/h for 15 min. K₂Si₄O₉ has a median particle size of 13.2 µm, whereas all other compounds have particle sizes lower than 32 µm. All compositions in wt %. Images captured at the end of the experiments.
Table 3.3 Equilibrium composition of the model fly ash compounds at different temperatures. Furnace temperature = 1450 °C, flue gas temperature in the bottom chamber = 968 °C, probe surface temperature = 475 °C. Thermochemical equilibrium calculations performed using Factsage\textsuperscript{113} with the model fly ash mixture in air (with 400 ppm CO\textsubscript{2} and 50% relative humidity) at experimental stoichiometric conditions. The number in the parenthesis indicates the number of moles. Components with a concentration lower than 0.2 mol % have been ignored.

<table>
<thead>
<tr>
<th>Model fly ash mixture</th>
<th>Temperature (°C)</th>
<th>Equilibrium composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solid</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (100)</td>
</tr>
<tr>
<td>K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (100)</td>
<td>968</td>
<td>K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (100)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>KCl (97) + KOH (3) + HCl (3)</td>
</tr>
<tr>
<td>KCl (100)</td>
<td>968</td>
<td>KCl (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>KCl (100)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>CaO (100)</td>
</tr>
<tr>
<td>CaO (100)</td>
<td>968</td>
<td>CaO (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>CaO (100)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>SiO\textsubscript{2} (100)</td>
</tr>
<tr>
<td>SiO\textsubscript{2} (100)</td>
<td>968</td>
<td>SiO\textsubscript{2} (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>SiO\textsubscript{2} (100)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>KOH (100)</td>
</tr>
<tr>
<td>KOH (100)</td>
<td>968</td>
<td>KOH (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>KOH (100)</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>K\textsubscript{2}SO\textsubscript{4} (31.8) + KOH (136.4) + SO\textsubscript{2} (68.2)</td>
</tr>
<tr>
<td>K\textsubscript{2}SO\textsubscript{4} (100)</td>
<td>968</td>
<td>K\textsubscript{2}SO\textsubscript{4} (100)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>K\textsubscript{2}SO\textsubscript{4} (100)</td>
</tr>
</tbody>
</table>

*Table continues on the next page*
### 3.4 Results and Discussion

<table>
<thead>
<tr>
<th>Model fly ash mixture</th>
<th>Temperature (°C)</th>
<th>Equilibrium composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solid</td>
<td>Liquid/Glass</td>
</tr>
<tr>
<td>KCl (76.1) + K$_2$Si$_4$O$_9$ (23.9)</td>
<td>1450</td>
<td>K$_2$Si$_4$O$_9$ (23.9)</td>
</tr>
<tr>
<td></td>
<td>968</td>
<td>K$_2$Si$_4$O$_9$ (22.6) + K$_2$Si$_2$O$_5$ (2.6)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>KCl (76.1) + K$_2$Si$_4$O$_9$ (23.9)</td>
</tr>
<tr>
<td>CaO (57.1) + KCl (42.9)</td>
<td>1450</td>
<td>CaO (57.1)</td>
</tr>
<tr>
<td></td>
<td>968</td>
<td>CaO (57.1)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>KCl (42.9) + CaO (57.1)</td>
</tr>
<tr>
<td>SiO$_2$ (55.3) + KCl (44.7)</td>
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<td>SiO$_2$ (49.1)</td>
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<td>968</td>
<td>SiO$_2$ (33.5)</td>
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<td></td>
<td>475</td>
<td>KCl (44.6) + SiO$_2$ (55.4)</td>
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<tr>
<td>K$_2$SO$_4$ (29.9) + KCl (70.1)</td>
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<td>KCl (10.2) + K$_2$SO$_4$ (29.9)</td>
</tr>
<tr>
<td></td>
<td>968</td>
<td>KCl (70.1) + K$_2$SO$_4$ (29.9)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>KCl (48.7) + K$_2$SO$_4$ (20.8) + K$_2$Si$_4$O$_9$ (30.5)</td>
</tr>
<tr>
<td>KOH (19.1) + K$_2$Si$_4$O$_9$ (80.9)</td>
<td>1450</td>
<td>K$_2$Si$_4$O$_9$ (80.9)</td>
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<tr>
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<td>968</td>
<td>K$_2$Si$_4$O$_9$ (71.4) + K$_2$Si$_2$O$_5$ (19.1)</td>
</tr>
<tr>
<td></td>
<td>475</td>
<td>K$_2$Si$_4$O$_9$ (71.4) + K$_2$Si$_2$O$_5$ (19.1)</td>
</tr>
</tbody>
</table>
Table 3.4 Deposit formation rates of model fly ash mixtures. Weighted average deposit formation rate calculated from the deposit formation rate of pure compounds constituting the model fly ash mixture. Furnace temperature = 1450 °C, flue gas temperature in the bottom chamber = 968 °C, probe surface temperature = 475 °C. All compositions in wt %.

<table>
<thead>
<tr>
<th>Model fly ash mixture</th>
<th>Experimental deposit formation rate (g/m²/h)</th>
<th>Weighted average deposit formation rate (g/m²/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂Si₄O₉</td>
<td>1365</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>1972</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>1326</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>3086</td>
<td></td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>2853</td>
<td></td>
</tr>
<tr>
<td>KCl + K₂Si₄O₉ (50%)</td>
<td>2017</td>
<td>1669</td>
</tr>
<tr>
<td>KCl + CaO (50%)</td>
<td>1716</td>
<td>1361</td>
</tr>
<tr>
<td>KCl + SiO₂ (50%)</td>
<td>2011</td>
<td>1649</td>
</tr>
<tr>
<td>KCl + K₂SO₄ (50%)</td>
<td>1807</td>
<td>2412</td>
</tr>
<tr>
<td>KCl (25%) + K₂SO₄ (25%) + K₂Si₄O₉ (50%)</td>
<td>1921</td>
<td>1889</td>
</tr>
<tr>
<td>KOH (10%) + K₂Si₄O₉ (90%)</td>
<td>3159</td>
<td>1537</td>
</tr>
<tr>
<td>Wood fly ash</td>
<td>1246</td>
<td>1223</td>
</tr>
<tr>
<td>Straw + wood cofired fly ash</td>
<td>2399</td>
<td>1296</td>
</tr>
<tr>
<td>Straw fly ash</td>
<td>3849</td>
<td>2364</td>
</tr>
</tbody>
</table>

Experiments using K₂SO₄ resulted in a high deposit formation rate (2853 g/m²/h), relative to the deposit formation rate of KCl and K₂Si₄O₉. Furthermore, deposition was observed on both sides of the steel tube, indicating deposition by inertial impaction as well as condensation/thermophoresis. This may possibly be attributed to the dissociation of K₂SO₄ into KOH and SO₂ in the furnace (see Table 3.3), as described by Equation 3.14. The equilibrium calculations suggest that the conversion of K₂SO₄ to KOH in the furnace at 1450 °C may be up to 68%. The short residence time of 0.08 s in the bottom chamber may not have allowed all of the dissociated KOH to recombine into K₂SO₄. As a result, KOH may have heterogeneously condensed on the steel tube or undergone homogeneous condensation to form submicron aerosols in the
bottom chamber, thereby forming deposits on the steel tube via thermophoresis. Furthermore, KOH may have heterogeneously condensed in-flight on K₂SO₄ particles, thereby increasing the sticking probability of the K₂SO₄ particles. Nevertheless, the high rate of deposit formation of K₂SO₄ is rather surprising and requires further investigation. Improved understanding of K₂SO₄ deposition may be achieved by liquid injection of a K₂SO₄–water slurry into the reactor, which may reduce mass transfer limitations and aid faster establishment of phase equilibrium in the furnace.

$$2\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 4\text{KOH} + 2\text{SO}_2 + \text{O}_2 \quad (3.14)$$

The results obtained from the aforementioned deposits concur with full-scale studies in straw-fired boilers, where increasing concentration of K and S in the fuel resulted in an increase in the formation of hard deposits.

**Model fly ash from mixtures of compounds**

Experiments conducted with a model fly ash generated from a mixture of KCl and K₂Si₄O₉ (50 wt %) revealed that the mixture of KCl and K₂Si₄O₉ had a higher rate of deposit formation, when compared to the weighted average deposit formation rate of pure KCl and pure K₂Si₄O₉ (see Table 3.4). This indicates that the addition of KCl influenced the sticking probability of K₂Si₄O₉ particles and/or the deposit surface. Equilibrium calculations suggest that the KOH released due to possible dissociation of KCl (see Equation 3.13) may react with K₂Si₄O₉ to form K₂Si₂O₅, as shown in Equation 3.15.

$$\text{K}_2\text{Si}_4\text{O}_9 + 2\text{KOH} \rightarrow 2\text{K}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O} \quad (3.15)$$

A condensation layer was observed on the downstream side, whereas a thick layer, formed primarily via inertial impaction, was observed on the upstream side of the steel tube. The thick layer was removed and analyzed using a Scanning Electron Microscope, revealing the following observations,

- As shown in Figure 3.10a, tiny KCl particles, approximately 5 µm in diameter, were observed on the surface of the K₂Si₄O₉ particles. In the bottom chamber, KCl may have existed as vapors, aerosols or molten droplets at the investigated conditions. The observed phenomenon is probably heterogeneous condensation of KCl vapors on K₂Si₄O₉ particles, or agglomeration/scavenging of KCl aerosols or tiny molten droplets on K₂Si₄O₉ particles. This may have occurred in-flight on K₂Si₄O₉ particles, prior to deposit formation, or on K₂Si₄O₉ particles present in the deposit. Nevertheless, a layer of partially molten KCl on the K₂Si₄O₉ particles decreases the surface viscosity (or increases the melt fraction) of the particles. In-flight heterogeneous condensation/scavenging of KCl on K₂Si₄O₉ particles may have increased the sticking probability of the K₂Si₄O₉ particles, whereas heterogeneous
condensation/agglomeration of KCl on K₂Si₄O₉ particles present in the deposit may have increased the sticking probability of the deposit surface. Therefore, due to the presence of KCl on the deposit surface, and possibly on the surface of in-flight K₂Si₄O₉ particles, the deposit formation rate of K₂Si₄O₉ increased.

- A majority of the K₂Si₄O₉ particles in the deposit were glued together by molten KCl, as shown in Figure 3.10b. This may have been due to molten KCl droplets impacting the deposit surface, and subsequently spreading out to form a neck between adjacent K₂Si₄O₉ particles in the deposit. Furthermore, condensation of KCl vapors on the deposit surface may have induced sintering, forming a bridge between adjacent K₂Si₄O₉ particles. Investigation of deposit composition and morphology in full-scale biomass boilers has shown that the Si and Ca rich particles, found in the intermediate and outer layers of the deposit, were glued together by KCl, agreeing with the experimental observations.

Figure 3.10 SEM image of deposit particles. Experiments performed with KCl + K₂Si₄O₉ (50 wt %) with a furnace temperature of 1450 °C, a flue gas temperature of 968 °C, probe surface temperature of 475 °C, gas velocity of 1 m/s, fly ash flux of 20412 g/m²/h for 15 min. K₂Si₄O₉ has a median particle size of 13.2 µm, whereas KCl has particle sizes lower than 32 µm. (a) Tiny KCl nuclei on K₂Si₄O₉ particles. (b) K₂Si₄O₉ particles in the deposit glued together by molten KCl.

Similarly, the model fly ash mixtures KCl + CaO (50 wt %) and KCl + SiO₂ (50 wt %) showed an increased deposit formation rate, when compared to their respective weighted average deposit formation rates (see Table 3.4). Deposition was observed on both sides of the steel tube (see Figure 3.9). Equilibrium
3.4 Results and Discussion

calculations indicated that KCl and SiO\textsubscript{2} may react to form K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} in the furnace (see Table 3.3), as described in Equation 3.16.

\begin{equation}
2 \text{KCl} + 4 \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{Si}_4\text{O}_9 + 2 \text{HCl}
\end{equation}

However, the model fly ash mixture KCl + K\textsubscript{2}SO\textsubscript{4} (50 wt %) showed a decreased deposit formation rate, when compared to its weighted average deposit formation rate (see Table 3.4). Deposition was observed on both sides of the steel tube (see Figure 3.9). Equilibrium calculations suggest the formation of a KCl – K\textsubscript{2}SO\textsubscript{4} eutectic melt at 968 °C (see Table 3.3), in addition to dissociation of KCl (see Equation 3.13) and K\textsubscript{2}SO\textsubscript{4} (see Equation 3.14). However, conclusive inferences cannot be obtained currently, and the deposition behavior of K\textsubscript{2}SO\textsubscript{4} requires further investigation.

The model fly ash mixture KCl (25 wt %) + K\textsubscript{2}SO\textsubscript{4} (25 wt %) + K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (50 wt %) showed an increased deposit formation rate, when compared to its weighted average deposit formation rate (see Table 3.4). Deposition was observed on both sides of the steel tube (see Figure 3.9). Equilibrium calculations suggest that dissociation of K\textsubscript{2}SO\textsubscript{4} into KOH (Equation 3.14), dissociation of KCl into KOH (Equation 3.13) and conversion of K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} to K\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} (Equation 3.15) may have occurred in the furnace.

Experiments conducted with a model fly ash containing KOH (10 wt %) and K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} (90 wt %) indicated that addition of KOH significantly increased the deposit formation rate of K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} at the investigated conditions (see Table 3.4). Visual observations of the deposit revealed that the majority of deposition occurred on the upstream side of the steel tube via inertial impaction, with a thin condensation layer present on the downstream side of the steel tube (see Figure 3.9). Heterogeneous condensation/agglomeration of KOH vapors/aerosols on K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} particles may have occurred, increasing the sticking probability of the K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} particles. Equilibrium calculations suggest that KOH may have reacted with K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9} to form K\textsubscript{2}Si\textsubscript{2}O\textsubscript{5} in the furnace (see Equation 3.15), which may have further influenced the sticking probability of the model fly ash. The presence of KOH in boiler deposits has been postulated in a few studies in literature.\textsuperscript{73,114} The results indicate that presence of even small quantities of KOH in the boiler may exacerbate fly ash deposition on boiler surfaces.

The results from this section suggest that interaction among the constituents of the model fly ash may significantly influence its overall deposition behavior. Addition of KCl/KOH to K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}, SiO\textsubscript{2}, and CaO resulted in increased deposit formation rates, when compared to their respective weighted average deposit formation rates. However, the deposition behavior of K\textsubscript{2}SO\textsubscript{4}, and the KCl–K\textsubscript{2}SO\textsubscript{4} system has not been understood completely, requiring further investigation.
Corrosion and adhesion strength of the investigated model fly ash deposits

Inspection of the deposits and the steel tube after the experiments showed that the steel tubes experienced corrosion if the model fly ash contained KCl or KOH. Furthermore, presence of KCl, K$_2$SO$_4$, K$_2$Si$_4$O$_9$ or KOH in the model ash fly mixture resulted in relatively strongly adherent deposits at the investigated conditions. However, presence of CaO or SiO$_2$ resulted in low adhesion strength of the formed deposits. The results agree with the subsequent investigations on deposit adhesion strength (see Chapter 4 and Chapter 5).[^91]

Fly ash obtained from biomass-fired boilers

Experiments comparing the deposit formation rates of three different boiler fly ashes (see Table 3.1) revealed that the investigated wood fly ash exhibited the least deposit formation rate, and the investigated straw + wood cofired fly ash exhibited a moderately high deposit formation rate, whereas the deposit formation rate of the investigated straw fly ash was significantly high (see Figure 3.9). Visual observations of the deposits indicated that wood fly ash and the straw + wood cofired fly ash formed a thin layer on the lateral sides of the steel tube, probably from thermophoretic deposition, whereas a porous, weakly adherent deposit layer was formed on the upstream side. However, no corrosion was observed at the deposit–tube interface. The deposition adhesion strength of the straw + wood cofired fly ash was slightly greater than the wood fly ash. The deposit formation rate of the wood fly ash was similar in magnitude to the weighted average deposit formation rate of its constituents, whereas the deposit formation rate of the straw + wood cofired fly ash was greater than the corresponding weighted average deposit formation rate (see Table 3.4).

The straw fly ash formed deposits on both sides of the steel tube, probably via condensation, thermophoresis and inertial impaction. The deposit was extremely dense and strongly adherent to the steel tube, causing corrosion at the deposit–tube interface. The deposit formation rate of the straw fly ash was greater than the weighted average deposit formation rate of its constituents (see Table 3.4). The high deposit formation rate of straw fly ash can be attributed to the high concentration of K, Cl and S in straw fly ash. Furthermore, the relatively low deformation temperature of straw fly ash (640 °C, see Table 3.1) indicates that the fly ash may have existed as molten droplets or vapor species, leading to a high rate of deposit formation. Moreover, the median particle size of the straw fly ash was relatively large.

The straw share in the boiler feed for generating the straw + wood cofired fly ash was approximately 10%. The high rate of deposit formation of the straw + wood cofired fly ash in the experiments, compared to the wood fly ash and the weighted average deposit formation rate, suggests that addition of relatively low
shares of straw in the feed, while cofiring straw and wood, may lead to a considerable increase in deposit formation.

The experimental results agree with full-scale studies on deposit formation, where increasing straw content in the feed resulted in increased deposit formation rates. Furthermore, full-scale studies have indicated that increasing alkali content in the fuel causes higher deposit formation rates. The results show that ash chemistry has a significant influence on deposit formation rates in biomass boilers. Furthermore, physical and chemical interactions between the components of the fly ash may increase or decrease deposit formation. However, further investigation is required to completely understand the effect of ash chemistry and ash transformations on deposit build-up in boilers.

3.5 Conclusions

The deposit formation of biomass fly ash on a steel tube in a laboratory-scale Entrained Flow Reactor was investigated in this study. Experiments were conducted using model biomass fly ash, prepared from mixtures of K$_2$Si$_4$O$_9$, KCl, K$_2$SO$_4$, CaO, SiO$_2$ and KOH, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The fly ashes were injected into the reactor, to form deposits on an air-cooled probe, simulating deposit formation on the first row of platen superheater tubes in biomass-fired boilers. The effect of flue gas temperature, probe surface temperature, flue gas velocity, fly ash composition, fly ash flux, fly ash particle size and probe residence time was investigated.

The results revealed that increasing the flue gas temperature from 589 – 968 °C increased the sticking probability of the model fly ash particles, thereby resulting in higher deposit formation rates. Furthermore, increasing the probe surface temperature from 300 – 450 °C increased the sticking probability of the deposit surface, resulting in increased deposit formation. However, varying the probe surface temperature from 450 – 550 °C did not influence the deposit formation rate at the investigated conditions. Increasing flue gas velocity from 0.7 – 3.5 m/s, and thereby the particle velocity, resulted in a decrease in the rate of deposit formation, since an increase in the kinetic energy of the particles results in increased particle rebound from the deposit surface after impaction.

The deposit formation rate increased with time, since an increasing deposit thickness led to higher temperatures at the deposit surface, thereby increasing the sticking probability of the deposit surface. However, the growth rate of the deposit was constant after 30 min at the investigated conditions. Furthermore, increasing fly ash flux resulted in a linear increase in the deposit formation rate. Increasing
the particle size of the fly ash resulted in an increased rate of deposit formation, since larger particles are more likely to detach from the gas streamlines around the steel tube and impact the tube surface.

A mechanistic model was developed to predict deposit formation in the reactor. The model was able to reasonably predict the influence of flue gas temperature and fly ash flux, suggesting that accounting for energy dissipation due to particle deformation, for predicting the sticking probability of incoming ash particles, seems to be fairly successful in predicting the influence of changes in local conditions on the deposit formation process. However, the model was unable to accurately predict the influence of probe surface temperature, gas velocity and probe residence time. Improvements in the prediction of the sticking probability of the deposit surface, as well as CFD simulations of the deposit formation process in the reactor, are desirable to improve model predictions.

Inertial impaction was the primary mechanism of deposit formation, when pure K$_2$Si$_4$O$_9$, SiO$_2$ or CaO was injected into the reactor, forming deposits only on the upstream side of the steel tube. However, feeding KCl, K$_2$SO$_4$ or KOH into the reactor resulted in deposit formation on both sides of the steel tube, via condensation, thermophoresis, and inertial impaction. The model fly ash containing pure KOH resulted in the largest rate of deposit formation, followed by K$_2$SO$_4$, KCl, K$_2$Si$_4$O$_9$, SiO$_2$ and CaO.

Addition of KCl to K$_2$Si$_4$O$_9$, SiO$_2$, and CaO resulted in an increased deposit formation rate, when compared to their respective weighted average deposit formation rates. Addition of KCl influenced the sticking probability of the deposit surface, and possibly the sticking probability the in-flight K$_2$Si$_4$O$_9$, SiO$_2$, and CaO particles. Moreover, addition of KOH to K$_2$Si$_4$O$_9$ in the model fly ash mixture resulted in a significant increase in the deposit formation rate. Experiments using three different boiler fly ashes revealed a low rate of deposit formation for the investigated wood fly ash, and a high rate of deposit formation for the straw fly ash. Analysis of deposits obtained using a model fly ash containing KCl and K$_2$Si$_4$O$_9$ (50 wt %), using a Scanning Electron Microscope, revealed the presence of tiny KCl nuclei on K$_2$Si$_4$O$_9$ particles. Furthermore, the K$_2$Si$_4$O$_9$ particles in the deposit were glued together by molten KCl.

