

CRANFIELD UNIVERSITY

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Formation of Corrosive Compounds from Biomass/Waste
Combustion

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PhD

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Abstract

Biomass/waste is a renewable energy source which can be fired in combustion power plants. These fuels can be used to replace coal combustion, with its associated environmental impacts, however challenges associated with biomass include accelerated fireside corrosion of heat exchangers (HX) due to producing different corrosive compounds; i.e. fireside corrosion is fuel dependent. As such compromises may be needed. For example, virgin wood fuels have lower fireside corrosion risks, although alternative biomass/waste fuels are cheaper.

This thesis compares the fireside corrosion influences of several biomass/waste fuel categories to further understand their attack mechanisms on conventional HX steels, T91 and 374HFG. The corrosive species generated during the fuels' combustion have been investigated using thermodynamic modelling by MTDData. Corrosion damage has been evaluated using high temperature corrosion furnace tests, conducted with isothermal conditions. In contrast to isothermal test conditions, further testing developed an alteration to the furnace setup to address heat gradient impacts on corrosion damage. In both fireside corrosion methodologies, the well-established deposit re-coat technique has been employed to simulate the deposition of representative salts. To evaluate corrosion trends influenced by the biomass/waste fuels with different exposure parameters, temperature, gas and deposition flux conditions have also been varied. Corrosion data evaluation is both quantitative (dimensional and weight changes of metals samples) and qualitative (scanning electron microscopy and energy dispersive X-ray spectroscopy).

Thermodynamic modelling shows higher partitioning of alkali metal species into the flue gas occurs for Wood Waste Fuels (WWF) than for Agricultural Plants & Residues (APR) and Herbaceous Grass Biomass (HGB) fuels. However, APR and HGB fuels release higher absolute amounts of these species in combustion. The high chloride percentages in APR and HGB deposits (69-89 mol.%) do not always correlate with higher corrosion rates as determined in the laboratory tests. Indeed, WWF deposits, with chlorides as low as 30 mol.%, have proven to be more destructive under certain operating conditions. Despite

this, the increased deposition flux on plant HXs of corrosive species from HGB and APR firing on plant HXs is responsible for their shorter operational lives as compared to WWF. This has implications for the type of biomass/waste fuel combusted for power generation.

Key words: Biomass/waste combustion, thermodynamic simulation, fireside corrosion, metal loss, heat flux, partitioning

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Dedication

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List of abbreviations

14ES	14 element system
15ES	15 element system
APR	Agricultural plants & residues
AM&S	Animal manure & sewage
ar	As received
A	Ash content
bal.	balance
BSE	Back scattered electron
BFB	Bubbling fluidised bed
CFB	Circulating fluidised bed
CHP	Combined heat and power
daf	Dry ash-free
db	Dry basis
EDX	Energy dispersive X-ray spectroscopy
EfW	Energy-from-waste
FB	Fluidised bed
GWe	Giga watt electricity
GW	Giga watt (heat)
GHG	Greenhouse gases
HGB	Herbaceous, grass biomass
HHV	High heating value
IFW	Industrial food waste
ICRC	International chemical recovery conference
IEA	International energy agency
KCP	Key condensed phase
LHV	Low heating value
m.pt.	Melting point
MC	Metal change

<i>MTCO_{2e}</i>	Metric tons of CO ₂ equivalent
<i>M</i>	Moisture content
<i>mol.%</i>	Mole percentage
<i>MSW</i>	Municipal solid waste
<i>PF</i>	Pulverised fuel
<i>ppm</i>	Parts per million
<i>RDF</i>	Refuse derived fuels
<i>RH</i>	Reheater
<i>SEM</i>	Scanning electron microscopy
<i>SE</i>	Secondary electron
<i>SMC</i>	Sound metal change
<i>SH</i>	Superheater
<i>SDS</i>	Sustainable development scenario
<i>TGA</i>	Thermogravimetric analysis
<i>vppm</i>	Volume parts per million
<i>wt.%</i>	Weight percentage
<i>WWF</i>	Wood waste fuels

1 Introduction, aims and objectives

This chapter gives the background to the PhD (**Section 1.1**), outlines the thesis structure (**Section 1.3**), presents the research aims and objectives (**Section 1.2**).

1.1 Background: Overview of energy production and CO₂ emission

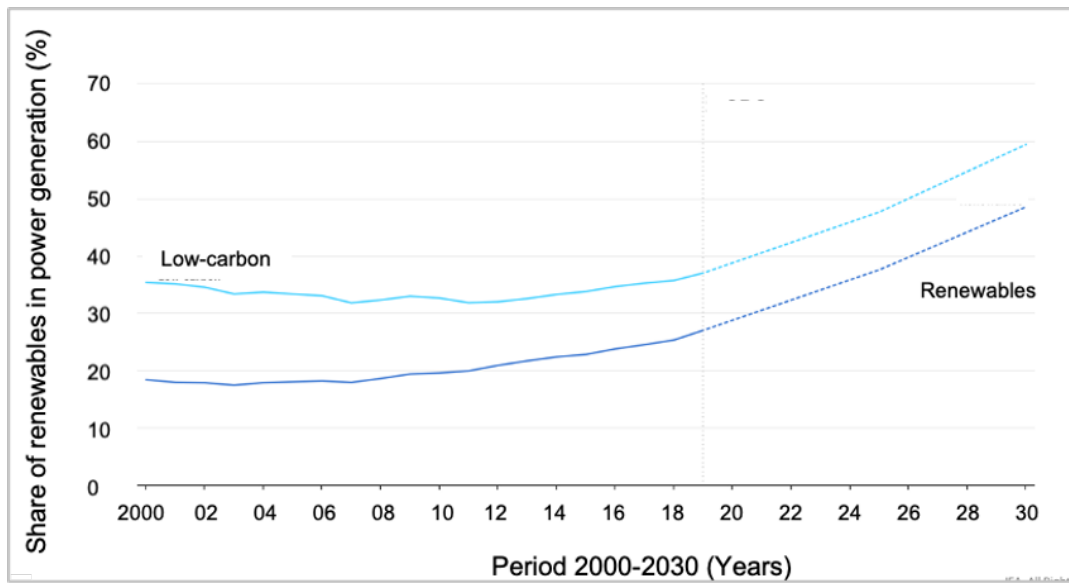


Figure 1-1: The percentage of renewable energy and other low carbon power generation sources employed in sustainability concepts [1]

The amount of renewable electricity generated globally in 2019 rose by 6% from the previous year's total, reaching a global electricity production share of nearly 27% [1]. Though this increasing renewables fraction (of global energy) may be encouraging, the target set by the International Energy Agency's (IEA) Sustainable Development Scenario (SDS), in-line with legally binding treaties on climate change, requires that approximately half of the electricity generated globally is produced via renewable sources by 2030 [1]. The 2030 renewables electricity generation projection in **Figure 1-1** reveals a steep deployment phase will be required to meet this target. As such there are ever pressing demands to improve these renewable technologies.

Carbon budgets are set with a view to achieving the 2050 CO₂ emission target, which is an 80% reduction in CO₂ emissions relative to 1990 levels [2]. The UK's CO₂ emissions, measured by greenhouse gases' (GHG) emissions, peaked in 2007 at approximately 1000 MTCO₂e (metric tons of CO₂ equivalent). Encouragingly, by 2016, emissions had lowered by 21% and current estimates show an increasing MTCO₂e margin below the peak values (of 2007) [3]. The EU has also included renewable energy in their environmental policies, setting achievable targets for its commitments towards CO₂ emission reduction [4].

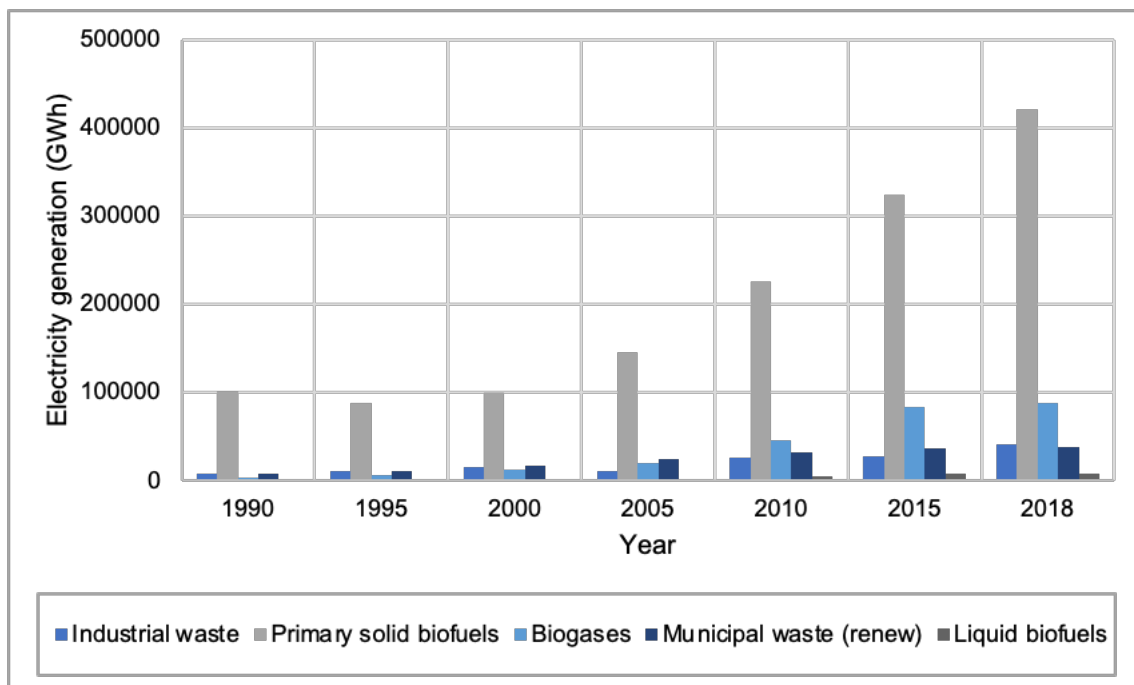


Figure 1-2: Global electricity generation from biofuels in 2018 [5]

Solid biofuels, also referred to as biomass, are the aggregate product of woods, vegetal matters, animal wastes and the renewable fractions of industrial waste that are used as a fuel for heat and electricity generation [5]. Global electricity generation from biomass and waste has more than doubled over the last decade [5]. Excluding biogas and liquid biofuels, the solid biomass share (which includes primary sources such as wood and energy crops, renewable

municipal waste, and industrial waste) produced over 500,000 GWh in 2018 (**Figure 1-2**). Globally, the heat production from solid biofuel combustion in 2018 was over 800,000 TJ [6], ranking 4th in renewable energy heat production that year [5]–[7]. The global utilisation of biomass as a combustion fuel thus continues to contribute to the catalogue of sustainable energy production means.

In the UK and the EU, the production of heat and electricity from biomass and biomass waste combustion continues to play a major role [4], [8]. As such, it is expected that the operations of biomass/waste plants will continue to improve, reducing the need for fossil fuel combustion.

In addition to pure biomass combustion, co-firing of up to 20% biomass/waste with coal has widely been adopted in the UK and EU [9]. Given its history in coal combustion, the UK has held one of the largest technical potentials in terms of available pulverised coal-fired boilers to exploit co-firing [9], [10]. Indeed, a variety of biomasses/wastes have been used in the UK's coal firing plants, including vegetal residues, energy crops (popularly miscanthus and short rotation coppice), forestry residue, and wood [11]. As such power plants, which were originally designed for 100% coal combustion, began introducing small fractions of biomass/wastes to the fuel stream, resulting in reduced coal fractions. However, this requires operational modifications, leaving room for research [9].

A number of policies have impacted the specifics of the exploitation of biomass over time; this has included Renewables Obligations Certificates, and the EU's Large Combustion Plant Directive [1], [5]. Currently it appears that large plants have reached an operable peak for co-firing, with many GWh of large plant shutting. Prior to this, plants could receive operational subsidies for co-firing. However, by 2010/2011, some coal power stations had either shutdown or fully converted to 100% biomass firing, encouraging smaller biomass boilers to spring up [11].

Over recent years, biomass combustion power plant operators have given attention to enhanced construction technologies to cope better with the different handling requirements and combustion properties of biomass as compared to

coal [8]. Indeed, biomass has lower energy contents and a wider range of chemical compositions than coal, making it problematic as a combustion fuel. The main driver for increasing renewable fuel usage, however, remains the imposition of countries' policies capping CO₂ emissions [10], [11].

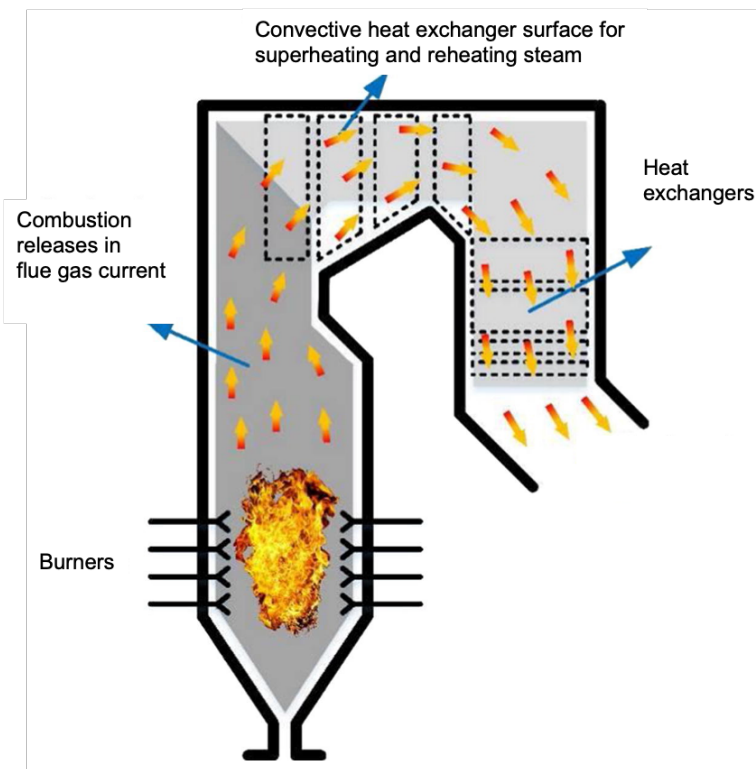


Figure 1-3: HX surfaces are exposed to flue gas contents following fuel combustion [12]

An outstanding challenge for biomass combustion technologies arises from deposition of the chemical components released during and post-combustion. Combustion power plants require a heat transfer from the combusted gas to a working fluid (steam), which is usually an array of high temperature alloy pipes. Such a heat conduit is collectively referred to as heat exchanger (HX) (see **Section 2.5**) (**Figure 1-3**). Deposition occurring on tube surfaces along the combustion gas stream has the tendency to impact the amount of heat energy recovered at the steam side. Fouling occurs when the

deposit layer built up on a HX surface causes an insulating effect which diminishes heat transfer [13]. Though deposit build-up on tube walls is experienced in coal combustion plants, compositional differences of non-fossil fuels make wall fouling a greater problem for the utilization of the latter fuels [14], [15]. In addition to fouling, chemical reactions occurring between the alloying elements, deposit and gas components, as well as the vapour in the gas stream, cause ‘fireside corrosion’ damage at high temperatures [16] (**see Section 2.5**).

Approaches for reducing deposit formation and thus the corrosion of HXs’ fireside surfaces include optimizing the metal surface temperatures, chemically modifying the fuel, and enhancing plant design and materials. The former two adaptations endeavour to avoid operation that puts alloy surface temperatures above a deposit’s melting temperatures, where molten deposits can react more rapidly (than solid phase components) [17], [18]. This, however, leads to lower energy conversion efficiencies, as steam temperatures must be lowered [19]. Lower temperature ranges for biomass firing, compared to coal, are listed later in **Table 2-3**.

High temperature corrosion control following biomass combustion requires multidisciplinary skill sets. Fireside corrosion occurring from the firing of biomass/waste, being relatively new and varied (types and compositions), is a complicated field with a significant number of knowledge gaps. Laboratory testing is usually aimed at understanding individual chemical component reactions or, at most, the firing conditions generated from specific fuels, such as conventional fuels. Biomass fuel combustion practices must, however, adapt to the use of less conventional fuels [20], such as from industrial, agricultural and urban wood waste, as these may have economic advantages [20]–[22]. The availability of these waste fuels may, however, be less predictable, compared to conventional fuels, due to seasonal and economic influences [20]. Though the use of fuels that lead to less corrosive deposits, such as virgin wood sourced from North America [23], remains very much in the foreseeable future for biomass combustion, costs and environmental life cycle impacts (such as land use, abiotic depletions and consumption of resources, for e.g., fertilizers) associated with growth, processing

and transportation have increased the desire to source biomass fuels more sustainably.

The combination of various waste biomasses is a likely approach for meeting supply levels [23], where fuels with similar chemical composition ranges can be co-fired. As such, there is further need for the investigation of the chemical environments generated from firing combined fuel category blends and their corrosion behaviours.

This study will entail the simulation of post-combustion compounds of pre-selected fuel groups, chosen based on their current or feasible application as combustion fuels. The molten compounds at HX fireside temperatures will be investigated to understand their chemical interactions with selected HX materials at high temperatures, thus evaluating corrosion behaviour trends within each fuel category. Conclusions from this PhD will thus enable improved understanding of high temperature corrosion behaviours of biomass/waste fuel ranges.

1.2 PhD aims and objectives

Aim

This PhD aims to identify and enhance understanding of the formation of corrosive compounds in pre-selected biomass/waste fuel categories with regards to their role in fireside HX corrosion.

Objectives

1. **Pre-selection of fuel categories:** To enable the delivery of a well-defined research scope by focusing on categories of economical and operationally feasible fuels.
2. **Identification of key corrosive species types in fuel categories:** The investigations of elemental distributions occurring within categories and thermodynamic modelling of post-combustion species enables identification of the condensed phase compounds which are likely to be molten on HXs for their surface temperature conditions. These molten

components are of fireside corrosion concern. This objective allows comparison of the corrosive deposits for the fuel categories, including trace element effects.

3. **Evaluation of fuel categories' post-combustion compound corrosion behaviour:** to investigate qualitatively and quantitatively the fireside corrosion behaviours of each fuel category on representative heat exchanger alloys for realistic fireside temperatures.
4. **Evaluation of corrosion data from a modified laboratory high temperature corrosion test setup:** To improve the interpretation of plant data, a novel test furnace setup will be designed to simulate the influence of heat flux.

1.3 Thesis outline

This thesis is organised in six chapters and as follows:

Chapter 2 is a literature review which outlines topic areas relating to this research

Chapter 3 provides the methodological approaches adopted to achieve the stated PhD objectives.

Chapter 4 presents all results generated from the experimental methods employed (procedures explained in **Chapter 3**) during this research.

Chapter 5 discusses the experimental results, making reference to each objective.

Chapter 6 concludes the thesis and proposes possible future work.

Chapter 7 gives the research recommendations

Appendix A documents fuel data, experimental parameters and experimental input calculations.

Appendix B presents the metal surface and sound metal changes of samples.

Appendix C presents the mass changes of samples.

Appendix D presents the error analysis carried out to determine the experimental errors range associated with dimensional metrology changes of metal samples.

Appendix E documents referenced microscopy images and element maps.

Appendix F is an attachment of referenced documents relevant to this thesis.

2 Literature review

This chapter reviews topics associated with the aim of this thesis, focusing on fireside corrosion, in particular, related to biomass and biomass waste combustion environments and HXs. It introduces fuel types (**Section 2.1**) and highlights their potentials and challenges as power plant combustion fuels (**Section 2.2**). The review highlights the major factors affecting fireside corrosion rates and mechanisms (**Section 2.3** to **Section 2.5**), and surveys popular methods adopted for quantifying that corrosion (**Section 2.6**). Knowledge gaps are then identified within the biomass fuel related fireside corrosion field (**Section 2.7**).

2.1 Introduction

A key aspect of power production, especially in solid fuel combustion systems, is the selected fuel, in particular, its physical and chemical properties. Fuel compositions and physical properties, such as grind particle size, will affect the conversion process and influence the choice of power generation system (e.g., fluidised, pulverised, grate). The fuel's supply and storage dictates the scale of the power plant unit (<30 MWe for biomass and 500-800 MWe for coal combustion boilers). Also, the chemical composition of the fuel will influence the target steam temperature, dictating the energy efficiency of the plant (typically up to 25% for biomass and 35-47% for coal fired systems [24]). Emissions capping and ash cleanout requirements are also affected by fuel composition. As such, the whole economic viability for plant running is largely dependent on fuel choice [24].

2.2 Fuel potentials and challenges

Fuel firing in combustion power plants come with pros and cons. Coal combustion has been employed for decades in power generation. Biomass and

waste firing is, however, relatively new and its exploitation as a combustion-based energy fuel is at a steep learning curve, compared to coal.

2.2.1 Coal as a combustion fuel

The term 'coal' defines a wide range of a solid fuels. The formation of coal may be described by a geo-chemical process called coalification whereby vegetal matter is formed into solid sedimentary rock material. It consists of both inorganic (from earth matter) and organic (from vegetation) material. The calorific values are higher than found in vegetation: attributed to the compact nature of the fuel whereby years of exerted pressure and temperature gradually decrease the moisture and volatile content (including the oxygen and hydrogen contents) [9]. Carbon content, which increases the calorific values, is thus more concentrated in coal fuels than biomass fuels [25].

Compositional ranges do occur within coal types, influenced by local geology and location. The organic matter content of coals are carbonaceous while major inorganic components consists of alkali metals and alkaline earth metal species/minerals including iron and chloride minerals [13]. Minerals of coal include carbonates, sulphides, sulphates, silicates, halogens, oxides and phosphates, and these make up part of the ash. Trace elements (with < 1000 parts per million (ppm) in the fuel) such as As, Ba, Mg, Ni, Ti and F, may also be associated with coals and may also be found in coal ash. These ash constituents can result in power plant operational problems such as high temperature corrosion (known as fireside corrosion; described in more detail in **Section 2.5**) and fouling. Cl and S, for example, can be present in ashes which may corrode power plant materials when they come in contact.

Historically, coal has been widely employed for power production, but non-fossil fuels are now playing an increasing role; combatting high CO₂ emissions while producing energy sustainably. Coal fuels are not considered to be

renewable as they emit CO₂ at rates higher than their formation takes up CO₂ [26].

2.2.2 Biomass/waste energy potential and challenges

Biomass is a derivative of organic matter from forests, agricultural practices and wastes [5]. It has been employed as a combustion fuel in energy production as part of the effort to lower CO₂ emission [1] by replacing coal. In 2012, over 60% of renewable energy consumed in the EU was supplied from biomass/waste [27]. The constraints of successfully harnessing energy from biomass (fuel supply and storage logistics; handling and preparation; availability; and economics) are determinant factors that influence their suitability as combustion fuels. These factors have contributed to the sourcing of combustion fuels from sustainable sources within realistic operational costs. In the search for such fuels, locally available fuels/wastes have gained the interests of energy providers, as a major proportion of the costs associated with sourcing these fuels is from transportation and logistics [20].

One of the main challenges in the use of these non-fossil combustion fuels is their widely varying chemical compositions [28]. This impacts their fireside performances [24], making it challenging to predict ash release, amongst other issues [9]. Furthermore, biomass has competition from other economic activities, such as agriculture [22] and, within the energy industry, liquid biofuel and biogas production. While this leads to incentives to widen the scope of biomass combustion fuel types, such action further extends the range of chemical compositions associated with biomass/waste combustion fuels [22], [29], [30]. To understand biomass/waste fuel behaviour during combustion, it has therefore become important to categorise the fuels (rather than simply relying on a specific single type) prior to evaluating their operational impacts. This is particularly important, as plants fired on biomass/waste fuels look likely to continue to use broader categories of fuel, due to availability and cost issues.

A major challenge associated with products formed from biomass/waste combustion, relative to coal combustion, is the high corrosion rates induced by them should they condense, forming deposits on power plant metal surfaces [24]. High temperature corrosion arises from chemical reactions between deposits, gases and metal components along the flue gas paths in combustion plants. These metals, or alloys, play a key role in combustion power plants where they serve as heat transfer conduits to the steam generation system, where the steam keeps the metal surface at a relatively lower temperature. Deposition of flue gas components onto these HX surfaces is thus difficult to prevent.

To curb the high material damage rates, biomass/waste plants run at lower metal temperatures than coal plants [19], [24] (see **Section 2.5.1**). Chemical reactions of species have been studied over the decades to understand their interactions with steels. Fireside corrosion can be understood from these reactions' mechanisms. Such studies have led to improved co-firing optimization [9], [24] enhanced metallurgical performance [31], [32] and improvement of fuel additives which influence melt behaviours when mixed with the combustion fuel [33]–[35]. There is, however, an on-going need to lower high temperature corrosion rates, especially where non-conventional fuel use (such as wastes) is concerned.

Higher fireside corrosion rates exist in biomass/waste combustion environments compared to coal [20]. These need to be understood. However, biomass/waste-related corrosion mechanisms are further complicated by the different chemical compositions of these fuels compared both to coal [22], [29], [30] and other biomasses/wastes. Extensive laboratory tests have been conducted to investigate corrosion linked to specific biomasses [36]–[39]. Furthermore, there are concerns about the differences in corrosion rates obtained between plants and laboratory exposure conditions [37], [40]. This implies the need to improve laboratory testing methods.

2.2.3 Categories of biomass fuels

Biomass fuels can be sourced directly from vegetation or indirectly via a waste stream. The difference between clean/virgin biomass fuels and waste biomass is the level of contaminant matter. For example, virgin wood sourced directly from wood felling will contain minimal heavy metal contaminants when compared with wood sourced from demolition activities [20] (some contamination sources are mentioned in **Section 2.2.3.1**). As a result, biomass from energy crop farms and forests are typically classified as clean biomass fuels, while biomass sourced from end-of-life activities, such as from agricultural and industrial processes, are classed as waste biomass. The chemical compositions of different clean biomasses can also vary distinctively. For example, higher chloride compositions are encountered in green plant parts and grasses than for woods [25]. These variations result in different handling and combustion characteristics, making it necessary to highlight major types of biomass/waste fuels in the following sections.

2.2.3.1 Wood and wood waste fuels

In 2014, approximately 300 TWh of electricity was produced globally from the combustion of wood chips (virgin wood) [41]. Currently, up to 500 TWh per annum of global biomass electricity is supplied from wood chips, accounting for up to 60% of the total biomass combustion contribution towards global electricity supply [5].

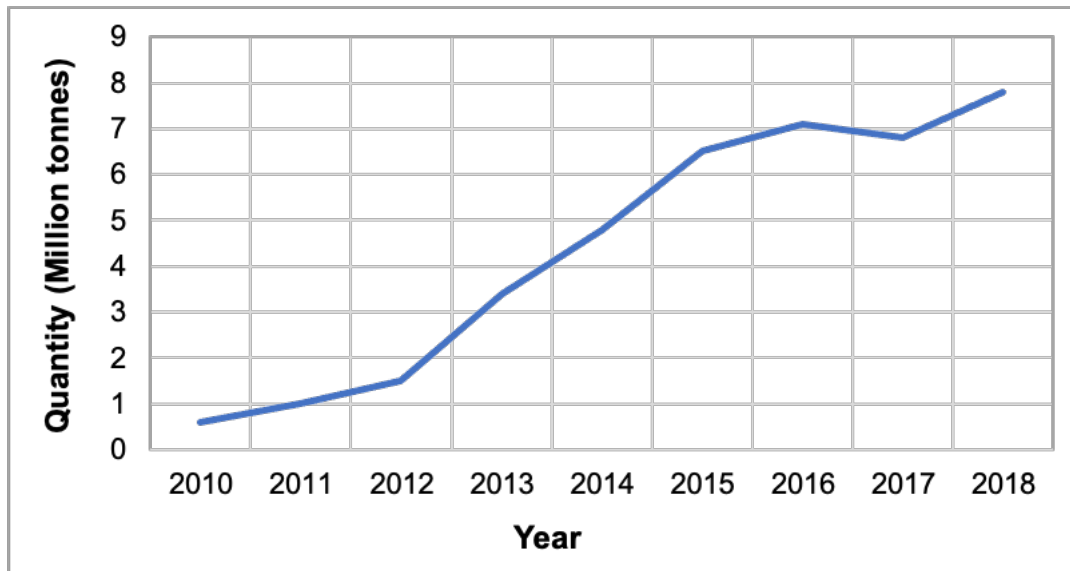


Figure 2-1: Wood pellet imports to UK within the last decade [42]

Wood, generally, is the most desired combustion fuel amongst biomass sources, from an operational point of view, as ash-contents and the related challenges are lower [20]. Sweden and the UK, amongst other countries, are the largest exploiters of biomass in the energy sectors and rely chiefly on wood fuels [43]. The importation of wood by the UK has risen steadily to meet energy demands [27]. With approximately 6.5 million tonnes imported in 2015, the UK held the largest (91%) market share of EU imports of North American virgin wood pellets [44]. In 2018, nearly 8 million tonnes of wood pellet were imported into the UK from North America (**Figure 2-1**).

As the UK's wood imports increased, a study was launched in 2014 [41]. This study enabled the evaluation of the true CO₂ emissions reduced by the use of biomass instead of fossil fuel for combustion energy. In addition to importation related CO₂ emissions, transportation and forest preparation charges/logistics are also of concern for imported wood. Smaller countries are less favoured with land availability for cultivating biomass fuels. As such, nearer-home, higher turnaround energy crops (which can be harvested annually [45]) and alternative fuels (e.g. wastes) are thus necessary options if renewable combustion fuel supplies are to be sustained in the future [23].

Clean wood causes fewer ash related operational challenges in biomass combustion in comparison with other biomass/waste fuels [46]. When comparing biomass fuels, Paneru et al. [47] and Vassilev et al. [14] highlighted wood's relatively lower moisture and ash contents compared to other biomass. The organic fraction of fuel ash has been linked to combustion issues, as detailed in **Section 2.4**. The chemical compositions of wood also showed lower concentrations of Cl, S and K containing species known cause or enhance corrosion [14]. This 'less problematic' wood is mostly desired by the high investment, larger power plants, where shutdown durations (for maintenance and repairs) significantly affect profit margins [4], [20], [28].

Smaller plants may, however, prefer to source fuels locally as supply quantities may be sufficient for such plants. For example, a 27.8 MWe capacity power plant developed in Kent, UK, by Estova Energy was launched in 2018 and powers 50,000 homes from the combustion of locally sourced wood [48].

Similarly, in February 2018, in Tansterne, Hull, UK, a plant was commissioned utilizing up to 150 metric tonnes per annum of locally supplied waste wood which would have otherwise become landfill [49]. The UK has an estimated annual availability of 4.2 - 6.6 million tonnes of waste wood per annum available for biomass combustion from 2020 to 2025, taking into consideration current reuse and recycle strategies to encourage the fuel's uptake [49], [50].

Varying levels of trace contaminants exists for wood wastes [51], [52]. Treated wood, for example, can be exposed to different compounds based on the treatment type, while demolition woods may have become mixed with metals and concrete. Most commonly, Zn and Cr contaminants in the wood waste fuels (WWF) category are related to adhesives employed for wood preservatives [51], [52]. Power plant developments are expected to further reduce the UK's reliance on wood biomass fuel imports [2]. Contaminants associated with waste wood fuels may, however, influence the suitability of these fuels for combustion where increased damage arising from chemical reactions of trace contaminants may occur [51].

2.2.3.2 Herbaceous and grass biomass (HGB)

The rising need to locally source biomass fuels has led to increased dedication of UK land to the cultivation of herbaceous plants and grasses [53]. Such plants may be termed ‘energy crops’ were they are grown specifically for biofuel use [53]. Approximately 3.9 million tonnes of energy crops were employed in UK electricity generation in 2015. By 2016, 12% of the UK’s overall heat energy production came from energy crop supplies, generating up to 18.8 TW.

This power comes from plants such as Snetterton (based in Lincolnshire) and Brigg (based in Norfolk), straw-fired biomass plants, which produced 44 MWe and 40 MWe respectively in 2016, while an additional 144 MWe was produced by several smaller capacity plants [2]. Advances in these areas have come from improved fuel processing technologies. For example, processing vehicles can simultaneously granulise while reaping. In addition, crop cultivation turnover periods have shortened over the past decade [45].

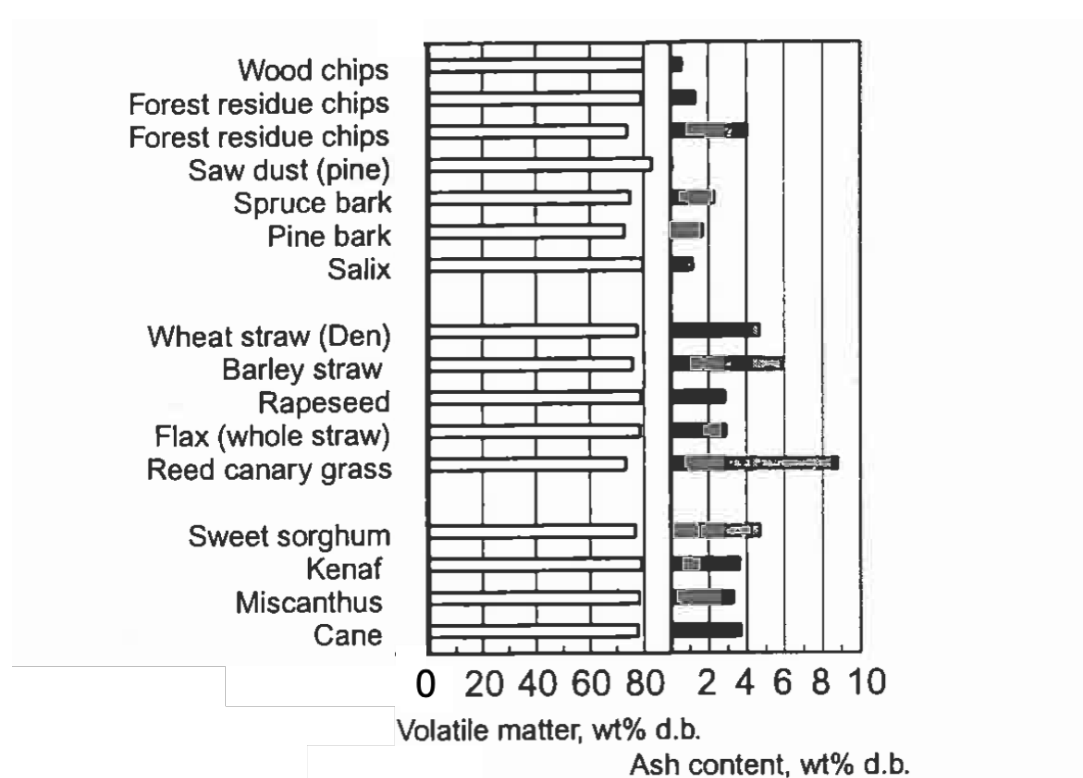


Figure 2-2: Comparison of wood and HGB fuels volatile matter and ash content (from proximate analysis) [54]

HGB fuels are typically characterised by relatively high moisture contents and thus low calorific values relative to wood [54]. Combustion compounds' release rates, which influence fireside corrosive conditions [34], [40] (see **Section 2.5**), are also higher for HGB fuels (**Figure 2-2**). Furthermore, HGB fuels are generally rich in K, whose level in plant (vegetal) matter is critical for the regulation of photosynthesis and the movement of nutrients and water. The K level varies for plants, being affected by geological, climatic and seasonal changes. This means that HGB fuels experience a wide range of K content. K is notorious for enhancing fireside corrosion rates [54] and, as such, different HGB fuels may have a wide range of fireside corrosion responses.

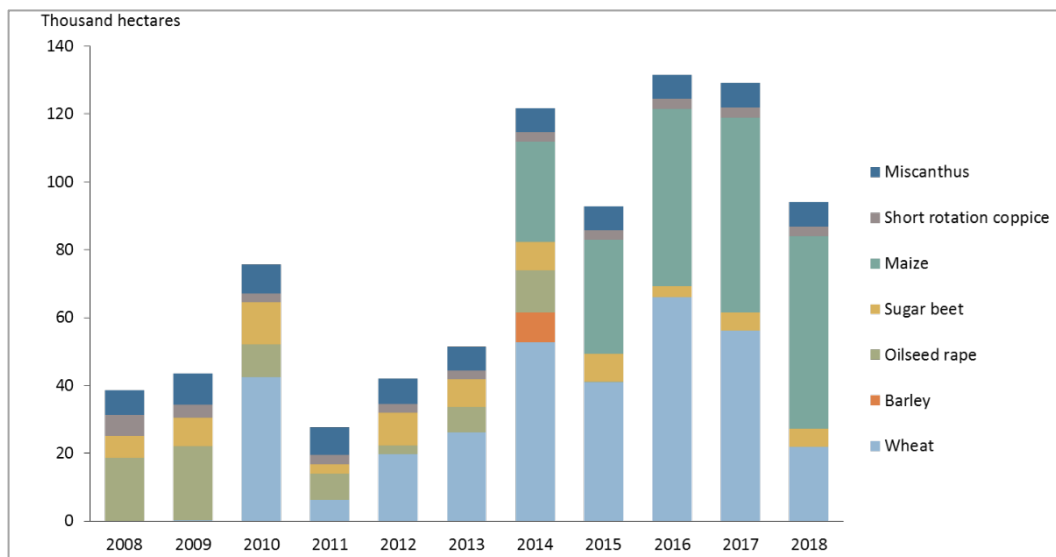


Figure 2-3: Overview of energy crop land area used in the UK over time [55]

In 2018, approximately 94,000 hectares of land was dedicated to energy crop cultivation in the UK (**Figure 2-3**), representing 1.6% of its arable land [55]. A total of 29% of the energy crop land usage is for bio-liquid fuels (biodiesel, bio

ethanol for the transportation industry [56]) and the rest is used for heat and power production [55].

Though the energy crop land space appears to have dropped in 2018, the decline is attributed to the bioethanol production fraction from wheat [55]. Popular combustion grasses (e.g. miscanthus) and straws (e.g. rapeseed, wheat, barley and canary straws) remain in use as combustion biofuels [54], [56] now and for the foreseeable future [55].

2.2.3.3 Agricultural and plant residues (APR)

The definition for 'agricultural plants and residues' can encompass a wide range of vegetal matter relating to agricultural practices. Waste generated from agricultural activities covers a large range of vegetal parts and the elemental distributions within these sections are particular to their biology. Furthermore, the cultivation process, geographical and climate conditions will influence the distribution of elements (the last two conditions are not particular to APR alone) [54]. These vegetal wastes include, but are not limited to: shells, husks, pruning and post-harvest residues. Such fuels show a wide range of operational behaviours and are possibly the most difficult to classify. Operational challenges are also more dramatic than are experienced with wood combustion [57]. However these fuels are locally available and, being wastes, they are relatively cheap which has economic benefits [58], [59].

In Crete, 2.7 million tonnes of olive pruning are generated annually, some of which provides electricity for homes via power plant combustion operations. Yet the majority of it is disposed in land fill/incinerated, leaving room for growth in heat and power production from APR fuel sources. In total, there is potential for these fuels to meet up to 27% of the country's electricity demand. Also, energy recovery from just 35% of Crete's crop disposed residues may meet their CO₂ emissions target [58], [59] by replacing the need for fossil fuels in power production, where the APR fuels are utilised.

Another example, in Turkey, is of approximately 3.2 million tonnes of fuels from a variety of tree pruning activities, sunflower shells, grape stalks, peels and tomato plant residues which are combusted annually for electricity generation [60]. However, the operational challenges encountered when utilizing these fuels in combustion plants require them to be co-fired with wood [60].

An evaluation of the fireside behaviour of APR fuels is required to improve their combustion performance and manage ash deposition rates.

2.2.3.4 Industrial food waste (IFW)

Caton et al. [29] explained that the moisture content of food waste is a major challenge to current technologies when IFW is employed as a combustion fuel; nonetheless it is possible to tackle this issue using systems that can direct exhaust heat to dry fresh food. Energy from waste (EfW) schemes indicate that heat and electricity generation via food waste combustion means have not been ruled out [61], though the fuel is currently utilised more in the production of biofuels and farming activities [62]. In the UK, in 2017, up to 7.3 million tonnes of food, amounting to £1.5 billion, was discarded [19], leaving room for exploring its feasibility as a combustion fuel.

2.2.3.5 Municipal solid waste (MSW)

MSW is waste disposed of, for example, at the municipal waste disposal sites, and includes, industrial, residential, construction and demolition wastes. In 2015, 14 TWh of electricity was generated from the combustion of 29 million tonnes of MSW fuels in the USA [64]. It is estimated that the UK generated MSW can potentially meet the electricity demand of over 15,000 homes daily, through combustion plant operations however, this practise has not gained popularity [65].

Burning of mixed municipal wastes in European EfW schemes exposes its widely varying properties and relatively large non-biomass proportions, for example where plastics and metals are mixed with waste streams [66]. The biomass types also vary and thus MSW remains a challenge to qualify.

Moora et al. [66], attempted to determine the average biomass fraction of MSW in Estonia, using a year-long manual sorting approach. The result was an estimated 52% biomass fraction of the waste stream was biomass. It was, however, concluded that a more standardised method is required for properly assessing both the MSW biomass fraction and the composition of the biomass fraction.

2.2.3.6 Animal manure & sewage (AM&S)

The availability of manure for its employment in energy production varies from one country/union to another. Under the Nitrate Directive for nitrate sensitive regions, there is a 170 kg N/Ha nitrate disposal restriction in EU, whereby a charge is incurred for exceeding this limit [67]. In this instance, manure is more easily sourced for energy generation but it becomes highly competitive where manure is scarce, for example, where manure shares its use in farming activities and in the production of biogas [67].

Sewage sludge finds its use in biomass gasifiers (syngas production) and, following recent interest in drying and palletisation of sewage sludge, this fuel can also be used in other renewable energy technologies such as bio-organic catalyst plants and biomethane production [2]. The use of sewage in biomass power plants has been shown to be problematic, requiring high maintenance to manage their high ash contents. Furthermore, preparation requirements are cumbersome and expensive due to their high moisture content [58], generally decreasing the desirability of this fuel type for heat and power production.

2.2.4 Biomass power plant applications

Several biomass/waste plant projects have, in recent years, been utilizing fuels from various categories [41], [48], [49]; to reduce CO₂ emissions from energy production. Reports from these plants emphasise that biomass/waste combustion is problematic because there are so many sources and thus a huge

variation in elemental composition which influences combustion release chemistries [68], [69].

The shift from coal to biomass/waste firing means a change in quantities of key elements, in particular S, Cl Na and K, which play significant roles in fireside corrosion [28], [38], [68], [70] (**Section 2.5**). The increased fluxes released in combustion and the nature of the combustion compounds formed increase fireside corrosion concerns. These factors also vary across biomass fuel types [69], [71], [72]. Biomass combustion plants thus operate for shorter durations compared to coal plants, and require longer downtimes for maintenance activities [20]. Furthermore, lower melting point deposits are encountered for biomass combustion than for coal. As such, HX temperatures are maintained at a lower level (~100-200°C lower) than those for coal power plants to reduce melting of deposits [38], [73]. This practice lowers the power production efficiency [24].

The mature technology of co-firing, which involves the joint combustion of coal and biomass fuels, is practiced worldwide. Plant design is a major factor to consider when optimizing the co-firing ratio. Cofiring has been successfully explored in most coal combustion plant types such as grate boilers, fluidised and fixed bed combustors, and pulverised fuel (PF) combustors (presented in **Figure 2-4**). Biomass fuels are mainly combusted in grate fired plants (also known as stokers) and fluidised bed (FB) plants (which can be circulating fluidised bed (CFB) or bubbling fluidised bed (BFB) boilers) chiefly for the generation of electricity, but also for heat energy production. In Poland there have been no less than eight conversions from pulverised fuel (PF) boilers into BFB boilers to allow for the combustion of 100% biomass [74], [75].

Grate plants (**Figure 2-4**) were created for low ash combustion fuels such as coals but also found to adapt well to fuels of high ash contents as found with biomass [66]. Also the coarser particles occurring for biomasses can be burned in stokers which can handle particle sizes >10 mm [13]. An upper grate receives fed in fuel which allows the fuel to dry to an extent before finally reaching the lower end of the combustion zone where it is burned. As the fuel travels along

the grate system, finer particles are burnt off and hoppers carry ash out of the combustion zone [40].

An advantage of FB boilers is the reduced amount of fuel preparation required [13]. FB combustion plants burn blown up fuel suspensions [40]. In BFBs, granular materials are suspended, creating a uniform mixture with the fuel particles, giving the effect of a fluid and aiding good thermal transfer to the HX tubes [40]. Low quality type fuels can be used in BFBs as they can handle larger volatile contents by operating with excess air [13].

For CFB plants, the fluidizing granular materials are separated from the flue gas (unlike BFB plants). These particles are directed out of the furnace by the combustion gases in a cyclone and then back to the lower end of the furnace. Inorganic ash is collected by cyclones into bottom ash hoppers, and fly ashes may also be collected by cyclones or other filtration techniques from along the flue gas stream [40]. Fluidised bed boilers may thus result in lower amounts of deposit formation on HXs. However, high alkali and chloride content in fuels can still cause highly corrosive environments.

The findings from co-firing operations have been useful for further understanding the complexities that arise from 100% biomass combustion. FB can be advantageous for biomass combustion due to their ability to cope with a wide range of fuel types. PF boilers, however, can reach greater biomass fractions with least modification to the existing coal fired plant [41], [75].

There are many types of biomasses (including biomass waste) combustion power plants world-wide, producing electrical and heat energy at a range of capacities. Fuel sourcing ranges from imports to localised supplies. Larger plants tend to employ the use of steadily supplied and easier managed fuels such as wood which are typically from distant sources. Smaller plants are, however, able to explore the use of a wider range of fuels and thus are not always challenged with the need to import from distant countries. The following subsections give examples of large and smaller plants (based on energy output), utilising the range of biomass and waste fuels introduced in **Section 2.2.3**.

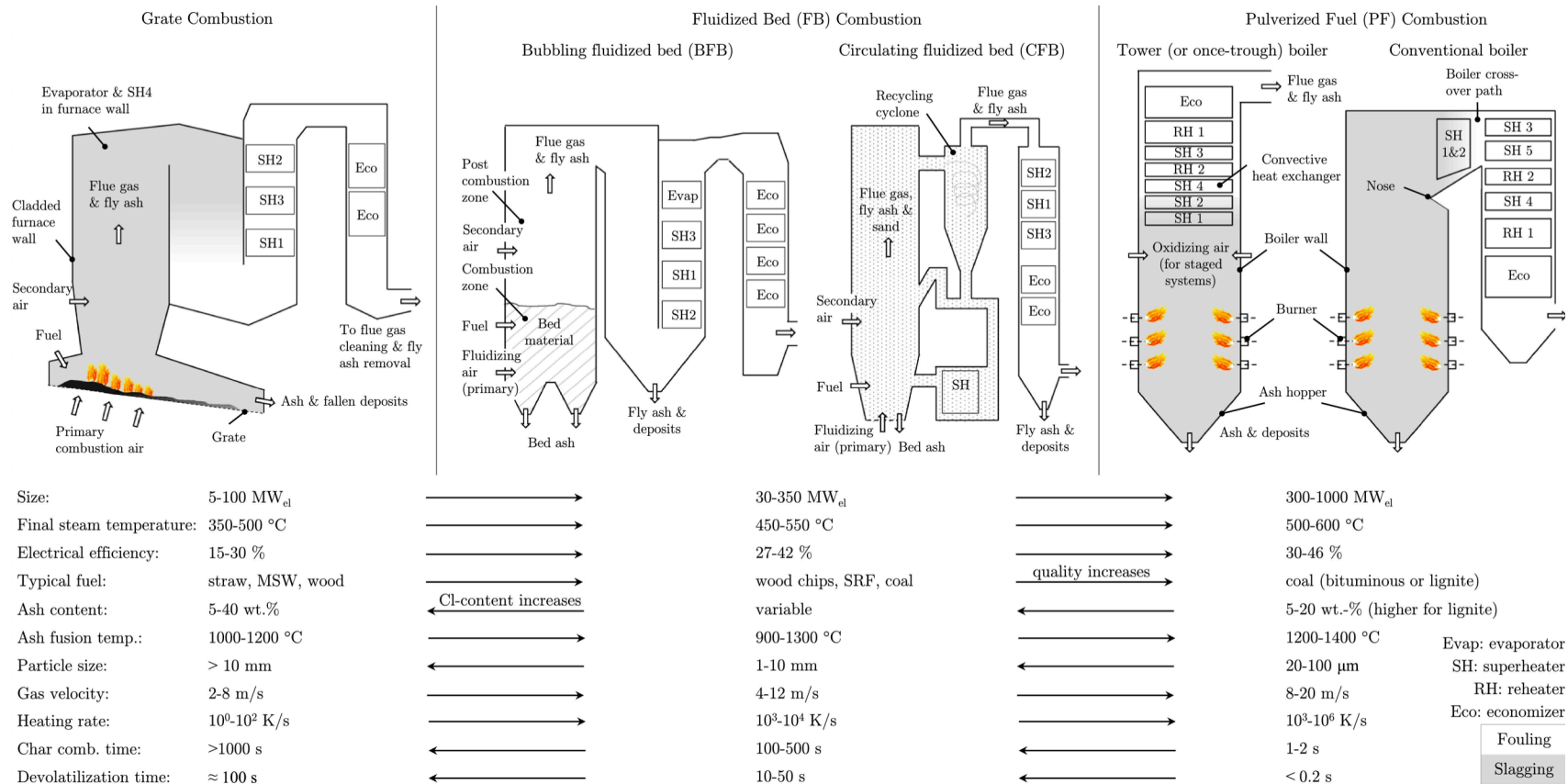


Figure 2-4: Solid fuel combustion systems showing HX positioning and highlighting areas of slagging (shaded) and fouling concern (no shade) [13]

2.2.4.1 Large scale biomass plants (global) case studies

- Drax power station in the UK, previously a coal-fired plant, now produces electricity from biomass combustion in three of its power generators. These generators have a total capacity of just under 2 GWe (total combination), using wood wastes such as sawmill and agricultural low grade woody residues, mainly imported from the USA. A recent, 2019, publication claims that Drax provides 15% of UK's renewable energy supply [76], [77].
- Avedøre Power Station in Denmark began producing combined heat and power (CHP) from coal combustion in 1990. From 2002, the power station was transformed to 100% wood pellet combustion, producing 648 MWh electricity and 856 MWh heat from two units [78].
- In the west of Finland, Alholmens Kraft Generator co-fires wood-based fuels and peat, operating at a capacity of 265 MWe. It provides energy to pulp, paper and timber manufacturing plants, and the local community. The Vaskiluodon Voima Oy gasification biomass plant, also in Finland, uses a range of biomass fuels and has a maximum capacity of 140 MWe [76].
- In Canada, the 200 MWe Atikokan Generating Station was modified from a coal-fired design to use wood pellets. It is the largest 100% biomass plant in North America [79].
- New Hope Power Partnership plant in Florida, USA, uses sugar cane fibre and urban waste wood, supplying 140 MW to 60,000 homes and a neighbouring sugar cane plant [76].
- Bilfinger Rodenhuize Plant in Ghent, Belgium, has operated as a fully converted biomass plant since 2010, with a capacity of 180 MW generated from the combustion of forest wood [80].
- Uniper Maasvlakte 3 is a co-firing (coal and wood) plant in Rotterdam, Netherlands that runs at 1,070 MWe. There are plans for its full conversion to 100% biomass combustion [81], [82].

2.2.4.2 Medium/small scale biomass plants (global) case studies

- E.ON's Stevens Croft BFB 44 MWe capacity plant in the UK utilizes locally sourced biomass fuels comprising of virgin and waste wood [83].
- Snetterton in the UK, with a capacity of 44 MWe, primarily burns cereal straw supplemented by miscanthus, oil seed rape and woodchips supplied by local farmers [84].
- The Briggs project in Lincolnshire, UK, generates 40 MWe and sources 250,000 tonnes of straw locally [85].
- The 38.5 MW Sleaford biomass power plant in the UK also utilises locally sourced straw [2].
- The 40 MWe design capacity, travelling grate stoker, Ridge Generating Station in the USA, combines the use of mainly urban wood wastes and tyres as fuel [20].
- The Eccleshall biomass power plant, UK, powers over 2,000 homes, producing an output capacity of 2.6 MWe chiefly from the combustion of locally sourced miscanthus [86].

2.2.5 Operational challenges encountered with biomass/waste combustion

This section briefly summarises **Section 2.2** and highlights the challenges encountered for biomass/waste combustion.

Although coal slagging and fouling were worse when compared to wood combustion at the Bay Front Station, USA, it was realised that co-firing coal and biomass created more severe ash issues than were encountered from the combustion of separate streams [20]. This was thought to be due to the combined effect of alkali from the wood and sulphur from the coal [20]. For this reason, the facility ended the co-firing of coal and wood [20]. Wood feed rates were then required at approximately twice that of coal (wt.%) to achieve comparable energy outputs [20].

The BFB of NRG Energy Inc. in Minnesota, USA, has burned over 35 types of wood, agricultural wastes (almond, vineyard pruning, corn and cotton stalks), forest wastes and HGB fuels (straws) in 100% biomass mixes (i.e., no coal). Their experience was that the BFB could handle some agricultural residues, although not all types. The most difficult of the fuels (identified to be straws and weeds) were combined at no more than 20% mass into the total mix. The less problematic agricultural residues, which burned successfully (which was not explained in the report, but found to refer to pits, shells, pomace, and stalks), were kept in the range of 20% to 50% mass of the total fuel mix [20]. Maintenance operations and outages were, however, required on a biweekly basis to clean/change deposit affected boiler tubes.

Due to the wide ranges of biomass classifications (both clean and waste), varying thermochemical properties of ash deposits on HX surfaces are encountered for different fuel mixes [20]. The thermochemical properties of the deposits on the metal surfaces was reported [17] to influence their corrosion mechanisms and damage rates.

In addition to the composition of the deposit, it is important when comparing biomass/waste performances against coal, to recognise that larger quantities of fuels from the former group are required to produce equivalent energy outputs. For example the gross energy value for UK coal is 32.7 MJ/kg while that of dried olive residue is 18.3 MJ/kg [24]. The employment of larger biomass/waste quantities increases the levels released during firing of undesired chemical species, relative to coal firing at matched energy outputs. Though much has been learnt from coal combustion, especially from co-firing technologies, increased maintenance costs and downtimes associated with biomass/waste firing leads to:

- i. The desire for improved HX material systems (alloys and coatings) that can cope with the degradation mechanisms encountered in the deleterious atmospheres.
- ii. More requirement for the studies of chemical release types of biomass/waste firing.

- iii. Further investigations of deposit formation on HX walls.
- iv. Furthering the understanding of corrosion mechanisms of key components.

2.3 Investigation of the combustion properties of fuels

Physical and chemical studies have investigated solid fuel combustion behaviour [87]. Ash and gas release information make up a fuel's unique fundamental code that will directly influence the problems related to its combustion such as slagging, fouling and fireside corrosion [46], [47], [88]. To optimize plant conditions and material technology against fireside corrosion, it is key to assess the post-combustion products formed [68], [69]. This section discusses fuel combustion characteristics and their composition properties.

2.3.1 Fuel combustion properties

The assessment of a fuel's initial water content, fixed carbon volatile matter, and ash content is useful for determining its combustion properties. These parameters make up the proximate analysis of such fuels [69]. The ash content is indicative of the inorganic fraction of the fuel which determines melt profiles at prevailing temperatures. The determination and characterization of the constituents of combustion products is an essential step for investigating the fuel combustion behaviour. For example, the molar distribution of inorganic fuel contents (Si, K and Na amongst others, including trace elements [69]) influence the composition and the type of the flue gas compounds formed, as well as the melting point of the ash.

The characterisation of fuel combustion properties can also be expressed by the ultimate analysis technique; commonly used for evaluating coals' and biomasses' compositions. The fraction of major elements, C, H, N, O & S (and sometimes Cl; used mostly in the case of biomass [89]) are determined using specialized analysers. The calorific value of the solid fuels (measured as 'high heating value' and 'low heating value' [25]) rise with increasing C and H contents and decrease with increasing O content [89]. Simplified by the reference, N and S contents are used to assess the potential releases of nitrous and sulphurous pollutants while Cl is indicative of the corrosivity of the fuel [90].

As an example, the ultimate analysis and proximate analysis compositions of peat (partially decayed organic matter, usually vegetation), bark and straw, analysed by Theis et al. [91], are compared in **Figure 2-5**. Peat shows lower volatile and O contents and higher C contents, characteristic of its higher high heating value.

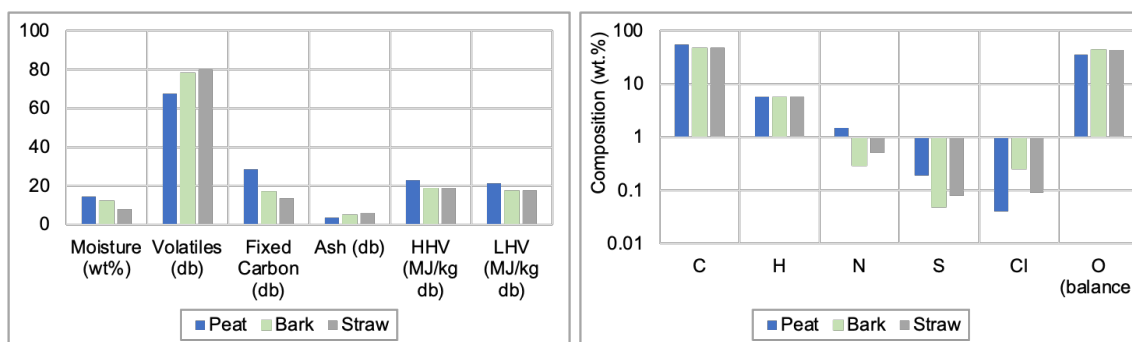


Figure 2-5: Proximate (left) and ultimate analyses (right) of fuels examined by Theis et al. [91]. db (dry basis); HHV (high heating value); LHV (low heating value)

The chemical compositions of non-fossil fuels vary significantly [28], [92]. Similar biomasses may show geographically and seasonally variable compositions [22], [93]. Furthermore, plant/tree parts (residues, branches, shells, husks, etc.) show large variations in moisture content as well as elemental values. A fuel's elemental data are thus commonly presented on a dry basis to lessen compositional variations with similar fuels [14], [28]. Research investigating fuel compositions have also found it useful to apply statistical ranges and averages [54], [94].

2.3.2 Elemental distribution in biomass/waste and ash

A fuel's S/Cl molar ratio has proved to be useful for predicting combustion release species. Higher molar S/Cl ratios have been seen to correlate with lower corrosion rates following the combustion of specific fuels [68], [72], [95], [96]. It has been proposed that S hinders the chloride deposition mechanism occurring

from gas phase, where alkali metals are sulphated to yield high melting point condensates [40], [97] relative to HX temperatures. This is further described in **Section 2.5.3**. In **Figure 2-6**, some fuel S/Cl molar ratios are compared. Biomass fuels typically have lower S/Cl molar ratios than coal. As such, co-firing biomasses and coal has been useful for increasing the S content of the combined fuels while keeping Cl content low.

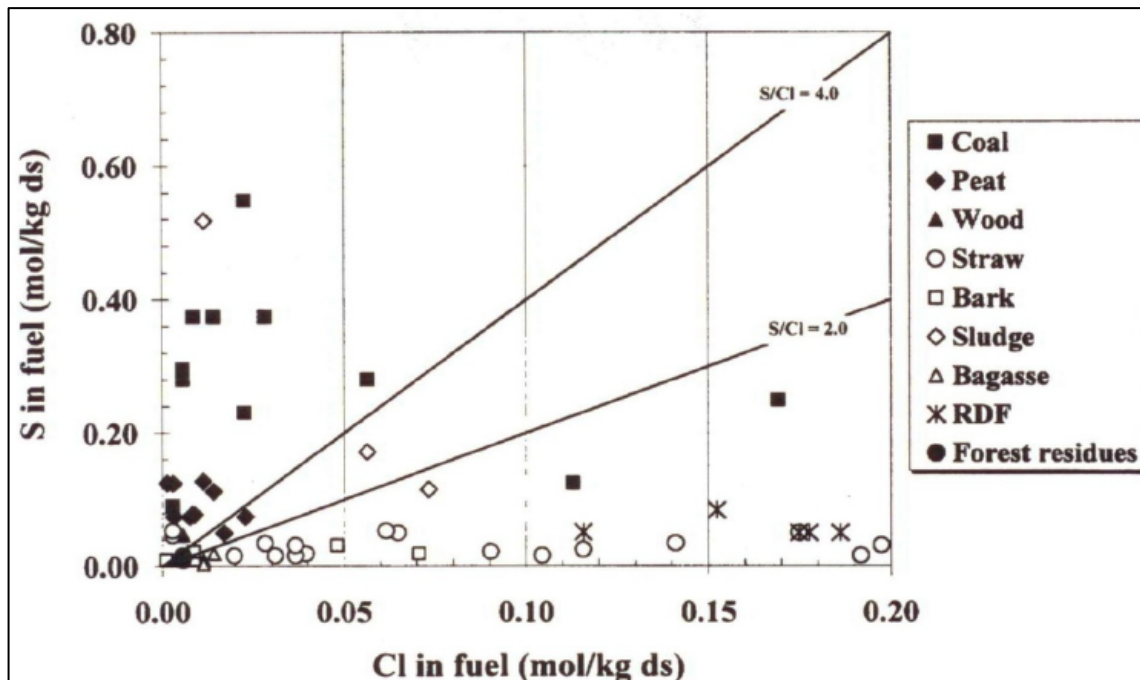


Figure 2-6: Dried combustion plant fuels (biomass, waste and coal) sulphur/chlorine molar ratios [40]. RDF (refuse derived fuels)

The use of S/Cl ratios in biomass fuels for the comparison of their post-combustion fireside corrosivity is, however, not sufficient due to other, varying, elements influencing the ash behaviours. The formation of low melting point inorganic fly ash components, which may be problematic to alloys, can however be predicted from the elemental analysis of fuel and ash. Such elements influence the transport of other established corrosion influencing elements [98]. For example, high Si and P values in straws influence the activity of K (in particular, its distribution between high and low melting point compounds) [57], while K may

determine the fate of Cl in gas phases (leading to the formation of HCl, which is easily lost to the environment, or KCl which may condense on metal surface) [47], [95].

The ash compositions of over 35 types of biomass/waste and fossil fuels were compared by Zajac et al. [93]. The ash compositions of biomass were confirmed to be influenced by geographical location and harvesting season. As such, elemental variations within similar fuels, and thus their ashes, occur. The virgin wood group showed the least K content in ash (amongst the non-fossil fuels). For example, the mean K levels in fuels within the virgin wood group were approximately 37,000 ppm (willow), 39,000 ppm (acacia), and 53,000 ppm (oak), with highest mean value being 116,000 ppm for pine.

Agricultural residues showed the highest mean K values in ash: ~193,000 ppm (cherry pits), ~185,000 ppm (walnut shell) and ~184,000 ppm (hazelnut shell). Compositional and ash quantity variations observed for the fuels were not limited to K only. Elemental distributions were observed for all elements listed in **Table 2-1** and for all fuel groups. Zajac et al [93] ranked the inorganic elements' mean concentrations for the 35 fuels analysed. Si, which also forms a major constituent of biomass/waste fuel ash [13], was however not included in their ranking.

Table 2-1: Inorganic ash content ranking by Zajac et al [93] for various biomasses/wastes

	Fuel	Elements (content ranking)
Wood and wood waste	Birch wood	Ca>K>P>Mn>Fe>S>Zn>Cu>Pb>Cr>Ni>As
	Pine wood	Ca>K>P>Mn>S>Fe>Cu>Zn>Cr>Ni>Pb>As
	Oak wood	Ca>K>P>Mn>Fe>S>Cu>Zn>Ni>Cr>Pb>As
	Hornbeam wood	Ca>K>Mn>P>Fe>S>Ni>Zn>Cu>Pb>Cr>As
	Ash wood	Ca>K>P>Mn>Fe>S>Zn>Cu>Cr>Ni>Pb>As
	Wood residue —Forest	Ca>K>P>Mn>Fe>S>Cu>Zn>Ni>Cr>Pb>As
	Wood residue—Municipal	Ca>K>P>S>Fe>Mn>Zn>Cu>Ni>Cr>Pb>As

	Poplar wood	Ca>K>P>S>Fe>Mn>Cu>Zn>Ni>Cr>Pb>As
	Willow	Ca>K>S>P>Fe>Mn>Zn>Cu>Cr>Ni>Pb>As
	Acacia wood	Ca>K>Fe>P>S>Mn>Zn>Cu>Ni>Cr>Pb>As
Energy crops (HGB)	Virginia mallow	Ca>K>P>S>Fe>Mn>Zn>Ni>Cu>Cr>Pb>As
	Jerusalem artichoke	Ca>K>P>S>Fe>Zn>Mn>Cu>Cr>Ni>Pb>As
	Multiflorous rose	Ca>K>P>S>Fe>Mn>Zn>Ni>Cu>Cr>Pb>As
	<i>Miscanthus giganteus</i>	K>Ca>P>S>Fe>Mn>Zn>Cu>Cr>Ni>Pb>As
	<i>Miscanthus sacchariflorus</i>	K>Ca>P>Fe>S>Mn>Zn>Cu>Cr>Ni>Pb>As
	Prairie cordgrass	Ca>K>P>Fe>S>Mn>Zn>Cu>Cr>Ni>Pb>As
	Common reed	Ca>K>P>Fe>Mn>S>Zn>Cr>Cu>Ni>Pb>As
	Switchgrass	K>Ca>P>Fe>S>Mn>Zn>Cu>Cr>Ni>Pb>As
HGB/ APR	Wheat straw	K>Ca>P>S>Fe>Mn>Zn>Cr>Cu>Ni>Pb>As
	Triticale straw	K>Ca>P>S>Fe>Mn>Zn>Cr>Cu>Ni>Pb>As
	Oat bark	K>Ca>P>S>Fe>Mn>Zn>Cu>Cr>Ni>Pb>As
	Barley straw	K>Ca>P>S>Fe>Zn>Mn>Cu>Cr>Ni>Pb>As
	Buckwheat straw	K>Ca>P>S>Fe>Mn>Zn>Cr>Cu>Ni>Pb>As
	Hay	K>Ca>P>S>Fe>Mn>Zn>Cr>Cu>Ni>Pb>As
Forest residue	Beech bark	Ca>K>P>Fe>S>Mn>Cu>Ni>Zn>Cr>Pb>As
	Oat bark	Ca>K>S>P>Fe>Mn>Cu>Zn>Ni>Cr>Pb>As
	Hornbeam bark	Ca>K>S>P>Fe>Mn>Zn>Ni>Cu>Cr>Pb>As
	Ash bark	Ca>K>P>S>Fe>Mn>Zn>Ni>Cu>Cr>Pb>As
	Acacia bark	Ca>K>P>S>Fe>Mn>Zn>Ni>Cu>Cr>Pb>As
IFW	Cherry pits	K>Ca>S>P>Fe>Zn>Cu>Mn>Cr>Ni>Pb>As
	Sunflower husk	Ca>K>P>S>Fe>Mn>Zn>Cu>Ni>Cr>Pb>As
	Rape pods	Ca>K>P>S>Fe>Mn>Zn>Cu>Ni>Cr>Pb>As
	Apple pomace	Ca>K>P>S>Fe>Cu>Zn>Mn>Ni>Pb>Cr>As
	Hazelnut shell	K>Ca>P>S>Fe>Cu>Zn>Mn>Ni>Cr>Pb>As
	Walnut shell	K>Ca>P>S>Fe>Cu>Mn>Zn>Cr>Ni>Pb>As

Ca, K and P have the highest concentrations for all categories of biomass/waste fuels, however the inorganic ash content of woody fuels and vegetation fuels (HGB and APR) are mostly led by Ca and K respectively. Some

energy crops may be burnt preferentially for their higher Ca content (instead of K), as Ca forms higher temperature melting salts than K post-combustion [99].

Vassilev et al. [68] carried out an overview of 86 different biomass species elements which included Si, K, Ca, P, Al, Mg and S. Variable combustion product compositions were noted, with decreasing ash yields in this order:

HGB, APR > woody biomass (virgin and waste)

The reviewed fuel data also showed that woods' inorganic contents were dominated by Ca, S and Mg, but that these were present in relatively low concentrations compared to the other biomass/waste fuel types. The APR and HGB fuel groups showed an abundance of Cl, K, Na and especially P and Si contents above other inorganic components.

K-rich fuels are still of major concern due to the cation's role in fireside corrosion [99]. Vassilev et al. [68], in their extended review of biomass ash characteristics, also noted K and Cl have high mobilities in biomass fuels, favouring the condensation of KCl and K₂SO₄ from gas and on HXs [47], [100]. Straw and grasses were characterised with relatively high alkali metal and Cl containing components, compared with wood [68].

The aforementioned elements are not the only components of concern regarding fireside corrosion issues. Trace elements such as Mn, Zn, Ni, Cr, Cu, Pb and As have been said to influence fireside corrosion [14]. Their compositions in specific fuels can only be defined on a case-by-case basis, as these elements tend to be associated with wastes [20].

2.4 Heat exchanger deposition

The nature of deposits on, and the ambient conditions of, HX surfaces influences fireside corrosion damage. Gas temperature influences the thermodynamically stable combustion product phases present in HXs' vicinities [9], where these compounds may either remain in the gas phase or condense [101]. While a significant portion of HX deposits are high melting point compounds [102], condensates which are molten at HX metal surface temperatures ranges are of primary concern for fireside corrosion [24] and are further discussed in **Section 2.5**. This section discusses the processes involved in depositing the combustion products on heat transfer surfaces.

2.4.1 Formation of fly ash

During combustion, inorganic fuel components undergo complex physiochemical transitions. In the initial stages, ash (as solid/liquid/gas) and the solid phase components may be intermediate species undergoing chemical transformations [12]. The inorganic content of biomass fuels can be categorised into:

- i. **Dissolved salts:** e.g. K, Na, Mg & Ca as sulphates, chlorides and phosphates [9], [12].
- ii. **Organically bound compounds which form ash:** compounds including K, Na, Mg, Fe, Mg & Al, and their covalent bonding non-metals such as Cl, S & P [102], [12].
- iii. **Extraneous mineral particles:** which may constitute up to 90 wt.% of the mineral matter. They become separated from organic matter during fuel preparation; are typically 4-40 μm in particle size [9]; and can be resistant to melting at HX temperatures.
- iv. **Inherent minerals:** represents up to 6 wt.% of the organic particle. They are metals bonded to the fuel matrix. Also, resistant to melting, they are mostly associated with slagging at the radiant section of the furnace [9], [102].

Bottom and fly ashes are formed during combustion. While bottom ash may remain within the combustion zone, fly ash tends to be carried with the flue gas [13]. Fly ash formation depends on various complex mechanisms which include the coalescence of minerals and fragmentation of particles as shown in **Figure 2-7**. [9], [13], [103].

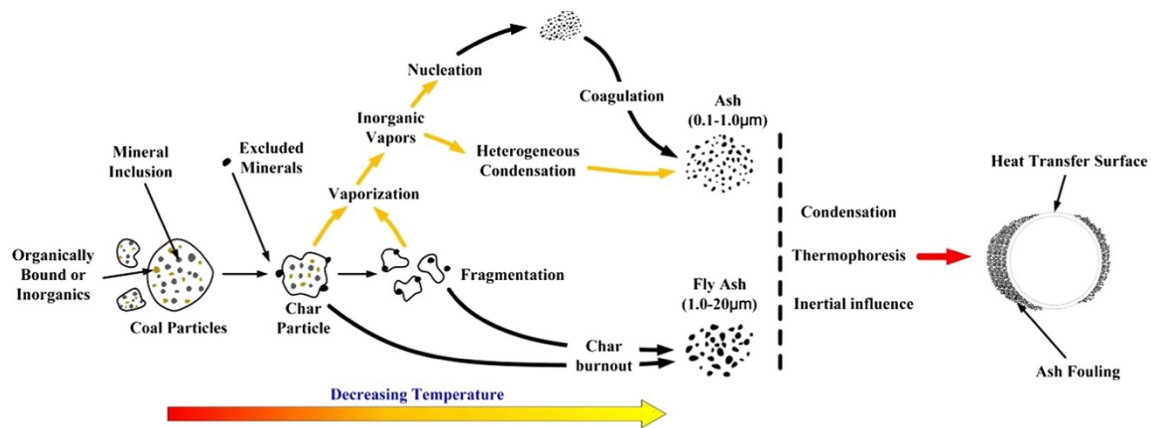


Figure 2-7: Transition of a pulverised fuel combustion particle transition to ash [12]

The quantities of inorganic vapours (composed of, for example, alkali and alkaline earth metals, P, S and Cl compounds) released are dependent on the fuel chemistry and ambient temperature conditions. Organically bound elements and dissolved salts may also vaporise to release inorganic vapours. The association of the inorganic components, size distributions and compositions of particulates are dependent on the fuel's physical and chemical characteristics, as well as the combustion conditions.

The type and conditions of intermediate (chemically transitioning) species formed influence bottom and fly ash partitioning, therefore dictating slagging, fouling, corrosion and emission behaviours during combustion [12]. The slagging mechanism of combustion components is not within the scope of this thesis,

though the partitioning of fly ash is an important factor to note when considering deposition on tube surface. The HX ash deposition process can be described in stages: the formation, transportation and adhesion of fly ash particles [12].

Released inorganic vapours are of concern to fireside corrosion as the vapours may condense onto ash as particles or aerosols [12], [9]. Aerosols can be physically and/or chemically transformed to yield fly ash [13]. The resulting ash species may be transported by convective heat transfer as gas, droplets and solids to the vicinity of the HXs. Other transport mechanisms also occur [9].

Shao et al. [75] noted an increased bottom ash fraction when the lignite ratio of a lignite/peat/vine 3-fuel blend was increased from 20% to 50%. This phenomenon was attributed to the increased formation of Mg-, Al-, Ca- and Si-containing minerals with high melting points. The bottom ash was low in S and K, suggesting that both elements were not associated with the higher melting point ash components.

Wang et al. [34] conducted combustion experiments for waste wood and straw (an HGB fuel type) in an entrained-flow reactor. The authors investigated the ash behaviours, including partitioning between fine fly ash (which may directly influence HX deposit fluxes) and bottom ash [13]. An air-cooled probe with the surface temperature maintained at 550°C was set up in the flue gas path, within the tube reactor at 1000°C to 1300°C. The condensed fine fly ash (<2.5 µm) collected on the probe during wheat straw firing was rich in S, K, Cl and P species, suggesting that K-chloride, -sulphate and -phosphate play a significant role in aerosol formation during wheat straw combustion. S and Cl were depleted in the bottom ash for the wheat straw combustion. By contrast, Si, Ca and K compounds were discovered in the wheat straw bottom ash. For the waste wood, Al, Cl and Ca remained in the bottom ash for the waste wood while the fly ash fraction contained significant quantities of Na, K, Cl and S. The volatility of ash compounds was linked to their ash partitioning tendencies for both fuels as the more volatile compounds at the temperature conditions were mainly located within the fly ash segment.

Si-rich additives and fuel mixtures can allow the binding of alkali metal chloride and sulphate species in high melting point complexes [34], [35]. Wu et al. [35] investigated the ash formation effect of an Si-rich additive (spent bleach earth) added to straw firing. The fuel blend showed lower KCl condensates compared to 100% straw firing, which consisted of K, S, P and Cl species in the fine fly ash ($< 2.5 \mu\text{m}$), suggesting that the Si component of fuel influenced the K partitioning. An indirect effect of low K-species content in gas phase is the loss of Cl (for example as HCl) during combustion [35]. As such, the elemental distributions occurring within fuels influence their ash partitioning behaviours [34], [35].

2.4.2 Heat exchanger deposits

The vapour conditions of fly ash determine the build-up of sticky HX deposits [9]. These deposits produce fouling, an active restriction of heat conduction through the HX surfaces caused by deposit build-up, as well as plugging up the flue gas paths [24].

In the previous section, the formation of fly ash components has been considered. During cooling, inorganic vapours may condense from saturated flue gas, when that flue gas temperature drops below the vapour dew point [13], and deposit on HXs. Particles transported to, and impacting on, the HX walls can be retained on their surfaces [13]. Also, partially and completely rebounding solid particles may also be cemented by molten particles [13]. HX deposits thus consist of component mixtures of varying melting points. Fly ash will continue to build up on the HX surfaces and may actively participate in fireside corrosion mechanisms. **Figure 2-8** is a graphical illustration of ash deposition on tube surface [13].

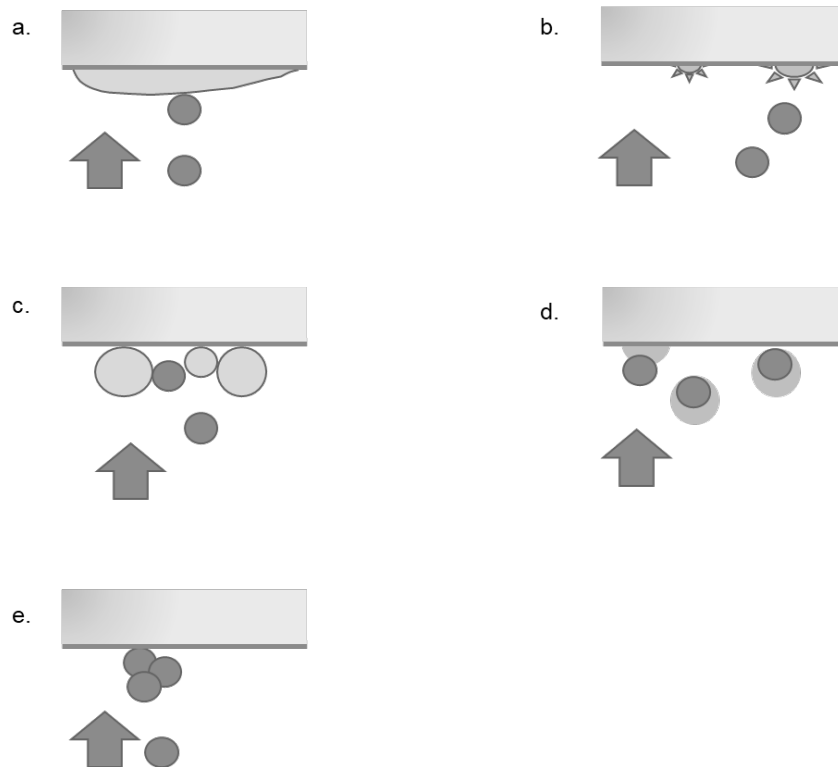


Figure 2-8: Fly ash particle interactions leading to tube deposit build-up such as solid particle sticking (a), condensation (b), trapping of particulates (c), nucleation of reacting species (d), and increased particle interaction (e). Adapted from [13]

The stages of particle interactions at the tube surface and vicinity as summarised:

- Sticking of solid particles with may occur on a molten HX deposit layer (**Figure 2-8a**). Initially, condensation creates a thin film of deposits with build-up rates depending on the sticky ash fraction of the deposit and particle as well as the velocity of the traveling particle. This has been observed in slag build-up. Agglomeration occurring between combustion particles may also rearrange their structure and become sticky rather than rebound from the tube surface [13].
- The heterogeneous condensation of particles may occur on the tube surface or on cooler fly ash component surfaces. When physicochemical properties are conducive, chlorides, which attain supersaturation at relatively lower

temperatures than sulphates [9], can condense directly on the tube surfaces. Above an inorganic compound's dew point, reactions will occur within all phases, and between flue gas and deposit components which may alter the melting temperatures and sticky fraction of the component surface.

Kleinhans et al. [13] suggested that K_2SO_4 begins to condense from below $1200^\circ C$. As HX surfaces are cooler [24], it was inferred that the condensation of K_2SO_4 particles will mostly occur on hotter fly ash particles within the HX vicinity or possibly within HX boundary layers penetrated by the vapour, before reaching the metal surface.

- c. In the cooler economizer tube region, where most inorganic compounds are solids, fine fly ash particles can become trapped within porous deposit structures, increasing the residence time of the fly ash and HX deposits [13].
- d. Homogenous nucleation may occur whereby an entirely new product is formed from particles reacting within the flue gas. Reactions can also occur at the deposit/gas interface. Flue gas components may also become agglomerated in flue gas aerosols, such that a film of liquid coats its surface.

A typical flue gas reaction summary occurring in biomass combustion is the formation of HCl from chlorinated hydrocarbons during combustion. The presence of species easily react with K in conditions favouring the formation of KCl and, in sufficient moisture content, KOH [104].

- e. The colliding of solid particles can increase their interaction time [9]. The deformation of joined sintering solid particles increases their contact area. Elastic deformation of the solid particle may also occur on the tube surface. The possibility of a surface interaction between the solid/solid interface increases in such conditions [13].

The chemical behaviour of the flue gas in a tube's vicinity significantly impacts the nature and mode of the prevailing deposition mechanisms. The vapor dew point of species is an important requirement for particle deposition. Alkali metal compounds are the primary inorganic vapours condensing at HX temperatures, the nature and concentration of which depends on the fuel type [13]. The vapour pressure of the alkali metal compounds is affected by the gas phase concentration, thus the salt condensation rates are affected by their gas composition mass fractions [9].

2.4.3 Temperature effect on deposit phase mobility

The chemical compositions of HX deposits can significantly alter melt behaviours. High fireside corrosion rates in biomass/waste combustion power plants are tied to the deposit composition of the fuels and the metal surface temperature. Fireside corrosion is the metal degradation that occurs as a result of thermochemical processes occurring in the tube's vicinity; **Section 2.5** [105]. A standard approach to minimizing the corrosion risk is to lower the HX surface temperature, avoiding deposit's melting temperatures. Eutectic and minima temperatures can, however, be significantly lower than individual deposit components' melting points.

Phase diagrams can be useful for estimating the lowest melting point occurring within specified chemical compositions. For example, the eutectic temperature of the NaCl-Na₂SO₄ system, in **Figure 2-9**, shows a eutectic melting point occurring at 626°C for 47 mol.% chloride. The KCl-K₂SO₄ binary system also has a eutectic melting point temperature which is lower than the melting points of the individual components (694°C at 74 mol.% chloride) [106].

In biomass combustion, K, Na, Cl and S are typical elemental constituents of HX deposits and their mixtures exhibit lower melting temperatures. As such, **Figure 2-10** can be applicable for the projection of liquidus temperature points occurring for these deposits. The phase diagram shows melts may occur at temperatures as low as 517°C [105]. The corrosive components, however, are

more complex than can be explained by deposit cation phase systems as interactions are not limited to the deposit components only.

Metal oxide layers formed by the oxidation of alloy substrates may also interact with deposits, resulting in lower melting point mixtures, where molten components exist within HX ranges 400-600°C [107].

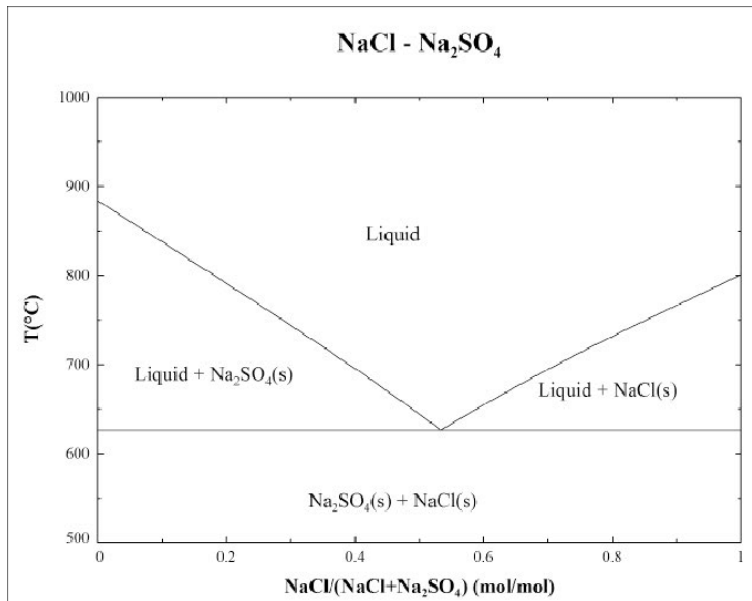


Figure 2-9: NaCl-Na₂SO₄ binary phase diagram [106]

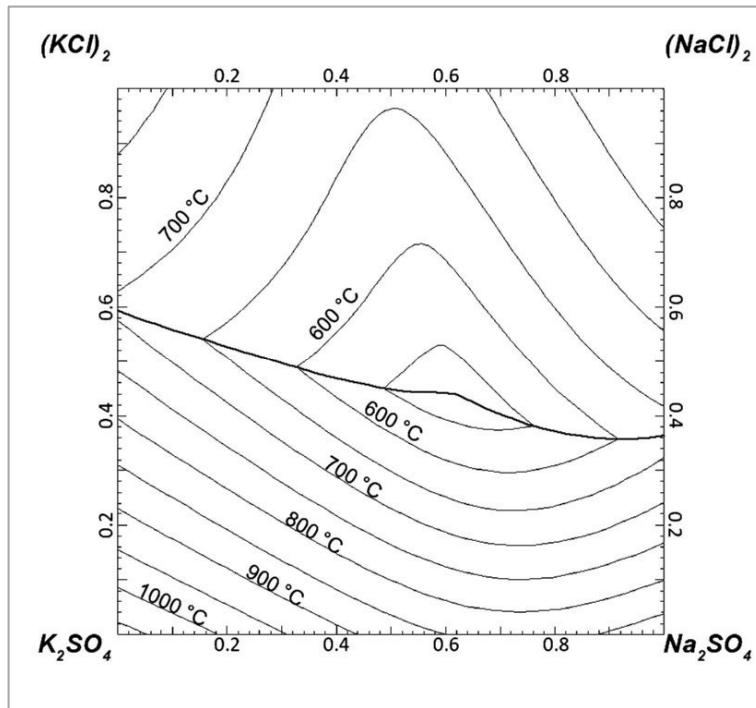


Figure 2-10: The liquidus projection diagram of the K-Na chloride and sulphate system [105]

Table 2-2 lists some eutectic melting points of alkali metals and chloride components resulting in low temperature melts. Such components are suggested to exist at various stages of fireside corrosion during on the degradation of metal surface during biomass/waste firing [106], [107]. The melting temperatures of the systems listed in **Table 2-2** make it impractical to target HX temperature conditions which are below the first (deposit species) melting point for biomass/waste firing, without operational efficiencies of power plants being significantly compromised [24], [108].

Niemi et al. [105] studied the fireside corrosion of synthetic ash-coated carbon and low alloyed steel rings inserted on a probe experiencing a temperature gradient in a hot furnace. Localised species within the ash deposit were noted, explained as the melt being able to migrate through pores and solidify at lower temperature locations. The melt compositions influenced the migration of these liquids. The migration of liquids led to the formation of eutectic melts as well as entirely new products.

Table 2-2: Melting temperatures for eutectic mixtures and compounds relating to low melting point alkalis and chloride melts in biomass/waste combustion

System	Eutectic/melting temperature (°C)	Alkali component at eutectic point (%)	Reference
KCl	772	n/a	[107]
FeCl ₂	677	n/a	[107]
FeCl ₃	300	n/a	[107]
KCl - FeCl ₂	340-393	45.8-91.8	[106], [107]
KCl - FeCl ₃	200-300	24-47	[106]
CrCl ₂	845	n/a	[107]
CrCl ₃	947	n/a	[107]
KCl - CrCl ₂	462-475	36-70	[107]
KCl - CrCl ₃	700-795	54-89	[107]
KCl - K ₂ CrO ₄	650	68.4	[107]
K ₂ CrO ₄	980	n/a	[107]
KCl - K ₂ Cr ₂ O ₇	366-368	25-27.5	[107]
K ₂ Cr ₂ O ₇	398	n/a	[107]
NaCl	801	n/a	[107]
NaCl - FeCl ₂	370	~56	[106]
NaCl - FeCl ₃	150	45.3	[106]
NaCl - CrCl ₂	437	~54	[107]
NaCl - CrCl ₃	544-593	68-95	[107]
NaCl - Na ₂ CrO ₄	557	-	[107]
Na ₂ CrO ₄	792	n/a	[107]
NaCl - Na ₂ Cr ₂ O ₇	356.7	30	[107]
Na ₂ Cr ₂ O ₇	592	n/a	[107]

Deposited species (on HXs) that reach their eutectic point temperatures are able to migrate through the deposit layers [40]. When the gas phase surrounding a deposit component such as KCl becomes saturated, the presence of a temperature gradient can induce a concentration gradient such that gas diffusion occurs to the less concentrated and cooler regions to balance this [17].

Condensation can thus reoccur over a distance such as across: deposit scale thickness, corrosion oxide layers, grain boundary features, as well as along the tube surface.

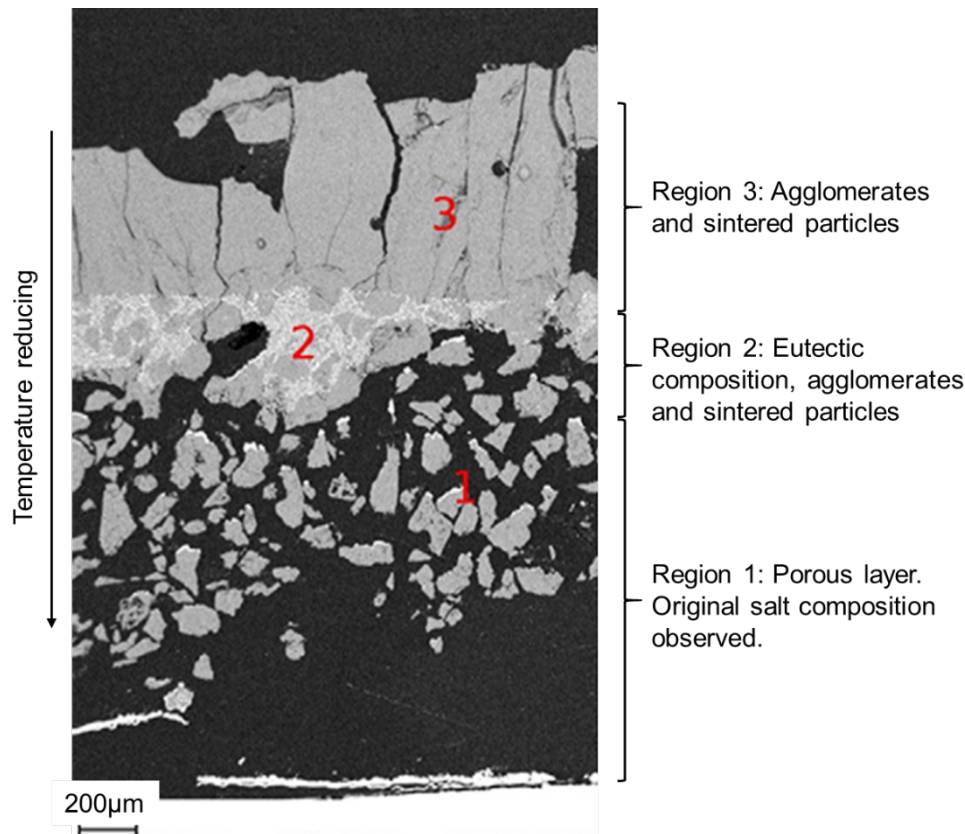


Figure 2-11: Three distinct morphology features of a salt deposit aged in a temperature gradient condition using an air cooled probe [17]

Lindberg et al. [17] demonstrated the time dependence of KCl transportation within deposit layers. The morphology studies were carried out using aged (heat exposed) salt coats of 5 mm thickness applied on the surface of an air-cooled probe sample fitting. The setup was placed in a furnace and the probe was maintained at 400-500°C, lower than the furnace wall temperature of 980°C. A temperature gradient was thus induced between the furnace wall and the probe. The atmosphere (composition not specified) just above the probe was ≈800°C. It was noted that alkali metal chlorides were evaporated and transported from the hotter outer deposit layer to the cooler metal surface deposit layer.

Three distinct features were identified by scanning electron microscopy (SEM), back scattered electron (BSE) analysis of the crossed section deposit layers as shown in **Figure 2-11**. A sintered and agglomerated region was observed in the outer deposit layer. Deposits closest to the steel surface were porous structures with particles that have sharp edges, indicating that melting had not occurred. It was suggested that the mid-deposit layer had undergone eutectic melting [17], whereas, components nearer the metal surface experienced temperature conditions lower than the eutectic melt temperature for the component mixture. The temperature gradients between flue gas and metal surface may thus influence changes in the fractions of molten deposits that are across a scale/deposit's thickness.

2.5 High temperature corrosion

High temperature corrosion occurs when temperatures are high enough to allow chemical interactions between a metallic component and chemicals in the environment, leading to the loss of metal from the bulk or surface [109]. Usually, a liquid phase is required; the deposit mentioned in **Sections 2.5.3**.

In the absence of a liquid phase, the alloy degradation is referred to as oxidation. Examples of oxidation reactions occurring in combustion environments include chlorination, oxidation, sulfidation and nitration [109]. Physiochemical reactions in high temperature combustion aid the formation of corrosive conditions which attack metal alloys. Extensive research is required to address the high temperature corrosion challenges on the fireside of HXs where high temperature conditions worsen the effect of mobile corrosive species.

Fireside corrosion of metals occurs at the combustion side of a power plant where HXs are exposed to the combustion species released from firing. Fireside corrosion is seen to be more difficult to define than the degradation observed on the steam side (internal tube surface exposed to superheated steam), chiefly due to the complexities of reactions occurring between a wider range of chemical components [34], [40]. A high yield of metal scale is particularly observed for annual crop biomass fuels with high alkali metal and chloride levels [40], [46], [88]. Major elements (Cl, S) and some minor elements are the typical focus for evaluating HX deposit compositions, in regard to corrosion. For waste fuels however, the influence of trace elements on combustion release and their role in fireside corrosion are sparingly evaluated [16], [110], [111].

Giggins et al. [112] suggested the high temperature degradation sequence follows two stages for metal attack. First is an initiation phase without severe attack, wherein a protective scale forms and corrosion of the metal surface is said to be incubating. Following this, the corrosion rate increases considerably; this is described as the propagation stage. The corrosion incubation phase for a metal corresponds with the formation and dissolution of the protective scales on the metal surface beneath the forming deposit layers. Initially, the metal surface

undergoes oxidation by the gaseous environment which could be air or steam or corrosion gases. The formation of the scale can be expressed by:



The integrity of this scale determines the deposit's ability to dissolve it and attack the underlying alloy. The scale, however, needs to be adherent, slow growing and non-porous to act as a barrier against metal attack. The thermodynamic stability of a metal oxide can be determined from the Gibbs' free energy change resulting from this reaction: if the dissociation pressure of the oxide in equilibrium with the metal is lower than the oxygen pressure at the vicinity of the metal surface, the formation of the metal oxide will be favoured. This is typically the case during fuel combustion as the excess of oxygen in the flue gas promotes oxidation (rather than reduction) reactions.

The Ellingham diagram in **Figure 2-12** expresses the standard free energies of formation of various oxides as a function of temperature, and their corresponding oxide dissociation pressures. The oxides formed with more negative Gibbs' free energies are more stable. Commonly formed oxides applicable to this research, in order of increasing stability, are:



The propagation stage of high temperature corrosion commences when the metal scales are no longer protective against corrosive deposits. In most cases, the scales have been fluxed away and the alloy below is too depleted to reform scales under the current exposure conditions. In highly corrosive environments, such as accelerated corrosion conditions created for laboratory tests (described in **Section 3.3**), the corrosion incubation stage is not observed at first sampling [37] (>200 hours exposure). Propagation involves a rapid rise in metal loss as well as morphology changes to the scale layers. Deposit components are distributed throughout the developing scale layers and can penetrate the alloy substrates, primarily driven by temperature gradients and local

chemical activities (**Section 2.4.3**) which govern their mobility. The rate of damage in propagation is thus controlled by temperature, and influenced by the chemical compositions and mobilities of corrosion species (their vapour pressures) [113]–[115].

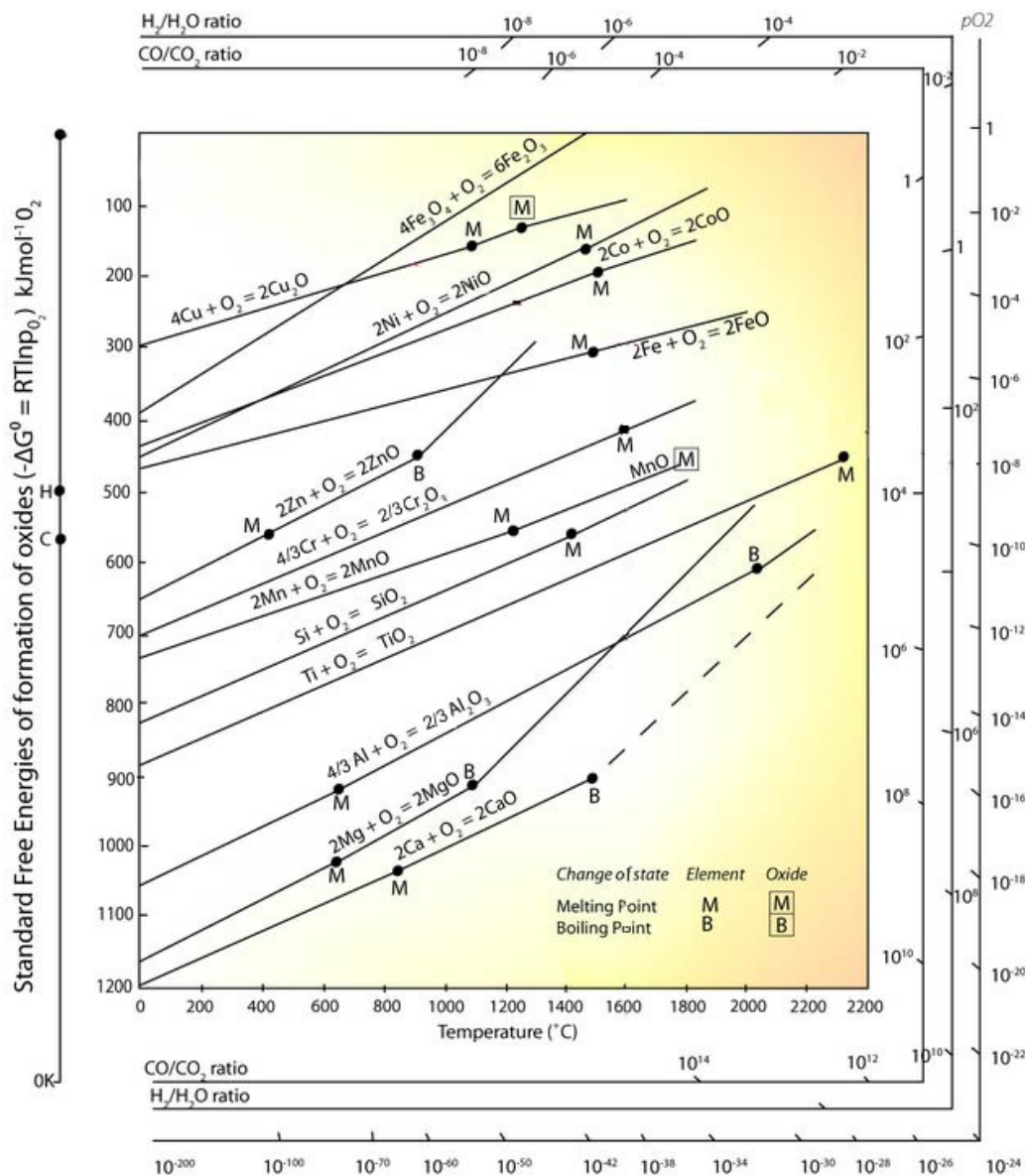


Figure 2-12 The Ellingham diagram exhibiting the standard free energy of formation of various metal oxides as a temperature function [116]

High temperature corrosion may occur where temperatures are high enough for molten deposit films to form [113]. High temperature corrosion may, however, also take place before deposits reach their individual melting points.

During deposit formation, lower melting salt complexes may be formed (**Section 2.4.3**) and localised across the metal surface. The stability of the melts are affected by the gas and also the integrity of the scale, which influences the transfer of molten deposit to the metal surface and other scale surfaces, enabling the incorporation of alloy elements (**Figure 2-11**, [17]). During biomass firing, as alkali metal sulphates and chlorides are released and deposited, corrosion occurs at temperatures lower than the melting points of the individual salts [57], [117] (see **Section 2.4.3**).

A peak in corrosion rate may also occur with increasing temperature where an initial formation, followed by a gas induced de-stabilization of a complex occurs. Hussain et al. [118] suggested that alkali-iron tri-sulphates, with a minimum melting point of 550°C, can be stabilized by SO₃. The authors concluded that the rate of metal loss increases with temperature in the presence of molten deposits under combustion exposure conditions from 600 to 650°C. Corrosion rates may, however, decrease as the deposit becomes unstable due to an increase in the gas SO₂/SO₃ balance between ~650 and 700°C in air-fired combustion plant conditions.

This demonstrates that the HX's surface temperature range is an important factor when determining the type of corrosion mechanisms occurring. For fireside corrosion to occur at the temperatures targeted for this research (<600°C, see **Section 2.5.1**), mechanisms will depend on the formation of eutectics as the pure salts, such as KCl, remain solid at these temperatures. The test temperatures employed in this research were set based on the initial review carried out in the following sub-section (**Section 2.5.1**). The formation of relatively low melting point eutectics tend to rely on the presence of alkali metals, chlorides [106], [107] and sulphates [99]. As such, the reaction mechanisms of alkali metal sulphates and chlorides are discussed in a following sub-section (**Section 2.5.3**). Also, alloys respond at different rates and mechanisms to corrosive environments [16], [102], [119]. As such, the selection of alloys employed for corrosion tests during this research is reviewed in **Section 2.5.2**.

2.5.1 Plant heat exchanger operational temperature

The design layout of a combustion plant boiler (**Figure 2-4**) influences the range of temperatures experienced by HX materials and hence the nature of deposits. It is necessary to be specific about the HX type, which determines the metal surfaces' temperature ranges.

The hottest tubes are superheaters and reheaters and these experience severe heat-related degradation due to the large flux of corrosive compounds depositing on their surfaces. Economisers and waters walls are relatively cooler and the deposits that form on them are associated with the finer fly ash particles. For this thesis, the term 'heat exchanger (HX)' refers to the superheaters and reheaters, as the temperatures focused on during this research correspond to their operational temperature conditions. Selection of specific HXs is important, as the temperatures will influence materials they are constructed from and hence the selection of candidate alloys for this research (see **Section 2.5.2**). Some of the qualities desired in superheater and reheater alloys include, but are not limited to, creep, strength, and fatigue.

Alkali metal chlorides, which have lower melting points than the corresponding sulphates, are found in biomass plant HX deposits [99]. Biomass plants operate at lower steam temperatures than coal combustion plants to limit the melting of these chlorides and the related fireside corrosion and the energy output from the biomass power plant is thus generally lower than for coal [24]. As such, setting of biomass/waste combustion plant HX steam temperature conditions is critical from an operational efficiency point of view. The melting temperature of biomass ash contents is influenced by the ash stoichiometry and therefore varies significantly for the vast number of biomass types [75].

Tran et al. [33] investigated the correlation between the first melting temperature (FMT) and the compositions of over 150 ash deposits. In increasing magnitude, sulphates, carbonates and most significantly, chlorides reduce the FMT. No notable change was seen with increased chloride concentration and it was argued that most deposits employed already had the chloride flux required for chlorine active oxidation (see **Section 2.5.3.1**).

Salmenoja et al. [120], in their study of the firing conditions favouring corrosion mechanisms in black liquor recovery boilers, concluded it best practice to avoid enhanced metal temperatures when optimising operational efficiency. It was advised that steam temperatures be maintained at least 50°C below the FMT of the heat exchanger deposits.

Alkali metal and alkaline earth metal salts may exhibit FMT ranging from 490–510°C. The FMT is further lowered by the presence of salt mixtures [33], [120]. Lower temperature fireside corrosion in biomass firing conditions (below 450°C) are thus common (relative to coal combustion) as these fuels tend to generate alkali metal salt-rich ashes during combustion [121].

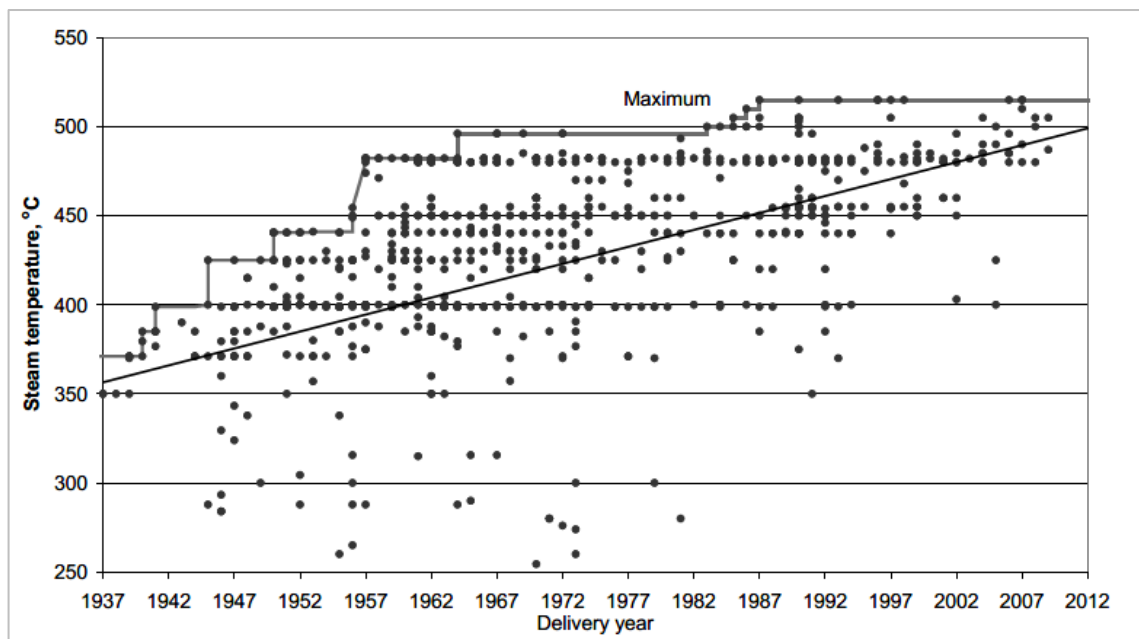


Figure 2-13: Recovery boiler (firing black liquor) main steam temperature trends [108]

In 2014, the International Chemical Recovery Conference (ICRC) celebrated the 50th year of recovery boiler operations' collaboration [19]. In 2009 [111] and 2014 [97], Vakkilainen et al. reviewed present and future recovery boiler steam temperatures which had risen slightly over the years from averages of ~350°C in the 1950s' to above 450°C by the 1990s' as shown in **Figure 2-13**. The June 2009 ICRC proceedings [108] concluded that relatively low rates of

corrosion of recovery boiler heat exchangers was seen when the temperature output of super-heated steam was managed around 450°C.

The corrosive damage to heat exchanger materials produced from wheat straw and coal firing conditions are compared over a temperature range in **Figure 2-14**. Corrosion damage is reported for two stainless steels exposed. The 100% biomass firing conditions produce a wide range of corrosion damage rates compared with coal combustion, and a co-fired mix of <10 wt.% biomass [24]. Corrosion rates heighten at 600°C for the biomass and co-fired conditions. The corrosion rates for the biomass firing remains relatively similar below 500°C.

Research and development, aiming to optimise metal performances in the high temperature corrosive environments of combustion power plants, focuses on potentially achievable and realistic steam temperature ranges. Chemical additives (e.g. ammonium based spent ash), which raise the FMT of low melting point salts, can permit higher metal operating temperatures [88], [121], [123]; improving energy output efficiencies without too much compromise on the metal lifetimes.

The targeted metal lifetimes, under various fuel firing conditions, vary; examples are listed in **Table 2-3**. These targets are based on the corrosiveness of the combustion environments generated by the selected fuels and the maximum acceptable metal loss rates. The accepted corrosion rate determines permissible metal temperature ranges set.

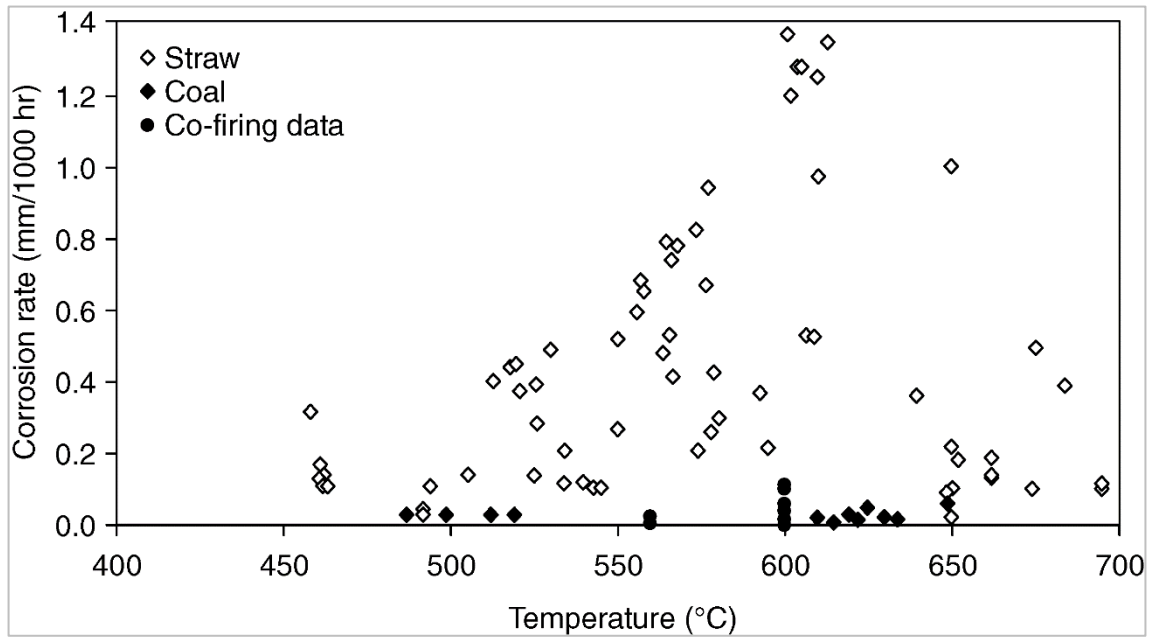


Figure 2-14: Metal temperature effect on corrosion rates biomass, coal and co-fired operations [24]

Table 2-3: HX aspirational target temperatures with corresponding metal target lifetimes for waste, biomass and coal firing [24]

Fuel	Target lifetime (hours)	Desired maximum steam temperature (°C)	Metal temperature (°C)	Maximum acceptable corrosion rate (µm/1000 hours)
Coal	100 000	650	680–700	20
Straw	20 000	580	610–630	100
Wood	40 000	580	610–630	50
Waste	40 000	500	530–550	50

The corrosion tests undertaken during this research (**Section 3.3**) were conducted at 500-600°C (metal temperature) to cover aspirational temperature ranges of HXs in biomass plants as listed in **Table 2-3**.

2.5.2 Alloys employed in biomass/waste combustion conditions

The selection of alloys employed for corrosion tests during this research is reviewed in this section.

Table 2-4: Four generations of ferritic steels and examples [124]

Year	Steel modification	10 ⁵ h creep rupture strength (MPa) at 600°C	Alloys e.g.,	Max. temp. (°C) at 100 MPa/10 ⁵ h
1960-1970 (1 st generation)	Mo increase or Nb addition, V addition to 12%, 9% Cr steel	60	Tempaloy F9, EM12, HCM9M, HT9, HT91	565
1970-1985 (2 nd generation)	Optimizing of Nb, C & V. HCM alloys are more cost effective and better creep strength than T22	100	T91, HCM12, HCM2S	593
1985-1995 (3 rd generation)	Improving creep strength: partially substituting Mo for W	140	P-62, P-122, P-911	620 (creep aspects)
Emerging	~ 3% W, 3% Mo, improved stabilization of nitride precipitates by addition of Ta & Nb (SAVE12)	180	NF12, SAVE12	650

It is necessary to be specific about the HX material in the evaluation of the fireside corrosion due to the vast range of alloy types employed and their range of thermochemical properties at high temperatures. A 9–12 wt.% Cr content is a basic requirement for high temperature oxidation and corrosion resistance alloys [31]. These materials undergo thermal stress and experience fatigue at high temperatures. Enhanced creep resistance, high thermal conductivity, low thermal expansion properties of steels are required to meet the challenges experienced in supercritical powerplant conditions.

Table 2-4 presents four ferritic steel generations, representing the alloys' performance innovation stages over past decades. Among the commercialised

9% Cr ferritic steels, T91 has been employed as steam pipes and superheater tubes in combustion plants operating at up to 593°C. In simulated fireside corrosion environments at 600°C, T91 has shown better corrosion resistance than lower Cr content ferritic steels T22 (~2.25 wt.% Cr) and T23 (~2.5 wt.% Cr) and 15Mo3 steel (0% Cr) [102], signalling the importance of Cr content in resisting fireside corrosion.

Though the latest ferritic steels are designed to offer high creep strength, Montgomery et al. [32] saw that both 9 and 12% Cr steels offered similar corrosion rates up to 50,000 hours, as illustrated in **Figure 2-15**, while carrying out fireside (coal combustion) corrosion studies in existing superheaters (steam temperatures averaging 555-568°C).

While the role of Cr is clear, the effects of the alloying element Mo on oxidation resistance is not well defined due to contradicting data [31]. Mo starts to oxidize significantly in air from 300°C. Below 400°C, an adherent MoO₂ scale which is relatively stable proceeds. Rapid oxidation begins from 500°C, and above this temperature the vapour pressure of MoO₃ increases significantly, depending on the partial pressure of O₂. The oxide is not protective, however, the scale may react with deposit/flue gas components.

In sulphidising environments, Mo may slowly transition to MoS₂ between 600-700°C [125], [126]. In contrast to most other functional metal sulphides, MoS₂ has an extremely low defect density and a relatively high melting point (~1200°C). It is for these reasons that Mo is highly resistant to sulphation. It is however not expected that these conditions will be reached under biomass/waste firing (H₂S atmosphere), as moisture is present.

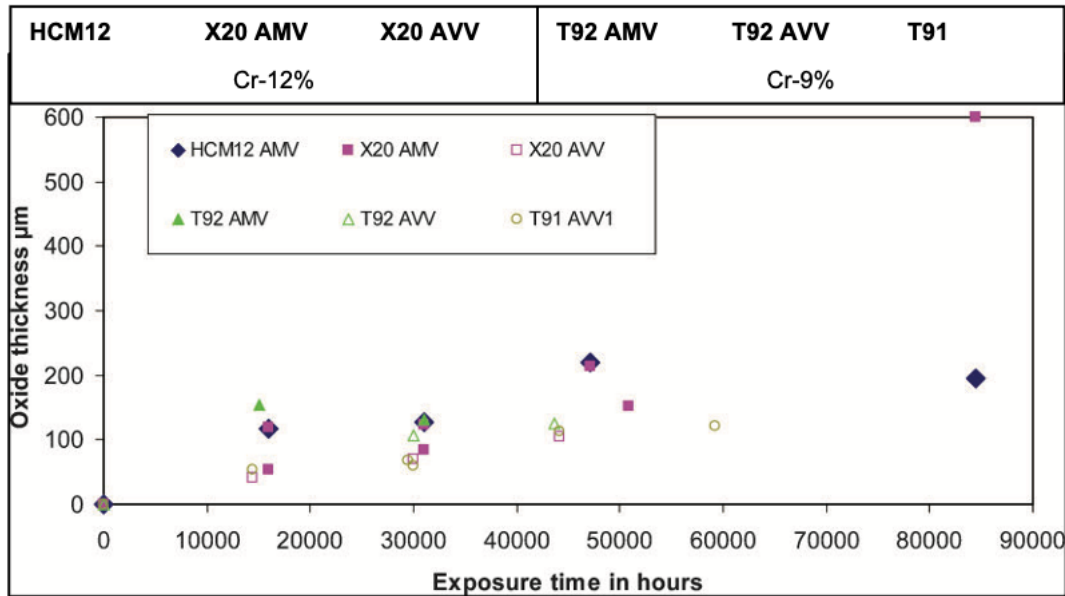


Figure 2-15: Martensitic steels oxide thickness formation rates at 555-568°C[32]

T91 shows creep strength limitations by 565°C and optimal corrosion resistance of commercialised ferritic steels are limited to use below 600°C (metal temperature) [124]. A difference between the alloy oxidation of a high Cr content steel and those of <15% Cr is the formation of a chromium-containing spinel oxide which is more protective than the ferric oxide formed in ferritic steels. Alloys based on 18% Cr, 8% Ni steels such as TP347 HFG are classified as austenitic steel with less than 20% Cr [113]. The ultimate tensile stress for these steels are intermediate between the ferritic steels and higher Cr content austenitic steels [124]. TP 347HFG austenitic alloy (18% Cr and 11% Ni) can exhibit acceptable corrosion rates at higher temperatures than T91 [16].

At 600°C, austenitic steels, which are face-centred cubic-crystalline structured stainless steels [113], may be required for their improved high temperature performances including corrosion resistance enabled by the high Cr content. They are also easier to weld and find applications on conventional plant superheaters. Ferritic steels, however, exhibit lower thermal expansion coefficients and good thermal conductivities. In addition, they are less expensive than most austenitic steels and as such remain desirable for biomass/waste combustion plant [127], [128].

Table 2-5 includes a list of high strength stainless steels. The stainless steels can be classed according to their Cr content: 15% Cr (15% Ni), 18% Cr (8% Ni), 20-25% Cr (15-32% Ni) and >25% Cr (high Ni) stainless steels. The optimization of these steels over the years has required a compromise between corrosion resistance and creep strength. Initially, Nb and Ti contents were increased to enhance corrosion resistance by stabilizing the steel. The element contents were then optimised to manage the comprised creep strength rather than corrosion. Further optimizations have included precipitation strengthening by addition of Cu, austenite solid phase stabilization with N and W, for tackling pitting corrosion [124].

Table 2-5: Range of austenitic steels employed of boiler super heater/reheater applications [124]

Cr-Ni content	Alloy examples
18% Cr, 8% Ni	TP 340H, Super 304H, TP 321H, TP 347 H, TP347 HFG, TP 316H, Tempaloy A-1
15% Cr, 15% Ni	17-14CuMo, Eshete 1250
20%-25% Cr, 15%-32% Ni	TP 310, HR3C, 800H
High Cr, high Ni	CR30A (30%-Cr, 50%-Ni), HR6W (43%-Cr, 23%-Ni)

Higher Cr alloys have been identified as leading candidates for use in high temperature operations (620-675°C). These include Super304H and SAVE 25. Exceeding 675°C, high Ni-content alloys perform better at high stress, such as Inco740 [124].

The selection of alloys used for corrosion testing during this research is not within the thesis scope which is aimed at investigating fireside corrosion behaviour of fuels. However, both selected steels, T91 and 347HFG, are employed in combustion power plants and were chosen by the PhD sponsors to represent plant conditions. Low Cr content ferritic alloys (such as T22) that have

insufficient corrosion resistance have shown unacceptable fireside corrosion rates and are not suitable for the highly corrosive environments experienced in biomass and waste firing [111]. The intermediate ferritic alloyed steel, T91 (9% Cr) is, however, commonly employed for use in biomass combustion power plants and in various metal performance focused research studies [31], [32], [102]. Thus, there is sufficient literature for comparison with the corrosion evaluations conducted within this PhD.

2.5.3 Fireside corrosion mechanisms of compounds and species

The various chemical species which may condense on heat exchanger surfaces following release after biomass/waste combustion have been discussed in earlier sections of this chapter. The various mechanisms for this, reported in the literature, are given in the following sub sections.

2.5.3.1 Chloride-based fireside corrosion mechanism

This section centres on the Cl-based corrosion mechanisms which favour attack of steels in a combustion environment.

2.5.3.1.1 Chlorine ‘active oxidation’

Grabke et al. [97] described the effects of chloride on steel oxidation at high temperatures, with the chloride attack proceeding via the following stages:

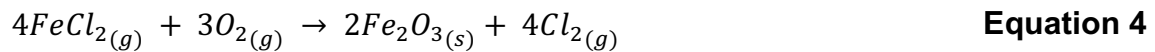
HCl or alkali metal-Cl can be oxidized in the presence of oxides in the flue gas path:



The evolved molecular chlorine gas can penetrate protective layers on a steel surface, through small cracks and faults, thus coming into contact with the metal surface beneath. This can lead to the formation of metal chlorides:



Depending on the metal temperature, if the vapour pressure of $FeCl_2$ is sufficient, its evaporation will occur. As $FeCl_2$ molecules make their way through the cracked/porous oxide layers, exposure to higher oxygen pressures will cause the oxidation of the chloride to iron oxide.



The iron oxides produced condense between the metal/scale layers. This process is termed 'active oxidation by chloride'. Grabke et al. [97] explains that the chlorine gas released by the oxidation of iron (**Equation 4**) at the metal surface will enable a repeat of the metal depletion process (**Equation 3**). The build-up of iron oxide is destructive to chromate protective layers, forming cracks, fractures, and complete delamination of the scale as components are transported through the scale paths. The internal depletion of metal cations also affects the integrity of the protective layer, and the collation of iron (III/IV) oxide forms a non-protective layer which leads to an increase in corrosion rate. Chloride thus acts as a catalyst for the reactions as the metal oxidation process releases chlorine at the alloy surface, inducing the active oxidation process again.

Grabke et al. [97] suggests the metal depletion is supported by diffusion processes.

For the active oxidation proposal, the rate of corrosion is enhanced by the diffusivity/ pore spaces of the alloy scale, and inversely proportional to the scale

thickness [97], [129]. The vapour pressure of metal chlorides increases with temperature, increasing the diffusion rates of molecules across the metal/deposit layers.

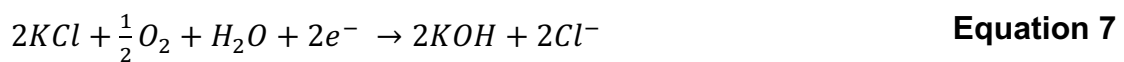
2.5.3.1.2 Ion diffusion Cl attack mechanism

Folkesson et al. [90] proposed an electrochemical mechanism for chloride ion damage involving a KCl deposit. Isothermal tests conducted at 400°C and 500°C showed that, at the higher temperature, the oxide growth rate on various steels diminished, corresponding with the depletion of K and Cl from the test environment. The proposed mechanism focused on corrosion reactions occurring for a low alloyed steel, T22, exposed to the deposit in the presence of CO₂, H₂O and N₂. Redox reactions stages (i.) and (ii.) are said to occur simultaneously during the initial oxidation phase, where the chloride deposit is present. Stage (iii.) involves an ion diffusion process which occurs after stages (i.) and (ii.):

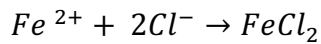
- i. **Equation 5** is the formation of Fe²⁺ ions at the alloy surface. This is coupled with the reduction of O₂ at an oxide surface as illustrated in **Equation 6**.



- ii. In the presence of water vapour, the reaction described in **Equation 7** is proposed to take place at the scale surface where **Equation 6** occurs.



- iii. The chloride ion may then diffuse inwards, through the scale, to the metal interface. It is as a result of this final ion diffusion stage that the metal chloride is said to form:



Equation 8

The proposed electrochemical process is summarised in **Figure 2-16**.

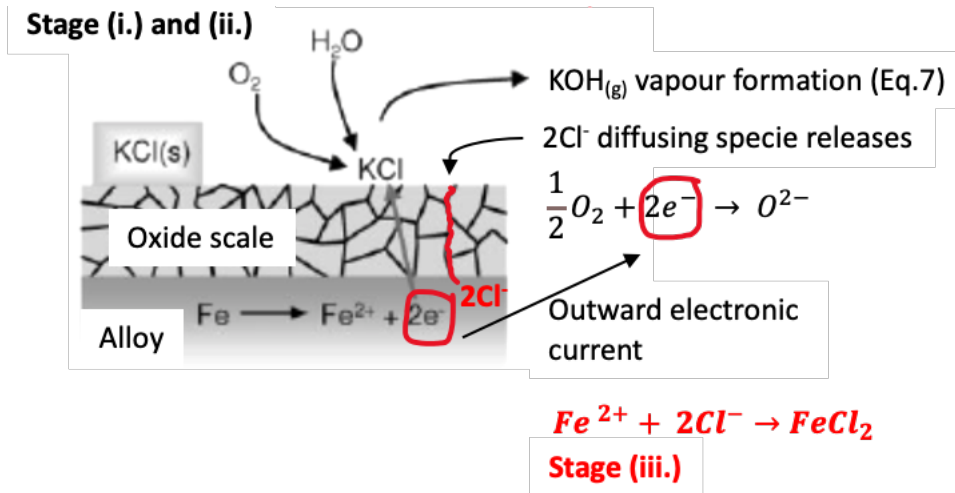


Figure 2-16: Folkson's proposed KCl dissociation and electrochemical ion diffusion Cl attack mechanism, modified from [90]

In the Folkson criteria, Cl is not recycled (as suggested by Grabke) to any significant extent, rather KOH and $FeCl_2$ are mostly vapourised and eventually depleted due to their high vapour pressures. This method of describing chloride attack in fireside corrosion thus requires the presence of the intermediate hydroxide (**Equation 7**), which may also be NaOH [107], for progressive corrosion rates.

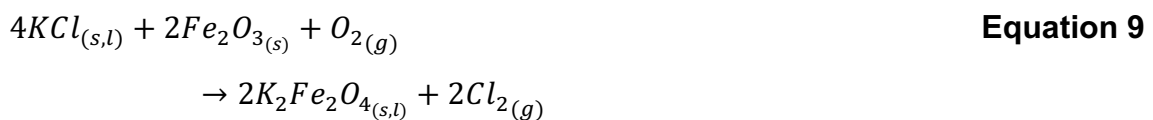
2.5.3.1.3 Factors influencing chloride corrosive attack

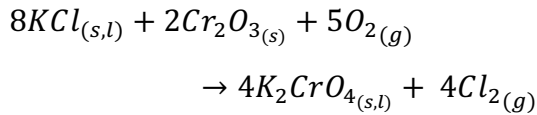
Several factors influence Cl damage rates during fireside corrosion. Researches have investigated the influences of temperature [90], [130]; time [90]; deposit flux and composition [115]; and alloy type [38], [130] on Cl damage.

i. Chemical influences

Gaus-Liu [130] associated the porous outer deposit scales formed during straw firing to the outward diffusion of FeCl_2 . The author observed that chlorine attack was more dramatic when temperature conditions were increased from 550 to 650°C. At the higher temperature, there was no evidence that Cr scale formation made a difference to metal loss, such that an austenitic steel with higher Cr content did not perform any better than a high alloyed ferritic steel. In addition, no internal attack was detected at 550°C, however by 650°C, internal corrosion of the ferritic steel T91 was observed, indicating that the damage mechanism may have changed. At the same temperatures, internal damage on the austenitic steel, 347HFG, featured Cr-depleted fissures within the metal matrix. It was proposed that this selective attack of Cr (in 347HFG) was caused by chloride, however, this was not confirmed, for example by SEM-EDX analysis, what type of chloride. It was suggested that chloride may have escaped, as advised by Folkesson et al. [90]. Ni and S were enriched at the metal/oxide interface, implying sulphates had influence on Ni migration. As such, the metal attack mechanism could not be attributed to Cl mobility alone. Cr, on the other hand, was found within detached multi-layered oxide scales while only iron oxide was observed in the porous oxide scale layer. The outer scale layer consisted of a mixture of ash and corrosion products. At 700°C, furthermore, no internal damage was observed on the steels exposed under coal firing (lower Cl conditions), signifying that the austenitic steel was more prone to Cl internal damage mechanisms.

Chloride release is kinetically favoured when molten chloride deposits are present on the alloy. Condensed alkali metal chlorides and other chlorides at the corrosion site can react with iron and chromium scales, releasing chlorine (or HCl in the presence of moisture) [131]. For example:





Equation 10

Corrosion in austenitic steels have been found to be more responsive to increasing Cl content than ferritic steels (not necessarily more damaged). Interaction between Cl and Cr in the alloy is said to occur, which may consume Cr-Fe spinels and Cr₂O₃ layers, exposing the alloy to further corrosion attack. Chromates can also form low melting point mixtures with KCl and with other chromates (e.g. K₂CrO₄-K₂Cr₂O₇ eutectic melting point, 393°C) [115].

In another study, Backman et al. [132] compared the fireside corrosion influences of alkali metal and alkali earth metals in a biomass/waste combustion plant. The concentrating of chlorides at the corroding alloy/deposit interface indicated the participation of Cl in first stages of metal damage. The metal elements present in the deposit varied with distance from the alloy surface. Alkali metals (K and Na) were closest to the alloy surface, while calcium species were more concentrated on the deposit's outer layer. This indicated that the alkali metals encouraged chloride attack of the alloy. The authors concluded that corrosion tendencies of species are of greater concern where the mobile alkali metals were present with Cl.

The formation of NaCl, which also influences Cl⁻ ion transport, is another concern when combusting Na-rich fuels. Deposits with melting points low enough that they occur within heat exchanger temperature ranges, may occur via the formation of eutectic mixtures of NaCl and metal oxides. In Na and K rich fuels, much lower eutectic temperatures may be reached [131]. The chemistry of deposits thus plays a significant role in chloride damage.

ii. Thermodynamic reactions in a chloridizing atmosphere

Grabke et al. [133] proposed a schematic of thermodynamically stable reactions that would occur during the degradation of alloy elements Fe, Cr, Ni, Mn and Mo in oxidizing and chloridizing environments at metal surfaces at 600°C. The oxidizing-chloridizing of alloy elements were explained by the using the Gibbs' free energy to arrange the corrosion attack rates, whereby the more negative the energy, the more favourable the reaction [101], [106].

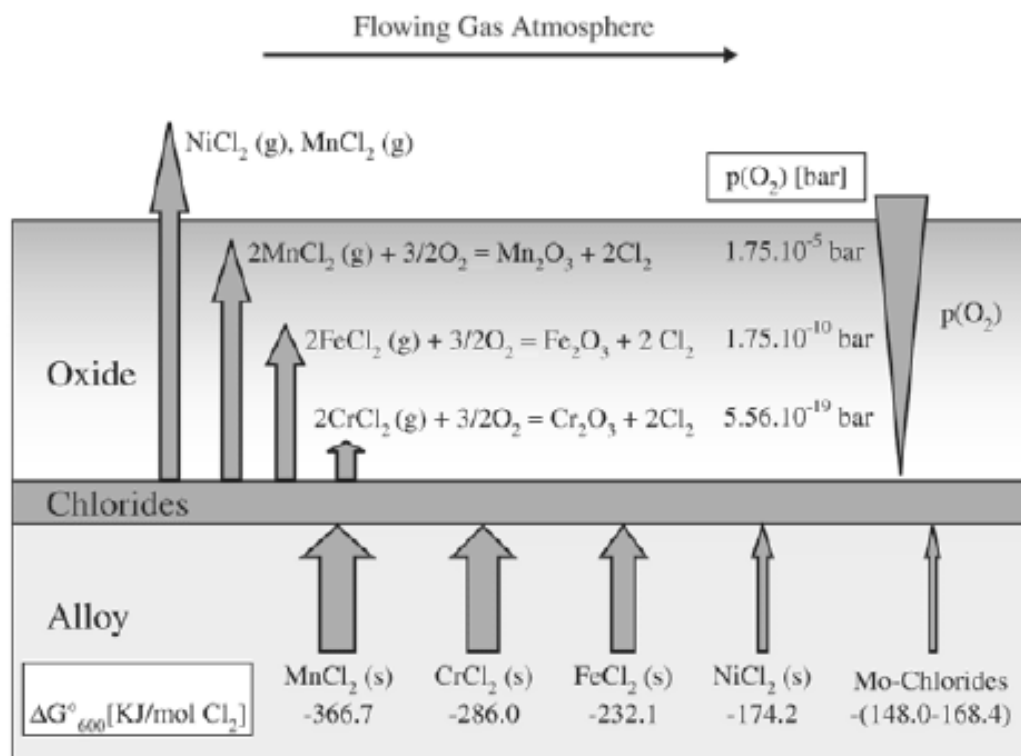


Figure 2-17: Fe, Ni, Cr, Mo and Mn corrosion explained by thermodynamics and reactions in a chloridizing and oxidizing environment [133]

From **Figure 2-17**, the susceptibility to corrosion attack of the elements occurs according to the sequence $\text{Mn} > \text{Cr} > \text{Fe} > \text{Ni} > \text{Mo}$, where the chloride attack of Mo is the thermodynamically least stable [133]. The author also explained that thermodynamic data can be used to explain the conversion of chlorides to oxides, based on the O_2 pressure required for this conversion. The higher the O_2 pressure required, the nearer to the metal surface the oxide formation (within the metal) occurred, as O_2 pressure decreases with distance

from the flue gas. The thermodynamic law also suggests that the transport of Ni and Mo chlorides can occur over a great distance, unoxidized by the gas stream. The authors confirmed that, according to thermodynamic laws, the vapour pressures of the chlorides also determine the fate of the corrosion products; whether they are oxidised or vapourised [133].



