# EFFECT OF TEMPERATURE GRADIENT ON SYNTHETIC ASH DEPOSIT CHEMISTRY, DEPOSIT MORPHOLOGY AND SUPERHEATER CORROSION

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# ABSTRACT

Deposit chemistry, deposit morphology and corrosion of steel in a temperature gradient were studied in laboratory scale. The objective of this study was to obtain a better understanding of the effects of temperature gradient on deposit chemistry, deposit morphology and corrosion as a function of deposit composition, steel temperature and time. Synthetic ash mixtures were applied on top of an air-cooled probe, which was placed in a tube furnace. The cross sections of the steel and ash were analyzed with Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDXA).

The parameters studied were the steel temperature, the exposure time and the ash composition. The steel temperatures in experiments were 300, 400 and 500 °C. The exposure times were 4, 24 and 72 h. The synthetic ashes were KCl/K<sub>2</sub>SO<sub>4</sub> or NaCl/Na<sub>2</sub>SO<sub>4</sub> mixtures in different ratios. The ratios were chosen so that the melt produced at the first melting temperature ( $T_0$ ) was either 20 wt-% or 100 wt-%.

Different region morphologies were observed in the deposit cross sections. The region formation was induced by the temperature gradient and the formation of the distinct regions was explained with the melting behavior of binary salt mixtures. Temperature gradients over the porous region were calculated from experimental data.

Alkali chloride migration towards the steel surface was observed and quantified from the SEM images. KCl was observed to migrate at a higher rate than NaCl. An alkali chloride transport model was developed based on Fick's first law of diffusion. The model correlated well with the experimental results suggesting that the alkali chloride transport occurred due to temperature induced concentration diffusion.

Corrosion of steel was studied by measuring the thickness of the oxide layer. The oxide layers were thicker than the oxide layers in other experiments at isothermal conditions. The steel temperature was observed to be the main contributor to the oxide layer thickness. KCl/K<sub>2</sub>SO<sub>4</sub> mixtures were observed to produce thicker oxide layers than NaCl/Na<sub>2</sub>SO<sub>4</sub> mixtures and the oxide layers grew as a function of time.

Keywords: temperature gradient, diffusion, KCl, NaCl, high temperature corrosion

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#### SVENSK SAMMANFATTNING

Förbränning av biobränsle och avfall erbjuder ett miljövänligt sätt att producera värme och el, men det finns förbättringsmöjligheter i förbränningstekniken. Användning av högre ångtemperaturer i förbränningsanläggningar ökar effektiviteten men det leder oftast till ökad korrosionshastighet av värmeväxlare, speciellt överhettare. Att minska korrosionen av värmeväxlarmaterial är en stor utmaning i samband med förbränning av biobränsle och avfall. Korrosion av värmeväxlare kan till exempel leda till oplanerade reparationer i förbränningsanläggningar. Vid förbränning av biobränsle och avfall frigörs stora mängder av askbildande ämnen vilket påverkar bildningen av beläggningar på värmeväxlarna. Beläggningarna ökar korrosionen av värmeväxlarmaterial. Stora mängder av askbildande ämnen kan alltså leda till ökad korrosionshastighet, speciellt i miljöer med hög temperatur. Dessa askbildande ämnen är orsaken till att pannor, som bränner biobränsle eller avfall, inte kan uppnå lika höga ångtemperaturer som till exempel pannor där det endast bränns kol.

Det finns mycket forskning om beläggningars inverkan på högtemperaturkorrosion men endast några av dessa undersökningar är gjorda med temperaturgradient över beläggningen. I det här diplomarbetet studerades temperaturgradientens påverkan på beläggningsmorfologi, beläggningskemi och korrosion av stål. Parametrar som användes i det här arbetet var ståltemperatur, tid och askbeläggningens sammansättning. Experimenten utfördes i laboratorieskala med en luftkyld sond som placerades i en rörugn. Syntetiska askbeläggningar (med tjockleken 2,5–7,5 mm) applicerades på sonden.

Blandningar av KCl/K<sub>2</sub>SO<sub>4</sub> och NaCl/Na<sub>2</sub>SO<sub>4</sub> användes som syntetiska askor. Dessa blandningar valdes på grund av att KCl, K<sub>2</sub>SO<sub>4</sub>, NaCl och Na<sub>2</sub>SO<sub>4</sub> är vanliga i beläggningar i samband med förbränning av biobränsle och avfall. Asksammansättningarna valdes så att smältan som bildas vid den första smälttemperaturen var endera 20 m-% eller 100 m-% av askan. Detta ledde till sex olika syntetiska askor: två eutektiska askor (KCl/K<sub>2</sub>SO<sub>4</sub> och NaCl/Na<sub>2</sub>SO<sub>4</sub>) KCl-rik aska, K<sub>2</sub>SO<sub>4</sub>-rik aska, NaCl-rik aska och Na<sub>2</sub>SO<sub>4</sub>-rik aska. Experimenten med den eutektiska NaCl/Na<sub>2</sub>SO<sub>4</sub>-askan misslyckades. Askornas sammansättningar och termodynamiska egenskaper räknades med mjukvaran FactSage.

Alla syntetiska askor testades med en ståltemperatur på 500 °C och testtid på 24 timmar. De sulfatrika askorna testades med ståltemperaturer på 300 °C, 400 °C och 500 °C med testtid på 24 timmar. De sulfatrika askorna testades även med testiderna 4 och 72 timmar med ståltemperatur på 500 °C. Eutektisk KCl/K<sub>2</sub>SO<sub>4</sub>-aska testades även med ståltemperatur 400 °C med testtid på 24 timmar.

Sonden bestod av tre koncentriska metallrör. Det yttersta röret fungerade som värmeisolering mellan ugnen och det mittersta röret. Till sonden hörde två stycken stålprovringar som blev en del av det mittersta röret. I båda stålprovringarna fanns det ett termoelement. Termoelementen användes för regleringen och mätningen av temperaturerna under experimenten. Det innersta röret förde in kylningsluften i sonden. Kylningsluften kylde ner stålprovringarna och flödade därefter ut ur sonden. Sondens temperatur reglerades med en PID-regulator som fick sin insignal från ett av de termoelement som var placerade i stålprovringarna. Regulatorn styrde en ventil som kontrollerade luftflödet in i sonden. Det fanns ytterligt ett termoelement som var placerat ovanpå sonden. Med det termoelementet mättes temperaturen i ugnen, cirka 1,5 cm ovanpå den syntetiska askbeläggningen.

Ugnstemperaturen under alla tester var inställd till 980 °C och temperaturen i ugnen mättes till 780–820 °C. I slutet av experimenten togs sonden ut ur ugnen och kyldes snabbt ner. När sonden hade kylts ner, applicerades några droppar av epoxi på askbeläggningen för att fästa beläggningen på stålringen. Epoxin fick stelna över natten. Sedan togs sonden isär och stålringen med askbeläggningen ingöts i epoxi. Efter det sågades stålringen av i mitten och tvärsnittet av ringen slipades och polerades. Tvärsnittet av askbeläggningen och stålringen analyserades med SEM/EDXA.

Utgående från SEM-bilderna på askbeläggningarnas tvärsnitt observerades några intressanta fenomen. I alla experiment fanns ett poröst lager närmast stålytan. I detta arbete kallas det här lagret för det porösa lagret. Ovanpå det porösa lagret hittades ett lager som under experimenten hade varit partiellt eller helt smultet. Det här lagret var sintrat och agglomererat och hade endera en sammansättning som var eutektisk eller en sammansättning som var ickeeutektisk. När sammansättningen var eutektisk kallades lagret för det eutektiska lagret och när sammansättningen var ickeeutektisk kallades lagret för det sintrade lagret. I några av experimenten observerades alla tre lager. I dessa fall hittades lagret når att ill ugnen.

I experimenten med de ickeeutektiska askorna observerades det i de flesta fallen ett poröst, ett eutektiskt och ett sintrat lager. Det konstateras att det eutektiska lagret hade uppkommit under experimenten. De eutektiska lagren hittades i experimenten med KCl-rik aska, NaCl-rik aska och Na<sub>2</sub>SO<sub>4</sub>-rik aska. Ett tunt eutektiskt lager hittades även i det 4 timmar långa experimentet med den K<sub>2</sub>SO<sub>4</sub>-rika askan, men likadana lager hittades inte i andra experiment med samma aska.

En sannolik förklaring varför det inte hittades något eutektiskt lager i de andra experimenten med den K<sub>2</sub>SO<sub>4</sub>-rika askan, är diffusion av KCl i ugnen. Med den K<sub>2</sub>SO<sub>4</sub>-rika askan förekommer en eutektisk sammansättning anrikad på KCl, jämfört med den ursprungliga sammansättningen. Den K<sub>2</sub>SO<sub>4</sub>-rika askan bildade ett mera poröst sintrat lager jämfört med de andra askorna. Detta skulle ha möjliggjort att de lättförångbara KCl-molekylerna diffunderade mot ugnen. Det förklarar varför ett eutektiskt lager endast hittades i det experimentet som hade varit i ugnen den kortaste tiden. Observationer med experimenten som var i ugnen 72 timmar, där det inte kunde hittas någon KCl-lager i temperaturer över 630 °C, stöder hypotesen om diffusionen av KCl mot ugnen.

De olika lagrens tjocklek mättes i SEM-bilderna. De uppmätta lagertjocklekarna normaliserades genom att dela de uppmätta värdena på tjocklekarna med beläggningstjockleken. Det observerades att NaCl/Na<sub>2</sub>SO<sub>4</sub>-askorna hade bildat tunnare porösa lager i förhållande till KCl/K<sub>2</sub>SO<sub>4</sub>-askor. Detta förklarades med skillnader i askornas första smälttemperaturer (KCl/K<sub>2</sub>SO<sub>4</sub>: 690 °C, NaCl/Na<sub>2</sub>SO<sub>4</sub>: 626 °C).

Vid gränsen mellan det porösa lagret och endera det eutektiska lagret eller det sintrade lagret konstaterades det att temperaturen varit den samma som den första smälttemperaturen. Det räknades ut värden på temperaturgradienten över de porösa lagren. Detta gjordes genom att dela skillnaden mellan askans första smälttemperatur och stålets temperatur med tjockleken på det porösa lagret. Temperaturgradienterna över de porösa lagren fick ett medeltal på 71,30 °C/mm och standardavvikelsen 18,45 °C/mm.

I det porösa lagret observerades alkalikloridtillväxt på den varmare sidan av partiklarna. Det observerades också att i vissa partiklar fanns det en porös yta på den kallare sidan. Den porösa ytan bestod endast av alkalisulfater. Hypotesen var att alkaliklorider förångades från partiklarna, diffunderade i gasfasen och deponerade på partiklar med kallare temperatur.

Alkalikloridtillväxten studerades med hjälp av SEM panoramabilder. I varje panoramabild där man kunde observera och särskilja alkalikloridtillväxt valdes det ut cirka 50 punkter med alkalikloridtillväxt. Dessa alkalikloridlagers tjocklek och distans från stålytan mättes i pixlar. För att kunna jämföra olika experiment med varandra ändrades distansen från stålytan från pixlar till temperaturenheter. Alkalikloridlagers tjocklek ändrades från pixlar till mikrometer.

Det observerades en klar skillnad mellan KCl/K<sub>2</sub>SO<sub>4</sub>- och NaCl/Na<sub>2</sub>SO<sub>4</sub>-askor i alkalikloridtillväxten i det poröra lagret. I experimenten där KCl/K<sub>2</sub>SO<sub>4</sub>-askor användes, var alkalikloridtillväxten mycket större än i experimenten där NaCl/Na<sub>2</sub>SO<sub>4</sub>-askor användes. Experimenten där samma aska användes och tiden i ugnen var samma men ståltemperaturen var olika, observerades inte större skillnader i alkalikloridtillväxten som funktion av den lokala temperaturen. Det fanns vissa skillnader mellan den eutektiska KCl/K<sub>2</sub>SO<sub>4</sub>-askan och den K<sub>2</sub>SO<sub>4</sub>-rika askan. I temperaturer över 580 °C var alkalikloridtillväxten i den eutektiska askan större än i den sulfatrika askan. I temperaturer under 580 °C var resultaten i de eutektiska och i de sulfatrika fallen mycket lika.

De skillnader som observerades mellan KCl/K<sub>2</sub>SO<sub>4</sub>- och NaCl/Na<sub>2</sub>SO<sub>4</sub>-askorna konstaterades bero på skillnader i mättnadstrycken av KCl och NaCl. KCl har märkbart högre mättnadstryck jämfört med NaCl i temperaturområden som användes i experimenten.

Resultaten beskrevs så at den naturliga logaritmen av alkalikloridlagertjockleken ritades mot inversen av den absoluta temperaturen. Detta gjordes på basis av Clausius-Clapeyronekvationen. Sedan anpassades en lineärfunktion till resultaten med minsta kvadratmetoden. Detta gjordes skilt för alla experiment och sedan ändrades skalan i figurerna tillbaka till µm mot °C.

I experimenten som utfördes med sulfatrika alkalisaltblandningar observerades att experimentens tid hade en påverkan på alkalikloridlagrens tillväxthastighet. I experimenten där sonden var i ugnen 4 timmar observerades det en snabbare alkalikloridlagertillväxt än i experimenten där sonder var i ugnen 24 timmar. Tillväxthastigheten hade minskat ännu mera i experimenten som tog 72 timmar.

