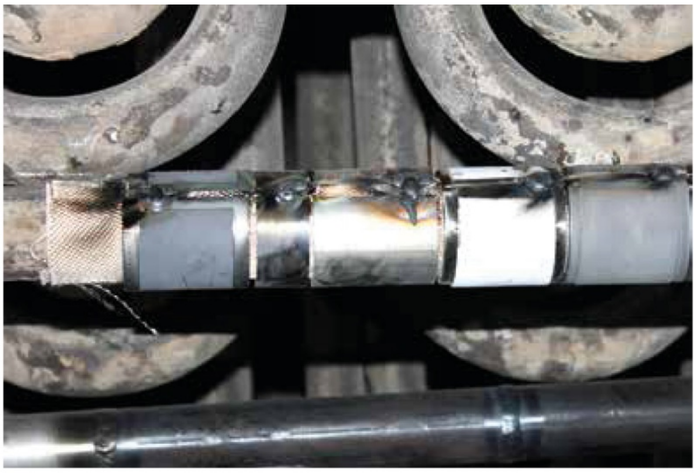
HIGH TEMPERATURE CORROSION IN USED-WOOD FIRED BOILERS – FUEL ADDITIVES AND COATINGS

KME-718



CONSORTIUM MATERIALS TECHNOLOGY
for thermal energy processes

KME

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High temperature corrosion in used-wood fired boilers

Fuel additives and coatings

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Preface

The project has been performed within the framework of the materials technology research programme KME, Consortium materials technology for thermal energy processes, period 2014-2018. The consortium is at the forefront of developing material technology to create maximum efficiency for energy conversion of renewable fuels and waste. KME has its sights firmly set on continuing to raise the efficiency of long-term sustainable energy as well as ensuring international industrial competitiveness.

KME was established 1997 and is a multi-cliental group of companies over the entire value chain, including stakeholders from the material producers, manufacturers of systems and components for energy conversion and energy industry (utilities), that are interested in materials technology research. 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 utilisation of renewable fuels and waste in power and heat production. The KME goals are to bring about cost-effective materials solutions for improved fuel flexibility, improved operating flexibility, increased availability and power production with low environmental impact.

KME's activities are characterised by long term industry and demand driven research and constitutes an important part of the effort to promote the development of new energy technology with the aim to create value and 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 %).

Bertil Wahlund, Energiforsk

Abstract

Corrosion tests have been performed in the furnace wall area and at the superheaters of recycled wood fired boilers. Analysis of the exposed samples through thickness measurements, chemical analysis of deposits and cross section analysis showed that:

1) Co-combustion of used wood with digested sewage sludge and fibre sludge reduces the corrosion rate (336 h corrosion tests) at furnace wall position for both low alloyed steel 16Mo3 and nickel base alloy Alloy 625.

2) Co-combustion of used wood with digested sewage sludge and fibre sludge reduces the initial corrosion (3 h deposit probe) also at superheater position.

3) There are interesting materials which could work better and possibly be more cost efficient than the commonly used overlay welded Alloy 625 as coating material at the furnace walls when firing used wood fuel. FeCrAl-alloys showed promising results.

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-NOx-förbränning). Projektet syftade till att undersöka om samförbränning av olika typer av slamtyper kan minska korrosionen hos vanligen använda material och på så sätt minska underhållskostnaderna och öka bränsleflexibiliteten. Även olika varianter av material lämpade som skydd (i form av påsvetsning) för de låglegerade tuberna utvärderades i tester där returträ eldades.

Korrosionstester med sameldning av olika slamtyper genomfördes i 336 h-försök i eldstadsposition och då studerades det låglegerade 16Mo3, vanligen använt som tubmaterial i eldstaden samt nickelbaslegeringen Alloy 625 som ofta används som ytbeläggning i pannorna. Kortare försök (3-timmars test) genomfördes också i överhettarposition.

Korrosionsprovning för att utvärdera material möjligen lämpliga som ytbeläggning utfördes av Vattenfall och E.ON (Uniper) i egna fluidiserad-bädd-pannor som använder returträ. I dessa beläggningstester provades många olika legeringar i eldstadsposition, bland annat FeCrAl-legeringar och termiskt sprutade skikt av modifierad nickelbaslegering Alloy 625, samt påsvets av nickelbaslegering Alloy 625 och Kanthal APMT. Solida prover av nickelbaslegeringen Alloy 625 som ofta tillämpas som ytbeläggning i eldstäder, användes som referens för testerna i Idbäcken. Tester genomfördes under ca 1000 h i Vattenfalls anläggning Idbäcken och under ca 7000 h i E.O.N (Unipers) anläggning Blackburn Meadows.

Proverna utvärderades efter exponering med avseende på avlagringskemi och korrosionsbeteende i tvärsnitt av Swerea KIMAB. Vattenfall AB utvärderade korrosionshastigeten på de prov som exponerats i Idbäcken genom tjockleksmätning.

<u>Resultaten visade att:</u>

(1) Sameldning av både rötat avloppslam och fiberslam minskar korrosionen för det låglegerade stålet 16Mo3 samt nickelbaslegeringen Alloy 625 när det exponeras i eldstadsposition. Även i överhettarposition visar sameldningen på positiva trender då den initiala korrosionen av testade material minskar.

(2) Flera av de testade materialen i ytbeläggningstesterna visade på bra korrosionsegenskaper, ibland bättre än det idag använda nickelbaslegeringen Alloy 625. Kanthal APMT samt FeCrAl-modellegeringar visade låga korrosionshastigheter när de testades som svetsade prover medan svetsat Alloy 625 inte riktigt nådde upp i samma goda beteende. Tester i Blackburn Meadows under längre tider visade på liknande korrosionsbeteende för nickelbaslegeringen Alloy 625 (Sanicro 60) och Kanthal APMT (jämfört med testerna som genomfördes i Idbäcken).

Projektet anses ha uppfyllt de satta målen på ett acceptabelt sätt. De positiva resultaten från slamtesterna resulterade dessutom i att Vattenfall AB numera samförbränner returträ med fiberslam för att minska korrosionsproblem i anläggningen.

<u>Nyckelord</u>: returträ, korrosion , eldstadsväggar , slameldning , FeCrAl legeringar, Ni-baserade legeringar

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 NOx combustion). This project aimed to evaluate if co-firing of different types of sludge can reduce the corrosion for commonly used materials and in that way save maintenance costs and increase fuel flexibility. In addition, different materials suitable for coatings should be evaluated when exposed during used wood firing.

Corrosion tests with co-firing of different sludges were performed during 336 h in furnace wall position. In these tests the low alloyed steel 16Mo3, usually used as tube material in the furnace, and the nickel base alloy Alloy 625, usually used as coating materials at the same position, were evaluated. Shorter tests (3h deposit tests) were also performed at superheater position.

Corrosion tests to evaluate materials suitable as coating materials were performed by Vattenfall and E.ON (Uniper) in their boilers firing used wood fuel. In these coating tests several alloys were tested at furnace wall position, for instance FeCrAl alloys, HVAF and HVOF-sprayed modified Alloy 625, as well as welded samples of Alloy 625 and Kanthal APMT. Alloy 625 as solid material was used as reference in the tests performed in Idbäcken. In Idbäcken the tests duration was approximately 1000 h and in E.ON (Unipers) boiler in Blackburn Meadows the test duration was approximately 7000 h.

After exposure the samples were evaluated by Swerea KIMAB with respect to deposit composition and corrosion behaviour in cross section. Vattenfall AB evaluated the corrosion rate for the samples exposed in Idbäcken through thickness measurements.

The results showed that:

(1) Co-firing of used wood with both sewage and fibre sludge decreased the corrosion rate of the low alloyed steel 16Mo3 and the nickel base alloy 625 when exposed at furnace wall position. Also at superheater position co-firing of the sludges showed positive effects with decreased initial corrosion of tested materials.

(2) Several of the tested materials in the coating campaigns showed good corrosion properties, sometimes better than the presently used nickel base alloy Alloy 625. Kanthal APMT and the model FeCrAl-alloys showed low corrosion rates when they were tested as welds while welded Alloy 625 did not reach as good corrosion behaviour. Tests in Blackburn Meadows with longer test times showed similar corrosion behaviour for the nickel base alloy 625 (Sanicro 60) and Kanthal APMT (compared to Idbäcken tests).

The project has in an acceptable way reached the set goals. The positive results from the sludge campaigns did result in that Vattenfall today is using co-firing of fibre sludge as a way to reduce corrosion problems in the furnace wall area when firing used wood fuel.

Keywords: used wood, corrosion, furnace walls, sludge, 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 wood and recovered building wood 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. It would be useful to reduce the amount of corrosion caused when burning used wood or reduce the operating costs still further.

Problems have been experienced with furnace wall corrosion with used wood contents as low as 20 % in combination with low-NOx combustion and advanced steam conditions of about 140 bar/540 °C (KME 508 final report). In Vattenfall's 100 MWth 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-base material Alloy 625 to reduce the corrosion, but even this alloy corrodes (albeit at a lower rate) so the problem is not solved. In addition, the raw material cost of Ni-base alloys is high. Long-term probe testing (1000 h) in KME 508, 708 (EM 39270-1) showed that an FeCrAl alloy from Kanthal AB had excellent corrosion resistance when tested as solid material, indicating its potential as a coating material. This alloy was evaluated as a weld overlay coating in this project, in parallel with testing of some other coatings. A particular benefit of highly corrosion resistant coatings is that they require less use of rare and expensive raw materials than the use of solid tubes of similar composition.

In KME 512 and 508 [3] short-term tests (8 and 14 hours respectively) with treated sewage sludge showed that adding digested sewage sludge to the fuel mix reduces the corrosion in low alloyed steel as well as high alloyed steels and Ni-base alloys.

In KME 708 [4] samples from short term tests showed that the co-firing of sewage sludge with recycled wood reduced the amounts of K, Na and Cl in the furnace wall deposits. This led to a reduction in the corrosion. Attack by a potassium-lead combination appeared to be the main corrosion mechanism in the Alloy 625 during used wood combustion. This resulted in the formation of a non-protective potassium-lead chromate. The addition of sewage sludge suppressed this attack and the protective chromia layer was maintained resulting in a lower corrosion rate. In the FeCrAl alloy Kanthal APMT, K attacked the pre-existing alumina layer, but the addition of sludge reduced this attack. It is thought that the presence of aluminosilicates in the sludge interacts with the alkali leading to a reduction in corrosion.

These short-term tests gave qualitative information. In this project longer term tests with sewage sludge have been performed in a boiler to obtain more quantitative information on the reduction in corrosion rates on furnace wall and the mechanism behind the effect of sewage sludge has been more closely analysed. In addition another fuel additive in form of a sludge with high-sulphur content (a waste product from the pulp and paper industry) has been investigated to see if it is suitable for long-term use and comparing its properties with sewage sludge.

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). 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. These materials has however been shown to be sensitive to corrosion.

Figure 1. Photograph of part of a furnace wall before being installed in a boiler.

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.

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 projects KME 508 and KME 708 [3, 4]. 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, [5]. 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. 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, [6, 7], although at different exposure conditions. These differences in corrosion properties are thought to be largely independent of the environment, but the mechanical properties, such as low temperature embrittlement and creep properties are worse for FeCrAl alloys, because of the formation of the Cr-rich alpha´ or sigma- phase, [7]. These materials, like Kanthal 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 [8, 9]. Short-term tests which have previously been performed with sewage sludge in KME 508 and evaluated in KME 708 have shown to decrease the initial corrosion [3, 4]. Longer tests are however needed to fully conclude the usefulness of a sludge-additive.

