# Combating superheater corrosion by new materials and testing procedures - Corrosion experiments in the waste fired CFB boiler P15 at Händelö.

### **Applying organisation**

HTC at Chalmers University of Technology Department of Biological and Chemical Engineering Division of Energy & Materials Organization number: 556479-5598

#### **Co-applicants**

E.ON Värme Sverige AB (EVS)
Foster Wheeler Energia OY (FW)
Sandvik Materials AB (SMT)
Sandvik Heating Technology AB (SHT)
MH-Engineering AB (MH)
Fortum Värme AB (FV)
Mälarenergi AB (Mäl)
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#### **Project leader**

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# **Project**

New

#### Title

Combating high temperature corrosion by new materials and testing procedures - Corrosion exposures in the waste fired CFB boiler P15 at Händelö

Minska högtemperaturkorrosion genom nya material och testprocedurer – Korrosionsexponeringar i den avfallseldade CFB-pannan P15 på Händelö

#### **Summary (max 1 000 characters)**

Compared to traditional waste fired CFB boilers, a newly built CFB boiler by Foster Wheeler is designed with a horizontal pass. With this design, a decreased corrosion rate of the superheater tubes is expected. However, no corrosion tests have been performed, showing if the horizontal pass design displays improved corrosion resistance.

We will investigate the corrosion attack of superheaters in the horizontal pass by testing a new class of materials (so called FeCrAl-alloys) as well as state-of-art stainless steels and conventional materials. In order to generate generic knowledge about the corrosion attack the flue gas chemistry, deposit chemistry and corrosion attack be closely monitored and coupled together. This is done by a novel alkali online system, comprehensive deposit analyses, advanced corrosion analysis and complementary equilibrium calculations. The goal is to increase the understanding how the corrosiveness of flue gas varies with temperature. A methodology development of the corrosion test program will be performed using three different corrosion test techniques having different complexity, cost and plant availability risk.

## **Motivation (max 5 000 characters)**

In order to increase green electricity production from combustion of biomass and waste high temperature corrosion of the pressure part materials in the boilers needs to be addressed. Compared to boilers burning fossil fuels, the electrical efficiency of biomass and waste fired boilers are considerably less. There is however a constant strive towards increasing the heat and power output from these boilers using renewable fuels or waste fractions.

#### **Energy relevance**

In the present project, we aim to investigate how the corrosivity of the flue gas varies with flue gas temperature and how the design of the superheater section of the CFB boiler (going from a vertical to a horizontal design) affects the corrosion of the superheaters. By lowering the corrosion rate through new boiler design, an increase in the boiler steam data is enabled for future plants. Furthermore, this projects aims to test a new class of materials for these types of boilers (so called FeCrAl-alloys) as a way towards decreasing the corrosion rate of the superheaters. The work will be coordinated in collaboration with the KME709 project, which also investigates the use of FeCrAl alloys for boiler applications. In addition, high performance stainless steels will also be investigated. The matrix will also include samples with different bulk properties, such as monotubes, compound tubes, overlay weldings and coatings. Special focus will put on coatings and a newly developed Ni-base self-fluxing coating including formation of hard-phase which will be tested with the new generation coating technology HVAF (High Velocity Air Fuel). By this two-pronged approach; decreasing the corrosion by boiler design and an optimized material selection, the aim is to generate new knowledge for the construction of future boilers with increased electrical efficiency. With increased electrical efficiency of biomass and waste fired power plants their competitiveness towards fossil fuelled plants is increased and thus, the share of renewable energy in the energy system can be increased.

### <u>Industrial relevance</u>, general applicability and implementation of the results

Since this project involves several industry partners, ranging from material manufactures to boiler manufactures and boiler owners, the project findings may rather swiftly be implemented or used by the project partners. The results are expected to visualize the corrosion performance of a set of new materials and coatings in relation to more conventional materials, the effect of a horizontal superheater pass on corrosion and also how the corrosivity of the flue gas is related towards its temperature. The knowledge generated within the project will aid the involved companies in improving their products and thus, the knowledge and improvements (of e.g. new materials or boilers) obtained will be of value also outside of this project.