The obtained results provide an improved understanding of deposit formation in boilers, describing the influence of operating conditions and ash chemistry. Furthermore, the experimental data may be used to develop novel sticking criteria to predict deposit growth in full-scale boilers.
This chapter has been written in a manuscript format. A slightly modified version has been published in the peer-reviewed journal *Energy & Fuels* as,


**Abstract**

Ash deposition on boiler surfaces is a major problem encountered in biomass combustion. Timely removal of ash deposits is essential for optimal boiler operation. In order to improve the understanding of deposit shedding in boilers, this study investigated the adhesion strength of biomass ash from full-scale boilers, as well as model fly ash deposits containing KCl, K₂SO₄, CaO, CaSO₄, SiO₂, K₂CO₃, Fe₂O₃, K₂SiO₃, and KOH. Artificial biomass ash deposits were prepared on superheater steel tubes and sintered in an oven with temperatures ranging from 500 to 1000 °C. Subsequently, the deposits were sheared off by an electrically controlled arm, and the corresponding adhesion strength was measured. The effects of sintering temperature, sintering time, deposit composition, thermal shocks on the deposit, and steel type were investigated. The results revealed that the adhesion strength of the ash deposits was dependent on two factors: ash melt fraction, and corrosion occurring at the deposit–tube interface. Adhesion strength increased with increasing sintering temperature, sharply increasing at the ash deformation temperature. However, sintering time, as well as the type of steel used, did not have a significant effect on the adhesion strength, under the investigated conditions. Addition of compounds which increase the melt fraction of the ash deposit, typically by forming a eutectic system, increased the adhesion strength, whereas addition of inert compounds with a high melting point decreased the adhesion strength. Furthermore, the study indicated that sulfation of ash deposits may lead to an increase in adhesion strength, while cooling down the deposits after sintering decreased the adhesion strength. Finally, it was observed that adhesion strength data followed a log-normal distribution.
Shear Adhesion Strength of Biomass Ash Deposits

4.1 Introduction

One of the major operational problems encountered in biomass-fired boilers is the formation of ash deposits on boiler surfaces. Ash deposition hinders the efficiency of heat transfer to the steam cycle and may completely block flue gas channels in severe cases, causing expensive unscheduled boiler shutdowns. Furthermore, ash deposits may cause severe corrosion of boiler surfaces. Therefore, timely and effective removal of ash deposits is essential for optimal boiler operation.

Natural as well as artificially induced shedding of ash deposits may be caused by several mechanisms including erosion, debonding, molten slag flow, and thermal and mechanical stresses in the deposits. Full-scale investigations have revealed that debonding is the dominant mechanism for shedding of dense and hard deposits in biomass boilers, occurring when the generated stress (e.g., by soot-blowing or due to the inherent weight of the deposit) exceeds the adhesion strength at the deposit–tube interface. Hence, quantification of the adhesion strength of ash deposits is crucial for understanding deposit shedding, and for optimizing artificial removal of deposits (e.g., by soot-blowing or application of thermal shocks). Soot-blowing in boilers produces both lateral (lift) and longitudinal (drag) forces on deposits, highlighting the importance of understanding the shear as well as tensile adhesion strength of ash deposits. Additionally, the adhesion strength at the interface is dependent on the contact area between the steel tube and the innermost layer of the ash deposit.

Previous studies have investigated the adhesion strength of deposits for coal ash as well as ash from kraft recovery boilers. Other studies have tried to quantify the inherent compression and bend strength of sintered ash deposits. However, there is a lack of understanding of the adhesion strength of biomass ash deposits to boiler surfaces. The literature lacks a detailed investigation, describing the effect of various parameters, such as sintering temperature, chemical composition, and sintering time, on the adhesion strength of biomass ash deposits.

The present work quantified the shear adhesion strength of biomass ash and salt rich deposits in a laboratory oven, in order to determine the effects of gas and steel surface temperature, deposit chemical composition, sintering duration, steel type, and thermal shocks brought about by a rapid change in sintering temperature. The study simulated the conditions present at the deposit–tube interface, under different deposit properties and boiler conditions. Apart from providing a better fundamental understanding of deposit shedding, the outcome of this study may facilitate boiler operation by
4.2 Experimental section

4.2.1 Materials

Experimental analysis was carried out using fly ash obtained from the electrostatic precipitator / bag filter of a straw-fired grate boiler (Avedørevarket unit 2, 100 MWth), a wood-fired suspension boiler (Avedørevarket unit 2, 800 MWth), and a straw + wood cofired suspension boiler (Amagervarket unit 1, 350 MWth). The fly ash properties are provided in Table 3.1.

While the straw fly ash was rich in K and Cl, the wood fly ash and the straw + wood cofired fly ash were rich in Ca and Si. As a result, the ash deformation temperature,\(^{89}\) which is the temperature at which the ash first softens and therefore becomes sticky,\(^{116}\) of straw fly ash was low (640 °C), whereas the ash deformation temperature of wood fly ash and straw + wood cofired fly ash was rather high (1240 and 1220 °C). Additionally, model fly ash deposits were prepared using mixtures of KCl (Sigma-Aldrich, CAS number: 7447-40-7), K\(_2\)SO\(_4\) (Sigma-Aldrich, CAS number: 7778-80-5), K\(_2\)CO\(_3\) (Sigma-Aldrich, CAS number: 584-08-7), CaO (Sigma-Aldrich, CAS number: 1305-78-8), CaSO\(_4\) (Alfa Aesar, CAS number: 7778-18-9), SiO\(_2\) (Sigma-Aldrich, CAS number: 60676-86-0), Fe\(_2\)O\(_3\) (Sigma-Aldrich, CAS number: 1309-37-1), K\(_2\)Si\(_4\)O\(_9\) (Alfa Aesar, CAS number: 1312-76-1), and KOH (Sigma-Aldrich, CAS number: 1310-58-3), in order to understand the effects of different components constituting a typical biomass fly ash. The melting point / eutectic point / glass transition temperature of the model fly ash compounds is provided in Table 4.1. Each of the different components was milled and sieved individually to obtain a particle size distribution in the range 32 – 90 \(\mu\)m. However, it should be noted that fly ash in boilers typically form a bimodal particle size distribution, consisting of submicron particles, as well as larger particles (-10 – 200 \(\mu\)m).\(^{38,50}\) Although the deposits prepared in this study did not contain any submicron particles, it was ensured that the particle size lied within the second peak of the characteristic bimodal size distribution. Since KCl and K\(_2\)SO\(_4\) are the major species found in the inner layer of typical biomass ash deposits,\(^{5}\) all investigated model fly ash deposits contained KCl and K\(_2\)SO\(_4\).
Table 4.1 Eutectic temperature / melting point / glass transition temperature of the investigated model fly ash compounds. Data obtained from multiple sources.\textsuperscript{5,113,117}

<table>
<thead>
<tr>
<th>Composition</th>
<th>Eutectic temperature\textsuperscript{a} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl\textsuperscript{b}</td>
<td>770</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4}\textsuperscript{a}</td>
<td>690</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + CaO\textsuperscript{a}</td>
<td>690</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + CaSO\textsubscript{4}\textsuperscript{a}</td>
<td>644</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + SiO\textsubscript{2}\textsuperscript{a}</td>
<td>690</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + K\textsubscript{2}CO\textsubscript{3}\textsuperscript{a}</td>
<td>580</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + Fe\textsubscript{2}O\textsubscript{3}\textsuperscript{a}</td>
<td>577</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}\textsuperscript{c}</td>
<td>650</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + KOH\textsuperscript{a}</td>
<td>288</td>
</tr>
</tbody>
</table>

Experiments were carried out using three different types of steel, TP347HFG (Salzgitter Mannesmann), 316SS (Sandvik), and 3R69BT (Sandvik), as well as tubes made from pure iron. The tubes had an outer diameter of 38 mm and a thickness of 5 mm. The chemical composition of the steel tubes is provided in Table 4.2. The addition of Cr, Mo and Mn in steel reduces oxide scale growth,\textsuperscript{118,119} improving overall corrosion resistance,\textsuperscript{99} while Ni acts as a deterrent for Cl induced corrosion.\textsuperscript{54} Preoxidation of steel tubes is beneficial for hindering corrosion,\textsuperscript{120,121} and provides a more accurate replication of operational boiler tubes.\textsuperscript{122,123} Thermogravimetric analysis of the TP347HFG steel tubes at 600 °C revealed that the majority of the oxidation occurs in the first few hours, after which the rate of oxidation significantly slows down (see Figure 4.1). Therefore, the tubes were preoxidized for 24 hours at 600 °C prior to conducting experiments.
4.2 Experimental section

### Table 4.2 Composition of the investigated steel tubes

<table>
<thead>
<tr>
<th>Steel type</th>
<th>Cr (wt %)</th>
<th>Ni (wt %)</th>
<th>Fe (wt %)</th>
<th>Others (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>316SS</td>
<td>16–18</td>
<td>10–14</td>
<td>balance</td>
<td>C = 0.08, Si = 0.75, Mn = 2, P = 0.045, S = 0.03, Mo = 2.5</td>
</tr>
<tr>
<td>TP347HFG</td>
<td>17–20</td>
<td>9–13</td>
<td>balance</td>
<td>C = 0.08, Si = 0.75, Mn = 2, P = 0.04, S = 0.03, Nb+Ta = 1</td>
</tr>
<tr>
<td>3R69BT</td>
<td>17.5</td>
<td>12.5</td>
<td>balance</td>
<td>C = 0.03, Si=0.4, Mn = 1.7, P = 0.03, S = 0.015, Mo = 2.2</td>
</tr>
</tbody>
</table>

**Figure 4.1** Thermogravimetric analysis of steel used (TP347HFG), exposed to air at 600 °C. Most of the oxidation occurs within the first few hours, after which the oxidation rate significantly slows down. Sample mass of 2059 mg, heating rate of 10 K/min.

#### 4.2.2 Sample preparation

In order to obtain tightly packed and adherent deposits, the ash particles were mixed with a 50% isopropanol solution to prepare a thick slurry, and molded into a cubical shaped deposit on the surface of the tube, using a Teflon mold (see Figure 4.2). The deposits were 15 mm × 15 mm × 10 mm, (W×D×H) in size, leading to a contact surface area of 223 mm². The use of deposit slurries was in accordance with EU guidelines⁴,¹²₅,¹²₆ for high temperature corrosion testing, providing a better representation of deposits in
power plants. However, it should be noted that the deposit formation process and the typical particle size distribution of fly ash in boilers are different from the case of the samples prepared in this study.\textsuperscript{5,38,30}

![Figure 4.2 Experimental setup for adhesion strength measurements. The superheater steel tube was placed inside the oven while the load cell was outside the oven. The actuator arm sheared off the artificial ash deposit, while the load cell measured the corresponding adhesion strength. Image not to scale.}

4.2.3 Deposit Sintering and Adhesion Strength Measurement

The deposits were heated up and sintered inside an oven for a fixed duration. A purge air flow of 15 NL/min was injected into the oven, to protect the oven heating elements from corrosion.

After sintering, the deposits were cooled down to the required measurement temperature at a rate of 15 °C/min, subsequently followed by shear adhesion strength measurements. An electrically controlled arm was used to debond the artificial ash deposit from the superheater steel tube, as shown in Figure 4.2. The arm was controlled using a linear actuator, and the corresponding force applied on the ash deposit was measured using a load cell. Shear adhesion strength was calculated by dividing the measured force by the contact area between the deposit and the superheater steel tube. Standard experiments were performed by sintering the deposits at 650 °C for 4 hours, while the adhesion strength was measured at 600 °C. These parameters were chosen providing consideration for typical sintering temperatures of the inner layers of the deposit,\textsuperscript{5} typical boiler steam temperatures,\textsuperscript{9,76,101,127} temperature gradients across the steel tube, resulting in the steel surface temperature to be 20 – 50 °C higher than the steam temperature,\textsuperscript{5,100,128} a reasonable experimental time, and the deposit formation process.\textsuperscript{9,38} In order to account for the scatter observed while measuring adhesion strength, measurements were conducted on at least four deposit samples for each instance of experimental conditions.
Selected samples were analyzed using Scanning Electron Microscopy to observe the deposit–tube interface. The steel tubes, along with deposits, were cast in epoxy and polished, without any exposure to water, thereby preventing any dissolution, recrystallization and removal of salts.

Further information on the experimental setup can be found in Appendix B.

### 4.3 Results and Discussion

#### 4.3.1 Effect of Sintering Temperature

Figure 4.3 shows the effect of sintering temperature on adhesion strength. Experiments were performed with pure KCl, as well as three different boiler fly ashes (see Table 3.1). It was observed that adhesion strength increases with increasing temperature, with a sharp increase near the melting point / ash deformation temperature,\(^8^9\) i.e., 640 °C for straw fly ash, and 770 °C for KCl.

A sharp increase in adhesion strengths for wood fly ash and the straw + wood cofired fly ash was been observed in this study, due to their high ash deformation temperatures, 1220 and 1240 °C respectively (see Figure 4.3). Furthermore, it should be noted that increasing the temperature of the oven to temperatures significantly higher than the melting point (or ash deformation temperature) led to completely molten deposits, whose adhesion strength could not be measured.
Figure 4.3 Effect of sintering temperature on shear adhesion strength for KCl and biomass fly ashes. Shear adhesion strength increased sharply near the melting point / ash deformation temperature. Deposits sintered for 4 hours, measured at 600 °C, superheater steel (TP347HFG) preoxidized for 24 hours, average of 4 data points.

4.3.2 Effect of Eutecticity

The constituents of fly ash typically form eutectic systems, leading to melt formation at temperatures lower than the melting point of the individual components. The aforementioned results seem to indicate that the adhesion strength of an ash deposit is dependent on its melting point. Previous studies in literature have indicated that the melt fraction of the deposit, especially at the deposit–tube interface, influences its adhesion strength. In order to better understand this phenomenon, experiments were performed with model fly ash compounds containing KCl and K$_2$SO$_4$. KCl and K$_2$SO$_4$, with individual melting points of 770 and 1069 °C, form a eutectic system with a eutectic temperature of 690 °C (see Table 4.1). However, other experimental studies have identified melt formation at 683 °C for a 50 wt % KCl–K$_2$SO$_4$ system. In the experiments, the amount of K$_2$SO$_4$ in KCl was varied at 650 °C, and the corresponding results are shown in Figure 4.4, along with the KCl–K$_2$SO$_4$ phase diagram. The phase diagram was obtained using FactSage.
The results indicate that while pure compounds did not have much adhesion strength at 650 °C, mixing of the components caused a large increase in the adhesion strength. Since KCl and K$_2$SO$_4$ form a eutectic system, mixing the two components led to an increase in the melt fraction of the deposit. Therefore, it can be inferred that a higher melt fraction at the deposit–tube interface probably increased the adhesion strength of the deposits. However, the experiments were carried out at 650 °C, which is lower than the eutectic temperature of the KCl–K$_2$SO$_4$ system. This indicates the presence of a secondary phenomenon influencing deposit adhesion strength, which has been explored in the following section by conducting a SEM analysis of the deposit–tube interface.

![Graph showing adhesion strength vs. temperature](image)

**Figure 4.4** Effect of varying concentration of K$_2$SO$_4$ in KCl on the shear adhesion strength. Deposits sintered at 650 °C for 4 hours, measured at 600 °C, superheater steel (TP347HFG) preoxidized for 24 hours, average of 4 data points (24 for 50 wt %). Mixing of KCl and K$_2$SO$_4$ causes an increase in adhesion strength.

### 4.3.3 SEM Analysis of the Deposit–Tube Interface

In order to determine the morphology of the deposits at the deposit–tube interface, SEM analysis of the interface was carried out for the model fly ash deposit containing KCl and K$_2$SO$_4$ (50 wt %). The analysis revealed the formation of a dense, partially molten layer at the interface, as seen in Figure 4.5. As the temperature increased, corrosion started to occur at the interface. As a result, corrosion products, such as Fe/Cr chlorides, oxides, chromates, etc., were formed. Most of the corrosion products form a complex eutectic system with the components present in the deposit. This led to a lower eutectic
temperature at the interface, compared to the outer layers of the deposit. The partially molten layer probably caused increased surface wetting and adsorption, leading to high surface adhesion.

It should be noted that debonding always occurred in the corrosion layer throughout all experiments, exposing a fresh layer of steel tube after deposit removal.

![SEM Image of Deposit-Tube Interface](image)

**Figure 4.5** SEM image of the deposit–tube interface. KCl–K$_2$SO$_4$ (50 wt %) deposit, sintered at 650 °C for 4 hours, superheater steel (TP347HFG) preoxidized for 24 hours. Partially molten corrosion layer observed at the deposit–tube interface.

### 4.3.4 Effect of Composition

Experiments were conducted with model fly ash deposits to understand the role of different components present in a typical biomass fly ash. The model fly ash deposits were made up of particles larger than 32 µm and smaller than 90 µm.

The results highlight the effect of sulfation on adhesion strength, as seen in Figure 4.6. The deposit containing KCl and K$_2$SO$_4$ (50 wt %) exhibited much higher adhesion strength compared to a deposit containing pure KCl. Similarly, the deposit containing KCl, K$_2$SO$_4$ and CaSO$_4$ (33 wt % each) showed a higher adhesion strength than the deposit containing KCl, K$_2$SO$_4$ and CaO.
Figure 4.6 Effect of composition on adhesion strength using model fly ash compounds. Deposits sintered at 650 °C for 4 hours, measured at 600 °C, superheater steel (TP347HFG) preoxidized for 24 hours, 4 data points (24 for KCl + K₂SO₄). All compositions in weight %.

The increase in adhesion strength of deposits containing sulfur can be attributed to the fact that KCl–K₂SO₄ and KCl–K₂SO₄–CaSO₄ form a eutectic system (see Table 4.1). Therefore, sulfation lowers the eutectic/deformation temperature of the ash deposit, increasing the melt fraction at 650 °C.

In boilers, KCl can undergo sulfation in the gas phase prior to deposition, or in solid phase after deposition on boiler surfaces. While gas phase sulfation is faster than solid phase sulfation, the deposit is exposed to the flue gas for a longer period of time, making both sulfation mechanisms relevant. Similarly, CaO can undergo sulfation to form CaSO₄.

Sulfation of KCl in deposits can occur as a gas–solid or gas–liquid reaction by SO₂ or SO₃ as shown in the following equations.

\[2 \text{KCl} + \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2 \text{HCl}\] (4.1)

63
Iron oxide may catalytically convert \( \text{SO}_2 \) to \( \text{SO}_3 \),\textsuperscript{57,137} or react with \( \text{SO}_2 \) to form Fe(III) sulfites or sulfates,\textsuperscript{138,139} thereby catalyzing the overall sulfation reaction and increasing the concentration of \( \text{K}_2\text{SO}_4 \) near the steel surface.

The present results suggest that sulfation may result in an increase in adhesion strength at the investigated conditions. However, these results are not conclusive, since the sulfate-forming reactions occurring inside the deposit have not been explored in the conducted experiments. Further investigation of deposit sulfation is required to completely understand the influence of the overall sulfation process on deposit adhesion strength. Nevertheless, it is speculated that reactions occurring between the deposit and the flue gas may contribute to adhesion strength variations in boilers.

Furthermore, the results portray the effect of \( \text{CaO} \), \( \text{SiO}_2 \), \( \text{K}_2\text{CO}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{K}_2\text{Si}_4\text{O}_9 \), and KOH (see Figure 4.6). While Ca and Si are widely present in biomass ash deposits, the presence of \( \text{K}_2\text{CO}_3 \) has been identified in only a few studies in literature.\textsuperscript{73,140} The addition of \( \text{CaO} \) to a model fly ash deposit containing \( \text{KCl}–\text{K}_2\text{SO}_4 \) decreased its adhesion strength. \( \text{CaO} \) does not form a eutectic melt with the \( \text{KCl}–\text{K}_2\text{SO}_4 \) system, effectively reducing the melt fraction, and thereby decreasing the adhesion strength. However, the addition of \( \text{SiO}_2 \) did not seem to significantly affect the adhesion strength, under the conditions examined.

The addition of \( \text{K}_2\text{CO}_3 \) to the model fly ash deposit containing \( \text{KCl} \) and \( \text{K}_2\text{SO}_4 \) considerably increased the adhesion strength. Addition of \( \text{K}_2\text{CO}_3 \) decreased the eutectic temperature of the \( \text{KCl}–\text{K}_2\text{SO}_4 \) system (see Table 4.1), increasing the melt fraction of the ash deposit at 650 °C, and thereby increasing the adhesion strength. Furthermore, \( \text{K}_2\text{CO}_3 \) may react with the steel, leading to the formation of a potassium–chromium compound, most likely \( \text{K}_2\text{CrO}_4 \),\textsuperscript{132,141,142} which forms a low-temperature melt with \( \text{KCl} \),\textsuperscript{143} further increasing the melt fraction at the deposit–tube interface.

Moreover, the addition of \( \text{Fe}_2\text{O}_3 \) significantly increased the adhesion strength of the ash deposits, bolstering the aforementioned theory correlating corrosion with high adhesion strength. Apart from decreasing the melting point of the mixture (see Table 4.1), the presence of \( \text{Fe}_2\text{O}_3 \) in the deposit may cause increased formation of corrosion intermediates, such as \( \text{FeCl}_2 \) or \( \text{FeCl}_3 \), according to the following proposed reaction. The reaction mechanism has been verified using Factsage.\textsuperscript{113}

\[
\text{Fe}_2\text{O}_3 + 6 \text{KCl} \rightleftharpoons 2 \text{FeCl}_3 + 3 \text{K}_2\text{O}
\]  \hspace{1cm} (4.3)

Moreover, in full-scale boilers, where HCl present in the flue gas may be oxidized to \( \text{Cl}_2 \), the following reaction may occur, leading to the formation of \( \text{FeCl}_2 \).\textsuperscript{54,104,144}

\[
\text{Fe}_2\text{O}_3 + 2 \text{Cl}_2 \rightleftharpoons 2 \text{FeCl}_2 + 1.5 \text{O}_2
\]  \hspace{1cm} (4.4)
Since FeCl$_2$, as well as FeCl$_3$, forms a eutectic system with the ash deposit, the corresponding increase in melt fraction probably results in an increase in adhesion strength.