1.3 RESEARCH TASK

In this project, ways of reducing furnace wall corrosion, while combusting used wood, have been investigated. Two approaches have been utilised in a 100 MW power boiler; decreasing the corrosion by co-firing with an additive and decreasing the corrosion by using coating materials.

Long-term corrosion tests (up to 336 h) with co-firing of two sludge additives have been performed in a 100 MW power boiler on the standard wall coating alloy, Alloy 625, and the low alloyed steel 16Mo3 commonly used as tube material in the furnace region.

Corrosion tests with a duration of 1000 h were performed for selected coating materials in the same 100 MW power boiler. In addition, a one-year campaign testing suitable coating materials in a 130 MW power boiler was conducted and the duration of this test was approximately 7000 operational hours.

1.4 GOAL

The overall aim of the project is to reduce operation and maintenance costs in heat and power boilers that burn predominantly used (recycled) wood by the use of additives to the fuel and the use of new coating materials. The effort will be directed towards furnace walls. In general this will result in increased fuel flexibility and make biomass a more attractive and financially competitive energy source.

Specifically the project aims at acquiring new knowledge from longer term studies on the effect of using sewage sludge as fuel additive on furnace wall corrosion. It further aims at finding a sludge that can be used as an alternative to sewage sludge and investigate the effects of it and evaluate whether it is suitable for longer term use.

The project aims at acquiring in-depth knowledge on the corrosion behaviour of materials typically used for furnace walls both when fuel additives are used and when firing the reference fuel. It also aims at investigating the corrosion properties of some new coating materials and their related performance with respect to furnace wall protection.

The academic goal of this project includes one licentiate (Annika Talus 2017), as well as giving additional contribution to her PhD thesis (estimated 2018). The results will be published in one to two scientific papers.

1.5 PROJECT ORGANISATION

The project organisation is described below:

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

Management of Vattenfall activities. 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 analyses. Corrosion measurement and deposit analysis. Data analysis and reporting.

In-kind contribution 1 170 kSEK.

AB Sandvik Materials Technology –Jesper Ederth. Provision of materials and technical support. In-kind contribution 60 kSEK.

Kanthal AB, (former Sandvik Heating Technology AB), Susanne Selin. Provision of materials, overlay welding, technical support. Development of a welding procedure for Kanthal APMT™. In-kind contribution 60 kSEK.

E.ON Värme Sverige AB and E.ON Business Heat and Power Solutions UK- Anna Jonasson, Patrick Cook and Colin Davis. In-kind contribution 60 kSEK. Corrosion testing (coated furnace wall tube) in Blackburn Meadows.

Andritz, Christophe Gruber, In-kind contribution 60 kSEK, Expertise knowledge about boilers.

Sumitomo SHI FW (former Amec Foster Wheeler OY), Edgardo Coda Zabetta, Jouni Mahanen and Kyösti Vänskä. In-kind contribution 60 kSEK, Expertise knowledge about boilers.

Stockholm Exergi (former Fortum Värme), Eva-Katrin Lindman and Jukka Meskanen. In-kind contribution 60 kSEK, Expertise knowledge about boilers.

MH Engineering: Matti Huhtakangas, In-kind contribution, 50 kSEK, Material delivery of coated samples.

KIMAB – Rikard Norling and Ph.D student Annika Talus. Budget 1 053 kkr

Overall project management and supervision of Ph.D student at KIMAB. Deposit analysis and initial corrosion studies of exposed samples.

Reference group. This consisted of the participants from the above mentioned companies/organisations and a representatives from boiler manufacturers Babock & Wilcox Völund and from the High Temperature Corrosion Competence Centre at Chalmers, 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 peformed in this plant. Situated some 120 km south of Stockholm, the Idbäcken CHP plant provides energy to the city of Nyköping. Nyköping has about 30 000 inhabitants and the Idbäcken plant provides half of its electricity requirements. It also supplies some 14000 households with district heating. The plant is owned and operated by Vattenfall AB and consists of a Bubbling Fluidised Bed (BFB) steam boiler (Boiler 3) for Combined Heat and Power (CHP) operation, two circulating Fluidised Bed (CFB) boilers (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 of 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. The holes, separated by 30 cm, are situated in the boiler between seconday and tertiary air. A cross-section of the plant with the testing positions is shown in Fig. 2.

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 runs on 100% used wood. It is owned and operated by E.ON Business Heat and Power Solutions UK. The boiler is a 97 MW bubbling fluidized bed which produces 30 MW electricity and has been retrofitted to export up to 25MW heat. The final steam data is 82 bar/487°C. A cross-section of the boiler with testing positions is shown in Fig. 3.

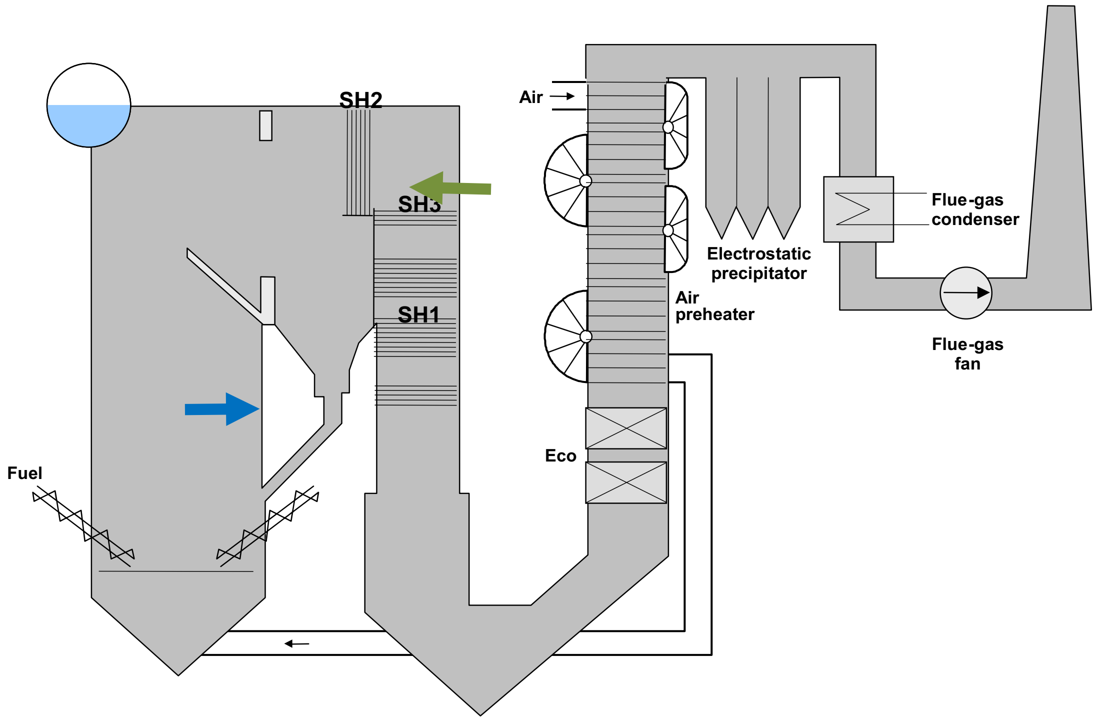


Figure 2. Cross-section of the BFB plant in Nyköping showing testing points. Wall corrosion blue arrow, short-term superheater deposit probes green arrow above superheater 3. (Superheater 2 no longer in use – has been removed)

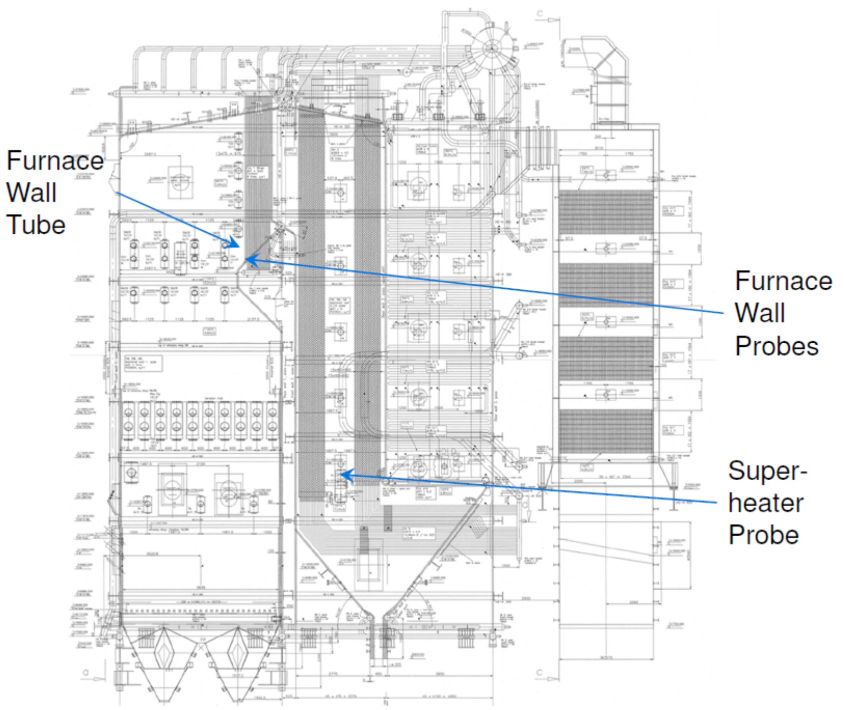


Figure 3. Cross-section of the BFB plant in Blackburn Meadows showing the testing points.

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 Fig. 4.) 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 approximately 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, assuming a difference between the surface temperature and the steam of approximately 50-60 °C. For long term coating corrosion testing the total exposure time at temperature was about 1000 hours (6 weeks) and for sludge testing the exposure time was 330 h (2 weeks).

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.

Figure 4. 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).

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 Fig. 5. The deposit probe was used during the sludge 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.

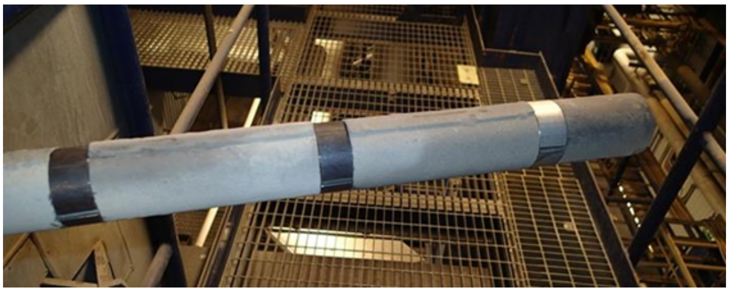


Figure 5. Vattenfall's deposit probe before exposure.

2.2.2 E.ON's coated wall tube test

In addition to plant testing with probes performed by Vattenfall, E.ON also installed a furnace wall tube coated with a number of different materials. The tube was installed on 1 July 2016 and remained in operation for one year. The position of the coated tube is close to that of the wall probes in Blackburn Meadows shown in Fig. 3.

Five different coatings were applied by different companies in different parts of the world including Kanthal APMT™ and Alloy 625 (Sanicro 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 the former project KME708 and the evaluation of the tube in this project KME718. A photograph of the tube is shown in Fig. 6, a table of coatings in Table 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 for material characterization by microscopy etc. Since this is a tube not only with materials from this project only reference material, Kanthal APMT and Sanicro 60 will be reported in this report.

