KME

CONSORTIUM MATERIALS TECHNOLOGY for demonstration and development of thermal energy processes

Study of corrosion memory in boiler heat surfaces by field tests with biomass fuel mixes including sulphur and refuse fractions

Maria Dolores Paz, Torbjörn Jonsson, Jesper Liske, Sofia Karlsson, Colin Davis, Anna Jonasson, Tom Sandberg

KME 608

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KME-608

Preface

The project has been performed within the framework the fifth stage of the material technology research programme KME.

KME, Consortium Materials technology for demonstration and development of thermal Energy processes, was established 1997 on the initiative of the Swedish Energy Agency. In the consortium, the Swedish Energy Agency, seven industrial companies and 18 energy companies participate. The programme stage has been financed with 60.2 % by participating industrial companies and with 39.8 % by Swedish Energy Agency. The consortium is managed by Elforsk.

The programme shall contribute to increasing knowledge to forward the development of thermal energy processes for various energy applications through improved expertise, refined methods and new tools. The programme shall through material technology and process technology developments contribute to making electricity production using thermal processes with renewable fuel more effective. This is achieved by

- Forward the industrial development of thermal processes through strengthen collaboration between industry, academy and institutes.
- Build new knowledge and strengthen existing knowledge base at academy and institutes
- Coordinate ongoing activities within academy, institutes and industry

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

Abstract

There is a vast potential to optimize and correlate the boiler operation to current fuel quality and continuously within an advanced boiler. A key phenomenon to do this can be referred to as the corrosion attack during operation due to historic boiler operation (corrosion memory). By studying both the kinetics of artificial deposits in real boiler as well as actual corrosion probe test in two commercial boilers new knowledge about the corrosion memory effect have been obtained.

Sammanfattning

Ökad kunskap om sambandet mellan dynamiska korrosionsmekanismer, bränslespecifikation och ångdrifttemperatur utgör en plattform för hur man ska genomföra glidande ångtemperaturkontroll. Det finns en stor ekonomisk potential för att optimera och korrelera pannan till varierande bränslekvalitet och kontinuerligt använda den ökade nettoinkomstens potential i en avancerad panna. Detta fenomen kan kallas korrosionminne på grund av att den påverkas främst av den historiska driften (som har resulterat i vissa avlagringar och korrosionsprodukter) snarare än bränslemixen som för närvarande används (korrosionsminne). Således påverkar oxidskickt och tjocka avlagringar från det förflutna korrosionen. En följd av detta är att korrosionsminneseffekten kan delas upp i två underområden; nämligen ökad korrosion på grund av irreversibel utarmning av stål och dels av omvandling av korrosivaavlagringar. En panna som körs med glidandeångtemperatur konceptet är mer mottagliga för denna typ av accelererad korrosion jämfört med konventionella pannor. Detta eftersom förändringen av ångtemperaturen måste väljas inte bara med avseende på korrosiviteten av den aktuella bränsleblandningen utan även med avseende på tidigare bränslemixar.

Detta projekt är ett första steg för att öka kunskapen om materialtekniska processlösningar för att minimera överhettarkorrosion med avancerade ångdata i pannor. Projektet består av två exponeringskampanjer, d.v.s. en förstudie och en huvudstudie. Det främsta syftet med förstudien var att undersöka kinetiken av reaktioner i samband med beläggningsbildning. Då främst uppbyggnad och konvertering som en funktion av materialtemperatur, d.v.s. i ett av de två delområden som beskrivs ovan. Förstudien visade att ökad exponeringstid och temperatur innebär att omvandlingen av KCl till K_2SO_4 också ökas. En icke-korrosiv beläggning (som representeras av ren K_2SO_4) kan bilda en skyddande barriär mellan en korrosiv beläggning och legeringen när de exponeras i en korrosiv miljö såsom i en avfallseldad panna (P14 i Norrköping). Alla icke-korrosiva beläggningar hade en tendens att flagna av, det vill säga både den konstgjorda beläggningen K_2SO_4 och den som bildas i den bioeldade pannan (P13 i Norrköping). Huvudstudien visade att korrosionshastigheten var lägre för provet som exponerats i P13 - P14 - P13 jämfört med provet exponerats i P14 trots längre exponeringstid vilket visar en positiv "minneseffekt" av beläggningen som bildas i P13. En av utmaningarna i projektet var att alla icke-korrosiva beläggningar hade en tendens att flagna av, det vill säga både den konstgjorda insättning K_2SO_4 och den som bildas i P13 pannan, vilket påverkar resultatet. Detta bör beaktas i framtida projekt då detta är en inledande undersökning beträffande korrosionsminneseffekt. Dessa studier av både kinetiken för artificiella beläggningar i verkliga pannor samt faktiska korrosionssondstest i två kommersiella pannor har generat ny kunskap om korrosionsminneseffekten.

Nyckelord: Avfallsförbränning, Biomassförbränning, Korrosionsminne, Sonder

Summary

An increased knowledge of the relationship between dynamic corrosion mechanisms, fuel specification and possible steam operation temperatures can form a platform for how to implement gliding steam temperature control. There is a vast economic potential to optimize and correlate the boiler operation to current fuel quality and continuously use the increased net income potential within an advanced boiler. This phenomenon can be referred to as the corrosion attack during operation due to historic boiler operation (which have resulted in certain deposits and corrosion products) rather than the fuel mix currently being used (corrosion memory). Thus, the formations of oxide scales and thick deposits from the past dictate the corrosion further on. As a consequence, the corrosion memory effect can be divided into two sub-areas; namely increased corrosion due to irreversible depletion of the steel and secondly the rate of conversion of corrosive deposits. A boiler using the gliding temperature concept is more susceptible for this type of accelerated corrosion compared to conventional boilers. This since the change of steam temperature needs to be chosen, not only with respect to the corrosiveness of the current fuel mix, but also with respect to former corrosion history.

The present project is a first step to increase the knowledge of materials technology process solutions to minimize superheater corrosion with advanced steam data in boilers. The project consists of two major exposure campaigns, namely the “pre-study” and the “main study”. The main aim of the pre-study was to investigate the kinetics of reactions related to deposit build-up and conversion versus material temperature. Thus, increasing the knowledge in one of the two corrosion memory two sub-areas described above; namely the rate of conversion of corrosive deposits. The pre-study showed that increasing the exposure time and the temperature implies that the conversion of KCl to K_2SO_4 is also increased. A non-corrosive deposit (represented by pure K_2SO_4) may form a protective barrier between a corrosive deposit and the alloy when exposed in a corrosive fuel such as in a waste fired boiler (P14 in Norrköping). However, all non-corrosive deposits had a tendency to spall off, i.e. both the artificial deposit K_2SO_4 and the one formed in the co-fired boiler P13 in Norrköping, co-firing forest residue, tyre derived fuel and recycled wood waste. The main study showed that the corrosion rate was lower for the sample exposed in P13-P14-P13 compared to the sample exposed in P14 despite longer exposure time showing a positive “memory effect” of the deposit formed in P13. One of the challenges in the project was that all non-corrosive deposits had a tendency to spall off, i.e. both the artificial deposit K_2SO_4 and the one formed in the P13 boiler, which influences the results. This should be taken into account in future projects, as this is an initial investigation regarding the corrosion memory effect. These studies of both the kinetics of artificial deposits in a real boiler as well as actual corrosion probe test in two commercial boilers new knowledge about the corrosion memory effect have been obtained.

Keywords: Waste combustion, Biomass combustion, Corrosion memory, Probes

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1 Introduction

1.1 Background

Power plants represent major capital investments for power utility companies and, as such, the plant owners will always seek to maximise the return on their investment. In order to achieve this goal, the plants are required to operate on demand, often for extended periods and at peak efficiency. In practical terms this means the highest sensible steam operating conditions of temperature and pressure which does not result in too much plant damage. Ultimately there is a trade-off between increasing plant output / efficiency and minimising the maintenance required in order to keep the plant operational between overhaul / inspection shutdowns.

For biomass fired boilers the limits to steam temperatures and pressures are governed by the composition of the fuel fired and the resulting corrosivity of the combustion environment. Power plant boilers will be specified and designed with a specific fuel compositional range, with boiler manufacturers being able to offer plant performance guarantees for the specified fuels. Fuels with greater concentrations of aggressive elements such as alkali (sodium / potassium) or heavy (lead / zinc) metals and chlorine must be fired with relatively modest final steam conditions in order to avoid excessive fireside corrosion of either the steam generating furnace section, or the superheater and reheater sections of the boiler.

Changes to the fuel burnt within a specific boiler can have either positive or negative effects. Reductions in heavy metals and chlorine will result in less furnace fireside corrosion, whilst reductions in alkali metals and chlorine will lead to reduced superheater and reheater damage. In such a situation it may be possible to operate the boiler at higher efficiency, with greater steam temperature and pressure, whilst still maintaining acceptable fireside corrosion rates. However, in practise, power plants will often seek to reduce costs by sourcing cheaper fuels wherever possible. This often leads to the firing of more aggressive fuels with higher concentrations of aggressive ash forming species. In this situation, fireside corrosion rates in the boiler will increase relative to that ordinarily encountered with the cleaner design fuel, resulting in reduced boiler tubing operating lives, increased maintenance costs, the potential for unexpected tube leaks and forced shutdowns and the need for more frequent planned maintenance outages.

Where it is known that the fuel composition has become more aggressive, proactive preventative measures may be taken to prevent additional corrosion. One method frequently applied is to use, or increase the rate of dosing additives or opportunity fuels, that limit fireside corrosion damage. These frequently contain sulphur species that bind to alkali metals and prevent the formation and deposition of alkali chloride rich ash. Where additives are deployed there will be an associated cost for the additional additives if already used, or if not already used, there will also be an additional capital cost associated with the installation of dosing equipment. It is known that the dosing of sulphur containing additives has a significant

positive effect for power plants operating with final steam temperatures of up to 540ºC, although the benefits are as yet uncertain for plant operating with higher final steam temperatures. Where steam temperatures exceed 540ºC, there remains the risk of forming molten sulphatic compounds, which whilst less aggressive than molten chlorides, still pose a significant threat to superheaters and reheaters. Other potential fuel additives include alumino-silicate materials which can combine with alkali metals effectively preventing them from forming alkali chloride deposits. The use of additives for reduction of furnace corrosion has been investigated in the KME512 project and is reported separately.

For boiler plant having multiple fuel sources of varying composition, this brings the possibility of varying the final steam temperatures, so called gliding temperature operation, using reduced temperatures when it is known that dirtier fuels are being fired. The situation within the boiler is however complicated by the presence of the existing ash deposits. During operation with benign fuels, ash deposits will be formed that are also relatively benign, causing relatively low rates of corrosion. The introduction of a dirtier fuel and the formation of more aggressive ash deposits may not lead to an immediate increase in fireside corrosion rates. It was considered likely at the proposal stage for the corrosion memory project, that a period of time would be required for the more aggressive ash deposits to form and displace or transform the existing benign ash deposits. Brief periods of operation with aggressive fuels may not cause significant additional damage and therefore may not require a reduction in steam conditions.

Conversely, on changing from an aggressive fuel requiring reduced steam temperatures, to a benign fuel, it may not be possible to immediately increase the final steam temperature. If for example a significant period is required to displace the aggressive ash deposits with more benign ash deposits, an as yet unquantifiable period would be required before final steam temperatures could be increased. The situation could be further complicated by the possibility of sulphation of existing chloride rich ash deposits, resulting in the release of additional chlorine vapour in close proximity to the boiler tubing surface. It has been speculated that such a process could lead to a locally enhanced chlorine concentration compared to the bulk combustion environment chemistry, and a temporary enhancement of fireside corrosion rate.

1.2 Description of the research field

In project KME 601, Reference power plant project, some remaining R&D issues have been listed and one of these issues is related to “corrosion memory”. This phenomenon can be referred to as the corrosion attack during operation due to historic boiler operation (which have resulted in certain deposits and corrosion products) rather than the fuel mix currently being used. Thus, the formations of oxide scales and thick deposits from the past dictate the corrosion further on. As consequence, the corrosion memory effect can be divided into two sub-areas; namely increased corrosion due to irreversible depletion of the steel and secondly the rate of conversion of corrosive deposits. A boiler using the gliding temperature concept is more susceptible for this type of accelerated corrosion compared to conventional

boilers. This since the change of steam temperature needs to be chosen, not only with respect to the corrosiveness of the current fuel mix, but also with respect to former corrosion history.

1.3 Research task

The main scope of the project is to investigate how the corrosion is affected by changing the environment, by means of e.g. changed fuel mix, if the samples already have been exposed for a long time and formed a corrosion product layer and deposit. Will the corrosion attack accelerate directly if the samples are going from a moderate corrosive environment towards a highly corrosive environment? Or will the formed deposit layer act as protection against the flue gas? What is the temperature dependence of these reactions? Should the temperature kept low (slower change of the deposit and less release of HCl/minute) or should the temperature be kept high so that the reactions of the deposit is fast? Furthermore, if the samples first experiences a corrosive environment (by e.g. deposits rich in alkali chlorides) will the corrosion attack be mitigated by e.g. a higher SO_2 content in the flue gas or will the attack initially be accelerated further by the release of HCl when the alkali chlorides are being sulphated? By generating knowledge about the temperature dependence on the kinetics of the most important deposit reactions and at the same time measure the extent of corrosion, the importance of the corrosion memory effect can be determined.

Recent laboratory studies have shown that the transformation of KCl to K_2SO_4 is very fast at 600°C in O_2, H_2O and SO_2 [1]. In that case, 50% of the applied KCl was transformed into K_2SO_4 during the first 15 minutes in the presence of 300ppm SO_2 at 600°C. Is this kinetics also valid for the complex environment in the boiler? Furthermore, how will this affect the corrosion attack?

1.4 Goal

The aim of this project is to aid boiler owners in operating boilers with a wide fuel range/variation and, still, have a control of corrosion. This is done by generating knowledge about the dynamic corrosion processes occurring when the fuel mix is changed during operation and how this relates to the operation history (i.e. is it more corrosive with a wider fuel mix during start-up compared to after long term operation?).

This relates to existing plants in general and new plants, designed for advanced steam data for a specified fuel range, in particular. In the new plants, operation outside the specified fuel window will occur depending on variations in fuel quality or that the specified fuel quality could not be purchased to a reasonable price (during the guarantee period, normally 24 months, the plant owner must use fuels within the contract specifications). It is therefore of great importance and interest to generate knowledge about how the boiler surfaces are affected by fluctuations in fuel specification, allowing the boiler operator to run the boiler in “safe mode” when there is a risk for high corrosion rates and “advanced steam data mode” whenever the

corrosiveness caused by the current fuel mix and factors affected by earlier operation history are acceptable low (i.e. “gliding temperature”).

There are at least three main important questions to be answered;

1. Can the corrosion rate be maintained low after a change to a more corrosive fuel if the steam temperature is lowered at the same time?

2. Is there a memory effect (resulting in increased corrosion rate) after the return to high steam temperature and less corrosive fuel?

3. Is there an “incubation time” (before the corrosion rate increases) for materials exposed at high steam temperature and less corrosive fuel after a change to low steam temperature and more corrosive fuel?

This project is expected to give a first set of answers as a platform for further work.

1.5 Project organisation

The project has involved the following organisations and staff:

Project management / administration
Pöyry Swedpower,
Lars Wrangensten and Tom Sandberg

Probe tests, material analysis and evaluation
High Temperature Corrosion Centre at Chalmers University of Technology,
Jesper Liske, Torbjörn Jonsson, Sofia Karlsson, Maria Dolores Paz and Dongmei Zhao.

Field tests with planning/execution etc.
E.ON Värme Sverige,
Anna Jonasson

Material samples
AB Sandvik Material Technology,
Mats Lundberg

Reference group
Annika Stålenheim (Vattenfall), Bertil Wahlund (ELFORSK), Mats Åbjörnson EON Värme), Pamela Henderson (Vattenfall), Paul Cho (Valmet Power), Sonja Enestam (Valmet Power), Rikard Norling (Swerea KIMAB).

Project finance
This project has been financed by 60 % from industry as cash and in-kind and 40 % through the KME programme. See the detailed budget below:

Company *)	In kind effort (kSEK)
E.ON Värme Sverige	415 (in kind) + 225 (cash)
E.ON C&R	145 (in kind)+ 225 (cash)
Sandvik Materials Technology	40 (as in kind)
Total industry contribution (60%)	1050
State cash from KME, 40 %	700
Total project costs:	1750

2 Project description

This projects work packages and phases have been performed according to the description below:

Pre-study of the kinetics in the boiler

In order to examine the kinetics of the key reactions in the boiler a pre-study was performed during spring 2013. By using pre-oxidised highly alloyed samples with simulated KCl or K_2SO_4 deposits the rate of conversion (i.e. chlorination or sulphation) was studied. The pre-oxidation was performed in furnaces at Chalmers to form a protective oxide. The pre-study focused on the rate of deposit conversion and temperature in order to facilitate the selection of relevant parameters for the corrosion tests. Analyses of the samples were carried out by HTC. During two reference group meetings the final set-up for the main study was decided.

Main study - Corrosion tests in the boilers

These corrosion exposures where carried out during November 2013. EON Värme hosted the tests at their plant and participated in the planning and set-up of the tests. Analyses of the samples were carried out by HTC but EON Climate & Renewables contributed with SEM-EDX analysis of the Sanicro samples.

This final report has been elaborated by HTC, EON Värme, EON Climate and Renewables as well as Pöyry Swedpower.

3 Description of the plants

To simulate the change of fuel two boilers where utilised and test probes where moved in between them. For this purpose boiler P13 and P14 at Händelö were suitable because P13 has a corrosion benign environment with sulphur rich fuel and P14 has a highly corrosive environment with a lot of chlorides and alkali in the flue gas. In section 3.1 and 3.2 P13 and P14 are described and section 3.3 describes the fuel mix during the test period.

3.1 Description of P13 at Händelö

The boiler is a Circulating Fluidised Bed (CFB) boiler with a thermal capacity of 131 MW supplied by Tampella. The boiler produces steam, primarily used for production of electricity, industrial process steam, and district heating.

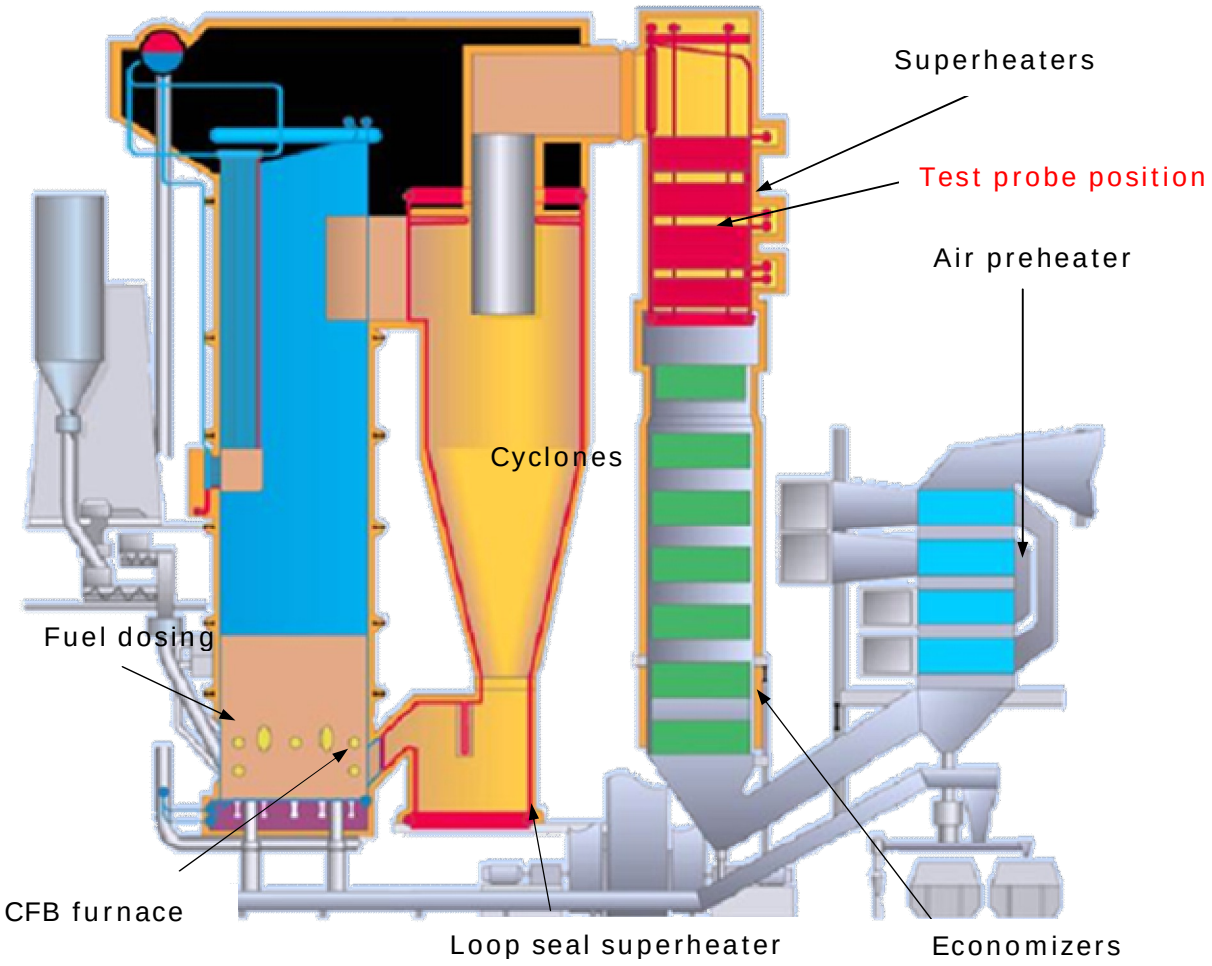


Figure 1. Händelö/Norrköping P13 CFB boiler

The boiler was originally constructed as a combined biofuel and coal fired boiler (60 % coal and 40 % biofuel, chipped wood). But since 1993 when the boiler was new, different kinds of biofuels have been used. Waste fuels like tyre derived fuel and recycled wood are also now part of the fuel mix which is used in P13. Light fuel oil is used as the start and reserve fuel. The boiler plant is installed in a separate boiler house.

The boiler's original design data is as follows:

Maximum continuous load (coal/wood fuel)		41.7 kg/s
Minimum continuous load		10.4 kg/s
Feed water temperature	Min.	110°C
	Max.	135°C
Turbine steam pressure		110 bar (excess pressure)
Steam temperature		540°C
Net thermal power		125 MW
Thermal power with light oil		48 MW

The steam boiler is a natural circulation boiler suspended from the top. The combustion air is preheated with district heating coils of flanged pipes and flue gas preheaters with smooth pipes. Part of the fly ash is collected from the second and third draught's base in cones and transported to an ash pallet via a screen. The boiler also has a four-field electrostatic precipitator and lime injection devices. The boiler has been supplied with catalyte that has been removed.

To feed solid fuel into the bed, there are two separate transport lines for coal and wood fuel. The boiler is also fitted with a light oil combustion device with which around 40% boiler power is achieved. The fluid bed's start burners (2+2) are on both side walls, around 3 m above the bed.

Combustion air, which, if required, can also be preheated with district heating water, is supplied to the boiler using fluid and secondary air fans. The design capacity of both fans is 1 x 100%. The design capacity of the flue gas fan is 1 x 100%.

The operation of boiler P13 started in 1993 and the first years there were some problems with the boiler. For example there were a number of broken vortex finders in the steam cooled cyclones and damage on the air pre-heaters which happened a few times because of low temperature corrosion. The construction of the vortex finders has been changed and the final construction which was installed 1998 has been very good. The air preheaters are reconstructed, also, and the new solution is satisfying.

The original tertiary superheater suffered from high temperature corrosion, but since the change of material to SS2338, it has resisted the corrosion attacks. The co-firing with chipped tyres also, has proven to be beneficial to mitigate corrosion on the superheaters.

