Contamination and Decontamination of Steel Components

A thesis submitted to the University of Manchester for the degree of Doctor of Philosophy in the Faculty of Science and Engineering

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<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AGR</td>
<td>Advanced Gas Reactor</td>
</tr>
<tr>
<td>AR</td>
<td>As Received</td>
</tr>
<tr>
<td>bcc</td>
<td>body centred cubic</td>
</tr>
<tr>
<td>bct</td>
<td>body centred tetragonal</td>
</tr>
<tr>
<td>BDM</td>
<td>Bockris-Devanathan-Müller</td>
</tr>
<tr>
<td>CRR</td>
<td>Centre for Radiochemistry Research</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
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<td>EBSP</td>
<td>Electron Backscattering Patterns</td>
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<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
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<td>EQCM</td>
<td>Electrochemical Quartz Crystal Microbalance</td>
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<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
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<td>ETD</td>
<td>Everhart-Thornley Detector</td>
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<td>fcc</td>
<td>face centred cubic</td>
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<td>FEG-SEM</td>
<td>Field Emission Gun Scanning Electron Microscope</td>
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<tr>
<td>GCIB</td>
<td>Gas Cluster Ion Beam</td>
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<tr>
<td>GD-OES</td>
<td>Glow Discharge-Optical Emission Spectrometry</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal closed packed</td>
</tr>
<tr>
<td>HLW</td>
<td>High Level Waste</td>
</tr>
<tr>
<td>HMO</td>
<td>Hydrous Metal Oxide</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma-Mass Spectrometry</td>
</tr>
<tr>
<td>IGC</td>
<td>Intergranular Corrosion</td>
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<td>Description</td>
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<tr>
<td>ILW</td>
<td>Intermediate Level Waste</td>
</tr>
<tr>
<td>IPA</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>LIBS</td>
<td>Laser Induced Breakdown Spectroscopy</td>
</tr>
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<td>LLW</td>
<td>Low Level Waste</td>
</tr>
<tr>
<td>LMIG</td>
<td>Liquid Metal Ion Gun</td>
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<tr>
<td>LTE</td>
<td>Local Thermodynamic Equilibrium</td>
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<td>NDA</td>
<td>Nuclear Decommissioning Authority</td>
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<td>Nuclear Power Plant</td>
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<tr>
<td>OECD</td>
<td>Organisation for Economic Co-operation and Development</td>
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<td>OES</td>
<td>Optical Emission Spectroscopy</td>
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<tr>
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<td>ppm</td>
<td>parts per million</td>
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<td>PUREX</td>
<td>Plutonium Uranium Redox Extraction</td>
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<td>Pressurised Water Reactor</td>
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<td>SCE</td>
<td>Standard Calomel Electrode</td>
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<td>Secondary Electron</td>
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<td>SFE</td>
<td>Stacking Fault Energy</td>
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<td>THORP</td>
<td>Thermal Oxide Reprocessing Plant</td>
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<td>TOF-SIMS</td>
<td>Time of Flight- Secondary Ion Mass Spectrometry</td>
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<td>VLLW</td>
<td>Very Low Level Waste</td>
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<td>WNA</td>
<td>World Nuclear Association</td>
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<tr>
<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>XRD</td>
<td>X-ray Diffraction</td>
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Abstract

Nuclear plant stainless steel can become contaminated by radionuclides during normal operation whereby the final disposition of these materials then becomes a major decommissioning challenge to address. Characterisation of the chemical and metallurgical processes that underpin contamination is essential in consideration of developing cost effective decontamination and prevention methods, as are in situ measurement techniques that allow assessment of contamination. To address these issues, contamination experiments to simulate the nitric acid-based reprocessing streams of the PUREX (Plutonium Uranium Redox Extraction) process, and alkaline spent fuel storage ponds were investigated. Solution and surface spectroscopic measurements were performed to characterise the sorption behaviour of stable analogues of two high yield fission products, Sr-90 and Cs-137, on as received and 30 % cold rolled AISI Type 304 stainless steel, respectively. In addition Laser Induced Breakdown Spectroscopy (LIBS) was also investigated as a standoff contamination assessment technique. Fission product accumulation was modelled to a second order kinetic fit that considers chemisorption, typically to a hydrous metal oxide surface, as rate controlling. This process is observed to be independent of solution composition and strain processing regime. This behaviour reflects complexation to the passivating surface chromium oxide film, and as determined by depth elemental analysis, effectively inhibits contaminant migration into the bulk material. Environment chemistry and microstructural variables that destabilise the Cr-rich passive film however reduces the passive layer capabilities to effectively inhibit fission product bulk diffusion. The importance of corrosion phenomena towards radionuclide sorption processes necessitates the consideration of metallurgical and chemical factors during the implementation of decontamination approaches to treat affected plant material at nuclear licenced sites. LIBS was found to be a satisfactory technique for measurement of Sr sorbed to steel but Cs could not be detected at the concentrations used in this experimentation. Furthermore, EDX and TOF-SIMS elemental mapping indicated ablated material may be redistributed into the crater profile during elemental analysis. This process has clear implications for the deployment of LIBS for in situ characterisation of nuclear materials as the uncontrolled redistribution of radioactive material certainly violates decommissioning principles.
Declaration

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1. Introduction

This chapter presents the background and rationale for the thesis. Particular attention is devoted to reprocessing of spent nuclear fuel and resulting contamination of nuclear plant steel materials. An outline of the thesis structure is also provided.

1.1. Thesis Rationale

The generation of radioactive waste is an unavoidable by-product of the commercial production of nuclear power. The majority of the radioactivity is concentrated within the spent fuel (OECD, 2005), where the presence of extremely long-lived radionuclides means the waste will have to be managed on a timescale of > 1 million years. Reflecting this, the storage, management, and final disposal of the nuclear legacy is a major technological challenge. In the UK, the estimated cost of for managing our existing legacy is > £110 billion (over 120 years; NDA, 2016A), although this value will inevitably increase as a result of new nuclear build.

In an effort to minimise the UK waste volume, and in order to recover uranium (U) and plutonium (Pu) from spent fuel (which are seen as assets), spent fuel reprocessing is undertaken at the Sellafield Ltd. Nuclear Licensed site in West Cumbria (Wilson, 1996). Reprocessing first requires an initial underwater storage period of spent fuel in storage ponds for a minimum of 12 months to allow for the radioactive heat decay of relatively short-lived fission products (IAEA, 2006). In most instances, spent fuel is stored in these on-site ponds for many years, and in some cases up to tens of years, depending on the pond’s storage capacity. Wet storage is chosen because in addition to excellent shielding properties, water’s high specific heat capacity enables the thermal heat of the spent fuel to be efficiently dissipated. At Sellafield, Advanced Gas Reactor (AGR) and Magnox (Magnesium non-oxidising) fuels are stored in ponds. This thesis partially examines steel contamination in Magnox ponds (as directed by Sellafield). Of note, the ponds are maintained at a pH of ~ 11 (via addition of NaOH) in order to prevent corrosion of the magnesium alloy (Magnox) fuel cladding (Wilson, 1996).

Once the total activity has declined sufficiently, the spent fuel is removed from the storage ponds and then transferred to either of the Magnox Plant (Magnox fuels and fuel retrieved from Calder Hall) or Thermal Oxide Reprocessing Plant (THORP; for AGR and Pressurised Water Reactor (PWR) fuels) at the Sellafield Ltd. site (Wilson, 1996). At both plants the fuel elements are controllably separated from the more persistent waste fission
products and minor actinides by the Plutonium Uranium Reduction Extraction (PUREX) process, a sophisticated and effective solvent extraction method based on nitric acid media. In order to safely contain these chemically aggressive solutions, stainless steel alloys are extensively used materials for storage vessels and piping network. Steel is also used for storage of spent fuel in ponds (pond furniture).

The adsorption and or incorporation of radionuclides onto stainless steel structural components during storage and reprocessing operations is an undesirable process because if left untreated, it necessitates the classification of contaminated material as nuclear waste (NDA, 2016B). The large volume of radioactively contaminated steel waste generated over several decades of storage and reprocessing activities, and the inability to easily compact these materials, means they will be costly to dispose. Interestingly, little is known about stainless steel radionuclide contamination mechanisms in alkaline and acidic matrices at Sellafield (or similar international facilities). As part of the Sellafield Ltd. Doctoral Training Centre, they requested a project that would extend knowledge of the chemical and metallurgical processes controlling steel contamination phenomena as they believed that data generated in this area would be fundamental to decide upon appropriate decontamination mechanisms in an effort to minimise final waste volumes.

As a result, the overarching aim of this thesis was to provide detailed mechanistic accounts of the sorption of radionuclides from the alkaline storage ponds and HNO₃ reprocessing streams onto stainless steels surfaces. Sellafield dictated that research should focus on two high-yield fission products: particular, ⁹⁰Sr (t½ = 28.8 yrs) and ¹³⁷Cs (t½ = 30.2 yrs). These radionuclides were chosen as they dominated the spent fuel activity within the first hundred years after reactor discharge (Choppin et al., 2002) and internal data from Sellafield indicated that there were taken up onto steel plant and pond furniture surfaces.

The approach adopted in this thesis was to characterise laboratory contamination systems utilising stable analogues of the radionuclides of interest. To reflect the conditions of on-site contamination and provide direct relevance, the steel materials and solution conditions used in this work were selected to be as representative as possible to the specifications of the pond furniture and reprocessing plant infrastructure. The extent and sorption characteristics of contamination were then determined using a combination of independent solution and surface spectroscopic techniques. The effect of steel metallurgy was also investigated by characterising strontium (Sr) and cesium (Cs) sorption onto stainless steel that had been subjected to strain hardening treatment prior to contamination. The knowledge obtained from these results will support informed decision making for the
selection of candidate decontamination strategies to counter the deleterious effects of radionuclide deposition.

1.2. Outline of Thesis Structure

This thesis initially provides a review of the relevant literature and discusses the aims and hypothesis of the thesis (Chapter 2). Chapter 3 provides an overview of the methods used during research. This is followed by three research chapters (Chapters 4-6) that are formatted for external publication. As such, these chapters also include sub-sections of supplementary information as dictated by the target journal styles. These chapters and author contributions are summarised below:

Chapter 4 is a reproduction of a paper that has been submitted for publication in the Journal of Hazardous Materials titled “Analysis of Contaminated Nuclear Plant Steel by Laser-Induced Breakdown Spectroscopy.” The research focuses on the development of laser induced breakdown spectroscopy (LIBS) for performing in situ quantitative analysis of strontium and cesium sorption and/or incorporation into a stainless steel matrix under conditions relevant to the nuclear industry. Author contributions to this manuscript are as follows: The experiments described in this Chapter were designed by A. Lang, D. Engelberg, and G. T.W. Law. Data collection and data processing was performed by A. Lang. The manuscript was written by A. Lang under the guidance of D. Engelberg and G. T.W. Law. Analytical assistance and proof reading of the manuscript was provided by N. T. Smith, D. Trivedi, O. Horsfall, and A. Banford. Technical advice and proof reading of the manuscript was provided by P.A. Martin and P. Coffey. Analytical assistance was provided by W.R. Bower, C. Walther, M. Weiß, and H. Bosco. Technical advice and analytical assistance was provided by A. Jenkins.

Chapter 5 is a reproduction of a paper prepared for submission to Chemistry of Materials titled “Cesium and Strontium Contamination of Nuclear Plant Stainless Steel”. It presents a comprehensive investigation of Sr and Cs contamination of 304 stainless steel in model laboratory systems representative of interim storage Magnox ponds and the Magnox and THORP reprocessing streams. In this chapter, independent spectroscopic measurements were performed to characterise the extent, kinetics, local bonding environment, depth, and distribution of contamination on 304 stainless steel. Author contributions to this manuscript are as follows: The experiments described in this Chapter were designed by A. Lang, D. Engelberg, and G. T.W. Law. Data collection and data processing was performed by A. Lang. The manuscript was written by A. Lang under the guidance of D. Engelberg
and G. T.W. Law. Analytical assistance was provided by Walther, M. Weiß, and H. Bosco. Technical advice and analytical assistance was provided by A. Jenkins.

Chapter 6 is a reproduction of a paper prepared for submission to Corrosion Science titled “Effect of Cold Work on Cesium and Strontium Contamination of Nuclear Plant Stainless Steel”. It investigates the significance of the steel microstructure on the Sr and Cs contamination processes. In this work, the contamination behaviour of strain hardened 304 stainless steel was investigated using an analogous approach as outlined in Chapter 5. In particular, a series of spectroscopic techniques were used to correlate strain-induced modifications of the steel microstructure to the observed changes in contamination behaviour. Author contributions to this manuscript are as follows: The experiments described in this Chapter were designed by A. Lang, G. T.W. Law, and D. Engelberg. Data collection and data processing was performed by A. Lang. The manuscript was written by A. Lang under the guidance of G. T.W. Law and D. Engelberg. Analytical assistance was provided by Walther, M. Weiß, and H. Bosco. Technical advice and analytical assistance was provided by A. Jenkins.

Chapter 7 then summarises the research described in this thesis and discusses its implications for the safe and cost effective management of fission product contaminated stainless steel. Finally, recommendations for further research and lines of enquiry are given.

2. Literature Review

2.1. Nuclear Power Generation in the United Kingdom

The large energy release associated with the fission of heavy atomic nuclei was first discovered in 1938 by Hahn and Strassman during experiments involving irradiation of U with thermal neutrons (Choppin et al., 2002). The original application of U fission reactions for military purposes during the Second World War has since been superseded by the preference for commercial electricity production. This transition highlights the urgent problem facing mankind to create a low carbon based economy whilst satisfying growing energy demands. The production of nuclear power in the United Kingdom (UK) first began at Calder Hall in 1956 (Bolton, 2012). In the intervening 60 years additional nuclear power stations of various reactor designs have since been constructed. The 15 reactors in current operation have a combined capacity of 70 TWh, corresponding to approximately 21 % of the UK’s total electricity production (WNA, 2016).
A source of contention hindering public acceptance of nuclear power are the difficulties surrounding the safe and cost effective disposal of nuclear waste. The extremely high cost associated with waste management (Figure 2.1) is associated with the incredibly long half-lives of many radionuclides which dictate the longevity of the waste for > 1 million years. The current nuclear legacy in the UK is estimated to be $6.27 \times 10^6 \text{ m}^3$, which is broadly categorised into four categories based on activity level and heat generating capability: $2.72 \times 10^6 \text{ m}^3$ of very low level waste (VLLW); $1.60 \times 10^6 \text{ m}^3$ of low level waste (LLW); $0.45 \times 10^6 \text{ m}^3$ of intermediate level waste (ILW); and $1.50 \times 10^6 \text{ m}^3$ of high level waste (HLW) (which requires heat to be considered during disposal) (NDA, 2016B). It is important to note that despite the relatively small volume, HLW contains approximately 95 % of the total radioactivity of all waste forms. Hence, the disposal of HLW is of principal concern and proposed schemes come under great scrutiny prior to approval. The current waste management programme involves the concentration and vitrification of radionuclides in spent fuel into glass, a more stable waste form for transport, storage, and eventual disposal purposes. Vitrified material is currently created and stored indefinitely at the Sellafield site pending approval of an underground geological disposal facility (GDF) to isolate the waste from the biosphere (NDA, 2010).

**Figure 2.1.** Breakdown on the Nuclear Decommissioning Authority (NDA) expenditure of £119 billion for the financial year 2015-2016 for addressing the nuclear legacy 2016 (Adapted from NDA, 2016A).

### 2.2. The Nuclear Fuel Cycle

The generation of electricity from U involves a sequence of interrelated processes that are collectively referred to as the nuclear fuel cycle. There are two common types of fuel cycle that are distinguished by their different methodologies of handling spent fuel. Arguably the
simplest approach is direct disposal (open fuel cycle), where the fuel is classified in its entirety as waste and handled accordingly. A technologically more ambitious alternative is to reprocess the fuel in order to controllably separate unreacted U and Pu from the minor actinides and fission products (Silverio et al., 2011). The potential to transmute the minor actinides in order to reduce their impact on the back end of the fuel cycle has not yet been exploited in the UK. Rather these elements, in addition to the fission products, eventually become incorporated into vitrified HLW. The history of reprocessing dates back to the pioneering work of fission research when Pu was specifically isolated so that it may be harnessed for military use (Wilson, 1996). In the 21st century, U and Pu material is principally recovered in the UK for reducing the total volume of HLW (the closed fuel cycle; Figure 2.2). This is possible due to the large fraction of the spent fuel composition (~ 96 %) comprised of U and Pu, although a significant fraction of the activity remains associated with the fission products (Choppin et al., 2002). Reprocessing operations in the UK are currently undertaken at the Sellafield nuclear licensed site.

**Figure 2.2.** Summary of the closed nuclear fuel cycle (Adapted from NDA, 2016B).

Uranium ores are present at many sites around the world and are currently an important source of feedstock material for the fleet of PWR and AGR reactors operating in the UK that use uranium dioxide (UO₂) fuel. Mining operations are primarily undertaken in Canada, Kazakhstan, Australia, Niger and Russia (Sharrad et al., 2011). Open pit and underground mining were once the most prevalent mining methodologies, collectively accounting for approximately 72 % of U ore production in 2002 (OECD, 2005). The attractiveness of these approaches were evaluated as high productivity in combination with low output costs, although their severe environmental impact has since seen a decline in
their popularity. *In situ* leaching is now considered a more sustainable alternative, which entails crushing the ore into a manageable size followed by the selective dissolution of U with an appropriate leaching agent e.g. sulphuric acid. The U mill product is subsequently extracted from the leach liquor by precipitation with magnesia or ammonia. After the filtered precipitate is dried, the end product is an impure mixture of U₃O₈ that is often referred to as “yellowcake” due to its visibly bright yellow appearance. Chemical refinement then reduces the concentration any impurities to an acceptable level for nuclear grade specifications.

Natural U consists of only 0.71 % of the fissile isotope, ²³⁵U, where the remainder is almost exclusively the ²³⁸U isotope which is not fissionable by thermal neutrons. Therefore, isotopic enrichment of natural U, typically to 4-5 % ²³⁵U, is needed to yield respectable fuel efficiencies (Sharrad et al., 2011). This is achieved by exploitation of the subtle differences in the physical properties of the 235 and 238 isotopes in either gas centrifuges or more commonly by gas diffusion methods. In the latter case, uranium hexafluoride (UF₆) vapour is passed through a permeable membrane and separation occurs as the two isotopes are eluted at different rates.

Once the fuel material satisfies chemical and isotopic requirements, the fuel is then fabricated into a designated chemical form. The first generation of commercial power reactors in the UK used U metal as nuclear fuel (Wilson, 1996). Undesirable phase transformations associated with U metal during burn-up has since resulted in UO₂ becoming the generally preferred fuel type. In addition, UO₂ has a significantly higher melting point than metallic U, permitting higher operation temperatures and an improved thermal output. In the case of AGR and PWR reactors operating in the UK, the isotopically enriched UF₆ feed material is converted to UO₂ powder and is uniaxial pressed and sintered into ceramic pellets. In order to conform to the precise dimensions of the pellet required to fit into the cladding, the UO₂ powder is initially pressed to a slightly exaggerated size and then carefully ground to the desired specification (OECD, 2005). The fuel pellets are encapsulated in either a zirconium alloy (Zircaloy) or stainless steel cladding which provides containment of the fuel elements and fission products whilst acting as a transfer medium for thermal energy from the fuel to the coolant (Antill et al., 1975).
2.3. Nuclear Spent Fuel

After several years of electricity production, the U fuel becomes less efficient power source and the continuation of fuel burn-up is no longer considered economically practical. As a result, spent fuel is continuously removed from the reactor and new fuel is emplaced.

In the United Kingdom, spent fuel is ultimately stored at the Sellafield nuclear licensed site for many years in fuel ponds, where the total fuel activity and temperature declines as short lived fission products undergo radioactive decay. In order to inhibit degradation of the fuel cladding, pond solutions are maintained at ~ pH 11 by a continuous replenishment with sodium hydroxide (Wilson, 1996) for Magnox fuels. AGR fuels are nominally stored in ponds with water at pH 8, but in some instances they can be made more alkaline to limit corrosion.

Afterwards, separation of the desired fuel elements from the waste by-products is universally accomplished by solvent extraction techniques which rely on the inconsistent complexation behaviour of the actinides, fission products, and other unwanted elements. By far the most popular extraction method is based on the PUREX (Plutonium Uranium Redox Extraction) process, as demonstrated by its application in reprocessing operations worldwide (Benedict et al., 1981; Dey et al., 2006). PUREX is used in the UK at both the Magnox Reprocessing Plant and the Thermal Oxide Reprocessing Plant (THORP) (Wilson, 1996). Here, irradiated fuel is initially leached from the cladding by dissolution in 6-12 M HNO₃. The dissolved fuel liquor is only then transferred to the chemical separation plant, where the acidity of the streams is reduced to 3-4 M HNO₃. The addition of an extractant, 30 % tributyl phosphate (TBP), partitions U(VI) and Pu(IV) species into an organic phase of odourless kerosene by the formation of neutral nitrate-TBP adducts. In comparison, the minor actinides and fission products interact weakly with the hard TBP oxygen donor atoms owing to their lower oxidation states in aqueous solution. Hence, U and Pu are effectively isolated from the waste products upon removal into the kerosene phase. The selective complexation of the TBP ligands to hard Lewis acids is further exploited as U and Pu are separated from each other by reduction of Pu(IV) to Pu(III), with Pu(III) repartitioning back into the aqueous phase. In order to maximise the purity of the recovered product, several cycles of extraction and back scrubbing are necessary. In the first iteration > 99.8 % U(VI) and Pu(IV) are co-extracted from 3-4 M HNO₃ into the organic phase, leaving behind > 99 % of the minor actinides and fission products in the aqueous phase (Raj et al., 2006). Several further iterations gradually improve purity of U and Pu to acceptable levels to be used as nuclear fuel.
2.4. Contamination of Nuclear Plant Construction Material

Approximately 75% of the global production of commercial stainless steels are the 300 series austenitic stainless steels, where the primary iron (Fe) phase is γ-austenite i.e. face centred cubic (fcc) (Beddoes et al., 1999). The commercial success of these alloys arises from the high chromium (Cr) and nickel (Ni) alloying content which impart a high tensile strength and in Cr’s case, excellent corrosion resistance that are considered ideal for industrial applications. The accumulation of radionuclides onto austenitic stainless steel nuclear plant components however is responsible for significantly raising the total amount of ionising radiation emitted from the plant during its operational lifetime (Adeleye et al., 1995). Unfortunately the immense scale of plant infrastructure within the Sellafield site provides large volumes of steel construction material susceptible to contamination. In particular, AISI Type 304L stainless steel is one of the main structural materials (Shaw, 1990) and accordingly becomes an important material for radioactive contamination. Significantly, the final disposition of these materials is determined largely by the relative success of subsequent decontamination treatments. The scheduled completion of Magnox and THORP reprocessing operations in 2017 and 2018 (NDA, 2016C) respectively, intensifies the urgency to develop effective decontamination techniques to minimise waste but direct investigations of the relevant contamination phenomena are difficult and thus limited. This is due to the additional radiation dose concerns for onsite personnel and because of the difficulty in conducting on and/or off-site analysis of these active materials.

Previous investigations of radioactive contamination on structural steel surfaces have typically not studied sorption and or incorporation reactions under reprocessing conditions. Nevertheless, the results presented have shown that contamination phenomena is a multi-elemental problem involving a large range of radioactive contaminants such as: fuel elements (Dombovári et al., 2007), activated corrosion products (Hirschberg et al., 1999; Varga et al., 2001), and fission products (Kádár et al., 2011). This thesis focuses on the deposition of two high yield fission products, $^{137}$Cs ($t_{1/2} = 30.2$ yrs) and $^{90}$Sr ($t_{1/2} = 28.8$ yrs) respectively, under conditions representative of alkaline fuel storage ponds and HNO$_3$ reprocessing streams. These relatively long lived fission products contribute a significant fraction of the total solution activity at Sellafield and their accumulation onto the surfaces of steel components is strongly associated with the increased plant activity.
2.5. Stainless Steel Sorbent Properties

When radionuclides accumulate onto stainless steel materials, sorption behaviour is controlled by a combination of chemical and surface speciation effects (Kádár et al., 2010). Although the chemical form of depositing radionuclides may be readily determined by knowledge of solution pH and redox potential, characterisation of the steel surface state is not at all straightforward. This is because the surface physico-chemistry properties of a steel material are derived from the passive layer, a surface oxide film that spontaneously forms under oxidising conditions. It is now known that this film is intimately related to metallurgical variables (Sedriks, 1986), where concerted efforts have been made to enhance corrosion performance by careful control over the concentrations of alloying elements and their distribution within the microstructure. Furthermore, the elemental constituents of the oxide layer possess distinct chemical properties in contact with aqueous solution. The solution composition can therefore be expected to play a key role in determining both the elemental composition and structure of the passive layer, and the chemical identity of accumulating species.

2.6. The Passive Layer

A characteristic feature of stainless steels is that these alloys do not readily corrode in mildly oxidising environments and hence maintain a “stainless” appearance. Under these conditions, the material is then described as being in a “passive” state. The term passivity was first used by Schönbein in 1836 (Groysman, 2010) to describe the diminished corrosion rate of Fe in nitric acid after a brief but intense period of initial metal dissolution. As this apparent inertness was in direct contradiction with thermodynamic principles it became clear that this behaviour was a kinetic phenomenon. It was later realised that passivity was a consequence of the spontaneous formation of a several nanometre thick, surface oxide layer that protects the underlying material from its corrosive medium. The formation of this strongly adhering film is derived from the continuous adsorption of oxide corrosion products that are rapidly produced as the material undergoes intense active dissolution. Over time the adsorbate concentration becomes sufficiently high that an interconnected, 3D oxide film completely covers the metal surface. In this instance further reaction ceases as the bulk material is adequately shielded from its aggressive environment.

Although it has been known for a long time that alloying Cr to Fe dramatically improves corrosion performance, practical experience preceded scientific understanding and Cr’s
exact function was not immediately clear. The term passivity has since become synonymous with Cr as corrosion resistance is now attributed to the spontaneous formation of a Cr rich surface oxide layer. The experimentally observed 13 wt. % Cr content needed for complete passivity (Haupt et al., 1995) has been rationalised in Monte Carlo simulations as the minimum number of Cr atoms required to form an interconnected 3D network (Qian et al., 1990; Diawara et al., 2004). Diffraction studies have confirmed the correctness of a percolation interpretation by revealing an interconnected amorphous oxide network forms at the expense of a spinel-like structure above this threshold Cr concentration (McBee et al., 1972). Therefore, these results collectively suggest that surface oxide morphology is a key contributing factor in determining its protective capabilities.

An interesting facet of the passive film is its dynamic capacity to respond to modifications in its environment. The elemental structure, composition, and thickness are all adjusted by the film’s constant exchange with components of the passivating medium, thus providing protection to the underlying material across a broad range of environmental conditions. A consequence of this adaptive behaviour however, is that the development of universal models to comprehensively describe the passive layer character is not straightforward. For this reason investigations have typically been conducted on an individual basis relevant to the environments of interest, where the total number of studies that describe general characteristic features is much smaller by comparison.

Half a century ago a gel like structure was proposed in which incorporated water molecules were considered to play a critical role in the passive layer’s formation and maintenance (Okamoto et al., 1965). In this model it was assumed that bridging between individual metal oxide clusters is augmented by the mutual sharing of bound water molecules (Figure 2.3A). As the film ages, H$_2$O deprotonation yields the interconnected (-O-M-O-) structure as identified in the aforementioned diffraction studies (Figure 2.3B). The special importance attached to water in this model suggests that the construction of this network configuration may be inhibited by nucleophilic substitution reactions as the film initially develops. The authors considered that the replacement of H$_2$O by Cl$^-$ (Figure 2.3C) for example will produce soluble metal chloride complexes (Figure 2.3D) that creates localised breaches within the oxide film. Hence, this “bound water” model provides a rationale for the pitting phenomenon of stainless steels in chloride containing media that, although studied extensively, is not fully understood (Schultze et al., 2000). In comparison, basic species such as OH$^-$ and CO$_3^{2-}$ may assist in the deprotonation of the bridging H$_2$O
units without becoming incorporated into the film (Shibata, 2007). Accordingly, these acid-base processes can accelerate the formation of, and if necessary repair of, the passive layer, thus improving corrosion resistance.

![Diagram of acid-base processes](image)

**Figure 2.3.** Okamoto’s “bound water model” illustrating the significance of incorporated water molecules in the construction of the passive layer 3D network (Adapted from Okamoto, 1973).

Considerable progress in the characterisation of the passive layer was made possible in the late 1970’s by the commercial availability of electron based spectroscopic techniques. The determination of the depth distribution and local bonding environment of the elemental constituents has revealed interesting subtleties about the passivity phenomenon. Electron spectroscopy for chemical analysis (ESCA) of atmospheric passivated metallic elements has identified a common bilayer structure consisting of an oxide layer underneath and an outer layer rich in metal hydroxides (Barr, 1978). It was also found that this terminal hydroxide layer is composed of the metal in a higher oxidation state than the inner layer if one is commonly available. The analogous deconvolution of the stainless steel passive layer into layered components is more complicated as multiple alloying elements in various oxidation states may be assimilated into the film. On the results of X-ray photoelectron spectroscopy (XPS) measurements, there is broad consensus that atmospheric passivation yields an inner Cr$_2$O$_3$ layer and an outer layer of Fe(III) oxides and hydroxides (Asami et al., 1977; Storp et al., 1977). Thus, the fundamental bilayer structure as described for pure metals appears to be maintained for more complex alloys. A similar result has also been obtained for stainless steels passivated in neutral and slightly alkaline solutions (Castle et al., 1977; Carmezim et al., 2005), suggesting that humidity is a controlling factor in atmospheric passivation behaviour. Interestingly, in these studies the authors did not observe selective oxidation of Cr relative to Fe, where the relative proportions of these two elements mirrored bulk concentrations. These results strongly suggest that concentration gradients are responsible for the observed passive layer elemental composition under atmospheric conditions. Furthermore, it has been postulated
that the enrichment of Fe in the terminal scale is due to a higher diffusion rate through the developing passive layer than Cr (Olsson, 2003).

