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KME-509

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Improved determination of service life of superheaters in boilers burning biomass and waste

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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

In summary, the project has demonstrated how corrosion rates change over time, the importance of having the probe exposures mimicking the thermal and environmental history of the superheaters, compared the corrosion rate at the existing temperature and at an elevated temperature, 80 °C higher than the existing one. The conclusion is that probe exposures can be used for estimating the potential corrosion rate of superheaters.

Sammanfattning

Nyckelord: Sondförsök, korrosionshastighetsmätningar, korrosion i avfallspannor

Detta projekt har haft som mål att förbättra anläggningars ekonomi genom att ta fram grundläggande kunskap hur sondförsök kan användas för att estimerar livslängden hos överhettare. Det är allmänt känt att sondförsök överdriver den verkliga korrosionshastigheten hos de överhettare som sondförsöken syftar till imitera. Detta kan bero på ett flertal parametrar, vilka detta projekt har undersökt. Den kunskap som uppkommit inom projektet är till nytta för flertalet aktörer inom kraftvärmebranschen så som pannägare, panntillverkare samt materialtillverkare.

Projektet har framgångsrikt genomfört en omfattande exponeringsmatris i den avfallseldade pannan P14 vid Händelöverket. Detta inkluderande 5 sondförsök samt 6 testsektioner i den befintliga överhettaren exponerade tidsupplöst upp till 5600 timmar. Vidare har 6 st olika material undersökts vid två olika materialtemperaturer, vilket gett korrosionshastigheter både vid befintlig materialtemperatur på dagens överhettare samt en temperatur som syftar till framtida pannor med höjda ångdata.

Resultaten från projektet visar att korrosionshastigheterna vid den valda positionen (ÖH2) i pannan är överlag låga, vilket överensstämmer med korrosionshastigheten som uppmäts på de befintliga överhettarna, som hitintills har haft en livslängd på 12 år. Korrosionshastigheten för Sanicro28, vilken som testades i sondförsök hade i princip samma korrosionshastighet som den Sanicro28 som i dagsläget sitter i överhettaren, 0,02 mm/år jämfört med 0,03 mm/år. Korrosionshastigheten ökade för 2 av 3 material då materialtemperaturen ökades från 420 °C (i dag befintlig materialtemperatur) till 500 °C. För Sanicro28 exponerad vid 500 °C var korrosionshastigheten 0,3 mm/år.

Projektet undersökte också om det fanns någon inneboende skillnad mellan korrosionshastigheten av sondexponerade prover och överhettare. Enligt resultaten, verkar det inte föreligga en sådan skillnad. Dock krävs det att sondförsöken i möjligaste mån efterliknar överhettarens termiska och miljömässiga historia. Speciellt fokus bör riktas på hur sondexponeringarna startas. Resultaten indikerar att en start med kalla sonder direkt in i en varm panna påverkar korrosionsangreppet negativt.

Sammanfattningsvis har vi inom projektet visat på hur korrosionshastigheter förändras med tiden, effekten av hur viktigt det är att genomföra sondexponeringarna på sådant sätt att de i möjligaste mån efterliknar överhettarens situation samt tagit fram underlag för korrosionen vid befintlig temperatur och vid en temperatur satt 80 °C högre än den befintliga. Slutsatsen är att sondexponeringar är ett möjligt sätt för att undersöka den potentiella korrosionshastigheten av överhettare.

Summary

Keywords: probe exposures, corrosion rate determination, corrosion in waste fired boilers

The main aim of this project has been to improve the plant economy by generating fundamental knowledge about how probe exposures can be used in order to estimate the lifetime of the superheater. The corrosion rate obtained from the probe exposures usually exaggerates the actual corrosion rate of the superheaters. The reason for this is probably related to several parameters, of which this project has aimed to investigate the effect of start-up, the effect of exposure time and if there is any inherent difference between probe and tube exposures. The knowledge generated within the project is beneficial to several actors within the power industry, e.g. boiler owners, boiler manufacturers and materials producers.

The project has successfully executed a comprehensive exposure matrix in the waste fired boiler (P14) at Händelöverket, Norrköping. This includes 5 probe exposures and 6 test sections in the existing superheater exposed in time resolved manner up to 5600 hours. The exposure matrix contained 6 different materials exposed at two different material temperatures, where corrosion rates were obtained for materials at the existing material temperature of today's superheaters as well as a temperature aimed at future boilers with higher steam data.

The results show that corrosion rates of the probe exposed samples are generally low, which is consistent with the corrosion rate measured on the existing superheaters (the current lifetime is 12 years). The corrosion rate of Sanicro28, exposed on the probes had basically the same corrosion rate as the Sanicro28 currently installed in the superheater, 0.02 mm/year and 0.03 mm/year, respectively. The corrosion rate increased for two of the three materials investigated when the material temperature was increased from 420 °C (existing superheater material temperature) to 500 °C. For Sanicro28 exposed at 500 °C, the corrosion rate was 0.3 mm/year.

The project also investigated if there was any inherent difference between the corrosion rate of probe exposed samples and the superheaters. According to the results, it does not seem to exist such a difference. Hence, probe exposures are a possible way of investigating the potential corrosion rate of superheaters. However, it is important to stress that the probe exposures needs to, as far as possible, mimic the thermal and environmental history of the superheater. This includes for instance how the probe exposures are started and handling during shorter stops. The results indicate that a startup with cold probes directly into a hot boiler affect corrosion attack negatively.

In summary, the project has demonstrated how corrosion rates change over time, the importance of having the probe exposures mimicking the thermal and environmental history of the superheaters, compared the corrosion rate at the existing temperature and at an elevated temperature, 80 °C higher than the existing one. The conclusion is that probe exposures can be used for estimating the potential corrosion rate of superheaters.

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1 Introduction

1.1 Background

Renewable energy sources such as biomass and waste are important for the Swedish energy supply. However, these fuels are challenging to combust because of their heterogeneous nature and the relatively high levels of alkali and chlorine. The fuel composition results in a flue gas environment which is more corrosive compared to fossil fuels. Actually, fireside corrosion is the main lifetime limiting factor for the superheaters in these plants and puts an upper limit to the steam data. In addition, the high ash content results in the formation of deposits on heat-exchanging surfaces (fouling) that limits power production.

Much research has been directed towards fireside corrosion and fouling in these plants in order to decrease maintenance costs and enable increased power efficiency. The in-plant work has mostly used cooled probes in order to investigate e.g. the influence of fuel composition, fuel additives, material composition and material temperature on fireside corrosion. The work has resulted in great improvement of the level of knowledge, e.g. concerning the influence of fuel composition and certain fuel additives on the rate of fireside corrosion. Much remains to be done however, for example concerning predicting the service life of superheaters.

1.2 Description of the research field

It is well-known that the fireside corrosion rates measured in cooled probe exposures are usually higher (sometimes much higher) compared to corrosion rates of tubes in real superheater bundles. The causes behind this discrepancy are largely not understood and have not been subjected to systematic study. This is a huge drawback limiting the usefulness of cooled probe exposures for predicting superheater lifetime. One central aim of this work is to address this problem and to analyse different parameters that may explain this discrepancy. Within this type of corrosive environments, i.e. biomass or waste combustion, there have been a great number of tests throughout the years where probe testing directed towards quantitative corrosion rate measurements has been performed [1-18].

In order to achieve as realistic corrosion rate values as possible, with respect to comparing the corrosion rates of the probes as with the corrosion rate of the superheaters, some issues needs to be addressed. One crucial factor is that while cooled probe corrosion exposures are seldom longer than 1000 hours, the lifetime of the superheater is several years. Thus, the corrosion rate is linearly extrapolated from the corrosion rate during the first 1000 hours of exposure. Another factor that may be of importance of the overall corrosion rate is the start-up sequence. For superheaters, the start-up is slow, following the boiler start-up sequence, and the environment is non-corrosive (usually oil is used as fuel). In contrast, probes are usually started directly into the hot boiler, directly exposed towards the corrosive environment.

Because these factors are not known, it is necessary to study corrosion kinetics in order to better extrapolate the cooled probe data for lifetime prediction. The present project therefore involves time-resolved cooled probe exposures at different temperatures as well as tangent test sections of the superheater.

1.3 Research task

The main aim of this project is to generate new knowledge about corrosion testing in order to facilitate the development of models for determination of the service life of superheater materials as a function of material temperature. Today, much of the high temperature corrosion related research in boilers is performed by corrosion probe measurements up to 1000 hours. The results obtained, in the form of corrosion rates, are extrapolated to estimate the service life of superheaters.

The project addresses the KME goal to verify an increase of the steam temperature by at least 50°C from 450 to 500°C for waste fractions in 2013. Furthermore, these tests aim to provide long term corrosion data for several superheater materials to be evaluated for the new superheater bundle that E.ON plans to install.

The project focuses on understanding the discrepancy between corrosion rate measurements using cooled probes and the corrosion rate of the real superheater. This is done by comparing time resolved cooled probe corrosion rate measurements with exposures of sample materials installed in the superheater tube loop.

In order to fulfil these tasks, a comprehensive exposure matrix consisting of both tube and probe exposed samples have been carried out. The matrix consisted of time resolved probe exposures (24, 336, 1000, 2000 and 5600 hours) and 6 test sections installed in the superheater bundle (one section per material and 5600 hours exposure time). Both probes and tubes have been installed and setup by Metso. During operation, the probes were monitored by E.ON. HTC at Chalmers have performed material loss evaluations of the samples as well as conducted a detailed corrosion analysis primarily by means of SEM/EDX analysis of cross sections.

1.4 Goal

The overall goal of the project is to improve plant economy by enabling an increased electricity production and enhancing fuel flexibility. This will be achieved by generating new knowledge to facilitate the development of models for determination of the service life of superheater materials as a function of material temperature.

The project addresses the KME goal to verify an increase of the steam temperature by at least 50 °C from 450 to 500 °C for waste fractions in 2013. The project focuses on understanding the discrepancy between corrosion rate measurements using cooled probes and the corrosion rate of the real superheater. This is done by comparing time resolved cooled probe corrosion rate measurements with exposures of sample materials installed in the superheater tube loop. Additionally, the initial corrosion (after 24h) will be

measured and evaluated concerning the corrosion mechanism. This frequent exposure approach render with a comparatively good understanding of how the corrosion rates vary with exposure time.

1.5 Project organisation

The project is jointly performed by E.ON, Metso and HTC at Chalmers. The distribution of work was:

Part	Participants role in the project
E.ON Värme Sverige	Responsible for operation and gas analysis. Responsible for probes during operation.
Metso Power	Providing probes and sample materials for probes and tubes. Responsible for probe and tube mantling and dismantling.
Mälarenergi	Participating in the project group
Chalmers/HTC	Project management. Responsible for corrosion evaluation and service life assessment.

Table 1. Participating partners in the KME-509 project

The members of the reference group were, besides members of the project;

Dilip Chandrasekaran	Sandvik Heating Technology
Pamela Henderson	Vattenfall Research & Development
Anette N. Hansson	DONG Energy (Until end of 2012)
Sören Aakjaer Jensen	Force Technology (During 2013-2014, appointed by Dong Energy instead of Anette N. Hansson)

The project was financed within the frame work of KME by the Swedish Energy Agency. The total project budget was 3 491 kSEK.

2 Plant description

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.



Figur 1. Den avfallseldade förbränningsanläggningen P14 vid Händelöverket

Figure 1. The waste incinerator plant P14 at Händelöverket

2.1 The boiler

The boiler, Figure 2, is a Circulating Fluidised Bed (CFB) boiler with a thermal capacity of 75 MW supplied by Kvaerner Power (today: Metso Power). The boiler produces steam, primarily used for production of electricity, industrial process steam, and district heating. Some boiler data are shown in Table 2, Table 3 and Table 4.

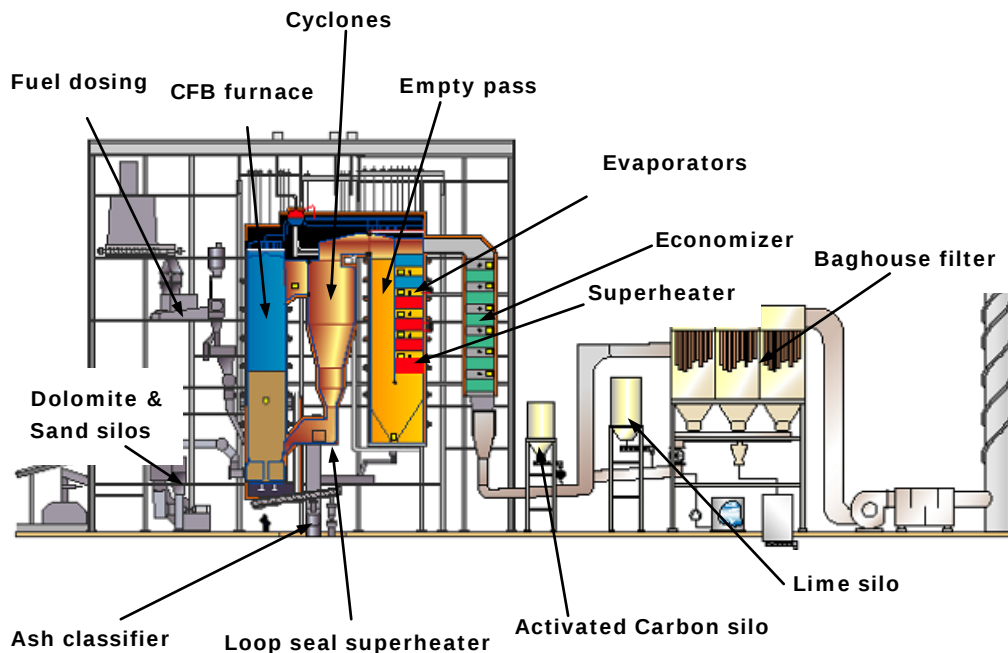


Figure 2. Händelö/Norrköping P14 CFB panna

Figure 2. 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 Metso CFB boiler used for combustion of MSW/RDF (Municipal Solid Waste, Refused Derived 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 2. 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 characterized 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 13CrMo4-5 (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 2. Operating data at MCR (Maximum Continues Rate)

Boiler part	Material	Max gas temperature °C	Max steam or water temperature °C
Furnace	Sanicro28 / St45.8/III	900	290
Radiation cavity (empty pass)	St45.8/III	850	290
Tertiary superheater	TP347H	900	450
Evaporator bank	St45.8/III	650	290
Secondary superheater gas inlet	Sanicro28 / St45.8/III	630	400
Secondary superheater gas outlet	Sanicro28 / St45.8/III	500	340
Primary superheater gas inlet	13CrMo4-5	500	370
Primary superheater gas outlet	16Mo3	440	290
Evaporator bank	St45.8/III	440	290
Economiser	St 35.8/III	350	240

Table 3. 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	

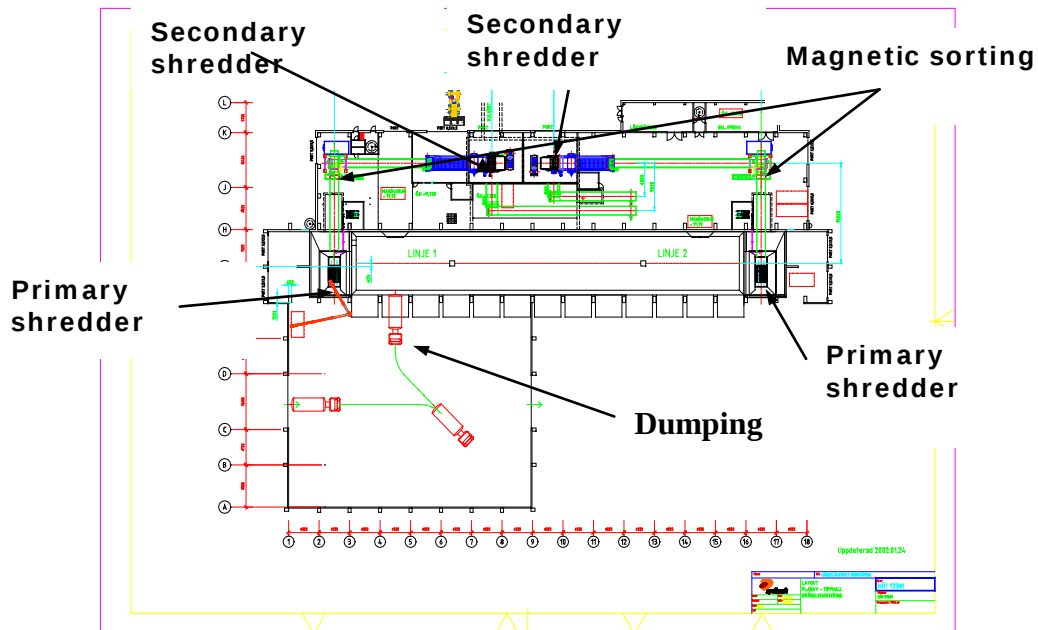
Table 4. Max tube and fin surface temperature at MCR

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.

2.2 The fuel preparation

The fuel preparation plant, Figure 3, consists of a receiving bunker (78 m long, 12 m wide and 8 m deep) with a total volume of more than 7000 m³. 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.