To be able to use recycled wood as a fuel a number of tests were performed. After the tests, it was easier to know how to rebuild the boiler to prepare it for the new fuel. The bottom of the furnace and the bottom ash system were rebuilt during 2009.

The P13 boiler is integrated with the other boilers at the plant. The water treatment, district heating system, steam turbine and the condenser are commonly used. The plant is supervised from one control room.

3.2 Description of P14 at Händelö

The waste fired plant P14 at Händelö has a capacity of 200 000 metric tonnes/year. The plant is a modern Energy-from-Waste plant with great fuel flexibility. The waste burned is household waste and industrial waste. It is also possible to burn 20% sewage sludge from sewage water treatment plants. The plant consists of a boiler, steam turbine, flue gas cleaning and fuel preparation.

Figure 2. The waste incinerator plant P14 at Händelöverket

The boiler is a Circulating Fluidised Bed (CFB) boiler with a thermal capacity of 75 MW supplied by Kvaerner Power (today: Valmet Power). The boiler produces steam, primarily used for production of electricity, industrial process steam, and district heating. Some boiler data are shown in Table 1, Table 2 and Table 3.

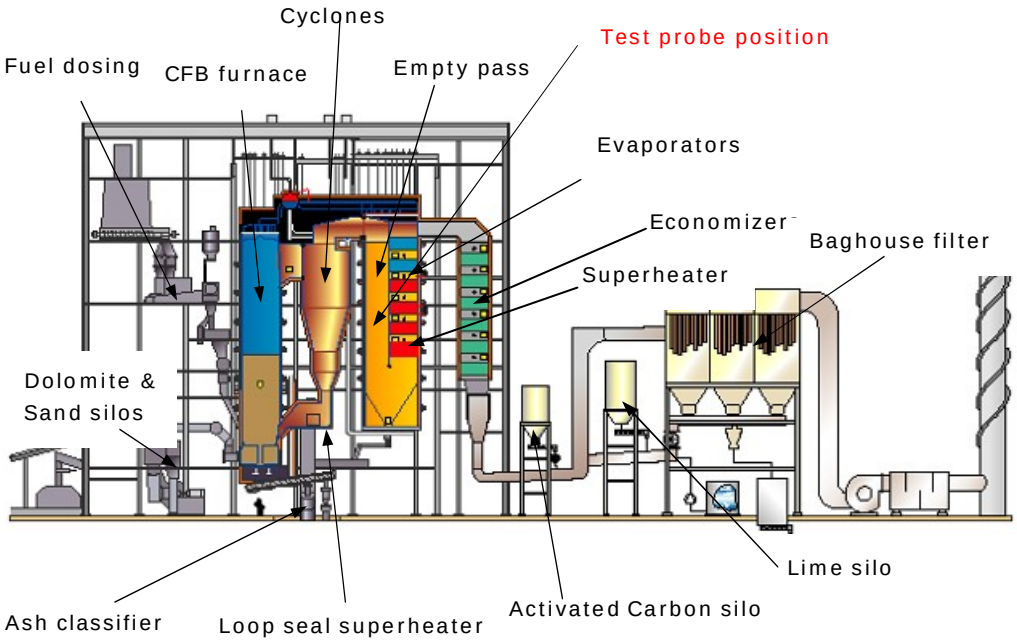


Figure 3. Händelö/Norrköping P14 CFB boiler

The boiler is designed for fuel flexibility, using a fuel mix of 30-50% combined household waste, 50-70% classified industrial waste and up to 20% sewage sludge.

The design of the Valmet CFB boiler used for combustion of MSW/RDF (Municipal Solid Waste, Refused Devised Fuels) fuels comprises some characteristic features to be outlined in the following text. The main parts in the boiler system are a water-cooled furnace with two integrated water cooled cyclones and loop seals, containing the final superheaters, and an external ash-classifier, Figure 3. The cyclones are followed by a single pass radiation cavity (empty pass) and a convection pass with superheater banks, boiler banks and economizer banks. The boiler is equipped with a conventional steam soot blowing system cleaning the banks in the convection pass. Afterwards the empty pass has been equipped with two water cannons and the economizer with sonic cleaning, which is used together with the original installed steam soot blowers.

The boiler is top supported and designed for natural circulation characterised by the steam separating system including the steam overflow headers, in combination with the downcomers, which run from the top to the bottom of the boiler. Saturated water from the drum is distributed through a number of downcomers to the bottom part of the boiler, the wall tubes in the furnace, the cyclone loop seal and the radiation cavity/back pass enclosure. The water/steam mixture is transferred back to the steam drum by a number of steam separating connecting pipes. The circulating system is integrated between all components.

The furnace front and rear wall are bent into a U-shape to form a water cooled windbox for primary air, below the fluidized bed furnace. The primary windbox also serves as a combustion chamber for the start-up burner, located at the furnace front wall.

All four walls of the furnace are refractory lined, except for a smaller surface area on the upper part of the sides and front wall, for erosion protection and to sustain furnace temperature above 850°C during 2 seconds after the last injection of air. The latter is a European requirement when firing waste. It is also required to install auxiliary burners in the furnace to secure the furnace temperature 850°C before adding the RDF during start up and in case of a sudden drop in the furnace temperature during boiler operation.

Coarse fuel ash entering the furnace is transported through the bottom bed, by means of the directed primary air nozzles, to discharge openings in the bottom plate from where it is fed to the ash classifier. The classifier operates as a high velocity fluidized bed, which elutriates the small bed particles from the coarse particles in the discharged ash and send them back to the furnace. In addition, the coarse ash is cooled by the added air before it leaves the classifier, which minimizes the loss of sensible heat.

The boiler features two hot gas cyclones for separation of the bed material entrained by the flue gas and leaving the furnace at the furnace top. The separated material is returned to the lower part of the furnace via a loop seal. The loop seal contains a bubbling fluidized bed and is equipped with a number of air nozzles to ensure material transport. Moreover, it is designed to prevent flue gas from the furnace entering the cyclones through the bed material return leg.

The loop seal, which is a feature of the CFB process, offers a location of the final superheater (SH) for two reasons; *1.* The heat transfer coefficient in the bubbling bed is 5 to 10 times higher than in the back pass. Hence, the SH area required is reduced by 80 to 90%. *2.* The gaseous atmosphere in the loop seal contains less of chlorine and water vapor since the chlorine and water released during the combustion of the RDF is in a gaseous form in the cyclone and therefore follows the flue gas to the back pass. Only the particles separated by the cyclone reach the loop seal.

The cyclones are constructed from water-cooled membrane walls, which form part of the water circulation system. The feature of this design is that the cyclones are part of the natural water circulation circuit and therefore expand in the same way as the furnace and back pass enclosure. This feature allows the cyclones to be gas-tight welded to the furnace and the back pass, thus avoiding all expansion bellows of huge dimensions always causing a lot of maintenance problems and costs. The cyclone interior is fully refractory lined with a thin layer for erosion protection, which minimizes the amount/thickness of refractory and further reduces the maintenance costs and shortens the start-up time. An SNCR-system is installed, with ammonia injection in both cyclones.

The cyclones are followed by an empty pass for lowering the flue gas temperature to a temperature, which makes the ash ”dry” and non-sticky to the back pass tube banks. This will minimize deposit formation and corrosion attacks. The bottom of the empty pass is equipped with an ash extraction conveyor system.

The risk of combined corrosion and erosion in the back pass calls for low flue gas velocities and low flue gas temperature. This will result in large superheater and evaporator surfaces.

A new evaporator bundle has been installed 2006 before the secondary superheater to reduce the flue gas temperature by 50°C. This bundle and four additional rows of boiler tubes protect the secondary superheater at the gas inlet side.

The secondary superheater in the back pass has compound tubes with Sanicro28/ St45.8/III and three loops of Sanicro63/St45.8, no 1, 14 and 26. The steam temperature increases from approximately 350°C and controlled up to 400°C in parallel flow with the gas.

The primary superheater was replaced in the spring 2007. It now has tube materials 16Mo3 (the cold part) and 13CrMo44 (the warmer part). The steam temperature increases from 290°C up to approximately 370°C in counter flow with the gas. The gas inlet temperature is about 500°C. All superheater tubes in the first and last rows, near the soot blowers, are protected by tube shields.

Water/steam		
Feed water temp	°C	135
Steam flow	kg/s	27.5
Steam pressure	MPa	6.5
Steam temperature	°C	450
Miscellaneous		
Boiler efficiency	%	89.7
Exit flue gas temperature	°C	165-170
Unburned in bottom ash	%	<0,1
Unburned in fly ash	%	< 0,5

Table 1. Operating data at MCR (Maximum Continues Rate).

Boiler part	*Material*	*Max gas temperature °C*	*Max steam or water temperature °C*
Furnace	Sanicro 28 / St45.8/III	900	290
Radiation cavity (empty pass)	St45.8/III	850	290
Tertiary superheater	TP347H	900	450
Boiler bank	St45.8/III	650	290
Secondary superheater gas inlet	Sanicro 28 / St45.8/III	630	400
Secondary superheater gas outlet	Sanicro 28 / St45.8/III	500	340
Primary superheater gas inlet	13CrMo44	500	370
Primary superheater gas outlet	16Mo3	440	290
Boiler bank	St45.8/III	440	290
Economiser	St 35.8/III	350	240

Table 2. Boiler material and temperatures at MCR.

Boiler part	*Tube surface temperature °C*	*Fin temperature °C*
Furnace	315	340
Radiation cavity gas inlet	300	310
Radiation cavity gas outlet	295	300
Tertiary superheater	500	
Boiler bank	295	
Secondary heater gas inlet	360	
Secondary superheater gas outlet	415	
Primary superheater gas inlet	380	
Primary superheater gas outlet	300	

Table 3. Max tube and fin surface temperature at MCR.

The P14 boiler is integrated with the other boilers at the plant. The water treatment, district heating system, steam turbine and the condenser are commonly used. The plant is supervised from one control room.

The fuel preparation plant, consists of a receiving bunker (78 m long, 12 m wide and 8 m deep) with a total volume of more than 7000 m^3. Two overhead travelling cranes with crab buckets feed the two redundant preparation lines. The crushing/ grinding is performed in two steps and magnetic sorting in three steps, before the boiler. M & J delivered the primary shredders and there are also two secondary shredders, which have replaced the hammer mills. The prepared waste is transported to an intermediate storage, an A-barn, before it is transported to the boiler silos. Sydkraft (today E.ON) has

designed the waste preparation system, while the parts are delivered from a number of suppliers.

3.3 Fuel specifications in P13 & P14 during the test period

P13 has a corrosive benign environment thanks to fuel mix containing the sulphur rich tyre derived fuel as opposed to P14 where household and industrial waste makes the environment in the flue gas very corrosive containing chlorides and alkali. Below is the composition of fuel feed to boiler P13 during the test campaign.

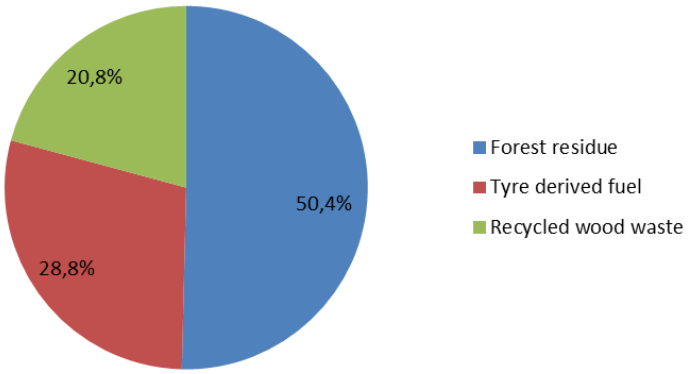


Figure 4. Distribution of fuel mix in Boiler P13, November 2013

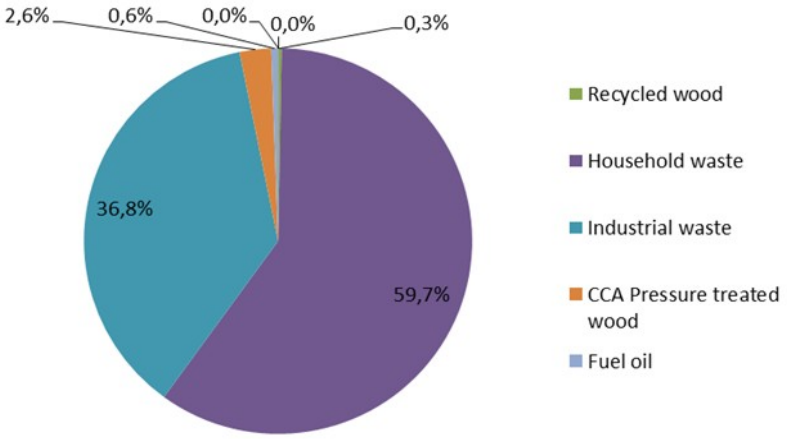


Figure 5. Distribution of fuel mix in Boiler P14, November 2013

In figure 5, the total distribution of fuels burnt in P14 during the test period can be seen. The fuel consists of a mix of municipal solid waste, industrial waste and some percentage of different types of bio fuels. The distribution of fuels reveals that in total, the fuel consists of more than 95% waste fuel. During normal operation, the fraction of waste fuels is 100%. The other types of fuels are related to the startup sequence of the boiler when, according to the incineration directive, no waste fuels are allowed. The bio fuels are also used when the regular fuel feeding system is out of order.

The different fuels, composing the fuel mix, can be described as:

- Forest residues: Forest residues are defined as the biomass material remaining in forests that have been harvested for timber, and are almost identical in composition to forest thinnings. Because only timber of a certain quality can be used in lumber mills and other processing facilities, biomass material/forest residue is left in the forests during harvesting operations. Forestry residues include logging residues, excess small pole trees, and rough or rotten dead wood. These residues could be collected after a timber harvest and used for energy purposes.

- Tyre derived fuel: Fuel derived from used tyres.

- Recycled wood: Recycling wood chips are produced from shredded and screened used wood.

- Household waste: Solid waste comprising of garbage that originates from private households. Also called domestic waste or residential waste.

- Industrial waste: Solid, semi-solid, liquid, or gaseous fuel that consists of unwanted or residual materials (not including hazardous or biodegradable wastes) from industrial operation.

- CCA Pressure treated wood: Used wood which has been treated with chromated copper arsenate.

- Fuel oil: Fuel oil is a fraction obtained from petroleum distillation, either as a distillate or a residue. Number 1 fuel oil is used in P14. Number 1 fuel oil is a volatile distillate oil intended for vaporizing pot-type burners. It is the kerosene refinery cut that boils off right after the heavy naphtha cut used for gasoline.

Table 4 below shows the average values of several fuel analyses performed 2010-2011. The samples are taken on mixed waste after fuel preparation and storage, on the way into the boiler.

	H_i MJ/kg	Water content %	Ash %	Carbon %	Oxygen %	Hydrogen %
As delivered	12,3	32,3	11,3	32,9	46,4	8,0
Dry sample			16,7	48,6	26,2	6,4
	Sulphur %	Chlorine %	Nitrogen %			
As delivered	0,14	0,7	0,5			
Dry sample	0,21	1,1	0,8			

Table 4. Typical fuel data, P14, Händelö

4 Experimental conditions

Within the project two major exposure campaigns were performed, namely the “pre-study” and the “main study”. The main aim of the pre-study was to investigate the kinetics of reactions related to deposit build-up and conversion versus material temperature. The results from the pre-study were used in order to sett up relevant parameters for the main study.

4.1 Probe exposures

The pre and main-study was performed during 2013 in boiler P13 and P14 at E.On´s plant in Händelö, Norrköping. These boilers were chosen in order to expose the samples towards two different types of corrosive environments:

- Highly corrosive environment in the waste fired P14 boiler. The fuel mix is around 50% household and 50% industrial waste.
- Moderate corrosive environment in the partly biomass fired P13 boiler. The fuel mix is 30% tyre derived fuel, 25-30% recycled wood and 45-50% forest residues.

The probes used for both main study and pre-study are cooled probes, which hold 3x3 samples in three temperature zones, as it is presented in Figure 6. A PID controller controlled each temperature zone individually, and pressurized air was used as cooling agent. The probes were exposed in P13 boiler (moderate corrosive environment) and P14 boiler (fuel mix of household and industrial waste).

Figure 6. Detail of the samples placed in the probes and temperature zones

The temperatures and loads of P14 and P13 boiler were measured and are presented in Figure 7 and Figure 8. All the general data about the boilers is already presented in section 3, but the data in this figures, corresponds to the dates when the probes stayed in. In P13 boiler the detectors are at the same level as the probes but on the other side of the boiler, the same happens for P14 so the data from the images could be taken as representative of the boiler environment. Regarding to the P14 boiler, two measurements were taken in account for the temperature, the lowest and the highest, so the temperature in the probe environment never went further those temperatures.

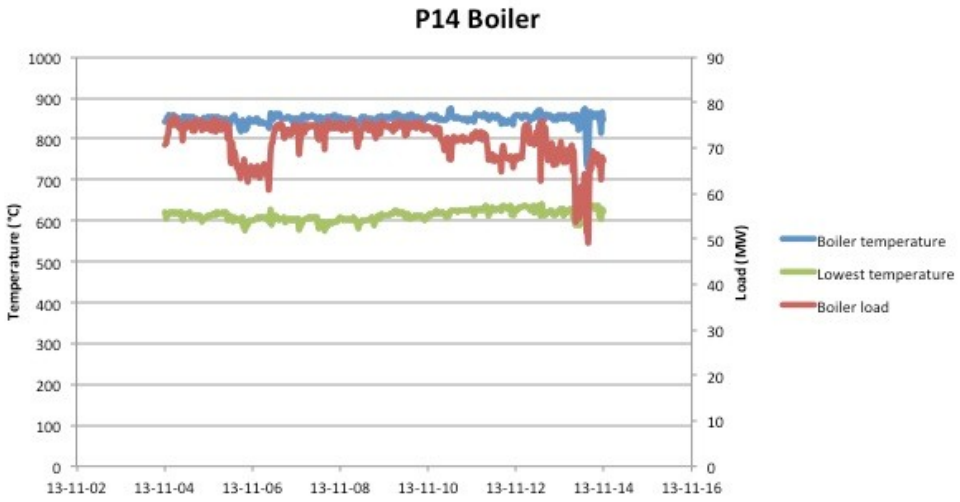


Figure 7. Temperature and load measured in the P14 boiler

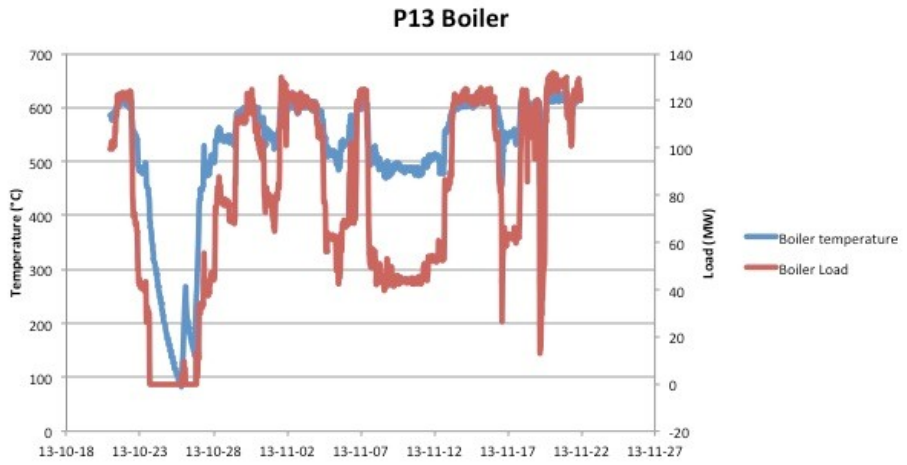


Figure 8. Temperature and load measured in the P13 boiler

4.2 Materials

An overview of the tested materials and their chemical composition are given in Table 5. The balance is mainly Fe. The content of Si and Mn is small.

	SIS	DIN/EN	%C	%Fe	%Cr	%Ni	%Mo
T22	2218	10CrMo9-10	0.12	bal	2.25		1
304L	2352	X2CrNi 19 11	0.012	bal	18.47	10.12	
Sanicro28	2584	X1NiCrMoCu N 31 27 4	0.014	bal	26.68	30.56	3.39

Table 5. Composition of the materials used in the project

The alloys can be described as:

- T22, 10CrMo9-10 (SS2218) is commonly used Cr-Mo alloyed low alloy steel in superheaters.
- 304L is a standard austenitic stainless steel alloyed with Cr and Ni. It has been used as water wall composite tubes in mainly Black Liquor Recovery Boilers. This is the low cost alternative both as austenitic stainless steel and composite tube.
- Sanicro 28 is a Fe-Cr-Ni alloy, which has shown promising results in waste incineration environments. It is highly alloyed with Cr (27%) and Mo (3,5%), which make the alloy sensitive for inter-metallic phases such as σ phase. Thus, the alloy is less suitable as ordinary mono tube, at least above 500°C. This is one reason why it is used as composite tube. However, its high Mo and Cr content make it suitable in high Cl containing environments.

4.3 Pre-study

The pre-study was performed during spring 2013 using pre-oxidized Sanicro28 samples. The main aim of the pre-study was to investigate the kinetics of reactions related to deposit build-up and conversion. The Sanicro28 samples were therefore pre-oxidized to form a protective chromium rich oxide prior to the exposure. Thus, the effect of corroding samples on the deposit chemistry was minimized. The pre-oxidation was performed in well-controlled laboratory furnaces at Chalmers. After the pre-oxidation, the samples were either covered with 100 μm thick KCl, K_2SO_4 deposit, or used as references (i.e. no artificial deposit was applied prior to exposure). The artificial deposit was applied by means of spraying the sample rings with a water/ethanol mixture containing the desired salt. The amount of artificial deposit was controlled by means of gravimetry, the average weight of the applied salt corresponded to 1,987 $\mu g/cm^2$ (KCl) and 2,66 $\mu g/cm^2$ (K_2SO_4).

The pre-study was performed with cooled probes (holding 3x3 samples) in the boilers P13 (fuel mix of biomass, TDF and recovered wood waste) and P14 (fuel mix of household and industrial waste). The material temperatures of the three temperature zones on the probe were set to 450, 525 and 600 °C, respectively. A PID controller controlled each temperature zone individually and pressurized air was used as cooling agent. The exposure time was set to 1 and 24 hours. The setup of the pre-study is summarized in Figure 9.

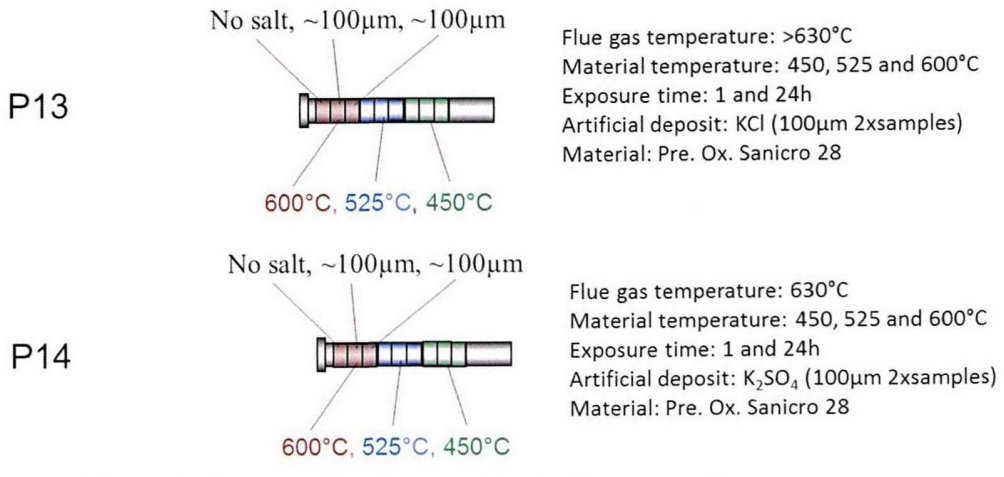


Figure 9. Evolution of the temperature in the P13 boiler during the step 1 measured in probe 1

4.4 Main study

The main-study was performed during autumn 2013 in boiler P13 and P14 at E.On´s plant in Händelö, Norrköping. Based on the results in the pre-study the following parameters were selected:

- First exposure executed in P13 to produce a protective deposit lasted for 313 hours.
- The second exposure (both P13 and P14) lasted for 256 hours.
- The third exposure in P13 for lasted for 162 hours.

