Sulfur recirculation and improved material selection for high temperature corrosion abatement – Investigating different aspects of corrosion memory

Applying organisation

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

Co-applicants

Götaverken Miljö AB (GMAB)
B&W Vølund (BWV)
Dong Energy (DE)
Technical University of Denmark (DTU)

Project leader

PL HTC:	Jesper Liske, +4631-7722843, jesper.liske@chalmers.se
	Torbjörn Jonsson, +4631-7722835, torbjorn.jonsson@chalmers.se
dPL GMAB:	Sven Andersson, +46 31 501981, sven.andersson@gmab.se
dPL BWV	Thomas Norman, +45 43 26 58 43, tno@volund.dk
dPL DE	Ove Jespersen, +45 99559260, ovjes@dongenergy.dk
dPL DTU	Kristian Vinter Dahl, +45 45252218, kvd@mek.dtu.dk

Project

This project is new but is based on 1000 h full scale sulfur recirculation tests done at Waste Refinery project WR07 and ProEnviro project SulphurR, where it received very high scores by an independent international expert evaluation committee. This project includes a permanent sulfur recirculation installation operated during two years.

Title

Sulfur recirculation and improved material selection for high temperature corrosion abatement – Investigating different aspects of corrosion memory

Svavelrecirkulation och bättre materialval för minimering av högtemperaturkorrosion – Undersökning av olika aspekter av korrosionsminne.

Summary (max 1 000 characters)

The project aims at demonstrating the first permanent full-scale installation of the corrosion mitigation technique "Sulfur recirculation" [1] and simultaneously investigating the phenomenon "corrosion memory. Corrosion memory refers to "*the present corrosion attack is due to historic corrosion rather than the fuel mix currently being used" [2]*. The phenomenon can be divided into two sub-areas; increased corrosion due to irreversible changes in the steel and the rate of conversion of corrosive deposits and the project will investigate both aspects. The sulfur recirculation will be installed in one of two nearly identical boilers sharing same fuel feeding system. The dynamic interplay between changes in fuel mix and corrosion attack can thus be studied effectively. The material aspect will be investigated through the aging response of the steel. The aim is to generate knowledge how precipitation occurring over time will influence corrosion.

Motivation (max 5 000 characters)

The overall goal of the project is to increase green electricity production from combustion of biomass and waste. In order to do so 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 lower. Consequently, better corrosion mitigation techniques in biomass and waste fired boilers are highly needed. The knowledge today of useful mitigation techniques have in several cases been based on the corrosion research performed within former KME projects. However, most of the research performed has primarily been investigating the initial (up to 6 months) aspects of the attack. By better understanding the long-time behaviour of the superheaters in this environment, improved mitigation techniques can be suggested or mitigation techniques present today can be optimized. Thus, the combined corrosion memory effect of environment and material needs to be studied as limited research has been performed considering this aspect.

Program relevance

This project is directly focussed on goal 1, 3, 5 and 6, specified in the program description. Furthermore, the results obtained within the project could aid in fulfilling goal 2 and 9. Thus, the project is in good agreement with goals of the program. The overall goal of the project is to increase green electricity production from combustion of biomass and waste.

Goal 1: This project will examine how the corrosion attack is changed when the sulfur recirculation technique is deployed. This knowledge/data will show if the electrical efficiency could be increased with maintained corrosion rates.

Goal 3: This project will examine how already aged materials perform in this type of environment. This could assist in an improved material selection of optimum superheater materials and influence of precipitation reactions on long-term superheater lifetime.

Goal 5: This project will examine how successful the corrosion mitigation technique "Sulfur Recirculation" is on decreasing corrosion of superheaters in a waste fired boiler.

Goal 6: This project will examine how the corrosion mitigation technique "Sulfur Recirculation" is affecting the flue gas chemistry of a waste fired boiler (primarily with respect to HCl and SO_2), and thus, if successful, the fuel flexibility and/or the availability can be increased. Furthermore, by an improved knowledge how the corrosion attack is affected over time (not only the initial attack) by environmental- and material specific parameters new design solutions, operating parameters and tools can be suggested.

Energy relevance

Due to the general national targets of increasing renewable energy, the share of virgin biomass decreases and the share of more difficult fuels increase. These difficult fuels severely limit steam parameters and thereby electricity efficiency. The beneficial effect of sulfur addition on high temperature corrosion is well documented, but sulfur recirculation avoids the disadvantages of additional residue production. The sulfur recirculation aims to change the environment at the superheaters in order to limit the high temperature corrosion. A parallel route to reach the national targets would be to aid boiler owners in a better material selection for the superheaters. Steels or Ni alloys with more than 15-18 wt% Cr suffer from selective internal corrosion. However, very little is known about the mechanism behind the selective internal corrosion. The present project will therefore in addition study the influence of bulk microstructure on the corrosion attack in different environments. The overall aim is to be able to generate more electricity in existing and new plants by increasing the steam parameters (i.e pressure and temperature) of the superheaters. This should be achieved by better understanding the link between environment and material over time, i.e. the corrosion memory effect.

Industrial relevance, general applicability and implementation of the results

The Sulfur Recirculation technology will, if proven successful over time, enable higher steam data and/or lower high temperature corrosion rates in boilers burning corrosive fuels such as municipal, industrial waste as well as waste wood and to some extent biomass. The sulfur recirculation technique is not dependent on any specific boiler type (e.g. CFB, BFB or grate fired boiler) since the technique is working on changing the flue gas chemistry rather than the bed or grate chemistry. However, the flue gas cleaning system needs to contain a wet scrubber. The obtained results with respect to corrosion memory and an increased SO_2 content are generic and thus, applicable for other types of sulfur dosing systems and/or co-combustion with a sulfur rich fuel. At sites with a combination of waste fired and biomass-fired boilers, the surplus sulfur from the waste fired boiler could be dosed into the biomass fired boiler, decreasing corrosion rates also in this boiler. However, a prerequisite for the sulfur recirculation technique to be installed is a wet flue gas cleaning system.

