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Trends in fireside corrosion damage to superheaters in air and oxy-firing of coal/biomass ☆

T. Hussain *, A.U. Syed, N.J. Simms

Centre for Energy & Resource Technology, Cranfield University, Bedfordshire MK43 0AL, UK

HIGHLIGHTS

- T92, 347HFG, HR3C and 625 have been tested in simulated air-fired and oxy-fired combustion gases at 600–750 °C.
- In both firing conditions characteristic “bell-shaped” curves of fireside corrosion damage was observed.
- The highest damage levels (peaks) were observed at 650 °C in air-fired conditions and 700 °C in oxy-fired conditions.
- The increase in peak corrosion damages in oxy-firing environment was due to the higher levels of SOx gases.
- Generally, the alloys had the following ranking (most to the least damage): T92 > 347HFG > HR3C > 625.

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ABSTRACT

This paper compares the laboratory-based fireside corrosion tests on superheater/reheater materials in simulated air-firing combustion conditions with oxy-firing combustion conditions (with hot gas recycling before flue gas de-sulphurisation). The gaseous combustion environment was calculated based on a specific co-firing ratio of CCP with Daw Mill coal. The fireside corrosion tests were carried out using the “deposit recoat” test method to simulate the damage anticipated in specific environments. A synthetic deposit (Na_2SO_4:K_2SO_4:Fe_2O_3 = 1.5:1.5:1 mol.) which has commonly been used in fireside corrosion screening trials and is a mix that forms alkali-iron tri-sulphate (identified in many investigations as a cause of fireside corrosion) was used in these tests. The air-fired tests were carried out at temperatures of 600, 650 and 700 °C and oxy-fired tests were carried out at temperatures of 600, 650, 700 and 750 °C to represent the superheater/reheater metal temperatures anticipated in future power plants with and without synthetic deposits, with four candidate materials: T92, HR3C and 347HFG steels; nickel-based alloy 625 (alloy 625 was only tested with screening deposits). The progress of the samples during their exposures was measured using mass change methods. After the exposures, the samples were examined by SEM/EDX to characterise the damage. To quantify the metal damage, pre-exposure micrometre measurements were compared to the post-exposure image analyser measurements on sample cross-sections. The trends in corrosion damage in both air and oxy-firing conditions showed a “bell-shaped” curve, with the highest metal damage levels (peak) observed at 650 °C for air-firing and 700 °C for oxy-firing tests. However, at 600 and 650 °C similar damage levels were observed in both environments. The shift in peak corrosion damage in oxy-firing condition is believed to be the presence of higher levels of SOx, which stabilised the alkali-iron tri-sulphate compounds. Generally, in both air and oxy-firing conditions the mean metal damage was reduced with increasing the amount of Cr in the alloys. However, at the highest temperatures in both air-firing (700 °C) and oxy-firing conditions (750 °C) the metal damage of nickel based superalloy 625 was higher than HR3C.

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1. Introduction

Conventional fossil fuel fired power plants are believed to be significant contributors to the enhanced greenhouse effect/global warming [1,2]. CO_2 is one of the major greenhouse gases and various national, EU and international legislations are in place to reduce the CO_2 emissions from fossil fuel fired power plants. The UK government has an ambitious target of reducing CO_2 emissions to 80% of their 1990 levels by 2050 [2]. To meet this target a combination of renewable fuels such as biomass, which can be classed as carbon neutral, and carbon capture and storage (CCS) technologies such as oxy-fuel combustion will be necessary. A potentially carbon negative power generation is possible if co-firing of biomass and carbon capture technologies can be used together.

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* Corresponding author. Tel.: +44 1234750111.
E-mail address: t.hussain@cranfield.ac.uk (T. Hussain).

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Further reductions in CO_2 emissions from pulverised coal-fired power plants can be achieved by increasing the operating pressures and temperatures of their steam systems (which in turn increases the overall efficiency of the plants) [3], since each 1% increase in absolute efficiency results in as much as a 3% reduction in CO_2 emissions [4].

Co-firing low levels of biomass in conventional pulverised coal-fired power plants has proved to be a successful way to introduce carbon neutral biomass fuels into the electricity generation market to meet national and EU legislation. Biomass is a major contributor to renewable energy production, accounting for approximately 70% of worldwide renewable energy production [5]. Power plants burning biomass alone as fuel face significant issues with fouling, deposition, agglomeration and corrosion, which restricts the steam temperatures that can be used and so reduce the overall efficiency of the plants. However, these issues can be significantly reduced by the co-firing of biomass and coal [5–9]. The existing pulverised coal fired power plants are much larger in capacity and more efficient than dedicated biomass fired plants, so a few percentages of biomass co-fired with coal will provide more biomass derived renewable energy than a dedicated biomass plant using the same amount of biomass. Co-firing low levels of biomass can be achieved without making any major modifications (except fuel feeding and storage) to the existing coal-fired power plants.