A similar increase in adhesion strength was observed when K$_2$Si$_4$O$_9$ was added to the KCl–K$_2$SO$_4$ system. The presence of alkali silicates has been identified in mature and sintered deposits in straw-fired boilers.$^5$ K$_2$Si$_4$O$_9$ is known to form a glass phase at high temperatures, gradually decreasing in viscosity with increasing temperature.$^{145}$ Analysis of the K$_2$Si$_4$O$_9$ samples using Differential Scanning Calorimetry (DSC) revealed that K$_2$Si$_4$O$_9$ has a glass transition temperature of 650 °C (see Figure 4.7). The formation of a semi-molten glass phase probably caused an increase in surface wetting, and increased adhesion of the deposit to the steel tube.

![Figure 4.7 Differential Scanning Calorimetry analysis of K$_2$Si$_4$O$_9$. The silicate forms a glassy phase, with a glass transition temperature of 650 °C. Sample mass of 10.5 mg, heating rate of 10 K/min.](image)

The presence of KOH in deposits has been postulated in a few studies in literature.$^{73,114}$ In the present study, it was observed that even the addition of a small amount of KOH (2.5 wt %) to the model fly ash deposit caused a large increase in adhesion strength. This can directly be attributed to the low melting point of KOH (360 °C) and the formation of a eutectic system with KCl–K$_2$SO$_4$ (see Table 4.1), causing increased melt formation and adhesion strength.

From this section, it can be concluded that addition of compounds which increase the melt fraction of the ash deposit, usually by forming a eutectic system, increased the adhesion strength at the investigated
conditions. However, addition of inert compounds with a high melting point, such as CaO (melting point of 2572 °C), decreased the adhesion strength at the investigated conditions.

### 4.3.5 Effect of Sintering Time

Varying the sintering time seemed to have a negligible effect on adhesion strength up to 24 hours at the investigated conditions, as seen in Figure 4.8. It should be noted that all the experiments were subjected to an additional 30 minutes of heating time prior to sintering, and 5 minutes for strength measurement after sintering.

![Figure 4.8](image)

**Figure 4.8** Effect of sintering time on adhesion strength. KCl–K₂SO₄ (50 wt %) deposits, sintered at 650 °C, measured at 600 °C, superheater steel (TP347HFG) preoxidized for 24 hours, 4 data points (24 for 4 hours).

The results suggest that the initial, partially molten corrosion layer was probably formed rather quickly, and significant changes in adhesion strength did not occur after the formation of the initial corrosion layer at the interface, within 24 hours. Several studies in literature indicate that the onset of corrosion is typically within a few minutes, and the rate of corrosion decreases exponentially over time.⁴,⁵,³,¹⁴ The marginal changes in melt fraction, due to increasing corrosion, was probably not significant enough to observe reliable changes in adhesion strength. However, further investigation is required prior to arriving at conclusions, especially considering that sintering in boilers may occur for longer durations.
Nevertheless, an increase in deposit adhesion strength may be observed in boilers due to sintering caused by reactions occurring in the deposit, e.g., sulfation, which have not been investigated in this study. Sulfation does not occur in the experimental setup, due to the absence of SO₂ in the gas stream.

### 4.3.6 Effect of Thermal Shocks

Application of thermal shocks to induce deposit shedding is a technique commonly used to remove heavily sintered deposits from superheater tubes. This study further investigated the effect of thermal shocks by cooling down the deposit after sintering. Deposits were cooled down at a rate of 15 °C/min.

As seen in Figure 4.9, cooling down the deposits resulted in a decrease in the adhesion strength. Thermal stresses were induced at the deposit–tube interface, owing to differences in the thermal expansion coefficients between the deposit/corrosion layer and the steel tube. As a result, cracks may have developed at the interface, leading to a decrease in the adhesion strength.

![Figure 4.9](image)

**Figure 4.9** Effect of strength measurement temperature on adhesion strength. KCl–K₂SO₄ (50 wt %) deposits, sintered at 650 °C for 4 hours, superheater steel (TP347HFG) preoxidized for 24 hours, 4 data points (24 for 600 °C).
4.3.7 Effect of Steel Type

In order to understand the effect of the type of steel used, experiments were carried out using a model fly ash deposit containing KCl–K₂SO₄ (50 wt %) on 3 different types of steels, as well as pure iron tubes (see Table 4.2). Experiments were carried out for 4 hours at 650 °C.

The results indicate that the type of steel used did not have a strong influence on the adhesion strength at the investigated conditions, considering the scatter in data (see Figure 4.10). Previous studies have shown that KCl induces corrosion at the steel surface, irrespective of the type of steel, although the depth of the corrosion layer might be different. Furthermore, the onset of the corrosion layer is typically within a few minutes. However, since the Cr and Ni content of the investigated steels was similar in magnitude, a similar degree of corrosion may be expected.

Nevertheless, the adhesion strength of deposits to pure iron tubes appears to be slightly higher, when compared to the investigated steels, indicating that the presence of corrosion inhibiting elements in steel might play a role in influencing adhesion strength. Further investigation, spanning over a larger range of steel types, is required prior to arriving at conclusions.

Figure 4.10 Effect of steel type on adhesion strength. KCl–K₂SO₄ (50 wt %) deposits, sintered at 650 °C for 4 hours, measured at 600 °C, steels preoxidized for 24 hours, 4 data points (24 for TP347HFG).
4.3 Results and Discussion

4.3.8 Analysis of Scatter in Adhesion Strength Data

In order to better understand the significant scatter observed in the data, 24 experiments were conducted using KCl–K$_2$SO$_4$ (50 wt %) deposits. The experiments revealed that adhesion strength data roughly followed a log-normal distribution, as seen in Figure 4.11. This is similar to observations made using deposits from kraft recovery boilers. Moreover, experiments conducted in full-scale biomass-fired boilers indicate similar trends.

![Figure 4.11](image)

**Figure 4.11** Log-normal distribution of adhesion strength data. KCl–K$_2$SO$_4$ (50 wt %) deposits, sintered at 650 °C for 4 hours, measured at 600 °C, superheater steel (TP347HFG) preoxidized for 24 hours, 24 data points.

The stochastic nature of debonding has significant implications on deposit shedding in boilers. The results suggest that even though soot-blowing may remove the majority of the deposits, the strongly adherent deposits might not be removed. Subsequent accumulation of strong deposits probably results in the eventual fouling of boiler surfaces.

The adhesion strength of biomass ash deposits observed in this study is comparable in magnitude to coal ash deposits from lab-scale investigations, as well as biomass ash deposits from full-scale studies, as shown in Table 4.3. However, previous lab-scale investigations indicate that deposits from kraft recovery boilers are more strongly adherent, when compared to biomass and coal ash deposits.
Table 4.3 Adhesion strength of different types of deposits.

<table>
<thead>
<tr>
<th>Deposit type</th>
<th>Adhesion strength (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass ash deposits, current lab-scale investigation</td>
<td>1 – 350</td>
</tr>
<tr>
<td>Biomass ash deposits, full-scale investigations(^6)</td>
<td>20 – 250</td>
</tr>
<tr>
<td>Coal ash deposits, lab-scale investigations(^6)(^2)(^-)(^4)</td>
<td>35 – 350</td>
</tr>
<tr>
<td>Deposits from kraft recovery boilers, lab-scale investigations(^5)</td>
<td>1000 – 16000</td>
</tr>
</tbody>
</table>

4.3.9 Practical Application of the Study

The results allow a better understanding of the process of deposit shedding, both qualitatively and quantitatively. Furthermore, the obtained data may be used to develop a tool for analyzing the effect of fuel composition on adhesion strength, and suggesting boiler operating conditions to prevent the formation of strong deposits. For example, the study identifies that maintaining steel temperatures below the ash deformation temperature may result in the formation of weaker deposits. Furthermore, the study quantifies the degree of thermal shocks needed to weaken the strongly adherent deposits. Moreover, the study analyzes the effect of composition of the fly ash, which could be used to estimate fuel quality. However, further work is required prior to arriving at conclusions.

Additionally, the obtained data may be used to optimize soot-blowing in boilers by recommending soot-blowing frequencies and pressures, based on the fuel and operating conditions. This may be done by modeling the log-normal distribution of adhesion strength data, incorporating the effect of deposit composition, flue gas temperature and steam temperature. However, further experimental work is required for the development of a detailed model.

4.4 Conclusions

This study investigated the shear adhesion strength of biomass ash deposits from full-scale boilers, as well as model fly ash deposits containing KCl, K\(_2\)SO\(_4\), CaO, CaSO\(_4\), SiO\(_2\), K\(_2\)CO\(_3\), Fe\(_2\)O\(_3\), K\(_2\)Si\(_4\)O\(_9\) and KOH.
Deposits were prepared on superheater steel tubes and sintered in a laboratory oven. The effects of sintering temperature, sintering time, deposit composition, thermal shocks on the deposit, and steel type were investigated.

Increasing sintering temperatures resulted in higher adhesion strengths, with a sharp increase observed near the ash deformation temperature / melting point. Sintering time did not significantly affect adhesion strengths up to 24 hours at 650 °C, using a model fly ash deposit containing KCl–K_2SO_4 (50 wt %). Furthermore, it was substantiated that cooling down the deposit after sintering reduces the adhesion strength, due to thermal stresses induced at the deposit–tube interface.

Deposits containing sulfates showed increased adhesion strengths, indicating that sulfation may cause the formation of stronger deposits. The addition of K_2CO_3, Fe_2O_3, K_2Si_6O_19 and KOH to the model fly ash deposit increased the ash melt fraction at the deposit–tube interface, thereby increasing the adhesion strength, whereas the addition of CaO decreased the ash melt fraction, thereby decreasing the adhesion strength.

Furthermore, the type of steel used did not seem to have a considerable effect on the adhesion strength. Finally, experiments revealed that the adhesion strength data roughly followed a log-normal distribution.

This study identified that the adhesion strength of ash deposits is probably dependent on two factors: the ash melt fraction, and corrosion occurring at the deposit–tube interface. A higher ash melt fraction at the deposit–tube interface may increase the adhesion strength of the deposits. Furthermore, corrosion products generated at the deposit–tube interface, may form a eutectic system with the inner layer of deposit and increase the local melt fraction, thereby increasing the adhesion strength.
This chapter has been written in a manuscript format. A slightly modified version has been published in the peer-reviewed journal *Energy & Fuels* as,


**Abstract**

Replacing coal with biomass in power plants is a viable option for reducing net CO$_2$ emissions and combating climate change. However, biomass combustion in boilers may exacerbate problems related to ash deposition and corrosion, demanding effective deposit removal. The tensile adhesion strength of model biomass ash deposits, containing mixtures of KCl, K$_2$SO$_4$, CaO, CaSO$_4$ and K$_2$Si$_2$O$_5$, has been investigated in this study. The deposits were prepared on superheater steel tubes, and sintered in an oven. The superheater steel tube was cooled by air, incorporating a temperature gradient across the deposits. After sintering, the deposits were removed using an electrically controlled arm, and the corresponding tensile adhesion strength was measured. The effects of flue gas temperature (500 – 700 °C), steel surface temperature (500 – 650 °C) and deposit composition were investigated. The results revealed that increasing the flue gas temperature, as well as the steel surface temperature, led to a sharp increase in the tensile adhesion strength of the model deposits. The sharp increase was typically observed near the melting temperature (or deformation temperature) of the investigated model deposits. Furthermore, migration of molten/vapor species from the outer layer of the deposit to the deposit–tube interface, causing liquid state sintering was observed at high flue gas temperatures, leading to an increase in the tensile adhesion strength. Varying the ash chemistry of the model deposits revealed that the melt fraction of the deposit was highly influential in determining the deposit adhesion strength. Addition of compounds which increased the melt fraction of the deposit increased the tensile adhesion strength, whereas addition of inert compounds with a high melting point, such as CaO, decreased the tensile adhesion strength. Moreover, the results suggested that the adhesion strength of the deposits was influenced by the corrosion occurring at the deposit–tube interface.
5.1 Introduction

Following the Paris Agreement at COP21,148 global efforts to mitigate climate change have accelerated. Being a CO₂ neutral fuel, biomass can potentially replace coal for providing flexible electricity and heat production. Globally, the supply of biomass for energy has been growing at 2.5% every year since 2010, with bioenergy contributing 10.5% of the global primary energy consumption.149 With Denmark aiming to replace coal with biomass in pulverized fuel power plants by 2030,2 biomass-firing and cofiring are gaining increased importance. However, biomass-fired boilers encounter numerous operational challenges, several of which are related to the critical volatile ash forming elements, such as K and Cl, causing severe ash deposition and corrosion on boiler surfaces.1,150 Ash deposition on boiler surfaces hinders heat transfer to the steam cycle, thereby reducing boiler efficiency.50 Moreover, ash deposition may completely block the flue gas channels in severe cases, resulting in expensive boiler shutdowns. Therefore, timely and effective deposit removal is essential for maximizing boiler efficiency and availability.

Shedding of ash deposits in boilers may occur naturally, without any operational influence, or may be induced artificially (e.g., using soot-blowing, or load changes). Deposit shedding may occur through several mechanisms, including erosion, debonding, molten slag flow, and thermal and mechanical stresses within the deposits.1 Erosion occurs when sharp-edged fly ash particles collide with non-molten deposits, resulting in deposit removal through chipping or repeated deformation. Debonding occurs when the generated stress (e.g., by soot-blowing, or due to the weight of the deposit) exceeds the adhesion strength at the deposit–tube interface, resulting in deposit removal from the tube surface. If the temperature of the outer layer of the deposit is sufficiently high for the formation of low-viscosity slags, molten phases may flow off the deposit. Thermal shocks caused by temperature changes in the boiler may induce deposit shedding due to differences among the thermal expansion coefficients of the tube, the corrosion layer, and the deposit. Full-scale investigations have identified that debonding is the dominant mechanism for deposit shedding in suspension-fired biomass boilers.60 Hence, quantification of the adhesion strength of ash deposits is essential for understanding deposit shedding, and for optimizing artificial removal of deposits (e.g., by soot-blowing) in boilers. Since soot-blowing in boilers may produce both lateral (lift) and longitudinal (drag) forces on deposits,58 it is important to quantify both the shear and the tensile adhesion strength of ash deposits.

The adhesion strength of coal ash deposits64,135,132 and deposits in kraft recovery boilers58 has been investigated in previous studies, while a few studies have quantified the compression and bend strength of ash deposits.55–68 The authors have previously investigated the shear adhesion strength of biomass ash deposits to superheater steel tubes, describing the influence of sintering temperature, sintering time,
5.2 Experimental section

5.2.1 Materials

Artificial biomass ash deposits were prepared using mixtures of KCl (Sigma Aldrich, CAS number: 7447-40-7), K$_2$SO$_4$ (Sigma Aldrich, CAS number: 7778-80-5), CaO (Sigma Aldrich, CAS number: 1305-78-8), CaSO$_4$ (Alfa Aesar, CAS number: 7778-18-9), and K$_2$Si$_4$O$_9$ (Alfa Aesar, CAS number: 1312-76-1). The materials were milled and sieved individually to obtain a particle size distribution in the range 32 – 90 µm. However, it should be noted that fly ash particles in biomass boilers typically form a bimodal size distribution, containing submicron particles as well as larger particles with sizes up to 200 µm. Accurately reproducing the typical bimodal size distribution of fly ash for the experiments is a tedious process. Therefore, a fixed particle size distribution in the range 32 – 90 µm was adopted for comparing the influence of ash chemistry. The materials were mixed in different combinations to create model deposits, as shown in Table 5.1, along with their eutectic temperature/glass transition temperature.
Table 5.1 Eutectic temperature/glass transition temperature of the investigated model deposits. Eutectic data obtained from Janz et al.\textsuperscript{117}

<table>
<thead>
<tr>
<th>Composition</th>
<th>Eutectic temperature\textsuperscript{a} /glass transition temperature\textsuperscript{b} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4}\textsuperscript{a}</td>
<td>690</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + CaO\textsuperscript{a}</td>
<td>690</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + CaSO\textsubscript{4}\textsuperscript{a}</td>
<td>644</td>
</tr>
<tr>
<td>KCl + K\textsubscript{2}SO\textsubscript{4} + K\textsubscript{2}Si\textsubscript{4}O\textsubscript{9}\textsuperscript{b}</td>
<td>650</td>
</tr>
</tbody>
</table>

Furthermore, an experiment was performed using straw fly ash obtained from the bag house filter of the grate-fired boiler in Avedøreværket unit 2.\textsuperscript{1,76} The steam cycle of the 100 MW\textsubscript{th} boiler was operated at 580 °C and 300 bar, with approximately 25 tons/h of wheat straw utilized at full load. Straw was fed to the boiler on a vibrating grate, and primary air was supplied through the grate, whereas secondary air was injected in the freeboard.\textsuperscript{1} The fly ash composition and ash melting analysis\textsuperscript{89} of the straw fly ash is provided in Table 3.1. The fly ash was rich in KCl and K\textsubscript{2}SO\textsubscript{4}, with an ash deformation temperature of 640 °C, slightly lower than the eutectic temperature of the KCl–K\textsubscript{2}SO\textsubscript{4} system of 690 °C. The particle size distribution of the fly ash is provided in Figure 5.1. It should be noted that submicron particles were not detected in the investigated fly ash, probably due to agglomeration during storage.

The deposits were prepared on a superheater steel tube (TP347HFG, Salzgitter Mannesmann), with an outer diameter of 38 mm, a thickness of 5 mm and a length of 200 mm. The chemical composition of the tube can be found in Chapter 4, Table 4.2. TP347HFG is characterized by its high Cr, Mn and Ni content. The presence of Cr and Mn in steel reduces oxide scale growth by forming Cr-Mn-spinels,\textsuperscript{118,119} improving the overall corrosion resistance,\textsuperscript{99} while Ni deters Cl induced corrosion.\textsuperscript{54}

Apart from hindering corrosion, preoxidation of steel tubes provides a more accurate replication of operational boiler tubes.\textsuperscript{121–123,144} Thermogravimetric analysis of the steel tubes at 600 °C in a previous investigation\textsuperscript{91} has indicated that the majority of the oxidation occurs rapidly in the first 10 hours, with the oxidation rate slowing down significantly after 24 hours. Therefore, the steel tubes were preoxidized for 24 hours at 600 °C prior to sample preparation.
5.2 Experimental section

Figure 5.1 Particle size distribution of the investigated straw fly ash, obtained using a Malvern Mastersizer 3000. $D_{10} = 8.01 \, \mu m$, $D_{50} = 51.7 \, \mu m$, $D_{90} = 142 \, \mu m$.

5.2.2 Sample Preparation

The required components constituting the model deposit were thoroughly mixed with 50% isopropanol solution to prepare a slurry. The use of slurries to prepare ash deposits is in accordance with EU guidelines.\textsuperscript{4,125,126} The slurry was molded into 8 cubical shaped deposits on the superheater steel tube using a Teflon mold, as shown in Figure 5.2. The superheater steel tube was placed inside the mold, and the mold was securely closed using clamps. During the molding process, hooks used for tensile strength measurements were inserted into the mold, for allowing the deposit to be debonded perpendicular to the steel tube. Subsequently, the deposit slurry was injected into the mold, and shaped into cubical pellets, with sides of 15 mm each, leading to a contact surface area of 223 mm$^2$. Thereafter, the Teflon mold was opened, leaving the superheater steel tube with 8 deposits.

It should be noted that the deposit formation process in boilers is different from the samples prepared in this study.
Tensile Adhesion Strength of Biomass Ash Deposits

Figure 5.2 Teflon mold used for sample preparation. After the superheater steel tube was positioned (a), the hooks were inserted into the mold, followed by injection of the deposit slurry. Subsequently, the deposits and the superheater steel tube were removed, by opening the Teflon mold (b).

5.2.3 Deposit Sintering

The superheater steel tube containing the deposits was placed around a double annular cooling probe in an oven, and the deposit hooks were connected to the corresponding strength measurement arms, as shown in Figure 5.3. Air flowed through the channels of the cooling probe, with the primary air flowing in through the innermost channel and flowing out through the outermost channel, while the secondary air flowed through the annular region of the cooling probe, as shown in Figure 5.4a.

The following nomenclature has been used for referring to the different measured temperatures in the experimental setup (see Figure 5.4a).

- Flue gas temperature: The gas temperature in the oven heating chamber (oven temperature).
- Cooling probe temperature: Temperature at the outer surface of the cooling probe (and the inner surface of the superheater steel tube), measured at the axial centerpoint of the superheater steel tube. The flow rate of the primary air was controlled electronically, such that the cooling probe temperature is maintained at a desired value. The cooling probe could be maintained at a temperature up to 200 °C lower than that of the flue gas (oven temperature). The cooling probe temperature in the experimental setup is analogous to the steam temperature in boilers.
5.2 Experimental section

- Steel surface temperature: Temperature at the outer surface of the superheater steel tube, measured at the centerpoint of the deposit–tube interface. Eight deposits correspond to eight steel surface temperatures. The steel surface temperatures were higher than the cooling probe temperatures, due to the presence of a vertical temperature gradient ($\Delta T_v$) across the steel tube. Furthermore, the steel surface temperature varied along the length of the superheater steel tube, due to the presence of a horizontal temperature gradient ($\Delta T_h$).

![Experimental setup for adhesion strength measurements. The superheater steel tube with the deposits was placed around the air-cooled probe inside the oven, and the deposits were connected to the strength measurement arms.](image)

Figure 5.3. Experimental setup for adhesion strength measurements. The superheater steel tube with the deposits was placed around the air-cooled probe inside the oven, and the deposits were connected to the strength measurement arms.

