A Study of Anaerobic Corrosion Behaviour of Carbon Steel in a Canadian Used Nuclear Fuel Repository

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Abstract

The Canadian nuclear waste management concept envisages using carbon steel as a primary engineered barrier for isolating nuclear waste in a deep geological repository (DGR) located in sedimentary rock. Steel corrosion in anticipated repository environments has been studied, but was mostly focused in two main areas: (i) aerobic or oxygen containing environments (both in vapour and liquid phases); and (ii) anaerobic, solution environments. The atmospheric corrosion behaviour of steel in a humid, anaerobic or anoxic environment, is a new topic, with virtually no published data to on which to rely.

This study was undertaken to improve the existing knowledge of anaerobic, atmospheric corrosion of carbon steel. Atmospheric corrosion testing was conducted on carbon steel wires in anoxic atmospheres at various temperature and relative humidity (30-100% RH), with and without sodium chloride (NaCl) contamination of the wire surfaces. Hydrogen evolved from corrosion was monitored and converted to an estimated corrosion rate. With salt on wire surfaces, sustained final corrosion rates in the range of 0.01 to 0.8 µm·y⁻¹ were observed over test durations of 935 to 1725 hours. Without salt contamination, the corrosion rates are very low, and can only be detected using a solid-state electrochemical hydrogen sensor. The hydrogen sensor can detect the pressure increase down to a limit of ca. 0.1 Pa, corresponding (depending on the exact procedure) to a corrosion rate as low as ca. 0.0001 µm·y⁻¹. The estimated corrosion rates for the degreased and pickled wires were found to be < 0.01 µm·y⁻¹.

In parallel with the corrosion experiments, corrosion product surface analyses were performed using different techniques. Oxides formed on steel surfaces consist mostly of the mixed Fe²⁺/Fe³⁺ spinel oxide Fe₃O₄. The experimental results of this study will be applied to assess the corrosion behaviour of carbon steel containers during the anoxic, unsaturated phase of a deep geological repository in Canadian sedimentary rock.
Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given in the list of sources.

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1.0 Introduction

The Canadian nuclear waste management concept envisages using carbon steel as a primary engineered barrier for isolating nuclear waste in a deep geological repository (DGR) (McMurry et al. 2003) as illustrated in Figure 1. A deep geological repository is an approach being considered for long-term management of nuclear fuel waste in many countries such as Sweden, Switzerland, the United Kingdom, Canada and the United States. In a DGR, used nuclear fuel would be sealed in durable metal containers and placed in an engineered repository constructed deep in stable host rock. The layout of the Canadian repository would be a network of tunnels and emplacement rooms designed to accommodate the rock structure and stresses, the groundwater flow system, and other subsurface conditions at the site. A clay buffer material would surround each container, and backfill material and other seals would close off the rooms. The rock and groundwater that surround the repository would provide stable mechanical and chemical conditions that would also promote containment of the wastes for long times.

Steel corrosion in anticipated repository environments has been studied, but was mostly focused in two main areas: (i) aerobic or oxygen containing environments (both in vapour and liquid phases); and (ii) anaerobic, immersed solution environments (King 2007). The long term behaviour of steels, in particular the less corrosion-resistant carbon steel, in humid, non-immersed, anaerobic or anoxic conditions, has not been studied. The lack of such data may be due to the relatively slow corrosion rates and difficulties in precise measurements. This condition (i.e. humid and anoxic) has nonetheless been repeatedly reported in various Canadian sedimentary host rock studies to span from thousands to millions of years after DGR closure (Mazurek 2004, King 2007). The urgency for addressing the anaerobic steel corrosion issue in humid, vapour phase condition is evident.
1.1 Objective
The objective of this study is to improve the existing understanding of anaerobic, unsaturated corrosion of carbon steel with the following underlying considerations:

i. Study the kinetics and mechanism of long-term aerobic, unsaturated corrosion of carbon steel as a function of the relevant variables;

ii. Evaluate the effect of time-dependent oxide film formation on the corrosion rate.