The project in addition aims to generate increased understanding of selective internal corrosion in biomass firing and the influence of precipitation reactions on long-term superheater lifetime. This could enable directly implementable guidelines for selection of optimum superheater materials. These results could in addition aid material manufacturers in designing new steels with improved long-term corrosion behaviour.

News value of the project

The news value of this project covers several different aspects. It will study several aspects of the corrosion memory effect. In a previous KME project [2] the corrosion memory effect was addressed. Running exposures in two boilers mimicking the effect of different fuels showed interesting results and we aim to continue this type of research questions within this project. The sulfur recirculation makes it possible to do this in a much more sophisticated way. For instance, the possibility to change the environment during the exposure without introducing thermal cycling will generate important knowledge about the performance of these materials in this type of environments. Furthermore, we aim to generate new knowledge about selective internal corrosion in biomass firing and linking this to the environment. Finally, this project will act as a demonstration project for the first permanent installation of the Sulfur Recirculation technique. The Sulfur recirculation technique has previously been tested for shorter time spans (up to 1000 hours) at the Renova Waste-to-Energy facility in Göteborg. Corrosion probe measurements showed that corrosion rates were reduced by 50% or more [1]. More importantly, corrosion probe tests done at two different material temperatures showed that sulfur recirculation lowered the corrosion rates even when the material temperature was raised from 450 °C to 525°C. In the present project, we will investigate if these positive effects persist over time.

Environmental goals

This project aims to meet the following environmental goals:

- Goal 1. Reduced Climate Impact: A decrease in deposit formation from higher sulfur levels will lead to higher heat transfer. Higher steam data and higher electrical efficiency from biogenic fuels is the ultimate goal of this project.
- Goal 2. Clean Air: Emissions of CO and ammonia have been shown to decrease from sulfur recirculation, while other components are unchanged [1].
- Goal 4: A Non-Toxic Environment: A decrease in dioxin formation has been observed in previous pilot and full-scale tests. By sulfating of the deposits, the chlorine available for the de Novo synthesis at the temperature window of 200-450°C is reduced. [1,3].

- Goal 7: Zero Eutrophication: A decrease in ammonia slip emissions to the atmosphere by changing the scrubbing liquid in the flue gas cleaning from Na_2SO_4 to H_2SO_4 [1].
- Goal 1, 8 and 9: The amount of sulfate water which is today transported to Langøya is reduced to a small fraction or even eliminated totally (Goal 1, 8 and 9). One option is to inject the excess sulfur from this process into the neighbor straw fired boiler, reducing corrosion also in this boiler (Goal 1).

Background (max 7 500 characters)

The selection of fuel has a great impact on the total budget of a CHP plant. By choosing less expensive fuels (like different fractions of biomass or waste) the profit of the plant can increase greatly. Cheaper fuels are however usually more corrosive and the profit is decreased by increased maintenance costs, due to corrosion. In order to keep these costs low, the steam parameters are lowered, resulting in not only lower corrosion rates but also a drop in electrical efficiency. Hence, in order to increase the green electricity production from these corrosive fuels, more effective corrosion mitigation techniques are needed. This project aims to demonstrate one such technique, namely the sulfur recirculation technique.

The corrosiveness of specific fuel types have been studied rather extensively and the boiler manufacturers use different boiler designs for different fuel mixes. However, little is known about how the corrosiveness varies over time with variations in the fuel mix. How much of the current corrosion attack is due to the corrosion history (i.e. previous deposit buildup and oxide scale formation) rather than the current flue gas composition (i.e. current fuel mix being used)? This effect can be referred to as a “corrosion memory”. Another aspect of corrosion memory is related to the bulk material. How will long term changes in alloy microstructure and composition influence the high temperature corrosion resistance? The corrosion memory effect can thus be divided into two aspects, i.e. environment and material.

<u>The sulfur recirculation technique</u>

The sulfur recirculation technique has previously been tested and evaluated for short term operation in a waste fired boiler [1]. The purpose of the sulfur recirculation technique is to reduce the corrosion rate of the superheaters in waste to energy plants by recirculating sulphur from the wet flue gas cleaning back to the boiler. The recirculated sulphur will increase the gas concentration of SO_2 in the boiler and decrease the Cl/S ratio of the deposits and ashes, thus producing a less corrosive environment for the superheaters [3]. The innovative, patented sulphur recirculation process, for which GMAB has a world-wide exclusive license, was invented by Hans Hunsinger at Karlsruhe Institute of Technology (KIT). The proposed technology is unique in the way that it, contrary to other methods, only uses the existing sulphur in the fuel and does not increase the amount of residues produced. The Sulfur recirculation technique has previously been tested for shorter time spans (up to 1000 hours) at the Renova Waste-to-Energy facility in Göteborg. Corrosion probe measurements showed that corrosion rates were reduced by 50% or more [1].

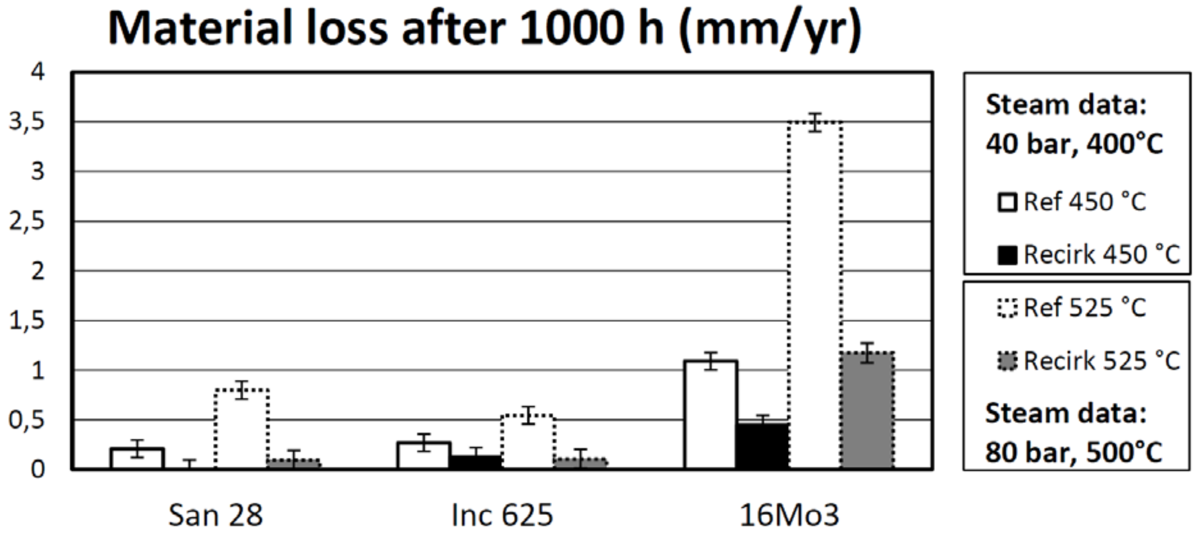

Figure 1: *Corrosion rate in mm/year calculated from 1000 hours exposures for 16Mo3, Sanicro28 and Inconel625 exposed at 450 and 525°C.*