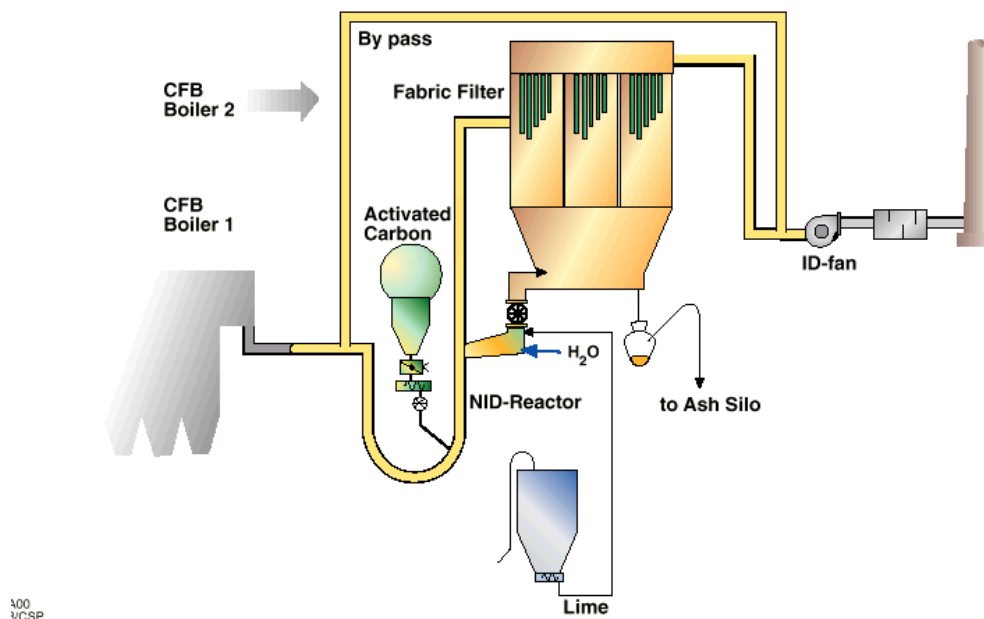


Figur 3. Bränsleberedningen

Figure 3. The fuel preparation

2.3 The flue gas cleaning

Alstom Power has delivered the flue gas cleaning system, Figure 4, which is a semidry system without flue gas condensation. The NID-system includes a mixer, a reactor and a fabric filter. Burnt lime is mixed with water in an extinguisher. The hydrated lime is mixed with recirculated filter ash and additional water in a mixer. Next, the moisturized dust is fed into the flue gases in a reactor chamber where activated carbon is added. The particles are removed from the flue gas by a fabric filter. The lime binds to chlorine and sulphur while the activated carbon is used to remove dioxins and heavy metals. The major part of the removed fly ash is recirculated through the mixer and reactor system.



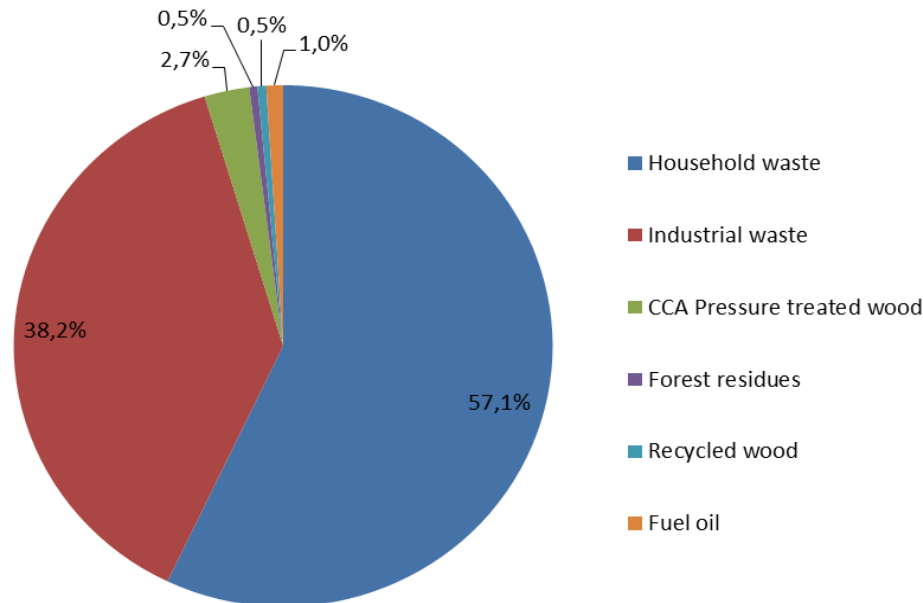
Figur 4. Rökgasreningen

Figure 4. The flue gas cleaning

2.4 Fuel specification

The fuel consists of a mix of municipal solid waste, industrial waste and some percentage of different types of bio fuels. In Figure 5, the total distribution of fuels during the period July 2011 – March 2012 is presented. 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.

Fuel, Boiler P14, July 2011 - March 2012



Figur 5. Bränslefördelning i Panna 14, juli 2011 – mars 2012

Figure 5. Distribution of fuel mix in Boiler P14, July 2011 – March 2012

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

- 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.
- 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.
- Recycled wood: Recycling wood chips are produced from shredded and screened used wood.
- 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 5 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. The complete fuel analyses are shown in Appendix A and were performed by SP.

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

Table 5. Typical fuel data, P14, Händelö

3 Experimental conditions

The exposures performed within the KME509 project started during the fall 2011 and was completed during the spring 2012. The exposure matrix consisted of time resolved probe exposures (24, 336, 1000, 2000 and 5600 hours) and 6 test sections installed in the superheater bundle (one section per material and 5600 hours exposure time).

3.1 Description of materials and placement of tubes and probes

An overview of the tested materials and their chemical composition are given in Table 6. The balance is mainly Fe. The content of Si and Mn is small.

	<i>DIN/EN</i>	<i>%C</i>	<i>%Fe</i>	<i>%Cr</i>	<i>%Ni</i>	<i>%Mo</i>	<i>%Si</i>	<i>%Mn</i>	<i>%Al</i>
13CrMo4-5		0.14	Bal	1		0.5			
TP347H	1.4912	0.06	Bal	18	11		0.4	1.8	
KanthalAPMT/ 13CrMo4-5*		0.8	Bal	21		3	0.7	0.4	5
TP310HCBN	1.4952	0.06	Bal	25	20		<1	<2	
Inconel625/ 16Mo3**		0.1	5	23	58	10	0.5		
Sanicro28 /St45.8/III***	1.4563	0.01	Bal	27	31	3	0.4	1.8	

* APMT applied as a HVOF coating **Inconel625 welded on 16Mo3 *** Compound tube

Table 6. Types of tested materials and chemical composition in weight %.

The chosen materials are typical for superheaters, from low alloyed ferritic steel to nickel-based alloys. The choice of materials for the superheater depends on the quality of the fuel, placement of the superheater (dependent on the flue gas temperature), material temperature (dependent on the steam temperature), material cost etc. Chromium is often used to increase the corrosion resistance of the steel. Steels with more than 13 % chromium are often referred to as stainless steels. Nickel alloys are also commonly used in order to improve the corrosion resistance of the superheater. The price of low alloy steels may be up to 8 times cheaper than high nickel based alloys. However, the availability of the high alloy steel can be limited or the delivery time long.

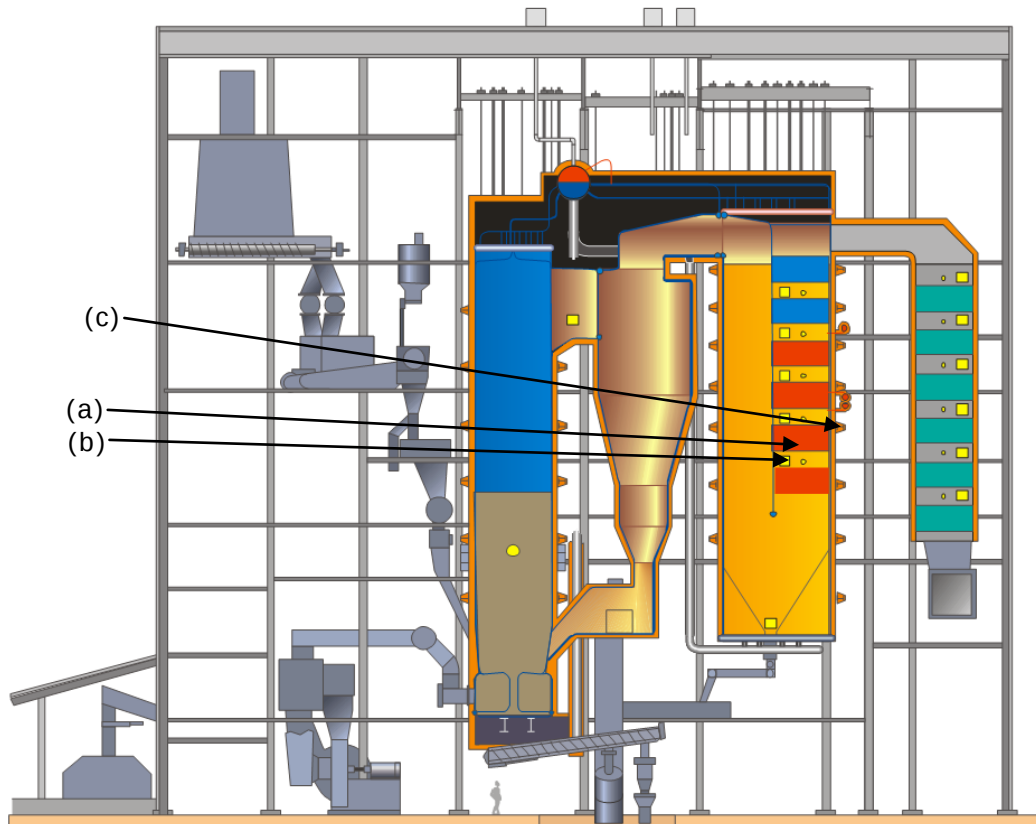
The alloys used within this project can be described as:

- 13CrMo4-5 is a commonly used Cr-Mo-alloyed low alloy steel in superheaters. It has better creep strength than non-alloyed steel.
- TP347H, is an austenitic stainless steel and it has good combination of strength and corrosion resistance.
- FeCrAl, (Kanthal APMT) is an advanced powder metallurgical, dispersion strengthened, ferritic iron-chromium-aluminium alloy. Typical applications

for Kanthal APMT are as radiant tubes in electrically or gas fired furnaces. Kanthal APMT forms, depending on environment and temperature, a protective layer containing Al_2O_3 . This protective layer makes this alloy interesting to use as superheater tubes. Within this project, the APMT samples were manufactured by thermally spraying Kanthal APMT wire on to a 13CrMo4-5 tube.

- TP310HCbN is a pressure vessel approved high Cr austenitic stainless steel.
- Inconel 625, (sometimes denoted alloy 625) exhibits good corrosion resistance in chloride containing environments. This material was overlay welded on 16Mo3 tubes. The overlay welded tube was manufactured in Metso's workshop in Gothenburg.
- Sanicro28 is a Fe-Cr-Ni alloy, similar to AC66. Often used in black liquor and waste firing boilers.

The placement of the test tubes and probes was chosen in between secondary superheater bundle; where the flue gas temperature is expected to be about 550 °C, see Figure 6. The probes were placed on both sides of the man doors and the test tubes were installed on the second row from bottom of the superheater bundle (due to tube shields on the first row tubes). Both test tubes and probes have been, as far as possible, subject to the same environmental conditions. The material temperatures of the test tubes were measured on the tubes (same coil as the test tubes) outside of the water wall to show if any differences in steam temperatures between test tubes due to different tube thickness.

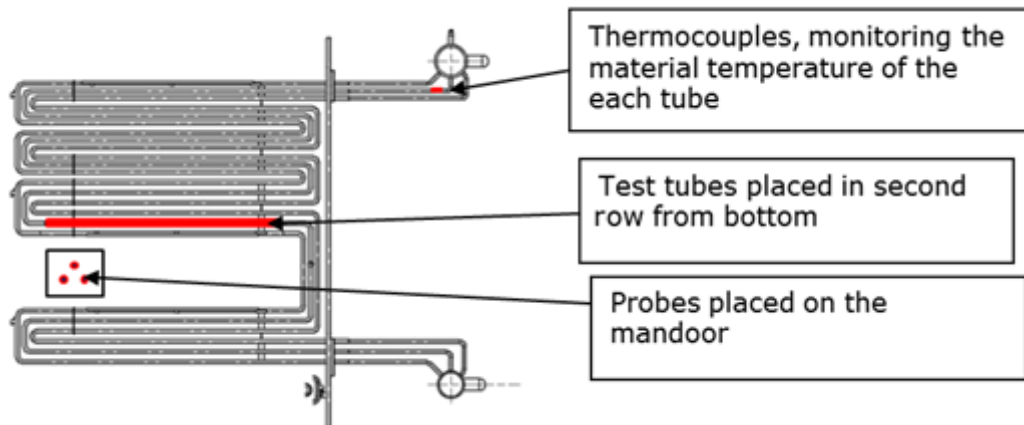


Figur 6. Placering av (a) testtuber, (b) sonder och (c) termoelement för mätning av testtubernas materialtemperatur.

Figure 6. Placement of the (a) test tubes, (b) probes and (c) thermocouples on the test tubes.

3.2 Probe exposures

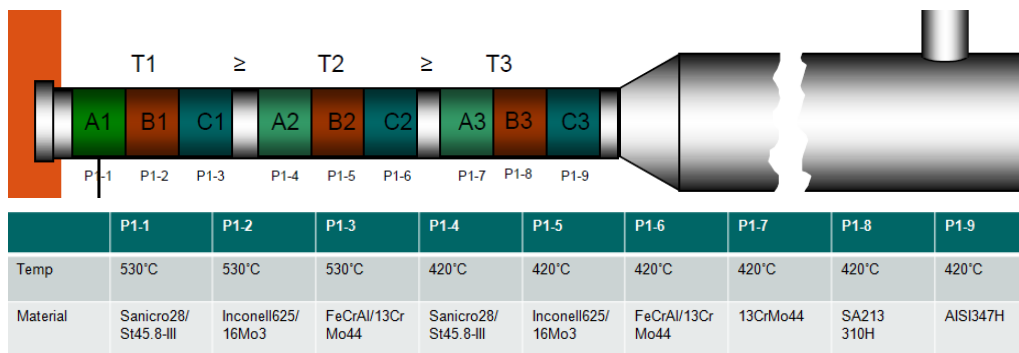
The test plan was to place five probes with identical test rings at the end of July, together with test tubes. The probe exposure times were 24 h, 336 h, 1000 h, 2000 h, and 4000 h. The 4000 h probe was planned to be taken out under short autumn revision together with test tubes. In that way, both test tubes and 4000 h probe have been subject to same conditions during test period. A soot blower was situated in middle of the empty part of the secondary super heater bundle, i.e. both test tubes and probes were affected by soot blower steam. In Figure 7, placement of the test ring, material, and set temperature is shown.



Figur 7. Placering av testtuber, sonder och termoelement för mätning av testtubernas materialtemperatur i detalj

Figure 7. Placement of the test tubes, probes and thermocouples on the test tubes in detail

In Figure 8, the placement of samples, material and set temperature is shown. The set temperature of the first set of samples (three samples) on the probe was 500 °C (planned 530 °C) and the rest in 420 °C. However, the set temperature of the first set was adjusted to 500 °C when the flue gas temperature couldn't reach the expected 550 °C. All five probes were placed in the cold boiler during revision. 24 hours exposure time was defined as 24 hours after waste was introduced to the boiler.



Figur 8. Placering av prover, material och set-temperatur

Figure 8. The placement of the samples, material, and set temperature

3.3 Tube exposures

Six test tubes were prepared, 2 m long, welding ends made of Sanicro28/St45-8 (except for Sanicro28/St 48-8 tube) were pre-welded on both ends of the test tubes in the workshop to simplify the welding procedure during the revision, see Figure 9. The test tubes were placed on second row from bottom, due to tube shield on the first row tubes, see Figure 6.



Figur 9. Testtuber med svetsändar. Nerifrån och upp i bilden: Sanicro28/St48-8, TP347H, TP310HCbN, Inconel625/St48-8, FeCrAl/13CrMo4-5, and 13CrMo4-5.

Figure 9. Test tubes with weld ends. From bottom of the picture, Sanicro28/St48-8, TP347H, TP310HCbN, Inconel625/St48-8, FeCrAl/13CrMo4-5, and 13CrMo4-5.

3.4 Evaluation of exposed samples

The exposed samples were investigated by means of quantitative as well as qualitative analytical techniques. The quantitative measures have involved material loss determination and the quantitative analysis have primarily involved cross sectional SEM/EDX analysis. All analyses were performed by HTC/Chalmers.

3.4.1 Metal loss measurements

3.4.1.1 Tubes

The tube thickness was measured both at Chalmers and at Metso. At Chalmers, the tube thickness of the samples was measured using cross-sectional samples and SEM. Measurements were done in 12 different locations along the ring, rotating the ring every 30° clockwise. The initial thickness was the nominal value given by the tube producer. At Metso, the diameter of the samples was measured before and after the exposure in two directions. In addition, the exposed samples were cut in two and photographed. An imaging program, Cell-D, was used in order to measure the diameter and thicknesses of the samples.

3.4.1.2 Probes

To determine the material loss the thickness of the samples was measured with micrometer screw before the exposure. The micrometer screw had a round measuring surface for the best measurement of curved objects. The sample thickness was measured at eight points evenly distributed around the mantle surface. The hole for the thermocouple, which was located on the windward side, was in the middle between the first and the last measuring point. After exposure, the samples were cut in two with a precision saw to obtain a cross section of each sample ring. With a high resolution camera each sample ring were photographed. The images were then digitalized using the engage software. The sample thickness was measured in approximately 400 individual positions; this enables a more realistic evaluation of the material loss compared with the measurements done in 8 positions with the micrometer screw.