### News value of the project

The news value of this project covers several different aspects. For instance, the comparably large matrix of materials (both new and commercial alloys) to be tested will generate important knowledge about the performance of these materials in this type of environment. Furthermore, we aim to generate new knowledge of how corrosion testing is performed in an optimum way for lifetime prediction. In previous KME projects (KME509 and KME514) corrosion testing methodology was addressed and we aim to continue this type of research questions within this project. Focus will be put towards different types of testing methods, i.e. corrosion exposures will be performed with probes, coils/tube replacements and "clamping". The latter testing technique is developed by Foster Wheeler and the test material is placed on top of the ordinary superheater tube and the material temperature of the test piece is controlled by the amount of insulation between the test clamp the superheater. In addition, the effect of startup sequence of probe exposures (both short term and long term) on corrosion rate and deposit formation will be addressed.

# **Background (max 7 500 characters)**

Traditional waste fired CFB boilers are designed with vertical superheater banks after a radiation pass/empty shaft. With this design, the superheater bundle is usually subject towards flue gases with high velocity and thus, the risk of erosion damages. Furthermore, due to the geometry of the tubes, ash removal from the tubes is usually performed by steam generated soot blowers. This may further enhance the risk of erosion. A newly built CFB boiler, boiler P15 at Händelöverket (see figure 1), by Foster Wheeler is designed with a horizontal pass. Hence, the superheaters in the flue gas in P15 are arranged hanging in a horizontal path. With this design, the flue gas velocity is much lower and cleaning by hammers instead of steam soot blowers can be deployed. This is expected to decrease the corrosion rate of the superheater tubes installed in this section. Furthermore, the horizontal design enables a relatively fast and easy exchange of the superheaters. However, so far no corrosion tests have been performed, showing if the horizontal pass design actually displays improved corrosion resistance.

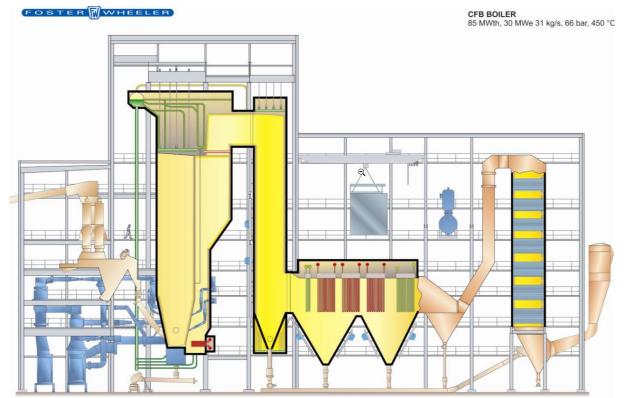


Figure 1: Boiler P15 at Händelöverket

E.ON Värme Sverige AB, Norrköping, Sweden

In addition to the horizontal pass design, this project aims to investigate how the radiation pass or empty shaft is affecting the corrosion of the downstream superheaters. Today, boilers designed for waste fired fuels utilise a radiation pass after the separation of bed material where the flue gas is cooled by radiation to a metallic water wall down to temperatures to  $600~^\circ\text{C}$  before entering the superheaters. Practical experiences have shown that the corrosivity of the flue gas follow the flue gas temperature, even if the material temperature of the superheater is the same. However, this is not fully understood why this is the case.