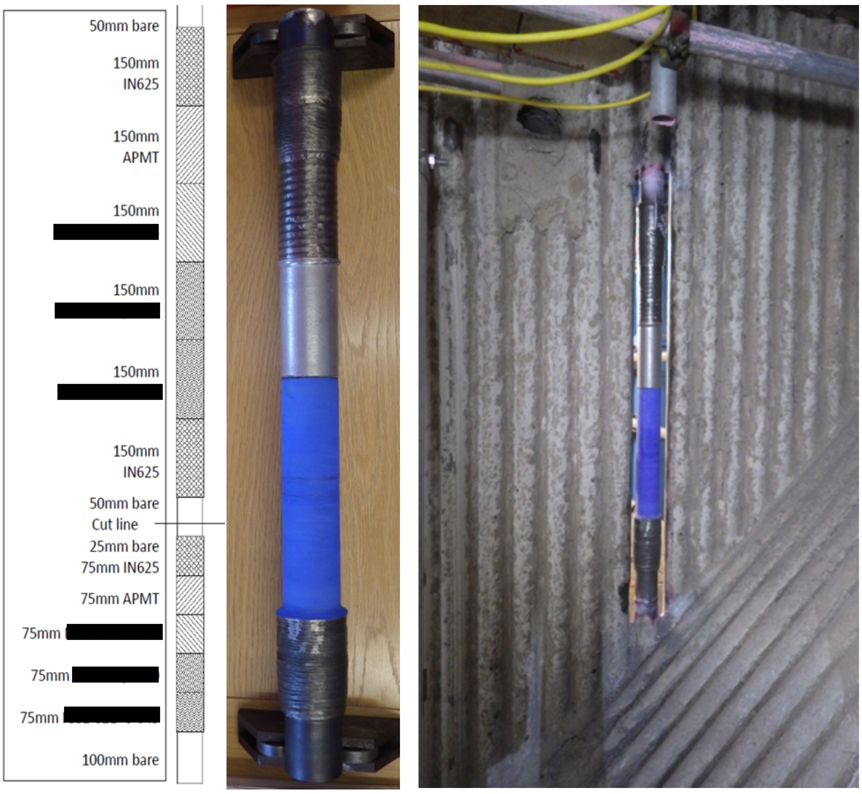


Figure 6. Sketch of coated tube showing dummy tube at bottom and furnace wall tube at top (left). Photograph of the wall tube before being welded into position (middle). Photograph of the tube in position in furnace wall (right).

Table 2. Name and position of coatings on the furnace wall tube exposed for KME718.

Materials (and position) on tube	**Application Method**	**Nominal Thickness**
Sanicro 60 (Alloy 625) Top	Weld Overlay	4mm
Kanthal APMT™	Weld Overlay	2mm
Sanicro 60 (Alloy 625) Bottom	Weld Overlay	4mm

2.3 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. 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. These techniques are described in more detail below.

2.3.1 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.

2.3.2 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 MATERIALS TESTED

The compositions of the alloys tested are given in Tables 3 and 4.

Table 3. Materials tested on probes by Vattenfall.

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
TP304L	Cr 18, Ni 10, Mo 0.3, Mn 1.2	SS 2352
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
Alloy 625 weld	Not disclosed	From wall tube
Kanthal APMT™	Cr 21, Al 5, Mo 3 Fe Bal	Kanthal AB
Kanthal APMT™ weld	Not disclosed	Kanthal AB
Sanicro [X]	Not disclosed	Sandvik Mat. Techn.
4971-74	Not disclosed	Kanthal AB
MH2, MH5	Alloy 625 (Modified, increased hardness)HVAF and HVOF sprayed	Si-based sealant
MH1, MH3	Alloy 625 (Modified, increased hardness) HVAF and HVOF sprayed	Al-based sealant

Table 4. Nominal chemical compositions of the coatings on coated wall tube in Blackburn Meadows.

Name	Chem comp wt%	Other
Sanicro 60	Cr 22, Mo 9, Nb 3.5, Si 0.2 Fe <1, Mn 0.2 Ni bal	
Kanthal APMT™	Cr 20.5-23.5, Al 5, Mo 3 Fe Bal	Rare Earth

3 Results

3.1 FUEL ADDITIVES IN IDBÄCKEN

Two different sources of sludges were co-fired with used wood fuel in the boiler in two separate campaigns. Each campaign consisted of furnace wall corrosion probe testing for 2 weeks and superheater deposit probe exposure for 3 hours. The original used wood fuel had a composition with high Cl and Pb levels (used in previous project KME708) and the sludges were sewage sludge and fibre sludge. The chemical compositions of the final fuel mixtures are given in table 5. Into the two fuel mixtures, 18 wt% sewage sludge and 13 wt% fibre sludge were mixed respectively.

Table 5. Compositions of the fuels used for the two-week additive tests.

		UW Fuel	Sewage sludge	Fibre sludge
Moisture –as rec.	%	22	76	72
Ash content – as rec	%	5.8	8.3	2.7
S	[% ds]	0.07	1,27	0.68
Cl	[% ds]	0.20	0.05	0.03
Al	[mg/kg ds]	1 262	18 200	8 200
Ca	[mg/kg ds]	5 117	23 400	9 200
K	[mg/kg ds]	900	3 860	890
Mg	[mg/kg ds]	538	3220	1 100
Na	[mg/kg ds]	976	1940	2 500
Si	[mg/kg ds]	15 247	28 700	20 000
Cu	[mg/kg ds]	45	259	17
Pb	[mg/kg ds]	136	15	5
Zn	[mg/kg ds]	122	524	170
P	[mg/kg ds]	118	27 100	3200

3.1.1 Furnace wall probes

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 16Mo3 (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. It is clear that both sludges decrease the corrosion dramatically for both materials compared to the reference fuels UW1 and UW2 (results obtained in KME708). The greatest effect is observed at the higher temperatures, above 350 °C, see Fig. 7.

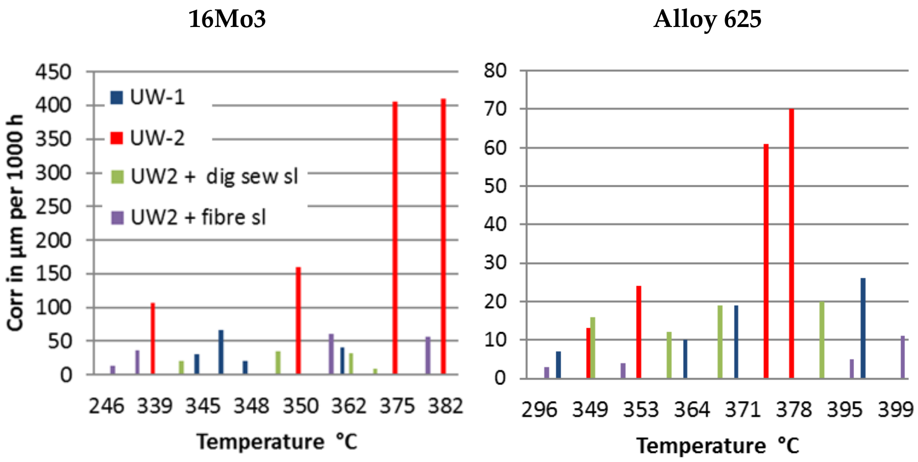


Figure 7. Corrosion rate in µm per 1000 h for 16Mo3 (left) and alloy 625 (right). Testing time 333 h in both cases. Note the difference in scales.

Chemical composition of the deposits shows a clear effect of the additive in terms of decreasing the Cl-content in the deposit, see Fig. 8. In this figure, the results from Alloy 625 are presented. The deposits on 16Mo3 were spalled to a great extent but in the cases deposit was still adherent, the results showed similar results to Alloy 625.

The surface analysis reflects the composition of the sludges with increased amounts of Al, Ca, Si, Na and P in the deposit when firing with sludge. There are however differences observed for the two sludges. For the sewage sludge, Al, Mg, Si and P seem to play an important role while for the fibre sludge an increased amount of Na and S is more observed. However, the results from the surface analysis need to be interpreted with care due to the uneven character of the deposits resulting in difficulties to fairly compare the two sludges.

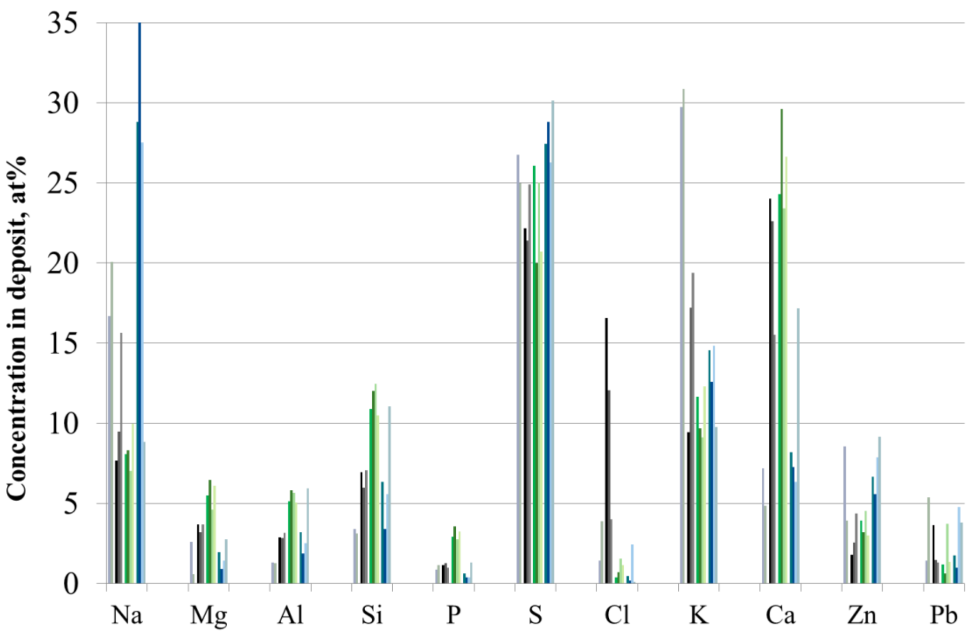


Figure 8. Deposit composition from EDS-analysis for Alloy 625 samples, light and dark grey used wood fuel 1 and 2, green bars used wood + sewage sludge and blue bars used wood + fibre sludge.

From the XRD-results alkali sulphates and calcium sulphates are observed for both sludges although there is an indication that $CaSO_4$ is more often present for the sewage sludge samples. For the fibre sludge samples alkali sulphates (both sodium sulphate and potassium sulphate) are more often observed. Traces of alkali alumina silicates are observed both for sewage and fibre sludge samples but to a greater extent on the sewage sludge samples. In general very little alkali chlorides are present at the sample surfaces.

Cross section analysis confirms the corrosion rate measurements with a clear decrease of corrosion products. For both materials, co-firing of sludge additives considerably decrease the thickness of the corrosion product layer, Fig. 9. For Alloy 625 pitting corrosion was observed for the reference samples (KME708) but when firing sludge no pitting corrosion was observed. At 400 °C the result showed similar results for Alloy 625 with no or negligible corrosion observed. For 16Mo3 only the temperature around 350 °C was evaluated in cross section due to a fairly large temperature spread on the probe for this material.

