Kurzfassung
Lebensdauerverlängerung für Kesselwandrohre in biomassebefeuerten Kesseln

Introduction
A 100% biomasse fired Bubbling Fluidised Bed (BFB) boiler began operations in 2014, supplying heat and power in a European Union country. Greater than anticipated boiler tube wall thickness losses were identified in the furnace chamber beyond the regions protected by the originally installed refractory and Alloy625 weld overlay. To mitigate future wastage and maintain reliability of the unit, the boiler was retrofitted with additional Alloy625 weld overlay, and additionally, the operator wanted to consider alternative tube protection technologies in case further protection might be required. Any solution adopted needed to be fit for the intended purpose, and provide a high degree of reliability over an extended period for this fuel-boiler-combination. Laboratory performance evaluations are somewhat limited in accuracy, being at best only a ranking tool, often neglecting critical variables such as heat flux and fluctuations in operating environment common in commercial boiler plant. Accordingly, a 1 m long tube insert was made having several different corrosion resistant materials and application technologies for evaluation in a detailed, in-service test enabling assessment of their relative performance over an extended period.

Boiler and exposure details
The trial of the corrosion resistant coating and cladding systems was completed in the waste wood fired, BFB boiler that operated year-round at base load. With a drum pressure of ~88 bar it was estimated to have a tube metal surface temperature of ~350°C. The 1 m long trial tube was installed in the upper furnace side wall adjacent to a retrofit Alloy625 clad panel, located downstream of all combustion air input and the urea injection used for NOx control, Fig. 1. Whilst not measured during the exposure, the boiler drawings suggested an approximate mean gas temperature at this position of 1,070°C and a velocity of 6 m/s, although given the position at the side wall, the actual gas temperature and velocity would likely have been lower. Whilst this area of the furnace wall would not be considered the most corrosive within the furnace section, and as such, was not protected by any corrosion resistant coating or cladding, it was possible to conduct an exposure for an extended period with a minimum risk of causing a tube leak and without compromising any existing corrosion protection systems or warranties associated with the refractory and Alloy625 cladding. The trial tube was installed during a planned annual maintenance and inspection outage and removed during the following annual outage after exposure for a total of 7,965 operating hours.

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Fig. 1. Schematic location of the trial tube insert.

The furnace walls at this location comprised membraned PG235GH plain carbon steel tubing having dimensions 57.0 mm outside diameter x 5.0 mm wall thickness. Periodic cleaning of the furnace walls was achieved using a shower cleaning system. The wood fuel fired was predominantly demolition wood and contained an average 21% moisture, 3% ash, 0.06% sulphur and 0.12% chlorine on an as received basis, with a Net calorific value (Lower Heating Value) of ~14 KJ/kg. The mean ash composition included ~890 mg/kg sodium, 980 mg/kg potassium, 210 mg/kg lead and 125 mg/kg zinc. The wood fuel excluded materials such as railway sleepers, telegraph poles or any material treated with...
Chlorine in the fuel readily reacts with volatile chloride rich corrosion scale is observed being a function of fuel chemistry and whether combustion is complete. Boiler furnace and final steam design temperatures are limited by the fuel to be combusted, with different manufacturers adopting particular firing methods and temperature limits for a given fuel chemistry. Design temperatures progressively decrease as the fuel chlorine, alkali and heavy metal contents increase. Chlorine in the fuel readily reacts with volatile alkali metals to produce alkali metal chlorides, (Na+K)Cl, in the gaseous vapour phase. This readily condenses as ash deposits on to the relatively cold (compared to the gas) tube metal surfaces, where it interacts with the normally protective oxide scales. The chloride rich ash inhibits the growth of a dense, duplex oxide scale which would ordinarily act as a diffusion barrier to limit further corrosion. Frequently a chloride rich corrosion scale is observed between the oxide scale and the metal surface, that under the influence of a heat flux leads to rapid diffusion of corrosives and corrosion products, with chlorine being continuously recycled within the corrosion scale.