All exposure conditions and temperatures are summarized in Table 6. During each step the three samples placed closest to the tip of the probe were removed and new samples were installed.

The Figure 10 shows the distribution of the probes in the boilers during the exposures.

	1st exposure			2nd exposure			3rd exposure		
Materials	T22 304L Sanicro28			T22 304L Sanicro28			T22 304L Sanicro28		
Temperature	450°C	600°C	600°C	450°C	600°C	600°C	450°C	600°C	600°C
Time	313 hours			236 hours			162 hours		
Boiler	P13			P13/P14			P13		

Table 6. Summary of the characteristics of the exposures

The temperature of the samples on the probes was recorded during all exposures. During the first exposure in P13 the boiler was shut down after two days of exposure. The probe with all samples was left within the boiler during the stop (for one week). The recorded sample temperatures for probe 1 can be seen in Figure 11. The equivalent temperatures recorded in probe 2 are presented in Appendix III.

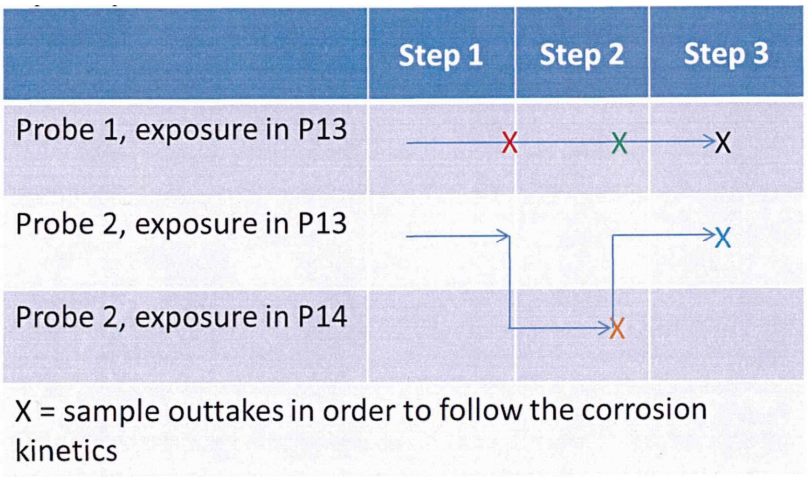


Figure 10. Distribution of the probes in the boilers for the different exposure steps

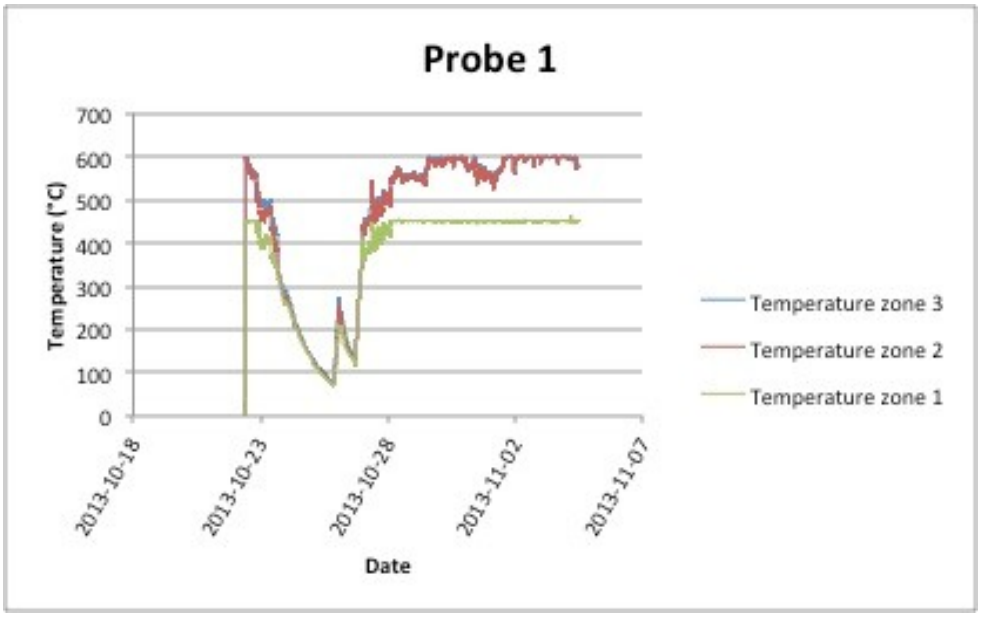


Figure 11. Evolution of the temperature in the P13 boiler during the step 1 measured in probe 1

During the second exposure probe 1 was exposed in P13 while probe 2 was exposed in P14. Both probes were handled the same way to be able to compare the results. The temperature of the samples in P14 was very stable during the whole exposure while this was not the case for the samples in P13 where it was impossible to reach the highest target temperatures due to how the boiler was run, see Figure 12 and Figure 13.

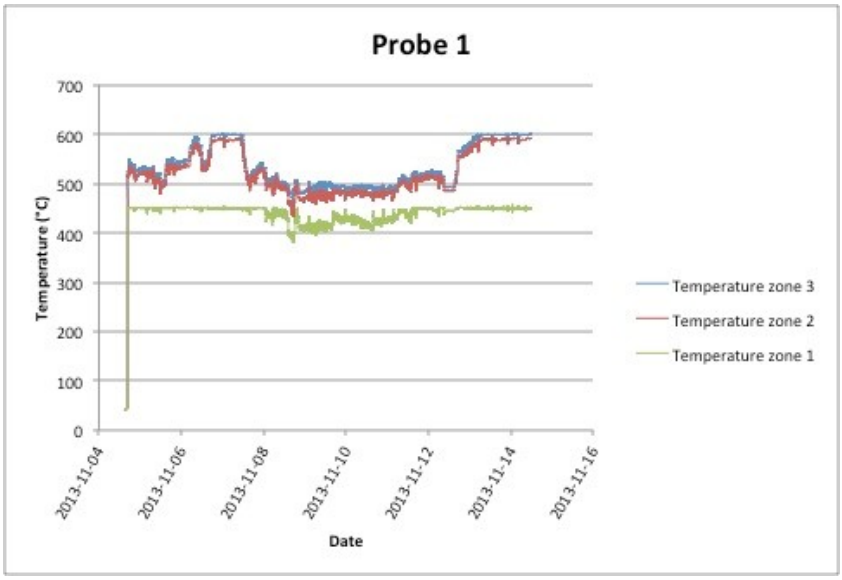


Figure 12. Evolution of the temperature in the P13 boiler during the step 2

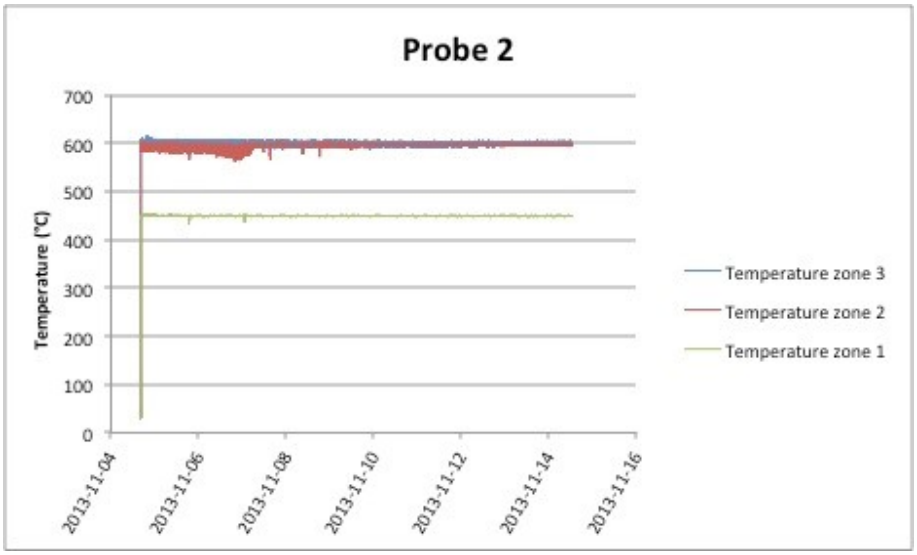


Figure 13. Evolution of the temperature in the P14 boiler during the step 2

The final exposure of both probes was performed in P13. During this exposure there were some problems with the thermocouples in probe 2. This can be seen in Figure 15. The exact temperature control of these samples is therefore not reliable. However the temperatures are estimated to be close to the pre set values. This because the average temperature of the P13 boiler in this exposure period was 591,89°C, between 481°C and 627°C. Due to the malfunctioning of the thermocouples, the probe was not cooled properly during this exposure step. It could therefore be assumed that the samples reached the flue gas temperatures in the boiler. This means that the temperature was not maintained at 600°C or 450°C. For the samples of the temperature zones 2 and 3, at 600°C, there is only a small difference given the average temperature in P13. On the other hand, the samples of the temperature zone 1, set to 450°C, were exposed at higher temperature during this step. These samples were not investigated in detail.

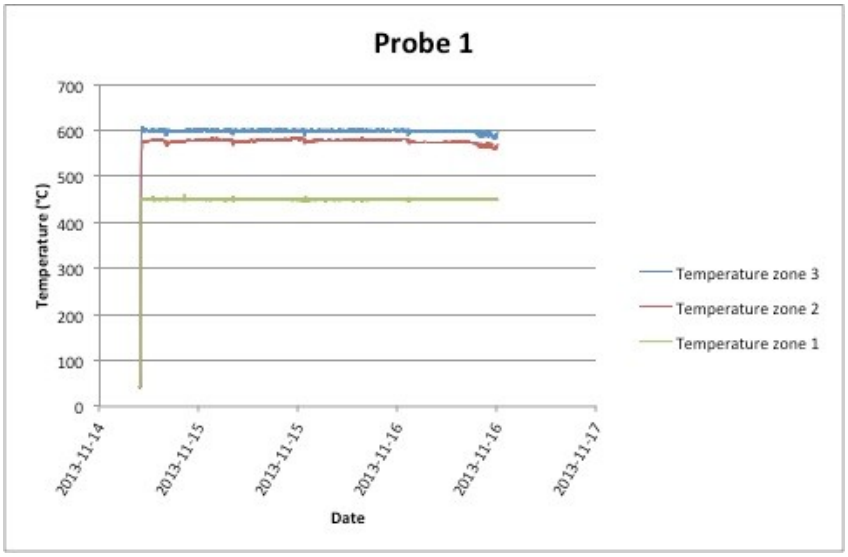


Figure 14. Evolution of the temperature in the P13 boiler during the step 3 measured in probe 1

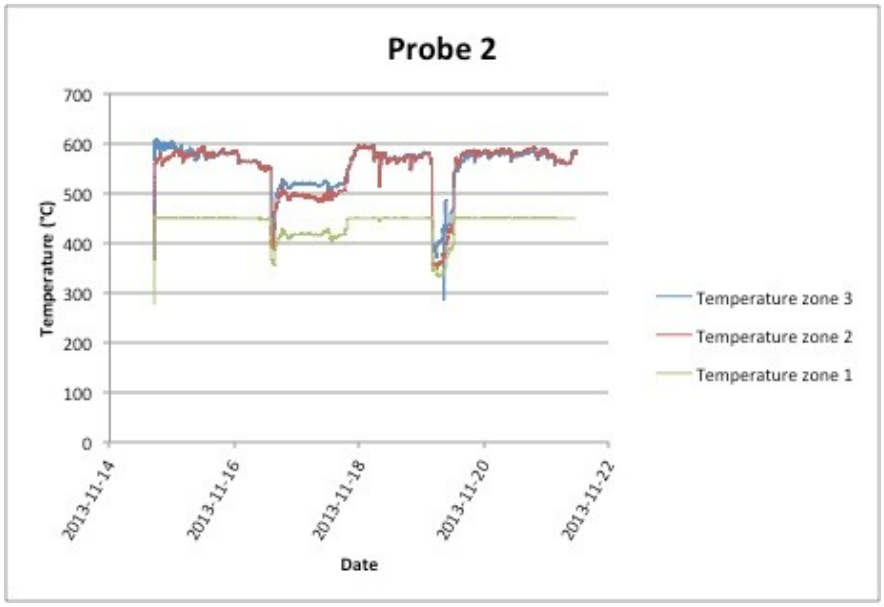


Figure 15. Evolution of the temperature in the P13 boiler during the step 3 measured in probe 2

4.5 Analytical techniques

4.5.1 Qualitative analysis

All samples were investigated by visual inspection after exposure and documented by photographs. The color, thickness and adherence of the deposit/corrosion product layer give rough information of the overall condition and performance of the exposed sample. All samples were stored in desiccators together with phosphorous pentoxide drying agent awaiting their analysis.

All the photographs are presented in Appendix IV.

4.5.2 Ion Chromatography (IC)

To determine the amount of water-soluble anions (Cl^-, SO_4^{2-} and CrO_4^{2-}) on the exposed samples, a Dionex ICS-90 system was used. The anions were analysed with an IonPac AS4A-SC analytic column and 1.8mM $NaHCO_3$/1.7mM$NaHCO_3$ was used as eluent. The flow rate was 2ml/min.

4.5.3 Scanning Electron Microscopy/ Energy Dispersive X-Rays (SEM/EDX)

After the boiler exposures the samples were casted in epoxy, cut and polished prior to the SEM/EDX investigation.
The rings were casted in epoxy resin. After the including in the epoxy, both sample and mould, were submitted to a 10 bar pressure to avoid the formation of bubbles during the hardening of the resin. The hardening time was fixed in 24 hours. After that time, using a silicon carbide disc and a lubricant without any water due to the delicate corrosion products, the samples were cut. After that the samples were polished dry with Silicon Carbide P4000. The cross-section was coated with platinum to avoid charging in the SEM.
The polished cross-sections of the samples were investigated by scanning electron microscopy, SEM. The SEM is equipped with an Energy Dispersive X-rays system enabling analysis of the elemental composition in small areas of the sample. In this work a FEI 200 Quanta FEG ESEM was used. It is equipped with a field emission electron gun (FEG) and an Oxford Inca energy dispersive X-ray (EDX) system. SEM/EDX was used for imaging, elemental mapping and quantification. An accelerating voltage of 20kV was used for all analysis.

4.5.4 Material loss measurements

The samples were evaluated by means of metal loss determination, performed by micrometer screw and SEM imaging. Prior to exposures, the samples of the three different materials were measured in thickness by using a digital micrometer. The measurements were taken twice, every 45° avoiding the edges in the gap of the ring. After the exposures the 304L samples were measured in thickness by using the SEM. The cross-section of the casted samples was measured each 45° avoiding the edges of the ring and, in the samples which lost its shape during the exposure, the deformed areas were avoided as well. The thicknesses before and after the exposure were compared and the materials loss was determined in the terms of microns lost. The error in measurements is estimated to 10 microns.

5 Results

5.1 Pre-study

The main aim of the pre-study was to investigate the kinetics of reactions related to deposit build-up and conversion versus material temperature. The results from the pre-study were used in order to sett up relevant parameters for the main study.

5.1.1 Conversion of KCl in P13

In order to investigate the kinetics of the sulphation reaction of a KCl rich deposit, samples pre-deposited with KCl (about 1,987 $\mu g/cm^2$) was exposed in the biomass-fired boiler P13.

IC measurements

In order to quantify the amount of chloride and sulfate ions that were present on the sample rings after exposure Ion Chromatography (IC) analysis was performed. With the IC analysis the aim is to try to follow the conversion of the applied salt by comparing the amount of salt still remaining after exposure. In order to know how fast the deposit formed on a sample without any pre-deposited salt, reference samples of pre-oxidized Sanicro28 were exposed during each temperature and exposure time. Due to the difficult experimental conditions, the results are to various extents affected by spallation and errors related to local variations of the deposit buildup.

The amounts of Cl^- and SO_4^{2-} analyzed by IC on the samples treated with KCl and the reference samples exposed in P13 without any pre-deposited coating are presented in Figure 16 and Figure 17.

The table with all the calculated data is presented in Appendix V.

For the reference samples, i.e. without any pre-deposited KCl, the amount of detectable Cl^- and SO_4^{2-} after 1 hour is low, see Figure 16 and Figure 17. The sulphur to chlorine ratio (S/Cl) is measured to be 1.3, 9.3 and 2.3 for three temperatures (450, 525 and 600 °C, respectively). The reference samples exposed for 24 hours have increased the presence of sulfate whereas the chlorine content is roughly the same. Hence, the S/Cl ratios have increased dramatically compared to the 1 hour samples, being for the 24 hours sample in the range of 50-120.

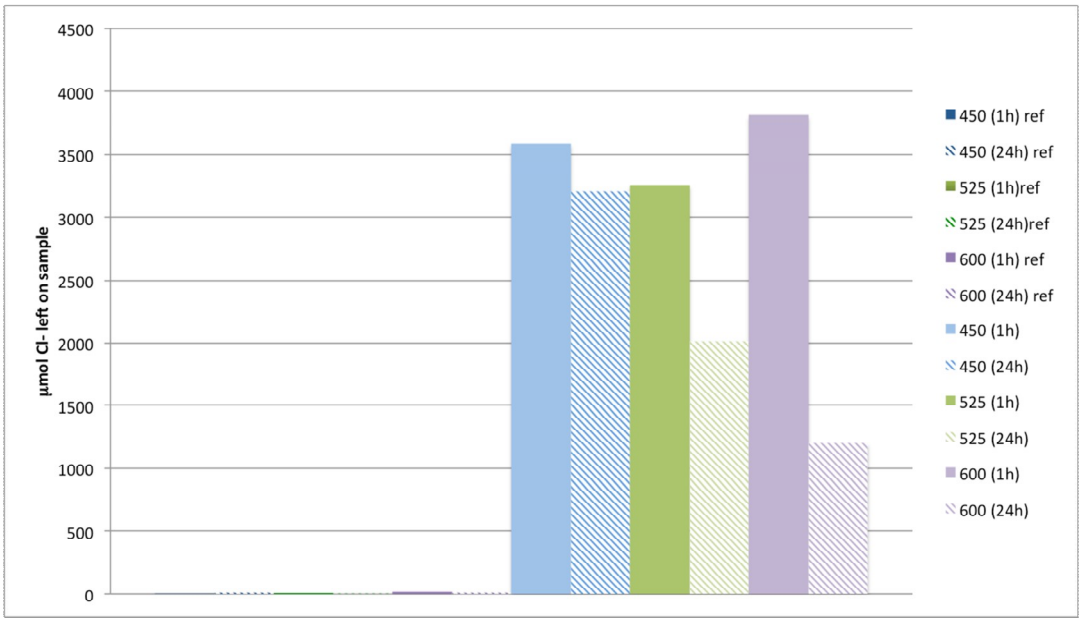


Figure 16. Amount of Cl^- measured in mol of the KCl treated sample after being exposed at different temperatures and times

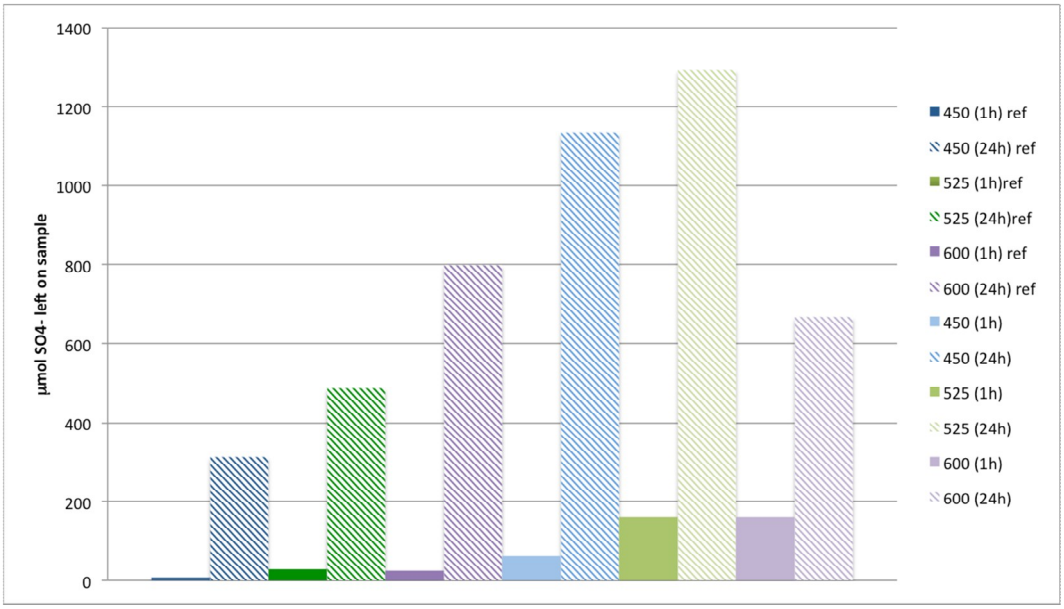


Figure 17. Amount of SO_4^{2-} measured in mol left on the KCl treated sample after being exposed at different temperatures and times

The samples pre-deposited with KCl, all show an increased presence of sulphate compared to the corresponding reference samples, see Figure 17. This indicates that the KCl pre-deposited on the samples have been partly sulphated. Since the samples experienced sizeable spallation (between 36-88% of the applied KCl is not accounted for, taken the sulphation into account), it is difficult to estimate the degree of sulphation. However, from the IC analysis, it can be seen that the amount of remaining chlorine on the sample decreases with time and temperature, showing the lowest amount of chlorine for the sample exposed for 24 hours at 600 °C, see Figure 18. Thus, increasing the exposure time and the temperature implies that the conversion of KCl to K_2SO_4 is also increased.

