MATERIAL- OCH KEMITEKNIK 1174

Material för högre ångtemperaturer (upp till 600°C) i bio- och avfallseldade anläggningar

Annika Stålenheim, Pamela Henderson

värmeforsk
VÄRMETEKNISK FORSKNING OCH UTVECKLING

Materials for higher steam temperatures (up to 600°C) in biomass and waste fired plant.
– A review of present knowledge

Material för högre ångtemperaturer (upp till 600°C) i bio- och avfallseldade anläggningar

Annika Stålenheim and Pamela Henderson

M08-833

VÄRMEFORSK Service AB
101 53 STOCKHOLM · Tel 08-677 25 80
Februari 2011
ISSN 1653-1248

Abstract

Results from probe testing simulating 600˚C steam or steam loop testing with 600˚C steam have been found for wood- based biomass fuels. TP 347H FG, HR3C and AC66 were shown to be suitable for further investigation because they have adequate strength, fireside corrosion and steam-side corrosion resistance at 600˚C. No information on corrosion testing at 600˚C steam in straw-fired boilers could be found.

No actual tests performed on furnace walls with higher pressures/temperatures could be found, although Ni-base coatings were shown to give good corrosion resistance with corrosive biofuels at lower pressures. In fluidised bed boilers Ni-base alloys mixed with a ceramic were used with some success. Much less work has been performed on furnace corrosion compared to superheater corrosion.

Sammanfattning

Ett mål för Svensk värmekraftindustri är att senast 2015 bygga en demonstrationsanläggning för biobränsle med en ångtemperatur på 600°C. Värmeforsk har också ett mål att identifiera material som kan användas i en sådan anläggning. I föreliggande rapport överblickas dagens kunskaper och publicerade artiklar om material som kan vara användbara i pannor som eldas med biobränsle eller sopor/avfall där ångtemperaturen kan uppgå till 600°C. Information har också samlats in från anläggningar i drift och från tidigare utförda fälttester med sonder. Anläggningar som enbart eldar hushållsavfall har exkluderats från denna sammanställning. De komponenter som speciellt studerats är vattenkylda väggar/eldstadsväggar (påverkade av högre ångtryck) och överhettare. Korrosion på rökgassidan och oxidation på vatten-/ångsidan har överblickats. Materialkandidater (eller ytbeläggningar) är föreslagna och områden för framtida forskning har identifierats. Avsikten med detta arbete är att ge en ”state-of-the-art” information om vilka material som skulle kunna användas i biobränsle och avfalls eldade anläggningar och då klara en ångtemperatur på max 600°C. Denna rapport vänder sig till leverantörer av pannor och material, energiföretag och andra som är engagerade i att bygga nya värmekraftanläggningar med högre ångtemperaturer än vad som idag är vanligt.

I enlighet med målsättningen för detta arbete, har följande noterats:

- Material lämpliga för användning i anläggningar med högre ångtemperaturer (upp till 600°C) med träbaserat bio- och avfallsbränsle har identifierats. Dessa är här de austenitiska rostfria stålsorterna HR3C, TP 347 HFG och AC66 som har adekvata hållfastheter, ångsideoxidations- och rökgaskorrosionsmotstånd för att kunna användas i överhettare. AC66 och HR3C har bättre ångside oxidationsmotstånd än TP 347 HFG, som å andra sidan har ett bättre rökgaskorrosionsmotstånd. Det kan rekommenderas att TP 347 HFG kulblästras på ångsidan för att förbättra oxidationsmotstånd om detta material används med ång temperaturer över 580°C.
- Eldstadsväggar belagda med Ni-bas legeringar eller en blandning av Ni-legering och keram uppvisar bra korrosions motstånd vid lägre temperaturer och borde utvärderas vid högre tryck och temperatur.
- Ferrit/martensitiska stålsorter lämpar sig inte för överhettare på grund av deras dåliga rökgaskorrosionsmotstånd.
- Möjligheter att reducera korrosion har föreslagits. Dessa är användningen av additiv och att flytta den slutliga överhettaren till områden med mindre aggressiv omgivning.
- Mer arbete krävs för eldstadsväggar vid högre tryck och temperaturer och andra höglegerade austenitiska rostfria stålsorter, med adekvata kryphållfastheter borde också utvärderas.

- För halm som bränsle, har inte material testats med 600°C ånga. Legeringar med högt krominnehåll bör undvikas och TP 347 HFG är det material som så här långt har identifierats att ha lägst korrosionshastighet.

Nyckelord : 600°C ånga, högtemperatur ånga, rökgassidig korrosion, ångsidig korrosion, biobränsle, rostfria stål, nickelbaserade legeringar.

Summary

A goal for the Swedish power industry is to build a demonstration biomass-fired plant with 600°C steam data in 2015. Värmeforsk also has a goal to identify materials that can be used in such a plant. This project involves a survey of present knowledge and published articles concerning materials that are suitable for use in biomass and waste-fired plants with steam data up to 600°C. The information has been gathered from plants presently in operation, and from field tests previously performed with probes. Plants firing only household waste are excluded. The components considered are waterwalls/furnace walls (affected because of higher steam pressures) and superheaters. Fireside corrosion and steam-side oxidation are dealt with. Candidate materials (or coatings) are suggested and areas for further research have been identified.

The purpose of this project is to give state-of-the-art information on what materials could be used in biomass and waste-fired plant to reach a maximum steam temperature of 600°C. This report is aimed at suppliers of boilers and materials, energy utility companies and others involved in building new plant with higher steam data.

In accordance with the goals of this project:

- Materials suitable for use at higher steam temperatures (up to 600°C steam) in wood-based biomass and waste-fired plant have been identified. Austenitic stainless steels HR3C, TP 347 HFG and AC66 all have adequate strength, steam-side oxidation and fireside corrosion resistance for use as superheaters. AC66 and HR3C have better steam-side oxidation resistance than TP 347 HFG , but TP 347 HFG has better fireside corrosion resistance. It is recommended that TP 347 HFG be shot-peened on the inside to improve the oxidation resistance if in service with steam temperatures above 580°C.
- Furnace walls coated with Ni-based alloys or a mixture of Ni- alloy and ceramic show good corrosion resistance at lower temperatures and should be evaluated at higher pressures/temperatures
- Ferritc/martensitic steels are not suitable for superheaters because of their poor fireside corrosion resistance
- Ways of reducing corrosion have been suggested. They are the use of additives and moving the position of the final superheaters to a less aggressive environment.
- More work is needed on furnace walls at higher pressures/temperatures and other (super) austenitic stainless steels, with adequate creep strength should also be evaluated.
- For straw, materials have not been tested with 600°C steam. Alloys with high chromium contents should be avoided and TP 347 HFG is the material with the lowest corrosion rate which has been identified so far.

Key words : 600°C steam, high temperature steam, fireside corrosion, steam-side corrosion, biomass, stainless steels, nickel-based alloys.

Contents

1 INTRODUCTION 1

1.1 BACKGROUND 1
1.2 DESCRIPTION OF THE RESEARCH AREA 4
1.3 THE PURPOSE OF THE RESEARCH ASSIGNMENT AND ITS ROLE WITHIN THE RESEARCH AREA 5
1.4 TARGET AND TARGET GROUP 6

2 WATERWALLS / FURNACE WALLS 7

2.1 CORROSION 7
2.2 MATERIALS 10
2.3 COATINGS 11
2.4 ADDITIVES AND OTHER PREVENTIVE MEASURES 14
2.5 PLANT EXPERIENCES 15
2.6 MATERIAL TESTS 17

3 SUPERHEATERS 19

3.1 CORROSION MECHANISMS 19
  3.1.1 Fireside corrosion 19
  3.1.2 Steamside corrosion 19
3.2 MATERIALS 21
  3.2.1 Creep strength 22
3.3 ADDITIVES AND OTHER PREVENTIVE MEASURES 23
3.4 MATERIAL TESTS AT ELEVATED TEMPERATURES 27
  3.4.1 Fireside corrosion 27
    3.4.1.1 Nässjö, 600°C (convective pass) and 650°C (sand loop seal) 27
    3.4.1.2 Nässjö 640°C. 650°C and 670°C 31
    3.4.1.3 Jordbro 33
    3.4.1.4 Masnedø – 585°C steam loop 35
    3.4.1.5 Nyköping – 600ºC steam loop 36
    3.4.1.6 Enstedsvaerket 40
  3.4.2 Steamside corrosion 41
    3.4.2.1 Nyköping 41
    3.4.2.2 Esbjerg 42
    3.4.2.3 Masnedø 44
    3.4.2.4 Comparison Esbjerg (256 bar) and Masnedø (91 bar) 44
    3.4.2.5 Avedøre 1 and Amager 3 44
    3.4.2.6 Effect of steam pressure 46
    3.4.2.7 Ways of reducing steam-side oxidation 46

4 DISCUSSION 48

4.1 FURNACE WALLS 48
4.2 SUPERHEATERS 49

5 CONCLUSIONS 52

6 RECOMMENDATIONS FOR FUTURE WORK 53

7 REFERENCES 54

1 Introduction

1.1 Background

A goal for the Swedish power industry is to build a demonstration biomass-fired plant with 600°C steam data in 2015. Värmeforsk also has a goal to identify materials that can be used in such a plant. This project involves a survey of present knowledge and published articles concerning materials that are suitable for use in biomass and waste-fired plants with steam data up to 600°C. The information has been gathered from plants presently in operation, and from field tests previously performed with probes. Plants firing only household waste are excluded. The components considered are waterwalls/furnace walls (affected because of higher steam pressures) and superheaters. Fireside corrosion and steam-side oxidation are dealt with. Candidate materials (or coatings) are suggested and areas for further research have been identified.

Three years ago a report [1] was published by Värmeforsk, which gave a review of fireside corrosion mechanisms in biomass and waste-fired boilers and suggestions on how to reduce the damage. This project has built on the information given in the report and updated it with specific reference to higher steam temperatures, up to 600°C.

Increasing the steam temperature of the plant will lead to increased demands on the materials used. Higher steam temperatures are usually associated with more corrosion, especially of the superheaters, and this is one of the problems to be tackled before the plant can be built. At the higher steam temperatures, steam-side oxidation becomes important and higher pressures also mean that higher temperatures are reached in the waterwalls/evaporaters/furnace walls. The corrosion resistance is not the only consideration in choosing a superheater material for higher steam temperatures. The creep strength (or proof stress) is also of prime importance.

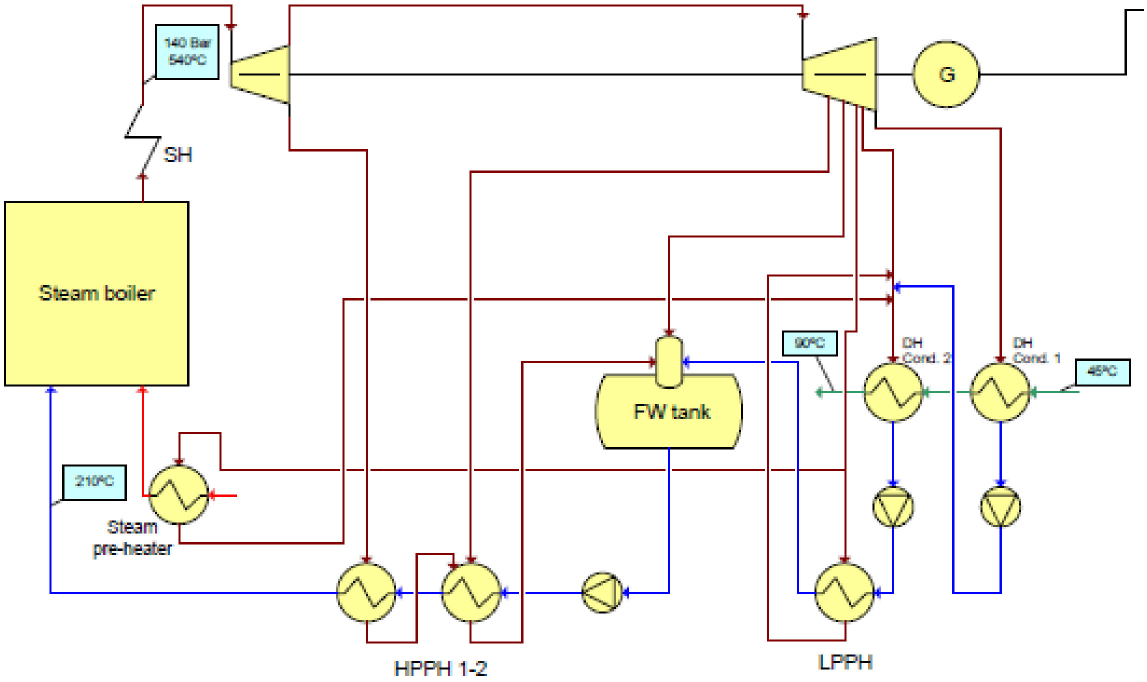
Elforsk, via KME, has started a four-year R&D programme on “More efficient electricity production with renewable fuels”. The final goal of the programme is to build and operate a bio-CHP demo plant with high electrical efficiency. Sponsors of the programme are utilities, suppliers and the Swedish Energy Agency. Fortum Värme, E.ON Värme and Vattenfall are the largest utilities involved. Among the boiler manufacturers, Metso Power will participate. The steam turbine manufacturer Siemens and the material manufacturers Outokumpu, Sandvik and Kanthal have also joined the programme.

In the pre-study for the Elforsk programme, three basic systems for the demo plant have been assumed and defined for further analysis. One based on today’s commercially available technology (state-of-the-art or benchmark) and two possible demonstration systems (so called reference power plants, RPP, both on year 2017/18 perspective and on longer term). A CFB boiler is assumed. The three systems are presented below. [4]

Benchmark: 140 bar/540°C, no reheat, feed water temperature 210°C, two HP feed water heaters and one LP feed water heater (Figure 1)

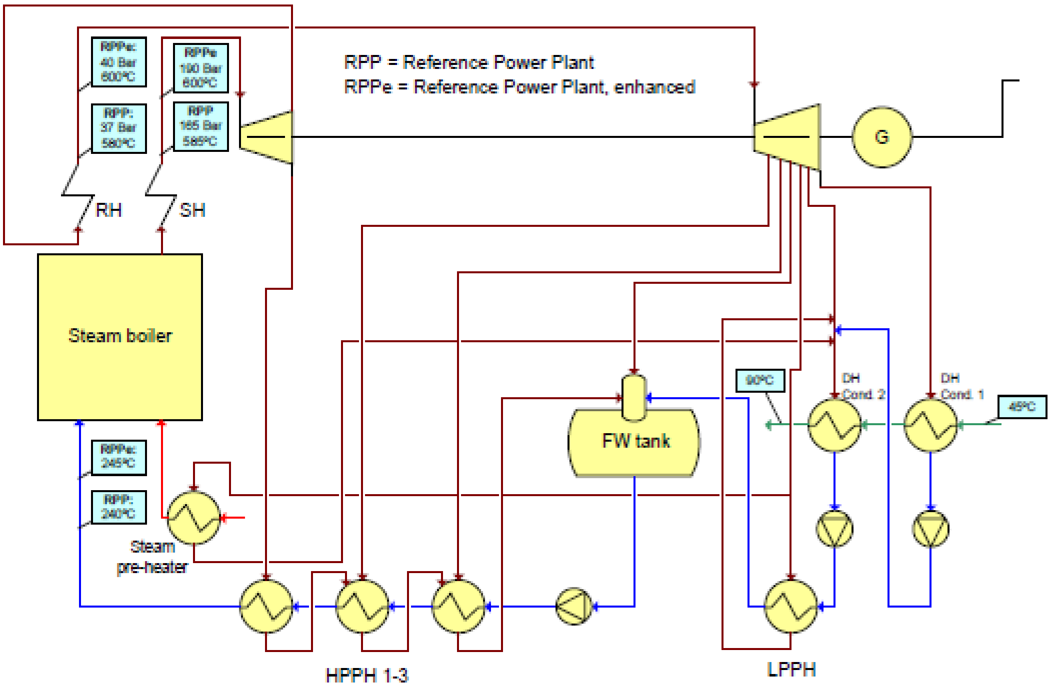
RPP: 165 bar/585°C, reheat 37 bar/580°C, feed water temperature 240°C, three HP feed water heaters and one LP feed water heater. (Figure 2)

RPP enhanced: 190 bar/600°C, reheat 40 bar/600°C, feed water temperature 245°C, three HP feed water heaters and one LP feed water heater (Figure 2)



Figur 1. Schematiskt processdiagram för benchmark-systemet [4]

Figure 1 Schematic process diagram of benchmark system [4]



Figur 2. Schematiskt processdiagram för RPP-systemet [4]

Figure 2 Schematic process diagram for RPP systems [4]

The resulting steam temperatures and pressures (Table 1) have been used to determine what temperatures and pressures are relevant to investigate in the present study. These figures are calculated for virgin biomass, if waste wood or other waste fuels are used the steam parameters have to be lowered.

Tabell 1. Tryck och temperatur i olika delar av pannan i de tre systemen

Table 1. Pressures and temperatures in different parts of the boiler in the three systems

	Benchmark	**165 bar/585°C/580°C**	**190 bar/600°C/600°C**
To steam turbine	540°C/140 bar	585°C/165 bar	600°C/190 bar
From SH	541°C/142 bar	586°C/168 bar	601°C/193 bar
From RH	No reheat	580°C/37 bar	600°C/40 bar
To boiler drum from evaporator	343°C/151 bar	356°C/178 bar	368°C/205 bar
Feedwater to boiler	209°C/157 bar	239°C/185 bar	244°C/213 bar

1.2 Description of the research area

Improved electrical efficiency can be obtained by many measures. The major improvements are gained by more advanced steam data, in terms of increased temperature and pressure in the steam cycle, combined with reheat. These measures are usually used in larger fossil fired plants, but very limited in CHP plant sizes 20-50 MWe, due to economic reasons but mainly due to corrosion risks. [4]

Some of the main measures for increasing efficiency are listed below:

- Steam temperature
- Steam pressure
- Turbine isentropic efficiencies (in different parts), tightening/leakage steam, handling moisture in last stages, mechanical- , generator losses
- Process configuration (Reheat, no. of pre-heaters and heat condenser stages, etc)
- District heating return and supply temperature
- Boiler efficiency (flue gas temperature / material choices / flue gas cleaning / auxiliary power requirements)
- Reduction of auxiliary power (pumps, fans, pressure drop water and flue gas side, fuel preparation, auxiliary systems)
- Maintenance (optimisation / status controlled maintenance)
- Improved dynamics and control
- Improved part load efficiency (control, design)

One of the largest potentials for increased electrical efficiency is to introduce more advanced steam data and configuration for biomass CHP plants in this scale. The potential would be defined by the technology used for large coal and natural gas fired condensing plants, where ultra superheated data with single or double reheat is used ($>600^{o}$C, 300 bar). The main limitations for the biomass applications in the CHP scale 20-50 MWe are [4]:

- High temperature fouling and corrosion in the boiler from alkali chlorides and other compounds formed from firing biomass fuels
- Less cost effectiveness for advanced configurations and measures in the actual CHP scale

Some technical limitations to increasing the steam parameters are :

- Boundary losses in HP stages (pressure related)
- Moisture in last turbine stages (pressure related)
- Creep strength in steam tubes, pipes and turbine
- Corrosion (temperature related)

The problems with high temperature corrosion are related to a number of critical compounds in the biomass fuels. Volatile metals and chlorine are involved in causing fouling and corrosion problems especially at furnace walls and in superheaters.

Virgin biomass fuels is a relatively heterogeneous fuel, depending on type of origin (from forestry, agriculture, vegetable waste, etc), growing conditions, handling, preparation, moisture content, impurities as soil and sand, etc. This increases the problems for controlling the combustion and optimising required measures for avoiding high temperature corrosion. Widening the fuel specification such as introducing used or recycled wood (RT), will further increase the problems by adding impurities such as metals (Zn, Pb) and chemical treatment compounds.

Furnace wall corrosion is especially a problem for recycled wood (RT), but also with agro-fuels. The solutions so far have been to reduce the steam pressure, but protective coatings are also possible solutions.

Boiler are in service today with steam data of up to 170 bar/ 560ºC for virgin wood. These numbers are far from what is possible for fossil fired plants. [4]

1.3 The purpose of the research assignment and its role within the research area

The purpose of this project is to give state-of-the-art information on what materials could be used in biomass and waste-fired plant to reach a maximum steam temperature of 600°C.

