High temperature corrosion in a biomass-fired power boiler

Reducing furnace wall corrosion in a waste wood-fired power plant with advanced steam data

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Licentiate Thesis in Corrosion Science
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To my father
Abstract

The use of waste (or recycled) wood as a fuel in heat and power stations is becoming more widespread in Sweden (and Europe), because it is CO₂ neutral with a lower cost than forest fuel. However, it is a heterogeneous fuel with a high amount of chlorine, alkali and heavy metals which causes more corrosion than fossil fuels or forest fuel.

A part of the boiler which is subjected to a high corrosion risk is the furnace wall (or waterwall) which is formed of tubes welded together. Waterwalls are made of ferritic low-alloyed steels, due to their low price, low stress corrosion cracking risk, high heat transfer properties and low thermal expansion. However, ferritic low alloy steels corrode quickly when burning waste wood in a low NOₓ environment (i.e. an environment with low oxygen levels to limit the formation of NOₓ). Apart from pure oxidation two important forms of corrosion mechanisms are thought to occur in waste environments: chlorine corrosion and alkali corrosion.

Although there is a great interest from plant owners to reduce the costs associated with furnace wall corrosion very little has been reported on wall corrosion in biomass boilers. Also corrosion mechanisms on furnace walls are usually investigated in laboratories, where interpretation of the results is easier. In power plants the interpretation is more complicated. Difficulties in the study of corrosion mechanisms are caused by several factors such as deposit composition, flue gas flow, boiler design, combustion characteristics and flue gas composition. Therefore, the corrosion varies from plant to plant and the laboratory experiments should be complemented with field tests. The present project may thus contribute to fill the power plant corrosion research gap.

In this work, different kinds of samples (wall deposits, test panel tubes and corrosion probes) from Vattenfall’s Heat and Power plant in Nyköping were analysed. Coated and uncoated samples with different alloys and different times of exposure were studied by scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX), X-ray diffraction (XRD) and light optical microscopy (LOM). The corrosive environment was also simulated by Thermo-Calc software.

The results showed that a nickel alloy coating can dramatically reduce the corrosion rate. The corrosion rate of the low alloy steel tubes, steel 16Mo3, was linear and the oxide scale non-protective, but the corrosion rate of the nickel-based alloy was probably parabolic and the oxide much more protective. The nickel alloy and stainless steels showed good corrosion protection behavior in the boiler. This indicates that stainless steels could be a good (and less expensive) alternative to nickel-based alloys for protecting furnace walls.

The nickel-alloy coated samples were attacked by a potassium-lead combination leading to the formation of non-protective potassium lead chromate. The low alloy steel samples corroded by chloride attack. Stainless steels were attacked by a combination of chlorides and potassium-lead.
The Thermo-Calc modelling showed 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. Consequently chlorine can attack low alloy steels by gaseous hydrogen chloride rather than chlorine gas as previously proposed. This is a smaller molecule than chlorine which could easily diffuse through a defect oxide of the type formed on the steel.

Keywords: High temperature corrosion, Waterwalls, Power plant corrosion, NO\textsubscript{x} reducing enviroments, Biomass, Waste wood, Thermodynamic calculation modelling, corrosion-resistance alloy, Furnace wall corrosion
Sammanfattning

Användningen av returträ som bränsle i kraftvärmeverk blir allt vanligare i Sverige (och Europa), eftersom det är koldioxid-neutralt med en lägre kostnad än skogsbränsle. Det är dock ett heterogent bränsle med höga halter av klor, alkali och tungmetaller som orsakar mer korrosion än fossila bränslen eller skogsbränsle.

En del av pannan som drabbats av en hög korrosionrisk är eldstadsväggen som bildas av rör som svetsas samman. Eldstadsväggar är tillverkade av ferritiska låglegerande stål på grund av deras låga pris, goda spänningskorrosionsmotstånd, låga värmearmutning och höga värmekapacitet. Men ferritiska låglegerade stål korroderar snabbt vid förbränning av returträ i en låg NOx-miljö (dvs. en miljö med låga syrehalter för att begränsa bildandet av NOx). Två av de viktigaste korrosionsmekanismerna förutom ren oxidation, som tros ske i avfallseldade miljöer, är klor- och alkali-inducerad korrosion.

Även om finns det ett stort intresse från kraftverksägare för att minska kostnaderna kopplade till eldstadskorrosion, har mycket lite rapporterats om eldstadskorrosion i biobränsleledade pannor. Korrosionsmekanismer i eldstäder undersöks vanligtvis i laboratorier, där analysen av resultaten är lättare. I kraftverk är det mer komplicerat. Svårigheterna med att studera korrosionsmekanismer orsakas av flera faktorer såsom avlagringssammansättning, rökgasflödet, pannutformning, förbränning och rökgassammansättning. Därför varierar korrosionen från anläggning till anläggning och laboratorieexperiment bör kompletteras med fältförsök. Detta projekt kan således bidra till att fylla denna lucka i korrosionsforskningen kopplad till kraftverk.

I detta arbete har olika typer av prover (avskrapade avlagringar, provrörpanel och korrosionssonder) från Vattenfalls kraftvärmeverk i Nyköping analyseras. Belagda och obela prover med olika material och olika exponeringtider studerades genom svepelektronmikroskopi (SEM), energidispersiv röntgenanalys (EDX), röntgendiffraktion (XRD) och optisk mikroskopi (LOM). Den korrosiva miljön har också modellerats med hjälp av Thermo-Calc programvara.


gasformig väteklorid. Följaktligen kan klor attackera lågerat stål genom gasformig väteklorid snarare än klorgas som tidigare föreslagits. HCl är dessutom en mindre molekyl än Cl₂, som därför kan diffundera lättare genom ett defekt oxidskal som bildats på stål.

Nyckelord: Högtemperatekorrosion, Eldstadsväggar, kraftverks korrosion, låg Nox mijöer, biomassa, returträ, Termodynamisk modellering, korrosionsbeständighet legering, eldstadskorrosion
Preface

This Thesis is based on the following appended papers:

Paper I


The author did most of the SEM and XRD analyses. The author collected all the samples. The paper was mainly written by P. Henderson.

Paper II


The author did all thermodynamic modelling, conducted all SEM analyses. The paper was mainly written by the author.

Paper III


The author did all experimental work, SEM and LOM as well as thermodynamic modelling. The paper was mainly written by the author.
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1 Introduction

The use of biomass as a fuel for power production has continued to rise in the last few decades, because it is a renewable energy source and CO₂ neutral; in contrast fossil fuels have a green house effect [1]. In June 2006 the government of Sweden agreed that by year 2020, 50% of the energy needed should be provided by clean renewable energy resources [2-3]. One kind of biomass is waste wood (recycled wood). Waste wood is a heterogeneous fuel and contains alkali metals, heavy metals and chlorine which lead to more corrosion problems in boilers compared to forest fuel or fossil fuel combustion (Table 1).

Table 1. Mean value of key elements of waste wood, Forest wood and Coal [4]

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

A part of the boiler suffering from a corrosion risk is the furnace walls, so-called water walls. Different types of corrosion attack are thought to occur in a waste wood-fired power plant. The chlorine cycle (i.e. diffusion of chlorine molecules through a defect oxide) has been reported as the main reason for corrosion [5-7]. Chlorine may also diffuse as chloride ions instead of in the gas phase [8]. Some suggested the hydrated form (i.e. gaseous HCl) may act as the corrodant [9]. This is a smaller molecule than chlorine, so diffuses easier through the oxide scale via pores and cracks [9]. Other authors reported that low melting point chloride-containing salts increase the corrosion rate [10-13].

Power plant owners wish to reduce maintenance costs corresponding to corrosion, but less work has been reported on waterwall corrosion compared to superheater corrosion. Moreover, corrosion mechanisms have usually been studied in laboratories. In power plants corrosion investigations are more difficult. Several factors such as deposit composition, flue gas flow, boiler design, combustion characteristics, gas flue composition and frequency of cleaning process such as soot-blowing cause difficulties in the study of corrosion mechanisms. Therefore, the corrosion varies from plant to plant and the laboratory experiments should be complemented with field ones.
These two major gaps encouraged us to perform this project. In this work we have studied corrosion in a power plant, but have also modelled thermodynamically.
2 Aim of this work

Power plant owners wish to reduce the costs associated with high temperature corrosion. This project goal is to lead to a better understanding of the corrosive processes happening at the power station furnace walls, and thereby be able to propose some solutions to the corrosion problem.

