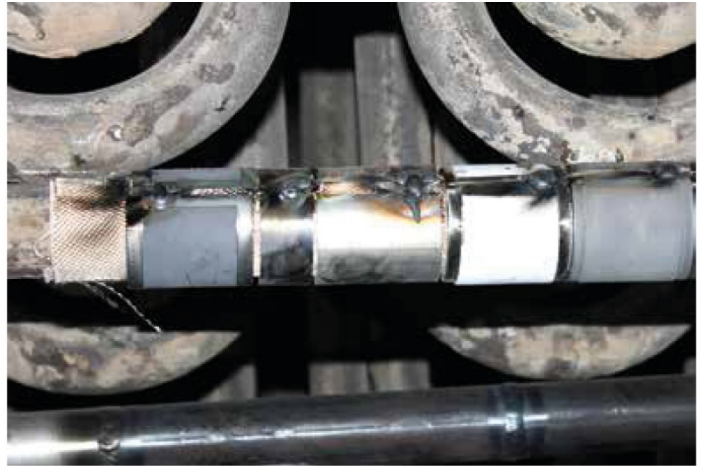


HIGH TEMPERATURE CORROSION IN USED-WOOD FIRED BOILERS

KME-708



CONSORTIUM MATERIALS TECHNOLOGY
for thermal energy processes



KME
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for thermal energy processes

High temperature corrosion in used-wood fired boilers

Part 1. KME-708

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Preface

The project has been performed within the framework of the sixth stage of the material technology research programme KME, Consortium Materials technology for development of thermal Energy processes, that is ongoing 2014-2018. KME was established 1997 and in the current programme stage eight industrial companies and 14 energy companies participate in the consortium. The consortium is managed by Energiforsk.

The programme shall contribute to increasing knowledge within materials technology and process technology development to forward the development of thermal energy processes for efficient use of renewable fuels and waste in the production of power and heat. The KME goals are to bring about increased power production, improved fuel flexibility and improved operating flexibility.

KME's activities are characterised by long term industry driven 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 long term sustainable energy society. The industry has participated in the project through own investment (60 %) and the Swedish Energy Agency has financed the academic partners (40 %).

Pamela Henderson, Vattenfall AB R&D, was the project manager. Other project participants: Mattias Mattsson, Vattenfall AB R&D, Carl Nordenskjöld, Vattenfall AB Värme Norden, Yousef Alipour and Peter Szakalos, KTH, Rikard Norling and Annika Talus, Swerea KIMAB, and Anders Hjörnhede and Fredrik Niklasson, SP.

Vattenfall, E.ON Värme, Amec Foster Wheeler, Fortum Värme, Sandvik Heating Technology and Sandvik Materials Technology have participated in the project through own in-kind contributions. the Swedish Energy Agency has financed academic partners KTH, Swerea KIMAB och SP. The project has also had a reference group consisted of the project participants and representatives from Babcock & Wilcox Vörlund, Andritz and Chalmers HTC.

Bertil Wahlund, Energiforsk

Abstract

Corrosion tests have been performed in the furnace wall area and at the superheaters of recycled wood fired boilers. It was found that:

- 1) Low alloyed steels exhibited high corrosion rates, while austenitic stainless steels, FeCrAl alloys and Ni-base alloys gave good results (low corrosion). Some alloys were identified that showed similar corrosion rates to Alloy 625. These alloys are not nickel-based and are therefore cheaper than Alloy 625.
- 2) Small differences in the chlorine and lead content of a fuel resulted in large differences in the corrosion rate. (Higher Cl- and Pb-levels give higher corrosion rates). This means that corrosion can be reduced by careful control of the fuel composition.
- 3) Co-combustion of used wood with digested sewage sludge reduces the initial corrosion which means that longer exposures will be performed in stage 2 of the project.

Sammanfattning

Andelen returträ som används som bränsle i kraftvärmeverk ökar hela tiden, eftersom det är billigare än jungfruligt träbränsle såsom skogsflis. Returträ orsakar dock mer korrosionsproblem, särskilt i eldstaden i syrefattiga områden (orsakade av låg-NO_x-förbränning). Projektet syftade till att hitta kostnadseffektiva sätt att minska korrosionen, för att minska underhållskostnaderna eller öka bränsleflexibiliteten och för att öka elverkningsgraden i nya pannor.

Korrosionsprovning med sonder har utförts huvudsakligen av Vattenfall och E.ON i egna fluidiserad-bädd-pannor som använder returträ. Många olika legeringar provades, bland annat aluminiumbildande legeringar och austenitiska rostfria stål från svenska tillverkare. Alloy 625, en nickelbaslegering som ofta tillämpas som ytbeläggning i eldstäder, användes som referens.

Korrosionstester genomfördes också med olika kvaliteter av RT-flis (hög Pb och Cl respektive lägre Pb och Cl) som är kommersiellt tillgängliga. Tvåveckors tester genomfördes i eldstaden och 3-timmars tester vid överhettare i Vattenfalls panna och 8-timmars försök genomfördes i laboratorieskala med samma bränslen i SP:s fluidiserad-bädd-reaktor. Proverna (sonderna) utvärderades efteråt av Swerea KIMAB.

KTH och Swerea KIMAB analyserade sondprover från korttidsprovning med tillsats av rötat avloppsslam (som härrörde från ett tidigare projekt, KME-508).

Resultaten visade att

- (1) Låglegerade stål visade höga korrosionshastigheter, medan austenitiska rostfria stål, FeCrAl-legeringar och Ni-bas-legeringar visade bra resultat (låg korrosion). Några legeringar uppvisade lika bra korrosionsegenskaper som Alloy 625, men var billigare.
- (2) Små skillnader i klorhalt i bränslet (i spannet 0,1-0,2 vikts %) orsakar stora skillnader i korrosionshastighet (högre Cl-halt ger högre korrosionshastighet). Korrosionshastigheten kan minskas med bra kontroll av bränslekemin.
- (3) Samförbränning med rötat avloppsslam minskar den initiala korrosionen vilket betyder att ytterligare försök, där korrosionen på längre sikt studeras, kommer att genomföras i etapp 2 (KME-718).

Dessutom har Sandvik Heating Technology AB påsvetsade en eldstadstub med den FeCrAl-legeringen Kanthal APMT™. En tub med flera ytbeläggningar, inklusive Kanthal APMT™ har installerats i en fluidiserad-bädd panna för långtidsutvärdering i etapp 2 (KME-718).

Nyckelord: returträ, korrosion, eldstadsväggar, stål, FeCrAl-legeringar, Ni-baslegeringar

Summary

Increasing use is being made of used (recycled) wood as a fuel in heat and power boilers, because it is cheaper than virgin wood. However, used wood causes more corrosion problems, especially in the furnace where there is a lack of oxygen (low NO_x combustion). This project sought to find cost effective ways of reducing the corrosion, thus saving maintenance costs, increasing fuel flexibility or increasing the electrical efficiency.

Corrosion testing with probes has been performed mainly by Vattenfall and E.ON in their own fluidized bed boilers which used recycled wood. Many different alloys were tested, including alumina-forming alloys and stainless steels from Swedish manufacturers. Alloy 625, a nickel-base alloy which is often applied as a coating on furnace walls, was used as a reference.

Corrosion tests were also performed with different qualities of used wood (high Cl, high Pb and lower Cl, lower Pb) which were commercially available. Tests lasting 2 weeks were performed at the furnace walls and tests lasting 3 hours were performed at the superheaters in Vattenfall's power plant. Tests lasting 8 hours were performed in SP's laboratory reactor with the same fuel batches. The probe specimens were evaluated afterwards by Swerea KIMAB.

KTH and Swerea KIMAB analysed specimens from short-term testing with additions of digested sewage sludge (obtained during the previous project KME-508).

The results showed that:

- (1) Low alloyed steels exhibited high corrosion rates, while austenitic stainless steels, FeCrAl alloys and Ni-base alloys gave good results (low corrosion). Some alloys were identified that showed similar corrosion rates to Alloy 625.
- (2) Small differences in fuel chlorine content (in the range 0.1 to 0.2 weight %) resulted in large differences in the corrosion rate. (A higher Cl- level gives higher corrosion rates). Corrosion can be reduced by careful control of the fuel composition.
- (3) Co-combustion of used wood with digested sewage sludge reduced the initial corrosion which means that longer exposures will be performed in stage 2.

In addition, Sandvik Heating Technology AB has overlay welded the FeCrAl-alloy Kanthal APMT™ on to a waterwall tube. A tube with several coatings, including Kanthal APMT™ has been installed in a fluidized bed boiler for long-term exposure and will be evaluated in KME-718.

Keywords: used wood, corrosion, furnace walls, steels, FeCrAl alloys, Ni-base alloys.

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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. In order to reduce operating costs (which is especially important when electricity prices are low) low quality fuels like used (recycled) wood are often utilized instead of forest residues (virgin biomass). Used wood consists of by-products from consumption, like demolition and building waste and often contains traces of paint or plastics or other polymers. This 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, when compared to virgin biomass, [1,2]. This project sought to find cost effective ways of reducing the corrosion, thus saving maintenance costs, or increasing fuel flexibility.

Problems have been experienced with furnace wall corrosion with used wood contents as low as 20% in combination with low-NO_x combustion and advanced steam conditions of about 140bar/540°C [7]. In Vattenfall's 100MWth bubbling fluidized bed boiler using 100% used wood in Idbäcken, Nyköping, corrosion rates of up to 1.5 mm a year were measured on the low-alloy steel walls made of 16Mo3. This corrosion rate gives a lifetime of 3 years and a new furnace wall for a boiler of this size costs around 25 MSEK.

The walls have since then been overlay welded with the nickel –based alloy Alloy 625 to reduce the corrosion, but even this alloy corrodes (albeit at a lower rate) so the problem is not solved, [9]. In addition, Ni-based alloys are expensive. KME-508 resulted in a number of recommendations to reduce furnace wall corrosion, but the work needs to be taken further [7]. This project will be a continuation of KME-508 (and also of KME-512).

Work within KME-508 showed that coatings of austenitic stainless steels can be a competitive alternative to Ni-base alloys and preliminary results with alumina forming alloys (as opposed to chromia-forming ones) showed that these FeCrAl alloys had very low corrosion rates at boiler wall temperatures (400°C), matching those of the Ni-base alloys. These alternatives need to be evaluated further so that boiler owners and manufacturers can have the confidence to use them instead of traditional Ni-base alloys. New alumina forming alloys manufactured by Sandvik Heating Technology AB and advanced steels from AB Sandvik Materials Technology have been evaluated in the new project. KME-508 also showed that sewage sludge can have positive effects by reducing the initial furnace wall corrosion. The specimens obtained from short-term testing were more closely examined in this project to determine whether long-term testing with sewage sludge should be performed in the future.

Initial results from KME-512 showed that the Pb content of the fuel influences the corrosion rate of the low alloy steel (more lead gives more corrosion). The lead and chlorine levels in waste wood vary according to origin /supplier of the fuel. While the suppliers cannot be mentioned (because this is competitive information) the corrosion caused by used wood having different characteristic chemical compositions has been investigated.

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 pressurised 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 more rapidly when burning fuel in a low NO_x environment (i.e. an environment with low oxygen levels to limit the formation of NO_x), [1,2]. Used wood is a more corrosive fuel than forest fuel, but it is cheaper. Used wood, (also known as demolition wood, waste wood or recycled wood), consists of by-products from consumption, the major sources being demolition and construction of buildings. It 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 the key elements which form corrosive salts in used wood and forest fuel is given in Table 1.2.1.

It is only in recent years that studies have been undertaken into furnace wall corrosion in waste- and biomass-fired boilers, firstly through Värmeforsk, [1,2] and then via the previous project KME-508. Previously most studies had focused on fireside corrosion of superheater tubes and there was little or no information available on the use of fuel additives or blends to reduce corrosion in the furnace region.

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 the nickel based alloy, Alloy 625 which seems to work well at lower steam temperatures, [1,2]. However, problems are observed at higher steam temperatures and pressures, [9]. In addition, nickel-based alloys are expensive (because of the relatively high price of nickel) and finding coating alloys which are cheaper, but as effective, would be advantageous.

Table 1.2.1 Mean values of key elements in forest residues and used wood and the spread in used wood analyses. From 16 analyses of forest residues and 12 analyses of used wood. Data reproduced from information in Ref. 10.

Parameter	Forest residues	Used wood	Used wood Spread
Total moisture (weight %)	44	23	11 - 39
Total ash (weight % dry)	2.6	5.8	3.2 - 15
C (wt %) dry ash-free	51	52	50 - 56
N (wt %) dry ash-free	0.4	1.2	0.12 - 1.5
S (wt %) dry ash-free	0.04	0.08	0.04 - 0.3
Cl (wt %) dry ash-free	0.02	0.06	0.04 - 0.22
K (wt %) in ash	7.2	2.0	1.0 - 2.6
Na (wt %) in ash	0.7	1.4	0.6 - 1.9
Zn (mg/kg) in ash	2047	10393	2420 - 184167
Pb (mg/kg) in ash	63	544	140 - 28611

It has been found, for example, 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 α' or sigma- phase, [4]. These materials, like APMT, can be used as coatings, but need more long-term evaluation.

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 [5,6]. Short-term tests which have previously been performed with sewage sludge in KME-508 have been more fully evaluated to assess the effectiveness of long-term usage.

Mechanisms of wall corrosion also need to be further studied. Different types of corrosion attack are thought to occur in a used 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 (Cl₂) under a deposit, and this is a smaller molecule than chlorine, which could more easily diffuse through a defect oxide [8,14]. 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].

1.3 RESEARCH TASK

In this project, ways of reducing furnace wall corrosion, while combusting used wood, have been investigated. Long-term corrosion tests have been performed in power boilers on the standard wall coating alloy, Alloy 625, and on different candidate coatings or materials that could be applied as coatings.

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.

Tests with two different sorts of used wood have been made in a 100 MW power boiler and a 10 kW laboratory rig and the results compared.

1.4 GOAL

The aim of the project is to reduce high temperature corrosion in heat and power boilers that burn predominantly used (recycled) wood. Most of the effort has been directed towards furnace walls.

A secondary goal is to evaluate materials suitable for superheaters when burning recycled wood. Superheaters close to the furnace region experiencing high flue gas temperatures (and therefore susceptible to high corrosion rates) are the main focus.

The main goal is to reduce furnace wall corrosion caused by combustion of used wood in a cost-effective way. This has been achieved by :-

- (1) finding wall coating materials that are more cost-effective than conventional nickel-base alloys (i.e. cheaper or more corrosion resistant). A cost or corrosion rate reduction of 20% is aimed at.
- (2) obtaining a better understanding between fuel quality (fuel chemistry) and corrosion
- (3) from results of short-term testing (performed in 508) with digested sewage sludge decide to proceed (or not) with long-term testing of sludge as an additive, i.e decision to run part 2 (KME-718).

As the results reveal, these goals have been fulfilled.

1.5 PROJECT ORGANISATION

The project organisation is described below:

Vattenfall AB, Research and Development (VRD) and Nordic Heat (VNH) - Pamela Henderson, project manager, Mattias Mattsson, Carl Nordenskjöld, Annika Stålenheim and Håkan Kassman, plus support from many other colleagues.

Overall project management, management of Vattenfall activities and supervision of PhD student at KTH. Plant testing - construction and provision of corrosion and deposit probes, long-term (six weeks) testing, short-term (two weeks) testing and 3 hour measurements in Idbäcksverket, Nyköping. Boiler operation and provision of operational data. Fuel and fly ash analyses. Corrosion measurement and deposit analysis. Data analysis and reporting.

In-kind contribution 2 830 000 kr.

AB Sandvik Materials Technology – Jan Högberg and Jesper Ederth. Provision of materials and technical support. In-kind contribution 340kSEK.