2.7. Passivity Behaviour at High pH

The corrosion behaviour of steel materials in alkaline media is frequently examined within the framework of reinforced steels in cement structures. The concrete pore solutions are comprised mainly of alkali metal hydroxides, where the resulting pH is typically between 12 and 13 (Freire et al., 2010). Under basic conditions Cr₂O₃ is oxidised to slightly soluble Cr(VI) species, where Cr dissolution accordingly concentrates Fe in the passive layer. XPS depth characterisation has shown at high pH the inner Cr layer is a spinel type structure consisting of small amounts of Fe and Ni. Importantly, this oxide has been shown by Mott-Schottky analysis to be highly defective and as a result, provides inferior corrosion resistance than Cr₂O₃ (Freire et al., 2010). For this reason, additional significance is now attached to the outer Fe layer as a source of passivity. On the basis of the determined 2:1 Fe(III)/Fe(II) ratio, a proposed Fe oxide is magnetite (Fe₃O₄), a cubic inverse spinel comprising a closed pack array of oxide anions (Freire et al., 2012). In this structure the Fe(III) ions reside in the tetrahedral and half of the available octahedral sites. The remaining octahedral positions are subsequently occupied by the Fe(II) ions. The formation of magnetite has been observed with cyclic voltammetry experiments at approximately -0.8 V vs. SCE, in accordance with the following reactions.

\[ 3Fe(OH)_2 + 2OH^- \rightleftharpoons Fe_3O_4 + 4H_2O + 2e^- \]  
(Equation 2.1)

\[ 3FeO + 2OH^- \rightleftharpoons Fe_3O_4 + H_2O + 2e^- \]  
(Equation 2.2)

The detrimental role of carbonate on the corrosion behaviour of mild steels in chloride containing alkaline solution is related to its destabilising effect on the protective Fe₃O₄ layer (Freire et al., 2011). As solution pH is reduced by CO₂ dissolution, Fe(II) is destabilised and accordingly Fe₃O₄ is converted to γ-Fe₂O₃. This transformation has been reported to occur within the pH range 9.4-10 (Huet et al., 2005) where in the absence of the protective Fe₃O₄ film, active corrosion is often prevalent. Some authors have also suggested the effect of carbonate is more complex and may kinetically inhibit oxidation to Fe(III) if present in high solution concentrations (Moreno et al., 2004).
The analogous decomposition of Fe$_3$O$_4$ under mildly alkaline conditions for 304L stainless steel was later observed to be irrelevant in maintaining corrosion resistance (Freire et al., 2011). This was despite the inclusion of 10 wt. % NaCl in the model concrete pore systems studied. The superior corrosion performance of the austenite grades is due to the increasing Cr$_2$O$_3$ stability that accompanies the oxidation of Fe$_3$O$_4$ under less basic conditions. The positive influence of alloying small amounts of Cr on corrosion resistance was demonstrated by a study of the corrosion behaviour of Fe-Cr alloys in chloride-carbonate environments at pH 10.5 (Liu et al., 2017). Here, the authors recorded severe intergranular corrosion (IGC) and pitting of carbon steel and 1.5Cr steel (Figure 2.4), attributed to insufficient Cr levels to produce an extensive Cr$_2$O$_3$ film. This assessment was supported by complementary cyclic voltammetry analysis which yielded intense anodic peaks characteristic of an unstable passive layer. In contrast, the absence of IGC for 3Cr and 5Cr steel (Figure 2.4C and D) indicates the formation of a significantly more effective Cr-passive film.

**Figure 2.4.** Variation in corrosion morphology after immersion in pH 10.5 simulated carbonated concrete pore solution for (A) carbon steel, (B) 1.5Cr steel, (C) 3Cr steel, and (D) 5Cr steel. The total immersion time for all systems was 60 days (Adapted from Liu et al., 2017).

**2.8. Passivity Behaviour at Low pH**

For an acidic solution, Cr$_2$O$_3$ is stabilised whereas the solubility of Fe is much higher than in neutral or alkaline media. Therefore, the observed enrichment of Cr in the passive layer
at low pH may be considered an artefact of selective Fe dissolution. In addition, these Cr rich films have typically been measured to be significantly thinner than those grown at elevated pH (Hoppe et al., 1994), which may be related to the increased stability of the Fe oxide components in alkaline solution. The study of passivation kinetics at low pH to monitor this transformation is somewhat limited since reaction times are usually conducted on an hour timescale. Nevertheless, XPS measurements have observed an increasing surface Cr: Fe ratio of austenitic stainless steels within minutes of initial HNO$_3$ immersion (Liu et al., 2015). This behaviour is consistent with previous passivation studies in other acid systems (Wallinder et al., 1999; O’Laoire et al., 2006). The increased film thickness in HNO$_3$ however has been correlated to the continued growth of Cr$_2$O$_3$ under more oxidising conditions (Hamm et al., 2002). Although an equilibrium elemental composition was frequently not observed in these kinetic investigations, it is clear that the oxide growth and dissolution processes that underpin passivation are rapidly initiated. Cabrera and Mott have for example described growth kinetics by an inverse exponential rate law, controlled by the slow diffusion of ions through the film (Cabrera et al., 1949). Subsequent research has shown this kinetic model may be applied to accurately describe the passivation behaviour of stainless steels in acidic (Hamm et al., 2002) and alkaline media (Marshall et al., 1983). The diminishing rate of Cr enrichment over time is possibly a consequence of the increased difficulty of ion migration through an outwardly expanding film.

As might be expected, pronounced Fe leaching at reduced pH produces an extremely thin Fe oxide scale above a thick Cr(III) layer at the metal-oxide interface (Olefjord et al., 1982; Haupt et al., 1995; Keller et al., 2004). Regardless, the Fe-Cr bilayer structure as previously described for atmospheric passivation is apparently maintained across a large solution pH range. This is despite clear evidence that metal oxide stability is highly sensitive to the solution composition.

2.9. Solid Solution Alloying

In addition to environment chemistry, passivity is also highly sensitive to the elemental composition and distribution within the steel microstructure. The influence of minor alloying elements on passivity behaviour is usually considered from the viewpoint of their chemical interaction with Cr. Common examples of this include sulphur and phosphorous impurities, which are both viewed as a source of potential material failure due to their formation of Cr precipitates (Armijo, 1968). This has been related to generation of Cr depleted zones in the surrounding areas that often become initiation sites for corrosive attack (Sedriks, 1986). In a similar manner, the “sensitisation” of stainless steels by the
precipitation of Cr carbides (e.g. Cr$_{23}$C$_6$) during the manufacturing process is characterised by attack at the grain boundaries. It is known that these precipitates are only thermodynamically stable at elevated temperatures (Sedriks, 1986), and as a result optimisation of heating times and quench annealing temperatures may prove valuable in inhibiting their formation. An arguably simpler control measure is to minimise the alloying carbon (C) content whilst maintaining sufficient amounts to impart strength onto the material. Hence, the most widespread austenitic stainless steels grades employed for nuclear plant material are the low C (< 0.03 %) alloys.

Regarding silicon (Si) content, corrosion resistance has been reported to increase and decrease, depending on the total amount alloyed and the nature of the corrosive environment. The high Si Uranus S1N stainless steel contains comparable Cr levels to the 300 series but nevertheless is less resistance to uniform corrosion in highly concentrated HNO$_3$ (Ghiban et al., 2008). XPS analysis has shown this to be due to the introduction of SiO$_2$ into the passive film at the expense of Cr$_2$O$_3$, thus reducing the film’s protective capabilities (Robin et al., 2008). As the rate of general corrosion was proportional to the Si content, this may be considered indicative of a continuous replacement of Cr by Si in the oxide layer. On the other hand, under high potentials that destabilise Cr, Si incorporation provides an alternative oxide composition that is somewhat resistant to IGC (Wilde, 1988). An increased immunity to intergranular degradation has also been attributed to Si segregation at the grain boundaries, increasing the electronegativity of the solid solution and thus hindering the undesirable chemisorption of Cr-withdrawing impurities (Kasprova, 2004).

The exact function of alloyed molybdenum (Mo) on enhancing the pitting resistance of stainless steels is unclear. There is some evidence that Mo becomes an important constituent in the passive layer (Figure 2.5) and has been postulated to act as a bridge to facilitate Cr reconnection during the repair of small pits (Oleffjord et al., 1982; Olsson et al., 1994). This interpretation may be considered an extension of Okamoto’s model that only considered bound H$_2$O as a possible bridging agent to re-establish lost connectivity of the interconnected passive film. Interestingly, in these studies a Mo depth distribution was reported that is consistent with the ESCA study of metallic elements i.e. Mo(VI) and Mo(IV) concentrated within the terminal and inner oxide, respectively (Olsson et al., 1994). The issue is complicated however by contradictory Auger Electron Spectroscopy (AES) and XPS studies that do not observe any discernible levels of Mo incorporation in the passive film (Olsson, 1995; Abreu et al., 2015). These results have prompted some
authors to propose an indirect stabilising mechanism in which Mo(VI) adsorption modifies the passive film’s electronic properties as to promote Cr₂O₃ formation (Yun et al., 2012). It is not clear if these inconsistent results are related to the non-identical steel compositions and solution conditions studied in the studied cited.

![Figure 2.5](image_url)

**Figure 2.5.** XPS analysis of passive film formed in 0.1 M HCl + 0.4 M NaCl. The model structure shows three distinct regions of non-uniform elemental composition: bulk metal, apparent metal, and oxide (Adapted from Olefjord et al., 1982).

In contrast, the role of Ni is much better understood. The principal function of alloying Ni in to the microstructure is to stabilise the metastable austenite phase at room temperature. The contribution of this element towards passivity is considered negligible because from a thermodynamic perspective, the associated free heat of Ni oxidation is significantly smaller than that for Fe and Cr (Castle, 2008). For this reason, elemental Ni is enriched at the metal-oxide interface rather in the oxide itself. A similar Fe enrichment phase was also reported for Fe-Cr alloys in acidic solutions (Bardwell et al., 1993) where Cr is selectively incorporated into the oxide film. On this basis, this effect is likely an artefact of the selective oxidation of other alloying elements at the near surface.

**2.10. Cs Contamination of Fuel Cladding Material**

During the late 1960’s and early 1970’s austenitic stainless steels were employed as fuel cladding material due to a strong clad integrity at 650 °C, the maximum inner temperature of the fuel pins (Tateishi et al., 1988). A fuel-cladding chemical interaction was later implicated in the severe IGC observed during reactor operation (Adamson et al., 1985). It was concluded on the basis of electron micrograph analysis that localised breakdown of the fuel cladding passive layer was intimately related to a chemical reaction with the volatile
fission product, $^{137}\text{Cs}$, to yield $\text{Cs}_2\text{CrO}_4$ (Bradbury et al., 1978; Figure 2.6A). The resulting defect in the passive film subsequently facilitates corrosive attack and Cs penetration into the bulk material (Antill et al., 1975).

Ferritic steel grades are currently considered a more reliable cladding material in recognition of their better swelling properties under heavy neutron irradiation (Mansur et al., 1991). In spite of this, analogous corrosion processes have been identified that are associated with the formation of $\text{Cs}_2\text{CrO}_4$ at the surface (Sasaki et al., 2013; Figure 2.6B). Utilisation of thermodynamic calculations led to the following reaction scheme being proposed:

$$2\text{Cs} + \frac{5}{2}\text{O}_2 + \frac{1}{2}\text{Cr}_2\text{O}_3 \rightleftharpoons \text{Cs}_2\text{CrO}_4$$

$$\Delta G_{650^\circ\text{C}} = -637.5 \text{ kJ mol}^{-1}$$

(Equation 2.3)

**Figure 2.6.** Proposed mechanism of Cs assisted internal cladding corrosion for: A) austenitic stainless steel (Adapted from Bradbury et al., 1978) and B) ferritic steel (Adapted from Sasaki et al., 2013).

Furthermore, Cs diffusion was found to be accompanied by the surface enrichment of Fe precipitates, a possible by-product of the selective reaction of Cr according to Equation 2.3 at the sub-surface (Sato et al., 2002). The regions of localised Cr depletion are considered favourable sites for the inwards transportation of unreacted elemental Cs into the bulk material. In this instance, a rapid oxidation step accompanies Cs transportation to produce the familiar Cr(VI) species:
\[ Cr_2C_6 + 4Cs + 46O_2 \rightleftharpoons 23Cs_2CrO_4 + 6C \]

\[ \Delta G_{650°C} = -25018.1 \text{kJmol}^{-1} \]

(Equation 2.4)

It is important to note that C is a by-product of this contamination phenomenon. This element is known to extract Cr from neighbouring areas to precipitate \( Cr_2C_6 \) (Sedriks, 1986) and thus introduces the possibility of establishing a catalytic cycle in association with Equation 2.4 to systematically remove Cr from the microstructure. Accordingly, the collective action of Cs, O, and C may be responsible for the initiation of extensive IGC. The high O:Cs stoichiometric ratio of Equation 2.4 suggests that O potential, and not fission product concentration, is rate controlling for this process. This interpretation has been demonstrated in corrosion experiments where trace amounts (10 ppb) of Cs were sufficient to induce severe intergranular attack (Gotzmann et al., 1974).

It has been reported that the aforementioned Cs related corrosion processes do not occur below \( \sim 550°C \) (Antill et al., 1975). This has been rationalised by the unfavourable enthalpy change associated with \( Cs_2CrO_4 \) formation at ambient temperatures (Equation 2.5). Therefore, the \( Cr_2O_3 \) layer is preserved, and the steel material remains in a passive state (Sasaki et al., 2013).

\[ Cs_2O + \frac{1}{2}Cr_2O_3 + \frac{3}{4}O_2 \rightleftharpoons Cs_2CrO_4 \]

\[ \Delta G_{25°C}^0 = +486.5 \text{kJmol}^{-1} \]

(Equation 2.5)

Not surprisingly ion bombardment studies have reported slow Cs diffusion rates into the microstructure at room temperature (Matzke et al., 1977). As the calculated diffusion coefficient was comparable to those of Fe and Cr (Smith et al., 1969), Cs transportation into the steel matrix was postulated to be propagated by available cation vacancies in the austenite lattice. The authors considered Cs would not be able to penetrate the passive layer for diffusion into the bulk material to occur and as a result, the steel substrate was etched to the zero valence state prior to Cs bombardment. The absence of relevant depth resolved contamination studies within the literature makes it difficult to accurately evaluate the correctness of this assumption.
2.11. Surface Complexation Modelling

The effect of temperature on the dominant contamination pathway indicates that alternative mechanisms are controlling the documented contamination of spent fuel storage and transport materials. However, the accumulation of radionuclides from aqueous solution on steel materials at low temperature is not as well researched. It has been suggested on the basis of spatial mapping (TOF-SIMS) analysis that Sr and Cs contamination of simulated pond furniture selectively occurs along the grain boundaries but the poor resolution of the data makes interpretation difficult (Woodhouse, 2008). A similar intergranular Cs diffusion mechanism has been proposed at elevated temperatures (Matzke et al., 1983). The Sr and Cs solution concentrations employed (0.5 wt. %) in the Woodhouse low temperature study however are not representative of onsite pond conditions and as a consequence, the direct relevance of these results is not clear.

As stainless steels are covered by the passive layer, it has been postulated that these alloys possess analogous sorbent properties to hydrous metal oxide (HMO) suspensions. The motivation for this comparison is that the immobilisation of aqueous radionuclides by sorption onto metal oxide minerals has been studied much more extensively (Parks et al., 1962; Strumm et al., 1976; Farley et al., 1985; Dzomak et al., 1986; Brown Jr. et al., 1999). This is because an understanding of groundwater transport mechanisms of accidently released radioactive material is of fundamental importance to satisfy immediate public health concerns. In these studies researchers adopt surface complexation models which describe sorption as an electrostatic interaction between metal ions and available surface sites. Here the oxide surface is charged due to the amphoteric nature of the surface hydroxyl groups in aqueous solution:

\[
\equiv MOH + H_3O^+ \rightleftharpoons \equiv MOH_2^+ + H_2O
\]

(Equation 2.6)

\[
\equiv MOH + OH^- \rightleftharpoons \equiv MO^- + H_2O
\]

(Equation 2.7)

where \( \equiv M \) is a surface metal atom.

The sign and magnitude of the surface potential is determined by solution pH as this parameter governs the equilibrium positions of the aforementioned acid-base surface reactions. The pH of point zero charge (pH_{pzc}) corresponds to the solution acidity that
generates an electro-kinetically neutral surface in which the concentration of protonated and deprotonated sites are perfectly balanced. When the pH is raised above this value, hydroxyl dissociation is favoured and the resulting negatively charged surface promotes metal ion deposition. At low pH (< pH_{pzc}), the increasing number of protonated surface sites will inhibit cation sorption. This behaviour has been experimentally verified for a large number of metal ions in several sorption experiments, where uptake on various HMOs was indeed observed to increase with increasing pH (His et al., 1985; Dzomabk et al., 1986; Mishra et al., 1999; Pathak et al., 2006).

Sorption processes at metal oxide surfaces are inherently complex and the aforementioned surface complexation model adequately accounts only for monolayer coverage of ions and neglects possible chemical interactions at the surface. These possibilities are more comprehensively described by the Bockris-Devanathan-Müller model (BDM) (McCafferty, 2006), which accounts for the sorption of both metal ions and polar solvent molecules (Figure 2.7).

**Figure 2.7.** Bockris-Devanathan-Müller model of a metal oxide showing ion adsorption at the oxide-solution interface. The pH of the solution is assumed to be higher than the pH_{pzc} of the metal oxide and hence the positively charged surface favours anion sorption (Adapted from Brown Jr. et al., 1999).

The BDM model can be classified into three main regions as follows. At the oxide-solution interface, opposite charged ions and solvent molecules are maintained in the so called inner
Helmholtz layer at the surface. This monolayer coverage of chemisorbed species effectively screens the surface charge of the metal oxide and as a result the second layer, the outer Helmholtz layer, consists of only hydrated ions that interact non-specifically with the surface. It is considered that the driving force for the formation of this layer is the charge neutralisation of the inner Helmholtz layer, and not the surface potential directly. Finally, a third layer exists that is composed of ions and solvent molecules in the aqueous phase that are loosely associated with the surface. Under thermal motion these species are mobile and hence this outermost layer is often referred to as the “diffuse layer”.

2.12. Ambient Temperature Contamination

The description of room temperature adsorption of radionuclides on stainless steels has subsequently evolved from these surface complexation models that were originally invoked to characterise metal ion sorption onto minerals. Investigation of the pH dependence of cobalt (Co) and Cs contamination of steel materials has found, analogous to the sorption onto HMOs, that uptake increases with increasing pH (Adeleye et al., 1996). In accordance with the relative charge densities of the two accumulating metal ions, the surface affinity for Co\(^{2+}\) sorption exhibit a much stronger pH dependence than for Cs\(^{+}\). In a separate study, a sharp increase in the rate of Co accumulation was observed above pH 8, attributed to the likely precipitation of Co(OH)\(_2\) (Adeleye et al., 1995). As particulate matter is deemed too large to penetrate the Helmholtz layers, Co(OH)\(_2\) must remain in the diffuse layer and forgo the slow process of approaching the metal oxide surface. Hence, the surface complexation model attaches some significance to the chemical form of the adsorbing species, in particular its occupied volume.

The pH\(_{\text{pzc}}\) values for bulk Cr and Fe oxides are typically within the near neutral range (Hubbard, 2002; Kulczycki et al., 2005) and as a result it may be expected that radionuclide deposition from acidic media will be minimal. The extent of accumulation of several fission products (e.g. \(^{140}\text{La}, \(^{143}\text{Ce}\) and \(^{239}\text{Np}\)) on 304L stainless steel from 3 M HNO\(_3\) was indeed insufficient to be detected by \(\gamma\)-spectroscopy, likely due to this unfavourable charge interaction (Fuji et al., 2002). On similar principles, fission products that form anionic oxide complexes (e.g. \(^{99}\text{Mo}, \(^{131}\text{I}, \(^{132}\text{Te}\)) are electrostatically attracted towards the protonated oxide layer and thus yield a measurable gamma signal at the surface. In a similar approach, \(^{133}\text{Cs}\) contamination of 304L stainless steel has also been described using a series of equilibrium reactions between contaminants, other dissolved ions and free surface sites (Rouppert et al., 2000). By utilisation of Fourier transform–
infrared spectroscopy, three fundamental chemical processes were identified by their signature vibrational frequencies:

\[
CsOH \rightleftharpoons Cs^+ + OH^- \]  
(Equation 2.8)

\[
\equiv MOOH \rightleftharpoons \equiv MOO^- + H^- \]  
(Equation 2.9)

\[
\equiv MOO^- + Cs^+ \rightleftharpoons \equiv MOOCs \]  
(Equation 2.10)

In accordance with Le Chatelier’s principle, the equilibrium positions of these reactions, and hence the extent of Cs contamination, is influenced by modifications to the solution composition. An increase in acidity displaces Equation 2.9 to the left and thus reduces Cs adsorption; a result also predicted by surface complexation modelling. The observed persistence of Cs-O-M vibrational stretches at pH 2 is somewhat unexpected as the physical interactions are certainly unfavourable for sorption under acidic conditions. Therefore, it should be appreciated that a chemical sorption component contributes to Cs contamination behaviour at low pH. This is an important result to be considered during the decommissioning of THORP and Magnox infrastructure.

2.13. Paks Nuclear Power Plant

A significant fraction of the room temperature adsorption studies available within the literature have examined the accumulation of radionuclides from model boric acid solutions on stainless steel and zirconium (Zr) surfaces. This research was motivated by the challenges arising after damaged fuel assemblies at Paks Nuclear Power Plant (NPP) released fission material into the primary cooling circuit of a pressurised water reactor. A comprehensive investigation was subsequently undertaken to characterise the extent and kinetics of radionuclide accumulation from the boric acid coolant onto the inner surfaces of structural materials (Kádár, 2009). A noteworthy result from these studies was for all radionuclides investigated, an equilibrium sorption capacity was reached within one day of initial contact with the metallic surfaces. This observation is reasonably consistent with a previous pH dependence kinetic study that reported equilibrium within ten days of immersion in nitric acid and sodium hydroxide solutions (Adeleye et al., 1995).
The inconsistent surface concentrations of the investigated metal ions as documented on AISI Type 321 stainless steel were principally ascribed to chemical speciation effects (Kádár et al., 2011). Two broad classifications of sorbing species were identified: cationic species (e.g. Cs\(^+\) and PuO\(_2\)\(^+\)) that are repelled from the similarly charged surface, and colloidal/disperse material (e.g. Cerium (Ce) and Curium (Cm)) that are insensitive to electrostatic effects. As expected, the deposition of colloidal and disperse material was more prevalent than for the corresponding cationic species. Owing to its diverse solution chemistry, the appropriate assignment of U is influenced by solution composition. In good agreement with the aforementioned study, a pH dependence sorption study reported maximum U surface coverage at pH 6, corresponding to colloidal UO\(_2\)(OH)\(_2\) precipitation (Dombovári et al., 2007). An alteration in solution pH was observed to reduce U surface concentration as hydrolysis yielded anionic complexes that were repelled from the surface. Furthermore, complimentary Fe, Cr, and U solution profiles prompted the authors to consider contamination as a co-precipitation mechanism involving corrosion species. In contrast, the incorporation of \(^{110m}\)Ag, into the steel passive layer from boric acid was shown by in situ solution analysis to involve the simultaneous release of Fe and Cr (Hirschberg et al., 1999) (Figure 2.8).

![Figure 2.8. Proposed mechanism for accumulation of \(^{110m}\)Ag onto AISI Type 321 stainless steel from boric acid solution (Adapted from Hirschberg et al., 2001).](image-url)

The importance of corrosion processes in the contamination process was further highlighted in the aforementioned Paks NPP investigation during the comparison of the contamination behaviour of 304 and 321 stainless steel (Kádár et al., 2011). Despite identical solution chemistry of the accumulating radionuclides, inconsistent sorption affinities were exhibited between the two steel materials. The markedly different surface elemental composition of the two passive layers, as determined by electron microscopy,
was postulated to have a contributing effect on the strength of the surface-sorbate interaction. A similar importance was attached to surface roughness in a study comparing the sorption properties of Zr and stainless steel structural materials (Répánszki et al., 2007). However, no concerted attempt was made in either of these studies to explain the effect of surface parameters for the sorption of certain radionuclides relative to others.

These collective findings clearly highlight an important contribution of metallurgical factors, and in particular corrosion processes, towards radionuclide contamination phenomena. The participation of corrosion processes in the initiation and propagation of Cs fuel cladding contamination is particularly noteworthy. Based on these results, it is imperative to characterise chemical and metallurgical factors that may influence corrosion behaviour for a comprehensive understanding of the contamination of structural materials. Nevertheless, a detailed study correlating steel metallurgy and its derived sorbent properties has not been reported yet.

2.14. Corrosion Behaviour in HNO₃

The concentration of the nitric acid media handled at the Magnox and THORP facilities typically promote the formation of the protective Cr(III) oxide layer and accordingly the austenitic stainless steels structural materials remain in a passive state. However, certain solution conditions may destabilise the passive layer and induce a shift of the corrosion potential towards the transpassive domain, where IGC and other forms of degradation are initiated. The identification of the electroactive species and the associated HNO₃ redox pathways is therefore essential to understand and subsequently control the corrosion processes of stainless steel that can lead to material failure. The absence of an exact mechanistic solution within the literature however is attributed to the large number of plausible HNO₃ reduction products that are available. Further complications arise from an apparent dependence of the initial nitric acid concentration on the dominant reduction mechanism. As a result, conclusions from independent corrosion studies often appear contradictory and irreconcilable with one another. Nevertheless, there is general consensus that the HNO₃ reduction process is autocatalytic, initiated by the generation of NO⁺:

$$HNO_3 + 2H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$$

(Equation 2.11)

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O$$

(Equation 2.12)
The fate of NO\textsuperscript{+} to close the catalytic cycle is not clear and has been the focal point for intense debate. Currently two competing mechanistic schemes exist as originally described by Vetter and Schmid, respectively (Vetter, 1959; Schmid, 1959). Vetter considered the autocatalytic mechanism to proceed by a series of surface bound intermediates that regenerate NO\textsubscript{2}, the electroactive species, as follows:

\[
(HNO_2)_{ads} + H^+ \rightleftharpoons (NO^+)_{ads} + H_2O
\]  
(Equation 2.13)

\[
(NO_3^-)_{ads} + (NO^+)_{ads} \rightleftharpoons (N_2O_4)_{ads}
\]  
(Equation 2.14)

\[
(N_2O_4)_{ads} \rightleftharpoons 2(NO_2)_{ads}
\]  
(Equation 2.15)

\[
(NO_2)_{ads} + e^- \rightleftharpoons (NO_2^-)_{ads}
\]  
(Equation 2.16)

\[
(NO_2^-)_{ads} + H^+ \rightleftharpoons (HNO_2)_{ads}
\]  
(Equation 2.17)

where the subscript “ads” corresponds to a surface adsorbate at the electrode surface.

Vetter’s mechanism was later shown to be inaccurate when researchers observed a concentration dependence of NO, and not NO\textsubscript{2}\textsuperscript{-} (Balbaud et al., 2000A) on the stainless steel corrosion rate. A more recent interpretation of Vetter’s concepts adequately accounts for this by describing three elementary reactions involving the reaction and regeneration of HNO\textsubscript{2}, the precursor to NO (Balbaud et al., 2000A; Fauvet et al., 2008):

\[
(HNO_2)_{ads} + H^+ + e^- + s \rightleftharpoons (NO)_{ads} + H_2O
\]  
(Equation 2.18)

\[
HNO_3 + (NO)_{ads} \rightleftharpoons HNO_2 + (NO_2)_{ads}
\]  
(Equation 2.19)
\[ HNO_3 + (HNO_2)_{ads} + 2s \rightleftharpoons 2(NO_2)_{ads} + H_2O \]

(Equation 2.20)

where \( s \) is an available site on the surface electrode.

For less concentrated acid systems (< 8 M), the progression of Equation 2.19 is sufficiently slow as to allow for a significant build-up of NO adsorbates at the steel surface. In this instance, the authors proposed an alternative reaction route:

\[ HNO_3 + 2(NO)_{ads} \rightleftharpoons 3(HNO_2)_{ads} + H_2O + 2s \]

(Equation 2.21)

Thus the fate of \((NO)_{ads}\) and its apparent reaction lifetime dictates the dominant \(HNO_2\) regeneration pathway. This is best illustrated by a comparison of the \((NO)_{ads}\) : \(HNO_3\) stoichiometric ratios of the two proposed reaction schemes; the rapid consumption of NO in highly acidic systems permits only a 1:1 reaction (Equation 2.19). In comparison, under less acidic conditions a 2:1 stoichiometric reaction now dominates (Equation 2.21) owing to an increased NO longevity.

