

OBJECTIVES

The objectives of this project were;

- To determine the effect of co-firing biomass with coal on boiler tube fireside corrosion rates in existing subcritical coal fired power plants.
- To determine the likely fireside corrosion rates that could be expected on boiler tubing in future advanced (ultra) supercritical power plant.

SUMMARY

Typical and potential boiler tube alloys have been exposed to simulated furnace wall and superheater/reheater environments in the 1MW_{Th} Combustion Test Facility (CTF) at Power Technology.

A total of four nominally 50 hour duration exposures have been completed. Specimens were exposed to a range of metal temperatures, heat fluxes and gaseous environments, representative of pulverised coal combustion under low NO_x conditions with biomass additions. Biomass was co-fired with Daw Mill coal on 20% and 10% thermal or heat input basis (approx 35% and 17% by mass). Specimens were exposed to the combustion environment on air-cooled, precision metrology, corrosion probes.

When co-firing with wood there was no discernable worsening of either furnace wall or superheater / reheater corrosion when compared with firing coal alone. As would be expected, the austenitic stainless steel superheater/reheater specimens exhibited corrosion rates substantially reduced compared to low alloy ferritic T22 specimens. Co-firing with Cereal Co-Product (CCP) yielded high



Figure 1. Superheater Tube Failure due to Fireside Corrosion

furnace corrosion rates under reducing conditions, comparable with that expected when firing coal alone. Under oxidising conditions the furnace corrosion rates were modestly increased from the expected low rates normally encountered. The T22 superheater/reheater specimens also exhibited metal wastage rates slightly increased compared with those measured previously. However, a marked increase in the corrosion was noted in the case of the austenitic superheater/reheater samples, where localised pitting attack resulted in peak wastage rates similar to those measured for the T22 samples.

The data indicate that plant operating at relatively low final steam temperatures ($\sim 540^{\circ}\text{C}$), employing only low chromium containing ferritic alloys, could safely operate whilst co-firing CCP or similar fuel, and expect only slight worsening of existing corrosion rates. However, plant operating at higher steam temperatures ($= 560^{\circ}\text{C}$), which contains austenitic alloys, are potentially vulnerable to greatly enhanced superheater and reheater fireside corrosion attack. Such enhanced attack would lead to a marked reduction in expected tube operating lives when compared to plant firing only coal.

With only two biomass fuels examined it is impossible to fully identify the reasons for the changes in corrosion rates measured. However, it is likely that high alkali metal contents, and specifically potassium, in some biomass materials, are particularly aggressive. Potassium in biomass tends to be bound organically and hence is very

reactive. This compares with potassium in coals, which tends to be un-reactive, being well bound to mineral matter.

Consideration should be given to extending the scope of this work to include other potential biomass fuels, in order to confirm the effects of the fuel composition on wastage rates and identify which fuels can be burnt safely without adversely affecting the operating life of superheater and reheater stages. Corrosion probe exposures in actual operating plant would be required to confirm whether the high wastage rates observed in the short term CTF trials are reproduced over the longer term.

BACKGROUND

With the current environmental pressures to reduce the net carbon dioxide emission to atmosphere from power plant, the co-firing of non-fossil fuels such as biomass is seen as an effective way of delivering targets.

Biomass is regarded as effectively a zero net emitter of carbon dioxide, only releasing recently fixed carbon when combusted. Co-firing biomass in existing boilers is seen as a potential low cost option which achieves the benefits of the high efficiencies achieved in

such plant. Additional benefits may be realised by the burning of biomass in future advanced plant, designed to operate with final steam temperatures approaching 700°C, and achieving even greater efficiencies. The large scale utilisation of biomass in existing coal fired boilers is also seen as a useful way to kick start the energy from biomass industry.

Whilst many years of operational experience and testing have enabled a good understanding of fireside corrosion problems when firing coal, there remains considerable uncertainties regarding the effects of biomass additions to fuel streams. The burning of biomass on its own within power plant can often lead to severe corrosion of boiler tubing. This has resulted in restricted final steam temperatures, reduced efficiency and poor economic viability. The experience in dedicated biomass plant raises concerns as to the corrosive effects when co-firing.