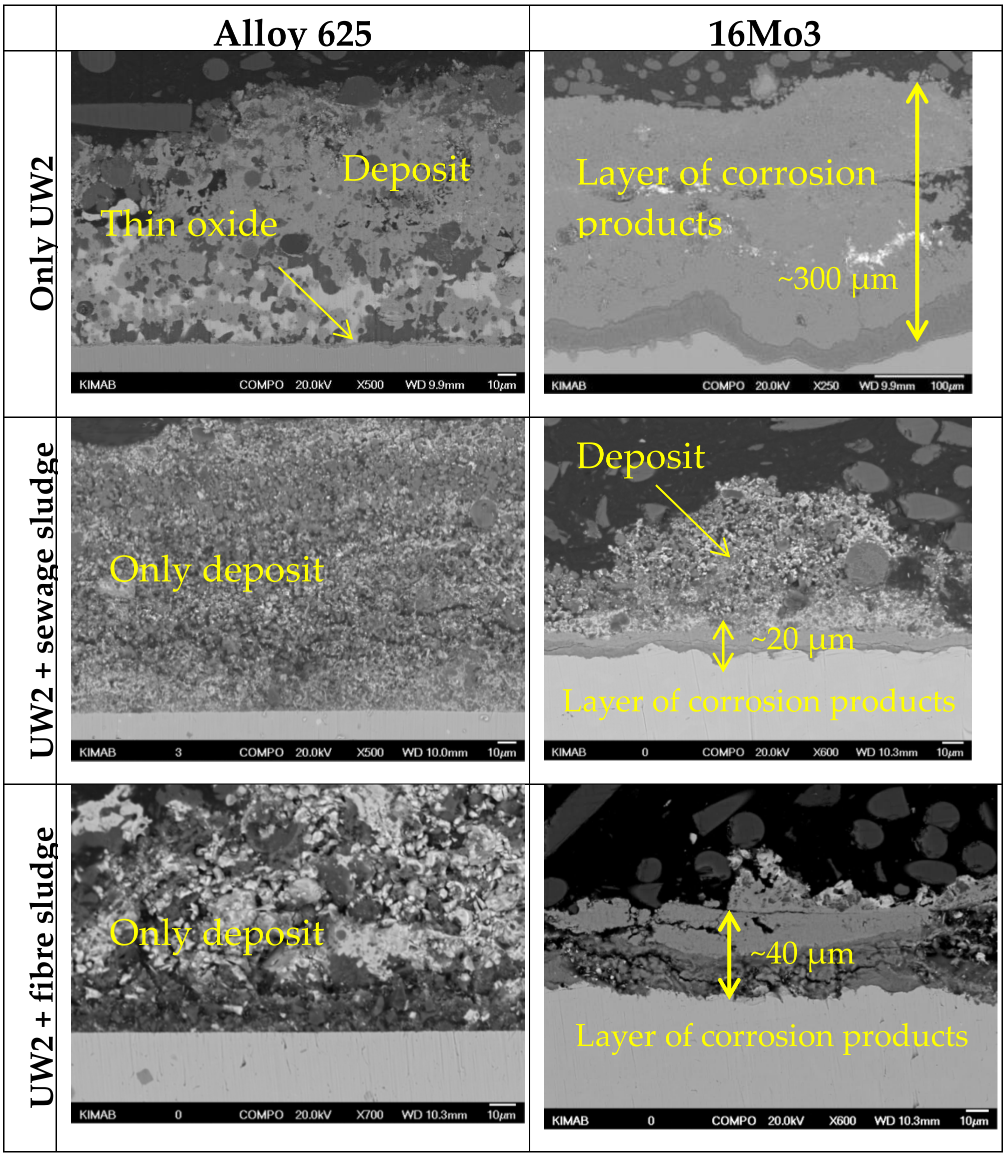


Figure 9. SEM images of cross-sections of Alloy 625 and 16Mo3 at 350 °C

3.1.2 Superheater deposit probes

The results from the 3 h deposit probes located at superheater position also showed a positive effect with co-firing of sludge. A decrease in chlorine content in the deposit is observed for both sludges at the same time as the sulphur in the deposit increases indicating sulphation of the alkali chlorides at super heater position, Fig.10. XRD-results shows the presence of $CaSO_4$ and Alkali sulphates (Na/KSO_4) and only very little alkali chlorides for the sludge samples while for the UW2 samples the relation between alkali chlorides and sulphates where reversed.

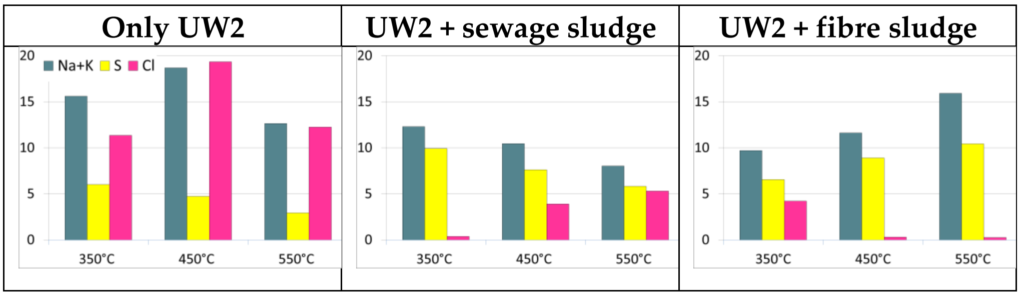
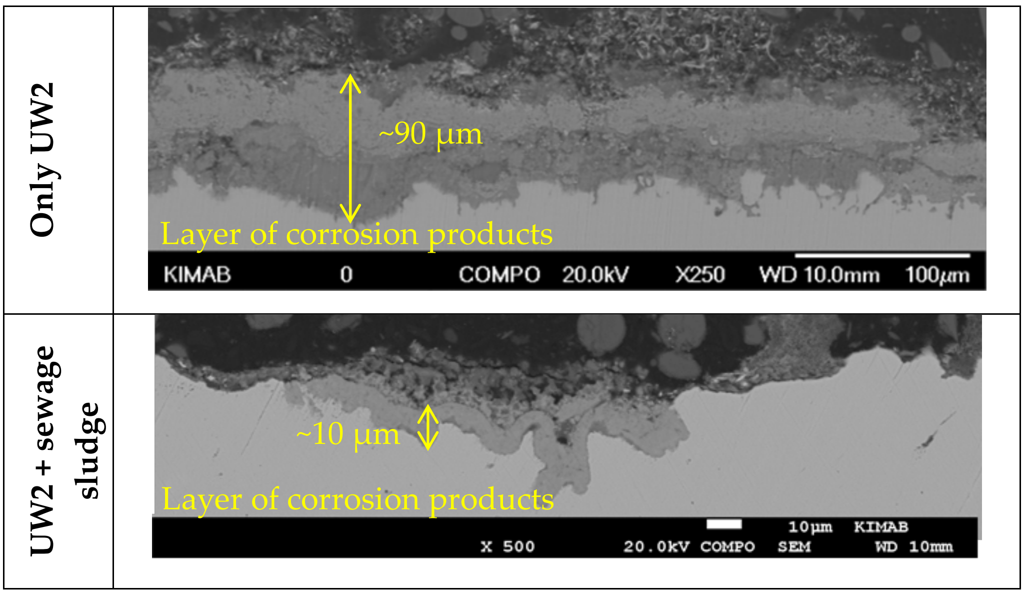


Figure 10. Deposit composition from superheater samples (EDS-analysis).

Cross section analysis of the superheater probe samples shows that the initial corrosion of material 2216 decreases, Fig.11. When exposed to only used wood fuel the corrosion product layer is at least 100 µm. For the sample at 350 °C the oxide has probably spalled but severe internal corrosion is observed. When co-firing both sewage and fibre sludge the thickness of the corrosion product layer decrease. Note the difference in scales in the figures.



UW2 + fibre sludge

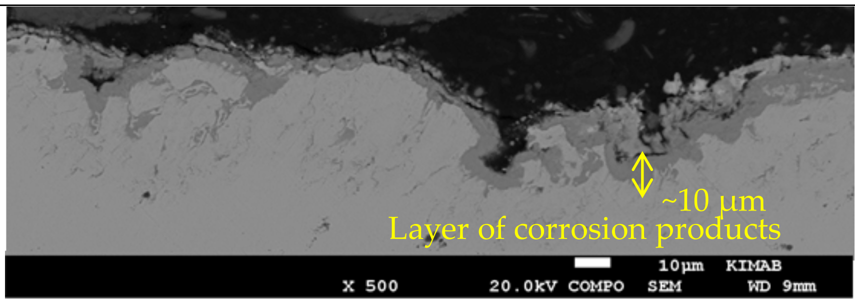


Figure 11. SEM images of cross-sections of 2216 at 450 °C located for 3 h at superheater position.

3.2 COATING CAMPAIGNS IN IDBÄCKEN

Two probes were used in parallel for the two coating campaigns, both with a control temperature 400 °C. There were several materials and coatings tested, see Table 3 in chapter 2 for details. There was some spread in temperatures along the probes, but the temperature of each specimen was measured individually.

On each probe Alloy 625 solid was always present as reference and it can be seen that the average corrosion rates for this reference samples have been similar throughout the tests, although slightly temperature dependent as is seems with higher corrosion rate at the higher temperature (443 °C), Fig. 12. Interesting is that welded Alloy 625 does not behave as well as the solid material showing a corrosion rate around 3-4 times higher.

The FeCrAl alloys showed very low corrosion rates in these tests. Both the model alloys 4971-74 and Kanthal APMT showed low corrosion rates, similar to the Alloy 625. Also SanX behaved in a similar way. Interesting is also that the welded Kanthal APMT and the solid Kanthal APMT showed similar results.

