



# BELENUS

## Lowering Costs by Improving Efficiencies in Biomass Fueled Boilers: New Materials and Coatings to Reduce Corrosion

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## BELENUS

Dissemination level		
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## Executive Summary

One of the technologies aimed at producing an energy source that is carbon neutral; cost effective with security of supply is biomass combustion to generate either or both heat and power. One of the main issues of biomass from an operational view is the corrosive nature of the combustion products and the variable nature of these products depending on the biomass source.

To counteract the corrosive threat to the integrity of the plant corrosion resistant coating can be applied to the surface areas of the plant that are at most risk. Coating have been used in biomass and waste to energy plant for over 20 years with reasonable success but in order to achieve a commercial life of the plant the operating conditions are maintained significantly lower than those for pulverised coal plant. The aim of the BELENUS project is to investigate the effectiveness of a number of coatings to protect the substrate materials against the corrosive biomass combustion products at higher operating temperatures than previous experienced, i.e. up to 650°C where current plant operate at or below 540°C.

A survey has been conducted, as reported in the below sections, of existing biomass operating plant and experimental studies in order to identify candidate alloy/coating systems with the potential to meet the 650°C target and still provide an economic plant life expectancy. This survey included various biomass types and various potential solutions to mitigating biomass related corrosion, e.g. fuel additives, sootblowers and shielding as well as the use of high grade alloy substrates and corrosion resistant coatings.

A significant body of knowledge and experience has been accumulated over the last 20 years but there are two areas where there is a gap in the knowledge that are going to be addressed during the BELENUS project: how the alloys and coating systems cope with elevated temperatures from both a combustion product consideration and the mechanical integrity consideration.

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## 1. Introduction

One of the main factors driving energy policy is climate change, and in this respect, the utilisation of coal as a fuel for power generation is becoming increasingly controversial. The concern about increasing greenhouse gas (GHG) emissions has given rise to several directives such as the Large Combustion Plant Directive (European Commission, 2016) and the Kyoto Protocol (United Nations Climate Change, 2019). This has led to national initiatives to reduce the use of coal, for example, the closure of many coal-fired plants in the United Kingdom (Toporov, 2014); the decline of coal utilisation in the United States (Mooney and Dennis, 2019), and mounting pressure on companies to divest from coal in France (Baxter et al., 2018).

Reports from the 2018 World Energy Outlook predicts a 3.7% compound annual decline in the global thermal coal trade (Roker, 2018a). The International Energy Agency (IEA), in its 'sustainable development scenario' cited by Roker (2018a), forecasts an 80% decrease in coal consumption in the global power sector, down to 732 million tonnes in 2040 (Roker, 2018a). In some emerging economies priority has been given to expansion of new coal builds to match the growing energy demands (e.g. China, Brazil, India, Indonesia, Mexico, South Africa) (Power Technology, 2017; International Energy Agency, 2018a). As examples of the high usage of coal are India's 60% of electricity produced from coal, and South Africa's 82% of electricity generated from coal (IEA, 2018b).

There are different approaches to reduce carbon dioxide emissions, such as co-firing coal with biomass or a complete switch to renewables and other sustainable fuels (Simms, 2011b). Biomass combustion is gradually gaining popularity as an alternative to coal-firing, where the range of biomass fuel species employed as fuel for power generation includes wood pellets, olive cake and pellets, palm kernel expellers, citrus pulp expellers, sunflower husk, sawdust, energy crops (e.g. willow, poplar, miscanthus, straws and grasses) and sewage sludge (Vassilev et al., 2010; The Biomass Energy Centre, 2011).

Biomass is regarded as inherently low carbon given that plants absorb an amount of carbon equivalent to that released to the atmosphere when biomass fuels are burnt (The National Council for Air and Stream Improvement, 2015). Fireside corrosion of superheater and reheater components becomes more challenging in boilers burning pure biomass than for coal-fired boilers, as the flue gas contains corrosive gases, high concentrations of low melting alkali metals and chlorides that severely damage and reduce the life of boiler tube materials. Hence steam conditions in biomass-fired plants are generally lower than those of coal-fired plants, typically  $\leq 540^{\circ}\text{C}$  vs  $620^{\circ}\text{C}$ , if the boiler must continue its operation over an extended period (Simms, 2011a).

Operating plant at higher steam temperatures than currently used will both increase the plant efficiency, i.e. more cost effective, and increase corrosion rates. In order to mitigate the effects of Biomass derived corrosion species the Belenus project aims to expose a number of superheater and reheater materials with protective coatings in some representative biomass environments up to temperatures of  $650^{\circ}\text{C}$ . Representative samples from Agricultural Waste, Industrial Waste and Wood Residues will be analysed for their combustion gases and residues to allow coated samples to be laboratory pilot scale tested in simulated biomass environments. The most promising coatings will be down selected for exposure in commercial plant as part of work package 7 of this project. This report provides some details of the performance of typical coatings used in boilers today and laboratory performance of potential coating that could be used at these higher temperatures.

## 2. Results and Discussion

### 2.1. Overview of corrosion in biomass environments

Biomass is regarded as inherently low carbon given that plants absorb an amount of carbon equivalent to that released to the atmosphere when biomass fuels are burnt (The National Council for Air and Stream Improvement, 2015). Biomass, however, is less energy dense than coal and would require a significant land mass to grow the amount needed to replace coal completely. As an example, the Department of Energy's (DOE) 2016 billion-ton model (BT16) (Langholtz et al., 2016) states that for the commercialisation of biomass to energy crops, the maximum eligible pastureland required is about 47 million acres (or 11% of pastureland). More specifically, a report from Partnership for Policy Integrity (2016), citing the aforementioned DOE's billion-ton model, states that forest harvesting will require clear-cutting up to 4.7 million acres per year to produce a 100 million dry tons of (forest) biomass for the production of wood pellets.

Biomass is a multifarious term covering a range of solid organic products, and to a lesser extent, inorganic matter, generated from natural and anthropogenic processes (Vassilev et al., 2015). One way of classifying is by grouping into six groups based on the structure of the organic and inorganic constituent (Vassilev et al., 2010; The Biomass Energy Centre, 2011; Hustad and Barrio, 2015):

- Agricultural residues (from crops, food processing and animals).
- Biomass mixtures.
- Dedicated energy crops (high yield crops are grown specifically for energy applications).
- Industrial waste and co-products.
- Municipal waste/food waste.
- Wood residues (from forest residues, wood processing, arboriculture activities, and the paper and furniture industry).

All solid biomass is made up of three main components: cellulose, hemicellulose and lignin. The organic part of biomass (mainly C, H, N and O) is present in the molecular structure of the cellulose, hemicellulose, and lignin component of biomass matter. The inorganic matter (0.1 – 46 wt.% on a dry basis) is made up of various minor species from different mineral groups and classes such as phosphates, carbonates, silicates, chlorides, sulphates, oxyhydroxides, nitrates; as well as some amorphous inorganic phases (Vassilev et al., 2010, 2013).

Although the literature on the chemical composition of different biomass varieties reveals similar contents of C, H and O (dry ash fuel basis), there are significant differences in the contents of N, ash-forming elements, and moisture. For instance, the wood-derived fuels show lower values of ash, Cl, K, N, S and Si, and higher concentrations of C and Ca. Straws and grasses, on the other hand, have a relatively high level of Cl, K, N, S, Na, S and Si (Vassilev et al., 2010). Si and Cl content is high in herbaceous biomass relative to other classes of biomass fuels (Jenkins et al., 1998). The agricultural derived and contaminated biomass group shows the most significant difference in levels of ash, moisture, C, Cl, H, Na, N, S and occasionally Al, Fe, P and Ti. These distinctions are a result of their original geographic location and handling process (pesticides, harvesting and storage) (Vassilev et al., 2010).

The alkali and alkaline earth metals in biomass fuels are very volatile and thus easily released at combustion temperatures (Hurley et al., 1993; Jenkins et al., 1998). Also, Cl facilitates the mobility of many compounds, especially K which is present in the form of water-soluble inorganic salts which can easily volatilise during combustion; thus the tendency for fouling of boiler tubing may increase in biomass combustion (E.ON UK, 2004;

Shao et al., 2012). The implication is that, during combustion, these species are released into the flue gas and interact with the boiler components and almost always result in erosion, deposition or/and corrosion of superheater/reheaters (Wright et al., 1997), thus creating significant maintenance issues in industrial steam raising boilers.

Fireside corrosion of evaporator, superheater and reheater components is more challenging in boilers burning pure biomass than for coal-fired boilers, as the flue gas contains corrosive gases, high concentrations of low melting alkali metals and chlorides that severely damage and reduce the life of boiler tube materials. Hence steam conditions in biomass-fired plants are generally lower than those of coal-fired plants if the boiler must continue its operation over an extended period (Simms, 2011a).

Sulphur plays a crucial role in the fireside corrosion mechanism. During combustion, pyrite ( $\text{FeS}_2$ ) burns to form  $\text{SO}_2$  and  $\text{FeO}$  which can be further oxidised to  $\text{SO}_3$  in the flue gas as it cools. Laboratory experiments have revealed that higher  $\text{SO}_3$  partial pressures can be generated by catalytic oxidation of  $\text{SO}_2$  beneath the tube deposits hence ensuring the stability of complex sulphates up to 700 °C (Wright and Shingledecker, 2015). Fireside corrosion studies reveal that the rate of dissolution of the protective scale increases when the local partial pressures of  $\text{SO}_3$  in flue gas increases from 1000 ppm to 5000 ppm (Wright et al., 1997). However, if the metal temperature is raised above the decomposition temperature for iron sulphate, the molten sulphate layer ceases to exist, and the corrosion rate drops (Weele, 1991), as shown schematically below.

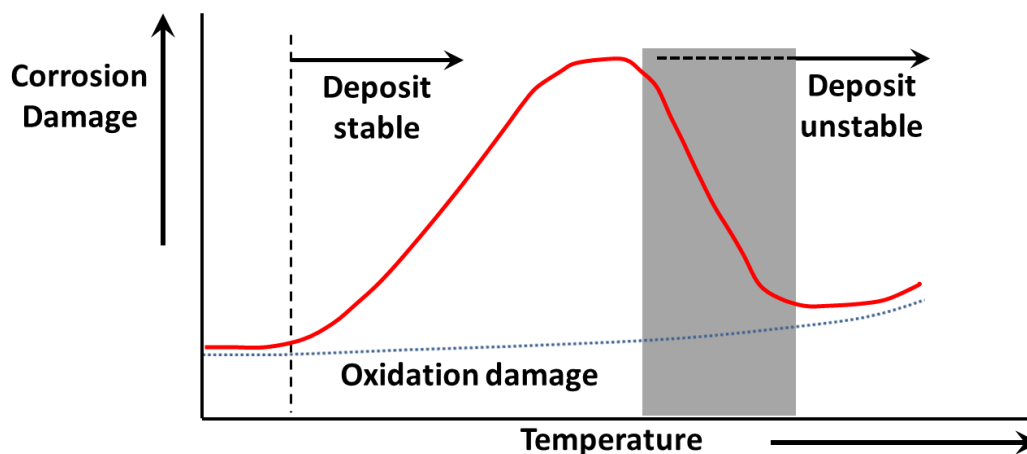
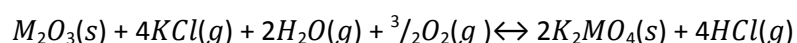


Figure 1. Effect of metal temperature on the fireside corrosion rate.

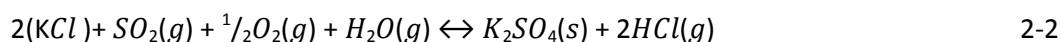
Although it is generally accepted that high Cl fuels may speed up the fireside corrosion process, it has been difficult to predict the degree to which the Cl content contributes to fireside corrosion. In biomass combustion, different mechanisms are observed particularly when burning low S biomass fuels (Cl attack), as the fireside corrosion is mainly attributed to alkali chloride deposits (Shao et al., 2012; Okoro et al., 2017). Deposition of the alkali chloride occurs via condensation mechanism, which is driven by the temperature difference between the gas and the boiler tubes (superheaters/reheaters) (Uniper Technologies, 2016). The KCl in the deposit can react with the oxide of the alloy elements transforming it to a fast growing oxide (equation 2-1) (Okoro et al., 2017; Petterson et al 2005; Petterson et al 2011)) or with the gaseous species in the gas stream (equation 2-2) (Okoro et al., 2017).



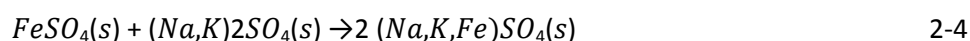
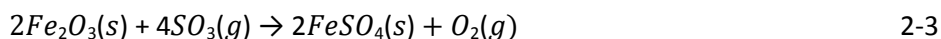
2-1

where M = oxide of the alloying element





Biomass contains more water-soluble K but lower amounts of S and Na when compared to coal. If the furnace temperature is high enough, K can be released into the combustion gas (Hurley et al., 1993). If the alkali content is high, this could lead to the deposition of alkali sulphate ((Na/K)2SO<sub>4</sub>) which could form a low-melting point compound with another species, e.g. Fe<sub>2</sub>O<sub>3</sub>, on the oxide scale on the tube surface or from the ash which melts at 560°C (Weele, 1991) (equations 2-3 and 2-4).



As heat is being transferred from the gas to the working fluid in the heat exchangers, the flue gases are cooled and, subsequently, alkali metal sulphates (Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>) form in the furnace and condense on the tube surface (Simms et al., 2007; Lant et al., 2010; Wright and Shingledecker, 2015). The alkali compounds can be deposited via direct condensation on the tube surface, or impaction of fly ash particles carrying the condensed alkali, or by thermophoresis of smaller particles (Wright and Krause, 1997). These deposits will eventually grow to the extent that they insulate the tube surface from the gas stream thereby impeding heat transfer to the tubes (Hurley et al., 1993). Above 580°C, and in the presence of SO<sub>3</sub>, the mixed deposits become molten at the tube surface, react with another constituent of the deposit and form a layer of highly corrosive alkali iron trisulphate mixture (2Na<sub>3</sub>Fe(SO<sub>4</sub>)<sub>3</sub>) beneath the ash deposit. The molten alkali iron sulphate dissolves the protective oxide scale thereby causing accelerated oxidation and sulphidation (Wright and Krause, 1997).

Fireside corrosion in biomass boilers has been the subject of much research activity in recent decades. A brief summary can be seen below of several predominantly European projects which have conducted work in this area.

## 2.2. ASPECT Project

A United Kingdom, Technology Strategy Board (TSB) co-funded, multi partner collaborative project entitled “Advanced Surface Protection Enabling Carbon abatement Technologies” (ASPECT), was conducted by academic and industrial partners including Doosan Babcock Limited (DBL) and E.ON Engineering Limited, now renamed Uniper Technologies Limited (UNIPER). Whilst much of the work was directed towards coal firing, oxy-fuel firing or biomass co-firing, a portion of the work undertaken included the installation of protective corrosion resistant coatings in the Steven’s Croft 44MW<sub>e</sub> Bubbling Fluidised Bed (BFB) boiler that is fired with a mixture of forestry waste and relatively clean recycled wood fibre. This boiler operates with final steam conditions of 165bar and 540°C. The coatings were installed in the boiler on trial tubes exposed as part of the boiler steam circuit and accumulated 16,000 hours exposure by the time of their removal during the March 2013 outage. The analysis of the corrosion rates suffered by the coatings and the associated unprotected base metal tubing, together with the characterisation of the ash deposits, provided valuable information on the wastage rates suffered in different parts of the superheater circuit.

The exposures in the low alloy primary superheaters highlighted the likely corrosion problems that could occur in wood fired boilers under adverse conditions. In particular, the deposition of chloride containing ash has been identified, either associated with alkali or heavy metals. The aggressive chloride deposits resulted in the formation of poorly protective, defective corrosion scales that were mechanically weak and easily removed at locations suffering enhanced gas velocities. Such attack is referred to as corrosion-erosion damage and can result in severe localised gouging of the boiler tubing, particularly in hard to access areas within close pitched tubing /

elements. This can be further exacerbated by partial blockages of the gas pass causing laning, something which should be controlled with good sootblower usage.

In contrast the unprotected HR3C austenitic stainless steel superheaters performed well with only very minor fireside corrosion damage. The applied coatings similarly performed well with only very minor wastage rates.

### 2.3. ASPIRE Project

A United Kingdom, Technology Strategy Board (TSB) co-funded, multi partner collaborative project 101167, entitled “Advanced Surface Protection Improved Renewable Energy” (ASPIRE), was conducted by academic and industrial partners including Doosan Babcock Limited (DBL), E.ON Engineering Limited, now renamed Uniper Technologies Limited (UNIPER) and RWE npower. The project was primarily aimed at biomass fired boilers with testing of coatings and substrates undertaken at laboratory, pilot and plant scale. In addition to isothermal laboratory scale tests, corrosion probe exposures were conducted in pilot scale combustors and pulverised fuel fired power plant boilers at Tilbury and Ironbridge. These boilers were originally coal fired and had been converted to fire clean, I2 grade industrial wood fuel pellets. The coatings and unprotected tube alloys on probes and trial tubes exposed in the boilers converted to clean wood pellet firing were found to suffer only minimal wastage rates even with final steam operating conditions of 165bar and 568°C .

The pilot scale exposures were conducted in a 1MW<sub>th</sub> pulverised fuel fired combustor and were conducted whilst firing either eucalyptus wood pellets, or a blend of clean wood pellets and hemp straw. Furnace wall corrosion rates for the unprotected low alloys steels were found to be in general relatively low, with benign conditions occurring under both oxidising and reducing environments. The applied coatings for the most part were also found to suffer negligible or only minor corrosion damage, although exceptions were found with chromium occasionally being leached from some HVOF coatings. The specimens exposed to superheater type conditions with metal temperatures of up to ~680°C were found to suffer significant damage, both to the unprotected ferritic and austenitic substrates and the protective coatings, with this occurring under the influence of chloride containing ash deposits. It was found that there was no clear pattern to the corrosion performance of the various coatings exposed.

DBL undertook bending and forming trials of a number of substrate tube and coating combinations. This highlighted several of the trial coatings to be brittle and unable to be successfully formed using normal industrial tube bending practise. For welded / laser clad coatings failures of the substrate tube also occurred, these originating within the cladding Heat Affected Zone (HAZ). This was found to be more problematic in materials such as T24 and T91 that typically require post weld heat treatment to reduce the material hardness after welding.

### 2.4. LÜbkorr project

Isothermal laboratory tests of base material corrosion under ashes and fluegas with Lignite, hardcoal and biomass co-firing conditions. A multi partner collaborative project was conducted receiving co-funding from the German Federal Ministry for Economic Affairs and Energy (BMWi) from 2014 -2018 under funding number 03ET7012D. Research was carried out by DECHEMA, Frankfurt and Salzgitter Mannesmann Forschungszentrum (SZMF), Duisburg. Partners included Babcock Borsig Steinmüller, Alstom Power Systems (now GE), E.ON Anlagenservice (now UNIPER), Sandvik, ThyssenKrupp VDM, Salzgitter Mannesmann Stainless Tubes, Vallourec & Mannesmann, Benteler, Uhlig, Vattenfall Europe Generation and RWE Power.

The project aimed at coal and co-firing boilers with isothermal testing of different martensitic, austenitic and nickel-base materials. Materials were tested under operational and artificial ashes from lignite and hard-coal fired boilers with artificial flue gas mixtures with typical compositions of these boilers in laboratory furnaces. Further tests were conducted under artificial ashes and flue gases with a chlorine content to simulate a biomass co-firing condition. Tests were conducted with respect to the tested material grades at 600, 650, 700 and 750°C for up to 10,000 h. Results described material loss and corrosion mechanisms for the different materials in tested temperature ranges and atmospheres.

## 2.5. Corretec Korrosionssonde Project

A multi partner collaborative project was conducted receiving co-funding from the German Federal Ministry for Economic Affairs and Energy (BMWi) from 2013 -2016 under funding number 03ET7023. Research was carried out by Technical University Darmstadt, Institut für Energiesysteme und Energietechnik, Darmstadt. Partners included Alstom (now GE), EON (now UNIPER), Hitachi Power Europe (now Mitsubishi Hitachi Power Service Europe), Steag, Salzgitter Mannesmann Forschungszentrum, Vattenfall (now LEAG), Vallourec & Mannesmann, Laborelec, Babcock Borsig Steinmüller and RWE Power.