In contrast, Schmid describes the autocatalytic \(HNO_3\) reduction process as an entirely solution phase phenomenon based on the reaction of NO with \(HNO_3\) to close the catalytic cycle as opposed to Equation 2.12:

\[ (NO)_{ads} \rightleftharpoons NO \]

(Equation 2.22)

\[ 2NO + HNO_3 + H_2O \rightleftharpoons 3HNO_2 \]

(Equation 2.23)

A similar heterogeneous mechanism was later suggested by Lange with the distinction that NO is quenched by \(NO_2\), rather than \(HNO_3\) (Lange et al., 2013):

\[ HNO_2 + HNO_3 \rightleftharpoons N_2O_4 + H_2O \]

(Equation 2.24)

\[ N_2O_4 \rightleftharpoons 2NO_2 \]

(Equation 2.25)
\[ NO_2 + NO + H_2O \rightleftharpoons 2HNO_2 \]

(Equation 2.26)

In contrast to the Fauvet and Balbaud homogeneous mechanism, no special importance is attached to the initial acid concentration in these proposed solution based processes. The decreasing thermodynamic stability of the NO\(_2\) reduction product in more dilute acid systems however would suggest that this assumption is not reasonable (Fauvet et al., 2008; Balbaud et al., 2000B). Furthermore, under less acidic conditions, Equation 2.23 may proceed at an insufficiently fast rate as to close the cycle in tandem with Equation 2.12. Therefore, on thermodynamic and kinetic principles, Schmid’s reaction mechanism is unlikely to be correct at low acid concentrations.

In an attempt to clarify these uncertainties, the corrosion behaviour of 316L stainless steel as a function of HNO\(_3\) concentration was investigated by polarisation and EQCM studies (Woodhouse et al., 2013). Abrupt changes in electrochemical behaviour in combination with the emergence of an apparent reduction current dependency on solution stirring rate were observed in 20 % HNO\(_3\) (~ 4.6 M). Below this acid concentration the current density was found to be independent of solution stirring, as demonstrated by rotating disk experiments. This inconsistent behaviour was interpreted as a transition from a predominately solution-phase (Schmid) to a surface orientated (Fauvet and Balbaud) mechanism as the chemical behaviour of surface adsorbates would be expected to be insensitive towards electrode rotation speed. Also discussed by the authors, this conclusion is in agreement with previous studies that highlighted the imperfections of the heterogeneous mechanism under less acidic conditions.

2.15. Transpassive Conditions

An important limitation of these proposed HNO\(_3\) reduction mechanisms is that they do not adequately describe stainless steel corrosion behaviour in highly concentrated acid systems (i.e. > 10 M HNO\(_3\)). As the acid concentration exceeds this value, additional redox processes must be considered as the corrosion potential shifts from a passive to a transpassive domain (Wijesinghe et al., 2006). Transpassive conditions are typically characterised by pronounced intergranular attack, afforded by the partial dissolution of the passive layer:

\[ Cr_2O_3 + 4H_2O \rightleftharpoons Cr_2O_7^{2-} + 8H^+ + 6e^- \]

(Equation 2.27)
The reprocessing operation within the Magnox and THORP reprocessing plant initially involves the dissolution of irradiated fuel in concentrated nitric acid (~ 12 M HNO₃) (Wilson, 1996). Although these acidic molarities are normally considered within safe operational limits of austenitic stainless steels (Fauvet et al., 2008), under suboptimal processing conditions Cr dissolution may nevertheless still occur. The corrosion resistance of stainless steels is known to greatly diminish in poorly renewed or confined nitric acid solution (Schosger et al., 1996). Here, the accelerated rate of aqueous Fe(III) and Cr(VI) production elevates the cathodic component of the HNO₃ reduction current-potential curve to transpassive potentials (Weast, 1988-1989; Ningshen et al., 2011). Furthermore, analogous redox processes have also been invoked to rationalise the detrimental effects of electroactive fission products such as neptunium (Np) (Motooka et al., 2003) and Ce (Bague et al., 2009) on stainless steel corrosion performance. The proposed Np(VI) catalytic reduction cycle is remarkably similar to the autocatalytic HNO₃ reduction cycle as described by Fauvet and Balbaud (Figure 2.9 A and B). Due to the catalytic nature of the HNO₃ reduction process, small concentrations (< 10 mM) of the aforementioned external redox couples were found to be sufficiently polarising to induce the development of transpassive corrosion (Figure 2.9 C and D):
Figure 2.9. Proposed HNO₃ reduction processes involving 304L stainless steel for (A) Np catalysed reaction in 9 M HNO₃ (Adapted from Motooka et al., 2003), and (B) HNO₃ autocatalytic mechanism > 8 M HNO₃ (Adapted from Fauvet et al., 2008). SEM images of 304L stainless steel after exposure to (C) 9 M HNO₃ + 3.8 mM ²³⁷Np (Adapted from Motooka et al., 2003) and (D) 8 M HNO₃ + 7.14 mM Ce(IV) (Adapted from Bague et al., 2009).

For nitric acid condensates, the ratio of the exposed steel area to the liquid volume is several orders of magnitude higher than the corresponding bulk liquid volume (Balbaud et al., 2000A). This property allows the increasing corrosion product concentration to occur at a comparable rate to stagnant solution conditions and thus leads to similar corrosion behaviour of stainless steels in the condensate phase. In recognition of these results, the reprocessing streams at nuclear facilities are frequently renewed in order to suppress the accumulation of corrosion products in a stagnant solution medium. The possibility of condensate formation during the dissolution of the fuel cladding cannot be eliminated however, and the consequences of this must be carefully considered during the assessment of contamination phenomena.

2.16. Cold Rolling

The specification of austenitic stainless steel construction material for nuclear plant facilities typically involves the inclusion of a small amount of residual cold work (20-30 %) in order to improve the final material’s strength (Elayaperumal et al., 1972). The
strain hardening of austenitic stainless steels by cold rolling is well known to be related to
the partial transformation of $\gamma$-austenite to body centred tetragonal (bct) $\alpha'$-martensite
(Hadji et al., 2002), although there remain uncertainties surrounding the mechanisms of
deformation. This is because the predominant mode of strain response is highly sensitive to
the austenite stacking fault energy (SFE), a parameter that governs how facile cross slip is
during deformation. The exact SFE value is dependent on alloying composition and
deformation temperature (Chowdhury et al., 2005) and is therefore characteristic to an
individual system. For low to moderate SFE materials, such as austenitic stainless steels,
deformation twins and shear band intersections generally dominate deformation behaviour
(Choi et al., 1997; Kumar et al., 2004). In some instances however, hexagonal closed pack
(hcp) $\varepsilon$-martensite formation has also been reported as a possible deformation pathway of
304 stainless steel during ($\gamma \rightarrow \alpha'$) transformation (Hadji et al., 2002).

The widespread use of austenitic stainless steel components for the transport and storage of
corrosive liquors, at nuclear sites for example (Shaw, 1990; Wilson, 1996), has prompted
researchers to better understand the influence of strain induced microstructural
transformations on general corrosion performance. It has been shown that martensite
selectively corrodes at lower potentials and thus becomes a potential source of weakness
for cold worked steels in both acidic (Hahin et al., 1976; Alvarez et al., 2013) and alkaline
media (Semino et al., 1979). In addition, atomic force microscopy (AFM) analysis has
revealed cold deformation may induce undesirable changes in the chemical structure and
composition of the surface oxide layer that compromises passivity integrity (Barbucci et
al., 2002; Souier et al., 2012). These findings has been supplemented by Mott-Schottky
experiments that have demonstrated cold rolling produces a highly defective passive layer
(Jinlong et al., 2015), possibly due to an increasing dislocation concentration that catalyses
oxygen vacancy formation (Yamamoto et al., 2010). It is important to note that beneficial
effects of mechanical deformation on corrosion properties of austenitic stainless steels
have also previously been reported (Navai et al., 1999; Haanappel et al., 2001). These
results have since been attributed to an increased long range Cr migration rate augmented
by cold working. Although an exact mechanism has not been clarified, several
microstructural factors have been linked to the enhancement of Cr diffusivity. This
includes mechanical stresses (Vignal et al., 2010), $\alpha'$-martensite (Kain et al., 2004) passive
layer vacancies (Singh et al., 2003), crystallographic texture (Kumar et al., 2005B), and
grain boundary network length (Chui et al., 2011).
The lack of a clear understanding of the effect of cold deformation on corrosion performance highlights the complex stress-strain response of stainless steels. This in turn has made it difficult to accurately assess the significance of an individual microstructural variable, where it is probable that multiple factors are simultaneously influencing corrosion behaviour. It is therefore not surprising that under different environments investigated non-monotonous variation of corrosion behaviour with thickness reduction has been observed. Examination of the literature reveals the transition from an overall negative to a positive influence of cold deformation on corrosion resistance generally occurs at ~ 60% thickness reduction (Phadnis et al., 2003; Singh et al., 2003; Kumar et al., 2004; Peguet et al., 2007; Jinlong et al., 2015). An improved corrosion resistance recorded > 60% thickness reduction suggests at high deformation levels an increased Cr mobility is the most significant factor controlling corrosion behaviour. On the other hand, the introduction of deleterious lattice defects into the microstructure, such as martensite and dislocations, likely dominate corrosion resistance at low to moderate thickness reductions. It has been reported for example that the crystallographic evolution of high density closed packed planes in 304L stainless steel is not particularly pronounced after low deformation treatments (< 60%) (Kumar et al., 2005B; Kumar et al., 2007). As a result the authors concluded that the positive effects of texture on corrosion behaviour do not fully compensate for the adverse effects of residual stresses after the application of small levels of strain.

2.17. Laser-Induced Breakdown Spectroscopy (LIBS) Analysis of Nuclear Materials

The chemical processes that govern contamination in many cases are poorly understood and this has subsequently restricted the development of safe and cost effective decontamination and prevention methods. The optimisation of novel decontamination solutions logically demands that treatments are tailored to the individual radionuclides of concern. Therefore, the rapid and quantitative analysis of contaminating elements on steel materials is a necessary step in the realisation of successful decommissioning strategy. Laser-Induced Breakdown Spectroscopy (LIBS) is a promising candidate technique to meet these requirements, as demonstrated by the numerous investigations that have utilised in situ measurements for the quantification of radioactive impurities in surrogate materials (Wachter et al., 1987; Kim et al., 2002; Sakar et al., 2008; Barefield II et al., 2013; Williams et al., 2016; Sengupta et al., 2017). LIBS is an atomic emission spectroscopic technique that employs a highly energetic laser pulse as the excitation source (Cremers et al., 2013). The focused laser pulse ablates a small volume of sample material, generating a
plasma of ionised matter at temperatures of up to 10,000 K (Hussain et al., 2016) at the sample surface. As the expanding plasma rapidly cools the resulting light emissions are characteristic of the chemical composition of the plasma plume. Therefore, analysis of the plasma’s radiation emissions permits a real time, multi-elemental quantitative determination of the sample material (Noll, 2012).

An important feature of LIBS is that unlike many commercially available spectroscopic techniques, no rigorous sample preparation is required for characterisation. Consequently, elemental analysis of materials in the solid (Lasheras et al., 2011), liquid (Al-Adel et al., 2013), and gaseous state (Sturm et al., 2003) have previously been demonstrated to a reasonable detection limit. The broad range of industrial applications of LIBS may be attributed in part to the technique’s requirement of only optical access to the target material, where as a result, sample condition is not critical. On this principle it is possible to conduct measurements at large working distances, where potential LIBS applications for the remote analysis of hazardous materials have been tested. This includes the analysis of trace elements in explosive residues (Gaona et al., 2014A), biological weapons (Gottfried et al., 2008), and high radiation environments (Davis et al., 1995; Martin et al., 2012; Gaona et al., 2014B).

The capabilities of LIBS for the characterisation of nuclear plant steel as the surrogate matrix is not well researched. In the few published results available, investigations have been limited to the quantitative determination of chemical impurities such as chloride (Xiao et al., 2017) and copper (Cu) (Whitehouse et al., 2001), and the detection of trace level radionuclides has not been documented. In comparison, the application of LIBS for the quantification of major alloying elements in steel materials has been studied extensively due to the industrial importance of rapid classification and quality assurance (Lopez-Moreno et al., 2007; Zaytsev et al., 2014; Kashiwakura et al., 2015; Lorenzetti et al., 2015; Karki et al., 2016; Meinhardt et al., 2016). The small number of trace analyte studies is related to the difficulties arising from discrimination of the spectral features of interest with the more pronounced emission lines of the alloying elements. Therein lies a fundamental disadvantage of the LIBS technique for the analysis of complex mixtures; the identification capability of a material is strongly dependent on its bulk elemental composition (Gaona et al., 2014B). This is because a fraction of the underlying supporting matrix is inevitably ablated together with the analyte of interest and thus contributes to the measured LIBS emission. Accordingly, the resulting emission spectra of stainless steels are
typically convoluted where the high probability of spectral interference may yield unsatisfactory results.

Nevertheless the correctness of this assumption is specific to the elements of interest and their signature emission wavelengths. Therefore the absence of LIBS investigations of contaminated steel materials presents an interesting avenue of research to pursue. The possibility of obtaining depth resolved information by multi-pulse ablation (Cabalín et al., 2011; Lefebvre et al., 2016; Cerrato et al., 2017; Syvilay et al., 2017) is an additional motivation for further investigation. Knowledge of the depth distribution of radionuclides within the steel matrix would assist in the clarification of appropriate decommissioning strategy as a number of promising decontamination treatments for removing surface bound contaminants are already available (Rufus et al., 2004; Samuleev et al., 2013; Castellani et al., 2014).

2.18. Thesis Aims and Hypotheses

The overarching aim of this research is to develop a mechanistic understanding of Sr and Cs uptake mechanisms onto 304 stainless steel under conditions representative of alkaline spent fuel ponds (i.e. relevant to pond furniture) and HNO₃ reprocessing streams (representative of Magnox and THORP steel plant). Therein, the depth, distribution, and speciation of Cs and Sr contamination will be probed as well as corrosion processes for the steel in the solution matrices. Further, a sub-aim is to develop the use of LIBS spectroscopy for Sr and Cs detection on steel surfaces as this technique could be used to assess Sr and Cs contamination of steel materials at nuclear sites, or during their decontamination.

The hypotheses tested in this thesis are:

- Laser-Induced Breakdown Spectroscopy (LIBS) can be utilised for the accurate identification and depth characterisation of Sr and Cs incorporated into the stainless steel matrix.

- The stainless steel passive layer possess analogous sorbent properties to hydrous metal oxides, where the extent of Sr and Cs contamination will be higher from the alkaline storage ponds than the nitric acid reprocessing streams.
• Sr and Cs contamination of 304 stainless steel is an exclusively surface based phenomenon in which fission products do not diffuse into the bulk material for all solution chemistries studied.

• The effect of cold rolling treatment on metallurgical variables will universally reduce the steel’s affinity for Sr and Cs contamination under identical solution conditions.
2.19. References


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3. Materials and Methods

In this thesis, a series of experimental techniques have been employed to characterise Sr and Cs contamination processes involving 304 stainless steel. The methods are briefly discussed in each research chapter (Chapters 4-6), as they are reproductions of self-contained manuscripts submitted for publication in Scientific Journals. However, in this chapter the theoretical basis of each technique is discussed more fully.

3.1. Base Material

In this work, model laboratory contamination systems were established to simulate the documented conditions of spent nuclear fuel storage and reprocessing of UK spent nuclear fuel. All experiments used austenitic type 304 stainless steel as the base material. The chemical composition of this material is given in Table 3.1, and was considered to be as representative as possible of the structural materials used throughout the Sellafield site (Shaw, 1990).

Table 3.1. Chemical Composition (wt. %) of AISI Type 304 Stainless steel used throughout this thesis

<table>
<thead>
<tr>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.15</td>
<td>8.6</td>
<td>0.055</td>
<td>1.38</td>
<td>0.45</td>
<td>0.04</td>
<td>0.005</td>
<td>0.038</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

For microstructural characterisation and contamination studies, individual steel coupons were cut from a base material with a Brilliant 250H cutting machine using a silicon carbide (SiC) grinding wheel rotating at 3000 rpm. Individual coupons of dimensions 10 mm x 10 mm x 13 mm (l x w x t) were cut for use in experiments described in Chapters 4-6. In addition, strips of dimensions 100 mm x 20 mm x 13 mm (l x w x t) were also cut and then uni-directionally cold rolled at room temperature under the lubrication of machine oil. After several rolling steps, the final thickness was 9.1 mm i.e. a reduction of 30 %. The strain hardened material was then cut into individual coupons of dimensions of 10 mm x 10 mm x 9.1 mm (l x w x t) to use in experiments discussed in Chapter 6.

All coupons were mechanically ground on a single 1 cm² face using SiC emery paper rotating at a constant speed of 200 rpm on EXTEC ® Labpol Duo 8-12 Convertible Twin Grinding Polishing & Machine, with water as the lubricant. Here, individual surfaces were sequentially contacted with 320, 600, 1200, 2400, and 4000 emery paper to remove surface
deformation, which has been shown to have a marked influence on the radionuclide retention properties of stainless steel materials (Kádár et al., 2011). Residual scratches from the grinding treatment were removed thereafter by polishing with 3 µm and then 1 µm diamond paste on a velvet cloth lubricated with ethanol rotating at 200 rpm. To prepare samples for electron backscatter diffraction measurements (Section 3.11), an additional polishing stage was included to generate a highly flat surface necessary to maximise data quality. This consisted of polishing with a 0.25 µm diamond paste first, and then with colloidal silica in an identical procedure as outlined earlier. Colloidal silica is a polishing solution consisting of silicon dioxide in an alkaline suspension that is frequently used to prepare surfaces to a 100 nm mirror finish (Petzow, 1999). In all instances, the polished surfaces were degreased with ethanol and distilled water prior to further use.

3.2. Contamination Experiments

Strontium and Cs contamination of as received and 30% cold rolled 304 stainless steel was achieved using 40 mL sorption experiments performed in triplicate. 3, 6 and 12 M HNO₃ solution matrices were selected to simulate the composition of the UK reprocessing streams (IAEA, 2006). Contamination from 1mM NaOH was also carried out to investigate contamination phenomena involving pond furniture at the Sellafield site (IAEA, 2006). Stock solutions were prepared using chemicals diluted with Milli-Q 18.2 MΩ deionised water to the required concentrations. For all experiments, Sr(NO₃)₂ and CsNO₃ salts were dissolved to give an initial solution concentration of both contaminants of 500 mg L⁻¹. Stable isotopes were used throughout to increase the number of analytical techniques available for surface characterisation afterwards. All chemicals used in the preparation of laboratory contamination experiments were Aristar grade.

40 mL aliquots of the prepared solutions were transferred to a 60 mL polypropylene centrifuge tube. Individual steel coupons were then carefully inserted so that only the polished surface was in contact with the Sr and Cs bearing liquors. The tubes were tightly sealed and the systems were heated at 60 °C (Figure 3.1) for a minimum of 30 days to allow for contamination to occur. In order to monitor the progression of Sr and Cs sorption, solution aliquots were removed at fixed intervals and prepared for elemental analysis by inductively coupled plasma spectrometry (ICP-MS; Section 3.3). After the designated period of reaction had elapsed, steel samples were removed from solution and washed with deionised H₂O and isopropyl alcohol (IPA) prior to surface characterisation.
3.3. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is a useful analytical technique for trace metal analysis of liquid samples. The sample is transferred into a nebulizer by a peristaltic pump where it is converted into a fine aerosol before being delivered to the plasma torch. Here, sample droplets are sprayed onto a high temperature (6,000-8,000 K) plasma generated by the ionisation of argon (Ar) gas in a strong electromagnetic field (Hill, 2006). Analyte molecules are ionised in the plasma and are then transferred to a high vacuum quadrupole mass spectrometer for detection. The quadrupole mass spectrometer is a scanning mass analyser comprised of four parallel rods that exploits the inconsistent stabilities of ion trajectories in an oscillating electric field to separates ions based on their mass to charge (m/z) ratio (Taylor, 2001). The electric field strength is selected so that ions with the desired m/z ratio are permitted to pass through the spectrometer whilst simultaneously filtering out interfering ions and non-analyte species. As atoms of different elements have different masses, knowledge of m/z may be converted into elemental identification. A collision cell is placed in the ion beam path in order to obstruct photon emissions from the plasma discharge to minimise background interferences, thus improving mass resolution.

In this thesis, samples were prepared by centrifugation (13,150 g) for 45 minutes to remove suspended matter, and then diluted into 2 % nitric acid to an acceptable concentration (1-100 ppb) for ICP-MS analysis. Elemental analysis was performed using an Agilent 7500cx ICP-MS coupled to a MicroMist nebuliser to determine the solution concentration of Sr and Cs in experiments studying sorption of fission products onto stainless steel surfaces. Furthermore, the solution concentrations of the major alloying elements (Fe, Cr, Ni) were also measured at the same time intervals to evaluate the steel corrosion behaviour in the various solution chemistries investigated.
3.4. Laser-Induced Breakdown Spectroscopy (LIBS)

Laser Induced Breakdown Spectroscopy (LIBS) is a type of atomic emission spectroscopy (AES) that utilizes a highly energetic laser pulse as the excitation source (Cremers et al., 2006). The output laser pulse ejects a small volume of sample material in both thermal and non-thermal processes (i.e. ablation), simultaneously generating a micro-plasma at the sample surface. Within this plasma, the ablated material is promoted to a higher electronic energy level. As the plasma rapidly cools and expands, excited atomic, ionic, and molecular species return to the ground state by the emission of photons of characteristic to the elemental composition of the plasma plume. Separation and spectral analysis of the plasma emissions using an appropriate spectrograph allows for rapid, multi-elemental analysis of the sample material (Noll, 2012). Because LIBS is fundamentally an optical technique, the physical condition of the sample is largely unimportant in terms of data quality. Quantitative elemental analysis of materials in the solid, liquid, and gaseous state can be achieved often to parts per million (ppm) sensitivity (Musazzi et al., 2014). This unique feature of LIBS also introduces the possibility to perform in situ measurements remotely. This has the advantage over conventional AES techniques which require physical contact with the sample as LIBS stand-off measurements can readily be performed under conditions not suitable for direct human exposure (Davis et al., 1995; Gaona et al., 2014).

In this work, a Q-switched 1064 nm Nd:YAG pulsed laser system (10 Hz, 3-6 ns beam width) operating at an output energy of 50 or 100 mJ pulse⁻¹ was used as the excitation source. Initially, identifiable Sr and Cs emission lines within the LIBS spectra of contaminated 304 stainless steel were established. This was deemed necessary as a fraction of the supporting matrix is inevitably ablated with the analytes of interest and therefore the spectral features of the more abundant elements in the plasma plume (Gaona et al., 2014). Experiments were thereafter performed to evaluate the capabilities of LIBS instruments to perform depth resolved characterisation of contaminated stainless steel materials. This involved delivering multiple laser pulses over a single point on the sample surface to monitoring the variation in Sr and Cs signal intensity as a function of pulse number.

3.5. Glow Discharge Optical Emission Spectrometry (GD-OES)

Elemental depth profile analysis of contaminated steel samples was conducted with GD-OES using a GD-Profiler 2 (Horiba Jobin Yvon) in order to identify the depth distribution of contamination within the steel matrix. GD-OES is a depth profiling technique that
involves the uniform sputtering of a solid sample. The elemental composition of ejected material is then analysed by optical emission spectroscopy (OES), utilising an Ar glow discharge as the excitation source. Sputtering in this context is the liberation of atoms, molecules, and ions from a sample material as a result of particle bombardment. The advantages of the GD-OES technique are the ability to generate elemental depth profiles at a high depth resolution and within a short (several minutes) measurement time. This is possible for ultrathin films (< 10 nm) (Shimizu et al., 2003), interfaces (Vadillo et al., 1998), and µm-thick layers (Anfone et al., 2001). The majority of the elements in the periodic table can easily be analysed to a ppm detection limit, including light elements such as hydrogen which are inaccessible to certain spectroscopic methods (Payling et al., 1997). The first modern direct current glow discharge instrument was constructed by Grimm for the analysis of conductive materials (Grimm, 1967) although radiofrequency (r.f) glow discharge sources have since become more popular. The principle reason behind this is that r.f GD-OES instruments can sputter and analyse non-conductive and conductive samples (Nelis, et al., 2007).

Regardless, the basic principles behind modern GD-OES spectrometers are fundamentally identical as for the Grimm model. Here, the sample is pressed against a silicone O-ring so that only a single surface is exposed to the GD plasma contained in the anode tube. The cathodic sputtering of the surface by low energy Ar$^+$ ions (< 50 eV) produces sample fragments that diffuse into the plasma discharge. In a similar process as described for the LIBS technique (Section 3.4), excitation and subsequent recombination events results in signature radiation emissions that can be utilised for multi-element determination as a function of sputtering time.

3.6. Time-of-Flight Mass Spectrometry (TOF-SIMS)

A TOF-SIMS instrument (IONTOF GmbH, Germany) was used to determine the elemental spatial distribution of the sample surface. The basic principle of this technique is the bombardment of a solid by an energetic primary ion beam to induce emission of secondary ions that are detected by a mass spectrometer. As only the uppermost layers participate in this process, TOF-SIMS is primarily considered a surface sensitive, quasi non-destructive technique (Fearn, 2015). The liberated ions that constitute a fraction of the ejected material are separated using an external electrical field and their chemical identities are analysed in a mass spectrometer by their m/z ratio. That is, TOF-SIMS utilises the same fundamental concepts as previously outlined in ICP-MS (Section 3.3) for ion detection. An important difference however, is that for TOF-SIMS ions are analysed in a time of flight analyser.
This is so that high resolution full mass range spectra of complex matrices can be acquired within a satisfactory time period. The time of flight mass spectrometer operates on the principle that ions with a distribution of masses travel at different velocities towards a detector if their kinetic energies are identical. During a TOF-SIMS measurement, sputtered ions are accelerated to a common kinetic energy by a homogeneous applied electrostatic field before entering a field free drift region, known as the flight tube, in order to pass to the detector. The time taken to traverse the field free drift region is given as:

\[ t = l \times \sqrt{\frac{m}{2 \times KE}} \]

(Equation 3.1)

where \( t \) is time taken to travel from the ion source to the detector, \( l \) is length of flight tube, \( m \) is the ion's mass, \( KE \) is the ion's kinetic energy.

By raster scanning the primary ion beam over the sample surface it is possible to construct a \( \mu \text{m} \)-scale chemical map of the sample. Furthermore, TOF-SIMS can also provide depth characterisation information by monitoring the signal intensity of a given mass signal as a function of sputtering time. In this work, depth analysis was performed using two pulsed ion beams that work in tandem with one another. Here, the first ion beam sputters a crater, whereas the second beam systematically analyses the crater bottom. The reason behind this approach is to ensure a uniform etching rate by avoiding elemental analysis of the crater wall (Vickerman et al., 2013). The principle advantage of this method over the GD-OES techniques is an increased sensitivity (Suzuki et al., 2005), where analytes present in sub-ppm concentrations can be detected. This was considered important as the detection limits of GD-OES was considered unsatisfactory to reliably measure Cs deposited onto the steel surface.

3.7. X-ray Photoelectron Spectroscopy (XPS)

XPS can provide detailed information about the surface chemistry of a material by analysing the kinetic energy distribution of emitted photoelectrons when the sample is irradiated with soft X-rays under vacuum. The low inelastic mean free path of ejected electrons determines that XPS is primarily a surface sensitive technique that is not well suited for bulk analysis. The photoelectron kinetic energy is related to the incident X-ray photon energy by Einstein’s photoelectric equation:
\[ h\nu = E_K + E_B + \phi_{\text{spec}} \]

(Equation 3.2)

where \(h\nu\) is the photon energy, \(E_K\) is the photoelectron kinetic energy, \(E_B\) is the electron binding energy measured relative to the Fermi level, and \(\phi_{\text{spec}}\) is the spectrometer work function.

The spectrometer work function is an instrumental correction factor that accounts for the energy required to transfer a liberated electron from the specimen surface to the spectrometer detector under vacuum and is assumed to be a constant for a given experiment. Because monochromatic X-rays such as Al K\(\alpha\) (1486.7 eV) and Mg K\(\alpha\) (1253.6 eV) are used, experimentally measured photoelectron kinetic energies can therefore be directly correlated to the binding energies of once bound electrons.

Quantisation of an atom’s electronic energy levels means that electron binding energies are characteristic to that element, although a small dependency (0.1-10 eV) on the local chemical bonding environment exists (Briggs, 1977). This is because a more oxidising coordination sphere reduces the charge density surrounding the parent atom, and as a result increases the Coulombic attraction between the positively charged nucleus and a bound electron. This effect is reflected by the increasing binding energy values recorded for more electronegative systems. The capabilities of XPS to provide direct information about the chemical state of an element was used in this work to determine the local chemical bonding environments of fission product contaminants incorporated into the steel matrix.

XPS measurements were also conducted to identify the chemical composition of the steel oxide layer after passivation in the various contaminating matrices. High resolution scans were performed using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical) which employed a monochromatic Al X-ray source (1486.69 eV). In order to account for specimen charging that occurs during XPS analysis, the binding energy scale was corrected by normalisation to the ubiquitous hydrocarbon C 1s peak at 284.6 eV.

3.8. X-Ray Diffraction (XRD)

X-ray diffraction is a non-destructive analytical technique that can be used for phase identification of crystalline samples. When X-rays interact with a crystalline material, they are reflected at the same angle upon which they strike the atomic planes. Two scattered X-rays undergoing interference will combine constructively when the path difference is equal to an integer multiple of the wavelength (Figure 3.2). This phenomenon is summarised by
Bragg’s law (Equation 3.3), which utilises trigonometric principles to correlate the interlayer spacing of atoms in the crystal structure to the incident striking angle:

\[ n\lambda = 2d \sin \theta \]

(Equation 3.3)

where \( n \) is the diffraction order, \( \lambda \) is incident X-ray wavelength, \( d \) is the spacing between diffracting planes and \( \theta \) is the diffraction angle. The path difference between two scattered X-rays undergoing interference is given as \( 2dsin\theta \).