3.4.2 Qualitative corrosion analyses of the probe samples

All samples were investigated by visual inspection after exposure and photographs of the windward (0°) and leeward (180°) side of the sample rings were taken. The colour, thickness and adherence of the deposit/corrosion product layer give rough information of the overall condition and performance of the exposed sample. Some of the samples were mounted in epoxy for subsequent analysis by SEM/EDX.

3.4.2.1 Scanning electron microscopy (SEM)

The morphology of the samples was investigated by scanning electron microscopy, SEM. The resolution and depth of focus in an SEM is much higher than in an optical microscope, revealing more details of the corrosion attack. In addition, the SEM can be equipped with an Energy Dispersive X-rays system enabling analysis of the elemental composition of the sample. The samples were examined with an FEI Quanta 200 FEG ESEM. The SEM has a field emission electron gun (FEG) and is equipped with an Oxford Inca energy dispersive X-ray (EDX) system. SEM/EDX was used for elemental mapping and quantification. For imaging and EDX analysis an accelerating voltage of 20 kV was used.

4 Results

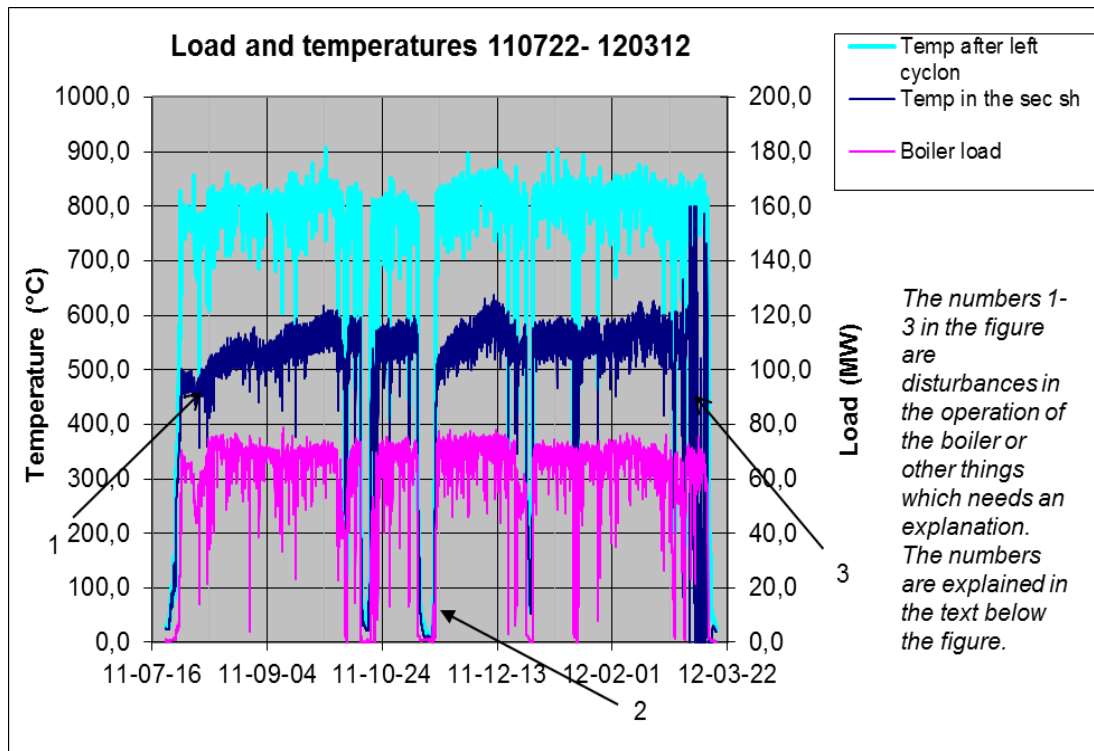
4.1 Boiler operation

4.1.1 *Boiler parameters*

The exposure of the changed tubes in the secondary superheater and the five probes started after the overhaul of the boiler in July 2011. The operation conditions for P14 during the whole exposure have been relatively stable, with a few exceptions. The most important deviations of normal conditions are explained in the text below

The exposures of probes and tubes were started during the overhaul in July 2011 to March 2012. The tubes were changed back to the ordinary material and the last probe was taken out from the boiler in March 2012. In general, the operation conditions for P14 during this time have been relatively stable. In Figure 10, the load and flue gas temperatures at two positions in the boiler are shown. The temperatures are measured by thermocouples in the flue gas, protected by metallic tubes. Some disturbances did occur during the tests and are marked by numbers in the figure. The numbers referred to in Figure 10 are related to:

- 1 Planned reductions in load; cleaning of the fuel feeding lines
- 2 Problems with the flue gas cleaning plant
- 3 Disturbances connected to the fuel feeding system



Figur 10. Last och temperaturprofiler över utvalda positioner i P14 under försöksperioden juli 2011 – mars 2012.

Figure 10. Load and temperature profiles for relevant positions in P14 during the exposure time July 2011 – March 2012.

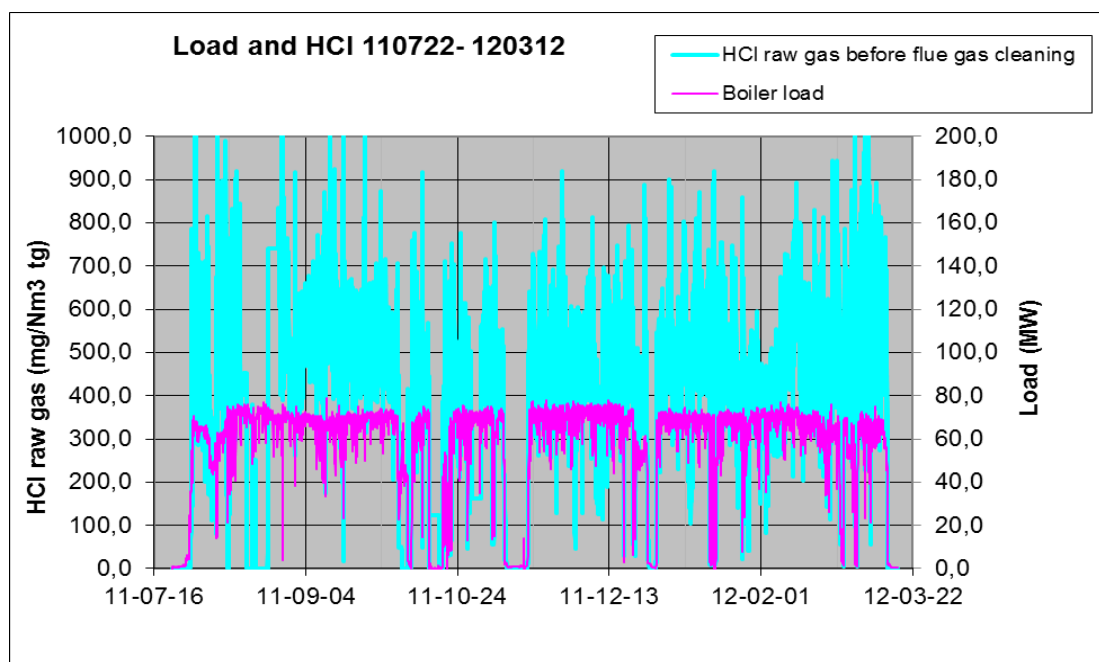
The exceptions in the exposure referred to in Figure 10 are further explained below:

- 1 During the overhaul of the boiler in the summer, the walls in the empty pass were replaced with new ones (the front wall and part of the side walls). Consequently, the boiler started up with some walls which were completely clean. Thus, it took rather long time for the temperatures in the boiler to reach "normal" levels, since the new clean walls was effectively cooling down the flue gas. Thus, during the initial stages of the exposure the highest probe temperature, 530°C, was not reached. It was decided within the project group to lower the set temperature of the probes to 500 °C.
- 2 Overhaul shut down, one week. Change of baghouse filter. The 5600 hours probe was removed from the boiler temporarily during the cleaning of the superheaters and the tubes, which were still in the boiler, were as far as possible untouched during cleaning of the superheater bundles.
- 3 The thermocouple in the secondary superheater was broken in the end of the exposure. As a consequence, the signal is going up and down.

The reasons for the load reductions in the beginning of the exposure are the problems with the baghouse filter. There was a need for maintenance of the filters, and the change of the filters could not be done until November (2011). So until the overhaul when the whole filter was changed, a lot of maintenance had to be done during operation of the boiler, with reductions in load as a result. Every week there were also planned reductions in load, when the fuel feeding lines were cleaned, one at a time (there are three).

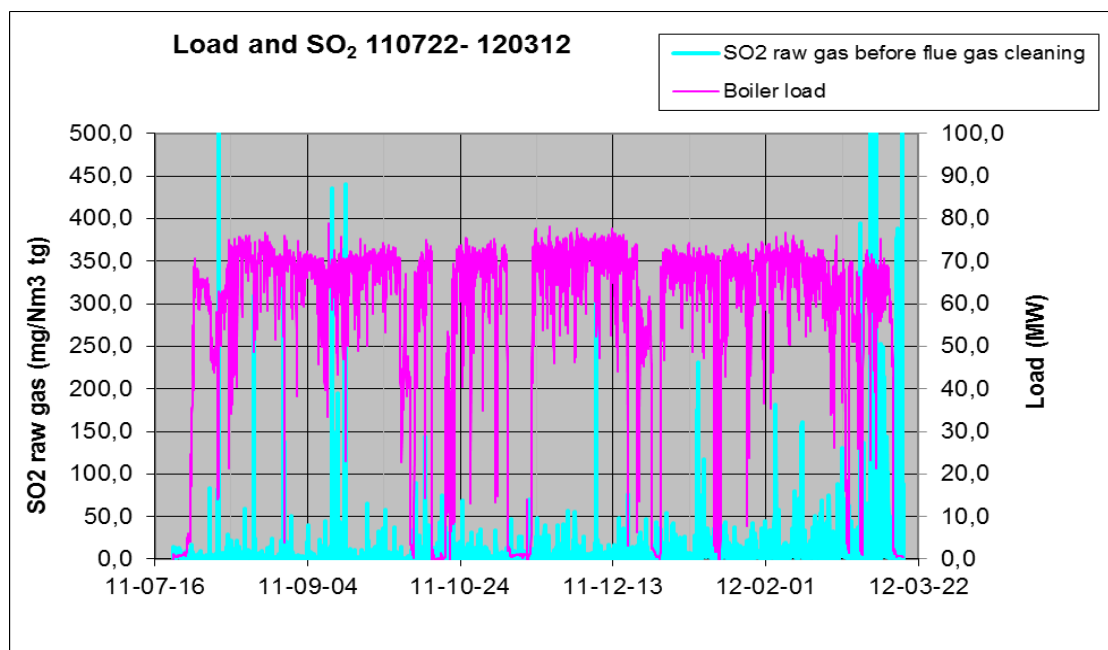
Except for the above mentioned reasons for load reductions there were a few problems with the flue gas cleaning plant but the disturbances on the second half of the exposure were mainly connected to the fuel feeding system and bottom ash system.

Other parameters of interest are the HCl and SO₂-concentrations in the flue gas before the flue gas cleaning. These two parameters are measured in the raw flue gas (SO₂ extractive) and the amounts are shown in Figure 11 and Figure 12.



Figur 11. HCl-halt och pannlast, under exponeringen av utbytta sekundäröverhettartuber och sonder 2011-2012.

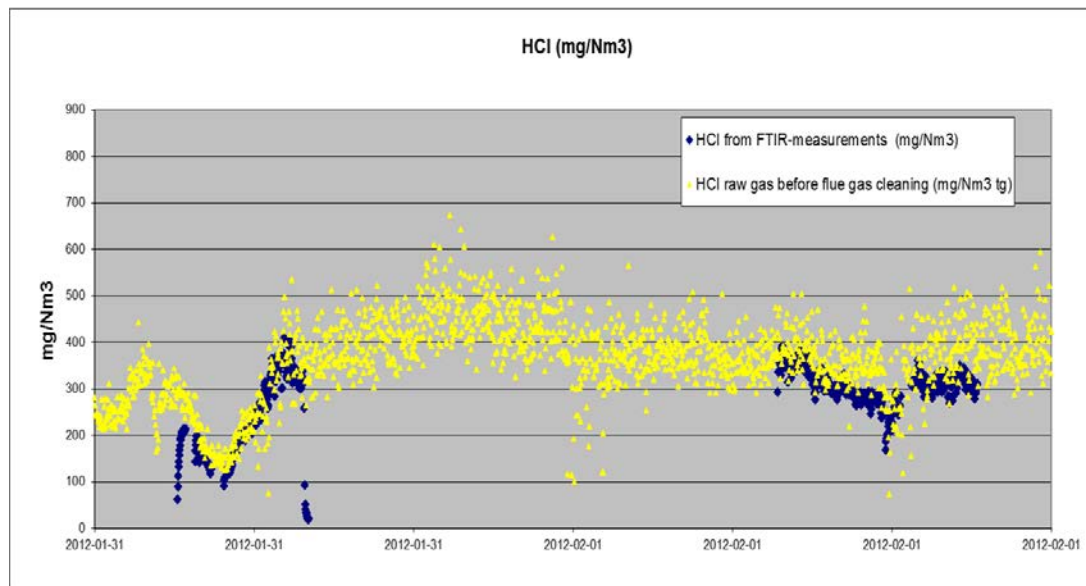
Figure 11. Amount of HCl and load during the exposure of changed secondary superheater tubes and probes in 2011-2012.



Figur 12. SO₂-halt och pannlast, under exponeringen av utbytta sekundäröverhettartuber och sonder 2011-2012.

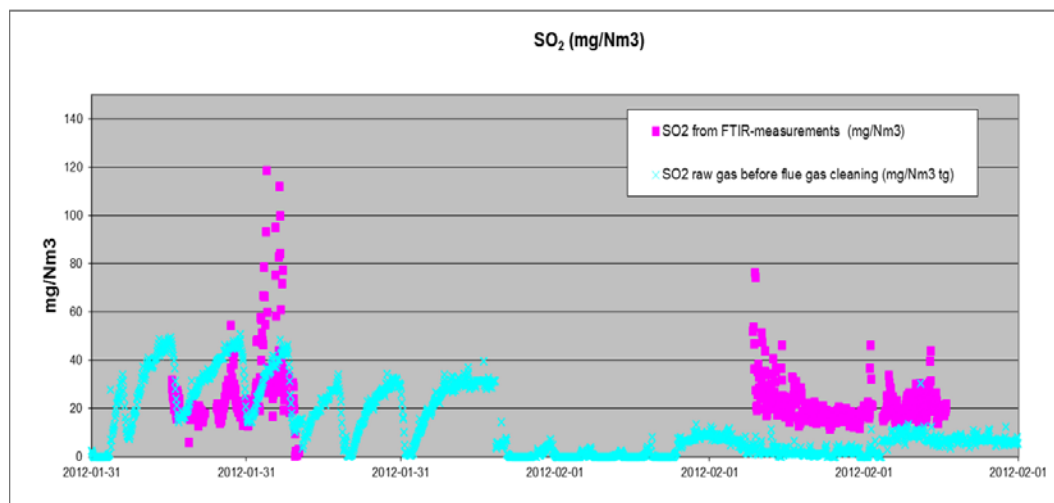
Figure 12. Amount of SO₂ and load during the exposure of changed secondary superheater tubes and probes in 2011-2012.

In order to verify that the measured content of HCl and SO₂ in the raw gas were correct, measurements with an FTIR-instrument were performed on the 31st of January and on the 1st of February 2012. The measurements were performed at the same position as of the 5600 hours probe, at the secondary superheater. The flue gas passes the secondary superheater a while before the position of the continuous measurements of HCl and SO₂, but the amounts should be approximately the same. In Figure 13 and Figure 14, the measurements of the FTIR are compared with the regular measurements of HCl and SO₂, respectively, values from exactly the same time. The FTIR-measurements were performed by Vattenfall R&D.



Figur 13. HCl-halt uppmätt både med FTIR-instrument och den vanliga rågasmätningen i pannan, den 31 januari och 1 februari 2012. FTIR-mätningen pågick under några timmar varje dag.

Figure 13. HCl concentrations, measured both with FTIR-instrument and the usual measurement of raw gas in the flue gas channel, on the 31 of January and the 1st of February. The FTIR-measurement was running a couple of hours each day.



Figur 14. SO₂-halt uppmätt både med FTIR-instrument och den vanliga rågasmätningen i pannan, den 31 januari och 1 februari 2012. FTIR-mätningen pågick under några timmar varje dag.