The project aimed at coal and co-firing boilers with the development and trial of an online corrosion sensor for membrane walls including the development of models of corrosive agents in flue gases and scales.

Sensors were developed with typical membrane wall materials. Trials were conducted in laboratory furnaces and laboratory combustion chambers under coal and co-firing conditions. Sensors were installed for trials runs in hard-coal and lignite fired boilers.

## 2.6. Gramat

The GRAMAT project, July 2013 to June 2017 conducted research on innovative corrosion resistant gradient tubes for biomass power generation installations, with circa €2.34M subsidy support from the European Union Research Program for Coal and Steel (RFCS), the European Research Fund for Coal and Steel, under Subsidy Contract No. RFSR-CT-2013-00005.

The main objective of the project was to acquire the knowledge necessary for the development of a new low-cost technology of production of semi-finished pipes with through thickness gradient chemical composition. This ensures the creep strength (low-alloyed material - tube core) and corrosion resistance (high-alloyed material - tube jacket). The gradient tubes were rolled on the existing production lines from the semi-finished product produced by the unique casting technology. The selected material combination for tube production was 347H as a jacket and 11CrMo9-10 as a tube core. After preliminary testing of gradient material at lab scale, tube samples were installed in a recirculation loop at Äänevoima BFB boiler (157 MW<sub>th</sub>) The overall performance of the gradient tube was satisfactory, though some refining of manufacturing process would be needed, mainly due to slag inclusions affecting detachment of the austenitic layer observed at the austenite-ferrite interface, and surface defects of the most outer layer enabling corrosion pitting.

## 2.7. HTC 2014 - 2017 & HTC 2018-2021 corrosion phenomena in boilers fired with biomass and waste

HTC is a Swedish centre of competence for high temperature corrosion research and is hosted by Chalmers University of Technology. In addition, the Royal Institute of Technology (KTH) and two institutes (Swerea KIMAB and Swerea IVF) take part.

High temperature corrosion is a key issue in energy production, engines and many industrial processes. It limits the useful life of installations and obstructs the development of more economical and environmentally sustainable processes and systems. HTC's research programme "High temperature corrosion – research for a sustainable society" is jointly funded by the Swedish Energy Agency, Chalmers and 16 member companies. HTC research is carried out in close cooperation with the member companies. HTC helps solve critical high-temperature corrosion issues, and provides tools to address new corrosion problems in the development of a sustainable energy system.

The programme is focused on the following areas:

- Renewable fuels – increasing the efficiency of power production and gasification
- Corrosion resistant materials for the energy system of the future
- Energy conversion

The project goal is to generate new knowledge that helps solve critical corrosion issues in biomass- and waste-fired boilers and to provide guidance for mitigating corrosion, for example avoiding corrosion problems when burning potentially corrosive fuels in plants. Such measures include changing the flue gas chemistry, optimizing materials selection (including new, more corrosion resistant materials and coatings) and improving boiler operation routines. The key factor for finding ways to mitigate corrosion in the complex boiler environment is a detailed knowledge of the corrosion processes. To achieve such knowledge, the fundamental laboratory work addressing the detailed mechanisms of corrosion, carried out within this project, with in-plant corrosion investigations. Research is directed towards the corrosion of superheaters and waterwalls and includes a wide variety of materials including commercial steels, model alloys and coatings.

## 2.8. KME Project

The Swedish Energy Agency in association with industrial partners has sponsored the Consortium Materials Technology (KME) for demonstration and development of thermal energy processes. The consortium comprises industrial and academic partners conducting research projects with the ultimate aim to demonstrate more effective electricity production from biomass fuels. This was to be achieved through the construction of demonstration power plant by ~2017 having 3 – 4% improved thermal efficiency compared to current state of the art biomass fired power plant as operating at the start of the process. Two fluidised bed burner, wood fired projects were being pursued, one firing recycled wood fibre and a second "large virgin wood" project with potential supercritical steam conditions and final steam temperatures of 600°C. These steam conditions are quite ambitious compared to current clean wood new build conditions of 150bar 540°C, and significantly above that of the design conditions for many existing coal fired boilers undergoing conversion to wood firing.

KME is dedicated to funding Swedish materials research connected to thermal energy processes and is sponsored by the Swedish Energy Agency. Titles of projects carried out within program the 2014-2017 period are:

- High temperature corrosion in waste-wood fired boilers;
- Increased steam temperature in grate fired boilers – Steamboost
- Combating superheater corrosion by new materials and testing procedures
- Corrosion exposures in the waste fired CFB boiler P15 at Händelö
- Sulfur recirculation and improved material selection for high temperature corrosion abatement – Investigating different aspects of corrosion memory
- Composite Metal Polymer (CMP) for non-stick improvements in CHP plants;
- Intermediate temperature corrosion in used-wood fired boilers – the influence of lead, zinc and their chlorides

- High temperature corrosion in waste-wood fired boilers. Part 2
- The effect of increased fractions of waste wood on water wall- and superheater corrosion - Combating corrosion by new materials and improved material selection.

## 2.9. US Project: Improving Heat Recovery in Biomass-Fired Boilers

The aim of this project was to identify the mechanisms responsible for rapid degradation of superheater tubes operated above the melting point of the inorganic deposits. Once these mechanisms are understood, the aim was to identify alloys and/or coatings that gave improved resistance to superheater tube degradation and/or work with manufacturers to find improved superheater designs to minimize degradation. Biomass boilers and their superheater components in particular, are less efficient than those fired by fossil fuels due to the concern that biomass fuel contaminants such as potassium, chlorine, sulphur, and sodium can deposit on superheater tubes that have been exposed to combustion exhaust gases. Some of these deposits will have low melting points and can, in their molten state, lead to accelerated corrosion of superheater tubes. To avoid this problematic corrosion, the standard industry practice has been to reduce the temperature in the superheater. However, reducing the superheater temperature also reduces the potential efficiency of the boiler. Through this project corrosion mitigation strategies and related methods to improve the efficiency of biomass-fuelled boilers was investigated. The development of more-efficient biomass-fired boilers with improved efficiency was estimated to potentially result in the following annual benefits to the US:

- Displacement of 227 trillion BTUs of primary energy
- Displacement of 4.4 million tons of CO<sub>2</sub> emissions
- Fuel cost savings of \$1.4 billion

The project team was quite large consisting of boilermakers, material suppliers, research centres and end users (Keiser).

### 3. Experience of Biomass Firing

#### 3.1. Biomass Fuels Characterisation and Classifications

Biomass materials to be used as fuels can be loosely grouped into one of three generalised categories, these being wood, grasses and waste materials. Sources of information regarding the analyses of biomass fuels can be freely accessed via the internet. The BIODAT database is a development of the Phyllis database in cooperation with European partners within the Phydades project, and was co-funded by the EU 7<sup>th</sup> Framework Programme through the BRISK project, and is being funded by the H2020 Programme (Grant Agreement Number 731101) through the BRISK-2 project (BIODAT, PHYLLIS2). This database currently holds approximately 3000 records, the vast majority of which refer to non-fossil fuels and is updated and extended annually. For each fuel the Proximate, Ultimate and calorific values are reported together with the chemical analyses including halides, major, minor and other elements, plus the bulk density. The Technical University of Vienna (TUWien) has developed and maintains a similar database called BIOBIB, which contains over 300 records (BIOBIB). This again breaks down the fuel into the three major groups of wood, grasses and waste materials and then breaks this down further into the eight groups wood, straw, biomass-waste, bark, energy crops, husks and shells, grass and others. In addition to the data presented in the BIODAT database, the BIOBIB database also records where available the ash thermal behaviour as determined using DIN 51 730 in oxygen atmosphere, i.e. the temperatures at which the ash exhibits sintering, softening, hemispherical slumping and flow.

Biomass derived fuels are very diverse in nature and chemical composition. Herbaceous fuels are typically derived from fast growing, annual crops such as various straws, whilst woody fuels are typically grown over longer periods of a few years to decades. Herbaceous fuels typically have low bulk and energy densities meaning that large volumes are required to achieve the necessary heat input to boilers. As they are fast growing, they can often contain significant / high levels of inorganic, ash forming elements such as alkali metals, chlorine or phosphorous. Woody fuels also exhibit variable compositions with chemistry differences between old heartwood (low impurity) and outer sappy / green wood and bark (high impurity). As such, removal of bark can reduce the impurities present within a woody fuel. Moisture contents can also vary greatly with some woody fuels being in excess of 50% moisture. Harvesting during the winter months when the herbaceous or woody plants are dead / dormant can dramatically reduce moisture and impurity contents. This can further be beneficial to the environment with trace elements / fertiliser type compounds having been taken back into the soil. Biomass fuels can further be defined in terms of energy crops or waste fuels, with different incentives applied to utilise these materials dependent upon current political strategies.

Biomass fuels have wide ranging characteristics and chemistries. Some are more challenging to fire in power plant boiler than others and, as such, biomass boilers take many forms. Relatively clean fuels with minimal ash and aggressive constituents may be fired in boilers closely resembling conventional coal fired boilers. At the other extreme, fuels having a high ash content and high concentration of aggressive impurities such as chlorine, alkali and heavy metals, will require firing in a boiler similar to a municipal waste incinerator.

Cleaner fuels such as virgin wood are easiest to fire, give the least operational problems and have the most scope for efficient (high steam temperature) plant and, as such, these attract a premium fee. Increasing levels of impurities lead to fuels which are more difficult to fire, have greater propensity for fouling and corrosion and consequently are utilised in less efficient boilers with relatively low final steam temperature and pressures. As a result, these latter fuels are much cheaper than the clean fuels, and in some cases might even attract a gate fee. Some of the dirtier, waste biomass streams such as poultry litter, meat and bone meal, food wastes or by-

products of other bio-fuel production (glycerine) can be extremely aggressive when fired, but form a considerable percentage of the fuel fired in some boilers as they would otherwise have been directed to landfill.

For biomass fuels there remain many non-standard classifications, with this often varying from one country to another. In addition to fuel quality there are other requirements which must be met such as sustainability, no impact of bio-diversity and no impact on indigenous populations in the area from which they are sourced (Laborelec). In the UK wood pellets for firing large scale converted coal fired boilers are often specified according to the Initiative Wood Pellets Buyers: Industrial wood pellets specification, to grade I2 Industrial. This limits sources to forest, plantation and other virgin wood or wood that does not contain chemically treated residues. The specification covers the pellet physical parameters as well as imposes limits to the elementary composition.

Waste woods are typically divided into four categories rated A – D (DEFRA, 2012), or 1 – 4, with A or 1 being the cleanest and most benign and 4 or D being the dirtiest and most aggressive. Category A wood may contain nails and metal fixings and minor amounts of paints or surface coatings. Category B may also contain some plastics, glass, grit, coatings, binders and glues. Category C may additionally contain coated and treated timber without copper, chromium, arsenic or creosote. Category D is the worst grade that can also include preservatives containing copper, chromium, arsenic or creosote.

In comparison to fossil fuels such as most coals, the inorganic constituents of the fuel are much more volatile and easily released during combustion. For example biomass derived alkali metals are most often present as simple ionic compounds, whereas in coal the majority of the alkali metals are tightly bound to alumina-silicate minerals, where they are relatively inert. Calcium in biomass is often found as simple carbonate as opposed to more complex inorganic compounds. When determining the metals present in the fuel, often expressed as the oxide matrix after ashing a fuel sample at high temperature, care is required to ash biomass fuels at lower temperature (<600°C) so as to avoid converting the calcium carbonate to oxide.

### **3.2. Limitations to Steam Conditions for Biomass Fired Plants**

Warneke (2004) developed a diagram representing gas and metal temperatures within the municipal waste fired boiler at Flingern, Düsseldorf, Germany. The diagram, an example of which is shown in Figure 2, has been used by biomass boiler makers to define safe operating gas and metal temperatures for the different stages of evaporator and superheater in biomass fired boilers. For each boiler stage the expected tube metal temperature range and range of expected combustion gas temperatures are plotted. Wastage rates are not predicted from the diagram, rather areas of low (shown as white), indifferent (pale grey) and high wastage rates (dark grey) are predicted, with a further qualification of these zones according to local gas velocities. The diagram is used as a design tool, with the aim being to maintain the tube metal temperatures within the benign (white) areas, or, where this cannot be avoided, to identify vulnerable tubing that will likely require higher alloy tubing or the use of protective coatings.



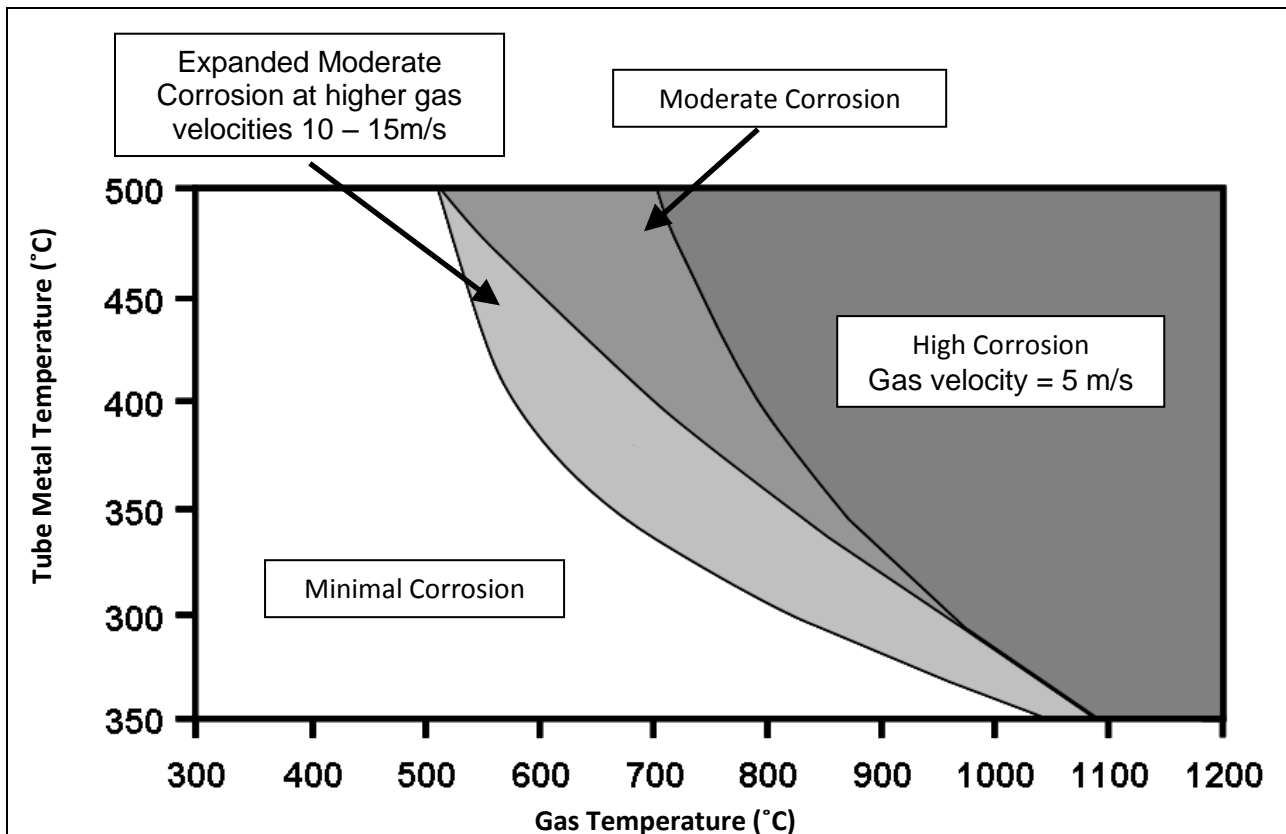


Figure 2. Flingern corrosion diagram after Warneke

### 3.3. Pulverised Fuel Fired Boilers

Limited information has been published in the open literature or made available regarding the pulverised fuel firing of wood pellets. Much information is little more than hearsay, for example related to topics such as the deposition of reflective ash within furnace sections which reduce heat absorption / evaporation rate and lead to higher furnace exit temperatures and difficulties in controlling steam temperatures. It should also be noted that until recently, most if not all wood fired power plants had a maximum steam pressure of 145bar and temperature of 540°C, this being approximately 20bar and 28°C lower than the normal steam temperature for typical sub-critical coal fired boilers. Most wood fired plants are also relatively small and therefore have no reheater sections in contrast to large coal fired boilers. Thus, where superheater and reheater steam temperatures are maintained at 568°C in converted plants originally designed to fire coal, these will have the most advanced steam conditions currently in use for any wood fired boilers. The main limitation for steam conditions in wood fired power plants is the fireside corrosion occurring as the result of the formation and deposition of potentially aggressive ashes, with water / steam temperature and hence tubing metal temperatures being the key factor in determining allowable steam conditions. Thus the increase in operating pressure and hence saturation temperature will increase the metal temperatures experienced by the furnace tubing when compared to purpose built wood fired boilers, potentially giving rise to heavy metal chloride induced corrosion under the influence of ash deposit condensation within the furnace. Ordinarily sulphur containing compounds are used in wood / biomass fired boilers as a means to promote the formation of alkali sulphate ash deposits in preference to the more aggressive alkali chloride deposits that can be produced in the superheater regions of biomass fired boilers. Whilst this method is successful in boilers operating up to 540°C, at which temperature sulphates are solid, boilers with final steam temperatures of 568°C can form molten sulphatic deposits. These can cause scale fluxing and rapid fireside corrosion damage. As such, this area is of great concern to converted boilers originally designed to fire coal which requires close monitoring post conversion to ensure excessive fireside corrosion is presented. It is possible that



the retained coal ash deposits and existing coal derived corrosion scales may at least offer some initial protection to the tubing post conversion, although extended wood fired operation would likely result in a greater influence of the biomass ash with time.

### 3.4. Drax

Drax Power have progressively increased their biomass firing capability from a single mill in one boiler, through single mills in all boilers to full conversion of four 660MW<sub>e</sub> units to 100% biomass firing using clean wood pellets by August 2018. Drax has significant experience of firing many different biomass types, including “challenging” fuels such as straw pellet, but the majority of this has been co-firing at a range of levels (6-60%) with coal. Plans for conversion were subject to frequent changes as a result of changes in the Renewable Obligation Certificate system (ROCS). It is understood that the converted units have continued to operate with the same 165bar and 568°C final steam conditions previously employed when coal firing and have achieved continuous operation for extended periods without the need for frequent shutdowns for deslagging / ash removal. Drax Power suggest that they have investigated additives to control ash or corrosion behaviour although again there is no information published regarding the success or otherwise of this strategy. It is believed that one additive employed is coal ash, this being used to capture alkali metals within the alumino-silicate phases contained in the ash.

### 3.5. Tilbury

Tilbury power station, operated by RWE Generation until final closure in 2013, comprised 3 x 330MW<sub>e</sub> units originally designed to fire coal but was modified to burn wood pellets in 2011. Tilbury have retained their original vertical coal mills and are using these for milling biomass with minor modification. On biomass operation the declared capacity is 750MW<sub>e</sub> for the 3 boilers, although higher load has been possible.

Limited work was carried out on the firing system so flame ignition problems have been experienced which have required a level of oil support for safe operation. Boiler performance has been good with boiler efficiencies similar to coal being achieved. As no boiler modifications were carried out as part of the switch to biomass operation, back end gas temperatures are elevated above that observed when coal firing, but steam temperatures have been achieved without major problems.

No major ash problems were experienced during the initial phase of the project but it was recognised that for re-licensing the boiler would need to be cleaned. During initial wood firing a white deposit was noted through the furnace which reduces heat pickup and evaporation rate in that section of the boiler. For the Industrial Emissions Directive (IED) compliance a method of keeping the furnace clean was required. No major slagging, fouling or corrosion problems were reported. As noted above in the ASPIRE project, the boilers did not suffer any significant corrosion damage when firing clean wood pellets.