The corrosion probe tests performed at two different material temperatures showed that sulfur recirculation lowered the corrosion rates even when the material temperature was raised from 450 °C to 525°C. In this current project, we aim to demonstrate the first permanent full-scale installation of the corrosion mitigation technique "Sulfur recirculation" and investigate if these positive effects on high temperature corrosion persist over time.

Corrosion memory - environment

The beneficial effect of sulfur addition on high temperature corrosion is well documented, see below. However, in contrast to other corrosion mitigation techniques based on sulphur containing species, the sulfur recirculation avoids the disadvantages of additional residue production. In fact, the residual fractions (e.g. sulphate water from the desulfurization part in the flue gas cleaning step) can be decreased by applying the sulfur recirculation technique. The sulfur recirculation aims to change the environment at the superheaters in order to limit the high-temperature corrosion. This is primarily done by decreasing the presence of alkali chlorides. The issue of alkali chloride induced corrosion has been previously studied and different ways to mitigate its effect have been addressed in recent years. A successful way to minimize the corrosiveness of alkali chlorides is to sulfate them to corresponding alkali sulfates. This can be done by using elemental sulfur, sulfur-rich additives or by co-combustion with a suitable fuel, e.g. sludge and coal [4-10]. The presence of sulfur in the fuel changes the flue gas chemistry; alkali chlorides react with SO_2/SO_3 forming alkali sulfates, and chlorine is released as HCl. There are several papers that investigate the gas phase reactions between alkali chlorides and sulfur containing species [5,8]. In addition to these publications, an investigation of the sulfation of solid alkali chlorides (i.e. deposits) and how they affect the corrosion has recently been published [5].

This project aims to increase the knowledge of the dynamic relationship between flue gas chemistry, deposit build up and corrosion mechanisms, focusing on how these parameters change with time.

Corrosion memory - materials

The term memory effect for the material is related to the microstructural changes of bulk material that occur with exposure time at elevated temperature. Fujikawa et al. [11] investigated high temperature NaCl induced corrosion of austentic stainless steels and found that the depth of internal corrosion increased with C-content due to interaction between the corrosion and Cr-rich carbides. When the steels were first aged at 650°C to further precipitate carbides and then exposed to NaCl, the corrosion response was worsened. In effect this means that materials with good (short-term) performance in as delivered condition will perform worse with time/ temperature as a result of microstructure changes (memory effect). Experiences with biomass (KCl) induced corrosion from Danish plants strongly indicate that similar mechanisms could play a significant role.

Experiences from research and plant exposures including cooled probes, test superheaters and test tubes in existing superheaters [12,13] have led to the choice of 18% Cr steels as the most suitable material for superheaters in biomass fired units. Exposure of steels and nickel based alloys with varying Cr contents indicate that there is a minimum in the chlorine induced corrosion attack around 15-18% Cr. With lower Cr content the alloys exhibit a high material loss while alloys with higher Cr contents are characterized by severe internal corrosion and chromium depletion [14,15]. The measured corrosion rates are presented in Figure 1.

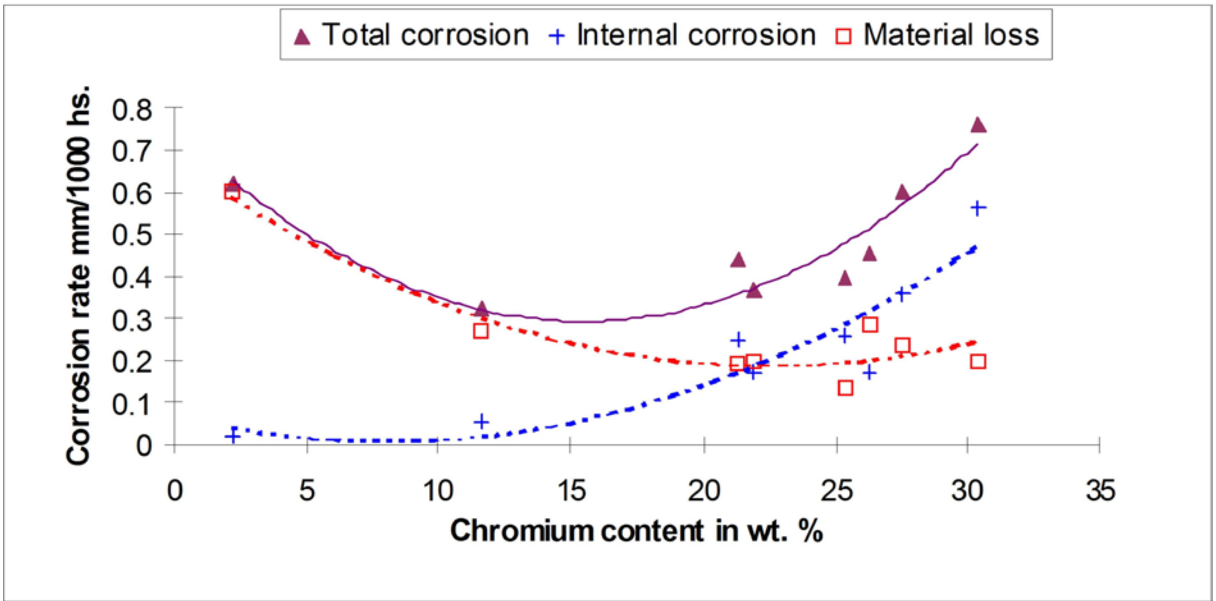

Figure 2: *Effect of chromium content on corrosion rate, data from water-cooled probes in the superheater of a straw-fired CHP plant [14]. Flue gas temperature 700-800°C; metal temperature (average) 510-527°C; metal temperatures from 450-600°C were measured; exposure time was 1392 hours.*