This will be achieved by analysing the deposits scraped from the furnace walls and from short term deposit probes and longer term corrosion probes and tube samples. In this work reported here the compositions of deposits forming on the waterwalls have been analysed, the effect of alloy composition has been investigated and corrosion products have been studied, when burning waste wood.
3 Fuel

Fuel is defined as a substance that stores energy which can later be extracted. Chemical fuels are able to release energy by reacting with the surrounding environment. Fossil fuel and biofuel are two types of chemical fuel.

3.1 Fossil fuel

Fossil fuels are made by natural processes over a long period of time, contain high amounts of carbon and can be burned as a source of heat or power [14]. Coal, petroleum and natural gas are some examples [14]. Energy Information Administration estimated that around 80% of the energy used world-wide in 2011 came from fossil fuels [15]. Fossil fuels produce around 23 billion tonnes of carbon dioxide per year [15]. CO₂ is one of the main greenhouse gases that leads to global warming. [16] A main goal of several European countries in energy is to reduce the use of fossil fuels and replace them with renewable energy.

3.2 Biofuel

Biofuel is any fuel with energy produced from biological carbon fixation (i.e. reduction of CO₂ to organic compounds) [17]. Oil price inflation and environmental politics are the main reasons for using biofuels. Biomass is a type of biofuel which is said to be a renewable energy source [18]. The difference between biomass and fossil fuel is the time scale. The age of fossil fuels is usually millions of years, whereas for biofuels it is less than 80 years (a human lifetime). This leads to biomass being called CO₂ neutral.

3.2.1 Waste wood

A less expensive type of biomass is waste wood (recycled wood). As the price of virgin wood increases, more waste wood is being used [19]. The main source of waste wood is from construction, so waste wood can contain paint, other chemicals or plastics. Therefore, this fuel contains alkali metal, heavy metals and chlorine [20].
4 Heat and power station

A general definition of a boiler is a closed vessel in which water or another fluid is heated. The heated or vaporized fluid exits the boiler for use in various processes or heating applications [21]. In power plants a boiler with superheaters is used to drive a turbine. The turbine converts steam energy to rotational energy and then the turbine generator produces electrical energy. The excess heat can be used to heat the water of the district-heating network. So the process can produce both heat and electricity. Boilers without superheaters cannot produce electricity and are used to produce only heat [22]. Some important types of boiler technology are grate firing, pulverised firing, fluidised bed, circulating fluidised bed and bubbling fluidised bed.

4.1 Grate firing technology

This system is employed for the combustion of solid fuels in small and medium sized units. Grate construction varies due to different fuels, although the basic principle for all of them is drying, devolatilising and finally burning the fuel. The fuel moves from the feeding section to the ash removal section on the other end of the fireside. The grate can be stationary or vibrating [23]. Depending on grate size they can be air-cooled or water-cooled. Small grates are generally air-cooled. The positive points of this technology are namely low fuel preparation costs and continuous fuel supply. On the other hand the narrow range of fuels and the restriction to a bale type are disadvantages of the technology [24].

4.2 Pulverised firing technology

The name is after the form of fuel in this firing technology. It is very common in power plants with coal combustion. A mill is used to grind the fuel into the particle with the proper size for burning. The fuel particles get suspended in the combustion chamber, so burning is more efficient compared with grate firing [24].

Figure 1. Schematic view of different firing technology a) grate b) pulverised
4.3 Fluidised bed technology

In fluidised bed combustion (FBC) a fluidised bed suspends solid fuels on upward-blowing jets of air during the combustion process. Special design of the air nozzles at the bottom of the bed allows air flow without clogging. The result is a turbulent mixing of gas and solid. They can be fired on coal and biomass. Some benefits of such kind of combustion are as follows:

1. Production of NO\textsubscript{x} is temperature dependant. In FB combustion the temperature is less than in other combustion processes hence it results in lower production of NO\textsubscript{x}.
2. FBC reduces the amount of sulphur emitted in the form of SO\textsubscript{x} [25].

Bubbling bed, deep bed and circulating bed are three common types of fluidised bed. All boilers use the same principle. Air blows through a grate and fluidises the fuel. The temperature should not become higher than the fusion point of the bed material and ash produced during combustion.

4.3.1 Bubbling fluidised bed

In BFB air mixes the fuel and bed material and keeps them in a fluidised state. Bed or fuel particles are surrounded by hot gas. The bed material (often coarse sand) is heated by the burning fuel, which is the heat source for new fuel particles [25].

4.3.2 Deep bed

An alternative of the bubbling bed system is the deep bed (i.e. pressurised bed reactor), where the entire system is enclosed in a pressure vessel. This technique helps to combust toxic wastes at lower temperatures than in atmospheric pressure. Both circulating bed and deep bed reactors have higher maintenance costs and are more expensive than the atmospheric bubbling bed type [25].

4.3.3 Circulating fluidised bed

CFB is a relatively new and evolving technology that has become a very popular method of generating low-cost electricity with very low emissions and environmental impacts [25]. This type of bed consists of a boiler and a high-temperature cyclone. A coarse fluidizing medium and char in the flue gas are collected by the high-temperature cyclone and returned to the furnace for recirculation. The hot gases from the cyclone pass to the heat transfer surfaces and go out of the boiler.

Figure 2 shows a schematic view of different types of fluidised beds.
Figure 2. Various types of air distributor commonly employed within FBC a) bubbling bed b) deep bed c) circulating bed
5 Possible oxidation and corrosion mechanisms in the furnace wall when burning waste

A part of the boiler which is subjected to a high corrosion risk is the furnace wall. The furnace wall, so-called waterwall, is formed of tubes welded together. They contain water. The tubes 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. Figure 3 presents two tubes of a furnace wall.

![Figure 3. Cross section of waterwalls](image)

However carbon steels corrode rapidly when burning waste in a low NO\textsubscript{x} environment (i.e. an environment with low oxygen levels to limit the formation of NO\textsubscript{x}) [26].

Different forms of corrosion are thought to happen in a waste fired environment.

5.1 Chlorine/chloride corrosion

Chlorine from both chloride-rich deposits and flue gas exists in the boiler environment when burning waste wood and corrosion can initiate [27]. Grabke et al. [6] suggested that chlorine corrosion can occur by diffusion of gaseous chlorine through the oxide scale via pores and cracks and reaction with metal at the oxide-metal interface where the oxygen activity is low, while the outer part of the scale (high pO\textsubscript{2}) contains mainly metal oxides. Iron (II) chloride then diffuses outwards and oxidises, according to Equation 1 (M stands for metal).

\[ XMC\textsubscript{2}(g) + Yo\textsubscript{2}(g) \rightarrow M\textsubscript{x}O\textsubscript{2y}(s) + XCl\textsubscript{2}(g) \] (1)

The released chlorine can then participate again in the corrosion process, the so-called chlorine cycle. It is also named active oxidation due to the creation of a porous non-protective oxide layer [7]. Alternatively, HCl may act as the corrodant. This is a smaller molecule than chlorine which could more easily diffuse through a defect oxide [9].
Chlorine may also diffuse as chloride ions instead of in the gas phase, according to Folkeson et al [8]. In this mechanism the chloride ions diffuse along the oxide grain boundaries. It is postulated that the iron chloride formed at the grain boundaries increases the rate of transport of oxygen and iron ions [8]. The cathodic process can be clarified by the following Equations [28, 8]:

\[ Fe \rightarrow Fe^{2+} + 2e^- \quad (2a) \]

then

\[ 2HCl + \frac{1}{2}O_2 + 2e^- \rightarrow 2Cl^- + H_2O \quad (2b) \]

or

\[ 2KCl + \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2Cl^- + 2KOH \quad (2c) \]

5.2 Alkali corrosion

Alkali products such as chlorides, sulphates and carbonates exist at the waterwall’s deposits and can have a role in the corrosion problem. For example potassium chloride can attack the protective chromia scale and form the non-protective chromate [29], Equation 3:

\[ 2KCl(s) + \frac{1}{2}Cr_2O_3(s) + H_2O(g) + \frac{3}{4}O_2(g) \rightarrow K_2CrO_4(s) + 2HCl(g) \quad (3) \]

It is also reported that NaCl [30] or K₂CO₃ [31] can have the same behaviour in reaction with chromia.

