High-Temperature Fireside Tube Corrosion during Oxy-Fuel Combustion of Low Rank Coal

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A thesis submitted for the degree of
Doctor of Philosophy

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Abstract

With the diminution of high-rank coals, natural gas and petroleum, the use of low-rank coal has received increasing attention in the energy and mining industries. There are large reserves of low-rank brown coal in both Australia and China, and in other parts of the world, and Victorian brown coal is the single largest source of electricity generation in Victoria. However, its combustion in air causes notoriously high carbon emissions, due to its large moisture content (approximately 65 wt. %). Compared with the conventional air-firing process, oxy-fuel combustion is one of the most promising technologies for the purpose of carbon capture and storage (CCS). In this process, high-purity oxygen (derived from an air-separation unit) is used instead of air in the boiler. As a result, high-purity CO₂ is produced, which can be subsequently sequestered or utilized with minimal treatment.

With the replacement of air with a mixture of high-purity oxygen and flue gas, the overall process is nitrogen-lean, and it can generate a flue gas rich in CO₂ and ready for CCS. Since the physical properties (e.g. specific heat capacity and thermal conductivity) of CO₂ differ from those of N₂, the heat profile and gas flow pattern in an oxy-firing boiler are remarkably different from those in the conventional air-firing boiler. This in turn affects ash formation/slagging/fouling, deposition and tube corrosion in the boiler.

The scope of this research involves both experimental and modelling studies. For the experimental aspects of this research, a set of corrosion tests was conducted on different tube materials and different ash samples in both oxy-fuel and air-firing mode. The first part of this research involved the investigation of the effect of flue gas and fly ash deposition formed during the oxy-fuel combustion of low-rank coal, and explored the science underpinning the solid-to-solid interaction between the tube material and the ash species. Moreover, this research project aimed to evaluate the possibilities of two fuel quality control techniques on the tube corrosion rate, under both conventional air-firing and oxy-fuel combustion conditions: the addition of silica to low-rank coal and prior washing of low-rank coal. Finally, long-term high-temperature corrosion tests and oxidation kinetics were conducted and modelled to understand the overall tube corrosion rate, the rate-limiting steps, the reaction mechanisms, the metal oxide crystal structure, oxide composition, and oxide microstructure and morphology. To achieve the project aims, a number of advanced experimental, analytical and modelling techniques were used. First, a horizontal furnace was used for tube corrosion tests for 50-200 h. In the project, many characterization facilities were involved to quantitatively/qualitatively analyze the samples. The tube corrosion depth and oxidation layer thickness were obtained from
optical microscopy (OM) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDX) to map the penetration/diffusion of elements of interest through the ash-tube interface; the X-ray diffraction (XRD) for the bulk surface was identified using Rigaku MiniFlex600. The XRD spectra obtained were analyzed quantitatively using Siroquant 3.1 based on the Redfield least-squares fitting method and Jade software. Synchrotron X-ray near-edge structure (XANES) was used for the oxidation states of iron (Fe), sulphur (S) and chromium (Cr) on both bulk and cross-section surfaces and individual particles/spots. Finally, thermodynamic equilibrium modelling was conducted using Factsage 6.4 for the prediction of melting behaviour, while kinetic modelling was conducted by fitting based on the diffusion-controlled model.

The outcomes of this project which conducted the pilot-scale experiments on ash deposition behaviour for high-moisture VBC and other low-rank coals under oxy-fuel combustion and the characterisation of corroded tube surface will contribute significantly to accelerating the deployment of oxy-fuel combustion technology for low rank coal. These findings will provide a theoretical reference and technical support for understanding tube corrosion mechanisms and, allow the deployment or retrofit of advanced tube materials and maintain a long lifetime for an oxy-firing boiler.
Declaration by Author

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes six original papers published in peer-reviewed journals. The core theme of the thesis is the investigation of the characteristics of tube corrosion caused by low-rank coal during oxy-fuel combustion. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the Department of Chemical Engineering under the supervision of A/Prof. Lian Zhang and Dr. Barbara Etschmann.

The inclusion of co-authors reflects the fact that the work came from active collaboration between the researchers and acknowledges input into the team-based research.

In the case of Chapters 4, 5, 6, 7, 8 and 9 my contribution to the work involved the following:

<table>
<thead>
<tr>
<th>Thesis chapter</th>
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<td>4</td>
<td>High-temperature tube corrosion upon the interaction with Victorian brown coal fly ash under the oxy-fuel</td>
<td>Published</td>
<td>Experimental design and conduct, writing (90%)</td>
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<td>5</td>
<td>Effect of silica additive on the high-temperature fireside tube corrosion during the air-firing and oxy-firing of lignite (Xinjiang coal) – Characteristics of bulk and cross-sectional surfaces</td>
<td>Published</td>
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<td>7</td>
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Spatial distribution of Cr-bearing species on the corroded tube surface characterized by synchrotron X-ray fluorescence (SXRF) mapping and micro-XANES: exposure of tubes in oxy-firing flue gas

Kinetic Study of Long-Term T23 Tube Corrosion upon Low-Rank Coal Ash Deposition under Oxy-Fuel Combustion Conditions

Published Experimental design and conduct, writing (90%)

Published Experimental design and conduct, writing (90%)

Sections of submitted or published papers have been renumbered in order to generate a consistent presentation within the thesis.

**Student signature:**

Date: 01.02.2020

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the student and co-authors’ contributions to this work.

**Main supervisor’s signature:**

Date: 01.02.2020

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<th>Description</th>
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<tbody>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>AET</td>
<td>Acoustic Emission Technique</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon dioxide Capture and Storage</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine-Structure</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
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<tr>
<td>FGD</td>
<td>Flue Gas Desulfurization</td>
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<tr>
<td>Mg</td>
<td>Magnesium</td>
</tr>
<tr>
<td>S</td>
<td>Sulphur</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Emission</td>
</tr>
<tr>
<td>IGCC</td>
<td>Integrated-Gasification-Combined-Cycle</td>
</tr>
<tr>
<td>PPC</td>
<td>Post Combustion Capture</td>
</tr>
<tr>
<td>OM</td>
<td>Optical microscopy</td>
</tr>
<tr>
<td>QXRD</td>
<td>Quantitative X-Ray Diffraction</td>
</tr>
<tr>
<td>RFG</td>
<td>Recirculated Flue Gas</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SEM/BSE</td>
<td>Backscattered electron of Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Scanning Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SXRF</td>
<td>Synchrotron X-ray fluorescence</td>
</tr>
<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
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<tr>
<td>XANES</td>
<td>X-ray Absorption Near Edge Structure</td>
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<tr>
<td>µ-XANES</td>
<td>Micro-X-ray absorption near-edge structure</td>
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<tr>
<td>VBC</td>
<td>Victorian Brown Coal</td>
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**Nomenclature**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
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<tbody>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Iron (III) oxide</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>Magnetite</td>
</tr>
<tr>
<td>FeS₂</td>
<td>Pyrite</td>
</tr>
<tr>
<td>k</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>R²</td>
<td>Correlation coefficient</td>
</tr>
<tr>
<td>Na₂S₂O₄</td>
<td>Sodium dithionite</td>
</tr>
<tr>
<td>Na₂S</td>
<td>Sodium sulphide</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>SO₄</td>
<td>Sulphate</td>
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<tr>
<td>T</td>
<td>Temperature</td>
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<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>wt. %</td>
<td>Weight percentage</td>
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CHAPTER 1

Introduction
Chapter 1 Introduction

1.1 Overview

Coal is the most abundant fossil fuel in the world. According to Statistics 2006, the recoverable reserves of coal are estimated to be approximately 120 billion tons [1]. The Latrobe Valley (Victoria), has one of the largest brown coal reserves in the world [2]. Worldwide energy demand is forecast to increase by about 40% by 2030 [3]. Energy production from brown coal, the most common resource, is the most carbon-intensive [4]. Increases in anthropogenic CO₂ emission are very likely to have caused most of the increases in global warming since the mid-20th century [5]. Public awareness and legislation have led to a policy of reduction of greenhouse gas emissions in most developed countries [6]. Countries such as Australia, China, India and South Africa produce between 65% and 94% of their electricity and heat through the combustion of coal [7]. In Australia, CO₂ emissions have received increased attention, especially with the recent introduction of a carbon price.

The amount of coal consumed by the combustion process in power plants results in CO₂ emissions, which contribute to global warming [8]. In order to reduce the CO₂ produced by coal-fired power plants, a variety of technologies have been used for carbon capture and storage (CCS) [9]. Oxy-fuel combustion is an attractive technology to curtail greenhouse gas emissions from coal combustion [10].

Compared with the conventional air-firing mode, oxy-fuel combustion provides a different atmospheric environment in the boiler. Apart from the high concentrations of CO₂ and steam derived from wet flue gas recycling, trivial but corrosive components, including SO₂ and HCl, also potentially accumulate in the furnace due to the recycling of the uncleaned flue gas [5, 11]. In nearly all the pulverized coal-fired boilers in Australia, downstream gas cleaning units do not exist. Therefore, high-temperature tube corrosion in the heat-exchanger zone is expected to be altered significantly under the oxy-fuel combustion mode for Australian coals, including Victorian brown coal [12]. In relation to high-temperature tube corrosion, coal quality is the major factor. A major piece of the equipment in the power plant is the boiler, and the dominant locations for boiler tube corrosion include the water walls, superheater pendants and economizer tubes [13].

In addition to corrosives gases such as SO₂ and HCl which result in the oxidation, chlorination, sulphation/sulphidation and even carburization of tube materials [14], ash deposits also cause
wastage, and disfigure the tube surface due to the large weight of deposits, and the formation of new species such as carbonates which are highly corrosive [15]. This situation is conducive to promoting the formation of other species such as sulphates and chlorides which lower the melting point of tube materials by forming new eutectics. An investigation of oxy-fuel combustion in a pilot-scale furnace found that the oxy-firing mode did not significantly affect ash chemistry or particle size distribution. Slight changes in slagging /fouling propensity and deposition rates were observed [6]. However, ash deposition and tube corrosion caused by coal oxy-firing have been less studied, and a generalized conclusion has not been reached. Several researchers have investigated the applicability of the oxy-fuel combustion system [11, 16, 17]. However, the fundamental issues of brown coal, such as high-temperature tube corrosion, have not been widely studied to date.

This study focuses on the utilization of different types of fly ashes and six tube materials. The aim of this research is to outline a scientific understanding of superheater corrosion mechanisms upon ash deposition under the oxy-fuel combustion of Victorian brown coal, to explore and clarify the suitability of new techniques, including the use of fuel additive (e.g. silica) and prior coal washing, on the minimization of tube corrosion, to reveal the effect of newly-formed gaseous species (e.g. H₂S) on tube corrosion, and to clarify the solid-to-solid interaction between ash species and tube materials. Understanding the high-temperature tube corrosion mechanisms under oxy-fuel combustion will provide a significant contribution to the design of heat-exchange boilers, which is an important parameter for the control of corrosion in superheater/reheater tubes.

1.2 Research Aim and Objectives

With the deployment of low-emission technologies such as oxy-fuel combustion, the properties of both flue gas and ash deposits are remarkably altered from those achieved using the conventional air-firing mode. Therefore, the establishment and control of tube corrosion under the oxy-fuel combustion mode are essential for the successful development of this low-emission technology. Ultimately, the study aims to promote the deployment of oxy-fuel combustion technology for Victorian brown coal, which is believed to have much more abundant reserves than high-rank coal in Australia and the rest of the world. The overall aim of this study is to develop a greater understanding of the high-temperature tube corrosion mechanisms related to the distinctive flue gas and fly ash depositions formed during the oxy-fuel combustion of Victorian brown coal.
The specific research objectives are as follows:

1. To understand the chemistry underpinning the interaction between fly ash deposit species and the tube surface upon the oxy-fuel combustion of VBC;
2. To study the mechanisms of the inhibitive effects of silica additives and coal pre-washing on the control of tube corrosion during the oxy-fuel combustion of low-rank coal;
3. To use XRFM & μ-XANES techniques to characterize the tube interface;
4. To investigate and clarify the roles of Sulphur (S) in both lignite ash deposits and bulk flue gas on tube corrosion during oxy-fuel combustion;
5. To study oxidation kinetics modelling under oxy-fuel combustion mode vs. air-firing mode.

1.3 Thesis Outline

The thesis consists of ten chapters as follows:

**Chapter 1** gives an overview of the area of research and highlights the main research aims and an outline of the thesis structure.

**Chapter 2** presents a review of the research literature on the tube corrosion of low-rank coal, brown coal and lignite upon oxy-fuel combustion. This review ultimately led to the identification of research gaps that formed the foundation of this PhD project.

**Chapter 3** summarizes the experimental and analytical facilities used during this research project, and the experimental methodology, including details of the alloys investigated. Detailed descriptions are provided on the tube corrosion experimental set-up, as well as each of the characterization techniques employed to assess oxide scale morphology and growth rates.

**Chapter 4** examines the corrosion of tubes exposed to Victorian brown coal fly ash under the oxy-fuel combustion mode. A temperature of 650 °C, flue gas composition (steam 30 vol%, O₂ 5%, SO₂ 3000 ppm, HCl 1000 ppm, N₂ 5% and CO₂ balanced), and an exposure time of 50 h were employed.

**Chapter 5** conducts tests of six tubes made from carbon steel SS400 to high-Cr-Ni austenitic steel SUS347 under the fixed exposure conditions, i.e. 650 °C, 50 h and fixed flue gas compositions. This
part of the study examines the flue gas-related tube corrosion rate, the role of the fly ash deposit and the inhibitory effect of silica additive under both air-firing and oxy-firing conditions.

Chapter 6 investigates the corrosive behaviour of selected tubes with different Cr contents and coated with lignite ash deposits during oxy-fuel combustion. The ash deposits were derived from the combustion of lignite and washed coal. The corroded tube’s surface and the ash samples used were characterized using X-ray absorption spectroscopy (XAS). Thermodynamic equilibrium calculations were also carried out to elucidate the experimentally observed phenomena.

Chapter 7 explores the effects of lignite ash deposits, in particular the Ca-bearing species in the ash, on tube corrosion under the oxy-firing mode. Two tubes, of low-alloy steel T23 and austenite SUS347, were coated with two ash deposits and exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The ash deposits were collected from the combustion of a lignite mixed with and without silica additive in a 30MW\(_{th}\) pulverized-coal-fired boiler.

Chapter 8 reports the results of using synchrotron X-ray fluorescence mapping and \(\mu\)-XANES to characterize the spatial distribution of individual elements and the speciation of Cr on a cross-section of various tubes exposed to oxy-fuel flue gas at 650 °C, 1 bar for 50 h. The gas composition tested is close to that of the flue gas produced from oxy-firing of low-rank coal in pilot-scale tests. Multi-layered scales with an uneven distribution were observed for individual elements on both the top surface and the spalled layer of carbon steel SS400.

Chapter 9 aims to investigate the oxidation kinetics of the high-temperature corrosion under the oxy-fuel combustion mode for low chromium ferritic steel material (T23) Apart from blank flue gases, four different types of fly ashes were also coated on tube surface for a detailed examination on their influence on the tube corrosion rate. Different kinetic models are examined in detail to understand the overall growth of the oxide scale and the controlling steps for different scenarios.

Chapter 10 summarizes the overall study and the implications of the major findings. Limitations of the current research are identified and suggestions for future research are discussed.
Figure 1.1 Thesis outline summary
References

1. Z. Li, X. Zhang, Y. Sugai j. Wang. Properties and developments of combustion and
gasification of coal and char in a CO₂-rich and recycled flue gases atmosphere by rapid
3. EIA, U., Annual energy outlook 2013. US Energy Information Administration, Washington,
DC, 2013
(CCC/147) International Energy Agency Coal Research, 2009
5. R. Stanger, and T. Wall, Sulphur impacts during pulverized coal combustion in oxy-fuel
technology for carbon capture and storage. Progress in Energy and Combustion Science,
combustion—State of the art research and technology development. Chemical Engineering
7. S. Soimakallio, and L. Saikku, 2012. CO₂ emissions attributed to annual average electricity
consumption in OECD (the Organisation for Economic Co-operation and Development)
8. A. Hjörnhede, M. Montgomery, M. Bjurman, P. Henderson, A. Gerhardt, J. Lecomte-
Beckers, Preliminary experiences with materials testing at the oxyfuel pilot plant at
9. G. Stein-Brzozowska, J. Maier, and G. Scheffknecht, Impact of the oxy-fuel combustion on
4: p. 2035-2042.
11. G. Scheffknecht, L. Al-Makhadmeh, U. Schnell, and J. Maier, Oxy-fuel coal combustion—A
12. R. Abang, A. Lisk, and H.J. Krautz, Fireside corrosion of superheater materials under oxy-
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CHAPTER 2

Literature Review
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Chapter 2 Literature Review

Scope of Literature Review

Chapter 2 provides a comprehensive and systematic review of research carried out to date on the properties of low-rank coals, CO₂ capture, oxy-fuel combustion and the mechanism of high-temperature tube corrosion.

2.1 Low Rank Coal

In general, coals can be categorized as high-rank coal and low-rank coal. [1]. Low-rank coal is rich in oxygen. Because of its porous structure, low-rank coal has high moisture content in the range of 30–70% [2, 3]. Most low-rank coal is run-of-mine material, and the quality can always be upgraded by drying. Selective mining is implemented in some places to improve the quality of low-rank coals. However, the utilization of low-rank coal including brown coal has received more consideration in the energy and mining industries due to the depletion of high-rank coal in the world [3].

Less than 15% of the worldwide production of low-rank coal is washed or dried [4]. The content of ash in low-rank coals differs very widely, with most falling within the range 5–50%. Low-rank coal contains less fixed carbon than high-rank coals such as anthracite and bituminous. However, the high moisture and ash content in low-rank coal lower the heating value, and the efficiency of combustion is affected. The properties of low-rank coals from diverse countries are shown in Figure 2.1 [5]. Lignite is brown in colour, and it frequently shows a woody structure. Subbituminous coal is black. It has bright surfaces, and a laminar structure. These coals are softer than high-rank coals and they can be easily pulverized.
Figure 2.1 Moisture and ash contents and calorific values of different low-rank coals [5]
2.1.1 Victorian Brown Coal (VBC)

Victoria has major reserves of brown coal not only in Australia but also in the world [6]. It is estimated that this brown coal reserve could last for at least 500 years at the current rate of consumption. Due to its abundance and low cost, VBC has been widely used as one of the main energy sources in Australia, supplying more than 90% of the electricity produced in the state [7]. In contrast, bituminous coal is the most commonly used coal for utility boilers in many countries, including the United States [5]. In many respects, the structure, chemical properties and physical properties of VBC are unique. VBC also has many benefits. For instance, the production cost for this brown coal is low, and it has high reactivity, and low ash content. The most obvious difference between brown coal and bituminous coal is the price. The price of VBC is around AU$ 2-7 per tonne [8] whereas bituminous costs around AU$ 80-110 per tonne, depending on quality.

An important feature of VBC is its high moisture content of more than 65 wt. %. This makes it burning not very economically feasible, and high costs can incurred for its transportation. In addition, it has low thermal efficiency during the combustion process [9]. Despite these disadvantages, VBC has very low ash and low Sulphur, and a considerable amount of ion-exchangeable alkali and alkaline earth metals such as Na, Mg and Ca linked with the carboxyl groups which constitute part of the organic coal substance [10]. In addition, aluminum and silicon, which are lean [11] soluble salts (mostly NaCl), can be found in low-rank coals, mainly linked with the moisture in the coals [12, 13]. Most of the sodium (Na) in the VBC is found as sodium chloride (NaCl) as a result of the geographical location of the coal in the Latrobe Valley in Victoria [14]. Corrosion issues may occur during its utilization if the concentration of chlorine in the coal is approximately ~0.25 wt. % or more [15].

A study using new technique, x-ray absorption fine spectroscopy (XAFS) reported that organic chlorine is not present in VBC possibly linked to the sodium (Na⁺) in as-mined VBC (containing over 65 wt.% of H₂O) in a form comparable to that of chloride anions in aqueous solution [12]. VBCs are structurally complex and heterogeneous because of their detrital origin and early stage of coalification. This coal is extensively used for power generation in Australia but its full potential for other uses largely remains to be realized [16]. Low-rank coal combustion differs from bituminous coal combustion, where very few inorganic elements are released during pyrolysis [17]. This gives organically-bound minerals a greater potential to form wall slag or escape air pollutant control devices. Therefore, more studies need to deal with low-rank coal in relation to its combustion issues.


### 2.2 The Capture and Sequestration of CO₂

Carbon dioxide capture and sequestration (CCS) has been recognized as an approach which holds great promise to reduce the CO₂ emitted from stationary power stations, thus stopping it from entering the environment. The CCS process requires the storage of CO₂ in geological storage facilities such as deep saline aquifers (porous rock layers containing salty water deep underground), depleted oil/gas reservoirs, and others [18]. This process would sequester CO₂ for thousands of years. The CO₂ would be pumped as a supercritical fluid with higher density to maximize the utilization of the storage space. Air impurities such as O₂, and N₂ can dilute the CO₂ stream and thus increase the volume required for storage. Other impurities such as gases like SOx and NOx are process-dependent and may have impacts on other diluents [19].

Three main CCS technological pathways are available to capture CO₂ from power plants or large-scale industrial facilities, as shown in Figure 2.2. The three CCS technologies are post-combustion capture (PCC), pre-combustion, and oxy-fuel combustion. In PCC, CO₂ is captured from the exhaust of the combustion process by absorbing it in a suitable solvent. The CO₂ absorbed is liberated from the solvent and then compressed for transportation and storage. In contrast, the pre-combustion process, usually known as Integrated-Gasification-Combined-Cycle (IGCC), involves first converting solid, liquid and gaseous fuel to a mixture of hydrogen and carbon dioxide by one of a number of processes, such as gasification or reforming. Lastly, in the oxy-fuel combustion process, the fuel is burned in a high purity oxygen stream which includes slight or no N₂ generated from air separation units (ASUs). PCC is used primarily in coal-fired boiler plants, while IGCC is used in gasification plants, whereas oxy-fuel combustion technology can be implemented in new plants or retrofitted to existing plants [20].
2.2.1 Oxy-Fuel Combustion

Oxy-fuel combustion is a combustion process which removes N₂ from the combustion cycle by burning the fuel in a mixture of high-purity oxygen (greater than 95%) and recirculated flue gas (RFG) to generate a capture-ready CO₂-rich stream from power plants. Both the properties of the flue gas and ash deposits are remarkably altered from those when the conventional air-firing mode is used [21]. The concept of this technique was suggested by Abraham in 1982 to produce CO₂ for coal-fired processes to enhance oil recovery [22]. Figure 2.3 depicts a basic diagram of this process. The addition of recirculated flue gas is necessary to lower the temperature of coal combustion, as the burning of fuel in high purity oxygen results in extremely high combustion temperatures that are not necessary in pulverized coal boilers [23, 24]. This configuration has been widely applied to control the temperature of the flame and to reconstruct the volume of flue gas to ensure proper heat transfer in the boiler. The oxy-fuel technique can be modified for present conventional coal combustion plants, and it allows carbon dioxide to be readily stored without costly scrubbing of flue gas as in the PPC process [24].

The efficiency of producing electricity by air-firing combustion is higher than that of oxy-fuel combustion. However, the air-firing process is less efficient than oxy-fuel combustion with sequestration of CO₂ because of the remarkable energy desired to scrub the dilute gas stream before
compression. Therefore, a large number of studies have reported that oxy-fuel technology is the most favourable in terms of the cost of CO₂ abatement, due to its technological and economic feasibility [24].

With a stricter requirement on CO₂ purity for pipeline transportation and storage, pollution control equipment has been again considered in the flue gas recycle configurations [30]. Specifically, remarkable challenges are predicted in the combustion process itself, since higher concentrations of CO₂, H₂O and SO₂ in the flue gas may accumulate due to flue gas recirculation, which results in 2/3 times higher concentration than in conventional air-firing combustion as an oxidizer. As a result, not only sulphation can be expected in the combustion process but also carbonization may occur on ash deposit surfaces under oxy-fuel combustion conditions [25]. Aggressive gases, such as SO₂ and HCl, cause remarkable corrosion in superheater and reheater tubes, and increase the decomposition temperature of carbonates with high partial pressures of CO₂. This form of corrosion is known as fireside corrosion and is caused by the formation of melt deposits on the tube surfaces of superheaters and reheaters, and therefore raise potential corrosion issues in the coal mill and flue gas pipes [26].

Up to the present time, very few studies have focused on the corrosion of oxy-fuel mode, partially due to the necessity for long-term exposure tests [27]. Based on preliminary tests, it has been concluded that oxy-fuel mode may increase the risk of corrosion in superheater/reheater tubes by surface chromium depletion, due to the enhanced formation of chromium carbide on austenitic alloy tubes [27]. However, tube corrosion can be minimized by using low-sulphur, low-chlorine coal and flue gas, which desulfurized in the recycled gases to reduce SO₂ and Cl concentrations in the furnace. However, in another study, it was suggested that oxy-firing is no more corrosive than air firing [28].
2.2.2 Speciation of Sulphur and Its Impacts on Oxy-Fuel Combustion

Four main elements in fuels are considered to be crucial reasons for corrosion in coal-fired boilers. They are sulphur, vanadium, alkalis sodium and potassium. Vanadium is present only in fuel oils. Sodium and potassium can be found in coal, whereas sulphur exists in both coal and fuel oils. Generally, sulphur exists as an impurity in fuels or feedstock. It is a serious corrosive contaminant in the high-temperature industrial environment. Excessive air is used to ensure the complete combustion of fuel for the generation of heat in many industrial processes. Oxygen can react with sulphur in the fuel to form SO$_2$ and SO$_3$. The corrosive effects of sulphur gases on boiler tube alloys rely largely on their oxygen concentration. Greater concentrations of SO$_x$ are of notable interest because they have significant effects on the corrosion process and on sulphur retention in fly ash. In a coal-fired boiler, the existence of sulphur gases substantially increases the corrosion rate [29], [30]. Zheng et al. [31] reported that a dry cold flue gas recycles FGR may be the best option for high-sulphur coal. The FGR is usually processed in a flue gas desulfurization unit (FGD) and a flue gas condenser. Therefore, most of the SO$_x$ will be eliminated. In contrast, a wet, hot recycle prior to the FGD is predicted to expedite tube corrosion in boilers [31].

Many studies have investigated the speciation of sulphur in coal combustion in air-fired power plants [32-36]. Many mechanisms and paths of sulphur to react in a combustion environment are known and
are anticipated to be comparable for oxy-fuel combustion. Sulphur enters the combustion system and is bound to both organic and inorganic portions of the coal. The concentration of SO$_3$ was initially shown to be lower in air-fired than in oxy-fuel conditions [30]. Others proposed that the temperature of the acid dew point is increased from 20 to 30 K under oxy-fuel conditions, because of the higher SO$_3$ and H$_2$O content in the flue gas [37]. **Figure 2.4** illustrates the acid dew-point temperature versus the SO$_3$ concentration at different H$_2$O concentrations for the following cases: air-firing (9% H$_2$O), oxy-fuel with dry recycle (12% H$_2$O), and oxy-fuel with wet recycle (37% H$_2$O).

![Figure 2.4 Dew point temperature vs. SO$_3$ and H$_2$O concentration [37].](image)

**2.3 High-Temperature Corrosion Mechanisms**

High temperature corrosion in boilers is a major concern in the operation of coal fireside plants. It causes shutdowns in coal fireside plants, accompanied by issues such as slagging and/or fouling in the boiler, and excessive refractory and metal wear. High-temperature tube corrosion is estimated to account for up to 75% of waste to energy plant shutdowns [39] and corrosion-related conservation costs account for one third of the yearly conservation budget, which may be as high as 10% of the yearly turnover [39]. In this section, the corrosion sensitive areas are identifying various corrosion mechanisms so as to outline the probable approaches to curtail tube corrosion issues.
High-temperature corrosion does not involve the existence of an electrolyte liquid. Alloys often depend on the oxidation reaction to form a protective oxide which is resistant to corrosion attacks, such as sulfidation and carburization. Generally, the corrosion mechanism is derived from the major components, including oxidation for oxides, sulfidation for sulfides, and carburization for the formation of carbides.

The properties of high-temperature oxide films, such as thermodynamic stability, and the ionic defect structure, play a major role in determining the oxidation resistance of a metal or an alloy in a particular environment [40]. The most important feature for oxide formation is their thermodynamic stability which is considered first.

2.3.1 Thermodynamic Considerations

2.3.1.1 Oxidation of metals

Oxidation is the most common reaction of high-temperature corrosion, creating an oxide film on the surface. Stainless steels are alloys typically utilized for boiler tubes, which are able to form a protective and adherent oxide scale on the tube surface.

A solid (metal) M, reacts with gases, such as oxygen, at a high temperature by initial absorption of oxygen and a chemical reaction to produce oxide. The underlying metal may be protected by the subsequent oxide nucleation and lateral growth resulting in the formation of a continuous film. The film may also thicken into a non-protective scale with defects such as cavities, micro-cracks and porosities [41]. Oxidation in air by oxygen proceeds according to the following Equation (2.1):

\[ M + O_2 = MO_2 \quad Eq. (2.1) \]

The prediction of the spontaneous occurrence of such a reaction can be derived from the second law of thermodynamics. Under conditions that both temperature and pressure are constant, the second law of thermodynamics can be written in terms of Gibb’s free energy as shown in Equation (2.2) [42]:

\[ \Delta G = \Delta H - T\Delta S \quad Eq. (2.2) \]
where, the driving force for the reaction is given by the change in Gibb’s free energy $\Delta G$ with $\Delta H$ being the difference in enthalpy, $T$ the temperature of the system and $\Delta S$ the entropy change. Under these conditions, the second law states of thermodynamic, that the Gibb’s free energy change is as follows:

$\Delta G < 0$: spontaneous reaction expected, $\Delta G > 0$: the reverse reaction is favoured, $\Delta G = 0$: reaction in equilibrium.

$$\Delta G = \sum \Delta G_{\text{product}} - \sum \Delta G_{\text{reactant}} \quad \text{Eq. (2.3)}$$

With the approximation for ideal gas where the oxygen activity is identical with its partial pressure, the Gibb’s free energy for the oxidation reaction can be written as Equation (2.4):

$$\Delta G = \Delta G^\circ + RT \ln K_{eq} \quad \text{Eq. (2.4)}$$

where, $\Delta G^\circ$ is the standard Gibb’s free energy, $R$ is the gas constant, and $K_{eq}$ is the equilibrium constant for the reaction. At equilibrium ($\Delta G = 0$). Equation (2.4) can be transformed as:

$$PO_2 = e^{\Delta G^\circ} RT \quad \text{Eq. (2.5)}$$

where, $PO_2$ is the dissociation pressure of the oxide, which can be interpreted as the lowest pressure of the oxygen needed for the oxide to be stable at a given temperature.

Equation (2.5) allows the calculation of the dissociation pressure of a given oxide as a function of temperature. This value can easily be determined from the Ellingham-Richardson diagram in Figure 2.5. Figure 2.5 plots the standard free energies of the formation of oxides versus the temperature. The thermodynamic stabilities of different oxides are compared in this diagram. The lower the position of the line in the diagram, the more stable the oxide is. For example, the line for Fe (formation of Fe$_2$O$_3$) is above the line for Al (oxidation of aluminum). The diagram refers to 1 mole O$_2$. For example, the line for the oxidation of chromium shows $\Delta G$ for the reaction $\frac{3}{2}Cr_{(s)} + O_{2\text{(g)}} \rightleftharpoons \frac{2}{3}Cr_2O_3_{(s)}$, which is $2/3$ of the molar Gibb’s energy of formation $\Delta G^\circ$ (Cr$_2$O$_3$). In addition, a significant conclusion which can be drawn from this diagram is that metal oxides become thermodynamically less stable when the temperature increases [43].
Figure 2.5 Ellingham diagram of metals and metal oxides [44]
2.3.2 Kinetics of Oxidation

The Ellingham diagram has a major disadvantage as the kinetics of reactions are not taken into consideration. Based on the equilibrium diagram, we understand that only under certain parameters such as temperature and partial pressure of oxygen, can an oxide be formed. There is a possibility that the kinetics of the process are so slow that it is even possible for the reaction to occur thermodynamically, and it will take a long time to form. Hence, it seems that the reaction of oxidation has not taken place. Therefore, it is essential to understand the kinetics of oxidation reactions. Moreover, the diagrams are not able to predict what type of oxide will be formed due to the formation of several oxides concurrently under a given condition. The reaction kinetics of the formation of different oxides need to be taken into consideration. To better understand the behaviour of an oxide, a combination of the knowledge of both thermodynamic and kinetics is crucial. Moreover, to further understand the reaction mechanisms, knowledge of the reaction rates is essential [44].

A number of various influences, such as temperature, oxygen pressure, surface preparation and the pretreatment of the metal, affect the reaction rates and the corresponding rate equations for the oxidation of a metal. It is very important to understand the kinetics of oxidation when estimating the lifespan of the metal in any engineering design. Various rate laws including linear, parabolic, and others are generally encountered [92].

2.3.2.1 Logarithmic Law

Oxidation can be characterized by a thin layer system. The kinetics generally follow logarithmic behaviour in the case of metals which are heated at low temperatures, in general, up to 400 °C. The reaction rate increases rapidly at the start and then decreases, following either a direct or inverse logarithmic law [44, 45]:

**Direct logarithmic law:** \[ x = K \log t + A \quad \text{Eq. (2.6)} \]

**Inverse logarithmic law:** \[ \frac{1}{x} = B + K' \log t \quad \text{Eq. (2.7)} \]

where, \( x \) is the change in weight (the amount of oxygen consumed per unit surface area) or the thickness of oxide formed (the amount of metal converted to oxide) as a result of oxidation, \( t \) represents the time, \( K \) and \( K' \) are the rate constants for logarithmic and inverse logarithmic process.
respectively, whereas A and B are the integration constants. Figure 2.6 shows the plotted values of \( x \) vs. time. A number of theories elucidate the two logarithmic laws. These depend on the transference of either ions or electrons.

### 2.3.2.2 Parabolic Oxidation

The parabolic law is very important in the oxidation of metals. According to this law, oxide growth takes place when the oxidation rate decreases. The reaction rate is therefore inversely proportional to the scale thickness or the weight of oxide which is formed. This can be expressed as [92]:

\[
\frac{dx}{dt} = \frac{k_p}{x} \quad \text{Eq. (2.8)}
\]

or after integrating:

\[
x^2 = 2k_p t + C \quad \text{Eq. (2.9)}
\]

where, \( k_p \) is the parabolic rate constant and the different values of \( x \) vs. \( t \) are plotted in Figure 2.7. At high temperatures, most metals and engineering alloys follow parabolic kinetics. The process of oxide growth is commonly ruled by the diffusion of ions or electrons across the oxide scale which is initially formed. Wagner was the first to propose the parabolic law, assuming the diffusion of charged species across the oxide layer [92].
Figure 2.6. Kinetics of logarithmic oxidation [92]

Figure 2.7. Kinetics of parabolic oxidation [92]
2.3.2.3 Linear Rate Law

The oxidation rate stays constant with time and does not rely on the amount of gas or metal previously expended in the reaction in certain metals. In such a case, the reaction rate is directly proportional to time:

\[
\frac{dx}{dt} = K_1 t \quad \text{Eq. (2.10)}
\]

or

\[
x = K_1 t + D \quad \text{Eq. (2.11)}
\]

where, \( x \) is the scale thickness and \( K_1 \) is the rate of the reaction. These reactions generally occur due to surfaces or boundary reactions. The steady-state reaction is governed by the formation of oxide at the metal oxide interface at a steady state. Such reactions may involve diffusion through a protective layer of constant thickness. Metals such as alkali/alkaline earth metals follow the linear rate law when a protective scale cracks, which leads to the evolution of gas to metal, followed by rapid oxidation rates by linear kinetic mechanisms [92].

2.3.2.4 Combination of Simple Rate Equations

In many examples, it has been observed that kinetics is not ruled by the three laws referred to above. Instead, a different oxidation law seems to be followed. Many metals at a low temperature follow a cubic law. This can, however, be elucidated in terms of the combination of logarithmic and parabolic laws. It is assumed that the reaction follows the logarithmic law in the initial stages of oxidations but changes to the parabolic law at some time.

Another important rate law which is always noticed at high temperature is the combination of parabolic and linear laws. The reaction progresses linearly during the initial stages and parabolically afterwards. In the reverse case, the kinetics of oxidation following a parabolic rate law suddenly change to linear kinetics; this occurs when the scale is partially cracked, or when micro-cracks occur at the scale interface. A very rapid oxidation rate, following linear kinetics, results from a direct access of gas.
2.3.3 Characterization and Identification of Scales

Kinetics of reaction enables researchers to understand how rapidly oxidation will take place or how long a metal will last at a certain temperature in an atmosphere. If we aim to understand the mechanism of oxidation so that the oxidation behaviour of a metal or alloy can be amended, we must have detailed information about the scale constituents, scale structure, and composition. This information can be obtained using a number of techniques.

Visual and stereo-microscopic analysis are the two simplest techniques which are used to produce details about scale cracks, spallation, exfoliation, etc. The scale is then exposed to either X-ray diffraction analysis to detect the various oxides formed through oxidation or secondary ion electron microscopy (SIMS) coupled with energy-dispersive X-ray analysis (EDAX) for surface topography, surface morphology, and surface composition. Information such as nodule formation, convoluted layers, and type of oxide (whether it is crystalline or amorphous) can be found from Scanning Electron Microscopy (SEM). Optical microscopy (OM) and SEM/EDAX analysis of scale cross-sections are used to observe the number of oxide layers, scale adherence, inter-layer scale adherence, and the distribution of diverse elements in the scale. Layers of the scale formed have been investigated by both electron spectroscopy for chemical analysis (ESCA) and SIMS to understand oxide structure along with depth profiles. The acoustic emission technique (AET) is another important technique used to provide details of scale spallation, scale adherence or, in general, the integrity of the scale and coatings. It relies entirely on the acoustics of the process during oxide growth and the information obtained is complementary to the information gained from other techniques of analysis and kinetics [92].

2.3.4 Active Oxidation

In general, chlorine-containing compounds are considered one of the major corrosive components of the fireside environment. The active oxidation mechanism, also known as the chlorine cycle, usually explains the effect of these corrosive compounds. The mechanism of active oxidation includes the following stages: 1) chlorine formation at the scale surface, 2) chlorine permeates inside the scale to the oxide/metal interface, 3) chlorides form on the metal surface components, 4) chlorides diffuse outwards, and 5) chloride reacts with existing oxygen in the environment to form chlorine and metal oxide [46]. The active oxidation mechanism is demonstrated in Equations (2.12) and (2.13).
1. Formation of chlorine: Chlorine is formed from the oxidation of HCl and catalyzed by the oxides of the scale, or from the reaction of chlorides such as NaCl with the oxides of the scale, as shown in Equations (2.12) and (2.13) [46]. Abels et al. [47] reported that Cl2 is the main aggressive species for a short-exposure test. The equilibrium of reaction (2.12) is established in the gas phase, but metal oxides act as catalysts for the reaction. Therefore, it may be assumed that the equilibrium of reaction (2.12) is approached on and in the oxide layer.

\[
2 \text{HCl}_{(g)} + \frac{1}{2} \text{O}_2 = \text{Cl}_2 + \text{H}_2 \text{O}_{(g)} \quad \text{Eq. (2.12)}
\]

\[
\text{NaCl}_{(g)} + \text{Fe}_2\text{O}_3 + 0.5\text{O}_2 \rightleftharpoons \text{Na}_2\text{Fe}_2\text{O}_4 + \text{Cl}_2 \quad \text{Eq. (2.13)}
\]

2. Permeation of chlorine and formation of metal chlorides: Thermodynamic calculations [48] of the dissociation constant of HCl as a function of temperature indicate that chlorine exists as Cl2 up to a temperature of 600°C, whereas the formation of HCl is enhanced above 600°C in the presence of steam (H2O). Thermodynamic calculations also indicate that metals also react directly with HCl to form metal chlorides as shown by reaction (2.14):

\[
\text{Fe} + 2\text{HCl} \rightleftharpoons \text{FeCl}_2(s) + \text{H}_2(g) \quad \text{Eq. (2.14)}
\]

Gaseous chlorine diffuses to the oxide layer through its cracks and pores, thus allowing the formation of metal chlorides at the metal-oxide interface. The formation of chloride is also thermodynamically favourable because its Gibb’s free energy (ΔG) has a negative value. The metal chloride is more stable than the oxide scale due to the low oxygen partial pressure on the tube surface. Grabke et al. [46] determined that Cl2 partial pressure is much below that of chloride at about (10^{-10}-10^{-13}) bar. The partial pressure of chlorine allows it to react with the metal and therefore, metal chloride is formed, as given below:

\[
\text{Fe} + \text{Cl}_2 \rightleftharpoons \text{FeCl}_2(s) \quad \text{Eq. (2.15)}
\]

At the interface, the vapor pressure of FeCl2 is moderately high, even at low temperatures. Vapour pressures are primarily dependent on the temperature and the concentration of HCl in the gas [49].
3. Diffusion of metal chlorides outward: Because of the volatility of iron chloride, continuous evaporation takes place by reaction (2.16). Subsequently, the resultant volatile metal chloride diffuses outward through the cracks and pores in the scale. On its way outward, chloride is oxidized to Fe$_2$O$_3$ and/or Fe$_3$O$_4$ by reactions (2.17) and (2.18) as the oxygen partial pressure increases near the oxide/gas interface. These oxides do not form as a perfect layer. Instead, they are porous and non-protective. By means of reactions (2.17) and (2.18), chlorine is released and diffused to bulk gas. However, a fraction of the liberated chlorine migrates back through the oxide-deposit interface to react with the metal at the oxide/metal interface and form metal chlorides again. Thus, a cycle is formed, providing continuous transport of metal away from the metal surface towards higher oxygen partial pressure.

\[
FeCl_2(s) \rightleftharpoons FeCl_2(g) \quad Eq. \ (2.16)
\]
\[
FeCl_2 + 1.5O_2 \rightleftharpoons Fe_2O_3 + 2O_2 \quad Eq. \ (2.17)
\]
\[
3FeCl_2 + 2O_2 \rightleftharpoons Fe_3O_4 + 3Cl_2 \quad Eq. \ (2.18)
\]

The rate of this phenomenon relies on the rate of chlorine diffusion between the metal and the gas phase. It is believed that the diffusion of the gas across the scale is the rate-controlling step in the corrosion process [46]. Figure 2.8 shows a phase stability diagram of the system of Fe-O-Cl at 500°C, which shows the stability of FeCl$_2$ corresponding with the Fe/Fe$_3$O$_4$ phase boundary.

The fact that reactions (2.12), (2.14), and (2.16) - (2.18) include the principal reaction path in the active corrosion of iron and low alloy steels has been observations: a) ferrates produced by the interaction of solid alkali chlorides on the scale, b) formation of solid metal chlorides, mostly FeCl$_2(g)$ at the metal/oxide interface and c) the appearance of scales after some time of active oxidation and Fe$_2$O$_3$. Figure 2.9 illustrates a diagram path of the circuit reaction of the active oxidation of iron.
Figure 2.8 Phase stability diagram of Fe-O-Cl system at 500°C [46]

Figure 2.9 Schematic mechanism for active oxidation reactions
2.3.5 Corrosion Due to Molten Salts

Deposits with low melting points, particularly alkali salts, are considered to be the main cause of the high-temperature tube corrosion and fireside corrosion in coal-fired boilers. The contents of sulphur (S), chlorine (Cl), and alkali metals in a fuel are crucial factors affecting fireside tube corrosion.

At the temperature of interest in advanced combustion systems, mixtures of alkali chlorides control the fireside deposits. The temperature regimes in which this corrosion happens are illustrated in Figure 2.10. The impact of boiler deposits on the tube corrosion of structural materials has been reported in a previous study [50]. With respect to ash deposit on tube surface, corrosion may occur by the formation of low-temperature eutectics, including chlorides (e.g. NaCl - CrCl₂ with a melting point of 437°C), chloride - chromate (e.g. NaCl-Na₂CrO₄ melts at 557°C, [51, 52], pyrosulfates (e.g. Na₂S₂O₇) with the involvement of SO₃ formation catalyzed by the presence of Fe₂O₃ in the ash deposit, and alkali-metal-trisulphate (e.g. Na₃Fe (SO₄)₃ melting at 624°C [37, 53]. The corrosion caused by these ash-related reactions is maximized at 650°C [32], at which a melting solution is formed at its maximum amount to dissolve the protective scale. Furthermore, sulphide can be formed, which enhances the break-down and even spallation of the protective scale due to the higher diffusion rates in sulphides, the greater tendency of sulphides to form low melting eutectics and the low solubility of sulphur [54]. The reaction mechanisms are elucidated below:

1. Formation of pyrosulfates: The generic reaction for the formation of a liquid phase containing pyrosulfates can start with the reaction of alkali chloride deposits on the metal-oxide interface, following the equation below (2.19) [53]:

\[
2NaCl_{(s,l)} + 2SO_2 \rightleftharpoons Na_2S_2O_7(s) + Cl_2(g) \quad (\Delta G^\circ) = -137 + 0.308T \ (K) \ \text{kJ/mol}
\]

\textit{Eq. (2.19)}

The (\Delta G^\circ) of this reaction has a negative value under 723K (450°C), and therefore this reaction will occur below this temperature. When sufficient SO₂ exists in the flue gas, the oxides (iron oxide) can catalyze the oxidation of SO₂; hence, SO₃ can be formed, as shown in reaction (2.20):

\[
SO_2 + 0.5O_2 \rightleftharpoons SO_3
\]

\textit{Eq. (2.20)}
Pyrosulfates can be formed subsequently, according to reaction (2.21) below [55]:

\[ Na_2SO_4 + SO_3 \rightleftharpoons Na_2S_2O_7 \]  \hspace{1cm} Eq. (2.21)

2. Formation of alkali-metal-trisulphate: The most common form of enhanced corrosion of the superheater tubes in conventional coal-fired boilers is caused by the existence of liquid phase alkali-metal trisulphate. The deposited alkali sulfates react with sulphur dioxide (SO\(_2\)) and iron oxide to produce liquid alkali-iron sulfates, according to reactions (2.22) and (2.23) below:

\[
3Na_2SO_4 + 3SO_3 + Fe_2O_3 \rightleftharpoons 2Na_3Fe(SO_4)_3(s,l) \hspace{1cm} Eq. (2.22)
\]

\[
3Na_2SO_4 + 3SO_3 + Fe_2O_3 \rightleftharpoons 2Na_3Fe(SO_4)_3(s,l) \hspace{1cm} Eq. (2.23)
\]

At around 500°C and above, the protective metal oxide can be attacked by tri-sulfate, according to the reactions (2.24 and 2.25) [37, 53]:

\[
3Na_2SO_4 + 3SO_3 + Fe_2O_3 \rightleftharpoons 2Na_3Fe(SO_4)_3(s,l) \hspace{1cm} Eq. (2.24)
\]

\[
K_2SO_4 + 3SO_3 + Fe_2O_3 \rightleftharpoons 2K_3Fe(SO_4)_3(s,l) \hspace{1cm} Eq. (2.25)
\]

The SO\(_3\) can be liberated once more and react and with sodium sulphate (Na\(_2\)SO\(_4\)), leading to a cyclic corrosion reaction, as shown in the following reactions:

\[
Na_2S + O_2 \rightleftharpoons Na_2SO_4 \hspace{1cm} Eq. (2.26)
\]

\[
3FeS + 5O_2 \rightleftharpoons Fe_3O_4 + 3SO_2 \hspace{1cm} Eq. (2.27)
\]

\[
2SO_2 + O_2 \rightleftharpoons 2SO_3 \hspace{1cm} Eq. (2.28)
\]
2.4 Formation of Solid Oxides upon High-Temperature Corrosion

The heat resistance of tubes and their rate of corrosion are highly reliant on the oxide scale formed on their surface. Generally, the scale consists of a broad variation of oxides that differ from one another in crystal structure and ion diffusivity as well as the capacity to resist corrosion attacks. The features of the main oxide forms are listed below.

**Hematite [Fe₂O₃]**

Hematite is present in two forms: α-Fe₂O₃ and β-Fe₂O₃. Above 400°C, Fe₂O₃ oxidizes to form α-Fe₂O₃ and only this structure is present at high temperatures. α-Fe₂O₃ has a corundum-type structure. A hexagonal close-packed lattice, two third are located at the octahedral sites, and formed by the oxygen ions in the structure. The oxide behaves as an n-type semiconductor at temperatures ranging from 650 to 800°C and as a p-type semiconductor at higher temperatures [57].
**Magnetite [Fe₃O₄]**

Magnetite is a mineral and one of the three common naturally-occurring oxides of iron. It is a member of the spinel structure group and contains both divalent and trivalent iron (Fe²⁺ and Fe³⁺), consisting of a face-centred cubic array of oxygen anions [44]. One-eighth of the tetrahedral holes are occupied by half of the trivalent ions and the octahedral holes are occupied by the rest of the ions. On both sites where iron ions may diffuse, defects can be detected. The oxide has a low degree of non-stoichiometry. However, it behaves as a p-type semiconductor [55].

**Wustite [Fe₁₋ₓO]**

Wustite is a mineral form of iron (II) oxide which is found in meteorites and native iron. It is stable above 570°C and reduces oxygen activities. The oxide is a p-type of semiconductor with metal vacancies, and it is highly non-stoichiometric. Its composition varies from Fe₁₋₀.₈₅O to Fe₁₋₀.₉₅O. Because of the high concentrations of defects, the mobility of cations and electrons via metal vacancies and electron holes is extremely high [58].

**Eskolaite [Cr₂O₃]**

At high temperature, the single solid chromium oxide can remain stable as eskolaite or chromia. It is a corundum structure spinel, considered to be a p-type semiconductor [36]. Solid-state diffusion is much slower than that of iron oxides. Hence, Cr₂O₃ is considered to be the best protective oxide scale at elevated temperatures and the principal protective oxide produced on stainless steel alloys.

**Corundum-type solid solution [(Fe, Cr)₂O₃]**

Eskolaite, Cr₂O₃, is completely soluble in Fe₂O₃ and the oxide formed on stainless steels is generally a solid solution to both, i.e. (Fe₁₋ₓCrₓ)₂O₃. The chromium content determines the protectiveness of this type of oxide.

**Spinel-type solid solution [Fe, Cr, Ni]₃O₄**

Oxides based on Fe, Cr and Ni may produce solid solutions with a spinel-type structure e.g. Fe, Cr, Ni₃ and O₄. Compared with magnetite, some of the Fe (III) ions may be substituted by Cr (III) ions,
whereas some of the Fe (II) ions may be replaced by Ni (II) ions. The actual composition relies on the plentiful supply of Fe, Cr and Ni, as well as the oxygen activity in the oxide/metal interface. Spinel-type oxides with other compositions may also produce, for example, \((\text{Fe, Cr})_3\text{O}_4\) and \((\text{Cr, Mn})_3\text{O}_4\) [59].

### 2.5 Effect of Steam on High-Temperature Tube Corrosion

It is widely known that the Fe-Cr alloys and stainless steels utilized as construction materials in heat-exchanging components depend on the formation of scale, namely \(\text{Cr}_2\text{O}_3\) or Fe-Cr spinel oxide, to provide resistance to oxidation. The existence of water vapour (\(\text{H}_2\text{O}\)) in the atmosphere enhances the volatilization of \(\text{Cr}_2\text{O}_3\) [68], [69]. In addition, it is very common for the oxidation rates at high temperature to increase considerably in steam-containing environments [54], [70, 71]. For instance, a higher growth rate of the oxide scale under oxy-fuel combustion was detected because of the increase in the steam content of the flue gas [72] and Asteman et al. [73] noted that high vapour pressure of \(\text{CrO}_2\) \((\text{OH})_2\) can be formed by reacting \(\text{Cr}_2\text{O}_3\) with steam in an \(\text{O}_2\) containing environment, as shown in reaction (2.29).

\[
\text{Cr}_2\text{O}_3(s) + 2 \text{H}_2\text{O}(g) + 1.5 \text{O}_2(g) \rightleftharpoons 2 \text{CrO}_2(\text{OH})(g) \quad \text{Eq. (2.29)}
\]

**Figure 2.11** clearly shows that corrosion is strongly influenced by the water vapour concentration. At a constant flow rate (1000 ml/min) for 168 h at 873K, the mass gain of tube 304L increases by a factor of five as the water vapour content increases from 10 to 20% by volume.

The effect of the flow rate is due to the fact that the rate of evaporation is surface-controlled. Volatile species diffuse out of the surface through a stagnant gas-phase layer, separating the surface from the bulk gas, and they are subsequently carried away by the gas flow. As the flow rate increases, the depth of the diffusion layer reduces, leading to an increased evaporation rate. As shown in **Figure 2.12**, the mass gain of tube 304L for 168 h at 873K in dry oxygen does not depend on the flow rate. In contrast, it is observed that the mass gain is dependent on flow rate when water vapour (\(\text{H}_2\text{O}\)) is present.

Graham and Davies [74] studied the flow-rate dependence of \(\text{CrO}_3(g)\) evaporation from sintered \(\text{Cr}_2\text{O}_3(s)\) in oxygen at 1473 K. They reported that the addition of 2.5 vol% of \(\text{H}_2\text{O} (g)\) resulted in a 50% increase in the evaporation rate, due to the formation of \(\text{CrO}_2\text{OH}(g)\). However, recent theoretical
calculations on the stability of various Cr species [75] predicted that this species was much less stable than the hexavalent CrO$_2$ (OH)$_2(g)$. Johnson and Panas [76] showed that CrO$_3$ immediately forms CrO$_2$(OH)$_2$ if it encounters H$_2$O, suggesting that CrO$_3(g)$ is not likely to be stable when water vapour (H$_2$O) is present.

In addition, Fe-base alloy research by Castle and Masterson [77] showed that the formation of volatile species Fe (OH)$_2$ clarified the oxidation mechanism of carbon steel in the presence of high-water content in the atmosphere, as shown in reaction (2.30):

\[
Cr_2O_3(s) + 2H_2O(g) + 1.5O_2(g) \rightleftharpoons 2CrO_2(OH)_2(g) \quad Eq. (2.30)
\]

![Figure 2.11 Mass gain versus P$_{H2O}$ content in atmosphere [72]](image-url)
2.6 Effect of CO$_2$ on High-Temperature Tube Corrosion

The carburization reaction may be enhanced on the tube surface because of the large amounts of CO$_2$ present in oxy-fuel combustion. Early investigations showed that the Cr steels exposed to a CO$_2$ environment tend to form a non-protective oxide scale similar to the scale formed during oxidation in a water vapour atmosphere [78-80]. It has also been found that carbide may form in the sub-scale region when these steels are oxidized in high CO$_2$-containing gas environments. Several researchers [81, 82] claim that carbide formation triggers the formation of iron oxide base scales because carbides tie up the free chromium in the steel matrix, which would otherwise be available for the formation of a protective, chromium-rich surface oxide scale.

A study of Fe-Cr and Ni-Cr alloys exposed to CO$_2$/CO environments [83, 84] demonstrated that if protective chromia-base scales are formed, the carburization reaction is inhibited. These scales act as obstacles preventing the permeation of the carbon. The transfer of carbon through the oxide layers may be caused by two mechanisms: diffusion and molecular transport through physical detects. A severe form of corrosion known as metal dusting occurs due to high carbon activity in the gas, leading to the formation of iron carbide (Fe$_3$C). As shown in reaction (2.31) below, this mechanism is attributed to the absorption of carbon into the metal [85]:

![Figure 2.12 Mass gain versus flow rate in various P$_{H_2O}$ content atmospheres [72]](image-url)
\[
\text{FeO} + \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe(OH)}_2(g) \quad \text{Eq. (2.31)}
\]

### 2.7 Summary of Literature Review and Gap in Research

Ash-related slagging/fouling and water tube corrosion are the most crucial issues encountered by coal-fired power generators. This issue is highly interrelated with changes in the oxy-coal burner design/configuration. In comparison to other issues such as ignition [86, 87], char oxidation [88] and pollutant emission [89], [90], [91], ash deposition and tube corrosion upon coal oxy-firing have been less studied. In particular, corrosion is a critical issue undermining the performance of coal-fired boilers, and responsible for shutdowns of power plants. Due to the complex reactions among the tube materials, corrosive gases such as (HCl/Cl\textsubscript{2} or SO\textsubscript{2}/H\textsubscript{2}S) and molten salt deposits which contain mainly sulphates and chlorides [46].

Results of numerous studies have been reported in the literature, mainly comparing the corrosion resistance of alloys and coatings in the fireside atmospheres of coal-fired utility boilers. However, the results of most of these studies were generated from laboratory studies under comparatively simplified test conditions. Since knowledge of the actual combustion environments present in coal-fired boilers is generally lacking, especially for those species most critical to fireside corrosion, most laboratory studies have applied conditions derived from either thermodynamic calculation of combustion systems or measurements of the product gases. With regard to oxy-fuel combustion, various corrosion data from extensive research studies were found from previous studies. However, these data are often inconsistent and at times debatable. A careful review of these studies shows that the majority have undertaken tests under conditions that did not fully reflect those anticipated for oxy-combustion in coal-fired commercial boilers. In fact, some of the laboratory tests were implemented under environments that deviated so greatly from those anticipated for oxy-coal combustion that they should not even be considered relevant. Specifically, with the employment of oxy-firing mode, impurities in the flue gas can accumulate, due to the recycling of the dirty, wet flue gases that are thought to enhance the formation of corrosive sulphates/sulphides under the same exposure times as the air-firing case, and even result in the formation of new species. The increased amounts of Na sulphates and chlorides in oxy-firing ash deposits [19] may further enhance the formation of sulphates/sulphides. However, the roles of the other species in ash, if any, have not been reported.
According to past studies on high tube corrosion under oxy-firing conditions, the extent of tube corrosion is very distinct for the diverse tests, and varies widely, depending on the samples of coal/ash utilized and the exposure parameters of the tests, such as time and temperature. A generalized conclusion is therefore yet to be achieved. In particular, corrosion tests under the oxy-fuel combustion of VBC are yet to be explored. Clarification of this is pivotal for the successful deployment of oxy-fuel combustion technology in the Latrobe Valley, where the combustion of VBC for power generation releases carbon dioxide at the highest rate in Australia.

With regard to the chemistry underpinning the speciation of the corroded tube surface and its interaction with ash deposition, nearly all previous studies relied on the use of bench-scale analytical facilities such as optical microscopy (OM), scanning electron microscopy (SEM), and X-ray diffraction (XRD), supplemented by thermodynamic equilibrium calculations using commercial software such as FactSage. The disadvantage of these techniques is the inability to pinpoint and specify the oxidation states of the metals of interest on the oxide scale/interface that is usually on the sub-micron scale. Jiao et al. [93] addressed the potential formation of toxic Cr (VI) and the variation of the quantities of Cr (III)-bearing species with flue gas composition. In contrast, Low et al. [94] examined the emission and characterisation of twelve trace elements (As, Ba, Be, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn) in the ash deposits from diverse sections of an industrial pulverized lignite-fired boiler and in the flue gas. Therefore, understanding is still incomplete with respect to the interaction between tube surface and ash deposit. In particular, understanding the roles of calcium-bearing species such as sulphates and free oxides is still far from complete.

Moreover, scientific knowledge of the effect of CO₂ and the speciation of chromium upon corrosion is still unclear. It is still unknown if carburization is the only reaction to the existence of abundant CO₂ in the flue gas stream. Real oxy-fuel flue gas has yet to be tested for the presence of carbides, as the oxygen partial pressure. The effect of ash deposits on the carburization reaction has also not been investigated. The conclusions regarding the carburization reactions are also quite contradictory in the literature. For example, one study [95] concluded that 9–12% Cr steels cannot exhibit a protective oxide scale due to the preferential formation of carbide in 30% H₂O/ 70% CO₂ at 500–700 °C. In contrast, another study using 2.25–20% Cr ferritic alloys in argon-20% CO₂–20% H₂O revealed the formation of a protective chromium oxide scale at 650 and 800 °C [96]. Moreover, previous studies either relied on microscopies that only focused on individual locations, or on XRD, which is unable to pinpoint the tube cross section which is generally on the micron scale. Chemical analysis methods
can detect and/or quantify carbides [96, 97, 98, 99], but fail to specify the spatial distribution and the partitioning of Cr between carbides and others.

References

4. G.R. Couch, Coal upgrading to reduce CO$_2$ correction required emissions, IEA Clean Coal Centre UK, 2002.


38. S. Chou, P. Daniel, A. Blazewicz, R. Dudek, Hydrogen sulfide corrosion in low-NOx
44. N. Birks, G.H. Meier, F.S. Pettit, Introduction to the high temperature oxidation of metals, Cambridge University Press, 2006
53. A. Karlsson, P.J. Møller, V. Johansen, Iron and steel corrosion in a system of O2, SO2 and alkali
chloride. The formation of low melting point salt mixtures, Corrosion Science, 30 (1990), pp. 153-158.


64. A.N. Hansson, M. Montgomery, M.A. Somers, Oxidation of X20 in water vapour: The effect of temperature and oxygen partial pressure, Oxidation of Metals, 71 (2009), pp. 201


89. E. Croiset, and K. Thambimuthu, NOx and SO$_2$ emissions from O$_2$/CO$_2$ recycle coal combustion. Fuel, 80(14) (2001), pp. 2117-2121


94. F. Low, A. De Girolamo, X. Wu, B. Dai, L. Zhang, Inhibition of lignite ash slagging and fouling upon the use of a silica-based additive in an industrial pulverised coal-fired boiler: part 3–
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CHAPTER 3

Experimental and Analytical Methods
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This chapter provides the general standard information on all the experimental and analytical methods and facilities. Specific details on the parameters are given in the relevant chapters.

**Research Methodologies**

This chapter summarizes all the experimental and analytical methods used in this thesis into three groups: experimental facilities, sample characterization methods, and modelling methodology. The experimental facilities included a high-temperature horizontal furnace for corrosion tests and a number of advanced equipment were employed for sample characterization. In addition, the modelling approaches are also briefly discussed, with more details included in the subsequent chapters. A snapshot of all the experimental facilities employed in this study is given below.

![Experimental Facilities Diagram](image)

**Figure 3-1 Snapshot of facilities employed in this research**
3.1 Sample Preparation

3.1.1 Ash Sample Properties

Four different types of fly ash sample were used for experiment in this study. These ash sample has different properties. Both the VBC Hazelwood fly ash (HW) and Yallourn fly ash (YL) fly ash were sourced from the brown coal-fired power plants in the Latrobe Valley, Australia. However, the HW-NaK synthetic fly ash had a typical ash composition to clarify tube corrosion under the worst scenario (80 wt. %) +Na₂SO₄ (10 wt. %) +K₂SO₄ (10 wt. %). Other samples include Xinjiang coal (XJC), a sub-bituminous coal found in Xinjiang, China and Xinjiang coal ash mixed with 4% silica. The properties of the ash samples were tested by X-ray fluorescence (XRF), and the results are shown in Table 3.1.

3.1.2 Tube Material Properties

Six steel specimens with the properties shown in Table 3.2 were tested, and photographs of the specimens are shown in Figure 3.2. The flat tube specimens (2 cm × 2 cm × 2 mm) were prepared by ion-beam cutting on the cross-sections of commercial-sized tubes. They were then degreased and cleaned in acetone and ethanol using an ultrasonic bath. For the corrosion test in flue gas only, the tube specimen was tested as it was. For the ash deposit-related corrosion test, fly ash powder (~100 mg per tube specimen) was spread uniformly over the surface to mimic ash deposition on a real steam tube surface, yielding a slightly compacted ash density of approximately 11 mg/cm² which was lower than but comparable with tests elsewhere [1]. The ash-laden tube specimen was then loaded on a quartz sample holder and pushed to the middle zone in the hot furnace. Subsequently, flue gas was fed at a continuous flow rate of 300 mL/min into the furnace. Each test lasted 50 h and two replicas were conducted for each condition. After the test, the particle-laden tube specimen was either scratched carefully to remove the ash particles to weigh its mass change, or quickly mounted (together with the ash particles) and solidified in epoxy resin to avoid surface oxidation. Note that the brushing of ash from the tube surface also removed the dusted species which were spalled off from the corroded tube surface.
Table 3.1 Elemental compositions of five fly ash samples tested, \textit{wt. %}

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Ash samples</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XJ (Ash 1)</td>
<td>10.4</td>
<td>12.46</td>
<td>8.27</td>
<td>16.24</td>
<td>0.45</td>
<td>10.58</td>
<td>0.45</td>
<td>38.82</td>
<td>0.38</td>
</tr>
<tr>
<td>XJC (Ash 2)</td>
<td>6.62</td>
<td>9.1</td>
<td>12.11</td>
<td>34.83</td>
<td>0.27</td>
<td>6.49</td>
<td>0.87</td>
<td>24.55</td>
<td>3.75</td>
</tr>
<tr>
<td>HW (Ash 3)</td>
<td>0.2</td>
<td>29.3</td>
<td>3.01</td>
<td>5.82</td>
<td>0.0</td>
<td>12.8</td>
<td>0.17</td>
<td>32.4</td>
<td>14.0</td>
</tr>
<tr>
<td>HW-NaK (Ash 4)</td>
<td>4.53</td>
<td>23.4</td>
<td>2.4</td>
<td>4.6</td>
<td>0.0</td>
<td>12.8</td>
<td>5.6</td>
<td>25.9</td>
<td>11.2</td>
</tr>
<tr>
<td>YL (Ash 5)</td>
<td>3.12</td>
<td>23.95</td>
<td>3.03</td>
<td>2.91</td>
<td>0.0</td>
<td>6.25</td>
<td>0.15</td>
<td>9.67</td>
<td>49.0</td>
</tr>
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</table>

Table 3.2 Tube materials tested in this study

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Steel grade</th>
<th>Compositions</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS400</td>
<td>Carbon steel (JIS SS400-ASTM A283)</td>
<td>Nil</td>
<td></td>
</tr>
<tr>
<td>12Cr1MoVG</td>
<td>Low chrome ferritic steel</td>
<td>1.25 Cr - 1 Mo-V</td>
<td>0.9-1.2</td>
</tr>
<tr>
<td>T23</td>
<td>Low-alloy steel</td>
<td>2.25Cr-1.6W-V-Nb</td>
<td>2.25</td>
</tr>
<tr>
<td>T91</td>
<td>High chrome ferritic steel</td>
<td>9Cr-1Mo-V-Nb</td>
<td>9</td>
</tr>
<tr>
<td>SUS304</td>
<td>Austenite stainless steel (JIS SUS304-ASTM S30400)</td>
<td>18 Cr-8 Ni</td>
<td>18-20</td>
</tr>
<tr>
<td>SUS347</td>
<td>Austenite stainless steel</td>
<td>18Cr-8Ni-Nb</td>
<td>17-19</td>
</tr>
</tbody>
</table>
Figure 3.2 Sample preparation
3.2 Experimental Facilities

3.2.1 High-Temperature Horizontal Furnace (HF)

A horizontal test furnace was used for the tube corrosion tests, and its schematic diagram is shown in Figure 3.3. The temperature in the furnace was fixed to mimic post-combustion flue gas temperatures with a range of 500-800°C, which is similar to the conditions near the super-heater and re-heater in an industrial furnace. For each run, the ash sample was placed on the square specimen plate made of typical steel to mimic ash deposition on a real steam tube surface. The ash specimens were located on a quartz sample holder inside the corrosion furnace. The gas control system (at the furnace entry) and the flue-gas analyzer system (at furnace rear) were connected to the furnace. A thermocouple was used to record the on-line temperature of the specimen. All ash specimens were tested under 50 h exposure for tube surface corrosion.

The gas compositions were fixed to mimic typical air-firing and oxy-firing conditions (refer to Table 3.3). The gas flow rate was 300 mL/min. The furnace was kept at 650 °C since this is the most critical temperature for tube surface corrosion. The ash-free, flue gas-related corrosion tests were conducted under the same conditions without ash on the tube surface.

![Figure 3.3 Schematic diagram of hot corrosion furnace](image)
Table 3.3 Gas compositions used in air-firing vs. oxy-firing

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Air-firing</th>
<th>Oxy-firing</th>
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<tr>
<td>O₂ [vol%]</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CO₂ [vol%]</td>
<td>15.0</td>
<td>Bal.</td>
</tr>
<tr>
<td>SO₂ [ppm]</td>
<td>300</td>
<td>3000</td>
</tr>
<tr>
<td>HCl [ppm]</td>
<td>260</td>
<td>1000</td>
</tr>
<tr>
<td>H₂O [vol%]</td>
<td>8.0</td>
<td>30</td>
</tr>
<tr>
<td>N₂ [vol%]</td>
<td>Bal.</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3 Sample Characterization

3.3.1 X-Ray Fluorescence Spectroscopy (XRF)

The elemental compositions of the ash samples were quantified using a pre-calibrated XRF (SPECTRO IQ II). XRF is a technique used for the quantification of major ash-forming elements, which can characterize the sample in a solid powder at around 10 μm. Such fine particles can be achieved by using a dual mixer/mill (SPEX 8000D). In this research, XRF was mainly employed for the quantification of iron (Fe), magnesium (Mg), calcium (Ca), aluminium (Al) and silicon (Si). The XRF was fully calibrated for fly ash by using three different fly ash standard materials: SARM 1633a, SARM 1633c and SARM 2690.