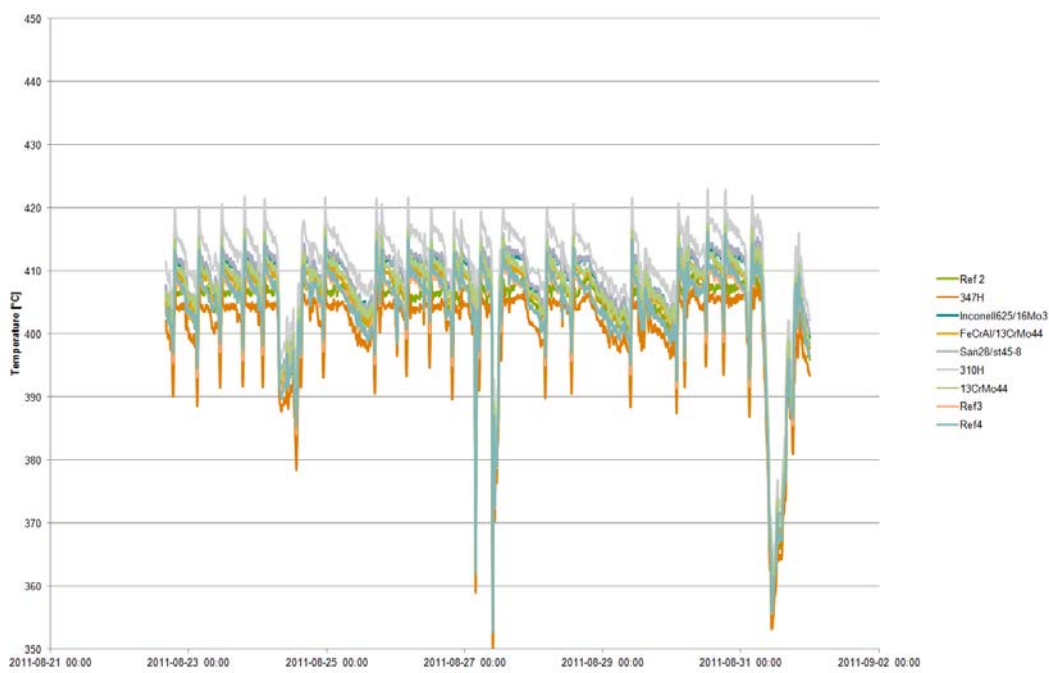
Figure 14. SO₂ concentrations, measured both with FTIR-instrument and the usual measurement of raw gas in the flue gas channel, on the 31 of January and the 1st of February. The FTIR-measurement was running a

couple of hours each day.

According to the gas analysis measurements, there is excellent agreement between the HCl-levels obtained by the external FTIR measurement and the permanently installed HCl analysis. For the SO₂ measurements the agreement is also good. However, a difference between the two measurements can be seen with respect to changes in the amplitude of the curve. The conclusion after the FTIR-measurements is that the permanently installed measurements of the raw gas are possible to use in order to obtain an overview of the concentrations of these gases.

4.1.2 Tube and probe exposures

The temperature of the material, measured on the tubes outside the waterwall screen is shown in Figure 15. Totally 10 thermocouples were placed (6 on the test tubes and 4 as reference). However, one of the reference thermocouple failed (Ref1). The temperature data for the whole test period could not be logged due to computer failure. The obtained data showed however that the temperature differences between tubes were small, about 5 °C. The average temperature during a 10 day period shown in Figure 15 was around 405 °C and max/min standard deviation was 4/2.



Figur 15. Materialtemperaturer av överhettaren uppmätta med termoelement utanför pannan.

Figure 15. Material temperatures of the superheater tubes measured with thermocouples outside the boiler.

The planned total exposure time was about 4000 h (same as for probe Nr. 5 (P5)). However, due to unplanned stop of the boiler during the test period,

the probe exposure time of the last probe (P5) was prolonged as test campaign continued. In Table 7, the planned time and actual exposure time of the probe exposures are shown.

Probe Number	Planed time [h]	test duration [h]
P1	24	24
P2	336	336
P3	1000	1008
P4	2000	1992
P5	4000	5568

Table 7. Planed probe exposure time and outcome of the test duration

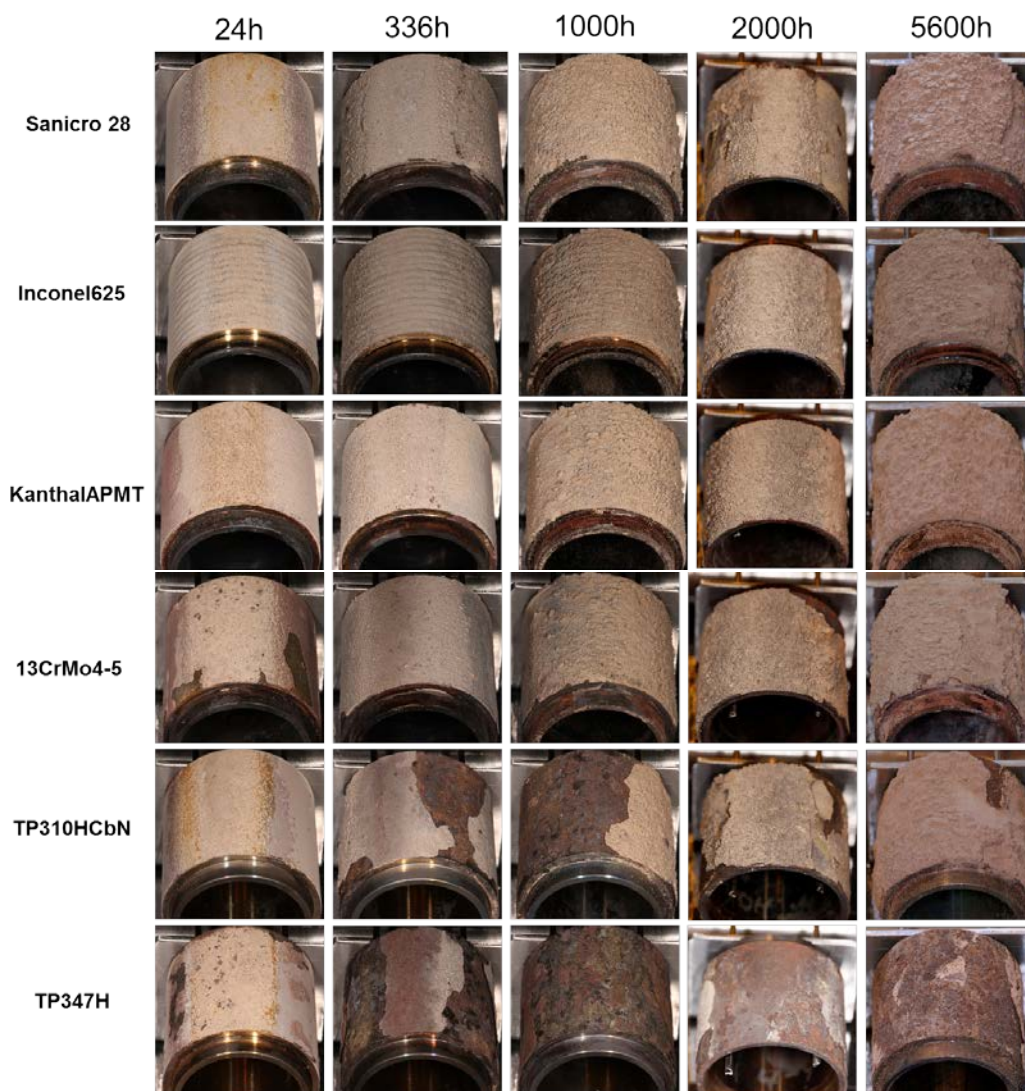
The measured temperature in the sample rings on the probes showed good match compared to set temperatures, typical min/max standard deviation were 4/12 °C.

In the middle of March 2012, the final probe as well as the test tubes was dismantled from boiler. The total exposure time of the test tube and probe (P5) was about 5600 h (5568 h). All the samples from the probes were transported together with moister absorbing medium to HTC at Chalmers prior to analyses. The test tubes were also transported together with moister absorbing medium to Metso's workshop where the 2 meter long tube sections were cut down to manageable pieces. From every test tube, 4 pieces with 10 cm length were kept for analyses, whereof the ones from center part of the test tubes were sent to HTC in Chalmers for comparing analyses with the probe test rings. Corrosion evaluation of probe exposures

The main aim for this project has been to perform long term corrosion testing with multiple probes in order to obtain more accurate corrosion rates and thereby compare if there is a difference between probe and tube exposures (with respect to the corrosion rate).

4.1.3 Optical investigation

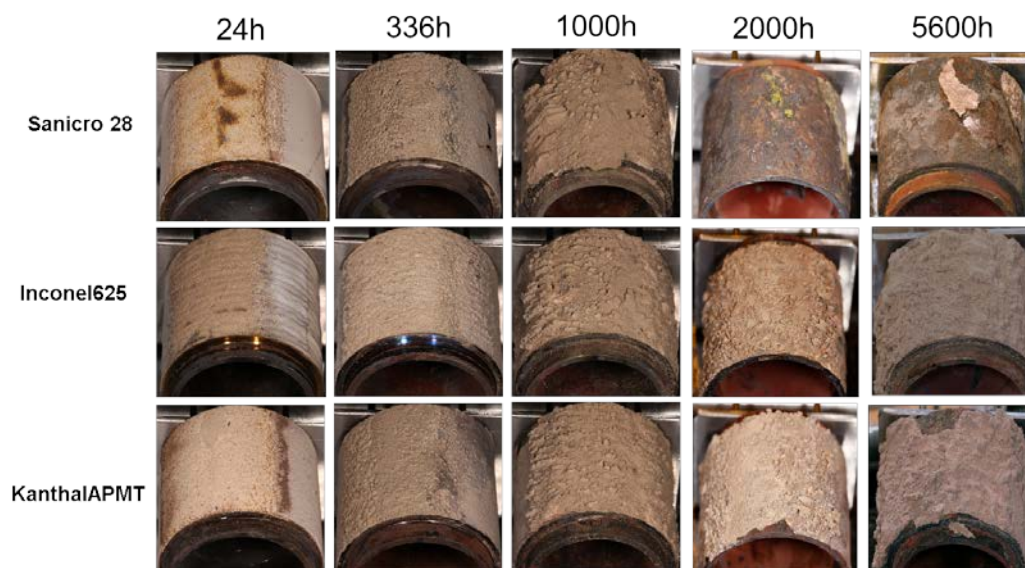
In Figure 16 - Figure 17 the probe sample rings are shown after exposure, at 420 °C and 500 °C respectively. The probe samples exposed at the lower temperature (Figure 16) reveals a beige/brown deposit which grows with exposure time. The deposit layer after 5600 hours is still in the sub-cm range. However, some of the samples experienced spallation and a black and reddish layer, indicating the corrosion product layer, could be seen. The spallation is especially pronounced on the TP347H material. The spallation is expected to have primarily occurred during air-quenching after exposure.



Figur 16. Optiska bilder av provringarna exponerade vid 420 °C.

Figure 16. Optical images of the samples exposed at 420 °C.

In Figure 17 the probe sample rings exposed at 500 °C are shown. At this temperature only Sanicro28, Inconel625 and KanthalAPMT were exposed. Compared to corresponding exposures at 420 °C, the deposit layer is thicker, especially after 5600 hours. The colour of the deposit is however similar as for the deposit formed on the corresponding samples at 420 °C. Furthermore, some spallation is detected on the Sanicro28 sample after longer times.

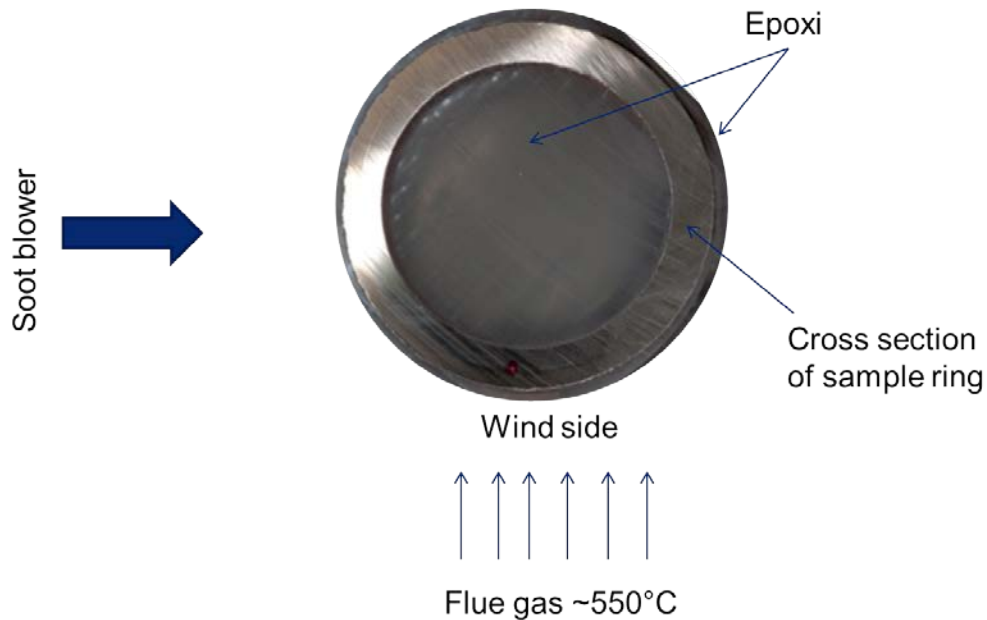


Figur 17. Optiska bilder av provringarna exponerade vid 500 °C.

Figure 17. Optical images of the samples exposed at 500 °C.

Prior to material loss determination, the sample rings were mounted in epoxy and cut into two with subsequent polishing of the obtained cross section. The position of the samples with respect to flue gas direction and soot blower is seen in Figure 18.

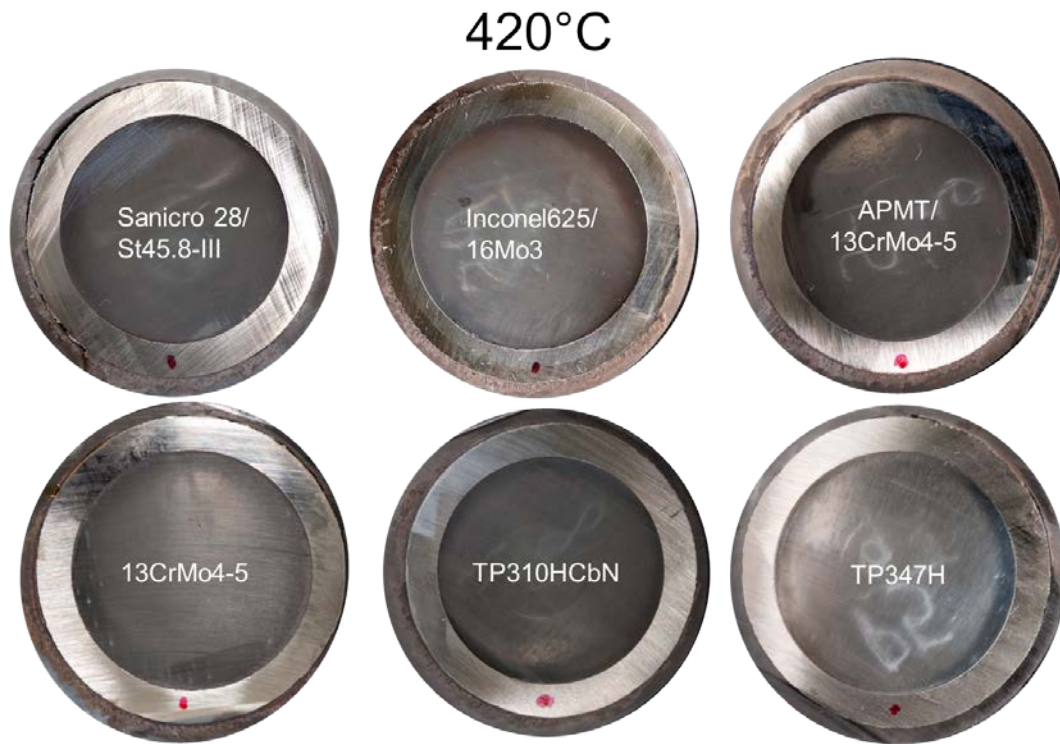
Exposure with probes



Figur 18. Schematisk bild av hur provringarna har suttit i förhållande rökgasflöde och ångblåsare.

Figure 18. Schematic image of the placement of the probe samples in relation to the flue gas direction and soot blower.

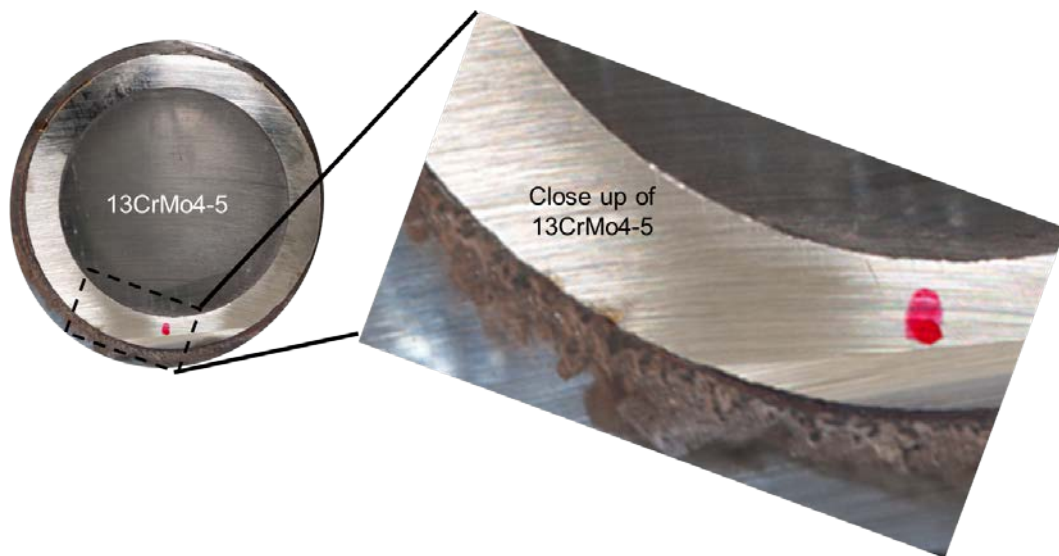
The optical cross sectional images shown in Figure 19 show all samples exposed for 5600 hours at 420 °C. The images reveal no or little signs of corrosion. Still after 5600 hours, the outer part of the sample rings exhibits a rather smooth and unattacked surface. For the samples exposed at 420 °C the material loss seems uniform around the ring and no preferential direction (e.g. wind side) of the corrosion attack can be seen.