En matematisk modell konstruerades för att förklara alkalikloridtransporten i det porösa lagret. Modellen baserade sig på Ficks första diffusionslag. Med hjälp av modellen räknades diffusionsflödet ut av alkaliklorider i gasfasen från varmare temperatur mot kallare temperatur. Gasfasen var antagen att vara mättad med alkaliklorider. Mättnadstrycken på

alkaliklorider användes för att räkna ut alkalikloridkoncentrationer i gasfasen. Diffusionsflödet räknades ut för KCl, (KCl)<sub>2</sub>, NaCl och (NaCl)<sub>2</sub>. Diffusionsflödet räknades vidare om till tjocklek av kompakt KCl eller NaCl lager per tidsenhet.

Resultaten från modellen stämde väl överens med de experimentella resultaten. Speciellt experimentella resultat med KCl i 4 och 24 timmars experiment stämde väl överens med modellen. Med NaCl gav modellen lägre resultat än experimenten. Det konstaterades även att 72 timmars experiment med både KCl och NaCl gav lägre resultat än modellen. Känsligheten för modellen testades med att ändra på vissa parametrar i modellen. Det konstaterades att modellen inte är speciellt känslig för ändringar i parametrarna.

Korrosionen av stålringen mättes så att en representativ punkt i oxidskiktet valdes ut och tjockleken av oxidskiktet mättes i µm. Ståltemperaturen hade en stor påverkan på oxidskiktens tjocklek. I experimenten där ståltemperaturen var 300 °C observerades inget oxidskikt efter 24 timmar. I experimenten där ståltemperaturen var 400 °C observerades oxidskikttjockleken vara 2–6 µm efter 24 timmar. I experimenten med ståltemperatur 500 °C observerades öxidskikttjockleken vara 12–27 µm efter 24 timmar. Det observerades även ett oxidskikt med tjocklek på 80 µm men detta konstaterades vara en avvikelse.

Det observerades skillnader i oxidskikttjocklek mellan olika askor. KCl/K<sub>2</sub>SO<sub>4</sub>-askor ledde i allmänhet till tjockare oxidskikten än NaCl/Na<sub>2</sub>SO<sub>4</sub>-askor. Detta var ett intressant fenomen eftersom KCl och NaCl i isoterma förhållanden har visats vara nästan lika korrosiva. Askor med högre alkalikloridhalt producerade tjockare oxidskikt jämfört med askor med lägre alkalikloridhalt men samma alkalimetall. Skillnaderna mellan sulfat- och kloridrika askor var dock så små att detta kan bero på mätosäkerheten. Tjockleken på oxidskiktet konstaterades växa som funktion av tiden.

Temperaturgradienten observerades påverka beläggningens morfologi och kemi, och vidare forskning behövs för att bättre kunna förklara dessa fenomen. Temperaturgradienten observerades även påverka korrosionen av stål, men för att bättre förstå temperaturgradientens roll i högtemperaturkorrosion behövs ytterligare forskning.

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## PREFACE

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# SUMMARY OF ABBREVIATIONS

BS	Backscatter (electron)
CFD	Computational Fluid Dynamics
DTA	Differential Thermal Analysis
EDXA	Energy-Dispersive X-ray Analysis
FCC	Face-Centered Cubic
GIMP	GNU Image Manipulation Program
НСР	Hexagonal Close Packing (structure)
PID	Proportional-Integral-Derivative (controller)
RCP	Random Close Packing
RLP	Random Loose Packing
SEM	Scanning Electron Microscopy
TIR	Temperature Indicator Recorder
с	Concentration, mol/m <sup>3</sup>
Ē	Mean speed, m/s
d	Molecule diameter, m
D	Diffusion coefficient, m <sup>2</sup> /s
J	Diffusion flux, mol/(s m <sup>2</sup> )
k <sub>B</sub>	Boltzmann constant, 1.381*10 <sup>-23</sup> J/K
М	Molar mass, g/mol
р	Pressure, Pa or bar

<i>q</i>	Heat flux, W/m <sup>2</sup>
R	Gas constant, 8.314 J/(mol K)
t	Time, s or h
Т	Temperature, K or °C
T <sub>0</sub>	Solidus temperature (first melting temperature), K or °C
T <sub>15</sub>	Sticky temperature, K or °C
T <sub>70</sub>	Flow temperature, K or °C
T <sub>100</sub>	Liquidus temperature, K or °C
Х	Distance, mm or µm
x <sub>i</sub>	Mole fraction
λ	Thermal conductivity, W/(m K)
$\lambda_{mfp}$	Mean free path, m

 $\rho$  Density, kg/m<sup>3</sup>

# 1. INTRODUCTION

# 1.1. General

The energy production of the world is going to increase in the future due to the improvement in the living standards across the world. At the same time there is a lot of pressure to decrease the amount of heat and power produced by combusting fossil fuels due to the risk of global warming. Biofuels and waste fuels are considered  $CO_2$  neutral and viable to replace at least part of the fossil fuels. For example, in Finland in the year 2012, 24% of the heat and power produced was from wood.<sup>1</sup>

Biofuels and waste derived fuels are attractive as energy sources but combusting them also introduces a wide range of challenges. For example the high amount of water and the varying chemical composition may lead to challenges. The high amount of ash forming matter often leads to slagging and fouling in the boilers, which may increase the corrosion rate and therefore lead to unplanned shutdowns and repairs.<sup>2</sup>

One way of increasing the heat and power production is to increase the steam temperatures in boilers. For example, increasing the steam temperature from 400 °C to 500 °C in a condensing turbine leads to approximately 20% more power generated from the same amount fuel.<sup>3</sup> On the other hand, increasing the steam temperatures lead to many challenges from the corrosion point of view.

High temperature fireside corrosion is one of the main factors limiting steam temperatures, especially in boilers combusting biofuel and waste derived fuels.<sup>4</sup> Out of the heat exchanger surfaces the superheater surfaces (Figure 1, Location 1) are exposed to the highest temperatures in the boiler and are most prone to corrosion.



Figure 1. A schematic picture of a bubbling fluidized bed boiler. Locations with flue gas temperatures are indicated in the picture. Location 1 indicates the location of superheaters. From Vainikka,<sup>5</sup> with permission.

Due to the high fireside corrosion rate, the steam temperatures in boilers combusting solid biofuels and waste fuels are notably lower than in boilers combusting coal. Steam temperatures in black liquor recovery boilers are usually within the range of 480–490 °C.<sup>6</sup> Boilers combusting biofuel may have steam temperatures as high as 535 °C while boilers combusting waste derived fuels have steam temperatures of approximately 420 °C.<sup>7</sup> Steam temperatures in boilers combusting coal may be as high as 580 °C.<sup>7</sup> High corrosion rates cause unscheduled shutdowns and repairs in the boilers. This means increased costs and lost revenues for the energy companies. It is important to understand the corrosion mechanisms taking place in the boilers so that the challenges associated with high temperature corrosion can be minimized.

There are a number of studies of high temperature corrosion in combustion processes. The two main aspects increasing the corrosion rate of steel, in boilers combusting biofuels and black liquor, are the amount of melt in contact with the heat exchanger material and the amount of Cl species present.<sup>6</sup> Both of these aspects are dependent on the operating

conditions. For example fuel type, boiler type and operating temperature affect the deposit behavior and the amount of Cl species present in the boiler.

It is important to understand the deposit behavior on the heat exchanger tubes to be able to understand fireside corrosion in boilers. Heat exchanger deposits are formed by slagging or fouling. Deposits formed by slagging are formed when relatively big partly molten particles hit the heat exchanger surfaces and stick to them. Slagging takes place on superheaters and furnace walls. Fouling takes place on all heat exchanger surfaces. Fouling mechanisms are thermophoresis, condensation, chemical reaction and diffusion.<sup>8</sup> Depending on the buildup mechanism the deposits have different properties. For example the density and the chemical composition of the deposit vary depending on the buildup mechanism.

Particle stickiness is essential for deposit buildup by slagging. For the particles to be sticky, they have to be at least partly molten. Four different temperatures are used to describe the melt behavior of the deposits.  $T_0$  is the first melting temperature (solidus temperature) where the first melt is formed.  $T_{15}$  is the temperature where 15% of the particle's mass is in the molten phase.  $T_{15}$  is also called the sticky temperature. When particles are above this temperature they become sticky and the slagging on heat exchanger tubes is increased.  $T_{70}$ , also called the flow temperature, is the temperature where 70 percent of the particle's mass is in the molten phase. When the outer layer temperature of the deposit reaches  $T_{70}$ , the deposit starts to flow and the deposit thickness stops to increase.  $T_{100}$  is the liquidus temperature where 100% of the particle's mass is in the molten phase.<sup>9</sup>

The chemical composition of the deposit defines the melting properties of the deposit. Trace elements in boilers may affect the melting behavior of deposits remarkably. For example in black liquor recovery boilers the presence of K and Cl decrease the  $T_0$  of deposits.<sup>10</sup> In boilers combusting waste derived fuels there are usually some trace metals, such as Zn, Pb, As, Cr, Cu and Hg, present.<sup>4</sup> For example Zn and Pb with Cl decrease the  $T_0$  of deposits considerably, which may lead to enhanced corrosion rate.<sup>11</sup>

Alkali chlorides are one of the key contributors to high temperature corrosion of heat exchanger tubes. K is the most common alkali metal in the most biomass and it induces corrosion especially when associated with Cl.<sup>2</sup> Na is more common in black liquor recovery boilers and may also lead to severe corrosion when associated with Cl.<sup>12</sup> Mixtures of alkali chlorides and alkali sulfates were used as synthetic ash deposits in the experimental part of this study.

During boiler operation there is a temperature gradient over the heat exchanger deposits. However laboratory scale corrosion experiments have so far often been conducted in isothermal conditions. Some studies have considered the temperature gradient. Brossard et al<sup>3,13</sup> carried out corrosion tests in a presence of temperature gradient. The tests were run in a laboratory scale pilot unit that simulates municipal solid waste incineration. The temperature gradient was produced by having a fluid–cooled metal tube placed in a combustion chamber. The combustion chamber was heated by a gas burner. The set-up considers the effects of flue gas temperature, flue gas flow and the composition of the synthetic ashes used in the tests.

Kawahara<sup>14</sup> conducted corrosion experiments in a presence of temperature gradient. In Kawahara's corrosion test apparatus, the temperature gradient was produced by cooling the corrosion samples with air. In Kawahara's apparatus, it is possible to apply deposits on top of the corrosion samples. In addition, the apparatus makes it possible to feed reactive gases into the furnace.

Covino et al<sup>15</sup> conducted laboratory scale corrosion experiments in a presence of temperature gradient. They studied the corrosion of cobalt and their research points out diffusion effects within the oxide layer. Their apparatus uses air cooling and they report heat fluxes of 40-50  $kW/m^2$  through their sample. The ashes they used as deposits were obtained from a municipal incinerator. The ashes had complex chemical compositions. Covino et al conducted their experiments in both isothermal conditions and in a presence of temperature gradient. They also applied synthetic gas atmosphere in their experiments.

Engblom et al<sup>16</sup> and Lindberg et al<sup>17</sup> conducted salt deposit studies in a presence of a temperature gradient. Experiments were conducted with steel temperatures at 400 °C and 500 °C with test time of 24 h. Lindberg et al reported formation of molten regions in eutectic NaCl/Na<sub>2</sub>SO<sub>4</sub> and Na<sup>+</sup>,K<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>,Cl<sup>-</sup> salt mixtures in a presence of a temperature gradient. Engblom et al reported similar results with eutectic NaCl/Na<sub>2</sub>SO<sub>4</sub> salt deposits. Both studies reported alkali chloride transport effects within the deposits. The studies reported a computational fluid dynamics (CFD) model that describes gas phase transport of alkali chlorides within the deposit. The work reported in this thesis is a continuation of the work reported by Lindberg et al and Engblom et al.

#### **1.2.** Purpose of this study

Corrosion is a major challenge in boiler heat exchanger tubes and corrosion research on the effect of temperature gradient is still scarce. Better understanding of the effect of the temperature gradient on superheater corrosion is needed. The purpose of this study is to gain a better understanding of the effects of temperature gradient on deposit morphology, deposit chemistry and corrosion of steel. The effects of temperature gradient were studied as a function of steel temperature, exposure time and ash deposit composition. The effects were studied by using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Analysis (EDXA) and image analysis.

The effects in the synthetic ash deposit induced by the temperature gradient were recognized and studied. For example different deposit morphologies were observed. The connection between the deposit morphology and the melting behavior of the binary salt mixtures were established in this study.

Different temperature gradient induced transport mechanisms were observed in the synthetic ash deposits. The purpose of this study was to gain a better understanding of the gas phase transport of alkali chlorides in the synthetic ash deposits. The alkali chloride gas phase transport was studied quantitatively and a model was developed to describe the phenomenon. The model was based on Fick's first law of diffusion.

Corrosion of steel was studied and the results were compared to the results in isothermal corrosion tests conducted by others<sup>6,18,19</sup>. The corrosion of steel was quantified by measuring the oxide layer thickness from SEM images. The purpose of this study was to study the effect of time, steel temperature, synthetic ash composition and temperature gradient to high temperature corrosion of steel.

# 2. EXPERIMENTAL PROCEDURE

Figure 2 shows a flow chart of the experimental part of this work. Six synthetic ashes with different chemical compositions were prepared for the experiments. The experiment set-up consisted of an air-cooled probe, a tube furnace and a Proportional-Integral-Derivative (PID) regulator that controlled an air valve. The samples were prepared for the SEM/EDXA and then analyzed.



Figure 2. A flow chart of the experimental procedure. The arrows indicate the order of the steps.

## 2.1. Synthetic ash deposits

#### 2.1.1. Synthetic ash composition

Mixtures of KCl/K<sub>2</sub>SO<sub>4</sub> and NaCl/Na<sub>2</sub>SO<sub>4</sub> were used to produce synthetic ash deposits. Alkali chlorides and sulfates were chosen because they are both relatively common in different combustion power plants.<sup>2</sup> K compounds are common in biofuel combustion and Na compounds are common in for example municipal waste combustion.<sup>18</sup> NaCl and Na<sub>2</sub>SO<sub>4</sub> are also common in black liquor combustion.<sup>20</sup> The chemical compositions of the synthetic ashes were chosen so that the melt fraction at the T<sub>0</sub> was either 20 wt-% or 100 wt-%.

