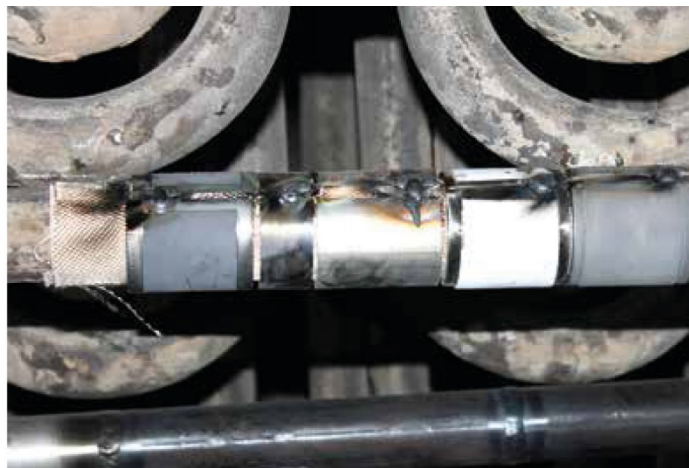


BOILER CORROSION AT LOWER TEMPERATURES – THE INFLUENCE OF LEAD, ZINC AND CHLORIDES

KME-717



CONSORTIUM MATERIALS TECHNOLOGY
for thermal energy processes



KME
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Boiler corrosion at lower temperatures

The influence of lead, zinc and chlorides

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Preface

The project has been performed within the framework of the materials technology research programme KME, Consortium materials technology for thermal energy processes, period 2014-2018. The consortium is at the forefront of developing material technology to create maximum efficiency for energy conversion of renewable fuels and waste. KME has its sights firmly set on continuing to raise the efficiency of long-term sustainable energy as well as ensuring international industrial competitiveness.

KME was established 1997 and is a multi-cliental group of companies over the entire value chain, including stakeholders from the material producers, manufacturers of systems and components for energy conversion and energy industry (utilities), that are interested in materials technology research. In the current programme stage, eight industrial companies and 14 energy companies participate in the consortium. The consortium is managed by Energiforsk.

The programme shall contribute to increasing knowledge within materials technology and process technology development to forward the development of thermal energy processes for efficient utilisation of renewable fuels and waste in power and heat production. The KME goals are to bring about cost-effective materials solutions for improved fuel flexibility, improved operating flexibility, increased availability and power production with low environmental impact.

KME's activities are characterised by long term industry and demand driven research and constitutes an important part of the effort to promote the development of new energy technology with the aim to create value and an economic, environmentally friendly and long term sustainable energy society.

The industry has participated in the project through own investment (60 %) and the Swedish Energy Agency has financed the academic partners (40 %).

Bertil Wahlund, Energiforsk

Abstract

The aim of the project was to find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150- 420°C in boilers firing used wood, and if the attack is worsened by the use of sulphur containing additive. Based on the results in this project, the use of a particular sulphur containing additive is not believed to increase the corrosion at lower temperatures. This enables it to be used to combat alkali chloride induced superheater corrosion not only for biomass fired boilers, but for boilers firing used (recycled) wood containing heavy metals as well.

Sammanfattning

På senare år har returträ blivit ett intressant bränsle med anledning av ett lågt pris jämfört med jungfruligt träbaserat bränsle. Returträ är ofta förorenat av färg, plast och metallföremål resulterande i förhöjda halter av tungmetaller, såsom zink och bly, klor och natrium i rökgasen och avlagringar. Ett sätt att minska överhettarkorrosion orsakad av alkaliklorider är att använda ett svavelinnehållande additiv som reagerar med alkaliklorider och bildar alkalisulfater och gasformig HCl. Dock så har tidigare beräkningar visat att tillsats av svavel till ett bränsle såsom returträ kan resultera i en ökning av $ZnCl_2$ och $PbCl_2$ i rökgasen. Det förmodas att dessa ämnen kan orsaka korrosionsproblem vid lägre temperaturer än vad som är fallet för alkaliklorider.

Projektets mål var att undersöka om bly, zink och deras klorider orsakar allvarliga korrosionsproblem i temperaturintervallet 150-420 °C i anläggningar som eldar returträ, samt om angreppen förvärras genom användning av svavelinnehållande additiv, genom exempelvis metoden ChlorOut®. Utifrån kunskap erhållen från fullskaliga sondförsök och resultat ifrån modellering och laboratorieprovning, så avsågs lösningar för minskning av potentiella problem föreslås.

Forskningsprojektet har utförts av en projektgrupp med representanter från Vattenfall, Andritz, Stockholm Exergi, Åbo Akademi och Swerea KIMAB. Projektet koordinerades av Swerea KIMAB.

Resultat ifrån projektet har påvisat förekomsten av bly och zink i avlagringar och korrosionsprodukter. Deras andel verkar dock inte öka när ChlorOut används. Korrosionen ökar inte signifikant av användningen av additivet. (Notera att långtidstest endast genomförts med och inte utan ChlorOut.)

De samlade resultaten indikerar att sulfatering av Cl-innehållande salter minskar korrosionen.

Utifrån resultaten ifrån detta projekt så förmodas ChlorOut inte öka korrosionen vid låga temperaturer. Detta möjliggör att ChlorOut används för att motverka alkalikloridförsakad överhettarkorrosion inte bara för biomasseldade pannor, utan också för pannor som eldar returträ innehållande tungmetaller.

Det konkluderas att projektmålen har uppfyllts acceptabelt.

Nyckelord: Returträ, korrosion, svaveladditiv, tungmetaller, klorider

Summary

In recent years, used (recycled) wood has become a fuel of interest due to low price compared to virgin wood-based fuels. Used wood is often contaminated with paint, plastic and metal components, leading to elevated concentrations of heavy metals, such as zinc and lead, chlorine and sodium in flue gases and deposits. One way to reduce superheater corrosion caused by alkali chlorides is to use a sulphur containing additive that reacts with the alkali chlorides and forms alkali sulphates and gaseous HCl. However, earlier calculations have shown that the addition of sulphur to a fuel such as used wood may result in an increase in ZnCl_2 and PbCl_2 in the gas phase. It is thought that these components could cause corrosion problems at lower temperatures than what is the case with alkali chlorides.

The aim of the project was to find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150- 420°C in boilers firing used wood, and if the attack is worsened by the use of sulphur containing additive, by for example the method ChlorOut®. Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems was intended to be suggested.

The research project has been carried out by a project group having representatives from Vattenfall, Andritz, Stockholm Exergi, Åbo Akademi and Swerea KIMAB. The project was coordinated by Swerea KIMAB.

Results in this project show the presence of lead and zinc in deposits and corrosion products. Their presence does however not seem to increase when ChlorOut is used. The corrosion does not increase significant by use of the additive. (Note that long time tests only have been performed with and not without ChlorOut).

The overall results give an indication that sulphation of Cl-containing salts decreases corrosion.

Based on the results in this project, the use of ChlorOut is not believed to increase the corrosion at lower temperatures. This enables ChlorOut to be used to combat alkali chloride induced superheater corrosion not only for biomass fired boilers, but for boilers firing used (recycled) wood containing heavy metals as well.

It is concluded that the goals have been acceptably well fulfilled.

Keywords: Used wood, corrosion, sulphur additive, heavy metals, chlorides

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1 Introduction

1.1 BACKGROUND

Combustion of biomass reduces the dependence on non-renewable energy sources, and thus the CO₂ emissions. In recent years, used (recycled) wood has become a fuel of interest due to low price compared to virgin wood-based fuels. However, used wood is often contaminated with paint, plastic and metal components, leading to elevated concentrations of heavy metals, such as zinc and lead, chlorine, sodium and sometimes sulphur in flue gases and deposits relative to those from virgin wood. In several cases, boilers burning used wood have experienced increased fouling and corrosion of furnace walls, superheaters and economisers, problems attributed to the content of chlorine, zinc, lead and alkali metals in the deposits. To minimize corrosion problems, the steam temperature is currently kept at a relatively low level and that limits electric power production efficiency.

Much work has been conducted on high temperature corrosion (> 450°C) caused by KCl and NaCl which are present in wood fuels. By contrast, much less is known about corrosion in the range 150-420°C and corrosion caused by Pb and Zn and their chlorides, which are found in used wood. Results from laboratory testing showed that ZnCl₂ is more corrosive than KCl in the temperature region 250-400°C on the low alloy superheater steel 10CrMo9-10 [1]. Laboratory tests also indicate that mixtures of salts, such as lead, zinc and alkali chlorides are more corrosive than the salts separately [2].

One way to reduce superheater corrosion caused by alkali chlorides is to use a sulphur containing additive that reacts with the alkali chlorides and forms alkali sulphates and gaseous HCl. However, results from calculations performed in KME 512 showed that the addition of sulphur to a fuel such as used wood could result in a sharp increase in ZnCl₂ and PbCl₂ in the gas phase under certain oxidising conditions [3]. It is thought that these components could cause corrosion problems at lower temperatures than what is the case with alkali chlorides.

1.2 DESCRIPTION OF THE RESEARCH FIELD

Very limited amount of field testing, if any, has been made to investigate corrosion by lead and zinc chlorides in the intermediate temperature range for CHP plants operating on used wood and how it is influenced by sulphur additives.

This means that the research field is very open and it is not possible to foresee if severe corrosion problems are to be expected or if the risk of corrosion will be low. Investigating this in detail is crucial to enable the use of sulphur additives, by for example the method ChlorOut®, to combat alkali chloride induced superheater corrosion not only for biomass fired boilers, but for boilers firing used (recycled) wood containing heavy metals as well. In case severe problems arise it will allow for solutions to be proposed, and in case not it will allow regimes of operational conditions to be identified where the corrosion risk becomes low.

1.3 RESEARCH TASK

As the field is almost unexplored one obstacle is to set the test parameters to investigate the most challenging situation. Through probe testing spanning the approximate temperature range 150-420°C in a real boiler firing used wood, with and without the use of additive, necessary input will be achieved to set the target for laboratory testing in the right direction. This will further be supported by modelling performed as thermodynamic equilibrium calculations. The probe testing will contain short term deposit testing with and without the use of ChlorOut, as well as long term corrosion testing with the use of ChlorOut. Considering the high risk of superheater corrosion long term testing without the use of ChlorOut, to serve as a reference for corrosion at lower temperatures, is not technically and economically possible. The combined results from probe testing, modelling and laboratory testing will be considered together and support each other.

1.4 GOAL

The overarching aim of this project is to increase the efficiency of boilers firing used wood and increase the fuel flexibility of boilers. The project will examine opportunities and obstacles to achieve greater steam data; perform exposures of materials to bring about greater fuel flexibility; suggest measures to reduce boiler corrosion; and propose suggestions for new design solutions and operating parameters to achieve enhanced fuel flexibility and availability.

A specific goal of the project is to find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150- 420°C in boilers firing used wood, and if the attack is worsened by the use of additive that reduce alkali chloride corrosion on superheaters at higher temperatures. Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems will be suggested.

Further, a scientific goal is to investigate and describe the ongoing corrosion processes and make an attempt to explain the mechanisms behind them to some extent. The results are aimed at being published in at least one scientific peer-reviewed article and are intended to be presented at an international conference as well. One Licentiate degree is expected to be achieved during the programme period followed by a Ph.D. degree shortly after.

1.5 PROJECT ORGANISATION

The project organisation is described below:

Vattenfall, Annika Stålenheim, Pamela Henderson and Mattias Mattsson, plus support from many other colleagues.

Management of Vattenfall activities. Plant testing - construction and provision of corrosion and deposit probes, long-term (six weeks) testing, short-term (two weeks) testing and 3 hour measurements in the boiler in Jordbro. Boiler operation and provision of operational data. Fuel analyses. Corrosion measurement and deposit analysis. Data analysis and reporting.

In-kind contribution 2 020 kSEK.

Andritz, Christoph Gruber, Responsible for ChemSheet-calculations.

In-kind contribution 500 kSEK.

Stockholm Exergi, Eva-Katrin Lindman and Jukka Meskanen. In-kind contribution 50 kSEK.

Åbo Akademi, Patrik Yrjas, budget 700 kSEK

Laboratory testing – isothermal tests and gradient deposit probes with the aim to study the influence of SO₂ in gas phase on corrosion behaviour.

Swerea KIMAB – Rikard Norling and Ph.D student Annika Talus. Budget 1 221 kkr

Overall project management and supervision of Ph.D student at KIMAB. Deposit analysis and initial corrosion studies of exposed samples. Scientific evaluation of the combined results from the different project parts.

Reference group. This consisted of the participants from the above mentioned companies/organisations and representatives from MH Engineering, the boiler manufacturers Babcock & Wilcox Völund, Sumitomo SHI FW, and from the High Temperature Corrosion Competence Centre at Chalmers, Gothenburg.

2 Experimental

2.1 FIELD TESTS

The BFB boiler in Jordbro is a commercial boiler in which exposures in field atmosphere has been performed. In Figure 1, a schematic picture of the boiler with illustration of the test positions used for the exposure (upper and lower) is shown. The flue gas temperatures at the upper and lower positions were measured to be approximately 420 °C and 550 °C, respectively.

Ring specimens of the tested alloys have been exposed on air-cooled probes, placed close to the superheaters, in the boiler. Different locations in the boiler have been tested in order to study the effect of flue gas temperature and also in order to be able to test a wide range of metal temperatures. The probes have been temperature controlled in order to achieve wanted metal temperature for the ring specimens given in each exposure. Used wood fuel has been used in all tests and the additive ChlorOut has both been in use and not. When in use, it was added according to the normal dosing level and operation procedure for the plant.

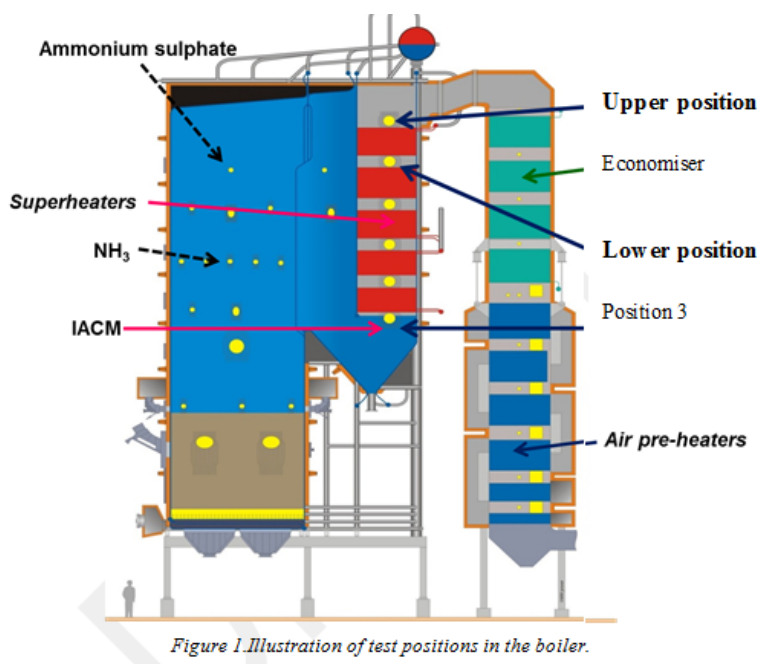


Figure 1. Illustration of the 63 MW BFB boiler in Jordbro.

2.1.1 Corrosion and deposit tests

Short term tests, 8h gradient probe

In this campaign two probes were tested in different positions (Upper and Lower position in Figure 1) and with a metal temperature range of 190 – 440 °C. In both positions, exposures with and without ChlorOut was performed. The gradient probe used with mounted ring specimen can be seen in Figure 2.



Figure 2. Probe used in the 8h gradient probe tests.

After exposure the samples were evaluated by Swerea KIMAB with respect to deposit composition and cross section analysis.

Long term tests, 6 weeks gradient probe and 3 h deposit probes

In this campaign two probes were tested in different positions (Upper and Lower position in Figure 1) and with the metal temperatures set to 250, 300 and 350 °C for both probes. Another probe type was used in this test, see Figure 3. The time duration was 6 weeks and ChlorOut was used during the exposure. Shorter deposit tests were performed before and after the long term tests for the same temperatures. In these tests exposures with and without ChlorOut were performed.