### 3.6. Ironbridge

Ironbridge Power Station was owned and operated by E.ON UK (later renamed Uniper) and comprised 2 x 500 MW units originally designed to fire coal. The plant underwent conversion from coal to 100% clean white wood pellet firing with these being supplied to I2 grade industrial wood pellet standard. With the exception of the firing system (bunkers, mills, pulverised fuel pipe work and burners), the boiler remained unchanged from the configuration designed and optimised for coal firing. For both boilers, five of the six original coal mills were replaced with ten biomass hammer mills and the fuel bunker segregated such that the volume feeding the retained coal mill was separate from the bunker volume feeding the wood mills. The boilers continued to operate with the original final steam design parameters of 568°C temperature and 165bar pressure, although at a reduced

maximum load of approximately 370MW<sub>e</sub>. The maximum load was reduced due to limitations in supplying combustion air to the boilers. Operation up to the point of closure under the requirements of the Large Combustion Plant Directive (LCPD) was intermittent, primarily base load during the week with weekend shutdowns. This arrangement permitted off-load refurbishment of the hammer mills and aided spalling of ash fouling deposits within the pendant superheater sections. The assessment of corrosion rates using installed trial tubes within the furnace wall evaporators and the pendant superheaters revealed very low fireside corrosion rates when compared to the historic rates experienced when firing coal, this without the use of any fuel or combustion additives.

### 3.7. Avedore Block 2

Energie E2, later DONG Energy and now names Orsted, in Denmark have several years' experience of operating the Avedore Block 2 boiler using a blend of fuels containing biomass. Originally designed with advanced supercritical steam conditions of 300 bar and 600°C final steam with pulverised coal corner firing in a tower boiler, the plant was commissioned on a blend of natural gas, Heavy Fuel Oil (HFO) and wood pellets. Significantly, from commissioning the final steam temperature was reduced to 540°C, although this may have been raised in more recent years, but this cannot be confirmed. The fuels used during early operation were relatively clean wood pellets with the HFO being included to increase the sulphur concentration of the blend so as to avoid chloride induced corrosion. It is not known what fuel blends have been used in more recent years. In addition to sulphur from the HFO, coal Pulverised Fly Ash (PFA) sourced from the adjacent Block 1 coal fired boiler was also injected into the furnace through small ports located directly above the top level burners as a means to capture alkali metals within the fly ash mineral matter. The boiler made extensive use of TP347HFG tubing in the superheaters and reheaters that would be expected to have similar corrosion performance to that of other 300 series austenitic stainless steels.

A series of corrosion probe exposures were conducted by E.ON under contract to Energi E2 between December 2005 and June 2006 [Davis 2008, 1]. The project was part financed by the Danish state and the results made public. The conclusions of this report were as presented below:

1. Corrosion of the various specimens can be characterised according to the type of material. Low alloy ferritic specimens suffered general metal loss forming duplex corrosion scales. Martensitic steels initially formed chromia scales which suffered irregular breakdown and wastage with slight subsurface attack and the growth of duplex corrosion scales. The austenitic stainless steels and the nickel based weld overlay also formed chromia scales that suffered isolated breakdown to give rise to pitting and internal attack, with duplex corrosion scale growth.
2. The specimens exposed at higher temperatures showed greater tendency for corrosion scale and ash interaction, with the outer scale being defective, losing chromium into the outer scale and ash, and the finding of low levels of ash derived elements in the inner corrosion scales.
3. With the formation of duplex corrosion scales it would be most likely that corrosion rates would follow parabolic rather than linear kinetics, although rates would likely remain higher than would be the case without corrosion scale and ash interaction.
4. With the range of materials exposed, and the variations in coal fly ash additions, it has been impossible to quantify the effects of changes in fuel composition. However, in general, operation of the Avedore boiler with higher percentage blends of wood fuel resulted in greater wastage rates.
5. The higher alloy materials in general performed significantly better than the low alloy ferritic materials. Questions remain as to the performance of copper containing austenitic materials such as SAVE25 which performed worse than the TP347HFG when exposed at the highest wood fuel blend,

but performed better when lower proportions of wood were fired. Careful consideration of the future fuel mix would be required prior to the selection of SAVE25 as an alternative tubing material.

6. No clear trends in ash compositions could be discerned with changes in fuel composition. Most ash deposits comprised mixtures of inert, alumino-silicate, coal fly ash derived particulate material, together with amorphous / sintered material containing greater proportions of alkali metals and sulphur. Only low levels of vanadium were found (<3%) in any of the ash examined. Trace levels of potentially aggressive elements including chlorine, zinc, arsenic and lead were occasionally identified.
7. In comparison with the probe exposures conducted in the wood and straw fired Amager boiler, the Avedore specimens generally exhibited lower wastage rates, although the rates measured following the first exposure with the highest percentage wood content were greater and similar to those measured after exposure in Amager.
8. In comparison with the probe exposures conducted at pilot scale, the Avedore wastage rates were slightly lower than those measured after exposure to the softwood fuels and substantially lower than those measured after exposure to the straw and hardwood fuels.

### 3.8. Amager Block 2

Originally owned and operated by Energie E2, the Amager power plant was assigned to Vattenfall upon the formation of DONG Energy. The Block 2 boiler is a 1½ pass boiler that is operated through the winter heating system delivering power and heat in to the Copenhagen district heat system. Originally the boiler was designed to operate with pulverised coal firing from the front wall but was converted initially to fire straw through the pulverised burners. The plant has final steam conditions of 110bar and 480°C. Straw firing resulted in considerable furnace fouling which overwhelmed the ash hopper and required regular shutdowns in order to dig the ash out of the boiler when the level approached the bottom burners. Fouling was reduced by firing a blend of approximately 2/3 wood and 1/3 straw by mass, with each fuel fed through separate mills and associated burners. E.ON (Uniper) were contracted to supply a pair of superheater corrosion probes for exposure within the Amager boiler during March 2007, with the outcome of the testing summarised as below [Davis, 2008,2]:

1. Corrosion of the various specimens can generally be characterised according to the type of material. The low alloy ferritic specimens suffered general metal loss and enhanced grain boundary attack, forming duplex, but defective corrosion scales. The formation of a dark phase / scale at the metal / scale interface was associated with locally enhanced wastage and was attributed to the presence of chlorine. The martensitic steels suffered uniform wastage and slight subsurface attack with the growth of dense duplex corrosion scales. Occasional dark phase scale was again associated with locally enhanced wastage. The austenitic stainless steels generally suffered slight general and grain boundary attack, again forming dense duplex scales. Only the nickel based weld overlay formed a chromia scale, although it too suffered isolated, irregular breakdown to form duplex scales with slight sub-surface attack.
2. The austenitic material Sanicro25 suffered considerably greater wastage than the other austenitic materials despite higher chromium content. This manifested as subsurface attack within metal grains, and grain boundary penetration, leading to surface metal exfoliation.
3. The specimens exposed at higher temperatures showed greater tendency for corrosion scale and ash interaction, losing chromium into the outer scale and ash, with low levels of ash derived elements in the inner corrosion scales.
4. The defective and hence un-protective nature of the corrosion scales formed by the ferritic specimens suggests that para-linear or linear corrosion kinetics would likely apply to these materials, with corrosion rates remaining high even after extended exposure periods.

5. With the formation of dense duplex corrosion scales by the higher alloy materials, it would be most likely that corrosion rates would follow parabolic rather than linear kinetics, although rates would likely remain higher than would be the case without corrosion scale and ash interaction.
6. With the exception of the copper containing Sanicro25 material, the higher alloy materials containing greater chromium contents performed better than the lower alloy materials, despite increased exposure temperatures. Questions remain as to the performance of copper containing austenitic materials particularly in aggressive biomass derived combustion environments, and as such, Sanicro25 would not be recommended in this application.
7. The dense, predominantly potassium sulphate ash deposits would be considered aggressive at metal temperatures in excess of approximately 560°C, above which molten salt attack would be likely, although the ash would be significantly more aggressive had it contained greater quantities of potassium chloride.
8. In comparison with the probe exposures conducted in the wood and straw fired Amager boiler, the Avedore specimens generally exhibited lower wastage rates, although the rates measured following the first exposure with the highest percentage wood content were greater and similar to those measured after exposure in Amager.
9. In comparison with the probe exposures conducted at pilot scale, the Amager wastage rates were slightly lower than those measured after exposure to the softwood fuels and substantially lower than those measured after exposure to the straw and hardwood fuels.

### 3.9. Atikokan

Ontario Power Generation is phasing out the use of coal in their thermal power plants. The 211MW<sub>e</sub> Atikokan Generating Station was converted from low sulphur, Western Canadian lignite firing to pulverised wood firing in the summer of 2014; it is believed without a reduction in load. However, as lignite fuels are nearer to wood in terms of composition and calorific value than hard coals, and indeed have considerably higher moisture contents, it is perhaps unsurprising that full boiler load could be achieved. Doosan Power Systems were awarded the contract to undertake the conversion process. The plant is believed to be only operated for peak power production and is anticipated to burn up to 90,000 tonnes of wood pellets per year.

It has been reported that initial 100% wood fired trials in 2008 showed a significant drop off in superheater and reheater steam temperatures. However trials were curtailed following an explosion in the bunker house. The quantities of wood pellet that was fired were not sufficient to make a proper assessment of ash behaviour, but the limited evidence gathered suggested that impacts of ash deposition were insignificant.

#### 3.9.1. Nanticoke Generating Station

Ontario Power Generation have also conducted biomass trials at Nanticoke Generating Station and have achieved 100% biomass firing, with natural gas support, on one unit, during a test in 2008. With a design output of 500 MW<sub>e</sub>, a minimum load of 175 MW<sub>e</sub> can be achieved. Using all mills, the opposed wall fired boiler was gradually switched over from coal to wood pellets as the bunker contents were fed through to the burners. Ultimately 145 MW<sub>e</sub> was achieved using the wood fuel and 30 MW<sub>e</sub> was due to the gas support. The limit to the load was the availability of primary air. The unit was decommissioned in 2013.

#### 3.9.2. Thunder Bay Generating Station

From 1984 the Thunder Bay generating station, operated by Ontario Power Generation, comprised two coal fired power plants firing a mixture of lignite and sub-bituminous Powder River Basin coals, achieving a combined output of 326 MW<sub>e</sub>. As of 2015, one unit was closed with the second unit maintained as a peak lopping plant and

converted to fire “advanced biomass”, a steam treated (torrefied) wood pellet termed biocoal sourced from Arbaflame, Norway. Despite having accumulated limited operating hours, approximately 2.5days/year, in July 2018 it was announced that the plant would close, due to the identification of “an area of the boiler that had incurred some significant corrosion damage ... to the point where we are no longer able to operate the unit without significant repair”. The position and extent of corrosion was not detailed, but given the expected limited future operation, the costs of the required repairs rendered the plant uneconomic to operate.

### 3.9.3. Helsingborg

The Helsingborg power plant was originally a 200 MW<sub>th</sub> pulverised coal fired boiler that was converted to 100% wood pellet firing from 2006. The boiler now achieves 138 MW<sub>th</sub> from wood fuel and operates at 130bar and 540°C. The plant is owned by Oresundskraft and is located at the Port of Helsingborg which is the second largest container harbour in Sweden. Most of the pellet import comes from Canada. The heat and power plant consists of two interconnected units – the wood fired steam boiler with a steam turbine and a gas fired combined cycle unit. The combined effect of the two units is 126 MW<sub>e</sub> and 186 MW<sub>th</sub> for the district heating. The plant has operated for 6 years since conversion with little or no operational problems reported in the open literature.

### 3.9.4. Hasselby

The Hasselby Heat and Power Plant in Stockholm, Sweden was commissioned in 1959 and was originally oil fired but operated on coal until 1993 when it was converted to 100% wood pellet firing. The plant comprises 3 x 100 MW<sub>th</sub> boilers and continues to operate with little published evidence of problems. There have been no significant ash deposition related issues at Hasselby since conversion, and it has been reported that the furnace is cleaner with less sootblowing required than when running on coal. However there have been reports of light coloured deposits on furnace surfaces – similar to those noted at Tilbury. These have not caused operational issues [Livingston, 2012]. However, it should be considered that these units are relatively small and no doubt operate with considerably reduced final steam conditions compared with plants converted from coal to wood firing.

### 3.9.5. Rodenhuize Unit 4

GDF Suez’s Rodenhuize Unit 4 tower boiler, near Ghent in Belgium, was converted from HFO and blast furnace gases to coal firing in 1989, to firing 100% wood pellet in several stages between 2005 and 2011, with full conversion in 2011. The boiler has three opposed rows of pulverised fuel burners, 24 burners in total with a capacity of 120tonnes / hour fuel throughput and also retains the ability to introduce blast furnace gases. During the conversion, the boiler was derated from 279 MW<sub>e</sub> to 242 MW<sub>e</sub> (gross output), as a result of both technical concerns and market conditions. In the full year it has been operating on wood pellet to 2013, it has been reported as “reliable”. A number of (generally short-term) tests have been undertaken at this plant under the EU FP7 “DEBCO” project, Grant Agreement No. TREN/FP7EN/218968/“DEBCO [DEBCO]. It was reported that there was minimal ash deposition in the superheater section on 100% wood pellet. Corrosion probes were also used in the superheater section (with a flue gas temperature of ~1000°C and probe temperature of 550°C to 650°C) for 94 hour trial. On ferritic rings, a clear iron oxide scale was observed below a KCl deposit layer. This scale was considered to offer protection against corrosion. Dust emissions post-ESP were reported to be <1mg/m<sup>3</sup>, with ESP efficiency around 99.8% (after a refurbishment) and most of the emitted dust very fine (67% as PM<sub>1</sub>). At present, all ash is land filled.

### 3.9.6. Electrabel AWIRS Unit 4

A corner fired two-pass boiler with 3 burner levels, originally commissioned in 1967 to fire oil and gas, later converted to coal and gas firing in 1982. The output and steam conditions were originally 125 MW<sub>e</sub>, 390t/h steam at 145bar 545°C.

From 2005 the plant has fired wood pellets, at 350 - 400ktonnes/year, 50 tonnes / hour, generating 80 MW<sub>e</sub> at 34% efficiency. The steam temperatures have been reduced to 510°C. The conversion can be fully reversed to enable coal firing during a 3 week period.

There are no reported fireside corrosion issues found in published literature, but it should be noted that the final steam temperatures are relatively modest and, as such, the plant would be expected to tolerate the clean wood pellet fuels used.

### 3.9.7. Herning Multifuel CHP, Denmark

The Burmeister & Wain Energy A/S designed pulverised coal and oil fired boiler was originally commissioned in 1982. The option to fire coal was removed in 2002 such that only gas and oil could be fired through the burners. In addition, a vibrating grate was retrofitted for wood chip firing. In 2009 further modification permitted wood dust firing through PF burners. The boiler now operates with a total output of 240 MW<sub>th</sub> from biomass (70% wood chips / 30% wood pellets), producing 95 MW<sub>e</sub>.

### 3.9.8. Amer, NL

Amer Unit 9 (RWE) was commissioned 1993 with 700 MW<sub>e</sub> and was originally designed as a pulverized coal boiler burning hard-coal. In a first co-firing period from 2003 to 2006 with high bio-mass share the membrane walls experienced some corrosive attack and had to be repaired with cladding. Now the boiler is converted to co-firing 35% biomass with a future perspective to raise the biomass share until end of 2019 to 50%. A further increase of the future biomass share is considered.

### 3.9.9. Eemshaven, NL

Eemshaven Units A&B (RWE) were commissioned 2015 with 1628 MW<sub>e</sub> and were originally designed as a pulverized coal boiler burning hard-coal. Now the boiler is going to be converted to co-firing biomass with an initial biomass share of 15%. A further increase of the future biomass share is considered.

## 3.10. Fluidised Bed and Grate / Stoker Fired Boilers

Many biomass plants are relatively small and traditionally employ fluidised bed, grate or stoker firing. Too many plants exist to produce an exhaustive list but some examples are listed in the subsections below.

### 3.10.1. Steven's Croft

The Steven's Croft plant in Scotland is a Metso (now Valmet) designed and supplied, bubbling fluidised bed combustor owned and operated by E.ON. Considerable experience of operating and managing wastage of this boiler has been gained. The boiler steam conditions are quite advanced for wood fired boilers at 145bar and 535°C and not much reduced compared to that which is expected to be maintained in converted coal fired power plants.

Water cannons have been retrofitted to control furnace slagging where previously no sootblowers existed. Progressive furnace fouling had previously resulted in excessive furnace exit gas temperatures which ultimately



led to excessive superheater temperatures that could not be controlled using the desuperheater sprays, necessitating shutdown to deslag the furnace.

Partial blockages in the convective section and design features that have given rise to locally enhanced gas flows have caused corrosion-erosion tube leaks. This occurs due to the formation of mechanically weak, defective and laminated corrosion scales under the influence of heavy metal chloride containing ash deposits. Such scales are easily removed by relatively fast flowing combustion / flue gases and provide little or no protection from further corrosive attack. The damage manifests as local gouging of individually affected tubes within convective tube banks, or the systematic removal of metal local to specific flow enhancing features such as tube bank wall supports or penetrations through walls. In Steven's Croft this coincides with the saturated steam tubes and the close pitched primary superheaters. The final superheaters were produced using the HR3C austenitic stainless steel which has in this case suffered only very slight corrosion damage. In contrast, excessive fireside corrosion rates in the carbon steel furnace wall section has necessitated the replacement of the lower furnace, up to the tertiary air level, with tubing that was overlaid with IN625 weld overlay.

### 3.10.2. Markinch

The Markinch plant in Scotland is a Metso (now Valmet) designed circulating fluidised bed CHP boiler, commissioned in 2014 and operated by RWE. The steam conditions are 90 bar at 520°C, delivering a total of 155 MW<sub>th</sub>. The fuel diet at Markinch consists of both virgin and recycled wood which will be mainly sourced locally. It is expected that the ratio of fuel will be about 85% recycled and 15% virgin wood. The station delivers a net capacity of 55 MW<sub>e</sub> and also provides steam to a papermaking facility adjacent to the site.

The boiler is refractory clad to protect it from erosion and fireside corrosion from the continually circulating bed material, however there is concern for potential corrosion issues in the rear pass tube banks, after the cyclone separators, which are unclad. In addition there are concerns for the tertiary superheater, which is situated in the loop seal operating at 520°C in a separate fluidised bed at the bottom of the cyclone separator, where both corrosion and erosion could be an issue. As such, the superheaters are all designed as modular units that are easily replaceable. If there are issues with corrosion in the superheater tube banks there could be commercial incentive to use a coating to prolong the longevity of the tubes and decrease the frequency of replacement.

## 3.11. Biomass Power Plants Built by Various Manufacturers

Biomass boiler manufacturers tend to favour particular design types and firing methods with their boilers firing a diverse range of fuels and operating over a range of final steam temperatures and pressures that are limited by the design fuel chemistry. A summary of boiler offerings and the fuels combusted for a number of manufacturers is summarised below. No particular boiler design is guaranteed to cope any better than another design offered by another manufacturer for a particular fuel or range of fuels, and the list below does not imply any preference.

Standard Kessel typically construct stoker-fired boilers capable of firing all types of wood. The plants are typically of less than 100 MW<sub>th</sub> output with final steam conditions of less than 100bar and 500°C.

Valmet, previously known as Metso, build several design types. Their Hybex boilers (such as Steven's Croft) are Bubbling Fluidised Bed (BFB) boilers firing a range of fuels and achieve final steam temperatures of up to 535°C at a pressure of 145 bar. Their Cymic boilers (such as Markinch) are based on Circulating Fluidised Bed (CFB) firing and can range widely in thermal output and final steam conditions. The final superheaters in this latter design are typically located in a separate fluidised bed where heat is extracted from the bed material before it is returned to the furnace. In this arrangement a high heat flux is achieved due to the thermal mass of the bed material (often

sand), but the environment is relatively benign as the material is fluidised with clean air. As such, this arrangement permits relatively high final steam temperatures for slightly more aggressive fuels than would be achieved in a BFB boiler.

Sumitomo Heavy Industries - Foster Wheeler also specialise in CFB boilers that are reportedly able to fire a wide range of fuels from hard coals to difficult biomasses and blends of many fuels. These boilers can often be relatively large with capacities in excess of 100 MW<sub>e</sub> and high final steam conditions / efficiencies. For smaller boilers of a few tens of MW<sub>e</sub> capacity and aggressive fuels, stoker boilers can be offered operating at more modest steam conditions.

Burmeister & Wein offer a wide range of plants including large scale, advanced pulverised fuel fired boilers (Avedore). For smaller scale boilers firing difficult biomass fuels such as straw, cotton stalks or some wood, the boilers offered are typically grate fired with capacities of tens to a few hundred tonnes an hour steam at approximately 100 bar and up to 542°C temperature.