The chemical compositions, phase diagrams and melting behaviors of the synthetic ashes were determined using thermodynamic calculations. Computer software Factsage, version 6.3, was used to perform the calculations.<sup>21</sup> The FTsalt database was used as the thermodynamic source data. The calculated chemical compositions,  $T_0$  values,  $T_{100}$  values and fractions of the

first melt are presented in Table 1. The binary phase diagrams are presented in Figure 3 and the melting curves are presented in Figure 4.

The melting behaviors of the synthetic ashes were studied with Differential Thermal Analysis (DTA). The DTA tests were done with a TA Instruments SDT Q600. Approximately 10 mg of the ash was analyzed by heating the sample to a temperature approximately 20 °C above the  $T_{100}$  of the ash (the SO<sub>4</sub> rich ashes were not heated above  $T_{100}$ ). The sample was subsequently cooled to 500 °C, followed by additional heating and cooling cycles. The heating and cooling rates were 20 °C/min. Values for the  $T_0$  and  $T_{100}$  were extracted from the raw data and the results are shown in Table 1.

Ash no.	Composition	Pre-melt	Pre-melt	T <sub>0</sub>	<b>T</b> <sub>100</sub>	Melt
	(wt-%)	furnace	time	(°C)	(°C)	produced
		temperature	(min)			at T <sub>0</sub>
		(°C)				(wt-%)
1	KCl 55.5 /	740	30	690	690	100
	K <sub>2</sub> SO <sub>4</sub> 44.5			(685)	(685)	
2	KCl 91.1 /	810	30	690	758	20
	K <sub>2</sub> SO <sub>4</sub> 8.9			(681)	(760)	
3	KCl 11.1 /	950	25	690	969	20
	K <sub>2</sub> SO <sub>4</sub> 88.9			(681)	(-)	
4	NaCl 32.0 /	750	20	626	626	100
	Na <sub>2</sub> SO <sub>4</sub> 68.0			(627)	(627)	
5	NaCl 86.4 /	830	20	626	780	20
	Na <sub>2</sub> SO <sub>4</sub> 13.6			(625)	(778)	
6	NaCl 6.4 /	880	20	626	818	20
	Na <sub>2</sub> SO <sub>4</sub> 93.6			(624)	(-)	

Table 1. A table of the synthetic ashes, the ash properties and the pre-treatment parameters



Figure 3. Calculated phase diagrams of KCl/K<sub>2</sub>SO<sub>4</sub> (left) and NaCl/Na<sub>2</sub>SO<sub>4</sub> (right).



Figure 4. The calculated melt fractions of the synthetic ashes plotted against temperature. Melt fractions for the KCl/K<sub>2</sub>SO<sub>4</sub> ashes (upper) and NaCl/ Na<sub>2</sub>SO<sub>4</sub> ashes (lower) are shown in separate pictures.

The synthetic ashes were pre-treated, to achieve homogeneity, in a way that is consistent with the previous work at the Laboratory of Inorganic Chemistry at Åbo Akademi University.<sup>22</sup> The pre-treatment procedure consisted of weighing, mixing, melting, grinding and sieving the salt mixtures.

The pure synthetic salts were weighed in the ratios presented in Table 1. The total amount of salts weighed per mixture was 50 g. The weighed salts were mixed roughly by shaking. The crude mixed salt was poured into a porcelain crucible. The salt mixture and the crucible were placed into a furnace that was heated up to 200 °C and kept in that temperature for 15 minutes. The crucible was subsequently moved into a furnace that was pre-heated to a higher temperature. This temperature was different for each synthetic ash (Table 1). Very high temperatures were avoided to minimize evaporation of alkali chlorides. The temperature still needed to be high enough for the salt mixture to melt and mix. All synthetic ashes, except for the K<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 3), were pre-melted in a temperature where approximately 80% of the mixture's mass consisted of melt.

The pre-melted salt mixture and the crucible were taken out of the furnace and quenched to room temperature. The salt mixture was grinded and sieved. The sieving fraction with particle size of 53–250  $\mu$ m was collected and the particles with the size greater than 250  $\mu$ m were grinded and sieved again. This procedure was repeated until practically no particles with size greater than 250  $\mu$ m were left. The sieving fraction of 53–250  $\mu$ m was used in the experiments. This grain size interval was chosen to be consistent with previous corrosion tests carried out at the Laboratory of Inorganic Chemistry at Åbo Akademi University.<sup>6,22</sup>

#### 2.2. Set-up

The probe used in the experiments is similar in design to the deposit probe described by Laurén.<sup>8</sup> The main differences are that the probe used in this study is smaller in size, approximately 60 cm in length, and it has an additional thermally insulating protective tube. The air-cooled probe used in the experiments consisted of three concentric metal tubes. A schematic picture of the probe is presented in Figure 5. The outermost metal tube functioned as a protective tube (Figure 5, C) and prevented a direct contact of the hot air and the middle tube. The sample rings were a part of the middle tube (Figure 5, B and D). The cooling air

entered the system through the innermost tube (Figure 5, A) and was then released into the space between the innermost tube and the middle tube, cooling down the middle tube and the sample rings (Figure 6). The cooling air flowed through the space between the middle and innermost tube and then exited through an exhaust tube. The exhaust tube was placed outside the furnace so it did not affect the temperature inside the furnace.



Figure 5. A schematic picture of the probe used in the experiments. Different parts of the probe (the innermost tube (A), the middle tube (B), the outermost tube (C), the exhaust tube (D) and the sample rings (E)) are shown in this picture.



Figure 6. A schematic picture of the set-up. The picture shows the probe (without the outermost tube), the PID regulator, the temperature indicator recorder (TIR) and the air valve. Based on Bankiewicz.<sup>23</sup>

The sample rings were located at the end of the probe (Figure 6). The outermost tube had an opening (Figure 5, C) so that the sample rings were in direct contact with the furnace environment. A thermocouple was placed in each of the sample rings. One of the thermocouples was used for regulating the air flow into the probe and the other was used for recording the sample ring temperature during the experiments. The ring closer to the exhaust tube was used for regulating the probe temperature and the other ring was used for recording the temperature. The synthetic ash deposit was applied on the regulating ring. In addition, in some experiments a synthetic ash deposit was applied on both of the rings.

The probe temperature was controlled by a PID regulator. The set temperature of the sample ring was the input value for the regulator and the signal from the regulating thermocouple was the in-signal for the regulator. The PID regulator controlled a valve that regulated the flow of compressed cooling air into the probe (Figure 6).

The furnace used in the experiments was a regular tube furnace. An  $Al_2O_3$  tube was placed inside the furnace and the other end of the tube was sealed. The probe was inserted into the  $Al_2O_3$  tube as shown in Figure 7. During experiments, the furnace temperature was set to 980 °C. The air temperature was measured approximately 1.5 cm above the ash deposit and was in the range of 780–820 °C. In other experiments, conducted prior to the work described in this thesis, the air temperature inside the  $Al_2O_3$  tube near the tube surface was measured to be approximately 830 °C.



Figure 7. Two pictures of the probe inside a tube furnace. A schematic picture of a crosssection of the  $Al_2O_3$  tube and the probe with typical temperatures (left) and a photograph of the probe in the furnace (right).

#### 2.3. Experiments

The parameters for the experiments conducted for this study were chosen so that a broader understanding of the deposit chemistry, deposit morphology and corrosion in a presence of a temperature gradient was obtained. The studied parameters were ash composition, steel temperature and time. The different ash compositions are explained in detail in Chapter 2.1. The studied steel temperatures were 300, 400 and 500 °C. The studied exposure times were 4, 24 and 72 h. The conducted experiments are presented in Table 2.

Table 2. The conducted experiments. The rows indicate conducted experiments and the parameters for the conducted experiments (synthetic ash no., steel temperature, exposure time, steel and A/B)

Ash no.	Steel	Time	Steel	A/B	Notes	
	temperature	( <b>h</b> )				
	(°C)					
1	400	24	10CrMo9-10	А	Same experiment as below	
1	400	24	P235GH	В	Same experiment as above	
1	500	24	10CrMo9-10	А	Same experiment as below	
1	500	24	10CrMo9-10	В	Same experiment as above	
2	500	24	10CrMo9-10	А		
3	300	24	10CrMo9-10	А		
3	400	24	10CrMo9-10	А		
3	500	24	10CrMo9-10	А		
3	500	24	10CrMo9-10	В		
3	500	4	10CrMo9-10	А		
3	500	72	10CrMo9-10	А		
4	500	24	10CrMo9-10	А	Experiment failed	
5	500	24	10CrMo9-10	А		
6	300	24	10CrMo9-10	А		
6	400	24	10CrMo9-10	А		
6	500	24	10CrMo9-10	А		
6	500	24	10CrMo9-10	В		
6	500	4	10CrMo9-10	A		
6	500	72	10CrMo9-10	А		
	Ash no; $1 = et$	itectic KC	$l/K_2SO_4, 2 = KC$	l rich, 3	$B = K_2 SO_4$ rich,	
$4 = eutectic NaCl/Na_2SO_4$ , $5 = NaCl rich$ , $6 = Na_2SO_4$ rich						

In this thesis the experiments are referred to in the following way: Ash no./Steel temperature/Time/A or B. For example 1/400/24/A refers to the experiment with eutectic

 $KCl/K_2SO_4$  ash (ash no. 1), set temperature of the sample ring at 400 °C, exposure time of 24 h and the experiment A. The A and B indicate a difference between experiments that were conducted with otherwise identical parameters. The A and B refer either to parallel or duplicate experiments. Parallel experiments were in the furnace at the same time and duplicate experiments were in the furnace at different times.

The 24 h experiment with the eutectic NaCl/Na<sub>2</sub>SO<sub>4</sub> ash (ash no. 4), with steel temperature at 500 °C, was repeated three times in total and it failed every time. The failure was due to the fact that the synthetic ash deposit applied on the steel ring had vanished during the experiment. The experiment was conducted two times with similar results. Then a new synthetic ash was prepared. The third experiment was conducted with the new ash but the same failure occurred again. In all of the experiments it seemed that the failure was due to a leakage of the ash. Due to the failures, no results with ash no. 4 were acquired.

#### 2.3.1. Procedure

The synthetic ash and the sample rings were prepared first. The sample rings were rinsed with acetone in ultrasound bath for 5 min to remove impurities on the surface of the steel. Subsequently the sample rings were dried in air and the probe was assembled. Fire sealant paste was used to form a holder for the synthetic ash deposit. Glass fiber rope was used to further insulate the middle tube of the probe. After the fire sealant paste had hardened, the thermocouples were connected to the PID regulator and to the temperature recorder. The cooling air feed tube was connected to the probe. Approximately 500 mg synthetic ash was applied on the sample ring. The probe was placed into the furnace and the furnace was turned on with a set temperature of 980 °C. The assembled probe with the synthetic ash deposit is presented in Figure 8.

The experiment was considered to start when the steel temperature reached its set temperature. This took approximately 30 min from the moment the furnace was turned on. At the end of the experiment, the probe was taken out of the furnace and quenched to room temperature. When the steel temperature had dropped to  $60 \,^{\circ}$ C, a few drops of epoxy hardener were applied on the synthetic ash deposit to attach it to the steel surface. The epoxy was left to harden overnight and the next day the probe was dissembled and the sample ring with the synthetic ash deposit was cast in epoxy and left to harden overnight. Different stages of the experiment are presented in Figure 8.



Fire sealant paste

Ash deposit with epoxy

Figure 8. Photographs of a synthetic ash deposit in different stages of the experiment. Before entering the furnace (left), after furnace exposure (middle) and after epoxy addition (right). The ash deposit, fire sealant paste and glass fiber rope are shown in the photographs.

The sample ring was cut with a high speed saw to get a cross section of the ring and the synthetic ash deposit. Subsequently the sample was soaked in petroleum ether to cleanse it of the oil used in the cutting. The sample cross-section was polished using sandpaper. Kerosene was used as a lubricant in the polishing process and after polishing the kerosene was washed away. The cleansing was done with petroleum ether in ultrasound bath. The sample was subsequently placed in a vacuum. The cleansing and vacuum sequences were repeated until the sample was clean of kerosene. The clean sample was coated with a thin carbon layer in order to make it conductive for the SEM/EDXA.<sup>22</sup>

## 2.3.2. SEM/EDXA

SEM is a method used to get information on the surface of the samples. SEM working principle is based on producing electrons and focusing them to a beam and scanning the sample surface with the electron beam. The electrons react with the sample surface and produce a wide range of different signals. The signals used in this work are the signals from backscatter (BS) electrons and the element characteristic X-rays which are used in EDXA.<sup>24</sup>

The BS electrons are used to produce an image of the sample surface where different elements appear in different shades of gray. The heavier elements appear in lighter color and the lighter

elements appear in darker color. SEM BS images were taken from every sample in places of interest. In addition, panoramic SEM BS images of the samples were taken to obtain a better understanding of the morphology of the synthetic ash deposits. The panoramic images are contained in the Appendix. The element characteristic X-rays were used for elemental analysis of specific spots and areas of the sample surface and also for producing elemental maps of specific areas in the samples.

In this study SEM/EDXA was used to get information on the sample ring and the synthetic ash deposit after the experiment. The SEM/EDXA was used to analyze deposit chemistry, deposit morphology and corrosion. Different regions in the synthetic ash deposit and oxide layer were recognized with SEM and the chemical compositions of the regions were analyzed with EDXA. In addition, thicknesses of the different regions were measured from the SEM BS images.