Figure 3. Probe used in the long term tests.

After exposure the samples were evaluated by Vattenfall AB with respect to metal loss and by Swerea KIMAB with respect to deposit composition and cross section analysis.

Long term tests, 6 weeks control probe

Due to anomalies observed in the second campaign a control test was performed for the selected temperature 300 °C. The time duration was 6 weeks and ChlorOut was used during the exposure. In this campaign all the samples on the probe was set to the same temperature and the position used was position 2 (see Figure 1).

After exposure the samples were evaluated by Vattenfall AB with respect to metal loss.

2.2 LABORATORY EXPOSURE

2.2.1 Isothermal corrosion tests

Three boiler materials were used in the isothermal corrosion tests. Table 1 presents the compositions of the tested steels (weight %).

Table 1: . The compositions of steels (wt-%)

Material	Fe	Cr	Ni	Mn	Si	Mo	C	N	P	S	Cu	Other
10CrMo9-10	95,96	2,24		0,45	0,25	1,00	0,07		0,01	0,01		
P235GH	97,17	0,30	0,30	1,20	0,35	0,08	0,16	0,01	0,03	0,02	0,30	Ti, V, Nb, Al
16Mo3	98,70	0,30	0,30	0,35	0,35	0,90	0,20	0,01	0,03	0,01		Co

The materials were cut to coupons with a size of approximately 20 x 20 x 5 mm. The top surfaces were subsequently polished by a 320 and a 1000 grid silicon carbide grinding paper to get a smooth surface. Then the specimens were cleaned in ethanol in ultrasound bath and further pre-oxidised in 200 °C for 24 h. A pre-determined salt mixture, simulating a simplified deposit, was then placed on each coupon before exposure (0.25 g/specimen). Three salt mixtures were used in the tests. The salts were put on the top surface of the steel and shaped as pillar.

Eight tests were carried out in the horizontal tube furnace, Figure 4, for 168 h at 300 and 350°C. The furnace was equipped with a pre-heater, water pump, and gas lines. The water was heated-up up to 200 °C and then introduced into the furnace together with the gas mixture.

The chemical compositions of the of the salt mixtures and of the gas mixtures used are shown in Table 2 and Table 3, respectively.

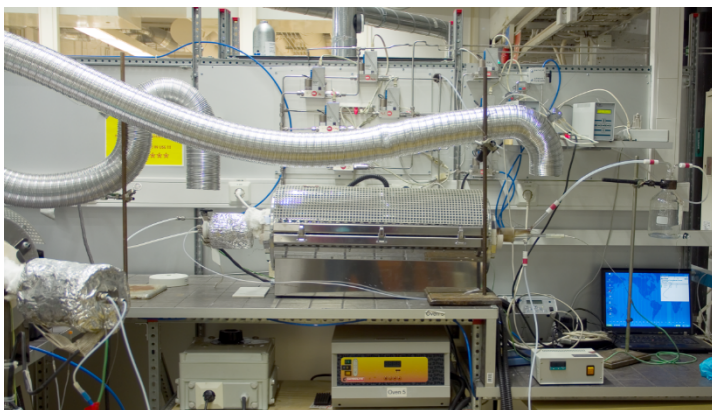


Figure 4: The horizontal tube furnace used for the corrosion tests.

Table 2: The compositions of synthetic deposits.

#	Salts	Compositions (mol.%)
1	PbCl ₂	100
2	KCl-PbCl ₂	80/20
3	KCl-PbCl ₂ -ZnCl ₂	80/10/10

Table 3: The compositions of the gas mixtures used in the corrosion tests (vol.% or ppm).

	O ₂	CO ₂	H ₂ O	SO ₂ , ppm	N ₂
Gas 1	5	15	15	0	rest
Gas 2	5	15	15	500	rest

After 168 h (1 week), the furnace and the injection of H₂O and SO₂ were turned off and after 30 minutes, the preheater was turned off. The specimens were allowed to cool down to room temperature inside the furnace in a continuous flow of a O₂-N₂. The samples were then taken out from the furnace, placed in a mould and cast in epoxy, then cut off in the middle to reveal the specimen's cross-section. The cross-section surfaces were further polished by a 320, a 1000 and a 1200 grid SiC paper using kerosene as lubricant. After polishing, the specimens were cleaned in petroleum ether in an ultrasonic bath and sputtered with carbon. The specimens were then analyzed with SEM/EDXA. The corrosion layer thickness was determined using scanning electron microscope back-scatter images. Several SEM images were combined into one panoramic image. After that, the panoramic images were digitally treated by using contrast differences. An example of the treatment stages of a typical SEM panoramic picture is shown in Figure 5.

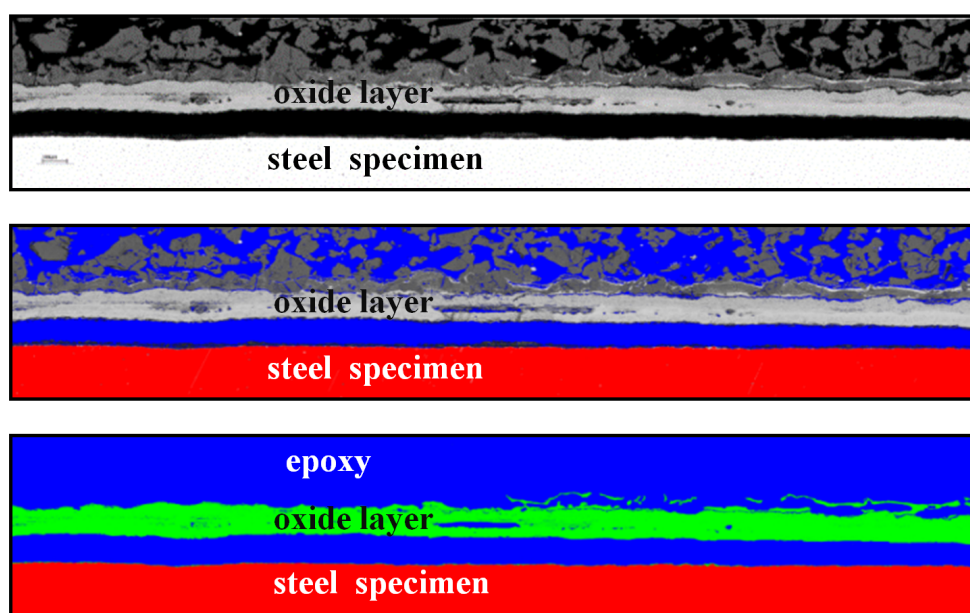


Figure 5. A schematic view of the colouring stages of the SEM images in order to determine oxide layer thickness.

After the panoramic images have been colored, the thickness of the oxide layer is determined for each vertical line of pixels and recalculated into μm . The corrosion layer is defined as the thickness of the oxide layer for each line and the corrosion attack is expressed as the mean thickness of the oxide layer [4, 5]. A specific area chosen from corrosion layer were analysed by SEM backscatter electron mode to identify the distribution and relative amount of the elements.

2.2.2 Temperature gradient tests

Rings of 10CrMo and P235GH were chosen for the temperature gradient corrosion tests. The tests were carried out in a specific experimental setup [6]. A short corrosion probe was placed into the reactor equipped with a pre-heater, water pump and a SO_2 injection line. The corrosion probe as shown in Figure 6 consists of an inner probe holding the ring samples and a protective probe surrounding the inner probe. The air was injected into the inner probe to adjust the temperature of one of the steel rings. In addition, the temperature of the other steel ring temperature was monitored by a second thermocouple. A third thermocouple was installed above the salt to measure the temperature of the gas above. In the tests done in this study, the gas temperature was adjusted to 550°C . The steel temperature on the probe was set to 350°C . The same synthetic deposits KCl-PbCl_2 and $\text{KCl-PbCl}_2\text{-ZnCl}_2$ as used in the isothermal tests were used in these tests too. The gas atmosphere in the gradient contained air with 15% water with or without 100 ppm SO_2 . The SO_2 was lower than in the isothermal tests due to safety reasons with an “open” reactor system.

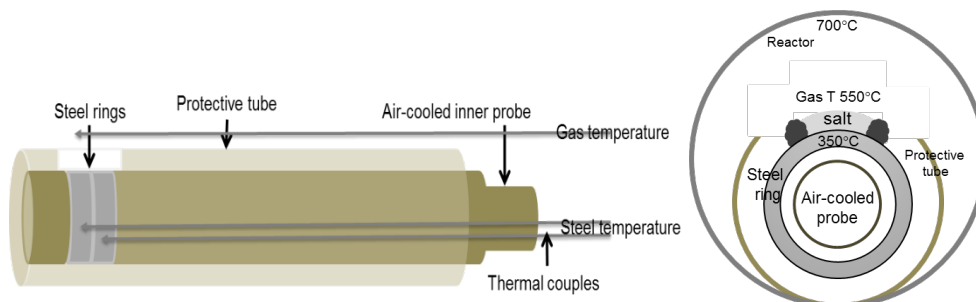


Figure 6: Outline of the corrosion probe and a schematic drawing of the cross-section of the probe. Results from simulation

After the rings were placed on the probe, the salt mixture was placed on the rings. In order to keep the salt on the ring, a fireproof paste was used and shaped around the salt. The probe was then inserted into the reactor and heated. Once the gas temperature reached 200°C , the water injection started. When the target temperature of steel was reached (350°C) the SO_2 was turned on.

Each test lasted for 24 h after which the probe was removed from the reactor and cooled down to room temperature. The rings were removed from the probe and cast in epoxy resin. A similar procedure as in the isothermal tests was used to cut, polish and clean the rings, which were then characterized by SEM-EDXA.

2.3 CHEMSHEET SIMULATIONS

Simulation was done to support the project main goals and find out general limitations in advance for the following tasks:

- To find out if lead, zinc and their chlorides cause serious corrosion problems in the temperature range 150-420°C in boilers firing used wood
- is this attack, if any, worsened by the use of additive (S-based) that reduce alkali chloride corrosion on superheaters at higher temperatures

For simulation a tool called "ChemSheet" was used. It works as an add-in program of general thermodynamics in Excel. As basis the thermochemical programming the library "ChemApp" is used in combination with its application-specific thermochemical data. ChemSheet is straightforward and requires no programming skills other than normal Excel use. Andritz has a tailor-made database from Åbo Akademi University ("Andritz Melt"). That includes that Åbo made a preselection of thermodynamic data to some extent to avoid not plausible calculation results. Some limitations or specifics are described below in brief:

The thermodynamic data is not so accurate with mixtures containing lots of alkalis, so problems may arise if there's a lot of K, Si and only small amount of Al.

Silicate has a certain impact and its behavior has to be considered from case to case e.g.:

- Organic silicate (straw) is obviously more reactive than "sand" so one should consider case by case the source of the silicate and accordingly decide whether to take it into the system and calculations or not because the silicate seems to capture all the alkalis
- Åbo told about a case (straw) where model showed that there shouldn't be KCl but in measurement it was present.

Thus, any calculation has to be checked for its plausibility.

In general the calculation takes into account fuel ultimate analysis (C, H, N, O) and ash impurities containing the following elements: Cl, S, Na, K, Ca, Mg, Zn and Pb. P and Si was added additionally during course of this project. Calculations were done under oxidizing conditions in general.

3 Results

3.1 RESULTS FROM FIELD TESTS

3.1.1 Short term test, 8h deposit probe

The aim of the test was to screen several metal temperatures in order to study the deposit at different temperatures and depending on the use of ChlorOut. However, the temperature profile was not fully successful and there was not a gradient along the whole probe but still temperatures in the wanted interval 190 – 450 °C with more samples at some temperatures, Figure 7.

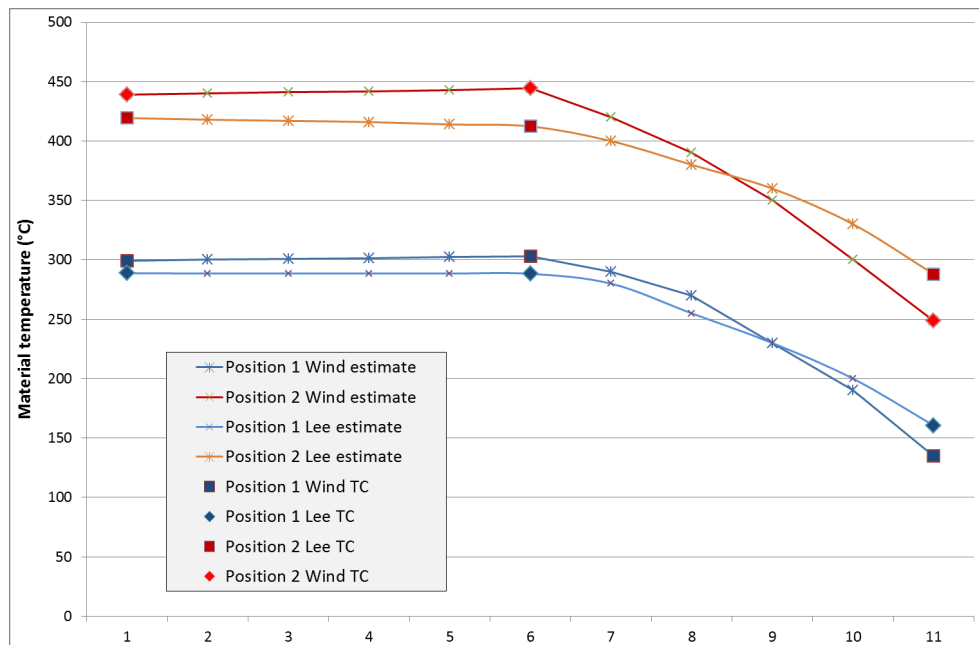


Figure 7. Temperature profile for the probe, wind and lee side.

The deposit analysis on the windward side of the samples showed an effect of the ChlorOut with less Cl and more S in the deposit when the additive was used, Figure 8. At higher temperature the effect was not as clear. No distinct difference was observed for the heavy metals depending on whether the ChlorOut system was used or not. Some of the samples flaked before analysis in SEM-EDS and in those cases the analysis is performed on flakes taken at wind position, marked with a star in the bar diagram. The analyses were made from the top (plan view), which means that by necessity the contents of elements predominantly present at the surface of the deposit will be enhanced compared to contents of those deeper into it.

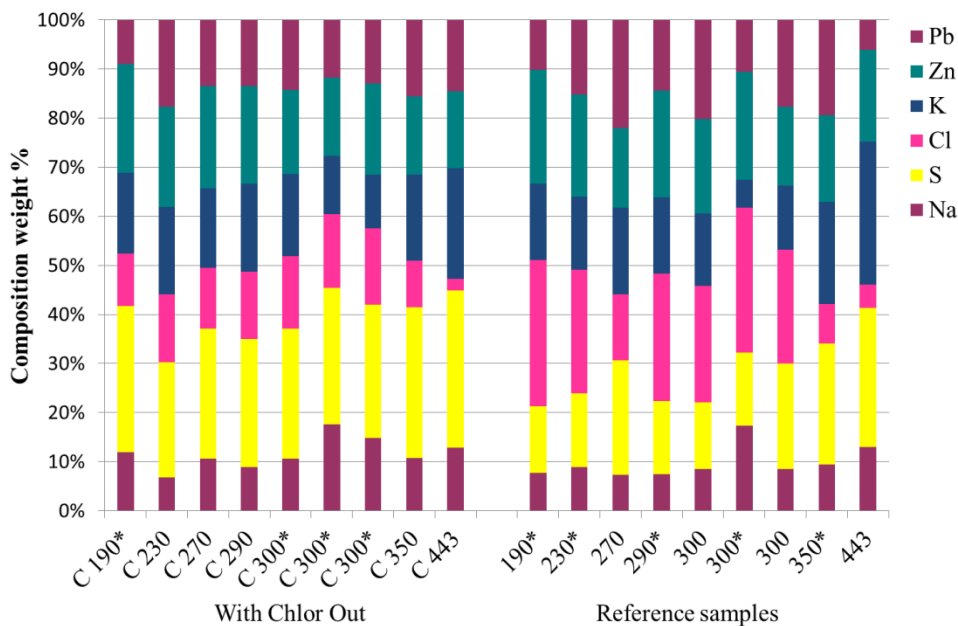


Figure 8. Deposit analysis in SEM/EDS. Normalised with presented elements.