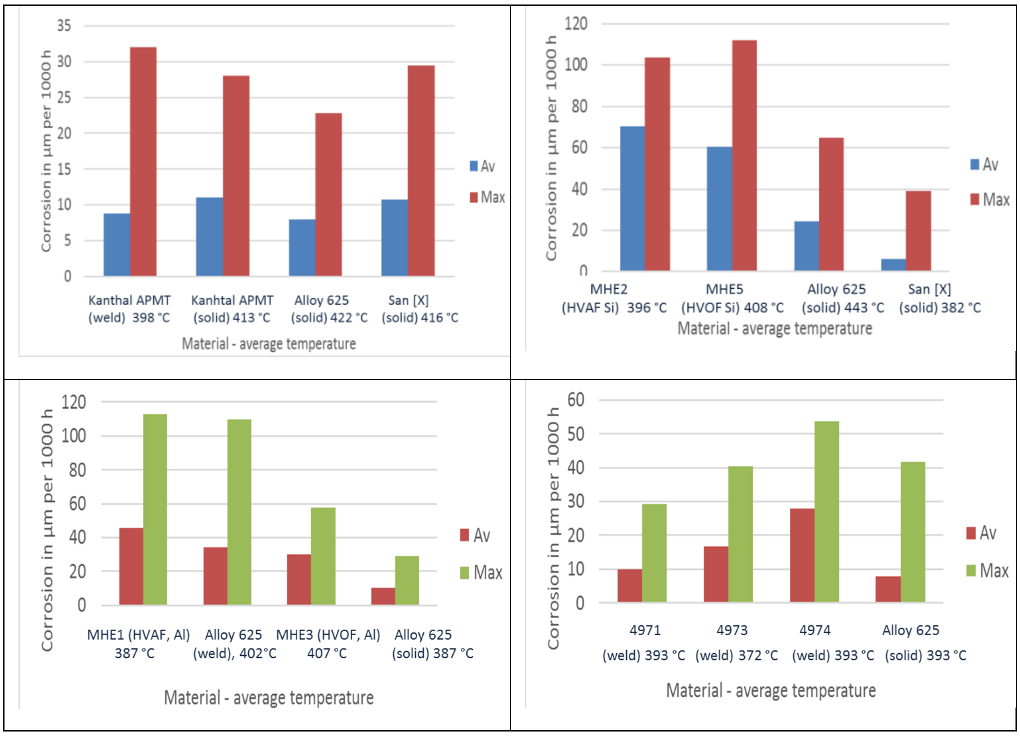
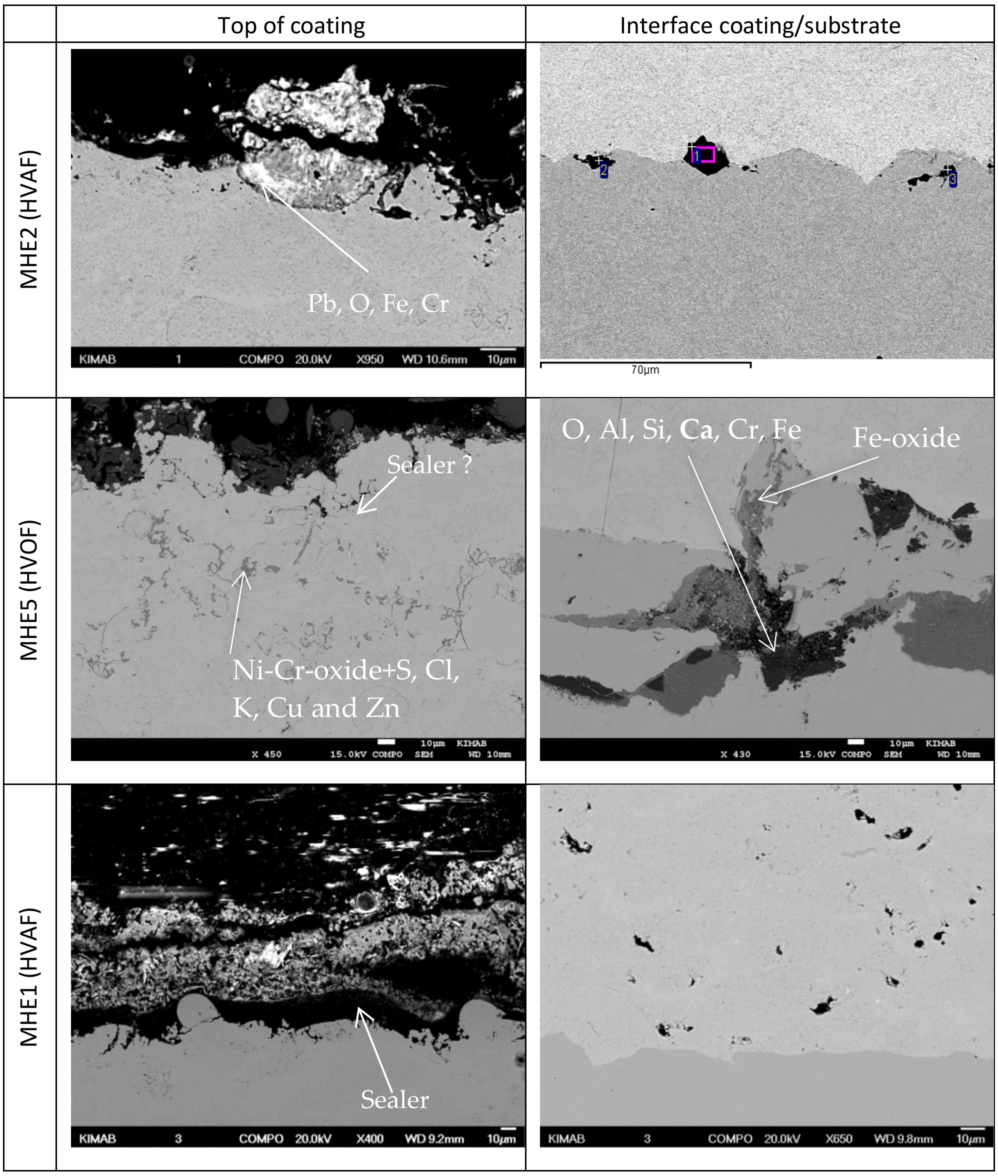


Figure 12. Corrosion rate results for tested samples.

3.2.1 Cross-section analysis

MH Engineering samples

MH Engineering samples are 16Mo3 coated with Alloy 625 using two deposition techniques. Samples MHE2 and MHE1 were coated with high velocity air fuel (HVAF) technique with a thickness of 380-400 µm. Samples MHE5 and MHE3 were coated with high velocity oxygen fuel (HVOF) technique with a thickness of 320-350 µm. The coatings on samples MHE2 and MHE5 were sealed with a silica based sealer and the ones on MHE1 and MHE3 were sealed with an alumina based sealer. MHE2 and MHE5 were field exposed in Idbäcken during November-December 2016 and then MHE1 and MHE3 were inserted in January-February 2017. Fig.13 shows SEM images of the top of the coating and the coating-substrate interface.



MHE3 (HVOF)

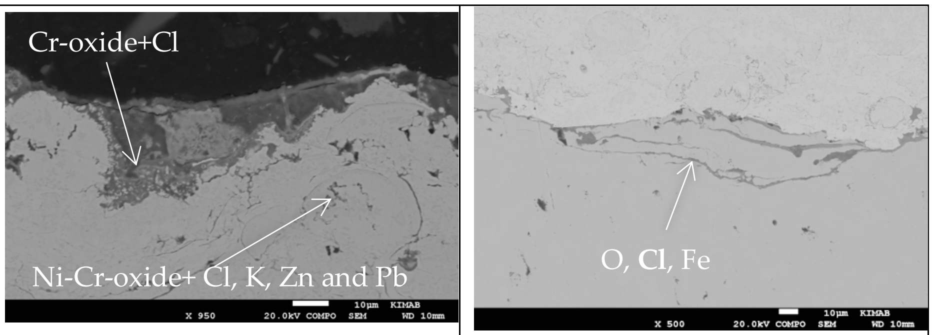


Figure 13. SEM images of cross-sections of MHE samples.

The top of the coatings are covered by a deposit mostly containing O, Al, Si, S, Cl, K, Ca, Zn and Pb. MHE5 is partially covered by a Si-oxide, which could be the remaining sealer. The deposit on MHE1 and MHE3 is much thicker than the other two samples.

For MHE2 some local corrosion pits are observed. The whiter area on the SEM image contains: Pb 35 wt%, O 21 wt%, Ni 20 wt% and Cr 9 wt%. MHE1 is covered by deposit but there is no visible internal corrosion. Some of the sealer on MHE1 was found and featured in the SEM images.

Darker grey areas in MHE5 coating are shown to contain mostly oxygen, nickel and chromium and traces of S, Cl, K, Cu and Zn, meaning an oxide has formed in the coating and the corrosive elements are likely to have diffused into the coating. Similar oxides were found in MHE3: O, Ni, Cr and traces of Cl, K, Zn and Pb. There is some local corrosion on top of MHE3 with the formation of a Cr-oxide containing some Cl.

The coatings did resist the corrosive environment; however it seems HVAF coatings were a better protection for the substrate underneath. There is no new phase, different from substrate or HVAF coating at the interface and no visible penetration of corrosive elements into the substrate.

For HVOF coatings there is a formation of different phases at the interface, which appears in the dark grey and black areas on the SEM images. Traces of Ca (at%) were found with EDS analysis at the interface of MHE5. MHE3 has a mix between Fe-oxide and Cl. The presence of these elements means species from the environment have penetrated the coating and started to corrode the sample underneath. The lines in MHE3 suggest the corrosion propagates further into the substrate.

The darker areas at the interface of MHE2 and MH5 are alumina and silica oxides remaining from the blasting step previous to the coating step.

Kanthal AB samples

Three welded coatings on steel substrates. The coatings are FeCrAl material with 10-15 wt% Cr, 3-5 wt% of Al and some also contained Si. The thickness of the weld is approximately 2 mm for all samples. All samples were exposed together in Idbäcken during January to February 2017. The samples were cut and prepared for cross-section analysis with SEM and EDS. Fig.14 shows SEM images of the top of the coatings.

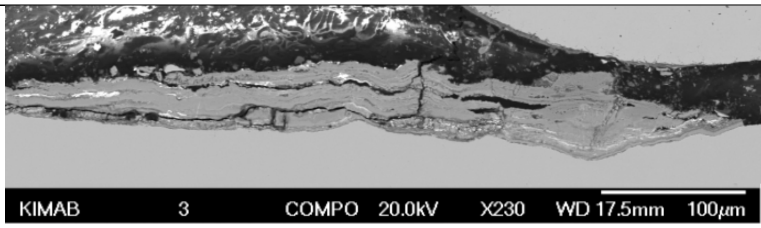
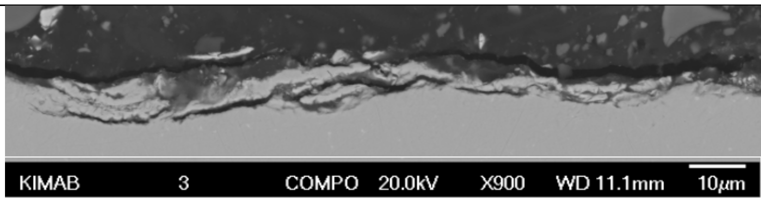
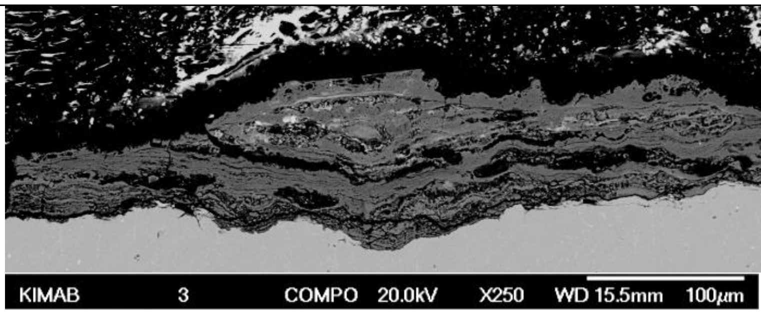
Coating	Top of coating
4971	
4973	
4974	

Figure 14. SEM images of cross-sections of FeCrAl samples.

On top of the coating there is formation of a multi-layered oxide. The layer closest to the welded coating is a Fe-Cr-Al oxide. The other layers also contain Fe, Cr Al and O with some traces of Cl, K, Ca Pb and Zn. The total thickness of the oxide layers varies from sample to sample but also along the cross-section. For 4971 the average thickness is 50 µm, for 4973 10 µm, for 4974 100 µm.

At the coating-substrate interface, for all samples, there are no new phases or any corrosion products. There is no sign of delamination either. The coating did protect the substrate from the corrosive environment.

Kanthal APMT material, also a FeCrAl material was introduced in the November exposure. Two samples were prepared: Kanthal APMT coating welded on a steel substrate and a solid Kanthal APMT sample.

All samples are cut and prepared for cross-section analysis with SEM and EDS. Fig.15 shows SEM images of the top of the coating.