Sandvik Heating Technology AB, Johanna Nockert Olovsjö, Susanne Selin. Provision of materials, overlay welding, technical support. Development of a welding procedure for Kanthal APMT™. In-kind contribution 400kSEK.

E.ON Värme Sverige AB and E.ON Business Heat and Power Solutions UK- Anna Jonasson and Colin Davis. In-kind contribution 340 kSEK. Corrosion testing (superheaters and furnace walls) in Blackburn Meadows. Characterisation and installation of coated tube in furnace wall of Blackburn Meadows.

Amec Foster Wheeler OY, Edgardo Coda Zabetta and Jouni Mahanen. In-kind contribution 340 000 kr. Corrosion testing.

AB Fortum Värme samägt med Stockholms stad: Eva-Katrin Lindman. In-kind contribution 140 000kr. Technical support.

Göteborg energi AB: Cash contribution 30 000kr.

Researchers receiving financing and activities:

KTH, Division of Surface and Corrosion Science – Peter Szakalos (part time), Ph.D student Yousef Alipour (full-time). Budget 1 885 007 kr

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 and PhD student Annika Talus. Budget 833 000kr

Deposit analysis and initial corrosion of short-term probe specimens from Idbäcken and SP’s combustion rig.

SP - Anders Hjörnhede and Fredrik Niklasson. Budget 275 000kr

Short-term (8 hour) tests in a laboratory-scale fluid bed rig using recycled wood provided by Vattenfall AB.

Reference group. This consisted of the participants from the above mentioned companies/organisations and a representatives from boiler manufacturers Babcock & Wilcox Völund and Andritz and from the High Temperature Corrosion Competence Centre at CTH, Gothenburg.

2 Experimental

2.1 DESCRIPTION OF PLANTS

2.1.1 Idbäcken P3, Nyköping, Sweden. Owned by Vattenfall AB.

Most of the testing has been performed 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 (Boilers 1 and 2) for hot water production and a hot water accumulator.

Boiler 3, the CHP unit, which was used for the testing, was taken into operation in 1994 and originally operated on a mixture of biomass and coal. Over the years the amount of coal has been reduced and the amount of used wood increased. Since the summer of 2008, the plant has been run on 100% recycled 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. Holes for probe testing were made on the back wall in an area of high corrosion. Previous testing in KME-508 was made in the centre of the back wall, but this hole was not easily accessible outside the boiler causing safety issues. There two new holes, separated by 30 cm, were made at a distance of about 2 metres from the original position, but at the same level in the boiler between secondary and tertiary air. A cross-section of the plant with the testing positions is shown in Figure 2.1.1.

2.1.2 Blackburn Meadows, Sheffield, UK. Owned by E.ON Business Heat and Power Solutions UK.

This plant was taken into operation in May 2014 and also runs on 100% used wood. It is owned and operated by E.ON Business Heat and Power Solutions UK. The boiler is a 97MW bubbling fluidized bed which produces 30MW electricity, but no heat. The final steam data is 82 bar/487°C. A cross-section of the boiler with testing positions are shown in Fig. 2.1.2.

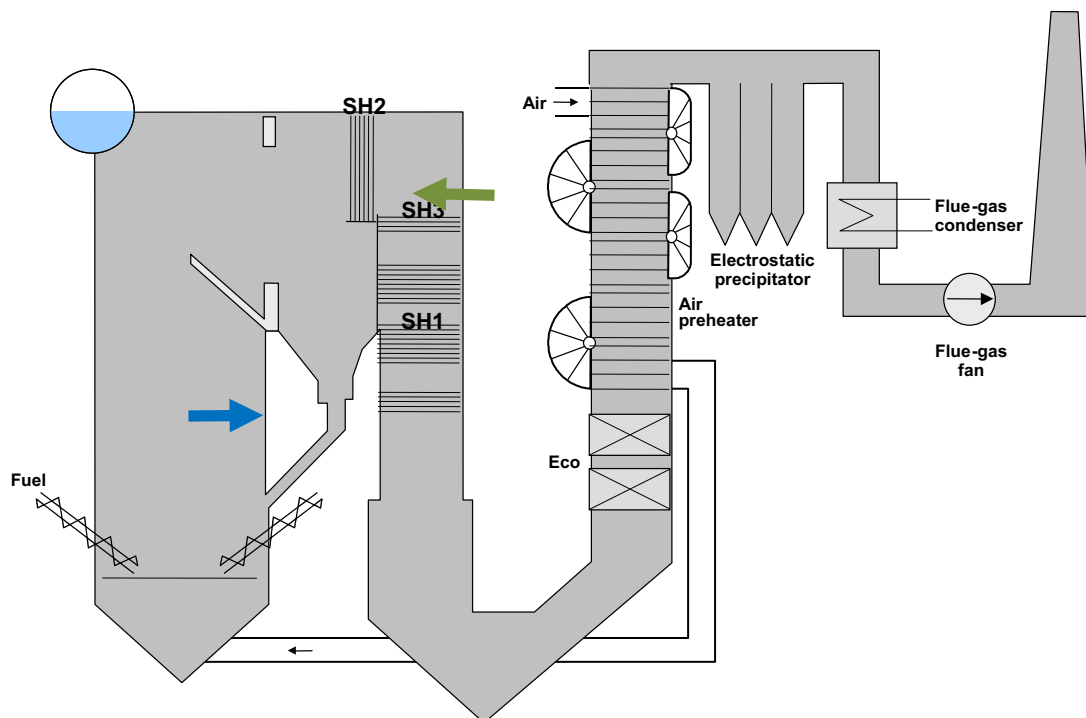


Fig. 2.1.1 Cross-section of the BFB plant in Nyköping showing testing points. Wall corrosion blue arrow, short-term superheater deposit probes green arrow above superheater 3. (Superheater 2 no longer in use – has been removed)

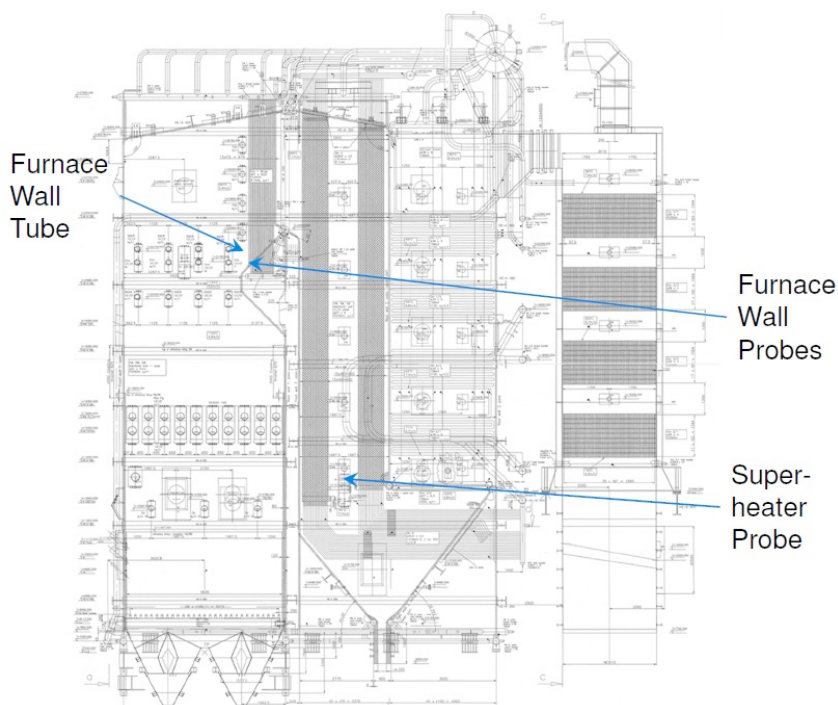


Fig. 2.1.2 Cross-section of the BFB plant in Blackburn Meadows showing the testing points.

2.1.3 Händelö P15, Norrköping, Sweden. Owned by E.ON Värme Sverige AB.

This plant is owned and operated by E.ON and is situated near the city of Norrköping. It is a circulating fluidized bed boiler running on 100% waste derived fuel and produces 85 MW heat

and 30 MW electricity. The final steam data is 66 bar and 450 °C. The plant was built by Amec Foster Wheeler who performed probe tests at the furnace wall. A sketch of the boiler showing the location of the probes is given in Fig. 2.1.3.

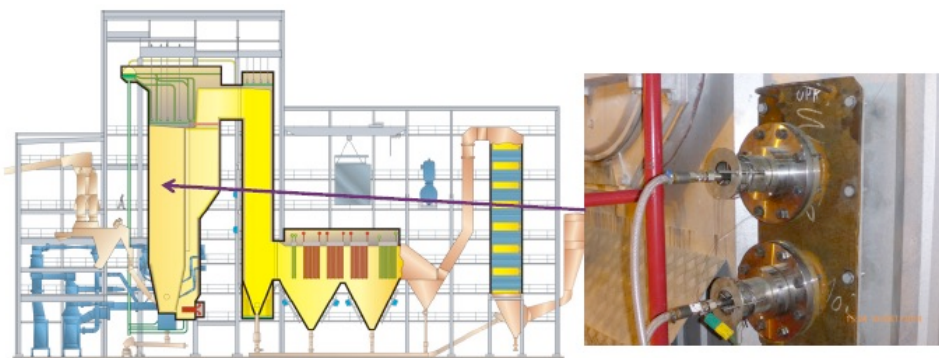


Fig. 2.1.3. Cross-section of Händelö CFB showing position of wall probes.

2.2 PLANT CORROSION AND DEPOSIT PROBE TESTING

2.2.1 Vattenfall's probes

Long-term material corrosion testing and fuel quality testing in the furnace region was performed with two air-cooled probes, each containing four specimens which were exposed simultaneously in the furnace region of the Idbäcken power plant. These two probes were separated by a distance of 30 cm and were positioned on the back wall at a height of 16 m. The wall probes, which were designed and built by Vattenfall Research and Development are long and thin (as can be seen in Figure 2.2.1) and were inserted vertically into slits made in the fins between two tubes. The probes each contained four specimens, placed vertically under each other. The specimens were of dimensions 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 350 °C or 400 °C, depending on the type of test. 400 °C simulates the temperature of the tube wall at 140 bar (the design pressure of the plant) and 350 °C the temperature of the tube wall at a reduced pressure of 90 bar. For long term material corrosion testing the total exposure time at temperature was about 1000 hours (6 weeks), for fuel quality testing the exposure time was 330h (2 weeks) and for short-term deposit testing with and without digested sewage sludge was about 15 hours.

Before exposure in the boiler, the thickness of each 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. (One cut, near the top, was made without water and that part of the specimen was reserved for further analysis in a scanning electron microscope). Four remaining parts of each sample were mounted in resin and used for metal thickness measurement by light optical microscope with a micrometer measuring gauge. A total of 20 points were measured after testing.

No coated specimens were tested on Vattenfall's probes, although all the materials tested were suitable for use as coatings.



Fig. 2.2. 1. Vattenfall's wall probe after exposure (left). The probes sit vertically in a slit in the fin between two tubes, here seen from outside the furnace, (right)



Fig. 2.2.2. Vattenfall's deposit probe before exposure.

Deposit probe testing at the superheaters was performed with a triple temperature air-cooled probe with temperature zones 350, 450 and 550°C. The probe is shown in Figure 2.2.2. The deposit probe was used during the fuel quality tests and exposed for three hours. The individual rings were weighed before and directly after exposure to determine deposit growth and the deposit analysed afterwards in a scanning electron microscope.

2.2.2 E.ON's probes

E.ON performed corrosion testing in their boiler at Blackburn Meadows power station, UK. E.ON have also designed and built their own furnace wall probe (air-cooled) which is shown in Figure 2.2.3. Their superheater probe, also air-cooled, is shown in Figures 2.2.4 and 2.2.5. Corrosion testing in the furnace lasted 70 h with mean probe metal temperatures of 355-358°C. At the superheaters testing lasted 890 h. The superheater probe contained 26 rings of different materials and a temperature gradient ranging from 435°C at the probe tip (ring 1) to 530°C (ring 26). Both coated and uncoated specimens were tested in Blackburn Meadows.

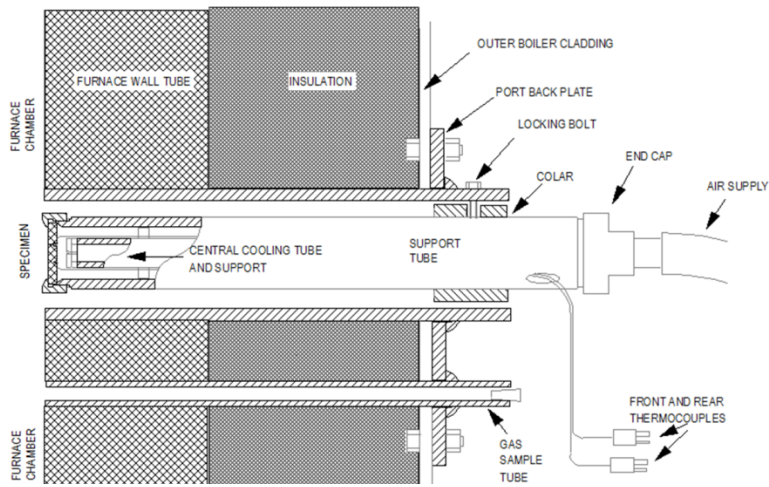


Fig. 2.2.3 A sketch of E.ON's wall probe inserted through the furnace wall. The probe is 31 mm in diameter.

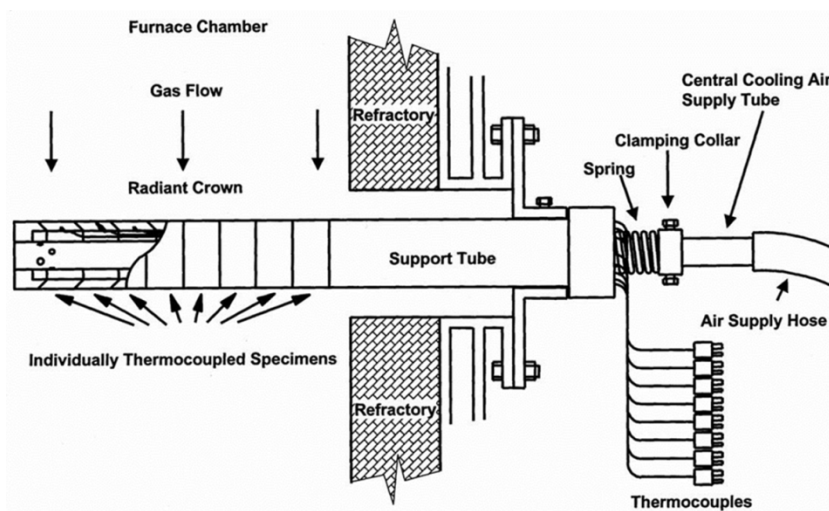


Fig. 2.2.4 A sketch of E.ON's superheater probe. The probe rings have an outer diameter of 37 mm.



Fig. 2.2.5 . E.ON's superheater probe after 890 hours exposure (close up of probe tip with ring specimens).

2.2.3 Amec Foster Wheeler's probe

AFW's furnace probe, which is air-cooled, is 70 cm long and shown in Figure 2.2.6. Three specimens (55mm x 15 mm) can be accommodated. Two probes with temperature 330°C and 360°C were exposed simultaneously during a four month period. No coated materials were tested.