5.3 Molten salt corrosion

Low melting point or liquid chloride-containing salts in the deposits may increase the corrosion rate because of increased reaction kinetics and transport of ions [32]. Table 2 shows the melting point of some salts or eutectic mixtures [33-34]. The salts attack the oxide by a fluxing mechanism whereby protective oxides dissolve in the salt. Corrosion by molten salts is also named hot corrosion which is in two types. In hot corrosion type I, the salt is molten. In contrast, type II corrosion occurs below the melting point of the salt [35].

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl-ZnCl₂</td>
<td>230</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>283</td>
</tr>
<tr>
<td>KCl-FeCl₂</td>
<td>355</td>
</tr>
<tr>
<td>KCl-PbCl₂</td>
<td>412</td>
</tr>
<tr>
<td>NaCl-CrCl₂</td>
<td>437</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>489</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>884</td>
</tr>
</tbody>
</table>
5.4 Thermodynamic background

Metals are thermodynamically unstable with respect to the surrounding environment and will form oxides, sulphides, carbides, etc. or mixtures of products [35]. In the case of ambient oxygen, the oxide layer will be created only if the ambient oxygen pressure is more than the dissociation pressure of the oxide, Equation (4) [35].

\[ PO_2 \geq \exp \left\{ -\frac{2 \Delta G^0(M_aO_b)}{bRT} \right\} \] (4)

\( \Delta G^\circ \) (M\textsubscript{a}O\textsubscript{b}) represents the standard free energy change of the metal oxide at temperature T. The values of \( \Delta G^\circ \) are generally termed as a function of T.

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \] (5)

Where \( \Delta H \) and \( \Delta S \) are enthalpy change and entropy change respectively. The standard free energy of formation of the oxides of metals and alloys per mole of oxygen can be plotted against temperature, in the so-called Ellingham/Richardson diagram [36]. The diagram can be plotted for carbides, chlorides, etc. in the same way. The diagram can help to predict which element in an alloy can react with the surrounding environment, i.e. the most stable oxides in the diagram have the largest negative values of \( \Delta G^\circ \) [35].

5.4.1 Oxide formation and growth

Most metals react with oxygen to form oxides. The oxidation rate increases with increasing temperature. Oxidation initially begins by the absorption and dissociation of oxygen on the surface from the atmosphere, followed by nucleation. The nuclei grow on the metal surface until a continuous film is formed [35]. Once the metal is covered by a thin oxide layer, oxidation can continue by the transportation of reactants through that layer. If the layer is pore or crack free, the transport must be by diffusion in the solid state (i.e. by diffusion of electrons and ions).

\[
\begin{align*}
O_2(g) + 4e^- &\rightarrow 20^2^-(\text{ions}) \\
O_2(g) &\rightarrow O_2^2^- (\text{ions}) \\
O_2(g) &\rightarrow O_2^2^- (\text{ions}) \\
M(s) &\rightarrow M^{x^+} (\text{ions})
\end{align*}
\]

Figure 4. Schematic view of oxidation a) initial formation b) nucleation c) formation of the continuous film

High temperature materials are often exposed to environments containing mixtures of oxidants rather than single-oxidant environments. In most cases environments contain both oxygen and sulphur, consequently oxides, sulphates and sulphides form. CO, CO\textsubscript{2}, H\textsubscript{2}O, H\textsubscript{2}S, H\textsubscript{4}C\textsubscript{2}, O\textsubscript{2}, SO\textsubscript{3} and SO\textsubscript{2} are present in the combustion of sulphur-bearing fuels in power
plants. In oxidation conditions where sulphur and oxygen are present together with some source of alkali, alkali sulphates may deposit on the metal, for instance:

$$2NaCl(g) + SO_2(g) + \frac{1}{2} O_2(g) + H_2O \rightarrow Na_2SO_4(S) + 2HCl(g) \quad (6)$$

Chlorine containing species are also of great interest in high temperature corrosion, which can lead to chlorination of the metal. Metal chlorides are more corrosive because they are excellent ionic conductors, they may form low melting point salts and they easily volatilize. Another example for oxidation in mixed-gas environments is air which contains nitrogen and oxygen. So nitrides may form as well as oxides. Similarly atmospheres containing carbon and oxygen gases may result in both carbides and oxides [37].

Oxidation growth rates (i.e. weight gain or increase in oxide thickness) can be divided into three kinetics laws for most of metals and alloys, parabolic, linear and logarithmic [38]. Figure 5 presents weight gain as a function of time for the three laws.

![Figure 5. Time against weight gain for common metal oxidation [35]](image)

For several metals at low temperatures (below 350°C) the reaction is quite fast at the beginning and then falls down to a low speed. This manner is often described by logarithmic rate equations, Equation (7) and (8).

$$x = k_{log} \log(t + t_0) + A \quad (7) \text{ direct logarithmic}$$

$$\frac{1}{x} = B - k_{ii} \log t \quad (8) \text{ Inverse logarithmic}$$

$x$ represents the oxide thickness or oxide surface area. $t$ is the time. $k_{log}$ and $k_{ii}$ denote rate constants, and $A$ and $B$ are constants.

At high temperatures the oxidation of many metals is found to follow a parabolic time dependence. Equations (9) and (10) show the differential and integral forms of the parabolic equation.
Where $k_p^r$ and $k_p$ present the rate constants and $C$ is the integration constant.

Parabolic oxidation occurs when the oxide is an effective barrier and cations or oxygen ions have to diffuse through the scale to react with each other. As the scale becomes thicker, diffusion takes longer and the oxidation rate falls [35].

In parabolic and logarithmic equations reaction rates decrease with time. But in linear oxidation, the rate is constant with time and is therefore independent of the amount of gas or metal. Linear oxidation kinetics are given by

\[
\frac{dx}{dt} = k_1 t \tag{11}
\]

\[
x = k_1 t + C \tag{12}
\]

Where $k_1$ and $C$ are the rate constant and the integration constant respectively [39].

Linear oxidation occurs when the oxide layer does not form an effective barrier, for example if it is cracked or porous [38].

5.5 Oxidation of different alloys

When an alloy containing different metals is surrounded by air, the oxide of metal, which has the lowest Gibbs free energy, is the more stable. An alloy’s constituents differ with respect to oxygen affinity and diffusivity in the alloy and in the oxide scale. These differences are used in the design of oxidation-resistant alloys. Thus, high temperature alloys contain constituents (e.g. chromium, aluminium, silicon) with a high oxygen affinity intended to form an external protective scale ($\text{Cr}_2\text{O}_3$, $\text{Al}_2\text{O}_3$, $\text{SiO}_2$). However these materials may produce oxide in the form of precipitates in the interior of the alloy, so-called internal oxidation [40].

5.5.1 Low alloy steels

Ordinary steels are essentially alloys of iron and carbon with small additions of elements such as manganese and silicon added to provide the requisite mechanical properties. Low alloy steel is widely used as a waterwall material. But low alloy steels corrode a lot both at low and high temperature. In some conditions, adding 0.3% copper to the alloy can decrease the corrosion rate by one quarter [41]. The elements phosphorus, chromium and nickel may also improve resistance to corrosion. Formation of a dense, tightly adhering rust scale is a factor in lowering the rate of attack. Oxidation of pure iron forms a multilayer scale and below 570°C the oxides $\text{Fe}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3$ are stable. Over this temperature $\text{FeO}$ can also be formed [41].
5.5.2 **Nickel alloys**

Nickel alloys are employed for both high strength and outstanding corrosion resistance. This is due to high chromium activity and diffusion rates at higher nickel contents [35]. Alloy 625 is a well-known commercial nickel-base alloy with high strength and high resistance against pitting and high temperature corrosion. The strength of this alloy is a solid solution effect of niobium and molybdenum which prevails during high temperature exposure.