The secondary air allowed additional cooling and reduced $\Delta T_h$. The flow rate of the secondary air was controlled manually using a rotameter, and was optimized to minimize $\Delta T_h$. It was identified that a secondary air flow rate of 50 NL/min, which was the maximum possible flow rate, resulted in minimum temperature gradients across the steel tube, advocating the use of 50 NL/min of secondary air throughout all experiments.
Figure 5.4 (a) Cross-sectional view of the mounted air-cooled probe. The cooling probe temperature was measured on the outer surface of the cooling probe (below the superheater steel tube) at the axial centerpoint of the superheater steel tube. Steel surface temperatures refer to the temperatures at the outer surface of the superheater steel tube. Horizontal and vertical temperature gradients exist along/across the superheater steel tube and the deposits. (b) Temperature gradients along the outer surface of the superheater steel tube, with a flue gas temperature of 650 °C. Axial position measured from the left edge of the superheater steel tube.
The steel surface temperatures were measured by mounting 6 thermocouples on the outer surface of the superheater steel tube. The temperature gradients along the steel tube at a flue gas temperature of 650 °C, and cooling probe temperatures of 450 – 650 °C, are shown in Figure 5.4b. It was observed that a horizontal temperature gradient of up to 64 °C existed along the steel surface (\(\Delta T_h = 0 – 64 \, ^\circ\text{C}\)). It should be noted that the air supply to the cooling probe was shut off for the measurement corresponding to a cooling probe temperature of 650 °C, resulting in isothermal conditions. Furthermore, the mean steel surface temperature was up to 88 °C higher than the cooling probe temperature (\(\Delta T_v = 0 – 88 \, ^\circ\text{C}\)). Both \(\Delta T_h\) and \(\Delta T_v\) decreased with increasing cooling probe temperature. Previous studies in full-scale boilers have identified that the steel surface temperature is typically around 20 – 50 °C higher than the steam temperature.\(^{100,155}\) The larger difference between the steel surface temperature and the cooling probe temperature in this experimental setup was probably due to the presence of air gaps between the cooling probe and the superheater steel tube, reducing the heat transfer efficiency.

It should be noted that the measurements to quantify the steel surface temperatures were performed in the absence of the deposits. The presence of the deposits might result in slight differences. Furthermore, the steel surface temperature was measured at 6 locations, whereas the superheater steel tube contained 8 deposits. The steel surface temperatures at the center of the deposits were interpolated linearly, wherever required, using the measured data.

After placing the superheater steel tube with the deposits around the cooling probe, the oven was heated to the required temperature at a uniform heating rate of 10 °C/min. Subsequently, the deposits were allowed to sinter for 2 hours. A purge air flow of 25 NL/min, acting as the flue gas, was injected into the oven, in order to protect the heating elements from corrosion. Baseline experiments were performed with a flue gas temperature of 650 °C, and a cooling probe temperature of 500 °C, using a model deposit containing KCl and K\(_2\)SO\(_4\) (50 wt %). Typical steam temperatures in biomass boilers range from 440 – 580 °C, while typical flue gas temperatures in the superheater/tube bank region range from 580 – 1300 °C.\(^{76,100,101,150}\)

### 5.2.4 Measurement of Tensile Adhesion Strength

After sintering, tensile adhesion strength measurements were performed using a movable actuator and load cell system mounted on the frame of the oven. For each measurement, the actuator was connected to the required strength measurement arm, pulling it slowly at a speed of 2.5 mm/s to debond the deposit, while the corresponding force was measured using the load cell. The tensile adhesion strength was calculated by dividing the measured force by the contact area between the deposit and steel tube.
The strength measurement arms were directed through an air-cooled plate heat exchanger installed in the outer shell of the oven. The heat exchanger absorbed the heat leaking from the top of the oven, thereby protecting the heat-sensitive actuator and the load cell. Heat may influence the tensile adhesion strength measurements and possibly damage the load cell.

Further information on the experimental setup can be found in Appendix C.

5.2.5 Statistical Data Analysis using Welch’s t-test

The two-tail Welch’s t-test\textsuperscript{157} for unpaired data with unequal variances was performed on the experimental data to analyze the statistical difference between two data sets. The test compared the two data sets, calculating the t-value ($T$) as shown below,

$$T = \frac{\mu_1 - \mu_2}{\sqrt{\frac{\sigma_1^2}{N_1} + \frac{\sigma_2^2}{N_2}}}$$

(5.1)

where $\mu$ and $\sigma$ are the mean and standard deviation of the data sets, and $N$ represents the sample size. Thereafter, the p-value ($p$) was calculated, as shown below,

$$p = P(|T| \leq t_{1-\alpha/2,v})$$

(5.2)

$t_{1-\alpha/2,v}$ is the critical value of the t distribution, where $v$ represents the degrees of freedom and $\alpha$ is the significance level. A typical value of 0.05 was chosen for the significance level, corresponding to a confidence level of 95%, indicating that the data sets in consideration are significantly different if $p \leq 0.05$. A higher $p$-value indicates that the data sets are statistically similar, whereas a low $p$-value indicates that the data sets in consideration are different from each other, with $p \leq 0.05$ being conclusive for significant statistical difference. Previous studies\textsuperscript{58,91} have indicated that adhesion strength data for boiler deposits typically follows a log-normal distribution. Since the Welch’s t-test requires that the data follow a normal distribution, the t-test was performed using the logarithmic values of the measured adhesion strength data.

5.3 Results and Discussion

5.3.1 Effect of Steel Surface Temperature

Figure 5.5 shows the effect of the steel surface temperature on the tensile adhesion strength of the investigated model deposit, containing KCl and K$_2$SO$_4$ (50 wt %), which was sintered for 2 hours with a
5.3 Results and Discussion

The cooling probe temperature was varied from 450 °C to 650 °C, resulting in the corresponding steel surface temperatures varying from 501 °C to 650 °C. The experiments revealed that the tensile adhesion strength of the model deposits was low (<12 kPa) at steel surface temperatures below 600 °C at the investigated conditions. Several deposits did not adhere to the steel tube, resulting in zero adhesion strength. However, the adhesion strength increased sharply at a steel surface temperature of 650 °C, with a mean tensile adhesion strength of 31.79 kPa.

![Graph showing effect of steel surface temperature on tensile adhesion strength.](image)

**Figure 5.5** Effect of steel surface temperature on tensile adhesion strength. KCl-K$_2$SO$_4$ (50 wt %) deposits, sintered with a flue gas temperature of 650 °C for 2 hours. Superheater steel (TP347HFG) preoxidized for 24 hours.

The two-tail Welch’s t-test\textsuperscript{137} for unpaired data with unequal variances was performed on the experimental data, as shown in Table 5.2. The results revealed that statistically significant difference did not exist between cooling probe temperatures of 450 – 500 °C, and 500 – 600 °C. However, adhesion strength data at a cooling probe temperature of 650°C was significantly different from adhesion strength data at 600 °C, as well as 450 °C, with p-values of 0.0425 and 0.0019 respectively. The results from the t-test substantiate the sharp increase in adhesion strength at 650 °C.
### Table 5.2 Statistical analysis of data sets with varying cooling probe temperature. Two-tail Welch’s t-test for unpaired data with unequal variances, α = 0.05. KCl–K₂SO₄ (50 wt %) deposits, sintered with a flue gas temperature of 650 °C for 2 hours.

| Compared data sets                          | T     | p = P(|T| ≤ t_{1-α/2,ν}) | Data significantly different? (p ≤ 0.05?) |
|--------------------------------------------|-------|--------------------------|----------------------------------------|
| Cooling probe temperature, mean steel surface temperature (°C) | Cooling probe temperature, mean steel surface temperature (°C) |                       |                                        |
| 450, 538                                   | 500, 562 | -0.5281                | 0.6089                                  | No                                     |
| 500, 562                                   | 600, 628 | -0.7199                | 0.4881                                  | No                                     |
| 600, 628                                   | 650, 650 | -2.2932                | 0.0425                                  | Yes                                    |
| 450, 538                                   | 650, 650 | -3.9671                | 0.0019                                  | Yes                                    |

Previous investigations have shown that corrosion leads to the formation of a partially molten layer at the deposit–tube interface, resulting in a sharp increase in adhesion strength. Corrosion occurs at the deposit–tube interface, resulting in the formation of Fe/Cr chlorides, oxides, chromates, etc., with increasing steel surface temperatures causing a higher degree of corrosion. Since most of the corrosion products form a complex eutectic system with the KCl-K₂SO₄ model deposit, a partially molten layer was probably formed at the deposit–tube interface, even below the eutectic temperature of the KCl–K₂SO₄ system (690 °C). The partially molten layer increased the physical contact area between the deposit and the tube on a molecular scale, thereby increasing adsorption. Furthermore, the corrosion reactions occurring between the deposit and the steel tube may have increased surface adhesion. Visual observations of the deposit–tube interface after debonding indicated the presence of a thick corrosion layer at steel surface temperatures of 650 °C.

It should be noted that debonding always occurred at the deposit–tube interface for the aforementioned experiments. The results concur with previous lab-scale investigations, where a sharp increase in adhesion strength was observed near the melting temperature/ash deformation temperature of the ash deposit, as well as full-scale deposit probe investigations, where deposits formed on a steel tube at higher steel surface temperatures required larger soot-blowing peak impact pressures to be removed. Furthermore, the mean tensile adhesion strength of the KCl–K₂SO₄ (50 wt %) deposits measured in this study at 650 °C and isothermal conditions (31.79 kPa), is similar in magnitude to the mean shear adhesion strength of KCl–K₂SO₄ (50 wt %) deposits at 650 °C (30.82 kPa), measured in a previous study.
A high degree of scatter was observed in the present experimental data. Previous lab-scale\textsuperscript{58,91} as well full-scale\textsuperscript{60} studies have also indicated that adhesion strength data for boiler deposits display a high degree of scatter, typically following a log-normal distribution.

### 5.3.2 Effect of Flue Gas Temperature

In order to investigate the effect of flue gas temperature on the tensile adhesion strength of ash deposits, experiments were carried out with model deposits containing KCl and K\textsubscript{2}SO\textsubscript{4} (50 wt %). The deposits were sintered for 2 hours, with the cooling probe temperature maintained at 500 °C, while the flue gas temperature was varied from 500 – 700 °C.

As seen in Figure 5.6, it was observed that the tensile adhesion strength of the model deposits did not change significantly with flue gas temperatures of 500 – 650 °C, at the investigated conditions. The mean steel surface temperature varied from 500 – 558 °C, when the flue gas temperature was varied from 500 – 650 °C. However, when the flue gas temperature was increased to 700 °C, a sharp increase in tensile adhesion strength was observed. At a flue gas temperature of 700 °C, and a cooling probe temperature of 500 °C, the steel surface temperature was 576 °C. Statistical analysis of the obtained experimental data using Welch’s t-test (see Table 5.3) confirmed that the data set corresponding to a flue temperature of 700 °C was significantly different from the data set corresponding to 650 °C, whereas no statistically significant difference could be observed from 500 – 650 °C.

In order to understand the increase in tensile adhesion strength at a flue gas temperature of 700 °C, the corresponding deposit was analyzed using Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy. The debonded deposit was cast in epoxy and polished, without any exposure to water, thereby preventing any dissolution, recrystallization, and removal of salts. The images revealed the presence of a thick molten layer at the deposit–tube interface, as shown in Figure 5.7. K\textsubscript{2}SO\textsubscript{4} particles were suspended in the KCl–K\textsubscript{2}SO\textsubscript{4} melt, where the composition of KCl in the melt was 8 wt %. However, KCl particles could be identified in the outer layer of the deposit (see Figure 5.7a).
Figure 5.6 Effect of flue gas temperature on tensile adhesion strength. KCl-K₂SO₄ (50 wt %) deposits, sintered with a cooling probe temperature of 500 °C for 2 hours. Mean steel surface temperatures varied from 500 – 576 °C. Superheater steel (TP347HFG) preoxidized for 24 hours.

Table 5.3 Statistical analysis of data sets with varying flue gas temperature. Two-tail Welch’s t-test for unpaired data with unequal variances, α = 0.05. KCl-K₂SO₄ (50 wt %) deposits, sintered with a cooling probe temperature of 500 °C for 2 hours. Mean steel surface temperatures varied from 500 – 576 °C.

| Compared data sets | T     | p=|P(|T|≤t_{1-α/2,v}) | Data significantly different? (p ≤0.05?) |
|--------------------|-------|---|-------------------|----------------------------------------|
| Flue gas temperature (°C) | Flue gas temperature (°C) |     |                   |                                         |
| 500 | 550 | 1.2965 | 0.2514 | No               |
| 550 | 600 | -1.1280 | 0.3024 | No               |
| 600 | 650 | -0.3018 | 0.7684 | No               |
| 650 | 700 | -2.5395 | 0.0294 | Yes              |
Figure 5.7 SEM image of a KCl–K$_2$SO$_4$ (50 wt %) deposit, sintered with a flue gas temperature of 700 °C, a steel surface temperature of 576 °C (cooling probe temperature of 500 °C) for 2 h, at (a) the outer layer of the deposit, in contact with the flue gas, and at (b) the inner layer of the deposit, in contact with the superheater steel tube.
The high molten content at the deposit–tube interface may be attributed to several factors. At a flue gas temperature of 700 °C, the outer layer of the KCl–K₂SO₄ model deposit became partially molten, since KCl and K₂SO₄ form a eutectic system with a eutectic temperature of 690 °C (see Table 5.1). As a result, the molten outer layer probably trickled down through the pores of the deposit, due to capillary and gravitational forces, solidifying at lower temperatures near the deposit–tube interface. This phenomenon is observed in full-scale boilers in the form of liquid state sintering, resulting in the formation of hard and strongly adherent deposits, and has been observed in previous experimental investigations.

Sintering increases the bulk density and thermal conductivity of the deposits, thereby increasing the temperature of the deposit over time, and further increasing the molten content at the deposit–tube interface. Furthermore, significant gas phase migration may have occurred within the deposit, where species on the outer layer of the deposit vaporized, diffused through the pores of the deposit, and eventually condensed near the deposit–tube interface. Therefore, the high molten/condensed content at the deposit–tube interface increased the surface wetting and therefore, increased the tensile adhesion strength.

It should be noted that the dissolution of KCl and K₂SO₄ in the 50% isopropanol solution during sample preparation may have increased the molten content at the deposit–tube interface. Furthermore, corrosion occurring at the deposit–tube interface may have contributed towards the formation of the molten layer. However, with a steel surface temperature of 576 °C, the corrosion layer is not expected to cause a significant increase in the tensile adhesion strength, as suggested by the results described in Figure 5.5.

Increasing the flue gas temperature to 750 °C led to a high degree of molten content, which severely reduced the deposit thickness, such that the adhesion strength could not be measured.

The results suggest that a temperature gradient across the deposit may induce migration of molten/vapor species from the outer layer of the deposit to the deposit–tube interface, causing liquid state sintering, and possibly leading to an increase in deposit adhesion strength. However, further investigation, spanning over a larger range of flue gas temperatures and time is required to completely understand the effect of sintering on adhesion strength.

### 5.3.3 Effect of Deposit Composition

In order to understand the effect of different components present in ash deposits, the composition of the model deposits was varied by adding CaO, CaSO₄ and K₂Si₄O₉ to the KCl–K₂SO₄ model deposit. Furthermore, experiments were conducted with the straw fly ash obtained from the Avedørekræket grate-fired boiler (see Table 3.1 for fly ash properties and Figure 5.1 for particle size distribution).
5.3 Results and Discussion

Figure 5.8 shows the effect of deposit composition on the tensile adhesion strength. The addition of CaO to the model deposit containing KCl and K$_2$SO$_4$ considerably decreased the adhesion strength at the investigated conditions, with several deposits not adhering to the steel tubes. Comparing the adhesion strength data of the model deposit containing KCl and K$_2$SO$_4$ (50 wt %) with the model deposit containing KCl, K$_2$SO$_4$ and CaO (33 wt %) using Welsh’s t-test, the obtained p-value was 0.0011 (see Table 5.4), implying that the difference in the data sets is statistically significant.

Calcium is widely present in deposits formed in coal and wood-fired boilers, primarily as oxides and sulfates.\(^\text{155,161}\) Since CaO does not form a eutectic melt with the KCl–K$_2$SO$_4$ system, the addition of CaO reduced the melt fraction, thereby decreasing adhesion strength.\(^\text{91}\)

However, as shown in Figure 5.8, the addition of CaSO$_4$ significantly increased the adhesion strength of the model deposit containing KCl and K$_2$SO$_4$. The increase in adhesion strength, which was determined to be statistically significant (see Table 5.4), can be attributed to the fact that KCl–K$_2$SO$_4$–CaSO$_4$ form a eutectic system, with a eutectic temperature of 644 °C (see Table 5.1). As a result, a molten layer at the deposit outer surface was formed, which probably trickled down through the deposit pores to induce deposit sintering and therefore, increased the tensile adhesion strength of the deposits. Furthermore, corrosion occurring at the deposit–tube interface may have resulted in an increased melt fraction at the interface, since the corrosion products form a complex eutectic system with KCl, K$_2$SO$_4$ and CaSO$_4$.\(^\text{117}\)

CaO in boilers may react with SO$_2$ or SO$_3$ in the flue gas to undergo sulfation, forming CaSO$_4$.\(^\text{24,25,162}\)

\[
\begin{align*}
\text{CaO} + \frac{1}{2} \text{O}_2 & \rightarrow \text{CaSO}_4 \quad (5.3) \\
\text{CaO} + \text{SO}_3 & \rightarrow \text{CaSO}_4 \quad (5.4)
\end{align*}
\]

Sulfation may occur in the gas phase prior to deposition, or in solid phase after deposition on boiler surfaces.\(^\text{91}\) Furthermore, iron oxide in the steel may catalytically convert SO$_2$ to SO$_3$,\(^\text{57,137}\) thereby catalyzing the overall sulfation reaction and increasing the concentration of CaSO$_4$ near the steel surface.

Replacing CaO with CaSO$_4$ in the model deposit resulted in an increase in deposit adhesion strength, indicating that sulfation of Ca in boilers may result in the formation of strongly adherent deposits. Previous investigations have also indicated that sulfation of ash deposits may increase their adhesion strength.\(^\text{91}\) However, further investigation is required to completely understand the effect of sulfation on ash deposits.
Figure 5.8 Effect of deposit composition on tensile adhesion strength. Deposits sintered with a flue gas temperature of 650 °C, a cooling probe temperature of 500 °C, and a mean steel surface temperature of 562 °C for 2 hours. Superheater steel (TP347HFG) preoxidized for 24 hours.

Table 5.4 Statistical analysis of data sets with varying deposit composition. Two-tail Welch’s t-test for unpaired data with unequal variances, $\alpha = 0.05$. Deposits sintered with a flue gas temperature of 650 °C, a cooling probe temperature of 500 °C, and a mean steel surface temperature of 562 °C for 2 hours.

| Compared data sets | T        | p = P(|T| $\leq$ t$_{\alpha/2,\nu}$) | Data significantly different? (p $\leq$ 0.05?) |
|--------------------|----------|---------------------------------|-----------------------------------------------|
| Composition (wt %) | Composition (wt %) |                                  |                                               |
| KCl + K$_2$SO$_4$ (50%) | KCl + K$_2$SO$_4$ + CaO (33%) | 6.7866 | 0.0011 | Yes |
| KCl + K$_2$SO$_4$ + CaO (33%) | KCl + K$_2$SO$_4$ + CaSO$_4$ (33%) | -12.4072 | 0.0002 | Yes |
| KCl + K$_2$SO$_4$ (50%) | KCl + K$_2$SO$_4$ + K$_2$Si$_4$O$_9$ (33%) | -5.7502 | 0.0003 | Yes |
| KCl + K$_2$SO$_4$ (50%) | Straw fly ash | -0.3627 | 0.7237 | No |
The presence of silicates has been identified in slagging deposits, and in sintered biomass ash deposits. The addition of K$_2$Si$_4$O$_9$ to the model deposit containing KCl and K$_2$SO$_4$ increased its adhesion strength, as shown in Figure 5.8. The increase in tensile adhesion strength was statistically significant (see Table 5.4). Differential Scanning Calorimetry (DSC) analysis of K$_2$Si$_4$O$_9$ in a previous investigation has revealed the formation of a glass phase at 650 °C. The formation of glass phase probably caused deposit sintering and increased the contact area between the deposit and the tube, thereby increasing the tensile adhesion strength of the deposits.

The tensile adhesion strength of deposits prepared from straw fly ash was similar in magnitude to model deposits containing KCl and K$_2$SO$_4$ (50 wt %). Statistical analysis using Welch’s t-test indicated that significant statistical difference between the corresponding two data sets did not exist (see Table 5.4). This can be attributed to the composition of the straw fly ash, which is dominated by KCl and K$_2$SO$_4$ (approximately 50 wt % each). The results further suggest that the difference in particle size distribution of the straw fly ash and the model deposit did not significantly influence the tensile adhesion strength.

The tensile adhesion strength of biomass ash deposits investigated in this study is similar in magnitude to the shear adhesion strength of biomass ash deposits, as seen from a comparison with previous lab-scale investigations (1 – 350 kPa) and full-scale investigations (20 – 250 kPa), as well as coal ash deposits from lab-scale investigations (35 – 350 kPa). However, the deposits from kraft recovery boilers possess a higher adhesion strength, as seen from lab-scale investigations (1000 – 16000 kPa).

The present results allow better understanding of deposit shedding in boilers, and recognize the influence of melt fraction at the deposit–tube interface, corrosion and sintering on deposit adhesion strength in boilers.

5.4 Conclusions

The tensile adhesion strength of model deposits containing KCl, K$_2$SO$_4$, CaO, CaSO$_4$, K$_2$Si$_4$O$_9$, as well as straw fly ash obtained from a grate-fired boiler, was investigated in this study. Artificial ash deposits were prepared on superheater steel tubes, and sintered in an oven under the influence of a temperature gradient across the deposits. The effects of flue gas temperature, steel surface temperature and deposit composition were investigated.

The results revealed that the tensile adhesion strength of the model deposits containing KCl and K$_2$SO$_4$ (50 wt %) was low (< 12 kPa) at steel surface temperatures below 600 °C, with several deposits not
adhering to the steel tube. However, the tensile adhesion strength increased sharply at a steel surface temperature of 650 °C at the investigated conditions, with a mean value of 31.79 kPa. Corrosion products formed at the deposit–tube interface may form a eutectic system with the deposit, thereby forming a partially molten layer at the deposit–tube interface and increasing adhesion strength.