**Figure 3.2.** Diffraction of X-rays by crystalline atomic planes (Adapted from West, 2014).

In a typical XRD measurement, a sample is rotated at a constant angular velocity whilst being irradiated with a monochromatic source of X-rays (Suryanarayana, 2013). As the sample slowly rotates, constructive interference of scattered waves will occur at specific scanning angles that satisfy the Bragg equation. In these instances, a so called ‘Bragg reflection’ will be recorded by the detector that converts a photon signal into an electrical output. Importantly, scattering from a single crystal phase occurs independently of other phases present in the sample. That is, illumination of a complex mixture will produce an overall diffraction pattern that is the summation of all the contributions from each individual phase present (West, 2014). Furthermore, the integrated peak intensities are proportional to the amount of X-ray scattering contributing to that reflection. Thus, XRD can be used to perform quantitative analysis of crystalline phases present, although in practice this technique is somewhat limited by a detection limit of 5 wt. %. In this thesis, steel samples were mounted on a goniometer of a Philips X’pert XRD and were irradiated with a Cu-K\( \alpha \) (\( \lambda = 1.540598 \) Å) source. Diffraction patterns were collected at \( 35 ^\circ \leq 2\theta \leq 150 ^\circ \) with a step size of 0.03\(^\circ \). A search of the literature afterwards permitted identification of the recorded diffraction peaks of steel samples as either the austenite (fcc) or martensite (bct) iron phases (Cullity, et al., 1978; Bentley, et al. 1986).
3.9. Confocal Laser Scanning Microscopy

Confocal laser scanning microscopy is an optical imaging technique that, in addition to producing higher resolution images than conventional light microscopy, also possesses capabilities for the acquisition of 3D image data (Sheppard et al., 1997). In this thesis, optical sectioning of craters that were generated from LIBS analysis of steel surfaces were analysed with a Keyence VK-X200K 3D laser confocal microscope.

Two dichromatic mirrors are orientated within the confocal microscope to focus the laser beam through a pinhole aperture onto a single point on the material investigated. The resulting fluorescence and emission signals originating from the sample are transferred back into the eye piece of the microscope and are detected by a photomultiplier tube. The placement of a second pinhole aperture in front of the detector eliminates light contributions from above and below the focal plane that would compromise the sharpness and contrast of the final image. The detection of light signals only associated with the focal plane is a characteristic feature of confocal microscopy that allows for the imaging of a thin optical slice of the sample (Sheppard et al., 1997). In comparison, conventional optical microscopy analyses a much larger volume of light at any given instant, including out of focus fluorescence, thus limiting the resolution and sharpness of images obtained by this technique. In a typical confocal measurement the dichromate mirrors are tilted in a raster fashion to systematically analyse light emissions corresponding to different focal planes (Rochow et al., 1994). This procedure therefore generates a series of optical slices that individually correspond to a different depth of the sample. A compilation of these optical images produces a 3D reconstruction of the sample in which the resulting profile contains information about the morphology and depth characteristics of the scanned area.

3.10. Scanning Electron Microscopy (SEM)

SEM is a technique that uses a scanning primary electron beam to produce a high resolution image of the surface topography of a given material. The excellent resolution (nm) of electron microscopy images is due to the much shorter de Broglie wavelength of electrons than visible light (Zhou et al., 2007). In order to investigate the effect of solution composition of the steel surface morphology in this work, SEM was carried out using FEI Quanta 200 (E)SEM and FEI XL30 200 (E)SEM-FEG microscopes.

The microscopes are equipped with a tungsten filament at the top of a column that emits electrons of narrow energy dispersion when a potential difference is applied. These electrons are accelerated to a common velocity and focussed through an aperture into a fine
spot onto the sample surface using a series of electromagnetic lenses. These lenses consist of a Cu wire inside an iron pole piece with a constant current passing through it. When the primary beam interacts with the surface, low energy secondary electrons (SE) are produced at a rate that varies with the surface topography of the sample. The SE signal is the most commonly used signal to construct a high resolution image (Shindo et al., 2002) and this was the selected mode for analysis in this thesis. However, an alternative signal produced is due to the backscattering of the incident electron beam, a phenomenon that is dependent on the atomic number (Z) of the sampling volume. Since electrons are backscattered to a greater extent by heavier nuclei, the presence of such elements in the sample increases the brightness of the image. As a result, it becomes possible to obtain some qualitative elemental information in backscattered mode. The primary electron beam is scanned in a rectangular raster in a series of horizontal lines backwards and forwards. The electron signal intensities generated by interactions between the incident beam and sample surface are recorded by a detector as a function of the scanning beam position and is converted into an image on the screen by the computer.

3.11. Energy Dispersive X-ray (EDX) spectroscopy

In addition to secondary and backscattered electrons, X-rays are also generated by primary electron irradiation during SEM imaging. In this instance, sufficient energy is transferred from the beam to the target material so that a core electron within the sample is promoted to an excited state. An electron from a higher-energy level almost instantaneously fills the newly created vacancy, releasing an X-ray photon in the process (Figure 3.3). The energy of this photon is equivalent to the energy difference between the initial and final electron levels of the transition, thus conserving total energy of the system. The quantisation of an atom’s electron energy levels determine that only X-rays of discrete energies are measured by the detector. Therefore, electron bombardment can promote signature X-ray emissions that can provide quantitative elemental information of a bulk material (Shindo et al., 2002). This is the basic principle underlying EDX. In this project, EDX was performed on a FEI XL30 200 (E)SEM-FEG microscope at an accelerating voltage of 15 kV (Section 3.10) using an EDAX Gemini EDS Spectrometer to determine the chemical composition of steel surfaces after laser ablation. Only analysis of the major elements in steel specimens were examined (Fe, Cr, Ni, O) as EDX typically requires a 0.1 wt. % concentration to yield a detectable line in the resulting X-ray spectrum (Suryanarayana et al., 2013).
3.12. Electron Backscatter Diffraction (EBSD)

EBSD is a technique that used in conjunction with SEM to characterise microstructural properties of inorganic crystalline materials. The EBSD phenomenon was first observed by Kikuchi during the electron irradiation of calcite crystals at an incidence angle of 6° (Kikuchi, 1928). A diffraction pattern consisting of paired black and white lines was seen on photographic plates normal to the primary electron beam. These features were later called Kikuchi bands in recognition of their discoverer. Unique electron backscatter diffraction patterns (EBSP) were recorded during the characterisation of other crystalline materials, demonstrating that the EBSP is intimately related to the lattice parameters of the specific crystal under investigation (Nishikawa, 1928). On this basis, characterisation of the Kikuchi bands formed in an EBSP may be transferred into knowledge of the microstructural characteristics of a given crystalline material.

In this work, EBSD measurements were performed to characterise the microstructure of as received and 30% cold rolled 304 stainless steel. Modern EBSD instruments are inevitably coupled with SEM functionality. EBSD operates by irradiating a highly polished sample with a primary electron beam focussed at an incident angle of 20°. When the beam interacts with the surface, a small amount of energy is transferred to the crystal lattice as low energy loss electrons are backscattered towards the original direction of the electron gun. Analogous to XRD, diffraction patterns form by the constructive and destructive interference of electrons subject to different path lengths as they are scattered by adjacent crystallographic planes. A phosphor screen collects the scattered electrons and converts the
diffraction pattern into an electronic signal that is recorded by a CCD camera. Specialised computer software facilitates data analysis and interpretation by automatically detecting numerous Kukuchi bands using an optimised Hough transform (Stojakovic, 2012). With prior information about the possible candidate phases computed, all possible orientations with each phase are processed by the software in order to identify the best candidate fit. In this instance, the EBSP is reported as indexed when the most probable orientation and phase are determined. By rastering the electron beam over the sample surface, it becomes possible to construct a 3D pattern as multiple points on the sample are scanned by the electron beam. An image of the microstructure can then be constructed by measuring Kukuchi bands as a function of the scanning electron beam position on the sample surface. Such a map contains quantitative information regarding grain boundary character, grain morphology and orientation, and phase composition.
3.13. References


4. Analysis of Contaminated Nuclear Plant Steel by Laser-Induced Breakdown Spectroscopy

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4.1. Abstract

Laser Induced Breakdown Spectroscopy (LIBS) has the potential to allow direct measurement of contaminants on nuclear plant. Here, LIBS is evaluated as an analytical tool for measurement of Sr and Cs contamination on type 304 stainless steel surfaces. Samples were reacted in model acidic (PUREX reprocessing) and alkaline (spent fuel ponds) Sr and Cs bearing liquors, with LIBS multi-pulse ablation explored to measure contaminant penetration. The Sr II (407.77 nm) and Cs I (894.35 nm) emission lines could be separated from the bulk emission spectra, though only Sr could be reliably detected at surface loadings $> 0.5$ mg cm$^{-2}$. Depth profiling showed decay of the Sr signal with time, but importantly, elemental analysis indicated that material expelled from LIBS craters is redistributed and may interfere in later laser shot analyses.
4.2. Highlights

• The use of LIBS for the analysis of contaminated nuclear plant steel is demonstrated at 45mm range (laser/emission collection optics to sample), illustrating the potential for ‘standoff’ (several mm to several metres) in-situ characterisation; here, the Sr II 407.77 nm and Cs I 894.35 nm emission lines can be used to positively identify Sr and Cs against the steel bulk emission matrix.

• Multi pulse LIBS can provide depth resolved information on contaminant distribution but material redistribution into LIBS craters must be considered as it can introduce artefacts.

4.3. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a quasi-non-destructive technique that operates on the fundamental principle of the ablation of a small amount of sample by a laser pulse that is focused onto the surface. The ablated material then forms a plasma of excited atoms, ions, and free electrons that, on cooling, emits radiation at characteristic wavelengths dependent upon the elemental composition the sample. Increasingly, LIBS is being recognised as a promising technique for elemental analysis, including in industry [1]. Examples of use include: elemental analysis in space exploration programs [2], quality control use in pharmaceuticals [3], and forensic and archaeological sample analysis [4]. This diverse range of LIBS applications is largely driven by the technique’s capability to perform fast, multi-elemental analysis of solids [5], liquids [6], and gases [7], with virtually no sample preparation, and with low ppm sensitivity.

LIBS is also used in the nuclear industry as the technique permits standoff (millimetres to tens of metres) analysis of radioactive samples. Therein, a rapidly emerging application is elemental analysis of radioactive waste processing materials for the assessment of radionuclide contamination. Positive identification of fission products, actinides, and activated corrosion products has been demonstrated for a range of nuclear materials, including mixed oxide fuels [8], molten salt electrolytes [9], and graphite [10]. LIBS has also been used for analysis of nuclear plant steels; however, work here has focussed on analysis of steel alloying components for quality control during manufacturing [11-12], or for discrimination between different kinds of steel for the rapid identification and sorting of unknown materials [13-14]. To our knowledge, LIBS has not been used to quantify radionuclide uptake onto steel components.
The radioactive contamination of steel components is a key decommissioning challenge at nuclear reprocessing facilities [15]. Deposition of radionuclides from reprocessing streams onto steel components incurs a radiation dose to nearby workers and, if left untreated, can generate large volumes of radioactive waste. In turn, these wastes are difficult and costly to characterise, dispose, or decontaminate. It is therefore highly desirable to develop analytical techniques that permit rapid assessment of contaminated plant components in order to limit human exposure and to allow evaluation of materials needing decontamination and or sentencing. LIBS presents an attractive option to meet this task as it only requires optical access to samples. Accordingly, radiologically and chemically hazardous areas such as hot cells may be readily analysed without incurring an additional dose penalty. This is in sharp contrast to wet techniques currently employed for the quantitative analysis of nuclear materials [16-17] which by comparison require comparatively long analysis times. Further, these methods are often commercially expensive and hence not economically suited for the analysis of industrial volumes of material. Such issues are overcome with LIBS, which can perform real-time quantitative analysis of multiple elements with minimal restrictions on sample condition. An additional possibility of LIBS is its potential to perform high-resolution depth profiling of materials by multi-pulse laser excitation [1]. In turn, this could yield useful information of contaminant penetration into nuclear plant steels or other contaminated materials.

For successful application of LIBS to nuclear plant steels, the discrimination of analyte emission lines from the supporting matrix spectrum must be possible. The large number of alloying elements typically present in steel reduces this probability of satisfying this prerequisite condition. However, in this contribution we evaluate the ability of LIBS to reliably measure Sr and Cs contamination in AISI Type 304 stainless steel, a common construction material used throughout nuclear reprocessing facilities owing to its excellent corrosion resistance properties [18]. The selection of these two elements reflects the dominant contribution of the fission products $^{90}$Sr $(t_{1/2} = 28.8$ yrs) and $^{137}$Cs $(t_{1/2} = 30.2$ yrs) to the total initial (< 200 years) activity of spent fuel (and resulting spent fuel reprocessing liquors and storage pond waters) after removal from reactors [19]. In addition, we also assess the potential of LIBS to be used as a depth profiling technique for Sr and Cs penetration into steels using LIBS multi-pulse analysis over a single position, as previously documented for other materials [20-21].
4.4. Experimental Section

4.4.1. Materials and Procedure

The chemical composition of the AISI Type 304 stainless steel used in experiments is provided in Table 4.1. Steel coupons with dimensions of 10 x 10 x 13 mm (l x w x t) were mechanically polished to 4000 grit using SiC paper on a single 10 x 10 mm face. This surface was then polished to 1 µm mirror finish and degreased with ethanol before contamination experiments commenced. Here, the coupons were exposed to the contaminant bearing liquors, either 3 M HNO₃, representative of the PUREX-derived nitric acid reprocessing liquors [22], or 1 mM NaOH, representative of alkaline fuel ponds at Sellafield Ltd. site. Aristar grade chemicals were used, and only the polished steel surface was exposed to the aqueous solutions that also contained stable CsNO₃ (500 mg L⁻¹) and Sr (500 mg L⁻¹). Contamination experiments were maintained at 60 °C for 30 days; thereafter the coupons were removed and washed briefly with deionised water and then isopropyl alcohol (IPA) prior to LIBS analysis. ICP-MS Solution analysis revealed that the total amount of Sr deposited onto the steel surfaces after acidic and alkaline contamination was 0.36 and 1.10 mg cm⁻², respectively (see Section 5.4.2 and Figure 5.4). In comparison, Cs accumulation was 0.50 and 0.56 mg cm⁻², respectively.

Table 4.1. Chemical Composition (wt. %) of AISI Type 304 Stainless steel used in experiments

<table>
<thead>
<tr>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.15</td>
<td>8.6</td>
<td>0.055</td>
<td>1.38</td>
<td>0.45</td>
<td>0.04</td>
<td>0.005</td>
<td>0.038</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

4.4.2. LIBS Analysis

Commercially available LIBS instruments (Applied Photonics Ltd., UK) were used in this work. A LIBSCAN 100 and a LIBS-8 instrument were used in scoping work with unreacted steel samples (Figure 4.1); a LIBSCAN 100 was used for all work with contaminated steel samples. Q-switched Nd:YAG pulsed lasers (LIBS-8: EKSPLA Nanosecond E/O laser model NL301G-10; LIBSCAN 100: Quantel Big Sky CFR Ultra GRM) with a fundamental wavelength of 1064 nm were used as the excitation source. The laser pulse energy was set to 100 mJ, a starting energy that was proven to be useful, and was later adjusted as required. The temporal laser beam width was 3 – 6 ns (LIBS 8) and 5 – 9 ns (LIBSCAN 100), each with a repetition rate of 10 Hz. For the LIBS 8, he light
emitted from the cooling plasma was collected by a plano-convex quartz lens with focal length of 75 mm plano-convex quartz lens with focal length of 75 mm collected the light emitted from the cooling plasma into the entrance slit of a 0.5 m focal length Fiber Optic Spectrometer (AvaSpec-2048-USB2-APL27; equipped with indexable gratings of 1200, 1800, 2400, and 3600 grooves mm\(^{-1}\)). For the LIBSCAN 100, the light emitted from the cooling plasma was collected by six quartz lenses, and refocused into each of the fibre optic spectrometers (AvaSpec-2048- USB2-APL range; see the Supporting Information Section 4.9 for a more detailed description). In both cases the plasma light was detected using a charge coupled device (CCD) detector (2048 pixel), with controls to enable setting of the delay and integration times. Emission spectra within the regions of 182-1011 nm (LIBS 8) and 185-904 nm (LIBSCAN 100) were generated, each from a single laser shot, which permitted identification of the necessary elements through their unique spectral features. The gate-width was 1.1 ms and the delay time for analysis was fixed at the minimum value of 1.27 µs, a standard time delay.

4.4.3. Glow Discharge Optical Emission Spectroscopy Depth Analysis

Elemental depth profile analysis was conducted with GD-OES (Glow Discharge Optical Emission Spectroscopy), using a GD-Profiler 2 (Horiba Jobin Yvon) at an applied power of 35 W and an Ar gas pressure of 635 Pa. A 4 mm diameter Cu anode was used. The elemental emission lines used were 371.999 nm for Fe, 425.439 nm for Cr, 341.482 nm for Ni, 130.223 nm for O, 460.739 nm for Sr, 455.329 nm for Cs, and 396.157 nm for Al. These lines were detected using a polychromator focal length of 500 mm and with 30 optical windows. The photon detector was calibrated using a 1 mm Al sheet. In order to maintain the vacuum seal at the O-ring-sample interface, larger, analogue steel coupons of dimensions 20 mm x 20 mm x 13 mm thickness were used for GD-OES analysis.

4.4.4. Electron Microscopy and Energy Dispersive X-ray Elemental Analysis

To determine the morphology of the steel surface after the ablation process, SEM analysis was undertaken on the resulting craters that formed upon laser impact. Electron microscopy images were obtained using a FEI XL30 200 (E)SEM-FEG microscope at an accelerating voltage of 15 kV under high vacuum, utilising either an Everhart-Thornley detector (ETD) or a Circular Backscatter detector (CBS). An EDAX Gemini EDS Spectrometer was used to determine the distribution of major elements (Fe, Cr, Ni, O) on the steel surface at a spot size of approximately 1 µm.
4.4.5. Laser Confocal Microscopy Analysis

The morphology and depth of craters that resulted from LIBS analysis of steel surfaces were analysed with a Keyence VK-X200K 3D laser confocal microscope at 200x magnification using a 0.5 µm step size and superfine resolution (2048 x 1536 pixels). The area analysed by the laser confocal microscopy of the LIBS crater was approximately 2.0 mm x 1.5 mm.

4.4.6. Time of Flight Secondary Ion Mass Spectrometry

Elemental distribution of the LIBS crater (including Sr and Cs) was analysed using a TOF-SIMS instrument (IONTOF GmbH, Münster, Germany) of the reflectron-type. The system was equipped with a 30 kV Bi/Mn liquid metal ion gun (LMIG) as the primary ion source and was operated at an emission current of 0.8 µA. The pulse width of the primary ion bunch was set to 30 ns at a 100 µs cycle time, which yielded a mass resolution of secondary ions >8000 amu. Prior to analysis, in situ sputter cleaning of the surface was undertaken with an Ar gas cluster ion beam (GCIB) in order to remove surface bound hydrocarbon contamination. The scanning area of the LIBS crater was set to 500 µm x 500 µm, the maximum area size for high resolution imaging. The major isotopes of the elements of interest were selected for analysis.

4.5. Results and Discussion

4.5.1. Strontium Identification

Initially, Sr and Cs emission lines were identified within the LIBS spectrum of contaminated coupons. A fraction of the underlying stainless steel support matrix is also ablated in tandem with the target elements, and therefore lines corresponding to elements in the substrate will also be observed in the emission spectrum. For this reason the possibility of spectral interference must be considered when selecting analyte lines for positive elemental identification. In contrast to many previous LIBS investigations of nuclear materials, the 304 stainless steel matrix comprises a large number of alloying elements and thus it yields a complex LIBS spectrum, irrespective of the surrounding atmosphere, as shown in Figure 4.1. The number of Sr and Cs spectral features that are free of interference can be expected to be low within the spectrum of stainless steel due to its multi-element composition. Accordingly, the choice of elemental line for positive detection must be carefully considered as those employed for other materials may not be suitable on the steel matrix.
Figure 4.1. LIBS emission spectra for -uncontaminated (as received) AISI Type 304 stainless steel measured under air (A) and argon (B) atmospheres. The output laser energy, gate-width, and delay time were 100 mJ, 1.1 ms and 1.27 µs, respectively.

Previous research has used 407.77 nm for Sr measurement (407.77 nm represents Sr II; \( ^2\text{S}_{1/2} \rightarrow ^2\text{P}_{3/2} \)) in LIBS experimentation [2, 8, 23-24], and in accordance this emission line was first tested in this work. As shown in Figure 4.2A, a 407.77 nm spectral line observable in the contaminated material is absent in the reference uncontaminated specimen, suggesting that this is the Sr line that is useful for measurements. Owing to the large number of alloying elements present in the matrix, the LIBS spectra of stainless steel materials are inherently complex and subsequently peak assignment can often be a challenging task. In consideration of this, a LIBS spectrum of a standard Sr salt (Sr(NO\(_3\))\(_2\)) was also recorded to support our assignment as Sr II 407.77 nm. The nitrate salt was deemed an appropriate reference Sr material as it was considered that nitrogen and oxygen do not contribute to the signal of interest. This was based on the omission of the 407.77 nm spectral feature in the open air spectrum of the uncontaminated steel material, despite an abundance of N\(_2\) and O\(_2\) in the surrounding atmosphere. Hence, the observation of this line in the salt spectrum validates our designation as Sr II 407.77 nm and strongly suggests that the steel alloying elements also do not contribute to the signal. Therefore, the Sr II 407.77 nm line can be satisfactorily utilised for the positive identification of Sr within the steel matrix.
Figure 4.2. Comparison of LIBS emission spectra of standard nitrate salts, uncontaminated 304 stainless steel, and 304 stainless steel after being exposed to various contaminant bearing liquors. Spectra are presented in the regions of interest for (A) Sr, and (B) Cs detection. The arrow shows the position of the Sr II 407.77 nm line. Measurement was performed under open air conditions at a laser output energy of 100 mJ. The spectra in (A) were normalised to 1 for ease of comparison.

A comparison of the normalised intensities of the Sr line in the contaminated LIBS spectra reveals uptake to be significantly enhanced in the alkaline contamination matrix, consistent with the ICP-MS solution data (see Section 5.4.2 and Figure 5.4). This is also in accordance with previous contamination studies that reported an increasing affinity for metal ion sorption onto steel surfaces in alkaline media [25-26], although no consensus of the mechanisms involved was provided. In order to quantify the observed pH dependence on Sr deposition, construction of calibration curves using standard samples would be necessary to convert signal intensity into concentration [23, 27], which is beyond the scope of this work.

4.5.2. Cesium Identification

The lack of LIBS investigations in the literature with Cs as the target element has previously been attributed to its poor limit of detection [10], and as a result studies have largely been limited to the analysis of samples where Cs is a major constituent of the substrate [27, 28]. Here, the prominent Cs I 852.11 nm line was almost exclusively selected for quantification but in this study interference with the atmospheric (air) Ar I line at 852.14 nm was observed [29; Figure 4.1], necessitating the selection of another candidate line. The prominent Cs I 455.53 nm and 459.32 nm lines [30] were discarded for identification purposes on similar grounds as spectral interference with the Cr I 455.48 [31] and Fe I 459.52 nm [32] matrix lines was observed [Figure 4.1]. The Cs I 894.35 nm line
\( ^2S_{1/2} \rightarrow ^2P_{1/2} \) was considered as an appropriate alternative in this work due to its applicability for a number of supporting matrices that have previously been tested [30]. As seen in Figure 4.2B the LIBS emission spectrum of contaminated 304 includes a line centred at 894.33 nm that is not present in the uncontaminated spectrum. To confirm this, we completed complimentary analysis of CsNO₃, and found that the Cs I 894.35 nm line was observed. This line, however, only becomes visible when the solution concentrations are increased by one to two orders of magnitude in both the alkaline and acidic systems, respectively. No detectable quantities of Cs could be found on the steel surface using contamination solution conditions representative of conditions found at nuclear reprocessing facilities. Hence, the sensitivity of LIBS with regards to Cs detection is not satisfactory in our study [10].

4.5.3. Chemical Depth Profiling

A fundamental challenge associated with depth profiling techniques is the correlation of analyte removal rate with depth of analysis. LIBS is no exception to this, and currently no established method for depth quantification exists. A relatively simple calibration procedure employed in previous studies involved calculation of the average ablation rate by dividing the thickness of a standard material by the corresponding number of shots required to ablate from top to bottom [21, 33]. Subsequent measurement of crater depth by electron microscopy and stylus profilometry demonstrated this approach to be dubious, by the observation of an obvious non-linear ablation rate [34]. A decreasing ablation rate at greater depths has subsequently been attributed to stronger absorption of the laser pulse by the plasma as it penetrates further into the material, reducing its capacity to remove material upon contact with the crater bottom [35]. Adding to these difficulties is apparent irregular crater morphology where the crater bottom typically does not have a flat surface, thus making it difficult to accurately determine depth by direct measurement [36].

The procedure used to obtain LIBS chemical depth information in this work is described as follows. The spontaneous formation of a passive surface Cr₂O₃ layer on stainless steel materials is exploited in an analogous approach to the aforementioned studies of coated systems, using O as the reference element confined to the surface. Using this approach, the decreasing oxygen signal in the initial pulses corresponds to the ablation of the passive layer and thus can be monitored to evaluate contamination relative to this surface film. To avoid contribution of the LIBS signal by atmospheric O, analysis must be performed under an inert atmosphere. Many of the plasma properties including size, temperature and expansion rate are strongly influenced by its surrounding atmosphere and therefore the
choice of atmosphere must be carefully selected to be complimentary with the nature of analysis. Argon is reported to yield intense spectral lines whilst simultaneously possessing a low surface ablation rate [37], attributed to its low thermal conductivity that subsequently heats the plasma more effectively by inverse Bremsstrahlung. The resulting plasma also acts as a protective barrier, optically shielding the surface and thus reducing the volume of ablation. The combination of intense spectral lines corresponding to smaller volumes of ablated material for each individual shot affords improved depth resolution for chemical analysis and for this reason Ar was chosen as the atmosphere for depth profiling analysis in this study.

LIBS depth profiles of Sr contaminated steel coupons are shown in Figure 4.3. To overcome poor accuracy, normalization of analyte signals to the Fe I 404.56 nm matrix line was performed; a common practice in elemental analysis [1]. In order to demonstrate the correctness of this approach, the Cr I emission line at 425.39 nm was also monitored, where the relatively stable signal observed suggests that the assumption of a uniform Fe distribution within the bulk matrix is reasonable. It is important to note that the ablation depth of a single pulse at 50 mJ laser energy, as determined by confocal laser scanning microscopy, is approximately 0.5 µm (see below). As a result, Fe concentration gradients in a nanometre scale passivating oxide layer cannot be expected to significantly affect the accuracy of our normalisation approach. Operating at a laser energy of 100 mJ shot\(^{-1}\) reveals a maximum Sr concentration within the initial pulses. However, strong fluctuation in the Sr signal for the alkaline system, where contamination is much more pronounced, makes it infeasible to accurately evaluate Sr contamination depth. This observation is much less pronounced for a laser energy of 50 mJ shot\(^{-1}\), suggesting it to be a consequence of matrix effects intrinsic to the LIBS experimental configuration, rather than a correct reflection of Sr contamination behaviour. In addition, inconsistent O depth profiles were also observed between the acidic and alkaline systems at high laser fluence, where the signal was significantly diminished for the high pH specimen. This effect was not observed at lower laser fluence. A possible explanation for the apparent significance of the laser parameters is addressed later. Measuring at a reduced laser output it also becomes apparent that O persists for at least an equal number of shots as the corresponding Sr signal. This observation now becomes possible only by the smoother decline of the Sr signal in the associated depth profiles. From this result it would seem that Sr is maintained within close proximity to the surface, and does not diffuse into the bulk material.
Figure 4.3. Comparison of LIBS depth profiles measured in an Ar environment for acidic and alkaline contaminated stainless steel at 100 mJ and 50 mJ laser energy. The Sr signal in (C) was scaled by a factor of 0.1 for clarity.

To check the validity of our proposed method, complimentary depth-resolved analysis of the contaminated steel coupons was undertaken using a commercial GD-OES spectrometer. The separation of sample removal and excitation processes in glow discharge techniques is a key distinction from LIBS that, in tandem with a stable discharge, is responsible for the reduction of matrix effects. Hence, suitable algorithms are available for the quantification of glow discharge emission yields [38] and for the conversion of sputtering rate to depth information [39]. As a result, GD-OES to date remains a more universal technique for elemental depth analysis, as demonstrated by the widespread investigations reported involving steel materials [40-43].

The GD-OES depth profiles of the steel coupons after contamination are shown in Figure 4.4. By monitoring the O signal, the interface position was located after a sputtering time of approximately 0.20 and 0.30 seconds for the low and high pH contaminating solutions, respectively. In both instances, Sr enrichment was observed within the Cr$_2$O$_3$ passive layer, as indicated by the alignment of the Sr, Cr, and O signal maxima. This finding is consistent with the LIBS result in that contamination diffusion is effectively inhibited by the passive
layer. An important distinguishing feature however is the improved depth resolution afforded by the GD-OES technique, which is capable of discriminating between surface complexation and passive layer embedment. This is a clear advantage over LIBS which in this study, is only sufficient to classify contamination as a surface phenomenon. Furthermore, no Cs signal could be detected during GD-OES characterisation, irrespective of contamination conditions. This result further emphasises that optical emission based spectroscopic techniques are currently not sensitive enough for the analysis of Cs [10].