3.3.2 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDX)

SEM and EDX were employed on the ash samples and the corroded tube samples to observe the surface characteristics of individual particles or the cross-sections of samples. A small amount of a solid powdered sample was loaded onto carbon tape fixed onto a sample stub for the analysis of particle surface morphology. The sample was coated with Platinum (Pt) using a sputter coater (QUORUM SC7620) prior to SEM analysis. The cross-section of the tube was obtained by cutting the tube using ion beam cutting. The SEM experiments including the element mapping were conducted at the Monash Centre for Electron Microscopy (MCEM) using a JEOL 7001F in backscatter mode.
3.3.3 Synchrotron X-ray Absorption near Edge Spectroscopy (XANES)

Fe K-edge XANES spectra were collected at the National Synchrotron Radiation Research Centre (NSRRC) BL16AI beamline in Hsinchu, Taiwan. The X-ray beam was diffracted by fixed-exit double-crystal Si (III) monochromators to vary the X-ray energy. The energy scale was calibrated with reference to an elemental Fe K-edge absorption peak with an energy of 7112 eV. Each spectrum was recorded from 200 eV below the edge to 250 eV above the edge. Spectra of standard compounds of various speciation and oxidation states were used to compare or quantitatively fit sample spectra to obtain information on the speciation of a particular element in the sample.

3.3.4 Synchrotron X-Ray Fluorescence (SXRF) and μ-XANES Analysis

SXRF and μ-XANES analysis were conducted at the XFM beamline, Australian Synchrotron. SXRF maps were collected at 15.8 keV with a Si (111) monochromator and an energy resolution (ΔE/E) of 2 × 10−4 and the Maia detector [2]. Kirkpatrick-Baez (KB) mirrors were used to focus the beam down to ~1.5 μm [3, 4, 5]. For each tube cross-section, an overview map, with areas ranging from 2.8 × 3.4 to 2.8 × 7.6 cm², was mapped using a pixel size of 100–200 μm² and a dwell time of 10 to 25 ms per pixel. Detailed maps were then collected over a ~2 × 0.4 cm² area using 2 μm² pixels and a dwell time of 0.4 ms per pixel. XANES stacks were generated by collecting SXRF images (~0.2 × 0.4 cm², 4 μm² pixels, and dwell times of 1 to 4 ms/pixel) at 77 monochromators energies spanning 100 eV across the Cr K-edge. Cr metal foil and a pellet of chromium oxide (Cr₂O₃) diluted in boron nitride were used to determine the energy shift for XANES analyses. SXRF data were analyzed using the dynamic analysis (DA) method in GeoPIXE II [2]. The DA approach fits multiple lines per element and separates overlaps and subtracts background, escape peaks and other detector artefacts. Note that light elements including C, Na and O cannot be detected by the Maia. The extracted XANES spectra were processed in ATHENA. Linear combination fitting (LCF) was used to qualitatively determine the mineral compositions, by using a variety of standards, including pure Cr metal oxide (Cr₂O₃), carbide (Cr₂S₃), hydroxide (Cr(OH)₃), chloride (CrCl₃), sulphide (Cr₂S₃), chromates (MgCr₂O₄, CaCr₂O₄, FeCr₂O₄) and Ca chromite (CaCrO₄). Note that the spectra for chromium carbide (Cr₃C₂) [6] and chromium sulphide (Cr₂S₃) [7] were cited elsewhere, whereas spectra for the other standards were collected from our previous studies [8-11]. Regarding the accuracy of analysis by SXRF and μ-XANES, the complete analysis of all measured quantities by SXRF based on GeoPIXE II and the relevant Maia detector was conducted by measuring a number of standard metal foils, such as Mn.
and Pt. The spectral fitting was further conducted based on the DA method which yields a relatively accurate quantification. Concentrations of individual elements (up to 52 in number) were calibrated using the known Fe concentration of the various tubes as an internal standard [12, 13]. Regarding the accuracy of μ-XANES and the relevant LCF method, our previous work based on the analysis of pure oxide mixtures [10] has shown a relative standard deviation of around 10% for this method.

3.4 Modelling Approach

3.4.1 FactSage Thermodynamic Calculation

The commercial thermodynamic equilibrium program, Fact Sage 6.5 (Equilib module) [14], was used to specify all the probable interactions between ash species and the tube surface. For each calculation, three scenarios were considered for the input: the co-existence of ash species and flue gas; the existence of ash species only; and the existence of flue gas components only. The first scenario mimics the ash-particle interface, which is exposed to both ash and bulk flue gas. The second scenario represents the interface where the bulk gas, particularly the oxidizing components, does not reach the tube surface, due to the diffusion resistance of the ash layer. The last scenario clarifies flue gas-related corrosion.

3.4.2. HSC 7.1 Thermodynamic Calculation

The commercial thermodynamic equilibrium program, HSC Chemistry 7.1 (Reaction equation module) [15] was employed to calculate the standard Gibbs function values (DG) for the potential corrosion reactions at 650 °C. The calculation is straightforward, with the input of all the reactants and products at stoichiometric ratios. The gas pressure was set at 1atm, and the built-in Main Database (MainDB7.HSC) was used. All the gases were assumed to be ideal gases.

3.5 Experimental Error Calculation

For the experiments conducted in this project, three replicates of a particular condition were performed. Errors associated with mass loss from HTF experiments were accounted by obtaining the standard deviation (SD) of the data from three replicates. For data obtained from XRF, three replicates of each sample analysis were taken, which resulted in a relative standard deviation (RSD). Errors for XANES fitting resulted in R-squared values.
References


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Monash University

Declaration for Thesis Chapter 4

Declaration by candidate

In the case of Chapter 4, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
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</thead>
<tbody>
<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
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<th>Name</th>
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<th>Extent of contribution (%) for student co-authors only</th>
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<tr>
<td>Juan Chen</td>
<td>Experimental work</td>
<td>10 %</td>
</tr>
<tr>
<td>Yoshihiko Ninomiya</td>
<td>Comments for my work</td>
<td>External co –author</td>
</tr>
<tr>
<td>Barbara Etschmann</td>
<td>Editing and data processing</td>
<td>Supervisor</td>
</tr>
<tr>
<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*

Candidate’s Signature

Main Supervisor’s Signature

Date
01.02.2020

*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
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CHAPTER 4

Tube Corrosion upon the Interaction with Victorian Brown Coal Ash Deposition
The literature review in Chapter 2 has shown that there is a lack of studies on tube corrosion of low rank coal upon oxy-fuel combustion. Specific research is required to examine the corrosion of tubes exposed to Victorian brown coal fly ash under the oxy-fuel combustion mode. This chapter specifically focuses on the understanding of the chemistry underpinning the interaction between fly ash deposit species and the tube surface upon the oxy-fuel combustion of Victorian brown coal. This chapter has been reformatted from the following published manuscript: I. Ja’baz, J. Chen, B. Etschmann, Y. Ninomiya, L. Zhang. High-temperature tube corrosion upon the interaction with Victorian brown coal fly ash under the oxy-fuel combustion condition. Proceedings of the Combustion Institute, 36 (2017) p. 3941–3948
Abstract

This study has examined the corrosion of tubes exposed to Victorian brown coal fly ash under the oxy-fuel combustion mode. The temperature of 650 °C, flue gas composition (steam 30 vol%, O₂ 5%, SO₂ 3000 ppm, HCl 1000 ppm, N₂ 5% and CO₂ balanced), and an exposure time of 50 h were employed. Through the joint use of advanced instruments such as synchrotron X-ray adsorption spectroscopy and thermodynamic equilibrium calculation, it has been confirmed that, from both mass loss and penetration rate perspectives, the corrosion of low-Cr tubes under the oxy-firing mode is severe compared to the respective air-firing mode. Both flue gas-related and ash-related corrosions are responsible for tube corrosion. In contrast, the corrosion rate of high-Cr tubes (∼20% for SUS304 and SUS347) is comparable between the two modes, due to the protective effect of Cr-oxide. The existence of fly ash on tube surface suppressed the chlorination reaction. Oxygen is the principal element permeating into tube under the air-firing mode, whereas both oxygen and sulphur penetrated into the tube under the oxy-firing mode, accelerating sulphation/sulphidation reactions for a rapid corrosion. Although Cr₂O₃ forms a protective layer under the air-firing mode, it broke down due to the accelerated corrosion attack caused by sulphates/sulphide under the oxy-firing mode. The interaction between ash and tube surface promoted the formation of pure oxides and oxide complexes with the involvement of Na and Ca as well. The presence of alkali sulphates in ash promoted the sulphidation reaction, the extent of which is however tube-specific and correlates little with Cr content. The use of advanced material SUS347 was found to be the most suitable candidate for heat-exchange tubes to be used in the oxy-firing boiler burning low-rank coal such as Victorian brown coal which is rich in alkali and alkaline earth metals.

Keywords: Oxy-fuel combustion; Victorian brown coal; Tube corrosion; XANES Fe and S K-edges


4.1 Introduction

Coal is the most abundant fossil fuel in the world and would expect to remain so for the rest of the century. The total amount of coal used is predicted to increase by 5% in 2040 [1]. Victoria, Australia is one of the largest brown coal reserves in the world [2]. Although bearing a very low amount of ash-forming elements in brown coal, the large amount of inherent moisture (up to 70 wt.%) within it results in a notoriously high CO$_2$ emission rate, compared to black coal [3]. Deploying the low-emission technologies such as oxy-fuel combustion is pivotal for the sustainable use of brown coal in the carbon-constrained future.

Compared to conventional air-firing mode, the oxy-fuel combustion provides a different atmospheric environment in the boiler. Apart from the high-concentrations of CO$_2$ and steam derived from wet flue gas recycle, the trivial but corrosive components including SO$_2$ and HCl are also potentially accumulated in the furnace, due to the recycle of the uncleaned, dirty flue gas [4,5].

In nearly all of the pulverized coal-fired boilers in Australia, the downstream gas cleaning units do not exit. In light of this, the high-temperature tube corrosion in the heat-exchanger zone is supposedly altered remarkably [6], under the oxy-fuel combustion mode for Australian coals including Victorian brown coal. With regard to the high-temperature tube corrosion, coal quality is the major player on the fire-side [7]. In addition to the afore-mentioned corrosives gases resulting in the oxidation, chlorination, sulphation/sulphidation and even carburization of tube material [8], the ash deposits also cause the wastage of tube surface, due to the formation of new species such as carbonates that are highly corrosive [9], and the promoted formation of other species such sulphates and chlorides that lower the melting point of tube material by forming new eutectics. As summarized in [9] and further discussed by the studies in an IEAGHG workshop [10], most of the previous studies on high-temperature tube corrosion focused on the effects of gaseous components such as CO$_2$, H$_2$O and SO$_x$. The ash-related corrosion, however has been much less examined. Even for the studies conducted to date, the conclusions achieved are far from generalized [11–14], due to the fact that the high-temperature tube corrosion is highly coal-specific. Victorian brown coal is different from German lignites [10, 15] and American coals tested previously [10, 16, 17], due to the high contents of inherent moisture and sodium within it.
In this study, we presented the results for the ash-related tube corrosions in the typical gas environment encountered during both the air-firing and oxy-fuel combustion of Victorian brown coal. That is, apart from the accumulated \( \text{SO}_2 \), a steam content of 30 vol% in flue gas is also probable for the recycle of wet flue-gas and the burning of partially dried coal. HCl was also added into the flue gas, to mimic the co-firing scenario in which biomass is blended with brown coal for a zero, and even negative carbon emission. The test temperature was fixed as 650 °C, at which the tube corrosion rate is maximum [9], and a test duration of 50 h have been conducted. Two typical fly ashes from Victorian brown coal-fired power plants were tested, and six tube materials with a chromium (Cr) content up to 20 wt.% have been tested. After each test, apart from weighing the mass change of a tube, a variety of advanced analysis was also conducted, optical microscope (OM) for the cross-section observation to quantify the corrosion depth, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analyzer (EDX) to map the penetration/diffusion of elements of interest through the ash-tube interface, X-ray diffraction (XRD) for the bulk surface, and synchrotron X-ray near-edge structure (XANES) for the oxidation states of iron (Fe), and sulphur (S) on both bulk and cross-section surfaces. Finally, thermodynamic equilibrium modelling was conducted to interpret the experimental observations. Such a study is expected to determine the suitability of and thus optimize the performance of tube materials. Ultimately, it aims to promote the deployment of oxy-fuel combustion for low-rank coal.

4.2 Experimental Procedure

4.2.1 Tube Corrosion Test Set-Up and Test Conditions

The experimental set-up is illustrated in Figures S1 and S2 in the supporting information (SI) document. A horizontal test furnace was used for tube corrosion test, which was first heated up to 650 °C. The fresh tube specimen, 2 cm \( \times \) 2 cm \( \times \) 0.2 mm, were prepared by a wire-electrical discharge machine. The oxidized outer surface was ruled out for testing. Photo of the fresh tube specimen is demonstrated in Figure S2 in the SI. Fly ash powder (~100 mg per run) was spread uniformly over the fresh tube plate surface to mimic the ash deposition on a real steam tube surface. The ash-laden tube specimen was then loaded on a quartz-made sample holder and pushed to the middle zone in the hot furnace. Subsequently, flue gas (as shown in Table 4.1) was fed at a flow rate of 300 mL/min continuously into the furnace. Each test lasted 50 h and two replicas were conducted for each condition. After the test, the particle-laden tube specimen was either scratched carefully to remove
the particles to weigh its mass change, or quickly mounted (with ash particles together) and solidified into epoxy resin to avoid the surface oxidation. Photos for ash coating, and corroded tube surfaces are further illustrated in Figure S3. Note that, such a testing procedure is consistent with the literature studies related to ash deposit-related tube corrosion [10, 15–17].

A total of six tube materials were tested, with a Cr content ascending sequence of SS400 (0% Cr), 12Cr1MoV (0.9–1.2%), T23 (2.25%), T91 (9%), SUS347 (17–19%) and SUS304 (18–20%). The elemental compositions of three fly ash samples tested are shown in Table 4.2, including Hazelwood fly ash (HW), modified Hazelwood ash (HW-NaK) for the raw Hazelwood fly ash mixed with Na₂SO₄ (10 wt.%) and K₂SO₄ (10 wt.%), and Yallourn fly ash (YL). Both HW and YL were sourced from the brown coal-fired power plants in the Latrobe Valley, Australia. The HW-NaK has a typical ash composition to clarify the tube corrosion under the worst scenario, in which the formation of alkali sulphate was enhanced due to the recycling of SO₂ in the dirty flue gas [18, 19]. Moreover, the fly ash samples tested here are similar with the ash deposits collected on the super-heater tube surface, in terms of the high contents of alkali sulphates [20]. The concentration of sulphates (as suggested by SO₃ content) decreases in a sequence of (YL) < HW < (HW-NaK). The ash-free, flue gas-related corrosion tests were conducted under the same conditions with the absence of ash on the tube surface.

Table 4.1 Flue gas compositions

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Air-firing [vol%]</th>
<th>Oxy-firing</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>CO₂</td>
<td>15</td>
<td>Bal.</td>
</tr>
<tr>
<td>SO₂</td>
<td>300</td>
<td>3000</td>
</tr>
<tr>
<td>HCl</td>
<td>260</td>
<td>1000</td>
</tr>
<tr>
<td>H₂O</td>
<td>8</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 4.2 Elemental compositions of three fly ash samples tested in this study, (wt.%)

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>0.2</td>
<td>29.3</td>
<td>3.01</td>
<td>5.82</td>
<td>0.0</td>
<td>12.8</td>
<td>0.2</td>
<td>32.4</td>
<td>14.0</td>
</tr>
<tr>
<td>HW-NaK</td>
<td>4.53</td>
<td>23.4</td>
<td>2.40</td>
<td>4.6</td>
<td>0.0</td>
<td>12.8</td>
<td>5.60</td>
<td>25.9</td>
<td>11.2</td>
</tr>
<tr>
<td>YL</td>
<td>3.12</td>
<td>24.0</td>
<td>3.03</td>
<td>2.91</td>
<td>0.0</td>
<td>8.03</td>
<td>0.15</td>
<td>9.67</td>
<td>49.0</td>
</tr>
</tbody>
</table>
4.2.2. Characterization of Corroded Tube Surfaces

For each un-mounted tube, its surface, namely bulk surface hereafter, were subjected to XRD analysis to qualitatively determine the crystallized species (Rigaku, Miniflex 600), under 40 kV voltage and 15 mA current, and the scanning speed was 1°/min with a step size of 0.01°. The peak identification was achieved by the search–match function in the JADE software. The XRD patterns are provided in Figures S4 and S5 in the SI. Additionally, each bulk surface was subjected to S K-edge XANES, the energy scale of which was calibrated with reference to elemental sulphur K-edge absorption peak with energy of 2472 eV. The data collection and interpretation processes are identical with our previous work [21].

For each epoxy-mounted tube, it was cut by wire-meshing and the resultant cross-section surface was analyzed by OM (Olympus) to establish the thickness of scale and depth of intergranular penetration, if any in the alloys; SEM-EDEX (JEOL 7001F) for micro-structure and the mapping of individual elements; and Fe K-edge XANES analysis and spectra interpretation by following our previous method [22]. The original and fitted Fe XANES spectra are further provided in the SI.

4.2.3 Thermodynamic equilibrium calculations

The commercial thermodynamic equilibrium program, FactSage 6.5 (Equilib module) was used to specify all the probable interactions between ash species and tube surface. The database FToxid-Slag in the program was used. For each calculation, three scenarios were considered for the input: the co-existence of ash species and flue gas; the existence of ash species only; and the existence of flue gas components only. The first scenario mimics the ash-particle interface which is exposed to both ash and bulk flue gas. The second one stands for the interface where the bulk gas particularly the oxidising components do not reach the tube surface, due to the diffusion resistance from ash layer. The last one clarifies the flue gas-related corrosion. The temperature was set at 650 °C for all the calculations.

4.3 Results and Discussion

4.3.1 Mass Change and Penetration Rate for Tube Corrosions

The mass change is the first index evaluating the tube corrosion rate. As illustrated in Figure 4.1
where the x-axis is listed in the ascending sequence of Cr content, oxy-fuel combustion led to the enhanced mass loss (thus corrosion) for almost all the tubes, irrespective of fly ash type. However, the enhancement is more obvious for the low-Cr tubes including SS400, 12Cr1MoVG and T23. For the other three tubes, there is a considerable overlap between air-firing and oxy-fuel modes, particularly for SUS347 in which the two modes are superimposed largely in the case of YL fly ash which contains least alkali sulphates. With respect to the fly ash-related corrosion, it is higher than the flue gas-only mode for the low-Cr SS400, and high-Cr tubes from T91 through to SUS347. Interestingly, for the two low-Cr tubes 12Cr1MoVG and T23, the flue gas-related corrosion is predominant over the ash-related corrosion, suggestive of the predominance of chlorination reaction for low-Cr tubes. Upon the increase in the Cr content in the tube material, the mass loss rate decreases considerably, implying the suppression of chlorination reaction.

The typical cross-sectional structures for corroded tubes are illustrated in Figure 4.2 where the tube T23 exposed to HW ash in air, flue gas only in air, HW ash in oxy-fuel and flue gas only in oxy-fuel mode were included. Clearly, apart from the formation of a thick interface denoting the penetration of oxidizing elements, a scale layer was also observed for the exposure to both ash and oxy-fuel flue gas. However, upon the co-existence of ash and flue gas in the air-firing mode, the penetration interface formed is much thinner, and a scale layer was not found either. Such a discrepancy echoes the significant corrosion under the oxy-fuel mode for this low-Cr tube. With respect to the flue gas-related corrosion, the interface was not observed. Instead, the tube surface turned rough and molten, implying the formation of low-melting eutectics such as chlorides [23]. Statistical analysis was further conducted to quantify the thickness of the corrosion interface depth, the corrosion rate or interface growth rate was further calculated by dividing by the exposure time, 50 h employed in this study. As depicted in Figure 4.3, the Cr content in tube material is in reverse proportion to the growth rate, irrespective of fly ash type. This is consistent with the literature finding [6]. For the tube T23 alloyed steel exposed to (HW) fly ash with the lowest Cr content, it was found to have the highest oxide thickness that is consistent with the literature [24]. The effect of fly ash type is marginal, given the fact that the experimental error is relatively large. In addition, the growth rate 0.2–1 μm/h found here is broadly consistent with the literature report on the tested alloy tubes with the similar Cr contents [25]. Moreover, the flue gas-related corrosion rate is comparable to that caused by fly ash only, 0.1–0.45 μm/h, further implying the enhanced corrosion upon the exposure of tube to both fly ash and flue gas.
Figure 4.1 Mass loss of different tubes for both ash-related and flue gas-related corrosion.

Figure 4.2 Macrostructure for T23 exposed to HW ash in air (a), flue gas only in air (b), HW ash in oxy-fuel (c) and flue gas only in oxy-fuel (d).
Figure 4.3 Penetration rate of different tubes calculated based on OM analysis

Figure 4.4 Elemental mapping for the cross-section of SUS347 exposed to flue gas only (a) and HW ash (b) in the oxy-firing mode.
4.3.2. Micro-Structure for the Cross-Section of Corroded Tubes

Figure 4.4 demonstrates the distributions of individual elements along the tube SUS347 cross-section, upon the exposure to flue gas without (a) and with fly ash loading (b) under the oxy-fuel mode. Clearly, the flue gas only resulted in the oxidation of Cr and Fe. The resultant oxides should break down and thus failed to form a protective layer. This could be due to the formation of chloride eutectics, as suggested in Figure 4.2. Therefore, oxygen (O) penetrated deeply into the Fe metal matrix. Such a phenomena was not confirmed for the air-firing flue gas only (data not shown), reflecting the high concentrations of corrosive gases, CO₂, H₂O, SO₂ and HCl within the oxy-fuel flue gas. For the fly ash-laden case, a Cr-rich protective layer was observed on the top of the interface, implying the resistance of fly ash layer against the attack of corrosive gases particularly HCl in flue gas. This could be due to the preferential chlorination of alkali and alkaline earth metals in the ash layer, and therefore, the molten chlorides were not formed on tube surface. Instead, both O and S permeated through the interface, suggestive of their overwhelming role on the ash-related tube corrosion, causing oxidation, sulphation and/or sulphidation of iron and other metals. In addition, since the creeping of S was not observed in the flue gas only case, the S in fly ash was apparently the major source accounting for the sulphation/sulphidation across the interface. Its interaction with iron metal could be due to the direct reaction between alkali sulphates and iron metal, as depicted in Eq. (4.1), or the combined reaction between alkali sulphates, SO₃ (derived from SO₂ and O₂ in flue gas) and iron oxide (Fe₂O₃), as shown in Eq. (4.2) [26].

\[
2(Na,K)₃Fe(SO₄)₃ + 17Fe \rightleftharpoons 8Fe₂O₃ + 3FeS + 3(Na,K)₂S \quad Eq. (4.1)
\]
\[
mNa₂SO₄ + nK₂SO₄ + 0.5Fe₂O₃ + 1.5SO₃ \rightleftharpoons 2(Na,K)₃Fe(SO₄)₃, m+n=1.5 \quad Eq. (4.2)
\]
Table 4.3 XRD results for the corroded tube surface exposed to HW ash.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Mode</th>
<th>Major</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS400</td>
<td>Air</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Pyrrhotite (FeS)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Magnetite (Fe$_3$O$_4$)</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>wustite (FeO)</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
</tr>
<tr>
<td>12Cr1MoVG</td>
<td>Oxy</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
<td>Eskolaite (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>Magnetite (Fe$_3$O$_4$)</td>
<td>Ferric tungstate (Fe$_2$WO$_6$)</td>
</tr>
<tr>
<td>T23</td>
<td>Oxy</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Magnetite (Fe$_3$O$_4$)</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>Magnetite (Fe$_2$O$_4$)</td>
<td>Eskolaite (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td>T91</td>
<td>Oxy</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Eskolaite (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td>SUS304</td>
<td>Oxy</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
</tr>
<tr>
<td>SUS347</td>
<td>Air</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
<td>Eskolaite (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe$_2$O$_3$)</td>
<td>Maghemite (Fe$_2$O$_3$)</td>
</tr>
</tbody>
</table>
4.3.3. Characteristics of Fe-Bearing Species by XRD and XANES

Table 4.3 lists the crystal species on the bulk surfaces of the corroded tubes upon the exposure to HW fly ash. Hematite/maghemite ($\text{Fe}_2\text{O}_3$) is the sole major species detected for all of the tubes under the oxy-fuel mode, whereas magnetite ($\text{Fe}_3\text{O}_4$) and wustite ($\text{FeO}$) are dominant for the air-firing tube surfaces. Clearly, apart from bulk $\text{O}_2$, the other gases including $\text{CO}_2$ and $\text{H}_2\text{O}$ in oxy-firing flue gas are also the sources causing the full oxidation of tube surfaces under the oxy-firing mode. In addition, compared to 12Cr1MoVG being the only tube with eskolaite ($\text{Cr}_2\text{O}_3$) on its surface under the oxy-fuel mode, $\text{Cr}_2\text{O}_3$ was found for the high-Cr tubes from T91 through to SUS347 in the air-firing mode, corresponding to the probable formation of Cr oxide-rich protective layer under the mild environment (e.g. low $\text{HCl}$, low steam and low $\text{SO}_2$ in the air-firing mode). Such a protective layer was either too thin to be detected (as shown in Figure 4.4), or fully broke down under the oxy-fuel mode, due to the higher content of $\text{HCl}$ that can permeate through the oxide scale once defects or cracks develop in it. In addition, pyrrhotite ($\text{FeS}$) was the only crystal detected by XRD on the SS400 tube exposed in the air-firing mode, which supports Eq. (4.1).

Figure 4.5 provides the quantified XANES results for the distribution of Fe-bearing species across the tube cross-sections. Clearly, the distribution of Fe is highly tube-dependent. Under the air-firing mode, the fully oxidized hematite was only observed on the SS400 tube, suggestive of the ease of the diffusivity of oxygen into it. For the low Cr-content tubes from 12Cr1MoVG to T91, the partially oxidized species including magnetite and wustite were dominant, confirming the protection effect of Cr-bearing scale against the penetration of oxygen. However, hematite was further back for two high-Cr tubes, which could be in a spinel form such as $\text{Fe}_2\text{Cr}_2\text{O}_6$. The un-oxidized Fe metal was also back to predominance, confirming the strong protection effect of Cr. Upon the shift of air-firing to oxy-fuel mode, the variation of above-mentioned oxides with tube materials is similar. However, augite ($(\text{Ca, Na}) (\text{Mg, Fe, Al, Ti}) (\text{Si, Al})_2\text{O}_6$) was observed. Clearly, the interaction between ash and oxidized tube surface is much more complex than the above two equations. Apart from alkali sulphates, the other oxides in ash are also available to react with the oxidized tube surface. This should occur after the oxidized surface of tube cracked, and the resultant fragments were blended with ash particles consequently. The thermodynamic equilibrium prediction, as tabulated in Table 4.4, confirmed the preferential formation of oxide complexes in the scenario of fly ash only on the surfaces of both low-Cr (T23) and high-Cr tube (SUS347). In the other two scenarios for the existence of flue gas with and without the co-existence of ash, the pure oxides including hematite ($\text{Fe}_2\text{O}_3$) and eskolaite
(Cr₂O₃) are formed, irrespective of the Cr content. Clearly, the oxidation of tube surface upon flue gas is superior over its interaction with solid fly ash. In addition, the thermodynamic equilibrium prediction confirmed the absence of chlorides under the experimental conditions. This further proved the suppression of this reaction by the abundant SO₂ used here. As has been suggested, increasing the molar ratio of sulphur to chlorine can make corrosion very unlikely [27].

Table 4.4 Thermodynamic equilibrium predicted species for two tubes exposed to HW-NaK under the oxy-fuel mode. Unit: mol based on a total input of 5.5E−5 mol Fe for a single tube specimen.

<table>
<thead>
<tr>
<th></th>
<th>Tube T23</th>
<th></th>
<th>Tube SUS 347</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Scenario 1</td>
<td>Scenario 2</td>
<td>Scenario 3</td>
</tr>
<tr>
<td></td>
<td>Ash + flue gas</td>
<td>Ash only</td>
<td>Flue gas only</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.76E-02</td>
<td>2.75E-02</td>
<td>2.26E-02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.89E-04</td>
<td>4.89E-04</td>
<td>2.25E-02</td>
</tr>
<tr>
<td>CaFe₂O₄</td>
<td>2.83E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₂Fe₂O₅</td>
<td>1.78E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCr₂O₄</td>
<td>5.00E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeS</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.5 Quantified XANES results for the distribution of Fe-bearing species across tube cross-section exposed to HW ash
4.3.4 Characteristics of S-Bearing Species by XANES

Although XRD has detected the Fe-bearing species on the corroded tube surface, it failed to clarify the role of S. On the other hand, Table 4.4 for thermodynamic equilibrium prediction suggests the potential presence of sulphide upon the interaction between ash and tube surface. In light of this, the XANES results in Figure 4.6 provide complementary information that is critical in revealing the tube corrosion upon the attack of S. Under the air-firing mode, sulphate is the predominant S-bearing species on the corroded tube surface, which should denote $\text{Fe}^{2+}/\text{Fe}^{3+}$ sulphate, and/or $(\text{Na, K})_3 \text{Fe} (\text{SO}_4)_3$ having a same energy position of $\sim 2480$ eV [14]. Apart from it, the peak at $2470$ eV for sulphide is also obvious for all the tubes except SS400, T23 and SU347. The altitude of sulphide peak shows little dependence on the Cr content in the tubes. Upon the shift to oxy-fuel combustion mode, the relative altitude for the peak of $\sim 2470$ eV was enhanced for almost all the tubes. This should be due to the enhanced formation of $(\text{Na, K})_3 \text{Fe} (\text{SO}_4)_3$, which in turn promoted the reaction Eq. (4.1).

Figure 4.7 further proved this. Compared to flue gas only and YL ash with the least alkali sulphates, sulphide is the principal S-bearing species on the tube surface exposed to HW ash. Adding extra alkali sulphates further enhanced the altitude for the peak related to sulphide, as well as the peak for sulphates.

The formation of sulphides should also be responsible for the break-down of $\text{Cr}_2\text{O}_3$ layer on the tube surface, as it provides paths for rapid outward diffusion of metals such as Ni, Cr, and Fe which in turn accelerate the corrosion attack. In combination with all the results achieved, it is clear that SUS347 is the most suitable tube to be used under the oxy-fuel combustion of low-rank brown coal which is rich in alkali and alkaline earth metals.
Figure 4.6 S K-edge XANES spectra for all the tubes exposed to HW fly ash.

Figure 4.7 S K-edge XANES spectra for SUS347 exposed to three ashes in the oxy-fuel mode.
4.4 Conclusion

The major conclusion from this study can be drawn as follows:

1. From both mass loss and penetration rate perspectives, the tube corrosion for the low-Cr tubes under the oxy-firing of Victorian brown coal is severe compared to the respective air-firing mode. Both flue gas-related and ash-related corrosions are responsible for tube corrosion. In contrast, the corrosion rate of high-Cr tubes (∼20% for SUS304 and SUS347) is comparable between the two combustion modes, due to the protective effect of Cr-oxide.

2. The existence of fly ash on tube surface suppressed the chlorination of tube surface. Oxygen is the principal element permeating into tube under the air-firing mode, whereas both oxygen and sulphur penetrated into the tube under the oxy-firing mode, accelerating sulphation and sulphidation reactions for the tube corrosion. Although Cr₂O₃ forms a protective layer under the air-firing mode, it broke down due to the accelerated corrosion attack caused by sulphates/sulphide under the oxy-firing mode.

3. The interaction between ash and tube surface promoted the formation of pure oxides and oxide complexes with the involvement of Na and Ca as well. The presence of alkali sulphates in ash promoted the sulphidation reaction of tube surface. However, the extent of sulphide is highly tube-specific and correlates little with Cr content.
Chapter 4 Tube Corrosion upon the Interaction with Victorian Brown Coal Ash Deposition

References


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Monash University

Declaration for Thesis Chapter 5

Declaration by candidate

In the case of Chapter 5, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juan Chen</td>
<td>Experimental work</td>
<td>10 %</td>
</tr>
<tr>
<td>Yoshihiko Ninomiya</td>
<td>Editing</td>
<td>External co-author</td>
</tr>
<tr>
<td>Barbara Etschmann</td>
<td>Editing and data processing</td>
<td>Supervisor</td>
</tr>
<tr>
<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

Candidate’s Signature

Main Supervisor’s Signature

Date 01.02.2020

Date 01.02.2020

*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
CHAPTER 5

Effect of Silica Additive on the Tube Corrosion
In Chapter 4 we have investigated the mechanism of the interaction between fly ash sample and tube materials. This chapter further examines the possibilities of fuel quality control techniques (addition of silica to low rank coal) on tube corrosion under both conventional air-firing and oxy-fuel combustion conditions. This chapter has been reformatted from the following published manuscript: Ja’baz, I., J. Chen, B. Etschmann, Y. Ninomiya, L. Zhang, *Effect of silica additive on the high-temperature fireside tube corrosion during the air-firing and oxy-firing of lignite (Xinjiang coal)—characteristics of bulk and cross-sectional surfaces for the tubes*, *Fuel* **187** (2017): p. 68–83.
Abstract

Detailed speciation analysis has been conducted on the corroded tubes coated with two different ash deposits collected from the combustion of a lignite, namely Xinjiang coal mixed with and without external silica in both air- and oxy-firing modes. The exposure conditions are of temperature of 650 °C, 50 h and the use of different flue gases (i.e. pure CO$_2$, air, air-firing flue gas and oxy-firing flue gas). Apart from the lab-based XRD used for the characterization of the top surface, synchrotron XANES was employed to determine the oxidation states of Fe, S and Cr on both top and cross-sectional surfaces of the corrode tubes. The results indicate that, irrespective of the Cr content, the tubes exposed to pure CO$_2$ underwent oxidation, which is most likely due to the reaction CO$_2$ + M = CO + MO where M stands for Fe or Cr. Cr in the Cr-bearing tubes were oxidized more rapidly than Fe in the pure CO$_2$. The combined use of silica additive and Cr-bearing tubes with a minimal Cr content of 2 wt.% (i.e. T23) is beneficial in inhibiting the tube surface oxidation as well the penetration of oxygen and sulphur. Except alkali sulphates, the free oxides in ash deposit can also trigger the reactions for the formation of new species such as augite ((Ca, Na) (Mg, Fe, Al, Ti) (Si, Al)$_2$O$_6$) on the carbon steel tube surface. The oxidation states of sulphur on the tube surface is highly tube-specific and dependent on ash deposit composition as well, with the abundance of pyrite (FeS$_2$) on the carbon steel tube coated with the raw coal ash deposits, whilst the enrichment of troilite (FeS) upon the coating of ash deposits derived from the combustion of coal mixed with silica additive, due to the shortage of free sulphur in ash deposit and a preferential scavenging of Fe into chromite. For the Cr-bearing tubes, sulphate is the only S-bearing species due to the inhibited inward diffusion of S by the Cr-oxide layer, irrespective of ash deposit type. In addition, spatial organization of the oxidation state of Cr suggests a slightly accelerated outward diffusion of Cr by the ash coating, thereby leading to a dense Cr-O layer that is highly protective on the tube top outer surface.

**Keywords:** Synchrotron XANES, Oxy-fuel combustion, Tube Corrosion, Chromium, Sulphide
5.1 Introduction

Chemical speciation of metals on corroded tube surfaces is pivotal to understanding the mechanisms underpinning the interaction between tube surface and flue gas, as well as the solid-to-solid interaction related to hot corrosion at high temperatures. This is particularly important for a new combustion process such as oxy-fuel combustion in which flue gas composition and ash deposit properties are altered remarkably compared to the conventional air-firing mode. To date, the knowledge is still sparse regarding metallic speciation on the corroded tubes that are exposed to the ash-laden oxy-firing flue gas [1].

To date, most of the knowledge with regard to the metallic speciation on the corroded tube surfaces was merely achieved from studies based on conventional air-firing cases, where nitrogen is predominant (nitride formation is thus probable), and the contents of impure SO\textsubscript{2}, steam and CO\textsubscript{2} are lean. However, upon employment of the oxy-firing mode, impurities accumulate due to the recycling of the dirty, wet flue gas that are supposed to enhance the formation of corrosive sulphates/sulphides under the same exposure time as under the air-firing case, and even result in the formation of new species. Table 5.1 summarizes all the past studies that have been conducted for the tube corrosions under the oxyfuel combustion mode. As can be seen, the tube corrosion extents were distinctively different for the different tests, varying broadly with the coal/ash sample and exposure conditions tested. A generalized conclusion regarding the tube corrosion in the oxy-firing mode has yet to be achieved. For instance, studies using German lignite ash deposit reported no carbonation or carburization reactions, and the high CO\textsubscript{2} content had little effect on the increase in tube corrosion. In contrary, the study using synthetic ash confirmed the carburization reaction. With regard to the effect of ash deposit, the increased deposition rate has been reported for the oxy-fuel combustion mode, leading to the accelerated tube corrosion that was mainly caused by sodium sulphates and its synergetic interaction with steam in the flue gas. However, the roles of the other species in ash, if any, have not been reported.

For the analyses of the corroded tube surface, only lab-based facilities were used, which were also listed in Table 5.2, including optical microscopy (OM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) coupled with energy-dispersive analysis (EDAX) [2–5]. However, for the tube cross-section which is on the micro and even submicron meter scale, lab-based XRD and XPS are not able to focus to such small areas. Thus,
the information based on these two techniques is a mixing of both the corroded and the uncorroded area. In addition, although the SEM-EDS is capable of analyzing the individual spots with a size down to 1 µm or even less, it only provides the elemental compositions of single particles. The information for the chemical speciation based on it is rather empirical and semi quantitative.

In this work, our primary goal is to clarify the changes on the chemical speciation of six tubes coated with lignite ashes, so as to understand the roles of CO₂ and oxy-firing flue gas on the tube corrosion chemistry, as well as their synergetic effect, if any, with ash deposit on tube corrosion. Two ash deposits were tested, which were collected from the super-heater tube surfaces in a 30 MWth pulverized coal-fired boiler burning a lignite namely Xinjiang (China) mixed with and without external silica. By doing this, we also aim to address the effect of silica additive to coal on the mitigation of tube corrosion, which is the extension of our previous works on the ash slagging and fouling during the combustion of the same coal [6,7]. To characterize the speciation of the corroded tube surfaces, the synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy was employed, which is able to probe the oxidation states of the elements of interest including Fe, S and Cr on both the top and cross-sectional surfaces of the corroded tubes that is only 0.2 cm in width. In particular, the spatial distribution of the oxidation states of Cr was revealed along the corroded tube cross-section. These analyses are expected to shed new light in understanding the chemistry underpinning the interaction between the ash deposit and tube surface, as well as the mechanisms for the inhibitive effect of silica additive on the control of tube corrosion during the oxy-fuel combustion of low – rank coal.
### Table 5.1 Summary on the literature studied on tube corrosion during the oxy-fuel combustion

<table>
<thead>
<tr>
<th>Reference</th>
<th>Purpose</th>
<th>Testing methods</th>
<th>Coal</th>
<th>Key findings</th>
</tr>
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<tbody>
<tr>
<td>G. Stein-Brzozowska et al., 2011 [26]</td>
<td>Investigate the influence of an oxy-fuel combustion of a hard-coal on the surface of selected super-heater materials</td>
<td>SEM-EDS</td>
<td>Dry lignite from Germany, hard-coal from South America</td>
<td>Increase in sulphur induced corrosion for tubes exposed to the oxy-combustion atmosphere.</td>
</tr>
<tr>
<td>G. Stein-Brzozowska et al., 2013 [10]</td>
<td>Study the interactions between flue gas atmosphere, deposits and heat exchanger materials during oxy-fuel firing</td>
<td>SEM/ ICP-OES/XRD</td>
<td>Bituminous coal</td>
<td>No Sulphur induced corrosion is detected on the alloy specimens exposed under real fly ash - and pure CaCO$_3$ - deposits</td>
</tr>
<tr>
<td>G.R. Holcomb et al., 2013 [27]</td>
<td>Compare air-firing and oxy-firing conditions on the tube corruptions</td>
<td>OM, SEM-EDS/XRD</td>
<td>Synthetic ash</td>
<td>The observed corrosion behavior shows accelerated corrosion even with sulphate additions that remain solid at the tested temperatures</td>
</tr>
<tr>
<td>K. Natesan and Z.t. Zeng 2011 [2]</td>
<td>Addresses the potential fireside corrosion issues in environments typical of USC boilers and oxy-fuel combustion system</td>
<td>OM, SEM-EDS/XRD</td>
<td>Synthetic ash</td>
<td>NaCl in the deposit led to catastrophic corrosion at 650 and 800°C. Corrosion rates for Ni-base alloys were significantly less than those of Fe-base alloys under the same exposure conditions.</td>
</tr>
<tr>
<td>Study</td>
<td>Methodology</td>
<td>Ash Composition</td>
<td>Result</td>
<td></td>
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<td>----------------------------------------------------------------------</td>
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<tr>
<td>L. Fryda et al., 2013 [28] Study ash formation and deposition of selected coal/biomass blends under oxy-fuel and air conditions in a lab scale pulverized coal combustor (drop tube furnace).</td>
<td>SEM-EDS/ICP/thermodynamic calculation using FactSage software</td>
<td>South African coal blended with shea meal (cocoa)</td>
<td>Deposition propensity was higher under oxy-fuel mode; however, ash chemistry was not changed</td>
<td></td>
</tr>
<tr>
<td>R. Abang et al., 2013 [11] Investigate the fireside corrosion behavior of superheater alloys under the oxy-fuel combustion mode</td>
<td>OM/SEM-EDS/XRD</td>
<td>Lignite from Germany</td>
<td>No carbonation observed; although sulfidation was observed, high CO₂ content in oxy-firing did not result in an increase in corrosion</td>
<td></td>
</tr>
<tr>
<td>S. Tuurna et al., 2010 [17] Investigate the performance of superheater alloys under the oxy-fuel combustion conditions</td>
<td>OM/SEM-EDS/GDOES</td>
<td>85% CaCO₃ + 15% CaSO₄</td>
<td>The corrosion resistance increased when the Cr content increased; no severe corrosion under oxy-fuel than the air-firing conditions</td>
<td></td>
</tr>
<tr>
<td>A. Hjornhede et al., 2010 [29] Corrosion test in both oxy-fuel and air-firing conditions</td>
<td>LOM/SEM-EDS</td>
<td></td>
<td>Found evidence for increased deposition rates of ash during oxyfuel combustion compared with air-firing; no significant difference between oxyfuel and air-firing corrosion rates or carburization.</td>
<td></td>
</tr>
<tr>
<td>A. Robertson et al., 2010 [30] Identify the tube corrosion mechanisms under the oxy-fuel conditions, and determine the effect of sulfur on boiler materials</td>
<td>SEM-EDS</td>
<td>Low – S coal, Med – S coal, High – S coal</td>
<td>The oxy-fired corrosion rates were typically no worse, and often less than air–fired rates</td>
<td></td>
</tr>
</tbody>
</table>
### Chapter 5 Effect of Silica Additive on the Tube Corrosion

<table>
<thead>
<tr>
<th>Authors</th>
<th>Description</th>
<th>Methods</th>
<th>Deposit</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Scheffkneckt et al., 2009 [31]</td>
<td>Study the fireside corrosion behavior of different alloys</td>
<td>SEM-EDS</td>
<td>Synthetic ash</td>
<td>Carburization and oxide scale morphology differences were confirmed between air and oxy-firing environments for austenitic materials</td>
</tr>
<tr>
<td>Y. Tang et al., 2014 [32]</td>
<td>Investigate the corrosion behavior of pure Fe under a Na$_2$SO$_4$ deposit in an atmosphere of H$_2$O + O$_2$</td>
<td>SEM-EDS/XRD</td>
<td></td>
<td>Corrosion rate is accelerated of the pure Fe significantly under a Na$_2$SO$_4$ deposit in atmosphere of H$_2$O + O$_2$ at 500º C</td>
</tr>
<tr>
<td>M. Montgomery et al., 2015 [34]</td>
<td>Study the corrosion resistance of various alloys in an oxy-fuel process</td>
<td>OM/SEM-EDS/XRD</td>
<td>Lignite</td>
<td>Corrosion rate decreases with increase in alloying elements. The oxy-fuel ash deposit is similar to that found in conventional air-firing plant</td>
</tr>
<tr>
<td>M. Mobin and S.K. Hasan 2012 [34]</td>
<td>Study the reaction of Fe$_2$O$_3$ with Na$_2$SO$_4$ in the presence of SO$_2$(g) at 800 and 900 ºC</td>
<td>SEM-EDS</td>
<td>UK Coal</td>
<td>Constituents in the reaction products were presented as distinct phase</td>
</tr>
<tr>
<td>A.U. Syed et al., 2012 [35]</td>
<td>Assess the effects of increasing heat exchanger surface temperature on the fireside corrosion</td>
<td>OM/SEM-EDS</td>
<td>Biomass/coal mix</td>
<td>A significant increase in metal damage when moving from 600 to 700 º C was confirmed for both alloys with and without ash deposit coverage</td>
</tr>
<tr>
<td>K. Natesan and J. H. Park, 2007 [36]</td>
<td>Evaluate the corrosion performance of Fe-base and Ni-base alloys in coal ash</td>
<td>OM/SEM-EDS</td>
<td></td>
<td>Ni-base alloys generally exhibited less corrosion than Fe-base alloys under the similar exposure conditions. However, localized pitting was confirmed on the Ni-based tube surface. surface. However, localized pitting was confirmed on the Ni- based tube surface.</td>
</tr>
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</table>
5.2 Experimental

5.2.1 Tube Corrosion Test Set – Up and Test Conditions

Horizontal furnace as shown in Figure 5.1 was used for tube corrosion test. The furnace temperature was fixed at 650 °C, considering that the ash deposit-related corrosion is maximized at this temperature. This temperature is also the typical surface temperature for the superheater/reheater tubes (650–700 °C) [8]. The flat tube specimen, 3 cm x 3 cm x 2 mm, were prepared by a wire electrical discharge machine to cut on the cross-sections of six commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. For the corrosion test in flue gas only, the tube specimen was tested as they were. For the ash deposit-related corrosion test, fly ash powder (~100 mg per tube specimen) was spread uniformly over the surface to mimic ash deposition on a real steam tube surface, yielding a slightly compacted ash density of approximately 11 mg/cm² that is lower than but comparable with the test elsewhere [8]. The ash laden tube specimen was then loaded on a quartz-made sample holder and pushed to the middle zone in the hot furnace. Subsequently, flue gas was fed at a flow rate of 300 mL/min continuously into the furnace. Each test lasted 50 h and two replicas were conducted for each condition. A short exposure time was chosen, considering that the flue gas as shown below is highly corrosive. After the test, the particle-laden tube specimen was either brushed carefully to remove the ash particles to weigh its mass change by a high-precision balance with a readability of 0.1 mg, or quickly mounted (with ash particles together) and solidified into epoxy resin to avoid surface oxidation.

With regard to the flue gas composition, pure CO₂, air and two typical flue gas compositions (as shown in Table 5.2) were tested. The two flue gas compositions represent the air-firing and oxy firing modes, respectively. As has been confirmed by our pilot scale test [9], the steam content in flue gas can rise to 30 vol% and SO₂ is also highly accumulated during the oxy-firing of low-rank brown coal. The steam content tested here is close to the oxy-fuel flue gases tested elsewhere [4,5,8,10,11], however, the SO₂ content in flue gas here is lower. The HCl was also tested here, because some Xinjiang coals contain high Cl. The addition of HCl into flue gas can also mimic the co-firing scenario in which biomass is blended into coal for a zero and even negative carbon emission. Note that, the HCl has yet to be tested for the oxy-fuel combustion of coal in the literature. The total gas pressure is 1 atm.
A total of six tube materials in Table 5.3 were tested, with an increasing Cr content of SS400 (0% Cr), 12Cr1MoV (0.9–1.2%), T23 (2.25%), T91 (9%), SUS347 (17–19%) and SUS304 (18–20%). Two ash deposits were tested, which were collected from the convective superheater surface in a 30 MWth pc-fired boiler for the combustion of Xinjiang lignite [6, 7]. The two samples were labelled XJ and XJ_S for the ash deposit derived from raw coal and coal mixed with silica additive, respectively. The elemental of the two ash samples are shown in Tables 5.4. Note that, the mineralogical compositions for the two ashes are shown in Figure S1 for the XRD patterns and further tabulated in Table S1 in Supporting Information (SI). Upon the addition of silica, the total contents of Na and S in sulphate are reduced, so are the other metals in the oxide form. This is mainly attributed to the immobilization of these elements into the silica matrix.

5.2.2 XRD and SEM-EDX Analysis of Bulk Surface

For each un-mounted corroded tube, its top surface, after the ash powders were removed, were subjected to XRD analysis to qualitatively determine the crystallized species (Rigaku, Miniflex 600), under 40 kV voltage and 15 mA current; the scanning speed was 1°/min with a step size of 0.01° and the wavelength of 0.15418 nm for Cu – alpha was used. The peak identification was achieved by search-match function in the JADE software. The species used for the XRD fitting are listed in Table 5.5. As can be seen, these probable species highly overlap with one another. Efforts have thus been made to distinguish them as much as possible. For each epoxy-mounted tube, it was first halved by a disc – cutter. The resulting cross-section surface was then polished by SiC paper. It was analyzed by OM (Olympus) to establish the thickness of scale and depth of intergranular penetration, if any in the alloys; and by SEM-EDAX (JEOL 7001F) for microstructural observation of the cross-section and the mapping of individual elements on the cross-section as well. Samples were carbon coated prior to the SEM-EDAX observation.

5.2.3 Synchrotron XANES Analysis

The K-edge XANES spectra of Fe, S and Cr were obtained from beamline BL16A1 at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. BL16A1 has a fixed exit double crystal Si (1 1 1) monochromators with a nominal beam size of 0.25 by 0.25 mm at sample. For the analysis of Fe and Cr, pure elemental Fe and Cr were used respectively for the calibration at a K-edge absorption energy of 7112 eV and 5989 eV. Pure elemental Mo was used for the calibration of S at a
K-edge absorption energy of 2481 eV. The peak energy absorption (white-line) position was taken as the base (0 eV), with all subsequent spectra recorded 200 eV below and 800 eV above this point in fluorescence mode. Additionally, some reference Cr XANES spectra were recorded at the wiggler XAS beamline at the Australian Synchrotron. This beamline has a Si (111) double crystal monochromator which was fully tuned. Higher harmonics were rejected using mirrors. Data were collected with Oken ion chambers under He flow (1.5 L/min) with 250 V and a 100 element HP-Ge detector (Canberra).

The analysis of S was only conducted for the top surfaces, as the signal for S from the cross-section of the tubes was too weak and very noisy. For the other two metals, the speciation along the cross-sectional surface of the corroded tubes was conducted. Definition of the two surfaces is shown in Figure 5.2. Additional attempts were also made to reveal the spatial organization of the oxidation state of Cr along the tube cross-section. This was done by moving the synchrotron beam from the centerline of the tube where the Cr signal is maximum through to the oxide scale where the Cr signal tends to disappear since the oxide scale is next to ash deposit/epoxy resin that is lean in Cr. Once the positions for the maximum and minimal Cr signals were recorded, one or two extra positions in between, defined as 0.4 cm and 0.7 cm away from the centerline were further analyzed.

All spectra were normalized using ATHENA which is part of the DEMETER package [12]. Linear combination fitting (LCF) was used on the normalized sample spectra to determine the mineral composition by using a large number of standards that were detailed in the SI. The details for the LCF methodology were also given in the SI.
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**Figure 5.1 Tube corrosion test set-up**

**Cross-sectional Surface**

**Top Outer Surface**

Flue gas

Bulk tube

Oxide scale

Flue gas

Centerline

In between 1

In between 2

Oxide scale

Figure 5.2 Top outer surface and Cross-section surface of the corroded tube specimen mounted in resin and the analysis of the spatial distribution by synchrotron XANES
5.3 Results and Discussion

5.3.1 Tube Surface Oxidation in Pure Gases without Ash Deposits

The typical micro-structure for the cross-section of the corroded tube T23 in pure CO$_2$ is illustrated in Figure 5.3. Clearly, CO$_2$ is not an inert gas, as it contributes to the tube corrosion. Such a finding has also been previously reported [8]. The top surface of the tube T23 became flawed and porous, implying the formation of defects and cracks that aid gaseous diffusion. The elemental mapping results confirm the abundance of O and Fe on the corroded surface, with the existence of trivial Cr and Si as well. It is clear that oxidation of Cr and Si took place in the oxide layer, exerting a protective role to minimize the wastage of iron. Regarding the existence of C on the tube surface, due to the carbon coating prior to the SEM observation, it is unclear if the C detected here is due to the carburization reaction caused by the Boudouard equilibrium (CO$_2$ + C = CO) [4].

Figure 5.4 confirms the enhanced corrosion for the tube T23 exposed to the two flue gases. The top surface is even spalled off, particularly in the oxy-firing flue gas. This reflects the high concentrations of HCl and steam within this gas. With regard to the air-firing flue gas, the spalled layer is dominated by Fe, whereas the other three elements are present in low concentrations. However, the carburization reaction may still be unlikely for T23 studied here, as it is difficult to achieve the Boudouard equilibrium in the presence of steam and oxygen with CO$_2$ [4]. In contrast, upon exposure to the oxy-firing flue gas, oxygen is the most abundant element in the oxide layer, demonstrating an enhanced diffusion of O into the metal. CO$_2$ has been suggested to be able to increase the transport of reactants within the oxide scale [8], although a theory has yet to be established to confirm this. Moreover, upon the spallation of oxide layer by the attack from steam, HCl and/or SO$_2$, the diffusion of oxygen towards the un oxidized metal was accelerated. Interestingly, for both flue gases, the distribution of S in the oxide layer is weak, implying little sulfation/sulfidation reaction caused upon the exposure to flue gas only, for an experimental temperature of 650 °C and 50 h only.
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Figure 5.3. Typical micro-structure for the cross-section of T23 specimen exposed to pure CO$_2$

![Typical micro-structure for the cross-section of T23 specimen exposed to pure CO$_2$](image)

Figure 5.4

Typical micro-structure for the cross-section of T23 specimen exposed to flue gases with the absence of fly ash.
5.3.2 Tube Surface Oxidation upon the Exposure to Ash Species

A typical microstructure for the corroded tube T23 is shown in Figure 5.5, for the exposure to XJ ash in the oxy-firing mode. Apart from a porous layer attaching to the bulk tube, a spalled scale was found detaching away from the bulk tube. The top layer is dominated by oxides, as indicated by the EDX mapping results that show O is the most abundant element, followed by Cr, S, and Fe. Clearly, both O and S diffused inwards, whereas Cr and Fe diffused outwardly for the corrosion and spallation of the tube. The faster diffusion of Cr than Fe resulted in the formation of a Cr-rich protective layer. The absence of Cl should be due to the volatilization of chlorides from the tube surface, or the inhibition of the formation of chloride in the co-existence of S and Cl in flue gas [14]. More interestingly, compared to the other elements especially O distributing evenly in the whole top layer, S is preferentially present in the boundary/interface between the metal/oxide layer and the bulk tube. This should be due to a faster diffusion for S than O through the tube lattice [15, 16].

Figure 5.5 The typical micro-structure for the cross-section of T23 specimen exposed to oxy-firing flue gas, with the coating of XJ fly ash on the surface.
Additionally, the S in the tube/metal boundary should be formed under the assistance of the ash sample, e.g. via reaction Eqs. (5.1) and (5.2) shown below.

\[
3Na_2SO_4(s) + 3SO_2 + Fe_2O_3 \rightleftharpoons 2Na_3Fe(SO_4)_3(S,l) \quad \text{Eq. (5.1)}
\]

\[
2Na_3Fe(SO_4)_3 + 19Fe \rightleftharpoons 6Fe_3O_4 + 3FeS + 3Na_2S \quad \text{Eq. (5.2)}
\]

**Figure 5.6** demonstrates the typical microstructure for the tube corroded surface upon the coating of XJ_S ash. Clearly, multiple oxide layers were formed on the tube surface. Compared to the top and spalled layers for the XJ ash in **Figure 5.5**, the multiple layers are dense and less porous. Therefore, their protection on the bulk tube is effective. The top layer attaches intimately to the bulk tube, mainly consisting of Fe and Cr. With respect to the middle scale, apart from the abundance of Fe and Cr, the presence of S and Cl was also confirmed. In particular, S is the most prevalent, which is also preferentially present on the left-hand surface of the middle scale. This suggests that S easily traverses through the interstitial space between top layer and the middle scale.

**Figure 5.6** Typical micro-structure for the cross-section of T23 specimen exposed to oxy-firing flue gas, with the coating of XJ_S fly ash on its surface.
Statistical analysis was conducted to quantify the thickness of the corrosion interface for each corroded tube, based on the micro-structures for the cross-sections observed by SEM. Furthermore, based on the interface depth, the corrosion rate or interface growth rate was calculated by dividing by the exposure time, 50 h employed in this study. As shown in Figure 5.7 with the X-axis being the increasing Cr content in the tubes, the oxide layer growth rate decreases monotonously upon the increase of Cr content in the tube, either in flue gas only or upon the coating of fly ash. Note that, the observed growth rate 0.2–1 μm/h here is broadly consistent with the literature report on the tested alloy tubes with the similar Cr contents [17].

![Figure 5.7 Oxide layer growth rate of the tubes.](image-url)

For the exposure of tubes in gas only, as shown in panel (a), the oxide growth rates for a tube are comparable for the four gases with the absence of ash deposit, based on the considerable overlapping of their error bars. Since oxygen is the principal oxidant for the gas-related tube corrosion, the results here indicate that the total partial pressure of all the oxidants in a flue gas is insignificant in the oxide layer thickness. In other words, the growth of the oxide layer should be controlled by the reaction rate...
for the oxidation of the metals such as Fe. For the pure CO₂ with an equilibrated O₂ partial pressure reaching 9.1 × 10⁻⁹ atm at 650 °C, it is still far higher than the equilibrium partial pressure of O₂ (7.1 × 10⁻⁹ atm) based on Fe + 1/2 O₂ = FeO (wüstite). In addition, the other reaction without the involvement of oxygen (O) may also be responsible for the oxidation of metals in CO₂. This will be further discussed based on the tube surface characterization later.

With respect to the effect of fly ash coating on the oxide layer thickness, both panels (b) and (c) are strong signs of an enhanced thickness for the oxide layer upon the coating of XJ fly ash, irrespective of the combustion mode. In the air-firing mode panel (b), the coating of XJ_S ash decreases the oxide layer thickness down to the same level as the gas only cases, further confirming its inhibited diffusion for the two elements O and S. However, in the oxy-firing mode, the tube thickness of SS400 and even low-Cr 12Cr1MoVG with the coating of XJ_S is still considerably larger than the flue gas only case. This should be due to the higher concentrations of impure components in the oxy-fuel flue gas, which interplayed with the ash to attack the tube surface.

5.3.3 XRD Analysis of the Top Surfaces for SS400, T23 and SUS304

The original XRD patterns for these three tubes are shown in Figures, S2–S4. Taking the carbon steel XRD patterns in Figure, S2 as the example, it is obvious that the tube surface oxidation is limited in pure air, with iron metal still being the principal species, followed by a small amount of magnetite (Fe₃O₄). Upon the use of air-firing flue gas that has a lower oxygen partial pressure (5%) but a lot of impurities, the peak intensity for Fe (110) decreases dramatically. Magnetite is still the only discernible oxides, suggestive of an active oxidation of the tube surface by steam and/or CO₂. With regard to the coating of fly ash deposits, it is clear that the oxidation is enhanced in the XJ ash case, with the abundance of fully oxidized hematite (Fe₂O₃) being dominant. This could be attributed to the catalytic effect of the free oxides in the ash, which plays an oxygen-shuttling role for the transfer of the bulk oxygen. The use of XJ_S ash is protective, providing a shield to mitigate the oxidation on the surface, as evident by the re-appearance of unreacted iron metal and abundant magnetite on the XRD pattern in Figure, S2. Again, this is caused by the capture of the free oxide by the silica additive in the combustion process [7, 18].

The results for oxy-fuel mode in Figure, S2 are more intriguing. The pure CO₂ is clearly non-inert, as is evident by the appearance of numerous peaks for magnetite. The same phenomenon has been
observed for a variety of tubes exposed to Ar/CO$_2$ for 1000 h [19]. Carbides were not found in the pure CO$_2$ case, suggesting that the Boudouard reaction (CO$_2$ + C = CO) may have not taken place in the exposure time 50 h tested here. For the pure CO$_2$ with a pressure of 1 atm at 650 °C, the equilibrium calculation results suggest an equilibrated C(g) partial pressure of $1.68 \times 10^{-47}$ atm, which is far lower than the equilibrated O$_{2(g)}$ partial pressure that reaches $9.1 \times 10^{-9}$ atm at 650 °C. However, extra analysis of experiment is still necessary to prove this, considering that the exposure time is very short and the XRD analysis was only conducted on the top surface, rather than along the cross-section of the tubes. Similar to the air-firing mode, the remaining three cases in the oxy-firing mode show an enhanced oxidation of the surface to magnetite in the flue gas, which was further enhanced upon the coating of XJ ash, as evident by the high intensity for the 2nd line of magnetite (440) at 62.515°. Again, the coating of XJ_S ash shielded the tube effectively, as evident by the abundance of the unreacted iron metal.

Similar observations were obtained for the two Cr-containing tubes shown in Figures S3 and S4. The most noteworthy phenomenon is the confirmation of oxidation of chromium that leads to the formation of chromium oxide on both T23 and SUS304. Similar to iron metal, chromium in the tube was also partially oxidized, even under the exposure to pure CO$_2$. Such a phenomenon is intriguing, and it even contradicts our assumption that this gas is inert in only 50 h exposure time. To further view the significance of CO$_2$, the intensity of the most intense peak for the oxides, observed in the XRD patterns in Figures S2–S4, was divided by the intensity of the most intense peak for the respective pure metal, and plotted in Figure 5.8. Interestingly, except the carbon steel tube SS400 which has a lower oxidation extent in pure CO$_2$ than the air, the other two tubes were oxidized more intensively in CO$_2$ than in air. With respect to the oxidation extent in CO$_2$, it increases with increasing Cr content in the tube. Again, these phenomena cannot be simply explained by the dissociation of CO$_2$ to active oxygen for the reaction (M + O$_2$ = MO, M for Fe or Cr), since the equilibrated partial pressure of oxygen is extremely low. Instead, a direct involvement of CO$_2$ in a reaction such as M + CO$_2$ = MO + CO may occur. CO$_2$ can dissociate into CO upon being trapped on the adsorption site on the tube surface [20]. To prove the thermodynamic potential for this reaction, the standard Gibbs functions were calculated and plotted in the right-hand side of Figure 5.8. As can be seen, the standard Gibbs free energy for the formation of Cr$_2$O$_3$ via the reaction of M + CO$_2$ = MO + CO is far lower than the formation of wüstite (FeO) via the same reaction route. The formation of Fe$_2$O$_3$ even bears a positive Gibbs free energy in CO$_2$, which hints that wüstite and its derivatives such as chromite (Fe$^{2+}$CrO$_4$) would be preferentially formed rather than hematite in the oxy-firing combustion mode.
In addition, Figure 5.8 confirms that all the three oxidation reactions \((M + O_2)\) are highly thermodynamically available, as expected. Cr is also more easily oxidized than Fe, thereby providing a protective layer.

![Figure 5.8](image)

**Figure 5.8** The intensity ratio of oxide to metal, \(I_{\text{oxide}}/I_{\text{metal}}\) in air versus \(\text{CO}_2\) (a), and the Gibbs free energy for the probable reactions of tube surface in the two pure gases (b).

### 5.3.4 XRD Analysis of the Tube Top Surfaces Coated with Ash Deposits

To further clarify the effect of ash deposit on tube corrosion, all six tubes coated with two fly ashes were analyzed using XRD. The resulting XRD patterns are illustrated in Figures. S5 and S6 for air firing and oxy-firing modes, respectively. Table S2 lists the two most abundant species with the strongest intensity for their first peaks in the XRD patterns. The three parameters, tube material, ash deposit type and combustion mode interplayed considerably to affect the tube corrosion. To clarify these effects, the molecular weight (MW) for the first major species was plotted versus the tube material type in Figure 5.9. Note that, the MWs of the species were normalized based on the unit molecule of iron (Fe). For instance, the MW of magnetite \((\text{Fe}_3\text{O}_4)\) is 77, rather than 232 because each
Fe$_3$O$_4$ consists of three molecules of Fe. In addition, for two species such magnetite and chromium oxide which have overlapping peaks, the larger MW was used. As shown in Figure 5.9, in the conventional air-firing flue gas where the impurities including CO$_2$, SO$_2$ and HCl are lean, the tube surface is far from being fully oxidized in 50 h, irrespective of the tube material. This further proves the superior shielding effect of fly ash over its catalytic effect on the oxygen shuttling in the air-firing mode. For the SS400 carbon steel, magnetite (Fe$_3$O$_4$) rather than hematite (Fe$_2$O$_3$) was formed. For the remaining Cr-bearing tubes, the stainless-steel Fe-Cr dominates over the 12Cr1MoVG tube, whereas wüstit (FeO), magnetite/chromium oxide (Cr-O) and austenite (Cr$_{0.19}$Fe$_{0.7}$Ni$_{0.11}$) were observed on T23, SUS304, T91 and SUS347, respectively. Except for the tube SUS304, a general decreasing trend was observed for the MW of the principal species with increasing Cr content in the tube, demonstrating the strong protective effect of Cr/Ni on the inhibition of the oxidation of iron, as expected. SUS304 is an exception, which may be due to the absence of Nb, although its Cr and Ni contents are similar to that in SUS347. Upon the coating with XJ_S ash deposit which is less corrosive, the above-mentioned oxides completely disappeared on the Cr-bearing tubes from T23 through to SUS347. The oxidation layer is thus slightly lighter than that formed on the tubes coated with XJ ash. Regarding the indiscernible discrepancy between the two fly ashes on the surface chemistry of SS400 and 12Cr1MoVG, it suggests a minimum 2wt.% Cr in the alloy tube even in the case that silica is mixed with coal for the combustion in air. However, one has to be aware that the XRD analysis here is only for the top surface.

The oxidation of tube surface is more obvious in the oxy-firing mode, and the oxides were formed regardless of ash deposit type. For the SUS400 carbon steel, magnetite is still the dominant species formed upon the coating of XJ ash, whereas the pure iron (Fe) was observed in the XJ_S ash case. In Table S2, one can see that the most intense peak for magnetite (Fe$_3$O$_4$) is the second highest upon the coating of XJ_S ash, relative to pure iron with its most intense peak being the second strongest in the XJ ash case. This further demonstrates the effect of using silica additive is more influential when the Cr-bearing tubes were used. For the remaining Cr-bearing tubes, the principal oxide is magnetite or chromium oxide for the XJ ash, whereas it turned to iron chromium oxide ((Fe$_{0.6}$Cr$_{0.4}$)$_2$O$_3$) and/or eskolaite (Cr$_2$O$_3$) for the XJ_S ash. Its MW is thus slightly larger than the respective oxide formed in the XJ ash case. This in turn makes the tube surface dense and less porous, thereby decreasing the inward diffusion of oxidant inside the tube.
Figure 5.9 Molecular weight of the principal species on the tube surface versus the tube type, determined by XRD in Figures. S5 and S6.

5.3.5. XANES Speciation of Fe on Tube Cross-Sectional Surfaces

Figure 5.10 illustrates the Fe K-edge XANES spectra and the respective fitting results for the cross-section of carbon steel tube SS400. Clearly, in either combustion mode, the coating of XJ_S ash deposit resulted in a lower oxidation extent for iron along the tube cross section, i.e. a thinner oxidation layer. In the air-firing mode, relative to a molar fraction of 0.38 for hematite observed for the XJ ash case, none of the oxides was observed in the XJ_S ash case, proving an effective protection of this ash deposit against the corrosion of this low-quality tube material. Moreover, compared to Figure 5.9 where magnetite (Fe₃O₄) was detected for the top surface for the same tube, the negligible content of oxide on the cross-section suggests that the oxidation layer should be very thin. The discrepancy between the two ash deposits was more obvious in the oxy-firing mode. For the coating of XJ ash, except hematite and magnetite that were also detected by the XRD in Figure 5.9, two extra species were found here, including augite ((Ca, Na) (Mg, Fe, Al, Ti) (Si, Al)₂O₆) and pyrite (FeS₂).
The former species is a direct evidence of the complex interaction between ash and tube surface, which includes a number of elements other than Na and S from the ash deposit that attack and penetrate through the tube surface. On the other hand, the latter species proves the importance of S that is able to break the oxide layer upon the formation of sulphide.

Upon the coating of the XJ_S ash deposit, these two species were however not detected, suggestive of a slower diffusion of SO$_2$ and its derivative S (g) through this ash deposit. The SEM-EDS mapping analysis in Figure 5.5 confirmed a deep and uniform distribution of S in the oxide layer and even the spalled scale caused by the coating of XJ ash. In contrast, the S is preferentially present in at the bottom of the spalled scale in the XJ_S ash case in Figure 5.6, suggestive of a grain-boundary diffusion route for S.

Figure. 5.10. Fe K-edge spectra for the cross-section of the carbon steel tube SS400 coated with the two fly ash deposits. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena.
The protective effect of silica additive was further confirmed for the low-alloy tube T23, as evident in Figure 5.11. In the air-firing case, no oxide was observed in the case of the XJ_S ash coating, suggestive of the formation of a super-thin oxide layer that is too thin to be pinpointed by the synchrotron beam. More oxide species were formed under the oxy-fuel mode, in particular for the coating of XJ ash, as expected. Interestingly, the S-bearing species were not detected, confirming the strong protective role of Cr in the tube.