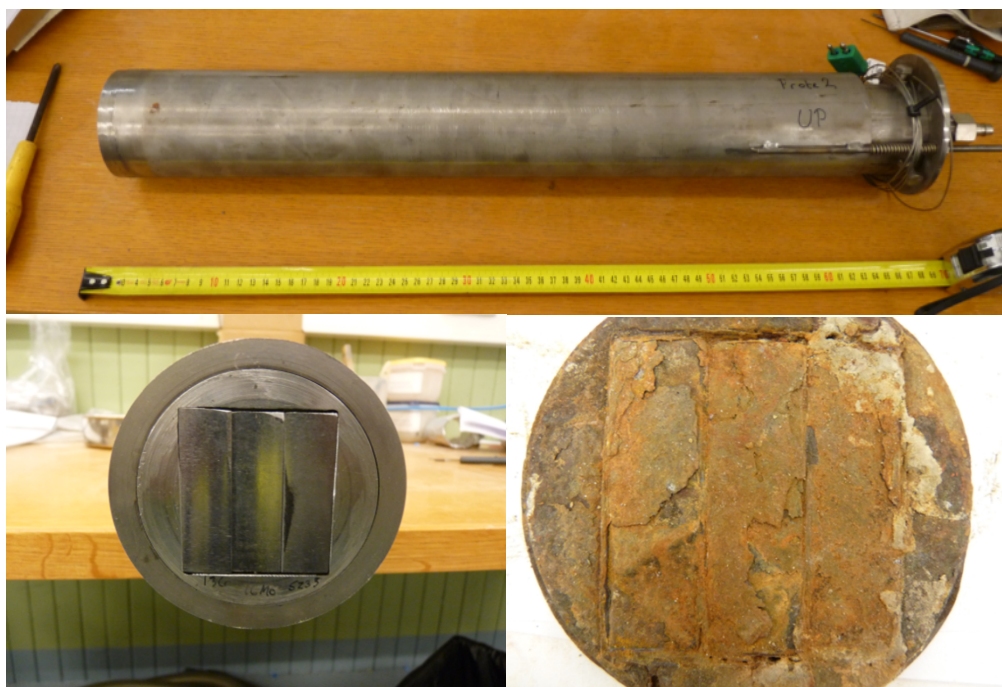


Fig. 2.2.6. AFW's furnace probe. Longitudinal view (upper).
Probe tip with three specimens before exposure (lower left).
Probe tip with three specimens after exposure at 330°C (lower right).

2.2.4 E.ON's coated wall tube test

In addition to plant testing with probes performed by Vattenfall, Amec Foster Wheeler and E.ON, the latter has also installed a furnace wall tube coated with a number of different materials. The tube was installed on 1 July 2016 and will remain in operation for one year or more. The position of the coated tube is close to that of the wall probes in Blackburn Meadows and is shown in Fig. 2.1.2.

Five different coatings were applied by different companies in different parts of the world including Sandvik's Kanthal APMT™ and Alloy 625 (San 60) as a reference. The ability to produce a quality overlay weld on a tube using Kanthal APMT™ (without needing a post weld heat treatment) was part of the experimental development work of this project. A photograph of the tube is shown in Fig. 2.2.7, a table of coatings in Table 2.2.1 and their chemical compositions in Table 2.2.2.

The tube was made of the plain carbon steel P235GH. The thickness of the coatings was measured before the tube was welded into the boiler. A "dummy" tube was also coated and will be retained for material characterization by microscopy etc. The tube will be evaluated during the continuation project KME-718.



Fig. 2.2.7. Sketch of coated tube showing dummy tube at bottom and furnace wall tube at top (left).
 Photograph of the wall tube before being welded into position (middle).
 Photograph of the tube in position in furnace wall (right).

Table 2.2.1 Name and position of coatings on the furnace wall tube.

Materials (and position) on tube	Application Method	Nominal Thickness
Sanicro 60 (Alloy 625) Top	Weld Overlay	4mm
Kanthal APMT™	Weld Overlay	2mm
Nanosteel (Weartech SHS7574HV)	Laser Clad	1mm
IGS5-460 (Ni-based)+ Al based sealant. Under cobalt blue coating	HVTS + Brush	0.5mm (+ sealant)
IGS1-021 (Alloy 625) + Al base sealant. Under cobalt blue coating	HVOF + Brush	0.35mm (+ sealant)
Sanicro 60 (Alloy 625) Bottom	Weld Overlay	4mm

Table 2.2.2. Nominal chemical compositions of the coatings on the furnace wall tube.

Consumable	C	Si	Mn	Cr	Ni	Mo	Fe	Nb	W	B	Al	Other
Sanicro60 (IN625)	≤0.03	0.2	0.2	22	≥60	9	≤1	3.5				
Kanthal APMT™	≤0.08	≤0.70	≤0.40	23.5 20.5		3	≥67.3				5	Rare Earth
Nanosteel	<3	<2	<5	<25		<20	Bal.		<10	<5		
IGS5-460		<3		22	Bal	5			3	<3		
IGS1-021	2 - 4			35 30	55 45	7 5	4 0	2 1				
IGS Sealant	CoAl ₂ O ₄ , AlPO ₄ + aluminium (as oxide)											

2.3 LABORATORY CORROSION AND DEPOSIT PROBE TESTING PERFORMED BY SP

The corrosion test comparing two fuel qualities in Idbäcken was performed for approximately 330 h and the tested materials were 16Mo3 and Alloy 625. In order to study the corrosion for these materials under more controlled conditions, a laboratory test using the same fuels as in the field test was performed at SP. Materials were exposed for 8 h in positions resembling both furnace wall position (16Mo3, IN625 and Sanicro28) and superheater position (2.25Cr, 304L and Sanicro28). The equipment used was a laboratory 10 kW fluidised bed boiler with a height of 3 m. The inner diameter of the reactor was 10 cm and the fuel was fed to the bed below the secondary air inlet. The metal ring samples had an outer diameter of 24 mm and were exposed on an air-cooled probe in between the secondary and tertiary air inlet (furnace wall samples) and after the tertiary air inlet (superheater samples). The metal temperatures tested were 380 °C (furnace samples) and 550 °C (superheater samples). Illustrations of the laboratory test rig and the sample probe are shown in Figure 2.3.1.

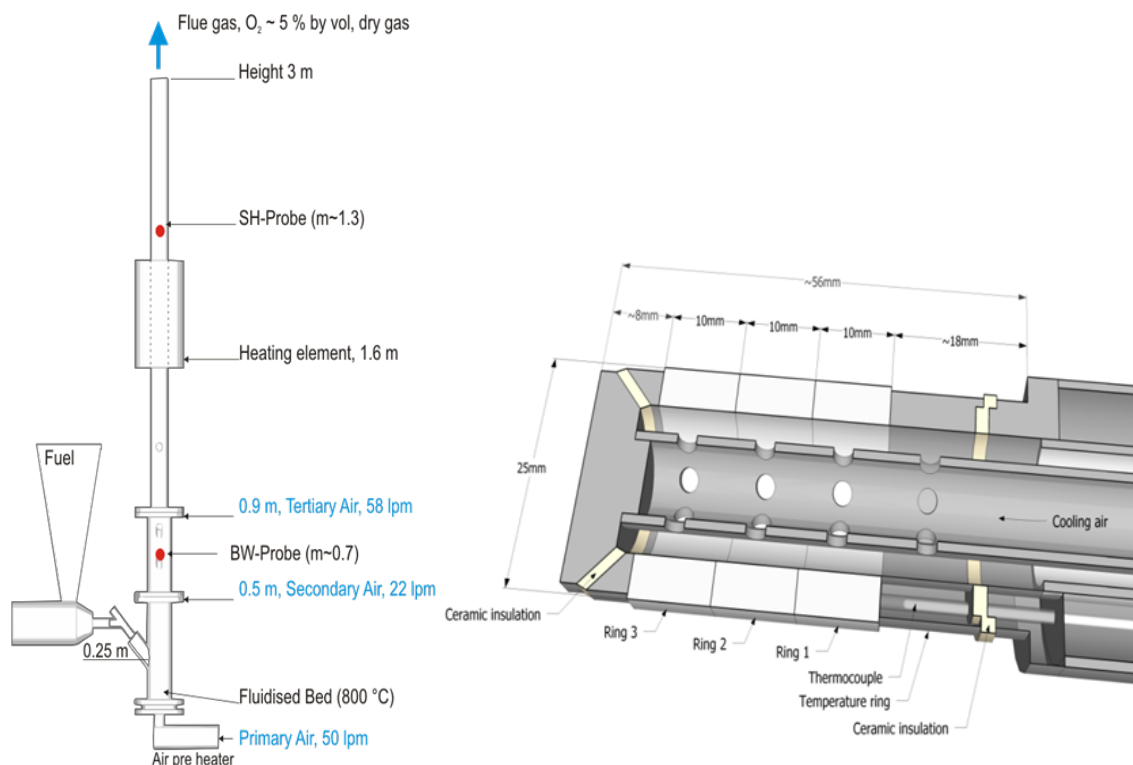


Figure 2.3.1. Illustration of SP's laboratory fluidised bed boiler (left) and air cooled sample probe (right).

The fuel used in the laboratory test was delivered from Vattenfall and had been sampled during the field test where two fuel qualities were tested. In order to be able to use the recycled wood in the laboratory test rig, it was first milled and then made into pellets with 8 mm diameter. The probe rings were weighed before exposure. After exposure loosely sitting ashes/deposit was removed from the rings and the rings were weighed again.

2.4 METALLOGRAPHIC AND CHEMICAL ANALYSES

A number of different techniques were utilised in the project. For cross section analysis and imaging scanning electron microscopy (SEM) was used. In order to make cross sections without exposing the sample to air and moisture focused ion beam (FIB) milling was used. For chemical analysis both of surface deposit composition and in cross sections, energy dispersive spectroscopy (EDS) and wave dispersive spectroscopy (WDS) were used. In addition, X-ray diffraction (XRD) was performed to obtain information of crystalline phases present in the deposits. Glow discharge optical emission spectroscopy (GD-OES) was used in order to obtain depth profiles of the chemical composition in the deposits. These techniques are described in more detail below.

2.4.1 Scanning Electron Microscopy (SEM) and Energy/Wavelength Dispersive Spectroscopy (EDS/WDS)

Scanning electron microscopy (SEM) was used frequently in the evaluation of samples. This technique uses electrons to produce an image. A focused electron beam scans a specimen, and when electrons hit the sample, they interact with the atoms in the sample and send different signals back. Commonly used signals for imaging and analysis are secondary electrons (SE), backscattered electrons (BSE) and X-rays. These signals originate from different depths within the specimen and are often used in combination in order to get the most out of an analysis. Secondary

electrons escape from the sample in areas close to the surface and are thus useful for topographical studies. Backscattered electrons have higher energy compared to secondary electrons and give elemental contrast of a sample; an element with a higher atomic number will appear lighter compared to an element with a lower atomic number. When primary electrons interact with the specimen, X-ray signals are also formed. The energy of these signals and the wavelengths are characteristic for each element and, thus, the signal can indicate the chemical composition of a specimen by using an energy dispersive spectrometer (EDS) or a wavelength dispersive spectrometer (WDS). WDS is useful when a sample contains elements whose X-ray signals are overlapping because they have similar energies. Sulphur (S), molybdenum (Mo) and lead (Pb) are typical elements which can be difficult to separate and one example of when WDS can be useful.

2.4.2 Focused Ion Beam (FIB)

The preparation of a cross section for analysis in SEM often results in some exposure to air and humidity. Even though dry sample preparation is used some corrosion products are very sensitive and the humidity in the air can cause a reaction before the sample is put under vacuum in the SEM. In order to avoid this, the focused ion beam (FIB) technique can be used. This is a technique that performs ion milling of the sample under vacuum. Chemical analysis of the sample can then be performed without any exposure to air humidity as long as some kind of chemical analysis equipment, like EDS or WDS, is installed in the microscope.

2.4.3 X-ray diffraction (XRD)

In order to study crystalline phases in the deposits on exposed samples, X-ray diffraction (XRD) was used. This gives information about what has formed or has been deposited on the samples during the exposures. The technique is based on irradiating a sample with monochromatic X-rays that are diffracted in a certain pattern, depending on the crystalline phase that is being irradiated.

2.4.4 Glow discharged optical emission spectroscopy (GD-OES)

To study the chemical profile from the top of a deposit towards the oxide/metal interface and into the metal, glow discharged optical emission spectroscopy (GD-OES) can be used. This technique gives a relatively fast response to the chemical profile through the deposit, and, in general, very little sample preparation is necessary.

The specimen is bombarded with argon ions on a circular area of 2-4 mm in diameter. When the argon ions hit the sample, the atoms on the specimen surface are sputtered away layer by layer. The characteristic light emission from this process is analysed with an optical emission spectrometer and the depth profile of the chemical concentrations in the deposit and oxide are, thus, obtained.

2.5 MATERIALS TESTED

The compositions of the alloys tested are given in Tables 2.5.1 and 2.5.2

Table 2.5.1 Materials tested on probes by Vattenfall and SP in Sweden

Name	Chem comp wt%	Notes
16Mo3	Mn 0.55, Si 0.22, Mo 0.3.	
13CrMo44	Cr 0.9, Mn 0.8, Si 0.22, Mo 0.5.	SS 2216
10CrMo9 10 /2.25Cr	Cr 2.25, Mn 0.5, Mo 1.0, Si <0.5,	
TP304L	Cr 18, Ni 10, Mo 0.3, Mn 1.2	SS 2352
San 28	Cr 27, Ni 31, Mo 3.4, Mn 1.7, Cu 1.0	Sandvik
Alloy 625 (Harald Pihl)	Ni 60, Cr 22, Mo 9, Nb 3.5, Fe 4, Mn 0.06, Ti 0.28, Al 0.17, Ta 0.01	Deutsche Nickel
Kanthal APMT™	Cr 21, Al 5, Mo 3 Fe Bal	Sandvik
Alkrothal 14	Cr 14, Al 4.3, Mn 0.15, Si 0.13, Fe Bal	Sandvik
Nikrothal PM 58	Fe 20, Cr 18, Al 5, Ni bal	Sandvik
Sanicro [X]	Not disclosed	Sandvik

Table 2.5.2 Materials tested on probes by E.ON in UK. Coatings are highlighted in yellow. FW= furnace wall coatings. SHTR= Superheater coatings.

Alloy wt%	Al	Si	V	Cr	Mn	Fe	Ni	Nb	Mo	Others
16Mo3 (Furnace)				0.2	0.5	98.6	0.2		0.3	Cu:0.2
FW FeCrAl	5.4	1.7		19.9	0.8	70.3				O:1.8
FW IN625	0.3	1.4		19.8	0.5	7.8	55.5	3.9	9.1	O:1.8
FW 50Cr50Ni	0.3	2.8		36.5		19.0	39.2			O:2.2
FW C276	0.4	1.4	0.4	13.9	1.3	8.5	51.4		16.5	O:1.6, W:1.6
16Mo3 (SHTR)		0.3		0.2	0.7	98.4			0.4	
10CrMo910				2.4	0.5	95.4	0.2		1.0	
X20CrMoV121		0.3	0.39	12.4	0.5	84.5	0.6		1.2	
Esshete1250		1.6	0.3	15.3	6.6	66.4	9.3	0.5		
DMV310N		0.6		25.2	1.3	51.6	20.5	0.4		N:0.3
Super625		0.4		21.8	0.3	16.0	51.6	0.5	8.8	Al:0.2, Ti:0.2
HR11N		0.3		29.9	0.7	28.4	39.1			N:0.3
SHTR FeCrAl	3.3	1.2		17.9	0.9	69.0	4.3			O:2.8
SHTR IN625		0.9		21.1	0.7	6.2	56.3	3.4	9.7	O:1.6
SHTR 50Cr50Ni		1.8		31.3		33.7	29.7			O:1.7

3 Results

3.1 FUEL QUALITY TESTING IN IDBÄCKEN

Two different sources of fuel were used which were fired in the boiler for two consecutive 3-week periods. Furnace wall corrosion probes were exposed for 2 weeks during each 3-week period and superheater deposit probes were exposed for 3 hours during each 2-week corrosion test. The fuels were obtained from different suppliers/sources and their chemical compositions (averages of 4-6 samples collected over each 3-week test period) are given in Table 3.1.1. It can be seen that Fuel 1 has a lower Cl and Pb content, but a higher moisture and Zn content than Fuel 2.