In cross section, metal chlorides were found at the metal interface independently on whether the ChlorOut additive was used or not. It was not possible to tell if there was a negative effect or not when using ChlorOut. Pb, Zn and Cl-rich compounds were sometimes found in the corrosion products but no trend was seen. In Figure 9 the visual appearance of selected samples are presented at similar magnification.

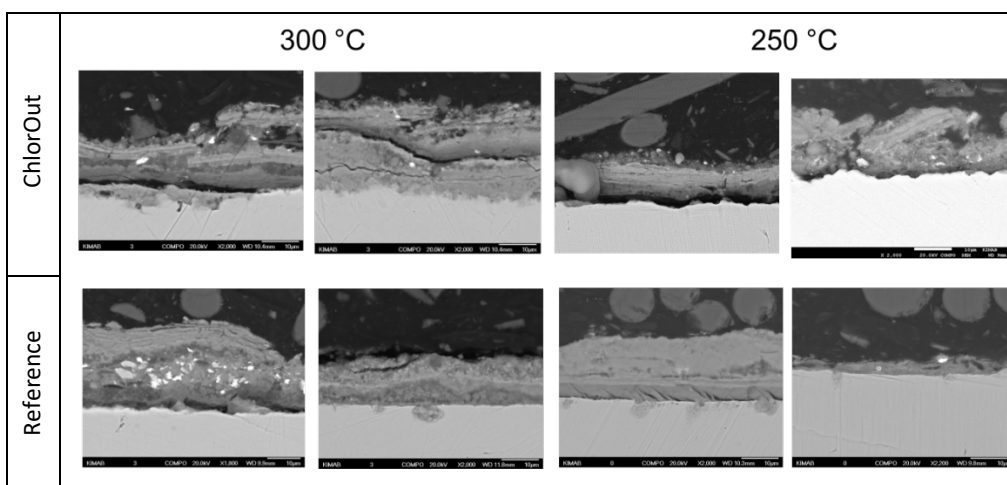


Figure 9. Selected samples in cross section.

Slightly more flaking was observed when using ChlorOut at 300 °C and this lead to the selection of the temperatures 250, 300 and 350 °C for the long term test.

3.1.2 Long term tests, 6 weeks gradient probe and 3 h deposit probes

The 3 h deposit probe test shows that deposit growth is similar for most of the samples but slightly higher for the samples with highest metal temperature. Specimen appearances and growth rate figures are given in Appendices I and II. The deposit analysis shows no difference for selected elements (normalised) depending on position (hot or cold flue gas), Figure 10.

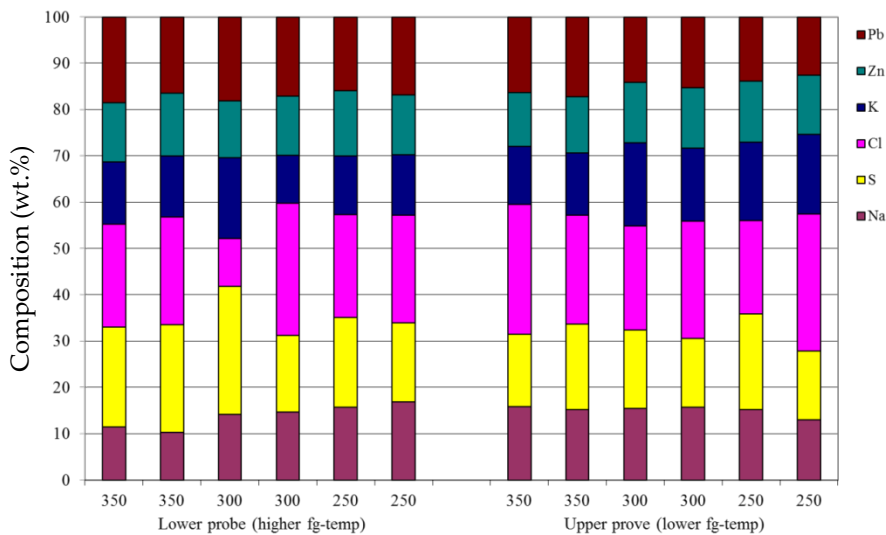


Figure 10. Normalised deposit composition, 3h test with ChlorOut made before long term test.

Similar results were observed for the upper 3 h deposit probe also after the long term test. However, the lower probe unfortunately was turned in the wrong direction and the temperature regulation was placed at lee side. This resulted in much higher temperature than intended at the wind side and thus it is difficult to compare the data before and after the long term test. For the two locations it was however possible to compare the 3h deposit probe with and without ChlorOut after exposure. The results of the upper probe are presented in Figure 11. No clear trends is observed for the presence of lead and zinc rich chlorides.

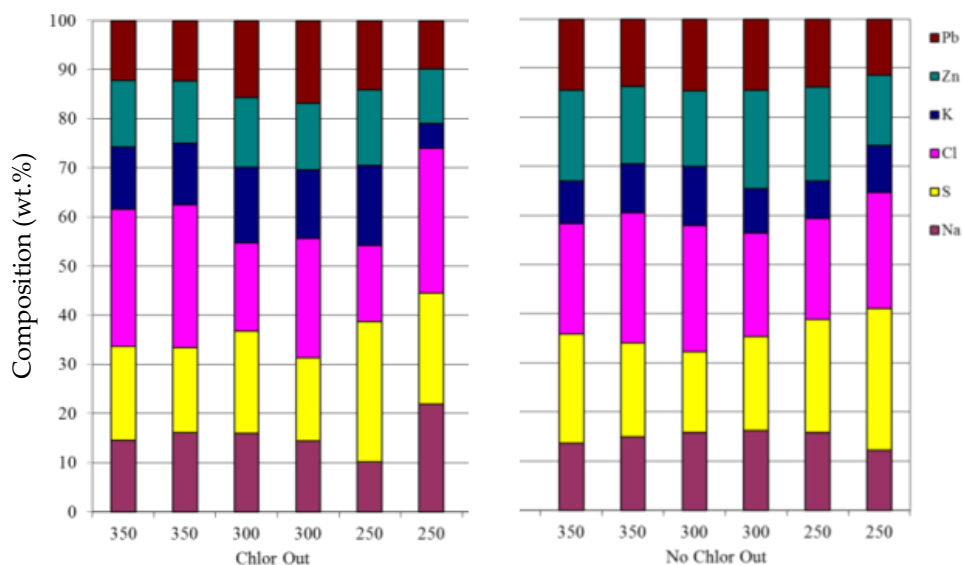
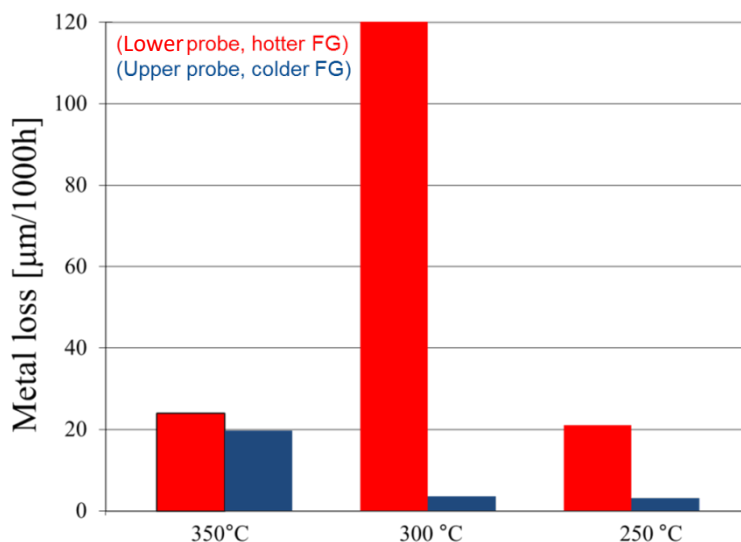


Figure 11. Comparison of deposit tests (upper probe) made after long term exposure with/without ChlorOut.

For the long term test the corrosion rate was measured by Vattenfall AB. The result is shown in Figure 12. For the colder flue gas similar corrosion rates are measured for 250 and 300 °C while the 350 °C sample show slightly higher corrosion rate. For the hotter flue gas the corrosion rates are similar for the highest and lowest temperature while a



very high corrosion rate was measured for the 300 °C sample.

Figure 12. Average metal loss after 6 weeks exposure. Note that the highest loss is a result of soot blowing.

Further evaluation of the 300 °C sample showed that the corrosion behaviour looked like erosion corrosion, probably caused by soot blowing in the boiler. The metal loss profile for the ring is shown in Figure 13. In order to ensure that this behaviour was an effect of soot blowing a third campaign with all samples on the probe at metal temperature 300 °C was run in the same position. These results showed that the same sample (middle on the probe) suffered from erosion corrosion and this result could be concluded.

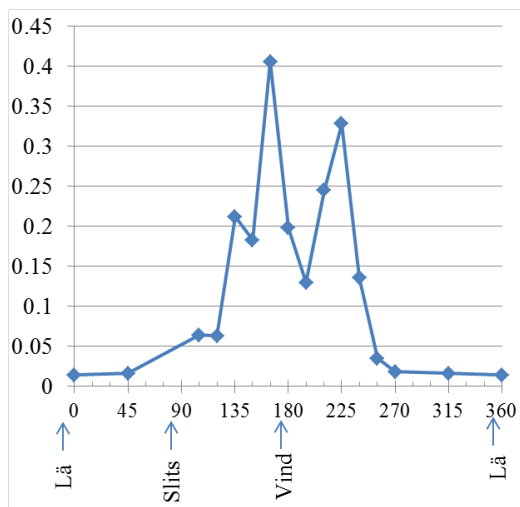


Figure 13. Metal loss profile for the 300 °C exposed in high temperature flue gas.

For the samples that had been exposed to the colder flue gas cross section analysis were performed. The measurements in cross sections confirmed the corrosion rate results with a thicker corrosion product layer for the 350 °C sample, Figure 14.

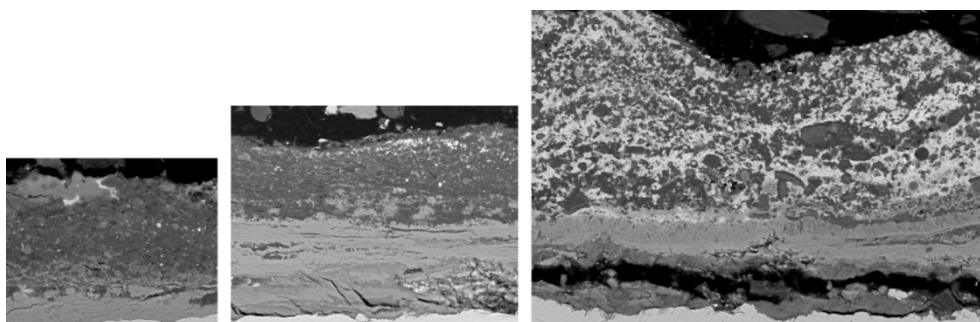


Figure 14. Cross section analysis of the cold probe samples at the same magnification. (Left 250°C, middle 300°C, right 350°C)

EDS-analysis of the corrosion products and deposits, Figure 15 - Figure 17, show that at the lower temperature zinc chloride is indicated to be present in the deposit and some iron chloride is present at the metal substrate interface. The amount of the metal chloride increased with temperature indicating increased corrosion with temperature. Interesting is that with increasing temperature the lead content increases in the deposit. At the lower temperatures the lead (and zinc when present) is present in combination with chlorine while at higher temperature sulphur seems to be in contact with the lead as well.

XRD-results of the deposits analysis also show that more lead sulphate is present at the higher temperature while more of the alkali sulphates are present at lower temperatures.

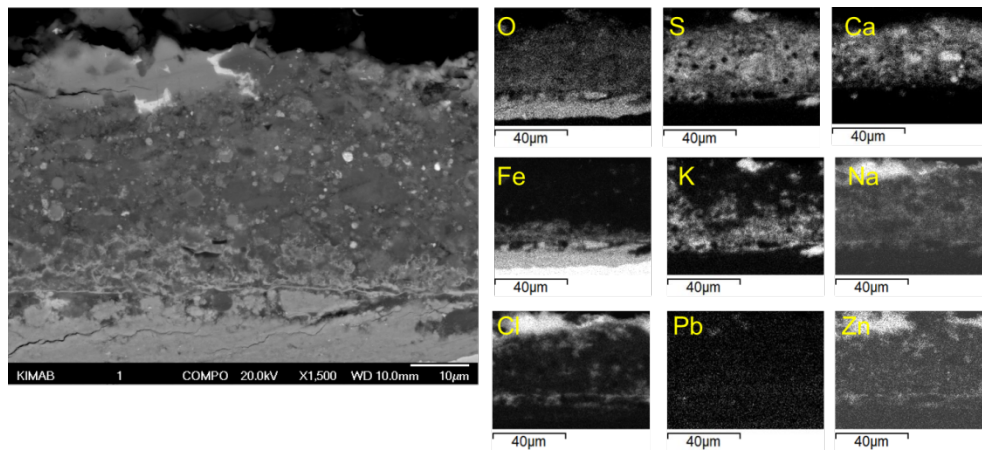


Figure 15. EDS-Mapping in cross section of 250 °C-sample.

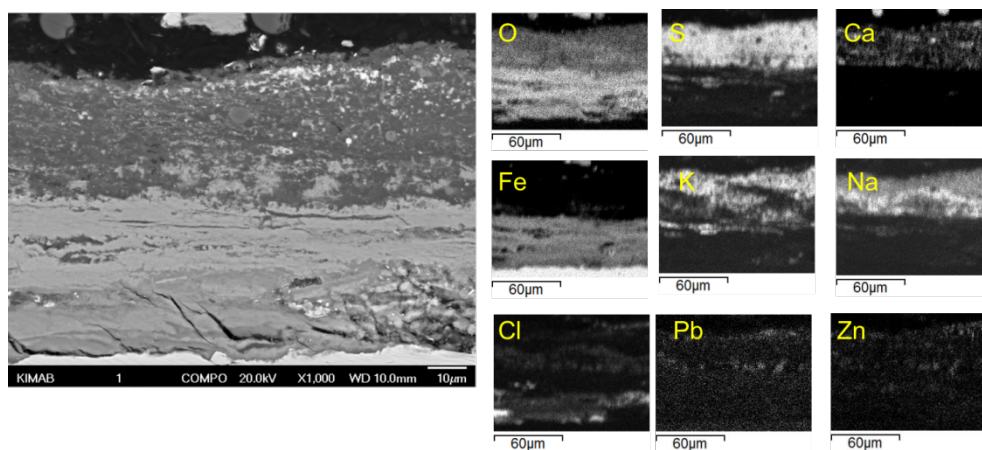


Figure 16. EDS-Mapping in cross section of 300 °C-sample.

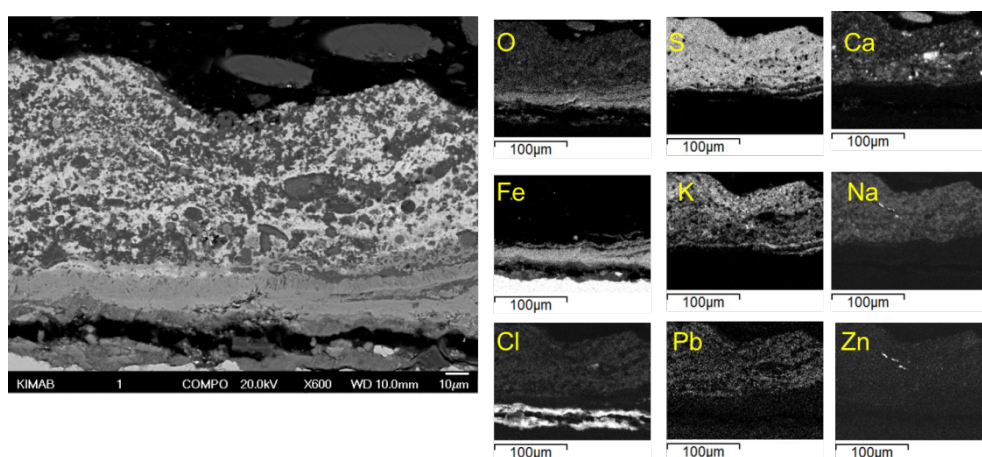


Figure 17. EDS-Mapping in cross section of 350 °C-sample.