A goal for the Swedish power industry is to build a demonstration biomass-fired plant with 600°C steam data in 2015. Värmeforsk also has a goal to identify materials that can be used in such a plant. Higher steam temperatures are usually associated with more corrosion and this is one of the problems to be tackled before the plant can be built.

In 2006 a report was published by Värmeforsk, [1], which gave a review of fireside corrosion mechanisms in biomass and waste-fired boilers and suggestions on how to reduce the damage. However, higher steam temperature was not considered in that report. This project has built on the information given in the report and updated it with specific reference to higher steam temperatures, up to 600°C, in biomass and waste-fired plant. At the higher steam temperatures steam-side oxidation becomes important and higher pressures mean that higher temperatures are reached in the waterwalls/evaporators/furnace walls.

This project has involved a survey of present knowledge and published articles concerning materials that are suitable for use in biomass and waste-fired plants with steam data up to 600°C. Information has been gathered from plants presently in operation, and from field tests previously performed with probes. Plants firing only household waste have been excluded.

The components considered have been superheaters and waterwalls/furnace walls. Fireside corrosion and steam-side oxidation has been dealt with. Candidate materials (or coatings) have been suggested and areas for further research have been identified.

This project supports the Värmeforsk goal to give recommendations of materials that could be used in combined heat and power plants with higher steam temperatures, up to 600ºC.

1.4 Target and target group

The goals of the project have been to identify:

- Materials suitable for use at higher steam temperatures (up to 600°C steam) in biomass and waste-fired plant
- Materials that are not suitable and should be avoided
- Ways of reducing corrosion
- Problem areas and gaps in our knowledge where more work is needed

Target groups for the project are suppliers of boilers and materials, energy utility companies and others involved in building new plant with higher steam data.

2 Waterwalls / furnace walls

Furnace wall corrosion is especially a problem for waste wood, but also with agro-fuels. The solutions so far have been to reduce the steam pressure, but protective coatings are also possible solutions. [4] Furnace wall corrosion is a limiting factor even at today's steam parameters. A compromise has to be made between the desired steam pressure and corrosion.

Increasing the steam parameters from 140 bar/540°C to 190 bar/600°C/600°C will mean that the outgoing temperature and pressure of the steam from the furnace walls will increase from 343°C/151 bar to 368°C/205 bar, an increase in temperature of 25°C. (Table 1). By a general rule of thumb, the wall metal temperature is assumed to be 50°C higher than the steam temperature, [40].

2.1 Corrosion

Corrosion can be caused by many different species and through several different mechanisms. These are strongly linked to the type of material used and to the temperature and environment where the material is placed. In the furnace three dominating corrosion mechanisms can be identified, oxidation, corrosion caused by a reducing atmosphere and chlorine induced corrosion. [1]

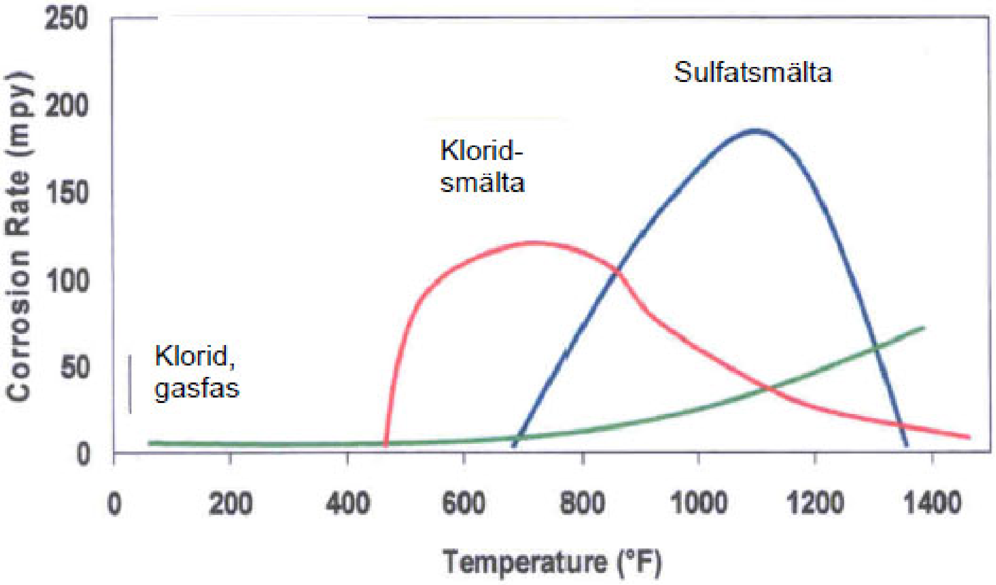
Oxidation is the reaction of oxygen with the metals (e.g. iron and chromium) in the steel under the formation of metal oxides. Mainly Fe_2O_3 (hematite, rust brown), and Fe_3O_4 (magnetite, black) are formed. When the conditions are good, a thin, dense and homogenous layer of magnetite is formed, that protects the steel from further oxidation and the oxidation rate is slowed down. This occurs on the water- or steam-side. However, on the fireside, the formation of the protecting oxide layer can be disturbed and a protecting oxide layer can be destroyed by e.g. corrosive species and reducing conditions (lack of oxygen) near the metal surface as well as thermal and mechanical factors.

Staged combustion increases the risk of reducing conditions near the furnace walls dramatically. This means that the passivating oxide layer on the steel surface cannot be maintained and the metal surface is exposed to attack from the corrosive species in the flue gases.

Chlorine can cause severe corrosion in oxidising as well as reducing environments. [1] Bio-fuels contain high amounts of alkali and chlorine, which form highly corrosive compounds during combustion. Alkali chlorides are released as gas during combustion, but may condense as a liquid on the cooler furnace walls. Other chlorides, such as zinc chloride and lead chloride may also form as well as large amounts of HCl. All these species may take part in the corrosion.

Mixtures of salts often have a lower melting point than the single salts have on their own, so called eutectic mixtures. Chlorine, zinc, lead and alkali metals are components that can lower the melting point significantly. This means that a molten phase can form on surfaces at relatively low temperatures. [13] Waste and waste wood can contain large amounts of heavy metals, such as zinc and lead. Salt melts containing heavy metals can have as low melting temperatures as 250°C. [6] Melts on the tube surfaces cause severe corrosion.

In Figure 3, below, a schematic diagram of the temperature ranges where different types of corrosion occurs can be seen. No chloride melt corrosion occurs below ~250°C, since there are no molten chlorides below this temperature. The melting temperature for sulphates is much higher than for chlorides, which is why chloride melt corrosion is the predominant corrosion process on the furnace walls. [5]

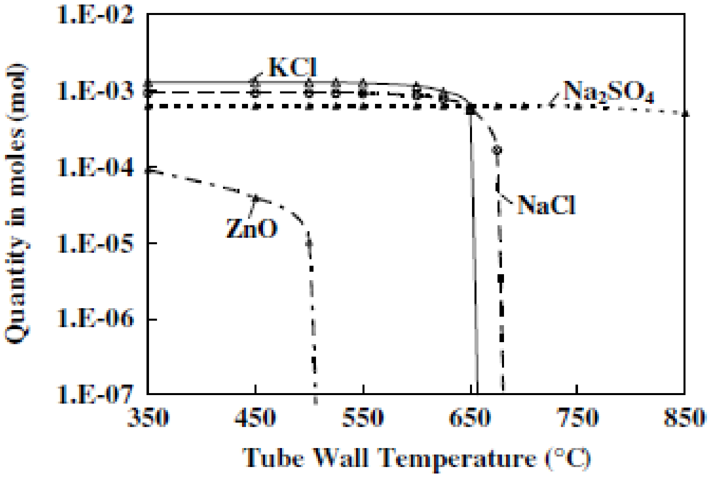


Figur 3. Korrosionshastighet som funktion av temperatur för kolstål som exponerats kloridsmälta och klorid i gasfas samt sulfatsmälta (observera temperaturen i °F) [5]

Figure 3 Temperature vs corrosion rate for carbon steel exposed to molten (red) and gaseous (green) chloride as well as molten sulphate (blue) Note temperature in °F [5]

Thermodynamic equilibrium calculations have been conducted to understand the effects of tube wall temperature, flue gas temperature, and waste chemistry on the type and amount of vapour-condensed ‘‘corrosive” salts from flue gas on superheater and waterwall tubes in waste incinerators. The amount of vapour-condensed compounds from flue gases at 650–950°C on tube walls at 350–850°C was calculated. Flue gas temperature, rather than tube wall temperature, influenced the deposit chemistry of boiler tubes significantly. Chlorine, sulphur, sodium, potassium, and calcium contents in waste affected it as well. It was demonstrated that NaCl and KCl, usually found at the innermost zone of tube deposits, are vapour-condensed from flue gas. Lead and zinc chlorides and sulphates, often detected in waterwall tube deposits, are vapour-condensed from flue gas as solid solution with other salts as well. Vapour-condensation of lead and zinc chlorides and sulphates is possible for flue gas at above 750°C and for tube surfaces at below 350°C, [24]

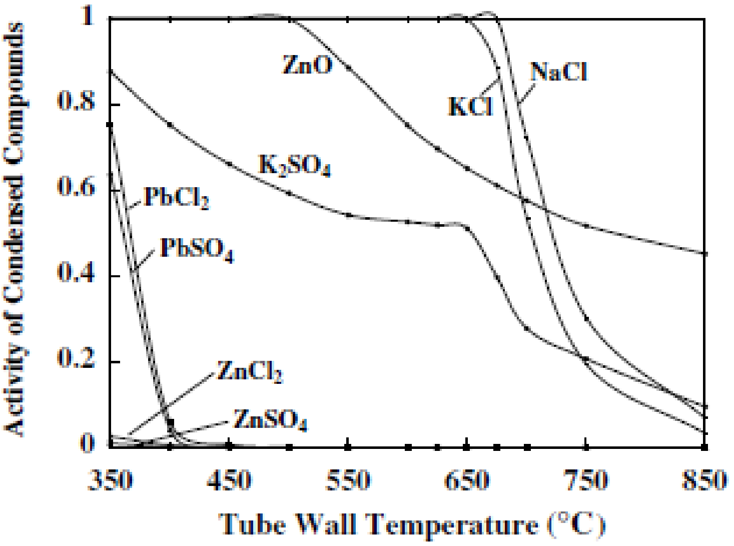
In Figure 4 the quantities in moles of pure vapour-condensed deposits from flue gas at 950°C on tube wall temperatures at 350–850°C are presented. For tube wall temperatures lower than 650°C, vapour-condensation of KCl, NaCl, and Na_2SO_4 occurred. Zinc oxide became involved as well at below 500°C. At 350–650°C, the amount of KCl, NaCl, and Na_2SO_4 remained generally constant and was not influenced by the tube wall temperature. Note that pure solid NaCl and KaCl became unstable and disappeared from the deposit at higher than 650°C. Hence, pure sodium and potassium chlorides cannot vapour-condense onto tube surfaces at higher than 700°C. [24]



Figur 4. Beräknad mängd i mol som kondenserat från rökgaser vid 950°C som funktion av tubväggens temperatur, vid förbränning av 100g avfall innehållande 0,5% Cl och 0,02%S. [24]

Figure 4 Calculated quantity in moles of pure vapour condensates from flue gas at 950°C as a function of tube wall temperature, upon burning 100 g waste containing 0.5% Cl and 0.02% S. [24]

Vapour-condensed salts of less than 0.99 activity, which were stable at 350–850°C upon quenching the 950°C flue gas, are presented with their activity values in Figure 5. These compounds are considered capable to be present as solid solution with other salts. At temperatures lower than 400°C, $PbCl_2$, $PbSO_4$, $ZnCl_2$, and $ZnSO_4$ became involved in vapour-condensed deposits. These salts can lower the melting-point temperature of the tube deposits, and hence are considered to be responsible for the fireside corrosion of waterwall tubes, the tube wall temperatures of which are generally below 400°C. Note that vapour-condensation of these lead and zinc salts can only be possible on tube surfaces lower than 400°C. [24]



Figur 5. Beräknad aktivitet för kondenserade föreningar från rökgas vid 950°C som funktion av tubväggens temperatur, vid förbränning av 100g avfall innehållande 0,5% Cl och 0,02%S. [24]

Figure 5 Calculated activity of vapour condensates from flue gas at 950°C as a function of tube wall temperature, upon burning 100 g waste containing 0.5%Cl and 0.02%S. [24]

In FB boilers, the sand in the bed is highly erosive and removes the protective oxide layer on the waterwalls, which aggravates corrosion problems. [2]

Corrosion of weld overlays can be separated into i) general corrosion, ii) selective corrosion (e.g. in dendrites) and iii) local corrosion in the form of pits caused by salt melts. In addition to this, galvanic corrosion in the interface between weld material and the carbon steel of the tube can also occur. [6]

2.2 Materials

Furnace walls consist of tubes that have been welded together. Between the tubes are membranes, also called fins, around 20 mm wide. The furnace walls are usually made of carbon steel or low alloyed steel. Traditionally these have been the best materials, since they are cheap, have high heat conductivity and, through their protective magnetite layer, do not corrode much in an oxidising environment if the fuel is moderately corrosive. An important quality is also their resistance to stress corrosion cracking. With the introduction of the more corrosive fuels used today and a reducing environment, a need for more corrosion resistant materials have risen. Unfortunately, most corrosion resistant materials have insufficient heat conductivity or strength. This has led to the use of different coating materials, [5], [13].

The most commonly used coating material is refractory lining. There is also increasing use of corrosion resistant metallic coatings applied by various techniques such as welding and thermal spraying.

Composite tubes are made up of two components, an inner tube of carbon steel and an outer tube of higher alloyed material, usually a Ni-based alloy or an austenitic steel. The thickness of the outer layer is usually around 1.6 mm, but can be slightly less. A composite tube has the advantages of the good heat conductivity of the inner tube and the corrosion resistance of the outer tube and is cheaper than a solid tube of a higher alloyed material, [5].

2.3 Coatings

When burning bio-fuel, the refractory used needs to resist alkali, which otherwise can penetrate into the coating and cause cracking and scaling. Somewhat more acidic materials with relatively low content of aluminium oxide and relatively high content of silicon oxide have the best resistance against alkali intrusion, [5].

Different types of alloys can be used as weld-on materials. The most commonly used type is Ni-base alloys, especially in waste-fired boilers. Austenitic steels are also sometimes used. In general, Ni-based alloys have good corrosion properties as well as good weldability and this makes them less prone to crack during welding or in service. Their coefficient of expansion is also close to that of carbon steel, making the thermal tensions small. Austenitic materials are usually much cheaper than Ni-based alloys, but the coefficient of expansion differs significantly to that of carbon steel and the corrosion resistance is not as good as for Ni-based alloys. The difference in thermal expansion does not have to be a problem, but the weld-on layer has to be significantly thinner than the tube wall and the number of starts and stops of the boiler per firing season has to be kept to a minimum. Austenitics can be a good alternative in bio- coal- and co-fired boilers, but in waste-fired boilers, the environment is usually too aggressive for this type of material. In Table 2 a few materials that are used as weld-on materials are presented, [5].

Tabell 2. *Sammansättningar för svetstillsatsmaterial som används till påsvetsning i eldstäder, riktvärden för grundmaterial anges i tabellen. [5]*

Table 2. *Typical compositions for weld materials that can be used as overlays on boiler tube walls, parent metal standard compositions are given in the table. [5]*

Material	**Ni**	**Cr**	**Mo**	**Fe**	**W**	**Nb**	**Co**	**C**	**Others**
C-276	Bal.	14,5-16,5	15-17	4-7	3-4,5	-	2,5 max	0,02 max	V; 0,35 max
C-22, 622	Bal	20-22,5	12–14,5	2 - 6	2,5-3,5	-	2,5 max	0,015 max	V; 0,35 max Cu; 0,5 max
686	Bal	19-23	15-17	1 max	3,0–4,4	-	-	0,005	Ti; 0,02 – 0,25
C-2000	Bal	23	16	2	-	-	-	0,005	Cu; 2,6
625	58 min	20-23	8-10	5 max	-	3,15-4,15	-	0,1 max	
625_{mod}	58 min	20-23	8-10	5 max	3,0-4,4	-	-	0,1 max	
50	Bal	18-21	9,5-12,5	12-16	0,5-2,5	0,05-0,5	-	0,03 max	Al; 0,05 – 0,5 N; 0,05 – 0,2
59	Bal	22-24	16,5 max	1,5 max	-	-	-	0,006 max	Al; 0,1 – 0,4
309L	12-14	23-25	-	Bal	-	-	-	0,03 max	
310	20-22,5	25,28	-	Bal	-	-	-	0,08-0,15	
312	8-10,5	28-32	-	Bal	-	-	-	0,15 max	
Sanicro 28	31	27	3,5	Bal	-	-	-		Cu; 1,0

Thermal spraying is an alternative to welding. This is a fast method which can give coatings of high hardness and durability, especially when the wear is caused by erosion.

The greatest potential lies in boilers where erosion is the main problem (i.e. CFB boilers). Usually arc spraying is used today, since this method has the highest capacity and the lowest costs, however, HVOF (High Velocity Oxygen Fuel) gives the best quality. [5]

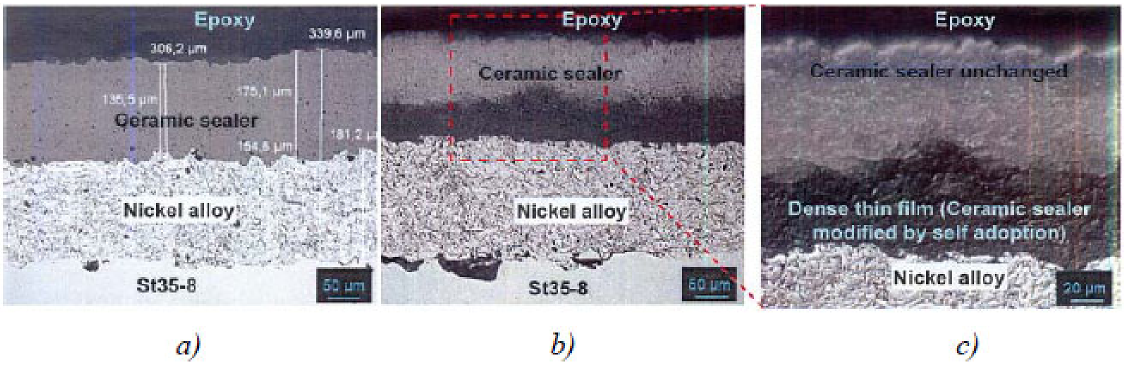
Below are examples of materials that are used for thermal spraying [5]:

- CoCrAlY
- CoNiCrAlY
- FeCrAlY
- NiCrAlY
- NiCoCralY
- Exotermisk MCrAlY
- Nickel-krom legeringar
- Inco 718
- IN-625
- René 41
- NiCrWSiB

There are also some recent developments of water wall corrosion protection methods. One way is to flame spray relatively thick layers onto water wall sections. Then these sections are heat treated by induction heating to make the spray layers sinter. The sinter material consists of 15 % Cr, 4,3 % Si, 3.1 % B and 2,5% Mo which gives very high hardness, HV = 815. Three years service exposure of test panels in a waste fired boiler gave no significant corrosion at all, whereas carbon steel tubes exposed at the same time corroded 1.5 mm. In addition, the output of the boiler increased as a result of flame spray + sintering method. [6]

Thermal spraying with ceramic constituents mixed into the metallic powder has been tested successfully. A TiO_2-Al_2O_3 / 625 cermet that had been applied with HVOF showed no significant material loss after 2 years operation (13 800 h). A ZrO_2 / 625 dual layer system applied with plasma jet also showed good results. [6]

In a laboratory test a ceramic material was sprayed onto a Ni-base coating. By diffusion and thermal dissolving processes, the ceramic layer and the Ni base layer forms a dense intermediate layer. (Figure 6) The idea is that this should happen during operation of the plant. The coating should then be self repairing when cracks appear in the ceramic layer. However, the temperature used in the test is somewhat high, and it is possible that this makes the coating unsuitable for use on waterwalls. [6]



Figur 6. Komposit av termiskt sprutade skikt a) efter sprutning b) i drift förenas nickel- och det keramiska skiktet genom diffusion (500 h 540°C) c) visar det bildade täta mellanliggande skiktet i högre förstoring [6]

Figure 6 Composite of thermal sprayed coatings with a) after spraying b) the nickel and the ceramic coating will bond to each other by diffusion in service (500 h 540°C) c) shows the dense thin intermediate in larger magnification [6]

In Table 3 life times of different coatings used in waste fired boilers are presented. [23]

Tabell 3. *Livslängd för korrosionshärdiga ytbeläggningar i avfallseldade pannor [23]*

Table 3. Durability of corrosion-resistant coatings in WTE boilers [23]

		Applied condition, °C			
Coating process	**Chemical composition, materials**	**Parts**	**Metal**	**Gas**	**Durability, yr**
Widely overlay					
MIG	21Cr-9Mo-3.5Nb-Al,Ti-Ni base (Alloy 625)	WW, SH	270-330	700-1000	>10
PPW	18Cr-14Mo-4W-Ni base (C-276M, 625M)	SH	470-510	510-650	(≈625)
MIG	23Cr-16Mo-1.6Cu-Ni base (HC-2000)	WW, SH	260-480	870-1730	(0.52mm/y) (>625)
PAW	Alloy 625	SH	470-530	510-650	>1
Laser cladding	625, HC-22, NiCr 309L, 686 etc	WW	(Coal fired black liquor)		…
Spray coating, Flame					
Flame	Al/80Ni20Cr	WW	230-300	700-900	>3
Flame/fused	10Cr-Si, B-Ni base (12C)	SH	370-540	…	>1
Spray coating, Plasma					
Plasma/fused	15Cr-Si, B, Fe-75Ni base	WW	230	700-800	4
Spray coating, HVOF					
Hybride cap	18Cr-5Fe-5Nb-6Mo-Ni base (diamalloy)	SH	370-540	…	>0.4
DJ-1000	17Cr-4Fe-3.5B-4Si-Ni base (no-fused)	WW, SH	230-330	700-900	>3
DJ-Gun DJ-1000	50TiO_2-50 Alloy 625 (cermet)	SH	430-460	500	>3
JP-5000	17Cr-4Fe-3.5B-4Si-Ni base	WW	230	700-900	>3
Spray coating, Plasma jet					
Modified PJ	ZrO_2/Alloy 625, NiCrSiB alloy	SH	430-500	510-650	>3

WW (Waterwall), SH (Superheater).