Figur 19. Optiska bilder av tvärsnittet av provringarna exponerade vid 420 °C i 5600 timmar. Den röda pricken markerar vindsida.

Figure 19. Optical images of the cross section of the samples exposed at 420 °C for 5600 hours. The red dot marks the wind side.

The corrosion front of 13CrMo4-5 after 5600 hours is shown in Figure 20 displaying a close up of the sample ring. A thin oxide layer (closest to the metal in dark grey) can be seen above the steel surface, covered in a relatively thin deposit layer (beige/brown in color). The evenness of the steel sample's circumference indicates that the corrosion attack has been mild.



Figur 20. Förstoring av 13CrMo4-5 provet som visades i Figur 19

Figure 20. Close up of the 13CrMo4-5 sample shown in Figure 19

Three materials (i.e. Sanicro28, KanthalAPMT and Inconel625) were tested at the higher material temperature (i.e. 500 °C). These samples exposed at 500 °C for 5600 hours are shown in Figure 21. Of these three samples, it is clear that the 13CrMo4-5 sample sprayed with KanthalAPMT performed worst. On this sample black/dark grey oxide layers could be seen and the circumference of the steel ring appears nugget and uneven. However, there is a remarkable difference between left and right side of the sample, where the left side is much more corroded. This could also be seen on the Sanicro28 and Inconel625 samples. However, the difference between the two sides was not equally pronounced as for the APMT sample. The more corroded side of the sample rings has been subject towards the nearby soot blower, see Figure 18.

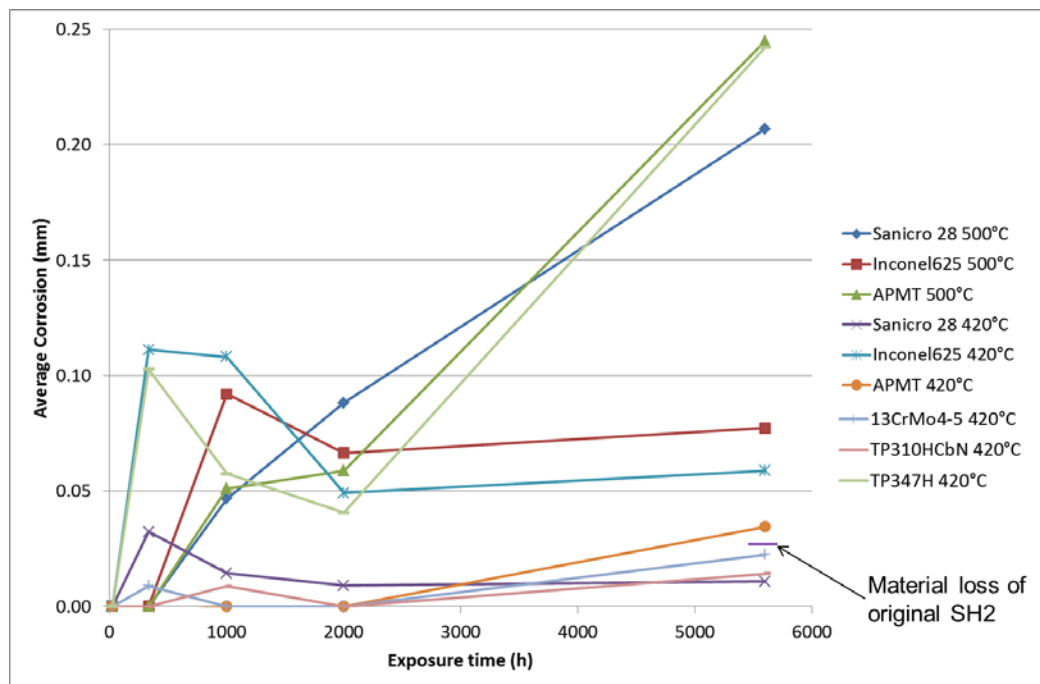


Figur 21. Optiska bilder av tvärsnittet av provringarna exponerade vid 500 °C i 5600 timmar. Den röda pricken markerar vindsida.

Figure 21. Optical images of the cross section of the samples exposed at 500 °C for 5600 hours. The red dot marks the wind side.

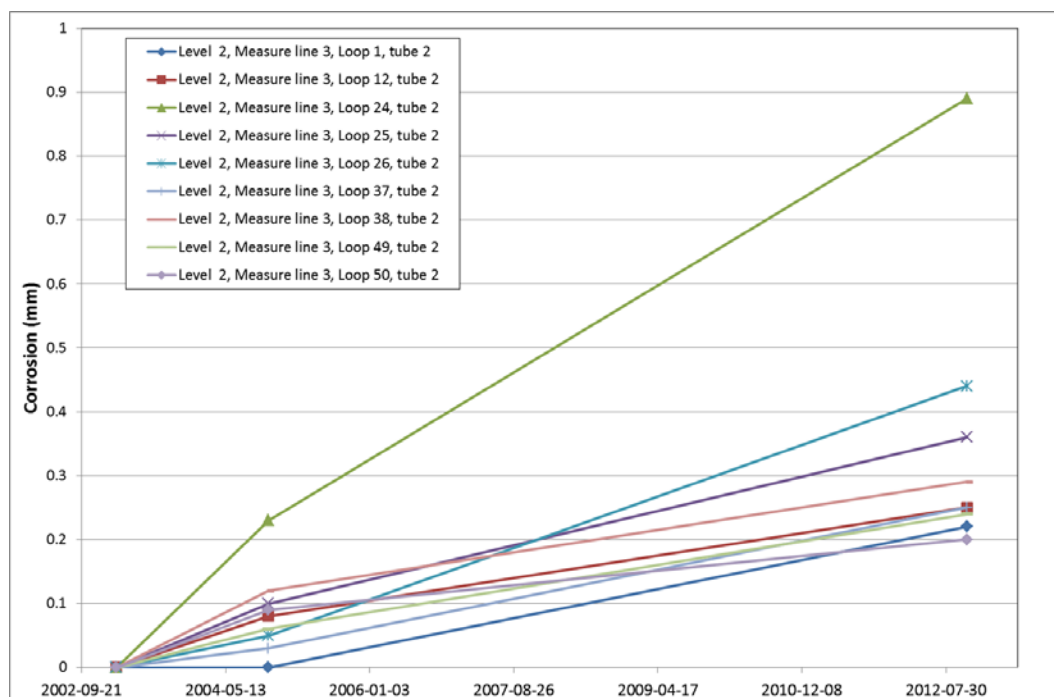
4.1.4 Material loss determination

In Figure 22, the material loss in mm versus the exposure time is plotted for all probe samples. Overall the corrosion rate of the majority of exposed samples after 5600 hours was below 0.1 mm/year, which often is referred to as an acceptable level of corrosion. The uncertainty of the material loss data is ± 0.03 mm with respect to the measuring method used. The uncertainty of the method was calibrated in a former project [3]. All data points refer to a single sample, hence 5 probes were exposed for 24, 336, 1000, 2000 and 5600 hours respectively. Hence, the scatter between different data points is expected to slightly higher than ± 0.03 mm. The 24 hours exposed sample was not evaluated by means of material loss. The samples exposed at the higher material temperature, i.e. 500 °C, showed higher mass loss compared to the samples exposed at 420 °C. The exception being the TP347H steel exposed at 420 °C which experienced the highest mass loss of all tested materials, around 0.25 mm after 5600 hours. The measured corrosion rate of the corrosion probes correlates rather well with the corrosion rate of the superheaters currently installed (life time today is nearly 12 years). The marked line in Figure 22 shows the material loss of currently installed superheaters, calculated as an average value from the thickness measurements of P14 presented in Figure 23.



Figur 22. Materialavverkning i mm (medelvärde) vs exponeringstid i timmar. Osäkerheten i mätningen är $\pm 0,03$ mm.

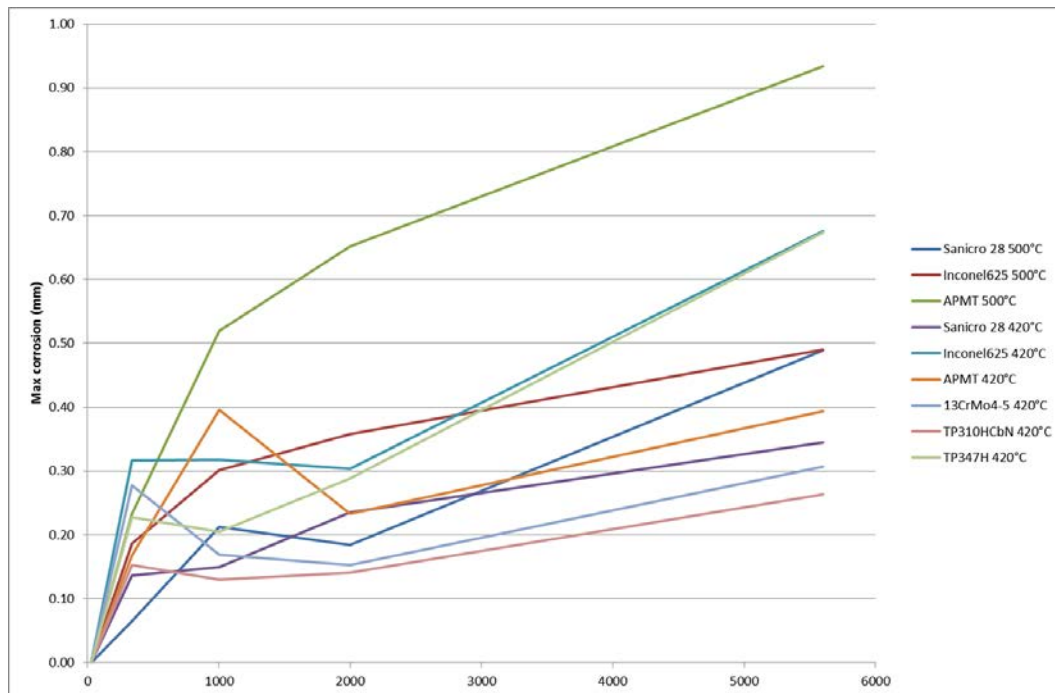
Figure 22. Average materials loss in mm versus exposure time in hours. The uncertainty of the measurement is ± 0.03 mm.



Figur 23. Materialavverkning i mm uppmätt mellan 2002-2012 på överhettare 2

Figure 23. Material loss in mm measured on the SH2 between 2002-2012

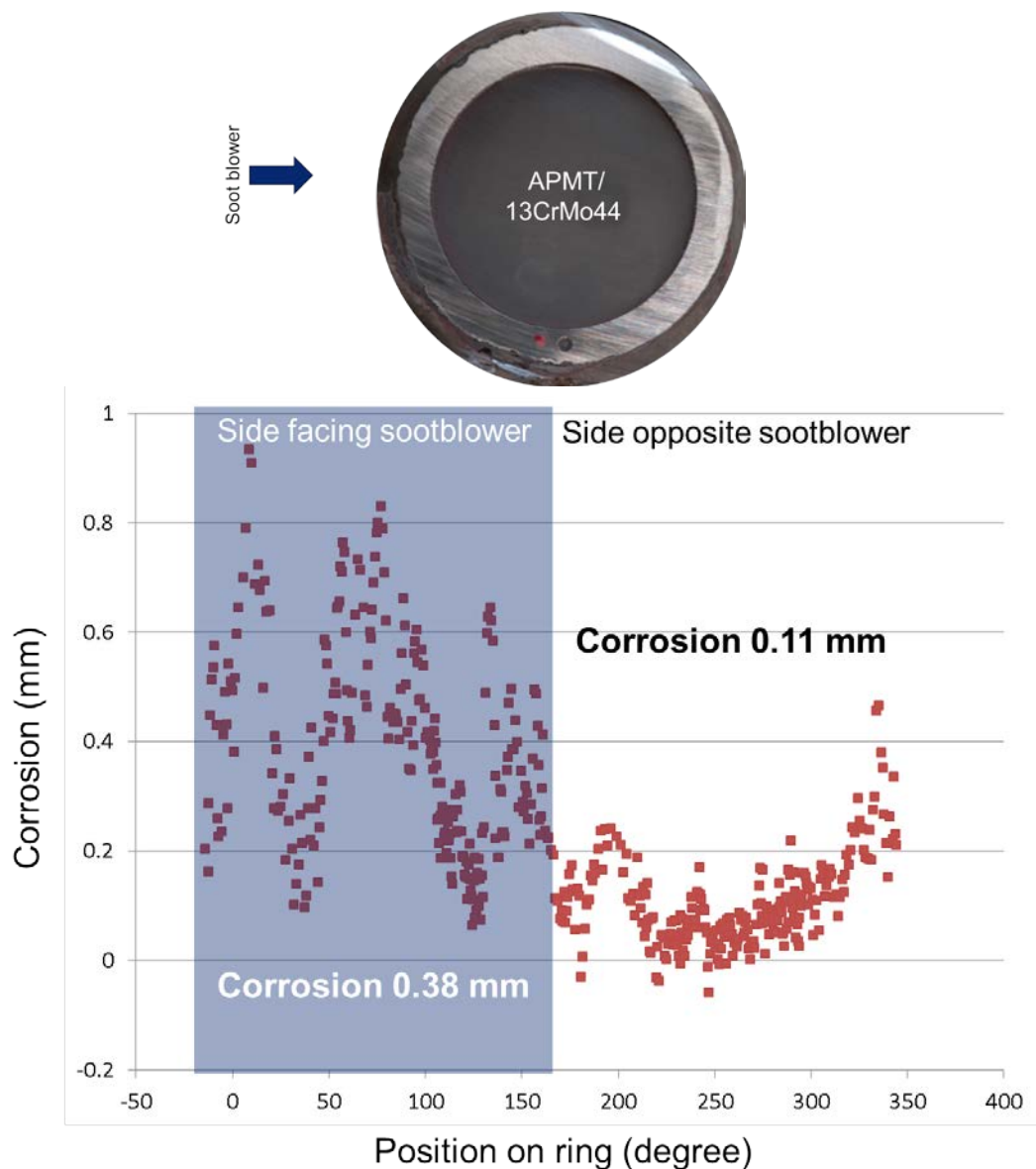
The maximum corrosion rates, by means of material loss measurements, are shown in Figure 24. The APMT coated sample (13CrMo4-5) exposed at 500 °C experienced the highest material loss of all tested materials. After 5600 hours the highest material loss in any single measuring point is slightly above 0.9 mm, corresponding to material wastage of about 1.4 mm/year. The maximum material loss, for most samples, is between 0.2 and 0.5 mm (corresponding to 0.3 – 0.8 mm/year). With the exception of the APMT coated sample, there is no major effect of the material temperature on the maximum material wastage. In fact, the difference in material loss between the two temperatures is only 0.15 mm for both Sanicro28 and Inconel625, where the lower temperature for Inconel625 actually experiences a higher maximum material loss compared to the corresponding sample exposed at higher temperature. The APMT coated sample (having the low alloyed 13CrMo4-5 as base material) experiences a much higher difference, around 0.55 mm or more than twice as high material loss for the sample exposed at 500 °C compared to the sample at 420 °C. However, the APMT sample exposed at 500 °C show signs of damage which could be related to the nearby soot blower. Hence, part of the corrosion rate on the 500 °C sample could be related towards the effect of the soot blower, see Figure 25.



Figur 24. Maximal materialavverkning i mm vs exponeringstid i timmar. Osäkerheten i mätningen är $\pm 0,03$ mm.

Figure 24. Maximum materials loss in mm versus exposure time in hours. The uncertainty of the measurement is ± 0.03 mm.