3.2 RESULTS FROM LABORATORY TESTING

3.2.1 Isothermal tests results part

The test matrix from the isothermal tests is presented in Table 4 and a summary of all the isothermal test results is presented in Figure 18.

Table 4: The test matrix for isothermal experiments at 300 °C and 350 °C.

Temp	Salt	Gas atm	Material
300°C	PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
300°C	PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-500ppm SO ₂ -N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
300°C	KCl-PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
300°C	KCl-PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-500ppm SO ₂ -N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3

Table 4 cont.: The test matrix for isothermal experiments at 300 °C and 350 °C.

Temp	Salt	Gas atm	Material
350°C	KCl-PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
350°C	KCl-PbCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-500ppm SO ₂ -N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
350°C	KCl-PbCl ₂ - ZnCl ₂	5%O ₂ -80ppm SO ₂ -15% H ₂ O-N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3
350°C	KCl-PbCl ₂ - ZnCl ₂	5%O ₂ 15%CO ₂ -15% H ₂ O-500ppm SO ₂ -N ₂	10CrMo9-10
			16Mo3
			P235GH
			10CrMo9-10
			16Mo3

When exposed to 300 °C without SO₂, only thin oxide layers were formed on the steels (Figure 18), except for 16Mo3 (Figure 19 (a)), which developed a 20 µm thick oxide layer. When the temperature was increased to 350 °C, very heavy corrosion occurred on all three steels, with oxide layer thicknesses over 110 µm. Figure 20 (a) and Figure 21 (a) show 16Mo3 after being exposed to KCl-PbCl₂ and KCl-PbCl₂-ZnCl₂, respectively. Both 10CrMo and P235GH corroded to a significantly lower degree in the case when exposed 350°C and KCl-PbCl₂-ZnCl₂ in a gas without SO₂. This may, however, be a cause of uneven corrosion, which not reflects the corrosion behavior correctly (Figure 22 (a) and Figure 23). As can be seen from the figures there are non-corroded surfaces in both cases while the surfaces around has been clearly corroded. This naturally influences the calculated oxide layer thickness average value.

In all tests with SO₂ in the gas phase the corrosion layers were very thin, and the positive effect is obvious. Very low corrosion attacks were detected after exposure to 350 °C with KCl-PbCl₂ and KCl-PbCl₂-ZnCl₂ as shown in Figure 19 (b), Figure 20 (b), Figure 21 (b) and Figure 22 (b). In the tests with PbCl₂, there was no measureable oxide layer at 300 °C in either gas atmosphere.

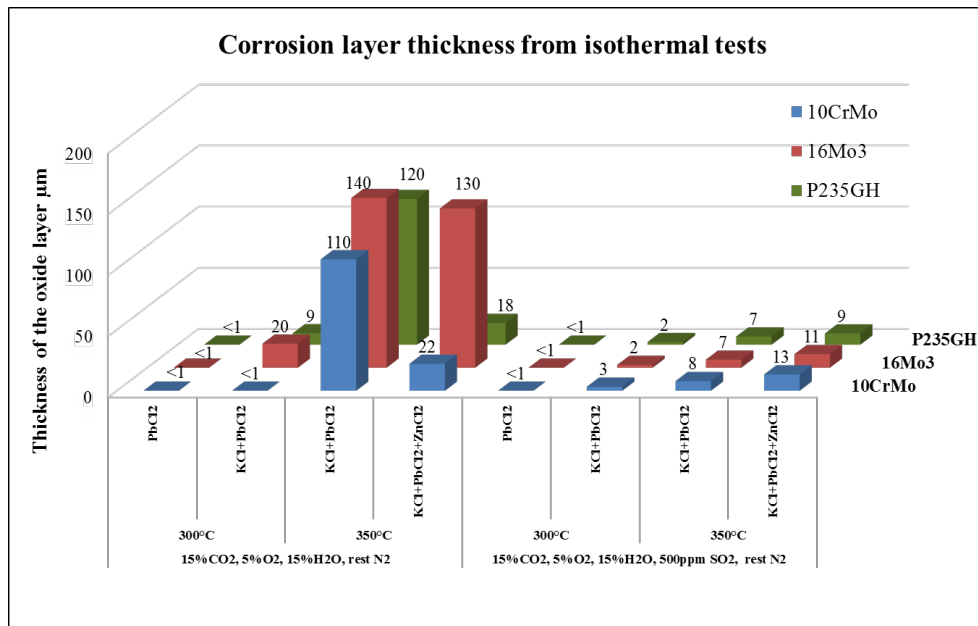


Figure 18: Results from all isothermal tests at 300 °C and 350 °C in two gas atmospheres with three salts.

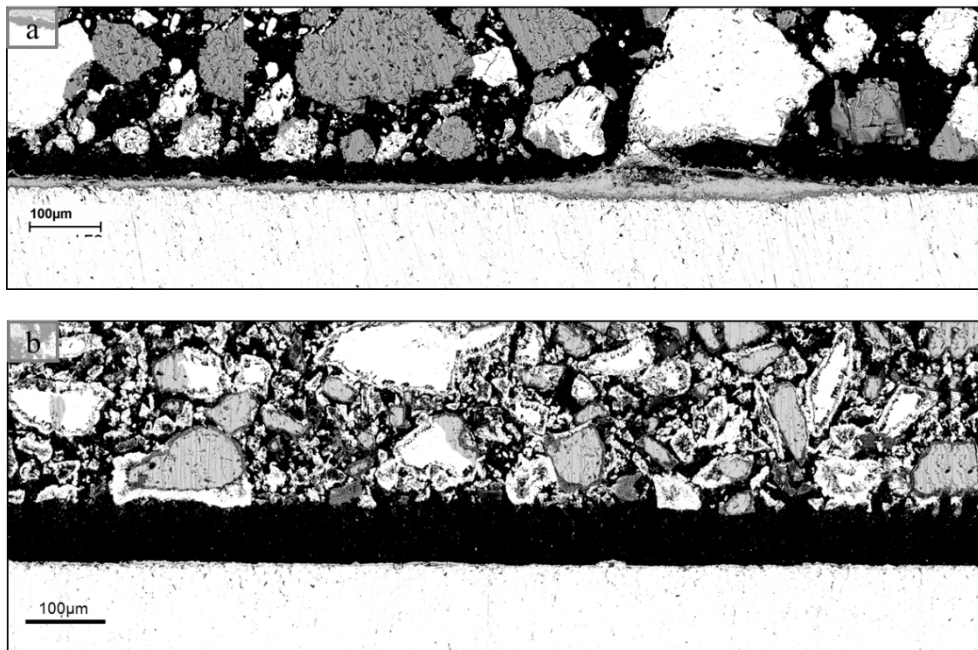


Figure 19: Panorama images of 16Mo3 after exposure to KCl-PbCl₂ a) without SO₂ and b) with SO₂ at 300 °C.

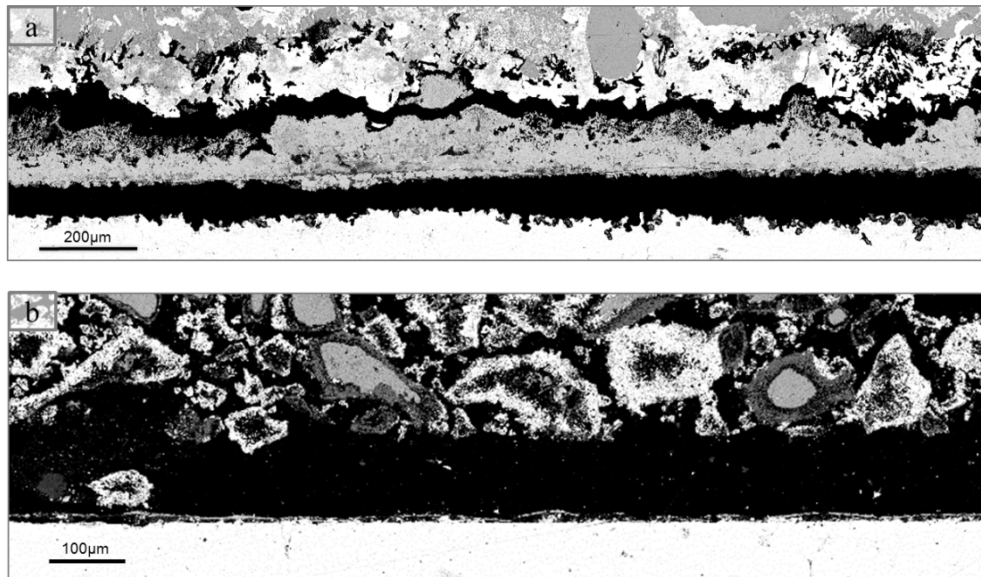


Figure 20: Panorama images of 16Mo3 after exposure to KCl-PbCl₂ a) without SO₂ and b) with SO₂ at 350 °C.

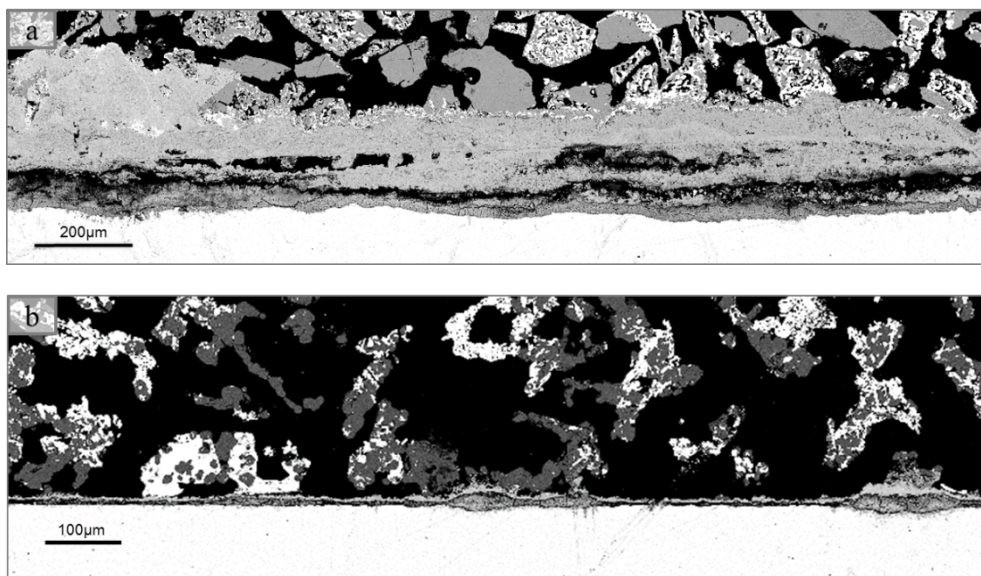


Figure 21: Panorama images of 16Mo3 after exposure to KCl-PbCl₂-ZnCl₂ a) no SO₂ and b) with SO₂ at 350 °C.

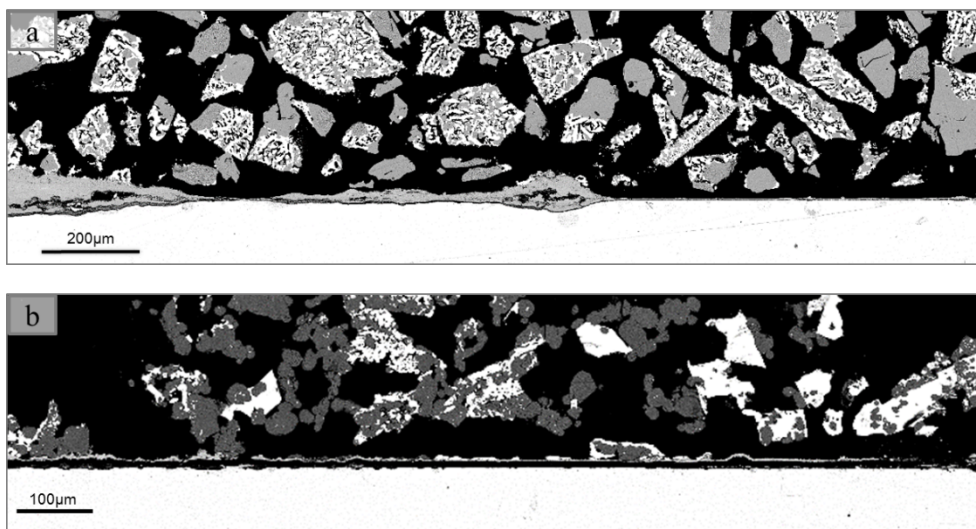


Figure 22: Panorama images of 10CrMo after exposure to KCl-PbCl₂-ZnCl₂ a) no SO₂ and b) with SO₂ at 350 °C.



Figure 23: Panorama image of P235GH after exposure to KCl-PbCl₂-ZnCl₂ without SO₂ at 350 °C.

3.2.2 Temperature gradient test results

Table 5 presents the matrix of temperature gradient corrosion tests performed.

Table 5: The test matrix for temperature gradient experiments.

Temperature	Salt	Gas atm	Material
550°C/350°C	KCl-PbCl ₂	air-15% H ₂ O	10CrMo9-10 P235GH
550°C/350°C	KCl-PbCl ₂	air-15% H ₂ O-SO ₂	10CrMo9-10 P235GH
550°C/350°C	KCl-PbCl ₂ -ZnCl ₂	air-15% H ₂ O	10CrMo9-10 P235GH
550°C/350°C	KCl-PbCl ₂ -ZnCl ₂	air-15% H ₂ O-SO ₂	10CrMo9-10 P235GH

The oxide layer thicknesses of 10CrMo and P235GH after 24 h exposures are presented in Figure 24. KCl-PbCl₂ appeared to be less corrosive than KCl-PbCl₂-ZnCl₂. 10CrMo showed very low corrosion when exposed to KCl-PbCl₂ in both atmospheres but when exposed to KCl-PbCl₂-ZnCl₂, the oxide layer thickness increased dramatically. In addition, in the case with P235GH the oxide layer increased dramatically when changing from KCl-PbCl₂ to KCl-PbCl₂-ZnCl₂ in the absence of SO₂, while in the presence of SO₂ the difference between the two salts was not that significant. The observation that with KCl-PbCl₂ and P235GH the presence of SO₂ increased the corrosion, while with the ternary salt the corrosion decreased is for now unclear.

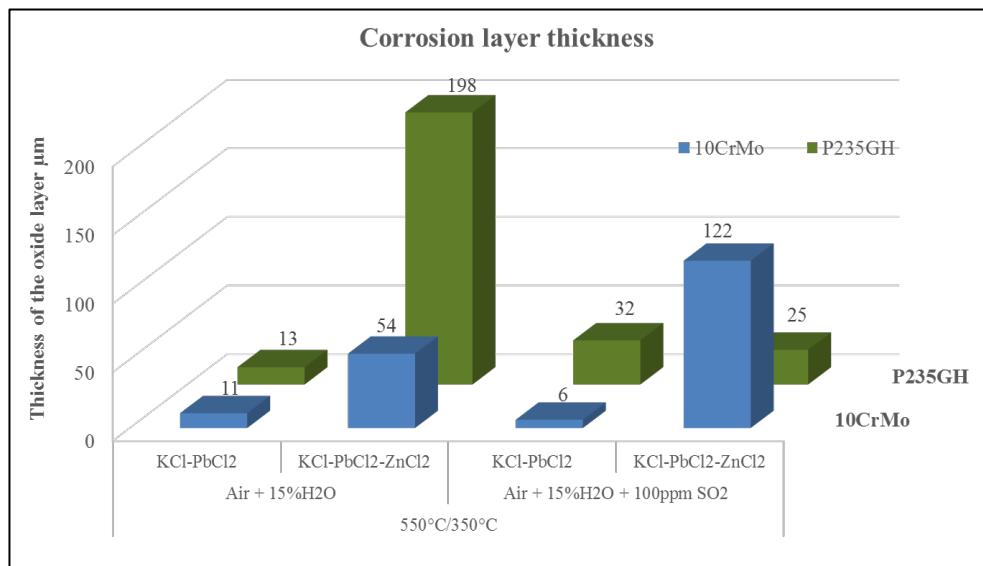


Figure 24: The mean oxide layer thickness of 10CrMo and P235GH after exposed to 550 °C/350 °C in air + water with/without SO₂.