Aalborg Boilers A/S typically build small grate fired boilers of approximately 10 – 20 MW<sub>e</sub> capacity operating with relatively low final steam temperatures of less than 500°C which are capable of firing difficult fuels such as straw, poultry litter or Meat and Bone Meal (MBM).

Andritz Energy offer Ecofluid (BFB) and Powerfluid (CFB) boilers, both of which are capable of efficiently combusting a diverse range of often difficult fuels. For waste wood fuels relatively high final steam temperatures can be achieved through protecting the final stage superheater tubing by encasing it in refractory. This effectively forms a physical barrier between the high temperature tubing and the aggressive combustion environment.

Some of the above are known to suffer significant corrosion for which methods such as corrosion resistant metal coating, cladding or overlays, design or operating practise changes, have been used to manage the corrosion problem to an acceptable level.

### **3.12. Occurrence/diagnosis of slagging, fouling, erosion and corrosion**

This section on slagging and fouling has been included due to implications for biomass fired boilers.

#### **3.12.1. Slagging and Fouling**

As noted in previous sections, the ash content and composition of biomass can vary widely depending on its origin. Whilst coal ash is dominated by alumina-silicate, iron and calcium, most biomass ashes tend to be rich in compounds of calcium, potassium, silicon, phosphorous, sodium and magnesium. This inorganic matter can be grouped into two categories; inherent and extraneous. Inherent inorganic material exists as part of the organic structure of the fuel and is most commonly associated with oxygen, sulphur and nitrogen containing groups in the organic structure. Biomass is generally high in oxygen-containing groups and a significant fraction of the inorganic material in most biomass fuels is in this form. Elements such as phosphorous, potassium and sodium often appear as part of the cell matrix of plants and elements such as calcium and silicon are embedded in the plant fibres. Extraneous inorganic material has been added to the biomass through harvesting, handling and processing of the fuel – for example, soil and sand may be a contaminant of biomass.

These elements can be further divided into non-volatile elements such as silicon, calcium, magnesium, semi volatile elements such as phosphorous and volatile elements such as potassium and sodium. During combustion semi-volatile and especially volatile elements are partly released from the fuel and are free to react with other elements in the flue gas such as sulphur, chlorine and CO<sub>2</sub>.



An appropriate choice of biomass fuel based on the ash content and its inorganic constituents is the primary means of ensuring successful operation and minimising deposition and corrosion rates. Wood ash is very rich in calcium as calcite or carbonate (50-60%) with minor amounts of silica <10% and low levels of alkali metals and chlorine compared to most other biomass fuels and is generally considered to be the lowest risk biomass for most operational issues.

### 3.12.2. Ash & Aerosol Formation

During the combustion of solid biomass fuels, the fuel is first dried and the volatile matter is released. Subsequently the remaining fixed carbon is combusted. During these processes, inorganic elements will behave in different ways depending on their volatility, non-volatile elements will tend to fuse and coagulate and once all organic material has combusted, these species remain as ash structures in a molten or solid form depending on composition & temperature. More volatile species such as potassium, sodium, as well as chlorine and sulphur will tend to be released to the gas phase where they undergo complex gas-gas and gas-liquid (melt) phase reactions and later will start to nucleate (formation of submicron aerosols) or condense onto surfaces of solid particles in the flue gas or onto heat exchanger surfaces.

Due to the processes described above, the ash deposits that form on downstream gas-side surfaces of biomass combustion systems therefore tend to be rich in salts of the volatile alkali metals (primarily potassium), principally as chlorides and sulphates, depending on fuel composition and gas / metal temperatures. The chemistry of the deposits tends therefore to be very different from that of coal ash deposits, particularly in terms of chlorine / sulphur ratio and alkali metal content.

### 3.12.3. Ash Deposition

Traditionally biomass has been fired in relatively small scale stoker/grate and fluidised bed furnaces. Problems experienced with regard to ash behaviour with these technologies has primarily been around sintering, fusion and agglomeration of ash particles, particularly with regard to bed de-fluidisation and grate performance, although slagging and fouling of heat exchange surfaces has also been reported. Due to the relative novelty of 100% biomass firing in PF combustors, virtually no published work is available on biomass ash impacts specific to this technology. However, the work reported on deposit formation on heat exchange surfaces from the radiant furnace zone, through the high temperature convective pass, and on through to the lower temperature economiser tubes and air heater baskets in grate and fluidised bed technologies should in general be applicable to the PF system, although combustion temperatures in the PF furnace are generally higher than grate and fluidised beds.

### 3.12.4. Slagging

Slagging is caused by the deposition of molten particles on the furnace walls and radiant platens and deposit growth occurs via viscous sintering of these droplets under viscous flow to give a heavily fused deposit. This can have a serious effect on heat transfer as well as potentially building up to the extent where such deposits can detach and fall into the ash hopper potentially damaging tubing and blocking the hopper throat. Deposits can also form on burner quarls affecting flame shape, combustion performance and NO<sub>x</sub> formation.

The potential for slagging is based on the ash fusion behaviour, both of individual fly ash particles and of the surface of the slag itself. The fusion behaviour of ash is a complex process and is best described in terms of a melting curve. Ash fusion testing has been applied for the characterisation of coal ashes for many years and is

based on the determination of four temperatures on this curve. This test has been widely applied for alumina-silicate coal ash systems, but the results of this application for biomass ashes may not be appropriate.

Most coal ashes are composed primarily of alumina-silicate minerals which are refractory by nature. The main fluxes that will act to reduce the viscosity of an alumina-silicate melt and promote slagging are the oxides of iron, calcium and sodium and high levels of these elements in the ash will tend to increase slagging propensity. Iron can occur in either the  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  oxidation states and it is well recognised that reducing conditions promote slagging because of the greater solubility of ferrous oxide in an alumina-silicate melt.

In very general terms, three types of biomass ash system have been described by Bryers, in terms of general ash chemical composition and fusion behaviour [Bryers 1996]:

1. High silica / high potassium / low calcium ashes, with low-medium fusion temperatures, including many agricultural residues.
2. Low silica / low potassium / high calcium ashes, with high fusion temperatures, including most woody materials.
3. High potassium / high phosphorus ashes, with very low fusion temperatures, including most manures, poultry litters and animal wastes.

A number of indices have been developed for assessment of the propensity of ash to form slagging deposits in PF furnaces, including base / acid ratio and slagging index which also takes account of the iron content. As these indices have been developed from the assessment of coal with predominantly aluminosilicate ashes, the application to biomass ash systems, which are chemically very different, should be treated with care. Slagging deposits in PF combustion systems are generally higher in concentration of the less volatile elements, such as silicon, aluminium, iron, calcium and magnesium compared to the more volatile elements (sodium, potassium, phosphorous) as the temperatures in this region of the furnace are sufficiently high for these species to still exist in the vapour phase.

It should be noted that the introduction of low  $\text{NO}_x$  burners and two-shifting / non-base load operation to coal fired plant has reduced the incidence of slagging in recent years. Low  $\text{NO}_x$  burners have resulted in lower peak temperatures in the furnace zone of PF-fired boilers reducing the susceptibility to slagging, whilst the thermal stresses induced on formed deposits during the start-up/shut down cycle of two-shifting often results in natural shedding of material. However, even with low  $\text{NO}_x$  burners, PF flame temperatures will remain significantly higher than the flames in fluidised bed or stoker fired boilers.

Despite the uncertainty of applying coal-based predictions to biomass, the very low ash content of wood pellets and relatively benign ash composition / high ash fusion temperature, is expected to result in few issues with slagging converted PF boilers.

### 3.12.5. Fouling

Whereas slagging is a bulk phenomenon, fouling is the formation of deposits as a result of the inertial impaction of fly ash with low melting point compounds (dominant mechanism for coal) and deposition of sticky volatile species by a condensation or thermophoresis mechanism (more important for biomass). The volatile species will condense onto heat exchange surfaces as they pass through the furnace, initiating deposit growth and acting as a chemical bond between non-volatile ash particles which adhere to the deposit. This is most likely to arise in the high temperature convective pass starting at what is normally the secondary superheater pendant tube bank. The build-up of deposits in this area can lead to “laning” and higher metal temperatures due to forcing the gas flow through a reduced area, reduced load due to loss of ID fan power, and ultimately to a forced outage.

For coal, the main source of the low melting point compounds is the sodium in the ash. Potassium is present in coal, but in low quantity and is not freely released on heating. However for biomass, potassium is normally present in much higher quantities and is quickly volatilised, subsequently reacting to form species such as of simple salts ( $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ), as well as more complex binary  $\text{K}_2\text{O-SiO}_2$ , and ternary  $\text{K}_2\text{O-CaO-SiO}_2$ ,  $\text{K}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$  and  $\text{K}_2\text{O-P}_2\text{O}_5\text{-CaO}$  systems, which can have melting points lower than  $700^\circ\text{C}$ , depending on relative concentrations of individual species in the melt [Wang, 2012]. Fouling deposits will contain much higher levels of the volatile elements than slagging deposits, although much of the fouling deposit will still be made up from bulk ash in the form of solid PFA that has adhered to the initial sticky substrate.

Although fouling indices for coal are mainly based on sodium content, those for biomass are based on total alkali content. One index is based on the mass in kg of alkali metal oxides ( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ) introduced into the system per GJ heat input to the furnace. At index values above  $0.17 \text{ kg.GJ}^{-1}$ , significant fouling of the boiler convective section is probable. At index values in excess of  $0.34 \text{ kg.GJ}^{-1}$ , severe fouling is to be anticipated. Most biomass materials, and particularly those from fast-growing plants, will have index values in excess of  $1 \text{ kg.GJ}^{-1}$ , whereas most coals have relatively low values, generally less than  $0.1 \text{ kg.GJ}^{-1}$  [Miles, 1996].

Following deposition, there is a tendency for the alkali metal compounds and other inorganic species to undergo further reaction. Among the most important reactions with respect to ash deposition are sulphation, alkali absorption and oxidation. The principal sulphating species are potassium and sodium, particularly their oxides and chlorides reacting with sulphur species in the flue gas. This can add significantly to the mass and volume of the deposit. Silica absorbs alkalis to form silicates; these have lower melting points than silica and can induce sintering, although these reactions are slow compared to sulphation.

Normally the fouling deposition efficiency and deposition rate is relatively low and the resultant deposits tend to be well-adhered to the tube surface, relatively dense and of low porosity, particularly as the deposit builds up and its surface temperature increases. The deposits may be partly fused at the entry to the superheater and can be tenacious and hard to remove. As the flue gas temperature decreases, the fouling deposits tend to be un-fused and more friable in nature and are easier to remove on and off-line.

The risk of fouling in plants fired with commercially produced clean wood pellets is judged to be low, given the very low ash content of the wood pellet.

#### 3.12.6. Reflective Ash

This is a very unusual phenomenon in PF combustion systems which have been observed with certain coal types including very high silica content coals from Australia (Queensland) and high calcium / magnesium content low rank coals from America (Powder River Basin) and South Africa. For both coal types, a highly reflective ash made up of very fine solid oxide and silicate particles was deposited onto the furnace walls, resulting in poor heat transfer, higher furnace exit temperature and high superheater / reheater metal temperatures. It should be noted that this is not 'slagging behaviour', as the material responsible is highly refractory and hence in solid not liquid form. Although the ash composition of the coals from Australia is not at all typical of biomass ash, the low rank PRB coal ash composition is much closer to that expected from a biomass ash and in particular woody biomass. Issues of reflective ash have been seen in a UK PF converted biomass station where the boiler observed a 'white out' of the reflective ash and caused issues with  $\text{NO}_x$  control.

#### 3.12.7. Erosion

Erosion within boilers is closely related to the gas velocity, with erosion being proportional to the velocity raised to the power of 2 to 4. The erosivity of the ash is also closely related to the amount of hard materials such as quartz contained within it. Coals frequently contain 10 – 15% ash, of which a large percentage is either aluminosilicate material or quartz. In comparison wood fuels contain substantially less ash (~1%), of which silica is frequently a lower proportion. Erosion is not expected to be an issue for converted PF boilers and to date no issues have been reported elsewhere firing 100% wood pellet. With the exception of some materials (e.g. rice husk), biomass generally normally contains lower levels of silica & quartz than coal and biomass fly ash is not considered to be erosive in nature. Contamination of the biomass with quartz-rich sand (possible during harvesting) is likely to be the biggest risk to operation – however, this is considered highly unlikely given the relatively tight ash content specified biomass pellet production.

Tube erosion in the combustion chamber and high temperature superheater / reheater region of PF furnaces is not normally a problem, mainly due to the plastic nature of the bonded-slag-type deposits which absorb the kinetic energy of the ash particles and partly due to the nature of the particles themselves. In the convective superheater and reheater areas where bonded deposits cease to be a problem, the erosion propensity will increase as the temperature drops and the ash particles solidify. Even so, generally erosion has not been reported as a significant problem in UK PF coal fired boilers.

Inappropriate sootblowing practice can also affect erosion rates; insufficient sootblowing can result in increased temperature and velocity of ash laden gases leaving the combustion chamber – if coupled with partial blockage of the heat transfer surfaces then this will increase velocities further. Conversely, excessive sootblowing (or sootblowers in the wrong position) can cause erosion by the entrained ash particles in the sootblower jet impacting on boiler tubes. Too aggressive sootblowing of tenacious calcium rich ash deposits can also be problematic, this being associated with local ash deposit removal and localised erosion, whilst much of the tubing retains the deposits.

Also beneficial to converted PF boilers is the anticipated reduced load when wood firing. This implies that the total gas throughput for the boiler will also be reduced thereby reducing the average propensity for erosion damage. However, the situation is further complicated by the nature of the corrosion scales formed on the tubing in biomass fired environments. These are often more defective and mechanically weak than those grown in coal fired environments and, as such, are likely to be more easily removed in a process termed corrosion-erosion.

### 3.12.8. Corrosion

As noted above, different biomass fuels have distinct and variable compositions and ash forming chemistries which drive / dominate the corrosion mechanisms that will be observed in plant. Whilst the fuels may be relatively low in ash, they typically contain potentially significant levels of a number of chemical species which have implications for boiler performance and lifetime, in particular the alkali metals (potassium and sodium) and chlorine. Straw and other annual crops are usually considered to present a significantly higher corrosion risk than clean wood fuels. Waste fuels such as Meat and Bone Meal (MBM) or demolition wood can also contain significant levels of chlorine through contamination by common salt, plastic or wood treatments and coatings. The latter contaminants are often associated with heavy metal contamination (lead and zinc). Alkali metals and chlorine are almost completely volatilised in the boiler and combine in the vapour phase to form low-melting point alkali chloride species. These can condense onto boiler tubes, in the furnace and superheater sections, and undergo chemical reactions to produce chlorine in close proximity to the boiler tubing surface where it can react with tube metal to form iron chloride salts. It is concentration of these elements and compounds which typically

limit the design steam pressures and temperatures for biomass fired boilers as a result of the fireside corrosion damage that will occur.

Fireside corrosion in pulverised wood fired boilers will be associated with aggressive species in the fuel such as chlorine and alkali or heavy metals. In the case of biomass fuels, the presence of sulphur in the fuel may have positive benefits in terms of reducing attack by chlorine containing phases, but may also have negative impacts due to corrosion scale fluxing under molten alkali sulphatic ash phases in plant with final steam temperatures greater than 540°C.

Chlorine can adversely affect the corrosion in three separate ways. In pulverised coal firing boilers, increasing coal chlorine content was linked to increased furnace wall fireside corrosion under reducing gases coupled with a high heat flux. Such conditions promote the diffusion of gaseous chlorine to the scale metal surface where it forms a chloride rich phase that allows rapid diffusion of corrosive species and metals at the corroding metal surface. The chloride rich phase formed has limited thermal stability and, under the influence of the heat flux, the outer higher temperature part of the scale becomes unstable, releasing the chlorine to diffuse back to the metal surface where it takes part in further corrosion. This process is often referred to as active oxidation and results in very high wastage rates that can cause tube failures after approximately 1 year of operation. Given the common clean wood fuel compositional specification for industrial pellet production, it is very unlikely that sufficient chlorine will be present in the fuel to enable this mechanism to be active.

Alkali or heavy metal chloride containing ash phases can also be condensed onto the tubes from the gas phase. At relatively low temperatures these may be in solid form and serve to moderately increase the corrosion rate through increasing the concentration of chlorine in the environment local to the tube surface. In this case the chlorides inhibit the growth of the desired dense and protective oxide corrosion scale that would otherwise form on the tube surface. The scale formed in these circumstances is less dense, more defective, and mechanically weak and does not provide an effective diffusion barrier to limit further corrosion damage. Rather than the corrosion process forming iron oxides, the formation of iron oxychloride ( $\text{FeOCl}$ ) may be favoured, with this phase having a layered structure which may be intercalated with additional metal ions such as potassium. It is this layered structure that is mechanically weak and it is relatively common when examining corrosion scales formed under biomass combustion conditions to find chlorine and potassium in close proximity to the corroding metal surface with iron and oxygen. This, coupled with high gas velocities, leads to the phenomenon of corrosion-erosion in which the mechanically weak scales are easily removed into the gas stream revealing fresh, unprotected metal to be corroded by the aggressive combustion environment.

At higher tube metal temperatures the alkali or heavy metal chloride ash deposits can be molten. In this instance, the corrosion rates can be dramatically increased as the molten ash deposits actively dissolve the protective corrosion scales that would ordinarily have formed on the tube surface. This effectively removes any diffusion barrier that might have existed between the tube metal and the combustion environment, allowing free access for the corrosive environment to interact with the bare tube metal. Such molten chloride attack can result in catastrophic wastage rates ( $>200\text{nm/h}$ ) causing tube failures in less than one year of operation. In some plants firing straw where the ash is dominated by alkali chloride containing ash, it is the practise of some boiler manufacturers to design the pendant superheater stages such that they operate without sootblowing. Instead, the widely spaced elements operate continuously fouled by a layer of alkali chloride ash, the outer layers of which approach the local gas temperature, this permitting the molten ash to run off of the stage. In this situation, an equilibrium condition is set up with relatively inert and cool ash in contact with the tube surface under which the fireside corrosion rates are tolerably low.

The best defence to combat corrosion under chloride containing ash deposits is to select clean fuels with low chlorine, alkali and heavy metal content. Ideally the ash formed in the high temperature superheaters and reheaters should be diluted with relatively inert ash species such as alumino-silicates, reducing the risk of high temperature superheater /reheater corrosion damage. As noted above, and further detailed in the following sections, the sulphur in the fuel can also be considered beneficial as this preferentially reacts with alkali metals to form alkali sulphates instead of alkali chlorides. This keeps the chlorine in the gas phase as HCl where it takes little part in the corrosion process.

Converted coal boilers may also have an additional benefit in that the existing boiler tubing surfaces should for the most part have retained dense and protective corrosion scales grown during this earlier operating period and still retain considerable coal ash deposits. The coal ash deposits may further act to extend the onset of typical biomass firing fireside corrosion as these will be relatively inert due to the high alumino-silicate content and may take some considerable period to develop the more aggressive typical biomass ash deposits. There is the possibility of a significant initiation period for breakdown of existing dense, protective coal firing derived corrosion scales to form less protective, more defective biomass influenced corrosion scales and, as such, a delay in onset of biomass driven corrosion. Thus there may be a progressive upturn in the observed wastage rates encountered in converted boilers which should be monitored as far as possible at opportunity outages.

### **3.13. Measurement of furnace and heating surface slagging or fouling**

Slagging and fouling of the boilers is best monitored on-line by following trends in furnace exit gas temperatures, superheater and reheater metal temperatures, de-superheater flow rates, differential pressures across tube banks and trends in rate of steam generation and superheating.

It would be prudent to take ash samples for chemical analysis during off-load visual inspections as a means to determine the tenacity and corrosivity of the deposits. In particular the proportion of alkali, alkaline earth and heavy metals, together with any chlorides or sulphates present could be used to determine whether the ashes from particular areas within boilers are relatively benign or aggressive. Ash samples may also be gathered using cooled deposition probes if suitable boiler openings are available.

### **3.14. Measurement of tube wastage (erosion / corrosion)**

With the perceived difficulties in predicting boiler wastage rates prior to commencing operation, it can be seen that there is a need to monitor fireside corrosion rates in an effort to understand areas of the boiler that are at risk, to determine wastage rates and hence predict tube lives and maintenance requirements, in order to identify the need for corrosion mitigation strategies.