Table 3.1.1 Compositions of the fuels used for the two-week comparison tests

		Fuel 1	Fuel 2
Moisture –as rec.	%	34,8	22,2
Ash content – as rec	%	3,6	5,8
S	[% ds]	0.07	0.07
Cl	[% ds]	0.13	0.20
Al	[mg/kg ds]	1 534	1 262
Ca	[mg/kg ds]	4 044	5 117
K	[mg/kg ds]	995	900
Mg	[mg/kg ds]	1 055	538
Na	[mg/kg ds]	1 611	976
Si	[mg/kg ds]	9 540	15 247
Cu	[mg/kg ds]	46	45
Pb	[mg/kg ds]	38	136
Zn	[mg/kg ds]	398	122
P	[mg/kg ds]	89	118

3.1.1 Superheaters

The growth rates of the deposits near the superheaters obtained from Fuel 2 were higher than those from Fuel 1, especially at the highest temperature, as can be seen from Fig. 3.1.1. Fig. 3.1.2 shows that more Cl was present in the deposits from Fuel 2 and more S was present in the deposits from Fuel 1. No Pb was detected in the deposits from Fuel 1 at the two highest temperatures of 450°C and 550°C. Sections through the rings to examine the initial corrosion showed that more corrosion was caused by Fuel 2, (see Figs. 3.1.3 and 3.1.4) on 13CrMo44 (SS2216) at 350°C and 450°C after 3 hours.

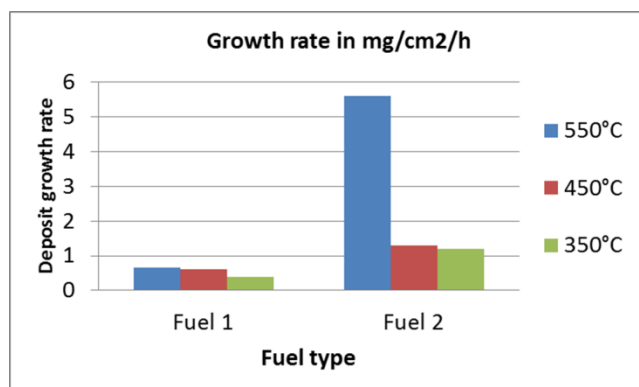


Fig. 3.1.1 Deposit growth rates at three different ring temperatures obtained from probe testing near the superheaters. Exposure time 3 hours.

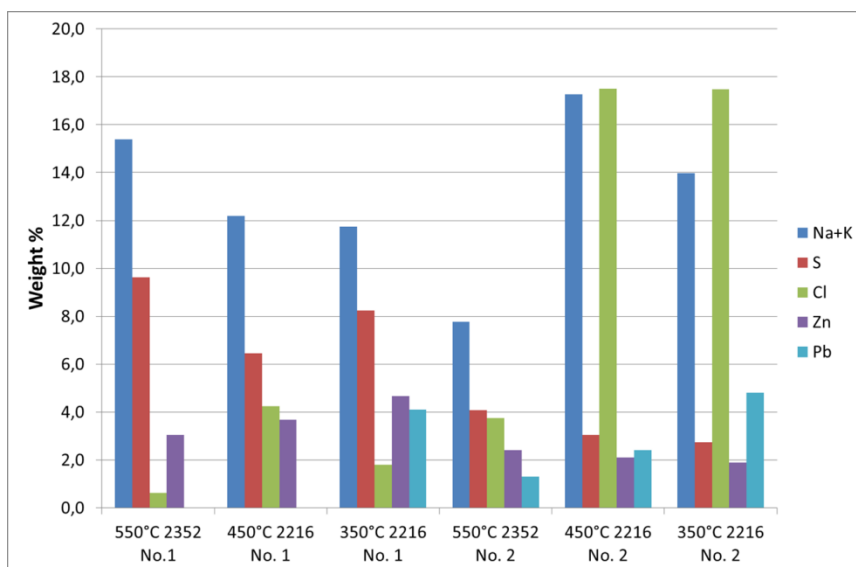


Fig. 3.1.2 Amounts of key elements in the probe deposits at three different temperatures. Exposure for 3 hours near the superheaters. The rings used at 550°C were made of stainless steel (SS 2352) and the rings used at 350°C and 450°C were made of a low alloy ferritic steel (SS 2216).

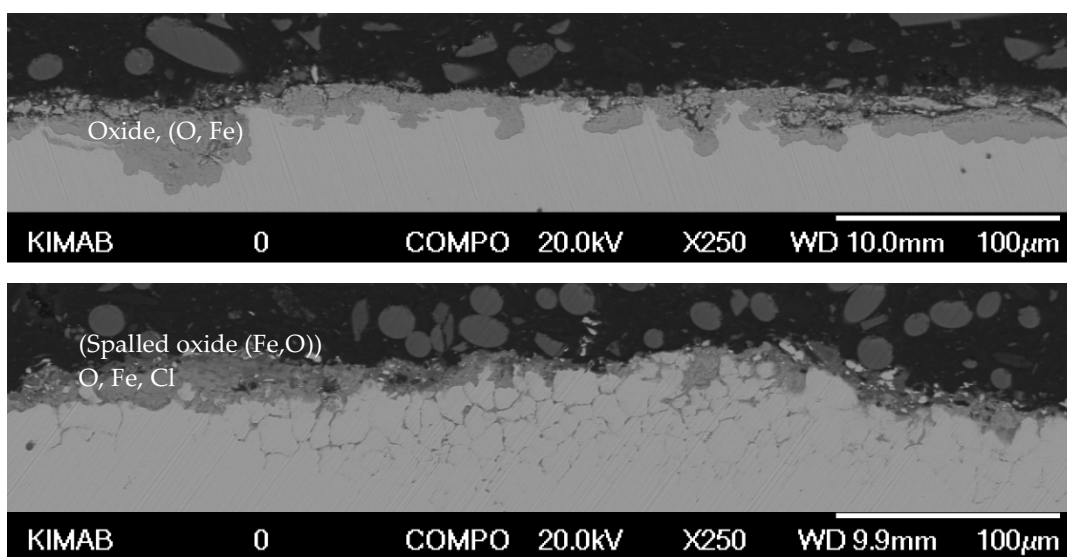


Fig. 3.1.3 Section through the 13CrMo44 (SS2216) deposit rings exposed for 3h at 350°C. Upper- Fuel 1, Lower-Fuel 2. More corrosion (grain boundary attack) caused by Fuel 2.

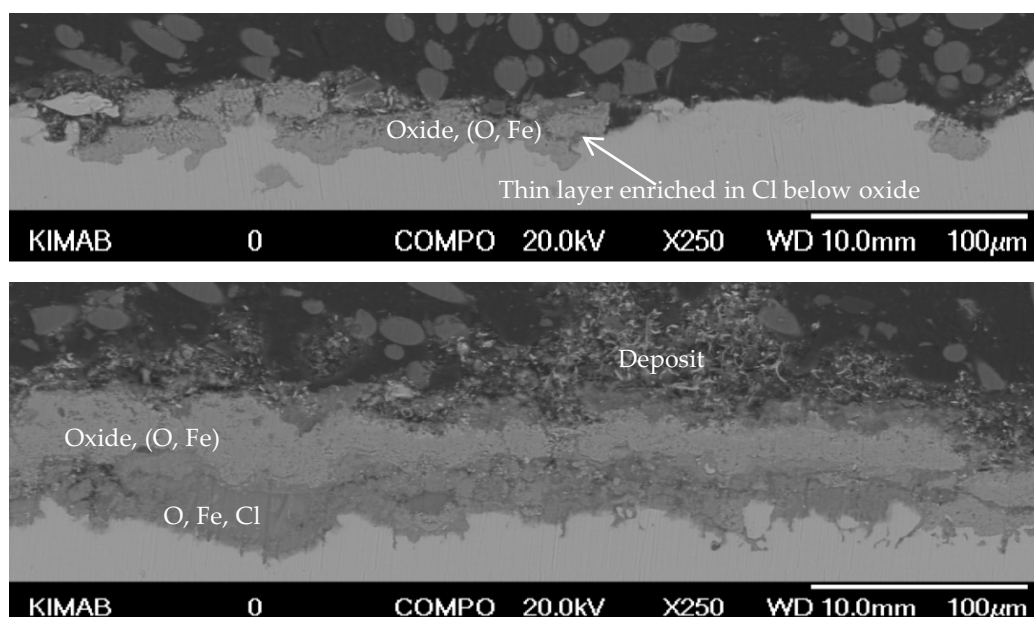


Fig. 3.1.4 Section through the 13CrMo44 (SS2216) deposit rings exposed for 3h at 450°C. Upper- Fuel 1, Lower-Fuel 2. More corrosion and thicker chloride layer caused by Fuel 2.

Areas with high concentrations of Pb and Cl were found in the cross sections for samples exposed to the Fuel 2 (high Pb/Cl fuel) at 350°C and 450°C. For the stainless steel exposed at 550°C (not shown) a slight increase of internal corrosion was observed with chlorine present in grain boundaries for the sample exposed when firing Fuel 2.

3.1.2 Furnace wall

The deposits on the wall probes were of course much thicker (after 2 weeks testing) although uneven because of spalling. Some deposits from the wall corrosion probes were analysed and the results for chlorine given in Fig. 3.1.5. More Cl was found in the wall deposits from Fuel 2 which agrees with the 350°C results from the superheater probe deposits in Fig. 3.1.2. The lead concentration was found to increase in the deposit closer to the metal substrate for all samples, which meant that a thinner (spalled) deposit showed higher lead levels.

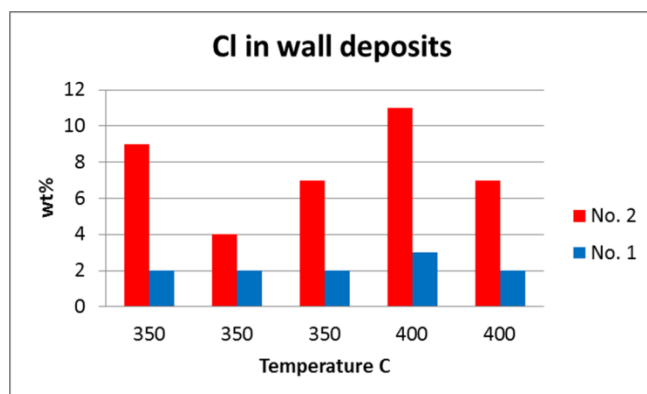


Fig. 3.1.5 Amount of Cl in the deposits on the wall probes after 333 h exposure.

Two probes were used in parallel for each fuel case, one with a control temperature of 350°C and one at 400°C. There were two specimens of the low alloyed steel 16 Mo3 (tube steel) and two of the nickel-based alloy Alloy 625 (coating material) on each probe. (Alloy 625 is used to coat the boiler tubes in the furnace wall, but for this corrosion test specimens of solid Alloy 625 – i.e. not coated, were used.) There was some spread in temperatures along the probes, but the temperature of each specimen was measured individually. The corrosion caused by Fuel 2 was greater than that caused by Fuel 1 and also more temperature dependent, see Fig. 3.1.6.

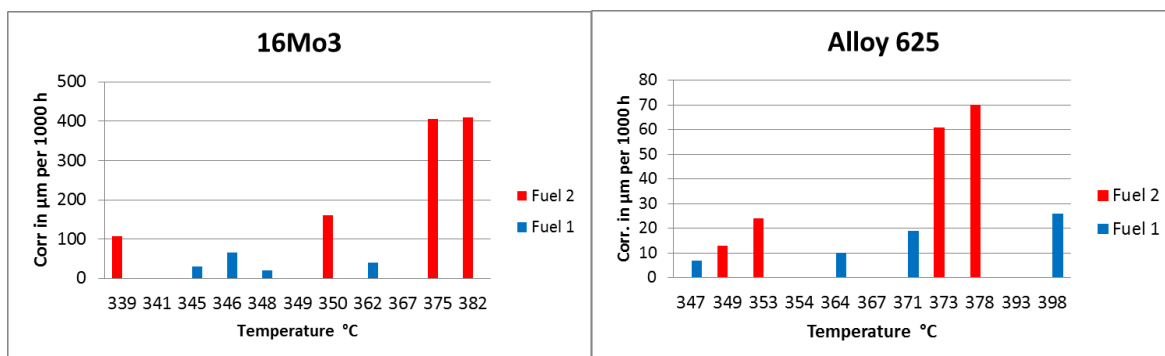


Fig. 3.1.6. Corrosion rate in µm per 1000 h for 16Mo3 (left) and alloy 625 (right). Testing time 333 h in both cases. Note the difference in scales. Fuel 2 caused more corrosion than Fuel 1.

Metallographic analysis confirmed these results. For 16Mo3, iron oxide and iron chloride were found as corrosion products and Pb-rich compounds were found in the samples exposed to Fuel 2, but not Fuel 1, see Fig. 3.1.7

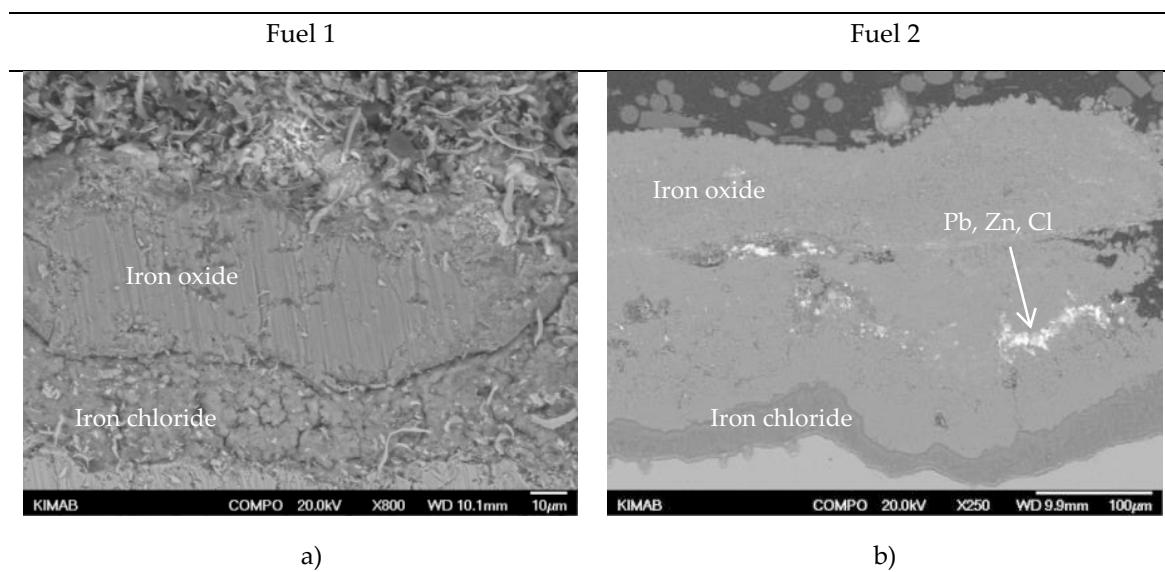


Fig. 3.1.7. Corrosion products on 16Mo3-samples with a metal temperature of 350 °C exposed on the furnace wall probe when firing a) Fuel 1 and b) Fuel 2. (Note: a) is at higher magnification x800 than b) x250.)

For the Alloy 625 samples local corrosion attack with nickel oxide and chromium oxide was observed and the numbers increased with increasing temperature. In addition lead molybdate, PbMoO_4 , was found on the surface and in the cross-sections of the Alloy 625 samples exposed in Fuel 2 at temperatures greater than 370°C, see Figure 3.1.8. This compound was identified by EDS analysis and X-ray diffraction. At lower temperatures (350 °C) no lead molybdate was found in the corrosion products.