Furthermore, the results showed that varying the flue gas temperature from 500 – 650 °C did not have a significant effect on the adhesion strength of the model deposits. However, at a flue gas temperature of 700 °C, a sharp increase in tensile adhesion strength was observed. The temperature gradient across the deposits at a flue gas temperature of 700 °C induced migration of molten/vapor species from the outer layer of the deposit to the deposit-tube interface, causing liquid state sintering, increasing the tensile adhesion strength.

Variation of the chemistry of the model deposits revealed that the melt fraction of the ash deposit is an important parameter for determining deposit adhesion strength. Addition of compounds which increased the melt fraction of the deposit increased the tensile adhesion strength, whereas addition of inert compounds with a high melting point, such as CaO, decreased the tensile adhesion strength. Furthermore, the tensile adhesion strength of the deposits prepared using straw fly ash was similar in magnitude to model deposits containing KCl and K₂SO₄.
This chapter reports the experiments conducted for heterogeneous sulfation of model biomass ash deposits. The experiments were performed in three different experimental setups to quantify the shear as well as tensile adhesion strength of model deposits containing KCl. The influence of sulfation time, $SO_2$ concentration and sintering temperature was investigated.

The motivation for investigating heterogeneous sulfation of biomass ash deposits arose from an analysis of boiler deposits, conducted by the Danish energy company, Ørsted. The investigation revealed the formation of heavily sintered sulfur-rich deposits, which were strongly adherent to superheater steel tubes. The sulfur-rich deposits were probably formed due to sulfation of K and Ca species in the boiler, which may have occurred prior to deposit formation, or after deposit formation. The influence of sulfation, prior to deposit formation, on the deposit adhesion strength has been simulated in Chapter 4 and Chapter 5. The influence of heterogeneous sulfation, after deposit formation, on the deposit adhesion strength has been explored in this chapter.

### 6.1 Introduction

In boilers, KCl and KOH may undergo sulfation in the gas phase,\(^{21}\) or in the condensed phase after deposition on boiler surfaces.\(^{51}\) While gas phase sulfation is significantly faster than condensed phase sulfation,\(^ {21,23,51}\) the deposit is exposed to the flue gas for a longer period of time, making both sulfation mechanisms relevant. Similarly, CaO can undergo sulfation to form $CaSO_4$.\(^ {24,25}\)

Sulfation of KCl in deposits may occur as a gas-solid or a gas-liquid reaction by $SO_2$\(^ {135}\) or $SO_3$\(^ {136}\) as shown below. KCl may be present in the deposits in solid or molten phase.

\[
2 \text{KCl} + \text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2 \text{HCl}
\]  
\[(6.1)\]

\[
2 \text{KCl} + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2 \text{HCl}
\]  
\[(6.2)\]

In the absence of water vapor, KCl may react with $SO_2$ to release $Cl_2$, according the following reaction,\(^ {57}\) although water vapor is usually present in the boiler chamber.
\[ 2 \text{KCl} + \text{SO}_2 + \text{O}_2 \rightarrow \text{K}_2\text{SO}_4 + \text{Cl}_2 \] (6.3)

The rate of KCl sulfation depends on temperature and partial pressures of \( \text{SO}_2 \), \( \text{O}_2 \) and \( \text{H}_2\text{O} \).\(^{163} \) Several studies have identified an increase in the rate of sulfation with increasing temperature, with a sharp increase in the rate of sulfation near the melting point of KCl (770 °C), suggesting that the gas-liquid reaction is faster than the gas-solid reaction.\(^{21,57,136,163,164} \) However, a study has identified a slight decrease in the rate of sulfation from 450 – 600 °C.\(^{165} \)

While the rate of sulfation increases with increasing \( \text{SO}_2 \) and \( \text{O}_2 \) partial pressure, varying \( \text{H}_2\text{O} \) partial pressure has exhibited a negligible effect on the rate of sulfation.\(^{21,51,135} \) However, some studies claim a dependence of the rate of sulfation on \( \text{H}_2\text{O} \) partial pressure.\(^{163} \) The availability of \( \text{SO}_3 \) in the flue gas significantly accelerates the sulfation reaction.\(^{21,166} \) Therefore, the conversion of \( \text{SO}_2 \) to \( \text{SO}_3 \) in the gas phase may potentially be the rate limiting step for the overall sulfation reaction.\(^{135,167} \) However, other studies have indicated that the oxidation of potassium sulfite to potassium sulfate may be the rate limiting step.\(^{168} \) Nevertheless, iron oxide may catalytically convert \( \text{SO}_2 \) to \( \text{SO}_3 \) or react with \( \text{SO}_2 \) to form Fe(III) sulfites or sulfates,\(^{138,139} \) thereby catalyzing the overall sulfation reaction and increasing the concentration of \( \text{K}_2\text{SO}_4 \) near the steel surface.

Sulfation of alkali chlorides can strongly influence ash deposition, corrosion and shedding in boilers. Sulfation of KCl may reduce overall deposit growth in boilers.\(^{26} \) Investigations cofiring biomass with coal,\(^{27-29} \) elemental sulfur,\(^{30} \) ammonium sulfate,\(^{30-32} \) ferric sulfate,\(^{33,34} \) aluminum sulfate\(^{34,35} \) and ferrous sulfide\(^{36} \) have indicated that sulfation of KCl prior to deposit formation may reduce corrosion in boilers. However, heterogeneous sulfation of KCl in the deposit, resulting in the liberation of HCl or Cl\(_2\), may increase corrosion of superheater tubes.\(^{37} \) Investigations in Chapter 4 and Chapter 5 have indicated that sulfation of KCl and CaO prior to deposit formation may increase the adhesion strength of biomass ash deposits. However, the effect of heterogeneous sulfation, after deposit formation, on the adhesion strength of biomass ash deposits has not been investigated previously, to the best of the authors’ knowledge.

In this chapter, heterogeneous sulfation of biomass ash deposits has been investigated. Model deposits containing KCl were prepared on superheater tubes and sintered in three different experimental setups, followed by adhesion strength measurements. The effect of sulfation time, \( \text{SO}_2 \) concentration and sintering temperature on the shear/tensile adhesion strength of the deposits was investigated.
6.2 Experimental section

6.2.1 Materials

Artificial biomass ash deposits were prepared using pure KCl (Sigma Aldrich, CAS number: 7447-40-7), milled and sieved to obtain a particle size distribution in the range 32 – 90 µm. However, it should be noted that fly ash particles in biomass boilers typically form a bimodal size distribution, containing submicron particles (typically rich in K, Cl and S), as well as larger particles (typically rich in Si and Ca) with sizes up to 200 µm. Accurately reproducing the typical bimodal size distribution of fly ash for the experiments is a tedious process. Therefore, a fixed particle size distribution in the range 32 – 90 µm was adopted in the experiments.

The deposits were prepared on superheater steel tubes (TP347HFG, Salzgitter Mannesmann), with an outer diameter of 38 mm, a thickness of 5 mm. The chemical composition of the tube can be found in Chapter 4, Table 4.2. TP347HFG is characterized by its high Cr, Mn and Ni content. The presence of Cr and Mn in steel reduces oxide scale growth by forming Cr-Mn-spinels, improving the overall corrosion resistance, while Ni deters Cl induced corrosion.

Preoxidation of the steel tubes provides a more accurate replication of operational boiler tubes. Thermogravimetric analysis of the steel tubes at 600 °C in Chapter 4 (see Figure 4.1) has indicated that the majority of oxidation occurs rapidly in the first 10 hours, with the oxidation rate slowing down significantly after 24 hours. Therefore, the steel tubes were preoxidized for 24 hours at 600 °C prior to sample preparation.

6.2.2 Sample Preparation

KCl was thoroughly mixed with a 50% isopropanol solution to prepare a slurry. The use of slurries to prepare ash deposits is in accordance with EU guidelines. The slurry was molded into cubical shaped deposits on the superheater tube using a Teflon mold (see section 4.2, and section 5.2). The contact surface area of each deposit to the superheater tube was 223 mm².

6.2.3 Deposit Sintering and Adhesion strength measurements

Experiments were carried out in three different setups,

Setup 1

The setup described in Chapter 4 (Shear Adhesion Strength Setup) was modified to enable SO₂ injection into the oven. Details on the setup can be found in Appendix B. The setup allowed two model deposit...
samples to be simultaneously heated to a fixed temperature (500 – 650 °C). The deposits were then sintered for a specified time (2 – 4 hours), with SO₂ present in the gas stream (50 – 500 ppm). Subsequently, shear adhesion strength measurements were performed at the sintering temperature.

**Setup 2**

SO₂ was injected into the setup described in Chapter 5 (Tensile Adhesion Strength Setup). Details on the setup can be found in Section 5.2.3 and Appendix C. Eight deposits were heated to a fixed temperature, and subsequently sintered for a specified time (0 – 24 hours), with SO₂ in the gas stream (0 – 600 ppm). The flue gas was maintained at 775 °C, and the cooling probe was maintained at 550 °C, incorporating a temperature gradient across the deposit. Subsequently, tensile adhesion strength measurements were performed in the setup.

**Setup 3**

The setup consisted of an electrically heated horizontal quartz tube (outer diameter = 66 mm, thickness = 3.2 mm, length = 1000 mm), a gas mixing panel and a flue gas cleaning system. A schematic representation of the setup is shown in Figure 6.1. N₂, O₂ and CO₂ streams were injected into the quartz tube through a water bath at 50 °C, whereas SO₂ was injected directly into the quartz tube. The moisture content (at saturation) in air at 50 °C is 83 g/m³. The flow rate of the gases was controlled using mass flow controllers. The gas line from the water bath to the oven was heated to 150°C, in order to prevent condensation of water vapor. The flue gas cleaning system consisted of a condensate trap, an NaOH scrubber and a drying tube filled with silica gel.

Eight deposits samples were placed inside the quartz tube, and heated to the desired temperature (550 – 650 °C). During heat-up, N₂, O₂ and CO₂, saturated with water vapor, were injected into the oven. When the desired temperature was reached, SO₂ injection (0 – 500 ppm) was turned on, and the deposit samples were sintered for a specified duration (1 – 24 hours). However, after sintering, the deposits were cooled down, and the shear adhesion strength of the deposits was measured in Setup 1 at room temperature. Further details on the setup, sample preparation, and deposit sintering can be found in Appendix D.
6.3 Results and Discussion

6.3.1 Effect of sulfation time

The effect of sulfation time on adhesion strength was investigated in Setup 2 and Setup 3.

Figure 6.2 shows the effect of sulfation time on the tensile adhesion strength in Setup 2. Experiments were performed with a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C using 60 ppm SO₂.

It was observed that the tensile adhesion strength of the deposits gradually increased with increasing sulfation time. Visual observations of the deposit–tube interface after debonding indicated that that a slightly thicker and more widespread corrosion layer can be observed, while comparing the deposits sulfated for 0 hours and 24 hours (see Appendix C, Figure C.10).

Statistical analysis using Welch’s t-test was performed on the experimental data, assuming that the data follow a log-normal distribution. Information on Welch’s t-test can be found in Section 5.2.5. The results from the statistical analysis indicated that the adhesion strength data corresponding to a sulfation time of 24 hours (mean adhesion strength = 29.58 kPa) was significantly different from the adhesion strength data for a sulfation time of 0 hours (mean adhesion strength = 7.40 kPa), although significant difference could not be observed while comparing adjacent data sets (see Table 6.1).

Figure 6.1 Electrically heated horizontal quartz tube.
**Figure 6.2** Influence of sulfation time on shear adhesion strength, Setup 2. KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C, a mean steel surface temperature of 611 °C, using 60 ppm SO\(_2\). Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

**Table 6.1** Statistical analysis of data with varying sulfation time, Setup 2. Two-tail Welch’s t-test for unpaired data with unequal variances, \(\alpha = 0.05\). KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C using 60 ppm SO\(_2\). Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

| Compared data sets | \(p = P(|T| \leq t_{1-\alpha/2,\nu})\) | Data significantly different? (\(p \leq 0.05\)?) |
|--------------------|----------------------------------------|-----------------------------------------------|
| Sulfation time (h) | Sulfation time (h)                     |                                               |
| 0                  | 2                                      | 0.92                                          | No                                           |
| 2                  | 4                                      | 0.06                                          | No                                           |
| 4                  | 8                                      | 0.59                                          | No                                           |
| 8                  | 24                                     | 0.36                                          | No                                           |
| 0                  | 24                                     | 0.02                                          | Yes                                          |
However, Energy-dispersive X-ray Spectroscopy (EDS) of the deposits sulfated for 24 hours using 600 ppm SO$_2$, revealed a Sulfur content of 1 wt %, indicating a low degree of sulfation at the investigated temperatures. Since the SO$_2$ concentration in the aforementioned experiments was 60 ppm, an even lower Sulfur content is expected. Therefore, the observed increase in adhesion strength with sulfation time cannot be conclusively attributed to the ongoing sulfation reaction, and may possibly be the effect of sintering and corrosion layer growth with time. Repeating the experiments in the absence of SO$_2$ will provide an insight into this issue. However, the results presented in Section 4.3.5 indicated that sintering model KCl–K$_2$SO$_4$ deposits in the absence of SO$_2$, did not significantly influence the adhesion strength of the deposits, up to 24 hours at 650 °C. Therefore, further investigation is required to understand the effect of sulfation time on the adhesion strength.

However, two theories, describing the possible effect of sulfation on the deposits, are hypothesized:

- The mean steel surface temperature at the investigated conditions is 598 °C, which is probably too low for significant sulfation to occur at the deposit–tube interface. However, the iron oxide present in the steel tube may catalyze the sulfation reaction, by catalytically converting SO$_2$ to SO$_3$,\textsuperscript{57,137} or by reacting with SO$_2$ to form Fe(III) sulfites or sulfates,\textsuperscript{138,139} resulting in the formation of K$_2$SO$_4$ at the deposit–tube interface. K$_2$SO$_4$ forms a complex eutectic system with KCl and the corrosion products formed at the deposit–tube interface (Fe/Cr chlorides, oxides, chromates, etc.).\textsuperscript{56,57,91} This may result in the formation of a partially molten layer at the interface at the investigated conditions, increasing surface wetting and adsorption,\textsuperscript{134} and leading to an increase in adhesion strength. The formation of a corrosion-induced partially molten layer at temperatures below the eutectic temperature of the KCl–K$_2$SO$_4$ system has been described in Section 4.3.3.

- At the outer surface of the deposit, in contact with gas at a temperature of 775 °C, sulfation of KCl may occur as a heterogeneous reaction, leading to the formation of K$_2$SO$_4$. Since K$_2$SO$_4$ forms a eutectic system with KCl, with a eutectic temperature of 690 °C,\textsuperscript{117} a partially molten layer may have formed at the outer surface of the deposit. The partially molten layer may then trickle down through the pores of the deposit, solidifying at lower temperatures inside the deposit. This phenomenon is observed in full-scale boilers in the form of liquid state sintering,\textsuperscript{1,49,158} resulting in the formation of hard and strongly adherent deposits. Sintering increases the density and thermal conductivity of the deposits,\textsuperscript{48} thereby gradually increasing the temperature of the deposit with time. As a result, the partially molten layer may reach the deposit–tube interface, increasing the surface wetting and therefore, the tensile adhesion strength.

Figure 6.3 shows the effect of sulfation time on the shear adhesion strength of the deposits in Setup 3. Experiments were performed at a sintering temperature of 600 °C using 50 ppm SO$_2$. The samples were cooled down after sintering, followed by shear strength measurements at room temperature.
Contrary to the inferences obtained from Setup 2, it was observed that increasing the sulfation time from 1 – 2 hours drastically decreased the mean adhesion strength of the deposits (57.93 – 1.92 kPa). Further increasing the sulfation time from 2 – 24 hours resulted in a gradual decrease in the mean adhesion strength (5.08 – 1.92 kPa). The decrease in adhesion strength from 2 – 24 hours was statistically significant (see Table 6.2). However, similar to observations in Setup 2, a thicker and more widespread corrosion layer, at the deposit–tube interface, was observed with increasing sulfation time (see Appendix D, Figure D.3).

The two key differences between Setup 2 and Setup 3 were:

a) A temperature gradient across the deposits was present in Setup 2, whereas the isothermal conditions prevailed in Setup 3.

b) Adhesion strength measurements were performed at high temperatures in Setup 2, whereas the deposits were cooled down to room temperature in Setup 3, followed by adhesion strength measurements at room temperature.

It is speculated that cooling down the deposits prior to adhesion strength measurements in Setup 3 may be the reason for the observed decrease in adhesion strength with sulfation time. Cooling the deposits after sintering induces thermal stresses at the deposit–tube interface, owing to differences in the thermal expansion coefficients between the steel tube, the corrosion layer and the deposit.\(^1\) The corrosion layer, typically dominated by Fe/Cr oxides, has a thermal expansion coefficient \((8 – 12 \cdot 10^{-6} /\text{K})\)\(^{169}\) lower than the steel TP347HFG \((16 – 18 \cdot 10^{-6} /\text{K})\)\(^{124}\) and the KCl rich deposit \((36 – 55 \cdot 10^{-6} /\text{K})\)\(^{170}\) in the investigated temperature range (25 – 600 °C). Investigations in Section 4.3.6 have indicated that cooling down the deposits after sintering causes a reduction in the adhesion strength of the deposits.

The corrosion layer thickness increased with increasing sulfation time (see Appendix C, Figure C.10). Furthermore, previous studies in Chapter 4 have indicated that increasing corrosion increases the contact area between the deposit and the steel tube. It appears that the corrosion layer in the experiments corresponding to larger sulfation times was unable to absorb the thermal stresses, while the deposits were cooled down to room temperature. As a result, increasing sulfation time probably led to an increase in the probability of cracks developing at the deposit–tube interface, and thereby a decrease in the measured adhesion strength.

Application of thermal shocks to induce deposit shedding is a commonly used technique to remove heavily sintered deposits from superheater tubes.\(^{149}\) The results suggest that thermal shocks might be more effective in deposit shedding if a thick corrosion layer, possibly due to heterogeneous sulfation, is formed at the deposit–tube interface.
Figure 6.3 Influence of sulfation time on shear adhesion strength, Setup 3. KCl deposits sintered at 600 °C using 50 ppm SO$_2$. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

Table 6.2 Statistical analysis of data with varying sulfation time, Setup 3. Two-tail Welch’s $t$-test for unpaired data with unequal variances, $\alpha = 0.05$. KCl deposits sintered at 600 °C using 50 ppm SO$_2$. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

| Sulfation time (h) | Sulfation time (h) | $p = P(|T| \leq t_{1-\alpha/2,\nu})$ | Data significantly different? ($p \leq 0.05$?) |
|-------------------|-------------------|-----------------------------------|------------------------------------------|
| 1                 | 2                 | 0.0006                            | Yes                                      |
| 2                 | 4                 | 0.56                              | No                                       |
| 4                 | 24                | 0.08                              | No                                       |
| 2                 | 24                | 0.045                             | Yes                                      |
The deposits sintered for 1 hour in Setup 3, possess a high adhesion strength (mean adhesion strength = 57.93 kPa), compared to the deposits sintered in Setup 2, for 0 hours (mean adhesion strength = 7.40 kPa). This may possibly be attributed to presently unknown processes occurring during deposit cooldown. Another possible reason may be the presence of water vapor in the gas stream, during heat-up and cooldown, in Setup 3, which might have resulted in additional corrosion of the superheater steel tubes. However, further investigation is required to understand the effect of water vapor on adhesion strength.

In order to quantify the degree of sulfation occurring in the deposits, selected samples were investigated using Inductive Coupled Plasma (ICP) analysis. Table 6.3 shows the sulfur content of the investigated deposit samples. Furthermore, a kinetic sulfation model proposed by Sengeløv et al. was constructed to predict the degree of sulfation in the deposits. The kinetic model estimates conversion of KCl to K$_2$SO$_4$, as described by Equation 6.4.

$$\frac{dX}{dt} = 2.7 \cdot 10^7 \exp\left(\frac{-18911}{T}\right)(1-X)^{2/3} \frac{Y_{SO_2}}{1+708 \cdot Y_{SO_2}} \left(Y_{SO_2}^{0.37}\right)$$  \hspace{1cm} \text{(6.4)}$$

where $X$ is the fractional conversion of KCl, as shown in Equation 6.5, and $Y_{SO_2}$ is the mole fraction of SO$_2$.

$$X = \frac{m_0 - m}{m_0}$$  \hspace{1cm} \text{(6.5)}$$

$m_0$ and $m$ are the initial and final mass of KCl (kg).

The sulfur content predicted from the model simulations is presented in Table 6.3.

The results revealed a low degree of sulfation in the experiments at the investigated conditions, compared to predictions by the kinetic model, indicating that the sulfation reaction in the experiments was probably mass transfer controlled. Nevertheless, an increasing sulfur content with sulfation time was observed, while comparing the deposits sulfated for 4 hours and 24 hours, in Setup 3. However, considering that only 0.2% of KCl is converted into K$_2$SO$_4$ after 24 hours in Setup 3, the cause of the observed change in adhesion strength cannot be ascertained without further investigation.

The results from Setup 2 and Setup 3 indicate that heterogeneous sulfation of boiler deposits may be extremely slow at relatively low flue gas temperatures ($<775^\circ$C), and may occur only in severe cases, where the deposits sinter in the boiler for long durations. Since sintering in boilers may occur for weeks or even months, experiments spanning for longer durations are desirable.
Table 6.3 Sulfur content of selected deposit samples obtained through ICP analysis.

<table>
<thead>
<tr>
<th>Setup</th>
<th>Experimental conditions</th>
<th>Sulfur content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Sulfation time (h)</td>
</tr>
<tr>
<td>Setup 1</td>
<td>600</td>
<td>4</td>
</tr>
<tr>
<td>Setup 3</td>
<td>600</td>
<td>4</td>
</tr>
<tr>
<td>Setup 3</td>
<td>600</td>
<td>24</td>
</tr>
<tr>
<td>Setup 3</td>
<td>650</td>
<td>24</td>
</tr>
</tbody>
</table>

6.3.2 Effect of SO₂ concentration

The effect of SO₂ concentration on adhesion strength was investigated in Setup 1, Setup 2, and Setup 3. Figure 6.4 shows the effect of SO₂ concentration on the shear adhesion strength of the deposits in Setup 1. Experiments were performed at a sintering temperature of 600 °C for 4 hours. Adhesion strength measurements were performed at 600 °C after sintering.