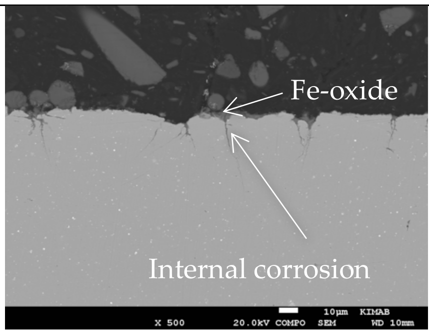
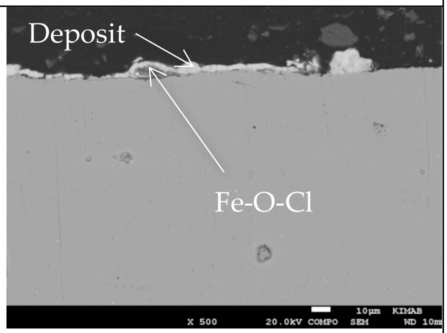
	Kanthal APMT-weld November 16	Kanthal APMT-solid November 16
Top of coating		

Figure 15. SEM images of cross-sections of Kanthal APMT samples

The welded Kanthal APMT shows some internal corrosion with propagation of Cl into the coating. The maximum propagation depth of chlorides is 40 µm approximately. The solid Kanthal APMT is covered with the deposit and at the interface there is a formation of a mixed Fe-oxide and Fe-chloride.

A chemical analysis was performed from the top of the samples both for welded and solid to compare alloying differences. Fig. 16 shows the Fe, Cr and Al wt% in the welded Kanthal APMT and solid Kanthal APMT, starting from the top of the sample down to the weld line and the same distance for the solid material. The solid material has a lower Fe content than the weld (~65 wt%) and a higher Cr (~21 wt%) and Al (~5 wt%) content than the welded material which had the following values: Fe ~73 wt%, Cr~17 wt%, Al ~4 wt%. In total three profiles where made along the cross section for the analysed samples and are in the legend named 1-3.

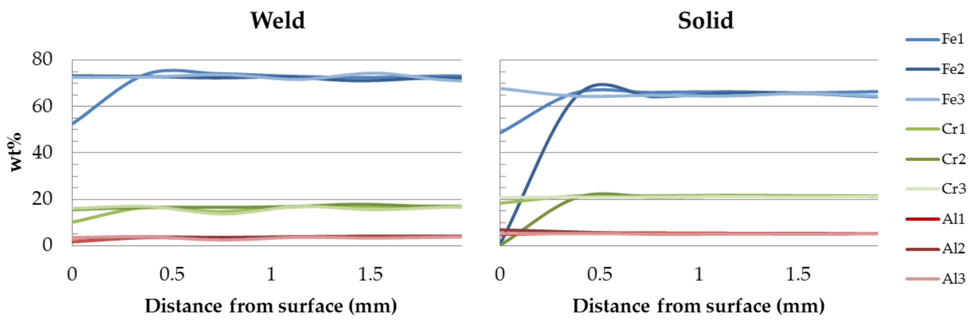


Figure 16. Fe, Cr and Al wt% of Kanthal APMT weld and Kanthal APMT solid vs distance from surface, 1-3 in legend represent three different profiles along the sample cross section.

Reference samples: Alloy 625

The reference material Alloy 625 was tested as a solid on all probes and one sample with welded Alloy 625 was tested in one campaign. The thickness of the weld was 3 mm. The samples are cut and prepared for cross-section analysis with SEM and EDS. Fig. 17-18 features SEM images of the top of the coating and the coating-substrate interface.

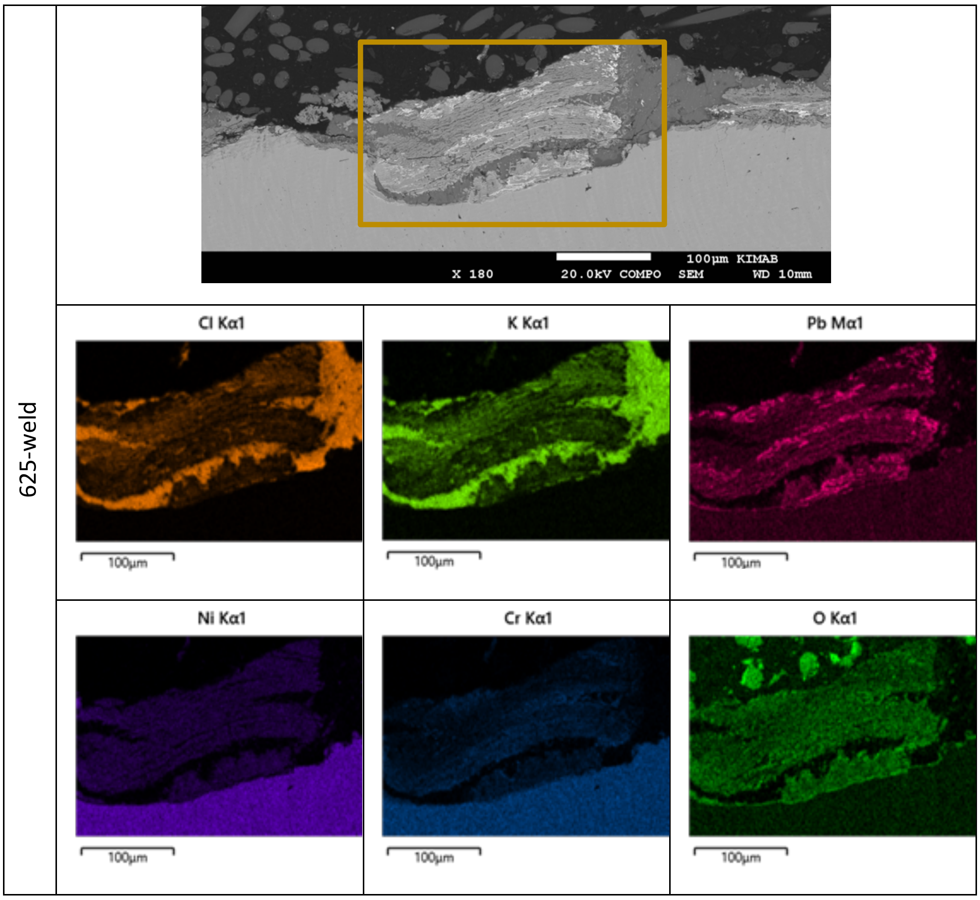


Figure 17. SEM images of cross-sections of reference samples Alloy 625

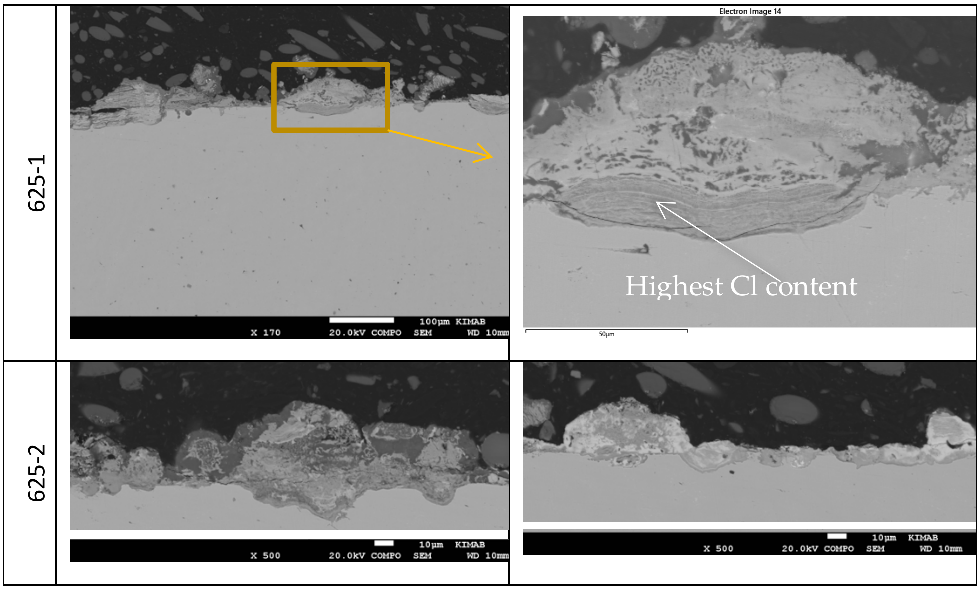


Figure 18. SEM images of cross-sections of reference samples Alloy 625

The corrosion products are a thick oxide formed rich in Ni and Cr. The thickness of the corrosion products is uneven for all 3 samples but the average thickness of the oxide for the weld is 80 µm whereas the solid material oxide has an average thickness of 30 µm approximately. The elements Cl, K, S and Pb are mixed with the oxide. Closest to the substrate (weld or solid Alloy 625) the corrosion product is rich in Cl indicating metal chlorides.

A chemical analysis was performed from the top of the samples both for welded and solid to compare alloying differences. Fig. 19 shows the Ni, Cr, Mo and Fe wt% in the 625weld and 625solid, starting from the top of the sample down to the weld line and the same distance for the solid material. Both materials have a similar Ni, Cr, Mo and Fe content in the area closest to the surface (0-1 mm). When approaching the weld line, the Fe content increases and the Ni and Cr content decreases slightly. In total three profiles where made along the cross section for the analysed samples and are in the legend named 1-3.

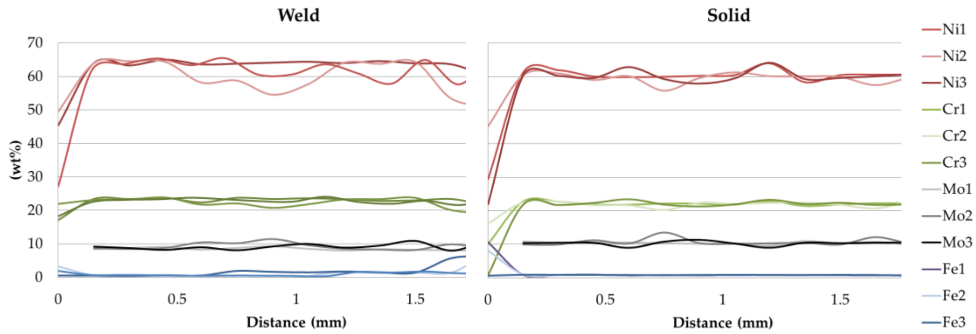


Figure 19. Ni, Cr, Mo and Fe wt% in Alloy 625 weld and Alloy 625 solid vs distance (mm), 1-3 in legend represent three different profiles along the sample cross section.

The microstructure was also studied in order to determine differences between the welded Alloy 625 and the solid. The samples were polished with oxide polishing suspension (OP-S) and then analysed in SEM. Fig. 20 and 21 shows SEM images of the top of the sample after polishing. The corrosion of the welded sample seem to be horizontal in the area closest to the surface (0-10 µm), following the lines revealed by the OP-S polishing. The solid sample is submitted to pitting corrosion, with formation irregularly over the sample. The microstructure is much more defined than the welded material: clear grains with low size distribution.