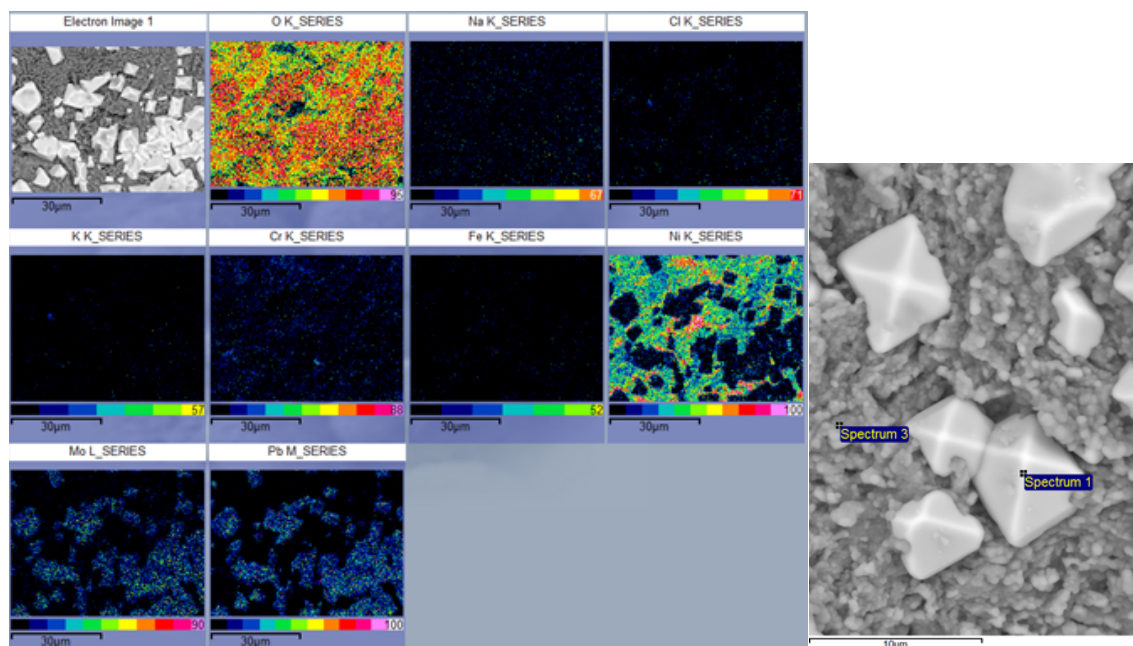


Fig. 3.1.8. The surface of Alloy 625 after 333 hours exposure at 373°C to Fuel 2 on a furnace wall probe.
(Left) Mapping diagrams showing the presence of oxygen, molybdenum and lead rich areas.
(Right) High magnification photo of lead molybdate crystals.

3.2 FUEL QUALITY TESTING IN THE LABORATORY

Two different sources of fuel were used which were fired in two separate tests. Furnace wall deposit probes and superheater deposit probes were exposed for 8 h. The fuel originated from the fuel quality tests in Idbäcken and was subsequently pelletised for the laboratory tests. The chemical compositions of the two fuels as pellets are given in Table 3.2.1 and compared with the power plant fuel. Some differences from the power plant fuel can be seen but it needs to be kept in mind that only a small part of the plant fuel was sampled to be used in the laboratory exposures and there can be large variations within each used wood fuel. In similarity to the field exposure, test Fuel 1 has a lower Cl and Pb content compared to Fuel 2.

Table 3.2.1 Compositions of the fuels used for the two-week comparison tests

		Fuel 1 (field)	Fuel 2 (field)	Fuel 1 (lab-pellets)	Fuel 2 (lab-pellets)
Moisture –as rec.	%	34,8	22,2	15,3	12,3
Ash content – as rec	%	3,6	5,8	5,7	4,2
S	[% ds]	0.07	0.07	0.07	0.07
Cl	[% ds]	0.13	0.20	0.08	0.11
Al	[mg/kg ds]	1 534	1 262	2600	1600
Ca	[mg/kg ds]	4 044	5 117	5100	6000
K	[mg/kg ds]	995	900	1500	1000
Mg	[mg/kg ds]	1 055	538	1100	600
Na	[mg/kg ds]	1 611	976	1700	1100
Si	[mg/kg ds]	9 540	15 247	14 400	11 500
Cu	[mg/kg ds]	46	45	64	56
Pb	[mg/kg ds]	38	136	59	170
Zn	[mg/kg ds]	398	122	550	850
P	[mg/kg ds]	89	118	100	100

As described in the experimental, loosely sitting ash/deposit was removed from the rings after exposure. In Figures 3.2.1 and 3.2.2 the visual appearance of the probes after exposure and before removing the loose ash is shown.



Fig. 3.2.1 Furnace wall probe at 380°C directly after removal from the test rig. Fuel 1 (left); Fuel 2 (right)

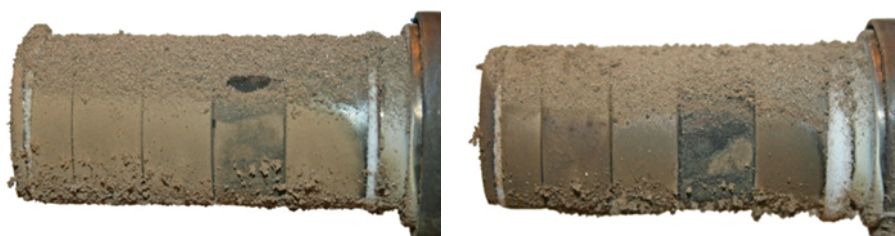


Fig. 3.2.2. Superheater probe at 550°C directly after removal from the test rig. Fuel 1 (left); Fuel 2 (right).

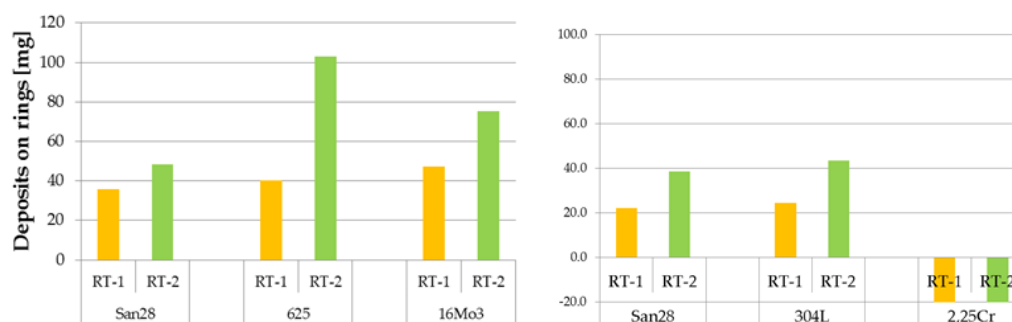


Fig. 3.2.3. Weight gain for each ring after the loose ash has been removed. Furnace wall probe at 380°C (left). Superheater probe at 550°C (right). In each case the weight gain is greater for the Fuel 2 case. The weight loss seen for 2.25Cr at 550°C (far right) indicates spalling of the oxide scale and that the temperature is too high for this steel.

In general more deposits were present on the samples exposed when firing Fuel 2 both at the furnace wall position and at the superheater position, see Figure 3.2.3. For 2.25Cr-material spallation occurred in the oxide layer when removing the loosely sitting ash/deposit and these samples thus showed a weight loss after exposure.

3.2.1 Furnace wall sample analyses

For the samples exposed at the furnace wall position, lower concentrations of sulphur and sodium, but higher calcium concentrations were measured in the deposit for Fuel 2. A slight increase of lead was measured in the deposit for samples exposed to Fuel 2 but no clear trend could be seen for chlorine.

Metallographic investigations showed very little or no corrosion for Alloy 625. For 16Mo3 severe corrosion occurred for both fuels. The appearance of corrosion products was a layer of iron

chloride closest to the metal substrate, Figure 3.2.4. Above this a layer rich in iron, sulphur and zinc was observed. On top of these two layers, compounds rich in sulphur and lead are present. Compared to the innermost layers this compound did not show high chlorine concentrations. Outermost a deposit rich in alkali chlorine and sulphur is present. Similar corrosion products were observed for both fuels. However, the sample exposed when firing Fuel 2 show a thicker layer of iron chloride closest to the metal substrate, indicating more corrosion.

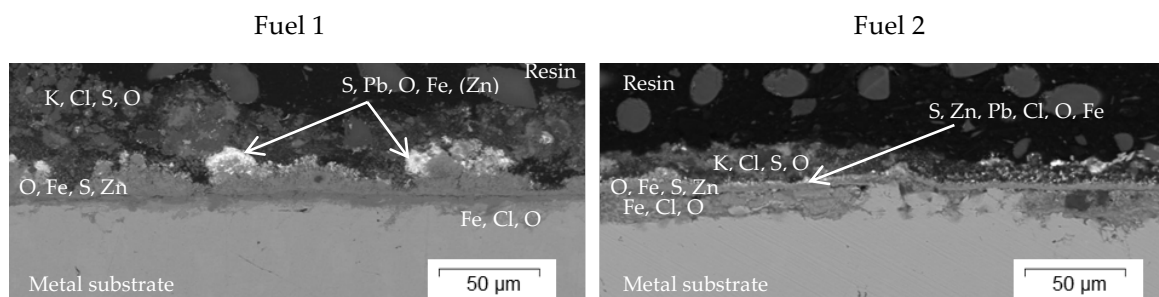


Fig. 3.2.4. Cross section appearance for 16Mo3 after exposure at 380°C in the furnace wall position.

3.2.2 Superheater samples analyses

The analysis of surface deposits on samples exposed to Fuel 2 showed higher chlorine contents and lower sulphur contents compared to samples exposed to Fuel 1. The lead concentration in the surface deposit was for both fuels very low. Cross-section analysis showed severe corrosion for the low alloyed steel when exposed to both fuels. Due to spallation of the oxide layer only the internal corrosion is presented in Figure 3.2.5. The corrosion products mainly consist of iron, sulphur and oxygen for the sample exposed when firing Fuel 1. When firing Fuel 2 chlorine becomes present and the internal corrosion increases.

A similar behaviour was observed for the stainless steel 304L, although less corrosion was observed in general. For the sample exposed when firing Fuel 1 not so much corrosion was observed. When firing Fuel 2 internal corrosion with chlorine present in corrosion products increased.

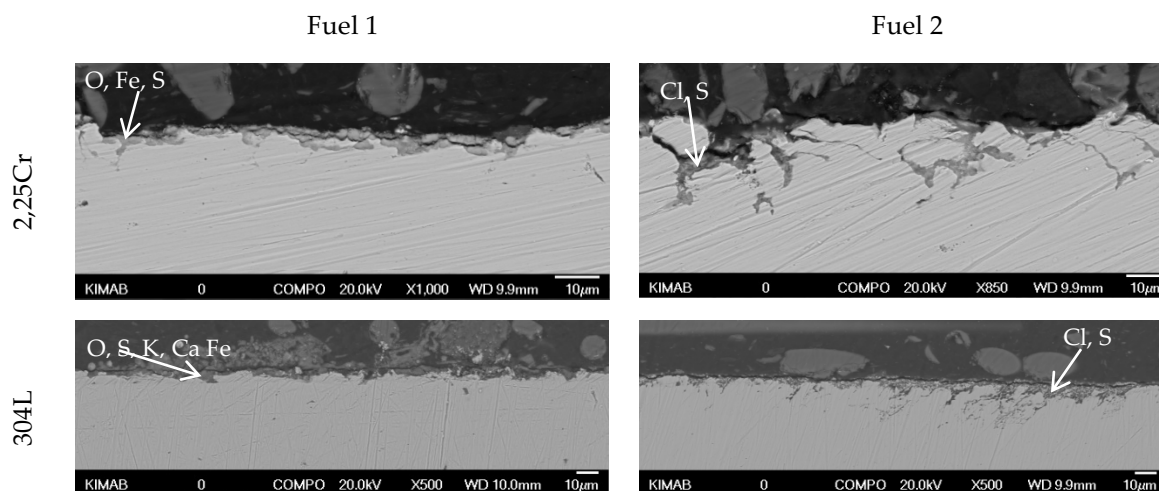


Fig. 3.2.5. Cross section appearance of 2.25Cr and 304L exposed at 550°C in the superheater position.

3.3 ANALYSIS OF SHORT-TERM TESTING WITH SEWAGE SLUDGE

The results of short-term (15 h) testing with digested sewage sludge have been published in refs. 31 and 32 and a review of the results is given here. During the previous project, KME-508, wall probes containing the low alloy steel 16Mo3 (the usual base of furnace walls), the nickel-base alloy Alloy 625, an iron-chromium-aluminium alloy APMT and the stainless steel 310S were exposed for about 15 h at 400°C with and without sewage sludge added to the used wood. Scanning electron microscopy revealed that the amount of chlorine in the deposit was reduced when co-firing sludge, while the amount of aluminium and phosphorous is higher. It was also found that the addition of sewage sludge had reduced the initial corrosion. More advanced analyses were performed in this project.

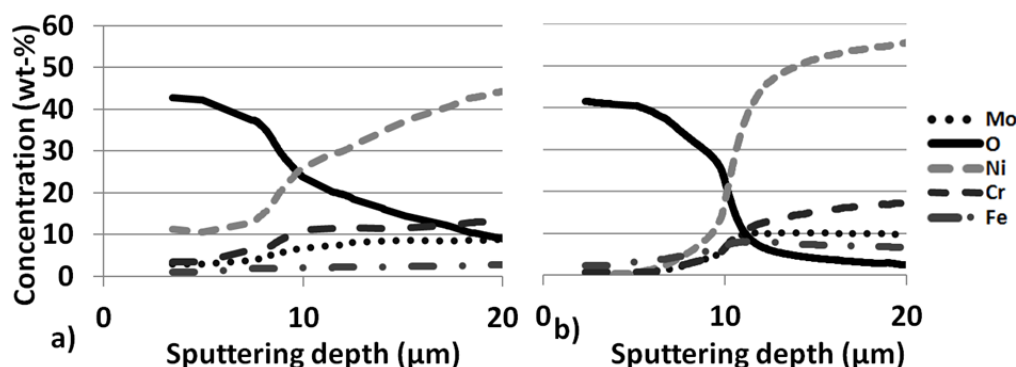


Fig. 3.3.1 GD-OES data for Alloy 625 samples a) when burning used wood b) when burning used wood+sludge

GD-OES revealed that higher amounts of Ni, Cr and Mo from Alloy 625 were found in the corrosion product of the used wood sample, compared to the mixture of used wood and sludge, indicating that the sludge had reduced the corrosion.

Results of x-ray diffraction on deposits of all the samples are given in Table 3.3.1.

