KME

CONSORTIUM MATERIALS TECHNOLOGY for demonstration and development of thermal energy processes

Furnace wall corrosion in biomass-fired boilers at higher steam temperatures and pressures

Pamela Henderson, Yousef Alipour,
Mattias Mattsson, Annika Stålenheim,
Christer Forsberg, Carl Nordenskjöld,
Jesper Ejenstam, Peter Szakalos,
Michal Glazer, Sonja Enestam, Paul Cho,
Anders Hjörnhede, Annika Talus, Rikard Norling,
Colin Davis and Anna Jonasson

KME-508/515

Furnace wall corrosion in biomass-fired boilers at higher steam temperatures and pressures

Pamela Henderson, Yousef Alipour,
Mattias Mattsson, Annika Stålenheim,
Christer Forsberg, Carl Nordenskjöld,
Jesper Ejenstam, Peter Szakalos,
Michal Glazer, Sonja Enestam, Paul Cho,
Anders Hjörnhede, Annika Talus, Rikard Norling,
Colin Davis and Anna Jonasson

KME-508/515

Preface

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

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

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

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

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

Abstract

It was found that furnace wall corrosion in recycled wood fired boilers can be reduced by coating the walls with the Ni-base alloy IN 625. Stainless steel coatings also worked well and an Fe-Cr-Al alloy showed potential. Overlay weld coatings had better adherence than thermally sprayed coatings. The use of treated sewage sludge changed the composition of the deposits and reduced corrosion during short-term testing.

Sammanfattning

Större användning av bränslen av låg kvalitet som t.ex. returträ (rivningsvirke), i kombination med kraven på minskade utsläpp av kväveoxider, gör det mycket svårt att undvika korrosion i reducerande miljöer vid eldstadsväggarna (vattenväggar). Returträ har ett högt innehåll av alkalimetaller och klor, samt tungmetaller som bly och zink, vilket ökar risken för korrosion. Därför är eldstadskorrosion redan ett stort problem i kraftvärmeanläggningar som eldar returträ, särskilt vid höga ångtryck som 140 bar. Korrosionshastigheter på upp till 1,5 mm per år har uppmätts på låglegerat stål eldstadsväggar, vilket ger en livslängd på bara 3 år, om inga åtgärder vidtas. En ny eldstadsvägg för en 100MWth panna kan kosta 20 miljoner kronor.

Försök inom korrosionsforskning utförs till största delen i laboratoriemiljö under simulerade pannförhållanden, men för att generera resultat som kan implementeras i pannanläggningar krävs att dessa försök kompletteras med försök i verkliga pannor. Det finns behov av långsiktig korrosionsprovning vid eldstadsväggar på olika materialbeläggningar vid olika temperaturer. Användning av additiv och andra metoder för att minska väggkorrosion bör övervägas. Dessa behov har tagits upp i detta projekt, som har som mål att ge rekommendationer om hur man undviker eldstadkorrosion i pannor vid hög elektrisk verkningsgrad / höga ångdata.

Målgruppen för denna forskning omfattar kraftproducenter, panntillverkare och materialleverantörer och det är denna konstellation, tillsammans med institut och ett universitet som har genomfört projektet.

Resultaten visade att om man ytbelägger eldstadstuber av låglegerat stål (16Mo3) med en nickelbaserad legering (Alloy 625) så minskas drastiskt korrosionshastigheten. En FeCrAl- (Kanthal - APMT) legering som innehåller 21% Cr visade också låga korrosionshastigheter. Denna legering visade försprödning i driftstemperaturområdet, 400-500°C, men FeCrAl-legeringar med cirka 10% Cr var inte spröda och bör utvärderas i framtiden. Austenitiska rostfria stål såsom TP310, San 28, 153 MA och 253MA visade måttliga korrosionshastigheter och kan vara ett alternativ till Ni-baserade legeringar för att skydda eldstadsväggar.

Metoden för att applicera ytbeläggningen visade sig vara viktigt. Vanligtvis hade de termiskt sprutade ytbeläggningarna sämre vidhäftning än de svetsade ytbeläggningarna.

Rör och sondprover belagda med nickelbaslegering attackerades av en kombination av kalium och bly vilket ledde till bildandet av icke-skyddande kaliumblykromat. Rör och sondprover av låglegerat stål korroderade av Cl-angrepp. De preliminära resultaten från undersökning av FIB-producerade tvärsnitt visade att järnklorid bildas som ett separat lager under oxiden och oxi-klorider upptäcktes inte. Korrosionshastigheten för 16Mo3 var temperaturberoende.

Thermocalcmodelleringen visade att HCl (g) gynnas framför Cl_2 (g) som korrosiv species. Även FeCrAl-legeringen (Kanthal) attackerades av klorider, även om denna legering uppvisade mycket låga korrosionshastigheter. Rostfritt stål angreps av en kombination av klorider och kalium-bly.

Preliminära resultat från användning av rötat avloppsslam som blandades med returträet visar att halterna av Pb, K, Na och Cl minskades i avlagringarna på eldstadsväggen. Detta ledde till en minskning av korrosionshastigheten under korttidstester, förhindrade bildandet av kaliumblykromat i Alloy 625 så att det skyddande kromoxidskiktet bibehölls. Avloppsslam kan vara ett användbart sätt att minska korrosion och bör utredas ytterligare.

Termodynamisk modellering med HSC-chemistry av faser som förväntas i rökgaserna och jämförelse med SteaMax (baserad på FACTData) visade att reducerande miljöer simulerades på ett liknande sätt av de båda beräkningsverktygen. Resultaten stämde i stort sett överens med sammansättningen av de avlagringar som samlats in från väggarna i Idbäcken pannan.

Inledande försök med GD-OES och FIB-instrument visade att dessa var användbara för att framställa eller analysera korrosionsfronten och dessa bör användas mer i framtiden.

Nyheter
från detta arbete inkluderar

- långtidssondprovning vid eldstadväggar i verkliga pannmiljöer,
- utvärdering av FeCrAl -legeringar för användning på eldstadsväggar,
- identifiering av kalium och bly i kombination som delaktig i korrosionsprocessen för Ni –legeringar
- användning av rötat avloppsslam som additiv, vilket förhindrade att kromoxid angrips av kalium och bly och som resulterade i en reduktion av korrosionshastigheten
- visar att HCl (g) gynnas framför Cl_2 (g) som de korrosiv art för järnbaserade legeringar
- användning av FIB och GD-OES instrument på prover som exponerats i pannor

Resultaten från detta projekt kan användas av kraftindustrin för att minska eldstadskorrosion. Till exempel har eldstaden i Idbäcken påsvetsats med Alloy 625.

Målet med projektet var att ge rekommendationer om hur man undviker eldstadskorrosion i pannor vid hög elektrisk verkningsgrad / höga ångdata, vilket har uppfyllts.

Nyckelord: returträ, korrosion, eldstadsväggar, stål, Ni-baserade legeringar

Summary

Wider use of low quality fuels like waste wood (demolition wood), in combination with the requirements of reduced NOx emissions, makes it much more difficult to avoid corrosion in reducing atmospheres adjacent to the furnace walls (water walls). Waste wood has a high content of alkali metals and chlorine, as well as heavy metals like lead and zinc, which increases the risk for corrosion. As a result, furnace wall corrosion is already a major problem in combined heat and power plant burning waste wood, especially at high steam pressures like 140 bar. Corrosion rates of up to 1.5 mm a year have been measured on low-alloy steel furnace walls giving a lifetime of only 3 years if no action is taken. A new furnace wall for a 100MWth boiler can cost SEK 20 million.

Most corrosion research is performed in the laboratory under simulated boiler conditions, but there is also a need to perform corrosion and deposit tests in real boilers. There is a need for long-term corrosion tests at the furnace walls on different material coatings at different temperatures. The use of additives and other methods for reducing wall corrosion should be considered. These needs have been addressed in the present project which has the goal to give recommendations regarding how to avoid water wall corrosion at high boiler electrical efficiency/ steam data.

The target group for this research includes power producers, boiler manufacturers and material suppliers and it is this constellation, together with institutes and a university that have performed the project.

The results showed that coating the low alloy steel (16Mo3) furnace wall tubes with a nickel base alloy (Alloy 625) drastically reduced the corrosion rate. An FeCrAl (Kanthal - APMT) alloy containing 21%Cr also showed low corrosion rates. This alloy was found to be susceptible to embrittlement in the temperature range of service, 400-500°C, but FeCrAl alloys with Cr contents of about 10% were not embrittled and should be evaluated in the future. Austenitic stainless steels like TP310, San 28, 153 MA and 253MA showed moderate corrosion rates and could be an alternative to Ni-base alloys for protecting furnace walls.

The method of applying the coating was found to be important. In general, the thermally sprayed coatings did not adhere as well as the weld overlay coatings.

The nickel alloy coated tubes and probe samples were attacked by a potassium-lead combination leading to the formation of non-protective potassium lead chromate. The low alloy steel tubes and probe samples corroded by Cl attack and K and Pb were not found at the corrosion front. Initial results from examination of a FIB –produced section showed that iron chloride formed as a distinct layer under the oxide and oxy-chlorides were not detected. The corrosion rate of 16Mo3 was highly temperature dependent.

The Kanthal FeCrAl alloy was also attacked by chlorides, although this alloy showed very low corrosion rates. Stainless steels were attacked by a combination of chlorides and potassium-lead.

Preliminary results from the use of digested sewage sludge which was mixed with the waste wood indicated that levels of Pb, K, Na and Cl were reduced

on the furnace wall deposits. This led to a reduction in the corrosion rate during short-term tests and suppressed the formation of potassium-lead chromate in Alloy 625 as the protective chromia layer was maintained. This sludge could be a useful means of reducing corrosion and should be further investigated.

Thermocalc modelling showed that HCl(g) is favoured over Cl_2(g) as the corrosive species. The initial work with Thermocalc showed that many of the phases formed by the corrosive environment could be predicted.

Thermodynamic modelling of phases expected in the flue gases using HSC-Chemistry and SteaMax (based on FACTData) showed that the reducing conditions cases were characterized in a similar way by both calculation tools. The results were in broad agreement with the composition of the deposits collected from the walls of the Idbäcken boiler.

Initial experiments with GD-OES and FIB- instruments showed that these were useful for preparing or analysing the corrosion front and should be used more in the future to facilitate more precise mechanistic studies.

The novel aspects from this work include :-

- the use of long-term testing of probes at the furnace wall in real boiler environments,
- evaluation of FeCrAl alloys for use on furnace walls,
- identification of potassium and lead in combination as participants in the corrosion process for Ni-base alloys
- the use of treated sewage sludge as an additive which prevented the attack of chromia by potassium and lead to form chromate, resulting in a reduction in the corrosion rate
- showing that HCl(g) is favoured over Cl_2(g) as the corrosive species for iron-based alloys
- use of FIB and GD-OES instruments on samples exposed in boilers

The results of this project can be utilised by the power industry to reduce furnace wall corrosion. For example, furnace walls have already been overlay welded with Alloy 625.

The goal of the project was to give recommendations on how to how to avoid water wall corrosion at high boiler electrical efficiency/ steam data, which has been fulfilled.

Keywords: waste wood, corrosion, furnace walls, steels, Ni-base alloys

Table of contents

1 Introduction

1.1 Background

The combustion of biomass and waste is making an increasing contribution to Sweden's energy production and reduces the dependence on non-renewable sources. To further increase the electricity generation there is a drive to increase steam temperatures and this is supported by the KME sub-programmes "Materials technology solutions for boilers" and "More efficient electricity production from renewable fuels".

In order to increase turbine efficiency, not only must the maximum steam temperature be raised, but also the steam pressure, which affects the water temperature in the waterwalls/furnace walls. Increasing the steam parameters from 140 bar/540°C to 190 bar/600°C/600°C (the goal for forest fuel) will mean that the outgoing steam temperature and pressure from the boiler will increase from 343°C/151 bar to 368°C/205 bar, an increase in temperature of 25°C. This is no dramatic change, but enough to increase the corrosion even further in the furnace region which already operates at its limits. For waste wood the pressure and temperature goals are somewhat lower and the testing conditions have been fixed to correspond to 140 bar (water temperature of 343°C or wall temperature of 400°C).

Water wall corrosion is already a major problem in CHP plant burning low quality wood fuels (like demolition wood) For example in Idbäcken, Nyköping, operating at 140 bar, the furnace walls were replaced in 2008 for the first time since the plant was built in 1994, but recent measurements showed that wall corrosion rates are now 1.5 mm a year which gives a lifetime of only 3 years if no action is taken.

The plant has been in operation since the end of 1994 and originally operated on a mixture of biomass and coal, but over the years the amount of coal has been reduced and the amount of waste wood increased. Since the summer of 2008, the plant operates on 100% waste wood. The waste wood is sourced from Sweden, Great Britain and Norway. This dramatic increase in corrosion rate has therefore coincided with an increase in the amount of waste wood in the fuel mix from 50% to nearly 100% (as the use of forest fuel has been reduced). A new furnace wall for a 100MWth BFB boiler like Idbäcken costs around 20 MSEK (2 MEuro).

Wider use of waste wood for fuel, in combination with the requirements of reduced NOx emissions, makes it much more difficult to avoid corrosion in reducing atmospheres adjacent to the furnace walls (water walls). Waste wood has a high content of alkali metals and chlorine, as well as heavy metals like lead and zinc, which increases the risk for corrosion.

Most corrosion research is performed in the laboratory under simulated boiler conditions. Therefore there is a need to also perform corrosion tests in real boilers. There is a need for deposit tests and long-term corrosion tests at the furnace walls on different material coatings at different temperatures. The use of additives and other methods for reducing wall corrosion should be

considered. Mechanisms of wall corrosion need to be further studied. These needs have been addressed in the present project and recommendations regarding how to avoid water wall corrosion at increased boiler electrical efficiency/increased steam data are presented.

1.2 Description of the research field

A part of the boiler which is subjected to a high corrosion risk is the furnace wall. The furnace wall, or so-called waterwall, is formed of tubes welded together, separated by a fin (see Fig. 1.2.1). The tubes contain pressured water before it separates into steam and are usually made of carbon steel or low alloy steel, due to the low price, low stress corrosion cracking risk, high heat transfer properties and low thermal expansion of this steel.

Fig 1.2.1. Photograph of part of a furnace wall before being installed in a boiler.

However carbon steels corrode rapidly when burning waste in a low NOx environment (i.e. an environment with low oxygen levels to limit the formation of NOx) [7]. Waste wood is a more corrosive fuel than forest fuel. Waste wood, (also known as recycled wood), consists of by-products from consumption, the major sources being demolition and construction of buildings. Waste wood often contains traces of paint or plastics which gives rise to an increase in the amount of chlorine, zinc and lead in the fuel and increases the corrosion risk to the boiler components. A comparison of waste wood, forest fuel and coal is given in Table 1.2.1

It is known that co-firing wood fuel with a small amount of coal decreases the corrosion rate [8,9]. The removal of coal from the fuel mix in the power plant contributed to an increase in the corrosion rate. The switch from forest residues to waste wood increased the problem further adding approximately 5

Euro /MWh to maintenance costs at the plant in Nyköping. However, waste wood is approximately half the price of forest residues, about 10 Euro/MWh as opposed to 20 Euro/MWh for forest residues, and so the overall costs are reduced.

Table 1.2.1 Mean values of key elements in forest residues and waste wood and coal (demolition wood) and the spread in waste wood analyses. From 16 analyses of forest residues and 12 analyses of waste wood. Data reproduced from information in [10].

Parameter	Waste wood	Waste wood (Min-Max)	Forest wood	Coal
Total moisture (W%)	23	11-39	48	3
Total ash (W% dry)	5.8	3.2-15	2.7	10.3
C (W% dry ash-free)	52	50-56	53.1	75.5
N (W% dry ash-free)	1.2	0.12-1.5	0.31	1.2
S (W% dry ash-free)	0.08	0.04-0.3	0.04	3.1
Cl (W% dry ash-free)	0.06	0.04-0.22	0.02	trace
K (W% in ash)	2.0	1.0-2.6	7.6	0.06
Na (W% in ash)	1.4	0.6-1.9	0.86	0.027
Zn (mg/kg in ash)	10393	2420-184167	2047	--
Pb (mg/kg in ash)	544	140-28611	63	--

Different types of corrosion attack are thought to occur in a waste wood-to-energy power plant. Chlorine/chloride corrosion is suggested to accelerate the corrosion rate; however, the exact attack mechanism is still a matter of debate [11]. A well-known explanation is the chlorine cycle (i.e. diffusion of chlorine molecules through a defect oxide) [12, 13]. However, hydrogen chloride (HCl) has been shown to be more thermodynamically stable than chlorine (Cl_2) under a deposit, and this is a smaller molecule than chlorine, which could more easily diffuse through a defect oxide [14]. The presence of low melting point chloride salts can also increase the corrosion rate [15, 16]. Alkali metals such as potassium, sodium and calcium have been found to react with protective chromia scale to form non-protective chromates [17,18].