Figure 5.11. Fe K-edge spectra for the cross-section of T23 tube coated with the two fly ash deposits. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5.3.6. XANES Speciation of the Oxidation States of S and Cr

The speciation of S was conducted to clarify if any other S-bearing species such as sulphates formed on the tube surface. For the speciation of S, only the results for the top surfaces exposed to the oxy-
firing mode are discussed here, because the signal for S on tube cross-section was very weak and noisy. In addition, the air-firing tubes were found to bear a very low signal to noise ratio even for its top surface. The SEM-EDS analysis also failed to detect any S on the air-firing tubes.

**Figure. 5.12** illustrates the S K-edge XANES spectra for three tubes coated with the two fly ashes in the oxy-firing mode. The peak located at ~2481 eV is the distinctive fingerprint for a compound containing the (SO$_4$)$_2^-$ group, whereas the peak located at ~2470 eV is the feature for pyrite (Fe$_2$S). This peak is a direct evidence for the sulfidation of the SS400 tube surface. Moreover, the intensified, broad peak locating at 2477 eV features the formation of troilite with a simple formula of FeS. It belongs to the pyrrhotite (Fe$_{1-x}$S, x = 0–0.2) group with an iron deficiency. It represents the transition of S to its p-like states in the conduction band hybridised with Fe 4sp states [21].

**Figure 5.12** S K-edge XANES spectra for the outer surfaces of three tubes exposed to XJ ash and XJ_S ash in the oxy-firing flue gas.
With respect to the coating of XJ_S ash, sulphate is the predominant S-bearing species in most of the cases except the carbon steel tube SS400. Interestingly, this species was indiscernible in the XRD, suggesting an amorphous state for the existence of molten sulphate eutectics. It was not detected on the narrow tube cross section in Figures. 5.10 and 5.11 for Fe either. Clearly, the molten sulphate eutectics preferentially stick on the outmost surface of the tubes, which dissolves the metals as well as increases the resistance against the inward diffusion of the gaseous components.

With respect to the sulphide formation, its content varies greatly with the tube type as well as ash deposit. For the carbon steel tube SS400, sulphide was formed in conjunction with sulphates, irrespective of the ash deposit type. However, for the two Cr-bearing tubes, sulphide is indiscernible, which should be due to the protective effect of Cr-oxide layer that was formed preferentially on the top of the tube. This further indicates the necessity of the use of Cr-bearing tubes even in the case that silica additive is mixed with coal for the combustion.

![Delta G function for a number of sulfidation reactions at 650 °C.](image)

Figure 5.13 Delta G function for a number of sulfidation reactions at 650 °C.
It is interesting to explore the probable reactions that have occurred during the sulfidation of the pure metal iron in the SS400 tube. **Figure 5.13** lists all the probable sulfidation and sulphation reactions and the Gibbs free energy of formation at 650 °C. These reactions include the solid-to-gas reactions between a metal and S\(_{(g)}\) that is derived from the reaction \(\text{SO}_2\ (g) = \text{S}(g) + \text{O}_2(g)\), and the solid-to-solid reaction (No. 5–8) for the interaction between Na sulphate, Fe/Cr sulphate and the pure metal (Fe/Cr). Here the Fe/Cr sulphates can be derived from the solid-to-gas reactions No. 3 and 5. In comparison to the sulfation reactions 3 and 4, the first two solid-gas reactions numbered 1 and 2 can be ruled out here, considering that the equilibrated S\(_{(g)}\) partial pressure is extremely low under the given exposure conditions. The exposure to flue gas only has confirmed this. The solid-to-solid reactions numbered 5–8 are the only probable causes for the formation of sulphides. In other words, the inherent Na sulphate in ash is the key component that drives the sulfidation reaction. It forms molten eutectics with iron surface to promote the outward diffusion and sulfidation of metals (Fe and Cr) within the molten eutectics. The use of Cr-bearing tube inhibited the formation of sulphate eutectics, and hence, the coating of XJ_S ash caused little difference against the speciation of S for T23 and SUS304 in **Figure 5.12**. However, the discrepancy between the two ash deposits for SS400 is intriguing. Although the content of Na sulphate is lower in the XJ_S ash (**Table S1**), the troilite (FeS) with a broad peak at ~2477 eV is nearly the only species observed upon the coating of SS400 with XJ_S ash. On the one hand, this substantiates the inhibitory effect of silica additive on the formation of molten alkali-metal sulphates. On the other hand, this may hint the alleviation of the resistance against the inward diffusion of SO\(_2\) due to the absence of molten sulphates. Therefore, the dissociation of SO\(_2\) inside the tube result in a relatively high partial pressure for S\(_{(g)}\) to promote the sulfidation extent of Fe.

The difference of the sulfidation potentials between the two pure metals Fe and Cr, as shown in **Figure 5.13** is also interesting. If the sulfidation rates of these two metals are comparable, the Cr oxide protective layer would break down by the spallation, thereby accelerating the overall corrosion rate for the tube. Since it is not possible to differentiate between Cr-S and Fe-S by the S K-edge XANES spectra, the XANES was conducted on the Cr K-edge for the top layer of the two tubes T23 and SUS347. As demonstrated in **Figure 5.14**, Cr\(^{3+}\) oxide and chromite (Mg\(^{2+}\)/Fe\(^{2+}\)) are the only two species observed, which were balanced by the Cr metal. This suggests that the amounts of Cr sulphide and sulphate are extremely low on the tube cross-section, or the sulfidation and sulphation rate of Cr is kinetically slower than its counterpart metal Fe, irrespective of the tube material and ash deposit type. Moreover, **Figure 5.14** suggests an enhanced formation of chromite upon the coating of XJ_S.
ash on the two tubes. This is consistent with the XRD results in Figures. S2–S4.

Figure 5.14. Cr K-edge XANES spectra and the fitting results for two tubes coated with the two fly ashes in the oxy-firing mode. Cr metal is the third species to balance the whole Cr on the cross-sectional surface of the tubes. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Last effort was made to clarify the oxidation states of Cr along the cross-section of the low-alloy tube T23 coated in the oxy firing mode, so as to quantify the penetration depth of oxygen and its promotion effect on the oxidation of Cr. At the XAS measurement, the sample was moved from the centreline of the tube through to the outer surface where the signal of Cr tends to disappear. The tube was analysed for two cases including the flue gas only case and the coating of JX_S ash. The resultant Cr K-edge XANES spectra are shown in Figure 5.15, whereas the respective fitting content for Cr$^{3+}$ including both chromium oxide and chromite was plotted versus the distance from the tube centreline.
in Figure 5.16. Interestingly, the exposure of the tube T23 in flue gas only resulted in a very slow diffusion of oxygen inside the tube, therefore, the oxidation extent of Cr on the outer layer surface only reaches ~8% of the total Cr, which gradually decreases to less than 5% for the Cr in the centreline of the tube. However, upon the coating of the XJ_S fly ash, the oxidation extent of the Cr inside was increased slightly compared to the flue gas case, reaching approximately 10% on the metal/oxide interface.

Figure 5.15. Cr K-edge XANES spectra along the width of the cross-sectional tube T23 from its centreline to the oxidation scale. The tube T23 was exposed in the oxy-firing mode. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the oxide scale, the oxidation extent of Cr in the ash deposit case is even slightly higher than the flue gas case. This confirms the catalytic effect of fly ash on the oxidation of chromium, either via
the oxygen-shuttling role of the free oxides within it, or the interaction with Cr-oxide layer to form the respective chromite, as indicated the Eqs. (5.3) and (5.4) below:

\[
M_xO \rightleftharpoons xM + O \quad \text{Eq. (5.3)}
\]

\[
M_xO + Cr + O \rightleftharpoons MxCr_2O_4 \quad \text{Eq. (5.4)}
\]

where \( M \) in Eq. (5.3) denotes a metal, which is mainly alkali and alkaline earth metals (Na, K, Ca and Mg) in ash possess a larger reducibility to accept the electrons released from dissociation of bulk oxygen. Our previous research [22] and the past studies [23, 24] using pure oxides for the oxidation of Cr at 600–1000 °C has proven this. Due to this catalytic effect, the dissociation of bulk oxygen and its inward diffusion rate were enhanced, whilst the relative diffusion of Cr outwards was enhanced simultaneously. Although this helps form a denser protective layer, it may cause some side effects such as the breakaway of the chromite layer over a longer exposure time [25]. Efforts will be made by us to clarify this and the probability for the formation of chromium carbide in the future.

Figure 5.16. The curve-fitting results for the content of Cr\(^{3+}\) including oxide and chromite along the width of the T23 tube cross-section. The respective XANES spectra were given in Figure. 5.15.


5.4 Conclusion

Detailed speciation analysis has been conducted on the corroded tubes coated with two different ash deposits, in air-firing versus oxy-firing mode, at an exposure temperature of 650 °C, 50 h and different flue gases, i.e. pure CO₂, air, air-firing flue gas and oxy-firing flue gas. The two ash deposits were collected from the surface of superheater tubes in a pc-fired boiler burning a low-rank coal (from Xinjiang, China) with and without silica additive.

The major conclusions achieved include:

1. Irrespective of the Cr content, the tubes exposed to pure CO₂ underwent oxidation, which is likely due to the reaction CO₂ + M = CO + MO where M stands for Fe or Cr. Cr in the Cr-bearing tubes were oxidized more rapidly than Fe.

2. The combined use of silica additive and Cr-bearing tubes with a minimal Cr content of 2 wt.% (i.e. T23) is beneficial in inhibiting the tube surface oxidation as well the penetration of oxygen in the air-firing flue gas.

3. Oxygen is the principle element diffusing inside the tube upon the exposure to flue gas only. Upon the deposition of ash on the tube surface, the penetration of sulphur was enhanced. Compared to the sodium sulphate - rich XJ ash causing the formation of pyrite (FeS₂) on the tube surface, the ash deposit derived from coal mixed with silica additive resulted in the preferential formation of troilite (FeS) that is deficient in S, thus less corrosive. For the Cr-bearing tubes, sulphate is the only S-bearing species due to the inhibited inward diffusion of S by the Cr-oxide layer, irrespective of ash deposit type.

4. Apart from sulphur, sodium and other metallic elements in ash deposits also interacted with the tube surface to form new species such as augite, which may cause the tube breakdown as well.

5. Spatial organization of the oxidation state of Cr suggests a slightly accelerated outward diffusion of Cr by the ash coating, due to the catalytically enhanced oxygen-shuttling of the free oxide in ash. This led to a dense Cr-O layer that is highly protective on the tube top surface.
Chapter 5 Effect of Silica Additive on the Tube Corrosion

References


27. G. Stein-Brzozowska, H. Díaz, J. Maier, G. Scheffknecht. Impact of oxy-fuel combustion on
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Monash University

Declaration for Thesis Chapter 6

Declaration by candidate

In the case of Chapter 6, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
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<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
</tr>
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</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
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<tbody>
<tr>
<td>Facun Jiao</td>
<td>Experimental work</td>
<td>10 %</td>
</tr>
<tr>
<td>Xiaojiang Wu</td>
<td>Editing and feedback</td>
<td>External co-author</td>
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<tr>
<td>Dunxi Yu</td>
<td>Editing and feedback</td>
<td>External co-author</td>
</tr>
<tr>
<td>Yoshihiko Ninomiya</td>
<td>Comments on my work</td>
<td>External co-author</td>
</tr>
<tr>
<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

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<th>Main Supervisor’s Signature</th>
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Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
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CHAPTER 6

Influences of Gaseous SO$_2$ and Sulphate-Bearing Ash Deposits on the High-Temperature Tube Corrosion of Heat Exchanger Tube during Oxy-Fuel Combustion
In chapter 5, we have used one fuel control method such additive of silica to inhibit the tube corrosion. However, this chapter used different control method which is coal washing prior combustion, aimed to clarify the roles of sulphur (S) in both lignite ash deposits and bulk flue gas on high-temperature tube corrosion during oxyfuel combustion. In particular, the potential synergism between these two different S sources during the oxy-fuel combustion was explored. The ash deposits were derived from the combustion of a Xinjiang lignite (from China) and its water and acid washed coal samples. This chapter has been reformatted from the following published manuscript: I. Ja'baz, F. Jiao, X. Wu, D. Yu, Y. Ninomiya, and L. Zhang. Influences Influence of gaseous SO$_2$ and sulphate-bearing ash deposits on the high-temperature corrosion of heat exchanger tube during oxy-fuel combustion Fuel Processing Technology, 167, p.193-204.
Chapter 6 Influences of gaseous SO$_2$ and sulphate-bearing ash deposits

Abstract

This study aims to clarify the roles of sulphur (S) in both lignite ash deposits and bulk flue gas on high-temperature corrosion. In particular, the potential synergism between these two different S sources during the oxy-fuel combustion was explored. The ash deposits were derived from the combustion of a Xinjiang lignite and its water and acid washed coal samples. It was found that the amount of S permeated inside the tube is predominantly limited by the availability of sulphates in the ash deposits, under both air-firing and oxy-firing combustion modes. However, the participation of flue gas in particular SO$_2$ and steam is essential, although their participation extent is very low. The lignite ash deposit functions as a medium which transfers the S from bulk gas to tube surface, via the formation of intermediate molten sulphates or sulphides. The formation of sulphides is highly dependent on ash properties (i.e. the content of sulphates) and tube composition. The high- S ash deposits with >8 wt.% sulphate have no propensity to cause the formation of sulphide. By contrast, for the low-S ash deposits with >8wt.% sulphate, the co-precipitation of Fe sulphide and even CaS in the molten melt was observed. The inherent Ca is believed to be a key element causing the sulphidation of tube surface. Compared to water washing, the use of acid to wash coal is able to remove the free Ca oxide, and hence, eliminates the formation of sulphide on the tube surface. For the tubes tested, the medium-Cr tube, T91 is most easily sulphided, due to the low Cr content. The Cr-O protective layer formed on the tube top surface is also porous enough for the gases to permeate and form a reducing environment deep inside that promotes the formation of sulphide. Upon the use of washed coal ashes, the tube corrosion rate was much lower than the use of silica additive and even comparable to the pure flue gas.

Keywords: Oxy-fuel combustion, High temperature corrosion, Lignite ash deposits, Sulphur, XANES
6.1 Introduction

Tube corrosion in the fireside is one of the critical issues negating the performance of a coal-fired boiler [1]. Apart from the nature of the material, the wastage of a tube is induced by flue gas and ash deposits in both of which sulphur is one of the most critical elements. In a typical coal-fired combustion environment, the majority of the inherent Sulphur converts into a gaseous oxide, which subsequently partially reacts with ash-forming elements to form sulphates. If the flue gas pollutants are recirculated, such as in oxy-fuel combustion, the concentration of SO$_2$ could be raised 3–4 times compared to air-firing combustion [2]. The high-temperature corrosion rate in the boiler will thus be accelerated [3–5].

The theory underpinning the role of sulphur on tube corrosion in the superheater zone has been well established under the conventional air-firing mode. In brief, the alkali sulphates in ash deposit are critical in accelerating the tube corrosion [6], due to the formation of alkali iron trisulphate eutectics such as Na$_3$Fe(SO$_4$)$_3$ and K$_3$Fe(SO$_4$)$_3$ that have a melting point close to and even lower than the tube surface temperature in the superheater and re heater zones [7]. The resultant trisulphate can further promote the sulfidation reaction under the tube surface, as shown in Eqs. (6.1) - (6.2) below [4]. Similar to alkali sulphates, calcium sulphate and SO$_2$ in bulk gas are also detrimental on high-temperature tube corrosion, causing the formation of iron sulphide at an environment of 593 °C, according to Eqs. (6.3) and (6.4) below [8, 9]. When sulphide reacts with oxides of iron, the binding of oxide layer to the bulk metal weakens [10]. Additionally, the sulfidation reaction may proceed at a linear rate in contrast to oxide formation which is approximately parabolic [11, 12]. Thus, more metal is consumed by sulphide formation [13]. The resultant sulphides are not protective, because they are usually porous and highly defective. The transport of gases/metals through the sulphide scale are also very high [14].

\[
\begin{align*}
3Na_2SO_4(s) + 3SO_2 + Fe_2O_3 & \rightarrow 2Na_3Fe(SO_4)_3 & \Delta G_{650^\circ C} = -199.21 \text{ KJ} & \text{Eq. (6.1)} \\
2Na_3Fe(SO_4)_3 + 19 Fe & \rightarrow 6Fe_3O_4 + 3FeS + 3Na_2S & \Delta G_{650^\circ C} = -1673.58 \text{ KJ} & \text{Eq. (6.2)} \\
4Fe + CaSO_4 & \rightarrow 3FeO + CaO + FeS & \Delta G_{650^\circ C} = -186.48 \text{ KJ} & \text{Eq. (6.3)} \\
3Fe + SO_2(g) & \rightarrow 2FeO + FeS & \Delta G_{650^\circ C} = -224.30.21 \text{ KJ} & \text{Eq. (6.4)}
\end{align*}
\]
These theories are qualitatively applicable to the oxy-fuel combustion environment. Through experimental study using sulphur–lean bituminous coal (3.77 wt.% in the ash deposit) and sulphur-rich bituminous coal (6.49 wt.%) in the ash deposits, Stein-Brzozowska et al. [15] found that, the fireside corrosion for the combustion of high-S coal was subjected to a higher corrosion rate than the low-S coal which was burnt under the same conditions. This hints the importance of inherent sulphur present in the coal ash that has more influence on corrosion than its gaseous counterpart in the oxy-fuel combustion mode. Stein-Brzozowska et al. [15] also reported that both the high temperature corrosion rate and sulfidation rate increased with temperature. However, by varying the concentration of bulk SO₂ from 1000 ppm to 3000 ppm, the same authors confirmed that the gaseous SO₂ is superior over the inherent S in coal, causing more corrosion on the tube surface. Clearly, this leaves an open and unclear question regarding how the gaseous SO₂ and solid sulphur in ash deposit interfere and even compete between one another to attack the tube surface. Upon the shifting of bulk gas from once-through air to recirculated flue gas in oxy-firing mode, the concentration of SO₂ in bulk gas is expected to increase rapidly than the content of S in ash deposit. Clarifying the importance of sulphur from different sources and their synergism, if any is thus critical for the control of tube corrosion in the oxy-fuel combustion process.

The present study aims to clarify the synergism between gaseous SO₂ and ash deposit on tube corrosion under the typical superheater conditions in an oxy-firing boiler. The tube exposure conditions were fixed at a temperature of 650 °C and 50 h duration, and the flue gas was made up of 3000 ppm SO₂, 30% steam, 1000 ppm HCl, 5% O₂, 10% N₂ and the balance CO₂. Efforts were made to vary the compositions of ash deposits that were produced from a lignite coal, namely Xinjiang and its respectively washed coals. Since Na and/or Ca are the major elements that were washed away whereas the other elements have little change, the use of such a series of ash samples is expected to minimize and even eliminate the effect of the metals other than Na and Ca on tube corrosion. The use of these ash deposits can also help us to reveal the effect of coal washing on the minimization of tube corrosion. Additionally, four different tubes with different chromium content (SS400, 12Cr1MoVG, T91 and SUS304) coated with raw/washed fly ash were tested. Special attention was paid to the medium-Cr tube T91 with around 9.1 wt.% Cr, based on the hypothesis that this medium-Cr tube has the potential to replace the commonly used low-Cr alloy such as 12Cr1MoVG under the harsh conditions that can be encountered during the oxy-fuel combustion.
Apart from weighing the mass change of a corroded tube, a variety of advanced analysis was also conducted on both tube surface and used ash deposits, including optical microscope (OM) for the cross-section observation to quantify the corrosion depth, scanning electron microscopy equipped with energy dispersive X-ray detector (SEM-EDX) to map the penetration/diffusion of elements of interest through the ash-tube interface, X-ray fluorescent spectrometer (XRF), and synchrotron XANES for the oxidation states of Sulphur (S) and chromium (Cr). Thermodynamic equilibrium calculation was also conducted to interpret the experimental observations. The results achieved are expected to shed new lights on the mechanisms underpinning the role of sulphur on tube corrosion during the oxy-fuel combustion.

6.2 Experimental procedure

6.2.1 Ash Deposit Compositions

The fly ash of Xinjiang (XJ) coal, known as a low - rank coal in Xinjiang, China was used as the baseline sample for high temperature corrosion test. As listed in Table 6.1, the raw coal ash, namely XJ is a typical low-rank lignite ash rich in around 10 wt.% sodium (Na) in its oxide form. It is accompanied by abundant calcium (Ca) of 39.21 wt.% and 10.86 wt.% sulphur (S). The typical low rank coal composition is 24.5 wt.% moisture, 6.9 wt.% ash, 30.2 wt.% volatile, 62.9 wt.% FC and 0.02 wt.% chlorine [16]. The ash sample was collected from the surface of the super-heater tube surfaces [17]. The same coal was washed by the use of water and 1 M hydrochloric acid (HCl) [16, 18]. For water washing, a three-stage counter-current process was applied, leading to the formation of three washed coals, W1-W3. On the other hand, for the acid washing, a two-stage counter-current with acid in stage 1 and water in stage 2 was employed, yielding two samples, A1 and A2 from the two stages, respectively. Regarding the ash samples from the water-washed coals, the content of Na was reduced remarkably. The use of acid further slightly reduced the content of Ca, whereas Na has little change compared to the water-washed coal samples. This is because Na in this coal is mostly present as water-soluble species that can easily dissolve into the neutral water [16].
Table 6.1 Elemental compositions of the fly ash samples tested in this study

<table>
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<tr>
<th>Compositions</th>
<th>Raw coal</th>
<th>Water washed</th>
<th>Water+ Acid (1 M HCl) washed</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>XJ 16.67</td>
<td>W1 47.59</td>
<td>W2 45.57</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>W3 45.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A1 46.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2 47.27</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>XJ 8.49</td>
<td>W1 21.16</td>
<td>W2 20.83</td>
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<td></td>
<td></td>
<td></td>
<td>W3 20.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A1 19.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2 19.10</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>XJ 0.39</td>
<td>W1 3.41</td>
<td>W2 2.88</td>
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<td></td>
<td></td>
<td></td>
<td>W3 2.71</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>A1 2.11</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>A2 3.46</td>
</tr>
<tr>
<td>CaO</td>
<td>XJ 39.21</td>
<td>W1 13.78</td>
<td>W2 16.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>W3 15.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A1 12.67</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2 11.18</td>
</tr>
<tr>
<td>MgO</td>
<td>XJ 12.79</td>
<td>W1 4.63</td>
<td>W2 5.05</td>
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<td></td>
<td></td>
<td></td>
<td>W3 4.96</td>
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<td></td>
<td></td>
<td></td>
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<tr>
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<td>XJ 10.86</td>
<td>W1 7.79</td>
<td>W2 7.33</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>W3 7.93</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>A1 8.79</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>A2 8.21</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>XJ 0.46</td>
<td>W1 0.12</td>
<td>W2 0.1</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>W3 0.15</td>
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<td>A2 0.17</td>
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<tr>
<td>Na₂O</td>
<td>XJ 10.67</td>
<td>W1 1.01</td>
<td>W2 1.58</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>W3 1.81</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>A1 1.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2 1.79</td>
</tr>
<tr>
<td>K₂O</td>
<td>XJ 0.46</td>
<td>W1 0.51</td>
<td>W2 0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>W3 0.49</td>
</tr>
<tr>
<td></td>
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<td>A1 0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A2 0.64</td>
</tr>
</tbody>
</table>

6.2.2 Tube Corrosion Test Set-Up and Test Conditions

The tube corrosion test was detailed in our previous work [4]. The furnace temperature was fixed at 650 °C in this study, the flat tube specimen, 3 cm × 3 cm × 2mm were prepared by a wire electrical discharge machine to cut on the cross-sections of four commercial tubes. Each test lasted 50 h and three repetitions were conducted for each condition. With regard to the oxy-firing flue gas composition, it is made up of 3000 ppm SO₂, 30% steam, 1000 ppm HCl, 5%O₂, 10% N₂ and CO₂ in balance, flue gas was fed at a flowrate of 300 mL/min continuously into the furnace. As confirmed by our pilot-scale test [19], the steam content in flue gas can go up to 30 vol% and SO₂ is also highly accumulated during the oxy-firing of low-rank brown coal. The steam content tested here is close to the oxy-fuel flue gases tested elsewhere [20–22]. A total of four tube materials in Table 6.2 was tested, with a Cr content in the ascending order of stainless steel SS400 (Cr% nil), low-chrome ferritic steel 12Cr1MoVG (0.9–1.2%), high-chrome ferritic steel T91 (9%), and austenite stainless steel SUS304 (18–20%). For each test, around 100 mg ash was loaded on the tube surface. The ash coating was conducted by putting the ash powders into a plastic mold that is the same size as the tube specimen. The ash powder amount remained almost the same throughout all the tests. The ash powder was also gently pressed by hand to ensure that there is no loss during the test. After it, the plastic mold was removed whereas the ash powder was left on the tube surface. Finally, the ash laden tube
specimen was loaded on a quartz-made sample holder and pushed to the middle zone in the hot furnace where the temperature is constant and the same as the set temperature. A thermocouple was further inserted above the tube specimen to record and control the temperature. After each test, the used ash was generally brushed away using a soft brusher (to avoid surface scratching) and saved for the characterization. The used tube was either weighed for its mass change and saved for the future characterization on the top surface, or quickly mounted together with the ash into epoxy resin to measure the cross-section.

Table 6.2 Tube materials tested in this study

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Mo</th>
<th>V</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS400</td>
<td>0.02</td>
<td>0.03</td>
<td>Bal</td>
<td>0.01</td>
<td>-</td>
<td>0.17</td>
<td>0.09</td>
<td>0.36</td>
<td>0.004</td>
<td>0.013</td>
</tr>
<tr>
<td>12Cr1MoV</td>
<td>0.90-1.20</td>
<td>-</td>
<td>Bal</td>
<td>0.25-0.35</td>
<td>0.15-0.30</td>
<td>0.08-0.15</td>
<td>0.17-0.37</td>
<td>0.40-0.70</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>T91</td>
<td>1.91</td>
<td>-</td>
<td>Bal</td>
<td>0.93-0.94</td>
<td>-</td>
<td>0.11</td>
<td>0.21</td>
<td>0.39-0.38</td>
<td>&lt;0.001</td>
<td>0.009-0.13</td>
</tr>
<tr>
<td>SUS304</td>
<td>18-20</td>
<td>8-12</td>
<td>Bal</td>
<td>-</td>
<td>-</td>
<td>0.03-0.08</td>
<td>0.75</td>
<td>2</td>
<td>0.030</td>
<td>0.045</td>
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</tbody>
</table>

6.2.3 Analytical Techniques for Characterization of the Surface of Corroded Tubes

The cross-sections of the corroded tubes were observed by an optical microscopy (Olympus) to establish the thickness of scale and depth of intergranular penetration. The oxidation thickness was evaluated using sketchbook software, where 10 lines were drawn across the interface. The length of each line was measured and used to calculate the average thickness and standard deviation which subsequently gave the interface thickness. From the interface thickness, the oxidation rate was calculated by dividing the interface thickness by the exposure time, 50 h. Prior to the analysis, the tube cross-sections were polished by the use of silicon carbide paper with a grit of 2400. In addition, scanning electron microscope (SEM) was used to map the elemental distribution on the tube cross-section. The analysis was conducted by JEOL 7001F to identify the distribution of major elements of interest, including Fe, S and O. Prior to the SEM observations, the tubes were also carbon sputtered. The K-edge X-ray adsorption near-edge spectroscopy (XANES) spectra of S and chromium (Cr) were conducted to specify the oxidation state of these two elements on the tube top surface. Compared to
bench-scale X-ray diffraction (XRD), XANES is highly sensitive and able to detect the elements with a concentration on the ppm level [23]. The beam size of around 1 μm can also easily pinpoint the tube ash interface which is generally on the sub-micron scale. The XANES spectra were collected from beamline BL16A1 at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. BL16A1 had a fixed exit double crystal Si (111) monochromators with a nominal beam size of 0.25 by 0.25mm on a sample. For the analysis of Cr, pure elemental Cr was used for the calibration at a K-edge absorption energy of 5989 eV. Pure elemental Mo was used for the calibration of S at a K-edge absorption energy of 2481 eV. The peak energy absorption (white-line) position was taken as the base (0 eV), with all subsequent spectra recorded 200 eV below and 800 eV above this point in fluorescence mode. The analysis of S and Cr was only conducted for the top surfaces, as the signal for S from the cross-section of the tubes was very weak and noisy. All spectra were normalized using ATHENA which is part of the DEMETER package [24]. Linear combination fitting (LCF) was used on the normalized sample spectra to determine the mineral composition by using a large number of standards that have been detailed in our previous papers [4, 25].

6.2.4 Analytical Techniques for Characterization of the Used Ashes

After the tube exposure tests, some of the used ash samples were also gently collected from the tube surface, further ground and characterized by X-ray fluorescence (XRF) for the composition as well as XANES for the oxidation of S. The XANES results are expected to supplement the results for the respective tube surfaces so as to draw an overall picture on the partitioning of S between tube and ash.

6.2.5 Thermodynamic Equilibrium Calculations

The “Equilib” module in a commercial thermodynamic equilibrium program, Factsage [26] was used to calculate and establish the species in equilibrium that can be formed upon the interaction between flue gas, ash deposit and the alloying elements in the tube. The input for each calculation includes the amounts of alloying elements in a tube, individual elements (as a form of oxide) in the ash, and individual components in flue gas based on the compositions of tube, ash and flue gas, masses of a tube and ash, flow rate (300 mL/min) of flue gas and a total exposure time of 50 h. The temperature was set at 650 °C and the total pressure was 1 bar absolute. Apart from the pure substances, the built-in databases FToxid Slag A or FToxid - Slag B were also ticked during the calculation. Slag A is
made up of sulphide whereas Slag B is dominated by sulphates in the FactSage database. The calculation using Slag B only converged for the raw XJ ash deposit that is rich in sulphate. In contrast, both two slag databases converged for the washed coal ashes that are lean in sulphates. However, the use of Slag B database gives a much lower slag formation propensity, because sulphate is less prone to melt than sulphide at 650 °C. Since the formation of sulphide is more of interest and is also confirmed experimentally in this study, the results using Slag A database for the washed coal ashes were only interpreted hereafter.

6.3 Experimental Results

6.3.1 Mass Changes and Oxidation Growth Rates

Figure. 6.1 illustrates both the mass loss and oxide layer growth rate for the four tubes coated with different ashes, where x-axis refers to the ascending sequence of Cr content in the tubes. The tube mass loss value is the average of the two replicate samples. Instead of mass gain, mass loss was observed for all the testes here, which is expected and can be explained by the evaporation of the metals as chloride/hydroxide, and the spallation of oxide/sulphide fragments which are ductile. For comparison, the blank test without ash coating was also included in Figure 6.1, as well as the XJ_S referring to the ash deposit collected from the combustion of Xinjiang coal blended with around 4 wt.% silica [17,27]. The use of silica additive has proven to be able to mitigate the fouling and tube corrosion in the industry-scale boilers, due to the immobilization of Na and Ca in the silica matrix [17,27].

As indicated by the mass loss results in Figure 6.1 panel (a), the mass loss decreases considerably with increasing the Cr content in the tube, irrespective of ash type. This agrees with our expectation, as Cr and the other addition metals such as Ni preferentially form a protective oxide layer on the tube surface [22]. Regarding the influence of ash type, it is evident that the raw coal XJ ash is most detrimental, causing the largest mass loss for each tube. The mass loss in the case of XJ ash is also 1.5 to 8 times higher than the blank flue gas case, demonstrating the significance of solid ash over flue gas on the tube corrosion. The use of silica additive reduces the tube mass loss, but the respective tube mass loss is still higher than the blank flue gas case except the tube SS400. In contrast, the coating of washed ashes, irrespective of its type is much more effective, mitigating the tube mass loss to a level that is even below the blank case, irrespective of the tube type.
The oxide layer growth rate is shown in Figure 6.1 panel (b). The oxide layer growth rate was calculated by dividing the corrosion product thickness (as shown in Figure 6.2) by the exposure time, 50 h. The results here further confirm that coal washing is more effective than silica addition in the prevention of tube oxidation. Instead of attacking tube surface, the washed coal ashes, in particular those washed by acid can even function as an extra shield, in combination with the medium-Cr tubes including T91 and SUS304 to decrease the tube oxidation layer dramatically. The typical cross-sectional structures for the corroded low-chrome ferritic tube 12Cr1MoVG are illustrated in Figure 6.2. Compared to the case of raw coal XJ ash coating, the other two cases for the coating of W1 and A2 yield a narrower corrosion product thickness which also refers to as the oxide layer that is formed by the penetration of corrosive components, in particular the oxidizing gases such as O₂ and H₂O. Moreover, considering that the tube corrosion is directly related to the penetration depth of oxygen (O) and sulphur (S) [1], efforts were made to map these two elements on the corroded tube
cross-section. As shown in Figure 6.3 for the tube T91, the two elements of O and S show distinctly different distribution along the cross-section. O is overwhelmingly dominant and distributes uniformly across the interface, demonstrating that oxidation is one of the principal mechanisms underpinning the tube corrosion [1,28]. In contrast, S has a non-continuous distribution, with the preference of the formation of thin strips on the boundary between interface and bulk tube/substrate, or even inside the interface layer. Taking W1 as the example, one can clearly see that a thin S-rich layer, labelled as strip No 1 in the S map adheres closely to the tube surface. However, the remaining two strips labelled as No 2 and 3 are embedded deeply inside the interface. Regarding another washed ash W2, only one thin layer was observed on the boundary between tube surface and the interface. For the acid washed ash A1, the distribution of S is barely discernible.

Figure 6.2. Typical micro-structure for the cross-section of 12 Cr1MoVG specimen exposed to different fly ash upon oxy-fuel combustion.

The S observed in the ash-tube interface demonstrates the penetration of this corrosive element either from SO₂ in bulk gas, or from solid sulphates in ash deposits. Regardless of the sulphur source, the resultant S in the interface should be partially ductile and easy to fragment into small pieces that are eventually mixed up with ash deposit, as evident in Figure 6.3. In light of this hypothesis, the contents of S on the corroded tube top surfaces (after the ash was brushed away) were quantified by XRF, and plotted versus the respective mass losses of the tubes. Considering the measurement error related to the mass of the tubes, a reasonably linear trend is evident in Figure 6.4. For the most advanced tube
SUS304, its mass losses are the least, so are the contents of S remaining on its surfaces. The tube T91 bears a medium-Cr content, and the S content remaining on its surface mostly falls in the medium range. As expected, the low-Cr tube 12Cr1MoVG bears the largest mass loss as well as the highest content of S. More interestingly, an identical linear correlation even holds for the three Cr-containing tubes, substantiating that S is the principle element causing the tube wastage. Furthermore, **Figure 6.5** for the used ash W1 on tube T91 demonstrates the abundance of ductile S-bearing fragments that are fully mixed with the other particles. The quantified composition for the used ash W1 on tube T91, as listed in **Table 6.3**, confirmed a remarkable rise on the concentrations of Fe and S, whereas the concentrations of Na and Ca were decreased significantly. Apparently, S is mainly affiliated with Fe, whereas the inherent Na and Ca should partially diffuse out of ash matrix and transfer into the corrosion product or even deep inside the bulk tube, forming eutectics that easily melt, flow and fill in the pores within bulk tube and ash deposit.

![Figure 6.3: Elemental mapping for tube T91 exposed to washed coal.](image)

**Figure 6.3** The elemental mapping for tube T91 exposed to washed coal.
Table 6.3 Elemental compositions of the W1 fly ash samples before and after corrosion exposure

<table>
<thead>
<tr>
<th>Composition, wt.%</th>
<th>W1 before corrosion exposure</th>
<th>W1 after corrosion exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.59</td>
<td>31.11</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.16</td>
<td>14.73</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.41</td>
<td>31.56</td>
</tr>
<tr>
<td>CaO</td>
<td>13.78</td>
<td>9.27</td>
</tr>
<tr>
<td>MgO</td>
<td>4.63</td>
<td>0.10</td>
</tr>
<tr>
<td>SO₃</td>
<td>7.79</td>
<td>12.98</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.12</td>
<td>0.00</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.01</td>
<td>0.03</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.51</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 6.4. Correlation between tube mass loss and the content of S on the corroded tube surface.
6.3.2 XANES Speciation of S and Cr on Tube Surface and/or Used Ash

Figure 6.6 illustrates the S K-edge XANES spectra for the three corroded Cr-bearing tubes. Irrespective of the tube material, the peak located at ~2485 eV is the predominant and single peak for 12Cr1MoVG and SUS304. This peak is the fingerprint of sulphates which can be assigned as iron sulphate [29]. Such a species should be formed by the direct sulphation of iron oxide by bulk flue gas, or via the formation of Na-Fe trisulphate according to the reaction Eq. (6.1). Since no other peaks were found for S remaining on the tubes 12Cr1MoVG and SUS304, it is referable that Eq. (6.2) for the reaction between sulphates and iron metal to form sulphide did not proceed on the surface of both low- and high-Cr tubes. This is however not the case for the tube T91 with a medium Cr content. From the panel b for T91 coated with W1-W3 ashes, one can clearly see a tiny but non-negligible peak located at 2470 eV or ~2472 eV. The similar phenomena were observed for the used ashes coated on the same tube. As evident in Figure 6.7 for both the fresh and used ashes, although sulphate is the single, dominant species in the fresh ashes and the used ones on the tubes 12Cr1MoVG and SUS304, the three washed ashes, W1-W3 on tube T91 are exceptional that display the unique feature peaks at 2470–2472 eV. This peak is close to the feature peaks for a variety of sulphide standards shown in Figure 6.8. The difference between these sulphide standards is subtle and thus, the sulphides detected in Figure 6.7 can refer to as Fe₂S₃, FeS, NiS, Cr₂S₃, or even CaS/MgS. To rule out the
formation of $\text{Cr}_2\text{S}_3$, synchrotron XAS was further conducted on the speciation of Cr on the top tube surfaces, following exactly the same analytical and calculation procedures for S. The Cr-bearing standards used include oxide, carbide, sulphide and spinel, as detailed elsewhere [4]. Figure 6.9 for the Cr K-edge XANES spectra suggests that chromite/spinel is the predominant Cr-bearing species on the tube surface. The resultant chromite/spinel should function as the protective layer against the oxidation of iron and its corrosion. In light of this, the sulphides in Figures 6.6 and 6.7 are very likely related to the metals Fe, Ca and Mg.
Figure 6.6 S K-edge XANES spectra and the fitting results for the top surfaces of three tubes exposed to different washed coal. In each panel the solid curves refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from ATHENA. Panels (a) to (c) are for the tube 12Cr1MoVG, T91 and SUS304, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Figure 6.7 S K-edge XANES spectra and the fitting results for the ash samples before and after the tube exposure tests. In each panel the solid curves refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from ATHENA. Panels (a) - (d) are for the fresh ash samples, used ash on tube 12Cr1MoVG, used ash on tube T91 and on tube SUS304, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Figure 6.8 S K edge XANES spectra for sulphide standards. Peak at 2481 eV indicated by the dotted line is spurious sulphate caused by oxidation [47].
Figure 6.9 Cr-species composition from XANES fitting of on the tube T91 surface.
Figure 6.10 Schematic (a) for the formation of melt, sulphide and sulphate in the melt; FactSage predicted slag composition (b) for XJ raw coal ash deposit on tube T91, based on the use of database BSlag + Sulphates; and (c) for the FactSage predicted slag composition for W1 ash deposit on tube T91, based on the use of database ASlag + Sulphide
6.4 Discussion on the Mechanisms Governing the Partitioning of Sulphur

Based on the results above, the behavior of S is clearly the most critical factor accelerating the high-temperature tube corrosion under the oxy-fuel combustion mode. This broadly agrees with the observations achieved in the conventional air-firing mode [30]. However, three key and new phenomena have been explored from this study, 1) co-existence of sulphate and sulphide on both corroded tube surface and used ash deposit; 2) ash-dependent formation of sulphide, and 3) the unique formation of sulphide on tube T91 upon the coating with washed coal ashes that are lean in sulphates. All these phenomena have yet to be reported. In particular, the last phenomena related to T91 is for the first time reported here. As summarized in Table 6.4 for the past researches on the use of T91, the previous findings are mainly composed of the general trends such as the tube corrosion rate versus tube composition, and the comparison between different tubes.

With regard the first phenomena for the splitting of S between sulphate and sulphide, they should be formed according to the reaction Eqs. (6.1) - (6.4) mentioned before. In particular, the formation of sulphate by Eq. (6.1) needs to take place firstly upon the contact between loose ash particles and oxide layer formed on the tube top surface. Subsequently, the resultant Na-Fe sulphates, as evident in Figures 6.6 and 6.7 partially melt and stick to the tube surface. The molten sulphates can further act as a solvent pool to dissolve the inherent metals such as Fe, Cr and others in the tube according to the fluxing mechanism [31]. The dissolved metals in turn react with the molten sulphates to form the respective sulphide, as suggested by Eqs. (6.2) and (6.4). This mechanism is explained virtually in Figure 6.10 panel (a), where the grey, black and light green colours refer to the bulk tube, molten species and loose ash particles, respectively. Note that, HCl in the bulk gas has been ignored, although it has the potential to cause the formation of sodium chloride which in turn reacts with SO₂ and O₂ into alkali sulphate [32]. After sulphation, the reaction mechanism is similar to that of fluxing scheme induced by SO₂. A thin Cr-O layer is expected to remain in between the grey and black colours, as has been confirmed in our previous studies [4] and Figure 6.9 in this study. With respect to the formation of molten species, the FactSage prediction results, as shown in Figure 6.10, panels (b) and (c) respectively for raw XJ coal ash and W1 ash on tube T91, confirmed the thermodynamic possibility for the melting of sulphates/sulphides at 650 °C. Note that, the melt fraction accounts for 5 wt.% and 10 wt.% of the total ash in panels (b) and (c), respectively. For the sulphate-bearing melt shown in Figure 6.10 panel (b), the oxides are instead much more abundant than sulphates, due to the fact that sulphates are more difficult to melt. The molten sulphates are also dominated by alkali
and iron sulphates. In contrast, for the sulphide-bearing melt in **Figure 6.10 panel (c)**, sulphide is predominant, which is followed by Cr and Fe oxides. The sulphide is also mainly made up of CaS and FeS that can be formed thermodynamically via Eq. (6.3).

The detection of sulphide in **Figures 6.6 – 6.7** experimentally confirmed a direct involvement of ash deposit on the tube corrosion. For the blank test using pure flue gas only, our previous test has proven that the formation of sulphide was indiscernible [3]. However, the role of flue gas on the formation of sulphide cannot be ruled out here. Although having no direct contact with tube surface, the flue gas can react with ash deposit first, forming sulphates that subsequently attack the tube surface according to the fluxing mechanism in **Figure 6.10 panel (a)**. The abundant CaO in ash samples in **Table 6.1** plus the free oxides derived from Eqs. (6.2) – (6.4) are able to capture SO\(_2\) at 650 °C [33].

To quantitatively clarify the extent of flue gas participating on the tube corrosion, thermodynamic equilibrium calculation was further conducted to evaluate the influences of three flue gas components, SO\(_2\), O\(_2\) and steam/H\(_2\)O on the formation of slag. A kinetic modelling was not attempted here because of the lack of the kinetic parameter and the complexity of the oxy-firing flue gas used here. **Figure 6.11 panel (a)** demonstrates the results for the extent of dry gas (SO\(_2\) and O\(_2\)) whereas panel (b) is for the participation extent of steam when the extent of two dry gas components are fixed at 0.2%. Note that, the ashW1 was used for calculation here, and the two dry gas components, O\(_2\) and SO\(_2\) are assumed to have an identical participation extent in the formation of slag and sulphide.

As shown in **Figure 6.11(a)**, the attendance of dry flue gas is critical in affecting the amounts of total slag and the two key sulphides, Fe sulphide and Cr sulphide. Compared to the predominant formation of Cr sulphide in the absence of flue gas, the introduction of dry flue gas decreases the formation of Cr sulphide quickly, which drops to nil in the case that < 0.2% of dry flue gas participates in the reactions. Simultaneously, the total slag amount and Fe sulphides increase quickly to their maximum when > 0.5% dry flue gas is involved. However, in the case that >2.5% dry flue gas attends the reactions, the slag amount and sulphide drop dramatically to nil, due to the formation of dominant sulphates that are difficult to melt. Back to **Figure 6.9** where Cr sulphide was not found, it is obvious that the participation extent of dry flue gas should range between 0.2 and 2.5%. Regarding the **Figure 6.11 panel (b)**, it demonstrates the remarkable influence of steam on the formation of molten slag and sulphides. Under the exposure conditions tested here, the participation extent of steam is not negligible, but <3.5%, otherwise the formation of solid sulphates and gaseous H\(_2\)S will be superior. Interestingly, the formation of Cr sulphide is insignificant, irrespective of the steam percentage. This
further demonstrates the stability of this protective element in the wet flue gas. However, the total amount of melt decreases while the fraction of Fe sulphide increases upon the rise of steam fraction to participate in the tube corrosion.

Considering that the participation extents of flue gas components are very small, and the solid-state reactions are more critical in attacking the tube directly for the corrosion, it might be the case that the concentration of SO$_2$ in bulk gas is insignificant. At least, it is not the controlling limit for the tube corrosion. If that is the case, the shift from air-firing flue gas to oxy-fuel gas causes little difference on the penetration rate of sulphur, i.e. the concentration of S remaining on the corroded tube surface. To confirm this, efforts were made to correlate the content of S (in its most stable oxide form, SO$_3$) in ash deposit with the content of S remaining on the corroded tube surfaces exposed to both combustion modes. The air-firing flue gas is made up of 300 ppm SO$_2$ only, 260 ppm HCl, 8% steam, 4%O$_2$ and N$_2$ in balance [19]. The concentration of SO$_2$ is ten times less than in the oxy-firing flue gas. The ash deposits tested in air-firing mode are also different lignite ashes which called Victorian Brown coal fly ash, named Hazelwood and Yallourn which collected from Australia, the composition of SO$_3$ in Hazelwood fly ash was higher than the fly ash samples prior washing [3]. In spite of these differences, a good and identical trend was found between the two combustion modes for each tube. Clearly, in terms of the S penetration rate, bulk flue gas is much less influential than the content of S in ash deposit, under the exposure conditions tested here. Furthermore, one can see Figure. 6.12 that the slope for the correlation trend decreases upon the rise on the content of Cr in the bulk tube, further confirming the protective role of this element against the penetration of S and tube wastage.
### Table 6.4 Literature survey on tube corrosion during the oxy-fuel combustion.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Purpose</th>
<th>Characterisation methods</th>
<th>Material</th>
<th>Key findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.M. Sahib [38]</td>
<td>Investigation of the corrosion behavior of the T91 ferritic steel in air and the coating of Na$_2$SO$_4$-60%V$_2$O$_5$ at temperature of 900°C in cyclic manner.</td>
<td>TG/SEM-EDS/ XRD</td>
<td>T91</td>
<td>The hot corrosion behavior of T91 steel was found to be milder in air condition than oxidation under salt condition.</td>
</tr>
<tr>
<td>X. Zhang et al. [39]</td>
<td>Investigation of morphology, chemical composition and phase structure of oxide scale formed on T91 super-heater tube after long-term service in an USC coal power plant.</td>
<td>LOM/SEM-EDS/XRD</td>
<td>T91</td>
<td>Cracks and exfoliation were observed at the interface between Fe-rich outer layer and Cr-rich inner layer of the oxide scale.</td>
</tr>
<tr>
<td>Y. Chen et al. [40]</td>
<td>To test and evaluate the corrosion performance of T91 steel in a supercritical water environment at a temperature of 500 °C and a pressure of 25 MPa, and to investigate the effects of dissolved oxygen concentration on supercritical water corrosion</td>
<td>SEM-EDS-EBSD / XPS</td>
<td>T91</td>
<td>The oxide is composed of three different layers; hematite layer containing some chromium followed by a magnetite, and spinel oxide layer. In tests performed in low oxygen content supercritical water (CSW), it was noted to affect the oxidation of T91 alloy by changing the oxide grain orientation and reducing the oxide thickness.</td>
</tr>
<tr>
<td>P. Ampornrat et al. [41]</td>
<td>To characterised and understand the corrosion and stress corrosion cracking behavior of ferritic martensitic alloys in supercritical water for potential application as core components in the supercritical water reactor.</td>
<td>SEM-EDS/XRD</td>
<td>HT-9,</td>
<td>Temperature has a major impact on corrosion with weight gains at 500°C of around 4-5 times that at 400°C</td>
</tr>
<tr>
<td>T. Dudziak et al. [42]</td>
<td>To study the influence of different chemical compositions of the deposits on the ferritic steels in simulated fireside corrosion tests</td>
<td>SEM-EDS</td>
<td>15Mo3,</td>
<td>Corrosion degradation decreases with increasing Cr content in the alloys for all six deposits</td>
</tr>
<tr>
<td>P. Ampornrat and G. S Was [43]</td>
<td>Study the oxidation behavior of ferritic–martensitic F–M alloys in supercritical water (SCW) to evaluate the suitability of these alloys for use in supercritical water reactor (SCWR) concept.</td>
<td>SEM/ EDS Thermodynamaic calculation</td>
<td>T91, HCM12A, HT-9</td>
<td>T91 experienced the highest weight gain, followed by HCM12A and then HT-9.</td>
</tr>
</tbody>
</table>
### Chapter 6 Influences of gaseous SO\(_2\) and sulphate-bearing ash deposits

<table>
<thead>
<tr>
<th>Authors</th>
<th>Description</th>
<th>Methodology</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>D.Gond et al. [44]</td>
<td>Investigate the oxidation behavior of T91 steel and T22 steel in air has been studied under isothermal conditions at a temperature of 900°C in a cyclic manner.</td>
<td>OM/SEM-EDS/XRD</td>
<td>T91, T22</td>
</tr>
<tr>
<td>D.Gond et al. [45]</td>
<td>Investigate the oxidation behavior of T91 steel and T22 steel in salt of 75wt% Na(_2)SO(_4) + 25wt% NaCl under isothermal conditions at a temperature of 900°C in a cyclic manner.</td>
<td>SEM-EDS/ XRD</td>
<td>T91, T22</td>
</tr>
<tr>
<td>N Nishimura et al. [46]</td>
<td>Investigate the oxidation behavior of advanced heat-resistant steel tubes in power boilers.</td>
<td>SEM-EDS</td>
<td>T91, T22</td>
</tr>
</tbody>
</table>
Figure 6.11. Thermodynamic equilibrium modelling on the formation of melt and sulphides on tube T91 surface. Panel (a) is for the percentages of Cr/Fe sulphides upon the ash deposit W1 as a function of dry flue gas reacting with tube surface; (b) for the percentages of Cr/Fe sulphides upon the ash deposit W1 as a function of steam reacting with tube surface. The percentages of O\textsubscript{2} and SO\textsubscript{2} reacting with tube surface were fixed at 0.2%.
Figure 6.12. The correlation between SO$_3$ in ash samples with the sulphur on different corroded tubes surface. Panels (a)–(c) are for tube 12CrMoVG, T91 and SUS304, respectively.
Chapter 6 Influences of gaseous SO\(_2\) and sulphate-bearing ash deposits

6.13 Sulphide composition from XANES fitting of tube T91 and ash sample coated with wash fly ash.

The second phenomena for the ash-dependent sulphide formation is intriguing. To reflect the effect of ash composition on the formation of sulphide, Figure 6.13 was plotted by merging Figures 6.4, 6.6 and 6.7 to correlate the content of S in ash versus the contents of sulphide formed on both corroded tube surface and used ash, as well as the total content of S remaining on the tube surface. Note that, the contents of sulphides were quantified by the LCF for Figures 6.6 and 6.7. It is interesting that the total amount of S on the tube surface and the fraction of sulphides follow the same trend. That is, the three water washed ashes in particular W1 are more influential in the adherence of S and the formation of sulphide on the tube surface, whereas the other two acid-washed ashes bearing a relatively large amount of S are not in favour of the sulphidation reaction. This difference should be due to the greater reduction on the amount of CaO by acid washing. Therefore, the extent of reaction Eq. (6.3) for A1–A2 is less than for W1-W3. The panel (c) in Figure 6.10 also suggests a predominance of CaS in the slag formed from the low-S ash deposit. Additionally, although XANES spectra for S in Figures 6.6–6.8 failed to distinguish different sulphides, it is clear that CaO has a higher white line position (close to 1472 eV) than iron sulphide. It is thus very likely that the smallest peak for S in Figures 6.6 and 6.7 should be assigned as CaS.
Chapter 6 Influences of gaseous SO$_2$ and sulphate-bearing ash deposits

The last phenomena related to the unique formation of sulphide only on the tube T91 is also noteworthy. Thermodynamically, the rise on the contents of Cr and Ni in a tube depreciates the formation of molten slags. As evident in Figure 6.14, one can see a sharp decrease on the amount of total slag and even the fraction of Fe$_2$S$_3$ once the Cr content in the tube increases up to 10% that is close to T91. Interestingly, the fraction of FeS in the total slag is slightly increased from the Cr content of 10%. This to certain extent indicates that the sulphides found by XANES should be mainly referred to as FeS. However, the thermodynamic prediction fails to explain the absence of sulphide on the low-Cr tubes. This should be due to the diffusion control inhibiting the formation of sulphides inside a tube. From the gas diffusivity perspective, the top oxide, shown as Cr-O layer in Figure 6.10(a) is supposedly protective against gas diffusion [1]. However, for the low-Cr alloy 12Cr1MoVG, the shortage of Cr resulted in a porous and even partially damaged protective layer (as shown in Figure S1) that is in favour of all the gases including oxygen. This in turn creates an oxidizing environment that favours the over-growth of sulphate over sulphide. In contrast, for the highest Cr-tube austenite

Figure 6.14. Effect of Cr content in bulk tube on the formation of total melt and Fe sulphides, predicted by FactSage. Ash W1 was used as the ash deposit, 0.2% flue gas was assumed to take part in the reactions with tube surface.
tube SUS304, its Cr-rich, protective scale is too tenacious for any gas/molten species to permeate through (see Figure S1). The medium Cr-tube T91 studied here should fall in between these two extreme tubes, creating a porous layer and reducing environment to promote the formation of sulphides inside. Such a unique feature for 9Cr steel has also been noticed in the other studies on the permeation of C/CO$_2$ for the formation for carbide [34–36].

6.5 Implications of This Study

This study casts important implications on the high-temperature tube corrosion during the oxy-fuel combustion. For a short exposure time 50 h referring to as the initial stage of tube corrosion, the accelerated concentrations for SO$_2$ and steam in oxy-firing flue gas are clearly insignificant in terms of the penetration of S inside the tube, bearing a maximum 0.2% percentage to interact with ash deposit to promote the tube corrosion. The penetration rate of S inside a tube is broadly identical between air-firing and oxy-fuel combustion modes [37]. The content of S in ash deposit is more critical than bulk gas, acting as a carrier to transfer the gaseous SO$_2$ inside the tube for both sulphation and sulfidation of the inherent elements in the tube. For the original ash deposit bearing an S content larger than 10 wt.%, the formation of sulphate bearing melt is favoured on the surface of the commercial low-Cr tube, due to the thermodynamic inability of the formation of sulphide. A prior washing of coal to reduce the S content down to 1 wt.% in ash deposit is greatly beneficial on mitigating the tube corrosion. In particular, its combination with the use of medium-Cr tube such as T91 is able to mitigate the tube corrosion rate down to a level that is even lower than the pure flue gas. However, the selection of coal washing reagent is critical. Instead of using water, the use of acid to remove Ca is even beneficial in eliminating the formation of ductile, molten sulphide.

6.6 Conclusions

This study focused on the exposure test of a number of tubes with different Cr content and coated with lignite ash deposits in typical oxy-fuel combustion flue gas at 650 °C for 50 h. The ash deposits were derived from the combustion of a Xinjiang lignite and its water and acid washed coal samples. The corroded tubes as well as the fresh and used ash samples were characterized by conventional lab-based instruments and synchrotron XANES for the speciation of S and Cr. Thermodynamic equilibrium calculation was also carried out to interpret the experimentally observed phenomena. The major conclusions can be drawn as follows:
1. Both water-washing and acid-washing are effective in decreasing the contents of S and Na/Ca. Consequently, the tube corrosion rate was mitigated significantly for all the tubes tested. Upon the use of washed coal ashes, the tube corrosion rate was lower than the use of silica additive and even comparable to the pure flue gas.

2. The amount of S permeated inside tube is predominantly limited by the availability of the inherent sulphates in ash deposits. However, the participation of flue gas is essential for the tube corrosion. Based on thermodynamic equilibrium assessment, the contribution extent of flue gas is estimated to range from 0.2% to maximum 3.5%. The lignite ash deposit functions as a medium which transfers the S from bulk gas to tube surface, via the formation of intermediate sulphates or sulphide.

3. The formation of sulphide is highly dependent on both ash properties and the tube composition. The high-S ash from raw coal has no potential causing the formation of sulphide. For the low-S ash deposits, the content of free oxide is critical since they can assist in the transfer of S from bulk gas to solid ash on the tube surface. Compared to water washing, the use of acid is able to remove the water insoluble free oxide, and hence, eliminates the potential for the formation of sulphide.

4. The medium-Cr ferritic tube T91 is most readily sulphided than the other tubes from both the thermodynamic equilibrium and gas diffusion perspectives. Its Cr content is not high enough to fully avoid the formation of sulphide-bearing melts. Additionally, its protective layer is porous for the gases to permeate and to form a reducing environment to promote the formation of sulphide inside the tube.
10. H. Cabibil, Sulfur-Induced Corrosion at Metal and Oxide Surfaces and Interfaces, in, University of North Texas, 1997https://digital.library.unt.edu/ark:/67531/metadc277765/m1/74/.


41. P. Ampornrat, C. Bahn, G. Was, Corrosion and Stress Corrosion Cracking of Ferritic-


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Monash University

Declaration for Thesis Chapter 7

Declaration by candidate

In the case of Chapter 7, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (%) for student co-authors only</th>
</tr>
</thead>
<tbody>
<tr>
<td>Song Zhou</td>
<td>SXRF &amp; μ-XANES analysis</td>
<td>6 %</td>
</tr>
<tr>
<td>Facun Jiao</td>
<td>XRF analysis</td>
<td>4 %</td>
</tr>
<tr>
<td>David Paterson</td>
<td>SXRF &amp; μ-XANES analysis</td>
<td>External co-author</td>
</tr>
<tr>
<td>Dunxi Yu</td>
<td>Editing and feedback</td>
<td>External co-author</td>
</tr>
<tr>
<td>Yoshihiko Ninomiya</td>
<td>Comments for my work</td>
<td>External co-author</td>
</tr>
<tr>
<td>Barbara Etschmann</td>
<td>Editing and data processing</td>
<td>Supervisor</td>
</tr>
<tr>
<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

Candidate’s Signature

Date 01.02.2020

Main Supervisor’s Signature

Date 01.02.2020

*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
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CHAPTER 7

Spatial Distribution of Chromium on the Corroded Tube Surface Characterised by Synchrotron X-Ray Fluorescence (SXRF) Mapping and μ-XANES: Co-Existence of Ca-Rich Ash Deposits and Oxy-Firing Flue Gas
Chapter 6 aimed to clarify the roles of sulphur (S) in both lignite ash deposits and bulk flue gas on high-temperature tube corrosion during oxyfuel combustion. However, this study aims to explore the effects of lignite ash deposit, in particular the Ca-bearing species in ash on the tube corrosion under the oxy-firing mode. This chapter has been reformatted from the following published manuscript: I. Ja'baz, S. Zhou, L. Zhang, F. Jiao, D. Yu, B. Etschmann, Y. Ninomiya, and D. Paterson. *Spatial distribution of chromium on the corroded tube surface characterised by synchrotron X-ray fluorescence (SXRF) mapping and μ-XANES: Co-existence of Ca-rich ash deposits and oxy-firing\textit{ }flue gas* Fuel Processing Technology, 2018. (167): p.31-42.
Chapter 7 SXRF and μ-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

Abstract

This study aims to explore the effects of lignite ash deposit, in particular the Ca-bearing species in ash on the tube corrosion under the oxy-firing mode. Two tubes, low-alloy steel T23 and austenite SUS347 have been coated with two ash deposits and exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The ash deposits were collected from the combustion of a lignite mixed with and without silica additive in a 30MW pulverized coal-fired boiler. In this study, the roles of Ca-bearing species including sulphate, free oxide/calcite have been first time revealed by using synchrotron-based X-ray fluorescence (SXRF) and μ-XANES to detail the spatial distribution of individual elements, and in particular the speciation of Cr on the cross-section of tubes. Carburization of Cr by \( \text{CO}_2 \) is inhibited remarkably upon the co-existence of flue gas and ash deposit. However, the attack from the species in ash deposit other than sodium sulphate is more influential in accelerating the tube corrosion. Calcium sulphate is corrosive against the Cr-rich protective layer formed on the tube surface, resulting in the formation of Cr sulphide even in an exposure time of 50 h. Sulfidation of Cr by calcium sulphate is thermodynamically possible under the exposure conditions tested. Moreover, the free calcium oxide and even calcite in raw coal ash deposit are detrimental, accelerating the breakdown of the two tubes upon the formation of Ca chromite (\( \text{Cr}^{3+} \)) and even chromate (\( \text{Cr}^{6+} \)). The resultant chromite penetrated underneath the protective layer that is rich in Cr-rich oxide and Fe-Cr spinel, as well as merged intimately with ash deposits. The detrimental effect of free calcium oxide/calcite is more pronounced than calcium sulphate in the 50 h tested here. The use of silica additive to coal combustion immobilized the free Ca oxide, thereby forming an extra protective layer that minimized the oxidation of Cr. Consequently, the whole tube remained intact with little being damaged.

Keywords: synchrotron XRF, μ-XANES, Chromium, Lignite ash deposit, Calcium sulphate, Calcium oxide
7.1 Introduction

Oxy-fuel combustion is one of the promising carbon capture and storage (CCS) technologies that could be deployed to secure the sustainable use of coal in the carbon-constrained future [1]. High-temperature tube corrosion in the convective zone is one of the most critical issues that has been receiving increased attention [1–3]. Apart from the augmented concentrations of carbon dioxide (CO₂), steam (H₂O) and impure components including sulfuric oxide (SO₂) and hydrogen chloride (HCl) in the recirculated flue gas [1,4], properties of ash deposits in the convective section are also reportedly changed, which could in turn affect the tube corrosion. To date, knowledge is still sparse regarding the speciation on the corroded tube surface that is exposed to the ash-laden oxy-firing flue gas.

As summarized in our previous work [5], a wide variety of ashes, either collected from power generation stations or synthesized in the laboratory have been tested. In a typical bench-scale test, the tube is first loosely coated with ash powder or immersed into molten ash. Subsequently, it is exposed to an oxy-fuel flue gas at high temperatures for a duration of minimum 50 h. The corrosion of the tube is expressed as weight loss rate, or growth rate of the oxidation scale on the top surface. With regard to the chemistry underpinning the speciation of the corroded tube surface and its interaction with ash deposition, nearly all the studies relied on the use of bench-scale analytical facilities such as optical microscopy (OM), scanning electron microscopy (SEM), and X-ray diffraction (XRD), which are further supplemented by thermodynamic equilibrium calculation using commercial software such as FactSage. The drawback of these techniques is the inability to pinpoint and specify the oxidation states of the metals of interest on the oxide scale/interface that is usually on the sub-micron scale. Therefore, understanding is still incomplete with respect to the interaction between tube surface and ash deposit.

In this study we report the corrosion of two tubes, low-alloy steel T23 and austenite stainless steel SUS347 that are coated with two ash deposits collected from a 30 MWth pulverized-coal fired boiler burning lignite with and without the addition of silica additive. This is a continuation of our previous work on the properties of these two ash deposits and their effect on tube corrosion, based on the bulk analysis techniques. Dai et al. [6] for the first time reported the overall properties of ash deposits collected from the combustion of this lignite mixed with silica additive, in a 30MWth pulverized-fuel
boiler with sub-critical steam conditions. This work clarified the mechanism of inhibition of the slagging upon the addition of silica additive. The ash deposit-laden tubes are further exposed under the oxy-fuel flue gas that is similar to the compositions achieved from our pilot-scale testing on the oxy-fuel combustion of wet brown coal [7]. Synchrotron X-ray fluorescence (SXRF) microscopy and micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy were employed to capture the fine structures and details on the cross-section of the tubes at a resolution of 2 μm [8–10]. The spatial distribution of the chromium-bearing species was determined to reveal the interaction between tube metal (Cr) and the ash deposit, in particular the Ca-bearing species in the two ash deposits. To date, extensive studies have been conducted to understand the corrosive nature of alkali sulphates and their interaction with tube surfaces at high temperatures [11] as well as, Jiao et al. [17] addressed the potential formation of toxic Cr (VI) and the variation of the quantities of Cr (III)-bearing species with flue gas composition. Whereas, Low et al. [20] examined the emission, and characterization of twelve trace elements (As, Ba, Be, Co, Cr, Cu, Mn, Ni, Pb, Sr, V, and Zn) in the ash deposits from diverse sections of an industrial pulverized lignite-fired boiler and in the flue gas. Understanding the roles of calcium-bearing species such as sulphate and free oxide is still far from complete. This will be focused on in depth in this study.

### 7.2 Experimental

#### 7.2.1 Tube Corrosion Conditions

The tube exposure was conducted in a horizontal furnace that was fixed at 650 °C for a duration of 50 h. The flue gas flow rate is fixed at 300 ml/min. The flat tube specimen, 3 cm × 3 cm × 2 mm, were prepared by a wire-electrical discharge machine to cut the cross-sections of two commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. Fly ash powder of around 100 mg per tube sample was spread uniformly over the tube surface to mimic ash deposition on a real steam specimen surface, yielding of around 11mg per cm² that is similar to the other studies [12]. The ash coating was achieved by putting the ash powders into a plastic mould that is the same size as the tube specimen. The ash powder was also gently pressed by hand to ensure that there is no loss during the test. The oxy-fuel flue gas tested is made of 4.0 vol% O₂, 3000 ppm SO₂, 1000 ppm HCl, 30 vol% H₂O, 10 vol% N₂, and the rest is CO₂. The pressure for flue gas is 1 bar. Such a flue gas composition was confirmed in our pilot-scale test on the oxy-fuel...
combustion of a local Victorian brown coal [7]. The details for experimental conditions and sample preparation are given elsewhere [11,13].

Two tubes were tested, low-alloy steel T23 (2.25 wt.% Cr) and austenite stainless steel SUS347 (17–19 wt.% Cr). The remaining elements in the two tubes include C (0.04–0.1 in T23 vs 0.08 in SUS347), Mn (0.1–0.6 in T23 vs 2.0 in SUS347), Si (0.5 in T23 vs 1.0 in SUS347), Mo (0.05–0.3 in T23), V (0.2–0.3 in T23), W (1.45–1.75 in T23), Nb (0.02–0.8 in T23 vs 10 in SUS347), Al (0.03 in T23) and Ni (9–13 in SUS347). All these values are expressed as weight percentage. The former tube is the material which is being used generally in a pc-fired boiler, whereas the use of the latter one is expected to address if the use of high-Cr tube (as well as high in Ni/Nb) is essential in the oxy-fuel combustion mode. After the corrosion test, tube specimen was quickly mounted and solidified in epoxy resin to avoid surface oxidation. Subsequently, the sample was halved by a disc-cutter. The resulting cross-sectional surface was finally polished by SiC paper with 2400 grit.

Table 7.1 Properties of the two ashes tested in this study, copy right from our previous work published in Fuel, Elsevier [11].

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Na2O</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>P2O5</th>
<th>SO3</th>
<th>K2O</th>
<th>CaO</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>XJ</td>
<td>10.4</td>
<td>12.46</td>
<td>8.27</td>
<td>16.24</td>
<td>0.45</td>
<td>12.53</td>
<td>0.45</td>
<td>38.82</td>
<td>0.38</td>
</tr>
<tr>
<td>XJ_S</td>
<td>6.62</td>
<td>9.1</td>
<td>12.11</td>
<td>34.83</td>
<td>0.27</td>
<td>7.9</td>
<td>0.87</td>
<td>24.55</td>
<td>3.75</td>
</tr>
</tbody>
</table>

7.2.2 Ash Deposit Properties

These two ash samples were collected from the convective super-heater surface in a 30 MWth pulverized-coal fired boiler burning a Chinese lignite, the same as the ash samples tested in our previous work [6]. The two samples were labelled XJ and XJ_S for the ash deposit derived from raw coal and coal mixed with silica additive, respectively. The elemental compositions of the two ash samples are shown in Table7.1. Upon the addition of silica, the content of Na, Ca and S are decreased remarkably. This should be due to the immobilization and even dilution of these elements particularly Na by the silica additive. As further evident in Table 7.2 for the quantified XRD results (original patterns are shown in the supporting information Figure S1), the contents of Na-bearing sulphates are reduced considerably upon the use of silica additive. So are the free oxides which are mostly captured by silica into amorphous species [6].
Chapter 7 SXRF and μ-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

7.2.3 SXRF and μ-XANES Analysis

SXRF and μ-XANES analysis were conducted at the XFM beamline, Australian Synchrotron. SXRF maps were collected at 15.8 keV with a Si (111) monochromator and an energy resolution (ΔE/E) of 2 × 10⁻⁴ and the Maia detector [14]. The Kirkpatrick-Baez (KB) mirrors were used to focus the beam down to ~1.5 μm [2,9,10]. For each tube cross-section, an overview map with areas ranging from 2.8 x 3.4 to 2.8 x 7.6 cm² were mapped using a pixel size of 100–200 μm² and a dwell time of 10 to 25 ms per pixel. Detailed maps were then collected over ~2 x 0.4 cm² area using 2 μm² pixels and a dwell time of 0.4 ms per pixel. XANES stacks were generated by collecting SXRF images (~0.2 x 0.4 cm², 4 μm² pixels, and dwell times of 1 to 4 ms/pixel) at 77 monochromators energies spanning 100 eV across the Cr K-edge. Cr metal foil and a pellet of chromium oxide (Cr₂O₃) diluted in boron nitride were used to determine the energy shift for XANES analyses. SXRF data were analyzed using the Dynamic Analysis (DA) method in GeoPIXE II [14]. The DA approach fits multiple lines per element that separates overlaps and subtracts background, escape peaks and other detector artefacts. Note that, the light elements including C, Na and O cannot be detected by the Maia. The extracted XANES spectra were processed in ATHENA. Linear combination fitting (LCF) was used to qualitatively determine the mineral compositions, by using a variety of standards including pure Cr metal, oxide (Cr₂O₃), carbide (Cr₂S₃), hydroxide (Cr (OH)₃), chloride (CrCl₃), sulphide (Cr₂S₃), chromates (MgCr₂O₄, CaCr₂O₄, FeCr₂O₄) and Ca chromite (CaCrO₄). The spectra for these standards are included in the Figure S2. Note that, the spectra for chromium carbide (Cr₃C₂) [15] and chromium sulphide (Cr₂S₃) [16] were cited elsewhere, whereas spectra for the other standards were collected from our previous studies [17–20].