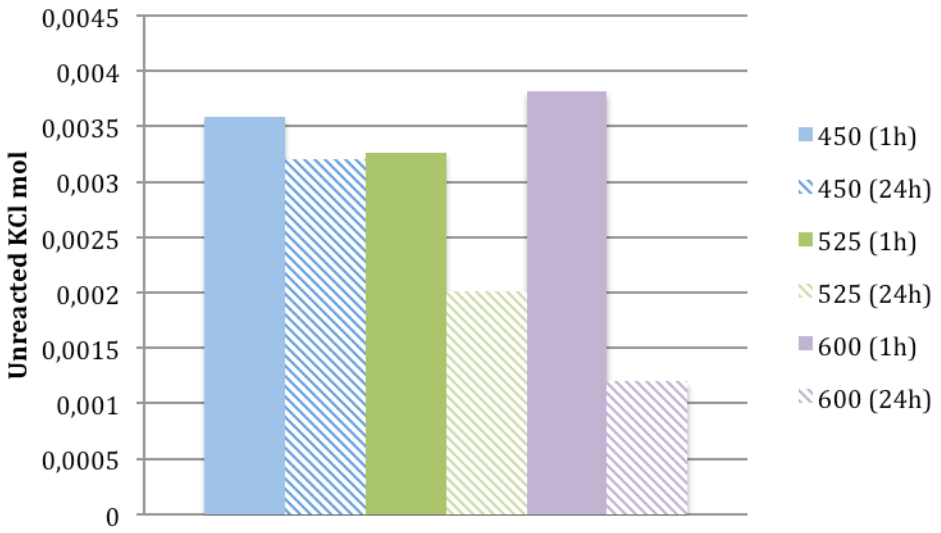


Figure 18. Unreacted mols of KCl in the samples for different exposure temperatures and times

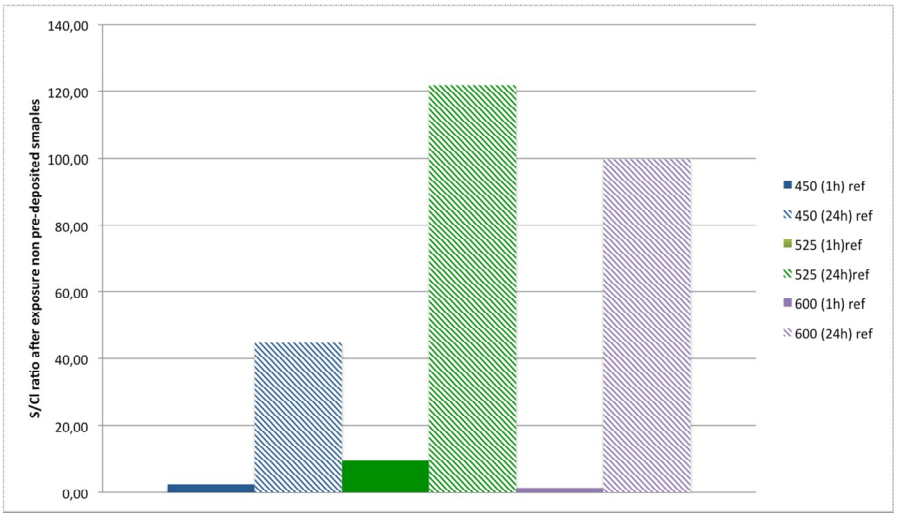


Figure 19. ***S/Cl ratio reference exposures***

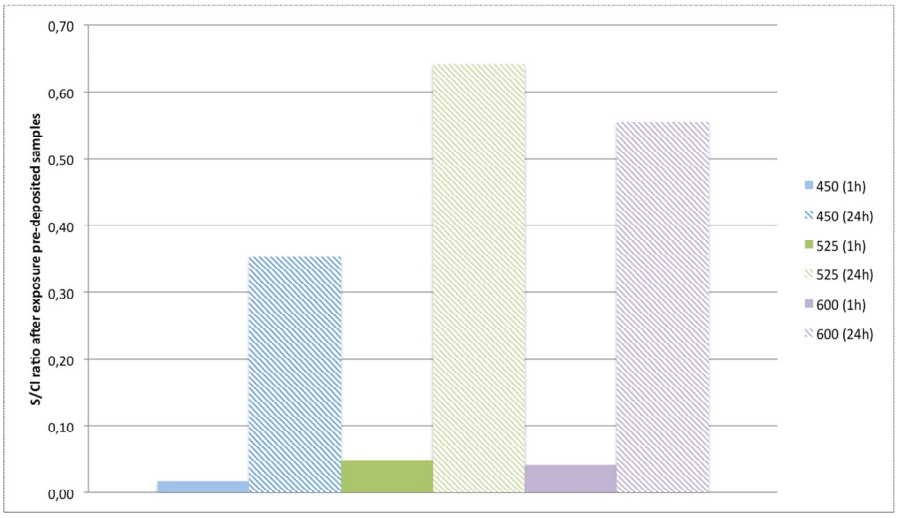


Figure 20. ***S/Cl ratio samples pre-deposited with KCl exposures***

Microstructural investigation of deposits (SEM/EDX)
Selected samples were investigated with SEM/EDX in order to better study the kinetics of the transformation. For this analysis the samples exposed for 1 and 24 hours at 600 °C were selected. There is local variation on all investigated samples and therefore only representative part each sample has been selected for analysis.

A low magnification SEM BSE image of polished cross-sections of the pre-deposited KCl sample exposed at 600 °C for 1 hour in the P13 boiler is shown in Figure 21. It shows that after 1 hour exposure at 600 °C an approximately 80 micron thick KCl layer can be seen on the sample. This should be compared with a calculated KCl thickness of 100 micron that was deposited on each sample. On some parts of the sample the KCl layer is detached probably due to sample preparation, see Figure 21.

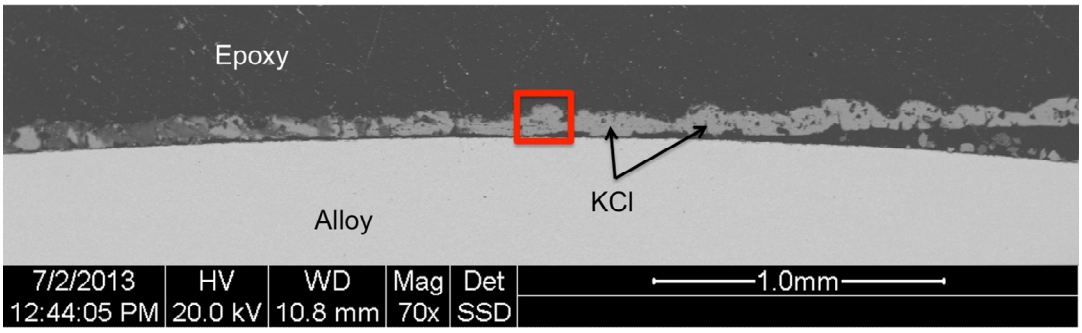


Figure 21. Backscattered SEM image of the KCl treated sample exposed at 600°C 1 hour

A high magnification SEM BSE image showing the marked region in Figure 21 indicates that typically four different layers cover the alloy (see Figure 22). Closest to the alloy a very thin oxide layer can be observed and above that the much thicker KCl layer is present. The outer part of the KCl layer has a different contrast and above this layer some deposits can be observed. The SEM/EDX results of this area are presented in Figure 23. The thin layer closest to metal is according to the EDX analysis rich in chromium and oxygen, i.e. the oxide formed during the pre-oxidation. The pre-deposited KCl layer is dominating the scale and according to the sulphur map, the sulphation of KCl have not occurred to any major extent. However on the top of the KCl layer, a thin sulphur enrichment can be seen, indicating that the KCl layer have started to be converted into K_2SO_4. This was difficult to see in the EDX map but was instead concluded from point analysis and the BSE image giving a different contrast. However this layer is thin and it is therefore difficult to

quantify the exact composition. On top of this thin layer some areas enriched in sulphur can in addition be observed. Most of them are enriched calcium according to the quantitative analysis, indicating the presence of $CaSO_4$, i.e. deposit formed on top of the KCl layer. These results are in the line with the IC results where about half of the KCl was unaccounted for and only a small fraction had sulfated.

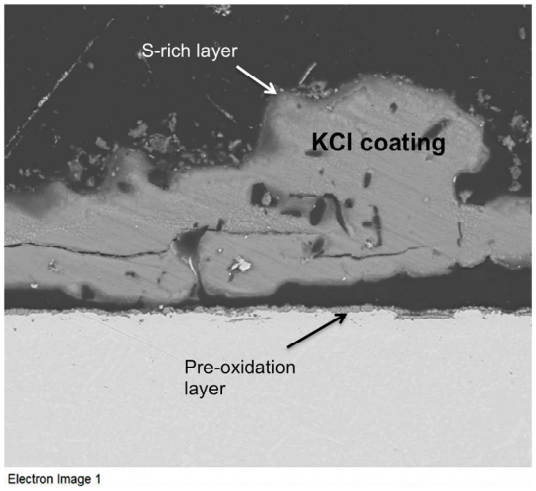


Figure 22. Composition of the previously marked area (Figure 6)

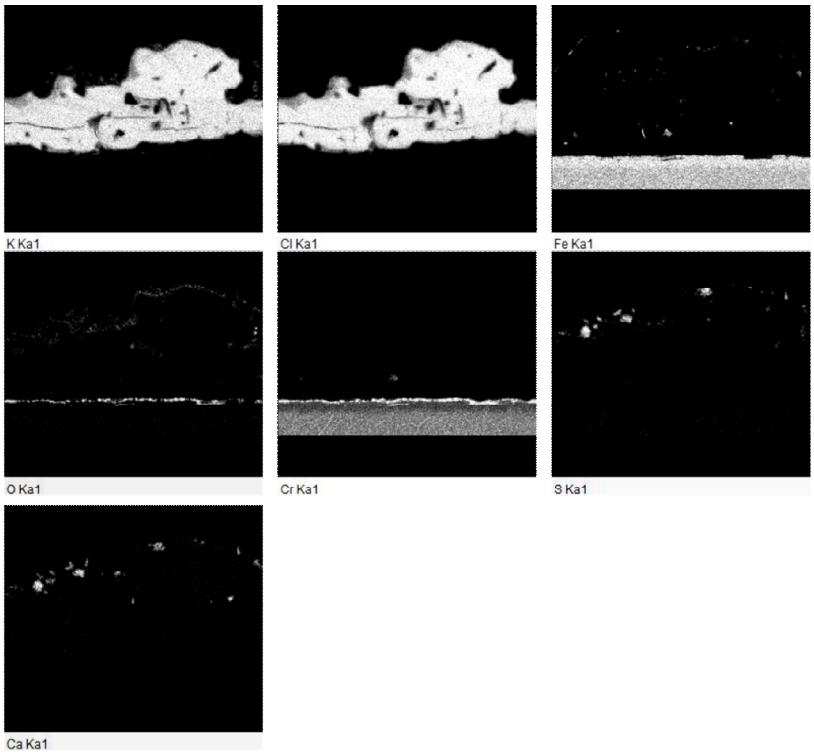


Figure 23. Composition of the previously marked area (Figure 6)

In order to investigate the kinetics of the initial reactions of the pre-deposited KCl samples at 600°C a cross-section of the 24 hours exposure was in addition investigated with SEM/EDX. The SEM BSE image in Figure 24, shows that a majority (80-90%) of the sample ring was covered by a 30 micron thick deposit layer after 24 hours of exposure. From the EDX analysis, presented in Figure 25, it is concluded that the deposit layer consists primarily of potassium, calcium, sodium, sulphur and oxygen, indicating the presence of different sulphate phases. In contrast, the chlorine content was below the detection limit. Thus, there are no signs of the pre-deposited KCl layer, which has either been converted into K_2SO_4 or has spalled off. Probably a combination of these has occurred. The chromium rich oxide formed during the pre-oxidation before depositing the KCl layer is still intact beneath the deposit layer.

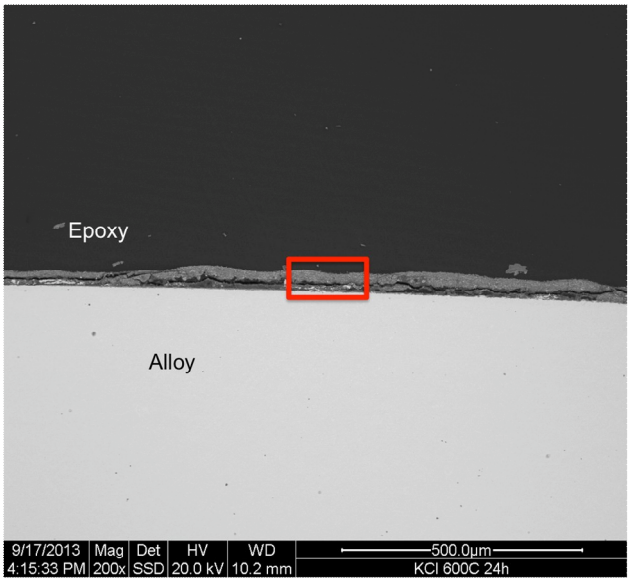


Figure 24. Backscattered SEM image of the KCl treated sample exposed at 600°C 24 hours

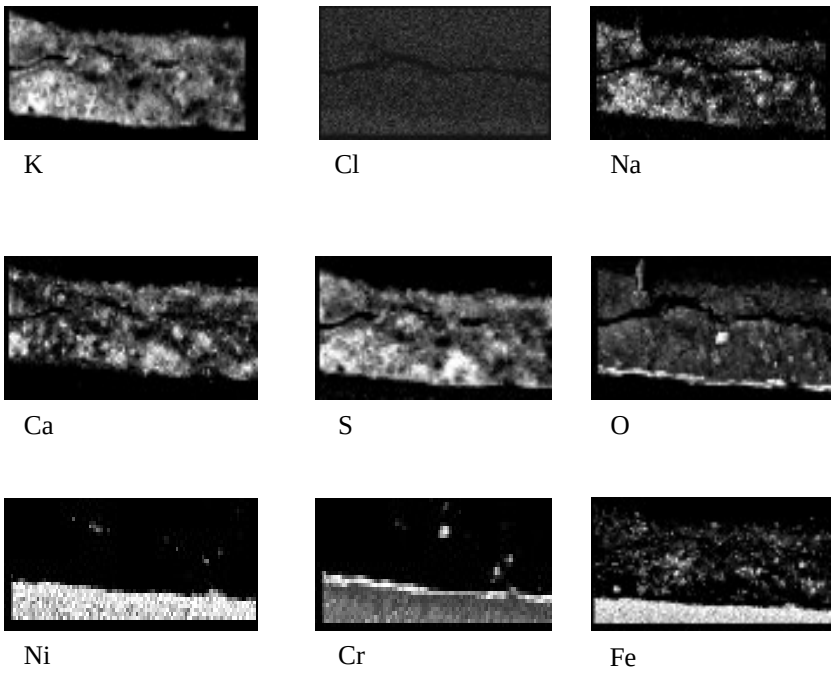


Figure 25. EDX mapping analysis of the KCl treated sam exposed at 600°C 24 hour

Figure 26 shows the remaining part (10-20%) of the sample ring exposed for 24 hours at 600 °C with a pre-deposited KCl layer. In these parts, the KCl layer is almost intact (75 micron) underneath a thicker deposit layer. Hence, after 24 hours of exposure, not all of the applied KCl has been converted to K_2SO_4. The deposit layer is consisting of sulphur containing compounds, probably K_2SO_4 and $CaSO_4$ or mixtures of them. Also the 24 hours microstructural investigation are in line with the IC results. Some KCl is still present (under a thick deposit) while more of the KCl has sulphated and/or spalled off.

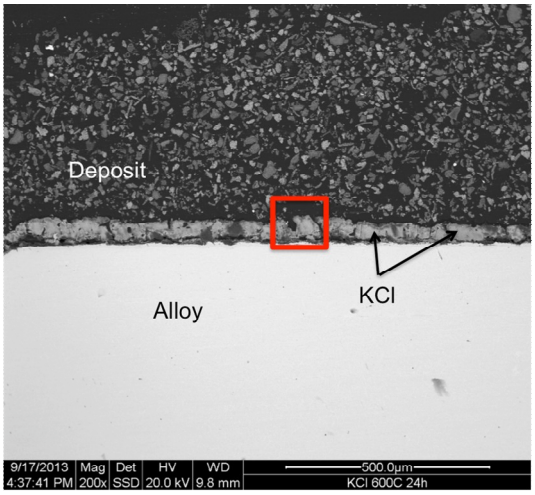


Figure 26. Backscattered SEM image of the minority area in the KCl treated sample exposed at 600°C 24 hours

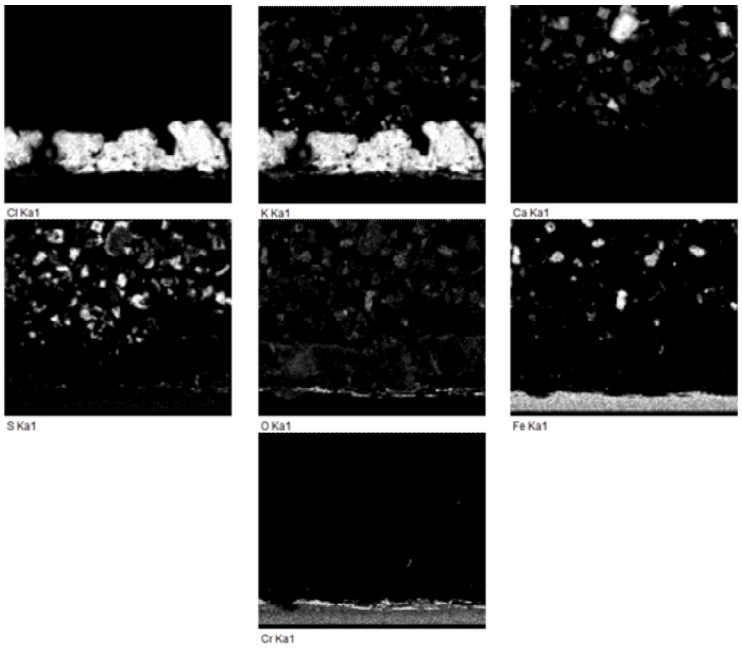


Figure 27. EDX mapping analysis of the minority area of the KCl treated sam exposed at 600°C 24 hours

5.1.2 Conversion of K_2SO_4 coating in P14

In order to investigate the kinetics of the chlorination of a sulphate rich deposit, samples pre-deposited with an about 100 micron thick K_2SO_4 deposit was exposed, in the same way as the KCl treated samples. However, instead of being exposed in the biomass-fired boiler P13, the K_2SO_4 treated samples were exposed in the waste-fired P14 boiler. The adhesion of the K_2SO_4 deposit was poor as some deposit spalled off already during handling of the samples.

IC measurements

The IC measurements for the K_2SO_4 treated samples does not give any significant information in the sense of improving or decreasing of sulphation, as they do for the KCl treated samples, due to the high spallation of the deposit.

The SO_4^{-2}/SO_4^{-2} ref ratio is calculated and presented in the Figure 28. Almost all the samples present a ratio minor than zero. The amount of SO_4^{2-} respect to the references decreases in all cases, except for the 600°C 24 hour and the 500°C 24 hour exposure samples. So, it seems that the SO_4^{2-} coming from the K_2SO_4 coating is lost or spalled off during the exposure time. This spallation of the K_2SO_4 is corroborated by the SEM images.

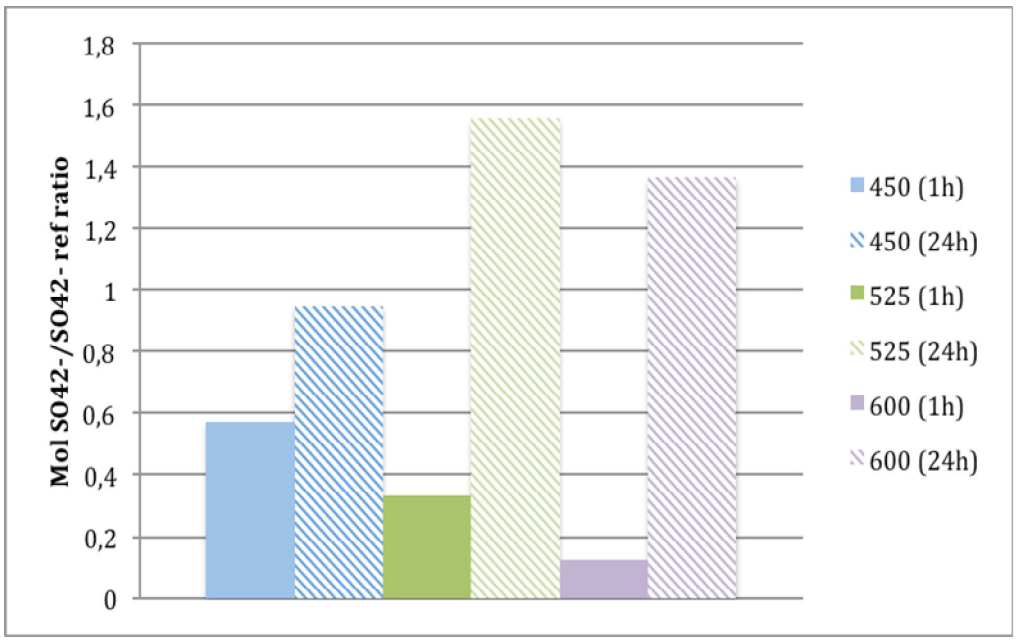


Figure 28. ***Mol SO_4^{2-} detected in the K_2SO_4 treated samples related to the mol SO_4^{2-} detected on its reference materials***

Microstructural investigation of deposits (SEM/EDX)
Selected samples were investigated with SEM/EDX in order to better study the kinetics of the transformation. For this analysis the samples exposed for 1 and 24 hours at 600 C were selected as with the study of the KCl deposit. There is again local variation on all investigated samples and representative part has been selected for analysis. However on the samples with a K_2SO_4 deposit the adhesion was generally very low which resulted in spallation and/or deposits that have been expanded during sample preparation. This makes it more difficult to interpret the SEM/EDX results and especially the quantitative data.

The sample pre-deposited with K_2SO_4 exposed for 1 hour at 600°C suffered from severe spallation. No or very small amounts of deposits was observed with SEM/EDX. The spallation was not as severe for the K_2SO_4 samples exposed for a longer exposure time (i.e. 24 hours). A SEM BSE image of the sample pre-deposited with K_2SO_4 and exposed for 24 hours is shown in Figure 29. This type of morphology covered about 70 % of the sample. The SEM/EDX analysis had to be interpreted because of the difficult morphology and outer part of the deposit layer was concluded to contain more chloride. Beneath this layer, an inner layer containing less amounts of chlorine and more sulphure could be observed. It is suggested that the inner layer is the remnants of the originally deposited K_2SO_4 layer. Since no corrosion is observed beneath the pre-deposited layer it is proposed that this layer have been acting as a barrier layer of the corrosive alkali chloride deposit formed on top.

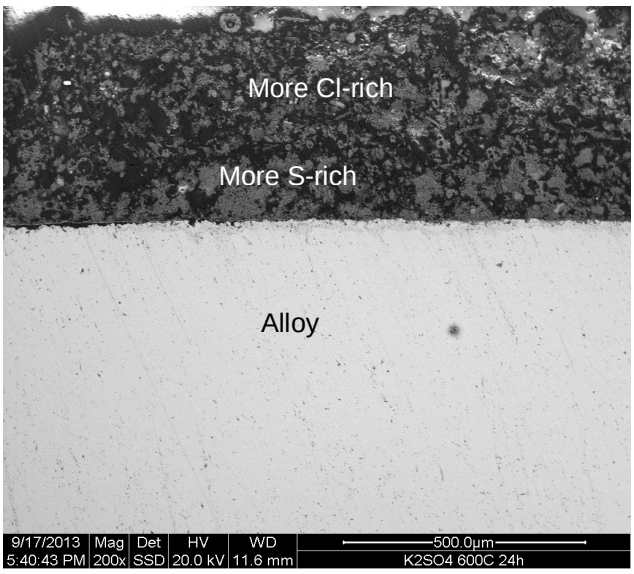


Figure 29. Backscattered SEM image of the K_2SO_4 sample exposed at 600°C for 24 hours

Figure 30 shows a BSE image of the typical morphology of the remaining 30% of the sample. In this region, there are no signs of the pre-deposited K_2SO_4 layer and a deposit rich in alkali chlorides can be seen. A thick oxide scale with signs of an alkali chloride induced corrosion attack has replaced the thin pre-oxidized formed Cr rich oxide. There are a large difference compared to the regions where there were signs of a intact K_2SO_4 layer (compare Figure 29 and Figure 30)

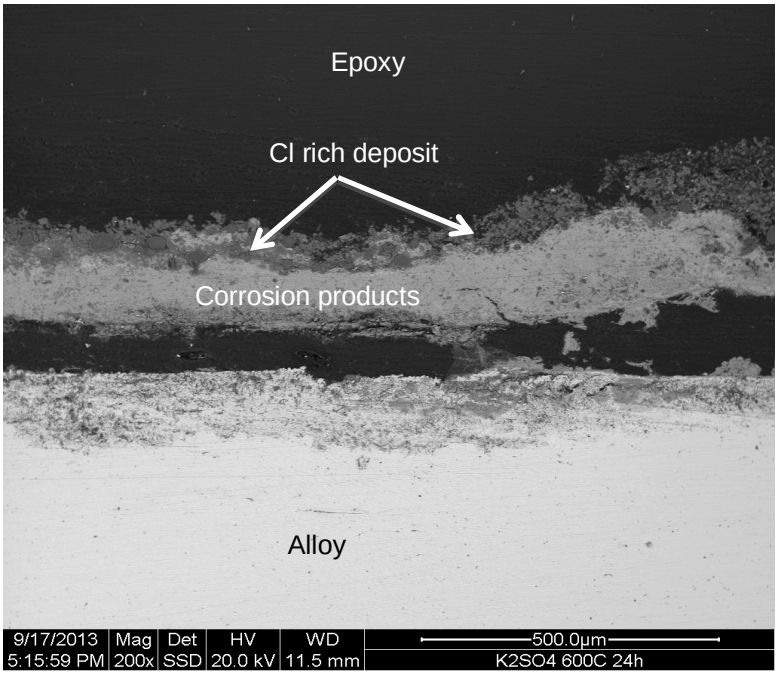


Figure 30. Backscattered SEM image of the minority area of the K_2SO_4 sample exposed at 600°C for 24 hours

5.1.3 Summary pre-study

The pre-study investigates the "memory effect" of two artificial deposits in two different boilers (one representing a corrosive environment (P14) and one representing a non-corrosive environment (P13)). The results from the study of a corrosive deposit (represented by pure KCl) indicates that it will be sulphated in a flue gas from a less corrosive fuel in the P13 boiler. The IC results show a larger fraction of SO_4 ions and less Cl ions after longer exposure times and at higher exposure temperatures. Thus, increasing the exposure time and the temperature implies that the conversion of KCl to K_2SO_4 is also increased. This was in addition supported by the results from the SEM/EDX investigation. However, a large part of the KCl could not be accounted for which indicates spallation of the deposit during the exposure.