Investigations into corrosion mechanisms have previously been performed in the laboratory under simplified simulated boiler conditions. However it is also important to perform tests in real environments to check the suitability of the laboratory tests.

1.3 Research task

Apart from recent studies by Värmeforsk on furnace wall corrosion, [1,2] most studies have focused on fireside corrosion of superheater tubes. There is little or no information available on the use of fuel additives or blends to reduce

corrosion and little information on deposit chemistry at the furnace walls and how it influences corrosion.

The traditional water wall materials – ferritic low alloyed steels – are not easy to replace because of their outstanding heat transfer properties, ability to form a protective oxide layer on the inside of the tubes and low thermal expansion. For this reason, corrosion protection generally involves the use of some kind of coating on the tubes, for example Inconel 625 or Sanicro 28, depending on the fuel and these seem to work well at lower steam temperatures, [1,2]. However, problems are observed at higher steam temperatures and pressures.

It has been found that ferritic FeCrAl alloys that form alumina have superior oxidation resistance compared with materials that form chromia even at temperatures as low as 300-600°C, [3,4]. These differences in corrosion properties are independent of the environment, but the mechanical properties, such as low temperature embrittlement and creep properties are worse for FeCrAl alloys, because of the formation of the Cr-rich alpha´ or sigma- phase, [4]. These materials, like APMT, can be used as coatings, but have real potential as a construction material for waterwalls, if the mechanical property limitations can be overcome. It is also noteworthy that the alloy APMT showed better corrosion resistance to KCl at the relatively low temperature of 600°C than both Sanicro 28 and TP 304L when compared in KME project 414, [33]. The APMT was not tested at temperatures below 600°C. The APMT also performed well in a waste-fired boiler.

In this project, ways of reducing furnace wall corrosion have been investigated. The wall deposit chemistry and furnace flue gases have been characterised to get a better understanding of the environment. Long-term corrosion tests of standard wall material have been performed at different temperatures. Long-term corrosion tests of different candidate coating materials have also been performed.

There is also a need to consider the use of additives. It has been suggested that a fuel additive, such as sewage sludge, can change the flue gas chemistry and deposit composition, and consequently reduce high temperature corrosion problems [6]. Short-term deposit and corrosion tests have been performed with sewage sludge. Mechanisms of wall corrosion also need to be further studied.

The FeCrAl alloy AMPT has been tested in the boiler wall and long-term aging experiments have been performed with FeCrAl alloys to find candidate materials that do not suffer from embrittlement at 400-500°C.

The use of modelling as a complement to experimental work has been investigated. Thermodynamic equilibrium modelling to predict the formation and condensation of Cl, S, K, Na, Zn and Pb compounds has been performed using the fuel composition as input. Thermodynamic equilibrium modelling of the phases formed by the corrosive environment has also been performed.

The use of new techniques to look at corroded samples has been investigated – in this case , sample preparation by FIB and GD-OES instruments.

1.4 Goal

The overriding goal is to give recommendations about how to avoid water wall corrosion at increased boiler electrical efficiency /increased steam data when burning biomass and waste wood mixes.

1.5 Project organisation

The project organisation is described below.

Vattenfall Research and Development (VRD) - Pamela Henderson, project manager. Mattias Mattsson, Annika Stålenheim, Michal Glazer. In-kind contribution 3 MSEK. Cash contribution 240kSEK (plus 181 kSEK cash in KME 515)

Tasks performed at VRD include :

- Overall project management, management of Vattenfall activities
- Supervision of Ph.D student,
- Plant testing - construction and provision of corrosion and deposit probes, provision of flue gas measuring equipment, long-term testing and short-term measurement campaigns in Idbäcksverket, Nyköping
- Analysis of plant/operationsal data. Corrosion measurements.
- Evaluation of HSC Chemistry programme to calculate chemical composition of compounds in the ash at different temperatures. Comparison to experimental results and results from Metso
- Delivery of final report to Elforsk

Vattenfall Nordic Heat (VNH) - Christer Forsberg, Calle Nordenskjöld, Seppo Simola. In-kind contribution 1.8 MSEK

- Boiler operation and provision of operational data. Testing support. Fuel and fly ash analyses
- Extra cost for different fuel mixes (e.g sewage sludge)
- Provision of coated test panels and wall material for evaluation
- Provision of deposits from furnace walls
- Provision of holes in furnace walls for corrosion probe, fuel gas measurement and impactor measurements

Valmet Power (formerly Metso Power) - Sonja Enestam, Paul Cho. In-kind contribution 500kSEK

- Thermodynamic equilibrium calculations using chemical composition of fuel to predict the formation and condensation of K, Na, Cl, Zn and Pb compounds at different temperatures. 4 fuel cases. Comparison with experimental results.

Sandvik Materials Technology - Mats Lundberg. In-kind contribution 360kSEK.

Sandvik Heating Technology - Johanna Nockert Olovsjö, Fernando Rave In-kind contribution 300kSEK.

Outokumpu Stainless - Rachel Pettersson, Fredrik Olsson. In-kind contribution 360kSEK.

Tasks performed by all material suppliers

- Provision of material for testing.
- Material competence and support

E.ON Sweden and UK - Anna Jonasson and Colin Davis. In-kind contribution 380 kSEK.

- Provision of deposits from various parts of the furnace walls of waste-wood fired boilers. Information on corrosion and tube failure investigation.

Researchers receiving financing and activities

KTH Division of Surface and Corrosion Science – Peter Szakalos (part time), Ph.D students Jesper Ejenstam (part-time) and Yousef Alipour (full-time). Budget 3630 kSEK

- Evaluation of FeCrAl alloys for wall construction and coatings. Long-term studies in furnace to verify alloys' good mechanical properties.
- Evaluation of FeCrAl alloys after exposure in power plant
- Metallographic analysis of furnace walls (deposits and corrosion) from different power plants and/or different parts of the furnace wall with known differences in corrosion tendencies. For example parts of a furnace wall with no, a small amount and large amount of corrosion.
- Evaluation of different alloys and coatings after testing in a boiler Evaluation of deposit chemistry and short-term corrosion results after additive tests in boiler
- Use of "ThermoCalc" thermodynamic equilibrium modelling on alloys in the corrosive environment

KIMAB – Rikard Norling, Ph.D students Peter Viklund (part-time until Sept 2012) and Annika Talus (part-time from Nov. 2012). Budget 950kSEK.

- Deposit analysis and initial corrosion of short-term probe specimens obtained at different temperatures, using GD-OES (Glow Discharge Optical emission Spectroscopy). Development of GD-OES technique.
- Using methods developed in KME project KME 504.

SP - Anders Hjörnhede. Budget 600kSEK

- Impactor measurements in furnace for particle size and chemical composition

Reference group. This consisted of the participants from the above mentioned companies/organisations and a representative from the High Temperature Corrosion Competence Centre at CTH, Gothenburg.

2 Experimental

2.1 Description of plants

2.1.1 Idbäcken Combined Heat and Power Plant , Nyköping

Most of the testing has been peformed in this plant. Situated some 120 km south of Stockholm, the Idbäcken CHP plant provides energy to the city of Nyköping. Nyköping has about 30 000 inhabitants and the Idbäcken plant provides half of its electricity requirements. It also supplies some 14000 households with district heating. The plant is owned and operated by Vattenfall AB and consists of a Bubbling Fluidised Bed (BFB) steam boiler (Boiler 3) for Combined Heat and Power (CHP) operation, two circulating Fluidised Bed (CFB) boilers for hot water production and a hot water accumulator. It has been in operation since the end of 1994.

Boiler 3, the CHP unit, originally operated on a mixture of biomass and coal. Over the years the amount of coal has been reduced and the amount of waste wood increased. Since the summer of 2008, the plant operates on 100% waste demolition wood.

The CHP unit produces 35 MW of electricity and 69 MW of heat. A flue-gas condensor yields 12 MW additional heat at full boiler load. The final steam temperature is 540°C and the pressure 140 bar.

The furnace walls are made of the low alloy steel 16Mo3, which have been progressively coated with the Ni-base alloy Alloy 625. Test-tubes, coated with a number of different alloys for evaluation, were welded into the furnace wall on the right hand-side (motorway side - seen from the front looking towards the back wall) as shown by the blue rectangle in Fig. 2.1.1. Holes for probe testing were made near the coated tubes on the right, where corrosion is considered to be moderate (known as position B) and also on the back wall in an area of high corrosion (position A).

The boiler runs at relatively low oxygen levels, 2-2.5%, but these can sometimes be as low as 1%. This is in order to increase efficiency and reduce NOx emissions (the Swedish NOx tariff is about 5 Euros per kg). These levels are measured after the superheaters. In some parts of the furnace, which uses staged combustion, oxygen levels of less than 0.5% have been measured. The control of the oxygen levels comes at a cost as it is believed that chlorine rich fuels cause more corrosion under reducing and low oxygen conditions, below 0.5%.

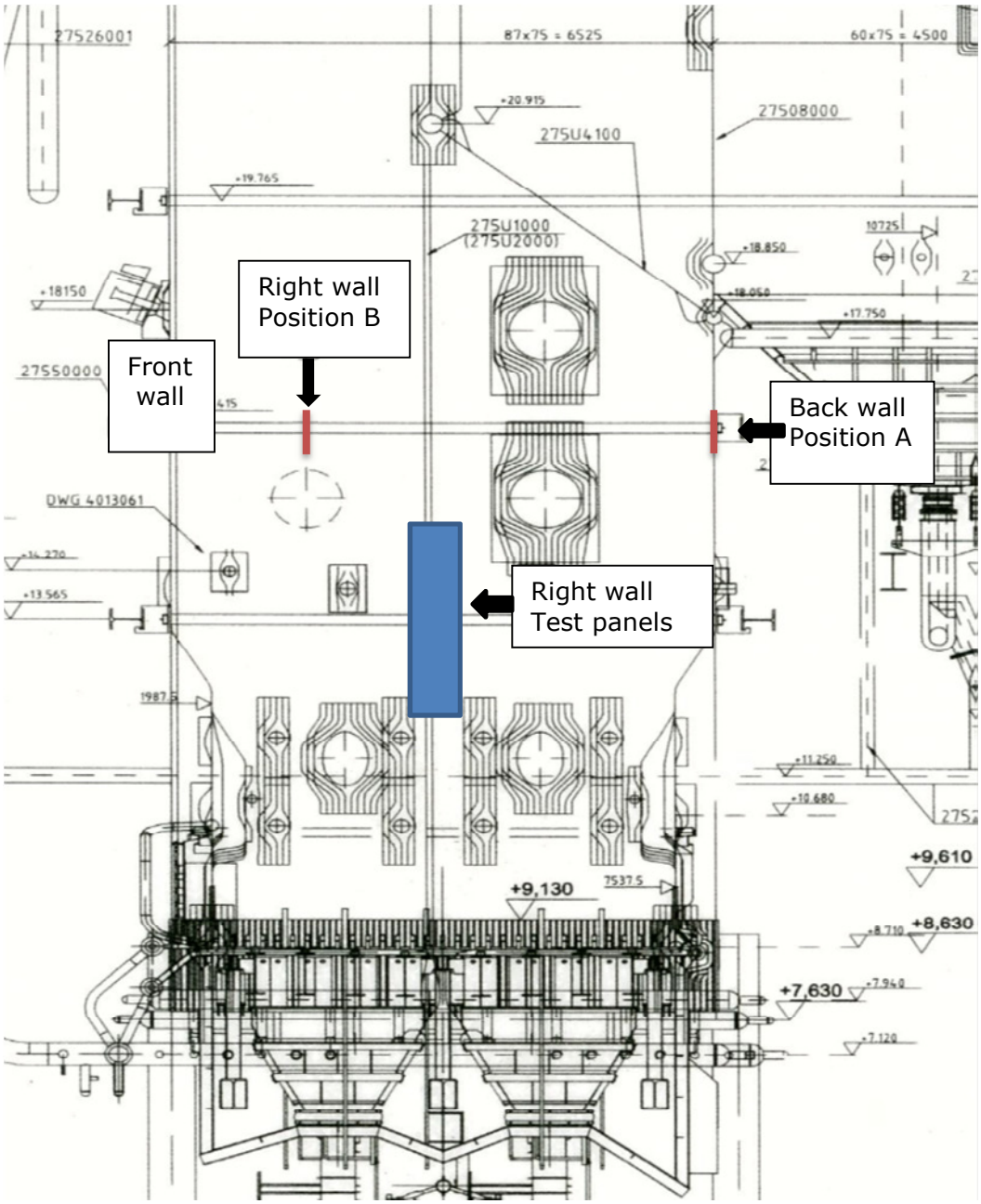


Fig. 2.1.1 **Schematic diagram showing a section through the Idbäcken boiler, viewed from the right wall. The right wall with the position of the test panels and probe postion B is shown at the front of the figure. The back wall is on the right.**

The average metal loss at the furnace walls was found to be 0.6 mm over a period of 9 years from start of operation in 1994 to 2003, i.e. a metal loss rate of 60-70 µm per year. In 2006 the average metal loss over the 12 year period since start was 1.5 mm, i.e. an increase in 0.9 mm over a three year

period. This is equivalent to a metal loss rate of 300 µm per year in the period 2003-2006.

The furnace walls were completely replaced in 2008 and the corrosion rate continues to be high when firing 100% waste wood at moderate to low oxygen levels. Locally, metal loss rates of 1.5 mm per year have been measured in the worst affected areas. With an operating time of 6500-7000 hours per year this amounts to a metal loss rate of 0.2 mm per 1000 h. Since 2012 all of the walls have been weld overlay coated with the nickel-based alloy, Alloy 625.

2.1.2 Händelö boiler 11

This is a grate boiler, themal power 85 MW. The final steam data are 110bar/535°C. It was built in 1982 and initially ran on coal, but in 1997 was converted to wood. For the first few years it ran on over 90% waste-wood, but this was subsequently reduced to 70-80% waste-wood (on an energy basis), the rest being forest fuel. Since 2008 small amounts of shredded rubber (from tyres) have been mixed with the fuel (3-4%).

The plant was one of the first in Sweden to run on waste-wood. The material in the furnace walls is the carbon steel St 35.8 and corrosion soon became a problem.

The plant started to use waste-wood in 1997, and already in 2000 some of the back wall and all of the side walls had to be replaced, (with the same material). Part of the back wall (the nose) was covered with refractory. The front wall was replaced in 1999.

From 2001 to 2003 the side walls have successively been replaced with Sanicro 63 and Sanicro 28 compound tubes. The extent of the refractory has been increased. In 2007-2008 the back wall was replaced by 16Mo3.

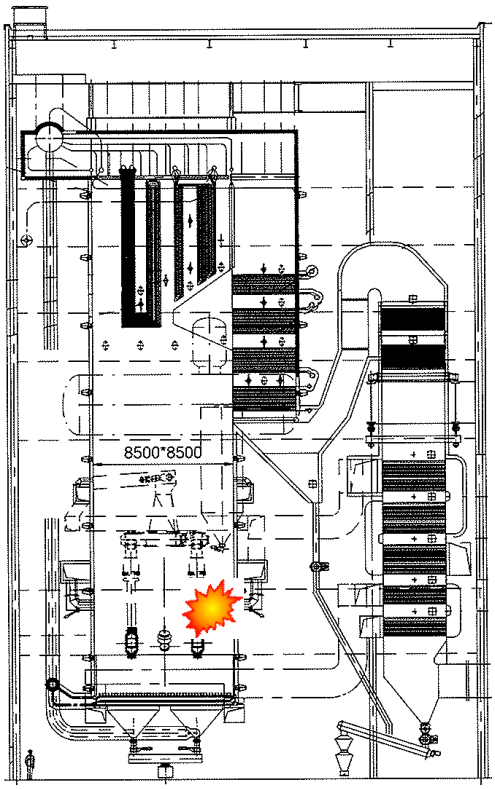
Today the plant runs on 70-80% waste wood, 20-30% forest fuel and 3% rubber. Corrosion problems are considered to be under control.

2.1.3 Steven's Croft

Stevens Croft is a 40 MWel bubbling fluidised bed boiler, owned and operated by E.ON and located in Lockerbie, Southern Scotland. The plant was taken into operation in 2007 and is the largest biomass power plant in Scotland. The steam data are 137 bar / 537°C and the fuel consists of a mixture of 85% forest fuel and 15% waste wood in the form of recycled wood fibre. The furnace walls are made of 16Mo3 and corrosion problems became apparent in 2013. Figure 2.1.2 shows a cross-section of the boiler and the position of the tube failure.