## 2.3.3. Image analysis

The SEM BS images were further studied with the help of the GNU Image Manipulation Program (GIMP). GIMP was used to measure distances and thicknesses of distinct regions within the synthetic ash deposits. The different regions of the ash deposit and their meaning are explained further in Chapter 3.1. In addition, GIMP was used to analyze alkali chloride transport within the deposit by recognizing and marking approximately 50 alkali chloride layers for every sample where the transport was observable. The thickness of an individual transported alkali chloride layer and the distance of the layer from the steel surface were measured in px. An example of the manually recognized alkali chloride layers is presented in Figure 9.



Figure 9. A SEM BS image of a cross-section of a synthetic ash deposit showing marked particles with KCl layers on top of them.

The procedure was not done with the chloride rich experiments (2/500/24/A and 5/500/24/A) and with one eutectic KCl/K<sub>2</sub>SO<sub>4</sub> experiment (1/400/24/A). The experiment 1/400/24/A had so aggressive alkali chloride layer buildup that the particles had agglomerated together and it was nearly impossible to distinguish the buildup layers and the original particles from each other. Experiments 2/500/24/A and 5/500/24/A were so rich in alkali chlorides that it was impossible to distinguish the buildup layer and the original particles from each other.

An effort was made to recognize the alkali chloride layers with computer software developed by Silvander L. Some of the panoramic SEM BS images were analyzed with the software. The software recognizes the transported alkali chloride areas in the images on basis of the light color of the alkali chloride layers and then calculates the light px in the alkali chloride area. The software also measures the distance of the recognized area from the steel surface, the height of the area and the width of the area in px. The challenge with the software was that it recognized also other light areas in the SEM BS images. For example left over kerosene and oxide layer appear light in the SEM BS images. The software also recognized areas, which were fairly uniform, as multiple areas. This led to cases where the height and the width of the recognized areas did not agree with the visual inspections of the SEM images. The results gained with the software are not reported in this thesis.

# 3. EXPERIMENTAL RESULTS AND DISCUSSION

## **3.1.** Synthetic ash deposit

#### 3.1.1. Deposit morphology

In the synthetic ash deposit SEM BS images three different types of regions were observed. The regions are presented in Figure 10. The region, found closest to the steel surface, was porous and the particle edges were sharp, which indicates that the region had only experienced temperatures below  $T_0$ . In this thesis this region is referred to as the porous region. In the next region from the steel, the particles were observed to have agglomerated and sintered together. It was interpreted that the ash particles had been molten or partly molten during the experiment, indicating that the ash particles had experienced temperatures above T<sub>0</sub>. With the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1), the KCl rich ash (ash no. 2) and all of the Na ashes (ashes 5–6) this region had a near eutectic composition. Similar region was also observed in the 4 h experiment with  $K_2SO_4$ -rich ash (ash no. 3). In this thesis this region is referred to as the eutectic region. An example of the eutectic region and its composition is shown in Figure 11. The third region, observed in the experiments, was found farthest away from the steel surface. This region was sintered and agglomerated, indicating it had at some point of the experiment been molten or partly molten. This region did not have near eutectic composition distinguishing it from the eutectic region. In this thesis this region is referred to as the sintered region and it was observed in all of the experiments with non-eutectic ashes (ashes 2, 3, 5 and 6).

	Region	Temperature range	Properties
3	Sintered	$T_0 - T_{Furnace}$	Sintered and agglomerated. Depleted of one component.
2	Eutectic	~T <sub>0</sub>	Sintered and agglomerated. Eutectic composition.
	Porous	T <sub>Steel</sub> -T <sub>0</sub>	Sharp particle edges. Bulk chemical composition is near the original. Pure alkali chloride layers observed on the hotter side of the particles.
200µm Mag = 30 X EHT = 15.00 kV			

Figure 10. A SEM BS image of a deposit cross-section showing three distinct regions and a table with region properties and temperature range. The porous region (1), the eutectic region (2) and the sintered region (3) were always observed in this order from steel to furnace.



Figure 11. A SEM BS image of the eutectic region of the experiment with  $Na_2SO_4$  rich ash, at steel temperature 500 °C and exposure time of 72 h (6/500/72/A). The EDXA results of the marked area are presented in the table. The marked area has near eutectic composition.

Only two distinct regions (porous and eutectic) were observed in synthetic ash deposits with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1) (Figure 12). The deposit morphology is explained with the melting behavior of the binary eutectic mixtures. Below  $T_0$  the particles were 100% of solid phase and mostly detained their original form during the experiment. Above  $T_0$  the particles were 100% in molten phase and they agglomerated together forming a dense region

with eutectic composition. Agglomeration was also observed in the porous region but it was considered to have occurred due to gas phase sintering of KCl.<sup>25</sup>



Figure 12. A SEM BS image of a synthetic ash deposit cross-section with eutectic  $KCl/K_2SO_4$  ash (ash no. 1) and the binary phase diagram of  $KCl/K_2SO_4$ . The vertical red line in the phase diagram indicates the chemical composition of ash no 1. The horizontal arrows indicate the chemical composition in the deposit at certain temperatures.

In synthetic ash deposits with non-eutectic composition (ashes 2, 3, 5 and 6) two or three regions were observed. The  $K_2SO_4$  rich ash (ash no. 3) was the only ash with which only the porous and the sintered regions were observed in the deposit (Figure 13). In the rest of the non-eutectic ash deposits all three regions were observed. The three regions were also observed in the 4 h experiment with the  $K_2SO_4$  rich ash (ash no. 3). The deposit morphologies are explained with melting behavior of binary eutectic mixtures. Below  $T_0$  the particle edges are sharp and the deposit is not agglomerated. Above  $T_0$  the particle edges are less sharp and the deposit is agglomerated and sintered.



Figure 13. A SEM BS image of a synthetic ash deposit cross-section with the  $K_2SO_4$  rich ash (ash no. 3). The sintered region, the porous regions and the estimated location in  $T_0$  are marked to the image.



Figure 14. A SEM BS image of a synthetic ash deposit with Na<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 6) and the binary phase diagram of NaCl/Na<sub>2</sub>SO<sub>4</sub>. The vertical red line in the phase diagram indicates the chemical composition of ash no. 6. The horizontal arrows indicate the chemical composition of the deposit in different temperature regions.

The fact that eutectic regions were observed in synthetic ash deposits with non-eutectic bulk compositions suggests that the eutectic regions were formed during the experiment. In the experiments with Na<sub>2</sub>SO<sub>4</sub> rich ash (6/500/4/A, 6/300/24/A, 6/400/24/A, 6/500/24/A, 6/5

region was observed to be different. In the 4 h experiment (6/500/4/A), some NaCl was observed in areas with eutectic composition within the sintered region. In the 24 and 72 h experiments with the same ash (6/300/24/A, 6/400/24/A, 6/500/24/A, 6/500/24/B and 6/500/72/A), similar eutectic areas were not observed in the sintered region. The effect of time is shown in Figure 15.



Figure 15. SEM BS images of  $Na_2SO_4$  rich ash (ash no. 6) deposit cross-sections with different exposure times. The images show the eutectic and sintered regions. NaCl was observed in the sintered region in the 4 h experiment but not in the 24 and 72 h experiments.

The experiments with alkali chloride rich ashes (2/500/24/A and 5/500/24/A) showed similar behavior to experiments with Na<sub>2</sub>SO<sub>4</sub> rich ash. In the experiment with the KCl rich ash (2/500/24/A) the sintered region was uniform and depleted of K<sub>2</sub>SO<sub>4</sub> and the eutectic region was enriched with of K<sub>2</sub>SO<sub>4</sub>. An EDX analysis map of the sintered region of the deposit is presented in Figure 16. In the experiment with NaCl rich ash (5/500/24/A) the eutectic region was enriched with Na<sub>2</sub>SO<sub>4</sub> and the sintered region was depleted of Na<sub>2</sub>SO<sub>4</sub>. Small areas with near eutectic composition were observed within the compact sintered region. This was similar to the 4 h experiment with the Na<sub>2</sub>SO<sub>4</sub> rich ash (6/500/4/A). The compositions of these areas were studied with EDXA and the results are presented in Figure 17.



Figure 16. Elemental maps of the sintered region in the experiment with KCl rich ash, with steel temperature at 500 °C and exposure time of 24 h (2/500/24/A). Most of the sintered region was observed to be KCl, however some K<sub>2</sub>SO<sub>4</sub> was observed in areas with near eutectic compositions.

	Spot	SO <sub>4</sub>	Cl	Ratio
		( <b>m-%</b> )	( <b>m-%</b> )	(SO <sub>4</sub> /Cl)
	1	0.0	58.7	0.0
	2	50.8	14.9	3.4
	3	47.4	16.0	3.0
	4	58.5	7.2	8.2
	Eutectic	46.0	19.4	2.4
200μm Mag = 30 X EHT = 29.99 kV Aperture Size = 60.00 μm Date :30 Oct 2013 LEO 1530 WD = 13 mm Signal A = QBSD Image Pixel Size = 3.906 μm	composition			

Figure 17. A SEM BS image of the sintered region in the experiment with NaCl rich ash, with steel temperature at 500 °C and exposure time of 24 h (5/500/24/A) and the EDX analysis results of the marked spots. The bulk composition was observed to be pure NaCl and the darker gray regions were observed to have near eutectic compositions.

A eutectic region was observed in the 4 h experiment with the  $K_2SO_4$  rich ash (3/500/4/A) but not in the other experiments with the same ash. The eutectic region of 3/500/4/A is presented in Figure 18. In the points A and B, areas with near eutectic composition were observed. In the points C and D, almost pure KCl layers were observed on top of the ash particles. The eutectic compositions in Figure 18 had either formed during the experiment or they were a part of the original ash composition. The overall size of the agglomerated particle around point A is larger than the original ash particle size (250 µm). This implies that the agglomeration had taken place during the experiment and thus the eutectic region had also likely been formed during the experiment. On the basis of the presence of the eutectic region in the experiment 3/500/4/A, it is possible that similar regions had also been present in the other experiments with the K<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 3).



Figure 18. A SEM BS image of the eutectic region in the 4 h experiment with the  $K_2SO_4$  rich ash (3/500/4/A). The spots A and B have near eutectic compositions. On top of the particles C and D almost pure KCl layers were observed.
The transport of compounds within the synthetic ash deposit takes place in gas or molten phase. Alkali sulfates have low volatility, suggesting that the formation of the eutectic region in the alkali chloride rich ashes (ashes 2 and 5) occurred by molten phase transport. Alkali chlorides are more volatile than alkali sulfates. At 700 °C, KCl has a saturation pressure of  $8.2*10^{-5}$  bar and K<sub>2</sub>SO<sub>4</sub> has a saturation pressure of  $1.7*10^{-9}$  bar. The values were calculated using FactSage software, version 6.3.<sup>21</sup> The high volatility of alkali chlorides enables a possibility for gas phase transport in the alkali sulfate rich ashes (ashes 3 and 6).

The absence of eutectic region in the 24 and 72 h experiments with the  $K_2SO_4$  rich ash (3/300/24/A, 3/400/24/A, 3/500/24/A, 3/500/24/B and 3/500/72/A) is explained with the high volatility of KCl. The KCl in the eutectic region has the possibility to diffuse towards the steel or into the furnace. Gas phase diffusion of alkali chlorides is discussed further in Chapter 3.2 and in Chapter 4.

The hypothesis of the molten phase transport is following: The melt that is formed in the temperatures above  $T_0$  fills the void spaces between the original ash particles and is transported towards the steel surface. The transport into the void spaces is due to gravitational and capillary forces. Sharp shapes were observed within the eutectic region in most of the experiments with non-eutectic ashes. An example is shown in Figure 19. These shapes are similar to the particle shapes observed in the porous regions. According to the hypothesis, a melt with eutectic composition had flowed into the void spaces between the original ash particles. When the melt reached an area where the temperature was below  $T_0$ , it solidified there. The filling of the void spaces between the particles is supported by the fact that in all of the experiments in this study, the melt had a lower density when compared with the solids. The densities were calculated using FactSage<sup>21</sup> and the results are contained in the Appendix. If there were no void spaces to fill, the melt would stay on top of the solid phase due to the density differences.



Figure 19. A SEM BS image of the eutectic region in the 24 h experiment with the  $Na_2SO_4$  rich ash with steel temperature at 400 °C (6/400/24/A).  $Na_2SO_4$  particles with sharp shapes were observed within the eutectic region.

# 3.1.2. Region thicknesses

The thicknesses of the different regions were measured from the SEM BS images. The measured thickness values varied depending on the horizontal position in the image. The maximum and minimum region thicknesses were measured and the average was used as the reported value. The thicknesses of all the regions within one sample were summed and that value was reported as the total thickness of the synthetic ash deposit. The region thickness results are presented in Figure 20.

The region thickness results were normalized by dividing the region thicknesses with the deposit thickness. The normalized region thicknesses are presented in Figure 21. The main observation from the normalized thicknesses was that the porous region was relatively thinner

for non-eutectic Na ashes (ashes 5 and 6) when compared to non-eutectic K ashes (ashes 2 and 3). It was also observed that an increase in steel temperature lead to a decrease in normalized porous region thickness.



Figure 20. The thicknesses of different regions within the synthetic ash deposit. The thicknesses of porous, eutectic and sintered regions make up the total deposit thickness.





In some of the SEM BS images, a dark void was observed between the porous region and the steel surface. These voids were considered to have been formed in the sawing phase. It is likely that the epoxy, used to cast the sample, did not penetrate all the way to the steel surface.