In addition to the alkali metals found in clean wood fuels, waste wood fuels frequently contain heavy metals such as lead and zinc. These metals similarly react readily with chlorine and further contribute to the transport of chloride rich ash to the tube metal surface, increasing the corrosivity of the ash deposit and combustion environment.

Under these conditions the dense corrosion scales are frequently disrupted forming instead defective, multi-laminated scales that have much reduced mechanical properties. These scales are vulnerable to erosion damage and loss in a process termed corrosion-erosion, in which the corrosion scales only are lost, leaving the underlying tube metal with significantly reduced protection from further corrosion. Any feature within a boiler that increases the local gas velocity will very likely increase the corrosion-erosion rate. This effect was summarized by Wannecke in the intended “Flingern corrosion diagram” [1].

**Damage mechanisms**

Furnace wall tubing metal loss in biomass fired boilers is dominated by fireside corrosion, influenced by metal temperature (boiler pressure), gas temperature (heat flux) and combustion environment, the latter being a function of fuel chemistry and whether combustion is complete. Boiler furnace and final steam design temperatures are limited by the fuel to be combusted, with different manufacturers adopting particular firing methods and temperature limits for a given fuel chemistry. Design temperatures progressively decrease as the fuel chlorine, alkali and heavy metal contents increase. Chlorine in the fuel readily reacts with volatile alkali metals to produce alkali metal chlorides, (Na+K)Cl, in the gaseous vapour phase. This readily condenses as ash deposits on to the relatively cold (compared to the gas) tube metal surfaces, where it interacts with the normally protective oxide scales. The chloride rich ash inhibits the growth of a dense, duplex oxide scale which would ordinarily act as a diffusion barrier to limit further corrosion. Frequently a chloride rich corrosion scale is observed between the oxide scale and the metal surface, that under the influence of a heat flux leads to rapid diffusion of corrosives and corrosion products, with chlorine being continuously recycled within the corrosion scale.

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**Solutions in the market**

The most tried and trusted solution to manage excessive fireside corrosion in the furnace section is to apply nominally 2 mm of Alloy625 weld cladding to the plain carbon steel tubing, either in the workshop prior to installation or, within the boiler during a maintenance outage. Ordinarily Alloy625 can be expected to have an order of magnitude lower wastage rate than plain carbon or low alloy steels. To avoid distortion the tubes must be water filled during the cladding process and have a remaining wall thickness of at least 2 mm. Cladding does have the advantage of a metallurgical bond to the substrate tube ensuring no risk of spallation.

The use of thermally sprayed coatings is gaining greater acceptance as an alternative to Alloy625 weld cladding. Initial attempts to employ traditional twin arc wire spray (TWAS) with NiCrMo alloy wire feedstock have been relatively unsuccessful. High levels of coating permeation by corrosive species in high moisture content environments can cause corrosion at the coating interface and delamination. Coating permeation may occur through a number of chemical and structural weaknesses in a coating. These are simple porosity, high oxide content, particle micro-cracking and through coating macro-cracking due to elevated stresses.

More recently, the use of High Velocity Thermal Spray processes ensure that coating thickness is comprised of a more finely structured coating, with lower porosity and greater homogeneity. Changes in feedstock chemistry have further improved performance by significantly reducing stress, increasing bond strength and mitigating oxide content. By addressing the root cause of these microstructural defects through process and material chemistry, thermal spray may be successfully employed in the field, during shutdowns, with higher production rates and lower costs [2]. As with welding and other coating technologies, that are more commonly understood than thermal spray, surface preparation, material, process and procedure criteria should be well defined in coating specifications.

**Test description**

Five different commercial, near commercial and development coatings were applied to a 1m length of PG235GH plain carbon steel tubing as used in the furnace walls, with coatings fully characterised and measured prior to installation and exposure.