Also, Cl vapour pressures and oxygen partial pressures influence the transport distance of components from the metal surface. The lower the O_2 pressure required, the nearer to the metal surface the oxide formation (above the metal) occurred. This explains why Fe-oxide scale layers are deposited further into the scale than Cr-oxide scales layers from the metal surface.

Figure 2-18 presents the influence of oxygen pressure on Ni corrosion in Cl_2 . Volatilization of $NiCl_2$ formed in such an atmosphere may occur via the routes described by **Equation 11** and **Equation 12** where the rate of corrosion of Ni is accelerated by oxygen via a $NiCl$ gas intermediary, confirmed spectroscopically by [134].

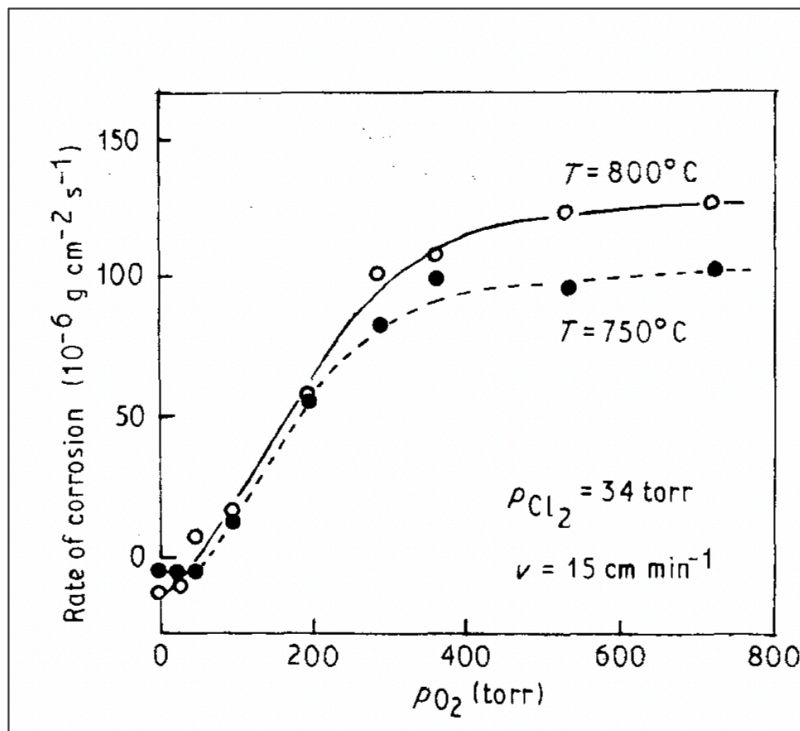


Figure 2-18: Effect of oxygen pressure on Ni corrosion in chlorine gas at 750°C and 800°C [134]

These studies show that the corrosive mechanisms of individual compounds/elements should not be investigated independently. Rather, thermodynamic and chemical properties of the interacting deposit and gases, as well as the alloy type, will strongly influence corrosion rates.

2.5.3.2 Sulphate fireside corrosion mechanism

Sulphates influence high temperature corrosion attack mechanisms and are often encountered in coal combustion. Following 1000 hours of exposure to simulated fuel combustion conditions at 650°C, Hack et al. [135] recorded average metal thickness losses ranging from 0.4-1.2 % and 0.6-2 % in low and high sulphur coals, respectively (dimensions not provided). The sulphate species available in both condensed (deposit) and gas phases vary in their damage influence extents [37], [115].

2.5.3.2.1 Gas sulphate attack processes

Corrosion data generated from laboratory tests employing four SO_2 concentrations showed that the concentration of various S-containing species in a flue gas environment is a significant factor for high temperature degradation [127].

The degradation of Inconel 740 H superalloy was evaluated by Jin-Tao et al. [136] at 750°C with SO_2 present in the corrosion test atmosphere. Corrosion rates were increased with SO_2 increment from 0.1-1.5 vol.%. Formation of the Ti and Al oxide scale, located by SEM-EDX analysis, beneath a Cr-rich oxide scale, was accelerated for higher SO_2 levels which may have fractured the chromium scale as volatile corrosion products were transported from the metal towards the scale surface. The results indicated that the high temperature damage was strongly linked to the gas SO_2 concentration.

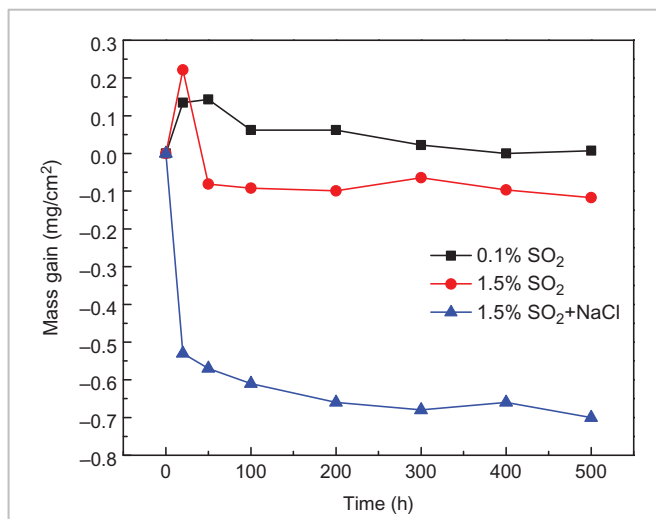
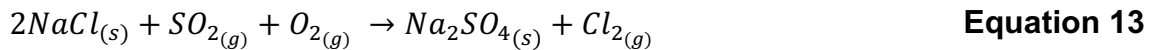
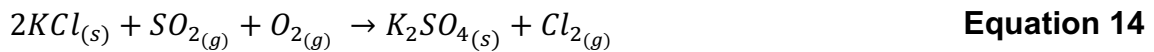


Figure 2-19: Sulphate and NaCl salt effects on Inconel 740 H superalloy at 750°C for 500 hours. Study conducted by [136]

The same authors also examined the corrosive effect of NaCl additions (in the presence of sulphate) on the integrity of the Cr₂O₃ scale. The oxide layer became porous and easily spalled, confirming the different mechanisms of damage between chloride and sulphate attack, and the supporting role of the chloride: hot corrosion accelerated with Cl (**Figure 2-19**) influenced scale loss (likely by decomposition and evaporation), allowing a penetrative attack of sulphates within the alloy matrix [136].

It is suggested that the role of the sulphate in fireside corrosion is also indirect: sulphate formation permits the release of chlorine/chloride for its continued use in active corrosion [40], [137] as described in **Equation 13** and **Equation 14**.



Chloride loss to the gas stream may be promoted by these reactions, which occur in the deposit surface region [97]. For this assumption, higher SO₂ concentrations favour Cl loss from the system. This is an example of how increased SO₂ concentration in the gas stream may hinder chloride attack.

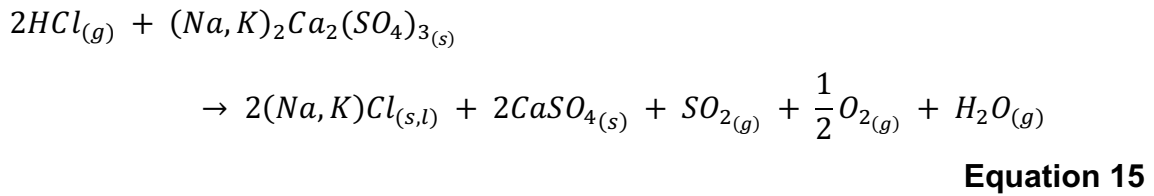
James et al. [137] observed the concentration of chloride species at a metal oxide scale/alloy interface. As time elapsed, it was observed that the chlorides had become sulphates and chlorine gas was released. This may suggest that SO₂ can diffuse through scales, or mix with components to become molten, to react with the chlorides, e.g., FeCl₂.

Karlsson et al. [138] carried out laboratory tests where an alloy was exposed to KCl, Fe₂O₃, Cr₂O₃ mixtures, heated in a static 1:1 SO₂/O₂ gas environment. The Fe₂O₃/KCl mixture began reacting with the gas from 310°C, then the reaction rate decreased at 500 - 650°C, after which no further reaction was observed. The presence of K₃Fe(SO₄)₃ was confirmed by X-ray

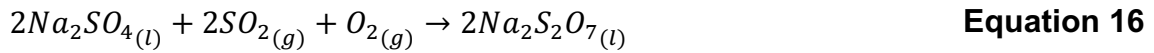
diffractometry. Though chlorine was produced in the reaction, FeCl_2 was not detected. The authors suggest that the SO_2 -led corrosion attack may have been helped by a FeCl_3 intermediary.

2.5.3.2.2 Combined deposit and gas attack mechanism

Sulphates may be converted to chlorides where the HCl partial pressure is sufficient (**Equation 15**), inducing an active chloride process via ion transfers and possibly form the eutectic mixtures [97].



Pyrosulfate (melting point 325°C) can also be formed from direct SO_2 interactions with molten deposits, explained in **Equation 16** [97].



Melted Na and K pyrosulfates are converted to complex sulphates from reactions with the iron (III) oxide scale, as demonstrated in **Equation 17**. The mass of scale increases and becomes more susceptible to spallation and delamination, thus exposing a fresh and unprotected layer [97].



An accelerated high temperature corrosion experiment, conducted by Syed et al. [37], observed corrosion damage of T92 and 347HFG samples exposed to a synthetic deposit mixture (Na_2SO_4 and K_2SO_4 at 37.5 mol.% each and Fe_2O_3 at 25%) in a corrosive gas environment (gas composition: 59 vol.% N_2 , 31 vol.% CO_2 , 4 vol.% H_2O , 6 vol.% O_2 , 6260 vol. ppm SO_2 and 1700 vol. ppm HCl) at 600, 750 and 700°C. An exposed sample with no deposit experienced a third of the median metal loss at all temperatures than the deposit-coated samples, highlighting that the sulphate deposit (with no chloride) accelerated the metal damage. The corrosion rates of the steels exposed without deposit were similar at all temperatures. In contrast, no protective scales were expected to have formed on the deposit-coated samples at any of the temperatures, as the corrosion rates were steady with time (indicating immediate progression).

Dudziak et al. [102] proposed relatively high S diffusion rates through the scale-substrate interface of a ferritic steel sample, though K and sulphate were indicated by SEM/EDX to be retained at the deposit region. The sample was exposed to the same deposit, as the previous author [37], in a gas of composition 1298 vol. ppm- SO_2 , 399 vol. ppm- HCl , 74 vol.%- N_2 , 4 vol.%- O_2 , 14 vol.%- CO_2 and 8 vol.%- H_2O . A S-rich interface was observed following exposure at 600°C and was less noticeable by 650°C, a similar trend observed by Karlsson et al. [138]. The concentration of S at the interface was considered to have risen again at temperatures > 700°C, a point where the deposit region consisting of K-S-O interactions (likely deposit K_2SO_4 component) had become porous.

The above investigations suggest higher temperature requirement (> 700°C) in the corrosive gas conditions described, for deposit sulphate attack. At these lower temperatures, however, sulphate gas content may be responsible for sulphate attack.

2.5.3.3 Carbonate and water vapour fireside corrosion processes

Carbonate damage processes in high temperature corrosion are less often discussed than chloride- and sulphate-influenced attack. However, the damage of chromium scale has been considered to also occur under carbonate exposure conditions. Alkali metal-carbonates may react with Cr-rich oxides to form a non-protective K-Cr-O, as was noted for chlorides [115]. The differences in the damage rates are, however, attributed to the ability for CO_3^{2-} and Cl^- reactions to form the resulting chromate and the relative stability of the leaving groups, CO_2 and HCl respectively.

Pettersson et al. [115] reported the similarities in corroded sample morphologies and corrosion rates for an austenitic steel coated with either KCl or K_2CO_3 and exposed to a gas mix (of H_2O , CO_2 and N_2) at 500°C and 600°C. The author explained that the cations may have played a more significant role in dictating the corrosion rates occurring while suggesting that the anions induced similar corrosion rates.

Lehmusto et al. [139] however reported that, though both salts, KCl and K_2CO_3 , were corrosive to alloys including a ferritic steel (10CrMo type) and an alloy 625-type nickel-based steel, the corrosive damage on the KCl exposed samples were greater in both wet and dry high temperature conditions, illustrated in **Figure 2-20**. Both reports [115] & [139], however, conclude that the presence of K-cations played the main role in promoting corrosion.

It is also noted that both Pettersson et al. [115] and Lehmusto et al. [139] relied on mass change and oxide thickness data (observed by SEM-EDX) for investigating corrosion rates. However, literature has shown that reliance on these factors may be flawed due to oxide spallation encountered under Cl attack [140]. The later author, however, distinguished the carbonate-induced scale by its good adherence, whereas the Cl attacked sample had multi-layered and poorly adhered scales. Lehmusto et al. [139] thus concluded that, following accelerated corrosion initiation, the presence of chloride is essential for corrosion propagation.

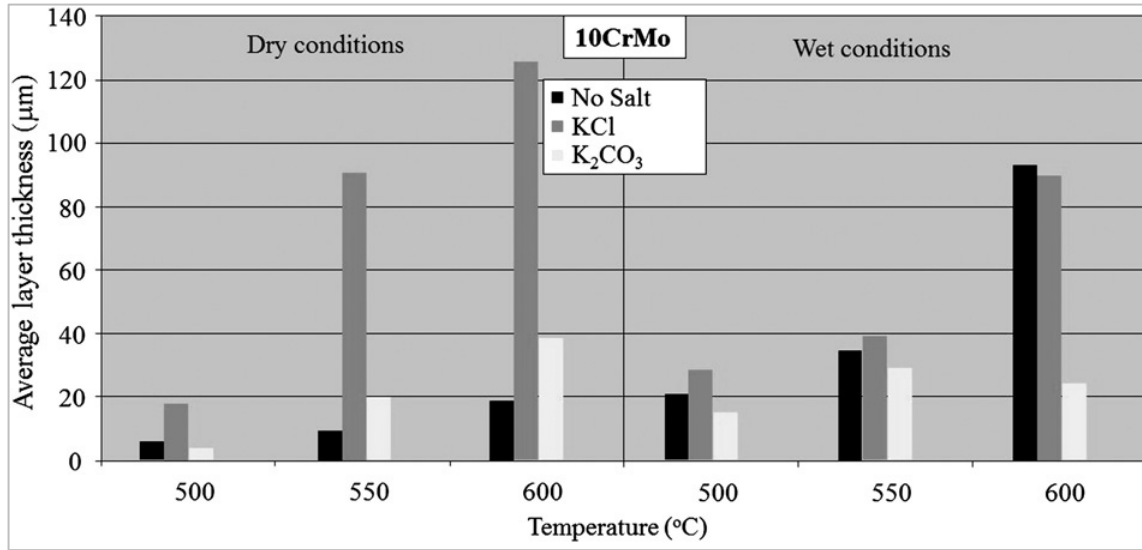


Figure 2-20: Average scale thickness of ferritic steel (10CrMo) under dry and wet (30% H_2O) air conditions as a function of temperature [139]

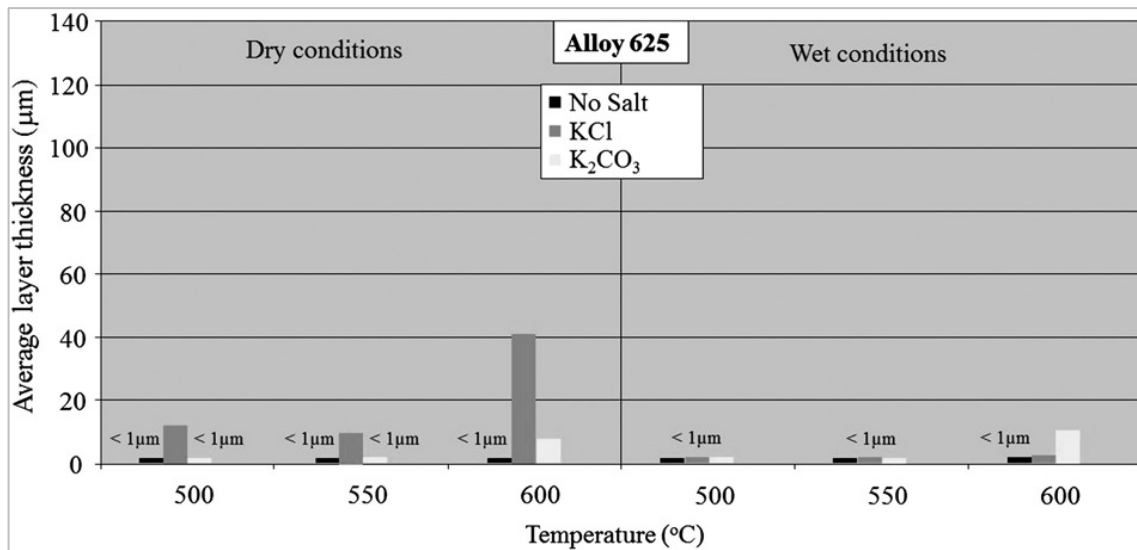


Figure 2-21: Average scale thickness of a Ni based steel (Alloy 625) under dry and wet (30% H_2O) air conditions as a function of temperature [139]

The difference between carbonate and Cl attack rates is not straightforward where water vapour plays a role. Lehmusto et al. [139] observed thicker scales for the KCl exposed 10CrMo sample under dry conditions than under wet (~30 vol.% H_2O) conditions, although at 500 $^{\circ}\text{C}$ and 550 $^{\circ}\text{C}$, the 10CrMo steel coated with K_2CO_3 showed reduced scale thickness under dry conditions.

The response of a 625 Ni-based steel sample under wet exposure conditions had a similar damage trend to the ferritic steel. In wet conditions at 500°C and 550°C, any oxide layer formed on the KCl exposed sample was too thin to be detected, whereas in dry conditions, the KCl exposed sample experienced severe corrosion at all test temperatures (500°C, 550°C and 600°C).

It should be noted that the test conducted by Pettersson et al. [115] was under a 40 vol.-%-H₂O atmosphere which could explain the extensive scale formation noticed on the carbonate exposed sample, as it has been observed that vapour assisted K₂CO₃ corrosion may be more severe than in dry conditions [139].

The K compounds' corrosivity differences were attributed to the cation attack in a carbonate environment where the formation of K-Cr is the main destructive mechanism, such that accelerated corrosion is dependent on the available Cr. In the case of KCl, both elements have their selective routes for metal damage; the influence of Cl⁻ ion on metal loss is not only limited to the Cr attack. The exact role of water vapour in enhancing K₂CO₃ attack and reducing KCl was not established, however it was suggested that vapour will enable the formation of volatile HCl [139] and KOH [90].

2.5.3.4 Heavy metal contaminants: their fireside corrosion influence

There is presently a need for the investigation of the fireside corrosion role of trace contaminants associated with waste fuels. These contaminants tend to be heavy metals at concentrations below 1000 ppm [141]. For example, wood preservatives may contain significant quantities of Zn and Cr [51], [52]. The proportion of heavy metal contaminants can vary by economic trends and by location [74]. There is therefore a potentially wide variation in the extents of fuel contaminant levels.

As, Cd, Cr, Cu, Pb, and Hg levels in wood, wood bark, fruit shell, mushroom, and lichen were analysed by Demirbas et al. [141], using atomic absorption spectrophotometrically. While the authors investigated toxic

emissions during combustion, finding these often below detection limits, the fireside corrosion influences of the element components (formed compounds/species) were not within the authors' work scope.

The heavy metal levels (trace levels) in biomass ashes (beech wood, switchgrass, corn cobs, rice husks, plum pits, sunflower shells, marine macroalgae and walnut shells), produced at 500°C, were also analysed by Vassilev et al. [14] using SEM/EDX, inductively coupled plasma/laser ablation mass spectrometry and other methods. Associations of the heavy metals with different constituents (such as silicates, oxides, hydroxides, sulphates, chlorides phosphates and carbonates) in the fuels and their ash were presented. Their conclusions were, however, also limited to the ecological challenges related to the firing of fuels with heavy metal contaminants.

The employment of less conventional biomass combustion fuels, which may be contaminated fuels (wastes), need further research, targeted at understanding trace element roles fireside corrosion.

2.6 Approaches for investigating fireside fuels' corrosion properties

Fireside corrosion investigation encompasses a range of study types which may include power plant design/engineering, heat exchanger materials, their exposure conditions (chemical and thermal), and metal change responses [24]. The study of exposure conditions experienced by alloys and their metal change responses require the investigation of fuel combustion properties and their deposit chemistries at heat exchanger surfaces [142]. This section highlights some methods adopted for investigating the fireside corrosion properties of fuels and the damage they cause (**Section 2.6.1**). Also, current challenges with laboratory and plant corrosion data agreeing are reviewed (**Section 2.6.2**).

2.6.1 Laboratory practises

Experimental methods may address the fireside corrosion impact of fuel combustion. Such investigations can focus on the nature of post-combustion products (**Section 2.6.1.1**) and the corrosion damage they influence (**Section 2.6.1.2**).

2.6.1.1 Determination of deposit and gas environment by thermodynamic simulation approach

Conventional experimental procedures for evaluating fireside corrosion have relied on power plants' post-combustion release data [111], [128], [143]. Long and short term analysis of corrosion risks can be measured with probes set up in combustion plants [144] and pilot-scale experimental setups [95], [145]. Collated data may be used to determine deposits and combustion gas releases from fuel combustion [95]. This data is then interpreted for the formulation of synthetic deposits. As such, compounds, based on their prominent role in high temperature corrosion, are selected for corrosion evaluation [105].

During fireside corrosion experiments, synthetic deposit (potential heat exchanger deposits) formulations can be varied by chemical ratios [34], [38]

(changing the element values, such as for Cl, S and K, or changing compositions such as for chlorides and sulphates [95]) to simulate specific conditions (e.g., fuel specific) or investigate fireside corrosion trends occurring across chemical composition ranges (e.g. for various fuel deposit compositions).

Alternatively, thermodynamic simulation is a well-applied tool for calculating the behaviour of complex chemical systems' components [101], [143], [146], [147]. The Gibbs minimization energy principles form the basis of thermodynamic calculations, which are carried out by modern software programming [101], [146].

Rizvi et al. [147] employed thermodynamic equilibrium calculations of existing liquid and solid phase ratios, occurring at various temperatures, in their study of the four biomass fuels' slagging and fouling tendencies during combustion. Post-combustion compositions were the simulation input data, using a multiphase equilibria mode to establish melt fractions of the ash at a temperature range of 700-1500°C in 100°C successions. Thermodynamic calculations were found useful for this purpose.

Lindberg et al. [146] acknowledged thermodynamic calculations as an important approach for modelling corrosion ash chemistry in combustion systems. Pejryd et al. [148] applied thermodynamic calculations in the prediction of post-combustion releases in recovery boilers. The furnace bed and gas compositions were calculated. The calculations included input data of 15 graphite and alkali metal salt compounds (stoichiometric solids), a 14-component liquid phase of K and Na salts, and a 47-species gas phase (consisting of Na, K, C, O, N, H, Cl and S). Calculated compositions of species and compounds were expressed as a function of temperature. Links between the thermodynamic calculations and furnace process evaluations were identified, such as melt compositions.

Limitations in the dependency of thermodynamic data generated by Rizvi [147] and Pejryd [148] have, however, been identified. Some phenomena cannot be interpreted by thermodynamics alone. Both authors suggest that component

mass transfer and kinetics are also controlling factors in the formation of post-combustion products. Perfectly mixed isothermal processes, where equilibrium reactions are attained, are assumed by the theoretical thermodynamic equilibrium calculations but are, however, unachievable in a combustion system [149].

Although such conditions are not reached in any part of a boiler, some conclusion can be inferred from the generated data:

- i. Compositions of post-combustion products that could form are determined.
- ii. The temperature dependence of these products are determined as there is the likelihood of forming a product at extreme temperatures which occurs in a different form or product in cooler temperatures [149].

In this thesis, both approaches to interpreting thermodynamic simulations have been applied for the investigation of corrosive species phases at heat exchanger and heat exchanger-vicinity temperatures. This concept is based on the physical state of post-combustion compounds which have a significant impact on their corrosion role (see **Section 2.4**). Thermodynamic simulations have thus been selected for the predictions of potentially corrosive compounds that could form from the combustion of a range of fuel groups categorized during this research.

2.6.1.2 Evaluation of the corrosive behaviours of fuels and alloy responses

The pre-evaluation of fuels' fireside corrosion influences may save industries from extensive trials, provide data for the investigation and optimisation of combustion additives and for HX material performances. Pre-estimations of fuel combustion behaviours have been attempted by mathematical calculations called indices. Indices are mathematical ratios which employ the understanding of combustion product formation for the estimation of, gas, condensed and ash compound formation [96]. Currently there is no clear understanding of the most useful fuel indices for predicting biomass/waste post-combustion components or

the HX deposits forming (nor their corrosion influences). Efforts have however been made to adapt coal-originated combustion indices. Some indices have been used to estimate coals' corrosion performance during combustion. Such formulas are usually adopted on the basis of the ash corrosion behaviour expected. Coals are sedimentary rocks and have lower Na and K contents, trapped within thin rock layers. The alkali metals are mainly bound in aluminosilicate complexes and thus their combustion release patterns differ from the alkali metal-rich biomass fuels which are not typically associated with aluminosilicates [24]. As earlier mentioned (**Section 2.2**), the S and Cl contents in coal and biomass/waste fuels differ considerably. The unique and vastly ranged compositions occurring for biomass/waste fuels (relative to coal) make coal combustion prediction-indices mostly inaccurate for describing the non-fossil fuel combustion and corrosion behaviours [70], [96].

The application of indices in predicting biomass firing conditions is relatively novel. However there are current efforts to validate links with some coal indices [96]. It is generally agreed that other analysis techniques for predicting biomass/waste fuels firing behaviour are required to support and compare with indices predictions [96], [143], [150].

Relating fireside corrosion to fuel combustion release chemistries is challenging under fluctuating fireside conditions. The fluctuating parameters include temperature (influencing the physiochemical properties of combustion components [100]), gas flow rates (influencing component mass transfer and ash deposit rates [9]), and fuel batch/type (influencing combustion chemistry [100]). Investigation of the material degradation rates therefore requires specified exposure parameters which may only be achievable under a controlled laboratory environment.

The combustion parameter effects of high temperature corrosion have been experimentally investigated by varying metal exposure temperatures [100], [128] to study thermal effects on deposit behaviour. Pilot- and laboratory-scale combustion tests generate real deposits on probes and are found useful for evaluating specific fuel fireside properties [57]. The probes may also be cooled

to target temperature ranges desired [17], [105]. Defined deposits compositions cannot be generated via the combustion methods. Controlled deposition flux and composition changes, however, can be applied to produce a range of data which may be used to understand the effects of these parameter variations on metal change [20].

A deposit recoat technique has been applied in fireside corrosion testing whereby deposit-coated corrosion samples are exposed to simulated combustion conditions in a furnace over series of timed test cycles. Following each cycle, samples are recoated with deposits, depicting continuous deposition of post-combustion release components on HX surface [36]–[39]. This technique allows the application of specific deposit mixes, permitting controlled deposition fluxes and metal temperatures.

Sumner et al. [36] studied the effect of varying the furnace cycle length when employing the deposit recoat method. Alloy samples were exposed in type II hot corrosion conditions at repeated deposit application flux. The length of exposures was however varied. Dimensional measurements of metal loss, carried out post-exposure, confirmed insignificant differences in metal loss comparison for the varied cycle length samples (which underwent the same total exposure duration). The authors defended the repeatability of the deposit-recoat method, which has been employed for this PhD research. As such the generated corrosion data for this work can be compared across literature for samples with shared exposure conditions.

2.6.2 Heat flux corrosion furnace testing

Temperature plays a significant role in high temperature corrosion (see **Section 2.4.3** and **Section 2.5.3**). Temperature gradients at the vicinity of a HX is not limited to within the flue gas stream. These gradients are experienced across deposit, scale layers and alloy thickness [105], [151] and may impact and vary corrosion mechanisms, where species/compounds respond to the prevailing temperature condition [105].

Conventional furnace-based corrosion testing carried out in the laboratory (**Section 2.6.1**) are setup for isothermal conditions whereby any temperature gradient existing between alloy/scale/deposit layers may be considered negligible.

Also employing the furnace corrosion test setup adopted for this PhD, Potter [113] reported a temperature range of $\pm 6.35^{\circ}\text{C}$ within the 6 cm extremities of the furnace hot point (at 700°C). This equates to a temperature variation of $\sim 1^{\circ}\text{C}/\text{cm}$. In a combustion plant, the difference between the steam temperature in a HX pipe and its fireside exposed surface is $\sim 50^{\circ}\text{C}$ [24]. With a pipe thickness $< 5\text{mm}$ [9], [119], a much larger temperature gradient exists across the pipe thickness than a coupon sample thickness (coupons employed in corrosion furnace test).

Lindberg et al. [17] employed cooled samples probes in a furnace to investigate the temperature gradient effect on condensate transport and deposit morphology at a tube surface.

Niemi et al. [105] investigated the effect of temperature gradients on eutectic melt formation. The experimental setup included alloy ring samples inserted on a probe which enabled cooling of the rings from beneath while their deposit coated surface experienced a higher temperature (exerted by the walls of a furnace which encased the probe). Localised species within the deposit layers were noted, however, (as also for Lindberg et al. [17]), the extent of metal corrosion variations (compared to that occurring under isothermal exposure) was not determined. The influence of heat gradients on fireside corrosion of steels thus require investigation.

2.7 Summary

This literature review has pinpointed the importance of biomass/waste combustion as a means of renewable energy production (**Section 2.2**). It has collated a catalogue of challenges associated with use of these fuels for combustion purposes in power plants (**Section 2.2.5**). This review also highlights

the challenges of reliance on conventional renewable fuels such as virgin wood (**Section 2.2.3**). As such, other biomass/waste fuels have, and may gain further, interest for sustaining combustion-based power-generation in a more sustainable manner (**Section 2.2.4**).

The use of less conventional fuels, however, further increases the knowledge gaps existing in operational performance optimization, with a major concern being fireside corrosion. This thesis thus focuses on improving the understanding of the fireside corrosion influences of biomass/waste combustion fuels. As these combustion fuels are highly varied, the thesis addresses fuel behaviour using a fuel category outlook (rather than single specified fuel types), whereby any fireside corrosion peculiarities of a fuel group may be identified and corrosion trends within the fuel group can be assessed. Literature (e.g., [35], [38], [75], [114], [115], [123]), commonly provide fuel or deposit/component specific data which may not address fireside corrosion mechanisms prevalent in renewable fuel blends (or categories). Using combined fuels when firing is, however, becoming a more common practice for biomass/waste combustion plants, especially where fuel shortages exist. (**Section 2.2.4**).

Current corrosion mechanisms related to particular compounds, established for their roles in fireside corrosion, have been documented in **Section 2.5.3**. The review has, however, identified a knowledge gap, regarding the limited data on the specific fireside corrosion role of heavy metals associated with biomass/waste (**Section 2.5.3.4**). The role of such elements in fireside corrosion need investigation, as such this thesis has carried out evaluations for selected heavy metal elements associated with the biomass/waste.

The review also highlights there may be a need to simulate fireside exposure conditions more closely when replicating fireside corrosion tests in the laboratory (see **Section 2.6.2**). This research thus explores a laboratory test setup which investigates corrosion in non-isothermal conditions (see methodology, **Section 3.5**), enabling corrosion damage data generated from this setup to be compared with data obtained from isothermal exposures, such as

conventionally employed for fireside corrosion testing [37], [111], [119], [127], [152].

3 Methodology

The procedures carried out during the work stages to meet the individual PhD objectives are described in this chapter. In brief, the work stages are listed as points a-d below:

a. Fuel categorisation and pre-selection (linked to Objective 1, **Section 3.1**)

A review was carried out to select which of the categories would be evaluated. This involved assembling a database of biomass and waste fuels. These fuels were grouped into categories, based on their type (for example, waste type). The fuel data selected in this point served as input to thermodynamic calculations (see point b) and, after this, were used to set parameters in the corrosion tests needed to evaluate fuels fireside corrosion behaviours (see points c and d).

b. Thermodynamic simulation of post-combustion compounds (linked to Objective 2, **Section 3.2**)

The Metallurgical and Thermochemical Databank multiphase thermodynamic software (MTData) was selected to simulate each fuel category's post-combustion releases at specific temperatures. The compositions of key condensed phase (KCP) compounds and gases, in relation to HX corrosion, were fed into the corrosion simulation and evaluation work stage (for points c & d). Using the MTData calculations, synthetic deposits and test gas compositions were formulated for carrying out corrosion testing.

c. Fireside corrosion investigation of fuel categories (linked to Objective 3, **Section 3.3** and **Section 3.4**)

The corrosion damage induced by the deposits were evaluated using the well-established deposit-recoat method [16], [36], [127], [153] in an atmosphere controlled corrosion furnace (**Section 3.3**). The corrosion testing and analysis phases were as follows:

- i.) Deposit and test gas formulation using MTDData calculations
- ii.) Alloy sample preparation and pre-measurements
- iii.) Deposit application, furnace exposures (recoat, and cycling)
- iv.) Post-exposure alloy preparation for analysis
- v.) Post-exposure alloy analysis

Thermogravimetric analysis of the formulated deposits derived from point b was carried out (**Section 3.4**) to study their evaporation rates to support the investigation of the corrosive influences of the deposits.

- d. Evaluation of novel corrosion testing technique (linked to Objective 4, **Section 3.5**)

An air-cooled probe was configured for furnace testing to evaluate the corrosion of T91 steel rings (probes), subjected to a temperature gradient of $>50^{\circ}\text{C}$ difference across its wall thickness. This contrasts with corrosion tests carried out under Objective 3 (point c) which were setup under isothermal conditions such that no appreciable heat gradient existed across samples. The exposure conditions (gas and deposit chemistries and metal surface temperature on the deposit-covered side) employed in part d were matched with one of the samples analysed in Objective 3 (point 3) to enable comparison.

3.1. Fuel categorisation and pre-selection

A database of biomass and biomass waste fuel data was compiled, consisting of the ultimate, proximate and chemical analysis of minor and trace element compositions for over 120 fuels. Fuel data were sourced mainly from the ECN Phyllis 2 biomass databank [25] and reported in **Section A-1** along with the ECN Phyllis 2 fuel reference numbers, were applicable. References are also provided for fuel data collated from other sources.

3.1.1. Fuel data sourcing and collation

Data were sourced in either 'as received' (ar), 'dried basis' (db) and/or 'dried ash-free basis' (daf) formats. Major elements, C, H, N, O, S and Cl (ultimate analysis) were expressed as percentage weight (wt.%). The moisture, ash, volatile matter, and fixed carbon contents (proximate analysis) were also expressed in wt.%. Elemental compositions of minor elements were expressed in mg/kg fuel db. The minor elements were those with concentrations >100 mg/kg, excluding the major elements. For all categories, these elements were Al, Ca, Fe, K, Mg, Na, P and Si. The trace elements were also presented in mg/kg of fuel, db. Their concentrations in fuel were <100 mg/kg. For all fuel categories, these elements were found to be Ti, As, B, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se, Mn, Sr, V, Sn and Zn.

3.1.2. Fuel categorization and selection

The fuels were grouped into categories based on their sources and physical properties. For example, fuels typically grown as energy crops, waste wood generated fuels, agricultural plant waste, and industrial food waste (plant based) fell under four separate categories. All fuel groups fell within waste sources or were specifically grown fuels.

All fuel data encountered were integrated in this initial data collation stage. To define the scope of this research, and to target the completion of the project within the PhD allocated timeframe, currently employed and potential fuel categories were carefully selected during this research. The fuel category selection process was influenced by fuel usage projections (as combustion fuels), where consultation with the PhD project industrial sponsors was sought. Categorization decisions were finalised following consultation with the project's industrial stakeholder. The meeting minutes and a fuel selection justification report can be found in **Appendix F**.

3.1.3. Fuel category statistics

The median, mean, maximum and medium elemental values for each selected fuel category were calculated from the collated fuel database. The high and low heating median values (ar and db) were calculated from the median fuel values using the formulas in **Equation 18** to **Equation 21** [25].

$$\begin{aligned} HHV_{(ar)} = & 0.341C_{(ar)} + 1.322H_{(ar)} - 0.12O_{(ar)} - 0.12N_{(ar)} \\ & + 0.069S_{(ar)} - 0.153A_{(ar)} \end{aligned} \quad \text{Equation 18}$$

$$\begin{aligned} HHV_{(db)} = & 0.341C_{(db)} + 1.322H_{(db)} - 0.12O_{(db)} - 0.12N_{(db)} \\ & + 0.069S_{(db)} - 0.153A_{(db)} \end{aligned} \quad \text{Equation 19}$$

$$LHV_{(ar)} = HHV_{(ar)} - 2.442 \left[(8.936 H_{(ar)}/100) + (M_{(ar)}/100) \right] \quad \text{Equation 20}$$

$$LHV_{(db)} = HHV_{(db)} - 2.442 \left[(8.936 H_{(db)}/100) + (M_{(ar)}/100) \right] \quad \text{Equation 21}$$

LHV: Low heating value, MJ/kg

HHV: High heating value, MJ/kg

ar: As received

db: Dry basis

A: Ash content

M: Moisture content

3.2. Thermodynamic simulation of post-combustion compounds

The fireside corrosion influence of combustion fuels are related to their gaseous releases which could potentially form condensates on HX surfaces [13]. To understand the corrosion behaviour of fuels, a necessary step would be to determine the combustion releases particular to each fuel category [96]. Products from thermodynamically feasible chemical reactions occurring in a defined system can be determined by simulations. Thus, the generated species, which may be formed post-combustion, were determined for each fuel category by thermodynamic software simulations.

3.2.1. MTData application

MTData software uses a robust algorithm for the assessment of thermodynamic data whereby the equilibrium phases in a system are determined. The equilibrium calculations are based on the Gibb's free energy minimization principle. These calculations have been found applicable to this research in the computation of chemical compositions at specific temperatures in multi-component systems. The MTData MULTIPHASE module has been employed. The module calculates equilibria of the phases occurring within a system of components and particularly includes a combination of gases, molten and solid salts, aqueous solutions, and pure stoichiometric components. Such phases and components are required for the post-combustion simulations [101], [154].

The MTDATA database accessed generated comprehensive ranges of compounds, phases and their compositions within the set temperature range (300°C to 1300°C) and these were:

- (i) SGTE Solution Database for the calculation of the compositions of phases. This database consists of non-ideal solutions data with over 450 binary phase systems, as well as ternary and higher-order phase systems' combinations.
- (ii) SGTE Pure Substance, which enabled the calculation of the Gibbs free energy as a function of temperature. This database consists of pure substance phases' data, such as their standard entropy at 298.15 K, element enthalpy of formation and specific heat capacities to enable thermodynamic calculations.
- (iii) SGTE Unary Database enabled the calculations of stable phases occurring from 298.15 K using data from more than 70 elements.

3.2.2. Post-combustion simulation parameters

Standard atmospheric condition was specified for all simulations. The simulation input data assumed a 1 kg/hour fuel feed rate. The input data also made allowance for air composition, based on air-combustion requirements. As such, air/fuel ratios were adjusted to achieve a 7-8 mole percent (% moles)

excess oxygen yield in the simulated flue gas composition; this being an operational target for ensuring complete combustion during biomass firing [20]. To accommodate air, both fuel (median category values) and air data were expressed as total moles of elements (where fuel input was maintained at 1 kg). The simulation input data was thus elemental moles of all elements entering the system. The calculations of total element moles fed into thermodynamic simulation for each fuel category are documented in **Section A-3. Table A-8** provides the input data of all simulations carried out in this study.

3.2.2.1. Post-combustion simulation based on category median values

The use of mean values was avoided to limit errors that would be caused by extreme element concentrations. Instead, median element concentration values were employed. The fuel category median values (ar) of the six ultimate analysis elements (C, H, S, O, N and Cl) and eight minor elements (Si, Al, Ca, Mg, K, Na, Fe and P) served as inputs for the simulations to generate the post-combustion release compositions for each fuel category. The simulations of median element value inputs of 14 element systems (14ES) provides each fuel category's 'base composition' of post-combustion release. The variations of simulation input values provided other compositions within the fuel category.

3.2.2.2. Post-combustion simulations based on fuel categories varied element concentrations and the impact of trace element addition to simulations

To investigate the influences of varying the element concentration ranges within the fuel categories, specifically for those elements with key roles in fireside corrosion [155], other MTDData simulations were performed, in addition to the category base (14ES median values) simulations (**Section 3.2.2.1**). In this case, the 14ES simulations were carried out with 13 elements maintained at median values while varying only the fourteenth element from its median value to explore the impact of its extreme fuel category concentration. This was carried out, in

turn, for each of the 14 elements, however, only those which influenced the simulation outputs were presented in this thesis.

To investigate the influence of trace elements on post-combustion release for each category, 14ES+1 (15ES) (median values) inputs were employed for thermodynamic simulations, where the additional element was the trace element. The trace elements assessed were those whose data were available for the fuels listed in **Table A-1**.

3.2.3. Key post-combustion data selection criteria

The MTData simulation outputs represent the post-combustion data for each assessment and were expressed in moles/kg of fuel. These output concentrations were yielded across a specified temperature range, 300-1300°C, covering the data range applicable to gas and condensed phases at a HX vicinity (1000-1200°C) and surface (450-600°C) [24].

All possible output phases that could be calculated by MTData were selected. This generated 900-1000 phase species and compounds' composition data per temperature interval for each simulation. A selection of a fuel category's simulated post-combustion output by MTData is displayed in **Figure A-1**. A data processing phase was thus required to narrow down the number of species obtained and, enable the selection of compounds with fireside corrosion influencing tendencies based on assumptions explained in **Section 3.2.3.1** and **Section 3.2.3.2**.

3.2.3.1. Gas phase selection

- i. Gas phase compounds with concentrations below 1×10^{-5} moles/kg of fuel were omitted. In addition to data simplification, gas compositions below this range would fall below the calibration range of the gas flow meters which would later be employed for corrosion tests. Such low concentrations are also beyond the calibration specification of the gas

cylinder supplier. Therefore, the use of trace gas concentrations would introduce experimental errors which may impact the validity of test data.

- ii. Gas phase compounds selected for corrosion testing were those present at 1100°C, being an average flue gas temperature condition occurring at the vicinity of HXs [20], [24].

3.2.3.2. Key condensed phase selection

The term 'condensed phase' is used, as the MTDData software version employed does not distinguish between solid and liquid states which make up deposits.

Condensed phase compounds with concentrations below 1×10^{-5} moles/kg of fuel were omitted. This enabled further data simplification, allowing focus on the dominant species for each fuel category.

- i. A molten phase is typically required for fireside corrosion. Condensed phases not present within 400°C to 600°C were not considered, this being the typical HX fireside surface temperature range maintained in biomass power plants [20], [24]. Thus, species not present in their condensed phase at this HX temperature range cannot be molten within this temperature range.

Condensed phases present at 450°C to 600°C but maintaining stable concentrations or transiting to other condensed phases that have stable concentrations beyond 1100°C (average temperatures at HX vicinity) were not considered. It is expected that these compounds will not be molten at the target test temperatures (within 450-600°C) as such, limiting their ability to participate in corrosion interactions.

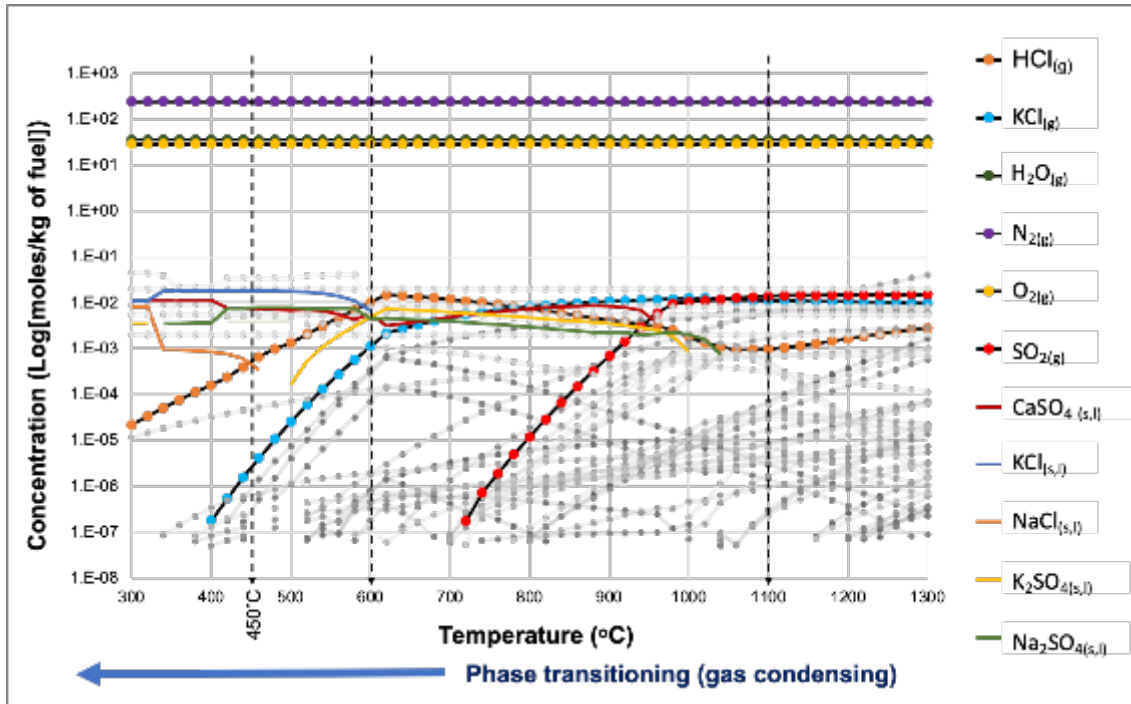


Figure 3-1: MTData calculated post-combustion outputs of a biomass fuel category. The black lines with coloured markers are selected gas phases. The coloured lines with no markers are the selected condensed phases

It is expected that a condensed phase component present between 450-600°C represents the total concentration of that compound at a specified temperature. As such, the present gas phase (at 1100°C) of the condensate would not be included in the gas composition. Examples of condensed phases (coloured lines with no markers) and gas phases (coloured lines with markers) meeting these selection criteria are illustrated in **Figure 3-1**.

The following assumptions were also made when selecting the KCP compounds of corrosion concern:

- i.) Condensed phases which meet the selection will have a liquid phase present within 450-600°C.
- ii.) Compounds (and their varied oxidation states, for e.g., CaMgSiO_6 and CaMgSiO_4) which maintain their condensed phase concentration

between 450-1100°C are in solid phase within 450-600°C and will promote little to no corrosive damage while in solid phase.

3.2.4. Interpreting thermodynamic simulation graphs

Cooling is experienced by combustion products, in combustion plants, as they travel along the flue gas path from the hottest zone. MTDData simulation results have thus been interpreted as phase transitioning from gas to condensed phase, as shown in **Figure 3-1**. The resulting data has been presented in post-combustion species mole/kg of fuel against the simulation temperature range resulting in a range of condensed and gas phase profiles.

3.3. Furnace corrosion tests

This section describes the methods adapted for carrying out laboratory-based corrosion furnace testing and evaluating the corrosion damage undergone by each sample. The corrosion test plan is listed in **Section 3.6**.

3.3.1. Deposit and test gas formulation

The KCP and 'key gas phase compound' compositions derived for each post-combustion simulation from the processes described in **Section 3.2.3.1** and **Section 3.2.3.2** were employed in the formulation of deposits and test gas compositions. These formulations thus represent the compositions of potentially corrosive fractions of deposits and gas exposure conditions experienced by a HX surface during firing. These mixes were determined for each fuel category.

3.3.1.1. Deposit formulation

The selected condensates (**Section 3.2.3.2**) compositions were normalised to 100 mol.%. The resulting deposit compositions employed for the corrosion tests are presented in **Table 4-6**. Pure salts (>99% purity) were

employed for mixing up the synthetic deposits. The salts were mixed in thick slurries using deionised water to enable homogeneous sampling of the mixtures. Eight deposit mixes in total were made to represent deposits from different fuel categories. The slurries were each stored in sealed plastic bottles to retain moisture and prevent contamination.

3.3.1.2. Gas formulation

The gas feed rates required to achieve each gas mix were calculated and are documented in **Section A-4**. The molar outputs of gas compounds selected (**Section 3.2.3.1**) were balanced with N₂ (mol.%). Gas cylinders were supplied as CO₂/O₂/N₂, HCl/N₂ and SO₂/N₂. A peristaltic pump supplied moisture to the test furnace at a rate corresponding to the simulated gas moisture content occurring at 1100°C, also detailed in **Section A-4**. The gas compositions representing flue gas conditions at 1100°C, and employed for the corrosion tests, are listed in **Table 3-3**.

3.3.2. Candidate material

Two candidate materials were selected for corrosion testing; an austenitic steel, TP 347HFG, and a ferritic steel, T91, used in high temperature combustion plant applications [156]. The use of two alloy materials allowed comparison of their responses to the test parameters and deposit mixes. **Table 3-1** presents the nominal elemental compositions of both alloys.

Table 3-1: The nominal compositions in weight percent (wt.%) of T91 and TP 347HFG employed for corrosion tests [127], [157]

Material	C	Cr	Ni	Mo	Mn	V	Nb	Fe
TP 347HFG	0.07	18.0	10.0	-	2.0	-	1.0	Balance
T91	0.14	9	0.4	1	0.5	0.25	0.1	Balance

3.3.3. Alloy sample preparation and measurements

This activity involves cleaning, pre-exposure measurement, and deposit coating (**Section 3.3.4**) of the alloy samples prior to the furnace exposure. A contractor was employed to cut the alloy samples from long tubes, firstly into cross-sectioned rings, then into curved coupons of approximately 1.5 cm chord length x 1.5 cm height and ~ 0.5 cm wall thickness. The coupons' surfaces were ground to a UK 600-grit finish and a mid-reference point was drilled into one side. This circular shallow hole enabled the identification of the coupon mid-line during sample measurements. An example of the cut samples is presented in **Figure 3-2**.



Figure 3-2: An alloy tube, ring, and curved samples [111]

The coupon pre-exposure dimensional measurements were required for calculating the deposition fluxes for salt application, and later on for calculating the metal thickness change to analyse the extent of corrosion damage. Prior to measurement, the coupons were cleaned in two stages. To remove any oil-based contaminants, the coupons were placed in a beaker of acetone, which was placed in an ultrasound bath for 10 minutes. Next, the samples were transferred to a

beaker of propanol and again placed in an ultrasound bath for 10 minutes. This further removed contaminants and any acetone left on the coupons. Crucibles, which served as the sample holders for positioning in the furnace, were cleaned in the same sequence after being water washed. All samples were allowed to air dry prior to measurements.

Dimensional measurements of each sample were carried out using a digital micrometre with a resolution of $\pm 1 \mu\text{m}$. Three measurement points each were taken for the thickness, length, and breadth as shown in **Figure 3-3**.

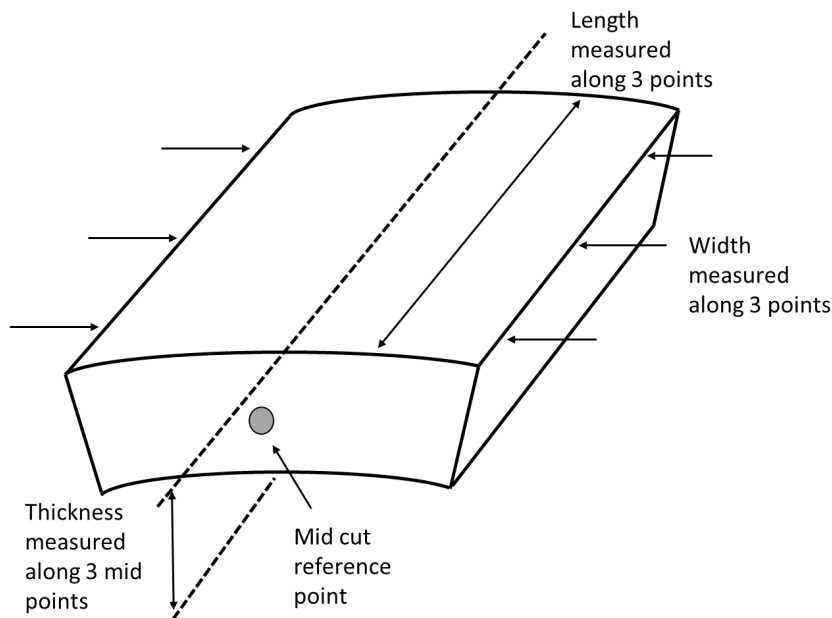


Figure 3-3: Illustration of dimensional measurement positions

3.3.4. Sample coating and furnace cycling

3.3.4.1. Deposit application: deposit recoat technique

A number of studies have used the deposit recoat method for hot corrosion tests [24], [36], [158] and this research has adopted its application as well. In this method, deposits are applied up to a specified flux for each furnace cycle. This is done at the start of the cycle and re-applied between furnace cycles until the desired exposure lengths are achieved. Each furnace cycle was maintained at

100 hours and the maximum exposure time any sample received was 1000 hours.

Coupons were weighed using a calibrated balance ($\pm 10 \mu\text{g}$ resolution) prior to deposit coating, and placed on a hotplate to heat up between 100-120°C. The mixed salt slurries, representing deposits, were spread over the convex surface of the coupon using a spatula. The heated coupons facilitated quick drying of the deposit slurry. Re-application and subsequent drying of the samples followed by reweighing were repeated until the required deposition fluxes were achieved (within a $\pm 10\%$ error margin). Each sample was placed in the crucibles and the overall weight was measured for identification of samples by mass if needed, after which samples were set for a 100-hour furnace cycle.

3.3.4.2. Furnace temperature profiling

Prior to testing, the hottest zone of the furnace was determined to allow the positioning of the samples within $\pm 5^\circ\text{C}$ of the target temperature. The furnace controller was first set to the test temperature then a graduated thermocouple was used to measure the actual furnace temperature and the corresponding position within the furnace liner. This was repeated for each test program following post-test cleaning of the furnace liner with water. Temperature profiling enabled the factoring of the difference between the temperature controller reading and the measured furnace hot zone temperature.

3.3.4.3. Furnace operation

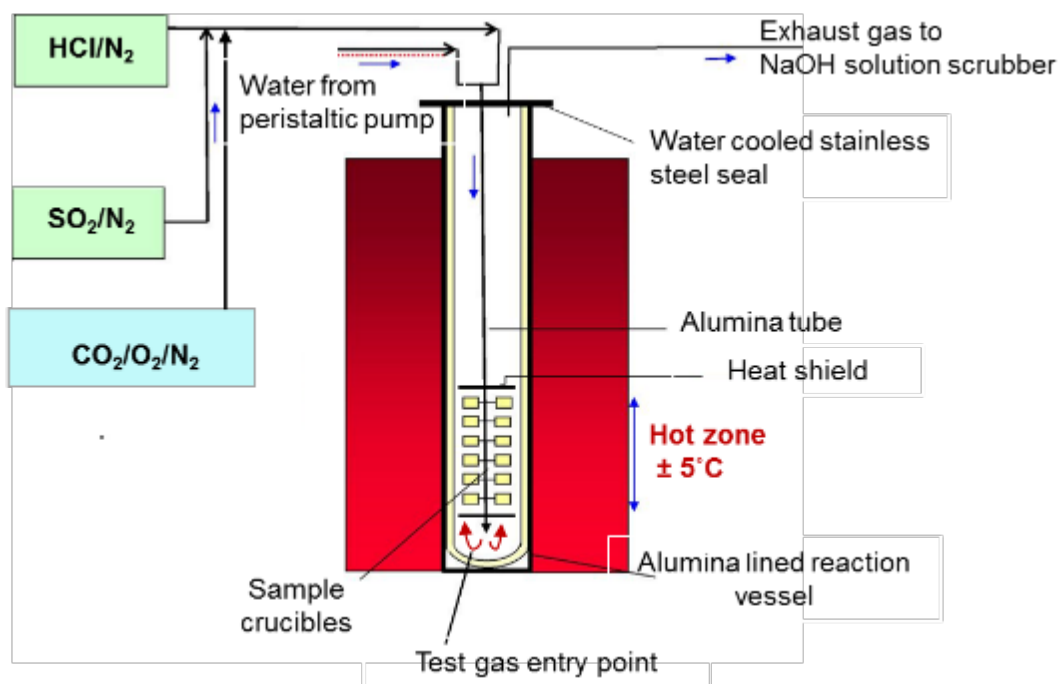


Figure 3-4: A schematic representation of the furnace test setup [111]

Each furnace cycle (100 hours, not including heating and cooling times) was set at a 6°C/min heating program ramp to avoid thermal shock and cracking of the ceramic components. The sample crucibles were placed on ceramic plates fitted within the furnace liner. The exposure tests were conducted in the ceramic-lined reaction vessel of a vertically positioned furnace. **Figure 3-4** shows the furnace and apparatus setup used for the corrosion tests. Test gases, metred by mass flow controllers, and water, introduced from an adjustable flow rate cylindrical or peristaltic pump, were passed through the furnace seal via a central ceramic tube entering at the bottom of the corrosion vessel and exhausting from the top. The exhaust gas was fed through a NaOH scrubber solution to remove acid gas, such as HCl before being expelled to the building exterior.

Following the tests, the samples were removed after the hot zone had sufficiently cooled (<150°C). **Figure 3-5** shows an example of a deposit-coated pre-test and post-exposure sample. Following each 100-hour furnace cycle,

sample to be re-inserted to the furnace were re-coated by repeating the initial deposit application technique.



Figure 3-5: Deposit coated sample before and after 1000 hours exposure

3.3.5. Post-exposure alloy preparation for analysis

Dimensional metrology and image analysis of the corrosion samples required the coupons to be mounted in a rigid structure to secure corrosion products and any remaining deposit on the alloy surface. The positioning of the coupon within the mount also ensured correct cross-sectioning of the sample length (**Figure 3-3**) and facilitated its handling and positioning during analysis. It was necessary to cross-section the coupon samples such that corrosion depth was measured on a freshly exposed surface.

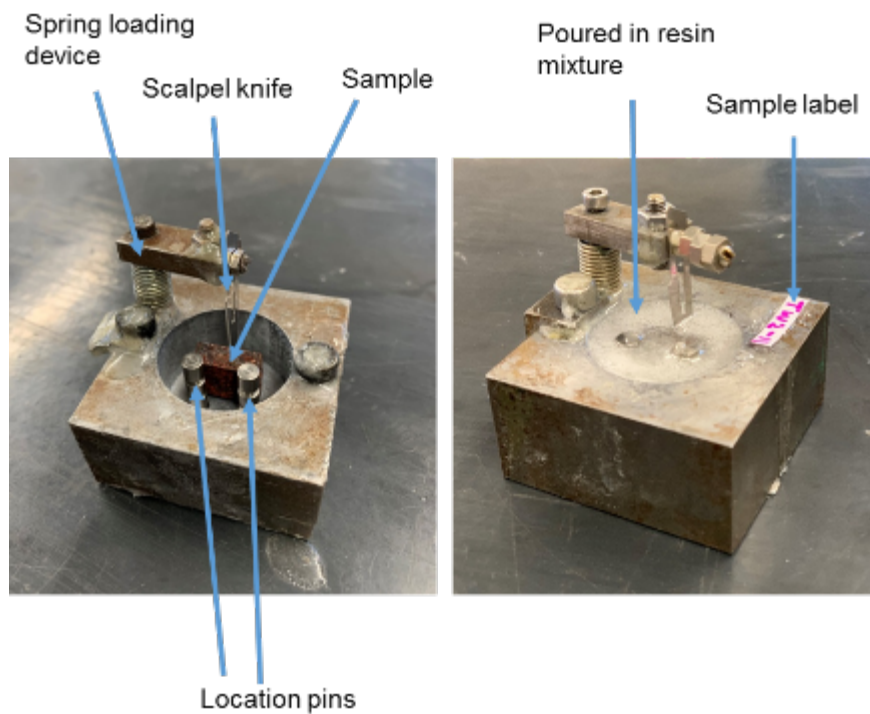


Figure 3-6: Post-exposure sample resin-mounting in a jig

Sample mounting was achieved using a jig, shown in **Figure 3-6**, which secured the coupon in position while it was fixed in a cold setting epoxy resin mixture. The sample was supported in a vertical position by the aid of two locating pins and a spring-loaded scalpel blade to ensure the coupons were cross-sectioned along the intended plain. The mid-reference point of the coupons faced an orientation opposite to the mounting pins, pointing towards the scalpel blade spring. The encasing resin was prepared with silica beads of an average diameter of ≈ 0.055 mm to reduce the shrinkage of the setting resin, which could have an effect on the fragile sample surface scales. Following the fixture of the samples in the jig setups, the units were exposed to a low vacuum for three minutes to minimise the presence of trapped air bubbles in the resin mixture, which could cause undesired air pockets at the sample surface. The resin mixture was left to set over a period of 24 hours, following which the resin mounted sample was removed from the jig.

A precision saw consisting of a diamond blade and an aligned sample holding vice was employed for cutting the samples. The ends of the locating pins

allowed positioning of the samples on the aligned vice at right-angle to the blade, while in operation. A cutting lubricant, which also served to keep the sample cool, removed debris from the blade-sample interface. To target the middle cross-section plain of the sample, the cut was positioned slightly (≈ 2 mm) above the midpoint of the sample to account for the metal loss during later grinding and polishing.

Table 3-2: Grind grits and polish sizes used during post-sample preparation

Grind grit (μm)	Run time (seconds)	Rotation speed (rpm)	Grind/Wheel Direction
120	150	125	opposite
240	150	125	opposite
1200	120	125	same
2500	120	125	same
6	80	120	same
1	60	120	same

Stages of grinding of the cut sample surface were carried out using different sizes (in a descending order format) of silicon carbide papers with a lubricant oil, followed by polishing with an abrasive polishing compound. The grinding and polishing grades are listed in **Table 3-2**.

Samples were cleaned with oil and stored in small sealable bags for shorter intervals, while samples were still being analysed, and stored in airtight units after analysis. At no time were samples exposed to aqueous fluids, thus limiting contact with moisture.

3.3.6. Post-exposure alloy analysis

Dimensional and weight change data of the post-exposure samples were generated from the corrosion tests. The mass change data were not used for corrosion evaluation as the unpredictable nature of spallation occurring on the samples limits its reliability in measuring corrosion. Corroded surfaces could become loose and fall off some samples while remaining on others, thus affecting the weight change data. Mass change also does not give much indication of internal damage. Dimensional measurement proved more useful in determining the extent of metal change resulting from the tests.

3.3.6.1. Dimensional metrology

Dimensional metrology was used to determine the new/regressed metal surface position (metal/scale interface), which was then compared with the pre-exposure dimensions measured with the micrometre. The sample was mounted on the motorised stage of an optical microscope with a 20x magnification lens and a digital image analyser controlled by Axion Vision software. The motorised stage consists of x-y coordinates with a location accuracy of 1 μm . The software produced sets of micrographs at a set number of equally spaced points around the perimeter of the sample. x-y coordinates were collected for each micrograph, ensuring that no fewer than 25 data points were positioned along the alloy edge for all samples. The instrumentation enabled the location of metal surfaces and the depth of internal damage occurring beneath the surface. These features are shown in **Figure 3-7**. Note that the spherical features on the secondary electron (SE) images may also be seen on the energy dispersive X-ray (EDX) maps and show the positions of the ballotini spheres in the mount resin. For the metal damage surface being measured, the x-axis was fixed for each micrograph's measurements; hence all measurements were equally spaced across the metal surface. These x-y coordinates were entered into spreadsheets where they were compared with the original coupon dimensional measurements.

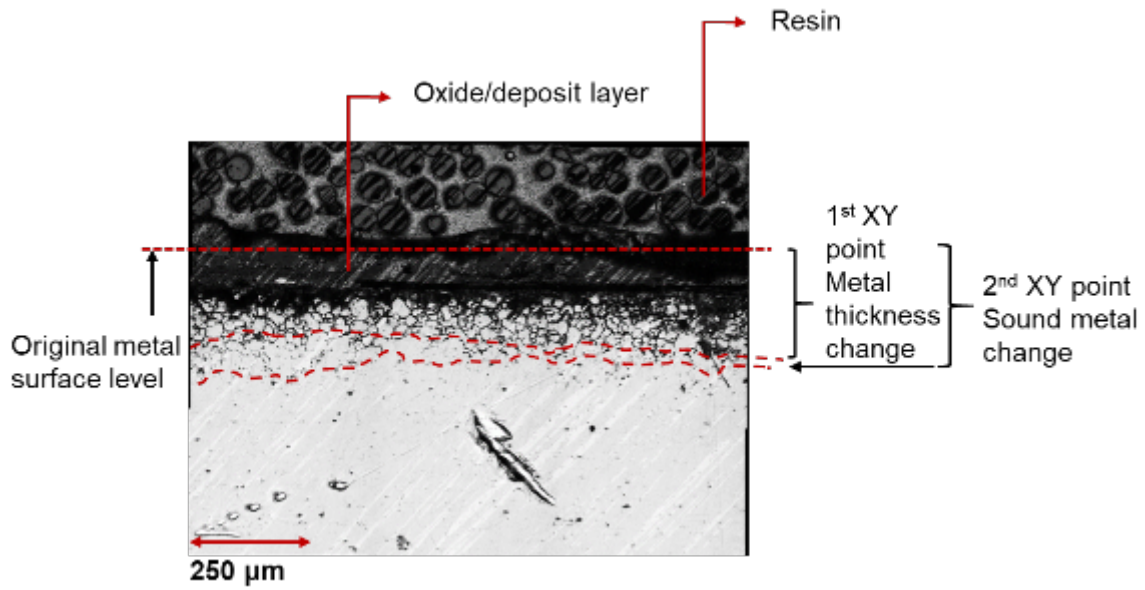


Figure 3-7: An example of a cross-section post-exposure sample image showing metal surface internal damage measurement plains. Note, the original metal surface location cannot be determined from the image, but only after dimensional metrology

The metal loss and sound metal change values were calculated by subtracting post-test sample measurements from the pre-exposed metal thickness measurements. Firstly, the orientation of the post-test sample was set to align with the pre-exposure measurements using rotational and translation sequences. A macro tool program rearranged the metal loss points in the order of a percentage cumulative probability (**Equation 22**) such that metal change data were ranked in order of magnitude as shown in **Figure 3-8**. The sound metal change coordinates were rearranged in the same format.

$$\text{Cumulative probabiity (\%)} = 100 \times N_r / (N_t + 1) \quad \text{Equation 22}$$

N_r : Rank order number

N_t : Total number of measurement points

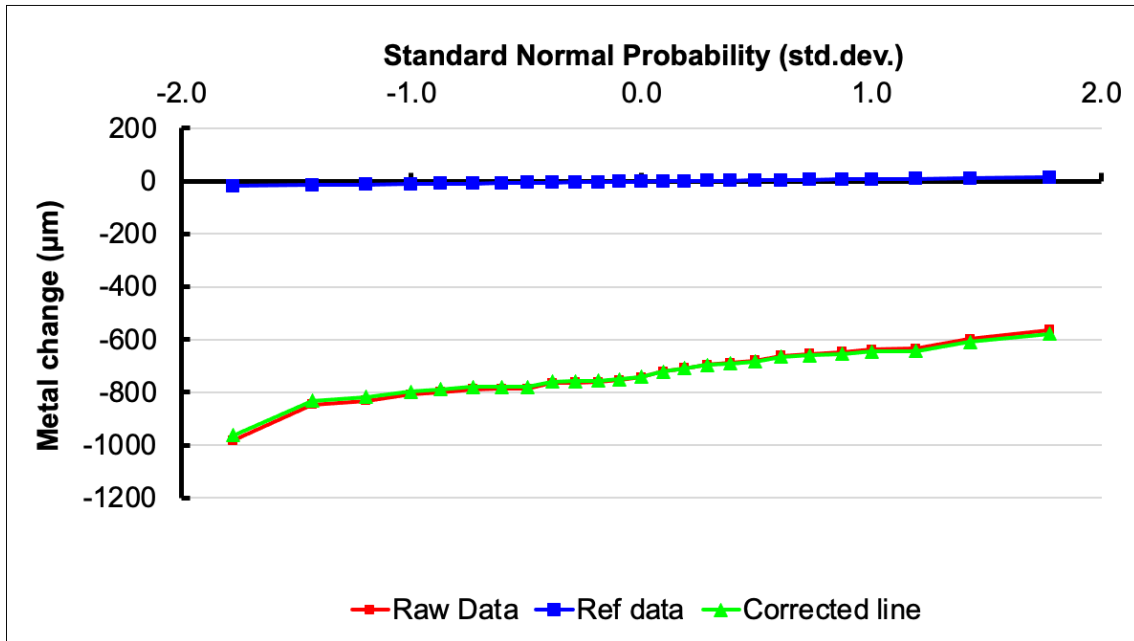


Figure 3-8: A metal change cumulative probability plot example showing raw, reference, and corrected data

Uncoated samples for each alloy type were used to provide correction factors to rectify metal loss data attributed to random and systematic errors. These samples were present in each corrosion test and exposed for 1000 hours (10 completed cycles). Reference sample measurements were also taken for bare unexposed samples to account for sample roughness, which could be mistaken as corrosion damage. The raw measurement data for each sample was thus expressed as a corrected measurement as shown in **Figure 3-8**.

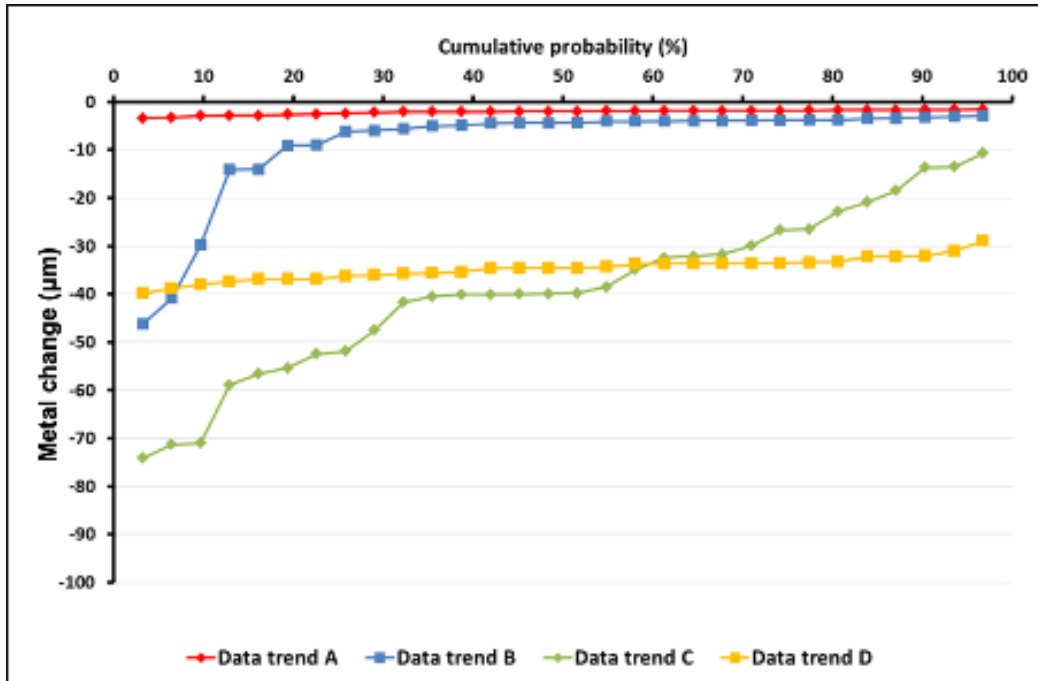


Figure 3-9: Metal loss cumulative probability plots for four datasets with distinct metal change features [113]

The corrected line data for various samples can be plotted together to compare degrees of metal loss and corrosion features. Using **Figure 3-9**, the cumulative probability plots of four corrosion datasets were compared by Potter et al. [113]. Each data point denotes the percentage probability of metal change exceeding the indicated value. Metal loss values are thus represented as a metal loss exceedance percentage value. The standard deviation from the mid metal loss value is proportional to the gradient, which gives indication of the range of metal change across the metal surface.

Dataset A shows a sample with no significant metal change. This is indicative of the sample surface having remained entirely in incubation during exposure. Scatter data inherent in the tests may be the main cause of metal change data seen and thus can be treated as negligible.

Data B expresses two distinct features. A majority of the metal surface has remained in an incubatory corrosion stage while a significant degree of metal loss, indicated by the steep gradient, occurs at lower probability levels. This

uneven distribution of metal loss is characteristic of pit features occurring across parts of the metal surface, which have proceeded to propagation corrosion stage.

Significant metal changes across the entire metal surface can occur with a combination of pits forming as represented by dataset C.

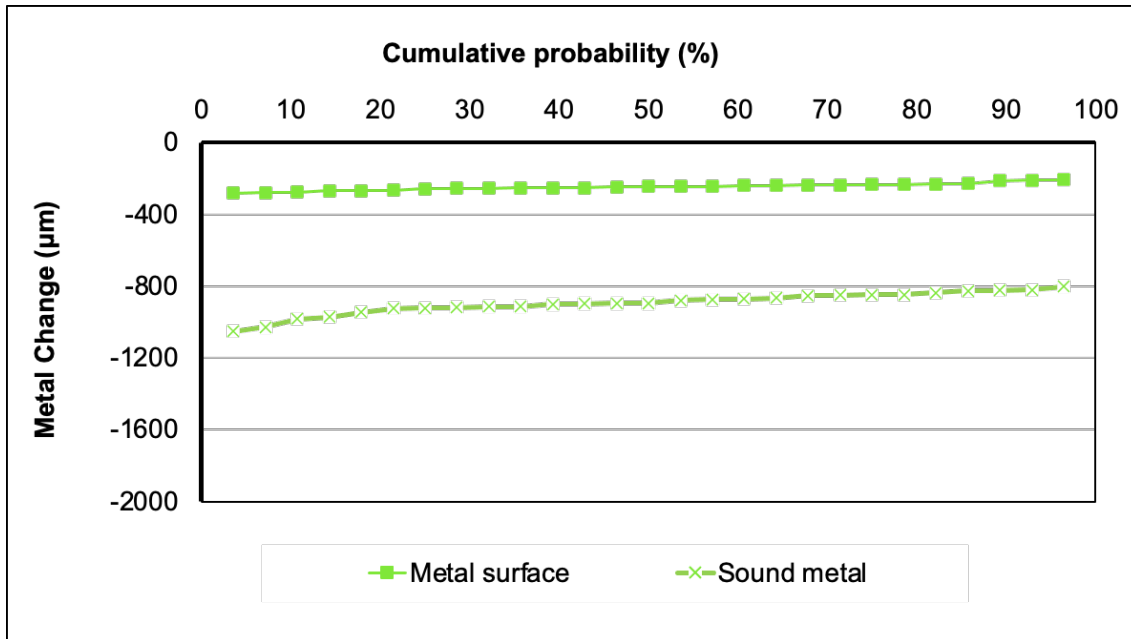


Figure 3-10: A cumulative plot example for a sample undergone severe internal damage

In addition, significant metal loss can occur with no distinctive pit formation seen post-exposure. In this case, metal loss is evenly distributed across the metal surface as represented in dataset D. The formation of several pits could occur initially, but as the sample is further exposed to a corrosive environment, areas with less metal depletion can undergo a faster rate of damage, thus evening out the corrosion distribution. The second x-y coordinate points were also plotted as cumulative probability plots to express the internal damage degrees detected with the microscope. Sound metal changes typically occur along grain boundaries. **Figure 3-10** compared metal surface changes and internal damage. For this

case, internal damage is severe as there is a significant depth of damage compared with the metal surface.

3.3.6.2. Microscopy analysis

The cross-section surfaces of the samples were analysed by a scanning electron microscope (SEM) to study the material changes occurring. The SEM was fitted with an energy dispersive X-ray (EDX) system, which was useful for elemental analysis. The sample surfaces were first coated with 10 nm of gold to improve its conductivity, therefore preventing the build-up of electrons on non-conductive deposits and corrosion products.

SEMs use a focused beam of electrons to scan a specimen. The electrons are able to excite the surface atoms of the specimen which then emit SE. These electrons are detected by the SEM leading to the provision of surface information of the specimen being examined. Interactions can occur between the primary beam of the SEM and the atomic nuclei of the specimen that have reacted in a quasi-elastic manner. The resulting electrons are reflected back and are called backscattered electrons (BSE) which can be detected by BSE detectors. The denser the elements of the specimen, the more strongly the electrons reflect, thus generating brighter images [113], [159]. This can be observed in **Figure 3-11** whereby Fe, with a higher atomic number of 26 is mapped in sections of lighter shades on the BSE image while O (atomic number 8) map corresponds with dark shaded areas. The BSE images have been used in this thesis as they provide information on the atomic number of distributed phases across the cross-sectioned specimen micrograph.

EDX was used to identify the elements present on the surface of the specimen. Electrons in the higher energy electron shells occupy the lower energy inner electron shells previously occupied by the now excited inner shell electrons. The energy difference between the two shells is emitted in the form of x-rays which are specific to each element [159]. An EDX detector receives these signals and scanned maps are created for each element. The emitted energy levels for

some elements can overlap, leading to some ambiguity; however, the element maps created for these were distinct. Though EDX can detect elements present, it does not determine the chemical formulas and thus cannot identify compounds present.

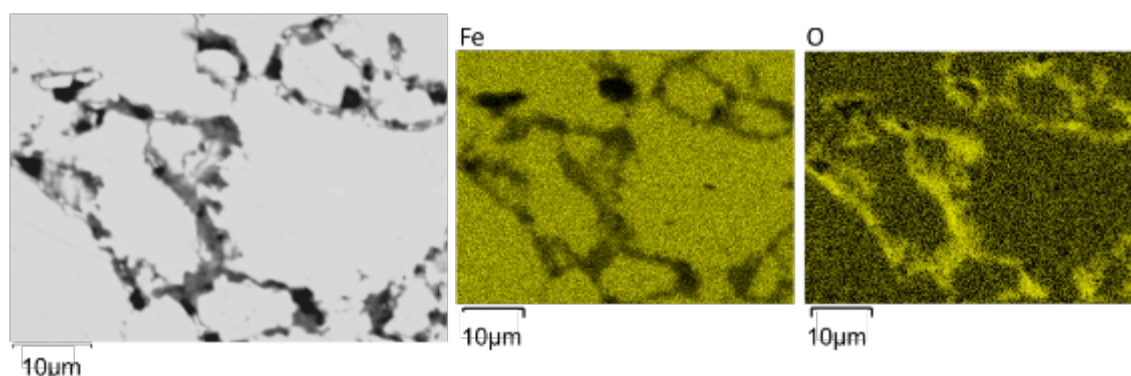


Figure 3-11: SEM BSE image (left) and EDX maps for Fe (atomic no. 26) and O (atomic no. 8) of a cross-section corroded 347HFG sample

3.4. Thermogravimetric analysis (TGA)

The SDT 650 operated by the TRIOS software (**Figure 3-12**) was employed for the thermal analysis of the deposit mixtures evaluated during this research. This analysis provides mass loss (or evaporation) rates of the deposits which can be used to support corrosion data evaluations by providing information on the possible phases present at the set temperature. The equipment is calibrated to a temperature precision of $\pm 0.5^{\circ}\text{C}$, a calorimetric precision/accuracy of $\pm 2\%$ and a weighing precision/accuracy of $\pm 0.1\%/\pm 0.5\%$. The instrument setup consists of an autosampler, a furnace unit and a connected computer processor for controlling the TGA operations and analysing the TGA data. The autosampler unit consists of a tray with 30 sample pan position slots. An empty ceramic pan is tared while positioned on a tray slot. A mechanised system loads/unloads and transfers each pan between the tray slots and the balance.

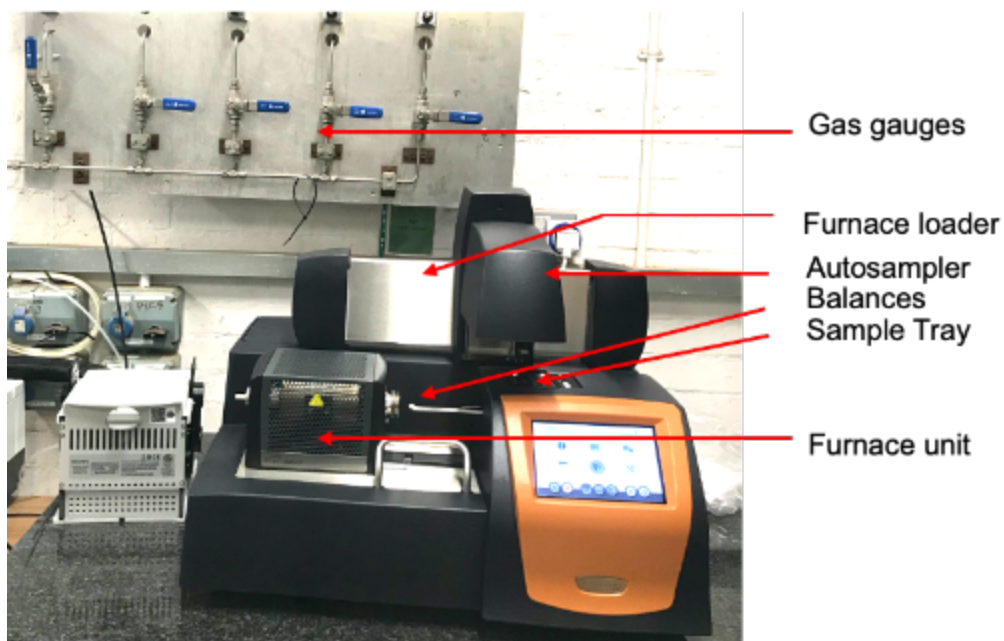


Figure 3-12: TA Instruments Discovery SDT 650 TGA instrument, Cranfield University

The gas employed for the tests was N_2 which enabled a simplistic comparison of the deposit evaporation rates. The gas flow rate was set at 100 ml/min which is the minimal flow requirement specified for setup, otherwise the SDT would not proceed with taring and analysis. The run program set for each sample analysis is described in **Figure 3-13**. The deposits were exposed at temperatures matching their corrosion evaluation exposure temperatures. The initial hold temperature (110°C) allowed time for the removal of any moisture left in the sample. The temperature ramp rate was set high, at $50^\circ\text{C}/\text{min}$, to limit changes in the deposit chemistry and/or to minimise evaporation occurring before the set test temperature was attained. However, this rate was low enough to prevent overshooting the desired test temperature. The ramp rate also matched that employed for the furnace corrosion tests. The 25 minutes hold duration at the test temperature was found to be sufficient for observing a steady mass loss rate.

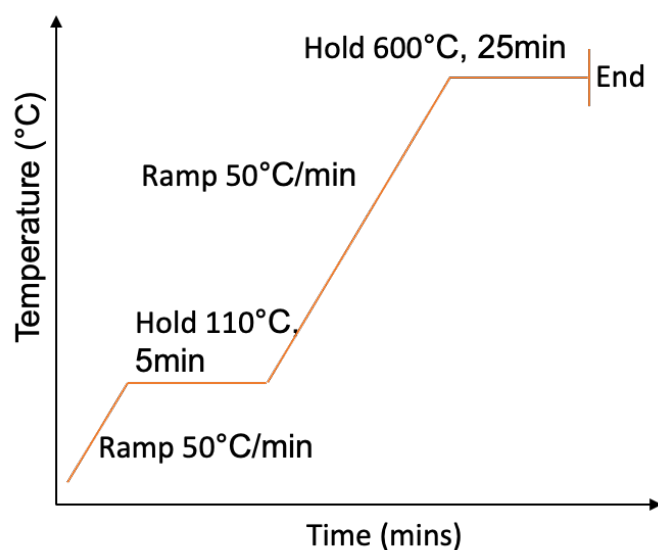


Figure 3-13: TGA heating program employed for deposit mass loss

The deposit samples tested in the TGA were from the same deposit batch employed for the deposit coating of the corrosion coupons (**Section 3.3.4.1**), as such samples were available as slurries. A 5 ml scooping spatula was employed for sampling from the slurry. The scooped specimen underwent drying in a ceramic dish placed on a hot plate ($\sim 80^{\circ}\text{C}$) for up to 60 minutes until all visible moisture had evaporated. Next, the resulting salt granules were crushed into a fine powder using a pestle.

The ceramic pan was tared following sequential cleaning with an ethanol spray for rinsing off residues and a blow torch to burn off any adhered contaminant. The taring program was initiated while the sample was placed in a set position on the sample tray. Next, the tared ceramic pan was half loaded with the dried deposit (25-40 mg), carefully ensuring the pan was not filled to prevent any of the salt being blown away by the gas flow. The loaded pan was then replaced at the same location on the sample tray to commence the analysis. The weight change and temperature trend data were exported to EXCEL for evaluation.

3.5. Novel heat flux corrosion testing

This modified furnace test was configured to evaluate the impact of heat fluxes on fireside corrosion damage. The setup introduces compressed air-cooling to corrosion samples via an 'air-cooled probe setup' while being heated from its outer surface by a furnace. As such, the sample experiences cooler internal surfaces, simulating the cooler steam sides and hence a tube wall heat flux is experienced by HXs.

3.5.1. Furnace test setup

Figure 3-14 demonstrates the compressed air and test gas currents within the air-cooled probe setup. For the air-cooling, compressed air (flow rate specified in **Section 3.5.2**) entry and exit connections are positioned at either ends of the probe. Inside the outer pipe is an inner tube which channels the air through the probe (**Figure 3-14**). The compressed air-tubing (inner tubing) enables air flow over the interior surfaces of the two interlocked samples. As such, the samples are cooled from their inner surfaces and heated from their outer surface during furnace operation. The outer and inner surface temperatures of the sample are determined by two thermocouples attached to the sample surfaces.

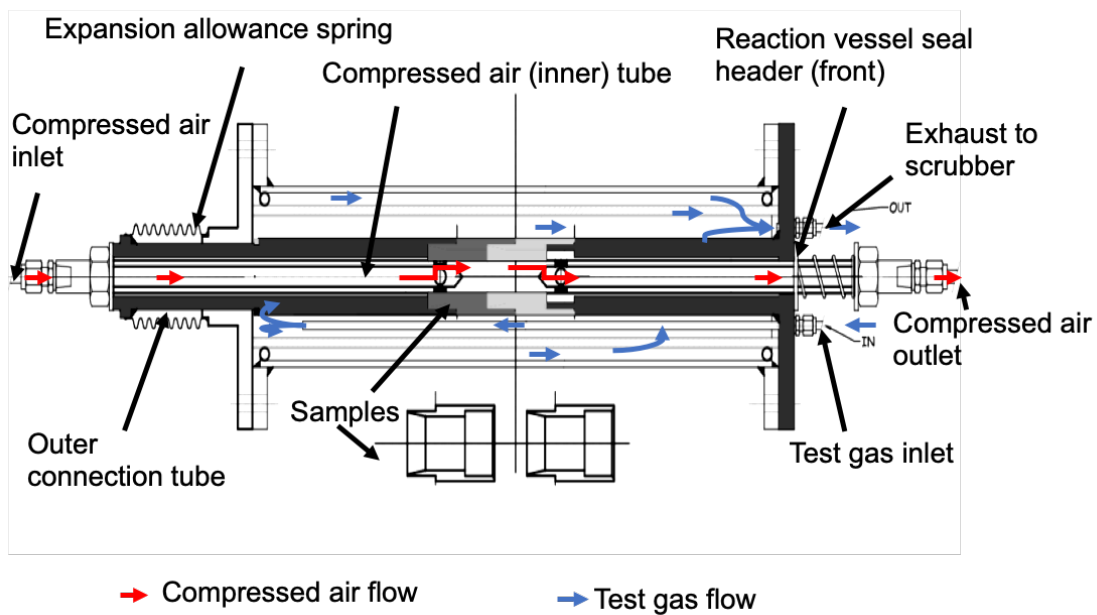


Figure 3-14: Schematic diagram of air-cooled probe setup displaying compressed air and test gas flow directions

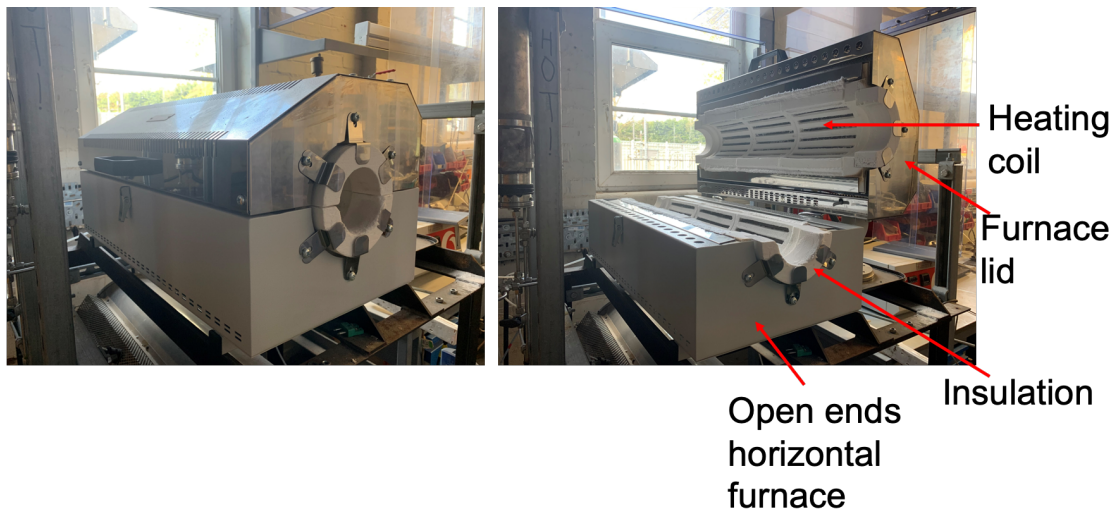


Figure 3-15: Horizontal corrosion furnace employed for air-cooled probe setup (left, closed; right open positions)

Similarities between the standard fireside corrosion furnace setup described in **Section 3.3.4.2** and this setup are: the exhaust connection which is

via a NaOH scrubber; the connection valves for test gas and moisture entry which are fed by mass flow controllers; and the use of a peristaltic pump (as employed in **Section 3.3.4.2**). The system consists of a horizontal furnace (**Figure 3-15**) and a steel reaction vessel with an alumina liner which can be opened and sealed at both ends to allow insertion of the probe (**Figure 3-16**).

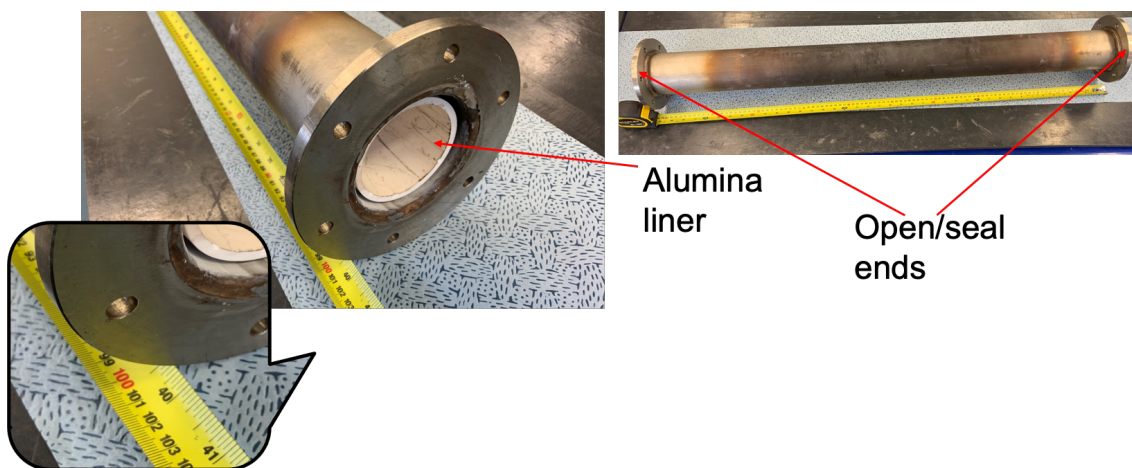


Figure 3-16: Reaction vessel showing sealing positions at both ends (length 101 cm)

The probe installation (**Figure 3-17**) is positioned in the reaction vessel. It consists of two interlocking T91 corrosion samples (dimension: ~40 mm exposure length by ~37.5 mm diameter, ~2.7 mm mean thickness) which are spring held between two other connection tubes.

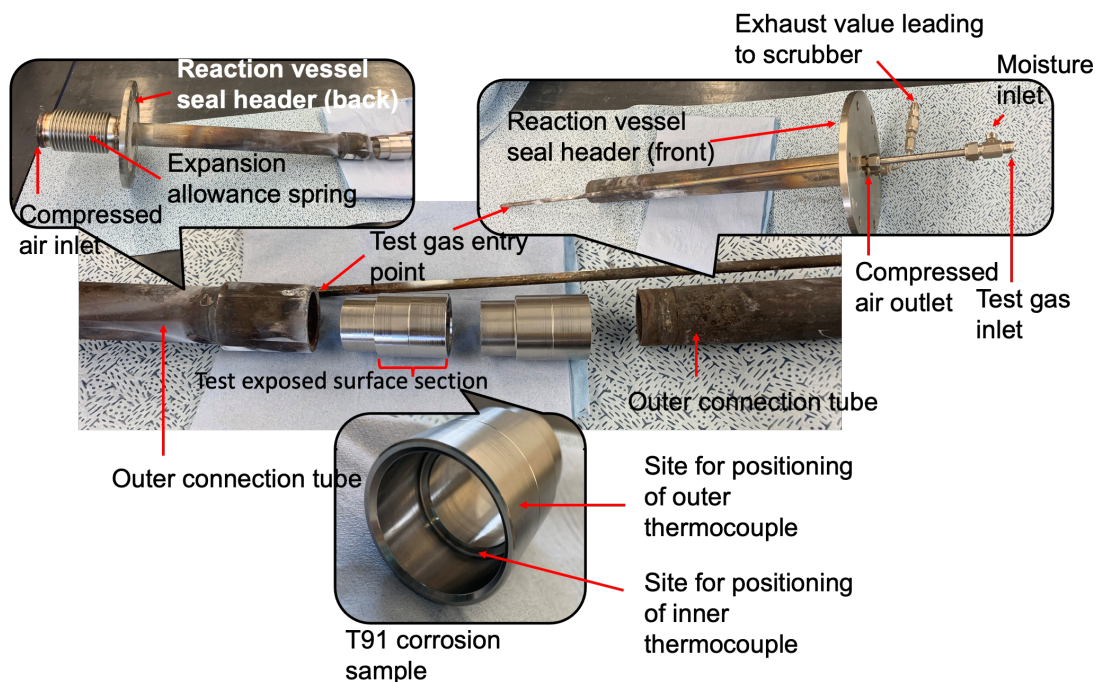


Figure 3-17: Air-cooled probe exterior tubing components. Outer connection tubes and corrosion test samples interlock to form a single tube.

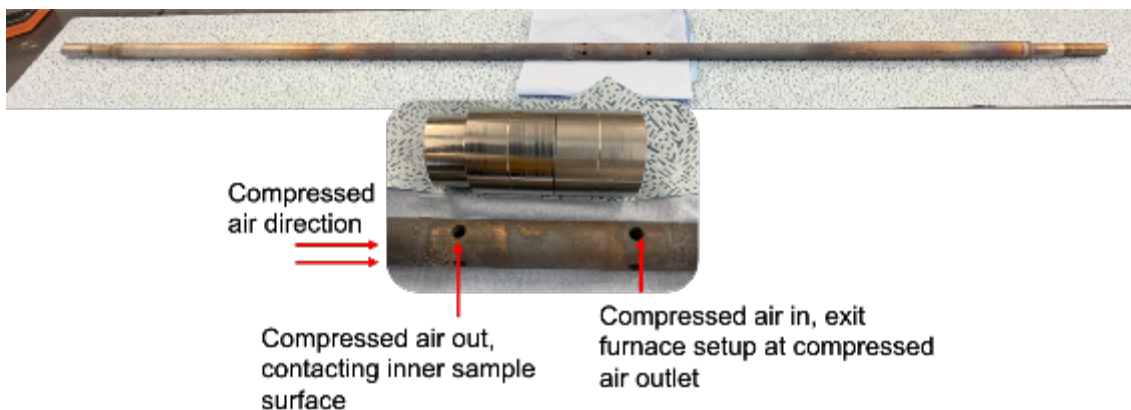


Figure 3-18: Air-cooled probe interior tube showing compressed air pathway

The tube in **Figure 3-18** admits the test gas and moisture (test atmosphere is specified in **Table 3-3**, test TW7) to the far end of the reaction vessel, such that the gas flows back over the exterior samples surfaces as it exits through the exhaust connections at the front end of the probe and via the scrubber solution.

3.5.2. Operational parameters

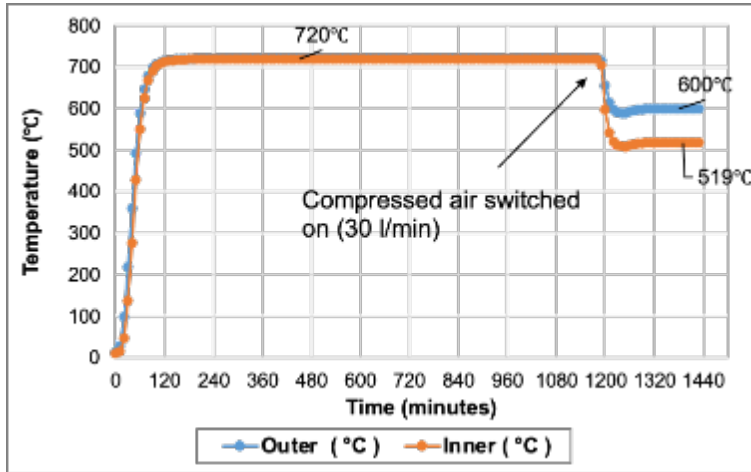


Figure 3-19: Temperature profiles before and after compressed air is switched on at an air flow rate of 30 l/min. Outer and inner sample surface thermocouple readings taken over 24 hours

Temperature profiling was carried out to establish the furnace controller temperature settings and the compressed air flow rate required to achieve the target exterior sample surface temperature and a cooler interior surface of $>50^{\circ}\text{C}$. Temperature measurements were taken using two K-type thermocouples positioned at the inner and outer surfaces of the test sample. To attain an outer sample surface temperature of 600°C while running the compressed air through the compressed air tube, the furnace temperature was ramped higher than the target test temperature (600°C). At the lowest feed rate setting of the compressed air gauge (30 l/min), an 81°C difference between the inner (519°C) and outer (600°C) surface temperatures was achieved (**Figure 3-19**). As such the existing temperature gradient across the sample thickness of $\sim 2.7\text{ mm}$ was 81°C ($30^{\circ}\text{C}/\text{mm}$).

3.5.3. Sample preparation and deposit coating

The samples were cleaned and weighed as described in **Section 3.3.3**. Dimensional measurements were carried out using a digital calliper with a resolution of $\pm 1 \mu\text{m}$. Eight measurement points each were taken for the thickness, length and diameter as demonstrated in **Figure 3-20**. The deposit re-coat method and furnace cycling technique were also employed for these tests (**Section 3.3.4**). The deposition flux applied was $100 \mu\text{g}/\text{cm}^2\text{h}$ and exposures were carried in 100 hours cycles for a total of 500 hours.

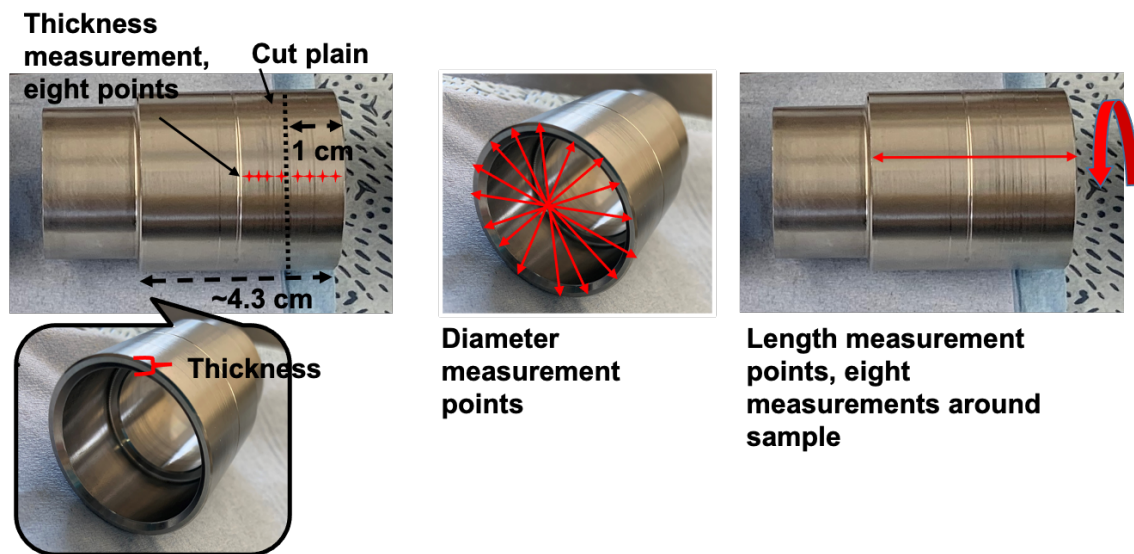


Figure 3-20: Probe sample measurement points for thickness, diameter and length. The cutting plain is also indicated

3.5.4. Post-exposure sample preparation and analysis

The samples required mounting in a resin to secure corrosion products, cutting with a precision saw, and polishing as described in **Section 3.3.5**. However, a vertical positioning of the sample was achieved by standing the sample on its flat face on flat surface. As such a jig was not required. The sample was then sectioned along the plain indicated in **Figure 3-20**.

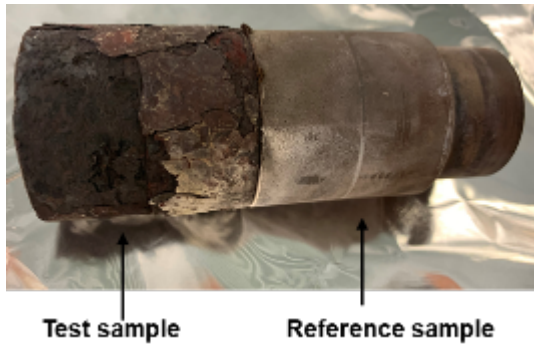


Figure 3-21: Spallation of test sample surface occurring. Sample had been exposed for 400 hours (4 cycles) in WWF gas conditions and with HGB deposit mix.

Again, the mass change data was not employed for evaluating corrosion as it could be visibly observed that significant spallation of the sample surface had occurred **Figure 3-21** (see **Section 3.3.6**). Dimensional metrology was employed for determining the post-exposure metal surface positioning and internal penetration depths. These readings were measured against pre-exposure dimensions to obtain metal change data (see **Section 3.3.6.1**)

3.5.4.1. Dimensional metrology

Dimensional metrology was used to determine the new metal interface position, which was then compared with the pre-exposure dimensions measured with the micrometre. The optical microscope and digital image analyser setup described in **Section 3.3.6.1** was employed for post-measurements of the radial x-y coordinates of the probe samples. 60 data points were positioned around the circumference for each sample, locating both metal surface and internal penetration depths. The larger number of measurement points taken for the probe sample was due to its larger size, compared to the coupons in **Section 3.3.6**. The x-y coordinates generated were entered into spreadsheets where they were compared with the original sample dimensional measurements.

The metal loss and sound metal change values were calculated by subtracting post-test sample measurements from the pre-exposure metal thickness measurements (see **Section 3.3.6.1**).

3.6. Furnace test parameter summary

Seven corrosion tests have been carried out during the course of this research. The experimental parameters for each test are outlined in **Table 3-3**. The test gas and water flow rate calculations are documented in **Section A-5** and, the deposit compositions were calculated from thermodynamic simulations as discussed in **Section 3.2**. These deposit compositions are listed in **Table 4-6**.

Test parameters set for furnace test TW1, TW2, TW3 & TW4 simulated hot corrosion conditions encountered in WWF combustion. TW1 (600°C), TW2 (550°C) & TW4 (500°C) enabled the investigations of temperature change effect on the extent of corrosion damage while TW3 was carried out at 600°C to evaluate effects of varied deposition fluxes of test TW1. TW5 & TW6 simulated fireside corrosion conditions encountered following HGB and APR combustion respectively. The procedures covering tests TW1-TW6 may be referred to in **Section 3.3**. TW7 experimental conditions were identical to TW1 and involved testing using the air-cooled probe setup. TW7's test procedure is covered under **Section 3.5**.

Table 3-3 Furnace tests experimental parameters. See Section 4.1.4 for deposit compositions. Deposition flux, 100 $\mu\text{g}/\text{cm}^2\text{h}$ unless otherwise stated

Test code	Materials ($\approx 15'' \times 15'' \times 5''$ coupons)	Atmosphere	Deposit	Temperature (°C)
TW1	T91 347HFG	WWF test gas		
		N ₂ 70.2 mol. %		
		O ₂ 8.5 mol. %		
		CO ₂ 10.0 mol. %		
		SO ₂ 41.0 vol. ppm		
		HCl 3.0 vol. ppm		
		H ₂ O 10.5 mol. %		
			D1-D6	600

TW2	T91 347HFG	WWF test gas	D1, D6	550
TW3	T91 347HFG	WWF test gas	D1, D6, flux 100, 50, 25, 10 $\mu\text{g}/\text{cm}^2\text{h}$	600
TW4	T91 347HFG	WWF test gas	D1, D6	500
TW5	T91 347HFG	HGB test gas N ₂ 58.6 mol. % O ₂ 7.3 mol. % CO ₂ 7.3 mol. % SO ₂ 41.0 vol. ppm HCl 8.0 vol. ppm H ₂ O 26.6 mol. %	D1, D6, D7	600
TW6	T91 347HFG	APR test gas N ₂ 70.3 mol. % O ₂ 6.2 mol. % CO ₂ 11.8 mol. % SO ₂ 96.0 vol. ppm HCl 53.0 vol. ppm H ₂ O 11.6 mol. %	D1, D6, D8	600
TW7	T91	WWF test gas	D6	600

4 Results

The results generated from the experimental methods employed for this research (procedures explained in **Chapter 3**) are presented in this chapter. Data provided are from the:

- Fuel classification and thermodynamic modelling of the biomass/waste fuels combustion products (**Section 4.1**),
- Furnace corrosion testing (**Section 4.2**),
- TGA of synthetic deposits (**Section 4.3**),
- Heat flux furnace corrosion tests (**Section 4.4**)

MTData thermodynamic simulations of the fuel categories' fireside combustion products have enabled the formulation of deposit mixtures for all later testing. These synthetic deposits have been evaluated with respect to their corrosion influence at temperatures within biomass combustion plant HX range. The corrosion test data are provided as weight change (μg), metal dimension change (μm), and SEM/EDX imaging.

4.1. Biomass/waste fuels classification and post-combustion release data

This section presents the specific fuel types selected to make up each biomass/waste fuel category (**Section 4.1.1**), the collective properties of the fuel categories which may impact their suitability as combustion energy fuels (**Section 4.1.1**), and the post-combustion data generated from MTData thermodynamic simulations (**Section 4.1.2** and **Section 4.1.3**).

4.1.1. Categorized Fuel Data

This section reports the HGB, IFW, APR and WWF categories' analysis data.

4.1.1.1. Selected fuel categories

Table 4-1 gives of the fuel categories selected for evaluation, summarising the fuel types compiled for these categories. A complete list of individual fuels and each source's reference, elemental and combustion characteristics data (totalling 120 fuels) are documented in **Table A-1**. The fuel list comprises a range of commonly employed feedstock such as energy crops (e.g. miscanthus, reed canary grass [21], [98]) and some residues (e.g. olive residues). The list also includes uncommonly employed fuels (e.g. coffee residues more-frequently found in Brazil [160]) and a variety of non-conventional fuels of potential benefit as combustion fuels [20]. The IFW category fuels are limited to vegetation-based ones as elemental analysis can vary significantly between plant and animal-based wastes. Elemental analysis for vegetal wastes from food processing has also been more available [25].

4.1.1.2. Fuel properties

Figure 4-1 presents the heat of combustion values, calculated for each fuel category on median 'as received' (ar) and 'dry basis' (db) values. The low heating value, LHV, is employed alone for a plant design where no secondary condenser exists. The assumption is that water vapour generated from fuel combustion will exit with the exhaust stream. In the case of secondary/tertiary condensers being present, the high heating value, HHV can account for the recoverable latent heat of vaporisation lost from hydrogen rich fuels which can release water during combustion [24]. The numerical difference between the HHV and LHV of a fuel is approximately the latent heat of vaporisation which is recoverable in a secondary condenser per unit of the combusted fuel.

Table 4-1: Types of fuels listed in each fuel category and category totals (see appendix for complete list and source references)

	HGB	APR	IFW	WWF
Fuel types	Switchgrass	Sunflower residues	Sugarcane fibre	Demolition wood
	Reed canary	Plum pits	Onion peel	Particle board
	Cane	Cotton husks	Olive residues	Treated woods
	Barley straw	Olive tree residue	Oil palm fruit	Painted wood
	Wheat straw	Rice residues	Mango waste	Railway wood
	Sweet sorghum	Groundnut shells	Longan waste	
	Kenaf	Palm kernel	Litchi waste	
	Rapeseed straw	Oat residues	Grains	
	Miscanthus	Mustard husks	Coffee	
	Flax	Grass seed chaff		
	Aubergine plant	Cotton residues		
	Bean plant	Almond residues		
	Brassica	Cacao residues		
	Courgette plant	Coconut residues		
	Cucumber plant	Hazelnut shell		
	Melon plant	Cotton husks		
	Pepper plant	Prune pits		
	Tomato plant	Pistachio residues		
	Watermelon	Walnut residues		
	Thistle	Soya husks		
	Tobacco, Burley	Coffee residues		
	Threshed hay	Greenhouse waste		
	Grass pellets	Cornstalk		
		Tomato plant		
Total fuels in group	31	52	14	23

The proximate and ultimate analysis of the four biomass/waste categories are presented in **Figure 4-2** to **Figure 4-5** and data ranges are tabulated in **Table A-2-Table A-5**. The IFW fuel category's relatively lower Cl contents (**Figure 4-4**) is desirable from a corrosion point of view as Cl is notorious for causing metal damage following fuel combustion [115], [131]. This is important as Caton et al. [29] suggested that the recoverable energy from vegetal-food waste combustion can be higher than that of wood. However, the basis of comparison was for a dry fuel feed and included cost/economic benefits associated with employment of waste in place of wood importation. Supporting with the authors, the IFW heating energy (~17 MJ/kg db) is comparable with that of WWF (~18 MJ/kg db) on a dry basis (**Figure 4-1**), however, the high moisture content for IFW (57 wt.%, **Figure 4-4**; relative to WWF, 15 wt.%, **Figure 4-5**) remains undesirable as fuel preparation for combustion can be challenging [29].

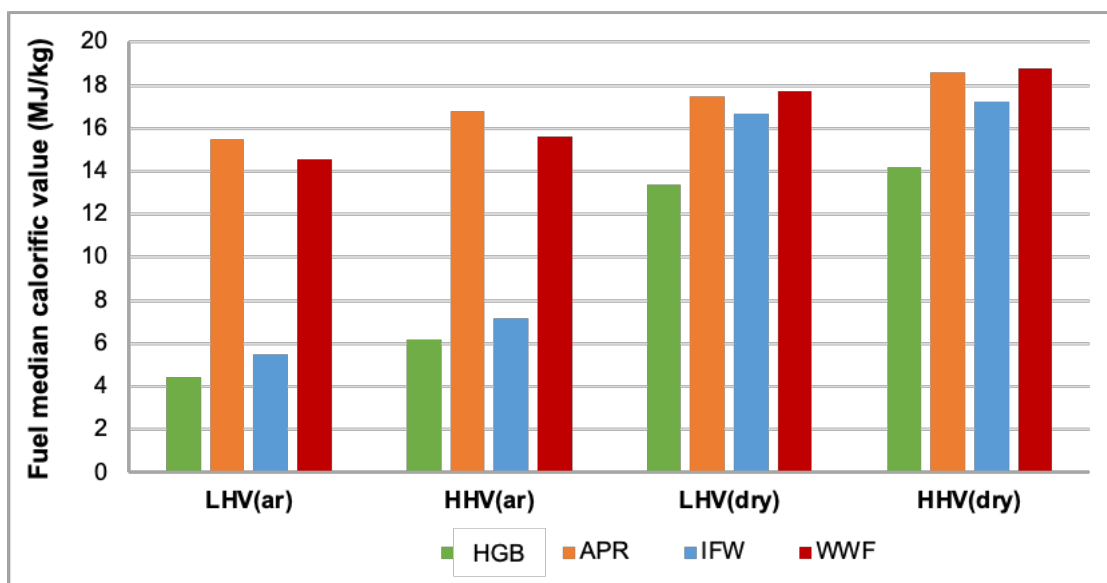


Figure 4-1: The calculated (see Equation 18- Equation 21) median low heating values (LHV) and high heating values (HHV) of fuel categories on 'as received' (ar) and 'dry basis' (db)

Individual fuel ar water content is dependent on several factors including the pre-handling process, storage conditions, nature of fuel and, the time elapsed

between harvesting and analysis [25]. As such, large variations in moisture (ar) content are observed for each category. Where median and mean values are considerably different and maximum/minimum ranges are large, it is likely that the ranges are affected by erroneous data. Larger differences between mean and median category S and Cl values are observed for the WWF (**Figure 4-5**), IFW (**Figure 4-4**) and APR (**Figure 4-3**) fuel categories where mean values are inclined towards extreme data.

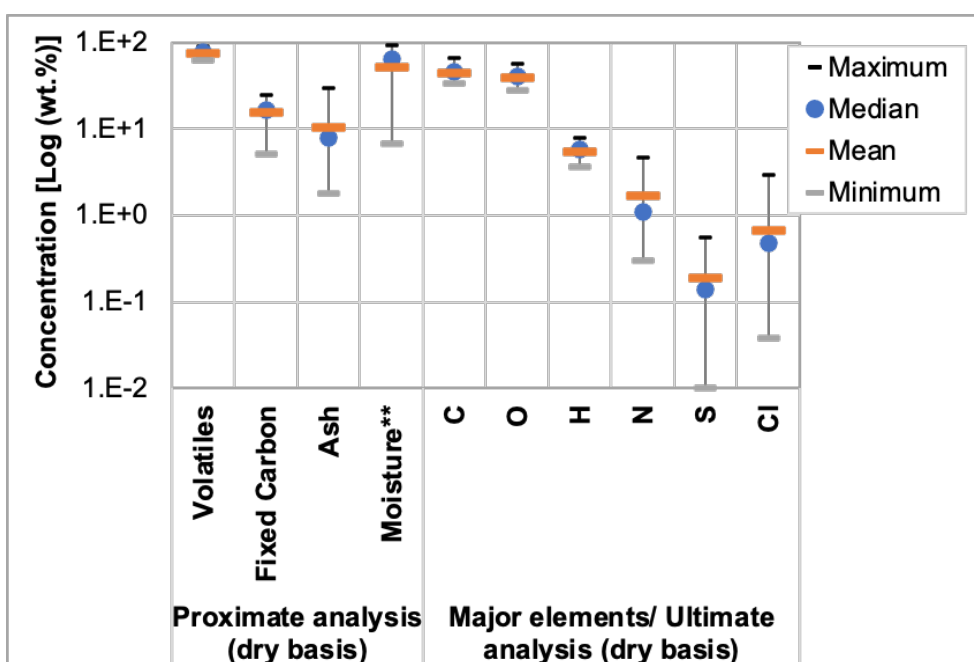


Figure 4-2: HGB fuel category properties, **as received. Values based on collated data, detailed data in A-1

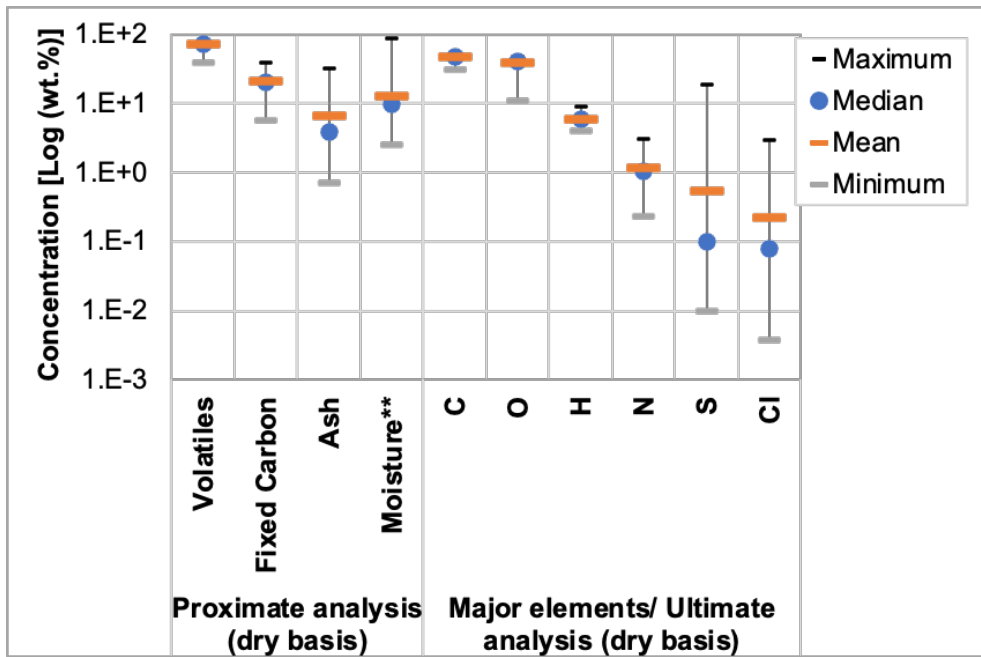


Figure 4-3: APR fuel category properties, **as received. Values based on collated data, detailed data in A-1

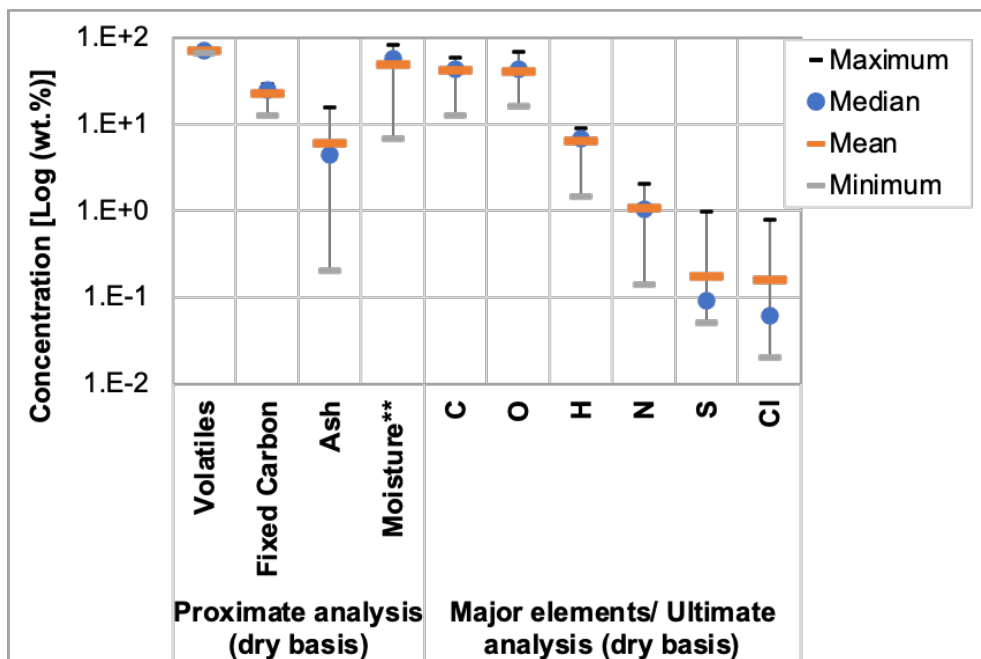


Figure 4-4: IFW fuel category properties, **as received. Values based on collated data, detailed data in A-1

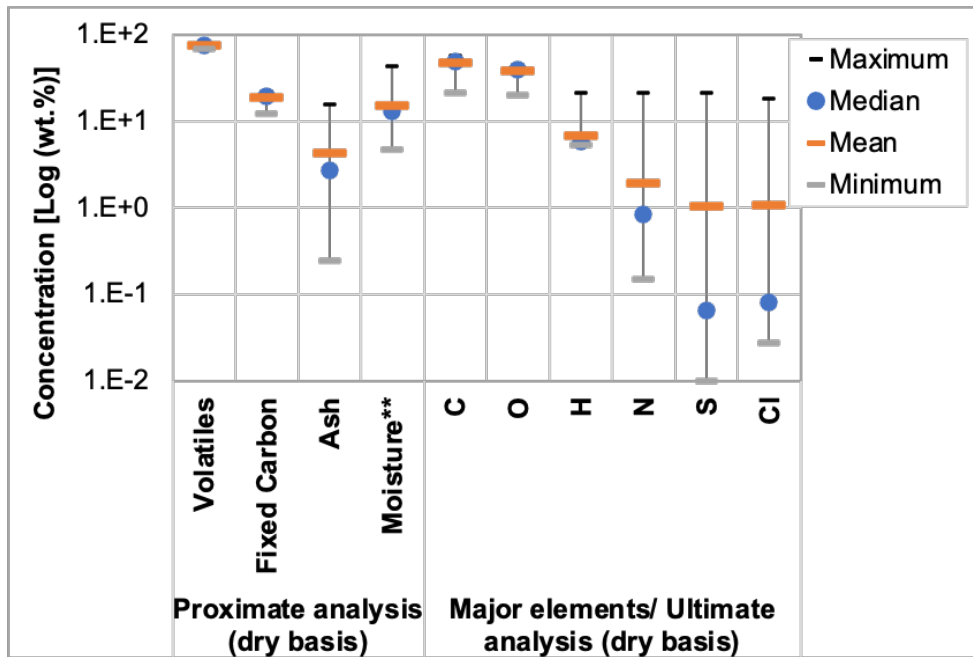


Figure 4-5: WWF fuel category properties, **as received. Values based on collated data, detailed data in A-1

Extreme data can also be influenced by the inclusion of fuels which may fit more than one category. This is especially true for forestation residues where wood chips, which consist of intermingled leaves, have been grouped in both virgin wood and WWF categories [25].

The median ash (db) contents of the fuel categories decrease as:

$$HGB (7.91 \text{ wt.}\%) > IFW (4.37 \text{ wt.}\%) > APR (3.83 \text{ wt.}\%) > WWF (2.7 \text{ wt.}\%)$$

The fixed carbon (db) median values decrease as:

$$IFW (25 \text{ wt.}\%) > APR (20.45 \text{ wt.}\%) > WWF (19.30 \text{ wt.}\%) > HGB (16.50 \text{ wt.}\%)$$

S wt.% (db) median values decrease as:

$$HGB (0.14 \text{ wt.}\%) > APR (0.10 \text{ wt.}\%) > IFW (0.09 \text{ wt.}\%) > WWF (0.07 \text{ wt.}\%)$$

Cl wt.% (db) median values decrease as:

$$HGB (0.47 \text{ wt.}\%) > APR (0.08 \text{ wt.}\%) > WWF (0.08 \text{ wt.}\%) > IFW (0.06 \text{ wt.}\%)$$

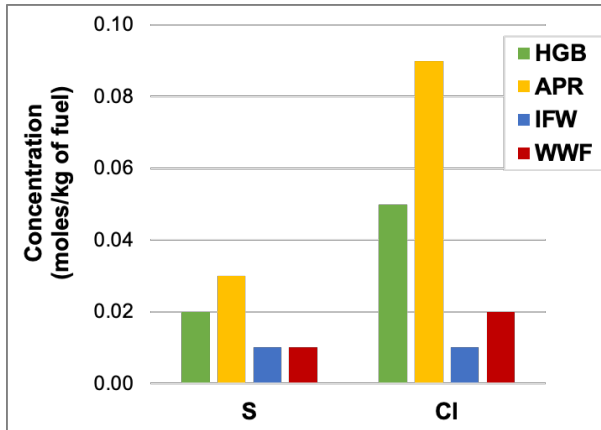


Figure 4-6: Fuel categories' median S and Cl concentrations normalised to per kg dry weight of fuel

In **Figure 4-6**, the Cl and S contents per kg of dry fuel feed (as fed into thermodynamic simulations), are compared for the fuel categories.

Per kg of fuel (db), the Cl concentration decreases as:

$$APR (0.09 \text{ moles/kg}) > HGB (0.05 \text{ moles/kg}) > WWF (0.02 \text{ moles/kg}) > IFW (0.01 \text{ moles/kg})$$

While the S concentration decreases as:

$$APR (0.03 \text{ moles/kg}) > HGB (0.02 \text{ moles/kg}) > WWF (0.01 \text{ moles/kg}), IFW (0.01 \text{ moles/kg})$$

This means that, though higher fractions of S and Cl exist in HGB as compared to APR, higher absolute quantities of the elements occur for the latter fuel category.

The minor element values employed for thermodynamic post-combustion calculations are presented in **Figure 4-7**. The IFW category has lower concentrations for most elements, however K and Mg levels within the category are comparable with the other fuel groups. Na median levels are lower in the IFW category, while APR and WWF show relatively similar levels. Median values of K are significantly higher in the HGB fuel category. APR fuels display wider ranges

of values for most elements. Si and P contents are also significantly higher for the HGB median category while WWF and IFW have lower levels.

4.1.1.3. Minor and trace elements of fuel categories

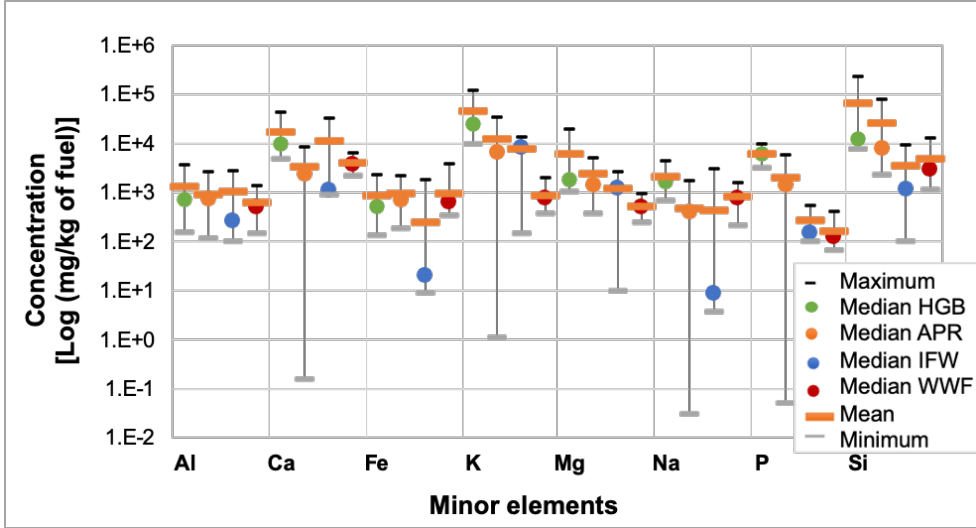


Figure 4-7: Minor element values for fuel categories HGB, APR, IFW and WWF based on dry feedstock analysis data

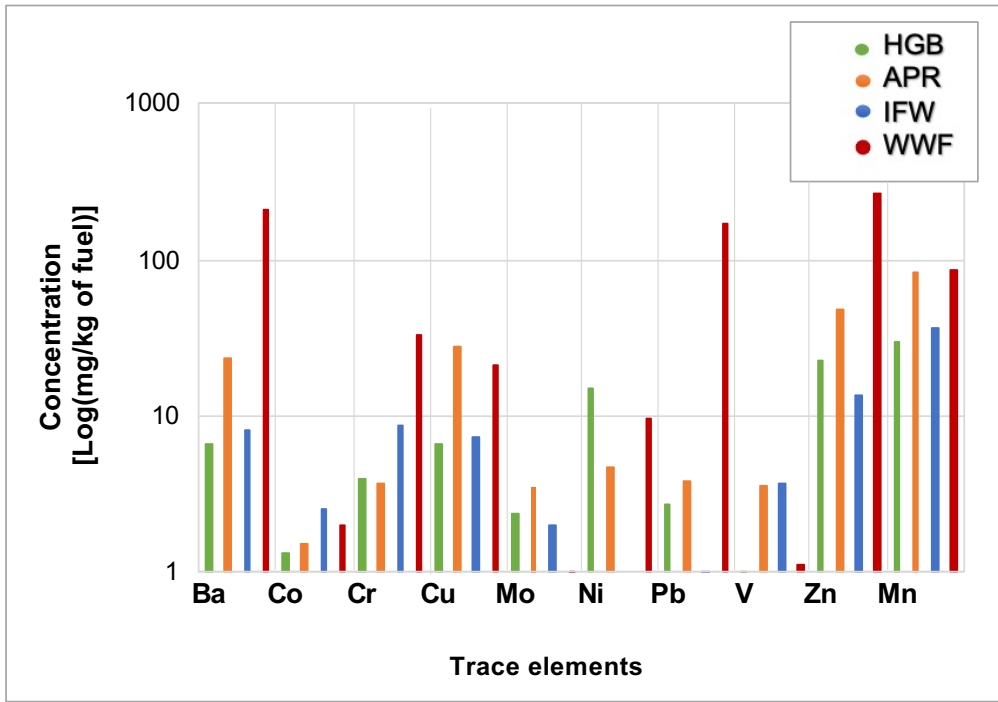


Figure 4-8: Heavy metal element median values for fuel categories HGB, APR, IFW and WWF based on dry feedstock analysis data

The median heavy metal element values are all within trace levels (<1000 ppm fuel concentration; **Figure 4-8**). Higher trace contaminant levels are observed for the WWF category where Ba, Pb, Zn (200-300 ppm) show the highest concentrations. HGB, IFW and APR have minimal heavy metal contaminant levels (<50 ppm).