2.4 Additives and other preventive measures

Little information has been found on the use of additives for corrosion reduction in the furnace. This does not seem to be a very common approach to attacking the problem.

Additives such as $Ca(OH)_2$ or $Mg(OH)_2$ can be injected into the furnace to reduce the concentration of HCl in the flue gases and to facilitate the removal of deposits and reduce their corrosivity. Drawbacks of this method are increased costs and an increase in the amount of fly ash. [6]

ICA 5000 is an additive, developed for waste fired boilers, that is injected with the secondary air. It is a powdery, synthetic aluminium layered silicate of a very large surface that is covered by silanol groups. The silanol groups (-Si-OH) reacts with the vaporous metal (e.g. K, Na) chlorides in the flue gas according to (1), binding the metal to the additive and releasing chloride as less corrosive HCl. In the combustion chamber the metal silicates are forming a protecting layer of molten glasses on the refractory. [25]

$$@\text{-Si-OH} + \text{MeCl} = @\text{-Si-OMe} + \text{HCl} \qquad (1)$$

Addition of sulphur is often mentioned as a means to reduce superheater corrosion by converting alkali chlorides into alkali sulphates. The authors have not found any references claiming that sulphur additives can reduce corrosion in the furnace, but if alkali chlorides are involved in the corrosion process in the furnace, this could still be the case. It has been found, that during the combustion of fossil fuels, the amount of chloride deposits formed is reduced and that these chloride-containing deposits can only form under reducing conditions. Once formed they are found to be highly corrosive under mildly reducing and oxidizing conditions, [42].

Sulphur can be added as elemental sulphur to the fuel, as a sulphur-containing additive, or by co-combustion with a sulphur containing fuel, e.g. peat, tyres or coal. However, there is a risk that the flue gas temperature is too high in the furnace for formation of sulphates, but this has not yet been investigated, as far as has been found in this literature study.

Another additive used to reduce the amount of alkali in the flue gases is kaolin ($Al_2Si_2O_5(OH)_4$). Kaolin is relatively expensive, but it can also be added by co-combustion with kaolin-containing fuels. Kaolin can be found in peat, sludges from the forest industry, paper, plastics, paint, rubber and cement. [1]

Cleaning methods where MgO is applied directly on exposed surfaces have been tested. The idea is that the added MgO will react with the deposits to make them fall off or be more easily removed. [6]

In reference [1], a number of measures to reduce corrosion have been identified. It is not always clarified if they reduce corrosion on superheaters, on furnace walls or in the entire boiler, but the measures mentioned below should have an effect on furnace wall corrosion:

- Work with control of and demands on fuel quality, especially the chlorine content.
- Make sure that the fuel is well mixed. Variations in moisture and heating value can increase the corrosion considerably.
- Improve fuel feeding to obtain a more even spread of the fuel over the cross section of the boiler.
- Work with combustion technological measures to achieve a stable oxygen level in the flue gases near the furnace walls. Control the result using measurement methods with fast response time (e.g. lambda probes).
- Perform tests with coated wall panels in parts of the furnace that experience the worst corrosion. There are many commercial coatings available.

During co-combustion it is of importance that the different fuel fractions are well mixed and that the quality and moisture content of the fractions of the fuel fluctuate as little as possible over time. This is to avoid local overtemperatures and/or reducing conditions, leading to CO spikes. It is also important that the fuel is fed evenly into the boiler. [1]

The temperature distribution in the boiler is affected if different fuel fractions with varying moisture content and heating values are mixed. Addition of drier fuels (higher heating value) than the standard fuel can lead to uneven combustion and CO emissions. This could be because the control system is adjusted to moist fuel. When a drier fraction with higher heating value is used, the temperature increases and the control system reduces the air supply to reduce the temperature. Actually, more air is needed for this fuel and the reduced air supply could lead to incomplete combustion and increased CO emissions. [1]

One measure to protect the furnace walls from corrosion could be to insert air in so called "air curtains" to achieve oxidising conditions along the walls, [1].

2.5 Plant experiences

No references have been found on investigations of wall corrosion when using steam pressures higher than the ones used today.

In a recently finalised Värmeforsk study, experiences from some waste and bio-fuelled plants are presented. [5], [6] In another Värmeforsk report, experiences of waterwall corrosion are also presented. [1] The experiences are presented below and short descriptions of the plants are presented in Table 4.

Tabell 4. Beskrivning av pannor som ingick i erfarenhetsinventeringen [5], [6], [1]

Table 4. Description of plants included in the experience survey [5], [6], [1]

Plant	Description	Fuel	Materials
Händelö P14	CFB, delivered 2002, Steam parameters 470°C/65 bar, final SH in loop seal	Industrial waste 50-70%, sorted household waste 30-50%, sludge 0-20%	San 28 composite tubes above refractory lining
Händelö P11	Grate boiler, 115MWth, steam parameters 540°C/110bar	Waste wood	Originally St 35.8, changed in 2001 to composite tubes with San 63
Högdalen P6	Compact CFB, started 1999, Steam parameters 480°C/60 bar, effect 92 MWth	Sorted industrial waste and waste wood	Weld overlay Alloy 625
Tekniska Verken, Linköping, P1	Oil boiler built 1964, converted to solid fuels in 1984, Steam parameters 475°C/60 bar, effect 80 MW	Coal, rubber, wood	Originally St 45.8 (III), since 2003 composite tubes with San 63
Igelsta P1	Grate boiler built 1982, water temperature ~200°C	Mainly sorted industrial waste	St 35.8/I, metal sprayed with Inconel 625
Västhamnsverket	PF boiler, built 1982, steam parameters 540°C/130 bar,	Biofuel (between 1997 and 2005 coal and biofuel, before that coal and oil)	Thermally sprayed coating with 45% Cr, 2% Ti, bal Ni
Uppsala KVV	Benson boiler built 1973, converted from oil to solid fuels in 1985, Steam parameters 520°C/125 bar, effect 120 MWel/245 MWth	Wood, peat	13CrMo44

Händelö P14:
There are problems with corrosion of the composite tubes and the panels have been reversed after four years operation in the most affected positions. [5], [6]

Händelö P11:
The side walls in the furnace above the gas neck have been severely corroded, which has resulted in rapid thinning of the tube walls leading to frequent changes of the wall panels. The corrosion has been related to the fuels high content Cl, Zn and lead as well as to the fact that in connection to shaking of the grate, there are periods with very low oxygen content in the flue gas. In 2001 corroded panels of the original material, St 35.8, were

exchanged for composite tubes with Sanicro 63. During the summer stop in 2002 a reduced material loss was observed, but in the area around the gas neck, small pits were found in the new material. Some additional parts of the original material were changed to Sanicro 28. [1]

Högdalen P6:
The plant has experienced problems with erosion in the bed bottom and tube leakages in the panel walls. Tube leakages have especially occurred near soot blowers. In the most damaged parts of the empty draft, tubes with a weld-on coating of Alloy 625 were installed in 2007. The main cause of the damages in the empty draft was erosion. The welding in the furnace has functioned well the past few years. [5], [6]

Tekniska Verken, Linköping, P1:
As the aggressiveness of the fuel used has increased over the years, so have the corrosion damages. They are thought to be caused mainly by reducing conditions. Thermally sprayed coatings have been tested, but did not last over one firing season. Test panels have been welded in testing the materials 304L, San 63, San 28 and Duroc F16. Only San 63 could withstand the corrosive environment. [5], [6]

Igelsta P1:
Large material losses were discovered in 2001. After that, the furnace walls have been thermally sprayed. Repairs are performed every year, renewing about 125 m^2 of the coating. [5], [6]

Västhamnsverket:
The size of the coated area has been increased over the years. The solution seems to function satisfactorily. Repairs have to be made every year and in 2009 the coating had to be renewed in large parts of the furnace. [5], [6]

Uppsala KVV:
There have been severe problems with corrosion, especially around the burners, caused by reducing conditions. After changing burners, the corrosion has decreased substantially. Also the use of the lowest soot blowers has been stopped, since they rather caused damage than being useful. [5], [6]

2.6 Material tests

Corrosion testing was performed in a CFB boiler at Korstaverket in Sundsvall, Sweden. During the test, the fuel used was 100% refuse derived fuel (RDF). The corrosion of alloys ranging from carbon steel to nickel based alloys was tested in oil-cooled test panels in the waterwall for 738 h. Two metal temperatures were tested, 300°C and 338°C. The compositions of the materials tested are presented in Table 5. Deposits on the samples and corrosion products were also analysed. [27]

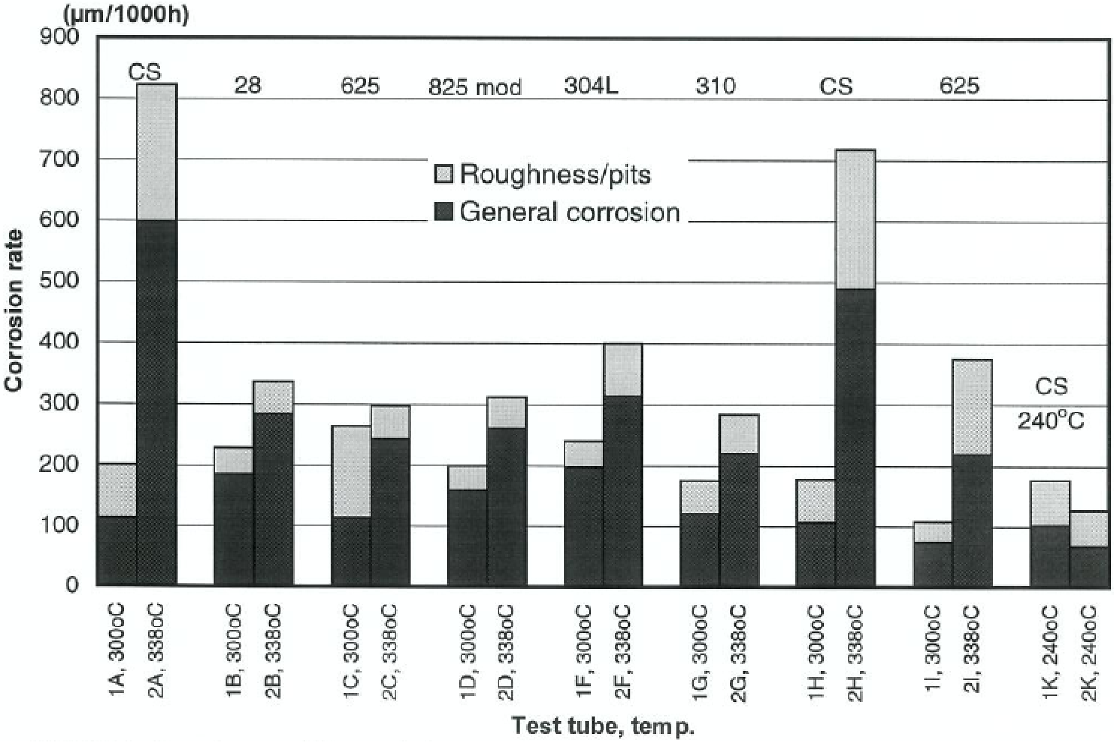
Tabell 5. Sammansättning i vikt-% hos de testade materialen [27]

Table 5. Composition in weight-% of the tested materials [27]

Position	Alloy designation	UNS	C	Fe	Cr	Ni	Mo	Si	Mn	Cu	Al	Ti	Nb	Co	N
A, H, K	CS ST35.8		.09	bal (99)				0.23	0.64						
B	Alloy 28*/SA210-A1	N08028	.01	bal (36)	26.7	30.4	3.33	.43	1.74	1.06					.08
C, I	Alloy 625*/SA210-A1	N06625	.013	bal (2.9)	22.2	61.8	9.12	.06	0.06		.12	.21	3.49	.04	
D	Alloy 38*/SA210-A1	N08825 mod	.014	(35.8)	19.9	38.3	2.54	.22	0.60	1.57	.096	.68		.04	.011
F	TP310*/T22	S31008	.015	bal (51)	25.4	21.2	0.20	.40	1.66	0.09					
G	TP304L*/SA210-A1	S30403	.009	bal (70)	18.4	10.1		.44	1.13						
Core	SA210		.18					.3	0.7						
Core	T22		.11		2.11		0.94	.22	0.49						

*Composite tube: outer alloy/core

The corrosion rates were higher at the higher material temperature for all materials tested. Especially the carbon steel showed a dramatic increase in corrosion rate. TP310 had the lowest corrosion rate at both temperatures (176 and 284µm/1000 h). The highest corrosion rate at 300°C was 264µm/1000 h for Alloy 625. At 338°C, the highest rates were 823µm/1000 h for the carbon steel and 400µm/1000 h for 304L, (see Figure 7). The outer deposits mainly consisted of KCl, NaCl and $CaSO_4$. A layer of mainly potassium oxide was found within the Fe_2O_3 on the carbon steel. For alloy 28 and alloy 625 a layer of KCl was found in connection to the Cr-Ni-Fe oxide, [27]. (The observant reader may note that specimens F and G have changed places between Table 5 and Figure 7. According to Ref 27 the Figure is correct).



Figur 7. Korrosionshastigheter för de testade materialen beräknade från 738 timmars exponeringstid. [27]

Figure 7 Corrosion rates of the tested materials calculated from 738 h exposure. [27].

3 Superheaters

The corrosion resistance is not the only consideration in choosing a superheater material for higher steam temperatures. The creep strength (or proof stress) is also of prime importance in order to keep tube thicknesses at reasonable levels. For normal superheater tube dimensions a pressure of 200 bar would require a creep strength of about 85 MPa, [8] [10]. For superheaters in the convective pass or the sand loop seal the metal temperature is taken to be the steam temperature plus 35°C or 80 °C respectively, [40].

3.1 Corrosion mechanisms

3.1.1 Fireside corrosion

Fireside corrosion of the superheaters is mainly caused by chlorine compounds, but at higher material temperatures, sulphur can also take part in the corrosion process. High temperature corrosion in the form of oxidation also occurs. Corrosion is not often caused by a single mechanism, but different mechanisms occur in parallel and can also support each other.

Some mechanisms and theories are briefly described below:

- The most commonly described mechanism is called active oxidation. This is a cyclic process where gaseous chlorine (HCl or Cl_2) attacks the metal and forms metal chlorides. The chlorine gas could either come from the flue gases or from reactions in the deposits. The metal chlorides evaporate and diffuse out into the oxide layer. They react with oxygen, forming chlorine gas and metal oxide. The chlorine gas then migrates to the metal surface and attacks it again. Gaseous HCl or Cl_2 can attack the material directly. Especially metal without a protecting oxide layer is attacked, but at high chlorine concentrations and/or low oxygen concentrations, oxides can also be attacked, [34], [35].
- Alkali chlorides deposited on the metal surface can react directly with the tube material. Potassium and sodium have more central roles in the corrosion process, causing the breakdown of the protective chromia layer in stainless steels by the formation of potassium (or sodium) chromate K_2CrO_4, [36], [37].

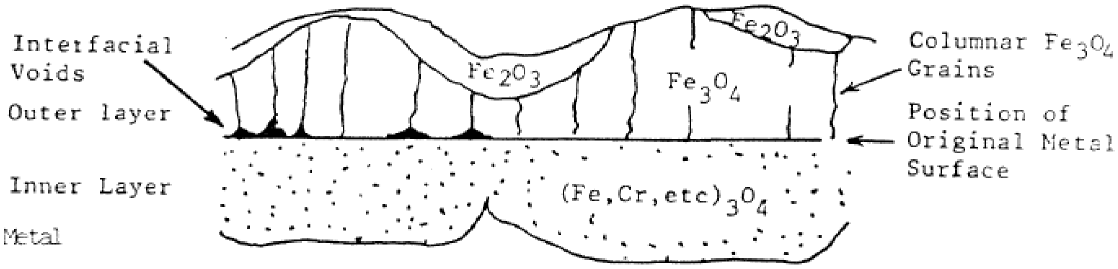
Large variations in temperature caused by e.g. soot blowing or variations in fuel quality can increase the corrosion rate dramatically. Erosion, especially in combination with corrosion, can also increase the material loss substantially, [1].

3.1.2 Steamside corrosion

Higher steam temperatures may result in thicker steamside oxide layers on the superheater tubes, which will further increase the metal temperature, and thereby the corrosion and creep degradation of the steel tubes. Furthermore, thick oxides are more susceptible to spallation, [18].

The austenitic materials are more prone to stress corrosion cracking (SCC) than the ferritic materials. The number of failures has however been fairly limited. The failures are usually caused by misshappenings during operations like regeneration of ion exchangers, acid cleaning etc. It does not seem that SCC is caused by the ordinary chemical environment in a plant with a normally accepted steam/water chemistry. [15]

Oxidation of austenitic materials in steam leads to the formation of an outer and an inner oxide layer. The outer oxide layer mainly consists of magnetite and the inner layer mainly consists of spinel. The interface between the two types of oxide coincides with the original metal surface. (Figure 8) [15] Due to the higher chromium content, the thicknesses of the oxides are lower than those for the ferritic steels with only 9-12 % Cr. [14].