Regarding the accuracy of the analysis by SXRF and μ-XANES, the complete analysis of all measured quantities by SXRF based on GeoPIXE II and the relevant Maia detector has been conducted by measuring a number of standard metal foils such as Mn and Pt. The spectral fitting was further conducted based on the dynamic analysis (DA) method, which yields a relatively accurate quantification capacity. Concentrations of individual elements (up to 52 elements) were calibrated by using the known Fe concentration of the various tubes as an internal standard [21,22]. Regarding the accuracy of μ-XANES and the relevant LCF method, our previous work based on the analysis of pure oxide mixtures [19] have proven a relative standard deviation of around 10% for this method.
7.2.4 Thermodynamic Equilibrium Calculations

The commercial thermodynamic equilibrium program, FactSage [23] was used to calculate and establish the FeO–Cr₂O₃–CaO phase diagrams under the tube exposure conditions, 650 °C and a total pressure of 1 bar for the flue gas. Apart from the pure substances, the built-in database for spinel species and slag in FactSage was also included in the calculation. In addition, the Gibbs function for the solid-state reactions were calculated by the ‘Reaction Equations' module in HSC Chemistry.

7.3 Experimental and Synchrotron Analytical Results

7.3.1 Tube Mass Loss Results

Mass losses for the two tubes are first reported in Table 7.3, which is supplementary to the oxide scale growth rate reported previously [11]. For T23 that is a common tube used in the pc-fired boiler, shifting the combustion mode to oxy-firing accelerated its mass loss for both ash deposits, due to the co-existence of highly concentrated and corrosive steam, SO₂ and HCl in the oxy-firing flue gas.

Table 7.2 Chemical compositions of the two ash deposits, copy right from our previous work published in Fuel, Elsevier [11]

<table>
<thead>
<tr>
<th></th>
<th>XJ</th>
<th>XJ_S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anhydrite (CaSO₄)</td>
<td>2.2</td>
<td>3.1</td>
</tr>
<tr>
<td>Glauberite (Na₂Ca (SO₄)₂)</td>
<td>3.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Thenardite (Na₂SO₄)</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>Marialite (Na₃SO₄ 10H₂O)</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>Periclase (MgO)</td>
<td>3.4</td>
<td>1</td>
</tr>
<tr>
<td>Lime (CaO)</td>
<td>3.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>3.1</td>
<td>1</td>
</tr>
<tr>
<td>Periclase (MgO)</td>
<td>3.4</td>
<td>1</td>
</tr>
<tr>
<td>Magnete (Fe₃O₄)</td>
<td>0</td>
<td>0.8</td>
</tr>
<tr>
<td>Quartz (SiO₂)</td>
<td>0</td>
<td>2.2</td>
</tr>
<tr>
<td>Ketatite (SiO₂)</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Gehlenite (Ca₂(Al(Si,Al)₂O₇)</td>
<td>3.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Merwinitite (Ca₃Mg (SiO₄)₂</td>
<td>3.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Amorphous amount</td>
<td>70</td>
<td>82</td>
</tr>
</tbody>
</table>
However, the use of silica additive is effective, reducing the mass loss by more than half in both flue gases. Similar results were confirmed for the high-Cr austenite tube SUS347. Clearly, the reduction of sulphates and free oxide in the ash deposit is of benefit to the mitigation of tube corrosion, as expected. By comparing with the case of no ash deposition on tube surface, it is clear that the coexistence of XJ ash deposit and flue gas accelerated the tube mass loss, irrespective of the combustion mode. Instead, the existence of XJ_S ash deposit provides a shield to mitigate the tube mass loss to a level that is considerably lower than that caused by flue gas exposure only, in particular under the oxy-fuel flue gas. Obviously, the evaporation of tube metals upon the attack of corrosive gases including HCl, steam and/or SO\textsubscript{2} is mitigated upon the use of silica additive. This will be further explained by the detailed speciation analysis in the following sections.

Table 7.3 Mass loss (mg/cm\textsuperscript{2}) of the two tubes T23 and SUS347 tested in this study

<table>
<thead>
<tr>
<th></th>
<th>Air-firing</th>
<th>Oxy-firing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no ash</td>
<td>XJ</td>
</tr>
<tr>
<td>T23</td>
<td>31.5</td>
<td>25.5</td>
</tr>
<tr>
<td>SUS347</td>
<td>20.7</td>
<td>17.0</td>
</tr>
</tbody>
</table>

7.3.2 Cross-Section of T23 Coated with XJ Ash Deposit

Figure 7.1 illustrates the SXRF maps for individual elements on the cross section of T23 coated with XJ ash deposit. The concentration distribution of individual elements is represented qualitatively by colour scale, in which black and white refer to the minimum and maximum concentration of an element, respectively. The Fe map clearly shows the breakdown of tube T23 upon XJ ash deposition. As amplified on the very left side of Figure 7.1, a multi-layered interface was formed between the bulk tube and ash deposit. The top layer that is adhered to bulk tube is in red, indicating the outward diffusion and subsequent oxidation of Fe by the bulk flue gas on the tube surface. By looking at the maps for the other elements, it is further evident that Cr is the second most abundant on this protective layer, which should for an oxide layer to resist against the inward diffusion of corrosive gases. Next to the top layer is a thicker, spalled layer which even bulked and fragmented into thinner, smaller scales that are also highly curled. Such a layer is also rich in Co, suggestive of the non-protective role of this inherent metal in the tube. Moreover, the spalled scale is in close contact with the most abundant element Ca in ash deposit, as evident by the Ca map. Signal for the last two elements S and Cl is rather weak, it is thus unclear if they are associated with any inherent metals in the original tube.
Figure 7.1 SXRF mapping for the major elements across the cross-section of tube T23 coated with XJ raw coal ash deposit. Concentrations listed are the maximum concentrations.

Efforts were made to zoom in and reveal the details of both the top/adherent layer marked as rectangle 1 and the spalled scale marked as rectangle 2 in Figure 7.1. Moreover, the spatial distribution of Cr-bearing species was mapped by XANES Cr K-edge on the two selected areas. As demonstrated in Figure 7.2, the top layer is around 20 μm in thickness, which is dominated by both Cr and V, proving the strong protective effect of these two additives in the bulk tube. Ti is rarely spotted, due to its extremely low concentration in the tube. Moreover, S was detected with a relatively strong signal on the Cr/V-dominating interface, proving an inward diffusion of this element inside the tube. It may be derived from SO₂ in flue gas or sulphates in the ash deposit. With respect to Ca from the ash deposit, its presence on the top layer should be much lower but not negligible, as evident by the scattered spots that coexist with Cr and V in the interface. This implies some probable association of Ca and Cr/V.

The XANES energy distribution of Cr, as shown on the right-hand side of Figure 7.2, suggests the predominance of the species that has the dominant peak located at the energy of 6.009 keV, as is the case for oxide (Cr₂O₃) and spinels from MgCr₂O₄ through to CaCrO₄ [17–20]. In contrast, the low intensity at 5.992 keV suggests that there is little to no pre-edge thus there should be little Cr carbide
and/or Cr-metal. This is further evident in Figure 7.3 that shows the XANES speciation of the points of interest. As can be seen, point No 1 located deep inside the bulk tube is dominated by pure metal and carbide, the oxide/spinel is rare. The formation of carbide is due to the carburization effect of CO\textsubscript{2} in the flue gas [5,24]. However, such a species was not detected in the orange-yellow interface. Instead, Cr in the interface is dominated by Fe-Cr spinel, the concentration of which even increases stably with the rise in the number of the points analyzed from No 2 (for the bottom of the interface) to No 7 referring to the top of the interface. This echoes the preferential oxidation of these two elements upon the exposure to flue gas that consists of a number of oxidizing components, including O\textsubscript{2}, H\textsubscript{2}O, and CO\textsubscript{2}. More interestingly, the Ca-Cr spinel was also found for the spots No 5–7 located on the very top layer that is in blue. Such a layer is in close contact with the ash deposit and thus has the opportunity to interact. Clearly, Ca in the XJ ash deposit is highly reactive and has the capability to react with Cr oxide. Cr-Sulphide/sulphate was not detected, and hence, it is assumed that the S in Figure 7.2 should be mainly associated with V and/or Ca.

Figure 7.2 SXRF maps of the selected area rectangle 1 in Figure 7.1 and the Cr K-edge distribution across the whole cross-section of tube T23 coated with XJ raw coal ash deposit.
Figure 7.4 shows the amplified map for the rectangle No 2 labelled in Figure 7.1. Due to the multi-layered scaling nature of this area, three small sub areas were further amplified and analyzed. For the sub-area 2–1 located in the middle of the multi-layered scale, the amplified SXRF map demonstrates the abundance of Cr, S and Ca. Interestingly, these three elements are split in between a narrow strip that is about 10–20 μm in width and a large lump. For Cr in the narrow strip in red, it is in a close contact but does not overlap with the strip rich in Ca and S, as indicated by the straight dashed reference line. For the remaining Cr in a form of curled thin scale, it is partially merged into the large lump dominated by Ca and S. The close association of Ca and S in both strip and lump is indicative of gypsum/anhydrite in the original fly ash. The merging of Ca/S and Cr is more evident for the sub-area No 2–2 shown on the right-hand side of Figure 7.4. The sub-area No 2–2 refers to a spalled narrow scale of 20–30 μm in width, which is dominated by both Cr and V. It has been fully merged into the large ash lump. This should be caused by counter current diffusion of ash and the inherent metals Cr and V upon their interaction in the tube-ash interface.

Figure 7.5 shows the XANES K-edge spectra for a number of points on the tube scales, with the quantified results for Cr speciation. The results further confirmed the existence of a Ca-Cr spinel across all the scales. Apart from CaCr₂O₄ in which Cr is trivalent, the hexavalent Cr⁶⁺ as a form of CaCrO₄ was also observed in the spots No 1, 3, 6 and 10. The total contents of these two Ca-Cr spinels are also much higher than the Fe-Cr spinel, demonstrating a high mixing of ash with the spalled tube scales. The presence of hexavalent Cr⁶⁺ also indicates a deep oxidation of Cr upon its mixing with the XJ ash deposit.
Chapter 7 SXRF and μ-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

Figure 7.3 Cr K-edge XANES spectra for various points on the selected area No 1 in Figure 7.7
Figure 7.4 SXRF maps for the selected area No 2 in Figure 7.1

(Cr 0.123%, V 192 ppm, Ti 599 ppm, S 1.23%, Ca 0.654%)
Figure 7.5 Cr K-edge XANES spectra for various points on the selected area No 2_3 in Figure 7.4
7.3.3 Cross-Section of SUS347 Coated with XJ Ash Deposit

SXRF mapping for the SUS347 coated with the XJ ash deposit is illustrated in Figure 7.6. Surprisingly, this high-Cr austenite tube was also severely corroded by the XJ ash, with the formation and detachment of a thick scale that is rich in Fe, Mn and even Co. This scale is also in close contact and even partially mixed with the ash deposit that is represented by the Ca map. In addition, similar to the low-Cr tube T23 in Figure 7.1, Cr forms a protective layer that is still adhered to the tube top surface, with only a few areas such as No 2 in the spalled scale.

Figure 7.6 SXRF maps of the major elements across the cross-section of tube SUS347 coated with XJ ash deposit

XANES speciation for Cr on the adherent/top layer, No 1 and the spalled fragment No 2 on Figure 7.6 was conducted, and the results are shown in Figures 7.7 and 7.8, respectively. With respect to the top adherent layer in Figure 7.7, Fe-Cr spinel is dominant across the whole cross-section the same as for the top layer of T23 in Figure 7.3. This species should be formed by the interaction between oxides of Fe and Cr upon the exposure to the oxidizing flue gases, exerting a protective role against the inward diffusion of corrosive components inside the tube. In addition, the Ca-Cr spinels including
chromite (Cr\(^{3+}\)) and chromate (Cr\(^{6+}\)) were observed with considerable fractions. In particular, the former species was even detected for the spots No 1–3 that are underneath the oxide layer. This is the evidence for the penetration of Ca inside the tube, through the oxide layer. Chromate for the presence of hexavalent Cr\(^{6+}\) was observed on the oxide layer (spots No 5–6) and its outer surface, No 7. Clearly, excessive oxygen is present inside the oxide layer and of benefit to the local oxidation of trivalent Cr\(^{3+}\).

The association of Ca-Cr is more obvious in the spalled scale (still dominated by Fe-Cr spinel) demonstrated in Figure 7.8. Regarding Ca chromite hosted by Cr\(^{3+}\), its fraction is relatively constant across the points from No 1 through to No 10, except the point No 11 which is in light blue for a low Cr concentration but possesses a highest fraction for Ca chromite. Ca chromate was detected in the spots from No 2 through to No 9, bearing a noticeable fraction. Moreover, the unreacted Cr metal was detected in No 5–7, suggestive of a simultaneous breakdown of the unreacted tube with the oxide/spinels.
Figure 7.7 SXRF map and Cr K-edge XANES analysis for the area of interest No 1 in Figure 7.6.
Figure 7.8 SXRF map and Cr K-edge XANES analysis for the area of interest No 2 in Figure 7.6.
7.3.4 Cross-Section of Tubes T23 and SUS347 Coated With XJ_S Ash Deposit

Figure 7.9 illustrates the SXRF maps for individual elements on the tube T23 coated with XJ_S ash deposit. Clearly, this tube remains intact, with a very thin layer formed on its top surface. Such a layer is rich in Cr and Mn due to their preferential oxidation to protect the bulk Fe. It is also in contact with the ash deposit that is dominated by Ca. The signal for S and Cl is discernible on the tube-ash interface. This is confirmed by the XANES point analysis for Cr in Figure 7.10. Irrespective of the point location, the fraction of sulphide is non-negligible. However, such a species was not found in the case of T23 coated with XJ ash deposit. The Ca-Cr spinel was not found either. Instead, the unreacted Cr metal is predominant across the whole interface, which is accompanied by carbide and a small amount of Fe-Cr spinel. The non-corrosive nature of the XJ_S ash deposit was further evident for the austenite tube SUS347. As demonstrated in Figure 7.11, the whole tube (represented by Fe here) remains intact, with an extremely thin layer formed upon the contact with ash deposit. Cr is enriched in the interface, with the pure metal being dominant across the whole interface. Clearly, the use of silica additive during coal combustion is of benefit to mitigate the tube corrosion.

![Figure 7.9 SXRF maps of the major elements across the cross-section of tube T23 coated with XJ_S ash deposit](image-url)
Figure 7.10 Cr K-edge XANES spectra for various points on the cross-section of T23 tube coated with XJ_S ash deposit in Figure 7.9
Chapter 7 SXRF and μ-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

Figure 7.11 SXRF map and Cr K-edge XANES analysis for the tube SUS347 coated with XJ_S ash
7.4 Discussion on Ca-Induced Corrosion Mechanisms

Compared to the XJ_S ash deposit generated from the combustion of coal added with silica additive, the raw coal ash deposit, namely XJ ash in this study is clearly highly corrosive, as evident in Table 7.3 and Figures 7.1–7.8. The higher content of sodium, in particular the high content of sodium sulphate should be one of the major causes [11,13]. The S map in Figure 7.2 for the tube T23 coated with XJ raw coal ash deposit is most likely attributable to sodium sulphate, since the Ca map was not associated with S. As further evident in Tables 7.1 and 7.2, the total Na in XJ ash accounts for 10.4 wt.%, relative to only 6.62 wt.% in its counterpart XJ_S ash deposit. In particular, sodium sulphates, namely thenardite and marialite were reduced from 6.5 wt.% to 1.9 wt.% upon the combustion of coal mixed with silica additive. This in turn reduced the probability for the formation of molten Na-Fe sulphates that proves to be a major trigger for the tube breakdown. To date, the mechanisms underpinning the formation of Na-Fe sulphates has been studied extensively.

Calcium sulphate has also been confirmed to be corrosive for the tubes exposed under the conditions that are typically encountered in the fluidized bed combustor, i.e. 650–950 °C in the air-fired flue gas [25,26]. At the flue gas temperatures of 800–950 °C [25], chromium sulphide was found to be formed underneath the protective Cr-rich layer on the top surfaces of Fe-20Cr and Fe-25Cr, accounting for the breakaway of the tubes. Additionally, a layer for finely mixed Cr$_2$O$_3$ and CaO was formed on the Cr-rich top layer, which was interpreted as CaCr$_2$O$_4$, but is yet to be confirmed directly [25]. For another tube corrosion test using 1018 plain carbon steel and at 650 °C that is exactly the same as this study [26], calcium sulphate was found to be protective against flue gas corrosion in the first 50 h, which however turns corrosive after 50 h, by attacking iron metal to form the resultant iron sulphide according to the reaction Eq. (7.1) below:

$$4Fe + CaSO_4 \rightarrow 3FeO + CaO + FeS$$

*Eq (7.1)*

The results observed for the formation of a Ca-Cr spinel in this study, under the exposure time of 50 h have not been found before. Although the exposure time is short, the deteriorating effect of Ca-bearing species is obviously profound, as demonstrated by the mixing of Ca, S, Cr and V in the spalled scale for the tube T23 coated with XJ ash in Figure 7.4. Even for the ash deposit XJ_S, its coating
on T23 caused the penetration of sulphur as a form of chromium sulphide inside the protective Fe-Cr spinel layer on the tube top surface, as demonstrated in Figure 7.10. The amplified view of such a layer, as visualized as RGB (Cr – red, S – green and Ca – blue) maps in Figure 7.12, further proves the association of Cr–S, Ca-S and Ca-Cr (see the dashed ovals) in the ash layer that stays above the protective layer. Clearly, it should be formed by the interaction between calcium sulphate and Cr/Cr$_2$O$_3$ on the tube-ash interface where Cr prefers to diffuse outwards to mix with and even merge into the ash deposit.

The formation of chromium sulphide is also thermodynamically possible at 650 °C, which even bears the largest potential in terms of the standard Gibbs free energy among all the probable reactions between Cr metal and calcium sulphate. This is evident in Figure 7.13, where the Gibbs free energy for the above reaction (8.1) was also included for comparison. Irrespective of the metallic type, the
formation of sulphide is more thermodynamically favoured than its counterpart sulphate. This explains the absence of Cr sulphate in all the Cr XANES spectra. Moreover, from the reaction kinetic perspective, the formation of chromium sulphide should be rather slow, as indicated by its extremely low molar fraction of the total chromium in Figure 7.7. Since sulphide was not detected for the high-Cr austenite tube SUS347, it is also inferable that the solid-state reaction equation (3) in Figure 7.13 should be controlled by the outward diffusion rate of Cr metal through the protective layer that is rich in Cr-Fe spinel. The Cr-rich layer should be denser for the tube SUS347, and hence, completely inhibit the reaction (3). Even for the spalled scale that is fully mixed with calcium sulphate, as evident in Figure 7.4, Cr sulphide was not detected either (see Figure 7.5), suggestive of the more likely occurrence of the other reactions over the sulfidation of Cr. In light of this, the existence of calcium sulphate in ash deposits not critical, at least less critical than sodium sulphate for the corrosion of both tubes in 50 h. Otherwise, the XJ_S ash deposit rich in calcium sulphate (see Table 7.2) should be more corrosive.

The other predominant Ca-bearing species such as free oxide in ash deposit should be more critical in affecting the speciation of Cr, accounting for the Ca-Cr spinels including both Ca chromite and chromate found in Figures 7.3, 7.5, 7.7 and 7.8 for the two tubes coated with XJ ash deposit rich in free Ca oxide. The Ca-Cr spinels were formed as a dominant Cr bearing species in the spalled pieces that are fully mixed with fly ash (Figures 7.5 and 7.8), and even on the top protective layer that is adherent to bulk tube and dominated by a Fe-Cr spinel (Figures 7.3 and 7.7). These spinels should be formed between the reaction between Ca oxide and Cr oxide that was formed upon the oxidation of Cr. Moreover, Ca in free oxide should be more competitive against Fe oxide (from the bulk tube) once it has a good contact with the tube surface, as is evident by the preferential formation of a Ca-Cr spinel on the tube SUS347 coated with XJ_S ash. This phenomenon was supported by the thermodynamic equilibrium phase diagram for CaO-FeO-Cr$_2$O$_3$ at 650 °C in Figure 7.14. Due to the fact that chromate is not included in the database of FactSage, prediction for the Ca chromate is unavailable here. However, the fraction of this species is very small, and hence, its lack in the database should be insignificant in interpreting the results here. The elemental compositions were also included in Figure 7.14 for the points analyzed in Figures 7.3 and 7.7 for the adherent surfaces, and Figures 7.5 and 7.8 for the spalled scales of the two tubes. Note that, the elemental compositions were conducted by the SXRF, and concentrations of the three elements, Fe, Ca and Cr were normalized in their most stable oxide form. As demonstrated in Figure 7.14, the top layers that are still adhered firmly to the two tubes fall into the zone No 1 for the co-existence of A Spinel referring to Fe chromite...
in FactSage, metallic Fe and calcium ferrite. This is in agreement with Figures 7.3 and 7.7, further proving the preferential interaction between the oxides of Cr and Fe and the protective role of the resultant Fe-Cr spinel against the tube corrosion. In contrast, for the spalled scales that is rich Ca, the points analyzed either fall into zone No 4 for T23 or zone No 2 for tube SUS347. For both zones, the formation of Ca chromite is favoured. This explains the abundance of this species as detected by XANES in Figures 7.5 and 7.8.

The Ca chromite formed should be detrimental and accelerated the corrosion of both tubes considerably. As evident in Figure 7.3, this species should be initially formed upon the contact between free oxide in the ash deposit and the oxide layer adhered on the bulk tube surface. However, the resultant Ca chromite deteriorated the crystal structure of Cr rich oxide and/or Cr-Fe spinel, resulting into the fragmentation of the protective layer, and consequently, break-down of the tube surface. The resultant fragments even merged into the ash deposit intimately, as evident in Figures 7.4 and 7.8. Moreover, the presence of Ca chromite underneath the top oxide layer, as evident in Figure 7.7 for SUS347 further implies that this species also penetrated deep down inside the tube. Although the reason for this is unclear, it is very likely that this species might be present in a molten phase, which can thus easily flow inter-granularly in the ash-tube interface layer. It then further broke the tubes from inside, causing a compressional stress to detach and buckle off the top layer, even for the high-Cr austenite tube SUS347. In this sense, the free calcium oxide in XJ ash deposit is comparably corrosive with sodium sulphate. Upon the use of silica additive during coal combustion, this species was reduced significantly in the ash deposit, as evident in Table 7.2. Moreover, the free oxide should be fixed by silica into an amorphous species, which forms a protective layer on the tube surface against the attack of flue gas, in particular, attack from CO₂ resulting in the formation of ductile carbide underneath the protective layer. Therefore, the two tubes remained intact, and less of Cr was oxidized as well, as demonstrated by the presence of unreacted Cr metal in Figures 7.10 and 7.12.

Finally, the formation of Ca chromate (Cr⁶⁺) in the spalled layer of tube T23 (Figure 7.5) and even the top surface of tube SUS347 (Figure 7.7) is intriguing. Its fraction is non-negligible. Such a species should be formed from reaction between oxides under the aid of bulk oxygen from the flue gas, as shown in Eq. (7.5) below.
Chapter 7 SXRF and \( \mu \)-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

\[
Cr_2O_3 + 2CaO + 1.5 \ O_2 \rightarrow 2CaO\text{Cr}O_4 \quad Eq. (7.5)
\]

In this reaction, alkali and alkaline earth metal oxide functions as the catalyst promoting the oxygen activation and shuffling from bulk gas to metals, as proven by the studies on model compounds in our previous work [19]. Interestingly, although the exposure temperature here is lower than the optimum temperature (800 °C) for the formation of Cr\(^{6+}\) as confirmed in pure air [19], the fraction of Ca chromate found on the tube surface is non-negligible. This hints at the promoting influence of other gas components such as steam and even HCl in the flue gas. Potassium chloride in biomass-derived ash deposit has proven to promote the formation of potassium chromate at the temperatures up to 700 °C [27]. Nevertheless, the resultant Ca chromate should also be easy to break down, as suggested by the small discrete fragments spalled from the tube SUS347 coated with XJ_S ash deposit in Figure 7.12. However, as its fraction is much lower than the chromite counterpart, the detrimental influence of Ca chromate is insignificant under the exposure conditions studied here.

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**Figure 7.13** Delta G function values for the four probable reactions between Cr/Fe metal and calcium sulphate at 650°C

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Figure 7.14 CaO-FeO-Cr2O3 phase diagram generated by FactSage. The reaction temperature is 650°C.
7.5 Conclusions

Synchrotron-based X-ray fluorescence and μ-XANES were used to detail the spatial distribution of individual elements, and the speciation of Cr on the cross-section of various tubes that had been coated with two ash deposits and exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The ash deposits were collected from the combustion of a lignite mixed with and without silica additive. The major conclusions can be drawn as follows:

1. Upon the co-existence of flue gas and Ca-rich ash deposit, the carburization of Cr by the abundant CO$_2$ in oxy-fuel flue gas is inhibited remarkably. However, the attack from the species in ash deposit other than sodium sulphate is more influential in accelerating the tube corrosion.
2. Calcium sulphate is corrosive against the Cr-rich protective layer formed on the tube surface, resulting in the formation of Cr sulphide even in an exposure time of 50 h. Sulphidation of Cr by calcium sulphate is thermodynamically possible under the exposure conditions tested.
3. The free calcium oxide is detrimental, accelerating the breakdown of the two tubes upon the formation of chromite and even chromate. The resultant chromite even penetrated underneath the protective layer that is rich in Cr-rich oxide and a Fe-Cr spinel, as well as merged intimately with ash deposits.
4. The detrimental effect of free calcium oxide/calcite is more pronounced than calcium sulphate. The use of silica additive immobilized the former Ca-bearing compounds remarkably, thereby forming an extra protective layer that even minimized the oxidation of Cr. Consequently, the whole tube remained intact.
Chapter 7 SXRF and μ-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

References


23. FactSage, website http://www.crct.polymtl.ca/factsage/FactSage_Applications/.
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Monash University

Declaration for Thesis Chapter 8

Declaration by candidate

In the case of Chapter 8, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
</tr>
</tbody>
</table>

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

<table>
<thead>
<tr>
<th>Name</th>
<th>Nature of contribution</th>
<th>Extent of contribution (% ) for student co-authors only</th>
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<tbody>
<tr>
<td>Song Zhou</td>
<td>SXRF &amp; μ-XANES analysis</td>
<td>10%</td>
</tr>
<tr>
<td>David Paterson</td>
<td>SXRF &amp; μ-XANES analysis</td>
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<td>Yoshihiko Ninomiya</td>
<td>Comments on my work</td>
<td>External co-author</td>
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<tr>
<td>Barbara Estchmann</td>
<td>Editing and data processing</td>
<td>Supervisor</td>
</tr>
<tr>
<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

<table>
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<th>Candidate’s Signature</th>
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<th>Main Supervisor’s Signature</th>
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*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
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CHAPTER 8

Spatial Distribution of Cr-Bearing Species on the Corroded Tube Surface Characterised by Synchrotron X-Ray Fluorescence (SXRF) Mapping and μ-XANES: Exposure of Tubes in Oxy-Firing Flue Gas
In chapter 7 we studied the effects of lignite ash deposit, in particular the Ca-bearing species in ash on the tube corrosion under the oxy-firing mode. However, this study, Synchrotron X-ray fluorescence mapping and μ-XANES were employed to characterize the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that were exposed to oxy-fuel flue gas only. This chapter has been reformatted from the following published manuscript: "I. Ja’baz, S. Zhou, B. Estchmann, D. Paterson, Y. Ninomiya, and L. Zhang. Spatial distribution of Cr-bearing species on the corroded tube surface characterised by synchrotron X-ray fluorescence (SXRF) mapping and micro-XANES: exposure of tubes in oxy-firing flue gas" Journal of Materials Science, 53(16): p.11791-11812.
Abstract

Synchrotron X-ray fluorescence mapping and micro-XANES were employed to characterize the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that were exposed to oxy-fuel flue gas at 650 °C, 1 bar for 50 h. The gas composition tested is close to the flue gas produced fromoxy-firing of low-rank coal in pilot-scale tests. Multi-layered scales with an uneven distribution were observed for individual elements on both the top surface and spalled layer of carbon steel SS400. Oxidation is the major reaction causing the scaling of the tube, whereas the other reactions such as sulphidation and chlorination led to the buckling of tube surface. The use of Cr, even at a low concentration of 1.2 wt. % in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion rate, as well as minimize the difference between oxy-fuel and air-firing flue gases on the tube mass loss rate. The CO$_2$ cycle with the involvement of oxidation (mainly of iron) and carburization (of chromium) took place simultaneously for the Cr-bearing alloy, even under the coexistence of CO$_2$ and a number of oxidizers in the flue gas tested here. The fast diffusion of CO$_2$ and its derivatives facilitated a preferential occurrence of carburization under the oxide scale. However, upon the closure of gas passage channels in the oxide scale of a high-Cr tube such as austenite SUS304, the reductants CO and carbon can flow back to tube top surface, causing the formation of carbide on the most outer scale that further fragments into fugitive pieces. Carburization is also the major cause of corrosion of high-Cr tubes. In contrast, for a tube with medium Cr content, such as high-chrome T91 tube with 9 wt. % Cr, it undergoes both oxidation and carburization successively on the metal/oxide interface. The gas passage channels mostly remain open, and hence, the resultant carbide and carbon precipitate penetrated deep inside the tube.
8.1 Introduction

Oxy-fuel combustion process is one of the most promising low-emission clean coal technologies that could be deployed to secure the sustainable use of coal in the carbon-constrained future [1]. High-temperature tube corrosion in boiler zone is one of the most critical issues of concern in the operation of coal-fired plants [2]. Compared to the conventional air-firing combustion where nitrogen is abundant, oxy-fuel combustion brings in augmented concentrations of carbon dioxide (CO\textsubscript{2}), steam (H\textsubscript{2}O) and impure components including sulphuric oxide (SO\textsubscript{2}) and even hydrogen chloride (HCl), due to the recirculation of wet, dirty flue gas back into the furnace [1, 3]. All these components have been reported to enhance the tube corrosion rate considerably.

Since CO\textsubscript{2} is most abundant in the oxy-fuel flue gas, several studies have been conducted to clarify its role on tube corrosion. Table 8.1 summarizes the related studies and their key findings, based on the use of either pure CO\textsubscript{2} stream or CO\textsubscript{2} mixed with steam. In brief, CO\textsubscript{2} is proposed to react with metallic iron (Fe) and chromium (Cr) to form oxide scales on a tube, according to Eqs. (8.1) and (8.2) below [3–6].

\begin{align*}
3Fe + 4CO\textsubscript{(g)} & \rightarrow Fe\textsubscript{3}O\textsubscript{4} + 4 CO \quad \text{Eq. (8.1)} \\
2.3Fe + 0.7Cr + 4CO\textsubscript{(g)} & \rightarrow Fe\textsubscript{2.3}Cr\textsubscript{0.7}O\textsubscript{4} + 4CO\textsubscript{(g)} \quad \text{Eq. (8.2)} \\
3Fe + 4CO\textsubscript{(g)} & \rightarrow Fe\textsubscript{3}O\textsubscript{4} + 4 C \quad \text{Eq. (8.3)} \\
2CO\textsubscript{(g)} & \rightarrow CO\textsubscript{2(g)} + C \quad \text{Eq. (8.4)}
\end{align*}

The resultant CO from Eqs. (8.1) and (8.2) can react with Fe to form oxide and carbon precipitates, according to Eqs. (8.3) and (8.4). Carbon precipitate can further combine with metals to form the respective carbides that are more brittle than the oxide scale, leading to the breakdown of the tube surface. The formation of carbide is dominant under reducing conditions [7–9] and is favoured by elevated CO\textsubscript{2} partial pressure [10] and a high carbon reactivity at the local scale-alloy equilibrium. It is also governed by the molecular diffusion of the dissolved carbon [5]. In contrast, in an oxidizing environment, oxide scale is formed preferentially on the tube surface [7]. The resultant Fe-based oxide is permeable to carbon [7], whereas chromium oxide formed on the Cr-rich tube surface is resistant to carbon diffusion [11]. The permeability of the tube is also highly dependent on the gas temperature. Cr is virtually immobile and non-protective below 600 °C. At temperatures above 600
°C, Cr is able to diffuse outwards into the Fe based oxide to form a protective layer [4]. However, when the temperature is too high and reaches 1200 °C, the carburization of Cr is enhanced, which in turn degrades the tube [9].

The real oxy-fuel flue gas has yet to be tested for the presence of carbides, as the oxygen partial pressure is generally around 5 vol% that is far higher than the gases tested in Table 8.1. The effect of ash deposits on the carburization reaction has not been investigated either. The conclusions regarding the carburization reactions are also quite contradictory in the literature. One study [12] concluded that the 9–12% Cr steels cannot exhibit a protective oxide scale due to the preferential formation of carbide in 30% H₂O/70% CO₂, at 500–700 °C. To the contrary, another study using 2.25–20% Cr ferritic alloys in argon-20% CO₂–20% H₂O revealed the formation of a protective chromium oxide scale at 650 and 800 °C [5]. Moreover, the previous studies either relied on microscopies that only focused on individual spots, or on X-ray diffraction (XRD) that is unable to pinpoint the tube cross section which is generally on the micron scale. The chemical analysis methods can detect and/ or quantify the carbides [5, 10, 11, 13], but fail to specify the spatial distribution and the partitioning of Cr between carbides and other species.

In this study, we reported the corrosion of a variety of tubes including carbon steel and 1.2–18 wt. % Cr alloys exposed under the oxy-fuel flue gas that is similar to the compositions achieved from our pilot scale test [14]. Apart from the bench-scale analytical facilities including X-ray diffraction (XRD) and scanning electron microscope (SEM) coupled with energy-dispersive X-ray analyzer (EDX), the synchrotron X-ray fluorescence (SXRF) microscopy and micro X-ray absorption near-edge structure (µ-XANES) spectroscopy were employed to capture the fine structures and details on the cross section of the tubes at a resolution of 2 μm [15–17]. The spatial distribution for chromium oxide and carbide was used to quantify the penetration of carbon and the carburization extent of chromium across the whole tube cross section. As far as the authors are aware, such advanced technologies have yet to be used on tube corrosion studies.
# Table 8.1 Literature review of flue gas corrosion related to CO$_2$ and oxy-fuel combustion

<table>
<thead>
<tr>
<th>Reference no</th>
<th>Purpose</th>
<th>Testing tubes</th>
<th>Gas environment</th>
<th>Temperature, $^\circ$C</th>
<th>Exposure time, h</th>
<th>Analytical methods</th>
<th>Key findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schnaas and Grabke [11]</td>
<td>Carburization test</td>
<td>NiCr 3220 and NiCrSi 6016</td>
<td>CH$_4$, CO, CO$_2$, H$_2$O, H$_2$</td>
<td>900-1000</td>
<td>up to 900</td>
<td>Gravimetric measurement, SEM-EDS</td>
<td>Internal carbides formed by carbon diffusion, A stable chromium oxide layer to resist against carburization, Premature failures occur by carburization, followed by internal oxidation and formation of cracks, voids and holes.</td>
</tr>
<tr>
<td>Meier et. al [7]</td>
<td>Corrosion in atmospheres containing carbon and oxygen</td>
<td>Ferritic and austenitic alloys (Fe-24Cr, Ni-46Cr, Co-27Cr) and Argon-10% CH$_4$/CO/CO$_2$; Hydrogen-10% CH$_4$/CO/CO$_2$.</td>
<td>621-1093</td>
<td>50-100</td>
<td>XRD, Optical microscopy, SEM-EDS</td>
<td>Fe-containing oxides cause the scales to be permeable to carbon. Carbon transport through oxide scales by diffusion and molecular transport through physical defects. In gases containing CO and CO$_2$, chromium carbide is stable, and chromium oxide forms at the carbide-alloy interface by oxygen transport.</td>
<td></td>
</tr>
<tr>
<td>Tawancy and Abbas [8]</td>
<td>Carburization mechanism</td>
<td>Wrought alloys including 310ss, Haynes alloy no.556 and Haynes alloy no. 214</td>
<td>Argon - 5% H$_2$-55 CO-5% CO$_2$</td>
<td>870-980</td>
<td>24-215</td>
<td>XRD, SEM-EDX, Optical microscopy</td>
<td>The alloy capable of forming Al$_2$O$_3$, developed and maintained a protective surface oxide scale as an effective barrier to C diffusion</td>
</tr>
<tr>
<td>Authors</td>
<td>Title</td>
<td>Reagents</td>
<td>Temperatures</td>
<td>Techniques</td>
<td>Notes</td>
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<tr>
<td>Barnes et al. [13]</td>
<td>Effect of sulphur on the internal carburization of Fe-Ni-Cr alloys</td>
<td>25Cr-20Ni alloy, HK40, 25Cr-35Ni cast alloy, HP40Nb and 25Cr-35Ni-40Fe alloy</td>
<td>H₂CH₄(0.75-1.4%) - H₂S (0-500 ppm)</td>
<td>950-1050</td>
<td>100</td>
<td>XRD, SEM-EDX, Optical microscopy Stain-etching with Murakami's reagent for the depth of carburization, Interference film technique using vapor-deposited ZnSe for the identification of phases, Nuclear microprobe technique for the distribution of carbon within the alloy. The addition of low level H₂S resulted in the reduction of tube corrosion rate. High level H₂S promoted the formation of a surface layer of chromium sulphide which reduced internal carburization but became a problem itself.</td>
<td></td>
</tr>
<tr>
<td>Chu and Rahmel [9]</td>
<td>Conversion of chromium oxide to carbide</td>
<td>Pure Cr₂O₃ tablet</td>
<td>CO and use of graphite felt to promote the Boudouard reaction</td>
<td>1200</td>
<td>N/A</td>
<td>Thermodynamic calculation, measurement of pressure versus time, and use of XRD. C₉O₃ conversion to carbide above a critical temperature which depends on CO pressure. Conversion rate is rather low, even at 1200 °C. The reaction rate is increased by carbon deposition on the Cr₂O₃ surface. The Fe-base oxides are permeable to CO₂ molecules for a substantial carburization under the oxide scale. &lt;600°C chromium is virtually immobile. &gt;600°C, chromium diffuses into Fe-base oxide to form a more protective layer to reduce carbon ingress. Humidity higher than 1500 ppm was corrosive for all steels with Cr contents below 12%. Direct evidence for carburization was not confirmed. Desulphurization is most critical for oxy-fuel flue gas.</td>
<td></td>
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<tr>
<td>Piron Abellan et al. [4]</td>
<td>Scale formation of martensitic steels in high CO₂/H₂O- environment</td>
<td>Martensitic steel 9-12% Cr</td>
<td>Air, argon-CO₂, argon-H₂O, 70% CO₂, 30% H₂O</td>
<td>550-700</td>
<td>24-500</td>
<td>Laser Raman spectroscopy (LRS), SEM-EDX, transmission scanning microscopy (TEM).</td>
<td></td>
</tr>
<tr>
<td>Kranzmann et al. [3]</td>
<td>Challenges on the corrosion mechanism s under oxyfuel combustion conditions</td>
<td>Different ferritic-martensitic and austenitic steels</td>
<td>Various compositions of CO₂-H₂O-O₂-SO₂</td>
<td>5-650</td>
<td>up to 600</td>
<td>OM, SEM-EDX, with thermodynamic equilibrium calculation.</td>
<td></td>
</tr>
</tbody>
</table>
### Chapter 8 SXRF and μ-XANES Characterization of Cr species in flue gas only

<table>
<thead>
<tr>
<th>Huenert and Kranzmann [12]</th>
<th>Impact of H₂O/CO₂/O₂ and H₂O/CO₂ on oxidation of ferritic-martensitic and austenitic steels</th>
<th>Ferritic-martensitic and austenitic steels</th>
<th>H₂O/CO₂/O₂ (30/70/0, 30/69/1)</th>
<th>500-700</th>
<th>250-1000</th>
<th>OM, SEM-EDX</th>
<th>Formation of protective chromium oxide layer is hampered due to carburization</th>
<th>Only austenitic steel can form dense and protective oxide scale</th>
<th>The 9-12% chromium steels cannot exhibit protective oxide scale due to the formation of carbidite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gheno et al. [5]</td>
<td>Carburization by low carbon activities gases</td>
<td>Synthetic ferritic alloy with 2.25-20 wt.% Cr</td>
<td>Ar-20% CO₂, Ar-20% CO₂, 20% H₂O</td>
<td>650 and 800</td>
<td>120</td>
<td>XRD, SEM-EDX, TEM with EDX and selected area diffraction (SAD)</td>
<td>Etching by a solution of 1% picric acid and 5% hydrochloric acid in ethanol to reveal grain boundaries and internal carbides</td>
<td>Carbon activities are controlled by the local scale-alloy equilibrium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Corrosion of 9Cr steel in CO₂ - Mechanism of carburization</td>
<td>T91 (9% Cr-1% Mo)</td>
<td>Pure CO₂ 1-250 bars</td>
<td>550</td>
<td>up to 1000</td>
<td>Etching by oxalic acid to show carbides</td>
<td>Under CO₂ at 1 atm, carburization accelerates with time slowly</td>
<td>A chromia scale is more effective to resist carbon than does an iron-rich oxide</td>
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<td></td>
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<td></td>
<td></td>
<td>Radiofrequency GDOES to quantify carbon ingress</td>
<td>At high pressures, high carbon depositions occur in the inner Fe-Cr rich spinel oxide layer</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>Combustion with infrared detector to determine the total carbon uptake EFTEM</td>
<td>Carburization occurs through the Boudouard reaction at the oxide/metal interface.</td>
<td>The degree of CO accumulation impacts</td>
<td></td>
</tr>
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8.2 Materials and Methods

8.2.1 Tube Corrosion Conditions

The tube exposure experiments were conducted in a horizontal furnace that was fixed at 650 °C for 50 h. The flue gas was fed into the furnace continuously at a rate of 300 ml/min. The flat tube specimen, 3 cm × 3 cm × 2 mm, was prepared by a wire-electrical discharge machine to cut on the cross sections of six commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. The oxy-fuel flue gas tested is made of 4.0 vol% O₂, 3000 ppm SO₂, 1000 ppm HCl, 30 vol% H₂O, 10 vol% N₂, and the rest being CO₂. The pressure for flue gas is 1 bar. Such a flue gas composition was confirmed in our pilot-scale test on the oxy-fuel combustion of a local Victorian brown coal [14]. The details for tube exposure conditions and sample preparation have been given elsewhere [18, 19].

A total of six tube materials were tested, with an increasing Cr content including SS400 (0% Cr), 12Cr1MoVG (0.9–1.2%), T23 (2.25%), T91 (9%), SUS347 (17–19%) and SUS304 (18–20%). For the SXRF and μ-XANES characterization, only four tubes were chosen: SS400, 12Cr1MoVG, T91 and SUS304. After the corrosion test, the tube specimen was quickly mounted and solidified into epoxy resin to avoid surface oxidation. Subsequently, it was halved by a disc cutter. The resulting cross-sectional surface was further polished by SiC paper with 2400 grit.

8.2.2 SEM–EDX and XRD Analysis

The SEM–EDX analysis is complementary to SXRF, as it is not possible for the SXRF to map oxygen and carbon on a hard X-ray beamline in Australian Synchrotron. Prior to the analysis, the cross section of the tubes was further polished using diamond paper (1 µm) and carbon-coated. A JEOL 7001F SEM was used for microstructural observation of the tube cross section and elemental mapping. XRD analysis was conducted on the top surface of the tube SS400, with a Rigaku Miniflex 600 setup at 40 kV and 15 mA, scanning rate of 1°/min, a step size of 0.01° and a wavelength of 0.15418 nm (Cu Ka). The software Jade was used for peak identification.

8.2.3 SXRF and μ-XANES Analyses
SXRF and μ-XANES analyses were conducted at the XFM beamline, Australian Synchrotron. SXRF maps were collected at 15.8 keV with a Si (111) monochromator and an energy resolution (ΔE/E) of $2 \times 9 \times 10^{-4}$. The Kirkpatrick-Baez (KB) mirrors were used to focus the beam down to $\sim 1.5 \, \mu\text{m}^2$ [16, 17]. For the cross section of each tube, an overview map with areas ranging from $2.8 \times 3.4$ to $2.8 \times 7.6 \, \text{cm}^2$ was achieved using a pixel size of $100–200 \, \mu\text{m}^2$ at a dwell time of $10–25 \, \text{ms} / \text{pixel}$. Detailed maps were then collected over $\sim 2 \times 0.4 \, \text{cm}^2$ area using $2 \, \mu\text{m}^2$ pixels and a dwell time of $0.4 \, \text{ms} / \text{pixel}$. XANES stacks were generated by collecting SXRF images ($\sim 0.2 \times 0.4 \, \text{cm}^2$, $4 \, \mu\text{m}^2$ pixels, and dwell times of $1–4 \, \text{ms} / \text{pixel}$) at 77 monochromators energies spanning 100 eV across the Cr Ka edge. Cr metal foil and a pellet of chromium oxide (Cr$_2$O$_3$) diluted in boron nitride were used to determine the energy shift for XANES analyses.

SXRF data were analyzed using the dynamic analysis (DA) method (Ryan 2000) in GeoPIXE II [20]. The DA approach fits multiple lines per element that separates overlaps and subtracts background, escape peaks and other detector artefacts. The extracted XANES spectra were processed in ATHENA. Linear combination fitting (LCF) was used to qualitatively determine the chemical compositions by using the Cr-bearing standards shown in Figure 8.1. Except for chromium carbide (Cr$_3$C$_2$) [21] and chromium sulphide (Cr$_2$S$_3$) [22] those were extracted from the references, spectra for the remaining standards were collected from our previous studies [23–26]. Additionally, we validated the LCF method by analyzing the mixture of standards at different molar ratios. The fitted data showed a maximum error of about 5% [25, 26]. It is also noteworthy that, as carbide and ferrite have varying stoichiometric ratios, the LCF fitting results based on the standards listed in Figure 8.1 should only be taken as those for a general carbide/ ferrite group, rather than for any specified chemical formulas such as Cr$_3$C$_2$ and FeCr$_2$O$_4$. The XANES analysis primarily aims to reveal the oxidation state of the elements of interest, which is independent of the atomic ratio for a given oxidation state. Concerning the similarity of a variety of standards such as Cr metal and carbide in Figure 8.1, an effort was further made to validate the sensitivity of LCF upon the selection of standards for the fitting of Cr in tube T23. As demonstrated in Figure 8.2a, exclusion of the carbide standard overestimated the intensity for the shoulder peak located at $\sim 5.992 \, \text{keV}$ (in the dashed cycle), where both Cr metal and carbide overlap significantly. Upon the inclusion of carbide, the measured spectrum was well fitted at the shoulder peak. The resulting Chi-square value dropped from 0.1708 to 0.0314 with the inclusion of carbide. Figure 8.2b further illustrates the details of the fit, showing the spectra in relative proportions.
Figure 8.1 Cr-bearing standards that have been used for the LCF fitting via Athena in this study

Figure 8.2 Athena LCF fitting for the tube T23 exposed to flue gas. Panel (a) is for the comparison between two fittings with and without the inclusion of carbide, and Panel (b) is for the detailed fitting results with the inclusion of carbide.
8.2.4 Thermodynamic Equilibrium Calculations

The commercial thermodynamic equilibrium programme, FactSage [27], was used to calculate and establish the Fe–Cr–CO$_2$ phase diagrams under the tube exposure conditions, 650 °C and a total pressure of 1 bar for CO$_2$. Apart from the pure substances, the built-in database for spinel species in FactSage was also included for the calculation.

8.3 Results and Discussion

8.3.1 Tube Mass Loss upon Exposure into Flue Gas

The mass losses of individual tubes in oxy-fuel flue gas versus the air-firing flue gas are shown in Figure 8.3. The composition of the air-firing flue gas is 5 vol% O$_2$, 10 vol% steam, 15% CO$_2$, 300 ppm SO$_2$, 100 ppm HCl and the remainder being N$_2$. It is obvious that oxy-fuel combustion is more corrosive than the air firing flue gas, especially for carbon steel and the two low-Cr steels, 12Cr1MoVG and T23. The mass loss in pure air and CO$_2$ was undetectable (data not shown). However, the CO$_2$ is still very reactive upon the interaction with the tube material. This is partially due to the oxidation of metals (both Fe and Cr) by CO$_2$, according to reaction Eqs. (8.1) and (8.2) mentioned above. The resultant oxides and spinel have been confirmed by XRD analysis [18]. However, carbides were not found by the previous XRD analysis. This could be due to the reasons that the top surface was not polished off, or a significant peak overlap in XRD does not warrant a good identification of any minor species such as carbides, which will be further evident later.

8.3.2 SXRF Mapping of Carbon Steel SS400

The SXRF map of tube SS400 exposed to the oxy-fuel flue gas is illustrated in Figure 8.4, where the spatial distribution of individual elements is represented by a colour scale in which black and white refer to the minimum and maximum concentrations of individual elements, respectively. Regarding the spatial distribution of the most abundant element, Fe shown on the left-hand side of Figure 8.4, it is obvious that the carbon steel was too weak to withstand the corrosive oxy-fuel flue gas. This agrees with its largest mass loss shown in Figure 8.3. It has broken down severely, with the formation of a spalled layer that buckled off and the detachment of the top scale as well, as suggested by the formation of a narrow ditch underneath the top surface. More interestingly, a close-up view in the
Chapter 9 SXRF and μ-XANES Characterization of Cr species in flue gas only

right-hand side demonstrates a rather wide ditch formed between the top scale and the spalled layer. Since Fe leans on both sides of the wide in between ditch (as evident by the blue colour), it is apparent that the corrosive gases such as O₂, steam and even SO₂/HCl penetrated inside the tube, forming volatile species that quickly diffused out. Consequently, the tube was spalled and buckled down by the compressive stress induced from the volatile gases. Additionally, it is clear that there is a formation of multi-layered structure for both top scale and the spalled layer, and a non-uniform spatial distribution of individual elements in each sub-scale/layer. For the principal element, Fe in the spalled layer, it is made up of three sub-scales. The very thin top subscale in yellow refers to the highest abundance of Fe (88 wt.% Fe), with a red medium sub-scale for a concentration of 45 wt.% Fe and a blue inner sub-scale (18 wt.% Fe) that is much thicker and lean in Fe. Such a colour order proved a fast-outward diffusion of Fe upon the oxidation on the tube surface. Regarding the top thin sub-scale for Fe in yellow, it also coexists with Mn, Co and even a small amount of Ti. This confirms the protective role and the fast-outward diffusion of these three minor elements, due to their larger oxidation potential than Fe. The oxidation potential decreases in the order of V > Ti > Mn > Fe (FeO) > Co > Fe (Fe₃O₄) at 650 °C [6]. However, compared to Mn and Co, V and Ti had a slow diffusion rate, and hence, most of them are still present in the bulk tube and on the top surface that is still attached to the bulk tube and have not spalled off yet. These two elements are thus less protective. Moreover, the concentrations of S and Cl are quite low in the spalled layer, implying that oxides are the principal components.
Figure 8.3 Mass loss and oxidation growth rate for the six tubes that have been exposed in four different flue gases, at 650°C for 50 h.
Figure 8.4 XFM mapping for the cross-section of carbon steel tube SS400 exposed to oxy-fuel flue gas. The Fe map is shown on the left.

The top scale is further amplified and marked on the top left corner of Figure 8.4. As can be seen, the principal element Fe in this figure is made up of multiple sub-scales in different colour/concentration. The blue scale refers to the most outer sub-scale with 17.6 wt.% Fe; a yellow medium sub-layer contains 73.2 wt.% Fe; a narrower ditch stays between the above two scales, and the most inner subscale contains 62 wt.% Fe that is still closely attached to the bulk tube. All these sub-layers have a comparable width that is around 120 µm. With regard to the top sub-scale in blue (next to the wide ditch), it comprises Fe and V, Ti, S and Cl. The lack of Mn and Co suggests a complete diffusion of Mn and Co out of the bulk tube, in comparison with the other two additives Ti and V that mostly reside in the bulk tube, as suggested by the red spots in their distribution. Furthermore, the existence of S and Cl here proved the preferential penetration of these two elements.
inside the tube, probably via the intra-granular diffusion through the pores. Fe in the medium sub-scale (yellow in colour, 73.2 wt.% Fe) is most abundant. Even so, its distribution is still uneven in this subscale, as evident by a reddish strip on the left edge and a dark yellowish ditch inside. The reddish strip on the left edge is accompanied by Mn and Co, whereas the bulk yellowish Fe coexists with V, Ti, S and Cl. This further confirmed the different diffusion rates for the elements studied here. Regarding the most inner sub-layer that is still attached closely to the bulk tube, it is covered with a Fe-rich thin top surface, which is followed by a dark yellowish strip of lower Fe concentration with a width of around 120 µm. However, none of the other elements show this unique pattern. In light of this, it may be due to the formation of carbide; carbon cannot be detected on a hard X-ray beam line. Carbides have been reported to preferentially form internally in the voids and cracks inside the tube. This will be further discussed for the speciation of Cr in the other tubes.

As S and Cl are related to bulk flue gas, efforts were made to clarify their affinity with the principal element Fe, by SEM mapping of the zoomed microstructure of spalled layer in Figure 8.5 and XRD analysis of top scale in Figure 8.6. From the SEM map in Figure 8.5, one can see the abundance of iron and oxygen, and their close affinity in the spalled layer. This confirms the preferential formation of iron oxide, which is further evident from the strong peaks for magnetite (Fe₃O₄) in Figure 8.6. For the two corrosive elements S and Cl, one can only see some S embedded deep in the Fe-dominated layer, whereas Cl is undetectable (data thus not shown). XRD analysis shown in Figure 8.6 confirmed the formation of troilite (FeS). These sulphide species are also preferentially present at the left edge of the spalled layer that is next to the ditch formed in between the top scale and the spalled layer in Figure 8.4, rather than being exposed to the bulk flue gas. Apparently, once diffusing inside the oxygen-depleted ditch, the accumulated SO₂ was partially dissociated into S( g) that in turn diffused outwards through the oxide scale. The inward diffusion of SO₂ and S( g) should be much more difficult, due to the dense nature of the bulk tube, compared to the porous Fe-based oxide scale [7]. Moreover, carbide was not detected in the XRD pattern in Figure 8.6. This could be due to the superimposition of its peaks with the other species and also the presence of carbide underneath the top surface (as suggested by the dark yellowish stripe on the left side of the top surface in Figure 8.4).
Chapter 9 SXRF and μ-XANES Characterization of Cr species in flue gas only

Figure 8.5 RGB map of the cross-section of carbon steel tube SS400 and SEM maps for the top layer spalled from the bulk tube

Figure 8.6 XRD pattern for the top surface of SS400 exposed to oxy-firing flue gas
8.3.3 SXRF Mapping and μ-XANES Analysis of Low-Alloy Steel 12Cr1MoVG

Figure 8.7 depicts the spatial distribution of the elements of interest on the cross-sectional surface of 12Cr1MoVG, a low-alloy steel containing 1.2 wt.% Cr. Surprisingly, the tube remained non-spalled, with the formation of only a very thin, reddish layer of high Fe concentration on top, as evident on the left-hand side. The layer formed is estimated to have a width of around 0.16 mm, which is much thinner than the carbon steel shown in Figure 8.4. A second reddish layer underneath the top layer was also observed, which can be attributed to the cracks formed by the outward diffusion of volatile species out of the bulk tube. However, it is much thinner and did not lead to the formation of any deep ditch in the 50-h exposure time. This proved the protectiveness of this low-Cr alloy against the oxy-fuel flue gas attack. The zoomed pictures shown on the right-hand side revealed an uneven spatial distribution of all the elements of interest. The principal element Fe is composed of four sub-scales on the tube surface, a super thin, blue subscale (~10.6 wt.% Fe) on the most top of the tube, followed by an orange sub-scale (51.6 wt.% Fe), a light-yellow sub-scale (79.2 wt.% Fe), and a ditch in orange with increasing distance from the tube surface. Such a multi-layered distribution is strong evidence for the different inward diffusivities of gases and the different outward diffusivities of metals out of the tube, thereby causing the formation of different species at different depths inside the tube. For Fe on the most top blue sub-scale, it is accompanied by Mn and some Co, S and Cl. The coexistence of the former two elements further confirmed their protective role which is even more pronounced than Cr and their faster diffusion outwards the bulk tube, the same as has been found for carbon steel. Mn is the second most abundant element in both the light-yellowish sub-scale and the orange sub-scale/ditch of Fe. The presence of S and Cl resulted in a very weak signal on the most top sub-scale of Fe.

The spatial distribution of Cr is intriguing in the cross section of this low-Cr alloy. Except for a few regions where some Cr coexisted with Mn and Co, its majority remained in the bulk tube. However, a subscale (2.78 wt.% Cr on average) formed by the mixing of yellowish dendrites and reddish one (marked as white rectangle on Cr map in Figure 8.7) was observed for Cr, which is present underneath the narrow, shallow ditch dominated by Fe and Mn. It might be formed by the sulphation/sulphidation of Cr, or even the carburization of Cr which was reported to occur preferentially over Fe and internally underneath the top layer of the tubes, due to the molecular diffusion of reductive carbon through the oxide grain boundary. The resultant carbide precipitated inside the voids, forming a deep penetration inside the tube [8–10].
Efforts were made to clarify the association between Cr and S/Cl/C, as well as the speciation of Cr by XANES mapping. For the association between these two elements, the RGB map on the left-hand side of Figure 8.8 suggests a close affinity of Fe and S forming a violet strip (top surface of the tube). Cr, however, has no association with S (on the top surface). Instead, the Cr-rich strip is slightly green in the RGB picture, suggesting the merging of green (for Cr) and red (for Fe) due to the dilution effect of the latter element. This is supported by the XANES distribution results shown on the top right corner of Figure 8.8. One can clearly see that the energy at approximately 6.009 keV is the brightest for Cr, which is one of the featuring peaks for standard oxide/hydroxide (Cr$_2$O$_3$, Cr (OH)$_3$), spinel (FeCr$_2$O$_4$), and chloride (CrCl$_3$) shown in Figure 8.1. The last species can be ruled out, since the Fe–Cr–Cl RGB map (data not shown) did not find any association between Cr and Cl. Regarding chromium carbide that has a shoulder peak centred around 5.991 keV (which should mainly attributed to carbide rather than Cr metal, as suggested by Figure 8.2), it is rather weak in the Cr K-edge XANES energy distribution map, suggesting that oxide is predominant for Cr, and the light-yellow dendrite on Cr map (in Figure 8.7) was not fully attributed from carbide. Or the carbide formed is well mixed up with oxides and failed to form its own strip with a clear boundary separating from the other species.

The XANES speciation results of Cr for seven individual spots are shown on the bottom right corner of Figure 8.8. Note that these spots were chosen randomly from different layers/scales of the tube. Therefore, the LCF results here only intend to provide indication on the presence of different Cr-bearing species, rather than suggesting an averaged composition for each location. Nevertheless, all the spots analyzed prove the formation of chromium carbide for almost all the locations except spot 5 which is located on the most outer surface of the tube. Moreover, it coexists with ferrite that has a central peak at 6.009 keV and a shoulder one at 6.024 keV. The LCF results as shown on the bottom right corner revealed the fractions of individual species. The fraction of pure Cr metal has a maximum at 0.4 (i.e. 40%), suggesting a severe penetration of the corrosive gases causing oxidation and carburization of Cr deep inside the bulk tube. The amplified microstructure for the cross section in Figure 8.9 confirmed the scaling and even creeping of the tube caused by the penetration of oxygen and carbon, which is a strong indicator for the large porosity of the thin scale formed on the tube surface, as further amplified on the left-hand side. It was not possible to map Cr with the SEM as the Cr concentration was below the detection limit of the EDS detector. With regard to the two Cr-bearing species, ferrite and carbide in Figure 8.8, both show a non-uniform distribution across the whole cross section. That is, carbide was preferentially present in the yellowish, dendritic strip that
penetrated underneath the top layer (in blue for Cr), accounting for around 0.4 in mass fraction for the locations No 1 and No 2 inside the tube, and around 0.3 on the strip. For [18], ferrite is dominant. The carbon map observed in SEM in Figure 8.9 also suggests the lack of carbon on the top thin scale which is mainly composed of Fe and O.

The formation of carbide is most intriguing here. As shown in Eqs. (8.3) and (8.4), the reductant should be the carbon, whereas the reactant CO in these two equations should be produced from Eqs. (8.1) and (8.2) for an initial oxidation of metals by CO$_2$. The reduction reaction for the carbide formation should also occur deep inside the tube, rather than on the gas/tube interface where the partial pressure of CO is extremely low, accounting for maximum 10–6 bar for a total pressure of 1 bar pure CO$_2$ [18]. Figure 8.9 shows individual crystals and the presence of nanoscale gas channel in between different grains on the amplified inset picture (on the most top left corner of the left photograph). Clearly, such a narrow channel favours the entry and exit of gas produced on the surface of individual grains. The slow desorption of CO from an oxide grain (after the completion of reactions (8.1) and (8.2) and/or the build-up of CO gas in the void are essential for the carbide to be formed, according to the void-induced duplex oxide formation mechanism proposed elsewhere [10, 28, 29].

Once the CO is consumed in the voids, the CO$_2$ will be regenerated via reaction Eq. (8.4) and in turn, diffuses either outwards through the pre-existing porous oxide layer, or further inwards inside the tube, depending on the porosity and structure of the bulk tube. The former diffusion created an internal pressure and thus the formation of a shallow ditch underneath the oxide layer. In contrast, the latter diffusion induced the successive oxidation and deep precipitation of the resultant oxides and carbides that are also highly mixed together inside the tube, as suggested by the yellowish strip (in the dashed rectangle) for Cr in Figure 8.7.
Figure 8.7. XFM mapping for the cross-section of carbon steel tube 12Cr1MoVG exposed to oxyfuel flue gas.
Figure 8.8 Fe-Cr-S RGB map, XANES spectra and LCF quantification results.
8.3.4 SXRF Mapping and µ-XANES Analysis of High-Chrome Ferritic T91 and Austenite SUS304

The speciation of Cr averaged over the cross section of a tube, for three different Cr-bearing tubes, is depicted in Figure 8.10. As can be seen on the left-hand side of Figure 8.10, Cr in the two high-Cr tubes formed a continuous protective scale (in red for a higher concentration) that is much thicker than the top scale (in blue due to the lower concentration of Cr). In comparison, Cr in 12Cr1MoVG failed to form a continuous layer to protect the principal element Fe, due to the low Cr content in this tube. Moreover, similar to the 12Cr1MoVG tube, Cr in both tubes with high Cr concentration shows a multi over-layered distribution, with the formation of top sub-scale in blue, a red–orange medium sub-scale and a dark yellowish sub-scale that penetrates inside the tube. For the top blue sub-scale that is depleted in Cr, it only accounts for around 13 µm in depth on the two high-Cr tubes, which is much thinner than the respective sub-scale formed for 12Cr1MoVG that is about 41 µm in depth. Regarding the red–orange medium sub-scale, it should be dominated by the Cr-based oxide that is dense and protective against the diffusion of corrosive gases. The dark yellowish sub-scale underneath the medium...
one is obviously most interesting. For the high-chrome ferritic T91, the dark yellowish subscale is much wider, covering plenty of discrete spots that are deep inside the bulk tube. These discrete spots may refer to the voids that are occupied by carbides and carbon precipitates that preferentially diffused inwards. If that is the case, the fraction of carbide formed on T91 is apparently larger than that found on the low-Cr alloy 12Cr1MoVG. Regarding the austenite tube SUS304, the formation of dark yellowish sub-scale is also evident. However, it is much thinner than on the T91 tube. There are also much less discrete precipitates formed deep inside the SUS304 tube.

Figure 8.10 Spatial distribution of Cr on the cross-sections of three tubes exposed to oxy-firing flue gas, and the averaged speciation of Cr on the interfaces

XANES analysis for the averaged Cr speciation on the whole top scale, as circled on each tube, was conducted to confirm the above concerns. Note that, analysis on the bulk cross section of T23 tube at the beamline 16A in National Synchrotron Radiation Research Center (NSRRC), Taiwan, was also included here. As depicted on the right-hand side of Figure 8.10, Cr on
121MoVG is dominated by ferrite that has a sharp central peak around 6.009 keV, whereas the carbide formed only accounts for a maximum molar fraction of 0.2. Cr on the bulk cross section of T23 possesses a similar fraction for the carbide, but has a much lower fraction for the ferrite, with the majority of Cr remaining as unreacted metal. For the other two high-Cr tubes, the fraction of ferrite is still low and comparable to T23. However, the fraction of carbide is much higher, accounting for 0.3–0.4 on average. This agrees with the presence of dark yellowish subscale and discrete precipitates on the cross sections of these two tubes, particularly T91. The phase diagram for Fe–Cr–CO$_2$ at 650 °C in Figure 8.11 confirmed the preferential carburization of chromium over iron from thermodynamic principles. The formation of carbide is also theoretically favored upon increasing the content of chromium in the bulk tube, as well as decrease in the fraction of CO$_2$. For the low-Cr alloy including 12Cr1MoVG and T23, the formation of ferrous oxide (FeO) and ferrite is highly favored, whereas CO$_2$ only converts to carbon precipitate (in zone 4) and then chromium carbide (in zones 1–3) in the case that the fraction of CO$_2$ is further lowered.

![Cr-Fe-CO$_2$ phase diagram](image)

Figure 8.11 Cr-Fe-CO$_2$ phase diagram created by FactSage$^{6,1}$, at the temperature of 650°C and a total pressure of 1 bar for CO$_2$. 

(1) Cr(s) + Fe(s) + Cr$_2$O$_3$(s) + Cr$_4$C(s)
(2) Fe(s) + Cr$_2$O$_3$(s) + Cr$_4$C(s) + Cr$_3$C$_2$(s)
(3) C(s) + Fe(s) + Cr$_2$O$_3$(s) + Cr$_4$C(s)
(4) C(s) + Fe(s) + FeO(s) + FeCr$_2$O$_4$(s)
(5) gas_real + C(s) + Cr$_2$O$_3$(s) + FeCr$_2$O$_4$(s)
(6) gas_real + C(s) + FeO(s) + FeCr$_2$O$_4$(s)
(7) gas_real + Cr$_2$O$_3$(s) + FeCr$_2$O$_4$(s)
(8) gas_real + FeO(s) + FeCr$_2$O$_4$(s)
(9) gas_real + Spinel + FeCr$_2$O$_4$(s)
(10) gas_real + Spinel + FeO(s) + FeCr$_2$O$_4$(s)
From the gas diffusivity perspective, the top oxide layer that is supposedly protective against gas diffusion also plays a role. Its composition rather than the thickness is critical in impeding the carbide formation. To reiterate, for the low-Cr alloy 12Cr1MoVG and even T23, the top layer rich in iron-based oxide is highly porous and even partially damaged by the attack of SO$_2$ and HCl. Consequently, both the inward diffusion of CO$_2$/O$_2$/H$_2$O and outward diffusion of the resultant CO are favored. The local environment is thus oxidizing that favours the overgrowth of oxide/sulphide/chloride over carbide inside the oxide/metal scale. For the highest Cr tube austenite tube SUS304 studied here, the whole tube and its Cr-rich, protective scale is dense (as demonstrated by the SEM maps in Figure 8.12), thus creating a strong local reducing environment around the oxide/metal grains. The resultant carbide and carbon precipitates quickly fill in and block the gas passage channels in the scale, thereby impeding the successive diffusion of gases deep inside the bulk tube. However, for the medium Cr tube T91, its oxide/metal scale formed is less dense and possesses creeps inside the tube (see Figure 8.12). The passage channel for CO$_2$ and its derivatives thus always remain open, as suggested by the strong penetration of oxygen inside the T91 tube in Figure 8.12 and the local environment on the oxide/metal scale boundary shift between oxidizing and reducing alternatively, according to the successive consumption and generation of CO$_2$ based on reactions (8.1) – (8.4). This in turn promotes the penetration of carbide/carbon precipitate inside the tube. The local carburization of T91 steel further accelerated the oxidation growth. Such a unique feature for 9Cr steel in CO$_2$ has also been noticed in the other studies using pure CO$_2$ or CO$_2$/H$_2$O mixed gases [10, 28, 29].
Analysis was also made to explore the detailed structure and spatial distribution of Cr-bearing species along the cross sections of T91 and SUS304. Figure 8.13 illustrates an amplified cross section of tube T91, the Cr K-edge XANES spectra for several spots typical along the tube cross section, and the resultant LCF fitting results. To iterate, these spots were chosen randomly from different location/colour on the tube cross section. The fitting results are thus only an indicator and evidence of the certain species rather an averaged quantitative result for different location. Similar to the tube 12Cr1MoVG, ferrite is most abundant on the orange interface that resides between the top blue sub-scale and the underneath dark yellowish sub-scale. Apart from pure metal, ferrite and carbide, the tiny amounts of chloride and even hydroxide were also observed on location nos. 4 and 5 on the orange oxide scale. This further proves a continuous open passage for gases in the oxide scale, and hence, a variety of species can be formed on the metal/oxide scale interface. More interestingly, the fraction of carbide is rather constant along the width of the tube, rather than being uneven as that has been found for 12Cr1MoVG in Figure 8.7. In particular, the fraction of carbide is still noticeable on tube top surface, i.e. the blue gas/metal interface. This indicates a relatively strong reducing environment on the tube surface. It should be caused by the back flow of the reducing gases (e.g. CO) and carbon derived from Eqs. (8.1)–(8.4). The carbide fraction for SUS304 was much higher on the top blue sub-scale, as evident for the location nos. 4 and 5 in Figure 8.14. The resultant carbide is apparently
brittle and thus, broke down into small fragments that were further carried over by the bulk flue gas, as suggested by no. 6 and those in the white circle on Figure 8.14.