#### State of the art

In this project we will investigate the corrosion performance of new materials and coatings, based on alumina forming alloys, in relation to more conventional materials. The ability of an alloy to resist high temperature corrosion is due to its capacity to form a protective oxide scale and corrosion properties depend on the growth rate, adhesion, chemical reactivity and mechanical properties of that scale. Only few oxides form protective scales, e.g., SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub> and their solid solutions, spinel oxides and α-Al<sub>2</sub>O<sub>3</sub>. However, in practice the number of oxides responsible for corrosion protection in biomass and waste fired boilers are far less and iron and chromium oxides are dominating. In the most corrosive parts of the boiler (i.e. the hottest part of the steam superheater) different classes of Cr<sub>2</sub>O<sub>3</sub>-forming alloys (i.e. stainless steels) are used. This is because chromia scales are far more protective than the iron oxide scales formed on, e.g. low alloy steels. Unfortunately, most chromia forming alloys behave relatively poorly in alkali chloride rich environments, which commonly is the case in biomass and waste fired boilers. Hence, when a chromia-forming alloy is exposed to alkali chlorides in the presence of water vapour and oxygen, the protective oxide reacts to form alkali chromate (Pettersson 2005, Jonsson 2009). Because this process depletes the protective scale in chromium, the chromia scale tends to be replaced by an iron-rich scale, causing a sudden acceleration of oxidation. The resulting "breakaway scale" is providing a much poorer corrosion protection compared to a chromia rich scale and is susceptible towards chlorine induced corrosion.

Alumina ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) scales are expected to be superior to chromia scales in biomass and waste combustion. However, alloys forming alumina scales are not widely used in combustion of biomass and waste. Also, commercial alumina formers are designed for higher temperatures and are known to be affected by internal oxidation and nitridation in the temperature range of interest (<700°C). However, recent (unpublished) research implies that the corrosion behaviour of commercial FeCrAlMo alloys may be superior to the best NiCr-base alloys in biomass and waste combustion environments. Since this class of materials has limited load bearing capacity at high temperatures and limited ductility at low temperature, they will likely be used as coatings or as the outer part of compound tubing, rather than as load bearing material, but applied in this way they have the potential to improve corrosion resistance dramatically. The coating technology has recently made advances and the project aim to investigate coatings performed with a new generation of coating technology, HVAF (High Velocity Air Fuel).

#### Goal (max 2 500 characters)

The overall goal of the project is to improve plant economy by enabling an increased green electricity production and optimum material selection. The material matrix includes commercial steels available today as well as future materials developed for this type of environment. This will be achieved by generating new knowledge about the following topics:

- To correlate the corrosivity of the flue gas with the flue gas temperature in respect to the material temperature.
- To verify and quantify the corrosion rates for different superheater materials in superheaters with a horizontal design.
- Verify and compare the corrosion properties of commercial superheater materials as well as state-of-the-art stainless steels and FeCrAl alloys.
- Verify and compare the corrosion properties of coatings performed with the new generation coating technology HVAF (High Velocity Air Fuel).
- Compare different corrosion testing methods (i.e. probes, coils/tubes and clamping) with respect towards their complexity, cost and plant availability risk.

Project goals in relation to KME goals

This project proposal contributes to the following KME goals:

- Verifying novel solutions in boiler design with respect towards corrosivity.
- Increased steam parameters and thereby higher electrical efficiency.
- Test improved material solutions including alumina forming alloys and coatings.

# **Project plan (max 5 000 characters)**

In this project several activities will be performed in order to achieve the stated goals. These activities can be divided into three major areas, focusing on different research and technical issues, namely;

- How does the corrosiveness of the flue gas varies with flue gas temperature and changes in the flue gas chemistry? What role does the radiation pass in the boiler play?
- Investigate the corrosivity of the superheaters in a boiler with horizontal design of the superheater section using three different corrosion testing methods (i.e. probes, coils/tubes and clamping).
- Test the usability of novel FeCrAl alloys and coatings and compare these materials towards state-of-the-art stainless steels as well as conventional stainless steels and steels.

# How does the corrosiveness of the flue gas varies with flue gas temperature and changes in the flue gas chemistry? What role does the radiation pass in the boiler play?