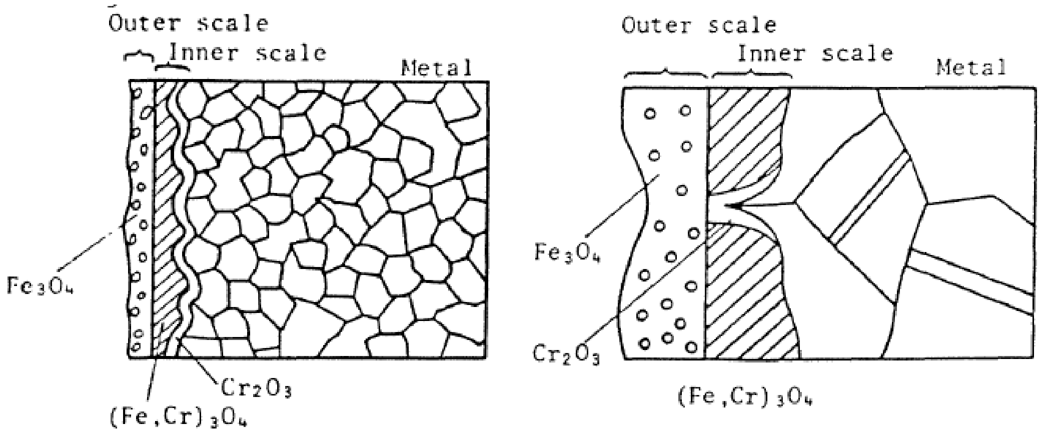
Figur 8. Oxidskikt på austenitiskt rostfritt stål efter exponering i högtemperaturånga [15]

Figure 8 Oxide layers on austenitic stainless steel after exposure in high temperature steam [15]

For the ferritic and martensitic steels (i.e. X20CrMoV12-1), a duplex oxide is formed where the outer layer predominantly contains iron and oxygen (probably magnetite and sometimes hematite is formed) and the inner layer additionally contains chromium (forming probably a chromium rich iron oxide). The interface between the inner and outer oxides is the original metal interface assuming that spallation has not already occurred. The oxidation rate for these types of steels can be described in general by a parabolic equation where oxidation decreases with increasing chromium. For the 9-12 % chromium steels the silicon content also affects the oxidation rates. [14]

For high temperature metallic components in power plants, the surface oxide is ideally relatively thin, protective and adherent in order to optimise materials behaviour. For superheater tubes, the adherence of the inner steamside oxide is especially important as spallation of this oxide results in a) blockage of loops which cause insufficient steam flow through the superheaters and subsequent overheating and tube failure and b) spalled oxide can cause erosion of turbine blades. Oxide spallation is a serious problem for austenitic steels where the significant differences of the thermal expansion coefficients of steel and oxide cause relatively high thermal stresses. [14]

Scaling makes the outer magnetite layer spall off. The reason is thought to be differences in heat expansion coefficient resulting in stress, especially upon cooling. Chromium oxide has a great influence on the growth of the oxide layer and the risk of spallation. In fine grained materials, as in cold worked materials, a thin chromium oxide layer is formed between the metal and the spinel layer. In both cases, the reason is that the diffusion of chromium is facilitated. In coarse grained material, no continuous layer of chromium oxide is formed. A continuous layer of chromium oxide reduces the oxidation rate and reduces the risk of spallation. In Figure 9 a schematic illustration of the oxide layers of a fine grained and a coarse grained austenitic material is shown. [15]



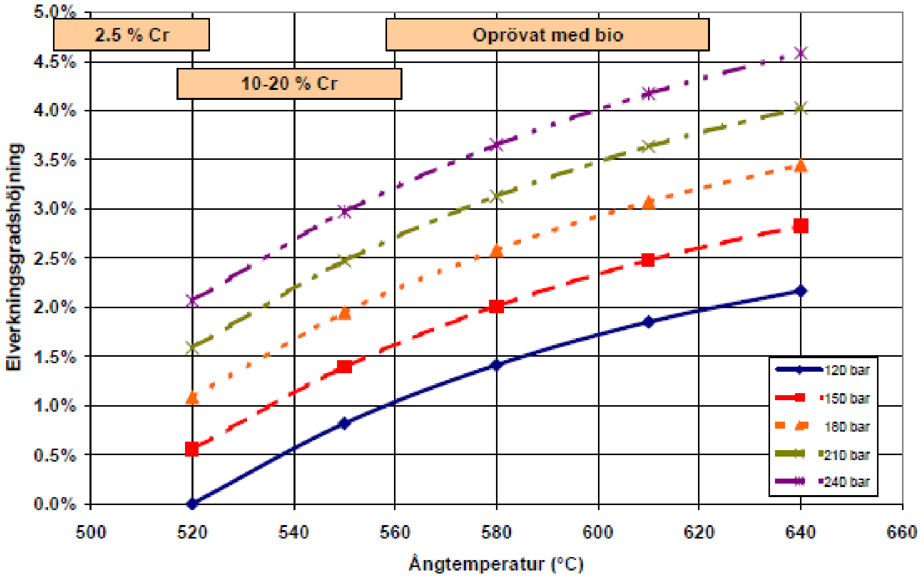
Figur 9. Oxidstrukturen i ett finkornigt austenitiskt material (vänster) och i ett grovkornigt austenitiskt material (höger) [15]

Figure 9 The oxide structure in a fine grained austenitic material (left) and in a coarse grained austenitic material (right) [15]

The risk of spallation increases with increasing metal temperature. The metal temperature is dependant on steam temperature, flue gas temperature, steam and flue gas flow and the heat conductivity of the material. [15]

3.2 Materials

A major restriction to increasing the electrical efficiency is the availability of commercial, corrosion resistant superheater materials for use in bio fuelled boilers. In the diagram below (Figure 10), approximate ranges for the chromium content of materials used in superheaters in commercial applications have been marked. At temperatures below ~520°C 2,5% Cr steels can be used. At steam temperatures between ~520-560°C 10-20% Cr steels are used, [3]. Both austenitic and ferritic materials are used in superheaters. Materials must have a stable microstructure and not form brittle phases.



Figur 10. Elverkningsgradshöjning som funktion av ångtemperatur vid olika ångtryck för en"avancerad" ångcykel med indikerade materialval [3]

Figure 10 Increase of electric efficiency as a function of steam temperature at different steam pressures for an "advanced" steam cycle with indicated material choices

Austenitic steels such as TP347H have had growing utilisation to accommodate the higher steam data in ultra supercritical coal-fired power plants. Sumitomo developed a fine-grained version of the TP347H steel which results in improved steam oxidation rates. Due to its fine-grained structure, there is increased chromium diffusion to the metal surface to form a more chromium rich oxide, which is thinner and a better barrier against further anion and cation diffusion. In addition with respect to fireside corrosion, it has been established that TP347H type steel gives good corrosion protection in biomass fired plants. Thus for a biomass plant with high steam temperatures, TP347H FG is a steel that combines the optimal corrosion resistance with the advantageous steamside oxidation features. [20]

3.2.1 Creep strength

Design values are the yield strength of the material or the stress which causes creep failure after 100,000 h (whichever is the lower). Tabell 6 shows 100,000 hour creep or tensile strength values for some steels. For normal superheater tube dimensions a pressure of 200 bar would require a creep strength of about 85 MPa (this includes a safety factor of 1.5), [8].

Tabell 6. Spänningen som orsakar krypbrott i 100,000 timmar (σ_{B10^5h}) i MPa vid metalltemperaturer 600°C, 650°C och 670°C, Sträckgränsen, $\sigma_{0.2}$, är given om den är mindre än σ_{B10^5h} [8], [10]

Table 6. The stress which causes creep failure in 100,000 hours (σ_{B10^5h}) I MPa at metal temperatures of 600°C, 650°C and 670°C. The 0.2% proof stress, $\sigma_{0.2}$, is given instead if it is less than σ_{B10^5h} [8], [10]

Steel	**Cr (wt %)**	**Ni (wt %)**	**600°C (σ_{B10^5h})**	**650°C (σ_{B10^5h})**	**670°C (σ_{B10^5h})**
10CrMo910	2.1	--	34	--	
X20CrMoV12 1	10.5	0.73	59	23	--
HCM12A	12.0	0.26	134*	70*	
Esshete 1250	14.9	9.65	133$\sigma_{0.2\%}$	100	74
TP 347H FG	18.5	11.9	132$\sigma_{0.2\%}$	105	
AC 66	27.3	31.7	90$\sigma_{0.2\%}$	85$\sigma_{0.2\%}$	74
TP 321	17.2	10.1	94	58	50
Alloy 800H	20.3	30.2	95σ0.2%	77	67
HR3C	25	20	158σ0.2%	113	96

* extrapolated values

3.3 Additives and other preventive measures

There are several different types of additives used for reduction of superheater corrosion. However, the goal of using any of these additives is to reduce the amounts of corrosive alkali chlorides in the flue gases. The main types of additives are sulphur based additives, silicon/aluminium based additives and calcium phosphate based additives.

Sulphur based additives work by converting alkali chlorides in the flue gases into less corrosive alkali sulphates and HCl. Silicon/aluminium based additives reacts with alkali chlorides to form alkali silicates and/or alkali aluminium silicates. Silicon can exist in many different forms and crystalline silica, such as quarts, can be assumed to be less reactive than amorphous silica. Some products that contain amorphous silica are bentonite and coal fly ash. Coal fly ash is a very cheap alternative, but it could lead to problems with the by-products due to its content of heavy metals. Calcium phosphate based additives works by forming $CaKPO_4$. However, if there is a deficit of Ca, low melting alkali phosphates are formed. An excess of Ca should therefore be aimed at so that higher melting calcium phosphates are formed. [26]

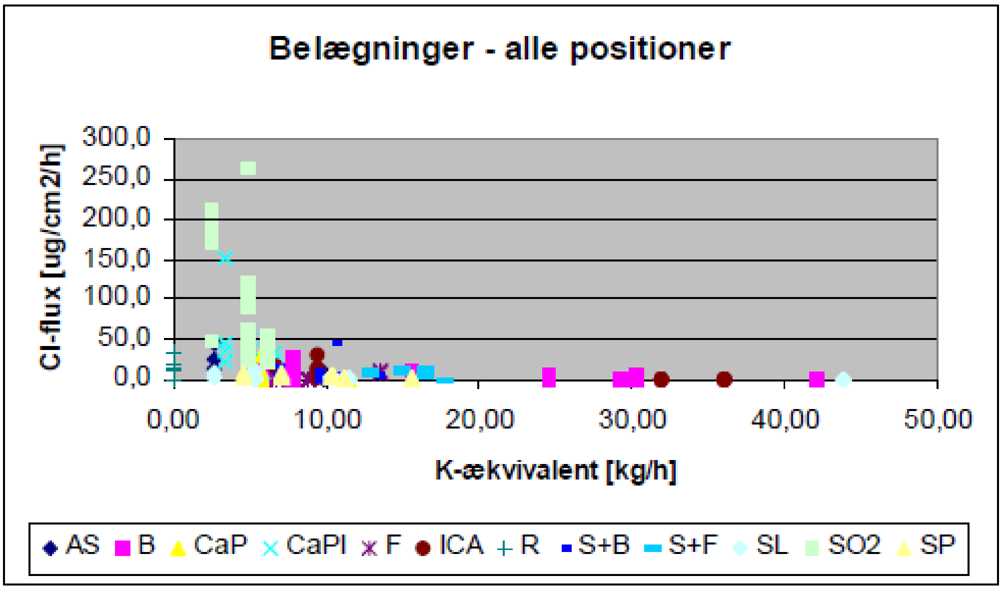
In a wood chip fired grate boiler at Ensted in Denmark, different measures to reduce superheater corrosion have been tested and evaluated. The methods tested are removal of chlorine containing fuel fractions, optimisation of air and fuel supply and additive dosing. It was found that removal of chlorine containing fuel fractions was not practically feasible at a reasonable cost. The purpose of optimising the air and fuel supply was to reduce the amount of KCl released from the grate. However, it could not be shown that optimisation would have any such effect. The only method which is practically and economically feasible and which ensures the requested effect at the same time, is the use of additives. [26]

Different types of additives and different methods of injecting them were tested. The types of additives tested were sulphur based additives, silicon/aluminium based additives and calcium phosphate based additives. It was also tested to combine different types of additives to see if there were any synergies, leading to an increased effect. The additives tested are shown in Table 7.

Tabell 7. Additiv som testats i Enstedsverkets fliseldade panna [26]
Table 7. Additives tested at the wood chip fired plant at Enstedsverket [26]

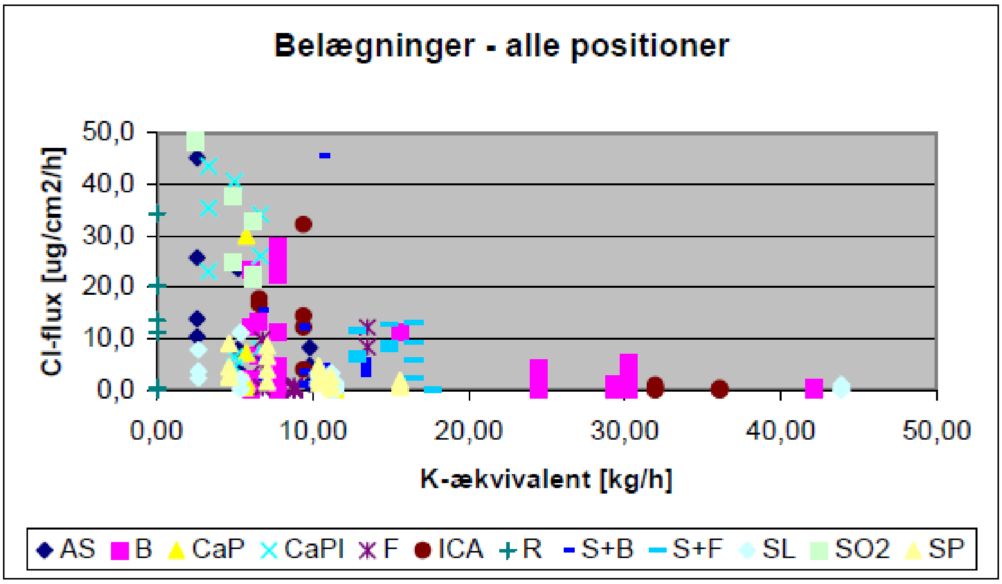
Type of additive	Additive	Form	In diagram
Sulphur	Sulphur	Granules	S
	Sulphur	Powder	SP
	SO_2	Gas	SO_2
	Ammonium sulphate	Solid?	AS
Silicon/aluminium	Bentonite	Powder	B
	Bentonite	Slurry	
	ICA 5000	Powder	ICA
	Coal fly ash	Powder	F
Calcium phosphate	Calcium hydrogen phosphate	Powder	CaP
	Calcium phosphate	Solution	CaPl
Combination	Sulphur + Bentonite	Powder	S + B
	Sulphur + Coal fly ash	Powder	S + F

The effect of the additives was measured by the use of deposit probes. The Cl content of the deposits was then compared for the different additive cases. The amount of additive used has been recalculated to an equivalent amount of alkali that the additive can react with and bind. A clear effect of the use of additives can be seen, with an increase in the amount of alkali that is bound causing a decrease in the amount of Cl in the deposits, (see Figure 11 and Figure 12). There is a large scatter in the results and this is probably caused by variations in the fuel or the additive. Since the fuel flow cannot be monitored continuously, it will be necessary to use an additive flow that is high enough to give a good result during variations of the fuel flow. It is considered that a flow of 15 kg K equivalents will be an adequate flow. All additives tested had about the same KCl reducing effect, except SO_2 gas, which actually increased the amount of KCl in the deposits, [26].



Figur 11. Mängd klor i beläggningen som funktion av mängden additiv omräknad till potentiell kaliuminbindning (beteckningar enligt Tabell 7, R står för referens). [26]

Figure 11 Amount of chlorine in deposits as a function of amount of additive recalculated as potential potassium binding (denotations according to Table 7, R is for reference). [26]



Figur 12. Mängd klor i beläggningen som funktion av mängden additiv omräknad till potentiell kaliuminbindning (beteckningar enligt Tabell 7, R står för referens).Samma data som i ovanstående figur, men med en annan skala på y-axeln. [26]

Figure 12 Amount of chlorine in deposits as a function of amount of additive recalculated as potential potassium binding (denotations according to Table 7, R is for reference). The same data as in previous figure but with a different scale on the y-axis. [26]

An economic evaluation of different additive alternatives was also performed. Factors that have been included in the evaluation are amount of additive needed, price for additive, costs for increased amounts of ash, increased emission fees (sulphur additives), investment and operation costs. The fly ash of the plant is deposited and an increased amount of fly ash will lead to increased deposit fees. The bottom ash is not deposited, but it is assumed that the use of coal fly ash will mean that the bottom ash will have to be deposited as well.

A summary of the economic evaluation is shown in Table 8. The full economic evaluation can be found in Appendix A. The two cheapest alternatives are fly ash and sulphur, with an annual cost of approximately 600 kDKK. If the bottom ash does not have to be deposited when using coal fly ash, the cost for that alternative will be as low as ~400 kDKK per year. Alternative actions to using additives are to lower the steam data or welding on corroded parts in the boiler. It is assumed that welding will cost ~10-25 MDKK every three years. This means that the use of additives is a very good alternative. [26].

It was calculated for the German market that if ammonium is used to reduce NOx this can be replaced by ammonium sulphate for the double reduction of NOx and alkali chlorides at similar consumable costs, [31]. Although 2.5 times more ammonium sulphate solution (37%) has to be used to get the same NOx reducing potential as ammonia solution (24%) the ammonium sulphate solution cost 40 Euros per tonne, whereas the ammonia solution cost 100 Euros per tonne.

Tabell 8. Kostnader i DKK för olika additiv i flispannan i Enstedsvaerket. [26]

Table 8. Costs in DKK for different additives tested at the wood chip fired plant at Enstedsverket [26]

	Coal fly ash	**Bentonite**	**ICA 5000**	**CaP**	**Sulphur**
Additive cost	28.636	1.260.000	1.354.839	1.086.207	129.098
Increased amount of fly ash	223.841	196.980	158.855	169.810	6.025
Increased amount of bottom ash	162.641	0	0	0	0
Increased emission fees	0	0	0	0	344.262
Investment and operation	187.120	180.707	171.604	174.220	137.262
Total	**602.238**	**1.637.687**	**1.685.298**	**1.430.237**	**616.647**

Ammonium sulphate, (as ChlorOut) has been proven to greatly reduce corrosion in long-term tests on biomass and waste fired boilers, but has not been tested at steam temperatures as high as 600°C. Sewage sludge, which contains Si and P has also been shown to be effective, [32].

3.4 Material tests at elevated temperatures

3.4.1 Fireside corrosion

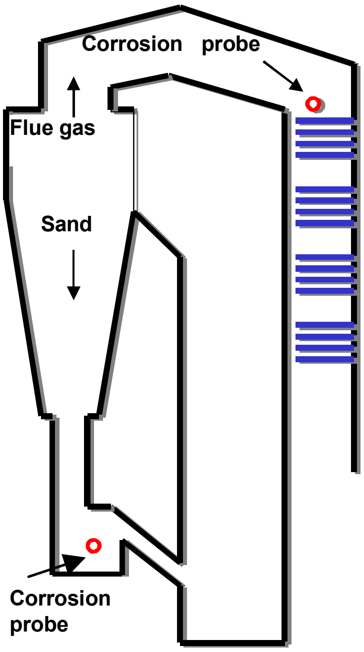
3.4.1.1 Nässjö, 600°C (convective pass) and 650°C (sand loop seal)

Corrosion testing of candidate superheater materials was performed using cooled probes in a 30MWth wood-fired circulating fluidised bed (CFB) boiler in Nässjö, Sweden. The fuel used in Nässjö was forest fuel (logging residues). The chromium content of the steels ranged from 2% to 28%. The alloys tested were 10CrMo910, X20CrMoV12 1, HCM12A, Esshete 1250, TP 347H FG, AC 66 and Sanicro 28 (composite tube). The compositions of the materials are shown in Table 9. Two probes, temperatures 530°C and 600°C, were exposed near the final superheater in a convective pass and therefore heated by the flue gas. Two probes, temperatures 600°C and 650°C, were placed in the cyclone loop seal and were heated by the sand, which is at the same temperature as the flue gas, and which is then circulated back into the bottom of the furnace (Figure 13). As the heat transfer coefficient between sand and superheater tube wall is greater than that between the flue gas and the tube wall, the temperature of the probes in the loop seal was set at 50°C higher than the other probes. This was done to simulate the same steam temperature. [8]

Tabell 9. Sammansättning i vikt-% hos de testade stålen i Nässjö. [8]

Table 9. Chemical composition, in wt %, of the steels tested in Nässjö. The balance is Fe. [8]

Steel	**Cr**	**Ni**	**Mo**	**Mn**	**Other**
10CrMo910	2.1	--	0.92	0.43	C 0.12, Si 0.22
X20CrMoV12 1	10.5	0.73	0.89	0.6	C 0.18, Si 0.24, V 0.27
HCM12A	12.0	0.26	0.32	0.65	W 1.9, Si 0.3, Nb 0.06, N 0.06, V 0.02, B 0.003, C 0.08
Esshete 1250	14.9	9.65	0.94	6.25	C 0.084, Si 0.58, Nb 0.86, V 0.22, B 0.004
TP 347H FG	18.5	11.9	--	1.5	Si 0.42, Nb 0.9, C 0.09
AC 66	27.3	31.7	--	0.49	Ce 0.06, Nb 0.8, Si 0.2, C 0.05
Sanicro 28	26.7	30.6	3.32	1.73	C 0.015, Si 0.42, Co 0.06, Cu 0.87, N 0.07

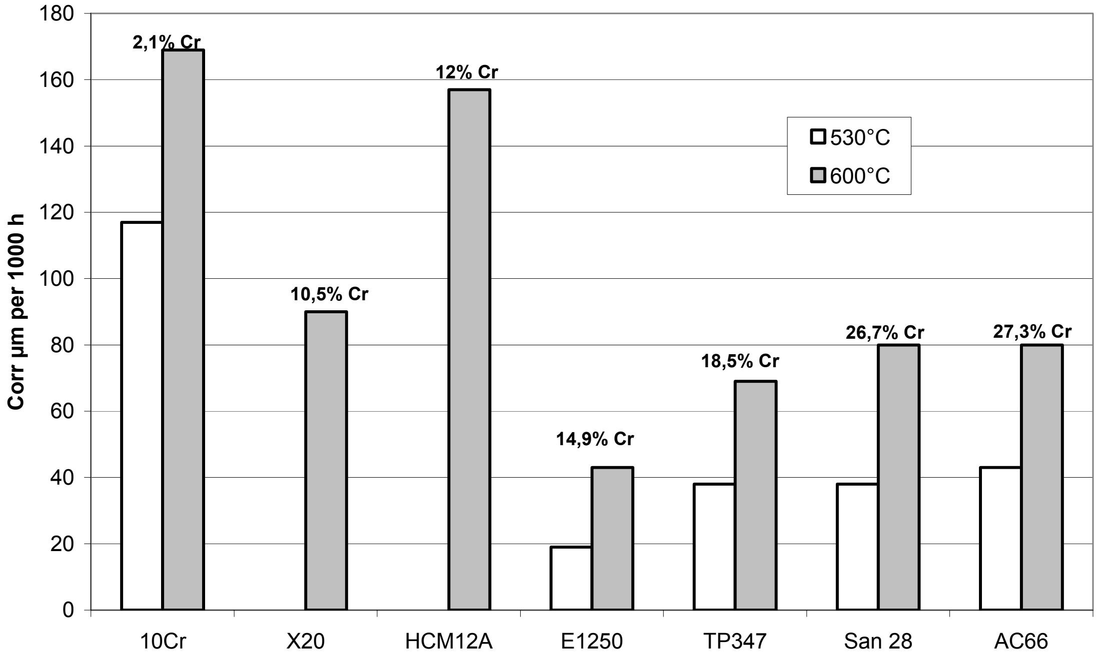


Figur 13. Schematisk bild av pannan i Nässjö. Positionerna för korrosionssonderna visas, dels högst upp i pannan, vid överhettarna och dels längst ner, i sandlåset. [8]

Figure 13 Schematic diagram of the Nässjö CFB boiler showing one corrosion probe near the top of the boiler at the superheaters and one at the bottom in the cyclone loop seal [8]

The chemical composition of the flue gas at the superheaters and the environment in the cyclone loop seal was determined by FTIR (Fourier Transform InfraRed Spectroscopy). Deposits were collected on probes and analysed by SEM-EDX (energy dispersive x-ray analysis in a scanning electron microscope).