4.1.2. MTData thermodynamic post-combustion simulation data

The thermodynamic simulations of stable species occurring within 300-1300°C are reported in this section and have been used to represent the post-combustion behaviours of fuels. Data generated are gas and condensed phase concentration yields from 1 kg of fuel and excess air (**Section 3.2**), outputs which are later applied to generate representative deposit and gas formulations for fireside corrosion testing. Also, the post-combustion composition changes, influenced by the inclusion of a trace element (heavy metal, median values) to the simulations, are reported. The range of species evolved during combustion for each fuel category (based on median category compositions) is based on their 14ES (**Section 3.2.2**). Where heavy metal trace elements are evaluated, the calculation input data are based on 15ES (14ES + 1, see **Section 3.2.2**).

4.1.2.1. Alkali combustion release

The release of alkali metals during combustion to the gas phase is useful for determining the potentially condensable molten salts which may form within the combustion gas stream. For this purpose, species stable at 1000-1200°C (HX-vicinity gas temperature range) were chosen. The types of alkali metal phases formed are important because alkali metals may react with sulphates, chlorides and carbonates (for e.g.) to form salts with melting points occurring within HX surface temperature ranges (400-600°C).

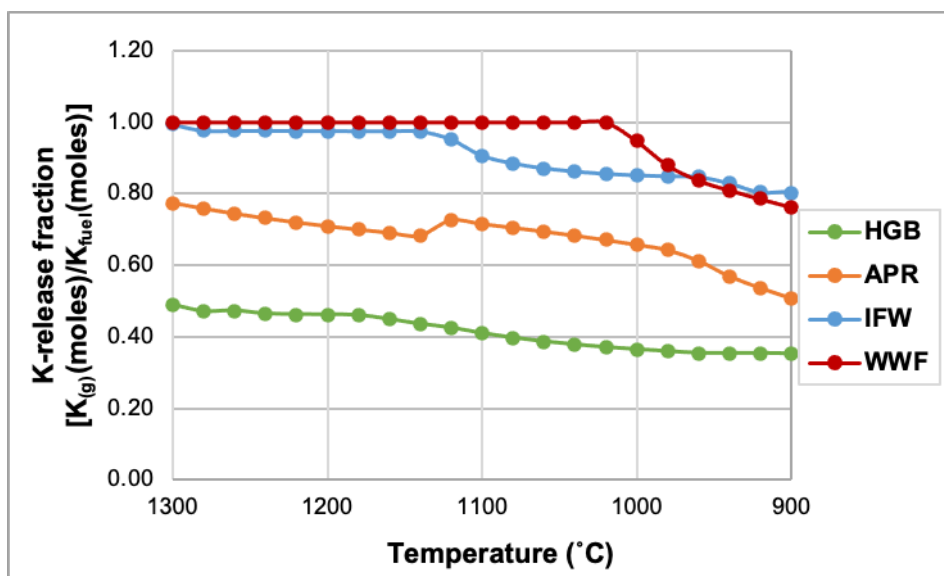


Figure 4-9: Fuel categories' K-release fractions

The K-release fraction, which is the fraction of K that ends up as gas phase compounds compared to the total K in the fuel, for the four fuel categories are compared in **Figure 4-9**. The groups may be divided into two, based on K-release at 1100°C: high K-release fuels, WWF (100%) and IFW (91%), and average K-release fuels, APR (71%) and HGB (41%). The term 'release' refers to the element becoming a component in the gas phase.

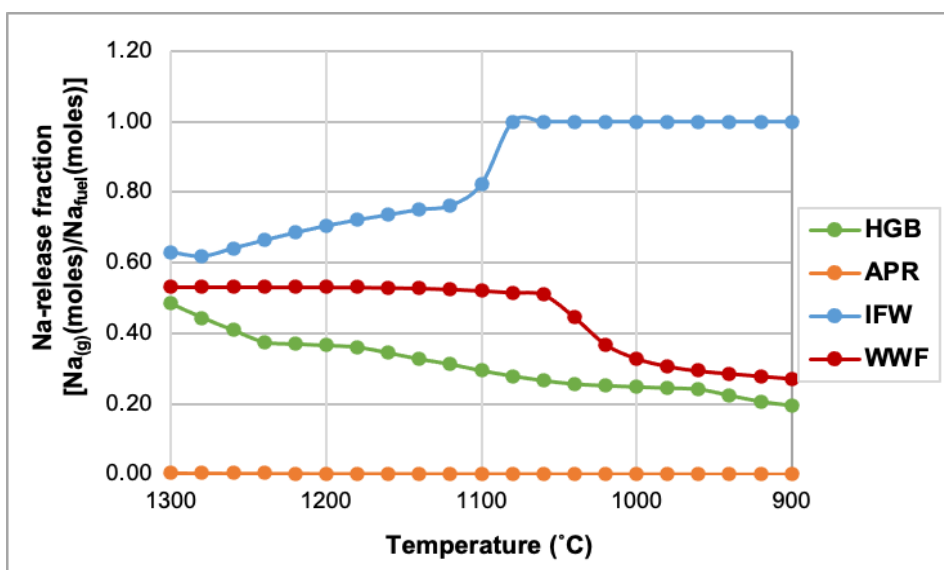


Figure 4-10: Fuel categories' Na-release fractions

The Na-release fraction for the four fuel categories is given in **Figure 4-10**. Na-release remains highest for both WWF and IFW categories at 1000-1200°C, though WWF falls within an average Na-release fraction (52% at 1100°C). HGB Na-release remains comparatively low (29% at 1100°C) while APR shows negligible quantities of gas phase Na compounds present at 1100°C.

Alkali metal compounds in gas phase, which may be present ($> 10^{-4}$ moles/kg fuel) within HX vicinity temperature ranges, are presented in **Figure 4-11**. $\text{KOH}_{(g)}$, $\text{KCl}_{(g)}$ and $\text{K}_2\text{SO}_{4(g)}$ are formed in each fuel category. $\text{Na}_2\text{SO}_{4(g)}$, $\text{NaCl}_{(g)}$ and $\text{NaOH}_{(g)}$ are predicted to exist within the HGB and WWF categories' gas phase components. The relatively high $\text{KOH}_{(g)}$ concentration for the IFW fuel category at 1100°C, compared to the fuel category's $\text{KCl}_{(g)}$ and $\text{K}_2\text{SO}_{4(g)}$ concentrations, correlate with the high moisture contents of the fuels (**Figure 4-4**), which favours hydroxide formation [161]. Similarly, within the HGB category, K in gas phase is mostly present as the hydroxide and chloride at high temperatures, which may also be reflective of its relatively high moisture content.

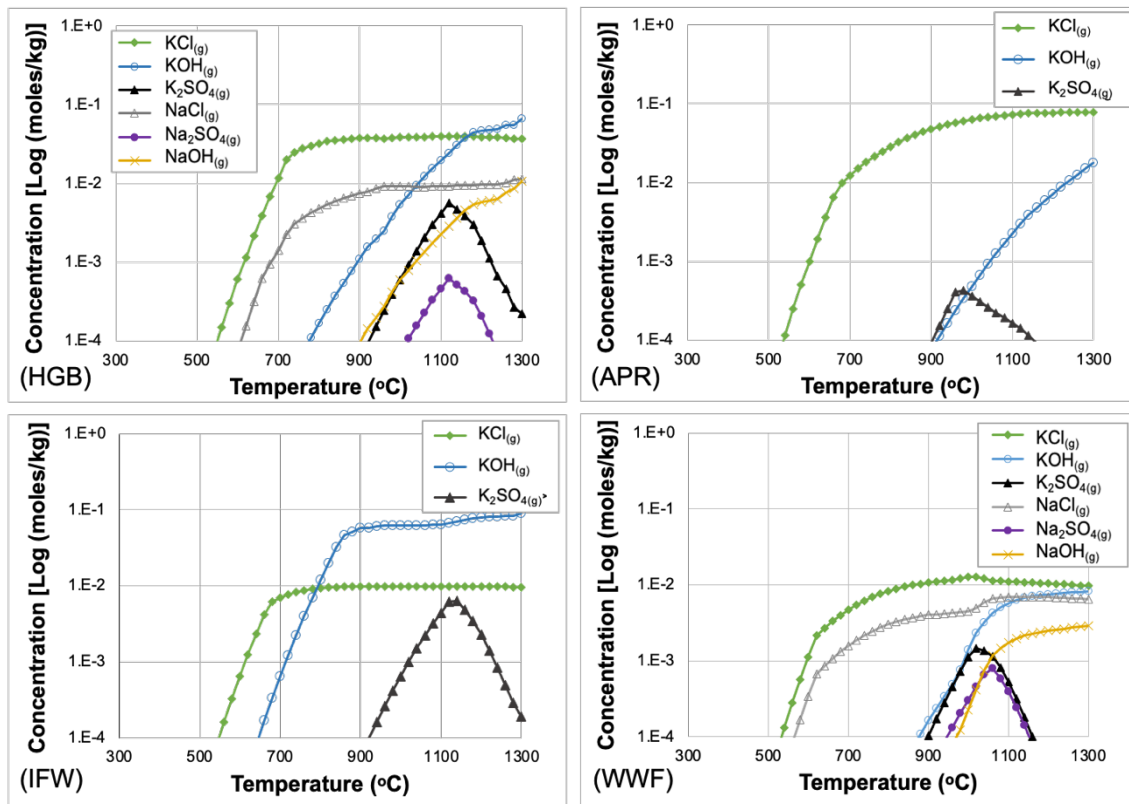


Figure 4-11: Chloride and sulphate alkali and alkaline earth metal vapours ($<10^{-4}$ moles per kg of fuel) existing from 300°C to 1100°C

The dry gas compositions existing at 1100°C and which do not condense within 400-600°C are presented in **Figure 4-12**. These gas species are less able to impact fireside corrosion as their contact period with HX surfaces is limited, compared to molten components. The excess O₂ yields achieved at 1100°C were 7.5 mol.% (HGB), 6.3 mol.% (APR), 7.6 mol.% (IFW) and 8.5 mol.% (WWF) for the 14ES median thermodynamic simulation input values. With the inclusion of heavy metals (trace element contaminants) to the simulations, the excess O₂ yields achieved were within ±0.1 mol.% of that obtained for the 14ES simulations for each category. These values fall closely within the recommend excess O₂ targets (7-8 mol.%) for biomass combustion practices in power generation plants [24].

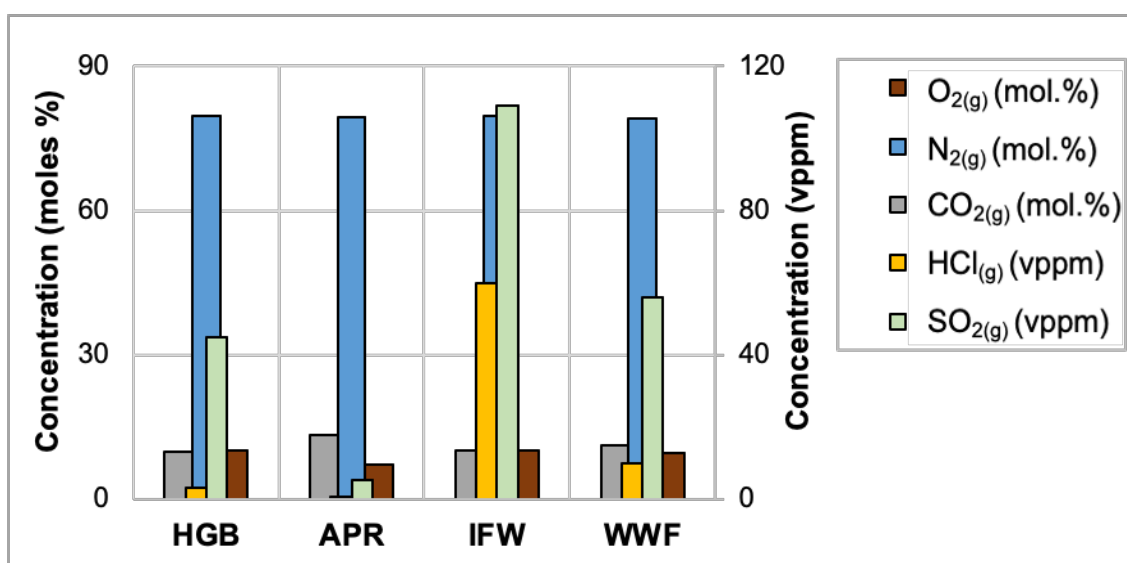


Figure 4-12: Dry gas concentrations (moles %) occurring at 1100°C. SO₂ and HCl concentrations are expressed in volume ppm; other gases in moles %.

4.1.3. Non-gaseous phase, thermodynamic simulation outputs

MTData thermodynamic outputs are designated as gaseous or non-gaseous species/compounds (no differentiation between solid and liquid). High temperature stable compounds and condensates with molten tendencies at HX

temperatures, within the 14ES thermodynamically predicted non-gaseous species, are reported for each category in this section.

4.1.3.1. Non-gaseous compounds compositions: silicates, phosphates and simple salts

Table 4-2: 14ES simulated condensed phase compositions ($>10^{-4}$ moles) at 600°C from different fuel categories. Values expressed in mol./kg of fuel

HGB		IFW		APR		WWF	
Component	mole/kg	Component	mole/kg	Component	mole/kg	Component	mole/kg
*K ₃ PO ₄	0.19	K ₂ CO ₃	0.031	SiO ₂	0.101	*CaSiO ₃	0.034
*CaSiO ₃	0.16	*CaMgSiO ₄	0.011	KCl	0.069	*CaMgSiO ₄	0.02
*CaMgSi ₂ O ₆	0.08	K ₂ SO ₄	0.01	MgSiO ₃	0.052	KCl	0.018
KCl	0.05	KCl	0.01	K ₂ SO ₄	0.03	Na ₂ SO ₄	0.008
K ₂ SO ₄	0.02	*Mg ₂ SiO ₄	0.009	*Ca ₃ P ₂ O ₈	0.018	CaSO ₄	0.007
*Na ₂ SiO ₃	0.02	*K ₃ PO ₄	0.002	*Al ₂ Na ₂ SiO ₁₆	0.008	*CaFe ₂ O ₄	0.005
*Al ₂ Na ₂ SiO ₁₆	0.015	*Al ₂ MgO ₄	0.002	Al ₂ K ₂ Si ₆ O ₁₆	0.007	*Al ₂ Na ₂ SiO ₁₆	0.005
*K ₂ Si ₂ O ₅	0.005	*AlKSiO ₄	0.0014	Fe ₂ O ₃	0.006	*Al ₂ Ca ₃ SiO ₁₂	0.004
Fe ₂ O ₃	0.005	*CaFe ₂ O ₄	0.0001	*K ₃ PO ₄	0.006	*Ca ₃ P ₂ O ₈	0.002
*CaFe ₂ O ₄	0.0001			*Mg ₃ P ₂ O ₈	0.0001	K ₂ SO ₄	0.00016
Total moles/kg	0.545		0.077		0.297		0.103

* MTData predicted compounds still condensed by 1300°C. Denoted compounds are expected to be in solid phase at HX temperature range. Compounds not denoted are in gas form at temperatures higher than 1100°C

The non-gaseous compounds (present at 600°C) are presented in **Table 4-2**. The proportions of alkali metal silicates and phosphates, which tend to exhibit higher melting points relative to HX temperatures, can indicate the available alkali metal fractions for salt formation. Larger proportions of metal-phosphates and silicates are observed for HGB and APR within the non-gaseous phase compounds. Alkali metal silicates and phosphates in the IFW and WWF

categories are of reduced concentrations, as fuel P and Si contents are relatively low (**Figure 4-7**).

4.1.3.2. Condensed phase: K^+ , Na^+ & Ca^+ salts

The KCP compounds (methodology described in **Section 3.2.3.2**), obtained from the analysis of the non-gaseous (condensed) phase components, for each fuel category are presented in **Figure 4-13**.

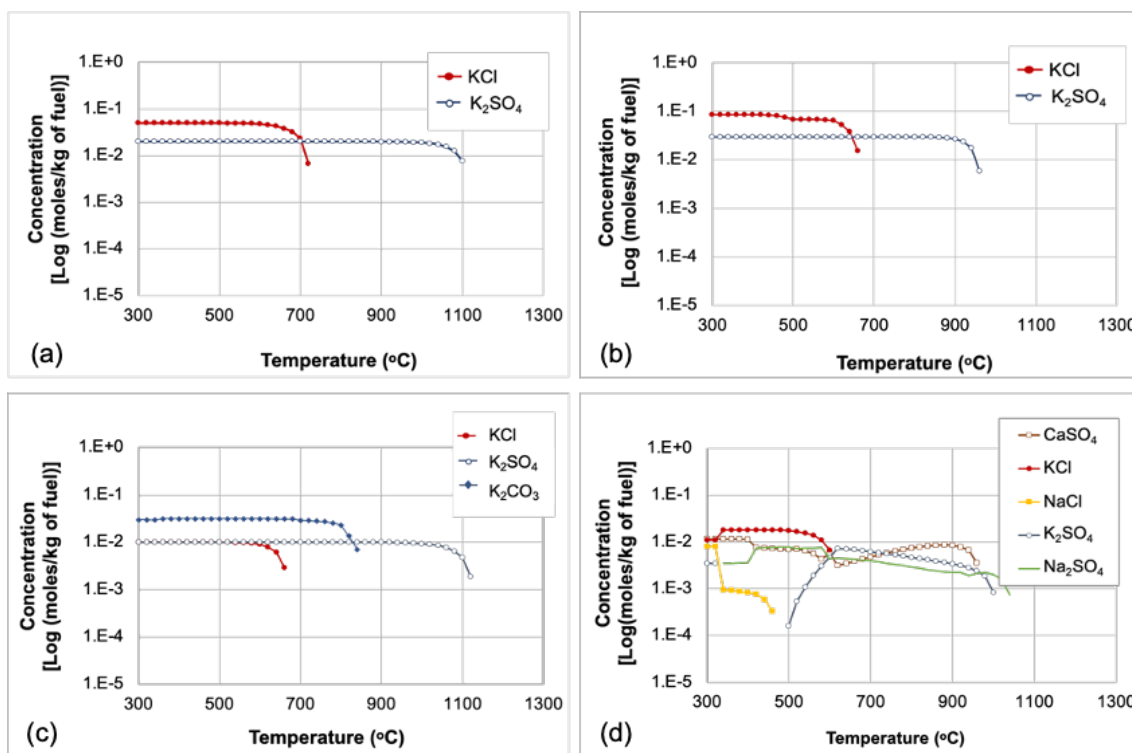


Figure 4-13: (a) HGB, (b) APR, (c) IFW & (d) WWF fuel category KCP compounds ($>10^{-4}$ moles/kg of fuel) simplified from MTData thermodynamic calculations of combustion releases

MTData simulations show variations in the KCP compositions and quantities between each category. KCl and K_2SO_4 condensates are common to all four fuel categories and are the only KCP compounds present for the HGB and APR categories. IFW and WWF may contain more component types.

In **Figure 4-14**, the condensed phase KCl and K_2SO_4 concentrations are compared between the four fuel categories. At 600°C, APR has over double the amount of KCl and K_2SO_4 of HGB. K_2SO_4 quantities are comparable for HGB and IFW. IFW shows the least KCl. K_2SO_4 and KCl concentrations are, however, similar for the IFW category below 550°C. K_2CO_3 is included within KCP compounds for the IFW category (**Figure 4-13**). The relatively high K_2CO_3 combustion yield corresponds with the high KOH gas fraction observed at 1100°C (**Figure 4-11**), whereas for other three categories, alkali metal gas concentrations is dominated by KCl (**Figure 4-11**).

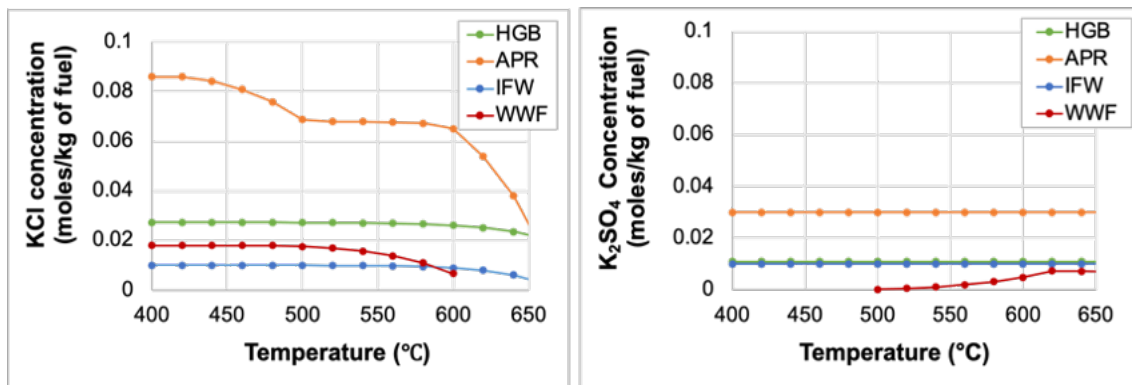


Figure 4-14: A comparison of fuel categories KCl and K_2SO_4 post-combustion temperature profiles occurring within the HX surface temperature range

The KCP composition of the WWF fuel category is distinctly different from that of the other fuel categories (**Figure 4-13**). In addition to K species, the category's KCP includes Na- and Ca-salts. The concentration profiles of KCP salts also vary significantly with temperature, whereas KCP compositions for HGB, APR and IFW are relatively stable up to their gas transition temperature region (temperature region where the condensed phase profile tends to zero concentration, while gas phases appear).

4.1.3.3. Trace element composition effects

The 15ES thermodynamic simulations were performed to assess the influence of ten heavy metals, present as trace contaminants in fuels, (listed in **Table 4-3**) on KCP compositions. These elements were introduced as median fuel category values. Their post-combustion associations are listed in **Table 4-3**.

Table 4-3: Trace element associations at 500°C ⁽⁵⁾ and 600°C ⁽⁶⁾ in 15ES post-combustion simulation for fuel categories

Elements	HGB	IFW	APR	WWF
Zn	Zn ₂ SiO ₄ ^{5,6}	ZnO ^{5,6}	Zn ₂ SiO ₄ ^{5,6}	ZnAl ₂ O ₄ ^{5,6}
V	-	Na ₄ V ₂ O ₇ ^{5,6} , Ca ₃ V ₂ O ₈ ⁵	Mg ₂ V ₂ O ₇ ⁵ , Ca ₂ V ₂ O ₇ ⁶	Ca ₃ V ₂ O ₈ ^{5,6}
Pb	PbO ^{5,6}	-	-	PbSO ₄ ⁵
Ni	NiFe ₂ O ₄ ^{5,6}	-	NiFe ₂ O ₄ ^{5,6}	NiO ^{5,6}
Mo	-	-	CaMoO ₄ ^{5,6}	MoO ₃ ^{5,6}
Mn	Mn ₂ O ₃ ^{5,6}	Mn ₂ O ₃ ^{5,6}	Mn ₂ O ₃ ^{5,6}	Mn ₂ O ₃ ^{5,6}
Cr	K ₂ CrO ₄ ^{5,6}	K ₂ CrO ₄ ^{5,6}	K ₂ CrO ₄ ^{5,6}	K ₂ CrO ₄ ^{5,6}
Cu	CuFe ₂ O ₄ ^{5,6}	CuAl ₂ O ₄ ^{5,6}	CuAl ₂ O ₄ ⁵ , CuFe ₂ O ₄ ⁶	CuAl ₂ O ₄ ^{5,6}
Co	CoFe ₂ O ₄ ^{5,6}	*Co ₃ O ₄ ^{5,6}	CoFe ₂ O ₄ ^{5,6}	Co ₃ O ₄ ^{5,6}
Ba	BaSi ₂ O ₅ ^{5,6}	BaCO ₃ ^{5,6}	BaSO ₄ , BaSi ₂ O ₅ ⁶	BaSO ₄ ^{5,6}

In **Table 4-4**, the KCP compounds generated for each fuel category (14ES thermodynamic simulations) are listed in moles. **Table 4-4** allows comparison of the changes to the KCP compositions at 500°C by the inclusion of heavy metal elements in MTData calculations. Thermodynamic input data are documented in **Table A-8**. KCP concentrations are significantly altered within the WWF category for simulations which include Cr, Pb or Ba. The KCP compositions remained unchanged for the IFW, APR and HGB fuel categories when the trace elements were included in the thermodynamic simulations.

Table 4-4: Trace element effects on fuel categories' KCP compositions at 500°C. Concentrations <10⁻⁴ moles are not included. Values expressed in moles/kg of fuel

Fuel Group	KCP	Moles/kg fuel										
		14ES	15ES									
			Ba	Mn	Co	Zn	Cr	Cu	V	Ni	Pb	Mo
HBG	K ₂ SO ₄	0.020	0.020	0.020	0.020	0.020	0.020	0.020	-	0.020	0.020	-
	KCl	0.048	0.048	0.048	0.048	0.048	0.048	0.048	-	0.048	0.048	-
APR	K ₂ SO ₄	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030
	KCl	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069	0.069
IFW	K ₂ CO ₃	0.031	0.031	0.031	0.031	0.031	0.031	0.031	0.031	-	-	-
	K ₂ SO ₄	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	-	-	-
	KCl	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	-	-	-
WWF	KCl	0.018	0.018	0.018	0.018	0.018	0.017	0.018	0.018	0.018	0.017	0.018
	K ₂ SO ₄	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0005	0.0002
	Na ₂ SO ₄	0.008	0.008	0.008	0.008	0.008	0.015	0.008	0.008	0.008	0.008	0.008
	CaSO ₄	0.007	0.006	0.007	0.007	0.007	0.007	0.007	0.007	0.007	0.006	0.007
	Na ₂ CO ₃	-	-	-	-	-	0.007	-	-	-	-	-
	NaCl	-	-	-	-	-	0.007	-	-	-	-	-
	PbSO ₄	-	-	-	-	-	-	-	-	-	0.0009	-

Affected KCP compound concentration in bold, larger font size. Results are not provided (dash) for simulations not carried out due to insufficient trace element data

Table 4-5: Trace element effects on fuel categories' KCP compositions at 600°C. Concentrations <10⁻⁴ moles are not included. Values expressed in moles/kg of fuel

Fuel Group	KCP	Moles/kg fuel											14ES	
		14 ES	Ba	Mn	Co	Zn	Cr	Cu	V	Ni	Pb	Mo	Ca-max	Na-max
HBG	K ₂ SO ₄	0.020	0.020	0.020	0.020	0.020	0.020	0.020	-	0.020	0.020	-	-	-
	KCl	0.048	0.048	0.048	0.048	0.048	0.048	0.048	-	0.048	0.048	-	-	-
APR	K ₂ SO ₄	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	-	-
	KCl	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	0.065	-	-
IFW	K ₂ CO ₃	0.032	0.032	0.032	0.031	0.032	0.032	0.032	0.032	-	-	-	-	-
	K ₂ SO ₄	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010	-	-	-	-	-
	KCl	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.010	-	-	-	-	-
WWF	KCl	0.007	0.007	0.007	0.007	0.006	0.015	0.007	0.007	0.007	0.005	0.007	0.012	0.016
	K ₂ SO ₄	0.005	0.005	0.005	0.005	0.005	-	0.005	0.005	0.005	0.006	0.005	0.002	0.015
	Na ₂ SO ₄	0.004	0.005	0.004	0.004	0.007	0.015	0.004	0.004	0.004	0.005	0.004	0.013	0.015
	CaSO ₄	0.006	0.005	0.006	0.006	0.003	0.006	0.006	0.006	0.006	0.005	0.006	-	0.004

Altered KCP compositions in larger font size & bold. Omitted results (dash) were not carried out due to insufficient trace element data

At 600°C (Table 4-5), 14ES and 15ES post-combustion KCP compound ratios are relatively similar for HGB and APR. Some changes to KCP compositions are noted for IFW when Co or V is included (median contaminant

values) in the 15ES post-combustion simulation. KCP composition changes are also noted for WWF where Ba Cr, Pb or Zn is added to the post-combustion simulation.

4.1.4. Application of thermodynamic simulation data

The KCP compositions predicted for each fuel category at 600°C from both 14ES and 15ES thermodynamic simulations have been applied to the formulations of deposit salt mixtures for later experimental fireside corrosion evaluation (Section 3.2.3). Each KCP compound's concentration has been expressed in mol.% (**Table 4-6**). The gas compositions from the 14ES simulations, occurring at 1100°C, have been employed for the corrosive test gas formulations, to replicate the combustion gas chemistry generated by the fuels.

Table 4-6: Synthetic deposit mole ratios generated from MTDData thermodynamic post-combustion simulations

Deposit Name	Simulation specification	KCP composition (mole%)				
		KCl	K ₂ SO ₄	Na ₂ SO ₄	CaSO ₄	NaCl
D1	WWF 14ES	30%	20%	20%	30%	
D2	WWF 15ES (+Cr)	48%		48%		4%
D3	WWF 14ES (Ca max value)	46%	8%	46%		
D4	WWF 14ES (Na max value)	50%		50%		
D5	WWF 15ES (+Zn)	28%	29%	29%	14%	
D6	HGB 14ES	71%	29%			
D7	HGB 14ES (Cl mean value)	89%	11%			
D8	APR 14ES	67%	33%			

4.2. Furnace corrosion tests

In this section, test results from the vertical furnace fireside corrosion tests are presented (methodology described in **Section 3.3**). Data includes mass changes, dimensional metrology changes, and qualitative assessments by SEM/EDX.

4.2.1. Introduction

Cross-sectioned post-exposure samples, measured with the image analyser, provided coordinate points for the post-exposure dimensions of the remaining metal (and also the remaining sound metal). The new metal surface points were compared with those recorded from the pre-exposure (**Section 3.3.6.1**). The terms 'metal thickness change' is interchangeably referred to as 'metal surface change'. Dimensional metrology and SEM/EDX results generated during the corrosion testing phase have been presented by test gas environments: WWF (**Section 4.2.2**), HGB (**Section 4.2.3**) and APR (**Section 4.2.4**).

WWF deposit, D1, and HGB deposit, D6, were included for all furnace tests to consider the influence of gas conditions on the deposits' corrosivity.

In **Appendix B**, all samples' dimensional metrology metal thickness change and sound metal change plots are presented on individual graphs, highlighting each median cumulative probability metal and sound metal change (**Figure 3-7**) value. These graphs allow more simplistic comparison between metal surface and sound metal depth profiles and may be referred to for evaluating median penetration depths as such:

$$\text{penetration depth} = \text{sound metal change} - \text{metal thickness change}$$

Energy peak overlap of Mo/S and Nb/S in the EDX spectrum have been encountered during microscopic element map for the exposed T91 and 347HFG steel samples. As such the BSE image brightness, which relates to the atomic numbers, has been used, in some instances, to differentiate between S and the heavy metals.

4.2.2. Metal changes in wood waste fuel test gas conditions

This section presents results generated from furnace test programs TW1, TW2, TW3 and TW4, for evaluating the corrosive effects of WWF deposits D1 - D5 and HGB deposit D6, exposed in WWF-firing gas conditions. The furnace tests' experimental conditions, sample alloys and test parameters are listed in **Table 3-3**. For ease of comparison, data from TW1 to TW4 have been presented by deposition flux. Some weight change data examples have also been provided in this section. All weight change measurements have been documented in **Appendix C**, while experimental errors associated with sample weighing are evaluated in **Section D-3**.

4.2.2.1. Metal changes at 600°C in wood waste fuels combustion gas conditions

Furnace tests conducted under the simulated WWF combustion gas conditions employed 4 deposition fluxes, 100, 50, 25 and 10 $\mu\text{g}/\text{cm}^2\text{h}$, for deposits, D1 and D6. Other deposits were evaluated only at 100 $\mu\text{g}/\text{cm}^2\text{h}$.

4.2.2.1.1. Weight change

The weight change measurements of each sample were taken, following each 100-hour furnace cycle. Example weight change data are presented in this section, while others are documented in **Appendix C**.

Figure 4-15 - Figure 4-17 present weight changes for 347HFG samples with applied deposits D1 - D6, exposed at 600°C in simulated WWF test gas conditions at a deposition flux of 100 $\mu\text{g}/\text{cm}^2\text{h}$. The 100-hour exposure samples (**Figure 4-15**) show weight increase (excluding 347HFG-D3), while some longer exposure (500-hour total) samples (**Figure 4-17**) underwent weight loss by 200 hours. The weight change is inconsistent for replicates even at the same exposure time. For example, at 200 hours, 347HFG-D5 gained 130 mg/cm^2 and 30 mg/cm^2 for the 200- and 500-hour samples respectively. Likewise, 347HFG-D3 and 347HFG-D4 experienced more than 200 mg/cm^2 weight loss after 200

hours, for the 500-hour samples; whereas their weight changes are $\leq 90 \text{ mg/cm}^2$ for the 200-hours samples at the same exposure duration.

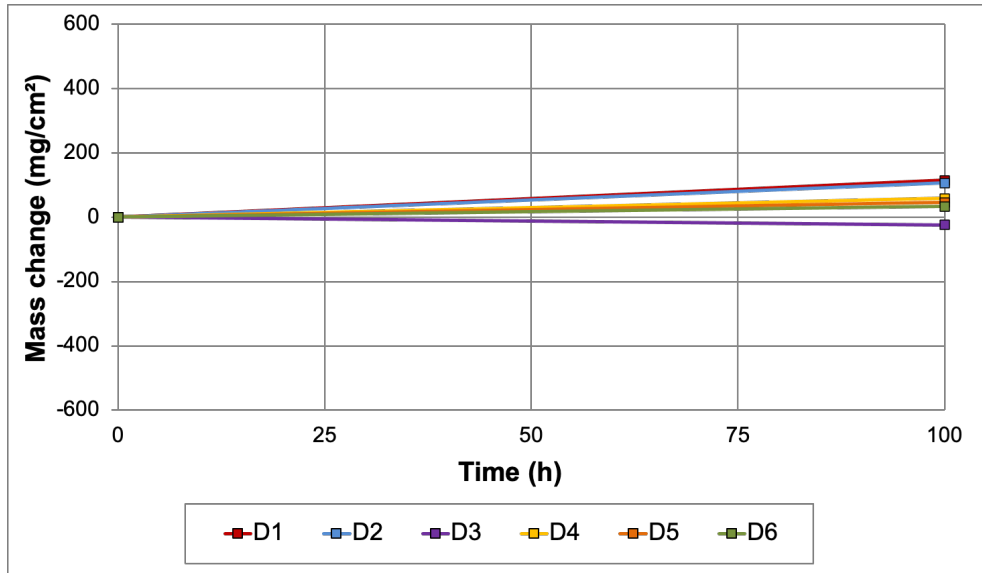


Figure 4-15: Mass changes in 347HFG samples exposed in wood waste fuels' simulated gas environment at 600°C with deposit D1-D6 (flux 100 $\mu\text{g/cm}^2\text{h}$) following 100 hours exposure

Figure 4-16 shows the 200-hour samples' weight changes after each 100 hours exposure cycle. It illustrates different weight change trends at the 100-hour interval compared to the 1000-hour samples (**Figure 4-15**).

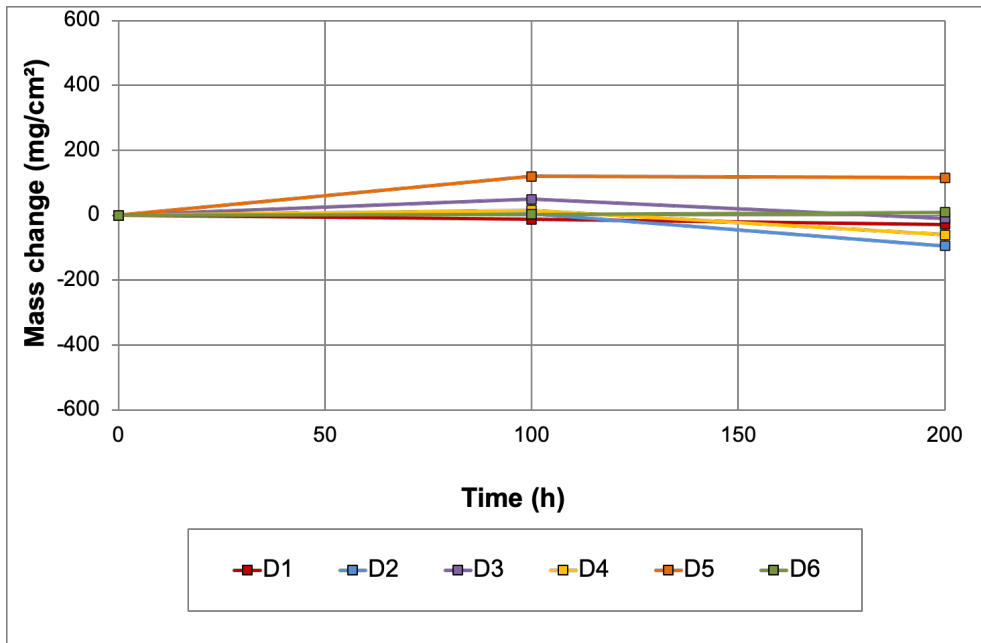


Figure 4-16: Mass changes in 347HFG samples exposed in Wood waste fuels' simulated gas environment at 600°C with deposit D1-D6, flux 100 $\mu\text{g}/\text{cm}^2\text{hour}$ following 200 hours exposure

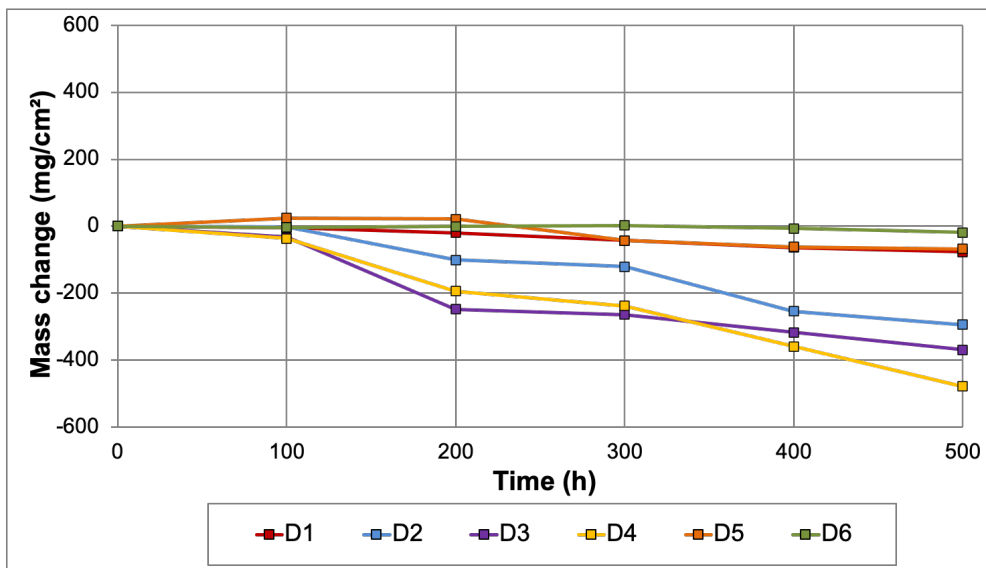


Figure 4-17: Mass changes in 347HFG samples exposed in Wood waste fuels' simulated gas environment at 600°C with deposit D1-D6, flux 100 $\mu\text{g}/\text{cm}^2\text{hour}$ following 500 hours exposure

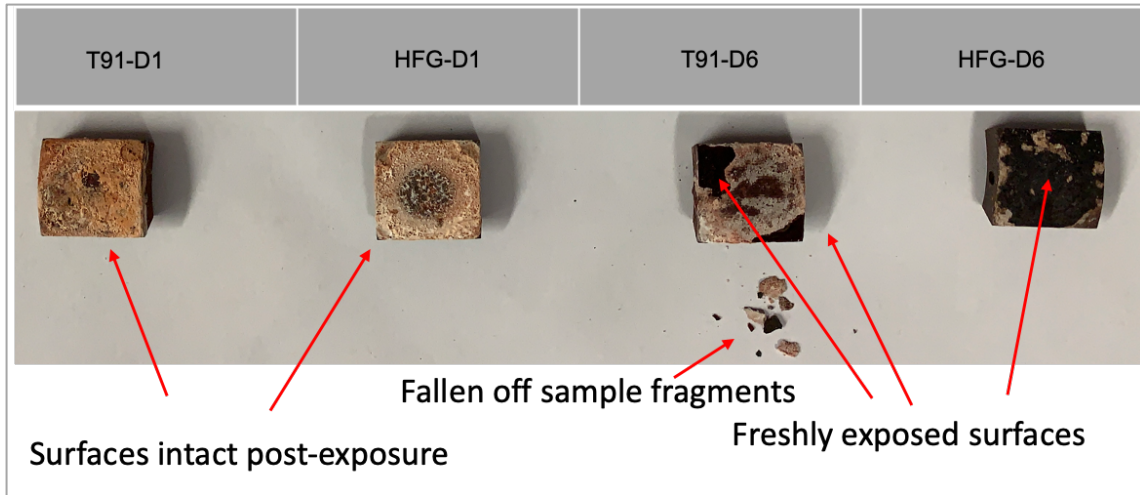


Figure 4-18: Evidence of spalled metal surfaces following furnace corrosion testing

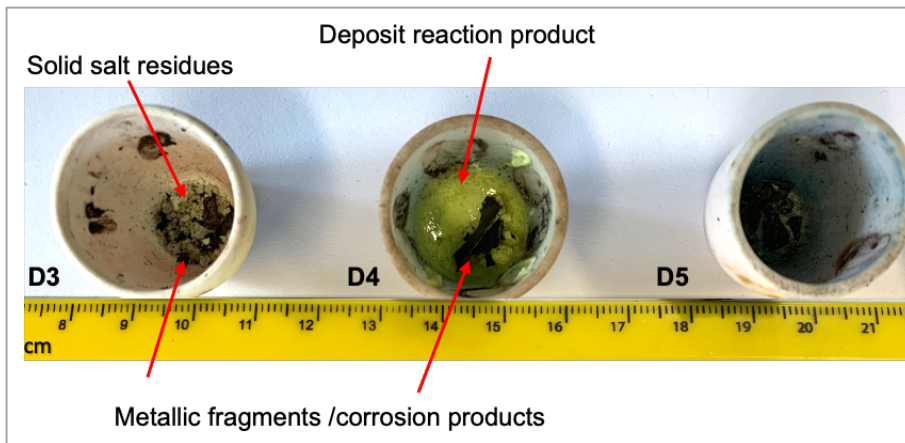


Figure 4-19: Crucibles for three 347HFG samples following 500 hours exposure with deposits D3, D4 & D5, flux $100 \mu\text{g}/\text{cm}^2\text{hour}$, in Wood waste fuels' simulated gas environment at 600°C

Figure 4-18 presents post-exposure images of some 500-hour exposure samples, including those coated with D3 and D4. Sample fragments collected in the crucibles (**Figure 4-19**) indicate spallation of scales occurred for these samples. Some fragments were loosely held on the metal surface and detached during sample analysis. Surface spallation was difficult to predict although samples were handled with reasonable care between tests. There was also no correlation between spallation and exposure time for the samples exposed up to

500 hours. The 1000-hour samples exposed at $100\ \mu\text{g}/\text{cm}^2\text{hour}$, however, demonstrated higher spallation tendencies (see **Figure C-1** and **Figure C-5**).

Following these observations, it was decided that the weight change data obtained from the samples would not be an accurate method for evaluating metal damage, although some correlation between excessive sample spallation and erroneous metal loss measurements have been noted.

4.2.2.1.2. Metal loss

The metal changes encountered by each sample, tested in the WWF test gas conditions at 600°C , are presented as cumulative probabilities (**Section 3.3.6.1**) in the following subsections. Metal change data are presented under the sections grouped by deposit flux level. The metal loss trends over time, deposition flux and temperature are described in **Section 5.2**.

i. Deposition flux $100\ \mu\text{g}/\text{cm}^2\text{h}$ for deposits D1, D2, D3, D4, D5 & D6

T91 and 347HFG were exposed with deposits D1 to D6 at flux $100\ \mu\text{g}/\text{cm}^2\text{h}$ at 600°C , generating 1000-, 500- and 200-exposure hours samples. The metal and sound metal change data for exposed alloys are presented from **Figure 4-20** to **Figure 4-31**.

Deposit D1

Figure 4-20 presents the post-exposure metal surface changes for both alloys coated with deposit D1 at flux $100\ \mu\text{g}/\text{cm}^2\text{h}$. By 200 hours, all T91 surface points experience metal change $>100\ \mu\text{m}$.

At all exposure times, T91 (659 μm , 451 μm , 196 μm , in order of decreasing exposure duration) undergoes more than twice the median metal changes experienced by the 347HFG samples (355 μm , 112 μm , 26 μm , in order of decreasing exposure duration). 347HFG-D1, exposed for 200 hours, has ~half

of its surface remaining within incubation phase of corrosion: i.e., metal loss error measurements may account for $\leq 13.5 \mu\text{m}$ (see error analysis, **Section D-4**). 347HFG also shows more evenly distributed metal change for the three samples, than T91.

The sound metal change plots for the six samples are presented in **Figure 4-21**. Minimal metal penetration is detected by dimensional metrology for the 500- and 1000-exposure hours samples. The sound metal penetration depths (**Appendix B**) are $12 \mu\text{m}$ and $17 \mu\text{m}$ respectively, for the 1000- and 500-exposure hour 347HFG samples. The median sound metal penetration depths of the T91 samples fall within $5 \mu\text{m}$ which is just above instrument resolution range (**Section D-1.2.3**).

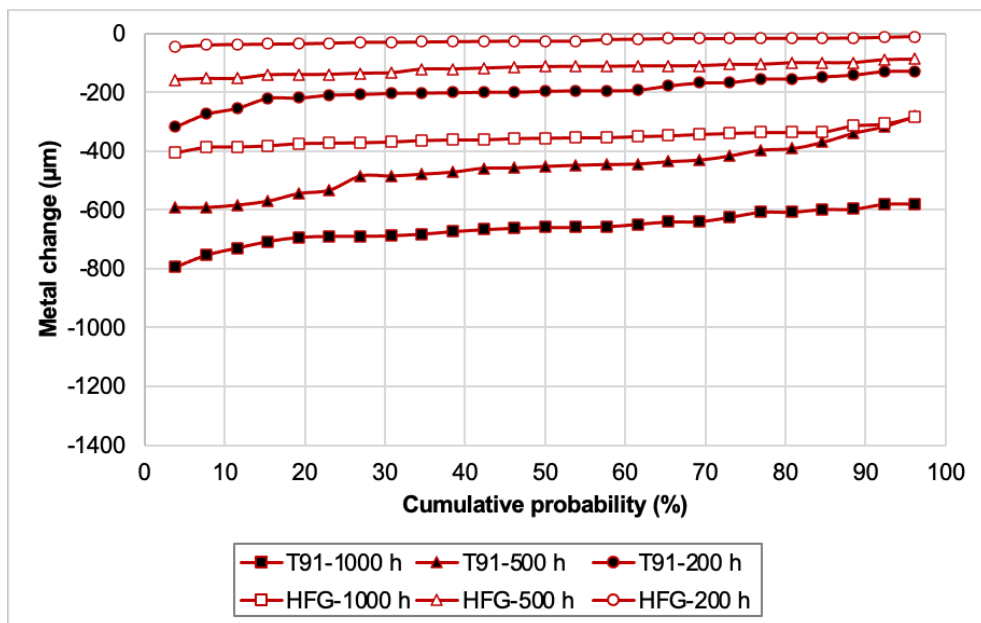


Figure 4-20: Metal change plot of T91 and 347HFG with deposit D1 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

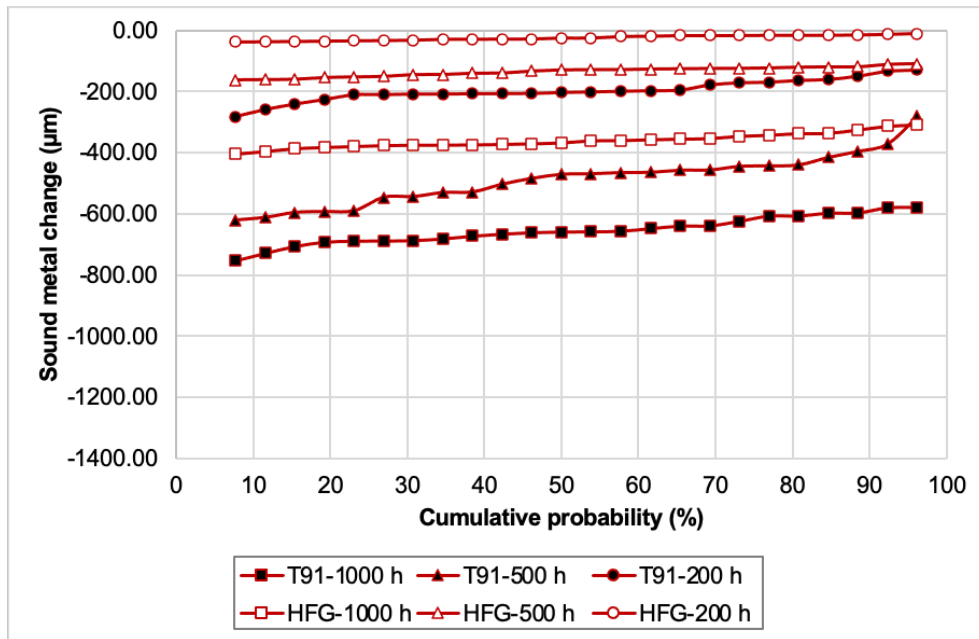


Figure 4-21: Sound metal change plot of T91 and 347HFG with deposit D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

Deposit D2

Figure 4-22 presents the metal surface change for both alloys coated with D2 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$. T91, at 1000 hours of exposure, suffers significant damage relative to 347HFG. The T91 metal changes at median values are -792 μm , -307 μm and -220 μm in order of decreasing exposure duration. The 347HFG metal changes at median values are -404 μm , -514 μm and -145 μm , in order of decreasing exposure duration. The mass change of the 1000-hour T91-D2 sample (Figure C-1) at 100-hours is $>100 \mu\text{m}/\text{cm}^2$. This mass change may be indicative of sample surface spallation having occurred. Such scale loss may expose fresh metal surfaces to deposits, increasing corrosion rates. The cumulative metal change profile for T91-D2, at 500 hours exposure, shows that $> 20\%$ of the metal surface has experienced a faster corrosion rate which may occur at spalled scale locations.

Median metal loss for the 200-hour samples (T91 and 347HFG) are $>150 \mu\text{m}$. It is possible that some degree of spallation had occurred for the 500-hour 347HFG sample, which underwent greater damage ($>100 \mu\text{m}$ median metal

loss difference) than its 1000-hour equivalent. The same sample (347HFG-D2, 500-hour exposure) also experienced a notable weight drop ($240 \mu\text{g}/\text{cm}^2$) after 500 hours exposure (**Figure C-6**), contrary to slight weight gain observed at 500 hours for the 1000-hours exposure sample equivalent (**Figure C-5**).

Exposure hour trends correlate better with internal damage for 347HFG (**Figure 4-23**). Median penetration depth and median sound metal change at 1000 hours are $-339 \mu\text{m}$ and $-743 \mu\text{m}$; and, at 500 hours, $-107 \mu\text{m}$ and $-622 \mu\text{m}$ respectively. Median penetrative damage for T91-D2 are 61 and $27 \mu\text{m}$ for the 1000- and 500-hour exposure samples respectively.

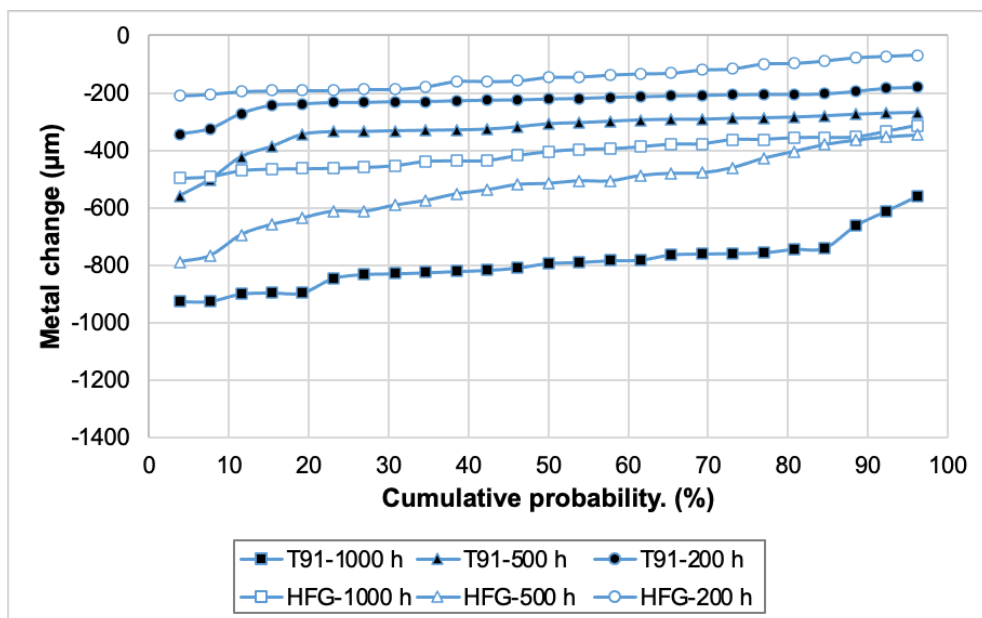


Figure 4-22: Metal change plot of T91 and 347HFG with deposit D2 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

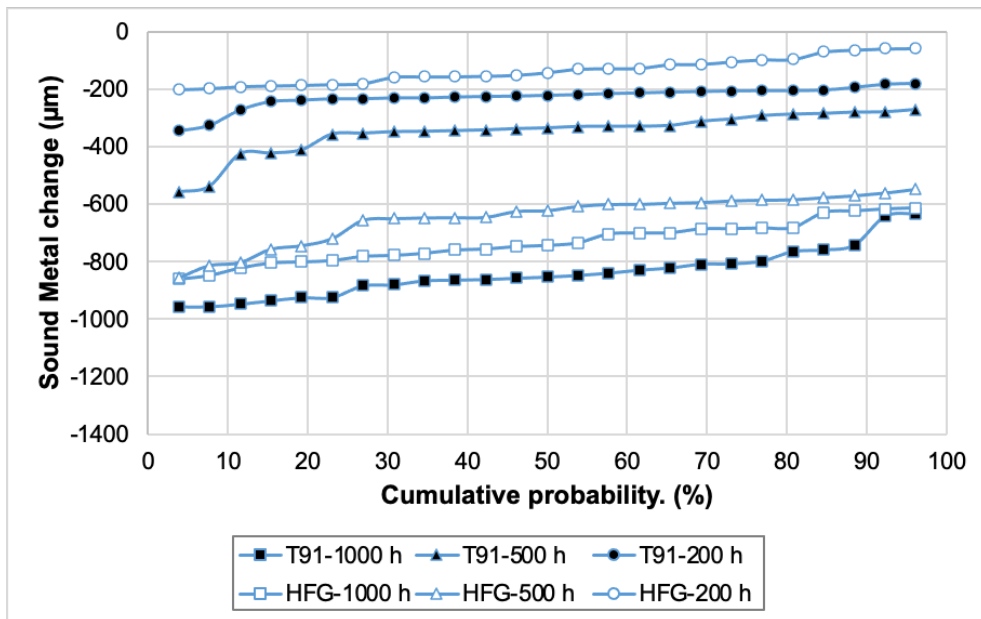


Figure 4-23: Sound metal change plot of T91 and 347HFG with deposit D2 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

Deposit D3

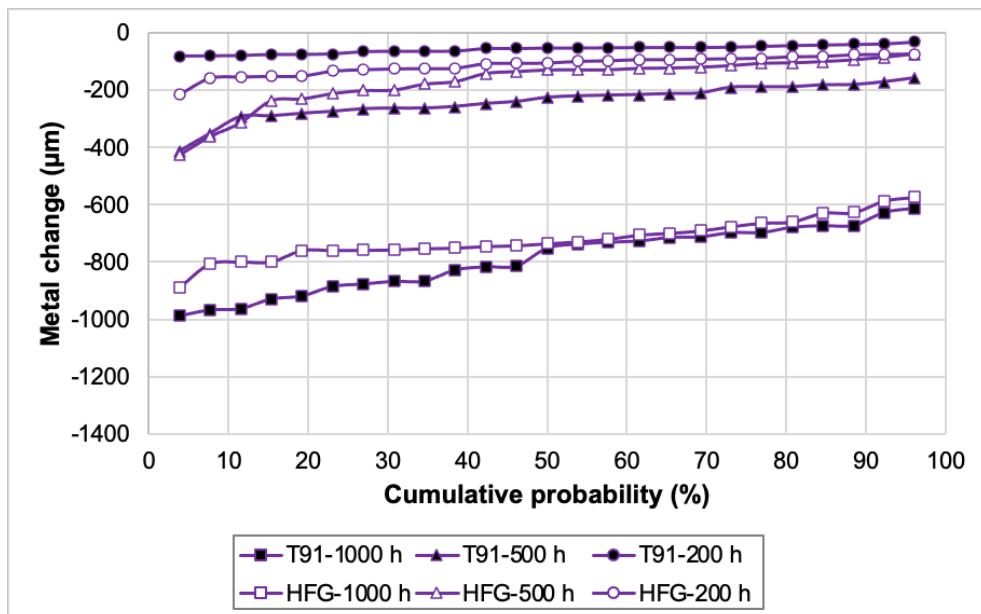


Figure 4-24: Metal change plot of T91 and 347HFG with deposit D3 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

Figure 4-24 presents the metal surface changes for both alloys coated with D3 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$. The median metal changes are $-752 \mu\text{m}$, $-226 \mu\text{m}$, $-52.5 \mu\text{m}$, for T91-D3 and, $-735 \mu\text{m}$, $-129 \mu\text{m}$, $-106 \mu\text{m}$ for 347HFG-D3, in order of decreasing exposure duration. Median metal loss values for the 1000-hour samples are much greater than those of the 500-hour samples. This is especially true for 347HFG, which also experienced significant weight changes compared to the T91 equivalent samples at 1000 hours (compare **Figure C-1** and **Figure C-5**).

The sound metal penetration depths for 347HFG are $41 \mu\text{m}$, $55 \mu\text{m}$ & $59 \mu\text{m}$, in order of increasing exposure duration, The internal oxidation for T91 is minimal at the initial exposure times (**Figure 4-25**). T91 penetrative depths are $<1 \mu\text{m}$, $21 \mu\text{m}$ & $110 \mu\text{m}$ in order of increasing exposure duration.

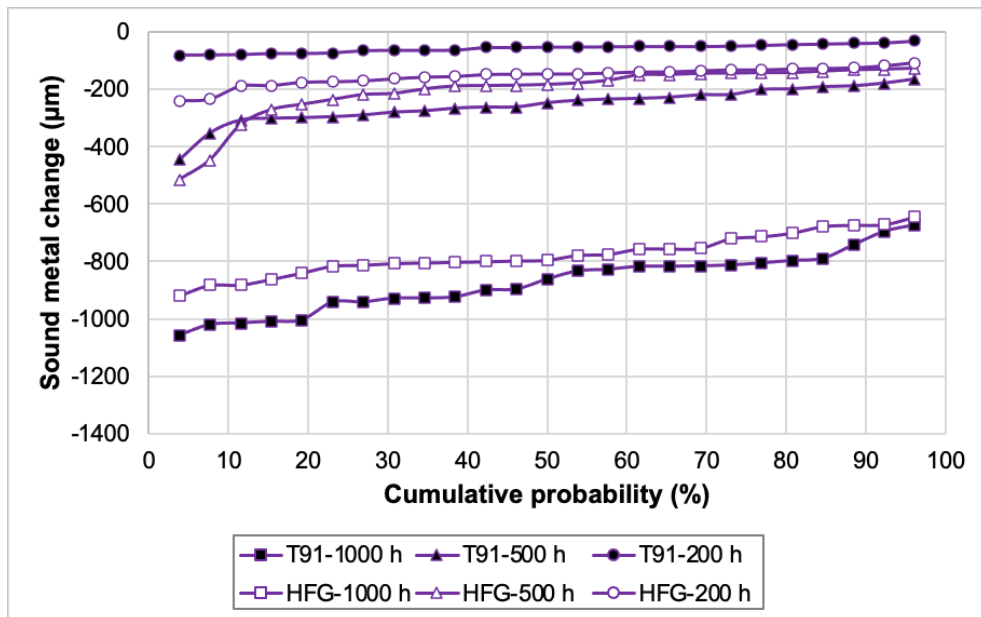


Figure 4-25: Sound metal change plot of T91 and 347HFG with deposit D3 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

Deposit D4

Figure 4-26 presents the metal surface change profiles for T91-D4 and 347HFG-D4 following exposure in WWF gas conditions at 600°C at a deposition flux of 100 $\mu\text{g}/\text{cm}^2\text{h}$. The metal change values measured across the T91 500-hour sample surface fall within -532 μm and -307 μm and are not far off those of the T91 200-hour sample; -435 μm to -301 μm . This may suggest that spallation could also occur at lower exposure times. A steep weight change (400 mg/cm^2) after the first furnace cycle (100 hours) was recorded for the 200-hour T91-D2 sample (**Figure C-3**). The 500-hour sample also shows considerable mass change (-230 mg/cm^2 at 500 hours exposure), although lower than for the former sample. These weight change differences may reflect variances in level of sample surface spallation which may have occurred for both samples, being lesser for T91-500 hours (**Figure C-4**). The weight increase in the case of the 200-hour sample (T91-D2) may reflect enhanced oxidation rates occurring, following spallation. Also, the 1000-hour sample shows a sharp drop in weight following 100 hours exposure (130 mg/cm^2 , (**Figure C-1**) which may suggest further corrosion exposure due to spallation and explain the wide gap between damage occurring for this sample and the 500-hour sample equivalent (**Figure 4-26**).

The 347HFG metal change trends also lack correlation with exposure duration. The 200-hour sample (median metal change, -302 μm) undergoes greater metal loss than its 500-hour sample equivalent (median metal change, -149 μm). Metal penetration depths are 29 μm , 106 μm , 57 μm , for 347HFG and 66 μm , 14 μm , 19 μm for T91, in order of decreasing exposure duration (**Figure 4-27**).

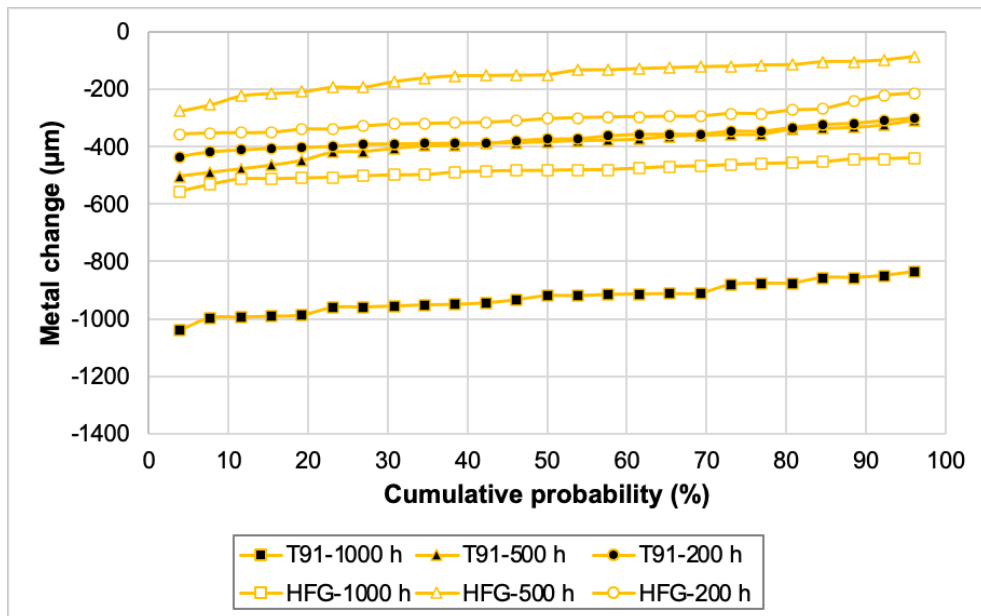


Figure 4-26: Metal change plot of T91 and 347HFG with deposit D4 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

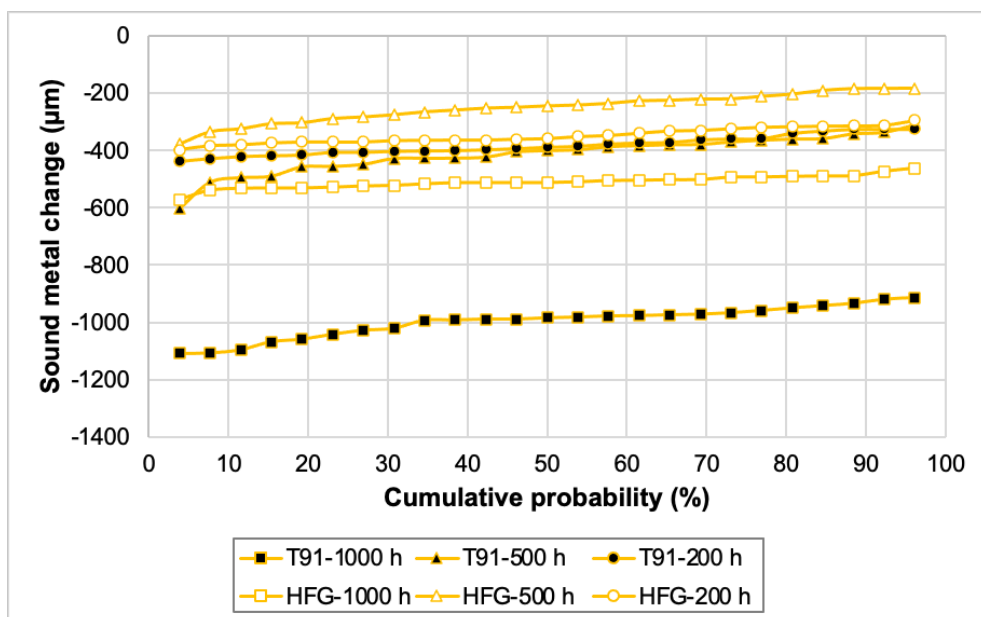


Figure 4-27: Sound metal change plot of T91 and 347HFG with deposit D4 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

Deposit D5

The metal surface change profiles for the D5 exposed steels in WWF gas conditions at 600°C are presented in **Figure 4-28**. Again, the 1000-hour exposed T91 sample undergoes dramatic metal change ($\sim 1200 \mu\text{m}$). The 500-hour and

200-hour median metal surface changes are -247 μm and -161 μm respectively. Metal loss for the latter two samples is localised on up to 20% of the surfaces.

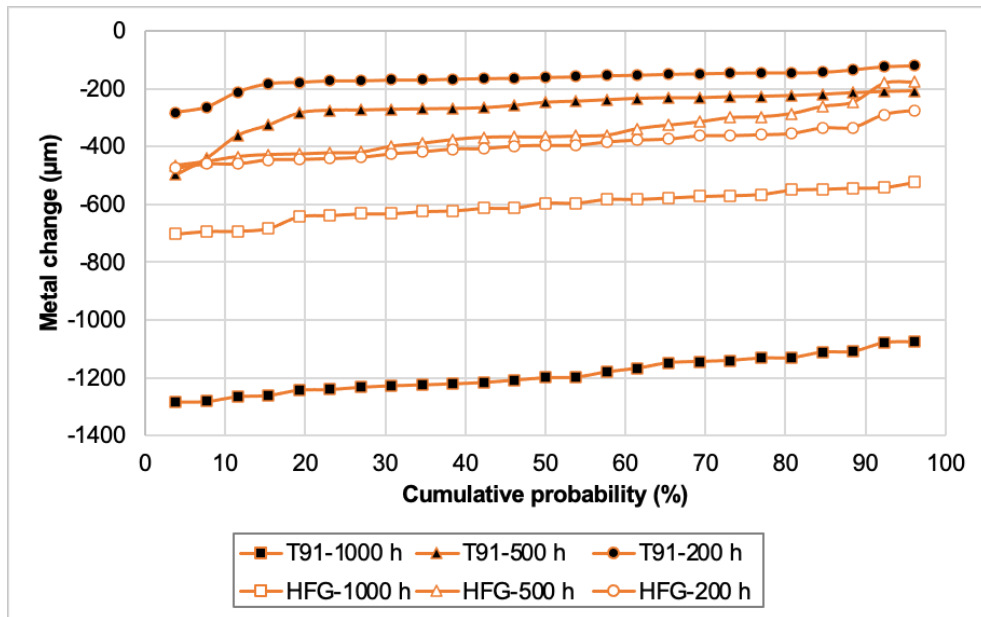


Figure 4-28: Metal change plot of T91 and 347HFG with deposit D5 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

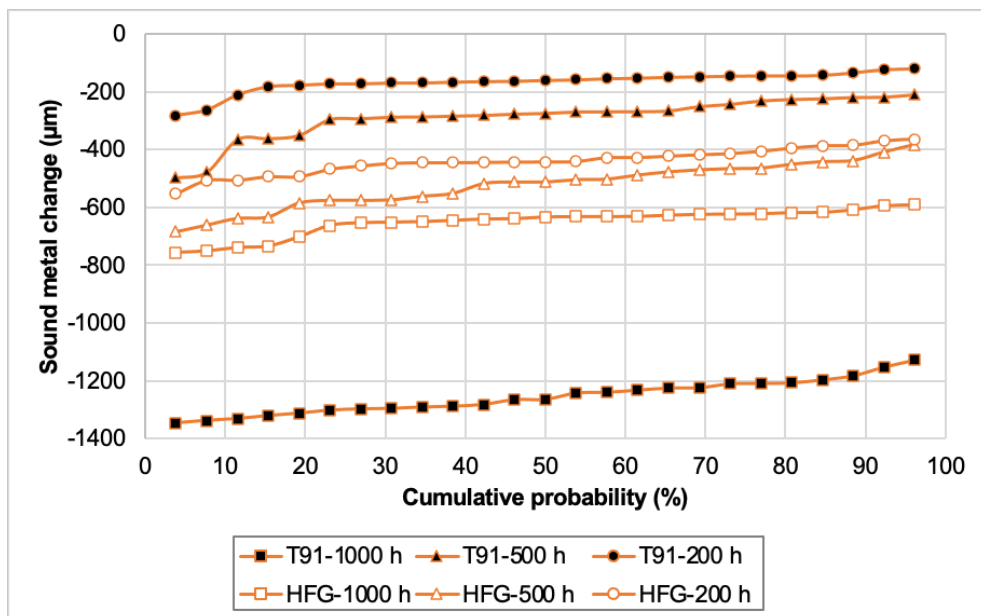


Figure 4-29: Sound metal change plot of T91 and 347HFG with deposit D5 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

The 200- and 500-hour exposure 347HFG-D5 samples experienced greater damage than the T91 samples equivalents which is not the case for the

previous. Erroneous metal change data is suspected of the former samples (347HFG-D5) as median metal loss was greater at 200-hours (396 μm) compared to that occurring at 500 hours (369 μm). Their sound metal changes were, however, more reflective of their exposure durations; 442 μm , 513 μm at 200 and 500 hours respectively (**Figure 4-29**).

Deposit D6

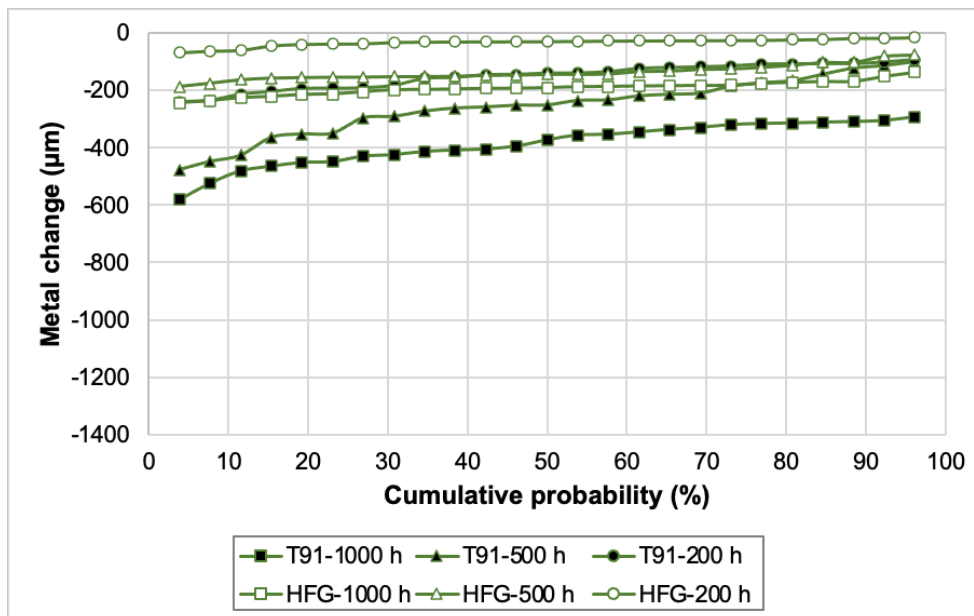


Figure 4-30: Metal change plot of T91 and 347HFG with deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

The metal change and sound metal changes for both alloys coated with the HGB deposit, D6, in WWF test conditions at 600°C are presented in **Figure 4-30** and **Figure 4-31** respectively. The 347HFG-D6 median metal loss at 200 hours remained within incubation corrosion stage for over 50% of its metal surface. 347HFG-D6 median metal loss values are 196 μm , 147 μm and 30 μm with decreasing exposure time.

Metal surface change is more evenly distributed across the 347HFG sample surfaces compared to the T91-D6 samples on which localised surface damage has occurred. By 200 hours, metal surface loss is progressed beyond 100 μm for all measured points on the T91-D6 sample. The median metal change values for the T91 samples in decreasing order of exposure duration are 374 μm , 251 μm and 145 μm . Median penetration depths are negligible ($< 2 \mu\text{m}$) at 200, 500 and 1000 hours for the 347HFG-D6 samples. Median penetration depths range between 22-54 μm for T91-D6, exposed for 1000 hours.

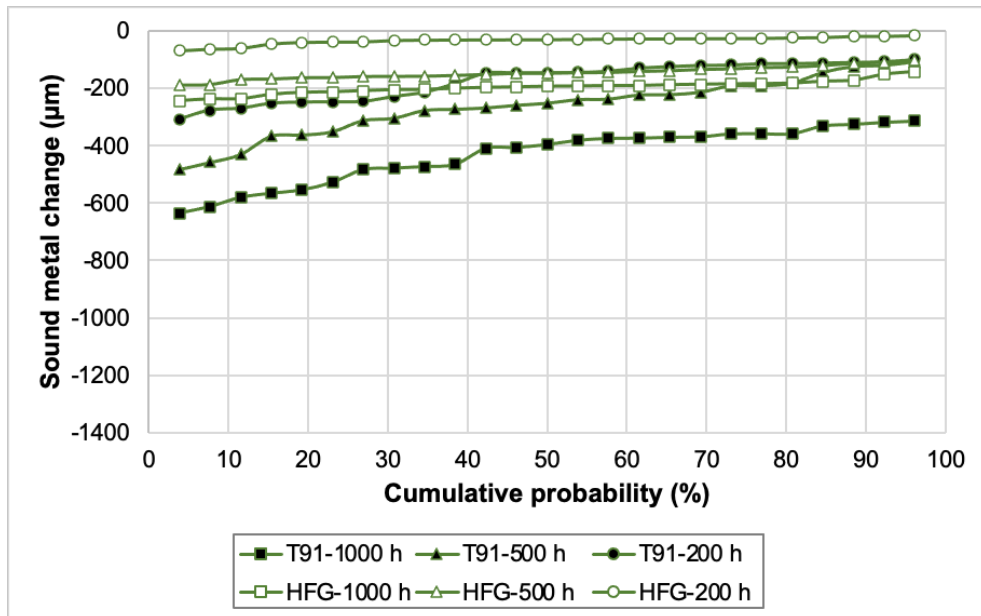


Figure 4-31: Sound metal change plot of T91 and 347HFG with deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed in simulated WWF test gas conditions at 600°C

ii. Deposition flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ for D1 & D6

T91 and 347HFG were corroded under exposure to deposit D1 and D6 at 50 $\mu\text{g}/\text{cm}^2\text{h}$ deposition flux. The tests were conducted in the WWF test gas conditions at 600°C, generating 1000- and 500-hour exposure samples. The metal and sound metal change data of the exposed alloys are presented from **Figure 4-32 to Figure 4-35**.

Figure 4-32 shows the metal changes occurring following 500 hours of exposure. The D1-covered samples experienced similar levels of metal change distributions. The metal surface change range as; -231 μm to -341 μm for 347HFG and, -234 μm to -341 μm for T91. D1 also promoted greater metal loss than D6.

Metal loss occurring for both D6-covered alloys, T91 (median value -180 μm) and 347HFG (median value -119 μm), show more damage occurring on the ferritic steel. The metal change range across the 347HFG-D6 sample cross-section is -86 μm to -60 μm , a more evenly distributed damage than experienced by 347HFG-D1. The damage range across the T91-D1 sample surface (-225 μm to -118 μm) suggests a less evenly distributed metal loss occurs, compared to T91-D1.

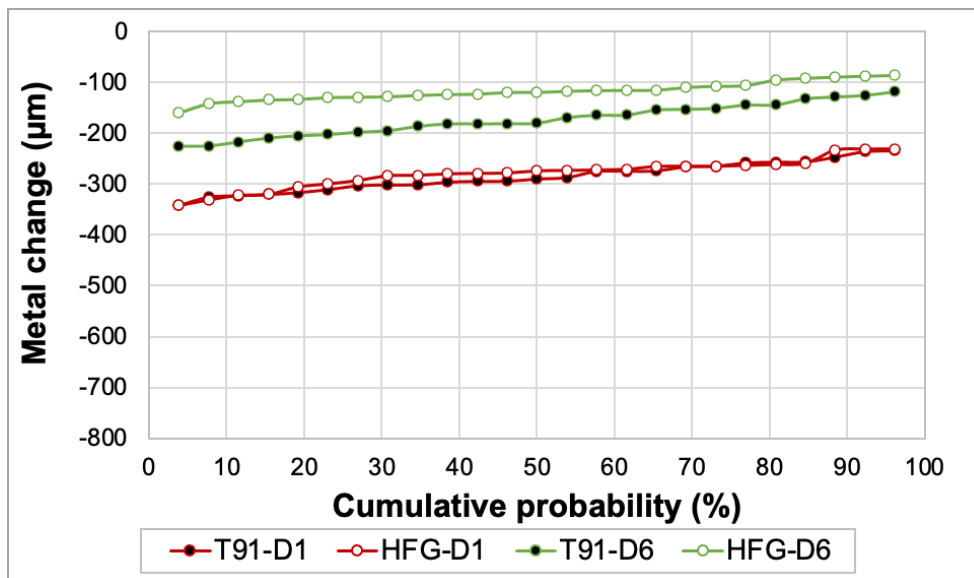


Figure 4-32: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

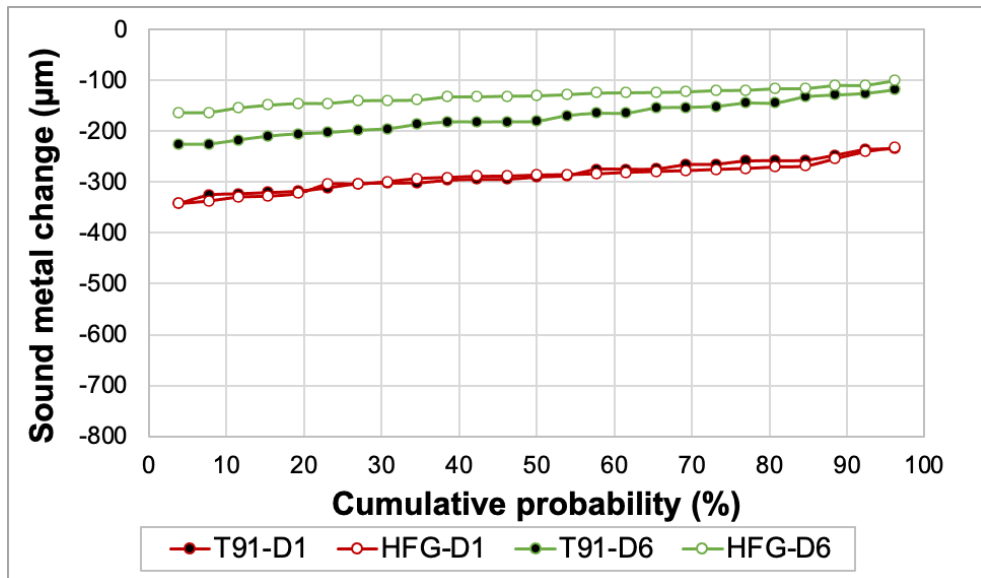


Figure 4-33: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

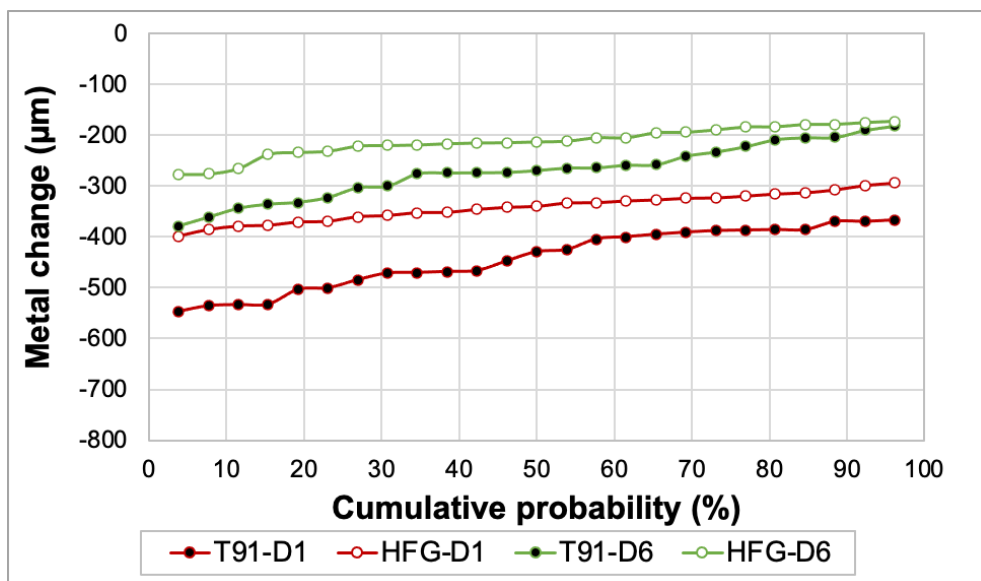


Figure 4-34: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 600°C

Minimal sound metal penetration is detected for both 347HFG samples at 500°C (**Figure 4-33**); median penetration depths of 12 μm (347HFG-D1) and 11 μm (347HFG-D6) occurs. No internal damage is measured on the ferritic steel samples.

At 1000 hours, deposit D1 (T91, 429 μm ; HFG347, 340 μm median metal loss) influences greater surface metal damage than D6 (T91, 270 μm ; 347HFG, 213 μm median metal loss) for both alloys (**Figure 4-34**). Also, all samples' surface points are corroded beyond incubation stage at a deposit flux of 50 $\mu\text{g}/\text{cm}^2\text{h}$ by 1000 hours exposure (173 μm metal loss for 347HFG-D6, which experiences the least change). Greater ranges in metal loss occur across the surfaces of the T91 samples (metal loss ranges: 179 μm , T91-D1; 196 μm , T91-D6) compared to those of 347HFG (metal loss ranges: 105 μm , 347HFG-D1; 104 μm , 347HFG-D6) which experience more evenly distributed surface metal changes. T91 exhibits slightly greater responses to the deposit change: the median metal loss values of 347HFG-D1 and 347HFG-D6 differ by 127 μm , those of T91 differ by 160 μm . There is however no sound metal penetration detected for T91, whereas for 347HFG, approximately 20 μm of median value sound metal penetration depth is recorded for the D1 exposed sample.

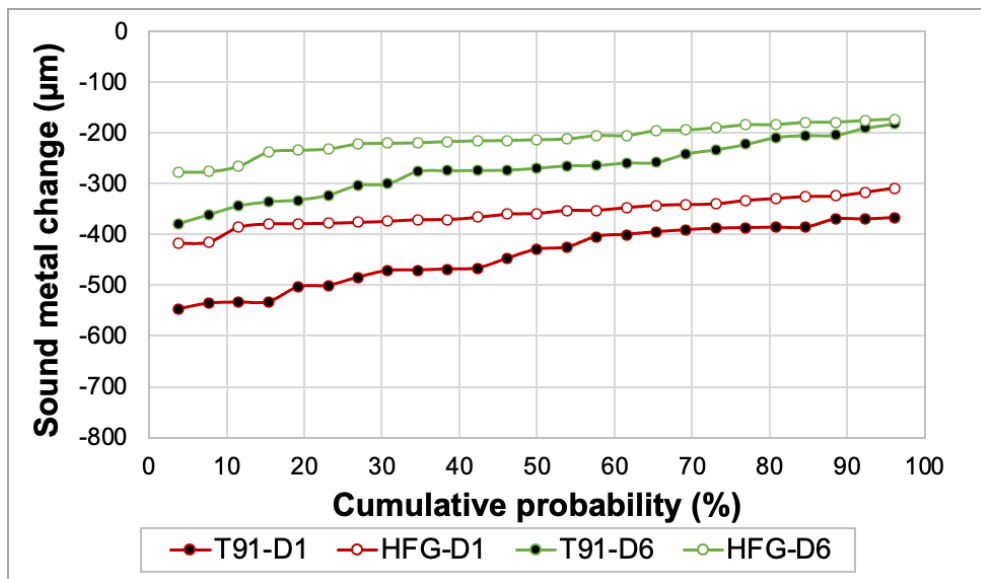


Figure 4-35: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 600°C

iii. Deposition flux 25 $\mu\text{g}/\text{cm}^2\text{h}$ for D1 & D6

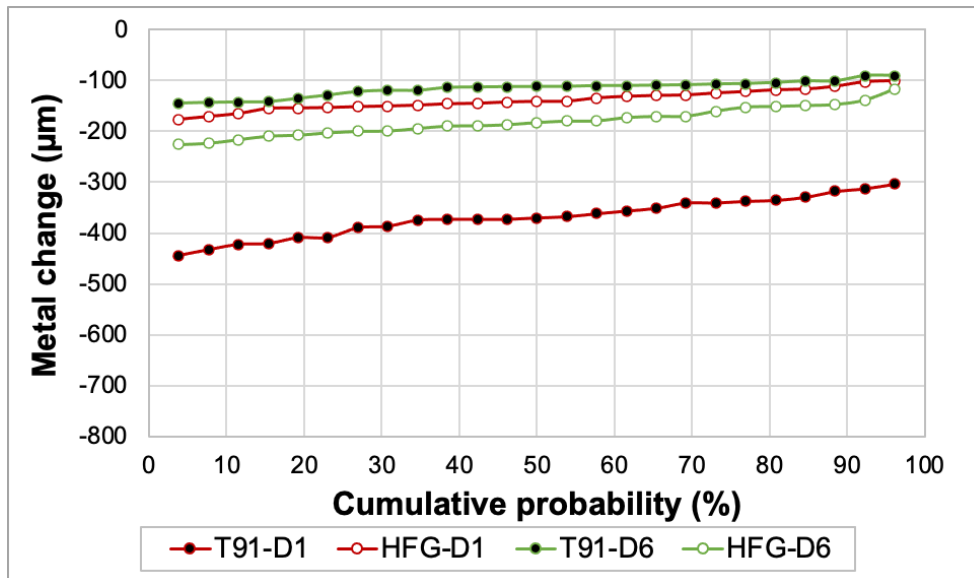


Figure 4-36: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 25 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

Both alloys were exposed with a deposition flux of 25 $\mu\text{g}/\text{cm}^2\text{h}$ under WWF test gas conditions at 600°C. Two 500- and 1000-hour samples were generated for each alloy. The metal and sound metal change data for the exposed alloys are presented from **Figure 4-36** to **Figure 4-39**.

Figure 4-36 displays the metal changes undergone, following 500 hours of exposure. Metal changes occurring across most measured points of the T91-D6, and the 347HFG sample surfaces (for both deposits) are within -230 μm . The median metal loss undergone by T91-D1 (370 μm) however, is higher than that of the equivalent sample exposed at a flux of 50 $\mu\text{g}/\text{cm}^2\text{h}$ (273 μm , **Figure 4-32**). The suspected flaw in the corrosion data for T91-D1 (25 $\mu\text{g}/\text{cm}^2\text{h}$) follows the observation of the inconsistent weight changes occurring after 200- and 300-hours exposure (**Figure C-10**). Sound metal changes are minimal (<10 μm) for both 347HFG samples and not detected on the T91 samples at 500 hours exposure (**Figure 4-37**).

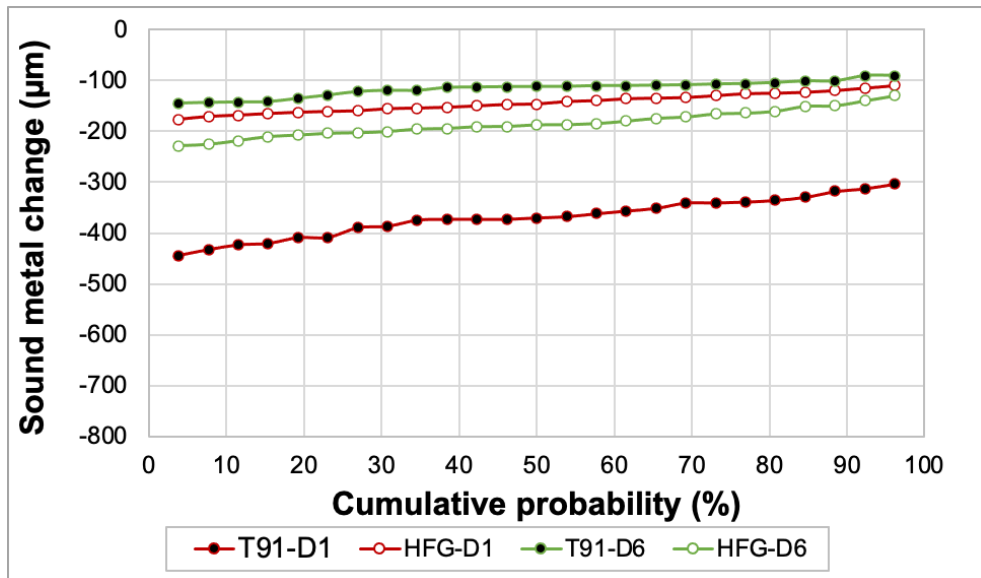


Figure 4-37: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $25 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

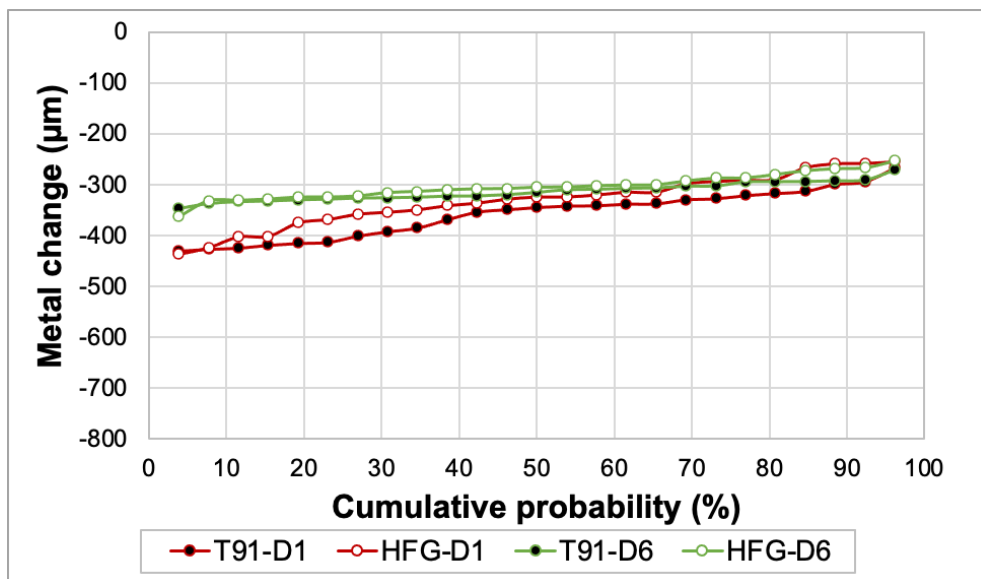


Figure 4-38: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $25 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 600°C

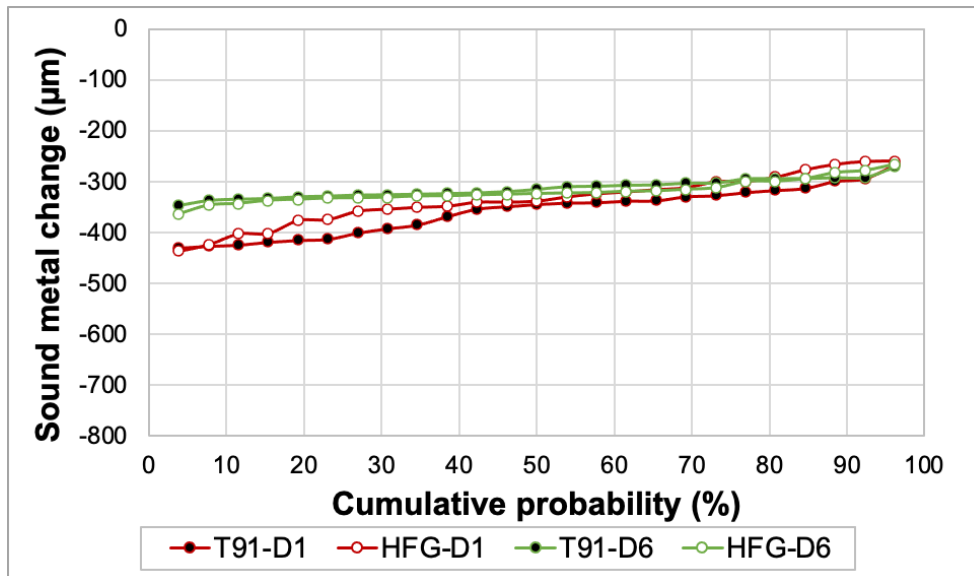


Figure 4-39: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 25 µg/cm²h exposed for 1000 hours in simulated WWF test gas conditions at 600°C

After 1000 hours, the samples display similarities in their metal change profiles for each deposit exposure. Median metal surface changes are: 348 µm & 328 µm and; 314 µm & 304 µm for T91-D6 & 347HFG-D6 respectively. D1 influences relatively more unevenly distributed surface loss on both alloys (~40% of the metals surfaces may have experienced localised damage; **Figure 4-38**). Sound metal change is mostly negligible for the austenitic steel samples, at all measurement points, and non-detected for the ferritic steel samples (**Figure 4-39**).

iv. Deposition flux 10 µg/cm²h for D1 & D6

The metal and sound metal changes for exposed 347HFG and T91 samples, coated with deposits D1 or D6 at a flux of 10 µg/cm²h, are presented from **Figure 4-40** to **Figure 4-43**. These tests were also conducted in WWF test gas at 600°C, generating 500- and 1000-hour exposure samples.

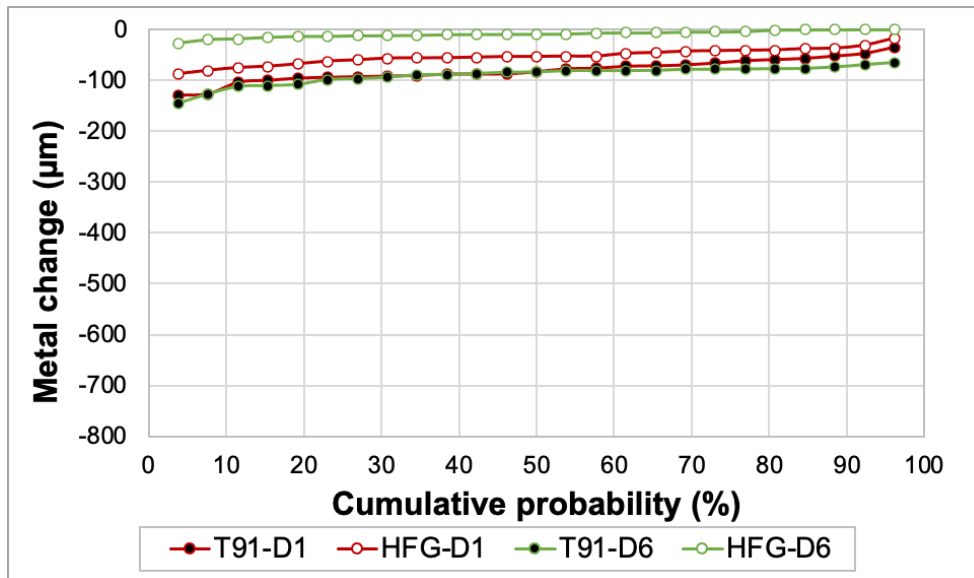


Figure 4-40: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $10 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

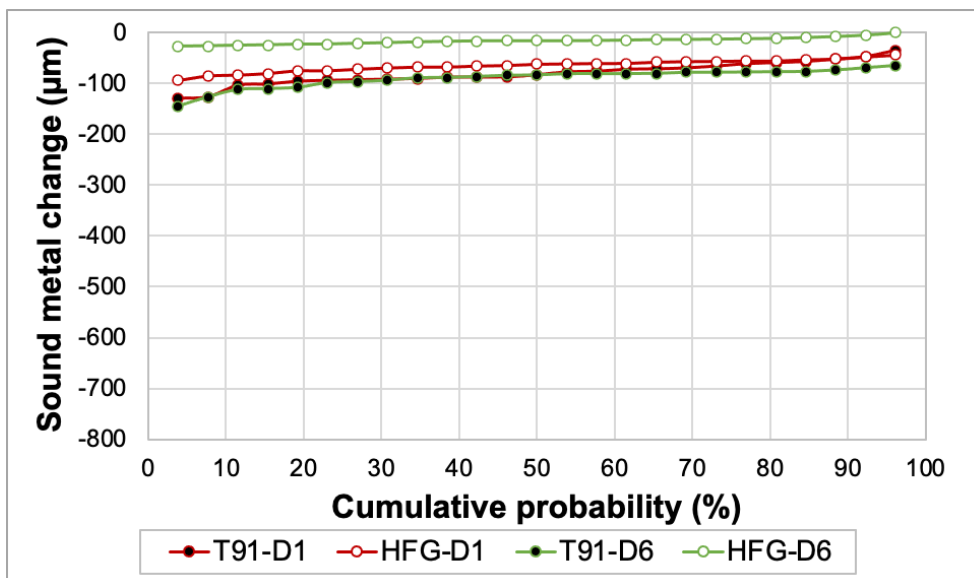


Figure 4-41: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $10 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 600°C

The metal changes, in **Figure 4-40**, show that most of the 347HFG-D6 sample remains within the incubation stage (metal loss range, 0-28 μm and median metal loss, 10 μm). Deposit D1, however, promotes propagative damage on most of the 347HFG steel's surface by 500 hours (metal loss range, 18-88 μm

and median metal loss, 54 μm). T91's responses to D1 and D6 are also at within propagation metal loss phase (up to 100 μm metal loss for most surface points measured). Sound metal penetration is not detected at the low deposition flux for all four samples (**Figure 4-41**).

After 1000 hours exposure (**Figure 4-42**), the median metal loss of 398 μm for T91-D1, is comparable with those of higher deposition flux exposed samples (e.g., sample T91-D1, exposed for 1000 hours at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$, in **Figure 4-34**, is 429 μm). The relatively high metal loss is observed alongside weight change anomalies (-148 mg/cm^2 after 300 hours cycle) (**Figure C-1**). Sample 347HFG-D1 experienced a median metal surface loss of 187 μm , while the D6 coated samples underwent less corrosion damage (metal surface loss ranging between 84-182 μm for both 347HFG-D6 and T91-D6). A median metal loss of 117 μm and 123 μm was recorded for 347HFG-D6 and T91-D6 respectively. Minimal sound metal penetration has been recorded for the four samples (**Figure 4-43**).

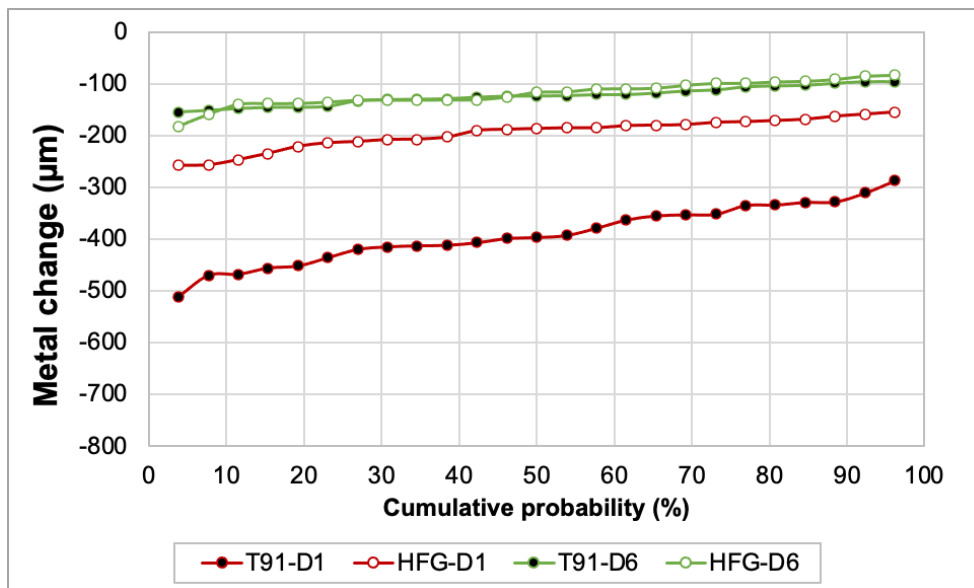


Figure 4-42: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 10 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in WWF test gas conditions at 600°C

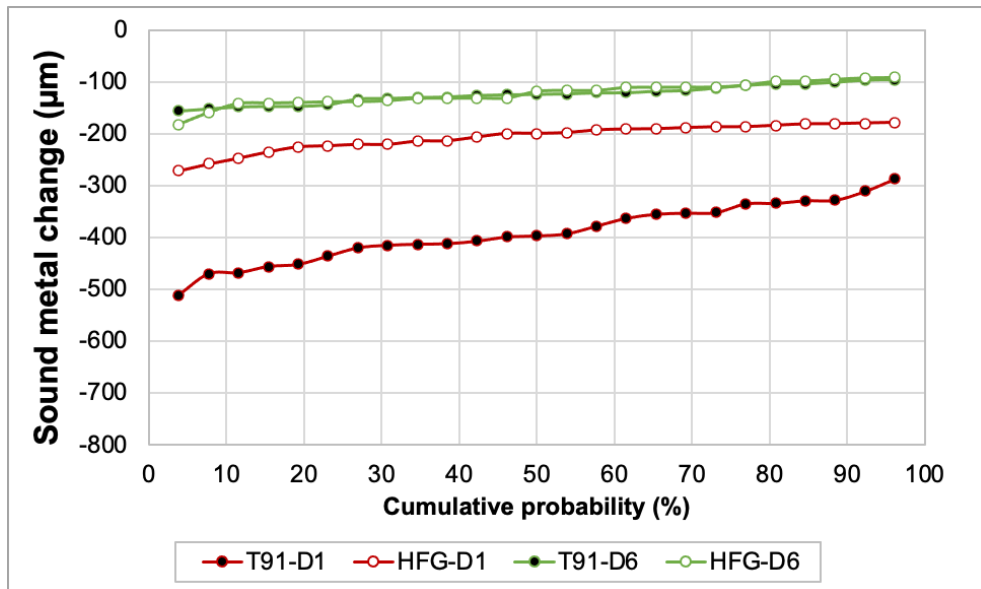


Figure 4-43: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 10 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in WWF test gas conditions at 600°C

4.2.2.1.3. SEM/EDX evaluation of WWF deposit samples in WWF test gas at 600°C

The SEM/EDX images of the cross-sectioned reference samples and the exposed samples (the 'no applied deposit' samples and samples assessed in **Section 4.2.2.1.2**) are presented in this section. All images captured represent typical views of the sample unless otherwise specified.

i. Reference samples (unexposed)

The BSE images and EDX maps of the unexposed T91 (**Figure 4-44**) and 347HFG (**Figure 4-45**) samples illustrate the alloy components as listed in **Table 3-1**. Nb precipitates are clustered in approximately 5 μm lengths within the austenitic steel matrix. These features are not observed on the T91 sample, making it easier to distinguish between both alloys.

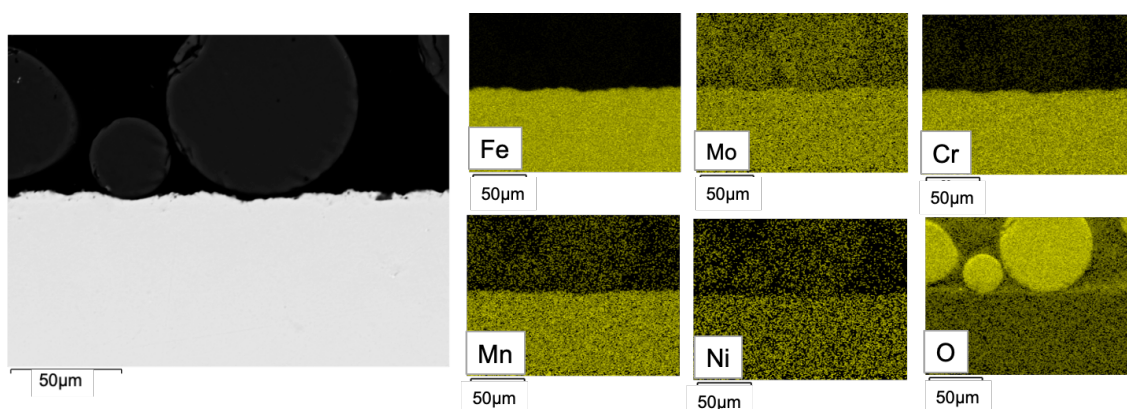


Figure 4-44: BSE image and EDX map of reference T91 sample (unexposed)

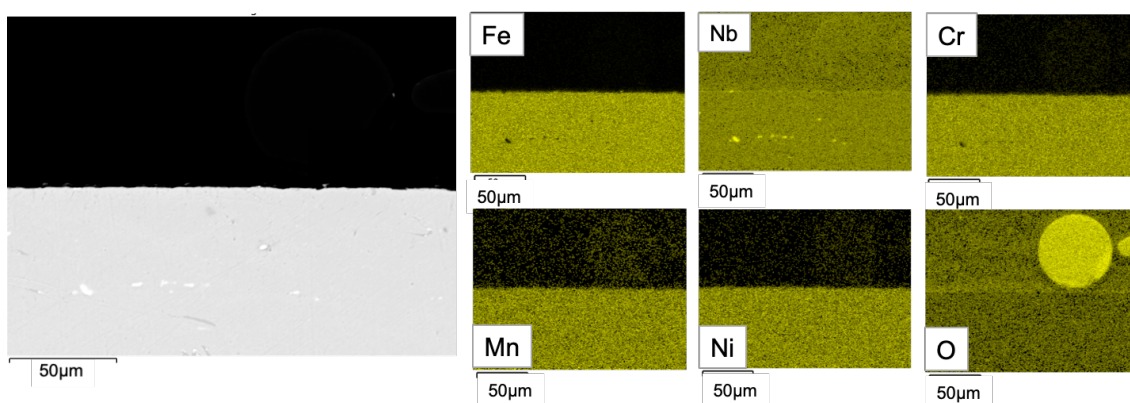


Figure 4-45: BSE image and EDX map of reference 347HFG sample (unexposed)

ii. No deposit samples (exposed)

The BSE images of the cross-sectioned T91 and 347 HFG steels exposed with no applied deposit for 1000 hours at 600°C in WWF test gas are presented in **Figure 4-46** and **Figure 4-47**.

T91 reveals a multi-layered scale, thicker than 100 µm. The mid-scale region is Cr and Mn-rich while the top scale region is Fe-rich. Different extents of porosity can be observed across the thickness of the scale, with the bottom scale layer appearing the most porous. The scale is delaminated from the alloy surface and the scale at the delamination layer is rich in Cr. When analysing EDX data, peak overlaps are encountered for Mo and S, whose characteristic X-rays have similar

kinetic energies ($L\alpha$ 2.293 eV; $K\alpha$ 2.307 eV respectively). A stronger electron beam deflection and a corresponding brighter BSE image is expected for heavier nuclei elements such as Mo, compared to S which appears darker [119]. These contrast features make it possible to distinguish between both elements' maps. Mo forms a predominant layer at the metal/scale boundary and is also encountered within the scale layers. S, condensed from the flue gas and positioned at the upper scale region, is presented as brighter clusters at the sintered scale region. It is also likely that S is present at the scale/metal interface, where delamination occurred.

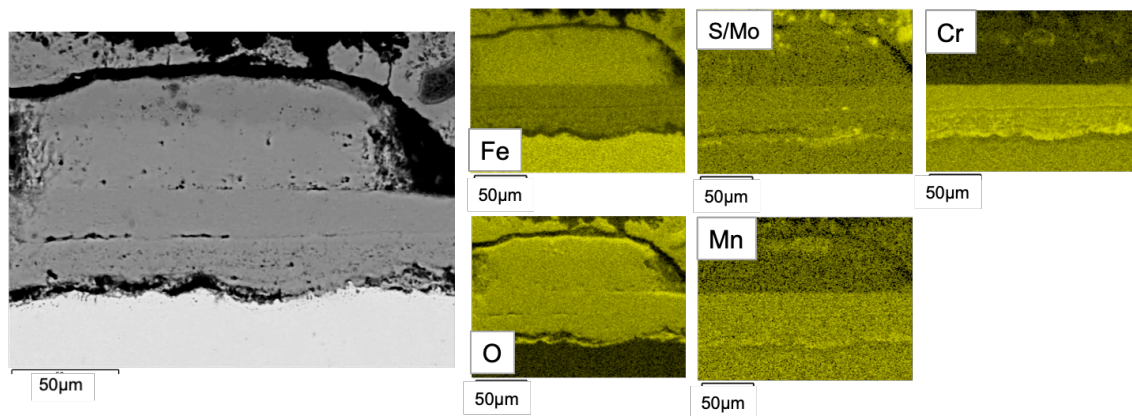


Figure 4-46: BSE image and EDX element maps of no applied deposit T91 sample, following 1000 hours exposure in WWF simulated combustion gas environment at 600°C. S is presented as brighter clusters at the sintered scale region

The average scale thickness across the austenitic steel sample (**Figure 4-47**), exposed in WWF test gas conditions at 600°C for 1000 hours, is under 60 µm. The reference to 'scales' in this thesis addresses regions of alloy components which have migrated from the bulk metal. Damage occurs in a more penetrative pattern into the bulk metal for this steel, which may be along the alloy's grain boundaries.

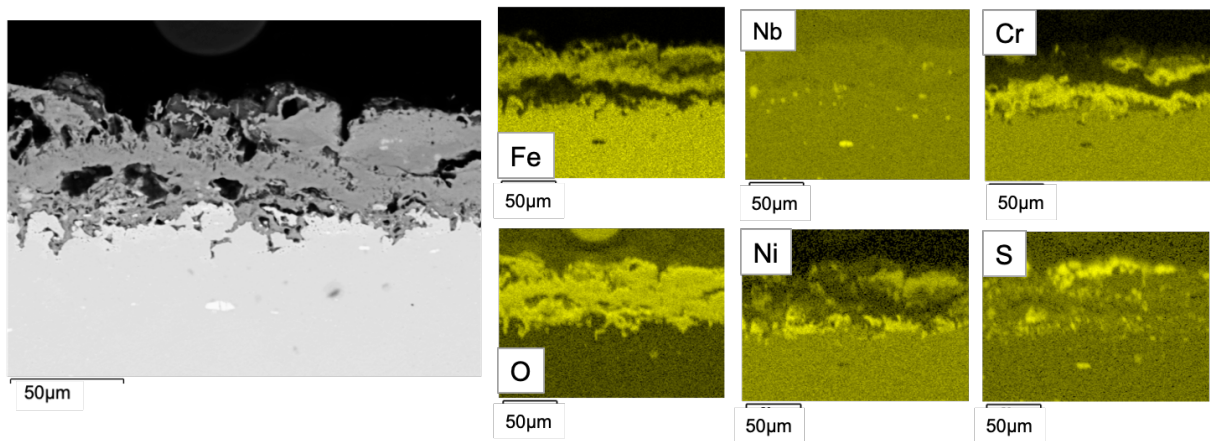


Figure 4-47: BSE image and EDX map of ‘no applied deposit’ cross-sectioned 347HFG sample following 1000 hours exposure in WWF simulated combustion gas environment at 600°C

Also, voids within the scale may result from depleted/corroded grains which may have detached from the bulk metal. The EDX mapping confirms layers of Fe and Cr-rich scales, the latter being nearer to the bulk metal. Ni however, forms a scale at the metal/scale interface. Some overlap is noted for Nb and S EDX peaks, as the outer shell energy levels of Nb is $L\alpha$ 2.166 eV (similar to that of S). In this case, the element maps may indicate the presence of S at the scale/gas interface as the heavier nuclei, Nb, gives poorer signals.

i. 100 $\mu\text{g}/\text{cm}^2\text{h}$ deposition flux samples

Deposit D1

The BSE images of the cross-sectioned D1-coated samples exposed for 1000 and 500 hours are presented in **Figure 4-48**. Scales were not recovered for the T91 1000-hour sample due to delamination. At 500 hours, scales of $>50\ \mu\text{m}$ thickness are observed. Corrosive attack is observed within the bulk alloy region for both T91 samples (**Figure 4-48**). At 500 hours, small cavities are observed along the metal surface (up to $20\ \mu\text{m}$ depth). By 1000 hours, the penetrative depth is $\sim 50\ \mu\text{m}$ at some localised regions.

Porous upper scales are noted on both 347HFG samples. At 500 hours, scales are $>50\text{ }\mu\text{m}$ thick. The lower scale layer is comparably less porous than the upper scale regions. Intergranular penetration into the remaining metal region of the austenitic steel samples is pronounced, especially at 1000-hour exposure where the penetration depth is $\sim 50\text{ }\mu\text{m}$ on average.

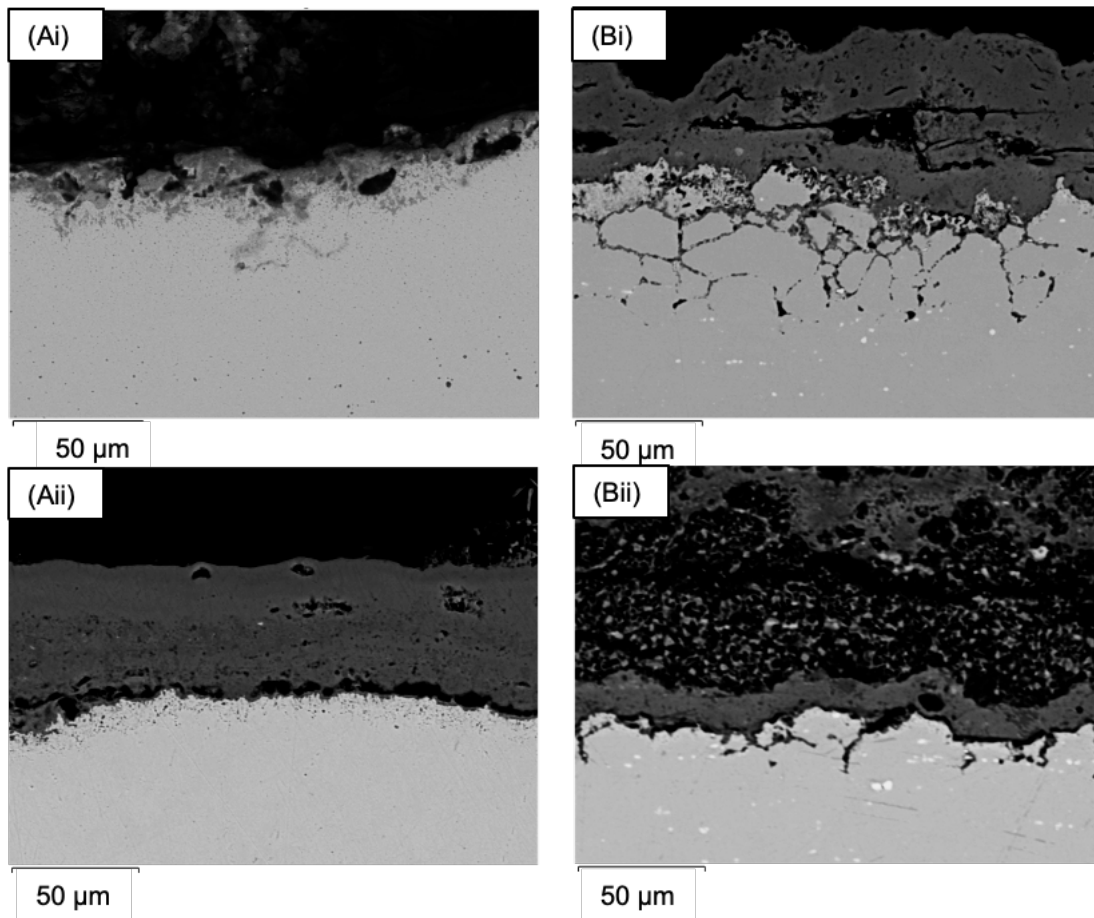


Figure 4-48: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples covered with deposit D1 at flux $100\text{ }\mu\text{g}/\text{cm}^2\text{h}$ following (i) 1000 and (ii) 500 hours of exposure in WWF simulated combustion gas environment at 600°C

Deposit D2

The BSE images of the cross-sectioned D2-coated steels, exposed for 1000 hours, are presented in **Figure 4-49**. Scales were not recovered for any of

the samples. The images show grain boundary attack depth of approximately 150 μm on 347HFG and localised damage occurring for T91.

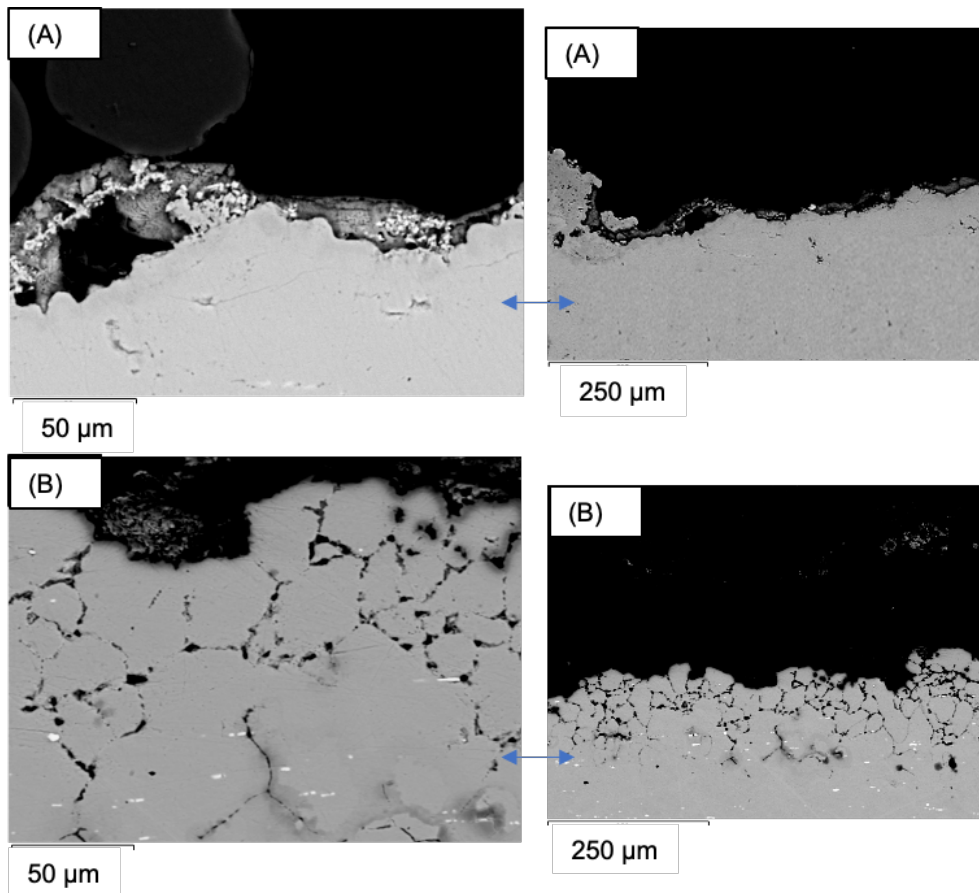


Figure 4-49: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples coated with deposit D2 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Images have been captured at two magnifications

Deposit D3

The BSE images of the cross sectioned D3 coated samples exposed for 1000 hours are presented in **Figure 4-50**. Wider views are presented on the right. Both steels have experienced significant damage. Delaminated multi-layered scales may be observed on T91, and the sound metal region displays corrosive features of up to 200 μm in vertical depth. The sample EDX maps

(Figure E-1, T91-D3) confirm the presence of damaged Cr oxide scales which may have been attacked by deposit components.

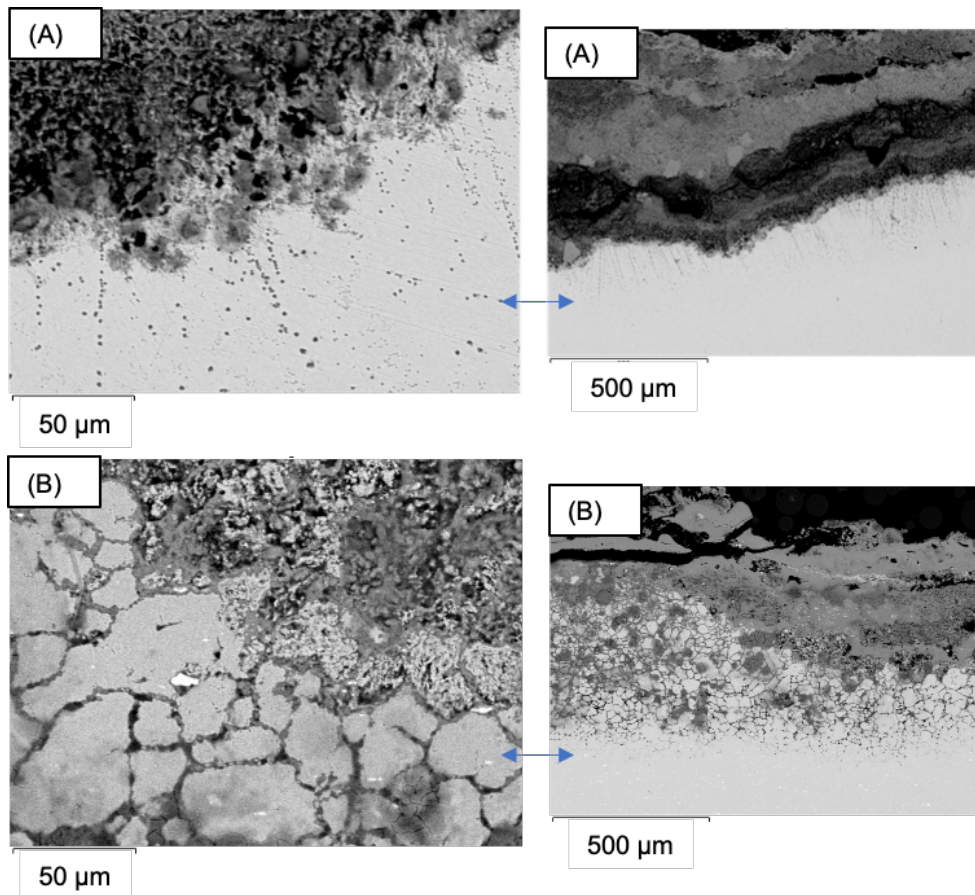


Figure 4-50: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples covered with deposit D3 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C . Images have been captured at two magnifications. Sample oil residue, which may be difficult to prevent for severely corroded samples, may have affected image resolution

Multi-layered fractured scales of varying porosities are observed on the 347HFG sample. Two distinct damage features are documented in **Appendix E** for the 347HFG sample (in **Figure E-2**): Intergranular attack regions featuring Fe depletion and, grain attack at the alloy/scale interface featuring Cr and Fe depletion. The damaged Cr oxide scales and grain boundary regions consist of deposit elements (K, Na, Cl and S).

Deposit D4

The BSE images of the cross-sectioned D4-coated samples exposed for 1000 hours are presented in **Figure 4-51**. Wider view images are presented on the right.

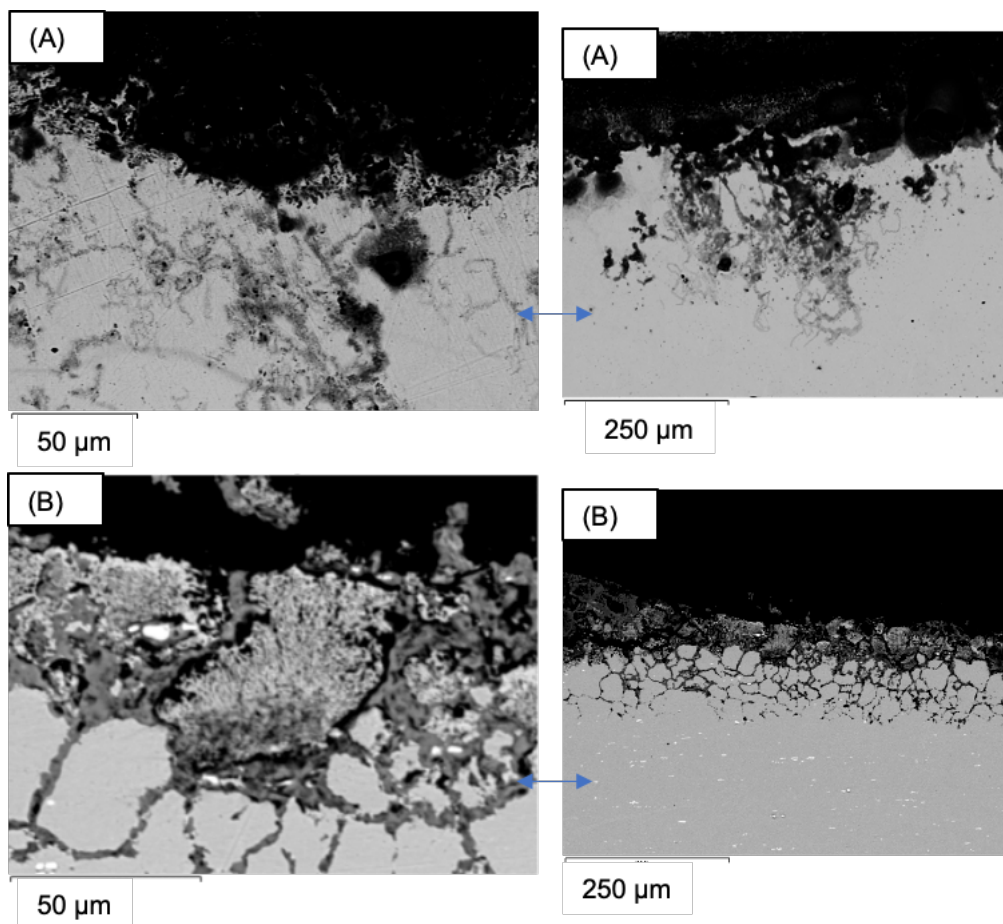


Figure 4-51: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples covered with deposit D4 at 100 µg/cm²h following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Images have been captured at two magnifications for both alloys

Extensive damage is encountered across the T91-D4 metal surface, correlating with the high metal loss data (**Figure 4-27** and **Figure 4-28**). No notable scale was recovered for this sample. The 347HFG-D4 sample damage

features are similar to those of 347HFG-D3 (**Figure E-2** and **Figure E-3**) although, damage occurs to greater extents for the later sample.

Deposit D5

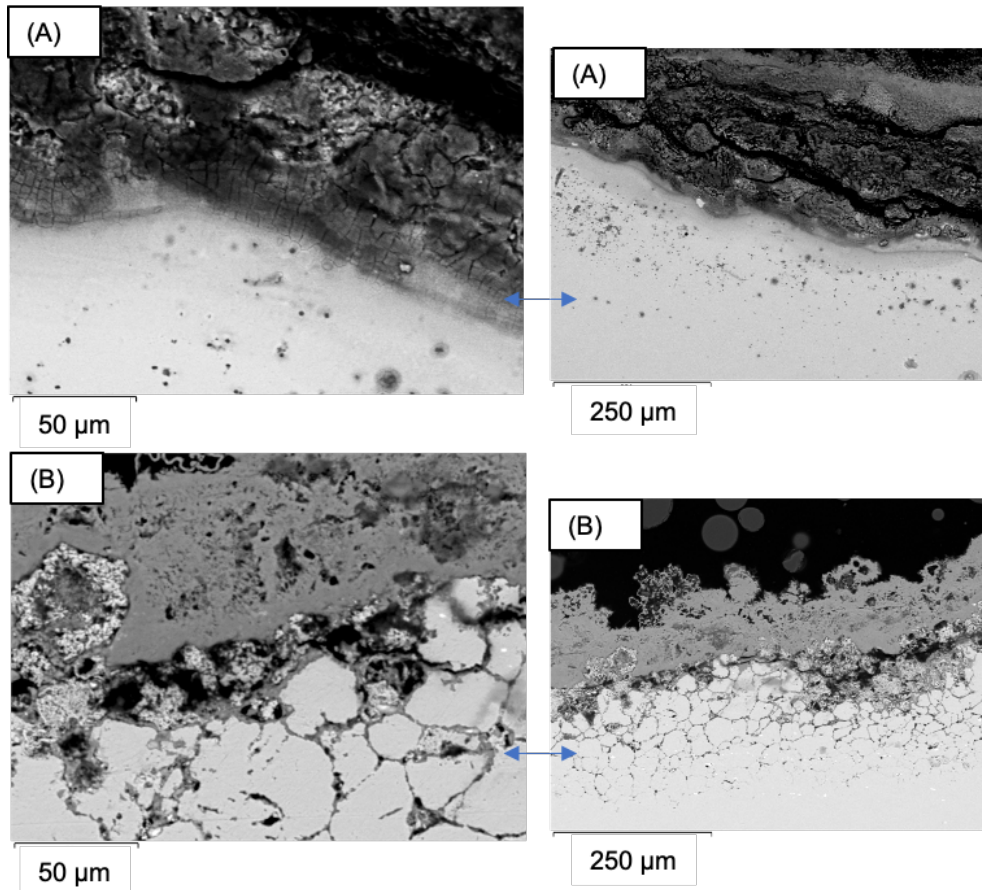


Figure 4-52: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples covered with deposit D5 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C . Images have been captured at two magnifications

The BSE images of the cross-sectioned D5 coated samples, exposed for 1000 hours, are presented in **Figure 4-52**. There are multi-layered scales present on the T91 sample and delamination from the metal surface also occurs for this sample. Scales are fractured and porous structures are observed. Damage feature on the ferritic steel are otherwise similar to those encountered on sample

T91-D4 at 1000 hours. Sound metal attack is also evident on 347HFG-D5, with up to a 150 μm vertical depth. However, there is noticeably less damage than the 347HFG-D4 sample at the same exposure time (**Figure 4-51**). EDX maps (**Figure E-4**) suggest Ca (in D5) remains within the deposit region for 347HFG-D5, whereas other deposit elements (K, Na, S and Cl) have been encountered in scale and grain boundary regions.