5.5.3 **Stainless Steels**

Resistance to oxidation of stainless steels is related to the chromium content, Figure 6. Most austenitic steels have at least 18% chromium and can be used at temperatures up to 870°C. Ferritic steels have usually lower oxidation resistance. When a high amount of chromium is added to iron as an alloying element, a spinel oxide Fe(Fe,Cr)₂O₄ is formed. Spinel oxides such as (Mg,Fe)(Al,Cr)₂O₄ may also form on stainless steels. Diffusion through this scale is very slow and it is thus reduced the oxidation rate dramatically [28].

![Figure 6. Effect of Chromium content on corrosion rate, test temperature 980 °C [42]](image-url)
6. Experimental

All samples in this project were exposed in the Idbäcken heat and power plant. Idbäcken is located in Nyköping, Södermanland, Sweden and supplies electricity and hot water for the city. The plant consists of three boilers, two circulating fluidized bed boilers for hot water and one bubbling fluidized bed boiler for combined heat and power (CHP). The latter was the sample exposure place. The CHP boiler generates 35 MW of electricity and 69 MW of heat. The final steam data is 540 °C and 140 bar. The pressure of 140 bar gives a maximum water temperature of 340 °C and the tubes are assumed to have a metal temperature of 390 °C. Since 2008 the plant has used 100% waste wood as the fuel which increased the corrosion rate rapidly. The boiler runs at quite low excess oxygen levels of 2-2.5%, but in some parts of the boiler even lower than 1%. This helps to decrease NOx emissions and increase efficiency.

6.1 Deposit samples

During the summer shutdown of 2011, deposits were scraped off from different positions on the top of tube furnace walls. Figure 7 shows the position of all samples from different walls. Most of the deposits were taken from areas in the boiler between the secondary and tertiary air ports (height 11.5 to 18 m), where corrosion is worst. Two samples (F6 and F7) were scratched from above the tertiary air ports (height 18 m). The samples vary in size, number of particles, shape and colour.

6.2 Test panel tube samples

Test panels of the low alloy steel 16Mo3 were welded into the right wall of the boiler in August 2008. Some of the tubes were arc-weld overlay coated with Alloy 625 and some were left uncoated. Two tube specimens were cut out in August 2011. One sample is the uncoated 16Mo3 sample as the reference tube (P4) and the other is the coated sample (P1). The nominal chemical compositions of low alloy steel and coating material are shown in Tables 3 and 4.

Table 3. Nominal chemical composition of 16Mo3 [43]

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Cu</th>
<th>N</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>0.12-0.2</td>
<td>0.4-0.9</td>
<td>0.00-0.05</td>
<td>0.00-0.025</td>
<td>0.00-0.01</td>
<td>0.00-0.035</td>
<td>0.00-0.030</td>
<td>0.00-0.012</td>
<td>0.00-0.020</td>
<td>Balance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Nominal chemical composition of Alloy 625 [44]

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>Nb+Ta</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>Ti</th>
<th>Co[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt% min</td>
<td>58</td>
<td>20</td>
<td>5.0</td>
<td>8.0</td>
<td>3.15</td>
<td>0.10</td>
<td>0.50</td>
<td>0.50</td>
<td>0.015</td>
<td>0.015</td>
<td>0.40</td>
<td>0.40</td>
<td>1.0</td>
</tr>
<tr>
<td>max</td>
<td>23.0</td>
<td>10.0</td>
<td>4.15</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td>max</td>
<td></td>
</tr>
</tbody>
</table>

[a] If determined
Figure 7. Schematic drawing of a) left wall, samples position L1 to L5 b) right wall, samples position R1 to R5 c) front wall, samples position F1 to F7 d) back wall, samples position B1 to B3

6.3 Fin wall probe samples

To compare the tube samples results with more controlled samples, air-cooled probes were designed which can be inserted into the fin wall between two tubes. One probe (A2) was installed in the back wall where the corrosion was thought to be highest. The other probe (B2) was installed in the right wall, close to the test panels, where corrosion was known to be less. They were exposed inside the boiler for 934 hours. Four specimens can be attached on each probe, only some of the results are reported here (Table 5). The samples’ dimensions are 48mm length, 6 mm thickness and 7 mm width. The temperature was measured by a thermocouple placed centrally at the back of each specimen and could be controlled by
adjusting the amount of cooling air. It was fixed to 400 °C to simulate the temperature of the tube walls.

Figure 8. a) Sketch of a fin wall test in field exposure b) a fin wall probe after exposure inside the boiler

Table 5. Probe samples and measuring chemical compositions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Chemical composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2-2</td>
<td>16Mo3</td>
<td>Shown in Table 3 (nominal)</td>
</tr>
<tr>
<td>A2-3</td>
<td>Alloy 625</td>
<td>Shown in Table 4 (nominal)</td>
</tr>
<tr>
<td>A2-4</td>
<td>310S(2520)</td>
<td>Ni19.2, Cr25.4, Mo0.11, Mn0.84, Si0.55, Ti0.001, S0.001, C0.046, Cu0.08, P0.015, Ce0.004, N0.04, Fe balance</td>
</tr>
<tr>
<td>B2-1</td>
<td>304L</td>
<td>Ni8.1, Cr18.1, Mo0.29, Mn1.63, Si0.35, S0.004, C0.02, Cu0.32, P0.03, N0.067, Fe balance</td>
</tr>
<tr>
<td>B2-2</td>
<td>16M03</td>
<td>Showed in Table 3 (nominal)</td>
</tr>
</tbody>
</table>
7 Analytical techniques

7.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was the main analysis method in this work, as it provides a combination of high resolution imaging and large depth of focus. In SEM, a high-energy-electron beam (1-30kV) is generated by the electron gun. The electron beam is focused by some electromagnetic lenses and apertures to a fine probe (1-10 nm diameter). The fine probe is aimed at a sample surface and scans it by scanning coils. When the fine electron beam hits the sample, a variety of signals are generated, most importantly secondary electrons, backscattered electrons, and X-rays, Figure 9 [45].

![Figure 9. Schematic figure of the exited volume from the interaction between the electron beam and specimen surface [45]](image)

Secondary electrons (SE) are a result of inelastic interaction between the primary electrons and the atoms in the specimen. SE can escape only from a thin region (less than 20 nm), so they offer information on the surface topography.

Backscattered electrons (BE) are a result of the backward scattering of the primary electrons and can escape from a larger region compared with SE. They offer information about specimen composition.

When electrons interact with an atom, energy can be emitted as secondary electrons, an electron from the outer shell can fill this vacancy. The corresponding energy to this transition is released in the form of an X-ray photon, Figure 10. X-ray photons are characteristic for each element and can be used to both quantify and qualify the elements [46-47].
Figure 10. A backward direction of scattered electron as characteristic radiation [48]

SEM can combine with some techniques for chemical analyses, e.g. Energy dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS). In EDS the detected X-ray signals can be shown in the form of a spectrum. The spectrum is the number of photons by photon energy (keV). Each X-ray peak in the spectrum is related to a specific element. EDS can be applied on a specimen to obtain a sample point (point analysis), in a chosen area (area analysis) or the spatial distribution of the elements (traditional map or QuantMaps map). WDS employs the X-rays diffraction on a crystal, so only photons with a specific wavelength will drop onto the detector [49]. Table 6 shows differences between EDS and WDS [48].

<table>
<thead>
<tr>
<th></th>
<th>EDS</th>
<th>WDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Resolution</td>
<td>80-180 eV</td>
<td>around 5 eV</td>
</tr>
<tr>
<td>Acquisition time</td>
<td>1 min</td>
<td>5-30 min</td>
</tr>
<tr>
<td>Use</td>
<td>Easy</td>
<td>difficult</td>
</tr>
<tr>
<td>Peak to background ratio</td>
<td>100:1</td>
<td>1000:1</td>
</tr>
</tbody>
</table>

In this work a JEOL 7001F and a JEOL 7000F were employed, with both EDS and WDS. The devices were connected to an INCA system from Oxford Instruments. SEM parameters were 15-20 keV and 16-18 A.

7.2 X-ray diffraction (XRD)

X-ray diffraction can be used to identify polycrystalline solids. In XRD a beam of monochromatic X-rays is aimed at the specimen surface at an angle of θ. When Bragg’s law, Equation (12) and related Figure 11, is satisfied constructive interference occurs. By the angles, different phases can be identified based on their d_{hkl} [50].
\[ n\lambda = 2d_{hkl} \sin \theta \] (12)

Figure 11. \( \theta \) is the angle between incident beam and the crystallographic plane, \( d \) is the space between crystallographic planes \( hkl \) and \( \lambda \) is the wavelength of X-rays [50]

In this work a Bruker D8 X-ray diffractometer with CuKα-radiation was employed to analyse corrosion products.

