

The interactions of coal-biomass ash with supercritical boiler materials

Final report for BCURA Project B91 (1 January 2008 – 31 December 2009)

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Executive Summary

New alloys are being developed for the higher superheater and reheater tube metal temperatures involved in supercritical or oxy-fired plants. These alloys, engineered to provide improved strength and creep resistance at temperatures above 700°C, are based on advanced steels and nickel alloys. Previous work on the characterisation of the tube-side layers of coal ash deposits has shown that the interaction between iron-rich ash particles and boiler tubes is important in initiating a deposit. Although the oxidation of these high-temperature alloys has been studied (Viswanathan and Coleman, 2006), the interaction of ash with different tube alloys under relevant conditions is not currently well understood.

Supercritical operation will increase the metal temperatures of the superheater and reheater elements, and oxy-firing will also change the gas conditions and probably the corrosion mechanisms. Depositing ash particles will transform more rapidly, and the resulting deposits may have lower melt viscosities and show different phase equilibria. Both the deposition and the removal of boiler slags may be affected, and this may have an important impact on the corrosion processes occurring under the gas-side deposits.

The aim of this project was to explore the interactions between coal ash and superheater/reheater materials in oxy-fired boilers, initially by characterising samples from corrosion trials at Doosan Babcock. These long-term corrosion tests have taken place at Doosan Babcock Energy, with whom Imperial College has had a long working relationship.

The activities of this project have been seriously delayed, and ultimately frustrated, by the non-availability of samples from Doosan Babcock. In the absence of metal samples and associated data a researcher could not be appointed, research activities could not start and the literature survey could not be focussed. Alternative samples have been sought elsewhere, but the corrosion samples needed to make progress this project are not available. The project has therefore been terminated.

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1 Introduction

New alloys are being developed by UK, EU and US projects for the higher superheater and reheater tube metal temperatures involved in supercritical plants. These alloys, engineered to provide improved strength and creep resistance at temperatures above 700°C, are based on advanced steels and nickel alloys. Previous work on the characterisation of the tubeside layers of coal ash deposits has shown that the interaction between iron-rich ash particles and boiler tubes is important in initiating a deposit. Although the oxidation of these high-temperature alloys has been studied (Viswanathan, 2006), the interaction of ash with different tube alloys under relevant conditions is not currently well understood; the proposed work would add value to existing projects on supercritical boiler development.

Supercritical operation will increase the metal temperatures of the superheater and reheater elements. Depositing ash particles will transform more rapidly, and the resulting deposits will have lower melt viscosities and show different phase equilibria. Both the deposition and the removal of boiler slags may be affected, especially with higher alkali concentrations resulting from biomass co-firing, and this may have an important impact on the corrosion processes occurring under the gas-side deposits.

The relevant long-term corrosion tests will take place at Doosan Babcock Energy, and Imperial College have a long track record of working with Doosan Babcock. The novelty of this project lies in the choice the boiler materials and temperature ranges under which ash behaviour will be investigated, both of which extend beyond current knowledge.

The initial aim of this project was to explore the interactions between coal-biomass ash and superheater/reheater materials in supercritical boilers. Feedback from industrial partners during the period between submitting the proposal and starting the project was that co-firing biomass in supercritical boilers was not a likely short-term development in the UK, but that interactions between coal ash and superheater/reheater materials in oxy-fired boilers was a pressing concern

where value could be added to planned trials at Doosan Babcock. The aim and objectives were modified accordingly.

The objectives of this project were to:

- Investigate the changes in ash interaction with wall materials under oxy-fired combustion conditions through laboratory experiments
- Explore this ash interaction and corrosion through characterisation of experimental samples
- Predict the impact of oxy-fired combustion conditions on metal corrosion and coal ash behaviour

2 Project activities

All project activities have been delayed, and ultimately frustrated, by the non-availability of corrosion trial samples. In the absence of metal samples and associated data a researcher could not be appointed, research could not start and the literature survey could not be focussed.

2.1 Acquisition of samples from Doosan Babcock

Doosan Babcock Energy agreed to provide results and samples from their OxyCoal-UK Phase 1 corrosion trials, as well as untreated superheater metal samples. Fraser Wigley has liaised with Doosan Babcock Energy through progress meetings on the OxyCoal-UK Phase 1 project, over the first 18 months of this project. Although delayed, the Doosan Babcock corrosion tests took place and corrosion rates were measured by mid-2009. Doosan Babcock trials involved the following test materials:

- T91 9% Cr (modified), superheater/reheater tube material
- X20 12% Cr, superheater/reheater tube material
- Esshete 1250 15 % Cr Austenitic superheater material
- Super 304H 18Cr-10Ni-Cu
- TP347 HFG 18Cr-10Ni-Cb
- HR 3C 25Cr-20Ni-Cb-N, ASME coded
- IN 740 Advanced Ni tube material
- Sanicro 25 22Cr-25Ni

The materials were tested at temperatures between 550 and 810°C over a standard period of 1000 hours. Materials were exposed to synthetic ash consisting of Na₂SO₄, K₂SO₄ and Fe₂O₃ (1.5:1.5:1 mole basis) in accurately controlled, synthetic gas atmospheres. Corrosion rate measurements employed microscopic techniques, and full metal thickness loss-temperature curves were plotted.

Three trials, involving different gas atmospheres, were conducted under OxyCoalUK Phase 1:

1. High SO₂ *Dirty air* (1.5% SO₂, 6.0% O₂, 14.6% CO₂, 73.0% N₂, 5.0% H₂O)
2. High SO₂ and CO₂ *Dirty recycle* (1.5% SO₂, 6.0% O₂, 77.5% CO₂, 10.0% N₂, 5.0% H₂O)
3. High CO₂ *Clean recycle* (0.3% SO₂, 6.1% O₂, 78.4% CO₂, 10.1% N₂, 5.1% H₂O)

Uncorroded test materials, and baseline test materials with corrosion rates were potentially available from previous *Clean air* trials.