Therefore the ash particles closest to the steel were detached from the sample in the sawing phase. It is also possible that the deposit was elevated from the steel surface during the quenching but it is unlikely. As seen in Figure 22, the rest of the ash deposit does not follow the shape of the void. Especially the boundary between the sintered region and the eutectic region is fairly straight. This implies that the void was not caused by elevation during cooling. The void was assumed to have been part of the porous region during the experiments.



Figure 22. A SEM BS image of a synthetic ash deposit cross-section with a void. The sintered, eutectic and porous regions are marked to the image. It is observed that the boundary between the sintered and eutectic region does not follow the shape of the void.

The differences in normalized porous region thicknesses between the non-eutectic K and Na ashes are explained with the difference in  $T_0$  values (KCl/K<sub>2</sub>SO<sub>4</sub>:  $T_0$ =690 °C, NaCl/Na<sub>2</sub>SO<sub>4</sub>:  $T_0$ =626 °C). It was also observed that the Cl rich and SO<sub>4</sub> rich ashes with the same alkali metal behaved similarly. The results with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash however differed from the non-eutectic results. Figure 23 shows the normalized porous region thicknesses of the ash



deposits plotted against steel temperature. Experiments with different exposure times are included in Figure 23.

Figure 23. The normalized porous region thicknesses plotted against steel temperature.

In Figure 24 the normalized porous region thicknesses are plotted against the temperature difference between  $T_0$  of the ash and steel temperature. A linear function was fitted to the results. The function had a boundary condition to intercept the y-axis at origo. This boundary condition corresponds to the situation where the steel temperature is the same as the  $T_0$  of the ash and no porous region is present in the deposit due to melt formation. Only the results from experiments conducted with non-eutectic ashes (ashes 2, 3, 5 and 6) are presented in Figure 24. The results with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1) deviated noticeably from the other results and are therefore not presented in Figure 24.



Figure 24. The normalized porous region thicknesses plotted against the temperature difference between  $T_0$  and  $T_{steel}$ . The linear function with a boundary condition to intercept the y-axis at origo was fitted to the data points.

### 3.1.3. Temperature gradient

The temperature gradient through the porous region was calculated for all of the experiments with Equation 1.

$$\frac{dT}{dx} = \frac{T_0 - T_{steel}}{x_{porous}} \tag{1}$$

where

 $\frac{dT}{dx}$  is the temperature gradient over the porous region, [°C/mm]  $T_0$  is the first melt temperature of the ash, [°C]  $T_{steel}$  is the temperature of the steel surface, [°C]  $x_{porous}$  is the thickness of the porous region, [mm]

It was assumed that the temperature at the steel–ash interface was equal to the set temperature of the steel ring. It was assumed that the temperature gradient over the porous region of the ash deposit was constant in radial direction. The temperature gradient results are presented in Table 3.

It was observed that the sintered region–eutectic region interface was linear in tangential direction in all of the samples. Also the distance between steel and the first sintered particles was fairly constant in tangential direction within the samples. This implies that particles with the same distance from steel had experienced similar temperatures during the experiment. This means the temperature gradient values in tangential direction have also been fairly constant during the experiments.

Differences between the temperature gradient values over the porous region were observed in different experiments. Especially when comparing the values for the experiments with the  $K_2SO_4$  rich ash (ash no. 3) and the  $Na_2SO_4$  rich ash (ash no. 6), differences were observed. The experiments with ash no. 3 had an average temperature gradient of 58 °C/mm over the porous region while the experiments conducted with ash no. 6 had an average temperature gradient of 87 °C/mm over the porous region.

Table 3. The global temperature gradients over the porous regions of the ash deposits and the parameters used to calculate the temperature gradients ( $T_0$ , steel temperature and porous region thickness)

Experiment	T <sub>0</sub>	Steel temperature	Porous region	Temperature
	(°C)	(°C)	thickness	gradient
			( <b>mm</b> )	(°C/mm)
1/400/24/A	690	400	4.07	71.3
1/400/24/B	690	400	5.03	57.7
1/500/24/A	690	500	2.05	92.7
1/500/24/B	690	500	2.20	86.4
2/500/24/A	690	500	3.60	52.8
3/300/24/A	690	300	5.60	69.6
3/400/24/A	690	400	4.90	59.2
3/500/24/A	690	500	4.78	39.8
3/500/24/B	690	500	2.80	67.8
3/500/72/A	690	500	3.32	57.3
3/500/4/A	690	500	3.61	52.6
5/500/24/A	626	500	2.20	56.8
6/300/24/A	626	300	3.53	92.2
6/400/24/A	626	400	2.25	100.0
6/500/24/A	626	500	1.82	68.7
6/500/24/B	626	500	1.49	83.8
6/500/72/A	626	500	1.83	68.3
6/500/4/A	626	500	1.18	106.4
Average				71.3
Standard				18.5
deviation				
	Ash no; 1 = eutectic KCl/K <sub>2</sub> SO <sub>4</sub> , 2 = KCl rich, $3 = K_2SO_4$ rich,			

 $4 = eutectic NaCl/Na_2SO_4$ , 5 = NaCl rich,  $6 = Na_2SO_4$  rich

## 3.2. Gas phase alkali chloride transport in the porous region

Alkali chloride transport in the porous region of the ash deposit was observed in all of the experiments. Alkali chloride layers were observed on the hotter side of the synthetic ash particles in the porous region. In addition in some experiments alkali chloride depleted areas were observed on the cooler side of the synthetic ash particles. The alkali chloride depleted scaffolds were common in K ashes (ashes 1 and 3). Typical alkali chloride buildup layers and alkali chloride depleted areas are presented in Figure 25. The alkali chlorides were assumed to have sublimated from the colder side of the ash particles, then diffused in the gas phase and deposited on the hotter side of the underlying ash particle or on the steel surface.



# KCl depleted area

Figure 25. SEM BS images showing the alkali chloride transport in the porous region. Transported NaCl layers (upper left), transported KCl layers (upper right) and particles with KCl depleted scaffolds (lower left and lower right). The alkali chloride transport was quantified as described in Chapter 2.3.3. The alkali chloride transport was quantified for experiments with eutectic and  $SO_4$  rich ashes (ashes 1, 3 and 6). The alkali chloride layer thicknesses were converted from px to  $\mu$ m and the distances from the steel were converted from px to mm. The results for the Na<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 6) with different steel temperatures and exposure time of 24 h are shown in Figure 26.



Figure 26. NaCl layer thicknesses in the  $Na_2SO_4$  rich ash (ash no. 6) deposits plotted against the distance from steel. Results from experiments with different steel temperatures with exposure time of 24 h are presented.

The results with the Na<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 6) show similar behavior with all of the tested steel temperatures. The thickest NaCl layers were found near the eutectic region and the thicknesses decreased towards the steel surface. However with different steel temperatures the transported NaCl layers were found from different distances from the steel. The other synthetic ashes showed similar behavior. The distance from steel values were converted from mm to °C by using the temperature gradient values calculated in Chapter 3.1.3. The results for the Na<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 6) with different steel temperatures and exposure time of 24 h are shown in Figure 27.



Figure 27. NaCl layer thicknesses in the  $Na_2SO_4$  rich ash (ash no. 6) deposits plotted against the local temperature in the deposits. Results for experiments with different steel temperatures with exposure time of 24 h are presented.

The results with different steel temperatures are similar when plotted against temperature instead of distance. The alkali chloride transport seems to be controlled by temperature. It was also observed that the synthetic ash deposit composition had a role in the alkali chloride layer formation. The KCl layer thickness results of experiments with KCl/K<sub>2</sub>SO<sub>4</sub> ashes (ashes 1 and 3), with different steel temperatures and exposure time of 24 h are presented in Figure 28. The KCl layers were noticeably thicker than the NaCl layers in the same temperatures. At 600 °C the thicknesses of KCl layers were 10–150  $\mu$ m and the thicknesses of NaCl layers were 10–25  $\mu$ m.



Figure 28. KCl layer thicknesses in deposits with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1) (upper) and with the K<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 3) (lower) plotted against local temperature in the deposits. The results from the experiments with 24 h exposure time are presented.

The alkali chloride layers were thickest with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1). The ash no. 1 had the highest Cl content of the ashes where the alkali chloride layer thicknesses were measurable. In addition, the Cl was associated with K. The K<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 3) produced the second thickest alkali chloride layers. In temperatures above approximately 580 °C the experiments with ash no. 1 have clearly thicker KCl layers than the experiments with ash no. 3. Below temperatures approximately 580 °C the ashes 1 and 3 showed similar KCl

thicknesses. The thinnest alkali chloride layers were observed in experiments with the  $Na_2SO_4$  rich ash (ash no. 6).

KCl has higher saturation pressure than NaCl in temperatures between 300-700 °C. The higher saturation pressure explains why the alkali chloride transport in KCl/K<sub>2</sub>SO<sub>4</sub> ash deposits is greater than in the NaCl/Na<sub>2</sub>SO<sub>4</sub> ash deposits. Higher saturation pressure means more alkali chloride molecules in the gas phase and thus more molecules are viable to gas phase transport. The saturation pressures of KCl, (KCl)<sub>2</sub>, NaCl and (NaCl)<sub>2</sub> are presented in Figure 29. The saturation pressures were calculated using computer software FactSage, version 6.3.<sup>21</sup>



Figure 29. Saturation pressures of KCl,  $(KCl)_2$ , NaCl and  $(NaCl)_2$  presented in two different axis. The saturation pressures were calculated using FactSage<sup>21</sup> software.

The results were handled based on the hypothesis that the alkali chloride saturation pressures control the transport process. According to Clausius–Clapeyron relation, natural logarithm of saturation pressure is a linear function of inverse temperature.<sup>26</sup> Natural logarithms were taken of the alkali chloride layer thickness values in each experiment. The logarithmical layer thicknesses were plotted against inverse temperature. A linear function was fitted to the results using the least squares method. Confidentiality bounds with 95% certainty were also calculated. Figures with the fitted functions are contained in the Appendix. The fitted curves were converted back to  $\mu m$  vs °C scale and plotted with the original data points. These figures are also contained in the Appendix. The data points and the fitted function for the experiment with Na<sub>2</sub>SO<sub>4</sub> rich ash, steel temperature at 400 °C and exposure time of 24 h (6/400/24/A) are presented in Figure 30.



Figure 30. An example of the quantified NaCl transport data, the fitted function and the 95% confidentiality bounds presented in two different axis. The data points are from the experiment with  $Na_2SO_4$  rich ash (ash no. 6), steel temperature at 400 °C and with exposure time of 24 h (6/400/24/A).

Results from experiments with the same synthetic ash and exposure time were also plotted together and treated as a group. This was done for the experiments with the  $K_2SO_4$  rich ash (ash no. 3) and with the  $Na_2SO_4$  rich ash (ash no. 6). The measurement points from 24 h experiments and the fitted functions are shown in Figure 31.



Figure 31. The alkali chloride transport results, the fitted functions and the 95% confidentiality bounds for 24 h experiments with the  $K_2SO_4$  rich ash (ash no. 3) (left) and with the  $Na_2SO_4$  rich ash (ash no. 6) (right).

The effect of exposure time to the alkali chloride layer thickness was also studied. Figure 32 shows the alkali chloride layer thickness results for the SO<sub>4</sub> rich ashes (ashes 3 and 6). The results from the experiments with the  $K_2SO_4$  rich ash (ash no. 3) show a clear effect as a function of exposure time. In the 4 h experiment the KCl layers were observed at temperatures above 580 °C while in the 24 and 72 h experiments the layers were observed at temperatures above 490 °C. The KCl layer thicknesses increased as a function of time.



Figure 32. The alkali chloride transport results for the  $K_2SO_4$  rich ash (ash no. 3) (left) and for the  $Na_2SO_4$  rich ash (ash no. 6) (right) with different steel temperatures and exposure times.

Similar behavior was observed with the  $Na_2SO_4$  rich ash (ash no. 6). In the 4 h experiment the NaCl layers were observed in temperatures above 570 °C. With exposure times 24 and 72 h the NaCl layers were observed in temperatures above 490 °C. The NaCl layer thicknesses increased as a function of time.

It was observed that with the  $K_2SO_4$  rich ash (ash no. 3) the exposure time also affected the maximum temperature where KCl layer were observed (Figure 32). Increased exposure time decreased the maximum temperature where KCl layers were observed. Alkali chloride diffusion into the furnace was considered to be the cause for this phenomenon. The absence of the eutectic regions in the 24 and 72 h experiments with the ash no. 3 support the diffusion hypothesis.

The same effect was not observed in the experiments with the  $Na_2SO_4$  rich ash (ash no. 6). NaCl has noticeably lower saturation pressure than KCl and thus not as much of the NaCl species diffused to the furnace. In addition, the ash no. 6 formed in all of the experiments dense eutectic and sintered regions. These dense regions were considered to have worked as protective layers that prevented the NaCl species of the porous region from diffusing into the furnace.

The alkali chloride layer growth rate was observed to decrease as a function of time. Figure 33 shows the layer growth rate with the  $SO_4$  rich ashes (ashes 3 and 6) as a function of temperature. The 4 and 24 h experiments with the  $K_2SO_4$  rich ash (ash no. 3) with steel temperature at 500 °C had similar KCl layer growth rates. In the 72 h experiment the growth rate had decreased noticeably. The experiments with the  $Na_2SO_4$  rich ash (ash no. 6), with steel temperature at 500 °C, showed similar trend. However with NaCl, the decrease in growth rate was observed already in the 24 h experiments and the decrease was even greater in the 72 h experiment.





Figure 33. Alkali chloride transport rates for the  $K_2SO_4$  rich ash (ash no. 3) (upper) and for the  $Na_2SO_4$  rich ash (ash no. 6) (lower) with steel temperature at 500 °C plotted against local temperature in the deposit.