Fig. 2.1.2

Section of Stevens Croft boiler showing postion of tube failure that occurred in January 2013 at 4.3 m above refractory, 6 m above bed.



2.2 Corrosion and deposit probe testing

Long-term corrosion testing and short-term deposit collection was performed with an air-cooled probe containing four specimens which was exposed either at the back wall of the furnace in Idbäcken (position A) or on the right wall (position B). These two postions were at a height of 16 m. Initially two holes for testing were made at positions A and B, but due to problems with installing the probe only one hole in each position could be used. The probe, which was designed and built by Vattenfall Research and Development is long and thin (as can be seen in Figure 2.2.1) and was inserted vertically into slits made in the fins between two tubes. The probe contained four specimens, placed vertically under each other. The probe specimens had dimensions of 48 mm length, 7 mm width and 6 mm thickness. The temperature was measured by a thermocouple placed centrally at the back of each specimen and normally controlled to 400 °C. This simulates the temperature of the tube wall at 140 bar (the operating pressure of the plant). For long term corrosion testing the total exposure time at temperature was about 1000 hours and for short-term deposit testing the exposure time was about 15 hours.

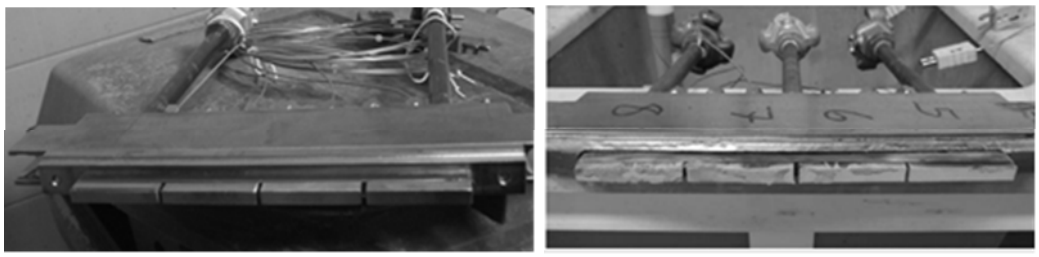


Fig. 2.2.1 The wall probe (left) before and (right) after exposure. The probe contains four specimens.

Before exposure in the boiler, the thickness of each probe specimen was measured with a micrometer at four equally spaced distances along the centre line. After testing, the specimens were cut at the measuring positions without water. Four parts of each sample were mounted in resin and used for metal thickness measurement by light optical microscope with a micrometer measuring gauge. One part of each sample was left unmounted for analysis in a scanning electron microscope. The chemical compostions of the alloys used for probe testing are given in Table 2.2.

The unmounted part of each sample was then polished without water by a polishing machine at 450 rpm at an angle of 45 degrees, according to Figure 2.2.2. Polishing in this method avoids washing away oxide products and chlorides and facilitates the analyses of the substrate, oxide and interface.

Fig. 2.2.2 Polishing of the unmounted part of sample

The samples were then chemically analysed under a scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS) with 15 KeV and 16 A parameters. The device was JEOL 7001 Oxford equipped with Inca program. Mapping, point analyses and QuantMaps were used at all areas of the samples.

Table 2.2 Specimens for fin probe and chemical compositions. Balance is Fe

Name	Chem comp wt%	Notes
16Mo3	Mn 0.55, Si 0.22, Mo 0.3, C 0.15	
13CrMo44	Cr 0.9, Mn 0.8, Si 0.22, Mo 0.5, C 0.12	
153MA	Cr 18.7, Ni 9.4, Mo 0.2, Mn 0.6, Si 1.3, N 0.14, C 0.05 + Ce	Outokumpu
253MA	Cr 20.8, Ni 10.8, Mo 0.2, Mn 0.4, Si 1.6, N 0.17, C 0.08 + Ce	Outokumpu
304L	Cr 18.2, Ni 8.1, Mo 0.3, Mn 1.6, Si 0.4, N 0.07, C 0.02	Outokumpu
3R12/TP304L	Cr 18, Ni 10, Mo 0.3, Mn 1.2	Sandvik
25-20/310S	Cr 25.4, Ni 19.2, Mn 0.8, Mo 0.1, Si 0.5, N 0,04, C 0.05	Outokumpu
San 28Cu	Cr 27, Ni 31, Mo 3.4, Mn 1.7, Cu 1.0	Sandvik
Alloy 625	Ni 61, Cr 21, Mo 8.5, Nb 3.4, Mn 0.4, Ti 0.28, Al 0.18, Ta 0.02	Sandvik
Alloy 625 (standard)	Ni 63, Cr 21 Mn 0.35, Si .02, Mo 9.0, Ti .25, Al .19, Nb+Ta 3.5	From welded tube
APMT	Cr 21, Al 5, Mo 3, Mn 0.4, Si 0.7, C 0.08	Sandvik

2.3 Summary of work performed

Summer/Autumn 2011

- Deposits collected from many different positions on the furnace walls of Idbäcken P3 and analysed (published in VGB PowerTech 12 2012) VNH, VRD, KTH and KIMAB
- New coated panels were welded into the right wall in Idbäcken. Samples cut from the existing wall and from the existing coated panels, delivered to the project and analysed. Report written (Memo U11-119). VNH and VRD
- Holes for testing made in the furnace wall in Idbäcken. VNH
- The fin wall probe was successfully modified and an extra probe manufactured to increase the testing capacity. VRD
- Deposits from furnace walls Händelö P11, delivered to the project and analysed. There were no deposits on the furnace walls of P13 (a 131 MWth CFB boiler running on forest residues, wood chips, shredded tyres and a small amount of waste wood). E.ON and VRD

- Materials for corrosion testing received from steel manufacturers and specimens manufactured. Sandvik MT and HT and Outokumpu.

Winter 2011/12

- November 2011. Measurement campaign was performed at Idbäcken with waste wood. Flue gas composition and temperature, impactor measurements, and deposit probe measurements were made at the furnace wall and 0.8-1 m from wall . Results have been analysed. (Memo U13-03). VNH, VRD SP and KTH
- Jan 2012 Corrosion probes (fin wall probes) prepared for long-term testing. VRD
- Feb 2012 Deposits from Steven's Croft delivered to the project and analysed summer 2012. (Memo U12-62) E.ON and VRD.

Spring 2012

- Idbäcken P3 suffered from 4 un-planned outages (tube leakages front wall and back wall uncoated areas) in Jan-Feb 2012 which delayed the long-term corrosion probe testing.
- First long-term probe test at 400°C in Idbäcken. A1 (back wall) and B1 (right wall). Start 14 Feb. 3 days exposure before plant shut-down. Re-started 15 March. Overheated 2 April due to short circuiting (water accident). Removed 4 April. Not evaluated
- Second probe test at 400°C in Idbäcken. A2 and B2 Installed 11 April. Removed 22 May. Approx 1000 h Position A Back wall. Position B, right hole seen from outside . VNH and VRD
- Analysis of deposits from Stevens Croft. (Memo U12-62) VRD
- Journal paper and conference paper written. Initial thermodynamic modelling of corrosion with ThermoCalc. KTH

Summer/Autumn 2012

- Summer 2012 – Samples cut from coated panels welded in during 2011 in Idbäcken. Samples cut from the existing wall and from the older coated panels in Idbäcken. Delivered to the project and analysed. (Memo U13-18). VNH and VRD.
- Third probe test 400°C in Idbäcken . A3 and B3 Installed 10 Oct and removed 18 Nov. Approx 1000 h. VNH and VRD.

Winter 2013

- Jan - Feb 2013 Measurement campaign was performed at Idbäcken with waste wood and waste wood + sewage sludge. Flue gas composition and temperature, impactor measurements, and deposit probe measurements were made at the furnace back wall. Results have been analysed, but not published. VNH, VRD, SP, KTH
- Analysis of tube failure in Stevens Croft. E.ON

Spring-Summer 2013

- Fourth probe test in Idbäcken. Probe test no. A4 (none in position B right wall) Probe installed 26 January and removed 16th April. Material 16Mo3. Gradient 250-400°C
- March- April Writing of Licentiate thesis KTH
- March-September. Deposit analysis of samples with and without sewage sludge. Investigation of initial corrosion. KTH
- May-September GD-OES measurements, on some short term probes from 2011, to check suitability of the technique. Development of technique. KIMAB
- May-September Thermodynamic equilibrium modelling of condensation behaviour of key elements from the fuel. SteaMax – based on FACT data (Valmet) and HSC Chemistry (Vattenfall) using same input data. 4 different fuel inputs and different lambda values. Comparison of results from SteaMax and HSC. Memo U13-57. Valmet and VRD.
- June Licentiate seminar by Yousef Alipour KTH
- September-October Analysis of deposit chemistry and corrosion on gradient probe.

3 Results

3.1 Analysis of deposits scraped from furnace walls

Deposits were scraped from the furnace walls of the 3 boilers during maintenance shut-downs. The parts of the deposit nearest the tube were analysed using energy dispersive x-ray spectroscopy (EDS). The scanned area was 2.5 x 2 mm in each case (corresponding to a magnification of 50x) and three separate areas (or pieces of deposit) were analysed for each deposit position. Some deposits were chosen for further examination at higher magnifications and some by x-ray diffraction (XRD).

3.1.1 Idbäcken

Deposits were taken from a 20 different positions on the furnace wall in Idbäcken and chemically analysed. Most of the deposits were from areas in the boiler between the secondary and tertiary air ports, i.e. the lower part of the wall (height 11.5 to 18 m), where corrosion is worst. Two samples were taken from above the tertiary air ports at a height of 22m (samples F6 and F7 on the front wall). The deposits were removed only from the tubes and not the fins between the tubes on the membrane wall.

The deposits showed a wide spread in chemical composition , although Cl was found in all the samples, sometimes at very high levels (27 atomic %). K and S were found in all the deposits samples and Na was found in most. A higher K content was always associated with a high Cl content. Zn was found in three-quarters of the samples at low concentrations and Pb was found in a third of the samples at low average concentrations, but high concentrations locally. The results for the front wall are shown in Fig. 3.1.1.

Scanning electron microscopy showed that lead, when it was present in a deposit, was heterogeneously distributed and could be observed as "islands" of pure lead or in mixtures containing oxygen, for example Pb-Cl-O mixtures or Pb-K-S-O mixtures. Zinc was less frequently observed, but was occasionally seen as crystals of zinc chloride.

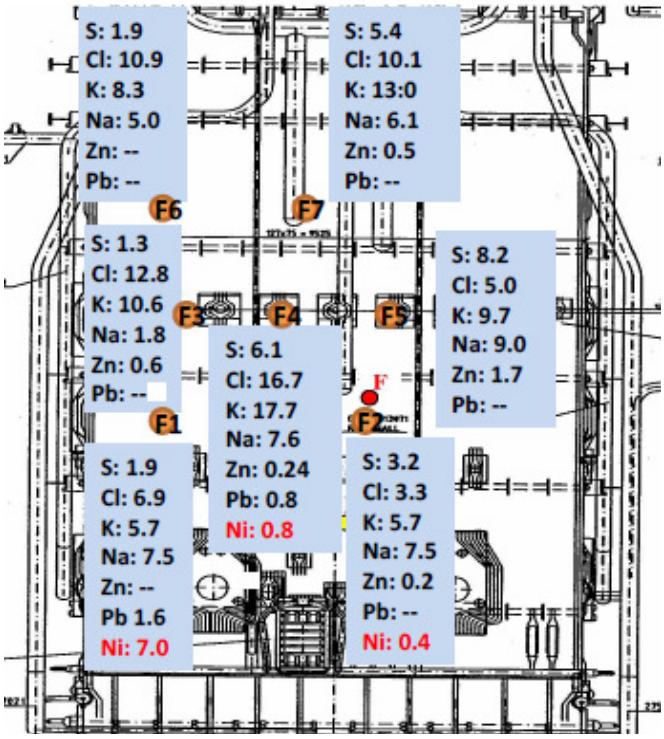
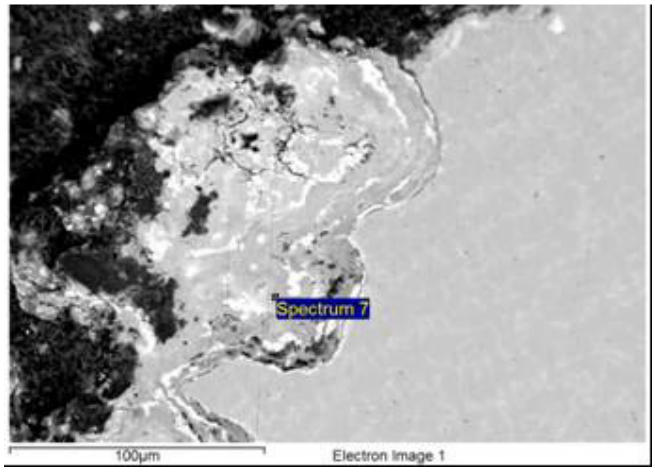


Fig. 3.1.1 **Sketch of front wall showing the positions, F1 to F7, from where deposits were removed and chemical composition in atomic % of key elements in the deposits. The nickel comes from the Alloy 625 coating which had found its way into the deposits. F6 and F7 are above the tertiary air ports**

In samples with a low chlorine content, sulphates dominated the x-ray diffraction results. As expected, potassium chloride dominated in deposits with medium to high chlorine contents. Potassium-lead compounds, such as potassium - lead chromate were also detected. Table 3.1.1 shows the compounds detected by x-ray diffraction.

Table 3.1.1. Compounds identified by x-ray diffraction in some deposits.

	Compounds detected
Low chlorine. High Pb. Cl = 0.6, Pb =1.1 at %	
Strong intensity/high concentrations	$(K,Na)SO_4$, $K_2Pb(SO_4)_2$
Medium intensity/medium concentrations	Pb_2OSO_4
Medium Cl. High Pb. Cl=6.9, Pb = 1.6 at%	
Strong intensity/high concentrations	KCl
Medium intensity/medium concentrations	NaCl, $K_3Na(SO_4)_2$, NiO, $K_2Pb(CrO_4)_2$
High Cl. Med-low Pb . Cl=14.5, Pb = 0.6 at%	
Strong intensity/high concentrations	KCl
Medium intensity/medium concentrations	NaCl, $K_3Na(SO_4)_2$, NiO, $(Cr_{1.6}Fe_{1.4})O_4$



Element	Wt%	At%
O K	19.99	51.68
S K	5.60	7.23
Cl K	0.46	0.54
K K	5.09	5.39
Cr K	4.92	3.91
Fe K	0.41	0.30
Ni K	35.32	24.88
Zn K	1.00	0.63
Pb M	27.22	5.43

Fig. 3.1.2 **A section through the surface of weld overlay IN 625 and the chemical composition of the analysed spot. The micrograph shows a pit filled with a mixture of deposit and corrosion products, with the un-corroded alloy on the right and the outer surface on the left. The spot analysis was made by WDS.**

Initial metallographic investigation of corroded Ni-alloy coated tubes, revealed that lead was greatly concentrated at the corrosion front in the pits, see Figure 3.1.2.

X-ray diffraction revealed the presence of K-Pb compounds such as $K_2Pb(SO_4)_2$ and $K_2Pb(CrO_4)_2$, Cr in the latter coming from coated tubes.

Coating the furnace wall tubes with the Ni-base alloy, Alloy 625, reduced the corrosion rate and metallographic examination using SEM and WDS showed that there was very little chlorine at the corrosion front in this alloy. However, although only small amounts of lead were found generally in the deposits, the lead together with potassium, was concentrated at the corrosion front in the pits and appeared to be highly active in the corrosion process on the nickel-based alloy coating.

The results are fully detailed in Appendix A "The analysis of furnace wall deposits in a low NOx waste wood fired bubbling fluidised bed boiler" by Yousef Alipour, Peter Viklund and Pamela Henderson and published in VGB PowerTech 2012.

3.1.2 Händelö Boiler 11

Deposit samples were taken from the lower part of the furnace at a distance of 0.7-3.5 m from the grate and contained no or very little chlorine. Less than 0.5% Cl (atomic or weight%) was found in deposits on the back wall, but none from the other walls.

Sulphur, lead, zinc and potassium were found in all the deposits. S in the range 5-14 wt%, 6-10 at %. Pb in the range 4-16 wt%, 0.5-2 at%. Zn 4-15 wt%, 1.5-6 at% and K 5-11 wt% , 3-7 at%.

The lack of Cl in the deposits and the reduced amount of K (compared to the deposits from Idbäcken) results in a much less corrosive environment. Corrosion was a problem when the boiler was firing 100% waste wood, but since then most of the walls have been coated with corrosion resistant alloys. It is believed that reducing the amount of waste wood to 70% and possibly the use of shredded tyres has removed much of the KCl. However it it difficult to speculate on this. Händelö differs from Stevens Croft and Idbäcken in that it is a grate boiler while the latter two are bubbling fluidised bed boilers.