A partial financial contribution by the Swedish Energy Agency, via the KME718 project “High Temperature Corrosion in Waste Wood Fired Boilers”, enabled Sandvik Material Technology (SMT) to use weld overlay techniques to apply Sanicro60, an equivalent of Alloy625, and the iron based Kanthal APMT alloys. Integrated Global Services (IGS) used a thermal spray technique to apply an iron based nanosteel type coatings, Weartech SHS7574.

Duplicate samples of each coating were also applied to a second 0.5 m length of tubing which was used to characterise the cladding and coatings in the as applied, unexposed condition. Each of the coatings were applied in full circumferential bands nominally 150 mm wide, leaving 50 mm uncoated “green ends” to enable site welding into the boiler furnace wall. Two bands of the Sanicro60 alloy were applied, one at each end of the insert. This arrangement provided both unprotected plain carbon steel and Alloy625 equivalent reference bands at ends of the trial tube. To avoid damaging the applied coatings, instead of using membrane fins to make a gas seal, a box was welded to the outside of the furnace wall which was then packed with refractory, Figure 2.

![Fig. 2. Trial tube welded into position before fitting of the external refractory filled box.](image)

Following exposure, the trial and surrounding tubes were found to be covered with a pale coloured ash deposit. The trial tube could only be distinguished by the oversize weld overlay and a slight reduction in brown colouration associated with the inclusion of iron based corrosion products on the adjacent unprotected tubing, Figure 3.

After removal the majority of the ash deposit was removed from the exposed half of...
the trial tube to reveal the trial coatings and unprotected tube ends, Figure 4. Whilst the unprotected tube ends had undergone obvious fireside corrosion damage, the weld and laser clad sections still exhibited the original surface profile. The seal coat applied to the thermal spray coats also appeared to have suffered no visible damage.

**Laboratory Assessment**

Upon receipt at the Uniper Technologies laboratory, the tube was first encapsulated in epoxy resin prior to the removal of circumferential and axial specimens as required for detailed metallography and metal loss determinations. Where possible the samples were cut and prepared without water based lubricants so as to preserve any water-soluble ash species. This was not always practical for the harder coatings such as the NanoSteel and carbide/boride filled thermal spray coatings, which were instead cut using flood cooled abrasive wheels.

After mounting in cold curing, glass filled, epoxy resin, the samples were ground, then polished to a 1 µm diamond finish.

The samples were examined using optical microscopy and Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Elemental Analysis (EDX).

The unprotected tube sections at the top and bottom of the insert exhibited irregular general attack over the full exposed surface, the greatest damage occurring at the tube crown (12 o’clock position). The top unprotected section (remote from the nose slope) appeared in worse condition with greater obvious surface roughening/wastage than the bottom unprotected end, Figure 5a. Corrosion was associated with the formation of an oxide scale which included minor (<1 a/o) indications of sulphur, chlorine, the alkali metals sodium and potassium, and heavy metals zinc and lead. The remaining ash deposit comprised a complex mixture of alkali and heavy metals, most probably present as sulphates and chlorides. Lead was the most common heavy metal detected, typically present at ~6 a/o concentration, with zinc and copper detected at varying lesser concentrations.