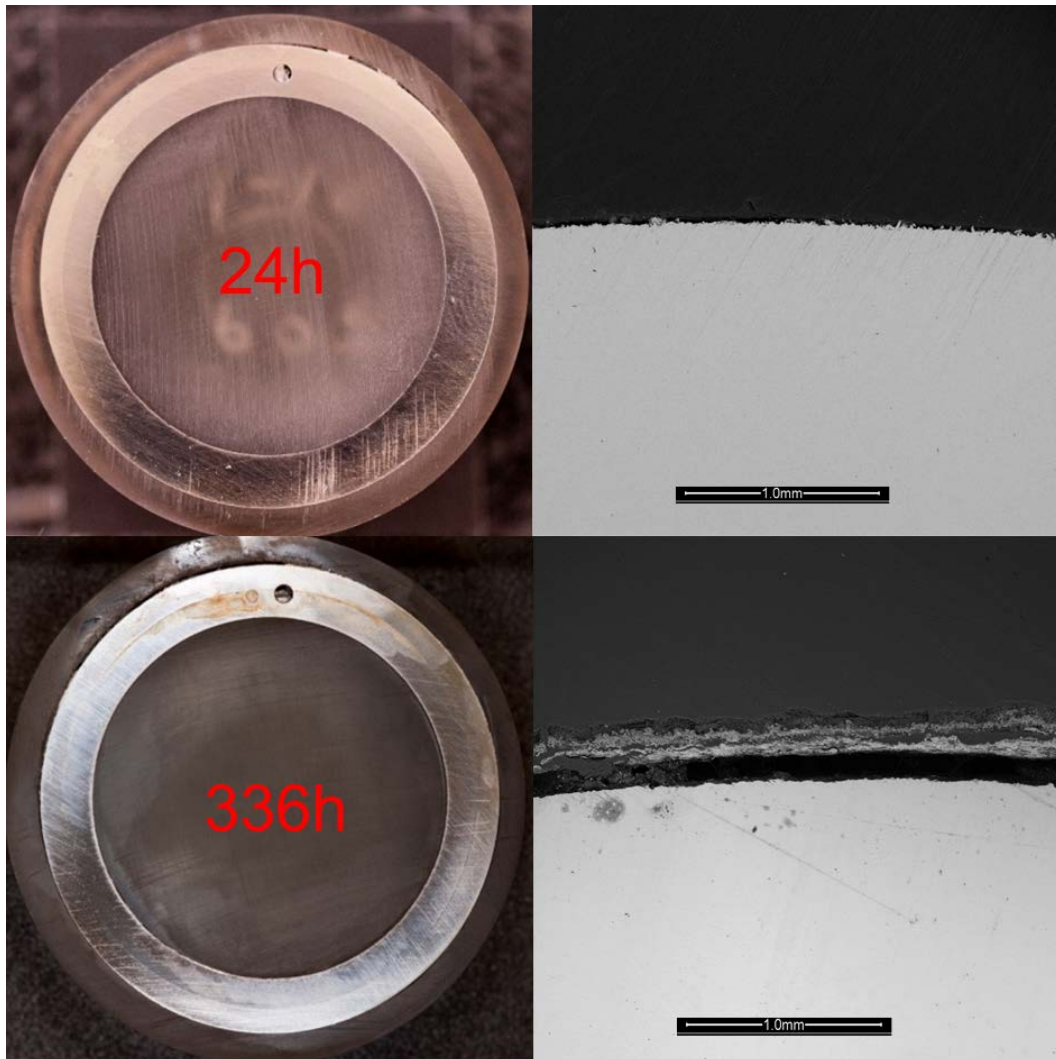
In Figure 25, the optical image of the cross section sample ring together with the material loss measurements versus position on the sample is shown for the APMT sample exposed at 500 °C for 5600 hours. From the material loss determinations, it is shown that there is a factor about 3.5 between the two sides with respect to material loss (0.38 mm and 0.11 mm, respectively). The increased material loss may refer to both erosion and corrosion or, more likely, a combination of these two effects. For the tube exposed samples, see section 4.2, the results do not reveal any tendency for being unevenly attacked with respect to the position to the soot blower. However, the tube samples were installed further from the soot blower than the probe samples. In addition, some shielding from the lower tube row may have also have decreased the erosive effect of the soot blower.

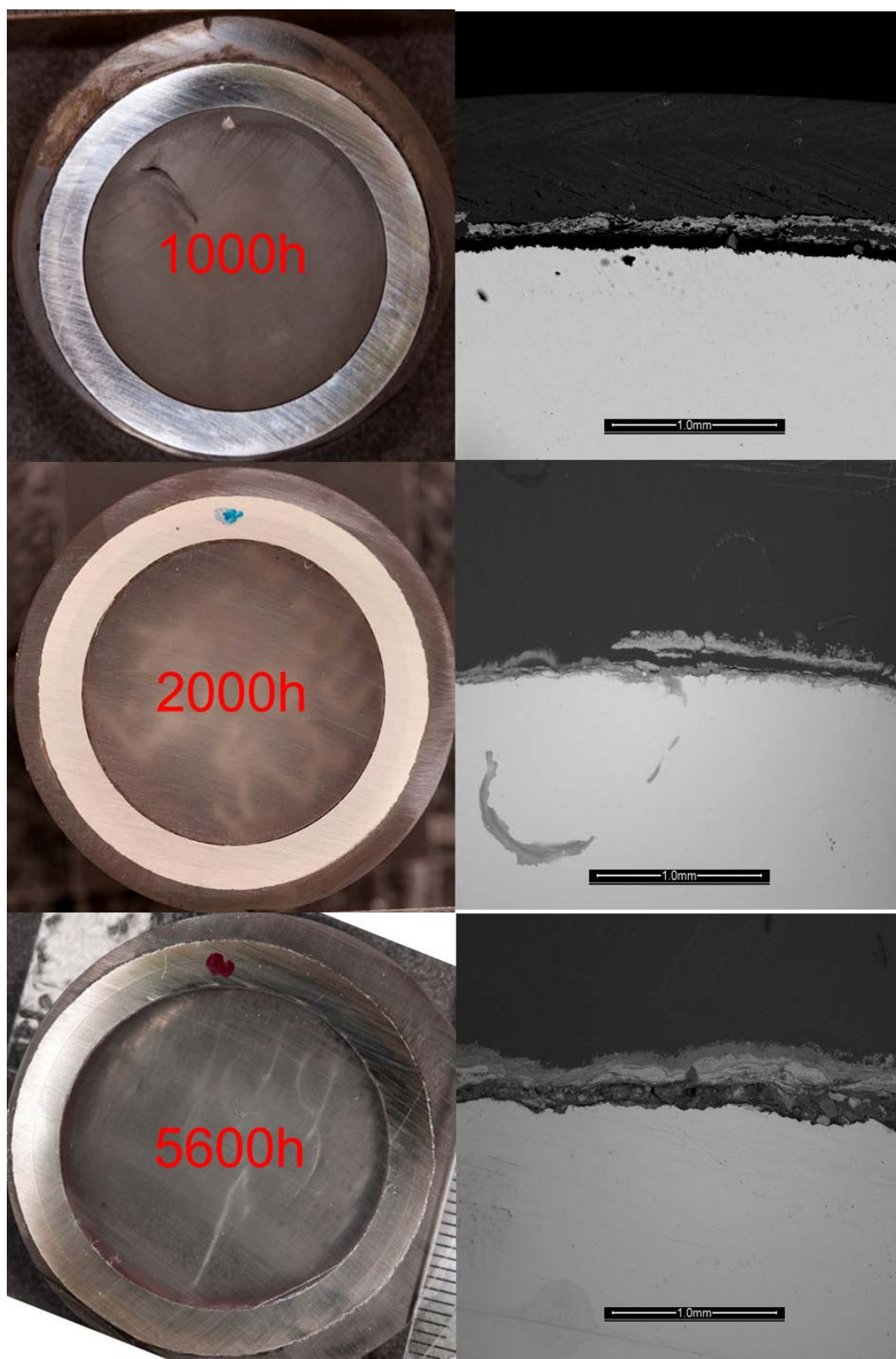


Figur 25. Effekt av sotblåsare på materialförlustmätningen av APMT provet exponerad vid 500 °C i 5600 timmar.

Figure 25. Effect of soot blower on material loss on the APMT sample exposed at 500°C for 5600 hours.

In Figure 26 cross sectional analysis of Sanicro28 exposed at 500 °C in a time resolved manner can be seen. The optical images on the left side show that the extent of corrosion has been rather mild. However, the steel surface seems somewhat nugget after 5600 hours. The SEM images reveal that the corrosion attack started already after 336 hours and progressed during the exposure towards 5600 hours, by an increasingly unevenness of the steel surface. This implies well with the material loss determination analysis which measured the highest material loss (0.21 mm corresponding to 0.33 mm per year) on the 5600 hours sample.



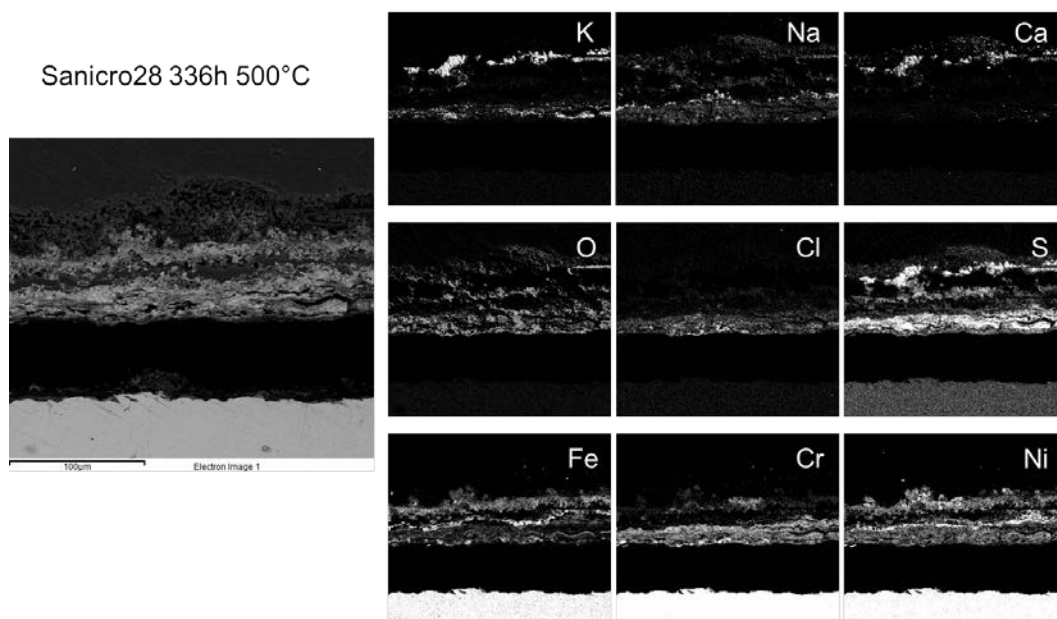


Figur 26. Tvärsnitt av Sanicro28 exponerad vid 500 °C i 24 – 5600 timmar.

Den vänstra kolumnen visar optiska bilder och den högra kolumnen visar SEM bilder.

Figure 26. Cross sections of Sanicro28 exposed at 500 °C for 24 – 5600 hours. The left column shows optical images and the right column shows SEM images.

In order to further investigate the corrosion attack SEM/EDX analysis was performed on the Sanicro28 samples exposed at 500 °C, see Figure 27 - Figure 31. As was shown by the cross sectional images in Figure 26, the degradation of the initial protective oxide seems to occur between 24 and 336 hours. In Figure 27, the SEM/EDX analysis of Sanicro28 exposed at 500 °C for 336 hours is shown. The corrosion product layer is approximately 50 µm thick consisting of an inner part being chromium rich and an outer part rich in iron and nickel. In addition, deposit related elements are detected throughout the corrosion product layer, such as K, Na, Cl and S. From the EDX analysis it is hard to distinguish what phases that is present. Further out, in the deposit layer, the correlation between K, Ca and S indicates the presence of $K_2Ca_2(SO_4)_3$. In addition, areas with only Ca and S (and O) exits, indicating the presence of $CaSO_4$. Due to the chromium enrichment of the inner part of the oxide some protective properties may be attributed to the corrosion product layer. However, the adherence of the oxide is poor and with thermal cycling of the boiler, this layer is expected to detach and spall.

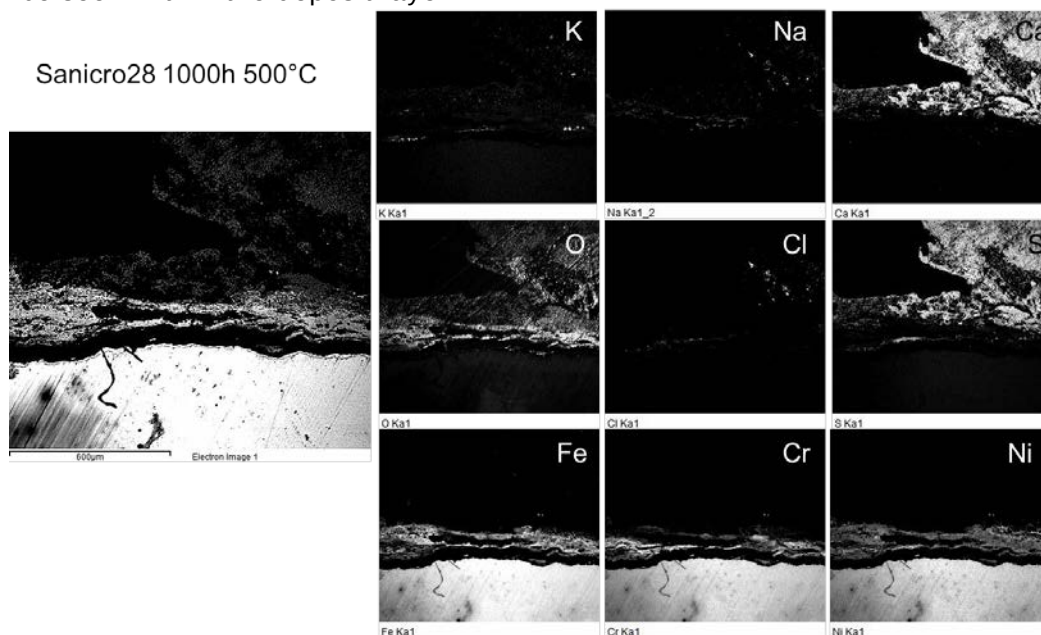


Figur 27. SEM/EDX analys av ett tvärsnitt av Sanicro28 exponerad vid 500 °C i 336 timmar.

Figure 27. SEM/EDX analysis of the cross section of Sanicro28 exposed at 500 °C for 336 hours.

After 1000 hours, the corrosion product layer has grown to about 200 µm, see Figure 28. The rather dense chromium rich inner layer seen after 336 hours is

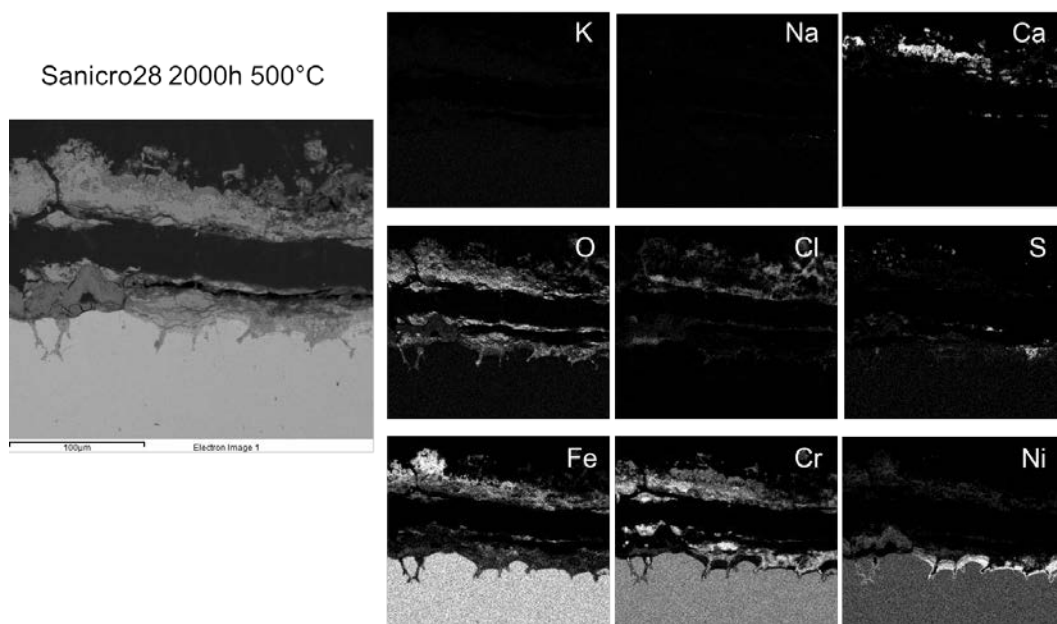
not equally pronounced after 1000 hours. Instead, the level of chromium is lowered and more dispersed in the oxide. The deposit is dominated by calcium and sulphur, indicating the presence of CaSO_4 . In addition, small enrichments of sulphur could be seen within the corrosion product layer, associated with chromium and/or nickel. Besides CaSO_4 , dispersed NaCl and KCl particles can be seen within the deposit layer.



Figur 28. SEM/EDX analys av ett tvärsnitt av Sanicro28 exponerad vid 500 °C i 1000 timmar.

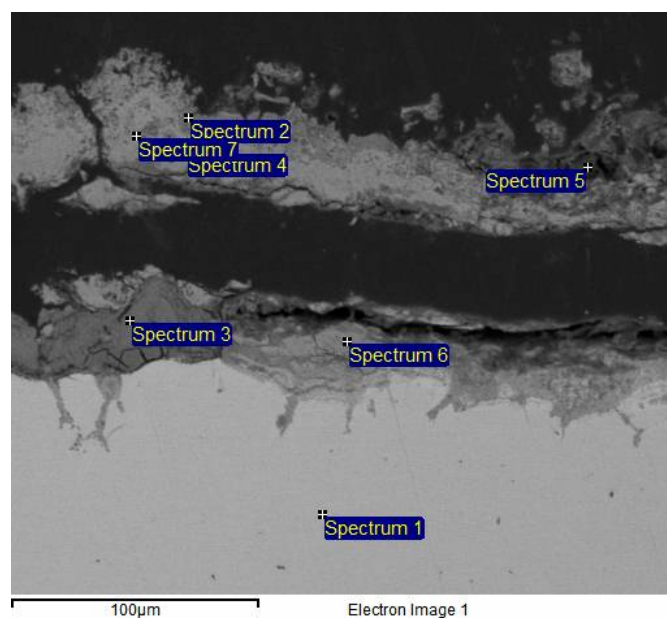
Figure 28. SEM/EDX analysis of the cross section of Sanicro28 exposed at 500 °C for 1000 hours.