3.1.3 Stevens Croft

Samples were taken from two levels in the boiler, level 1 at 3 m and level 5 at 25 m above the bed, from all four sides of the boiler. (N.b tube failure later occurred at 6m). Level 5 is above the tertiary air inlets. The outer parts of the deposits that were facing the flue gases as well as the inner parts that were facing the tubes were analysed.

The dominating species in the outer, light brown part of the deposit were Ca, K, S, Na, Si, Zn and in some cases Pb. In the samples from level 1 there were also substantial amounts of Cl and more Zn than in the level 5 samples. The samples from the outer deposits at level 5 contained 0-0.2 wt% Cl whereas the deposits at level 1 contained 5-12 wt%. There was generally more sulphur at level 5 and the oxygen content of the outer deposits was 30-40 wt% at level 1 , but 40-50 wt% at level 5. Figure 3.1.3 shows some key elements in the outer parts of the deposits.

The parts of the deposit facing the tubes (inner deposits) were black or in some cases rusty red. The outer part of the deposits contained 2-6 wt% iron, whereas the inner part of the deposits contained 20-46 wt% iron indicating that the inner part probably contained corrosion products and oxide from the tube surfaces. Magnetite (Fe3O4) is black and hematite (Fe2O3) is reddish brown which ties in with appearance of the inside of the deposit. As with the outer part of the deposit, the chlorine content was much higher in the samples from level 1 than in the samples from level 5 Figure 3.1.4 shows some key elements in the inner parts of the deposits.

More detailed information on the chemical analysis of the deposits from Stevens Croft can be found in Appendix B Vattenfall Memo U12-62 " Analysis of deposits from Steven's Croft" by Annika Stålenheim.

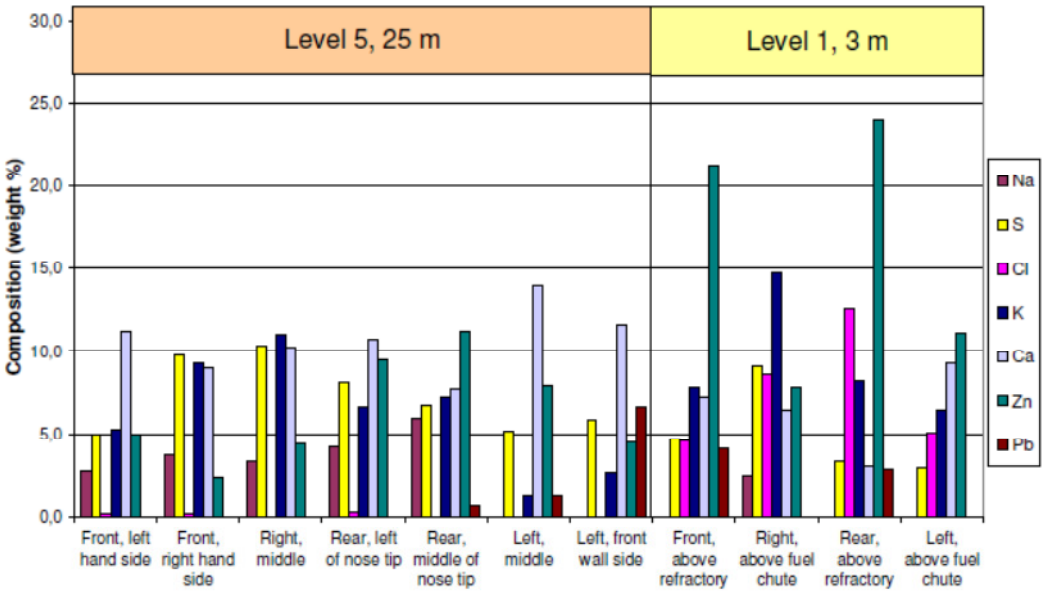


Fig. 3.1.3 **Content of some selected elements in deposit samples from Steven's Croft, outer, light brown part of deposit**

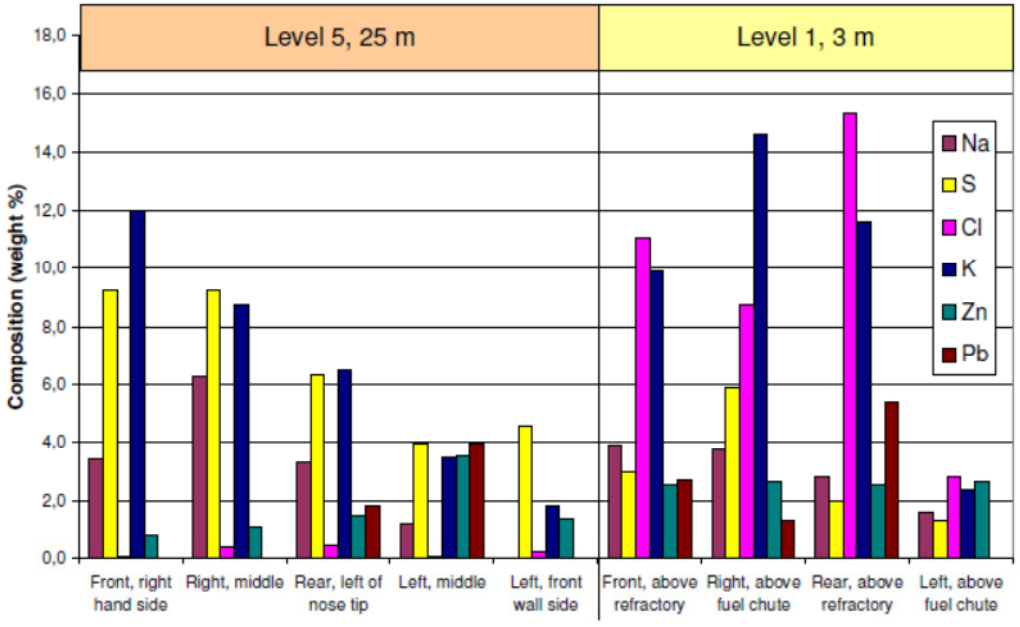


Fig. 3.1.4. **Content of some selected elements in deposit samples from Steven's Croft, inner, black part of deposit**

3.2 Corrosion of tubes in the furnace wall

3.2.1 Steven's Croft tube failure

During January 2013 the boiler was taken out of service with a tube leak in the lower furnace. The leak was located in the right hand side wall, twelve tubes from the rearmost corner and 4.3m above the refractory. Microstructural examination revealed no indication of microstructural degradation or overheating. The prepared section exhibited external fireside surface wastage with substantial thinning to a minimum of 1.3mm wall thickness, equivalent to 5 mm metal loss. The boiler had been in operation for 32,000 hours, giving a maximum corrosion rate of about 156 µm per 1000h. This wastage together with slight subsurface, intergranular penetration to a maximum depth of 50µm was the result of fireside corrosion.

The retained corrosion scales were predominantly oxides, and often exhibited a defective, more heavily laminated and cracked layer at the scale metal interface. An elemental analysis of the corrosion scales revealed these to contain low levels of lead, sulphur, potassium, zinc and copper, with these frequently being concentrated at more defective, inter-lamellae bands. In addition, chlorine was found at low levels throughout the corrosion scales, with concentrations increasing to a maximum of 33 at % at the scale metal interface.

3.2.2 Furnace tubes and wall coatings in Idbäcken

During the summer of 2008 test panels were installed in the waterwalls of the Idbäcken P3 boiler and samples were removed during the summers of 2009, 2010 and 2011. In 2011 parts of the furnace walls were exchanged and some extra test panels were installed. The test panels were installed on the right wall (motorway side) of the boiler. Amstar AMS 888, one of the coatings installed in 2008, was consumed during the first firing season. Tube specimens were cut out from the test panels in the summer 2012. The coatings on the test panels that were investigated are given in Table 3.2.1 In addition, uncoated tubes of 16Mo3 were also investigated.

The results from 2011 (after 3 years exposure of the tubes installed in 2008) showed that all three Ni-base coatings had very low corrosion rates.

Table 3.2.1 Investigated test panels and coatings

Coating	Tube nr
Arc welded hard facing (overlay weld) by Burmeister and Wain Energy A/S, BWE, consisting of Inconel 625. The intended thickness is > 1,5 mm (2008)	39-42
A metal sprayed coating using HVOF (High Velocity OxyFuel) applied by Sulzer Metco. The alloy is SumeBoil70C (Inconel625 + carbides) with an intended thickness of 0,3 mm (2008)	45-48
FlameSpray, FlameSeal WW (a ceramic seal on top of a thermal sprayed coating). The thermal sprayed alloy is Alloy C-276 (Ni16Cr16Mo5Fe4W) with the intended thickness 0,3 mm (2008)	52-54
A coating that was plasma sprayed in workshop by Häuser. The alloy used is HS4, Häuser's own corrosion erosion resistant Ni-alloy (NiCrWBSi). Intended thickness 0.4 mm. (2011)	55-58
Coating plasma-sprayed in workshop by MH engineering. The alloy used was TP316 stainless steel. (2011)	59-60, 62-63
Coating applied by MH engineering on site. Material used is CorrEr (A variation of Alloy 625). Only one tube coated. (2011)	65
Coating applied by MH engineering on site. Material used is alloy 625. Only one tube coated. (2011)	67

The original thickness of the IN625 welded coating on the tube samples was about 4 mm, but being a welded structure it was difficult to measure accurately and may have been greater or less than 4 mm in a number of areas. After 3 years exposure (about 20,000 hours) the average thickness of the examined section was 3.8 mm (average of 8 equally spaced measurements) and the minimum thickness 3.4 mm. This gives an estimated average metal loss rate of 10 µm per 1000 h and a maximum metal loss rate of 30 µm per 1000 h.

The original wall thickness of the 16Mo3 test panel tubes was 7 mm and after 3 years exposure the average thickness of the examined section was 5.35 mm and the minimum 5.0 mm. This gives an estimated average metal loss rate of 80µm per 1000 h and a maximum loss rate of 100 µm per 1000 hours, about 3 times greater. These values are of course, only approximate.

The results from 2012 showed that all the coatings except the overlay weld were damaged. The two thermally sprayed coatings (Sulzer and FlameSpray) applied in 2008 were mainly intact, but were damaged in the area near the weld repair after the 2011 sampling. There was also one large hole in the coating of each of these panels one or a few decimetres from the weld repair. The cause of these holes is not known, but the local nature of the damages indicated that they were caused by some external factor, rather than

deterioration of the material from corrosion caused by the flue gases and deposits. Except for these holes the coatings do not seem to have suffered any thickness loss.

The coatings that were installed in 2011 (all thermally sprayed) were all severely damaged. Two coatings, Häuser HS4 and MH Engineering 316, had some areas in good condition, indicating that the break down was not caused by corrosion of the coating, but rather physical damage, such as cracking and delamination. This could indicate that stainless steel might be an alternative to Ni-base.

As regards metal loss (corrosion), the nickel-based alloys showed negligible loss (too small to be measured accurately) and the stainless steel showed a loss of 35-90 µm per year (less than 0.1 mm), also very small.

The reference sample analysed in 2011 experienced a maximum metal loss of 2 mm (0.65 mm per year) during the three year period 2008-2011 and an average metal loss of 1.65 mm (0.55mm per year). The maximum metal loss of the reference sample analysed in 2012 was about 1 mm after one firing season (152µm per 1000 h) and the average was 0.65mm (100µm per 1000h), indicating a marginally higher corrosion rate.

Full details of the tube investigations can be found in Appendix C Vattenfall Memo U 13-18 " Evaulation of Waterwall Materials from test panels 2012" by Annika Stålenheim and Mattias Mattsson.

3.3 Furnace environment measurements with waste wood

3.3.1 Flue gas and deposit measurements when burning waste wood

A measurement campaign was performed at Idbäcken with waste wood in November 2011. The measurements were made during the period 8-10 November with the boiler running at 65-80% of full load.

The flue gas composition and temperature were investigated at seven positions in the boiler, on the back wall, right wall and front wall of the furnace at a height of + 16 m, between the secondary and tertiary air- ports. The measurements were taken at a distance of 10 cm and 80 cm from the boiler wall at each postion. An FTIR was used to measure the flue gas content of CO, SO_2, NH_3, HF, CH_4, NOx, H_2O, HCl, and CO_2 and a Sick-May instrument was used the measure the O_2 content and flue gas temperature.

Impactor measurements were made by SP on the back wall and right wall at the same positions as the flue gas sampling. The measurements were made at the wall and 80 cm from the wall, using a Dekati low pressure impactor.

Six deposit probe exposures were performed at the wall, on the back wall and right wall (same positions as flue gas and impactor measurements). Each deposit probe contained four cooled specimens where the deposits were collected. Probe specimens were 48 mm long, 7 mm wide and 6 mm thick. The probes were inserted into slits in the fins between two tubes in the furnace wall. The exposure time was 12-15h.

Two alloys were used, 13CrMo4-5 (ferritic steel) and 310 (austenitic stainless steel) at a range of metal temperatures from 250 to 460°C.

The lower furnace region of a boiler, where combustion is occurring, is a difficult area to make tests in. The combustion conditions fluctuate rapidly leading to a heterogeneous distribution of flue gases and particles landing on the furnace walls. Additionally, the operating conditions were not constant with time leading to a variation in bed and flue gas temperature in the furnace over the measurement period.

The back wall of the boiler experiences a higher corrosion rate than the right wall. The main differences between these two positions seemed to be a higher flue gas temperature and a greater fluctuation in the oxygen content at the back wall.

Very low O_2 levels were detected, sometimes below 0.5%, and the fluctuation over time was large. The fluctuation was greatest at the back wall and least on the right wall. The temperatures were lower close to the wall than 1 m into the furnace. The CO levels were high. When the ChlorOut system was turned off the KCl level near the superheaters was 19-28 ppm.

Average values of flue gas measurements 10 cm from furnace wall, at an elevation of + 16 m (between secondary and tertiary air ports) are as follows:-

SICK O_2 0.9%, CO (out of range for many readings, i.e. > 1.3%)

FTIR, average values: CO 1.7%, SO_2 46 ppm, HCl 15 ppm, HF 1 ppm, CH_4 (methane) 1360 ppm, NOx 96 ppm, H_2O 19.6 %, CO_2 8.9%

IACM (with no ChlorOut additive) at superheaters : KCl 19-28 ppm, SO_2 32-49 ppm

It was expected that the deposit composition might vary with metal substrate temperature, type of steel, or position in boiler. However, no such correlation could be found. K, Cl, S, Pb and Zn were found in the deposits. The levels varied considerably and in a seemingly random manner as can be seen in Fig. 3.3.1.

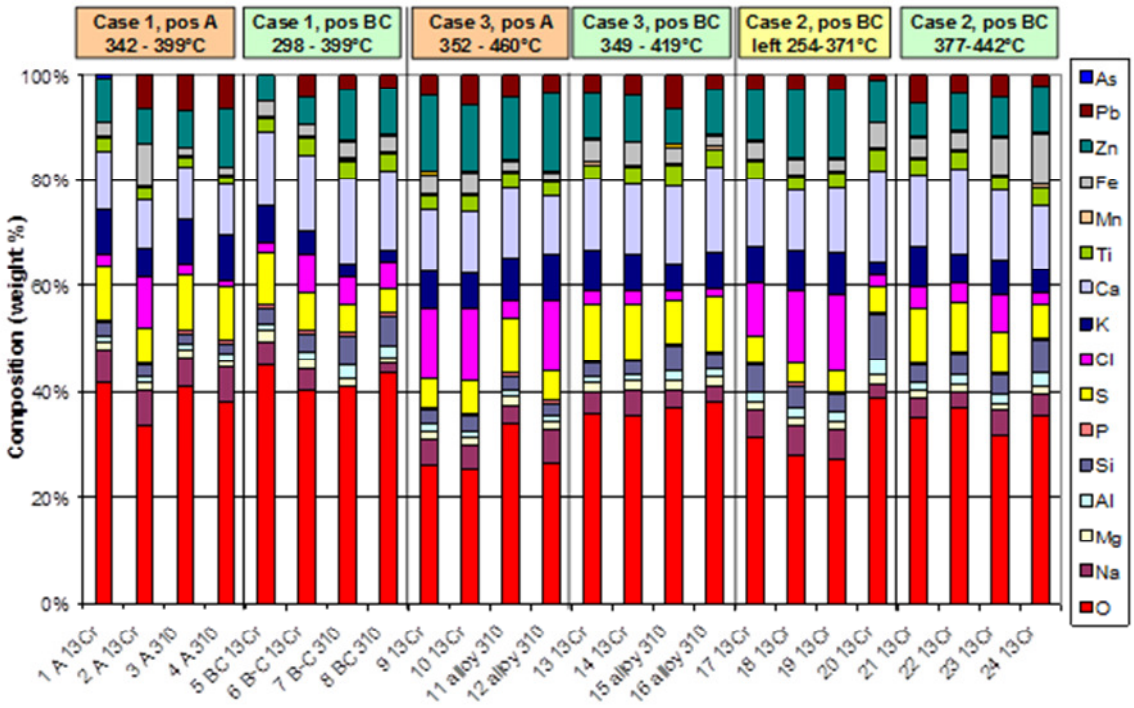


Fig. 3.3.1 Composition of the deposits collected on probes at the different positions on the wall.