![Graph](image)

**Figure 4.4.** GD-OES depth profiles of 304 stainless steel contaminated in 3 M HNO₃ and 1 mM NaOH. For clarity the Sr signals have been multiplied by a factor of 100.

### 4.5.4. Crater Analysis

The analysis of major element distribution (Fe, Cr, O, Ni) around LIBS craters, as a function of total number of laser shots delivered is shown in Figure 4.5. In all cases, the craters produced were approximately 1 mm in diameter. The study was carried out using alkaline pH contaminated steel samples using 100 mJ shots in an Ar medium because fluctuation of the Sr signal was most evident under these conditions. It can clearly be seen that with an increasing number of shots a distinct crater geometry develops in which discrete concentric rings of non-uniform elemental composition form. A prominent feature is the increasing O concentration at the crater rim with shot number, which may be attributed to material being expelled from the crater and accumulating around the perimeter as a solidified oxide melt.

The absence of the major steel alloying elements in the melt however suggests that the nature of this laser-matter interaction is not dominated by the relative concentrations of the matrix elements within the plasma plume. Taking into consideration the irregular Sr and O depth profiles recorded at high laser fluence (Figure 4.3), it is possible that Sr (which could
not be reliably detected by EDX) redistribution processes are also occurring during the LIBS measurement. This was investigated via complementary elemental spatial distribution analysis with TOF-SIMS. The crater surface morphology was also characterised by confocal microscopy to identify potential regions of settled debris. As shown in Figure 4.6, Sr enrichment is observed both within the central position and around the rim of the crater formed from a single 100 mJ shot. In addition to the depletion of Fe, Cr, and Ni, these identifiable regions of Sr deposition are raised above the unablated surface, as demonstrated by the colour coded height map. These results collectively indicate that Sr is also being expelled from the crater and is subsequently returned as a concentrated form of settling debris.

Figure 4.5. SEM image and SEM-EDX elemental maps of LIBS craters formed on the high pH contaminated steel surface after a different number of 100 mJ shots under argon: (A) 2 shots, (B) 3 shots, (C) 5 shots, and (D) 10 shots.

The homogenous distribution of oxygen within the crater is consistent with the EDX result that accumulation of oxide debris is insignificant for a low number of shots. Nevertheless,
this result excludes the likelihood of Sr being deposited as SrO, where the exact chemical composition of the debris is subsequently not clear. Regardless, the presence of settled Sr and O material on the specimen surface may subsequently be re-analysed in tandem with ablation of deeper regions, producing a residual tailing of the analyte signals that in turn leads to a compromised depth resolution. This possibility has been considered previously in studies that reported analogous crater morphologies on metallic alloys [44], where in one instance direct observation was possible by electron probe microanalysis [45]. Furthermore, in the aforementioned studies the severity of the tailing effect was often exacerbated by alterations to experimental parameters that increase laser fluence. This includes tightening the beam focus and reducing working distance, which in turn yielded more irregular crater profiles.
Figure 4.6. (A) SEM morphology and (B) confocal microscopy analysis of a crater formed on an alkaline contaminated steel sample from a single 100 mJ laser shot under an Ar atmosphere. TOF-SIMS elemental analysis of the highlighted region in (B) for the elements (C) Fe, (D) Cr, (E) Ni, (F) O, (G) Sr, and (H) Cs.
It is not the purpose of this paper to explain LIBS crater morphology or its formation in detail, which has been described elsewhere in published literature for nanosecond laser ablation [46]. Of note, Cs could also be detected with TOF-SIMS (Figure 4.6) and here the Sr and Cs spatial distribution profiles were also inconsistent, indicating that the redistribution behaviour is unique to each individual element and therefore cannot reliably be inferred from the surface response of another material. A more comprehensive study of crater morphology and evolution is clearly necessary to better understand the surface-laser interaction that is fundamental to LIBS as a characterisation technique. This undertaking is particularly prudent for applications in nuclear decommissioning, since this analysis technique could potentially reintroduce radioactive material onto the material surface.

In addition, it has previously been suggested that laser irradiance treatments may also deteriorate the corrosion resistance of austenitic stainless steels [47]. This behaviour has been attributed to a localised discontinuity of the passive layer under the heating effect of the laser at high fluence [48]. If similar corrosion phenomena are initiated during the LIBS measurement this will present a serious problem for in situ characterisation as a reduced corrosion performance will increase the likelihood of material failure. Further investigation is therefore required to evaluate the effect of the ablation process on the corrosion resistance of stainless steels.

4.6. Conclusions

We have shown that LIBS can be used to identify Sr and Cs contamination on 304L austenitic stainless steel, a material widely used in the nuclear waste storage and reprocessing operations. Here, the Sr II (407.77 nm) and Cs I (894.35 nm) emission lines can be separated from the overall steel emission spectrum. However, whilst LIBS can reliably measure Sr contamination on steel at levels representative of those found in the nuclear industry (≥ 0.4 g cm⁻²), Cs detection at these levels is challenging. LIBS depth profiling of Sr contamination in steel also appears possible; however here, at an output laser energy of 100 mJ shot⁻¹ material ablated from the steel surface can be redeposited in the LIBS crater, causing tailing in the Sr signal. Reducing the laser output to 50 mJ shot⁻¹ lessens this problem and at this energy LIBS results for Sr depth penetration into steels were in good agreement with complimentary GD-OES analysis. As such, LIBS offers reliable standoff analysis for Sr contamination in nuclear plant steels at loadings representative of industry. This an intriguing possibility due to the requirement of minimal sample preparation and handing associated with the LIBS technique.
4.7. Acknowledgments

This work was supported by the Sellafield Ltd. Centre of Expertise for Decontamination and Effluent Treatment and the RCUK grants ST/N002474/1 and NE/M014088/1. Smith is funded by a Royal Society Industry Fellowship, and Banford, Horsfall, Smith and Trivedi acknowledge support from NNL’s Waste Management and Decommissioning IR&D Programme.
4.8. References


4.9. Supporting Information for:

**Analysis of Contaminated Nuclear Plant Steel by Laser-Induced Breakdown Spectroscopy**

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4.9.1. LIBS Experimental Setup

The experimental setup for the acquisition of LIBS spectra is shown in Figure 4.7. For all measurements, the distance from the emission light collection optics to the samples investigated was 45 mm.

Figure 4.7. Laser-induced breakdown spectroscopy experimental set up. (i) laser focus optics, (ii), (iii) collar to aid sample positioning. (iv) sample.

4.9.2. Plasma Parameters

For a quantitative assessment of the relationship between contamination behaviour and solution pH, it is necessary to demonstrate that the plasma is in local thermal equilibrium (LTE). To confirm this condition the plasma temperature and electron density must be calculated. In this work, the plasma temperature is determined using the Boltzmann plot method. Assuming that the population of electronic states in the plasma plume follows a Boltzmann distribution, the integrated intensity of a spectral line $I_{mn}$ is related to the plasma temperature $T$ accordingly:

$$I_{mn} = \frac{A_{mn} g_m h \nu(T)}{\lambda_{mn}} e^{-\frac{E_m}{k_B T}}$$

where $A_{mn}$ is transition probability (s$^{-1}$), $g_m$ is the statistical weight of the upper level, $\lambda_{mn}$ is the wavelength of the spectral lines (nm), $E_m$ is the energy of the upper level (eV), $U^s(T)$ is the total number density (m$^{-3}$), $h$ is Planck’s constant (Js), $c$ is the speed of light in a vacuum (ms$^{-1}$) and $k_B$ is Boltzmann’s constant (JK$^{-1}$). The linear form is expressed as:

$$\ln \left( \frac{I_{mn} \lambda_{mn}}{A_{mn} g_m} \right) = -\frac{E_m}{k_B T} + \ln(h \nu U^s(T))$$
When the left hand term is plotted against $E_m$, a linear plot of gradient $-1/k_B T$ is obtained [1]. In this experiment, six Fe I lines were selected (Table 4.2) that are insensitive towards self-absorption and saturation effects at elevated plasma temperatures [2]. Figure 4.8 shows the Boltzmann plots obtained from measurement at 50 mJ laser energy under atmospheres of air and Ar. Plasma temperatures of 6,854 K and 7,734 K were calculated respectively, thus in accordance with previous studies citing hotter plasmas in Ar atmospheres [3-4].

Table 4.2. Wavelengths and associated spectroscopic constants of the Fe I lines used in the Boltzmann plot method [5]

<table>
<thead>
<tr>
<th>$\lambda$ / nm</th>
<th>$E_m$ / eV</th>
<th>$A_{mn}$ / $10^8$ s$^{-1}$</th>
<th>$g_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>532.418</td>
<td>5.54</td>
<td>0.15</td>
<td>10</td>
</tr>
<tr>
<td>532.804</td>
<td>3.24</td>
<td>0.0115</td>
<td>7</td>
</tr>
<tr>
<td>537.150</td>
<td>3.27</td>
<td>0.0105</td>
<td>5</td>
</tr>
<tr>
<td>538.337</td>
<td>6.62</td>
<td>0.59</td>
<td>13</td>
</tr>
<tr>
<td>539.713</td>
<td>3.21</td>
<td>0.00259</td>
<td>9</td>
</tr>
<tr>
<td>540.578</td>
<td>3.28</td>
<td>0.0109</td>
<td>9</td>
</tr>
</tbody>
</table>
Figure 4.8. Boltzmann plots obtained from the selected neutral Fe lines (left) and associated Voigt fits of the Fe I 426.05 nm line (right) for the corresponding LIBS plasma formed in air and Ar. The output laser energy was 50 mJ.

The dominant contribution of spectral line broadening is considered to a consequence of electric field interactions within the plasma i.e. Stark broadening. Assuming Doppler effects are negligible, broadening is directly proportional to the electron number density, \( N_e \), as follows:

\[
\Delta \lambda = 2\omega \left( \frac{N_e}{10^{16}} \right)
\]

where \( \Delta \lambda \) is the Stark contribution to the line broadening (nm), \( \omega \) is the electron impact parameter (nm) and \( N_e \) is the electron number density (cm\(^{-3}\)). For calculation of the electron density, the Fe I line at 426.05 nm was used, with a corresponding impact parameter value of 0.011 nm [6]. The Stark broadening contribution can be computed from the Lorentz FWHM, de-convoluted from the Gaussian component with an appropriate Voigt fit. Lorentzian widths were calculated as 0.028 and 0.074 nm for air and Ar respectively. The corresponding electron densities are therefore 1.28 \( \times 10^{16} \) and 3.35 \( \times 10^{16} \) cm\(^3\).

The McWhirter criterion for LTE is the lower limit for electron number density, calculated as:

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\[ N_e \geq 1.6 \times 10^{12} (\sqrt{T})(\Delta E)^3 \]

where \( \Delta E \) (eV) is the highest energy transition of the chosen element. In this work, \( \Delta E = 2.91 \) eV for Fe. Imputing the plasma temperatures of 6,854 K and 7,734 K yields a minimum electron density of the order of \( 10^{15} \) cm\(^{-1}\) in both instances. Therefore, the McWhirter criterion is satisfied [8].
4.9.3. References


5. Cesium and Strontium Contamination of Nuclear Plant Stainless Steel

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5.1. Abstract

The incorporation of radioactive species into nuclear plant stainless steel materials is a key decommissioning challenge that generates large volumes of waste. The chemical processes that underpin contamination in many instances are not well understood and this has subsequently restricted the development of safe and cost effective decontamination treatments. Here, we perform model contamination experiments with \textsuperscript{90}Sr and \textsuperscript{137}Cs to understand AISI Type 304 stainless steel contamination mechanisms in nitric acid-based reprocessing streams representative of the PUREX (Plutonium Uranium Redox Extraction) process, and alkaline spent fuel storage ponds. Solution and surface spectroscopic measurements were used to characterise Sr and Cs uptake to the steel surface using stable analogues. In addition, the chemical composition and structure of the passive layer formed on the steel surfaces were examined. Experiments show that under passivating conditions Sr and Cs are maintained at the surface by the selective incorporation into the Cr-rich passive film. This behaviour was found to be independent of solution pH despite apparent chemical and surface speciation effects that promote contaminant uptake under alkaline conditions. In concentrated nitric acid, a shift in corrosion potential to a transpassive region led to severe intergranular attack that was accompanied by Sr diffusion into to the bulk material. The accumulation of Sr and Cs also occurs with the re-adsorption of once dissolved corrosion products. These results collectively demonstrate that contamination and corrosion phenomena are intimately related and should not be examined independently of one another.

KEYWORDS: strontium, cesium, stainless steel, nuclear plant, decommissioning
5.2. Introduction

In recognition of the detrimental impact of fossil fuel emissions on the environment, development of a low carbon based energy economy is now a priority (Brumfiel, 2011). Nuclear power is a cheap, efficient, low carbon energy source. However, the unavoidable generation of radioactive waste and its costly management is a fundamental concern that inhibits full exploitation of nuclear energy (Rivasseau et al., 2013). A major source of waste arises from the accumulation of radioactive species from aqueous solution onto surfaces of reactors, plant, and fuel handling equipment (IAEA, 2006). This “plate-out” process, if not effectively controlled, creates further challenges for final material disposal whilst simultaneously posing additional radiation issues for on-site personnel. The advancement of reliable and cost effective decommissioning and decontamination programmes is consequently of great importance to provide cost savings and ensure the sustainability of civil nuclear power.

The widespread use of austenitic stainless steels, such as AISI Type 304, as structural materials (Shaw, 1990) at nuclear sites mean that these alloys become an important source of contaminated material over a plant’s operational lifetime. The selection of these materials is based on a combination of high tensile strength and excellent corrosion resistance, the latter afforded by the spontaneous formation of a nanometre scale passivating surface chromium oxide layer (Olsson et al., 2003). It has been assumed that radionuclides become impregnated in this passive layer during the accumulation process (Bayri et al., 1994; Rufus et al., 2004), although this phenomenon has not been fully demonstrated. In order to make informed decisions regarding the design and optimisation of decontamination treatments for these materials, an understanding of the principal chemical interactions driving radionuclide uptake onto or into the steel is highly desirable.

The contamination phenomena witnessed during transport and storage of radioactive liquors are not completely understood. It is known that on contact with aqueous solution the passivating surface oxide layer of stainless steel materials, like many natural sorbents, is charged and interacts electrostatically with dissolved metal ions (McCafferty, 2006). On this basis, surface complexation models initially constructed for making reliable predictions for radionuclide groundwater transport (Dzomabk et al., 1986; Mishra et al., 1999) have since been applied to describe the sorption properties of stainless steels (Rouppert et al., 2000; Fujii et al., 2002). Recent investigations of the contamination of Pressurised Water Reactor (PWR) materials have shown sorption phenomena to be more complex, where complete characterisation is not possible by utilisation of charge principles.
alone (Kádár et al., 2011). Here, the elemental composition and morphology of the passive layer was considered to control a chemical component to the accumulation process that may facilitate sorption from boric acid coolant, despite repulsive electrostatic interactions with the surface. No comprehensive attempt was made in this study to elucidate an exact mechanism correlating the nature of the surface oxide layer to the dominant sorption mode. Nevertheless, the importance of the passive layer condition on the character of contamination strongly suggests that sorbent properties of stainless steels are inherited from this surface oxide film. It is clear that an assessment of the passivation state of the steel material is essential in understanding radionuclide sorption phenomena. A complicating issue, however, is that the elemental composition, structure, and thickness of the surface oxide layer varies with the composition and potential of the passivating medium (Castle, 2008). Accordingly, the derived sorbent properties are expected to be a synergy between steel composition and environment chemistry, and therefore “plate-out” phenomena must be investigated on an individual basis under the specific conditions of contamination.

The reprocessing of spent nuclear fuel to recover U and Pu is a major activity at the back end of the nuclear fuel cycle and has also been implicated in “plate-out” processes involving stainless steel storage and piping material (Adeleye et al., 1996). Uranium and plutonium recovery is achieved using the PUREX process, a solvent extraction method based on nitric acid (Sood et al., 1996). The high acidity and strong oxidising power of the reprocessing streams will likely modify the steel passivation state so that contamination processes cannot be reasonably expected to be comparable with those described for the PWR cooling circuits (Hirschberg et al., 1999; Varga et al., 2001; Kádár et al., 2011). In spite of this, there remain many uncertainties surrounding the mechanisms of contamination of reprocessing plant material. To address these issues, it is necessary to characterise the surface chemistry of the steel materials in contact with HNO₃, and identify the relevant chemical sorption processes that are promoting radionuclide accumulation.

In this work we seek to better understand ⁹⁰Sr (t½ = 28.8 yrs) and ¹³⁷Cs (t½ = 30.2 yrs) (Flynn et al., 1964) uptake onto AISI Type 304 stainless steel surfaces across a range of solution chemistries representative of those found in the UK waste reprocessing stream and in alkaline fuel storage ponds. The selection of these two high yield fission products was motivated by their domination of the reprocessing streams activity (Choppin et al., 2002) where their subsequent accumulation provides a significant fraction of the total deposited activity (IAEA, 2006). Model contamination systems were established to simulate
documented conditions on site and contamination was subsequently characterised using solution uptake data and analysis of the contaminated steel surfaces. In addition to a series of nitric acid matrices to model the reprocessing streams, a further solution matrix comprising of 1 mM NaOH was established to simulate the conditions found in fuel ponds, where steel pond furniture is used to store spent fuel (Wilson, 1996). In analysing the sorption behaviour in both acidic and alkaline media, this study may also provide useful information regarding the significance of solution composition, where previous studies have shown contamination behaviour to be highly sensitive towards the pH of the contacting solution (Adeleye et al., 1996).

5.3. Experimental Section

5.3.1. Materials and Procedures

AISI Type 304 stainless steel material with a chemical composition of (wt. %) 18.15 Cr, 8.6 Ni, 1.38 Mn, 0.055 C, 0.45 Si, 0.04 P, 0.038 N, 0.005 S was used in this study. Individual specimens of dimensions 10 mm x 10 mm x 13 mm (l x w x t) were cut from a base material and were mechanically ground using 4000 SiC emery paper on a single 10 mm x 10 mm face in order to remove surface deformation. This surface was then polished to a 1 µm mirror finish and was degreased with ethanol and distilled water.

Contamination was achieved by contacting the polished surface with solutions containing stable Sr(NO$_3$)$_2$ (500 mg L$^{-1}$) and CsNO$_3$ (500 mg L$^{-1}$) in a sealed polypropylene container. Solutions of 3, 6 and 12 M HNO$_3$ and 1 mM NaOH (Aristar grade chemicals diluted with 18.2 MΩ deionised H$_2$O to the desired concentration) were selected as the contamination matrices to simulate reprocessing waste streams at the Sellafield site and the pond furniture respectively (IAEA, 2006). Although it is known that the Sr solution concentrations are significantly lower in the pond furniture than in the reprocessing streams, it was decided to operate under identical solution concentrations. In doing so, these results would permit a more comprehensive account of the importance of solution composition on the contamination process and also permit spectroscopic characterisation of the steel surfaces. The solutions were then maintained at 60 °C during the contamination experiments. All steel samples were contaminated for 30 days thereafter the samples were removed and washed with deionised H$_2$O and IPA prior to surface characterisation.
5.3.2. Electron Microscopy Analysis

The morphology of the steel surface after immersion in the Sr and Cs bearing liquors was characterised by scanning electron microscopy (SEM). Electron microscopy images were obtained using a FEI Quanta 200 (E)SEM microscope at an accelerating voltage of 20 kV operated under high vacuum. SEM images were recorded at a magnification of 1600x, corresponding to a scanning area of approximately 150 µm x 150 µm.

5.3.3. Glow Discharge Optical Emission Spectroscopy (GD-OES) Analysis

Elemental depth analysis of steel coupons was performed with GD-OES (Glow Discharge Optical Emission Spectroscopy), using a GD-Profiler 2 (Horiba Jobin Yvon). The glow discharge area was 4 mm in diameter and operated at an applied power of 35 W under an Ar gas pressure of 635 Pa. The elemental emission lines (nm) used for detection were Fe I 371.999, Cr I 425.439, Ni I 341.482, O II 130.223, Sr II 460.739, Cs I 455.529, Al I 396.157. The photon detector was calibrated using a 1 mm Al sheet prior to analysis and operated at polychromator focal length of 500 mm and with 30 optical windows. In order to maintain the vacuum seal at the O-ring-sample interface, 304 stainless steel coupons of dimensions 20 mm x 20mm x 13mm (l x w x t) were employed for GD-OES analysis.

5.3.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Solution Analysis

Sr and Cs adsorption onto the steel surfaces was tracked by removing 1 mL aliquots of solution at the following time intervals (0.17, 1, 6, 24, 168, 336, 504, 672 h) followed by centrifugation (13,150 g for 45 minutes). Thereafter, 500 µL of the resulting supernatant was withdrawn and diluted into 2% HNO₃ for ICP-MS analysis. Elemental analysis was conducted using an Inductively Coupled Plasma Mass Spectrometer (Agilent 7500cx). Solution analysis was also carried out on the main alloying elements (Fe, Cr, Ni) to assess the corrosion behaviour of the steel surfaces under these contaminating conditions. All solutions were stored at 4 °C prior to analysis to inhibit loss of material by evaporation. Each sorption experiment was performed in triplicate and the average values are provided. The amount sorbed at time t, \( q_t \) (gm⁻²) was calculated as follows:

\[
q_t = \frac{(c_0 - c_t) \times V}{A}
\]

where \( c_0 \) and \( c_t \) are the solution concentrations at time = 0 and t, respectively (g L⁻¹), \( V \) is the volume of solution (L) and \( A \) is the surface area of the exposed steel surface (m²).
5.3.5. X-ray Photoelectron Spectroscopy (XPS) Analysis

The composition of the surface oxide layer and the chemical environments of the fission product contaminants were assessed using XPS. High resolution scans were recorded using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical) using a monochromatic Al X-ray source (1486.69 eV). The relative fractions of chromium and iron in the passive film were calculated as the relative mass ratio (e.g. \( \text{Cr}_{\text{oxide}} / (\text{Cr}_{\text{oxide}} + \text{Fe}_{\text{oxide}}) \)) using the Cr 2p peaks at approximately 575 and 584 eV, and the Fe 2p peaks located at approximately 710 and 723 eV, respectively. Spectra were recorded in duplicate and the resulting surface Fe/Cr ratios were averaged. Peak positions were charge corrected by normalisation with the C 1s ubiquitous hydrocarbon peak at 284.6 eV.

5.3.6. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) Analysis

The elemental distribution of the fission product contaminants and the alloying elements on the steel surface was assessed using a TOF-SIMS instrument (IONTOF GmbH, Münster, Germany) of the reflectron-type. All measurements were carried out using a pulsed Bi/Mn liquid metal ion gun (30 keV) operated at a 0.8 µA emission current. A 30 ns pulse width of the primary ion bunch at a 100 µs cycle time enabled a mass resolution of secondary ions in excess of 8000 amu. To remove ubiquitous hydrocarbon surface contamination, specimens were sputtered with an Ar gas cluster ion beam for 5 minutes prior to measurement. High resolution imaging was performed on scanning areas of 50 µm x 50 µm. In all cases the most abundant isotopes were selected for characterisation.

5.3.7. Laser Confocal Microscopy Analysis

The depth of the craters that resulted from GD-OES analysis of steel surfaces was quantified with a Keyence VK-X200K 3D laser confocal microscope at superfine resolution (2048 x 1536 pixels). Operating at a 200x magnification and a 0.5 µm step size, the area analysed by the laser confocal microscopy of the GD-OES crater was approximately 6.0 cm x 6.5 cm.

5.4. Results and Discussion

5.4.1. Physical and Chemical Alteration of Steel Surfaces in Contaminant Solutions

In order to better understand the contamination mechanism, it was considered necessary to first study the physical state and elemental composition of the passive layer and the
resulting corrosion state of the steel materials after exposure to the various contaminating matrices.

Electron microscopy (Figure 5.1) revealed no discernible features of the surface morphology after immersion in the alkaline and less concentrated acid contaminating matrices at 60 °C for 30 days. An important exception to this behaviour was the 12 M HNO₃ matrix, where preferential corrosion attack at the grain boundaries was observed (Figure 5.1C) after an identical contact time. Type 304 stainless steel also typically contains a small volume fraction of remaining δ-ferrite (Shankar et al., 2012), and corrosion at these ferrite interface regions is also apparent. The onset of intergranular corrosion (IGC) under strongly oxidising conditions is well known to be characteristic of a shift in the corrosion potential from the passive towards the transpassive region (Priya et al., 2014). Under these circumstances, transformation of insoluble Cr(III) to soluble Cr(VI) species can occur, where the subsequent depletion of Cr in the passive layer deteriorates the film’s protective capabilities at the most susceptible sites first (Robin et al., 2008). Hence, corrosion phenomena are typically initiated at defects, interfaces, or grain boundaries, and may result in material failure if left untreated (Mudali et al., 1993).
Figure 5.1. Typical morphology of 304 stainless steel surfaces after immersion in (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH aqueous solution, at 60 °C for 30 days. The arrows show the attacked ferrite stringers.

Although the acid systems investigated here are normally considered within the safe limits of use, the onset of corrosion phenomena in 12 M HNO₃ as shown, is nevertheless in good agreement with previous corrosion studies of austenitic stainless steels in the presence of confined and weakly renewed nitric acid solutions (Balbuad et al., 2000). The apparent deterioration of corrosion performance in stagnant acidic media has previously been attributed to the uninterrupted build-up of Fe and Cr corrosion products which can catalyse the anodic dissolution reaction. In this event, the corrosion potential of stainless steel may be sufficiently polarised as to induce transpassive behaviour where IGC is usually prevalent. An important distinction to note here is that the reprocessing streams are typically renewed (IAEA, 2006), where it is subsequently not clear if passive behaviour is maintained throughout the entire duration of plant operations. This limiting factor should be taken into consideration during the assessment of contamination processes occurring on site.

In this work, depth analysis of the contaminated steel material was undertaken using a GD-OES spectrometer. As shown in Figure 5.2, the O signal is initially intense, where the
overlapping of the O and Cr maximum signal after a short sputtering time coincides with the steel passive layer. Further measurement results in the complete removal of the O signal, thus corresponding to the bulk material. The GD-OES compositional depth profiles are also presented in terms of sputtered depth in the Supporting Information (see Supporting Information Section 5.8.1 and Figure 5.12). Of note, the O signal diminishes after treatment in 12 M HNO₃ (Figure 5.2C), which suggests that a stable surface oxide layer cannot be maintained under such strongly oxidising conditions. The absence of the protective passive film is expected to greatly increase the steel’s susceptibility to various forms of corrosive attack, a result that is confirmed by SEM analysis.

**Figure 5.2.** GD-OES elemental depth profiles of 304 stainless steel after contamination in (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH aqueous solution, at 60 °C for 30 days. The O and Sr signals have been scaled by a factor of 10 and 100 respectively, for clarity. Note the graphs have different x-axis. Figures 5.2(A) and (D) have been adapted from (Lang et al., 2017).

Furthermore, it was found that after alkaline contamination the passive layer became substantially thicker than those grown under acidic conditions. This is shown by the increased persistence of the O signal in Figure 5.2D, which is accompanied by a significant Fe signal at this early sputtering stage. The growth of thicker films in alkaline media is
related to the bilayer models generally accepted for the steel passive layer structure. Several researchers have experimentally shown the passive layer to be comprised of an outer layer rich in various Fe oxides and an inner layer composed of Cr₂O₃ (Storp et al., 1977; Castle et al., 1997; Carmezim et al., 2005). Whilst this outermost oxide layer is relatively stable in neutral and alkaline solution, dissolution rapidly occurs in acidic solutions owing to Fe’s high solubility at acidic pH (O’Laoire et al., 2006; Liu et al., 2015). Thus, the passive film will contract in acidic media as the Fe oxide component is selectively leached into solution.

This behaviour is confirmed by in situ solution analysis that recorded a significant increase in iron solution concentration within 6 hours of the Sr and Cs sorption study (Figure 5.3A). The decreasing solution concentration afterwards is interesting and is indicative of precipitation or re-adsorption of Fe corrosion products onto the steel surface. The dissolution of Cr in 12 M HNO₃ may be considered characteristic of the transpassive behaviour, as it is known that effectively no Cr is released within passive potential regions (Haupt et al., 1987). Chromium re-adsorption was also observed (Figure 5.3A) during experimentation; however, owing to a reduced initial solution concentration, this effect was not as evident as that for Fe.

Another important artefact of selective Fe dissolution in acidic solution is the enrichment of Cr in the passive layer, as shown by XPS measurements (Figure 5.3B). It should be noted that the relative fraction of oxidised Cr is largely independent of acid molarity, suggesting small variations in the acid molarities used in this study does not significantly influence Fe solubility. On the other hand, the low solubility of Fe in alkaline solution yields a surface composition that is similar to the air passivated material. According to the literature, the slight increase in surface Fe concentration at alkaline pH is due to the higher Cr solubility under basic conditions (Freire et al., 2012) although in this work the presence of Cr in solution could not be detected. An examination of the binding energy positions of the Fe and Cr 2p photoelectron peaks to identify the chemical forms of the passive layer components is provided in the Supporting Information (see Supporting Information Section 5.8.2 and Figure 5.13).
Figure 5.3. (A) Time dependence of Cr (left axis) and Fe (right axis) solution concentration in 3 M, 6 M, and 12 M HNO₃ during the Sr and Cs sorption study onto 304 stainless steel at 60 °C, and (B) Variation in the oxide content of 304 stainless steel as a function of passivation treatment.