1.2 Scope of Study
At the time the study was planned, it was anticipated that anoxic atmospheric corrosion might show a kind of feedback or autocatalysis effect, where the development of a porous, conducting corrosion product enhances the kinetics of hydrogen evolution and thus the corrosion rate. In the event, even though conducting surface oxides were formed, no evidence for such effects was observed, so this aspect was not pursued in detail.

It was also not practicable to study alloy composition effects, because the corrosion rates were so low that only bundles of thin wires of generic steel gave sufficient metal surface area. However, some evidence was obtained for a lack of effect of hydrogen partial pressure ($P_{H2}$) on corrosion rate, over a certain range; but high $P_{H2}$ values were not practicable to study.

The experimental work started in November 2007, with the initial aims being to evaluate the optimal corrosion cell setup, hydrogen detection techniques and testing protocols. Two
approaches were taken to monitor the hydrogen evolved from anaerobic corrosion of steel. In the first, a corrosion system equipped with a high sensitivity pressure gauge was constructed to directly measure the amount of hydrogen evolved from the anaerobic corrosion of carbon steel. In cases where pressure increases were not detectable by the pressure gauge, a solid-state electrochemical hydrogen sensor was employed to measure traces of hydrogen evolved. This second detection method had a sensitivity of at least an order of magnitude better than the pressure gauge system. Intensive data collection using the preferred techniques continued until February 2010. In parallel with the corrosion experiments, the structures and chemical compositions of the oxides formed during the anaerobic corrosion studies were analyzed using various surface analyses. This thesis presents the detailed results of the study and discusses the probable carbon steel performance in the expected Canadian repository conditions.

1.3 Layout of Thesis

This thesis is structured as follows:

Chapter 1 provides background information including the purposes, objectives and the scope of the study. Chapter 2 provides an overview of the evolution of environmental conditions within a Canadian deep geological repository in sedimentary rock. The three (3) major phases that the repository is anticipated to go through and their expected timescales are presented. Chapter 3 documents the results of a thorough literature review on the corrosion behaviours of carbon steel in various environmental conditions. Experimental details and results are presented in Chapter 5, followed by results discussion and conclusions in Chapters 6 and 7.

2.0 The Canadian Deep Geological Repository (DGR) and Carbon Steel Corrosion

The Canadian deep geological repository concept entails encapsulating bundles of used nuclear fuel in durable containers and sealing the containers in a repository located at sufficient depth in a stable geological setting, either within the placement rooms or in boreholes drilled from the placement rooms. Clay-based sealing materials would surround the containers of used fuel and would completely fill all remaining voids in each placement room to ensure low-permeability and chemically and biologically benign conditions. Carbon steel has been proposed as a candidate container material for the disposal of used nuclear fuel in a deep geological repository in sedimentary rock. Carbon steel is being considered because of
the relative ease and flexibility of fabrication, good corrosion performance, extensive industrial experience, and relatively low cost.

Since the use of carbon steel for a used fuel container was first proposed in the 1980’s, much has been learnt of the corrosion behaviour under expected repository environments. An international consensus on the important corrosion processes for carbon steel in a backfilled DGR has emerged (JNC 2000, Johnson and King 2003, King 2005b). Certain aspects of the chemical and physical environment to which the used fuel containers are exposed change over time as the conditions within the deep geological repository evolve. In general, this evolution of conditions can be described in terms of the changes in (i) temperature, (ii) redox conditions, and (iii) the degree of saturation (water). In terms of the evolution of temperature and redox conditions, the repository environment is classically divided into an initial warm, oxidizing period and subsequent, long-term cool, anoxic phase (Figure 2). In terms of the degree of saturation of the repository, the evolution can be alternatively described by an initial dry-out period, followed by a transition phase during which the bentonite-based sealing materials take up moisture, and a long-term saturated phase. In terms of the corrosion behaviour of the used fuel container, the container will be subject to uniform corrosion, which initially could take the form of uneven or localized attack. The degree of localization is expected to diminish with time. Hydrogen produced by anaerobic corrosion will be absorbed by the container material, but proper selection of material should preclude effects such as hydrogen-induced cracking (HIC) or blistering. Similarly, stress corrosion cracking (SCC) and microbiologically influenced corrosion (MIC) can be ruled out based on proper container fabrication and repository design.

