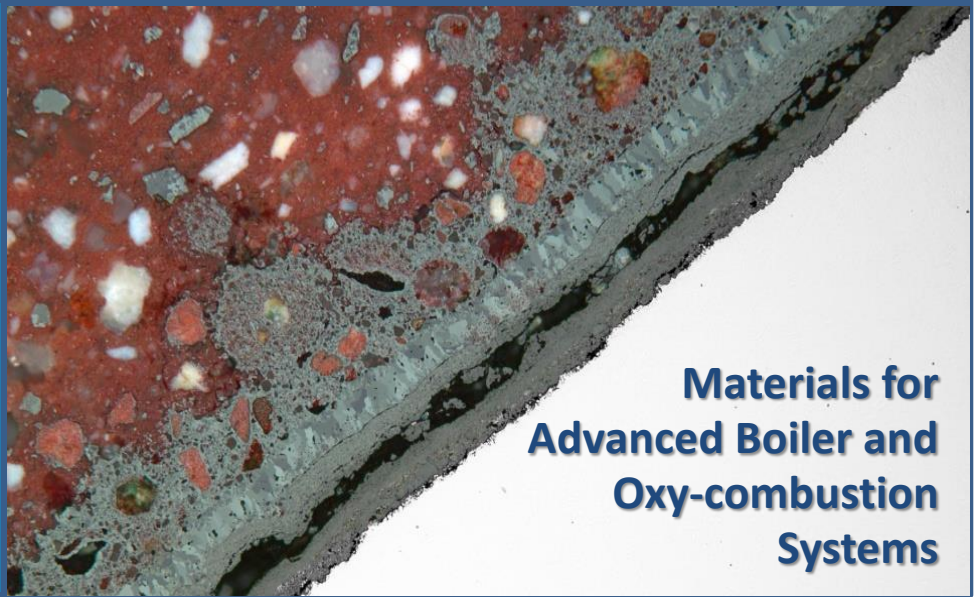**Project duration**
2010-2016

**Project Partners**
**UK:**
Cranfield University*
National Physical Laboratory
**US:**
Argonne National Laboratory
National Energy Technology Laboratory*
Reaction Engineering International
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# Materials for Advanced Boiler and Oxy-combustion Systems

## Background

The ability to control corrosion of the fireside surfaces of boiler components to acceptable levels is a major prerequisite for the successful development of advanced coal-fired boilers operating at advanced steam temperatures, oxy-fuel combustion and boilers with the capability to co-fire biomass materials at high co-firing ratios. Consequently, there has been a significant increase worldwide in research and development activities on fireside corrosion associated with coal/biomass-fired boiler plants.

*Figure 1. Corrosion risk areas related to a coal-fired oxy-combustion plant.*
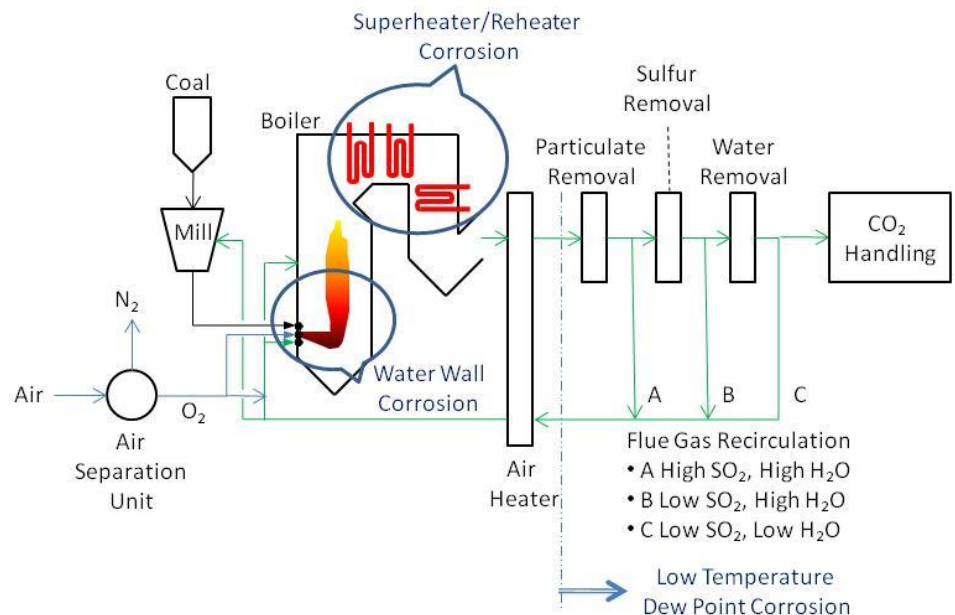