#### **3.14.1. Off-Line Assessment and Measurement**

Boiler internal visual / tactile surveys should be undertaken at routine planned plant outages. Such surveys can be used to direct more detailed ultrasonic thickness surveys should these prove necessary in areas noted to be suffering unexpected or significant corrosion damage. This approach compliments the normally undertaken tube thickness surveys in the furnace and superheater / reheater sections during plant maintenance overhauls.

#### **3.14.2. Temporary Corrosion Probes**

No standard method exists for design, installation or operation of fireside corrosion probes. A number of different temporary corrosion probe systems are available that can offer a range of sensitivities, accuracies and measurement intervals in furnace wall or superheater type applications. All temporary probe systems are inserted



in to the furnace environment through small boiler openings. The boiler openings typically need to be slightly larger than the probe systems to facilitate probe insertion and particularly removal whilst retaining at least some of the associated ash deposits. With corrosion probe sensors or coupons normally constructed using standard boiler tube stock materials, these most frequently have dimensions/external diameters in the range 38.1-50.8mm (1.5-2"). As such, a boiler opening of 75mm internal bore (3") is sufficient for most, if not all corrosion probe systems. Existing furnace wall openings such as viewing windows or redundant soot blower / dosing ports may be used with only minor modifications. Alternatively openings can be made through man access doors or furnace walls by the installation of appropriate tube joggles at positions of interest.

For boilers having a membrane wall construction, probes can be installed in slots in the membranes between tubes, or screwed into drilled and taped holes in them membrane. The latter type can be very simple, relying on the cooling effect of the membrane and adjacent wall tubes to maintain the desired exposure temperature, although close temperature control is not easily achieved. Such probes are offered by DNV KEMA and Doosan Babcock and make use of post exposure laboratory assessment to determine metal losses and wastage rates. Alternatively temporary probes may be air, water or steam cooled, although these systems are more complex and hence more expensive than the passively cooled probes.

As part of the Belenus project, power plant based medium to long term exposures are to be made by Doosan and UNIPER using metrology corrosion probes equipped with a number of bare alloy and coated corrosion coupons. These are relatively simple probes that use post exposure measurement and assessment to accurately determine wastage rates, see below.

Metrology corrosion probes can be used to monitor both furnace wall and superheater / reheater corrosion rates. These temperature controlled, air cooled probes can be installed and removed whilst the plant is on load and have no impact on the boiler operation. Metal losses and hence wastage rates are determined from post exposure laboratory measurement using digital image analysis techniques. The technique is very accurate ( $\pm 1\mu\text{m}$ ) but can only give an average rate over the duration of the test exposure, which may range from periods as short as 50 hours to many thousands of hours. Where it would be anticipated that high wastage rates are likely to occur, probe exposures of fifty to a few hundred hours would be adequate to obtain reliable wastage rate determinations. Schematic diagrams of the probes can be seen in [Figure 3](#) and [Figure 4](#) below.

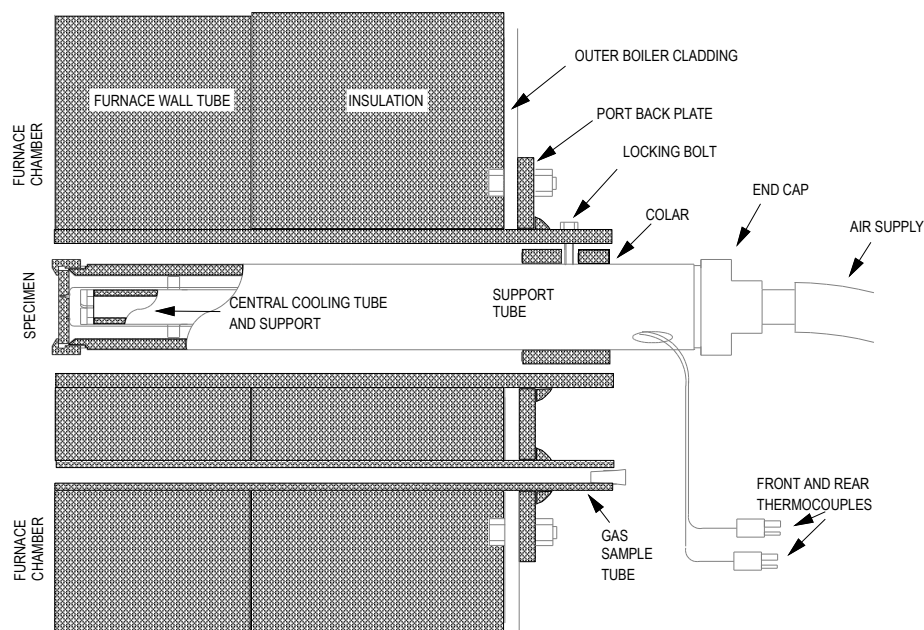


Figure 3. Precision Metrology Furnace Wall Corrosion Probe

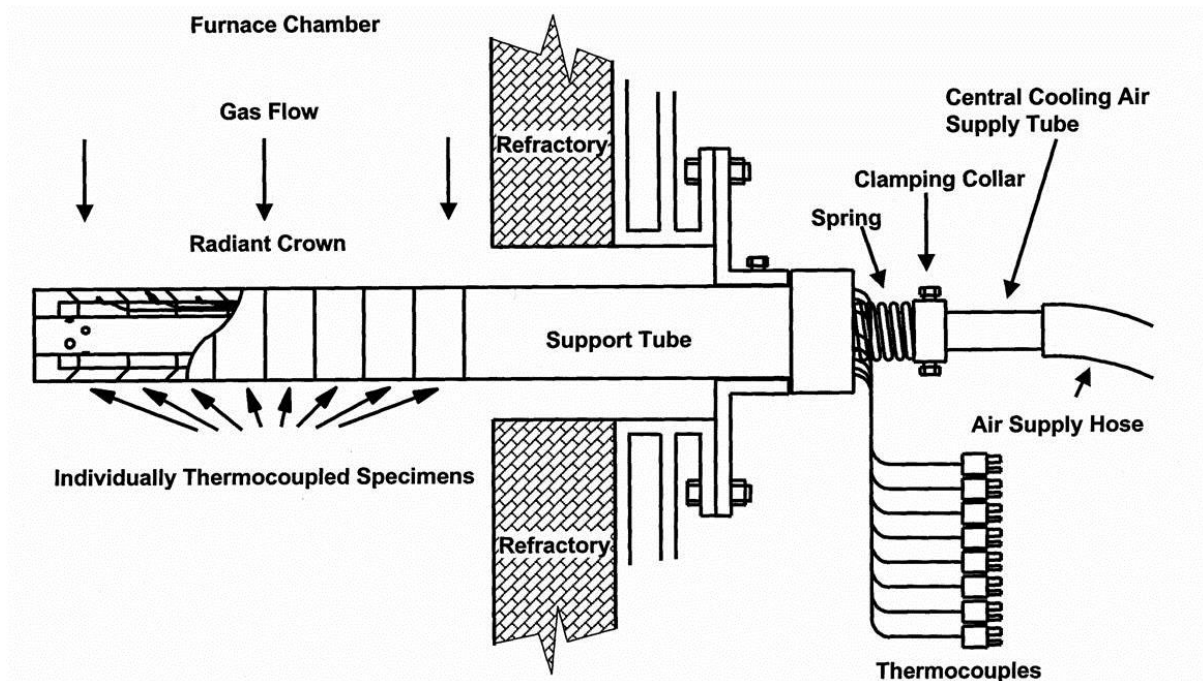


Figure 4. Precision Metrology Superheater Corrosion Probe

Both precision metrology corrosion probes use power plant supplied compressed air typically at 1-2 bar pressure to provide cooling and enable temperature control of the corroding coupons. The test coupons can be exposed at typical tube metal temperatures or over a range of temperatures to examine the effect of increasing or decreasing boiler pressure and steam temperature. The air is exhausted external to the furnace and has no impact on the local combustion environment. The furnace wall probes are each equipped with a single corrosion coupon typically produced from low alloy ferritic steels as used for the furnace wall tubing. Alternative high alloy materials, sprayed corrosion resistant coatings or corrosion resistant weld overlays can also be used to study the benefits obtained when utilising these materials. The superheater probes are equipped with between 8 and 26 specimens which can be produced from a range of tube materials or corrosion resistant coatings/overlays.

The probes used by Doosan Babcock are similar to those shown in Figure 4, although in this case the cooling air used to control the coupon temperatures exhausts from the end of the probe into the furnace.

### 3.14.3. Temporary On-line Corrosion Probes

Online corrosion probes rely on electrical resistance, impedance or electrochemical noise measurements to determine metal losses and or wastage rates of their sensor corrosion coupons. As with metrology probes, these are temperature controlled usually with air cooling. These probe systems provide an indication of wastage rates with a lesser degree of accuracy than the metrology probes, but can give an indication of changes in fireside corrosion rates over time as a function in changes in fuel composition or plant operation. As part of the Belenus project UCM aim to develop and prove an on-line corrosion sensor which should be demonstrated in an operating biomass fired boiler.

Electrochemical noise probes probably provide the most rapid response (measured in a few hours), but with probably only order of magnitude changes in rates being indicated rather than accurately measured. It is likely that these probes are reacting to changes in the combustion environment, i.e. a transition from solid to molten ash deposits, rather than absolute changes in wastage rates. The systems often rely on complex “black box” fast Fourier analysis and, as such, the results are not readily interpreted without expert assistance. The corrosion



probes can be exposed for periods extending to years in low wastage rate environments, after which they can be dismantled and subject to laboratory examination in order to confirm average metal losses over the exposure periods.

Resistance probes respond more slowly as these rely on the increase in resistance associated with the loss in metal coupon cross section as a result of corrosion. There is a trade off in terms of sensitivity and probe longevity, with more sensitive probes having thinner sensors that are consumed more rapidly by corrosive attack. As an example, the resistance probes offered by Rowan Technologies will require approximately 1 month to determine a low wastage rate of approximately 2 nm/h (5mm wall tube life measured in decades) with a good degree of confidence, but only 7 to 10 days to determine a wastage rate of 70 nm/h (5mm wall tube life 8 years) and shorter periods still to determine severe or catastrophic wastage rates [ROWAN].

As with any probe system, metrology, electrochemical noise or electrical resistance, it would always be recommended that the probes are destructively examined under laboratory conditions in order to confirm the extent of metal loss after testing has been completed. This not only enables confirmation, or otherwise, of any indicated metal losses derived from on-line probes, but also enables the corrosion scales and associated ash deposits to be examined using light and electron microscopy. The later technique can also be coupled with elemental x-ray analysis which enables the active corrosion mechanism to be ascertained together with the fate of the metal and combustion derived elements within the corrosion scale and ash deposit.

#### 3.14.4. Permanent Fixed Corrosion Measurement Systems

Rowan Technologies also produce an Installed Scanner Array system. This is a non-intrusive, permanently installed electrode array attached to the cold side of membrane furnace walls that requires no boiler openings. The electrodes are stud or TIG welded to the rear of the tubing with the connections then feeding out through the furnace insulation and cladding. The resistance between individual electrodes is scanned at 60 second intervals with changes in resistance over time again being used to determine the extent of metal loss. Such systems have not been widely employed but there is some good operational experience in the UK with one coal fired power plant having three systems installed over a period of several years, with this reportedly being expanded in boilers having undergone conversion to wood pellet firing. The results from the largest system installed after Boosted Over Fire Air (BOFA) was installed in the boiler to control NO<sub>x</sub> emissions have been verified through the use of EMAT ultrasonic thickness checks at routine overhauls. This has shown the system to produce relatively reliable and quantifiable (with a scaling/averaging factor) results even in boilers suffering low wastage rates (Figure 5).

For the boiler represented in Figure 5 having a tube wall thickness of 6mm and a temperature uncertainty of approximately  $\pm 5^{\circ}\text{C}$ , it was possible to determine a mean relatively low metal loss rate of 0.5mm.y<sup>-1</sup> (57nm.h<sup>-1</sup>) after approximately 40 days of data acquisition.

The system is also supposed to be able to detect circumferential thermal fatigue cracking in weld overlays and distinguish this damage from general metal loss with this having been demonstrated in the Brunner Island supercritical coal fired boiler, Pennsylvania, USA. The installed electrodes can be fitted either singly or as pairs to the rear side of the membranes between the furnace wall tubes at intervals of approximately 1 m. As such the measurements yield average wastage over areas of  $\sim 1\text{m}^2$ . Given remote data access the system can be monitored without any operator intervention on site. The systems are reportedly rugged and operate for extended periods without any need for maintenance. It is unknown whether this system would be suitable for installation in a furnace wall having tangent tube construction rather than membrane walls. As adjacent tubes are not connected by membranes and therefore not in effective electrical contact with each other, it would be assumed that any such installation would only be sensitive to wastage on individual tubes. As such, it must be

assumed that this technique would only be capable of measuring corrosion losses over vertical lengths with multiple individual arrays required to monitor a number of tubes.

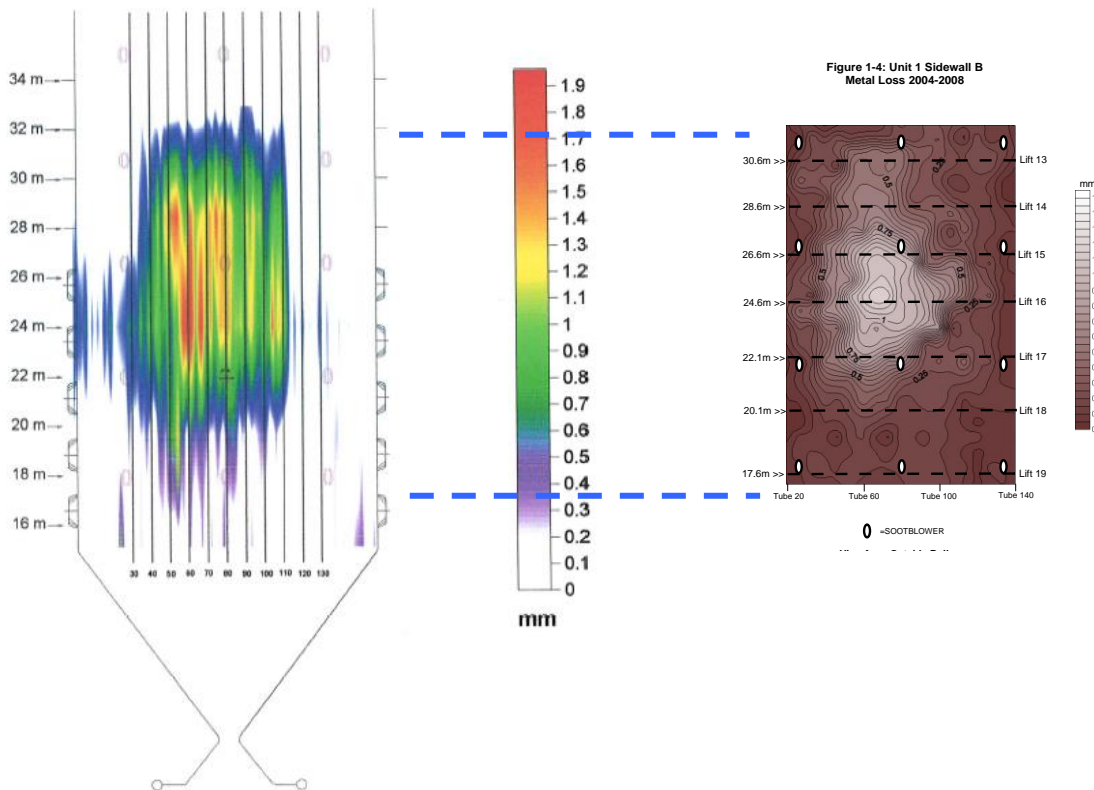


Figure 5. Comparison with the output from the Rowan resistance scanner (left) and routine ultrasonic thickness checks (right) in a large-scale UK coal fired boiler.

### 3.14.5. Indirect measurement of corrosivity

Ash deposition probes can give a good indication of the corrosivity of the combustion environment in relatively short time. Ash samples would be collected over a period of up to a few hours using temperature controlled, water or air cooled probes. The deposition probes would need cooling to temperatures similar to the boiler tubing so as to encourage the condensation of any aggressive chlorides from the gas phase. With knowledge of the concentrations / partial pressures of the various chlorides in the combustion environment and the local gas temperatures, it would be useful to determine at which temperature these compounds begin to condense from the gas phase in order to characterise this process and highlight any deleterious operating conditions.

The deposits would be analysed to determine the extent of alkali metal and / or heavy metal chloride deposition, with the presence of these compounds being indicative of a high risk of severe corrosion. In contrast, the absence of chlorides from the ash deposits would be indicative of benign conditions. This technique could be used for instance in association with a ChlorOut injection system during its commissioning in order to gauge its effectiveness in preventing chloride deposition, see below. The probing system would be relatively simple / inexpensive and would not require extended periods of post exposure assessment. As with corrosion probes, the deposition probes would be constructed from tubing with dimensions of approximately 38mm and, as such, the probes would be inserted into the boiler using carrier tubes / ports as available around the boiler. Samples would be collected with and without any furnace dosing or other mitigation strategies operating to assess their relative performance. Sample positions would range from the furnace through to the areas of the primary superheaters and reheaters.

### 3.15. Remnant tube life estimation

The assessment of remaining tube life for all stages in the boiler is subject to considerable uncertainty and something that is best assessed by giving close attention to particular tube stages after temperatures and wastage rates under the influence of biomass firing is known.

Furnace wall tubes in subcritical boilers are not subject to creep and for the most part will be life limited only by the fireside corrosion damage. With the maintenance of good combustion conditions that achieve oxidising conditions at the tube walls and using relatively clean biomass fuel such as I2 grade industrial wood pellets, there should be little risk of fireside corrosion in the furnace walls. This situation may fall down if poor combustion control occurs and reducing conditions are experienced at the furnace walls. For biomass fuels with ash dominated by alkali and heavy metal chlorides the furnace walls will likely suffer from the corrosion-erosion mechanism as described above.

Primary superheater and reheater tubing may similarly be affected by the deposition of alkali and heavy metal chlorides and degradation in corrosion scale integrity. This would likely become an issue if there are any partial ash blockages within the tube banks that cause locally enhanced flue gas velocities as this could result in local corrosion-erosion damage. Similarly local design features that promote acceleration of the gas velocity or turbulence could also promote localised corrosion-erosion problems.

The higher temperature penultimate and final superheaters and reheaters may be subject to high temperature fireside corrosion and fluxing of the corrosion scales by molten ash deposits. Provided that relatively clean fuel is fired, it would be hoped that there would be no alkali chloride deposition, assuming that sufficient sulphur is available to react with all of the available alkali metal. Should molten alkali chlorides be deposited, the fireside corrosion rates would likely be very severe and could result in tube failures within short time scales of one year's operation, even for high alloy austenitic stainless steel tubing. Whilst alkali sulphates are less aggressive than alkali chlorides, they may still be present in an aggressive molten state in the final superheater and reheater stages of plant operating at a temperature of 568°C or greater. A reduction in steam temperatures to 540°C would greatly reduce any sulphatic corrosion damage as at these lower temperatures the alkali metal sulphates formed would be in a solid form and not able to flux the corrosion scales present on the tubing. Indeed, the use of sulphur containing additives is commonly used in biomass boilers operating at temperatures of less than 540°C as a means to prevent molten chloride corrosion.

The rate of long term creep failures in high temperature superheater and reheater tubing will be greatly dependent upon the steam and metal temperatures, irrespective of any associated fireside corrosion wastage. Any reduction in tube metal temperatures will be beneficial in extending anticipated tube creep life. As a rule of thumb, a decrease in metal temperatures of 10°C will result in a doubling of anticipated tube life. Conversely, an increase of 10°C will result in a halving of the tube life. It should also be noted that metallurgically bonded coatings such as weld overlay and laser cladding, may also poses significant strength which may contribute to the load carrying capability of tubing subject to creep damage. In this instance a metallurgically bonded coating would have the benefit of reducing corrosion and effective stress, thereby increasing the anticipated tubing creep / operating life. In contrast, mechanically bonded coatings such as those produced by thermal spray processes could not be expected to be load bearing.