Of particular interest for the present project is the increase in internal corrosion with the increase of Cr content. The mechanism behind this increase is not fully understood. Interestingly, the minimum in corrosion lies at the solubility limit of Cr in the steels (i.e. at higher Cr-contents Cr-rich precipitates will form), which makes it of high interest to study the influence of Cr-rich precipitates on the selective corrosion. It was hypothesized that the increase is coupled to the volatility of chromium chloride and that there might be a relation to the presence of Cr carbides [14]. Unfortunately no characterization of the bulk microstructure was done for the investigated alloys and therefore it is difficult to ascertain whether there were differences in carbide or other precipitate types, which are related to the Cr-content. Thermodynamic equilibrium calculations can help elucidate, whether such effects could be expected. Table 1 shows the Cr-content, the selective/internal corrosion rates and calculated phase fractions. From the data it can be seen that selective corrosion as a general trend follows the Cr-content but there are discrepancies, such as the poor performance of the Fe36Ni38Cr21 alloy. Remarkably the three alloys with the highest observed selective corrosion attack all have the tendency to form the very Cr-rich bcc α-Cr (Calculated composition given in wt% for alloy Fe28Ni40Cr30: Cr 92.0, Mo 0.9, Fe 6.9, Ni 0.2).

	Cr wt%	Cr at%	Selective corrosion rate mm/1000h	FCC	ALFA-Cr	SIGMA	P_PHASE	NBNI3	NI3TI	M23C6	TiC
Fe28Ni40Cr30	30.3	32.5	0.58	0.802	0.188	-	0.004	-	-	0.006	-
Fe37Ni30Cr28	27.5	29.7	0.37	0.675	0.082	0.238	-	-	-	0.004	-
Fe36Ni38Cr21	21.3	22.8	0.26	0.808	0.064	0.098	-	-	0.026	-	0.003
Fe53Ni20Cr26	25.4	26.9	0.26	0.677	-	0.307	-	-	-	0.015	-
Fe3Ni63Cr22	21.9	24.9	0.18	0.695	-	-	0.199	0.080	0.004	0.022	-
Fe53Ni20Cr26	26.3	27.9	0.18	0.616	-	0.352	-	0.013	-	0.020	-
X20CrMoV121	11.6		0.05								
10CrMo910	2.2		0.02								

Table 1: *Results of thermodynamic equilibrium calculations at 550°C for the alloys tested in [14].*

The present project aims to look further into the role of the bulk microstructure on response to the chlorine-induced corrosion seen during biomass firing. It is hypothesized that an approach using a combination of modeling and controlled laboratory exposures can help elucidate the mechanism lying behind the increased selective corrosion seen for high Cr containing alloys.

Goal (max 2 500 characters)

The overall goal of the project is to improve plant economy by enabling an increased green electricity production. This should be achieved through research in a full-scale installation of a novel corrosion mitigation technique called sulfur recirculation. The aim is to show how the corrosion attack of the superheaters is altered when the sulfur recirculation technique is activated. The aim is in addition to generate new knowledge in order to better select materials for the superheaters. By demonstrating the success of these two aspects of corrosion memory this project may lead to improved plant economy by:

- Increased fuel flexibility
- Increased steam data
- Better material selection in order to improved long term corrosion resistance

Furthermore, the project will deploy a unique approach in corrosion testing. In order to investigate the long-term behavior of selected superheater materials, well-controlled pre-treatments will be performed to samples prior to the exposures. Thus, linking environment to the development of the different alloys gives a unique possibility to predict the long time behavior in different types of environment.

This project is directly working towards fulfilling the following KME Goals:
Goal 1: *To examine opportunities and obstacles with regard to how plants in Sweden can achieve greater steam data corresponding to the long-term ambition of electrical efficiency that is 3-4 percentage units higher than the best technology for a given fuel at present.*

This project will examine how the corrosion attack is changed when the sulfur recirculation technique is deployed. This knowledge/data will show if the electrical efficiency could be increased with maintained corrosion rates. It is anticipated that the sulfur technique will lead to a decrease in deposit formation, resulting in a higher heat transfer of the superheater tubes. Higher steam data and higher electrical efficiency from biogenic fuels is the ultimate goal of this project.

Goal 3: *To evaluate exposures and application tests of various solid and composite materials and/or coated materials with the aim to develop improved material solutions which help to bring about greater fuel flexibility and increased electricity production.*
This project will examine how already aged materials perform in an environment that mimic biomass and waste combustion. The aged materials will include materials with different precipitate distributions. The results will assist in an improved material selection of optimum superheater materials for prolonged lifetime and may aid material manufacturers in producing steels with optimized microstructural properties.

Goal 5: *Suggestions for measures and solutions in order to reduce superheater and furnace corrosion, erosion-related problems and low temperature corrosion should have been developed.*
This project will examine how successful the corrosion mitigation technique “Sulfur Recirculation” is on decreasing corrosion of superheaters in a waste fired boiler.

Goal 6: *Suggestions for new design solutions, operating parameters and tools for assessing what technical demands a specific fuel places on the plant should have been developed for CHP plants with the aim to help achieve enhanced fuel flexibility and availability*.
This project will examine how the corrosion mitigation technique “Sulfur Recirculation” is affecting the flue gas chemistry of a waste fired boiler (primarily with respect to HCl and SO_2), and thus, if successful, the fuel flexibility and/or the availability can be increased. Furthermore, by an improved knowledge of how the corrosion attack is affected over time (not only the initial attack) by environmental- and material specific parameters new design solutions, operating parameters and tools can be suggested.