It was observed that varying SO₂ concentration did not have a significant effect on the shear adhesion strength of the deposits at the investigated conditions. Furthermore, a visually significant change in the corrosion layer thickness at the deposit–tube interface, with increasing SO₂ concentration, was not observed (see Appendix B, Figure B.8).
Figure 6.4 Influence of $SO_2$ concentration on shear adhesion strength, Setup 1. KCl deposits sintered at 600 °C for 4 hours. Shear strength measurements performed at 600 °C. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

Figure 6.5 shows the effect of $SO_2$ concentration on the tensile adhesion strength in Setup 2. Experiments were performed at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C for 2 hours (Figure 6.5a), 4 hours (Figure 6.5b), and 24 hours (Figure 6.5c).

Irrespective of the sulfation time, varying $SO_2$ concentration did not have a significant effect on the tensile adhesion strength at the investigated conditions. This inference was bolstered by statistical data analysis using Welch's t-test (see Table 6.4). Furthermore, similar to observations in Setup 1, a visually significant change in the corrosion layer thickness at the deposit–tube interface, with increasing $SO_2$ concentration, was not observed (See Appendix C, Figure C.II). However, the steel tube appeared extremely corroded in the experiment corresponding to 24 hours of sulfation using 600 ppm $SO_2$. 
6.3 Results and Discussion

Figure 6.5 Influence of SO₂ concentration on shear adhesion strength, Setup 2. KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C, a mean steel surface temperature of 611 °C, for (a) 2 hours, (b) 4 hours, and (c) 24 hours. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.
Table 6.4 Statistical analysis of data with varying SO$_2$ concentration, Setup 2. Two-tail Welch’s t-test for unpaired data with unequal variances, $\alpha = 0.05$. KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C for (a) 2 hours, (b) 4 hours, and (c) 24 hours. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

| Compared data sets | $p = P(|T| \leq t_{1-\alpha/2,\nu})$ | Data significantly different? ($p \leq 0.05$?) |
|--------------------|---------------------------------|---------------------------------------------|
| SO$_2$ concentration (ppm) | SO$_2$ concentration (ppm) |
| 2 hours            |                                 |                                             |
| 0                  | 60                              | 0.77                                        | No                                           |
| 60                 | 600                             | 0.12                                        | No                                           |
| 0                  | 600                             | 0.10                                        | No                                           |
| 4 hours            |                                 |                                             |
| 60                 | 300                             | 0.13                                        | No                                           |
| 300                | 600                             | 0.11                                        | No                                           |
| 60                 | 300                             | 0.74                                        | No                                           |
| 24 hours           |                                 |                                             |
| 60                 | 600                             | 0.53                                        | No                                           |

A possible justification for the observed phenomenon may be attributed to the lack of ongoing sulfation in the experiments, probably due to mass transfer limitations within the setup and the deposit. EDS analysis revealed a Sulfur content of 1 wt % for the deposit subjected to the harshest conditions (600 ppm SO$_2$ for 24 hours). Further investigation, using higher temperatures and longer sulfation times, is required to understand the effect of SO$_2$ concentration on heterogeneous sulfation and adhesion strength.

Figure 6.6 shows the effect of SO$_2$ concentration on the shear adhesion strength of the deposits in Setup 3. The deposits were sintered at a temperature of 600 °C for 4 hours. The samples were cooled down after sintering, followed by shear strength measurements at room temperature.

The results did not show any specific trend with varying SO$_2$ concentration. Increasing the SO$_2$ concentration from 0 – 50 ppm caused a decrease in the mean value of the adhesion strength (from 64.67 – 3.45 kPa). Furthermore, the adhesion strength data corresponding to an SO$_2$ concentration of 0 ppm exhibits a surprisingly large amount of scatter. However, increasing the SO$_2$ concentration from 50 – 250 ppm increased the mean adhesion strength of the deposits, from 3.45 – 30.97 kPa. Further increasing the SO$_2$ concentration from 250 – 500 ppm led to a decrease in the mean adhesion strength, from 30.97 – 1.98 kPa.
Figure 6.6 Influence of SO$_2$ concentration on shear adhesion strength, Setup 3. KCl deposits sintered at 600 °C for 4 hours. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

Table 6.5 Statistical analysis of data with varying SO$_2$ concentration, Setup 3. Two-tail Welch’s t-test for unpaired data with unequal variances, $\alpha = 0.05$. KCl deposits sintered at 600 °C for 4 hours. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

| Compared data sets | p=P(|T|\leq t_{1-\alpha/2,\nu}) | Data significantly different? (p ≤0.05?) |
|--------------------|-------------------------------|----------------------------------------|
| SO$_2$ concentration (ppm) | SO$_2$ concentration (ppm) |                                   |
| 0          | 50               | 0.13                                | No                                      |
| 50         | 100              | 0.15                                | No                                      |
| 100        | 250              | 0.07                                | No                                      |
| 250        | 500              | <0.01                               | Yes                                     |
| 0          | 500              | 0.03                                | Yes                                     |
Statistical analysis of the data indicated that significant difference in adhesion strength did not exist from 0 – 250 ppm (see Table 6.5). However, the adhesion strength data corresponding to an SO$_2$ concentration of 500 ppm was significantly lower than the adhesion strength data for 0 ppm and for 250 ppm.

Contrary to observations in Setup 1 and Setup 2, increasing the SO$_2$ concentration in Setup 3 from 0 – 250 ppm, led to an increase in the corrosion layer thickness (see Appendix D, Figure D.4). However, the corrosion layer of the deposit corresponding to an SO$_2$ concentration of 500 ppm was slightly lower than the deposit corresponding to 250 ppm SO$_2$.

The reason for the observed phenomenon is not understood presently. The initial decrease in adhesion strength with sulfation might have been due to the formation of a corrosion layer, which was not able to absorb the thermal shocks induced while cooling down the deposit. However, the observed trend from an SO$_2$ concentration of 50 – 500 ppm is surprising. The difference may likely be due to unknown processes occurring during heat-up or cooldown of the deposits. Therefore, owing to the thermal shocks exerted on the deposit prior to strength measurement, the results from Setup 3 should be taken with a pinch of salt, and should not be used for comparing the effect of different operational parameters on the adhesion strength of the deposit. The results highlight the importance of conducting adhesion strength measurements at high temperature, subsequently after sintering.

### 6.3.3 Effect of sintering temperature

The effect of sintering temperature on adhesion strength was investigated in Setup 1 and Setup 3.

Figure 6.7 shows the effect of sintering temperature on the shear adhesion strength of the deposits in Setup 1. Experiments were performed for 2 hours, and 4 hours, using 50 ppm SO$_2$. Shear strength measurements were performed at the sintering temperature.

It was observed that the measured adhesion strength did not change significantly, while varying the sintering temperature from 500 – 650 °C, irrespective of the sulfation time. Furthermore, a significant change in the corrosion layer thickness, with increasing temperature, was not observed from 500 – 600 °C at the investigated conditions (See Appendix B, Figure B.9). However, the deposits sintered at 650 °C, appeared to have a slightly larger corrosion layer.
Results and Discussion

Figure 6.7 Influence of sintering temperature on shear adhesion strength, Setup 1. KCl deposits sintered for (a) 2 hours, and (b) 4 hours, using 50 ppm SO\textsubscript{2}. Shear strength measurements performed at the sintering temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

The justification for the observed phenomenon may possibly be attributed to the mass transfer limitations in the deposit. The overall rate of sulfation in the experiments was probably too low to observe substantial changes in adhesion strength at the investigated conditions. ICP analysis indicated that deposits sintered at 600 °C, for 4 hours using 50 ppm SO\textsubscript{2}, contained only 0.031 wt % S (see Table 6.3). Furthermore, previous studies have indicated that the rate of sulfation significantly increases only after the formation of a molten phase,\textsuperscript{21,57,136,163,164} which was not formed in the aforementioned experiments. Nevertheless, further investigation, at higher temperatures, and for longer durations, is required to understand the effect of temperature on the deposit adhesion strength. However, steel surface temperatures in boilers rarely exceed 650 °C.

Figure 6.8 shows the effect of sintering temperature on the shear adhesion strength of the deposits in Setup 3. The deposits were sintered for 4 hours using 60 ppm SO\textsubscript{2}. The samples were cooled down after sintering, followed by shear strength measurements at room temperature.

The results indicate that increasing sintering temperature from 550 – 600 °C decreased the mean adhesion strength of the deposits from 64.67 – 3.25 kPa. Further increasing the sintering temperature to
650 °C increased the mean adhesion strength to 20.62 kPa. Statistical analysis of the data indicated a significant difference between the data sets corresponding to 550 – 600 °C, and 600 – 650 °C (see Table 6.6). However, no statistically significant difference was observed while comparing the data sets corresponding to 550 – 650 °C. Furthermore, an increasing corrosion layer thickness was observed while increasing the sintering temperature from 550 – 650 °C (see Appendix D, Figure D.5).

The irregular behavior of adhesion strength with varying sintering temperature in Setup 3 may be attributed to unknown processes occurring during heat-up and cooldown of the deposits. Further investigation is required to understand the observed variation of adhesion strength with sintering temperature.

Higher temperatures were not investigated in the present study in Setup 1 and Setup 3, since higher sintering temperature could have induced melting of the deposits, and potentially damaged the setup. Furthermore, flue gas temperatures higher than 775 °C in Setup 3 led to partially molten deposits, where the hooks used for strength measurement (see Figure C.9) fell off, such that the tensile adhesion strength could not be measured.
Figure 6.8 Influence of sintering temperature on shear adhesion strength, Setup 3. KCl deposits sintered for 4 hours using 50 ppm SO$_2$. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

Table 6.6 Statistical analysis of data with varying sintering temperature, Setup 3. Two-tail Welch’s t-test for unpaired data with unequal variances, $\alpha = 0.05$. KCl deposits sintered for 4 hours using 50 ppm SO$_2$. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours.

| Compared data sets | $p=P(|T|\leq t_{1-\alpha/2,\nu})$ | Data significantly different? ($p \leq 0.05$?) |
|--------------------|----------------------------------|---------------------------------------------|
| Sintering temperature (°C) | Sintering temperature (°C) | | |
| 550 | 600 | <0.01 | Yes |
| 600 | 650 | <0.01 | Yes |
| 550 | 650 | 0.34 | No |
6.4 Conclusions

Model biomass ash deposits, containing KCl, were prepared on superheater steel tubes, and subjected to heterogeneous sulfation, to investigate the effect of sulfation time, SO$_2$ concentration and sintering temperature on the shear/tensile adhesion strength of the deposits.

Specifically, the three experimental setups investigated:

1. Shear adhesion strength of sulfated model deposits at sintering temperatures ranging from 500 – 650 °C, for 2 – 4 hours, with SO$_2$ concentrations in the gas phase from 50 – 500 ppm. The shear adhesion strength was measured at the sintering temperature.

2. Tensile adhesion strength of sulfated model deposits, with a temperature gradient across the deposit layer. Experiments were performed at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C for 0 – 24 hours, with SO$_2$ concentrations in the gas phase from 0 – 600 ppm. The tensile adhesion strength was measured at the sintering temperature.

3. Shear adhesion strength of sulfated model deposits at sintering temperatures of 550 – 650 °C, for 1 – 24 hours, with 0 – 500 ppm SO$_2$ in the gas phase. The deposits were cooled down, and the shear adhesion strength was measured at the room temperature.

Table 6.7 Effect of sulfation time, SO$_2$ concentration, and sintering temperature on the mean adhesion strength in Setup 1, Setup 2, and Setup 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effect on mean adhesion strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Setup 1</td>
</tr>
<tr>
<td>Increasing sulfation time</td>
<td>Not studied</td>
</tr>
<tr>
<td>Increasing SO$_2$ concentration</td>
<td>No significant effect from 50 – 500 ppm</td>
</tr>
<tr>
<td>Increasing sintering temperature</td>
<td>No significant effect from 500 – 650 °C</td>
</tr>
</tbody>
</table>
6.4 Conclusions

Table 6.7 summarizes the effect of the sulfation time, SO\textsubscript{2} concentration, and sintering temperature on the adhesion strength in the three experimental setups.

The results from Setup 3 indicate an irregular trend, probably due to unidentified processes occurring during deposit cooldown prior to strength measurement, and should be disregarded for understanding the effect of operating conditions on the adhesion strength of the deposits.

Increasing sulfation time in Setup 2 gradually increased the adhesion strength and the corrosion layer thickness at the deposit–tube interface. However, Energy-dispersive X-ray Spectroscopy of the deposits indicated a low degree of sulfation (1 wt % S for deposits sulfated for 24 hours, using 600 ppm SO\textsubscript{2} with a flue gas temperature of 775 °C, and a mean steel surface temperature of 598 °C). Therefore, it is uncertain if the observed increase in adhesion strength was due to the ongoing sulfation reaction, or due to the effect of sintering and corrosion layer growth over time.

Varying SO\textsubscript{2} concentration in Setup 2 and Setup 3 did not have a significant influence on the adhesion strength of the deposits, and the corrosion layer thickness, at the investigated conditions. This may again be attributed to the low degree of observed sulfation in the experiments, probably due to mass transfer limitations in the experimental setup or within the deposits. ICP analysis indicated that deposits sintered at 600 °C for 4 hours using 50 ppm SO\textsubscript{2} contained only 0.031 wt % S (see Table 6.3).

Varying sintering temperature in Setup 1 did not have a significant impact on the adhesion strength of the deposits at the investigated conditions. Furthermore, a significant change in the corrosion layer thickness, was not observed from 500 – 600 °C. However, the deposits sintered at 650 °C, appeared to have a slightly larger corrosion layer.

Further investigation is required to understand the effect of operating conditions on the adhesion strength of ash deposits during heterogeneous sulfation. The investigations may ideally be performed in Setup 2, which allows experiments at relatively higher temperatures, under the influence of a temperature gradient across the deposits. Experiments should be performed at harsher conditions, such as longer sulfation times, higher SO\textsubscript{2} concentrations, and possibly higher sintering temperatures. Nevertheless, the obtained results indicate that heterogeneous sulfation of boiler deposits may be extremely slow at flue gas temperatures below 775 °C, and may occur only in severe cases, where the deposits sinter in the boiler for long durations.
This thesis is the culmination of three years of research on deposit formation, sintering, and shedding in biomass-fired boilers. This chapter summarizes the main conclusions of this thesis and provides suggestions for future work.

### 7.1 Summary of Conclusions

The second chapter of this thesis provided an overview of biomass combustion in boilers. The mechanisms behind formation of fly ash and aerosols, transport of ash species and deposit formation, deposit consolidation and sintering, and shedding of ash deposits, were discussed.

The third chapter presented the results of an investigation simulating deposit formation on superheater tubes in biomass-fired boilers. Experiments were performed in a laboratory-scale Entrained Flow Reactor, using model biomass fly ash, prepared from mixtures of K$_2$Si$_4$O$_9$, KCl, K$_2$SO$_4$, CaO, SiO$_2$ and KOH, as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood cofired fly ash. The model fly ash particles were mixed with air and injected into a 2 m long electrically heated furnace, to form deposits on an air-cooled probe at the outlet of the furnace. Furthermore, a mechanistic model was developed to predict deposit formation of K$_2$Si$_4$O$_9$ in the reactor. The following inferences were deduced:

- Increasing the gas temperature (589 – 968 °C) increased the sticking probability of the model fly ash particles, thereby resulting in higher deposit formation rates.
- Increasing the probe surface temperature from 300 – 450 °C increased the sticking probability of the deposit surface, resulting in increased deposit formation. However, varying the probe surface temperature from 450 – 550 °C did not significantly influence the deposit formation rate at the investigated conditions.
- Increasing gas velocity (0.7 – 3.5 m/s), and thereby the particle velocity, resulted in a decrease in the rate of deposit formation, since an increase in the kinetic energy of the particles results in increased particle rebound from the deposit surface after impaction.
Concluding Remarks

• The deposit formation rate increased with time, up to 30 min, since an increasing deposit thickness led to higher temperatures at the deposit surface, thereby increasing the sticking probability of the deposit surface. However, the growth rate of the deposit was approximately constant from 30 – 60 min at the investigated conditions.

• Increasing fly ash flux (10000 – 40000 g/m²/h) resulted in a linear increase in the deposit formation rate.

• Increasing the particle size of the fly ash (3.5 – 90 µm) resulted in a higher rate of deposit formation, since larger particles are more likely to detach from the gas streamlines around the steel tube and impact the tube surface.

• The model was able to reasonably predict the influence of flue gas temperature and fly ash flux, suggesting that accounting for energy dissipation due to particle deformation, for predicting the sticking probability of incoming ash particles, seems to be fairly successful in predicting the influence of changes in local conditions on the deposit formation process. However, the model was unable to accurately predict the influence of probe surface temperature, gas velocity and probe residence time.

• The deposit formation rate of the investigated species decreased in the following order: KOH > K₂SO₄ > KCl > K₂Si₄O₉ > SiO₂ > CaO, at the investigated conditions.

• Addition of KCl to K₂Si₄O₉, SiO₂, CaO, and K₂SO₄ moderated the sticking probability of the deposit surface, and possibly the sticking probability the in-flight K₂Si₄O₉, SiO₂, CaO, and K₂SO₄ particles, resulting in increased deposit formation rates, when compared to their respective weighted average deposit formation rates. Furthermore, addition of KCl induced rapid deposit sintering. Addition of KOH to K₂Si₄O₉ in the model fly ash mixture resulted in a significant increase in the deposit formation rate.

• The deposit formation rate of biomass fly ash increased in the following order: wood fly ash < straw + wood cofired fly ash < straw fly ash, at the investigated conditions.

• Inertial impaction was the primary mechanism of deposit formation on the upstream side of the steel tube, when the model fly ash was present as solid or semi-molten particles. However, presence of vapor species or submicron particles in the model fly ash resulted in the formation of deposits on both sides of the steel tube via condensation or thermophoresis.

The fourth chapter presented the results of an experimental investigation on the shear adhesion strength of biomass ash deposits. Artificial deposits were prepared on superheater steel tubes using mixtures of KCl, K₂SO₄, CaO, CaSO₄, SiO₂, K₂CO₃, Fe₂O₃, K₂Si₄O₉ and KOH, as well as straw and wood fly ash obtained from full-scale boilers. The deposits were sintered in a laboratory oven for a specified duration, followed by shear adhesion strength measurements at high temperatures. The main inferences deduced from the investigation were:
7.1 Summary of Conclusions

- Increasing sintering temperatures (500 – 1000 °C) resulted in increased adhesion strengths, with a sharp increase observed near the ash deformation temperature / melting point of the deposit.
- Increasing sintering time (0 – 24 hours) did not significantly influence the adhesion strength of the deposits at 650°C, using a model fly ash deposit containing KCl–K₂SO₄ (50 wt %).
- Cooling down the deposits after sintering reduced the adhesion strength of the deposits, due to thermal stresses induced at the deposit–tube interface.
- Deposits containing sulfates showed increased adhesion strengths, indicating that sulfation may cause the formation of stronger deposits.
- Addition of compounds which increase the melt fraction of the deposit, such as K₂CO₃, Fe₂O₃, K₂Si₄O₉ and KOH, increased the adhesion strength of the deposit, whereas the addition of compounds which decrease the melt fraction of the model deposit, such as CaO, decreased the adhesion strength of the deposit.
- Adhesion strength data roughly followed a log-normal distribution.
- Corrosion occurring at the interface may increase the adhesion strength of the deposits, since most corrosion products form a eutectic system with the inner layer of deposit (typically dominated by KCl and K₂SO₄), thereby increasing the local melt fraction.

The fifth chapter presented the results of an experimental investigation on the tensile adhesion strength of model deposits containing KCl, K₂SO₄, CaO, CaSO₄, K₂Si₄O₉, as well as straw fly ash obtained from a grate-fired boiler. Similar to the experiments described in Chapter 4, artificial ash deposits were prepared on superheater steel tubes, and sintered in an oven for a specified duration. However, the superheater steel tube was cooled, incorporating a temperature gradient across the deposits, leading to a more accurate simulation of boiler conditions. The primary inferences from the investigation were:

- Increasing the steel surface temperatures led to a sharp increase in the tensile adhesion strength of model KCl–K₂SO₄ deposits at 650 °C.
- Increasing the flue gas temperatures led to a sharp increase in the tensile adhesion strength of model KCl–K₂SO₄ deposits at 700 °C. The temperature gradient across the deposits at a flue gas temperature of 700 °C induced migration of molten/vapor species from the outer layer of the deposit to the deposit–tube interface, causing liquid state sintering, increasing the tensile adhesion strength.
- Addition of CaSO₄ or K₂Si₄O₉ to the model KCl–K₂SO₄ deposits increased the adhesion strength, whereas addition of CaO decreased the adhesion strength.

The findings from this study indicate similar inferences as Chapter 4, identifying corrosion at the deposit–tube interface, and the ash melt fraction, as the two main parameters determining deposit adhesion.
Concluding Remarks

strength. Adhesion strength increases sharply upon the formation of a molten phase, which is typically observed at the eutectic temperature / deformation temperature of the fly ash (690 °C for KCl–K₂SO₄). However, corrosion occurring at the deposit–tube interface lowers the local eutectic temperature.

Heterogeneous sulfation of biomass ash deposits was simulated in Chapter 6. Model biomass ash deposits, containing KCl, were prepared on superheater steel tubes, and subjected to heterogeneous sulfation at temperatures ranging from 500 – 650 °C, up to 24 hours, using 0 – 600 ppm SO₂ in the flue gas. Subsequently, the shear/tensile adhesion strength of the deposits was measured.