7.3 Light Optical Microscopy (LOM)

LOM is an instrument which uses visible light, with \( \lambda \) between 400 to 800 nm, and a system of lenses to magnify images of small samples. The maximum normal magnification under LOM is 1000x. A sample should be polished, free of any scratches, to become highly reflective. Producing image contrast, so-called etching, should be employed because incident light is uniformly reflected [51].

In this work a Leica DM IRM light optical microscope connected to microGOP 2000S software were used to measure internal corrosion.

7.4 Thermodynamic Calculation Modelling

Thermodynamic calculation modelling is used for phase diagram and thermodynamic computations for multi-component systems of practical importance. These calculations are based on the Gibbs energy for components and phases. In this work, thermodynamic modelling was performed with Thermo-Calc software using the substance database (SSUB) and the solution database (SSOL) produced by expert evaluation of experimental data. Each phase in databases is represented by its minimum Gibbs free energy [52].
8 Results

8.1 Deposit Samples

As a first step in identifying corrosion mechanisms, the parts of the deposit nearest to the tubes were analysed under EDS and some by XRD.

8.1.1. SEM/EDS

Three separate areas, or three pieces of deposit in the case of smaller deposits, were analysed under SEM. The scanned area was 5 mm². There was not too much spread in chemical composition within individual samples in these three areas under EDS, Figure 12.

Figure 12. Chemical compositions (at%) of three different particles in sample F4 (position four on the front wall)

The deposits were attached to carbon tape for analysis, so the carbon contents were not presented in analyses here. However, they were in the range 5 to 10 wt% for most of the particles.

The average contents of elements which are thought to be corrosive or form corrosive salts on all the furnace walls are presented in Table 7. An amount of nickel was detected in some samples from the front wall, and comes from the coating Alloy 625. It was shown in the table as well. The height value is from the bed of the boiler.

There was significant spread in chemical composition from position to position, but a higher content of potassium was always associated with a high chlorine content, e.g. L1, R3, F4 and B3. Potassium, chlorine and sulphur were found in all samples. However the amount varies a lot. It is between 0.6 and 27.9 at% for chlorine. Sodium was present in all deposits except R4. Lead was detected in 7 of 20 samples at low intensity, but high concentrations locally.
Lead was heterogeneously distributed and could be found as pure lead or in mixtures containing oxygen as shown in Figure 13.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wall</th>
<th>Height (m)</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Na</th>
<th>Ni</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>Left</td>
<td>+12.5</td>
<td>3.5</td>
<td>21.2</td>
<td>15.5</td>
<td>10.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>L2</td>
<td>Left</td>
<td>+12.5</td>
<td>4.4</td>
<td>4.4</td>
<td>7.1</td>
<td>5.5</td>
<td>--</td>
<td>0.9</td>
<td>0.5</td>
</tr>
<tr>
<td>L3</td>
<td>Left</td>
<td>+15</td>
<td>7.7</td>
<td>1.3</td>
<td>8.5</td>
<td>4.5</td>
<td>--</td>
<td>2.7</td>
<td>0.8</td>
</tr>
<tr>
<td>L4</td>
<td>Left</td>
<td>+15</td>
<td>3.8</td>
<td>2.0</td>
<td>5.0</td>
<td>3.7</td>
<td>--</td>
<td>0.9</td>
<td>--</td>
</tr>
<tr>
<td>L5</td>
<td>Left</td>
<td>+18</td>
<td>2.8</td>
<td>4.7</td>
<td>6.8</td>
<td>2.5</td>
<td>--</td>
<td>0.89</td>
<td>--</td>
</tr>
<tr>
<td>R1</td>
<td>Right</td>
<td>+14</td>
<td>5.6</td>
<td>0.8</td>
<td>4.6</td>
<td>1.0</td>
<td>--</td>
<td>0.6</td>
<td>--</td>
</tr>
<tr>
<td>R2</td>
<td>Right</td>
<td>+14</td>
<td>3.5</td>
<td>14.5</td>
<td>12.4</td>
<td>6.6</td>
<td>--</td>
<td>--</td>
<td>0.6</td>
</tr>
<tr>
<td>R3</td>
<td>Right</td>
<td>+18</td>
<td>2.4</td>
<td>27.9</td>
<td>15.4</td>
<td>18.1</td>
<td>--</td>
<td>--</td>
<td>0.4</td>
</tr>
<tr>
<td>R4</td>
<td>Right</td>
<td>+18</td>
<td>6.7</td>
<td>0.6</td>
<td>1.8</td>
<td>--</td>
<td>--</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>R5</td>
<td>Right</td>
<td>+18</td>
<td>5.6</td>
<td>0.9</td>
<td>6.3</td>
<td>2.9</td>
<td>--</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>F1</td>
<td>Front</td>
<td>+15</td>
<td>1.9</td>
<td>6.9</td>
<td>5.7</td>
<td>7.5</td>
<td>7.0</td>
<td>--</td>
<td>1.6</td>
</tr>
<tr>
<td>F2</td>
<td>Front</td>
<td>+15</td>
<td>2.2</td>
<td>3.3</td>
<td>5.7</td>
<td>7.5</td>
<td>0.4</td>
<td>0.2</td>
<td>--</td>
</tr>
<tr>
<td>F3</td>
<td>Front</td>
<td>+18</td>
<td>1.3</td>
<td>12.8</td>
<td>10.6</td>
<td>1.8</td>
<td>--</td>
<td>0.6</td>
<td>--</td>
</tr>
<tr>
<td>F4</td>
<td>Front</td>
<td>+18</td>
<td>6.1</td>
<td>16.7</td>
<td>17.7</td>
<td>7.6</td>
<td>0.8</td>
<td>0.24</td>
<td>0.8</td>
</tr>
<tr>
<td>F5</td>
<td>Front</td>
<td>+18</td>
<td>8.2</td>
<td>5.0</td>
<td>9.7</td>
<td>9.0</td>
<td>--</td>
<td>1.7</td>
<td>--</td>
</tr>
<tr>
<td>F6</td>
<td>Front</td>
<td>+21</td>
<td>1.9</td>
<td>10.9</td>
<td>8.3</td>
<td>5.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>F7</td>
<td>Front</td>
<td>+21</td>
<td>5.4</td>
<td>10.1</td>
<td>13.1</td>
<td>6.1</td>
<td>--</td>
<td>0.5</td>
<td>--</td>
</tr>
<tr>
<td>B1</td>
<td>Back</td>
<td>+16</td>
<td>2.0</td>
<td>1.6</td>
<td>3.4</td>
<td>2.4</td>
<td>--</td>
<td>0.7</td>
<td>--</td>
</tr>
<tr>
<td>B2</td>
<td>Back</td>
<td>+16</td>
<td>4.2</td>
<td>13.2</td>
<td>11.8</td>
<td>8.2</td>
<td>--</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>B3</td>
<td>Back</td>
<td>+16</td>
<td>2.6</td>
<td>16.3</td>
<td>10.1</td>
<td>13.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Figure 13. Island of Pb-Fe-Cl-O mixture in the sea of alkali chloride from sample F7, the analyses are in at%. 
Zinc was found in 15 of 20 samples at low concentrations. It was observed as crystals of ZnCl$_2$, Figure 14.

![Figure 14. Crystals of zinc chloride in sample of L3, the sample had the highest amount of Zn](image)

The nickel which was detected in some samples, F1, F2 and F4, comes from the Alloy 625 coating.