The knowledge obtained within the project may also aid in fulfilling the following KME goals:
Goal 2: *To further develop tools and techniques to facilitate the application of new material solutions in plants.*
The obtained generic knowledge about the long term material behaviour may aid the material manufacturers in producing steels with optimized microstructural properties
Goal 9: *To develop methods for quantifying process ability for new materials, as well as creating an understanding of microstructure development and mechanical properties for more efficient energy plants.*
The obtained generic knowledge about the long term material behaviour may aid the material manufacturers in producing steels with optimized microstructural properties

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 topics and technical issues, namely;

- Investigate the dynamic interplay between changes in the fuel mix and the corrosion attack over time (corrosion memory – environment).

- Investigate the influence of precipitates on the corrosion performance of alloys (corrosion memory – materials).
- Demonstrate corrosion mitigation using the sulfur recirculation technique in full-scale over a period of two years. The final goal is to demonstrate how the decreased corrosion rates can be used to increase steam data.

In order to study these effects, the project will include field exposures with corrosion probes, test materials installed in the superheaters, corrosion measurements made on the full scale superheater as well as laboratory exposures. The project will perform field tests in the waste fired boilers of Måbjergværket, Holstebro, Denmark. The Måbjergværket Waste-to-Energy plant consists of two parallel, almost identical incineration lines, with grate fired furnaces and boilers supplied by B&W Vølund. The capacity is approximately 2 x 10 tons/hour of municipal waste. Both lines are fed with the same fuel from the same fuel bunker, which eliminates one variability factor when comparing different operations of the two lines. The boilers are supplying steam of 80 bar superheated to 412 °C. This steam is superheated to 520 °C in an external superheater, fired with natural gas or biogas. One steam turbine converts the 520 °C steam from these two lines and another straw fired boiler with the same steam data, located at the same site. If this project is successful, both Waste-to-Energy boilers have the potential to be upgraded to produce higher steam temperatures, which will place this plant among the world leaders in terms of Waste-to-Energy electrical efficiency. To complement the field campaigns, laboratory exposures (primarily ageing-treatments) will be performed at DTU as well as HTC at Chalmers (primarily exposures of aged materials in KCl containing environments).

One of these boilers will be equipped with the first permanent installation of the corrosion mitigation technique "Sulfur recirculation", while the second line will continue with normal operation in order to enable a comparison. Thus, the boilers at Måbjergværket are chosen in order to expose the samples towards two different types of corrosive environments; highly corrosive environment in the boiler without the sulfur recirculation technique installed and moderately corrosive environment in the boiler with the sulfur recirculation technique installed. Characterization of material from real plant exposures with emphasis on internal/selective corrosion will in addition be performed.

Corrosion memory - environment

The main scope of this sub-project is to investigate how the corrosion is affected by changing the flue gas environment, by means of e.g. changed fuel mix, if the samples already have been exposed for a long time and formed a corrosion product layer and deposit. Will the corrosion attack accelerate directly if the samples are going from a moderate corrosive environment towards a highly corrosive environment? Or will the formed oxide and deposit scales act as protective layers against the flue gas? In opposite, will the poor corrosion resistance of a material continue after the corrosive environment has been mitigated by means of e.g. additives or can the material heal itself? These issues were already addressed in a previous KME project [2]. In the project referred to, the setup for exposing the probes were based on investigating the initiation of the corrosion due to the short project time. Furthermore, different exposure steps were chosen for mimicking the complete sequence of events leading to corrosion memory in a boiler. Hence, three steps were chosen; first the probes were exposed to a mild environment in order to form a protective oxide and non-corrosive deposit, thereafter the probes were exposed towards an highly corrosion environment and finally back into the mildly corrosive environment. The results from the KME608 project showed that a corrosion memory effect existed. Thus, the non-corrosive deposit and oxide scale formed in the mild environment decreased the corrosion rate, compared to the corresponding samples exposed only to the highly corrosive environment for shorter exposure times.

Within this project we will perform a 2-step exposure matrix. In this way, the effect of alterations in the flue gas composition (e.g. change in fuel mix) could be investigated in a detailed manner. Furthermore, since the main aim is to investigate the propagation of the corrosion attack, the exposure time in each step will be considerably longer (at least 1000 hours) compared to the KME608 project (in which the focus was more on the initiation). After the first step, some samples will be removed from the probes for analysis and evaluation and replaced by new samples. For the second step, the probes will switch boilers and the exposure continues for at least 1000 hours. Thus, the continued exposure would then mimic the situation occurring when a boiler switches from corrosive fuel to mildly corrosive fuel (or vice versa). The specific details about material, material temperature, flue gas temperature, exposure times etc. will be decided by the project group.

The environment aspect will consist of four parts according to the following list:

A) Installation of 2 identical probes (with respect to materials) in two different boilers (step 1)
B) Characterization of part of the samples exposed in step 1
C) Switch of boiler and continued exposure of samples from step 1 (step 2).
D) Characterization of samples exposed in step 2

Corrosion memory - materials

The other aspect of the corrosion memory will be studied through the influence of precipitates on the performance of alloys; the precipitates form with time as a result of the temperature history, hence the term memory. The reference material to be tested is TP347HFG in as delivered and service exposed conditions (presence of σ-phase). The performance of TP347HFG will be compared to that of Tempaloy AA1, which is a possible alternative to TP347HFG. Finally experiments will be made on alloy systems where short-term controlled heat treatments can result in widely different distributions of Cr-rich phases. Experiments will be performed on both high alloyed steel that can be heat treated to contain from 0-20 volume % of σ-phase and a NiCrNb model alloy system that can be heat treated to contain varying amounts of α-Cr. Laboratory testing will be performed at 600°C where the fractions of σ-phase or α-Cr will not change within the duration of the corrosion exposure (up to 168 hrs).

This yields a test matrix involving six materials, TP347HFG in as delivered condition, TP347HFG in aged condition (containing σ-phase), Tempaloy AA1 in as delivered condition, Fe24Cr20Ni and NiCrNb solution treated and precipitation heat treated. Samples will be exposed to KCl induced corrosion in a carefully controlled laboratory environment at 600°C in an atmosphere mimicking that of biomass firing for periods up to one week. The interaction of precipitates with the corrosion attack will be compared with predicted modelling results using Thermo-Calc.