While increasing sulfation time, resulted in a gradual increase in the adhesion strength of the deposits, varying SO₂ concentrations and sintering temperature did not significantly influence the deposit adhesion strength at the investigated conditions. A low degree of sulfation was observed in the experiments (<1 wt % S was detected in the deposit after 24 hours of sulfation using 600 ppm SO₂, with a flue gas and mean steel surface temperature of 775 and 598 °C.), suggesting that further investigation, especially using longer residence times, is required to understand the effect of varying operating conditions during heterogeneous sulfation on the adhesion strength.

7.2 Suggestions for future work

The obtained results in this PhD project provided an improved understanding of the formation, sintering and removal of deposits in biomass-fired boilers, describing the influence of operating conditions and ash chemistry on the deposit formation rates and deposit adhesion strength. However, an enormous amount of work may be performed in this field, which may aid further understanding. A few suggestions for further work are described below.

Additional deposit formation experiments with the Entrained Flow Reactor

Additional experiments may be performed for further understanding of the effect of ash chemistry and particle size on the deposit formation process. Furthermore, experiments may be performed using biomass fuels, with combustion occurring in the furnace prior to deposit formation. This will allow comparison of the model fly ash with in-situ fly ash and may allow deposit formation to be predicted as a function of fuel chemistry.

Improvements in modelling deposit formation in the Entrained Flow Reactor

The model requires improvements in the representation of the sticking probability of the deposit surface. Improvements in the heat transfer model, accounting for the decrease in local gas temperatures induced by the cooling probe may allow improved model predictions. Furthermore, CFD simulations of deposit
formation in the EFR may allow better understanding of the process. The accuracy of the different sticking probability models in literature may be compared. Furthermore, alternate sticking criteria may be developed, by comparing the model predictions with the obtained experimental data. Subsequently, the model may be expanded to predict deposit growth in full-scale boilers. The full-scale model may be validated using deposit formation data obtained from previous studies.

**Quantification of deposit surface temperatures during deposit growth**

Additional experiments may be carried out with an infrared camera installed in the bottom chamber, for determining the temperature at the surface of the deposit. This may aid justification of the observed effect of time and probe surface temperature on the rate of deposit formation. Furthermore, the obtained data may be used for validating heat transfer models across the deposit layer.

**Investigation of deposit composition and morphology**

Inductive Coupled Plasma (ICP) analysis and Scanning Electron Microscopy (SEM-EDS) of the obtained deposits may enable better understanding of the different deposit formation mechanisms, providing an insight into selective transport of ash species to the deposit surface.

**Deposit shedding model**

A model to predict deposit shedding in boilers may be developed by using the obtained experimental data. This may be done by modeling the obtained log-normal distribution, incorporating the effect of deposit composition, flue gas temperature and steam temperature. This model may be used to optimize soot-blowing in boilers by recommending soot-blowing frequencies and pressures based on the fuel and operating conditions. However, further experimental work, investigating a wider range of operating conditions and ash chemistry, is required for the development of a detailed model.

**Additional tensile strength experiments**

Further experiments may be performed using the tensile adhesion strength setup, using different ash chemistry, steel type and operating conditions. Heterogeneous sulfation may be carried out for longer durations, and possibly higher SO$_2$ concentrations and temperatures, to observe higher degrees of sulfation.

**Corrosion studies using the tensile adhesion strength setup.**

The tensile adhesion strength setup is ideal for corrosion studies, as it simulates a temperature gradient across the deposit layer. The sintered deposit layer may be analyzed using SEM-EDS to observe the corrosion layer at the deposit–tube interface. The effect of ash chemistry, temperature, SO$_2$ concentration, steel type, and sintering time may be investigated.
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Appendix A: Entrained Flow Reactor

In this Appendix, the setup used to perform deposit formation experiments has described. An air-cooled deposit probe, designed and constructed during this PhD project, has been described in Section A.1.3.

A.1 Experimental setup

The experimental setup consisted of a gas supply system, a screw feeder for injecting solids, a gas preheater, a 2 m long electrically heated furnace, and a fly ash deposition system comprising of an air-cooled deposit probe. A schematic representation of the setup is shown in Figure A.1.

![Schematic representation of the Entrained Flow Reactor.](image)

**Figure A.1** Schematic representation of the Entrained Flow Reactor.
A.1.1 Screw feeder

Fly ash was injected into the setup using a screw feeder (K-tron). The minimum and maximum feeding rate of the screw feeder was 50 – 2000 g/hr. The screw feeder was enclosed in a gas-tight chamber, where it was mixed with primary air. The flow rate of the primary air was controlled using a mass flow controller (maximum flow rate = 35 NL/min). During the experiments, the flow rate of the primary air was fixed at 15 NL/min.

A.1.2 Furnace

The Entrained Flow Reactor consisted of a gas preheater, containing two preheater zones, and a furnace, containing seven heating zones. A ceramic tube, with an inner diameter of 80 mm, acted as the inner wall of the furnace, surrounded by heating elements, insulation bricks and a metallic casing. The maximum operating temperature of the preheaters and the furnace was 1100 and 1450 °C respectively. A water-cooled feeding probe connected the furnace to the chamber containing the screw feeder. The feeding probe injected primary air + fly ash mixture directly into the furnace. Water-cooling of the feeding probe protected the metallic feeding probe from corrosion. Mixing the primary air with the fly ash was essential to prevent clogs in the feeding probe.

The secondary air was injected into the preheater. The flow rate of the secondary air was controlled using a mass flow controller (maximum flow rate = 200 NL/min). The preheated secondary heat was allowed to mix with the primary air + fly ash mixture in the furnace. The flow rate of the secondary air was varied during the experiments, to induce a change in the total gas velocity. Furthermore, a purge air stream (5 NL/min) was injected in the furnace through the heating elements, in order to protect the heating elements from the corrosive species present in the fly ash. The flow rate of the purge air stream was controlled using a mass flow controller (maximum flow rate = 10 NL/min).

After the furnace, the air + fly ash mixture entered a bottom chamber (see Figure A.1). The bottom chamber was made up of a water-cooled jacket for cooling the gases. Following the bottom chamber, the entrained flow entered an air-cooled cylindrical jacket, where the gas was cooled down to approximately 100 – 200 °C. Subsequently, the solid particles were separated from the entrained flow using a cyclone, located at the end of the air-cooled cylindrical jacket, and the air was vented out.

A.1.3 Deposit Probe

An air-cooled deposit probe was designed and constructed during this PhD project for deposit formation. The deposit probe (outer diameter = 8 mm) was inserted into the bottom chamber through a port. Furthermore, a camera was installed on a port, perpendicular to the deposit probe (see Figure A.1), and a light source was installed on a port diagonal to the deposit probe. Deposits were formed on a 316-stainless
steel tube (outer diameter = 10 mm, thickness = 1 mm, length = 140 mm), which was inserted around the deposit probe, as shown in Figure A.2.

![Diagram of air-cooled deposit probe](image)

**Figure A.2** Air-cooled deposit probe. Deposits are formed on the steel tube mounted on the probe.

Since the gases cooled down in the bottom chamber, the temperature of the gas was measured using a suction pyrometer. The temperature measured by the suction pyrometer has been referred to as the flue gas temperature. Measurements using the suction pyrometer were performed by replacing the deposit probe with the suction pyrometer, measuring the gas temperature at the deposit formation region. The variation of the flue gas temperature with the furnace temperature and the gas velocity is shown in Figure A.3. Increasing furnace temperatures resulted in increased flue gas temperatures. It should be noted that a gas velocity of 0.7 m/s was required to obtain a stable flue gas temperature. Lower gas velocities resulted in excessive cooling of the flue gas by the bottom chamber.
Figure A.3 Variation of flue gas temperature in the bottom chamber, with the furnace temperature and gas velocity. The flue gas was measured by replacing the deposit probe with a suction pyrometer.

The deposit probe was made up of two annular 316 stainless steel tubes, such that the cooling air flowed in through the inner steel tube (outer diameter = 4 mm, thickness = 1 mm), and flowed out through the outer steel tube (outer diameter = 8 mm, thickness = 1 mm). Five K-type thermocouples (diameter = 0.5 mm) were embedded on small channels on the surface of the deposit probe to measure the surface temperature. The position of the thermocouples (T₁ – T₅) along the surface of the deposit probe is provided in Figure A.4. The temperature measured by the thermocouple at the axial centerline of the furnace (T₃) has been referred to as the probe surface temperature. The flow rate of the air was controlled through a proportional solenoid valve (Burkert 2873) and a Eurotherm controller (3216). The controller was connected to the thermocouple measuring T₃ (see Figure A.4), such that the probe surface temperature is maintained at a desired value.

The cooling air was preheated to 200 °C during the experiments, in order to minimize the horizontal temperature gradients along the surface of the deposit probe. Typical temperature gradients present along the surface of the deposit probe at a flue gas temperature of 781 °C and a probe surface temperature of 475 °C are shown in Figure A.4.
Figure A.4 Temperature gradients along the surface of the deposit probe, for a flue gas temperature of 781 °C and a probe surface temperature of 475 °C. The thermocouples were mounted on the surface of the deposit probe. Probe surface temperature = T₃.

A PI diagram of the deposit probe is shown in Figure A.5. The building air supply was connected to a filter, a pressure regulator, a safety valve, and a 3-way valve. The 3-way valve allowed air into the air preheater or directly into the deposit probe. Direct supply of the air into the deposit probe allowed rapid cooling of the deposit probe. The solenoid valve and the controller were used for controlling the flow rate of the air into the air preheater. After the air preheater, the air flowed into the deposit probe through a heated line (at 200 °C).
Figure A.5 PI diagram of the air-cooled deposit probe.
A.2 Experimental procedure

The furnace was heated to the desired temperature. The model fly ash mixture was loaded onto the screw feeder, and the chamber containing the screw feeder was sealed. Subsequently, the air preheater and the tracing were turned on, and the deposit probe, containing the steel tube for deposit formation, was inserted into the bottom chamber. Subsequently, the primary air and the secondary air were turned on, heating up the bottom chamber. When, the deposit probe surface temperature reached the desired value, the camera was turned on to initiate video recording. Thereafter, the screw feeder was turned on to initiate the experiments. During the experiments, a negative pressure in the furnace of 0.1 – 0.5 mbar was maintained. Experiments in a slight vacuum ensured that the gases do not leak out of the furnace.

After a specified duration, the screw feeder was turned off. The primary air and the secondary air were turned off, and the deposit probe was retracted from the bottom chamber. When the deposit probe cooled down, the steel tube containing the deposits was carefully removed. Subsequently, the deposit layer was removed from the steel tube and weighed.
Appendix B: Shear Adhesion Strength Setup

In this Appendix, the setup used to measure the shear adhesion strength of ash deposits has been described. The setup was eventually modified to allow SO$_2$ injected to investigate heterogeneous sulfation of biomass ash deposits. The modifications have been described in Section B.3.

B.1 Setup description

The main components of the setup are shown in Figure B.1. The setup primarily consisted of an oven, a strength measurement arm, an air injection system, and a laptop for data collection.

**Figure B.1** Setup used for shear adhesion strength measurements. 1: Actuator, 2: Load cell, 3: Oven, 4: Laptop, 5: Temperature controller, 6: USB interface for load cell, 7: Actuator control box, 8, 10: Hand-held thermometers, 9: Rotameter for air flow control.
The oven, heated by six Kanthal U-shaped heating elements (located on the left and right walls of the heating chamber), and controlled by a Eurotherm 3504 dual loop temperature controller, was constructed in-house. The maximum allowable operating temperature and the maximum recommended operating temperature of the oven was 1600 and 1000 °C.

Figure B.2 Inside view of the oven. The superheater steel tubes with the deposits were placed in the support block, and the support block was positioned such that the strength measurement arm impacts the deposits.

The oven temperature was measured using an S-type thermocouple inserted through the back wall of the oven (see Figure B.2). An additional S-type thermocouple was positioned near the heating elements on the right wall of the oven. This was done to control the heating rate of the oven, such that high temperature gradients across the oven, and overheating, are prevented. In the experiments, the difference between the temperatures measured by the two aforementioned thermocouples was always maintained below 50 °C. During the experiments, the temperatures were recorded on a software in the laptop (see Figure B.1). Hand-held thermometers were used to measure the temperatures at additional locations in the oven, if needed.

Since the deposits investigated in this study may release corrosive vapors during heat-up, the heating elements are susceptible to corrosion. Therefore, the heating elements were protected using a steel plate (see Figure B.2). Furthermore, air was injected into the oven through the heating elements, using the rotameter (see Figure B.1), to ensure that the volatile vapors do not corrode the heating elements. Holes
in the steel plate allowed the air to enter the heating chamber. The air flow also aided minimization of the temperature gradients across the oven. In the experiments, an air flow of 15 NL/min was used.

The strength measurement arm consisted of a linear actuator and load cell (see Figure B.1), and a 253MA high temperature stainless steel rod (diameter of 6 mm) protruding into the oven through the left wall (see Figure B.2). The force applied on the steel rod was measured by the load cell (Nordic Transducer S Beam TCTN-9110-200N), which could measure forces up to 200 N. The data provided by the load cell was recorded by the laptop through a USB-Sensor Interface (Lorenz Messtechnik LCV-USB2, software = VS2). The force signal, in mV/V, could be converted to N (3 mV/V = 200 N). The actuator (LINAK LA23, 50 mm stroke length) was capable of applying forces up to 2500 N, moving at a maximum speed of 3.2 mm/s without load, and 2.5 mm/s at full load. However, the maximum force applied by the actuator, was limited to 200 N, while the speed of the actuator was fixed at 0.32 mm/s.

B.2 Experimental procedure

The deposit samples were prepared on superheater steel tubes, pre-oxidized for 24 hours, using a Teflon mold (see Figure B.3). The ash particles were mixed with a 50% isopropanol solution to prepare a thick slurry, and molded into two cubical shaped deposits on the surface of the tube. The tubes had an outer diameter of 38 mm, a thickness of 5 mm, and a length of 60 mm. The deposit samples were 15 mm x 15 mm x 10 mm, (W x D x H) in size, leading to a contact surface area of 223 mm$^2$. Subsequently, two steel tubes, containing a total of 4 deposit samples, were placed on a support block inside the oven. The support block was positioned such that the strength measurement arm faced the back-left deposit sample.

The oven was heated to the required sintering temperature, for a specified time. The followed heating program is described below, and shown in Figure B.4:

- Heating rate of 25 °C/min, from room temperature to 200 °C below the sintering temperature.
- Heating rate of 10 °C/min, from 200 °C below the sintering temperature, to 50 °C below the sintering temperature.
- Heating rate of 5 °C/min, from 50 °C below the sintering temperature to the final sintering temperature.

Furthermore, the heating was paused if the measured temperature difference between the center of the heating chamber and the region near the heating elements exceeded 50 °C. In practice, this rarely happened with the adopted temperature program.
Appendix B: Shear Adhesion Strength Setup

Figure B.3 Experimental setup for adhesion strength measurements. The superheater steel tube was placed inside the oven while the load cell was outside the oven. The actuator arm shears off the artificial ash deposit and the load cell measures the corresponding adhesion strength. Image not to scale.

Figure B.4 Temperature program used during heat-up.
After sintering, the temperature was reduced or increased (if needed) to the required strength measurement temperature at a rate of 15 °C/min. The actuator was turned on, to debond the deposit samples from the superheater tubes, as shown in Figure B.3. After the back-left sample underwent debonding, which could be identified from a peak in the measured force signal, the actuator was stopped, the oven door was opened, and the debonded deposit sample was removed. The actuator was turned on again to debond the back-right sample. Subsequently, actuator arm was retracted, and the front superheater tube was aligned with the steel rod, followed by the corresponding adhesion strength measurements.

Figure B.5 shows a typical force signal obtained from the load cell. The value of the peak was quantified, and converted to adhesion strength using the following equation,

\[
\text{Adhesion strength (kPa)} = \text{Peak value} \left( \frac{mV}{V} \right) \cdot \frac{200}{2.9954} \cdot \frac{10^3}{223}
\]

![Typical force signal obtained from the load cell.](image)

**Figure B.5** Typical force signal obtained from the load cell.

### B.3 Modifications to allow SO₂ injection

The oven, in its native state, was not gas-tight. SO₂ is a lethal gas, with an exposure Threshold Limit Value (TLV) of 0.5 ppm. Therefore, the oven was modified during this PhD project to allow SO₂ injection.

The modifications included the construction of a gas-tight chamber, and a gas supply and extraction system. A gas-tight chamber was constructed from 253MA stainless steel, as shown in Figure B.6.
Appendix B: Shear Adhesion Strength Setup

is a high temperature stainless steel, resistant to SO$_2$ corrosion up to 900 °C. The chamber was connected to the left wall of the oven such that the strength measurement rod was able to enter the chamber. A high temperature steel tube (diameter of 26 mm) was used to enclose the strength measurement arm, and connect the gastight box to the frame of the strength measurement arm outside the oven. The strength measurement arm was able to move freely inside the steel tube. The objective of the steel tube was to prevent gases from leaking out of the oven, through the left holes on the metallic chamber and the oven.

Figure B.6 Gas-tight chamber for SO$_2$ injection.

A PI diagram of the SO$_2$ injection system is shown in Figure B.7. SO$_2$ was supplied from a gas bottle (containing 7500 ppm of SO$_2$). A pressure reduction valve was used to reduce the pressure to 3.5 bar, followed by a solenoid valve and a ball valve. A safety system, consisting of an alarm monitor and an SO$_2$ sensor (resolution of 0.1 ppm), ensured that the solenoid valve shuts down if SO$_2$ is detected in the fume cabinet.

The mass flow rate of SO$_2$ was controlled using a mass flow controller (Bronkhorst, 2-100mNL/min). SO$_2$ was diluted with air prior to injecting it into the oven. The air flow rate was controlled using a mass flow
controller (Bronkhorst, 0.15-7.5 NL/min). The mass flow controllers were controlled using a laptop (LabView). During the experiments, the total flow rate of the gas stream was maintained at 1 NL/min. Air was saturated with water vapor using a heated water bath. The temperature of the water bath was maintained at 50 °C during the experiments. Air and SO₂ were fed into the oven through a heated gas line. The gas lines were heated in order to prevent condensation of water vapor.

SO₂ was injected into the metallic chamber through the front wall, using a ¼ inch 316 stainless steel tube (see Figure B.6). The primary gas outlet was through a ¼ inch 316 stainless steel tube from the back of the metallic chamber. The tubes wrapped around the box and the tubes entered/exited the oven through a slit in the oven door. The setup allowed for a secondary gas outlet from the steel tube enclosing the strength measurement arm. This outlet was used in order to prevent SO₂ from accumulating near the strength measurement arm. Both the outlets were connected to a suction vent. All components, except the alarm monitor, laptop, the controllers for water bath heating and tracing of gas lines, the SO₂ bottle, and the pressure reduction valve, were kept inside a fume cabinet.

The modified configuration allowed two deposit samples to be sintered simultaneously. The deposit samples were prepared on a superheater steel tube, and placed inside the metallic chamber in the oven (see Figure B.6). The lid of the metallic chamber was closed, and the oven was heated to a specified sintering temperature, using the temperature program described in Figure B.4. Air was injected into the oven through the heating elements, as well as into the metallic chamber during heat-up. When the specified temperature was reached, SO₂ injection into the metallic chamber was turned on, and the deposit samples were sintered for a specified duration. After sintering, SO₂ injection was turned off, and the shear adhesion strength of the deposits was measured at the same temperature.
Figure B.7 PI diagram for SO$_2$ injection into the oven.
Figure B.8 Influence of SO$_2$ concentration on the corrosion layer, Setup 1. KCl deposits sintered at 600 °C for 4 hours. Shear strength measurements performed at 600 °C. TP347HFG steel tubes preoxidized for 24 hours. No significant increase in corrosion layer.
Figure B.9 Influence of sintering temperature on the corrosion layer, Setup 1. KCl deposits sintered for (a) 2 hours, and (b) 4 hours, using 50 ppm SO₂. Shear strength measurements performed at the sintering temperature. TP347HFG steel tubes preoxidized for 24 hours. No significant increase in corrosion layer from 500 – 600 °C. Deposits at 650 °C appear to have a slightly larger corrosion layer.
Appendix C: Tensile Adhesion Strength Setup

In this Appendix, the setup used to measure the tensile adhesion strength of ash deposits has been described. The setup was designed and constructed during this PhD project. The setup allows sintering of ash deposits on a cooled probe in an oven, thus incorporating a temperature gradient across the setup. Compared to the Shear Adhesion Strength setup described in Appendix B, this setup provides a more realistic simulation of boiler conditions. Furthermore, SO₂ can be injected into the setup, for investigating heterogeneous sulfation of biomass ash deposits.

C.1 Setup description

The setup consisted of four main components: an oven, a cooling probe, a tensile adhesion strength measurement system, and an SO₂ injection system. An image of the setup is shown in Figure C.1.

C.1.1 Oven

The oven comprised a cuboidal heating chamber, with inner dimensions measuring 200 mm × 200 mm × 400 mm (W × H × D). 10 Kanthal globar SR (rod-type) heating elements were used for heating, and were located behind the left and right walls of the heating chamber. The maximum operating temperature of the oven was 1200 °C. The oven temperature was controlled using an S-type thermocouple, protruding into the heating chamber by 40mm through the back wall, and a Eurotherm 3508 dual loop controller.

Since the deposits investigated in this study may release corrosive vapors during heat-up, the heating elements are susceptible to corrosion. Therefore, the left and right walls of the heating chamber were constructed using SiC plates, and the heating elements were located behind the SiC plates. Each SiC plate contained 8 holes of diameter 5 mm near the bottom, in order to allow purge air to flow into the heating chamber. The purge air flow ensured that the corrosive vapors do not reach the heating elements. During heat-up in the experiments, a purge air flow of 25 NL/min, acting as flue gas was used.