The decrease in alkali chloride layer growth rate as a function of time is explained with the lack of alkali chlorides present. The alkali chloride amount in the deposit is limited and the alkali chlorides are simultaneously transported towards the steel surface and into the furnace. The decrease in the growth rate is observed more clearly in higher temperatures. This is logical because the diffusion into the furnace affects the higher temperature regions first. In addition, the diffusion flux towards the steel surface is higher in higher temperatures. This leads to a situation where the deposit is depleted of alkali chlorides in higher temperatures. This phenomenon was observed in the experiments with the  $K_2SO_4$  rich ash (ash no. 3). Further experiments with different ash compositions and exposure times are needed to gain a better understanding of the effect of the temperature gradient to the alkali chloride transport within the ash deposit.

## 3.3. Corrosion

Corrosion of the steel rings was analyzed from the SEM BS images. The oxide layer thickness was measured in a location where it was compact. An example from experiment with the  $K_2SO_4$  rich ash, steel temperature at 500 °C and exposure time of 72 h (3/500/72/A) is presented in Figure 34. Oxide layer thicknesses from the 24 h experiments are presented in Figure 35. In case of duplicate experiments (3/500/24 and 6/600/24) the average oxide layer thickness was plotted in Figure 35.

The experiment with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash, steel temperature at 400 °C, exposure time of 24 h and with P235GH steel ring (1/400/24/B) is not included in the Figure 35 due to the different steel used in the experiment. The measured oxide layer thickness was approximately 4  $\mu$ m. In addition, the experiments with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash, steel temperature at 500 °C and exposure time of 24 h (1/500/24/A and 1/500/24/B) were parallel but only the latter (1/500/24/B) is presented in Figure 35. In the experiment 1/500/24/A, a considerably thicker oxide layer compared with the other experiments in the same temperature was observed. The oxide layer thickness in the 1/500/24/A was over 80  $\mu$ m while the oxide layer thicknesses in the other experiment 35  $\mu$ m. The oxide layer thickness of the experiment 1/500/24/A was considered an outlier and it was not included in Figure 35. The possible reasons for this unusually thick oxide layer are discussed later.



Figure 34. A SEM BS image of the oxide layer cross-section in the experiment with the  $K_2SO_4$  rich ash, steel temperature at 500 °C and exposure time of 72 h (3/500/72/A).



Figure 35. The measured oxide layer thicknesses of experiments with exposure time of 24 h.

From the corrosion point of view it was observed that the steel temperature was the main factor contributing to the oxide layer thickness. With steel temperature at 300 °C practically

no corrosion was observed. Oxide layer thicknesses of 2–6  $\mu$ m were observed with steel temperature at 400 °C. With steel temperature at 500 °C, oxide layer thicknesses of 12–27  $\mu$ m were observed. Similar results have been shown in other studies in isothermal conditions. For example Skrifvars et al<sup>6</sup> have shown that an increase in temperature leads to an increase in corrosion rate of steel.

Some differences in oxide layer thicknesses were observed between the K and Na ashes. The experiments with Na ashes produced slightly thinner oxide layers than the K ashes. This is in contrast with previous work. For example according to Enestam et al<sup>18</sup> there are no main differences between the corrosiveness of KCl and NaCl. The differences in oxide layer thicknesses, observed in this study, between the different synthetic ashes were potentially due to the temperature gradient induced alkali chloride transport to the steel surface. As noted in Chapter 3.2. the KCl transport rate towards steel was greater than the transport rate of NaCl. The higher amount of KCl has possibly enhanced the corrosion rate and the transported KCl has possibly contributed to the oxide layer thickness. However, the current data is inconclusive and further research is needed.

The amount of alkali chlorides in the synthetic ash deposits made little difference to the oxide layer thickness. The experiments with the Cl rich ashes had slightly thicker oxide layers than the SO<sub>4</sub> rich experiments but the differences were small (Figure 35). The amount of alkali chlorides in the SO<sub>4</sub> rich ashes was still high (11.1 wt-% KCl and 6.4 wt-% NaCl). According to Skrifvars et al<sup>6</sup> the amount of 0.3 wt-% of Cl, associated with Na and K, induces high corrosion rates in temperatures below  $T_0$ . They reported oxide layer thicknesses of approximately 20 µm in 10CrMo9-10 steel after 168 h of exposure at 500 °C with deposit that is similar to the Na<sub>2</sub>SO<sub>4</sub> rich ash (ash no. 6) used in this thesis. Their results are in the same order of magnitude with the results of this work. However the different exposure times make it challenging to compare the results.

The thickest oxide layer was observed in the experiment with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash, steel temperature at 500 °C and exposure time of 24 h (1/500/24/A), but it is not presented in Figure 35. The thickness of the oxide layer was 80  $\mu$ m while the oxide layer thickness of the parallel experiment (1/500/24/B) was 25  $\mu$ m. The thickness of 25  $\mu$ m is consistent with other experiments at steel temperature 500 °C and therefore only the value of 25  $\mu$ m is presented in Figure 35. In the experiment 1/500/24/A, some Na species were observed near the steel surface. The Na species have possibly affected the corrosion rate of that sample and the

unusual oxide layer thickness is possibly explained with it. No Na contaminations were found in other experiments with the eutectic  $KCl/K_2SO_4$  ash (ash no. 1) and it is likely that only the experiment 1/500/24/A was contaminated.

In the experiments with the K<sub>2</sub>SO<sub>4</sub> rich ash and steel temperature at 500 °C (3/500/4/A, 3/500/24/A, 3/500/24/B, and 3/500/72/A) the oxide layer thickness was observed to increase as a function of the exposure time. A similar trend was observed in the experiments with the Na<sub>2</sub>SO<sub>4</sub> rich ash and steel temperature at 500 °C (6/500/4/A, 6/500/24/A, 6/500/24/B, and 6/500/72/A). The oxide layer thicknesses with the SO<sub>4</sub> rich ashes and steel temperature at 500 °C are presented as a function of time in Figure 36.



Figure 36. The oxide layer thicknesses with  $SO_4$  rich ashes (ashes 3 and 6) with steel temperature at 500 °C plotted against the exposure time.

Sundqvist<sup>19</sup> reported similar results with pure KCl deposits on 10CrMo9-10 steel in isothermal conditions. Sundqvist reports oxide layer thicknesses of 14.9  $\mu$ m at 24 h and 22.8  $\mu$ m at 72 h with steel temperature at 500 °C. The oxide layer thicknesses reported by Sundqvist are systematically lower than the oxide layer thicknesses reported in this work. The difference is potentially due to the temperature gradient, different ash compositions or difference in the method of measurement. Further research is needed to understand the effect of the temperature gradient to the high temperature corrosion of steel.

# 4. MODELLING

Modelling was carried out to gain a better quantitative understanding of the experimental data and observations. A model was developed to calculate the alkali chloride transport in the porous region. The model is based on Fick's first law of diffusion and it predicts the alkali chloride layer growth in a porous ash deposit. The Matlab code of the model is contained in the Appendix.

## 4.1. The modelling unit

In the model, the three dimensional synthetic ash deposit was simplified into a theoretical one dimensional modelling unit. This unit has one solid ash layer on top and one air layer at the bottom. In the unit the hotter side is the upper side and the colder side is the lower side. The unit is presented schematically in Figure 37. In the model, an ash layer thickness of 150  $\mu$ m was used. The thickness of 150  $\mu$ m was chosen on the basis of the ash particle sieving fraction (53–250  $\mu$ m) used in the experiments. The ash layer thickness and a theoretical packing fraction were used to calculate the thickness of the air layer in the modelling unit. The default packing fraction used in the model was the Random Close Packing (RCP) with a value of  $\eta_{RCP} = 0.64^{27}$ . The calculated default air layer thickness used in the model was 84.4  $\mu$ m.



Figure 37. A SEM BS image of the deposit structure (left) and a scematic picture of the theoretical modelling unit (right, inside the dashed line). The vertical arrows indicates the alkali chloride transport direction.

The particle to particle distance of 84.4  $\mu$ m agrees well with the particle to particle distances in theoretical close packing structures. In close packing structures, the hexagonal close packing structure (HCP) and the face centric close packing structure (FCC), there are two kinds of holes in the structures. There are tetrahedral holes and octahedral holes.<sup>28</sup> These holes are presented schematically in Figure 38. Some distances regarding these holes were calculated using spheres with diameters of 150  $\mu$ m. The shortest distance between the points A and B (Figure 38) in an octahedral hole is approximately 62.1  $\mu$ m and in a tetrahedral hole approximately 94.9  $\mu$ m. The value of 84.4  $\mu$ m is between the two theoretical values.



Figure 38. Cross sections of theoretical close packing structures. The FCC structure with octahedral hole (left) and the HCP structure with tetrahedral hole (right). The distances between the points A and B were calculated (FCC 62.1  $\mu$ m and HCP 94.9  $\mu$ m) with particle diameters of 150  $\mu$ m.

## 4.2. Diffusion calculations

According to Fourier's law of heat conduction, the heat flux through the ash and the air in the deposit is the same and it is calculated using Equation 2. Equation 2 was manipulated into the form of Equation 3. Equation 4 shows how the temperature gradient is calculated in the ash deposit. Equation 5 was gained by combining Equations 3 and 4. Equation 5 gives the temperature difference over the air layer in the modelling unit when the temperature gradient over the porous deposit, the thicknesses of air and ash layers and the thermal conductivities of air and ash are known.

$$\dot{q} = \lambda_i \frac{dT}{dx} \tag{2}$$

$$\frac{\Delta T_{ash}}{\Delta T_{air}} = \frac{\lambda_{air} \Delta x_{ash}}{\lambda_{ash} \Delta x_{air}} \tag{3}$$

$$\frac{dT}{dx} = \frac{\Delta T_{air} + \Delta T_{ash}}{\Delta x_{air} + \Delta x_{ash}} \tag{4}$$

$$\Delta T_{air} = \frac{dT}{dx} * \frac{\Delta x_{air} + \Delta x_{ash}}{1 + \frac{\lambda_{air} + \Delta x_{ash}}{\lambda_{salt} \Delta x_{air}}}$$
(5)

where

 $\dot{q}$  is the heat flux, [W/m<sup>2</sup>]  $\lambda_i$  is the thermal conductivity of *i*, [W/(m K)]  $\frac{dT}{dx}$  is the temperature gradient over the porous deposit, [°C/m]  $\Delta T_{air}$  is the temperature difference through the air layer, [°C]  $\Delta T_{ash}$  is the temperature difference through the ash layer, [°C]  $\lambda_{air}$  is the temperature difference through the ash layer, [°C]  $\lambda_{air}$  is the thermal conductivity of the air, [W/(m K)]  $\lambda_{ash}$  is the thermal conductivity of the ash, [W/(m K)]  $\Delta x_{air}$  is the thickness of the air layer, [m]  $\Delta x_{ash}$  is the thickness of the ash layer, [m]

The modelling unit was applied to temperatures ranging from  $T_{steel}$  to  $T_0$ . The temperature of the colder side of the air layer in the modelling unit was decided and the temperature of the hotter side of the air layer was calculated by adding the  $\Delta T_{air}$  value.

The thermal conductivity of dry air varies from 0.026 to 0.051 W/(m K) in the temperature range of 300–700 °C.<sup>29</sup> No thermal conductivity data for the solid salts used in the experiments, at temperatures relevant for this work, were found. Figure 39 shows thermal conductivity values of KCl and NaCl in the temperature interval 0–400 K. The thermal conductivity values of KCl and NaCl do not change considerably in the temperatures above 0 °C, but stay close to approximately 5 W/(m K).<sup>30</sup> A similar trend is also observed with similar dielectric salts (NaF and LiF).<sup>31</sup>



Figure 39. The thermal conductivities of KCl and NaCl plotted against temperature in K.<sup>20</sup>

The thermal conductivity values of 5.0 W/(m K) for ash and 0.05 W/(m K) for air were used in the model. The layer thicknesses of 150  $\mu$ m for ash and 84.4  $\mu$ m for air were used. The modelling was conducted using several temperature gradient values (20, 40, 60, 80, 100 and 120 °C/mm), which were chosen on basis of the experimental values (see Chapter 3.1.3.).

The saturation pressures of different alkali chloride species were calculated as a function of temperature. According to Clausius–Clapeyron equation, natural logarithm of saturation pressure is a linear function of inverse temperature.<sup>26</sup> Natural logarithm was taken of the saturation pressure values that were calculated with FactSage (see Chapter 3.2.) and plotted against inverse temperature. A linear function was fitted to the points using least squares method to obtain a continuous function for the saturation pressures of different alkali chloride species. The species considered in this study were NaCl, (NaCl)<sub>2</sub>, KCl and (KCl)<sub>2</sub>.