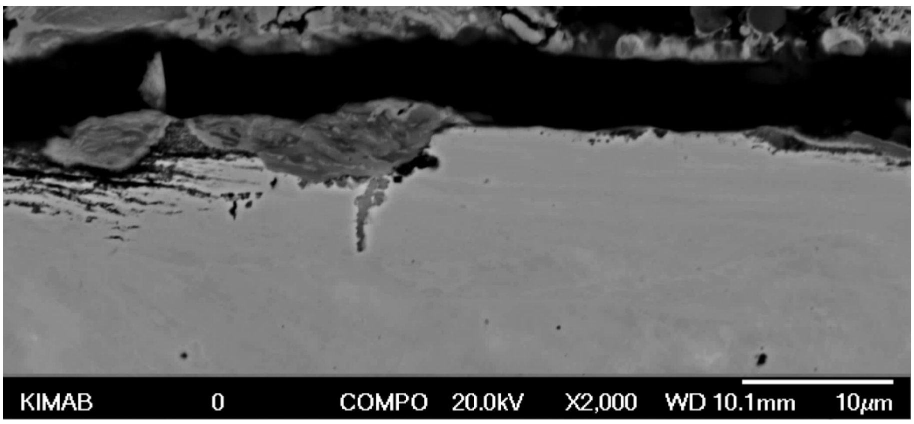


Figure 20. SEM images of 625-weld oxide polished.

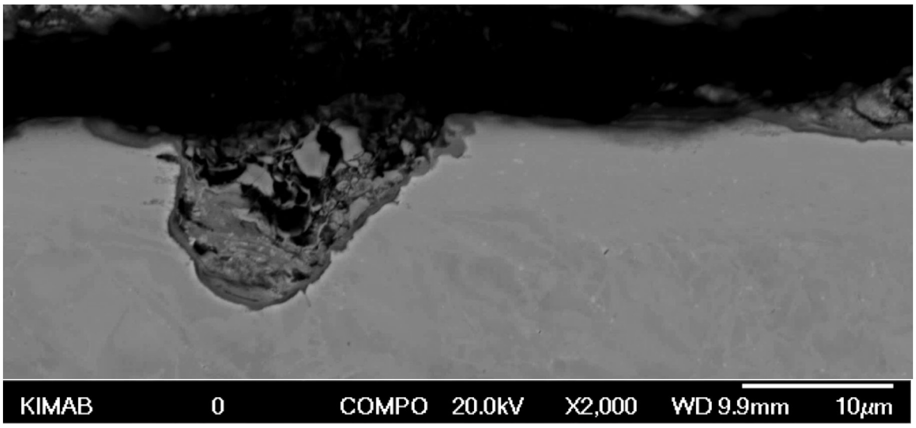


Figure 21. SEM images of solid alloy 625 (OPS-polished)

3.3 COATING CAMPAIGN IN BLACKBURN MEADOWS

The samples tested on the tube in Blackburn Meadows were exposed for approximately 7000 operational hours and the fuel fired in this boiler was used wood fuel. The approximate furnace tube metal temperature was 360 °C. Several materials were tested on this probe but only the reference steel (16Mo3), Sanicro 60 and Kanthal APMT belong to this KME-project and are presented in this report.

3.3.1 Cross-section analysis

In the cross section analysis it is clearly observed that the higher alloyed materials behave better with less corrosion observed in comparison with the reference material, 16Mo3, which was also expected. At the areas where deposit is still present at the reference sample the corrosion products are 100-200 µm thick and are covered with a deposit which closest to the corrosion products is rich in lead, Fig. 22.

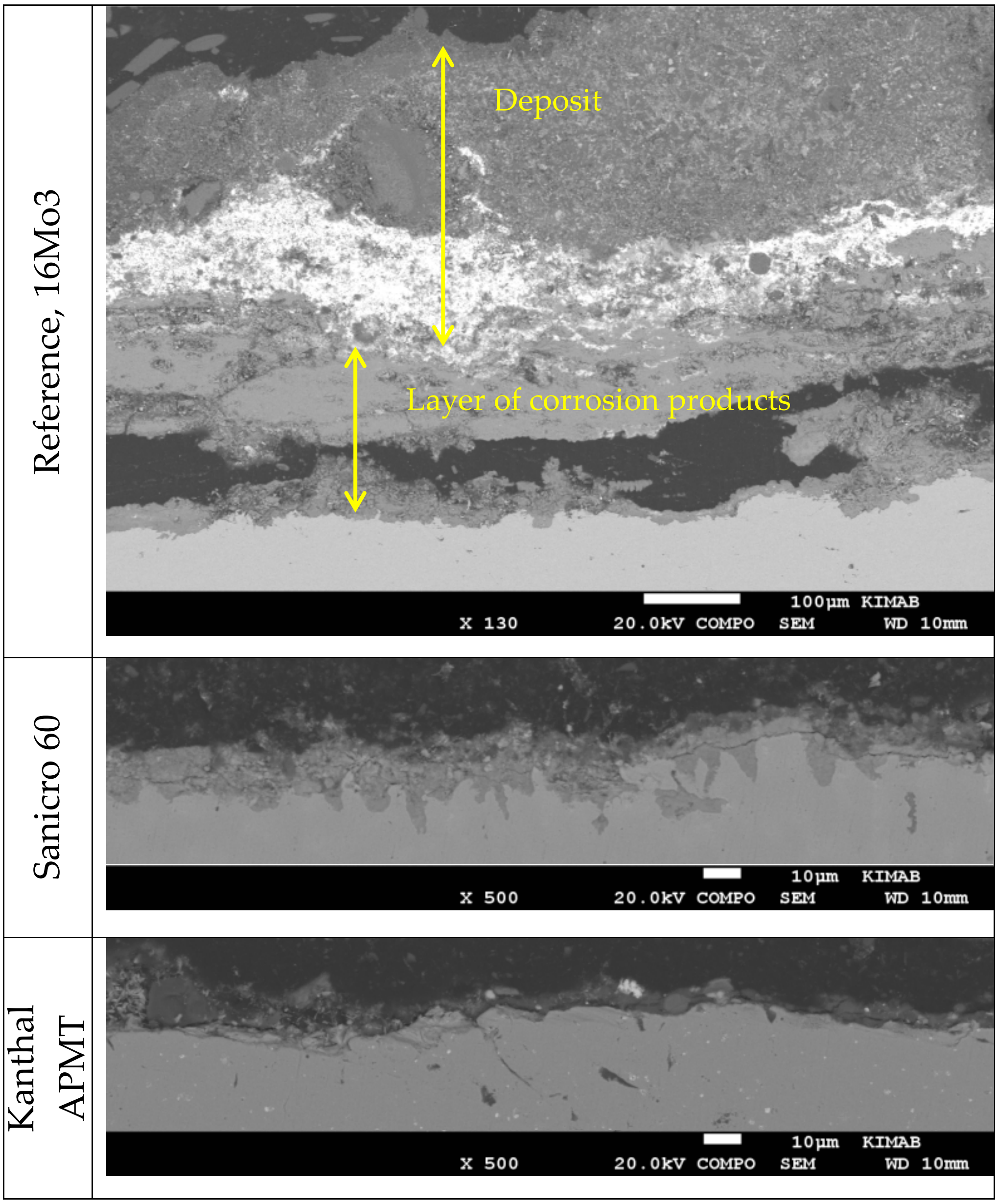


Figure 22. Cross section analysis of exposed materials.

For the higher alloyed materials the corrosion is not as severe. For welded Sanicro 60 the oxide layer visible is around 10-20 µm thick but varies locally. At some areas no clear layer is present, instead the oxide has formed locally. An interesting observation is that for the welded Kanthal APMT not so much oxide formation is present along the investigated cross section. Instead, internal corrosion is observed in similarity to what was observed for the samples tested in the Idbäcken campaign (3.2.1). The maximum propagation measured in the Blackburn Meadows campaign is of a similar magnitude.

EDS profiling

Fig. 23 features the Ni, Cr, Mo and Fe wt% in sample Sanicro 60-2a. The amount of the elements is similar through the weld, except for the lower content in the area closest to surface where an oxide has formed. The results for Sanicro 60-5a and Sanicro 60-1b are similar to the results featured in Fig. 23. In total three profiles where made along the cross section for the analysed samples and are in the legend named 1-3.

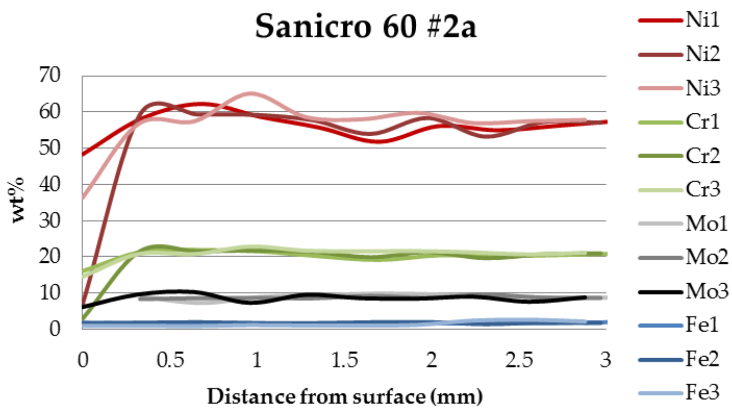


Figure 23. Ni, Cr, Mo and Fe wt% in Sanicro 60 #2a vs distance from surface (mm), 1-3 in legend represent three different profiles along the sample cross section.

Fig. 24 features the Fe, Cr and Al wt% in sample Kanthal APMT-3a. The amount of the elements is similar through the weld. The decrease in Cr and increase in Fe marks the weld-substrate interface (at 3 mm).

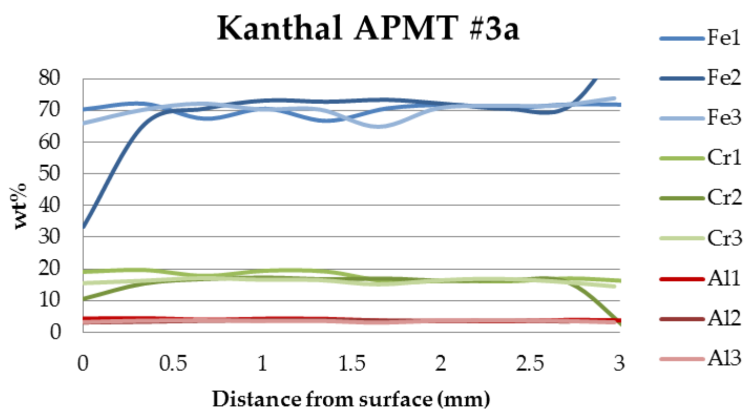


Figure 24. Fe, Cr and Al wt% in sample Kanthal APMT-3a vs distance from surface (mm), 1-3 in legend represent three different profiles along the sample cross section.

4 Analysis of the results

4.1 SLUDGE AS FUEL ADDITIVE

The results show a positive effect on furnace corrosion behaviour when a sludge additive is co-fired with a corrosive used wood fuel. These results are independent of material and sludge additive. Previous project KME708 investigated the corrosion depending on lead and chlorine content in a used wood fuel and showed that fuels high in Cl and Pb resulted in severe corrosion of the materials tested. The results from the present KME718 project where this corrosive fuel is used as a reference shows that using sludge additives (both sewage and fibre) results in less corrosion and thus opens up for a more flexible fuel usage since highly corrosive fuels can be made less corrosive by co-firing of a sludge additive.

There are some differences between the sludges but common for both of the sludges is that they have higher content of the elements sulphur (S) and phosphorous (P) which both are known for their capability to convert alkali chlorides to alkali sulphates or alkali phosphates [10-12]. Also calcium (Ca), Aluminium (Al), Silica (Si) and Magnesium (Mg) is higher in the sludges. Previous work has suggested that for instance alumina silicates in sewage sludge could capture alkali and in this way reduce the possibility for alkali to form alkali chlorides which would decrease the risk for corrosion [13-16].