The material aspect will consist of four parts according to the following list:

A) Initial heat treatments:
   DTU have access to all the materials and the facilities to do initial heat treatments of the Fe24Cr20Ni and NiCrNb material.

B) Laboratory exposures:
   HTC has laboratory facilities for testing the materials with and without addition of KCl in an atmosphere mimicking the atmosphere from biomass units. DTU have facilities for a limited amount of testing.

C) Characterization and comparison with modelling results:
   HTC and DTU have access to state of the art characterization facilities as well as thermodynamic and kinetic modelling tools, such as MatCalc, Thermo-Calc, DICTRA and Factsage.

D) Characterization of material from commercial plant exposures with emphasis on internal/selective corrosion (Dong/DTU).

The intention is in addition to link environmental and material aspects of the memory effect. Based on the laboratory study and the characterization of material from real plant aged material may therefore be exposed in the sulphur recirculation part. This is done by using aged material from the lab or samples exposed for a long time in a plant. The corrosion attack on lab samples can thereby compared with corroded samples from a commercial boiler.

The risks against a successful project are very limited, material for testing is already available through the project partners and all the facilities needed for carrying out exposures, characterization and calculations are available directly in-house to the partners.

<u>Demonstrate the sulfur recirculation technique in mitigating corrosion</u>

In addition to investigating the effect of corrosion memory, this project also aims to demonstrate how this first permanent installation of the sulfur recirculation technique affects the long term behaviour with respect to high temperature corrosion. Thus, the project will install test tubes, consisting of several different commercial alloys, in the superheater bundle at the position with the highest material temperature. The specific details about materials, position, exposure times etc. will be decided by the project group.

The test tubes will be removed and investigated after 1 respectively 2 years of operation. These test tubes will be compared to reference test tubes, installed in the waste fired boiler without the sulfur recirculation technique. Today the boilers are equipped with superheater tubes of low alloyed steel 16Mo3.

The test tubes will consist of the following material samples or similar. Both low alloyed and more highly alloyed materials will be selected. The exact material matrix will be decided by the project group.

Each material will be represented by a piece of steel tube, each 50 mm long in order to avoid the influence of welding on material properties in the middle of the test tube. After exposure, cross sections will be investigated in the middle of the test tubes, 25 mm from each weld.

Since these two boilers share the same fuel feeding system, the only difference between the boilers will be the sulfur levels originating from the sulfur recirculation technique.

The samples will primarily be analysed by means of material loss determination. However, additional qualitative analysis, such as e.g. SEM/EDX and XRD, of the deposit and corrosion product layers will be performed. Together with the probe samples exposed for a single step in the corrosion memory tests (see above) a comprehensive, time resolved study of the corrosion behaviour in the two boilers will be performed. Hence, the influence of the sulfur recirculation technique on the corrosive environment can be mapped over time.

Part	**Participants role in the project**
Götaverken Miljö AB	Responsible for installation of the sulfur recirculation technique and coil test. Evaluation of operation and corrosion.
B&W Vølund	Responsible for different types of testing (probes and coils), will perform corrosion evaluation
Dong Energy and Danish Technical University	DTU will develop and produce aged material. DTU will characterize materials exposed in field and lab exposures. Dong Energy is funding DTU.
Dong Energy, Måbjergværket	Plant operation
Chalmers/HTC	Project leader. Responsible for probe exposures and corrosion evaluation (both probe and coil tests)

Staff

The following personnel will be participating in the project:

HTC (Chalmers)	J. Liske T. Jonsson K. Hellström New Ph. D. student, Licentiate (2017)
GMAB	Sven Andersson
BWV	Thomas Norman Lars Mikkelsen Allan Hedegaard Olesen
DE	Ove Jespersen Staff at the Dong Måbjergværket
DTU	Kristian Vinter Dahl John Hald
All project members works part time within the project	

Time schedule

The project will start in February 2015 and end (including final scientific and economic reporting) in April 2018. The project will include both laboratory work as well as field tests.

	2015				**2016**				**2017**				**2018**	
	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2
Official start of project	X													
Superheater thickness measurement in the boiler		X				X				X				
Coil samples installation in superheaters		X												
SH coil samples outtake						X				X				
Wastage measurements coil samples							X				X			
Deposit and corrosion probe testing			X	X	X			X	X	X				
Scientific analysis of field samples			X	X	X	X	X	X	X	X	X	X	X	
Aging of model system materials up	X	X												

to 1000 hrs														
Laboratory exposures at DTU		X	X	X	X	X								
Laboratory exposures at HTC					X	X	X	X	X	X	X			
Characterization of lab exposed samples			X	X	X	X	X	X	X	X	X	X	X	
Final report													X	X

Industrial reference and financing

Götaverken Miljö will sponsor installation of a system for Sulfur Recirculation at Måbjergværket, without making any profit for the installation. A part of the direct costs for engineering, installation and components will eventually be paid for (year by year under 4 years) by Måbjergværket if the anticipated results can be realized and verified for DONG Energy. The remaining direct costs for the installation as well as for the research related activities are financed by Götaverken Miljö AB and will therefore be regarded as industrial financing and amount to at least 1927 kSEK over the project duration. This financing follows the principles of the Swedish Energy Agency described in "Riktlinjer för beräkning av motfinansiering…" from 2008-10-27, by not including any profits or overhead costs for Götaverken Miljö.

B&W Vølund will contribute with 300 kSEK. The above financing is confirmed from Götaverken Miljö and B&W Vølund. Måbjergværket has agreed to the installation, but need a formal final acceptance from their owners Dong Energy at a meeting on 2014-11-24. Dong Energy is, however, also a project partner in this project. DTU will take a more active role in the project on the behalf of Dong Energy.

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.