5.4.2. Sr and Cs Kinetic Studies

In all solution matrices studied, Sr and Cs accumulation on the steel surface was reasonably rapid (Figure 5.4) with significant uptake of both elements occurring within 24 hours. Uptake then continued but at a diminished rate before an apparent equilibrium sorption capacity was obtained at 30 days. Alkaline contamination conditions led to the maximum amount of Sr and Cs removed to the surface, measured at ~ 11.0 g m⁻² and 5.6 g m⁻², respectively. Other radionuclide sorption studies have also reported fast deposition rates onto austenitic stainless steel materials from acidic and alkaline pH solution matrices (Adeleye et al., 1995; Kádár et al., 2011), suggesting that “plate-out” is an inherently rapid process.
Figure 5.4. Effect of contact time on Sr and Cs uptake ($q_t$) onto 304 stainless steel from (A) 3 M HNO$_3$, (B) 6 M HNO$_3$, (C) 12 M HNO$_3$, and (D) 1 mM NaOH solution, at 60 °C.

In an effort to describe the adsorption behaviour over time, the solution data were analysed by the Ho second order, Lagergren first order, and Elovich kinetic models (Lagergren, 1898; Taylor et al., 1952; Ho et al., 1999). As these models have previously been used to describe the removal of low valence metal ions from aqueous solution by solid substrates (Juang et al., 1997; Cheung et al., 2001; El-Rahman et al., 2006; Sharma et al., 2009; Kim et al., 2014; Yakout et al., 2014), it was postulated that the adsorption of Sr(II) and Cs(I) onto stainless steel may also be governed by similar kinetic descriptions. The Ho second order kinetic model is based on the adsorption capacity of the sorbent in which the driving force for sorption is proportional to the square of the number of unoccupied active sites (Ho et al., 1999):
\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

where \(q_e\) is the equilibrium sorption capacity (g m\(^{-2}\)) and \(k_2\) is the second order rate constant (m\(^2\) g\(^{-1}\) hr\(^{-1}\)). The integrated form over the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_t\) is

\[
\frac{1}{q_e - q_t} - \frac{1}{q_e} = k_2 t
\]

Rearranging into the linear form yields

\[
\frac{t}{q_t} = \frac{1}{q_e} - \frac{1}{k_2 q_e^2}
\]

and

\[
h = k_2 q_e^2,
\]

where \(h\) is the initial sorption rate (g m\(^{-2}\) hr\(^{-1}\)) as \(t \to 0\).

When the left hand term is plotted against \(t\), a linear plot of gradient \(1/q_e\) and a y-intercept of \(1/k_2 q_e^2\) is obtained. The adsorption second order kinetic plots are shown in Figure 5.5 for all for systems studied, where the values of \(q_e\) and \(k_2\) can be calculated from the slope and intercept of the fits, respectively.
Figure 5.5. Ho second order kinetic fits for the adsorption of Sr and Cs onto 304 stainless steel from (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH solution at 60 °C.

As shown in Figure 5.5, for all solution compositions investigated, consistently high correlation coefficients ($R^2 \geq 0.99$) are obtained for this second order kinetic model. In comparison, significantly inferior correlation coefficients were obtained when the experimental data was analysed with the Lagergren first order and Elovich equations. These results are presented in the Supporting Information Section 5.8.3. On this basis of these findings, it may be concluded that Sr and Cs contamination follows Ho second order kinetics over the entire sorption period. In addition, the theoretical $q_e$ values (Table 5.1) were found in all instances to be in excellent agreement with the experimentally measured values (Figure 5.4), further supporting the model selection. An interesting possibility not considered in the original derivation of the Ho kinetic model is that the overall second order reaction originates from the depletion of unoccupied sorption sites and a reducing sorbate solution concentration as the reaction progresses i.e. the simultaneous occurrence
of two first order processes. Further investigation is therefore required to better understand the individual components that contribute to the second order kinetic expression.

Table 5.1. Calculated equilibrium sorption capacity ($q_e$), second order rate constant ($k_2$), and initial sorption rate ($h$) from Ho second order kinetic analysis of Sr and Cs accumulation onto 304 stainless steel

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>$q_e$ / g m$^{-2}$</th>
<th>$k_2$ / $10^{-2}$ m$^2$ g$^{-1}$ hr$^{-1}$</th>
<th>$h$ / g m$^{-2}$ hr$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO$_3$</td>
<td>3.6 ± 0.1</td>
<td>1.5 ± 0.1</td>
<td>0.2 ± 0.1</td>
</tr>
<tr>
<td>6 M HNO$_3$</td>
<td>5.9 ± 0.2</td>
<td>1.1 ± 0.1</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>12 M HNO$_3$</td>
<td>6.8 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>11.0 ± 0.3</td>
<td>1.4 ± 0.1</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>

A comparison of the theoretical equilibrium sorption values showed a marked influence of contaminating solution composition on the extent of Sr contamination (Table 5.1), where uptake increases with HNO$_3$ molarity, and to a greater extent, under basic conditions. In contrast the amount of Cs sorbed was found to be largely independent of solution composition and was found to only marginally increase at elevated pH. Given that the chemical form of Cs in these aqueous solutions is expected to be Cs$^+$ (Takeno, 2005), this result indicates that any variation in the steel surface chemistry that is occurring does not significantly alter the steel’s affinity for Cs$^+$ sorption. This is clearly not the case for Sr, where the inconsistent sorption capacities may suggest Sr uptake is more sensitive to surface speciation derived from variations in the exact steel passivation condition. Alternatively, this result may be due to chemical speciation effects, where the dominant Sr chemical forms at high acid molarity and at alkaline pH possess a higher affinity for sorption. This possibility is examined in more detail in Section 5.4.5. It is well documented that adsorption of Sr$^{2+}$ and Cs$^+$ onto Hydrous Metal Oxide (HMO) sorbents is often promoted under alkaline solution conditions (Trivedi et al., 1999; Mishra et al., 2007; Liu et al., 2014). This behaviour has been rationalised by electrostatic surface complexation models based on the acido-basic properties of the surface hydroxyl groups of the sorbent (Music et al., 1983):
\[ \equiv M - OH + H^+ \rightleftharpoons \equiv M - OH_2^+ \]
\[ \equiv M - OH + OH^- \rightleftharpoons \equiv M - O^- + H_2O \]

where \( \equiv M \) is a surface metal atom.

The importance of similar charge effects for stainless steel surfaces has been discussed in previous radionuclide sorption studies (Fujii et al., 2002; Kádár et al., 2007) and may be responsible for the increase in Sr and Cs uptake at alkaline pH observed in this work. The pH of point of zero charge (pH_{pzc}) for austenitic stainless steels is known to be acidic, reportedly within the pH range of 3.0-4.8 (Fukuzaki et al., 1995; Exartier et al., 2004; Hedberg et al., 2013). It is important to note that these generally accepted values differ considerably with those reported for bulk Fe oxides (pH_{pzc}: 7.5-8.5) (Parks et al., 1962; Lee et al., 1989; Yao et al., 2014) and \( \alpha \)-Cr_2O_3 (pH_{pzc}: 6.2-7.6) (Yates et al., 1975; Lee et al., 1989; Wisniewska et al., 2013), suggesting a fundamentally different charging mechanism occurs for passive metals than for discrete metal oxides. Results from adhesion measurements have indicated that the surface potential of metallic alloys arises not by the dissociation of surface hydroxyl groups but rather through the adsorption of hydronium and hydroxide ions (Lefèvre et al., 2009):

\[ \equiv M - OH + H_3O^+ \rightleftharpoons \equiv M - (OH)(H_3O^+) \]
\[ \equiv M - OH + OH^- \rightleftharpoons \equiv M - (OH)_2^- \]

For the purposes of this work, the exact nature of the charging mechanism is not critical as it is clear that for the HNO_3 matrices, pH < pH_{pzc}, whereas the opposite is the case for the model pond furniture. Accordingly, in the alkaline matrix the steel sorbent will acquire an overall negative charge that will interact favourably with accumulating metal ions. As might be expected from the difference in charge density, the adsorption behaviour of Cs\(^+\) is less sensitive to electrical forces and hence the increased affinity for sorption at alkaline pH is more apparent for Sr\(^{2+}\). In addition, the accelerated initial Sr sorption rate from alkaline solution (Table 5.1) may also be attributed to an attractive electrostatic interaction with the surface. In the case of the nitric acid solutions, the steel surface now exerts a positive potential that will inhibit cationic sorption. Given that this effect is not so pronounced for Cs, it should be considered that electrical forces are only weakly influencing Cs sorption phenomena. Likewise, the higher affinity for Sr uptake under increasingly more acidic conditions cannot be accounted for by charge principles and suggests additional processes are controlling low pH sorption behaviour. This conclusion is
in agreement with a fundamental assumption of the Ho second order kinetic model which states that chemisorption involving valency forces between the surface and accumulating metal ions is rate controlling (Ho et al., 1999). A chemical bonding interaction has also been proposed to describe the accumulation of Cs and Pu onto AISI Type 321 stainless steel from boric acid, and interestingly in this study sorption behaviour was also related to metallurgical parameters (Kádár et al., 2011). On this basis the enhanced Cs sorption rate from 12 M HNO$_3$ (Table 5.1) may be a consequence of the transition from a passive to transpassive region of the steel sorbent, although further investigation is required to confirm this.

5.4.3. Contaminant Depth Distribution

In addition to alloy depth profiling analysis, the depth distribution of Sr and Cs within the steel matrix was also evaluated with GD-OES. Alignment of the Sr maximum signal with the corresponding O and Cr signals (Figure 5.2) demonstrates enrichment of this contaminant within the passive layer. This phenomenon was found to be independent of the contaminating solution composition, despite non-identical amounts of Sr depositing onto the steel surface and an inconsistent elemental composition of the passive layer. The stabilisation of the Fe oxide over-layer at high pH thus does not effectively inhibit inward diffusion of contamination into the material. Rather, the Cr$_2$O$_3$ component, which is traditionally considered the source of corrosion resistance, was observed to also afford protection of the underlying material from contamination phenomena. On this basis, it is not surprising that Sr bulk material diffusion was prominent after contamination in 12 M HNO$_3$ (Figure 5.2C), where IGC was also a characteristic feature for this specimen. It was determined by measurement of the GD-OES crater depth that the Sr penetrating depth from 12 M HNO$_3$ was approximately 150 nm (see Supporting Information Section 5.8.1 and Figure 5.12).

With regards to Cs depth characterisation, no signal could be detected for any of the acidic systems investigated. This is likely due to the small amounts accumulating onto the steel surface where some studies have shown optical based techniques currently do not yield acceptable Cs detection limits (Martin et al., 2012). Due to the slight increase in uptake at elevated pH, it was possible though to determine that Cs contamination is also a surface based phenomenon. As shown in Figure 5.6, Cs enrichment was observed within the Cr enriched oxide layer in similar fashion to Sr. Collectively these depth profiling results demonstrate that a stable Cr$_2$O$_3$ film is an adequate barrier against the mobilisation of contaminants into the bulk material. The total film thickness therefore itself is not of direct
importance as the Fe outer layer of the passive film provides inadequate resistance against Sr and Cs diffusion.

![Graph showing elemental depth profiles](image)

**Figure 5.6.** GD-OES elemental depth profiles of 304 stainless steel contaminated at alkaline pH at 60 °C for 30 days. The Cs signal has been scaled by a factor of 100 for clarity.

### 5.4.4. Spatial Distribution Analysis

Radioactive contamination experiments of stainless steel alloys have reported selective Cs deposition along grain boundaries at elevated temperatures (Bradbury et al., 1978; Matzke et al., 1983). The TOF-SIMS images of 304 stainless steel after contamination in 12M HNO₃ (Figure 5.7) however, shows no obvious enhancement of fission product accumulation at these interface positions. Rather, the most striking result obtained is the alignment of numerous Fe and Cr spherical hotspots that are consistently ~ 2 µm in diameter. Taking into account the solution data of the major alloying elements (Figure 5.3A), these distinctive features may be assigned as once dissolved Fe and Cr material that has re-precipitated onto the steel surface. The remarkably similar morphology and locations of Sr enrichment with Cr, and to a greater extent, Fe hotspots is noteworthy and suggests Sr contamination occurs with the co-adsorption of Fe species. The deposition of corrosion material onto the surfaces of stainless steel construction material during active operations is well documented (Lin et al., 1994; Hirschberg et al., 2001; Varga et al., 2001) and some authors have postulated this may involve co-precipitation with dissolved fuel elements (Dombovári et al., 2007). This possibility is consistent with the observed time dependence of Fe and Sr sorption as both solution profiles exhibit a significant decrease after 6 hours to reach an equilibrium state within 30 days. On this basis, the increasing Sr uptake under more acidic conditions solutions may be rationalised by the higher Fe
solution concentrations that are available to participate in the co-adsorption process. On the other hand, Cs accumulation appears much more homogeneous and no apparent correlation with the Fe and Cr spatial distribution profiles could be identified. This may explain the greatly reduced sensitivity of Cs uptake to acid molarity in comparison to Sr.

Figure 5.7. (A) Secondary electron image of the sputtered area and the corresponding TOF-SIMS maps of (B) Fe, (C) Cr, (D) Ni, (E) Mn, (F) O, (G) Sr, and (H) Cs. The 304 stainless steel specimen was contaminated in 12 M HNO₃ for 30 days at 60 °C. The arrows show the positions of the grain boundaries.
As expected, the decreased Fe and Cr solubility under passive potentials results in a marked reduction in the extent of alloying element re-adsorption, as shown in Figure 5.8 for the alkaline contaminated specimen. Nevertheless, the overlay of Fe and Sr hotspots is still apparent, although this behaviour is clearly not as pronounced as for the acid treated specimen. Instead, this effect is much more evident for deposited Cs, which exhibits a clear correlation with re-accumulating Fe species. The exact role of the re-adsorbing Fe species in facilitating Sr and Cs chemisorption is not clear and further research is clearly needed to better understand this phenomenon. It is important to mention here that similar to the acid contaminated specimen, no preferential accumulation of either Sr or Cs along the grain boundaries was observed. The reduced influence of grain boundaries on Sr and Cs sorption phenomena at both acidic and alkaline pH suggests the contamination mechanisms outlined at high temperature (Bradbury et al., 1978; Matzke et al., 1983) cannot be reasonably applied to our work here. Results of this present study reveal a fundamental contribution of corrosion processes to “plate-out” phenomena at low temperature and therefore reiterate the importance of corrosion performance optimisation. Minimisation of corrosion product solution concentrations by frequent renewal of the reprocessing streams and storage pond solutions may also prove an effective method to limit the extent of radionuclide contamination.
Figure 5.8. (A) Secondary electron image of the sputtered area and the corresponding TOF-SIMS maps of (B) Fe, (C) Cr, (D) Ni, (E) Mn, (F) O, (G) Sr, and (H) Cs. The 304 stainless steel specimen was contaminated in 1 mM NaOH for 30 days at 60 °C. The arrows show the positions of the grain boundaries.
5.4.5. Chemical Speciation Analysis

Strontium accumulation on the steel surface can be characterised by the corresponding Sr 3d3/2 and Sr3d5/2 XPS photoelectron peaks located at ~ 135 and 133 eV, respectively. It should be mentioned that the surface concentrations obtained from contamination in 3 M and 6 M HNO₃ were too low to detect the Sr 3d lines. As a result, data is only presented for the 12 M HNO₃ and 1 mM NaOH solution matrices (Figure 5.9), where Sr uptake was higher (Table 5.1). For the 12 M HNO₃ system, deconvolution of the Sr 3d core electron bands into the 3d3/2 and 3d5/2 components at 135.4 eV and 133.6 eV reveals the most probable bonding environment as SrCrO₄ (Baghni et al., 2004; Chen et al., 2015). This assignment is based on the fact that other plausible chemical forms, such as Sr(NO₃)₂ and SrO, have significantly different 3d5/2 binding energy positions, reported at 134.2 and 132.8 eV, respectively (Young et al., 1985). In combination with the GD-OES depth profile, this local bonding environment may be interpreted as the co-adsorption of Sr²⁺ with the Cr oxide passive layer. A comparison of the XPS spectrum obtained from high pH contamination reveals an additional component at 135.0 and 133.2 eV, corresponding to strontium carbonate (Sosulnikov et al., 1992). The surface complexation of SrCO₃ onto mineral phases has been characterised by X-ray Absorption Spectroscopy (XAS) (Sahai et al., 2000; Carrol et al., 2008) and results have shown aqueous carbonate complexes dominate sorption behaviour above pH 8.7. Therefore, the XPS result in our work is more likely to correspond to surface complexation of SrCO₃ rather than the uniform precipitation onto the steel surface. This result suggests that the co-adsorption of Sr with components of the contaminating solution occurs across a large pH range, and therefore may be an inherent feature to the Sr contamination process.

![Figure 5.9](image.png)

**Figure 5.9.** High resolution XPS spectra of the Sr 3d photoelectron lines for 304 stainless steel contaminated in (A) 12 M HNO₃ and (B) 1 mM NaOH at 60 °C for 30 days.
The local chemical environment of the Cs atoms on the steel substrate can be assessed by the corresponding Cs 3d$_{3/2}$ and Cs 3d$_{5/2}$ XPS lines located at approximately 738 and 724 eV, respectively. With regards to the alkaline matrix, the Cs 3d photoelectron lines could not be detected due to spectral interference with the Fe 2p photoelectron peaks associated with the Fe rich passive layer (see Supporting Information Section 5.8.2). For similar reasons as previously described for GD-OES characterisation, XPS analysis of Cs contamination under acidic conditions could not reliably be performed, where as a result data is only presented for the 12 M HNO$_3$ matrix. Figure 5.10 shows the high resolution XPS spectrum associated with the Cs 3d$_{5/2}$ and 3d$_{3/2}$ photoelectron peaks, which are observed at 723.9 and 737.8 eV, respectively. In comparison, the Cs 3d$_{5/2}$ binding energy positions of standard ionic Cs salts have been measured at 724.2 eV (Wagner et al., 1979). For heavy alkali metals a decreasing binding energy value is typically related to a more oxidising chemical environment (Baba et al., 2015), and hence the values reported here are indicative of a chemical bonding interaction that polarises Cs$^+$. XPS investigations of Cs are somewhat limited by characterisation of Cs(I) compounds and therefore little information is available for more oxidised chemical forms. An examination of the literature suggests that the most probable chemical state is Cs$_2$Cr$_2$O$_7$ (Allen et al., 1973), which analogous to the Sr assignment, may be interpreted as Cs complexation to the Cr rich steel passive layer.

**Figure 5.10.** High resolution XPS spectrum of the Cs 3d photoelectron lines for 304 stainless steel contaminated in 12 M HNO$_3$ at 60 °C for 30 days.
5.5. Conclusions

In this work, the accumulation of Sr and Cs on 304 austenitic stainless steel has been examined in model contamination systems representative of reprocessing conditions. Overall, the experimental results have showed the extent and character of contamination is intimately related to the corrosion state of the steel surface. For a passivated stainless steel material, contamination of these two important fission products was identified as a surface based phenomenon in which selective deposition in the Cr$_2$O$_3$ passive layer occurs. This behaviour was found to be independent of solution pH, despite clear evidence of speciation of the steel surface and accumulating Sr. Under transpassive potentials however, the dissolving passive layer provided poor protection against intergranular attack and was found to be an ineffective barrier against contaminant diffusion into the bulk material. Furthermore, the partial dissolution of the steel surface directly led to an enhanced removal of Sr and Cs from solution, as accumulation was found to occur in tandem with the re-adsorption of Fe. The available results do not permit a complete description of the exact function of once dissolved alloying elements in the Sr and Cs contamination process.

Nevertheless, these results clearly show that the breakdown of the passivating surface oxide layer can promote the initial adsorption and subsequent diffusion of contaminants into the steel matrix. Clearly the dissolution rate of the steel materials must be minimised for the dual purposes of optimising corrosion performance and also for limiting the severity of contamination phenomena. This has clear implications for the design and implementation of reprocessing schemes at nuclear licenced sites. If contaminant diffusion in the bulk material can be effectively inhibited, simultaneous removal of the surface oxide layer and any bound constituents may therefore prove a reliable decontamination technique. We further suggest that direct chemical decontamination treatments may in contrast not be effective due to the presumably strong chemical interaction between the surface and the contaminants that would necessarily have to be overcome for separation.

5.6. Acknowledgments

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5.7. References


5.8. Supporting Information for:

Cesium and Strontium Contamination of Nuclear Plant Stainless Steel

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5.8.1. GD-OES Depth Profiling

For a quantitative assessment of the elemental depth distribution of steel specimens, it is necessary to correlate the GD-OES measurement time with depth of analysis. In this work, the depth of a GD-OES crater generated after 20 seconds of sputtering is determined using laser confocal microscopy (Figure 5.11). Assuming a constant sputtering rate (Boumans, 1972), time can then be converted into depth by an appropriate scaling calculation.

![Figure 5.11](image)

**Figure 5.11.** (A) Optical image, and (B) surface topography profile of GD-OES crater formed on the surface of 304 stainless steel after 20 seconds of continuous sputtering. The steel specimen was contaminated in 1 mM NaOH at 60 °C for 30 days prior to GD-OES measurement.

The crater depth was measured to be 761 nm, corresponding to an average sputtering rate of 38.05 nm s\(^{-1}\). The presentation of GD-OES profiles as a function of sputtered depth (Figure 5.12) reveals the surface oxide thickness after acid and alkaline passivation treatment as 5.7 nm and 11.4 nm, respectively. This result is consistent with a 316L stainless steel passivation kinetic study which reported a film thickness of 4.8 nm after immersion in 6 M HNO\(_3\) for 24 hours (Liu et al., 2015). An equilibrium film thickness was not obtained in this 24 hour study and therefore our reported value of 5.7 nm after 720 hours appears reasonable. In comparison, the resulting oxide layer thickness after passivation in 0.5 M H\(_2\)SO\(_4\) is found to be no greater than 2 nm (Haupt et al., 1995). Hence, the thickness of films grown in HNO\(_3\) is governed by a high anodic potential that promotes Cr\(_2\)O\(_3\) growth, and not by solution acidity.
Figure 5.12. GD-OES elemental depth profiles of 304 stainless steel after contamination in (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and D) 1 mM NaOH aqueous solution, at 60 °C for 30 days. The O and Sr signals have been scaled by a factor of 10 and 100 respectively, for clarity. Note the graphs have different x-axis.

5.8.2. XPS Passive Film Analysis

X-ray photoelectron spectroscopic measurements were carried out to determine the elemental composition of the passive layers formed on 304 stainless steel, where the influence of solution composition was investigated. The XPS spectra of the Fe 2p and Cr 2p photoelectron positions for the four contaminating matrices are shown in Figure 5.13. It is clear that no significant deviation of the binding energy positions occurs, suggesting that the fundamental Fe and Cr oxide components are independent of solution composition. On the other hand, the relative proportion of the Fe and Cr in the film is strongly influenced by the passivating medium. The reduced Fe 2p signal after acid passivation treatment is due to an increased Fe solubility at low pH, whereas a similar effect occurs for Cr under basic conditions. The Fe $2p_{1/2}$ and $2p_{3/2}$ peaks at 724.6 and 710.7 eV, respectively, are associated with Fe$_2$O$_3$ (Yamashita et al., 2008). Furthermore, the contributions at 719.8 and 706.7 eV are due to metallic Fe (Brion et al., 1980; Tan et al., 1990), likely corresponding to
photoemission from bulk material. It is important to note that the feature at ~ 720 eV in the alkaline spectrum may also be ascribed to the Fe 2p\textsubscript{3/2} satellite, where the presence of the corresponding Fe 2p\textsubscript{1/2} satellite at 733.1 eV supports this assignment (Yamashita et al., 2008). In addition, the feature at ~ 742 eV may also be identified as a daughter peak of one of the Fe 2p peaks, although an exact assignment remains unclear (Aronniemi et al., 2005). The Cr 2p\textsubscript{1/2} and Cr 2p\textsubscript{3/2} peaks at 586.2 and 576.7 eV, respectively may be assigned as Cr\textsubscript{2}O\textsubscript{3} (Allen et al., 1973; Shuttleworth, 1980). For a similar reason outlined for Fe, elemental Cr was also identified by the corresponding photoelectron lines at 583.4 and 574.1 eV (Moffat et al., 1995). These results reveal that, in combination with the GD-OES data, a fundamental structure of the passive layer is a Cr\textsubscript{2}O\textsubscript{3} layer underneath a Fe\textsubscript{2}O\textsubscript{3} over layer. The relative concentrations of these two components are highly sensitive to the solution pH, where Cr grows at the expense of Fe oxide under acidic conditions. The surface enrichment of Fe after high pH treatment is also apparent, although this effect is more subtle owing to the high Fe oxide content in the passive film formed by atmospheric exposure. The increased Fe stability within the passive film under alkaline conditions has important ramifications for the identification of Cs present in the steel material as the Cs 3d photoelectron are likely to be masked by the more prominent Fe 2p peaks (Figure 5.13). Thus, despite an increased amount accumulating on the steel surface (see Table 5.1) no Cs could be detected on the steel surface after alkaline contamination.

![Figure 5.13](image-url) XPS high-resolution spectra of (A) Fe 2p, and (B) Cr 2p photoelectron peaks of 304 stainless steel as a function of passivation treatment.

5.8.3. Sr and Cs Kinetic Modelling

The rate of adsorption for the Lagergren first order model is dependent on the sorption capacity of the substrate, which is expressed as (Lagergren, 1898):
\[
\frac{dq_t}{dt} = k(q_e - q_t)
\]

where \(q_e\) is the equilibrium uptake (g m\(^{-2}\)) and \(k\) is the first order rate constant (hr\(^{-1}\)). The integrated form over the boundary conditions \(t = 0\) to \(t = t\) and \(q_i = 0\) to \(q_t = q_t\) is

\[
\log(q_e - q_t) = -kt + \log(q_e)
\]

Therefore, a plot of \(\log(q_e - q_t)\) against \(t\) will yield a linear relationship of gradient \(-k\) and a y-intercept of \(\log(q_e) / k^2 q_e^2\) is obtained. Therefore, a fundamental disadvantage of this kinetic model is that some knowledge of the equilibrium sorption capacity must be known. In this work, the maximum \(q_t\) value measured for each individual sorption was taken as \(q_e\). The first order kinetic plots are shown in Figure 5.14 for all systems studied, where the first order rate constant can be determined by the gradient of the fit.

**Figure 5.14.** Lagergren first order kinetic fits for the sorption of Sr and Cs on 304 stainless steel from (A) 3 M HNO\(_3\), (B) 6 M HNO\(_3\), (C) 12 M HNO\(_3\), and (D) 1 mM NaOH, at 60 °C.
Another kinetic model tested was the Elovich model (Figure 5.15). In the Elovich equation, the overall rate of analyte removal from solution is derived from competing adsorption and desorption processes (Low, 1960), which is expressed as:

\[
\frac{dq_t}{dt} = \alpha e^{-\beta q_t}
\]

where \(q_t\) is the amount sorbed at time \(t\), \(\alpha\) is the initial sorption rate (g m\(^{-2}\) hr\(^{-1}\)) and \(\beta\) is a constant related to the rate of desorption (m\(^2\) g\(^{-1}\)). The integrated form over the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_i\) is

\[
e^{\beta q_t} = \alpha t + \frac{1}{\beta}
\]

Rearranging into the linear form yields

\[
q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln t
\]

where

\[
t_0 = \frac{1}{\alpha \beta}
\]

In order to simplify this kinetic model, it is often assumed that \(\alpha \beta t > 1\) i.e. the contribution of \(t_0\) is negligible (Chien et al., 1980). The rate equation then becomes:

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]

When the \(q_t\) is plotted against \(\ln t\), a linear plot of gradient \(1/\beta\) and a \(y\)-intercept of \(\ln(\alpha \beta)/\beta\) is obtained. The corresponding kinetic plots are shown in Figure 5.15 for all for systems studied, where the values of \(\beta\) and \(\alpha\) can be calculated from the slope and intercept of the fits, respectively.
Figure 5.15. Elovich kinetic fits for the sorption of Sr and Cs on 304 stainless steel from (A) 3 M HNO$_3$, (B) 6 M HNO$_3$, (C) 12 M HNO$_3$, and (D) 1 mM NaOH at 60 °C.

The statistical results of the Ho, Lagergren, and Elovich kinetic fits are summarised in Table 5.2. It can clearly be seen that the Lagergren and Elovich equations do not give reasonable $R^2$ values and in all cases Sr and Cs sorption behaviour can be more accurately described by Ho second order kinetics.

Table 5.2. Comparison of the co-efficient of determination ($R^2$) values obtained from the linear plots of the Ho, Lagergren, and Elovich kinetic models used to characterise Sr and Cs sorption onto 304 stainless steel.