The BSE images presented in this section (and EDX mappings in **Appendix E**) demonstrate greater severity in the damage influences of deposits D2-D5 compared to that of D1, in WWF test gas at 600°C. Damage features for these samples are, however, similar.

Deposit D6

The BSE images of the cross sectioned D6 (HGB deposit) coated samples, exposed for 1000 hours, are presented in **Figure 4-53**. The wider view images are presented to the right. Fractured scales and vertical intrusions/cavities are also encountered on T91-D6. The scales, which may be observed on the EDX maps documented in **Appendix E (Figure E-5)**, are relatively compact (compared to scales of the D1-D5 T91 coated samples).

Grain boundary attack observed for 347HFG is also less extensive than those initiated by the WWF deposits, D1-D5 (also see the documented EDX maps in **Figure E-6**).

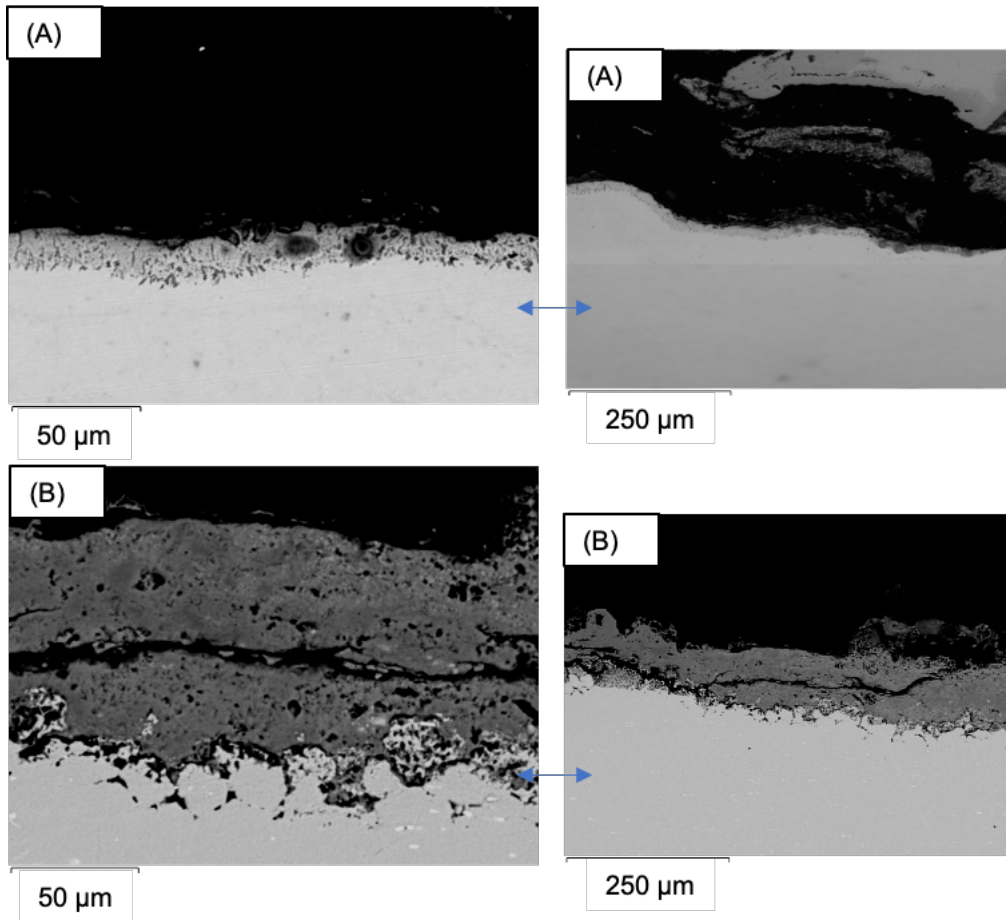


Figure 4-53: BSE image of cross-sectioned (A) T91 and (B) 347HFG samples covered with deposit D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Images have been captured at two magnifications

ii. 50 $\mu\text{g}/\text{cm}^2\text{h}$ deposition flux samples

The BSE image and EDX maps for the cross-sectioned T91 and 347HFG samples, exposed to D6 at deposition flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ for 500 hours, are presented in **Figure 4-54**.

Sample T91-D6 presents multiple scale features. Fe- and Cr-rich layers have been identified at the scale region. A Mo-oxide scale may also be present beneath the Cr oxide scale. Deposit components S and K are observed within the upper scale and sintered deposit/scale regions.

Sample 347HFG-D6 experienced ~30 μm metal penetration vertical depth, following 500 hours of exposure. The attacked grain boundary sites are Fe- and Cr-depleted, however, Ni-rich. Cl is detected at depleted pits within the grain boundary depths (up to 30 μm ; higher magnification SE/EDX image documented in **Figure E-7**). As with the reference sample (**Figure 4-45**), Nb-rich particulates are sited within the bulk metal. Deposit component K was not sighted on this sample (map not included). It is likely the element may have been present in the scales; however, scale recovery for this sample was minimal.

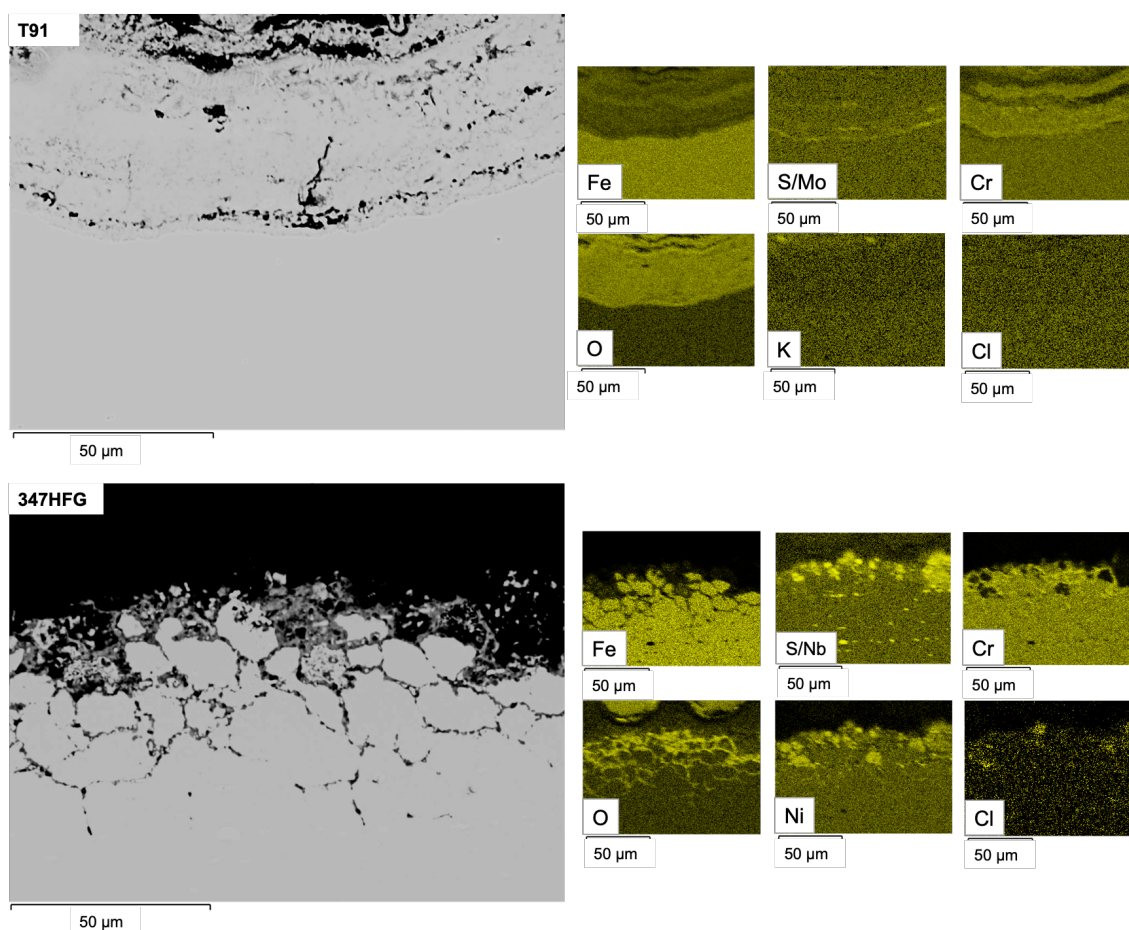


Figure 4-54: SE/EDX map of cross-sectioned T91 and 347HFG samples covered with deposit D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$, following 500 hours exposure in WWF simulated combustion gas environment at 600°C

The BSE image and EDX maps for the cross-sectioned T91 and 347HFG samples exposed to D1 at deposition flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ are presented in **Figure**

4-55. Sample T91-D1 damage features resemble those observed on the 100 $\mu\text{g}/\text{cm}^2\text{h}$ deposition flux exposed sample counterpart (**Figure 4-48**), however less severe. A multi-layered scale is observed which appears delaminated at the Mo-Cr- scale fronts. The Mo-rich zone is encountered along a penetrated metal surface (depth up to 15 μm).

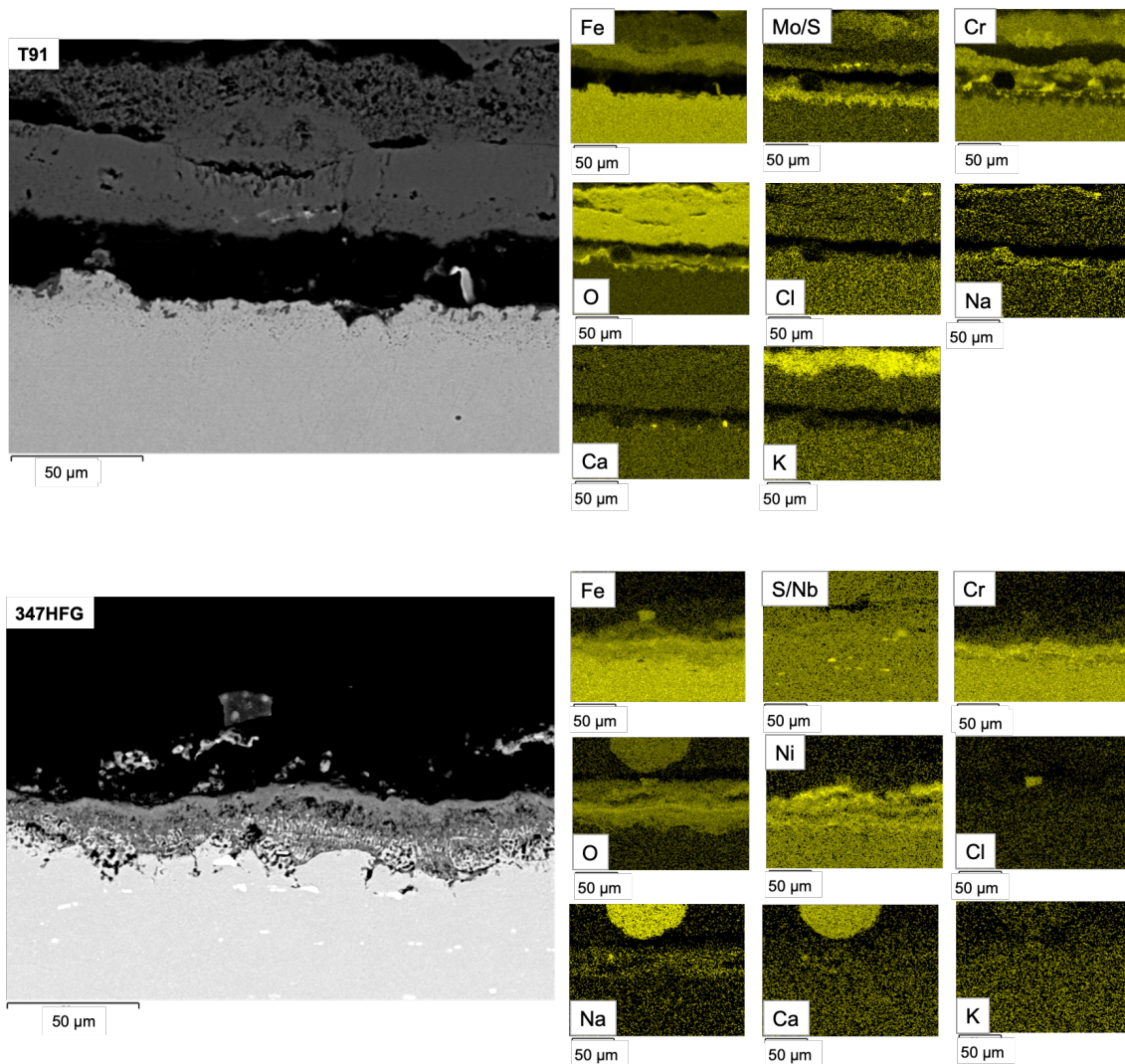


Figure 4-55: SE/EDX maps of cross-sectioned T91 and 347HFG samples covered with deposit D1 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours exposure in WWF simulated combustion gas environment at 600°C

At a porous scale/deposit interface region, deposit components, K, Na, S and Cl, are present. A Na-rich layer is encountered at the Mo- and Cr-oxide scale boundaries near to the metal surface, whereas K is not observed at the metal

damage sites. Ca deposits may also be spotted at the metal surface region, although the element map (**Figure 4-55**) show these deposit regions have rigid structures. The alkali metal deposition zones, however, present fluid structures on their element maps. The well-defined edges of deposits, corresponding to the Ca maps, suggest unmelted salts may be present and are able to migrate to voids.

347HFG-D1 (**Figure 4-55**) features grain boundary penetrations ($\sim 15\ \mu\text{m}$ depth at image capture section) and grain depletions in the form of vein-like penetrations into the metal lattice. It is noted that internal damage at this sample site is less penetrative than for 347HFG-D6 (**Figure 4-54**), where scale loss is severe, whereas in this case (347HFG-D1, **Figure 4-55**), the scale are well-adhered to the bulk metal surface. Again, the presence of Na at the metal surface region (347HFG-D1) is noted, whereas K was not detected at this site.

iii. $25\ \mu\text{g}/\text{cm}^2\text{h}$ deposition flux samples

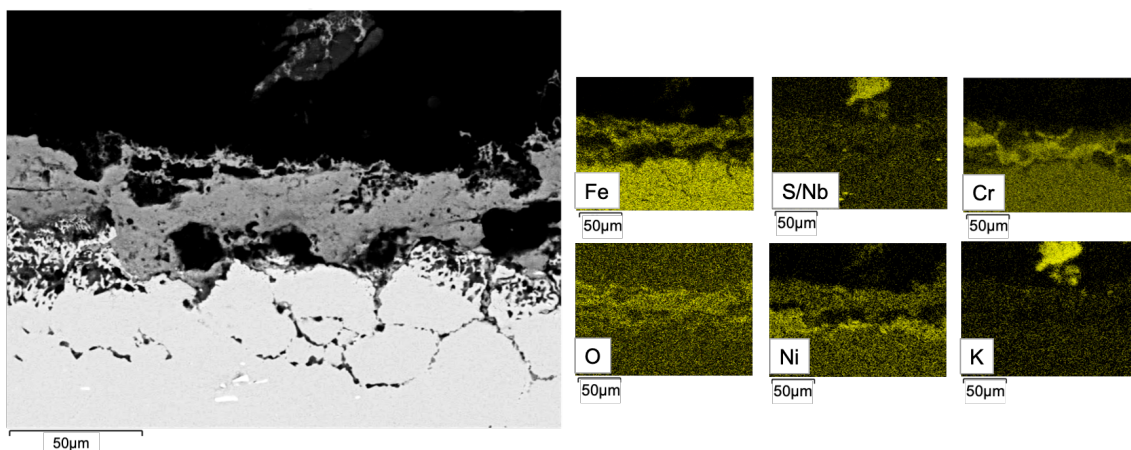


Figure 4-56: BSE image of cross-sectioned 347HFG sample covered with deposit D6 at flux $25\ \mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours exposure in WWF gas at 600°C

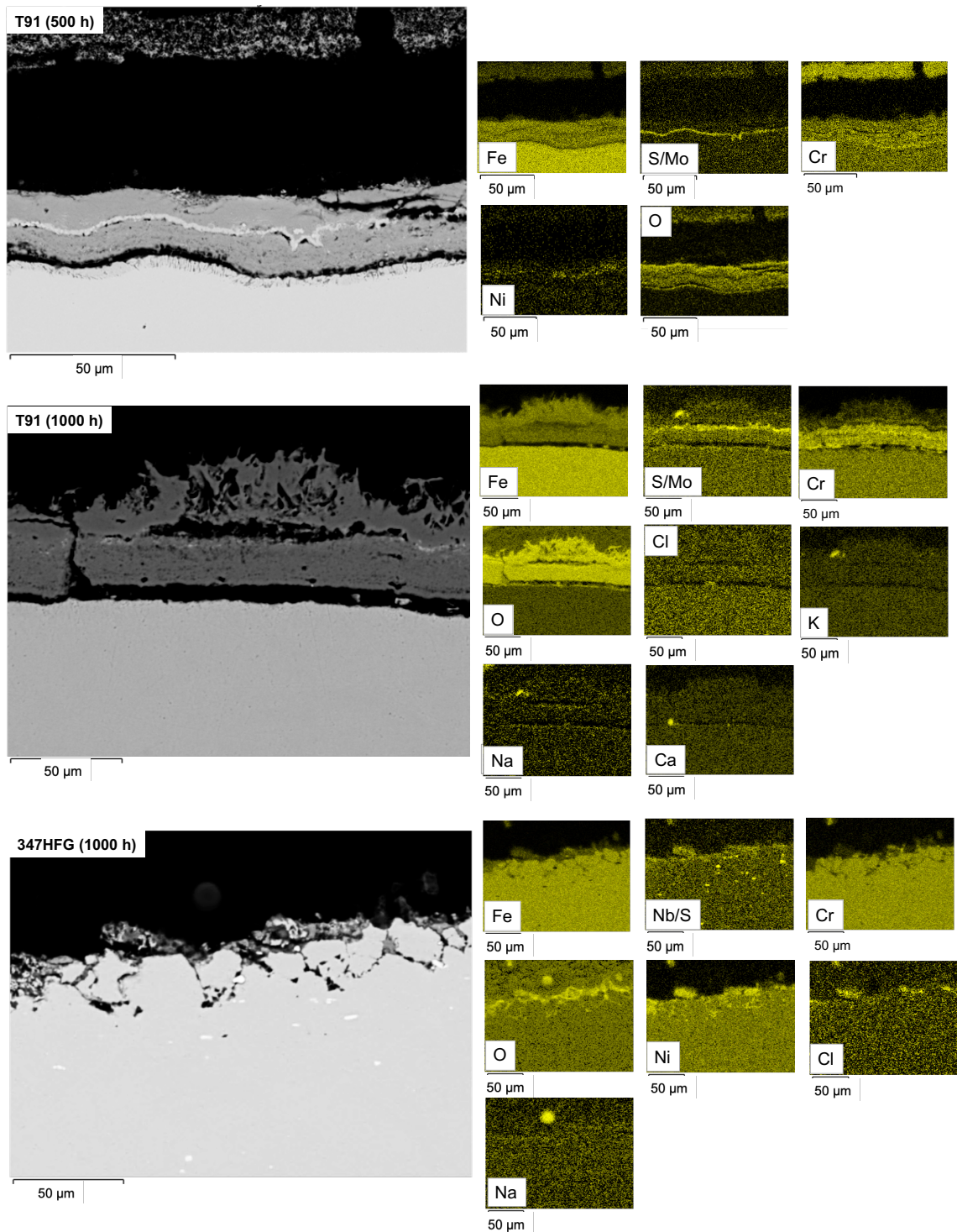


Figure 4-57: BSE and EDX maps of cross-sectioned T91-D1 and 347HFG-D1 samples at deposition $25 \mu\text{g}/\text{cm}^2\text{h}$, following exposure in WWF simulated combustion gas environment at 600°C

The corrosion features on the D6 sample in **Figure 4-56** are similar to those observed on the higher flux austenitic steel samples, however, grain

boundary penetration is only $\sim 20\text{ }\mu\text{m}$, following 1000 hours exposure. The lower penetrative damage may be suggestive of slower intergranular diffusion as the deposit flux is reduced. In this case, scales are also denser. It is also likely that internal penetration (via grain boundaries) may be exaggerated for such samples (reduced deposit exposure rates) where damaged metal surface is retained for longer prior to being spalled. In terms of chemistry of attack, K is observed within grain boundaries for this sample. A S-rich film is observed on the metal surface. Cl (map not included) was not identified within this image.

Figure 4-57 presents samples T91-D1 and 347HFG-D1 following exposure in WWF gas conditions with a deposit flux of $25\text{ }\mu\text{g}/\text{cm}^2\text{h}$ applied. A multi-layered scale on the T91-D1 sample exposed for 500 hours features a distinct Mo-rich film between layers of Cr and Fe rich scale layers. The scale can also be detached from the metal surface as observed for the higher flux T91 samples, however, the number of voids may be comparably lesser. The Mo-containing scale is also notably thicker at $25\text{ }\mu\text{g}/\text{cm}^2\text{h}$ with generally more compact scales forming. At the metal surface, vertical depletion patterns exist with a thickness of $\sim 10\text{ }\mu\text{m}$ across the metal. EDX mapping identifies a scanty Mo-rich scale at this location. Also, a faint Na map suggests this alkali metal may participate in degradation mechanisms resulting in poor Mo scales and delamination for T91 which has been seen to occur at the Mo interface for each sample. These features may be better examined on the higher BSE magnification image documented in (**Figure E-8**). The presence of K and Cl, post exposure, could not be confirmed at this site.

By 1000 hours (**Figure 4-57**), T91-D1, at applied deposition flux of $25\text{ }\mu\text{g}/\text{cm}^2\text{h}$, features two scanty Mo scales within Fe and Cr-rich scale zones and also at the metal surface. Though K is only encountered at the top scale/deposit region, Na and Cl may be observed at the metal surface.

347HFG-D1, following 1000 hours of exposure, features S and Cl at the metal surface, where damaged Ni scales may also be observed. With the sample having undergone a median metal loss of $324\text{ }\mu\text{m}$, it is likely that prominent scaling had developed. As the scale layer thickness observed is minimal, it is

likely scales delaminated from the bulk metal during testing/handling. Compared to the D6 exposed sample equivalent in **Figure 4-56**, wider gaps/pits are observed at the tail end of penetrations. SEM mapping shows the selective transfer of Fe and Cr occur from these locations. As deposit components have not been identified in these gaps, it is likely destructive components are evaporated from these regions along with Fe and Cr.

iv. **10 $\mu\text{g}/\text{cm}^2\text{h}$ deposition flux samples**

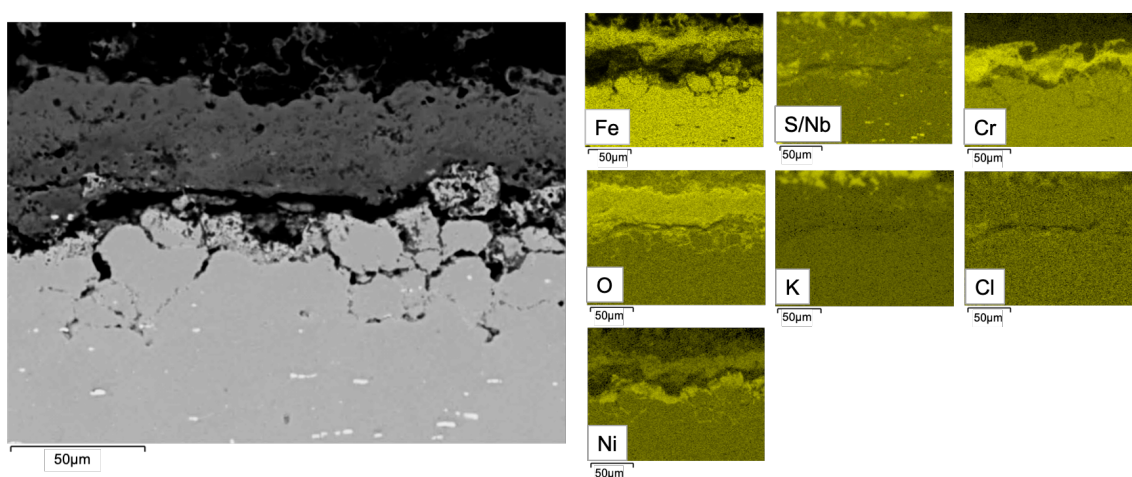


Figure 4-58: BSE image of cross-sectioned 347HFG sample covered with deposit D6 at flux 10 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours exposure in WWF simulated combustion gas environment at 600°C

At 10 $\mu\text{g}/\text{cm}^2\text{h}$, internal damage can still be observed on both authentic samples with D1 (**Figure 4-59**) and D6 (**Figure 4-58**) following 1000 hours exposure. In both cases, Ni scales are formed on the metal surface. The D6 exposed sample exhibits features of a more protective scale compared to the D1 exposed sample which shows broken Ni-scale which may be penetrable. For example, chloride attack is more evident within the grain boundaries of 347HFG-D1 compared to 347HFG-D6. The Cr scale for sample 347HFG-D6 is also more consistently

spread and thicker across the sample, unlike the Cr-scale for sample 347HFG-D1 which is depleted.

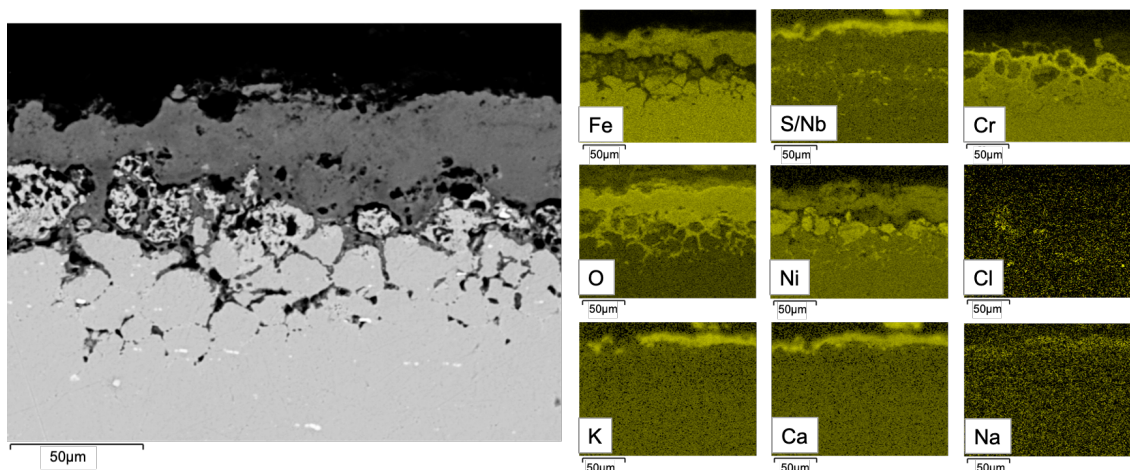


Figure 4-59: SEM image of cross-sectioned 347HFG sample covered with deposit D1 at flux 10 µg/cm²h following 1000 hours exposure in WWF simulated combustion gas environment at 600°C

4.2.2.2. Metal changes at 550°C in wood waste fuels combustion gas conditions

Tests were conducted at 550°C, also under the WWF gas conditions, to investigate the corrosive effects of D1 and D6 at this temperature. The deposition flux applied to each coupon samples was 100 µg/cm²h. The metal loss measurements and SEM/EDX analysis data are presented in this section.

4.2.2.2.1. Metal loss

Figure 4-60 to Figure 4-65 present the metal and sound metal changes of T91 and 347HFG, exposed to deposits D1 and D6 at 550°C. Samples have

been tested in WWF test gas conditions at 200, 500 and 1000 hours for each deposit.

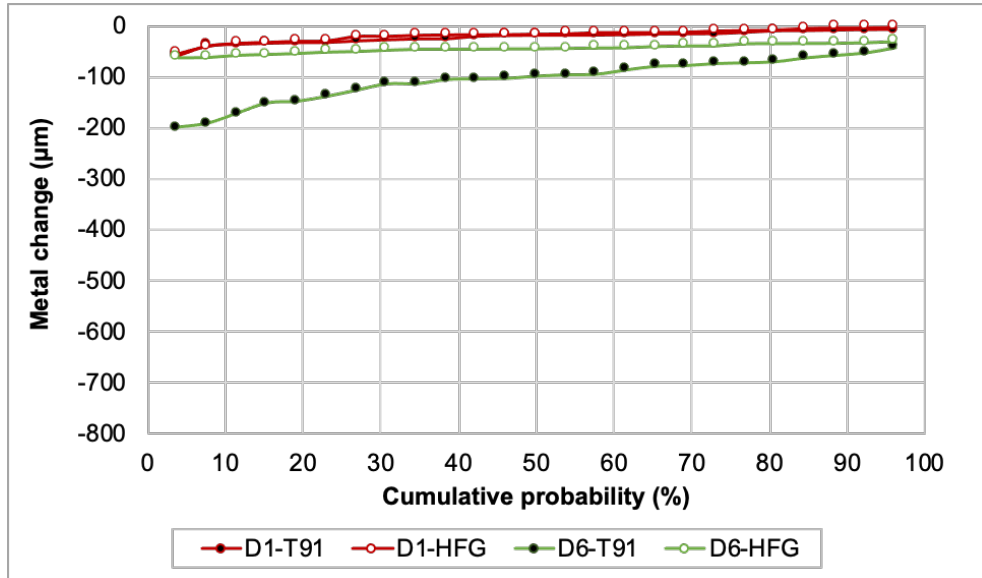


Figure 4-60: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 100 µg/cm²h exposed for 200 hours in simulated WWF test gas conditions at 550°C

The metal and sound metal changes for the 200-hour exposure alloy samples are presented in **Figure 4-60** and **Figure 4-61** respectively. Metal loss is under 65 µm for the T91 and 347HFG alloys with D1 deposit (median metal change -18 µm and -17 µm respectively), although over half of the measured points show metal changes within error analysis range (**Section D-4**). Both alloys covered with D6 experience higher degree of metal change than initiated by deposit D1. T91-D6 may exhibit localised corrosion damage tendencies as steep metal change gradients are observed for ~30% of the metal surface. D6 attack on T91 is however relatively spread across the alloy surface with a median metal change value of -44 µm. Negligible sound metal penetration on the 347HFG-D6 (**Figure B-15**) is recorded by dimensional metrology. No sound metal penetration was detected for T91-D1 (**Figure B-12**), T91-D6 (**Figure B-13**) and HFG-D1 (**Figure B-14**) at 200 hours of exposure.

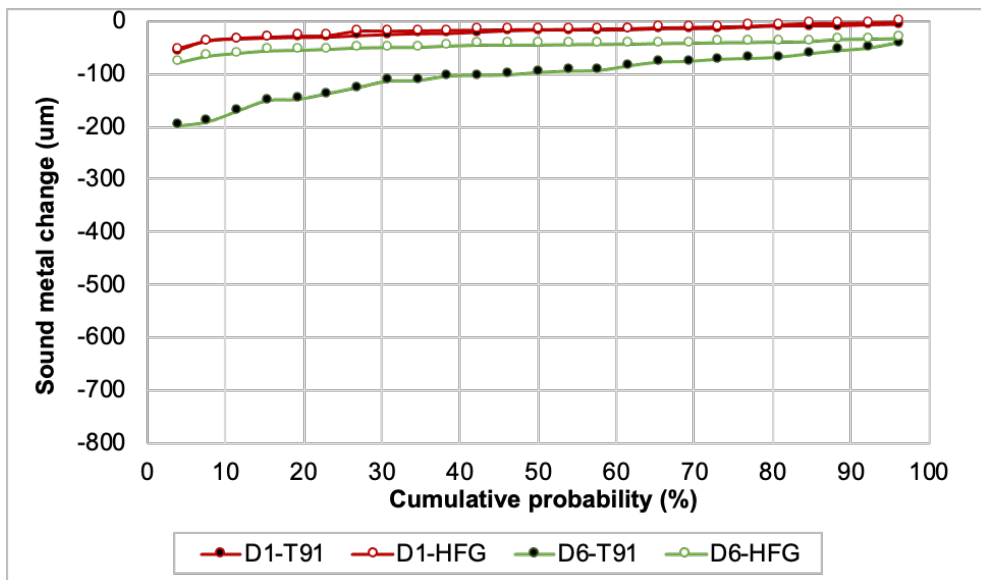


Figure 4-61: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated WWF test gas conditions at 550°C

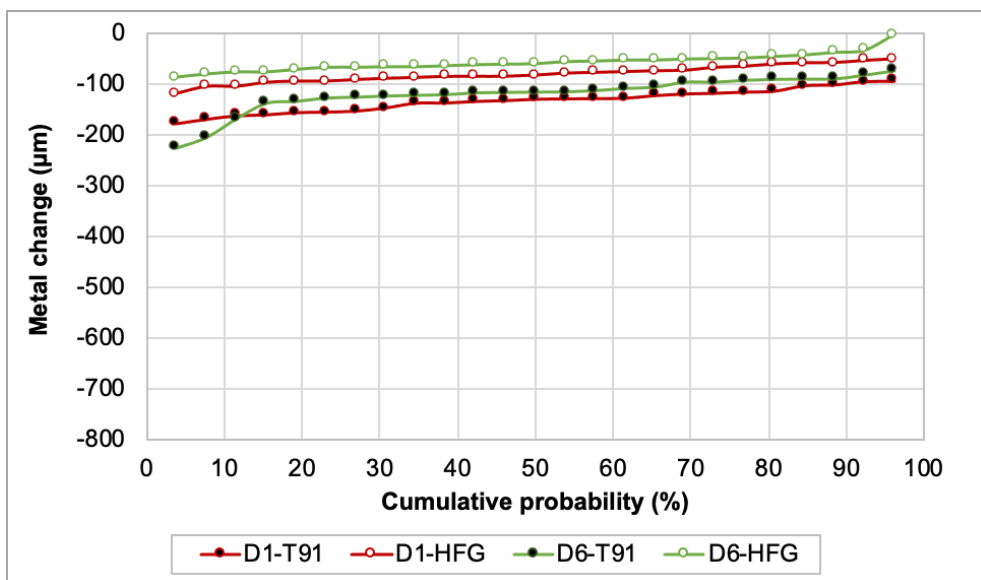


Figure 4-62: Metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 550°C

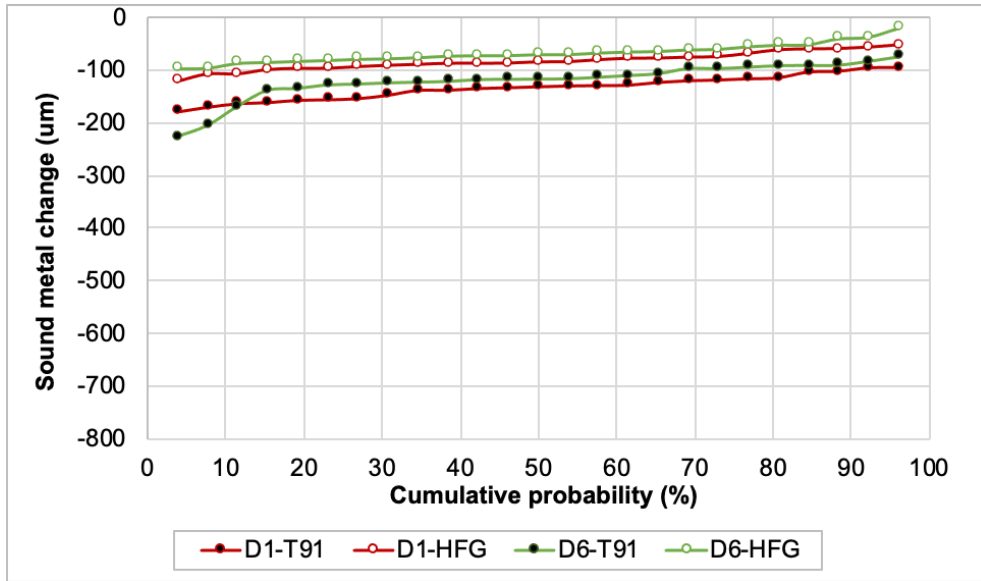


Figure 4-63: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 µg/cm²h exposed for 500 hours in simulated WWF test gas conditions at 550°C

The metal and sound metal change data of the 500-hour exposure samples are presented in **Figure 4-62** and **Figure 4-63**. Metal change is in the propagation stage across most metal surface for all four samples. The median metal loss is comparable for each alloy exposed to D1 (T91-D1, 116 µm; 347HFG-D1, 85 µm) and to D6 (T91-D6, 117 µm; 347HFG-D6, 62 µm). T91-D6 again exhibits localised corrosive damage at 500 hours, as was observed at 200 hours (**Figure 4-60**). Metal surface loss is however relatively uniform across the D1 exposed samples, and no sound metal penetration is detected for either of the D1 exposed samples at 500 hours (**Figure B-12** & **Figure B-14**). Minimal sound metal penetration is encountered on 347HFG-D6 (**Figure B-15**); however, no sound metal penetration observed for T91-D6 (**Figure B-13**).

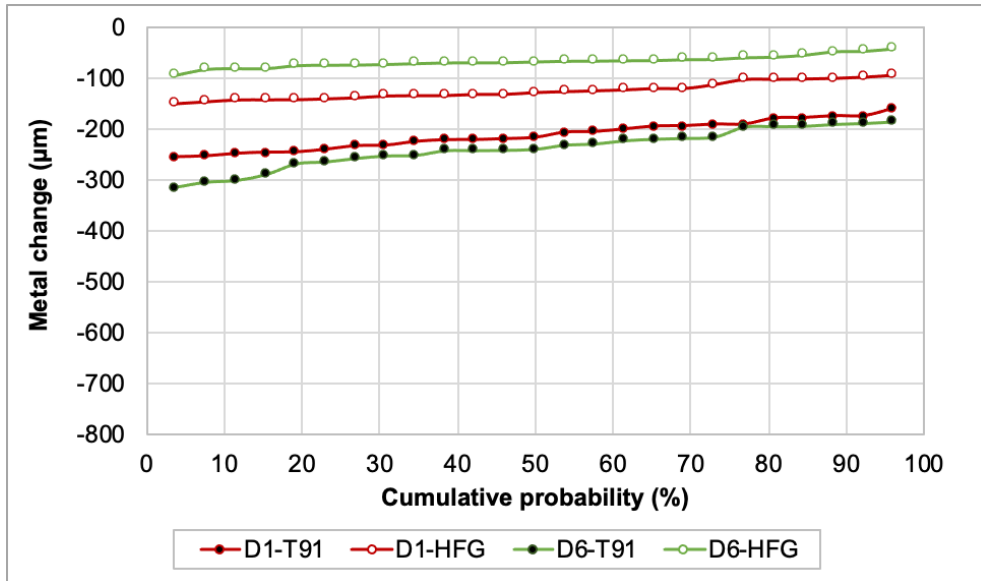


Figure 4-64: Metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 550°C

The metal and sound metal changes exhibited by the 1000-hour exposure samples are presented in **Figure 4-64** and **Figure 4-65**. Both steels experience median metal loss values of 127 μm (347HFG-D1) and 66 μm (347HFG-D6). T91-D1 metal loss range within 95 μm across the sample surface (median metal loss, 217 μm), while T91-D6 has a metal loss range of 131 μm across the metal surface, and comparable median metal change (-238 μm) with T91-D1. T91 demonstrates less responsiveness to the change in deposit type compared to 347HFG and exhibits greater damage than the 347HFG samples.

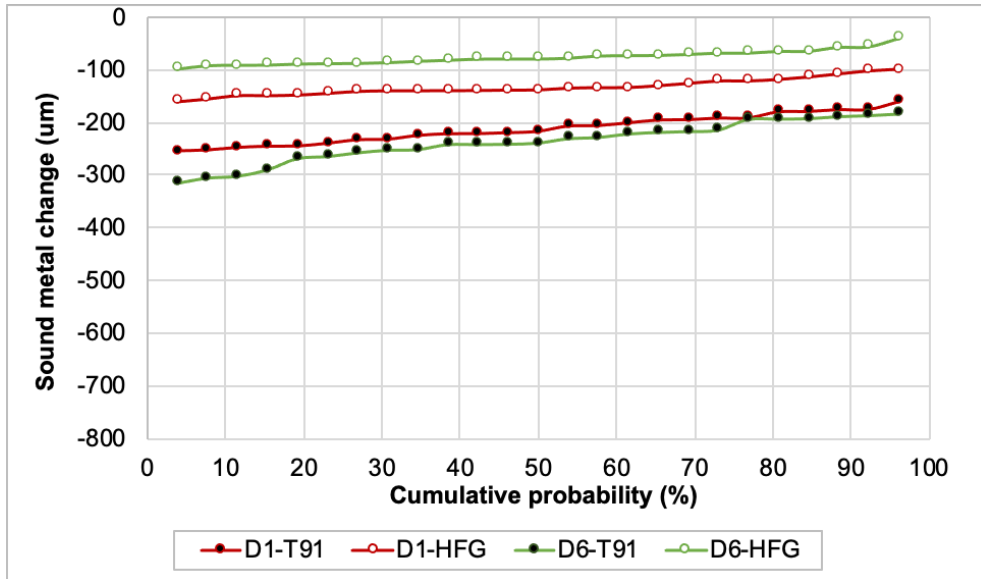


Figure 4-65: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in WWF test gas conditions at 550°C

Approximately 13 μm and 11 μm of sound metal penetration depths (based on media values) are recorded for the 347HFG-D6 (**Figure B-15**) and 347HFG-D1 (**Figure B-14**). No sound metal penetration was observed for either T91 sample (**Figure B-12** and **Figure B-13**).

4.2.2.2.2. SEM/EDX evaluations of 550°C exposure samples

The cross-sections SE/EDX images for both alloys exposed under WWF test gas conditions with deposits D1 and D6 at 550°C are presented within this section.

The 'no-deposit' exposed samples are presented in **Figure 4-66** and **Figure 4-67**. The cross-sectioned images show typical surface attack features on the T91 sample with some localised damage occurring. A multi-layered scale is confirmed by EDX. Mn and Cr rich layers are observed at compact scale regions. The porous Fe rich upper scale region shows S deposits which may have condensed from the test gas flow. S deposition is also likely to be positioned between the Cr scale/alloy interface where some degree of scale delamination

has occurred. As such, the test gas is able to initiate corrosive damage on T91 at 550°C.

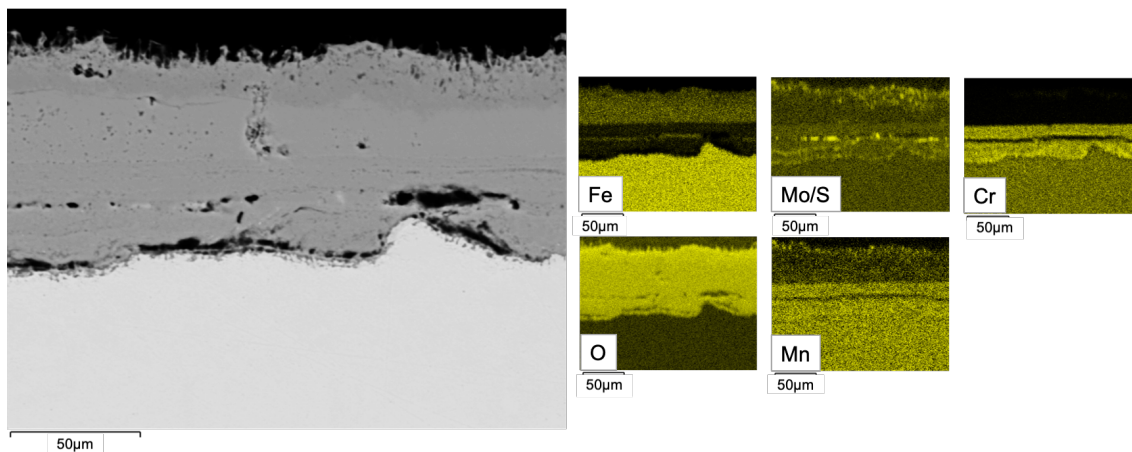


Figure 4-66: BSE image and EDX map of no applied deposit T91 sample following 1000 hours exposure in WWF simulated combustion gas environment at 550°C

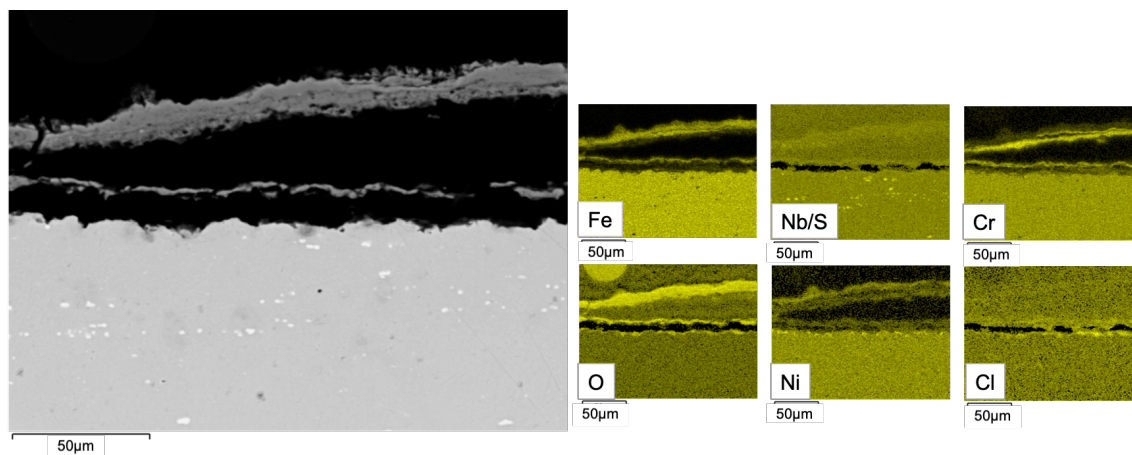


Figure 4-67: SE/EDX image of no applied deposit 347HFG sample following 1000 hours exposure in WWF simulated combustion gas environment at 550°C

The initial stages of grain boundary attack on 347HFG may be the increased roughness of the alloy surface (**Figure 4-67**) compared to the reference sample (**Figure 4-45**). A detached multi-layered scale of Cr, Fe and Ni

oxides are present and also an oxide layer exists on the metal surface. Cl (likely from the tests gas which contains HCl, 3 vppm) is deposited at the metal surface and is likely to have contributed to the metal surface roughness observed.

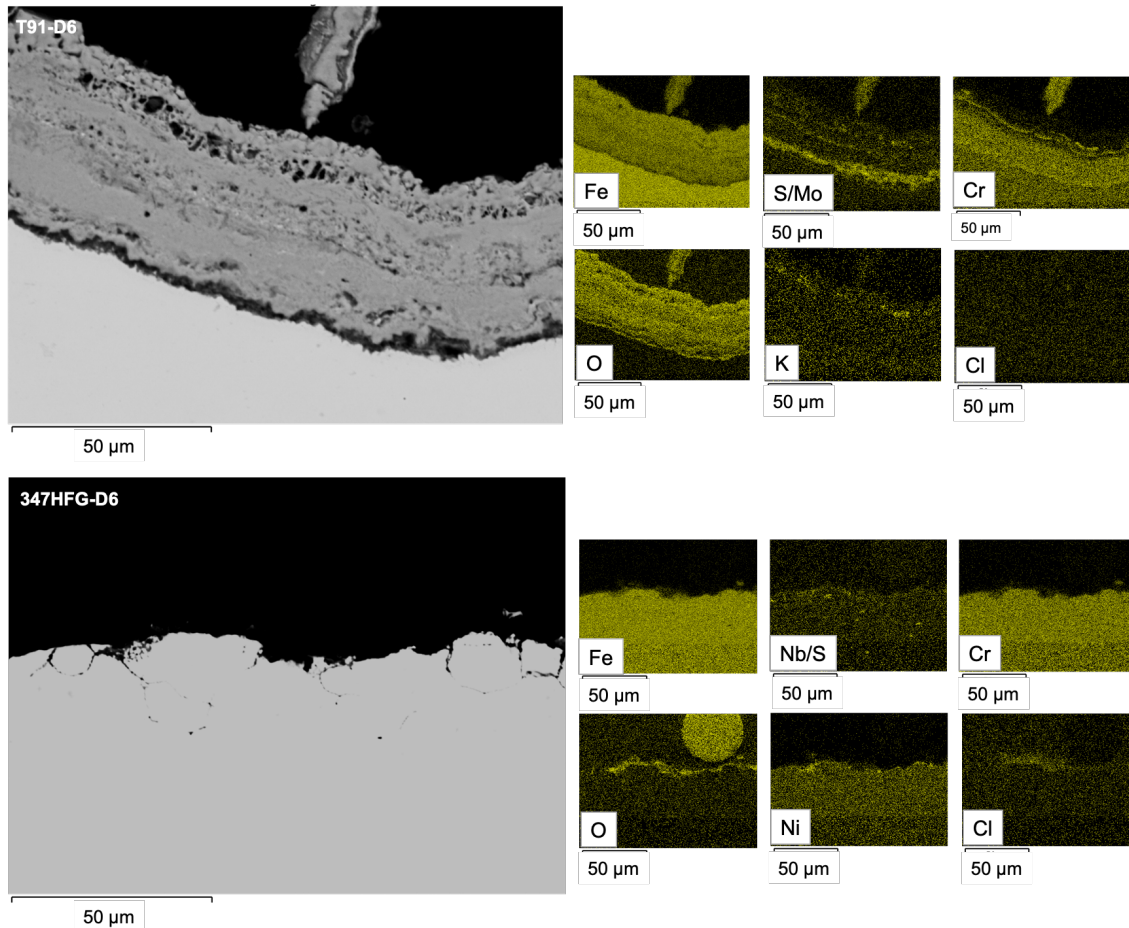


Figure 4-68: BSE/EDX image of T91-D6 and 347HFG-D6 post 200 hours exposure in WWF test gas conditions at 550°C and deposition flux of 100 µg/cm²h

Figure 4-68 presents the cross-section BSE/EDX images of the D6 exposed samples following 200 hours. Scales recovered on T91 feature multi-layered oxides as observed for previous samples under low deposition flux exposure conditions. Internal damage on 347HFG (~30 µm) is detected by BSE analysis, whereas these grain boundary intrusions were not discovered during dimensional analysis imagery. As such, higher magnifications may enable improved assessments of penetration depths.

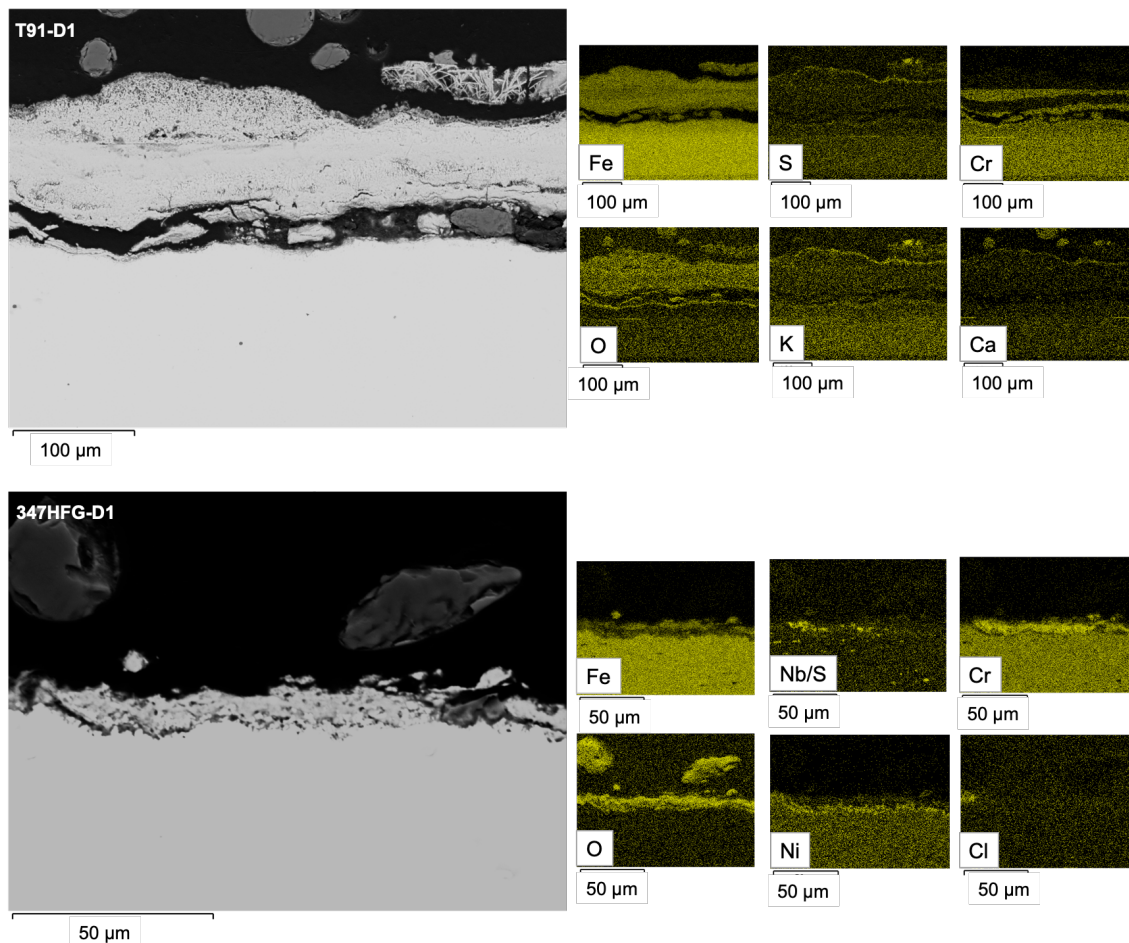


Figure 4-69: BSE image and EDX element maps of T91 and 347HFG after 200 hours exposure in WWF test gas at 550°C and with a deposition flux of 100 µg/cm²h.

For the D1 exposed samples, K and S rich layers are observed on T91 at the multi-layered scale surface (**Figure 4-69**). Two distinct Cr-scales are observed, one of which occurs within the upper Fe rich scale layer and the other closer to the alloy surface, as encountered on the T91-D6 samples. The continuous Ca-containing layer, which is positioned at similar locations to enrichments of K and S, may suggest the occurrence of melts for compounds containing this element. No internal damage has been spotted on 347HFG-D1 following 200 hours exposure.

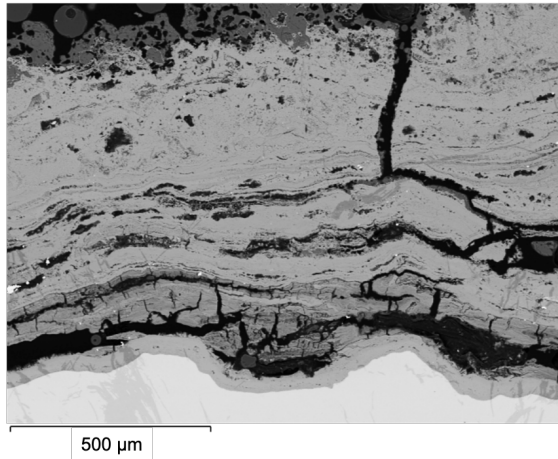


Figure 4-70: BSE image of cross-section T91 post 1000 hours exposure to deposit D1 in WWF simulated combustion gas environment at 550°C and deposition flux of 100 µg/cm²h

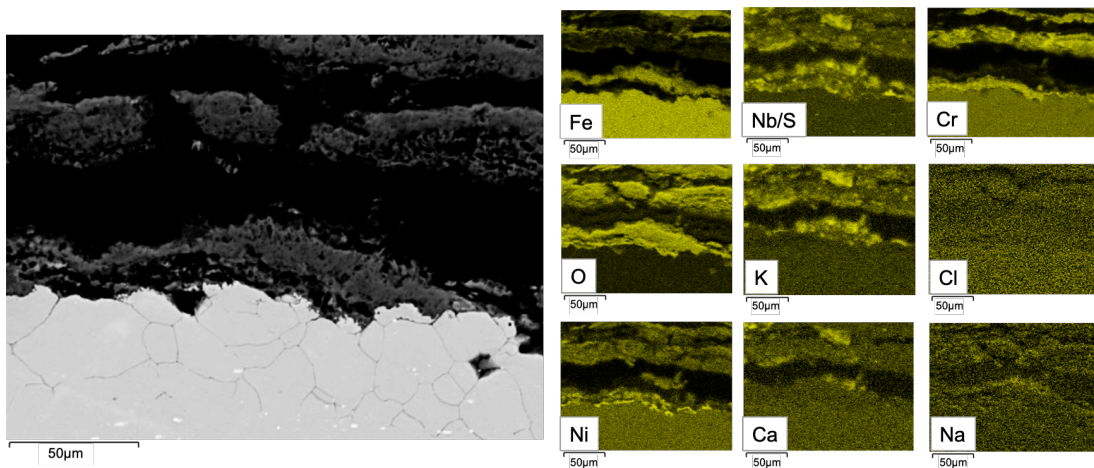


Figure 4-71: BSE image and EDX maps of cross-section 347HFG after 1000 hours exposure to deposit D1 in WWF test gas at 550°C and a deposition flux of 100 µg/cm²h

The samples exposed for 1000 hours at 550°C are presented in **Figure 4-70** (T91-D1), **Figure 4-71** (347HFG-D1) and **Figure 4-72** (D6 exposed samples). T91-D1 presents a compact scale formation adhered to the metal surface. Above this region however, the multi-layered scales are fractured/delaminated. Deposits are embedded within the different scale as a result of recoating with fresh deposit after every cycle (EDX images presenting deposit elements are documented in **Figure E-10**). Grain boundary damage on the 347HFG-D1, presented in **Figure 4-71**, is severe following 1000 hours

exposure. Deposit components Na, K, Ca and S are observed at the metal surface where the Ni scale lacks protective features.

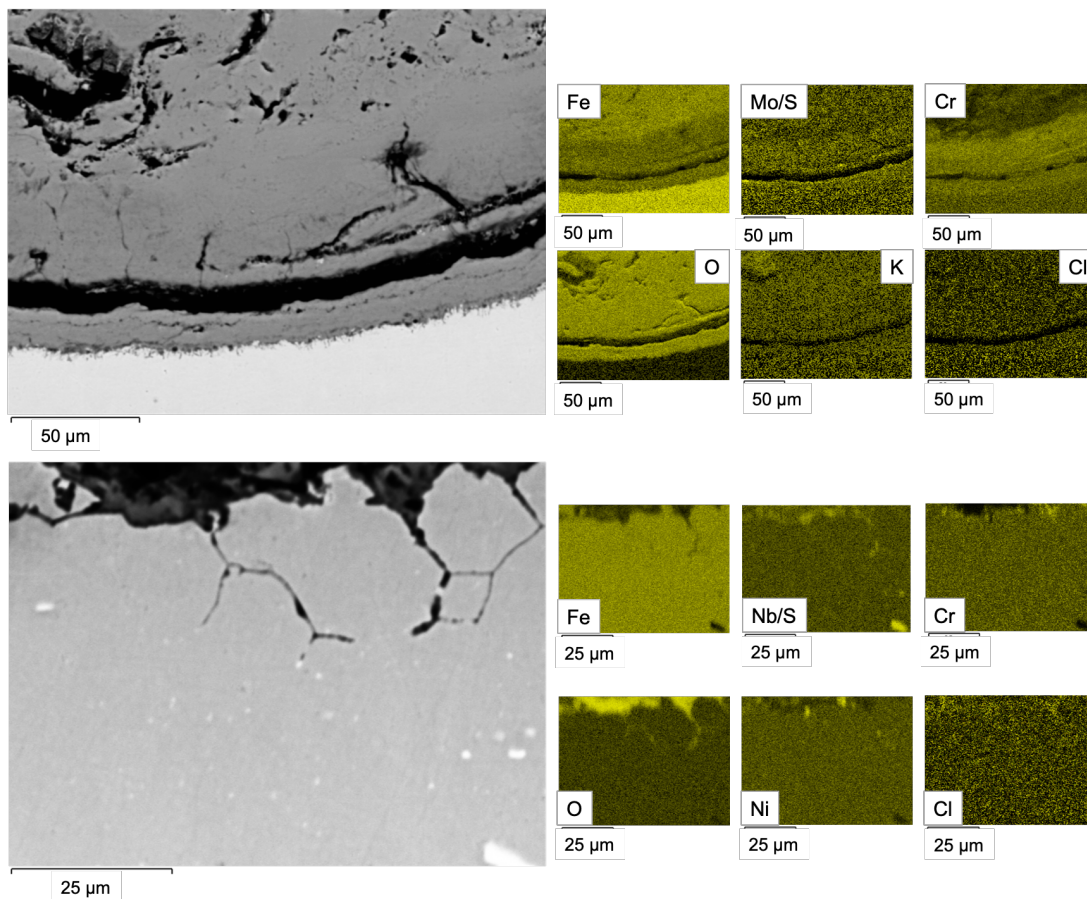


Figure 4-72: BSE image and EDX maps of cross-section T91 and 347HFG post 1000 hours exposure to deposit D6 in WWF test gas conditions at 550°C and deposition flux of 100 µg/cm²h

Deposit D6 is able to influence shallow vertical intrusions into the T91 lattice at 550°C and chloride intrusion within grain boundaries is observed for 347HFG at the same temperature (**Figure 4-72**).

4.2.2.3. Metal changes at 500°C in wood waste fuels' combustion gas conditions

Tests were conducted at 500°C under the WWF test gas conditions to consider the temperature effects of D1 and D6 on T91 and 347HFG corrosive damage while maintaining the deposition flux at 100 $\mu\text{g}/\text{cm}^2\text{h}$. The metal loss measurements and SEM/EDX analysis data are presented in this section.

4.2.2.3.1. Metal loss

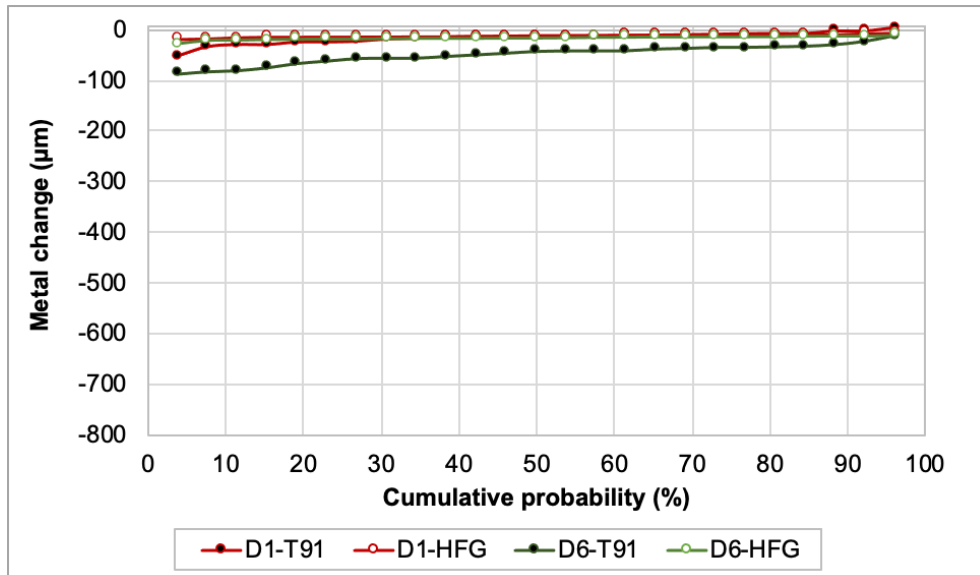


Figure 4-73: Metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated WWF test gas conditions at 500°C

Figure 4-73 to Figure 4-78 present the metal and sound metal changes of the alloys' responses to deposits D1 and D6 at 500°C.

The metal and sound metal change data for the 200-hour exposure alloy samples are presented in **Figure 4-73** and **Figure 4-74** respectively. Greater damage is observed on the T91-D6 sample with 10% and 50% metal loss exceedance values of -83 μm and -43 μm respectively. The 10% metal loss exceedance is -21 μm for both D1 covered samples and the 347HFG samples

respond similarly to both deposits: median metal changes are within -16 μm . At 200 hours, no sound metal penetration is recorded any of the samples (**Figure E-5**).

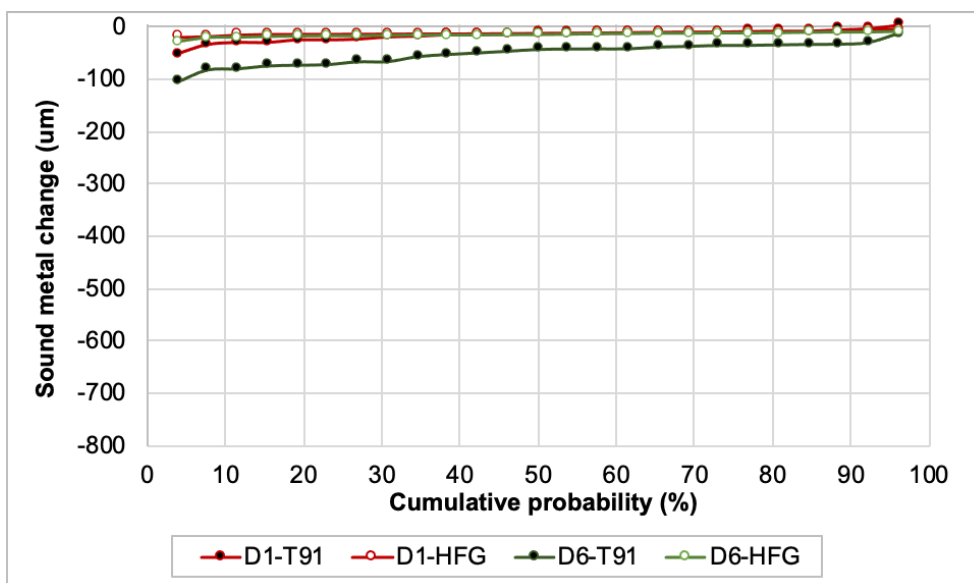


Figure 4-74: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated WWF test gas conditions at 500°C

The post-exposure metal and sound metal change data for the 500-hour exposure alloy samples are presented in **Figure 4-75** and **Figure 4-76** respectively. The metal change measurements are similar for most surface measurement points on both of the T91 samples and their metal thickness changes at median probabilities are approximately -44 μm for both samples.

Again, by 500 hours, sound metal penetration is also not detected for either alloy exposed to D1 or D6.

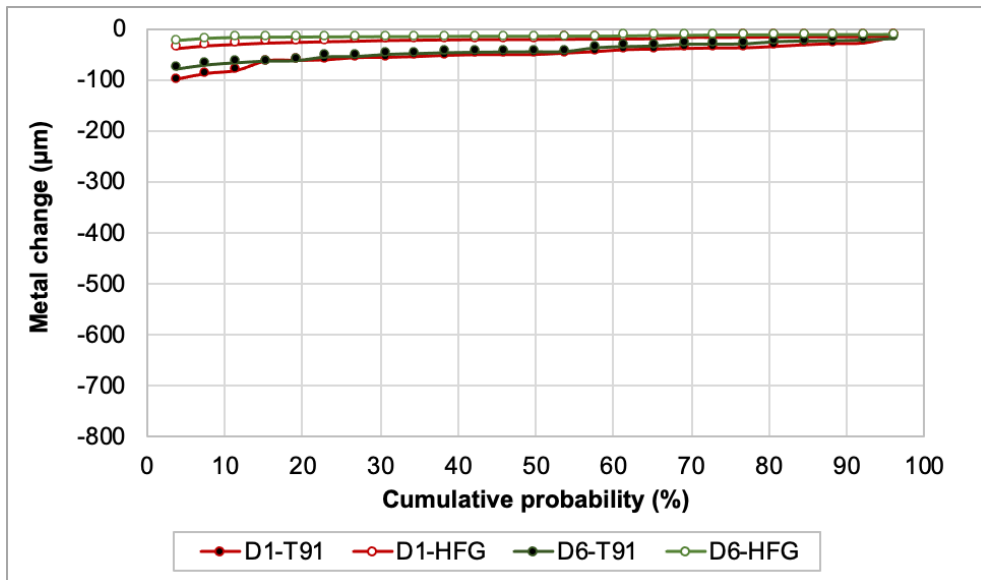


Figure 4-75: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 500°C

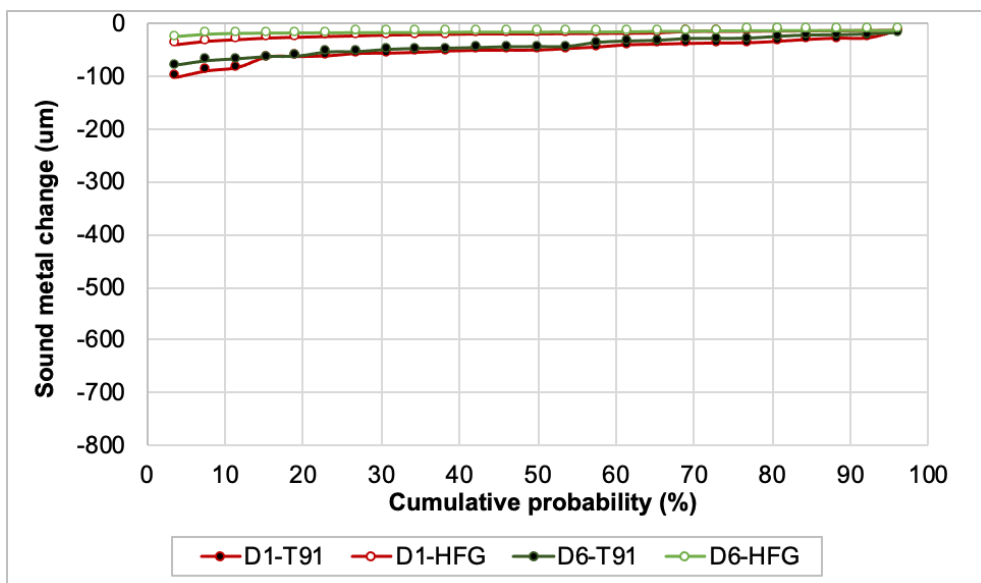


Figure 4-76: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated WWF test gas conditions at 500°C

Deviation from methodological procedure

During the 2020 UK COVID-19 pandemic shut down, the 1000-hour deposit coated, and no-deposit samples tested at 500°C were kept in a N₂ atmosphere at ambient temperatures which may have ranged between 10°C to 25°C. The samples were accessed after 3 months. Under standard practices, samples are not left unattended beyond a week prior to concluding samples preparation and dimensional metrology measurements.

The no-deposit T91 and 347HFG samples metrology data presented median metal thickness changes of -3.1 µm (T91) and -2.1 µm (347HFG) and are documented in **Figure B-1**. These values may be within expected ranges when compared corrosive changes undergone by samples of higher temperature exposures (**Figure B-1**). The metal and sound metal changes exhibited by the 1000-hour exposure alloy samples covered with deposits D1 and D6 are present in **Figure 4-77** and **Figure 4-78** respectively.

Metal loss was again most advanced for the T91-D6 sample at 500°C. Metal thickness change of T91-D6 (-160 µm) was doubled that of T91-D1 (-78 µm) at median value. At lower probability, 347HFG-D6 dimensional metrology data recorded steep metal thickness change at mid-metal surface section. The occurrence of the steep gradient may be initiated by the prolonged storage of sample as an unspent salt residue could remain actively corrosive. Most of the sample's surface, however, displays minimal metal thickness change similar to the 347HFG-D1 sample.

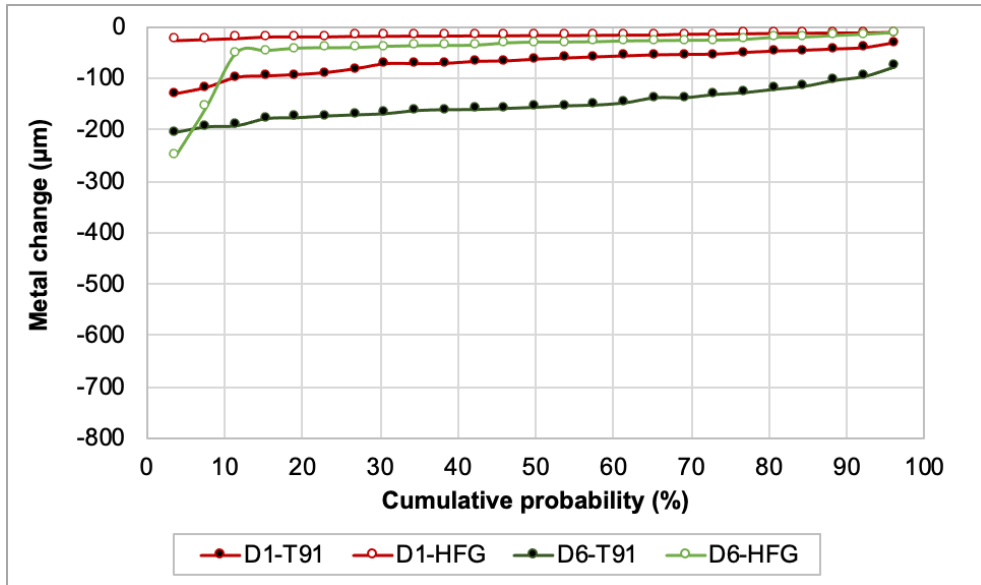


Figure 4-77: Metal change plot of T91 and 347HFG with deposits D1 and D6 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 500°C

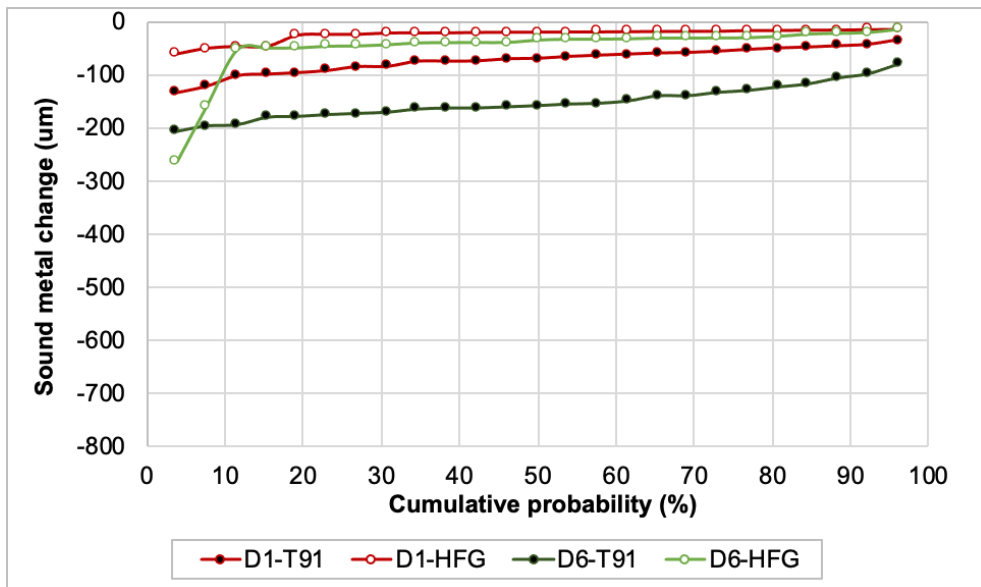


Figure 4-78: Sound metal change plot of T91 and 347HFG with deposits D1 and D6 at $100\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated WWF test gas conditions at 500°C

The sound metal change profile for 347HFG indicates some localised damage, albeit occurring at low cumulative probability levels.

4.2.2.3.2. SEM/EDX evaluation of 500°C exposure samples

Cross-sectioned images of the 500°C exposure samples are presented within this section. **Figure 4-79** presents the BSE cross-sectioned images of the alloys with no deposit following exposure for 1000 hours in WWF gas environmental at 500°C. Scale thickness on the T91 sample is about 50% less than observed on the higher temperature exposed no-deposit samples (**Figure 4-46** and **Figure 4-66**) and also remains adhered to the alloy surface. Scale thickness may indicate the severity of metal loss.

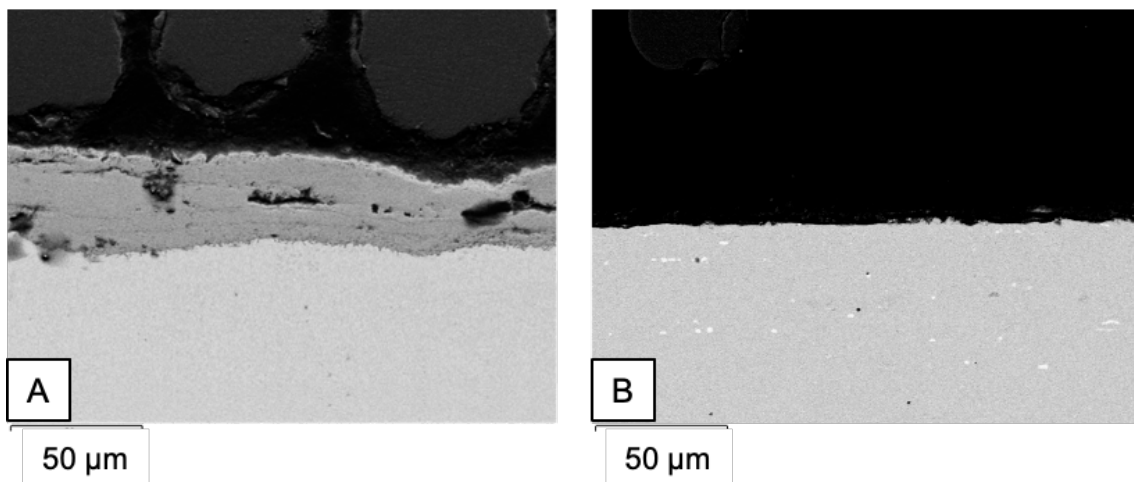


Figure 4-79: BSE images of cross-sectioned (A) T91 & (B) 347HFG with no deposit, following 1000 hours exposure in WWF simulated combustion gas conditions at 500°C

Figure 4-80 compares the BSE images of the cross-sectioned alloys surfaces exposed with deposits D1 and D6 for 500 hours in WWF test gas environment at 500°C. Multi-layered scale features are noted on both T91 samples, however, the scale thickness on the T91-D6 sample is more than doubled that seen on T91-D1. Delaminated scales and fractures are pronounced on the T91-D6 sample, whereas T91-D1 at 500°C shows better adhesion properties. Scale thickness on the austenitic steel is also greater for the D6 exposed sample. The deposit section of sample 347HFG-D1 features sharp edged particles which is indicative of non-melted deposit component. These unmelted salt components were not found on the D6 exposed sample (wide

overview SE image documented in **Figure E-11**). The deposit section of the D6-exposed sample showed Cl did not remain on the sample and deposit residue was K and S.

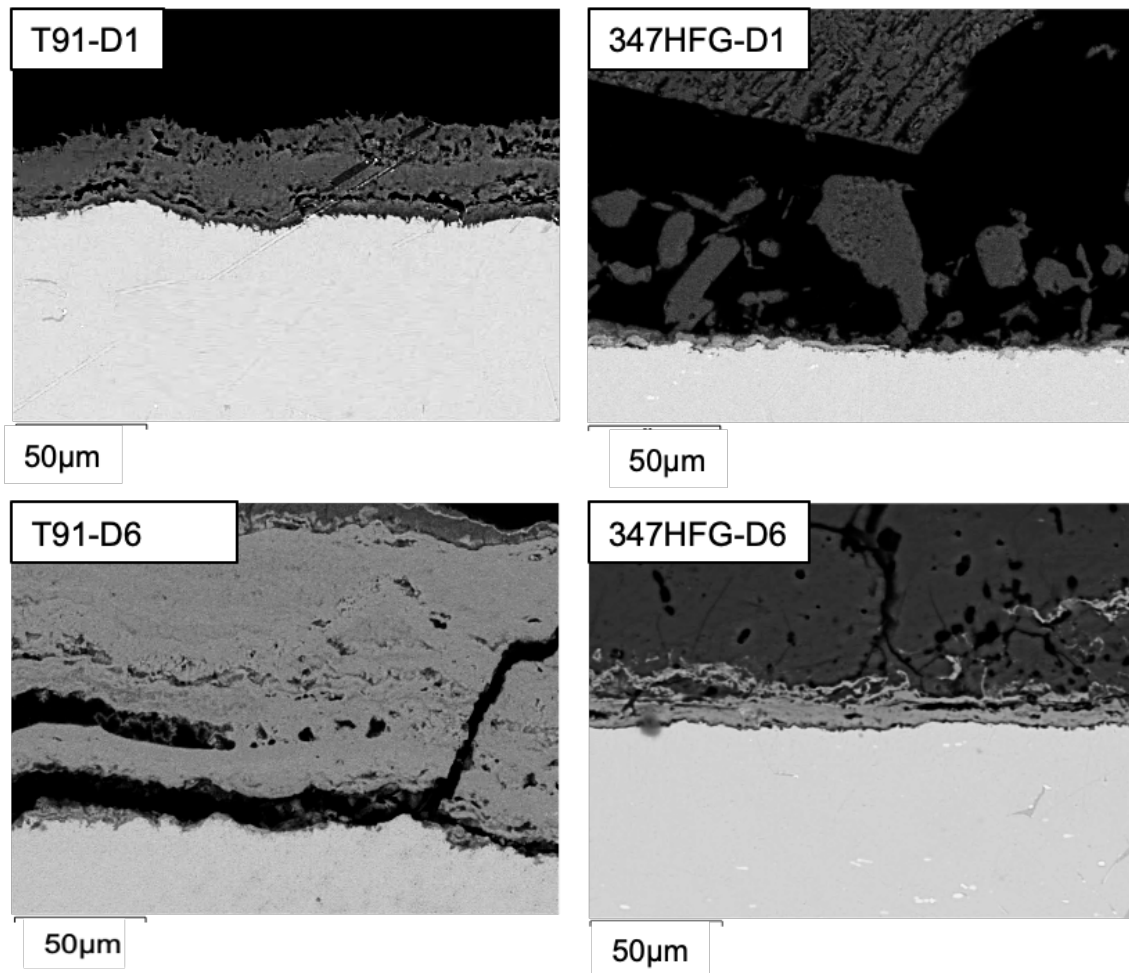


Figure 4-80: BSE images of cross-sectioned alloy samples following 500 hours exposure in WWF simulated combustion gas conditions at 500°C with D1 and D6 at a deposition flux of 100 µg/cm²h

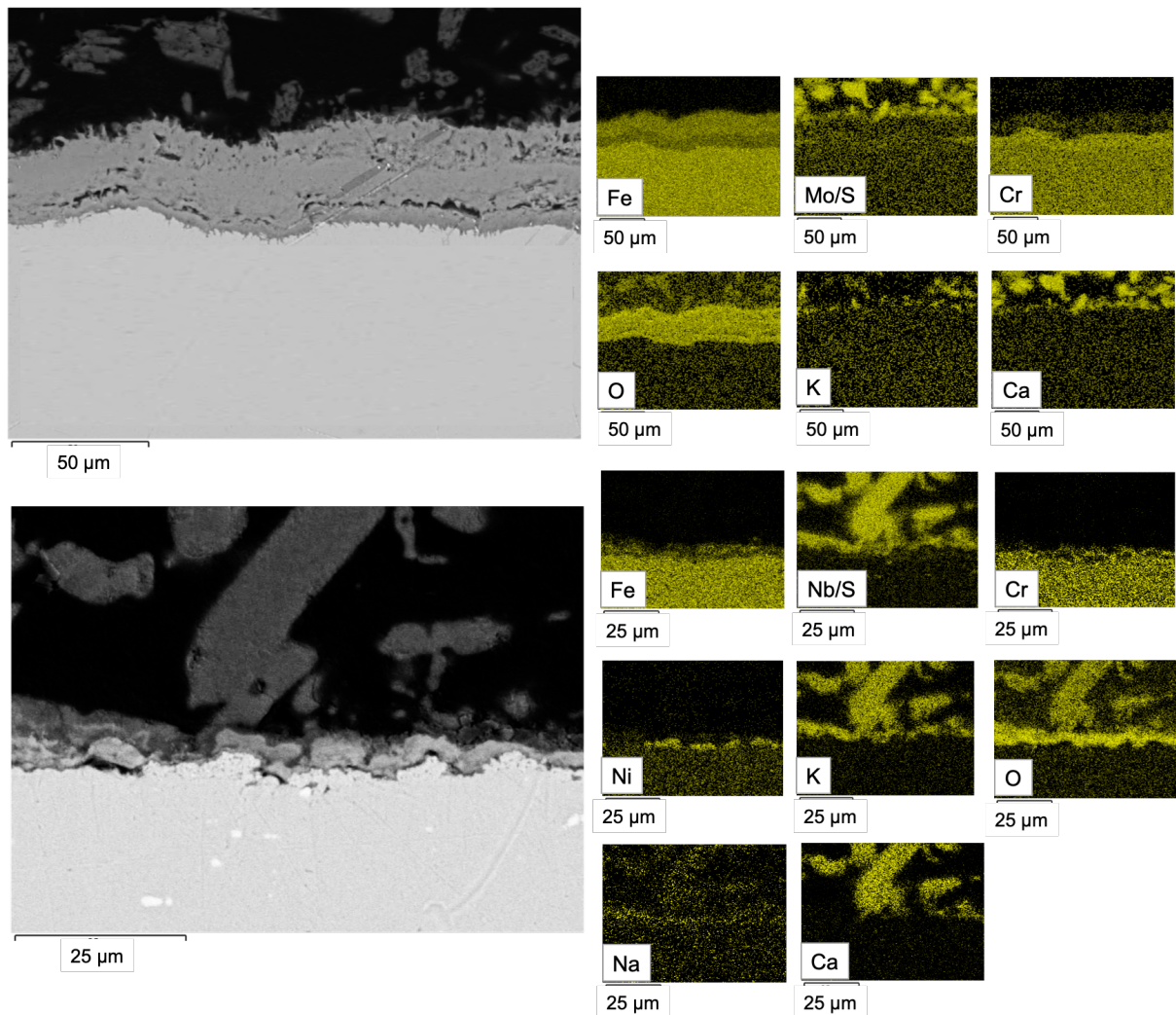


Figure 4-81: SEM image of cross-section T91-D1 and 347HFG-D1 samples post 500 hours exposure in WWF simulated combustion gas environment at 500°C and deposition flux of 100 µg/cm²h

The EDX maps in **Figure 4-81** confirm D1 deposit components; Ca, K, S and O, are concentrated at the unmelted deposit layer (rigid structures) for the T91 and 347HFG samples by 500 hours exposure. K is also present at the scale surface in a fluid-like layer, typical of components which have melted. Cl was not observed on the image and the map has not been included in **Figure 4-81**.

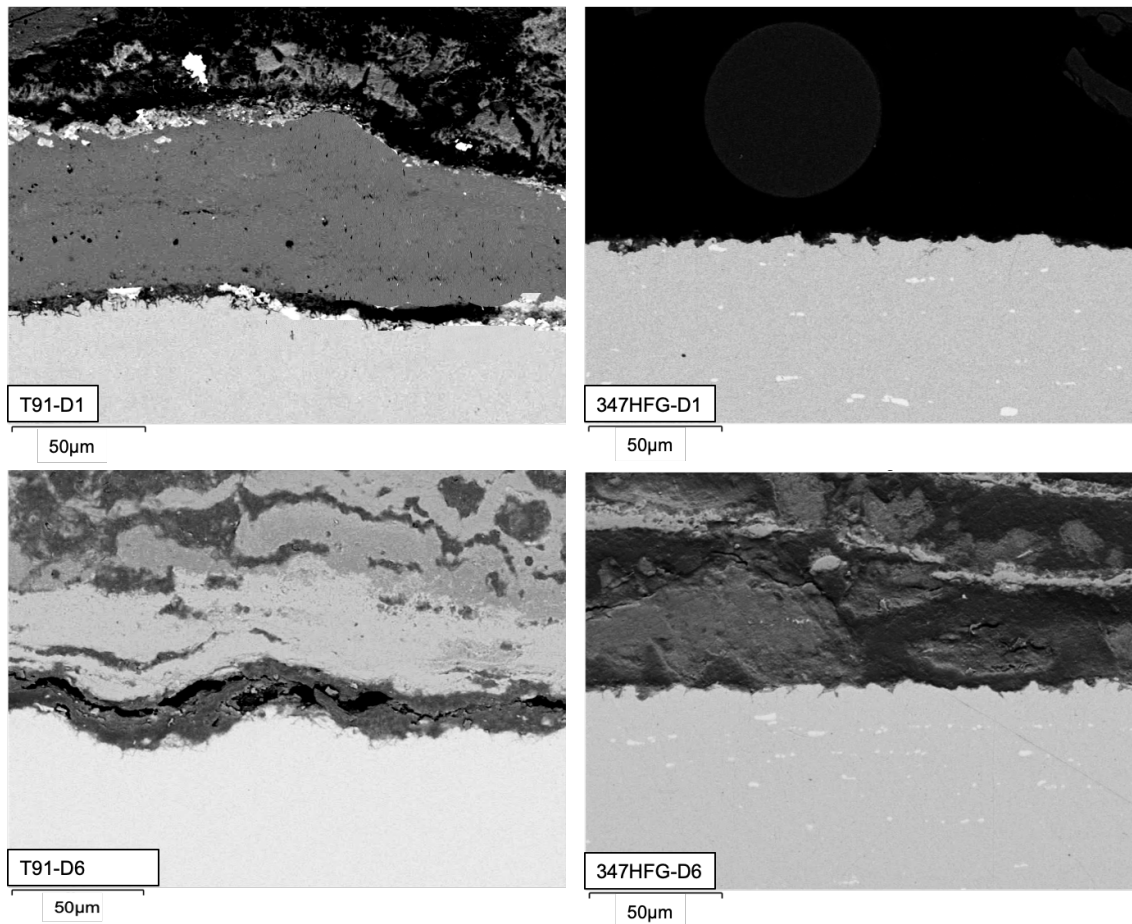


Figure 4-82: SEM image of cross-sectioned samples following 1000 hours exposure in WWF simulated combustion gas conditions at 500°C with D1 and D6 at deposition flux of 100 µg/cm²h

The BSE images of the deposit coated samples exposed at 500°C for 1000 hours are presented in **Figure 4-82**. 347HFG-D6 and T91-D6 scales are multi-layered and darker shades on their BSE images are indicative of low atomic number elements present such as included in the deposit (D6; K, S, Cl). These dark shades correspond with map for K and S as detected by EDX analysis in **Figure 4-83** (347HFG-D6) and in **Figure E-12**. The K- and S-rich regions for both samples (**Figure 4-8**) are embedded within the multi-layered metal scales in a compact and fluid-like pattern which may suggest that the test environment is conducive for eutectic melts occurring at 500°C. These scales are comparatively thicker than scale of the D1 exposed metals which may be also more uniform (T91-D1 as for the case) and compact, thus preventing deposit component

intrusion within the scale layouts. Cl was not detected on the sample following 1000 hours exposure at 500°C for the D6 exposed samples and the EDX maps have not been included in **Figure 4-83**.

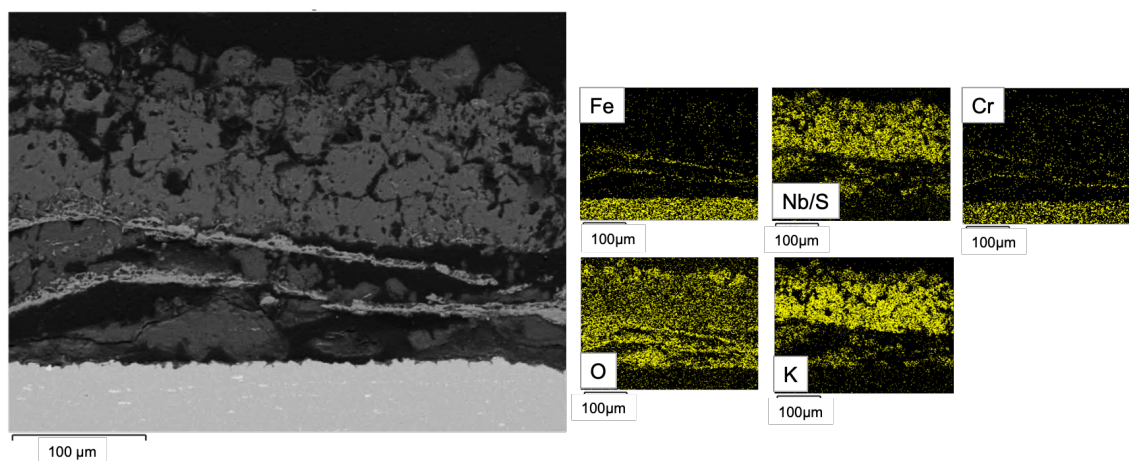


Figure 4-83: BSE image and EDX maps of cross-sectioned 347HFG-D6 sample post 1000 hours exposure in WWF simulated combustion gas environment at 500°C a deposition flux of 100 µg/cm²h

4.2.3. Metal changes in herbaceous grass & biomass test gas conditions

Tests were conducted at 600°C under the HGB test gas conditions to evaluate the corrosive effects of HGB deposits D6 and D7 and, WWF deposit D1 which were applied at a deposition flux of 100 µg/cm²h. The alloy metal changes are presented within this section. The HGB test gas has higher quantities of corrosive components (HCl and SO₂) compared to WWF (**Table 3-3**). Flow rates conditions are also higher for the HGB atmosphere (**Section A-5**).

4.2.3.1. Metal loss

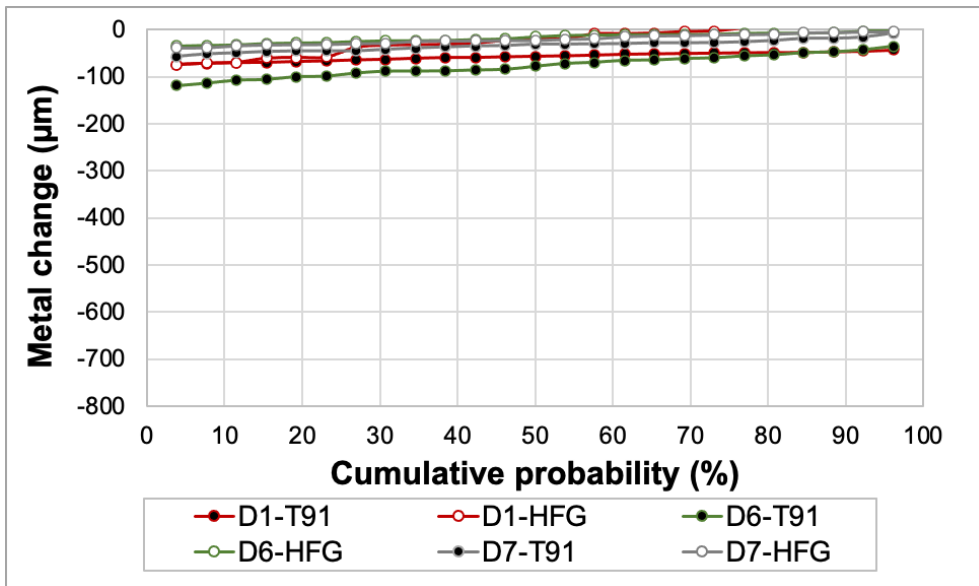


Figure 4-84: Metal changes of T91 and 347HFG with deposits D1, D6 and D7 at $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated HGB test gas conditions at 600°C

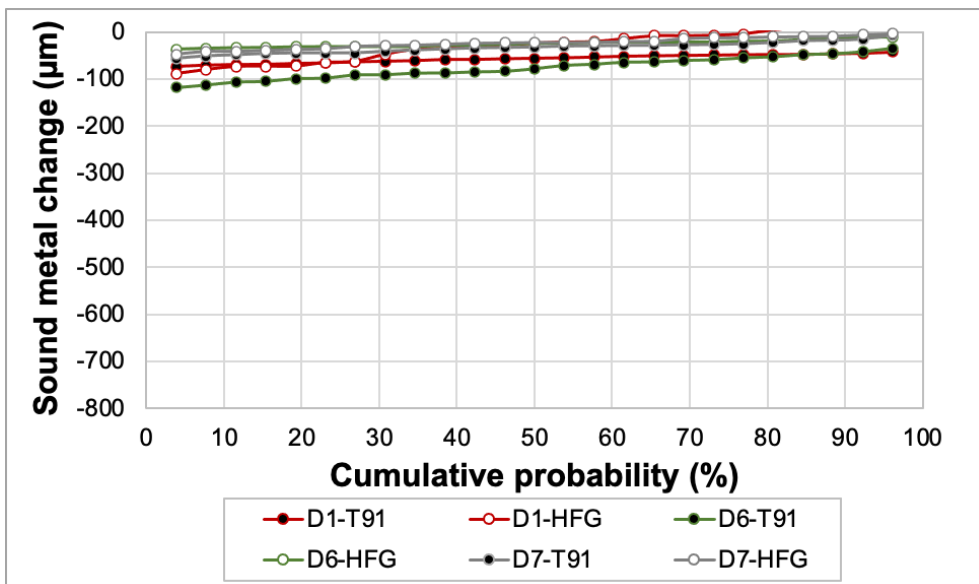


Figure 4-85: Sound metal changes of T91 and 347HFG with deposits D1, D6 and D7 at $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated HGB test gas conditions at 600°C

The metal and sound metal change data for the 200-hour exposure alloy samples are presented in **Figure 4-84** and **Figure 4-85** respectively. Most measurement points across each sample surface are less than 100 μm of metal loss (T91-D6 experiences a metal loss range within 96-118 μm and median metal loss of 78 μm . The metal change measurements above zero (347HFG-D1 and 347HFG-D6) lay within calculated metal change error margins (+13 μm to -13.5 μm) for these samples as detailed in **Section D-4**.

By 500 hours exposure, 347HFG-D1 is the least progressed in metal loss within 20% of its surface metal loss below 17 μm (median metal loss, 32 μm). The D6 and D7 covered 347HFG samples undergo similar damage extents (median metal loss; 176 μm , 165 μm respectively). While metal responses of samples T91-D1 and T91-D7 have similar values (median metal loss; 188 μm , 187 μm respectively), T91-D6 exhibits greater metal surface loss of all six samples (median metal loss; 290 μm). Median sound metal penetration depths for 347HFG exposed are 18 μm (D1), 8 μm (D6) and 11 μm (D7). Sound metal penetration for T91 were not detected during metrology analysis.

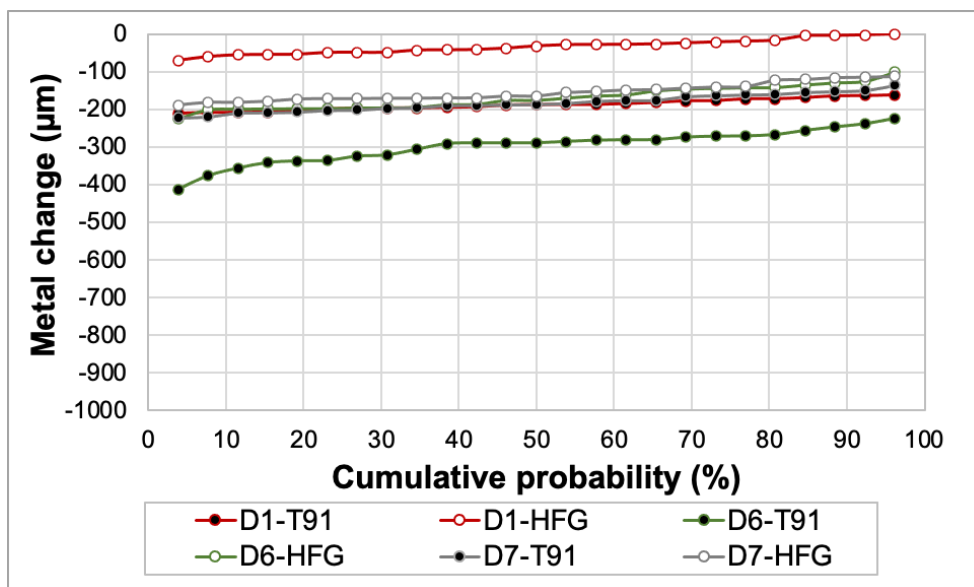


Figure 4-86: Metal change plot of T91 and 347HFG with deposits D1, D6 and D7 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated HGB test gas conditions at 600°C

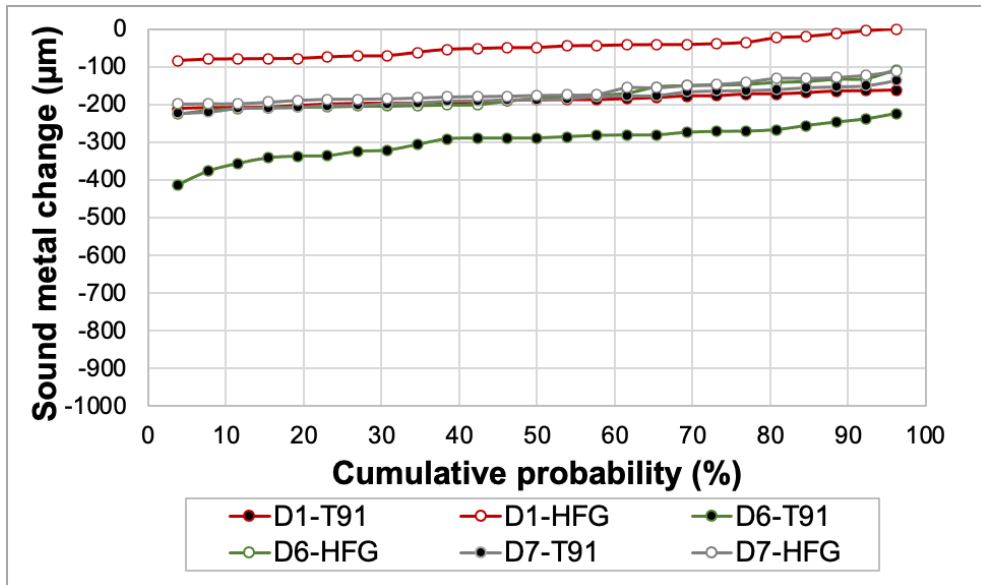


Figure 4-87: Sound metal change plot of T91 and 347HFG with deposits D1, D6 and D7 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in simulated HGB test gas conditions at 600°C

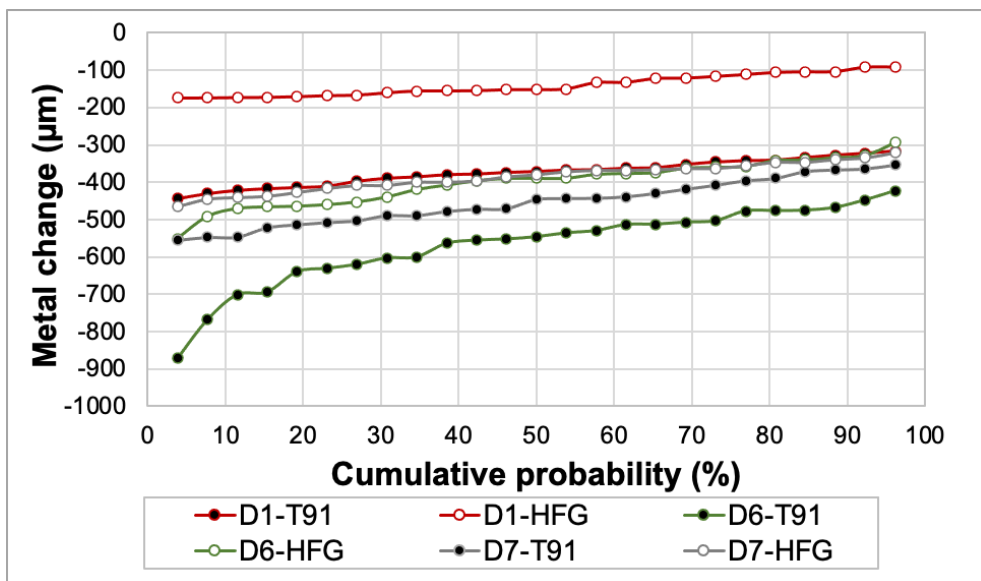


Figure 4-88: Metal change plot of T91 and 347HFG with deposits D1, D6 and D7 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated HGB test gas conditions at 600°C

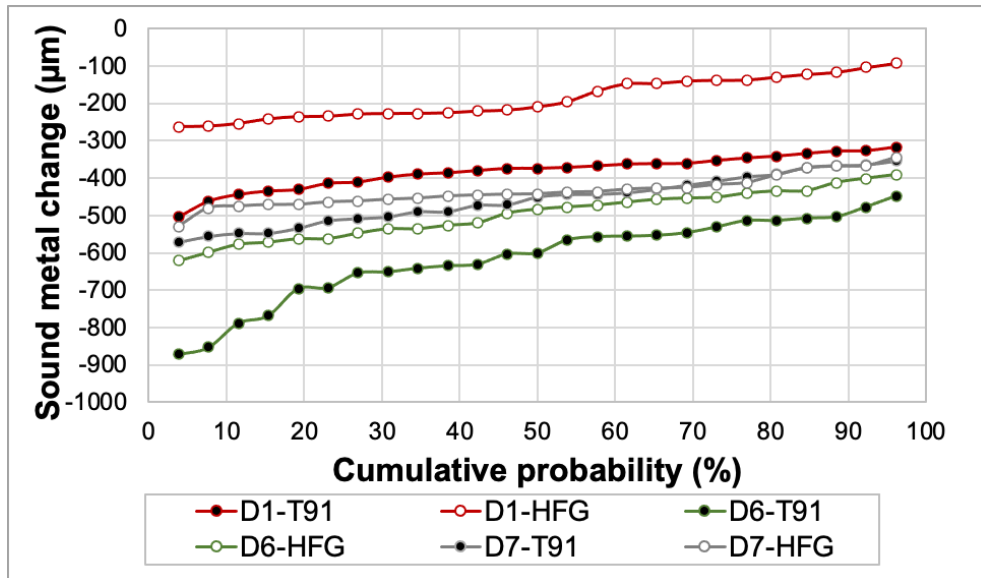


Figure 4-89: Sound metal change plot of T91 and 347HFG with deposits D1, D6 and D7 at 100 µg/cm²h exposed for 1000 hours in simulated HGB test gas conditions at 600°C

Figure 4-88 and **Figure 4-89** show that, at 1000 hours exposure, HFG-D1 (median metal loss; 152 µm) remains the least affected, while T91-D6 (median metal loss; 546 µm) remains the most corroded within the HGB test gas condition at 600°C as for the 500-hour exposure samples (the median metal loss for T91-D7 is 439 µm). T91 shows more localised damage tendencies with D6 exposure (**Figure 4-89**). Median sound metal damage are greater at 1000 hours exposure with D6 which results in greater internal penetration attack on both steels in HGB conditions at 600°C. With increasing exposure time, median sound metal penetrations depths are as follows: 57 µm (D1), 93 µm (D6) and 63 µm (D7) for 347HFG and, 3 µm (D1), 54 µm (D6) and 4 µm (D7) for 347HFG.

4.2.3.2. SEM/EDX evaluations of HGB test gas exposed samples

The no-deposit samples exposed to corrosive gas conditions of HGB at 600°C for 1000 hours are displayed in **Figure 4-90**. The 347HFG sample experienced ~20 µm internal damage penetration along grain boundaries. The HGB gas environment also influenced localised damage on the T91 sample surface.

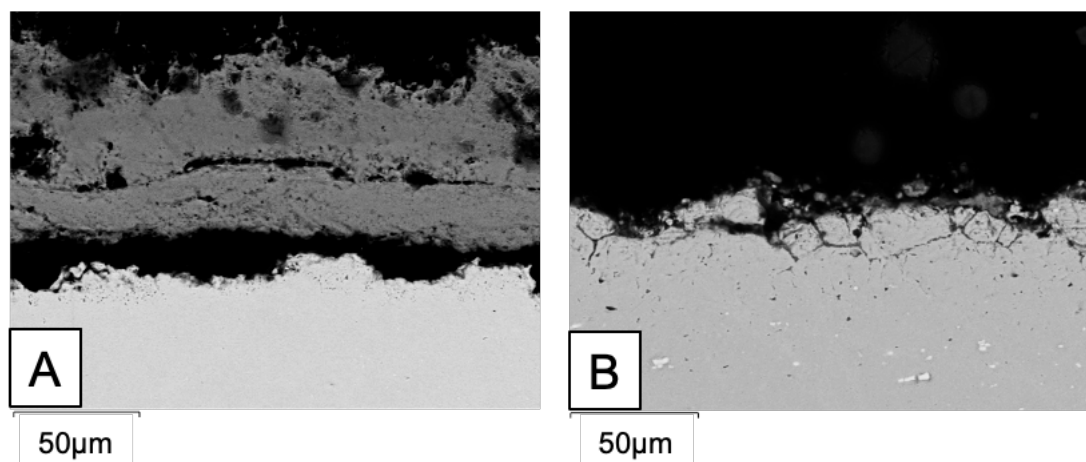


Figure 4-90: BSE image of no applied deposit samples (A) T91 and (B) 347HFG, following 1000 hours exposure in HGB test gas environment at 600°C

Figure 4-91, Figure 4-92 and Figure 4-93 presents the cross-sectioned images of T91 and 347HFG samples exposed at 500 hours to D1, D6 and D7 respectively. The T91 tend to produce more scales and have been presented at wider capture range to observe both metal damage and scale features within the same image.

Scale cover is observed for 347HFG-D1. These scales feature metal oxides, and some deposit components may also be observed within the scale. Na and K may be observed within grain boundaries and upper scale/deposit region respectively. Grain boundary intrusions are notably wider at the extreme depths, showing pit formations within the alloy. Chlorides have not been observed at these locations (Cl EDX map not included for 347HFG in **Figure 4-91**).

T91-D1 comprises of an adhered multi-layered scale. Na is seen to have penetrated these scale layers to the metal/scale interface, signifying its participation in the scale delamination process. Other scales present at the upper sample regions feature K and Na at the scale/void interfaces. Amongst the D1 deposit cations (Ca, K and Na), Ca is furthest from the metal surface and situated mainly within the deposit region and possibly where deposits have become covered with scales and re-coats within furnace run cycles. The granular

particulates of Ca, S and O are mapped at the deposit layer whereas, Ca-based deposits embedded within scales structure appear continuous, as would be expected for components which have melted, suggesting the Ca species had undergone melting.

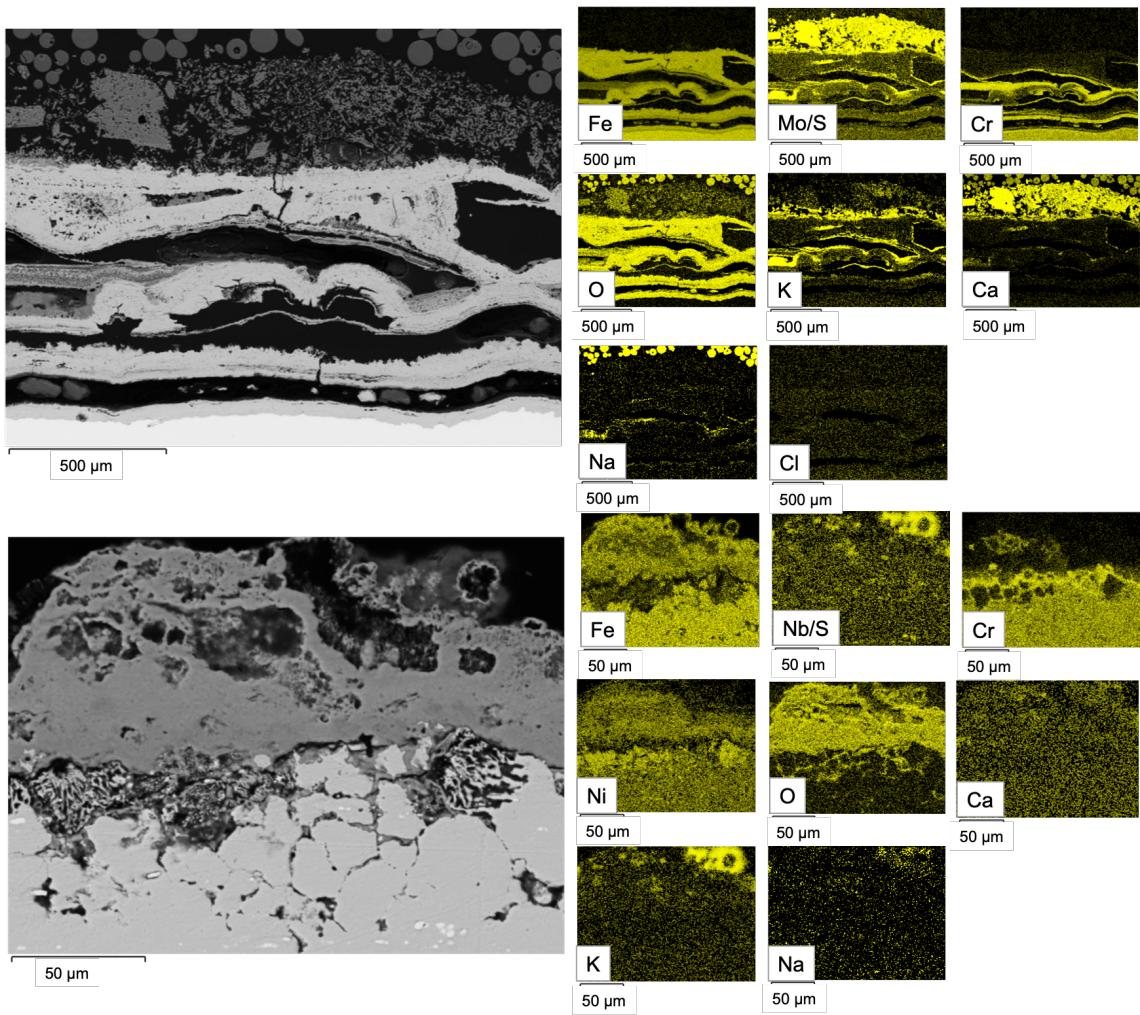


Figure 4-91: T91-D1 and 347HFG-D1 following 500 hours exposure in HGB test gas environment at 600°C

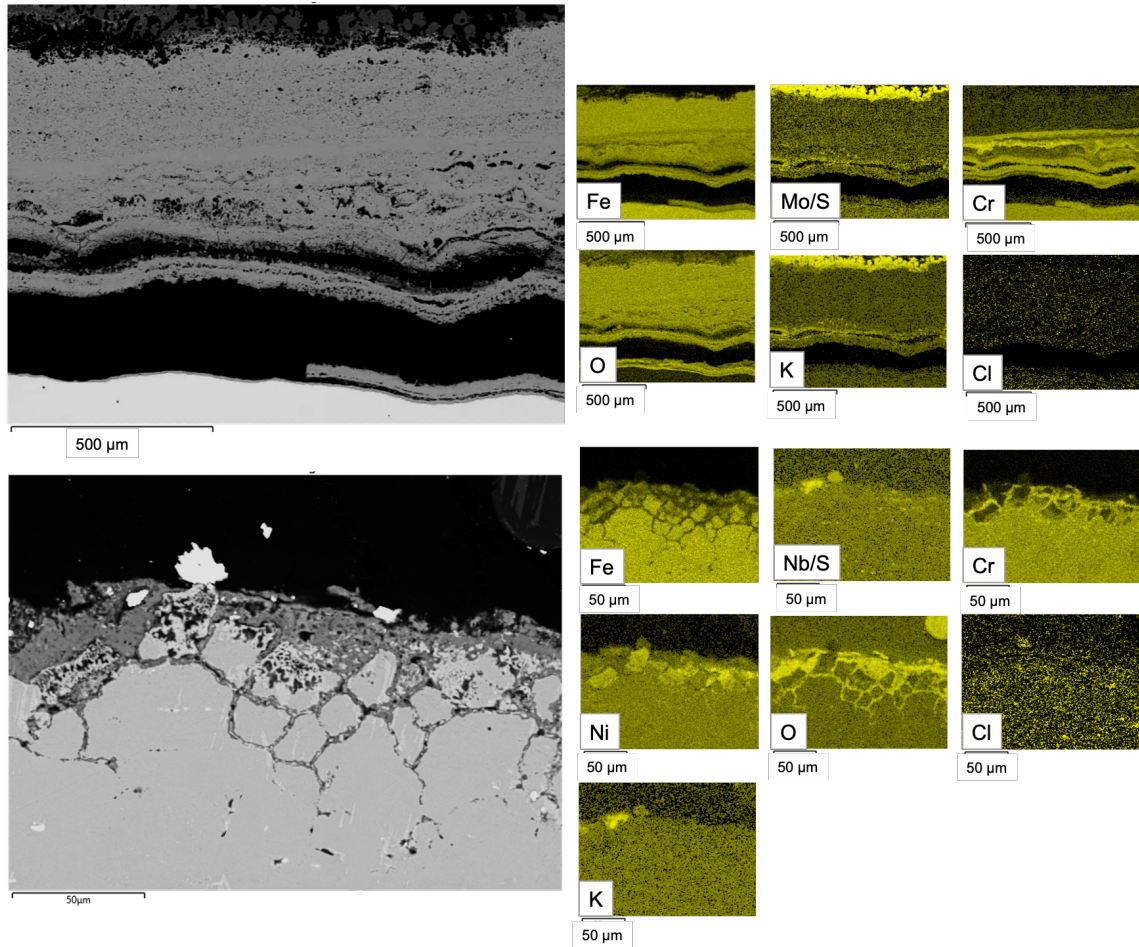


Figure 4-92: T91-D6 and 47HFG-D6 following 500 hours exposure in HGB test gas environment at 600°C

The image capture for T91-D6 in **Figure 4-92** is of a lower magnification (compared to that of 347HFG-D6) to allow the observation of all damage features occurring along the sample thickness. T91-D6 shows multi-layered scaling with fractures. The scale is also delaminated from the metal surface where further scale fracturing may have occurred. The Mo-rich scale interfaces seem to be weak scale layer boundaries favouring scale separation as similarly observed for T91-D1 in **Figure 4-91**. Ni and Cr oxides on the 347HFG-D6 sample surface are scanty/broken and don't appear protective against chloride penetration which is located at >50 µm below the metal surface.

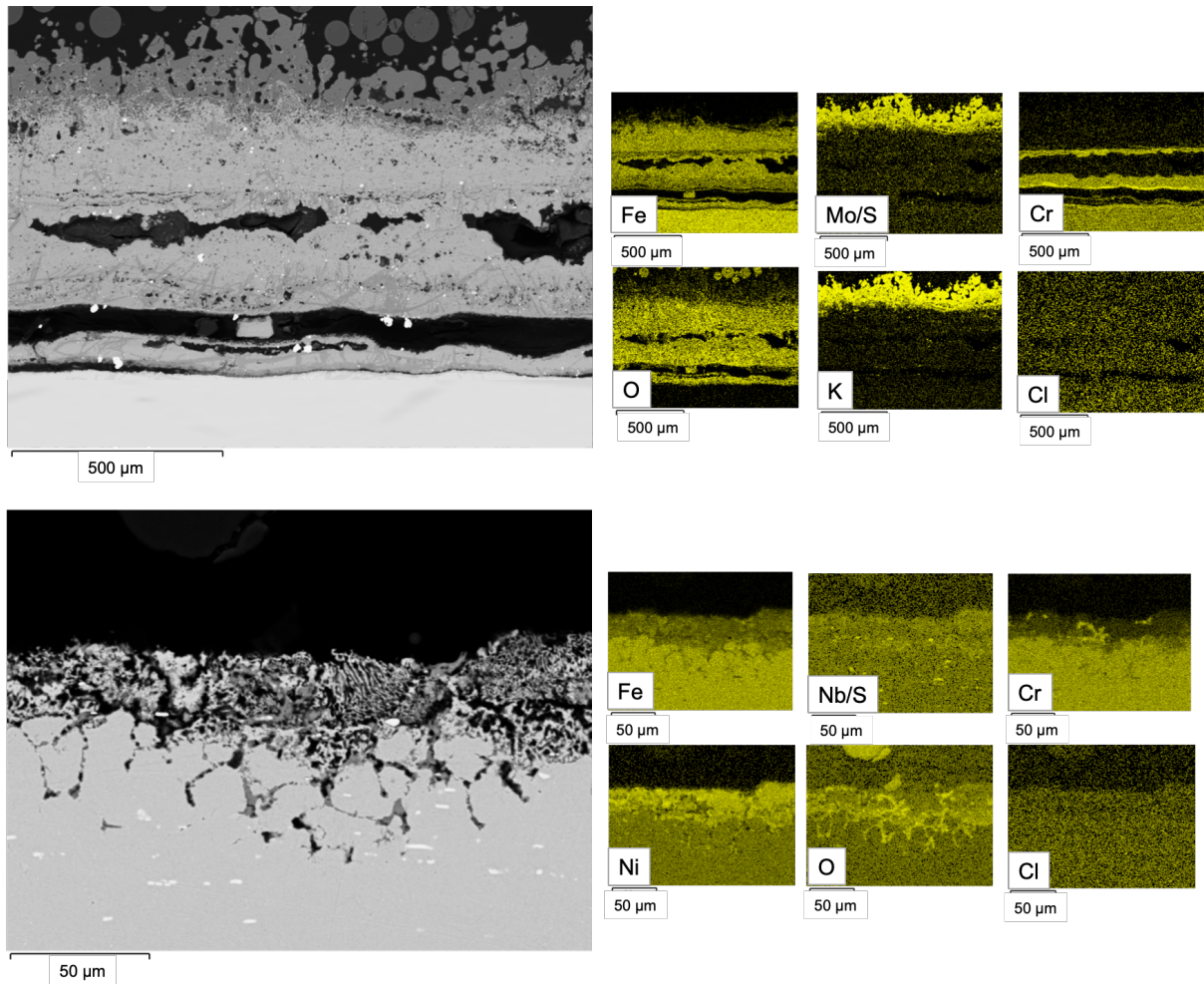


Figure 4-93: T91-D7 (top) and 347HFG-D7 (bottom) following 500 hours exposure in HGB test gas environment at 600°C

Again, a wider image view was preferred for sample T91-D7 to allow observations of damage feature along the sample depth as for 347HFG-D7 in **Figure 4-93**. Similar depths of penetration can be observed for the austenitic steels in **Figure 4-93** and **Figure 4-91**, though internal metal pitting at grain boundary depths may be more prominent for the D1-covered 347HFG steel (**Figure 4-91**). Ni-rich scales are ~30 μm thick, however Cr-rich scales may have not been recovered as it is suspected that spallation occurred which led to the loss of upper scale/deposit features (K map did not identify the presence of the element at the image capture region. This map has been excluded for sample 347HFG-D7 in **Figure 4-93**).

4.2.4. Metal changes in agricultural plants & residues test gas conditions

Corrosion tests were conducted at 600°C under the APR test gas conditions for T91 and 347HFG steel samples exposed with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$. Post-exposure sample dimensional metrologies and SEM-EDX images are presented within this section. The APR test gas has the highest quantities of corrosive components (HCl and SO_2) compared to HGB and WWF (Table 3-3). Flow rates conditions are also highest for the APR atmosphere (Section A-5).

4.2.4.1. Metal loss

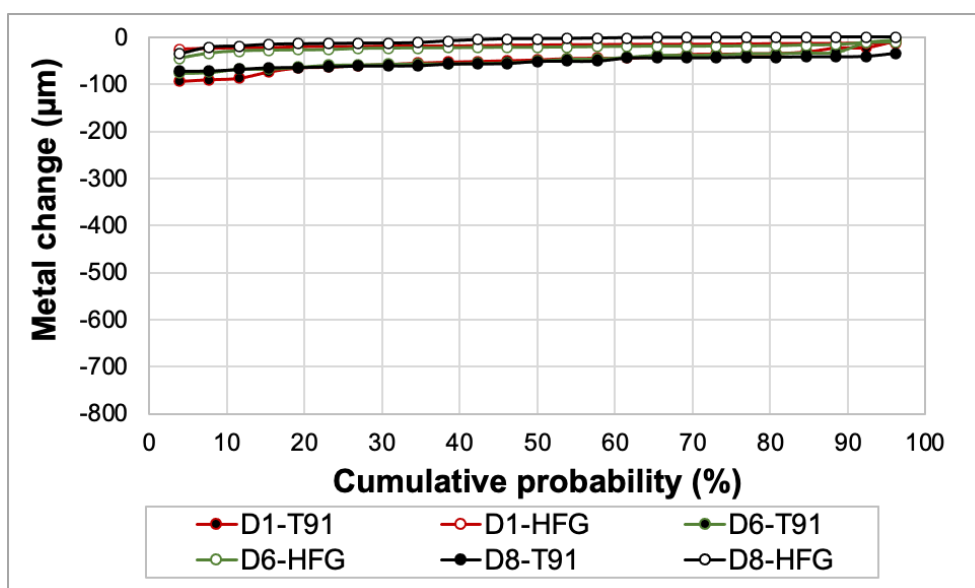


Figure 4-94: Metal changes of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in simulated APR test gas conditions at 600°C

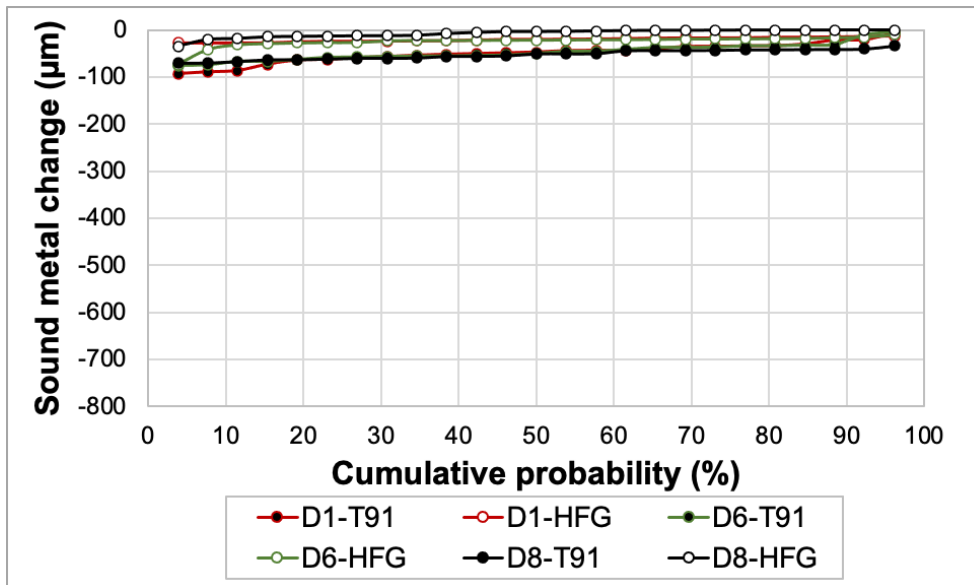


Figure 4-95: Sound metal changes of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 200 hours in APR test gas conditions at 600°C

The metal and sound metal change data for the 200-hour exposure alloy samples are presented in **Figure 4-94** and **Figure 4-95** respectively. All measurement points across each sample surface are within 100 μm of surface metal loss and within metal change error analysis range (+13 μm to -13.5 μm , **Section D-4**). No internal penetration below metal surface is detected by dimensional metrology at this exposure time (dimensional metrology median figure documented in **Section B.14**).

By 500 hours (**Figure 4-96** and **Figure 4-97**), internal damage is observed for the austenitic samples. Median metal loss for all samples are beyond incubation phase.

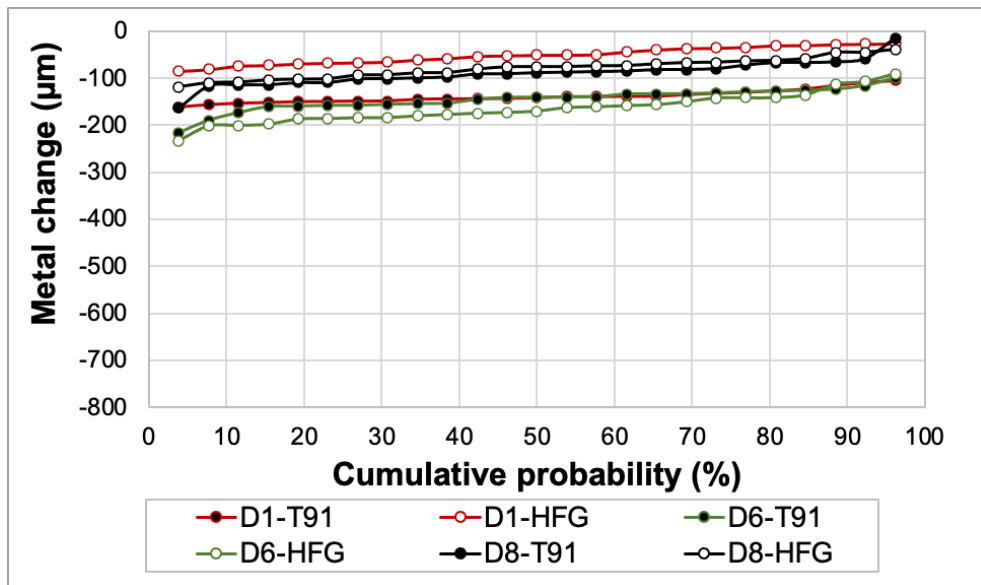


Figure 4-96: Metal change plot of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in APR test gas conditions at 600°C

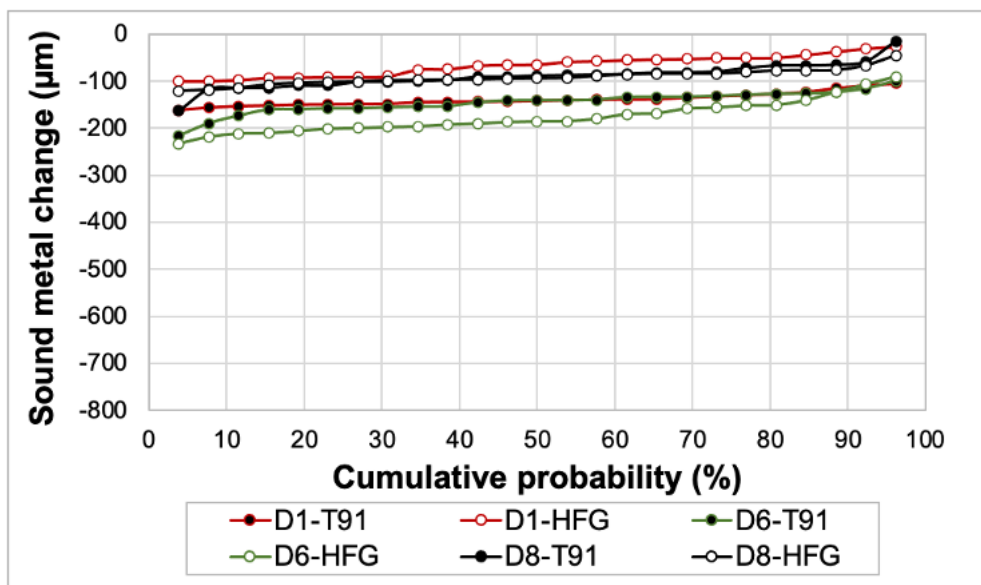


Figure 4-97: Sound metal changes of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in APR test gas conditions at 600°C

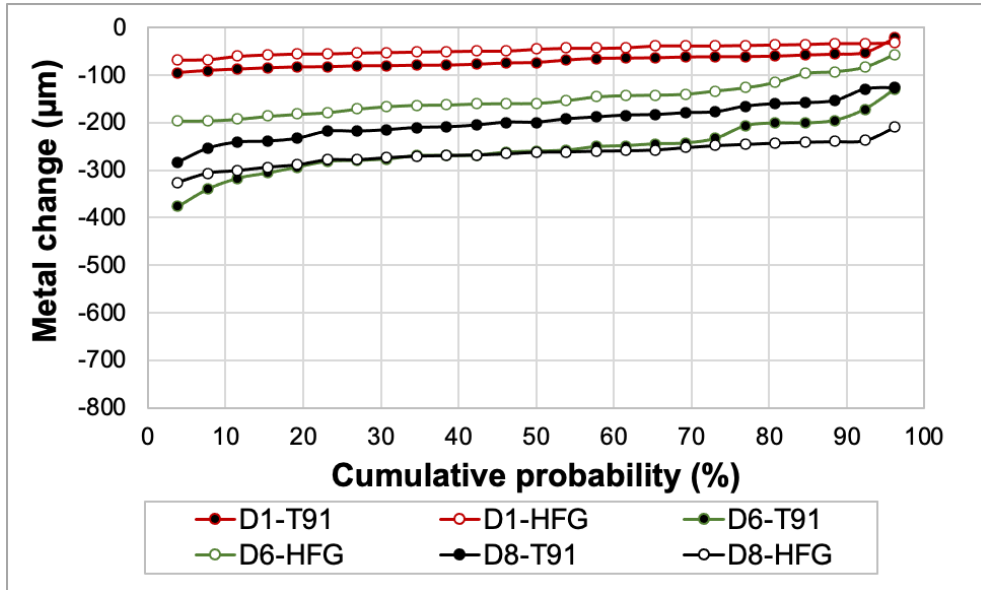


Figure 4-98: Metal change plot of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in simulated APR test gas conditions at 600°C

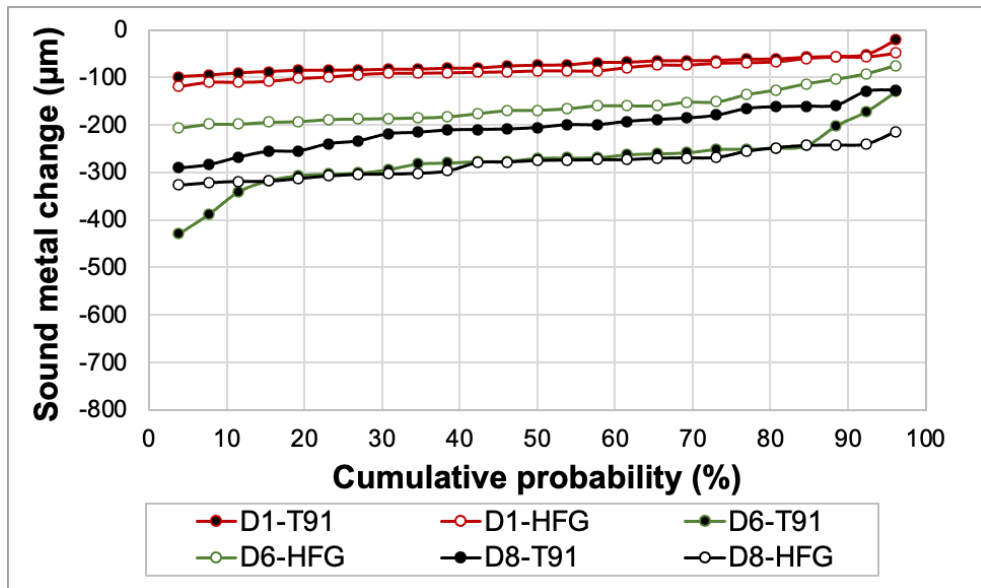


Figure 4-99: Sound metal change plot of T91 and 347HFG with deposits D1, D6 and D8 at 100 $\mu\text{g}/\text{cm}^2\text{h}$ exposed for 1000 hours in APR test gas conditions at 600°C

In **Figure 4-98** metal changes of the D6 exposed alloys are greater compared to metal changes for the D1 exposed alloys, as also observed for the samples exposed in HGB test gas conditions (**Section 4.2.3**). Following 1000 hours exposure, median metal losses for T91 are 73 μm (D1), 260 μm (D6) and 206 μm (D8) and, for 347HFG, 45 μm (D1), 159 μm (D6) and 261 μm (D8). Sound

metal changes presented in **Figure 4-99** indicate intrusive damage exist for the six samples. For T91, sound metal penetration depths are: 13 μm (D1), 10 μm (D6) and 6 μm (D8) and for 347HFG: 41 μm (D1), 10 μm (D6) and 14 μm (D8).