Both SMT applied Sanicro60 weld overlay sections, suffered only slight intermittent attack with approximately half of the exposed surfaces, biased towards the sides of the tube, remaining free from observable corrosion. The crown of Sanicro60 weld overlay did suffer slight irregular wastage, pitting or interdendritic attack, forming relatively dense, occasionally laminated corrosion scales, Figure 5b. Where corroded a nickel, chromium and molybdenum rich oxide scale formed that was intimately mixed with combustion derived elements such as sulphur (1 to 8 a/o), chlorine (2 to 4 a/o), alkali metals (0 to 4 a/o) and heavy metals (0 to 8 a/o). Lead was the most common combustion derived heavy metal present within the mixed scale and ash layers, although zinc and copper were commonly found at lesser percentage concentrations. The retained ash deposit exhibited distinct layers which were either essentially free from, or rich in, heavy metals. Where free from heavy metals the ash comprised either silica or alkali and alkali-earth (magnesium and calcium) silicates. The heavy metals were again dominated by lead, either as chlorides or sulphates, or in combination with potassium to form potas-
The UoN applied NanoSteel cladding similarly experienced attack over approximately half of the exposed surface and, in addition, also suffered slight corrosion at the substrate to coating interface via coating through-thickness fissures, Figure 5c. Such fissures were already present in the as clad, unexposed sample and there was no indication of propagation of these fissures into the substrate tube. Where corroded oxide scales formed they were mixed with, or incorporated varying quantities of combustion derived elements. Sulphur and chlorine were typically present at no more than 2 a/o, although occasionally up to 9 a/o sulphur was found, this in combination with alkali and heavy metals, particularly lead sulphate. The sample examined retained levels (<2 a/o) of alkali and (<1 a/o) heavy metals. The sample examined retained potassium-alkali metals. The sample examined retained chlorine, although occasionally the chlorine content was higher at up to 9 a/o. The corrosion scale was found to be a mixed iron, chromium and aluminium oxide, which again incorporated combustion derived elements into the metallic thermal sprayed portions of the IGS1-021 coating, there were very slight indications of alkali metal chloride penetration along interstitial oxides close to the surface of the IGS5-460 coating, and, at one isolated position close to the tube crown (12 o’clock position), alkali chloride was detectable at the substrate tube coating interface. The blue coloured seal coat was found to have been infiltrated by the combustion environment, incorporating low levels of sulphur, chlorine, alkali and heavy metals. In keeping with the observation of potential minor corrosion of the IGS 5460 coating, the associated seal coat was found to occasionally contain minor quantities of nickel oxide.

The assessment of metal losses was performed using optical microscopy. The unprotected upper and lower tube sections suffered maximum metal losses of 560 and 320 μm, corresponding to maximum linear wastage rates of 76 and 43 nm.h⁻¹. The adjacent Sanicro60 weld overlay coatings suffered much lower maximum losses of 62 and 35 μm, almost a magnitude lower than the steel substrate, corresponding to maximum wastage rates of 8 and 5 nm.h⁻¹. The iron based NanoSteel coating offered a degree of protection but still suffered a maximum metal loss of 191 μm, equivalent to a maximum wastage rate of 26 nm.h⁻¹. Despite also being iron based, the Kanthal APMT weld overlay performed very well suffering a maximum metal loss of only 15 μm, or 2 nm.h⁻¹. The best corrosion resistance was found for the sealed thermal spray coatings with the IGS5460 and IGS1021 coatings suffering approximately 3 μm and no discernible attack (<<1 μm) respectively, this equating to <1 nm.h⁻¹ wastage rates.

Discussion and conclusions

The environment local to the trial tube was moderately corrosive giving rise to a maximum wastage rate for the unprotected tube of 76 nm.h⁻¹, at which the wall tubing could be anticipated to achieve an operating life of approximately 60 khrs, or 7 years.

The trial weld overlays Sanicro60 (Alloy625) and Kanthal APMT both exhibited very good corrosion resistance and, given a nominal 2 mm overlay thickness, could be expected provide protection for periods of 200 khrs and 400 khrs, or 22 and 45 years, respectively in a similar environment.

Fireside corrosion of the laser clad NanoSteel was greater than that observed for the weld overlay coatings and despite offering up to 38 khrs, or 5 years, protection to the substrate tube, would likely be less cost effective than the weld overlay coatings. Further difficulties exist due to the through-wall fissuring which could ultimately result in the coating being undercut and spalling, or, the development of thermal fatigue cracking within the substrate tube if the boiler were to be subject to frequent stop start cycles.

The IGS thermal sprayed and sealed coating systems both demonstrated extremely good corrosion resistance with little or no indications of metal loss. With such small metal losses, it was impossible to determine a realistic operating life for these coatings, although it remains highly likely that this would be in excess of that achieved by the weld overlay coatings under similar operating conditions. The corrosion resistance coupled with the ease of application in-situ, makes the selection of such IGS coatings favourable in areas which may traditionally have been protected using Alloy 625 weld overlays.

References


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