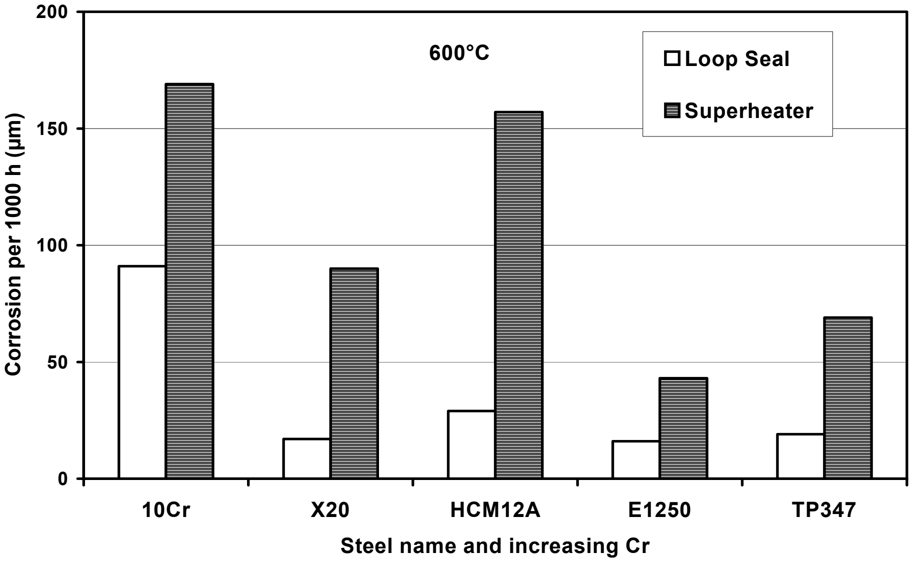
When positioned in the convective pass, austenitic steels containing 15-18% Cr performed much better than 2-12% Cr ferritic/martensitic steels and marginally better than high Cr/Ni alloys. (Figure 14) Considerable amounts of internal (selective) corrosion on the fireside were seen in some alloys, especially E1250, TP 347H FG and HCM12A in the superheater environment at 600°C, [8]



Figur 14. Korrosion per 1000 timmar för stål exponerade på sonder vid överhettarna med metalltemperaturerna 530°C *och* 600°C*. Korrosionshastigheten var högre vid* 600°C*. [8]*

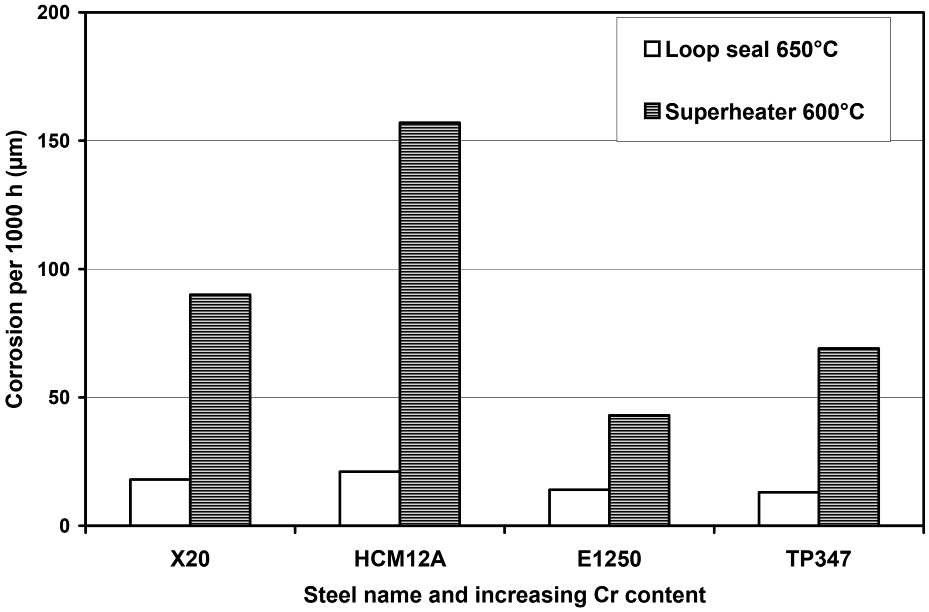
Figure 14 Total corrosion per 1000 hours for steels exposed in probes near the superheaters at metal temperatures of 530°C and 600°C. The corrosion rate was higher at 600°C [8]

In spite of a higher metal temperature the corrosion rate in the loop seal was at least 50% lower than that in the convective pass, for the same materials. For some materials, the corrosion rate is reduced 5-fold if the steel was positioned in the loop seal. (Figure 15 and Figure 16) The improvement in the corrosion resistance was explained on the basis that the water vapour content in the loop seal is much lower than in the convective pass and that the deposits formed were much thinner. FTIR spectroscopy showed that the moisture content of the gas in the loop seal was considerably lower than that of the flue gas at the superheaters, (5 vol. % as opposed to 25 vol. %) and oxygen levels were generally higher, although variable. All the steels tested in the loop seal, apart from 10CrMo910, performed well, [8]



Figur 15. Jämförelse av korrosionshastigheter vid 600°C för stål som exponerats på sonder vid överhettarna och i sandlåset. [8]

Figure 15 Comparison of corrosion rates at 600°C for steels exposed in probes near the superheaters and in the cyclone loop seal. [8]



Figur 16. Jämförelse av korrosionshastigheter för stål som exponerats på sonder vid överhettarna vid 600°C och i sandlåset vid 650°C för att simulera samma ångtemperatur på ca 565-570°C. [8]

Figure 16 Comparison of corrosion rates for steels exposed in probes near the superheaters at 600°C and in the cyclone loop seal at 650°C, simulating the same steam temperature of about 565-570°C. [8]

Another advantage to be gained by placing the superheaters in the loop seal, in addition to reduced corrosion, is that the superheater can be considerably smaller in size (about a third of the size of a conventional superheater) since the heat transfer per unit area of tube surface is more intensive in the loop seal. This leads to savings in material and labour costs. The heat transfer is greater in the loop seal because:

(i) the temperature drop in the sand, as it gives up its heat to the superheater, is much less than the temperature drop in the flue gas which means that a greater temperature difference between sand and steam is maintained and

(ii) the heat transfer coefficient is greater between sand and the superheater tube wall than between the flue gas and the superheater tube wall.

The result of this, and a possible disadvantage, is that the superheater wall temperature will be higher in the loop seal, for the same steam temperature. For superheaters heated by flue gas (but shielded from radiation from the furnace) the temperature difference between the steam and the tube wall, ΔT, is typically assumed to be 35°C. If a superheater is heated by sand, then ΔT can be about 80°C. This means that a steel with a superior creep strength is needed. However, it is expected that the cost savings by the reduction in size of the superheater will more than offset any increase due to the use of a more highly alloyed material. [8]

3.4.1.2 Nässjö 640°C. 650°C and 670°C

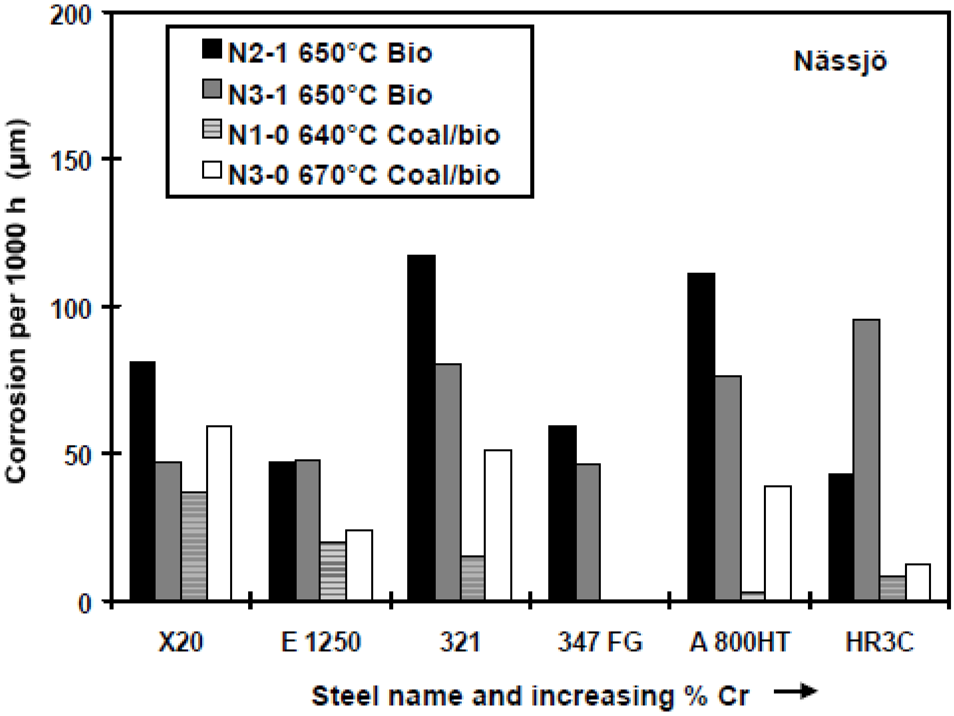
A number of austenitic stainless steels and one high chromium martensitic steel were tested in corrosion probes in the Nässjö boiler, in the same position in the convective pass as in the test described above, (Figure 13). Four probes were used with metal temperatures of 640-670°C simulating a steam temperature of about 600-635°C. Two of the probes were exposed to the flue gases of a wood/coal mixture (30% coal in term of thermal energy) and two probes were exposed to 100% wood. The wood fuel consisted of, in both cases, by-products from the forestry industry and had not been used in any industrial process. The fuel used, exposure times and temperatures of the four probes are shown in Table 10. [9]

Tabell 10. Bränsle, materialtemperatur och exponeringstemperatur för sonderna. [9]

Table 10. Fuel used, material temperature and exposure time for the probes. [9]

Probe name	**Probe N1-0**	**Probe N3-0**	**Probe N2-1**	**Probe N3-1**
Fuel	wood/30% coal	wood/30% coal	100% wood	100% wood
Nom. temp	640°C	670°C	650°C	650°C
Exp. time	3192 h	1776 h	4253 h	6159 h

Corrosion was assessed as the amount of metal loss plus the amount of internal/selective grain boundary attack. Changing from wood/30% coal to 100% wood approximately doubled the corrosion rate at similar metal temperatures. For many alloys the change of environment from bio/coal to 100% bio resulted in a large increase in the amount of internal corrosion. Generally, an increase in chromium content led to a decrease in corrosion in the wood/coal environment, but this was not the case when firing 100% wood. With 100% wood there was no clear relationship between alloying content and corrosion rate. It is thought that the sulphur content of the coal leads to a reduction in the chlorine content of the deposits and so reduces corrosion.



Figur 17. Korrosion (metallförlust plus intern korrosion) per 1000 timmar för olika stål testade i Nässjö. Korrosionen av Alloy 825 (visas ej här) var likartad den för Alloy 800HT. TP 347 H FG testades inte vid sameldning av kol och trä. [9]

Figure 17 Total corrosion (metal loss plus internal attack) per 1000 hours for various steels tested in the Nässjö boiler. Corrosion of Alloy 825 (not shown here) was similar to that of Alloy 800HT. TP 347H FG was not tested during co-firing of coal and wood. [9]

Chemical analysis showed a high Cl content and a lower S content in the deposits formed during firing with 100% bio compared with coal/bio (see Table 11). These results were typical and analyses of deposits from superheaters showed similar compositions.

Tabell 11. Innehåll i vikt-% i avlagringarna på sonderna N1-0 (kol/bio) och N2-1 (100% bio) [9]
Table 11. Content in weight percent of the deposits on the probes N1-0 (coal/bio) and N2-1 (100% bio). [9]

	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	S	Cl
Fuel											
Coal/ Bio	15.7	7.1	15.5	2.2	17.8	2.6	1.2	3.0	2.5	12.5	0.5
100% Bio	9.1	1.5	19.5	0.9	22.5	3.0	2.5	1.4	3.2	4.9	11.3

3.4.1.3 Jordbro

Several commercially available stainless steels for use as heat exchangers with 600°C/200-300 bar steam were exposed during 1994/5 on a probe placed in a utility boiler at Jordbro operating with 100% biomass. A conventional 10-12% Cr steel was also tested as a comparison. The compositions of the steels tested can be seen in Table 12. The probe was exposed in boiler 3 of Jordbro district heating station, near Stockholm. Jordbro is a 70MW hot water boiler fired with 100% biomass (pulverised wood). The exposure time was 1680 hours and the material temperature nominally 650°C, but the probe temperature varied between 640-660°C. Chemical analyses were obtained for the fuel, ash and deposits. The wall thickness of the specimens was measured before and after exposure. After exposure the specimens were examined using light optical- and scanning electron microscopy and energy dispersive x-ray analysis. Metal loss, oxide thickness and internal attack were measured, [10].

Tabell 12. Sammansättning i vikt-% för de testade ståleni Jordbro. [10]

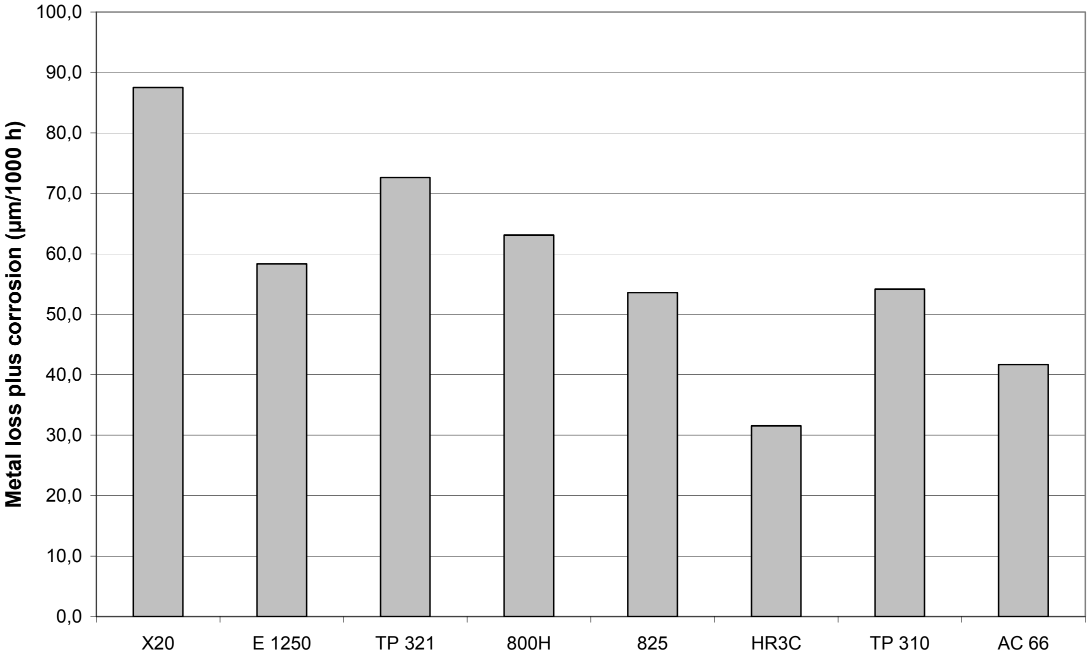
Table 12. Composition in weight % of the tested steels in Jordbro. [10]

Steel	**Cr**	**Ni**	**Mo**	**Mn**	**Other**
Esshete 1250	14.5	9.4	0.97	6.2	Si .46, Nb 1, V .27,B .006, C .08, N .04
X20	10.5	0.4	0.83	0.7	V 0.3, Si 0.3, V .29, Cu .19, C .19
TP 321	17.2	10.1		1.4	Ti 0.47, Si 0.36, C 0.05
TP 310NbSi	25.4	21.2	0.22	1.7	Si 1.17, C 0.18, N 0.03, Nb 0.67
Alloy 825	22.0	39.3	3.25	0.5	Ti 0.93, C 0.01, Si 0.32, Cu 1.83
Alloy 800H	20.3	30.2	--	0.6	Ti 0.53, Al 0.5, Si 0.49, C 0.07
HR3C*	25	20	0.25	1.1	Si 0.4, Nb 0.5, N 0.2., C 0.06
AC 66*	27	32	0.8	1.0	Si .2, Nb 0.8, Ce 0.07,

* standard chemical composition

Optical microscopy was used to measure the wall thickness of the samples as well as the depth of any internal corrosion. The results are given in Figure 18. X20 showed the highest corrosion rate followed by TP 321. A more detailed analysis in the SEM showed a well formed oxide of chromium near the metal interface, with a more porous layer of iron oxide on top, at the surface. A chromium depleted layer in the metal directly under the chromium oxide was detected.

The corrosion resistance is not the only consideration in choosing a superheater material for higher steam temperatures. The creep strength (or proof stress) is also of prime importance. X20, TP 321, 825 and 800H are not suitable for 600°C steam, where the metal temperature will be 635-650°C, but 825 has been used as the outer component in co-extruded tubes at lower temperatures and could be used at higher temperatures provided the inner component had sufficient creep strength. E 1250, HR3C and AC 66 are all suitable for metal temperatures up to 650°C. HR3C has the highest creep strength of all the materials tested, but has been found to suffer from cracking because of low ductility caused by cold working,[38].