### 8.1.2 XRD

Deposit particles of samples R4 (low chlorine content, 0.6 at%), F1 (medium chlorine content, 6.9 at%) and R2 (high chlorine content, 14.5 at%) were separately ground and analysed under X-ray diffraction. The X-ray diffraction results are shown in Table 8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Identified compound in strong intensity/high concentration</th>
<th>Identified compound in medium intensity/medium concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>(K,Na)SO$_4$, K$_2$Pb(SO$_4$)$_2$</td>
<td>Pb$_2$OSO$_4$</td>
</tr>
<tr>
<td>F1</td>
<td>KCl</td>
<td>NaCl, K$_3$Na(SO$_4$)$_2$, NiO, K$_2$Pb(CrO$_4$)$_2$</td>
</tr>
<tr>
<td>R2</td>
<td>KCl</td>
<td>NaCl, K$_3$Na(SO$<em>4$)$<em>2$, NiO, Cr$</em>{1.6}$Fe$</em>{1.4}$O$_4$</td>
</tr>
</tbody>
</table>

In sample R4 (low chlorine content), sulphates dominated the XRD results. In sample F1 with a medium and R2 with a high chlorine content, potassium chloride dominated the XRD results. Potassium-lead compounds were also identified. The presence of potassium lead chromate in the deposit of sample F1, means that lead together with potassium had reacted with the protective chromia layer and formed chromate, which is non-protective.

### 8.2 Test panel tube samples

#### 8.2.1. Corrosion rate measurement

The thickness of the tube samples was measured after exposure at eight equally spaced positions. The original wall thickness of the 16Mo3 tube sample (P4) was 7 mm and after three years exposure (about 20000 hours) the average thickness of the examined section was 5.35 mm and the minimum 5.0 mm. The original thickness of the Alloy 625 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 than 4 mm in a number of areas. After 3 years exposure the average thickness of the examined section was 3.8 mm and the minimum thickness 3.4 mm.

These approximate values are normalized to 1000 hours and presented in Table 9.

Table 9. Metal loss from tube samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average (μm/1000h)</th>
<th>Maximum (μm/1000h)</th>
<th>Position in boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>16Mo3 (P4) tube</td>
<td>82 (approx)</td>
<td>100 (approx)</td>
<td>Right wall</td>
</tr>
<tr>
<td>Alloy 625 (P1) coated tube</td>
<td>10 (approx)</td>
<td>30 (approx)</td>
<td>Right wall</td>
</tr>
</tbody>
</table>

8.2.2. SEM

The top of the two tube samples was polished by papers with grit P800, P1200, P2500 and P4000 respectively. A polishing machine with the speed of 450 rpm was used in a dry manner to avoid washing away the corrosion product on the tubes, especially chlorine which is soluble in water. Polishing in this way facilitated the study of the base metal, oxide and interface between oxide/substrate. The polishing method is shown in Figure 15.

![Figure 15. Schematic drawings of tube samples before and after polishing](image)

The elemental QuantMaps map for the Alloy 625 coated tube sample (see Figure 16) showed concentrations of Pb and K in the oxide and at the substrate/deposit interface, but no Cl was observed at interface. Low amounts of Cl (less than 1 wt%), were found in the oxide layer.

![Figure 16. QuantMaps of key elements on the nickel-alloy coated tube sample](image)
SEM/WDS results showed that high levels of lead were frequently seen at the corrosion front (see Figure 17 along with some point analyses, Table 10).

Figure 17. A section of Alloy 625 coated tube sample (P1), white areas indicates high amount of lead (up to 33 wt%). Three spot analyses are also shown

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>53.59</td>
<td>51.68</td>
<td>13.79</td>
</tr>
<tr>
<td>Mg</td>
<td>--</td>
<td>--</td>
<td>0.85</td>
</tr>
<tr>
<td>S</td>
<td>4.70</td>
<td>7.23</td>
<td>3.29</td>
</tr>
<tr>
<td>Cl</td>
<td>--</td>
<td>0.54</td>
<td>--</td>
</tr>
<tr>
<td>K</td>
<td>4.29</td>
<td>5.39</td>
<td>2.12</td>
</tr>
<tr>
<td>Ca</td>
<td>0.54</td>
<td>--</td>
<td>1.37</td>
</tr>
<tr>
<td>Ti</td>
<td>1.17</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cr</td>
<td>8.80</td>
<td>3.91</td>
<td>3.45</td>
</tr>
<tr>
<td>Fe</td>
<td>0.29</td>
<td>0.30</td>
<td>0.76</td>
</tr>
<tr>
<td>Ni</td>
<td>14.34</td>
<td>24.88</td>
<td>66.14</td>
</tr>
<tr>
<td>Zn</td>
<td>1.73</td>
<td>0.63</td>
<td>7.16</td>
</tr>
<tr>
<td>Nb</td>
<td>6.49</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Pb</td>
<td>7.19</td>
<td>5.43</td>
<td>1.07</td>
</tr>
</tbody>
</table>

Table 10. Chemical analysis (at%) of three spectra related to Figure 17

Figure 17 and related Table show lead was highly concentrated at the interface in the pits. Only a small amount of chlorine was found in the corrosion product. Sulphur and potassium were also found in the deposit and at the interface.

Figure 18 shows the element mapping for the uncoated 16Mo3 tube sample, P4. The level of chlorine found was much higher at the interface and in the deposit compared with the Alloy 625 coated tube sample, P1. Lead and zinc were not observed at the interface or in the deposit.

Area analysis by the SEM clarified that corrosion products were mainly chlorine, iron and oxygen. Some iron chlorides were found at the metal interface. Table 11 shows the average chemical composition results of the deposit and interface in four different 5 mm² areas.
Table 11. Average chemical composition results for the oxide and interface of the uncoated tube sample

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
<th>at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>30.82</td>
<td>57.99</td>
</tr>
<tr>
<td>Cl K</td>
<td>15.22</td>
<td>12.92</td>
</tr>
<tr>
<td>Fe K</td>
<td>53.96</td>
<td>29.09</td>
</tr>
</tbody>
</table>

8.2.3 LOM

One part of each tube sample (P1 and P4) was dry cut and then mounted by phenolic resins. The mounted samples were respectively polished by paper p1200, polishing cloths 3 μm and finally 1 μm. The samples were then chemically etched and analysed by light optical microscopy, Table 12.

Table 12. Microstructural etchants for tube samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Etchant</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4</td>
<td>16Mo3</td>
<td>2 ml HNO₃ and 98 ml alcohol</td>
<td>The sample was swabbed for 10 seconds.</td>
</tr>
<tr>
<td>P1</td>
<td>Alloy 625</td>
<td>94 ml dist. water, 18.75 ml H₂SO₄, 225 ml HCl, 62.5 ml HNO₃, 94 ml CH₃COOH, 95 gr FeCl₃</td>
<td>The sample was immersed for 15 seconds.</td>
</tr>
</tbody>
</table>

Figure 19 shows LOM results of the tube samples. P4, Alloy 625 coated tube sample shows dendritic structure, because it is a welded sample. P1, 16Mo3 low alloy steel shows pearlitic-ferritic microstructure. No internal corrosion was found in either sample.

Figure 19. Light optical microscopy results a) Tube sample 16Mo3 b) Tube sample Alloy 625 coated
8.3 Fin wall probe samples

8.3.1 Corrosion rate measurement

The thickness of each specimen was measured before and after exposure at 4 places along the centre-line. Before testing the thickness was measured with a micrometer. After testing the specimens were sectioned (dry cutting) at the four places. Then the four parts of each specimen were examined in an optical microscope with a micrometer measuring gauge. One part was left unmounted. Table 13 shows the maximum thickness loss and the average thickness loss which is normalised to 1000 hour.

Table 13. Metal loss from probe samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average (μm/1000h)</th>
<th>Max (μm/1000h)</th>
<th>Position in the boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>16Mo3 (A2-2)</td>
<td>116</td>
<td>133</td>
<td>Back wall</td>
</tr>
<tr>
<td>Alloy 625 (A2-3)</td>
<td>47</td>
<td>55</td>
<td>Back wall</td>
</tr>
<tr>
<td>310S (A2-4)</td>
<td>61</td>
<td>75</td>
<td>Back wall</td>
</tr>
<tr>
<td>304L (B2-1)</td>
<td>54</td>
<td>78</td>
<td>Right wall</td>
</tr>
<tr>
<td>16Mo3 (B2-2)</td>
<td>78</td>
<td>97</td>
<td>Right wall</td>
</tr>
</tbody>
</table>

Sample A2-3 has the lowest corrosion rate among all samples as one might expect. The metal loss of stainless steel samples are between the low alloy steel sample and the nickel alloy sample.

8.3.2 SEM

The unmounted part of each sample was dry polished on the edge at an angle of 45. The polishing technique was the same as for the tube samples and Figure 20 shows a sketch of samples before and after polishing.