Table 3.3.1 Compounds identified by x-ray diffraction in all deposits

Alloy/ fuel	Strong intensity	Medium intensity	Weak intensity
APMT used wood	KCl, CaCl ₂	K ₂ Al ₂ O ₄	K ₂ PbO ₂
APMT used wood + sludge	K ₂ Al ₂ Si ₂ O ₈	KCl	K ₂ Ca ₂ (SO ₄) ₃
Alloy 625 used wood	NiO	(Na,K) ₂ SO ₄	K ₂ SO ₄ , K ₂ Pb(CrO ₄) ₂
Alloy 625 used wood + sludge	K ₂ Ca ₂ (SO ₄) ₃ , Cr ₂ O ₃	Unidentified peaks	Fe ₂ O ₃
16Mo3 Used wood	Fe ₂ O ₃ , Fe ₃ O ₄ , NaCl,	KCl, CaSO ₄	K ₂ Ca ₂ (SO ₄) ₃
16Mo3 used wood + Sludge	CaSO ₄	Fe ₂ O ₃ , Fe ₃ O ₄ , KCl, NaCl, K ₂ Ca ₂ (SO ₄) ₃	
310S Used wood	Fe ₃ O ₄ , NaCl	KCl, Fe ₂ O ₃ , Ca(SO ₄), K ₂ Ca ₂ (SO ₄) ₃	Cr ₂ O ₃
310S Used wood + Sludge	CaSO ₄	Fe ₂ O ₃ , Fe ₃ O ₄ , NaCl, KCl, K ₂ Ca ₂ (SO ₄) ₃	Cr ₂ O ₃

The stability of different compounds in the deposit and interface at the flue gas was calculated based on thermodynamics data by using Thermo-Calc software with the TCFE7 and SSUB5 databases for the APMT and Alloy 625 cases. The thermodynamic equilibrium calculations were performed at 400 °C to simulate the temperature of the furnace wall. The calculation included all the elements in each compound found in corrosion products and/or deposits by XRD of APMT and Alloy 625 (Table 3.3.1). The oxygen amount was 1% (from the flue gas). The total amount of species was set to 1 mol with argon as the balance. Argon was used so as not to affect the composition. Based on thermodynamics laws and Gibbs free energy the most stable phase in the corrosion product/deposited layer can be suggested by Thermo-Calc regarding exposure of different alloys in the flue gas. For example in the case of nickel and oxygen the formation of NiO is most possible in the deposit of nickel metal at 400 °C in the low oxygen level rather than other compounds or materials, such as pure nickel, Ni₂O₃ or oxygen.

A summary of the results is shown in Tables 3.3.2 and 3.3.3.

Table 3.3.2 Summary of results for the APMT samples (Explanation of Yes, N/A, N/D given under Table 3.3.3.)

	SEM/EDS	XRD	GD-OES	Thermo-Calc
Alumina layer was absent in used wood sample	YES	YES	YES, compared to used wood and sludge sample where there was a clear alumina peak	YES
K ₂ Al ₂ O ₄ in used wood sample	YES	YES	N/A	YES
Al ₂ O ₃ in used wood+sludge sample	YES	N/D	YES	YES
Lower Cl in the deposit of sludge sample compare to used wood	YES	YES	YES	YES
Cr in mixed oxide/deposit area in waste wood sample	YES	N/D	YES	YES

Table 3.3.3 Summary of results for the Alloy625 samples

	SEM/EDS	XRD	GD-OES	Thermo-Calc
Cr & Ni in mixed oxide/deposit area in used wood sample	YES	N/D	YES, at least higher amount early comp. to sewage sludge sample	N/A
Chromia is present in sludge sample	YES	YES	N/A	YES
NiO (s) in used wood sample	N/D	YES	YES, at least higher amount early comp. to sewage sludge sample	YES
(Na,K) ₂ SO ₄ in used wood sample	N/D	YES	N/A	N/A
K/Pb-chromates in used wood sample	YES	YES	N/A	N/A

YES: Was detected by this technique

N/A: Not technically possible to detect with this technique/instrument i.e. the instrument is not suitable

N/D: Not detected by this technique, but is technically possible

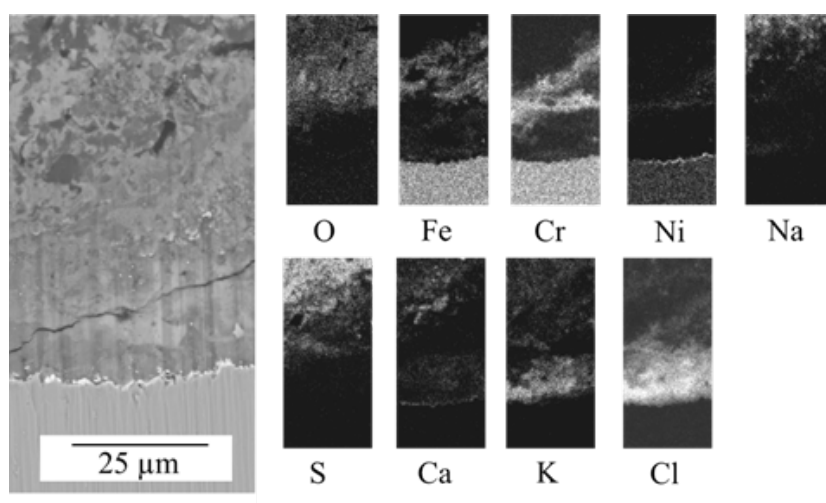


Figure 3.3.2. Element distribution by EDS mapping of 310S exposed to 100% used wood.

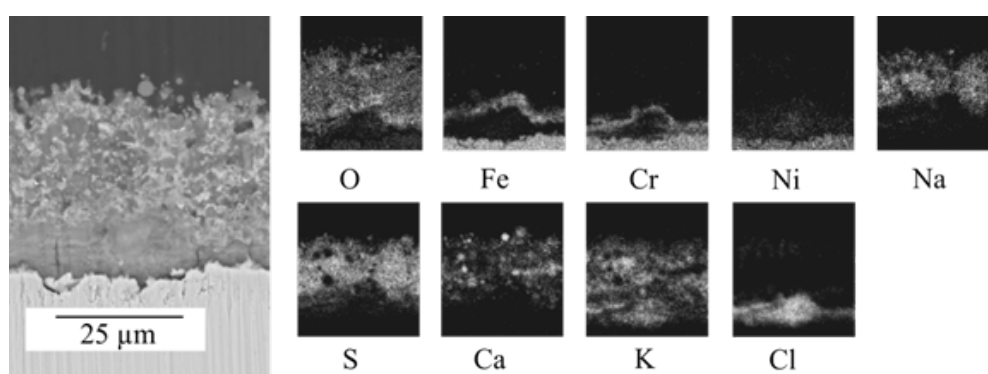


Figure 3.3.3. Element distribution by EDS mapping of 310S exposed to used wood + sludge.

Typical micrographs of the initial corrosion with and without sludge or shown in Figures 3.3.2 and 3.3.3. In the mapped area of the used wood sample, chlorine is shown close to the interface, Fig. 3.3.2. The chlorine is in combination with potassium at several places. In the deposit, sulphur, oxygen, calcium and potassium are dominant but a high iron content is also observed. Closest to the alkali chloride, chromium enrichment is seen in combination with a chlorine signal indicating chromium chloride. No continuous iron oxide layer is observed; instead the iron is located in the deposit. Close to the metal surface nickel enrichment is seen. For the sludge sample a similar behaviour is seen regarding the chemical analysis, Fig. 3.3.3. However, in general, the potassium chloride area is thinner for the sludge sample. Also for this sample a chromium layer together with chlorine is observed. In the deposit, sulphur, oxygen, calcium and potassium are dominant but compared to the 100% used wood sample, very little iron is seen in the deposit. Instead, the iron is located as an oxide on top of the chromium and chloride. Another difference is also that no nickel enrichment is seen in this sample.

For 16Mo3 samples, tested with or without sludge additions, it was found that the chlorine close to the metal surface was mainly correlated to iron and oxygen indicating that the corrosion product was an iron chloride which had been oxidised or hydrated (Fig. 3.3.4). Due to the hygroscopic nature of iron chloride this compound has most probably absorbed moisture during sample handling after grinding when exposed to air. In order to confirm the presence of iron chloride a

cross-sectional cut was performed in FIB on 16Mo3 where an elemental analysis was performed without exposing the cut to air. In the cross section of the sample exposed to 100% used wood, Fig. 3.3.5 and Table 3.3.4, it can be seen that there is no oxygen at the interface indicating that mainly iron chloride is present at the interface (point 1). The image also shows that the iron chloride is present as a continuous layer along the metal surface. Above this layer, iron oxides are present and further up some deposit has become mixed in with the oxide layer, (point 5). The main difference for 16Mo3 when sludge is added to the fuel is that less corrosion is observed. However, both with and without sludge addition the material showed severe corrosion considering the short exposure time of about 15 h.

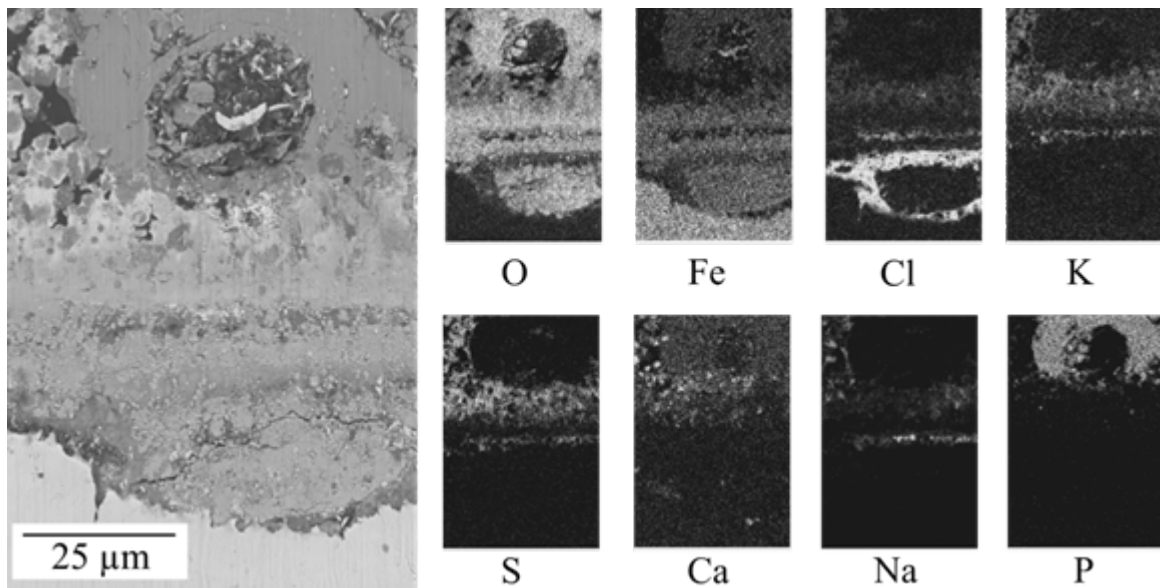


Figure 3.3.4 Element distribution by EDS mapping in cross section of 16Mo3 exposed to used wood + sludge.

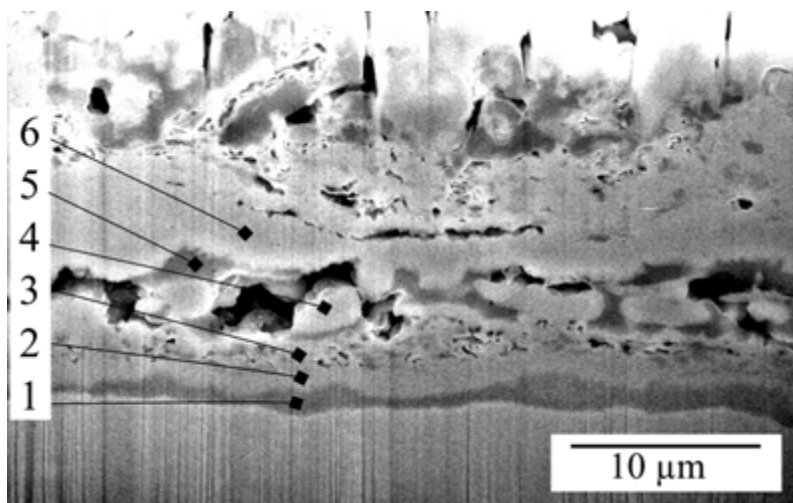


Fig. 3.3.5 FIB cross section of 16Mo3 exposed to 100% used wood.

Table 3.3.4. Semi-quantitative EDS results (at %) from analysed areas marked in Figure 3.3.5.

	O	Na	Si	S	Cl	K	Mn	Fe	Zn	Pb
1			0.6	0.4	33.2		0.5	65.2		0.1
2	24.4			1.4	8.3			65.7		0.2
3	29.4		0.4	0.8	2.1	1.1		66.0		0.2
4	26.9			0.4	1.9	0.8		69.8		0.2
5	7.0	4.2		0.6	23.3	20.1	0.6	42.7	1.2	0.3
6	27.5			0.3	0.9	0.6		70.5		0.2

3.4 MATERIAL PERFORMANCE CORROSION TESTING

All the material corrosion testing was performed with probes in-situ in the furnace region or near the superheaters in the three power boilers described in sections 2.1.1 to 2.1.3.

3.4.1 Wall material corrosion testing in Idbäcken

The alloys tested are all suitable for coatings, but were tested in solid (non-coated) condition in Idbäcken. Corrosion had previously been performed in the centre of the back wall (old position). Because of health and safety issues when installing probes at this point, two new holes for probes were made 3 metres to the left of the old holes, but at the same height. The new probe holes were separated by a distance of 30 cm. The first corrosion test, performed in November and December 2014, consisted of two probes containing the same materials in the same order on the probes; one probe was tested at the old position and one at the new position. The testing time at temperature was 986 h and the fuel was similar to Fuel 2. The results are shown in Fig. 3.4.1. The corrosion was higher in the new position, but no explanation could be found for this. Alkrothal 14 showed the highest corrosion rates in both cases. The pre-existing surface oxide had been removed prior to testing from APMT, which meant that all alloys were exposed in the same condition.

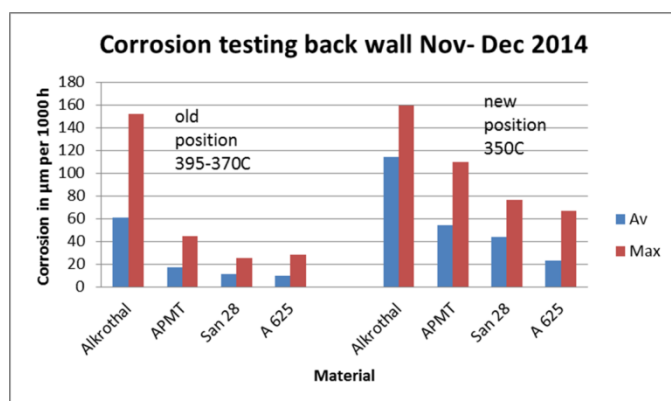


Fig. 3.4.1 Average and maximum corrosion rates for alloys tested on the furnace back wall of Idbäcken. Nominal temperature was 400°C. Testing time was 986 h.

The second long-term corrosion test was performed in December 2015. Both probes contained the same materials: APMT, Nikrothal PM58, Sanicro 28 and Alloy 625. The average temperatures of all specimens were in the range 380-400°C and the control temperature was 400°C. Exposure time at temperature was 1129 h. The results are displayed in Fig. 3.4.2. Sanicro 28 and Alloy 625 showed the lowest corrosion rates.

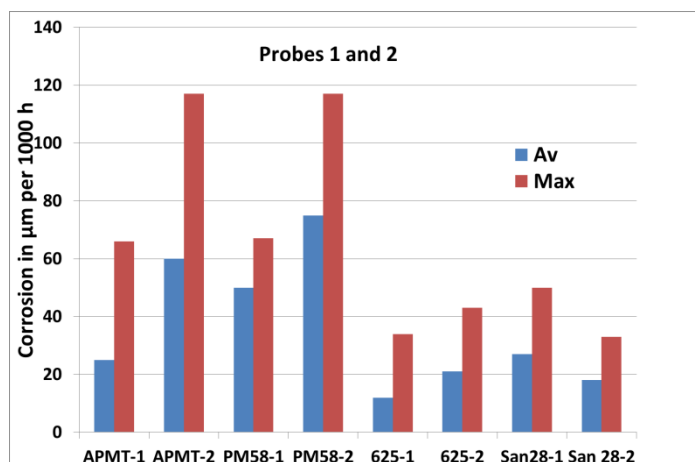


Fig. 3.4.2 Average and maximum corrosion rates for alloys tested on the furnace back wall of Idbäcken. Two probes (no. 1 and 2) were used which were exposed at the same time during December 2015 and January 2016. Nominal temperature was 400°C. Testing time was 1129 h. APMT-1 denotes APMT on probe 1 and APMT-2 denotes APMT on probe 2, etc.