Oxy-fuel firing is one of the possible routes for post-combustion capture where CO_2 is removed from the flue gas [1,8]. In oxy-fuel firing combustion is carried out in an O_2–CO_2–steam environment instead of air to produce a flue gas stream of minimal N_2 content and high CO_2 content which can be separated, compressed and stored in geological sites. Increased levels of CO_2 and H_2O coupled with higher levels of SO_2 and HCl (up to five times the levels of SOx found in conventional boilers using the same fuel, depending on the flue gas recycling configuration [1,8]) can lead to aggressive corrosion attack to the superheaters/reheaters. Oxy-fuel firing is expected to result in different gas chemistries and deposit compositions compared to conventional combustion systems.

Fireside corrosion (i.e., metal loss of heat exchangers due to chemical reactions with the combustion gases and deposits at high temperatures) has been a life-limiting factor for the pulverised fuel fired power plants. Fireside corrosion is one of the key reasons for tube failures in power plants. Fireside corrosion can lead to failure of superheaters/reheaters either by general metal loss or by the formation of cracks which can allow failure to occur by mechanical damage. Such failures are difficult to repair and results in unscheduled plant down time. In pulverised coal fired power plants molten alkali-iron tri-sulphates can form in the deposits on heat exchanger surfaces, which are very aggressive in nature [8,10]. However, when biomass is co-fired the combustion gases and deposits do not remain the same. Herbaceous biomass has higher levels of elements such as K and Cl but much less S compared to most coals [8,9,11,12]. Since the introduction of biomass, the issue of fireside corrosion has become more pronounced. Oxy-firing pulverised fuel power plants provides one potential route to enable post-combustion CO_2 capture, which in-turn requires higher temperature/pressure steam system to counter-act the energy required to run the CO_2 capture/compression units. Furthermore, the higher operating temperatures in future power plants will result in higher than acceptable metal damages for conventional superheater/reheater materials. In absence of preventative action, the increased steam system operating temperatures, co-firing of biomass and oxy-firing conditions will have a significant effect on the fireside corrosion of the heat exchanger materials; resulting in premature component failure and unscheduled shut-downs.

This paper reports the results of a comprehensive study of candidate superheater/reheater materials (a ferritic alloy: T92, two austenitic alloys: 347HFG and HR3C and a nickel based alloy: 625) in simulated air-fired and oxy-fired combustion gases (with hot gas recycling before flue gas de-sulphurisation) at metal temperatures higher than the average conventional temperatures (e.g., 540–560 °C [13,14]) of existing pulverised fuel power plants. The gas/deposit environments were selected based on co-firing a UK coal with cereal co-product. The performances of the alloys were investigated with/without a synthesis deposit to assess gas/deposit induced corrosion attack at 600–750 °C. This work was carried out using the "deposit recoat" technique that has been developed for high temperature corrosion [15–17]. Dimensional metrology has been used as the primary route to quantify the metal damage occurring due to fireside corrosion. After the exposures, the samples were examined by SEM with EDX mapping to characterise the damage. The data generated from these tests are now being used in an on-going programme that is developing models of fireside corrosion of superheater/reheater materials, as one element of life-time modelling of heat exchangers in advanced power generating systems [18].

2. Experimental methods

2.1. Materials

In this study, one ferritic steel (T92), two austentic steels (347 HFG, HR3C) and one nickel based alloy (625) were used to represent candidate materials for heat exchangers (supeheater/reheaters) in advanced pulverised fuel power plants. The nominal compositions of all four alloys are shown in Table 1. The materials were sourced as long tubes (i.e., boiler tubes) which were then cut and machined into tube segments with dimensions of ~15 mm chord, 15 mm long and 4 mm wall thickness. The surfaces of all the samples were prepared to a UK 600 grit surface finish.

2.2. Exposure conditions

The exposure conditions were determined following a detailed investigation of the gaseous environments and deposit conditions that could be found around superheater/reheaters in conventional pulverised coal fired UK plants using various biomass-coal fuel combinations [8,18]. The gaseous conditions for the fireside tests were based on co-firing 80:20 wt.% of a typical UK coal (Daw Mill) with cereal co-product (CCP). The compositions of these fuels are available in [19]. The gas compositions produced by these fuels in (a) air-firing and (b) oxy-firing (with hot gas-recycle following particulate removal but before flue gas de-sulphurisation) modes have been calculated from the fuel compositions, using models that have been validated through pilot and plant scale operations.

Table 1
Nominal composition of alloys used in fireside corrosion exposures (data in weight %).

Materials	Cr	Mo	Ni	Si	Mn	P	S	C	Fe	Others
T92	9.5	0.6		$\leqslant 0.5$	$\leqslant 0.6$	$\leqslant 0.02$	$\leqslant 0.01$	0.13	Bal.	0.25 V; 2 W; 0.09 Nb; 0.07 N
347 HFG	17–19		9–13	$\leqslant 0.5$	$\leqslant 2$	$\leqslant 0.045$	$\leqslant 0.03$	0.08	Bal.	0.6 < Nb + Ta < 1
HR3C	25		20	0.75	$\leqslant 2$	$\leqslant 0.04$	$\leqslant 0.04$	0.1	Bal.	0.4 Nb; 0.2 N
Alloy 625	20–23	8–10	Bal.	$\leqslant 0.5$	$\leqslant 0.5$	$\leqslant 0.015$	$\leqslant 0.015$	.01	5	1 Co; 0.4 Al

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