From the XRD-results alkali sulphates and calcium sulphates are observed for both sludges although there is an indication that $CaSO_4$ is more often present for the sewage sludge samples. For the fibre sludge samples alkali sulphate with sodium also present is more often observed. These results are also reflected in the surface analysis performed with SEM-EDS. Traces of alkali alumina silicates are observed both for sewage and fibre sludge samples but to a greater extent on the sewage sludge samples. In general very little alkali chlorides are present at the sample surfaces which strengthen the results that the alkali is captured in another form, sulphates and silicates. An interesting observation is that the amount of lead (Pb) and zinc (Zn) in the deposits (measured by SEM-EDS) was higher for some samples when sludges were co-fired. For the fibre sludge samples this was most pronounced and from the XRD analysis traces of lead sulphates and potassium-zinc silicates were observed. It is though important to mention that the possible presence of these compounds does not seem to influence the corrosion in a negative way. At least not in such a way that the general corrosion reducing effect of the sludges is notably affected.

The surfaces of the sewage sludge samples were smoother compared to the fibre sludge samples, Fig. 25, and thus the interpretation of the XRD and SEM-EDS data needs to be made with care since there are probably variations through the deposit.

Fibre sludge

Sewage sludge

Figure 25. Visual appearance of the sample surfaces after exposure when firing waste wood fuel and fibre sludge (upper) sewage sludge (lower).

A positive effect of co-firing the sludges is also observed at superheater position. Decreased initial corrosion is observed for the materials tested when both sludges are fired.

Before this project, tests with sewage sludge had been performed during limited test time and showed promising results. By extending the test time to 336 h, the results were strengthened. Also, the tests with fibre sludge as an additive showed that also this sludge have very promising corrosion reducing properties.

The positive outcome with decreased corrosion shows the potential in using both sewage and fibre sluge as additives. By co-firing these additives the fuel flexibility in used wood fired boilers increase markedly since more corrosive, often cheaper fuel, can be used which also affects the cost aspect in a positive way.

During the project, Vattenfall AB started to use fibre sludge as an additive in their boiler used in this project. This shows that the results from the project are useful.

4.2 COATING CAMPAIGNS

Two coating campaigns were performed in the project, one short (approx. 1000 h) and one longer (approx. 7000 h). These coating campaigns showed that there are several coating materials that are comparable and even better than the currently used nickel base alloy Alloy 625.

Analysis of the corrosion behavior of Alloy 625, reference material

In general the average corrosion rate for the reference material Alloy 625 was similar through the 1000 h tests, (except for one sample which was exposed to very high temperature (443 °C)) and this shows the repeatability of the tests. It is though observed in the cross section analysis of the samples that corrosion attack on this material is often local pits and this has an influence on the maximum measured corrosion rate. In the pits the presence of chlorine, lead and potassium is observed together with oxides formed from the base metal. This is expected when exposing this material when firing used wood fuel and the corrosion behavior has been shown also in previous work [5, 15]. Also in the longer test of 7000 h the corrosion was of the local character for a variant of this material (Sanicro 60) even though there was a thicker coherent oxide on top of the pits.

An interesting remark is that the welded sample of Alloy 625 exposed in the 1000 h test did not behave as well as the solid material. Both the average corrosion rate and the maximum measured corrosion rate were higher than for the solid samples.

In order to understand why the welded nickel base alloy 625 showed so much higher corrosion rate compared to the solid material, a composition analysis through the weld compared to the solid sample was made for Fe, Mo, Cr and Ni. However, no trend was observed which could explain the result. After a more detailed investigation of the microstructure it is believed that it mainly is the microstructure differences that contribute to the difference in corrosion rate.

It can be discussed also if there were local environmental effects but this is not believed to be the explanation since the metal temperature of the exposed samples have been similar and also the samples are located relatively close to each other. Thus, differences in deposition mechanisms are not expected.

It also needs to be kept in mind that the surfaces of the samples were milled before testing and it was not the as received surface that was tested (which most often is the case in a boiler) and the interpretation of the results needs to consider this detail.

Analysis of the corrosion behavior of MH-Engineering samples

In the case of MHE-samples, the coatings were applied with two techniques (HVAF and HVOF). Also, two sealers were tested, silica based and alumina based. This means that the four samples are different from each other. The two sealers had different surface appearances before entering the boiler. The silica based sealer was smooth while the alumina based was very irregular and had thick parts left that were ground down before exposure. This was made in order to better be able to measure the corrosion rates of the samples.

In general, it seems as if the samples with alumina sealer have the lower corrosion rates. However, it is difficult to draw any conclusions on the corrosion rates of the samples since the sealer present before exposure possibly could have had an effect on the reliability of the measured corrosion rates. However, it seems to be a difference in behaviour depending on deposition method. For the samples which were deposited with the HVOF method, traces of chlorine and other deposit related compound was found in the coating. For the samples deposited with the HVAF method this was not observed.

Analysis of the corrosion behavior of Kanthal AB model alloys and Kanthal APMT samples

The model alloys (FeCrAl-alloys) tested behaved well and showed low corrosion rates. An oxide consisting of Fe, Cr and Al seems to form and the three samples behave in a relatively similar way. The composition of 4973 and 4974 are the most similar and the increase in corrosion rate between the two could be reflecting an increased temperature for the sample showing the highest corrosion rate. Sample 4971 is also showing a good result and has a slightly different composition compared to the other two.

In previous work Kanthal APMT had shown promising results at furnace wall position [4]. Also in this project it showed good results with low corrosion rates. One solid and one welded sample were tested and they showed similar corrosion rates. The main difference was observed in cross section analysis and showed that the weld suffered from internal corrosion while the solid material formed a thin oxide. The penetration of chlorides and internal corrosion in the weld was measured to maximum 40 μm. Usually internal corrosion is not wanted due to its possible effect on the strength properties but in this case the material is not aimed to be load bearing and a certain amount of internal corrosion could be accepted as long as it does not grow with time. Studying the welded Kanthal APMT from the longer test (7000 h) also in this case internal corrosion is observed. The long term test was though performed at a lower temperature and can thus not be directly compared but the depth of the internal corrosion does not seem to increase a lot with respect to the longer exposure time. This gives strong indication that at the lower temperature the internal corrosion is acceptable. A chemical analysis of both the welded and solid samples showed that there was a slightly lower chromium content, a few wt%, in the welded samples.

Sanicro X was also behaving well but no further microstructural analysis was performed in the project; the samples were sent back to Sandvik after exposure in the boiler.

5 Conclusions

Corrosion tests have been performed in the furnace wall area and at the superheaters of used wood fired boilers in order to study how corrosion problems can be reduced. Tests with co-firing an additive have been performed with the aim to study their possible corrosion decreasing effect. Also different coating materials have been tested in order to evaluate their corrosion resistance.

5.1 SLUDGE CAMPAIGN

- Co-firing of both sewage sludge and fibre sludge show reduced chlorine content in deposits and reduced corrosion of all tested materials at both furnace wall position (336 h exposure) and superheater position (3 h deposit probe, initial corrosion).
- The use of sludge additives (both sewage and fibre) results in less corrosion and thus opens up for a more flexible fuel usage since highly corrosive fuels can be made less corrosive by co-firing of a sludge additive.
- A positive result from this project is that Vattenfall is now using the fibre sludge as an additive at the Idbäcken plant.

5.2 COATINGS

<u>Coating campaign Idbäcken</u>

- Solid Alloy 625 performed better than welded and one explanation to the higher corrosion rate observed for the welded sample is believed to be a result of the difference in microstructure compared to solid sample.
- All FeCrAl-alloys (model alloys, Kanthal APMT (both welded and solid)) performed well and were similar in their behaviour to solid Alloy 625.
- The model alloy San[X] performed well and similar to solid Alloy 625.
- Differences are observed between HVAF and HVOF sprayed modified Alloy 625 (hardness treated) but it is believed to be sealer dependent.

<u>Coatings in Blackburn Meadows campaign</u>

- Kanthal APMT and Sanicro 60 (both welded) both showed low corrosion rates and performed better than the reference material 16Mo3.
- Kanthal APMT showed best results with mainly some internal corrosion present while Sanicro 60 showed a slightly thicker oxide layer.

The project showed that there are interesting materials which could work better and possibly be more cost efficient than overlay welded Alloy 625 used today. FeCrAl-alloys seem promising.

6 Goal fulfilment

The overall aim of the project is to reduce operation and maintenance costs in heat and power boilers that burn predominantly used (recycled) wood by the use of additives to the fuel and the use of new coating materials. To achieve this, the following goals were set:

Technical and Scientific

1. Reduce operation and maintenance costs in boilers that burn predominantly used wood by the use of additives and coatings
2. Acquiring new and in-depth knowledge from longer term studies on the effect of using sewage sludge and one alternative sludge
3. Investigating the corrosion properties of some new coating materials and their related performance with respect to furnace wall protection

Academic

4. One licentiate degree (Annika Talus, latest 2017)
5. Contribution to one PhD thesis (Annika Talus, estimated 2018)
6. Publication of one to two scientific papers

The goal fulfilment is as follows:

1. The project has shown that by using additives and coatings, corrosion problems decrease. This is expected to lead to reduced operation and maintenance costs.
2. The project has shown that two types of sludges can be used in order to decrease corrosion problems of materials typically used for furnace walls and the effect on corrosion has been studied in detail after longer term exposures.
3. The project has shown promising results for some coating materials to be used in order to decrease furnace wall corrosion.
4. Licentiate seminar was held in December 2016
5. The project has produced results which will contribute to the thesis
6. No publication is finalized but results from the project are expected to be presented/published in some form during 2018

It is concluded that the goals have been acceptably well fulfilled.

7 Suggestions for future research work

The project resulted in useful and interesting results both for the use of sludge additive and for the use of new coating materials.

One very positive outcome from the project is that Vattenfall AB now is using one of the evaluated sludges (fibre sludge) in their boiler at Idbäcken plan. It could be interesting to study materials that have been exposed in the boiler for a longer time by collecting samples during tube change or other reparations in the boiler to fully evaluate the positive effect of the sludge additive.

The test of welded samples were limited in this project and could be of interest to study further to fully evaluate the material stated as promising choice for overlay welding.

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9 Publications

Talus, A. *"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, Chalmers University of Technology, 2016

High temperature corrosion in used-wood fired boilers

Corrosion tests have been performed in the furnace wall area and at the superheaters of recycled wood fired boilers. Analysis of the exposed samples through thickness measurements, chemical analysis of deposits and cross section analysis showed that:

1) Co-combustion of used wood with digested sewage sludge and fibre sludge reduces the corrosion rate (336 h corrosion tests) at furnace wall position for both low alloyed steel 16Mo3 and nickel base alloy Alloy 625.

2) Co-combustion of used wood with digested sewage sludge and fibre sludge reduces the initial corrosion (3 h deposit probe) also at superheater position.

3) The use of sludge additives (both sewage and fibre) results in less corrosion and thus opens up for a more flexible fuel usage since highly corrosive fuels can be made less corrosive by co-firing of a sludge additive.

4) There are interesting materials which could work better and possibly be more cost efficient than the commonly used overlay welded Alloy 625 as coating material at the furnace walls when firing used wood fuel. FeCrAl-alloys showed promising results.

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