The total concentration of the gas phase as a function of temperature was calculated using the ideal gas law.<sup>26</sup> The alkali chloride concentrations were calculated by multiplying the total gas concentration with the corresponding alkali chloride saturation pressure as shown in Equation 6.

$$c_i = x_i \frac{p}{RT} \tag{6}$$

where

c<sub>i</sub> is the concentration of *i*, [mol/m<sup>3</sup>]
x<sub>i</sub> is the mole fraction of *i* in gas phase, [-] *p* is the standard atmospheric pressure, [101 325 Pa] *R* is the gas constant, [8.314 J/(mol K)] *T* is the temperature, [K]

The diffusion coefficients for NaCl,  $(NaCl)_2$ , KCl and  $(KCl)_2$  were calculated. The kinetic theory of gases was used to calculate values needed for the diffusion coefficient calculations.<sup>26</sup> The equations are presented in Equations 7–9.

$$D_i = \frac{1}{3} \lambda_{mfp,i} \,\bar{c}_i \tag{7}$$

$$\lambda_{mfp,i} = \frac{k_B T}{\frac{1}{2^2} d_i^2 \pi p} \tag{8}$$

$$\bar{c}_i = \left(\frac{8RT}{\pi M_i}\right)^{\frac{1}{2}} \tag{9}$$

where

 $D_i$  is the diffusion coefficient of *i*, [m<sup>2</sup>/s]  $\lambda_{mfp,i}$  is the mean free path of *i*, [m]  $\bar{c}_i$  is the mean speed of *i*, [m/s]  $k_B$  is the Boltzmann constant, [1.381\*10<sup>-23</sup> J/K] *T* is the temperature, [K]  $d_i$  is the molecule diameter of *i*, [nm] *p* is the standard atmospheric pressure, [101 325 Pa] *R* is the gas constant, [8.314 J/(mol K)]  $M_i$  is the molar mass of *i*, [g/mol] Molecular diameters of the alkali chloride species were calculated based on the geometry of the molecules. For the alkali chloride monomer diameters the values of the bond lengths multiplied by two were used. The NaCl bond length of 0.24  $\text{nm}^{30,32}$  was used and the KCl bond length of 0.27  $\text{nm}^{30}$  was used.



Figure 40. The geometry of the alkali chloride dimer structure. Based on Torring.<sup>33</sup>

The (KCl)<sub>2</sub> and (NaCl)<sub>2</sub> are both rhombus shaped (Figure 40). The distance of the centers of the Cl ions (Figure 40,  $r_{ClCl}$ ) was calculated. The bond length of the alkali metal and the Cl (Figure 40,  $r_{MCl}$ ) in a dimer structure was added to the  $r_{ClCl}$ . In the model the molecular diameters of 0.63 nm for (NaCl)<sub>2</sub> and 0.65 nm for (KCl)<sub>2</sub> were used.<sup>32-34</sup>

The molar fluxes of alkali chloride species were calculated using Fick's first law of diffusion (Equation 10).<sup>26</sup>

$$J_i = D_i \frac{dc_i}{dx} \approx D_i \frac{\Delta c_i}{\Delta x} \tag{10}$$

$$\frac{\Delta c_i}{\Delta x} = \frac{c_{i,hot} - c_{i,cold}}{\Delta x_{air}} \tag{11}$$

where

$$J_i$$
 is the molar flux of *i*, [mol/(s m<sup>2</sup>)]  
 $D_i$  is the diffusion coefficient of *i*, [m<sup>2</sup>/s]  
 $\frac{\Delta c_i}{\Delta x}$  is the concentration gradient of *i*, [mol/m<sup>4</sup>]  
 $c_{i,hot}$  is the concentration of *i* in the hottest point of the air layer, [mol/m<sup>3</sup>]  
 $c_{i,cold}$  is the concentration of *i* in the coldest point of the air layer, [mol/m<sup>3</sup>]  
 $\Delta x_{air}$  is the thickness of the air layer, [m]

The diffused alkali chloride layer thickness was calculated with Equation 12. The total calculated alkali chloride thickness was gained by summing the layer thicknesses of monomer and dimer structures. The densities at 20 °C were used for solid NaCl (2170 kg/m<sup>3</sup>) and KCl (1990 kg/m<sup>3</sup>) in the calculations.<sup>30</sup> The modelled results for NaCl and KCl with 24 h diffusion time are presented in Figures 41 and 42.

$$\Delta x_i = \frac{tM_i J_i}{\rho_i} \tag{12}$$

where

 $\Delta x_i$  is the diffused layer thickness of *i*, [m] *t* is the diffusion time, [h]  $M_i$  is the molar mass of *i*, [g/mol]  $J_i$  is the molar flux of *i*, [mol/(s m<sup>2</sup>)]  $\rho_i$  is the density of solid *i* at 20 °C, [kg/m<sup>3</sup>]



Figure 41. The predicted KCl layer thickness with different temperature gradient values with diffusion time of 24 h.



Figure 42. The predicted NaCl layer thickness with different temperature gradient values with diffusion time of 24 h.

#### 4.3. Model sensitivity analysis

Sensitivity analysis of some of the model parameters was carried out. The parameters tested were the packing fraction, the thermal conductivity of the ash, the thermal conductivity of the air and the ash particle size. The effect of the temperature gradient was included to the model itself. The KCl layer thicknesses with diffusion time of 24 h and temperature gradient of 80 °C/mm were used as reference.

The model was run with packing fraction values of 0.60, 0.64 and 0.74. These are the packing fractions of Random Loose Packing (RLP), Random Close Packing (RCP) and Face Centric Close packing (FCC). The results are presented in Figure 43. The packing fraction affects the temperature gradient over the air layer. Higher packing fraction leads to higher temperature gradient over the air layer which leads to faster alkali chloride transport. The packing fraction values of 0.60 and 0.64 gave almost identical results. The packing fraction of 0.74 did lead to a slight increase in diffusion rate. The packing fraction of 0.64 was used as a default value in the model.



Figure 43. The effect of packing fraction value on the predicted KCl layer thickness values.

The effect of the ash particle size was tested by running the model with particle sizes of 50, 150 and 250  $\mu$ m. 150  $\mu$ m was the default particle size used in the model. The results are presented in Figure 44. Increasing the particle size in the model increased the estimated alkali chloride diffusion rate.



Figure 44. The effect of ash particle size on the predicted KCl layer thickness values

The model was run with ash thermal conductivity values of 1, 5 and 10 W/(m K). The value of 5 W/(m K) was used as the default value in the model. The results are presented in Figure 45. The thermal conductivity value of the ash was observed to have little effect on the results.



Figure 45. The effect of the thermal conductivity of ash on the predicted KCl layer thickness values.

The effect of the thermal conductivity of air was tested using values of 0.01, 0.05 and 0.10 W/(m K). The default value in the model was 0.05 W/(m K). The results are presented in Figure 46. It was observed that changing the thermal conductivity of the air made practically no difference to the modelling results.



Figure 46. The effect of the thermal conductivity of air on the predicted KCl layer thickness values.

Changing the thermal conductivities of ash and air had little effect to the modelling results. In the calculations, the ratio of the thermal conductivity values is used. In default conditions the ratio of  $\lambda_{air}/\lambda_{ash}$  is 0.01. If  $\lambda_{air}$  is increased to 0.1 the ratio increases to 0.02 and if  $\lambda_{ash}$  is decreased to 1 the ratio is increased to 0.05. The ratio is used in Equation 5, in calculating the temperature gradient over the air layer, in the nominator  $\left(1 + \frac{\lambda_{air}\Delta x_{ash}}{\lambda_{salt}\Delta x_{air}}\right)$ . The term  $\frac{\Delta x_{ash}}{\Delta x_{air}}$  is dependent on the ash particle size and the packing fraction, and is 1.78 with the default model parameters. When the ratio of  $\lambda_{air}/\lambda_{ash}$  is increased from 0.01 to 0.05, the nominator value is increased from 1.02 to 1.09. The change in the nominator value is insignificant, which explains why changing the thermal conductivity of ash or air has little effect to the modelling results.

The change in packing fraction or particle size affects the nominator term mentioned earlier. The packing fraction and particle size values also directly affect the concentration gradient value (Equation 11). The air layer thickness, used in Equation 11, is calculated using the packing fraction and the particle size.

### 4.4. Comparison between the model and experimental results

In this section the experimental results and the model predictions are compared. Figures 47–49 show experimental and modelling results for 24 h experiments. The model results agree well with the experimental data. The results with the eutectic  $KCl/K_2SO_4$  ash (ash no. 1) agree better in lower range of the temperature scale, while some deviation in the higher end of the temperature scale is observed. The results with the  $K_2SO_4$  rich ash (ash no. 3) seem to correlate well with the model in the lower end of the temperature scale. However in the higher temperatures the model predicts noticeably higher values than was observed in the experiments. The results with  $Na_2SO_4$  rich ash (ash no. 6) show similar trend as the model but it seems as if the temperature axis is offset.



Figure 47. Experimental KCl layer thickness results with the eutectic KCl/K<sub>2</sub>SO<sub>4</sub> ash (ash no. 1) and the modelled results with 24 h diffusion time.



Figure 48. Experimental KCl layer thickness results with the  $K_2SO_4$  rich ash (ash no. 3) and the modelled results with 24 h diffusion time.



Figure 49. Experimental NaCl layer thickness results with the  $Na_2SO_4$  rich ash (ash no. 6) and the modelled results with 24 h diffusion time.

In Figures 47–49, it was observed that the experimental alkali chloride layer thicknesses correlate with the temperature gradient values. In the model, higher temperature gradient leads to higher diffusion rates. In the experiments with higher temperature gradients, higher alkali chloride layers were observed.



Figure 50. The KCl layer thickness results of the 4 h (upper) and the 72 h (lower) experiments with the  $K_2SO_4$  rich ash (ash no. 3) plotted together with the modelled results.

Experimental results and model predictions of KCl transport for  $K_2SO_4$  rich ash (ash no. 3) with exposure times of 4 and 72 h are presented in Figure 50. The model agrees well with the 4 h results. The model predicts noticeably thicker KCl layer than were observed in the 72 h experiment. The predicted KCl layer thicknesses, with diffusion time of 72 h at temperatures above 650 °C with temperature gradient of 80 °C/mm, are over 500 µm. KCl layers with

thicknesses of approximately 500  $\mu$ m are impossible to form in these experiments. The void spaces where the KCl layers are formed are approximately 80  $\mu$ m thick. In addition there are not sufficient amounts of KCl present to form multiple layers that are 500  $\mu$ m thick.



Figure 51. The NaCl layer buildup results of the 4 h (upper) and the 72 h (lower) experiments with the  $Na_2SO_4$  rich ash (ash no. 6) plotted together with the modelled results.

Experimental results and model predictions of NaCl transport for  $Na_2SO_4$  rich ash (ash no. 6) with exposure times of 4 and 72 h are presented in Figure 51. The experimental results with exposure time of 4 h give higher values than predicted with the model. The model prediction agrees well with the experimental results with exposure time of 72 h. NaCl transport seems to be faster in the beginning and slow down as a function of time. Similar trend was also observed with KCl.


Figure 52. Experimental KCl layer thicknesses divided with the exposure time and the modelled KCl layer thickness growth rate plotted against temperature. The experimental results with the  $K_2SO_4$  rich ash (ash no. 3) with steel temperature at 500 °C are presented in this Figure.



Figure 53. Experimental NaCl layer thicknesses divided with the exposure time and the modelled NaCl layer thickness growth rate plotted against temperature. The experimental results with the  $Na_2SO_4$  rich ash (ash no. 6) with steel temperature at 500 °C are presented in this Figure.

The effect of time to the alkali chloride layer growth rate is presented in Figures 52 and 53. The alkali chloride layer growth rates were observed to decrease as a function of time with both of the  $SO_4$  rich ashes (ashes 3 and 6). The model does not consider changes in the diffusion rate as a function of time. Further research is needed to improve the existing model so that it takes into account the decrease in the transport rate as a function of time and the limiting factors within the deposit (for example deposit thickness, void size and alkali chloride amount).

### 5. CONCLUSIONS AND FUTURE WORK

### 5.1. Conclusions

The effects of a temperature gradient on a synthetic ash deposit chemistry, morphology and corrosion were studied in this thesis. Synthetic ash deposits were applied on an air-cooled corrosion probe, which was inserted into a tube furnace. The effects of steel temperature, synthetic ash composition and exposure time were studied. In this study, steel temperatures of 300, 400 and 500 °C were used. The exposure times were 4, 24 and 72 h. The synthetic ashes were KCl/K<sub>2</sub>SO<sub>4</sub> and NaCl/Na<sub>2</sub>SO<sub>4</sub> mixtures with different ratios. The steel and deposit crosssections were studied with SEM/EDXA. The melting properties of the synthetic ashes were calculated using computer software FactSage and studied with DTA measurements.

Temperature gradient was observed to have an effect on the deposit morphology. The presence of a temperature gradient led to a formation of different regions within the deposit. In experiments with ashes with eutectic composition, a region with porous morphology was observed closest to the steel. This region had the bulk chemical composition of the original ash. On top of the porous region there was a region with compact morphology and eutectic composition. With non-eutectic ashes, an additional region was observed on top of the minor component of the ash.

Temperature gradient had an effect on the deposit chemistry. Temperature gradient was observed to induce species transport within the synthetic ash deposit. Alkali chlorides were observed to transport towards the air-cooled steel surface. The phenomenon was modelled and the modelling results support the hypothesis that the alkali chlorides are transported by gas phase diffusion. The temperature gradient induces an alkali chloride gas phase concentration gradient in the ash deposit. This led to a gas phase diffusion of alkali chlorides towards the steel surface.

Corrosion of steel was quantified by measuring the oxide layer thickness. The oxide layers measured in this work were thicker than the oxide layers measured in isothermal conditions by others.<sup>6,18,19</sup> In the light of these results, the presence of a temperature gradient seems to lead to higher corrosion rates. However the data is inconclusive and further research is needed.

#### 5.2. Future work

Further research is needed to gain more comprehensive understanding of the effect of a temperature gradient on deposit chemistry, deposit morphology and corrosion. The alkali chloride diffusion into the furnace appears to be an important factor in the deposit morphology, but at the moment there are no quantitative measurements of the phenomenon. Further development of the experimental set-up is needed to be able to quantify the diffusion in to the furnace.

Experiments with different ash compositions are of interest. Experiments with KCl/K<sub>2</sub>SO<sub>4</sub> and NaCl/Na<sub>2</sub>SO<sub>4</sub> with different ratios are of interest to further approve the conclusions in this thesis. In addition, other binary eutectic and non-eutectic salt mixtures are of interests. Ternary systems offer interesting possibilities regarding the deposit chemistry and morphology. ZnCl<sub>2</sub> and PbCl<sub>2</sub> diffusion measurements are one possibility to further study the gas phase diffusion of Cl species. There is also a possibility to conduct the experiments in a reactive atmosphere and for example study the effects of water vapor to the deposit morphology.