For KCl-PbCl₂ and 10CrMo there are three distinct regions, a porous region close to the ring, an eutectic region with a white molten phase and a sintered region on the top (Figure 25 (a) and Figure 25 (b)). The oxide layer cannot be observed from these images since the magnification is too small.

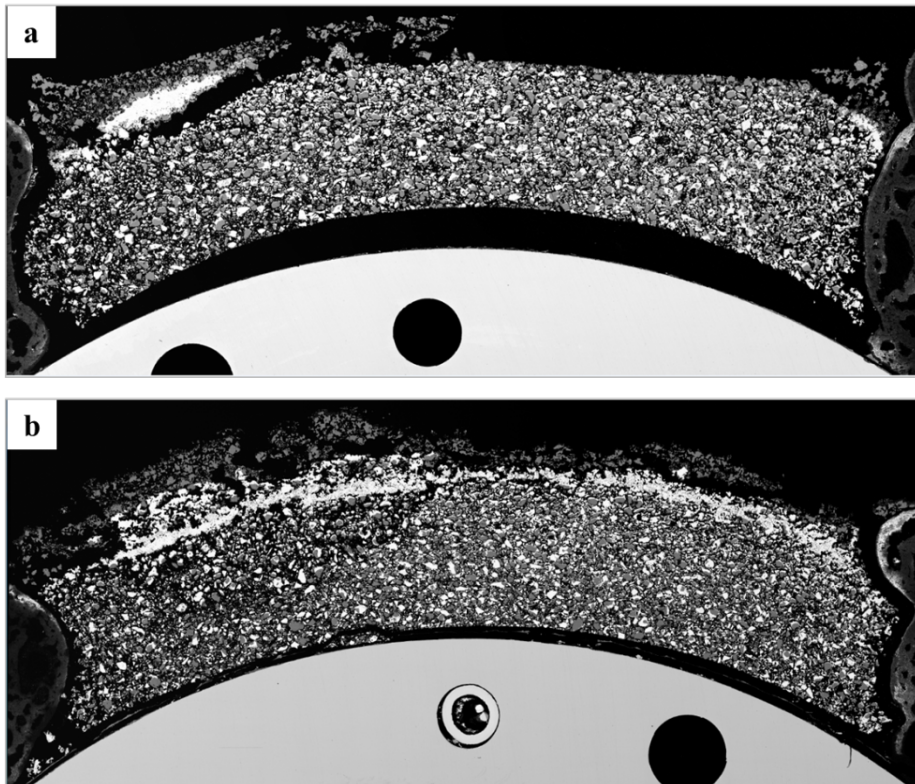


Figure 25: The panorama images of 10CrMo after exposure to KCl-PbCl₂ in air + water at 550/350 °C a) without SO₂, and b) with SO₂.

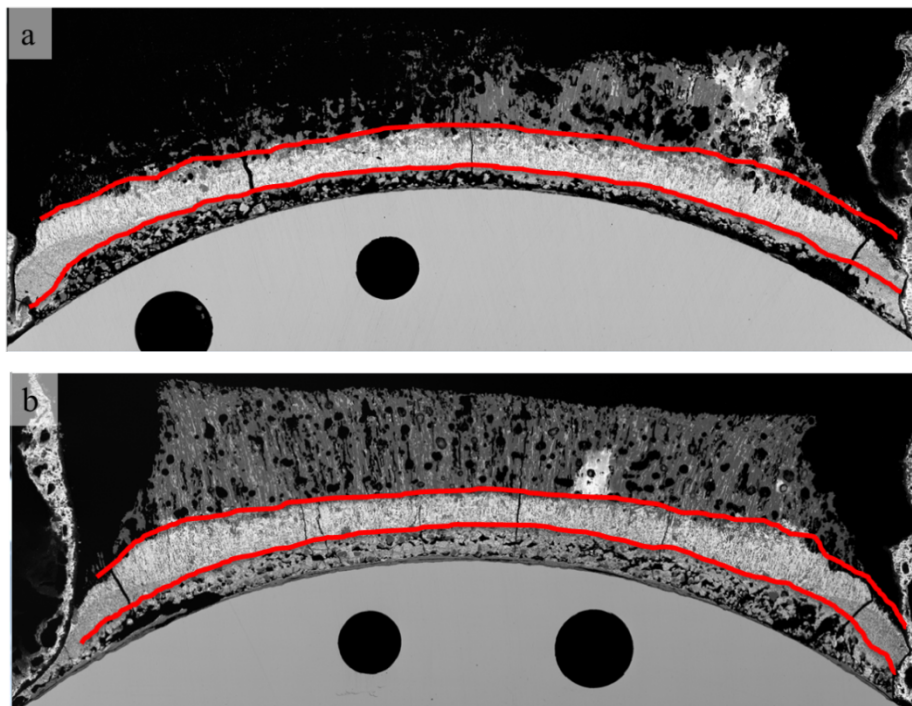


Figure 26: The panorama images of 10CrMo after exposure to KCl-PbCl₂-ZnCl₂ in air + water at 550/350 °C a) without SO₂, and b) with SO₂.

Figure 26 and Figure 27 show the panorama images of the cross sections 10CrMo and P235GH after exposure to KCl-PbCl₂-ZnCl₂. The images of the oxide layer and salt in the figures show three distinct regions. The regions are separated and illustrated with the red lines in the figures. The region closest to the ring surface seems to be “broken” and it could be that some of the oxide layers have been lost e.g. during cutting and/or polishing. This could be one reason for the somewhat unsystematic results concerning the oxide layer thicknesses presented in Figure 24.

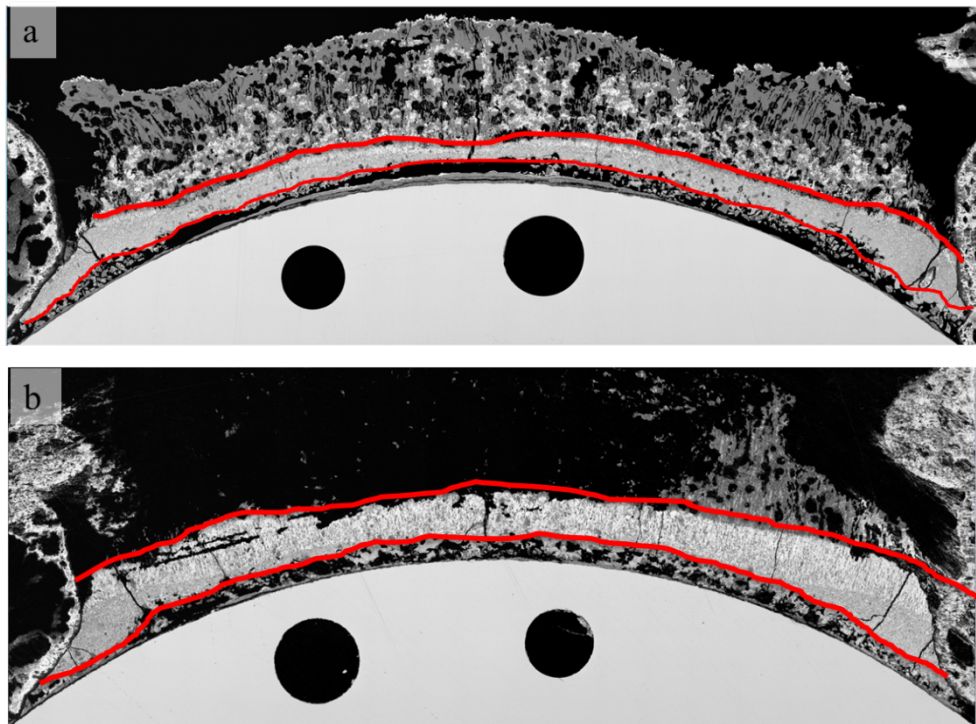


Figure 27: The panorama images of P235GH after exposure to KCl-PbCl₂-ZnCl₂ in air + water at 550/350 °C a) without SO₂, and b) with SO₂.

3.3 RESULTS FROM SIMULATION

The output of main chemical equilibrium calculation at different temperatures is shown in figures for:

- Salt melt (sulphate/chloride) fraction / Slag (silicate/oxide) melt fraction
- Salt melt composition
- Gaseous components: focus on Pb, Zn, S, Cl
- Condensed phase components: focus on Pb and Zn

The following typical analysis, Table 6, (100% waste wood) from Jordbro was used as a base input for the calculations, variations of fuel data provided by Vattenfall (Prov1-Prov3) were also used but not considered in this report.

Table 6: Typical fuel analysis from Jordbro waste fired boiler took for thermodynamic calculation.

Moisture content (105C)	% ar	22.0
Ash (550C)	% db	3.9
Net Calorific Value (NCV)	MJ/kg ar	13.8
(at constant pressure)	MJ/kg db	18.5
Carbon (C)	% db	48.6
Hydrogen (H)	% db	5.9
Nitrogen (N)	% db	1.4
Oxygen (O)	% db	39.9
Chlorine (Cl)	% db	0.09
Sulphur (S)	% db	0.07
Aluminium (Al)	mg/kg db	1,350
Silicon (Si)	mg/kg db	7,040
Titanium (Ti)	mg/kg db	1,250
Sodium (Na)	mg/kg db	1,012
Magnesium (Mg)	mg/kg db	686
Potassium (K)	mg/kg db	911
Calcium (Ca)	mg/kg db	4,771
Iron (Fe)	mg/kg db	1,083
Phosphorus (P)	mg/kg db	107
Manganese (Mn)	mg/kg db	96
Antimony (Sb)	mg/kg db	2.1
Arsenic (As)	mg/kg db	24
Barium (Ba)	mg/kg db	213
Lead (Pb)	mg/kg db	67
Bor (B)	mg/kg db	8.1
Cadmium (Cd)	mg/kg db	0.39
Cobalt (Co)	mg/kg db	1.14
Copper (Cu)	mg/kg db	44
Chrome (Cr)	mg/kg db	44
Mercury (Hg)	mg/kg db	0.04
Molybdenum (Mo)	mg/kg db	0.27
Nickel (Ni)	mg/kg db	2.3
Thallium (Tl)*	mg/kg db	0.02
Vanadium (V)	mg/kg db	2.1
Zinc (Zn)	mg/kg db	273

ChemSheet shall assist in answering the question if Pb and Zn makes the temperature region of 150-420°C more affected for corrosive attack especially in combination with S-containing additives (ChlorOut). One corrosion mechanism is based on salt melts and such salt melts can be easily calculated by thermodynamic equilibrium calculations.

A typical result of such a salt met analyses can be seen in Figure 28.

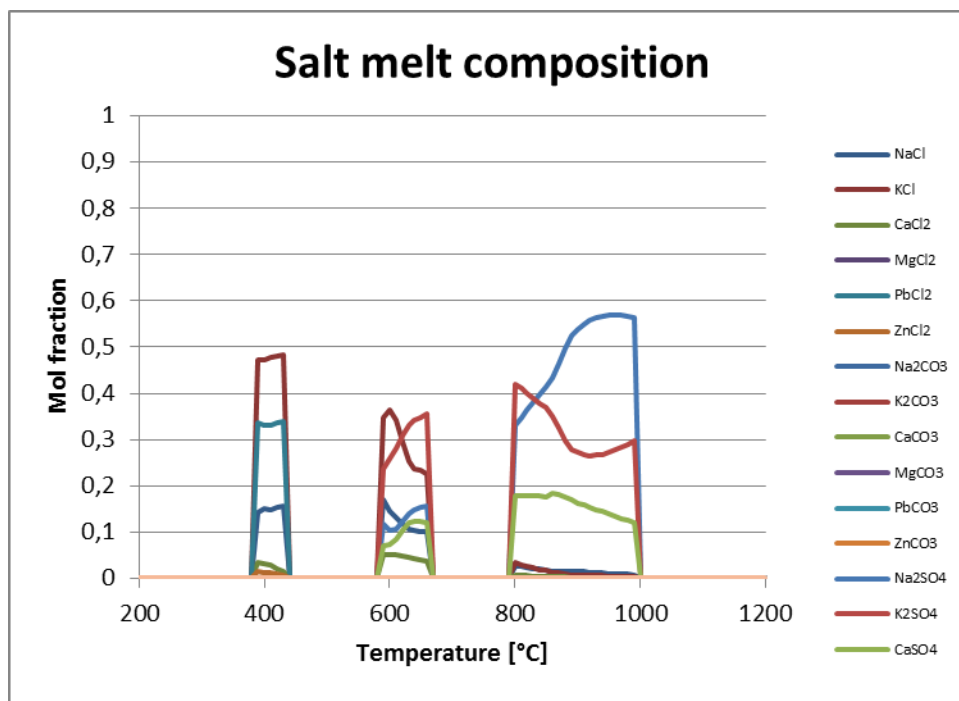


Figure 28: Typical temperature range of usual salt melt in a biomass / waste wood fired boiler

PbCl₂ and ZnCl₂ melting occurs in the region of 400°C but alkali sulphates are building the main portion in general.

With fuel data from Jordbro and also with variation of Pb, Zn and S amount (sensitivity analysis) no significant melt formation is observed below 800 °C (see Figure 29).

Salt melts at ~400 °C need higher concentrations of Pb and Zn compared to these typical data used for the calculations. Based on performed calculations it is not possible to give a temperature where ChlorOut possibly could be dangerous compared to when not using ChlorOut.

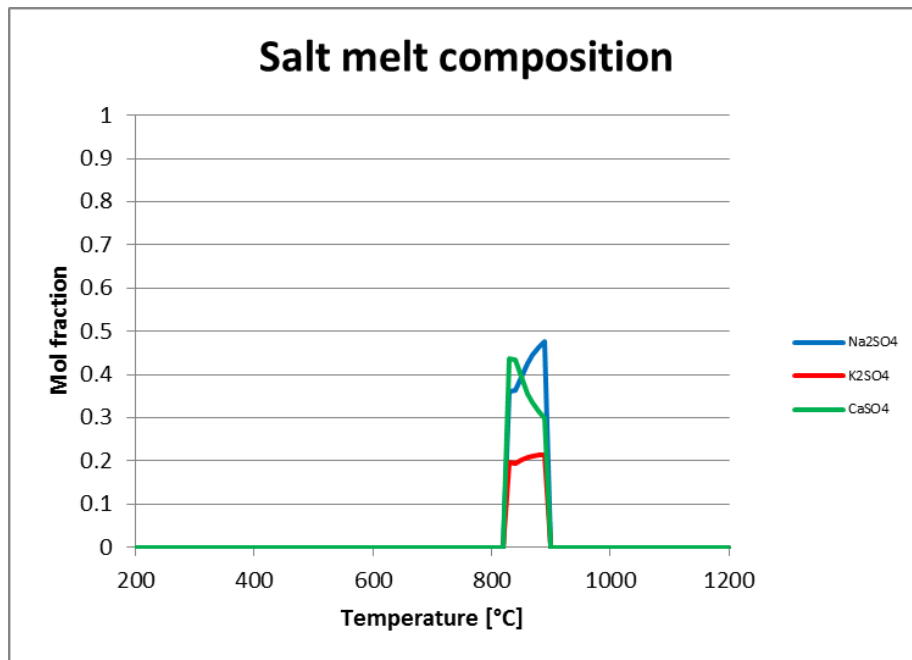


Figure 29: Typical result with Jordbro analysis regarding salt melts

Around 400°C typically alkali salts can be seen, salt liquids are generally low viscosity sulphate-chloride mixtures, see Figure 30. The other phases are mainly slag. Slag consists of silicate melts, which are generally high viscosity glass like mixtures. A distinction is made between slag1 and slag 2. There can be situation where the slag phase is separated into two - slag 2 does not form if slag 1 is not stable

The viscosity of slag determines the stickiness of the mixture but so far a method to guess/calculate the viscosity is not available. For this project the formation of slag is not of high relevance so there was no further investigation in that direction.