The results also indicate that the sulphation process slows down or stops under a dense deposit.

The results from the study of a non-corrosive deposit (represented by pure K_2SO_4) indicate that it can form a protective barrier between a corrosive deposit and the alloy when exposed in a corrosive fuel such as in the P14 boiler. However, the adhesion of the non-corrosive deposit was very poor and the results were difficult to interpret.

Based on the pre-study results the main study was planned. The aim was to create an as thick protective non-corrosive deposit as possible in P13 and therefore a two-week first exposure was planned in P13. The second and third exposure times had to be set to about one week based on the kinetics of the up 24 hours samples in the pre-study and in order to be able to have time to investigate the sample as the project was run during the final part of the program period. As the number of samples on the probes is limited the highest and lowest temperatures were selected.

5.2 Main study

The main-study was performed during autumn 2013 in boiler P13 and P14 at E.On´s plant in Händelö, Norrköping. The exposure times were based on the results in the pre-study and were performed in three steps:

- First exposure in P13 in order to produce a protective deposit lasted for 313 hours.
- The second exposure (both P13 and P14) lasted for 256 hours.
- The third exposure in P13 for lasted for 162 hours.

All exposure conditions and temperatures are summarized in Table 2.

5.2.1 General observations

The Figure 31 shows the probes after each exposure. The first exposure was carried out in P13 boiler for 313 hours. In general, all the samples showed a high degree of spallation of the deposit formed during the exposure. This was the same for all materials and temperatures. During the second exposure one probe was again exposed in P13 while the other probe was exposed in P14. Selected parts of the deposit spalled off on the probe exposed in P13 while the exposure in P14 generated large amounts of deposit on the probe. It is even hard to distinguish the temperature zones on the probe exposed in P14 and it was difficult to remove the samples. The probe tip was damaged and some force had to be used in order to be able to remove the samples. To be able to insert this probe for the final exposure in P13 it was necessary to manually remove the outer part of the deposit.

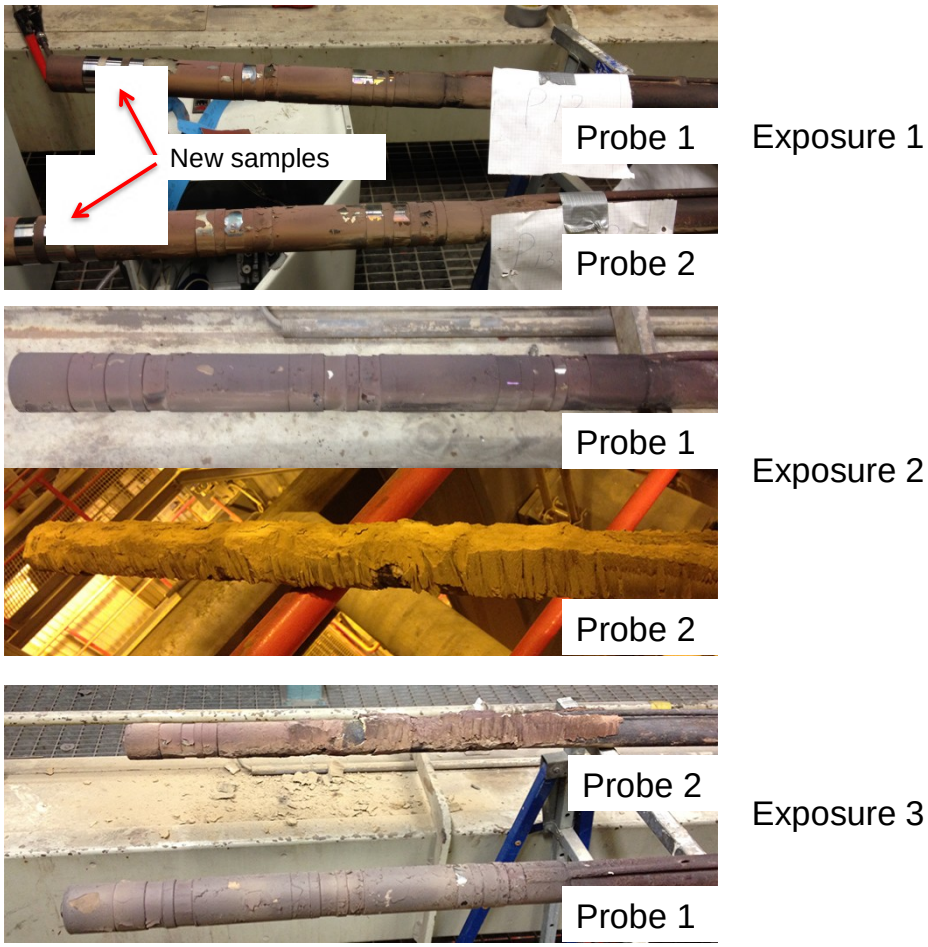


Figure 31. Probes after the different exposure steps

General observations after the exposures were:

- After exposures in P13 parts of the deposit spalled off on all samples.
- All exposures in P13 generated relatively small amounts of deposits.
- The exposure in P14 generated large amount of deposit. The deposit was very corrosive (damage the probe) and difficult to remove.

5.2.2 Characterization of deposits and the corrosion products

After each exposure the three samples placed closest to the tip of both probes were removed and new samples were mounted. This resulted in a large number of samples. All samples were optically investigated and documented, see Appendix IV. Based on the optical investigation some samples were

selected for a detailed investigation with SEM/EDX. The samples selected for a more detailed analysis were:

- Exposed only in P13 during the second exposure to be able to study the build up of the non-corrosive deposit.
- Exposed in P13-P13-P13 to be able to study the non-corrosive deposit after longer exposure time.
- Exposed in P14 during the second exposure to be able to study the effect of the corrosive environment without a preformed non-corrosive deposit.
- Exposed in P13-P14-P13 to be able to study the effect of a non-corrosive deposit when exposed to a corrosive environment.

During all exposures three different materials (Sanicro28, 304L and T22) were inserted at both temperatures. However, the first investigation showed that most of the low-alloyed steel (T22) samples were extremely corroded and it was decided together with the project group to further investigate only the 304L and San28 samples. It was in addition decided to focus the detailed investigation on the samples exposed at the high temperature (600°C).

Figure 32. Investigated 304L samples

Photos of the investigated 304L samples can be seen in Figure 32. All 304L samples were investigated at Chalmers and the San28 samples by Eon UK.

Exposure in P13 (second exposure) - Build up of the non-corrosive deposit
In order to study the build up of the deposit and the corrosion attack in the less corrosive environment (boiler P13) cross-sections were polished of the 304L and San28 samples exposed during the second exposure (236h) in P13. These samples can in addition be directly compared with the samples exposed during the second exposure in P14. As can be seen in Figure 33 the 304L sample is covered with a thin deposit with bad adhesion.

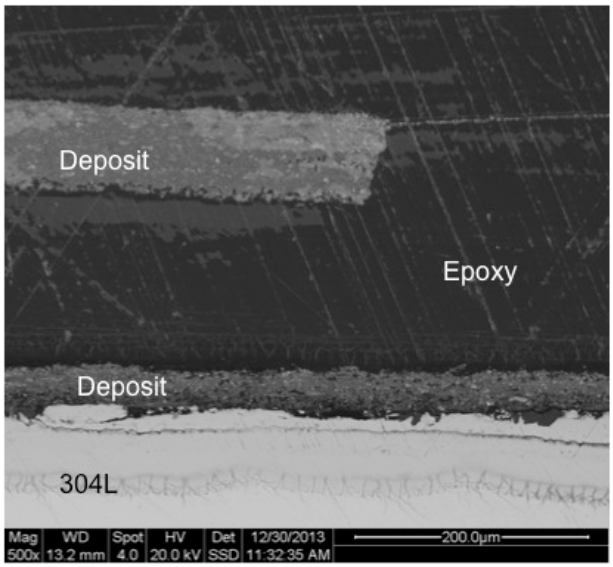


Figure 33. Backscattered SEM image of the 304L sample after one exposure step in P13. Detail of the spallation of the deposit

The cross-section of the sample shows that the deposit is approximately 80 µm thick, see Figure 34. The oxide scale is very thin and the deposit consists of sodium, calcium and potassium sulphates but very small amount of chlorine, see EDX maps in Figure 35. The non-corrosive deposit and thin oxide scale was in line with the material loss measurements which showed a material loss of 40 µm on the 304L sample.

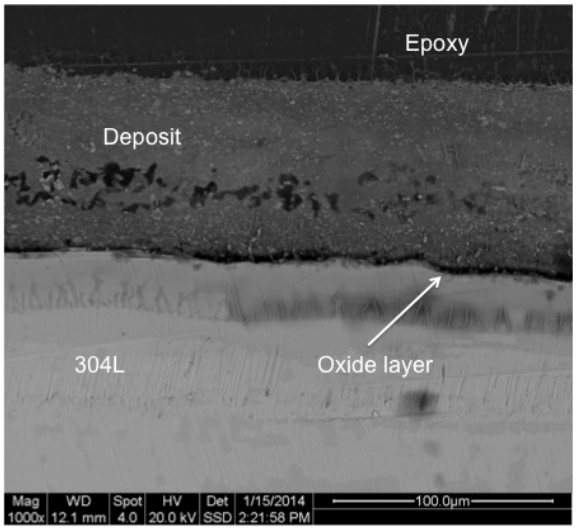


Figure 34. Backscattered SEM image of the 304L sample after one exposure step in P13

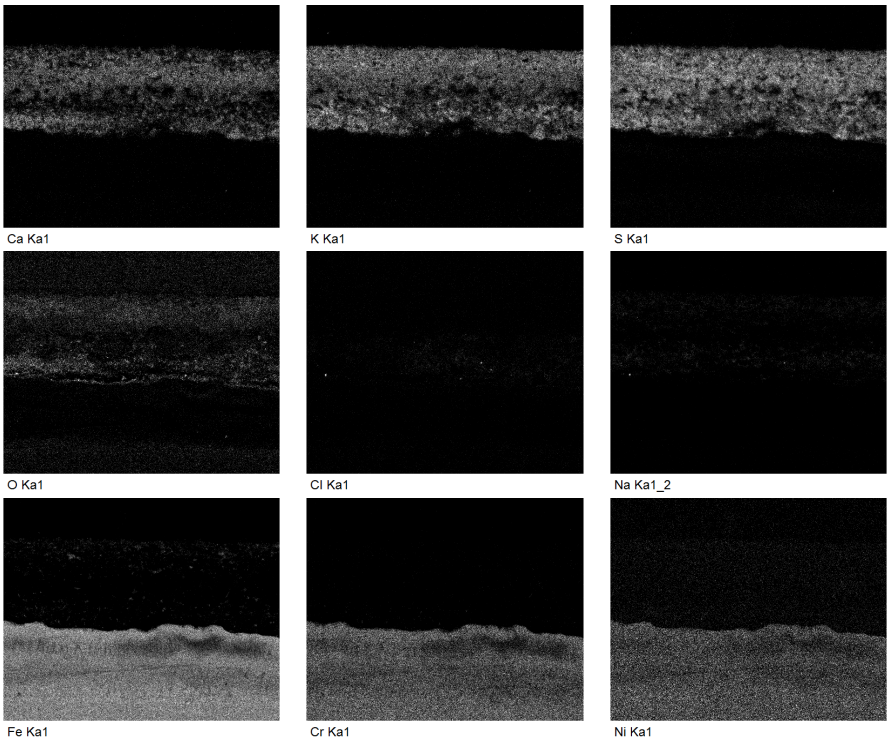


Figure 35. EDX mapping analysis of the 304L sample exposed in P13

Analysis performed on the San28 sample confirms the 304L results. The thickness and composition of the deposit is similar to the one formed on 304L, see Figure 36 and EDX maps in Appendix VI.

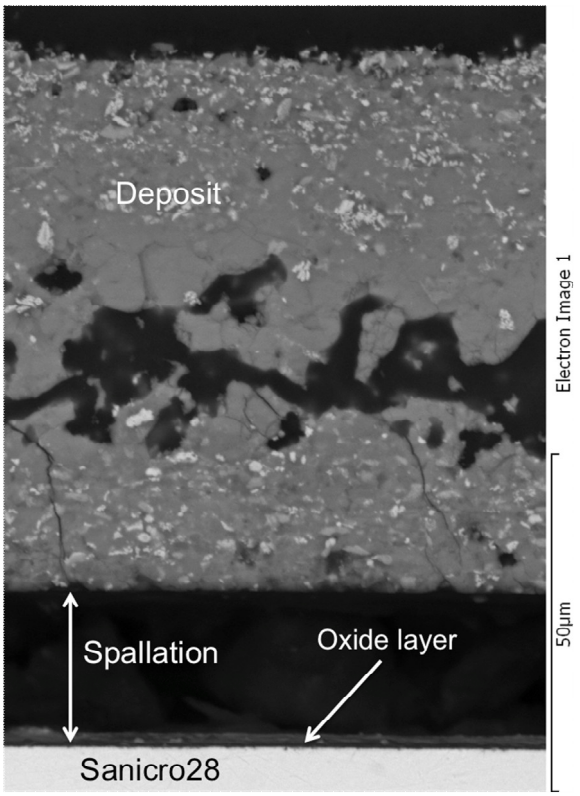


Figure 36. Backscattered SEM image of the Sanicro28 sample after one exposure step in P13

Exposure in P13-P13-P13 - The long time effect of the non-corrosive deposit
In order to characterize the deposit and corrosion attack after longer times in the less corrosive environment (boiler P13) cross-sections were polished of the 304L and San28 samples exposed during all exposures in P13. As can be seen in Figure 37 the 304L sample is covered with a relatively thin deposit with bad adhesion is some area of the surface.

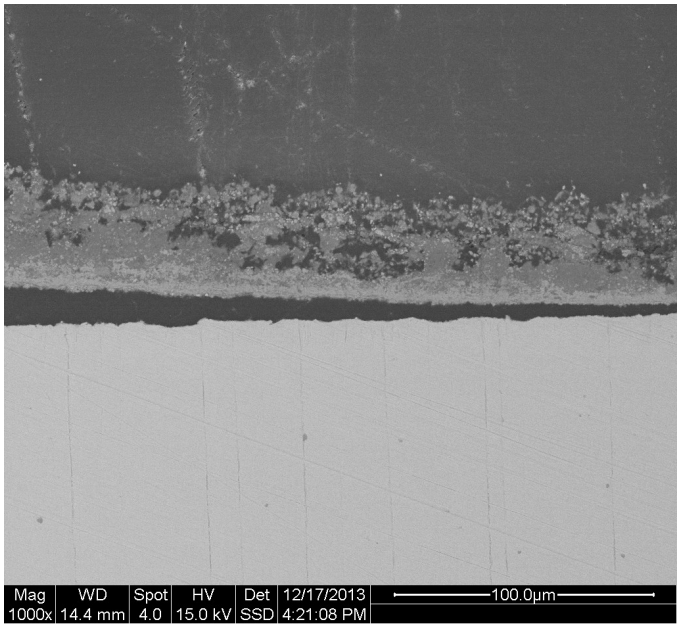


Figure 37. Backscattered SEM image of the 304L sample after three exposure steps in P13. Detail of spallation of the deposit

The cross-section of the sample shows that the deposit is approximately 100 µm thick, see Figure 38. The deposit can be divided into different layers corresponding to the different exposures. The corrosion scale is thin (about 5µm thick) and the deposit consists of sodium, calcium and potassium sulphates but very small amount of chlorine, see EDX maps in Figure 39. The non-corrosive deposit and relatively thin oxide scale was again in line with the material loss measurements which showed a material loss of 47 µm on the 304L sample after 313 + 267 + 167 hours exposure. Analysis performed on the San28 sample confirms the 304L results. Images of the polished cross-section performed on San28 in Figure 40 and EDX maps in Appendix VI.

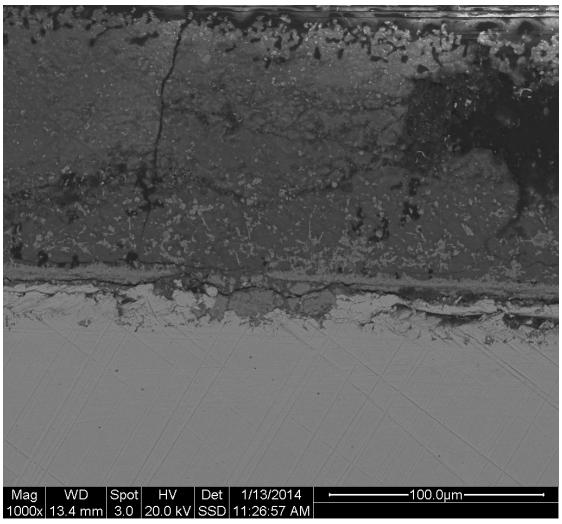


Figure 38. Backscattered SEM image of the 304L sample after three exposure steps in P13

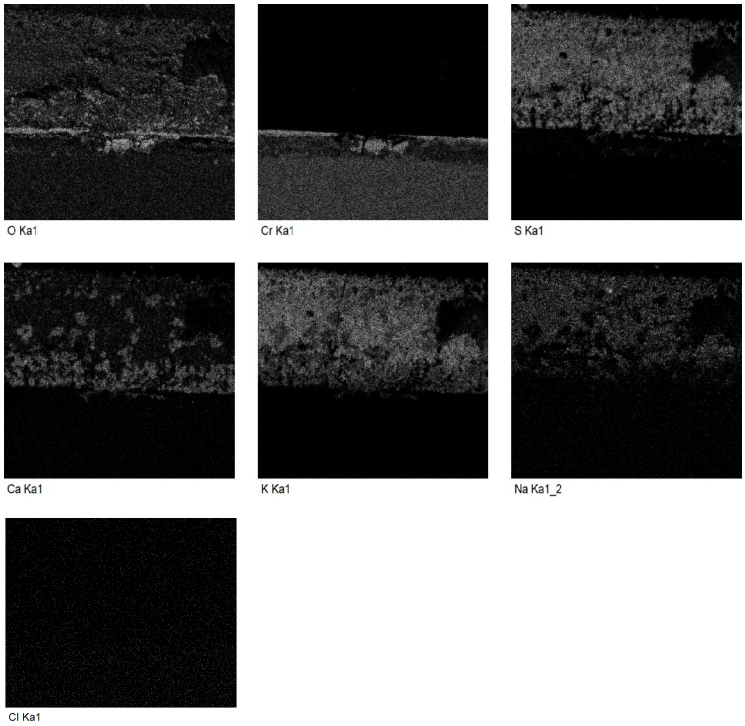


Figure 39. EDX mapping analysis of the 304L sample exposed during three steps in P13

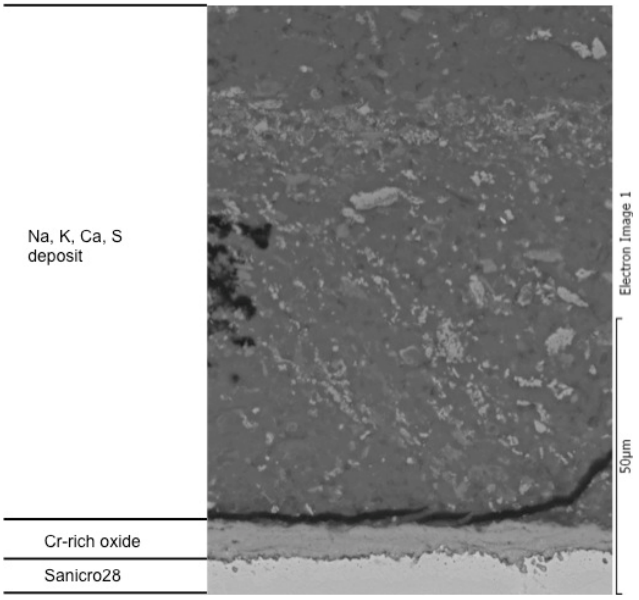


Figure 40. Backscattered SEM image of the Sanicro28 sample after three exposure steps in P13

5.2.3 Exposure in P14 – The effect of the corrosive deposit

In order to characterize the deposit and corrosion attack in the corrosive environment (boiler P14) cross-sections were polished of the 304L and San28 samples exposed during the second exposure in P14. As can be seen in Figure 41 the 304L sample is covered with a thick deposit. The probe was difficult to handle after the exposure in P14 and some force had to be used to shift samples. This resulted in that some/all deposit fell of the samples.

The cross-section of the 304L sample shows only the inner part of the corrosion products, which is approximately 100 µm thick (see Figure 41). It can be divided into several different layers metal chloride layers, see EDX in Figure 42. The corrosion attack is uniform over the whole sample and the part remaining on the sample in probably only the inner part. Due to this it was not possible to detect any deposit.

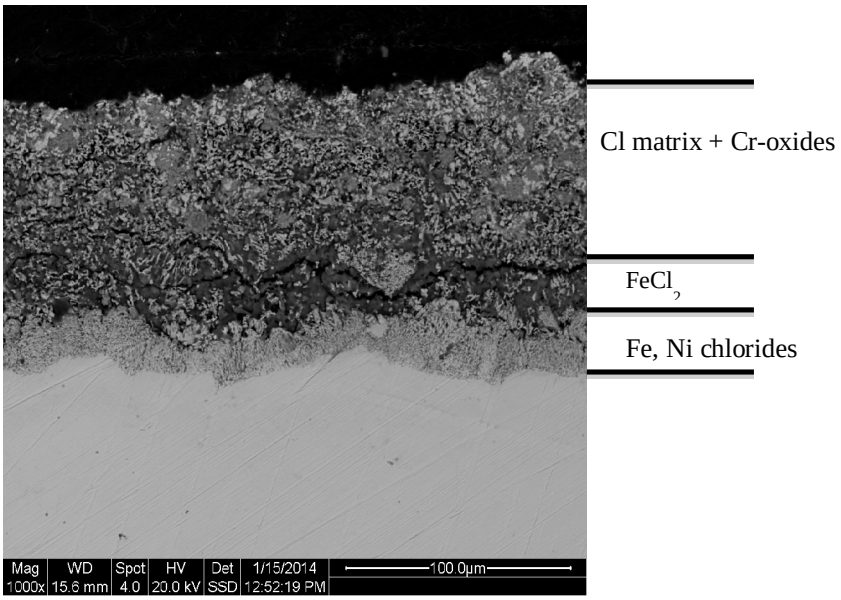


Figure 41. Backscattered SEM image of the 304L sample after one step exposure in P14

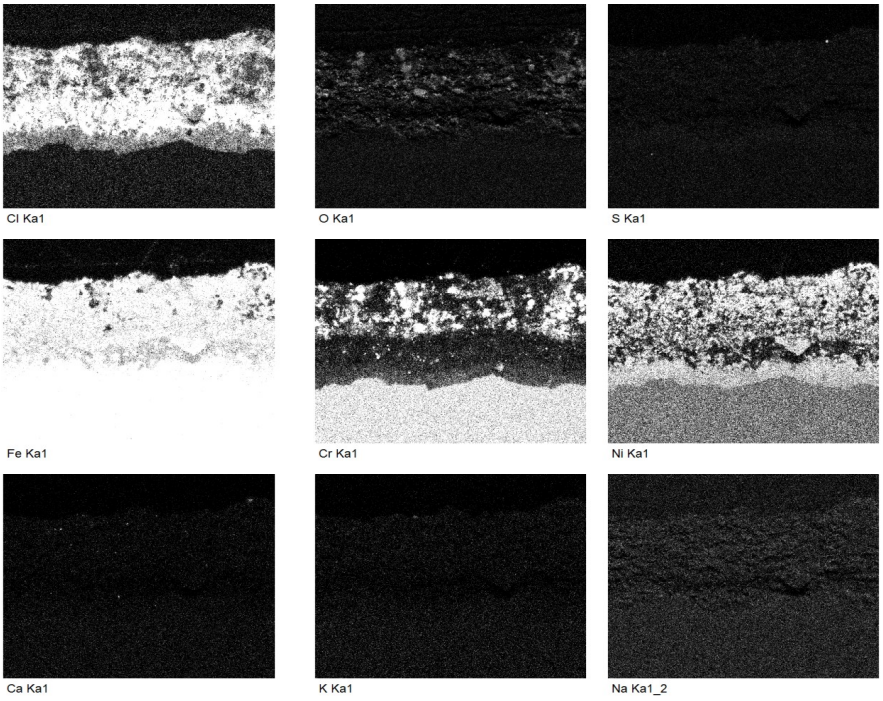


Figure 42. EDX mapping analysis of the 304L sample exposed in P14

The corrosive deposit and thick corrosion products were in line with the material loss measurements, which showed a material loss of 466 µm on the 304L sample. Analysis performed on the Sanicro28 sample confirms the 304L results of a very corroded sample with metal chlorides at the metal/oxide interface. Images of the polished cross-section performed on Sanicro28 can be seen in Figure 43 and EDX maps in Appendix VI.