For the purpose of comparison, Table 8.2 summarizes the major Cr-bearing species observed at the different scales for the three tubes, based on the SXRF and l-XANES results in Figures 8.8, 8.10, 8.13 and 8.14. Apart from the difference in the averaged Cr speciation that is usually measured by bench-scale facilities or bulk XANES, the three tubes also showed remarkable difference in the speciation of Cr at different scales.

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Top sub-scale (blue)</th>
<th>Medium sub-scale (orange)</th>
<th>Inside Defects</th>
</tr>
</thead>
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<tr>
<td>12Cr1MoVG</td>
<td>1st abundant</td>
<td>Ferrite</td>
<td>Ferrite</td>
<td>Cr3C2 ~ Ferrite</td>
</tr>
<tr>
<td></td>
<td>2nd abundant</td>
<td>Cr metal</td>
<td>Cr metal</td>
<td>Cr3C2</td>
</tr>
<tr>
<td></td>
<td>3rd abundant</td>
<td>Cr metal</td>
<td>Cr3C2</td>
<td>Cr metal</td>
</tr>
<tr>
<td></td>
<td>Trivial</td>
<td>Ferrite</td>
<td>Ferrite</td>
<td>Ferrite</td>
</tr>
<tr>
<td>T91</td>
<td>1st abundant</td>
<td>Cr metal</td>
<td>Cr metal</td>
<td>Cr metal ~Cr3C2</td>
</tr>
<tr>
<td></td>
<td>2nd abundant</td>
<td>Cr3C2</td>
<td>Cr3C2</td>
<td>Ferrite</td>
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<tr>
<td></td>
<td>3rd abundant</td>
<td>Ferrite</td>
<td>Ferrite</td>
<td>Ferrite</td>
</tr>
<tr>
<td></td>
<td>Trivial</td>
<td>Ferrite</td>
<td>Ferrite</td>
<td>Ferrite</td>
</tr>
<tr>
<td>SUS304</td>
<td>1st abundant</td>
<td>Cr metal</td>
<td>Cr metal</td>
<td>Cr3C2</td>
</tr>
<tr>
<td></td>
<td>2nd abundant</td>
<td>Cr3C2</td>
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<td></td>
<td>3rd abundant</td>
<td>Ferrite</td>
<td>Ferrite</td>
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</tr>
<tr>
<td></td>
<td>Trivial</td>
<td>Ferrite</td>
<td>Ferrite</td>
<td>Ferrite</td>
</tr>
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</table>

Oxide is more easily formed deep down inside the low-Cr 12Cr1MoVG tube, whereas the pure Cr metal is still strong and protective enough to remain as the principal Cr-bearing species on the top surface of T91 and SUS304. The only side effect of this is the creation of a strong carburizing environment inside the tube, which in turn promotes the simultaneous formation of both oxide and carbide, due to the roles of CO2 played in Eqs. (8.1)–(8.4).
Figure 8.13 Spatial distribution of Cr-bearing species on the interface of T91 exposed to oxy-fuel flue gas, Cr K-edge XANES spectra and LCF quantification results.
Figure 8.14 Spatial distribution of Cr-bearing species on the interface of SUS304 exposed to oxy-fuel flue gas, Cr K-edge XANES spectra and LCF quantification results.
8.4 Summary and Implications of This Study

The most interesting finding in this study is the confirmation of chromium carbide under the oxide/ferrite scale that is inaccessible to XRD unless the top scale is ground off [16, 17]. In addition, the significant overlaps of carbide’s peaks with the other species make it difficult to identify using XRD analysis. SXRF maps at 5.993 and 6.005 keV that are the energies of the shoulder of carbide and oxide/ferrite, respectively, demonstrate the presence of these two species, with the presence of a measurable width inside the tube. As illustrated on the left-hand side of Figure 8.15, the formation of carbide on 12Cr1MoVG is weak and highly miscible with other species including metal and oxide, compared to a clear thickness of 1.2 µm for oxide scale in orange, which is also around ten times thicker than oxide scale on the other two tubes. This is due to the depletion of Cr and fast oxidation of the principal metal Fe upon the attack of the flue gases. Instead, the carbide scale (blue strip at 5.992 keV) formed inside T91 is the thickest, accounting for around 0.45 µm which is nearly double the thickness for carbide formed on 18Cr SUS304. Since the thickness of the oxide scale is similar for the two high-Cr tubes, tube T91 thus bears the largest carbide-to-oxide ratio, suggestive of the dominance of carbide formation on its breakaway, compared to the predominance of oxide/sulphide/chloride for the buckling of low-Cr tube. Furthermore, from Figure 8.3 it is evident that the use of Cr, even at a low content of only 1.2 wt.% in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion, as well as minimize the difference between oxy-fuel and air firing flue gases after the exposure of 50 h in oxy-fuel flue gas. The high-chrome steel T91 also performed comparably to the two 18Cr austenite tubes, suggesting that the carbide formed inside may not be strong enough to degrade the ductility of T91, within 50 h of exposure. However, a much longer exposure time is essential to monitor the performance of T91. Previous studies have suggested a linear kinetic rate for tube carburization, and a much thicker carburization zone could be formed, e.g. approximately 40 µm for Fe–20Cr exposed at 600 °C for 120 h [5].

The strong reactivity of CO₂ under the coexistence of a variety of different gas components has also been confirmed in this study. This suggests the large potential of CO₂ for the oxidation and carburization of metals and the fast diffusion of CO₂ and its derivatives compared to oxygen and even other components in oxy-fuel flue gas. The similar phenomena have been observed in a previous study where both the thickness of scale and carbide layer were increased upon the doping of 1% O₂ in the CO₂–H₂O [3]. Another study even suggested that addition of
3% O\textsubscript{2} in Ar/CO\textsubscript{2} or CO\textsubscript{2}/H\textsubscript{2}O has no clear effect on carburization \cite{30}. The CO\textsubscript{2} cycle as depicted on the top right corner of **Figure 8.15** should be the key theory explaining the formation of carbide, both underneath and above the oxide scale. CO\textsubscript{2} and its derivatives including CO and carbon precipitate should diffuse rapidly through the channels formed in the oxide scale, compared to the other gaseous components. The other components such as steam and oxygen may even accelerate the cycle. Steam has been suggested to open cracks for the diffusion, whereas oxidation of internal carbide by Eq. (8.5) \cite{30} below may enhance the formation of CO and move the carbide front deep down inside the tube.

\[
Cr_{23}C_6 + 20 \frac{1}{4} O_2 \rightarrow 11 \frac{1}{2} Cr_2 O_3 + 6CO(g)
\]

Eq. (8.5)

The content of Cr in the tube is crucial. Although an increase in Cr content facilitates the formation of a dense oxide scale, the CO and carbon formed could be encapsulated, accumulated underneath the resultant dense oxide scale and thus further penetrate deep inside the tube. This applies to the 9Cr tube T91. Increasing the Cr content to 18 wt.\% for the use of austenite tube should make the oxide scale denser and narrow the gas passage channels. Consequently, the successive formation of oxide closes the pores and pushes the resultant CO and carbon back out of the tube, which even creates a strong carburizing environment on the tube surface to promote the formation of carbide that can further fragment into fugitive pieces. Consequently, the tube is still slightly corroded.

![Figure 8.15 Comparison of the averaged thickness of carbide/oxide and the proposed CO\textsubscript{2} cycle on tube surface](image-url)
8.5 Conclusions

Synchrotron-based X-ray fluorescence and μ-XANES were used to detail the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that had been exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The gas composition is close to the flue gas produced from the oxy-firing of a low-rank coal in our previous pilot-scale tests. The major conclusions can be drawn as follows:

1. Multi-layered scales with an uneven distribution of individual elements were observed for both the top surface and spalled layer of carbon steel SS400. Oxidation is the major reaction causing the scaling of the tube, whereas the other reactions such as sulphidation and chlorination led to the buckling of tube surface. The use of Cr, even at a low content of only 1.2 wt.% in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion, as well as minimize the discrepancy between oxy-fuel and air-firing flue gases in terms of mass loss rate.

2. The CO₂ cycle with the involvement of oxidation and carburization of metals took place for the Cr bearing alloy, even under the coexistence of CO₂ and oxidizers in the flue gas tested here. The fast diffusion of CO₂ and its derivatives facilitated a preferential occurrence of carburization under the oxide scale. However, upon the closure of gas passage channels in the oxide scale, the reductants CO and carbon can flow back to the tube top surface causing the formation of carbide on the most outer scale that then fragments into fugitive pieces.

3. Compared to the austenite SUS204 tube where the carburization is dominant for tube corrosion, chromium in the high-chrome T91 tube with 9 wt.% Cr undergoes both oxidation and carburization alternatively on the metal/oxide interface. The gas passage channels mostly remain open in the oxide scale, and hence, the resultant carbide and carbon precipitate penetrated deep inside the tube.
References


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Monash University

Declaration for Thesis Chapter 9

Declaration by candidate

In the case of Chapter 9, the nature and extent of my contribution to the work was the following:

<table>
<thead>
<tr>
<th>Nature of contribution</th>
<th>Extent of contribution (%)</th>
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<tr>
<td>Initiation, key ideas, experimental work, analysis of results, writing up.</td>
<td>90 %</td>
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The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

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<td>Experimental work</td>
<td>10 %</td>
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<td>Comments on my work</td>
<td>External co-author</td>
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<tr>
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<td>Editing and feedback</td>
<td>Supervisor</td>
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<td>Lian Zhang</td>
<td>Initiation, key ideas, editing</td>
<td>Supervisor</td>
</tr>
</tbody>
</table>

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate’s and co-authors’ contributions to this work*.

Candidate’s Signature  

Date 01.02.2020

Main Supervisor’s Signature  

Date 01.02.2020

*Note: Where the responsible author is not the candidate’s main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.
CHAPTER 9

Kinetic Study of Long-Term T23 Tube Corrosion upon Low-Rank Coal Ash Deposition under Oxy-Fuel Combustion Conditions
Abstract
The aim of this study was to understand the kinetics of high-temperature tube corrosion and its rate-limiting step in oxy-fuel combustion mode. Four different types of ash deposits collected from low-rank coal combustion boilers were tested, with varying contents of sulfur and metallic species. A typical stainless steel, low chromium ferritic alloy, T23, was tested at a metal surface temperature of 650 °C for up to 200 h. Compared with air-fired flue gas which is lean in SO₂ and steam, the aggressive flue gases formed under oxy-firing conditions enhanced T23 tube corrosion but to a marginal extent in a comparison with the S-rich ash deposit. The study found a positive correlation between the sulfur content within ash deposit and the thickness of the tube oxide layer. The sulfate in the ash deposit promoted the formation of molten and mobile sulfate complex and sulfides. The former species are predominant on the tube’s outer surface, while sulfides are preferentially formed inside the oxide layer where oxygen is lean and/or even absent. In addition, the study confirmed that the rate of growth of tube corrosion is controlled by both diffusion and phase boundary reactions. Regardless of the combustion mode, the gas diffusion coefficient decreases with the increase of sulfur content in the ash deposit, due to the enhanced formation of molten sulfates on the oxide layer. In contrast, no change was observed for the phase boundary reaction rate constant with increased sulfur content in the ash deposit. This is mainly because the solid-to-solid reactions are independent of the solid ash properties during the formation of molten sulfates and sulfides.

Keywords: XANES, Tube Corrosion, Long Term Test, Low Cr alloy, Oxidation Kinetics
9.1. Introduction

Oxy-fuel combustion has potential as a low-emission combustion technology for coal in the carbon-constrained world [1]. In this new process of combustion, coal is burnt in high-purity oxygen balanced by the recirculated flue gas inside a boiler in order to deliver high-purity CO₂ in the flue gas, which could be subsequently sequestered with a minimal pre-treatment [2]. Compared with other carbon capture and storage technologies, oxy-firing is more efficient in CO₂ capture, which has been reported to reach 100% [2]. However, the corrosive nature of CO₂ and other gaseous components of flue gas, in addition to changes in the operating temperatures and properties of the ash deposit, may trigger severe damage such as tube corrosion in the convective heat-exchange zones.

Oxidation is the principal mechanism of tube corrosion in a convective heat transfer zone in a coal-fired boiler. The initial step in oxidation is the adsorption of oxygen from flue gas, followed by the formation of oxide, the nucleation of oxide and its subsequent growth into a continuous scale/layer covering the tube surface [3]. Factors affecting the reaction rate and the respective rate equations include the surface property and pre-treatment of the metal, reaction temperature, oxygen partial pressure, and the duration of the reaction [3]. Two relatively simple models are currently applied to interpret the rate of oxidation of a metal, linear and parabolic [3,4]. Linear behavior is frequent under conditions where a surface or a phase boundary reaction is the rate-determining step and the oxide scale formed is porous and nonprotective [5]. The overall oxidation rate remains constant with increasing the exposure time. Linear behavior may be caused by cracking and spallation of the scale, since new metal is continuously exposed to the atmosphere. Linear behavior may also occur before the oxide layer is sufficiently thick to separate the reactants in the initial stages of oxidation [6]. In contrast, parabolic behavior predominates when the diffusion of ions or electrons through the oxide layer is rate limiting. Consequently, the rate of oxidation decreases as the layer thickens. The parabolic kinetic model was established by Wagner [7], based on a number of assumptions including stoichiometric, compact and adherent oxide scales, and only lattice diffusion as the rate-determinant. However, these assumptions are rarely valid. In practice, the oxidation for alloys with the presence of multiple passivation elements is usually complicated, and hence, deviations of the observed corrosion rate from these equations are common. Several studies have reported contradictory findings on whether the kinetics display linear, parabolic, or other
growth patterns, as summarized in a review by Wright and Pint [8]. Moreover, oxidation usually reveals different behaviors at different stages and therefore requires a combined rate law to explain the kinetics. To date, a number of research studies have kinetic studies of high-temperature tube corrosion under oxy-firing conditions are still lacking.

This paper reports the results for the oxidation kinetics of high-temperature corrosion for a low chrome ferritic steel material (T23). In addition to blank flue gases, four different types of fly ashes were applied to the tube surface to enable a detailed examination of their effects on the rate of tube corrosion. Similar with our previous studies [9–11], this study also employed a fixed temperature of 650 °C but different exposure times up to 200 h. Different kinetic models were assembled to interpret the tube oxidation rate and its controlling step under the different scenarios. In addition, the post-corrosion ash and tube samples were analyzed using different analytical methods, including scanning electron microscopy (SEM) together with energy dispersive X-ray (EDX), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). The study attempted to establish the corrosion rate of the T23 tube under typical long-term exposure in an oxy-fired boiler in order to gain insights into how the minimization of tube corrosion can be achieved under this low-emission combustion mode in its future deployment stage.

9.2. Experimental Section

9.2.1 Ash Deposit Compositions

The elemental compositions of the four ash samples are shown in Table S1 as determined by X-ray fluorescence (XRF). The two ash samples labeled XJ and XJ_S are the deposits collected from a superheater tube surface installed in a 30 MWth pc-fired boiler for the combustion of a low-rank Xinjiang coal. Sample XJ was derived from the combustion of Xinjiang coal alone, while XJ_S was derived from the combustion of the same Xinjiang coal blended with silica additive to reduce in-furnace slagging. The other two ash samples, Hazelwood fly ash (HW) and Yallourn fly ash (YL), were collected from the ash dam in Yallourn power station located in the Latrobe Valley, Australia. The XRD patterns for these four ash deposits and their mineralogical compositions are shown in Figure S1 and Table S2, respectively, in the Supporting Information (SI). As the results show, the four samples that were tested differed
greatly in the contents of individual species. In particular, the contents of thernadite (Na$_2$SO$_4$) and other sulfates varied widely. Note that these samples are exactly the same as those that were tested in our previous work [10].

**9.2.2 Tube Corrosion Test Set – Up and Test Conditions**

A horizontal furnace was used for tube corrosion testing. The testing temperature is kept at 650 °C for all the runs, since this temperature is most critical for the worst ash deposit-related tube corrosion [12]. It is also a typical surface temperature for superheater/reheater tubes (650–700 °C) [13]. The corrosion tests were done in 50–200 h at an interval of 50 h. The flue gas tested has two different compositions for the air-firing and oxy-firing conditions. The air-firing flue gas consists of 5 vol % O$_2$, 15 vol % CO$_2$, 8 vol % H$_2$O, and 300 ppm of SO$_2$ and N$_2$ in balance. In contrast, the oxy-firing flue gas is made up of 5 vol % O$_2$, 30 vol % H$_2$O, 10 vol % N$_2$, and 1000 ppm of SO$_2$ and CO$_2$ in balance. Finally, the tube material is mainly composed of 0.065 wt. % C, 2.2 wt. % Cr, 0.07 wt. % Mo, 0.21 wt. % V, and 0.32 wt. % Si and Fe in balance. The detailed tube sample preparation, corrosion test procedure, and post-test tube cutting were explained in our previous papers [9–11].

**9.2.3 Characterization of the Surfaces of Corroded Tubes**

**9.2.3.1 Cross-section preparation and observation**

Cross-Section Preparation and Observation. The cross-section of each corroded tube was prepared by initially mounting a tube in epoxy resin in a vacuum chamber. The resultant pellet was then halved along its height. The resultant cross-section was subsequently polished by silicon carbide papers and diamond paper. The oxide layer thickness, microstructure, and composition of the oxide layer including the ash-tube interface were determined using SEM-EDX (JEOL 7001F).

**9.2.3.2 X-ray Absorption Near-Edge Spectroscopy (XANES)**

The K edge X-ray absorption near-edge spectroscopy (XANES) spectra of iron (Fe) and sulfur (S) were collected to determine the state of oxidation of these two elements on both the outer
and inner surfaces of the tube. Note that the term “outer surface” hereafter refers to the outer top surface on which the ash sample was initially loaded. After the corrosion test, the ash powders were removed carefully to expose the outer surface. The inside of a tube was achieved by polishing the outer surface with carbide paper until the entire corrosion layer was removed and the surface became shiny. Again, the details of the beamline calibration were explained in our previous papers [9–1].

### 9.3. Results and Discussion

First of all, in order to validate the accuracy of our experimental results, the tube thickness and mass gain calculated under two typical conditions were compared with the results reported in the literature (see Table 9.1). Note that there is still scant research in this area; so far, no similar study with the same tube material and the same ash samples is available. As a result, Table 9.1 is merely a qualitative reference, rather than a quantitative benchmark. For the flue gas only case (no ash), the mass change for our tube T23 after 100 h reached $\sim 30 \text{ mg/cm}^2$, which is more than two times greater than the result for tube T91 (9.0 wt. % Cr, 1.0 wt. % Mo) tested with a similar flue gas composition. This is desired, since tube T91 is much more corrosion-resistant, due to its greater content of passivation elements. Different results for mass gain were also observed for another case with ash deposit on the tube surface. Apart from the differences in the properties of ash and tube material, the mass measurement is also believed to have a relatively large error, due to the use of very small amount of sample for the test in each single run, causing reproducibility to be low. Moreover, exfoliation may cause mass loss, although the oxidation scale/layer continues to grow. In contrast, the measurement of oxide layer thickness under the microscope is more accurate and the results are more comparable. As Table 9.1 shows, the XJ ash rich in sulfates reaches a value of 0.22 mm for the oxide layer thickness of T23 after 200 h, whereas the tube thickness for tube T91 is about 0.19 mm under similar conditions. On the basis of these results, it is clear that our measurement of oxide layer/scale thickness is reasonable, and the oxide layer thickness is also more consistent with the results reported in the literature. Therefore, the oxide layer thickness is used in the discussion hereafter.
Table 9.1 Comparison with Literature Studies on Tube Mass Change and Oxide Layer Thickness upon Corrosion

<table>
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<tr>
<th>Literature</th>
<th>Reference</th>
<th>Coal</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Mode</th>
<th>Material</th>
<th>Mass change (mg/cm²)</th>
<th>Thickness of oxide layer (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. R Holcomb et al., 2012 [13]</td>
<td>No ash</td>
<td>650</td>
<td>96</td>
<td>oxy-fuel (3.6%O₂, 30%H₂O, 6.4% Ar, 60%CO₂)</td>
<td>T91</td>
<td>14.08</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Present study</td>
<td>No ash</td>
<td>650</td>
<td>100</td>
<td>oxy-fuel (5%O₂, 30%H₂O, 0.1% SO₂)</td>
<td>T23</td>
<td>30.0</td>
<td>0.137</td>
<td></td>
</tr>
<tr>
<td>G. R Holcomb et al., 2012 [13]</td>
<td>Synthetic ash (5%Na₂SO₄+5%K₂SO₄)</td>
<td>700</td>
<td>200</td>
<td>oxy-fuel (3.6%O₂, 30%H₂O, 6.4% Ar, 60%CO₂)</td>
<td>T91</td>
<td>82.0</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>Present study</td>
<td>Xinjiang ash (XJ)</td>
<td>650</td>
<td>200</td>
<td>oxy-fuel (5%O₂, 30%H₂O, 0.1% SO₂)</td>
<td>T23</td>
<td>55.0</td>
<td>0.216</td>
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</table>
9.3.1 Oxidation Rate of Tube Corrosion

The typical cross-sectional microstructures for corroded tubes under oxy-firing mode are illustrated in Figure 9.1, where the tubes exposed to flue gas only and four different ash deposits are included for comparison. Note that the oxide layer shown is representative of the scale/layer which remained mostly intact after testing. However, exfoliation was also confirmed for some cases, and the resulting spalls mixed with the ash deposit. This was not counted into the scale/layer thickness here. As shown in Figure 9.1, both the corrosion environment (i.e., flue gas only versus ash deposit) and exposure time are influential in terms of the oxide scale thickness. Regardless of the corrosion environment, the scale thickness grows stably with increased exposure time. For the flue gas only case, all the scales remain intact on the tube top. However, the presence of ash deposit causes obvious exfoliation to varying extents for the four different ash deposits. For the two ash deposits, XJ and XJ_S, collected from the combustion of the same coal with and without the addition of silica [10,14], the tube scale remains intact at 50 h and starts to fragment slightly when exposure increases to 100 h. The difference in oxide scale thickness between the two cases is also negligible. However, with the increase of exposure time to 150 h and even longer, it is clear that the addition of silica mitigates tube corrosion remarkably, since the oxide scale in the XJ_S case remains firmly attached to the tube surface, relative to the highly fragmented scale in the XJ case. The scale of the other two ash deposit cases fragments in 50 h. The extent of fragmentation also varies remarkably for these two cases with increases in the exposure time. The HW ash deposit is clearly more corrosive than the YL ash, which is also more corrosive than the XJ_S ash deposit. These changes reflect the importance of the composition of the ash deposit, which is detailed later.

On the basis of SEM pictures taken, the average thickness of the oxide layer was further calculated for each corroded tube. Moreover, based on the oxide layer thickness, the corrosion rate or the oxide layer growth rate was calculated by dividing it by the respective corrosion time. Figure 9.2 shows the results for the five scenarios tested under the oxy-firing mode. Regardless of the testing scenario, the oxide layer growth rate increases monotonously with increased exposure time. However, the increase rate of the oxide layer differs greatly among the different scenarios studied. The flue gas only shows the lowest rate of increase, followed by XJ_S, YL, XJ, and HW in ascending order. This is consistent with the qualitative observations shown in Figure 9.1.
Figure 9.3 compares the oxide layer growth rate for the two combustion modes. Similar to the oxy-fuel combustion mode, air-firing results in a monotonous growth trend for all three scenarios. In each scenario, the oxy-fuel combustion mode causes an enhanced corrosion rate, which can be partially attributed to the introduction of high concentrations of SO₂, steam, and/or CO₂ in the flue gas. However, the discrepancy of the two combustion modes varies significantly with the corrosion environment. That is, the disparity in the flue gas only scenario remains nearly constant from 50 h up to 150 h but shrinks when the exposure time is further extended to 200 h. This is possibly due to the fragmentation and spalling-off of the oxide layer which occurred for the longest exposure time. It is clear that the discrepancy is more obvious in the case of XJ ash, indicating a strong synergy between oxy-fuel flue gas components (e.g., SO₂, steam, and/or CO₂) with this ash deposit which enhances tube corrosion. In contrast, the tube corrosion rate discrepancy is much smaller and even disappears in the XJ_S case. This strongly suggests that the ash deposit property is most influential. Depending on the properties of the ash deposit, the extent of its synergistic interaction with oxy-fired flue gas varies remarkably.

The elemental mapping in Figure 9.4 illustrates an enlarged cross-section of the tube coated with XJ ash deposit (the worst-case scenario in Figure 9.3) and exposed to oxy-fuel flue gas for 200 h. The fragmentation of the tube by corrosion was further confirmed, leading to the formation of a thick oxide layer dominated by oxygen and iron. More interestingly, the abundance of sulfur (S) was also confirmed. However, it is mostly distributed on two thin strings within the oxide layer. The left-most S-rich string is located at the left edge of the entire oxide layer that is next to the tube crack. Silicon (Si) is the most abundant element in the oxide layer, which should be partially derived from the ash deposit on its top surface and partially derived from the inherent Si (0.32 wt. %) in the original tube. Si has been shown to be an efficient passivator to protect the oxidation of iron (Fe) [10]. The other two elements, sodium (Na) and calcium (Ca), exhibit much weaker signals in the oxide layer, indicating that most remain unreacted and/or react with the mobile Fe-rich fragments in the ash deposit.
Figure 9.1. Typical microstructure of cross-section of corroded tube T23 under oxy-firing conditions.
Figure 9.2. Oxide layer growth rate of tubes in oxy-fuel combustion mode.
Figure 9.3. Comparison of oxide layer growth rate for oxy-firing and air firing modes

Figure 9.4. Elemental mapping of cross-section of tube coated with XJ ash deposit and exposed to oxy-firing flue gas for 200 h. and exposed to oxy-firing flue gas in 200 h.
9.3.2 XANES Speciation of S

To validate the importance of S in tube corrosion, the synchrotron K-edge XANES spectra for this element were collected. These are shown in Figure 9.5. As panel a for oxy-fuel flue gas only shows, the peak around 2482 eV is the sole peak observed for both the outer and inside surfaces of the tubes exposed for different times. This peak is a unique feature of sulfate (SO$_4^{2-}$), which is mainly bound with Fe$^{[15]}$. The sulfate ion is also small enough to penetrate the oxide layer to react with Fe, as evident by the sole peak for sulfate inside the tubes. With the deposition of ash on the surface (see panel b), sulfate still remains as the sole S-bearing species on the outer surface, demonstrating the initial formation of sulfates of iron and even Fe–Na complexes, as confirmed previously $[9,11]$. However, another major peak at 2470 eV was also confirmed for the inside of the tubes exposed for 100 h. This peak and the others located between 2470 and 2482 eV are the unique features for sulfides $[15]$. When a sufficient amount of SO$_2$ is present in flue gas, the oxides (iron oxide) can catalyze the oxidation of SO$_2$, and hence, SO$_3$ can be formed, as shown in Eq (9.1) $[16]$. It can further react with the inherent sulfate in the ash deposit and the oxide layer (rich in Fe$_2$O$_3$) to form sulfate complexes, as per Eq (9.2). Since the sulfates are also detected inside the tubes, it is clear that these sulfates are molten and mobile for inward diffusion. More interestingly, at temperatures of 500 °C and above, the resultant trisulfate can attack the protective metal oxide, according to reaction (9.3) $[17]$. Compared with sulfate, sulfide is brittle, thus causing the fragmentation of the oxide layer and its blending into the ash deposit in the longest exposure time of 200 h. This explains a decrease in the intensity of sulfide from 150 to 200 h in panel (b). In comparison to flue gas only in panel (a), it is also evident that the reactions (9.2) and (9.3) did not take place in the absence of ash deposit.

$$SO_2 + 0.5O_2 ⇌ SO_3 \quad \text{Eq. (9.1)}$$

$$3Na_2SO_4 + 3SO_3 + Fe_2O_3 \rightleftharpoons 2Na_3Fe(SO_4)_{3(s,l)} \quad \text{Eq. (9.2)}$$

$$2Na_3Fe(SO_4)_3 + 19Fe \rightleftharpoons 6Fe_3O_4 + 3FeS + 3Na_2S \quad \text{Eq. (9.3)}$$
9.3.3 Correlation of Oxide Layer Thickness and Ash Species

As confirmed by the microstructural observations, the penetration of oxygen and SO$_2$ in flue gas into a tube is the most influential factor affecting the growth of oxide layer and thus the wastage of the tubes. These two oxidants interplay rather than compete with each other, accelerating tube wastage. However, the ash deposit is clearly more influential. The oxide in the ash deposit may catalyze the dissociation of the bulk oxidants, including O$_2$, CO$_2$, and even steam, to produce the respective O radicals. In general, the dissociation of bulk oxygen is facilitated by alkali and alkaline earth (Na, K, Ca, Mg) metal oxide acting as the oxygen-shuttling agent via the redox reaction swing [14]. Since the creeping of S was not observed in the flue gas only case, the S in fly ash should be the principal source for the formation of sulphation/sulphidation across the oxide layer. It is possible that the sulfates in ash directly

Figure. 9.5. S K edge XANES spectra. (a) Oxy-fuel flue gas only. (b) HW ash deposit for tube inside (red) and outer surfaces (solid black).
interact with the iron metal as depicted in Eq (9.2) or via the Eq (9.3) that is the combination of alkali sulfates, \( \text{SO}_3 \) (derived from the gas-phase reaction of \( \text{SO}_2 \) and \( \text{O}_2 \)), and iron oxide (\( \text{Fe_2O_3} \)) [17].

**Figure 9.6** presents a positive correlation between the contents of \( \text{SO}_3 \), \( \text{Na}_2\text{O} \), and \( \text{CaO} \) in the original ash deposit and their respective amounts deposited firmly on the corroded tube surface. Again, the loose ash deposits were removed carefully prior to the quantification of the tube top surface by XRF. Regardless of the exposure time and elemental type, it is evident that the content of each of these elements increases nonlinearly as a function of its original content in ash deposit. \( \text{S} \) is the most abundant element on the tube surface, and its concentration on tube surface rises quickly with the change of ash deposit from XJ_S with the least \( \text{S} \) to YL at around 8 wt. % \( \text{SO}_3 \). Subsequently, its content almost levels off with a further rise of the original content of \( \text{S} \) in the ash deposit. This is particularly the case for exposures longer than 100 h. Clearly, a partitioning equilibrium exists between \( \text{S} \) in the original ash and the amount that can transfer into and be adsorbed by the oxide layer on the tube surface. A similar phenomenon was confirmed for the other two elements, \( \text{Na} \) and \( \text{Ca} \). However, their concentrations in the oxide layer are extremely low, accounting for a maximum of 1.2−1.6 wt. % even after exposure of 200 h. This implies that the sulfide is mainly in the form of iron sulfide in the corroded tube.
Figure. 9.6. Effect of ash properties on tube corrosion, SO$_3$ panel (a), Na$_2$O panel (b) and CaO panel (c)
9.3.4 Oxidation Kinetics

the oxidation rates for different scenarios. In general, the change on the tube scale thickness, \( x \) over time \( \frac{dx}{dt} = f(t) \) can be simplified based on the control step. In the case where the external diffusion of oxidizing gases is relatively slow compared to its internal diffusion and the phase boundary reaction rate, the entire oxidation rate can be expressed as \[18\].

\[
\frac{dx}{dt} = k_1 \quad \text{Eq. (9.4)}
\]

Eq. (9.4) can be integrated to yield

\[
X = k_1 t \quad \text{Eq. (9.5)}
\]

where \( k_1 \) is the linear rate constant with a unit of cm\(^2\)/h, and the integration constant is based on the assumption that \( X = 0 \) at \( t = 0 \) \[18\]. Under these conditions, diffusion inside the oxide scale can be so rapid that it makes no contribution to rate control.

In the case where internal diffusion is the control step, the overall rate of growth of the oxide scale is limited by the diffusion through the scale, following a parabolic equation \[19\].

\[
\frac{dx}{dt} = \frac{k_p}{x} \quad \text{Eq. (9.6)}
\]

\[
X^2 = 2k_p t \quad \text{Eq. (9.7)}
\]

where \( k_p \) is the parabolic rate constant with a unit of cm\(^2\)/h, and one initial condition solving these two equations is \( x = 0 \) at \( t = 0 \). If the data do not fit the parabolic rate law well, there may be defects such as voids in the protective oxide scale. Parabolic time dependence has been observed elsewhere \[20\].

In some cases, both diffusion and phase boundary reaction could control the overall oxidation rate, as the diffusion is initially rapid and slows down upon the increase on the scale thickness. Therefore, when the scale is thin, the scaling rate predicted from Eq (9.6) is faster than the experimental observation. However, as the scale thickens, the diffusion rate eventually decreases until it becomes slower than the constant phase boundary rate. Simultaneously, the
phase boundary process then approaches a local equilibrium. Therefore, the observed kinetics will be initially linear and subsequently parabolic, as evident by a study on the fitting of corrosion kinetics by a parabolic law at 650 °C and up to 200 h. This behaviour has been detailed elsewhere [3] and is simplified by the following rate equation (9.8).

\[ X^2 + LX = k_t + C \]

Eq. (9.8)

where L and C are the correlation constants. The symbol \( k_t \) denotes the overall diffusion coefficient while the value of L represents the reaction kinetic coefficient.

Figures 9.7 and 9.8 show the curve fittings for all the cases under the oxy-firing mode and air-firing mode, respectively. Panel (a) in each figure refers to a linear fitting of the oxide scale thickness x versus time t, as per Eq (9.5) panel (b) refers to a linear fitting of thickness square \( x^2 \) versus time t, as per Eq (9.7), while panel (c) refers to a polynomial fitting of x versus t, as per Eq 9.8. The correlation coefficients of \( R^2 \) for the fittings are listed in Tables 9.2 and 9.3 for Figures 9.7 and 9.8, respectively. Clearly, regardless of the existence of ash deposit, ash deposit type, and flue gas composition, the overall oxidation rate is controlled by both diffusion and the phase boundary reaction, as evident by the largest correlation coefficients which are mostly close to unity. Moreover, the diffusion should be mainly external diffusion for the oxidizing gases through the ash deposit or the gas film formed on the outer surface of the oxide scale, as evident by the relatively large correlation coefficient for the linear fitting between the oxide layer thickness versus exposure time in panels (a). This is consistent with Figures 9.2 and 9.3 which show a rapid increase in the oxide layer growth rate in the initial 50–100 h. Since the oxide layer is relatively thin, gas diffusion through the ash deposit dominates. With a further increase in the exposure time, the oxide scale grows thicker and hence, diffusion slows and reaches a local equilibrium as per Eqs (9.1) – (9.3). This is reflected by the relatively flat increase in the tube thickness growth rate from 150 h in Figures 9.2 and 9.3.

On the basis of the best fitting in Figures 9.7 and 9.8, efforts were then made to extract the diffusion coefficient (\( K_t \)) and the phase boundary reaction kinetic constant (L) for each case. Table 9.4 lists all the calculated values, while Figure 9.9 depicts the correlation between these two values versus the content of S (in terms of \( SO_3 \) in the ash deposit) on the x-axis, where the initial value of zero refers to the flue gas only case. The content of S in ash was taken as the
principal variable, since it is the most abundant element found in tube oxide scale, as evident in the previous section. Interestingly, the gas diffusion coefficient through ash deposit in panel a is independent of the flue gas composition. This is consistent with the fact that ash deposit is more influential in affecting the penetration of sulfur within the oxide scale in Figure 9.5. In another sense, the reaction rate of Eq 9.1 for the formation of SO$_3$ is not the rate-limiting step for tube corrosion or even independent of the partial pressure of SO$_2$ in flue gas. More interestingly, a reverse linear trend was observed for the dependence of $K_t$ on the content of S in ash. This is because more molten sulfates can be formed with the increase of S content in ash, as per the Eqs 9.2 and 9.3, which in turn makes it more difficult for the gases to diffuse through it. In contrast, the reaction kinetic constant, L, remains constant across all the ash samples, regardless of the S content. This holds true as the reaction rate for a solid-to-solid reaction proposed in Eqs 9.2 and 9.3 is independent of the solid ash properties.
Figure 9.7. Oxy-firing tube corrosion mechanisms and kinetic modeling. (a) Controlled by diffusion outside oxide scale. (b) Controlled by diffusion inside scale. (c) Diffusion and boundary phase reaction.
Figure 9.8. Air-firing tube corrosion mechanisms and kinetic modeling. (a) Controlled by diffusion outside oxide scale. (b) Controlled by diffusion inside scale. (c) Diffusion and boundary phase reaction.
Table 9.2 Correlation Coefficients for Fittings in Figure 9.7

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<th>Sample</th>
<th>Diffusion Control</th>
<th>Diffusion and Reaction Control</th>
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<tr>
<td></td>
<td>Outside ($R^2$)</td>
<td>Inside ($R^2$)</td>
</tr>
<tr>
<td>No ash</td>
<td>0.9600</td>
<td>0.7663</td>
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<tr>
<td>XJ</td>
<td>0.9552</td>
<td>0.7270</td>
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<td>XJ-S</td>
<td>0.9651</td>
<td>0.7610</td>
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<tr>
<td>YL</td>
<td>0.9553</td>
<td>0.7238</td>
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<td>HW</td>
<td>0.9602</td>
<td>0.7302</td>
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Table 9.3 Correlation Coefficients for Fittings in Figure 9.8

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<th>Diffusion Control</th>
<th>Diffusion and Reaction Control</th>
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<td>Outside ($R^2$)</td>
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<td>No ash</td>
<td>0.9523</td>
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<td>XJ-S</td>
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Table 9.4 Diffusion Coefficient (K) and Kinetic Reaction Coefficient (L) Values for Both Oxy-Fuel and Air-firing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air-Firing K (cm$^2$/sec)</th>
<th>Air-Firing L (cm$^2$/sec)</th>
<th>Oxy-Fuel K (cm$^2$/sec)</th>
<th>Oxy-Fuel L (cm$^2$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ash</td>
<td>1.90 x 10^{-3}</td>
<td>5.9 x 10^{-5}</td>
<td>2.1 x 10^{-3}</td>
<td>8.4 x 10^{-5}</td>
</tr>
<tr>
<td>XJ</td>
<td>1.5 x 10^{-3}</td>
<td>7.3 x 10^{-5}</td>
<td>1.6 x 10^{-3}</td>
<td>8.6 x 10^{-5}</td>
</tr>
<tr>
<td>XJ-S</td>
<td>1.0 x 10^{-3}</td>
<td>4.9 x 10^{-5}</td>
<td>1.1 x 10^{-3}</td>
<td>6.4 x 10^{-5}</td>
</tr>
<tr>
<td>YL</td>
<td>-</td>
<td>-</td>
<td>1.0 x 10^{-3}</td>
<td>6.3 x 10^{-5}</td>
</tr>
<tr>
<td>HW</td>
<td>-</td>
<td>-</td>
<td>9.1 x 10^{-4}</td>
<td>7.4 x 10^{-5}</td>
</tr>
</tbody>
</table>

Figure 9.9. Kinetic coefficients vs sulfur content in original ash sample. (a) K values vs SO$_3$ content in original ash sample. (b) L values vs SO$_3$ content in original ash sample upon oxy-fuel and air-firing reaction
9.4. Conclusions

This research was designed to facilitate the generation of oxide scale thickness and its growth rate for use in the life assessment of low ferritic chromium tubes in conventional air-firing and advanced oxy-fuel combustion technologies. The oxide growth rate of T23 was investigated at a metal surface temperature of 650 °C for up to 200 h. The major conclusions are as follows:

1. The aggressive flue gases formed under oxy-firing conditions enhanced T23 tube corrosion but to a marginal extent compared with the S-rich ash deposit. Kinetic simulation confirmed that both the coefficients of gas diffusion and the boundary phase reaction rate are constant for the two different combustion modes, demonstrating that the formation of sulfur trioxide (SO$_3$) from the reaction of SO$_2$ and O$_2$ in flue gas is not rate-limiting and is also independent of the partial pressures of these two gas components in flue gas.

2. A positive correlation was found between the sulfur content in ash deposit and oxide scale thickness. The sulfate in ash deposit promoted the formation of molten and mobile sulfate complex and sulphides. The former species are predominant on the tube outer surface, while sulphide is preferentially formed inside the tube where oxygen is lean and/or absent.

3. The oxide scale growth rate or oxidation rate is controlled by both diffusion and phase boundary reactions. Regardless of the combustion mode, the gas diffusion coefficient decreases with increased sulfur content in the ash deposit, due to the enhanced formation of molten sulfates on the oxide layer. In contrast, the phase boundary reaction rate constant remains unchanged with increased sulfur content in ash deposit, mainly because the solid-to-solid reactions for the formation of molten sulfates and sulfides are independent of the solid ash properties.
Chapter 9 Kinetic Study of Long-Term T23 Tube Corrosion

References

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CHAPTER 10

Conclusions and Recommendations for Future Work
This chapter provides summaries and major conclusions that are derived from prior working chapters in this thesis, and also provides recommendations for future works.
Chapter 10 Conclusions and Recommendations for Future Work

10.1 Conclusion and Innovation of Research

The main aim of this study is to develop a greater understanding of the high-temperature tube corrosion mechanisms related to the distinctive flue gas and fly ash depositions formed during the oxy-fuel combustion of low rank coal.

This research study is innovative in terms of the approaches, methods and techniques. Firstly, using Synchrotron-based X-ray fluorescence (SXRF) and μ-XANES to detail the spatial distribution of individual elements in the corrosion products. In addition, we have carried out modelling study and kinetic study as well.

This is a comprehensive tube corrosion study on low rank coal in oxy firing conditions. This study has provided a good understanding of high temperature tube corrosion mechanisms and has also provided ways to reduce tube corrosion in oxy-firing combustion, which is elucidated in the following sub-sections.

10.1.1 Tube Corrosion upon the Victorian Brown Coal Ash Deposition

This work has examined the tubes exposed to Victorian brown coal fly ash under the oxy-fuel combustion mode has been examined. The temperature of 650 °C, flue gas composition (steam 30 vol%, O₂ 5%, SO₂ 3000 ppm, HCl 1000 ppm, N₂ 5% and CO₂ balanced), and an exposure time of 50 h were employed. It was found that the tube corrosion in oxy firing combustion is more serious than that in the air-firing combustion. The use of advanced material (stainless steel), SUS347, was found to be the most suitable candidate for heat-exchange tubes to be used in the oxy-firing boiler when burning low-rank coal such as Victorian brown coal which is rich in alkali and alkaline earth metals.

10.1.2 Effect of Silica Additive on the High-Temperature Fireside Tube Corrosion

This work has examined the flue gas-related tube corrosion rate, the role of fly ash deposit and the inhibitory effect of silica additive under both air-firing and oxy-firing conditions of six tubes from carbon steel SS400 to high-Cr-Ni austenitic steel SUS347 under the fixed exposure conditions, i.e. 650 °C 50 h it was found the addition of silica to coal resulted in a sulphur - lean fly ash deposit, and therefore, mitigated the tube corrosion rate down to the same level as the flue gas only case.
10.1.3 Influence of Gaseous SO$_2$ and Sulphate-Bearing Ash Deposits

This work aims to investigate the corrosive behaviour of selected tubes with different Cr content and coated with lignite ash deposits during the oxy-fuel combustion. The corroded tube’s surface and the used ash samples were characterized by using X-ray Absorption Spectroscopy (XAS). Thermodynamic equilibrium calculations were also conducted to elucidate the experimentally observed phenomena. It was found that tube corrosion can be significantly mitigated by coal washing which reduces Sulphur content in tubes. Tube T91 was the only tube on which the sulphide was formed because its protective layer was porous enough for the gases to permeate and to form a reducing environment to promote the formation of sulphide inside the tube.

10.1.4 SXRF and $\mu$-XANES Characterization of Cr upon the Co-Existence of Ca-Rich Ash Deposits

This work explores the effects of lignite ash deposit, in particular the Ca-bearing species in ash on the tube corrosion under the oxy-firing mode. Two tubes, low-alloy steel T23 and austenite SUS347 have been coated with two ash deposits and exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The roles of Ca-bearing species including sulphate, free oxide/calcite have been first time revealed by using synchrotron-based X-ray fluorescence (SXRF) and $\mu$-XANES to detail the spatial distribution of individual elements, and in particular the speciation of Cr on the cross-section of tubes. It was found that carburization of Cr by CO$_2$ is inhibited remarkably upon the co-existence of flue gas and ash deposit.

10.1.5 SXRF and $\mu$-XANES Characterization of Cr Species in Flue Gas Only

In this work, Synchrotron X-ray fluorescence mapping and $\mu$-XANES were employed to characterize the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that were exposed to oxy-fuel flue gas at 650 °C, 1 bar for 50 h. It was found that the use of Cr, even at a low concentration of 1.2 wt. % in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion rate, as well as minimize the difference between oxy-fuel and air-firing flue gases on the tube mass loss rate.
10.1.9 Tube Oxidation Kinetics and Modelling

This work focused on study the kinetics for the tube corrosion rate and the rate-limiting step under the oxy-fuel combustion mode. Four different types of fly ashes were used (HW, YL, XJ, and XJ_S). One alloy such as (low chromium ferritic alloy T23) was selected for ultra-supercritical boilers, to investigate the corrosion tests under oxy-fuel conditions at a metal temperature of 650 °C. The specimens were exposed for long term tests: 50, 100, 150 and 200 h and fixed flue gas compositions. Apart from the combustion of the raw lignite, the combustion of coal mixed with 4 wt. % of a silica-based additive for the inhibition of the high-temperature corrosion was also conducted to investigate the influence of silica on the high-temperature corrosion resistance. Oxidation kinetic modeling under oxy-fuel combustion vs. air-firing mode has also been conducted to clarify the controlling steps for tube corrosion. Under the oxy-firing conditions, the tube corrosion growth rate was found to be controlled by both diffusion and phase boundary reactions.

10.2 Recommendations for Future Work

This research was based on the fundamental science of high temperature tube corrosion upon oxy-fuel combustion for low rank coal, especially Victorian brown coal. An innovative examination has been conducted to understand the mechanisms and the kinetics of high temperature tube corrosion. The following is a list of possible studies that are recommended for further research.

10.2.1 Testing of the Ni – Based Inconel Alloy

The alloy element Ni has good corrosion resistance. Therefore, the past research and engineering practice tell us that austenitic stainless steel TP347H is more resistant to corrosion than low-nickel steel such as 12Cr1MoVG or T91 due to its high alloy element chromium and nickel. In this thesis, the corrosion resistance mechanism and properties of alloy element Cr are systematically studied, while the corrosion resistance mechanism and properties of Ni are seldom systematically studied. It is suggested that systematic research in this field be carried out in the future. Ni alloys is generally favored, which is used for A-USC boilers: 700 – 760°C and up to 35 MPa steam inside. Inconel Alloy 740H: is high strength, high creep resistance, rupture strength, and large resistance to coal ash corrosion. It consists of Cr 23-25%, Co 15-20%, Al 0.2-2%, Nb 0.5-2.0%, Ni Bal. This alloy is highly recommended for boiler design in future work.
10.2.2 Tube Cladding/Coating/Thermal Spray

Thermal sprayed coatings can be the most cost-effective means of protecting substrate surfaces from wear or corrosion. This process produces high-performance surfaces with absolutely no risk of distortion or metallurgical changes to the component. The use of MCRAIL (metal, chromium, aluminium and yttrium) on steels or alloy substrates. This method is used to avoid Type I hot corrosion (850 - 950°C) where corrosion occurs through reaction with salts deposited from the vapour phase (from impurities in the fuel). Molten sulphates flux the oxide scales, and the microstructure is characterised by non-protective scales, extensive internal sulphidation and a depletion zone of scale-forming elements.

10.2.3 Long Term (up to 500 h) Testing at Different Temperatures

In this study, short term (200hr) tests at up to 650 degree were conducted, and future works can consider conducting long-term tests for up to 500hrs and a variety of wall temperature. The upshift of heat from the combustion zone increases the temperature rise on the superheater zone.
Appendix A

Supplementary Information of Chapter 4
Appendix A Supplementary Information of chapter 4

Contents

1. Experimental set-up and photos for the fresh and corroded tube surfaces
2. Fitted XRD patterns for corroded tube exposed to Hazelwood fly ash under oxy-fuel combustion vs. air firing mode
3. Experimental set-up and the XANES spectra for blank tubes and fitting results for blank tubes exposed to Hazelwood fly ash under oxy-fuel combustion vs. air firing mode.
1. Experimental set-up and photos for the fresh and corroded tube surfaces

A horizontal test furnace was used, and its schematic diagram is shown in Figure S1. The temperature in furnace is fixed to mimic post-combustion flue gas temperature with a range of 500-800°C, which is similar with the conditions near super-heater and re-heater in an industrial furnace. For each run, the ash sample were placed on the square specimen (plate) made of typical steels to mimic the ash deposition on a real steam tube surface. The ash specimens are located on a quartz-made sample holder inside the corrosion furnace, shown in panel (a). Panel (b) illustrates the gas control system (at furnace entry) and flue-gas analyzer system (at furnace rear) connected with furnace. There is a thermocouple to record the on-line temperature for the specimen. All ash specimens were tested under 50 h exposure for the tube surface corrosion.

Photographs of lab-scale bench are further illustrated in Figure S2, including (1) horizontal furnace outlook, (2) gas inlets (including steam nozzle), (3) sample holder and thermal couple, (4) The fresh specimen before the test. Photos for the ash-coated tube specimen, before and after the tests, are further illustrated in Figure S3.

![Figure S1](image1.png)

**Figure S1** Schematic diagrams of the hot corrosion furnace (a) samples and sampler holder inside the furnace; (b) Gas pipelines for the exposure time
Figure S2 Photographs of key parts of the corrosion test facility

Figure S3 Ash-coated tube specimens before and after the corrosion test
2. Fitted XRD patterns for corroded tube exposed to Hazelwood fly ash under oxy-fuel combustion vs. air firing mode

**Figure. S4** XRD Spectra for the corroded tubes exposed to Hazelwood fly ash under oxy-fuel combustion (a: Hematite (Fe$_2$O$_3$); b: Magnetite (Fe$_3$O$_4$); c: Maghemite (Fe$_2$O$_3$); d: Eskolaite (Cr$_2$O$_3$)).

**Figure. S5** XRD Spectra for the corroded tubes exposed to Hazelwood fly ash under air-firing combustion (a: Hematite (Fe$_2$O$_3$); b: Magnetite (Fe$_3$O$_4$); c: Maghemite (Fe$_2$O$_3$); d: Eskolaite (Cr$_2$O$_3$); e: Pyrrhotite (FeS); f: Wuestite (FeO); g: Ferric tungstate (Fe$_2$WO$_6$))
3. Experimental set-up and the XANES spectra for blank tubes and fitting results for blank tubes exposed to Hazelwood fly ash under oxy-fuel combustion vs. air firing mode.

The K-edge XANES spectra of Fe the cross-section of tube surface was obtained from beam line BL16A1 at the National Synchrotron Radiation Research Centre (NSRRC). The resin-mounted tube specimen holder with respect to the XANES analysis, a fixed exit double crystal Si (111) monochromators was used for the diffraction of the X-ray beam. For the analysis of Fe, pure elemental Fe was used for the calibration at a K-edge absorption energy of 7112 eV. The peak energy absorption (white-line) position was taken as the base (0 eV), with all subsequent spectra recorded 200 eV below and 800 eV above this point in fluorescence mode. The pre-edge scan was conducted from -200 eV to -20 eV, at a step of 2 eV and 1 s per step. Following it is the scan from -20 eV to 40 eV at a step of 0.25 eV and 2 s per step. The final step spanned from 40 eV to 800 eV, with a step of 0.06 eV and 4 s per step. For the XANES analysis of the cross-section of a tube surface, 3-5 spots along its cross-section were tested. As visualized in Figure S6, five spots examined for a tube cross-section include, bulk material (the centerline of the tube), bottom (interfacial surface caused by corrosion between ash and tube), middle (between interface and the center of the tube), bottom opposite (the surface exposed to flue gas side), and middle opposite (between flue gas side interface and tube center). The spectra for different tubes exposed to HW fly ash are shown in Figures S7 and S8 for oxy-firing and air-firing mode, respectively.

The standards were chosen include pure iron metal (Fe), hematite (Fe₂O₃), maghemite (Fe₂O₃), magnetite (Fe₃O₄), augite (NaFeO₂), wusetite (FeO), siderite (FeCO₃), ferrous sulphate (FeSO₄) and ferrous chloride (FeCl₂). All spectra were normalized using the ATHENA software (normalization order of 2, pre-edge range normalization range of -192 eV to -30 eV and post-edge range of +77.5 eV to +281 eV). Subsequently, the linear combination fitting (LCF) feature was used on the normalized sample spectra for the quantification of iron speciation. The LCF was done from -20 eV to +50 eV with respect to the peak energy absorption (white line) position (~7122 eV).
Figure S6 Visualized locations for the five spots examined along the cross-section of the tube.

Figure S7 XANS spectra and fitting results for the interfacial layer of tubes exposed to HW fly ash in oxy-firing mode.
**Figure. S8** XANS spectra and fitting results for the interfacial layer of tubes exposed to HW fly ash in air-firing mode.
Appendix B

Supplementary Information of
Chapter 5
Content

1. Original and fitted XRD patterns for two fly ash samples (Table S1 and Figure S1);
2. XRD patterns for the tubes SS400, T23 and SUS304 exposed to pure air/CO₂, flue gases and ash deposition (Figures S2-S4);
3. XRD patterns for the six tubes coated with XJ ash and XJ_S ash in air firing mode and oxy-firing mode (Figure S5) (Figure S6), and summary of the top two strong peaks in Table S2.
4. Detailed methodology for the quantitative XANES analysis (Figure S7).
1. Original and fitted XRD patterns for two fly ash samples (Table S1 and Figure S1);

Table S1 Chemical compositions of the two ash deposits.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>XJ</th>
<th>XJ S</th>
</tr>
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<tr>
<td>Gypsum (CaSO₄(H₂O)₂)</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Anhydrite (CaSO₄)</td>
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<td>3.1</td>
</tr>
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<td>Bassanite (2CaSO₄·H₂O)</td>
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<td>0</td>
</tr>
<tr>
<td>Glauberite (Na₂Ca(SO₄)₂)</td>
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<td>2.6</td>
</tr>
<tr>
<td>Thenardite (Na₂SO₄)</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>Marialite (Na₂SO₄·10H₂O)</td>
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<td>Periclase (MgO)</td>
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<td>1</td>
</tr>
<tr>
<td>Lime (CaO)</td>
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</tr>
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<td>Calcite (CaCO₃)</td>
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<td>1</td>
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<td>0</td>
</tr>
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<td>0</td>
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<td>0</td>
</tr>
<tr>
<td>Gehlenite (Ca₂(Al(Si, Al)₂O₇)</td>
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<td>1.3</td>
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<tr>
<td>Merwinite (Ca₃Mg(SiO₄)₂)</td>
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<td>2.4</td>
</tr>
<tr>
<td>Amorphous amount</td>
<td>70</td>
<td>82</td>
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</table>
Figure S1 XRD patterns for XJ_S (a) and XJ ash (b) deposits, with another two ashes Hazelwood fly ash (c) and Yallourn fly ash (d) for comparison.
2. XRD patterns for the tubes SS400, T23 and SUS304 exposed to pure air/CO$_2$, flue gases and ash deposition (Figures S2-S4);

Figure S2 XRD patterns for the outer surface of the carbon steel tube SS400 exposed to (a) pure air or CO$_2$, (b) flue gas only, (c), coated with XJ ash, and (d) coated with XJ_S ash.
Figure S3 XRD patterns for the outer surface of the low-alloy tube T23 exposed to (a) pure air or CO₂, (b) flue gas only, (c), coated with XJ ash, and (d) coated with XJ_S ash.
Figure S4 XRD patterns for the outer surface of the high–Cr austenitic tube SUS304 exposed to (a) pure air or CO$_2$, (b) flue gas only, (c), coated with XJ ash, and (d) coated with XJ_S ash.
3. XRD patterns for the six tubes coated with XJ and XJ_S ash in air-firing and oxy-firing mode (Figure S5), (Figure S6), and summary of the top two strong peaks in Table S2.

Figure S5 XRD patterns for the tube specimen exposed to the different ashes in the air-firing mode.
**Figure S6** XRD patterns for the tube specimen exposed to the different ashes in the oxy-firing mode.
Table S2 The top three most intense species on the outer surfaces of the corroded tubes with the coating of ash deposits, determined by XRD in Figures S5 and S6

<table>
<thead>
<tr>
<th>Ash type</th>
<th>First - peak</th>
<th>Second - peak</th>
</tr>
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<tbody>
<tr>
<td>SS400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XJ ash</td>
<td>Hematite (Fe₂O₃)</td>
<td>Iron (Fe)</td>
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<tr>
<td>XJ_S ash</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Iron (Fe)</td>
</tr>
<tr>
<td>12Cr1MoVG</td>
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<td></td>
</tr>
<tr>
<td>XJ ash</td>
<td>Stainless steel (Fe-Cr)</td>
<td>Chromium oxide (Cr-O)</td>
</tr>
<tr>
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<td>Stainless steel (Fe-Cr)</td>
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</tr>
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<td>T23</td>
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<tr>
<td>XJ ash</td>
<td>Wüstite (FeO)</td>
<td>Stainless steel (Fe-Cr)</td>
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<tr>
<td>XJ ash</td>
<td>Stainless steel (Fe-Cr)</td>
<td>Chromium oxide (Cr-O)</td>
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<td>Stainless steel (Fe-Ni)</td>
<td>Magnetite (Fe₃O₄)</td>
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<td>SUS304</td>
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<tr>
<td>XJ ash</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Chromium oxide (Cr-O)</td>
</tr>
<tr>
<td>XJ_S ash</td>
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<td>SUS347</td>
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<td>Chromium oxide (Cr-O)</td>
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<tr>
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Oxy-firing flue gas

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<tr>
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<td>Iron (Fe)</td>
</tr>
<tr>
<td>XJ_S ash</td>
<td>Iron (Fe)</td>
<td>Magnetite (Fe₃O₄)</td>
</tr>
<tr>
<td>12Cr1MoVG</td>
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<td></td>
</tr>
<tr>
<td>XJ ash</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Chromium oxide (Cr-O)</td>
</tr>
<tr>
<td>XJ_S ash</td>
<td>Iron chromium oxide (Fe₉Cr₉O₈)</td>
<td>Eskoliate (Cr₂O₃)</td>
</tr>
<tr>
<td>T23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>XJ ash</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Chromium oxide (Cr-O)</td>
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<td>SUS304</td>
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<td>Iron chromium oxide (Fe₉Cr₉O₈)</td>
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<td>SUS347</td>
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<tr>
<td>XJ ash</td>
<td>Magnetite (Fe₃O₄)</td>
<td>Chromium oxide (Cr-O)</td>
</tr>
<tr>
<td>XJ_S ash</td>
<td>Iron chromium oxide (Fe₉Cr₉O₈)</td>
<td>Eskoliate (Cr₂O₃)</td>
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4. Detailed methodology for the quantitative XANES analysis

X-ray Absorption Near-Edge Spectroscopy (XANES) arises from the excitation of core electrons to higher electronic states and provides information about oxidation state and coordination symmetry. The edge energy tends to shift to higher energy with increasing oxidation state and the spectral shape tends to vary with different coordination symmetry. XANES is a qualitative fingerprinting technique: by comparing spectra with those measured from known compounds it is possible to deduce symmetry and oxidation state [1,2]. XANES is the best available technique for in situ examination of metal speciation and associations in complex environmental media, has proven to be a powerful tool for critically characterizing the local atomic configuration as well as electronic state of absorbing atoms in materials of crystalline, amorphous, and liquid phases at ambient or high-pressure environment [3,4]. Analysis of XANES allows for the characterization of samples containing low concentrations of elements and for the determination of the chemical structure and association of elements involved.

Data reduction of the XAS spectra involves energy calibration, background subtraction and normalization. The final quantification performs involves the use of linear combination fitting (LCF) method by a commercial software Athena that was developed specifically for XANES data process [5,6]. LCF is a method for the quantification of oxidation states. LCF reconstructs the sample spectrum using a combination of selected model spectra via least-square fitting, and reports goodness of fit parameters (R-factor and reduced $\chi^2$) along with the percent that each model contributes to the fit. Each sample spectrum was fitted to the maximum number of standard spectra; the combination of standards that resulted in the best fit (smallest R-factor and reduced $\chi^2$) was chosen as the most likely representation of the sample. Combination that explained less than 5% of the fit were not considered.

The standards for Fe speciation include pure iron metal (Fe), hematite ($\text{Fe}_2\text{O}_3$), maghemite ($\text{Fe}_2\text{O}_3$), magnetite ($\text{Fe}_3\text{O}_4$), augite (NaFeO$_2$), wüstit (FeO), siderite (FeCO$_3$), ferrous sulphate (FeSO$_4$), ferrous chloride (FeCl$_2$) and pyrite (FeS$_2$) that have been collected previously by us at the same beamline [7,8]. The standards for S include ferrous sulphate (FeSO$_4$), and pyrite (FeS$_2$), whereas the standards for Cr include pure metal (Cr), eskolaite (Cr$_2$O$_3$), Cr-Fe spinel (FeCr$_2$O$_4$), magnesium chromite, Cr sulphate, Cr chloride, and Na chromate (Na$_2$CrO$_4$) collected from our previous works [9].
Figure S7 shows the components (hematite, magnetite, maghemite and metallic Fe) that were used in a least squares linear combination fit (dashed line) to the sample spectrum (solid line). So, we can see clearly how molar fractions are measured from the raw experimental data. In previous work we used the standard component which has confirmed the accurate of this method [10,11]. It is also noteworthy that, the peak-fitting method is also used for the quantification. However, the peak-fitting method generally overlooks the trail of the major peaks. Accordingly, its accuracy is not very high. In our past study on the speciation of sulphur by XANES, we have proven the accuracy of LCF method over the conventional peak-fitting method [12].

![Figure S7](image)

**Figure S7** Fe K-Edge XANES spectra of the cross-section of T23 tube exposed to XJ_S fly ash under oxy-fuel mode and the reference standards used for the LCF fitting.
References

Appendix C

Supplementary Information of Chapter 6
Content

1- SEM photographs of tubes (a) 12Cr1MoVG, (b) T91 and (c) SUS304 coated with washed fly ash sample W1 upon oxy-fuel combustion mode
1. Scanning Electron Microscopy (SEM) of tube 12Cr1MoVG, T91 and SUS304 coated with fly ash sample W1, upon oxy-fuel combustion mode.

**Figure S1** SEM photographs of tubes (a) 12Cr1MoVG, (b) T91 and (c) SUS304 coated with washed fly ash sample W1 upon oxy-fuel combustion mode
Appendix D

Supplementary Information for Chapter 7
Content

1  XRD patterns for ash deposits
2  Cr K-edge XANES spectra for standards
1. XRD patterns for ash deposits

XRD analysis was conducted under the conditions of 40 kV voltage and 15 mA current, scanning speed of 1°/ min with a step size of 0.01° and the wavelength of 0.15418 nm for Cu – alpha. The instrument used is Rigaku Miniflex 600. The peak identification was achieved by search-match function in the JADE software. Moreover, each sample was also mixed with 20 wt.% high-purity corundum (Al₂O₃) as an internal standard to quantify the content of amorphous species. The method has been detailed in our previous work [1].

![XRD patterns for the two ash deposits. Panel (a) is raw XJ fly ash and (b) is for the XJ_S ash deposit. Copy right from our previous work published in Fuel, Elsevier [2]](image)

Figure S1 XRD patterns for the two ash deposits. Panel (a) is raw XJ fly ash and (b) is for the XJ_S ash deposit. Copy right from our previous work published in Fuel, Elsevier [2]
2. Cr K-edge XANES spectra for standards

![Cr K-edge XANES spectra for standards](image)

**Figure S2** Cr K-edge XANES spectra for a variety of Cr-bearing standards used in this study

**References**


Appendix E

Supplementary Information for Chapter 9
Content

1- XRD patterns for original and fitted patterns.
2- Experimental set-up of corrosion test.
1. Original and fitted XRD patterns for two fly ash samples (Table S1 and Figure S1);

Figure S1 XRD patterns for XJ_S (a) and XJ ash (b) deposits, with another two ashes Hazelwood fly ash (c) and Yallourn fly ash (d) for comparison
### Table S1 Mineralogical compositions of the four fly ash samples, wt. % in total ash, determined by quantitative XRD

<table>
<thead>
<tr>
<th></th>
<th>Xinjiang coal fly ash, no clay (XJ)</th>
<th>Xinjiang coal fly ash, with clay (XJC)</th>
<th>Hazelwood fly ash (HW)</th>
<th>Yallourn fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gypsum (CaSO₄(H₂O)₂)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Anhydrite (CaSO₄)</td>
<td>2.2</td>
<td>3.1</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>Bassanite (2CaSO₄·H₂O)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Glauberite (Na₂Ca(SO₄)₂)</td>
<td>3.4</td>
<td>2.6</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td><strong>Thenardite (Na₂SO₄)</strong></td>
<td><strong>4.0</strong></td>
<td><strong>1.5</strong></td>
<td><strong>2.0</strong></td>
<td><strong>0.385</strong></td>
</tr>
<tr>
<td>marialite (Na₂SO₄·10H₂O)</td>
<td>1.9</td>
<td>0.0</td>
<td></td>
<td></td>
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<tr>
<td>Periclase (MgO)</td>
<td>3.4</td>
<td>1.0</td>
<td>23.2</td>
<td>2.77</td>
</tr>
<tr>
<td>lime (CaO)</td>
<td>3.4</td>
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<td></td>
</tr>
<tr>
<td>Calcite (CaCO₃)</td>
<td>3.1</td>
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<tr>
<td>Hemitite (Fe₂O₃)</td>
<td>1.4</td>
<td>1.2</td>
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<td>maghemite (γ-Fe₂O₃)</td>
<td>12.86</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>0.0</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂F (Ca₂Fe₂O₅)</td>
<td>0.0</td>
<td>0.0</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>C₄AF (Ca₂Fe₀.₂₈Al₁.₇₂O₅)</td>
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<td>0.0</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>Magnesioferrite (MgFe₂O₄)</td>
<td>0.0</td>
<td>0.0</td>
<td>1.5</td>
<td>49.51</td>
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<tr>
<td>Quartz (SiO₂)</td>
<td>0.0</td>
<td>2.2</td>
<td>17.2</td>
<td>1.46</td>
</tr>
<tr>
<td>Cristobalite (SiO₂)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>keatite (SiO2)</td>
<td>0.5</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mullite (3Al₂O₃·2SiO₂)</td>
<td>0.0</td>
<td>0.0</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Gehlenite (Ca₂(Al(Si,Al)₂O₇)</td>
<td>3.5</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merwinite</td>
<td>3.2</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Amorphous amount</strong></td>
<td><strong>70.0</strong></td>
<td><strong>82.0</strong></td>
<td><strong>3.8</strong></td>
<td><strong>23</strong></td>
</tr>
</tbody>
</table>
2. Experimental set-up of corrosion test.

![Horizontal tube furnace of corrosion test](image)

**Figure S2** Horizontal tube furnace of corrosion test
Appendix F

Published Versions of Thesis
High-temperature tube corrosion upon the interaction with Victorian brown coal fly ash under the oxy-fuel combustion condition

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Abstract

This study has examined the corrosion of tubes exposed to Victorian brown coal fly ash under the oxy-fuel combustion mode. The temperature of 650 °C, flue gas composition (steam 30 vol%, O2 5%, SO2 3000 ppm, HCl 1000 ppm, N2 5% and CO2 balanced), and an exposure time of 50 h were employed. Through the joint use of advanced instruments such as synchrotron X-ray adsorption spectroscopy and thermodynamic equilibrium calculation, it has been confirmed that, from both mass loss and penetration rate perspectives, the corrosion of low-Cr tubes under the oxy-firing mode is severe compared to the respective air-firing mode. Both flue gas-related and ash-related corruptions are responsible for tube corrosion. In contrast, the corrosion rate of high-Cr tubes (~20% for SUS304 and SUS347) is comparable between the two modes, due to the protective effect of Cr-oxide. The existence of fly ash on tube surface suppressed the chlorination reaction. Oxygen is the principal element permeating into tube under the air-firing mode, whereas both oxygen and sulphur penetrated into the tube under the oxy-firing mode, accelerating sulphation/sulphidation reactions for a rapid corrosion. Although Cr2O3 forms a protective layer under the air-firing mode, it broke down due to the accelerated corrosion attack caused by sulphates/sulphide under the oxy-firing mode. The interaction between ash and tube surface promoted the formation of pure oxides and oxide complexes with the involvement of Na and Ca as well. The presence of alkali sulphates in ash promoted the sulphidation reaction, the extent of which is however tube-specific and correlates little with Cr content. The use of advanced material SUS347 was found to be the most suitable candidate for heat-exchange tubes to be used in the oxy-firing boiler burning low-rank coal such as Victorian brown coal which is rich in alkali and alkaline earth metals.