One of the activities is to increase the knowledge of why a higher flue gas temperature is more corrosive for a given material temperature. In order to address this question tests at two different flue gas temperatures will be performed. In addition, this question will also be addressed altering the flue gas chemistry by means of sulphur containing additives. These tests will be done with broad palette of techniques in order to following the chemistry and kinetics of flue gas, deposit and corrosion chemistry. In addition, fuel analysis will be performed. The flue gas chemistry will be monitored by an on-line alkali probe (developed by Foster Wheeler and Metso Automation) together with HCl (g) and  $SO_2$  (g) downstream raw gas measurements. The deposit formation and the corrosion attack will be analysed by means of deposit probes and an in-situ corrosion probe (developed by Foster Wheeler), respectively. In addition, equilibrium calculations will be performed with aim to couple the fuel analysis with the deposit composition.

# Investigate the corrosivity of the superheaters in a boiler with horizontal design of the superheater section using three different corrosion testing methods (i.e. probes, coils/tubes and clamping).

This activity has a two-folded approach; the corrosion of the superheaters in a CFB boiler with a horizontal pass design is investigated at the same time as different corrosion testing methods (i.e. probes, coils/tubes and clamping) are evaluated. The corrosion tests will include commercial alloys well as newly developed alloys. The detailed selection of materials, exposure times, positions in the boiler, etc. will be decided by the project group. However, as far as possible, the different exposure parameters related to the different exposure techniques will be the same. Also, exposure times of the different techniques will be synced. Clamps and corrosion probe samples will be evaluated at different test times. The test tubes in the superheater will be measured for wastage at every maintenance stop and when taken out at the end of the test period. Foster Wheeler and HTC will provide necessary probes to the project.

# Test the usability of novel FeCrAl alloys and coatings and compare these materials towards state-of-the-art stainless steels as well as conventional stainless steels and steels.

In this project we will investigate a large matrix of different alloys relevant as superheater materials. This includes commercial steels available today but also newly developed materials by Sandvik (both Materials technology and Heating technology). The aim with this broad approach on material selection is twofold; seeking potential materials for future boilers with increased steam temperatures as well as finding more cost-effective materials for current steam data. In addition to testing different types of

materials, we will also within the project evaluate the potential of using some of the materials not as mono tubes but instead as coatings, overlay welds or compound tubes. All material suppliers (SHT, SMT and MH) will contribute to the project with these types of materials. For example, MH will supply a Ni-base self-fluxing coating including formation of hard-phase which will be tested with the new generation coating technology HVAF (High Velocity Air Fuel). Both alumina forming coatings as well as chromia forming coatings will be tested.

### **Evaluation of the exposed samples**

The proposed project plan will render in a considerable amount of samples to be analyzed. Depending of what type of investigation, a wide range of analytical tools is available. Analysis of the corrosion products can be performed with Scanning Electron Microscopy (SEM) using high-resolution FEG-SEMs. Energy Dispersive X-ray analysis (EDX) can be used for chemical analysis, while crystalline phases can be identified by Electron Backscattered Diffraction (EBSD). Cross sections of selected samples will, if applicable, be performed using a Broad Ion Beam (BIB). Transmission Electron Microscopy (TEM) and Focused Ion Beam (FIB) milling can be employed to analyze the specimens in more detail. A state-of-the-art 300 kV FEI Titan 80-300 TEM is installed and available at Chalmers. It provides unique opportunities for analyzing the oxide scales on the atomic level. Grazing incidence angle X-ray diffraction, GI-XRD can be used for characterization of crystalline corrosion products and in-situ diffraction. We will use a Siemens D-5000 instrument equipped with a Göbel mirror that allows us to detect 20 nm crystalline corrosion product layers. The composition of formed deposits will be evaluated by means of Ion Chromatography (IC) and Ion Coupled Plasma - Optical Emission Spectroscopy (ICP-OES). Material loss determination will be performed on selected samples. Samples will be analyzed both at Chalmers and at Foster Wheeler laboratories.