4.2.4.2. SEM/EDX evaluation of APR test gas exposure samples

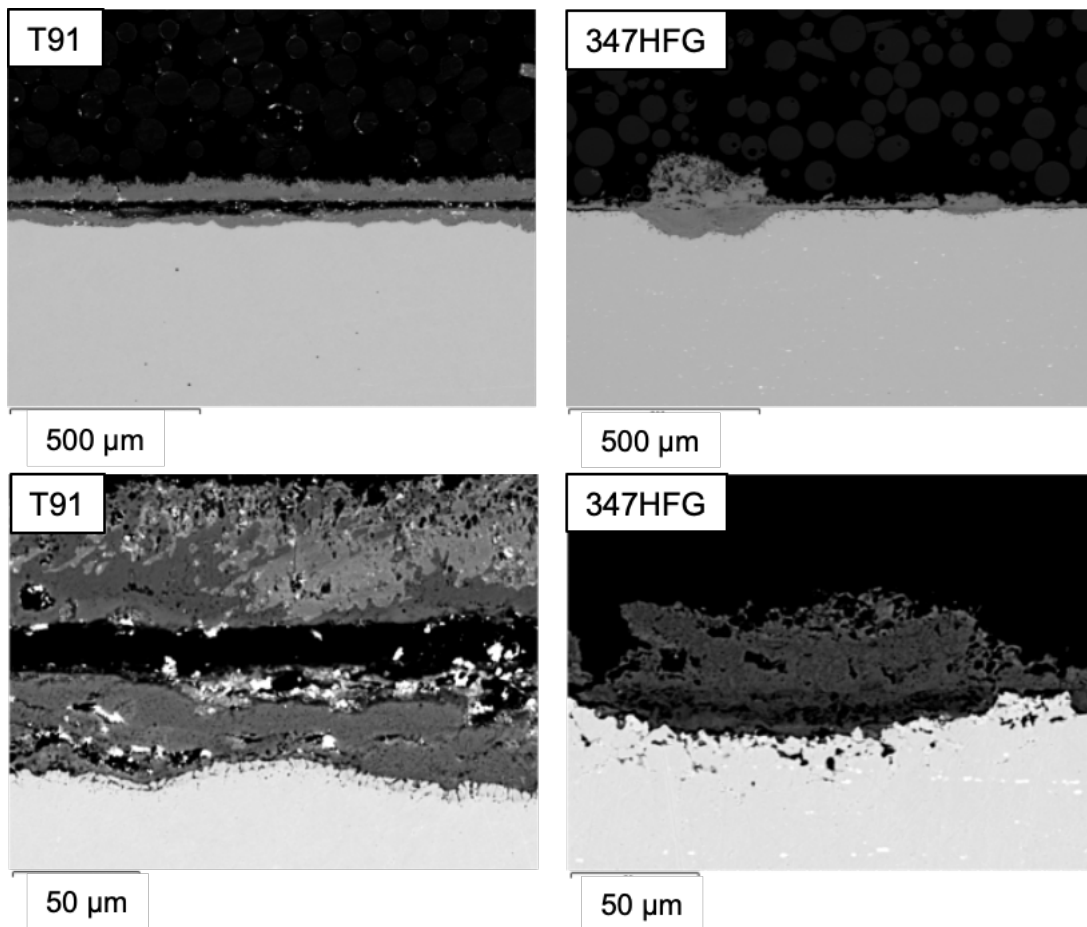


Figure 4-100: BSE images of no applied deposit alloy samples following 1000 hours exposure in APR test gas environment at 600°C. Sample cross-sectioned images have been presented in two magnifications

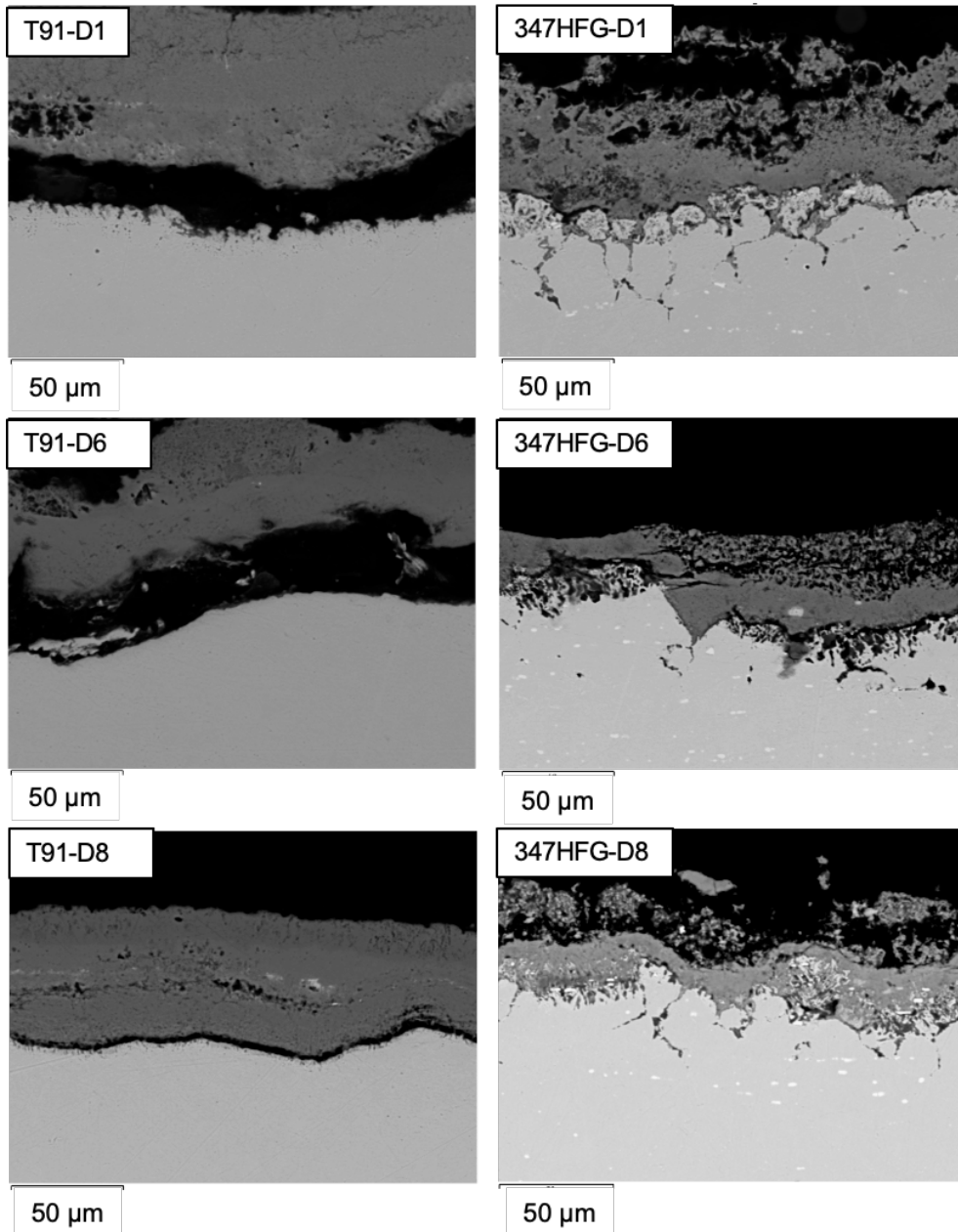


Figure 4-101: BSE image of alloy samples exposed for 500 hours with deposits D1, D6 and D8 in simulated APR combustion gas environment at 600°C

The cross-sectioned images of the no-deposit samples exposed in APR test gas for 1000 hours are displayed in **Figure 4-100**. The top row images present broader views of the samples, and the bottom row presents images captured at a higher magnification.

The T91 alloy surface is uneven and minuscule vertical penetrations intruding from the metal surface into the metal structure can be observed. The multilayered scales are thick (up to ~100 μm) and delaminated, possibly at scale interfaces, for T91. The 347HFG displays localized pits and grain boundary penetration depths of up to 30 μm across the alloy surface.

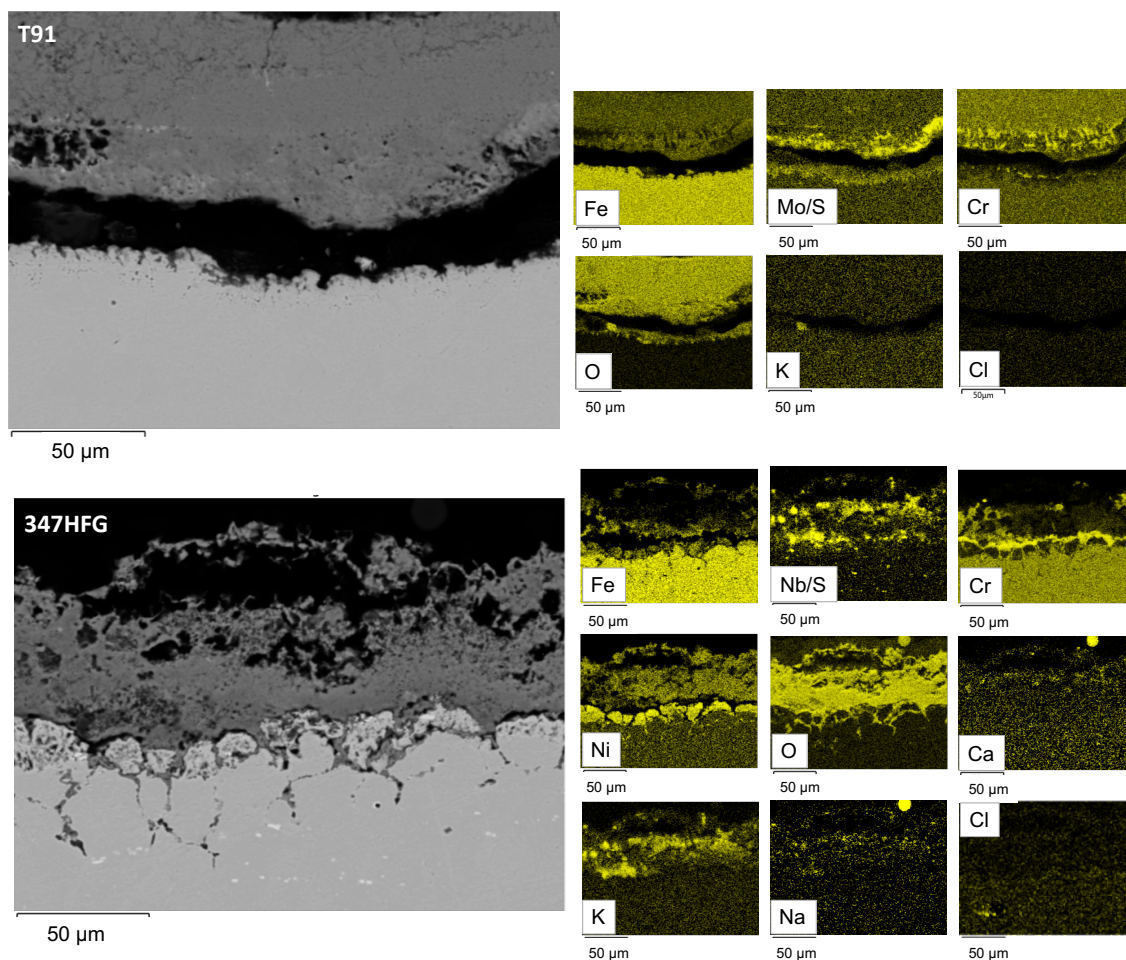


Figure 4-102: BSE/EDX images of T91 and 347HFG samples exposed for 500 hours to deposit D1 at flux 100 $\mu\text{m}/\text{cm}^2\text{h}$ in APR test gas conditions at 600°C

SE images of the 500-hour test samples exposed with D1, D6 and D8 can be compared in **Figure 4-101** and their EDX maps are presented from **Figure 4-102** to **Figure 4-104**. Vertical penetration depth is greatest for 347HFG-D1 and comparable for 347HFG-D6 and 347HFG-D8 amongst the austenitic steel

samples. The hierarchy is in line with penetration depths determined by dimensional metrology (**Section 4.2.4.1**).

Sample T91-D1 features porous Mo- and Cr-rich scales delaminated from the bulk metal. The metal surface reveals another Mo layer beneath which sound metal penetrations may be observed. A Ni scale, which features a penetrable layer, exists beneath a Cr scale layer for 347HFG-D1. Fe-S-K association are observed at the Ni-rich scale layer (left side of image) and Cl is located within grain boundaries (~30 μm below the metal surface). Ca is located at the deposit/scale interface.

Scale delamination occurs between the Mo and Cr scale boundaries in the case of sample T91-D6, and deposit components K and S are deposited within the void (**Figure 4-103**). A shallow and wide pit at the left side of the displayed sample section may have been propagated by chloride attack. The pits were however rarely encountered.

Similar damage features are observed on sample 347HFG-D6 (**Figure 4-103**) as seen on 347HFG-D1 (**Figure 4-102**); a Fe-K-S association, chloride attack at grain boundary region and a rich but non-continuous Ni scale. The damage distribution across the metal surface is, however, less even and the grain damage depths are shallower than encountered on the D1 exposed counterpart. Cl attack is also more spread across the alloy surface (based on the Cl map) as well as within grain boundaries, whereas Cl attack was mostly penetrative for sample 347HFG-D1 (**Figure 4-102**).

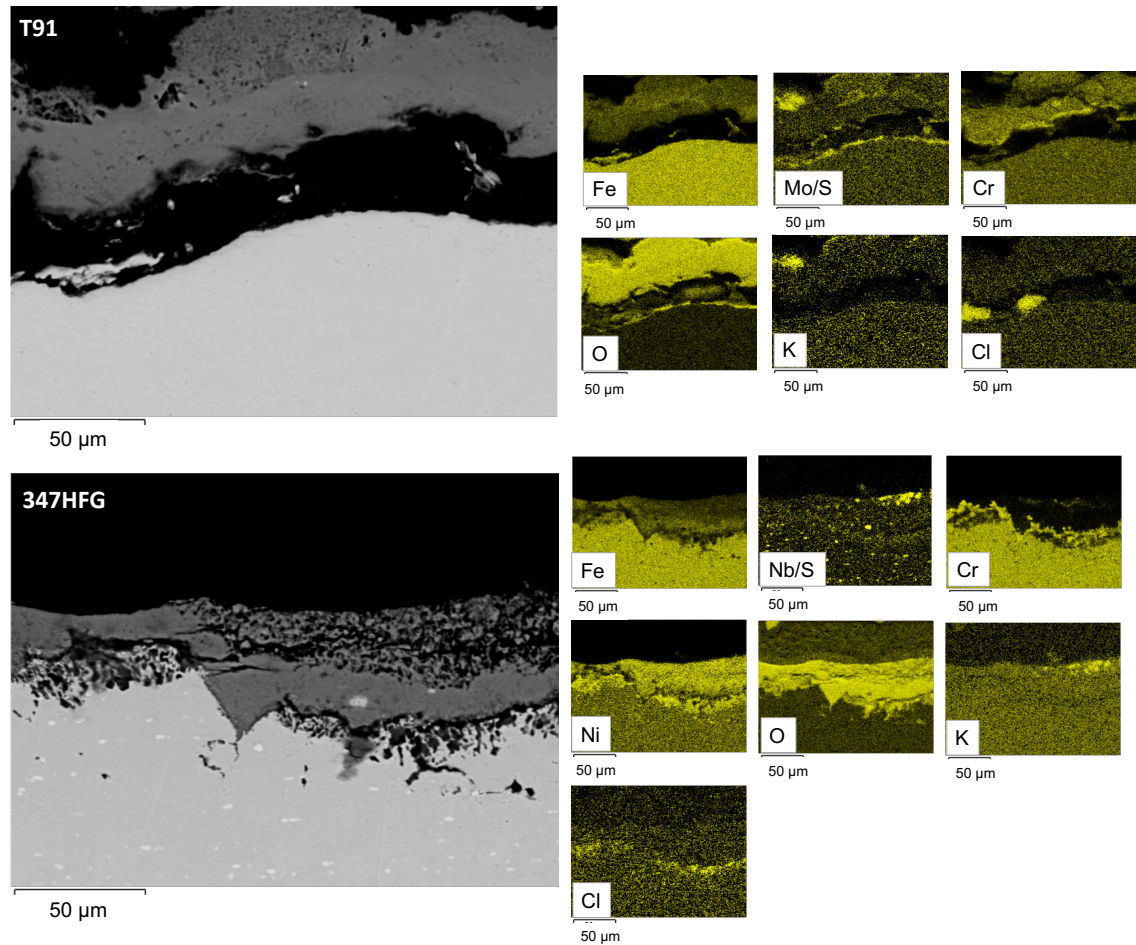


Figure 4-103: BSE/EDX images of T91 and 347HFG samples exposed for 500 hours to deposit D6 at flux 100 µm/cm²h in APR test gas conditions at 600°C

Scaling is more compact on the D8 exposed T91 sample in **Figure 4-104**, though separation of the scale from the bulk metal occurs at the Mo and Cr oxide scale interface. Sound metal is relatively less impacted by corrosive attack, compared to the corrosive damage experienced by the D1 and D6 exposed samples.

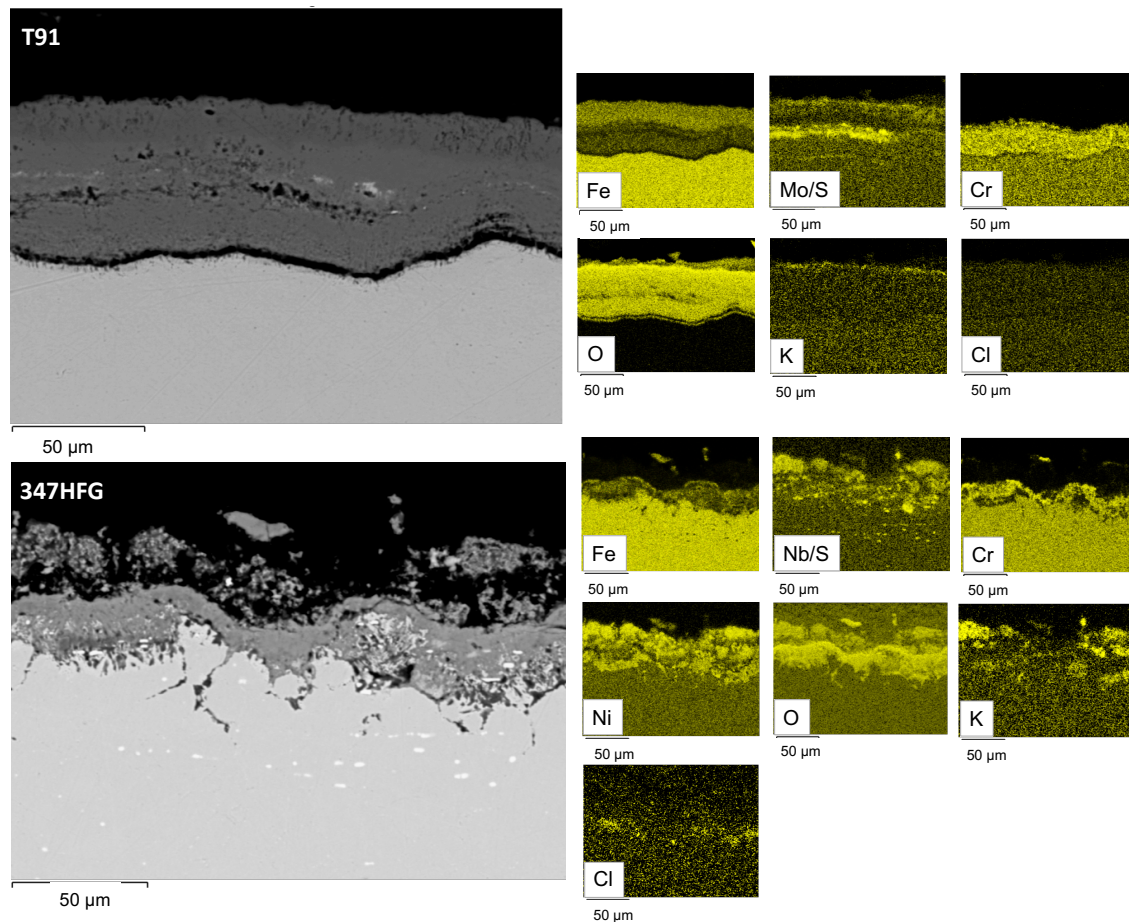


Figure 4-104: BSE/EDX images of T91 and 347HFG samples exposed for 500 hours to deposit D8 at flux 100 $\mu\text{m}/\text{cm}^2\text{h}$ APR test gas environment at 600°C

A similarly spread-out Cl attack at the metal/scale interface is encountered in 347HFG-D8 (**Figure 4-104**) as for sample 347HFG-D6 (**Figure 4-103**). Grain boundary chloride intrusions are less frequently observed compared to those of 347HFG-D1 (**Figure 4-102**). The Cr and Ni scales also feature porous structures; however, the Ni scale is comparably as thick as that of 347HFG-D6 (**Figure 4-103**). Grain boundary penetrations beneath these scales taper off into thinner cavities which may indicate a depletion of corrosive components been channeled through the metal structure.

4.3. Thermogravimetric analysis (TGA)

TGA analysis was carried out for each deposit in N₂ (see Section 3.4 for methodology). A blank TGA run was conducted to account for mass changes appearing as a result of the buoyancy effect (Figure 4-105). The mass loss profiles of the deposits D1-D8 are presented in Figure 4-106, Figure 4-107 and Figure 4-108.

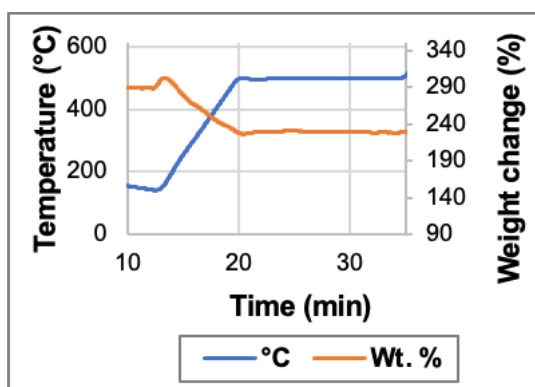


Figure 4-105: Blank TGA analysis run (no deposit). At zero minutes, weight change is 0% (not shown on graph). Bouyancy effect influences intial weight gain during heating

The mass change profiles of all samples show that most weight loss occurs at the initial heating stages. The mass loss at the first 15 mins occurs at temperature conditions which may favour water evaporation (temperature ramped up and held at 105°C for 5 minutes). Moisture loss at this initial heating stage (0-15 mins) suggests that initial salt drying on a hot plate prior to analysis did not thoroughly dry out the samples. The amount of moisture loss (mass loss) occurring during dehydration phase also varied across samples as the initial water contents of the slurries were non-specific, which meant that various levels of moisture were present in each sample to begin with. As such, the vaporisation phase for the mass loss tests differs across the samples.

The second mass change peaks, correspond with the second temperature ramp, prior to attaining a steady test temperature. A similar mass change profile was observed for the blank TGA run (empty sample pan used) (**Figure 4-105**). Also, for the blank run, the mass measurement exceeded the original mass, set at 100 wt.%. The increased weight may be indicative of a buoyancy effect occurring during both temperature ramping. For the deposit analysis, as moisture has been removed from the salts during the first stage ramping, the mass loss may negate buoyancy mass gain observed on the no-deposit run. Most informative to these analyses however are the mass change profiles occurring at the target test temperatures. At isothermal conditions, such as in **Figure 4-109**, minimal mass change is detected, as such mass changes occurring for the samples were compared on a % weight change (based on the initial sample mass at test temperature). Also, ~5 minutes allowance was given for the stabilisation of mass change measurements, following the second stage temperature ramping, to avoid using the weight change measurements which were influenced by buoyancy. The weight loss profiles of the deposits at targeted test temperatures are discussed in **Section 5.2**.

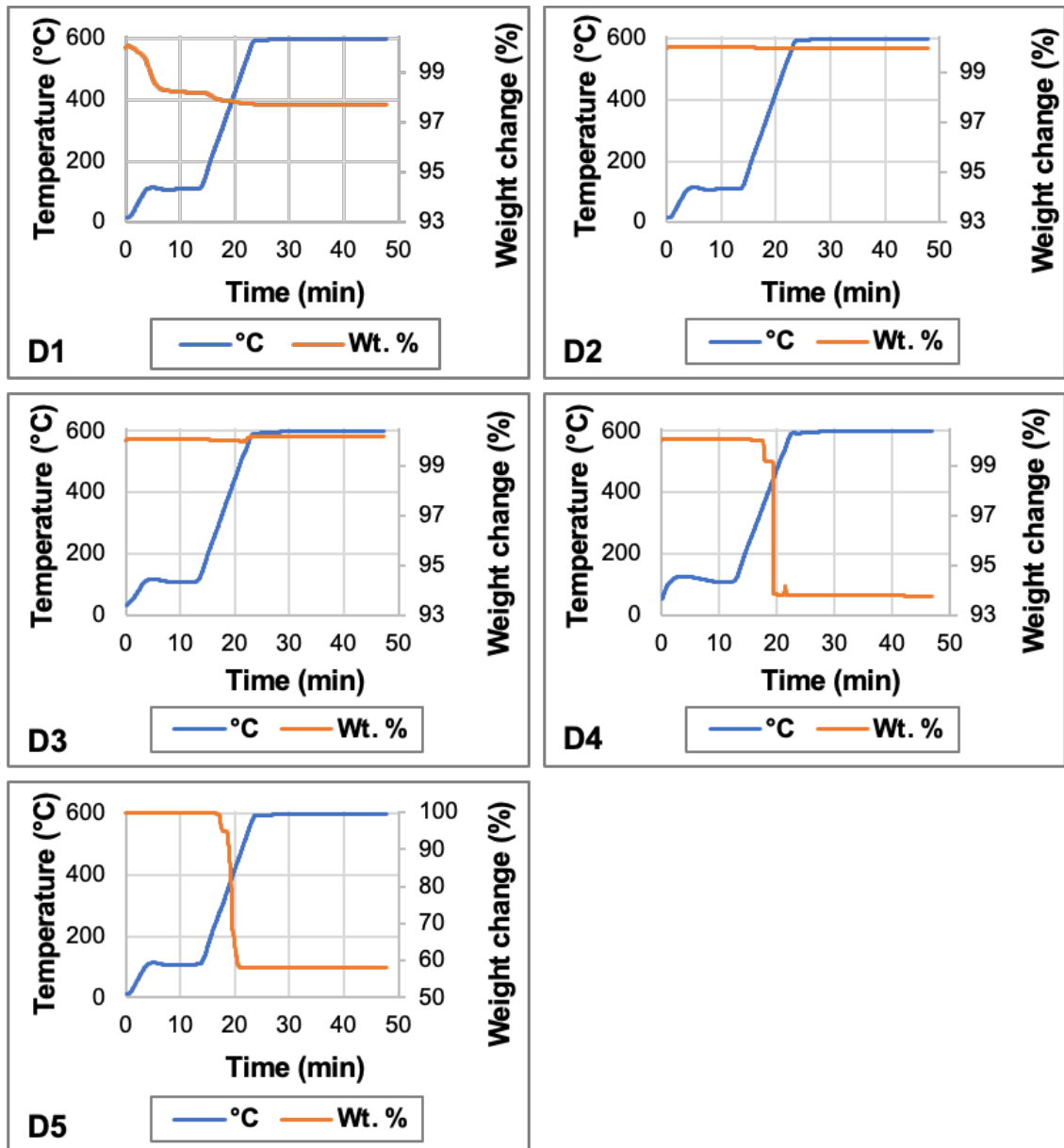


Figure 4-106: Mass change experimental data conducted for deposits D1, D2, D3, D4 & D5 (WWF deposits) by TGA analysis

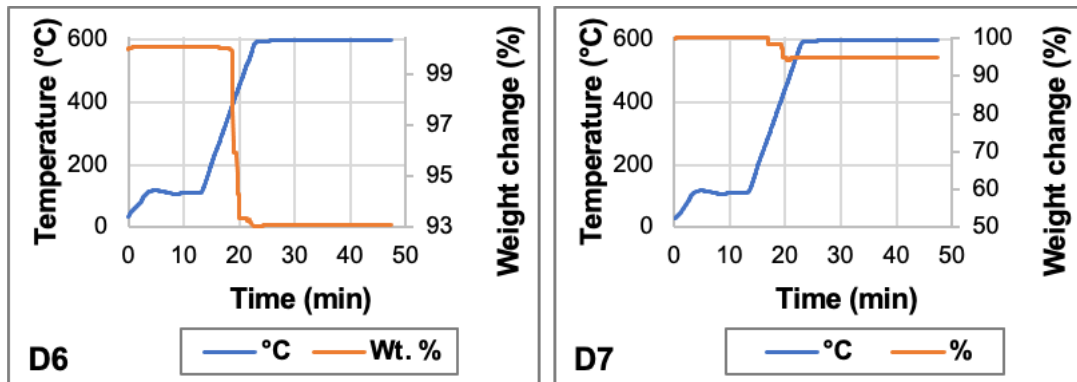


Figure 4-107: Mass change experimental data conducted for deposits D6 & D7 (HGB deposits) by TGA analysis

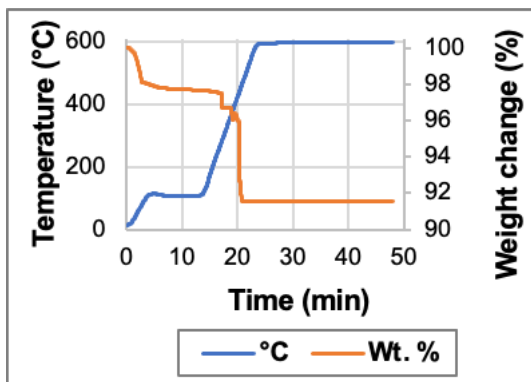


Figure 4-108: Mass change experimental data conducted for deposits D8 (APR deposits) by TGA analysis

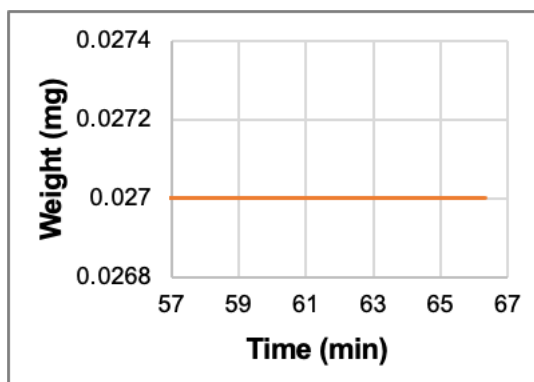


Figure 4-109: Blank TGA analysis run (no deposit) at 600°C

4.4. Heat flux furnace corrosion test

The metal and sound metal changes occurring for the T91 probe sample exposed in WWF test gas to deposit D6 ($100 \mu\text{g}/\text{cm}^2\text{h}$) at 600°C for 500 hours is presented in **Figure 4-110**. Metal changes are measured over $230\text{--}320 \mu\text{m}$ around the sample with median metal loss value at $270 \mu\text{m}$. Negligible sound metal penetration is observed for this sample.

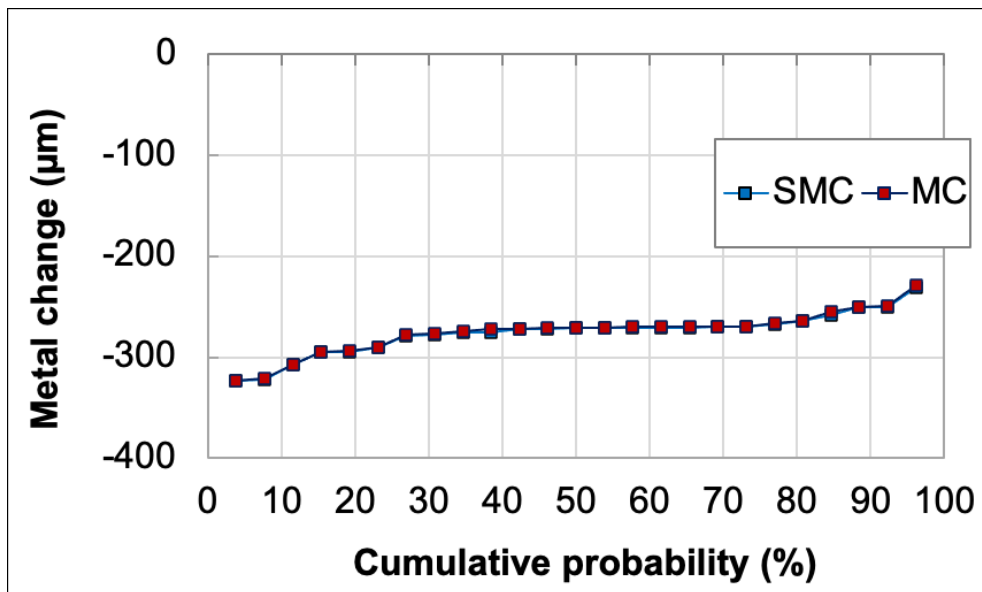


Figure 4-110: Metal change (MC) and sound metal change (SMC) plots for T91 with deposit D6 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ exposed for 500 hours in WWF test gas at 600°C . MC and SMC plots are superimposed

5 Discussions

This chapter qualitatively and quantitatively describes the fireside corrosion behaviours of biomass/waste fuel categories. It discusses the combustion chemical species released from the fuels, relating these species to fireside corrosion. Also, the corrosion influences of deposits, whose compositions were derived from thermodynamic calculations (by MTDData), are discussed.

5.1 Investigation of how biomass/waste fuel categories element distributions and combustion release behaviours differ

In this section, the chemical variations occurring within each fuel group are described. The main focus is on elements whose presence can potentially influence the compositions of corrosive deposits condensing on HX surfaces.

A wider range of elemental values exists within the APR and HGB categories compared to those of WWF and IFW (**Figure 4-2** to **Figure 4-5**). This may be as a result of larger quantities of data being gathered for the former fuel categories, however, this also representative of the variations in the categories (based on availabilities). Moisture and ash content are less varied within the WWF category (**Figure 4-5**), though a wide range of element values occur between its mean (1.02 wt.%) and median (0.07 wt.%) contents for S and Cl (mean, 1.08 wt.%; median, 0.08 wt.%).

The varying S and Cl levels within the HGB, APR and WWF categories may increase the challenges in describing the fuel categories' corrosive impact within the categories as both elements play key roles in fireside corrosion [115], [131] (**Section 2.5.3**). It becomes important, therefore, to evaluate the corrosion impacts of S and Cl at varying element concentrations (**Section 5.2.2.1**). As described in **Section 3.2.1**, this was achieved by, first, feeding varying elemental values into thermodynamic calculations and comparing trends in the resulting post-combustion species. Secondly, the fireside corrosion impact of the different post-combustion species was evaluated by corrosion testing. This enabled investigation of fireside corrosion trends occurring within the fuel categories. The

element distributions and post-combustion species' compositions occurring within each fuel category are thus discussed further in **Section 5.1.1** and **Section 5.1.2**.

5.1.1 Minor element distributions

The minor elements' distributions within fuel categories are distinctive (**Figure 4-7**). For example, the APR and HGB fuel categories show similarities in their Al contents (~ 0.02 mol./kg), which is noted for its involvement in the formation of high temperature stable complexes with alkali metals [94] as observed in **Table 4-2**. This may increase the solid phase fraction which results in lower corrosion exposures. Lower K and Na values however, which may form molten salts at HX temperatures ranges (450-600°C) [121], exist for the APR category, as shown in **Figure 4-7**. Finally, the Si content in fuels is of particular importance in the formation of complexes which may influence the availability/state of alkali metal species in the flue gas (EUBCE conference paper, **Appendix F**).

5.1.1.1 Alkali metal components in the gas phase

Though typically applied for estimating the bottom sag tendencies of fuel ash [96], [162], fuel K/Si ratios may be used to investigate K-release potential during fuel combustion [96] (**Section 4.1.2.1**). The higher the ratio, the lower the fuel K-fraction which may be retained in high melting point (relative to metal temperatures) silicates. The median fuel categories' K/Si ratios of the fuels were discussed in the EUBCE conference paper (documented in **Appendix F**) which investigates the alkali metal combustion release behaviours of the four fuel groups, analysed by thermodynamic simulations.

According to index predictions, higher K-release fraction for HGB is expected when compared to APR:

APR (K/Si index, 0.23) < HGB (K/Si index, 1.95)

However, the above K/Si index ranking is contrary to what thermodynamic simulations may suggest. **Figure 4-9** ranks the K-release fraction predicted by MTData at 1100°C as:

HGB (40 mol.% K release) < APR (70 mo.% K release)

As Ca and Mg may also form temperature stable Si-complexes [96], [162] (**Table 4-2**), both elements can be expected to influence K-release. The alkaline earth metal fuel contents of HGB (Ca, 9750 mg/kg; Mg 1800 mg/kg) are higher than those of APR (Ca, 2400 mg/kg; Mg 1400 mg/kg). As such, it is expected that there would be less available Si (in the case of HGB) for the retention of the alkali metals in higher melting point Si-complexes. However, MTData calculations reveal K-P associations (K_3PO_4 , m.pt., 1380°C) (m.pt is an abbreviation for melting point) also occur for these P-rich fuels (HGB). The K/Si index addresses silicates only, which are not the only compound types which influence the stability of alkali metal species. The use of this index should thus be treated with caution.

The condensable phase alkali metal species, listed in **Table 4-2**, indicate a higher preference for Na-Si complex formation (compared to K-Si complex formation) for the APR and HGB fuel categories. A Na-release prediction ratio, which can be simplified as Na/Si, ranks Na-release for APR and HGB categories in the same order as that calculated by MTData (**Figure 4-10**):

APR: 0 mol.% Na-release at 1100°C (MTData), 0.05 mole ratio (Na/Si index)

HGB: 29 mol.% Na-release at 1100°C (MTData), 0.13 mole ratio (Na/Si index)

More detailed analysis of thermodynamic data, however, suggests that within the HGB category, the Na species in the gas phase at 1100°C (**Figure 4-11**) cools to form both solid and molten compounds at the metal HX temperature range. This contrasts with K, where gas phase condensates, KCl

and/or K_2SO_4 , form only molten compounds within metal surface temperature ranges. While molten components can facilitate fireside corrosion, solid phase components may be relatively inactive.

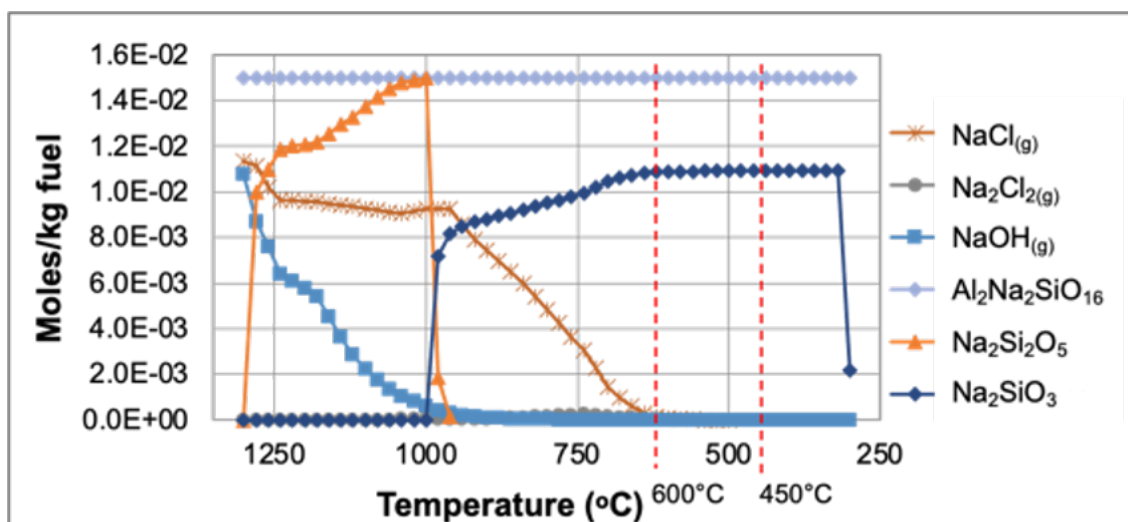


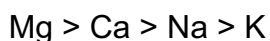
Figure 5-1: Na associations ($>10^{-4}$ mol./kg) at 1100°C HGB combustion temperature conditions. Temperature (x-axis) is scaled in decreasing order with condensation

The associations of Na across the cooling HGB combustion gas temperature gradient, as simulated by MTDData, are presented in **Figure 5-1**. The reduction of NaCl and NaOH gas concentrations correspond with the change in oxidation state of the Na-silicate, which does not to dissociate below 1250°C. Within the HX temperature range (450-600°C), Na is retained as stable Na-silicate compounds (m.pt. $>1100^{\circ}\text{C}$ [163]) and the formation of Na salts is not favoured. As such, the alkali metal species gas/condensed phase partitioning may not always be sufficient for predicting salt formation. The substitution of compound groups during condensation may influence the condensed phase composition (**Figure 5-1**) There will also be kinetics effects where components are not given adequate time to form.

The WWF post-combustion species data calculated by MTDData also indicate Na-Si complexes may form. For the low-level Si fuel, WWF (3000 mg/kg median Si value, **Figure 4-7**), no K-Si associations are thermodynamically

predicted. By 1100°C, 100 mol.% K-release is in gas phase (**Figure 4-9**). Mg (509 mg/kg) and Ca (3346 mg/kg) also compete for Si in the formation of Si-complexes (**Table 4.2**).

According to the reactivity series, the preference for silicate formation decreases as:



Where K is the most active of the elements and least likely to form silicates

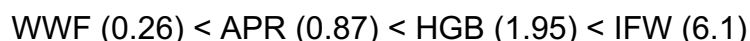
The relatively low Si component of WWF allows a higher gas phase release fraction of the alkali components, compared to the APR and HGB fuel categories. As the chemical activities of the elements reduce, the total moles of their salts (sulphates and chlorides, **Table 4-2**) formed during combustion decrease. For e.g., WWF:



In summary, the higher the element's chemical activity, the higher the salt forming ability. As such, the lower the chemical activity, the better the correlation between thermodynamic (MTData) and index (element/Si, for Mg, Ca, Na & K) predictions of volatile release predictions.

The K level of IFW is comparatively high, second to the HGB fuel category (**Figure 4-7**). Na level is negligible for this category (>0.4g/kg), a natural occurrence and requirement for foods [164], which may be beneficial for K-Si formation. The category also shows relatively low Mg values (**Figure 4-7**, Mg, 1100 mg/kg), thus there are fewer moles of Mg-Si complexes formed, relative to the other categories. The formation of K-Si is, however, limited by the significantly low Si fuel content (1200 mg/kg). The K/Si ratio (6.1) is thus high.

Overall, the K/Si mole ratios for the fuel categories increase as:



By contrast the thermodynamic predictions suggest an increase in K-release fraction as such (at 1100°C, **Figure 4.9**):

HGB (41 mol.%) < APR (71 mol.%) < IFW (91 mol.%) < WWF (100 mol.%)

While conducting single particle combustion experiments and atomic emission spectrometry, Clery et al. [72] found wood ranked highest for combustion K-release fraction (at 550°C) amongst the fuels investigated, as such:

Olive residue (APR, 40 mol.%) < wheat straw (HGB, 50 mol.%) < softwood (virgin wood, 80 mol.%)

Both Clery's work and the MTData investigations in this work suggest woods in general have high K-release potentials. Clery nevertheless recorded 0-30 mol.% K-release from wood combustion when a Si additive was in excess, explaining that the K-release fraction from wood combustion is strongly influenced by its Si level.

The IFW category has not been included in the following ranking as the fuel category's Na content is negligible. The Na/Si mole ratios for the fuel categories increase as:

APR (0.05) < HGB (0.13) < WWF (0.22)

While the thermodynamic prediction suggests an increase in Na-release fraction as such (at 1100°C, **Figure 4-10**):

APR (<1 mol.%) < HGB (29 mol.%) < WWF (52 mol.%)

Na/Si ranking thus corresponds with thermodynamically calculated combustion Na-release ranking. Thermodynamic predictions of element associations, which influence their release patterns, consider the influence of all components of the reaction which may not be simplified by silicate behaviours alone. Thermodynamic simulations confirm a preference for Na-Si associations compared to K-Si associations. K-release will therefore be subjected to more

complex interdependencies within the post-combustion development of species, more so, where other elements capable of forming high temperature, stable compounds, such as P, react with K [162] (as illustrated in **Table 4-2**).

5.1.1.2 Condensed phase compound distributions

Also important for understanding their fireside corrosion impact particularities is the chemical distribution of the condensed phase generated. Assuming equal condensate deposition rates, the IFW and HGB categories show the largest and smallest condensed phase alkali metal salt fractions (**Figure 5-2**). The condensed phase molar quantities for each category per kg of fuel, as predicted by MTData, are presented in **Figure 5-3**.

The HGB fuel category have a higher alkali metal salt molar output per kg fuel compared to WWF and IFW (**Figure 5-3**); but its high phosphate content (**Figure 5-2**) will favour K-retention. High P levels may also signify a major difference between APR and HGB fuel categories, considering the element's role in K-release. Though the molar combustion release outputs for the latter fuel may be close to double that of APR (**Figure 5-3**), the K chloride and sulphate fractions are considerably lower for HGB (higher K-P associations).

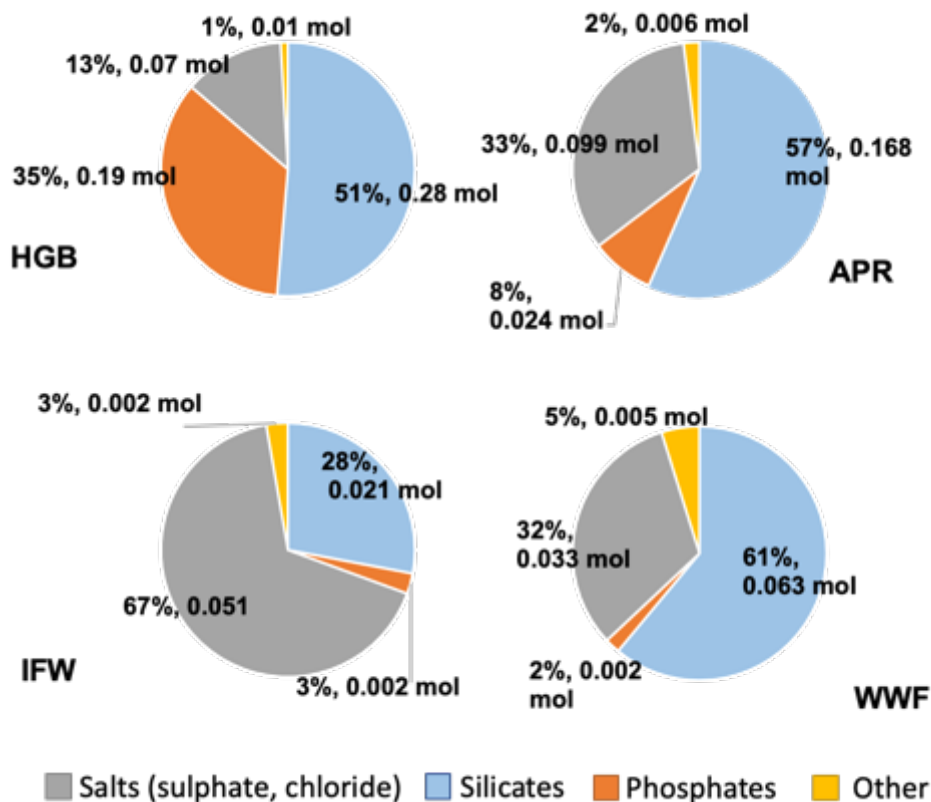


Figure 5-2: Post-combustion condensed phase fractions, by association, simulated by MTData at 600°C

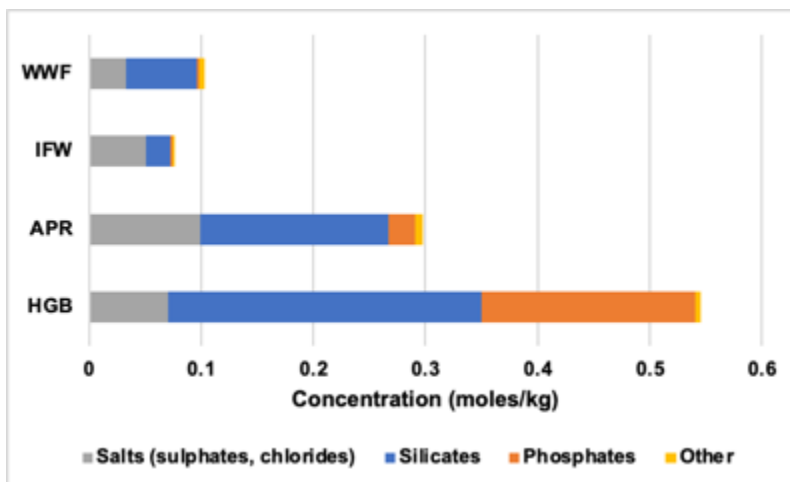


Figure 5-3: Condensed phase moles output at 600°C by association. Thermodynamic simulation based on category median ar values of 14 elements

5.1.1.3 Condensed phase alkali metal salt compositions

The condensed phase of fuel combustion species can damage HXs. The method adapted for distinguishing between solids and molten phase components calculated by MTDData (at applicable HX temperature range) has been described in **Section 3.2.3**, which distinguishes the KCP compounds as being of particular concern to fireside corrosion [98], [136].

Figure 4-13 demonstrates the variations of KCP compositions with temperature within the fuel categories. HGB and APR show similarities in their salt compositions: their KCP compounds are KCl and K_2SO_4 and their concentrations are relatively stable across HX surface temperature range. Several salt types are encountered in WWF firing conditions (a mixture of K, Na and Ca chlorides and sulphates). These salts also experience stoichiometric variations within 450-600°C; meaning the KCP compounds differ by type and concentration. These variations increase difficulties in investigating the fireside corrosion behaviour of the WWF category as corrosion mechanisms will vary more significantly within the temperature range compared to trends for the APR and HGB fuel categories.

The KCl condensation flux is of particular interest to this study, being a dominant KCP amongst the fuels and being notorious for its fireside corrosion role in biomass firing [99], [115], [165]. The fluctuating KCP compositions for WWF involve changes in KCl concentrations. The KCP concentrations within this section are reported from high to low temperatures, as condensation occurs.

From **Figure 5-4**, the KCl molten temperature for each fuel category varies differently. The highest temperature at which KCl condensate exists may define the temperature region at which the condensed phase KCl molten fraction peaks. At this temperature, the solid phase fraction is lowest or non-existent and above this temperature, KCl is completely in gas phase. As such, at this temperature, denoted as ' T_{cf} ', the first condensed phase transition from higher (gas) to lower (condensate) temperature, occurs.

From **Figure 5-4**, T_{cf} reduces across the fuel categories as:

$$\text{HGB} > \text{APR} > \text{IFW} > \text{WWF}$$

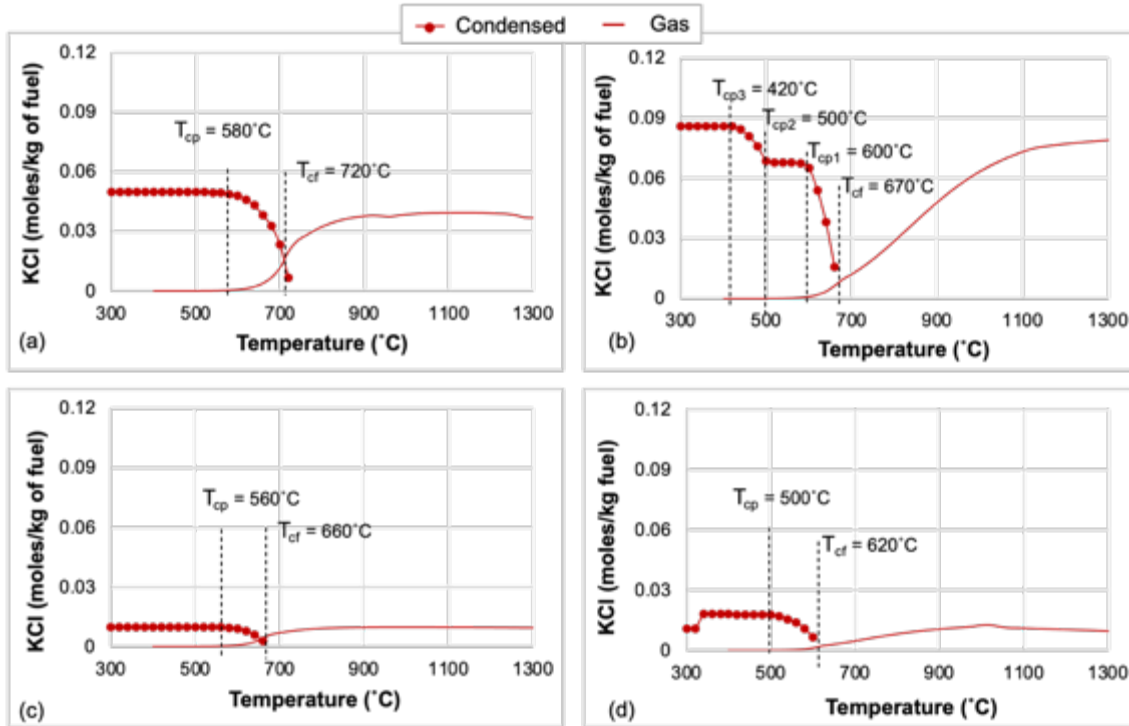


Figure 5-4: KCl condensed phase temperature-concentration profiles for fuel categories (a) HGB, (b) APR, (c) IFW and (d) WWF

' T_{cp} ', in **Figure 5-4**, denotes the highest temperature corresponding to the peak condensed KCl concentration. At metal temperature $T < T_{cp}$, the KCP compound is expected to be predominantly solid as observed from the steady concentration profile. When $T > T_{cp}$ but $T < T_{cf}$ (i.e., within the temperature range between T_{cf} and T_{cp} , **Figure 5-4**), the KCP component exists as a combination of solid and liquid phase, indicating a critical temperature window, ' T_{cw} ', where the highest molten fraction of KCl (and other KCP) will exist. As such, the wider the T_{cw} interval of a fuel group, the more challenging it will be to avoid its peak molten KCl temperature.

T_{cw} intervals specify the range of temperatures at which the molten phase of KCl exists. It reduces as:

$$\text{APR (250}^{\circ}\text{C)} > \text{HGB (140}^{\circ}\text{C)} > \text{WWF (120}^{\circ}\text{C)} > \text{IFW (100}^{\circ}\text{C)}$$

A much larger molten KCl window exists for the APR fuel category for which two KCl T_{cw} are observed: (i) within $T_{\text{cp1}} - T_{\text{cf1}}$ and (ii) within $T_{\text{cp2}} - T_{\text{cf2}}$. Between both windows, a steady molten fraction, less sensitive to temperature changes within 500-600°C may exist.

The KCl critical melt windows of fuels has not been previously investigated. Rather, much focus is on the deposits' FMT [33], [120], [121] (see **Section 2.5.1**) which may be related to the T_{cp} . As running metal temperatures below the T_{cp} to avoid KCl melts has a compromise on operational efficiency (**Section 2.5.1**), power plants are willing to compromise on acceptable metal loss rates while operating at temperatures higher than FMT [24]. Additives such as sulphates and silicates have also been applied to fuel feeds [35], [72], [145] which, in effect, push the FMT towards higher temperature ranges by restricting the formation of alkali-metal chlorides which exhibit comparatively lower melt temperatures than the chlorides.

Standard biomass plant HX temperature ranges (~450-600°C) do, however, fall within the deposit melt temperature regions for each fuel category (**Figure 5-4**). Even where additives are employed, further mitigating KCl attack may be improved where plants operate at metal surface temperatures avoiding peak KCl molten ranges. Such temperatures may, however, not be limited to below melting points, but possibly temperatures at which gas phase chlorides are predominant, and corrosion influences may be slightly lower. The gas components have less residual corrosive reaction time than their molten form, though a challenge may be where gaseous chlorides condense on cooler metal surface further up the flue current stream in combustion sites. Mechanical designs considerations, such as (for example) blowers, which can redirect flue gas components condensing, are beyond the scope of this work.

The approach to minimise HX damage (by working above peak KCl molten temperatures) may also be more suitable for the short range T_{cw} fuel groups such

as WWF and IFW. However, the wider the KCl T_{cw} and the higher the T_{cf} , the more impractical it becomes; avoiding peak corrosion temperature windows without permitting the formation of other molten components (e.g. sulphates [98]) which may otherwise have been less active at the KCl T_{cw} . The fireside corrosion severity at currently employed metal temperature ranges needs to be compared with corrosion rates at an optimised temperature where KCl is predominantly gas but at a low enough temperature to avoid severe melting of other potentially corrosive deposit components.

5.1.2 Trace element distributions

The other fuel groups have relatively low trace element contents (**Figure 4-8, Table A-8**) compared to the WWF category. Cr and Zn altered the KCP composition for WWF, as illustrated in **Table 4-5**, though neither element formed compounds melting within T_{cw} . Changing KCP compositions and/or quantities, however, may alter corrosion mechanisms. The role of the trace elements in WWF were thus seen to be indirect as the compounds they form, post-combustion, are more likely to be retained as solids which may be inert to metal scales. The corresponding KCP compositions for the 15ES simulations employing Cr and Zn (**Table 4-5**) were employed as corrosive test deposits, to investigate the indirect corrosion influence of Cr and Zn contaminants in WWF (**Section 5.2.2.2**).

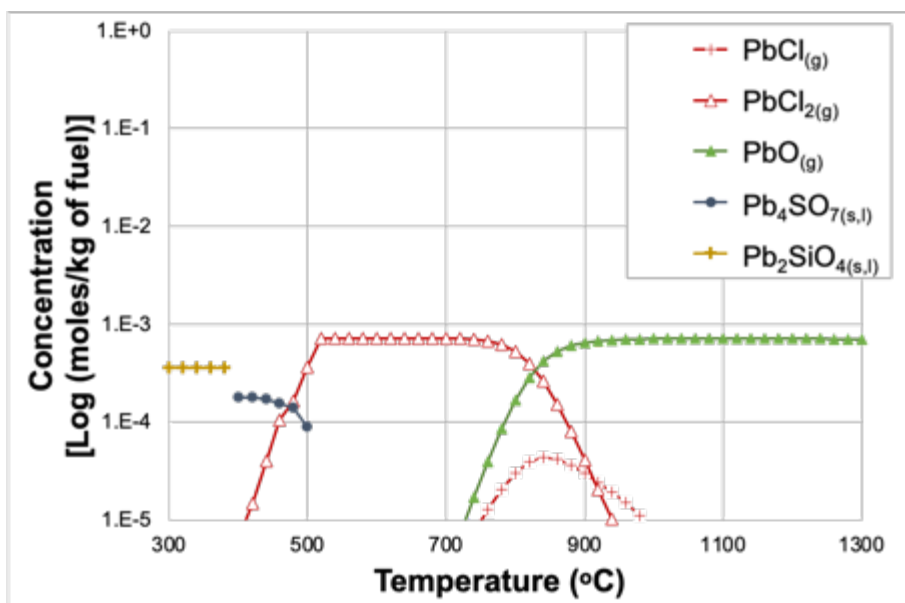


Figure 5-5: Pb post-combustion associations for WWF, determined by MTDData thermodynamic simulation

Pb sulphate within the WWF KCP composition was not investigated for corrosion effects as the safety requirements regulating working with Pb based compounds would have significantly impacted the corrosion analysis timeline for this PhD. In addition to laboratory testing safety concerns, combustion power plants would need to avoid the use of fuels with lead contamination to comply with regulations for lead emissions [56]. Weighed against the PhD objectives, it was decided that a detailed description of fireside corrosion peculiarities could be delivered, focussing on other element trends.

5.1.3 Summary

Thermodynamic simulations have been found useful for identifying the potentially corrosive fractions of post-combustion condensates particular to each fuel category. Variations of post-combustion condensate compositions between the fuel categories have been linked to their fuel analysis data. Si, P and alkaline earth metals play a major role in the corrosive releases associated with fuel combustion.

Thermodynamic data show that molten KCl temperature ranges of deposits differ for each fuel category. Below and above this temperature region, KCl is predominantly in solid phase and gas phase respectively. As such, HX surface temperatures which fall outside the molten phase may experience lesser extents of enhanced K assisted chloride attack. Because such temperature ranges differ for the fuel groups, and likely within fuel groups, it may be beneficial to perform pre-analysis of chloride phases for fuels, such as achieved by thermodynamic simulations employed in this research work. Such analysis may give first-hand information on HX temperature conditions to monitor, noting that such temperatures can be as low as (for example) 420°C, as predicted for the APR fuels. By 500-600°C however, condensed phase chlorides in gas phase may be lower (**Figure 5-4**).

Though the addition of additives to combustion fuels alleviates corrosion damage to notable extents [20], there may be more room for the optimization of target HX surface temperature ranges. Such optimisations will need to consider corrosion damage rates elevated by sulphate as well as NaCl (also predicted to be condensing species, **Figure 4-13**) which tend to melt at higher temperatures than KCl.

A limitation to the use of thermodynamic modelling to determine key molten temperatures of fuel groups is the sensitivity of the calculations to varying concentrations of fuel S and Cl content. This means that, for large fuel groups, where wider element concentration ranges exist, different melt profiles may be present. Such ranges in melt temperatures are also expected under trace element influences.

The quantities of Zn and Cr have been found to be high enough to indirectly influence changes in the compositions of the potentially corrosive components formed during WWF firing, without themselves forming molten deposits at HX temperature range. This is not to say that other trace elements (<1000 mg/kg fuel) do not directly impact corrosion trends. Indeed, thermodynamic simulations suggest Pb may occur as molten sulphates/chlorides at HX temperature conditions. However, the associations of these elements will

determine how they exist in combustion flue gas conditions and their concentrations in the fuel feed will determine how significant their fireside corrosion impact (if direct) may be.

Thermodynamic predictions show that most trace elements evaluated in this study are likely to form solid phase components at HX temperatures conditions for biomass firing. The main challenge however lies where the higher concentration alkali metal salts, established as fireside corrosion influencers [46], [54], [90], have their compositions altered in the presence of the trace elements. Past research, however, has primarily focused on the direct impact of these trace element compounds on fireside corrosion [14], [141], [146], whereas, the changes to the corrosive environment driven by changes to the alkali metal salt compositions may have larger impact.

The resulting stoichiometric shift in alkali salts' compositions is not limited to trace elements only. Indeed, results have shown that varying levels of minor and major elements in biomass fuels impact their alkali metal salt associations. It is thus important to place more emphasis on the fireside corrosion influences that these elements may indirectly impose.

Due to the characteristically high moisture contents of the collated IFW fuels, discussions were held, with this PhD's stakeholders, concerning combustion fuel usage projections (as given in **Appendix F**). These did not favour the continued evaluation of the fuel group due to energy expended drying the fuel and resulted in the decision to exclude the IFW fuel category from further investigations into fireside corrosion influences, thus allowing more time for corrosion studies of fuels more suitable for combustion.

5.2 Investigations into how biomass/waste post-combustion release deposits vary in their fireside corrosion impact

Metal damage data generated from the corrosion tests, for 347HFG and T91 exposed to synthetic deposits and test gas, are evaluated in this section. The potential influences of temperature and deposition flux variations on fireside corrosion damage are discussed. These evaluations are then applied to the assessments of HGB, WWF and APR fuel category fireside corrosion characteristics.

The discussions are separated into five sections. Experimental parameters are listed in **Table 5-1**.

- i.) **Comparison of corrosion behaviours of K (D6 & D8) and K-Na-Ca (D1) chloride/sulphate deposits (Section 5.2.1):** Tests were conducted at 600°C and deposition flux 100 µg/cm²hr.
- ii.) **Discussion of corrosive variations within K (D6 & D7) and K-Na (D1, D2, D3, D4 & D5) chloride/sulphate deposits (Section 5.2.2)**
Corrosion comparisons are made for two HGB deposits and five WWF deposits at 600°C and a deposition flux of 100 µg/cm²hr.
- iii.) **Discussion into temperature's influence on the corrosive behaviours of deposits (Section 5.2.3):** Corrosion test data generated at 500°C, 550°C and 600°C are evaluated for deposits D1 and D6.
- iv.) **Investigation of deposition flux effects on alloy damage (Section 5.2.4):** Corrosion trends from deposition flux variation are evaluated for alloy samples exposed to deposits D1 and D6.

- v.) **Investigation of the heat flux furnace corrosion test method (Section 5.2.5):** Comparisons made against the conventional isothermal furnace corrosion test method.

Table 5-1: Fireside corrosion test matrix and the related discussion sections within this chapter

Section	MTData simulation	Gas	Deposit	Temp. (°C)	Deposit flux (µg/cm ² hr)	Exposure (hours)
i	WWF 14ES	WWF	D1	600	100	200, 500, 1000
	HGB 14ES	HGB	D6			
	APR 14ES	APR	D8			
ii	WWF 14ES	WWF	D1	600	100	200, 500, 1000
	WWF 15ES (+Cr)		D2			
	WWF 14ES (Ca max)		D3			
	WWF 14ES (Na max)		D4			
	WWF 15ES (+Zn)		D5			
	HGB 14ES	HGB	D6			
	HGB 14ES (Cl mean)		D7			
iii	WWF 14ES	WWF	D1	600, 550,	100	200, 500, 1000
	HGB 14ES		D6	500		
iv	WWF 14ES	WWF	D1	600	100, 50,	500, 1000
	HGB 14ES		D6		25, 10	

5.2.1 Comparison of corrosion behaviours of K (D6 & D8) and K-Na-Ca (D1) chloride/sulphate deposits

Deposit formulations and gas compositions used to simulate the fuel categories are derived from thermodynamic calculations of anticipated post-combustion products, based on the median element values of the specific fuel

categories (**Section 5.1**). The fireside corrosion impact of the fuel categories' representative deposits (D1, D6 & D8, compositions listed in **Table 4-6**) on T91 and 347HFG at 600°C are discussed in this section.

In **Figure 5-6**, the metal damage trends are compared for T91 and 347HFG exposed with deposits D1, D6 and D8 in WWF, HGB and APR test gases respectively to simulate the 3 flue gas conditions. Median values are plotted with the metal change ranges representing extreme values for each (i.e., the highest and lowest metal change values on the cumulative probability plots presented in **Section 4.2**).

A progression model can be used to express corrosion rates over parameter trends. The ' R^2 ' values evaluate data points scatter around a fitted regression model line. Rates can thus be predicted more accurately by adjusting the regression line fit. A linear rate has been employed to compare the metal change rates and is expressed as:

$$y = Bx + C \quad \text{Equation 23}$$

Where ' y ' is metal change (μm), ' x ' is time (h), ' B ' is the coefficient (rate) and ' C ' is the intercept, which is typically at zero (metal change at time zero).

The best fits for linear progressive damage were achieved when the intercept was set at zero for T91. These samples were not at incubation phase of metal loss at 200 hours.

347HFG-D8, 347HFG-D6 and 347HFG-D1 remained within incubation phase by 200 hours (median metal loss $<20 \mu\text{m}$), so it is expected that a different equation would exist at the initial exposure time (different from another linear equation which would best describe the propagation corrosion stages of the samples). The linear equations explaining the propagation corrosion phases for the 347HFG samples were improved by forcing a positive intercept, as shown in **Figure 5-6**, to accommodate the effect of an initial incubation stage.

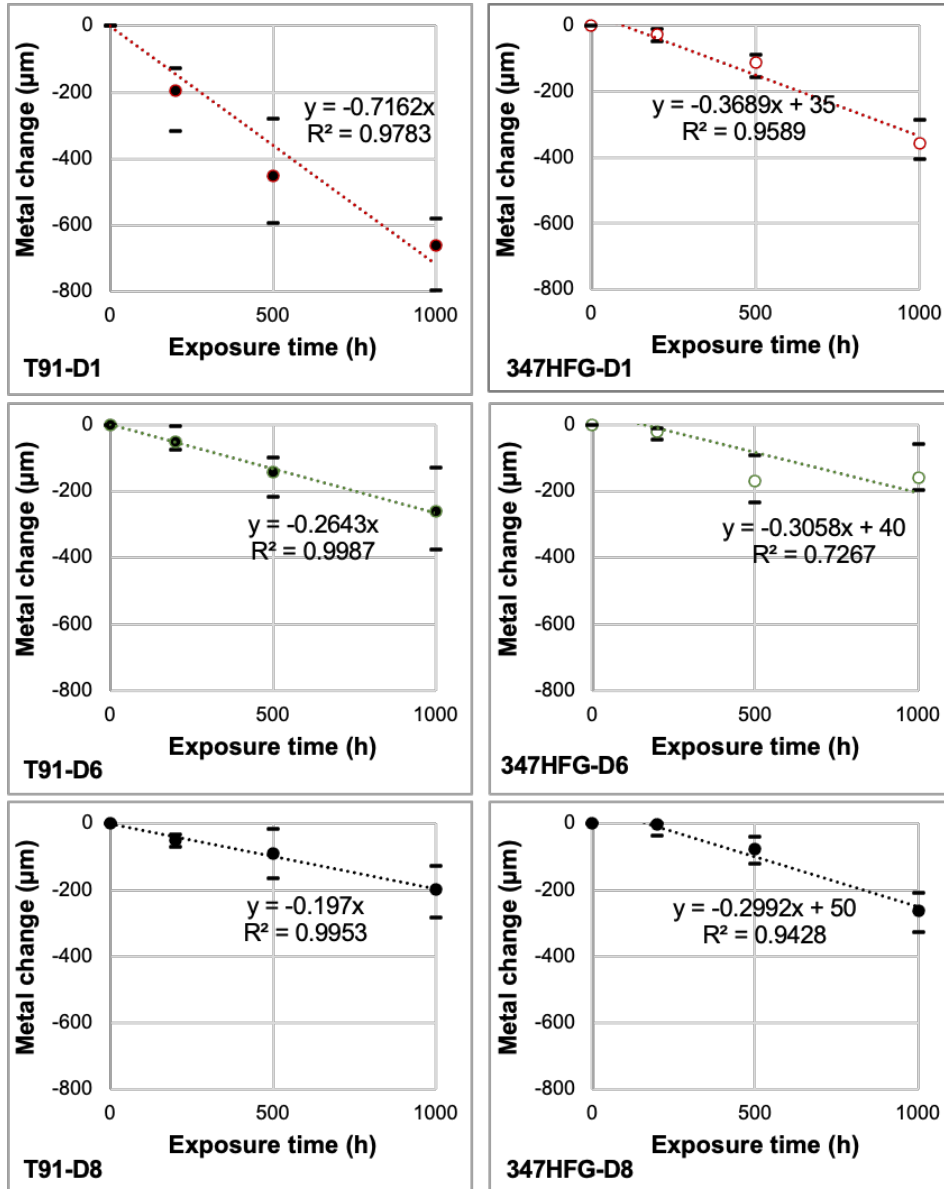


Figure 5-6: Median metal change trends of T91 and 347HFG samples exposed to D1, D6 and D8 in WWF, HGB and APR test gas respectively at 600C. Minimum and maximum metal loss are represented by error margins. Graphs show linear trendline equations

Initial incubation of 347HFG suggest metal loss onset may be explained by a parabolic law which has been employed for describing corrosion rates governed by an ion diffusion process through oxide films [119], [166]. The curve is thus influenced by parabolic scale growth, where corrosion rate diminishes with time as the scale thickness increases [119], [166]. At the higher exposure times for 347HFG, scales may have spalled from the metal surface, as the scale is a

non-protective growth. The metal oxidation rate becomes dominated by the deposits and gas reaction processes at the metal interface. Such a corrosion rate has a linear dependency on time as the scale ion diffusion is not the preponderating factor for metal attack.

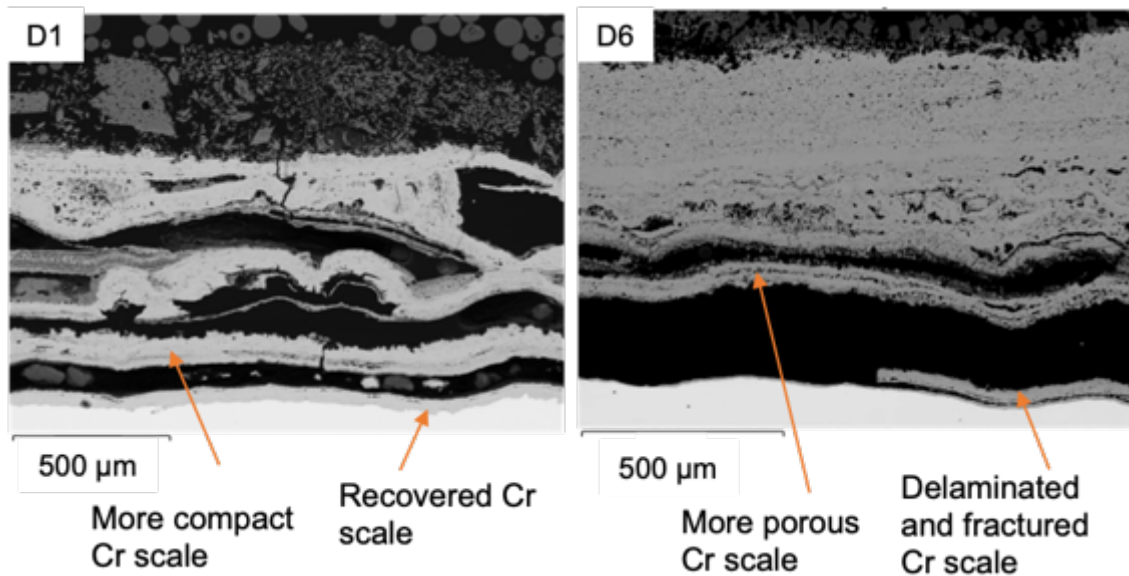


Figure 5-7: T91 steels exposed for 500 hours in HGB firing conditions. Regions of significant voids are more pronounced on the D6 exposed sample. Compositional notes informed by EDX (Figure 4-91 and Figure 4-92)

T91 samples scales were often delaminated from the metal surface, exposing the alloy to corrosion attack with minimal scale hindrances (**Figure 5-7**). As such, T91 attack was best described by linear corrosion rates from earliest exposure times for all samples. However, the scale damage and healing rates may be different for the deposit exposures as there appears to have been some improvement (recovery) of the Cr scale cover on the T91-D1 metal surface under HGB firing conditions (**Figure 5-7**).

By comparison of the corrosion rates (best fit equation coefficients, **Figure 5-6**), the deposit and gas influence on metal surface loss rates of T91 and 347HFG at 600°C increases as:

$$\mathbf{D8 < D6 < D1}$$

In APR, HGB & WWF test gas conditions respectively.

The comparison of the corrosivity of the deposits requires evaluation within the same test gas conditions. Under WWF test gas exposure, D1 also caused greater damage than D6 (D8 was not tested in WWF test gas). The cumulative probability plots measuring metal and sound metal changes of both alloys exposed to deposit D1 and D6 under WWF exposure conditions can be compared in **Figure 4-20**, **Figure 4-21**, **Figure 4-30** and **Figure 4-31** (Chapter 4).

Figure 4-96 and **Figure 4-97** show that, under higher flow rate conditions (APR test gas conditions), D6 remained more damaging (on both steels) than D8 as observed under WWF test gas conditions at 600°C, though to lesser extents. D1 was, however, less damaging than the other two deposits (D6 and D8). The order of corrosivity of high chloride deposits, D6 and D8, was thus less influenced by the gas environment than deposit D1.

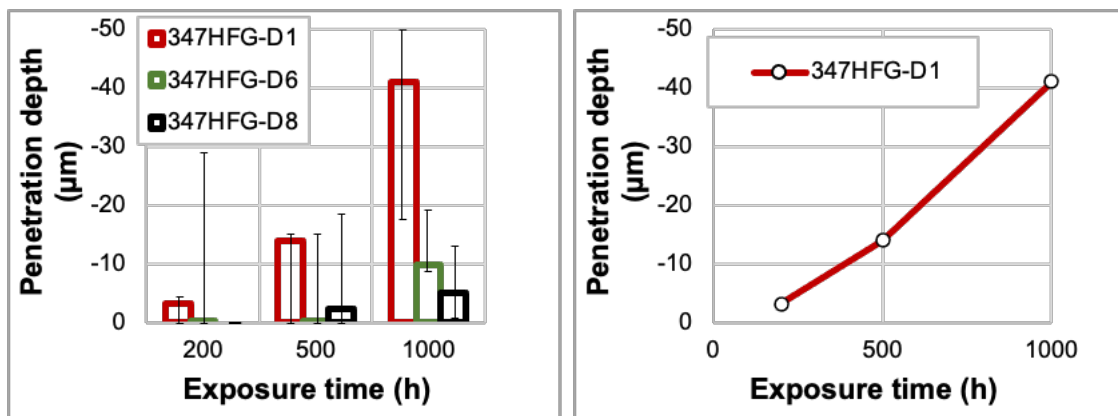


Figure 5-8: Median penetration depths of 347HFG with maximum and minimum values inclusive (left). Samples were exposed in APR test gas at 600°C. A high penetrative damage rate is observed for 347HFG-D1 (right)

In **Figure 5-8**, the penetration depth is less extensive for 347HFG-D6 and 347HFG-D8, compared to 347HFG-D1, in APR test gas. Penetrative depths influenced by these two deposits are also not significant by 500 hours (<3 μm). 347HFG-D1 however shows considerable penetrative damage at all exposure times.

By 1000 hours exposure, the deposit influence on the penetration depth of the austenitic steel samples increase as (**Figure 5-8**):

$$D8 < D6 < D1$$

In APR test gas conditions at 600°C

A similar order is observed for T91 in APR gas conditions, where the median penetration depth for T91-D1 (41 µm) is also greater than that occurring for T91-D6 and T91-D8 (~10 µm; **Section B.15**), following 1000 hours exposure (based on dimensional metrology median values).

The dimensional metrology method for the measurement of grain boundary intrusion depth into the austenitic steel samples have sometimes underestimated the sound metal damage extent when compared to SEM. The discrepancies may be related to the higher magnifications achievable by SEM evaluation, compared to the optical microscope employed for dimensional metrology. As sound metal damage can consist of miniscule vein-like features at their furthest depth, these regions are not always observable during dimensional metrology image captures.

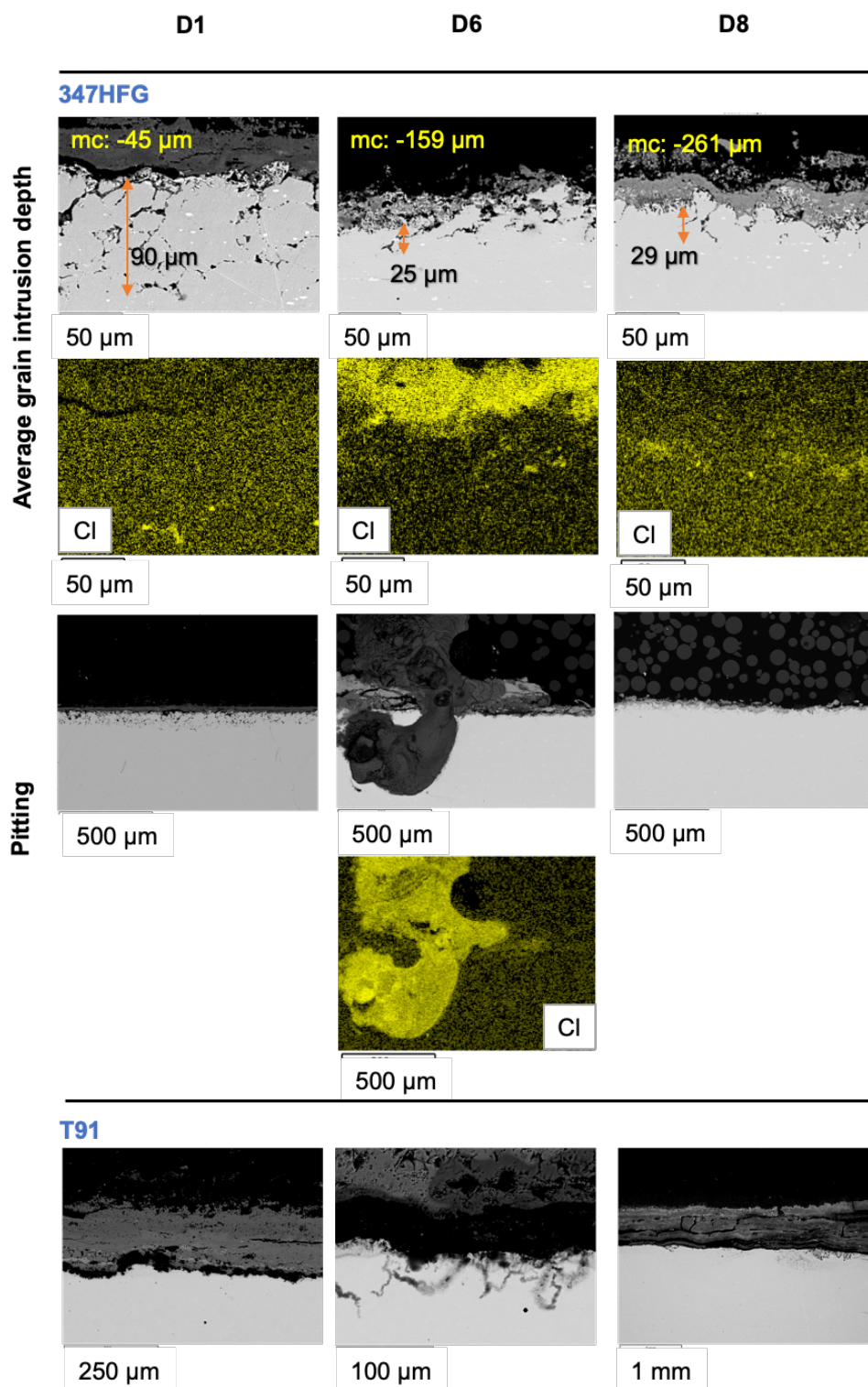


Figure 5-9: D1, D6 & D8 1000-hour exposure samples showing typical grain boundary damage (347HFG) and pit (T91 and 347HFG) views following exposure in APR test gas conditions at 600°C. *Mc (med): metal change, median value obtained from metal surface change dimensional metrology (Section B.15)

SEM images of the 1000-hour exposure 347HFG samples in **Figure 5-9**, taken at regions which represent the average damage features exhibited by the samples, confirm that D1 resulted in the greatest metal penetration amongst the three deposits in APR conditions. While grain boundary depletion is severe for 347HFG-D1, no pitting damage was detected on this sample by 1000 hours exposure, whereas significant pitting and greater metal surface loss were observed on 347HFG-D6 at 1000 hours (one pit region is shown in **Figure 5-9**).

The localised pit damage on 347HFG-D6 may be influenced by the high Cl content in D6, although, no pitting was encountered on 347HFG-D8 (which also has a high Cl content, **Table 4-6**). Metal loss was severe for 347HFG-D8, a likely explanation for lack of pitting on this sample could be the scale loss. The significant weight loss experienced by 347HFG-D8 (1000-hour exposure sample) at 400 hours (compared to the 500-hour sample at the same exposure time; see **Figure C-26**) suggests that indeed, scale spallation may have occurred. In this case, corrosive attack would be more evenly distributed across the metal surface than seen for a sample where scales remained intact (**Figure 5-9**) [167].

D8 demonstrates its ability to initiate pitting (as D6): at 500 hours (APR test gas exposure), pitting is encountered on both T91-D6 and T91-D8, whereas no pits were observed on T91-D1 (**Figure 5-9**). It can thus be agreed that there are differences in the corrosion damage types influenced by the K-cation high chloride deposit systems, D6 and D8, and the K/Na/Ca-cation low chloride deposit system, D1.

The following subsections focus on the descriptions of fireside corrosion mechanisms occurring under the same gas conditions to enable like-for-like comparisons of deposit induced metal damage. As such, the discussions in the subsections involve the deposit influences under HGB test gas conditions (comparing D1 and D6 corrosive behaviours), and APR test gas conditions (comparing D1, D6 and D8). Reference is also made to data from WWF test gas exposures.

5.2.1.1 KCl-K₂SO₄ deposit system corrosion mechanism of 347HFG and T91

This section discusses the KCl-K₂SO₄ deposit system's (D6 and D8) corrosion influence on 347HFG and T91 at 600 C.

5.2.1.1.1 Chloride transport in KCl-K₂SO₄ deposit system

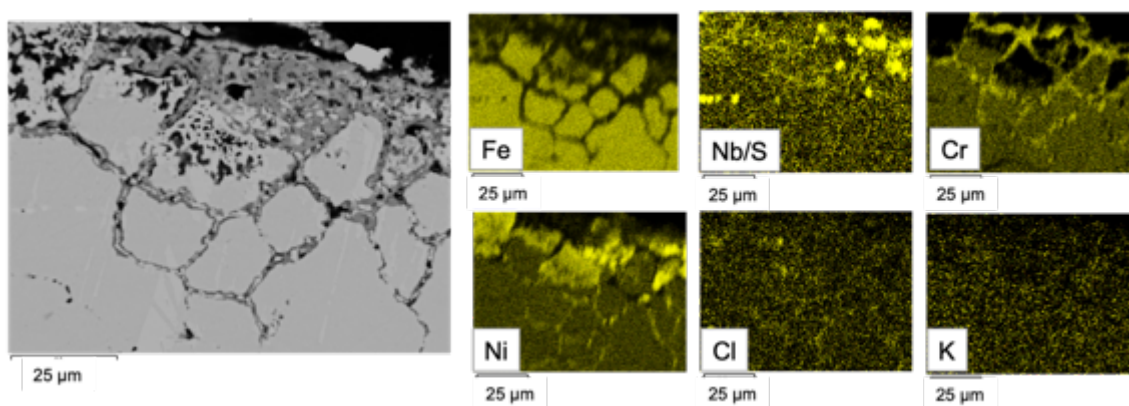


Figure 5-10: BSE/EDX images showing KCl-K₂SO₄ (D6) exposed 347HFG steel following 500 hours in HGB test gas conditions at 600°C

The corrosion damage observed for the KCl-K₂SO₄ deposit exposed 347HFG sample in **Figure 5-10** confirms Cl has migrated into the bulk metal. Individual deposit components' melting points (KCl, 774°C; and K₂SO₄, 1069°C) are, however, higher than the test temperature of 600°C. An explanation for this attack is that, in the initial stage of deposit attack, a KCl-K₂SO₄ eutectic may form, as described in the binary phase diagram in **Figure 5-11**. The binary system suggests eutectic melts of the deposit can occur at 690°C; this eutectic melt temperature still exceeds the test temperature. As such, other mixture will exist under D6 and D8 exposure conditions to promote chloride attack (**Figure 5-9**). Lower melting point compounds are known to form via interactions between the

deposit component and metal oxide scales Cr_2O_3 and Fe_2O_3 (the presence of metal oxide scale are confirmed in **Section 4.2**), as expressed in **Equation 24** and **Equation 25** [114]. These reactions will increase the chloride partial pressures at the reaction sites.

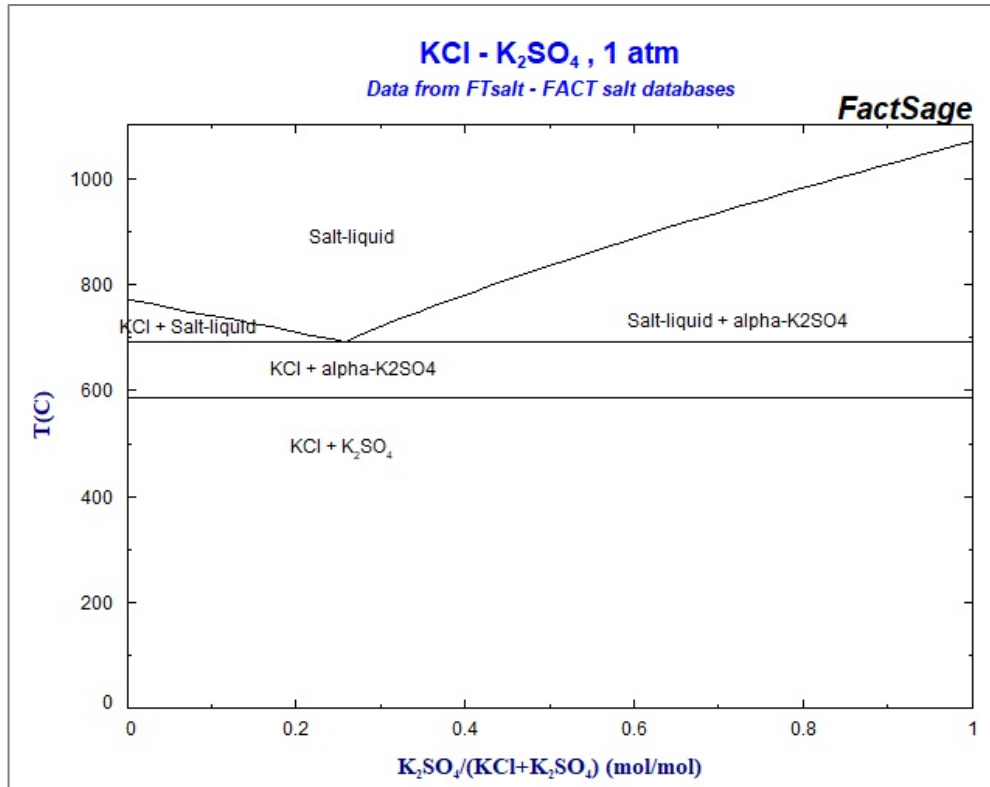
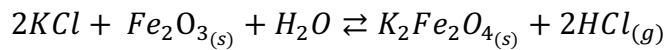
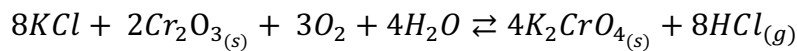


Figure 5-11: KCl-K₂SO₄ binary phase diagram [106]

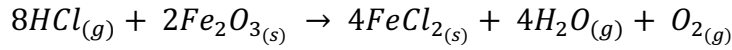


Equation 24

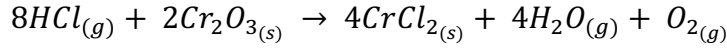


Equation 25

HCl may be released at a region of low oxygen potential, as it is expected that the oxygen partial pressure at this region would be reduced by the formation of the metal oxides. As such, the formation of thermodynamically stable FeCl_2 and CrCl_2 are favoured as described by **Equation 26** and **Equation 27**.



Equation 26



Equation 27

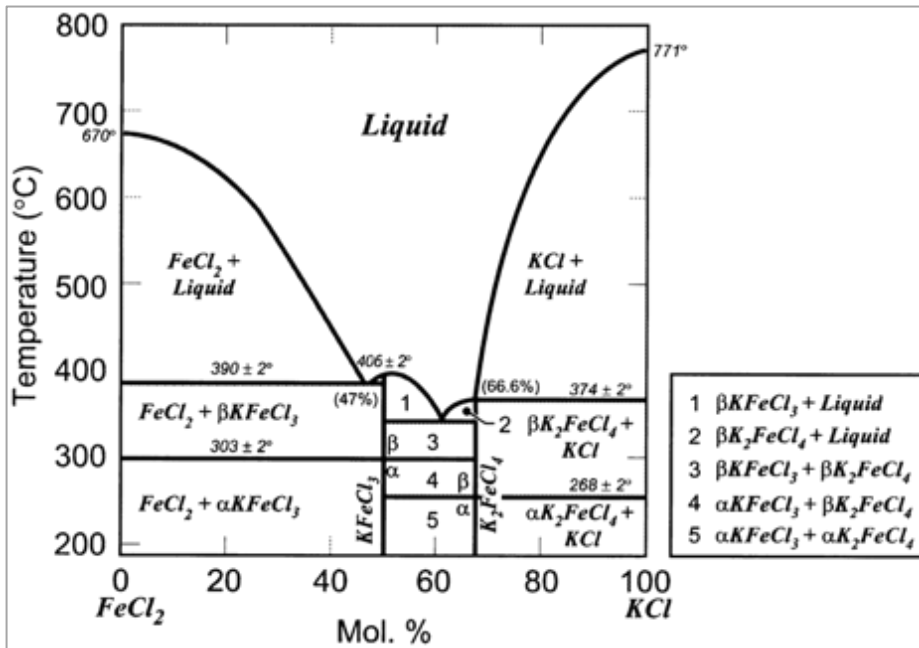
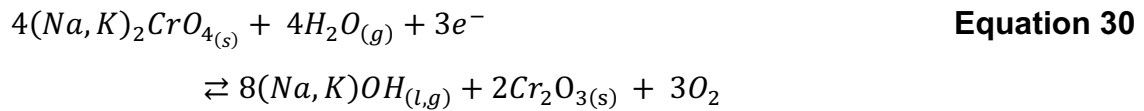
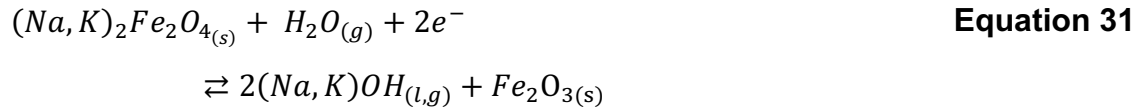


Figure 5-12: KCl-FeCl₂ binary phase diagram [107]

The pure metal chlorides CrCl₂ and FeCl₂ are also solids at 600°C [107], however, low eutectic melt temperature ranges are reached by the chloride interactions with KCl (462-475°C and 340-393°C respectively where >36 mol.% of the alkali metal is present) [107], [168]. The KCl-FeCl₂ binary phase diagram presented in **Figure 5-12** demonstrates eutectic melt temperatures, occurring well below the test temperature of 600°C for alkali metal chloride scales. The presence of a molten phase is thus likely to occur, within the test conditions described in this study, enabling the corrosion damage observed. As such, the

damage of alkali metal chromate or ferrite may release alkali metal-OH at the scale/gas interface (**Equation 30** and **Equation 31**) [90].

Equation 24 and **Equation 25** propose the formation of K-ferrite and chromate scales and further release of HCl [114], which is likely to occur at the scale/metal interface. Currents driven by Cr and Fe oxidation [90] in **Equation 28** and **Equation 29** provide electrons which promote the electrochemical decomposition of chromate scales (formed in **Equation 24** and **Equation 25**).



The reoccurring formation and dissociation of K-chromate and K-ferrite scales (in the case of the KCl-K₂SO₄ deposit systems) will certainly promote the weakening of compact scales via fractures and pores [114], [115]. The electron currents, induced by the ion exchange mechanisms, rely on the availability of oxygen whose partial pressure increases with distance from the metal/scale site. As such, the reformation of scale is deposited further from the bulk metal, leading to increasing layers of delaminated multi-oxide scales (as seen in **Figure 5-7**). These reaction mechanisms thus favour metal surface exposure to further corrosive attack.

5.2.1.1.2 Sulphur transport in KCl-K₂SO₄ deposit system

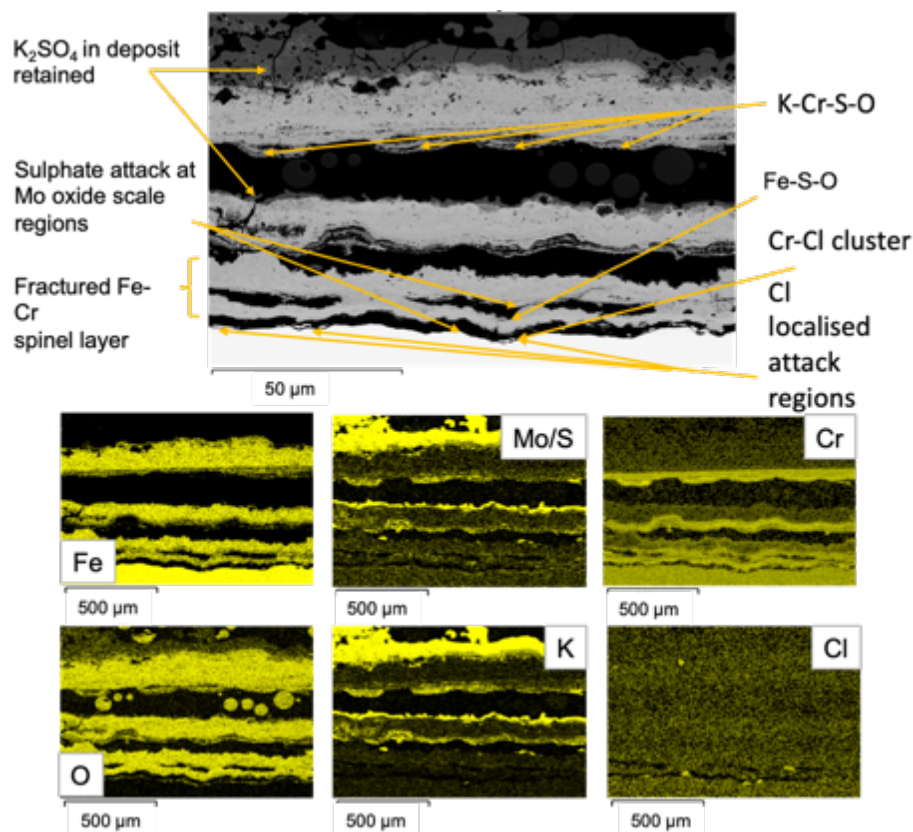
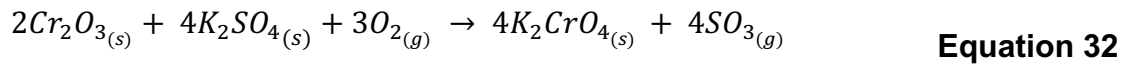


Figure 5-13: KCl-K₂SO₄ (D6) exposed T91 steel following 500 hours in HGB test gas at 600°C. Voids exist in this image. Note, furnace cycles, and deposit recoats encouraged trapping of deposit components within scales

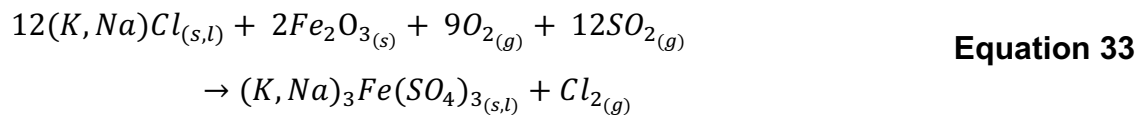
Metal attack by sulphate has been identified on samples, especially at delaminated scale regions (**Figure 5-13**). K₂SO₄ is, however, frequently encountered at the deposit region of the D6 and D8 exposed samples (also noted in **Section 4.2.4.2**). The retention of the salt at the deposit region may suggest that the thermochemical environments of the test conditions do not favour sufficient melting of K₂SO₄ within the KCl-K₂SO₄ system for D6 and D8. **Figure 5-13** presents the T91-D6 sample exposed for 500 hours at 600°C. K-S-O rich zones within the deposit layers, likely to be K₂SO₄, are observed.

Pettersson et al. [115] observed unmelted deposit regions while comparing the abilities of KCl and K₂SO₄ to react with the chromium scales (to form K-chromate) of an austenitic steel, 304L. The samples were exposed in a 5 mol.% O₂, 40 mol.% H₂O (bal-N₂) gas environment. Approximately 80% of K₂SO₄ remained unreactive at 600°C after 168 hours of exposure, whereas only about 15% of KCl was retained as deposit (quantified by ion chromatography). A reaction between the chromate oxide and K₂SO₄, expressed in **Equation 32** [115], was described as thermodynamically unfavourable at the test conditions.



$$\Delta G^{\circ}f = +135 \text{ KJ/mol}, p_{eq}(SO_3) = 8.9 \times 10^{-10} \text{ bar (600}^{\circ}\text{C, } pO_2: 0.05 \text{ bar)}$$

Karlsson et al. [138] heated (up to 500°C) alloy samples coated with a KCl, Fe₂O₃ and Cr₂O₃ deposit mixture in a 1:1 SO₂/O₂ gas environment. The rate of reaction for forming K₃Fe(SO₄)₃ (confirmed by XRD) reduced when the SO₂ within the test gas was spent. The authors concluded that corrosive attack by SO₂ can occur within the 310-700°C range, regardless of whether the corroding metal is alloyed with Cr or Ni. The conditions favouring the reaction were high alkali chloride concentrations and SO₂ content > 100 ppm in an oxidative atmosphere, such as employed for these corrosion studies, and as described by **Equation 33**



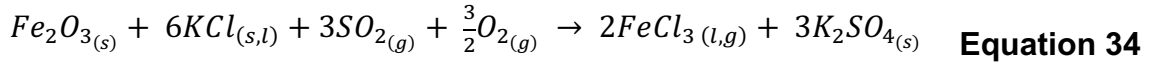
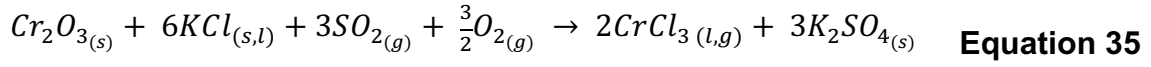
Sulphate migration into the metal substrate interface was observed by Dudziak et al [102] for a ferritic steel coated with a 37.5 mol.% Na₂SO₄, 37.5 mol.% K₂SO₄ and 25 mol.% Fe₂O₃ deposit mix, and exposed in a 1300 vppm

SO₂, 400 vppm HCl, 4 mol.% O₂, 13.4 mol.% CO₂, 8.6 mol.% H₂O, N₂ bal. gas at 600°C (bal. is an abbreviation for balance). The author attributed the sulphate present at the substrate region to a suggested deposit sulphate reaction [102].

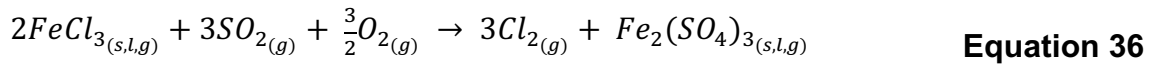
It may be inferred from observations made by Karlsson et al. [138] and Pettersson et al. [115], and within this research, that at 600°C, the sulphate attack at the metal substrate is not mainly dependant on the deposit sulphate but may be attributed to the SO₂ gas.

A porous Fe oxide scale, also showing S in EDX mapping, is spread across sample 347HFG-D6 (**Figure 4-103**). This suggests the presence of iron sulphate. Karlsson et al. [138] proposed that the formation of Fe₂(SO₄)₃ is favourable in an alkali metal-chloride rich oxidizing environment with SO₂ gas content >100 vppm. The APR test gas compositions contains 96 vppm SO₂ (**Table A-11**). As such, it is possible a similar formation occurred for 347HFG-D6 in **Figure 4-103**. Karlsson et al. [138] also proposed that the sulphate is generated from FeCl₃ released from alkali metal chloride attack of scales. The presence of the Fe-S interactions (**Figure 4-103**) may be an indication that FeCl₃ had existed, especially since severe metal attack is observed below the scale. The low melting point of the compound (FeCl₃ m.pt 310°C) and its high vapour pressure can accelerate scale damage and corrosion. Cl was however not confirmed to have been present at the corroded site.

Sulphate may be able to corrode metal grains. An attacked grain, nearer the metal surface of sample 347HFG-D6 (**Figure 5-10**), is Cr- and partially Fe-depleted (a porous Fe substrate is confirmed by the EDX map). The grain is however rich in Ni, suggesting the selective dissolution of Fe (partially) and Cr (almost completely) occurred at the grain. S is also observed at this damaged grain region. The reactions in **Equation 34** and **Equation 35** [107] are proposed to have occurred at the grain locations where KCl reduces the Fe and Cr oxide scales in the presence of SO₂.

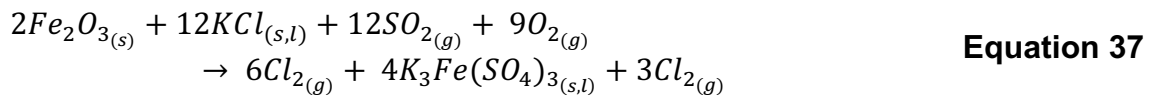


Another example of a sulphate aided damage is demonstrated in **Figure 4-125** which features a possible K-Fe-S-O association (from middle-centre to the middle-right image regions) around the metal/scale interface. A possible explanation for the lack of Fe-Cl associations on the EDX maps of the KCl-K₂SO₄ deposit exposed samples in **Figure 5-10** and **Figure 4-103** may be the sulfation of FeCl₃ as described by **Equation 36** [138].



In **Equation 36**, HCl is likely to form, giving the test gas moisture content (>1 mol.% [165]). As such, a HCl attack mechanism at the metal/scale interphase is most likely. The release of Cl⁻ ions may explain the presence of the Cl films on the D8 and D6 exposed 347HFG samples (**Section 4.2.4.2.**).

Combining **Equation 34** and **Equation 36** gives [107]:



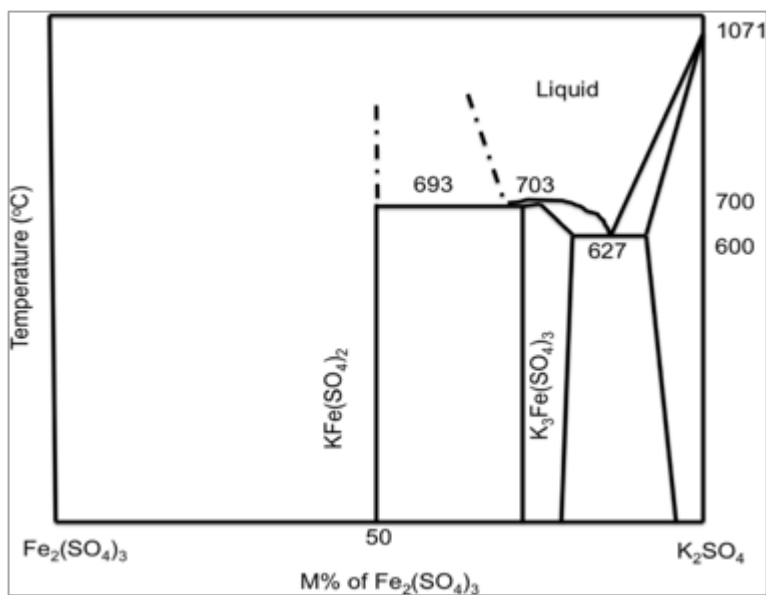


Figure 5-14: Fe (III) and K sulphate binary phase system showing eutectic melt occurring at 627°C [169]

The ferrous trisulphate formed in **Equation 37** may exhibit higher thermal stability (**Figure 5-14**) than FeCl₃ (m.pt.; 310°C) [165] in the test conditions. Thus, where sulphation of Fe-Cl does not occur (reaction terminates at **Equation 34**), Fe³⁺ ion loss (as metal chloride) may be more favoured. As such, the partial retention of Fe³⁺ ions (as ferrous trisulphate; **Equation 37**), may explain the presence of the porous Fe-scale zones in **Figure 5-10**.

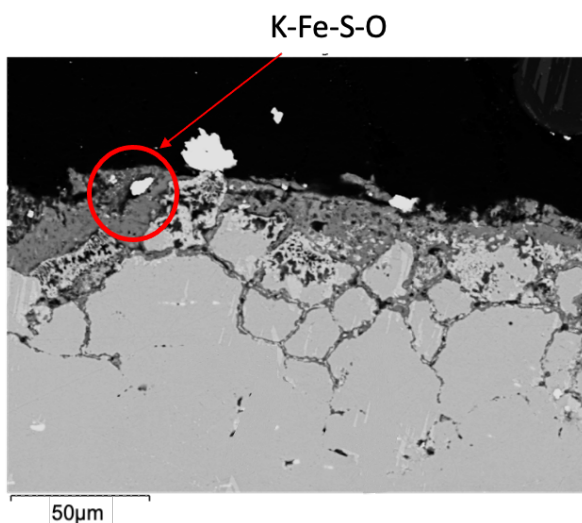


Figure 5-15: 347HFG-D6 following 500 hours exposure in HGB test gas environment at 600°C. Extracted from Figure 4-92 to highlight a scale region where Fe-K-S association is observed

Cr is not encountered at the highlighted scale region in **Figure 5-15** (image with EDX maps presented in **Figure 4-92**) where K, Fe, S and O species have been mapped by EDX. The absence of a Cr-K-S association may suggest that the reaction described in **Equation 37** did not occur for the chromium oxide.

5.2.1.1.3 Alloy components migration in KCl-K₂SO₄ deposit system

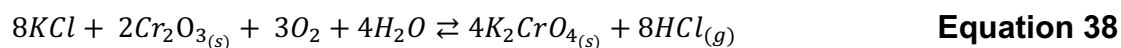
For this thesis, only the most common alloy precipitates for T91 (Fe, Cr, Mo) and 347HFG (Fe, Cr, Nb, Ni) have been discussed, as the associated elements have been more easily mapped during SEM/EDX analysis.

Fe and Cr interactions

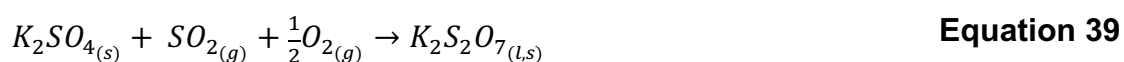
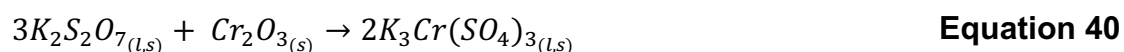
Figure 5-13 confirmed that alloy and deposit components interact. As discussed earlier, Fe sulphates and chlorides may be present. Cl clusters (**Figure 5-13**) mapped at similar locations with Cr, may indicate the presence of CrCl₃ (m.pt; 947 [107]), as described in **Equation 35** [107]. It is expected that the

release of Cl^- ions from CrCl_3 will be slower than from FeCl_3 as vapour pressures of the latter chloride is higher [107]. The KCl-CrCl_2 binary system, however, suggests the mixture may reach low eutectic temperature points of $\sim 460^\circ\text{C}$ [107], encouraging localised Cl attacks where such melts occur (**Figure 5-13**). The Cl attack mechanism is therefore promoted by Fe and Cr oxide damage where both chloride and sulphate play active roles.

Figure 5-13 also suggests the presence of a K-Cr-S-O specie(s) at scale surfaces. The formation of K_2CrO_4 , in similar conditions, has been considered, by Karlsson et al. [114], to occur without sulphate species present, via the reaction route in **Equation 38**:



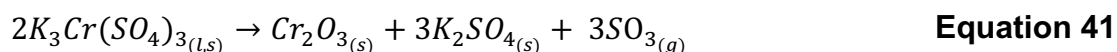
Also, Mayoral et al. [170] employed XRD analysis to confirm the presence of $\text{K}_3\text{Cr}(\text{SO}_4)_3$ on a high alloyed steel, I617 at 600°C . The alloy sample was initially pre-oxidised for 200 hours (in 5%- O_2/CO_2 , bal. N_2) prior to being exposed. The exposure condition was an 80 ml/min Ar atmosphere, an applied KCl coating (spray layer; 5 mg/cm), and a synthetic pyrosulphate, which has been mentioned to likely exist on HX [170] (**Equation 39**):



Thermogravimetric investigations of melted K-pyrosulphate activity, by Mayoral et al. [170], showed that the melts could solubilise oxides which would otherwise have not been soluble. The corrosion behaviour of the pyrosulphate was related to its high chemical activity towards both the metal and the oxides which may be dissolved to yield trisulphides.

An example of where a pyrosulphate may have been present and dissolved a chromium scale is illustrated in **Figure 5-13**. The K-Cr-S-O associations at the indicated scale sections suggest the presence of a K-Cr-sulphate which might have occurred (according to **Equation 40**). These deposit regions seem to have been detached in a domed pattern which may have influenced the unevenness of the T91 metal surface, observed on various samples.

Scale delamination may thus also be influenced by the decomposition of $K_3Cr(SO_4)_3$ (**Equation 41**), which may release sulphate at the scale region, promoting the sulphation (for e.g.) of chlorides.



The reaction stages described from **Equation 39** to **Equation 41** give an example of when a deposit sulphate may be transported (as melts) from the deposit region to a scale region (dissolving the scale), and released at the latter location (decomposed scale). In this case, the affected scale is chromate.

Mo interactions

Mo scaling over the ferritic steel is formed closer to the metal surface, relative to Cr-O and Fe-O (**Figure 5-13**), and has also been found within Fe and Cr spinel's (**Figure 5-16**). In **Figure 5-13**, Mo species within the scale layers often neighbour S-rich regions. At 600 C, porous and delaminated Mo scales are observed (**Figure 5-13**). S-rich clusters are noted at the Mo scale boundaries, suggesting the element's role in Mo scale damage. MoS_2 may, however, offer good protection from corrosive species (if sufficiently formed) due to the sulphide's high melting point [171], as discussed in **Section 2.5.2**. There is also insufficient evidence, from the EDX analysis of the T91 sample, to suggest that the formation of the sulphide occurred in any of the test gas conditions. Also, the

formation of MoS_2 is unlikely to occur at low H_2 partial pressure as expected in the simulated air fired combustion atmosphere.

The diffusion of Cl^- ions towards an alloy (**Equation 3**), and a subsequent cation release from the metal body (**Equation 4**), may affect the early onset of a proper Mo scale. Compared to the no-deposit exposed sample (**Figure 4-46**), by 500 hours, the deposit exposed samples (**Figure 4-92** and **Figure 4-93**) show Mo poor scales which may coincide with the scale delamination layers, at the metal surface. There is, however, no evidence to suggest chloride attack on the Mo scales has occurred. In addition, Mo retains reasonable inertness in a HCl containing gas even at low O_2 potential up to 900°C [172], and the MoCl_3 formation Gibbs' free energy confirms the chlorination reaction will not be feasible [125], [126].

The scales observed in **Figure 5-13** are more likely to be MoO_3 and not MoO_2 as the compound with the lower Mo oxidative state has greater thermal stability, which would likely have improved the scale compactness, as proposed by Lyon [171]. The presence of a relatively unstable MoO_3 may thus be considered as a Mo scale damage route in an oxidising environment, at the prevailing test temperature.

The exposure of Mo scale is likely dependent on the integrities of the upper Cr and Fe scales, which may have become damaged by reactions described in **Equation 26** and **Equation 27**. **Figure 5-16** presents an improved Mo scale, where the overlaying Cr scale shows improves protective features than observed in **Figure 5-13**. Mo scales may undergo a more complex damage mechanism which has not been understood by the analysis carried out in this work.

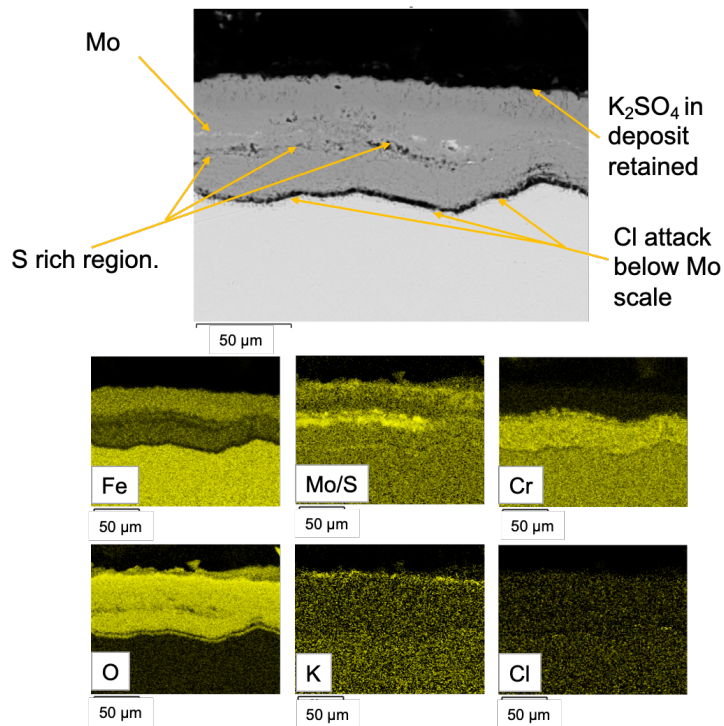


Figure 5-16: KCl-K₂SO₄ (D8) exposed T91 steel following 500 hours in APR test gas conditions at 600°C (Adopted from Figure 4-120)

Other interactions: Ni and Nb

The formation of a low melting point KCl-NiCl₂ eutectic mixture is illustrated on the binary phase diagram in **Figure 5-17**. This phase equilibrium suggests a molten Ni-Cl phase can be present below 600°C which may explain the presence of Ni-Cl at the metal/scale interface of 347HFG-D6 in **Figure 4-103**. Nb clusters may be well-retained within the austenitic structure (there have been no Nb precipitates observed within scales). There have been no trends observed for Nb behaviour in substrates.

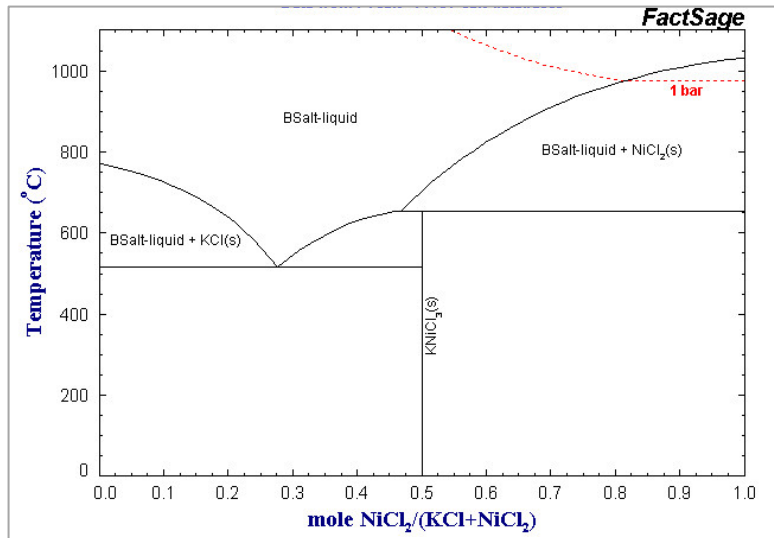


Figure 5-17: KCl-NiCl₂ binary phase diagram [106]

5.2.1.2 KCl-K₂SO₄-Na₂SO₄-CaSO₄ deposit system corrosion mechanism for 347HFG and T91

Deposit D1 is described by the KCl-K₂SO₄-Na₂SO₄-CaSO₄ system. The deposit system has more chemical reaction routes which can occur, given the increased number of elements in the deposit mix, compared to D6 and D8 (KCl-K₂SO₄). As deposit cations influence Cl corrosion attack mechanism, there may be more chloride assisted damage mechanisms occurring within the multi-cation deposit system, D1.

5.2.1.2.1 Chlorine transport in K-Na-Ca cation (sulphate/chloride) system: alkali metal activity

To understand the damage mechanisms of the alkali metals, it is necessary to describe the chloride damage observed. Chloride attack can occur under higher deposit chloride content. E.g., pitting at a metal surface location is facilitated where the Cl partial pressure is high [97], as encountered under D6 exposures in **Figure 5-18**. Cl induced damage will be more severe at metal surface location where the scale integrity is already compromised.

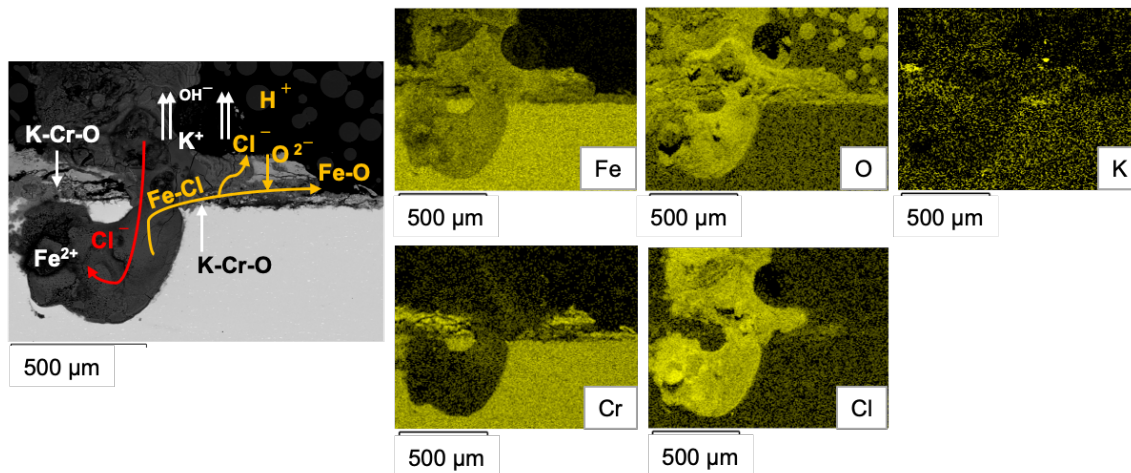


Figure 5-18: BSE/EDX image showing Cl attack mode on 347HFG-D6, exposed for 1000 hours in APR test gas conditions at 600°C

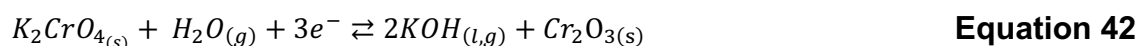
The targeted Cl attack via the compromised scale region may influence penetrative damage where scale healing at the attack location is not likely, due to the high Cl vapour pressure exerted on the metal-oxide scales. Cl^- ions may however be lost from the corrosion site, as illustrated in **Figure 5-18**.

Where chloride concentrations are lower, e.g., WWF deposits such as D1, the occurrence of pits may be less likely due to lower chloride partial pressures. Where corrosion rates are progressive under low chloride conditions, there must be a way of ‘recirculating’ the Cl^- ions. The following paragraph describes how.

Damage occurring within the D1 exposure conditions can be understood by considering the individual cation role in fireside corrosion. The previous section has discussed, at length, the ways K^+ ions may assist in anion attack. These descriptions are, however, not limited to K^+ ions. Folkeson et al. [90] proposed that a K^+ ion attack on metals is similar to that of a Na^+ ion.

The formation of KOH gas during biomass/waste combustion is thermodynamically favourable (as demonstrated by MTDData in **Figure 4-11**). It is

also likely to occur from the breakdown of chromate scales [114]. In this case, the activity of K^+ ions is influenced by the vapour pressure of the hydroxide. In a system, such as described in **Equation 42**, the vapour pressure of KOH is relatively high (equilibrium vapour pressure at 600°C; 4.9×10^{-5} bar [114]). As such K^+ ions may be evaporated from the corrosion site and lost in the flue gas (as KOH gas):



Subsequently, Cl^- ions released from ion exchange mechanism (**Equation 7**) (described in **Section 2.5.3.1.2** and illustrated with sample T91-D6 in **Figure 5-18**) may form HCl (gas at 600°C) (in the absence of KOH) and also be lost (**Equation 43**).



Where the cation is lost, high corrosion rates (by chloride attack) must be sustained by sufficient provision of chlorides from the deposit/gas. This could explain the aggressive chloride damage (in form of pits) encountered by the D8 and D6 coated samples (examples cited in, **Figure 5-9** and **Figure 5-18**).

In such a system, where the volume of chloride becomes the main factor governing corrosion rates, the S/Cl ratio, which influences the eutectic melt fraction of deposits [173], will determine the availability of chloride (from deposit) for attack in this scenario.

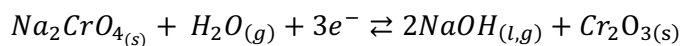
The previous paragraphs in this section have highlighted how K may assist in chloride damage. Following on, Na cation behaviour in fireside corrosion is

discussed to understand the damage mechanisms influenced by the D1 deposit system.

Despite having much lower chloride content, the multi-cation deposit (D1) system has caused significant grain boundary depletion depths in the case of 347HFG (**Figure 5-9**) and internal oxidation for the 1000-hour exposure T91-D1 sample (**Figure 4-48**) compared to the K-cation deposits (D6 and D8). In WWF gas, both metal loss and internal damage have been more severe for the D1 exposed sample (**Section B.15**, **Figure 5-6** and **Figure 5-8**).

5.2.1.2.1.1 Cation mobility in K- and K-Na-Ca cation (sulphate/chloride) systems

In a system where both Na and K form alkali metal chromate scales, both elements may assist Cl^- ion attack, thus more corrosion mechanisms may exist (compared to those occurring in a single-cation deposit system). Karlsson et al. [114] compared the formation rates of K- and Na-chromate, from interactions of alkali chloride salts with chromium oxide scales on 304L steel samples, by EDX analysis. The pre-oxidised alloy samples were exposed to KCl and NaCl in a 40 mol.% H_2O , 5 mol.% O_2 (N_2 bal.) atmosphere at 600°C. It was observed that both alkali metals formed chromate scales (K_2CrO_4 and Na_2CrO_4), though these scales decomposed at different rates. The rate variance was attributed to the equilibrium vapour pressure difference of the decomposition products, which are KOH and NaOH (**Equation 42** and **Equation 44**) (equilibrium vapour pressure of NaOH at 600°C; 5.3×10^{-7} bar [114]). Karlsson et al. [114] thus observed a higher rate of K loss (as KOH) than Na from the system.



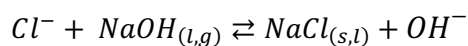
Equation 44

The higher volatility of KOH (than NaOH) may have promoted the high metal loss on the KCl-K₂SO₄ deposit exposed samples (**Figure 5-9**), where deposit chloride content is also high (**Table 4-6**). KOH and HCl may form, while exiting the reaction site towards the gas stream, causing further damage to the scales. In the lower chloride content exposure conditions, oxide recovery may occur to some extent, as demonstrated by sample T91-D1 in **Figure 5-7**. **Figure 5-9** also demonstrates thicker scales for the D1 exposed sample (~30 µm), compared to the scale thicknesses of the D6 (~5 µm) and D8 (~10 µm) exposed samples. The improved recovery of scale for 347HFG-D1 (compared to the KCl-K₂SO₄ deposit exposed equivalent samples) may be aided by the reduced volumes of volatile K species exiting the reaction site. Internal attack is, however, most severe for the D1 exposed 347HFG steels in all test gas conditions at 600°C, suggesting the attack is sustained internally at the target grain boundary regions (**Figure 5-9** and **Figure 5-18**) within their imperfect crystal lattice which are sites for enhanced diffusion of various species.

K⁺ ion depletion (evaporation as KOH) may be prominent within the Na/K sulphate/chloride system. In **Figure 5-19**, K species are mostly associated with S in the upper scale region. An explanation may be the sulphation of the hydroxide (KOH) released from the reaction described in **Equation 42**. Sulphate species may be provided by unspent deposit or from the gas stream.

The positioning of Na species nearer the metal surface in **Figure 5-19** suggests this element is effectively retained rather than evaporated. Also present at the Na-rich zone are chromium scales, suggesting the formation of Na-Cr scales had occurred. At the prevailing temperature (600°C), the breakdown of Na chromate (m.pt.; 357°C [107]) may occur as described in **Equation 44**; albeit at a slower release rate of NaOH (relative to KOH released from the decomposition of K-chromate). Also, the lower vapour pressure of NaOH, compared to KOH, would mean a lower evaporation rate. The simultaneous accumulation of NaOH and simultaneous presence of Cl⁻ ions (released from the ion exchange mechanisms as proposed by Folkesson et al. [90], **Section 2.5.3.1.2**) at the metal/scale interface may permit the condensation of chloride. The formation of

NaCl thus limits the loss of Cl^- ions, as HCl (**Equation 45**), where NaCl is likely to be molten (NaCl - Na_2CrO_4 eutectic m.pt 557°C [107]) rather than being in gas phase.