The chlorine content of the deposits varied between 2 and 14 wt % , zinc 5-15 wt%, lead up to 6.8 wt%, potassium 2-9 wt% , sodium up to 6.6 wt% and sulphur 4-11 wt%. There was no correlation between Cl content, measuring position (back wall or side wall), substrate temperature or alloy, but a high S content correlated with a low Cl content.

Impactor measurements showed that Cl, K, Pb and Zn and S were found in sub-micron particles. Si and Ca were found in particle sizes 1-10µm. The impactor measurements showed similar results at both 10 cm and 80 cm from the furnace wall.

Full details of the measurement campaign can be found in Appendix D, Vattenfall Memo. U13-03 "Measurement campaign November 2011, KME 508 Furnace wall corrosion" by Annika Stålenheim and Pamela Henderson.

3.3.2 Furnace measurements with digested sewage sludge

To study the effect of co-firing of sewage sludge, two air-cooled probes were exposed at the furnace back wall in the Idbäcken power plant for 14.25 hours. Both probes contained low alloy steel 16Mo3 (the usual base of furnace walls), nickel-base alloy Alloy 625, iron-chromium-aluminium alloy APMT and stainless steel 310S. The APMT sample was pre-oxidised by the supplier for 8 hours in air at 1050°C to produce a protective 1 µm thick alumina layer on the sample surface. The temperature of the probes was controlled to 400°C

which is assumed to be the metal temperature of furnace walls. The power plant was operated on 100% waste wood during exposure of one probe, and then 8.4 wt% (1.7 vol%) of sewage sludge, as received, was added when testing the second probe. This corresponded to 3.5 dry wt% or 1.5% of the total energy.

During firing with sewage sludge impactor measurements were made by SP on the back wall at the same positions as the probe. The measurements were made at the wall and 80 cm from the wall, using a Dekati low pressure impactor.

Results of deposit analysis showed that the amounts of lead, chlorine, potassium and sodium in the deposits was reduced when burning sewage sludge along with waste wood, while the amounts of aluminium, phosphorus and silicon were increased. The results of the impactor measurements showed that Cl, K, Pb and Zn and S were found in sub-micron particles both with and without sewage sludge. Si, and Ca were found in particle sizes 1-10µm and peaks of P containing particles were found at 0.1µm and in the range 1-10 µm. There were no differences in the impactor measurements between 10 cm and 80 cm from the furnace wall.

The initial corrosion was reduced on all the high alloy specimens with the use of sludge. The amount of corrosion caused with or without sludge was high on 16Mo3 so it was difficult to estimate the effect, however, the use of sludge reduced the width of the iron chloride layer at the metal interface, which implies a reduction in the corrosive environment. Sludge inhibited the formation of non-protective K-Pb chromates from protective chromia, which is believed to have contributed to the reduced corrosion on the high alloy specimens.

More information can be found in Appendix E "The effect of co-firing of sewage sludge with waste wood on furnace wall corrosion" by Yousef Alipour and Pamela Henderson.

3.4 Corrosion measurements with probes

Four long-term corrosion measurement campaigns with probes were performed and evaluated within the time-frame of this project. The testing was performed in Idbäcksverket with 100% waste-wood as the fuel. The first probes (probes A1 and B1) were not evaluated because of over-heating.

3.4.1 Effect of alloy composition on corrosion rate

The results from the second probe campaign are shown in Fig. 3.4.1. It can be seen that APMT, Alloy 625 and the stainless steels 153MA, 253MA and 310S perform better than 16Mo3 and that the corrosion rate was higher on the back wall, position A. This became the main position for future probe testing.

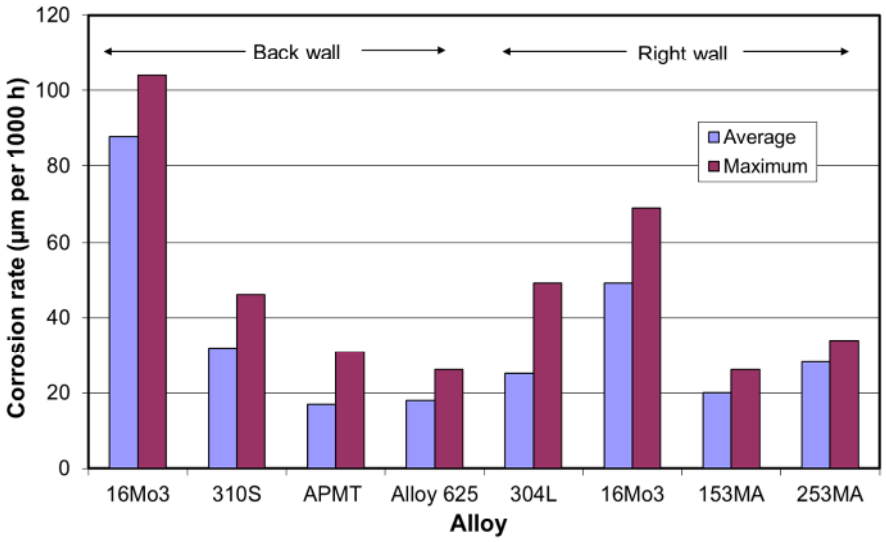


Fig. 3.4.1 Average and maximum corrosion rates for specimens on probe A2 (back wall) and B2 (right wall). Metal temperature 400°C. The corrosion rate was higher on the back wall.

The results for probe tests 2 and 3 on the back wall are presented in Figure 3.4.2 which shows that APMT, Alloy 625 and the stainless steels Sanicro 28 and 310S perform better than 16Mo3. The boiler load was higher in the autumn than the spring, which is why the corrosion rates for APMT, 16Mo3 and Alloy 625 on the right of the diagram are higher than those on the left. It also shows that the advantages of using a high alloy coating increase at increased boiler loads.

The dominant corrosion mechanism in the 16Mo3 specimen was found to be chloride corrosion, while attack by a potassium-lead combination seemed to be the main attack in the nickel alloy coating material. SEM analysis for the stainless steels showed chlorine, lead and potassium at the corrosion front. Lead and potassium were in connection together; however they were not in reaction with chlorine. The corrosion mechanism in the stainless steels therefore seems to be mixture of both mechanisms. The corrosion rate of the stainless steels is between of 16Mo3 (the highest corrosion rate) and Alloy 625 (the lowest corrosion rate). This indicates that stainless steels, could be a cheaper alternative to Ni-base alloys for protecting furnace walls.

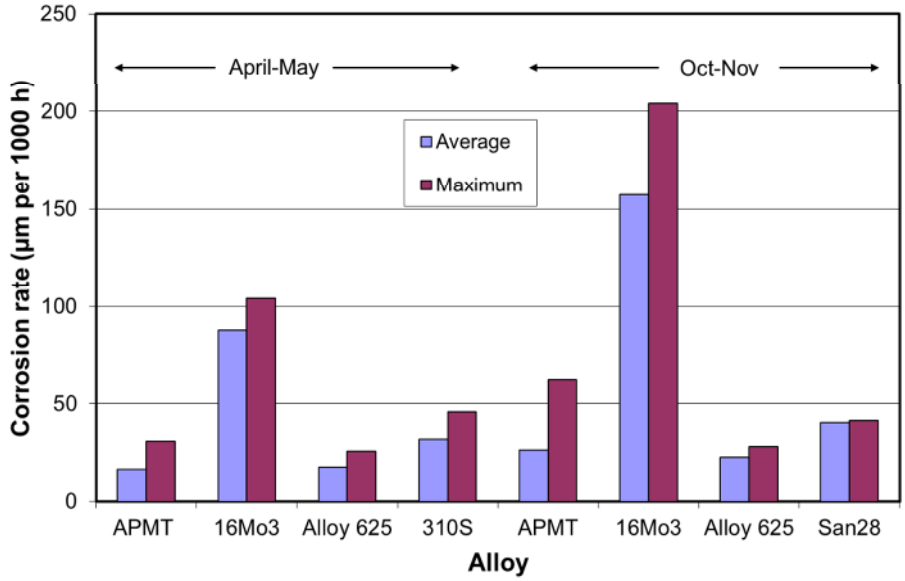


Fig. 3.4.2 Average and maximum corrosion rates for probes A2 (April-May 2012) and A3 (Oct-November 2012) in position A Idbäcken – centre of back wall, height 16 m. Metal temperature 400°C.

Kanthal APMT alloy had a very low corrosion rate which may be due to the pre-oxidation treatment or the presence of aluminium in the oxide, albeit at a low level. Potassium, zinc and chloride were all found at the corrosion front in this material. More information can be found in Appendix F "The effect of a nickel alloy coating on the corrosion of furnace wall tubes in a waste wood fired power plant" Y. Alipour, P. Henderson and P. Szakálos.

3.4.2 Effect of temperature on corrosion rate

The results of the fourth corrosion probe measurement are given in Fig 3.4.3. This probe (A4) contained four specimens of 16Mo3 and had a temperature gradient forced upon it to simulate different wall temperatures (boiler pressures). It can be seen that the corrosion rate of 16Mo3 increases steeply with temperature at the higher temperatures (above about 390°C).

The deposits on the samples were chemically analysed by XRD and SEM/EDS and the corrosion fronts of two samples were studied by FIB (focussed ion beam milling)/EDS.

The corrosion rate decreased with decreasing metal temperature and the amount of K and Cl in the deposit also decreased with decreasing temperature. However the amount of Pb peaked at about 360°C. XRD analysis of the deposit on the 360°C sample showed that the chloride was associated with alkali and the deposit mostly contained KCl and NaCl. Lead was detected as pure lead but some lead oxide was also present.

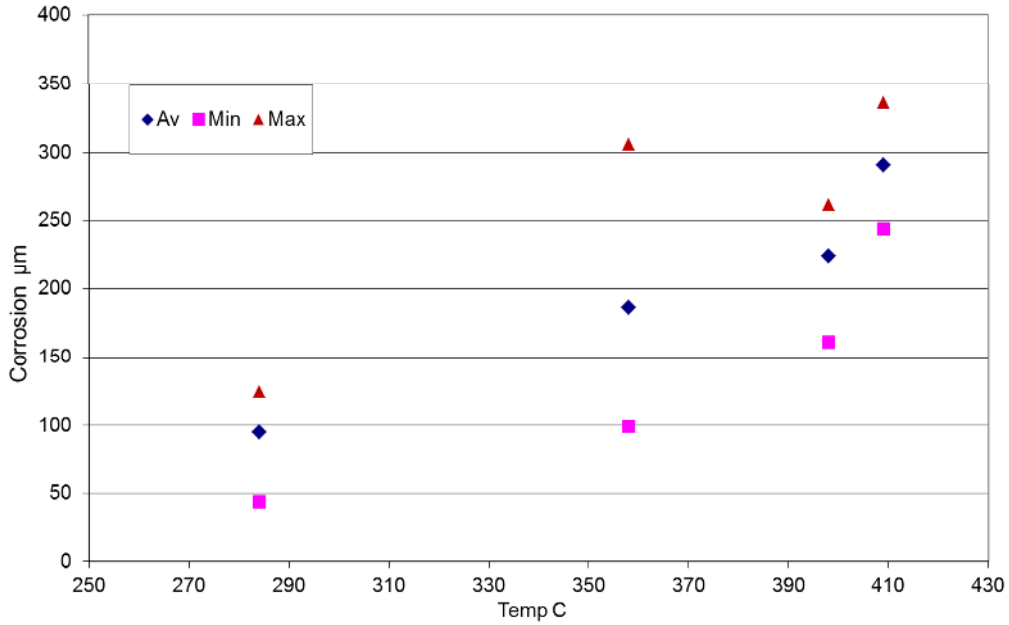


Fig. 3.4.3 **Variation of corrosion rate in µm per 1000 h with metal temperature in °C for 16Mo3. The average, maximum and minimum of 20 measuring points are shown.**

The FIB sections of the specimens at the highest and lowest temperatures showed very similar results. A band of iron chloride 2 µm wide was found next to the metal and no overlap of oxygen and chlorine signals was observed. An FIB section is shown in Fig. 3.4.4 and the measurement profile in Fig. 3.4.5.

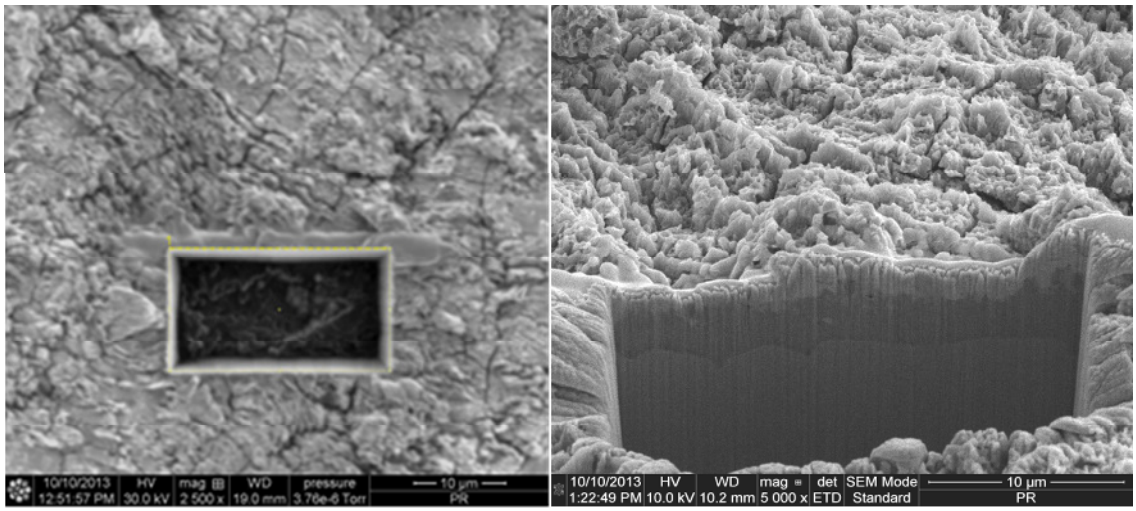


Fig. 3.4.4 **(Left)Surface view of hole made by FIB. (Right) After tilting by 52 degrees to expose cross-section in the 409°C 16Mo3 sample.**

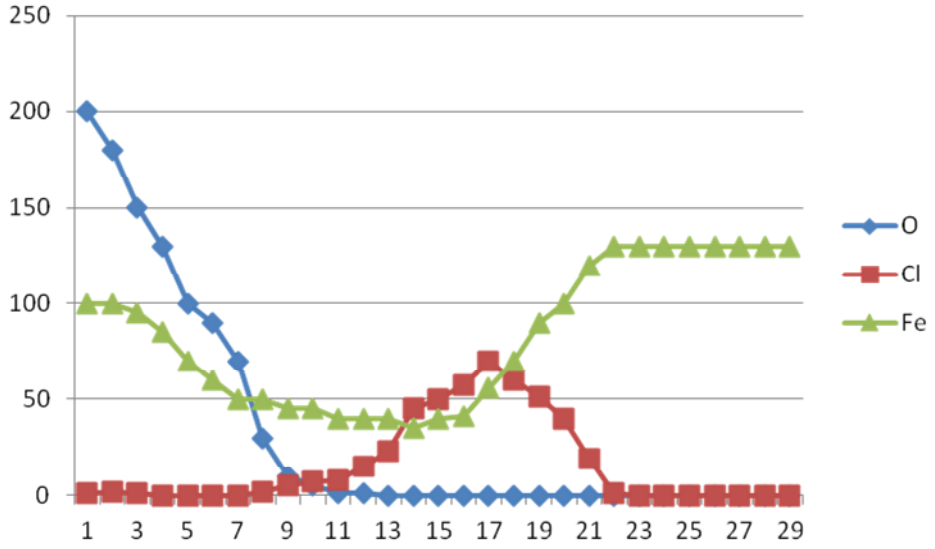


Fig. 3.4.5. **Measurement profile from 409°C 16Mo3 sample, 5µm deep, covering 29 measurement points, from the surface of the specimen in to the metal. The iron chloride band is 2µm wide. There is no overlap of oxygen and chlorine, i.e oxychlorides are not seen. The intensities of Fe, Cl and O are related to weight %, but have not been calibrated.**

More information can be found in Appendix G Vattenfall Memo U 13-66 "Corrosion of a low-alloy furnace wall material at different temperatures in a BFB boiler firing 100% waste wood", by Pamela Henderson, Yousef Alipour and Mattias Mattsson

3.5 Development of Fe-Cr-Al alloys that are resistant to 475-degree embrittlement

As shown in section 3.4.1 the Fe-Cr-Al alloy APMT shows very good corrosion resistance at 400°C and it is thought that Fe-Cr-Al alloys might make suitable coating materials or even structural wall materials to resist corrosion. Although these alloys are single-phased at high temperatures, they separate into two phases at temperatures of around 475 °C and below. This phenomenon is known as spinodal decomposition. The phase separation - into two phases, α (alpha, Fe- rich ferrite) and α' (alpha-prime, Cr-rich ferrite)- causes severe embrittlement of the steel, making it practically inapplicable for use at these temperatures.