Figur 18. Korrosion per 1000 timmar för stål exponerade på en sond i Jordbro med metaltemperaturen 650°C *[10]*

Figure 18 Total corrosion per 1000 hours for steels exposed in probes in Jordbro with a metal temperature of 650°C [10]

Tabell 13. Innehåll i vikt-% av huvudämnena i avlagringar på sonderna, bränsle och aska i pannan i Jordbro. [10]

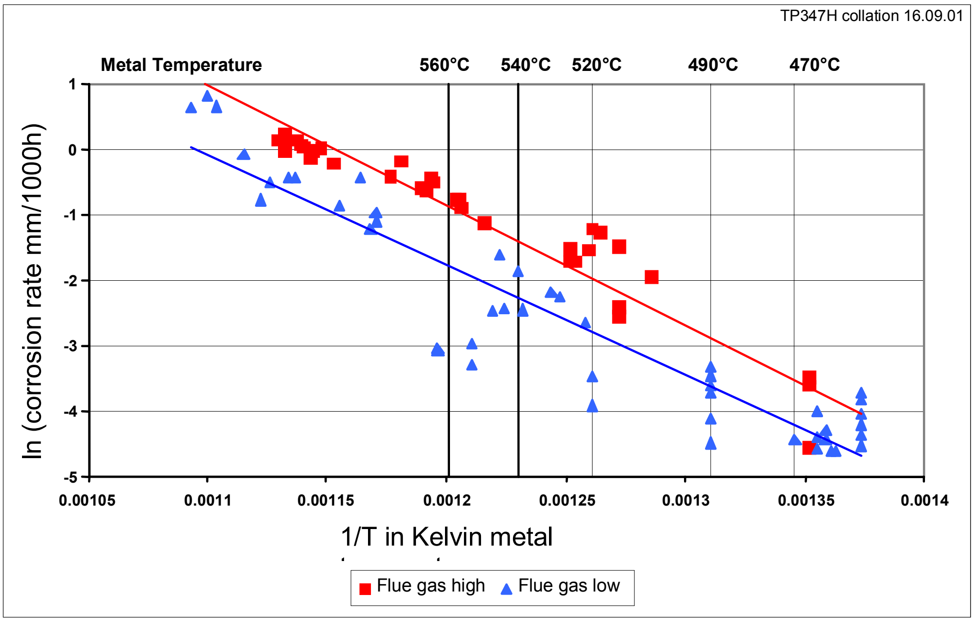
Table 13. Content in weight % of the main elements in the deposits on the probes, fuel and ash in Jordbro power station.. [10]

	Sulphur	Chlorine	Calcium	Potassium	Sodium
Deposits	4-7	0.2-0.8	17-23	8-17	0.5-1.4
Fuel (Dry)	<0.01	0.01	0.08	0.04	0.01
Fly ash	0.94	0.31	5.49	2.85	0.6

3.4.1.4 Masnedø – 585°C steam loop

Corrosion tests have been performed at the Masnedø straw-fired CHP Plant. This plant has an 8MWth moving-grate boiler and produces steam at 520°C and 80 bar. Some tubes were welded into place into a specially constructed test steam loop which had an outlet temperature of 585°C. Some tubes were exposed during 1998-99 for 3462 hours and others during 1998-2000 giving a total time of 8690 hours over 2 years. The flue gas temperature during 1998-99 was measured as 900-1050°C, but during 99-2000 it had decreased to around 850-900°C.

Corrosion, given as the sum of metal loss and internal (selective) corrosion, was measured at 24 points around the circumference of the tube samples. It can be seen in Figure 19 that the corrosion rate for TP 347H increased with calculated metal temperature (based on steam temperature), but also depended on the flue gas temperature. The corrosion rates were also higher if the superheater tubes were not shielded from the flue gas, [16]. At a metal temperature of 600°C (corresponding to a steam temperature of 570°C) TP347H (coarse or fine –grained, both were tested) showed a corrosion rate of 1.0-1.2 mm per 1000 h. The steel X3CrNiMoN17-13 (Cr 16-18, Mo 2-2.8, Ni 12-14) showed similar rates, [41]. It was found that alloys with higher Cr contents showed higher corrosion rates, [41].



Figur 19. Ln för korrosionshastigheten per 1000 timmar mot 1/T i Kelvin för TP347 H i överhettartuber i en halmeldad panna. Korrosionshastigheten var beroende av metaltemperatur men också av värmeflöde. [16]

Figure 19 Ln. corrosion rate in mm per 1000 hours against inverse temperature in Kelvin for TP347H superheater tubes in a straw fired boiler. The corrosion rate depended on the metal temperature, but also the heat flux. [16]

3.4.1.5 Nyköping – 600ºC steam loop

A steam loop for corrosion testing was constructed in Esshete 1250 and attached to one of the superheaters in a 100 MWth bubbling fluidised bed (BFB) boiler. (boiler 3) in Nyköping, Sweden. The Combined Heat and Power (CHP) unit produces 35 MW of electricity and 69 MW of heat. The final steam temperature is 540°C and the pressure 140 bar. A flue-gas condensor yields 12 MW additional heat at full boiler load. The plant has been in operation since 1994.

The loop raised the final steam temperature to about 600°C at 140 bar. A number of different test materials were welded into the loop for evaluation at low temperature (500°C steam) and high temperature (600°C steam). A number of sections were examined metallographically after exposure. The steam loop was in service for one firing season (about 5500 h) and the fuel mixture was initially a biomass mix co-firing with 15% coal. However, halfway though the firing season the coal was replaced with 15% packaging waste, containing plastic and aluminium. The latter mixture (biomass and waste) was highly corrosive and accounted for most of the corrosion. The biomass mix consisted of demolition wood, forestry residues and sawmill residues. In Table 14 the different materials tested and the calculated metal temperatures are presented. In Figure 20 the test loop before and after operation can be seen.

Tabell 14. Sammansättning i vikt-% för stålen i testslingan. X indikerar att stålet testades. De angivna temperaturerna är den beräknade metalltemperaturen mitt i ringens vägg. [17]

Table 14. Chemical composition in wt% of the steels tested in the loop. X indicates that the steel was tested. The temperatures given are the calculated metal temperatures at mid-wall thickness. [17]

Steel	**Dims (mm)**	**Cr**	**Ni**	**Mo**	**Mn**	**Other**	**500°C**	**610-620°C**
HR 11N	38 x 4.4	29.1	41.1	1.1	0.50	Si 0.12, N 0.17, C 0.01	X	
Esshete 1250	38 x 5	14.5	9.2	1.0	6.2	Si 0.4, Nb 1.0, V .27, B .005, C .08	X	X
HR3C	38.2 x 6.5	24.6	20.0	--	1.1	Si 0.4, Nb 0.5, N 0.2, C 0.06	X	X
TP347 HFG	38 x 7.1	18.5	11.0	--	1.8	Nb 0.7, Si 0.7 max, C 0.07	X	X
AC 66	33.7 x 4.5	27.6	32.0	--	0.51	Si 0.2, Nb 0.8, Al 0.1, Ce 0.09, C 0.47	X	X
Haynes 230	33.7 x 3.38	21.8	59.0	2.13	0.48	Al.35, B .003, Co .2, Fe 1.6, Si .38, W 13.9	X	X
X20	31.8 x 5.6	11.0	0.5	1.0	1max	V 0.3, Si 0.5, C 0.19	X	

Figur 20. Testslingan och delar av ÖH2 före drift (vänster) och efter en eldningssäsong (höger) [17]

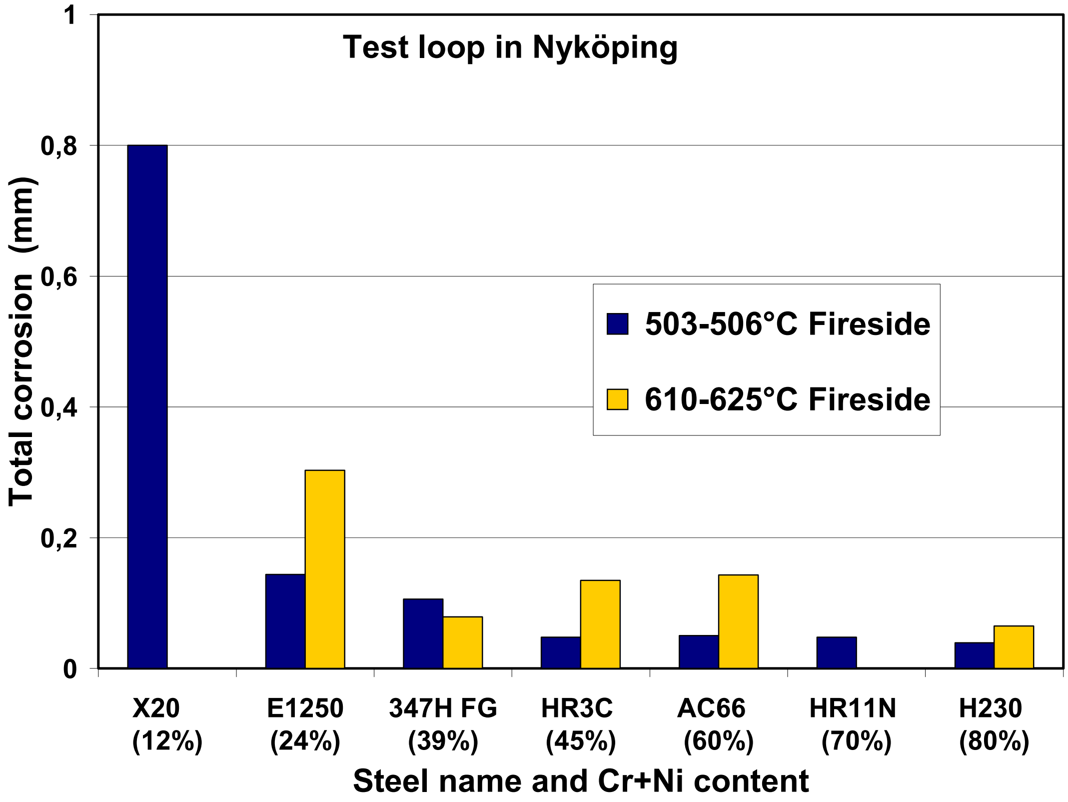
Figure 20 Test loop and part of SH2 before operation (left) and after one firing season, (right). [17]

Tabell 15. Ångsidiga- och rökgassidiga- korrosionsvärden från testslingan. Värdena är medel/maximum uppmätta. Temperaturerna är metalltemperaturerna i kontakt med ångan eller rökgaserna.

Table 15. Steam-side and fireside corrosion values for the test loop. The values given are average/maximum measured. The temperatures are the metal temperatures in contact with the steam or flue-gases.

Steel	**495-499°C**	**607-616°C**	**503-506°C metal temp. Fireside corrosion. Average/maximum**			**610-625°C metal temp. Fireside corrosion. Average/maximum**		
	Steam-side oxid. in µm	Steam-side oxid in µm	Selective corrosion µm	Metal loss µm	Av. Total corrosion µm	Selective corrosion µm	Metal loss µm	Av. Total corrosion µm
HR 11N	1/3	--	34/101	14/38	48	--	--	--
Esshete 1250	45/51	64/86	72/123	72/117	144	118/162	185/219	303
HR3C	10/20	10/30	41/175	7/28	48	86/171	49/114	135
TP 347 HFG	33/47	26/38	75/109	31/101	106	65/115	14/37	79
AC 66	1/2	2/4	13/50	27/90	50	83/167	60/114	143
Haynes 230	1/3	2/4	16/51	23/96	39	53/135	12/35	65
X20	46/90	--	0/0	800/969	800	--	--	--

Fireside corrosion values (as average metal loss plus average selective corrosion) are shown in Figure 21 and Table 15. The 11% chromium steel X20 and the nickel-base alloy HR11N were not tested at the higher steam temperature because of strength considerations. Regarding fireside corrosion at 500°C steam the alloys with the best corrosion resistance were Haynes 230, HR11N, AC 66 and HR3C followed by Esshete 1250 and TP 347 HFG. The corrosion rate of X20 was unacceptably high and this material is totally unsuitable for this fuel mix. At 600°C Haynes 230 showed the lowest corrosion rates, followed by TP 347H FG, HR3C, AC66, and Esshete 1250. Large amounts of internal corrosion were seen.



Figur 21. Total rökgassidig korrosion (medelmetallförlust plus medel av selektiv korrosion) för de olika stålen i testslingan. Materialtemperaturer vid ångtemperaturerna 500°C och 600°C. X20 och HR11N testades inte vid 610°C. [17]

Figure 21 Total fireside corrosion (as average metal loss plus average selective corrosion) for the different steels in the test loop. Material temperatures at steam temperatures 500°C and 600°C. X20 and HR11N were not tested at 610°C.[17]

Deposits up to 20 cm thick were formed on the superheater tubes. The majority of the deposits was built up by fly ash that was quite loose, but parts were hard and dominated by enrichments of Al, Ca, K, Si and some S and Cl. In all deposits from the superheaters high concentrations of Al could be found, in some places as much as 50 wt.% after firing with biomass and packaging waste. This compares to an Al content of 3-5% when previously firing biomass and coal. Investigation of the oxide layers gave a slightly different picture with chlorine in the percentage range indicating that the chlorine either has come to the tube in an early stage of condensation or has been transported through the deposit into the tube.

A feature of all the steels tested, (apart from X20, which has proved itself unsuitable for this application) is the large amount of internal (or selective) corrosion as a function of the toal corrosion. The internal corrosion amounts to 40-50% of the total in Esshete 1250 up to 80% in TP 347 HFG, HR3C and Haynes 230. If corrosion is being monitored by ultra-sonic testing, or other wall-thickness measurements, the amount of internal corrosion will not be seen and the total corrosion will be under-estimated. It is not known if the internal corrosion zone grows continuously during exposure or if it reaches a steady-state maximum depth below the oxide scale. It is clear though that as steam temperatures increase in biomass and waste-fired plant and more highly alloyed materials are used that the “unseen” internal corrosion will need to be taken into consideration. [17].

The materials mostly showed expected results with the corrosion rate decreasing with an increase in the chromium and nickel contents. The alloys with the best corrosion resistance produced well-formed Cr-oxide layers. That TP 347 HFG showed a slightly lower corrosion rate at the higher temperature could be explained by the formation of a more compact Cr-oxide layer at this temperature. In TP 347 HFG on the steam-side at 500°C the outer oxide was Fe-rich, while the inner oxide was Cr-rich. At 610°C this situation was reversed, with the outer oxide being Cr-rich. A Cr-oxide on top of an iron oxide is not usually observed. It was thought that the small grain size of 347H FG aids the diffusion of Cr and facilitates the formation of a compact Cr-oxide, [17].

The conclusion for 600°C steam was that Haynes 230 showed the lowest corrosion rates, followed by (surprisingly) TP 347H FG, and then HR3C/AC66 and Esshete 1250. In view of its lower alloying content and therefore cost TP 347H FG should be investigated further together with HR3C and AC66 for use in wood-based biomass plants with high steam temperatures, [17].

Increasing the metal temperature of a superheater steel does not always lead to an increase in the corrosion rate. Gradient probe tests performed in Nyköping running on 100% waste wood, with ammonium sulphate additive, showed that for stainless steels a maximum corrosion rate was reached at a metal temperature of 540-560ºC, [33] . An example of the results obtained for Esshete 1250 is given in Table 16, The decrease in corrosion rates at higher temperatures were explained on the basis of decreasing Cl levels in the deposits with increasing temperature and increasing diffusion allowing a protective Cr-rich oxide to be formed more effectively.

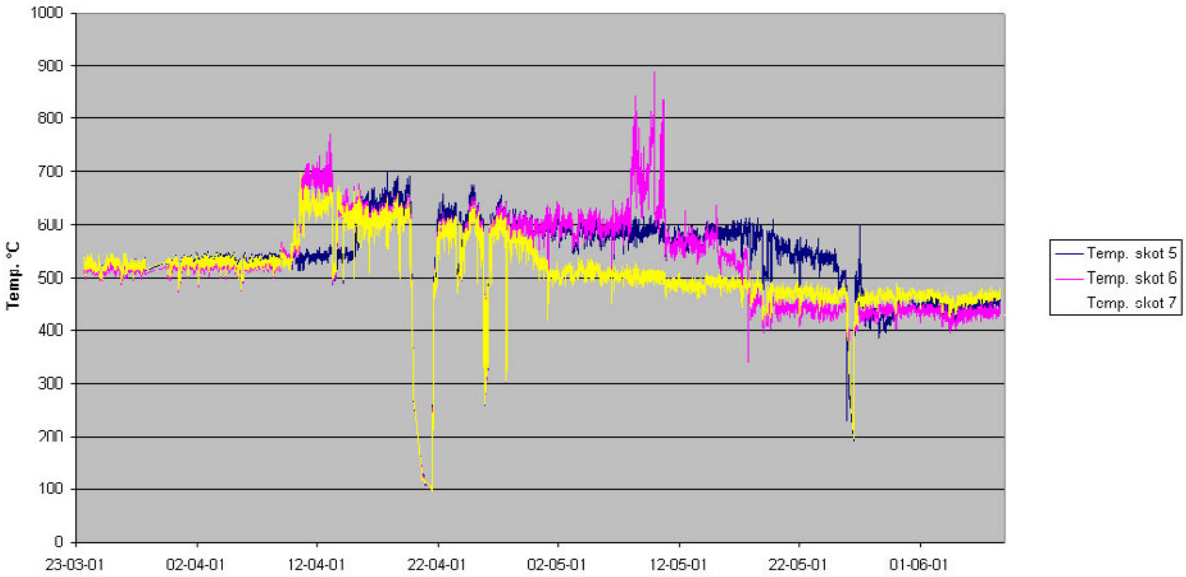
Tabell 16. Medel metallförlust vid oliks temperaturer för Esshete 1250 efter sondprovning i Nyköping,[33].

Table 16. Average metal loss at various metal temperatures for Esshete 1250 after probe testing in Nyköping, [33].

Av. Metal Temperature (ºC)	505	536	568	585	598	601
Av. Metal loss (µm per 1000 h)	77	100	94	78	39	23

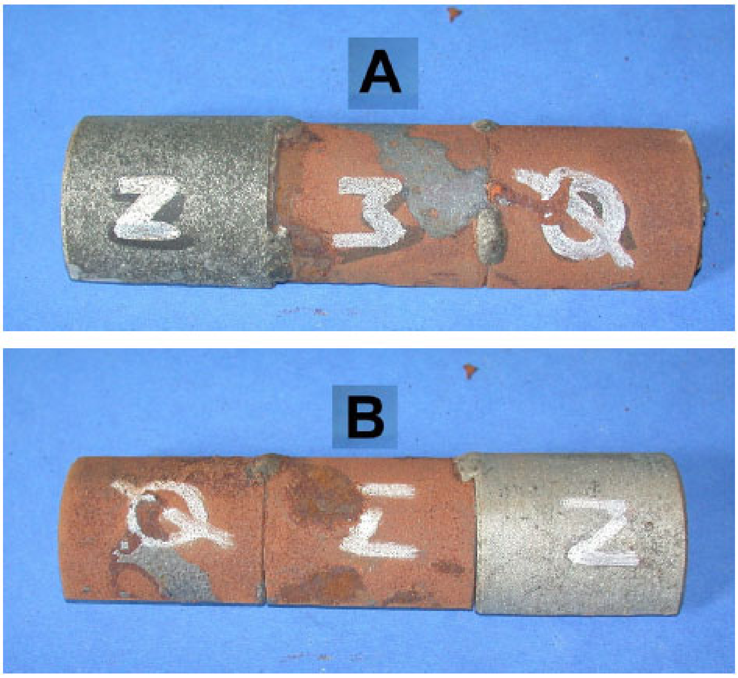
3.4.1.6 Enstedsvaerket

A test of welded-on Inconel 625 and two spray coatings in a wood-chip fired boiler at Enstedvaerket in Denmark has been performed, with the goal of testing the material at ~600°C- Tube parts were mounted onto the superheaters in order to achieve a higher material temperature than in the superheaters, where the material temperature is ~470-500°C. Three samples were installed, each containing three different materials. The material temperature of each sample was measured, (Figure 22). In one of the samples the temperature was in periods very high, >800°C, and this sample was excluded from further investigations. The two other samples are shown in Figure 23. Three different coating materials were tested in each sample, weld-on of Inconel 625 and two spray coatings, one was Inconel 625 and the other was not specified. The weld-on was polished to a smooth surface before exposure. [26]



Figur 22. Materialtemperaturer på de proverna som testats i Enstedsvaerkets träflispanna, [26].

Figure 22 Material temperatures of the samples tested in the wood fired boiler at Ensted, [26].