Dust erosion may or may not be a significant issue when biomass firing. The relatively low ash content in many biomass fuels when compared to coal means that the total throughput of ash in a boiler will be relatively low. For converted coal boilers any reduction in unit load will also result in lower gas velocities within the boiler reducing the propensity for dust erosion. The main obstacle to achieving a low erosion rate is the uncertainty with respect

to the fouling of the boiler and the associated requirements for sootblowing. Any reduction in sootblowing frequency is likely to be beneficial in reducing localised sootblower erosion damage. Conversely local accumulations of ash particularly in tightly pitched tube banks may require more frequent sootblowing leading to enhanced damage rates. The uncertainty with regard to the growth of defective and poorly protecting corrosion scales further complicates the effects that could be observed when sootblowing with cleaning potentially exacerbating any corrosion-erosion wastage rates.

### 3.16. Design and operational solutions to biomass firing issues

#### 3.16.1. Plant Equipment Solutions

##### Sootblowing

The principal means of on-line control of deposition is the use of sootblowers. The high velocity jet of steam, water or air employs a combination of mechanical impact and thermal shock to break up deposits and remove them. Sonic sootblowers are an alternative solution that may be deployed particularly for the removal of relatively weak deposits in the cooler parts of boiler convective sections, whilst Shock Pulse Generators (SPG) may also be used to prevent ash accumulations. Sootblowers are the most established technology for removing ash deposits from boilers surfaces and ensuring effective heat transfer.

Ash deposition effects heat absorption in the various sections of the boiler and can therefore be monitored to some degree by simply monitoring steam (superheat and reheat) and metal temperatures, and desuperheater spray flow values. Any ash deposition in a particular region will tend to reduce the heat transfer in that region and may increase gas temperatures to subsequent areas of the boiler requiring increased use of desuperheater sprays. It should be noted that deposits of light-coloured 'reflective' ash could have a magnified effect, reducing the radiant heat input in particular. The changes noted in superheater / reheater temperatures and spray flows following sootblowing episodes will further assist the plant operator in diagnosis of potential problem areas for ash deposition.

As well as steam and metal temperatures, monitoring furnace draughts where this information is available (e.g. convective zone inlet pressures and ID fan suction), will also provide a relatively crude measure of pressure drop across the furnace and hence degree of ash deposition / blockage formation.

##### Erosion Baffles and Shields

As well as control of fuel ash content, other measures are available to alleviate erosion. This includes the use of baffles and shields for high velocity or turbulent areas within the gas pass. The extent of erosion and the requirement for tube shielding should be accessed through visual and tactile surveys at routine plant outages. Areas or tubes found to be locally eroded can be targeted for additional erosion shield installation. Localised application of overlay or sprayed coatings can also be effective in reducing erosion rates.

##### Heat Exchanger Modification

The modification of heat exchangers to increase or decrease the amount of economiser, evaporative, superheat or reheat tube surface may be considered to:

- (i) Enable a reduction, increase or better control of steam temperatures
- (ii) Increase the pitch between convective tube bank tubing so as to reduce propensity for blockages
- (iii) Alter the proportion of heat absorbed between the furnace and convective sections.

The removal of tube surface area to prevent boiling in the economiser or reduce superheater / reheater steam temperatures may be relatively easily achieved. For example, this may be achieved through shortening tubes or completely removing individual tubes within elements / tube banks. Similarly bypassing loops in the convective section economiser, superheater or reheaters can effectively remove tube surface area and thereby reduce heat pick up.

The addition of tubing to increase tube surface area and increase heat absorption in specific areas is somewhat more difficult given the available space and existing access constraints within boilers. The addition of tubing is also likely to be problematic in terms of integrating with the existing heat exchanger and header systems and could also be prohibitively expensive.

Should further evaporative tubing be required to increase the rate of steam generation, it may be possible to convert surface such as radiant wall superheaters to evaporators, with a consequential reduction in the superheater surface area. Again such a modification would likely entail considerable expense.

Prior to undertaking any such changes to the surface area of the various stages it would be necessary to fully understand the implications in terms of altered heat pickup on the surrounding sections of the boiler. Modelling of any proposed changes would be strongly recommended to avoid any other adverse changes that may occur.

### 3.16.2. Materials Solutions for Fireside Corrosion Management

The range of tubing alloys currently installed in the gas pass of biomass boilers is essentially the same as that deployed in subcritical and supercritical fossil fuel fired boilers. These comprise low alloy ferritic (<2%Cr), bainitic steels (2 - 12%Cr), relatively low alloy austenitic stainless steels (15 – 21%Cr) and relatively high alloys stainless steels (>21%Cr). As in any other boiler design, biomass boilers are constructed using the cheapest, lowest alloy materials that are able to withstand the operational stresses associated with particular boiler section temperatures and water / steam pressures. Low alloy ferritic steels are most frequently deployed wherever possible. Typically, fireside corrosion is a secondary issue, although designers of biomass boilers try to anticipate problems and use design / arrangement of the different boiler stages to minimise the impact of tube wastage.

Given the difficulties in predicting wastage rates it is common for plants to be constructed using low alloys materials and put into service with the minimum corrosion protection that the equipment suppliers expect to be necessary. The extent of fireside corrosion damage is then assessed after approximately one year of operation and at this latter stage, options for corrosion protection would be considered to protect areas exhibiting significant corrosion damage.

The industry typical protection system is to use IN625 weld overlays, applied either in the workshop to new replacement tubing, or applied in-situ to existing damaged tubing. Other overlays, cladding or thermally sprayed corrosion resistant materials may be deployed, although these will need to have demonstrated cost benefits when compared to IN625 weld overlay protection. It would be anticipated that the Belenus project output would identify where this approach may be insufficient, particularly with the aim of extending operation to higher temperatures where alternative protection solutions may be better employed.

Alternative, cheaper overlay, clad or coating materials may be deployed provided these protective coating systems can be shown to offer sufficient corrosion protection, these may be formed for example from iron rather than nickel based materials. Similarly the use of Laser cladding and HVOF may be attractive given the lesser use of the relatively expensive coating materials given that these processes typically deposit 1mm or 0.3mm of material compared to the typical 2mm weld overlay cladding thickness. Again the output of the Belenus project,

and in particular the in plant exposures of coating systems, would be used to demonstrate the performance of such coating systems.

### 3.16.3. Operational changes

#### Opportunity Outage Inspection and Cleaning

Regular visual inspection of boiler surfaces for any sign of deposit formation, corrosion or erosion should be undertaken at routine or breakdown outages. This can provide invaluable information to determine the rates and nature of deposit build-up. It is also recommended that ash deposit samples are taken during internal furnace inspections to allow for further chemical characterisation.

Natural shedding or detachment of deposits occurs when deposits grow too large for the adhesive forces to support them or due to the effect of thermal expansion differences between the boiler tube and ash deposit during shut downs and load changes. During off-load periods it may also be advisable to routinely clean boiler areas known to have slagging or fouling problems.

#### Steam Conditions

Should corrosion under the influence of heavy metal deposition prove to be a problem in the furnace, one possible solution would be to reduce the boiler operating pressure. Whilst this may not reduce the propensity for heavy metal chloride deposition it would reduce the activity or corrosivity of any chloride containing deposits.

Similarly, if alkali sulphate containing ash leads to excessive molten sulphate attack in either the final superheater or reheater stages of plant operating with final steam temperatures in excess of 540°C, a reduction in final and reheat steam temperatures to this temperature should effectively remove the problem. This reduction in temperature should take the tubing metal surfaces outside of the temperature region in which complex alkali sulphates are molten and instead these will be present in the less aggressive solid phase. Such an approach would not be effective in preventing attack due to molten chloride containing ash deposits as these remain in this state to significantly lower temperatures.

Any reduction in operating pressure or temperature would however have a consequential impact on reduced unit output and efficiency.

#### Additives for Fouling

The use of additives to control biomass ash deposition behaviour and corrosion is fairly common in fluidised bed and grate combustion systems. Additives can change the ash chemistry, increase ash melting temperature, reducing fouling rates and decrease concentrations of aggressive species.

Three groups of additives have been identified that modify fouling behaviour. All three species have the ability to react with potassium and sodium chloride and create higher melting point crystalline phases; potassium and sodium chloride are also removed from the gaseous phase. The addition of alumino-silicates such as kaolin  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , or bentonite  $\text{Al}_2\text{O}_3(\text{SiO}_2) \cdot 2\text{H}_2\text{O}$  will cause reactions between potassium silicates to form higher melting point temperature potassium alumina-silicate systems, as well as reactions with KCl. As well as the commercially available additives noted above, simpler alumino-silicates such as those derived from coal ash have been investigated, although their reactivity would be expected to be less.

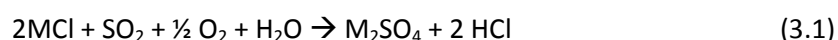


Sulphur based additives such as ammonium sulphate, or elemental sulphur have the effect of converting KCl into  $K_2SO_4$  which has a higher melting temperature, reducing deposition issues. In addition the chlorine is reduced in the fouling deposits, mitigating chlorine induced corrosion. Calcium based additives such as CaO,  $CaCO_3$ ,  $Ca(OH)_2$  and dolomite  $CaMg(CO_3)_2$  are relatively ineffective for fuels with high alkali and chlorine contents unless the biomass contains reasonable levels of phosphorous. The use of calcium and phosphorous together in the form of dicalcium phosphate (DCP) and monocalcium phosphate allows enhancement of calcium in potassium phosphates which can strongly increase their melting temperature (Wang, 2012).

Further, it is understood that additives to darken the colour of light coloured ash are under development from companies such as Baker Hughes, but these have generally been aimed at coal-fired applications burning high calcium content coals. Addition of an iron compound to the coal can result in the formation of dark coloured calcium ferrite in preference to calcium oxide. This is an option that may be considered if evaporation rates are too low and superheater / reheater steam temperatures are too high.

### Additives for Corrosion Protection

One key method to reduce the risk of chloride ash driven fireside corrosion is to limit the levels of alkali chloride species in the flue gas. In the presence of sufficient free sulphur, potassium and sodium will preferentially form sulphate rather than chloride, with the excess chloride forming HCl in the flue gas (Equation 3.1).



where M = K, Na.

Gaseous HCl plays little part in the high temperature superheater / reheater fireside corrosion process. The rate of sulphation is believed to be determined by the rate of  $SO_2$  conversion to  $SO_3$  (the active species in the reaction) – in most boilers the ratio of  $SO_3$  to  $SO_2$  is very low; although certain metal species can catalyse the conversion.

For effective sulphation, a free sulphur to chlorine ratio of 4:1 is generally recommended. However, native levels of sulphur in most biomass fuels are very low, and the level of free sulphur in the flue gas is reduced still further by reaction with any calcium carbonate which is a significant component of the majority of biomass ashes. If relying on this method, alternative sources of sulphur must therefore be considered when utilising biomass fuels with a high chlorine but low sulphur content.

Pulverised coal fired coal boilers have traditionally used  $SO_3$  injection in order to improve the performance of the electrostatic precipitators.  $SO_3$  also has great benefits in terms of reducing the tendency to form alkali chloride containing ash deposits and as such there could be benefits obtained through re-engineering  $SO_3$  injection system so that the gas can be introduced into the furnace area. This position is upstream of the superheaters and reheaters which would be offered a degree of protection using this technique. Preventing the deposition of alkali chlorides is greatly beneficial in reducing the influence of molten alkali chloride corrosion scale fluxing. However, if the final superheaters and reheaters operating at temperatures above the melting point of the alkali sulphate deposits, the tubing could be exposed to molten sulphate corrosion scale fluxing. Any molten sulphate corrosion would be restricted to a significantly smaller section of the boiler than would be the case if molten chloride corrosion were to occur, and would propagate at a reduced rate compared to molten chloride induced damage. It is not known what levels of  $SO_3$  injection might be required in order to provide full protection from alkali chloride ash formation but, as a rule, there would be a requirement for at least twice as much sulphur in the combustion environment than there is chlorine in order to prevent alkali chloride formation.

Sulphur containing additives are often used in power plant boilers operating with final steam temperatures of 540°C or less, and similarly work by forming alkali sulphates to prevent the formation of alkali chlorides. However, significantly greater quantities of sulphur are required as in normal combustion most of the sulphur is converted to SO<sub>2</sub>, whilst SO<sub>3</sub> is required to effectively remove the alkali metals through the formation of sulphates. Significant sulphur sources include waste tyres which also have significant heat content, or some sewage sludge sources. Both of these options would require a Waste Incineration Directive (WID) compliant boiler. UK sewage sludge contains little sulphur or sulphates as pozzolanic flocculants are used in preference to aluminium or ferrous sulphate and, as such, little or no benefit would be obtained through the firing of this material.

Other additives, such as kaolin (china clay) and coal ash, can be injected either with the fuel or local to the burners as a means to reduce alkali chloride deposits and reduce fouling as described above. Both these materials are alumino-silicates and readily form glassy ash phases that can absorb alkali metals effectively removing them from the combustion environment and preventing their reaction with chlorides and subsequent deposition in the superheater and reheater stages. Such an injection system is reported to function better in pulverised fuel fired boilers rather fluid bed fired boilers as a result of the higher flame temperature achieved.

The above methods have various efficiencies for removing alkali chloride from the ash deposits; however, none of these methods are thought to be effective in preventing heavy metal chloride ash formation and deposition.

### **Addition of Coal or Peat**

Depending on the source, coal and peat can contain significant levels of sulphur (2% sulphur as received is not uncommon for coal) and so relatively low levels are needed to provide the sulphur required. Peat is generally not transported over large distances and so its use is restricted to those plants which are located close to a peat source. Power plants using peat are also frequently ineligible for biomass firing incentives / subsidies largely as a result of the perceived environmental damage associated with the mining of the peat.

Co-firing coal to mitigate biomass induced fireside corrosion is a process that has been used for some time in countries such as Sweden where biomass fired boilers are more common. Co-firing fossil fuels will probably have some impact in terms of the eligibility to claim environmental subsidies.

### ***Tyres***

Tyres are a waste fuel source with relatively low levels of recovery at present and as such may be available at much lower cost than other potential sulphur sources, with typical sulphur levels from 1-3%. However, since the majority of rubber is now derived from fossil sources, tyres are likely to be considered a fossil fuel and so subject to the same limitations as other fossil fuels such as coal. Tyres may also contribute significant levels of metals such as zinc.

### ***Sewage Sludge***

Sewage sludge can be a low, zero or even a negative cost fuel depending on the situation and the level of pre-processing undertaken. Unlike other fuel sources of sulphur, sewage sludge may be classed as 100% biomass, although significant levels of heavy metals can be found in some sources. Levels of sulphur depend on the treatment process; it is believed that UK sewage sludge is treated with non-sulphurous chemicals and therefore would be of limited benefit, whereas in other countries including Sweden, flocculation of solids is achieved using sulphate based additives.



## Non-Fuel Additives

As an alternative to combusting high-sulphur fuels, elemental sulphur, chemical additives containing sulphur and certain minerals can all also be used to reduce the formation of alkali chlorides. Vattenfall have developed and patented the use of the “ChlorOut” system, which injects a sulphate solution (usually ammonium sulphate which has the co-benefit of NO<sub>x</sub> reduction activity) into the area of the furnace outlet, upstream of any superheater and reheater stages.

## Elemental Sulphur

Elemental sulphur addition can be considered a special case of a supplementary fuel; it does combust and has a calorific value (~9.1 MJ.kg<sup>-1</sup>) but doesn't contain fossil carbon. As with the use of other supplementary fuels, the feed rate required will be dependent on the concentrations of S and Cl in the flue gas. Combusting elemental sulphur in the furnace may be an inefficient process as the majority would be burnt to form SO<sub>2</sub> with only a minor increase in SO<sub>3</sub> concentration. As SO<sub>2</sub> the sulphur is less efficient at displacing the chloride and a large proportion simply contributes to the sulphur emissions from the stack.

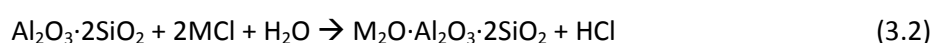
Addition of sulphur to the bed of FBCs has been applied by Foster Wheeler to new build plant, for example in the Irdalta plant of Solderenergie (Natunen, 2010). The plant was designed to burn a mixture of refuse derived fuels, woody biomass and waste wood, with steam conditions of 520-540°C, 90 bar (chosen because Foster Wheeler's experience with 100% demolition wood plants in Germany has shown minimal corrosion at 90 bar conditions). The design fuel chlorine content was 0.125% (dry basis). As well as boiler design measures to limit the corrosion risk, granulated elemental sulphur is added directly to the bed via pneumatic conveyance. To ensure that emission limits for SO<sub>2</sub> are met, there are separate handling and feed systems for both lime and sodium bicarbonate to be used for acid removal in the bag filter. The more expensive sodium bicarbonate is only added as required, for example if the flue gas temperature increases or improved SO<sub>x</sub> removal is needed. However, little information is currently available on the effectiveness of this system or feed rates used at this plant.

Sulphur addition for corrosion control has also been demonstrated by Metso Power in a bubbling fluidised bed plant converted from brown coal to biomass firing to allow higher levels of agro-fuels to be utilised (Silvennoinen, 2011). The 75 MW<sub>th</sub> plant in Poland has steam conditions of 138 bar, 540°C. Granulated sulphur was dosed into the fuel prior to the feed chutes, with a dosage rate of 2.9 g/s given for one experiment.

## Alkali-capture by Alumino-Silicate

Whereas sulphur containing additives function by the sulphation of the alkali metals, the use of alumino-silicate materials injected into the flame can avoid the formation of the chlorides by binding the alkali metals into the ash, preventing their release into the vapour phase. This method was trialled and subsequently adopted at Avedore Block 2 and is also believed to be used in the Drax boilers which have been converted to clean wood pellet firing.

A number of different minerals have been studied at laboratory and plant scale for fluid bed fired boilers, although these might find useful application in the higher temperature flame environment found in pulverised fuel fired boilers. In the majority of cases alumino-silicates such as kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O, also called china clay) have proved most effective (Steenari, 1998). These react with the potassium in the fuel according to Equation 3.2.



Kaolin is a naturally occurring mineral whose cost will depend on the purity and amount of pre-processing required. Alternative sources of aluminosilicates, including waste sources, are available, though the cost of these would have to be balanced against lower purities, resulting in higher throughputs, ash production and disposal costs. As with other mitigation options, the amount of material required will depend heavily on ash and flue gas chemistry, and the level of control that is needed as a consequence, but inputs equivalent to 30-50% of the fuel ash content have been suggested in some studies (Coda, 2001; Abo, 2001).

Potential materials that could be used as an alumino-silicate source include coal ash, sludge from paper pulp processing and sewage sludge. Coal ash is typically over 50% silica and 25% alumina, and so could be a low cost source of material. However, since coal ash can also contain unburnt fossil carbon, its use may affect eligibility for environmental subsidies.

Sludge from the paper/pulp processing industry has also been used as a supplementary fuel in Finnish wood-fired plants for a number of years with few corrosion problems (kaolin is a major component in the paper production industry) (Aho, 2004), but this option relies on a suitable source being identified within an economic radius of the biomass fired plant (some sludges can also contain significant chlorine content).

As with the sulphur additives, more HCl is released during alkali capture which could be an issue at plants with emission limits for HCl, but there is no extra formation of  $\text{SO}_x$  and resulting additional gas clean up plant. The highest operating cost, particularly when using low cost waste materials, is likely to be in the disposal of the additional ash produced.

## ChlorOut

ChlorOut is a process developed and patented by Vattenfall AB and now marketed by a spin out company Chlorout AB. A sulphate solution is sprayed into the freeboard of a boiler before the first superheater bank. The sulphate decomposes in the flue gas to release  $\text{SO}_3$ , which then reacts with the alkali chloride species to give HCl and alkali sulphate. Since  $\text{SO}_3$  is formed directly from the additive without the need for  $\text{SO}_2$  oxidation, the level of excess sulphur needed is lower than when using elemental / fuel sources of sulphur (see **Error! Reference source not found.**).