In order to avoid phase separation in this type of alloy, the composition has to be drastically changed. In theory, an FeCrAl alloy containing only 10 wt. % of chromium would be immune to spinodal decomposition and therefore a candidate material for use on waste-fired boilers.

Theoretical and experimental work was therefore carried out to show that FeCrAl alloys, containing only 10 wt. % chromium, are resistant to embrittlement in the temperature interval 350 °C to 600 °C. The investigated alloys were 21Cr-5Al and 10Cr-alloys containing 4.6 and 8 wt% Al.

In order to study phase separation in the interval 350 ° to 450 °C theoretical work had to be performed because phase separation kinetics exponentially decrease with decreased temperature, hence thermodynamic modelling tools (Thermo-Calc) was used. Thermocalc showed that, in theory, if enough aluminium is added, spinodal decomposition can be suppressed at all temperatures. It showed for 21Cr-5Al that at 450 °C and above the alloy is immune to α-α' phase separation. This was found to be incorrect experimentally (see paragraphs below). Therefore it clear that Thermo-Calc (TCFE5) overestimates the influence of aluminium.

Thermal aging was carried out at 450 °C, 475 °C, 500 °C, 550 °C and 600 °C in air. The change in the microstructure was monitored by hardness and the microstructure was investigated by atom probe microscope.

The hardness results showed that the reference alloy, 21Cr-5Al, was readily hardened in the interval 450 °C to 500 °C, (indicating phase separation). The 10Cr-alloys showed a decrease in hardness with time in the same interval. At 550 °C and 600 °C, all alloys showed a decrease in hardness, which was expected as the temperature is too high for α-α' phase separation.

Electrical resistance measurements were carried out on all alloys at 475 °C and 500 °C up to 48 h. The method is highly sensitive to macroscopic changes in the microstructure, hence if phase separation occurs at these temperatures it would be noted instantly. While the resistance of the 21Cr-5Al alloy decreased rapidly at both temperatures, the 10Cr-alloys were unaffected. The resistance drop was more pronounced at 475 °C, which was expected as α-α' phase separation is known to have its maximum around this temperature.

Two aged samples (10Cr-8Al & 21Cr-5Al) were analysed with atom probe tomography in order to study the homogeneity of the microstructure. The 10Cr-8Al was aged at 500 °C for 10,000 h, whereas the 21Cr-5Al-alloy sample originated from the 48 h electrical resistance measurement at the same temperature. By studying the 48 h sample, the drop in electrical resistance could be proven to originate from a phase separation. No indications of phase separation had been observed for the 10Cr-alloys in previous tests, hence the AP would provide the ultimate answer. Fig. 3.5.1 shows that the 21Cr-5Al alloy aged for 48 h in 500 °C, shows clear signs of phase separation. Chromium rich regions have been formed, and are evenly spread throughout the analyzed volume. The result clearly shows the fast phase separation at 500 °C for the 21Cr-5Al alloy. By contrast, no phase separation could be seen for the 10Cr-8Al alloy aged for 10,000 h.

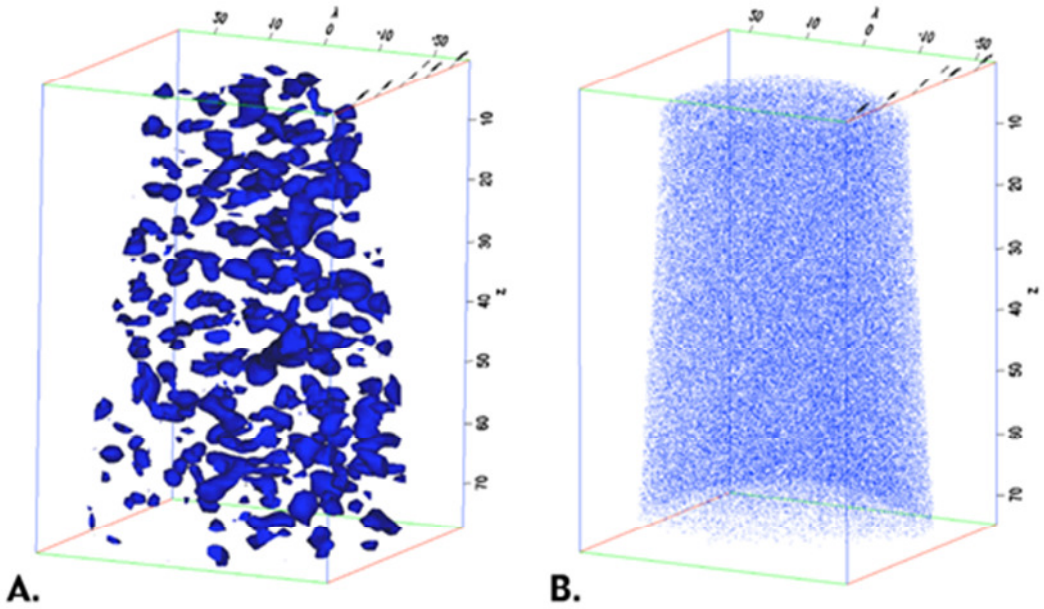


Fig. 3.5.1 **Computer reconstruction of analyzed volumes (50 x 50 x 75 nm3). The reconstruction of the 21Cr-5Al alloy aged for 48 h at 500 °C (A), show isosurfaces containing at least 30 % Cr atoms. The formation of Cr-rich α' clusters is typical for the phase separation. The 10Cr-8Al alloy (B), aged for 10,000 h at 500 °C shows a perfectly homogeneous structure, i.e. Cr atoms are evenly spread throughout the volume.**

The study thus shows that Fe10CrAl alloys are immune to α-α' phase separation at 450-600 °C. While the 21Cr-5Al alloy was clearly hardened at 450-500 °C, no signs of hardening or phase separation were observed for the Fe10CrAl alloys, at least up to 10,000 h.

At lower temperatures, 350-400 °C, the Thermo-Calc modelling showed no indication of phase separation in the Fe10CrAl alloy system, but the thermodynamic database does not give a completely correct picture of reality.

In order to use FeCrAl alloys in structural components in energy producing applications, such as waste-fired boilers, the microstructure has to completely stable at the process temperature of the plant. The work presented in this study have shown that this may be possible by reducing the chromium content, in FeCrAl alloys, to 10 wt. %.

More information is available in Appendix H, "Development of embrittlement resistant FeCrAl alloys" by J. Ejenstam, M. Thuvander, F. Rave, J.N. Olovsjö and P. Szakalos.

3.6 Thermodynamic equilibrium modelling using fuel composition

Thermodynamic equilibrium calculations using the chemical composition of fuel to evaluate the condensation behavior of K, Na, Cl, S, Zn and Pb compounds at different temperatures were performed and the calculation results compared to the experimental ones from deposit analyses at Idbäcken power plant. The objective was to find a correlation between the equilibrium calculations and the collected deposits in order to use the chemical equilibrium calculations to predict potentially corrosive fuel mixtures and operational conditions.

Calculations were performed by Vattenfall using HSC Chemistry software and by Valmet Power using the Valmet in-house tool SteaMax using the same input data. (SteaMax is based on the ChemSheet software, FACT database and Valmet's proprietary database modification and expertise.) The results were compared.

Calculations were performed for:

-Idbäcken fuel at lambda 0.8 and 1.2

-Reference (REF) fuel at lambda 0.8 and 1.2

-RPP Reference Power Plant fuel (as defined in KME 601) at lambda 0.8 and 1.2

-Steve's Croft fuel at lambda 0.8 and 1.2

The conditions represent oxidizing and reducing conditions present in real boilers. The reducing conditions simulate the conditions experienced at boiler walls and the oxidizing conditions at superheaters further downstream in the boiler. The work focused mainly on the reducing conditions and the Zn and Pb based system.

The comparison between the Valmet calculations (SteaMax) and Vattenfall calculations (HSC) revealed that the reducing conditions cases were characterized in a similar way by both calculation tools. The system was dominated with the pure elements of Zn and Pb or with their chlorides and lead sulphide, apart from the case of the RPP fuel, which had a lower Cl content. The chlorides are believed to be responsible for the corrosion of the boiler walls.

More differences between Valmet and Vattenfall were visible for the oxidizing conditions. Here the systems do not correspond as well. For Vattenfall the system was dominated by chlorides over the whole temperature range. For the Valmet calculations Pb was predicted to exist mainly as gaseous lead oxide at temperatures above 840 – 900 °C, depending on the chlorine content of the fuel, whereas lead chloride ($PbCl_2$) was the dominating lead compound at lower temperatures. The calculations performed by Vattenfall with HSC predicted lead chloride to be the most stable lead compound over the whole temperature range. This difference is most likely due to differences in the

thermodynamic data used; PbO(g) has a higher stability in the HSC database than in the FACT database [34].

Zinc behaves very differently from lead under oxidizing conditions. Whereas lead is fully volatilized in the whole investigated temperature range, either as PbO(g) or $PbCl_2$(g), depending on the availability of chlorine, zinc is predominantly present as ZnO(s). Only a small fraction of the zinc available in the boiler (a couple of %) forms gaseous compounds, mainly $ZnCl_2$(g). Increasing the lambda value above 1.2 did not change the results observed for the oxidizing conditions.

The HSC data revealed that for reducing conditions in the temperature range 800 – 1000°C Zn(g), $ZnCl_2$(g) and Pb(g) are dominant while for the wall temperatures (350°C – 450°C) chlorine based and sulphur based compounds were present at the highest concentration. SteaMax calculations showed that zinc is totally vaporized under reducing conditions at 800 – 1000°C. The thermodynamically most stable form of zinc is Zn (g), in all cases. In addition to Zn (g) a small amount of $ZnCl_2$ (g) is formed in all cases. Under reducing conditions, lead is fully volatized at 800 – 1000°C. Minor lead compounds formed in the reducing part of the furnace are PbS (g), PbCl (g) and very low concentrations of $PbCl_2$(g). Wall temperatures of 350°C – 450°C were not simulated by Valmet.

Comparing the results with the deposits collected from Idbäcken one could speculate that the Zn, Pb based compounds condense at the walls in the form of chlorides and sulphides or in metallic form creating a high risk of corrosion. Corrosive lead and zinc chlorides might also form in the deposits over time. In the deposits collected from the boiler walls substantial levels of chlorine were measured. The equilibrium calculations were qualitatively in reasonable agreement with the experimental results.

More information is available in Appendix I Vattenfall Memo U13- 57 "HSC modelling results for KME 508 project" by Michal Glazer and Appendix K Valmet Memo "Chemical equilibrium calculations" by Paul Cho and Sonja Enestam.

3.7 Preliminary work with Thermocalc

Thermodynamically stable phases were modelled regarding corrosion composition and flue gas composition at 400 °C, the temperature of waterwalls in the boiler at 140 bar, by Thermo-Calc software, using the substance database (SSUB) and the solution database (SSOL). For simplification, chromium and molybdenum were excluded in both cases and pure iron and pure nickel were used for the modelling.

The modelling was performed with a constant amount of iron (or nickel), hydrogen and chlorine, and increasing amounts of oxygen, sulphur, potassium and lead. The gas phase in equilibrium with the solid phases is not shown in the diagram. The gas phase contains mainly nitrogen, water vapour and a small amount of hydrogen chloride. At high oxygen partial pressures the gas phase also contains oxygen gas and at lower oxygen partial pressures it also contains hydrogen gas, basically controlled by the hydrogen-oxygen-water

equilibrium. The oxygen gradient (partial pressure) is shown at the x-axis, the average of oxygen levels measured in the flue gas (less than 1%) is marked with an arrow in the Fig 3.7.1. The expected stable phases in a corrosion product/deposited layer are shown in y-axis.

The amounts of chlorine in hydrated form (HCl) and gaseous molecule chlorine (Cl_2) are calculated in the iron case and are shown at three different positions in boxes, Figure 3.7.1. It can be seen from the modelling that chlorine gas exists at extremely low levels (less than 0.1 ppm) at the tube surface at different oxygen partial pressures; instead the hydrated form is thermodynamically favoured, i.e. gaseous hydrogen chloride. (This is a smaller molecule than chlorine which could easily diffuse through a defect oxide of the type formed on the steel). It seems that chlorine can attack low alloy steels by gaseous hydrogen chloride rather than chlorine gas.

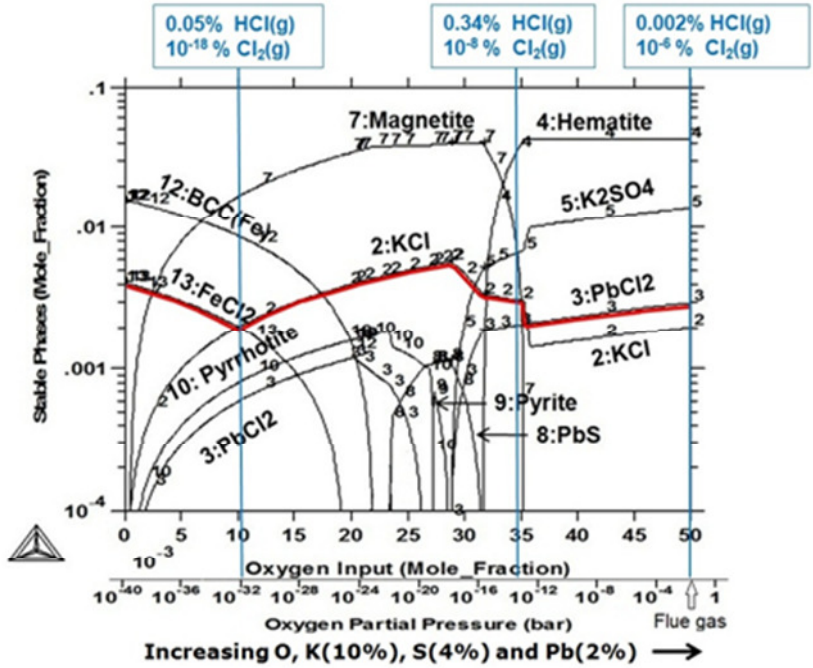


Fig. 3.7.1 **Modelling of iron in flue gas at 400ºC (input in 1 mole: 0.017Fe, 0.003Cl, 0.01H, balance N and gradient of O, K, Pb and S). The amount of K, Pb and S are related to the oxygen amount by factors 0.1, 0.02 and 0.04, respectively. The dominant Cl phases are shown by the red line. The amounts of HCl and Cl_2 at 3 different positions are shown in blue boxes.**

Fig. 3.7.1 shows that the calculated amount of HCl in the flue gas is 0.002% , or 20 ppm, which is similar to the value of 15 ppm measured by FTIR in the Idbäcken boiler (see section 3.3.1).