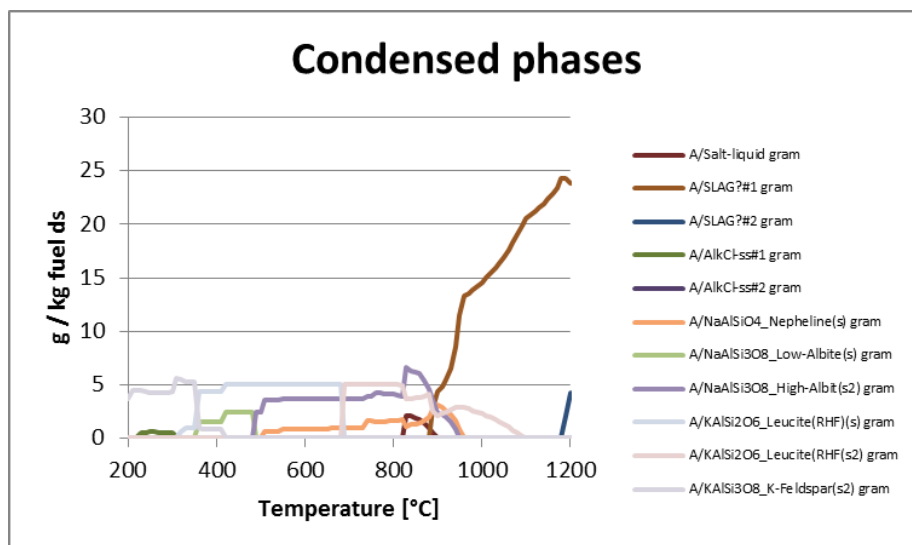


Figure 30: Typical composition of condensed phase from Jordbro fuel.

4 Analysis of the results

4.1 ANALYSIS OF FIELD TEST RESULTS

In the field tests different exposure times were used (3h, 8h and 1000 h). Most of the results from deposit measurements indicate that there is no great effect of ChlorOut usage on condensation of heavy metal salts. For the 8 h test a clear indication is that there is less alkali chlorides in the deposits in favor for sulphates which is the expected outcome when using the ChlorOut additive. However, these trends are not obvious for all campaigns, in the 3h deposit tests and the long term tests it is not as clear. This shows that there is a factor of natural variation when it comes to fuel and deposit composition for these types of field tests.

During the long term test there were some error factors during the exposure. In the end of the exposure (the last 24 h) the bed sintered in the boiler and a few hours before taking out the probes, the boiler was started again with used wood as fuel but without ChlorOut additive. This could have affected the deposit analysis but is not believed to have had any effect on the corrosion behavior since the total exposure time was approximately 1000 h. Also the deposit probes after exposure were slightly affected by this since the load of the boiler was not the same during the whole deposit exposure, (the load gradually increased from the first tests (without ChlorOut) to the last (with ChlorOut)). This could have had a minor effect on the deposit composition.

Despite the error factors during the long term tests all results from the field tests tell a similar story; there does not seem to be an increased risk for corrosion due to condensation of heavy metal salts when using ChlorOut. Lead and zinc are present in the deposit at all tested temperatures and in cross section analysis from long term tests more chlorides compared to sulphates (with these elements involved) are present but still no increase in corrosion is observed. A strong increase in corrosion is observed when the metal temperature is increased from 300 °C to 350 °C for the colder flue gas. In this case the heavy metals are present also in the form of sulphates at the higher temperature. Thus, a sulphation of the heavy metals could be indicated and the increased corrosion is believed to mainly be a result of the increased temperature and not condensation of heavy metal salts.

It was in general difficult to evaluate the difference in corrosion behaviour between colder and hotter flue gas. An indication is that hotter flue gas in general causes more corrosion but due to erosion corrosion effect of the middle sample on the probe this cannot be told for all temperatures. The largest effect is observed at the lowest tested temperature (250 °C) and may be expected also at 300 °C if not the erosion corrosion was present. At 350 °C there is no significant difference depending on flue gas temperature so the largest effect is observed at the lower temperature. It can be noted that this equals to the largest temperature difference to the flue gas.

4.2 ANALYSIS OF LABORATORY TEST RESULTS

4.2.1 Analysis of the result from the isothermal tests

The compositions of the oxide layers formed were analyzed by X-ray mapping and the results are shown in Figure 31-Figure 34. These images show that the corrosivities of the salt mixtures were quite the same for the three steels when exposed to similar gas

atmospheres. In the tests with KCl-PbCl₂ without SO₂, the oxide scale build-up on the steels consisted of two layers on top of each other. The upper layer composed entirely of Fe and O, while an iron chloride layer with some iron oxide Fe_xO_y was clearly observed close to the steel surface at 300 °C (Figure 31). When the temperature was increased to 350°C, the salt and the corrosion product mixture may have been partly molten and thus causing significant damage. In addition, some K and Cl were observed in the Fe depleted zone (Figure 32). As with KCl-PbCl₂ also with KCl-PbCl₂-ZnCl₂ and without SO₂, a high Cl concentration was detected in the inner oxidation layer as shown in Figure 33 and Figure 34 and the dual corrosion layers (FeCl₂ and Fe_xO_y) were detected. The presence of FeCl₂ may decrease the first melting point of the salt and corrosion product mixture and thus enhance the corrosion.

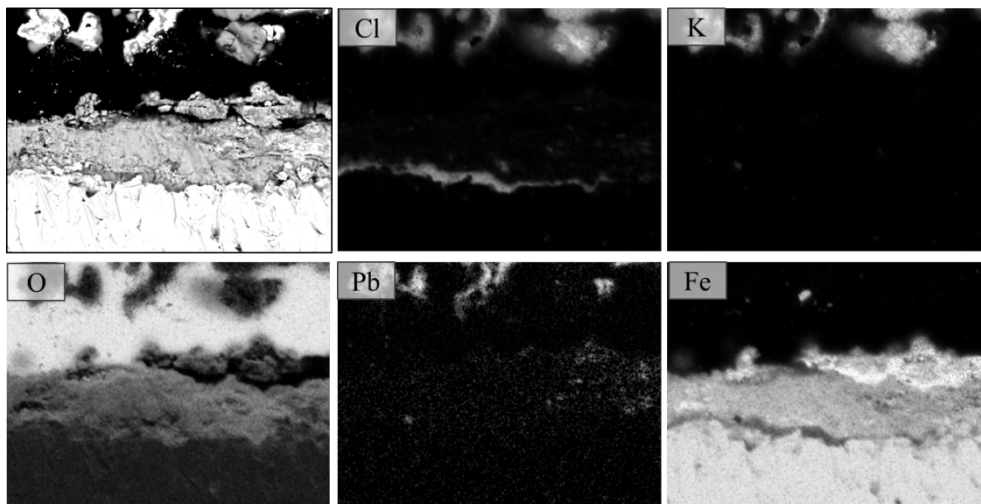


Figure 31: X-ray maps of 16Mo3 after exposure to simulated gas without SO₂ with KCl-PbCl₂ at 300 °C.

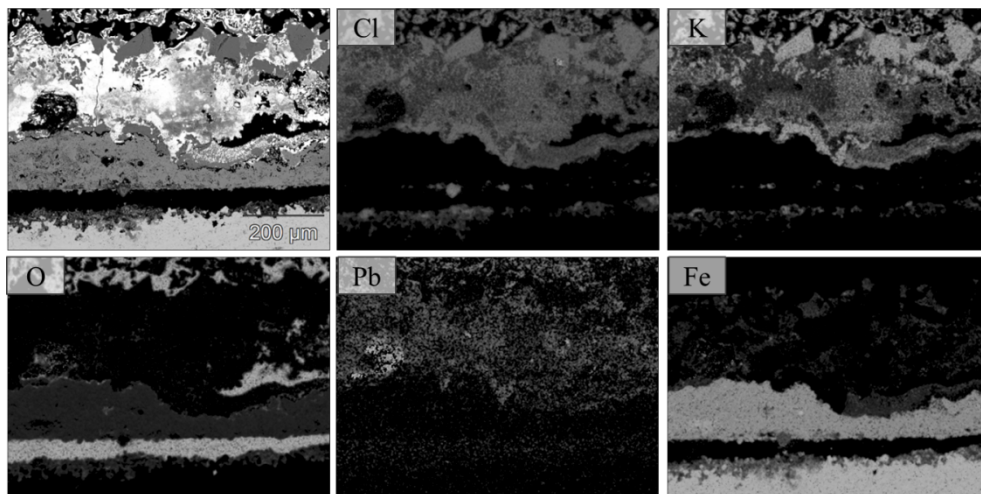


Figure 32: X-ray maps of 16Mo3 after exposure to simulated gas without SO₂ with KCl-PbCl₂ at 350 °C.

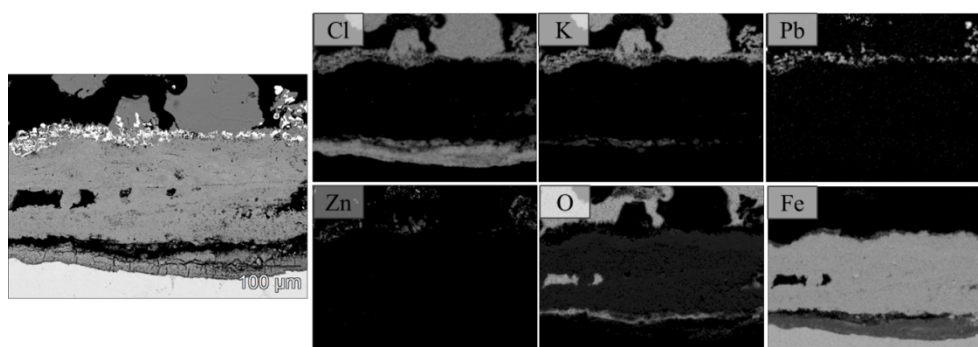


Figure 33: X-ray maps of 16Mo3 after exposure to simulated gas without SO₂ with KCl-PbCl₂-ZnCl₂ at 350 °C.

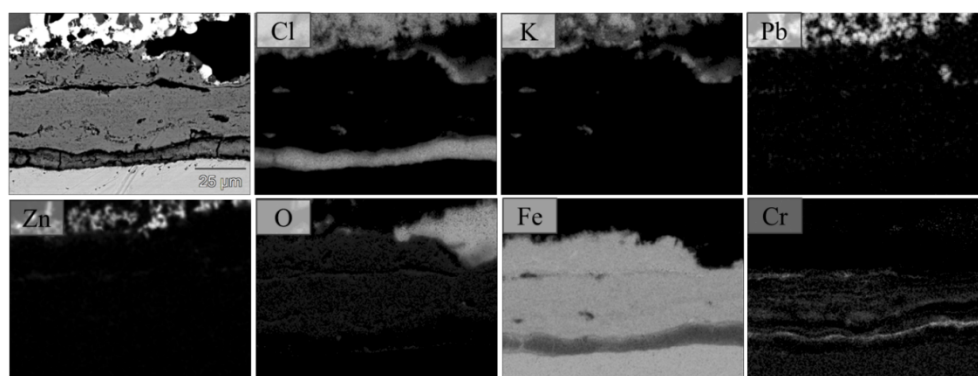


Figure 34: X-ray maps of 10CrMo after exposure to simulated gas without SO₂ with KCl-PbCl₂-ZnCl₂ at 350 °C.

In the tests containing SO₂, the presence of iron chloride close to the steel surface was observed. Nevertheless, the corrosion layers were considerably thinner than in the cases without SO₂. This can probably be explained with the sulphation of the metal chlorides, which is clearly observed from the X-ray maps (Figure 35-Figure 37). From the figures, it is clear that both K and Pb are present as sulphates and not chlorides, while the remaining chlorine is present as FeCl₂. Zinc only gives a weak signal, and possibly a part of it has evaporated and a part of it may have reacted to ZnO and/or ZnSO₄. The presence of ZnSO₄ is, however, not as obvious as the presence of K₂SO₄ and PbSO₄ from the X-ray maps.

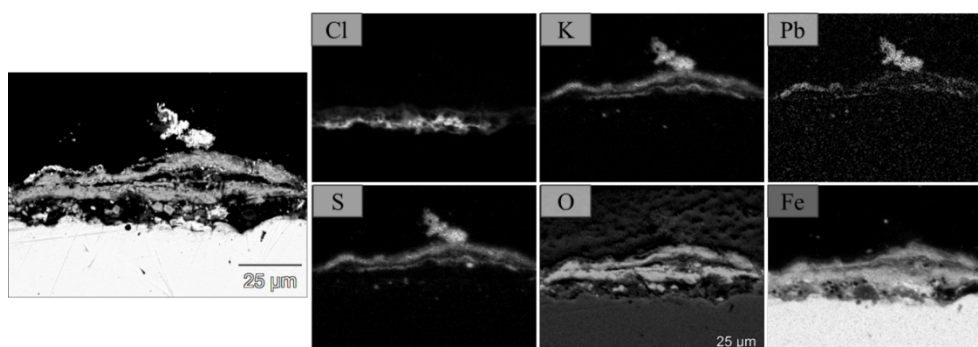


Figure 35: X-ray maps of 16Mo3 after exposure to simulated gas with SO₂ with KCl-PbCl₂ at 350 °C.

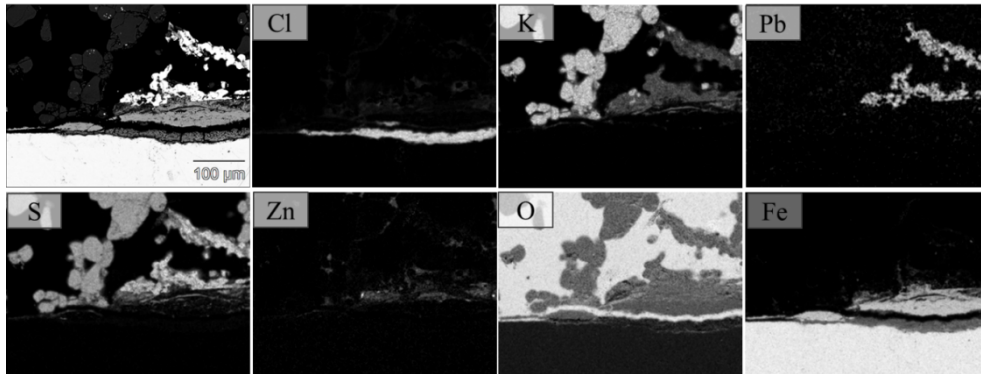


Figure 36: X-ray maps of 16Mo3 after exposure to simulated gas with SO₂ with KCl-PbCl₂-ZnCl₂ at 350 °C.

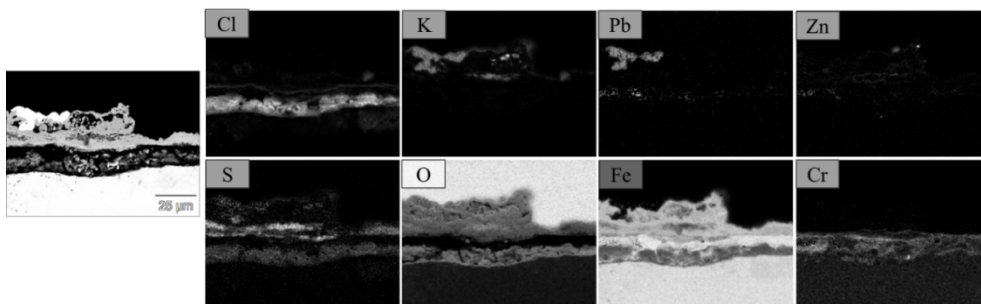


Figure 37: X-ray maps of 10CrMo after exposure to simulated gas with SO₂ with KCl-PbCl₂-ZnCl₂ at 350 °C.