Equation 45

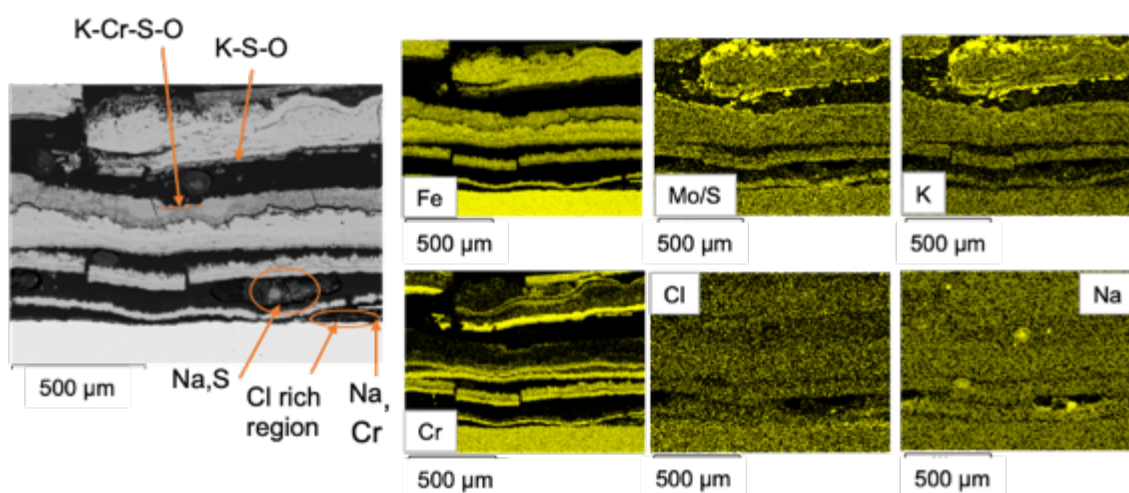


Figure 5-19: T91-D1 exposed for 1000 hours in HGB test gas conditions at 600°C , illustrating cation positioning relative to S and Cl species

Where the corrosion mechanism favours the condensation of chloride, its loss (Cl^- ions reduced to HCl gas) is deterred. The release of NaOH and KOH from the decomposition of alkali metal-Cr scales will likely occur at the metal/scale interface, where the initial chromate (Cr_2O_3) layers are formed. As such the hydroxide may be liquid/gas at the metal surface front, allowing targeted attacks, for example at weakened grain boundary regions as seen on the D1 exposed 347HFG samples.

The presence of NaOH (lower vapour pressure than KOH) may thus allow a more sustained chloride attack within grain boundary regions than expected for KOH, which may evaporate faster than KCl can be formed. **Figure 5-20** confirms

the presence of both alkali metals within grain boundary corrosion zones of a 347HFG-D1 sample following 1000 hours exposure. The Cl clusters in the EDX maps however overlay with Na (possibly via **Equation 46**) while K does not appear to have been retained as KCl.

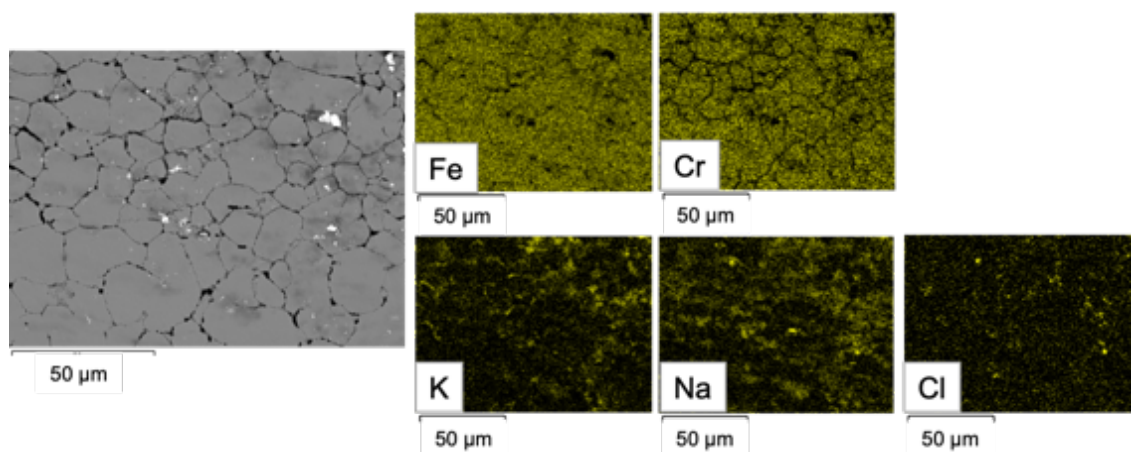


Figure 5-20: Alkali metal and chloride species condensed along grain boundary region in 347HFG-D1 sample post exposure at 600°C for 1000 hours in WWF test gas conditions



Although the chloride level in D1 is much lower than for D6 and D8, Cl^{-} ion loss is likely reduced for the D1 exposed samples. The increased sound metal penetration (**Figure 5-9**) may be favoured by the deposition of NaCl at the metal/scale interface.

5.2.1.2.1.2 Test gas influence on Na-assisted chloride attack

The flue gas compositions and flow rates were calculated based on fuel composition and the air flow rate required to achieved 7-8% excess O_2 (a standard biomass/waste firing power plant practice for ensuring complete combustion [24]) (see **Section A-3** and **Section 3.2.2**). In WWF gas conditions,

where the total gas flow rate (50 ml/min) is less than half that of the APR test gas (118 ml/min) (**Section A-5**), internal penetration and metal loss is more severe for D1 than D6 (**Section 4.2.2.1.2**). As deposit components nearer the metal surface may be less influenced by the flue gas flow, an increased residence time of NaOH and chlorides at the metal surface region may permit the formation of NaCl species before been expelled as NaOH.

In higher flow rate conditions (such as in APR gas conditions), chloride loss may be enhanced by the flow. For example, in **Figure 4-94**, metal damage occurring for the alloys exposed to deposits D1, D6 and D8 in APR test gas conditions at 600°C are relatively comparable at 200 hours (median metal loss is within 50 µm for all samples) and, metal penetration depths and surface damage become least for the D1 exposed samples, following 1000 hour of testing (**Figure 4-98** and **Figure 4-99**).

5.2.1.2.2 Chlorine transport in K-Na-Ca (sulphate/chloride) system: K-Na eutectics lead attack

Eutectic melts including both alkali metals (Na and K) from deposit D1 can achieve lower molten temperature ranges than the K-cation only system, according to the phase systems presented in **Figure 5-12** and **Figure 5-21**. The ternary phase diagrams show melts may occur in the triple chloride system at 310°C (at ~30 mol.% NaCl), whereas the lowest eutectic temperature for the FeCl₂-KCl system occurs at ~400°C.

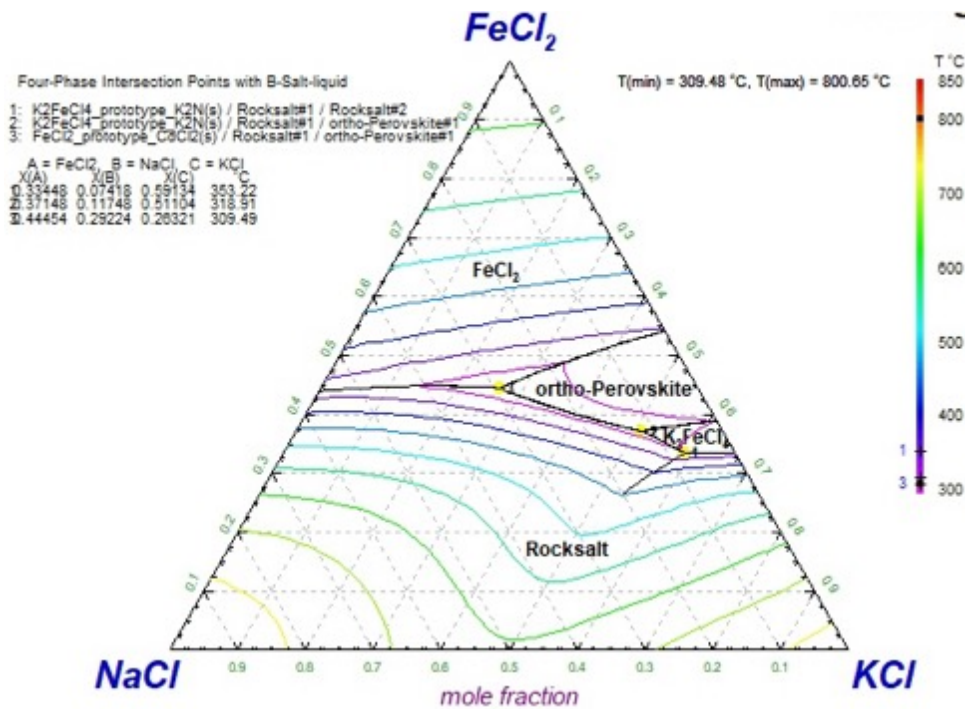


Figure 5-21: KCl-FeCl₂-NaCl ternary phase diagram [106], [173]

Figure 5-22 shows the likely presence of a Na-K-S association at the metal/scale interface region of sample T91-D1 exposed in APR conditions for 500 hours. A molten phase $K_3Na(SO_4)_2$ may exist as low as 493.3°C within the deposit, via the reaction route described in **Equation 47** [173]. The grain boundary penetration occurring below this region indicates Cl is present where the internal attack becomes wider at the tail end, located ~40 μm below the metal surface. The formation of the mixed alkali metal sulphate scale may have encouraged the penetrative Cl attack.

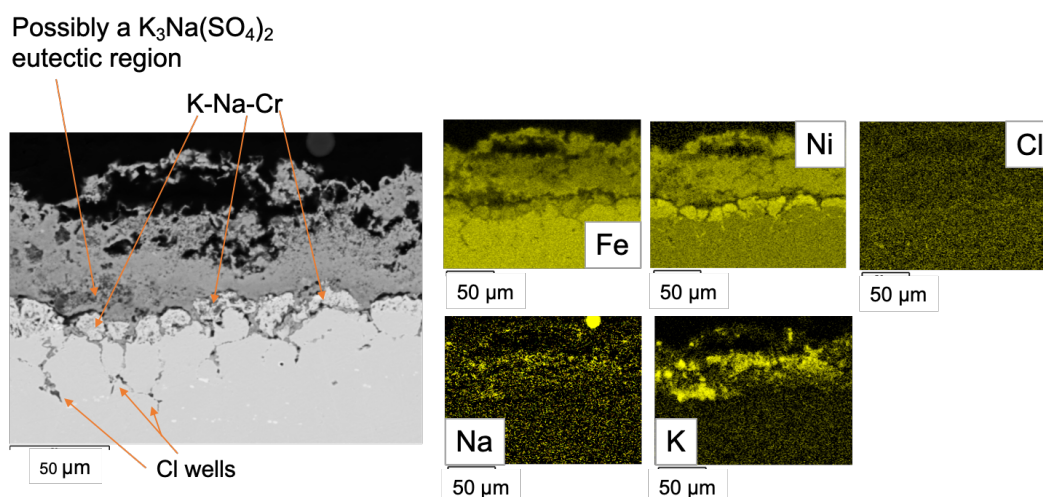
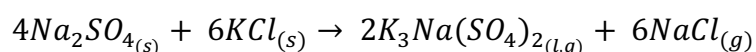


Figure 5-22: BSE/EDX image, K-Na eutectic suggested for Na-K EDX map overlap observed on 347HFG-D1 sample (deposit flux 100 $\mu\text{m}/\text{cm}^2\text{h}$) exposed for 500 hours in APR test gas conditions. Adopted from Figure 4-102



Equation 47

He et al. [131] observed the higher penetrative damage depth for a 12Cr1Mo steel exposed to 50/50 mol.% NaCl-KCl salt mix, compared to when the alloy was exposed to three other deposit mixtures: (a) $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$, (b) $\text{KCl}/\text{K}_2\text{SO}_4$ and (c) $\text{NaCl}-\text{Na}_2\text{SO}_4$ (50/50 mol.%). The test involved exposure in air at 700°C. The author also observed that the dual cation deposit mix (a) attacked the alloy more severely than the single cation deposit mixes (b) and (c), demonstrating that the cations played a major role in the extent of damage. The author's observation is in line with the increased grain boundary penetration by chloride species for 347HFG-D1 compared to the D6 and D8 exposed equivalent samples.

5.2.1.2.3 Role of Ca in the K-Na-Ca deposit system

There are illustrations provided (Section 5.2.1.1.2) which show that a considerable proportion of K_2SO_4 within the deposit is retained. The reasons suggested for the sulphate retention at the deposit layer have focused on the temperature phases of the compound, whereby its solid phase is prevalent at the test temperature conditions.

There has been no evidence to show Ca from the deposit has been able to interact with scales or metal components at the set test conditions, however, some interaction may be noted between K and Ca sulphates in the deposit.

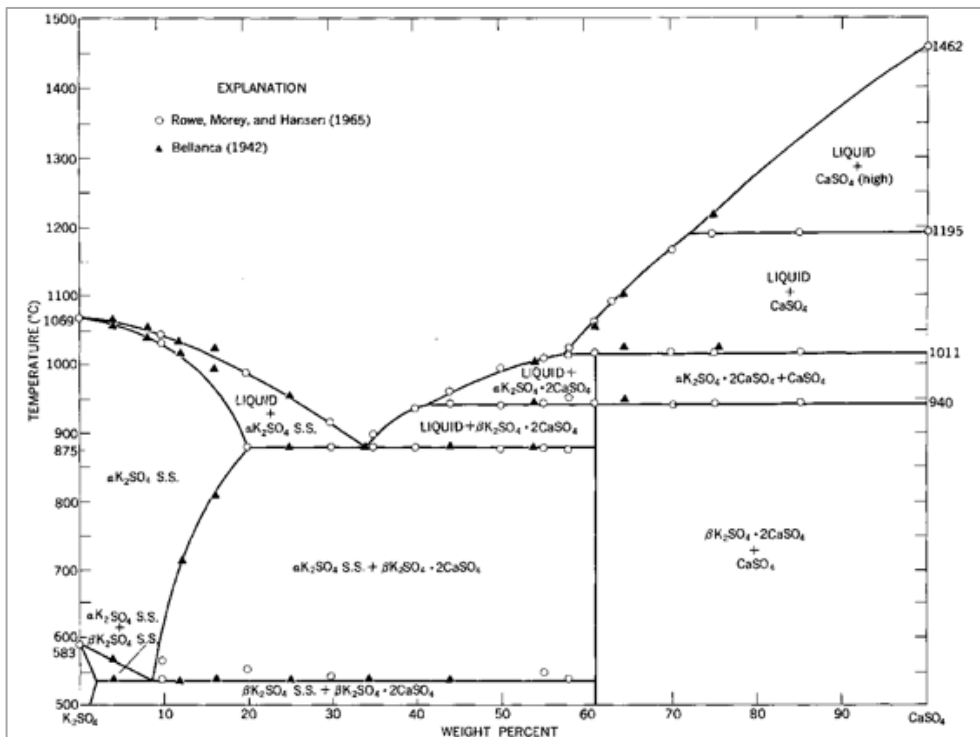


Figure 5-23: K_2SO_4 - $CaSO_4$ binary phase diagram [174]

A Ca_2SO_4 - K_2SO_4 binary equilibrium system (Figure 5-23), as explained by Rowe et al. [174], reports the lowest temperature melt phase occurs at 875°C. An intermediate crystalline phase, $K_2SO_4 \cdot 2CaSO_4$ (calcium langbeinite), is

present as the melting of K_2SO_4 within a solid solution of up to 24 mol.% CaSO_4 [174], [175]. The deposit region in **Figure 4-81** shows that a Ca-K-S association may exist. The relatively high melting point of the langbeinite (**Figure 5-23**) may suggest that, if present under deposit D1 exposure conditions, only solid phases will exist, as such, causes of corrosion involving interactions with Ca^{2+} ions are not expected.

5.2.1.3 Summary

The corrosivity of deposit D1 (K-Na-Ca sulphate/chloride), D6 and D8 (K sulphate/chloride), under the three test gas conditions at 600°C, have been compared to understand fireside corrosion behaviours of WWF, HGB and APR (respectively) biomass/waste fuels. Similarities in the damage extents for metal and sound metal loss are encountered for both alloy types (T91 and 347HFG) exposed to the single cation deposits, D6 and D8. BSE imaging confirms the sound metal attack of the D1 coated samples can be deeper and metal loss greater for both alloys than encountered for the D6 and D8 sample equivalents at 600°C (**Figure 5-9**). The severity of internal penetration is, however, much greater for the austenitic steel coated with the WWF deposit. The absolute metal loss is lower than that of the ferritic steel.

The relatively low chloride WWF deposit, however, leads to lower metal loss damage than the K-cation deposits (high chloride) in higher flow rate gas conditions (observed above 74 ml/min), which can be attributed to both chloride and alkali metal being swept away via the flue gas stream. Nevertheless, at 600°C, the presence of NaCl at the metal surface is still able to influence greater grain boundary attack, in the case of 347HFG, than where Na species are not deposited.

This PhD has identified that the differences in the temperature stabilities of alkali metal chromate scales (formed during sample exposures) and the vapour pressures of their hydroxides (when these scales decomposed) will influence

different fireside corrosion chloride attack mechanisms, attributed to these conditions:

- i. At 600°C, NaOH will cause chloride damage at the metal surface and at grain boundaries.
- ii. Vapour phase KOH will, at 600°C, be generated from the decomposing chromate scale region, influencing scale porosity, fracture and/or delamination. The loss (from the corrosion site, likely carried away with flue gas stream) of KOH will also favour the loss of chloride as HCl.

This means that, the presence or absence of K and Na may determine how chloride attack occurs on a HX surface. The implication is that WWF and non-wood-based fuels, such as APR and HGB, will result in different chloride attack mechanisms as the corrosive deposits of the latter fuel categories are predominantly K-salts (as determined by MTDData).

For WWF combustion, both Na and K salts may be present in deposits. The Na and chloride content likely to exist in WWF deposits are, however, relatively low, compared to HGB and APR. As such, Na species damage mechanisms (for WWF firing) may target compromised metal surface sections, such as grain boundary regions, as in the case of 347HFG. This signifies that alloys prone to grain boundary damage will be sensitive (fireside corrosion wise) to deposit Na content. In agreement with Tran et al. [33], the chloride fraction of the WWF deposit is sufficient for sustained chloride attack. Expanding further, Na plays a significant role in sustaining the corrosion rates observed at 600°C.

Damage influenced by evaporating species such as HCl and KOH (compared to damage encouraged by molten species in low chloride conditions) may be more easily observed in combustion power plant materials. This is because damage of scales by large volumes of K and Cl species vapours (as anticipated to occur during HGB and APR firing) will influence metal surface attack and pitting where the scales are partially vulnerable.

Furthermore, the fireside corrosion rates and mechanisms occurring during HGB and APR firing exposures partly depend on the hydroxide. Folkesson et al. [90] argued that KOH serves as an intermediary between a KCl molecule and a diffusing Cl^- ion. In this study, however, K_2CrO_4 is the intermediary between KCl and the Cl^- ion where the scale decomposition product (in this case -OH) supports scale damage. As such, it may be argued that both Cl^- ion diffusion (likely influencing pit formation) and alkali metal hydroxide transfers (influencing scale damage) contribute to corrosive damage.

Where both alkali metals are present, combined sound metal loss and metal loss damage mechanisms are expected. Another complication associated with deposits which contain both Na and K is the formation of lower melting point eutectics (compared to deposit systems with only K as cation). In agreement with Niu et al. [173], a low melting point K-Na-sulphate may form. Such compounds make K less volatile and increase the molten deposit fraction. The retention of alkali metal species is crucial for sustained chloride damages, especially for WWF deposits with relatively low chloride content. As such, this research establishes that the overall chloride content is not informative enough to predict its corrosive behaviours.

Recent research gives attention to the destructive behaviour of K in biomass firing, mostly attributed to its low melting temperature compounds formed [98]. Further studies on the behaviour of Na are discussed in the subsequent sections to better understand how this element behaves in combination with other components at varying fireside corrosion conditions.

5.2.2 Discussion of corrosive variations within K (D6 & D7) and K-Na (D1, D2, D3, D4 & D5) chloride/sulphate deposits

This section describes the differences in the corrosion influences of deposits formulated to represent chemical variations occurring within the WWF and HGB fuel categories. Deposit compositions for D1-D5 and D6 & D7 are formulated from the WWF and HGB fuel categories respectively (**Table 4-6**).

5.2.2.1 Comparison of deposits', D6 and D7, corrosion damage influences on T91 and 347FG

Corrosion variations between D6 (KCl/K₂SO₄; 71 mol.%/29 mol.%) and D7 (KCl/K₂SO₄; 89 mol.%/11 mol.%) were compared at 600°C in the HGB test gas environment. A decision to evaluate two deposits within the HGB category followed the observation of the range between the fuel median (0.18-Cl wt.%, ar) and mean (0.41-Cl wt.%, ar) Cl contents. The minimum and maximum fuel Cl contents ranged from 0.06-1 wt.% ar (**Figure 4-2**). D7 is thus formulated based on the fuel category mean Cl content and median values of other elements (14ES) input into combustion calculations by MTData. The Cl input rates were 0.05 moles/kg fuel and 0.11 moles/kg fuel for D6 and D7 respectively (**Table A-8**). The corrosion investigation of both deposits enabled the comparison of their impact on damage under HGB category mid-range (median and mean) Cl content.

Though the metal loss was reported to be similar for both 347HFG-D6 and 347HFG-D7, the former sample underwent deeper sound metal penetration at all three exposure times. (**Section 4.2.3.1**). From **Figure 5-24**, the metal surface loss of sample T91-D6 increases at a faster rate than that of T91-D7. Internal oxidation is also more severe under D6 influence: at 1000 hours, internal oxidation depth is ~50 µm (median value) for T91-D6 whereas, internal oxidation is <10 µm across all measurement points for sample T91-D7 (**Figure 5-24** and **Figure 5-25**).

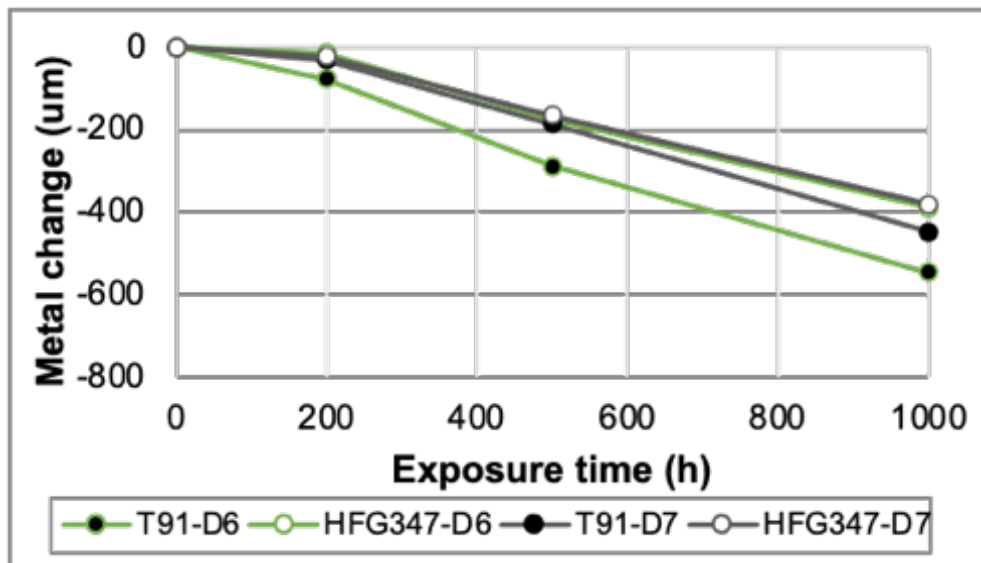


Figure 5-24: Median metal changes with exposure time for T91 and 347HFG samples exposed to D1 and D6 (deposit flux 100 $\mu\text{m}/\text{cm}^2\text{h}$) in HGB test gas at 600°C

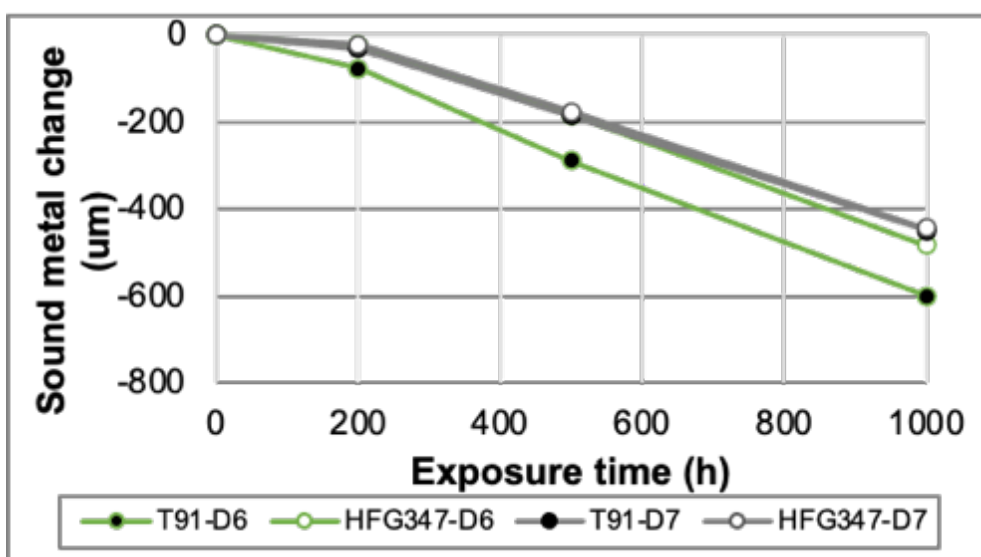


Figure 5-25: Median sound metal changes with exposure time for T91 and 347HFG samples exposed to D1 and D6 (deposit flux 100 $\mu\text{m}/\text{cm}^2\text{h}$) in HGB test gas at 600°C

The higher corrosivity of D6 than D7 within the same experimental conditions suggests that the sulphate/chloride ratio of the deposits is an important factor influencing the extents of corrosion damage of both alloys. The corrosion mechanisms which may occur for the KCl-K₂SO₄ deposit exposed samples have been discussed in **Section 5.2.1.1**. It has also been discussed in **Section**

5.2.1.1.1 that the deposit components may melt at test temperatures below their expected eutectic mixture melting point, were deposits interact with gas species and/or scales. Variations in corrosion extents influenced by the KCl-K₂SO₄ deposit systems however exist.

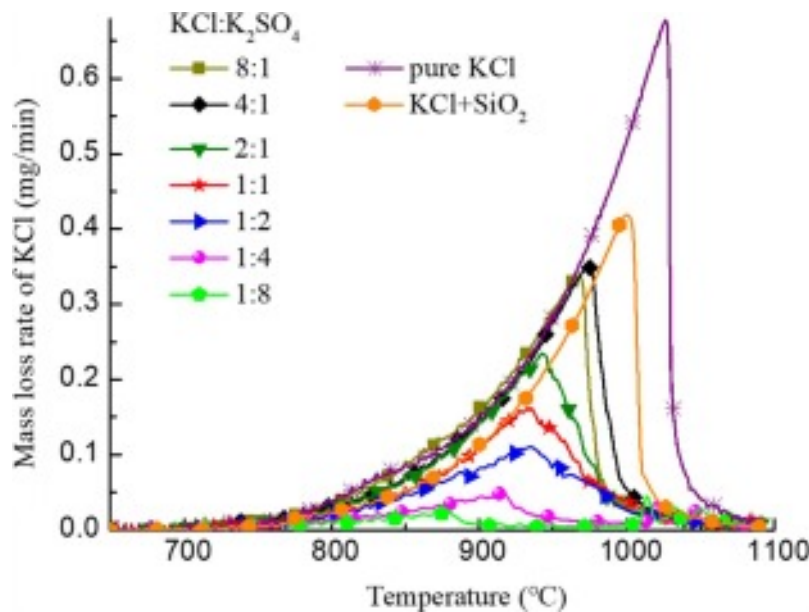


Figure 5-26: Derivative thermogravimetric (DTG) curve of pure salts and salt mixture showing increase in mass loss of KCl with increased KCl content [161]

Li et al. [161] noted that the evaporation rate of KCl was highest from two salt mixtures of 8:1 and 8:2 KCl/K₂SO₄ (mole fraction), compared to the mass losses from the 1:8 and 2:8 KCl/K₂SO₄ salt mixtures, which were heated to 1100°C at 10°C/min. The tests were conducted in air and N₂ (feed rates of 20 ml/min). It was concluded that the evaporation rates of KCl increased with KCl content as illustrated in **Figure 5-26**. Of all the KCl/K₂SO₄ salt ratios employed by Li et al. [161], the 8:1 KCl/K₂SO₄ ratio is most similar to that of deposit D7. The higher chloride content and lower corrosion influence of D7, compared to D6, suggests that chloride content and deposit evaporation rates could not be used to explain the fireside corrosion behaviours of these deposits.

Orlicka et al. [176] also investigated the thermal stabilities of sulphate and chloride pure salts and mixtures. Experiments were conducted in isothermal furnaces at 600°C in a 7%-O₂, 100 ppm-SO₂, 350 ppm-HCl, bal. N₂ mix. The double alkali metal salt mixtures exhibited higher mass loss than single alkali metal salt mixtures when the KCl content was >60 mol.% (**Figure 5-27**). At 40 mol.% KCl, both the single and double alkali metal salt mixtures demonstrated similar mass loss at 600°C, however, the determination of the melt fractions existing for both mixtures (at 40 mol.% KCl) were outside their work scope.

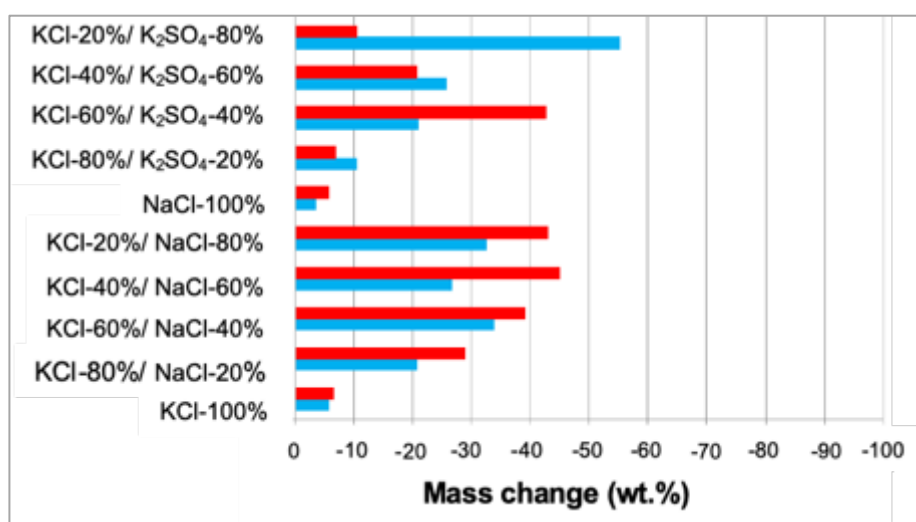


Figure 5-27: 50-hour mass changes of chloride and sulphate salt mixtures exposed at 500°C (red bars) and 600°C (blue bars) in a 7%-O₂, 100 ppm-SO₂, 350 ppm-HCl, balance N₂ gas mix [176]

The accelerated corrosion rates influenced by the low chloride deposit mixtures compared to the high chloride deposits (**Section 5.2.1.2**) do not correlate with the mass loss findings of Orlicka et al. [176] or Li et al. [161] (higher volatility with increased chloride ratio of mixture), though the former author noted an increased evaporation rate for the double alkali metal salt mixture at higher chloride content. The link between evaporation rates of salts and their corrosive influence is thus not clearly defined.

In addition to loss of chloride vapour via sulphation, the condensation of components will also be influenced by gas flow rates [9] and the temperature

gradients [113] experienced by the gas species. Thus, the evaporation of KCl from a corrosion attack site may or may not be able to participate further in corrosive attack, making it less straightforward when using mass transfer assessments to investigate potential corrosive damage. Nevertheless, evaporation having occurred, in most cases, is an indication that a molten phase had existed. The presence of a component in molten state will enhance the interaction of such a component with metal and scales. As such, the higher the molten fraction of a deposit, the greater the corrosive influence of the deposit [33], [120].

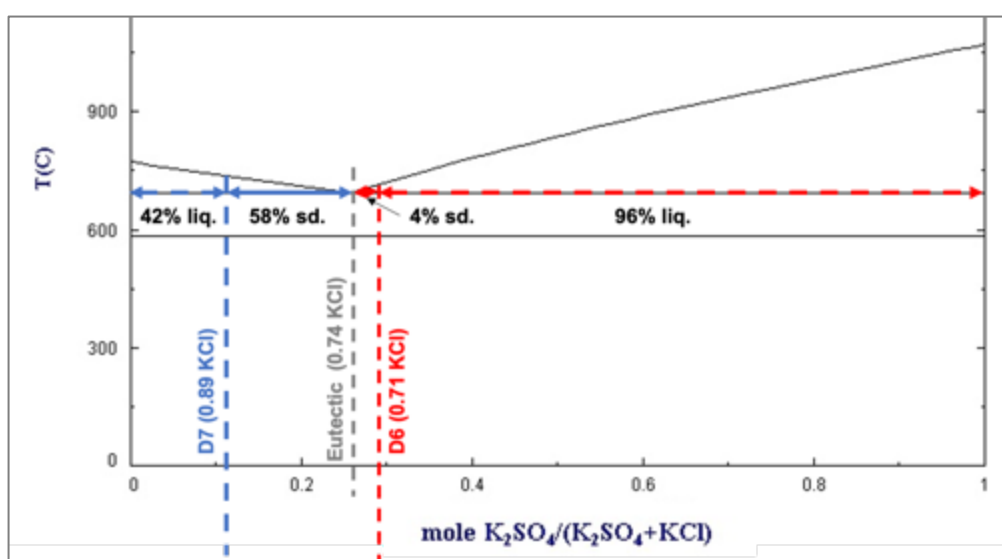


Figure 5-28: Position of deposits D6 and D7 on the KCl/K₂SO₄ binary phase diagram composition scale and the calculated deposits liquid (liq.)/ solid (sd.) percentages at the eutectic temperature. Adopted from [106]

The KCl and K₂SO₄ in a mixture will retain their individual physiochemical properties, by definition of a eutectic mixture [177]. This means that the molten KCl within a eutectic mixture present in D6 and D7 (and other occurring eutectics, e.g., **Figure 5-12**) will exhibit the chemical properties of its pure molten form. The molten KCl fractions of the deposits may thus be directly linked to the deposit corrosivity (molten KCl exposures). The molten/solid phase fractions of both deposits at the eutectic melting temperature can be calculated for the eutectic composition as illustrated in **Figure 5-28**.

The molten fraction for D6 is expressed as:

$$1 - \frac{\text{K}_2\text{SO}_4 \text{ mole fraction for D}_6}{\text{eutectic KCl mole fraction}} \quad \text{Equation 48}$$

$$1 - 0.29/0.74 = 0.96 \quad \text{Equation 49}$$

The molten fraction for D7 is expressed as:

$$1 - \frac{\text{KCl mole fraction for D}_7}{\text{eutectic K}_2\text{SO}_4 \text{ mole fraction}} \quad \text{Equation 50}$$

$$1 - 0.89/0.26 = 0.42 \quad \text{Equation 51}$$

D6 and D7 are 96% and 42% molten at eutectic temperatures respectively. The higher damage rates of D6 than D7 corresponds with the calculated deposit molten fractions, as alloys exposed to D6 will experience a higher molten deposition flux.

5.2.2.2 Comparison of deposits', D1, D2, D3, D4 and D5, corrosion damage influences on T91 and 347FG

The corrosion influences of deposits D1-D5 on T91 and 347HFG were compared following sample exposures at 600°C in WWF test gas conditions. From **Figure 5-29**, the corrosive damage of T91 influenced by the deposits at 600°C and at 1000 hours in WWF test conditions, increase as:

$$D1 < D2 < D3 < D4 < D5$$

While for 347HFG:

$$D1 < D2 < D4 < D5 < D3$$

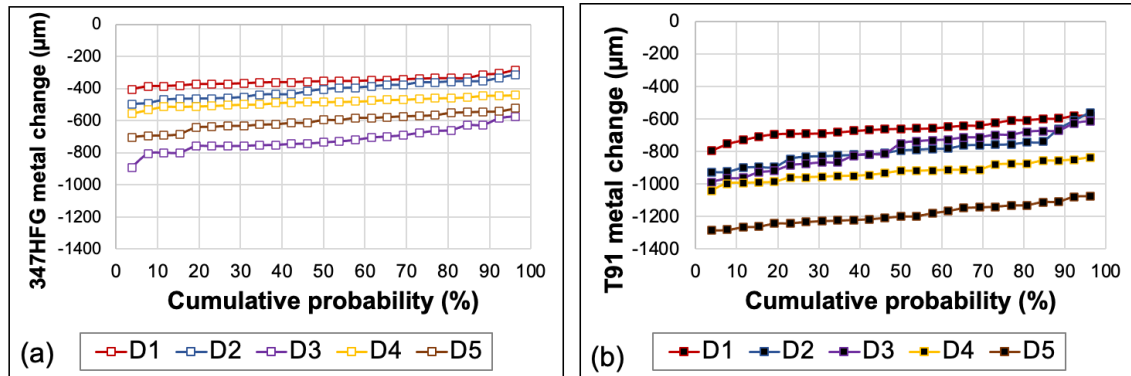


Figure 5-29: Metal surface changes of (a) 347HFG and (b) T91 samples exposed to deposits D1, D2, D3, D4 and D5 at a deposition flux of 100 µg/cm²h and at 600°C for 1000 hours in WWF test gas conditions

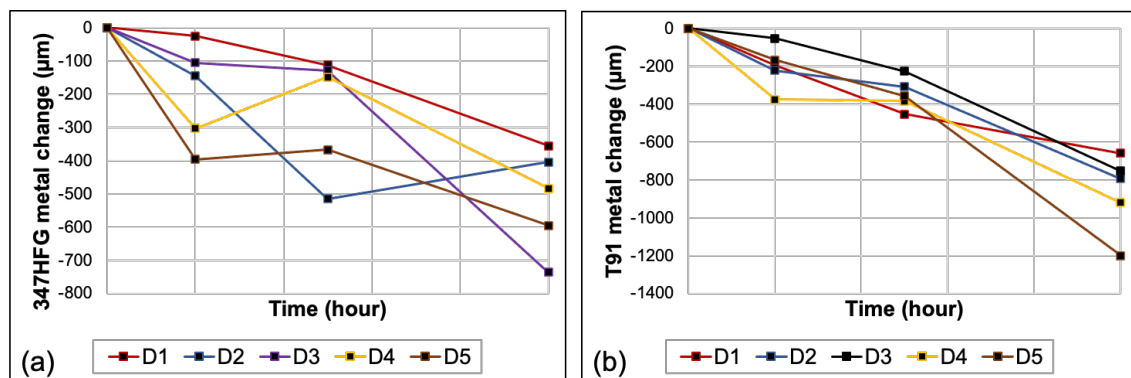


Figure 5-30: Metal surface change trends of (a) 347HFG and (b) T91 samples at 600°C exposed to deposits D1, D2, D3, D4 and D5 in WWF test gas conditions at a deposition flux of 100 µg/cm²h

Figure 5-30 presents the metal loss trends with exposure for the alloys coated with the WWF deposits corroded in WWF test gas conditions at 600°C. The order of deposit corrosiveness at 1000 hours (Figure 5-29) differs from that observed at the other, shorter, exposure times. As such, to simplify the discussion, the corrosion damage influences of the deposits are considered relative to that of D1 (WWF base deposit).

5.2.2.2.1 Corrosion trend within the KCl-K₂SO₄-Na₂SO₄ deposit systems D1, D3 and D5

In **Figure 5-30**, the median metal losses of 347HFG-D5 and 347HFG-D3, which consist of the same alkali metal salt components (KCl, K₂SO₄ and Na₂SO₄) at different chemical ratios), exceed 347HFG-D1 at each exposure time. At 1000 hours, the least metal loss of T91 is seen for the D1 exposure sample.

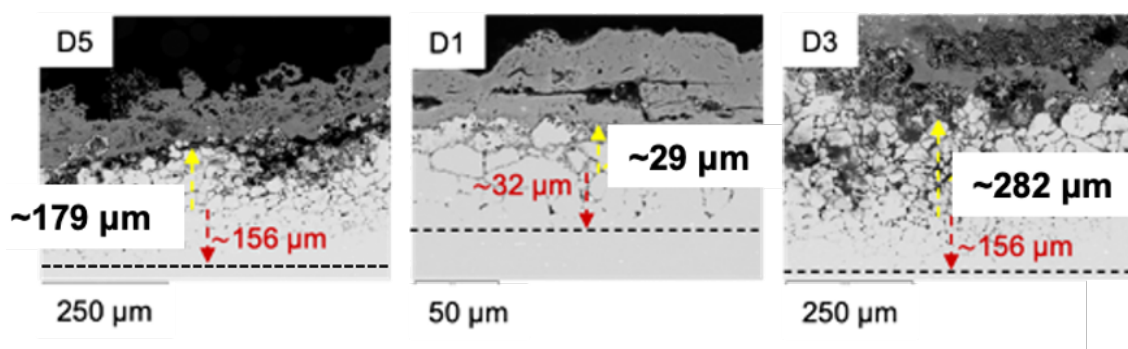


Figure 5-31: BSE images for 347HFG samples exposed to deposits D5, D1 and D3 (KCl-K₂SO₄- Na₂SO₄ deposit systems) at 600°C in WWF test gas condition for 1000 hours

The BSE images in **Figure 5-31** also confirm greater sound metal penetration depths for the D5 and D3 exposed 347HFG samples. At 1000 hours, metal loss is most severe for T91-D5. However, the risk of scale delamination increases with exposure time as the scale thickness increases. It could be that the scale loss of T91-D5 may have permitted the comparably high metal loss rate occurring at 1000 hours exposure (**Figure 5-30**). Though the metal loss of 347HFG-D5 is at least twice that of 347HFG-D1 at all exposure times, D1 and D5 influence comparable T91 metal loss at 200 and 500 hours.

The difference in the corrosive influence of deposit D1 and D5 on T91 and 347HFG may be explained as follows:

i. Corrosion exposures increase with the amount of potentially corrosive species:

The alkali metal salt concentration, which may be considered as the most corrosive fraction, in each 100 µg/cm²h deposit flux for D1 and D5 are:

18 µg-KCl, 28 µg-K₂SO₄ & 22 µg-Na₂SO₄ (32 µg -CaSO₄) for D1

16 µg-KCl, 38 µg-K₂SO₄, 31 µg-Na₂SO₄ (14 µg -CaSO₄) for D5

The alkali metal salt composition of D3, which contains no Ca salt, is already listed in (**Table 4-6**).

Table 5-2: Alkali salt percentages (of overall alkali salt content) in deposits D1 & D5

	KCl	K ₂ SO ₄	Na ₂ SO ₄
	mol.% of alkali salt		
D1	42.9	28.6	28.6
D5	32.6	33.7	33.7

In summary, the alkali metal salt fraction of D5 (86%, bal. CaSO₄) and D3 (100%) is higher than that of D1 (69%, bal. CaSO₄). The CaSO₄ component in D1 and D5 reduce the corrosive component of the deposit flux (**Table 5-2**), as CaSO₄ is mostly retained in deposit regions with no notable presence along grain metal/scale interface or grain boundaries (**Section 5.2.1.1** and **Section 5.2.1.1.2**).

ii. Corrosion component flux increase with molten alkali salt fractions:

The melting temperature region existing for these deposits have been located on the KCl-K₂SO₄-Na₂SO₄ equilibrium ternary phase diagram in **Figure 5-33** (based on the alkali metal salt compositions in **Table 5-2**). The contour lines closest to

D5 and D1 are described by a $\text{Na}_2\text{SO}_4\text{-K}_2\text{SO}_4$ mixture which, according to Niu et al. [173], is $\text{K}_3\text{Na}(\text{SO}_4)_2$ and exists in liquid phase at temperatures as low as 439.3°C [173]. Na-K-S interactions have been observed at regions of the $\text{KCl-K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ deposit exposed samples (exposed under WWF gas conditions at 600°C), as demonstrated by sample 347HFG-D1 (**Figure 5-22**). T91-D3 (**Figure 5-32**) shows Na-K-Cl rich sections within scales which have neighbouring/interlaying S-rich sections, possibly linked to a molten $\text{K}_3\text{Na}(\text{SO}_4)_2$ phase formed by the interaction of KCl with Na-sulphate salt as described in **Equation 47**.

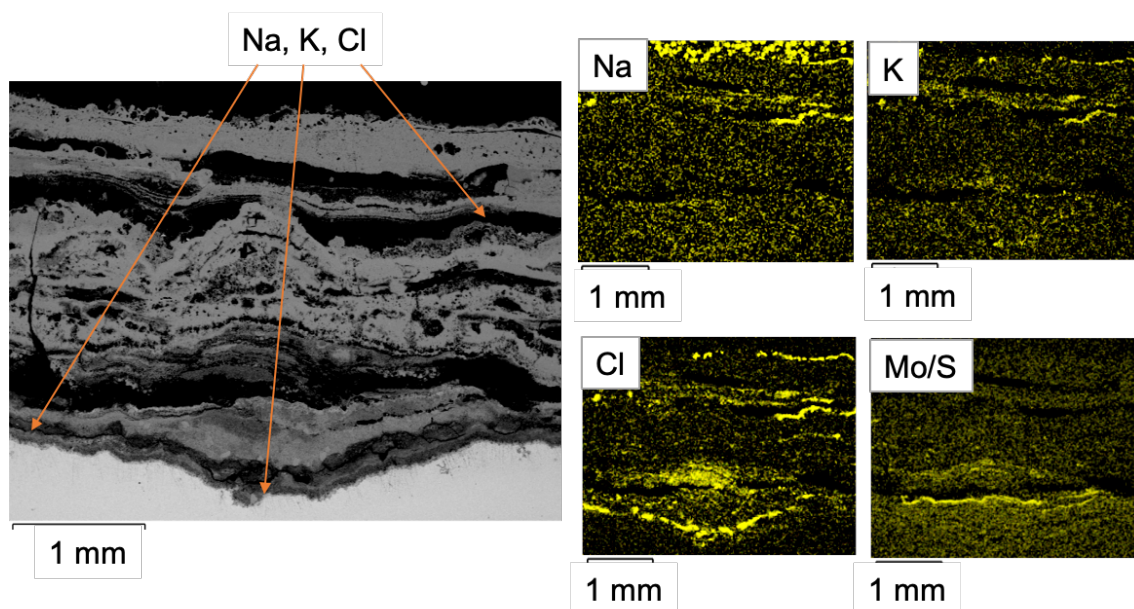


Figure 5-32: BSE/EDX image for T91-D3 (deposit flux $100 \mu\text{m}/\text{cm}^2\text{h}$) exposed at 600°C in WWF test gas condition for 1000 hours

In **Figure 5-33**, D5 and D1 are positioned (alkali metal salt compositions) on two successive contour lines of 25°C difference [106], [173]. D1 is positioned on the lower temperature contour, suggesting a higher molten fraction of D1 exists compared to D5 at the test temperature. This reduces the corrosive influence of D5 compared to D1, though the higher alkali metal salt content of the former deposit increases corrosive exposures, as earlier mentioned (point i.

above). This may explain the nearness in the corrosion extents imposed by both deposits at 200- and 500-hours exposure.

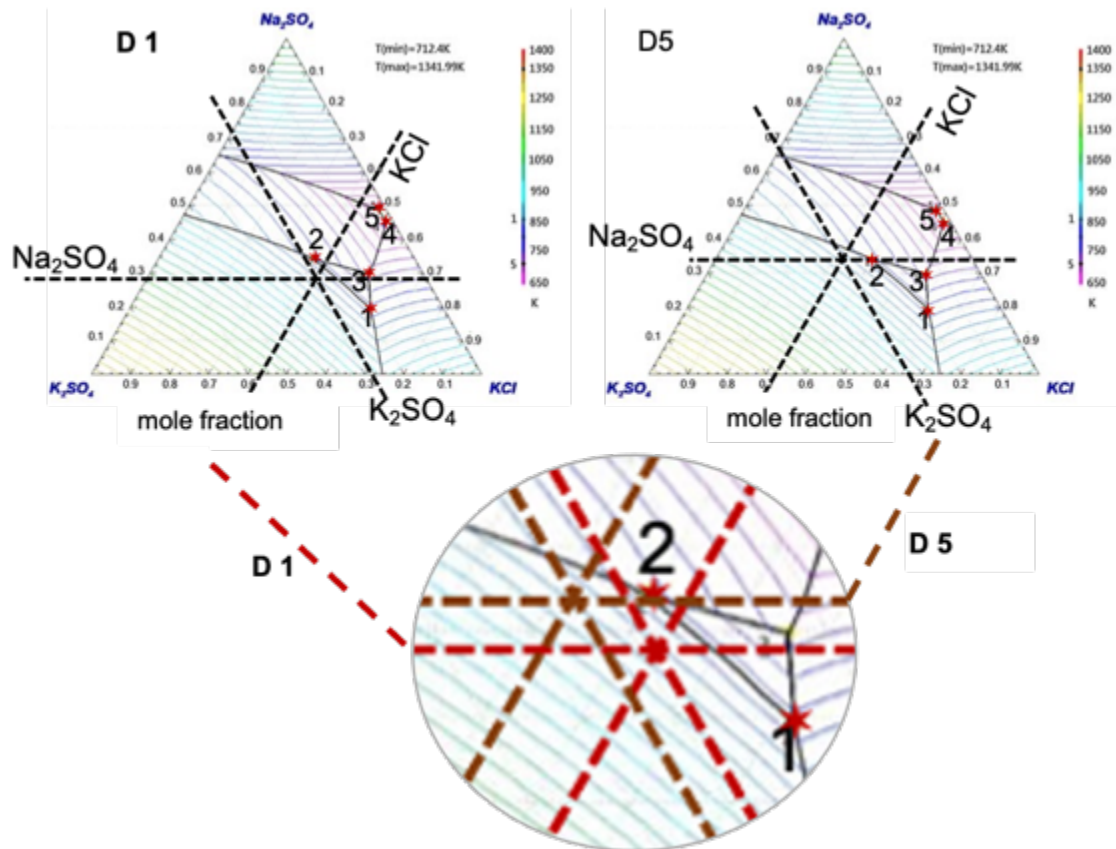


Figure 5-33: Deposits D1 and D5 composition fitting on the K_2SO_4 -KCl- Na_2SO_4 ternary equilibrium phase diagram. The temperature scales are in Kelvin (K). Contour lines represent 25°C increments [106], [173]

iii. Grain boundary penetration depths increase with Na deposit content

The increased Na content in deposit D5, however, may assist further penetrative attack of 347HFG (the role of Na is discussed in **Section 5.2.1.2.2**). The sound metal damage response of 347HFG is expected to be more sensitive (compared to that of T91) to the Na species concentration difference between deposit D1 and D5, as demonstrated in **Figure 5-31**.

The difference in the corrosive influence of deposit D1 and D3 on T91 and 347HFG may be explained as follows:

i. Corrosion exposures increase with the amount of potentially corrosive species:

D3 consists of 100% alkali metal-based salts, which is higher than that of D1 (69%). The corrosive deposit flux is thus higher for samples coated with D3.

ii. Corrosive component flux increase with molten alkali salt fraction, but the evaporation of deposit components reduces such flux:

D3 is positioned much further on from D1 (alkali metal species) on the eutectic phase diagram (**Figure 5-34**). The former deposit, possibly consisting of pyrosulphate ($K_3Na(SO_4)_2$, **Equation 47** [173]) molten phase, lies much closer to a lower temperature eutectic region ($<478^\circ\text{C}$), whereas D1 is positioned at a higher melt temperature region ($555.5\text{--}594.3^\circ\text{C}$). Metal surface loss however remains lower for T91-D3 compared to T91-D1 and also T91-D5 at 200 and 500 hours.

A possible explanation may be a case of higher evaporation rates existing for D3 at the test temperature (600°C). If this were the case, the metal/deposit interaction period is reduced for this deposit, compared to D5 and D1. The latter two deposits, however, are closer to eutectic temperatures which are just below the test temperature, indicating that higher melt fractions would indeed exist for both deposits compared to D3.

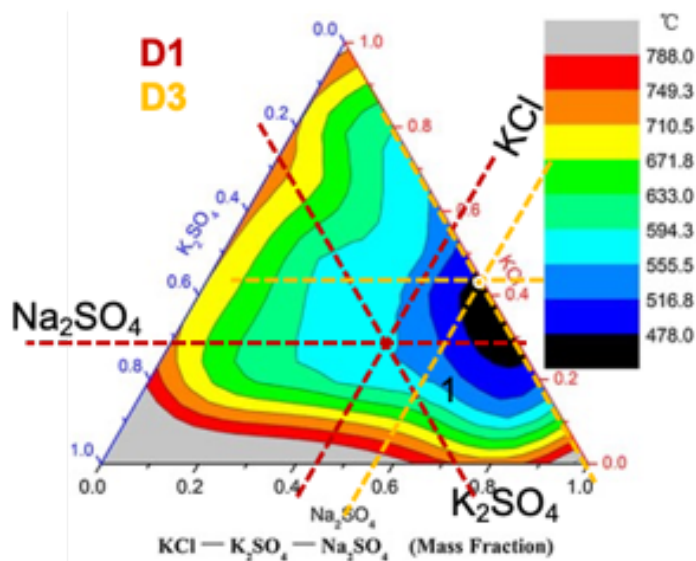


Figure 5-34: Deposits D1 and D3 composition fitted on the K_2SO_4 -KCl- Na_2SO_4 ternary equilibrium phase diagram. Adapted from [173]

5.2.2.2.2 Corrosion trend within the KCl- K_2SO_4 - Na_2SO_4 deposit system, D1 and KCl- Na_2SO_4 deposit system, D4

D4 causes greater metal loss on T91 and 347HFG than D1 at most exposure times at 600°C and thus is more damaging than the latter deposit (**Figure 5-30**). Three explanations are proposed for the greater corrosivity of D4 than D1:

i. **Amount of potentially corrosive species increases corrosion exposure:**

Similar reasons given for D3. (**Section 5.2.2.2.1**)

ii. **Grain boundary penetration depths increase with Na deposit content**

The higher Na-alkali metal content of deposit D4 (50 mol.%) compared to D1 (20 mol.%) may have favoured higher sound metal penetration rates as discussed in **Section 5.2.1.2**

iii. **Corrosive component flux increase with molten alkali salt fraction**

In **Figure 5-35**, the D4 composition is positioned within a significantly lower melting point range (478-516°C) of the K_2SO_4 -KCl- Na_2SO_4 equilibrium ternary phase system than D1 (556-593°C). It is thus likely that melting may be more

significant under the D4 exposure condition compared to that of D1. Evaporation may, however, be lower for D4 compared to D3 under similar conditions at 600°C.

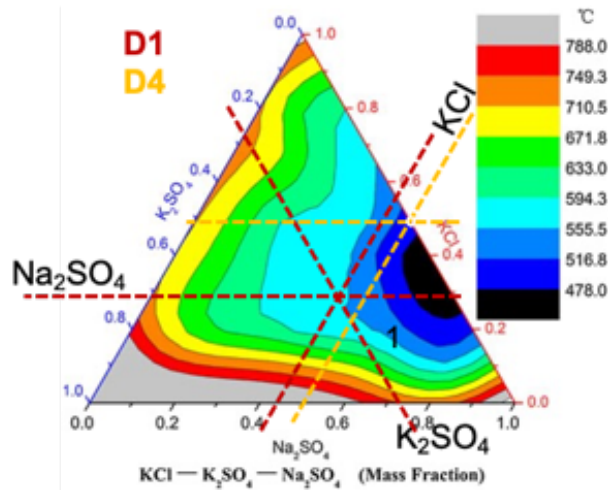


Figure 5-35: Deposits D1 and D4 composition fitting on the K_2SO_4 -KCl- Na_2SO_4 ternary equilibrium phase diagram [173]

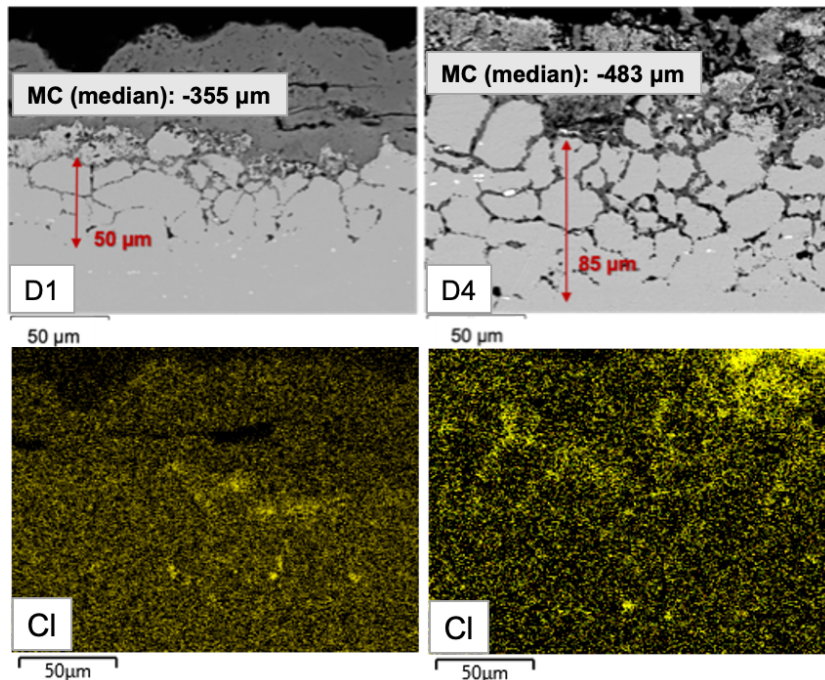


Figure 5-36: BSE/EDX showing chloride attack at grain boundary regions of 347HFG-D1 (left) and 347HFG-D4 (right) at 600°C in WWF test gas conditions

iv. Chloride attack may increase with deposit chloride content

Another notable feature of deposit D4 (50 mol.% chloride) is its higher chloride content compared to D1 (30 mol.% chloride) which may also increase chloride damage. For example, pitting is more severe for T91-D4 (**Figure 4-51**) than for T91-D1 (**Figure 4-48**) and chloride damage is more penetrative for 347HFG-D4 than for 347HFG-D1 as illustrated in **Figure 5-36**.

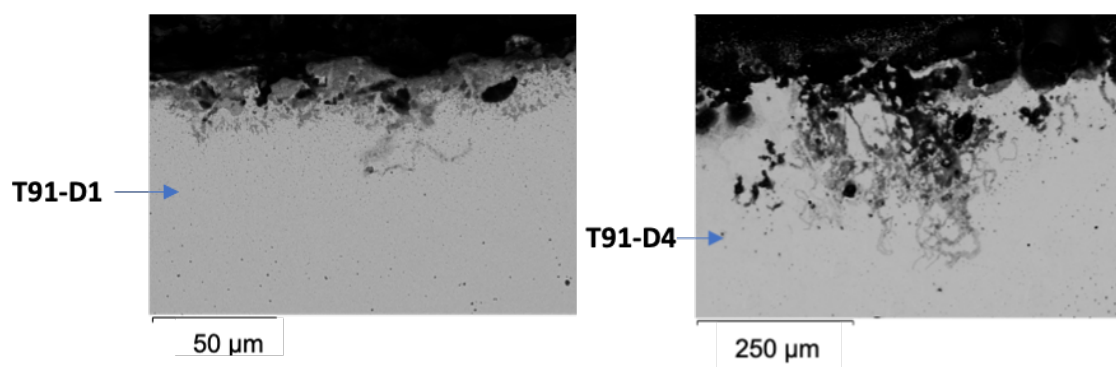


Figure 5-37: BSE image of cross-sectioned T91 samples covered with deposit D1 and D4 at 100 µg/cm²h following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Images were captured at two magnifications for both alloys

5.2.2.2.3 Corrosion trend within the KCl-K₂SO₄- Na₂SO₄ deposit system, D1, and KCl-Na₂SO₄-NaCl deposit system, D2

The generally higher corrosion damage of D2 compared to D1 for both alloys (**Figure 5-30**) may also be explained accordingly:

i. Amount of potentially corrosive species increases corrosion exposure:

Similar reasons given for D3 (**Section 5.2.2.2.1**).

ii. Grain boundary penetration depths increase with Na deposit content:

The higher Na-salt content of deposit D2 (52 mol.%) compared to D1 (20 mol.%) may have favoured higher sound metal penetrative rates as discussed in **Section 5.2.1.2**

iii. Chloride attack may increase with deposit chloride content:

Another notable feature of deposit D2 is its higher chloride content (52 mol.% chloride) compared to D1(30 mol.% chloride) which may also increase chloride damage.

Though the composition for D2 is closest to that of D4 (**Table 4-6**), the median metal loss of 347HFG-D2 is 100 μm greater than that of 347HFG-D4 at most exposure times. T91 corrosion is however less sensitive to the chemistry differences between both deposits. Further testing may be required to investigate 347HFG corrosion responses to Na/K salt ratios in such deposits.

5.2.2.3 Evaporation rates of deposits D1-D5: comparison of trends with corrosion test data

To establish any correlation between the evaporation rates of the WWF deposits and their damage severities, the deposit mass loss rates were studied by TGA (**Section 3.4**). **Figure 5-38** presents the weight change profiles for deposits D1-D5 occurring at 600°C. As explained in **Section 4.3**, the data presented in **Figure 5-38** have been extracted from mass changes occurring at the target temperature following ~5 mins at this temperature to avoid data influenced by buoyancy occurring during temperature ramping. As such, mass changes are relative to weight at the nominated temperature which in this case is 600°C.

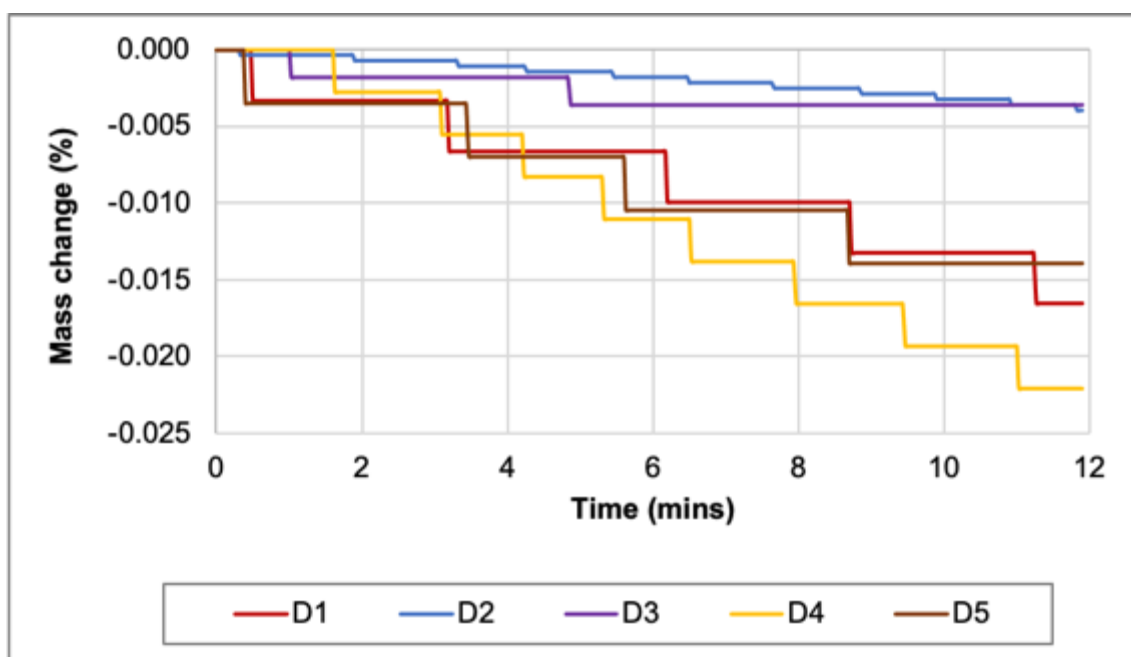


Figure 5-38: Deposits D1, D2, D3, D4 and D5 mass change profiles occurring at 600°C in N₂

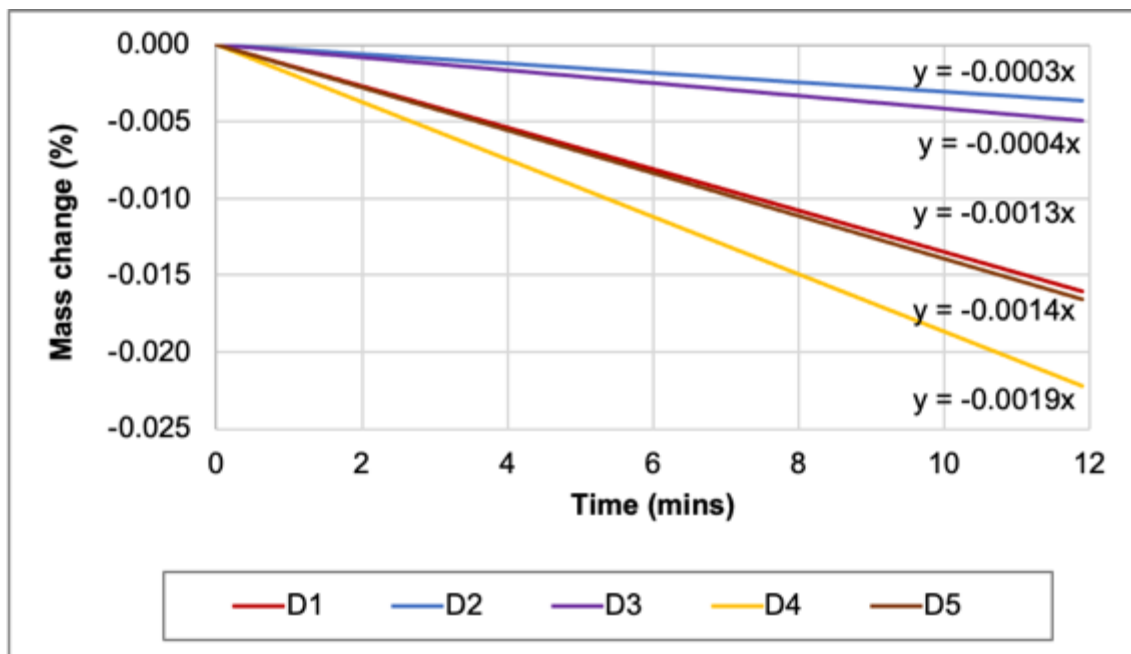


Figure 5-39: Deposits D1, D2, D3, D4 and D5 mass change (linear progressions) at 600°C in N₂

Figure 5-39 presents the deposit mass change linear progressions and equations. These progressions have enabled the determination of the mass change rates. The mass change rates are the coefficients, 'x', of each equation and are negative for the five samples, indicating that evaporation occurred for the five deposits at 600°C in N₂. Though the evaporation rates may not be truly reflective of the conditions experienced by the deposits during corrosion testing (under HGB, APR and WWF test gas exposures), mass changes would also be expected to occur under test gas conditions as deposit components will interact with gas phase species [161], [176]. In increasing order of negativity, the deposits evaporation rates may be ranked as:

$$D2 < D3 < D1 < D5 < D4$$

Evaluating the deposits' corrosion ranking against evaporation rates ranking, the damages experience by the deposit exposed alloys (**Figure 5-30**) show there may be some correlation between corrosion influence and evaporation rates at 600°C for D1, D4 and D5 on 347HFG at all corrosion exposure hours. Also, the similarities in corrosion damage extents experienced by T91-D1 and T91-D5 correspond with their similar evaporation rates (**Figure 5-39**). There are, however, no correlations seen between the corrosivity of D3, D2 and D1 on both alloys and their evaporation rates.

The lack of correlation may be explained by the limitations of the mass loss analysis which has only reflected the loss of volatiles in N₂. The deposit melt fractions, which may show better correlation with metal loss trends (as discussed in **Section 5.2.2.2.1** and **Section 5.2.2.2.2**), cannot be determined by this method. The evaporation rate investigation (**Figure 5-39**) however supports the discussion that molten phases do exist at 600°C.

The direction of mass changes (evaporation or condensation) is, however, difficult to predict where deposits are exposed under test gas conditions. The vapourised chloride may interact with SO₂ (in test gas) and condense. With sulphate salt being denser compounds than their chloride equivalent, a weight gain can occur. The condensation of alkali metal sulphates on the sample however is controlled by mass transfer rates and influenced by the gas flow rates. Whatever the mass change however (loss or gain), it is certain that chemical changes have occurred.

It is not understood why the evaporation rate of D3 would be lower than that of D1, given that the melt region for D3 is, at least, 100°C less than that of D1 (**Figure 5-34**). The higher corrosion influence of D1 compared to D3 suggests evaporation rates should indeed be higher for D3. The gas and scale conditions may however interfere with the decomposition/evaporation of deposit species.

The confirmation, by TGA, of mass loss occurring at 600°C in N₂, however, draws conclusion that the temperature is high enough for evaporation and thus lower melting point mixtures are likely to occur within the Na-K deposits in the absence of alloy scale (**Figure 5-28**).

Mass loss analysis of the K-cation deposits D6, D7 (HGB fuel category) and D8 (APR fuel category), however, suggested no evaporation had occurred at 600°C under N₂ conditions. A longer exposure time may be necessary to conclude, though these results show that lower melting points will exist in wood-based deposits compared to non-wood based.

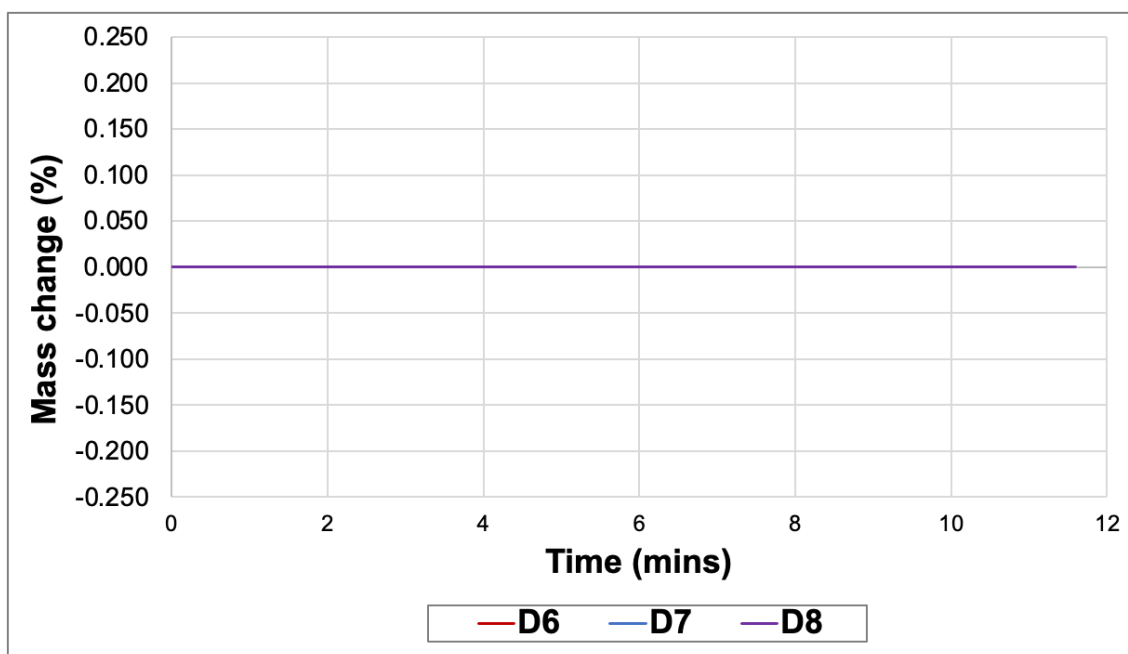


Figure 5-40: TGA of deposits D6, D7 & D8 at 600°C in N₂

5.2.2.4 Summary

The corrosion rates and mechanisms experienced by the K-cation (sulphate/chloride) deposit exposed T91 and 347HFG samples, under HGB test gas conditions at 600°C, have been evaluated in **Section 5.2.2.1**. Comparisons have been made for D6 and D7 corrosive effects, employing the same deposition flux, 100 µm/cm²h, and exposure durations (1000, 500 and 200 hours).

Li et al. [161] linked the chloride level of deposits to their thermogravimetric derivative curves, suggesting higher evaporation rates occur with increasing KCl content for KCl/K₂SO₄ mixtures. This PhD work however has demonstrated that at 600°C, D7, which represents the HGB fuel category at a chloride content of

0.41-Cl wt.% (ar), produces less damage than D6 which represents a lower chloride level of 0.18-Cl wt.% (ar) for the HGB fuel category. The KCl/K₂SO₄ phase diagram (**Figure 5-28**) has proved more accurate in explaining the higher corrosivity of D6 (69/31 mol.% KCl/K₂SO₄) compared to D7 (89/11 mol.% KCl/K₂SO₄) by predicting a higher molten fraction of D6 (96%) compared to D7 (42%).

The corrosion rates and mechanisms experienced by the multi-cation (sulphate/chloride) deposit exposed T91 and 347HFG samples under WWF test gas conditions at 600°C have been evaluated in **Section 5.2.2.2**. The deposition flux were maintained at 100 µm/cm²h, and exposure durations at 1000, 500 and 200 hours for each sample.

The extent of corrosion experienced by the multi-cation deposit exposed samples generally correspond with the deposit melt temperature profiles located on ternary phase diagrams, where greater corrosion (sound and/or surface metal depletion extent) is encountered for samples exposed to deposits able to form lower temperature melt mixtures.

Corrosion data show that composition variations occurring within the multi-cation deposits, and thus within the WWF category, will influence a wide range of fireside corrosion rates. The median metal loss differences between samples exposed to deposits D1-D5 have ranged up to 500 µm for 347HFG at all exposure hours. This is a greater range than observed for T91 (median metal loss differences between samples are within 400 µm at 200 hours and 300 µm at 500 hours; **Figure 5-30**). The corrosion of 347HFG is thus more sensitive to the varying deposit chemistries than T91 in WWF firing conditions, although greater metal loss (greater than 347HFG) is encountered for most T91 samples.

Such ranges in corrosion extents occurring within the WWF category deposits can be problematic for fuel combustion operations which rely on estimated corrosion rates for predicting the operational lives of steels. The challenge arises where WWF chemical compositions vary with waste streams. This research has shown that increasing Cr and Zn contaminant levels in WWF

will increase the fireside corrosion risks. So will the increase in Ca and Na fuel content.

Agreeing with Pettersson et al. [115] (**Section 2.5.3.3**), cations may play a more significant role in biomass/waste fireside corrosion encounters than anions as commonly concluded. Furthermore, changes to the anion compositions of deposits do not influence corrosion damages as much as variations in the alkali metal concentrations do. As observed for the single cation (K-cation) deposit systems, the higher chloride content deposits (46-53 mol.% chloride; D2, D3 and D4) do not always influence greater corrosion rates than the lesser chloride content deposits (30 mol.% chloride- D1 and 29 mol.% chloride-D5; **Table 4-6** and **Figure 5-30**). Chloride contents of fuels may thus be insufficient for ranking their corrosion tendencies in biomass/waste firing plants.

5.2.3 Discussion into temperature's influences on the corrosive behaviours of deposits

The metal change responses of T91-D1, 347HFG-D1, T91-D6 and 347HFG-D6 at 500, 550 and 600°C, exposed under WWF test gas conditions while maintaining a deposition flux of 100 $\mu\text{g}/\text{cm}^2\text{h}$, have been presented in **Section 4.2.2.2** and **Section 4.2.2.3**. **Figure 5-41** compares the metal loss responses to time with changing temperature from 600°C (left) to 550°C (middle) to 500°C (right).

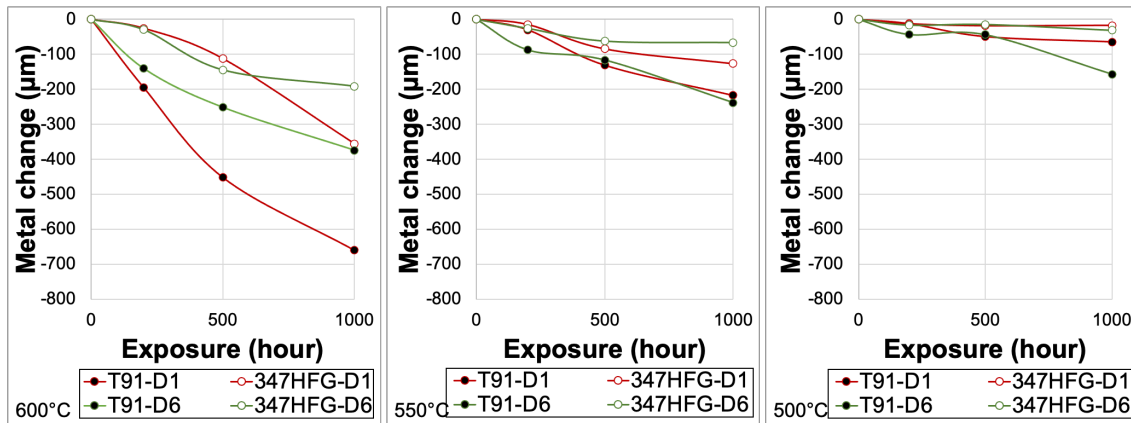


Figure 5-41: Metal surface changes (median values) of T91 and 347HFG samples exposed to D1 and D6 in WWF test gas as a function of time. Graphs are arranged from left to right in order of temperature; 600, 550 and 500°C respectively

As the exposure temperature is lowered, D1 becomes less corrosive, to T91, than D6. Following 1000 hours exposure (**Figure 5-41**):

- At 600°C, the median metal surface loss for T91-D1 is 659 μm and that of T91-D6 is 374 μm .
- By 550°C, the median metal surface loss for T91-D1 (218 μm) and T91-D6 (238 μm) are within comparable range.
- By 500°C, metal surface loss for T91-D6 (157 μm) is greater than for T91-D1 (65 μm).

A similar metal loss trend is observed for the exposed austenitic steels:

- At 1000 hours, the median metal loss gap between 347-HFG-D1 and 347HFG-D6 narrows as the temperature is reduced from 600°C to 550°C (**Figure 5-41**).
- By 500°C, similar median metal surface damage extents are experienced by both 347HFG samples exposed to either deposit (18 μm for 347HFG-D1 and 31 μm for 347HFG-D6).

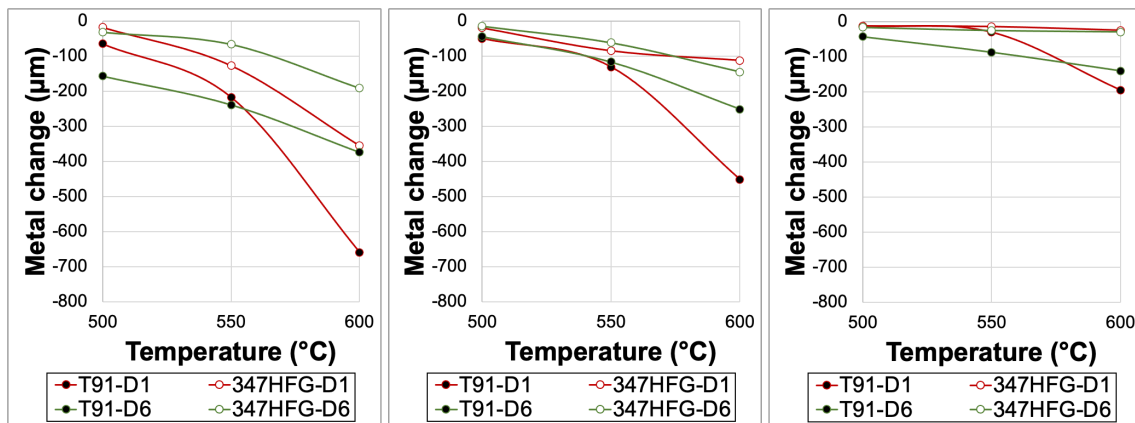


Figure 5-42: Metal surface changes (median values) of T91 and 347HFG samples exposed to D1 and D6 in WWF test gas at 500-600°C. Graphs are arranged from left to right in order of exposure time; 1000, 500 and 200 hours respectively

The arrhenius rate of the metal change for the samples (graphs positioned in decreasing exposure hours from left to right) may be compared in **Figure 5-42**. T91-D1 experienced the most change at all exposure times. At 1000 hours exposure, the austenitic steel is also more sensitive to temperature changes under D1 exposure. The steepest metal change occurs at 500°C. The sharp metal loss of the D1 exposed samples at this temperature might indicate a change in corrosion mechanism. In this section, the corrosion influences of both deposits under varied temperature conditions are related to the phases of deposit and scale components likely to be existing at the test temperature.

5.2.3.1 Temperature stability of alkali metal-Cr scales

The thermochemical responses of deposits and scales influence corrosion rates as these deposit/scales may or may not be stable at the presiding temperature [114]. The melt temperature ranges of alkali metal chromate scales vary and are influenced by the presence of other species (**Table 2-2**). Such melts can occur within practical HX temperature ranges (450-600°C) [105], [114]. Where temperature conditions change, the thermochemical response of a component may also vary [33], [120]. Such variations may trigger changes in the corrosion rates and mechanisms.

As temperature is lowered, the molten fraction of a deposit is reduced, restricting the mobility of the deposit components and thus lowering corrosive exposures of the deposit. As expected, the metal damage reduced with falling temperature for both steels (**Figure 5-41**).

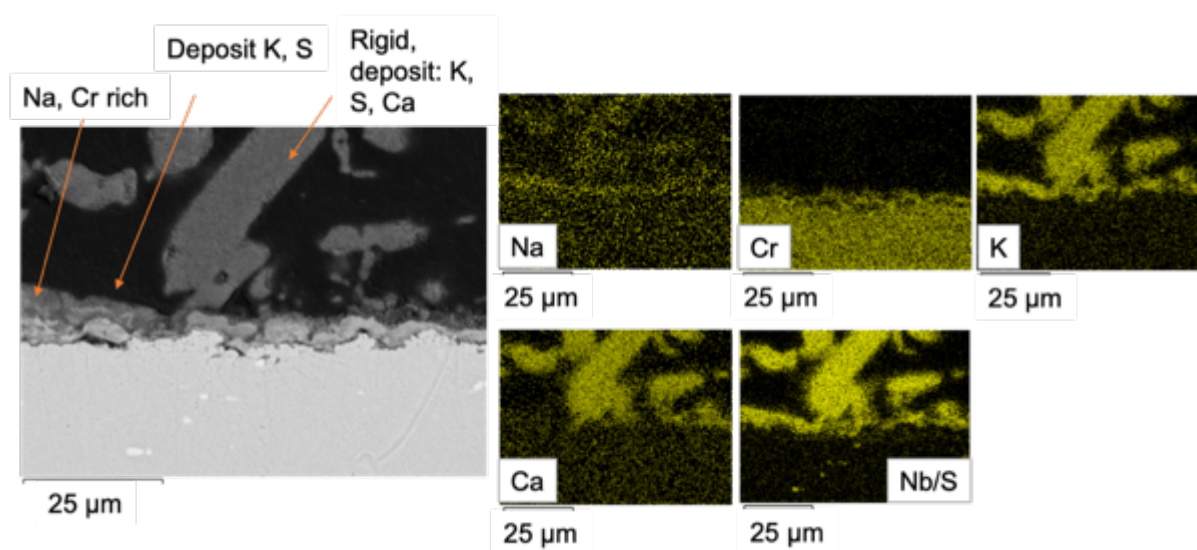


Figure 5-43: BSE/EDX images showing the likely presence of Na-chromate scaling on a 347HFG-D1 sample exposed for 500 hours in WWF test gas conditions at 500°C

The rate of decomposition of a K-Cr-O scale will exceed that of Na-Cr-O at 600°C given the same ambient conditions [114], [178]. Karlsson et al. [114] related the differences in decomposition rates to the different vapour pressures

of the corresponding hydroxides of the leaving group (discussed in **Section 5.2.1.2.1**). Also, at temperature conditions below melting points, scale decomposition reactions are not thermodynamically favoured [99]. K-Cr interactions have been difficult to identify on the EDX maps of the 600°C exposed samples (e.g. **Figure 5-18**), however, a Na and Cr containing zone is identified nearer the metal surface at 600°C (**Figure 5-19**).

By 500°C, Na and Cr are observed at the left side of the image in **Figure 5-43**. A K-Cr region may be present minimally at this temperature (**Figure 5-43**) for 347HFG-D1. This suggests that K species loss is still favoured at this temperature.

The melting temperatures of pure $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{K}_2\text{Cr}_2\text{O}_7$ are 592°C and 398°C respectively [107]. At 600°C, the temperature experienced by a $\text{Na}_2\text{Cr}_2\text{O}_7$ scale can favour a high molten fraction (9°C above m.pt.) of the scale. For a $\text{K}_2\text{Cr}_2\text{O}_7$ however, the vapour pressure exerted by the gas/liquid phase is relatively high [114], [179].

At test conditions of 500°C, $\text{Na}_2\text{Cr}_2\text{O}_7$ is 92°C below its melting temperature, thus lowering the test temperature from 600-500°C may influence a solidification of the scale. At 500°C, however, $\text{K}_2\text{Cr}_2\text{O}_7$ likely exists in a liquid/gas phase (102°C above m.pt). Reducing the test temperature from 600-500°C reduces the vapour pressure exerted by the $\text{K}_2\text{Cr}_2\text{O}_7$ scale, however, the existence of a solid phase of the scale is not likely at 500°C.

The reduced vapour pressure increases the liquid/gas ratio of the component. As such, at 500°C, a higher liquid fraction of the $\text{K}_2\text{Cr}_2\text{O}_7$ scale may exist compared to when at a temperature of 600°C. Where a combination of both alkali metal scale exists, as likely for the D1 exposed samples, a $\text{Na}_2\text{Cr}_2\text{O}_7$ scale may offer protection for the metal surface from corrosive components at 500°C. At 600°C, however, $\text{Na}_2\text{Cr}_2\text{O}_7$ may aid the sustenance of chloride attack (**Section 5.2.1.2.1**). The steeper metal loss slope occurring at 550°C for the D1 exposed sample (**Figure 5-42**) may signify a switch in phase (solid/liquid) of a $\text{Na}_2\text{Cr}_2\text{O}_7$ scale.

5.2.3.2 $\text{CaSO}_4\text{-K}_2\text{SO}_4$ role in fireside corrosion

At 600°C, Ca-K-S-O rich deposit regions were occasionally encountered on samples exposed to deposits containing Ca_2SO_4 (D1 and D5; for example, in **Figure 4-67**). The deposit features were fluid-like at this temperature, suggesting that some degree of melting had occurred during exposure. Nevertheless, Ca was retained within the deposit zones for those samples. At 500°C however, these deposit regions feature rigid structures (for example, in **Figure 5-43**). The SEM/EDX analysis suggest that the deposit components are retained in K-Ca-S-O crystalline structures, in line with [174] and as discussed in **Section 5.2.1.2.3**, during exposure at 500°C. A langbeinite may thus be present [175].

Figure 5-43 shows that, at 500°C, K_2SO_4 in D1 may:

- i. Partly exist as a fluid layer (having undergone melting) and also,
- ii. Associate with Ca in an unmelted state. At 500°C, the alkali metal is partially held in the crystalline structure.

By 600°C however, no rigid structures have been observed at the deposit region, indicating that both sulphates (K and Ca) in the deposit undergo some degree of melting at this temperature. As exposure temperatures are reduced, it is likely that CaSO_4 further inhibits the ability of K_2SO_4 to dissociate from the complex, as such limiting the ability for K_2SO_4 to interact at the lower temperatures with other deposit and scale components (e.g. in the formation of lower melting point eutectics with KCl and Fe_2O_3), or gas components (such as SO_2 for the formation of pyrosulphates; **Equation 17** [97]).

5.2.3.3 Summary

The corrosive influence of deposit D1 and D6 (compositions in **Table 4-6**) have been compared under WWF gas conditions at 600, 550 and 500°C. T91 and 347HFG show reduced corrosive damage under D1 and D6 exposure conditions with lowering temperatures (**Figure 5-41**). Tests also show that the

damage influence of D1 is more sensitive to temperature changes than that of D6.

Both Na-Cr and K-Cr associations are likely to have been present (following exposure, as observed by EDX) for the D1 exposed samples at 500°C (e.g. **Figure 5-22** and **Figure 5-43**). The presence of Na in biomass/waste fuels may, however, give some protection at 500°C exposures, when the Na-Cr scale formed is likely mostly solid. Such Na-Cr scales may hinder the migration of corrosive K species melts to a HX surface.

Molten fractions of $K_2Cr_2O_7$ (m.pt, 398°C) may exist at 500°C [114], whereas by 600°C, the vapour pressure exerted by this scale makes it unlikely to remain in solid or molten state [114]. Corrosion damage also occurs at 600°C when the K-Cr scales decompose. Deposits where K is the only cation may influence fireside corrosion damage in ways which are more predictable when temperature is varied between 500-600°C when compared to instances where both Na and K are present. The influence of K/Na ratios of deposits and their temperature sensitivities (regarding corrosion) needs further investigation for determining the corrosive damage ranges existing for WWF firing.

T91 at 550°C has demonstrated the steepest corrosion rate change in response to temperature changes when exposed to the multi-cation deposit. Fireside corrosion damage to low Cr steels up to T91's range have been attributed to scale losing protective properties [180]. This may, however, be viewed from the 'lack of' scale formation, as well as the 'decomposition of' scales already formed [114]. This work finds evidence of alkali metal-chromate scale formation on both steels (347HFG and T91) occurring at 500-600°C. The alkali metal-chromate scales formed by the alloys are suspected to be different, however, because the corrosion rates observed for the samples, which have been attributed to the melt properties of the scales, differ.

Table 2-2 lists the melting point of some alkali metal-chromate scales and eutectics which show varying melt temperatures. Within the 550°C range, where the corrosion rate of T91 exposed to the WWF deposit suddenly changes, a NaCl - Na_2CrO_4 eutectic melt occurs [106], [107]. Other alkali metal chromate scales

mentioned in the literature review (**Table 2-2**) have varying melting points. If different alkali metal chromate scales form on a sample, then scale decompositions should occur over a wider range of temperatures.

Ca-sulphate may impede corrosion rates, although across a wider temperature range than for Na salts, and via a different mechanism. It may be argued that the presence of Ca in fuels may also aid in the demobilization of K where both elements are present as salts on metal surfaces. EDX imaging of samples exposed between 500-600°C have confirmed K-Ca-S-O associations exist for K-Ca deposit exposed samples, suggesting the presence of a solid langbeinite structure in agreement with Tesfaye et al. [175].

5.2.4 Investigation of deposition flux effect on alloy damage

The T91 and 347HFG metal change effects of deposits D1 and D6 at varying deposition flux were investigated in **Section 4.2.2.1.2**. The exposure conditions are listed in **Table 3-3** (test TW3) and 500- and 1000-hour exposures samples were generated. The corrosion damage investigated are discussed in this section.

5.2.4.1 Comparing the corrosive damage extents of T91 and 347HFG in response to varying D1 and D6 deposition fluxes

Figure 5-44 represents the median metal loss trends (with varying deposition flux) where the minimum and maximum points display the metal loss range occurring on each metal's surface.

At 100 $\mu\text{g}/\text{cm}^2\text{h}$, both steels coated with D1 and D6 suffer the most severe localised damage ($>250\text{ }\mu\text{m}$ metal loss range); as the deposition flux is reduced, the metal loss ranges occurring for each sample is reduced ($<150\text{ }\mu\text{m}$ sample metal loss range). This indicates that the high deposition flux encourages pitting and thus the damage mechanisms influenced by such deposits are also dependant on the amount of deposit.

In power plants, HXs are required to survive for at least 100,000 hours of operation [24]. Laboratory testing for such a duration is impractical. As such, shorter duration tests which accelerate material damage are used to fit in laboratory time scales [102], [111], [113], [153], [176] (see **Section 2.6**). Such tests may hasten corrosion by increasing the exposure temperature, however, damage mechanisms are often temperature sensitive [116]. Another approach, adopted for this research, is to increase the applied flux of corrosive deposits.

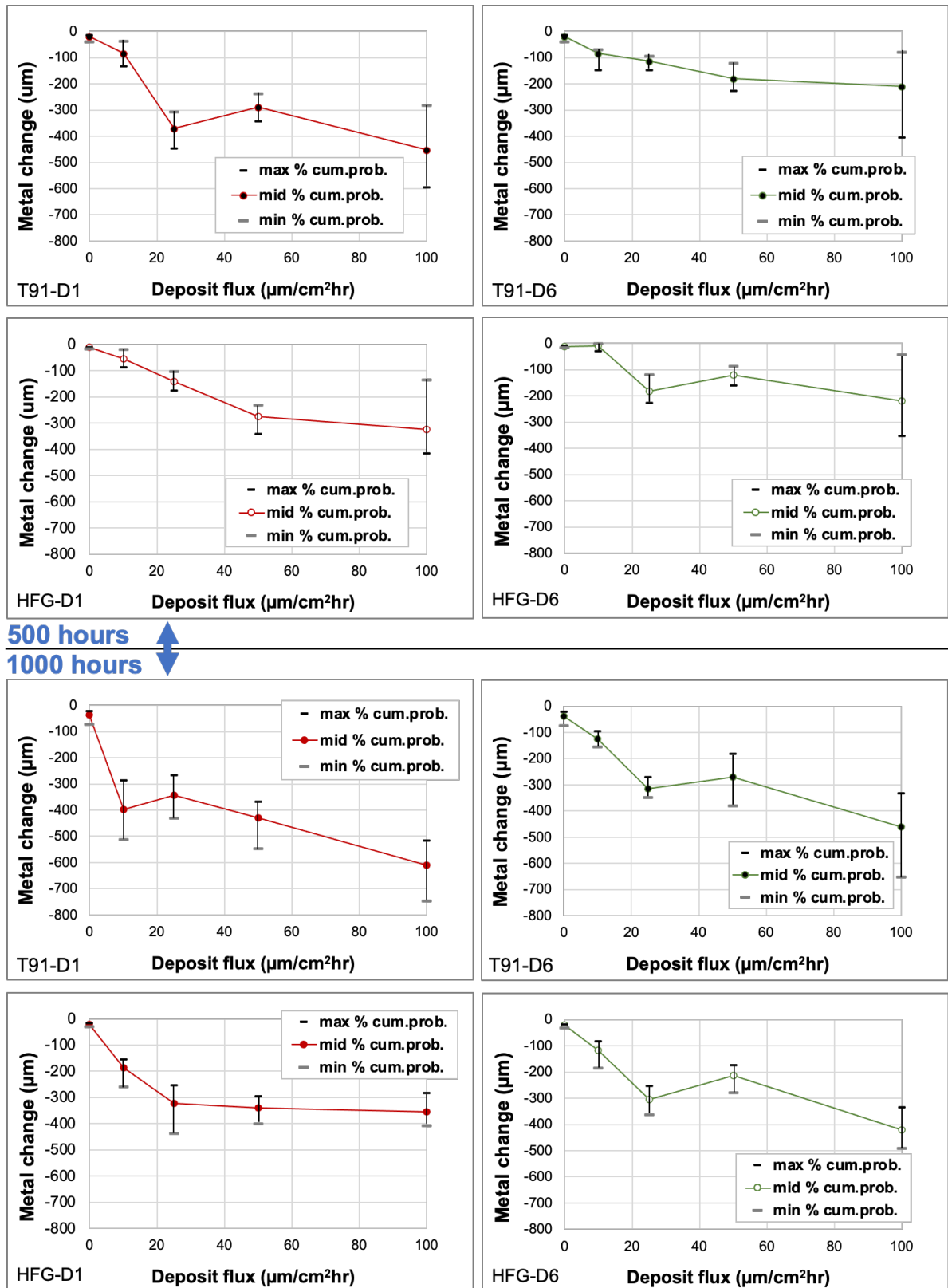


Figure 5-44: Deposits flux variation effect on metal change for T91 and 347HFG exposed to WWF test gas environment at 600°C

The latter approach allows testing at targeted power plant HX temperatures and enables exposures to similar deposit compositions and ambient gas conditions. A limitation for the increased deposit flux approach for inducing accelerated corrosion rates in laboratories may be where localised damage is partial to high deposition flux.

347HFG's corrosion rate (median metal loss) is steepest at deposition flux 0-25 $\mu\text{g}/\text{cm}^2\text{h}$ for both D1 and D6 exposures (**Figure 5-44**). As the deposition flux is increased, corrosion rate increments are smaller, meaning that the amount of deposit required to enable accelerated corrosion may be optimised at a lower value; especially where a change in corrosion mechanism attributed to higher deposition flux is to be avoided (e.g., above 50 $\mu\text{g}/\text{cm}^2\text{h}$ of corrosive components in the test conditions employed).

The influence of D1 deposition flux variation on T91's corrosion is most dramatic, compared to D6 exposure. By 50 $\mu\text{g}/\text{cm}^2\text{h}$, up to 75% (T91-D1) and 90% (T91-D6) of metal damage is already experienced by the alloy (relative to damage at 100 $\mu\text{g}/\text{cm}^2\text{h}$).

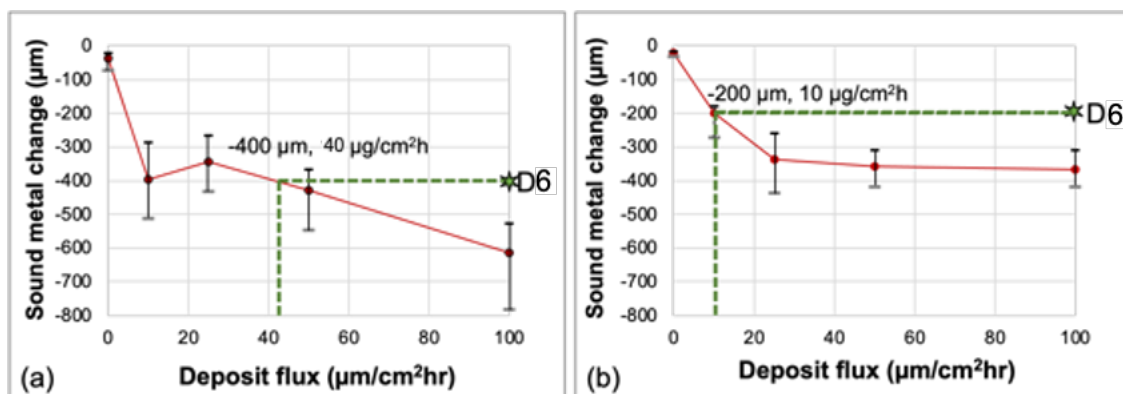


Figure 5-45: Sound metal changes of cross-sectioned (a) T91 and (b) 347 HFG samples exposed to deposit D1 at varying flux for 500 hours in WWF gas conditions at 600°C. Sound metal changes for the D6 deposit at a flux of 100 $\mu\text{g}/\text{cm}^2\text{h}$ plotted for comparison

From (**Figure 5-45**), the extent of metal damage of T91-D1 (400 μm) at a deposition flux of 40 $\mu\text{g}/\text{cm}^2\text{h}$ matches that of T91-D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$, demonstrating the greater impact of D1 compared to D6 in material damage.

5.2.4.2 Summary

Employing mass transfer rate calculations, Sanusi et al. (submitted for publication) compared the HX deposition flux of KCl released from firing WWF and HGB fuels. The KCl deposition rate was nearly 5 times greater for HGB firing per kg fuel. This range would be more where transfer rates were compared on a calorific output 'ar' basis as the WWF category has shown higher energy values (~ 14 MJ/kg LHV, ar; ~ 16 MJ/kg HHV, ar) than HGB fuels (~ 4 MJ/kg LHV, ar; ~ 6 MJ/kg HHV, ar) (**Figure 4-1**).

In practice, the HX deposition flux for WWF combustion is lower than that of APR and HGB [20]. As such, combustion plants experience lower corrosion rates where the former fuels are employed [20], [24]. However, at matched deposition flux, the deposit chemistries for WWF firing may cause greater damage than those of APR and HGB firing conditions.

The deposit compositions employed for these studies represent the corrosive fraction only, not considering the dormant ash deposit fraction. Simms et al. [38] employed a 92.5 wt.% fly ash, 7.5 wt.% corrosive component while investigating deposits' corrosion influences on alloys at 600°C. The fly ash represented the inert fraction of the deposit. The application flux of the potentially active deposit species, which were KCl and K_2SO_4 , were 5 and 2.5 $\mu\text{g}/\text{cm}^2\text{h}$ respectively. At 10% metal loss exceedance, a metal thickness loss of only ~ 20 μm for 347HFG was recorded, after being exposed for 1000 hours. In this research, only the corrosive condensates were considered for each deposit mix. A limitation to this approach may be increased localised pitting observed at the high fluxes which may not be the case if deposit fluxes were reduced.

Compared to target corrosion rates for HX materials in conventional combustion power plants (~ 45 $\mu\text{m}/1000$ hours [37]), the median metal loss

generated by these tests are high, even at lower deposition fluxes ($> 100 \mu\text{m}$ metal loss occurred at $10 \mu\text{g}/\text{cm}^2\text{h}$). Though other conditions such as temperature and flue gas compositions and flow rates contribute to these differences. Low corrosion rates in laboratory conditions may, however, result in smaller ranges of metal damage between deposits, making a comparison of deposits' corrosion influences difficult and likely subject to errors where metal loss differences are within error analysis range. The greater extents of damage enabled comparison of deposit corrosivity for varying exposure conditions in this work.

5.2.5 Investigation of the heat flux furnace corrosion test method

Corrosion damage occurring for T91 exposed to D6 in HGB gas conditions at 600°C have been compared for both furnace test methods (**Section 3.3** and **Section 3.5**) used in this research. This section highlights the similarities and differences between the corrosion data obtained, and challenges encountered using the novel air-cooled probe test method, and recommends design improvements for future research.

5.2.5.1 Metal thickness change difference between samples exposed in heat flux and isothermal furnace setups

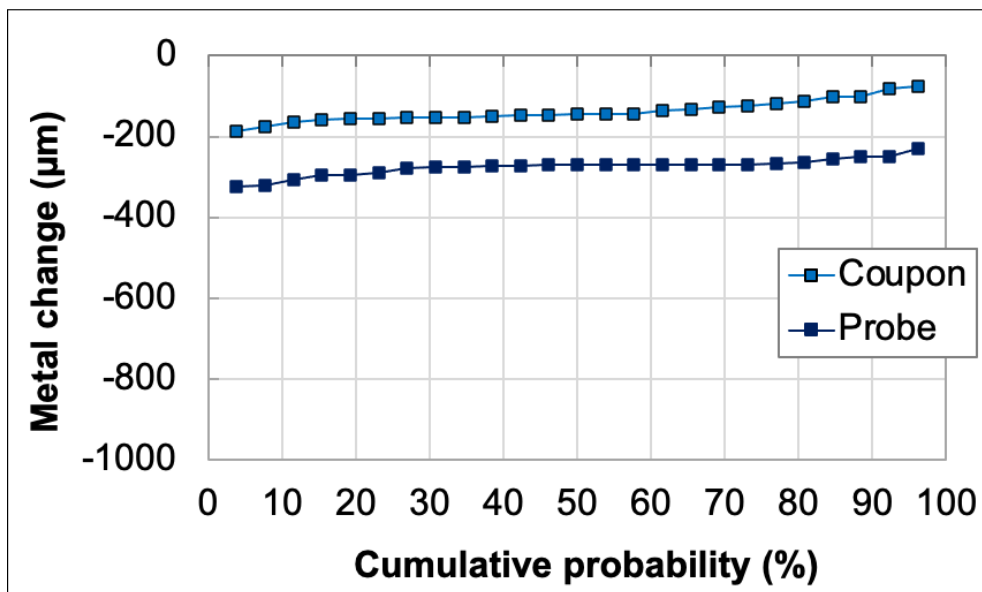


Figure 5-46: Comparing metal changes for probe (method, Section 3.5) and coupon (method, Section 3.3) T91 samples exposed to deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ for 500 hours in WWF test gas conditions at 600°C

Metal thickness loss occurring for the T91 probe sample exposed in the heat flux rig, was greater than occurred for the equivalent sample tested in the conventional vertical furnace, as illustrated in **Section 3.3**. The larger metal change for the probe sample followed the observations of significant scale loss

from sample during handling (between cycles) (**Figure 5-47**). If less scale loss had occurred, metal thickness losses may have been lower than those observed as there would be reduced reactant access to the metal (**Figure 4-110**), bringing the metal loss closer to that experienced by the equivalent coupon sample.

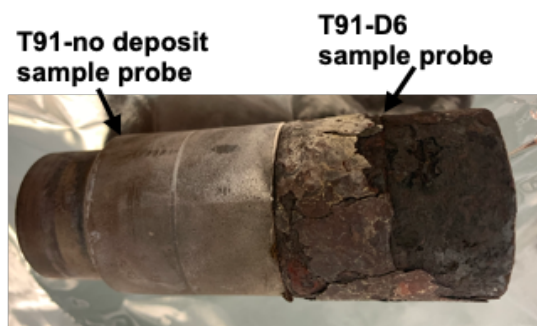


Figure 5-47: Scale fragmentation on the probe sample with deposit occurred with handling

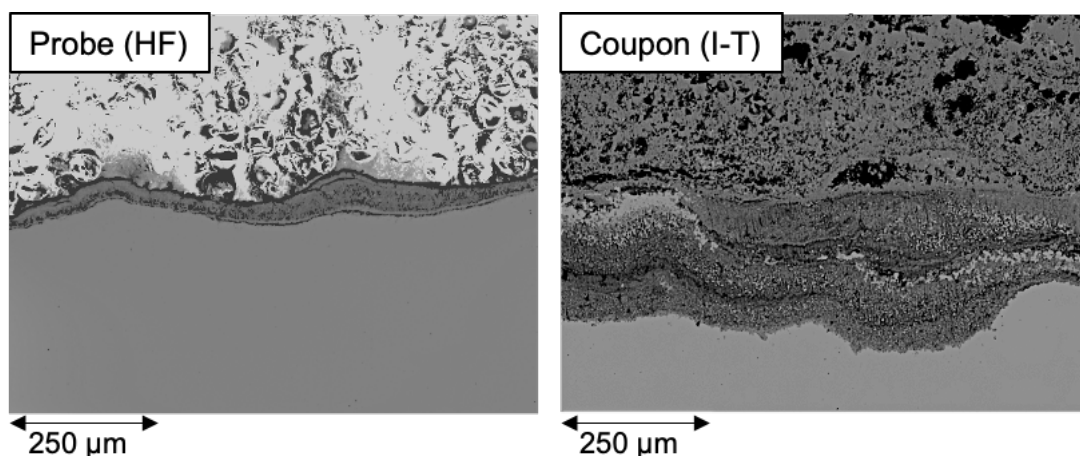


Figure 5-48: BSE images for the cross-sectioned T91-D6 (flux $100 \mu\text{g}/\text{cm}^2\text{h}$) heat flux (HF) and isothermal (I-T) exposure samples. . Exposed conditions are 600°C (fireside surface temperature) in WWF test gas for 500 hours. Resin region shown for the HF sample

The BSE images for both corroded samples can be compared in **Figure 5-48**. More localised damage on the isothermally exposed sample may have been influenced by scale cover, as corrosive components need to penetrate

further to the metal surface. The more evenly distributed damage on the heat flux exposed sample, however, may have been encouraged by the patchier scale cover. The difference in surface morphology for both samples may thus not be an indication that different damage mechanisms had occurred.

5.2.5.2 Recommendations for improving the probe setup design

On one end of the test sample, disconnecting the outer connection tube (**Figure 3-17**) (following an exposure cycle) required mechanical handling as corrosion products had built up where both samples connect (within the interlock). On the other end of the test sample, disconnecting the sample with no deposit (**Figure 5-47**) from the test sample was also problematic, although disconnection was not required as deposit recoating could proceed while both samples remained connected. Weight change measurements, however, were not possible as the combined weight of both probe samples exceeded the measurement limit of the digital scale employed. As such, the dried weight of salt required for the deposit recoat was measured then diluted for application on the test sample surface. As such, the deposit application flux was maintained.

The snug fit between the test sample and the outer tube was to prevent the mixing of the cooling air (in the inner tube) and test gas (outside the inner tube). Mixing could affect the probe surface temperature and corrode the inner surfaces of the tubes/probes, amongst a list of other issues that would invalidate the test (for probe setup, refer to **Figure 3-17** and **Figure 3-18**). An improvement to this model may consider a design which allows easier dismantling of the sample probe from the setup to reduce handling and thus minimise damage to scales. This could be achieved by:

- i. Reducing the interlock length of the alloy sample to reduce the metal overlap (**Figure 5-49**).

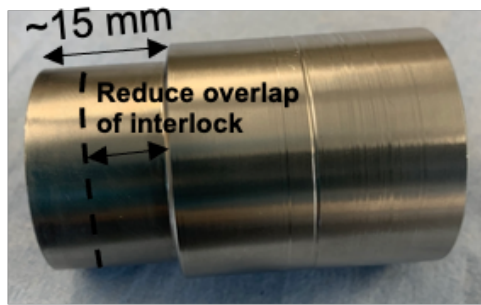


Figure 5-49: Reducing the overlap of probe interlock may facilitate dismantling of the probe setup

- ii. Create three sample probe positions instead of two such that the test sample sits between two uncoated (no deposit) samples and further away from the outer tubes. In this case, deposit recoat would be continued on the test (middle) probe sample even if stuck to the two samples at opposite ends. The outer setup tubes are less likely to stick to the uncoated samples.

If changing the probe design is not ideal, another recommendation is to test in less corrosive conditions such as by:

- i. Reducing corrosive salt flux
- ii. Lowering the test temperature
- iii. Reducing the test cycle lengths
- iv. Increasing the test gas flow rate to discourage corrosive recondensation onto the tube surface at/near the interlock.

5.3 The qualitative and quantitative descriptions of biomass/biomass waste fuel categories corrosion behaviours

This section links all discussions in this chapter to describe the fireside corrosion behaviours of biomass/waste fuel groups.

5.3.1 Formation of corrosive deposits when biomass/waste fuels are combusted

Section 5.1 discussed the elemental distributions occurring within four fuel categories, HGB, APR, IFW and WWF, relating their elemental compositions to their compound releases when combusted. Thermodynamic simulations of post-combustion compounds/species formed showed that relatively high Mg and/or Ca fuel contents in fuel inhibit the formation of Si-alkali metal complexes. This coincided with higher fractions of alkali metal sulphates and chlorides, forming post-combustion, for each fuel category.

The WWF category was uniquely identified as having Si levels similar to the total alkaline earth levels (Ca+Mg). This is typical with wood-based fuels [25]. This meant lesser Si-alkali metal complexes were formed for the WWF category and, subsequently, higher corrosive compounds were released (alkali metal sulphates and chlorides). A similar situation may be encountered for IFW fuels, however these fuels are generally low in Na. As such, corrosive species of concern may be predominantly K-salts. The corrosive deposits calculated for IFW are similar to those predicted for HGB and APR fuels, although at significantly lower concentrations (ten times less moles).

APR and HGB fuels are abundant in Si and P, enabling their associations with alkali metals, and subsequently, resulting in lower release fraction of corrosive (alkali metal) species during combustion. The emphasis is, however, a 'lower fraction release' and not 'release quantity', as the K levels in APR and HGB fuels are relatively high, such that their K-component concentrations in gas phase during combustion (per kg of fuel) can be up to 10 times greater than those of IFW and WWF.

Heavy metal in WWF can also influence the K- and Na-species' flue gas concentrations during fuel combustion. The difference between the effect of these elements on corrosive releases during biomass combustion may be related to the contaminant level as these species may not, by themselves, influence corrosion mechanisms as they have mostly been predicted (by MTData) to form relatively high temperature stable species. As WWFs have lower levels of inorganics, it has been observed that lower levels of heavy metals are required to influence alkali metal species (corrosives) concentrations in flue gas compared to amounts required in HGB and APR fuels. Also, increasing heavy metal contents of WWF fuels increases the alkali metal species concentrations in flue gas (and potentially increasing the corrosive deposition flux on HX surfaces). In particular, median quantities of Zn (270 mg/kg of fuel) and Cr (33 mg/kg of fuel) in WWF were able to increase the alkali metal salt quantities of corrosive deposits (30 mol% and 16 mol.% increments respectively) per kg of fuel.

In these investigations, heavy metal contaminants in APR and HGB fuels (up to 50 mg/kg of fuel, median content), were not able to influence alkali metal concentrations in flue gas. It is thus proposed that the corrosivity of WWF combustion releases is more susceptible to trace heavy metal contaminant levels, and the risk to fireside corrosion is always likely to be higher where these elements are present in WWF.

5.3.2 The formation of corrosive components when HX surfaces are exposed to corrosive deposits released from biomass/waste firing

The term 'corrosive compounds' in relation to fireside corrosion does not only encompass the corrosive components released from the combusting fuel. The type of alloy and scale formed, and how it interacts with the deposit will affect the formation/decomposition of components which may themselves influence further damage to the alloy. Indeed, the exposure temperature and gas conditions will affect the corrosivity of these components present at the metal surface. This work has observed the corrosion influences of deposits at varying temperature

and deposition flux conditions as well as within different gas compositions. Chromium scales have been of particular interest for both steels employed (T91 and 347HFG) as the scale tends to be positioned along with alkali metal, sulphates and chlorides.

Corrosion data generated (both dimensional and qualitative by SEM) in this research has enabled distinguishing between Na and K fireside corrosion behaviours. The corrosion influencing capabilities of the element species may be explained by the temperature response of their formed chromate scales and the decomposition products these scales generate. Decomposition product NaOH, from Na-Cr scales, has been linked to the penetrative chloride damage in samples exposed to WWF deposits (especially for 347 HFG steel samples) at 600°C. K-Cr scales have been linked to scale damage (and metal surface loss) at the same temperature. When temperature is varied, the melting point of the predominant alkali-chromate scales and/or vapour pressure of the decomposition products may significantly affect corrosion rates. As such, it becomes more difficult to predict corrosion attack when both alkali metals have dominant role in chromium scale attack such as anticipated for WWF firing.

5.3.3 Limitations of methods adapted in this PhD work

The work concluded in this PhD has employed methods whose limitations may impact the validity of the data produced. Understanding these limitations has however enabled accurate interpretation of the data.

5.3.3.1 Thermogravimetric analysis data

Data generated from thermodynamic calculations assume an infinite amount of time is available for species reacting to form an end product [101], [106]. During combustion, chemical release conditions change [100] and reactants may not have sufficient time to form end/stable products. Thermodynamic calculations have, however, been valuable for investigating the types of corrosive species and comparing the corrosives composition as the

variations within/between categories. Such species have also been determined across a temperature range to see how temperature influences the compositions and phases of these species.

Median Cl/sulphate ratios of HGB deposits closely resemble those of deposit samples collected by Michelson et al. [151] on air-cooled probes in a 10 MW straw fired boiler. Also, plant data have shown better correlation with thermodynamic calculations than mass transfer rate prediction models [9], [24], [103], as thermodynamic simulations consider multiple interactions which a component can undergo along a temperature gradient (such as the conversion of chlorides to sulphates).

5.3.3.2 Corrosion evaluation

Fireside corrosion tests were carried out in isostatic furnaces, whereas in combustion power plants, the HX surfaces experience a range of temperatures. Knowing this, tests have been conducted at varying temperatures to investigate the influence of temperature changes on deposit corrosivity.

The heat flux furnace corrosion tests were successfully designed to compare corrosion attack occurring across a temperature gradient. Although it could not be concluded that corrosion mechanisms were different for the isothermal and heat flux exposed samples, running the tests for five furnace cycles enabled the identification of design/procedure changes which could improve the method as listed in **Section 5.2.5.2**.

6 Conclusions and technology implications

There has been limited understanding of the fireside corrosion behaviours of biomass/waste combustion fuels. The corrosion influence of biomass/waste fuels has been found to be greater than that of coal, related to the different compounds formed from their combustion. The application of wastes may further complicate fireside corrosion challenges. As such, this research has investigated fireside corrosion arising from the use of less conventional biomass/waste fuels, with the view that such fuels may have increased demands in combustion power plants in the future, to achieve green energy production targets.

Addressing each objective listed in **Section 1.2**, this chapter highlights the main achievements of the research:

1. Clustering of biomass/waste fuels into different categories (**Section 6.1**, addressing objective 1);
2. Evaluating the elemental distributions post-combustion of various biomass/waste fuel categories, and investigating the combustion corrosive species compositions and fluxes for typical HX temperatures (**Section 6.1**, addressing objective 2);
3. Understanding how corrosive compounds may influence alloy damage and identifying the potential mechanisms of fireside corrosion influenced by these fuels (**Section 6.2**, addressing objective 3);
4. Comparing furnace test methods for simulating fireside corrosion conditions (**Section 6.2**, addressing objective 4).

6.1 Fuel clustering, combustion element release and technology implication

This section concludes on findings relating to objectives 1 & 2.

6.1.1 Summary of findings and related objective

Fuels of particular interest to this research were determined to fall into the categories of wood waste fuels (WWF), Industrial Food Waste (IFW), Agricultural

Plants & Residues (APR), and Herbaceous Grass Biomass (HGB), though several other fuels were grouped into other fuel categories in the initial stages of the study. The pre-selection of the four fuel categories for analysis enabled project delivery within the research scope by identifying economically and operationally feasible fuels. Clustering of a range of fuels' data into each category permitted the investigation of average and compositional ranges.

(This has met the requirements of objective 1)

Thermodynamic simulations of species/compounds formed during combustion were carried out with MTDData.

The two main findings, in relation to the release of corrosive component following WWF combustion, are:

- i. The relatively low Si content and comparable Ca+Mg levels (comparable to Si levels) of WWF favours the release of highly reactive alkali metal species into the gas phase where Si-Mg and Si-Ca complexes are formed.
- ii. The heavy metal contaminants mostly form stable species. The main challenges arising from these elements are that they encourage the release of alkali metal salts into the flue gas by displacing them from forming compounds stable at high temperatures.

Findings relating to corrosive component releases from the non-woody fuels (HGB, APR & IFW) are:

- i. For APR and HGB, the fuel Si levels (and P contents for HGB fuels) are similar or higher than the total alkaline earth metal concentration (based on each category's median). Therefore, the excess Si enables the retention of K and Na in temperature-stable solid phases by forming their silicates.
- ii. Although Na levels are considerably higher (relative to WWF quantities) in HGB and APR fuels, Na release in combustion is counteracted by excess Si levels meaning formation of corrosive Na deposits may not be a concern when firing these fuels. This is also true when firing IFW which contains negligible Na levels.

- iii. The main challenges with APR and HGB combustion remains the high K-salt flux in the flue gas following their combustion. This results in the categories' median corrosive condensates fluxes (based on alkali metal-salts) being up to 10 times those of WWF. IFW fuels, however, have lower concentrations of alkali metal salts which could form, thus exhibiting lower quantities of corrosive species in flue gas and deposit when combusted.
- iv. The fuels elemental makeup influencing the formation of potentially corrosive compounds during combustion have been summarised in points i-iii above. These compounds have been identified to be majorly alkali metal salts based on the melting temperature ranges of these compounds. For the non-woody biomass/waste, KCl and K_2SO_4 will be of primary concern for fireside corrosion. For WWF, corrosive condensates will also include Na and Ca (in addition to K) salts.

(This addresses the PhD objective 2.)

6.1.2 Technology implications

Combustion plants HX will encounter mainly Na- and K-salts, as molten deposit fraction, when WWFs are combusted. The corrosive deposits from non-woody fuels may be predominantly K-salts. Fireside corrosion mechanisms occurring in WWF firing may thus be governed by a wider variety of corrosive species (compared to the non-woody fuels), which may make it more difficult to describe or predict fireside corrosion damage occurring.

IFW fuels have the lowest flue gas and deposit corrosive concentrations, of the four categories analysed. Where technologies improve to tackle the high moisture content, the employment of this fuel in combustion energy generation should be encouraged.

6.2 Fireside corrosion characteristics of biomass/waste fuels and technology implications

This section concludes on findings relating to objectives 3 & 4

6.2.1 Summary of findings and related objective

Corrosion trends show that WWF deposits may indeed be more damaging than other biomass/waste deposits evaluated. The corrosivity of WWF deposits are, however, more sensitive to flue gas flow rates and temperature on steels, 347HFG and T91. The impact of the alkali metals, K and Na, on fireside corrosion had been thought to be similar [114], though previous explanations had focused on the alkali metals' ability to disrupt protective chromate oxides. Disagreeing with literature [114], Na and K salts influence metal degradation via different mechanisms. The alkali metal hydroxides, KOH and NaOH, produced from the decomposition of alkali metal-chromates at 600°C, have different vapour pressures, with the latter hydroxide more likely to be in molten state. Higher vapour pressures of KOH will influence scale damage while NaOH, were molten, will encourage penetrative metal damage.

Even where chloride levels are low (< 30 mol.% chloride fraction in corrosive deposits, e.g., in WWF), accelerated corrosive chloride damage remains likely; sustainable by NaOH (relative to KOH which has a higher vapour pressure). The lower evaporation rates of NaOH (compared to KOH) may enhance chloride retention, where NaCl is able to form at certain conditions applicable to biomass combustion.

This difference, identified in the corrosion mechanism and related to the alkali metal components, increases understanding of the dissimilarities in corrosion extents and mechanisms between wood-based biomass/waste fuels and non-woody fuels (e.g., APR and HGB which may lack Na-salts). Though the later fuels generally result in greater HX damage rates [24], this should not be attributed to the corrosivity of the molten deposits, but rather the amount of these species being deposited.

(This has met the requirements of objective 3.)

In addition to conventional laboratory testing of fireside corrosion, a heat flux corrosion furnace setup was successfully designed to simulate a thermal gradient through a deposit-coated sample (here T91). Though the corrosion rates occurring for the heat flux and isothermal exposed samples could not be readily compared (due to experimental difficulties encountered which may have impacted the heat flux sample's corrosion data), there was not sufficient data to indicate that the corrosion mechanisms differed. The successful completion of several furnace cycles enabled the identification of possible design and method improvements which may be beneficial for further testing.

(This has met the requirements of objective 4.)

6.2.2 Technology implications

HXs, at metal temperatures of ~550-600°C on the fireside, will encounter relatively high volumes of volatile K-containing species when HGB and APR fuels are combusted. Metal penetration rates (for alloys susceptible to this mode of damage) will, however, be high where the volatile components include Na-containing species. When utilising WWF for combustion (which will lead to deposits containing both Na and K salts), both penetrative damage and metal surface loss (per corrosive deposit flux) will be severe. The integrity of such alloys may thus be compromised under such conditions, despite the apparent loss of metal being limited to levels which are not easily detected.

The corrosivity of Na-species is more sensitive (than K-species) to flue gas flow rates (higher flow rates encourages the removal of decomposition products). This is related to the low levels of Na and Cl necessary for sustaining Na assisted chloride damage. Temperature also influences the decomposition of alkali metal-Cr scales) and the conditions of NaOH and a KOH (molten or gas). Optimizing both parameters (flow rate and temperature) to limit corrosion rates is expected to improve alloy performance against the fireside corrosion influences of these fuels.

7 Recommendations

This chapter makes recommendations based on the findings of this research. These recommendations may impact how the fireside corrosion influence of biomass/waste fuels is investigated.

7.1 Recommendations based on findings relating to combustion releases during biomass/waste firing

- The presence of heavy metal contaminants in WWF will likely increase alkali metal concentrations in flue gas. As a result, contaminated fuels will result in greater metal attack. Low Si fuels (such as WWF) are more susceptible to trace element levels (in terms of corrosive alkali components being released during combustion). Removal of contamination sources (e.g., nails) is recommended.
- Where pre-treated woods are employed, the nature of the adhesive used should be considered. This research has observed that 33 mg/kg of Cr or 270 mg/kg of Zn (employed in some wood adhesives) is able to increase the alkali metal concentration in flue gas after WWF combustion. It is recommended that further tests are carried out to establish the concentration limits of trace elements, beyond which alkali metal salt formation is favoured.
- The alkali metal and chloride contents are lowest for the IFW fuels. Where technologies improve to handle its high moisture content, it will be beneficial to investigate the fireside corrosion performances of these fuels.

7.2 Recommendations based on fireside corrosion trends evaluated in this research

- The post-combustion releases from different biomass/waste fuels lead to a wide range of material damage depths. The austenitic steel, 347HFG, is considerably more responsive than T91 to the changing chemical compositions of deposits, and thus T91 may be more suitable for WWF firing, where significant deposit composition variations occur (relative to the other fuel categories examined). 347HFG may completely fail under Na assisted chloride attack (likely to occur for WWF firing) due to grain boundary susceptibility to this mode of damage. The recommendation is attributed to more predictable damage rates experienced by the ferritic steel, though corrosion rates are higher than for 347HFG. It is important also to note that T91 corrosion rate is more sensitive to changing deposition flux and temperature (500-600°C) under WWF firing conditions (compared to 347HGH).
- The alkali metal Cr-scales formed on the T91 surface may be different from those on 347HFG under WWF firing conditions, as corrosion rates have been shown to differ. Further research on the alkali metal Cr-scale properties would be beneficial for understanding how these scales are different; especially those present at 550-600°C. The corrosion rates for T91, exposed under WWF firing conditions, change within this temperature range.
- It should be noted that higher corrosive damage of HGB and APR fuels compared to WWF in plant-firing experiences [20] is not attributed to the corrosivity of deposit molten components, but rather, the quantities of these melts. Indeed, WWF molten deposits can be twice as corrosive as those of HGB and APR under specific firing conditions.

Plants firing WWF are likely to experience greater penetrative damage rates (higher than those firing APR and HGB fuels) per molten deposition flux. Reducing metal damage rates in plants firing WWF will necessitate

considering the employment of alloys less susceptible to internal damage and depletion of protective elements from grains.

Specifically, 347HFG exposed to chlorides can undergo a more severe internal damage at lower chloride contents when Na is present in the deposit at the corrosion site.

Further investigation of the effects of alkali metal deposit ratio on chloride-related penetrative damage is required to establish the concentration resulting in peak damage. Similarly, it will be useful to establish the minimal chloride content required for chloride penetrative attack.

- Heavy metal contaminants will promote internal damage under WWF firing conditions as Na species concentrations in the flue gas are increased. Monitoring of the levels of Na species released/depositing may thus be critical when combusting such fuels.

7.3 Recommendations based on evaluation techniques employed for this research

- Thermodynamic simulations of HGB corrosive deposit compositions compare well with literature [151]. Published work on alternative fuel deposit compositions is encouraged to allow research comparisons. Thermodynamic calculations are beneficial as a pre-screening or comparison tool for alternative and contaminated fuels' combustion releases, where plant data is not available.
- The isothermal furnace test setup allows several samples to be tested in the same cycle, which saves time.

For more samples to be tested simultaneously, another design to permit the loading of several samples (such as where samples lengths are reduced) may be required for the heat flux furnace setup.

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Appendix A Fuel data, experimental parameters and calculation spreadsheet

This appendix chapter lists fuel data, thermodynamic output data and calculations (tables/spreadsheets and examples) for experimental data employed in **Chapter 3**.

A-1. Fuel categories, classification and group chemical properties

In **Table A-1**, the ECN Phyllis sourced data used in this project are denoted by a corresponding sample reference number as provided on the date of access. Data without a sample reference number where sourced from other references as denoted.