The third (and last) long-term corrosion test in Idbäcken was performed in February and March 2016. Two probes (3 and 4) were used in parallel, both in the new testing position. The probes contained the same materials: Sanicro [X], Nicrothal PM58, Sanicro 28 and Alloy 625. The average temperatures of specimens on probe 3 were in the range 395-410°C and on probe 4 360-415°C. The control temperature was 400°C and exposure time at temperature was 817 h. The results are displayed in Fig. 3.4.3. Sanicro [X] and Alloy 625 showed the lowest corrosion rates. One specimen of Sanicro 28 (San28-3) exhibited very high corrosion rates. However both Sanicro 28 specimens, San28-3 and San28-4 had similar temperatures, 398°C and 394°C respectively.

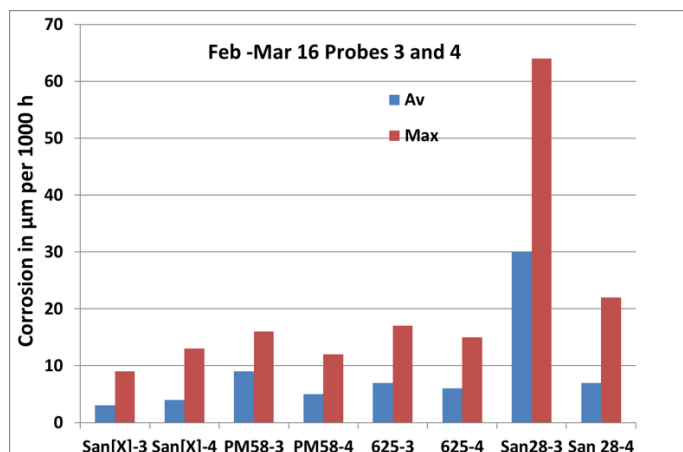


Fig. 3.4.3 Average and maximum corrosion rates for alloys tested on the furnace back wall of Idbäcken. Two probes (no. 3 and 4) were used which were exposed at the same time during February and March 2016. Nominal temperature was 400°C. Testing time was 817 h. San[X]-3 denotes Sanicro [X] tested on probe 3 and San[X]-4 denotes Sanicro [X] tested on probe 4, etc.

3.4.2 Wall material corrosion testing in Blackburn Meadows

Two wall probe tests were performed, each lasting 70 hours, during November 2014, with 100% used wood as the fuel. The average chlorine content of the used wood was in the range 0.13-0.15 %

(similar to Fuel 1 in Idbäcken) and the sulphur content was 0.02% (lower than Fuels 1 and 2). The lead and zinc contents were 229 and 133 mg/kg respectively which are similar to Idbäcken's Fuel 2.

The measured corrosion rates for 16Mo3 corresponded to linear rates of 19 and 26 μm per 1000 h. Coatings of FeCrAl- alloy and Alloy 625 showed corrosion rates of 4 and 3 μm per 1000 h respectively and the coatings of 50Cr50Ni and C276 suffered negligible corrosion (too low to measure).

3.4.3 Superheater material corrosion testing in Blackburn Meadows

Testing was performed with a probe containing a temperature gradient and the exposure time was 890 h. Several different types of alloys were tested.

Ferritic steels: 16Mo3 showed average corrosion rates of between 100 and 180 μm per 1000 h for metal temperatures in the range 430 to 510°C. The average corrosion rate of T22 varied between 100 and 240 μm per 1000 h in the temperature interval 450 to 515°C and X20 exhibited rates of 60 to 80 μm per 1000 h between 460 and 530°C.

For these materials the thick oxide scales were highly laminated and contained alternating oxide, sulphide and Cl-rich bands, indicating that the scales reacted strongly with the ash deposit.

Austenitic steels and nickel-base alloys: Esshete 1250 corroded 60 μm per 1000 h between 490 and 505°C, but at the higher temperature range of 520-535°C Esshete 1250, DMV 310N, Super 625 and HR11N all showed rates of 25 μm per 1000 h or under.

The austenitic steels showed a double layered oxide, the inner layer infiltrated by S and Cl, and the outer layer strongly interacting with ash deposit. There was selective internal oxidation of Cr that can lead to creation of pores. The Ni-base alloys showed a similar scale structure but the amount of selective oxidation of chromium at the grain boundaries was greater.

The laser clad coatings made of FeCrAl, 50Cr50Ni and IN625 showed the lowest rates of under 15 μm per 1000h in the range 520-535°C. (The laser cladding was performed by Nottingham University, UK). The surfaces of coatings were damaged/cracked during manufacture and during grinding leading to accelerated corrosion rates in some areas. Very thin protective chromia layer seen in some places.

Laser clad FeCrAl : Double layered oxide (inner Fe/Cr/Al rich and outer Fe/Ni rich). Selective internal oxidation of Cr. Some deep vertical branches of internal oxidation (up to ~100 μm).

Laser clad 50Ni50Cr : Similar double layered oxide. Extent of selective internal oxidation of Cr higher, leading to S/Cl infiltration and pitting.

Laser clad IN625 : Surface highly damaged, accumulating Nb-rich slag and deposit. Selective internal oxidation of Cr-rich dendritic phases leading to S/Cl infiltration and localised pitting, (see Fig. 3.4.4)

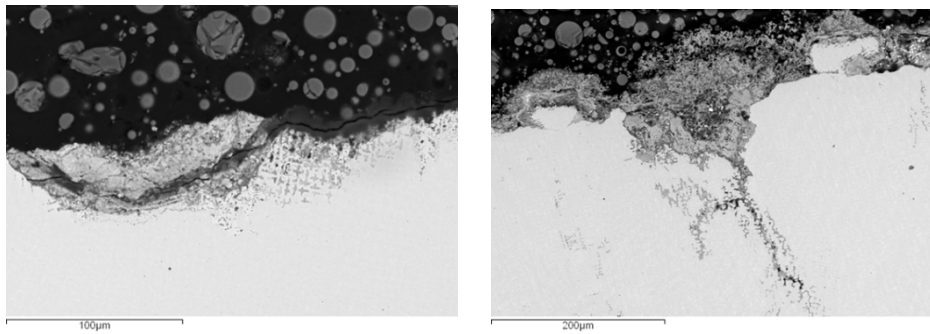


Fig. 3.4.4. Laser clad IN625 after exposure showing selective internal oxidation.

3.4.4 Wall material corrosion testing in Händelö

Amec Foster Wheeler performed their testing between October 2104 and February 2015.



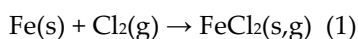
Fig. 3.4.1 Probes after removal from furnace.

C-steel, 16Mo3 and 13CrMo4-5 tested at 330 and 360°C. Because of the long testing time, severe corrosion had occurred and even the main body of the probe made of the high temperature alloy 253MA was severely corroded.

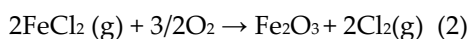
4 Analysis of the results

4.1 SCIENTIFIC BACKGROUND TO CORROSION IN USED-WOOD ENVIRONMENTS

In a used 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



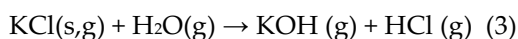
The volatile metal chloride then diffuses outwards through the oxide and reacts with oxygen in the outer part of the scale releasing chlorine, e.g.



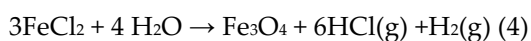
The chlorine is then able to diffuse back into the scale and cause more corrosion, the so-called chlorine cycle or “active oxidation” [13, 20]

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].

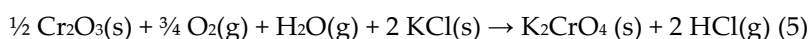
However, thermodynamic modelling shows that chlorine gas exists at extremely low levels (less than 0.1 ppm) at a tube surface and instead the hydrated form, HCl(g) , is thermodynamically favoured, [8, 14]. (This is a smaller molecule than chlorine which could easily diffuse through a defect oxide of the type formed on the steel). It seems that chlorine can attack low alloy steels by gaseous hydrogen chloride rather than chlorine gas. The HCl may be generated from KCl deposits or gas as shown in Eqn. 3.



The HCl reacts with the iron to form iron chloride under the magnetite scale. Water vapour molecules (oxygen carrier) which exist at the interface of iron chloride and magnetite then react with the iron chloride and release HCl according to equation 4.



For stainless steels it has been suggested that chlorine induced corrosion may occur [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:



It is believed that the presence of Zn and Pb in used wood also accelerates 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]. Additions of lead to forest

fuel were found to increase the corrosion of 16Mo3 in experiments using a laboratory scale fluidized bed boiler, [34].

Low melting point or liquid chloride-containing salts in the deposits also 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.

Any number of these mechanisms may be acting simultaneously, although one may dominate over the others.

4.2 FUEL QUALITY

4.2.1 Furnace wall corrosion

Fuel 2 (higher Cl and Pb) was much more corrosive than Fuel 1 and the corrosion rate increased more with increasing temperature for this fuel for both alloys tested. The corrosion caused by Fuel 2 was three times higher for Alloy 625 and six times higher for 16Mo3, compared with that caused by Fuel 1.

However, corrosion was much less on Alloy 625 (used as a coating material) than on 16Mo3 (boiler tube material). The maximum measured corrosion rate was 400µm per 1000h for 16Mo3 and 70µm per 1000h for Alloy 625 at a temperature of 380°C (see Fig. 3.1.6). This is because Nickel-based alloys are less prone to chlorine/chloride induced corrosion than 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].

If one assumes that a boiler is in operation for 7000 hours per year that is equivalent to a corrosion rate of 2.8 mm per year for 16Mo3 and 0.5 mm per year for Alloy 625. The corrosion tests only lasted 2 weeks (333 hours) and there is a certain risk in extrapolating these rates to 7000 h, however this risk is small for 16Mo3 as it experiences linear corrosion rates. For Alloy 625 which is assumed to corrode in a parabolic manner (i.e. corrosion is more rapid at shorter times) the rate of 0.5 mm is likely to be overestimated.

It has been shown previously that a possible way of reducing the corrosion is to reduce the boiler pressure, [33]. Reducing the boiler pressure from 140 bar to 90 bar is equivalent to reducing the metal temperature from 390°C to 360°C, (the water temperature is reduced from 340 to 310°C) giving a reduction in the corrosion rate. This method is more effective for Fuel 2 than Fuel 1 because of the greater temperature dependence of the corrosion rate, but this would still result in a corrosion rate of 1mm per year for 16Mo3. However the corrosion is reduced to 0.2 mm per year for Alloy 625, (see Fig. 4.1.1)

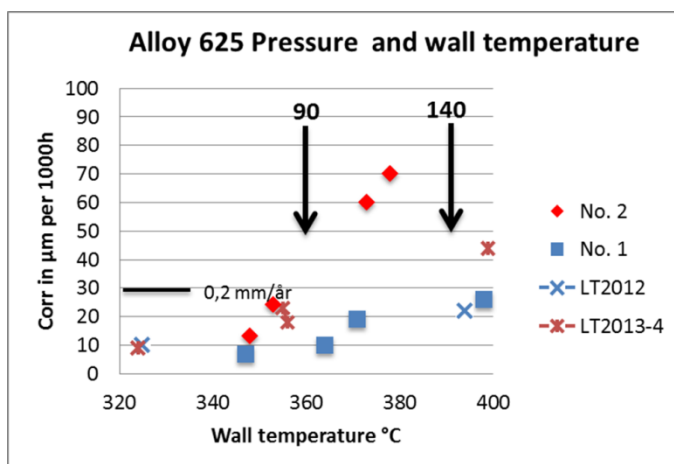


Fig. 4.2.1 Variation of corrosion rate for Alloy 625 with Fuels 1 and 2 (2 week tests) and comparison with long-term (6 week) testing performed during 2012 and 2013-4. Reducing final pressure from 140 to 90 bar reduces the wall temperature from 390 to 360°C.

The wall probe's deposit chemistry showed that the Cl-content from Fuel 2 was 2-3 times higher than that from Fuel 1, (see Fig. 3.1.5). It seems that chlorine has a strong influence on the corrosion rate and is reflected by the reduced corrosion observed at the lower Cl-contents of Fuel 1. However the chlorine content in Fuel 2 was only 50% higher than in Fuel 1 (0.20% and 0.13% respectively). It is difficult to judge how corrosive a fuel will be by only considering its chemical composition. As discussed previously lead as well as chlorine plays a role. Lead was 3.5 times higher in Fuel 2 than in Fuel 1, (136 and 38mg/kg d.s. respectively).

For 16Mo3, the initial corrosion observed in laboratory after 8 h showed that lead and sulphur-rich compounds were present on top of oxide islands. Below the oxide a layer of iron chlorides was present. The oxide islands seemed to grow larger and the thickness of the iron chloride layer clearly increased when exposing the material to a fuel with higher lead and chlorine content. A similar behaviour regarding the corrosion was observed for the samples exposed in the field exposure, indicating a similar corrosion mechanism. An oxide layer with a metal chloride layer below was present and seemed to grow when changing to a fuel with higher chlorine and lead content. In the oxide layer lead-rich compounds were found. However, in contrast to the laboratory exposure, chlorine, and not sulphur, was present in these compounds. Also, the compounds are found within the oxide layer and not in close connection to the deposit. In the laboratory they are located closer to the deposit and this could indicate that what is observed in the laboratory is the initial deposition of lead-compounds which after longer exposure (333 h in the field) will form other compounds.

For the nickel-base Alloy 625 a clear increase in corrosion was observed depending on fuel quality. When this material was exposed to Fuel 1, with lower lead and chlorine content, pitting corrosion occurred at some places on the samples. Exposing the material when firing Fuel 2, with higher chlorine and lead content, resulted in an increase of the corrosion. The corrosion products formed were oxides rich in nickel and chromium where the oxide rich in chromium is located closest to the metal substrate and nickel on top. Chemical analysis in cross sections also showed that a corrosion product consisting of lead, molybdenum and oxygen (lead molybdate, PbMoO_4) was formed. This was only seen in the field tests with Fuel 2 at temperatures higher than 370°C. In the laboratory test with a duration of 8 h no corrosion was observed for Alloy 625.

Regarding the laboratory exposure as a test method it was shown that most probably the 8 h exposure in tested condition is a too short exposure time for Alloy 625 to initiate corrosion and longer exposure times would be needed to study the initiation. For 16Mo3 on the other hand, the 8 h exposure seem to be too long in order to study the initial corrosion and shorter exposure times would be needed. Similar behaviour regarding the initial corrosion for both 16Mo3 and Alloy 625 has been observed in a previous study [34], where the initial corrosion as a function of lead concentration in a wood fuel was evaluated.

An interesting observation from the field exposure is the difference in temperature dependence for the corrosion behaviour between the fuels. For Fuel 2 the corrosion increases more depending on the temperature compared to Fuel 1. For Alloy 625 this was also clearly seen in cross-section analyses with an increased amount of pitting corrosion with nickel oxide and lead molybdate formation.

4.2.2 Superheater corrosion

Both the field test and the laboratory test comparing two fuel qualities showed that there is a risk for increased corrosion also at the superheaters when firing fuels with higher chlorine and lead concentrations. The analysis of surface deposits showed a clear increase of chlorine content and in the cross section analysis internal corrosion increased and lead rich compounds were found in the corrosion products. Not only the low alloyed steel showed increased corrosion for Fuel 2, also the stainless steels investigated showed a slight increase in corrosion. An increase of internal corrosion was the main feature observed when changing to a fuel with higher chlorine and lead concentration during these short-term tests.