4.2.2 Analysis of the result from the temperature gradient tests

The corrosion products on the 10CrMo after the gradient tests with KCl-PbCl₂-ZnCl₂ and without SO₂ composed mostly the oxides of iron and chromium with traces of metal chlorides and some K, based on the elemental distribution in the X-ray maps in Figure 38. After exposure to air with water and SO₂, a dense and compact layer enriched on K and Cl was formed close to the interface of the steel in Figure 39. The formation of this KCl-layer is, however, most likely not caused by the SO₂ since in the test in air with water on P235GH a similar layer was detected.

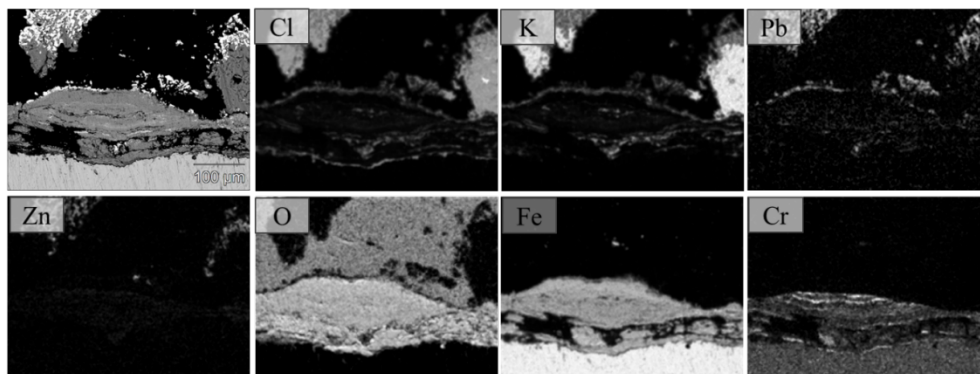


Figure 38: X-ray maps of 10CrMo after exposure to air + water with KCl-PbCl₂-ZnCl₂ at 350 °C.

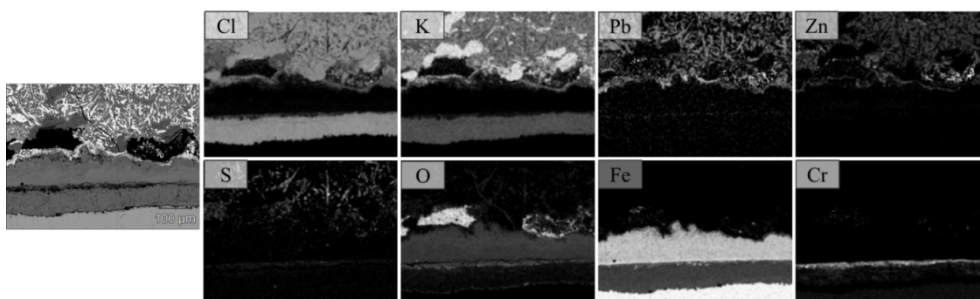


Figure 39: X-ray maps of salts on the top of 10CrMo after exposure to air + water + SO₂ with KCl-PbCl₂-ZnCl₂ at 350 °C.

As mentioned in the previous chapter, three distinct regions were observed in the tests due to the temperature gradient from the top of the salts (~550 °C) to the steel surface (~350 °C). The porous region close to the surface of steel seems to remain the original salt compositions without melting or sintering. The temperature in this region is below the first melting temperature (T_0) of the salts. Farther away from the steel surface, there is an eutectic region and a sintering region on the top. Figure 40 presents a detailed view of the eutectic region and its chemical composition at different points. In the lower part (spots 1, 3) and in the upper part (spot 14) of the eutectic region, pure KCl was detected. The eutectic region formed in the test in air with water consisted probably of K₂PbCl₄ in the grey area (spots 4, 8, 10), PbCl₂ in the white area (spots 2, 6, 9, 11, 13, 15) and KCl (spots 5, 7) in Figure 40 (a). When the salt mixture was exposed to air with water and SO₂, the upper part of eutectic region was partly sulphated based on the EDX analysis of area 6 in Figure 40 (b).

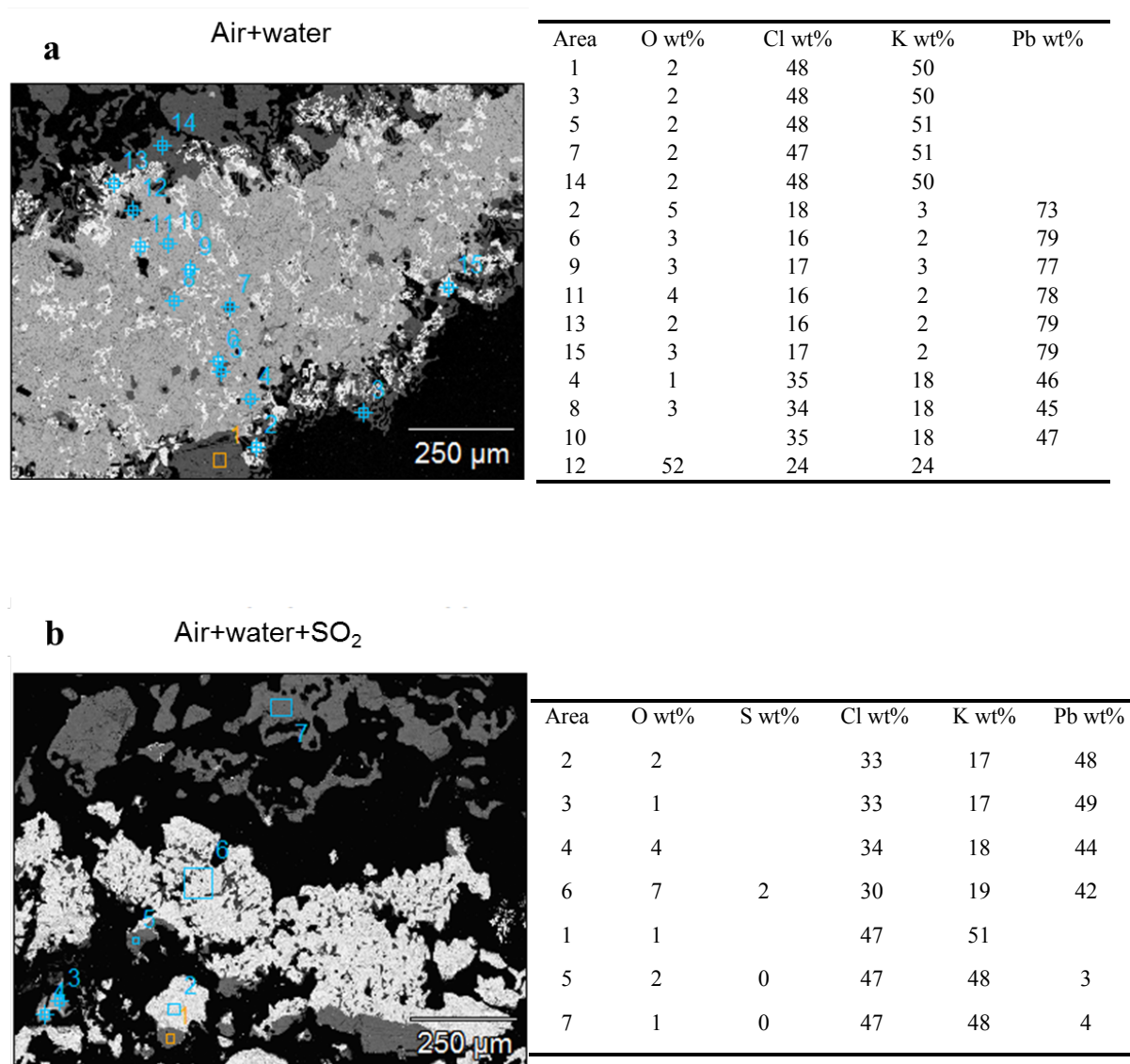


Figure 40: SEM images of the eutectic region of the salt on the top of 10CrMo after exposure to KCl-PbCl₂ in a) air + water and b) air + water + SO₂.

The X-ray maps in Figure 41 present the elemental distribution of the KCl-PbCl₂-ZnCl₂ salt mixture after being exposed to air with water and SO₂. Three separate regions are clearly observed and are here named the sintered region, the eutectic region and the porous region. The sintered regions were mostly depleted with PbCl₂ and ZnCl₂, leaving KCl in a molten phase. The ZnCl₂ may have evaporated towards the hot gas or been transported towards the cooler steel surface. The eutectic regions were enriched with Pb and Cl with traces of K. Some particle agglomeration was also observed in the porous region, most probably caused by metal-chloride vapour condensation [7, 8]. The structures of a sintered region and a eutectic region are shown in Figure 42 together with the EDX analysis of some points. K₂PbCl₄ and K₂ZnCl₄ are suggested to be present based on the atomic ratio of Cl-K-Pb/Zn in the white areas (spots 2, 4, 7, and 9 in Figure 25 (b)) and of KCl in the dark grey areas (spots 1, 3, 5, 6, and 8 in Figure 42 (b)). The sintered region shown in Figure 42 (a) consisted mainly of

KCl. When exposed to air with water and SO_2 , small amounts of sulphur was detected together with small amounts of Cl, K, Pb and Zn. Accordingly, some sulphation has occurred, although its extent seems to be limited. It is known that at least KCl reacts significantly faster with SO_3 than with SO_2 , and since the catalytic formation of SO_3 is more efficient on a metal surface it is more plausible that sulphates are formed closer to the steel surface. This may also partly be a reason to the low sulphation in the gradient tests, since the dense salt layer hinders the penetration of gaseous sulphur to the surface.

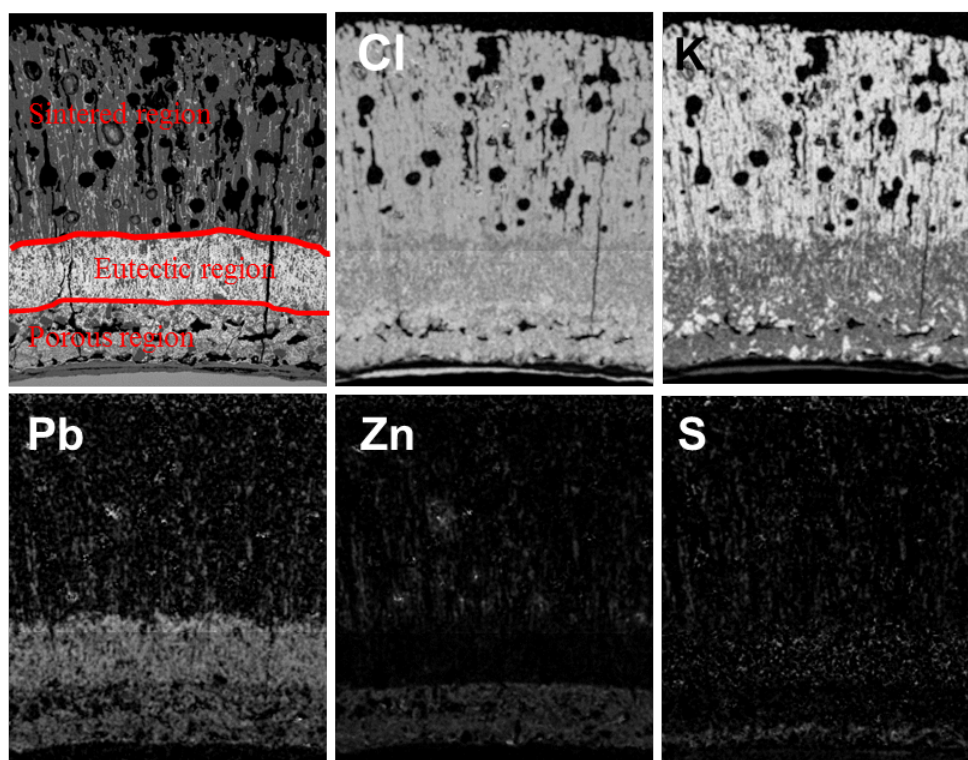
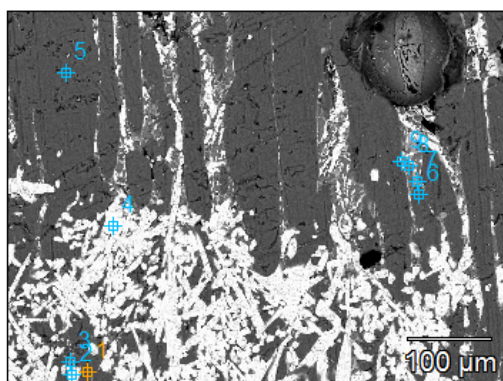
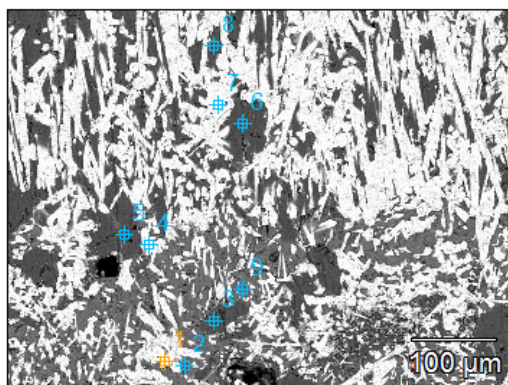


Figure 41: The X-ray maps of salts on the top of 10CrMo after exposure to air + water + SO_2 with KCl-PbCl₂-ZnCl₂ at 350 °C.



at%	O	S	Cl	K	Zn	Pb
1			50.5	49.5		
2			57.9	28.6		13.5
3	19.3	2.0	43.0	25.9	7.2	2.7
4			59.0	27.9		13.1
5			50.0	50.1		
6			50.8	49.2		
7	27.2	5.9	34.9	21.4	5.4	5.2
8		0.0	56.7	28.2	15.2	0.0
9	1.4		56.7	28.2	0.7	13.0



at%	O	Cl	K	Zn	Pb
1		58.4	28.7		12.9
2	1.4	56.2	28.4	14.0	
3	2.3	49.7	48.0		
4		59.9	27.1		13.1
5		50.6	49.4		
6	1.7	49.3	49.0		
7	0.4	57.4	29.5	0.3	12.3
8		50.0	50.0		
9		56.2	30.6	13.3	

Figure 42: SEM images of a) the sintered regions and b) the eutectic region of the salts on the top of 10CrMo after exposure to KCl-PbCl₂-ZnCl₂ in air + water + SO₂.

4.3 ANALYSIS OF SIMULATION RESULTS

Main focus was initially laid on salt melt formation, condensed phase composition and gas phase composition with typical fuel analysis from Jordbro as input data. During course of project more effort was done on critical analysis of influencing factors such as S content and possible formation hindrances of PbCl_2 and ZnCl_2 because of alkali/Pb/Zn ratios.

To gain a deeper understanding of the impact of S respectively the effect of ammonium sulphate (AS) addition – ChlorOut - should be considered in the simulation. Therefore, data from Jordbro where AS is added to overcome high temperature corrosion in superheater section was taken and an analysis was done in regard how S/Cl ratio can be influenced by dosing of AS, Table 7.

Table 7: Range of AS dosed and change of S/Cl ratio

Flow AS	Added S	Added S	Total S	S/Cl
l/h	kg/h	kmol/h	kmol/h	
200	23.8	0.74	1.10	2.65
100	11.9	0.37	0.73	1.76
50	5.95	0.19	0.54	1.31
40	4.76	0.15	0.51	1.22
20	2.38	0.07	0.43	1.04
0	0	0.00	0.36	0.86

Thus, 200 l/h respectively the S/Cl ratio of 2.65 should be sufficient for corrosion abatement. Analysis with different AS amount did not result in any significant change in gas phase composition what can be seen in Figure 43.