Table A-1: Biomass and wastes whose fuel data have been collated for evaluation in this PhD. ECN Phyllis 2 data are denoted by the inclusion of the website reference number for each fuel

Categories and fuels	Reference
Herbaceous & grass biomass	
Switchgrass	[14]
Switch grass	[25] № 896
Switch grass	[25] № 2426
Reed canary Grass	[181]
Reed canary Grass	[54]
Rapeseed Straw	[54]
Barley Straw	[54]
Barley Straw	[21]
Wheat Straw	[54]
Wheat straw	[4]
Sweet Sorghum	[54]
Kenaf	[54]
Cane	[54]
Miscanthus (Italy)	[54]
Miscanthus (Germany)	[54]
Flax whole straw	[54]
Flax shive	[54]
Aubergine plant	[25] № 2886
Bean plant	[25] № 2888
Brassica	[25] № 2811
Courgette plant	[25] № 2884
Cucumber plant	[25] № 2885
Melon plant	[25] № 2891
Pepper plant	[25] № 2889
Tomato plant	[25] № 2887

Watermelon plant	[25] № 2890
Thistle	[25] № 2295
Thistle	[25] № 2812
Tobacco, Burley	[25] № 2868
Threshed hay	[25] № 3064
Grass pellets	[25] № 2732

Industrial food waste

Sugarcane fibre	[25] № 2807
Onion peel	[25] № 3068
Olive pomice pellets	[25] № 2893
Oil palm empty fruit bunch	[25] № 2897
Mango seeds	[25] № 2925
Mango peel	[25] № 2922
Longan seeds	[25] № 2927
Longan peel	[25] № 2924
Litchi seeds	[25] № 2926
Litchi seeds	[25] № 2923
Grain screening	[25] № 2805
Coffee grounds	[25] № 1769
Spent coffee	[25] № 2190
Corn cobs	[14]

Agricultural plants & residues

Sunflower shells	[14]
Sunflower pellets	[4]
Sunflower husk	[25] № 1911
Sunflower shells	[25] № 2803
Sunflower seed shells	[25] № 2317
Sunflower seed husks	[25] № 378
Sunflower seed husks	[25] № 2149
Sunflower husks	[71]
Sunflower seed shells	[25] № 878
Plum pits	[14]
Cotton husks	[71]
Olive residue	[25] № 1764
Olive residue	[25] № 3054
Olive residue	[25] № 2177
Rice husks	[25] № 993
Rice hulls	[25] № 452
Groundnut shells	[25] № 375
Palm kernel	[25] № 2719
Oat screenings	[25] № 3485
Mustard husks	[25] № 1913
Grass seed chaff	[25] № 3063
Cotton seed husks	[25] № 370
Almond shells (hulls)	[25] № 357
Almond shells (hulls)	[25] № 350
Almond shells (hulls)	[25] № 2813
Almond shells	[25] № 707
Olive residue	[25] № 2176
Cacao shells	[25] № 1776
Cacao shells	[25] № 2736
Cacao	[25] № 884

Coconut shell	[25] № 1919
Hazelnut shell	[25] № 2875
Hazelnut shell	[25] № 2315
Rice husks	[14]
Rice husks	[25] № 3251
Rice husks	[25] № 2876
Cotton husks	[25] № 1912
Prune pits	[25] № 998
Pistachio shells	[25] № 995
Pistachio shells	[25] № 706
Walnut shells	[14]
Walnut blows	[25] № 996
Walnut hells and blows	[25] № 997
Soya husks	[71]
Coffee husks (Mbuni)	[71]
Coffee husks (parchment)	[71]
Greenhouse residues	[4]
Cornstalk derived fuel	[121]
Almond hulls	[25] № 708
Almond shells (hulls)	[25] № 353
Almond shells	[25] № 2314
Tomato plant	[25] № 2887

Wood Waste Fuels

Demolition wood pellets	[4]
Demolition wood (clean wood)	[25] № 855
Demolition wood (clean wood)	[25] № 856
Demolition wood-chipped	[25] № 676
Demolition wood-chipped	[25] № 679
Demolition wood	[25] № 848
Demolition wood	[25] № 1929
Demolition wood	[25] № 2900
Wood particle board	[25] № 79
Particle board-Chipped wood	[25] № 684
Wood-salt impregnated	[25] № 685
Wood, fir treated (salt imp.)	[25] № 394
Demolition wood	[25] № 2712
Demolition wood	[25] № 2901
Demolition wood	[25] № 2918
Demolition wood	[25] № 1448
Demolition wood	[25] № 1889
Wood-painted	[25] № 911
Wood-painted	[25] № 939
Waste wood	[25] № 2748
Railway ties	[25] № 2749
Railway ties	[25] № 407
Used wood-chemically treated	[25] № 3281

Table A-2: Herbaceous & grass biomass fuels combined group properties

Content	Basis	units	Median	Mean	Minimum	Maximum	Count
Heating Values		MJ/kg	4.44	6.25	-	19.58	17

LHV	ar	MJ/kg	6.19	8.00	0.56	21.18	17
HHV	ar	MJ/kg	13.40	13.61	7.94	23.14	17
LHV	dry	MJ/kg	14.21	14.23	8.00	24.60	17
HHV	dry	MJ/kg					

Proximate Analysis

Volatile	dry	wt. %	76.40	75.04	61.68	90.48	30
Fixed Carbon	dry	wt. %	16.50	15.69	5.20	24.97	30
Ash	dry	wt. %	7.91	10.34	1.81	29.75	31
Moisture	ar	wt. %	65.20	51.33	6.80	93.04	17

Major Elements

C	dry	wt. %	45.80	44.49	33.81	65.85	29
O	dry	wt. %	40.45	39.52	27.84	56.68	29
H	dry	wt. %	5.80	5.49	3.70	7.78	29
N	dry	wt. %	1.08	1.70	0.30	4.70	30
S	dry	wt. %	0.14	0.19	0.01	0.55	29
Cl	dry	wt. %	0.47	0.68	0.04	2.94	22

Minor elements

Al	dry	mg/kg	710	1318	151	3700	4
Ca	dry	mg/kg	9750	16861	4945	43000	4
Fe	dry	mg/kg	520	868	133	2300	4
K	dry	mg/kg	25405	45477	9600	121500	4
Mg	dry	mg/kg	1800	6115	1061	19800	4
Na	dry	mg/kg	1698	2124	700	4400	4
P	dry	mg/kg	6010	6200	3178	9600	4
Si	dry	mg/kg	12321	65610	7700	230100	4

LHV: Low heating value

HHV: High heating value

Table A-3: Agricultural plants & residues fuels combined group properties

Content	Basis	units	Median	Mean	Minimum	Maximum	Count
Heating Values		MJ/kg					
LHV	ar	MJ/kg	15.49	14.76	-	19.43	45
HHV	ar	MJ/kg	16.80	16.10	1.15	21.05	45
LHV	dry	MJ/kg	17.48	17.03	7.76	21.40	45
HHV	dry	MJ/kg	18.62	18.20	8.68	23.22	45
Proximate Analysis							
Volatiles	dry	wt. %	73.32	72.01	38.80	81.64	46
Fixed Carbon	dry	wt. %	20.45	21.13	5.64	38.60	46
Ash	dry	wt. %	3.83	6.63	0.70	31.79	53
Moisture	ar	wt. %	9.77	12.87	2.50	89.54	42
Major Elements							
C	dry	wt. %	48.28	46.82	31.44	53.65	52
O	dry	wt. %	40.11	38.85	11.18	47.30	52
H	dry	wt. %	5.97	6.02	4.08	9.18	52

N	dry	wt. %	1.03	1.15	0.23	3.05	51
S	dry	wt. %	0.10	0.55	0.01	19.00	45
Cl	dry	wt. %	0.08	0.23	0.00	2.94	24

Minor elements

Al	dry	mg/kg	735	925	115	2697	6
Ca	dry	mg/kg	2400	3365	0.16	8552	8
Fe	dry	mg/kg	720	959	186	2224	6
K	dry	mg/kg	6494	12244	1.11	34200	10
Mg	dry	mg/kg	1400	2396	383	4996	7
Na	dry	mg/kg	408	485	0.03	1750	10
P	dry	mg/kg	1449	1966	0.05	5900	8
Si	dry	mg/kg	7929	26072	2300	81180	7

LHV: Low heating value

HHV: High heating value

Table A-4: Industrial food waste fuels combined group properties

Content	Basis	units	Median	Mean	Minimum	Maximum	Count
Heating Values							
LHV	ar	MJ/kg	5.49	4.68	-	18.15	13
HHV	ar	MJ/kg	7.20	6.17	-	19.56	13
LHV	dry	MJ/kg	16.68	11.42	-	20.90	13
HHV	dry	MJ/kg	17.20	11.93	-	21.44	13
Proximate Analysis							
Volatiles	dry	wt. %	70.43	70.45	65.90	77.18	10
Fixed Carbon	dry	wt. %	25.00	22.82	12.71	29.11	10
Ash	dry	wt. %	4.37	5.96	0.20	15.65	13
Moisture	ar	wt. %	56.59	48.81	6.86	82.60	13
Major Elements							
C	dry	wt. %	43.10	41.52	12.55	59.68	13
O	dry	wt. %	43.72	41.12	16.23	69.54	13
H	dry	wt. %	6.79	6.46	1.46	9.12	13
N	dry	wt. %	1.04	1.07	0.14	2.07	13
S	dry	wt. %	0.09	0.18	0.05	0.98	13
Cl	dry	wt. %	0.06	0.16	0.02	0.78	10
Minor elements							
Al	dry	mg/kg	260	1060	100	2820	3
Ca	dry	mg/kg	1100	11488	900	32464	3
Fe	dry	mg/kg	20	248	9.0	1836	9
K	dry	mg/kg	8410	7737	150	13400	9
Mg	dry	mg/kg	1257	1202	10	2656	9
Na	dry	mg/kg	9	441	3.8	2985	7
P	dry	mg/kg	150	268	100	555	3
Si	dry	mg/kg	1200	3590	100	9469	3

LHV: Low heating value

HHV: High heating value

Table A-5: Wood waste fuels combined group properties

Content	Basis	units	Median	Mean	Minimum	Maximum	Count
Heating Values							
		MJ/kg					
LHV	ar	MJ/kg	14.57	14.90	8.37	20.56	17
HHV	ar	MJ/kg	15.58	15.33	-	22.31	18
LHV	dry	MJ/kg	17.72	18.05	13.66	23.81	17
HHV	dry	MJ/kg	18.78	19.17	14.66	25.24	17
Proximate Analysis							
Volatiles	dry	wt. %	76.40	75.76	68.80	80.10	14
Fixed Carbon	dry	wt. %	19.13	18.73	12.32	21.91	14
Ash	dry	wt. %	2.70	4.22	0.24	15.60	20
Moisture	ar	wt. %	12.95	15.32	4.65	42.90	17
Major Elements							
C	dry	wt. %	49.25	47.82	21.00	56.89	21
O	dry	wt. %	39.82	38.55	20.00	44.79	20
H	dry	wt. %	5.78	6.75	5.26	21.00	21
N	dry	wt. %	0.84	1.93	0.15	21.00	21
S	dry	wt. %	0.07	1.02	0.01	21.00	21
Cl	dry	wt. %	0.08	1.08	0.03	18.00	18
Minor elements							
Al	dry	mg/kg	519	631	150	1369	10
Ca	dry	mg/kg	3758	4045	2200	6537	10
Fe	dry	mg/kg	640	959	340	3800	10
K	dry	mg/kg	760	876	370	2000	11
Mg	dry	mg/kg	509	525	250	960	10
Na	dry	mg/kg	790	829	210	1613	11
P	dry	mg/kg	128	166	67	410	10
Si	dry	mg/kg	3000	4882	1135	13000	9

LHV: Low heating value

HHV: High heating value

A-2. Furnace temperature profiling

Profiling a furnace involves using a thermocouple to calibrate the actual temperature reached with the controllers set point value. **Table A-6** shows the achieved temperatures at the hottest furnace zone when the furnace controllers displayed the desired values for the furnaces employed during this research. The

furnaces controllers where then set at temperatures to account for this temperature difference.

Table A-6: Actual temperatures recorded at set furnace temperatures. Set temperatures were modified to account for the temperature differences

Set value	Temperature at hottest zone		
	600°C	550°C	500°C
Furnace A	586	539	493
Furnace B	613	-	-

A-3. Thermodynamic modelling input elemental data calculations

The MTData element input values (employed for **Section 3.2.2**) were calculated from air and median fuel compositions which were combined to give the total element feed rates.

i. Air elemental feed rate (moles/hour)

For each element in air:

$$\begin{aligned} \text{moles feed per hour} & \qquad \qquad \qquad \text{Equation 52} \\ &= \frac{\text{wt. \%}}{100} \times \text{air feed wt. (g)} \times \text{mole fraction} \end{aligned}$$

The air feed rate was varied for each fuel category to yield a thermodynamic simulation output of 7-8% excess O₂ (refer to **Section 3.2.2**), assuming a fuel feed of 1 kg/hour.

Table A-7: Air feed rate for 1 kg fuel (per hour) which yielded 7-8 mol.% excess O₂

Element		Air composition (wt.%)	HGB (mol./hr)	APR (mol./hr)	WWF (mol./hr)
Air feed (kg/hour)			5 kg/hour	6 kg/hour	8 kg/hour
N	From N ₂	74.91	214.03	308.26	428.06
H	From H ₂ O	0.80	3.56	7.11	7.11
C	From CO ₂	0.05	0.05	0.09	0.09
	From O ₂	22.96			
O	From H ₂ O	0.8	59.27	118.54	118.54
	From CO ₂	0.05			
Ar		1.28	1.28	2.56	2.56

ii. **Fuel elemental feed rate (moles/hour)**

For each median category element value (assuming a feed rate of 1 kg/hour):

$$mol. \text{ feed per hour} = \frac{wt. \%}{100} \times 1000 \text{ g} \times mol. \text{ fraction} \quad \text{Equation 53}$$

Table A-8: MTData element input values based on 1 kg fuel, and air ratio. The bold italic figures are trace elements assessed (Section 3.2.2.2)

	Element	HGB Base	HGB mean CI	APR Base	WWF Base	WWF Ca max	WWF Na max
		(moles)					
14 ES	N	0.41	0.41	0.60	0.44	0.44	0.44
	H	93.67	93.67	63.90	63.15	63.15	63.15
	C	13.28	13.28	35.74	33.97	33.97	33.97
	O	45.55	45.55	27.85	28.41	28.41	28.41
	S	0.02	0.02	0.03	0.01	0.01	0.01
	Cl	0.05	0.11	0.09	0.02	0.02	0.02
	Al	0.02	0.02	0.025	0.018	0.018	0.018
	K	0.50	0.50	0.155	0.018	0.018	0.018
	Na	0.05	0.05	0.016	0.026	0.026	0.061
	Mg	0.06	0.06	0.052	0.020	0.020	0.020
	P	0.18	0.18	0.042	0.004	0.004	0.004
	Fe	0.01	0.01	0.012	0.011	0.011	0.011

	Si	0.35	0.35	0.243	0.096	0.096	0.096
	Ca	0.22	0.22	0.054	0.084	0.148	0.084
15 ES	Mn	0.00050		0.00140	0.00130		
	Ba	0.00003		0.00015	0.00146		
	Co	0.00002		0.00002	0.00003		
	Cr	0.00005		0.00006	0.00060		
	Cu	0.00008		0.00041	0.00030		
	Mo	0.00002		0.00003	0.00001		
	Ni	0.00016		0.00007	0.00015		
	Pb	0.00001		0.00002	0.00072		
	V	0.00001		0.00006	0.00002		
	Zn	0.00026		0.00069	0.00344		

A-4. MTData's thermodynamic simulation output format

Figure A-1 presents an extract of species and their concentrations predicted by MTData for the APR fuel category 14ES median value (base) post-combustion simulation. The original output spreadsheet generated by MTData consists of a vast amount of data which cannot be clearly displayed within the chapters of this thesis.

Figure A-1: An extract of MTData post-combustion simulation outputs for APR fuel category

A-5. Fireside corrosion test gas flow rate calculation

The calculated test gas flow rates were employed for corrosion testing described in **Section 3.2** and **Section 3.3**. The gas concentrations specified for gas bottles ordered from a supplier are listed in **Table A-9**. The wet gas compositions were thermodynamically simulated (at 1100°C) for each fuel category, then converted to their respective dry compositions. EXCEL was used to calculate gas flow rates by adjusting bottle flows to achieve the thermodynamically predicted dry gas compositions as closely as possible. The EXCEL Solver tool enabled the achievement of the best bottle flow rate combinations by minimising the standard deviation between the dry gas and calculated bottle feed compositions. An example spreadsheet for the WWF test gas flow rate is presented in **Table A-10**.

Table A-9: Gas bottle specified concentrations

	N₂	O₂	CO₂	SO₂	HCl
Bottle	%v	%v	%v	vppm	vppm
1	99.97				100
2	99.96				400
3	99.95			500	
4	64.00	12	24		
5	76.00	12	12		

Table A-10: Spreadsheet sample for gas flow rate calculation

	Flow rates	N ₂	O ₂	CO ₂	SO ₂	HCl
	cc/min	%v	%v	%v	vppm	vppm
Bottle 1	1.4	99.99				100
Bottle 3	4.13	99.95			500	
Bottle 5	40.0	76	12	12		
total	45.5					

	Flow rates	N ₂	O ₂	CO ₂	SO ₂	HCl
Dry gas flows	cc/min	cc/min	cc/min	cc/min	cc/min	cc/min
Gas 1	1.4	1.369				0.00014
Gas 2	4.1	4.126			0.0021	
Gas 3	40.0	30.435	4.805	4.805		
Totals	45.5	35.930	4.805	4.805	0.0021	0.00014

	N ₂	O ₂	CO ₂	SO ₂	HCl								
	%	%	%	vppm	vppm	%error btw bottle supply and target							
Achieved from bottles' flow	78.89	10.55	10.55	45.32	3.01	O ₂ /CO ₂	SO ₂ /HCl	N ₂	O ₂	CO ₂	SO ₂	HCl	Sum of errors
WWF MTData Dry (target)	79.30	9.50	11.20	45.00	3.00	0.8	15.0	0.5	-11.1	5.8	-0.7	-0.2	156.9

Flow rates were adjusted to account for steam flow, employing the ideal gas law for converting water flow to steam:

$$nRT/P = V \quad \text{Equation 54}$$

'R' is rate constant (0.082 L.atm/mol.K), 'P' is the pressure (1 atm), 'T' is temperature (~373 K), 'n' is the amount of substance in 1 ml of H₂O, and 'V' is the calculated volume of steam in 1 ml of H₂O. **Equation 54** expresses the steam volume from 1 ml of water. The total steam entering the system (ml/min) is derived from the MTData calculated water vapour content. First the flow rate fractions of the individual gas components are determined:

$$f_{fi} = df_i \times \frac{100}{wConc_i} \quad \text{Equation 55}$$

Where ' f_{fi} ' is the flow rate fraction of component ' i ' in the wet gas stream, ' df_i ' the dry flow rate of component ' i ' (**Table A-10**), and ' $wConc_i$ ' is the wet mol.% of ' i ' obtained from MTData calculations.

Next the total flow rate is calculated from the average of the flow rate fractions

Figure A-2 presents the values of the terms in **Equation 55** for the WWF gas flow rates. The total flow rate of wet feed (Step 1) is calculated by averaging the dry gas component flow rate fractions and the flow rate fraction of steam. The total flow rate of wet feed includes moisture content, as such thus the steam flow rate may be determined by subtraction (Step 2). The water pump rate can thus be extrapolated from the steam volume equivalent of 1 ml (**Equation 54**).

Step 2

Total flow rate	N ₂	O ₂	CO ₂	SO ₂	HCl	H ₂ O
cc/min	cc/min	cc/min	cc/min	cc/min	cc/min	cc/min
50.25	35.93	4.81	4.81	0.0021	0.00014	4.71

Values required for calculating f_{fi}

Step 1

	N ₂	O ₂	CO ₂	SO ₂	HCl	H ₂ O
	mol%	mol%	mol%	vppm	vppm	mol%
Wet (MTData)						
mole%	70.97	8.47	10.03	41.00	3.00	10.48

Figure A-2: Gas flow rates and compositions for WWF test gas

The bottle feed dry flow rates are adjusted for moisture as such:

Adjusted bottle rate

Equation 56

$$= \frac{\text{dry bottle flowrate}}{\text{total bottle flowrate}} \times \text{total wet flowrate}$$

Total gas flow rates achieved for the WWF, HGB and APR test gas conditions are 50, 74 and 118 cc/min, moisture inclusive.

Table A-11: Gas flow rates and compositions for WWF test gas

Test gas	N ₂	O ₂	CO ₂	SO ₂	HCl	H ₂ O
WWF	35.93	4.81	4.81	0.001	0.0002	4.71
HGB	45.74	5.36	5.36	0.003	0.0006	17.67
APR	77.99	7.37	14.74	0.010	0.0060	18.41

Appendix B Metal thickness & sound metal change graphs

This appendix documents the cumulative probability plots for the metal thickness and sound metal changes measured for all corrosion samples.

B.1 Samples with no deposit in WWF gas conditions

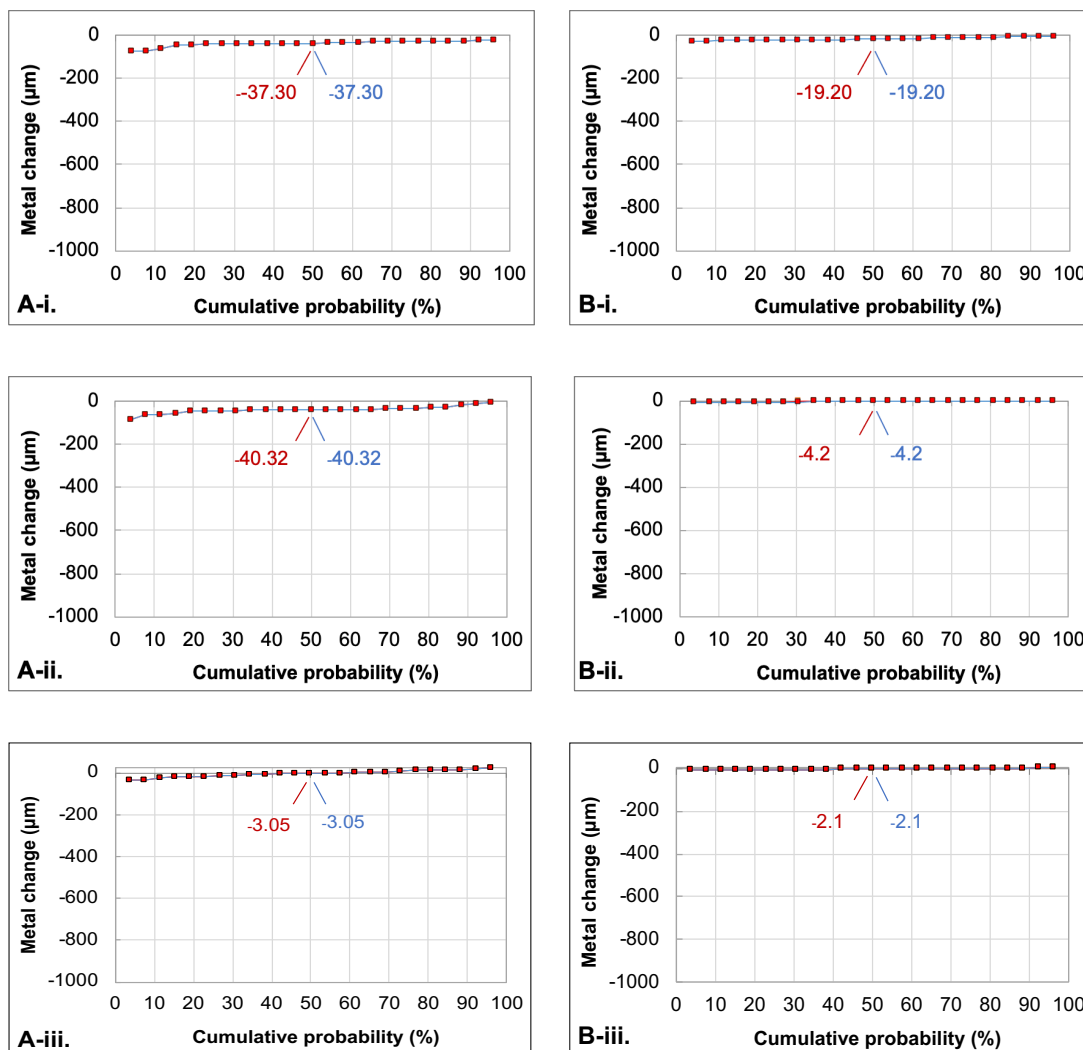


Figure B-1: Cumulative probability plot of (A) T91 and (B) TP 347HFG metal change (red data) and sound metal change (blue data) following 1000 hours exposure in WWF test gas (i.) at 600°C (ii.) 550°, (iii.) and 500°C

B.2 Samples with no deposit in HGB fuel gas conditions

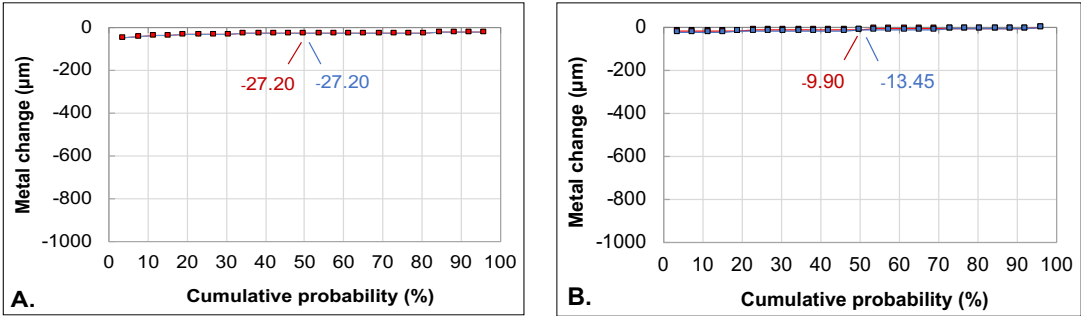


Figure B-2: Cumulative probability plot of (A) T91 and (B) TP 347HFG metal change (red data) and sound metal change (blue data) following 1000 hours exposure in HGB test gas

B.3 Samples with no deposit in APR fuel gas conditions

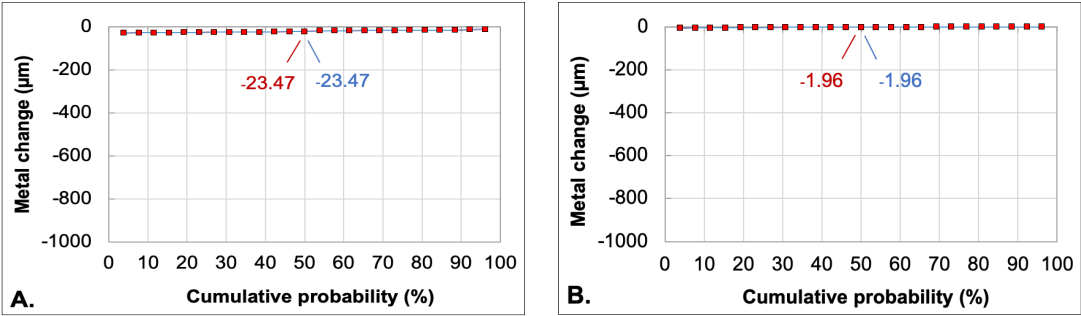
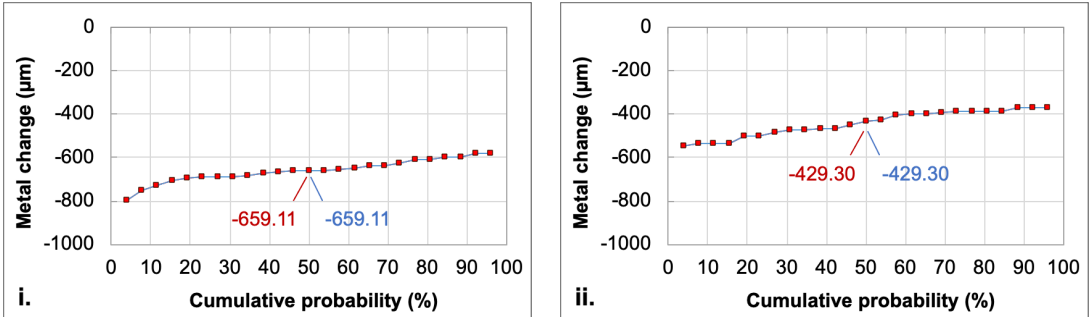


Figure B-3: Cumulative probability plot of (A) T91 and (B) TP 347HFG metal change (red data) and sound metal change (blue data) following 1000 hours exposure in HGB test gas

B.4 Deposition flux effect on T91



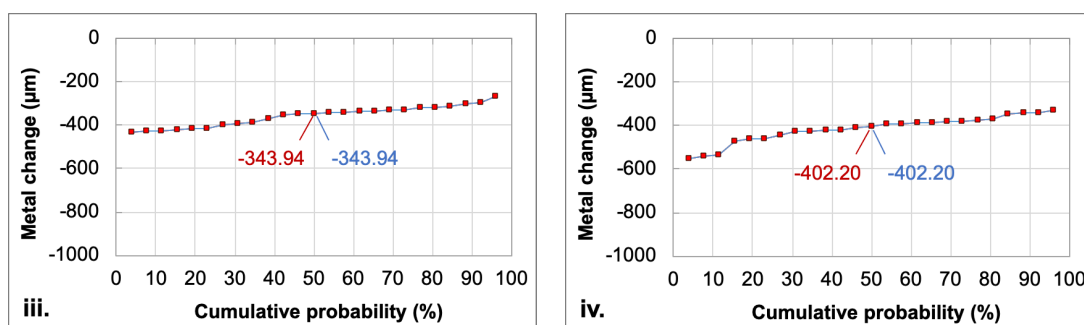


Figure B-4: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following 1000 hours exposure at 600°C in WWF test gas with applied deposit D1 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 μg/cm²hr

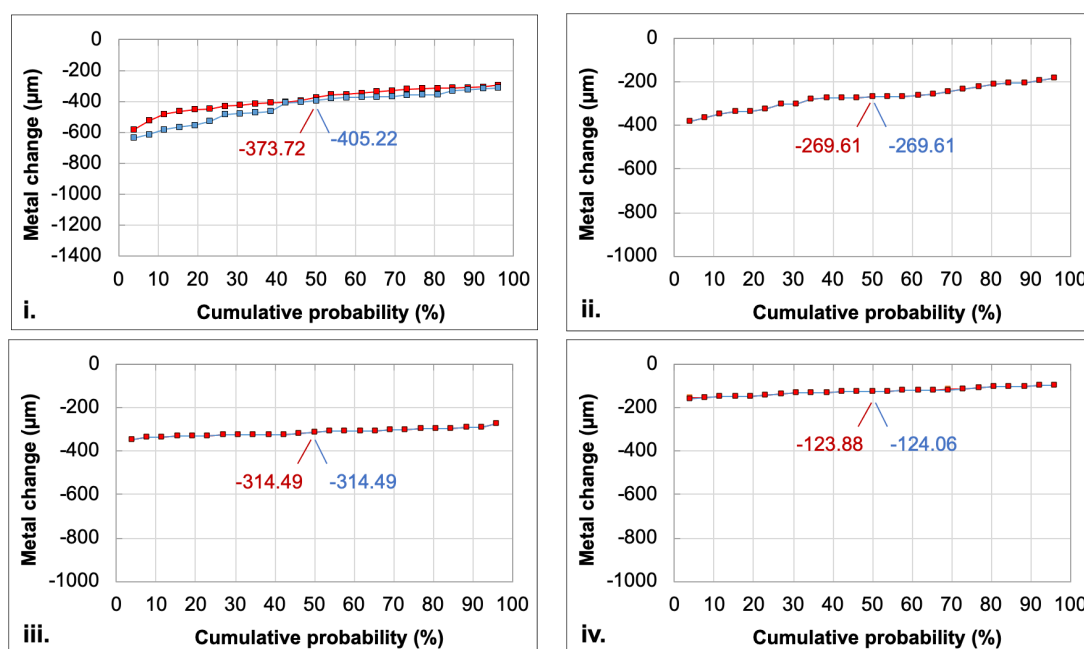


Figure B-5: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following 1000 hours exposure at 600°C in WWF test gas with applied deposit D6 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 μg/cm²hr

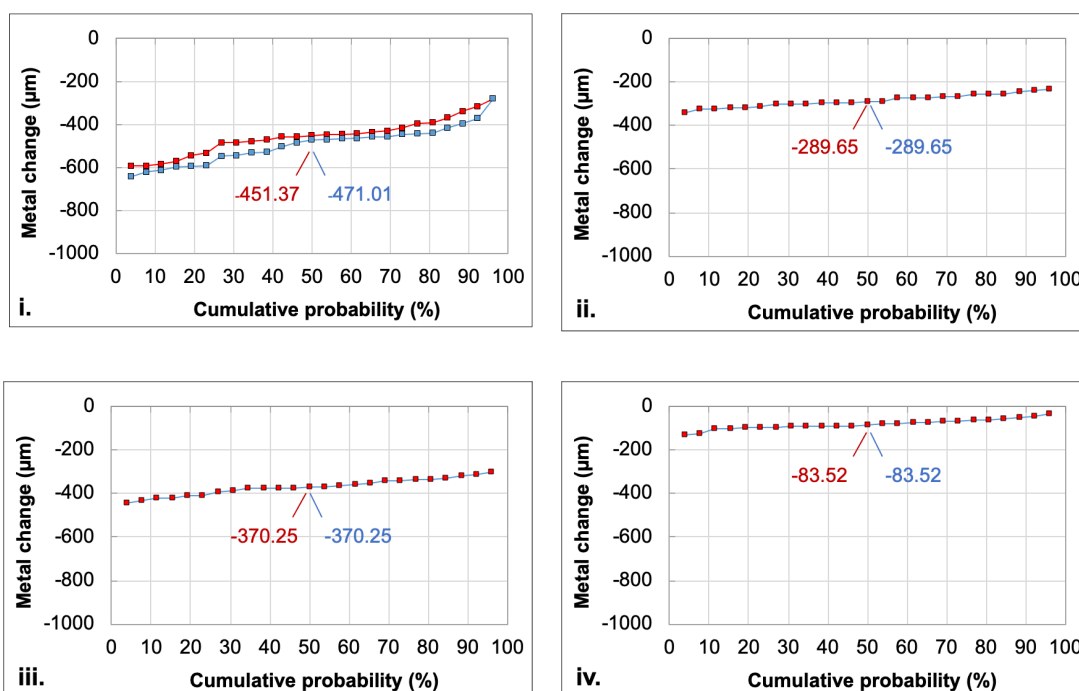


Figure B-6: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following 500 hours exposure at 600°C in WWF test gas with applied deposit D1 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 µg/cm²hr

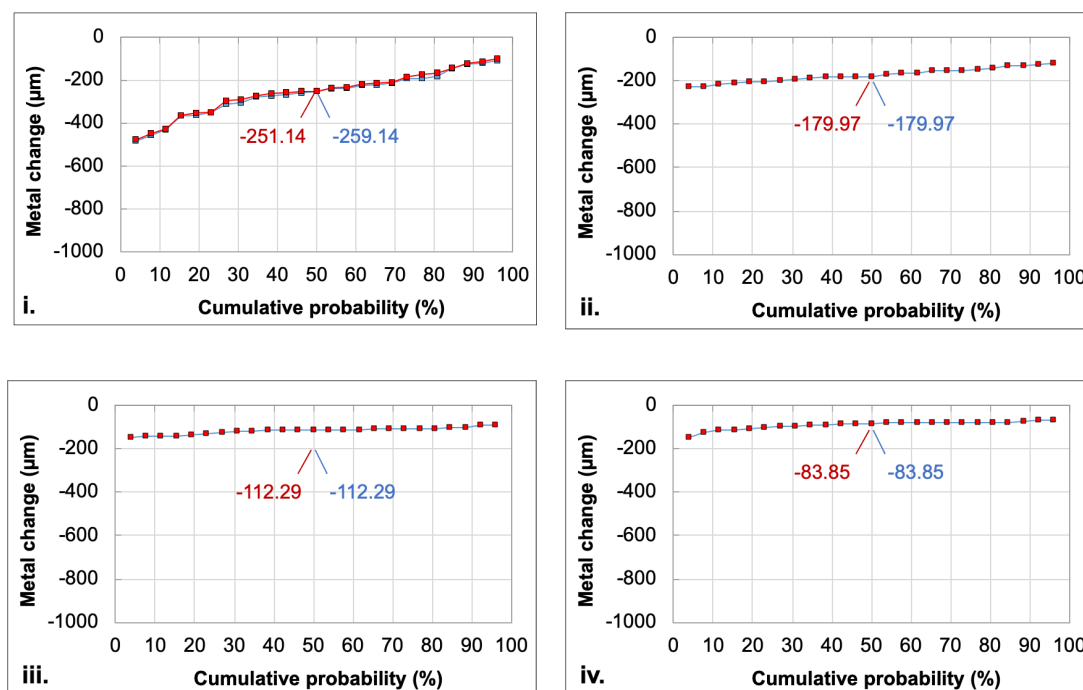


Figure B-7: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following 500 hours exposure at 600°C in WWF combustion gas with applied deposit D6 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 µg/cm²hr

B.5 Deposition flux variation effect on TP 347HFG

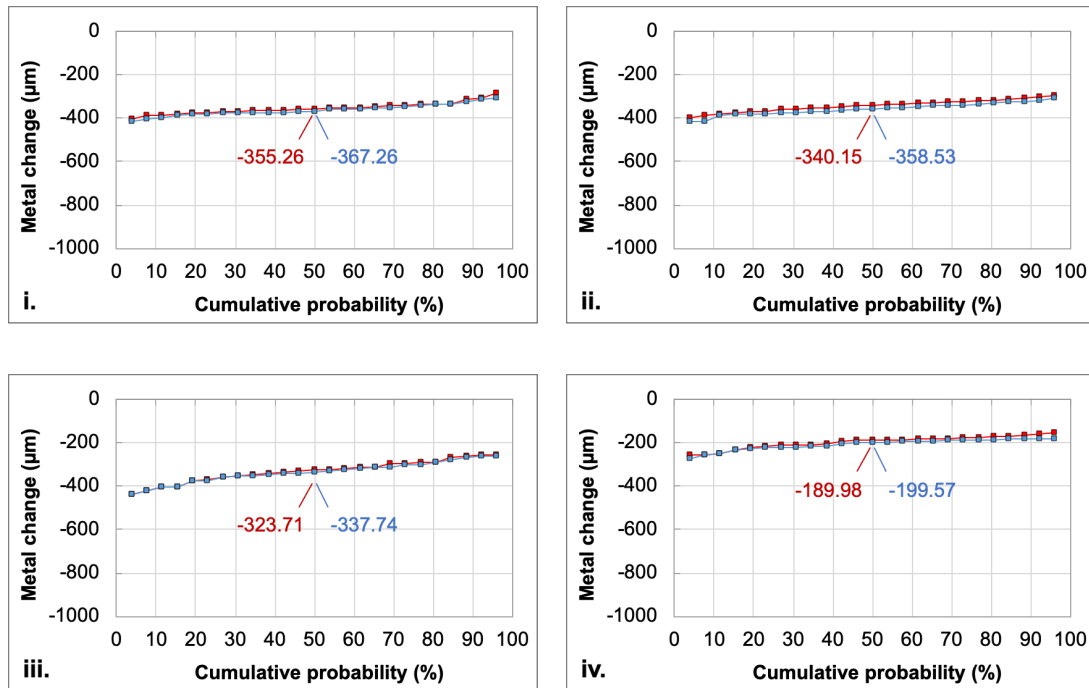
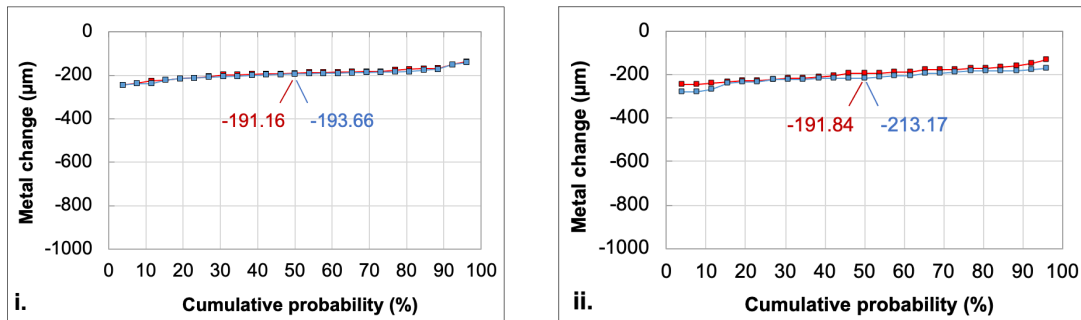


Figure B-8: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following 1000 hours exposure at 600°C in WWF test gas with applied deposit D1 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 μg/cm²hr



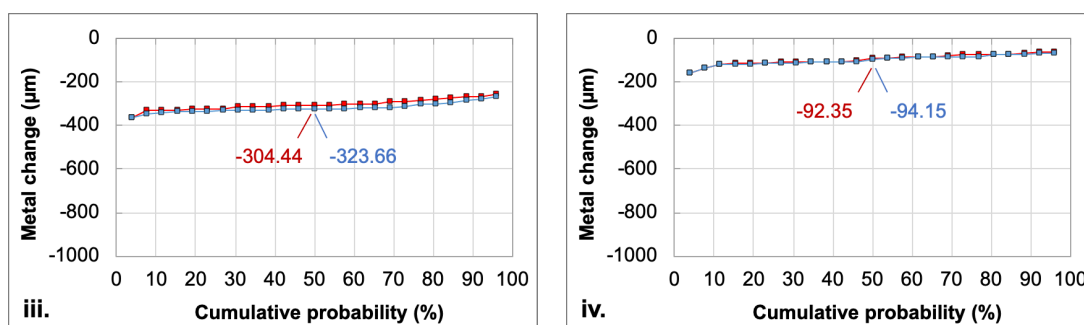


Figure B-9: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following 1000 hours exposure at 600°C in WWF test gas with applied deposit D6 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 $\mu\text{g}/\text{cm}^2\text{hr}$

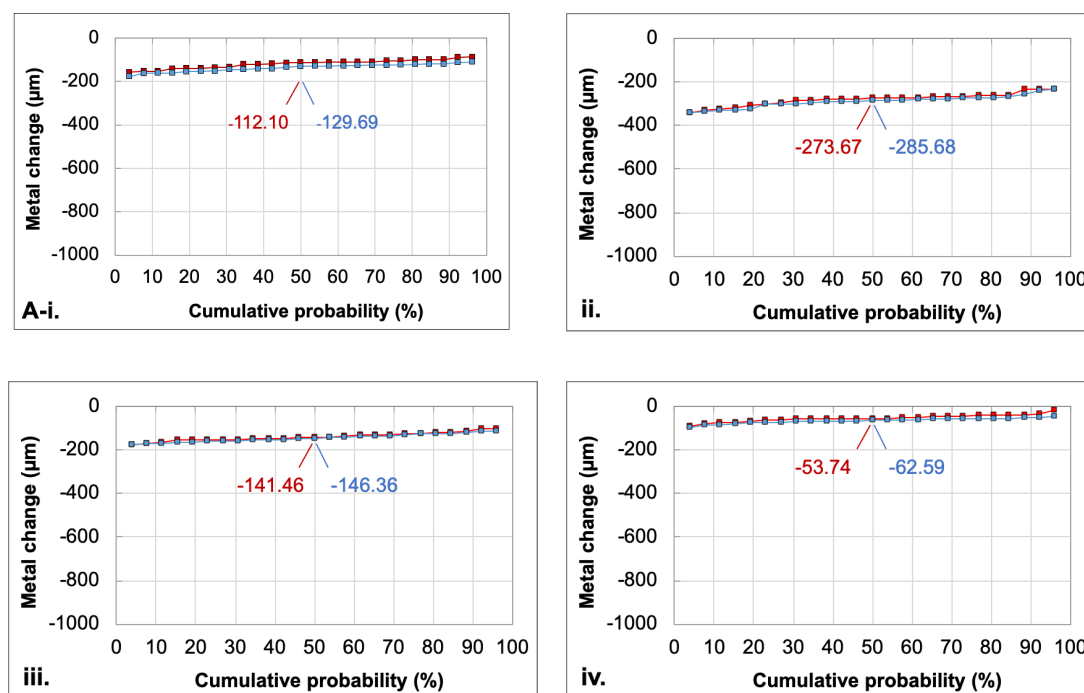


Figure B-10: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following 500 hours exposure at 600°C in WWF combustion gas with applied deposit D1 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 $\mu\text{g}/\text{cm}^2\text{hr}$

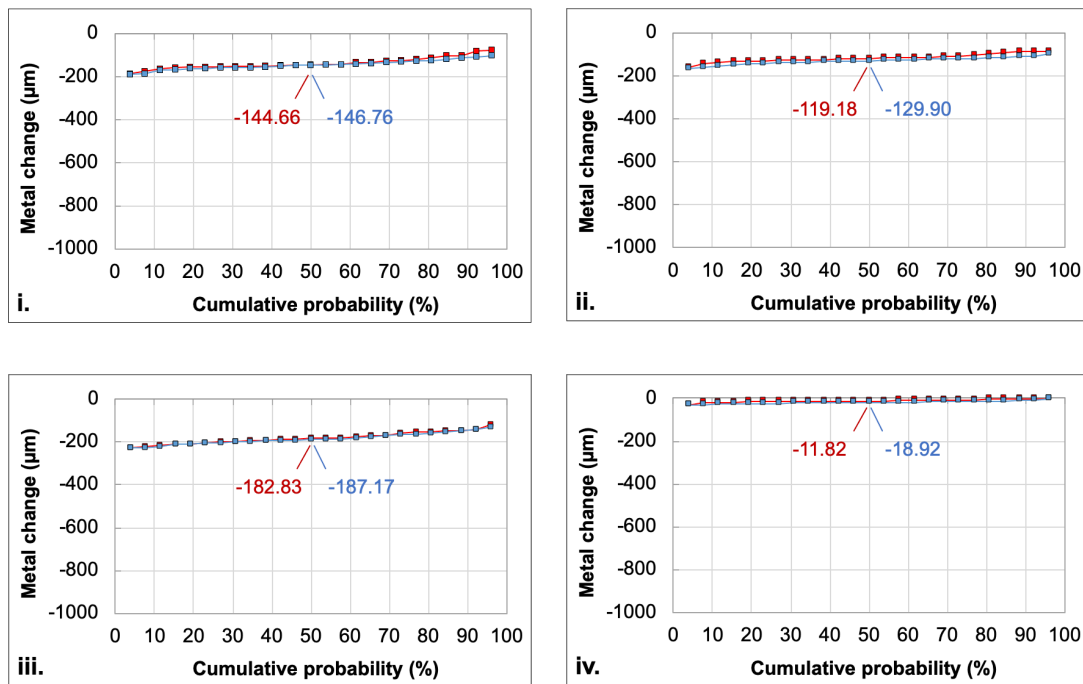
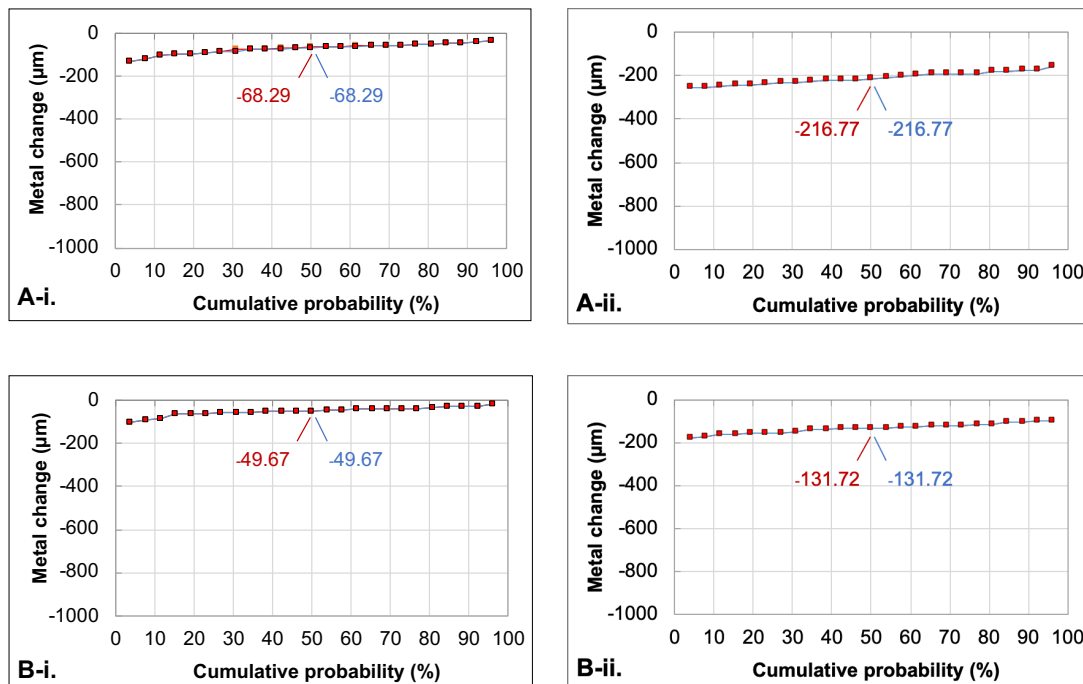


Figure B-11: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following 500 hours exposure at 600°C in WWF combustion gas with applied deposit D6 at flux (i.) 100, (ii.) 50, (iii.) 25 & (iv.) 10 $\mu\text{g}/\text{cm}^2\text{hr}$

B.6 Temperature change Effect on T91



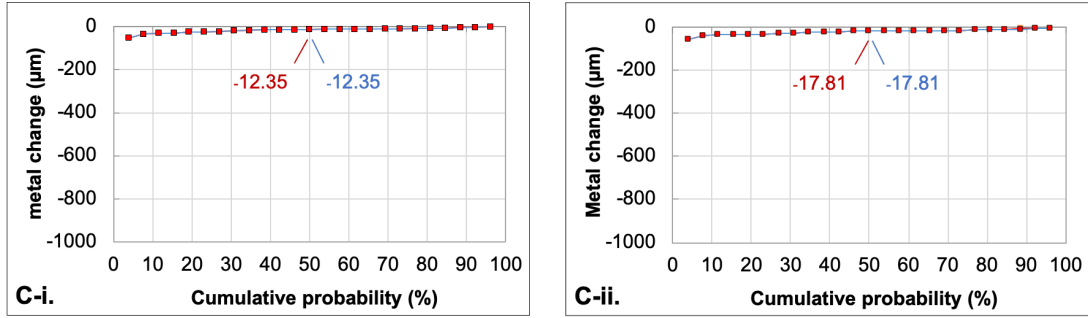


Figure B-12: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following (A) 1000, (B) 500 & (C) 200 hours exposure in WWF test gas with applied deposit D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at (i.) 500°C & (ii.) 550°C

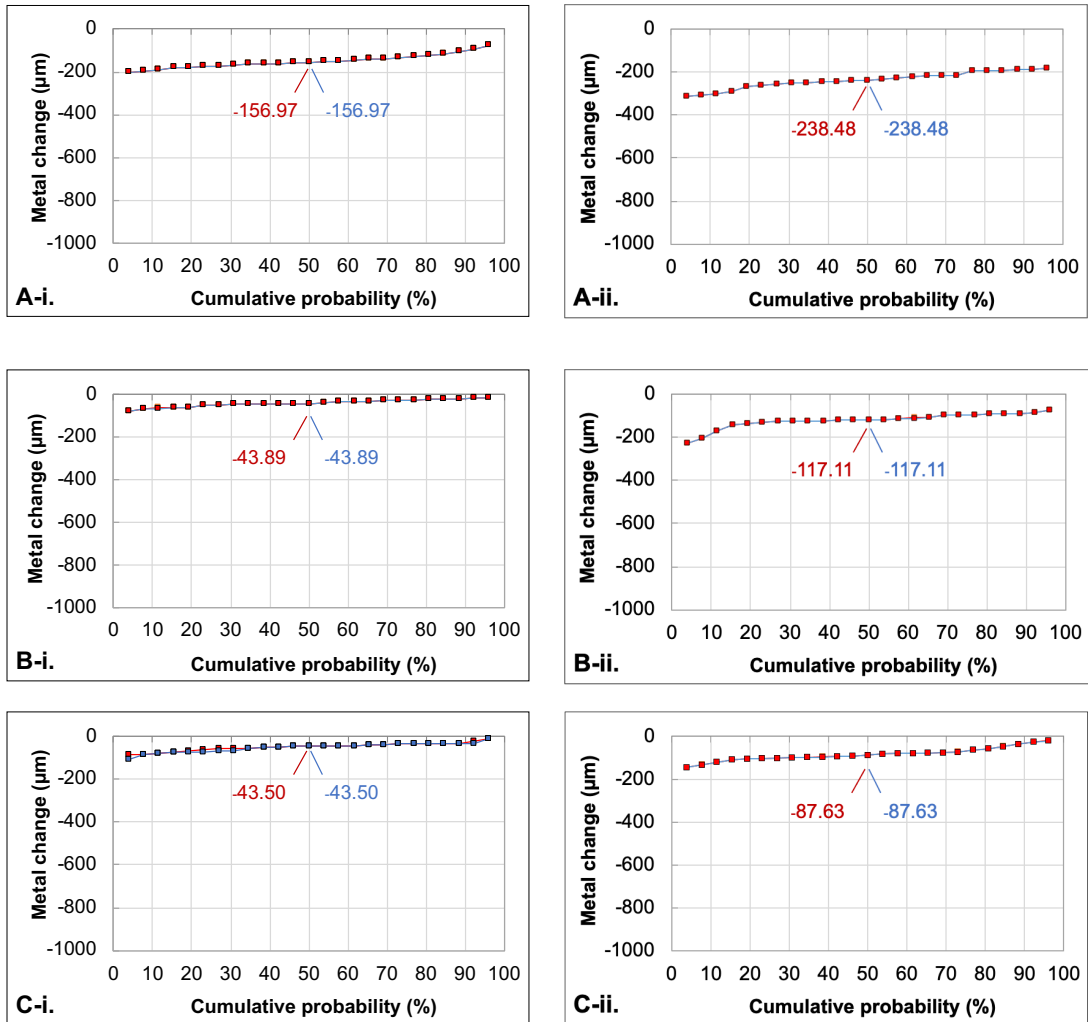


Figure B-13: Cumulative probability plot of T91 metal change (red data) and sound metal change (blue data) following (A) 1000, (B) 500 & (C) 200 hours exposure in WWF test gas with applied deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at (i.) 500°C & (ii.) 550°C

B.7 Temperature change effect on TP 347HFG

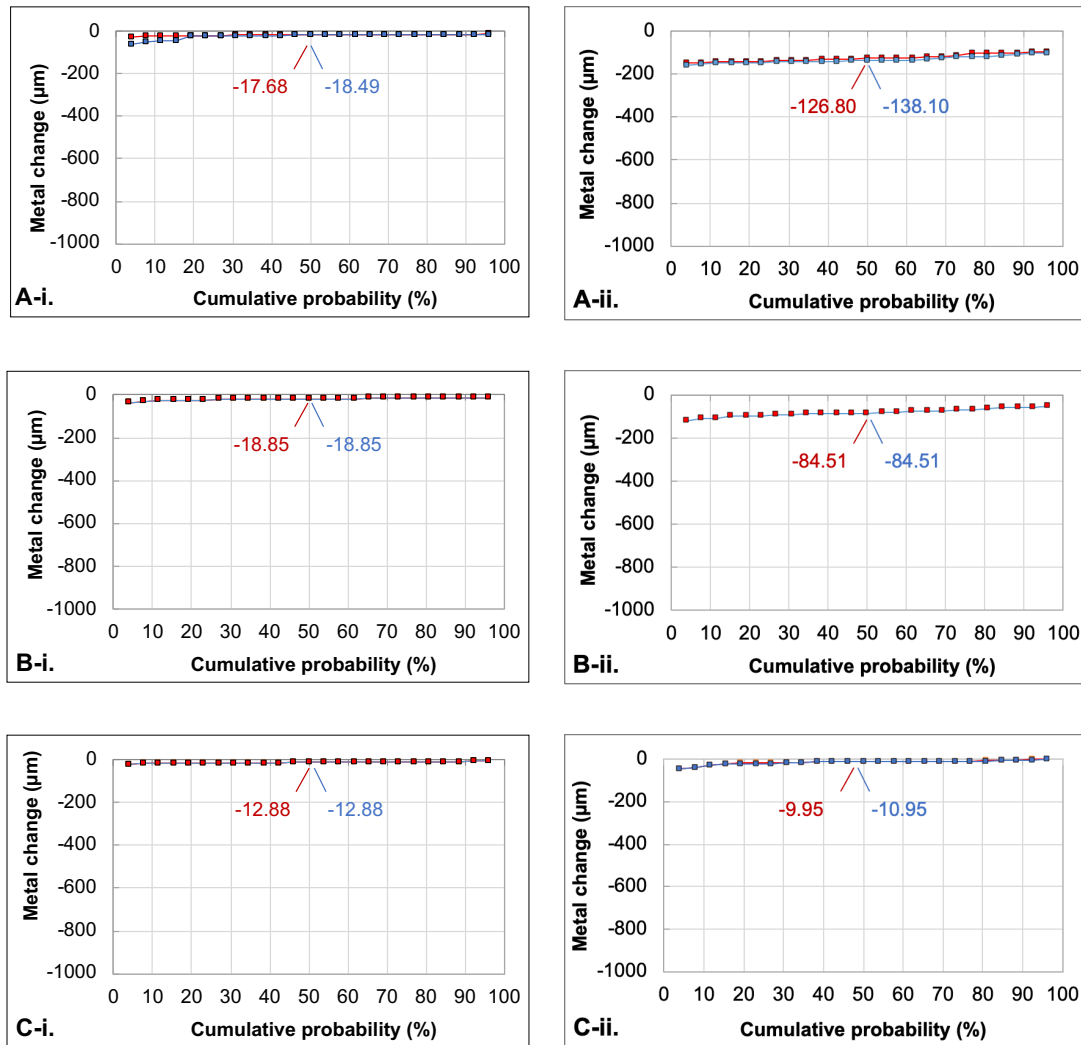
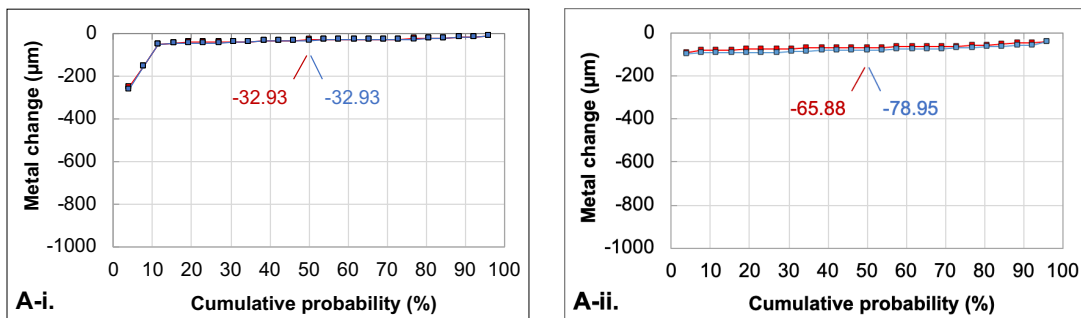


Figure B-14: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following (A) 1000, (B) 500 & (C) 200 hours exposure in WWF test gas with applied deposit D1 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at (i.) 500°C & (ii.) 550°C



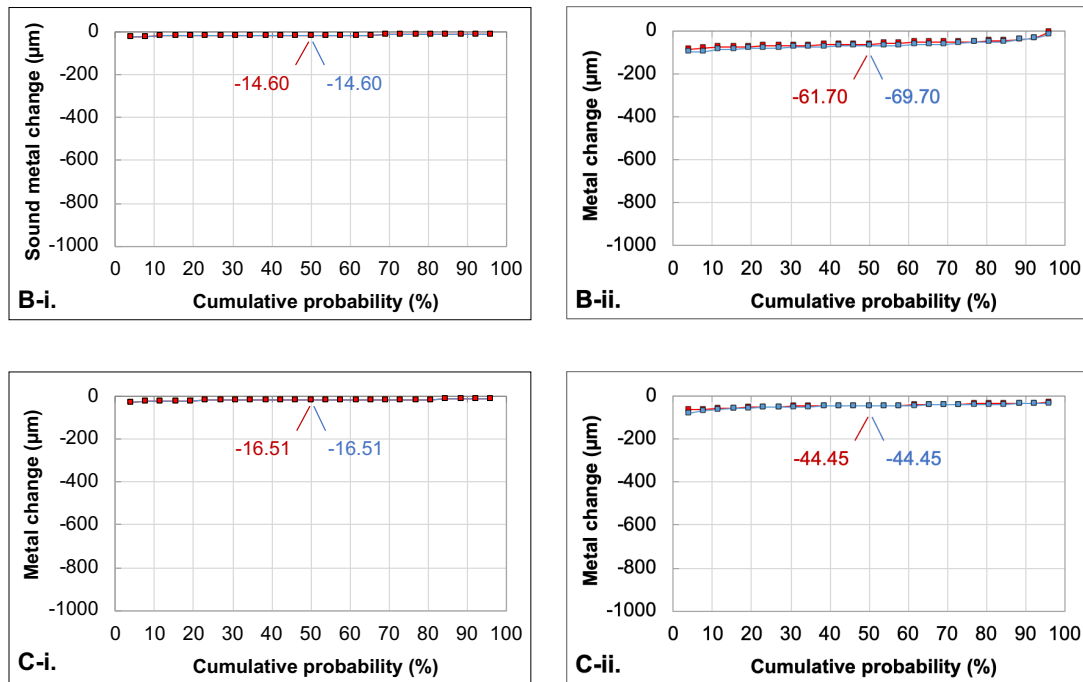


Figure B-15: Cumulative probability plot of TP 347HFG metal change (red data) and sound metal change (blue data) following (A) 1000, (B) 500 & (C) 200 hours exposure in WWF test gas with applied deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at (i.) 500°C & (ii.) 550°C

B.8 Deposit D1 in WWF test gas conditions

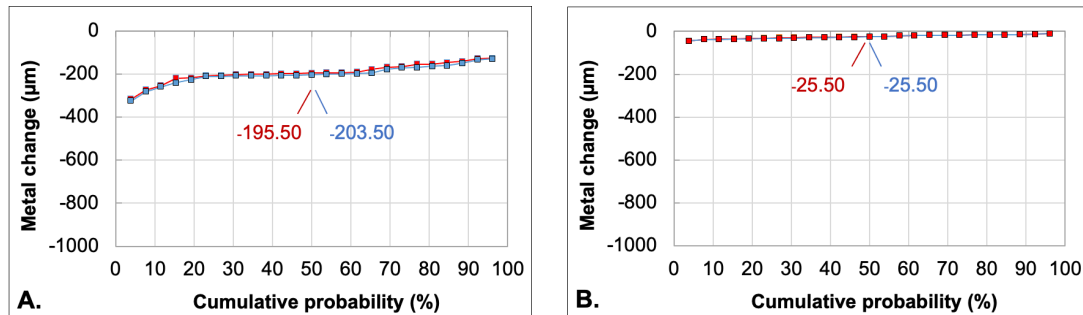


Figure B-16: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following 200 hours exposure in WWF test gas with applied deposit D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.9 Deposit D2 in WWF test gas conditions

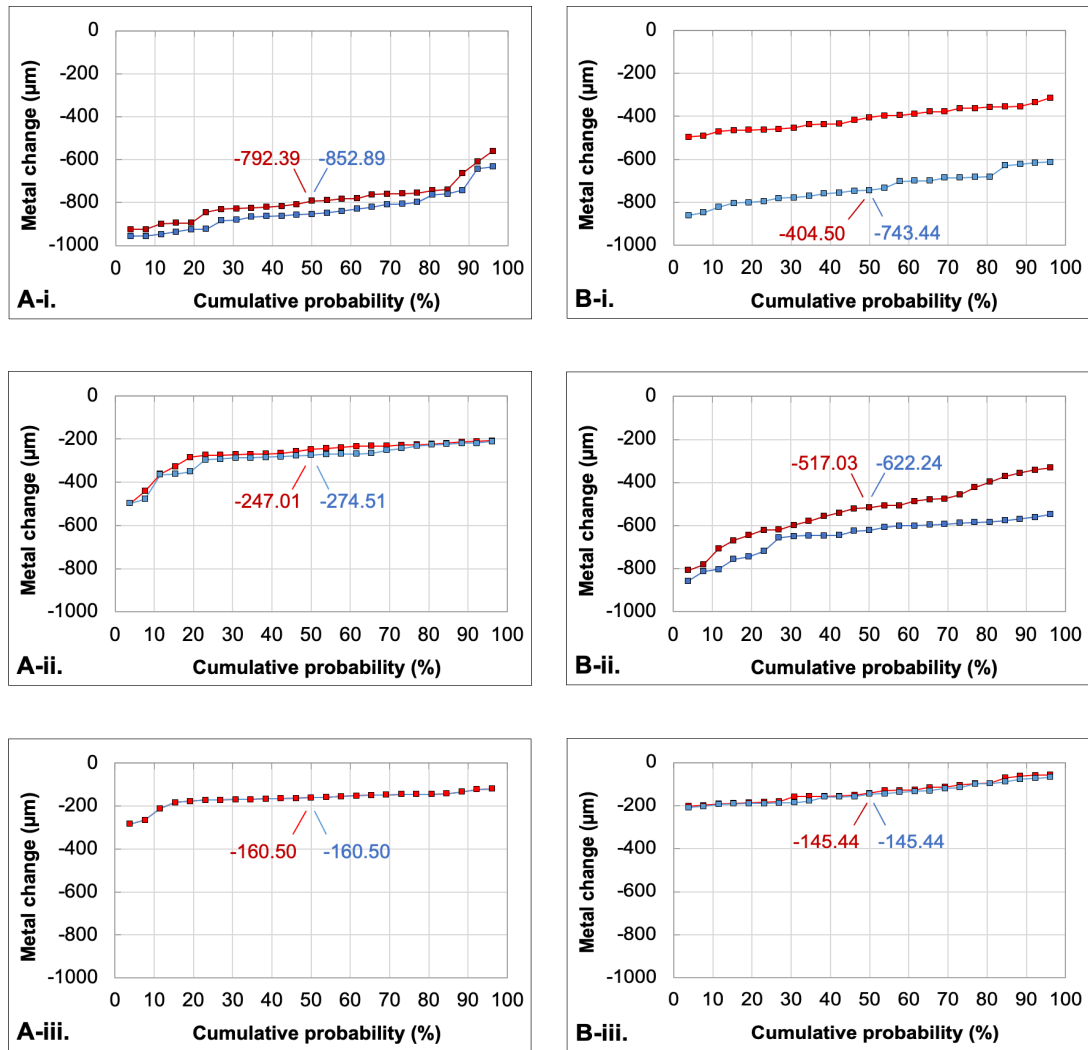


Figure B-17: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 exposure hours to simulated median WWF combustion gas conditions with applied deposit D2 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.10 Deposit D3 in WWF test gas conditions

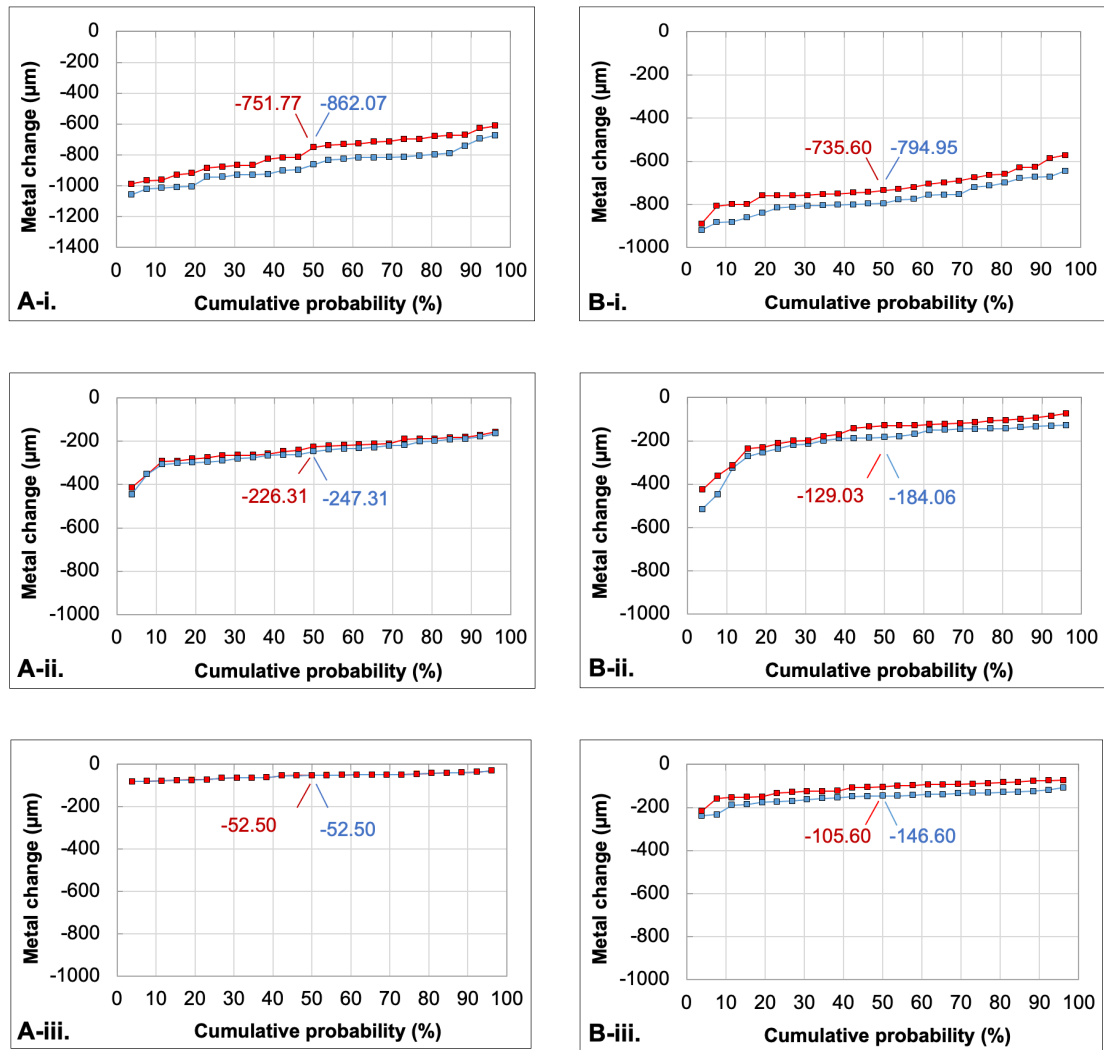


Figure B-18: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in WWF test gas with applied deposit D3 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.11 Deposit D4 in WWF test gas conditions

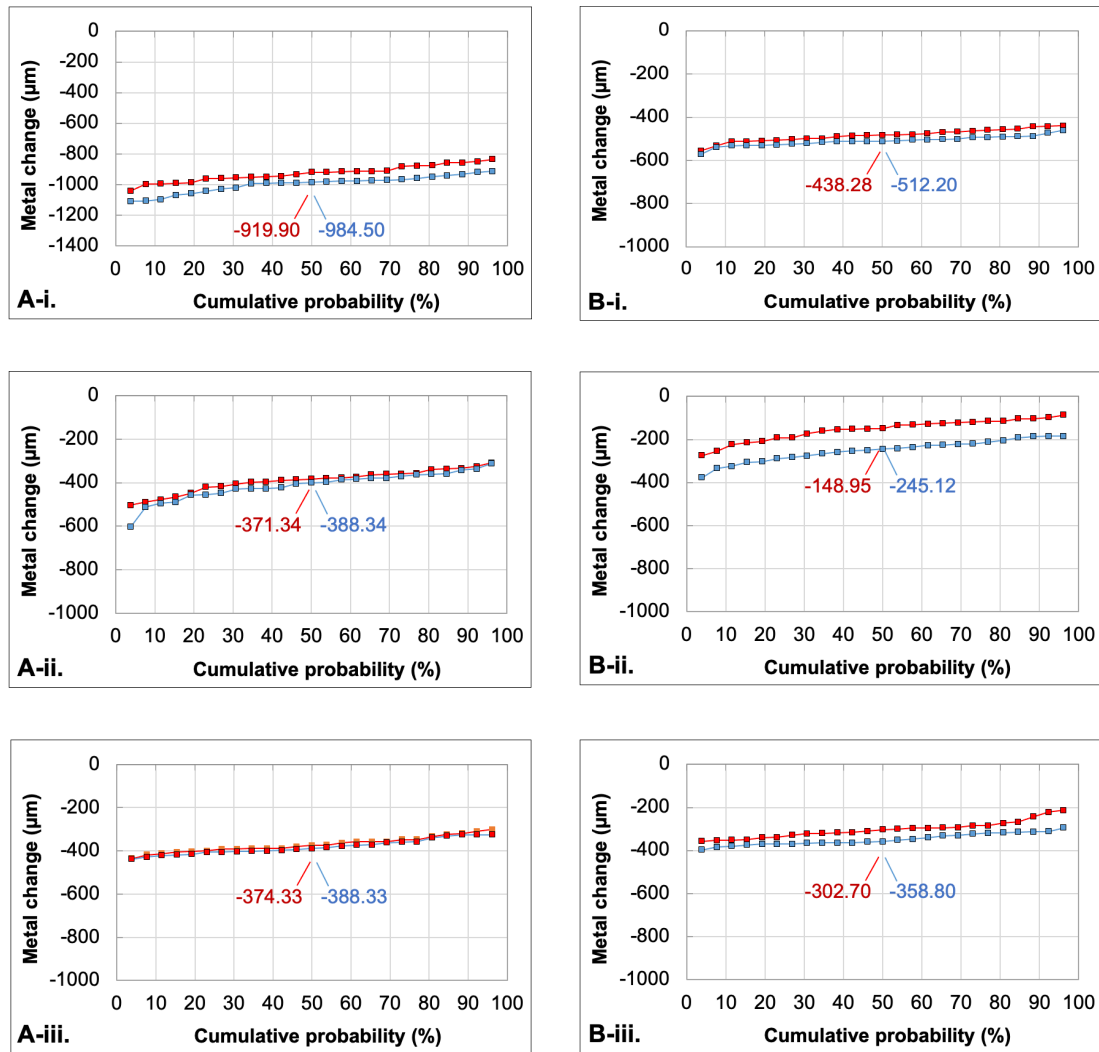


Figure B-19: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 exposure hours in WWF test gas with applied deposit D4 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.12 Deposit D5 in WWF test gas conditions

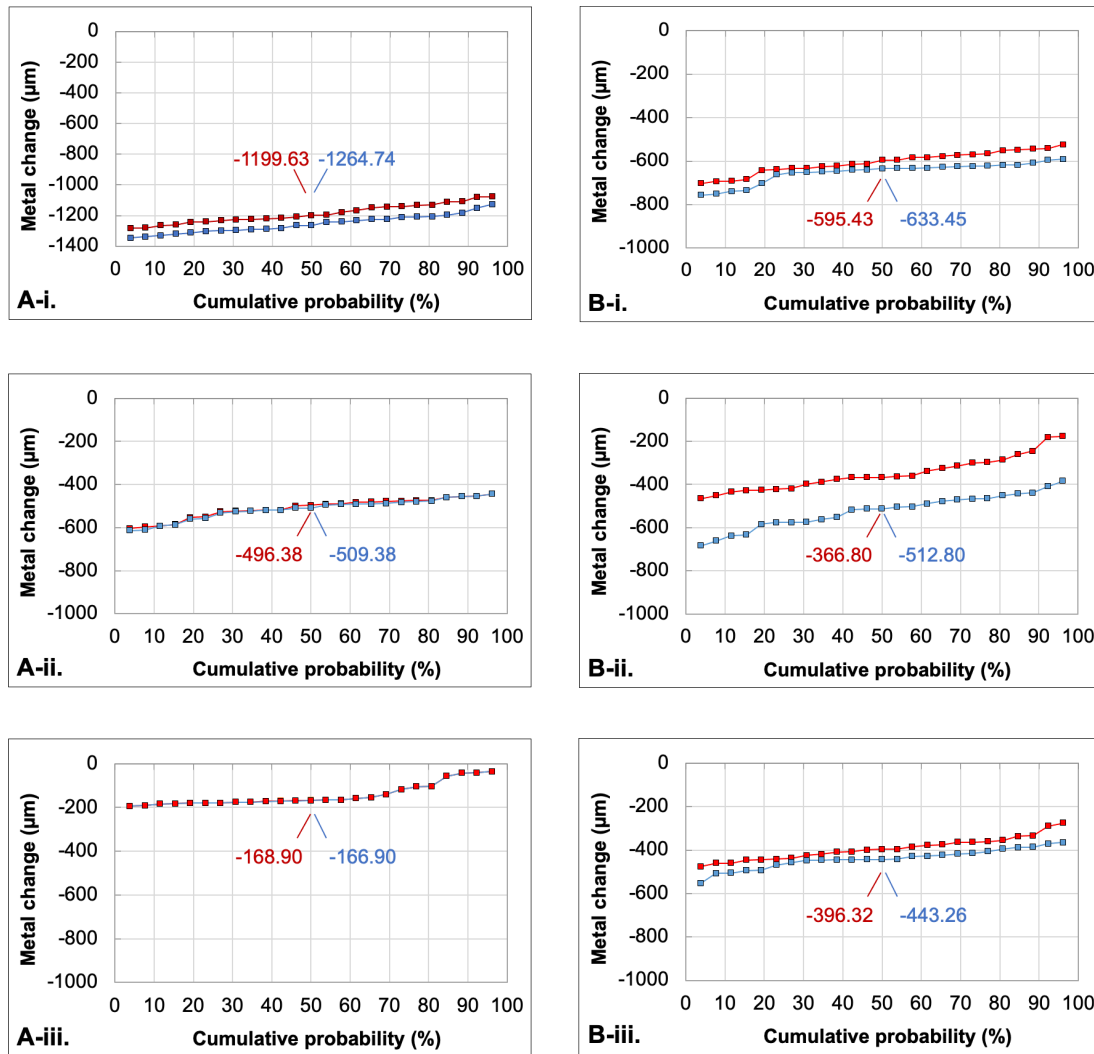


Figure B-20: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in WWF test gas with applied deposit D5 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.13 Deposit D6 in WWF test gas conditions

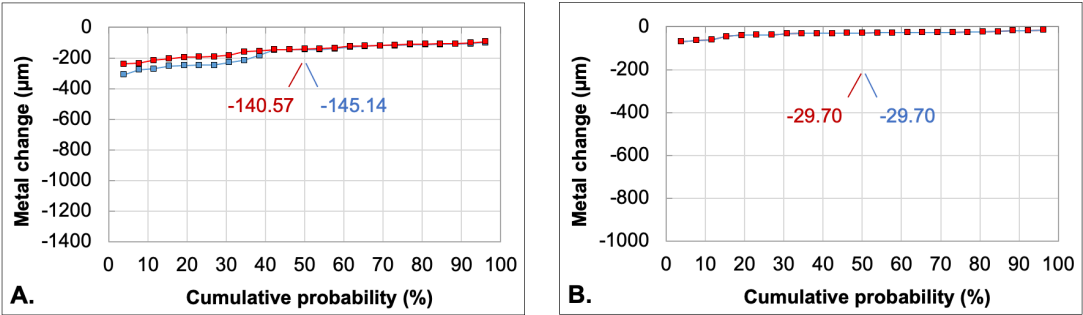
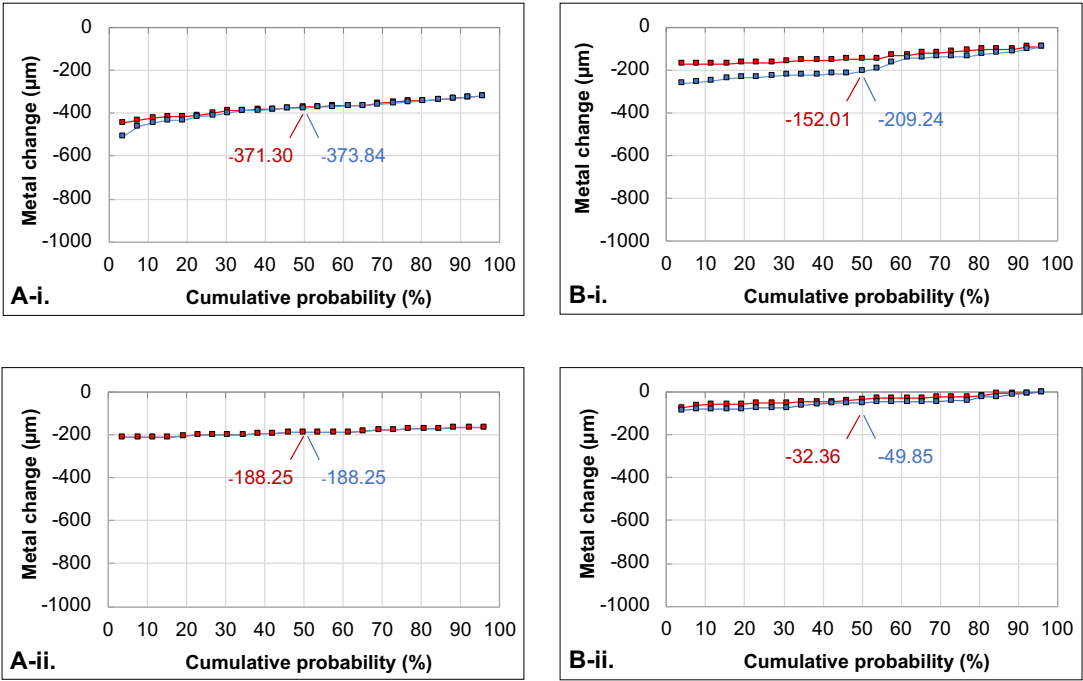


Figure B-21: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following 200 hours exposure in WWF test gas with applied deposit D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.14 Deposit D1, D6 and D7 effects in HGB fuel test gas conditions



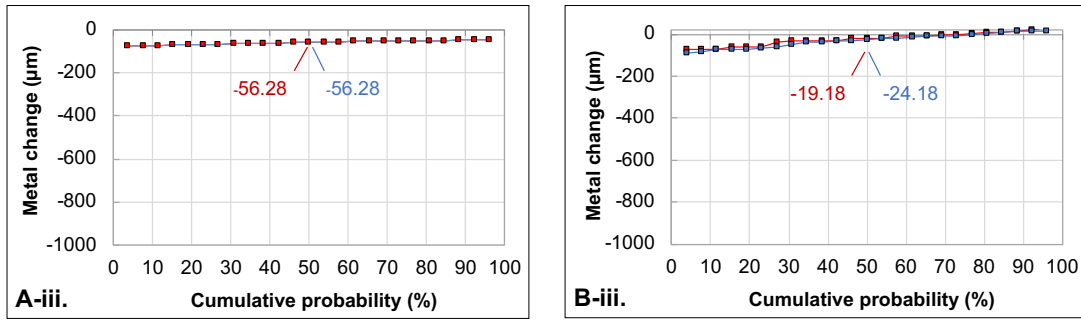


Figure B-22: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in HGB test gas with applied deposit D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at 600°C

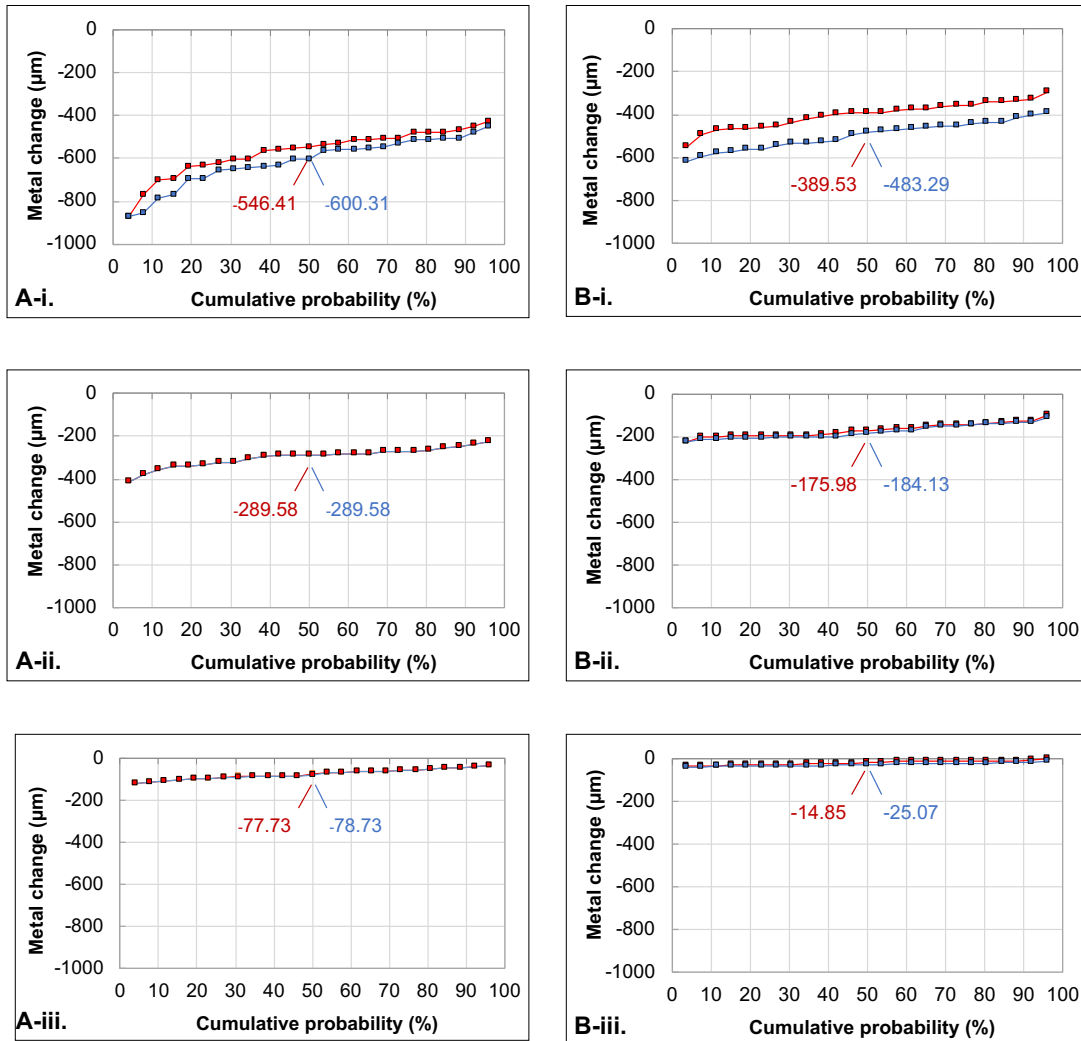


Figure B-23: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in HGB test gas with applied deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at 600°C

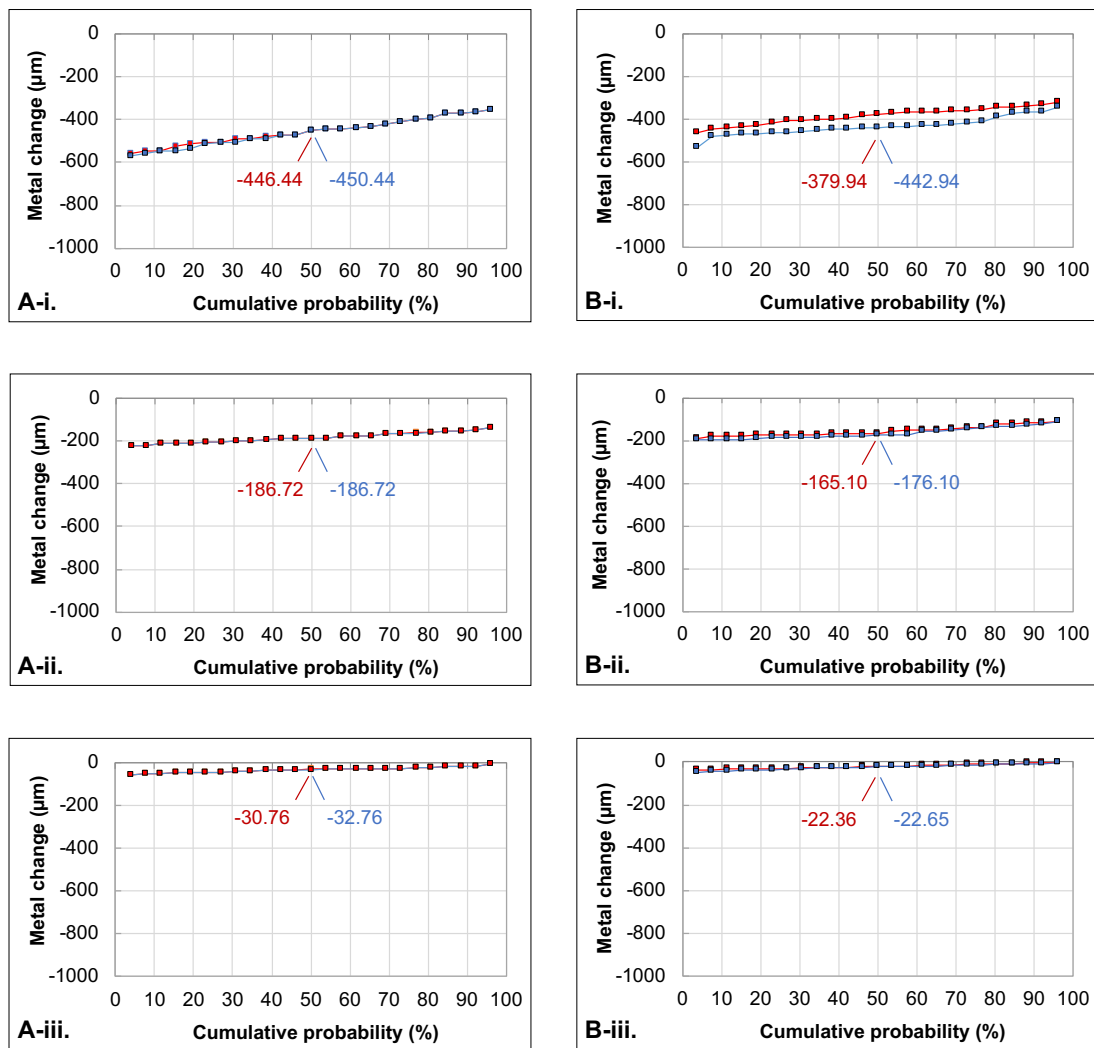
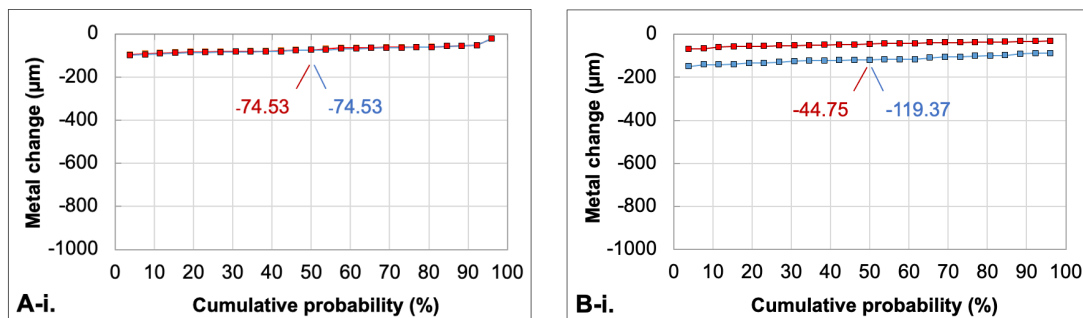


Figure B-24: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in HGB test gas with applied deposit D7 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ at 600°C

B.15 Deposit D1, D6 and D8 effects in APR fuel test gas conditions



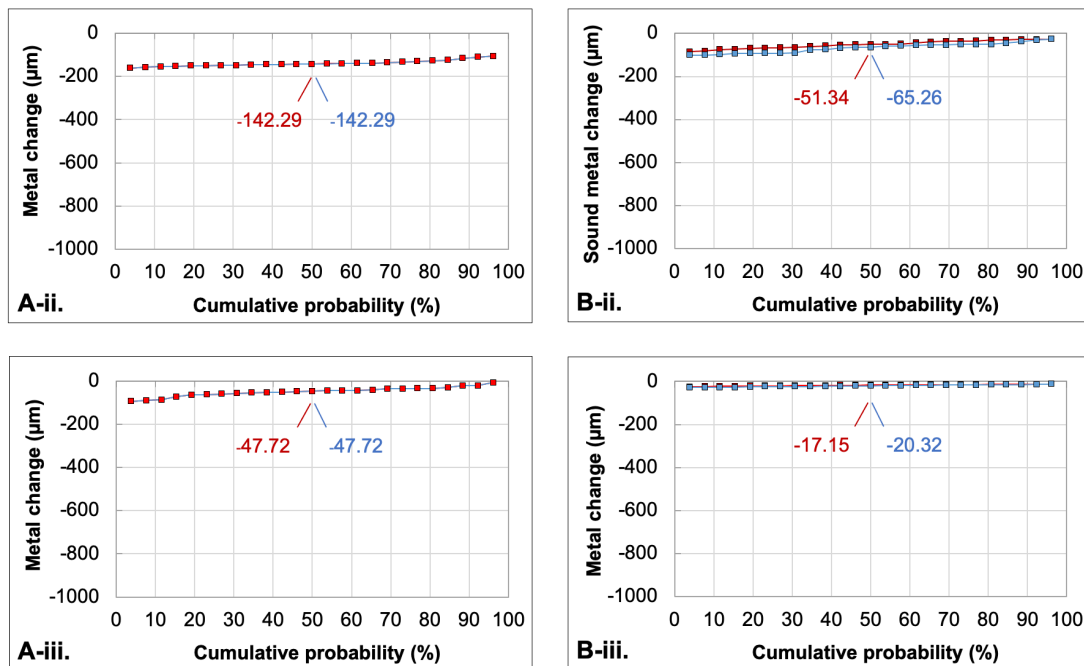
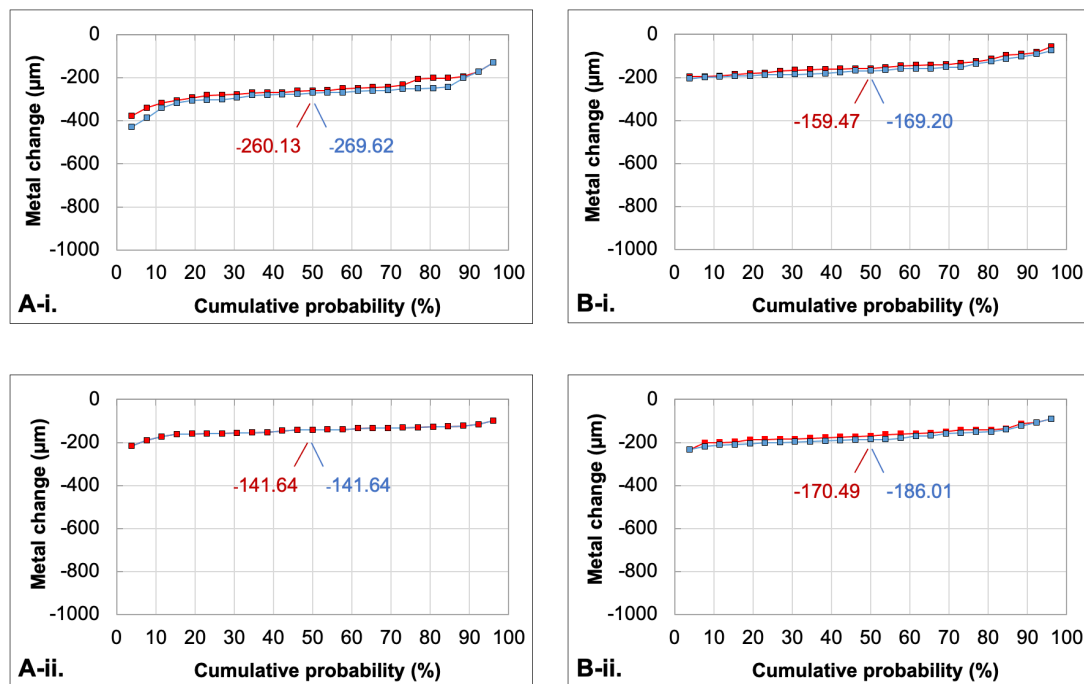


Figure B-25: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 exposure hours in APR test gas conditions with applied deposit D1 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C



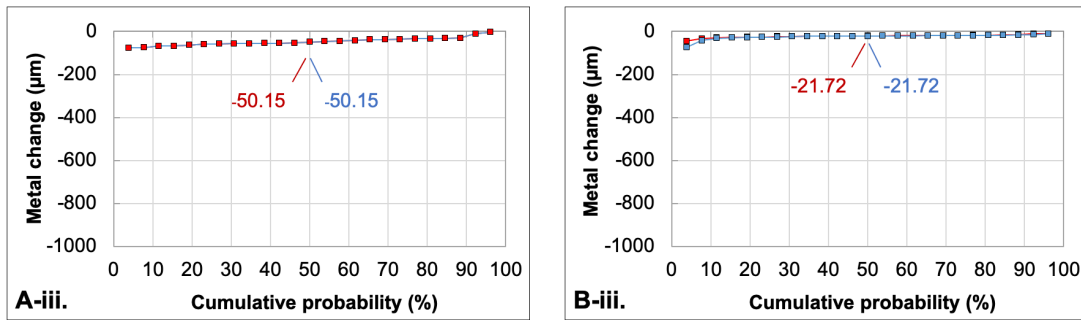


Figure B-26: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in APR test gas conditions with applied deposit D6 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

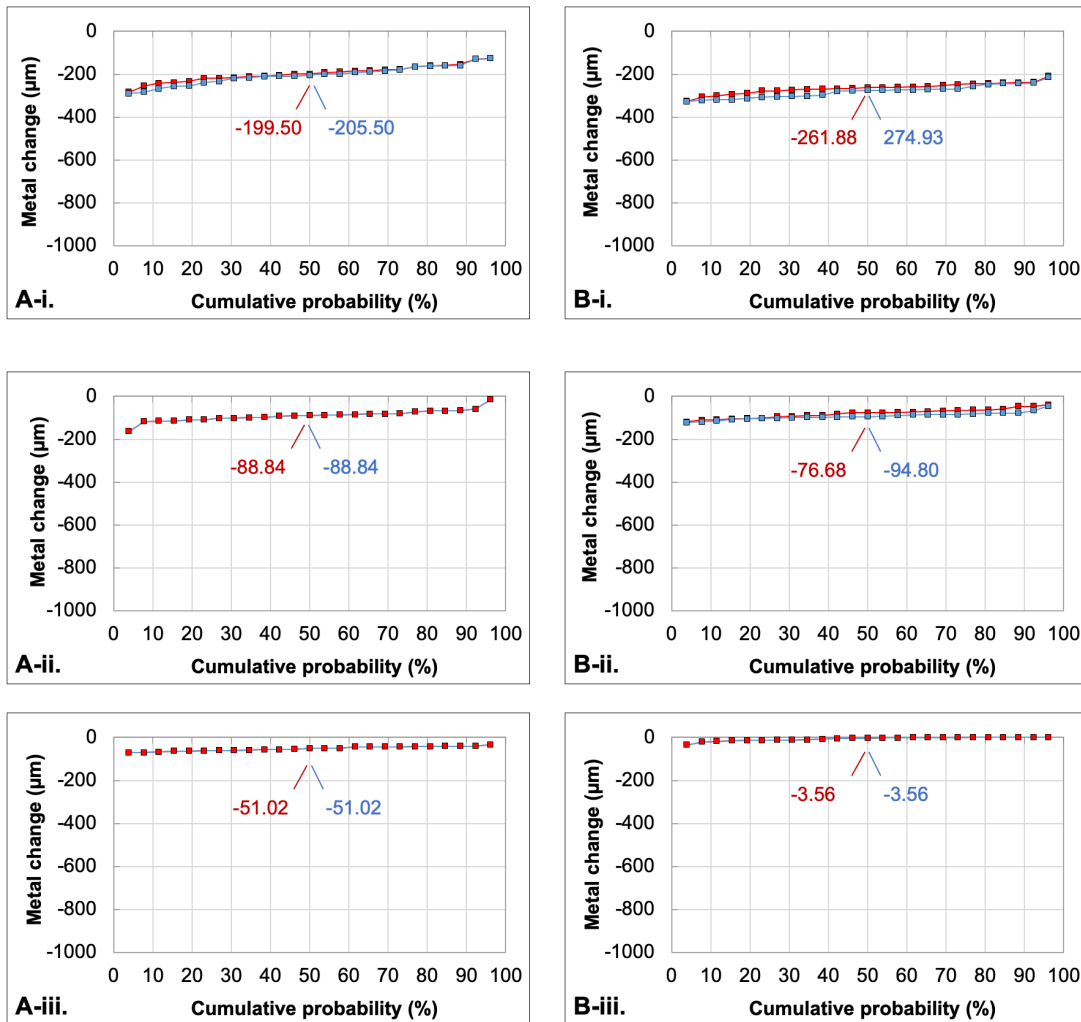


Figure B-27: Cumulative probability plot of (A) T91 & (B) TP 347HFG metal change (red data) and sound metal change (blue data) following (i) 1000, (ii) 500 & (iii) 200 hours exposure in APR test gas conditions with applied deposit D8 at flux $100 \mu\text{g}/\text{cm}^2\text{h}$ at 600°C

Appendix C
Weight change graphs

This chapter presents the weight changes measured for all corrosion samples.

C-1.
Samples exposed in WWF test gas environment at 600°C at deposition flux 100 μg/cm²hour

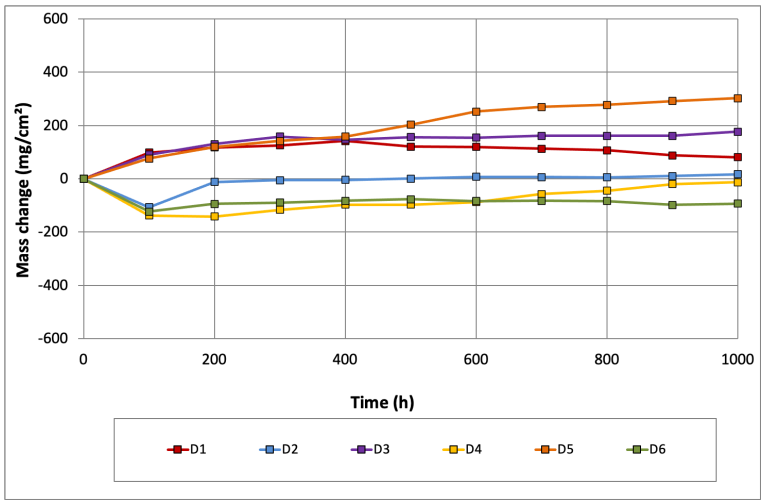


Figure C-1: Mass changes in T91 samples, deposits D1-D6, 1000 hours exposure

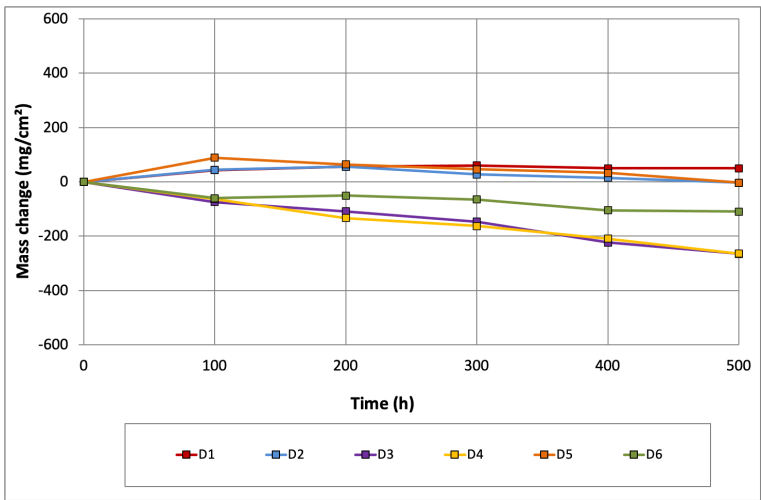


Figure C-2: Mass changes in T91 samples, deposits D1-D6, 500 hours exposure

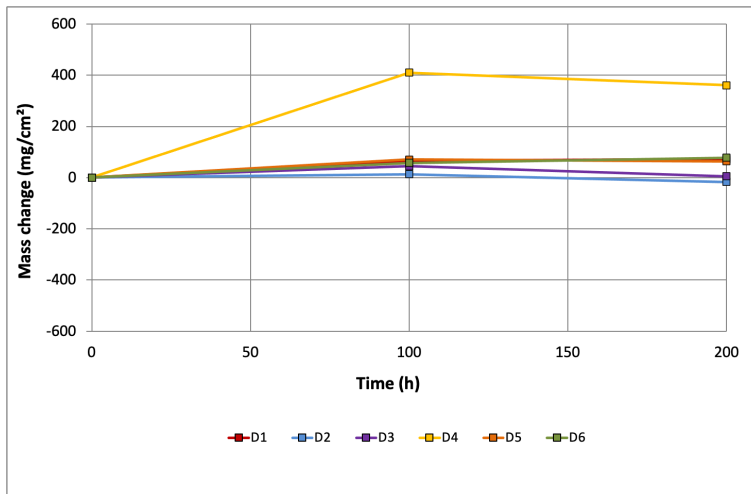


Figure C-3: Mass changes in T91 samples, deposits D1-D6, 200 hours exposure

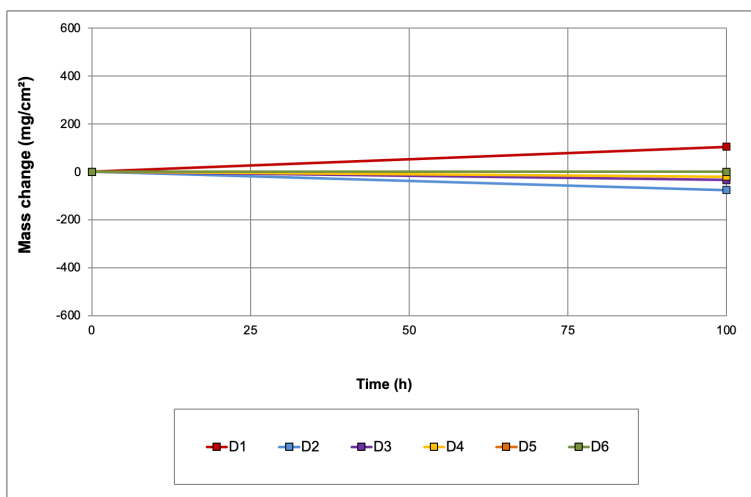


Figure C-4: Mass changes in T91 samples, deposits D1-D6, 100 hours exposure

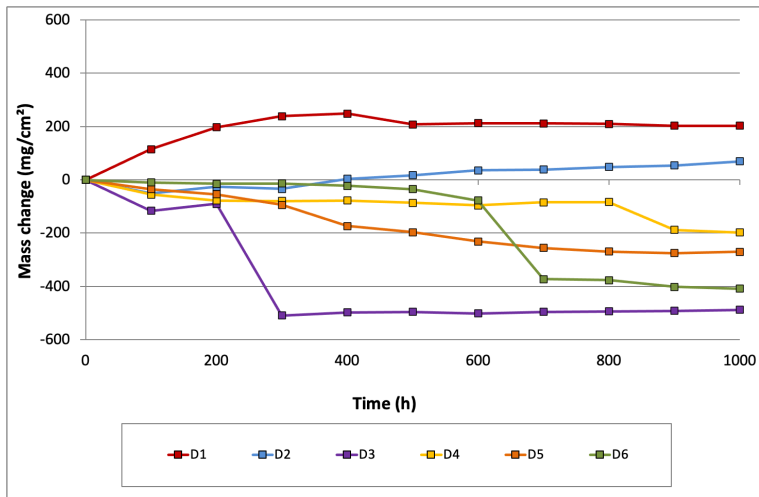


Figure C-5: Mass changes in TP 347HFG samples, deposits D1-D6, 1000 hours exposure

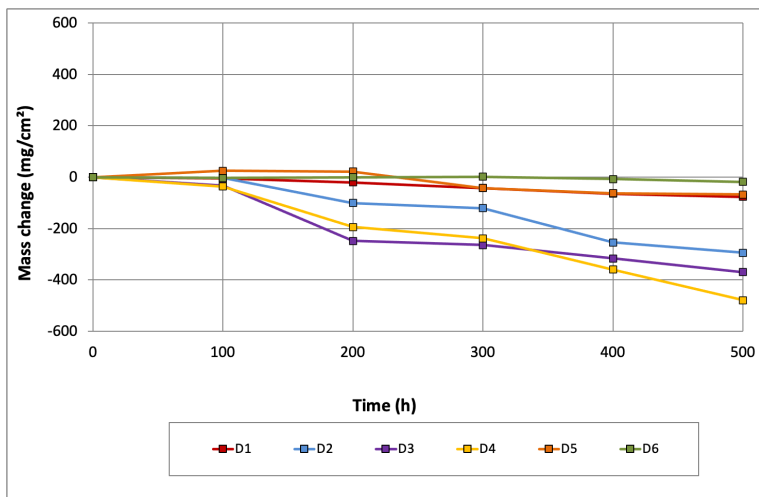


Figure C-6: Mass changes in TP 347HFG samples, deposits D1-D6, 500 hours exposure

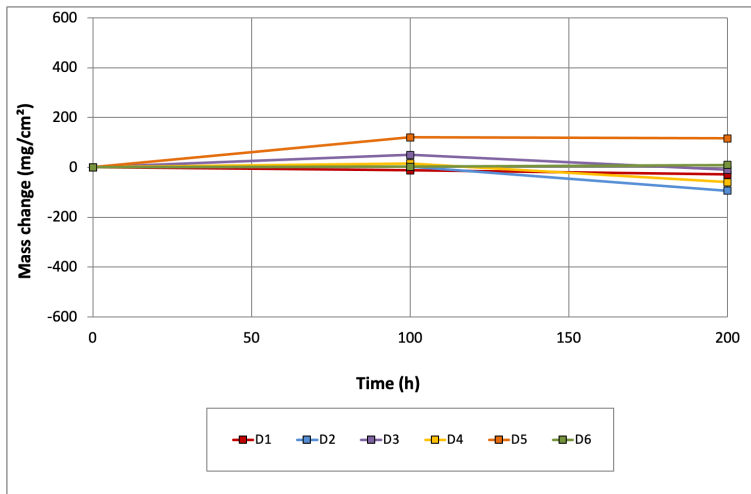


Figure C-7: Mass changes in TP 347HFG samples, deposits D1-D6, 200 hours exposure

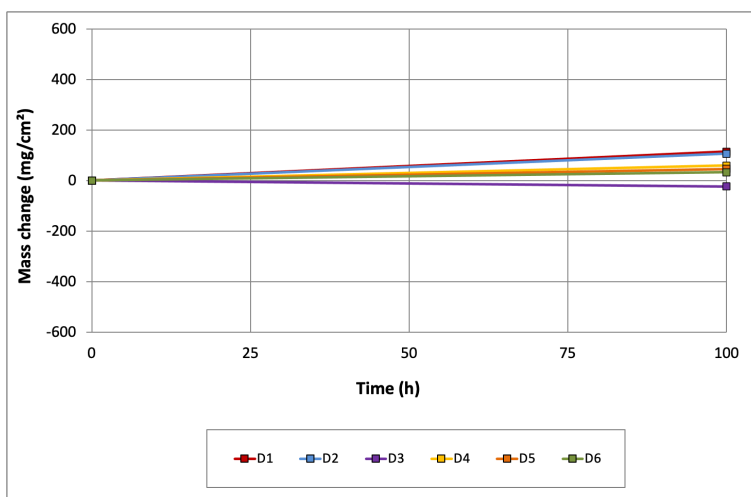


Figure C-8: Mass changes in TP 347HFG samples, deposits D1-D6, 100 hours exposure

C-2. Samples exposed in WWF test gas environment at 600°C at varying D1 and D6 deposition fluxes

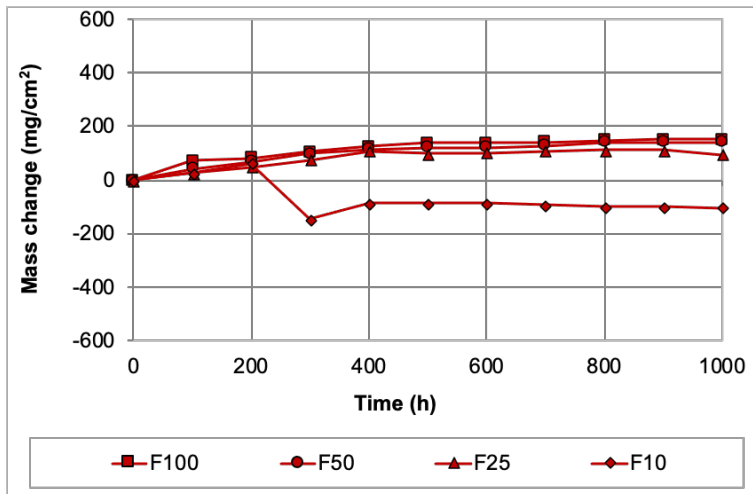


Figure C-9: Mass changes in T91 samples, deposit D1, 1000 hours exposure at deposition flux 10, 25, 50 & 100 $\mu\text{g}/\text{cm}^2\text{h}$

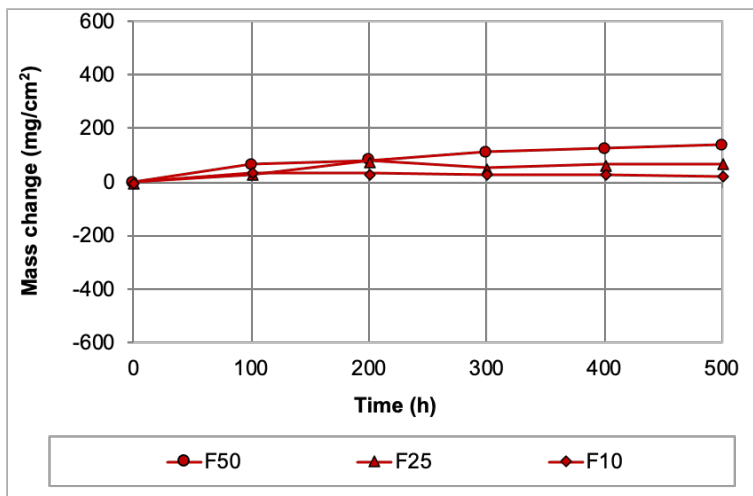


Figure C-10: Mass changes in T91 samples, deposits D1, 500 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

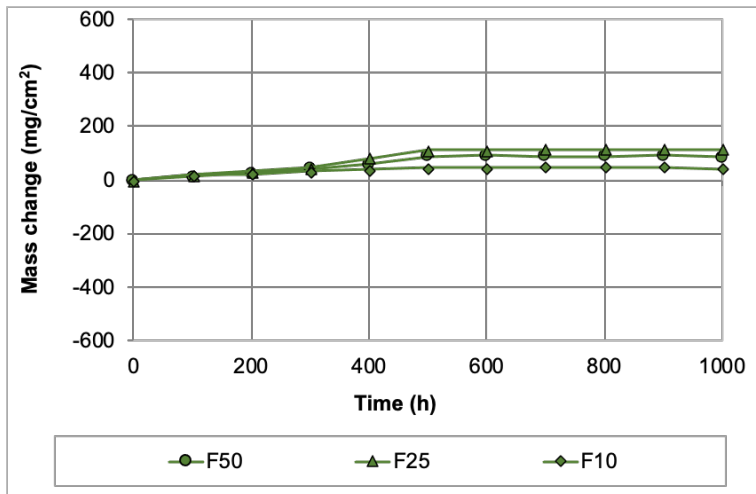


Figure C-11: Mass changes in T91 samples, deposits D6, 1000 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

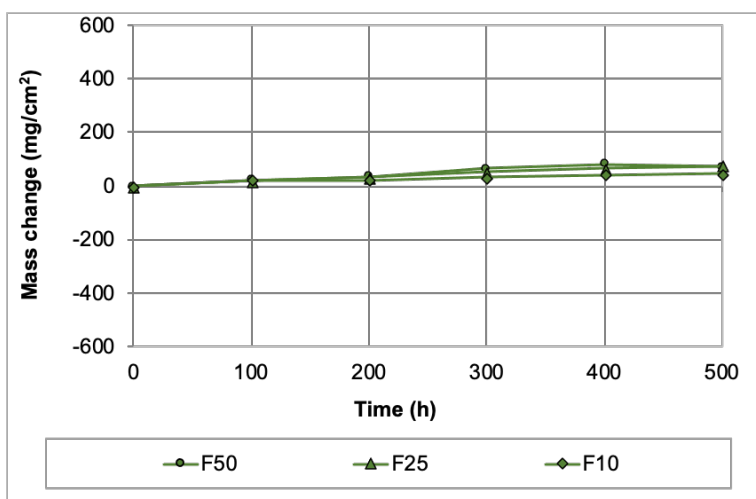


Figure C-12: Mass changes in T91 samples with deposits D6, 500 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

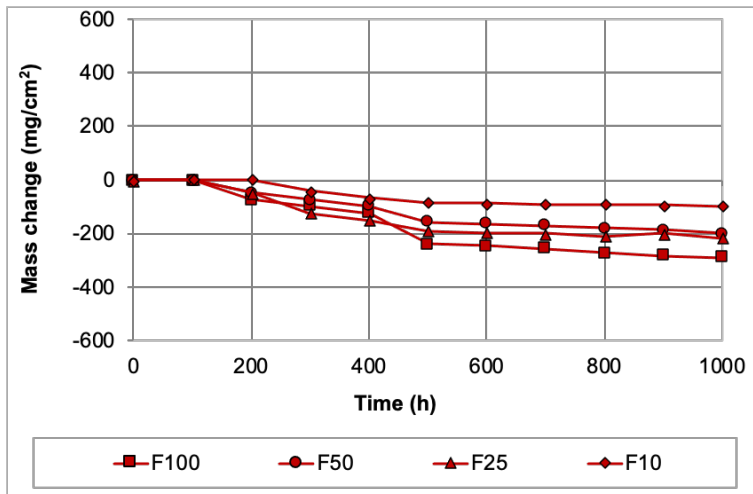


Figure C-13: Mass changes in TP 347HFG samples, deposits D1, 1000 hours exposure at deposition flux 10, 25 50 & 100 $\mu\text{g}/\text{cm}^2\text{h}$

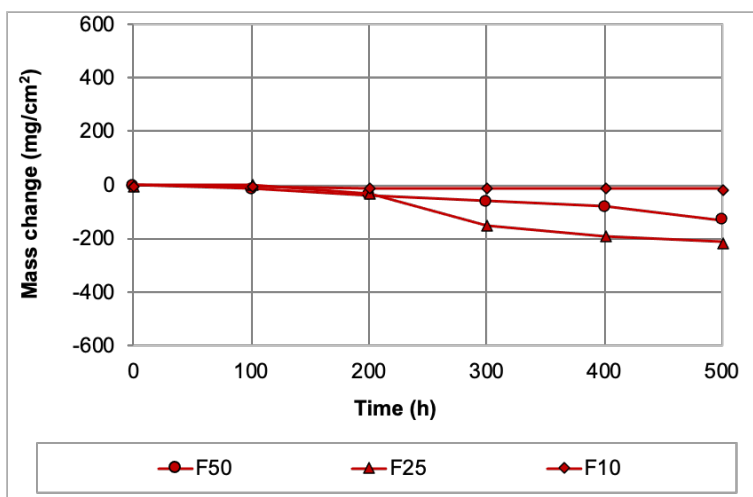


Figure C-14: Mass changes in TP 347HFG samples, deposits D1, 500 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

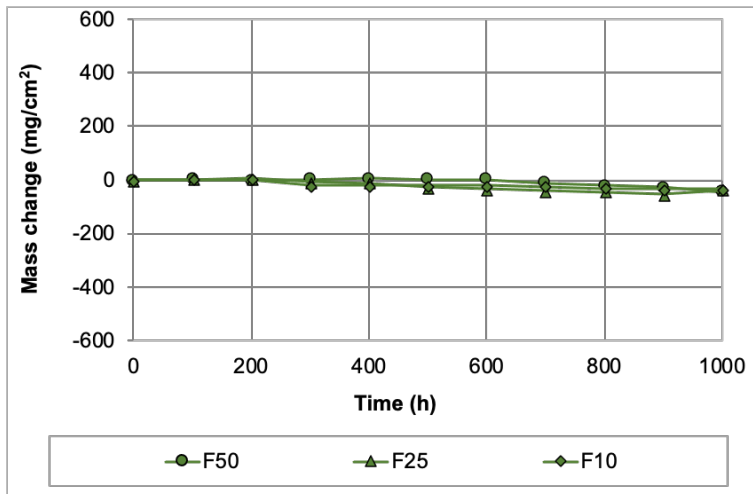


Figure C-15: Mass changes in TP 347HFG samples, deposits D6, 1000 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

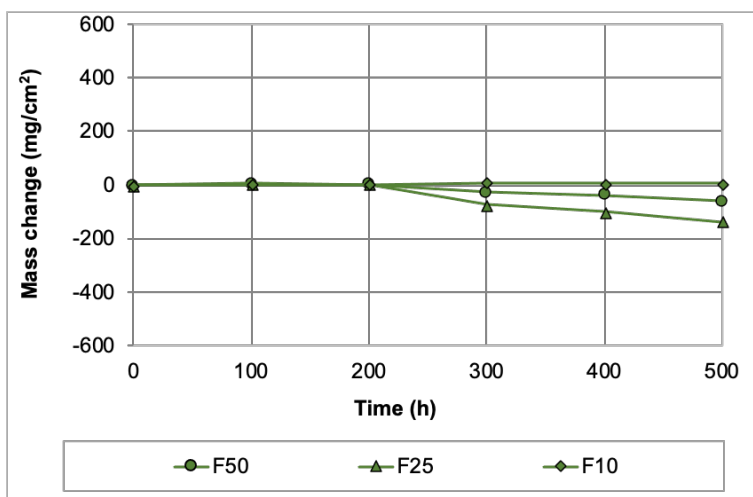


Figure C-16: Mass changes in TP 347HFG samples, deposits D6, 500 hours exposure at deposition flux 10, 25 & 50 $\mu\text{g}/\text{cm}^2\text{h}$

C-3. Samples exposed in WWF test gas environment at 550°C with deposit D1 and D6 at 100 $\mu\text{g}/\text{cm}^2\text{h}$

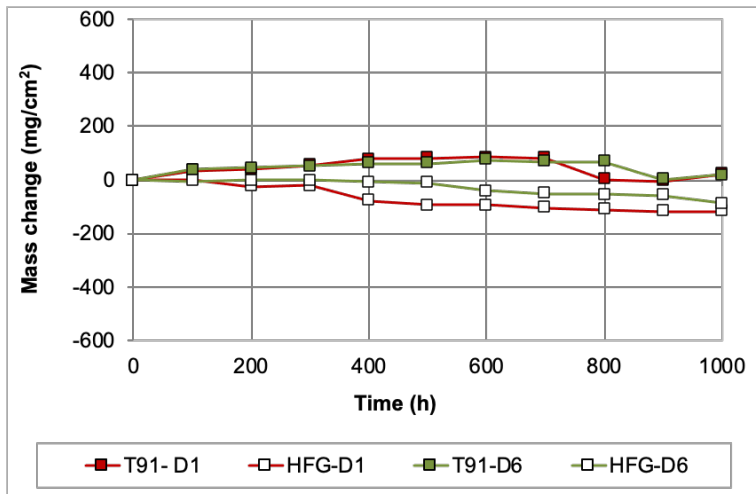


Figure C-17: Alloy mass change effects of deposits D1 & D6, 1000 hours exposure

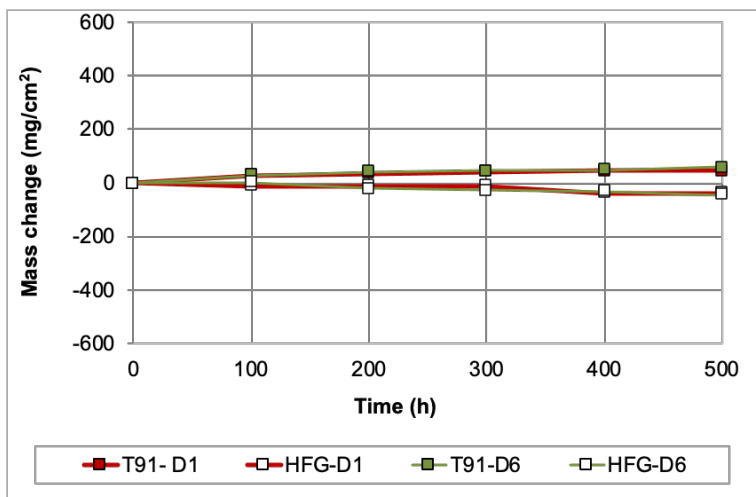


Figure C-18: Alloy mass change effects of deposits D1 & D6, 500 hours exposure

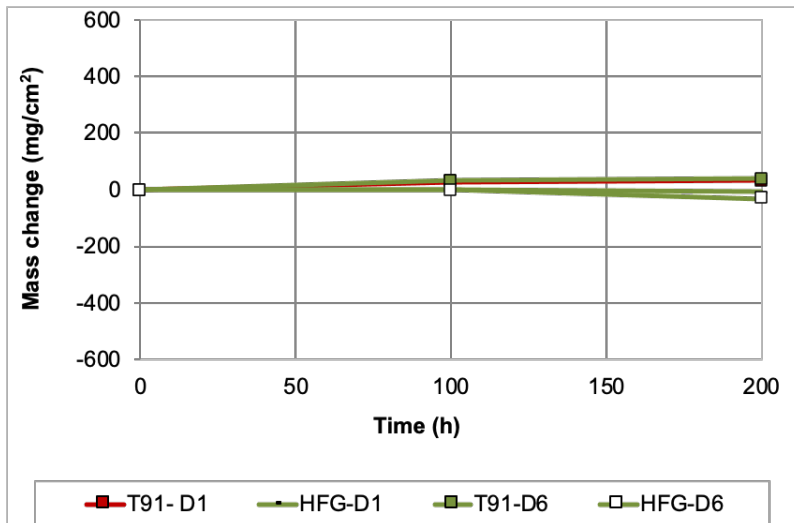


Figure C-19: Alloy mass change effects of deposits D1 & D6, 200 hours exposure

C-4. Samples exposed in WWF test gas environment at 500°C with deposit D1 and D6 at 100 μ g/cm²h

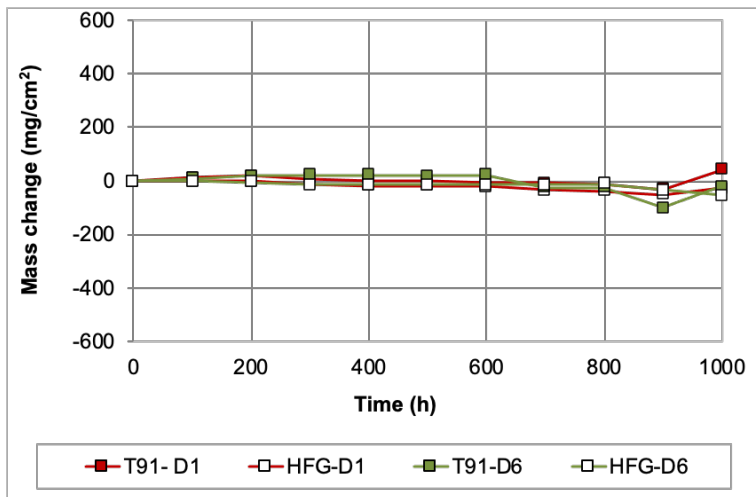


Figure C-20: Alloy mass change effects of deposits D1 & D6, 1000 hours exposure

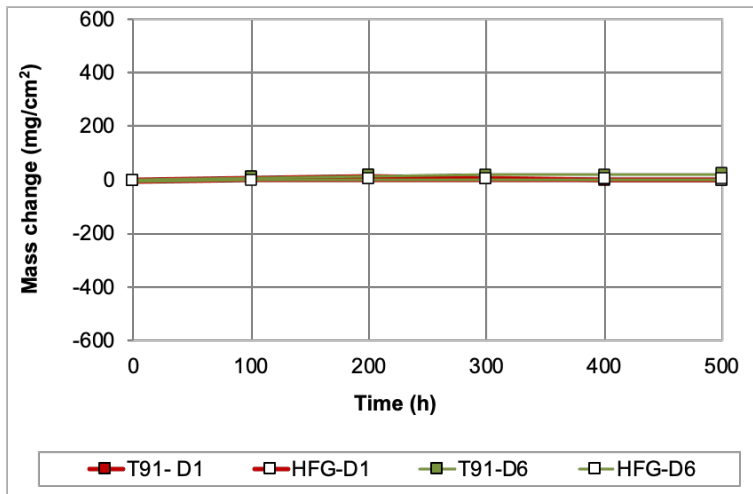


Figure C-21: Alloy mass change effects of deposits D1 & D6, 500 hours exposure

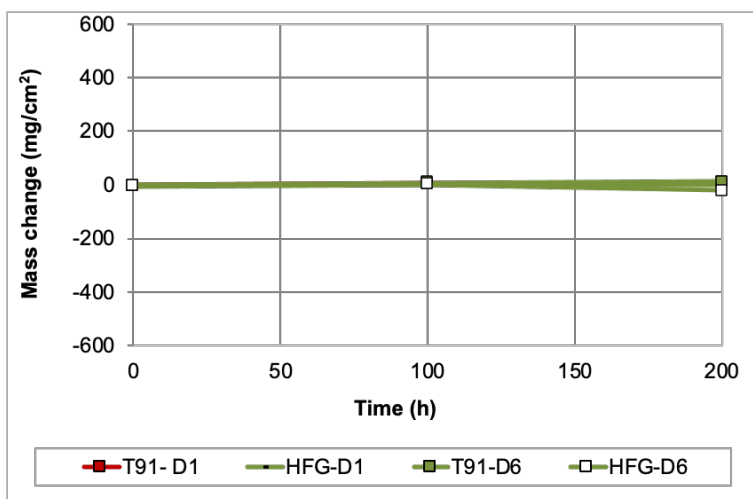


Figure C-22: Alloy mass change effects of deposits D1 & D6, 200 hours exposure

C-5. Samples exposed in HGB test gas environment at 600°C with deposit D1, D6 and D7 at 100µg/cm²h

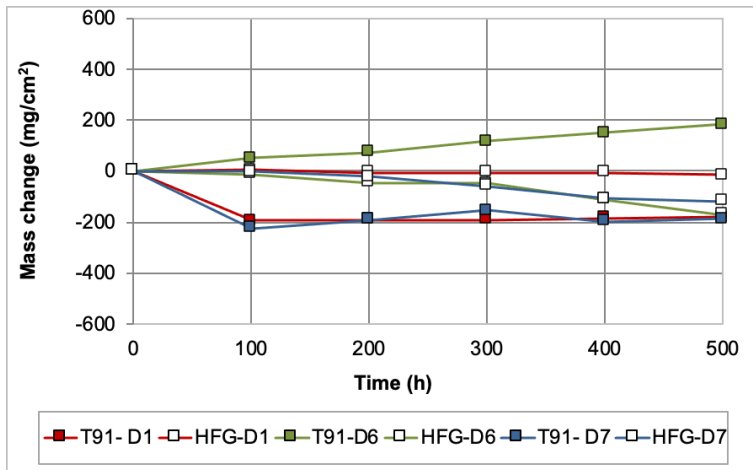


Figure C-23: Alloy mass change effects of deposits D1, D6 & D7, 1000 hours exposure

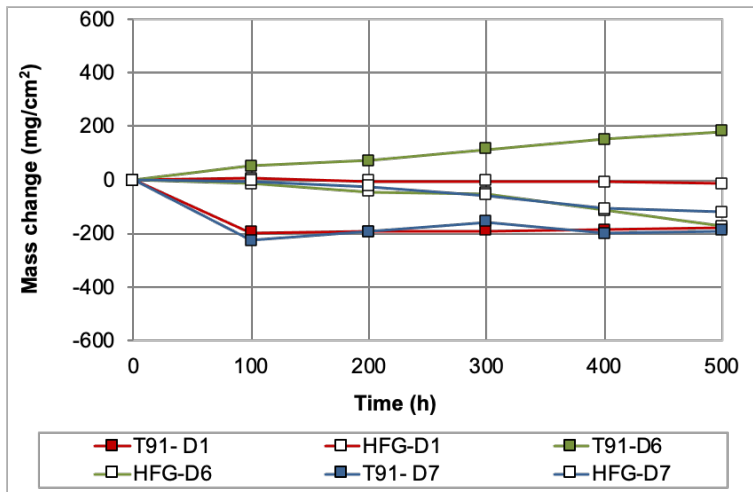


Figure C-24: Alloy mass change effects of deposits D1, D6 & D7, 500 hours exposure

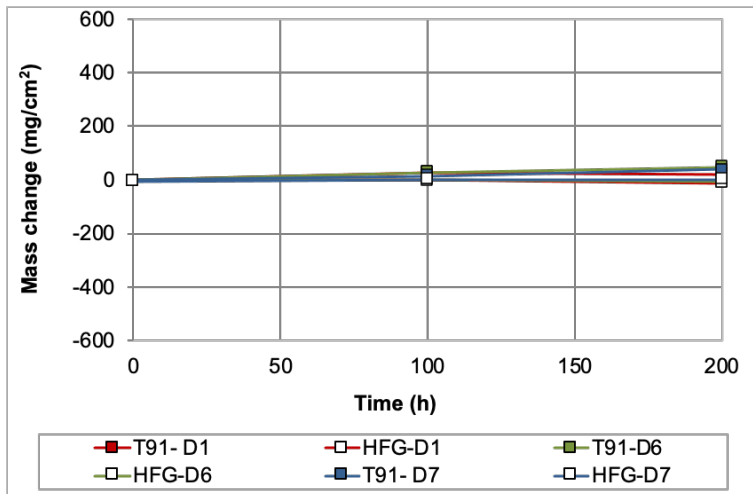


Figure C-25: Alloy mass change effects of deposits D1, D6 & D7, 200 hours exposure

C-6. Samples exposed in APR test gas environment at 600°C with deposit D1, D6 and D8 at 100μg/cm²h

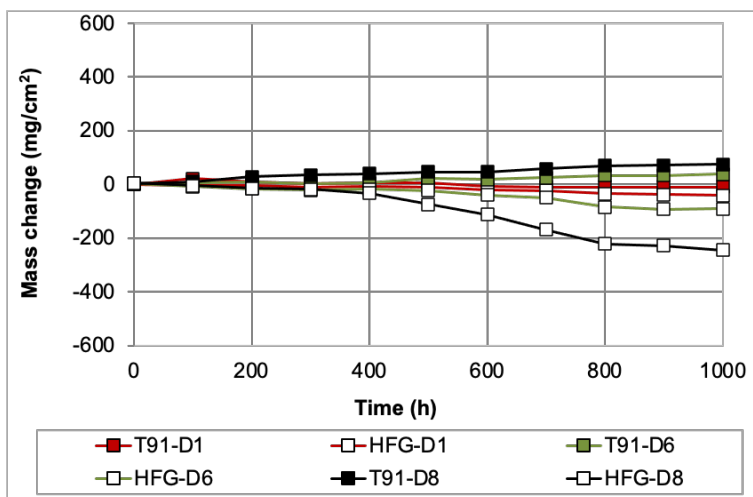


Figure C-26: Alloy mass change effects of deposits D1, D6 & D8, 1000 hours exposure

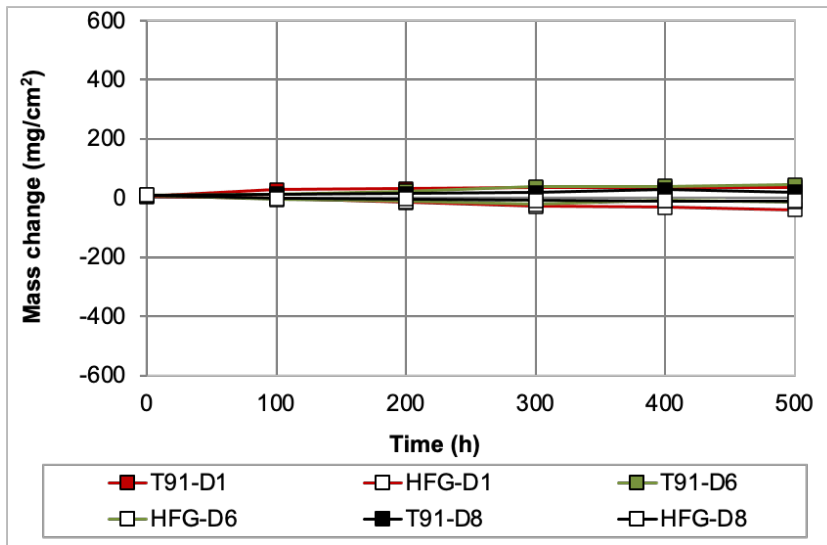


Figure C-27: Alloys mass change effects of deposits D1, D6 & D8, 500 hours exposure

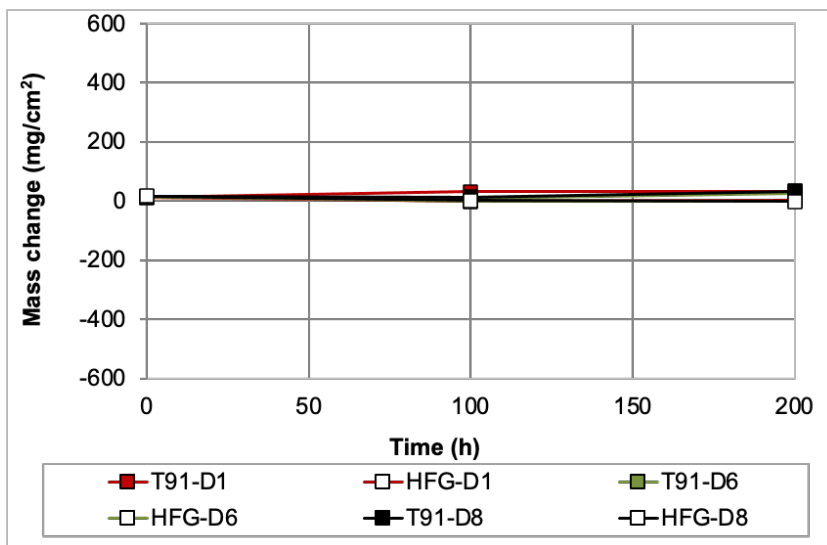


Figure C-28: Alloy mass change effects of deposits D1, D6 & D8, 200 hours exposure

Appendix D Error analysis

Experimental errors may be introduced from sample measurements, such as weights and dimensions. As the 'deposit recoat' method has been majorly employed in the evaluations undergone in this research, this chapter lists and discusses error sources inherent within the procedure.