Figur 23. Prover efter exponering.: N: påsvets av 625; M, Spray coated 625; Ø: spray coated med okänt material. [26]

Figure 23 Samples after exposure. N: Weld-on 625; M, Spray coated 625; Ø: spray coated with unspecified material. [26]

On the two spray coated samples, less than 25% of the coating remains. The weld-on coating still covers the entire surface and the material loss is 0.12-0.21 mm/1000 hours. The coating has an average thickness of 3 mm and a minimum thickness of 2mm. This means that with a corrosion rate of 0.1 mm/1000 hours, the coating will need repair after 20 000 hours, corresponding to 3 years operation. [26]

3.4.2 Steamside corrosion

3.4.2.1 Nyköping

During the test with the steam loop, described in section 3.4.1.5, steam side oxidation was also investigated on the materials Esshete 1250, HR3C, TP 347H FG, AC66 and Haynes 230 at 500°C and 600°C, see Table 15. The 11% chromium steel X20 and the nickel-base alloy HR11N were only tested at the lower temperature and not at the higher steam temperature because of strength considerations.

The alloys with the highest Ni and Cr contents, Haynes 230, AC 66 and HR11N, showed negligible steam-side corrosion. TP 347H FG formed an oxide layer about 30 µm thick (although thinner at 600°C than 500°C). X20 formed a Cr-Fe-Mn oxide on the steam-side at 500°C and evidence of spalling was seen. [17]

3.4.2.2 Esbjerg

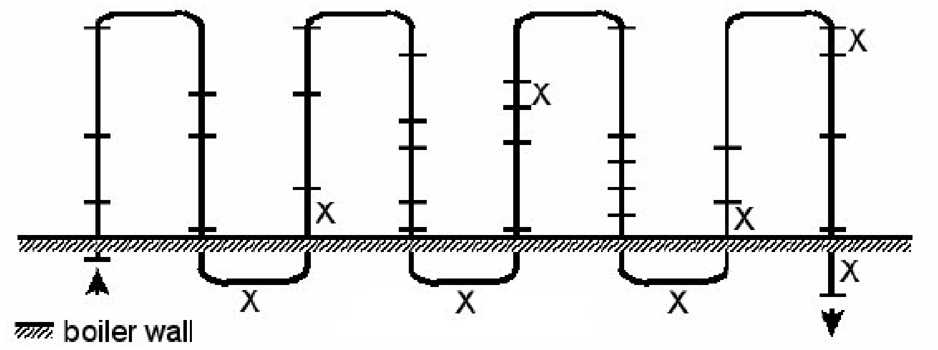
The long term oxidation behaviour of TP 347H FG was assessed by exposing the steel in test superheater loops in Esbjerg Power Plant, a Danish coal-fired power plant. The steamside oxide layer was investigated with scanning electron microscopy and energy dispersive X-ray diffraction in order to reveal the effect of oxidation time and temperature on the microstructure. The steel composition is given in Table 17. [18] [19]

Tabell 17. Sammansättning för TP 347H FG i vikt-.% [19]

Table 17. Alloy specifications of TP 347H FG in elemental wt.% [19]

	C	Cr	Ni	Si	Mn	Nb
TP347HFG	0.04– 0.10	17.0 – 20.0	9.0 – 13.0	<1.00	<2.00	NbxC<1.0

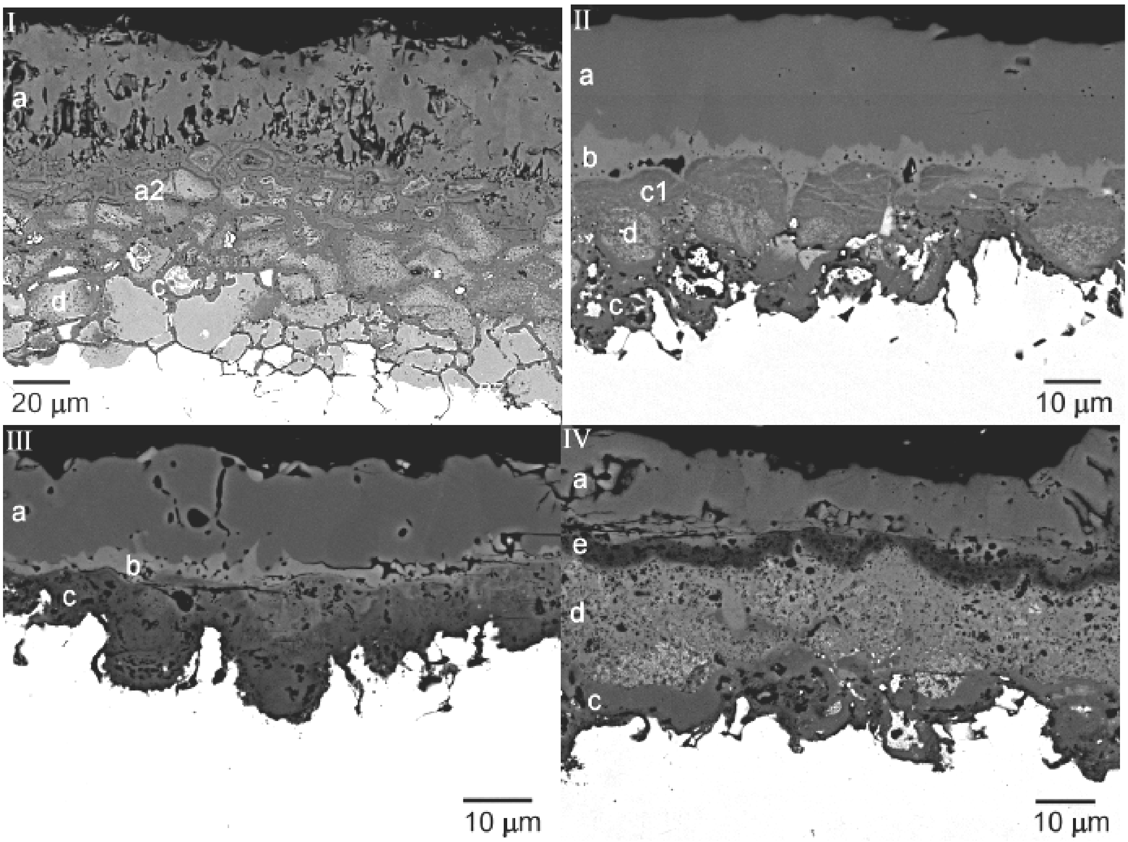
Samples were exposed in 4 test superheaters, each with 4 loops, in a coal-fired Danish power plant for 7720, 22985, 29588 and 57554 h, respectively. The location of the samples (x) within the test superheaters is sketched in Figure 24. The wall thickness was 5 mm for the samples exposed in loop 1 to 3, and 9 mm for the samples exposed in loop 4. The steam flow rate, the steam pressure (256 bar), and the inlet and outlet temperatures of each loop were recorded continuously. Metal temperatures at the location of each sample were calculated from these data. The calculated metal temperatures were between 499°C and 648°C, in the range of 20-40°C higher than the steam temperature. A total number of 24 TP 347H FG samples were investigated. [18] [19], [28].



Figur 24. Position (X) för prover som har exponerats i 7720 tim, 22985 tim och 57554 tim i testslingan [18]

Figure 24 The position (X) of the samples exposed in the 7720 h, 22985 h and 57554 h test superheaters [18]

A double layered oxide formed during steam oxidation. The interface between the inner and the outer oxide layer was reported to coincide with the original metal surface implying that the outer layer grows mainly by outward cation diffusion while the inner layer grows predominantly by inward transport of oxygen. The morphology of the inner Cr-containing layer was influenced by the oxidation temperature. At temperatures below approx. 585°C, it consisted of regions of Fe-Ni-Cr spinel surrounded by Fe-Cr oxide. At higher temperatures almost the entire inner oxide layer was composed of Fe-Cr oxide. The chromium rich oxide is a healing layer, which presumably reduces the oxidation rate significantly, [18], [28]. The oxide layers developed at different temperatures are shown in Figure 25.



Figur 25. BSE-SEM-tvärsnitt över oxidskiktet som bildats under 57554 timmars exponeringstid i ånga vid 256 bar och I: 506°C, II: 566°C, III: 615°C, IV: 648°C. a+a2 = Fe_3O_4, b = $(Fe_{1-x}Ni_x)_3O_4$, c+e = Fe-Cr oxide, d = Fe-Ni-Cr spinel. [18]

Figure 25 BSE-SEM cross-section showing the morphology of the oxide layer formed during 57554 h exposure in steam at 256 bar and I: 506°C, II: 566°C, III: 615°C, IV: 648°C. a+a2 = Fe_3O_4*, b =* $(Fe_{1-x}Ni_x)_3O_4$*, c+e = Fe-Cr oxide, d = Fe-Ni-Cr spinel. [18]*

It is suggested that faster Cr transport within the alloy at higher temperatures explains the change in morphology. The thickness of the inner oxide layer did not change significantly with oxidation time and temperature for exposures less than 30000 h; however after 57554 h the thickness had increased significantly at the lowest temperatures and slightly at the highest temperatures, [18], [28].

3.4.2.3 Masnedø

Tube specimens of TP 347 FG were exposed in a test superheater loop in Masnedø biomass plant in Denmark. The specimens were exposed to surface metal temperatures in the range of 455–568°C, steam pressure of 91 bar and exposure duration of 3500 and 8700 hours. The oxide thickness and morphology was investigated using light optical and scanning electron microscopy. The oxide present on the specimens is a duplex oxide with an inner chromium rich oxide and an outer iron rich oxide. The inner oxide consisted of a primary iron chromium nickel oxide in the original alloy grain and a chromium rich oxide, "healing layer", at the grain boundaries. This gave the appearance of uneven inner oxide and it was clear that the varying subsurface grain size affected inner oxide thickness, especially after longer exposure times. Longer exposure times from 3500 to 8700 hours resulted in increased pit thickness. Comparison of pit thickness revealed that increase of temperature from 455 to 525°C increases the oxidation rate, however a further increase in temperature did not result in thicker inner oxide, presumably due to the formation of a better healing layer at grain boundaries. [20]

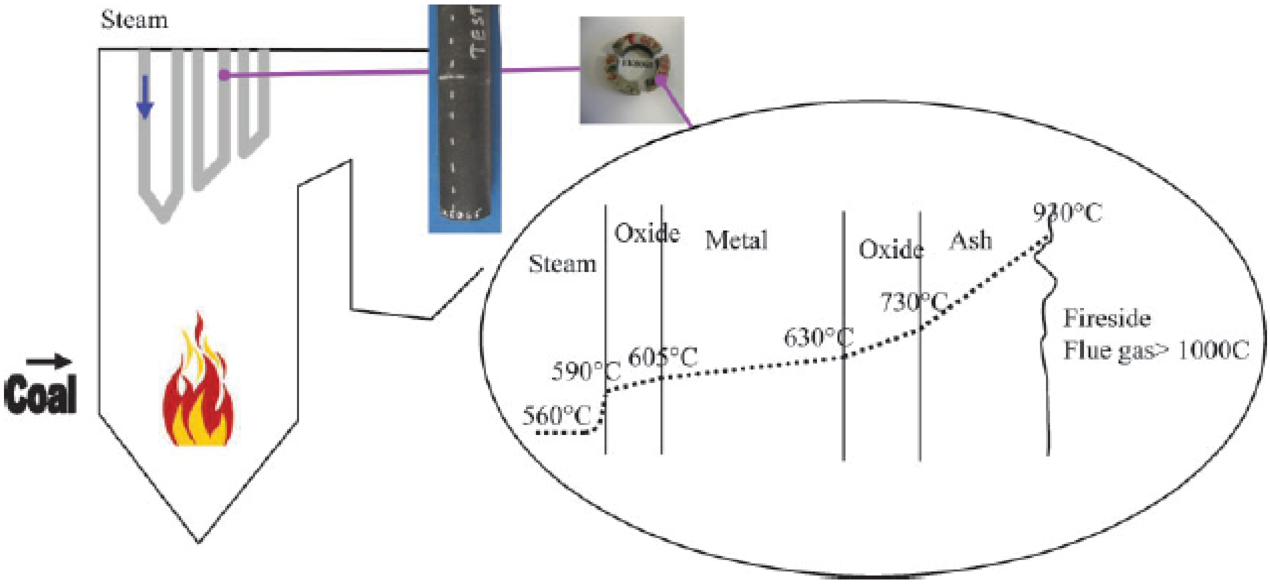
3.4.2.4 Comparison Esbjerg (256 bar) and Masnedø (91 bar)

The inner oxide thickness at 91 bar increases with temperature and time within the temperature range of 455 to 525°C. However, in the temperature range from 500-600°C for 91 and 256 bar, neither temperature increase or longer exposure times significantly increases the inner oxide thickness. Above 610°C, there is a decrease in inner oxide thickness, presumably due to increased grain boundary diffusion of chromium , resulting in a a better chromium rich healing layer and therefore lower oxidation rates. Thus the steam oxidation resistance of TP 347H FG is more suited to higher temperatures and pressures, and could give unacceptable oxidation rates at lower temperatures and pressures, [20] [22].

3.4.2.5 Avedøre 1 and Amager 3

To obtain long term steam oxidation data for the 9–12%Cr ferritic steels, test tube sections have been exposed in Amager 3 and Avedøre 1, coal fired power plants in Denmark. Thus direct comparisons can be made for T91 and T92 for the 9%Cr steels and X20CrMoV121 and HCM12 for the 12%Cr steels. [21]

The specimens have been welded into existing superheaters at Amager Unit 3 and Avedøre Unit 1. The sections investigated were located in the plant as shown in Figure 26 in a testing region 3-5 m long, close to the outlet of superheater 4. They were located at different levels in the superheater tube, and thus were exposed to varying steam temperatures in the region of 555–568°C. Exposure has been conducted over a ten year period (1994–2005).



Figur 26. Schematisk bild över placeringen av testslingorna in Avedøre och Amager. Temperaturerna är generella och visar den relativa temperaturökningen genom en överhettartub. [21]

Figure 26 Schematic showing specimens taken from Avedøre and Amager. Temperatures are arbitrary showing relative increase in temperature through superheater tube [21]

The elemental specifications of the steels are given in Table 18. Compared to the older steel types, T92 and HCM12 utilise tungsten to improve their creep strength.

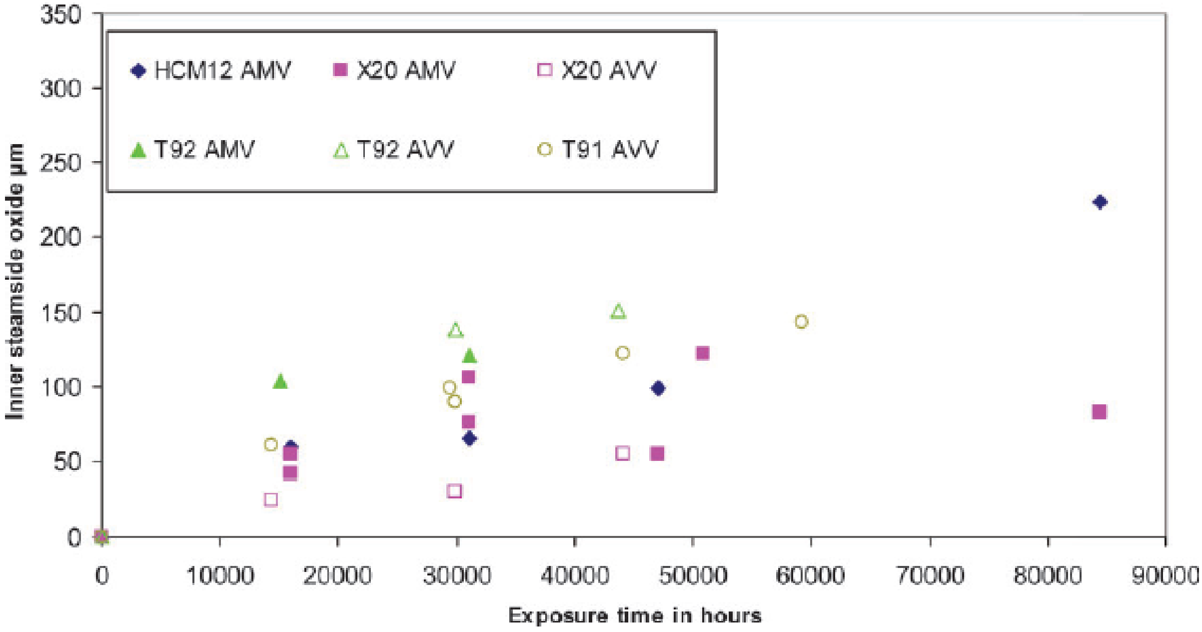
Tabell 18. Specifikationer för de undersökta legeringarna [21]

Table 18. Specifications of alloys investigated [21]

	C	Si	Mn	Cr	Mo	Ni	V	Nb	Others
T91	0·08–0·12	0·20–0·50	0·30–0·60	8·00–9·50	0·85–1·05	≤0·40	0·18–0·25	0·06–0·10	N 0·03–0·07, Al ≤0·040
T92	≤0·15	≤0·50	≤1·00	8·5–9·5	0·30–0·60	≤0·40	0·10–0·30	≤0·10	N 0·03–0·07, W 1·5–2·0, B 0·001–0·006
X20CrMoV121	0·17–0·23	≤0·5	≤1·0	10·0–12·5	0·8–1·2	0·3–0·8	0·25–0·35	–	–
HCM12	≤0·14	≤0·50	0·30–0·70	11·0–13·0	0·8–1·2	–	0·20–0·30	≤0·20	W 0·80–1·2

From Avedøre 1 testing, T91 and T92 can be compared for exposure times up to ~48 000 h. From Amager 3, X20, HCM12 and T92 were tested; T92 has been exposed for up to 31 000 h and X20 and HCM12 have had 84 500 h exposure. Tube sections were removed for various exposure durations such that steamside oxidation could be investigated with respect to exposure time. The growth of steamside oxide was assessed by inner oxide thickness. The microstructure and chromium content of the corroded layers has been investigated using light optical and scanning electron microscopy. HCM12 revealed high oxidation rates after the longest exposure time.

The average inner oxide thickness measurements are shown in Figure 27. With respect to the 9%Cr steels, it can be seen that T92 had the highest oxidation rate, compared to T91. For the 12%Cr steels, there is a marked difference for X20 exposed at Amager and Avedøre, where Avedøre has a lower oxidation rate. Reasons for this should be further investigated, and could be variations of alloy composition, variations in temperature, or variation in steam composition. In the first 45 000 h, HCM12 has similar oxidation rates to X20, however the final exposure of 84 500 h shows a marked difference in oxidation rates.



Figur 27. Medeltjocklek för inre ångsidig oxid mot exponeringstid, ångtemp. 555-568°C [21]

Figure 27 Average inner steamside oxide with respect to time, steam temperature 555-568°C *[21]*

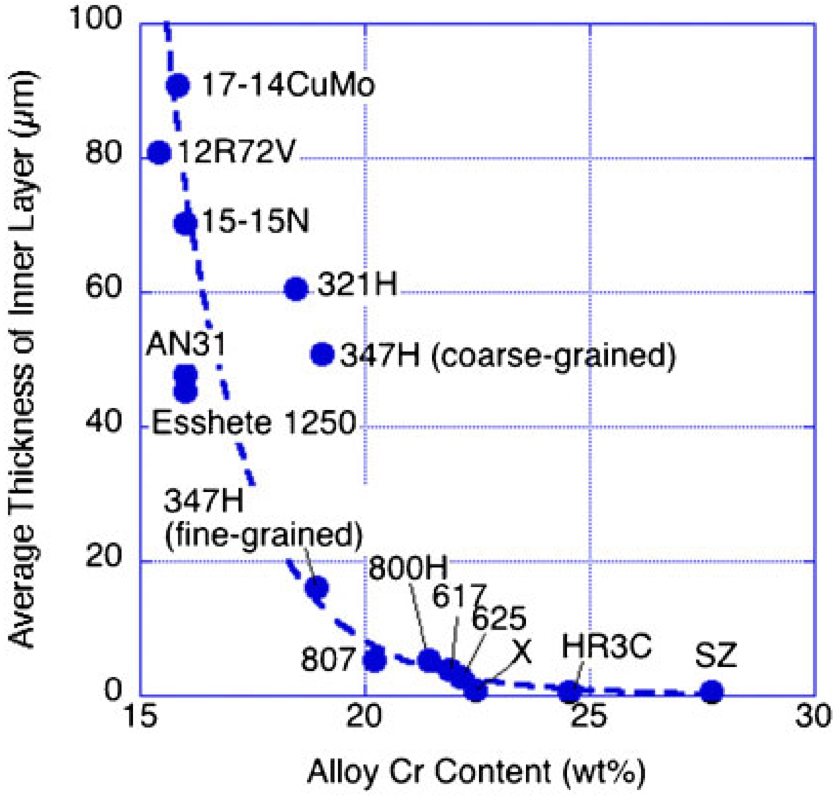
3.4.2.6 Effect of steam pressure

Some studies have shown that an increase in steam pressure leads to an increase in oxide thickness, [29]. On studies of T22 (10CrMo910) the oxide thickness increased by 50% when the pressure was increased from 19 bar to 121 bar, but other studies have shown smaller increases and it seems likely that the effect of pressure is low, [29].