	Cash contribution	**In-kind contribution**	
Götaverken Miljö AB		1 927 kSEK	
B&W Völund		300 kSEK	
Dong Energy		1 663 kDKK*	
Dong Energy, Måbjergværket		300 kSEK	
Energy companies through Elforsk**	76 kSEK		
Total industrial contribution	**76 kSEK**	**4 548 kSEK**	**= 4 624 kSEK**
STEM financing	**51 kSEK**	**3 032 kSEK**	**= 3 083 kSEK**
Total cash in project: (156+3 083)=3 239 kSEK, Total project volume: 7 707 kSEK			
* Corresponds to 2 021 kSEK at the time of writing this application ** Needs to be confirmed			

List of references

1. Andersson S., Blomqvist E., Bäfver L., Jones F., Davidsson K., Froitzheim J., Karlsson M., Larsson E., Liske J., Sulfur recirculation for Increased electricity production in waste-to-energy plants, Waste Management 34 (2014), pp. 67-78

2. Paz M.D, Jonsson T., Liske J., Karlsson S., Davis C., Jonasson A., Sandberg T., Study of corrosion memory in boiler heat surfaces by field tests with biomass fuel mixes including sulphur and refuse fractions, KME-report: 608, 2014.

3. Hunsinger H., Seifert H., Jay K., Reduction of PCDD/F Formation in MSWI by a Process-integrated SO_2 Cycle, IT3 Conference May 15-19, Savannah, USA (2006)

4. Henderson, P., Andersson, C., Szakalos, P., Pettersson, R., Högberg, J. (2006). "Reducing superheater corrosion in wood-fired boilers." Materials and Corrosion **57**(2): 128-134.

5. Karlsson, S., Pettersson, J., Svensson, J. -E., Johansson, L. -G. (2011). "KCl-Induced High Temperature Corrosion of Austenitic Stainless Steel 304L – The Influence of SO2." Material Science Forum **696**: 224-229.

6. Kassman, H., Pettersson, J., Steenari, B.-M., Åmand, L.-E. (2013). "Two strategies to reduce gaseous KCl and chlorine in deposits during biomass combustion – Injection of ammonium sulphate and co-combustion with peat." Fuel Processing Technology **105**: 170–180.

7. Krause, H. H., D. A. Vaughan, et al. (1975). "Corrosion and Deposits From Combustion of Solid Waste—Part III: Effects of Sulfur on Boiler Tube Metals." Journal for Engineering for Power **97**(3): 448-452.

8. Pettersson, J., Folkeson, N., Svensson, J.-E., Johansson, L.-G. (2011). "The Effects of KCl, K2SO4 and K2CO3 on the High Temperature Corrosion of a 304-type Austenitic Stainless Steel." Oxidation of Metals **76**(1-2): 93-109.

9. Vainio, E., Yrjas, P., Zevenhoven, M., Brink, A., Laurén, T., Hupa, M., Kajolinna, T., Vesala, H. (2013). "The fate of chlorine, sulfur, and potassium during co-combustion of bark, sludge, and solid recovered fuel in an industrial scale BFB boiler." Fuel Processing Technology **105**: 59-68.

10. Viklund, P., Pettersson, R., Hjörnhede, A. (2009). "Effect of sulphur containing additive on initial corrosion of superheater tubes in waste fired boiler." Corrosion Engineering, Science and Technology **44**(3): 234-240.

11. Fujikawa, H. and Maruyama, N., Corrosion behaviour of austenitic stainless steels in the high chloride-containing environment: Mater. Sci. Eng. A, 1989, vol. 20, pp. 301–306.

12. Larsen, O. H. and Montgomery, M., Materials Problems and Solutions in Biomass Fired Plant, Energy Materials: Materials Science and Engineering for Energy Systems, 2006. **1**(4): pp. 227-237.

13. Montgomery, M., Jensen, S.A.J, Borg, U., O. Biede, and Vilhelmsen, T., Experiences with high temperature corrosion at straw-firing power plants in Denmark: Materials and Corrosion, 2011. **62**(7): pp. 593-605.

14. Montgomery, M. and Karlsson, A., In-situ corrosion investigation at MasnedøCHP plant – a straw fired power plant: Materials and Corrosion 1999. **50**: pp. 579-584.

15. Montgomery, M., Karlsson, A. and Larsen, O. H., Field test corrosion experiments in Denmark with Biomass fuels. Part 1: Straw-firing: Materials and Corrosion 2002. **53**: pp. 121-131.

Updated time plan 40118-1/KME714

Sulfur recirculation and improved material selection for high temperature corrosion abatement – Investigating different aspects of corrosion memory

Svavelrecirkulation och bättre materialval för minimering av högtemperaturkorrosion – Undersökning av olika aspekter av korrosionsminne

Background

At the time of the project proposal, Dong Energy was the owner of the Måbjergværket plant, where the Sulfur Recirculation technology will be demonstrated in full scale. The time schedule has been delayed due to the fact that Dong Energy has sold the plant during 2015, and an ongoing project was unwanted during the process of changing owner. The new owners, MEC Bio Heat & Power, are very positive to the project and a contract for the installation was signed in late 2015. The KME714 project group has continuously informed the KME board about the status: see previous board information documents.

Project plan changes – influence on the project

The time schedule, which initially stretched over several years, has been somewhat compressed without sacrificing research quality, budget or scope. Some activities have been shifted in time, see original and new time plan below. The goals and projected results have not been changed with the new time schedule and the same number of analyses will be made, albeit at slightly different points in time.

Original time plan

	2015				**2016**				**2017**				**2018**	
	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2
Official start of project	X													
Superheater thickness measurement in the boiler		X				X				X				
Coil samples installation in superheaters		X												
SH coil samples outtake						X				X				
Wastage measurements coil samples							X				X			
Deposit and corrosion probe testing			X	X	X			X	X	X				
Scientific analysis of field samples			X	X	X	X	X	X	X	X	X	X	X	
Aging of model system materials up to 1000 hrs	X	X												
Laboratory exposures at DTU		X	X	X	X	X								
Laboratory exposures at HTC					X	X	X	X	X	X	X			
Characterization of lab exposed samples			X	X	X	X	X	X	X	X	X	X	X	
Final report													X	X