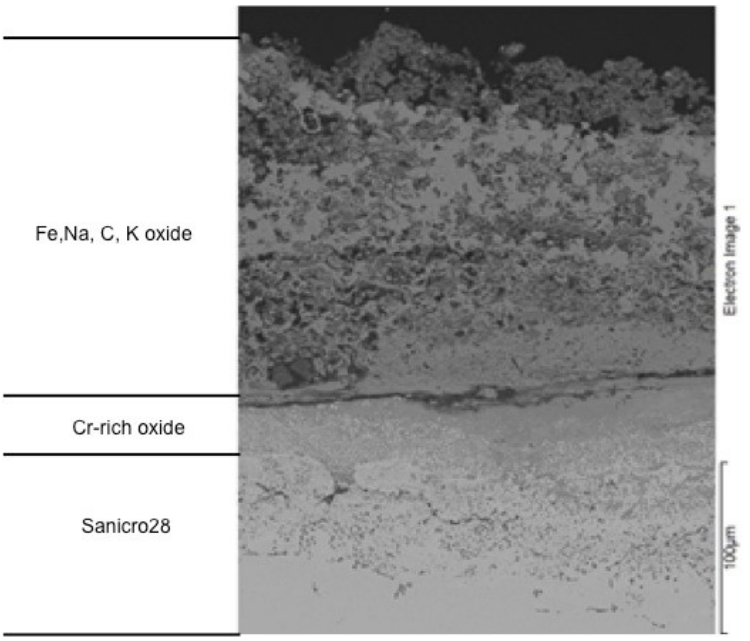


Figure 43. Backscattered SEM image of the Sanicro28 sample after one step exposure in P14

5.2.4 Exposure in P13-P14-P13 – The effect of a protective deposit in a corrosive environment

In order to characterize the deposit and corrosion attack of the samples exposed first in the non-corrosive environment (boiler P13) then the corrosive environment (P14) and finally in the P13 boiler cross-sections were polished of the 304L and Sanicro28 samples. As can be seen in Figure 44, the 304L sample is covered with a 40 µm corrosion layer of corrosion products. The cross-section images indicate that the outer part of the oxide scale has spalled of and it shows only the inner part of the corrosion products, which is approximately 50 µm thick (see Figure 44). The scale consists of a layer of corrosion products, covered by a chromium-rich oxide follow by the spalled

deposit, see EDX maps in 0. No or very small amount of Cl could be observed in the corrosion products. It was not possible to detect any deposit

in the cross-section due to spallation of the deposit.

The thickness of the remaining corrosion products was in line with the material loss measurements which showed a material loss of 329 µm on the 304L sample. Analysis performed on the San28 sample again confirms the 304L results. An images of the polished Sanicro28cross-section can be seen in Figure 45 and the EDX maps in Appendix VI. No or very small chlorine content could be found on the Sanicro28 sample as on the 304L sample.

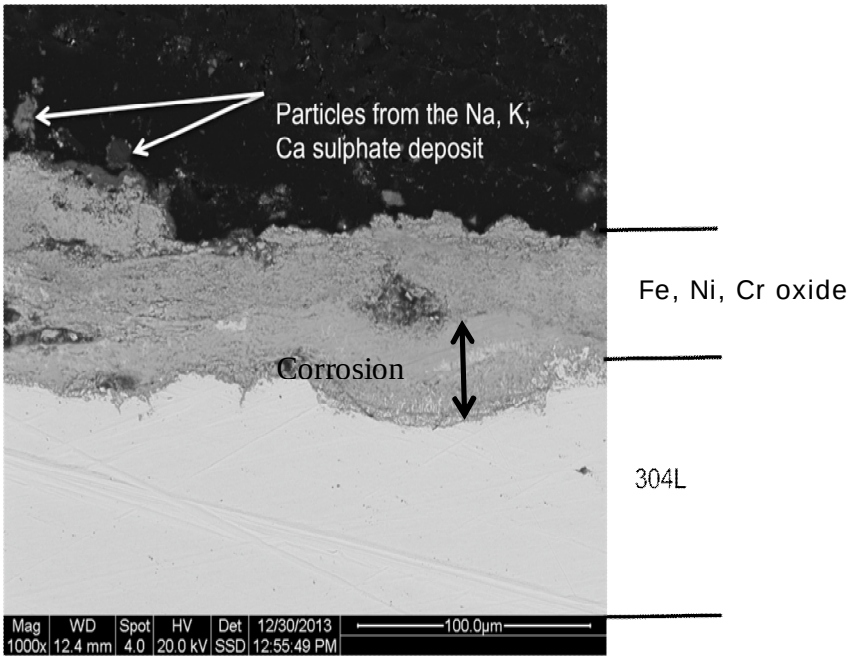


Figure 44. Backscattered SEM image of the 304L sample after one exposure step in P13, one in P14 and last one in P13

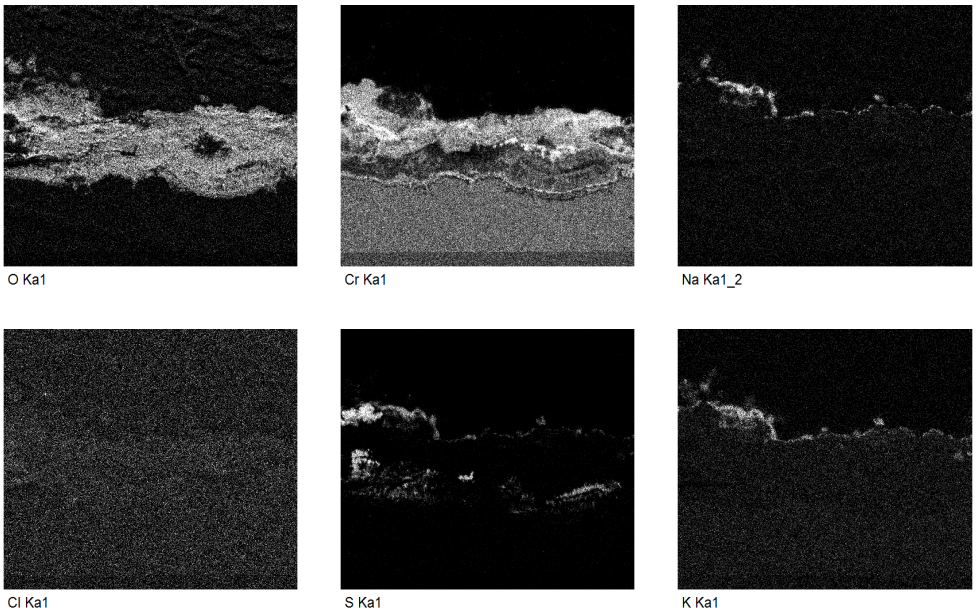


Figure 46. EDX mapping analysis of the 304L sample exposed for step in P13, one in P14 and last one in P13

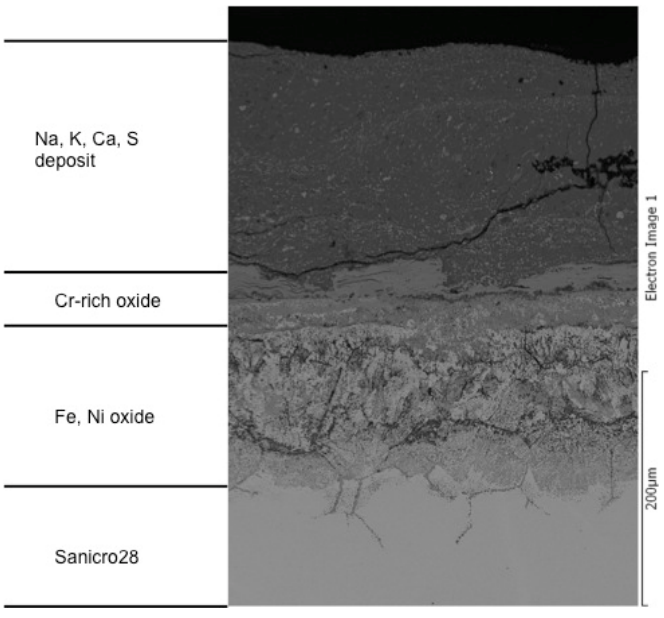


Figure 45. Backscattered SEM image of the Sanicro28 sample after one exposure step in P13, one in P14 and last one in P13

5.2.5 Summary main study

The results show that an exposure in the less corrosive boiler P13 resulted in a thin deposit that was dominated by sulphates. The formed deposit layer had poor adhesion, which resulted in spallation after outtakes. Despite this, the observed corrosion attack was minor even after longer exposure times. The material loss of 304L was very small and within the error of the measuring technique. The formation of protective scale on the stainless steels was confirmed by SEM/EDX. Exposure in the waste fired boiler P14 resulted in the formation of large amounts of very corrosive deposit. This resulted in a substantial corrosion attack and thereby a large material loss despite the short exposure time (256 hours). The detailed investigation revealed chlorine-induced corrosion with large amount of metal chlorides at the metal/oxide interface on the stainless steels.

The investigation of the samples exposed in the P13-P14-P13 sequence showed less material loss then the samples exposed only in the P14 boiler (450 µm/1000h compared to 1820 µm/1000h). This despite the much longer exposure time, 313+256+162 hours compared to 256 hours. Furthermore, the detailed investigation of the corrosion attack of the samples exposed in the P13-P14-P13 sequence revealed a different microstructure compared to the samples exposed only in the P14 boiler. In the former case, the presence of metal chlorides within the corrosion product layer was scarce. This despite the substantial spallation of the protective deposit observed prior to the exposure in the P14 boiler. The material loss (450 µm/1000h) is however larger than for the corresponding sample exposed only in the P13 boiler (64 µm/1000h). This is in addition supported by the microstructural investigation.

6 Analysis of the results

An increased knowledge of the relationship between dynamic corrosion mechanisms, fuel specification and possible steam operation temperatures can form a platform for how to implement gliding steam temperature control. There is a vast economic potential to optimize and correlate the boiler operation to current fuel quality and continuously use the increased net income potential within an advanced boiler. A potential limiting factor in this type of operation is periods of accelerated corrosion, severely decreasing the lifetime of e.g. the superheaters in the boiler.

This phenomenon is also one of the important issues listed in the KME project 601 and can be referred to as the corrosion attack during operation is due to historic boiler operation (which have resulted in certain deposits and corrosion products) rather than the fuel mix currently being used (corrosion memory). Thus, the formations of oxide scales and thick deposits from the past dictate the corrosion further on. As a consequence, the corrosion memory effect can be divided into two sub-areas; increased corrosion due to irreversible depletion of the steel (e.g. chromium depletion) and the rate of conversion of corrosive deposits, releasing corrosive species for further corrosion attack. It may however also be noted that there could exist a positive memory effects as well, non-corrosive deposits from earlier operation protects the underlying steel from the current flue gas composition. A boiler using the gliding temperature concept is more susceptible for this type of accelerated corrosion compared to conventional boilers. This since the change of steam temperature needs to be chosen, not only with respect to the corrosiveness of the current fuel mix, but also with respect to former corrosion history.

The present project aims to increase the knowledge of materials technology process solutions to minimize superheater corrosion with advanced steam data in boilers. The obtained results will contribute to the understanding of how a power plant with advanced steam data can be operated with variations in fuel quality. By addressing the corrosion memory effect, boiler operators will benefit twofold; by getting new knowledge how to optimize the electrical efficiency using gliding temperatures and getting tools to minimize the corrosion using a smart operational strategy.

The project consists of two major exposure campaigns, namely the “pre-study” and the “main study”. The main aim of the pre-study was to investigate the kinetics of reactions related to deposit build-up and conversion versus material temperature. Thus, increasing the knowledge in one of the two corrosion memory sub-areas described above; namely the rate of conversion of corrosive deposits. The results from the pre-study were also used in order to set up relevant parameters for the main study. The main study is a first attempt to study the dynamic corrosion mechanisms at play (i.e. not investigating the corrosion attack from a clean steel tube but

instead take the former operation into account). Hence, by the setup of these two studies, new knowledge regarding the corrosion memory effect has been obtained.

In the main study the combined effect of the corrosion memory was studied. The ambition was to be able to answer the following questions:

1. Can the corrosion rate be maintained low after a change to more corrosive fuel if the steam temperature is lowered at the same time?
2. Is there a memory effect (resulting in increased corrosion rate) after the return to high steam temperature and less corrosive fuel?
3. Is there any "incubation time" (before the corrosion rate increases) for materials exposed at high steam temperature and less corrosive fuel after a change to low steam temperature and more corrosive fuel?

6.1.1 Pre-study

Within the pre-study of this project pre-deposited artificial deposits have successfully been exposed on air-cooled probes in two commercial boilers. The aim with these exposures was to investigate the kinetics and temperature dependence of the reactions of two artificial deposits (KCl and K_2SO_4) in two different environments (one corrosive environment (in boiler P14) and one "non-corrosive" environment (in boiler P13)). In order to avoid corrosion of the samples used in the pre-study, peroxidised Sanicro 28 samples were used. The pre-study was focused on the initial reactions and lasted up to 24 hours. The results from the study of the corrosive deposit (represented by pure KCl) indicate that the sulphation process in a flue gas from a less corrosive fuel as in the P13 boiler is fast. These results are in line with recent laboratory studies that have shown that the transformation of small amounts of KCl to K_2SO_4 is very fast at 600°C in O_2, H_2O and SO_2 [1]. In that case, 50% of the applied KCl (0.10 mg/cm^2) were converted into K_2SO_4 during the first 15 minutes in the presence of 300ppm SO_2 at 600°C. This would explain the thin sulphur rich layer on top of the KCl after 1 hour's exposure (see Figure 19). The SO_2 content in the flue gas of P13 is however much lower (31 ppm in average) than in the lab exposures. The IC results also show a larger fraction of SO_4^{2-} ions and less Cl^- ions after longer exposure times and at higher exposure temperatures. Thus, increasing the exposure time and the temperature implies that the conversion of KCl to K_2SO_4 is also increased. This was in addition supported by the results from the SEM/EDX investigation. However, a large part of the KCl could not be accounted for which indicates severe spallation of the deposit during the exposure. The results also indicate that the sulphation process slows down dramatically under a dense deposit.
The results from the study of a non-corrosive deposit (represented by pure K_2SO_4) indicate that it can form a protective barrier between a corrosive deposit and the alloy when exposed in a corrosive fuel such as in the P14 boiler. However, the adhesion of the non-corrosive deposit was very poor which resulted in two different cases. Parts where the artificial deposit spalled off resulted in severe corrosion of the pre-oxidized Sanicro 28 samples. The parts where the deposit remained during the exposure no or were small amounts of Cl could be found close to the alloy and the thin oxide layer was still present.

6.1.2 Main study

Based on the pre-study results the parameters of the main study was decided. The aim was to create an as thick protective non-corrosive deposit as possible in P13 and therefore a first two-week long exposure was planned in P13. The second and third exposure times had to be set to about one week based on the kinetics in the pre-study and in order to be able to have time to investigate the sample as the project was set up during the final part of the program period. As the number of samples on the probes was limited, the highest (600 °C) and lowest (450 °C) temperatures were selected. As the pre-study also showed the difficulty in handling the samples with deposits on it was decided by the project group to minimize the handling of samples in-between exposures. Therefore only the samples in the outer temperature zone were switched in-between each exposure. The three questions posted above will therefore be addressed together.

The results show that an exposure in the less corrosive boiler P13 resulted in a thin deposit that was dominated by sulphates. The deposit layer had poor adhesion, which resulted in spallation of large parts of the deposit (see Figure 47). The deposit was as expected non-corrosive and the observed corrosion attack was minor even after longer exposure times. The material loss was very small and within the error of the measuring technique also after the long exposure time (313+256+162 hours). The stainless steels formed a thin chromium rich protective scale, which can be seen in the SEM image (Figure 49). Exposure in the waste fired boiler P14 resulted in the formation of large amounts of very corrosive deposit (see Figure 48). This resulted, as expected, in a substantial corrosion attack and thereby a large material loss despite the short exposure time (256 hours). The detailed investigation revealed chlorine-induced corrosion with large amount of metal chlorides at the metal/oxide interface on both the stainless steels.

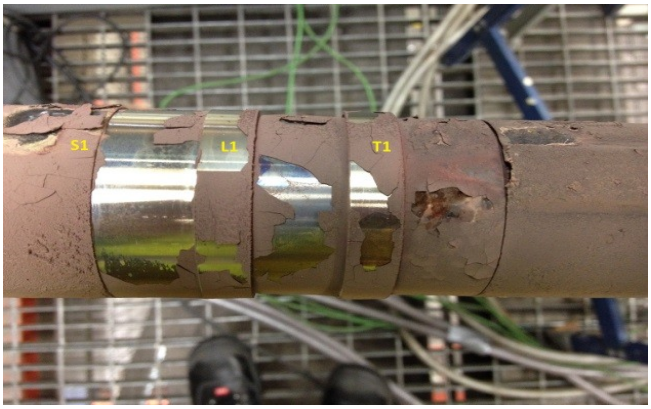


Figure 47. Some of the deposit spalls off after the exposure in P13

Figure 48. The thick deposit formed in P14

The investigation of the samples exposed in the P13-P14-P13 sequence showed less material loss than the samples exposed only in the P14 boiler (329 µm compared to 466 µm). This despite the much longer exposure time, 313+256+162 hours compared to 256 hours. Furthermore, the detailed investigation of the corrosion attack of the samples exposed in the P13-P14-P13 sequence revealed a different microstructure compared to the samples exposed only in the P14 boiler. In the former case, the presence of metal chlorides within the corrosion product layer was scarce. This despite the

substantial spallation of the protective deposit observed prior to the exposure in the P14 boiler. The material loss is however larger than for the corresponding sample exposed only in the P13 boiler (329 µm compared to 47 µm). This is in addition supported by the microstructural investigation, see cross-sections of all four 304L samples in Figure 49. The investigation revealed a thick oxide scale formed due to breakaway oxidation of the P13-P14-P13 sample while the scale still was chromium rich and protective in all P13 exposures.

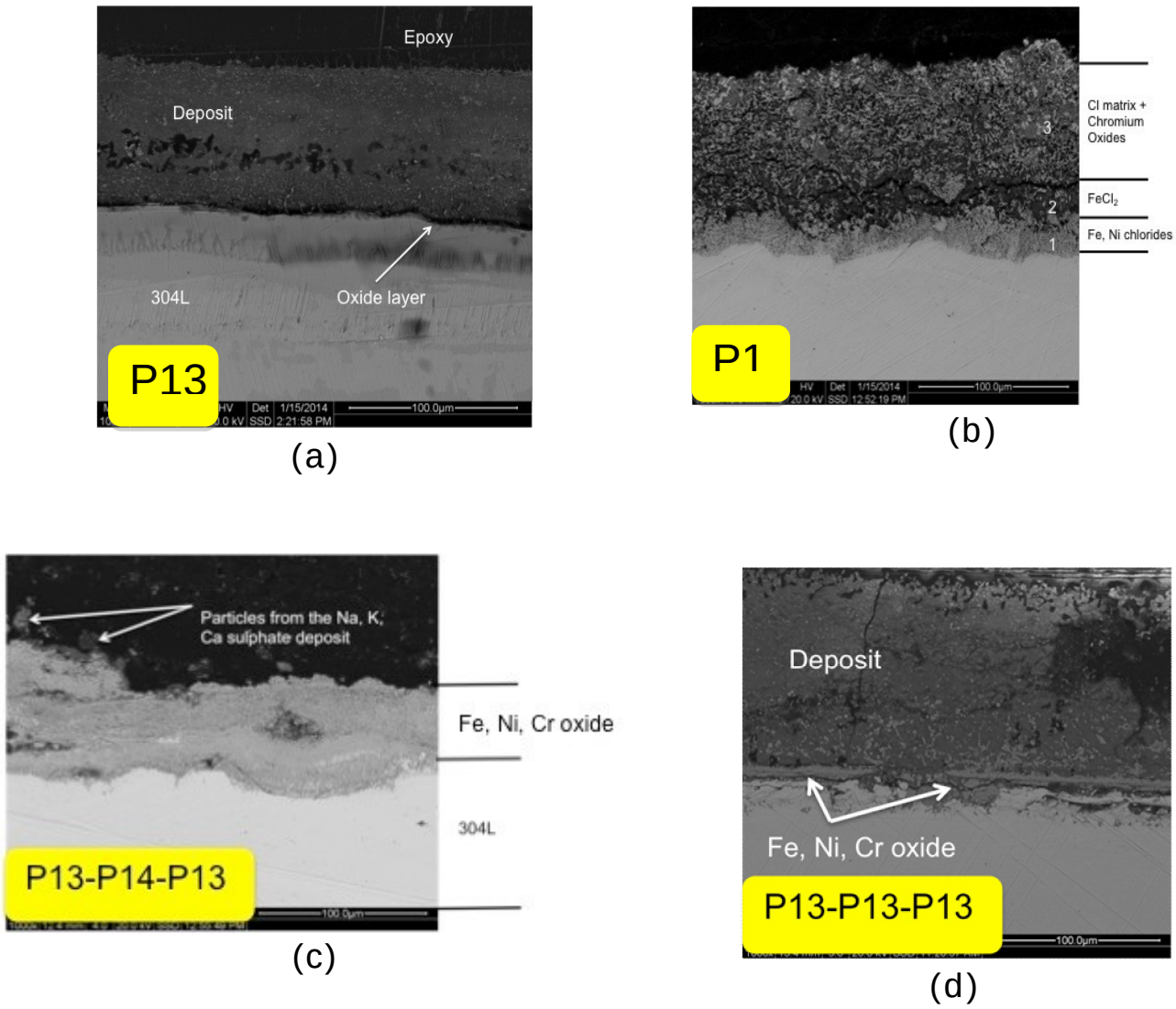


Figure 49. ***Cross section of 304L samples exposed at (a) P13 only, (b) P14 only, (c) P13-P14-P13 and (d) three exposure steps in P13***

The results indicate that the corrosion rate can be maintained low after a change to more corrosive fuel and back again (question 1, 2 and 3). The corrosion rate was indeed lower for the sample exposed in P13-P14-P13 compared to the sample exposed in P14 despite longer exposure time indicating a positive memory effect. This despite the problems with spallation of the protective deposit. Furthermore, during the main study the samples were exposed at high temperature also in the in the corrosive boiler (decided within the project group in order limit the number of changed parameters). With a decreased metal temperature in the corrosive boiler the corrosion rate is expected to be even lower. Now, the oxide scale microstructure indicates that a breakdown of the protective scale has occurred. However, there were no sign of metal chlorides. One of the challenges in the project was that all non-corrosive deposits had a tendency to spall off, i.e. both the artificial deposit K_2SO_4 and the one formed in the P13 boiler, which influences the results. This should be taken into account in future projects, as this is an initial investigation regarding the corrosion memory effect.