More work is also needed to better understand the rheology of the molten phase. To confirm the gravitational and capillary effects in the formation of eutectic regions in non-eutectic ashes is of interest. This could be tested for example by applying different original deposit morphologies, for example experiments with densely packed ash deposits with fewer pores.

To improve the existing diffusion model is of interest. The current diffusion model does not take into account the decrease in alkali chloride content on the colder side of the ash particles. The model does not take into account the condensation mechanisms and the crystal growth. In addition, the model is one dimensional and does not take into account diffusion to other directions. The alkali chloride diffusion into the furnace also seems to affect the diffusion rate towards the steel surface and it should be taken into account when the model is improved.

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### APPENDIX

# Appendix 1: Panoramic SEM BS images

Ash no./Steel temperature/Exposure time/A or B

1/500/24/A = Ash no.1, steel temperature at 500 °C, exposure time of 24 h and experiment A

Table of ash compositions

Ash no.	Composition (wt-%)	T <sub>0</sub>	T <sub>100</sub>	Melt produced at T <sub>0</sub>
		(°C)	(°C)	(wt-%)
1	KCl 55.5 / K <sub>2</sub> SO <sub>4</sub> 44.5	690	690	100
2	KCl 91.1 / K <sub>2</sub> SO <sub>4</sub> 8.9	690	758	20
3	KCl 11.1 / K <sub>2</sub> SO <sub>4</sub> 88.9	690	969	20
4	NaCl 32.0 / Na <sub>2</sub> SO <sub>4</sub> 68.0	626	626	100
5	NaCl 86.4 / Na <sub>2</sub> SO <sub>4</sub> 13.6	626	780	20
6	NaCl 6.4 / Na <sub>2</sub> SO <sub>4</sub> 93.6	626	818	20



1/400/24/A



1/400/24/B



1/500/24/A



1/500/24/B



2/500/24/A



3/300/24/A



3/400/24/A



3/500/24/A



3/500/24/B



3/500/4/A



3/500/72/A



5/500/24/A



6/300/24/A



6/400/24/A



6/500/24/A



6/500/24/B



6/500/4/A



6/500/72/A



Appendix 2: Synthetic ash densities calculated with FactSage



# Appendix 3: Fitted alkali chloride layer thickness results

Ash no./Steel temperature/Exposure time/A or B

1/500/24/A = Ash no.1, steel temperature at 500 °C, exposure time of 24 h and experiment A

Table of a	ash com	positions
------------	---------	-----------

Ash no.	Composition (wt-%)	T <sub>0</sub>	T <sub>100</sub>	Melt produced at T <sub>0</sub>
		(°C)	(°C)	(wt-%)
1	KCl 55.5 / K <sub>2</sub> SO <sub>4</sub> 44.5	690	690	100
2	KCl 91.1 / K <sub>2</sub> SO <sub>4</sub> 8.9	690	758	20
3	KCl 11.1 / K <sub>2</sub> SO <sub>4</sub> 88.9	690	969	20
4	NaCl 32.0 / Na <sub>2</sub> SO <sub>4</sub> 68.0	626	626	100
5	NaCl 86.4 / Na <sub>2</sub> SO <sub>4</sub> 13.6	626	780	20
6	NaCl 6.4 / Na <sub>2</sub> SO <sub>4</sub> 93.6	626	818	20






























## Appendix 4: Alkali chloride transport model code

```
%MIN 1=solid 2=air
   k1=5;
   k2=0.05;
   x1=150;
   z=0.64;
   x2=x1/z*(1-z);
   T block max=109*(x1+x2)*0.001; %132 K/mm * um
   a max=k2*x1/(k1*x2); %dT1/dT2
   T2 max=T block max/(1+a max); %K
   T1 max=T block max-T2 max; %K
   T block=34*(x1+x2)*0.001;
   a=k2*x1/(k1*x2); %dT1/dT2
   T2=T block/(1+a); %K
   T1=T block-T2; %K
%constans
R=8.3144621; %J/mol K
Pa=101300; %Pa
k=1.3806488E-23; %J/K the Boltzmann's constant
T 0=300+273; %K
T KCl=[573:10:1173];
T NaCl=[573:10:1173];
p KCl=[5.660000000000e-06;1.15000000000e-05;2.280000000000e-
05;4.400000000000e-05;8.330000000000e-
05;0.00015400000000000;0.0002790000000000;0.00049600000000000;0.0008660
000000000;0.00148000000000;0.00250000000000;0.00415000000000;0.0
06770000000000;0.010900000000;0.0173000000000;0.027000000000;0
.2100000000000;0.307000000000;0.442000000000;0.632000000000;0.89
5000000000;1.2500000000;1.74000000000;2.41000000000;3.2900000
000000;4.460000000000;6.010000000000;8.030000000000;10.70000000000;
14.10000000000;18.4000000000;24;31;39.9000000000;51;64.80000000000
0;82;103;129;161;199;246;302;369;450;546;659;793;951;1140;1350;1600;1900;22
40;2630;3080;35901;
p NaCl=[1.4265200000000e-07;3.2069800000000e-07;7.0109600000000e-
07;1.4925500000000e-06;3.0982500000000e-06;6.2786800000000e-
06;1.2436100000000e-05;2.4100600000000e-05;4.5744100000000e-
05;8.5117400000000e-
05;0.00015540500000000;0.00027863400000000;0.00049098800000000;0.0008509
4100000000;0.00145151700000000;0.0024385290000000;0.0040372790000000;0.0
0659116100000000;0.0106167390000000;0.0168813560000000;0.0265111990000000;0
.213571140000000;0.314206880000000;0.457877490000000;0.661134370000000;0.94
6186170000000;1.34258880000000;1.88936610000000;2.63765080000000;3.65394950
000000;5.02415200000000;6.85841960000000;9.29710910000000;12.5179030000000;
16.7443450000000;22.2559870000000;29.400400000000;38.6072950000000;50.4050
```

43000000;65.439911000000;84.498322000000;108.53253000000;138.690020000 00;176.34715000000;223.14729000000;281.04405000000;352.34996000000;427. 96378000000;516.82650000000;621.81394000000;745.41713000000;890.4410500 0000;1060.0344000000;1257.7211000000;1487.4331000000;1753.5457000000;2 060.9134000000];

p\_KCl\_d=[1.570000000000e-06;3.31000000000e-06;6.800000000000e-06;1.36000000000e-05;2.6600000000e-05;5.0700000000000e-05;9.450000000000e-05;0.0001730000000000;0.0003090000000000;0.00054200000000000;0.0009340 0000000000;0.00158000000000;0.00263000000000;0.0043100000000000;0.0 06950000000000;0.01110000000000;0.01730000000000;0.02680000000000;0. 04090000000000;0.0616000000000;0.09180000000000;0.1350000000000;0. 1970000000000;0.284000000000;0.405000000000;0.5720000000000;0.80 000000000;1.11000000000;1.53000000000;2.8100000 00000;3.77000000000;5.0200000000;6.64000000000;8.7100000000;2.8100000 000000;3.77000000000;5.0200000000;1.53000000000;2.4.2000000000;3.8000 0000000;3.77000000000;14.7000000000;18.9000000000;24.2000000000;30.8000 0000000;38.9000000000;48.9000000000;61.2000000000;76.1000000000 0;94.1000000000;116;142;173;210;254;306;367;439;522;619;731;860;1010;11 80;1370;1600];

p NaCl d=[7.860690000000e-09;1.926080000000e-08;4.5743100000000e-08;1.0546100000000e-07;2.3638000000000e-07;5.1578900000000e-07;1.0970600000000e-06;2.2772200000000e-06;4.6183400000000e-06;9.1607800000000e-06;1.7789900000000e-05;3.3854700000000e-05;6.3190000000000-05;0.000115777000000000;0.00020839400000000;0.00036877000000000;0.0006420 0300000000;0.00110031700000000;0.00185767900000000;0.00309138700000000;0.0 0507353100000000;0.0082162500000000;0.0131360160000000;0.0207438660000000; 0.0323705950000000; 0.0499385470000000; 0.0761948310000000; 0.115024700000000;0.171868450000000;0.25427088000000;0.37259860000000;0.540968470000000;0.7 78438670000000;1.11052460000000;1.57111190000000;2.20485370000000;3.0701494 0000000;4.24282300000000;5.82063010000000;7.92874450000000;10.7263940000000 ;14.4148340000000;19.246866000000;25.5381460000000;33.6805170000000;44.157 6610000000;57.5633690000000;74.6227340000000;96.2166390000000;123.409880000 000;157.483300000000;189.359440000000;225.945800000000;268.588240000000;318 .113450000000; 375.434840000000; 441.558410000000; 517.588690000000; 604.734690000000;704.315940000000;817.76840000000];

```
salt=input('salt K=1 Na=2')
t=input('time i h')
```

## %MONOMER

```
if salt==1
    x=T KCl.^(-1);
    y=transpose(log(p KCl));
    T 1=690+273;
    M=74.5513; %g/mol
    d=0.25*2; %nm
    rho=1.980; % g/cm^3
elseif salt==2
    x=T NaCl.^(-1);
    y=transpose(log(p NaCl));
    T 1=625+273;
    M=58.44; %g/mol
    d=0.24*2; %nm
    rho=2.165; % g/cm^3
end
[p s] = polyfit(x, y, 1);
```

%Temperature

```
T lin=[T 0:5:T 1]; %K
T x=T lin+T2; <sup>⊗</sup>K
%Temperature
T_x_max=T_lin+T2_max; %K
%Cl
[log p Cl lin delta]=polyval(p,(T_lin).^(-1),s);
[log p Cl x delta]=polyval(p,(T x).(-1),s);
[log p Cl x max delta]=polyval(p, (T x max).^(-1),s);
p Cl lin=exp(log p Cl lin); %Cl ppm
p_Cl_x=exp(log_p_Cl_x); %Cl ppm
p Cl x max=exp(log p Cl x max); %Cl ppm
c luft lin=Pa/R*((T lin).^(-1)); %mol/m^3
c luft x=Pa/R*((T x).^(-1)); %mol/m^3
c luft x max=Pa/R*((T x max).^(-1)); %mol/m^3
c_Cl_lin=c_luft_lin.*p_Cl_lin.*10^(-6); %mol/m^3
c_Cl_x=c_luft_x.*p_Cl_x.*10^(-6); %mol/m^3
c Cl x max=c luft x max.*p Cl x max.*10^(-6); %mol/m^3
%mean speed
c lin=((8*(T lin).*R)/(pi()*M*0.001)).^(1/2); %m/s
%mean free path
mfp=((T_lin).*k)/(sqrt(2)*pi()*(d*10^-9)^2*Pa); %m
%Diffusions koefficient
D=1/3*c lin.*mfp; %m^2/s
%dC/dx
dC_dx=(c_Cl_x-c_Cl_lin)*((x2*10^-6)^-1); %mol/m^4
dC_dx_max=(c_Cl_x_max-c_Cl_lin)*((x2*10^-6)^-1); %mol/m^4
%J
J=D.*dC dx; %mol/s m^2
J max=D.*dC dx max; %mol/s m^2
%DIMER
if salt==1
    y1=transpose(log(p KCl d));
    M1=74.5513*2; %g/mol
   d1=0.65;
elseif salt==2
    y1=transpose(log(p NaCl d));
    M1=58.44*2; %g/mol
    d1=0.63;
end
[p1 s1]= polyfit(x,y1,1);
```

```
%Cl DIMER
[log p Cl lin1 delta]=polyval(p1,(T lin).^(-1),s1);
[log p Cl x1 delta]=polyval(p1, (T x).(-1),s1);
[log_p_Cl_x_max1 delta]=polyval(p1,(T_x_max).^(-1),s1);
p Cl lin1=exp(log p Cl lin1); %Cl dimer ppm
p_Cl_x1=exp(log_p_Cl_x1); %Cl dimer ppm
p Cl x max1=exp(log p Cl x max1); %Cl dimer ppm
c Cl lin1=c luft lin.*p Cl lin1.*10^(-6); %mol/m^3
c_Cl_x1=c_luft_x.*p_Cl_x1.*10^(-6); %mol/m^3
c Cl x max1=c luft x max.*p Cl x max1.*10^(-6); %mol/m^3
%mean speed
c lin1=((8*(T lin).*R)/(pi()*M1*0.001)).^(1/2); %m/s
%mean free path
mfp1=((T lin).*k)/(sqrt(2)*pi()*(d1*10^-9)^2*Pa); %m
%Diffusions koefficient
D1=1/3*c_lin1.*mfp1; %m^2/s
%dC/dx
dC dx1=(c Cl x1-c Cl lin1)*((x2*10^-6)^-1); %mol/m^4
dC dx max1=(c Cl x max1-c Cl lin1)*((x2*10^-6)^-1); %mol/m^4
%J
J1=D1.*dC_dx1; %mol/s m^2
J_max1=D1.*dC_dx_max1; %mol/s m^2
%SUM
%Cl i 1 m^2
Cl g=J*t*60*60*M+J1*t*60*60*M1; %g
Cl_g_max=J_max*t*60*60*M+J_max1*t*60*60*M1; %g
%Cl volym
Cl V=Cl g/rho; %cm^3
Cl V max=Cl g max/rho; %cm^3
%Cl layer thickness
Cl h=(Cl V/10000) *10000; %µm=cm^3/m^2*10000
Cl_h_max=(Cl_V_max/10000)*10000; %µm
```

```
figure
plot((T_lin-273),Cl_h,'-',(T_lin-273),Cl_h_max,'-')
```