After repeated requests, 15 samples from a range of metals tested in 'normal' flue gas at various temperatures were offered in May 2009. It also became apparent that equivalent samples tested in synthetic oxy-coal flue gas could not be made available because they had been destroyed. The samples available from Doosan Babcock did not support this projects activities.

Almost all of the activities of this BCURA project depend on receiving these samples and information. In particular, appointing a researcher to start project activities before corrosion results and samples are available would be very unwise.

2.2 Acquisition of samples from E.ON

Following the inability of Doosan Babcock to provide suitable samples, useful discussions were held with Colin Davis at E.ON UK. The corrosion samples they have available can be summarised as follows:

Mounted and polished corrosion samples from oxy-coal combustion trials involving four coals were available from E.ON in late 2009, and samples from the combustion of two more coals are expected by early summer 2010. These six coals have a range of sulphur and chlorine contents. Corrosion rate measurements are available with the samples. Baseline corrosion samples from air-firing combustion trials conducted at the same time as the oxy-coal trials are only available for one of these six coals; historical air-fired corrosion samples are available for two more of the coals but may not be directly comparable. The only direct comparison between oxy-fired and air-fired corrosion samples is for one coal with very low S and Cl contents, where the flame temperatures were significantly lower than would be expected during oxy-coal combustion.

Each trial produced corroded samples of several different metals, some of which had been exposed at multiple temperatures. Almost all the sample cross-sections contain portions of metal oxide scale and ash deposit, and some show grain boundary cracking. However, the short duration of the corrosion tests (50 hours) means that element depletion at the corroded metal surface and along grain boundaries and cracks is likely to be too small to measure.

The lack of direct comparison between oxy-fired and air-fired corrosion samples is a serious drawback in the usefulness of the E.ON samples for this project. In addition, the short duration of the E.ON tests is justified by their use to produce qualitative rankings of corrosion rates, which correlate well with rankings of corrosion rates based on plant experience. The lack of fully quantitative reliance on these samples suggests that the relative importance of different corrosion mechanisms probably change between the initial 50 hours and more extended test periods. In addition, there is no corresponding plant experience for corrosion mechanisms under oxy-firing conditions.

It does not appear that further analysis of these E.ON samples would significantly advance the understanding of the difference in corrosion of superheater materials between air-fired and oxy-coal combustion conditions. The corrosion samples needed to make progress this project are simply not available.

2.3 Literature survey

A wide range of publications concerning the corrosion of superheater metals are available. The review by Bryers (1996) is both comprehensive and detailed. This and other publications noted that

higher concentrations of S, Cl and, to a lesser, extent alkalis in the combustion gas increased the potential for corrosion of boiler materials. These higher concentrations could arise from biomass co-firing, the flue gas recycle inherent in oxy-firing, or possible from both process operating together. Buhre et al (2005), amongst others, noted the potential importance for boiler corrosion of elevated SO₂ concentrations during oxy-firing. One common feature of trials in which detailed corrosion mechanisms are studied is that they have exposure times measured in hundreds of hours. As corrosion is a very broad topic, the results from the Doosan Babcock corrosion trials were needed to identify publications of particular relevance.

Projects that involved studying corrosion of boiler materials under oxy-firing conditions were announced by Panesar (2007), Dixon (2008) and others. Reports on oxy-firing corrosion projects that were in progress but without results (e.g. Cameron and Fitzgerald, 2008; Goh, 2008) were presented at the 3rd meeting of the Oxy-Fuel Combustion Network (4-6 March 2008 in Yokohama, Japan). The conference on the *Impacts of Fuel Quality on Power Production and the Environment* (29 September – 3 October 2008 in Banff, Canada) included descriptions of corrosion studies during biomass co-firing (e.g. Tillman et al, 2009; van Lith et al, 2009), but not during oxy-firing. Adamiec (2009) reported on the corrosion of boiler materials with high nickel content under biomass co-firing conditions.

Initial results of corrosion trials under oxy-firing conditions started to be presented in late 2009, particularly at the *First International Oxyfuel Combustion Conference* (8-11 September 2009 in Cottbus, Germany). Significant findings were:

- Oxide scale formation in CO₂-rich gasses shows significant differences from air-firing conditions (Kull et al, 2009)
- Calcium sulphate in ash deposits forms carbonates in CO₂-rich atmospheres, enhancing the availability of sulphur and promoting corrosion (Kull et al, 2009)
- Carburization occurs in CO₂-rich atmospheres for austenitic steels, with or without an ash layer; Cr is fixed in the carbide phases, reducing the protection against corrosion (Hünert et al, 2009; Kull et al, 2009)
- Creep and high-temperature corrosion can interact to reduce fatigue life under service conditions in both air-firing and oxy-firing combustion conditions (Klingelhöffer et al, 2009)

3 Conclusions

The activities of this project have been seriously delayed, and ultimately frustrated, by the non-availability of samples from Doosan Babcock. Alternative samples have been sought elsewhere, but the corrosion samples needed to make progress this project are simply not available. The project has therefore been terminated.

4 Further work

There is still a clear need for a systematic study of the behaviour of existing and candidate superheater/reheater materials at a range of temperatures, to compare corrosion and metal-ash

interactions between air-firing and oxy-firing conditions. Some of the corrosion rate data is available, allowing particular combinations of test material, temperature and gas conditions to be identified for further study. Sample characterisation is needed to identify the mechanisms for significant differences in behaviour between air-firing and oxy-firing. Other European groups are currently working towards this goal, and the possibility of world-leading research of industrial relevance appears to have been lost.

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