In Figure 29, the SEM/EDX analysis of Sanicro28 exposed at 500 °C for 2000 hours is shown. The adherence of the corrosion product layer is poor and the oxide layers have detached from each other. The oxides formed consist of a mixture of iron and chromium. The corrosion front also show signs of selective oxidation of the steel grain boundaries, i.e. internal oxidation. Both Cl and S are detected with small amounts within these internal oxide areas. Chlorine is detected throughout the whole oxide layer, indicating a less protective oxide. This is further strengthened by the presence of Ca, Cr and O in the top of the oxide layer. The EDX quantification reveals the composition to be 16% Ca, 16% Cr and 66% O, which correlates well with CaCrO_4 . The formation of chromate is known to decrease the protective properties of the chromium rich oxide normally formed on stainless steels [19-21]. However, despite the chromate formation, there are still areas within the oxide layers that are enriched in chromium (e.g. spectrum 4 and 6).



Figur 29. SEM/EDX analys av ett tvärsnitt av Sanicro28 exponerad vid 500 °C i 2000 timmar.

Figure 29. SEM/EDX analysis of the cross section of Sanicro28 exposed at 500 °C for 2000 hours.



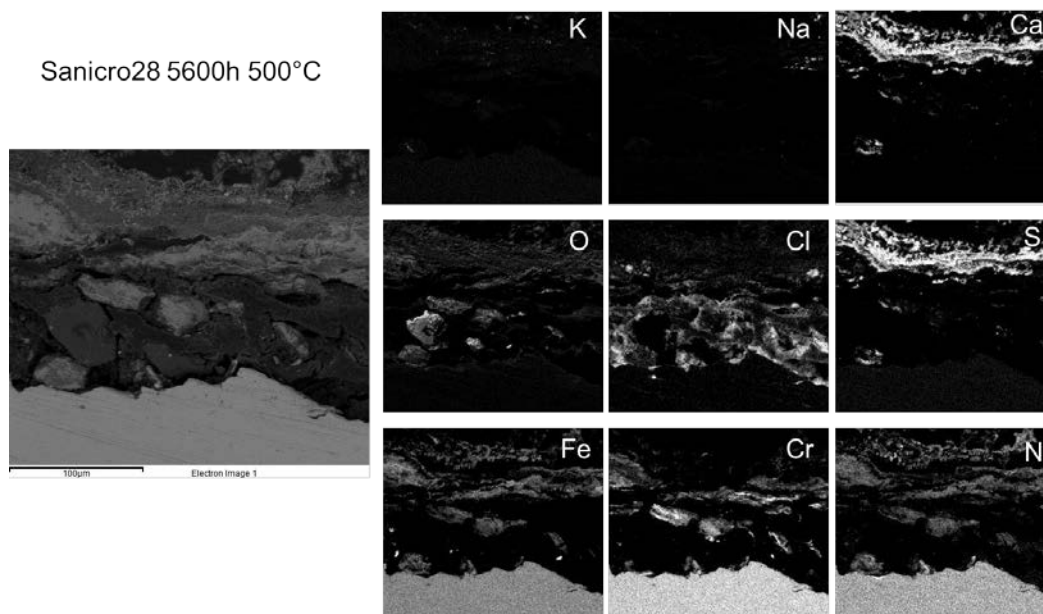
Figur 30. SEM/EDX punktanlys av ett tvärsnitt av Sanicro28 exponerad vid 500 °C i 2000 timmar.

Figure 30. SEM/EDX point analysis of the cross section of Sanicro28 exposed at 500 °C for 2000 hours.

(a%)	O	Na	K	Ca	S	Cl	Fe	Cr	Ni
Spectrum 1	0	0	0	0	0	0	38	31	31
Spectrum 2	66	0	0	16	0	1	1	16	0
Spectrum 3	52	0	0	2	4	6	6	4	26
Spectrum 4	55	1	0	0	2	1	10	26	5
Spectrum 5	77	1	0	5	0	11	2	3	1
Spectrum 6	59	1	0	0	1	1	5	31	2
Spectrum 7	53	0	0	1	2	2	18	15	9

Table 8. EDX quantification of the elemental composition of the points shown in Figure 30.

In Figure 31, the SEM/EDX analysis of Sanicro28 exposed at 500 °C for 5600 hours is shown. The progress of the corrosion attack continues on the same path as for the samples exposed for shorter time; the oxide layer has become more dispersed and the presence of chlorine in the corrosion product layer has increased further. From the SEM/EDX analysis a deposit dominated by Ca, S and O (probably CaSO_4) can be seen. The inner part of the loose oxide layer consists of Fe, Cr and Ni whereas the outer part only contains Fe and Ni. Throughout the whole oxide layer chlorine enrichments can be seen.



Figur 31. SEM/EDX analys av ett tvärsnitt av Sanicro28 exponerad vid 500 °C i 5600 timmar.

Figure 31. SEM/EDX analysis of the cross section of Sanicro28 exposed at 500 °C for 5600 hours.

4.1.5 The effect of start-up

Corrosion rate measurements are usually performed by means of exposing corrosion probes for various times, materials and temperatures. The exposure is often performed in such way that the cold probe is put into the boiler, through some type of measurement hole, during operation. Hence, the cold probe experiences directly the hot flue gases and plausibly intense condensation of various species is occurring during the initial stages. The ramping period can take up to 30 minutes until the desired material temperature is achieved. The right images in Figure 32 and Figure 33 are showing Sanicro28 exposed for 24 hours at 500 °C according to this type of startup (from KME411 [18]). The left images in Figure 32 and Figure 33 are also showing Sanicro28 exposed at 500 °C. However, the exposure history for this sample is different. The corrosion probe was mounted into the boiler during revision, i.e. into a cold boiler. During startup the boiler was fired with oil during 72 hours in order to dry out all new brick work installed during the revision. After this initial time, the fuel gradually changed to waste and the corrosion probe was exposed for an additional 24 hours after that the fuel-mix was 100% waste.

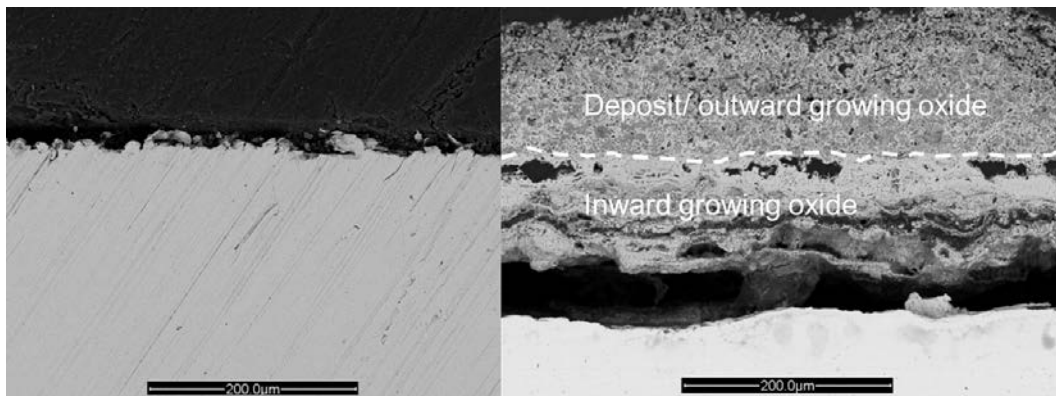


Figur 32. Optiska bilder av vindsidan av Sanicro28 exponerade med korrosionssond vid 500 °C. Till vänster: Långsam start (start från kall panna, ~72 timmar med oljeeldning innan 24 timmar med avfallsförbränning) Till höger: Snabb start (24 timmar med avfallsförbränning, kall sond installerades direkt in i en varm panna).

Figure 32. Optical images of the wind side of Sanicro28 exposed at 500 °C on a corrosion probe. To the left: Slow startup (start from cold boiler, ~72 hours oil then 24 hours waste) To the right: Fast startup (24 hours waste, cold probe going directly into the hot boiler).

Comparing these two Sanicro28 samples it is evidently so that the sample mounted during revision and experienced a slow heat up has suffered less from corrosion. This can clearly be seen in the SEM cross sections in Figure

33; the corrosion front of the Sanicro28 sample shown to the right is over 250 μm thick whereas the Sanicro28 sample to the left only have formed a thin and protective oxide layer in the submicron range. Both samples have been exposed in the same position and at same material- and flue gas temperature in the P14 boiler using 100% waste. However, the Sanicro28 sample to the right (i.e. startup during operation) was exposed in the former KME411 project in 2007 (compared to the exposure in KME509 in 2011). Hence, it cannot be ruled out that the difference in corrosion attack may be attributed to other effects, e.g. long term change in fuel composition or difference in local flue gas chemistry. In order to fully elucidate the effect of the starting sequence on the corrosion rate, new exposures are needed.

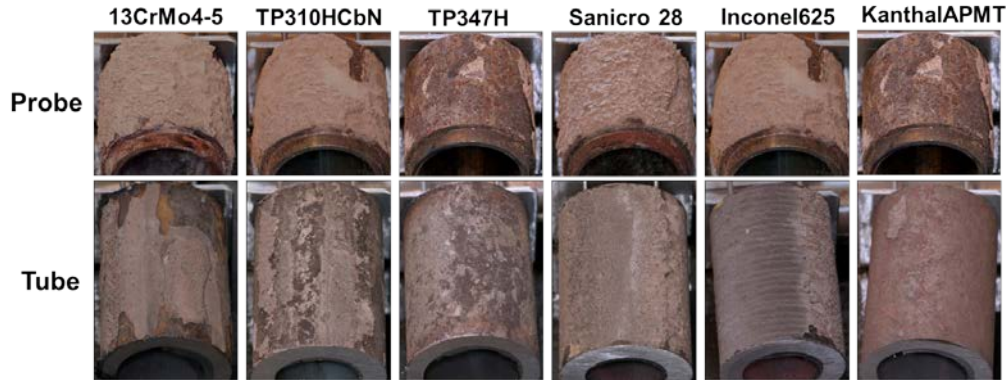


Figur 33. SEM bilder av vindsidan av Sanicro28 exponerade med korrosionssond vid 500 °C. Till vänster: Långsam start (start från kall panna, ~72 timmar med oljeeldning innan 24 timmar med avfallsförbränning) Till höger: Snabb start (24 timmar med avfallsförbränning, kall sond installerades direkt in i en varm panna).

Figure 33. SEM cross sectional images of the wind side of Sanicro28 exposed at 500 °C on a corrosion probe. To the left: Slow startup (start from cold boiler, ~72 hours oil then 24 hours waste) To the right: Fast startup (24 hours waste, cold probe going directly into the hot boiler).

4.2 Corrosion evaluation of tube exposures

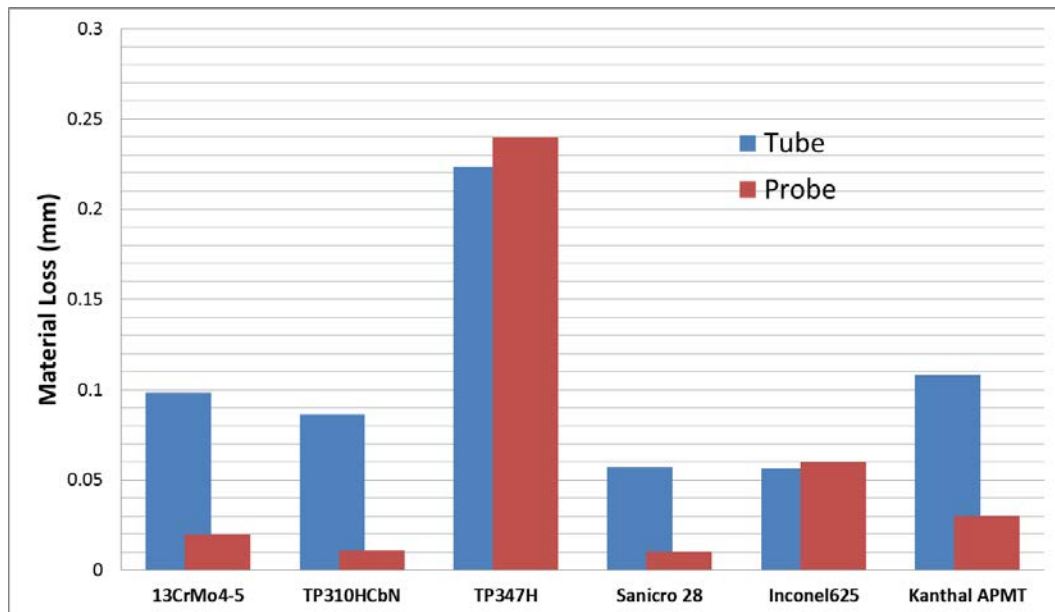
The comparison between the probe and tube exposures is shown in Figure 34 - Figure 36. In general, there were little or no difference between the samples exposed on a probe and the samples installed in the superheater tube bundle. There is a tendency of slightly thicker deposit layer on the probe samples compared to the tube samples. However, this may be an effect of the probes being mounted upstream the tube samples. Furthermore, the tube samples were mounted in row 2 and some shielding from row 1 is expected.



Figur 34. Optiska bilder av provringarna från sond (övre raden) och tub (nedre raden) exponerade vid 420 °C

Figure 34. Optical images of the probe samples (top row) and tube samples (bottom row) exposed at 420 °C

In Figure 35 the material loss data of tube and probe samples exposed for 5600 hours at 420 °C are shown. In general, the measured corrosion rate was low. The trend of the corrosion rates between the tested materials correlates well between the tube and probe exposures; 347H shows the highest corrosion rate and Sanicro28 shows the lowest corrosion rate. Some of the tested materials (e.g. 13CrMo4-5 and TP310HCbN) show rather large percentage deviation between the tube and probe exposures. However, due to the low corrosion rate, some of the measured values lie within the margin of errors (approximately 0.03 mm). Hence, the deviation shown is not statistically safe and it is hard to conclude if there exists any difference in material losses between probe and tube exposures. However, the lack of clear evidence of such a difference also indicates that it does not exist. For the samples with highest corrosion rate, (*i.e.* the 347H samples), the material losses are well above the margin of error level and here, the deviation between tube and probe exposed samples is much smaller.



Figur 35. Materialverkning i mm för sond och tubprov exponerade vid 420 °C i 5600 timmar

Figure 35. Material loss in mm measured on probe and tube exposed samples exposed at 420 °C for 5600 hours

In Figure 36, the optical images of Sanicro28 exposed on a probe (to the left) and as a tube (to the right) for 5600 hours at 420°C are shown. The optical images agree well with material loss measurements, showing small wastages and corrosion resistance.

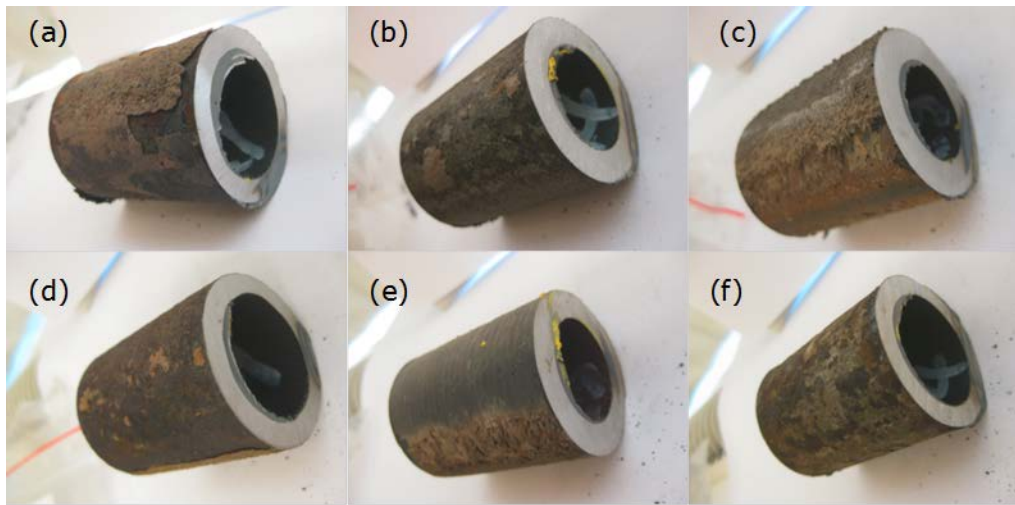


Figur 36. Tvärsnitt av Sanicro28 exponerad vid 420°C i 5600 timmar. Till vänster: sondprov. Till höger: Tubprov

Figure 36. Cross sections of Sanicro28 exposed at 420 °C for 5600 hours. To

the left: probe sample. To the right: tube sample.

In addition to the tube analysis performed at Chalmers, Metso was performing additional analysis of other sections of the test tubes, see Figure 37. In agreement with previous analysis of the tube samples, no sign of severe corrosion could be seen beside surface corrosion for all test tubes. The bright yellow colour shown on the tubes in Figure 37(b) and (e) came from mark-up pen.



Figur 37. Tubprovbitar efter exponering av (a) 13CrMo4-5, (b) TP310HCbN, (c) Sanicro28/St45-8, (d) APMT/13CrMo4-5, (e) Inconel625/16Mo3 (f) TP347H

Figure 37. Test tube samples after exposure, (a) 13CrMo4-5, (b) TP310HCbN, (c) Sanicro28/St45-8, (d) APMT/13CrMo4-5, (e) Inconel625/16Mo3 (f) TP347H

The outer diameter of the test tubes was measured with calliper before and after exposure. The results are shown in Table 9 below. The diameter shown in the table is an average number of 6 measurement and standard deviation is shown in brackets. The outer diameter of the test tubes was about 38 mm, and standard deviation of the APMT/13CrMo4-5 and Inconel625/16Mo3 were somewhat higher than others, as expected, due to manufacturing conditions (thermal spraying and overlay welding). The test tube pieces were brushed to remove deposits and then measured with calliper and with optical camera. For most of the test tubes except for APMT/13CrMo4-5, the outer diameter has increased slightly. This increase is referred to as an uncertainty in the measuring technique and that the material losses are generally low.