D-1 Dimensional metrology

Errors occurring from the measurements of a pre-exposure coupon's dimensions and measurements carried out post-exposure translate directly to metal change data. The likely errors that could be encountered are analysed in this section.

D-1.1 Pre-exposure metrology

Errors associated with alloy machining and dimensional measurements prior to furnace exposure tests can influence corrosion measurement data. Unsymmetrical segmentation can leave sample surface rough, however the samples employed were provided cut and polished to specific size and shape using specialised machinery.

The resolution and quantizing error of the micrometre employed for pre-exposure dimension measurements is provided in the instrument's documentation as $\pm 1 \mu\text{m}$ each. 1200 measurements of the same sample, led by Potter A. [119] were conducted to assess the measurement repeatability of cylindrical alloy samples. Three standard deviations from three different users were $0.97 \mu\text{m}$ (max. range, $5 \mu\text{m}$), $1.38 \mu\text{m}$ (max. range, $9 \mu\text{m}$) and $1.48 \mu\text{m}$ (max. range, $8 \mu\text{m}$). The initial metrology measurement error of $\pm 2 \mu\text{m}$ was calculated using **Equation D-1**.

$$\delta_i = \sqrt{(\delta_r)^2 + (\delta_q)^2 + (\delta_u)^2} = \pm 1.9 \text{ um} \quad \text{Equation D-1}$$

Where δ_i is the pre-exposure dimensions measurement error; ' δ_r ' is resolution error; ' δ_q ' is quantizing error and ' δ_u ' is the average standard deviation user error.

Though measurements done by Potter A. [119] were performed on cylindrical samples, the methods adopted for dimensional measurements as well as instrumentations are similar to those described within Chapter 3 of this thesis. It is thus expected that, similar levels of error will be encountered from pre-exposure dimensional measurements in this research.

D-1.2 Post-exposure metrology

Errors associated with post-exposure sample preparation and metrology are analysed in this section.

D-1.2.1 Sample mounting

As samples are cross-sectioned within a cured resin, it is essential that samples are placed parallel with the mount base to avoid unsymmetrically cross-sectioning which will impact post-measurement data. The mounts are designed such that a coupon sits fully to avoid non-parallel aligning of the mounted sample. However, the mounted alloy may shift prior to the resin setting if the scalpel blade loses its spring held grip on the sample surface as a result of a loosened screw. To avoid this problem, mounts and screws were visually inspected and prior to cutting, the scalpel thread position against the sample surface was confirmed to be in place.

D-1.2.2 Sample cutting, grinding and polishing

Errors from sample cutting and grind back can be associated with cross-sectioning away from the central point marked by the shallow drilled hole.

Assuming the equation of a circle, shown in **Equation D-2**.

$$x^2 + y^2 = r^2$$

Equation D-2

Where 'r' is the radius of the circle, 'x' is the horizontal distance from the central point and 'y' is the vertical distance from the central reference point.

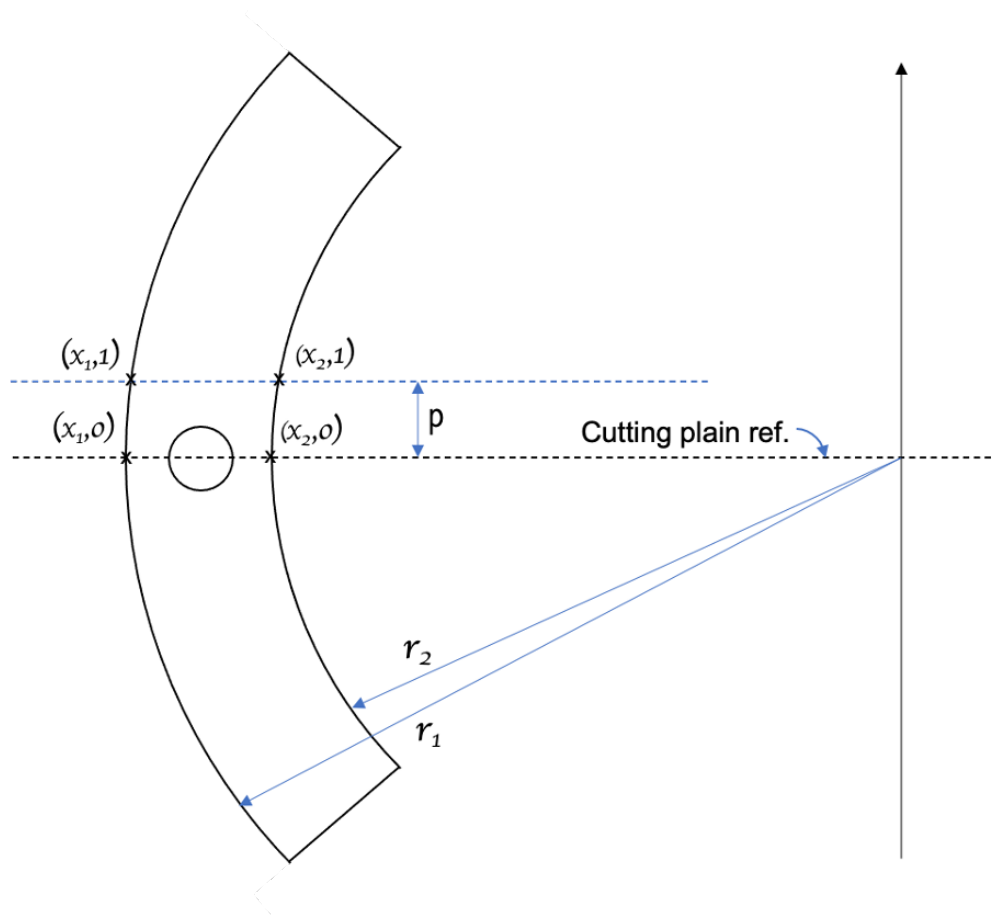


Figure D-1: Schematic of an alloy tube segment showing reference cross-sectioning plain and 1 mm above reference plain with x-y coordinate points. Adapted from [111]

Equation D-2 can be expressed as:

$$x^2 = r^2 - y^2 \quad \text{Equation D-3}$$

Assuming radius 'r₁' and 'r₂' for internal and external diameters respectively are 20 mm and 16 mm. The (x₁,y₁) and (x₂,y₂) coordinate points on the reference cutting plain are (20,0) and (16,0), thus the wall thickness (x₁ – x₂), is 4 mm. If the alloy is sectioned at a plane 'p' which is 1 mm above the reference point, 'y'=1 and the new wall thickness can be calculated using the following equations:

$$x^2 = r^2 - y^2 \quad \text{Equation D-4}$$

$$x_1 = \sqrt{20^2 - 1^2} = 19.9750 \text{ mm} \quad \text{Equation D-5}$$

$$x_2 = \sqrt{16^2 - 1^2} = 15.9687 \text{ mm} \quad \text{Equation D-6}$$

$$x_1 - x_2 = 4.0063 \text{ mm} \quad \text{Equation D-7}$$

$$\delta_c = 4 \text{ mm} - 4.0063 \text{ mm} = 6.3 \text{ } \mu\text{m} \quad \text{Equation D-8}$$

Were 'δ_c' is the post-exposure sample cross-sectioning error.

Thus, the effect of cross-sectioning 1 mm above the cutting reference plain is 6.3 μm and is indicated as a positive metal thickness gain. This is true for the assumed dimensions. Typically, samples are cut about 1mm before the reference point to give allowance for the ground back metal. Appearance of the drilled hole during grinding is an indication that the sectioned plane is within 1 mm, given that the hole diameter is within 2 mm. It is unlikely that the cut/grind level will be missed beyond 1 mm. Metal lost from polishing is considered negligible in this regard.

D-1.2.3 Acquiring post-exposure dimensions

The image analyser x-y stage movement may be subject to a degree of error. Potter A. [119] determined the average difference between repeated measurements of a sample which generate sample coordinates. The calculated user-based error, resulting from replotting the same image 10 times and generating a total of 300 measurements, was a standard deviation of 0.49 μm over 30 measurements (max. range 2.3 μm). The post-exposure sample metrology error can be calculated by:

$$\delta_{pm} = \sqrt{(\delta_s)^2 + (\delta_p)^2} = \pm 1.2 \mu\text{m} \quad \text{Equation D-9}$$

Where ' δ_{pm} ' is the post-exposure sample metrology error; ' δ_s ' is the microscope stage error ($\pm 1 \mu\text{m}$, manufacturer defined [119]) and ' δ_p ' is the user error associated with plotting sample coordinates.

D-2 Furnace Temperature

Temperature profiling measurements were conducted for each furnace and each set temperature. **Table D-1** shows the temperatures measured by a K-type thermocouple at 1 cm depth intervals prior to each furnace program, using furnace A and B. The measured temperature points cover the length of the positioned sample shelves. Six shelf levels with 4 crucible holder slots each are spread over 12 cm approximately, and a temperature gradient exists across this distance. The middle placement level (between shelf 3 & 4) is positioned at the hottest temperature point recorded by the thermocouple. The thermocouple manufacturer advise an error margin of $\pm 2.5^\circ\text{C}$ [182]. The measurement error and any error related to the positioning of the thermocouple within the furnace is likely to be negligible. The temperature ranges at the ± 6 cm extremities from the midpoint (presented in **Table D-1**) represent the maximum temperature difference

between any two samples in the same test. The errors associated with temperature differences experienced by samples at corresponding set temperatures can be calculated using **Equation D-10** and are given in **Table D-1**.

$$\delta_t = \sqrt{(\delta_{max})^2 + (\delta_{tk})^2}$$

Equation D-10

' δ_t ' is the error in sample temperature; ' δ_{max} ' is the maximum temperature difference between any two samples within the same test and ' δ_{tk} ' is the manufacturer guide K-type thermocouple error margin.

Table D-1: Temperature error analysis figures for furnaces used for fireside corrosion tests

		Temperature at ± 6cm from hot zone, ' δ_{max} ' (°C)	
		A	B
Temp. (°C) measured at hot zone	600°C	8	6
	550°C	5	
	500°C	3	

A worst-case temperature deviation will be achieved using Furnace A set at 600°C. As such,

$$\delta_t = \pm 8.4^{\circ}\text{C}$$

Equation D-11

The metal loss deviations that can be associated with temperature errors are not fixed for all conditions as chemistry conditions influencing metal loss is dependent on other factors such as gas and deposit

compositions, material characteristics and test duration. Data from literature provide corrosion information for different test conditions.

Potter A. [119] used a similar approach for quantifying the metal thickness change associated with temperature errors. It was estimated that the metal thickness loss for a super alloy exposed for 200 hours with a deposit of composition Na_2SO_4 -98% / NaCl -2% and a flux of $5 \mu\text{g}/\text{cm}^2\text{h}$ between is $1 \mu\text{m}/^\circ\text{C}$. The extrapolation was based on exposure temperatures between 600°C and 1000°C and 25°C measurement intervals, as described by Haight et al. [183].

For this research, T91-D1 exposed at 550°C and 500°C for 200 hours shows a metal thickness loss difference of $\sim 5 \mu\text{m}$ (median value) (D1 composition: 20%- K_2SO_4 , 30%- KCl , 20%- Na_2SO_4 , 30%- CaSO_4) (**Figure B-12**). A simple extrapolation of the 50°C temperature interval results in a rate of $0.1 \mu\text{m}/^\circ\text{C}$.

At 1000 hours exposure, the T91-D1 median metal loss difference between 600°C and 550°C is $\sim 178 \mu\text{m}$ and by extrapolation, the rate is $3.7 \mu\text{m}/^\circ\text{C}$ (**Figure B-12** and **Figure B-16**). These comparisons are based on samples exposed under $100 \mu\text{g}/\text{cm}^2\text{h}$ deposit application flux and WWF combustion gas conditions. These rate values show an increased temperature sensitivity of T91 corrosion response as the test temperature is increased.

D1 and D6 have been the most employed deposits for evaluating corrosion mechanisms and D1 has shown greater metal corrosion influence than D6 under WWF test gas conditions (**Section 5.2.1**). As corrosion rates are higher for T91 compared to 347HFG, the use of median corrosion values of T91-D1 exposed at 600°C represents samples analysed in this PhD which undergo the most severe of metal changes at the minimal exposure duration (200 hours). Thus, the worst-case median metal thickness change per degree temperature drop (where temperature reduces from the hot zone to

the sample position extremes) ' δ_m ', between 500-600°C in WWF conditions is:

$$\delta_m = -0.1 - 3.7/2 = -1.9 \mu\text{m} \quad \text{Equation D-12}$$

The total median metal change error, ' δ_{mt} ', can be expressed as:

$$\delta_{mt} = \delta_m \times \delta_t = -16 \mu\text{m} \quad \text{Equation D-13}$$

D-3 Weight measurements

Errors associated with weight measurements are described within this section.

D-3.1 Alloy weight measurements

The calibration specification for the balance on which the alloy samples and deposit salts were weighed states instrumentation repeatability and linearity values of $\pm 0.02 \text{ mg}$ and $\pm 0.03 \text{ mg}$ respectively. The combined error from the scale application can thus be estimated using **Equation D-14**.

$$\delta_b = \sqrt{(\delta_{rep})^2 + (\delta_{lin})^2} \quad \text{Equation D-14}$$

$$\delta_b = 0.036 \text{ mg} \quad \text{Equation D-15}$$

Where δ_b is the balance error per cycle, δ_{rep} is the repeatability error and δ_{lin} is the linearity error.

The weight changes of alloys are commonly applied to the quantitative evaluation of corrosion damage. Spallation of alloy surfaces introduce weight change errors which can be significant and difficult to

manage. The weight change effect of spallation has been discussed in **Section 4.2.2.1.1**. Discrepancies in weight change measurements do not correlate with metal thickness change data as spallation only affects loosely held surfaces which do not comprise of the metal thickness measured. As a result of these observations, weight change data were not considered for evaluating corrosion and metal loss error analysis is not required in this case.

D-3.2 Deposit application weight measurements

Errors associated with deposits include deposit makeup, deposit application technique and the amount of deposit applied (flux). The extents to which errors in deposition flux application can affect the corrosion rate varies as other factors such as temperature, material, deposit and gas compositions and exposure hours also influence corrosion rates. The uniformity of applying the deposit on the alloy surface, which ensures the entire coupon surface receives an evenly distributed deposit coating, is difficult to quantify. The deposit application method ensures that deposits are smeared as thick slurries on a moderately hot sample surface (~90°C). This way, the slurry is able to spread out to the edges of the sample as gradual salt dry-out occurs.

Deposit component mixing errors can also affect metal loss, whereby salt samples are inaccurately measured or not allowed to completely mix in the slurry. The effect of errors associated with weight measurements of deposit components (salts) on metal thickness is however complex, considering that this research employs several deposits of up to 4 salt components. Error analysis would require an evaluation of the metal change influence using a cumbersome algorithm to address all chemical composition combinations possible. To limit salt weight measurement errors, each salt component was measured separately before it was introduced to

the batch. Salt residues were decanted into the bulk with deionised water. Bulk slurries were stored in airtight containers at room temperature.

Errors associated with deposition flux measurements can be estimated from the instrumental error calculated in **Equation D-16** and user weighing repeatability.

The balance error effect on deposition flux can be estimated as such:

$$\delta_{bf} = \left(\frac{\delta_b(\mu g)}{Surface\ area(cm^2) \times Exposure(h)} \right) \quad \text{Equation D-16}$$

Where ' δ_{bf} ' is the balance flux error for a sample exposed for 1 furnace cycle (100 hours), using an average sample surface area of 2.22 cm².

Flux error from the balance thus varies with sample dimensions and exposure time.

$$\delta_{bf} = \left(\frac{0.36 \times 1000 (\mu g)}{2.22 (cm^2) \times 100(h)} \right) = 1.6 \mu g/cm^2h \quad \text{Equation D-17}$$

The user deposit weighing errors (δ_{WU}) were calculated for each sample using a deposit weight differences (W_d) from the target weights (W_t) (**Equation D-18**). Majority of deposit application weights (at 100 $\mu g/cm^2h$ flux) fell within 10 wt.% range. Examples of δ_{WU} weight errors measured for samples employed in this study are presented in **Table D-2**.

$$\delta_{WU} = \left(\sqrt{[(W_{final} - W_{initial}) - W_{target}]^2 / W_{target}^2} \right) \times 100\% \quad \text{Equation D-18}$$

Where W_{final} is the final sample weight, $W_{initial}$ is the initial sample weight and W_{target} is the target deposit weight.

Table D-2: Weigh measurement errors for deposit application flux

Sample details	TW3-1, Flux 100 ug/cm2h (0.02 g added)									
Total exposure time	1000 hours									
Initial weight ($W_{initial}$)	7.532	7.713	7.750	7.829	7.895	7.951	7.967	8.007	8.077	8.121
Final weight (W_{final})	7.552	7.734	7.770	7.849	7.918	7.971	7.986	8.026	8.096	8.141
Error (δ_{WU})	0%	6%	1%	1%	16%	3%	6%	7%	4%	2%
Sample details	TW3-23, Flux 10 ug/cm2h (0.002 g added)									
Total exposure time	1000 hours									
Initial weight ($W_{initial}$)	7.532	7.713	7.750	7.829	7.895	7.951	7.967	8.007	8.077	8.121
Final weight (W_{final})	7.536	7.579	7.591	7.617	7.631	7.638	7.663	7.671	7.677	7.683
Error (δ_{WU})	17%	6%	2%	1%	6%	16%	1%	3%	15%	17%

The user deposition flux error ' δ_{Wuf} ' may be expressed as:

$$\delta_{Wuf} = \delta_{WU} \times \text{flux } (\mu\text{g}/\text{cm}^2\text{h}) \quad \text{Equation D-19}$$

Applying ' δ_{WU} ' allowance of 10% at high flux (100 and 50 $\mu\text{g}/\text{cm}^2\text{h}$) and 20% at low flux (25 and 10 $\mu\text{g}/\text{cm}^2\text{h}$), at flux 100, 50, 25 and 10 $\mu\text{g}/\text{cm}^2\text{h}$, δ_{Wuf} is 10 5, 5 and 2 $\mu\text{g}/\text{cm}^2\text{h}$ respectively, with an average δ_{Wuf} value of 5.5 $\mu\text{g}/\text{cm}^2\text{h}$:

The total flux error, ' δ'_{tf} ', defined by user error ' δ_{Wuf} ' and the balance error δ_{bf} can be expressed as:

$$\delta_{tf} = \sqrt{(\delta_{bf})^2 + (\delta_{Wuf})^2} \quad \text{Equation D-20}$$

$$\delta_{tf} = \sqrt{(1.6)^2 + (5.5)^2} = \pm 5.73 \mu\text{g}/\text{cm}^2\text{h} \quad \text{Equation D-21}$$

The deposition flux error influence on metal change can be quantified by extrapolation from corrosion tests performed in this research. For deposit D1 at 10 µg/cm²h (closest applied flux to calculated flux error), the median metal thickness loss of 347HFG is 9.5 µm following 500 hours exposure of 347HFG in WWF gas conditions. Although the metal loss value is expected to be lower following 100 hours of exposure, in the absence of such data, 9.5 µm has been used to extrapolate the corresponding metal change.

Thus, a metal loss equivalent to the flux application error is:

$$\delta_f = 5.443 \text{ } \mu\text{m} \quad \text{Equation D-22}$$

Where δ_f is the overall flux application error metal change effect.

D-4 Combined error for metal change

This section combines the quantified individual metal change errors calculated in this chapter to arrive at the combined metal change error.

In Equation D-23 metal change values are expressed as metal thickness increment error.

$$\delta_{comb}(+) = \sqrt{(\delta_i)^2 + (\delta_c)^2 + -(\delta_{mt})^2 + (\delta_f)^2} \quad \text{Equation D-23}$$

$$\begin{aligned} \delta_{comb}(+) \\ = \sqrt{(1.9)^2 + (6.3)^2 + (1.2)^2 - (16)^2 + (5.73)^2} \end{aligned}$$

$$\delta_{comb}(+) = 13 \text{ } \mu\text{m}$$

In Equation D-24 metal change values are expressed as metal thickness loss error.

$$\delta_{comb}(+) = \sqrt{(\delta_i)^2 + (\delta_c)^2 + -(\delta_{mt})^2 + (\delta_f)^2}$$

Equation D-24

$$\begin{aligned} \delta_{comb}(+) \\ = \sqrt{(1.9)^2 + (6.3)^2 - (1.2)^2 - (16)^2 + (5.73)^2} \end{aligned}$$

$$\delta_{comb}(-) = \mathbf{13.5 \mu m}$$

Appendix E Image Analysis

This chapter documents referenced SEM/EDX imaging of corroded samples.

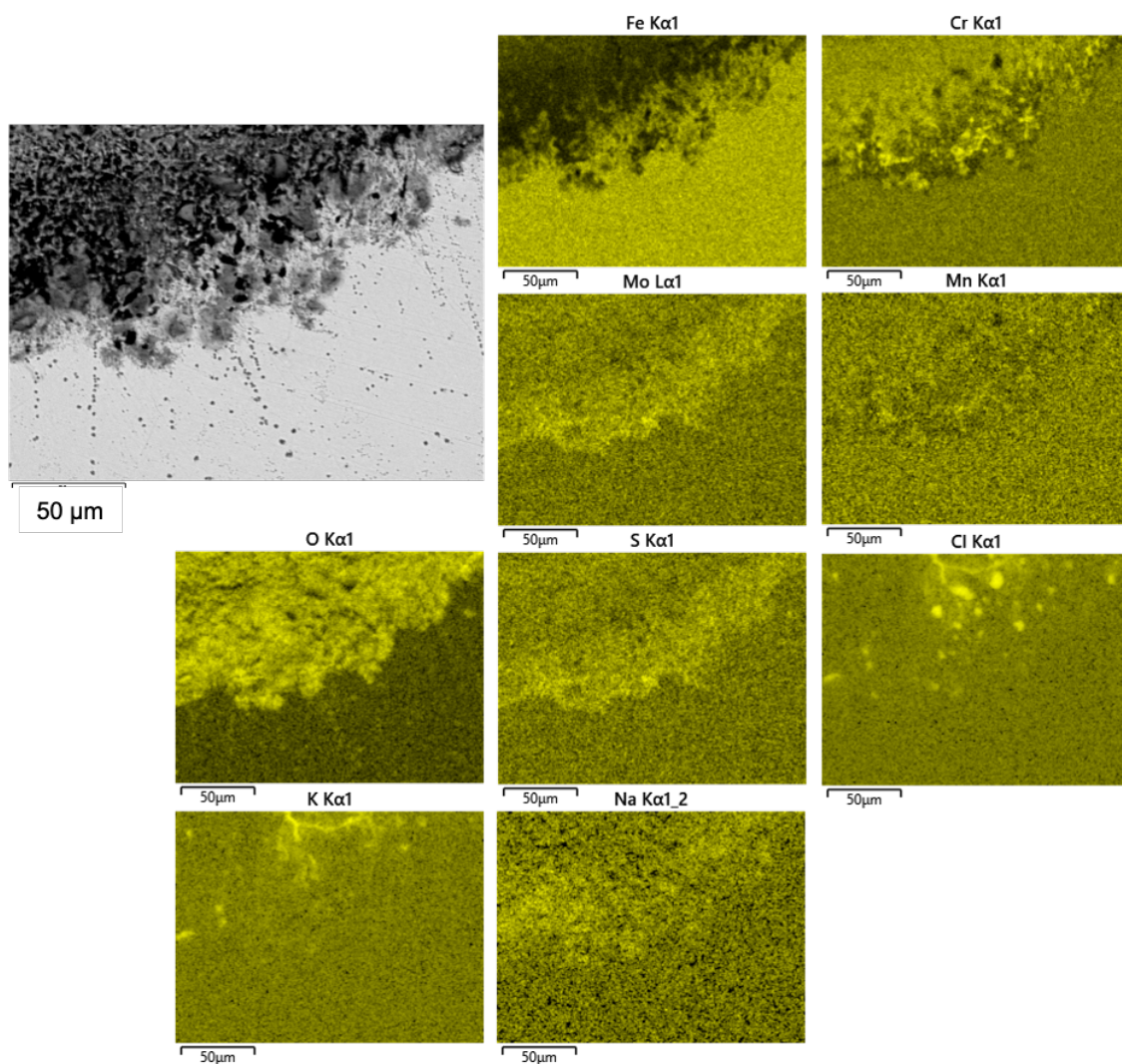


Figure E-1: SE/EDX imaging of cross-sectioned T91 sample covered with deposit D3 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Imaging captures a metal/scale interface

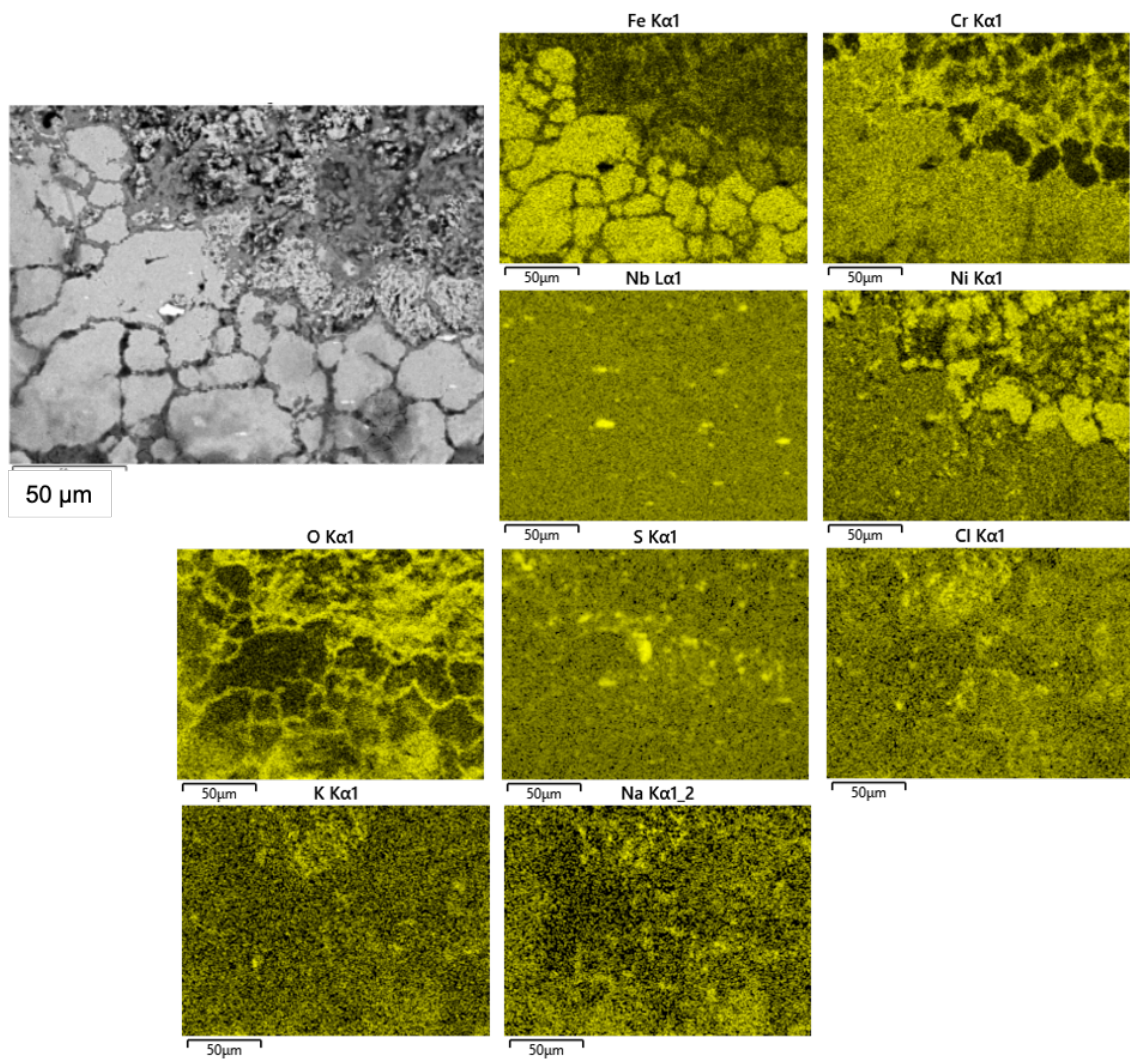


Figure E-2: SE/EDX imaging of cross-sectioned 347HFG sample covered with deposit D3 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Imaging captures a metal/scale interface section

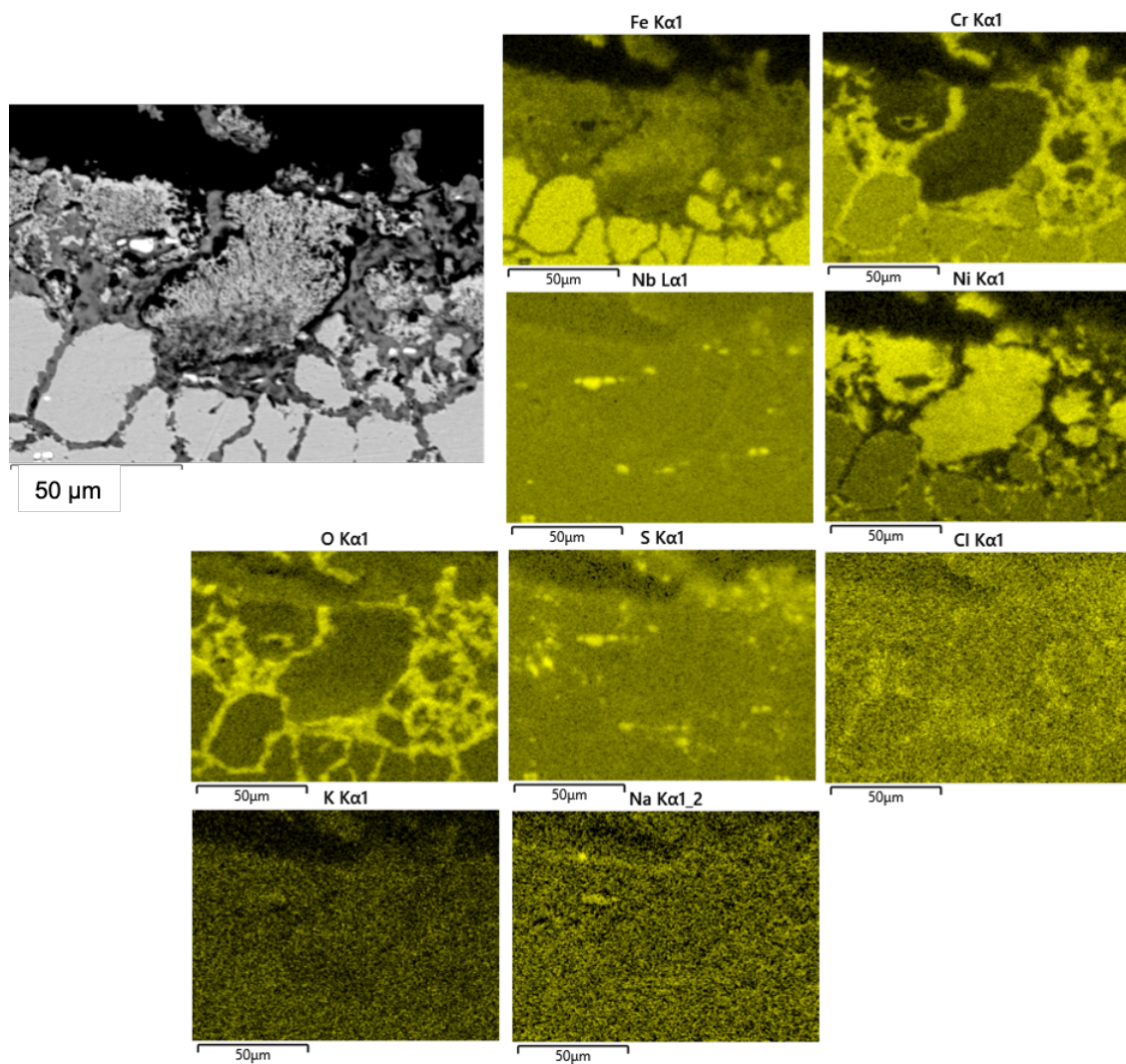


Figure E-3: SE/EDX imaging of cross-sectioned 347HFG sample covered with deposit D4 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Imaging captures a metal/scale interface section

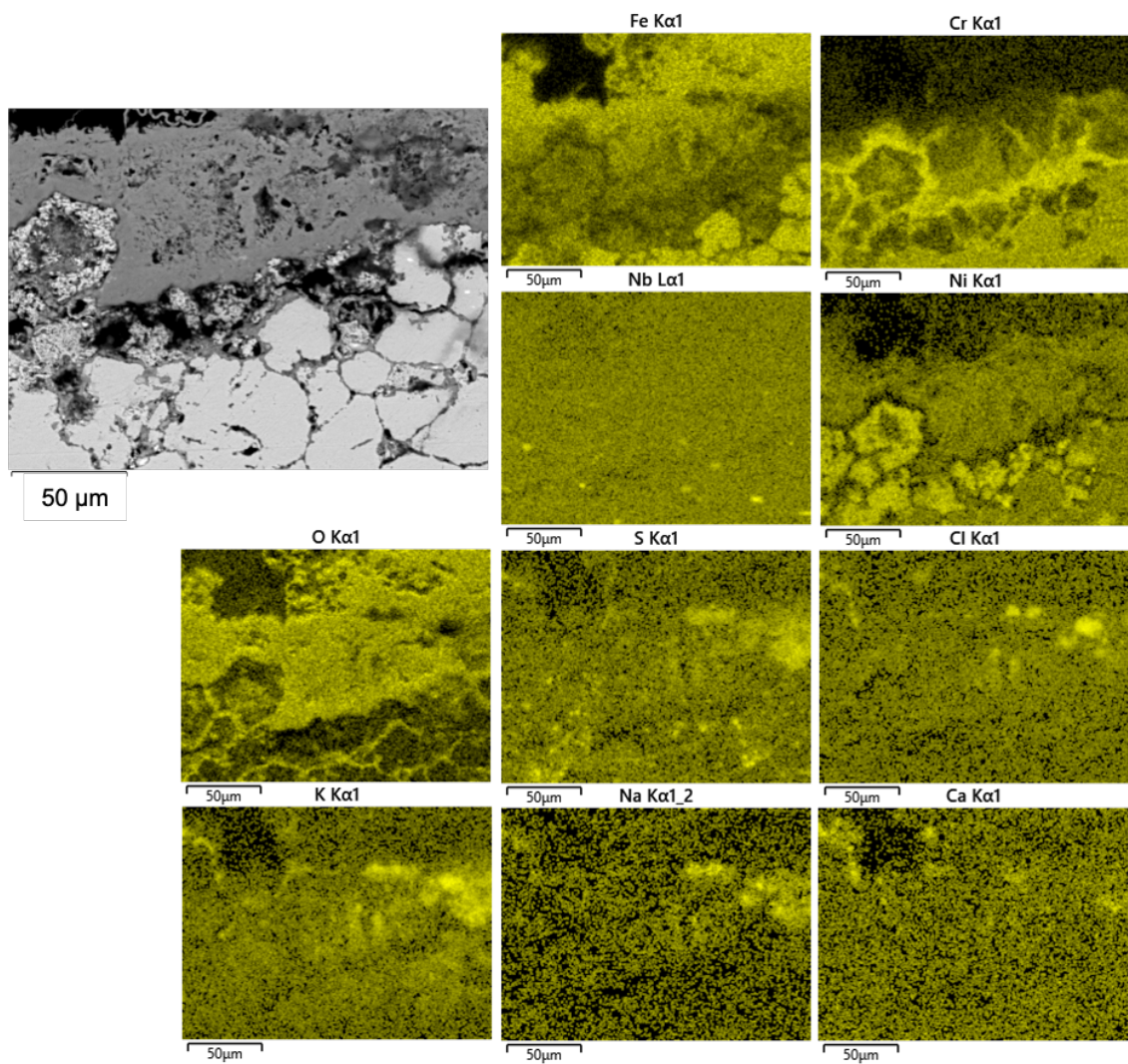


Figure E-4: SE/EDX imaging of cross-sectioned 347HFG sample covered with deposit D5 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C. Imaging captures a metal/scale interface section

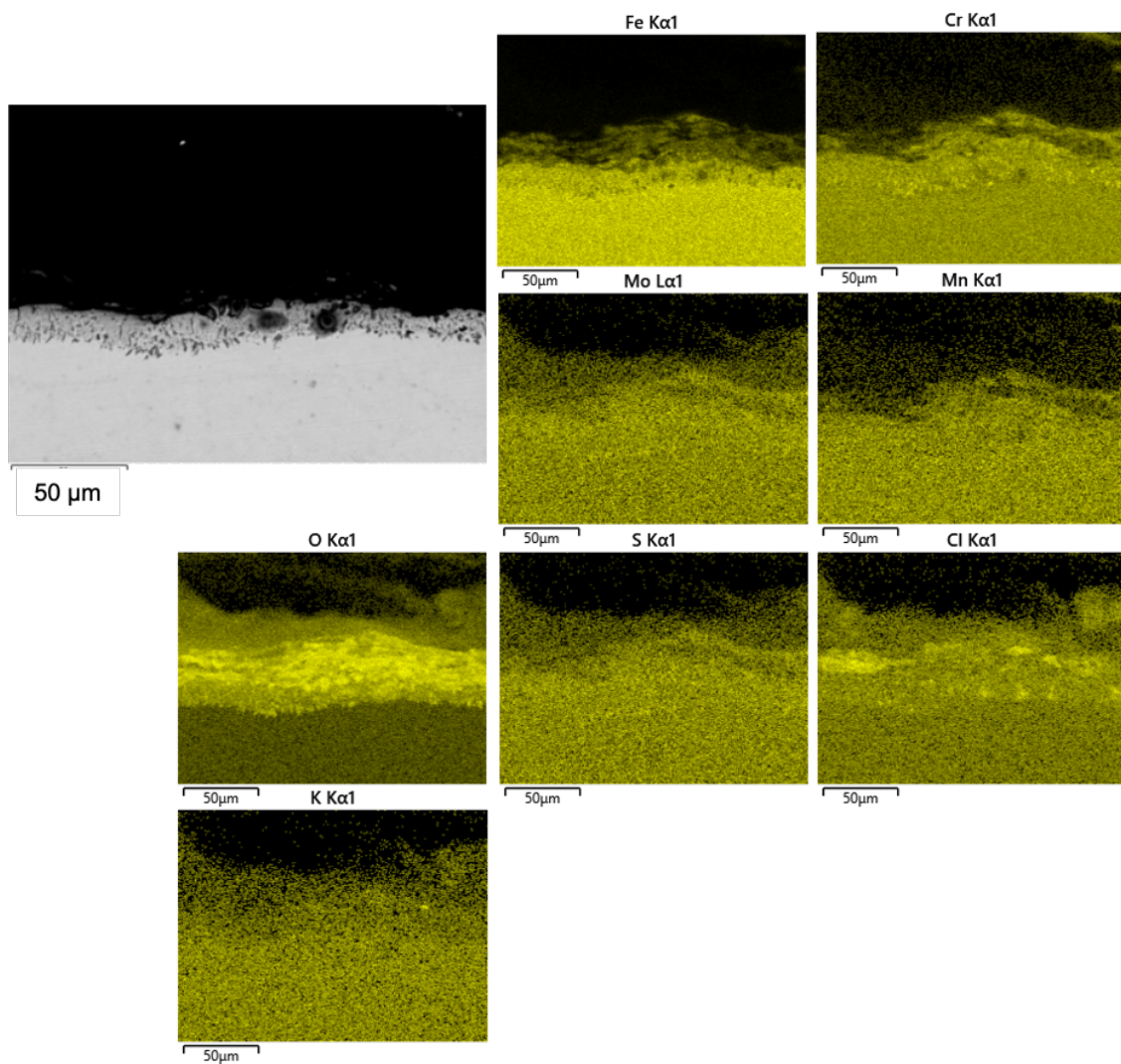


Figure E-5: SE/EDX imaging of cross-sectioned T91 sample covered with deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C

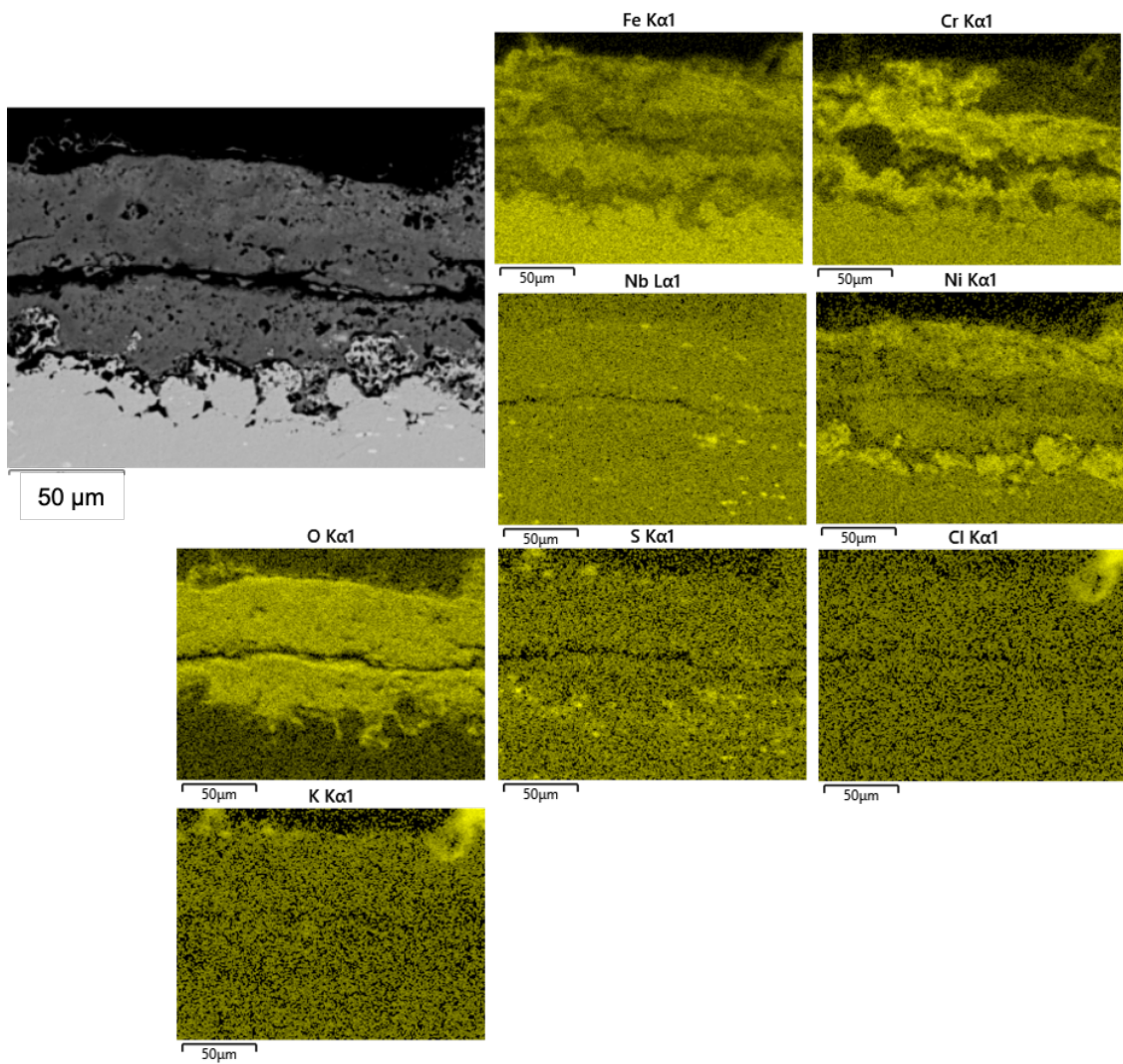


Figure E-6: SE/EDX imaging of cross-sectioned 347HFG sample covered with deposit D6 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours of exposure in WWF simulated combustion gas environment at 600°C

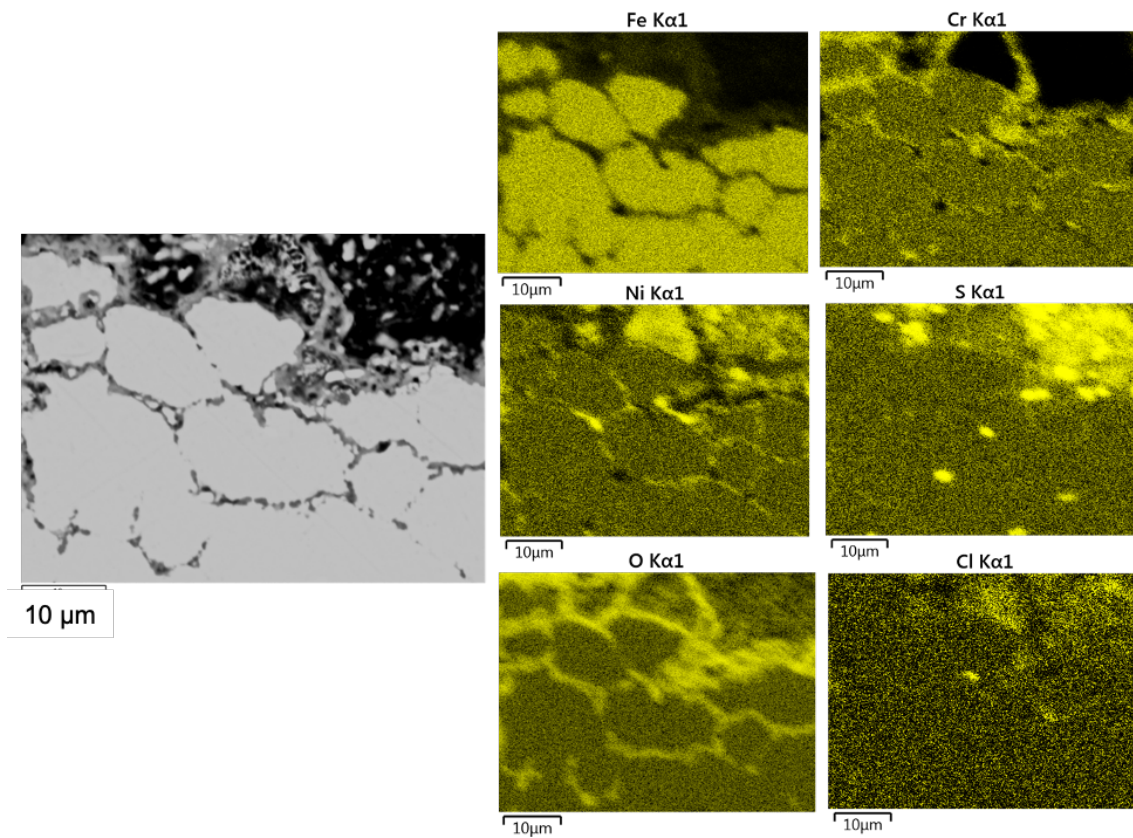


Figure E-7: BSE image and EDX map of grain boundary region of cross-sectioned 347HFG-D6 at flux 50 $\mu\text{g}/\text{cm}^2\text{h}$ following 500 hours exposure in WWF gas environment at 600°C

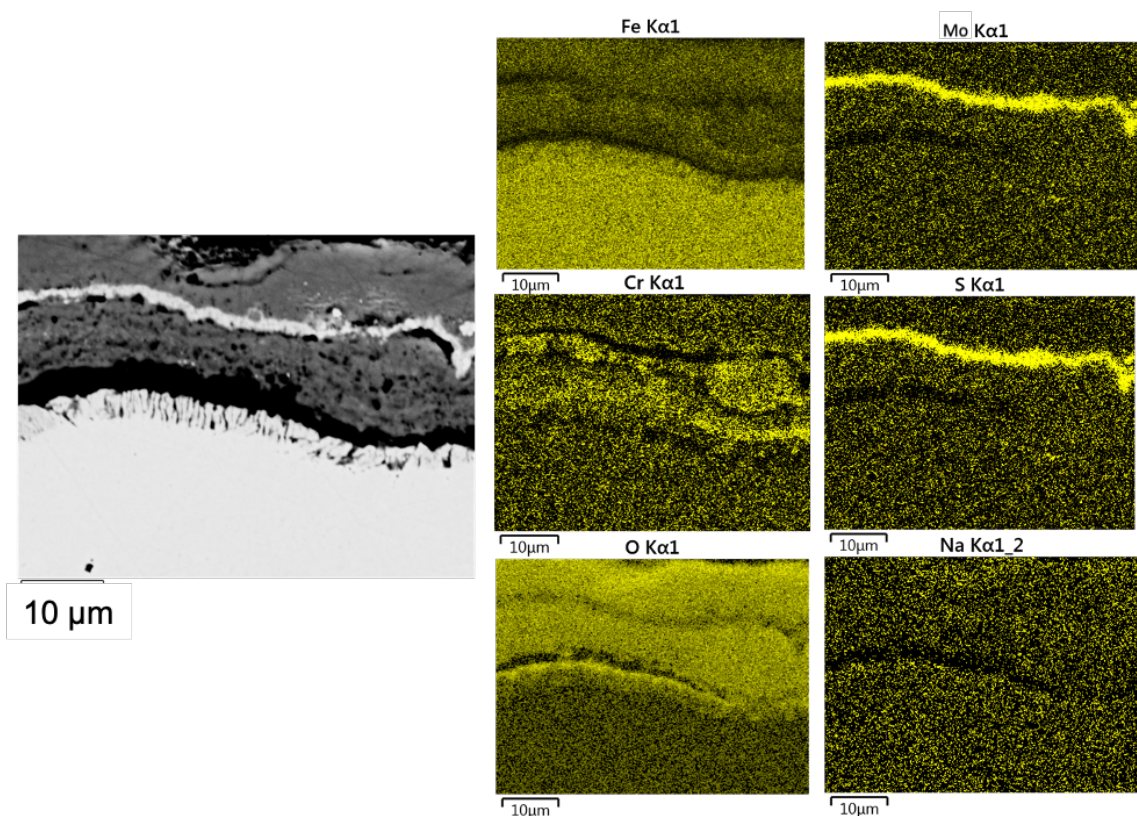


Figure E-8: BSE image and EDX map of grain boundary region of cross-sectioned 347HFG-D1 at flux 25 $\mu\text{g}/\text{cm}^2\text{h}$ following 500 hours exposure in WWF gas environment at 600°C

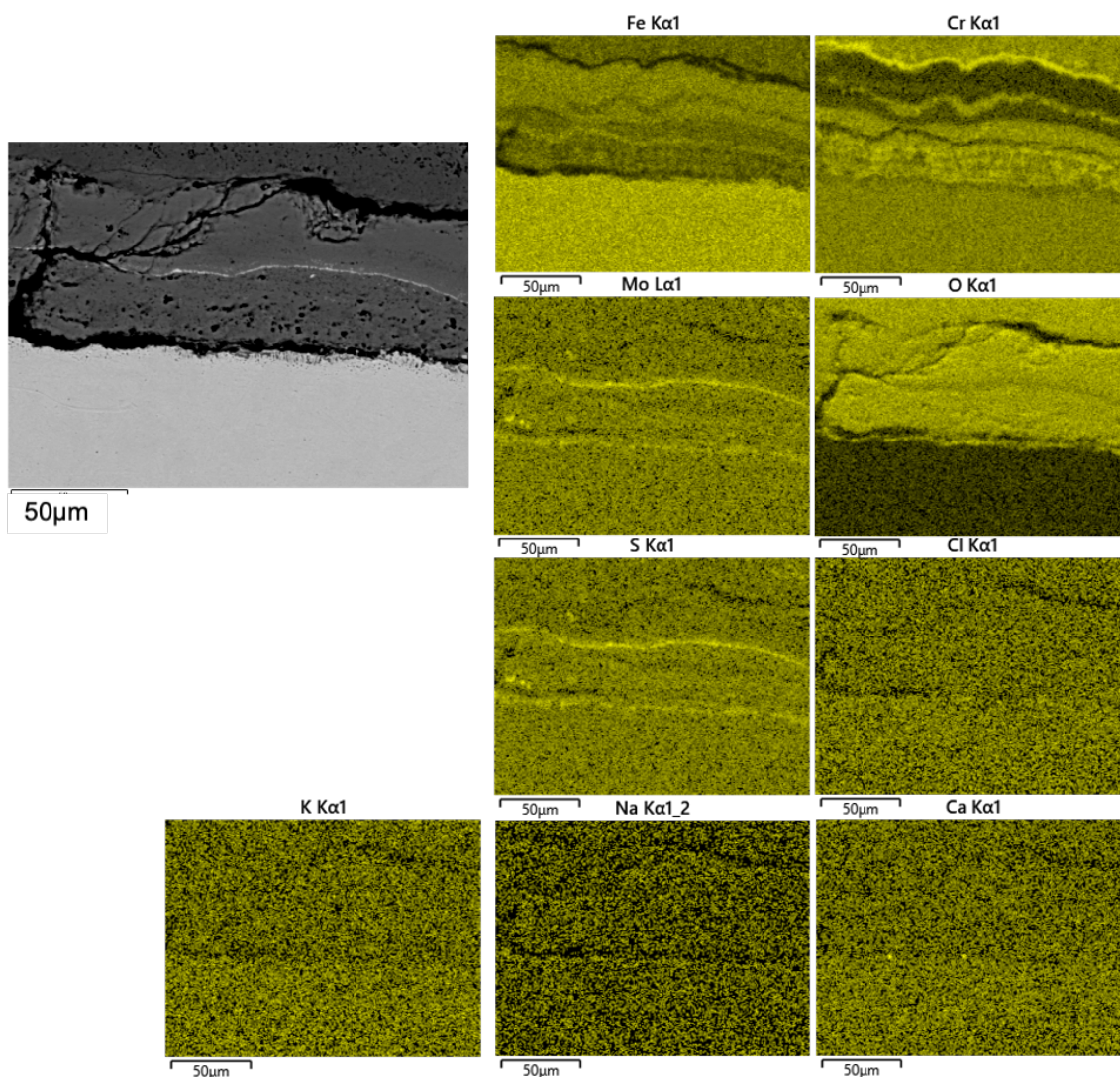


Figure E-9: BSE image and EDX map of grain boundary region of cross-sectioned T91-D1 at flux $10 \mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours exposure in WWF simulated combustion gas environment at 600°C

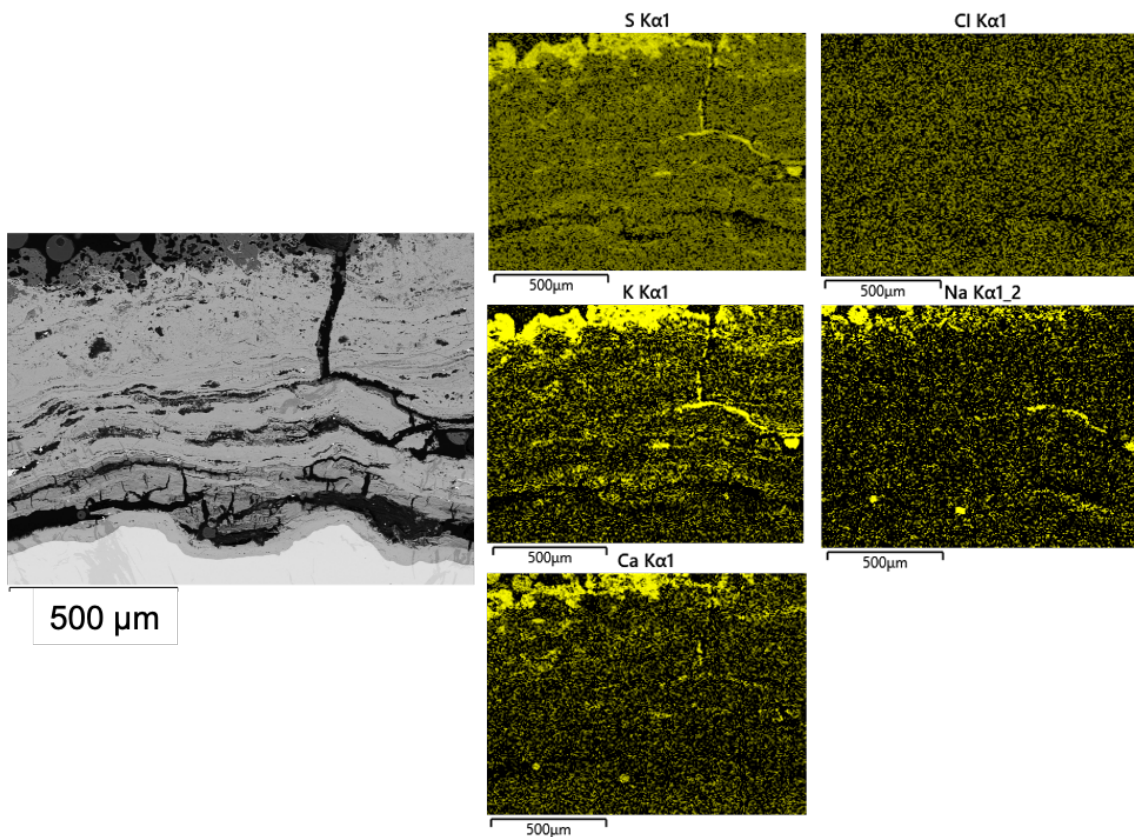


Figure E-10: BSE image and EDX map (deposit elements) of grain boundary region of cross-sectioned T91-D1 at flux 100 $\mu\text{g}/\text{cm}^2\text{h}$ following 1000 hours exposure in WWF simulated combustion gas environment at 550°C

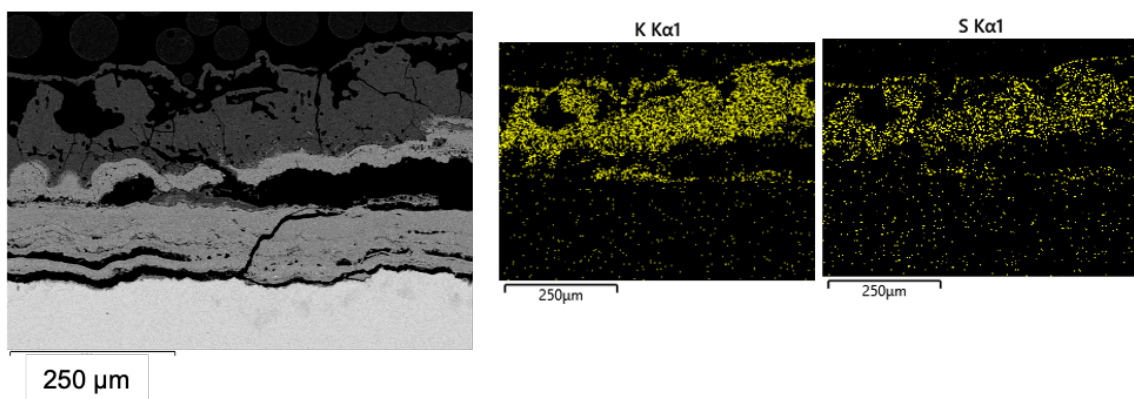


Figure E-11: Secondary image of cross-section T91-D6 sample post 500 hours exposure in WWF simulated combustion gas environment at 500°C and deposition flux of 100 $\mu\text{g}/\text{cm}^2\text{h}$

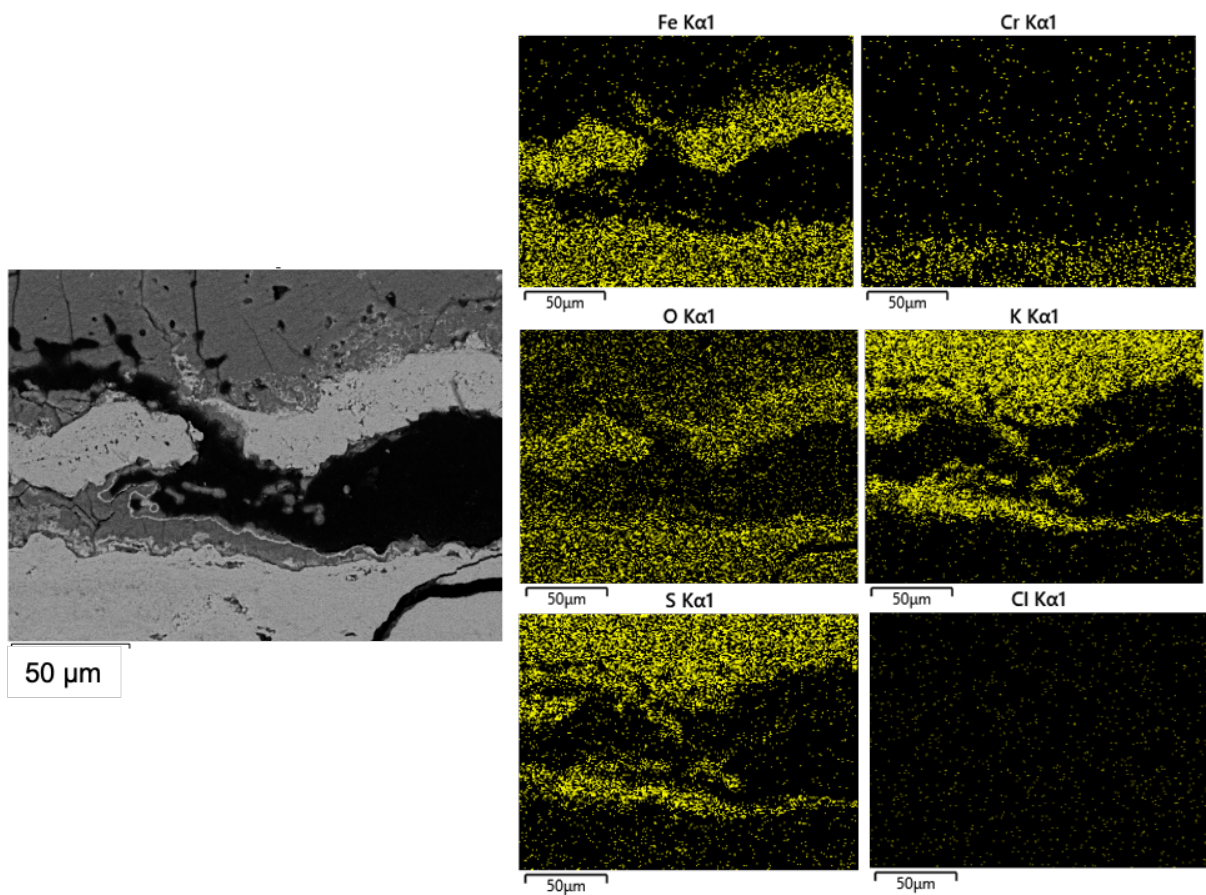


Figure E-12: Secondary image of cross-section T91-D6 sample post 500 hours exposure in WWF simulated combustion gas environment at 500°C and deposition flux of 100 µg/cm²h. Capture section features scale region

Appendix F Publications and ‘fuel justification’ report

F.1 EUBCE conference paper

INVESTIGATION OF THE COMBUSTION ENVIRONMENT GENERATED FROM COMBINED BIOMASS FUEL CATEGORIES

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ABSTRACT: Amongst the challenges encountered by biomass combustion plants providing renewable energy, is the securing of fuel supplies as competition for biomass fuel use increases. This has led to the adoption of “combined fuels”, including wastes. Biomass combustion, however, releases species promoting corrosive degradation and there is limited understanding about their formation and deposition on heat exchangers.

This study pre-evaluates the high temperature compounds’ releases from four fuel categories: herbaceous & grass biomass (HGB), industry food waste (IFW), agricultural plant & residue (APR), and wood waste fuels (WWF). It compares combustion release predictions from both biomass-applicable fireside indices (2S/Cl, Cl/K and K/Si) with MTDData thermodynamic simulations.

Indicators of increased fireside corrosion from fuel combustion include higher quantities of potassium species release (K-release) and lower 2S/Cl ratios. At 1100°C, MTDData predicts K-release values increased: IFW<HGB<APR; the fuels’ Cl/K index ratios follow the same trend. However the K/Si index ratios do not (APR<HGB<IFW), indicating that indices should be cautiously applied. The fuels’ 2S/Cl index ratios and MTDData simulated gas phase S-species/Cl⁻ ratios at 1100°C decreased: IFW>APR>HGB.

Unlike other categories, WWF generated a variety of salts with temperature-dependent interactions, making indices application difficult.

Keywords: biomass indices, combustion, corrosion, mixed biomass, thermodynamic simulation, waste

1 INTRODUCTION

1.1 Background

The thermochemical conversion of renewable fuels to produce heat energy is of growing interests to the energy industry [1]. One of the challenges affecting the shift from coal to biomass combustion technology is the associated increased fireside degradation rates and the formation of complex corrosion compound deposits (solid and molten) on heat exchanger surfaces [2]. These issues limit the heat exchanger’s operational temperatures to 530-630°C, depending on the biomass fuel type and the target alloy material’s lifetime [2]. The energy efficiency of the system is thus reduced.

Biomass fuels’ corrosion characteristics are associated with heat exchanger deposits’ melting temperatures, which are mostly determined by the presence of low melting point compounds. The combustion of plant residues from agricultural practices such as pellets, grass seeds, cereal grains, husks and hems, and oil-pressing residues, release low melting point alkali metal chloride

and sulfate deposits on the heat exchangers [3,4]. The high temperature corrosion role of sulfate species in biomass combustion is seen to have two main effects: (a) as a fireside corrosion rate reducer, whereby the sulfate layers form directly on the alloy surface and minimises the amount of KCl there [5] and, (b) as an active corrosion initiator, whereby sulfate ion in gas releases Cl from KCl [6]. The releases of the K, S and Cl species into gas phase are thus major indicators of biomass fuels’ fireside corrosion behaviours.

Another biomass-related challenge is the sustainability of biomass fuels in meeting combustion plant demands. Although, due to their low levels of fireside corrosion inducing species, virgin wood biomass fuels pose less heat exchanger corrosion issues than other renewable fuels [4], high demand and importation costs put a constraint on the supply of these fuels [7]. For improved fuel supply security, combustion plants will therefore benefit from: (1) the use of waste type biomass fuels in addition to economically feasible grown fuels, and (2) biomass firing plant adapted for combined biomass fuel combustion. The latter point, about plant specialisation, suggests a future

requirement for the grouping of fuels into categories based on supply sources.

Several biomass combustion plants have already been adapted to use mixed biomass fuels for improved fuel security and these include:

- The Ridge Generating Station in Auburndale, Florida, which doubles as a wood waste recycling and 40 MW capacity unit, and is able to adapt to variations in fuel processing and feeding requirements. The combustion plant accepts all waste wood types, with only the restriction of palm trees whose fibrous textures do not blend well with other woods. Its fuel processing requirements prior to feeding are relatively inexpensive and can deal with metals from wires for example [7].
- In 1983, the travelling grate stoker, Avista Kettle Falls Generating Station, became the first stand-alone biomass combustion plant of its size in the USA to produce energy solely from wood waste firing. Its current power capacity is 46 MW and relies mostly on the combustion of nearby milling by-products (slabs, shavings, sawdust and bark) [7,8].
- The bubbling fluidised bed, San Joaquin Valley Energy Partners facilities consumed biomass/waste fuel mixes of up to 50% APR fuels. These fuels included green waste, onion and garlic skins and grape pomace, not typically desired by wood consumers' biomass plants due to their K and Cl-rich compositions as well as high moisture contents. The plant owners operated the plants with large fuel flexibilities to reduce their average fuel cost below those of competitors combusting wood. This also improved fuel supply reliability during peak wood fuel demand seasons [7].

As there are concerns about the corrosive combustion environment generated from clean and waste biomass/mixed fuels, combustion plant efforts to enhance the operational and economic benefits of mixed biomass/waste fuel firing [7] need the evaluation of the post-combustion phases generated. Historically, the use of coal indices has been found useful for the pre-evaluation of fuels' post-combustion corrosion properties and there is interest in adapting these for biomass fuels [5,9,10]. Such indices often inform later extensive laboratory tests and small or large fireside corrosion trials [4]. Thermodynamic calculations can also be carried out to give first-hand information on the post-combustion products likely to form from those selected fuels over prevailing fireside combustion temperatures [9]. However, little research has been conducted to validate the use of fuel indices for the prediction of fireside corrosion post-combustion of mixed biomass/waste fuel.

This study thus compares the post-combustion high temperature compound release trends to fuel indices for four categories of mixed biomass fuels. This takes place in four phases:

- i. Grouping of biomass/waste fuels into categories.

- ii. Thermodynamic simulation of each fuel category's post-combustion phases.
- iii. Calculation of applicable biomass fireside fuel indices (intended to establish post-combustion ash corrosion behaviour).
- iv. Comparison of thermodynamic post-combustion trends with the biomass fuel indices.

1.2 Categories of Current & Potential Biomass Fuels

The renewable fuel types employed by biomass combustion plants vary by location. Energy crops such as herbaceous and grass biomass (HGB) and agricultural plants and residues (APR) are alkali rich fuels with K concentrations as high as 0.1 wt% of fuel (prior to drying). The HGB fuel category is also characterised by higher Si contents than the other fuel categories discussed in this study [11]. Wood compositions are typically characterised by lower alkali metal contents when compared to HGB and APR [11]. Wood waste fuels (WWF), however, contain varying types and quantities of trace elements depending on their previous employment. For example, wood preservatives may contain significant quantities of Zn and Cr [12,13]. Cleaner wood waste firing operations can benefit from higher deposit melting temperatures than those encountered with other biomass types. However, there is presently a need for the investigation of the fireside corrosion role of minor and trace contaminants associated with more challenging to use waste wood fuels. WWF plant consumers estimate 10-15% of materials are from highly contaminated industrial wood waste while the larger majority are sourced from relatively low contaminant level tree felling. The proportion can vary seasonally and by location, as some wood can be sourced from demolition [14]. There is therefore a potentially wider variation in the extents of fuel contaminant levels.

The makeup of vegetation grown specifically for combustion has changed over time to develop their combustion properties for biomass firing. In 2016, the UK dedicated up to 132,000 hectares to the cultivation of wheat, maize, sugar beet, miscanthus and other energy crops [15]. HGB supplies are, however, affected by seasonal changes.

Another potential fuel source, industry food wastes (IFW) which are of vegetation-based origin, are characterised by their high moisture and lean alkali and alkaline earth metals contents [11]. IFW fuels constitute over 20% of municipal waste in developed countries [16]. A study of the energy recovery potential of pelletized dry food waste fuel found these fuels consist of higher energy and ash content than wood (dry basis comparison) [16]. There were also relatively narrow composition ranges in the waste food fuels accessed. There is thus opportunity for the exploration of waste food as a potential biomass fuel.

APR fuels are K-rich and may be associated with trace contaminants as a result of the cultivation method employed. Though APR fuels are becoming more popular for combustion, they are characterised by a high ash

contents which increase plant maintenance requirements. They also consist of a wide variety of compositions [3] thus making their combustion qualities more challenging to define.

1.3 Fuel Makeup & Application of Corrosion Indices

There have been efforts to adapt some coal originated combustion indices, to biomass fuels. These indices have been employed to rank likely coals for their final corrosion performance after combustion. Such indices are usually based upon expected post-combustion ash corrosion behaviour. The indices are mathematical ratios employing the knowledge of combustion release element associations for the predictions of ash, condensed and gas phase compound formation [5]. Coals, which are sedimentary rocks, generally have lower alkali metal and Cl contents, and higher S contents, than biomass fuels [2]. The alkali compounds are trapped within thin sedimentary layers and mostly bound in aluminosilicate complexes which are not commonly associated with biomass fuels. These fundamental differences in the fuel makeup and the largely variable physiochemical properties of biomass fuels make coal methods of describing ash behaviour mostly non-applicable in the prediction of biomass fuel combustion ash behaviour [5].

To apply coal indices to biomass combustion release predictions, the target elements, which form the basis of the indices, have been linked to the specific biomass combustion behaviours being addressed. These indices are also validated against experimental/plant data leading to their further development and further exploration of their fireside combustion environment calculation limitations [5].

1.3.1 Indices Correlations with Combustion Species Release Trends

The suitability of employing indices to predict a fuel's impact on corrosion may vary across fuel types due to the abundance of other elements affecting ash behaviour and which are beyond the scope of the index. To correctly interpret index ash qualifications, it is important to observe the underlying gas phase release trends.

The $K/(Si + Al)$ ratio approach was evaluated by Clery et al. [17] to include the potassium partitioning influence of aluminosilicates, whereby higher Al content promotes K-retention, thus reducing K corrosion impact. The Al content in biomass fuel is however much lower relative to coal and these biomasses are not expected to form the aluminosilicates post-combustion. Thus the ratio is better served for coal than biomass firing evaluations.

Baxter et al. [18] studied the melt behaviour of straw ash and linked this to ratios in K/Si content. They noted a change in this ratio from 1:4 to 1:25 for the analysed molten ash region, depicting lower melting point ash and granular ash region, depicting higher melting point ash, respectively. Miller et al. further demonstrated the importance of fuel alkali and alkaline earth metals by comparing K/Si ratios. They observed a relatively controlled K/Si ratio in the ash melt up to 1609°C; the ash consisted largely of $K_2Si_4O_9$ over the entire temperature range [19].

Sommersacher et al. [5] compared fireside combustion indices with laboratory, pilot and plant scale combustion

data to evaluate and predict the release of K-containing species (K-release), comparing this to the K/Si ratios of APR and HGB type fuels. The experimental models were based on data for grate combustion conditions.

High Si contents in biomass fuels in comparison with their K quantities have been seen to favour the formation of K-Si complexes. Knudsen et al. [10] suggested K could be bound in bottom ash as K-Ca-Si and thus that fuels with similar Si and K compositions ($K/Si \sim 1$) may yield ashes with similar behaviours irrespective of the abundance of each element [10].

Although Si concentration has an influence on K-release, Knudsen et al. further investigated the effect of Cl on the K/Si ratio. Higher fuel Cl/K ratios showed higher K releases in the experimental evaluation of rice combustion, which has a low K/Si ratio. The rice was expected to show much lower K-release than a wheat straw fuel sample (which has a higher K/Si ratio), but the opposite was the case. This was attributed to the high Cl/K ratio resulting in the formation of KCl. Further addition of $HCl_{(aq)}$ in excess to the Si-rich fuel sample lead to a sharp rise in K-release to the gas phase [10]. It was seen that K-retention in Si-rich fuels can be counteracted by the relatively high presence of Cl in the fuel during combustion. This is as a result of the preferred K-Cl correlation yielding high KCl vapour pressures at the prevailing biomass firing temperatures [20,21]. It was concluded by Sommersacher et al. [5] that an insusceptible quantity of K to excess Cl will be retained in ash as high melting point compounds or complexes.

The formation of the K-Si complex is however competitive with other alkali and alkaline earth metals, and trace elements, which would form complexes with Si in the place of K [20]. Experimental studies may suggest there are varying levels of correlations between K/Si ratios and K-release. Cl on the other hand mostly condenses as $KCl_{(s)}$ in low contaminant biomass fuels, and thus the Cl content of fuel may be more reliable than K/Si in the prediction of the volatility of K [5].

Sommersacher et al. [5] compared the 2S/Cl ratios of eight biomass fuels' feed stocks with that of their combustion aerosol emissions for the prediction of corrosion risks. Sulfate rich fuel gas compositions favour the formation of K_2SO_4 over KCl, thereby promoting its build-up on heat exchangers in place of KCl. The thicker build-up of KCl on heat exchangers has been associated with HGB type fuels in comparison to other biomass types [22,23].

In addition to the higher melting point benefit of the sulfate over the chloride compound in biomass combustion, K_2SO_4 build-up reduces Cl^- transfer to the alloy surface, thus slowing down the active corrosion mechanism [5,22,24].

Indices predicting the biomass combustion releases of K, S and Cl can thus be linked to corrosion risks.

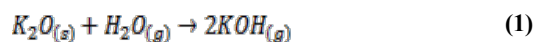
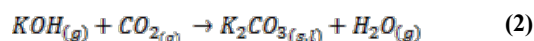
1.3.2 Corrosion Relation to Gas Phase Species' Releases

The biomass fireside combustion releases can be transferred to the heat exchanger surfaces where they can form deposits. The deposits constitute a variety of compounds with a range of physiochemical properties and thus, various operational impacts on the heat exchanger surfaces are expected. To investigate corrosion influence

of the fuel categories, it is important to evaluate the type of combustion releases and deposits formed which are characteristic of the fuels being combusted. Current combustion practices have led to heat exchangers in biomass combustion plants being kept below the “ T_{15} ash melt temperature”. This means 15% of the liquid phase melt of alkali and alkali earth salts exists in equilibrium with the solid phases [4]. Above T_{15} , ashes are considered sticky enough to adhere to the heat exchangers and hence pose corrosion risks. Low T_{15} ash temperatures have been characterised with the presence of K chlorides, carbonates and sulfates in the ash. Investigations have monitored the K-release of six HGB and APR type fuels tested in a laboratory reactor with conditions resembling grate biomass plant firing [10]. It was observed that the ash phase Si and Cl content had an effect on K-release and fireside corrosion. The release of Cl showed no correlation with ash compositions, but was dependent on temperature, with nearly 100% Cl-release from the fuels for temperatures over 800°C. K-release rates were seen to vary with temperature and a reduced rate at higher combustion temperatures corresponded with the release of K from higher melting point K-Si complexes. It is assumed that fast release rates of K at lower temperatures was from low Si content biomass fuels.

Clery et al. [17] noted the combustion K-release fraction at 550°C of wood, wheat straw, and olive residue samples were 80%, 50% and 40% respectively. Though wood fuels display higher K-release fraction than most biomass samples, their K-content is much lower compared to other biomasses, thus exhibiting lower heat exchanger corrosion risks [5,25]

K-release can lead to the formation of a range of K compounds. The presence of KOH in biomass fuel gas corresponds to high moisture content or low chloride content fuels as with wood fuels and can result in the condensation of K_2CO_3 (see Equation 1-2) [10]. Bloomberg et al. [26] concluded that the condensation of KCl on heat exchangers is a result of the reaction between gas phase KOH and HCl, suggesting that KOH is the major alkali specie occurring in the gas phase. Bloomberg described low melting point ashes had an abundance of KOH (melting point 406°C) instead of KCl (melting point 774°C). It is expected that IFW fuels can attain up to 90% K and Cl content loss, including other minerals, depending on the food preparatory process employed [21]. This limits the post-combustion chloride species able to form. KOH however may contribute to alloy depletion at temperatures lower than 500°C at considerable magnitudes [27].



The S-release is dependent on the association of S and the fuel makeup. Low temperature S-releases- at fuel devolatilization stage of combustion have been attributed to the decomposition of organically bound S, while temperature releases above 500°C are recognized as inorganically bound sulfates of alkali and alkaline earth metals [5,21]. S-release from inorganic sulfates has been seen to increase with higher Si content due to the preferred formation of Si-metal complexes and lower melting point alkali sulfate salts [10]. The release of S post-combustion thus is based on a number factors.

Though some variances are seen in the explanation of gas phase releases from biomass firing, it is generally agreed that the estimation of K-release is an important factor in fireside corrosion predictions. The fuel S and Cl contents determine the dominant condensed K compound directly on heat exchanger surface, while K in excess of S and Cl will lead to the formation of $KOH_{(g)}$ [26].

1.4 Summary

Biomass and waste biomass fuel sourcing may be improved by the employment of fuel mixtures which will reduce the demand strain on desired fuel stocks. Four fuel categories were identified based on sourcing correlations, however high temperature fireside heat exchanger corrosion remains an operational challenge to biomass plants. The use of fuel mixtures therefore requires an evaluation of the combined corrosion characteristics of that fuel category. This study uses thermodynamic calculations of post-combustion species to pre-evaluate four fuel categories' corrosion tendencies. Furthermore, it compares their thermodynamic post-combustion trends with the potential biomass fuel indices to indicate whether or not these are suitable for future use in predicting a biomass fuel's ability to induce fireside corrosion.

2 METHODOLOGY

2.1 Fuel Categorisation

A collection of 120 biomass (including waste biomass) fuels were selected for the WWF, HGB, IFW and APR fuel categories. Their specifications were provided by online fuel database, ECN Phyllis [11] and additional literature sources (Table I).

Table 1: List of fuels in the biomass/waste fuel categories, WWF, HGB, IFW and APR, and their data source. Material ID numbers have been included after the reference for fuels whose data have been sourced from ECN Phyllis 2.

Biomass/Waste Fuel	Reference	Biomass/Waste Fuel	Reference
<u>Herbaceous & Grass Biomass</u>			
Switchgrass	[28,29]	Flax whole straw	[30]
Switch grass	[11] № 896	Flax shive	[30]
Switch grass	[11] № 2426	Aubergine plant	[11] № 2886
Reed Canary Grass	[19]	Bean plant	[11] № 2888
Reed Canary Grass	[30]	Brassica	[11] № 2811
Rapeseed Straw	[30]	Courgette plant	[11] № 2884
Barley Straw	[30]	Cucumber plant	[11] № 2885
Barley Straw	[31]	Melon plant	[11] № 2891
Wheat Straw	[30]	Pepper plant	[11] № 2889
Wheat straw	[32]	Tomato plant	[11] № 2887
Sweet Sorghum	[30]	Watermelon plant	[11] № 2890
Kenaf	[30]	Thistle	[11] № 2295
Cane	[30]	Thistle	[11] № 2812
Miscanthus (Italy)	[30]	Tobacco, Burley	[11] № 2868
Miscanthus (Germany)	[30]	Threshed hay	[11] № 3064
		Grass pellets	[11] № 2732
<u>Industry Food Waste</u>			
Sugarcane fibre	[11] № 2807	Longan peel	[11] № 2924
Onion peel	[11] № 3068	Litchi seeds	[11] № 2926
Olive pomice pellets	[11] № 2893	Litchi seeds	[11] № 2923
Oil palm empty fruit bunch	[11] № 2897	Grain screening	[11] № 2805
Mango seeds	[11] № 2925	Coffee grounds	[11] № 1769
Mango peel	[11] № 2922	Spent coffee	[11] № 2190
Longan seeds	[11] № 2927	Corn cobs	[28,29]
<u>Agricultural Plants & Residues</u>			
Sunflower shells	[28,29]	Olive residue	[11] № 2176
Sunflower pellets	[32]	Cacao shells	[11] № 1776
Sunflower husk	[11] № 1911	Cacao shells	[11] № 2736
Sunflower shells	[11] № 2803	Cacao	[11] № 884
Sunflower seed shells	[11] № 2317	Coconut shell	[11] № 1919
Sunflower seed husks	[11] № 378	Hazelnut shell	[11] № 2875
Sunflower seed husks	[11] № 2149	Hazelnut shell	[11] № 2315
Sunflower husks	[33]	Rice husks	[28,29]
Sunflower seed shells	[11] № 878	Rice husks	[11] № 3251
Plum pits	[28,29]	Rice husks	[11] № 2876
Cotton husks	[33]	Cotton husks	[11] № 1912
Olive residue	[11] № 1764	Prune pits	[11] № 998
Olive residue	[11] № 3054	Pistachio shells	[11] № 995
Olive residue	[11] № 2177	Pistachio shells	[11] № 706
Rice husks	[11] № 993	Walnut shells	[28,29]
Rice hulls	[11] № 452	Walnut blows	[11] № 996
Groundnut shells	[11] № 375	Walnut halls and blows	[11] № 997
Palm kernel	[11] № 2719	Soya husks	[33]
Oat screenings	[11] № 3485	Coffee husks (mbuni)	[33]
Mustard husks	[11] № 1913	Coffee husks (parchment)	[33]
Grass seed chaff	[11] № 3063	Greenhouse residues	[32]
Cotton seed husks	[11] № 370	Cornstalk derived fuel	[34]
Almond shells (hulls)	[11] № 357	Almond hulls	[11] № 708
Almond shells (hulls)	[11] № 350	Almond shells (hulls)	[11] № 353
Almond shells (hulls)	[11] № 2813	Almond shells	[11] № 2314
Almond shells	[11] № 707	Tomato plant	[11] № 2887
<u>Wood Waste Fuels</u>			
Demolition wood pellets	[32]	Demolition wood	[11] № 2712
Demolition wood (clean wood)	[11] № 855	Demolition wood	[11] № 2901
Demolition wood (clean wood)	[11] № 856	Demolition wood	[11] № 2918
Demolition wood-chipped	[11] № 676	Demolition wood	[11] № 1448

Table II: Median values of fuel categories' proximate analysis, ultimate analysis, elemental compositions and heating values. Individual fuel references are listed in Table I

Content	Basis	units	Herbaceous and Grass Biomass	Industrial Food Waste	Agricultural Plants/ Residues	Wood Waste Fuels
Proximate Analysis						
Fixed Carbon	dry	(wt%)	16.50	25.00	20.45	19.13
Moisture		(wt%)	65.20	56.59	9.77	12.9
Ash	dry	(wt%)	7.91	4.37	3.83	2.70
Volatiles	dry	(wt%)	76.04	70.43	73.32	76.40
Major Elements						
C	dry	(wt%)	45.80	41.52	47.54	46.80
O	dry	(wt%)	40.45	41.12	39.76	39.03
H	dry	(wt%)	5.80	6.46	5.88	5.60
N	dry	(wt%)	1.08	1.04	0.93	0.70
S	dry	(wt%)	0.14	0.09	0.10	0.05
Cl	dry	(wt%)	0.18	0.06	0.08	0.08
Minor elements						
Al	dry	(mg/kg)	710	260	735	519
K	dry	(mg/kg)	25405	8410	6494	760
Na	dry	(mg/kg)	1698	8.7	408	790
Mg	dry	(mg/kg)	1800	1257	1400	509
P	dry	(mg/kg)	6010	150	1449	127
Fe	dry	(mg/kg)	520	20	720	640
Si	dry	(mg/kg)	12320	1200	7929	3000
Ca	dry	(mg/kg)	9750	1100	2400	3758

2.2 Thermodynamic Equilibrium Simulation

Thermodynamic simulations of the species formed post-combustion were performed for the four fuel categories. The thermodynamic simulation inputs were median fuel category values for ultimate analysis elements (C, H, N, O, S and Cl) and major elements (K, Na, Ca, Mg, Si, Al, P and Fe; Table II). A fuel feed rate of 1kg/hour and a temperature range of 300-1300°C was used assuming

standard atmospheric pressure, which are typical temperature and pressure conditions experienced during fuel combustion. A compilation of the dominant species for each category was reviewed using literature-based data. The median statistical tool was preferred over mean values to limit the errors by avoiding the extreme values; although there were some fuels with incomplete composition data. 'As received' fuel compositions were normalised to moles per hour feed rates assuming an oxidising combustion predefined atmosphere with calculated adjustments for combustion air with a target yield of 7-8% moles excess oxygen post-combustion. The comparison of the fuel category post-combustion thermodynamic predictions with indices was thus based on the 14-element thermodynamic equilibria calculations.

MTData Multiphase Thermodynamic Software

was selected for the calculation of multiphase thermodynamic equilibria for each fuel category's post-combustion simulation. Elimination of the thermodynamic output species with concentrations below 1×10^{-5} moles/kg allowed a focus on the evaluation of the fuel categories' predominant post-combustion species formation. The software employs the Gibbs free energy minimisation principle and a series of multi-components database for the calculations of phase equilibrium. The accessed database were: (i) SGTE Pure Substance Database which consists of data of pure substance phases, including their enthalpy of formation for pure elements and standard entropy at 298.15 K and the heat capacity which enable the Gibbs free energy calculation as a temperature function; (ii) SGTE Solution Database which consists of data of non-ideal solutions and uses data assessed for over 400 binary phase systems and higher order phase combinations; and (iii) SGTE Unary Database which contains over 70 element data for calculating their stability phases from 298.15 K.

2.3 Fuel Corrosion/K-Release Index Calculations

For each of the four fuel categories, the median as received chemical compositions have been used to calculate the following fuel indices:

- Cl/K

- ii.) K/Si
- iii.) 2S/Cl

The first two indices have been selected to: (a) compare the fuel categories' K-release and, (b) compare the correlation of K-release with fuels' Si and Cl contents. As aforementioned, the K-release is an indication of the ash melting properties of the deposits likely to form on the heat exchanger surfaces. The third index has been chosen to compare the fuel categories' sulfate/chloride ratios which impacts Cl mobility to the heat exchanger surfaces.

3 RESULTS & DISCUSSIONS

3.1 Fuel Categories' Thermodynamically Simulated Post-Combustion Release Trends

3.1.1 S and Cl Release

The release of chloride and sulfate species from biomass firing is paramount to the evaluation of the post-combustion fireside corrosion effects the biomass fuels may pose on heat exchangers.

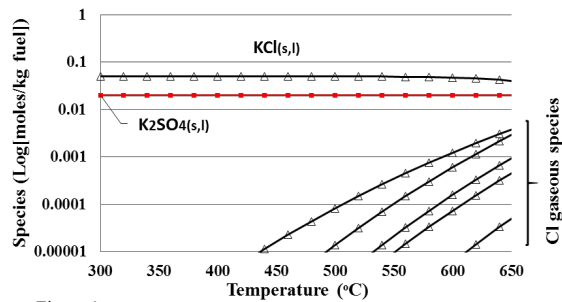


Figure 1a

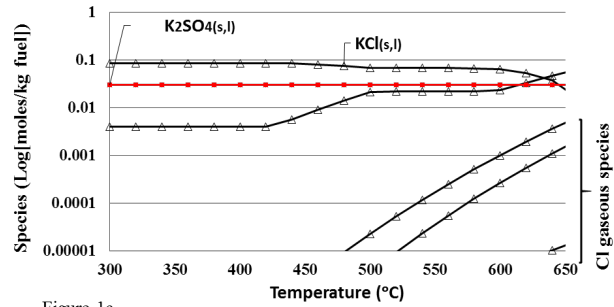


Figure 1c

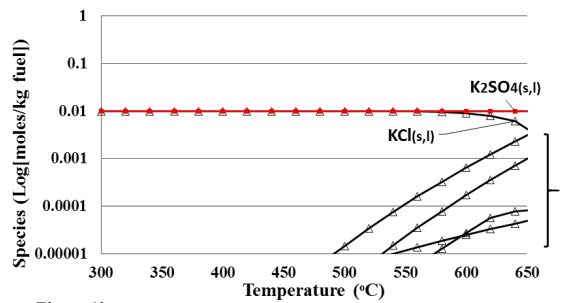


Figure 1b

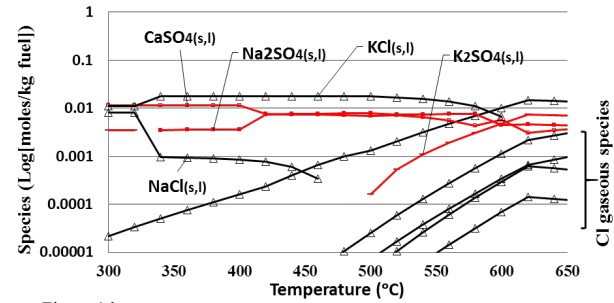


Figure 1d
 ▲ Cl species
 — S species

Figure 1: MTDData thermodynamic post-combustion Cl and S species outputs (moles/kg) of (1a) HGB, (1b) IFW, (1c) APR and (1d) WWF fuel categories using median as received (ar) compositions input values for 14 element (14ES): C, H, N, O, S, Cl, Si, K, Na, Ca, P, Mg, Al and Fe. All condensed phase species are labelled.

As previously discussed, higher 2S/Cl ratios of fuel feedstock can be related to heat exchanger deposits forming that are relatively higher in sulfate compounds, thus slowing down the migration of Cl to the corrosion zone [22]. To compare the fuel categories' thermodynamically predicted post-combustion gas environments at the vicinity of the heat exchanger, the total sulfate (SO_x and SO_4^{2-}) and Cl^- gas phase species occurring at 1100°C for the fuel categories were used to determine the gas phases S-species/ Cl^- ratios. Table III show these ratios decreased for the fuels according to: $\text{WWF} > \text{IFW} > \text{APR} > \text{HGB}$. These ratios suggest that HGB and APR fuels' gas compositions may favour the formation of larger amounts of chloride deposits than

sulfate deposits on the heat exchangers.

Table III: MTDData thermodynamic simulations of post-combustion sulfate (SO_4^{2-} and SO_x) and chloride gas phase releases at 1100°C for the fuel categories using 14ES median compositions input values.

Fuel Categories	Simulated gas phase species (moles/kg of fuel)		
	Sulfates	Chlorides	S-species/ Cl^-
Herbaceous Grass & Biomass	0.007	0.027	0.25
Industrial Food Waste	0.003	0.005	0.52

Agricultural Plants & Residues	0.010	0.029	0.33
Wood Waste Fuels	0.004	0.006	0.79

SO_x and Cl solid/molten compounds (above 10⁻⁵ moles/kg of fuel) occur only as K₂SO₄ and KCl for the IFW, HGB and APR fuel categories' condensed phase but not for the WWF category (Figure 1), for which NaCl, Na₂SO₄ and CaSO₄ are also included with the K compounds. There is therefore a variety of chloride and sulfate deposit compounds predicted to form for the WWF category dependent upon temperature. A 500°C snapshot of the fuel categories' condensed phases is presented in Table IV.

3.1.2 KCl Phase Transition Temperatures

The KCl gas to condensed (G-C) phase transition temperature ranges and KCl concentrations (moles/kg of fuel) for each fuel category differ (Figure 2). Two fuel-based mechanisms which may affect the transfer of KCl to the heat exchangers are addressed in this section:

- The overall KCl released during combustion will influence the amount of KCl condensing on the heat exchanger surfaces.
- The G-C KCl phase transition temperature may influence the KCl deposition temperature interval. According to Figure 2, it is expected that these intervals will vary for the fuel categories. It can be assumed that a biomass plant heat exchanger surface temperature is

between 530-630°C, with similar flue gas rates and temperatures (≈1100°C) in the vicinity of the heat exchanger. Then deposits of higher G-C phase transition temperatures will condense earlier as the combustion gas cools, based on a temperature/condensation mechanism. Thus, higher KCl G-C phase transition temperatures (which are below 1100°C) may initiate earlier deposit formation.

The temperatures corresponding to the equal KCl gas and condensed phases for the four categories increased as: WWF<APR & IFW<HGB (Figure 2). Similar KCl G-C phase transition temperatures are seen for APR and IFW, however, the APR category shows the highest KCl concentrations in gaseous and condensed phases of the four fuel categories.

3.1.3 K Release

The thermodynamic predictions of K in the gas phase have been evaluated against the overall fuel K for the fuel categories to compare their K-release tendencies. Figure 3 shows the K-release fraction is lowest for the HGB and APR categories. This is to be expected as higher concentrations of high temperature stable K-Si compounds (melting points of observed K-Si compounds >1300°C [36]) are formed (Table IV). Also, K₃PO₄ (melting point >1300°C [37]) dominates the condensed phase for the HGB fuels (Figure 4a).

Table IV: MTData thermodynamic post-combustion condensed phase compounds (>10⁻⁵ moles) (moles/kg) of fuel categories at 500°C using 14ES median compositions input values.

Herbaceous & Grass Biomass									
*K ₃ PO ₄	*CaSiO ₃	*CaMgSi ₂ O ₆	KCl	K ₂ SO ₄	*Na ₂ SiO ₃	*Al ₂ Na ₂ SiO ₁₆	*K ₂ Si ₂ O ₅	Fe ₂ O ₃	*CaFe ₂ O ₄
0.190	0.160	0.080	0.050	0.020	0.020	0.015	0.005	0.005	0.0001
Industry Food Waste									
K ₂ CO ₃	*CaMgSiO ₄	K ₂ SO ₄	KCl	*Mg ₂ SiO ₄	*K ₃ PO ₄	*Al ₂ MgO ₄	*AlKSiO ₄	*CaFe ₂ O ₄	Na ₂ CO ₃
0.031	0.011	0.010	0.010	0.009	0.002	0.002	0.0014	0.0001	0.00005
Agricultural Plants & Residues									
SiO ₂	KCl	MgSiO ₃	K ₂ SO ₄	*Ca ₃ P ₂ O ₈	*Al ₂ Na ₂ SiO ₁₆	Al ₂ K ₂ Si ₆ O ₁₆	Fe ₂ O ₃	*K ₃ PO ₄	*Mg ₃ P ₂ O ₈
0.101	0.069	0.052	0.030	0.018	0.008	0.007	0.006	0.006	0.0001
Wood Waste Fuels									
*CaSiO ₃	*CaMgSiO ₄	KCl	Na ₂ SO ₄	CaSO ₄	*CaFe ₂ O ₄	*Al ₂ Na ₂ SiO ₁₆	*Al ₂ Ca ₃ SiO ₁₂	*Ca ₃ P ₂ O ₈	K ₂ SO ₄
0.034	0.020	0.018	0.008	0.007	0.005	0.005	0.004	0.002	0.00016

*MTData predicted compounds with no gaseous phase below 1300°C.

**ar: as received

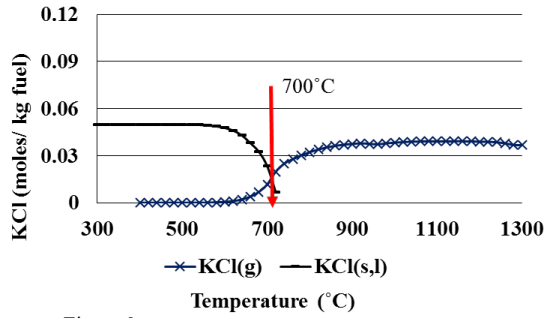


Figure 2a

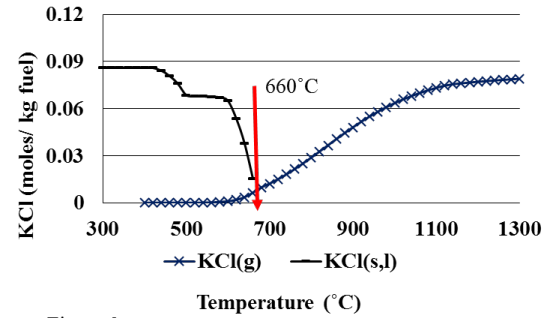


Figure 2c

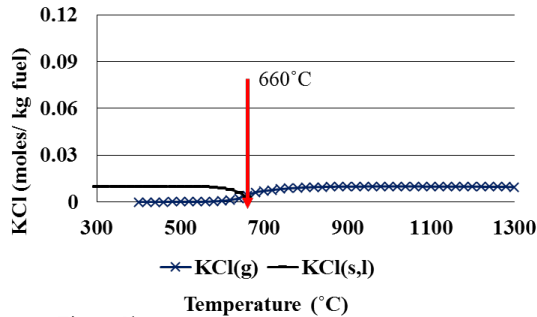


Figure 2b

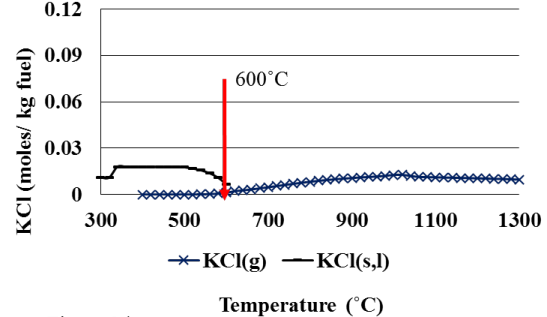


Figure 2d

Figure 2: KCl gas and condensed phase transition temperatures and corresponding concentrations of the (1a) HGB, (1b) IFW, (1c) APR and (1d) WWF fuel categories.

The formation of these high temperature stable compounds (relative to flue gas temperatures of $\approx 1100^\circ\text{C}$ in the vicinity of the heat exchangers) limit the availability of K in the formation of lower melting point K species, thus reducing the K-release fraction to gas phase.

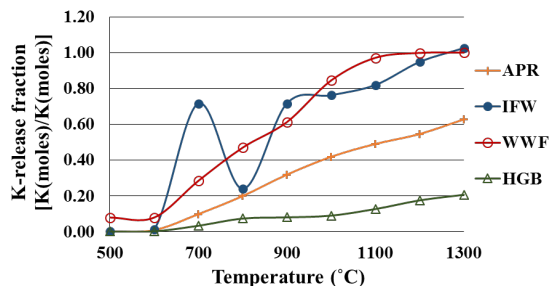


Figure 3: Comparison of the fuel categories' thermodynamically predicted K-release fractions.

Though the K-release fraction profiles are higher for the

IFW and WWF categories (Figure 3), their K fuel contents are relatively lower, as shown in Figure 2.

The thermodynamic prediction of the abundance of K_2CO_3 as the main condensate compound for the IFW category (Figure 4b) is due to its high KOH gas content, resulting from a high fuel moisture content (Table II) [10]. The higher KOH release is also favoured by the relatively lower Cl and S contents in the fuels.

For ease of illustration, K_2CO_3 , KCl and K_2SO_4 have been classed as the lower melting point K compounds (LMK) in relation to heat exchanger surface temperatures of $\approx 530\text{--}630^\circ\text{C}$. It is expected that, if compounds condense or adhere to the heat exchanger surface, they can become molten deposits. K-Si complexes and K_3PO_4 have, on the other hand, been identified as higher melting point K compounds (HMK) which are stable across the thermodynamic simulation temperature range (stable beyond 1300°C). They are thus not expected to be vapourised or molten in the heat exchanger's vicinity. K used in the formation of HMK compounds is considered to be retained as solid phases within a high melting point K (HMK) matrix. This potentially reduces the overall K-release, making K less available to corrosive degradation mechanisms. LMK distributions within the fuel categories have been used to compare the distribution of K between (i.) stable high melting point compounds (relative to combustion flue gas temperatures of $\approx 1100^\circ\text{C}$ in the

vicinity of the heat exchangers) and (ii.) deposits likely to form melts on the heat exchanger at operational temperatures of ≈ 530 - 630°C .

While the combustion K-release fractions for the fuels give an indication of the overall K in gas phase, they can include K compounds forming condensates or exiting the plant fireside with the flue gas vapours. As deposits

have direct and prolonged contact with heat exchanger surfaces than flue gas vapours, LMK and HMK can indicate the molten K compound proportions of the non-gaseous K formed from fuel combustion.

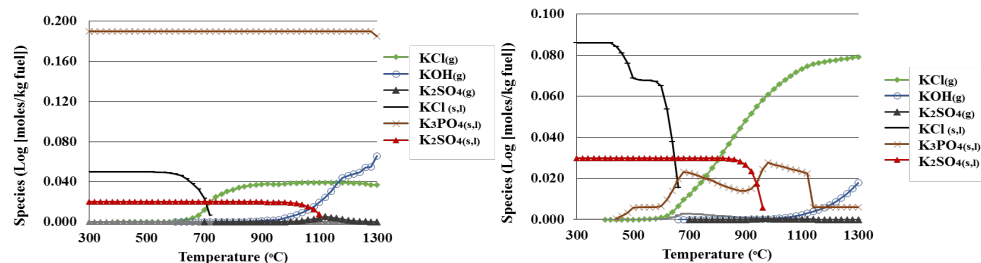


Figure 4a

Figure 4c

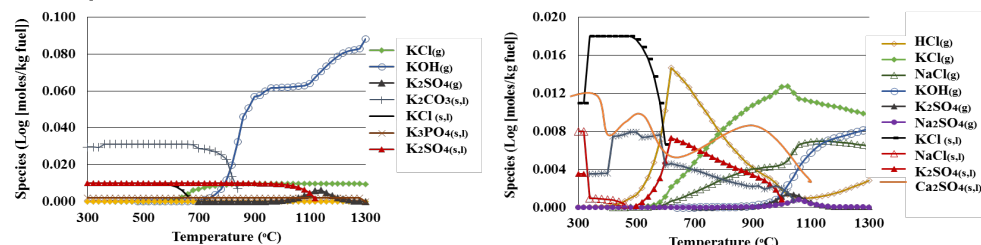


Figure 4b

Figure 4d

Figure 4: The thermodynamic predictions of the compounds containing alkali and alkaline earth metals, showing their condensed and gas phase compositions (with concentrations above 0.002 mole/kg fuel) in a) HGB, b) IFW, c) APR and d) WWF fuel categories.

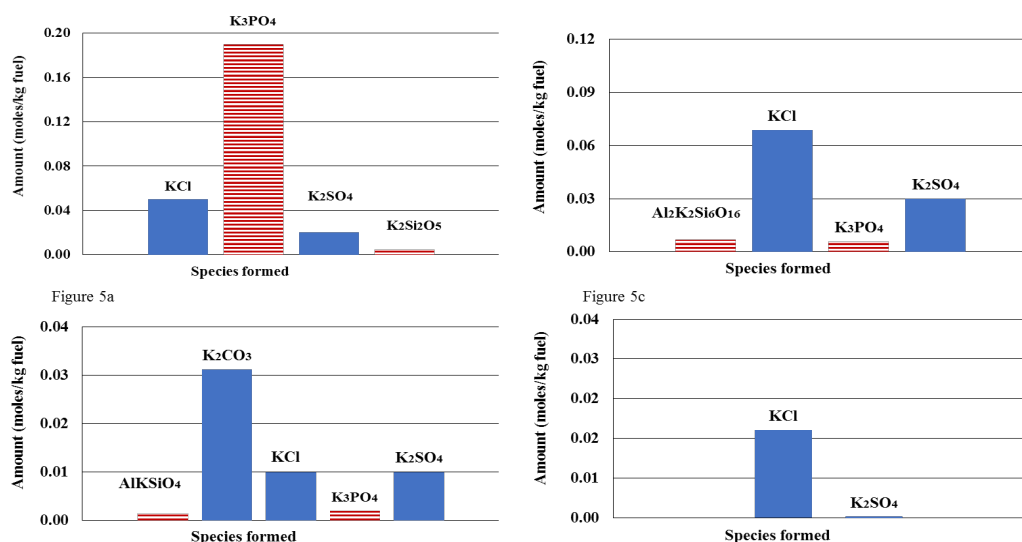


Figure 5a

Figure 5c

Figure 5b

Figure 5d



Figure 5: MTDData thermodynamic distribution prediction of the post-combustion high melting point K compounds (HMK), and heat exchanger corrosion prone low melting point K compounds (LMK) occurring at 500°C in biomass categories (a) HGB, (b) IFW (c) APR and (d) WWF. LMK compounds are likely to interact with heat exchanger fireside corrosion mechanisms.

The high P content of the HGB fuel category (Table II) favours the formation of K_3PO_4 (Figure 5), resulting in the HGB category having the highest HMK values amongst the four fuel categories (Figure 6b). Although WWF shows significantly lower K content than the other fuel categories, the thermodynamic post-combustion simulation indicates it results in 0% HMK compound formation; instead all of the K is associated as KCl or K_2SO_4 (LMKs) in the non-gaseous phase (Figure 6). Subsequently, 100% K-release to gas phase from the vapourisation of LMKs is available to condense from the flue gas current onto the heat exchanger surfaces for the WWF category. This predicted formation of 100% LMK for the WWF category can be explained by the significant amounts of Na and Ca in the fuel, which substitute for K in the formation of Si complexes and phosphates, thus K becomes available for the formation of chlorides and sulfates. The extent to which this would be expected to occur for the WWF category would depend on the availability of sufficient Si content to fix the K species, the abundance of K, as well as the alkali and alkaline earth metal levels of the fuels. The thermodynamic prediction of 0% occurrence of HMK compounds deviates from the minimal K-Si retention fraction [5]; however, it supports the exclusion of K from the formation of K-M-Si complexes, where M is Na, or an alkaline earth metal [10].

Further evaluation of systems with high Ca content and low Si and P, as typically encountered with wood based fuels [11], is required for the determination of their K-release patterns. The $(Ca+Mg)/Si$ index described by Knudsen et al. [10] becomes more relevant for the prediction of K-release from wood type fuels and may be further modified for the inclusion of metal contaminants associated with WWF combustion.

3.2 Fuel Indices for Biomass and Waste Fuel Categories.

Table V shows the calculated indices for the four biomass and waste fuel categories. These indices increase according to $IFW < HGB < APR$ for Cl/K; while the trend for K/Si is different, $APR < HGB < IFW$. The 2S/Cl index, which is indicative of the formation of a sulfate layer serving as a Cl attack inhibitor, suggests highest chloride ratios form for the HGB fuels.

Table V: Calculated fuel K-releases and corrosion prediction indices for the biomass categories. Using the 'as received' values of the fuel stock chemical analysis given in Table II.

Index	Fuel category			
	HGB	IFW	APR	WWF
Cl/K	0.09	0.06	0.12	0.98
K/Si	1.95	6.13	0.23	1.46
2S/Cl	0.58	3.72	2.59	1.39

3.3 Comparison of Thermodynamic & Indices Predictions

K-Release and K Condensed Phases

The same Cl/K fuel index trend is seen for the MTData thermodynamic predictions of the:

- gas phase K-release at 1100°C (Figure 7a) and,
- LMK mole fraction at 300-650°C (Figure 6a).

This suggests a relationship between the Cl/K fuel index and the thermodynamic predictions of the fraction of K involved in the formation of low melting point deposits (melts occurring below 650°C). The thermodynamic post-combustion simulations of 100% Cl release to gas phase, which forms solely KCl as condensate, supports the use of the Cl/K fuel index for the description of K-release.

The K/Si ratios trend of the HGB, IFW and APR fuels (Table V) do not agree with the thermodynamically predicted trends of K-release at 1100°C or with the fuel categories' LMK trend. This can be attributed to the use of Si in other complexes not involving K (Table IV), thus reducing the moles of K-Si complexes formed. The Si content of the fuel can therefore not alone represent the prediction of K that will be fixed in K-Si complexes. This limitation is not addressed by the K/Si index.

As 100% vaporisation of Cl is expected [20] and all Cl-condensates occur only as KCl for the HGB, IFW and APR fuel categories (Figure 4), the formation of KCl in condensed phases will therefore only be influenced by the Cl content. With KCl making up a significant proportion of the condensed phases of these fuels, Cl species post-combustion trends can better align with the amounts of K on the deposits forming from these fuels. Thus, a better correlation of the thermodynamic K-release and LMK predictions occur for the Cl/K fuel index than for the K/Si fuel index. This is in agreement with Knudsen et al. [10] who, in their experimental evaluation of some biomass fuels, observed a rise in K-release with increased Cl concentration despite the fuels' high Si contents.

The WWF category is an exemption to these predictions as its thermodynamically simulated K-release and LMK, and Cl/K fuel index calculations do not correlate with the trends shown to work for the other categories. The relatively low K/Si fuel index ratio for the WWF category (Table V) suggests a higher K-retention in the formation of K-Si complexes (HMK compounds), however this is not the case as K/Si does not consider the effect of other metals present which compete with K in the formation of Si complexes. This index is therefore not sufficient in the estimation of K-release in the case of WWF.

Sulfate/Chloride Ratios

The MTData simulated gas phase S-species/ Cl^- ratios of the HGB, IFW and APR fuel categories at 1100°C follow the same order ($IFW > APR > HGB$) as the 2S/Cl fuel index ratios (Figure 8). Again the WWF category is an exemption to this trend. Thermodynamic post-combustion

predictions for the HGB, IFW and APR categories suggest the condensed phase sulfate occurs only as K_2SO_4 . However, these post-combustion predictions show Na and Ca, as well as K, sulfates are included in the condensed phase predicted post WWF combustion (Figure 4). This suggests a different post-combustion sulfate and chloride distribution mechanism for the WWF category. This may relate to the association of other metal elements not considered by the indices and which may not be found in sufficient quantities in HGB, IFW and APR fuels to significantly alter their combustion species release behaviors.

3.3 Summary

- i. MTDData thermodynamic post-combustion predictions of the fuel categories suggest varying KCl G-C transition temperatures. This may influence the critical KCl condensation temperature on heat exchangers (Figure 2).

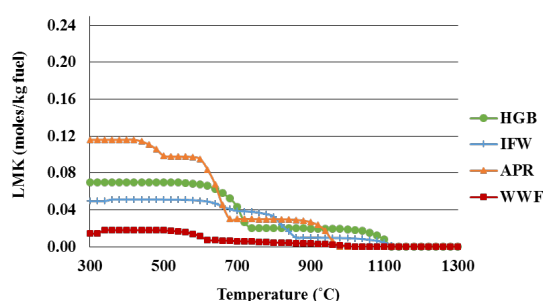


Figure 6a

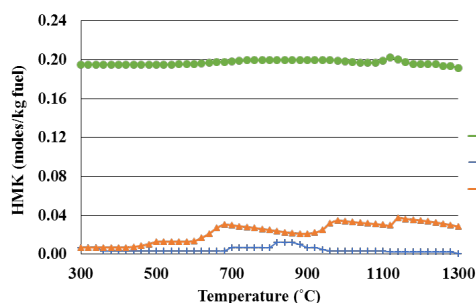


Figure 6b

Figure 6: MTDData simulation concentration profiles of combined (a) low melting point potassium (LMK) compounds of the fuel categories (LMK include KCl, K_2SO_4 and K_2CO_3) and; (b) high melting compounds (HMK) compounds (include K_3PO_4 and potassium silicate compounds).

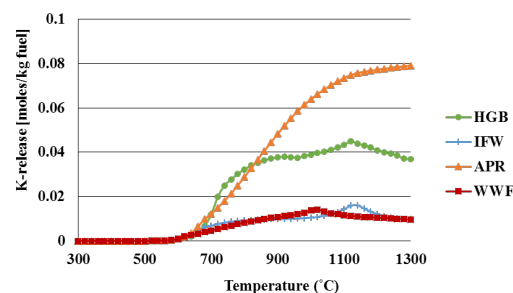


Figure 7a

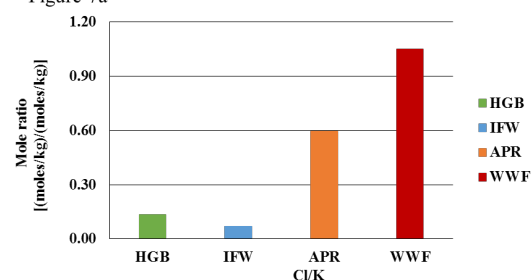


Figure 7b

Figure 7: (a) Summations of all MTDData simulated gas phase potassium-containing species reported as K-release in moles/kg fuel; (b) Cl/K ratios of the fuel categories.

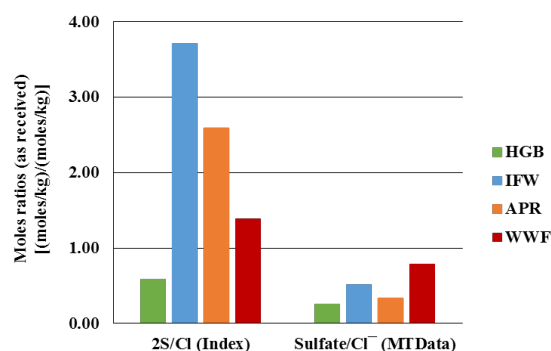


Figure 8: K/Si ratio depicting the K-release fraction of the fuel categories showing no correlation with thermodynamic prediction trends.

- ii. For the HGB, IFW and APR fuel categories' thermodynamic post-combustion simulations, condensed phases related to Cl and S are present only as KCl and K_2SO_4 . K is therefore key in for the migration of these post-combustion species to heat exchanger surfaces. For the WWF category however, Na and Ca sulfates/chlorides are also predicted (Figure 4).
- iii. For the IFW fuel category, KOH gas dominates the gas phase, condensing as K_2CO_3 , K_3PO_4 and

KCl dominate the condensed phases of the HGB and APR categories respectively. The highest KCl concentrations are noted for the APR fuel category and lowest in the WWF and IFW fuel categories.

- iv. The Cl/K fuel index ratios, the MTData thermodynamic post-combustion simulations of the LMK (at 300-650°C) and the K-release values (at 1100°C) all decrease from: APR>HGB>IFW.
- v. The 2S/Cl fuel index ratios and MTData thermodynamic post-combustion prediction for the gas phase S-species/Cl⁻ ratios at 1100°C agree: IFW>APR>HGB.
- vi. The indices applied do not consider the influence of Na and Ca in the prediction of WWF post-combustion release. Whereas thermodynamic simulation suggest Ca and Na will influence the WWF post-combustion K-release and LMKs' formation. This omission may lead to problems with the application of such indices to biomass/waste fuels.

4 CONCLUSION

Efforts have been made to pre-evaluate the key post-combustion compounds formed from the combined firing of biomass/waste fuels, to compare the corrosive releases of these fuels. Categorization of fuels for combined firing becomes more relevant as improving fuel supplies to biomass/waste combustion power plants increase in importance.

Thermodynamic simulations of the post-combustion K species' condensates formed for HGB, IFW and APR fuels are K₂SO₄ and KCl. Significant portions of K₂CO₃ is also present in the IFW category. Stable K compounds such as K-Si complexes and K₃PO₄ are also predicted for the post-combustion compounds formed from these three categories.

The thermodynamic predictions of the post-combustion gas phase S-species/Cl⁻ and the 2S/Cl fuel index ratios follow the same trend for non-WWFs. There have also been correlations between the thermodynamic predictions of K-releases to gas phase and the Cl/K index ratios of the fuel categories, suggesting the highest K-releases are for APR followed by HGB fuels. The Cl/K index shows better correlation than the K/Si with thermodynamic post-combustion K-release predictions due to the influence of Cl in the preferred formation of KCl rather than K-Si complexes. The element-rich fuels, HGB and APR, show higher concentrations of K species in gas phase but lower K-release fractions (in relation to the entire fuel K contents) than the other categories, the latter being due to the relatively high Si content. The overall K content in WWF as well as IFW fuels are however relatively lower than that of APR and HGB fuels, hence lower K-releases in general are expected for these categories.

WWF thermodynamic post-combustion predictions suggest that, in addition to K, Na and Ca will also form sulfate and chloride deposits as well as displace K from the formation of K-Si complexes. The indices applied during this work have failed to adequately describe the WWF post-combustion behavior due to the presence of other metals not considered by these indices.

The post-combustion releases of species, thermodynamically predicted for the fuel categories investigated during this work, are indicative of the types and ratios of deposits that could form on heat exchangers in combustion plants. These simulated post-combustion data are currently being applied to experimental fireside corrosion evaluations of the corrosion mechanisms effected by combustion of these combined biomass/waste fuels.

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F.2 Fuel selection justification report

PhD Project - Formation of Corrosive Compounds from Biomass/Waste Combustion

Fuel Categories Selection



An estimated two-fifths of the available worldwide biomass and waste resource is being utilised for energy production to meet legislative CO₂ emission caps [1]. In 2014, 354 TWh of electricity was generated from biomass combustion plants, mostly from agricultural residues, forest residues and wood chips [1]. Predicting the formation of corrosion causing species released from fuel combustion remain highly relevant for managing fireside corrosion [2]. The corrosion effect of alkali metals and chlorine has been well established by several reports [3,4], but there is limited work done on less common species found in many of these biomasses. Sustainability and cost play major roles in the final selection of a specific biomass fuel, however, the large variations in their properties and resultant fireside corrosion impact also need to be understood. Assessing fuels' corrosive behaviours will require analysing a large range of fuels and blends, generating large amounts of data. In order to deliver a well-defined research scope, it is important that this PhD is focused on fuels with favourable projections for future uptake.

2. Objective

To justify the selection of the following biomass/waste categories for future research work during this PhD:

Herbaceous and Grass Biomass -Agricultural Plant Residues -Industrial Food Waste - Contaminated Biomass and Waste

3. Discussion of Different Fuel Categories

It is believed that electricity production from fossil fuels is cheaper than that from non-fossil fuels; however, the energy potentials of biomass and waste have not yet been fully explored [5]. Energy crop international trade is encouraged by the EU, however the fact that such crops are in demand will increase costs. Improving Energy- from-Waste (EfW) schemes as well as energy crops thus has the potential to reduce energy costs and enhance environmental strategies. The estimated quantity of oven dried wood fuels employed in UK biomass plants in 2013/2014 was 0.8 million tonnes; 62.5% of which was derived from virgin-wood and the remaining from waste wood (0.3 million tonnes); biomass combustion plants have since been shifting towards more sustainable fuels which rely primarily on EfW [6]. Non-fossil fuels for biomass combustion could therefore be classified into two broad groups: Energy crops/natural resources and EfW fuels, in which various subdivisions, or categories, exist. The following fuel categories have been grouped based on their sources and physical properties:

3.1. Energy Crops/Natural Resources

Wood and Woody Biomass (WWB) NOT SELECTED

For the purpose of this research work, WWB consists of virgin-wood fuels, not pre-used wood whose chemical analysis shows higher contaminant levels, and which is included in the Contaminated Biomass and Waste category instead. The EU currently has the highest global demand for WWB and supplements their local supply by importing WWB from North America, Brazil and Russia [7]. Annually, an estimated 41 - 56 EJ of global biomass energy is supplied from forest wood, accounting for over 40% of the total biomass contribution towards global energy supply [1]. Sweden, the second largest exploiters of biomass in the energy sectors relies chiefly on WWB fuels [8]. With over 6.5 million tonnes imported in 2015, the UK held the largest (91%) market share of EU imports of USA WWB pellets [9]. WWB fuels are presently of primary interest to biomass boilers due to the relatively lower operational challenges experienced from their use [3,4].

WWB fuels have not been selected for future studies in this research as there are already considerable amounts of research work addressing the economic and operational subject matters of WWB fuels. It is also anticipated that WWB demand and therefore cost will rise [10].

Herbaceous & Grass Biomass (HGB) SELECTED

In the UK, large spans of land dedicated to the cultivation of herbaceous plants and grasses, which are used as energy crops, have increased in the recent years [11]. Approximately 1.4 million tonnes of HGB fuels were used in total for the UK's electricity generation in 2012. This rose to 3.9 tonnes in 2015. In 2016, 12% of overall heat energy production was brought about by HGB supplies, generating up to 18.8 TWh. In that year, the UK Snetterton and Brigg straw-fired biomass plant produced 100 MW while an additional 144MW was produced by several smaller capacity plants [12].

The makeup of HGB has changed over time. In 2016, UK dedicated 132,000 hectares to include: wheat (66,000 hectares), maize (52,000 hectares), sugar beet (3,000 hectares), miscanthus (7,000 hectares) and short rotation coppice (9,000 tonnes). 47% of the yields were used for electricity generation via plant combustion, leaving 53% for bioethanol and biodiesel production. This means that, since 2015, there had been a decrease in use of sugar beet and an increase for wheat, by over 60%. Similarly, miscanthus growth increased by 7% while short rotation coppice decreased by 38% compared to 2014. These trends show annual changes in the underlying fuels which are integrated under the HGB category. Changes are often driven by the challenges HGS fuel face which include: their encroachment into 'land for other uses' [7], their generally lower bulk densities and their higher corrosion tendencies [13,14].

Europe holds share of over 50% of agricultural land space [7]. The need for fuel importation is reduced as local sourcing of HGB is promoted. This research has selected HGB fuels for further studies as it is expected that the further assessment of their corrosion properties in biomass combustion will be beneficial to their promoted use as biomass combustion fuels.

3.2. Energy-from-Waste

Agricultural and Plant Residues (APR) SELECTED

APR fuels are crop-farm generated wastes. They cover a large range of materials with the fuel variation enhanced by large differences in the cultivation practices adopted locally. APR fuels include: shells, husks and discarded plant parts. As an example, 2.7 million tonnes of olive pruning is generated annually in Crete, some of which provides electricity for homes while majority of it is

disposed of. It has been estimated that if 35% of APR is recovered in Crete, it will meet their total electricity demand [15]. In another example, Turkey has been able to utilize approximately 3.2 million tonnes of APR fuels annually from a variety of tree pruning activities as well as sunflower shells, grape stalks, peels and tomato plant residues for electricity generation. Their estimated total APR reaches 15.3 million tonnes generated annually; this could meet 17 - 27% of their electricity demand [16,17].

This research has selected APR fuels for further studies as the trends above indicate their promising future prospects as biomass combustion fuels.

Industrial Food Waste (IFW) SELECTED

Food from crop-farm produce inevitably generate waste consisting of fruits trimmings, extract remnants and seeds.

Approximately 40% of food waste in UK ends up in landfill. In 2017, up to 7.3 million tonnes of food, amounting to £1.5 billion, was thrown away [19]. With the potential of generating electricity for 600,000 UK homes in 2020, EfW schemes now show more interest in IFW fuels [19]. However, one of the major challenges that faces the use of IFW fuels, is the competition for the use of this waste with its use as livestock feed [20]. This research has selected IFW fuels for further studies as it is expected that improving the sourcing of IFW fuels could encourage biomass industry to invest in them.

Animal Manure & Sewage (AMS) NOT SELECTED

Animal manures (primarily mixtures of animal waste and beddings of straws or wood forms) show lower combustion efficiencies due to their higher ash and moisture contents and lower energy densities; however, wood-bedding manures have been seen to perform better than straw bedding manures [21]. Another AMS fuel is sewage sludge, however competition may increase between biomass boilers and biomass gasifiers (syngas production) as, following recent interest in drying and palletisation of sewage sludge, this fuel can also be used in other renewable energy technologies, bio-organic catalyst plants and methane capping, potentially increasing its price [12]. For this reason, sewage sludge fuels have not been selected for further studies.

Also, animal manure fuels have not been selected for future studies as the required maintenance for managing their high ash contents as well as preparation requirements for their high moisture content increase plant running costs, making the use of animal manure fuels in biomass combustion plants unattractive [15].

Wood Waste Fuels (WWF) SELECTED

This section is mostly made up of commercial/ industrial wood wastes. Recent EfW developments such as the UK Wilton Complex at Redcar have led to a 10% increase in electricity generation (2.7 TWh) from waste [12]. In February 2018, in Tansterne UK, a plant has been commissioned that utilizes up to 0.15 million tonnes per annum of UK supplied wood waste [22]. The UK's economic progression have estimated an annual availability of 4.2- 6.6 million tonnes of waste wood will be available combustion from 2020 to 2025, taking into consideration current reuse and recycle strategies to encourage uptake [10,22]. Such developments are expected to further reduce the UK's reliance on biomass fuel exports.

WWF fuels have been selected for further studies during this research as the current projections for their use as biomass combustion fuels are favourable.

Municipal Solid Waste (MSW) Fuels NOT SELECTED

EfW plants can make use of municipal wastes consisting of organic and inorganic mixtures. It is estimated that UK generated municipal waste can meet the electricity demand of over 15,000 homes daily [23]. In 2015, 14 billion kilowatts of electricity was generated from the combustion of 29 million tonnes of MSW from EfW plants in USA. It was noted that the volume of landfill waste was considerably reduced [24].

MSW fuels show good potentials for their employment in biomass combustion however, there is limited analytical data available on these fuels. Large composition variations are also expected due to the ambiguous definition of ‘municipal waste’. The selection of this category is therefore put on hold following further review.

4. Conclusion – Summary of Fuel Categories Selection for Future PhD Research

- The final fuel categories selected for this PhD are given in section 2.
- The future of HGB, APR, IFW and WWF, selected for evaluation in this PhD looks promising. The waste-type fuels are largely available and their use will reduce landfill levels.
- WWB fuels pose relatively lower corrosion issues than other fuel categories. As such, they continue to be the top biomass fuel choice for plants; however, the economic, social and ecological aspects of WWB sustainability will reduce their realised projections, increasing export trade costs and forcing plants to shift their attention to other sources.
- The favourable projections for waste wood supplies may attract more WWB consuming biomass boilers. This could further reduce the requirement to import WWB fuels.
- - HGB cultivation requirements allow better in-country sourcing, reducing the need to import them (as compared to WWB fuels). EU-28 are the primary importers of WWB from USA, Brazil and Russia; however, Europe holds over half of the global land-crop area [7].
- Plant operational challenges with the use of manures make AMS fuels undesirable. In addition, the demands and costs of sewage sludge will most likely increase. As such, this fuel category will not be considered further.
- Finally, assessing the four selected fuels will enable the research of the high temperature degradation effects of rare elements from novel fuels.

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F.3 Presentations, publications and conference paper

Table F-1: List of presentations and reports

Event/Submission	Presentation/publication type
ERA summer showcase 2021, Cranfield (England)	• Oral
Fuel journal paper submission, 2021	• Submitted paper for publication
EUBCE conference 2019, Lisbon (Portugal)	• Poster • Conference papers
10 th International Charles Parsons Turbine Conference 2019, Cranfield (England)	• Poster • Oral
Tri-U symposium 2019, Jiangsu (China)	• Oral
Clean Energy Science Lecture 2019, London (England)	• Oral
Internal presentations	
Corrosion Seminar 2021, Cranfield (England)	• Oral
Cranfield University interim reviews: 4 th , 9 th , 24 th and 30 th month	• Oral • Review reports
BF2RA (sponsors) reviews	• Oral • Mid-year reports • End of year reports
Energy and Power research student's seminar 2020, Cranfield (England)	• Oral
Corrosion Seminar 2019, Cranfield (England)	• Oral