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>Ho 2nd order $R^2$</th>
<th>Lagergren 1st order $R^2$</th>
<th>Elovich $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO$_3$</td>
<td>0.997</td>
<td>0.137</td>
<td>0.778</td>
</tr>
<tr>
<td>6 M HNO$_3$</td>
<td>0.991</td>
<td>0.861</td>
<td>0.727</td>
</tr>
<tr>
<td>12 M HNO$_3$</td>
<td>0.994</td>
<td>0.819</td>
<td>0.947</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>0.995</td>
<td>0.850</td>
<td>0.930</td>
</tr>
</tbody>
</table>
5.8.4. References


6. Effect of Cold Work on Cesium and Strontium Contamination of Nuclear Plant Stainless Steel

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6.1. Abstract

The deposition of radionuclides onto nuclear plant stainless steel components is a major decommissioning problem that has historically been studied from a chemistry perspective. The advancement of satisfactory decontamination solutions requires a comprehensive understanding of the sorption mechanisms that underpin contamination processes. To this end, it is important from the viewpoint of safe waste management to characterise the role of metallurgical variables on radionuclide accumulation behaviour. This work investigates the effect of varying microstructural parameters by cold work on \(^{90}\text{Sr}\) and \(^{137}\text{Cs}\) accumulation into austenitic Type 304 stainless steel from nitric acid-based reprocessing streams and sodium hydroxide spent fuel storage ponds. Comparison with the findings of our previous contamination study of as-received 304 stainless steel reveals uptake is universally increased by cold working. This behaviour was rationalised by examining the relationship between metallurgical properties and corrosion behaviour. The relative Cr content of the passive layer after contact with concentrated HNO\(_3\) was found to increase with cold work, enabling the film to maintain Sr and Cs contaminants at the surface. In combination with alkaline passivation however, cold working has the opposite effect of depleting Cr from the surface. Under these conditions the passive layer becomes a less effective barrier against fission product diffusion into the bulk material. These results emphasise the synergistic effect of metallurgical and environmental factors towards contamination phenomena.
KEYWORDS: cesium, strontium, stainless steel, cold rolling, decommissioning

6.2. Introduction

Austenitic stainless steels are important structural materials within the nuclear industry owing to a combination of outstanding corrosion resistance, tensile strength, and mechanical properties (Shaw, 1990). The remarkable corrosion performance of these alloys is attributed to the spontaneous formation of a Cr rich surface oxide layer that passivates the underlying bulk material. The association of radioactive species with this passive film during normal operations is responsible for a significant fraction of legacy nuclear waste (Adeleye et al., 1996). The high economic cost associated with the continued storage of radioactive waste (e.g. NDA, 2016) dictates that the development of safe decontamination methodologies is a decommissioning priority. The optimisation of waste management strategies however requires a comprehensive analysis of key processes that control radionuclide sorption behaviour. For this reason, researchers have utilised laboratory contamination systems to elucidate valuable information about contamination phenomena as documented on-site (IAEA, 2006).

The initiation of severe IGC of stainless steel fuel cladding material at temperatures of approximately 650 °C has for example, been related to the deposition of the volatile product, $^{137}$Cs, onto the steel surface (Adamson et al., 1985). Electron-based spectroscopic measurements revealed Cs chemisorption creates local ruptures within the Cr$_2$O$_3$ passive film that are significantly less resistant to corrosive attack (Bradbury et al., 1978; Sasaki et al., 2013). In turn, these vulnerable sites act as efficient diffusion pathways for the transfer of unreacted Cs into the bulk material, a phenomenon propagated by Cr depletion from the microstructure. Thus, corrosion performance is further weakened as Cs penetrates into the material. Although these contamination processes are known to be thermodynamically unfavourable at low temperature (Antill et al., 1975), corrosion resistance has nevertheless been identified as an important factor controlling the radionuclide retention properties of austenitic stainless steels under ambient temperatures (Kádár et al., 2010). Radioactive contamination studies of PWR cooling circuits have reported a transition from physical to chemical sorption without modification to boric acid solution composition (Kádár et al., 2011). This behaviour was attributed to inconsistencies in the passive layer thickness and elemental composition of the steel materials investigated. Some information was also presented that suggested that radionuclide accumulation may induce modifications in the
passive layer composition by influencing metal dissolution (Hirschberg et al., 2001) and re-adsorption (Dombovári et al., 2007) processes at the steel surface. On the basis of these results, it is apparent that an unqualified, but important relationship between contamination and corrosion processes exists. This indicates that an evaluation of variables that may influence corrosion resistance is of great importance for obtaining a complete understanding of radioactive accumulation processes.

In order to obtain the required geometry for industrial environments, steel components are subject to machining and cold rolling treatments that inevitably introduce strain into the material (Elayaperumal et al., 1972). The uncontrollable modification of corrosion resistance by plastic deformation is not fully understood, where the corrosion performance of austenitic stainless steels has been reported to increase (Farkhutdinov et al., 1994), decrease (Barbucci et al., 2001), or be non-monotonously affected (Kumar et al., 2005; Kumar et al., 2007; Peguet et al., 2007) by cold work. This dispersion is likely due to a complex relationship between deformation behaviour of these materials and environmental interactions. The influence of cold work has been linked, for example, to changes in martensite content (Semino et al., 1979, Alvarez et al., 2013), grain morphology (Grabke et al., 1998), residual stresses (Vignal et al., 2010), and crystallographic texture (Phadnis et al., 2003; Kumar et al., 2007). Although elucidation of an exact deformation mechanism is unrealistic, it is clear that stainless steel corrosion resistance is highly sensitive to microstructure and cold working (Krawczyk et al., 2017). This correlation introduces unexplored implications on the character of contamination processes involving piping and other stainless steel components that are subjected to strain processing regimes prior during forming and manufacturing processes.

The reprocessing of irradiated nuclear fuel to isolate U and Pu is accomplished using the PUREX process, a series of complex chemical extractions using nitric acid as a matrix (Sood et al., 1995). To reduce radiation levels, spent fuel is initially stored underwater in alkaline cooling ponds prior to reprocessing (Wilson, 1996). The deposition of radionuclides onto stainless steel components, such as AISI Type 304, during these activities has previously been examined in terms of environment chemistry. The effect of solution pH (Rouppert et al., 2000), radionuclide chemical speciation (Adeleye et al., 1995), and liquid turbulence (Adeleye et al., 1996) on the extent of contamination has been studied. The influence of microstructural variables in contrast, has not been researched in any detail and therefore the importance of strain treatments on radionuclide sorption behaviour is unknown. To clarify these uncertainties, it is important to characterise the
effect of cold working on contamination phenomena under acidic and basic conditions representative of spent fuel storage and reprocessing activities.

To examine the relationship between steel microstructural parameters and radionuclide contamination processes, we investigate the radioactive contamination of 30% cold rolled type 304 stainless steel surfaces. The selection of this engineering strain was chosen to take into account a typical amount of cold work or service hardened steel components (Elayaperumal et al., 1972). A series of model experiments that mimic the nitric acid reprocessing streams of the PUREX process and alkaline spent fuel pond furniture were performed to investigate $^{90}$Sr and $^{137}$Cs sorption. These two high yield fission products collectively account for a significant fraction of the total deposited surface activity (Choppin et al., 2002) and therefore a better understanding of their accumulation properties is highly desirable. Results of these experiments are compared to data from our earlier contamination study of 304 stainless steel (Lang et al., 2017A) to identify alterations in sorption behaviour induced by cold working. Understanding the contribution of microstructure variables to the radionuclide retention properties of stainless steels may provide fundamental insights into contamination phenomena needed to support decontamination strategies.

6.3. Experimental Section

6.3.1. Materials and Procedures

As received (AR) AISI Type 304 stainless steel material with a chemical composition of (wt. %) 18.15 Cr, 8.6 Ni, 1.38 Mn, 0.055 C, 0.45 Si, 0.04 P, 0.038 N, 0.005 S was used in this paper. Strips with dimensions 100 mm x 20 mm x 13 mm (l x w x t) were cut from a base material and uni-directionally cold rolled at room temperature to a thickness of reduction of 30% (i.e. 9.1 mm) to introduce strain into the material. Cold worked samples, referred as 30% CW, were cut into individual specimens of dimensions 10 mm x 10 mm x 9.1 mm (l x w x t) and mechanically ground using 4000 SiC emery paper. This surface was then polished to a 1 µm mirror finish and was degreased with ethanol and distilled water prior to contamination.

The contamination of 30% CW 304 stainless steel was performed under identical experimental conditions as described in our earlier investigation of the contamination behaviour of AR 304 stainless steel (Lang et al., 2017A). In doing so, the results obtained in this contribution would permit a direct insight into the effects of steel metallurgy on Sr and Cs contamination behaviour across a wide pH range. All steel specimens were
contaminated for 30 days thereafter the samples were removed and immediately washed with deionised H₂O followed by IPA prior to surface analysis.

6.3.2. Electron Microscopy Analysis

The surface morphology of the cold rolled steel material after passivation in the Sr and Cs solution matrices was characterised by scanning electron microscopy (SEM). Electron microscopy images were obtained using a FEI Quanta 200 (E)SEM microscope operated at an accelerating voltage of 20 kV. SEM images were collected at a magnification of 1600x, corresponding to an area of approximately 150 µm x 150 µm.

6.3.3. X-ray Diffraction (XRD) Phase Analysis

The phase evolution after cold rolling treatment was evaluated using X-ray diffraction (XRD) with a Philips X’Pert Modular Powder using a Cu-Kα (λ = 1.540598 Å) radiation at 40 kV and 40 mA. A 2 hour scan with a step size of 0.03 for a total of 3381 data points was used during scanning. The procedure for quantitative phase composition analysis is presented in the Supporting Information Section 6.8.1.

6.3.4. Electron Backscatter Diffraction (EBSD) Analysis

The microstructural transformations induced by cold rolling were characterised by electron backscatter diffraction (EBSD). For the EBSD procedure, as received and cold rolled specimens surfaces were additionally polished to 0.25 µm diamond paste finish, followed by OPS colloidal silica fine polishing. EBSD analysis was performed using a FEI Quanta 650 field emission gun scanning electron microscope (FEG-SEM) equipped with a HKL Nordlys EBSD detector. Operating at an accelerating voltage of 20 kV and a step size of 0.5558 µm the area scanned for both specimens was approximately 500 µm x 400 µm. The collected data was analysed with Channel 5 software.

6.3.5. X-ray Photoelectron Spectroscopy (XPS) Analysis

The elemental composition of the steel passive layer and the local bonding environments of deposited fission product contaminants were evaluated using spectroscopy (XPS). High resolution scans were obtained using a Kratos AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical) that employed a monochromatic Al X-ray source (1486.69 eV). Calibration of the binding energy scale was performed using the C 1s hydrocarbon signal at 284.6 eV as the reference peak. The relative fractions of Cr and Fe cations in the oxide film were calculated as the relative mass ratio (e.g. Croxide / (Croxide +
Fe$_{\text{oxide}}$) using the integrated areas of the Cr 2p ($\sim$ 575 and 584 eV) and Fe 2p ($\sim$ 710 and 723 eV) peaks, respectively. Spectra were recorded in duplicate and the average surface composition ratios are presented.

**6.3.6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Solution Analysis**

The extent and kinetics of Sr and Cs removal onto the steel surfaces was monitored by quantitative elemental analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. Here, 1 mL aliquots of the contaminating matrices were removed at the following time intervals (0.17, 1, 6, 24, 168, 336, 504, 672 h) and were subject to centrifugation (13,150 g for 45 minutes). Thereafter 500 µL of the resulting supernatant was isolated and diluted into 2 % HNO$_3$. ICP-MS analysis was performed using an Inductively Coupled Plasma Mass Spectrometer (Agilent 7500cx), in which solution analysis was carried out on the two contaminants (Sr, Cs) and the major alloying elements (Fe, Cr, Ni). The purpose of this was to evaluate the effect of solution conditions on the corrosion behaviour of the steel surfaces. All solutions were stored at 4 °C prior to analysis to minimise loss of analyte material by evaporation. Each sorption experiment was performed in triplicate and the concentration values were averaged. The amount of Sr and Cs adsorbed at time $t$, $q_t$ (g m$^{-2}$) was calculated as follows:

$$q_t = \frac{(c_0 - c_t) \times V}{A}$$

where $c_0$ and $c_t$ are the solution concentrations at time = 0 and $t$, respectively (g L$^{-1}$), $V$ is the volume of solution (L), and $A$ is the surface area of the exposed steel surface (m$^2$).

**6.3.7. Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) Analysis**

The elemental distribution of Cs and Sr and the alloying elements on the steel surface was assessed using TOF-SIMS (IONTOF GmbH, Münster, Germany) of the reflectron-type. All measurements were carried out using a pulsed Bi/Mn liquid metal ion gun (30 keV) operated at a 0.8 µA emission current. A 30 ns pulse width of the primary ion bunch at a 100 µs cycle time enabled a mass resolution of secondary ions in excess of 8000 amu. High resolution imaging was performed on scanning areas up to 50 µm x 50 µm and 20 µm x 20 µm areas, as necessary. In all cases the most abundant isotopes were selected for characterisation. Depth resolved characterisation was performed by combining the Ar Gas Cluster Ion Beam (GCIB) for the continuous etching of the steel surface by the incident ion beam with the Liquid Metal Ion Gun (LCIB) in spectrometry mode. The experimentally
measured ion signals were normalised to the total ion count to account for variation in the incident ion current.

6.4. Results and Discussion

6.4.1. Microstructural and Surface Alteration of Steel Specimens by Cold Working

In general, corrosion behaviour is determined by the steel microstructure and environment chemistry (Sedriks, 1986). Hence, it was considered necessary to first characterise the effect of cold working on both microstructure variables and the passive layer elemental composition after immersion in the various contaminating matrices. These results may prove useful for rationalising any subsequent changes in Sr and Cs contamination behaviour that incur from cold working.

In our previous contribution, the AR specimen showed the onset of intergranular corrosion (IGC) after contact with 12 M HNO₃ (Figure 6.1A; Lang et al., 2017A). This phenomenon is characteristic of transpassive behaviour in strongly oxidising media such as concentrated nitric acid (Fauvet et al., 2008). It is known that in addition to IGC, the small amounts of delta (δ)-ferrite remaining within the microstructure are prone to preferential corrosive attack in concentrated HNO₃ (Shankar et al., 2012). Interestingly, this form of corrosion morphology is not observed for the cold worked surface after identical acid treatment (Figure 6.1B), where attack along the grain boundaries is also much less pronounced. Thus, corrosion resistance in HNO₃ is slightly improved by the introduction of strain into the microstructure. The suppression of intergranular attack in concentrated nitric acid by cold working has been noted previously (Mayuzum et al., 1998), and has been related to favourable structural modifications near the vulnerable grain boundaries during deformation (Hahin et al., 1976). One of the most important parameters influencing deformation behaviour is the stacking fault energy (SFE) of the austenite matrix. The SFE, a function of temperature and alloying composition, determines the ease of cross slip and thus becomes a controlling factor in the dominant deformation mode at different stages of deformation (Chowdhury et al., 2005). For low to medium SFE materials, such as 304 stainless steel, a combination of deformation twins and shear band intersections become prominent microstructural features after cold working (Choi et al., 1997; Hadji et al., 2002), as shown in Figure 6.1B. It is interesting that several studies have found cold working weakens stainless steel corrosion resistance in sulphuric media (Elayaperumal et al., 1972; Barbucci et al., 2001; Barbucci et al., 2002). The contrasting corrosion behaviour in acidic media demonstrates the overall effect of cold work on corrosion behaviour is
strongly dependent on environment factors. On this basis, one would expect the acidic and alkaline systems investigated in this study to experience different responses to cold rolling treatment (Krawczyk et al., 2017).

Figure 6.1. Surface morphology of (A) as-received (AR), and (B) 30 % cold worked (30 % CW) 304 stainless steel surface after immersion in 12 M HNO₃ aqueous solution, at 60 °C for 30 days. The black arrows mark ferrite stringers. Figure 1A is adapted from (Lang et al., 2017A).

It is well documented that many shear band intersections act as nucleation sites of martensite embryos in austenitic stainless steels (Chang et al., 1995). Comparison of the XRD diffraction patterns of AR and 30 % CW 304 stainless steel (Figure 6.2) clearly show an increase in diffraction peak intensities of bct α'-martensite after 30 % cold rolling treatment. In contrast, the corresponding fcc austenite diffraction peaks are suppressed after cold working. The extent of austenite transformation to α'-martensite is sensitive to many complex factors, such as strain rate (Kumar et al., 2007), rolling temperature (Jinlong et al., 2015), inclusion/exclusion of interpass cooling (Kumar et al., 2004), and alloying composition (Hadji et al., 2002). A detailed mechanistic discussion of strain induced α'-martensite formation has been described elsewhere (Celada-Casero et al., 2017) and is beyond the scope of this paper. Nonetheless, it was determined that cold working led to a volume fraction of α'-martensite of approximately 10 %, a value in good agreement with previous phase analysis of AISI 304L stainless steel subject to similar experimental conditions of strain engineering (Kumar et al., 2005; Kumar et al., 2007). The appearance of low intensity α'-martensite peaks in the diffraction pattern of the AR material may be attributed to small amounts of δ-ferrite present which yields similar diffraction peak...
positions as $\alpha'$-martensite. Furthermore, $\varepsilon$-martensite, a possible intermediate structure in the deformation of 304 stainless steel (Hadji et al., 2002), could not be detected. The inhibition of $\varepsilon$-martensite production in this work may be attributed to the low strain levels applied at room temperature (da Rocha et al., 2009), where the total amount present may be below the limit of detection for XRD analysis. Other workers have related the negative effects of cold working on corrosion performance to $\alpha'$-martensite formation (Alvarez et al., 2013) as it has been shown that $\alpha'$-martensite selectively corrodes at lower potentials than austenite in acidic media (Semino et al., 1979). As the detrimental corrosion effects of martensite have been found to be insignificant for low to moderate thickness reductions ($< 50 \%$) in HNO$_3$ (Hahin et al., 1976), this indicates other microstructural variables dominate corrosion behaviour in the PUREX reprocessing streams.

![Figure 6.2. Typical XRD patterns of AR and 30 % CW 304 stainless steel.](image)

The positive influence of cold work on corrosion resistance is mainly due to the formation of efficient diffusion pathways for Cr into the passive layer, accelerating film growth and repassivation processes. An exact mechanism describing Cr transportation through the rolled material has not been confirmed, where various microstructural variables such as grain boundaries (Trillo et al., 1995), texture (Phadnis et al., 2003) and vacancies and dislocations (Singh et al., 2003; Kain et al., 2004) have been proposed to dominate long range Cr diffusion kinetics. The beneficial effects of crystallographic orientations on corrosion resistance has been shown to be negligible for low to moderate thickness reductions ($< 60 \%$) (Kumar et al., 2005). The microstructures of the AR and 30 % CW steel specimens are shown in Figure 6.3. Overall, the grain morphology produced by cold
rolling is of a compressed and elongated character. Moreover, a reduction in grain size from $14.5 \pm 2.8$ to $7.1 \pm 2.2 \, \mu m$ was determined after cold work.

![Crystal orientation EBSD maps obtained for (A) AR, and (B) 30 % CW 304 stainless steel.](image)

**Figure 6.3.** Crystal orientation EBSD maps obtained for (A) AR, and (B) 30 % CW 304 stainless steel.

The increasing grain boundary density associated with grain refinement may therefore facilitate Cr replenishment in the passive layer, and thus play an important role in improving corrosion resistance in concentrated nitric acid. To investigate this possibility, the elemental composition of the as-received and 30 % CW surfaces were characterised by XPS using the ratio $\frac{Cr_{oxide}}{(Cr_{oxide} + Fe_{oxide})}$. The credibility of this approach relies on the assumption that the passive film is composed of Fe and Cr only (Asami et al., 1977; Storp et al., 1977). After air passivation, XPS showed the surface oxide formed on the deformed surface was depleted in Cr (Figure 6.4A), a result previously attributed to selective Fe oxidation under the heating influence of the rolling process (Houmard et al., 2007). After immersion in the model pond furniture, the Cr surface content is found to decrease for both specimen types as Cr is slightly soluble in alkaline solution (Olsson et al., 2003). Given that the $\frac{Cr_{oxide}}{(Cr_{oxide} + Fe_{oxide})}$ ratio for the cold rolled specimen remains noticeably lower
as compared to the AR specimen, it would seem that a synergistic coupling of metallurgical and environmental factors is promoting Cr depletion at alkaline pH.

In contrast, the contribution of overheating effects become negligible after acid passivation since Cr is observed to become the major constituent of the passive film. Such an inversion in the relative Fe and Cr concentrations is understood to be a consequence of Fe dissolution at acidic pH, leaving Cr enriched at the surface (Wallinder et al., 1999; O’Laoire et al., 2006; Liu et al., 2015). To confirm this, in situ solution analysis was performed to quantify the release of major alloying elements into the Sr and Cs bearing liquors. Significant amounts of Fe were released from both the AR and 30 % CW specimens, as shown in Figures 6.4B and C, respectively. Furthermore, small amounts of Cr are released into 12 M HNO₃ solution for both specimen types, a result consistent with the onset of IGC. The slight decrease of Cr emission from the worked material may be considered evidence of strengthened corrosion resistance. Since it is expected that a passive domain is maintained for the less acidic systems investigated (Fauvet et al., 2008), it is not surprising that Cr could only be detected in the most concentrated acid solution in this study. The increased tendency of Fe dissolution from the cold rolled specimen in acidic matrices may also account for the slight increase in the (Cr oxide/Cr oxide + Fe oxide) ratios, as indicated in Figure 6.4A.

A more distinctive feature of the solution data however is the time dependence of Fe and Cr concentrations. They differ significantly for specimens in the as received and worked condition. It is evident that the solution profiles of AR stainless steel exhibited a maximum Fe and Cr concentration after 6 hours, followed by a significant decline to an equilibrium value with the timeframe of the study (Figure 6.4B). In contrast, for the deformed material an initially intense period of active dissolution of main alloying elements is followed by release at a diminished rate before rapid equilibration is obtained (Figure 6.4C). Taking into account elemental spatial mapping, this result in our previous study was attributed to the co-adsorption of once dissolved corrosion species with Sr and Cs (Lang et al., 2017A). The noticeable absence of a decreasing Fe and Cr solution concentration in this present study indicates Fe and Cr dissolution dominates re-adsorption processes at the deformed surface. This suggests an alternative sorption mode is controlling Sr and Cs contamination.
Figure 6.4. (A) Evolution of $\text{Cr}_{\text{oxide}}/(\text{Cr}_{\text{oxide}} + \text{Fe}_{\text{oxide}})$ of AR and 30 % CW 304 stainless steel surfaces as a function of passivation treatment. Time dependence of Cr (left axis) and Fe (right axis) solution concentration for (B) AR and (C) 30 % CW 304 stainless steel. Data presented in Figure 4A and B is adapted from (Lang et al., 2017A).

6.4.2. Sr and Cs Kinetic Studies

Strontium and Cs uptake onto the varying steel surfaces is shown in Figure 6.5. It can be seen that significant amounts of Sr and Cs are removed onto the steel surface within 10 minutes of initial contact. In all instances a pseudo-equilibrium state was obtained within 30 days. It is important to mention here that previous studies investigating radioactive
contamination of stainless steel (Adeleye et al., 1995; Répánszki et al., 2007) have also recorded short equilibration times with qualitatively similar time-variation curves.

**Figure 6.5.** Effect of contact time on Sr and Cs uptake ($q_t$) onto 30% CW 304 stainless steel from (A) 3 M HNO$_3$, (B) 6 M HNO$_3$, (C) 12 M HNO$_3$, and (D) 1 mM NaOH solution at 60 °C.

In our previous paper, the Ho second order equation was used to describe the adsorption of Sr and Cs on AR 304 stainless steel surfaces from all solution compositions studied (Lang et al., 2017A). The reliability of this kinetic model to describe Sr and Cs sorption onto 30% CW stainless steel surfaces was subsequently tested in this contribution. This rate equation considers the driving force for sorption to diminish with time as the number of free surface sites decreases. The linear form of this kinetic description is written as (Ho et al., 1999):

\[
q_t = \frac{1}{k_f} 
\]
\[
\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2}
\]

where \(q_e\) is the equilibrium sorption capacity (g m\(^{-2}\)) and \(k_2\) is the second order rate constant (m\(^2\) g\(^{-1}\) hr\(^{-1}\)). If Sr and Cs adsorption follows this kinetic model then a kinetic plot of \(t/q_t\) against \(t\) will yield a linear relationship from which the equilibrium capacity, \(q_e\), and second order rate constant, \(k_2\), may be calculated. The initial sorption rate may also be calculated as follows:

\[
h = k_2 q_e^2,
\]

where \(h\) is the initial sorption rate (g m\(^{-2}\) hr\(^{-1}\)) as \(t \rightarrow 0\).

Figure 6.6 shows the kinetic plots of \(t/q_t\) against \(t\) for Sr and Cs sorption onto 30 % CW 304 stainless steel where in all instances, a linear relationship is observed. The consistently high coefficient of determination for all for systems investigated (R\(^2\) > 0.99) strongly suggests that the entire adsorption period can be accurately described by second order kinetics. Other kinetic equations investigated did not yield satisfactory correlation coefficient values in our study and were found to poorly describe Sr and Cs accumulation over the entire sorption period. These results are presented in the Supporting Information Section 6.8.2. The applicability of the second order equation to accurately describe Sr and Cs accumulation on AR and 30 % CW steel surfaces strongly suggests that the rate controlling interaction driving contamination is unperturbed by cold working. In particular, these results demonstrate that a chemisorption process involving valency forces between accumulating metal ions and the steel surfaces is rate controlling (Ho et al., 1999).
Figure 6.6. Ho second order kinetic fits for the adsorption of Sr and Cs onto 30 % CW 304 stainless steel from (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH solution at 60 °C.

The theoretical equilibrium sorption capacities (qₑ) obtained from the gradient of the linear plots (Table 6.1) are consistent with the experimental data, (Figure 6.5), thus providing additional support for the validity of our model selection. Other kinetic parameters calculated from the Ho second order equation are discussed in more detail in Supporting Information (see Supporting Information Section 6.8.2. and Tables 6.3. and 6.4).
Table 6.1. Calculated equilibrium sorption capacity \( (q_e) \) of second order kinetics of Sr and Cs accumulation onto 30 % CW and AR 304 stainless steel. The data for the as-received specimen is reproduced from (Lang et al., 2017A)

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>( q_e ) (g m(^{-2})) for 30 % CW 304</th>
<th>( q_e ) (g m(^{-2})) for AR 304</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sr</td>
<td>Cs</td>
</tr>
<tr>
<td>3 M HNO(_3)</td>
<td>11.2 ± 0.3</td>
<td>11.0 ± 0.2</td>
</tr>
<tr>
<td>6 M HNO(_3)</td>
<td>9.7 ± 0.7</td>
<td>9.7 ± 0.4</td>
</tr>
<tr>
<td>12 M HNO(_3)</td>
<td>9.9 ± 0.5</td>
<td>10.2 ± 0.6</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>19.5 ± 0.5</td>
<td>13.2 ± 0.1</td>
</tr>
</tbody>
</table>

This data indicates that the extent of Sr and Cs accumulation significantly increases with the introduction of strain into the material, irrespective of the composition of the solution matrix. Thus, microstructural factors clearly play an important role in contamination processes. Moreover, Sr contamination as a function of acid molarity is noticeably different after the two processing regimes. Whilst accumulation onto AR material is promoted under more acidic conditions, it is quite obvious that Sr sorption onto a deformed surface is largely unaffected by such subtle variations in solution composition. The reduced sensitivity of Sr uptake to acid molarity in this work suggests changes in metallurgical variables dominate contamination behaviour at acidic pH. In a similar manner, Cs uptake was also found to be effectively independent of solution composition across such a small pH range, although this behaviour occurred irrespective of processing regime. Therefore, the constancy of Cs uptake should be interpreted to be primarily a result of environmental factors.

The maximum Sr and Cs surface concentrations of the 30 % CW sample, determined as \( \sim 19.5 \) g m\(^{-2}\) and 13.2 g m\(^{-2}\) respectively, occurred under alkaline contaminating conditions. A similar tendency was observed for AR steel surfaces (Table 6.1), and was attributed to a minor electrostatic attraction that slightly enhances uptake at elevated pH. This interpretation is consistent with arguments that physical forces associated with surface acid-bases reactions are responsible for a pH dependence of metal ion sorption onto stainless steel (Fujii et al., 2002). The effect of surface speciation on Cs sorption affinity has been described using a series of chemical equilibria involving accumulating Cs and surface hydroxyl groups of 304L stainless steel sorbent (Rouppert et al., 2002):

\[
\equiv MOOH \rightleftharpoons \equiv MOO^- + H^-
\]
\[ \equiv MOO^- + Cs^+ \rightleftharpoons \equiv MOOCs \]

where \( \equiv M \) is a surface metal atom.

In accordance with these chemical equilibria, an increasingly more basic system creates additional negative surface sites that interact favourably with metal ions such as Cs\(^+\) and Sr\(^{2+}\). Surface speciation effects however should not be considered the only cause of higher \( q_e \) values at alkaline pH because analogous to the acid systems uptake is significantly more pronounced for the cold work specimen. As such, steel metallurgy plays an important role in the extent and character of contamination phenomena across a large pH range.

### 6.4.3. Contaminant Depth Distribution

In our previous investigation, depth analysis of AR steel specimens was carried out using glow discharge optical emission spectrometry (GD-OES) (Lang et al., 2017A). In this study TOF-SIMS analysis was performed to evaluate contaminant depth in 30\% CW specimens as the associated sample preparation requirements could be more readily satisfied. In order to investigate dependence of Sr and Cs contamination depth on solution pH, measurements were performed for AR and 30\% CW steel specimens contaminated in 12 M HNO\(_3\) and 1 mM NaOH, respectively. Results from the analysis of AR coupons were compared to GD-OES data to evaluate the depth resolution of TOF-SIMS in this study (Lang et al., 2017A).

To obtain quantitative depth information, it is necessary to measure the etching rate and calculate the depth scale. The surface roughness of the steel specimens however, made it challenging to accurately determine the total depth, meaning only a qualitative interpretation of results was possible. A procedure for qualitative depth analysis of stainless steel materials has been explained elsewhere (Lang et al., 2017B), and involves monitoring the decaying O signal to identify the sputtering time that corresponds to complete removal of the passive layer. Knowledge of the measurement time that coincides with the interface of the surface oxide and bulk material may then be used as a reference marker for a qualitative assessment of Sr and Cs contaminant depth.