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Keywords: Oxy-fuel combustion; Victorian brown coal; Tube corrosion; XANES Fe and S K-edges

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1. Introduction

Coal is the most abundant fossil fuel in the world and would expect to remain so for the rest of the century. The total amount of coal used is predicted to increase by 5% in 2040 [1]. Victoria, Australia is one of the largest brown coal reserves in the world [2]. Although bearing a very low amount of ash-forming elements in brown coal, the large amount of inherent moisture (up to 70 wt%) within it results in a notoriously high CO₂ emission rate, compared to black coal [3]. Deploying the low-emission technologies such as oxy-fuel combustion is pivotal for the sustainable use of brown coal in the carbon-constrained future.

Compared to conventional air-firing mode, the oxy-fuel combustion provides a different atmospheric environment in the boiler. Apart from the high-concentration of CO₂ and steam derived from wet flue gas recycle, the trivial but corrosive components including SO₂ and HCl are also potentially accumulated in the furnace, due to the recycle of the uncleaned, dirty flue gas [4,5]. In nearly all of the pulverised coal-fired boilers in Australia, the downstream gas cleaning units do not exist. In light of this, the high-temperature tube corrosion in the heat-exchanger zone is supposedly altered remarkably [6], under the oxy-fuel combustion mode for Australian coals including Victorian brown coal. With regard to the high-temperature tube corrosion, coal quality is the major player on the fireside [7]. In addition to the aforementioned corrosive gases resulting in the oxidation, chlorination, sulphonation/sulphidation and even carbonisation of tube material [8], the ash deposits also cause the wastage of tube surface, due to the formation of new species such as carbonates that are highly corrosive [9], and the promoted formation of other species such sulphates and chlorides that lower the melting point of tube material by forming new eutectics. As summarised in [9] and further discussed by the studies in an IEAGHG workshop [10], most of the previous studies on high-temperature tube corrosion focused on the effects of gaseous components such as CO₂, H₂O and SO₂. The ash-related corrosion, however, has been much less examined. Even for the studies conducted to date, the conclusions achieved are far from generalised [11,14], due to the fact that the high-temperature tube corrosion is highly coal-specific. Victorian brown coal is different from German lignites [10,15] and American coals tested previously [10,16,17], due to the high contents of inherent moisture and sodium within it.

In this study, we presented the results for the ash-related tube corrosion in the typical gas environment encountered during both the air-firing and oxy-fuel combustion of Victorian brown coal. That is, apart from the accumulated SO₂ or steam content of 30 vol% in flue gas is also probable for the recycle of wet flue-gas and the burning of partially dried coal. HCl was also added into the flue gas, to mimic the co-firing scenario in which biomass is blended with brown coal for a zero, and even negative carbon emission. The test temperature was fixed as 650 °C, at which the tube corrosion rate is maximum [9], and a test duration of 50 h have been conducted. Two typical fly ashes from Victorian brown coal-fired power plants were tested, and six tube materials with a chromium (Cr) content up to 20 wt% have been tested. After each test, apart from weighing the mass change of a tube, a variety of advanced analysis was also conducted, optical microscope (OM) for the cross-section observation to quantify the corrosion depth, scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analyser (EDX) to map the penetration/diffusion of elements of interest through the ash-tube interface, X-ray diffraction (XRD) for the bulk surface, and surface X-ray photoelectron spectroscopy (XPS) for the oxide states of iron (Fe), and sulphur (S) on both bulk and cross-section surfaces. Finally, thermodynamic equilibrium modelling was conducted to interpret the experimental observations. Such a study is expected to determine the suitability of and thus optimise the performance of tube materials. Ultimately, it aims to promote the deployment of oxy-fuel combustion for low-rank coals.

2. Experimental procedure

2.1. Tube corrosion test setup and test conditions

The experimental set-up is illustrated in Figs. S1 and S2 in the supporting information (SI) document. A horizontal test furnace was used for tube corrosion test, which was first heated up to 650 °C. The fresh tube specimen, 2 cm × 2 cm × 0.2 mm, were prepared by a wire-electrical discharge machine. The oxidised outer surface was ruled out for testing. Photo of the fresh tube specimen is demonstrated in Fig. S2 in the SI. Fly ash powder (∼100 mg per run) was spread uniformly over the fresh tube plate surface to mimic the ash deposition on a real steam tube surface. The ash-laden tube specimen was then sealed on a quartz-made sample holder and pushed to the middle zone in the hot furnace. Subsequently, flue gas (as shown in Table 1) was fed at a flow rate of 300 m³/min continuously into the furnace. Each test lasted 50 h and two replicates were conducted for each condition. After the test, the particle-laden tube specimen was either scratched carefully to remove the particles to weigh its mass change, or quickly mounted (with ash particles together) and solidified into epoxy resin to avoid the surface oxidation. Photos for ash coating, and corroded tube surfaces are further illustrated in Fig. S3. Note that, such a testing procedure is consistent with the literature studies related to ash deposit-related tube corrosion [10,15-17].
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Table 1
Flue gas compositions.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Air-firing (vol%)</th>
<th>Oxy-firing (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>CO₂</td>
<td>15</td>
<td>Bal.</td>
</tr>
<tr>
<td>SO₂</td>
<td>300</td>
<td>3000</td>
</tr>
<tr>
<td>HCl</td>
<td>260</td>
<td>1000</td>
</tr>
<tr>
<td>H₂O</td>
<td>8</td>
<td>30</td>
</tr>
<tr>
<td>N₂</td>
<td>Bal.</td>
<td>10</td>
</tr>
</tbody>
</table>

A total of six tube materials were tested, with a Cr content ascending sequence of SS400 (0% Cr), 12Cr1MoV (0.9–1.2%), T23 (2.25%), T91 (9%), SUS347 (17–19%), and SUS304 (18–20%). The elemental compositions of three fly ash samples tested are shown in Table 2, including Hazelwood fly ash (HW), modified Hazelwood ash (HW-NaK) for the raw Hazelwood fly ash mixed with Na₂SO₄ (10 wt%) and K₂SO₄ (10 wt%), and Yallourn fly ash (YL). Both HW and YL were sourced from the brown coal-fired power plants in the Latrobe Valley, Australia. The HW-NaK has a typical ash composition to clarify the tube corrosion under the worst scenario, in which the formation of alkali sulphate was enhanced due to the recycling of SO₂ in the dirty flue gas [18,19]. Moreover, the fly ash samples tested here are similar with the ash deposits collected on the super-heater tube surface, in terms of the high contents of alkali sulphates [20]. The concentration of sulphates (as suggested by SO₃ content) decreases in a sequence of (YL) < HW < (HW-NaK). The ash-free, flue gas-related corrosion tests were conducted under the same conditions with the absence of ash on the tube surface.

2.2. Characterisation of corroded tube surfaces

For each un-mounted tube, its surface, namely bulk surface hereafter, were subjected to XRDA analysis to qualitatively determine the crystallised species (Rigaku, MiniFlex 600), under 40 kV voltage and 15 mA current, and the scanning speed was 1.7º min with a step size of 0.01º. The peak identification was achieved by the search-match function in the JADE software. The XRDA patterns are provided in Figs. S4 and S5 in the SI. Additionally, each bulk surface was subjected to K-edge XANES, the energy scale of which was calibrated with reference to elemental sulphur K-edge absorption peak with energy of 2472 eV. The data collection and interpretation processes are identical with our previous work [21].

Table 2
Elemental compositions of three fly ash samples tested in this study (wt.%).

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW</td>
<td>0.2</td>
<td>29.3</td>
<td>3.01</td>
<td>5.82</td>
<td>0.6</td>
<td>12.8</td>
<td>0.2</td>
<td>32.4</td>
<td>14.0</td>
</tr>
<tr>
<td>HW-NaK</td>
<td>6.4</td>
<td>23.4</td>
<td>2.40</td>
<td>4.6</td>
<td>0.0</td>
<td>20.5</td>
<td>5.60</td>
<td>25.9</td>
<td>11.2</td>
</tr>
<tr>
<td>YL</td>
<td>3.12</td>
<td>24.0</td>
<td>3.03</td>
<td>2.91</td>
<td>0.0</td>
<td>8.03</td>
<td>0.15</td>
<td>9.67</td>
<td>40.0</td>
</tr>
</tbody>
</table>

For each epoxy-mounted tube, it was cut by wire-meshing and the resultant cross-section surface was analysed by OM (Olympus) to establish the thickness of scale and depth of intergranular penetration, if any in the alloys. SEM-EDEEX (JEOL 7001F) for micro-structure and the mapping of individual elements; and Fe K-edge XANES analysis and spectra interpretation by following our previous method [22]. The original and fitted Fe XANES spectra are further provided in the SI.

2.3. Thermodynamic equilibrium calculations

The commercial thermodynamic equilibrium program, FactSage 6.5 (Equilib module) was used to specify all the probable interactions between ash species and tube surface. The database FToxid-Slag in the program was used. For each calculation, three scenarios were considered for the input: the co-existence of ash species and flue gas; the existence of ash species only; and the existence of flue gas components only. The first scenario mimics the ash-particle interface which is exposed to both ash and bulk flue gas. The second one stands for the interface where the bulk gas particularly the oxidizing components do not reach the tube surface, due to the diffusion resistance from ash layer. The last one clarifies the flue gas-related corrosion. The temperature was set at 650°C for all the calculations.

3. Results and discussion

3.1. Mass change and penetration rate for tube corrosion

The mass change is the first index evaluating the tube corrosion rate. As illustrated in Fig. 1 where the x-axis is listed in the ascending sequence of Cr content, oxy-fuel combustion led to the enhanced mass loss (thus corrosion) for almost all the tubes, irrespective of fly ash type. However, the enhancement is more obvious for the low-Cr tubes including SS400, 12Cr1MoV and T23. For the other three tubes, there is a considerable overlap between air-firing and oxy-fuel modes, particularly for SUS347 in which the two modes are superimposed largely in the case of YL fly ash which contains less alkali sulphates. With respect to the fly ash-related corrosion, it is higher than the flue gas-only mode for the low-Cr SS400, and high-Cr tubes from T91 through to SUS347. Interestingly, for the two low-Cr tubes 12Cr1MoV and T23, the
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Fig. 1. Mass loss of different tubes for both ash-related and flue gas-related corrosion.

Fig. 2. Macrostructure of T23 exposed to HW ash in air (a), flue gas only in air (b), HW ash in oxy-fuel (c) and flue gas only in oxy-fuel (d).

Flue gas-related corrosion is predominant over the ash-related corrosion, suggestive of the predominance of chlorination reaction for low-Cr tubes. Upon the increase in the Cr content in the tube material, the mass loss rate decreases considerably, implying the suppression of chlorination reaction.

The typical cross-sectional structures for corroded tubes are illustrated in Fig. 2 where the tube T23 exposed to HW ash in air, flue gas only in air, HW ash in oxy-fuel and flue gas only in oxy-fuel mode were included. Clearly, apart from the formation of a thick interface denoting the penetration of oxidising elements, a scale layer was also observed for the exposure to both ash and oxy-fuel flue gas. However, upon the co-existence of ash and flue gas in the air-firing mode, the penetration interface formed is much thinner, and a scale layer was not found either. Such a discrepancy echoes the significant corrosion under the oxy-fuel mode for this low-Cr tube. With respect to the flue gas-related corrosion, the interface was not observed. Instead, the tube surface turned rough and molten, implying the formation of low-melting eutectics such as chlorides [23]. Statistical analysis was further conducted to quantify the thickness of the corrosion interface for each corroded tube. Based on the interface depth, the corrosion rate or interface growth rate was further calculated by dividing by the exposure time, 50 h employed in this study. As depicted in Fig. 3, the Cr content in tube material is in reverse proportion to the growth rate, irrespective of fly ash type. This is consistent with the literature finding [6]. For the tube T23 alloyed steel exposed to HW bul ash with the lowest Cr content, it was found to have the highest oxide thickness that is consistent with the literature [24]. The effect of fly ash type is marginal, given the fact that the experimental error is relatively large. In addition, the growth rate 0.2–1 μm/h found here is broadly consistent with the literature report on the tested alloy tubes with the similar Cr contents [25]. Moreover, the flue gas-related corrosion rate is comparable to that caused by fly ash only, 0.1–0.45 μm/h, further implying the enhanced corrosion upon the exposure of tube to both fly ash and flue gas.

3.2. Micro-structure for the cross-section of corroded tubes

Figure 4 demonstrates the distributions of individual elements along the tube SUS347 cross-section, upon the exposure to flue gas without (a) and with fly ash loading (b) under the oxy-fuel mode. Clearly, the flue gas only resulted in the oxidation of Cr and Fe. The resultant oxides should break down and thus failed to form a protective layer. This could be due to the formation of chloride eutectics, as suggested in Fig. 2. Therefore, oxygen (O) penetrated deeply into the Fe metal matrix. Such a phenomena was not confirmed for the air-firing flue gas only (data not shown), reflecting the high concentrations of corrosive gases, CO₂, H₂O, SO₂ and HCl within the oxy-fuel flue gas. For the fly ash-loaded case, a Cr-rich protective layer was observed on the top of the interface, implying the resistance of fly ash layer against the attack of corrosive gases particularly HCl in flue gas. This could
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Fig. 4. Elemental mapping for the cross-section of SUS347 exposed to flue gas only (a) and HW ash (b) in the oxy-firing mode.

be due to the preferential chlorination of alkali and alkaline earth metals in the ash layer, and therefore, the molten chlorides were not formed on tube surface. Instead, both O and S permeated through the interface, suggestive of their overwhelming role on the ash-related tube corrosion, causing oxidation, sulphation and/or sulphidation of iron and other metals. In addition, since the creping of S was not observed in the flue gas only case, the S in fly ash was apparently the major source accounting for the sulphation/sulphidation across the interface. Its interaction with iron metal could be due to the direct reaction between alkali sulphates and iron metal, as depicted in Eq. (1), or the combined reaction between alkali sulphates, SO₂ (derived from SO₃ and O₂ in flue gas) and iron oxide (Fe₂O₃), as shown in Eq. (2) [26].

\[
2(\text{Na}_x\text{K}_y\text{Fe}_z\text{(SO}_4)_w) + 17\text{Fe} = 8\text{Fe}_3\text{O}_4 + 3\text{FeS} + 3(\text{Na}_x\text{K}_y)\text{S}
\]  

(1)

\[
\text{mNa}_x\text{SO}_4 + \text{nK}_y\text{SO}_4 + 0.5\text{Fe}_3\text{O}_4 + 1.5\text{SO}_3 = (\text{Na}_x\text{K}_y)\text{Fe}(\text{SO}_4)_3, m + n = 1.5
\]

(2)

3.3. Characteristics of Fe-bearing species by XRD and XANES

Table 3 lists the crystal species on the bulk surfaces of the corroded tubes upon the exposure to HW fly ash. Hematite/magnetite (Fe₂O₃) is the sole major species detected for all of the tubes under the oxy-fuel mode, whereas magnetite (Fe₃O₄) and wustite (FeO) are dominant for the air-firing tube surfaces. Clearly, apart from bulk O₂, the other gases including CO₂ and H₂O in oxy-firing flue gas are also the sources causing the full oxidation of tube surfaces under the oxy-firing mode. In addition, compared to 12Cr1MoVG being the only tube with eskoltite (Cr₂O₃) on its surface under the oxy-fuel mode, Cr₂O₃ was found for the high-Cr tubes from T91 through to SUS347 in the air-firing mode, corresponding to the probable formation of Cr oxide-rich protective layer under the mild environment (e.g., low HCl, low steam and low SO₂ in the air-firing mode). Such a protective layer was either too thin to be detected (as shown in Fig. 4), or fully broke down under the oxy-fuel mode, due to the higher content of HCl that can permeate through the oxide scale once defects or cracks develop in it. In addition, pyrrhotite (Fe₃S₄) was the only crystal detected by XRD on the SS400 tube exposed in the air-firing mode, which supports Eq. (1).

Figure 5 provides the quantified XANES results for the distribution of Fe-bearing species across the tube cross-sections. Clearly, the distribution of Fe is highly tube-dependent. Under the air-firing mode, the fully oxidised hematite was only observed on the SS400 tube, suggestive of the ease of the diffusivity of oxygen into it. For the low Cr-content tubes from 12 Cr1MoVG to T91, the partially oxidised species including magnetite and wustite were dominant, confirming the protection effect of Cr-bearing scale against the penetration of oxygen. However, hematite was further back for two high-Cr tubes, which could be in a spined form such as
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Table 3
XRD results for the corroded tube surface exposed to HW ash.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Mode</th>
<th>Major</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS400</td>
<td>Air</td>
<td>Hematite (Fe₂O₃)</td>
<td>Pyrrhotite (FeS)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Wustite (FeO)</td>
<td></td>
</tr>
<tr>
<td>12Cr1MoVG</td>
<td>Air</td>
<td>Hematite (Fe₂O₃)</td>
<td>Magnetite (Fe₃O₄)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Wustite (FeO)</td>
<td></td>
</tr>
<tr>
<td>T23</td>
<td>Air</td>
<td>Magnetite (Fe₂O₃)</td>
<td>Ferritic tungstate (Fe₂WO₄)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe₂O₃)</td>
<td>Magnetite (Fe₃O₄)</td>
</tr>
<tr>
<td>T91</td>
<td>Air</td>
<td>Magnetite (Fe₂O₃)</td>
<td>Eskolite (Cr₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe₂O₃)</td>
<td></td>
</tr>
<tr>
<td>SUS304</td>
<td>Air</td>
<td>Hematite (Fe₂O₃)</td>
<td>Eskolite (Cr₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe₂O₃)</td>
<td></td>
</tr>
<tr>
<td>SUS347</td>
<td>Air</td>
<td>Magnetite (Fe₂O₃)</td>
<td>Eskolite (Cr₂O₃)</td>
</tr>
<tr>
<td></td>
<td>Oxy</td>
<td>Hematite (Fe₂O₃)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4
Thermodynamic equilibrium predicted species for two tubes exposed to HW-NaX under the oxy-fuel mode. Unit: mol based on a total input of 5.5E-5 mol Fe for a single tube specimen.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
<th>Scenario 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ash +</td>
<td>Ash only</td>
<td>Fine gas</td>
</tr>
<tr>
<td></td>
<td>flue gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.76E-02</td>
<td></td>
<td>2.75E-02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.89E-04</td>
<td>4.89E-04</td>
<td></td>
</tr>
<tr>
<td>CaFe₂O₅</td>
<td>2.88E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₃Fe₅O₁₁</td>
<td>1.79E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₉Cr₄O₁₉</td>
<td>5.00E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₅</td>
<td>2.26E-02</td>
<td>2.25E-02</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>5.99E-03</td>
<td>4.70E-04</td>
<td>5.99E-03</td>
</tr>
<tr>
<td>Ca₉Cr₄O₁₉</td>
<td>6.52E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>5.48E-04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Na₂O)(Cr₂O₃)</td>
<td>7.31E-05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Quantified XANES results for the distribution of Fe-bearing species across tube cross-section exposed to HW ash.

Fe₂Cr₂O₆. The un-oxidised Fe metal was also back to pre-dominance, confirming the strong protection effect of Cr. Upon the shift of air-firing to oxy-fuel mode, the variation of above-mentioned oxides with tube materials is similar. However, augite (Ca₂Mg₃Si₂O₆) was observed. Clearly, the interaction between ash and oxidised tube surface is much more complex than the above two equations. Apart from alkali sulphates, the other oxides in ash are also available to react with the oxidised tube surface. This should occur after the oxidised surface of tube cracked, and the resultant fragments were blended with ash particles consequently. The thermodynamic equilibrium prediction, as tabulated in Table 4, confirmed the preferential formation of oxide complexes in the scenario of flue ash only on the surfaces of both low-Cr (T23) and high-Cr tube (SUS347). In the other two scenarios for the existence of flue gas with and without the co-existence of ash, the pure oxides including hematite (Fe₂O₃) and eskolite (Cr₂O₃) are formed, irrespective of the Cr content. Clearly, the oxidation of tube surface upon flue gas is superior over its interaction with solid fly ash. In addition, the thermodynamic equilibrium prediction confirmed the absence of chlorides under the experimental conditions. This further proved the suppression of this reaction by the abundant SO₂ used here. As has been suggested, increasing the molar ratio of sulphur to chlorine can make corrosion very unlikely [27].

3.4. Characteristics of S-bearing species by XANES

Although XRD has detected the Fe-bearing species on the corroded tube surface, it failed to clarify the role of S. On the other hand, Table 4 for thermodynamic equilibrium prediction suggests the potential presence of sulphide upon the interaction between ash and tube surface. In light of this, the XANES results in Fig. 6 provide complementary information that is critical in
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4. Conclusions

The major conclusion from this study can be drawn as follows:

1. From both mass loss and penetration rate perspectives, the tube corrosion for the low-Cr tubes under the oxy-firing of Victorian brown coal is severe compared to the respective air-firing mode. Both flue gas-related and ash-related corrosion processes are responsible for tube corrosion. In contrast, the corrosion rate of high-Cr tubes (~20% for SUS304 and SUS347) is comparable between the two combustion modes, due to the protective effect of Cr-oxide.

2. The existence of fly ash on tube surface suppressed the chlorination of tube surface. Oxygen is the principal element permeating into tube under the air-firing mode, whereas both oxygen and sulphur penetrate into the tube under the oxy-firing mode, accelerating sulphation and sulphidation reactions for the tube corrosion. Although Cr₂O₃ forms a protective layer under the air-firing mode, it breaks down due to the accelerated corrosion attack caused by sulphates/sulphide under the oxy-firing mode.

3. The interaction between ash and tube surface promoted the formation of pure oxides and oxide complexes with the involvement of Na and Ca as well. The presence of alkali sulphates in ash promoted the sulphidation reaction of tube surface. However, the extent of sulphide is highly tube-specific and correlates little with Cr content.

Acknowledgement

The authors are grateful to BCLA and ANLEC R&D for the support. Appreciation is also extended to beamline scientists, Ling-Yun Jang and Bing-Jian Su at NSRRC of Taiwan for the XANES operation support.
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Supplementary materials

Supplementary material associated with this article can be found in the online version, at doi: 10.1016/j.proci.2016.08.076.

References

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Full Length Article

Effect of silica additive on the high-temperature fireside tube corrosion during the air-firing and oxy-firing of lignite (Xinjiang coal) – Characteristics of bulk and cross-sectional surfaces for the tubes

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HIGHLIGHTS

- The pure CO₂ caused the oxidation of Cr and Fe.
- The use of silica additive is effective in alleviating the diffusion rate of oxygen.
- Formation of amorphous oxides results between free oxides in ash and carbon steel surface.
- Speciation of S varies with ash deposit and tube material.
- A slightly accelerated outward diffusion of Cr by the ash deposit.

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ABSTRACT

Detailed speciation analysis has been conducted on the corroded tubes coated with two different ash deposits collected from the combustion of a lignite, namely Xinjiang coal mixed with and without external silica in both air- and oxy-firing modes. The exposure conditions are at temperature of 650 °C, 50 h, and the use of different fuel gases (i.e. pure CO₂, air, air-firing fuel gas and oxy-firing fuel gas). Apart from the lab-based XRD used for the characterisation of the top surface, synchrotron XANES was employed to determine the oxidation states of Fe, S and Cr on both top and cross-sectional surfaces of the corroded tubes. The results indicate that, irrespective of the Cr content, the tubes exposed to pure CO₂ underwent oxidation, which is most likely due to the reaction CO₂ + M = CO + MO where M stands for Fe or Cr. Cr in the Cr-bearing tubes were oxidised more rapidly than Fe in the pure CO₂. The combined use of silica additive and Cr-bearing tubes with a minimal Cr content of 2 wt% (i.e. 723) is beneficial in inhibiting the tube surface oxidation as well as the penetration of oxygen and sulphur. Except alkali sulphates, the free oxides in ash deposit can also trigger the reactions for the formation of new species such as alkali (Na, Mg, Fe,Al)(SO₄)₂ or (Al, Fe)₂O₃ on the carbon steel tube surface. The oxidation states of sulphur on the tube surface is highly tube-specific and dependent on ash deposit composition as well, with the abundance of pyrite (FeS₂) on the carbon steel tube coated with the raw coal ash deposits, while the enrichment of titania (TiO₂) upon the coating of ash deposits derived from the combustion of coal mixed with silica additive. Due to the shortage of free sulphur in ash deposit and a preferential scavenging of Fe into chromite. For the Cr-bearing tubes, sulphide is the only S-bearing species due to the inhibited inward diffusion of S by the Cr oxide layer, irrespective of ash-deposit type. In addition, spatial organisation of the oxidation state of Cr suggests a slightly accelerated outward diffusion of Cr by the ash coating, thereby leading to a dense Cr-rich layer that is highly protective on the tube outer surface.

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1. Introduction

Chemical speciation of metals on corroded tube surfaces is pivotal to understanding the mechanisms underpinning the interaction between tube surface and flue gas, as well as the solid-solid interaction related to hot corrosion at high temperatures. This
is particularly important for a new combustion process such as oxy-fuel combustion in which flue gas composition and ash deposit properties are altered remarkably compared to the conventional air-firing mode. To date, the knowledge is still sparse regarding metallic speciation on the corroded tubes that are exposed to the ash-laden oxy-firing flue gas [1].

To date, most of the knowledge with regard to the metallic speciation on the corroded tube surfaces was merely achieved from studies based on conventional air-firing cases, where nitrogen is predominant (nitride formation is thus probable), and the contents of impure SO₂, steam and CO₂ are lean. However, upon employment of the oxy-firing mode, impurities accumulate due to the recycling of the dirty, wet flue gas that is supposed to enhance the formation of corrosive sulphates/sulphides under the same exposure time as under the air-firing case, and even result in the formation of new species. Table 1 summarizes all the past studies.

### Table 1

Summary of the literature studied on tube corrosion during the oxy-fuel combustion.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Purpose</th>
<th>Testing methods</th>
<th>Coal</th>
<th>Key finding</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Szejn-Brozowska et al., 2011 [36]</td>
<td>Investigate the influence of an oxy fuel combustion on the surface of selected super heater materials</td>
<td>SEM-EDS</td>
<td>Dry ash from Germany, hard coal from South America</td>
<td>Increase in sulphur induced corrosion for tubes exposed in the oxy-fuel combustion atmosphere</td>
</tr>
<tr>
<td>G. Szejn-Brozowska et al., 2013 [37]</td>
<td>Study the interactions between fly gas atmosphere, deposits and heat, exchanger materials during oxy-fuel firing</td>
<td>SEM/EDS XRD</td>
<td>Recrystallised coal</td>
<td>No sulphur induced corrosion is detected at the alloy specimens exposed under real fly ash and pure CaCO₃ deposits</td>
</tr>
<tr>
<td>G.R. Helmschrott et al., 2013 [38]</td>
<td>Compare air-firing and oxy-firing conditions on the tube corrosion</td>
<td>OM/SEM-EDS XRD</td>
<td>Synthetic ash</td>
<td>The observed corrosion behavior shows accelerated corrosion even with sulphate additions that remain solid at the tested temperatures</td>
</tr>
<tr>
<td>R. Nstsas and Z.T. Zieg, 2001 [2]</td>
<td>Address the potential crevice corrosion issues in environments typical of UOE headers and oxy-fuel combustion system</td>
<td>OM/SEM-EDS XRD</td>
<td>Synthetic ash</td>
<td>No corrosion was detected in the deposit left to catastrophic corrosion at 650 and 600 °C</td>
</tr>
<tr>
<td>L. Fereda et al., 2010 [29]</td>
<td>Study ash formation and deposition of selected coal (lonas) blends under oxyfuel and air conditions in a lab scale pulsed coal combustor (deep tube furnace)</td>
<td>SEM-EDS</td>
<td>South African coal blended with biomass (wood)</td>
<td>Deposition propensity was higher under oxy-fuel mode, however, ash chemistry was not changed</td>
</tr>
<tr>
<td>R. Abar et al., 2013 [31]</td>
<td>Investigate the formation of superheater alloys under the oxy-fuel combustion mode</td>
<td>OM/SEM-EDS XRD</td>
<td>Lignite from Germany</td>
<td>No carbonization observed: although sulphidation was observed, high CO₂ content in efasting did not result in an increase in corrosion</td>
</tr>
<tr>
<td>S. Tuzca et al., 2011 [37]</td>
<td>Investigate the performance of superheater alloys under the oxy-fuel combustion conditions</td>
<td>OM/SEM-EDS GDOES</td>
<td>45% CaCO₃ &gt; 50% CaSO₄</td>
<td>The corrosion rate increased with the Cr content increased; no severe corrosion under oxy-fuel than the air-firing conditions</td>
</tr>
<tr>
<td>A. Hjortbø et al., 2010 [30]</td>
<td>Corrosion inbuilt steel and oxy-fuel air-firing conditions</td>
<td>LDSE/OM-S-EDS</td>
<td>Low - 5 vol% Mud - 5 vol% High - 5 vol%</td>
<td>Found evidence for increased deposition rates of ash during oxyfuel combustion compared with air firing: no significant difference between oxyfuel and air firing corrosion rates or carbonization</td>
</tr>
<tr>
<td>A. Robertson et al., 2010 [41]</td>
<td>Identify the tube corrosion mechanisms under the oxy-fuel condition, and determine the effect of sulphur on boiler materials</td>
<td>SEM-EDS</td>
<td>Low - 5 vol% Mud - 5 vol% High - 5 vol%</td>
<td>The oxy-fuel corrosion rates were typically as worse, and often less than air-firing rates</td>
</tr>
<tr>
<td>G. SchellRebneck et al., 2009 [32]</td>
<td>Study the tube corrosion behaviour of different alloys</td>
<td>SEM-EDS</td>
<td>Synthetic ash</td>
<td>Carbonization and oxide scale morphology differences were confirmed between air and oxy-fuel environments for automotive materials</td>
</tr>
<tr>
<td>V. Targ et al., 2014 [39]</td>
<td>Investigate the corrosion behaviour of pure Fe under a Na₂SO₃ deposit in an atmosphere of H₂O + O₂</td>
<td>SEM-EDS XRD</td>
<td>Lignite</td>
<td>Corrosion rate is accelerated by the pure Fe significantly under a Na₂SO₃ deposit in atmosphere of H₂O + O₂ at 500 °C</td>
</tr>
<tr>
<td>M. Montgomery et al., 2013 [34]</td>
<td>Study the corrosion resistance of various alloys in an oxy-fuel process</td>
<td>OM/SEM-EDS XRD</td>
<td>Lignite</td>
<td>Corrosion rate decreases with increase in alloying elements. The oxy-fuel ash deposit is similar to that found in conventional air-firing plant</td>
</tr>
<tr>
<td>M. Mehri and S.K. Ranaj, 2012 [35]</td>
<td>Study the reaction of Fe-Si with Na₂SO₃ in the presence of SO₂(g) at 500 and 600 °C</td>
<td>SEM-EDS</td>
<td>UC Coal</td>
<td>The reaction products were presented in distinct phases</td>
</tr>
<tr>
<td>A.I. Spald et al., 2012 [36]</td>
<td>Assess the effects of increasing heat exchanger surface temperature on the crevice corrosion</td>
<td>OM/SEM-EDS</td>
<td>Bioassay/evaluated</td>
<td>A significant increase in metal damage when moving from 600 to 800 °C was confirmed for both alloys with and without ash deposit coverage</td>
</tr>
<tr>
<td>R. Nitsas and Z. Zieg, 2007 [37]</td>
<td>Evaluate the corrosion performance of Fe-base and Ni-base alloys in coal ash environments</td>
<td>OM/SEM-EDS</td>
<td>Bioassay/evaluated</td>
<td>Ni-base alloy generally exhibited less corrosion than Fe-base alloys under the similar exposure conditions; however, localized pitting was confirmed on the Ni-based tube surface</td>
</tr>
</tbody>
</table>
that have been conducted for the tube corrosion under the oxy-fuel combustion mode. As can be seen, the tube corrosion extent was distinctly different for the different tests, varying broadly with the coal/ash sample and exposure conditions tested. A generalized conclusion regarding the tube corrosion in the oxy-firing mode has yet to be achieved. For instance, studies using German lignite ash deposit reported no carbonation or carbonisation reactions, and the high CO₂ content had little effect on the increase in tube corrosion. In contrast, the study using synthetic ash confirmed the carbonisation reaction. With regard to the effect of ash deposit, the increased deposition rate has been reported for the oxy-fuel combustion mode, leading to the accelerated tube corrosion that was mainly caused by sodium sulphates and its synergistic interaction with steam in the flue gas. However, the roles of the other species in ash, if any, have not been reported.

For the analyses of the corroded tube surface, only lab-based facilities were used, which were also listed in Table 1, including optical microscopy (OM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) coupled with energy-dispersive analysis (EDAX) [2-5]. However, for the tube cross-section which is on the micro- and even sub-micron meter scale, lab-based XRD and XPS are not able to focus to such small areas. Thus, the information based on these two techniques is a mapping of both the corroded and the un-corroded area. In addition, although the SEM-EDS is capable of analysing the individual spots with a size down to 1 μm or even less, it only provides the elemental compositions of single particles. The information for the chemical speciation based on it is rather empirical and semi-quantitative.

In this work, our primary goal is to clarify the changes on the chemical speciation of six tubes coated with lignite ashes, so as to understand the roles of CO₂ and oxy-firing flue gas on the tube corrosion chemistry, as well as their synergistic effect, if any, with ash deposit on tube corrosion. Two ash deposits were tested, which were collected from the superheater tube surfaces in a 350 MW, pulverized coal-fired boiler burning a lignite named Xinjiang (China) mixed with and without external silica. By doing this, we also aim to address the effect of silica additive to coal on the mitigation of tube corrosion, which is the extension of our previous work on the ash-shaping and fouling during the combustion of the same coal [6,7]. To characterise the speciation of the corroded tube surfaces, the synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy was employed, which is able to probe the oxidation states of the elements of interest including Fe, S and Cr on both the top and cross-sectional surfaces of the corroded tubes that is only 0.2 cm in width. In particular, the spatial distribution of the oxidation states of Cr was revealed along the corroded tube cross-section. These analyses are expected to shed new light in understanding the chemistry underpinning the interaction between the ash deposit and tube surface, as well as the mechanisms for the inhibitive effect of silica additive on the control of tube corrosion during the oxy-fuel combustion of low-rank coal.

2. Experimental

2.1. Tube corrosion test set-up and test conditions

A horizontal furnace as shown in Fig. 1 was used for tube corrosion test. The furnace temperature was fixed at 650°C, considering that the ash deposit-related corrosion is maximised at this temperature. This temperature is also the typical surface temperature for the superheater/reheater tubes (650-700°C) [8]. The flat tube specimen, 3 cm × 3 cm × 2 mm, were prepared by a wire-electrical discharge machine to cut on the cross-sections of six commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. For the corrosion test in flue gas only, the tube specimen were tested as they were. For the ash deposit-related corrosion test, fly ash powder (~100 mg per tube specimen) was spread uniformly over the surface to mimic ash deposition on a real steam tube surface, yielding a slightly compacted ash density of approximately 11 mg/cm² that is lower than but comparable with the test elsewhere [8]. The ash-laden tube specimen was then loaded on a quartz-made sample holder and pushed to the middle zone in the hot furnace. Subse-

![Diagram of tube corrosion test set-up](image-url)
quently, flue gas was fed at a flow rate of 300 ml/min continuously into the furnace. Each test lasted 50 h and two replicates were conducted for each condition. A short exposure time was chosen, considering that the flue gas as shown below is highly corrosive. After the test, the particle-laden tube specimen was either brushed carefully to remove the ash particles to weigh its mass change by a high-precision balance with a readability of 0.1 mg, or quickly mounted (with ash particles together) and solidified into epoxy resin to avoid surface oxidation.

With regard to the flue gas composition, pure CO₂, air and two typical flue gas compositions (as shown in Table 2) were tested. The two flue gas compositions represent the air-firing and oxy-firing modes, respectively. As has been confirmed by our pilot-scale test [9], the steam content in flue gas can rise to 30 vol% and SO₂ is also highly accumulated during the oxy-firing of low-rank brown coal. The steam content tested here is close to the oxy-fuel flue gas tested elsewhere [4.5,8,10,11], however, the SO₂ content in flue gas here is lower. The HCl was also tested here, because some Xinjiang coals contain high Cl. The addition of HCl into flue gas can also mimic the co-firing scenario in which biomass is blended into coal for a zero and even negative carbon emission. Note that, the HCl has yet to be tested for the oxy-fuel combustion of coal in the literature. The total gas pressure is 1 atm.

A total of six tube materials in Table 3 were tested, with an increasing Cr content of SNS400 (08 Cr), 12Cr1MoV (0.9–1.2%), T2 (2.25Cr), T91 (9Cr), SUS347 (17–18%) and SUS304 (18–20%). Two ash deposits were tested, which were collected from the convective superheater surface in a 30 MWth power-plant. Four different compositions were selected for the combustion of Xinjiang lignite [67]. The two samples were labelled X and X', of which one was a raw coal deposit and the other was a coal deposit mixed with silica additive, respectively. The elemental compositions of the two ash samples are shown in Table 4. Note that, the mineralogical compositions for the two ashes are shown in Fig. S1 for the XRD patterns and further tabulated in Table S1 in Supporting information (SI). Upon the addition of silica, the total contents of Na and S in sulphate are reduced, so are the other metals in the oxide form. This is mainly attributed to the immobilization of these elements into the silica matrix.

### Table 2
Gas compositions used in air-firing vs oxy-firing.

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Air-firing</th>
<th>Oxy-firing</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ [vol%]</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>CO₂ [vol%]</td>
<td>15.0</td>
<td>Bal.</td>
</tr>
<tr>
<td>SO₂ [ppm]</td>
<td>300</td>
<td>1000</td>
</tr>
<tr>
<td>HCl [gpt]</td>
<td>260</td>
<td>1000</td>
</tr>
<tr>
<td>H₂O [vol%]</td>
<td>8.0</td>
<td>30</td>
</tr>
<tr>
<td>N₂ [vol%]</td>
<td>Bal.</td>
<td>10</td>
</tr>
</tbody>
</table>

### Table 3
Tube materials tested in this study.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Steel grade</th>
<th>Compositions</th>
<th>Cr [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNS400</td>
<td>Carbon steel (JSN400-ASTM A283)</td>
<td>1.25G-1Mo-Y</td>
<td>0.5-1.2</td>
</tr>
<tr>
<td>12Cr1MoV</td>
<td>Low chrome ferrite steel</td>
<td>2.25Cr-1.0W-V-V</td>
<td>2.25</td>
</tr>
<tr>
<td>T23</td>
<td>Low-alloy steel</td>
<td>18Cr-1Mo-V-Nb</td>
<td>9</td>
</tr>
<tr>
<td>T91</td>
<td>High chrome ferrite steel</td>
<td>18Cr-1Mo-V-Nb</td>
<td>9</td>
</tr>
<tr>
<td>SUS304</td>
<td>Austenite stainless steel (JS SUS304-ASTM SUS304)</td>
<td>18Cr-8N</td>
<td>18-20</td>
</tr>
<tr>
<td>SUS347</td>
<td>Austenite stainless steel (JS SUS347-ASTM SUS347)</td>
<td>18Cr-8N</td>
<td>17-19</td>
</tr>
</tbody>
</table>

### Table 4
Elemental compositions of the fly ash samples tested, w/w%

<table>
<thead>
<tr>
<th>Ash samples</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>X' ash</td>
<td>5.4</td>
<td>12.4</td>
<td>8.27</td>
<td>10.24</td>
<td>0.45</td>
<td>12.53</td>
<td>0.45</td>
<td>36.82</td>
<td>0.38</td>
</tr>
<tr>
<td>X' s ash</td>
<td>6.2</td>
<td>9.1</td>
<td>12.11</td>
<td>34.63</td>
<td>0.37</td>
<td>7.9</td>
<td>0.87</td>
<td>26.55</td>
<td>3.15</td>
</tr>
</tbody>
</table>

### 2.2. XRD and SEM-EDX analysis of bulk surface

For each un-mounted combed tube, its top surface, after the ash powders were removed, were subjected to XRD analysis to qualitatively determine the crystallized species (Rigaku, Miniflex 6000, under 40 kV voltage and 15 mA current; the scanning speed was 1°/min with a step size of 0.01°) and the wavelength of 0.15418 nm for Cu – alpha was used. The peak identification was achieved by search-match function in the Jade software. The species used for the XRD fitting are listed in Table S1. As can be seen, these probable species highly overlap with one another. Efforts have thus been made to distinguish them as much as possible.

For each epoxy-mounted tube, it was first halved by a disc cutter. The resulting cross-section surface was then polished by SiC paper. It was analyzed by OM (Olympus) to establish the thickness of scale and depth of intergranular penetration, if any in the alloys, and by SEM-EDAX (JED 7001F) for microstructural observation of the cross-section and the mapping of individual elements on the cross-section as well. Samples were carbon coated prior to the SEM-EDAX observation.

### 2.3. Synchrotron XANES analysis

The K-edge XANES spectra of Fe, S and Cr were obtained on beamline 11.16A1 at the National Synchrotron Radiation Research Centre (NSRRC). BL16A1 has a fixed exit double crystal Si (1 1 1) monochromator with a nominal beam size of 0.25 by 0.25 mm at sample. For the analysis of Fe and Cr, pure elemental Fe and Cr were used respectively for the calibration at a K-edge absorption energy of 7112 eV and 5989 eV. Pure elemental Mo was used for the calibration of S at an K-edge absorption energy of 2481 eV. The peak energy absorption (white-line) position was taken as the base (0 eV), with both subsequent spectra recorded 200 eV below and 800 eV above this point in fluorescence mode. Additionally, some reference Cr XANES spectra were recorded at the wiggler XAS beamline at the Australian Synchrotron. This beamline has a Si (1 1 1) double crystal monochromator which was fully tuned. Higher harmonics were rejected using mirrors. Data were collected with 0.05 mm ion chambers under He flow (1.5 L/min) with 250 V and a 100 mm HP-Ge detector (Canberra).

The analysis of S was only conducted for the top surfaces, as the signal for S from the cross-section of the tubes was too weak and very noisy. For the other two metals, the speciation along the cross-sectional surface of the combed tubes was conducted. Definition of the two surfaces is shown in Fig. 2. Additional attempts were also made to reveal the spatial distribution of the oxidation state of Cr along the tube cross-section. This was done by moving the synchrotron beam from the centreline of the tube where the Cr
signal is maximum through to the oxide scale where the Cr signal tends to disappear since the oxide scale is next to ash deposit/epoxy resin that is low in Cr. Once the positions for the maximum and minimal Cr signals were recorded, one or two extra positions in between, defined as 0.4 cm and 0.7 cm away from the centreline were further analysed.

All spectra were normalised using ATHENA which is part of the DEMETER package [12]. Linear combination fitting (LCF) was used, on the normalised sample spectra to determine the mineral composition by using a large number of standards that were detailed in the SL. The details for the LCF methodology were also given in the SL.

2.4. Thermodynamic equilibrium calculations

The commercial thermodynamic equilibrium program, HSC Chemistry 7.1 (Reaction equation module) [13] was used to calculate the standard Gibbs function values (△G) for the potential corrosion reactions at 650 °C. The calculation is straightforward, with the input of all the reactants and products at stoichiometric ratios. The gas pressure was set at 1 atm, and the built-in Main Database (Main887:HSC) was used. All the gases were assumed as ideal gases.

3. Results and discussion

3.1. Tube surface oxidation in pure gases without ash deposits

The typical micro-structure for the cross-section of the corroded tube T23 in pure CO₂ is illustrated in Fig. 3. Clearly, CO₂ is not an inert gas, as it contributes to the tube corrosion. Such a finding has also been previously reported [8]. The top surface of the tube T23 became flawed and porous, implying the formation of defects and cracks that aid gaseous diffusion. The elemental mapping results confirm the abundance of O and Fe on the corroded surface, with the existence of trivial Cr and Si as well. It is clear that oxidation of Cr and Si took place in the oxide layer, exerting a protective role to minimise the wastage of iron. Regarding the existence of C on the tube surface, due to the carbon coating prior to the SEM observation, it is unclear if the C detected here is due to the carburisation reaction caused by the Boudard equilibrium (CO₂ + C ↔ CO + CO) [4].

Fig. 4 confirms the enhanced corrosion for the tube T23 exposed to the two flue gases. The top surface is even spalled off, particularly in the oxy-firing flue gas. This reflects the high concentrations of HCl and steam within this gas. With regard to the air-firing flue gas, the spalled layer is dominated by Fe, whereas the other three elements are present in low concentrations. However, the carburisation reaction may still be unlikely for T23 studied here, as it is difficult to achieve the Boudard equilibrium in the presence of steam and oxygen with CO₂ [4]. In contrast, upon exposure to the oxy-firing flue gas, oxygen is the most abundant element in the oxide layer, demonstrating an enhanced diffusion of O into the metal. CO₂ has been suggested to be able to increase the transport of reagents within the oxide scale [8], although a theory has yet to be established to confirm this. Moreover, upon the spallation of oxide layer by the attack from steam, HCl and/or SO₂, the diffusion of oxygen towards the un-oxidised metal was accelerated. Interestingly, for both flue gases, the distribution of S in the oxide layer is weak, implying little sulfidation/reduction reaction caused upon the exposure to flue gas only, for an experimental temperature of 650 °C and 50 h only.
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Fig. 3. Typical micro-structure for the cross-section of T23 specimen exposed to pure CO₂.

Fig. 4. Typical micro-structure for the cross-section of T23 specimen exposed to flue gases with the absence of O₂ anhy.
3.2. Tube surface oxidation upon the exposure to ash species

A typical microstructure for the corroded tube T23 is shown in Fig. 5, for the exposure to XJ ash in the oxy-firing mode. Apart from a porous layer attaching to the bulk tube, a spalled scale was found detaching away from the bulk tube. The top layer is dominated by oxides, as indicated by the EDX mapping results that show O is the most abundant element, followed by Cr, S, and Fe. Clearly, both O and S diffused inwards, whereas Cr and Fe diffused outwards for the corrosion and spallation of the tube. The faster diffusion of Cr than Fe resulted in the formation of a Cr-rich protective layer.

The absence of Cl should be due to the volatilisation of chlorides from the tube surface, or the inhibition of the formation of chloride in the co-existence of S and Cl in flue gas [14]. More interestingly, compared to the other elements, especially O distributing evenly in the whole (top layer, S is preferentially present in the boundary/ interface between the metal/oxide layer and the bulk tube. This should be due to a faster diffusion for S than O through the tube lattice [15, 16]. Additionally, the S in the tube/metal boundary should be formed under the assistance of the ash sample, e.g. via reaction Eqs. (1) and (2) shown below.

\[
3Na_2SO_4(s) + 35O_2 + Fe_2O_3 = 2Na_2Fe_2(SO_4)_{3.5}(s) \tag{1}
\]

\[
2Na_2Fe(SO_4)_{2.5} + 15Fe = 6Fe_2O_3 + 3FeS + 3NaS \tag{2}
\]

Fig. 6 demonstrates the typical microstructure for the tube corroded surface upon the coating of XJ S ash. Clearly, multiple oxide layers were formed on the tube surface. Compared to the top and spalled layers for the XJ ash in Fig. 5, the multiple layers are dense and less porous. Therefore, their protection on the bulk tube is effective. The top layer attaches intimately to the bulk tube, mainly consisting of Fe and Cr. With respect to the middle scale, apart from the abundance of Fe and Cr, the presence of S and Cl was also confirmed. In particular, S is the most prevalent, which is also preferentially present on the left-hand surface of the middle scale. This suggests S easily traverses through the interstitial space between top layer and the middle scale.

Statistical analysis was conducted to quantify the thickness of the corrosion interface for each corroded tube, based on the micro-structures for the cross-sections observed by SEM. Furthermore, based on the interface depth, the corrosion rate or interface growth rate was calculated by dividing by the exposure time, 56 h employed in this study. As shown in Fig. 7 with the X-axis being the increasing Cr content in the tubes, the oxide layer growth rate decreases monotonously upon the increase of Cr content in the tube, either in flue gas only or upon the coating of fly ash. Note that the observed growth rate 0.2–1 μm/h here is broadly consistent with the literature report on the tested alloy tubes with the similar Cr contents [17].

For the exposure of tubes in gas only, as shown in panel a, the oxide growth rates for a tube are comparable for the four gases with the absence of ash deposit, based on the considerable overlapping of their error bars. Since oxygen is the principal oxidant for the gas-related tube corrosion, the results here indicate that the total partial pressure of all the oxidents in a flue gas is insignificant in the oxide layer thickness. In other words, the growth of the oxide layer should be controlled by the reaction rate for the oxidation of the metals such as Fe. For the pure O2 with an equilibrated O2 partial pressure reaching 0.1 × 10^-2 atm at 650 °C, it is still far higher than the equilibrium partial pressure of O2 (7.1 × 10^-3 atm) based on Fe + 1/2 O2 = FeO (wustite). In addition, the other reaction without the involvement of oxygen (O) may also be responsible for the oxidation of metals in CO2. This will be further discussed based on the tube surface characterisation later.

With respect to the effect of fly ash coating on the oxide layer thickness, both panels (b) and (c) are strong signs of an enhanced
thickness for the oxide layer upon the coating of XJ fly ash, irrespective of the combustion mode. In the air-firing mode (panel b), the coating of XJ fly ash decreases the oxide layer thickness down to the same level as the gas only cases, further confirming its inhibiting diffusion for the two elements O and S. However, in the oxy-firing mode, the tube thickness of SS400 and even low-Cr 12CrMoVG with the coating of XJ fly ash is still considerably larger than the flue gas only case. This should be due to the higher concentrations of impure components in the oxy-fuel flue gas, which interplayed with the ash to attack the tube surface.

3.3. XRD analysis of the top surfaces for SS400, T23 and SUS304

The original XRD patterns for these three tubes are shown in Figs. S2-S4. Taking the carbon steel XRD patterns in Fig. S2 as the example, it is obvious that the tube surface oxidation is limited
in pure air, with iron metal still being the principal species, followed by a small amount of magnetite (Fe₃O₄). Upon the use of air-firing fine gas that has a lower oxygen partial pressure (5%) but a lot of impurities, the peak intensity for Fe (1 1 0) decreases dramatically. Magnetite is still the only discernible oxides, suggesting that an active oxidation of the tube surface by steam and/or CO₂.

With regard to the coating of fly ash deposits, it is clear that the oxidation is enhanced in the XJ ash case, with the abundance of fully oxidized hematite (Fe₂O₃) being dominant. This could be attributed to the catalytic effect of the free oxides in the ash, which plays an oxygen-shuttling role for the transfer of the bulk oxygen. The use of XJ ash as protective, providing a shield to mitigate the oxidation on the surface, as evident by the re-appearance of unreacted iron metal and abundant magnetite on the XRD patterns in Fig. 52. Again, this is caused by the capture of the free oxide by the silica additive in the combustion process [7,18].

The results for oxy-fuel mode in Fig. 52 are more intriguing. The pure CO is clearly non-inert, as is evident by the appearance of numerous peaks for magnetite. The same phenomenon has been observed for a variety of tubes exposed to Ar/CO₂ for 1000 h [19]. Carbides were not found in the pure CO case, suggesting that the oxidation reaction (Fe₃O₄ + C ↔ FeO + CO) may not have taken place in the exposure time 50h tested here. For the pure CO with a pressure of 1 atm at 650°C, the equilibrium calculation results suggest an equilibrium Cₐt partial pressure of 1.68 × 10⁻⁴ atm, which is far lower than the equilibrium O₂ partial pressure that reaches 8.1 × 10⁻⁸ atm at 650°C. However, extra analysis of experiments is still necessary to prove this, considering that the exposure time is very short and the XRD analysis was only conducted on the top surface, rather than along the cross-section of the tubes. Similar to the air-firing mode, the remaining three cases in the oxy-firing mode show an enhanced oxidation of the surface to magnetite in the free gas, which was further enhanced upon the coating of XJ ash, as evident by the high intensity for the 2nd line of magnetite (440) at 62.51°. Again, the coating of XJ ash shielded the tube effectively, as evident by the abundance of the unreacted iron metal.

Similar observations were obtained for the two Cr-containing tubes shown in Figs. 53 and 54. The most noteworthy phenomenon is the confirmation of oxidation of chromium that leads to the formation of chromium oxide on both T23 and SUS304. Similar to iron metal, chromium in the tube also partially oxidized, even under the exposure to pure CO₂. Such a phenomenon is intriguing, and it even contradicts our assumption that this gas is inert in only 50h exposure time. To further view the significance of CO₂, the intensity of the most intense peak for the oxides, observed in the XRD patterns in Figs. 52-54, was divided by the intensity of the most intense peak for the respective pure metal, and plotted in Fig. 8. Interestingly, except the carbon steel tube SS400 which has a lower oxidation extent in pure CO₂ than the air, the other two were oxidized more intensively in CO₂ than in air. With respect to the oxidation extent in CO₂, it increases with increasing Cr content in the tube. Again, these phenomena cannot be simply explained by the dissociation of CO₂ to active oxygen for the reaction (M + O₂ ↔ MO, M for Fe or Cr), since the equilibrium partial pressure of oxygen is extremely low. Instead, a direct involvement of CO₂ in a reaction such as M + CO₂ ↔ MO + CO may occur. CO₂ can dissociate into CO upon being trapped on the adsorption site on the tube surface [20].

To prove the thermodynamic potential for this reaction, the standard Gibbs functions were calculated and plotted in the right hand side of Fig. 8. As can be seen, the standard Gibbs free energy for the formation of Cr₂O₃ via the reaction of M + CO₂ ↔ MO + CO is far lower than the formation of wustite (FeO) via the same reaction route. The formation of Fe₂O₃ even bears a positive Gibbs free energy in CO₂, which hints that wustite and its derivatives such as chromite (Fe₃O₄) would be preferentially formed rather than hematite in the oxy-firing combustion mode. In addition, Fig. 8 confirms that all the three oxidation reactions (M + O₂) are highly thermodynamically available, as expected. Cr is also more easily oxidized than Fe, thereby providing a protective layer.

3.4. XRD analysis of the tube top surfaces coated with ash deposits

To further clarify the effect of ash deposit on tube corrosion, all six tubes coated with two fly ashes were analysed using XRD. The
resulting XRD patterns are illustrated in Figs. S5 and S6 for air-firing and oxy-firing modes, respectively. Table S2 lists the two most abundant species with the strongest intensity for their first peaks in the XRD patterns. The three parameters, tube material, ash deposit type, and combustion mode interplayed considerably to affect the tube corrosion. To clarify these effects, the molecular weight (MW) for the first major species was plotted versus the tube material type in Fig. S3. Note that, the MWs of the species were normalized based on the unit molecule of iron (Fe). For instance, the MW of magnetite (Fe₃O₄) is 77, rather than 232 because each Fe₃O₄ consists of three molecules of Fe. In addition, for two species such magnetite and chromium oxide which have overlapping peaks, the larger MW was used. As shown in Fig. 9, in the conventional air-firing flue gas where the impurities including CO₂, SO₂, and HCl are lean, the tube surface is far from being fully oxidized in 50 h, irrespective of the tube material. This further proves the superior shielding effect of fly ash over its catalytic effect on the oxygen shuttling in the air-firing mode. For the SS400 carbon steel, magnetite (Fe₃O₄) rather than hematite (Fe₂O₃) was formed. For the remaining Cr-bearing tubes, the stainless steel Fe-Cr dominates over the 12Cr1MoVG tube, whereas wustite (FeO), magnetite/chromium oxide (Cr₂O₃) and austenite (Cr₃Fe₂O₆N₊) were observed on T23, SUS304, FB1 and SUS347, respectively. Except for the tube SUS304, a general decreasing trend was observed for the MW of the principal species with increasing Cr content in the tube, demonstrating the strong protective effect of Cr/Ni on the inhibition of the oxidation of iron, as expected. SUS304 is an exception, which may be due to the absence of Nb, although its Cr and Ni contents are similar to that in SUS347. Upon the coating with XJ_S ash deposit which is less corrosive, the above-mentioned oxides completely disappeared on the Cr-bearing tubes from T23 through to SUS347. The oxidation layer is thus slightly lighter than that formed on the tubes coated with XJ ash. Regarding the indiscernible discrepancy between the two fly ashes on the surface chemistry of SS400 and 12Cr1MoVG, it suggests a minimum 2 wt% Cr in the alloy tube even in the case that silica is mixed with coal for the combustion in air. However, one has to be aware that the XRD analysis here is only for the top surface.

The oxidation of tube surface is more obvious in the oxy-firing mode, and the oxides were formed regardless of ash deposit type. For the SUS400 carbon steel, magnetite is still the dominant species formed upon the coating of XJ ash, whereas the pure iron (Fe) was observed in the XJ_S ash case. In Table S2, one can see that the most intense peak for magnetite (Fe₃O₄) is the second highest upon the coating of XJ_S ash, relative to pure iron with its most intense peak being the second strongest in the XJ ash case. This further demonstrates the effect of using silica additive is more influential when the Cr-bearing tubes were used. For the remaining Cr-bearing tubes, the principal oxide is magnetite or chromium oxide for the XJ_S ash, whereas it turned to iron chromium oxide (Fe₃O₄Cr₂O₃) and/or eskolaite (Cr₂O₃) for the XJ_S ash. Its MW is thus slightly larger than the respective oxide formed in the XJ ash case. This in turn makes the tube surface dense and less porous, thereby decreasing the internal diffusion of oxidant inside the tube.

3.5. XANES spectra of Fe on tube cross-sectional surfaces

Fig. 9 illustrates the Fe K-edge XANES spectra and the respective fitting results for the cross-section of carbon steel tube SS400. Clearly, in either combustion mode, the coating of XJ_S ash deposit resulted in a lower oxidation extent for iron along the tube cross-section, i.e. a thinner oxidation layer. In the air-firing mode, relative to a similar fraction of 0.38 for hematite observed for the XJ ash case, none of the oxides was observed in the XJ_S ash case, proving an effective protection of this ash deposit against the corrosion of this low-quality tube material. Moreover, compared to Fig. 9 where magnetite (Fe₃O₄) was detected for the top surface for the same tube, the negligible content of oxide on the cross-section suggests that the oxidation layer should be very thin. The discrepancy between the two ash deposits was more obvious in the oxy-firing mode. For the coating of XJ ash, except hematite and magnetite that were also detected by the XRD in Fig. 9, two extra species were found here, including augite (Ca₆Mg₃Fe₅Al₂(Si₂Al)₂O₁₈) and pyrite (FeS₂). The former species is a direct evidence of the complex interaction between ash and tube surface, which includes a number of elements other than Na and S from the ash.

![Fig. 9. Molecular weight of the principal species on the tube surface versus the tube type, determined by XRD in Figs. S5 and S6.](image-url)
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Fig. 10. Fe L-edge spectra for the cross-section of the carbon steel tube SS400 coated with the two fly ash deposits. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena.

deposit that attack and penetrate through the tube surface. On the other hand, the latter species proves the importance of S that is able to break the oxide layer upon the formation of sulphate. Upon the coating of the \( XJ_S \) ash deposit, these two species were however not detected, suggestive of a slower diffusion of SO\(_2\) and its derivative \( S_{\text{gas}} \) through this ash deposit. The SEM-EDS mapping analysis in Fig. 5 confirmed a deep and uniform distribution of S in the oxide layer and even the spalled scale caused by the coating of \( XJ \) ash. In contrast, the S is preferentially present in at the bottom of the spalled scale in the \( XJ_S \) ash case in Fig. 6, suggestive of a grain-boundary diffusion route for S.

The protective effect of silica additive was further confirmed for the low-alloy tube T73, as evident in Fig. 11. In the air-firing case, no oxide was observed in the case of the \( XJ \) ash coating, suggestive of the formation of a super-thin oxide layer that is too thin to be penetrated by the synchrotron beam. More oxide species were formed under the oxy-fuel mode, in particular for the coating of \( XJ \) ash, as expected. Interestingly, the S-bearing species were not detected, confirming the strong protective role of Cr in the tube.

3.6 XANES speciation of the oxidation states of S and Cr

The speciation of S was conducted to clarify if any other S-bearing species such as sulphates formed on the tube surface. For the speciation of S, only the results for the top surfaces exposed to the oxy-firing mode are discussed here, because the signal for S on tube cross-section was very weak and noisy. In addition, the air-firing tubes were found to bear a very low signal to noise ratio even for its top surface. The SEM-EDS analysis also failed to detect any S on the air-firing tubes.

Fig. 12 illustrates the S K-edge XANES spectra for three tubes coated with the two fly ash deposits in the oxy-firing mode. The peak located at ~2481 eV is the distinctive fingerprint for a compound containing the SO\(_2\) group, whereas the peak located at ~2470 eV is the feature for pyrites (FeS\(_2\)). This peak is a direct evidence for the oxidation of the SS400 tube surface. Moreover, the intensified, broad peak located at ~2477 eV features the formation of trolith with a simple formula of FeS. It belongs to the pyrrhotite (Fe\(_{1-x}\)S, \( x \sim 0.02\)) group with an iron deficiency. It represents the transition of S to its p-like states in the conduction band hybridized with Fe 4sp states [21].

With respect to the coating of \( XJ_S \) ash sulphate, the predominant S-bearing species in most of the cases except the carbon steel tube SS400. Interestingly, this species was indiscernible in the XRD, suggesting an amorphous state for the existence of molten sulphate eutectics. It was not detected on the narrow tube cross-section in Figs. 10 and 11 for Fe either. Clearly, the molten sulphate eutectics preferentially stick on the outermost surface of the tubes, which dissolves the metals as well as increases the resistance against the inward diffusion of the gaseous components.

With respect to the sulphide formation, its content varies greatly with the tube type as well as ash deposit. For the carbon steel tube SS400, sulphide was formed in conjunction with sulphates, irrespective of the ash deposit type. However, for the two C-bearing tubes, sulphide is indiscernible, which should be due to the protective effect of Cr-oxide layer that was formed preferen-
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Fig. 11. Fe K-edge spectra for the cross-section of T23 to be coated with the two fly ash deposits. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It is interesting to explore the probable reactions that have occurred during the sulfidation of the pure metal tube in the SS400 tube. Fig. 13 lists all the probable sulfidation and sulphation reactions and the Gibb’s free energy of formation at 650°C. These reactions include the solid-to-gas reactions between a metal and \( S_2 \), that is derived from the reaction \( \text{SO}_2(g) = \text{S}_2 + \text{O}_2(g) \), and the solid-to-solid reaction (No. 5–8) for the interaction between Na sulphate, Fe/Co sulphate and the pure metal (Fe/Cr). Here the Fe/Co sulphates can be derived from the solid-to-gas reactions Nos. 3 and 5. In comparison to the sulfation reactions 3 and 4, the first two solid-gas reactions numbered 1 and 2 can be ruled out here, considering that the equilibrated \( S_2 \) partial pressure is extremely low under the given exposure conditions. The exposure to flowing gas only has confirmed this. The solid-to-solid reactions numbered 5–8 are the only probable causes for the formation of sulphides. In other words, the inherent Na sulphate in ash is the key component that drives the sulfidation reaction. It forms molten eutectics with iron surface to promote the outward diffusion and sulfidation of metals (Fe and Cr) with the molten eutectics. The use of Cr-bearing tube inhibited the formation of sulphate eutectics, and hence, the coating of X JS ash caused little difference against the speciation of S for T23 and SUS304 in Fig. 12. However, the discrepancy between the two ash deposits for SS400 is intriguing. Although the content of Na sulphate is lower in the X JS ash (Table S1), the trillite (FeS) with a broad peak at ~2477 eV is nearly the only species observed upon the coating of SS400 with X JS ash. On the one hand, this substantiates the inhibitory effect of silica additive on the formation of molten alkali-metal sulphates. On the other hand, this may hint the alleviation of the resistance against the inward diffusion of SO\(_2\) due to the absence of molten sulphates. Therefore, the dissociation of SO\(_2\) inside the tube result in a relatively high partial pressure for \( S_2 \) to promote the sulfidation extent of Fe.

The difference of the sulfidation potentials between the two pure metals Fe and Cr, as shown in Fig. 13 is also interesting. If the sulfidation rates of these two metals are comparable, the Cr-oxide protective layer would break down by the spallation, thereby accelerating the overall corrosion rate for the tube. Since it is not possible to differentiate between Cr-S and Fe-S by the S K-edge XANES spectra, the XANES was conducted on the Cr K-edge for the top layer of the two tubes T23 and SUS304. As demonstrated in Fig. 14, Cr\(_{\text{III}}\) oxide and chromite (Mg\(_{\text{II}}\)(Fe\(_{\text{III}}\))\(_2\)) are the only two species observed, which were balanced by the Cr metal. This suggests that the amounts of Cr sulphide and sulphate are extremely low on the tube cross-section, or the sulfidation and sulphation...
rate of Cr is kinetically slower than its counterpart metal Fe, irrespective of the tube material and ash deposit type. Moreover, Fig. 14 suggests an enhanced formation of chromite upon the coating of XJ S ash on the two tubes. This is consistent with the XRD results in Figs. 52-54.

Last effort was made to clarify the oxidation states of Cr along the cross-section of the low-alloy tube T23 coated in the oxy-firing mode, so as to quantify the penetration depth of oxygen and its promotion effect on the oxidation of Cr. At the XAS measurement, the sample was moved from the centreline of the tube through to the outer surface where the signal of Cr tends to disappear. The tube was analysed for two cases including the flue gas only case and the coating of XJ S ash. The resultant Cr K-edge XANES spectra are shown in Fig. 15, whereas the respective fitting content for Cr²⁺ including both chromian oxide and chromite was plotted versus the distance from the tube centreline in Fig. 16. Interestingly, the exposure of the tube T23 in flue gas only resulted in a very slow diffusion of oxygen inside the tube, therefore, the oxidation extent of Cr on the outer layer surface only reaches ~8% of the total Cr, which gradually decreases to less than 5% for the Cr in the centreline of the tube. However, upon the coating of the XJ S fly ash, the oxidation extent of the Cr inside was increased slightly compared to the flue gas case, reaching approximately 10% on the metal/oxide interface. In the oxide scale, the oxidation
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Fig. 14. Cr K-edge XANES spectra and the fitting results for two tubes coated with the two fly ashes in the oxy-firing mode. Cr metal is the third species to balance the whole Cr on the cross-sectional surface of the tubes. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 15. Cr K-edge XANES spectra along the width of the cross-sectional tube T23 from its centerline to the oxidation scale. The tube T23 was exposed in the oxy-firing mode. The solid lines on the left two panels refer to the measured XANES spectra, and the dashed curves (in red) are the respective fitted results from Athena. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The extent of Cr in the ash deposit case is even slightly higher than the fly ash case. This confirms the catalytic effect of fly ash on the oxidation of chromium, either via the oxygen-shuttling role of the free oxides within it, or the interaction with Cr-oxide layer to form the respective chromium, as indicated in the Eqs. (3) and (4) below:

\[ M_2O = xM + O \]  
\[ M_2O + Cr + O = MCr_2O_4 \]

where \( M \) in Eq. (3) denotes a metal, which is mainly alkali and alkaline earth metals (Na, K, Ca and Mg) in ash possess a larger reducibility to accept the electrons released from dissociation of bulk oxygen. Our previous research [22] and the past studies [23,24] using pure oxides for the oxidation of Cr at 600–1000 °C has proven this. Due to this catalytic effect, the dissociation of bulk oxygen and its inward diffusion rate were enhanced, whilst the relative diffusion of Cr outwards was enhanced simultaneously. Although this helps form a denser protective layer, it may cause some side effects such as the breakaway of the chromeite layer over a longer exposure time [25]. Efforts will be made by us to clarify this and the probability for the formation of chromium carbide in the future.
4. Conclusions

Detailed speciation analysis has been conducted on the corroded tubes coated with two different ash deposits, in air-firing versus oxy-firing mode, at an exposure temperature of 650 °C, 56 h and different flow gases, i.e. pure O₂, air, air-firing flue gas and oxy-firing flue gas. The two ash deposits were collected from the surface of superheater tubes in a PC-fired boiler burning a low-rank coal (from Xinjiang, China) with and without silica additive. The major conclusions achieved include:

1. Irrespective of the Cr content, the tubes exposed to pure O₂ and air oxidation, which is likely due to the reaction \( \text{Cr}_2\text{O}_3 + \text{O}_2 = \text{Cr}_2\text{O}_4 + \text{O}_2 \) where \( \text{M} \) stands for Fe or Cr. Cr in the Cr-bearing tubes were oxidized more rapidly than Fe.

2. The combined use of silica additive and Cr-bearing tubes with a minimal Cr content of 2 wt% (i.e. T23) is beneficial in inhibiting the tube surface oxidation as well as the penetration of oxygen in the air-firing flue gas.

3. Oxygen is the principle element diffusing inside the tube upon the exposure to flue gas only. Upon the deposition of ash on the tube surface, the penetration of sulphur was enhanced. Compared to the sodium sulphate – rich XJ ash causing the formation of pyrite (FeS₂) on the tube surface, the ash deposit derived from coal mixed with silica additive resulted in the preferential formation of mobile (FeS) that is deficient in S, thus less corrosive. For the Cr-bearing tubes, sulphate is the only S-bearing species due to the inhibited inward diffusion of S by the Cr-oxide layer, irrespective of ash deposit type.

4. Apart from sulphur, sodium and other metallic elements in ash deposits also interacted with the tube surface to form new species such as augite, which may cause the tube breakdown as well.