Many potential biomass fuels are available which have widely differing properties and compositions. Plant operators primary concerns include fuel handling, performance impacts and availability of sufficient biomass to warrant undertaking plant modifications. Of the available potential fuels, wood type products and straw based products are two distinct types, are readily available in large quantities and are relatively easily handled in operational plant.

CORROSION TESTING

The techniques employed within the corrosion testing programme were developed as part of previous fireside corrosion programmes undertaken at Power Technology. The CTF enabled realistic furnace conditions to be simulated at pilot scale, whilst realising near laboratory control of exposure conditions. Precision metrology corrosion probes, coupled with metal loss measurement via digital image analysis, enabled metal loss determination to approximately 1µm accuracy, this being necessary in order to measure changes in corrosion rates from such short exposures.

It has previously been demonstrated that corrosion rates within the furnace section are adversely affected by reducing conditions (excess CO / no O₂), together with increasing fuel chlorine and heat flux. Within the superheater / reheater stages, increasing gas temperature / heat flux is also detrimental. Increasing alloy chromium content reduces wastage rates in both furnace and superheater / reheater stages.

Building upon earlier experience, the CTF was chosen to co-fire biomass with pulverised coal. A clean wood based product was co-fired as sawdust by blending with the coal prior to entering the burner. The straw based Cereal Co-Product (CCP) was co-milled with the coal. Up to 15 individual samples of carbon steel, HCM2S (2%Cr), E911 (9%Cr) and HCM12A (12% Cr) were exposed within the CTF furnace, whilst in the convective section a further 8 to 16 samples comprising T22 (2%Cr), TP316 (18%Cr) and HR3C (25%Cr) were exposed during each test.

WOOD CO-FIRING

The furnace wall corrosion specimens exhibited corrosion scales typical of those seen in full scale plant when firing coal only. Particulate ash deposits were for the most part also typical of those found in coal fired plant, although some evidence was found for amorphous / condensed ash in which sodium and potassium were found to be closely associated with sulphur, suggestive of potentially aggressive ash deposits.

No significant difference was found between the metal losses for the wood co-firing specimens and the losses that would have been expected under similar conditions firing only coal.

Both the ferritic and austenitic superheater specimens suffered general metal loss with the formation of protective corrosion scales. Only particulate type ash deposits were identified with no indication of aggressive molten ash formation.

Measured metal losses for the ferritic T22 specimens fell within the data scatter expected for firing only coal, whilst as would be expected, the austenitic specimens suffered substantially less attack.

CEREAL CO-PRODUCT CO-FIRING

The furnace wall corrosion specimens again exhibited corrosion scales typical of those seen in full scale plant when firing coal only. In addition to the expected particulate ash deposits, condensed / prior molten ash deposits were identified in intimate contact with the corrosion scales on several samples. Evidence for the ash having been molten took the form of precipitated iron oxide within the ash. Elemental analysis showed the prior molten ash to predominantly contain potassium, sodium and sulphur, together with iron from the corrosion scale.

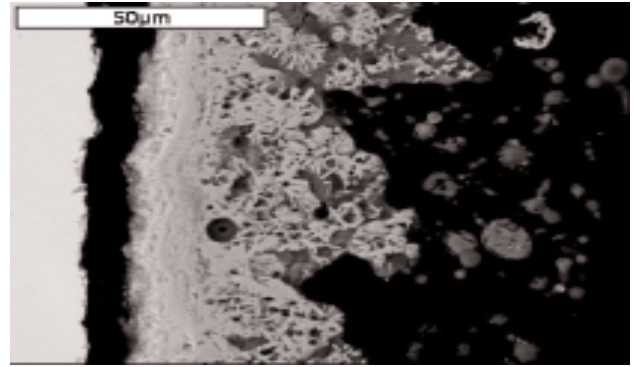


Figure 2. Corroded HCM12 alloy showing precipitated oxide in prior molten ash after exposure to furnace wall conditions

Under reducing conditions with a high heat flux, the greatest metal losses remained similar to that which would be expected firing coal only. However, there was an increase in the losses under less severe conditions that was attributable to interaction with the aggressive molten ash deposits.