**Staff**The following personnel will be participating in the project:

	Transfer with be participating in the project.
HTC (Chalmers)	J. Liske
	T. Jonsson
	K. Hellström
	M. Paz
	New Ph. D. student, Licentiate (2017)
EVS	Anna Jonasson
	Bengt-Åke Andersson
	Magnus Liljegren
	Operational staff
	Erik Skog, consultant
FW	Edgardo Coda Zabetta
	Jouni Mahanen
	Kyösti Vänskä
	Kari Peltola
	Vesna Barisic
SHT	Bosse Jönsson
SMT	Nicklas Folkeson
	Jan Högberg
MH	Matti Huhtakangas

	Operational staff						
FV	Eva-Katrin Lindman						
Mäl	Magnus Eriksson						
Söd Per Oxelmark							
All project members works part time within the project							

Part	Participants role in the project								
EON Värme Sverige	Responsible for boiler operation and coil test.								
Foster Wheeler Energia OY	Responsible for different types of testing (probes, clamps and coils), will perform corrosion evaluation and analysis								
Sandvik Heating Technology	Providing material development, material and know-how.								
Sandvik Materials Technology	Providing material and know-how.								
MH Engineering	Providing material and know-how.								
Fortum Värme	Attending meetings and provide knowledge to the project								
Mälarenergi	Attending meetings and provide knowledge to the project								
Söderenergi	Attending meetings and provide knowledge to the project								
Chalmers/HTC	Project leader. Responsible for probe exposures and corrosion evaluation and analysis								

#### Time schedule

The project will start in September 2014 and end (including final scientific and economic reporting) in April 2018. The project will include both long term (coils and clamps) and short term (probes) testing. Installation of clamps in the superheater will be performed during the maintenance stop 2014 and test tubes in the coils 2015.

Wastage measurements of the installed coils and clamps will be performed at the maintenance stops 2015, 2016 and 2017. Full corrosion analysis of the coil and clamp samples will be performed during 2017. Corrosion probe exposures will be performed during 2014, 2015 and 2016. Especially the probe exposures investigating the effect of start-up sequence will be performed as fast as possible (during 2014). Corrosion analysis will be performed continually as the exposed samples become available.

	2014			2015				2016				2017				2018		
	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q	Q
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2
Installation of clamps		Χ																
Official start of project			Χ															
Clamp testing		Χ	Χ	Х	Х	Χ	Χ	Χ	Χ	Χ	Χ	Χ	Х	Χ				
Outtake of clamps						Χ				Χ				Х				
In-situ corrosion probe		Χ	Χ	Χ	Χ	Χ	Χ	Χ	Χ	Χ	Χ	Χ	Х	Χ				

Sample outtake					Χ				Χ				Χ				
Test of startup seq.		Χ	Χ														
Coil installation					Х												
Coil tests					Х	Χ	Х	Χ	Х	Х	Χ	Χ	Х				
Wastage measurements of coils									Х				Х				
Deposit and corrosion probe testing		Х	Х		Х	Х	Х			Х	Х	Х					
Scientific analysis		Χ	Χ	Χ	Х	Χ	Х	Χ	Х	Х	Χ	Х	Х	Х	Х	Х	
Final report																Х	Χ

# **Industrial reference and financing**

The industrial partners that will participate in the project are listed in the table below together with the amount of cash or in kind they are contributing with. Since the revision of the boiler follows a commercial time plan the project needs to adjust its time plan accordingly. This implies that the involved companies may have costs before the official project start date. These costs are associated to the boiler revision stop in the summer of 2014 and installation of clamp test pieces.

	Cash	In-kind						
	contribution	contribution						
EON Värme Sverige		2 263 kSEK						
Foster Wheeler Energia OY		1 725 kSEK						
Sandvik Heating Technology		2 000 kSEK						
Sandvik Materials Technology		344 kSEK						
MH Engineering		125 kSEK						
Fortum Värme	100 kSEK	200 kSEK						
Mälarenergi	352 kSEK	96 kSEK						
Söderenergi	152 kSEK	96 kSEK						
Göteborg Energi	23 kSEK							
Total industrial contribution	627 kSEK	6 849 kSEK	= 7 476 kSEK					
STEM financing	418 kSEK	4 566 kSEK	= 4 984 kSEK					
Total cash in project:(4 984+ 627) = 5 611 kSEK, Total project volume: 12 459 kSEK								