Under strongly acidic conditions, it can clearly be seen that the passive film formed on the surface of AR material is an inadequate barrier against enhanced transfer of Cs and Sr contaminants into the bulk material (Figure 6.7A), a result that is in agreement with previous GD-OES characterisation. On the other hand, for the cold worked specimen, the oxide surface now effectively maintains Sr and Cs at the surface (Figure 6.7B), and thus
fundamentally alters the character of contamination. As Cr is usually considered the most important element influencing passivity strength, an increased Cr\text{oxide} content arising from cold rolling (Figure 6.4A) may give a plausible explanation for the film’s improved capabilities to mitigate contamination diffusion. This result is somewhat unexpected as uptake was found to be promoted by cold rolling, thus demonstrating \( q_s \) is not necessarily proportional to contaminant depth. Since Sr and Cs deposition and build up onto the worked material are related to the passive layer condition, alterations in contamination behaviour should be examined by considering the sensitivity of passive layer characteristics to deformation. In this work it is not possible to evaluate the contribution of each effect produced by cold rolling to the enhancement of contamination phenomena.

The combination of 30 \% CW with alkaline contaminating conditions was observed to have the opposite effect on Sr contaminating depth as noted at acidic pH. As indicated by a comparison of Figures 6.7C and D, cold rolling promotes Sr diffusion into the bulk, thus demonstrating the response of contamination behaviour to strain processing is strongly dependent on solution pH. Judging from the surface elemental analysis presented in Figure 6.4A, the cause of this may be the severe depletion of Cr in the surface oxide film. These results clearly show that the Cr content of the passive layer has become an important factor in the initial sorption behaviour and ultimate fate of accumulating Sr. Although Cs uptake also increases as a result of cold work, no apparent modification in depth distribution could be observed. It is not clear if the enhancement of Cs accumulation is related to the reduced competition for surface adsorption sites by the subsequent transfer of Sr into the bulk.
Figure 6.7. TOF-SIMS elemental depth profiles of 304 stainless steel: (A) AR + 12 M HNO₃, (B) 30 % CW + 12 M HNO₃, (C) AR + 1 mM NaOH, and (D) 30 % CW + 1 mM NaOH. In all instances, contamination experiments were conducted at 60 °C for 30 days. Elemental signals have been scaled as necessary, for clarity.

6.4.4. Spatial Distribution Analysis

For similar reasons as outlined in the section on depth analysis, specimens contaminated in 12 M HNO₃ and 1 mM NaOH were selected for TOF-SIMS spatial distribution analysis. Analogous characterisation was undertaken in our previous study with AR specimens and therefore our current selection permits a direct comparison between the two sample processing regimes.

Previous Cs contamination studies have proposed lattice defects such as vacancies (Matzke et al., 1977) and grain boundaries (Matzke et al., 1983; Woodhouse et al., 2008) act as preferential diffusion avenues for Cs penetration into stainless steel. The images obtained from TOF-SIMS measurements on the cold worked specimen contaminated at acidic pH (Figure 6.8) do not corroborate these findings as no obvious correlation between Sr and Cs deposition and crystalline defects could be observed. This includes both grain boundaries
and shear bands, as highlighted on the secondary electron (SE) image. Overall, a generally homogeneous distribution of all elements is observed, where few distinguishing features are apparent. The most noticeable of which is the presence of a small number of ~2 µm diameter spherical regions of elemental enrichment. It is important to mention that the observation and assignment of over 30 of these features to re-adsorbed corrosion species was made in our previous contamination study conducted under identical solution conditions (Lang et al., 2017A). In this earlier contribution, alignment with contaminant hotspots across a large pH range led to the suggestion that fission product accumulation occurred as a co-adsorption process with once dissolved steel elements. No such correlation is apparent with regards to the cold worked specimens in this study (Figure 6.8), a result consistent with the alloying element solution data (Figure 6.4C). It would therefore seem that in addition to contamination depth, cold working has also modified fission product sorption processes. Given the reliability of Ho second order rate equation to describe Sr and Cs sorption is unaltered by strain processing, it is unlikely that the rate controlling interaction for sorption onto the as received material involves the re-accumulating Fe and Cr species.
Figure 6.8. (A) Secondary electron image of the sputtered area of 30% CW 304 stainless steel and the corresponding TOF-SIMS maps of (B) Fe, (C) Cr, (D) Ni, (E) Mn, (F) O, (G) Sr, and (H) Cs. The steel specimen was contaminated in 12 M HNO₃ for 30 days at 60 °C. The arrows on image (A) highlight lattice defects such as grain boundaries and shear bands.
In contrast, the TOF-SIMS data for the alkaline pH contaminated 30 % CW specimen revealed a distinctive heterogeneous structure of many important elements, as in Figure 6.9. It can easily be seen that Sr and Cs are selectively incorporated into a region of approximately 10 µm diameter that is simultaneously Fe abundant and Cr poor. In contrast, Cr concentrated zones in the surrounding areas are noticeably depleted in Sr, Cs, and Fe. The homogeneous Ni distribution across the entire measurement area excludes the possibility that these Cr depleted regions are strain-induced martensite phases as one would also expect a similar removal of Ni relative to the austenite matrix (Cottrell, 1966). Taking into account the surface elemental composition data (Figure 6.4A) it is more reasonable that this Cr depleted feature is related to the low Cr levels in the passive surface film of cold rolled specimen at alkaline pH. These collective results are consistent with other literature findings (Bradbury et al., 1978; Sasaki et al., 2013) that identified important connections between contamination and Cr stability in the passive layer, albeit at elevated temperatures.
Figure 6.9. (A) Secondary electron image of the sputtered area of 30 % CW 304 stainless steel and the corresponding TOF-SIMS maps of (B) Fe, (C) Cr, (D) Ni, (E) Mn, (F) O, (G) Sr, and (H) Cs. The 30 % CW 304 stainless steel specimen was contaminated in 1 mM NaOH for 30 days at 60 °C.
6.4.5. Chemical Speciation Analysis

Strontium accumulation on the deformed steel surface initially results in coordination to the passive layer, as characterised by the Sr 3d\textsubscript{3/2} and 3d\textsubscript{5/2} XPS signals at 135.4 eV and 133.7 eV, respectively that correspond to SrCrO\textsubscript{4} (Baghni et al., 2004; Chen et al., 2015; Figure 6.10). The observed binding energy values related to this chemical state does not depend on the composition of the contaminating matrix. This constancy suggests that in all systems studied Sr\textsuperscript{2+} complexation to the Cr oxide rich passive is a key component to the contamination process, even when subsequent diffusion into the bulk occurs (Figure 6.7D).

The deconvolution of additional components after alkaline pH contamination conditions indicates a second Sr chemical environment exists within the steel surface film. Additional analysis and a search of the literature permitted the assignment of the 135.0 and 133.2 eV XPS lines as SrCO\textsubscript{3} (Vasquez et al., 1991; Sosulnikov et al., 1992). The determination of the SrCO\textsubscript{3}/SrCrO\textsubscript{4} ratio of the Sr XPS lines in Figure 6.10D using the relative intensities of the associated photoelectron signals result in a value of approximately 3. In comparison, a similar calculation for the AR specimen contaminated at alkaline pH (Lang et al., 2017A) yields a value close to unity. The decrease in the contribution of the SrCrO\textsubscript{4} signal to the overall Sr XPS lines reflects further emphasises that under alkaline conditions, a significant fraction of deposited Sr is transferred from the passive layer into the bulk material.
Figure 6.10. High resolution XPS spectra of the Sr 3d photoelectron lines for 30 % CW 304 stainless steel treated in (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH at 60 °C for 30 days.

The deposition of Cs on the 30 % CW steel surface can be identified by the Cs 3d XPS peaks, as shown in Figure 6.11. For all three acidic systems, the Cs 3d₃/₂ and Cs 3d₅/₂ lines are measured at 724.0 eV and 737.9 eV respectively, where no definitive changes in the binding energy positions were observed that would indicate multiple Cs bonding environments. A search of the literature data indicates that the most probable assignment of these lines to Cs₂Cr₂O₇ (Allen et al., 1973). Following the same principles utilised for the interpretation of the Sr XPS data, this bonding environment may be interpreted as Cs⁺ complexation to the passive layer. The assignment of these lines is in agreement with the data of Figure 6.7 which shows Cs contamination is a surface phenomenon. The binding energy values reported in this work are essentially identical to those reported for Sr and Cs deposition onto AR 304 stainless steel (Lang et al., 2017A). The absence of any clear peaks shifts suggests the introduction of strain into microstructure does not affect the dominant chemical forms of adsorbing contaminants. Hence the observed increase in uptake is related to changes in metallurgical factors. For similar reasons as described in our
previous contribution (Lang et al., 2017A) XPS analysis of Cs contamination on stainless steel was not considered possible for the alkaline matrix. This was due to spectral interference of the Cs 3d peaks with the Fe 2p photoelectron lines ascribed to the Fe$_2$O$_3$ component of the Fe-rich passive layer.

![XPS spectra](image)

**Figure 6.11.** High resolution XPS spectra of the Cs 3d photoelectron lines for 30 % CW 304 stainless steel treated in acid systems at 60 °C for 30 days.

### 6.5. Conclusions

Here the effect of 30 % CW on the Sr and Cs sorption onto 304 stainless steel from acidic and alkaline solutions has been investigated. It has been shown that alterations in the microstructure such as martensite nucleation and grain morphology significantly increase the uptake of Sr and Cs on steel surface for all systems studied. TOF-SIMS and ICP-MS data suggest that the propensity for the re-adsorption of dissolved alloying elements is severely diminished by cold working. This is an important finding as the co-adsorption of Fe and Cr species with accumulating Sr and Cs was postulated to be an intrinsic component to the fission product contamination of as received stainless steel under identical experimental conditions. The inconsistent sorption behaviour demonstrates the importance of steel metallurgy towards contamination phenomena and suggests that stainless steel structural materials subject to different levels of cold work may exhibit distinctive radionuclide retention properties.

The influence of metallurgical properties on the extent and character of contamination phenomena has been discussed in terms of their effect of the passive layer chemical composition. In combination with alkaline passivation, cold work had the effect of
incurring significant Cr removal from the passive layer, compromising the film’s ability to inhibit Sr diffusion into the bulk material. In contrast, Cr content in concentrated nitric acid was enhanced by cold working as an increased grain boundary length from plastic deformation provided efficient diffusion pathways for Cr diffusion into the surface film. This led to a transition of Sr and Cs contamination from a bulk to a surface based phenomenon. The available results do not allow for the increase in fission product passive layer at acidic pH to be fully clarified. Fission product deposition and build-up on stainless steel surfaces are certainly related to passive layer properties and further investigation is required to better understand the relationship between metallurgical composition and passive layer characteristics. Regardless, it is evident on the basis of these results that the effect of cold work on the passive film’s properties must necessarily be considered in the context of environmental parameters. These results have important ramifications for the future conduct of investigations of radioactive contamination phenomena associated with the nuclear industry as previous studies have typically been limited to the characterisation of chemical effects only.

6.6. Acknowledgments

This work was supported by the Sellafield Ltd. Centre of Expertise for Decontamination and Effluent Treatment and the Science and Technology Facilities Council Env-Rad-Net (ST/N002474/1).
6.7. References


Mayuzum, M.; Ohta, J.; Arai, T. Effects of Cold Work, Sensitization Treatment, and the


6.8. Supporting Information for:

Effect of Cold Work on Cesium and Strontium Contamination of Nuclear Plant Stainless Steel

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6.8.1. XRD Phase Analysis

The phase composition of steel specimens was determined from the relative integrated intensities of diffraction peaks using the following formula (Cullity, 1978; Bentley et al., 1986):

\[ V_\alpha = \frac{(1/n) \sum_{j=1}^{n} (I_{\alpha j}/R_{\alpha j})}{(1/n) \sum_{j=1}^{n} (I_{\gamma j}/R_{\gamma j}) + (1/n) \sum_{j=1}^{n} (I_{\alpha j}/R_{\alpha j})} \]

where \( n \) is the number of phases identified, \( I \) is the integrated intensity of diffraction plane and \( R_i \) is a constant related to the intensity factor of the diffraction line. The peaks used in the calculation and the associated \( Ri \) values are given in Table 6.2.

Table 6.2. X-ray reflections used in the quantitative determination of \( \alpha' \)-martensite volume fraction

<table>
<thead>
<tr>
<th>Reflection</th>
<th>d / Å</th>
<th>Diffraction angle / 2( \theta )</th>
<th>( R_i ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}( \gamma )</td>
<td>2.070</td>
<td>43.75</td>
<td>212</td>
</tr>
<tr>
<td>{200}( \gamma )</td>
<td>1.792</td>
<td>50.96</td>
<td>95</td>
</tr>
<tr>
<td>{220}( \gamma )</td>
<td>1.267</td>
<td>74.94</td>
<td>52</td>
</tr>
<tr>
<td>{110}( \alpha )</td>
<td>2.028</td>
<td>44.69</td>
<td>279</td>
</tr>
<tr>
<td>{200}( \alpha )</td>
<td>1.434</td>
<td>65.05</td>
<td>40</td>
</tr>
<tr>
<td>{211}( \alpha )</td>
<td>1.171</td>
<td>82.36</td>
<td>79</td>
</tr>
</tbody>
</table>

6.8.2. Sr and Cs Kinetic Modelling

The relevant kinetic parameters obtained from the Ho second order fit of the Sr and Cs solution data is summarised in Table 6.3 and Table 6.4, respectively. It should be noted that the consistently higher second order rate constants for the cold worked surface are a consequence of higher equilibrium sorption capacities. Thus, to gain a better understanding of the relative sorption kinetics of the rolling condition, it is more appropriate to compare the initial sorption rates. It can be seen these values obtained from acidic pH contamination are not markedly different from one another which suggests that the rate limiting step in the sorption process is independent of metallurgical variables. This result is consistent with one of the principal assumptions of the Ho model which states that chemisorption via the sharing of valency electrons is rate controlling (Ho et al., 1999). A noteworthy result
however, is that the initial rate of Sr sorption from alkaline solution is significantly enhanced by cold working. It is not clear if this result is related to the decreased Cr content in the passive layer.

Table 6.3. Calculated second order kinetic parameters for the adsorption of Sr on to 30 % CW and AR 304 stainless steel

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>( k_2 / \text{m}^{-2} \text{g}^{-1} \text{hr}^{-1} )</th>
<th>( h / \text{g} \text{m}^{-2} \text{hr}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO₃</td>
<td>0.4 ± 0.02</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>6 M HNO₃</td>
<td>0.5 ± 0.01</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>12 M HNO₃</td>
<td>0.8 ± 0.07</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>1.5 ± 0.1</td>
<td>1.4 ± 0.1</td>
</tr>
</tbody>
</table>

Table 6.4. Calculated second order kinetic parameters for the adsorption of Cs on to 30 % CW and AR 304 stainless steel

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>( k_2 / \text{m}^{-2} \text{g}^{-1} \text{hr}^{-1} )</th>
<th>( h / \text{g} \text{m}^{-2} \text{hr}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO₃</td>
<td>0.3 ± 0.01</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>6 M HNO₃</td>
<td>0.9 ± 0.07</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>12 M HNO₃</td>
<td>0.5 ± 0.07</td>
<td>6.5 ± 0.3</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>1.7 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
</table>

The rate of adsorption for the Lagergren first order model is dependent on the sorption capacity of the substrate, which in its linear form is expressed as (Lagergren, 1898):

\[
\log(q_e - q_t) = -kt + \log(q_e)
\]

A plot of \( \log(q_e - q_t) \) against \( t \) will yield a linear relationship of gradient \(-k\) and a y-intercept of \( \log(q_e) / k_2 q_e^2 \) is obtained. An important limitation of this kinetic model is that some prerequisite knowledge of the equilibrium sorption capacity \( (q_e) \) is required. In this work, the maximum \( q_t \) value determined for each individual sorption experiment was assumed to be \( q_e \). The first order kinetic plots are shown in Figure 6.12 for all for systems studied, where the corresponding first order rate constant can be calculated from the gradient of the fit.
Another kinetic model tested was the Elovich model. In the Elovich equation, the overall rate of analyte removal from solution is derived from competing adsorption and desorption processes, which is expressed as (Low, 1960; Chien et al., 1980):

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \]

When \( q_t \) is plotted against \( \ln t \), a linear plot of gradient \( 1/\beta \) and a y-intercept of \( \ln(\alpha \beta)/\beta \) is obtained. The corresponding kinetic plots are shown in Figure 6.13 for all for systems studied, where the values of \( \beta \) and \( \alpha \) can be calculated from the slope and intercept of the fits, respectively.

**Figure 6.12.** Lagergren first order kinetic fits for the sorption of Sr and Cs on 30% CW 304 stainless steel from (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH at 60 °C.
Figure 6.13. Elovich kinetic fits for the sorption of Sr and Cs on 30 % CW 304 stainless steel from (A) 3 M HNO₃, (B) 6 M HNO₃, (C) 12 M HNO₃, and (D) 1 mM NaOH at 60 °C.

The statistical results of the Ho, Lagergren, and Elovich kinetic fits are summarised in Table 6.5. It can clearly be seen that the Ho second order linear fit consistently gives coefficient of determination values that are closest to unit. In comparison, utilisation of the corresponding Lagergren and Elovich equations in their linear form without exception give yield inferior R² values. Thus, for all solution compositions studied, the adsorption of Sr and Cs from aqueous solution onto the surface of 30 % CW stainless steel can be more accurately described by Ho second order kinetics.
Table 6.5. Comparison of the statistical analysis of the Ho, Lagergren, and Elovich kinetic models tested to describe Sr and Cs sorption behaviour on 30 % CW 304 stainless steel

<table>
<thead>
<tr>
<th>Solution Composition</th>
<th>Ho 2\textsuperscript{nd} order $R^2$</th>
<th>Lagergren 1\textsuperscript{st} order $R^2$</th>
<th>Elovich $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 M HNO$_3$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
</tr>
<tr>
<td>6 M HNO$_3$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
</tr>
<tr>
<td>12 M HNO$_3$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.80</td>
</tr>
<tr>
<td>1 mM NaOH</td>
<td>0.99</td>
<td>0.99</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.60</td>
</tr>
</tbody>
</table>
6.8.3. References


7. Summary, Conclusions and Suggestions for Future Directions

7.1. Summary and Conclusions

The work presented in this thesis has explored Sr and Cs contamination processes involving stainless steel nuclear plant components. Employing laboratory scale contamination experiments throughout, the primary aim of this project was to elucidate mechanisms of Sr and Cs contamination of 304 stainless steel in 1mM NaOH and HNO₃ rich environments. A series of hypotheses were tested (see Chapter 2) and the results are summarised as follows.

The capabilities of LIBS to characterise Sr and Cs contamination of 304 stainless steel was explored in Chapter 4. Hypothesis 1 stated that: “Laser-Induced Breakdown Spectroscopy (LIBS) can be utilised for the accurate identification and depth characterisation of Cs and Sr incorporated into the stainless steel matrix.” This hypothesis was proven to be partially true. Although the Cs I 894.35 nm and Sr II 407.77 nm emission lines could be used to detect the presence of fission products within the steel matrix, the sensitivities of LIBS with regards to the two spectral features were observed to be markedly different. In the case of Sr, detection was possible after exposure of steel specimens to solution concentrations representative of industry (500 mg L⁻¹ Sr(NO₃)₂) at both low and high pH. In contrast Cs detection was only realised when elevated solution concentrations (≥ 5000 mg L⁻¹ CsNO₃) were used in contamination experiments. Higher Cs detection limits associated with the LIBS technique have been reported for other surrogate materials (Martin et al., 2012) and is therefore unlikely to be specific to the stainless steel supporting matrix used in this work.

LIBS multi-pulse analysis over a single position revealed that the O signal persisted for at least an identical number of laser shots as the corresponding Sr signal, suggesting Sr contamination is maintained at the surface by the passive layer. This result was consistent with complimentary GD-OES data. However, EDX and TOF-SIMS elemental mapping indicated that ablated material is redeposited within the crater profile where it can subsequently be reanalysed in subsequent shots. This effect was observed to produce a residual signal tailing of elements of interest, thus compromising depth resolution. Hence, LIBS was not considered a reliable technique to obtain accurate depth resolved information in this project.
Hypothesis 2 stated that: “The stainless steel passive layer possess analogous sorbent properties to hydrous metal oxides, where the extent of Sr and Cs contamination will be higher from the alkaline storage ponds than the nitric acid reprocessing streams.” This hypothesis was proven to be valid for both elements in Chapter 5. Here, extensive Sr and Cs uptake was observed for all solution chemistries where the highest levels of removal onto the steel surface occurred at alkaline pH. In addition, the uptake of Sr and Cs was observed to be rapid in all system, where an equilibrium sorption uptake was established within 30 days of initial exposure. Kinetic data revealed Sr and Cs contamination follows Ho second order kinetics over the entire sorption period, a rate equation which has previously been used to characterise the adsorption of Sr$^{2+}$ and Cs$^+$ onto metal oxide minerals (El-Rahman et al., 2006; Kim et al., 2014; Yakout et al., 2014). These results collectively highlight the similarities in sorption properties of the stainless steel surface oxide layer and those of a discrete metal oxide. This correlation may provide useful concepts for developing stainless steel contamination mechanisms.

Building on these results, Hypothesis 3 stated that: “Sr and Cs contamination of 304 stainless steel is an exclusively surface based phenomenon in which fission products do not diffuse into the bulk material for all solution chemistries studied.” This hypothesis was proven to be generally correct with an important exception. GD-OES and TOF-SIMS data collected revealed Sr and Cs selectively become incorporated into the Cr enriched component of the passive layer, suggesting that that the Cr$_2$O$_3$ film is important in retarding the inward diffusion of foreign contaminants. XPS analysis also identified SrCrO$_4$ and Cs$_2$Cr$_2$O$_7$ bonding environments of sorbed contaminants that is consistent with complexation to the Cr$_2$O$_3$ passive layer. However, contamination from the 12 M HNO$_3$ system was found to involve Sr and Cs penetration into the bulk material. SEM analysis of the steel specimen showed the onset of intergranular corrosion after 30 days of contact with 12 M HNO$_3$, likely due to the partial dissolution of Cr from the passive layer under strongly oxidising conditions (Fauvet et al., 2008). This could explain the increased contamination depth recorded under strongly acidic conditions and suggests that the steel corrosion state could be an important factor in determining the fate of accumulating radionuclides.

The effect of the steel microstructure on radionuclide retention properties was discussed in Chapter 6. Hypothesis 4 stated: “The effect of cold rolling treatment on metallurgical variables will universally reduce the steel’s affinity for Sr and Cs contamination under identical solution conditions.” This hypothesis was found to be false as the levels of Sr and
Cs uptake onto 30% cold rolled 304 stainless steel were observed to be higher than those on as received specimens for all systems investigated. TOF-SIMS depth analysis showed Sr and Cs uptake onto 30% cold rolled stainless steel from 12M HNO₃ is an exclusively surface phenomenon, a result in sharp contrast to the one obtained for the as received specimen. Taking into consideration the findings of Chapter 5, this difference may be due to an increased Cr stability in the passive layer formed on the cold worked material. An increase in the relative surface Cr concentration of the cold rolled specimens after 12M HNO₃ treatment was identified by XPS. EBSD data collected identified a reduction in the average grain size for the cold rolled material which could potentially increase the number of efficient diffusion pathways to facilitate Cr enrichment in the passive film. The exact reason for the increased contaminant uptake is not entirely clear but is likely related to changes in passive film electrochemical and electronic properties induced by cold working (Peguet et al., 2007).

In combination with passivation in alkaline media however, cold working was found to deplete Cr from the passive layer. This is likely due to a combination of overheating effects during the rolling process (Houmard et al., 2007) and an increased Cr solubility at high pH (Olsson et al., 2003) which individually promote surface Fe enrichment. Furthermore, TOF-SIMS data collected for the alkaline system showed significant amounts of Sr were present in the bulk of the cold worked material. This result compliments data presented in Chapter 5 which suggested an absence of Cr within the passive film creates opportunities for fission product bulk diffusion. The different response of sorption behaviour to cold work under acidic and alkaline conditions suggests a synergistic coupling of metallurgical factors and environment chemistry is controlling the nature of contamination phenomena. This coupling would indicate that characterisation of both metallurgical and chemical variables are required for a comprehensive mechanistic understanding of contamination processes.

7.2. Implications

Several key findings have emerged in this work which collectively has important implications for the safe management and disposal of contaminated steel nuclear plant components and pond furniture. This study highlights the important role of the passive layer character on 304 stainless steel adsorption behaviour and, therefore, the fate of accumulating Sr²⁺ and Cs⁺ ions. For example, it has been shown that Sr and Cs contamination mechanisms may be partially explained by surface complexation models originally used to characterise sorbent properties of metal oxide minerals (Parks et al.,
1962). This has beneficial implications for making predictions about the kinetics and extent of radionuclide adsorption as a function of solution pH. This in turn may assist in the selection and optimisation of decontamination techniques to combat contamination from the HNO$_3$ reprocessing streams and the alkaline pond furniture.

Furthermore, evidence presented in Chapter 6 reveals that a change in microstructural variables by cold working also influences adsorption behaviour, with data indicating a synergistic effect involving steel microstructural variables and environment chemistry. This is an important finding as the effect of steel metallurgy on contamination mechanisms has generally not been considered in previous studies. In this project, the effect of these variables on contamination phenomena has been discussed in terms of their mutual relationship with corrosion processes. For example, fission product diffusion into the bulk material has been observed under conditions that destabilise Cr within the passive film. In contrast, a Cr enriched film was found to maintain contaminants at the surface. Hence, corrosion control could be particularly important for mitigating the inward diffusion of radioactive contaminants into the steel matrix. There is also evidence to suggest that fission product co-adsorption occurs with once dissolved Fe and Cr species emitted from the steel surface, further highlighting the underlying role of corrosion processes in determining contamination behaviour.

The capability of LIBS to perform reliable standoff analysis for Sr contamination in nuclear plant steels has been demonstrated under conditions representative of industry. This presents attractive possibilities for LIBS to perform remote analysis of potentially contaminated steel components to rapidly confirm or exclude the presence of Sr contamination. Discouragingly, however, redistribution of analyte material into the crater profile creates a residual signal tailing effect that limits the potential of LIBS as a commercially competitive depth profiling technique. Moreover, the reintroduction of radioactive material into the melt breaches decommissioning principles, a previously unidentified problem that must be considered before the deployment of LIBS in nuclear environments.

Overall, the work presented in this thesis has demonstrated that knowledge of steel corrosion processes is essential to understanding the contamination mechanisms that is required for the elucidation of cost effective and reliable decontamination solutions. In addition, standoff LIBS measurements offers standoff characterisation of Sr contamination in nuclear plant steels. This work has implications for the future characterisation of
contamination phenomena as well as optimisation of candidate decontamination and prevention methods.

7.3. Directions for Future Work

The current UK programme for the storage and reprocessing of spent nuclear fuel has been in operation for several decades. The laboratory scale experiments utilised in this thesis are a simple methodology for investigating contamination phenomena under well-defined and carefully controlled conditions but are somewhat limited by the relatively short timescales. It would therefore be useful to perform surface characterisation (e.g. GD-OES, TOF-SIMS) on aged specimens collected from nuclear sites to better understand the effect of time on radionuclide contamination behaviour. Data obtained from such analysis would, for example, reveal if a stable and Cr enriched passive layer remains an effective barrier against radionuclide diffusion on timescales representative of industry.

During the LIBS multi-pulse measurements, a residual tailing effect of the analyte signals was observed that EDX and TOF-SIMS analysis suggested was due to redistribution of ablated material within the crater profile. To our knowledge, only one study has previously investigated this possibility (Mateo et al., 2001) and as a result it is unclear if this deleterious effect is intrinsic to the LIBS technique. In order to clarify these uncertainties and to determine satisfactory control measures, a more comprehensive study of crater formation as a function of laser parameters is necessary. Further SEM-EDX measurements and focused ion beam (FIB) cross section analysis for example may reveal an optimal LIBS experimental setup that mitigates these undesirable tailing effects.

The data presented in this thesis suggests that the passive layer character has a marked influence on stainless steel adsorption behaviour. Specifically, a stable Cr$_2$O$_3$ passive layer has been shown to act as sink for accumulating Sr$^{2+}$ and Cs$^+$ ions, a result consistent with a previous stainless steel contamination study (Hirschberg et al., 1999). However, the exact action of the passive film on accumulating radionuclides is unclear and clearly warrants further investigation. A better understanding of the interaction of the passive layer with radioactive contaminants is highly desirable for the development and optimisation of novel decontamination solutions. On this basis, obtaining local structural information for deposited fission products by X-ray adsorption spectroscopy (XAS) is highly desirable.

There is currently an absence of comprehensive investigations within the literature which have explored the effect of steel microstructure on radionuclide adsorption behaviour. One recent study has suggested that steel surface elemental composition, a parameter sensitive
to microstructural variables, may influence the extent of radionuclide accumulation from boric acid solution (Kádár et al., 2011). To date, there are no studies that have investigated the effect of grain boundary engineering by thermomechanical treatments on the radionuclide retention properties of stainless steels. Proposed methodologies for the controlled modification of the frequency of grain boundary characters have proven highly successful for corrosion control (Shimada et al., 2002) and thus would be a good line of enquiry to reduce initial contamination. The relative success or failure of these treatments on inhibiting radionuclide sorption processes may also further the understanding of contamination mechanisms required to develop more cost efficient decontamination programmes.
7.4. References