An additional S-type thermocouple was positioned near the heating elements, behind the right wall of the heating chamber. This was done to control the heating rate of the oven, such that an overshoot in the oven temperature during heat-up is prevented. In the experiments, the difference between the temperatures measured by the two aforementioned thermocouples was always maintained below 50 °C. During the experiments, the temperatures were recorded using a software.
Figure C.1 Experimental setup used for tensile adhesion strength measurement. The strength measurement arms are connected to the movable actuator + load cell setup, followed by adhesion strength measurements.

The heating chamber was enclosed in a metallic casing. Wiring and supplementary mechanical components were located in a chamber in the right wall of the oven. The oven door located in the front contained a window of diameter 50mm. The outer dimensions of the oven were 650 mm × 753 mm × 650 mm (W × D × H). A suction port for cooling the casing was located at the top right corner of the oven. The suction port also served towards removing gases (e.g., SO$_2$) out of the oven (see Figure C.1).

The heating chamber contained two holes on the back wall, one for accommodating the cooling probe (28 mm), and the other for allowing SO$_2$ injection (¼ inch). Furthermore, the heating chamber contained a 10 mm × 240 mm slit on the top wall for tensile strength measurements. A cooling plate heat exchanger was installed in the region between the heating chamber and the outer metal casing. The cooling plate cooled and safely guided the hot gases from the oven to the ventilation, thereby protecting the heat-
sensitive actuator and the load cell. Furthermore, heat may influence the tensile adhesion strength measurements and possibly damage the load cell. A drawing of the cooling plate is shown in Figure C.2. Cooling air was supplied to the cooling plate, which flowed down the channels in the side walls, in a counter-current manner. The hot gases coming from the oven may be extracted from the heating chamber to the ventilation system.

![Diagram of the cooling plate heat exchanger](image)

**Figure C.2** Exploded view of the cooling plate heat exchanger installed between the heating chamber and the metal outer casing.

### C.1.2 Cooling probe

A double-annular air-cooled tube, as shown in Figure C.3, was used to cool the superheater steel tube containing the ash deposits. The cooling probe entered the heating chamber though the back wall of the oven, and the weight of the cooling probe was supported by the frame surrounding the oven (see Figure C.1).
Appendix C: Tensile Adhesion Strength Setup

The following nomenclature has been used for referring to different measured temperatures, (see Figure C.3)

- Cooling probe temperature: Temperature at the outer surface of the cooling probe.
- Steel surface temperature: Temperature at the outer surface of the superheater steel tube, measured at the centerpoint of the deposit. Eight deposits correspond to eight steel surface temperatures.
- Flue gas temperature: The oven temperature measured by the oven thermocouple.
- $\Delta T_h$: Horizontal temperature gradient along the surface of the superheater steel tube.
- $\Delta T_v$: Vertical temperature gradient, temperature difference between the cooling probe temperature, and the mean steel surface temperature.

The temperature of the cooling probe was measured using four thermocouples, (Cooling probe temperature, $T_{\text{front}}$, $T_{\text{back}}$, $T_{\text{bottom}}$, see Figure C.4) present in grooves along the surface of the cooling probe. The values of $T_{\text{front}}$, $T_{\text{back}}$, $T_{\text{bottom}}$ were recorded via a USB-Data Acquisition Device (MCDAQ USB-TC).

The primary air flowed in through the innermost channel and flowed out through the outermost channel. The flow rate of the air was controlled through a proportional solenoid valve (Burkert 2873) and a Eurotherm controller (3216). The controller was connected to the thermocouple measuring the cooling probe temperature, such that the cooling probe temperature is maintained at a specified value.

**Figure C.3 Cross-sectional view of the mounted air-cooled probe.**
Figure C.4 Cross-sectional view of the mounted air-cooled probe, showing the temperatures measured on the cooling probe

The secondary air flowed in through the outer annular channel and flowed out through the inner annular channel. The flow rate of the air was controlled manually through a rotameter. During the experiments, the secondary flow rate was fixed at 50 NL/min.

The steel surface temperatures were measured by mounting 6 thermocouples on the outer surface of the superheater steel tube. The temperature gradients along the steel tube at a flue gas temperature of 650 °C and cooling probe temperatures of 400 – 650 °C are shown in Figure C.5. The temperature gradient along the steel tube at a flue gas temperature of 775 °C, and a cooling probe temperature of 550 °C is shown in Figure C.6. Measurements to quantify the steel surface temperatures were performed without the presence of deposits.
Figure C.5 Temperature gradients along the outer surface of the superheater steel tube, with a flue gas temperature of 650 °C. Axial position measured from the back edge of the tube.

Figure C.6 Temperature gradient along the outer surface of the superheater steel tube, with a flue gas temperature of 775 °C, and a cooling probe temperature of 550 °C. Axial position measured from the back edge of the tube.
C.1.3 Tensile Adhesion Strength Measurement System

A frame was built around the oven for measuring the tensile adhesion strength of the deposits. As shown in Figure C.1, the frame contained an actuator (Linak LA25, 50mm stroke length) and a load cell (S beam type, Nordic transducer TCTN-9363-50kg), on a linear motion system (Hepco HGH30). The actuator was controlled via a control unit (EM-236), whereas the load cell was connected to a laptop via an LDU 68.2 amplifier. During the experiments, the actuator moved at a speed of 0.32 mm/s.

The actuator and the load cell could be connected to the deposits in the oven via strength measurement arms (see Figure C.1). The strength measurement arms were constructed using high temperature stainless steel (MA253). The linear motion system could be aligned and locked in position, thereby connecting a hook at the bottom end of the load cell system to the required strength measurement arm.

C.1.4 Gas Injection and Extraction System

A PI diagram of the gas injection and extraction system is shown in Figure C.7.

The air supply from the building line was split into 5 lines. Two lines were used to supply air to the cooling probe, one through a solenoid valve (primary air), and the other through a rotameter (secondary air). The third air line was supplied to the oven through the heating elements via a rotameter (protective purge gas, see Section C.1.1). The fourth air line was used for the cooling plate (see Section C.1.1) through a rotameter. The fifth air line was connected to a mass flow controller and was used for diluting SO₂ with air, prior to injection into the oven.

SO₂ was supplied from a gas bottle (containing 7500 ppm of SO₂). A pressure reduction valve was used to reduce the pressure to 3.5 bar, followed by a solenoid valve and a ball valve. A safety system, consisting of an alarm monitor and an SO₂ sensor (resolution of 0.1 ppm), ensured that the solenoid valve shuts down if SO₂ is detected in the fume cabinet.

The mass flow rate of SO₂ was controlled using a mass flow controller (Bronkhorst, 2-100mNL/min). SO₂ was diluted with air prior to injecting it into the oven. The air flow rate was controlled using a mass flow controller (Bronkhorst, 0.15-7.5 NL/min). The mass flow controllers were controlled using a laptop (LabView). During the experiments, the total flow rate of the gas stream was maintained at 1 NL/min. Air was saturated with water vapor using a heated water bath. The temperature of the water bath was maintained at 50 °C during the experiments. Air and SO₂ were fed into the oven through a heated gas line. The gas lines were heated in order to prevent condensation of water vapor.
Figure C.7 PI diagram of the Tensile Adhesion Strength Setup.
SO₂ was injected into the heating chamber through the back wall, using a ¼ inch 316 stainless steel tube. SO₂ could exit the oven through the cooling plate, or through the suction port on the top-right corner of the oven (see Figure C.1). The other aforementioned gas lines were discharged to the ventilation system. All components, except the alarm monitor, laptop, the controllers for water bath heating and tracing of gas lines, the SO₂ bottle, and the pressure reduction valve, were kept inside a fume cabinet.

C.2 Experimental Procedure

C.2.1 Sample Preparation

The required components constituting the model deposits were thoroughly mixed with 50% isopropanol solution to prepare a slurry. The slurry was molded into 8 cubical shaped deposits on the superheater steel tube using a Teflon mold, as shown in Figure C.8. The superheater steel tube was placed inside the mold, and the mold was securely closed using clamps. During the molding process, hooks used for tensile strength measurements were inserted into the mold, for allowing the deposit to be debonded perpendicular to the steel tube. Subsequently, the deposit slurry was injected into the mold, and shaped into cubical pellets, with sides of 15 mm each, leading to a contact surface area of 223 mm². Thereafter, the Teflon mold was opened, leaving the superheater tube with 8 deposits.

Figure C.8 Teflon mold used for sample preparation. After the superheater tube is positioned (left), the hooks are inserted into the mold, followed by the injection of the deposit slurry. The deposits and the steel tube can be removed by opening the Teflon mold (right).
C.2.2 Heat-up and Deposit Sintering

The superheater tube containing the deposits was placed around a double annular cooling probe in an oven, and the deposit hooks were connected to the corresponding strength measurement arms, as shown in Figure C.9.

![Experimental setup for adhesion strength measurements. The superheater steel tube with the deposits was placed around the air-cooled probe inside the oven, and the deposits were connected to the strength measurement arms.](image)

After placing the superheater steel tube with the deposits around the cooling probe, the oven was heated to a specified temperature at a uniform heating rate of 10 °C/min. When the specified temperature was reached, SO$_2$ injection was turned on, and the deposit samples were sintered for a specified duration. The protective purge gas flow was turned off during sintering, in order to maintain a uniform SO$_2$ concentration in the heating chamber.

C.2.3 Tensile Adhesion Strength Measurement

After sintering, SO$_2$ injection was turned off, and tensile adhesion strength measurements were performed. For each measurement, the actuator was connected to the required strength measurement arm, and lifted up to debond the deposit, while the corresponding force was measured using the load cell.
The tensile adhesion strength was calculated by dividing the measured force by the contact area between the deposit and steel tube.

Figure C.10 Influence of sulfation time on the corrosion layer, Setup 2. KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C using 60 ppm SO₂. Superheater steel tubes (TP347HFG) preoxidized for 24 hours. Steel surface temperature for the rightmost deposit = 625 °C, for the leftmost deposit = 559 °C (see Figure C.6). Higher steel surface temperatures probably caused reduced deposit thickness due to melting. Few deposit samples could not be debonded due to experimental errors. Slight increase in corrosion layer with sulfation time.
Appendix C: Tensile Adhesion Strength Setup

Figure C.11 Influence SO$_2$ concentration on the corrosion layer, Setup 2. KCl deposits sintered at a flue gas temperature of 775 °C, a cooling probe temperature of 550 °C for (a) 2 hours, (b) 4 hours, and (c) 24 hours. Superheater steel tubes (TP347HFG) preoxidized for 24 hours. Steel surface temperature for the rightmost deposit = 625 °C, for the leftmost deposit = 559 °C (see Figure C.6). Higher steel surface temperatures probably caused reduced deposit thickness due to melting. Few deposit samples could not be debonded due to experimental errors. No significant effect of SO$_2$ concentration on corrosion layer.
Appendix D: Horizontal Quartz Oven

In this Appendix, a setup used for heterogeneous sulfation of model biomass ash deposits has been described. An existing setup was modified to accommodate the deposit samples.

The setup consisted of an electrically heated horizontal quartz tube (outer diameter = 66 mm, thickness = 3.2 mm, length = 1000 mm), an inlet gas mixing panel and a flue gas cleaning system. A schematic representation of the setup is shown in Figure D.1.

![Figure D.1 Electrically heated horizontal quartz tube.](image)

The quartz tube was placed inside an oven, which consisted of three heating zones, controlled using three temperature controllers (Eurotherm 2208). Furthermore, another temperature controller (Eurotherm 2132i) was installed as a safety measure, which shuts off the heating, if the temperature set point is exceeded. During operation, a small temperature gradient was present along the length of the quartz tube. The temperatures at different locations in the quartz tube were measured using thermocouples. Typical temperature gradients along the quartz tube, for an oven set point temperature of 650 °C, is shown in Figure D.2. In the operating region in the center of the tube, the maximum temperature gradient was ±5 °C.
Appendix D: Horizontal Quartz Oven

Figure D.2 Temperature gradients along the length of the quartz tube at 650 °C.

N₂, O₂ and CO₂ streams were injected into the quartz tube through a water bath at 50 °C (see Figure D.1). The moisture content (at saturation) in air at 50 °C is 83 g/m³. SO₂ was injected directly into the quartz tube, from a gas bottle containing 4930 ppm of SO₂ in N₂. The flow rate of the gases was controlled using mass flow controllers. Table D.1 shows the maximum flow rate of the mass flow controllers. During the experiments, the total flow rate of the gas stream was maintained at 0.5 NL/min. The gas line from the water bath to the oven was heated to 150°C, in order to prevent condensation of water vapor. The flue gas cleaning system consisted of a condensate trap, an NaOH scrubber and a drying tube filled with silica gel.

Table D.1 Maximum gas flow rates.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Maximum flow rate (NmL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>3000</td>
</tr>
<tr>
<td>O₂</td>
<td>500</td>
</tr>
<tr>
<td>CO₂</td>
<td>500</td>
</tr>
<tr>
<td>SO₂</td>
<td>100</td>
</tr>
</tbody>
</table>
Deposit samples were prepared on superheater steel tubes, pre-oxidized for 24 hours, using a Teflon mold. The deposit preparation methodology is described in Appendix B.2, with the only difference being that the superheater tubes were cut in half along the axial centerline, prior to sample preparation. A total of eight deposits, on four superheater steel half-tubes were placed inside the quartz tube. Subsequently, the tube was closed using gas-tight ground-glass joints, and secured using clamps.

The oven was heated to a specified temperature at a fixed heating rate of 5 °C/min. During heat-up, N₂, O₂ and CO₂ were injected into the oven. When the specified temperature was reached, SO₂ injection was turned on, and the deposit samples were sintered for a specified duration. After sintering, SO₂ injection was turned off, and the deposits were allowed to cool down to room temperature overnight. N₂, O₂ and CO₂ were allowed to flow through the quartz tube during cooldown. The rate of cooling was variable, and not recorded. Shear adhesion strength of the deposits was measured at room temperature in the setup described in Chapter 4 and Appendix B.
Figure D.3 Influence of sulfation time on the corrosion layer, Setup 3. KCl deposits sintered at 600 °C using 50 ppm SO\textsubscript{2}. Shear strength measurements performed at room temperature. TP347HFG steel tubes preoxidized for 24 hours. Corrosion layer at 24 h is larger than corrosion layer at 1h.
**Figure D.4** Influence of SO$_2$ concentration on the corrosion layer, Setup 3. KCl deposits sintered at 600 °C for 4 hours. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours. Increasing corrosion layer from 0 – 250 ppm. Smaller corrosion layer at 500 ppm.
Figure D.5 Influence of sintering temperature on the corrosion layer, Setup 3. KCl deposits sintered for 4 hours using 50 ppm SO₂. Shear strength measurements performed at room temperature. Superheater steel tubes (TP347HFG) preoxidized for 24 hours. Increasing corrosion layer with increasing temperature.
Appendix E: Deposit Formation Model

This Appendix provides supplementary information for the deposit formation model used for predicting deposit formation in the Entrained Flow Reactor. Further details may be found in Hansen et al.\textsuperscript{9}

### E.1 Estimation of Thermophoretic Velocity

The thermophoretic velocity $u_T$ of the particle was estimated as,\textsuperscript{102}

$$u_T(\theta) = \frac{2u_g C_c C_s \left( \frac{k_g}{k_p} + C_s Kn \right)}{(1 + 3C_m Kn) \left( 1 + 2 \frac{k_g}{k_p} + 2C_s Kn \right)} \frac{\nabla T(\theta)}{T}$$  \hspace{1cm} (E.1)

$\nabla T$ is the temperature gradient, whereas $C_m = 1.14$, $C_s = 2.28$ and $C_s = 1.17$

$C_c$ is the Cunningham correction factor, as shown in Equation E.2.\textsuperscript{102}

$$C_c = 1 + Kn \left( 1.257 + 0.4 \exp \left( \frac{-1.1}{Kn} \right) \right)$$  \hspace{1cm} (E.2)

$Kn$ is the Knudsen's number, as shown in Equation E.3.

$$Kn = \frac{2l}{d_p}$$  \hspace{1cm} (E.3)

where $l$ is the mean free path, and $d_p$ is the particle diameter.

### E.2 Estimation of Local Collision Efficiency

The local collision efficiency $\eta_l$ was estimated as,\textsuperscript{42}
Appendix E: Deposit Formation Model

\[
\eta_t = \frac{\pi}{2} \frac{\eta_i}{\theta_{\text{max}}} \cos \left( \frac{\pi \theta}{2 \theta_{\text{max}}} \right)
\]

(E.4)

The target efficiency \( \eta_t \), and the maximum collision angle \( \theta_{\text{max}} \) were estimated using Equations E.6 and E.7, as well as Table E.1.\(^{42} \)

The effective Stokes number is,

\[
Stk_{\text{eff}} = \frac{\rho_p d_p^2 u_s}{9 \mu_s D} \left( \sqrt{0.158 \frac{\nu}{\text{Re}_p}} - \tan^{-1} \left( \sqrt{0.158 \frac{\nu}{\text{Re}_p}} \right) \right)
\]

(E.5)

and

\[
\Gamma = \beta_1 \ln \left( 8 Stk_{\text{eff}} \right) + \beta_2 \left( Stk_{\text{eff}} - 0.125 \right) + \beta_3 \ln \left( Stk_{\text{eff}} - 0.125 \right)^2
\]

(E.6)

\[
\Gamma = \left[ 1 + \beta_1 \left( Stk_{\text{eff}} - 0.125 \right)^{-1} + \beta_2 \left( Stk_{\text{eff}} - 0.125 \right)^{-2} + \beta_3 \ln \left( Stk_{\text{eff}} - 0.125 \right)^{-3} \right]^{-1}
\]

(E.7)

Table E.1 Correlation coefficients for estimating local collision efficiency.\(^{42} \)

<table>
<thead>
<tr>
<th>Parameter, ( \Gamma )</th>
<th>Stk_{\text{eff}}</th>
<th>Equation</th>
<th>( \beta_1 )</th>
<th>( \beta_2 )</th>
<th>( \beta_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target efficiency, ( \eta )</td>
<td>0.125 – 0.5</td>
<td>E.6</td>
<td>0.01978749</td>
<td>0.5136545</td>
<td>-0.0482858</td>
</tr>
<tr>
<td>&gt; 0.5</td>
<td>E.7</td>
<td>1.54424</td>
<td>-0.538013</td>
<td>0.2020116</td>
<td></td>
</tr>
<tr>
<td>Max collision angle, ( \theta_{\text{max}} \frac{\pi}{2} )</td>
<td>0.125 – 0.5</td>
<td>E.6</td>
<td>0.696596</td>
<td>-1.822407</td>
<td>1.145275</td>
</tr>
<tr>
<td>&gt; 0.5</td>
<td>E.7</td>
<td>0.7722744</td>
<td>-0.271871</td>
<td>0.06049905</td>
<td></td>
</tr>
<tr>
<td>Impact velocity, (</td>
<td>u_p (0)</td>
<td>/U )</td>
<td>0.125 – 0.8</td>
<td>E.6</td>
<td>0.0209863</td>
</tr>
<tr>
<td>&gt; 0.8</td>
<td>E.7</td>
<td>1.038627</td>
<td>-0.327754</td>
<td>0.1115706</td>
<td></td>
</tr>
<tr>
<td>Impact velocity, (</td>
<td>u_p (\theta_{\text{max}})</td>
<td>/U )</td>
<td>0.125 – 0.8</td>
<td>E.6</td>
<td>1.925045</td>
</tr>
<tr>
<td>&gt; 0.8</td>
<td>E.7</td>
<td>-0.242589</td>
<td>0.2343417</td>
<td>-0.0446577</td>
<td></td>
</tr>
</tbody>
</table>
The impact velocity of the particle $u_p$ and the angle of impaction $\alpha_{impact}$ was estimated using Equation E.8 and Equation E.9.\textsuperscript{42}

$$u_p = \left[ u_p(0) - u_p(\theta_{max}) \right] \cos \left( \frac{\pi}{2} \frac{\theta}{\theta_{max}} \right) + u_p(\theta_{max})$$ (E.8)

$$\alpha_{impact} = \frac{\pi}{2} \left[ 1 - \left( \frac{\theta}{\theta_{max}} \right)^{1/\beta} \right]$$ (E.9)

$$b = 1 + \frac{0.1851488}{Stf_{eff}} + \frac{0.0205901}{Stf_{eff}^2} + \frac{0.001530146}{Stf_{eff}^3}$$ (E.10)

**E.3 Estimation of Model Parameters and Physical Properties**

**E.3.1 Heat transfer coefficient**

The heat transfer coefficient was estimated as,\textsuperscript{171} 

$$Nu = \frac{n \cdot d_{probe}}{k_\theta} = \begin{cases} 0.67 \cdot Re^{0.5} \cdot Pr^{0.35} \left( 1 + \cos \left( \frac{\pi}{180} \theta \right) \right) & \theta < 85^\circ \\ 0.67 \cdot Re^{0.5} \cdot Pr^{0.35} & 85^\circ < \theta < 180^\circ \end{cases}$$ (E.11)

where Re and Pr are the Reynolds and Prandlt numbers, based on the probe diameter.

**E.3.2 Surface tension**

The surface tension of the ashes was estimated using the equations described by Mills,\textsuperscript{172} to be 0.1644 at 1500 °C. A temperature dependence of 15 mN per 100 °C,\textsuperscript{172} was incorporated into the model.

**E.3.3 Emissivity**

The emissivity of K\textsubscript{2}Si\textsubscript{3}O\textsubscript{9} was estimated according to the model provided by Boow and Goard.\textsuperscript{173}

$$\varepsilon = 0.30 \log(d_p) + 0.16$$ (E.12)
E.3.3 Thermal conductivity

The thermal conductivity of $\text{K}_2\text{Si}_4\text{O}_9$ was estimated according to the model provided by Rezaei et al.\textsuperscript{174}

\[ k_p = 0.0015 \cdot T^{1.1} \]  \hspace{1cm} (E.13)