4.2.3 Fuel quality summary

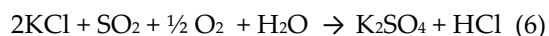
The results clearly showed that the fuel quality is of importance. The corrosion mechanisms are not fully understood but when an increase of chlorine and lead are measured in the fuel, both elements are found in the deposits and corrosion products, indicating that both play an important role. The increased corrosion observed in this study related to fuel composition not only at the furnace wall position but also at the superheater position for some selected materials, strongly showed the importance of regulating the fuel composition in order to avoid corrosion. Also, further investigations are needed to fully understand the role of lead in the fuel.

For all samples exposed in this fuel quality test it was observed that the lead concentration in the deposit increased towards the metal substrate. A thinner (spalled) deposit showed higher concentrations of lead indicating that the lead somehow is attracted to the metal substrate. This shows that evaluating the corrosion risk based on surface deposit composition needs to be performed with care and in combination with cross-sectional analyses.

4.3 SEWAGE SLUDGE ADDITIONS

The addition of digested sewage sludge was shown to reduce the amount of chloride in the deposit, reduce the amount or thickness of the iron chloride level in the iron-based alloys and reduce the initial corrosion. Sewage sludge contains sulphur and alumino-silicates and all previous work with sewage sludge additions has focused on superheater corrosion, [35-38]. In

these cases the amount of chlorine in the deposits decreased and there was a clear increase in the amount of sulphur. It is thought that corrosive alkali chlorides were converted to less corrosive alkali sulphates according to equation (6) :



leading to a reduction in corrosion.

In the furnace region the oxygen levels are low, because combustion is not complete and the testing was performed below the tertiary air ports. It is therefore not expected that large amounts of alkali chlorides were converted into sulphates (although this may occur to a limited extent). Rather, a reaction of alkali with aluminosilicates is expected, according to equation 7.



This also results in a reduction of chlorides and corrosion, without an equivalent increase in sulphates.

4.4 MATERIAL PERFORMANCE CORROSION TESTING

Furnace wall testing at 380-400°C in Idbäcken showed that Alloy 625 always performed well (under 20µm per 1000 h), but APMT, PM 58 and San 28 showed variable (and higher) corrosion rates. The new alloy Sanicro [X] showed good results (under 20µm per 1000h) from initial tests and more testing is needed to validate this.

Furnace wall testing at 350-360°C in Blackburn Meadows showed that the coatings of FeCrAl, Alloy 625, 50Cr50Ni and C276 all showed very low corrosion rates, (under 5µm per 1000h). Even 16Mo3 showed acceptable rates of under 30µm per 1000 h.

Long-term testing at the furnace wall in Idbäcken during the firing season 2015-16 showed some differences in the corrosion rates measured during December 2015- January 2016 and February – March 2016. The corrosion rates measured were higher for the Dec-Jan exposures and this was most marked for the nickel-based alloys, see Figures 4.4.1 and 4.4.2.

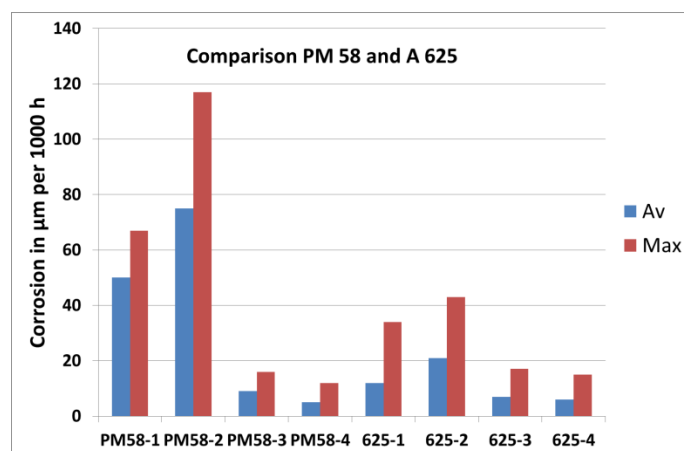


Fig. 4.4.1 Comparison of Nikrothal PM 58 and Alloy 625 for Dec-Jan (samples 1 and 2) and Feb –March (samples 3 and 4). Corrosion was greater during Dec-Jan.

A number of factors can affect corrosion rates, for example fuel composition, boiler load, flue gas temperature. A comparison of key boiler and fuel parameters is given in Table 4.2.1. It can be seen that the boiler load and flue gas temperatures were similar, but the Cl and Pb levels in the fuel and also the moisture content were slightly higher during testing in December and January. This probably explains the higher corrosion rates.

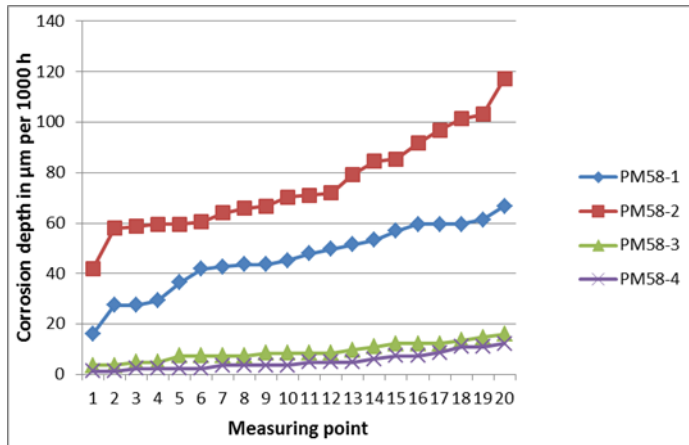


Fig. 4.4.2 Corrosion depth for each of the 20 measuring points on specimens Nikrothal PM58 1-4. The results show that corrosion in all points measured was higher for tests 1 and 2 than for 3 and 4.

Table 4.4.1 Key boiler and fuel parameters during tests 1-4.

	Probes 1 & 2	Probes 3 & 4
Dates (hours of exp. at temp)	17/12-> 02/02 (1129)	04/02-> 17/03 (817)
Av. Boiler load (MW)	65	64.7
Probe temp (°C)	381-396/381-401	395-409/362-415
Av gas temp in furnace (°C)	845	844
Fuel (Av Cl % DS)	0.08-0.09	0.05-0.08
Fuel (Av Pb mg/kg DS)	67-133	64-67
Fuel (Av moisture %)	19	14

For the material Nikrothal PM58, which showed the greatest variation in corrosion rate between the two campaigns, metallographic analysis by the use of SEM/EDS was performed. The result confirmed the higher corrosion rates observed for the samples exposed in Dec-Jan compared to the samples exposed in Feb-March, see Figure 4.4.3.

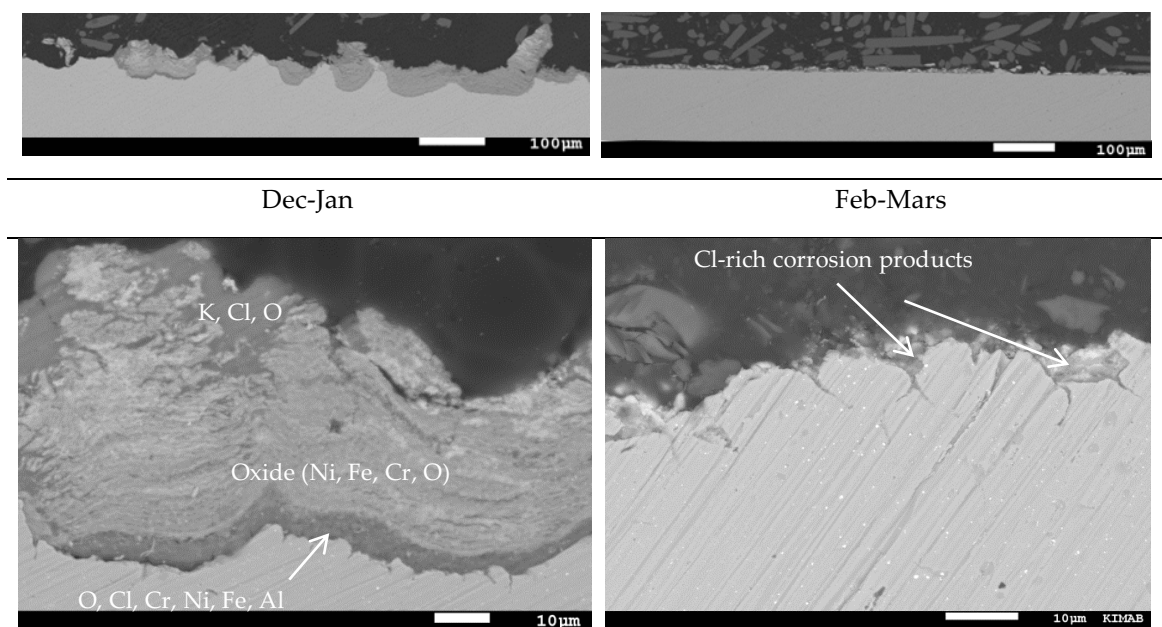


Fig. 4.4.3 Cross section of Nikrothal PM58 showing local corrosion attacks for samples exposed in dec-jan (left) and feb-mars (right). Upper low magnification, lower high magnification.

The corrosion is of a local character with pits that are filled with oxide, and below the oxide closest to the metal substrate, metal chlorides seem to be present, see Figure 4.4.3. For both samples exposed in Dec-Jan the main part of the deposit had spalled, but a thick oxide of Ni, Cr and Fe remained. The surface analysis showed that lead and chlorine was present in the corrosion products. For the samples exposed in Feb-Mar more deposit was adherent and the oxide scale was thinner. Again, it could be seen that the lead and chlorine concentration in the deposit in general increases further down in the deposit towards the metal.

Testing of superheater materials in Blackburn Meadows showed that:

- the ferritic/martensitic steels 16Mo3, T22 (2.25% Cr) and X20CrMoV121 (12% Cr) were all unsuitable for use in the temperature range 430°C -530°C with used wood because of their high corrosion rates (60-240 µm per 1000 h)
- the austenitic steels Esshete 1250, TP 310 and the nickel-based alloys HR11N and Super 625 performed well in the temperature range 520-535°C with corrosion rates of under 25µm per 1000h.
- the coatings of Fe20Cr5Al, 50Cr50Ni and IN 625 performed very well with corrosion rates of under 15µm per 1000 h in the temperature range 520-535°C.

5 Conclusions

Corrosion tests have been performed in the furnace wall area and at the superheaters of recycled wood fired boilers. It was found that:

- 1) Low alloyed steels exhibited high corrosion rates, while austenitic stainless steels, FeCrAl alloys and Ni-base alloys gave good results (low corrosion). Some alloys were identified that showed similar corrosion rates to Alloy 625. These alloys are not nickel-based and are therefore cheaper than Alloy 625.
- 2) Small differences in fuel chlorine and lead content resulted in large differences in the corrosion rate. (Higher Cl- and Pb-levels gave higher corrosion rates). This difference increased with increasing metal temperature. This means that corrosion can be reduced by careful control of the fuel composition and by reducing the furnace wall temperature (reducing boiler water pressure).
- 3) Co-combustion of used wood with digested sewage sludge reduced the initial corrosion of a number of different alloys. The amount of chlorine at the corrosion front was also reduced by the sludge addition which implies that even long-term corrosion is likely to be reduced. As sludge has a negative gate fee it could be an effective way of reducing operating and maintenance costs.

6 Goal fulfilment

The overall objective of the project was to reduce high temperature corrosion in heat and power boilers that burn predominantly used (recycled) wood. To achieve this the following goals were set

1. finding wall coating materials that are more cost-effective than conventional nickel-base alloys (i.e. Alloy 625). A cost or corrosion rate reduction of 20% was aimed at.
2. obtaining a better understanding between fuel quality (fuel chemistry) and corrosion.
3. evaluating materials that are suitable for high temperature superheaters
4. from results of short-term testing (performed in KME-508) with digested sewage sludge decide to proceed (or not) with long-term testing of sludge as an additive, i.e decision to run part 2 (KME-718).

The goal fulfillment is as follows:-

1. Sanicro [X] showed lower corrosion rates than Alloy 625, but only two tests were performed. Kanthal APMT™ and Sanicro 28 have been tested many times and showed similar (although more variable) corrosion rates to Alloy 625. These three alloys are estimated to be 25-30% cheaper than Alloy 625.
2. Recycled wood with a high chlorine and lead content (0.17%Cl, 119 ppm Pb) caused 3 times more corrosion on Alloy 625 and 6 times more corrosion on the low alloyed steel 16Mo3 than recycled wood with a lower chlorine and lead content (0.13%Cl, 36 ppm Pb). Pb and Cl compounds were found in the corrosion products and in greater concentrations in the high Cl-Pb fuel. Both these recycled wood types lie within the specification range for commercially available recycled wood. It is clear that a better control of wood chemistry when purchasing fuel can lead to reduced corrosion in both the furnace and at the superheaters.
3. Austenitic stainless steels and nickel-based alloys performed well as superheater materials or coatings for superheaters when firing recycled wood. Ferritic steels (up to 12% Cr) are not suitable in an uncoated condition.
4. The analysis of short-term testing with digested sewage sludge showed that corrosion was reduced and the amount of chlorides present in the corrosion products was also reduced in all the investigated specimens. It was therefore decided to proceed with Part 2 (KME-718).

It is concluded that the goals have been fulfilled.

7 Suggestions for future research work

Long-term testing of recycled wood with digested sewage sludge to determine quantitative corrosion rates.

Identification and long-term testing of an additional sludge waste product.

Sanicro [X] showed extremely low corrosion rates and should be further evaluated.

Kanthal APMT™ has been tested as a solid material (from plate) in this project. Sandvik Heating Technology has successfully welded this alloy as a coating on to 16Mo3 plate and tube. The next step is to test overlay coated specimens, both on probes (for accurate corrosion measurement) and long-term evaluation on a coated tube.

Identification and testing of other promising coatings to reduce corrosion.

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Y. Alipour, P. Henderson and P. Szakalos.

The effect of a nickel alloy on the corrosion of furnace wall tubes in a waste wood fired power plant. *Materials and Corrosion*, **65**, 217, (2014).

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Initial corrosion of 16Mo3 and 310S when exposed in a used fired boiler with and without sewage sludge additions. *Materials and Corrosion*, **67**, 683 (2016)

Y. Alipour

Furnace wall corrosion in a wood-fired boiler.

Doctoral thesis. Royal Institute of Technology, KTH, Stockholm, November 2015

A. Talus

Decreased furnace wall corrosion in fluidised bed boilers - The influence of fuel lead content and sewage sludge additive

Thesis for the degree of licentiate of engineering, CTH, Gothenburg, December 2016

High temperature corrosion in used-wood fired boilers – KME-708

Increasing use is being made of used (recycled) wood as a fuel in heat and power boilers, because it is cheaper than virgin wood. However, used wood causes more corrosion problems, especially in the furnace where there is a lack of oxygen (low NO_x combustion). This project sought to find cost effective ways of reducing the corrosion.

Corrosion tests have thus been performed in the furnace wall area and at the superheaters of recycled wood fired boilers. It was found that:

- 1) Low alloyed steels exhibited high corrosion rates, while austenitic stainless steels, FeCrAl alloys and Ni-base alloys gave good results (low corrosion). Some alloys were identified that showed similar corrosion rates to Alloy 625. These alloys are not nickel-based and are therefore cheaper than Alloy 625.
- 2) Small differences in the chlorine and lead content of a fuel resulted in large differences in the corrosion rate. (Higher Cl- and Pb-levels give higher corrosion rates). This means that corrosion can be reduced by careful control of the fuel composition.
- 3) Co-combustion of used wood with digested sewage sludge reduces the initial corrosion which means that longer exposures will be performed in stage 2 of the project (KME-718).