The aim of this work was to develop further understanding of the corrosion mechanisms found on heat exchanger surfaces present in oxy-combustion and coal/biomass co-fired combustion systems, and to develop a modelling capability to predict the effect of different fuels on the lifetimes of plant components.

Oxy-combustion is a process that has gained much international interest, but there was little information on the consequences of changing the combustion atmosphere on heat exchanger corrosion. To remove uncertainties and promote the adoption of low carbon approaches, it was necessary to conduct this test program to generate the critical data needed.

Fireside corrosion tests are normally performed under simplified exposure conditions. As conditions become more demanding, the synergistic effect of corrosion and mechanical loading is becoming more important. Testing approaches to combine these two conditions are required, and have been investigated in this program.

## Objectives

- ➤ To generate improved understanding of the fireside corrosion performance of low alloy steels, stainless steels and Ni-based alloys
- ➤ To determine the effect of (a) biomass/coal combustion and (b) oxy-fuel combustion on fireside corrosion and to understand better the associated degradation mechanisms
- ➤ To identify possible impacts that oxy-combustion could have on boiler operations and to consider potential mitigating measures
- ➤ To develop apparatus and procedures for measuring mechanical performance of materials under controlled atmospheres.

## Work Program

Laboratory studies were carried out to establish the effect of the oxy-combustion environment on the fireside corrosion of candidate superheater/reheater materials. These oxidising environments contain greatly elevated $CO_2$ levels, but with $H_2O$, and $SO_2$ levels that depend significantly on the boiler design and flue gas recycling/cleaning options. A series of candidate materials were tested to enable heat exchangers to be operated with surface temperatures of up to 800°C. A similar research program was carried out for fireside corrosion conditions resulting from combustion of selected coal/biomass mixtures, but to a maximum temperature of 700°C. For both programs of research, time dependant data were collected at each temperature to investigate corrosion incubation and propagation effects. Both mass change and dimensional metrology data were gathered as a function of exposure conditions, with the latter used as the basis for corrosion model development.
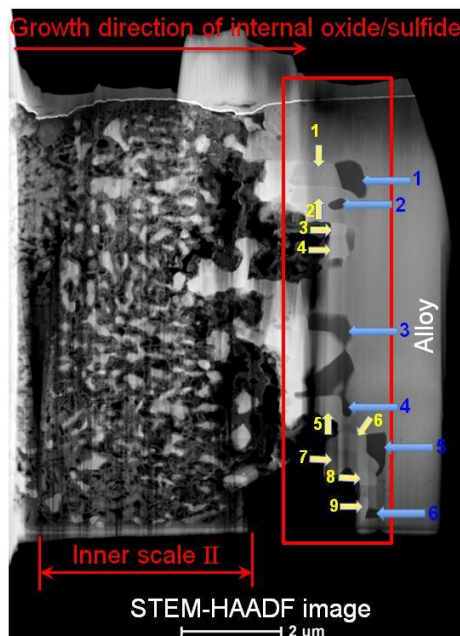


*Figure 2.
Internal sulfidation of Cr in IN617 after exposure in an oxy-combustion environment.*

Laboratory and plant exposures were carried out low alloy steel coupons under actual and simulated water-wall conditions for coal/biomass-fired combustion. Data from these were generated for the development of a neural network model to predict metal wastage rates as a function of alloy composition and fuel type.