3.4.2.7 Ways of reducing steam-side oxidation

An increase in chromium content of the alloy leads to a decrease in the thickness of the steam-side oxide layer, (see Figur 28). Cold working of the inner surface through shot peening, on alloys with lower chromium contents also reduces the steam-side oxidation via enhanced Cr-diffusion to the alloy surface which results in the formation of a protective Cr-rich oxide layer, [29]. The same effect, (enhanced diffusion) is seen in fine-grained alloys, [29], [30]. However, for steam temperatures greater than 580°C the VGB recommends that even TP 347 HFG be shot- peened, producing deformation to a depth of

70µm, [43]. Alloys with higher chromium contents, (20 wt% or more), do not need shot-peening.



Figur 28. Inre oxidtjocklek som function av Cr-halt i legeringen, vid 700ºC och 100 timmar,[29]

Figure 28 Inner steamside oxide as a function of Cr-content in the alloy after 100 hours at 700ºC, [29].

Tube blockages, caused by exfoliation of oxide layers on austenitic steels was found to occur when the magnetite thickness was between 100 and 150µm, [30], but a finer grain size and a higher Cr content can inhibit this. Exfoliation occurred in coarse grained TP 347 H in Esbjergvaerket after 45,000 hours service at 250bar/560ºC, when the oxide layer was 150µm thick. However, it also occurred in the same material at Skaerbackvaerket after only 8000 hours at 290bar/580ºC, because of thermal shock. The oxide was only 20µm thick in this case, [30]. In fine-grained steels it was found that the oxidation rate was unaffected by higher temperatures or even reduced at metal temperatures up to 620ºC, [30].

It seems well accepted that steam-side oxidation can be minimised by increasing the Cr-content, a reducing the grain size or increasing the surface deformation.

4 Discussion

4.1 Furnace walls

Corrosion by chloride attack is the predominant mechanism for furnace walls because of their relatively low temperature. From thermodynamic calculations it was found that the composition of the deposits on waterwalls will probably not be affected by the increase in material temperature. Major corrosive constituents, KCl, NaCl and NaSO4, will remain constant, however it is important that these calculations are verified by experimental data.

Reducing conditions can locally increase the corrosion rate and in fluidised bed boilers erosion is also a problem. The combination of erosion and corrosion, so-called "erosion-corrosion" leads to an increased corrosion rate because the protective oxide layer is removed or becomes cracked allowing an accelerated ingress of corrosive species, [39]. Most work has been performed in the temperature region of 550°C or higher and not specifically on furnace walls, [39].

Corrosion tests in a waste fired boiler showed that even a small increase in material temperature can lead to an increase in corrosion rate. This is especially true for low alloyed materials that are operating close to their corrosion limits which can have a dramatic increase in corrosion rate. The temperatures used in the test were 300°C and 338°C, but it is reasonable to assume that the same trend will be seen at higher temperatures in a boiler with less aggressive fuel, such as bio fuel, [27].

The use of additives or co-firing with corrosion reducing fuels, such as peat or sludge, to reduce waterwall corrosion has not been tried to any large extent. This should, however, be a method worth trying. Some of the additives used for corrosion reduction of superheaters could be worth testing also in the furnace. One must bear in mind, though, that the flue gas temperature in the furnace is much higher there than near the superheaters, and additives that work well to reduce the amount of chlorides near the superheaters might not work at all in the furnace.

Nickel-base alloys either in the form of compound tubes or welded or thermally sprayed coatings have been successfully used to reduce corrosion at pressures less than 140 bar. The coatings are sprayed on to plain carbon or low-alloyed steels, which would otherwise show excessive corrosion. There are many different methods for thermal spraying with a large variation both in price and in quality of the coating. There are also a very large number of alloys to be used for coating. This means that it can be difficult to find the optimum coating for a specific plant. However, thermal spraying a mixture of ceramic constituents and the Ni-based Alloy 625 showed promising results. Nickel-base alloys do suffer from pitting , whereas stainless steels showed more uniform corrosion. In some circumstances where corrosion in not too severe stainless steels like Sanicro 28 can be a good economic alternative to the more expensive Ni-base alloys like Sanicro 63. None of these systems have been tested at pressures higher than 140 bar, [6].

Compared to the amount of work performed on superheaters, only a small amount of work has been performed on furnace walls. A thorough investigation is needed to find out what types of coatings are most suitable for different fuels and types of boilers and a better understanding of the corrosion process and the effect of temperature, environment and alloy composition is needed.

4.2 Superheaters

Materials used for superheaters have to fulfil three demands, high enough corrosion resistance on the flue gas side, high enough creep strength and good steam side oxidation properties, at the material temperature in question.

Fireside corrosion of superheaters in biomass-fired boilers is mainly caused by chlorine, but at higher temperatures sulphur induced corrosion can become important.

At higher steam temperatures creep strength becomes important. Design values are the yield strength of the material or the stress which causes creep failure after 100,000 h (whichever is the lower). For normal superheater tube dimensions a pressure of 200 bar would require a creep strength of about 85 MPa (this includes a safety factor of 1.5). Fortunately alloys with higher nickel and chromium contents, like austenitic stainless steels and nickel-base alloys, have a higher creep strength than ferritic/martensitic materials and the highest creep strength is achieved for nickel base materials.

The stress required to cause creep failure at 10^5 h should be 85 MPa or higher at the required metal temperature. This is normally taken to be the steam temperature plus 35ºC for superheaters in the convective pass or the steam temperature plus 80ºC for superheaters in the sand loop seal, [40]. It may be difficult to find materials of the right strength for use in the loop seal.

Several additives have been tested for the reduction of superheater corrosion. Plant tests at Enstedsverket, [26], showed that sulphur based, Si/Al based and calcium phosphate based additives had similar effects in the reduction of the amount of Cl in the deposits. (Corrosion was not actually measured though). The cheapest additives to use are waste products like sewage sludge or fly ash from coal-firing. Sulphur-based additives are the next cheapest. If the plant has NOx reduction by SNCR using ammonia, this can be replaced by ammonium sulphate with a similar consumable cost for the same NOx reduction effect.

Most corrosion test results are from probes, but a TP 347 H steam loop for 585°C steam was built at the Masnedø straw-fired plant and a loop containing several materials was built in Nyköping, raising the final steam temperature to 600°C, [16], [17].

Results from probe tests performed over the years show a considerable scatter in results, but generally, austenitic steels performed much better than ferritic/martensitic steels. Probe testing probably overestimates the corrosion rate, but it is not known by how much. In the Nässjö wood-fired boiler at 600°C material temperature, austenitic steels containing 15-18% Cr performed much better than 2-12% ferritic/martensitic steels and marginally better than high Cr/Ni alloys. In the corrosion test in the same boiler with material temperature 650°C, X20, an 11% Cr martensitic steel, actually performed better than the high Cr/Ni alloys 800 HT and HR3C. However, the strength of X20 is too low to make it a candidate for high steam temperatures. The best result in both tests was obtained for the 15% Cr austenitic material Esshete 1250.

In the Jordbro biofuelled boiler at material temperature 650°C, the best result was obtained for HR3C. X20 had the highest corrosion rate, but the difference between this material and the austenitic 17% Cr material TP 321or the high Cr/Ni material 800H was not very large. In this test no clear correlation between material composition and corrosion rate can be seen.

In Nyköping firing a mixture of wood, waste wood and packaging waste the alloys with the best fireside corrosion resistance at 500°C steam were Haynes 230, HR11N, AC 66 and HR3C followed by Esshete 1250 and TP347HFG. The corrosion rate of X20 was unacceptably high and this material is totally unsuitable for this fuel mix. At 600°C Haynes 230 showed the lowest corrosion rates, followed by TP 347H FG, HR3C/AC66, and Esshete 1250. Large amounts of internal corrosion were seen.

In all tests performed in the convective pass a large amount of internal (or selective) corrosion has been observed for many steels. If corrosion is being monitored by ultra-sonic testing or other wall thickness measurements, the amount of internal corrosion will not be seen and the total corrosion will be underestimated. It is not known if the internal corrosion zone grows continuously during exposure or if it reaches a steady-state maximum depth beow the oxide scale. It is clears though that as steam temperatures increase in biomasss and waste-fired plant and more highly alloyed materials are used, that the “unseen” internal corrosion will need to be taken into consideration.

Corrosion depends on the metal (or steam) temperature, but also on the flue gas temperature. Corrosion is higher if the flue gas temperature is higher and if the superheater is exposed to the flue gas stream or the effects of a soot-blower.

Positioning of the final superheater in the sand loop seal of a CFB boiler reduces corrosion. The water vapour content is much lower here than in the convective passes and some fluidisation of the sand means that the oxygen levels are higher. Another advantage to be gained by placing the superheaters in the loop seal, in addition to reduced corrosion, is that the superheater can be considerably smaller in size (about a third of the size of a conventional superheater) since the heat transfer per unit area of tube surface is more intensive in the loop seal. This leads to savings in material and labour costs. The result of this, and a possible disadvantage, is that the superheater wall temperature will be higher in the loop seal, for the same steam temperature. For superheaters heated by flue gas (but shielded from radiation from the furnace) the temperature difference between the steam and the tube wall, ΔT, is typically assumed to be 50°C. If a superheater is heated by sand, then ΔT can be in the range 70-100°C. This means that a steel with a superior creep strength is needed.

The corrosion rates may not always increase with increasing steam temperature. The decrease in corrosion rates at higher temperatures can be explained on the basis of decreasing Cl levels in the deposits with increasing temperature and increasing diffusion allowing a protective Cr-rich oxide to be formed more effectively.

Steam-side oxidation of austenitic materials at higher steam temperatures leads to the formation of an outer and an inner oxide layer. The outer oxide layer mainly consists of magnetite and the inner layer mainly consists of spinel. The interface between the two types of oxide coincides with the original metal surface. Due to the higher chromium content, the thicknesses of the oxides are lower than those for the ferritic/martensitic steels with only 9-12 % Cr, (and these steels do not have sufficient fireside corrosion resistance).

Steam-side oxidation has been investigated at higher steam temperatures of 600°C. Alloys with the highest Ni and Cr contents, like Haynes 230, AC 66 and HR11 N showed negligible steam-side oxidation after 5500 hours. The long-term steam-side oxidation of TP 347 H FG has been evaluated at several temperatures. It was found that the oxide was thinner at 610°C than at lower steam temperatures of 450-525°C, presumably due to increased grain boundary diffusion of chromium.

Steam-side oxidation can be reduced by cold working (eg. Shot peening), using an alloy with a fine grain size (eg. TP 347 HFG) or a higher chromium content. For steam temperatures greater than 580°C the VGB recommends that even TP 347 HFG be shot-peened, producing deformation to a depth of 70µm, [43].

HR3C, AC 66 and TP 347 H FG are all suitable candidate alloys for superheaters with 580-600°C steam in a wood-based biomass-fired boiler and should be evaluated further. TP 347 H FG exhibited the lowest corrosion rate of about 15 µm per 1000 h or about 0.11mm per operating year (7500 h), [17]. AC 66 and HR3C showed higher rates of about 25µm per 1000 h or 0.19 mm per operating year. Other austenitic stainless steels, with adequate creep strength should be identified for evaluation.

At a steam temperature of 570°C in a straw-fired plant TP 347 corroded at a rate of 1.0 mm (1000 µm) per 1000 h. More materials need to be evaluated for testing in straw-fired plant.

5 Conclusions

Furnace walls suffer from chloride corrosion, especially in areas of reducing conditions and erosion is also a problem in fluidised bed boilers. Nickel-based coatings mixed with a ceramic component and applied by thermal spraying have been successful in reducing corrosion in some cases. However in some boilers Ni-alloys like IN 623/SAN 65 are subject to severe pitting whereas superaustenitic alloys like SAN 28 show more uniform corrosion. Most data is obtained from boilers with low pressures and there is a lack of information from pressures greater than 140 bar. Additives have not been investigated for use with furnace corrosion. Generally, not much research has been carried out into furnace corrosion, compared with superheater corrosion.

Fireside corrosion of superheaters in biomass-fired boilers is mainly caused by chlorine, but at higher temperatures sulphur induced corrosion can become important.

The stress required to cause creep failure at 10^5 h should be 85 MPa or higher at the required metal temperature. This is normally taken to be the steam temperature plus 35ºC for superheaters in the convective pass or the steam temperature plus 80ºC for superheaters in the sand loop seal. It may be difficult to find materials of the right strength for use in the loop seal.

Additives have been used to reduce corrosion of superheaters but no additives have been tested with steam temperatures higher than 560ºC.

Corrosion is reduced by placing the final superheater in the sand loop seal of a circulating fluidised bed boiler. However, creep strength considerations become more important here.

HR3C, AC 66 and TP 347 HFG have been tested in a high temperature steam loop. They are all suitable candidate alloys for superheaters with 580-600°C steam in biomass-fired boiler and should be evaluated further. They have suitable creep strength, fireside corrosion and steam-side corrosion rates. TP 347 HFG needs to be shot-peened on the inside.

Ferritic-Martensitic steels are not suitable for 580-600°C steam in biomass-fired boilers because of their high fireside corrosion rates.

In straw-fired boilers no materials have yet been identified as being suitable for use with 580-600°C steam.

6 Recommendations for future work

- More investigations in to furnace walls to find out what types of coatings are most suitable for different fuels and types of boilers
- Gaining a better understanding of the furnace wall corrosion process and the effect of temperature, environment and alloy composition.
- Furnace wall tests at higher pressures/temperatures
- Long-term testing of a superheater loop in the convective pass with 600˚C steam in a wood-fired boiler
- Evaluation of superheaters in the sand loop seal with 600˚C steam in a wood-fired boiler
- Identification and testing of materials for use with 580-600˚C steam in a straw-fired boiler

Acknowledgements

We are grateful for the information provided by our colleague Melanie Montgomery and for the input from the Värmeforsk reference group, especially Juha Sarkki.

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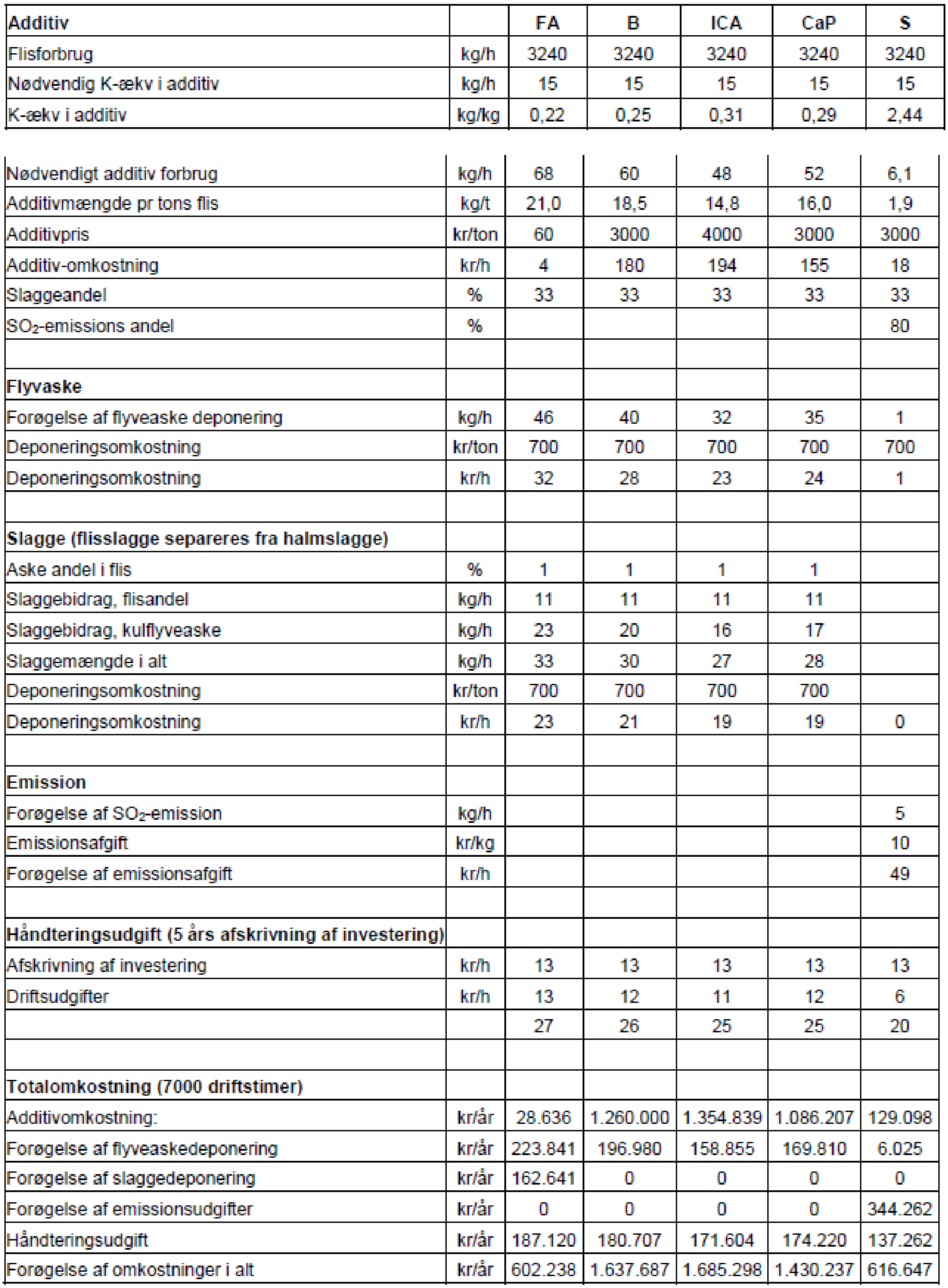
Appendix

A Economic evaluation of additive tests at Enstedsvaerket



Additiv		**FA**	**B**	**ICA**	**CaP**	**S**
Flisforbrug	kg/h	3240	3240	3240	3240	3240
Nødvendig K-ækv i additiv	kg/h	15	15	15	15	15
K-ækv i additiv	kg/kg	0,22	0,25	0,31	0,29	2,44
Nødvendigt additiv forbrug	kg/h	68	60	48	52	6,1
Additivmængde pr tons flis	kg/t	21,0	18,5	14,8	16,0	1,9
Additivpris	kr/ton	60	3000	4000	3000	3000
Additiv-omkostning	kr/h	4	180	194	155	18
Slaggeandel	%	33	33	33	33	33
SO_2-emissions andel	%					80
Flyvaske						
Forøgelse af flyveaske deponering	kg/h	46	40	32	35	1
Deponeringsomkostning	kr/ton	700	700	700	700	700
Deponeringsomkostning	kr/h	32	28	23	24	1
Slagge (flisslagge separeres fra halmslagge)						
Aske andel i flis	%	1	1	1	1	
Slaggebidrag, flisandel	kg/h	11	11	11	11	
Slaggebidrag, kulflyveaske	kg/h	23	20	16	17	
Slaggemængde i alt	kg/h	33	30	27	28	
Deponeringsomkostning	kr/ton	700	700	700	700	
Deponeringsomkostning	kr/h	23	21	19	19	0
Emission						
Forøgelse af SO_2-emission	kg/h					5
Emissionsafgift	kr/kg					10
Forøgelse af emissionsafgift	kr/h					49
Håndteringsudgift (5 års afskrivning af investering)						
Afskrivning af investering	kr/h	13	13	13	13	13
Driftsudgifter	kr/h	13	12	11	12	6
		27	26	25	25	20
Totalomkostning (7000 driftstimer)						
Additivomkostning:	kr/år	28.636	1.260.000	1.354.839	1.086.207	129.098
Forøgelse af flyveaskedeponering	kr/år	223.841	196.980	158.855	169.810	6.025
Forøgelse af slaggedeponering	kr/år	162.641	0	0	0	0
Forøgelse af emissionsudgifter	kr/år	0	0	0	0	344.262
Håndteringsudgift	kr/år	187.120	180.707	171.604	174.220	137.262
Forøgelse af omkostninger i alt	kr/år	602.238	1.637.687	1.685.298	1.430.237	616.647

Tabel 8.1 *Økonomi ved dosering af forskellige additiver. FA er kulflyveaske, B er bentonit, ICA er ICA 5000, CaP er calciummonofosfat og S er rent svovl.*

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