5. Spatial organisation of the oxidation state of Cr suggests a slightly accelerated outward diffusion of Cr by the ash coating, due to the catalytically enhanced oxygen-shuttling of the free oxide in ash. This led to a dense Cr-O layer that is highly protective on the tube top surface.

Acknowledgement:

This work was supported by Brown Coal Innovation Australia (BCIA), and the Partnership Program of Japan Society for the Promotion of Sciences (JSPS) and Australian Academy of Technological Science and Engineering (AATS). The first author is also grateful to the Iraq Government for providing the PhD scholarship. The XANES analysis on Fe, Cr and S was conducted at the beamline BL16A at Taiwan National Synchrotron Radiation Research Center (NSRRC) with the support of Dr. Long-Yan Jiang. Part of this research was undertaken at the XAS beamline in the Australian Synchrotron, Victoria, Australia.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2016.09.060.

References

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Influence of gaseous SO\(_2\) and sulphate-bearing ash deposits on the high-temperature corrosion of heat exchanger tube during oxy-fuel combustion

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High temperature corrosion
Lignite ash deposits
Sulphate
XANES

A B S T R A C T

This study aims to clarify the role of sulphur (S) in both lignite ash deposits and bulk flue gas on high-temperature corrosion. In particular, the potential synergism between these two different S sources during the oxy-fuel combustion was explored. The ash deposits were derived from the combustion of a Xinjiang lignite and its washed coal samples. It was found that the amount of S permeated inside the tube is predominantly limited by the availability of sulphates in the ash deposits, under both air-firing and oxy-firing combustion modes. However, the participation of flue gas in particular SO\(_2\) and steam is essential, although their participation extent is very low. The lignite ash deposits function as a medium which transfers the S from bulk gas to tube surface via the formation of intermediate molten sulphates or sulphides. The formation of sulphides is highly dependent on ash properties (i.e., the content of sulphates) and tube composition. The high-S ash deposits with high-S flue gas have no propensity to cause the formation of sulphide. By contrast, for the low-S ash deposits with low-S flue gas, the co-precipitation of Fe sulphide and even CaS in the molten melt was observed. The inherent Ca is believed to be a key element causing the sulphidation of tube surface. Compared to water washing, the use of acid in wash coal is able to remove the free Ca oxide, and hence, eliminates the formation of sulphide on the tube surface. For the tubes tested, the medium-C tube: 791 is most easily sulphided, due to the low C content. The Cr-O protective layer formed on the tube top surface is also porous enough for the gases to permeate and form a reducing environment deep inside that promotes the formation of sulphide. Upon the use of washed coal ashes, the tube corrosion rate was much lower than the use of silica additive and even comparable to the raw flue gas.

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1. Introduction

Tube corrosion in the furnace is one of the critical issues negating the performance of a coal fired boiler [1]. Apart from the nature of the material, the wastage of a tube is induced by flue gas and ash deposits in both of which sulphate is one of the most critical elements. In a typical coal-fired combustion environment, the majority of the inherent sulphur converts into a gaseous oxide, which subsequently partially reacts with ash-forming elements to form sulphates. If the flue gas pollutants are recirculated, such as in oxy-fuel combustion, the concentration of SO\(_2\) could be raised 3–4 times compared to air-firing combustion [2].

The high-temperature corrosion rate in the boiler will thus be accelerated [3–5]. The theory underpinning the role of sulphur on tube corrosion in the superheater zone has been well established under the conventional air-firing mode. In brief, the alkali sulphates in ash deposit are critical in accelerating the tube corrosion [6], due to the formation of alkali - iron trisulphates eutectics such as Na\(_2\)Fe\(_2\)(SO\(_4\))\(_3\) and K\(_2\)Fe\(_3\)(SO\(_4\))\(_3\) that have a melting point close to and even lower than the tube surface temperature in the superheater and reheater zones [7]. The resultant trisulphide can further promote the sulfidation reaction under the tube surface, as shown in Eqs. (3) and (4) below [8,9]. When
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Table 1

| Compounds (wt%) | Samples | Raw coal | Washed | Water + Acid | W+Acid
<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>W1</td>
<td>W2</td>
<td>W3</td>
<td>W4</td>
</tr>
<tr>
<td>S</td>
<td>5.67</td>
<td>47.59</td>
<td>45.57</td>
<td>45.42</td>
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<td>18.60</td>
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<td>4.96</td>
<td>7.71</td>
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<tr>
<td>SiO₂</td>
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<td>7.79</td>
<td>7.13</td>
<td>7.59</td>
<td>8.79</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.60</td>
<td>0.12</td>
<td>0.1</td>
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<td>0.18</td>
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<tr>
<td>Na₂O</td>
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<td>1.1</td>
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<td>1.18</td>
<td>1.93</td>
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<tr>
<td>K₂O</td>
<td>0.40</td>
<td>0.51</td>
<td>0.15</td>
<td>0.49</td>
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</table>

These results are qualitatively attributable to the oxy-fuel combustion environment. Through experimental study using sulphur – lean bituminous coal (3.77 wt%) and sulphur – rich bituminous coal (6.49 wt%) in the coal ash deposits, Stevi-Bzorzovskaia et al. [15] found that, the flue gas corrosion of the combustion of high S coal were subjected to a higher corrosion rate than the low-S coal which was burnt under the same conditions. This hints the importance of inherent sulphur present in the coal ash that has more influence on corrosion than its gaseous counterpart in the oxy-fuel combustion mode. Stevi-Bzorzovskaia et al. [15] also reported that both the high temperature corrosion rate and sulphidation rate increased with temperature. However, by varying the concentration of bulk SO₂ from 1000 ppm to 3000 ppm, the same authors confirmed that the gaseous SO₂ is superior over the inherent S in coal, causing more corrosion on the tube surface. Clearly, this leaves an open and unclarified question regarding to what extent the gaseous SO₂ and solid sulphur in ash deposit interfere and even compete between one another to attack the tube surface. Upon the shifting of bulk gas from once-through air to recirculated flue gas in oxy-fuel mode, the concentration of SO₂ in bulk gas is expected to increase rapidly than the content of S in ash deposit. Clarifying the importance of sulphur from different sources and their synergism, if any, is thus critical for the control of tube corrosion in the oxy-fuel combustion process.

The present study aims to clarify the synergism between gaseous SO₂ and ash deposit on corrosion under the typical superheater conditions in an oxy-firing boiler. The tube exposure conditions were fixed at a temperature of 650°C and 50 s duration, and the flue gas was made up of 3000 ppm SO₂, 30% steam, 1000 ppm HCl, 5% O₂, 10% N₂ and the balance CO₂. Efforts were made to vary the compositions of ash deposits that were produced from a lignite coal, namely Xinjiang and its respectively washed coals. Since Na and/or Ca are the major elements that were washed away whereas the other elements have little change, the use of such a series of ash samples is expected to minimize and even eliminate the effect of the metals other than Na and Ca on tube corrosion. The use of these ash deposits can also help us to reveal the effect of coal washing on the minimization of tube corrosion. Additionally, four different tubes with different chromium content (SS400, 12CrMoVG, T91 and SUS304) coated with raw/washed by ash were tested. Special attention was paid to the medium-Cr tube T91 with around 9.1 wt% Cr, based on the hypothesis that this medium-Cr tube has the potential to replace the commonly used low-Cr alloy such as 12CrMoVG under the harsh conditions that can be encountered during the oxy-fuel combustion.

Apart from weighing the mass change of a corroded tube, a variety of advanced analysis was also conducted on both tube surface and used ash deposits, including optical microscopy (OM) for the cross-section observation (to quantify the corrosion depth), scanning electron microscopy equipped with energy dispersive X-ray detector (SEM-EDX) to map the penetration/diffusion of elements of interest through the ash-tube interface, X-ray fluorescent spectrometer (XRF), and synchrotron XANES for the oxidation states of sulphur (S) and chromium (Cr). Thermodynamic equilibrium calculation was also conducted to interpret the experimental observations. The results achieved are expected to shed new lights on the mechanisms underpinning the role of sulphur on tube corrosion during the oxy-fuel combustion.

2. Experimental procedure
2.1. Ash deposit compositions

The fly ash of Xinjiang (XJ) coal, known as a low - rank coal in Xinjiang, China was used as the baseline sample for high temperature corrosion test. As listed in Table 1, the raw coal ash, namely XJ is a typical low-rank lignite ash rich in around 10 wt% sodium (Na) in its oxide form. It is accompanied by abundant calcium (Ca) of 39.21 wt% and 10.86 wt% sulphur (S). The typical low rank coal composition is 24.5 wt% moisture, 6.9 wt% ash, 30.2 wt% volatile, 31.7 wt% FC and 0.02 wt% chlorine [16]. The ash sample was collected from the surface of the super-heater tube surfaces [17]. The same coal was washed by the use of water and 1 M hydrochloric acid (HCl) [16,18]. For water washing, a three-stage counter-current process was applied, leading to the formation of three washed coals, W1-W3. On the other hand, for the acid washing, a two-stage counter-current with acid in stage 1 and water in stage 2 was employed, yielding two samples, A1 and A2 from the two stages, respectively. Regarding the ash samples from the water-washed coals, the content of Na was reduced significantly. The use of acid further slightly reduced the content of Ca, whereas Na has little change compared to the water-washed coal samples. This is because Na in this coal is mostly present as water-soluble species that can easily dissolve into the neutral water [16].

Table 2

<table>
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<tr>
<th>Specimen</th>
<th>C</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn</th>
<th>V</th>
<th>Cr</th>
<th>Si</th>
<th>S</th>
<th>P</th>
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<td>SS400</td>
<td>0.02</td>
<td>0.09</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.06</td>
<td>0.06</td>
<td>0.36</td>
<td>0.004</td>
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<tr>
<td>12CrMoVG</td>
<td>0.10</td>
<td>0.12</td>
<td>0.12</td>
<td>0.01</td>
<td>0.07</td>
<td>0.15</td>
<td>0.15</td>
<td>0.30</td>
<td>0.013</td>
</tr>
<tr>
<td>T91</td>
<td>0.50</td>
<td>0.01</td>
<td>0.03</td>
<td>0.04</td>
<td>0.11</td>
<td>0.21</td>
<td>0.39</td>
<td>0.38</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>SUS304</td>
<td>0.02</td>
<td>0.05</td>
<td>0.12</td>
<td>0.17</td>
<td>0.05</td>
<td>0.08</td>
<td>0.75</td>
<td>2</td>
<td>0.010</td>
</tr>
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</table>
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2.2. Tube corrosion test set-up and test conditions

The tube corrosion test was detailed in our previous work [4]. The furnace temperature was fixed at 650 °C in this study; the flat tube specimen, 3 cm × 3 cm × 2 mm were prepared by a wire electrical discharge machine to cut on the cross-sections of four commercial tubes. Each test lasted 30 h and three repetitions were conducted for each condition. With regard to the oxy-firing flue gas composition, it is made up of 3000 ppm SO₂, 30% steam, 1000 ppm NO, 5% O₂, 10% N₂, and CO₂ in balance. Flue gas was fed at a flow rate of 300 ml/min continuously into the furnace. As confirmed by our pilot scale test [19], the steam content in flue gas can go up to 30 vol.%; and SO₂ is also highly accumulated during the oxy-firing of low-rank brown coal. The steam content tested here is close to the oxy-fuel flue gas tested elsewhere [20–22]. A total of four tube materials in Table 2 were tested, with a Cr content in the ascending order of stainless steel SS400 (Cr-nil), low-chrome ferritic steel 12CrMo195 (0.9–1.2%), high-chrome ferritic steel 191 (1.9%), and austenitic stainless steel SS304 (18–20%). For each test, around 100 mg ash was loaded on the tube surface. The ash coating was conducted by putting the ash powders into a plastic mold that is the same size as the tube specimen. The ash power amount remained almost the same throughout all the tests. The ash powder was also gently pressed by hand to ensure that there is no loss during the test. After it, the plastic mold was removed whereas the ash powder was left on the tube surface. Finally, the ash laden tube specimen was loaded on a quartz-made sample holder and pushed to the middle zone in the hot furnace where the temperature is constant and the same as the set temperature. A thermocouple was further inserted above the tube specimen to record and control the temperature. After each test, the used ash was generally brushed away using a soft brush (to avoid surface scratching) and saved for the characterisation. The used tube was either weighed for its mass change and saved for the future characterisation on the top surface, or quickly mounted together with the ash into epoxy resin to measure the cross-section.

2.3. Analytical techniques for characterisation of the surface of corroded tubes

The cross-sections of the corroded tubes were observed by an optical microscopy (Olympus) to establish the thickness of scale and depth of intergranular penetration. The oxidation thickness was evaluated using sketchbook software, where 10 lines were drawn across the interface. The length of each line was measured and used to calculate the average thickness and standard deviation which subsequently gave the interface thickness. From the interface thickness, the oxidation rate was calculated by dividing the interface thickness by the exposure time, 50 h.

Prior to the analysis, the tube cross-sections were polished by the use of silicon carbide paper with a grit of 2400. In addition, scanning electron microscopy (SEM) was used to map the elemental distribution on the tube cross-section. The analysis was conducted by JOL 7001F to identify the distribution of major elements of interest, including Ti, S, and O. Prior to the SEM observations, the tubes were also carbon sputtered.

The K-edge X-ray absorption near-edge spectroscopy (XANES) spectra of S and chromium (Cr) were conducted to specify the oxidation state of these two elements on the top tube surface. Compared to bench-scale X-ray diffraction (XRD), XANES is highly sensitive and able to detect the elements with a concentration on the ppm level [23]. The beam size of around 1 mm can easily pinpoint the tube surface, which is generally on the sub-micron scale. The XANES spectra were collected from beamline BL16A1 at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. BL16A1 had a fixed exit double-crystal Si (111) monochromator with a nominal beam size of 0.25×0.25 mm on a sample. For the analysis of Cr, pure elemental Cr was used for the calibration at a K-edge absorption energy of 5898 eV.

Pure elemental Mo was used for the calibration of S at a K-edge absorption energy of 2481 eV. The peak energy absorption (white line) position was taken as the base (0 eV), with all subsequent spectra recorded 200 eV below and 800 eV above this point in fluorescence mode. The analysis of S and Cr was only conducted for the top surfaces, as the signal for S from the cross-section of the tubes was very weak and noisy. All spectra were normalized using ATHENA which is part of the IFEW/DESMER package [24]. Linear combination fitting (LCF) was used on the normalized sample spectra to determine the mineral composition by using a large number of standards that have been detailed in our previous papers [4,25].

2.4. Analytical techniques for characterisation of the used ashes

After the tube exposure tests, some of the used ash samples were also gently collected from the tube surface, further ground and characterised by X-ray fluorescence (XRF) for the composition as well as XANES for the oxidation of S. The XANES results are expected to supplement the results for the respective tube surfaces so as to draw an overall picture on the partitioning of S between tube and ash.

2.5. Thermodynamic equilibrium calculations

The 'Equilib' module in a commercial thermodynamic equilibrium program, FactSage [26] was used to calculate and establish the species in equilibrium that can be formed upon the interaction between flue gas, ash deposit and the alloying elements in the tube. The input for each calculation includes the amounts of alloying elements in a tube, individual elements (as a form of oxide) in the ash, and individual components in flue gas based on the compositions of tube, ash and flue gas, masses of a tube and ash, flow rate (300 ml/min) of flue gas and a total exposure time of 50 h. The temperature was set at 650 °C and the total pressure was 1 bar absolute. Apart from the pure substances, the built-in databases F-oxid Slag A or F-oxid - Slag B were also ticked during the calculation. Slag A is made up of sulphide whereas Slag B is dominated by sulphates in the FactSage database. The calculation using Slag B database gives a much lower slag formation propensity, because sulphate is less prone to melt than sulphide at 650 °C. Since the formation of sulphide is more of interest and is also confirmed experimentally in this study, the results using Slag A database for the washed coal ashes were only interpreted hereafter.

**Fig. 1.** Mass loss (panel a) and oxide layer growth rate (b) of the tubes exposed to washed coal ashes under the oxy-fuel combustion mode. The dashed lines are results for the respective blank ashes with flue gas only.
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3. Experimental results

3.1. Mass changes and oxidation growth rates

Fig. 1 illustrates both the mass loss and oxide layer growth rate for the four tubes coated with different ashes, where x-axis refers to the ascending sequence of Cr content in the tubes. The tube mass loss value is the average of the two replicate samples, instead of mass gain. Mass loss was observed for all the tests here, which is expected and can be explained by the evaporation of the metals as chloride-hydroxide, and the spallation of oxide/sulphide fragments which are ductile. For comparison, the blank test without ash coating was also included in Fig. 1, as well as the XJ5 referring to the ash deposit collected from the combustion of Xinjiang coal blended with around 4 wt% silica [17,27]. The use of silica additive has proven to be able to mitigate the fouling and tube corrosion in the industry-scale boilers, due to the immobilisation of Na and Ca in the silica matrix [17,27].

As indicated by the mass loss results in Fig. 1 panel (a), the mass loss decreases considerably with increasing the Cr content in the tube, irrespective of ash type. This agrees with our expectation, as Cr and the other addition metals such as Ni preferentially form a protective oxide layer on the tube surface [22]. Regarding the influence of ash type, it is evident that the raw coal XJ ash is most detrimental, causing the largest mass loss for each tube. The mass loss in the case of XJ ash is also 1.3 to 8 times higher than the blank flue gas case, demonstrating the significance of solid ash over flue gas on the tube corrosion. The use of silica additive reduces the tube mass loss, but the respective tube mass loss is still higher than the blank flue gas case except the tube SS400. In contrast, the coating of washed ashes, irrespective of its type, is much more effective, mitigating the tube mass loss to a level that is even below the blank case, irrespective of the tube type.

The oxide layer growth rate is shown in Fig. 1 panel b. The oxide layer growth rate was calculated by dividing the corrosion product thickness (as shown in Fig. 2) by the exposure time, 50 h. The results here further...
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Fig. 4. Correlation between tube mass loss and the content of S on the corroded tube surface.

Confirms that coal washing is more effective than silica addition in the prevention of tube oxidation. Instead of attacking tube surface, the washed coal ashes, in particular those washed by acid can even function as an anti-ash layer in combination with the medium-Cr tubes including T91 and SUS304 to decrease the tube oxidation layer drastically.

The typical cross-sectional structures for the corroded low-chrome ferritic tube 12Cr1MoVG are illustrated in Fig. 2. Compared to the case of raw coal fly ash coating, the other two cases for the coating of W1 and A2 yield a narrower corrosion product thickness which also refers to as the oxide layer that is formed by the penetration of corrosive components, in particular the oxidising gases such as O2 and H2O. Moreover, considering that the tube corrosion is directly related to the penetration depth of oxygen (O) and sulphur (S) [1], efforts were made to map these two elements on the corroded tube cross-section. As shown in Fig. 3 for the tube T91, the two elements of O and S show distinctively different distribution along the cross-section. 

interface and bulk tube/substrate, or even inside the interface layer. Taking W1 as the example, one can clearly see that a thin S-rich layer, labelled as strip No 1 in the map adheres closely to the tube surface. However, the remaining two strips labelled as No 2 and 3 are embedded deeply inside the interface. Regarding another washed ash W2, only one thin layer was observed on the boundary between tube surface and the interface. For the acid washed ash A1, the distribution of S is barely discernible.

The S observed in the ash tube interface demonstrates the penetration of this corrosive element either from SO2 in bulk gas, or from solid sulphates in ash deposits. Regardless of the sulphur source, the resultant S in the interface should be partially ductile and easy to fragment into small pieces that are eventually mixed up with ash deposit, as evident in Fig. 3. In light of this hypothesis, the contents of S on the corroded tube top surfaces (after the ash was brushed away) were quantified by XRF, and plotted versus the respective mass losses of the tubes. Considering the measurement error related to the mass of the tubes, a reasonably linear trend is evident in Fig. 4. For the most advanced tube SUS304, its mass losses are the least, so are the contents of S remaining on its surfaces. The tube T91 bears a medium-Cr content, and the S content remaining on its surface mostly falls in the medium range. As expected, the low-Cr tube 12Cr1MoVG bears the largest mass loss as well as the highest content of S. More interestingly, an identical linear correlation even holds for the three Cr-containing tubes, substantiating that S is the principle element causing the tube wastage. Furthermore, Fig. 5 for the used ash W1 on tube T91 demonstrates the abundance of ductile S-bearing fragments that are fully mixed with the other particles. The quantified composition for the used ash W1 on tube T91, as listed in Table 3, confirmed a remarkable rise on the concentrations of Fe and S, whereas the concentrations of Na and Ca were decreased significantly. Apparently, S is mainly affiliated with Fe, whereas the inherent Na and Ca should partially diffuse out of ash matrix and transfer into the corrosion product or even deep inside the bulk tube, forming eutectics that easily melt, flow and fill in the pores within bulk tube and ash deposit.

3.2. XANES speciation of S and Cr on tube surface and/or used ash

Fig. 6 illustrates the S K-edge XANES spectra for the three corroded Cr-bearing tubes. Irrespective of the tube material, the peak located at ~2485 eV is the predominant and single peak for 12Cr1MoVG and SUS304. This peak is the fingerprint of sulphates which can be assigned...
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### Table 3

<table>
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<tr>
<th>Composition</th>
<th>wt% Before corona exposure</th>
<th>wt% After corona exposure</th>
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<td>SO$_2$</td>
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</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>21.96</td>
<td>14.73</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
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<td>3.56</td>
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<td>C$_2$O</td>
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<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>0.51</td>
<td>0.10</td>
</tr>
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</table>

as iron sulphate[20]. Such a species should be formed by the direct
dissolution of iron oxide by bulk gas or via the formation of Na-Fe
trisulphide according to the reaction eq. 1. Since no other peaks were
found for S remaining on the tubes 12Cr1MoV and SUS304, it is
referable that eq. 2 for the reaction between sulphides and iron metal
to form sulphide did not proceed on the surface of both low- and
high-Cr tubes. This is however not the case for the tube 191 with a
medium Cr content. From the panel b for 191 coated with W1-W3 ashes, one
can clearly see a peak at 2470 eV or 2472 eV. The similar phenomena was observed for the used ashes
coated on the same tube. As evident in Fig. 8 for both the fresh and
used ashes, although sulphate is the single, dominant species in the fresh ashes and the used ones on the tubes 12Cr1MoV and SUS304,
the three washed ashes, W1-W3 on tube 191 are exceptional that display
the unique feature peaks at 2470-2472 eV. This peak is close to the feature peaks for a variety of sulphide standards shown in Fig. 8.

The difference between these sulphide standards is subtle and thus,
the sulphides detected in Fig. 7 can refer to as FeS$_2$, FeS, NiS, CrS$_2$, or
even CoS-MgS. To rule out the formation of CrS$_2$, synchrotron XAS
was further conducted on the speciation of Cr on the top tube surfaces,
following exactly the same analytical and calculation procedures for Cr.
The Cr-bearing standards used include oxide, carbide, sulphide and spintel,
as detailed elsewhere [4]. Fig. 5 for the Cr K-edge XANES spectra
sustains that chrome/spinels is the predominant Cr-bearing species
on the tube surface. The resultant chrome/spinels should function as
the protective layer against the oxidation of iron and its corrosion. In
light of this, the sulphides in Figs. 6 and 7 are very likely related to the
metals Fe, Cr and Mg.

### 4. Discussion on the mechanisms governing the partitioning of sulphur

Based on the results above, the behavior of S is clearly the most
critical factor accelerating the high-temperature tube corrosion under the
oxy-fuel combustion mode. This broadly agrees with the observations
achieved in the conventional air-firing mode [30]. However, three key
and new phenomena have been explored from this study, 1) the
existence of sulphate and sulphide on both corroded tube surface and
used ash deposit; 2) ash - dependent formation of sulphide, and 3) the
unique formation of sulphide on tube 191 upon the coating with
washed coal ashes that are lean in sulphates. All these phenomenon
have yet to be reported. In particular, the last phenomena related to
191 is for the first time reported here. As summarised in Table-4 for the
past researches on the use of 191, the previous findings are mainly
comprised of the general trends such as the tube corrosion rate versus
tube composition and the comparison between different tubes.

With regard to the first phenomena for the splitting of S between
sulphate and sulphide, they should be formed according to the reaction
eqs. 1-4 mentioned before. In particular, the formation of sulphate by
eq. 1 needs to take place firstly upon the contact between loose ash
particles and oxide layer formed on the tube top surface. Subsequently, the
resultant Na-Fe sulphates, as evident in Figs. 6 and 7 partially melt and
stick to the tube surface. The molten sulphates can further act as a solv
vent pool to dissolve the inherent metals such as Fe, Cr and others in
the tube according to the fluxing mechanism [31]. The dissolved metals
in turn react with the molten sulphates to form the respective sulphide,
as suggested by eqs. 2 and 4. This mechanism is exploited virtually in Fig. 10 panel a, where the grey, black and light green colours refer to
the bulk tube, molten species and loose ash particles, respectively.

Note that, HCl in the bulk gas has been ignored, although it has the
potential to cause the formation of sodium chloride which in turn reacts
with SO$_2$ and O$_2$ into allilodium sulphate [32]. After sulphation, the reaction
mechanism is similar to that of fluxing scheme induced by SO$_2$. A thin
Cr-O layer is expected to remain in between the grey and black colours,
as has been confirmed in our previous studies [4] and Fig. 9 in this study.

With respect to the formation of molten species, the FastRay prediction
results, as shown in Fig. 10, panels b, c, d respectively for raw XJ coal
ash and W1 ash on tube 191, confirmed the thermodynamic possibility
for the melting of sulphates/sulphides at 950 °C. Note that the melt
fraction accounts for 5 wt% and 10 wt% of the total ash in panels b and

![Fig. 6. S K-edge XANES spectra and the fitting results for the top surfaces of three tubes exposed to different washed coal. In each panel the solid curves refer to the measured XANES spectra, and the dashed curves (a and c) are the respective fitted results from ATHENA. Panels (a) and (c) are for the tube 12Cr1MoV, W1 and SUS304, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
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Fig. 7. S K-edge XANES spectra and the fitting results for the ash samples before and after the tube exposure tests. In each panel the solid curves refer to the measured XANES spectra, and the dashed curves in red are the respective fitted results from Athena. Panels (a) – (d) are for the fresh ash samples, used ash on tube 1200 MVG, used ash on tube 1500 MVG, and on tube 1500 MVG, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

c. respectively. For the sulphate-bearing melt shown in Fig. 10 panel c, sulphide is predominant, which is followed by Cr and Fe oxides. The sulphide is also made up of CuS and FeS that can be formed thermodynamically via eq. 3.

The detection of sulphide in Figs. 6–7 experimentally confirmed a direct involvement of ash deposit on the tube corrosion. For the blank test using pure flue gas only, our previous test have proven that the formation of sulphide was indiscernible [3]. However, the role of flue gas on the formation of sulphide cannot be ruled out here. Although having no direct contact with tube surface, the flue gas can react with ash deposit first, forming sulphates that subsequently attack the tube surface according to the fluxing mechanism in Fig. 10 panel a. The abundant CaO in ash samples in Table 1 plus the free oxides derived from eqs. 2–4 are able to capture SO$_2$ at 650 °C [33]. To quantitatively clarify the extent of flue gas participating on the tube corrosion, thermodynamic equilibrium calculation was further conducted to evaluate the influences of three flue gas components, SO$_2$, O$_2$, and steam/H$_2$O on the formation of sulphide. A kinetic modelling was not attempted here because of the lack of the kinetic parameter and the complexity of the oxy-firing flue gas used here. Fig. 11 (a) demonstrates the results for the extent of dry gas (SO$_2$ and O$_2$) whereas panel (b) is for the participation extent of steam when the extent of two dry gas components are fixed at 0.2. Note that, the ash W1 was used for calculation here, and the two dry gas components, O$_2$ and SO$_2$, are assumed to have an identical participation extent in the formation of sulphide and sulphide.

As shown in Fig. 11(a), the attendance of dry flue gas is critical in affecting the amounts of total slag and the two key sulphides, Fe sulphide and Cr sulphide. Compared to the predominant formation of Cr sulphide in the absence of flue gas, the introduction of dry flue gas decreases the formation of Cr sulphide quickly, which drops to nil in the case that ~0.2% of dry flue gas participates in the reaction. Simultaneously, the total slag amount and Fe sulphides increase quickly to their maximum when ~0.5% dry flue gas is involved. However, as the case that ~2.5% dry flue gas attends the reactions, the slag amount and sulphide drop dramatically to nil, due to the formation of dominant sulphates that are difficult to melt. Back to Fig. 9 where Cr sulphide was not found, it is obvious that the participation extent of dry flue gas should range between 0.2 and 2.5%. Regarding the Fig. 11 panel (b), it demonstrates the remarkable influence of steam on the formation of molten slag and sulphides. Under the exposure conditions tested here, the participation extent of steam is not negligible, yet ~3.5%, otherwise the formation of solid sulphates and gaseous H$_2$S will be superior. Interestingly, the formation of Cr sulphide is insignificant, irrespective of the steam
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percentage. This further demonstrates the stability of this protective element in the wet flue gas. However, the total amount of melt decreases while the fraction of Fe sulphide increases upon the rise of steam fraction to participate in the tube corrosion. Considering that the participation extents of Fe gas components are very small, and the solid-state reactions are more critical in attacking the tube directly for the corrosion, it might be the case that the concentration of SO2 in bulk gas is insignificant. At last, it is not the controlling limit for the tube corrosion. If that is the case, the shift from air-firing flue gas to oxy-fuel gas causes little difference on the penetration rate of sulphur, i.e. the concentration of S remaining on the corroded tube surface. To confirm this, efforts were made to correlate the content of S (in its most stable oxide form, SO3) in ash deposit with the content of S remaining on the corroded tube surfaces exposed

Table 4

<table>
<thead>
<tr>
<th>Reference</th>
<th>Purpose</th>
<th>Characterization methods</th>
<th>Material</th>
<th>Key findings</th>
</tr>
</thead>
<tbody>
<tr>
<td>S. M. Sabih [38]</td>
<td>Investigation of the corrosion behavior of the Ti6Al4V thoria coating in supercritical water for potential application as one component in the supercritical water reactor.</td>
<td>SEM, TGA, XRD</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>X. Zheng et al. [39]</td>
<td>To study the influence of different chemical compositions of the deposits on the metallic steels in simulated flue gas corrosion tests</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>Y. Chen et al. [40]</td>
<td>To study the initiation behavior of ferritic-martensitic alloys in supercritical water reactor (SCWR) environment.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>P. Amperger et al. [41]</td>
<td>Study the initiation behavior of ferritic-martensitic alloys in supercritical water reactor (SCWR) environment.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>T. D. Alba et al. [42]</td>
<td>To study the effects of dissolved oxygen content on supercritical water corrosion.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>G. W. Wang et al. [43]</td>
<td>To study the effects of dissolved oxygen content on supercritical water corrosion.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
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<tr>
<td>G. Wang et al. [44]</td>
<td>To study the effects of dissolved oxygen content on supercritical water corrosion.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>G. Wang et al. [45]</td>
<td>To study the effects of dissolved oxygen content on supercritical water corrosion.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
<tr>
<td>N. Nishiwaki et al. [46]</td>
<td>To study the effects of dissolved oxygen content on supercritical water corrosion.</td>
<td>SEM, EDS, TGA</td>
<td>Ti6Al4V</td>
<td>Corrosion deterioration decreases with increasing C content in the alloys at 600°C.</td>
</tr>
</tbody>
</table>

Fig. 5. Co-species composition from XANES binding of the tube. (a) Variation in Cr K-edge energy. (b) Variation in Fe L-edge energy. (c) Variation in O K-edge energy. (d) Variation in Ni L-edge energy. (e) Variation in Co K-edge energy.
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![Diagram](image)

Fig. 13: Schematic (a) for the formation of metal, sulphide, and sulphate in the melt; fuel ash predicted slag composition (b) for N1 raw coal ash deposit on tube TR1, based on the use of database slag + Sulphate and (c) for fuel ash predicted slag composition for W1 ash deposit on tube TR1, based on the use of database slag + Sulphate.

To both combustion modes. The air-firing flue gas is made up of 300 ppm SO₂ only, 280 ppm HCl, 8% steam, 41%O₂, and N₂ in balance [19]. The concentration of SO₂ is ten times less than in the oxy-firing flue gas. The ash deposits tested in air-firing mode are also different lignite ashes which called Victorian Brown coal fly ash, named Hazelwood and Yallourn which collected from Australia, the composition of SO₂ in Hazelwood fly ash was higher than the fly ash samples prior washing [3]. In spite of these differences, a good and identical trend was found between the two combustion modes for each tube. Clearly, in terms of the S penetration rate, bulk flue gas is much less influential than the content of S in ash deposit, under the exposure conditions tested here. Furthermore, one can see Fig. 12 that the slope for the correlation trend decreases upon the rise on the content of Cr in the bulk tube, further confirming the protective role of this element against the penetration of S and tube wastage.

The second phenomena for the ash-dependent sulphide formation is intriguing. To reflect the effect of ash composition on the formation of sulphide, Fig. 13 was plotted by merging Figs. 4, 6 and 7 to correlate.
the content of S in ash versus the contents of sulphide formed on both corroded tube surface and used ash, as well as the total content of S remaining on the tube surface. Note that, the contents of sulphides were quantified by the LCF for Figs. 6 and 7. It is interesting that the total amount of S on the tube surface and the fraction of sulphides follow the same trend. That is, the three water washed ashes in particular W1 are more influential in the adherence of S and the formation of sulphide on the tube surface. whereas the other two acid-washed ashes bearing a relatively large amount of S are not in favour of the sulphidation reaction. This difference should be due to the greater reduction on the amount of CaO by acid washing. Therefore, the extent of reaction eq. 3 for A1–A2 is less than for W1-W3. The panel (c) in Fig. 10 also suggests a predominance of CaS in the slag formed from the low-S ash deposit. Additionally, although XANES spectra for S in Figs. 6–8 failed to distinguish different sulphides, it is clear that CaS has a higher white line position (close to 1472 eV) than iron sulphide. It is thus very likely that the smallest peak for S in Figs. 6 and 7 should be assigned as CaS.

The last phenomena related to the unique formation of sulphide only on the tube 191 is also noteworthy. Thermodynamically, the rise on the contents of Cr and Ni in a tube deprecates the formation of molen slags. As evident in Fig. 14, one can see a sharp decrease on the amount of total slag and even the fraction of Fe2S3 once the Cr content in the tube increases up to 10% that is close to 191. Interestingly, the fraction of FeS in the total slag is slightly increased from the Cr content of 10%. This to certain extent indicates that the sulphides found by XANES should be mainly referred to as FeS. However, the thermodynamic prediction fails to explain the absence of sulphide on the low-Cr

![Diagram](image-url)

**Fig. 11.** Thermodynamic equilibrium modeling on the formation of melt and sulphides on tube 191 surface. Panel (a) is for the percentages of OFe sulphides on the ash deposit W1 as a function of dry flux gas reacting with tube surface; (b) for the percentages of CaS sulphides on the ash deposit W3 as a function of steam reacting with tube surface. The parameters of O2 and SO2 reacting with tube surface were fixed at 0.2%.

![Diagram](image-url)

**Fig. 12.** The correlation between S(2) in ash samples with the sulphide on different corroded tubes surface. Panels (a)-(c) are for tube 1201/MWC, 191 and 110304, respectively.
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5. Implications of this study

This study casts important implications on the high-temperature tube corrosion during the oxy-fuel combustion. For a short exposure time 50 h referring to as the initial stage of tube corrosion, the accelerated concentrations for SO₂ and steam in oxy-fuel flue gas are clearly insignificant in terms of the penetration of S inside the tube, bearing a maximum 0.25 percentage to interact with ash deposit to promote the tube corrosion. The penetration rate of S inside a tube is broadly identical between air-firing and oxy-fuel combustion modes [37]. The content of S in ash deposit is more critical than bulk gas, acting as a carrier to transfer the gaseous SO₂ inside the tube for both sulphation and solidification of the inherent elements in the tube. For the original ash deposit bearing as 5% content larger than 10 % wt., the formation of sulphate-bearing melt is favoured on the surface of the commercial low-Cr tube, due to the thermodynamic instability of the formation of sulphide. A prior washing of coal to reduce the S content down to 1 % wt. in ash deposit is greatly beneficial on mitigating the tube corrosion. In particular, its combination with the use of medium-Cr tube such as 191Cr is able to mitigate the tube corrosion rate down to a level that is even lower than the pure flue gas. However, the selection of coal washing reagent is critical. Instead of using water, the use of acid to remove Ca is even beneficial in eliminating the formation of ducile, molten sulphide.

6. Conclusions

This study focused on the exposure test of a number of tubes with different Cr content and coated with lignite ash deposits in typical oxy-fuel combustion flue gas at 650 °C for 50 h. The ash deposits were derived from the combustion of a Xinjiang lignite and its water and acid washed coal samples. The original ash deposit bearing as 5% content larger than 10 % wt., the formation of sulphate-bearing melt is favoured on the surface of the commercial low-Cr tube, due to the thermodynamic instability of the formation of sulphide. A prior washing of coal to reduce the S content down to 1 % wt. in ash deposit is greatly beneficial on mitigating the tube corrosion. In particular, its combination with the use of medium-Cr tube such as 191Cr is able to mitigate the tube corrosion rate down to a level that is even lower than the pure flue gas. However, the selection of coal washing reagent is critical. Instead of using water, the use of acid to remove Ca is even beneficial in eliminating the formation of ducile, molten sulphide.

1) Both water-washing and acid-washing are effective in decreasing the contents of S and Na/ Ca. Consequently, the tube corrosion rate was mitigated significantly for all the tubes tested. Upon the use of washed coal ashes, the tube corrosion rate was lower than the use of silica additive and even comparable to the pure flue gas.

2) The amount of S penetrated inside tube is predominantly impacted by the availability of the inherent sulphates in ash deposits. However, the participation of flue gas is essential for the tube corrosion. Based on thermodynamic equilibrium assessment, the contribution extent of flue gas is estimated to range from 0.2 % to maximum 3.5 %. The lignite ash deposit functions as a medium which transfers the S from bulk gas to tube surface, via the formation of intermediate sulphates or sulphide.

3) The formation of sulphide is highly dependent on both ash properties and the tube composition. The high-S ash from raw coal has no potential causing the formation of sulphide. For the low-S ash deposits, the content of free oxide is critical since they can assist in the formation of sulphide-bearing melt. In the case of water washing, the use of acid is able to remove the water-insoluble free oxide, and hence, eliminates the potential for the formation of sulphide.

4) The medium-Cr ferritic tube 191Cr is well suited to sulphidisation than the other tubes from both the thermodynamic equilibrium and gas diffusion perspectives. Its Cr content is not high enough to fully avoid the formation of sulphide-bearing melt. Additionally, its protective layer is porous for the gases to permeate and to form a reducing environment to promote the formation of sulphide inside the tube.

Acknowledgement

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were collected from the beamline BM16A in Taiwan National Synchrotron Radiation Research Center (NSRRC) via the help from Dr. Ting-Chan Chang and Mr. Yu-Peng Huang, and is particularly grateful to the NSRRC for her PhD scholarship. Lin Zhang is also grateful to National Natural Science Foundation of China (No. 51620105) for supporting the collaborative research with Prof. Dunxi Yu at Huazhong University of Science and Technology.

Appendix A. Supplementary data

The supporting information document associated with this paper includes the SEM pictures for the cross-section of the three C-bridge tubules. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.jprotec.2017.06.033.

References

Spatial distribution of chromium on the corroded tube surface characterised by synchrotron X-ray fluorescence (SXRF) mapping and μ-XANES: Co-existence of Ca-rich ash deposits and oxy-firing flue gas

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K E Y   W O R D S
Synchrotron SXRF μ-XANES Chromium Lignite ash deposit Calcium sulphate Calcium oxide

A B S T R A C T
This study aims to explore the effects of lignite ash deposit, in particular the Ca-bearing species in ash on the tube corrosion under the oxyfiring mode. Two tubes, low-alloy steel 122 and austenitic 316L have been coated with two ash deposits and exposed to oxy-fired flue gas at 650 °C for a total of 50 h. The ash deposits were collected from the combustion of a lignite mixed with and without silica additive in a 30 MWth pulverised coal-fired boiler. In this study, the role of Ca-bearing species including sulphate, free calcium oxide have been first time revealed by using synchrotron-based X-ray fluorescence (SXRF) and μ-XANES to detail the spatial distribution of individual elements, and in particular the speciation of Cr on the cross-section of tubes. Carbochromation of Cr by CO₂ is inhibited remarkably upon the co-existence of flue gas and ash deposit. However, the attack from the species in ash deposit other than sodium sulphate is more influential in accelerating the tube corrosion. Calcium sulphate is the major contributor in the formation of Cr sulphide even in an exposure time of 50 h. Sulphidation of Cr by calcium sulphate is thermodynamically possible under the exposure conditions tested. Moreover, the free calcium oxide and free calcium in raw coal ash deposit are detrimental, accelerating the breakdowns of the two tubes upon the formation of CaCr₂O₄ (Cr⁺³ and even chromium (Cr⁶⁺)). The resultant chanoide generated underneath the protective layer that is rich in CaO-Cr₂O₃ oxide and Fe-Cr spinel, as well as merged intimately with ash deposits. The detrimental effect of free calcium oxide/calcium is more pronounced than calcium sulphate in the 50 h tested here. The use of silica additive in coal combustion immobilised the free Ca oxide, thereby forming an extra protective layer that minimised the oxidation of Cr. Consequently, the whole tube remained intact with little being damaged.

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1. Introduction
Oxy-fuel combustion is one of the promising carbon capture and storage (CCS) technologies that could be deployed to secure the sustainable use of coal in the carbon-constrained future [1]. High-temperature tube corrosion in the convective zone is one of the most critical issues that has been receiving increased attention [1–3]. Apart from the augmented concentrations of carbon dioxide (CO₂), steam (H₂O) and impure components including sulfuric oxide (SO₂) and hydrogen chloride (HCl) in the recirculated flue gas [1–4], properties of ash deposits in the convective section are also reported to change, which could in turn affect the tube corrosion. To date, knowledge is still sparse regarding the speciation on the corroded tube surface that is exposed to the ash-laden oxy-firing flue gas.

As summarised in our previous work [5], a wide variety of ashes, either collected from power generation stations or synthesised in the laboratory have been tested. In a typical bench-scale test, the tube is first loosely coated with ash powder or immersed into molten ash. Subsequently, it is exposed to an oxy-fuel flue gas at high temperatures for a duration of minimum 50 h. The corrosion of the tube is expressed as weight loss rate, or growth rate of the oxidation scale on the top surface. With regard to the chemistry underpinning the speciation of the corroded tube surface and its interaction with ash deposition, nearly all the studies relied on the use of bench-scale analytical facilities such as optical microscopy (OM), scanning electron microscopy (SEM), and X-ray...
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diffraction (XRD), which are further supplemented by thermodynamic equilibrium calculation using commercial software such as FactSage. The drawbacks of these techniques is the inability to pinpoint and specify the oxidation states of the metals of interest on the oxide scale interface that is usually on the sub-micron scale. Therefore, understanding is still incomplete with respect to the interaction between tube and ash deposit.

In this study we report the corrosion of two tubes, low-alloy steel T23 and austenite stainless steel SUS347 that are coated with two ash deposits collected from a 30 MWth pulverised-coal fired boiler burning lignite with and without the addition of silica additive. This is a continuation of our previous work on the properties of these two ash deposits and their effect on tube corrosion, based on the bulk analysis techniques. Dai et al. [6] for the first time reported the overall properties of ash deposits collected from the combustion of this lignite mixed with silica additive, in a 30 MWth pulverised-coal fired boiler with sub-critical steam conditions. This work clarified the mechanism of inhibition of the slagging upon the addition of silica additive. The ash deposit-laden tubes are further exposed under the oxy-fuel flue gas that is similar to the compositions achieved from our pilot-scale testing on the oxy-fuel combustion of wet brown coal [7]. Synchrotron X-ray fluorescence (SRF) microscopy and micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy were employed to capture the line structures and details on the cross-section of the tubes at a resolution of 2 μm [8-10]. The spatial distribution of the chromium-bearing species were determined to reveal the interaction between tube metal (Cr) and the ash deposit, in particular the Ca-bearing species in the two ash deposits. To date, extensive studies have been conducted to understand the corrosive nature of alkali sulphates and their interaction with tubular surfaces at high temperatures [11] as well as Jiao et al. [17] addressed the potential formation of toxic Cr (VI) and the variation of the quantities of Cr (III)-bearing species with flue gas composition. Whereas, Low et al. [20] examined the emission, and characterisation of twelve trace elements (As, Ba, Be, Cu, Cr, Cs, Mn, Ni, Pb, Sr, V, and Zn) in the ash deposits from diverse sections of an industrial pulverised lignite-fired boiler and in the flue gas. Understanding the roles of calcium-bearing species such as sulphate and free oxide is still far from complete. This will be focused on in depth in this study.

2. Experimental

2.1. Tube corrosion conditions

The tube exposure was conducted in a horizontal furnace that was fixed at 650 °C for a duration of 50 h. The flue gas flow rate is fixed at 300 ml/min. The flat tube specimen, 3 cm × 3 cm × 2 mm, were prepared by a wire-electrical discharge machine to cut the cross-sections of two commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. Fly ash powder of around 100 mg per tube sample was spread uniformly over the tube surface to mimic ash deposition on a real steam turbine sample surface, yielding of around 11 mg per cm² that is similar to the other studies [12]. The ash coating was achieved by putting the ash powders into a plastic mould that is the same size as the tube specimen. The ash coating was also gently pressed by hand to ensure that there is no loss during the test. The oxy-fuel flue gas tested is made of 40 vol% O₂, 3000 ppm SO₂, 1000 ppm NO, 3000 ppm NH₃, 10 ppm H₂O, and the rest is CO₂. The pressure for flue gas is 1 bar. Such a flue gas composition was confirmed in our pilot-scale test on the oxy-fuel combustion of a local Victorian brown coal [7]. The details for experimental conditions and sample preparation are given elsewhere [11,13].

Two tubes were tested, low-alloy steel T23 (22.5 wt% Cr) and austenite stainless steel SUS347 (17-19 wt% Cr). The remaining elements in the two tubes include C (0.04-0.1 in T23 vs. 0.08 in SUS347), Mn (0.1-0.6 in T23 vs 2.0 in SUS347), Si (0.5 in T23 vs 1.0 in SUS347), Mo (0.05-0.3 in T23), V (0.2-0.3 in T23), W (1.45-1.75 in T23), Nb (0.02-0.8 in T23 vs 1.0 in SUS347), Al (0.03 in T23) and Ni (9-13 in SUS347).

All these values are expressed as weight percentage. The former tube is the material which is being used generally in a pc-fired boiler, whereas the use of the latter one is expected to address if the use of high - Cr tube (as well as high in Ni/Nb) is essential in the oxy-fuel combustion mode. After the corrosion test, tube specimen were quickly mounted and polished in epoxy resin to avoid surface oxidation. Subsequently, the sample was halved by a disc-cutter. The resulting cross-sectional surface was finally polished by SiC paper with 2400 grit.

2.2. Ash deposit properties

These two ash samples were collected from the connected superheater surface in a 30 MWth pulverised-coal fired boiler burning a Chinese lignite, the same as the ash samples tested in our previous work.

The two samples were labelled XJ and XL5 for the ash deposit derived from raw coal and coal mixed with silica additive, respectively. The elemental compositions of the two ash samples are shown in Table 1. Upon the addition of silica, the content of Na, Ca, and S are decreased remarkably. This should be due to the immobilisation and even dilution of these elements particularly Na by the silica additive. As further evident in Table 2 for the quantified XRD results (original patterns are shown in the supporting information Fig. S1), the contents of Na-bearing sulphates are reduced considerably upon the use of silica additive. So are the free oxides which are mostly captured by silica into amorphous species [6].

2.3. SRF and μ-XANES analysis

SRF and μ-XANES analysis were conducted at the XFM beamline, Australian Synchrotron. SRF maps were collected at 15.8 keV with a Si (111) monochromator and a energy resolution (ΔE/E) of × 10⁻⁴ and the Maida detector [14]. The Klöpfer-Baeyertz (KB) mirrors were used to focus the beam down to ~1.5 μm [2,10]. For each tube cross-section, an overview map with areas ranging from 2.8 × 3.4 to 2.8 × 7.6 cm² were mapped using a pixel size of 100-200 μm² and a dwell time of 10 to 25 ms per pixel. Detailed maps were then collected over ~2 × 0.4 cm² area using 2 μm² pixels and a dwell time of 0.4 ms per pixel. XANES spectra were gathered by collecting SRF images (~0.2 ×
Table 3

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<tr>
<th></th>
<th>T23</th>
<th>SUS347</th>
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<tr>
<td>Oxy-firing</td>
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<tr>
<td>N x 100</td>
<td>80.2</td>
<td>78.6</td>
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<td>Y x 100</td>
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<td>Z x 100</td>
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0.4 cm², 4 μm pixels, and dwell times of 1 to 4 ms/pixel at 77 monochromators energies spanning 100 eV across the Cr K-edge. Cr metal foil and a pellet of chromium oxide (Cr₂O₃) diluted in boron nitride were used to determine the energy shift for XANES analyses.

SRMF data were analysed using the Dynamic Analysis (DA) method in GeofDIE II [14]. The DA approach fits multiple lines per element that separate overlaps and substracts background, escape peaks and other detector artefacts. Note that, the light elements including C, Na and O cannot be detected by the Maia. The extracted XANES spectra were processed in ATHENA. Linear combination fitting (LCF) was used to qualitatively determine the mineral compositions, by using a variety of standards including pure Cr metal oxide (Cr₂O₃), carbide (Cr₃C₂), hydroxide (Cr(OH)₂), chloride (CrCl₂), sulphide (CrS₂), chromates (MgCrO₄, CaCrO₄, Fe₃CrO₄) and Ca chrome (CaCrO₄). The spectra for these standards are included in the Fig. 3. Note that, the spectra for chromium carbide (Cr₂C) [15] and chromium sulphide (CrS₂) [16] were cited instead, whereas spectra for the other standards were collected from our previous studies [17–20].

Regarding the accuracy of the analysis by SRMF and μ-XANES, the complete analysis of all measured quantities by SRMF based on GeofDIE II and the relevant Maia detector has been conducted by measuring a number of standard metal foils such as Mn and Pt. The spectral fitting was further conducted based on the dynamic analysis (DA) method, which yields a relatively accurate quantification capacity. Concentrations of individual elements (up to 52 elements) were calibrated by using the known Fe concentration of the various tubes as an internal standard [21,22]. Regarding the accuracy of μ-XANES and the relevant LCF method, our previous work based on the analysis of pure oxide mixtures [19] have proven a relative standard deviation of around 10% for this method.

2.4. Thermodynamic equilibrium calculations:

The commercial thermodynamic equilibrium program, FactSage [23] was used to calculate and establish the FeO–Cr₂O₃–CaO phase diagrams under the tube exposure conditions, 650 °C and a total pressure of 1 bar for the flue gas. Apart from the pure substances, the built-in database for spinel species and slag in FactSage was also included in the calculation. In addition, the Gibbs function for the solid-state reactions were calculated by the “Reaction Equations” module in HSC Chemistry.

3. Experimental and synchrotron analytical results

3.1. Tube mass loss results

Mass losses for the two tubes are first reported in Table 3, which is supplementary to the oxide scale growth rate reported previously [11]. For T23 that is a common tube used in the p-fired boiler, shifting the combustion mode to oxy-firing accelerated its mass loss for both ash deposits, due to the co-existence of highly concentrated and corrosive steam, SO₂ and HCl in the oxy-firing flue gas. However, the use of silica additive is effective, reducing the mass loss by more than half in both flue gases. Similar results were confirmed for the high-Cr austenite tube SUS347. Clearly, the reduction of sulphates and free oxide in the ash deposit is of benefit to the mitigation of tube corrosion, as expected. By comparing with the case of no ash deposition on tube surface, it is clear that the co-existence of ash deposit and flue gas accelerated the tube mass loss, irrespective of the combustion mode. Instead, the existence of ash deposit provides a shield to mitigate the tube mass loss to a level that is considerably lower than that caused by flue gas exposure only, in particular under the oxy-fuel flue gas. Obviously, the evaporation of tube metals upon the attack of corrosive gases including HCl, steam and/or SO₂ is mitigated upon the use of silica additive. This will be further explained by the detailed speciation analysis in the following sections.

3.2. Cross-section of T23 coated with Xf ash deposit

Fig. 1 illustrates the SRMF maps for individual elements on the cross-section of T23 coated with Xf ash deposit. The concentration distribution of individual elements is represented qualitatively by colour scale, in

![SRMF mapping for the cross-section of tube T23 coated with Xf ash deposit](image_url)
which black and white refer to the minimum and maximum concentration of an element, respectively. The Fe map clearly shows the breakdown of tube T25 upon X3 ash deposition. As amplified on the very left side of Fig. 1, a multi-layered interface was formed between the bulk tube and ash deposit. The top layer that is adhered to bulk tube is in red, indicating the outward diffusion and subsequent oxidation of Fe by the bulk flue gas on the tube surface. By looking at the maps for the other elements, it is further evident that Cr is the second most abundant on this protective layer, which should form an oxide layer to resist against the inward diffusion of corrosive gases. Next to the top layer is a thicker, spalled layer which even bulked and fragmented into smaller, smaller scales that are also highly curled. Such a layer is also rich in Ca, suggestive of the non-protective role of this inherent metal in the tube. Moreover, the spalled scale is in close contact with the most abundant element Ca in ash deposit, as evident by the Ca map. Signal for the last two elements S and Cr is rather weak, it is thus unclear if they are associated with any inherent metals in the original tube.

Efforts were made to zoom in and reveal the details of both the top/adherent layer marked as rectangle 1 and the spalled scale marked as rectangle 2 in Fig. 1. Moreover, the spatial distribution of Cr-bearing species was mapped by XANES Cr K-edge on the two selected areas. As demonstrated in Fig. 2, the top layer is around 20 μm in thickness, which is dominated by both Cr and V, proving the strong protective effect of these two additives in the bulk tube. Ti is rarely spotted, due to its extremely low concentration in the tube. Moreover, S was detected with a relatively strong signal on the Cr/V-dominating interface, proving an inward diffusion of this element inside the tube. It may be derived from SO2 in flue gas or sulphates in the ash deposit. With respect to Ca from the ash deposit, its presence on the top layer should be much lower but not negligible, as evident by the scattered spots that coincide with Cr and V in the interface. This implies some possible association of Ca and Cr/V.

The XANES energy distribution of Cr, as shown on the right hand side of Fig. 2, suggests the predominance of the species that has the dominant peak located at the energy of 6009 keV, as is the case for oxide (Cr2O3) and spinels from MgCr2O4 through to Cr2O3 [17–20]. In contrast, the low intensity at 5993 keV suggests that there is little to no pre-edge thus there should be little Cr carbide [15] and/or Cr-metal. This is further evident in Fig. 3 that shows the XANES speciation of the points of interest. As can be seen, point No 1 located deep inside the bulk tube is dominated by pure metal and carbide, the oxide/spinel is rare. The formation of carbide is due to the carburisation effect of CO2 in the flue gas [23-24]. However, such a species was not detected in the orange-yellow interface. Instead, Cr and the interface is dominated by Fe-Cr spinel, the concentration of which even increases stably with the rise in the number of the spots analysed from No 2 (for the bottom of the interface) to No 7 referring to the top of the interface. This echoes the preferential oxidation of these two elements upon the exposure to flue gas that consists of a number of oxidising components, including O2, H2O, and CO2. More interestingly, the Cr-Cr spinel was also found for the spots No 5–7 located on the very top layer that is in blue. Such a layer is in close contact with the ash deposit and thus has the opportunity to interact. Clearly, Ca in the X3 ash deposit is highly reactive and has the capability to react with Cr oxide. Cr-Sulphide/sulphate was not detected, and hence, it is assumed that the S in Fig. 2 should be mainly associated with V and/or Ca.

Fig. 4 shows the amplified map for the rectangle No 2 labelled in Fig. 1. Due to the multi-layered scaling nature of this area, three small sub-areas were further amplified and analysed. For the sub-area 2–1 located in the middle of the multi-layered scale, the amplified XSRF map demonstrates the abundance of Cr, S and Ca. Interestingly, these three elements are split between a narrow strip that is about 15–20 μm in width and a large lump. For Cr in the narrow strip in red, it is in a close contact but does not overlap with the strip rich in Ca and S, as indicated by the straight dashed reference line. For the remaining Cr in a form of curled thin scale, it is partially merged into the large lump dominated by Ca and S. The close association of Ca and S in both strip and lump is indicative of gypsum/anhydrite in the original fly ash. The merging of Ca/S and Cr is more evident for the sub-area No 2–2 shown on the right hand side of Fig. 4. The sub-area No 2–2 refers to a spalled narrow scale of 20–30 μm in width, which is dominated by both Cr and V. It has been fully merged into the large ash lump. This should be caused by counter current diffusion of ash and the inherent metals Cr and V upon their interaction in the tube-ash interface.

![Image](image-url)

Fig. 2. XSRF maps of the selected area rectangle 1 in Fig. 1 and the Cr K-edge distribution across the whole cross-section of tube T25 coated with X3 raw coal ash deposit.
Fig. 3. Cr K-edge XANES spectra for various points on the selected area No 1 in Fig. 1.

Fig. 5 shows the XANES K-edge spectra for a number of points on the tube scales, with the quantified results for Cr speciation. The results further confirmed the existence of a Ca-Cr spinel across all the scales. Apart from CaCr$_2$O$_4$, in which Cr is trivalent, the hexavalent Cr$^{VI}$ as a form of CaCr$_2$O$_4$ was also observed in the spots No 1, 3, 6 and 10. The total contents of these two Ca-Cr spinels are also much higher than the Fe-Cr spinel, demonstrating a high mixing of ash with the spalled tube scales. The presence of hexavalent Cr$^{VI}$ also indicates a deep oxidation of Cr upon its mixing with the XJ ash deposit.

Fig. 4. ESR maps for the selected area No 2 in Fig. 1.
3.3. Cross-section of SUS347 coated with XJ ash deposit

SXRF mapping for the SUS347 coated with the XJ ash deposit is illustrated in Fig. 6. Surprisingly, this high-Cr austenite tube was also severely corroded by the XJ ash, with the formation and detachment of a thick scale that is rich in Fe, Mn, and even Co. This scale is also in close contact and even partially mixed with the ash deposit that is represented by the Ca map. In addition, similar to the low-Cr tube T23 in Fig. 1, Cr forms a protective layer that is still adhered to the tube top surface, with only a few areas such as No 2 in the spalled scale.

XANES speciation for Cr on the adherent/top layer, No 1 and the spalled fragment No 2 on Fig. 6 was conducted, and the results are shown in Figs. 7 and 8, respectively. With respect to the top adherent layer in Fig. 7, Fe-Cr spinel is dominant across the whole cross-section, the same as for the top layer of T23 in Fig. 3. This species should be formed by the interaction between oxides of Fe and Cr upon the exposure to the oxidising flue gases, exerting a protective role against the inward diffusion of corrosive components inside the tube. In addition, the Ca-Cr spinels including chromite (Cr$_2$O$_3$) and chromate (CrO$_4^{2-}$) were observed with considerable fractions. In particular, the former species was even detected for the spots No 1–3 that are underneath the oxide layer. This is the evidence for the penetration of Cr inside the tube, through the oxide layer. Chromate for the presence of hexavalent Cr$^{VI}$ was observed on the oxide layer (spots No 5–6) and its outer surface, No 7. Clearly, excessive oxygen is present inside the oxide layer and of benefit to the local oxidation of trivalent Cr$^{III}$.

The association of Ca-Cr is more obvious in the spalled scale (still dominated by Fe-Cr spinel) demonstrated in Fig. 8. Regarding Ca
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chronite hosted by Cr\(^{3+}\); its fraction is relatively constant across the points from No 1 through to No 10, except the point No 11 which is in light blue for a low Cr concentration but possesses a highest fraction for Ca chromite. Ca chromate was detected in the spots from No 2 through to No 5, bearing a noticeable fraction. Moreover, the unreacted Cr metal was detected in No 5-7, suggestive of a simultaneous breakdown of the unreacted tube with the oxide/spinel.

3.4. Cross-section of tubes T23 and SUS347 coated with XL5 ash deposit:

Fig. 9 illustrates the SXRF maps for individual elements on the tube T23 coated with XL5 ash deposit. Clearly, this tube remains intact, with a very thin layer formed on its top surface. Such a layer is rich in Cr and Mo due to their preferential oxidation to protect the bulk Fe. It is also in contact with the ash deposit that is dominated by Ca. The signal
for S and Cl is discernible on the tube-ash interface. This is confirmed by the XANES point analysis for Cr in Fig. 10. Irrespective of the point location, the fraction of sulphide is non-negligible. However, such a species was not found in the case of T23 coated with XJ ash deposit. The Ca-Cr spinel was not found either. Instead, the unreacted Cr metal is predominant across the whole interface, which is accompanied by carbide and a small amount of Fe-Cr spinel.

The non-corrosive nature of the XJ ash deposit was further evident for the austenite tube SUS347. As demonstrated in Fig. 11, the whole tube (represented by Fe here) remains intact, with an extremely thin layer formed under the contact with ash deposit. Cr is enriched in the interface, with the pure metal being dominant across the whole interface. Clearly, the use of silica additive during coal combustion is of benefit to mitigate the tube corrosion.

4. Discussion on Ca-induced corrosion mechanisms

Compared to the XJ ash deposit generated from the combustion of coal added with silica additive, the raw coal ash deposit, namely XJ ash in this study is clearly highly corrosive, as evident in Table 3 and Figs. 1-8. The higher content of sodium, in particular the high content of sodium sulphate should be one of the major causes [11,13]. The S map in Fig. 2 for the tube T23 coated with XJ raw coal ash deposit is most likely attributable to sodium sulphate, since the Ca map was not associated with S. As further evident in Tables 1 and 2, the total Na in XJ ash accounts for 10.4 wt%, relative to only 6.62 wt% in its counterpart XJ ash deposit. In particular, sodium sulphates, namely thiosulphate and muriate were reduced from 6.5 wt% to 1.9 wt% upon the combustion of coal mixed with silica additive. This in turn reduced the probability...
for the formation of molten Na-Fe sulphates that proves to be a major trigger for the tube breakdown. To date, the mechanisms underpinning the formation of Na-Fe sulphates has been studied extensively.

Calcium sulphate has also been confirmed to be corrosive for the tubes exposed under the conditions that are typically encountered in the fluidised bed combustors, i.e. 650–950°C in the air-fired flue gas [25,26]. At the flue gas temperatures of 800–950°C [25], chromium sulphide was found to be formed underneath the protective Cr-rich layer on the top surfaces of Fe-20Cr and Fe-25Cr, accounting for the breakaway of the tubes. Additionally, a layer for finely mixed CaO and CaS was formed on the Cr-rich top layer, which was interpreted as CaCr2O4 but is yet to be confirmed directly [25]. For another tube corrosion test using 1018 plain carbon steel and at 650°C that is exactly the same as this study [26], calcium sulphate was found to be protective against flue gas corrosion in the first 50 h, which however turns corrosive after 50 h, by attacking iron metal to form the resultant iron sulphide according to the reaction Eq. (1) below:

$$4Fe + CaS = 3FeO + CaO + FeS$$ (1)

The results observed for the formation of a Cr-Cr spinel in this study, under the exposure time of 50 h have not been found before. Although

**Figure 11.** SXRF map and Cr K-edge XANES analysis for the tube SUS347 coated with XLS inh.

**Figure 12.** Cr-S-Ca RGB map for tube T23 coated with XLS inh shown in Fig. 5. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the exposure time is short, the deteriorating effect of Ca-bearing species is obviously profound, as demonstrated by the mixing of Ca, Sr, and V in the spalled scale for the tube T23 coated with XJ ash in Fig. 5. Even for the ash deposit XJ5, its coating on T23 caused the penetration of sulphur as a form of chromium sulphide inside the protective Fe-Cr spinel layer on the tube top surface, as demonstrated in Fig. 10. The amplified view of such a layer, as visualized as RGG (Cr - red, S - green and Ca - blue) maps in Fig. 12, further proves the association of Cr-S, Ca-S and Ca-Cr (see the dashed oval) in the ash layer that stays above the protective layer. Clearly, it should be formed by the interaction between calcium sulphate and Cr(III) on the tube-ash interface where Cr prefers to diffuse outwards to mix with and even merge into the ash deposit.

The formation of chromium sulphide is also thermodynamically possible at 650 °C, which even bears the largest potential in terms of the standard Gibbs free energy among all the probable reactions between Cr metal and calcium sulphate. This is evident in Fig. 13, where the Gibbs free energy for the above reaction (1) was also included for comparison. Irrespective of the metallic type, the formation of sulphide is more thermodynamically favoured than its counterpart sulphate. This explains the absence of Cr sulphate in all the Cr XANES spectra. Moreover, from the reaction kinetic perspective, the formation of chromium sulphide should be rather slow, as indicated by its extremely low molar fraction of the total chromium in Fig. 7. Since sulphide was not detected for the high-Cr austenite tube SUS347, it is also inferable that the solid-state reaction equation (3) in Fig. 13 should be controlled by the inward diffusion rate of Cr metal through the protective layer that is rich in Cr-Fe spinel. The Cr-rich layer should be denser for the tube SUS347, and hence, completely inhibit the reaction (3). Even for the spalled scale that is fully mixed with calcium sulphate, as evident in Fig. 4, Cr sulphide was not detected either (see Fig. 5), suggestive of the more likely occurrence of the other reactions over the sulphidation of Cr. In light of this, the existence of calcium sulphate in ash deposit is not critical, at least less critical than sodium sulphate for the corrosion of both tubes in 50R. Otherwise, the XJ ash deposit rich in calcium sulphate (see Table 2) should be more corrosive.

The other predominant Ca-bearing species such as free oxide in ash deposit should be more critical in affecting the speciation of Cr, accounting for the Ca-Cr spinels including both Ca chromate and chromite found in Figs. 3, 5, and 8 for the two tubes coated with XJ ash deposit rich in free Ca oxide. The Cr-Ca spinels were formed as a dominant Ca-bearing species in the spalled pieces that are fully mixed with fly ash (Figs. 5 and 8), and even on the top protective layer that is adherent to bulk tube and dominated by a Fe-Cr spinel (Figs. 3 and 7). These spinels should be formed between the reaction between Ca oxide and Cr oxide that was formed upon the oxidation of Cr. Moreover, Ca in free oxide should be more competitive against Fe oxide (from the bulk tube) once it has a good contact with the tube surface, as is evident by the preferential formation of a Ca-Cr spinel on the tube SUS347 coated with XJ5 ash. This phenomenon was supported by the thermodynamic equilibrium phase diagram for CaO-FeO-Cr2O3 at 650 °C in Fig. 14. Due to the fact that chromate is not included in the database of FactSage, prediction for the Ca chromate is unavailable here. However, the fraction of this species is very small, and hence, its lack in the database should be insignificant in interpreting the results here. The elemental compositions were also included in Fig. 14 for the points analysed in Figs. 3 and 7 for the adherent surfaces, and Figs. 5 and 8 for the spalled scales of the two tubes. Note that, the elemental compositions were conducted by the SR-EDX and concentrations of the three elements, Fe, Ca, and Cr were normalized in their most stable oxide form. As demonstrated in Fig. 14, the top layers that are still adhered firmly to the two tubes fall into the zone No 1 for the co-existence of Fe oxide referring to Fe chromite in FactSage, metallic Fe and calcium ferrite. This is in agreement with Figs. 3 and 7, further proving the preferential interactions between the oxides of Cr and Fe and the protective role of the resultant Fe-Cr spinel against the tube corrosion. In contrast, for the spalled scales that is rich in Ca, the points analysed either fall into zone No 4 for T23 or zone No 2 for tube SUS347. For both zones, the formation of Ca chromate is favoured. This explains the abundance of this species as detected by XANES in Figs. 3 and 8.

The Ca chromate formed should be detrimental and accelerated the corrosion of both tubes considerably. As evident in Fig. 3, this species should be initially formed upon the contact between free oxide in the ash deposit and the oxide layer adhered on the bulk tube surface. However, the resultant Ca chromate deteriorated the crystal structure of Cr-rich oxide and/or Cr-Fe spinel, resulting into the fragmentation of the protective layer, and consequently, break-down of the tube surface. The resultant fragments even merged into the ash deposit intimately, as evident in Figs. 4 and 8. Moreover, the presence of Ca chromate underneath the top oxide layer, as evident in Fig. 7 for SUS347 further implies that this species also penetrated deep inside the tube. Although the reason for this is unclear, it is very likely that this species might be present in a molten phase, which can thus easily flow inter-granularly in the ash-tube interface layer. It then further broke the tube from inside, causing a compressional stress to detach and buckle off the top layer, even for the high-Cr austenite tube SUS347. In this sense, the free calcium oxide in XJ ash deposit is comparably corrosive with sodium sulphate. Upon the use of silica additive during coal combustion, this species was reduced significantly in the ash deposit, as evident in Table 2. Moreover, the free oxide should be fixed by silica into an amorphous species, which form a protective layer on the tube surface against the attack of flue gas, in particular, attack from CO2 resulting in the formation of ductile carbide underneath the protective layer. Therefore, the two tubes remained intact, and less of Cr was oxidized as well, as demonstrated by the presence of unreacted Cr metal in Figs. 10 and 12.