Novel test facilities were designed and built to enable the application of mechanical loads under a controlled atmosphere. These rigs can record the load and strain on a sample whilst at high temperature in corrosive gases. Two approaches were taken; the first used small scale samples in instrumented small punch tests, while the second used a more conventional creep sample approach.

- Using a large database of fireside corrosion test data at water-wall conditions, a neural network model was developed to predict the corrosion rate of low alloy steels.

- Instrumented small punch and creep/tensile testing equipment were developed and used to measure the creep strain rate in controlled atmospheres, thereby enabling the combined effect of corrosion and stress to be evaluated.

- For many alloys an incubation period of relatively low corrosion rate occurs prior to establishment of a liquid phase mechanism and more rapid corrosion (propagation).

- For environments (and deposits) with high S/Cl ratios (for example resulting from the combustion of coal or many coal-biomass mixtures), the liquid salt that forms during the fireside corrosion of superheaters/reheaters is a $(Na,K)_2SO_4–Fe_2(SO_4)_3$ mixture (similar to those formed in Type II hot corrosion of Ni and Co-based alloys). Alkali iron trisulfates are not needed to form such liquid deposits.

- Carefully targeted laboratory furnace exposures using a deposit recoat technique showed that superheater/reheater fireside corrosion depended on the deposition flux and $SO_X$ level in the combustion environment, regardless of whether air or oxy-firing (i.e., $N_2$ or $CO_2$ dominated gases) was used.

- A 5-year DOE oxy-combustion multi-scale study found that oxy-fuel combustion led to corrosion that was similar to air-firing unless the flue gas recycle generated high $SO_2$ and $H_2O$ levels around the superheaters/reheaters. The ash aerosol properties and slagging behavior were also similar to air-firing.
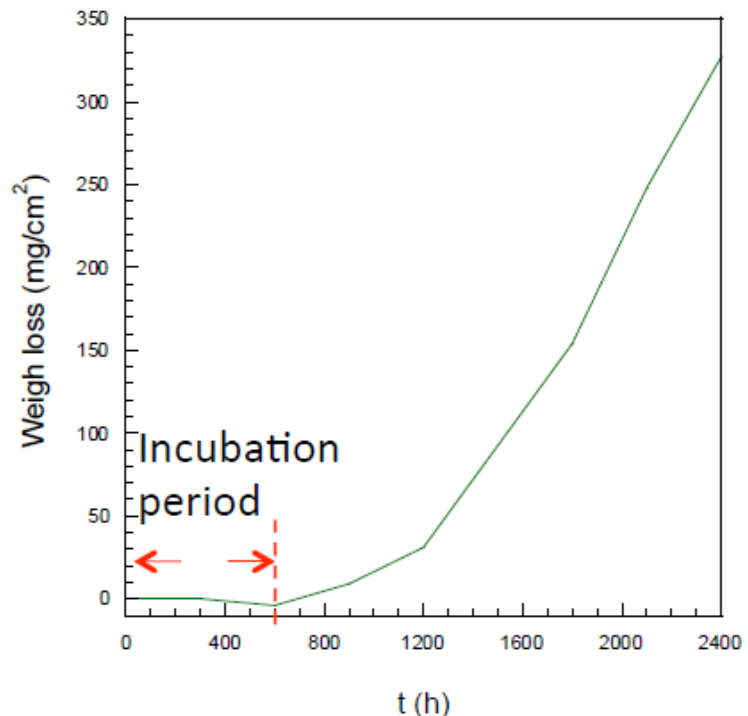
*Figure 3.*
*Graph showing the incubation period prior to more rapid corrosion associated with liquid salt formation.*

Development of improved models of all forms of fireside corrosion of a wider range of alloys and product forms, in virgin, post-fabrication and post-service conditions.

*For further information on the UK-US Collaboration on Energy Research and Development please visit – https://fossil.energy.gov/usuk/*