This analysis of the results was focused in the 304L material as, due to the high corrosion in P14 boiler and the problems to remove the samples from the probes, it was considered that the 304L samples were the most representative of the study. T22 resulted extremely corroded to give any good result or to be comparable with the other materials. Sanicro28 showed the same tendency as the 304L but in some cases a worst behaviour was found for this material, as it has already occurred in previous studies with Sanicro28 and 304L.

7 Conclusions

- The exposure matrix was executed successfully and both the kinetics and temperature dependence of the artificial deposits were investigated as well as the corrosion test in the main study.
- Increasing the exposure time and the temperature implies that the conversion of KCl to K_2SO_4 is also increased. The conversion is to be regarded fast; the pre-deposited KCl was converted to a great extent already after 24 hours.
- A non-corrosive deposit (represented by pure K_2SO_4) is suggested to act as protective barrier between a corrosive deposit and the alloy when exposed in a corrosive fuel such as in the P14 boiler.
- All non-corrosive deposits had a tendency to spall off, i.e. both the artificial deposit K_2SO_4 and the depsoit formed in the P13 boiler.
- The corrosion rate was lower for the sample exposed in P13-P14-P13 compared to the sample exposed in P14 despite longer exposure time showing a positive “memory effect” of the deposit formed in P13.
- One of the challenges in the project was that all non-corrosive deposits had a tendency to spall off, i.e. both the artificial deposit K_2SO_4 and the one formed in the P13 boiler, which influences the results. This should be taken into account in future projects, as this is an initial investigation regarding the corrosion memory effect.

8 Goal fulfilment

The overall goal of this project has been to increase the knowledge of materials technology process solutions to minimize superheater corrosion with advanced steam data in boilers. This executed by studying the dynamic corrosion processes occurring using two boilers representing different fuels under operation and relating this to the operation history. The obtained results will contribute to the understanding of how a power plant with advanced steam data can be operated with variations in fuel quality. Studying the kinetics of the conversion of artificial deposits exposed in full-scale boilers as well as performing corrosion have obtained probe testing new knowledge has been generated about the corrosion memory effect. The corrosion tests indicate a positive “memory effect” both from artificial and actual deposits. The work also identifies some of the challenges e.g. that the non-corrosive deposits had a tendency to spall off and thereby influences the results. This should be taken into account in future projects. The project was in addition expected to give a first set of answers as a platform for further work regarding the corrosion memory effect. Furthermore, three questions was addressed within the project and the following answers were obtained:

1. Can the corrosion rate be maintained low after a change to more corrosive fuel if the steam temperature is lowered at the same time?

According to the results, the highest corrosion rate was measured for the samples exposed only in P14 boiler, thus there exists a positive memory effect on the samples exposed in P13-P14-P13. If the temperature also would have been lowered during the exposure in the P14 boiler, it is expected that the corrosion rate would be even lower. This project indicates that the corrosion rate can be maintained low after a change to a more corrosive fuel. However, this needs to be further investigated.

2. Is there a memory effect (resulting in increased corrosion rate) after the return to high steam temperature and less corrosive fuel?

Again, the highest corrosion rate was observed for the samples exposed only in P14 boiler. If a “bad” memory effect would have been a dominating factor in the overall corrosion rate, the corrosion of the P13-P14-P13 exposed samples should have been more severe. However, to clearly investigate this effect, a two-step exposure has to be performed.

3. Is there any “incubation time” (before the corrosion rate increases) for materials exposed at high steam temperature and less corrosive fuel after a change to low steam temperature and more corrosive fuel?

Only one exposure time to the test the “incubation time” have been performed within the project. According to the results, the deposit formed in the P13 boiler did slow down (or delayed) the corrosion attack of the samples exposed in P13-P14-P13 compared to the samples exposed in P14. Again, the further elucidate this incubation time, more exposures are needed where samples with different exposure times can be investigated.

9 Suggestions for future research work

This project was a first step in investigating the corrosion memory effect. The results have enlightened various aspects and possibilities. However, the results obtained within the project have also raised many suggestions for further studies. Especially, if the questions addressed in the project should be scientifically answered a more extensive exposure matrix needs to be performed, investigating the different steps more thoroughly.

Taking in account the results obtained in the project and the analysis presented above, some further studies could be proposed to improve the knowledge about the dynamic corrosion and memory effect, which has started in this project. Both 304L and Sanicro28 materials could be used for further work but T22 should be retired for future experiments as it results too much corroded to give any good or comparable result in the analyses.

A two step exposure starting in P14 and changing to P13 will give the knowledge about how the bad corrosion memory affects the samples and could be comparable with the results of the samples without any memory effect, of which the knowledge is already have from this project.

A set of exposures at different times will be desirable to investigate how the kinetics of the “good corrosion effect” affects to the future corrosion when the fuel mix is changed.

In the present project only the 600°C could be compared in the different steps so more exposures setting more temperatures (i.e. 450°C) could be taking into account.

10 Publications

No publications has resulted from the project

11 Appendix

11.1 Appendix I – Field exposures data

MATERIAL	START DATA STEP1	HOUR	SAMPLE	PROBE	TEMPERATURE	BOILER
San 28	20131022	09:10	S1	Probe 1	450	P13
San 28	20131022	09:10	S2	Probe 1	600	P13
San 28	20131022	09:10	S3	Probe 1	600	P13
San 28						
San 28	20131022	09:10	S4	Probe 2	450	P13
San 28	20131022	09:10	S5	Probe 2	600	P13
San 28	20131022	09:10	S6	Probe 2	600	P13
San 28						
304L	20131022	09:10	L1	Probe 1	450	P13
304L	20131022	09:10	L2	Probe 1	600	P13
304L	20131022	09:10	L3	Probe 1	600	P13
304L						
304L	20131022	09:10	L4	Probe 2	450	P13
304L	20131022	09:10	L5	Probe 2	600	P13
304L	20131022	09:10	L6	Probe 2	600	P13
304L						
T22	20131022	09:10	T1	Probe 1	450	P13
T22	20131022	09:10	T2	Probe 1	600	P13
T22	20131022	09:10	T3	Probe 1	600	P13
T22						
T22	20131022	09:10	T4	Probe 2	450	P13
T22	20131022	09:10	T5	Probe 2	600	P13
T22	20131022	09:10	T6	Probe 2	600	P13
T22						

Table 7. Step 1 sample details

MATERIAL	START DATA STEP2	HOUR	SAMPLE	PROBE	TEMPERATURE	BOILER	REMOVING HOUR
San 28	20131104	16:28	S1	Probe 1	450	P13	10:41
San 28	20131104	16:28	S2	Probe 1	600	P13	10:41
San 28	20131104		S3	Probe 1		REMOVED	10:41
San 28	20131104	16:28	S7	Probe 1	600	P13	
San 28	20131104	16:05	S4	Probe 2	450	P14	10:30
San 28	20131104	16:05	S5	Probe 2	600	P14	10:30
San 28	20131104		S6	Probe 2		REMOVED	10:30
San 28	20131104	16:05	S8	Probe 2	600	P14	
304L	20131104	16:28	L1	Probe 1	450	P13	10:41
304L	20131104	16:28	L2	Probe 1	600	P13	10:41
304L	20131104		L3	Probe 1		REMOVED	10:41
304L	20131104	16:28	L7	Probe 1	600	P13	
304L	20131104	16:05	L4	Probe 2	450	P14	10:30
304L	20131104	16:05	L5	Probe 2	600	P14	10:30
304L	20131104		L6	Probe 2		REMOVED	10:30
304L	20131104	16:05	L8	Probe 2	600	P14	
T22	20131104	16:28	T1	Probe 1	450	P13	10:41
T22	20131104	16:28	T2	Probe 1	600	P13	10:41
T22	20131104		T3	Probe 1		REMOVED	10:41
T22	20131104	16:28	T7	Probe 1	600	P13	
T22	20131104	16:05	T4	Probe 2	450	P14	10:30
T22	20131104	16:05	T5	Probe 2	600	P14	10:30
T22	20131104		T6	Probe 2		REMOVED	10:30
T22	20131104	16:05	T8	Probe 2	600	P14	

Table 8. Step 1 sample details

MATERIAL	START DATA STEP4	HOUR	SAMPLE	PROBE	TEMPERATURE	BOILER	REMOVING HOUR
San 28	20131121		S1	Probe 1	450	REMOVED	11:27
San 28	20131121		S2	Probe 1	600	REMOVED	11:27
San 28							
San 28	20131121		S9	Probe 1	600	REMOVED	11:27
San 28	20131121		S4	Probe 2	450	REMOVED	11:27
San 28	20131121		S5	Probe 2	600	REMOVED	11:27
San 28							
San 28	20131121		S10	Probe 2	600	REMOVED	11:27
304L	20131121		L1	Probe 1	450	REMOVED	11:27
304L	20131121		L2	Probe 1	600	REMOVED	11:27
304L							
304L	20131121		L9	Probe 1	600	REMOVED	11:27
304L	20131121		L4	Probe 2	450	REMOVED	11:27
304L	20131121		L5	Probe 2	600	REMOVED	11:27
304L							
304L	20131121		L10	Probe 2	600	REMOVED	11:27
T22	20131121		T1	Probe 1	450	REMOVED	11:27
T22	20131121		T2	Probe 1	600	REMOVED	11:27
T22							
T22	20131121		T9	Probe 1	600	REMOVED	11:27
T22	20131121		T4	Probe 2	450	REMOVED	11:27
T22	20131121		T5	Probe 2	600	REMOVED	11:27
T22							
T22	20131121		T10	Probe 2	600	REMOVED	11:27

Table 9. Step 1 sample details

MATERIAL	START DATA STEP3	HOUR	SAMPLE	PROBE	TEMPERATURE	BOILER	REMOVING HOUR
San 28	20131114	16:42	S1	Probe 1	450	P13	11:42
San 28	20131114	16:42	S2	Probe 1	600	P13	11:42
San 28	20131114		S7	Probe 1		REMOVED	11:42
San 28	20131114	16:42	S9	Probe 1	600	P13	
San 28	20131114	16:56	S4	Probe 2	450	P13	11:57
San 28	20131114	16:56	S5	Probe 2	600	P13	11:57
San 28	20131114		S8	Probe 2		REMOVED	11:57
San 28	20131114	16:56	S10	Probe 2	600	P13	
304L	20131114	16:42	L1	Probe 1	450	P13	11:42
304L	20131114	16:42	L2	Probe 1	600	P13	11:42
304L	20131114		L7	Probe 1		REMOVED	11:42
304L	20131114	16:42	L9	Probe 1	600	P13	
304L	20131114	16:56	L4	Probe 2	450	P13	11:57
304L	20131114	16:56	L5	Probe 2	600	P13	11:57
304L	20131114		L8	Probe 2		REMOVED	11:57
304L	20131114	16:56	L10	Probe 2	600	P13	
T22	20131114	16:42	T1	Probe 1	450	P13	11:42
T22	20131114	16:42	T2	Probe 1	600	P13	11:42
T22	20131114		T7	Probe 1		REMOVED	11:42
T22	20131114	16:42	T9	Probe 1	600	P13	
T22	20131114	16:56	T4	Probe 2	450	P13	11.57
T22	20131114	16:56	T5	Probe 2	600	P13	11:57
T22	20131114		T8	Probe 2		REMOVED	11:57
T22	20131114	16:56	T10	Probe 2	600	P13	

Table 10. Step 1 sample details

11.2 Appendix II – Probe optical images

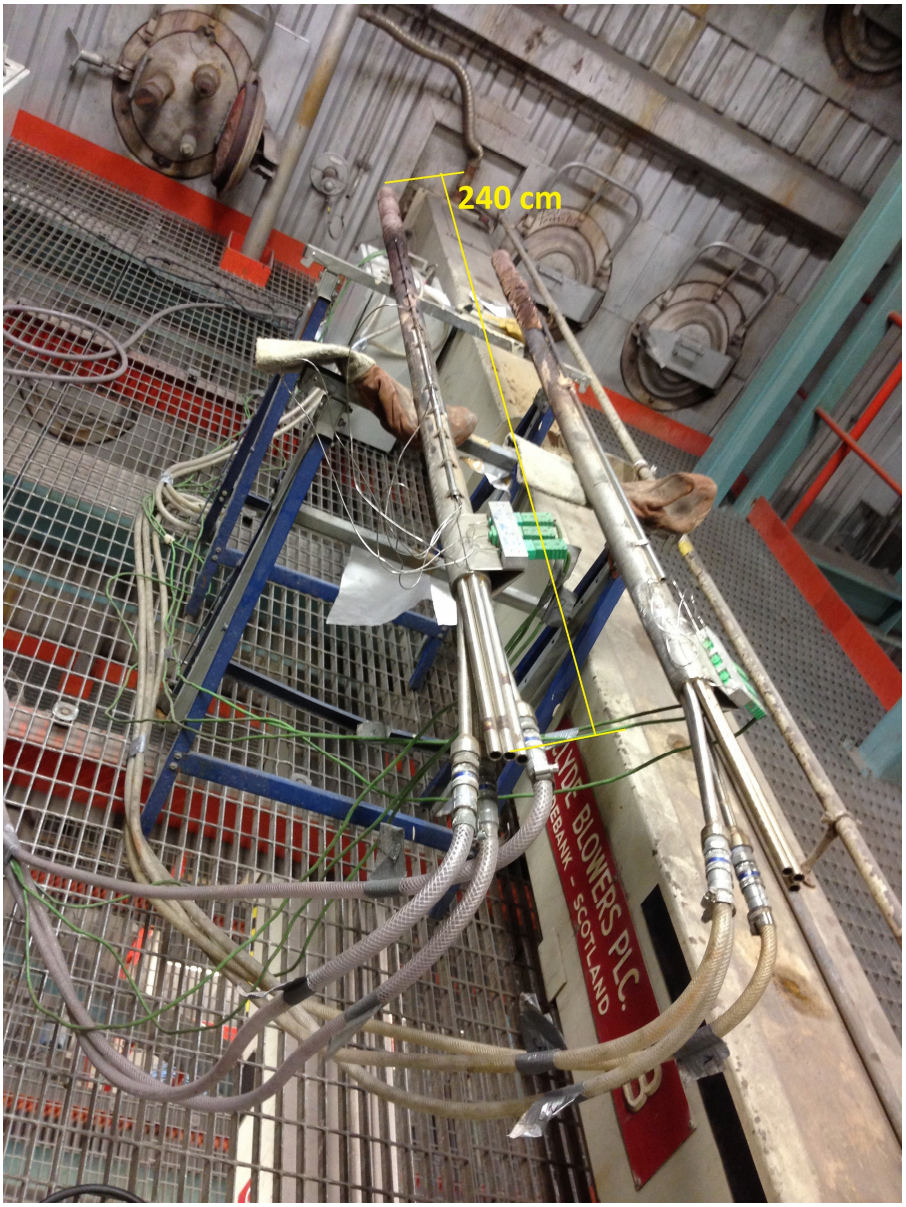


Figure 50. Probe 1 and probe 2 after the exposures in P13

Exposure 1

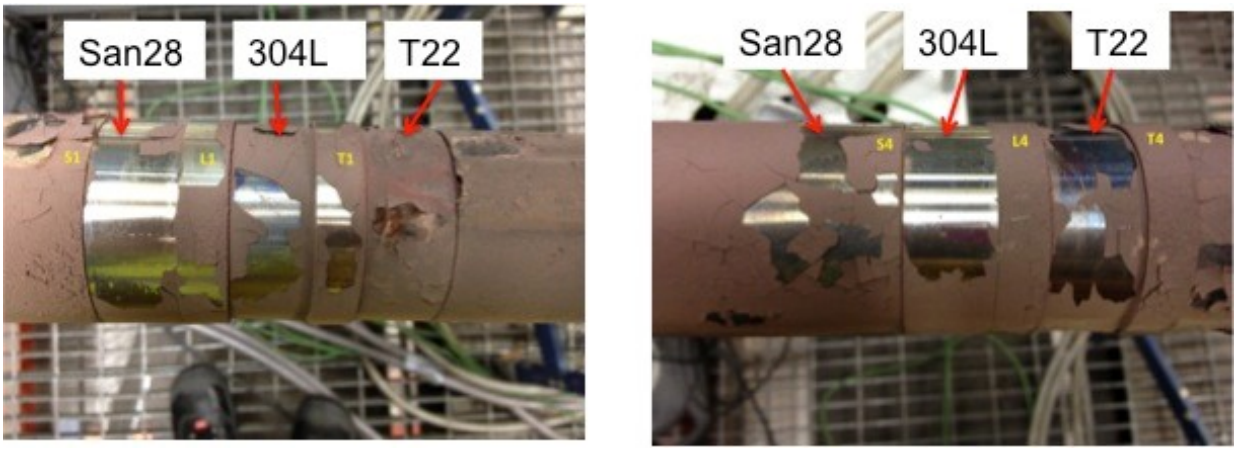


Figure 51. Samples placed in probe 1 (left) and probe two (right) after step 1 in temperature zone 1

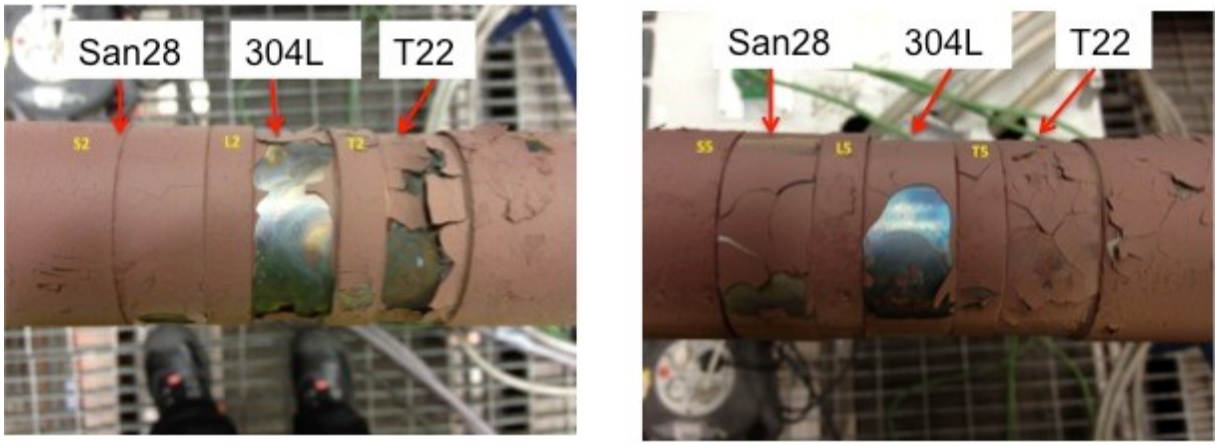


Figure 52. Samples placed in probe 1 (left) and probe two (right) after step 1 in temperature zone 2

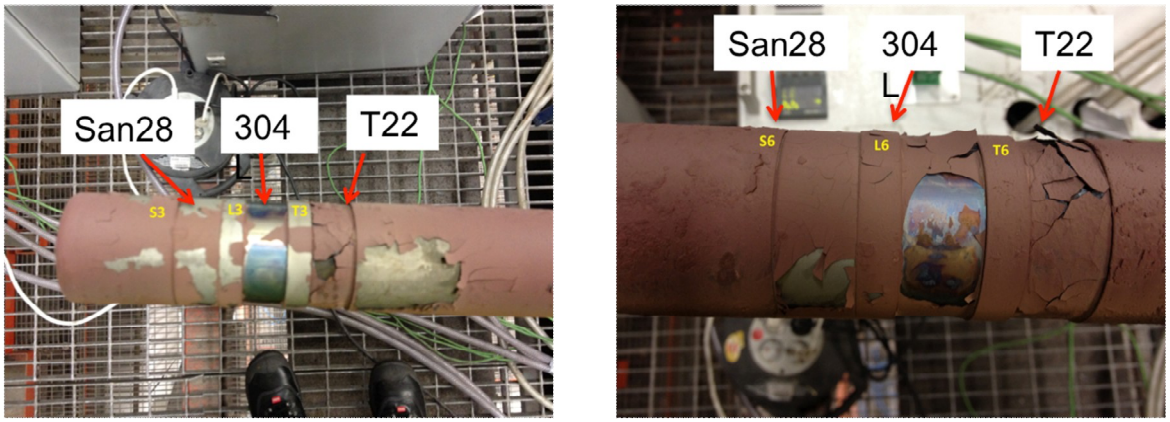


Figure 53. Samples placed in probe 1 (left) and probe two (right) after step 1 temperature zone 3

Exposure 2

Figure 54. Probe 1 after the step 2

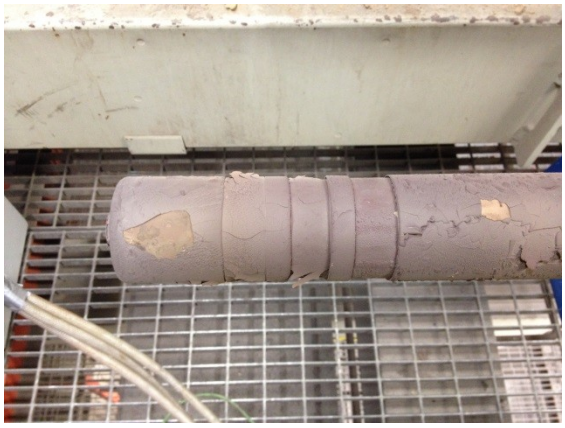
Figure 55. Probe 2 after the step 2

Figure 56. Probe 1 after the removing of the samples in step 2

Exposure 3

Temperature zone 1

Temperature zone 2



Temperature zone 3

Figure 57. Aspect of the probe 1 after step 3

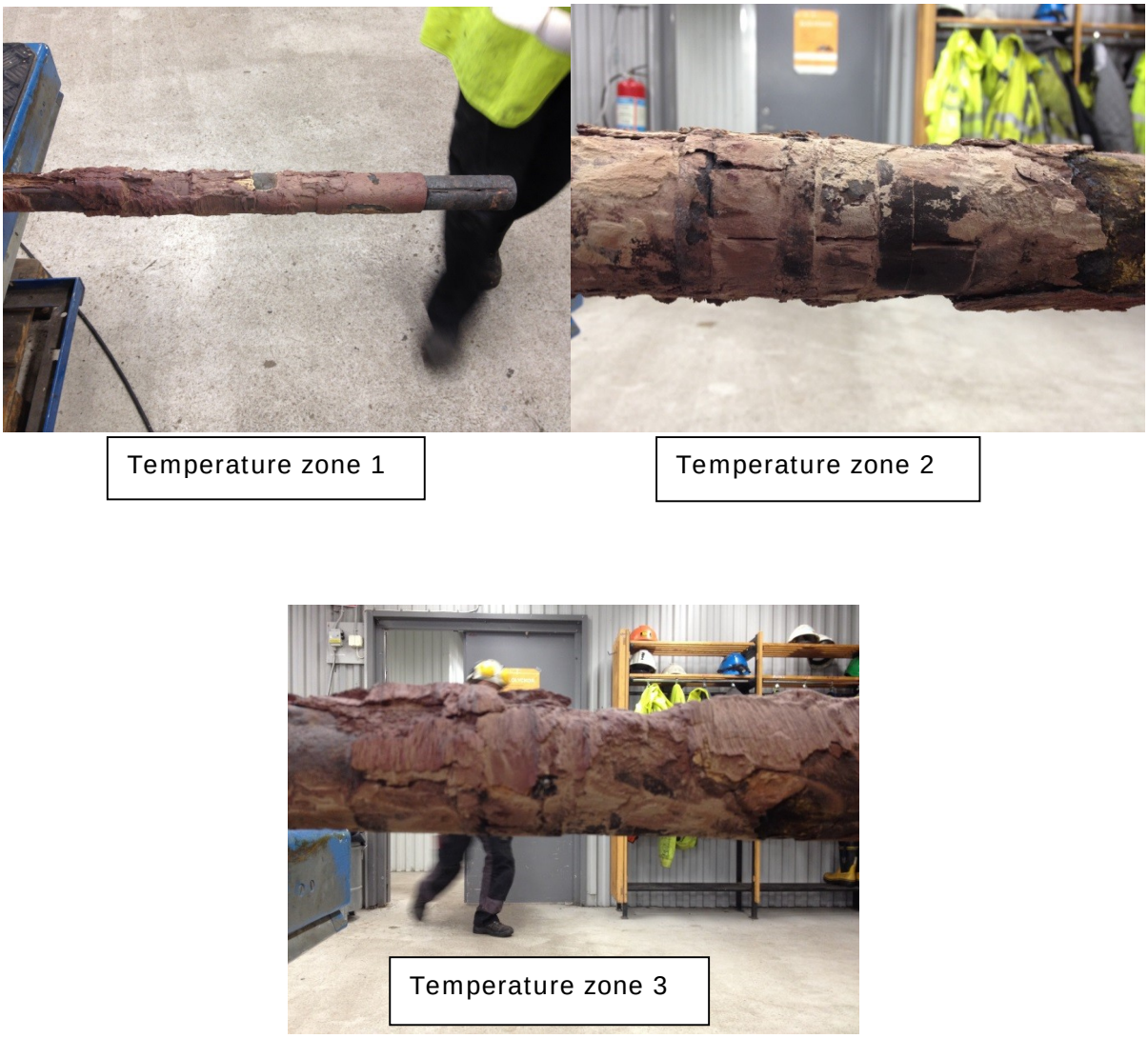


Figure 58. Evolution of the temperature in the P13 boiler during the step 1 measured in probe 1

11.3 Appendix III – Temperature charts

The Figure 59 shows the temperature chart taken from the thermocouples in probe 2 during exposure step 1 in P13. The chart is equivalent to the one in probe 1 presented in the section 2.