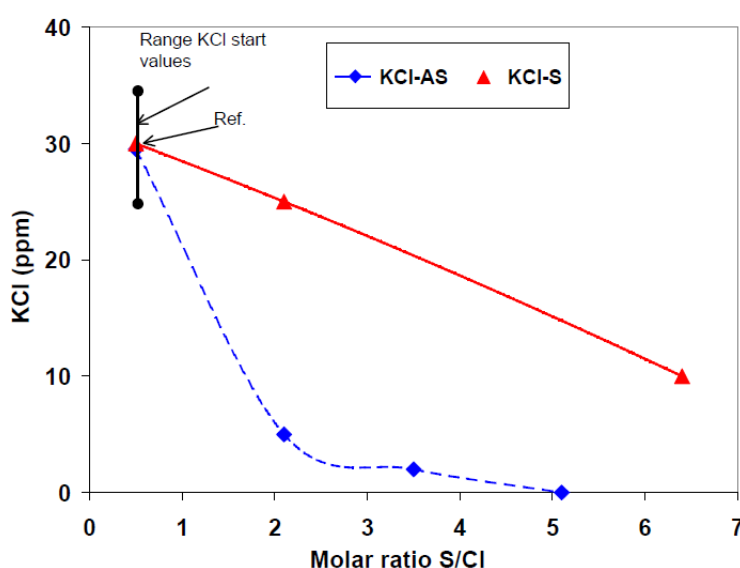
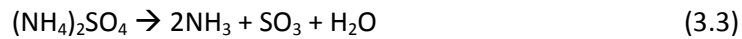


Figure 6. Reduction of KCl in flue gas during addition of ammonium sulphate (AS) (ChlorOut) and sulphur (S)

The Vattenfall patent covers the use of a number of sulphates, namely ammonium sulphate, ferrous sulphate and ammonium bisulphate, as well as sulphuric acid (Andersson, 2002). In most of the reference plant and tests the additive used has been ammonium sulphate, as the decomposition of this compound also generates ammonia (Equation 3.3), which can contribute to NO<sub>x</sub> reduction in a Selective Non-Catalytic Reduction (SNCR) process. Since the majority of plant where ChlorOut would be deployed also have to use SNCR to meet NO<sub>x</sub> limits, this reduces the amount of SNCR reagent required and so partially offsets the cost of the ChlorOut system.



The system has been tested in a number of fluidised bed (bubbling and circulating) and grate-fired plant burning a variety of fuels. These include HKW-Mittelfeld (waste wood and demolition wood) (Hjörnhede, 2010; Viklund 2011), Idbäcken CHP (wood chips, demolition wood) (Kassman, 2006), Munksand (bark, virgin wood, plastic wastes) (Henderson, 2006; Kassman, 2006; Broström, 2010), Nyköping (wood chip, waste wood, coal) (Henderson, 2006; Viklund, 2011) and Dåvamyran (household and industrial waste) CHPs (Broström, 2010). Boiler modifications needed for the ChlorOut system are very similar to those for SNCR, with a cross-duct system of nozzles prior to the first superheater bank. Depending on relative injection rates, uncontrolled emission levels and the level of reduction required, it may be possible to completely substitute the SNCR reagent with ammonium sulphate.

Figure 7 is a schematic of the ChlorOut process indicating the typical position of the spray and the on-line monitoring of alkali chlorides (for process control). **Error! Reference source not found.**8 shows a typical response of the alkali chlorides to the injection of the ChlorOut additive.

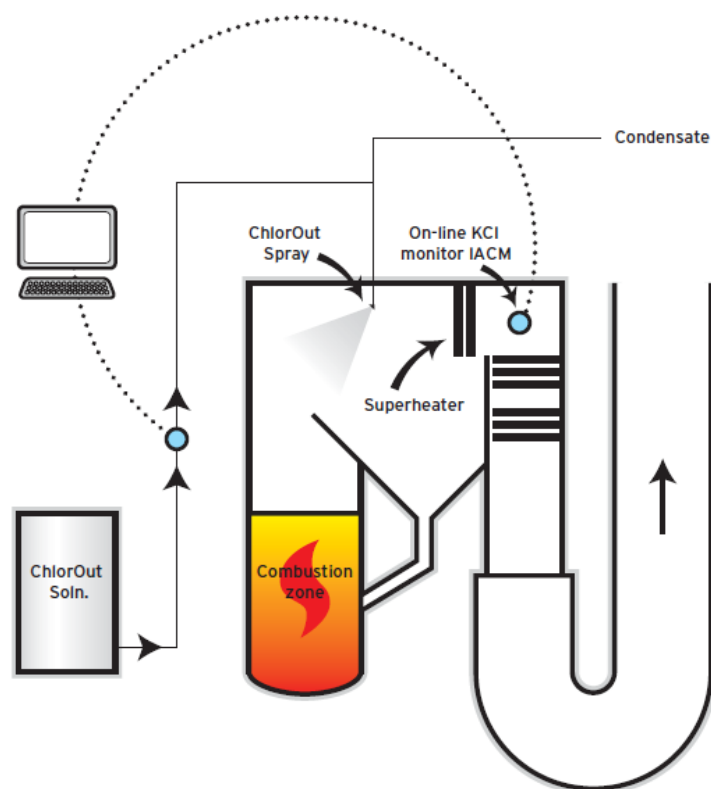
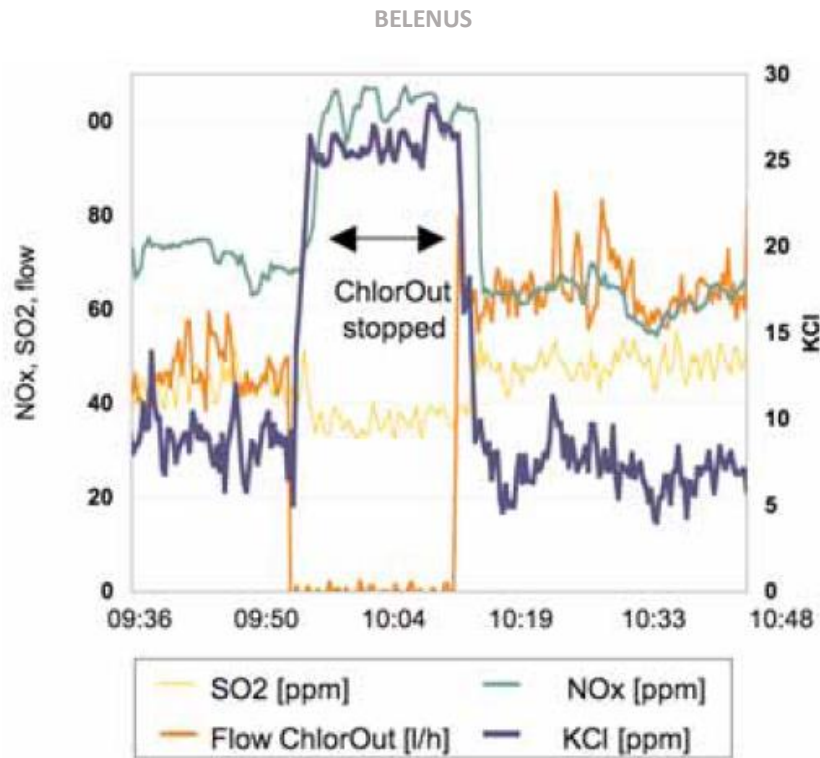


Figure 7. Schematic of ChlorOut process



Vattenfall has patented a raw combustion gas monitor called the In Situ Alkali Chloride Monitor (IACM) which can simultaneously monitor alkali chloride (Na+K)Cl levels and SO<sub>2</sub> (Andersson, 2001, Forsberg, 2009). The monitor has been demonstrated in a number of plants in conjunction with Vattenfall's ChlorOut injection system, and can be used to control the ChlorOut addition rate in response to variable flue gas alkali chloride levels.

IACM measures the sum of the KCl (g) and NaCl (g) concentrations on-line but is unable to distinguish between these two species. The result is expressed as KCl during biomass combustion. This is a cross-duct system, although depending on the dust burden in the flue gas, shorter path lengths may be required to reduce obscuration. The sender unit contains a UV light source (xenon lamp) which crosses the flue gas path and is received by a spectrometer in the receiver unit. Levels of (Na+K)Cl are determined by Differential Optical Absorption Spectroscopy at characteristic wavelengths. Quoted detection limits are 1 ppm for (K+Na)Cl and 4 ppm for sulphur across a 5 m path length. The system operates in a flue gas temperature window of 700-1100°C and is usually installed upstream of the first superheater bundle.

### Alternative Sulphur Additives

Alternative additives with similar effects to ChlorOut have been investigated by other research groups (often sponsored by boiler manufacturers). Ferric sulphate and aluminium sulphate are two of these chemicals; like ammonium sulphate the non-sulphate portion of the chemical is also claimed to also have beneficial reactivity in the flue gas path (Aho, 2008). The use of these chemicals, termed CorroStop, has been patented by Metso Power Oy, now Valmet, (Roppo, 2009), who propose the addition to the boiler to be via a cross-duct cooled cased hollow beam fitted with injection nozzles. As well as releasing SO<sub>3</sub> directly, ferric sulphate will also provide iron which will help the conversion of SO<sub>2</sub> from the fuel into SO<sub>3</sub>, and hence reduce the amount of extra sulphur addition required. In contrast, the aluminium sulphate will produce aluminium compounds which can bind the alkali metal into alkali aluminosilicates, as with the use of kaolin and similar materials in fluid bed systems. At present however it is unclear whether these materials have been tested in full-scale systems, with data at present restricted to bench and small pilot scale testing.

Metso (now Valmet) have identified an alternative measurement method based on particle size distribution of aerosols. In biomass combustion, submicron particles in the flue gas are primarily composed of alkali metal chloride, so the measurement of this particle size fraction by a particle impactor can be used as a surrogate for (Na+K)Cl (Palonen, 2010). This method has been used in a number of studies, particularly on pilot plants, where the effectiveness of measures to prevent alkali chloride formation has been monitored by measurement of sub-micron particles (Vainikka, 2011). A sample of flue gas is extracted from the boiler, diluted and pre-conditioned as necessary and passed to a particle impactor which counts the number of particles in specified size ranges. Various companies supply the impactor systems – the only in-duct equipment is the air-cooled permeable tube for sample extraction (Silvennoinen, 2011). These particle impactor systems tend to be expensive (~£100k) and can be difficult to keep in service. Questions also remain over the reliability of the assumption that all fine particulate is alkali chloride.

## 4. Overview of coatings for corrosion protection

An alternative to mitigate corrosion and allow operation at higher temperatures and pressures is the use of highly-corrosion resistant coatings that can significantly increase the life of Ni- base materials or even allow the use of lower cost alloys such as austenitic and ferritic steels. These include weld cladded, thermal spray and diffusion coatings among others (Kawahara, 2016). Some of these coatings are very protective, as for instance fused NiCrSiB applied by thermal spray (Matsubara, 2007) and composites incorporating ceramic materials such as SiC, Al<sub>2</sub>O<sub>3</sub>, Zr<sub>2</sub>O<sub>3</sub>, etc. (Kawahara, 2016). Alloy 625 (Lai, 1999) applied by weld overlay has been used for over 10 years in a biomass fuel plant operating at 500°C with a maximum corrosion rate of 200µm/year. In addition, a cermet coating composed of TiO<sub>2</sub> and alloy 625 was estimated to last 27,000h at a metal temperature of 448°C (Kawahara, 2016). Aluminium and Cr diffusion coatings were also protective relative to uncoated P91, when tested at 650°C in the laboratory (Fähsing, 2017) in contact with a mixture of salts including KCl. Other than pure coating corrosion, failure mechanisms are also related to erosion (alone or combined with corrosion) and the presence of porosity and defects that allow gases to reach the substrate (Kawahara, 2016).

There is no general agreement regarding the optimal compositions capable of withstanding biomass corrosion, likely due to biomass diversity. In general, protective coatings work by developing a stable protective oxide scale, usually based on Al or Cr, and the coating must have sufficient amount of these elements, so that if the oxide breaks and/or spalls it can be reformed immediately. Depending essentially on the atmosphere composition and the deposits to which the materials are exposed as well as the temperature, these scales can form (or not) and remain attached to the coating. For instance, it was suggested that Cr plays a detrimental role in molten chloride corrosion at 670°C when comparing the behaviour of Fe<sub>21</sub>Cr<sub>5</sub>Al and Fe<sub>45</sub>Al alloys (Li, 2005) but another group found that Fe<sub>22</sub>Ni<sub>10</sub>Cr<sub>13</sub>Al had higher corrosion resistance than Fe<sub>22</sub>Ni<sub>10</sub>Al when in contact with KCl at 650°C (Pan, 2011) and yet other authors demonstrated that chromized P91 behaved better than aluminized P91 embedded in a sulphates and chlorides mixture at 650°C (Fähsing, 2017). Moreover, as already mentioned, fused NiCrSiB (Matsubara, 2007) (21 wt. % in Cr) and also alloy 625 (20-23 wt. % in Cr) (Lai, 1999) exhibit a very protective behaviour at 500°C, and NiCr and FeCr coatings deposited by thermal spray, also show good results which were dependent, not only on the composition and Cr content but also on the quality of the coatings (Varis, 2013). It was also found that at 750°C tested in a biomass plant for 1300 h Ni<sub>46</sub>Cr and Ni<sub>46</sub>Cr<sub>1</sub>Ti deposited by thermal spray behaved significantly better than IN625 (22 wt. % in Cr) and Ni<sub>21</sub>Cr<sub>10</sub>W (Oksa, 2016). Sealing Ni based Cr containing alloys with an alumina based paint also proved to be beneficial in a 100% waste wood fired bubbling fluidized bed (Okoro, 2018). Finally detonation and HVOF sprayed Ni<sub>50</sub>Cr showed excellent results in the water walls of a waste incinerator for 7 years and when tested in the lab for 72 h at 600°C showed significantly better behavior than IN 625 and other Ni based alloys (Yamada, 2002)

Regarding Fe-Al intermetallics former of Al oxide, the results available in the literature do not show agreement, as for instance, an aluminide coating on P91 with the FeAl phase at the surface could form protective oxides whereas the richer Al containing phase Fe<sub>2</sub>Al<sub>5</sub> was attacked across the entire surface when KCl was present at 600°C under air (Kiamehr, 2017). In contrast, other work showed the opposite trend when exposing the same two phases to KCl/K<sub>2</sub>SO<sub>4</sub> at 550°C under a model oxycombustion atmosphere (Agüero, 2018), and other researchers observed that Fe<sub>45</sub>Al suffered from a significantly lower attack than Fe<sub>10</sub>Al and Fe<sub>20</sub>Al in contact with KCl at 650°C (Li, 2004). Moreover, it was found that the corrosion resistance of several coatings and materials immersed in a KCl/K<sub>2</sub>SO<sub>4</sub> mixture under air at 650°C depended on the Al content and on the distribution of Cr within the coatings (Vokál, 2008). In fact, the degree of corrosion of Fe<sub>2</sub>Al<sub>5</sub> on P91 was the lowest even when comparing it with lower Al containing coatings on other higher Cr substrates such as Alloy 800 and 17Cr-13Ni. Combining Cr and Al in FeCrAl coatings is another alternative that has been explored. Fe<sub>21</sub>Cr<sub>5</sub>Al<sub>3</sub>Mo showed excellent

performance at 330°C in a 100% waste wood fired bubbling fluidized bed boiler (Davis, 2018). The effect of Si has also been studied for instance in FeCrAl model alloys at 600°C in contact with KCl. Si contributed to resist breakaway corrosion and reduced the thickness of the corrosion products (Eklind, 2018) whereas peroxidation to form a protective  $\alpha\text{-Al}_2\text{O}_3$  scale also helped to improve its corrosion behaviour at 560°C in contact with KCl (Okoro, 2018).

Ni based intermetallic coatings have also been explored and  $\text{Ni}_2\text{Al}_3$  coatings have shown promising behaviour in the laboratory (Dahl, 2018) but tend to spall when tested on a boiler (Wu, 2018). It is very interesting however, that remains of detached coatings were found within the corrosion products and ashes, indicating that the problem for these coatings is the adhesion to the substrate rather than the composition. Ni31Al coatings applied by HVOF were also studied at 700°C in contact with KCl (Bai, 2018) whereas Ni5Al was exposed to KCl/ $\text{K}_2\text{SO}_4$  at 550°C and in both cases the coating failed due to oxidation at the coating substrate interface. The penetration of corrosive gases may have started from the samples edges of through pores and coating defects. The Ni5Al coating tested at 550°C also showed corrosion at coating surface. A NiCrAlY coating applied by HVOF was tested in contact with KCl at 600°C for 168h and showed evidence of inter-lamellar corrosion (Sadeghimeresht, 2018).

Summarizing the findings, welded IN625 is the current choice of the industrial sector at least up to 550°C. The general trends indicate that:

- Ni base materials rich in Cr are so far the best performers
- There are controversies regarding the behaviour of alumina formers, aluminide of FeCrAl type.
- It is clear that thermal spray coatings need to be either free of pores and defects or treated to avoid permeation of the corrosive species.

Since the main goal of BELNUS is to reduce costs referenced to welded IN625, efforts will be undertaken to develop less costly solutions based: 1) on lower cost deposition techniques such as thermal spray or slurry application or b) clarify the behaviour of aluminides and FeCrAls and study the behaviour of FeCr with higher Cr contents. The effect of minor alloying elements such as Si will also be explored in Belenus as well as the use of sealants and peroxidation treatments.

#### 4.1. Power plant operating experience with coatings for corrosion protection

Power plant boilers firing all types of fuel have often employed corrosion resistant materials as a corrosion protection system for the commonly employed low alloy tubing used to fabricate a large proportion of the boilers. Low alloy steels are used as the predominant construction material due to their low cost and ease of fabrication. Higher alloy and hence expensive materials are only used in circumstances where the properties of the low alloy steels do not provide adequate or economic design lives, for example at high temperature where creep effects are encountered, or where corrosion results in premature tubing failures. Where creep effects and minor to moderate corrosion rates are encountered ( $<100\text{nm/h}$ ), austenitic stainless steels are frequently utilised.

However, where corrosion rates are greater, the use of often relatively costly corrosion resistant materials as a protective coating is a commonly employed approach that enables lower alloy materials to be used in more aggressive environments.

The form of the coatings that have been used is varied, ranging from mechanically bonded sprayed systems applied by techniques such as (double) arc wire, plasma and High Velocity Oxy-Fuel (HVOF) and its variants, to metallurgically bonded systems such as weld overlays or co-extruded tubing. Each technique has its benefits and limitations and may be used to a greater or lesser extent in different parts of the boiler.



Sprayed coatings are frequently applied at thicknesses of less than 1mm, but can in some circumstances be applied to thicknesses of several mm. Arc wire coatings have a tendency to be porous and if not sealed may not be effective barriers between the tubing and the corrosive environment and not further over coated by some form of sealant material. The plasma spray process has been used since the 1980s but can be intolerant of poor application practises which can result in unexpectedly poor quality coatings that have excessive voidage or oxide content, and as a result, have been largely replaced by HVOF coatings. HVOF is in general more tolerant of operator error with fewer incidences of producing poor quality coatings. All sprayed coatings are mechanically bonded to the substrate tubing and, as such, require stringent controls on tube surface preparation, generally to Sa3 white metal. Sprayed coatings are also relatively brittle and therefore not amenable to tube manipulation or welding after coating application. However, sprayed coatings can be very useful for in-situ repairs of damaged boiler tubing provided good line of sight access is available to the affected area. Due to the relatively low heat input to the substrate tubing, it is possible to apply the coatings without requiring cooling (water filled) of the tubing to avoid distortion. The techniques can involve the generation of large quantities of noise, dust and fume which means that when coatings are being applied within boilers all other activities must be suspended. Operators frequently require forced clean air supplied helmets in addition to the normally expected personal protective equipment with the boiler fans also being used to expel fume and vapours from the boiler gas pass.

Weld overlay coatings are frequently applied by either Tungsten Inert Gas (TIG) or Metal Inert Gas (MIG) methods but other techniques such as Pulsed Arc Transfer (PAT) or, to a lesser extent laser cladding. These may use either wire or powder feed / consumables, the latter potentially having reduced application efficiencies. Weld overlay methods produce coatings that are normally fully dense and metallurgically bonded to the substrate tubing ensuring no loss or spalling in service, but this does result in a higher heat input during application. High heat input may limit application to tube materials such as the Creep Strength Enhanced Ferritic (CSEF) alloys such as T23, T24 or T91, or other 9% - 12% chromium variant alloys which ordinarily require post weld heat treatment to achieve acceptable hardness values. Due to the high heat input it is normal practise for tubing to be water filled whilst being clad in order to avoid distortion, with this potentially being in conflict with a requirement for weld preheating. Water cooling may be readily achieved in the workshop but if being applied in-situ / retrospectively within a boiler, requires the boiler section to be water filled. This can limit other boiler works given that the boiler would need to hold water. Weld overlay materials frequently, but not always, exhibit significant ductility and as a result, clad tubing may be manipulated and bent after cladding application, enabling tubing arrangements with relatively complex geometries to be fabricated.