Updated time plan

	2015				2016				2017				2018	
	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2	Q 3	Q 4	Q 1	Q 2
Official start of project	X													
Superheater thickness measurement in the boiler		*X*		*X*		*X*		*X*		*X*		*X*		
Coil samples installation in superheaters							*X*							
SH coil samples outtake										*X*		*X*		
Wastage measurements coil samples											*X*		*X*	
Deposit and corrosion probe testing							*X*	*X*	*X*	*X*	*X*	*X*		
Scientific analysis of field samples							*X*	*X*	*X*	*X*	*X*	*X*	*X*	
Aging of model system materials up to 1000 hrs	X	X												
Laboratory exposures at DTU		X	X	X	X	X								
Laboratory exposures at HTC					X	X	X	X	X	X	X			
Characterization of lab exposed samples			X	X	X	X	X	X	X	X	X	X	X	
Final report													X	X

Changes from the original time plan:
- Superheater thickness measurement in the boiler (increased number of measurements): Due to better access to the boiler we will be able to perform twice as many superheater thickness measurements in the boiler than planed for in the application.
- Coil samples installation in superheaters and SH coil samples outtake (shorter exposure time): The coil samples will be installed later than originally planned. We will still manage to have two outtakes as original planned. Deposit and corrosion probe testing will also complement the installations as planned. The shorter exposure time will only affect the SH coil samples (not the probe samples) and will not influence the ability to fulfil the goals of the project.
- Deposit and corrosion probe testing (only shifted in time): The deposit and corrosion probe testing will complement the installations as planned and will only be shifted in time.

Status, Sulfur Recirculation installation

- Component offers from sub-suppliers are currently being collected including instruments, H_2SO_4 pump and H_2O_2 storage tank. The SO_2 raw gas analyzer is currently being ordered. H_2O_2 and sulfuric acid piping is being engineered and planned.
- Project meeting 1 was held at Måbjergværket on 2016-02-03
- Project meeting 2 including risk analysis (HAZOP) will be held on 2016-04-05.
- A short planned maintenance stop (“pit stop”) will be held in May. All instruments in contact with the scrubbing liquid will have to be chemically resistance towards the new media, when Na_2SO_4 solution is exchanged for H_2SO_4 solution. Many instruments will be replaced, while some are already resistant. A few valves and pipes will also be exchanged. The SO_2 raw gas analyzer will be installed. NaOH dosage is moved from the SO_2-scrubber stage to the following stage. Flanges for corrosion probe testing will be mounted on manhole hatches of the boilers. The H_2SO_4 nozzle injection points will be installed.
- After the stop, the rest of the system components, not required for normal operation, will be installed in order to make startup of Sulfur Recirculation possible.

- Startup of Sulfur Recirculation will preliminarily take place during week 35 in order to test the system and build up a sulfuric acid buffer in the scrubber system before the maintenance stop in September-October.
- Maintenance stop in September-October: Material samples will be installed in the super heaters of both line 1 (Sulfur Recirculation) and line 2 (Normal operation) in order to enable comparison of the corrosion rates of several commercial steel grades during real operation with and without Sulfur Recirculation, but basically the same fuel. These samples will be extracted after ½ and 1 year of operation respectively.
- During the autumn and winter 2016, corrosion probe experiments with and without Sulfur Recirculation will be made. Corrosion probes will be used to expose material samples in the most corrosive environment of the boiler, i.e. the position upstream of the first superheater. Line 1 and 2 are situated just next to each other, which enables corrosion probes to be moved between the incineration lines very rapidly, virtually without cooling, which presents unique possibilities to expose samples first to a corrosive environment, and then a to protective, sulfur rich environment. Also the opposite order can be tested and compared with samples only exposed to one or the other environment. This will give new possibilities to isolate the effect of corrosion memory and corrosion protection memory.
- Short “pit stop” in May 2017, with super heater material sample extraction.
- Longer maintenance stop in September-October 2017, with super heater material sample extraction.

Original budget

	KKR	Lön	Konsult	Utrustning	Material	Laboratorie	Dator	Resor	Övrigt	Indirekta	**Summa**
Götaverken Miljö AB	2014										0
	2015	873		200				70			1 143
	2016	92						50			142
	2017	177						20			197
	2018	145									145
	Summa	1 287	0	200	0	0	0	140	0	0	1 627
B&W Vølund	2014										0
	2015	130			130			15			275
	2016	35						5			40
	2017	35						5			40
	2018	30						5			35
	Summa	230	0	0	130	0	0	30	0	0	390
Dong Energy/Technical University of Denmark	2014										0
	2015	539				38		5		163	745
	2016	557				38		5		167	767
	2017	539				38		5		170	752
	2018	123				9		5		60	197
	Summa	1 758	0	0	0	123	0	20	0	560	2 461
HTC vid Chalmers	2014										0
	2015	720			20	260		40		445	1 485
	2016	270			20	175		40		169	674
	2017	290			20	170		40		181	701
	2018	110				70		5		66	251
	Summa	1 390	0	0	60	675	0	125	0	862	3 112

Updated budget

	KKR	Lön	Konsult	Utrustning	Material	Laboratorie	Dator	Resor	Övrigt	Indirekta	***Summa***
Götaverken Miljö AB	2014										0
	2015	143						2			146
	2016	730		200				68			997
	2017	269						70			339
	2018	145									145
	Summa	1 287	0	200	0	0	0	140	0	0	1 627
B&W Vølund	2014										0
	2015										0
	2016	160			130			20			310
	2017	40						5			45
	2018	30						5			35
	Summa	230	0	0	130	0	0	30	0	0	390
Dong Energy/Technical University of Denmark	2014										0
	2015	471				38		5		141	655
	2016	488				38		5		146	677
	2017	470				38		5		141	653
	2018	123				9		5		39	176
	Summa	1 551	0	0	0	123	0	20	0	467	2 161
MEC Bio Heat & Power	2014										0
	2015										0
	2016	180									180
	2017	100									100
	2018	20									20
	Summa	300	0	0	0	0	0	0	0	0	300
HTC vid Chalmers	2014										0
	2015	150				75		20		93	338
	2016	720			30	215		40		447	1 452
	2017	395			30	275		40		245	985
	2018	125				110		25		77	337
	Summa	1 390	0	0	60	675	0	125	0	862	3 112