![Figure 20](image)

Figure 20. a) Schematic figure of an unmounted part of sample b) sample after polishing

The elemental QuantMaps for the Alloy 625 coated sample were similar to the coated tube sample ones, Figure 21. It can be observed that there is a concentration of lead in the oxide layer. The oxide layer is mainly free of chlorine (apart from an isolated area under the oxide). At the interface there is a correlation between lead and potassium.
Lead was present in the EDS point analysis, but not in combination with chlorine, Figure 22 and Table 14.

The 16Mo3 probe sample (A2-2, back wall) was analysed under SEM/EDS and QuantMaps for this sample are presented in Figure 23. Chlorine was present at the interface and in the deposit. No lead and sulphur was found at the corrosion front. Figure 24 and related table (Table 15) elucidated that corrosion product is mainly iron, chlorine and oxygen.
Figure 23. QuantMaps of the 16Mo3 probe sample

Figure 24. A section through the surface of 16Mo3 probe specimen on right wall with two marked spectra

These results are highly similar to those of the 16Mo3 probe sample on the right wall (B2-2). Figure 25 shows SEM quantmapping of the sample. No lead and sulphur were present in the corrosion product. Chlorine was observed in the deposit or at the interface between substrate and oxide.

Table 15. Chemical composition (atomic %) of two spectra related to Figure 24

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>26.10</td>
<td>61.21</td>
</tr>
<tr>
<td>Si</td>
<td>0.48</td>
<td>0.70</td>
</tr>
<tr>
<td>S</td>
<td>0.30</td>
<td>0.24</td>
</tr>
<tr>
<td>Cl</td>
<td>1.02</td>
<td>7.66</td>
</tr>
<tr>
<td>K</td>
<td>0.09</td>
<td>--</td>
</tr>
<tr>
<td>Cr</td>
<td>0.25</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>71.76</td>
<td>29.94</td>
</tr>
</tbody>
</table>
The results of 310S stainless steel showed both chlorine and lead are present at the corrosion front but not in combination together. Lead was found in connection with potassium. Sulphur was also observed at the interface. Spectra 1-5 in figure are placed at interface and spectra 6 and 7 are at the deposit of the sample 310S, Figure 26. Spot chemical analyses are presented in Table 16.

The results of 304L stainless steel show the same behavior as 310S. Chlorine is present at corrosion front but not in connection with heavy metals such as lead. Lead and potassium are in combination together in some areas at the interface and corrosion product.

Figure 27 shows QuantMaps results of the probe sample 304 (B2-1).
Four parts of each probe sample were cut, mounted and polished with the same technique as the tube samples. They then were etched, Table 17.

Table 17. Microstructural etchant and etching method for probe samples

<table>
<thead>
<tr>
<th>Sample Material</th>
<th>Etchant</th>
<th>Etching technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>16Mo3 (A2-2, B2-2)</td>
<td>2 ml HNO₃ and 98 ml alcohol</td>
<td>The sample was swabbed for 10 seconds.</td>
</tr>
<tr>
<td>Alloy 625 (A2-3)</td>
<td>94 ml dist. water, 18.75 ml H₂SO₄, 225 ml HCl, 62.5 ml HNO₃, 94 ml CH₃COOH, 95 gr FeCl₃</td>
<td>The sample was immersed for 15 seconds.</td>
</tr>
<tr>
<td>310S(A2-4)</td>
<td>200 ml H₂O, 200 ml conc. HCl and 20 ml conc. HNO₃</td>
<td>The etch solution was heated up to 60 °C while the sample was immersed in it. Some bubbles should be visible after one minute. Then the etchant was stirred and the procedure was again repeated.</td>
</tr>
<tr>
<td>304L(B2-1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 28 shows LOM results of the probe samples. No internal corrosion was observed in all samples. No big difference was found between P1 and A2-3 (Alloy 625 coated tube and probe sample). Probe and tube sample of 16Mo3 (A2-2, B2-2 and P4) were also the same under LOM.
8.4 *Thermo-Calcc results*

Thermodynamically stable phases were modelled regarding corrosion and flue gas composition at 400 °C by Thermo-Calcc software. For simplification, chromium and molybdenum were excluded from 16Mo3 alloy and Alloy 625 alloy. So, the simulation was done using pure iron and pure nickel, Figure 29 and Figure 30.

The modelling was performed with a constant amount of iron or nickel, hydrogen and chlorine, and increasing amounts of oxygen, sulphur, potassium and lead (It was not possible to perform modelling with more than four elements as variables). The total amount of species was set to one mole with nitrogen as balance. The gas species in equilibrium with the solid phases is not shown in the diagrams. The gas phase mainly contains 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 is less than 1% in both cases which is marked with an arrow in the Figures 29 and 30. The expected stable phases in a corrosion product/deposited layer are shown in the y-axis in both diagrams. The dominant Cl-containing phases are presented in both cases with a red line. The dominating Cl-containing phases from low to high oxygen partial pressure and sulphur partial pressure in Figure 29 are respectively FeCl₂, KCl and PbCl₂. In nickel modelling (Figure 30) the phases are HCl, KCl(NiCl₂), KCl, PbCl₂. The amounts of chlorine in hydrated form (HCl) and gaseous molecule chlorine (Cl₂) are calculated in the iron case and are shown at three different positions in blue boxes, Figure 29.
Figure 29. Modelling of iron in flue gas at 400 °C (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.

Figure 30. Modelling of nickel in flue gas at 400 °C (input in 1 mole: 0.017Ni, 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.
9 Discussion

Table 1 shows the key elements which form corrosive salts in waste wood, coal and forest wood. Waste wood contains more chlorine, zinc and lead than forest residues and coal, although it contains less alkali metals (Potassium and Sodium). It is suggested that both alkali and chlorine cooperate in the corrosion mechanism. Chlorine attack may occur by diffusion of gaseous chlorine [5] or chloride ions [8] through the defects, cracks or pores in the oxide scale. However the chlorine gas molecule (Cl₂) is larger than the gaseous hydrogen chloride. Therefore HCl can diffuse easier through a defective oxide [9]. This work has shown that HCl is thermodynamically favoured. Table 7 shows chlorine is present in all the deposit samples. Laboratory studies show potassium can change the protective chromia scale to the non-protective potassium chromate (K₂CrO₄) [13]. The same reaction can happen for lead and PbCl₂ can accelerate corrosion due to the formation of lead chromate (PbCrO₄) [53]. Table 8 shows that lead and potassium together react with the chromia protective layer and lead to the formation of potassium lead chromate. The presence of K₂Pb(CrO₄)₂ and K₂Pb(SO₄)₂ illustrate that potassium and lead are in reaction together.

Table 9 shows the Alloy 625 coated tube has a lower corrosion rate than the 16Mo3 tube. Nickel alloys are less prone to react with chlorine compared with iron or chromium. This behavior also agreed well with probe samples, Table 13. Alloy 625 probe sample has the lowest corrosion rate of all the samples. The Gibbs free energy of nickel chloride formation is less negative than iron chloride formation or chromium chloride formation; this leads nickel alloys to be more corrosion resistant in chlorine containing environments [7, 35-36]. The corrosion rate measured over a 20,000 hour period on the 16Mo3 tube on the right wall (sample P4, Table 9) agreed well with the rate measured over an only 934 hours period by 16Mo3 probe testing on the same wall (sample B2-2, Table 13). This points out that the corrosion rate of 16Mo3 low alloy steel is linear (about 1 mm per 10,000 hours) and the oxide layer is non-protective, so it is possible to extrapolate results from shorter term probe testing to longer term measurements on this material in this environment. It is more difficult to draw any such conclusions for the nickel alloy; no probe testing was made on the right wall and 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 indicate a parabolic corrosion rate and a protective oxide. Comparing the samples’ corrosion rates on the right wall with those on the back wall (see Table 13) shows that the corrosion rates on the back wall were 30-50% higher, which is in 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% although 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 increase in flue gas temperature close to the back wall may account for the difference, in the absence of any other factors.

Two forms of attack are thought to occur in waste environments: chlorine corrosion [5, 8-9, 27, 54] and alkali corrosion [29, 34], both initiating from the alkali- and chloride-rich deposits and flue gas. The results of our investigations are in agreement with the mechanisms.