Finally, the formation of Ca chromate (CrO3+) in the spalled layer of tube T23 (Fig. 5) and even the top surface of tube SUS347 (Fig. 7) is intriguing. Its fraction is non-negligible. Such a species should be formed from reaction between oxides under the aid of bulk oxygen from the flue gas, as shown in Eq. (5) below.

\[
\text{Cr}_2\text{O}_3 + 2\text{CaO} + 1.5\text{O}_2 = 2\text{CaCrO}_4
\]

In this reaction, alkali and alkaline earth metal oxide functions as the catalyst promoting the oxygen activation and diffusing from bulk gas to metals, as proven by the studies on model compounds in our previous work [19]. Interestingly, although the exposure temperature here is lower than the optimum temperature (800 °C) for the formation of
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CrO as confirmed in pure air [19], the fraction of Ca chromate found on the tube surface is non-negligible. This hints at the promoting influence of other gas components such as steam and even HCl in the flue gas. Potassium chloride in biomass-derived ash deposit has proven to promote the formation of potassium chromate at the temperatures up to 700 °C [27]. Nevertheless, the resultant Ca chromate should also be easy to break down, as suggested by the small discrete fragments spilled from the tube 5S5347 coated with Al2O3 ash deposit in Fig. 12. However, as its fraction is much lower than the chrome counterpart, the detrimental influence of Ca chromate is insignificant under the exposure conditions studied here.

5. Conclusions

Synchrotron-based X-ray fluorescence and pXANES were used to detail the spatial distribution of individual elements, and the speciation of Cr on the cross-section of various tubes that had been coated with two ash deposits and exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The ash deposits were collected from the combustion of a lignite mixed with and without silica additive. The major conclusions can be drawn as follows:

1) Upon the co-existence of flue gas and Ca-rich ash deposit, the carbonization of Ca by the abundant O2 in oxy-fuel flue gas is inhibited remarkably. However, the attack from the species in ash deposit other than sodium sulphate is more influential in accelerating the tube corrosion.

2) Calcium sulphate is corrosive against the Cr-rich protective layer formed on the tube surface, resulting in the formation of Cr sulphide even in an exposure time of 50 h. Sulfidation of Cr by calcium sulphate is thermodynamically possible under the exposure conditions tested.

3) The free calcium oxide is detrimental, accelerating the breakdown of the two tubes upon the formation of chromite and even chromite. The resultant chromite even penetrated underneath the protective layer that is rich in Cr oxide and a Fe-Cr spinel, as well as merged intimately with ash deposits.

4) The detrimental effect of free calcium oxide/carbonate is more pronounced than calcium sulphate. The use of silica additive immobilised the former Ca-bearing compounds remarkably, thereby forming an extra protective layer that even minimized the oxidation of Cr. Consequently, the whole tube remained intact.

Acknowledgement

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Appendix A. Supplementary data

The original X-ray diffraction (XRD) patterns for the two ash deposits and Cr K-edge XANES spectra for the standards are detailed in the Supporting information document. Supplementary data associated with this article can be found in the online version, at doi: http://dx.doi.org/10.1016/j.apusc.2017.06.018.

References

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Spatial distribution of Cr-bearing species on the corroded tube surface characterised by synchrotron X-ray fluorescence (SXRF) mapping and micro-XANES: exposure of tubes in oxy-firing flue gas

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ABSTRACT

Synchrotron X-ray fluorescence mapping and micro-XANES were employed to characterize the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that were exposed to oxy-fuel flue gas at 680 °C, 1 bar for 50 h. The gas composition tested is close to the flue gas produced from oxy-firing of low-rank coal in pilot-scale tests. Multi-layered scales with an uneven distribution were observed for individual elements on both the top surface and spalled layer of carbon steel SS400. Oxidation is the major reaction causing the scaling of the tube, whereas the other reactions such as sulphidation and chlorination led to the buckling of tube surface. The use of Cr, even at a low concentration of 1.2 wt% in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion rate, as well as minimize the difference between oxy-fuel and air-firing flue gases on the tube mass loss rate. The CO2 cycle with the involvement of oxidation (mainly of iron) and carburisation (of chromium) took place simultaneously for the Cr-bearing alloy, even under the coexistence of CO2 and a number of oxidizers in the flue gas tested here. The fast diffusion of CO2 and its derivatives facilitated a preferential occurrence of carburisation under the oxide scale. However, upon the closure of gas passage channels in the oxide scale of a high-Cr tube such as austenite SUS304, the reductants CO and carbon can flow back to tube top surface, causing the formation of carbide on the most outer scale that further fragments into fugitive pieces. Carburisation is also the major cause of corrosion of high-Cr tubes. In

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Introduction

Oxy-fuel combustion process is one of the most promising low-emission clean coal technologies that could be deployed to secure the sustainable use of coal in the carbon-constrained future [1]. High-temperature tube corrosion in boiler zone is one of the most critical issues of concern in the operation of coal-fired plants [2]. Compared to the conventional air-firing combustion where nitrogen is abundant, oxy-fuel combustion brings in augmented concentrations of carbon dioxide (CO₂), steam (H₂O) and impure components including sulphuric oxide (SO₂) and even hydrogen chloride (HCl), due to the recirculation of wet, dirty flue gas back into the furnace [1, 3]. All these components have been reported to enhance the tube corrosion rate considerably.

Since CO₂ is most abundant in the oxy-fuel flue gas, several studies have been conducted to clarify its role on tube corrosion. Table 1 summarises the related studies and their key findings, based on the use of either pure CO₂ stream or CO₂ mixed with steam. In brief, CO₂ is proposed to react with metallic iron (Fe) and chromium (Cr) to form oxide scales on a tube, according to Eqs. (1) and (2) below [3–6].

\[
\begin{align*}
3\text{Fe} + 4\text{CO}_2(g) & \rightarrow \text{Fe}_3\text{O}_4 + 4\text{CO}(g) & (1) \\
2.5\text{Fe} + 0.7\text{Cr} + 4\text{CO}_2(g) & \rightarrow \text{Fe}_2\text{Cr}_7\text{O}_3 + 4\text{CO}(g) & (2) \\
3\text{Fe} + 4\text{CO}(g) & \rightarrow \text{Fe}_3\text{O}_4 + 4\text{C} & (3) \\
2\text{CO}_2(g) & \rightarrow \text{CO}_2(g) + \text{C} & (4)
\end{align*}
\]

The resultant CO from Eqs. (1) and (2) can react with Fe to form oxide and carbon precipitates, according to Eqs. (3) and (4). Carbon precipitate can further combine with metals to form the respective carbides that are more brittle than the oxide scale, leading to the breakdown of the tube surface. The formation of carbide is dominant under reducing conditions [7–9] and is favoured by elevated CO₂ partial pressure [10] and a high carbon reactivity at the local scale-alloy equilibrium. It is also governed by the molecular diffusion of the dissolved carbon [5]. In contrast, in an oxidising environment, oxide scale is formed preferentially on the tube surface [7]. The resultant Fe-based oxide is permeable to carbon [7], whereas chromium oxide formed on the Cr-rich tube surface is resistant to carbon diffusion [11]. The permeability of the tube is also highly dependent on the gas temperature. Cr is virtually immobile and non-protective below 600 °C. At temperatures above 600 °C, Cr is able to diffuse outwards into the Fe-based oxide to form a protective layer [4]. However, when the temperature is too high and reaches 1200 °C, the carburisation of Cr is enhanced, which in turn degrades the tube [9].

The real oxy-fuel flue gas has yet to be tested for the presence of carbides, as the oxygen partial pressure is generally around 5 vol% that is far higher than the gases tested in Table 1. The effect of ash deposits on the carburation reaction has not been investigated either. The conclusions regarding the carburation reactions are also quite contradictory in the literature. One study [12] concluded that the 9–12% Cr steels cannot exhibit a protective oxide scale due to the preferential formation of carbide in 30% H₂O/70% CO₂ at 500–700 °C. To the contrary, another study using 2.25–20% Cr ferritic alloys in argon-20% CO₂/80% H₂O revealed the formation of a protective chromium oxide scale at 650 and 800 °C [5]. Moreover, the previous studies either relied on microscopies that only focused on individual spots, or on X-ray diffraction (XRD) that is unable to pinpoint the tube cross section which is generally on the micron scale. The chemical analysis methods can detect and/or quantify the carbides [5, 10, 11, 13], but fail to specify the spatial distribution and the partitioning of Cr between carbides and other species.

In this study, we reported the corrosion of a variety of tubes including carbon steel and 1.2–18 wt% Cr alloys exposed under the oxy-fuel flue gas that is similar to the compositions achieved from our pilot-scale test [14]. Apart from the bench-scale analytical facilities including X-ray diffraction (XRD) and
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scanning electron microscope (SEM) coupled with energy-dispersive X-ray analyser (EDX), the synchrotron X-ray fluorescence (SXRF) microscopy and micro X-ray absorption near-edge structure (μ-XANES) spectroscopy were employed to capture the fine structures and details on the cross section of the tubes at a resolution of 2 μm [15-17]. The spatial distribution for chromium oxide and carbide was used to quantify the penetration of carbon and the carburisation extent of chromium across the whole tube cross section. As far as the authors are aware, such advanced technologies have yet to be used on tube corrosion studies.

**Materials and methods**

**Tube corrosion conditions**

The tube exposure experiments were conducted in a horizontal furnace that was fixed at 650 °C for 50 h. The flue gas was fed into the furnace continuously at a rate of 300 mL/min. The flat tube specimen, 3 cm × 3 cm × 2 mm, was prepared by a wire-electrical discharge machine to cut on the cross sections of six commercial tubes. Subsequently, they were degreased and cleaned in acetone and ethanol using an ultrasonic bath. The oxy-fuel flue gas tested is made of 4.0 vol% O₂, 3000 ppm SO₂, 1000 ppm HCl, 30 vol% H₂O, 10 vol% N₂, and the rest being CO₂. The pressure for flue gas is 1 bar. Such a flue gas composition was confirmed in our pilot-scale test on the oxy-fuel combustion of a local Victorian brown coal [14]. The details for tube exposure conditions and sample preparation have been given elsewhere [18, 19].

A total of six tube materials were tested, with an increasing Cr content including SSS0 (0% Cr), 12Cr1MoVG (0.9-1.2%), T23 (2.25%), T91 (9%), SU53M7 (17-19%) and SU5304 (18-20%). For the SXRF and μ-XANES characterisation, only four tubes were chosen: SSS0, 12Cr1MoVG, T91 and SU5304. After the corrosion test, the tube specimen was quickly mounted and solidified into epoxy resin to avoid surface oxidation. Subsequently, it was halved by a disc cutter. The resulting cross-sectional surface was further polished by SiC paper with 2400 grit.
Figure 1. Cr-bearing standards that have been used for the LCF fitting via Athena in this study.

SEM–EDX and XRD analysis

The SEM–EDX analysis is complementary to SXRF, as it is not possible for the SXRF to map oxygen and carbon on a hard X-ray beamline in Australian Synchrotron. Prior to the analysis, the cross section of the tube was further polished using diamond paper (1 μm) and carbon-coated. A JEOL 7001F SEM was used for microstructural observation of the tube cross section and elemental mapping. XRD analysis was conducted on the top surface of the tube SS400, with a Rigaku Miniflex 600 setup at 40 kV and 15 mA, scanning rate of 1°/min, a step size of 0.01° and a wavelength of 0.15418 nm (Cu Kα). The software Jade was used for peak identification.

SXRF and μ-XANES analyses

SXRF and μ-XANES analyses were conducted at the XFM beamline, Australian Synchrotron. SXRF maps were collected at 15.8 keV with a Si (111) monochromator and an energy resolution (ΔE/E) of 2 × 10⁻⁴. The Kirkpatrick-Baez (KB) mirrors were used to focus the beam down to ~1.5 μm² [16, 17]. For the cross section of each tube, an overview map with areas ranging from 2.8 × 3.4 to 2.8 × 7.6 cm² was achieved using a pixel size of 100–200 μm² at a dwell time of 10–25 ms per pixel. Detailed maps were then collected over ~2 × 0.4 cm² area using 2 μm² pixels and a dwell time of 0.4 ms per pixel. XANES stacks were generated by collecting SXRF images (~0.2 × 0.4 cm², 4 μm² pixels, and dwell times of 1–4 ms/pixel) at 77 monochromators energies spanning 100 eV across the Cr Ka edge. Cr metal foil and a pellet of chromium oxide (Cr₂O₃) diluted in boron nitride were used to determine the energy shift for XANES analyses.

SXRF data were analysed using the dynamic analysis (DA) method [Ryan 2000] in GeoPIXE II [20]. The DA approach fits multiple lines per element that separates overlaps and subtracts background, escape peaks and other detector artefacts. The extracted XANES spectra were processed in ATHENA. Linear combination fitting (LCF) was used to qualitatively determine the chemical compositions by using the Cr-bearing standards shown in Fig. 1. Except for chromium carbide (Cr₃C₂) [21] and chromium sulphide (CrS₂) [22] those were extracted from the references, spectra for the remaining standards were collected from our previous studies [23–26]. Additionally, we validated the LCF method by analysing the mixture of standards at different molar ratios. The fitted data showed a maximum error of about 3% [25, 26]. It is also noteworthy that, as carbide and ferrite have varying stoichiometric ratios, the LCF fitting results based on the standards listed in Fig. 1 should only be taken as those for a general carbide/ferrite group, rather than for any specified chemical formulas such as Cr₂C₃ and FeCrₓOᵧ. The XANES analysis primarily aims to reveal the oxidation state of the elements of interest, which is independent of the atomic ratio for a given oxidation state. Concerning the similarity of a variety of standards such as Cr metal and carbide in Fig. 1, an effort was further made to validate the sensitivity of LCF upon the selection of standards for the fitting of Cr in tube T23. As demonstrated in Fig. 2a, exclusion of the carbide standard overestimated the intensity for the shoulder peak located at ~5.992 keV (in the dashed cycle), where both Cr metal and carbide overlap significantly. Upon the inclusion of carbide, the measured spectrum was well fitted at the shoulder peak. The resulting Chi-square value dropped from 0.1708 to 0.0314 with the inclusion of carbide. Figure 2b further illustrates the details of the fit, showing the spectra in relative proportions.

Thermodynamic equilibrium calculations

The commercial thermodynamic equilibrium programme, FactSage [27], was used to calculate and establish the Fe-Cr-CO₂ phase diagrams under the tube exposure conditions, 650 °C and a total pressure of 1 bar for CO₂. Apart from the pure substances, the
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Figure 2 Athena LCF fitting for the tube T23 exposed to flue gas. Panel a is for the comparison between two fittings with and without the inclusion of carbide, and Panel b is for the detailed fitting results with the inclusion of carbide.

Figure 3 Mass loss and oxidation growth rate for the six tubes that have been exposed in four different flue gases, at 650 °C for 50 h.

Results and discussion

Tube mass loss upon exposure into flue gas

The mass losses of individual tubes in oxy-fuel flue gas versus the air-firing flue gas are shown in Fig. 3. The composition of the air-firing flue gas is 5 vol% $O_2$, 10 vol% steam, 15% $CO_2$, 300 ppm $SO_2$, 100 ppm HCl and the remainder being $N_2$. It is obvious that oxy-fuel combustion is more corrosive than the air-firing flue gas, especially for carbon steel and the two low-Cr steels, 12Cr1MoVG and T23. The mass loss in pure air and $CO_2$ was undetectable (data not shown). However, the $CO_2$ is still very reactive upon the interaction with the tube material. This is partially due to the oxidation of metals (both Fe and Cr) by $CO_2$ according to reaction Eqs. (1) and (2) mentioned above. The resultant oxides and spinel have been confirmed by XRD analysis [18]. However, carbides were not found by the previous XRD analysis. This could be due to the reasons that the top surface was not polished off, or a significant peak overlap in XRD does not warrant a good identification of any minor species such as carbides, which will be further evident later.

SXRF mapping of carbon steel SS400

The SXRF map of tube SS400 exposed to the oxy-fuel flue gas is illustrated in Fig. 4, where the spatial distribution of individual elements is represented by a colour scale in which black and white refer to the minimum and maximum concentrations of individual elements, respectively. Regarding the spatial distribution of the most abundant element, Fe shown on the left-hand side of Fig. 4, it is obvious that the carbon steel was too weak to withstand the corrosive oxy-fuel flue gas. This agrees with its largest mass...
loss shown in Fig. 3. It has broken down severely, with the formation of a spalled layer that buckled off and the detachment of the top scale as well, as suggested by the formation of a narrow ditch underneath the top surface. More interestingly, a close-up view in the right-hand side demonstrates a rather wide ditch formed between the top scale and the spalled layer. Since Fe lewis on both sides of the wide in between ditch (as evident by the blue colour), it is apparent that the corrosive gases such as O\textsubscript{2} steam and even SO\textsubscript{2}/HCl penetrated inside the tube, forming volatile species that quickly diffused out. Consequently, the tube was spalled and buckled down by the compressive stress induced from the volatile gases. Additionally, it is clear that there is a formation of multi-layered structure for both top scale and the spalled layer, and a non-uniform spatial distribution of individual elements in each sub-scale/layer. For the principal element, Fe in the spalled layer, it is made up of three sub-scales. The very thin top sub-scale in yellow refers to the highest abundance of Fe (88 wt% Fe), with a red medium sub-scale for a concentration of 45 wt% Fe and a blue inner sub-scale (18 wt% Fe) that is much thicker and lean in Fe. Such a colour order proved a fast outward diffusion of Fe upon the oxidation on the tube surface. Regarding the top thin sub-scale for Fe in yellow, it also coexists with Mn, Co and even a small amount of Ti. This confirms the protective role and the fast outward diffusion of these three minor elements, due to their larger oxidation potential than Fe. The oxidation potential decreases in the order of V > Ti > Mn > Fe (FeCl\textsubscript{2}) > Co > Fe (Fe\textsubscript{3}O\textsubscript{4}) at 650 °C [6]. However, compared to Mn and Co, V and Ti had a slow diffusion rate, and hence, most of them are still present in the bulk tube and on the top surface that is still attached to the bulk tube and have not spalled off yet. These two elements are thus less protective. Moreover, the concentrations of S and Cl are quite low in the spalled layer, implying that oxides are the principal components.

The top scale is further amplified and marked on the top left corner of Fig. 4. As can be seen, the principal element Fe in this figure is made up of multiple sub-scales in different colour/concentration. The blue scale refers to the most outer sub-scale with
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Figure 5  RGB map of the cross section of carbon steel tube SS400 and SEM maps for the top layer spalled from the bulk tube.

Figure 6  XRD pattern for the top surface of SS400 exposed to oxy-fuel flue gas.

17.6 wt% Fe; a yellow medium sub-layer contains 73.2 wt% Fe; a narrower ditch stays between the above two scales, and the most inner sub-scale contains 62 wt% Fe that is still closely attached to the bulk tube. All these sub-layers have a comparable width that is around 120 μm. With regard to the top sub-scale in blue (next to the wide ditch), it comprises Fe and V, Ti, S and Cl. The lack of Mn and Co suggests a complete diffusion of Mn and Co out of the bulk tube, in comparison with the other two additives Ti and V that mostly reside in the bulk tube, as suggested by the red spots in their distribution. Furthermore, the existence of S and Cl here proved the preferential penetration of these two elements inside the tube, probably via the intra-granular diffusion through the pores. Fe in the medium sub-scale (yellow in colour, 73.2 wt% Fe) is most abundant. Even so, its distribution is still uneven in this sub-scale, as evident by a reddish strip on the left edge and a dark yellowish ditch inside. The reddish strip on the left edge is accompanied by Mn and Co, whereas the bulk yellowish Fe coexists with V, Ti, S and Cl. This further confirmed the different diffusion rates for the elements studied here. Regarding the most inner sub-layer that is still attached closely to the bulk tube, it is covered with a Fe-rich thin top surface, which is followed by a dark yellowish strip of lower Fe concentration with a width of around 120 μm. However, none of the other elements show this unique pattern. In light of this, it may be due to the formation of carbide; carbon cannot be detected on a hard X-ray beam line. Carbides have been reported to preferentially form internally in the voids and cracks inside the tube. This will be further discussed for the speciation of Cr in the other tubes.
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As S and Cl are related to bulk flue gas, efforts were made to clarify their affinity with the principal element Fe, by SEM mapping of the zoomed microstructure of spalled layer in Fig. 5 and XRD analysis of top scale in Fig. 6. From the SEM map in Fig. 5, one can see the abundance of iron and oxygen, and their close affinity in the spalled layer. This confirms the preferential formation of iron oxide, which is further evident from the strong peaks for magnetite (Fe₃O₄) in Fig. 6. For the two corrosive elements S and Cl, one can only see some S embedded deep in the Fe-dominated layer, whereas Cl is undetectable (data thus not shown). XRD analysis shown in Fig. 6 confirmed the formation of troilite (FeS). These sulphide species are also preferentially present at the left edge of the spalled layer that is next to the ditch formed in between the top scale and the spalled layer in Fig. 4, rather than being exposed to the bulk flue gas. Apparently, once diffusing inside the oxygen-depleted ditch, the accumulated SO₂ was partially dissociated into S(II) that in turn diffused outwards through the oxide scale. The inward diffusion of SO₂ and S(II) should be much more difficult, due to the dense nature of the bulk tube, compared to the porous Fe-based oxide scale [7]. Moreover, carbide was not detected in the XRD pattern in Fig. 6. This could be due to the superimposition of its peaks with the other species and also the presence of carbide underneath the top surface (as suggested by the dark yellowish stripe on the left side of the top surface in Fig. 4).

**SXRF mapping and μ-XANES analysis of low-alloy steel 12Cr1MoVG**

Figure 7 depicts the spatial distribution of the elements of interest on the cross-sectional surface of 12Cr1MoVG, a low-alloy steel containing 1.2 wt% Cr. Surprisingly, the tube remained non-spalled, with the formation of only a very thin, reddish layer of high Fe concentration on top, as evident on the left-hand side. The layer formed is estimated to have a width of around 0.16 mm, which is much thinner than the carbon steel shown in Fig. 4. A second reddish layer underneath the top layer was also observed, which can be attributed to the cracks formed by the outward diffusion of volatile species out of the bulk tube.

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(Springer)
However, it is much thinner and did not lead to the formation of any deep ditch in the 50-h exposure time. This proved the protectiveness of this low-Cr alloy against the oxy-fuel flue gas attack. The zoomed pictures shown on the right-hand side revealed an uneven spatial distribution of all the elements of interest. The principal element Fe is composed of four sub-scales on the tube surface, a super thin, blue sub-scale (~10.6 wt% Fe) on the most top of the tube, followed by an orange sub-scale (51.6 wt% Fe), a light-yellow sub-scale (79.2 wt% Fe), and a ditch in orange with increasing distance from the tube surface. Such a multi-layered distribution is strong evidence for the different inward diffusivities of gases and the different outward diffusivities of metals out of the tube, thereby causing the formation of different species at different depths inside the tube. For Fe on the most top blue sub-scale, it is accompanied by Mn and some Co, S and Cl. The coexistence of the former two elements further confirmed their protective role which is even more pronounced than Cr and their faster diffusion outwards the bulk tube, the same as has been found for carbon steel. Mn is the second most abundant element in both the light-yellowish sub-scale and the orange sub-scale/ditch of Fe. The presence of S and Cl resulted in a very weak signal on the most top sub-scale of Fe.

The spatial distribution of Cr is intriguing in the cross section of this low-Cr alloy. Except for a few regions where some Cr coexisted with Mn and Co, its majority remained in the bulk tube. However, a sub-scale (2.78 wt% Cr on average) formed by the mixing of yellowish dendrites and redish one (marked as white rectangle on Cr map in Fig. 7) was observed for Cr, which is present underneath the narrow, shallow ditch dominated by Fe and Mn. It might be formed by the sulphation/sulphidation of Cr, or even the carburisation of Cr which was reported to occur preferentially over Fe and internally underneath the top layer of the tubes, due to the molecular diffusion of reductive carbon through the oxide grain boundary. The resultant carbide precipitated inside the voids, forming a deep penetration inside the tube [8–10].
Efforts were made to clarify the association between Cr and S/Cl/C, as well as the speciation of Cr by XANES mapping. For the association between these two elements, the RGB map on the left-hand side of Fig. 8 suggests a close affinity of Fe and S forming a violet strip (top surface of the tube). Cr, however, has no association with S (on the top surface). Instead, the Cr-rich strip is slightly green in the RGB picture, suggesting the merging of green (for Cr) and red (for Fe) due to the dilution effect of the latter element. This is supported by the XANES distribution results shown on the top right corner of Fig. 8. One can clearly see that the energy at approximately 6.009 keV is the brightest for Cr, which is one of the featuring peaks for standard oxide/hydronitride (Cr₂O₃, Cr (OH)₃, spinel (FeCr₂O₄), and chloride (CrCl₃) shown in Fig. 1. The last species can be ruled out, since the Fe–Cr–Cl RGB map (data not shown) did not find any association between Cr and Cl. Regarding chromium carbide that has a shoulder peak centred around 5.991 keV (which should mainly attributed to carbide rather than Cr metal, as suggested by Fig. 2), it is rather weak in the Cr K-edge XANES energy distribution map, suggesting that oxide is predominant for Cr, and the light-yellow dendrite on Cr map (in Fig. 7) was not fully attributed from carbide. Or the carbide formed is well mixed up with oxides and failed to form its own strip with a clear boundary separating from the other species.

The XANES speciation results of Cr for seven individual spots are shown on the bottom right corner of Fig. 8. Note that these spots were chosen randomly from different layers/scales of the tube. Therefore, the LCF results here only intend to provide indication on the presence of different Cr-bearing species, rather than suggesting an averaged composition for each location. Nevertheless, all the spots analysed prove the formation of chromium carbide for almost all the locations except spot 5 which is located on the most outer surface of the tube. Moreover, it consists with ferrite that has a central peak at 6.009 keV and a shoulder one at 6.024 keV. The LCF results as shown on the bottom right corner revealed the fractions of individual species. The fraction of pure Cr metal has a maximum at 0.4 (i.e. 40%), suggesting a severe penetration of the corrosive gases causing oxidation and carburation of Cr deep inside the bulk tube. The amplified microstructure for the cross section in Fig. 9 confirmed the scaling and
even crooping of the tube caused by the penetration of oxygen and carbon, which is a strong indicator for the large porosity of the thin scale formed on the tube surface, as further amplified on the left-hand side. It was not possible to map Cr with the SEM as the Cr concentration was below the detection limit of the EDS detector. With regard to the two Cr-bearing species, ferrite and carbide in Fig. 8, both show a non-uniform distribution across the whole cross section. That is, carbide was preferentially present in the yellowish, dendritic strip that penetrated underneath the top layer (in blue for Cr), accounting for around 0.4 in mass fraction for the locations No 1 and No 2 inside the tube, and around 0.3 on the strip. For [18], ferrite is dominant. The carbon map observed in SEM in Fig. 9 also suggests the lack of carbon on the top thin scale which is mainly composed of Fe and O.

The formation of carbide is most intriguing here. As shown in Eqs. (3) and (4), the reductant should be the carbon, whereas the reactant CO in these two equations should be produced from Eqs. (1) and (2) for an initial oxidation of metals by CO₂. The reduction reaction for the carbide formation should also occur deep inside the tube, rather than on the gas/ tube interface where the partial pressure of CO is extremely low, accounting for maximum 10⁻⁶ bar for a total pressure of 1 bar pure CO₂ [18]. Figure 9 shows individual crystals and the presence of nanoscale gas channel in between different grains on the amplified inset picture (on the most top left corner of the left photograph). Clearly, such a narrow channel favours the entry and exit of gas produced on the surface of individual grains. The slow description of CO from an oxide grain (after the completion of reactions 1 and 2) and/or the build-up of CO gas in the void are essential for the carbide to be formed, according to the void-induced duplex oxide formation mechanism proposed elsewhere [10, 28, 29].

Once the CO is consumed in the voids, the CO₂ will be regenerated via reaction Eq. (4) and in turn, diffuses either outwards through the pre-existing porous oxide layer, or further inwards inside the tube, depending on the porosity and structure of the bulk tube. The former diffusion created an internal pressure and thus the formation of a shallow ditch underneath the oxide layer. In contrast, the latter diffusion induced the successive oxidation and deep precipitation of the resultant oxides and carbides that are also highly mixed together inside the tube, as suggested by the yellowish strip (in the dashed rectangle) for Cr in Fig. 7.

SXR and pXANES analysis of high-chrome ferritic T91 and austenite SUS304

The speciation of Cr averaged over the cross section of a tube, for three different Cr-bearing tubes, is depicted in Fig. 10. As can be seen on the left-hand side of Fig. 10, Cr in the two high-Cr tubes formed a continuous protective scale (in red for a higher concentration) that is much thicker than the top scale (in blue due to the lower concentration of Cr). In comparison, Cr in 12Cr1MoVG failed to form a continuous layer to protect the principal element Fe, due to the low Cr content in this tube. Moreover, similar to the 12Cr1MoVG tube, Cr in both tubes with high Cr concentration shows a multi over-layered distribution, with the formation of top sub-scale in blue, a red-orange medium sub-scale and a dark yellowish sub-scale that penetrates inside the tube. For the top blue sub-scale that is depleted in Cr, it only accounts for around 13 μm in depth on the two high-Cr tubes, which much thinner than the respective sub-scale formed for 12Cr1MoVG that is about 41 μm in depth. Regarding the red-orange medium sub-scale, it should be dominated by the Cr-based oxide that is dense and protective against the diffusion of corrosive gases. The dark yellowish sub-scale underneath the medium one is obviously most interesting. For the high-chrome ferritic T91, the dark yellowish sub-scale is much wider, covering plenty of discrete spots that are deep inside the bulk tube. These discrete spots may refer to the voids that are occupied by carbides and carbon precipitates that preferentially diffused inwards. If that is the case, the fraction of carbide formed on T91 is apparently larger than that found on the low-Cr alloy 12Cr1MoVG. Regarding the austenite tube SUS304, the formation of dark yellowish sub-scale is also evident. However, it is much thinner than on the T91 tube. There are also much less discrete precipitates formed deep inside the SUS304 tube.

XANES analysis for the averaged Cr speciation on the whole top scale, as circled on each tube, was conducted to confirm the above concerns. Note that, analysis on the bulk cross section of T23 tube at the beamline 16A at National Synchrotron Radiation Research Center (NSRRC), Taiwan, was also included.
here. As depicted on the right-hand side of Fig. 10, Cr on 121MoVG is dominated by ferrite that has a sharp central peak around 6.099 keV, whereas the carbide formed only accounts for a maximum molar fraction of 0.2. Cr on the bulk cross section of T23 possesses a similar fraction for the carbide, but has a much lower fraction for the ferrite, with the majority of Cr remaining as unreacted metal. For the other two high-Cr tubes, the fraction of ferrite is still low and comparable to T23. However, the fraction of carbide is much higher, accounting for 0.3–0.4 on average. This agrees with the presence of dark yellowish sub-scale and discrete precipitates on the cross sections of these two tubes, particularly T91. The phase diagram for Fe–Cr–CO\textsubscript{2} at 650 °C in Fig. 11 confirmed the preferential carburisation of chromium over iron from thermodynamic principles. The formation of carbide is also theoretically favoured upon increasing the content of chromium in the bulk tube, as well as decrease in the fraction of CO\textsubscript{2}. For the low-Cr alloy including 12Cr1MoVG and T23, the formation of ferrous oxide (FeO) and ferrite is highly favoured, whereas CO\textsubscript{2} only converts to carbon precipitate (in zone 4) and then chromium carbide (in zones 1–3) in the case that the fraction of CO\textsubscript{2} is further lowered.

From the gas diffusivity perspective, the top oxide layer that is supposedly protective against gas diffusion also plays a role. Its composition rather than the thickness is critical in impeding the carbide formation. To reiterate, for the low-Cr alloy 12Cr1MoVG and even T23, the top layer rich in iron-based oxide is highly porous and even partially damaged by the attack of SO\textsubscript{2} and HCl. Consequently, both the inward diffusion of CO\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O and outward diffusion of the resultant CO are favoured. The local environment is thus oxidising that favours the overgrowth of oxide/sulphide/chloride over carbide inside the oxide/metal scale. For the highest Cr tube
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Figure 11 Cr-Fe-CO$_2$ phase diagram created by FactSage$^\text{TM}$, at the temperature of 650 °C and a total pressure of 1 bar for CO$_2$.

(1) Cr(s) + Fe(s) + Cr$_2$O$_3$(s) + O$_2$(g)
(2) Fe(s) + Cr$_2$O$_3$(s) + CO$_2$(g)
(3) Cr(s) + Fe(s) + Cr$_2$O$_3$(s) + CO$_2$(g)
(4) Cr(s) + Fe(s) + FeO(s) + Cr$_2$O$_3$(s)
(5) gas + Cr(s) + FeO(s) + FeCr$_2$O$_4$(s)
(6) gas + Cr(s) + FeO(s) + FeCr$_2$O$_4$(s)
(7) gas + Cr$_2$O$_3$(s) + FeCr$_2$O$_4$(s)
(8) gas + FeO(s) + FeCr$_2$O$_4$(s)
(9) gas + FeO(s) + FeCr$_2$O$_4$(s)
(10) gas + FeO(s) + FeCr$_2$O$_4$(s)

Figure 12 Typical microstructures and the O and Fe maps for the three oxidizing tubes.

- Austenite tube SUS304 studied here, the whole tube and its Cr-rich, protective scale is dense (as demonstrated by the SEM maps in Fig. 12), thus creating a strong local reducing environment around the oxide/metal grains. The resultant carbide and carbon precipitates quickly fill in and block the gas passage channels in the scale, thereby impeding the successive diffusion of gases deep inside the bulk tube. However, for the medium Cr tube T91, its oxide/metal scale formed is less dense and possesses crevices inside the tube (see Fig. 12). The passage channel for CO$_2$ and its derivatives thus always remain open, as suggested by the strong penetration of oxygen inside the T91 tube in Fig. 12 and the local environment on the oxide/metal scale boundary shift between oxidizing and reducing alternatively, according to the successive consumption and generation of CO$_2$ based on reactions (1)-(4). This in turn promotes the penetration of carbide/carbon precipitate inside the tube. The local carburisation of T91 steel further accelerated the oxidation growth. Such a unique feature for 9Cr steel in CO$_2$ has also been noticed in the other studies using pure CO$_2$ or CO$_2$/H$_2$O mixed gases [10, 28, 29].

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![Image](image_url)

**Figure 13** Spatial distribution of Cr-bearing species on the interface of T91 exposed to oxy-fuel flue gas, Cr K-edge XANES spectra and LCF quantification results.

Analysis was also made to explore the detailed structure and spatial distribution of Cr-bearing species along the cross sections of T91 and SUS304. Figure 13 illustrates an amplified cross section of tube T91, the Cr K-edge XANES spectra for several spots typical along the tube cross section, and the resultant LCF fitting results. To iterate, these spots were chosen randomly from different location/colour on the tube cross section. The fitting results are thus only an indicator and evidence of the certain species rather than a quantitative result for different location. Similar to the tube 12CrMoV9, ferrite is most abundant on the orange interface that resides between the top blue sub-scale and the underneath dark yellowish sub-scale. Apart from pure metal, ferrite and carbide, the tiny amounts of chloride and even hydroxide were also observed on location nos. 4 and 5 on the orange oxide scale. This further proves a continuous open passage for gases in the oxide scale, and hence, a variety of species can be formed on the metal/oxide scale interface. More interestingly, the fraction of carbide is rather constant along the width of the tube, rather than being uneven as that has been found for 12Cr1MoVG in Fig. 7. In particular, the fraction of carbide is still noticeable on tube top surface, i.e. the blue gas/metal interface. This indicates a relatively strong reducing environment on the tube surface. It should be caused by the back flow of the reducing gases (e.g. CO) and carbon derived from Eqs. (1)-(4). The carbide fraction for SUS304 was much higher on the top blue sub-scale, as evident for the location nos. 4 and 5 in Fig. 14. The resultant carbide is apparently brittle and thus broke down into small fragments that were further carried over by the bulk flue gas, as suggested by no. 6 and those in the white circle on Fig. 14.

For the purpose of comparison, Table 2 summarises the major Cr-bearing species observed at the different scales for the three tubes, based on the SXRF and μ-XANES results in Figs. 8, 10, 13 and 14. Apart from the difference in the averaged Cr speciation that is usually measured by bench-scale facilities or bulk XANES, the three tubes also showed remarkable difference in the speciation of Cr at different scales.

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Figure 14: Spatial distribution of Cr-bearing species on the interface of SUS304 exposed to oxy-fuel flue gas, Cr K-edge XANES spectra and LCF quantification results.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Difference between the three tubes in terms of the averaged Cr speciation and its spatial distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>12Cr1MoVG</td>
<td>1st abundant</td>
</tr>
<tr>
<td></td>
<td>2nd abundant</td>
</tr>
<tr>
<td></td>
<td>3rd abundant</td>
</tr>
<tr>
<td>T91</td>
<td>1st abundant</td>
</tr>
<tr>
<td></td>
<td>2nd abundant</td>
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<td></td>
<td>3rd abundant</td>
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<td>SUS304</td>
<td>1st abundant</td>
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<td>3rd abundant</td>
</tr>
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</table>

Oxide is more easily formed deep down inside the low-Cr 12Cr1MoVG tube, whereas the pure Cr metal is still strong and protective enough to remain as the principal Cr-bearing species on the top surface of T91 and SUS304. The only side effect of this is the creation of a strong carburising environment inside the tube, which in turn promotes the simultaneous formation of both oxide and carbide, due to the roles of CO$_2$ played in Eqs. (1)-(4).

Summary and implications of this study

The most interesting finding in this study is the confirmation of chromium carbide under the oxide/ferrite scale that is inaccessible to XRD unless...
the top scale is ground off [16, 17]. In addition, the significant overlaps of carbide’s peaks with the other species make it difficult to identify using XRD analysis. SXRF maps at 5.993 and 6.005 keV that are the energies of the shoulder of carbide and oxide/ferrite, respectively, demonstrate the presence of these two species, with the presence of a measurable width inside the tube. As illustrated on the left-hand side of Fig. 15, the formation of carbide on 12Cr1MoVG is weak and highly miscible with other species including metal and oxide, compared to a clear thickness of 1.2 µm for oxide scale in orange, which is also around ten times thicker than oxide scale on the other two tubes. This is due to the depletion of Cr and fast oxidation of the principal metal Fe upon the attack of the flue gases. Instead, the carbide scale (blue strip at 5.992 keV) formed inside T91 is the thickest, accounting for around 0.45 µm which is nearly double the thickness for carbide formed on 18Cr SUS304. Since the thickness of the oxide scale is similar for the two high-Cr tubes, tube T91 thus bears the largest carbide-to-oxide ratio, suggestive of the dominance of carbide formation on its breakaway, compared to the predominance of oxide/sulphide/chloride for the buckling of low-Cr tube. Furthermore, from Fig. 3 it is evident that the use of Cr, even at a low content of only 1.2 wt% in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion, as well as minimise the difference between oxy-fuel and air-firing flue gases after the exposure of 50 h in oxy-fuel flue gas. The high-chrome steel T91 also performed comparably to the two 18Cr austenite tubes, suggesting that the carbide formed inside may not be strong enough to degrade the ductility of T91, within 50 h of exposure. However, a much longer exposure time is essential to monitor the performance of T91. Previous studies have suggested a linear kinetic rate for tube carburisation, and a much thicker carburisation zone could be formed, e.g. approximately 40 µm for Fe–20Cr exposed at 600 °C for 120 h [5].

The strong reactivity of CO2 under the coexistence of a variety of different gas components has also been confirmed in this study. This suggests the large potential of CO2 for the oxidation and carburisation of metals and the fast diffusion of CO2 and its derivatives compared to oxygen and even other components in oxy-fuel flue gas. The similar phenomena have been observed in a previous study where both the thickness of scale and carbide layer were increased upon the doping of 1% O2 in the CO2–H2O [5]. Another study even suggested that addition of 3% O2 in Ar/CO2 or CO2/H2O has no clear effect on carburisation [30]. The CO2 cycle as depicted on the top right corner of Fig. 15 should be the key theory explaining the formation of carbides, both underneath and above the oxide scale. CO2 and its derivatives including CO and carbon precipitate should diffuse rapidly through the channels formed in the oxide scale, compared to the other gaseous components. The other components such as steam and oxygen may even accelerate the cycle. Steam has been suggested to open cracks for the diffusion,
whereas oxidation of internal carbide by Eq. 69 [30] below may enhance the formation of CO and move the carbide front deep down inside the tube.

\[
\text{Cr}_2\text{C}_6 + 20\frac{1}{3}\text{O}_2 \rightarrow 11\frac{1}{3}\text{Cr}_2\text{O}_3 + 6\text{CO}_2
\]  

The content of Cr in the tube is crucial. Although an increase in Cr content facilitates the formation of a dense oxide scale, the CO and carbon formed could be encapsulated, accumulated underneath the resultant dense oxide scale and thus further penetrate deep inside the tube. This applies to the 9Cr tube T91. Increasing the Cr content to 18 wt% for the use of austenite tube should make the oxide scale denser and narrow the gas passage channels. Consequently, the successive formation of oxide closes the pores and pushes the resultant CO and carbon back out of the tube, which even creates a strong carburising environment on the tube surface to promote the formation of carbide that can further fragment into fugitive pieces. Consequently, the tube is still slightly corroded.

Conclusions

Synchrotron-based X-ray fluorescence and μ-XANES were used to detail the spatial distribution of individual elements and the speciation of Cr on the cross section of various tubes that had been exposed to oxy-fuel flue gas at 650 °C for a total of 50 h. The gas composition is close to the flue gas produced from the oxy-firing of a coal in our previous pilot-scale tests. The major conclusions can be drawn as follows:

1. Multi-layered scales with an uneven distribution of individual elements were observed for both the top surface and spalled layer of carbon steel SS400. Oxidation is the major reaction causing the scaling of the tube, whereas the other reactions such as sulphidation and chlorination led to the buckling of tube surface. The use of Cr, even at a low content of only 1.2 wt% in 12Cr1MoVG, is essential and can considerably reduce the tube corrosion, as well as minimise the discrepancy between oxy-fuel and air-firing flue gases in terms of mass loss rate.

2. The CO₂ cycle with the involvement of oxidation and carburisation of metals took place for the Cr-bearing alloy, even under the coexistence of CO₂ and oxidisers in the flue gas tested here. The fast diffusion of CO₂ and its derivatives facilitated a preferential occurrence of carburisation under the oxide scale. However, upon the closure of gas passage channels in the oxide scale, the reducants CO and carbon can flow back to the tube top surface causing the formation of carbide on the most outer scale that then fragments into fugitive pieces.

3. Compared to the austenite SUS204 tube where the carburisation is dominant for tube corrosion, chromium in the high-chrome T91 tube with 9 wt% Cr undergoes both oxidation and carburisation alternatively on the metal/oxide interface. The gas passage channels mostly remain open in the oxide scale, and hence, the resultant carbide and carbon precipitate penetrated deep inside the tube.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

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[18] Ja’buz I, Chen J, Etschmann B, Ninomiya Y, Zhang L (2017) Effect of silica additive on the high-temperature ferrite tube corrosion during the air-firing and oxy-firing of lignite (Xinjiang coal)—characteristics of bulk and cross-sectional surfaces for the tubes. Fuel 187:68–81


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Kinetic Study of Long-Term T23 Tube Corrosion upon Low-Rank Coal Ash Deposition under Oxy-Fuel Combustion Conditions

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ABSTRACT: The aim of this study was to understand the kinetics of high-temperature tube corrosion and its rate-limiting step in oxy-fuel combustion mode. Four different types of ash deposits collected from low-rank coal combustion boilers were tested, with varying contents of sulfur and metallic species. A typical stainless steel, low chromium ferritic alloy, T23, was tested at a metal surface temperature of 650 °C for up to 200 h. Compared with air-fired flue gas which is lean in O2 and steam, the aggressive flue gases formed under oxy-firing conditions enhanced T23 tube corrosion to a marginal extent in comparison with the S-rich ash deposit. The study found a positive correlation between the sulfur content within ash deposit and the thickness of the tube oxide layer. The sulfate in the ash deposit promotes the formation of molten mobile sulfate complex and sulfides. The former species are predominant on the tube’s outer surface, while sulfides are preferentially formed inside the oxide layer where oxygen is lean and/or absent. In addition, the study confirmed that the rate of growth of tube corrosion is controlled by both diffusion and phase boundary reactions. Regardless of the combustion mode, the gas diffusion coefficient decreases with the increase of sulfur content in the ash deposit, due to the enhanced formation of molten sulfates on the oxide layer. In contrast, no change was observed for the phase boundary reaction rate constant with increased sulfur content in the ash deposit. This is mainly because the solid-to-solid reactions are independent of the solid ash properties during the formation of molten sulfates and sulfides.

1. INTRODUCTION

Oxy-fuel combustion has potential as a low-emission combustion technology for coal in the carbon-constrained world. In this new process of combustion, coal is burnt in high oxygen concentration balanced by the recirculated flue gas inside a boiler in order to deliver high-purity CO2 in the flue gas, which could be subsequently sequestered with a minimal pretreatment. Compared with other carbon capture and storage technologies, oxy-firing is more efficient in CO2 capture, which has been reported to reach 100%. However, the corrosive nature of CO2 and other gaseous components of flue gas, in addition to changes in the operating temperatures and properties of the ash deposit, may trigger severe damage such as tube corrosion in the convective heat-exchange zones.

Oxidation is the principal mechanism of tube corrosion in a convective heat transfer zone in a coal-fired boiler. The initial step in oxidation is the adsorption of oxygen from flue gas, followed by the formation of oxide, the nucleation of oxide and its subsequent growth into a continuous scale/layer covering the tube surface. Factors affecting the reaction rate and the respective rate equations include the surface property and pretreatment of the metal, reaction temperature, oxygen partial pressure, and the duration of the reaction. Two relatively simple models are currently applied to interpret the rate of oxidation of a metal, linear and parabolic. Linear behavior is frequent under conditions where a surface or a phase boundary reaction is the rate-determining step and the oxide scale formed is porous and nonprotective. The overall oxidation rate remains constant with increasing the exposure time. Linear behavior may be caused by cracking and spallation of the scale, since new metal is continuously exposed to the atmosphere. Linear behavior may also occur before the oxide layer is sufficiently thick to separate the reactants in the initial stages of oxidation. In contrast, parabolic behavior predominates when the diffusion of ions or electrons through the oxide layer is rate limiting. Consequently, the rate of oxidation decreases as the layer thickens. The parabolic kinetic model was established by Wagner, based on a number of assumptions including stoichiometric, compact and adherent oxide scales, and only lattice diffusion as the rate-determinant. However, these assumptions are rarely valid. In practice, the oxidation for alloys with the presence of multiple passivation elements is usually complicated, and hence, deviations of the observed corrosion rate from these equations are common. Several studies have reported contradictory findings on whether the kinetics display linear, parabolic, or other growth patterns, as summarized in a review by Wright and Pint. Moreover, oxidation usually reveals different behaviors at different stages and therefore requires a combined rate law to explain the kinetics. To date, a number of research studies have been

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conducted under conventional air-fired conditions. However, kinetic studies of high-temperature tube corrosion under oxy-firing conditions are still lacking.

This paper reports the results for the oxidation kinetics of high-temperature corrosion for a low chrome ferritic steel material (T23). In addition to blank flue gases, four different types of fly ashes were applied to the tube surface to enable a detailed examination of their effects on the rate of tube corrosion. Similar to our previous studies, this study also employed a fixed temperature of 650 °C but different exposure times up to 200 h. Different kinetic models were assembled to interpret the tube oxidation rate and its controlling step under the different scenarios. In addition, the postcorrosion ash and tube samples were analyzed using different analytical methods, including scanning electron microscopy (SEM) together with energy dispersive X-ray (EDX), X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS). The study attempted to establish the corrosion rate of the T23 tube under typical long-term exposure in an oxy-fired boiler in order to gain insights into how the minimization of tube corrosion could be achieved under this low-emission combustion mode in its future deployment stage.

2. EXPERIMENTAL SECTION

2.1. Ash Deposit Compositions. The elemental compositions of the four ash samples are shown in Table S1 as determined by X-ray fluorescence (XRF). The two ash samples labeled XJ and XJL were the deposits collected from a superheater tube surface installed in a 30 MWw, pc-fired boiler for the combustion of a low-rank Xijining coal. Sample XJL was derived from the combustion of the same Xijining coal blended with silica additive to reduce in-hurnace slagging. The other two ash samples, Hailahou fly ash (HFY) and Yulin coal fly ash (YL), were collected from the ash dam in Yallourn power station located in the Latrobe Valley, Australia. The XRF patterns for these four ash deposits and their mineralogical compositions are shown in Figure S1 and Table S2, respectively, in the Supporting Information (SI). As the results show, the four samples that were tested differed greatly in the contents of individual species. In particular, the contents of thermitite (Na₂SO₄) and other sulfates varied widely. Note that these samples are exactly the same as those that were tested in our previous work.

2.2. Tube Corrosion Test Setup and Test Conditions. A horizontal furnace was used for tube corrosion testing. The testing temperature is kept at 650 °C for all the runs, since this temperature is most critical for the worst ash deposit-related tube corrosion. It is also a typical surface temperature for superheater/reheater tubes (650–700 °C). The corrosion tests were done in 50–200 h at an interval of 30 h. The flue gas tested has two different compositions for the air-firing and oxy-firing conditions. The air-firing flue gas consists of 5 vol% O₂, 15 vol% CO₂, 8 vol% H₂O, and 300 ppm of SO₂ and NOₓ in balance. In contrast, the oxy-firing flue gas is made up of 5 vol% O₂, 30 vol% H₂O, 10 vol% N₂, and 1000 ppm of SO₂ and NOₓ in balance. Finally, the tube material is mainly composed of 0.065% wt C, 2.2 wt % Cr, 0.07 wt % Mo, 0.21 wt % V, and 0.32 wt % Si and Fe in balance. The detailed tube sample preparation, corrosion test procedure, and post-test tube cutting were explained in our previous papers. The cross-section of each corroded tube was prepared by initially mounting a tube in epoxy resin in a vacuum chamber. The resultant pellet was then halved along its height. The resultant cross-section was subsequently polished with silicon carbide papers and diamond paper. The oxide layer thickness, microstructure, and composition of the oxide layer on the as-heated interface were determined using SEM-EDX (JEOL 7001F).

2.3. Characterization of Surfaces of Corroded Tubes. 2.3.1. Cross-Section Preparation and Observation. The cross-section of each corroded tube was prepared by initially mounting a tube in epoxy resin in a vacuum chamber. The resultant pellet was then halved along its height. The resultant cross-section was subsequently polished with silicon carbide papers and diamond paper. The oxide layer thickness, microstructure, and composition of the oxide layer on the as-heated interface were determined using SEM-EDX (JEOL 7001F).

3. RESULTS AND DISCUSSION

First of all, in order to validate the accuracy of our experimental results, the tube thickness and mass gain calculated under two typical conditions were compared with the results reported in the literature (see Table 1). Note that there is still scant research in this area, so far, no similar study with the same tube material and the same ash samples is available. As a result, Table 1 is merely a qualitative reference, rather than a quantitative benchmark. For the flue gas only case (no ash), the mass change for our tube T23 after 100 h reached ~30 mg/cm², which is more than twice the mass loss caused by the tube T91 (9.0 wt % Cr, 1.0 wt % Mo) tested with a similar flue gas composition. This is desired, since the tube T91 is much more corrosion-resistant, due to its greater content of passivation elements. Different results for mass gain were also observed for another case with ash deposit on the tube surface. Apart from the differences in the properties of ash and tube material, the mass measurement is also believed to have a relatively large error, due to the use of very small amount of sample for the test in each single run, causing reproducibility to be low. Moreover, exfoliation may cause mass loss, although the oxidation scale/layer continues to grow. In contrast, the measurement of oxide layer thickness under the microscope is more accurate and the results are more comparable. As Table 1 shows, the XJ ash rich in sulfates reaches a value of 0.22 mm for the oxide layer thickness of T23 after 200 h, whereas the tube thickness for tube T91 is about
0.19 mm under similar conditions. On the basis of these results, it is clear that our measurement of oxide layer/ scale thickness is reasonable, and the oxide layer thickness is also more consistent with the results reported in the literature. Therefore, the oxide layer thickness is used in the discussion hereafter.

3.1. Oxidation Rate of Tube Corrosion. The typical cross-sectional microstructures for corroded tubes under oxy-fuel mode are illustrated in Figure 1, where the tubes exposed to flue gas only and four different ash deposits are included for comparison. Note that the oxide layer shown is representative of the scale/layer which remained mostly intact after testing. However, exfoliation was also confirmed for some cases, and the resulting spalls mixed with the ash deposit. This was not counted into the scale/layer thickness here. As shown in Figure 1, both the corrosion environment (i.e., flue gas only versus ash deposit) and exposure time are influential in terms of the oxide scale thickness. Regardless of the corrosion environment, the scale thickness grows stably with increased exposure time. For the flue gas only case, all the scales remain intact on the tube top. However, the presence of ash deposit causes obvious exfoliation to varying extents for the four different ash deposits. For the two ash deposits, XJ and XJ_S, collected from the combustion of the same coal with and without the addition of silica, the oxide scale remains intact at 50 h and starts to fragment slightly when exposure increases to 100 h. The difference in oxide scale thickness between the two cases is also negligible. However, with the increase of exposure time to 150 h and even longer, it is clear that the addition of silica mitigates tube corrosion remarkably, since the oxide scale in the XJ_S case remains firmly attached to the tube surface, relative to the highly fragmented scale in the XJ case. The scale of the other two ash deposit cases fragments in 50 h. The extent of fragmentation also varies remarkably for these two cases with increases in the exposure time. The HW ash deposit is clearly more corrosive than the YL ash, which is also more corrosive than the XJ_S ash deposit. These changes reflect the importance of the composition of the ash deposit, which is detailed later.

On the basis of SEM pictures taken, the average thickness of the oxide layer was further calculated for each corroded tube. Moreover, based on the oxide layer thickness, the corrosion rate or the oxide layer growth rate was calculated by dividing it by the respective corrosion time. Figure 2 shows the results for

![Graph](image-url)
the five scenarios tested under the oxy-firing mode. Regardless of the testing scenario, the oxide layer growth rate increases monotonously with increased exposure time. However, the increase rate of the oxide layer differs greatly among the different scenarios studied. The flue gas only shows the lowest rate of increase, followed by X1_S, Y1, X1, and HW in ascending order. This is consistent with the qualitative observations shown in Figure 1.

Figure 3 compares the oxide layer growth rate for the two combustion modes. Similar to the oxy-fuel combustion mode, deposit which enhances tube corrosion. In contrast, the tube corrosion rate discrepancy is much smaller and even disappears in the X1_S case. This strongly suggests that the ash deposit property is most influential. Depending on the properties of the ash deposit, the extent of its synergistic interaction with oxy-fuel flue gas varies remarkably.

The elemental mapping in Figure 4 illustrates an enlarged cross-section of the tube coated with X1 ash deposit (the worst-case scenario in Figure 3) and exposed to oxy-fuel flue gas for 200 h. The fragmentation of the tube by corrosion was further confirmed, leading to the formation of a thick oxide layer dominated by oxygen and iron. More interestingly, the abundance of sulfur (S) was also confirmed. However, it is mostly distributed on two thin strings within the oxide layer. The left-most S-rich string is located at the left edge of the entire oxide layer that is next to the tube crack. Silicon (Si) is the most abundant element in the oxide layer, which should be partially derived from the ash deposit on its top surface and partially derived from the inherent Si (33.2 wt %) in the original tube. Si has been shown to be an efficient passivator to protect the oxidation of iron (Fe)\(^{10}\). The other two elements, sodium (Na) and calcium (Ca), exhibit much weaker signals in the oxide layer, indicating that most remain unreacted and/or react with the mobile Fe-rich fragments in the ash deposit.

3.2. XANES Speciation of S. To validate the importance of S in tube corrosion, the synchrotron K-edge XANES spectra for this element were collected. These are shown in Figure 5. As panel a for oxy-fuel flue gas only shows, the peak around 2482 eV is the sole peak observed for both the outer and inside surfaces of the tube exposed for different times. This peak is a unique feature of sulfate (SO\(_4^{2-}\)), which is mainly bound with Fe.\(^{11}\) The sulfite ion is also small enough to penetrate the oxide layer to react with Fe, as evident by the sole peak for sulfite inside the tubes. With the deposition of ash on the surface (see panel b), sulfite still remains as the sole S-bearing species on the outer surface, demonstrating the initial formation of sulfates of iron and even Fe-Na complexes, as confirmed previously\(^{10,11}\). However, another major peak at 2470 eV was also confirmed for the inside of the tubes exposed for 100 h. This peak and the others located between 2470 and 2482 eV are the unique features for sulfides.\(^{11}\) When a sufficient amount of SO\(_2\) is present in flue gas, the oxides (iron oxide) can catalyze the oxidation of SO\(_2\) and hence, SO\(_2\) can be formed, as shown in eq 1.\(^{11}\) It can further react with the inherent sulfate in the ash deposit and the oxide layer (rich in Fe-S-O) to form sulfate complexes, as per eq 2. Since the sulfates are also detected inside the tubes, it is clear that these
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Figure 5. S K edge XANES spectra. (a) Oxy-fuel fly ash only. (b) HW ash deposit for tube inside (red) and outer surfaces (solid black).

sulfates are molten and mobile for inward diffusion. More interestingly, at temperatures of 500 °C and above, the resultant trisulfate can attack the protective metal oxide, according to reaction 3.15. Compared with sulfite, sulfate is brittle, thus causing the fragmentation of the oxide layer and its blending into the ash deposit in the longest exposure time of 200 h. This explains a decrease in the intensity of sulfate from 150 to 200 h in panel b. In comparison to fly ash only in panel a, it is also evident that the reactions 2 and 3 did not take place in the absence of ash deposit.

\[
\begin{align*}
\text{SO}_3 + 0.5\text{SO}_2 & \rightleftharpoons \text{SO}_3 \\
3\text{Na}_2\text{SO}_3 + 3\text{SO}_3 + \text{Fe}_2\text{O}_3 & \rightleftharpoons 2\text{Na}_3\text{Fe}(\text{SO}_4)_2(\text{aq}) \\
2\text{Na}_3\text{Fe}(\text{SO}_4)_2 + 19\text{Fe} & \rightleftharpoons 6\text{Fe}_2\text{O}_3 + 3\text{FeS} + 3\text{Na}_2\text{S}
\end{align*}
\]

Equation 3.3. Correlation of Oxide Layer Thickness and Ash Species. As confirmed by the microstructural observations, the penetration of oxygen and \( \text{SO}_3 \) in fly ash into a tube is the most influential factor affecting the growth of oxide layer and thus the wastage of the tubes. These two oxidants interplay rather than compete with each other, accelerating tube wastage. However, the ash deposit is clearly more influential.

3.3.1. Oxide Layer Thickness, Oxidation of Sulfur, \& Ash Erosion. The oxide in the ash deposit may catalyze the dissociation of the bulk oxidants, including \( \text{O}_2 \), \( \text{CO}_2 \), and even steam, to produce the respective \( \text{O} \) radicals. In general, the dissociation of bulk oxygen is facilitated by alkali and alkaline earth (Na, K, Ca, Mg) metal oxide acting as the oxygen-shuttling agent via the redox reaction swing.19 Since the coupling of S was not observed in the fly ash only case, the S in fly ash should be the principal source for the formation of sulphonation/sulphidation across the oxide layer. It is possible that the sulfates in ash directly interact with the iron metal as depicted in eq 3, or via the eq 3 that is the combination of alkali sulfates, \( \text{SO}_3 \) (derived from the gas-phase reaction of \( \text{SO}_2 \) and \( \text{O}_2 \)), and iron oxide \( (\text{Fe}_2\text{O}_3) \).15

**Figure 6** presents a positive correlation between the contents of \( \text{SO}_3 \), \( \text{Na}_2\text{O} \), and \( \text{CaO} \) in the original ash deposit and their respective amounts deposited firmly on the corroded tube surface. Again, the loose ash deposits were removed carefully prior to the quantification of the tube top surface by XRF. Regardless of the exposure time and elemental type, it is evident that the content of each of these elements increases nonlinearly as a function of its original content in ash deposit.

S is the most abundant element on the tube surface, and its concentration on tube surface rises quickly with the change of ash deposit from \( \chi \) to \( \chi \) at around 8 wt % \( \text{SO}_3 \). Subsequently, its content almost levels off with a further rise of the original content of S in the ash deposit. This is particularly the case for exposures longer than 100 h. Clearly, a partitioning equilibrium exists between S in the original ash and the amount that can transfer into and be adsorbed by the oxide layer on the tube surface. A similar phenomenon was confirmed for the other two elements, Na and Ca. However, their concentrations in the oxide layer are extremely low, accounting for a maximum of 1.2–1.6 wt % even after exposure of 200 h. This implies that the sulfide is mainly in the form of iron sulfide in the corroded tube.

3.4. Oxidation Kinetics. An attempt was made to interpret the oxidation rates for different scenarios. In general, the change in the thickness of the oxide scale, \( \Delta X \), over time \( \Delta t = f(t) \) can be simplified, based on the control step. In the case where the external diffusion of oxidizing gases is relatively slow compared to its internal diffusion and the phase boundary reaction rate, the entire oxidation rate can be expressed as \( \frac{dX}{dt} = k_1 \).

**Equation 4** can be integrated to yield

\[
X = k_1 t
\]

where \( k_1 \) is the linear rate constant with a unit of \( \text{cm}^2/\text{h} \), and the integration constant is based on the assumption that \( X = 0 \) at \( t = 0 \). Under these conditions, diffusion inside the oxide scale can be so rapid that it makes no contribution to rate control.

In the case where internal diffusion is the control step, the overall rate of growth of the oxide scale is limited by the diffusion through the scale, following a parabolic equation.
where $k_p$ is the parabolic rate constant with a unit of cm²/h, and one initial condition solving these two equations is $x = 0$ at $t = 0$. If the data do not fit the parabolic rate law well, there may be defects such as voids in the protective oxide scale. Parabolic time dependence has been observed elsewhere. In some cases, both diffusion and phase boundary reactions may control the overall oxidation rate, as diffusion is initially rapid and then slows down upon the increase on the scale thickness. Therefore, when the scale is thin, the scaling rate predicted by eq 6 is faster than the experimental observation. However, in the process of scale thickening, the diffusion rate decreases until it becomes slower than the constant phase boundary rate. Simultaneously, the phase boundary process reaches a local equilibrium. Therefore, the kinetics are first linear and then parabolic, as evident by a study of the fitting of corrosion kinetics by a parabolic law at 650 °C and up to 200 h. This behavior has been detailed elsewhere and is simplified by the following rate: eq. 8

$$X^2 + LX = k_e + C$$

where $L$ and $C$ are the correlation constants. The symbol $k_e$ denotes the overall diffusion coefficient, while the value of $L$ represents the reaction kinetic coefficient.

Figures 7 and 8 show the curve fittings for all the cases under the oxy-fitting mode and air-fitting mode, respectively. Panel a in each figure refers to a linear fitting of the oxide scale thickness $x$ versus time $t$, as per eq 5; panel b refers to a linear fitting of thickness square $x^2$ versus time $t$, as per eq 7, while panel c refers to a polynomial fitting of $x$ versus $t$, as per eq 8. The correlation coefficients of $R^2$ for the fittings are listed in Tables 2 and 3 for Figures 7 and 8, respectively. Clearly, regardless of the existence of ash deposit, ash deposit type, and flue gas composition, the overall oxidation rate is controlled by both diffusion and the phase boundary reaction, as evident by the largest correlation coefficients which are mostly close to unity. Moreover, the diffusion should be mainly external diffusion for the oxidizing gases through the ash deposit or the gas film formed on the outer surface of the oxide scale, as evident by the relatively large correlation coefficient for the linear fitting between the oxide layer thickness versus exposure time in panels a. This is consistent with Figures 2 and 3 which show a rapid increase in the oxide layer growth rate in the initial 50–100 h. Since the oxide layer is relatively thin, gas diffusion through the ash deposit dominates. With a further increase in the exposure time, the oxide scale grows thicker and hence, diffusion slows and reaches a local equilibrium as per eq 1–3. This is reflected by the relatively flat increase in the tube thickness growth rate from 150 h in Figures 2 and 3.

On the basis of the best fitting in Figures 7 and 8, effects were then made to extract the diffusion coefficient ($k_e$) and the phase boundary reactions kinetic constant ($L$) for each case. Table 4 lists all the calculated values, while Figure 9 depicts the correlation between these two values versus the content of $C$ (in terms of SO$_3$ in the ash deposit) on the x-axis, where the initial value of zero refers to the flue gas only case. The content of $C$ in ash was taken as the principal variable, since it is the most abundant element found in tube oxide scale, as evident in the previous section.

Interestingly, the gas diffusion coefficient through ash deposit in panel a is independent of the flue gas composition. This is consistent with the fact that ash deposit is more influential in affecting the penetration of sulfur within the oxide scale in Figure 5. In another sense, the reaction rate of eq 1 for

$\frac{dx}{dt} = k_e \frac{x}{x}$

$X^2 = 2X + k_e t$

Figure 6. Effect of ash properties on tube corrosion, SO$_3$ panel (a), Na$_2$O panel (b), and CaO panel (c).
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![Graphs and tables from Energy & Fuels](image)

Figure 7. Oxidizing tube corrosion mechanisms and kinetic modeling. (a) Controlled by diffusion outside oxide scale. (b) Controlled by diffusion inside scale. (c) Diffusion and boundary phase reaction.

Figure 8. Air-oxidizing tube corrosion mechanisms and kinetic modeling. (a) Controlled by diffusion outside oxide scale. (b) Controlled by diffusion inside scale. (c) Diffusion and boundary phase reaction.

Table 2. Correlation Coefficients for Fittings in Figure 7

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diffusion Control Outside ($R^2$)</th>
<th>Diffusion Control Inside ($R^2$)</th>
<th>Diffusion and Reaction Control ($R^2$)</th>
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<tbody>
<tr>
<td>No ash</td>
<td>0.9600</td>
<td>0.7663</td>
<td>0.9963</td>
</tr>
<tr>
<td>XJ</td>
<td>0.9552</td>
<td>0.7770</td>
<td>1.0000</td>
</tr>
<tr>
<td>YL</td>
<td>0.9601</td>
<td>0.7619</td>
<td>0.9996</td>
</tr>
<tr>
<td>HW</td>
<td>0.9553</td>
<td>0.7238</td>
<td>0.9997</td>
</tr>
</tbody>
</table>
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Table 3. Correlation Coefficients for Fittings in Figure 8

<table>
<thead>
<tr>
<th>Sample</th>
<th>Outside (R²)</th>
<th>Inside (R²)</th>
<th>Diffusion and Reaction Control (R²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ash</td>
<td>0.9523</td>
<td>0.7326</td>
<td>0.9994</td>
</tr>
<tr>
<td>XJ</td>
<td>0.9442</td>
<td>0.7181</td>
<td>0.9942</td>
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<tr>
<td>XJ_5</td>
<td>0.8572</td>
<td>0.7170</td>
<td>0.9415</td>
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</tbody>
</table>

Table 4. Diffusion Coefficient (K) and Kinetic Reaction Coefficient (L) Values for Both Oxy-Fuel and Air-Firing

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxy-fuel</th>
<th>Air-firing</th>
</tr>
</thead>
<tbody>
<tr>
<td>K (cm²/sec)</td>
<td>L (cm/sec)</td>
<td>K (cm²/sec)</td>
</tr>
<tr>
<td>Na ash</td>
<td>1.0 × 10⁻⁸</td>
<td>2.1 × 10⁻⁸</td>
</tr>
<tr>
<td>XJ</td>
<td>1.5 × 10⁻⁸</td>
<td>6.6 × 10⁻⁸</td>
</tr>
<tr>
<td>XJ_5</td>
<td>1.0 × 10⁻⁸</td>
<td>6.4 × 10⁻⁸</td>
</tr>
<tr>
<td>YL</td>
<td>1.0 × 10⁻⁶</td>
<td>6.3 × 10⁻⁶</td>
</tr>
<tr>
<td>HW</td>
<td>1.0 × 10⁻⁶</td>
<td>6.3 × 10⁻⁶</td>
</tr>
</tbody>
</table>

Figure 9. Kinetic coefficients vs sulfur content in original ash sample. (a) K values vs SO₂ content in original ash sample upon oxy-fuel and air-firing reaction

4. CONCLUSIONS

This research was designed to facilitate the generation of oxide scale thickness and its growth rate for use in the life assessment of low ferritic chromium tubes in conventional air-firing and advanced oxy-fuel combustion technologies. The oxide growth rate of T23 was investigated at a metal surface temperature of 650 °C for up to 200 h. The major conclusions are as follows:

1. The aggressive flue gases formed under oxy-firing conditions enhanced T23 tube corrosion but to a marginal extent compared with the S-rich ash deposits. Kinetic simulation confirmed that both the coefficients of gas diffusion and the boundary phase reaction rate are constant for the two different combustion modes, demonstrating that the formation of sulfur trioxide (SO₃) from the reaction of SO₂ and O₂ in flue gas is not rate-limiting and is also independent of the partial pressures of these two gases components in flue gas.

2. A positive correlation was found between the sulfur content in ash deposit and oxide scale thickness. The sulfate in ash deposit promoted the formation of molten and mobile sulfate complex and sulfides. The former species are predominant on the tube outer surface, while sulfide is preferentially formed inside the tube where oxygen is lean and/or absent.

3. The oxide scale growth rate or oxidation rate is controlled by both diffusion and phase boundary reactions. Regardless of the combustion mode, the gas diffusion coefficient decreases with increased sulfur content in the ash deposit, due to the enhanced formation of molten sulfates on the oxide layer. In contrast, the phase boundary reaction rate constant remains unchanged with increased sulfur content in ash deposit, mainly because the solid-to-solid reaction for the formation of molten sulfates and sulfides are independent of the solid ash properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.9b01781.

XRD patterns for the fly ash samples, ash component of fly ash samples tested, mineralogical compositions of the four fly ash samples (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES


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