Co-extruded tubing is a particular case of metallurgically bonded corrosion resistant material applied to either a low alloy steel, or occasionally and historically, a high strength austenitic alloy. In instance the cladding material is applied during the production / drawing of the substrate tube. In furnace wall applications a Type 310 austenitic stainless steel was co-extruded with plain carbon steel core. The austenitic stainless steel provided fireside corrosion protection to the carbon steel tubing in pulverised fuel fired boilers that suffered severe (>200nm/h) wastage rates using high chlorine coals. The carbon steel core in turn protected the austenitic stainless steel from the risk of stress corrosion cracking from the internal waterside environment. Prior to the development of high creep strength austenitic steels such as HR3C (TP310Nb), boilers which required creep resistant alloys could make use of Eshette1250 austenitic stainless, although with only 15% chromium, this alloy had only marginally acceptable corrosion resistance. To remedy this situation Eshette1250 was co-extruded with the corrosion resistant, but creep weak TP310 austenitic stainless steel containing 25% chromium. A further specialist case of co-extruded boiler tubing was the combination of the austenitic Sanicro28 and the low alloy ferritic steel 10CrMo910 (T22) which was produced by Sandvik for use in the Kraft paper / black liquor boiler furnaces, which are particularly corrosive. Where alloys cannot be extruded due to cracking and tearing, in rare

instances tubing has been produced by co-compaction. A final superheater stage in a UK coal fired boiler was retrofitted with Alloy800 substrate tubing on to which had been co-compacted (hot iso-statically pressed) a dense, metallurgically bonded layer of IN617 (50Ni50Cr). Such an application would be considered extremely costly and has not been repeated.

Many corrosion resistant coating alloy compositions have been trialled in research projects to combat fireside corrosion as may occur in boilers firing a diverse range of fuels although a relatively small number of alloy types are commonly encountered. In coal fired boiler furnace sections 50Ni50Cr was commonly applied using plasma spray techniques. With more stringent NO<sub>x</sub> emission limits and deeply staged combustion environments (i.e. delayed combustion and expanded flame envelopes) corrosion protection was commonly provided by the weld overlay application of either Alloy625 or, latterly Alloy622. Alloy622 has a narrower freezing range than Alloy625 and is thus subject to less segregation / coring on solidification, this enabling the Alloy622 to better resist circumferential, interdendritic cracking. Thermal spray coatings, based predominantly on Alloy625, but also C276 may also be applied to protect low alloy steel tubing, and may in some instances also be used to repair corroded weld overlays.

For biomass and waste to energy plants, the most commonly selected corrosion protection system is Alloy625 weld overlay, with the performance of all other protective systems judged with reference to this “standard” protective system. Given its extensive use this cladding system is available commercially from a number of different suppliers internationally. Other weld overlay alloys have also been used such as Alloy59, Alloy686, 20-25Nb. Iron based coatings such as Kanthal APMT have been used in small scale trial applications but have yet to be used for large scale commercial protection. Thermal spray coatings, most frequently applied by HVOF or similar variants are offered by a number of commercial coating applicators operating within the power industry. Within Europe suppliers such as Castolin Eutectic, Hauser or Integrated Global Solutions (IGS) are employed by plant operators and boiler manufactures to apply protective coatings. Frequently the coatings used by such suppliers are proprietary and their compositions may not be known in great detail, although it is believed that many compositions are derivatives of the common Alloy625 or C276. As noted above the thermal spray coatings may also make use of sealant coatings which may be either brush or spray applied and based on ceramic systems, again frequently of unknown proprietary compositions. Double arc wire systems may also be encountered, again using proprietary materials which may include cored wire consumables containing (burnable) materials which form carbide or boride containing coatings for added erosion resistance.

## 5. Summary and Gap Analysis

Work Package 1 “Foresight & Definition of Requirements” has 7 sub-tasks with Task 1.2 being the “Selection of Alloys and Coating Systems”. One milestone and one deliverable covered the works conducted under Task 1.2. The milestone identifying/agreeing the alloys and coatings to be trialled/evaluated during this project namely M1.2 “Initial alloy and coating system selected” has been issued to the partners and included in appendix A for completeness. The deliverable D1.2 “Collation of data sources: coating performance” is an overview of the experimental and service experience taken into consideration when selecting the alloys and coating to be evaluated during the rest of the project and is considered as the final deliverable under this task.

From the data provided in previous sections a list of conclusions can be drawn.

- Cleaner fuels such as virgin wood are easiest to fire, give the least operational problems and have the most scope for efficient (high steam temperature) plant and, as such, these attract a premium fee. Increasing levels of impurities lead to fuels which are more difficult to fire, have greater propensity for fouling and corrosion and consequently are utilised in less efficient boilers with relatively low final steam temperature and pressures. Some of the dirtier, waste biomass streams such as poultry litter, meat and bone meal, food wastes or by-products of other bio-fuel production (glycerine) can be extremely aggressive when fired, but form a considerable percentage of the fuel fired in some boilers as they would otherwise have been directed to landfill.
- Whilst coal ash is dominated by alumina-silicate, iron and calcium, most biomass ashes tend to be rich in compounds of calcium, potassium, silicon, phosphorous, sodium and magnesium. These elements can be further divided into non-volatile elements such as silicon, calcium, magnesium, semi volatile elements such as phosphorous and volatile elements such as potassium and sodium. During combustion semi-volatile and especially volatile elements are partly released from the fuel and are free to react with other elements in the flue gas such as sulphur, chlorine and CO<sub>2</sub>.
- The ash deposits that form on downstream gas-side surfaces of biomass combustion systems therefore tend to be rich in salts of the volatile alkali metals (primarily potassium), principally as chlorides and sulphates, depending on fuel composition and gas / metal temperatures. The chemistry of the deposits tends therefore to be very different from that of coal ash deposits, particularly in terms of chlorine / sulphur ratio and alkali metal content.
- Alkali or heavy metal chloride containing ash phases can also be condensed onto the tubes from the gas phase. At relatively low temperatures these may be in solid form and serve to moderately increase the corrosion rate through increasing the concentration of chlorine in the environment local to the tube surface. At higher tube metal temperatures the alkali or heavy metal chloride ash deposits can be molten.
- The corrosion rates can be dramatically increased as the molten ash deposits actively dissolve the protective corrosion scales that would ordinarily have formed on the tube surface. This effectively removes any diffusion barrier that might have existed between the tube metal and the combustion environment, allowing free access for the corrosive environment to interact with the bare tube metal. Such molten chloride attack can result in catastrophic wastage rates (>200nm/h) causing tube failures in less than one year of operation.
- The potential for slagging is based on the ash fusion behaviour, both of individual fly ash particles and of the surface of the slag itself. The fusion behaviour of ash is a complex process and is best described in terms of a melting curve. Most coal ashes are composed primarily of alumina-silicate minerals which are refractory by nature. The main fluxes that will act to reduce the viscosity of an alumina-silicate melt and promote slagging are the oxides of iron, calcium and sodium and high levels of these elements in the ash will tend to increase slagging propensity. Iron can occur in either the Fe<sup>2+</sup> or Fe<sup>3+</sup> oxidation states and it is well recognised that reducing conditions promote slagging because of the greater solubility of ferrous oxide in an alumina-silicate melt.

- Whereas slagging is a bulk phenomenon, fouling is the formation of deposits as a result of the inertial impaction of fly ash with low melting point compounds (dominant mechanism for coal) and deposition of sticky volatile species by a condensation or thermophoresis mechanism (more important for biomass). The volatile species will condense onto heat exchange surfaces as they pass through the furnace, initiating deposit growth and acting as a chemical bond between non-volatile ash particles which adhere to the deposit. This is most likely to arise in the high temperature convective pass starting at what is normally the secondary superheater pendant tube bank. The build-up of deposits in this area can lead to “laning” and higher metal temperatures due to forcing the gas flow through a reduced area, reduced load due to loss of ID fan power, and ultimately to a forced outage.
- Although fouling indices for coal are mainly based on sodium content, those for biomass are based on total alkali content. One index is based on the mass in kg of alkali metal oxides ( $K_2O + Na_2O$ ) introduced into the system per GJ heat input to the furnace. At index values above  $0.17 \text{ kg.GJ}^{-1}$ , significant fouling of the boiler convective section is probable. At index values in excess of  $0.34 \text{ kg.GJ}^{-1}$ , severe fouling is to be anticipated. Most biomass materials, and particularly those from fast-growing plants, will have index values in excess of  $1 \text{ kg.GJ}^{-1}$ , whereas most coals have relatively low values, generally less than  $0.1 \text{ kg.GJ}^{-1}$  (Miles, 1996)
- One key method to reduce the risk of chloride ash driven fireside corrosion is to limit the levels of alkali chloride species in the flue gas. In the presence of sufficient free sulphur, potassium and sodium will preferentially form sulphate rather than chloride, with the excess chloride forming HCl in the flue gas. Gaseous HCl plays little part in the high temperature superheater / reheater fireside corrosion process. The rate of sulphation is believed to be determined by the rate of  $SO_2$  conversion to  $SO_3$ . For effective sulphation, a free sulphur to chlorine ratio of 4:1 is generally recommended. However, native levels of sulphur in most biomass fuels are very low, and the level of free sulphur in the flue gas is reduced still further by reaction with any calcium carbonate which is a significant component of the majority of biomass ashes.
- Three groups of additives have been identified that modify fouling behaviour. All three species have the ability to react with potassium and sodium chloride and create higher melting point crystalline phases, potassium and sodium chloride are also removed from the gaseous phase. The addition of aluminosilicates such as kaolin  $Al_2Si_2O_5(OH)_4$ , or bentonite  $Al_2O_3(SiO_2) \cdot 2H_2O$  will cause reactions between potassium silicates to form higher melting point temperature potassium alumina-silicate systems, as well as reactions with KCl.
- Sulphur based additives such as ammonium sulphate, or elemental sulphur have the effect of converting KCl into  $K_2SO_4$  which has a higher melting temperature, reducing deposition issues. In addition the chlorine is reduced in the fouling deposits, mitigating chlorine induced corrosion. Calcium based additives such as  $CaO$ ,  $CaCO_3$ ,  $Ca(OH)_2$  and dolomite  $CaMg(CO_3)_2$  are relatively ineffective for fuels with high alkali and chlorine contents unless the biomass contains reasonable levels of phosphorous. The use of calcium and phosphorous together in the form of dicalcium phosphate (DCP) and monocalcium phosphate allows enhancement of calcium in potassium phosphates which can strongly increase their melting temperature (Wang, 2012).
- $SO_3$  also has great benefits in terms of reducing the tendency to form alkali chloride containing ash deposits and as such there could be benefits obtained through re-engineering  $SO_3$  injection system so that the gas can be introduced into the furnace area. Sulphur containing additives are often used in power plant boilers operating with final steam temperatures of  $540^\circ\text{C}$  or less, and similarly work by forming alkali sulphates to prevent the formation of alkali chlorides. However, significantly greater quantities of sulphur are required as in normal combustion most of the sulphur is converted to  $SO_2$ , whilst  $SO_3$  is required to effectively remove the alkali metals through the formation of sulphates.
- ChlorOut is a process developed and patented by Vattenfall AB and now marketed by a spin out company Chlorout AB. A sulphate solution is sprayed into the freeboard of a boiler before the first superheater bank. The sulphate decomposes in the flue gas to release  $SO_3$ , which then reacts with the alkali chloride species to give HCl and alkali sulphate.

- Monitoring of corrosivity rates is conventionally conducted using corrosion probes inserted into the furnace either permanently installed or periodically, with probe sections either removed for examination or electrostatic noise summation. Indirectly the corrosivity may be estimated from ash samples where the composition of the ash gives an indication of the species present. Furnace wall tubes in subcritical boilers are not subject to creep and for the most part will be life limited only by the fireside corrosion damage.
- The principal means of on-line control of deposition is the use of sootblowers. The high velocity jet of steam, water or air employs a combination of mechanical impact and thermal shock to break up deposits and remove them. Sonic sootblowers are an alternative solution that may be deployed particularly for the removal of relatively weak deposits in the cooler parts of boiler convective sections, whilst Shock Pulse Generators (SPG) may also be used to prevent ash accumulations. Sootblowers are the most established technology for removing ash deposits from boilers surfaces and ensuring effective heat transfer.
- As well as control of fuel ash content, other measures are available to alleviate erosion. This includes the use of baffles and shields for high velocity or turbulent areas within the gas pass
- Erosion within boilers is closely related to the gas velocity, with erosion being proportional to the velocity raised to the power of 2 to 4. The erosivity of the ash is also closely related to the amount of hard materials such as quartz contained within it. Coals frequently contain 10 – 15% ash, of which a large percentage is either alumino-silicate material or quartz. In comparison wood fuels contain substantially less ash (~1%), of which silica is frequently a lower proportion. Erosion is not expected to be an issue for converted PF boilers and to date no issues have been reported elsewhere firing 100% wood pellet.
- Given the difficulties in predicting wastage rates it is common for plants to be constructed using low alloys materials and put into service with the minimum corrosion protection that the equipment suppliers expect to be necessary. The extent of fireside corrosion damage is then assessed after approximately one year of operation and at this latter stage, options for corrosion protection would be considered to protect areas exhibiting significant corrosion damage. The industry typical protection system is to use IN625 weld overlays, applied either in the workshop to new replacement tubing, or applied in-situ to existing damaged tubing.
- Warneke (2004) developed a diagram representing gas and metal temperatures within the municipal waste fired boiler at Flingern, Düsseldorf, Germany. The diagram has been used by biomass boiler makers to define safe operating gas and metal temperatures for the different stages of evaporator and superheater in biomass fired boilers. For each boiler stage the expected tube metal temperature range and range of expected combustion gas temperatures are plotted. Wastage rates are not predicted from the diagram, rather areas of low (shown as white), indifferent (pale grey) and high wastage rates (dark grey) are predicted, with a further qualification of these zones according to local gas velocities. The diagram is used as a design tool, with the aim being to maintain the tube metal temperatures within the benign (white) areas, or, where this cannot be avoided, to identify vulnerable tubing that will likely require higher alloy tubing or the use of protective coatings.
- An alternative to mitigate corrosion and allow operation at higher temperatures and pressures is the use of highly-corrosion resistant coatings that can significantly increase the life of Ni- base materials or even allow the use of lower cost alloys such as austenitic and ferritic steels. These include weld cladded, thermal spray and diffusion coatings among others. Some of these coatings are very protective, as for instance fused NiCrSiB applied by thermal spray and composites incorporating ceramic materials such as SiC, Al<sub>2</sub>O<sub>3</sub>, Zr<sub>2</sub>O<sub>3</sub>. Alloy 625 applied by weld overlay has been used for over 10 years in biomass fuel plant operating at 500°C with a maximum corrosion rate of 200 µm/year.
- There is no general agreement regarding the optimal compositions capable of withstanding biomass corrosion, likely due to biomass diversity. In general, protective coatings work by developing a stable protective oxide scale, usually based on Al or Cr, and the coating must have sufficient amount of these elements, so that if the oxide breaks and/or spalls it can be reformed immediately. Summarizing the current state of the knowledge for coatings, welded IN625 is the current choice of the industrial sector at least up to 550°C. The general trends indicate that:

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- Ni base materials rich in Cr are so far the best performers
- There are controversies regarding the behaviour of alumina formers, aluminide of FeCrAl type.
- It is clear that thermal spray coatings need to be either free of pores and defects or treated to avoid permeation of the corrosive species.

The main gap in the current state of the knowledge is how coating and alloys will behave at temperature up to 650°C, which is effectively the object of this project, i.e. to generate data in this area.

Another knowledge gap is the effect of the coating on the mechanical integrity of the tubes. With increasing temperature creep related failure mechanism may become significant. To date biomass plant failures have predominantly been associated with corrosion and/or erosion but with increasing temperature the high temperature mechanical properties of the alloy/coating system needs to be considered. Some of these issues will be addressed in WP3 “Lab Scale testing, Characterisation and Monitoring” and WP5 “New Welding and Structural Integrity Strategies: Assembly of Boiler Structures”.

## 6. Degree of Progress

Milestone M1.2 “Initial alloy and coating system selected” has previously been issued to the partners. With the issue of this report deliverable D1.2 is considered to be complete.

Consequently with M1.2 and D1.2 issued Task 1.2 “Selection of alloys and coating system” is completed.



## 7. Dissemination Level

Deliverable D1.2 “Collation of data sources: coating performance” will be issued to all BELENUS partners via email and copies lodged on the BELENUS database. Deliverable D1.2 will also be uploaded to the EU portal by the project Co-ordinator.

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## 9. Appendix

Milestone M1.2 “Initial alloy and coating system selected”

<b>Alloy Substrates</b>				
	Round Robin <sup>(1)</sup>	Main Programme	Pilot Plant	Commercial Plant
T24		X		
MarBN		X		
SVM12	X	X	X	X
HR3C		X	X	
347HFG		X		

(1) Round Robin between testing laboratories for calibration

<b>Coatings - INTA's Offering</b>		
	<b>Coating type and composition</b>	<b>Coating Acronym</b>
1	Fe slurry aluminide	<b>isFeAl</b>
2	Ni electrodeposited-slurry aluminide	<b>isNiAl</b>
3	Ni electrodeposited- slurry Cr aluminide	<b>isNiCrAl</b>
4	Si modified Fe slurry aluminide	<b>isSiFeAl</b>
5	SiCrAl slurry aluminide	<b>isSiCrAl</b>
6	Ni electrodeposited- slurry SiCr aluminide	<b>isNiSiCrAl</b>
7	Oxidized HVOF FeCr	<b>ihFeCrOx</b>
8	Oxidized HVOF NiCr	<b>ihNiCrOx</b>
9	HVOF FeCr + Al	<b>ihFeCr+Al</b>
10	HVOF NiCr + Al	<b>ihNiCr+Al</b>
11	HVOF HfS + Al	<b>ihHfS+Al</b>
12	HVOF IN625	<b>ihIN625</b>
13	HVOF FeCr + slurry aluminizing	<b>ihFeCr+sAl</b>
14	HVOF NiCr + slurry aluminizing	<b>ihNiCr+sAl</b>

<b>Coatings - TEandM's Offering</b>		
	<b>Coating type and composition</b>	<b>Coating Acronym</b>
15	HVOF IN625	<b>thIN625</b>
16	Laser clad IN625	<b>tlIN625</b>
17	HVOF Co28.5Mo17.5Cr3.4Si	<b>thCoMoCrSi</b>
18	Laser Co28.5Mo17.5Cr3.4Si	<b>tlCoMoCrSi</b>
19	HVOF Fe50Cr	<b>thFeCr</b>
20	Laser Fe50Cr	<b>tlFeCr</b>
21	EAWS Fe50Cr	<b>teFeCr</b>
22	APS ZrO <sub>2</sub> +24CeO <sub>2</sub> +2.5Y <sub>2</sub> O <sub>3</sub>	<b>taZrCeYO</b>

<b>Coatings - SMT (Kanthal) Offering</b>		
	<b>Coating type and composition</b>	<b>Coating Acronym</b>
23	Overlay welded FeCrAl1	<b>swFeCrAl1</b>
24	Overlay welded FeCrAl2	<b>swFeCrAl2</b>
25	Overlay welded Kanthal APMT	<b>swAPMT</b>
26	Overlay welded A625*	<b>swA625</b>
27	Bulk FeCrAl1	<b>sbFeCrAl1</b>
28	Bulk FeCrAl2	<b>sbFeCrAl2</b>
29	Bulk Kanthal APMT	<b>snAPMT</b>
30	Sandviken	<b>tba</b>
31	HVO/AF FeCrAl1	<b>shFeCrAl1</b>
32	HVO/AF FeCrAl2	<b>shFeCrAl2</b>
33	HVO/AF Kanthal APMT	<b>shAPMT</b>