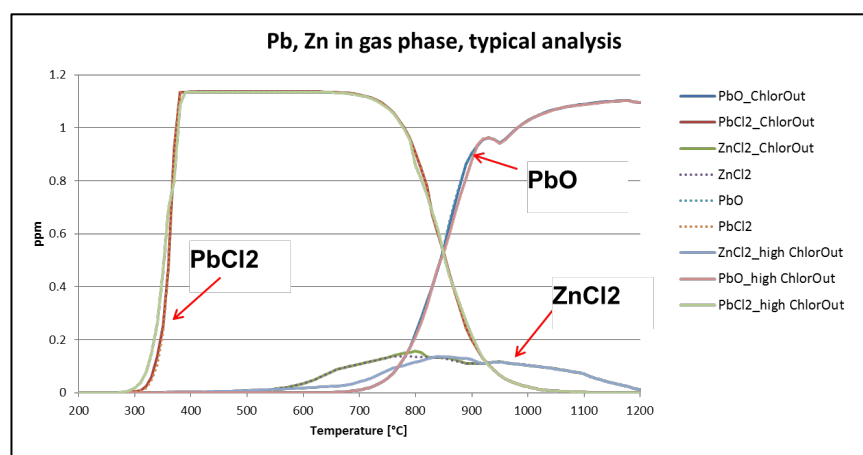


Figure 43: Gas phase analysis with ChlorOut sensitivity analysis with ammonium sulphate addition

For further sensitivity analysis to analyze critical factors, focus was not made on small fuel variations from the original Jordbro fuel, as there was no significant change expected. Thus, the fuel was changed for the calculations for S, Zn and Pb to higher and very high levels to see if there is a relevant change in melt behavior and/or in gas phase composition, Table 8.

Table 8: Input data changes on base fuel composition for sensitivity analysis of S, Zn and Pb

	S		Zn		Pb	
	g/kg	ratio	g/kg	ratio	g/kg	ratio
Fuel base	0.1		0.273		0.067	
high	2	20	0.5	2	0.4	6
high-high	4	40	2	7	1	15

Typical fuel in Jordbro results in formation of PbCl_2 and ZnCl_2 at lower temperature and PbO at higher temperature, Figure 44.

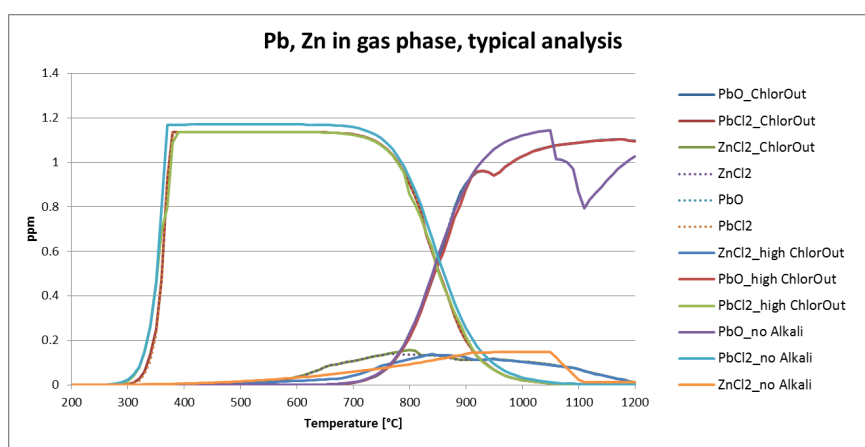


Figure 44: Gas phase analysis with the focus on alkali content

There is the possibility that Cl content in Jordbro fuel is too low in general that there cannot be any ZnCl_2 or PbCl_2 formed as alkalis are consuming all chlorine. Calculation without alkalis showed that there is enough Cl to form ZnCl_2 and PbCl_2 for all cases.

5 Conclusions

5.1 CONCLUSIONS FROM FIELD TEST RESULTS

Corrosion tests were performed in the super heater area with deposit and corrosion probes with the aim to evaluate the possibly increased risk for corrosion due to increased condensation of heavy metal salts when using ChlorOut. The field test campaigns showed that

- The amount of Pb, Zn and Cl in the deposits from short exposures (3 h and 8 h) does not show that more of these elements is deposited at the surfaces at lower temperatures (in the interval tested in this project) when ChlorOut is used.
- No increase in initial corrosion (3 h and 8 h) is observed in cross section analysis when ChlorOut is used.
- Increased corrosion is observed with increased temperature at the lower flue gas temperature (420 °C), but not for the higher flue gas temperature (550 °C).
- At lower temperatures (250 °C and 300 °C) more corrosion is observed when the flue gas is hotter (lower probes) and the temperature difference between metal and flue gas is larger.
- Pb-containing compounds in the deposit are increasing in amount with increasing metal temperature. At 250 °C and 300 °C in combination with chlorine and at 350 °C in combination with sulphur.

5.2 CONCLUSIONS FROM LABORATORY TEST RESULTS

The performed tests including isothermal tests and the temperature gradient tests were arranged to evaluate the corrosiveness of KCl, PbCl₂ and ZnCl₂ containing deposits at lower temperatures and to better understand the role of SO₂. The gradient tests additionally gave some insight in the effect of a temperature gradient on the salt deposit layers.

The results from isothermal tests showed that the presence of SO₂ (500 ppm) diminished the corrosion via sulphation of Cl-containing salt mixtures. Even though the addition of ZnCl₂ decreased the first melting temperature of the salt mixture, no melting was observed and the degradation of the steels was not accelerated. The initial reaction between the Cl-containing salts with the tested steels formed FeCl₂, which resulted in the presence of a molten phase of the salts KCl-PbCl₂.

The results from the gradient tests showed that ZnCl₂ had a remarkably negative impact on the corrosion behaviour of the steels, which was largely contradictory to the isothermal results. The addition of SO₂ (100 ppm) was controversial and its effect remained unclear in the temperature gradient tests. The gradient test is dynamic and complicated; hence, more tests and repetitions should be done in order to obtain accurate results.

Generally, despite the unclear results from the gradient tests concerning the influence of SO_2 , the results from the isothermal tests were consistent and clear and based on these it is concluded that SO_2 hinders corrosion under the tested conditions. It is also concluded that at 300 °C, the corrosion risk is very low, while at 350 °C, the risk may be substantial, and that no obvious difference concerning the corrosion susceptibility of the tested materials was observed.

5.3 CONCLUSIONS FROM SIMULATION RESULTS

Thermodynamic calculations in low temperature range, especially in the range between 180-400°C where this project is focusing on are limited in general. Results of calculation are available but there are hardly any significant differences to see between the different fuel data available from Jordbro and even if input data for fuel was changed massively to have some kind of sensitivity analysis for S, Zn and Pb.

From these analyses no significant salt melt formation is observed below 800 °C. Salt melts at ~400 °C need higher concentrations of Pb and Zn compared to these typical data used for the calculations. Sensitivity analysis of S, Zn and Pb showed no indication of salt melt formation in the respective temperature region even at relatively high concentration of Pb and Zn in a hypothetical fuel which cannot be found in real fuel mixtures.

The effect of alkali content in fuel in regard to the formation of ZnCl_2 and PbCl_2 was investigated and it was shown that there is enough Cl in fuel to allow formation of ZnCl_2 and PbCl_2 .

Sensitivity analysis of S content showed that even at high S amounts no significant change in gas composition in regard to NaCl or KCl could be found.

Based on performed calculations it is not possible to give a temperature where ChlorOut possibly could be harmful in terms of corrosion compared to when not using ChlorOut.

5.4 GENERAL PROJECT CONCLUSIONS

Results in this project show the presence of lead and zinc in deposits and corrosion products. Their presence does however not seem to increase when sulphur containing additive, in this case ChlorOut, is used. The corrosion does not increase significantly by use of the additive. (Note that long time tests only have been performed with and not without ChlorOut).

The overall results give an indication that sulphation of Cl-containing salts decreases corrosion.

Based on the results in this project, the use of sulphur containing additive, such as ChlorOut, is not believed to increase the corrosion at lower temperatures. This enables sulphur containing additive to be used to combat alkali chloride induced superheater corrosion not only for biomass fired boilers, but for boilers firing used (recycled) wood containing heavy metals as well.

6 Goal fulfilment

The overarching aim of this project was to increase the efficiency of boilers firing used wood and increase the fuel flexibility of boilers. To achieve this, the following goals were set:

1. To find out if lead, zinc and their chlorides causes serious corrosion problems in the temperature range 150-420°C in boilers firing used wood, and if the attack is worsened by the use of additive that reduce alkali chloride corrosion on superheaters at higher temperatures.
2. Based on the knowledge acquired by full-scale probe testing and the results of modelling and laboratory testing solutions for minimizing potential problems will be suggested.
3. To investigate and describe the ongoing corrosion processes and make an attempt to explain the mechanisms behind them to some extent.

The goal fulfilment is as follows:

1. Results in this project show the presence of lead and zinc in deposits and corrosion products. Their presence does however not seem to increase when ChlorOut is used. The corrosion does not increase significantly by use of the additive. (Note that long time tests only have been performed with and not without ChlorOut).
2. Based on the results in this project, the use of ChlorOut is not believed to increase the corrosion.
3. Indication that sulphation of Cl-containing salts decreases corrosion.

The results were aimed at being published in at least one scientific peer-reviewed article and to be presented at an international conference as well. However, at present no article has yet been prepared. One Licentiate degree was expected to be achieved during the programme period followed by a Ph.D. degree shortly after. The actual outcome with respect to this is that the results are in the process of being submitted for presentation at an international conference, one licentiate degree has been awarded during the programme period and continued work towards a Ph.D. degree is ongoing.

It is concluded that the goals have been acceptably well fulfilled.

7 Literature references

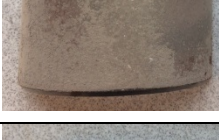
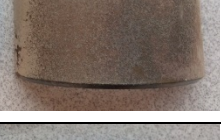
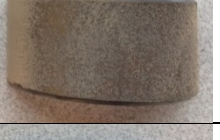
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8 Appendices

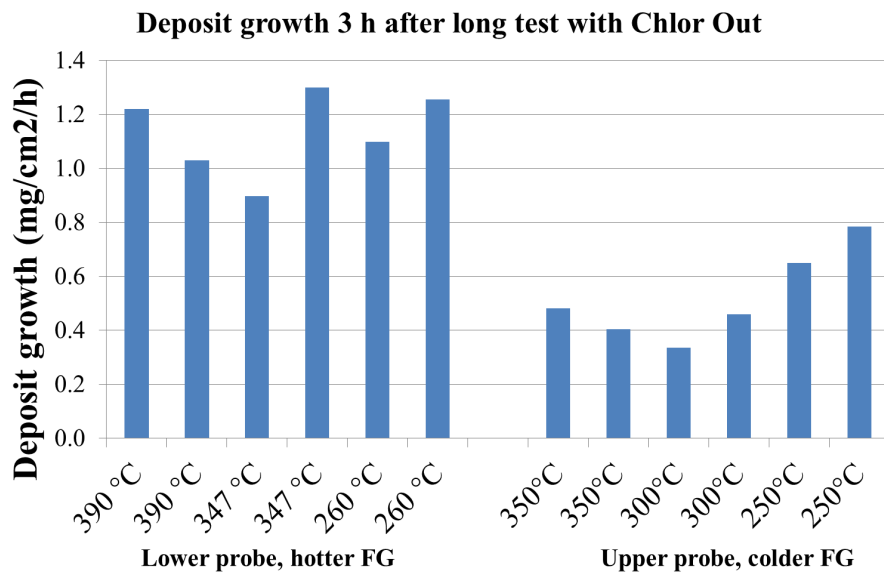
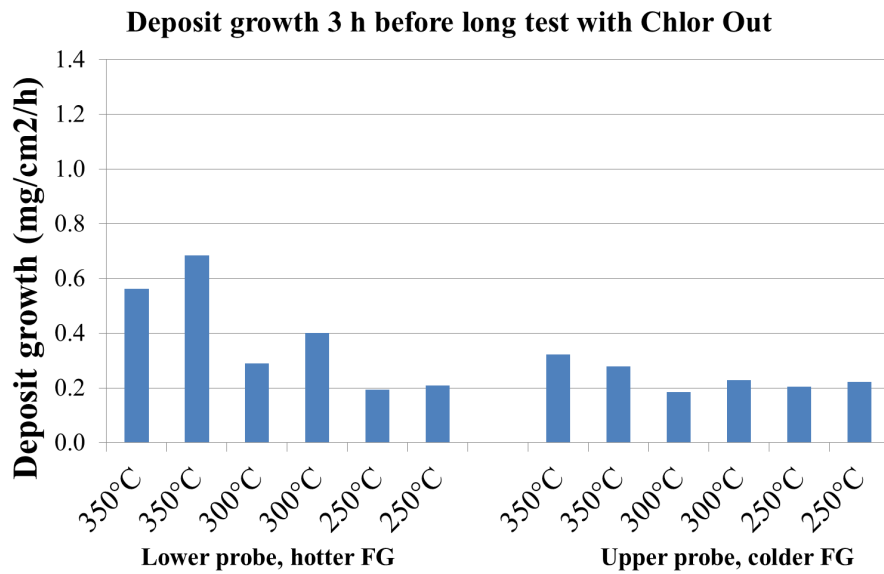
Appendix I – Visual appearance of samples

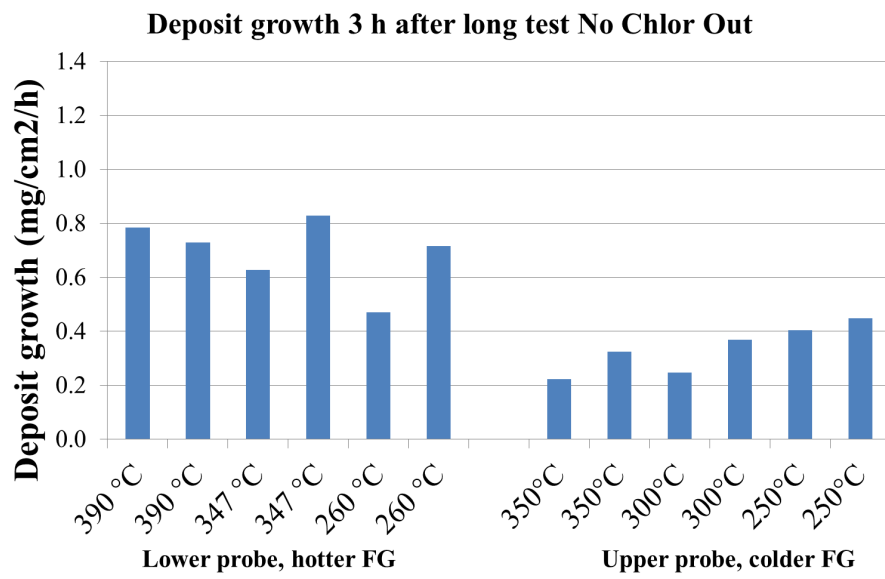
3h	before	#1		#2	
		Wind	Lee	Wind	Lee
350	Lower (hotter FG)				
300					
250					
350	Upper (cooler FG)				
300					
250					

3h	After	#1		#2	
	ChlorOut	Wind	Lee	Wind	Lee
350	Upper probe				
300					
250					
350	Lower probe				
300					
250					

3h	after	#1		#2	
	Ref	Wind	Lee	Wind	Lee
350	Upper probe				
300					
250					
350	Lower probe				
300					
250					

Appendix II – Deposit growth 3 h tests





Boiler corrosion at lower temperatures

The aim of the project was to find out if lead, zinc and their chlorides cause serious corrosion problems in the temperature range 150- 420°C in boilers firing used wood, and if the attack is worsened by the use of sulphur containing additive.

Results in this project show the presence of lead and zinc in deposits and corrosion products. Their presence does however not seem to increase when sulphur containing additive was used. The overall results give an indication that sulphation of Cl-containing salts decreases corrosion.

Based on the results in this project, the use of a particular sulphur containing additive is not believed to increase the corrosion at lower temperatures. This enables sulphur containing additive to be used to combat alkali chloride induced superheater corrosion not only for biomass fired boilers, but for boilers firing used (recycled) wood containing heavy metals as well.

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