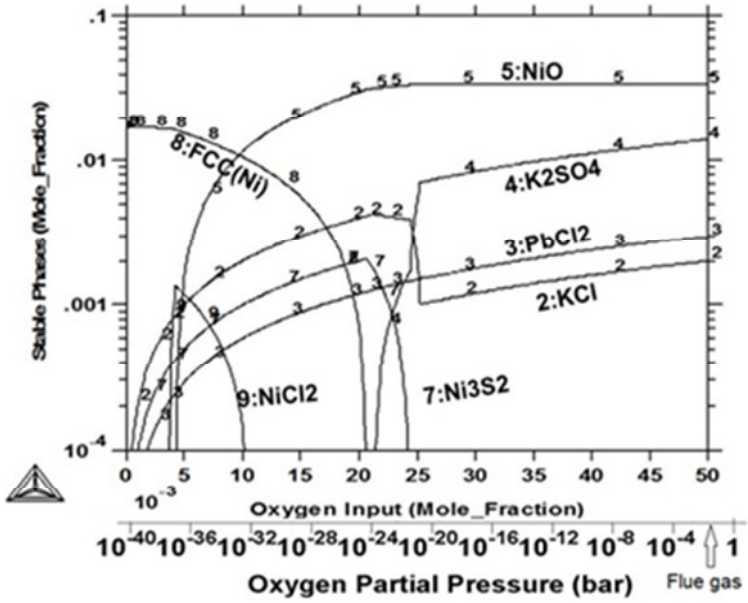


Fig. 3.7.2 Modelling of nickel. Input in mole: 0.017Ni, (instead of Fe). Otherwise same conditions as Fig. 3.7.1

As shown in the Thermo-Calc modelling, Figs 3.7.1 and 3.7.2, the stable phases in contact with the flue gas are metal oxides i.e. hematite and nickel oxide. (In the presence of chromium, spinel oxides containing chromium, iron and nickel are thermodynamically expected.) In the presence of heavy metals like zinc and lead, heavy metal chlorides may form as indicated in the modelling by lead chloride. However, at sufficiently high oxygen partial pressures other lead containing phases may form as shown by XRD data from the nickel coated tube, i.e. lead potassium chromate. This phase is unfortunately not included in the Thermo-Calc data bases. Alkali chlorides such as potassium chloride are also expected unless the sulphur and oxygen content is high enough to convert potassium chloride to potassium sulphate. This conversion tendency towards potassium sulphate can be observed in the modelling at higher oxygen partial pressures than 10^{-16} in the case of iron and 10^{-21} in the case of nickel, i.e. this process is thermodynamically more favoured in the case of nickel.

At lower oxygen partial pressures (i.e. closer to metal surface) the stability area of iron chloride is much larger than with nickel chloride. Obviously, nickel base alloys are expected to be less prone to chlorine induced corrosion from a thermodynamic point of view.

The simplified/preliminary thermodynamic modelling fitted well with the identified phases in the deposit/corrosion product, although thermodynamic data for some complex phases was missing in the databases.

3.8 Preliminary work with the GD-OES technique

The main aim with the investigation was to study the possibility of using GD-OES as an analysis method for samples exposed in short term tests where thin oxides is expected. Another scope was to study the distribution of elements in the deposit and if possible draw some conclusions regarding the initial corrosion. As a complement and for further development for studying the oxide thickness also minor analysis with FIB (Focused Ion Beam) was aimed to be performed.

Two methods were combined in order to achieve a depth profile for all wanted elements.

The Glow Discharge Optical Emission Spectroscopy (GD-OES) technique is based on the principle that optical emission is achieved when sputtering a sample surface with ions and atoms formed due to glow discharges in a low pressure Argon-plasma. By performing spectral analysis of the optical emission achieved when sputtering a sample, the composition of the sample can be determined. Most GD-OES instruments are equipped with up to 60 individual photomultiplier detectors which record a specific wave-length representing a specific material.

However, one problem was that no detector for the wave lengths of potassium was installed which meant that no information regarding potassium was achieved. Since potassium is an important and central element for these kinds of issues another technique was used to get data for potassium. To get information on the potassium distribution in the deposit a complementary CCD (charged coupled device)-detector was used which collected the whole light spectra. The light spectra was manually recorded every 15s and when the analysis was finished, the specific wave-lengths for potassium were manually evaluated and plotted in excel next to the GDOES spectra achieved. To confirm that this complementary technique gave comparable results two extra elements (Cl and Na) were plotted and compared with the data achieved from the GD-OES spectrum

The results showed that the selected elements, Cl and Na, showed a very good correlation in time when comparing the GD-OES and CCD techniques. This result implies that the potassium spectra from the CCD-camera can be used to study the distribution of the element in the deposit.

By comparing the signals of Na, K and Cl it was also shown that the potassium signal is following the signal of sodium and reaches its maximum at the same place. This result showed that the potassium signal could be read also from the GD-OES spectra if combined with the CCD-detector results.

No clear conclusions could be made regarding the oxide thickness of the samples exposed in the campaigns. Due to the complex and porous structure of the deposits it is rather difficult to get the depth information and sensitivity from only the GD-OES technique. One problem with these kinds of samples is that there is no element that only appears in the oxide. However, by combining the analysis with the FIB technique it was possible to tell that the oxide thickness was very thin, Fig. 3.8.1. It could also be seen that the deposits were porous and showed differences depending on position.

However, this was not further investigated but would be of great interest to work further within a future project.

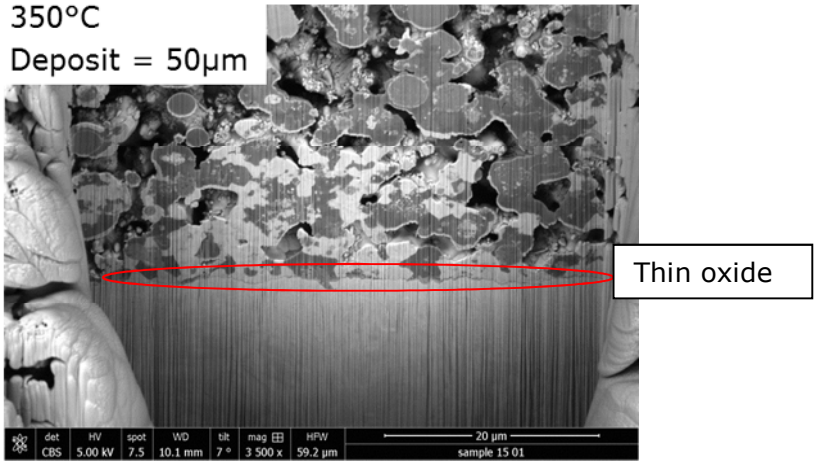


Fig. 3.8.1 Section produced by FIB technique on a 310 stainless steel sample exposed for 24 h at 350°C. The porous deposit and very thin oxide layer can be seen.

The results in the study show that GDOES is an analysis method that can be used in order to study the element distribution in deposit and oxide of a sample. However, due to the complexity of these kinds of samples it is not used for quantitative analysis today. The analysis could though be useful when studying for example corrosion mechanisms since the distribution of elements close to the metal surface can be detected. By developing the method further this technique could be a very useful tool. Since the analysis with this equipment is rather fast and gives good information of the deposit composition it is a tool that preferably could be used in the future when it comes to these kinds of samples

More information on the GD-OES development and results can be found in Appendix J, Swerea KIMAB report 702006 "GD-OES analysis of deposit probes" by Annika Talus.

4 Analysis of the results

4.1 Background to corrosion mechanisms in biomass combustion

In a waste wood combustion environment both alkali metals and chlorine (or chlorides) are present in the flue gases and deposits and can take part in the corrosion process. The most well-known mechanism is thought to occur by the diffusion of gaseous chlorine through a defect oxide scale [20] and reaction with the metal, where the oxygen partial pressure is low, at the metal-oxide interface to form a metal chloride. For example

$Fe(s) + Cl_2(g) \rightarrow FeCl_2(s,g)$ (1)

The volatile metal chloride then diffuses outwards through the oxide and reacts with oxygen in the outer part of the scale releasing chlorine, e.g.

$2FeCl_2\ (g) + 3/2O_2 \rightarrow Fe_2O_3 + 2Cl_2(g)$ (2)

The chlorine is then able to diffuse back into the scale and cause more corrosion, the so-called chlorine cycle or "active oxidation" [13, 20]

Other mechanisms proposed for chlorination include diffusion of chloride ions through the oxide scale or oxide grain boundaries [21] or a chlorine-modified non-protective oxidation process [22].

Our Thermo-Calc modelling, (section 3.7), showed that chlorine gas exists at extremely low levels (less than 0.1 ppm) at the tube surface at different oxygen partial pressures; instead the hydrated form is thermodynamically favoured, i.e. gaseous hydrogen chloride. (This is a smaller molecule than chlorine which could easily diffuse through a defect oxide of the type formed on the steel). It seems that chlorine can attack low alloy steels by gaseous hydrogen chloride rather than chlorine gas. This agrees with previous modelling [14].

It has been suggested that stainless steels may be attacked by chlorine induced corrosion [23], but others have suggested [17,18] that the chromia layer formed on stainless steels is attacked and dissolved in molten alkali or by heavy metal chlorides, i.e. by fluxing mechanisms, to form non protective chromates. For example, the following equation may occur at the corrosion front of austenitic stainless steels to produce a poor protective scale:

$½\ Cr_2O_3(s) + ¾\ O_2(g) + H_2O(g) + 2\ KCl(s) \rightarrow K_2CrO_4\ (s) + 2\ HCl(g)$ (3)

Low melting point or liquid chloride-containing salts in the deposits increase the corrosion rate because of increased reaction kinetics and transport of ions. [24-25] For example a potassium chloride-iron chloride eutectic mixture has a melting point in the range 340-393°C and the presence of zinc chloride and

lead chloride in an alkali chloride deposit can depress the first melting temperature to 200°C [16]. The salts attack the oxide by a fluxing mechanism whereby protective oxides dissolve in the salt. All these elements are present in waste wood.

4.2 Deposit chemistry and corrosion

The deposits taken from the three investigated boilers all contained K, Pb and Zn. The deposits taken from Idbäcken showed a wide spread in chemical composition , although Cl was found in all the samples, sometimes at very high levels (27 atomic %). K and S were found in all the deposits samples and Na was found in most. A higher K content was always associated with a high Cl content.

Deposits from Stevens Croft showed very high Cl levels, especially in the lower part of the boiler. Both Idbäcken and Stevens Croft suffer from extreme corrosion problems.

By contrast, the deposits taken from the walls of Händelö contained no or very little chlorine. Less than 0.5% Cl (atomic or weight%) was found in deposits on the back wall, but none from the other walls. This boiler does not suffer from corrosion problems. (Corrosion is considered to be under control – it can never be eliminated).

The effect of Cl is clear, although it is believed that the presence of Zn and Pb in waste wood also accelerate the corrosion. In a laboratory study it was observed that stainless steels exposed to lead chloride, $PbCl_2$, showed accelerated corrosion due to the formation of lead chromate, $PbCrO_4$, whereas $ZnCl_2$ was found to have only a marginal effect on the corrosion rate and no chromate was detected. (Chromate is non-protective, whereas chromia is a protective oxide) Both $PbCl_2$ and $ZnCl_2$ increased the corrosion rate on a low alloyed steel, but $PbCl_2$ was far more aggressive, [16,19].

In the present study it was found that lead and potassium together reacted with the chromia scale to form the chromate $K_2Pb(CrO_4)_2$. The presence of the sulphate $K_2Pb(SO_4)_2$ also shows that potassium and lead are reacting together.

Results of deposit analysis with the addition of sewage sludge showed that the amounts of chlorine, potassium and sodium in the deposits were reduced and the initial corrosion was reduced. Sludge inhibited the formation of non-protective K-Pb chromates from protective chromia, which is believed to have contributed to the reduced corrosion on the high alloy specimens.

4.3 Furnace environment and corrosion

In the Idbäcken boiler no correlation could be found between deposit composition and position in the furnace. However, comparison of the corrosion rates measured on the right wall with those on the back wall showed that the rates on the back wall are 30-50% higher. This is in general

agreement with the experience of the plant. No difference in deposit chemistry or flue gas chemical composition has been detected so far between these positions although extensive measurements have been performed at the plant. The average oxygen levels at both positions were less than 1%. Levels of below 0.5% were sometimes detected, and the fluctuation over time was large. The fluctuation was greatest at the back wall and least on the right wall.

Temperature measurements showed that the gas temperature varied between 855-895°C at probe A on the back wall and 667-766°C at probe B on the right wall. (The measuring points for the flue gas were 10 cm from the walls, measuring time 8 minutes, sampling interval 5 s). Metal loss in a power boiler furnace depends on a wide range of factors, for example gas flow rate, particle flows, flue gas chemistry, deposit chemistry and gas temperature or heat flux. In this case the higher flue gas temperature and the greater fluctuation in oxygen levels may account for the difference, in the absence of any other factors.

4.4 Alloy composition and corrosion

The corrosion rate measured over a 20,000 hour period on the 16Mo3 tube on the right wall of Idbäcken agreed well with the rate measured over a much shorter period of about 1000 hours by probe testing. This indicates that the corrosion rate is linear, the oxide formed non-protective and that it is possible to extrapolate results from shorter term probe testing to longer term measurements on this material in this environment. SEM analysis of polished 45° sections showed that chlorine appeared to be present in the oxides on the 16Mo3 steel tube and probe specimen. We were unable to detect any lead, and very little potassium. Use of the FIB technique (to make a fresh section in the materials) and subsequent rapid analysis by SEM showed that the chloride was formed as a separate layer under the oxide, but still no other elements could be detected (apart from Fe, of course).

It was more difficult to draw any such conclusions for the IN 625 coated tube; the uneven surface of the weld overlay on the tube meant that no accurate initial thickness measurements could be made. However, the very low average corrosion rate for the tube exposed for 20,000 hours may be representative and indicates a parabolic corrosion rate and a protective oxide. The results of probe testing showed that IN 625 had the lowest corrosion rates of all alloys tested. High amounts of lead were found at the corrosion front in the nickel alloy specimens and X-ray diffraction confirmed the presence of potassium-lead chromate. Very low or no amounts of Cl were found at the corrosion front in the IN 625 samples.

It appears then that the 16Mo3 steel is attacked by the diffusion of a chloride containing species, for example, chloride ions or gaseous hydrogen chloride while the nickel alloy is attacked by potassium and lead and possibly by fluxing of molten salts. The results for the stainless steels showed that they were attacked by mixture of both mechanisms. The IN625 showed the lowest corrosion rates (closely followed by the AMPT). Stainless steels 310, San 28,

153 MA and 253MA also showed low corrosion rates. The 16Mo3 experienced the highest corrosion rates.

Nickel-based alloys are expected to be less prone to chlorine/chloride induced corrosion that other alloys because the Gibbs free energy of nickel chloride formation is less negative than that of chromium chloride or iron chloride [12]. Alloy 625 overlay coating has been found to be acceptable in waste-firing boilers [26,27] and welding nickel alloys on to waterwalls is still the most popular method to reduce the waterwall corrosion problem in boilers [28,29]. Alloy 625 also has good weldability, and this gives it a lower risk of cracking during welding or in service [30]. Its coefficient of expansion is close to that of carbon steel, leading to lower thermal tensions [30].

The Kanthal APMT used in the exposure reported here had been given a pre-oxidation treatment of 8 hours in air at 1050 °C, by the material supplier, which produced an alumina-rich layer of about 1 µm thick. Alumina is known to exhibit excellent oxidation and corrosion resistance at high temperatures [31] and indeed FeCrAl alloys are predominately used at high temperatures. However, FeCrAl alloys have also recently been shown to form a type of alumina at temperatures as low as 400 °C and 500 °C and this oxide was sufficient to give protection against corrosion in oxygen-containing molten lead [32].

It is possible that the pre-oxidation treatment contributed to the low corrosion rate of the Kanthal APMT specimen even at the low temperature of 400 °C, although this effect would be expected to diminish at longer exposure times.

Previous laboratory studies at 600 °C for 168 h (one week) have shown that KCl accelerated the oxidation process in un-treated APMT and caused the formation of K_2CrO_4 which depleted the oxide in protective chromia causing Fe_2O_3 to be formed [33]. Under the same conditions the pre-oxidising treatment of 8 hours in air at 1050 °C had a tremendous positive effect on the corrosion resistance, leaving the protective oxide intact and totally suppressing chromate formation [33]. However, the opposite effect was found when Kanthal APMT was exposed at 600 °C for 860 hours in a waste-fired boiler. In that case the untreated material performed better than the pre-oxidised. It is also noteworthy that the alloy showed much better corrosion resistance than the stainless steel TP 304L [33]. Therefore it is unclear whether the pre-oxidation treatment always offers any benefits and no previous information is available on boiler exposures of this material at the low temperature of 400°C.

The results for APMT from this project showed that chlorine was present at the corrosion front (up to 5 at%) together with substantial amounts of zinc (up to 7 at%). Potassium was also present. It seems likely that potassium and zinc attacked part of the protective oxide and that chloride corrosion also occurred, albeit at a very low rate, indicating that the protective alumina-rich layer was continuing to exert some influence.

The ageing treatments on Fe-Cr-Al alloys showed that APMT is prone to embrittlement at 400-500°C. Testing should be continued on FeCrAl alloys with a lower chromium content. Kanthal APMT is produced by a power metallurgical route and may be suitable for use as a thermally sprayed coating.

4.5 Metal temperature and corrosion rate

Increasing the steam parameters from 140 bar/540°C to 190 bar/600°C/600°C means that the water temperature in the boiler will increase by 25°C. The results given in Fig 3.4.3 show that the corrosion rate increases steeply with temperature at temperatures above about 390°C, which is today's wall temperature. Reducing the pressure to 90 bar, gives a water boiling temperature of about 300°C and a corresponding metal temperature of 350°C and reduces the corrosion rate of 16Mo3 by 20-30% from today's level. Therefore reducing the boiler pressure is not an effective way of reducing the corrosion problems in a boiler, because a large reduction in pressure only results in a small reduction in the corrosion rates.