The nickel-alloy coated tube specimen (Figure 16) shows the presence of potassium and lead in the corrosion front. Only a small amount of chlorine was found in deposit. The nickel is spreading from the oxide into the deposit which might suggest a fluxing mechanism. High amounts of lead and potassium at the corrosion front on the nickel alloy coated tube are measured by the spot analyses shown in Figure 17 and related table. XRD results (Table 8) also show the formation of potassium lead chromate. The results of the Alloy 625 probe test (Figure 21) were highly similar to the results of the Alloy 625 tube test. In Figure 22 and related table (Table 14), the Alloy 625 probe sample also shows a concentration of lead in the nickel oxide, an area which is devoid of chlorine. It appears then that the Alloy 625 coated samples are suffering from corrosion by a lead-potassium combination.

By contrast, chlorine was present at the interface between substrate and deposit of all the 16Mo3 specimens, but we did not detect any lead and potassium (see Figure 18, Figure 23 and Figure 25). Only small amounts of potassium were detected under SEM by point or area analyses, Table 11 and Table 15. The dominant corrosion mechanism in 16Mo3 low alloy steel seems to be chloride attack.

Stainless steels results (Figure 26 and Figure 27) show chlorine, lead and potassium at the corrosion front. Lead and potassium are found together; however lead is not found with chlorine at the corrosion front. It seems that 304L and 310S are attacked by mix of both mechanisms: chloride containing species and lead-potassium combination. Table 13 shows that the corrosion rates of 304L and 310S stainless steels are in between of 16Mo3 and Alloy 625.

Figure 19 and Figure 28 show there is no internal corrosion in the tube or probe specimens. No special difference was observed in the structure of tube and probe Alloy 625 samples or of 16Mo3 samples under optical microscopy.

As shown in the Thermo-Calc modelling (Figure 29 and Figure 30) 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 (in the case of iron) and nickel (in the case of 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-alloy 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 [55]. 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 the metal surface) the stability area of iron chloride is much larger than that at nickel chloride. Obviously, nickel base alloys are expected to be less prone to chlorine induced corrosion from a thermodynamic point of view.

The amount of HCl and Cl₂ has been calculated by Thermo-Calc at different oxygen partial pressures and three of the results are presented in Figure 29 in blue boxes. This shows that chlorine gas exists at extremely low levels; instead the hydrated form is thermodynamically favoured. The amount of HCl is much higher than Cl₂ (or FeCl₂). It can be expected that the porosity (i.e. the gas phase in the deposit/oxide layer) is dominated by gaseous hydrogen chloride in the whole oxygen partial pressure range. Therefore it suggested that chlorine corrosion in the hydrated form can govern the chlorine induced corrosion under an oxide layer where no alkali is found.
10 Summary of presented papers

10.1 paper i

The use of biomass as a fuel for power production is increasing and as the price of virgin wood continues to rise, waste wood (recycled wood) is used more. However waste wood contains more chlorine, zinc and lead, which are believed to cause an increase in the corrosion rates.

Corrosion problems have occurred on the furnace walls of a fluidised bed boiler firing 100% waste wood under low NOx conditions. As a first step to understanding the impact of the fuel, deposits have been collected and analysed from a number of positions on the lower area of furnace walls. A large part of the walls have been coated with the Ni-base alloy Alloy 625.

There was considerable spread in the deposit composition, but a higher potassium content was always associated with a high chlorine content. Chlorine was found in all the deposit samples, sometimes at very high levels (27 atomic%). Potassium and sulphur were found in all the deposits samples and Na was found in most samples (19 of 20). Zinc was found in 15 of 20 samples at low concentrations. Lead was found in 7 of 20 samples at low average concentrations, but high concentrations locally.

X-ray diffraction results showed the presence of K-Pb compounds, such as K₂Pb(CrO₄)₂ in the deposit and initial examination of the Ni-alloy coated tubes showed that lead was greatly concentrated in pits at the corrosion front.

10.2 paper ii

In this work, furnace tubes coated with a nickel-based alloy were compared to the uncoated tubes of the low alloy steel 16Mo3 after three years of exposure in the boiler. The nickel alloy coating and uncoated material were also compared with more controlled testing on an air-cooled probe lasting for about 6 weeks at 400 °C. The corrosion rates were measured and the samples were chemically analysed by SEM/EDS/WDS and XRD methods. The corrosive environment was also modelled with Thermo-Calc software to predict thermodynamically the stability of the corrosion products.

The corrosion rates measured from the probe and tube samples of 16Mo3 agreed well with each other, implying linear corrosion rates. The results also showed that the use of nickel alloy coatings changes the corrosion mechanism, which leads to a dramatic reduction in the corrosion rate. The simplified Thermo-calc results are in agree with identified phases in corrosion product.
The combustion of waste wood is becoming more widespread in Europe, because it is carbon dioxide neutral and a renewable energy source, but with a lower cost than forest fuel. However it is a heterogeneous fuel with a high amount of chlorine, alkali and heavy metals which leads to more corrosion in boilers than with fossil fuel or forest fuel combustion.

In this work different alloys were exposed in the fin wall between two furnace wall tubes by air-cooled probes in a waste wood-fired fluidised bed boiler. The analysed materials were low alloy steel 16Mo3, nickel-alloy Alloy 625, stainless steel 310S and ferritic iron-chromium-aluminium Kanthal APMT. The exposure time was 934 hours at 400 °C to investigate corrosion rate, corrosion front, deposit compositions and corrosion mechanisms.

As expected 16Mo3 exhibited the highest corrosion rate. Alloy 625 and Kanthal APMT had the lowest corrosion rates (about 40% of the rate for 16Mo3), closely followed by 310S (50% of the 16Mo3 rate). The corrosion mechanisms were very different in different materials: chloride attack in 16Mo3, a combination of K-Pb attack in Alloy 625, a mixture of Cl and K-Pb attack in the stainless steel 310S, and Cl and K attack in Kanthal APMT.

Thermodynamic modelling showed chlorine gas exists at extremely low levels (less than 0.1 ppm); instead the hydrated form is thermodynamically favoured. Consequently chlorine can attack low alloy steels by gaseous hydrogen chloride rather than chlorine gas as previously proposed.
11 Conclusions

The deposit results showed a wide spread in chemical composition related to different positions, although chlorine, potassium and sulphur were found in all the samples. The results revealed the presence of K-Pb compounds.

The results showed that coating furnace tubes with Alloy 625 alloy reduces the corrosion rate of the waterwalls significantly.

The dominant mechanism in the 16Mo3 specimens was chloride corrosion, while attack by a potassium-lead combination appeared to be the dominant mechanism in the nickel-alloy coated samples. The corrosion mechanism in 310S and 304L stainless steels were mixture of both chlorine attack and potassium-lead attack.

The results revealed Alloy 625 has the lowest corrosion rate, the next lowest corrosion-rate material is Kanthal APMT, then 310S and 304L, and finally 16Mo3 corrodes fastest. The corrosion rate of the 16Mo3 low alloy steel seems to be linear. The Alloy 625 seems to have a parabolic corrosion rate.

The simplified thermodynamic modelling fitted well with the identified phases in SEM results. Thermo-Calc modelling revealed chlorine gas exists at extremely low levels (less than 0.1 ppm); instead the hydrated form is thermodynamically favoured, i.e. gaseous hydrogen chloride. So it suggested that chlorine corrosion in hydrated form can attack the low alloy steel 16Mo3 rather than chlorine gas.
12 Future work

As the maintenance cost is high in power plants, it would be valuable to find alloys which are more corrosion resistant than alloy 625 or less expensive.

Work is continuing to find fuel additives to reduce corrosion.

Depth profile of corrosion products will be analysed using Glow Discharge Optical Emission Spectroscopy (GDOES) to learn more about inner and outer oxide compositions.

Thermo-Calc modelling seems to be a promising tool also for such complex systems as corrosion in flue gas, but more work is needed to simulate alloy and flue gas chemical composition closer to each specific case. Additionally, it would be desirable that thermodynamic data of certain identified complex phases should be added to the thermodynamic databases in the future.
13 Acknowledgements

This study would not have been possible without the guidance and the help of several individuals and groups who extended their valuable assistance. This includes the coffee machine at KTH.

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14 References


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