Tube sample	Outer diameter Before exposure [mm]	Outer diameter after exposure [mm]	
	With calliper	With calliper	Optical camera measurement
13CrMo4-5	37,90 (0,05)	38,03 (0,48)	38,05 (0,30)

<i>TP347H</i>	37,72 (0,02)	37,55 (0,26)	37,67 (0,27)
<i>APMT/13CrMo4-5</i>	38,65 (0,10)	38,70 (0,44)	38,38 (0,19)
<i>TP310HCbN</i>	37,93 (0,04)	38,00 (0,14)	38,08(0,27)
<i>Inconel625/16Mo3</i>	37,43 (0,12)	37,27 (0,56)	37,34 (0,56)
<i>Sanicro28 /ST45.8/III</i>	38,01 (0,01)	38,70 (0,44)	38,25 (0,18)

Table 9. The average outer diameter of the test tubes before and after exposure. The average number of 6 measurements and standard deviation is shown in brackets.

5 Analysis of results

The background for this project is derived from the usually poor estimations on corrosion rate of the superheaters in biomass and waste fired boilers obtained by probe exposures. Better estimations of the superheater corrosion will lead to better plant economy as changing a superheater is usually associated with great costs. Today, the estimated corrosion rate of the superheaters is usually extrapolated from probe measurements, exposed for a certain time (e.g. 1000 hours). Due to the limitations of these estimations, the boiler owners are instead planning upcoming changes of the superheaters by performing thickness measurements of the superheater bundle during the yearly revision. This project has aimed for increasing the knowledge about corrosion testing in order to facilitate the development of models for determination of the service life of superheater materials as a function of material temperature. In order to improve the life prediction models of superheaters from probe exposures it is of utter importance that the probe exposures are performed in such a way that the correct corrosion attack is obtained. Several aspects then need to be taken into account. We have within the project focussed on the following aspects:

- **Time resolved probe exposures** – *if the corrosion rate is extrapolated from probe exposures, the slope of the corrosion curve will be a very important factor*
- **Probe versus tube exposures** – *Is there any difference if the sample is exposed on a probe or installed in the superheater tube bundle?*
- **Effect of start-up** – *How important is the start of exposure on the corrosion rate?*
- **How does the corrosion attack progress with time** - *Sanicro28 acts as an example*

Time resolved probe exposures

This project has successfully exposed corrosion probes up to 5600 hours in a time resolved manner. The exposure matrix started by having five probes mounted in the boiler during revision, together with installing 6 test sections in the superheater bundle. The probes have been removed from the boiler in consecutive manner after 24, 336, 1000, 2000 and 5600 hours, respectively. By having this frequent testing program, the aim was to obtain better information about the corrosion curve over time.

The results show that the corrosion rate of the materials exposed at 420 °C (the current material temperature of the superheaters today) is low. This was true for most of the tested materials (13CrMo4-5, TP310HCbN, Sanicro28, KanthalAPMT and Inconel625) with the exception of TP347H, which experienced somewhat higher corrosion rate. In fact, the corrosion rate was in many times within the margin of error of the used method in determining the material loss. However, these results are in line with the corrosion data of the

currently installed superheaters at this position, where Sanicro28 is currently installed. Until today, the superheaters at this position have been in operation for more than 12 years. According to the thickness measurements performed over the years during the revisions the corrosion rate is about 0.03 mm/year. From the Sanicro28 samples exposed on the probes the corresponding value is calculated to be 0.02 mm/year. Thus, the corrosion rate measurements agree well with the corrosion rate of currently installed superheaters.

At 500°C and long exposure times, a corrosive effect of the soot blower was observed on the probe exposed samples. The sample surface facing the soot blower was more corroded, for the APMT sample up to 4 times. This corrosion phenomenon was however not observed for the tube samples or the samples exposed at 420 °C. Since the probes, due to limitations in space, needed to be placed closer to the soot blower compared to the tube samples the corrosion rate of the probe samples may be accelerated with respect to the “true” corrosion rate of the installed superheater bundle.

Due to the small material loss and scatter between different exposure times, it is problematic to apply a generic mathematical expression to describe the corrosion rate. Furthermore, the kinetics of the corrosion attack, according to the corrosion rate measurements, does not appear to be unified for all samples. However, there is a tendency that the samples exposed at 500 °C exhibits a more linear growth rate whereas the samples exposed at 420 °C more follows a rate better described in terms of parabolic growth. Even though a general mathematical expression describing the corrosion of all materials is not obtained, the great number of exposed samples, resolved in time, leads to an improved estimation of the service life of the superheater. Hence, the prediction of the service life of the superheaters can be made with higher accuracy than just linearly extrapolating a single data point.

Probe versus tube exposures

One question addressed in the beginning of the project was if there exists an inherent arbitrary difference between samples exposed on probes and samples exposed as part of the superheater bundle. Thus, if such a difference exists, corrosion rate measurements by means of probe exposures are by default an inadequate method in estimating the service life of the superheater tubes. In order to answer this question, a location in the boiler needed to be selected where the probes were exposed to the same environmental conditions as the test sections in the superheater. As a result of this and availability in the boiler, the probes were mounted in the man door on level 6 which is located between two superheater bundles in superheater 2 (SH2), Figure 6. The samples that were installed in the superheater bundle were located above the probes. For 6 single tubes, a 2 meter long testing tube was installed, one for each material. Since the lowest rows were equipped with tube shields, the sample tubes were installed in Row 2. Since it is impossible to have the probes exactly in the same position as the tubes, this setup offered the most adjacent installation.

The results show that it is little difference between the probe and tube exposed samples with respect to corrosion rate. In both cases, 347H experiences the highest metal loss and Sanicro28 performs the best. The difference between probe and tube samples is, in average, a factor of two. However, this value is to some extent attached with an uncertainty affected

by that some measured material losses are within the margin of error of the method. For the material with the highest material loss, 347H, the deviation between the probe and tube measurements is less than 10%.

Based on the results, it is not expected that there exists an inherent difference between tube and probe exposed samples with respect to corrosion attack. The difference in corrosion rate between probe exposed samples and the superheater commonly referred to is thus an effect of the probe exposed samples not experiencing the same thermal and environmental history as the superheaters. Hence, if performing a probe exposure in which the aim primarily is to estimate the corrosion rate of the superheaters it is of great importance that the probes are exposed in such way that they truly mimics the superheaters. This includes for instance that the probes should be started from a cold boiler and during shorter stops the probes should remain inside the boiler (in similarity to the superheater tubes).

Effect of start-up

As mentioned earlier, the probes were mounted in the boiler during revision, i.e. the boiler was cold. The exposures were started as the boiler was ignited after revision. The startup sequence lasted for approximate 3 days when the boiler was heated by oil burners. The reason for this rather long period of time with oil burning was because of the hardening of the brick walls mounted during revision. After these days, waste fuel was fed to the boiler. As soon as normal waste firing conditions were achieved the exposure time was set to zero. The first probe was removed from the boiler after 24 hours from time equals zero, thus the total exposure time was about 96 hours for samples denoted "24 hours".

According to the results, it seems that the startup procedure (72 hours of oil burning) have mitigating effects on the corrosion of the materials. Sanicro28 exposed for 24 hours with waste, after the initial 72 hours with oil burning, is unaffected by corrosion, see Figure 26. If comparing this sample with a corresponding sample exposed earlier in KME411 (Same position, material temperature, material and exposure time with respect to fuel) the corrosion attack of the two samples are significantly different. For the Sanicro28 sample exposed directly to the waste environment (i.e. the sample exposed in KME411) the corrosion were immense and already after 24 hours the corrosion front is characterized by a thick, two layered oxide with a band of chlorine enrichment closest to the metal, see Figure 33. The corrosion product layer is at least 250 μm thick, compared to the oxide layer formed on the sample with 72 hours oil burning which is estimated to be in the sub micrometer range.

The reason or reasons behind the positive effect of starting the corrosion probes from a cold boiler can for now only be speculated around. The formation of a protective oxide layer in the mild environment during the startup is probably positive for the future corrosion protection material. Once waste is fed in to the boiler, the initial oxide layer is expected to some extent withstand the corrosive effect of the deposit layer formed on the sample. Another explanation to why the startup from a cold boiler may be beneficial in decreasing the initial corrosion attack is that there is a major difference in

corrosiveness of the environment during ramping up in material temperature. If started from a cold boiler, the probe is heated up in a mild environment characterized by low levels of e.g. alkali compounds and chlorine. For a sample heated up in an environment characterized by firing waste, the initial period of time would involve condensation of several corrosive species from the flue gas. Actually, during the really initial period of exposure, the probe temperature is raised from room temperature and before reaching the dew point of water vapour, a thin film of liquid water will form on the probe. By itself, this is not expected to cause any accelerated corrosion. However, if a liquid film of water is present, HCl(g) will immediately dissolve in it. Thus, the initial layer formed on the sample exposed directly towards a hot boiler is probably enriched in chlorine and expected to be highly corrosive. For a sample started from a cold boiler, the material temperature is already high when the waste is fed to the boiler and thus, condensation of water and subsequent dissolving of HCl will not occur. The effect of the startup sequence is however not yet fully understood and it suggested that this effect should be further investigated. This issue is closely related towards the corrosion memory effect addressed in the KME608 project.

How does the corrosion attack progress with time

The project has successfully performed a large exposure matrix which includes both long term testing (5600 hours is much longer time compared to what is normally achieved with probes) and detailed information of the corrosion rate in a time resolved manner. The project addressed the KME goal to verify an increase of the steam temperature by at least 50°C from 450 to 500°C for waste fractions in 2013. Three materials (Sanicro28, APMT coated on 13CrMo4-5 and Inconel625 welded on 16Mo3) were tested for both temperatures (i.e. 420°C and 500°C) in order to verify that an increase in steam temperature is possible. From the corrosion rate measurements, it is shown that for the Sanicro28 and APMT samples the increase in corrosion rate is significant for the 500°C samples compared to the 420°C samples, see Figure 22. For the Inconel625 samples there is almost no difference between the temperatures. For the APMT and Sanicro28 samples exposed at 500°C the corrosion is almost linear during the first 5600 hours, the corrosion rates corresponding to 0.39 and 0.33 mm/year, respectively. At 420°C , the samples follow a more protective behaviour and the corrosion rate after the initial corrosion is low, less than 0.05 mm/year for these materials. According to these results, there would be a much shorter lifetime of the superheater if it was operated at 500°C instead of 420°C . However, even though 5600 hours is a long time with respect towards probe testing, it is not necessarily so that the corrosion rate at 500°C would continue to be linear with time. In order to determine the condition of the corrosion resistance of the materials, SEM/EDX analyses of cross sections have been performed.

In Figure 27 - Figure 31, the progress of the corrosion attack of Sanicro28 exposed at 500°C is shown. According to the SEM/EDX analyses, the condition of the oxide layer is worsening with time. The chromium rich part of the oxide becomes more dispersed and on the 2000 hours sample, the presence of CaCrO_4 is detected. This indicates that the protective properties of the oxide layer are continually broken down. For the 5600 hours sample, the

oxide layer is enriched in chlorine. This is expected to further deteriorate the protective properties of the oxide layer as the diffusion of ions through this layer is expected to be greatly accelerated and thus, accelerating the corrosion rate. Hence, from the SEM/EDX analyses, there are no signs of the Sanicro28 material slowing down the corrosion attack with time. Instead, the composition of the corrosion product layer indicates that the corrosion rate may very well continue with the same rate or even higher. An alternative to Sanicro28 may be Inconel625 which exhibited better corrosion resistance at 500 °C according to the material loss measurements.

6 Conclusions

The project has successfully executed a comprehensive exposure matrix including 5 probe exposures and 6 test sections in the existing superheater exposed in time resolved manner up to 5600 hours. The exposure matrix contained 6 different materials exposed at two different material temperatures, where corrosion rates were obtained for materials at the existing material temperature of today's superheaters as well as a temperature aimed at future boilers with higher steam data. The following conclusions from the results of the project have been made:

- The corrosion rate was generally low and at 420°C (current superheater temperature) the corrosion was near the detection limit. This correlates well with corrosion rate of the superheaters installed today which show small material wastages (life time today 12 years).
- At 420 °C, there were little difference in corrosion rate between high and low alloyed steels, the low alloyed performed equally well as the more highly alloyed steels. The exception being TP347H which exhibited a more severe corrosion attack after long time compared to the other materials.
- At 500 °C, Sanicro28 and APMT exhibited the highest material loss. Inconel625 was performing much better. Furthermore, according to the slopes of the curves, it is expected that Inconel625 would continue to perform better compared to Sanicro28 and APMT.
- It does not seem to exist an inherent difference between probe and tube exposed samples. The corrosion rate of the probes and the tubes were similar, showing only small differences. However, it is of utter importance that the probes and the tubes experience the same thermal and environmental history.
- The startup of the corrosion probes seems to be of great importance for the overall corrosion rate (especially for shorter exposure times). Starting up the corrosion exposure directly into a hot boiler appears to give rise to a more severe corrosion attack.
- At 500°C and long exposure times, a corrosive/erosive effect of the soot blower was observed. The sample surface facing the soot blower was more corroded. This was especially true for the APMT coated 13CrMo4-5 sample.

7 Goal fulfilment

The overall goal of this project has been to generate new knowledge in order to facilitate the development of models for determine the service life of superheaters and thus, improve the plant economy. By the comparably large exposure matrix with both probe and tube samples, resolved in time, valuable information about the progress of the corrosion rate have been obtained. This has been directly useful for E.ON in their plans for an upcoming change of the secondary superheater, in which the tests were performed. Partly based on the results obtained within this project, E.ON was encouraged to choose a less alloyed (cheaper) steel, 13CrMo4-5 than the former selected Sanicro28. By choosing the cheaper material, a save in installation costs of several millions SEK can be made.

The project has also been evaluating the possibility to increase the steam temperature by at least 50 °C for waste fractions. According to the results, the corrosion rate will increase if the temperature is raised (from current 420 °C material temperature to 500 °C material temperature). Even though an increase in corrosion rate at the higher temperature was measured for two of the three materials tested, the corrosion rate was rather low. For a Sanicro28 compound tube, the lifetime of the Sanicro28 layer (2 mm thickness) is estimated to be about 6 years.

The project also investigated if there was any inherent difference between the corrosion rate of probe exposed samples and the superheaters. According to the results, it does not seem to exist such a difference. Hence, probe exposures are a possible way of investigating the potential corrosion rate of superheaters. However, it is recommended that efforts are made that the probes are installed and started in such way that they mimic, as far as possible, the situation of the superheater. This includes for instance start-up from cold boiler and more than one exposure time. Furthermore, the exposure time of the probes should preferably be longer than 1000 hours.

8 Suggestions for future research work

This project has enlightened various aspects that are of importance when performing probe exposures for quantitative estimations of the service life of the superheater tubes. However, the results obtained within the project have also raised some suggestions for further studies. One important aspect to investigate more thoroughly is the effect of the start-up procedure on the corrosion attack. As it seems, the corrosion attack is magnitudes more severe when the probe is started directly into a hot waste fired boiler compared to a sample heated up in a mild environment before being exposed towards the corrosive atmosphere characterized by a waste fired boiler. If the goal is to obtain corrosion rates for quantitative estimations of the service life of the superheater tubes, this needs to be addressed. Furthermore, addressing the issue of the start-up procedure would benefit from the conclusions of the KME608 project, which has been investigating related questions.

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10 Publications

This project has not yet led to any publications. However, part of the work will be included in the upcoming thesis of Sofia Karlsson.

Appendices

Appendix A

Fuel analyses for the P14 boiler at Händelö during 2010-2011

Water content %	Ash %	Ash % TS	Sulphur %	Sulphur % TS	Chlorine %	Chlorine % TS	H_i MJ/kg
2010 week 45-47	35,6	13,0	20,2	0,29	0,46	0,9	11,9
2010 week 50-52	41,8	11,2	19,2	0,22	0,37	0,4	9,4
2011 week 6-8	40,1	12,2	20,3	0,43	0,72	0,7	10,2
2011 week 12-14	39,2	10,3	17	0,31	0,51	0,9	11,7
2011 week 18-20	33,8	15,6	23,5	0,48	0,72	1,1	11,3
2011 week 25-27	32,1	16,0	23,5	0,58	0,85	0,7	11,9
Average	37,1	13,1	20,6	0,4	0,6	0,8	11,1

Carbon %	Carbon % TS	Hydrogen %	Hydrogen % TS	Nitrogen %	Nitrogen % TS	Oxygen %	Oxygen % TS
2010 week 45-47	30,3	47,1	8,0	6,2	0,8	1,2	23,9
2010 week 50-52	26,2	45,1	8,2	6,0	0,7	1,2	27,7
2011 week 6-8	27,3	45,5	8,0	6,0	0,7	1,1	25,6
2011 week 12-14	30,2	49,7	8,3	6,4	0,5	0,8	24,6
2011 week 18-20	29,8	45,0	7,6	5,7	0,7	1,0	22,9
2011 week 25-27	30,9	45,5	7,6	5,9	0,9	1,4	22,1
Average	29,1	46,3	8,0	6,0	0,7	1,1	24,5

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