4.6 Thermodynamic modelling

The chemical equilibrium analyses performed in this project proved to be useful tools for initial analyses of new fuels and their influence on the boiler. The equilibrium calculation itself takes into account only the chemistry of the system and based on the mathematical calculations tries to minimize the Gibbs free energy of the system to check at which composition the system is at equilibrium. The equilibrium calculation process assumes that an infinite amount of time is available for the chemical reactions to occur which is in contrary to the situation in real boilers. In reality some reactions will happen faster and some slower, all of them controlled by kinetics. One has to be careful analysing the results and a comparison with experimental data is always advisable. Another limitation of the chemical equilibrium method is that it does not take into account anything related to the flow conditions in the boiler and boiler geometry which may influence the deposits formation and composition. The initial work with Thermocalc showed that many of the phases formed by the corrosive environment could be predicted. However, some data was missing from the data-bases, for example lead potassium chromate. The Thermocalc modelling also showed that HCl (g) was thermodynamically more important than chlorine gas. Thermocalc modelling should be extended to include alloys of nickel and iron.

4.7 New experimental techniques

Both the FIB technique and the GD-OES technique are useful for studying corrosion mechanisms as they provide fresh analysis areas which have not previously been contaminated by the ambient atmosphere. Chemical analysis of layers below the surface occurs simultaneously in GD-OES as the alloy is sputtered. However the results obtained are an average of the whole analysis area which is then destroyed. The FIB technique is more time consuming; a new section has to be produced first and then analysed afterwards, but it is possible to select the areas of interest. Both techniques should be pursued and used in the future.

5 Conclusions

The results showed that coating furnace wall tubes with a nickel base alloy (Alloy 625) drastically reduces the corrosion rate. The corrosion rate of the low alloy steel tubes, steel 16Mo3, was linear, being about 100µm per 1000 h (0.1 mm per 1000 h) from the probe testing and about 1 mm per 10,000 hours (0.1 mm per 1000h) from long-term evaluation of tubes. The corrosion rate of the Ni-alloy decreased with time, indicating parabolic kinetics being about 20µm per 1000 h from the probe testing and over a 3 year period was about 0.1 mm per 10,000 hours (10µm per 1000h).

An FeCrAl (Kanthal - APMT) alloy containing 21%Cr also showed low corrosion rates. However this alloy is susceptible to embrittlement in the temperature range of service, 400-500°C. Ageing of an FeCrAl alloy with 10% Cr showed that this alloy did not embrittle at the service temperature. FeCrAl alloys with Cr contents of about 10% should be evaluated in the future.

Austenitic stainless steels like TP310, San 28, 153 MA and 253MA showed moderate corrosion rates; the long-term data for stainless steel 316 was 0.15 mm per 10,000 hours. Stainless steels could potentially be an alternative to Ni-base alloys for protecting furnace walls

The method of applying the coating was found to be important. In general, the thermally sprayed coatings did not adhere as well as the weld overlay coatings.

The nickel alloy coated tubes and probe samples were attacked by a potassium-lead combination leading to the formation of non-protective potassium lead chromate. It has long been known that lead oxide attacks nickel- chromium alloys and reduces the corrosion resistance by the formation of lead chromate and it has more recently been shown that alkali metals such as potassium and sodium can also attack the protective chromia scale and form the unprotective chromates, potassium chromate and sodium chromate. However our work shows that potassium and lead together have been found in the corrosion process and very high levels of lead were found at the corrosion front.

The low alloy steel tubes and probe samples corroded by Cl attack. Initial results from examination of a FIB –produced section showed that iron chloride formed as a distinct layer under the oxide and oxy-chlorides were not detected.

The corrosion rate of 16Mo3 was temperature dependent. At metal temperatures higher than 390°C the corrosion rate increased rapidly, indicating that this material, without a coating, is unsuitable for use at higher boiler pressures. The corrosion rate could be reduced by reducing the pressure, but this reduction is marginal compared to other methods, for example, application of a Ni-base or stainless steel coating.

The Kanthal FeCrAl alloy was also attacked by chlorides, although this alloy showed very low corrosion rates. Chlorine, potassium and lead were found at

the corrosion front in stainless steels, indicating that they took part in the attack of these materials.

In the classic Cl- corrosion mechanism gaseous Cl_2 is assumed to diffuse through the oxide scale via pores and cracks and react with metal iron at the oxide-metal interface where the oxygen activity is low. However the Thermo-Calc modelling using the actual gas chemical composition showed that chlorine gas exists at extremely low levels (less than 0.1 ppm) at the tube surface; instead the hydrated form is thermodynamically favoured, i.e. gaseous hydrogen chloride. (This is a smaller molecule than chlorine which could easily diffuse through a defect oxide of the type formed on the steel).

Thermodynamic modelling using HSC-Chemistry of phases expected in the flue gases and comparison with SteaMax (based on FACTData) showed that the reducing conditions cases were characterized in a similar way by both calculation tools. The results were in broad agreement with the composition of the deposits collected from the walls of the Idbäcken boiler. Although there are some differences in the data-bases of these two programmes they can provide useful information regarding corrosivity in the combustion region with regards to the fuel.

Preliminary results from the use of digested sewage sludge which was mixed with the waste wood indicate that levels of Pb, K and Cl were reduced on the furnace wall deposits. This led to a reduction in the corrosion of all alloys tested during short-term tests. The addition of sewage sludge suppressed the formation of the non-protective potassium-lead chromate in Alloy 625 and the protective chromia layer was maintained. This sludge could be a useful means of reducing corrosion and should be further investigated.

Initial experiments with GD-OES and FIB- instruments showed that these were useful for preparing or analysing the corrosion front and should be used more in the future to facilitate more precise mechanistic studies.

6 Goal fulfilment

The project goal was to give recommendations about how to avoid water wall corrosion at increased boiler electrical efficiency /increased steam data when burning biomass and waste wood mixes. This has been fulfilled.

The following recommendations can be given :

Coating with a Ni-base alloy such as IN 625 in highly corrosive environments

Use of an additive, for example digested sewage sludge

Do not use un-coated 16Mo3 (or similar low alloy steel)

Avoid high flue gas temperatures, low oxygen partial pressures and rapidly fluctuating oxygen levels

7 Suggestions for future research work

Long-term measurements with digested sewage sludge as a fuel additive to obtain quantitative information on corrosion rates

Investigation of additional alloys and coatings as an alternative to Alloy 625 coated tubes. For example Fe-Cr-Al alloys with Cr lower than 21% and the stainless steels 310, San 28, 153 MA and 253 MA which also showed good results.

A cost-benefit analysis of different alternatives should be calculated

Follow up long-term corrosion results on coated tubes

Further use of Thermo-Calc, for example to simulate Ni- and Fe-alloys , i.e with additional alloy components such as Cr, Al, Ni and Mo

Development and further use of FIB- and GD-OES instruments for production and analysis of corroded sections

8 Literature references

[1] Jan Storesund et al. "Countermeasures to furnace corrosion on boiler tubes". M06-601. Värmeforsk report 1023, December 2007.

[2] Jan Storesund, Ragna Elger, Magnus Nordling, Peter Viklund. "Countermeasures to corrosion on waterwalls Part 2". M08-806. Värmeforsk draft report 2010.

[3] Q. Lu, G Hultquist, T Åkermark. "In-situ SIMS analysis of the initial oxidation of a commercial FeCrAl alloy in H2O-O2 gas at 600-800K" Eurocorr proceedings1992, p. 581-590.

[4] Il Soon Hwang et al. "Development of Alumina Forming Ferritic Steels for Pb-Bi Eutectic Cooled Applications" International Workshop on Structural Materials for Innovative Nuclear Systems Daejeon, Republic of Korea 31 Aug. –3 Sep. 2010

[5] Karlsson, S., Åmand, L., E., Pettersson, J., "Reducing High Temperature Corrosion when Burning Waste by Adding Digested Sewage Sludge", Proc Swedish-Finish Flame Days, Piteå, January,(2011), pp. 1-19.

[6] Davidsson, K.O., Åmand, L. E., Elled, A. L., Leckner, B., "Effect of Co-firing Coal and Biofuel with Sewage Sludge on Alkali Problems in a Circulating Fluidized Bed Boiler", Energy Fuels, Vol. 21, No. 4, (2007), pp. 3180-3188.

[7] Deacon, J. DuPont, C. Kiely, A. Marder, P. Tortorelli, Oxid. Met.,72, 67, (2009)

[8] Henderson, P.J., Ljung P., Eriksson, Th., Westberg S-B, Hildenwall, B., and T. Åbyhammar, T.: Corrosion testing of superheater steels for biomass-fired boilers and the effects of co-firing with coal. Proc Conf "Advanced Materials för 21st Century Turbines and Power Plant". pp 1094-1104. Eds. A. Strang et al. Book 736, IOM Communications, London, UK, (2000).

[9] Montgomery, M. and Larsen, O.H.: Field test corrosion experiments in Denmark with biomass fuels Part II: Co-firing. Materials and Corrosion, 53, pp185-194 (2002).

[10] Strömberg, B. and Svärd, S.H.: Fuel Handbook 2012. Värmeforsk report 1234, (2012). Downloaded from http://www.varmeforsk.se/rapporter?action=show&id=2782 (In Swedish). An earlier version (2006), translated into English, is available at http://www.varmeforsk.se/reports?action=show&id=1945

[11] P. Viklund, PhD thesis, KTH Royal Institute of Technology, Stockholm, Sweden, 2013.

[12] A. Zahs, M. Spiegel,H. J. Grabke, Corros. Sci., 42, 2000, pp.1093-1122

[13] E. Reese, H.J. Grabke, Werkst. Korros., 43, 1992, pp.547-557

[14] P.Szakálos, P. Henderson, R. Petterson, Presented at Proceedings of the 16th international corrosion conference, Beijing, China, 19-24 September 2005.

[15] T. Ishituska, K. Nose, Corros. Sci., 44, 2002, pp. 247-263

[16] S. Enestam, Ph.D. Thesis, Åbo Akademi, Åbo, Finland, 2011

[17] J. Pettersson, H. Asteman, J. E. Svensson, L. -G. Johansson, Oxid. Met., 64 (112), 2005, pp. 23-41

[18] S. Karlsson, J. Pettersson, L. -G. Johansson, J. -E. Svensson, Oxid. Met., 78, 2012, pp. 83-102

[19] Bankiewicz, D., Enestam, S., Yrjas, P., and Hupa, M., Experimental studies of Zn and Pb induced high temperature corrosion of two commercial boiler steels. Fuel Processing Technology, vol 105, Jan 2013 pp 89-97.H.

[20] J. Grabke, E. Reese, M. Spiegel, Corros. Sci., 37(7), 1995, pp. 1023-1043

[21] N. Folkeson, L. -G. Johansson, J. –E. Svensson, J. Electrochem. Soc., 154, 2007, pp. 515-521

[22] P. Viklund, R. Pettersson, oxid. Met., 76, 2011, pp. 111-126

[23] Y.-N. Chang, F. –I. Wei, J. Mater. Sci. , 26, 1991, pp. 3693-3698

[24] H. P. Nielsen, F. J. Frandsen, K. Dam-Johansen, L. L. Baxter, Prog. Energy Combust. Sci. 2000, 26, 283.

[25] P. Kofstad, High Temperature Corrosion, Elsevier Applied Science, New York 1988.

[26] G. Y. Lai, Presented at NAWTEC 12, May 17-19, 2004 Georgia, USA

[27] P. Amador, G. Lai, Presented at NAWTEC 11, April 28-30, 2003 Florida, USA

[28] D. O. Albina, PhD Thesis, Colombia University, New York, USA, 2005

[29] R. F. A. Pettersson, J. Storesund, M. Nordling, Corros. Eng. Sci. Technol., 44(3), 2009, pp. 218-225

[30] A. Stålenheim, P. Henderson, "Materials for higher steam temperatures (up to 600 °C) in biomass and waste fired plant. A review of present knowledge" Värmeforsk report 1174, (2011). Downloaded from , http://www.varmeforsk.se/rapporter?action=show&id=2439.

[31] B. Jönsson, Q. Liu, D. Chandrasekaran, R. Berglund, F. Rave, Oxid. Met., 79, 2013, pp. 29-39

[32] A. Weisenburger, A. Jianu, S. Doyle, M. Bruns, R. Fetzer, A. Heinzel, M. DelGiacco, W. A. G. Müller, J. Nucl. Mater., 437, 2013, pp.282-292

[33] J. –E. Svensson, L. –G. Johansson, K. Hellström, J. Petterssson, N. Israelsson, B. Jönsson, D. Chandrasekaran, R. Norling, Final report on KME414 FeCrAl alloys for superheaters in biomass and waste fired boilers a feasibility study, Elforsk, 2009

[34] T. Talonen, "Chemical equlibria of heavy metals in waste incinerations: Comparison of thermodynamic databases, Åbo Akademi, report 08-02, 2008

9 Publications

1. The analysis of furnace wall deposits from a low NOx waste wood fired bubbling fluidised bed boiler. Y. Alipour, P. Viklund and P Henderson, VGB PowerTech, pp 96- 100, Dec (2012).
2. The effect of a nickel alloy coating on the corrosion of furnace wall tubes in a waste wood fired power plant. Y. Alipour, P. Henderson and P. Szakalos.. Materials and Corrosion, published online: 2 JUL 2013.
3. High Temperature corrosion in a biomass-fired power plant. Yousef Alipour. Licentiate thesis. June 2013. Available on http://www.diva-ortal.org/smash/get/diva2:617187/FULLTEXT01.pdf
4. Effect of temperature on the corrosion of furnace walls in a waste-to-energy boiler Yousef Alipour and Pamela Henderson. Abstract accepted for presentation at Microscopy of Oxidation-9, 14-16 April 2014, Nottingham, UK. Proceedings to be published in "Materials at High Temperatures"
5. The effect of co-firing of sewage sludge with waste wood on furnace wall corrosion. Yousef Alipour and Pamela Henderson. Extended abstract accepted for presentation at ISHOC-2014. International Symposium on High-temperature Oxidation and Corrosion 2014 23-27 June 2014. Hakodate, Hokkaido Japan.

10 Appendices

Appendix A

"The analysis of furnace wall deposits in a low NOx waste wood fired bubbling fluidised bed boiler" by Yousef Alipour, Peter Viklund and Pamela Henderson and published in VGB PowerTech 2012.

Appendix B

Vattenfall Memo U 12-62 " Analysis of deposits from Steven's Croft" by Annika Stålenheim

Appendix C

Vattenfall Memo U 13-18 " Evaulation of Waterwall Materials from test panels 2012" by Annika Stålenheim and Mattias Mattsson.

Appendix D

Vattenfall Memo U13-03 "Measurement campaign November 2011, KME 508 Furnace wall corrosion" by Annika Stålenheim and Pamela Henderson

Appendix E

"The effect of co-firing of sewage sludge with waste wood on furnace wall corrosion" by Yousef Alipour and Pamela Henderson. Extended abstract accepted for presentation at ISHOC-2014. International Symposium on High-temperature Oxidation and Corrosion 2014 23-27 June 2014. Hakodate, Hokkaido Japan.

Appendix F

"The effect of a nickel alloy coating on the corrosion of furnace wall tubes in a waste wood fired power plant" by Y. Alipour, P. Henderson and P. Szakálos. Materials and Corrosion 2013. Published on-line 02-07-2013.

Appendix G

Vattenfall Memo U 13-66 "Corrosion of a low-alloy furnace wall material at different temperatures in a BFB boiler firing 100% waste wood", by Pamela Henderson, Yousef Alipour and Mattias Mattsson

Appendix H

"Development of embrittlement resistant FeCrAl alloys" by J. Ejenstam, M. Thuvander, F. Rave, J.N. Olovsjö and P. Szakalos.

Appendix I

Vattenfall Memo U13- 57 "HSC modelling results for KME 508 project" by Michal Glazer.

Appendix J

Swerea KIMAB report 702006 "GDOES analysis of deposit probes" by Annika Talus.

Appendix K

Valmet Memo "Chemical equilibrium calculations" by Paul Cho and Sonja Enestam.

ELFORSK

SVENSKA ELFÖRETAGENS FORSKNINGS- OCH UTVECKLINGS - ELFORSK - AB

Elforsk AB, 101 53 Stockholm. Besöksadress: Olof Palmes Gata 31
Telefon: 08-677 25 30, Telefax: 08-677 25 35
www.elforsk.se