The ferritic superheater specimens again suffered general metal wastage with losses slightly greater than would have been expected firing coal only. The austenitic superheater specimens, however, were found to have suffered severe localised pitting damage, with corrosion rates having increased markedly to values similar to that measured for the ferritic samples. The severe pitting attack was associated with condensed / prior molten ash deposits which again predominantly comprised potassium, sodium and sulphur. Elemental analysis indicated that both potassium and sulphur had penetrated to within the pit, whilst chromium, which would normally be expected to be retained within the scale adjacent to the metal, had been leached out into the mixed scale and ash overlying the pit.

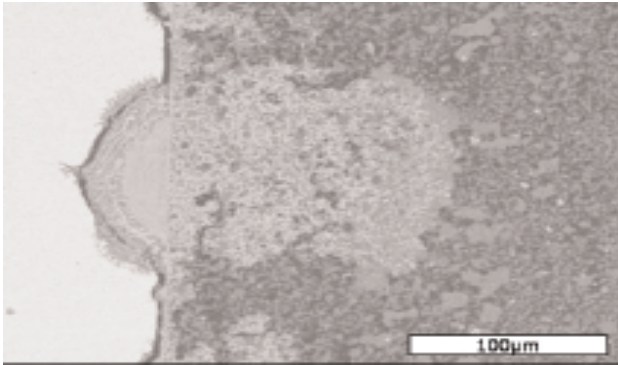


Figure 3. Corroded TP316 austenitic stainless steel specimen exhibiting severe localised pitting damage

CONCLUSIONS

- The highest furnace wall fireside corrosion rates when co-firing biomass continue to be caused by the synergistic effect of fuel chlorine and heat flux under reducing conditions, the same mechanism as is responsible when firing coal only.
- High percentages of wood can be co-fired without adverse corrosive effects at subcritical or (ultra) supercritical temperatures in both the furnace and superheater/reheater sections of plant.
- Within the furnace section, under normal oxidising conditions, co-firing with CCP is likely to result in moderate increases to the existing low rates of fireside corrosion.
- Co-firing with CCP can be expected to result in a slight increase in ferritic superheater / reheater tubing corrosion rates in comparison to plant firing only coal.
- Austenitic superheater / reheater tubing can be expected to suffer a dramatic increase in fireside corrosion rates when compared with firing coal only. Current data does not enable reliable long term wastage rate predictions, but in the worse case, with linear kinetics, metal losses in excess of 8mm per year are possible.

- Careful fuel selection, or a restriction of the biomass percentage burn, would be required to enable operation of advanced plant with tolerable superheater / reheater wastage rates.
- The biomass alkali metal content is implicated in the enhanced fireside corrosion process, but the current data is insufficient to permit a fully quantitative description of the aggressive components in the fuels. Fuel phosphorous or sulphur: chlorine ratios may also be important factors in determining fuel corrosivity.

POTENTIAL FOR FUTURE DEVELOPMENT

In order to determine the exact nature of the corrosive constituents in potential biomass fuels it would be necessary to conduct further 50 hour CTF trials on fuels with differing compositions. In particular, fuels with a range of alkali metal, sulphur and chlorine contents should be examined.

A further 50 hour CTF test conducted with lower percentage CCP content would determine whether a peak in superheater / reheater corrosion rate is found at lower temperatures and characterise any dilution effect attributable to excess coal ash.

In order to better ascertain the long-term effects of co-firing fuels such as CCP on the superheater / reheater corrosion of austenitic materials in actual plant, it would be necessary to conduct short and medium term probe exposures in operating plant.

Through selection of ferritic and austenitic alloy specimens, data would be relevant to sub critical plant operating with final steam temperatures of 540°C or 560°C, as well as (ultra) supercritical plant operating with advanced steam conditions.

COST

The total cost of this project is £187,000 with the Department of Trade and Industry (DTI) contributing £93,500. The balance of funding was provided by the participants.

DURATION

24 months - January 2002 to December 2004

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