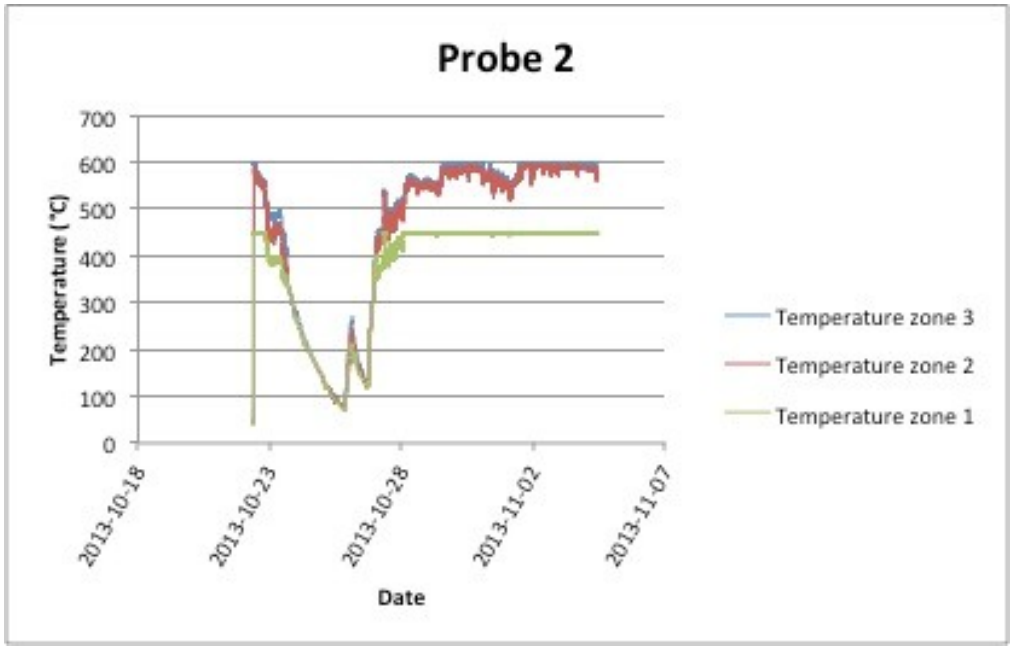


Figure 59. Evolution of the temperature in the P13 boiler during the step 1 measured in probe 2

11.4 Appendix IV – Sample optical images

Figure 60. ***Probe 1*** *– temperature zone 1 (450 °C) – S1, L1, T1 (313 h P13 + 236 h P13+ 162 h P13)*

Figure 61. ***Probe 1*** *– temperature zone 2 (600 °C) – S2, L2, T2 (313 h P13 + 236 h P13+ 162 h P13)*

Figure 62. ***Probe 1*** *– temperature zone 3 (600 °C) – S3, L3, T3 (313 h P13)*

Figure 63. ***Probe 1*** *– temperature zone 3 (600 °C) – S7, L7, T7 (236 h P13)*

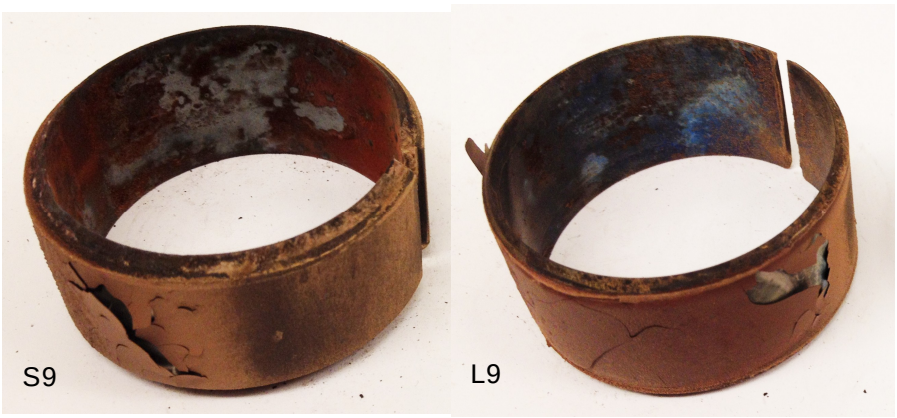


Figure 64. ***Probe 1*** *– temperature zone 3 (600 °C) – S9, L9, T9 (162 h P13)*

Figure 65. ***Probe 2*** *– temperature zone 1 (450 °C) – S4, L4, T4 (313h P13 +236h P14 + 162h P13)*

Figure 66. ***Probe 2*** *– temperature zone 2 (600 °C) – S5, L5, T5 (313h P13 + 236h P14+ 162h P13)*

Figure 67. ***Probe 2*** *– temperature zone 3 (600 °C) – S6, L6, T6 (313h P13)*

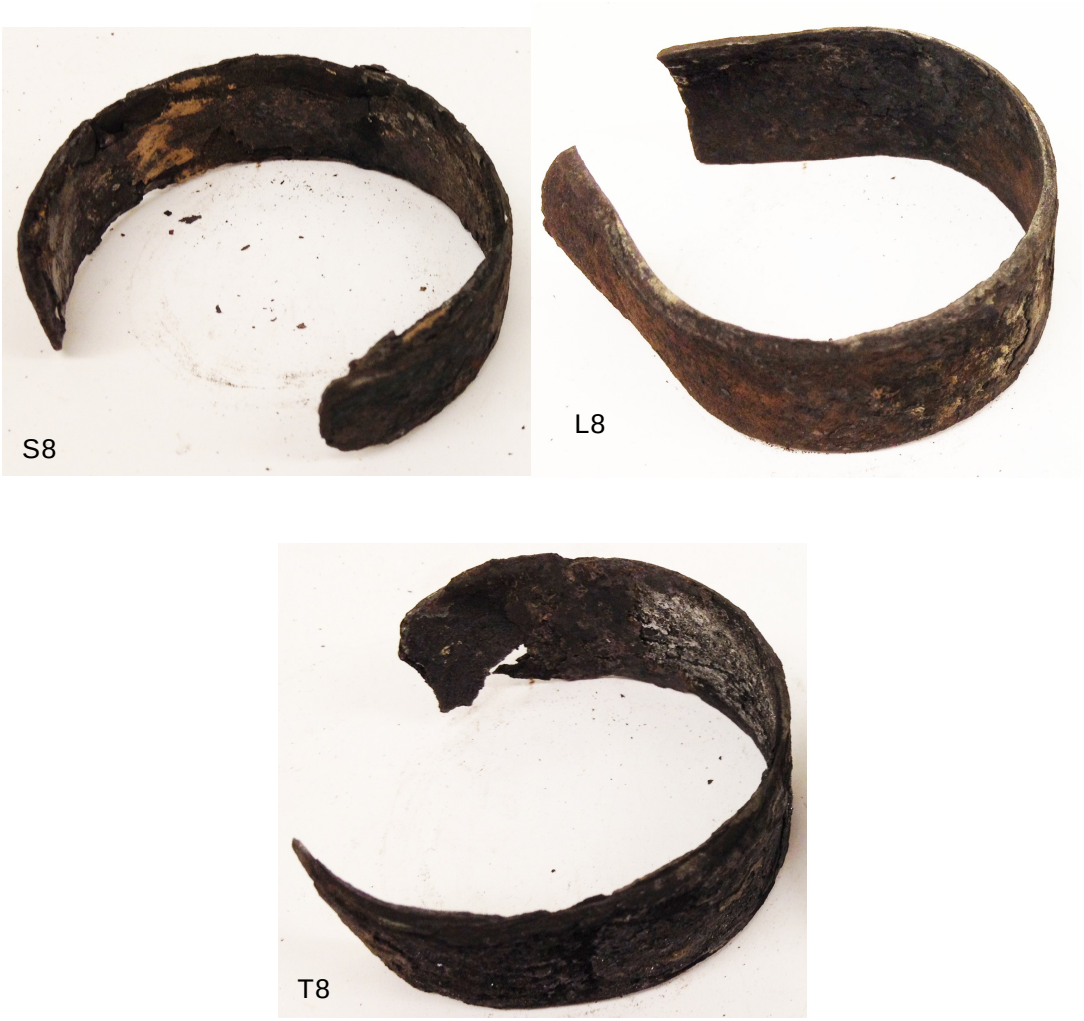


Figure 68. ***Probe 2*** *– temperature zone 3 (600 °C) – S8, L8, T8 (236h P14)*

Figure 69. ***Probe 2*** *– temperature zone 3 (600 °C) – S10, L10, T10 (162h P13)*

11.5 Appendix V – IC calculations

Time (hours)	Temperature (°C)	Amount Cl^- (µmol)		Amount SO_4^{2-} (µmol)
		Applied	After exposure	After exposure
1	450	-	3	7
1	450	7385	3589	63
1	525	-	3	28
1	525	7263	3256	161
1	600	-	19	25
1	600	8614	3813	159
24	450	-	7	313
24	450	7579	3209	1134
24	525	-	4	487
24	525	7830	2016	1292
24	600	-	8	798
24	600	7657	1200	666

All grey rows refer to reference samples without any pre-deposited KCl exposed in P13.

Table 11. Amounts of Cl^- and SO_4^- detected in the KCl treated samples exposed in P13.

11.6 Appendix VI – Sanicro28 EDX mapping

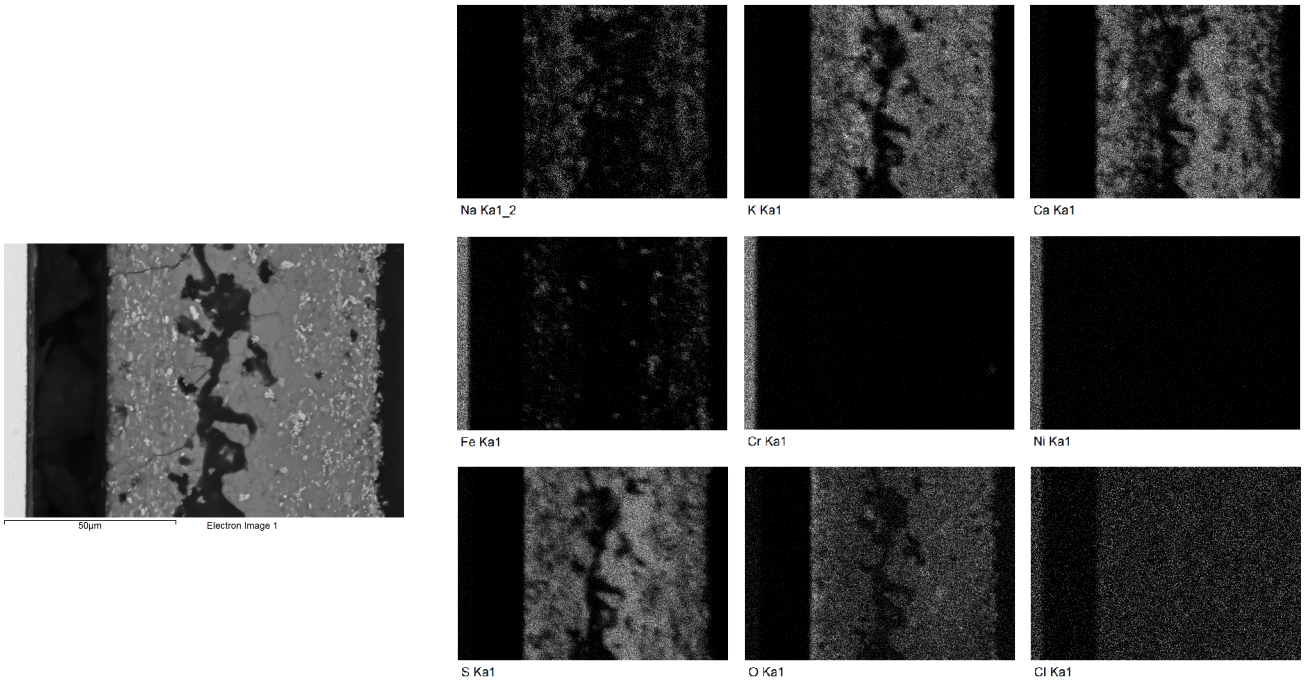


Figure 70. EDX mapping analysis of the Sanicro28 sample exposed in P13

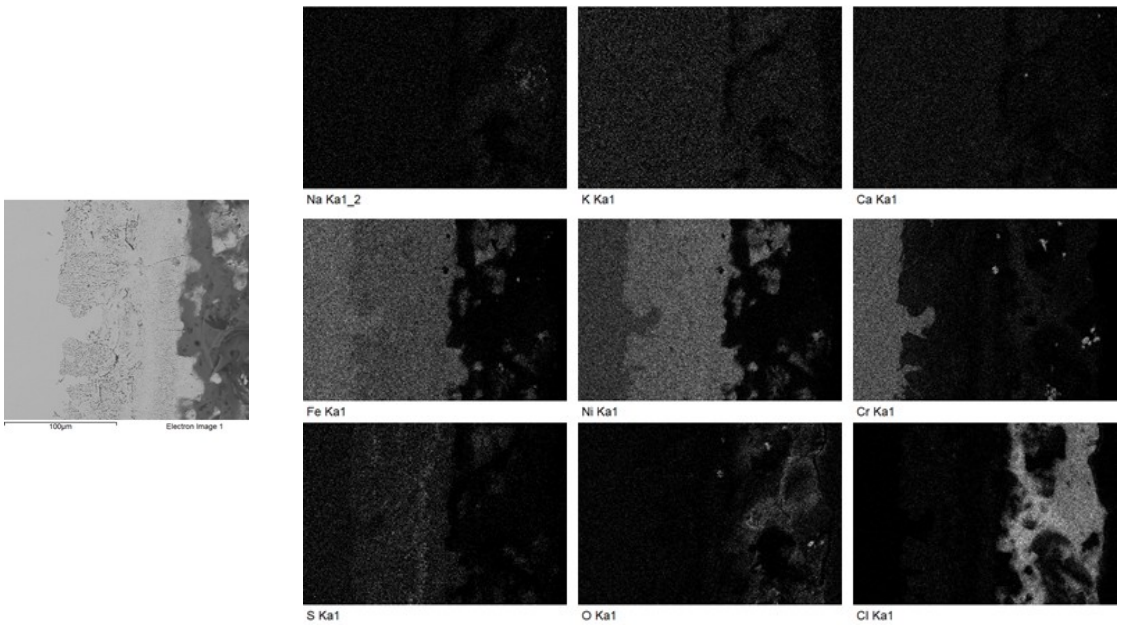


Figure 71. EDX mapping analysis in the area 1 of the Sanicro28 sample exposed in P14 for 236 h

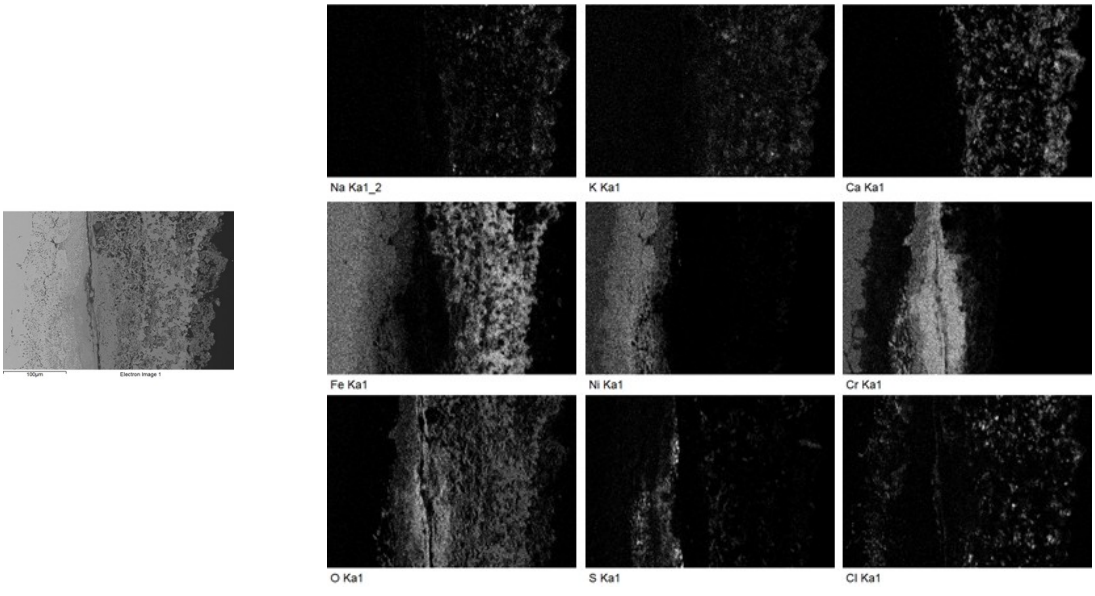


Figure 72. EDX mapping analysis in the area 2 of the Sanicro28 sample exposed in P14 for 236 h

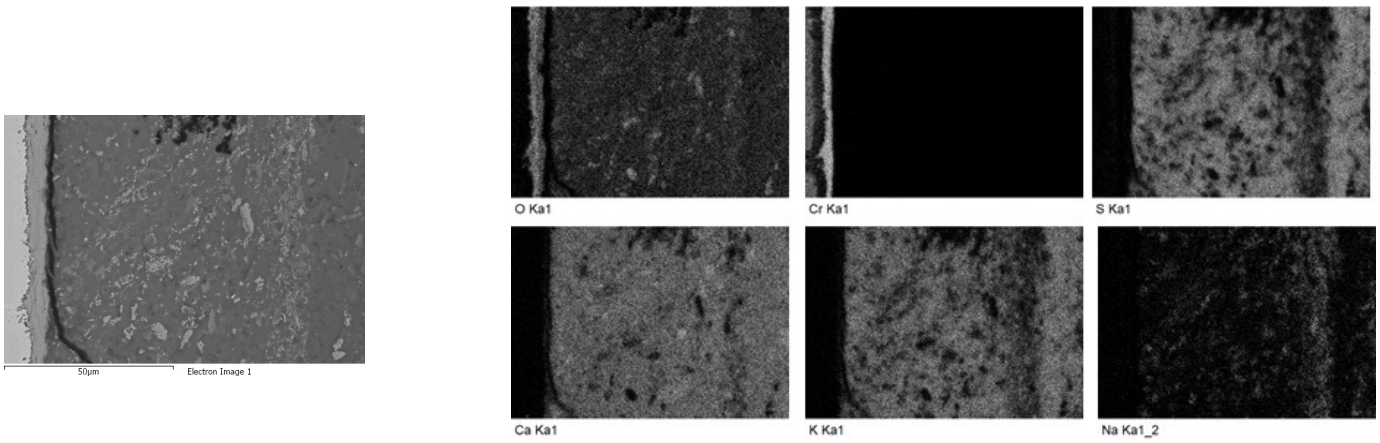


Figure 73. EDX mapping analysis of the Sanicro28 sample exposed during three steps in P13

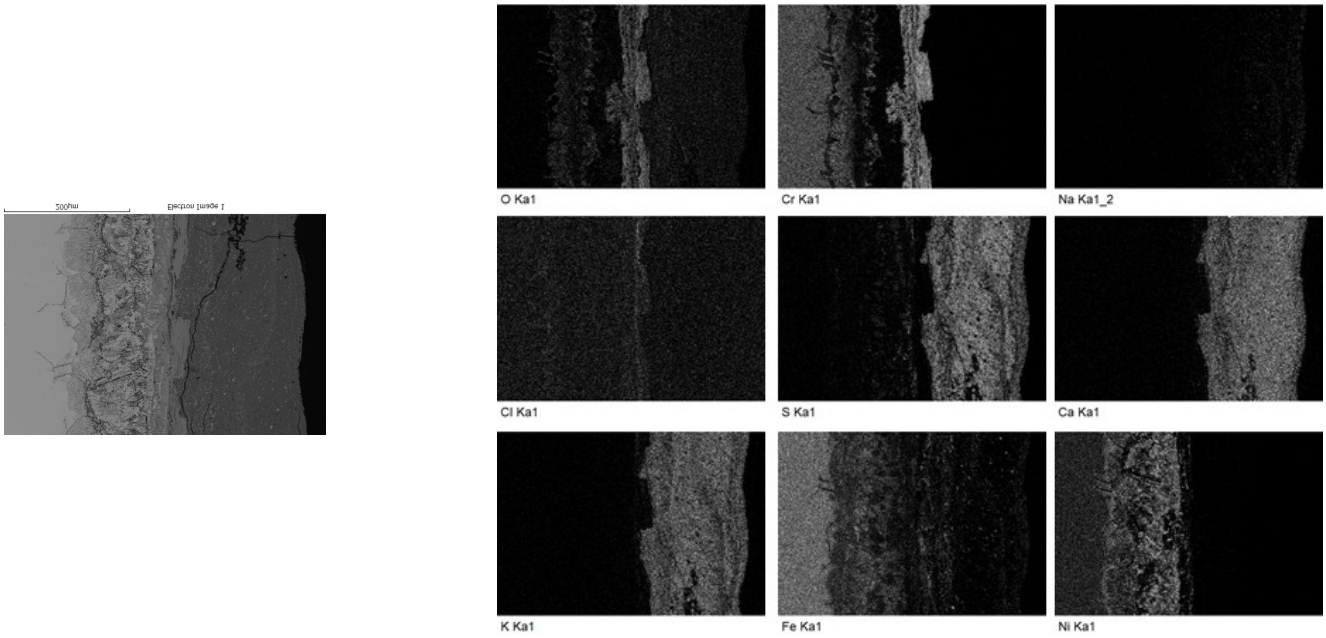


Figure 74. EDX mapping analysis of the Sanicro28 sample exposed for step in P13, one in P14 and last one in P13

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