2.1 Evolution of Environmental Conditions and Corrosion Reactions

Corrosion behaviour is determined by a combination of (a) the corrosion properties of the metal and (b) the corrosivity of the environment. The environment within a deep geological repository will continue to evolve over time and carbon steel behaves differently when the environmental condition changes. Initially, the used fuel container surface within the bentonite buffer will remain dry due to the hot used fuel (maximum surface temperature of 120°C). As the container surface temperature begins to drop, groundwater from the surrounding host rock will wet the bentonite buffer, and the trapped oxygen will be consumed by corrosion, by the microbes present in the bentonite, and by reaction with Fe(II) minerals.
The repository will gradually become anoxic. The timeframes of the three phases have been defined:

(i). An early unsaturated aerobic phase ~ 50 years after DGR closure,
(ii). An unsaturated anaerobic phase ~ 50-100’s of years after closure for crystalline rock and 50-100,000 years for sedimentary rock,
(iii). A long-term anaerobic phase > 100’s of years for crystalline rock and > 100,000 years for sedimentary rock.

These phases and schematic drawings of the container surface condition at various times are shown in Figure 2.

![Figure 2](image-url)

**Figure 2:** Schematic representation of the evolution of redox conditions in a Canadian deep geological repository (King and Kolar 2000)

2.2 Aerobic, unsaturated phase

In this phase, the container is placed in an emplacement cell where it is surrounded by bentonite blocks and granular bentonite backfill. This phase begins with a heat up period to the peak container surface temperature of about 100-120°C achieved after about 5-10 years. Following this heat up period is a long slow cool down period. This phase continues until the time when the container surface is first wetted with liquid water after about 20-40 years of emplacement.
For atmospheric corrosion of metals, there is a critical relative humidity (RH) for the formation of moisture on the metal surface and below which aqueous corrosion does not occur (Kucera and Mattson 1987). For clean, smooth metal surfaces, this critical RH is of the order of ~ 80%. Particulate covered and rough metal surfaces can significantly lower the critical RH to 60-70% although the exact value depends on the nature of the surface contaminants and the porosity of precipitated corrosion products (King 2006). At the time of emplacement, the initially low moisture content of the bentonite and the high temperature of the container surface maintain very low humidity values. Oxygen is consumed by corrosion of the container and access of oxygen to the container surface is expected to be uniform, despite the initial differences in density and moisture content of the bentonite blocks and pellets, because oxygen diffusion through partially saturated bentonite is rapid. At the end of this phase, all oxygen will be consumed through metal corrosion and by oxidation of pyrite in the excavation damaged zone (EDZ).

2.3 Anaerobic, unsaturated phase

During this phase, the container surface temperature decreases and the level of saturation of bentonite increases. The degree of saturation of the bentonite affects (i) the rate of transport of species to and away from the container surface (including gaseous H₂), (ii) the likelihood of precipitation and film formation, and (iii) the rate of the interfacial electrochemical processes. When the relative humidity rises above the critical RH, aqueous corrosion becomes possible. Under unsaturated conditions, precipitation of solids is more likely (than in bulk solution) because of the limited amount of water. Under anaerobic conditions, water acts as both the electrolyte and the oxidant. If the supply of water was rate limiting, the thin moisture film on the container surface would gradually dry out and electrochemical reactions cease until such time that the RH increases sufficiently to wet the container surface again. As the RH within the repository increases, the concentration of dissolved solutes decreases (assuming no gain or loss of solutes by transport or by reaction) and the probability of precipitation diminishes. Equilibration of the bentonite pore water with that in the surrounding host rock will continue and progressive saturation of the bentonite will create swelling of the clay. By the end of this phase, the bentonite reaches complete saturation.
2.4 Anaerobic, saturated phase
In this phase, the bentonite is completely saturated and all oxidized corrosion products formed at the container surface and other metal support structures within the DGR have been consumed. The only oxidant available in the system is water. Corrosion under these conditions yields hydrogen gas by reduction of protons and water. Metal ions formed by corrosion may precipitate as carbonates or oxides / hydroxides near the container surface or react with the bentonite.

3.0 Literature Review
There is a large amount of published information on the corrosion of carbon steel in natural environments. The scope of this review is limited to the behaviour of carbon steel under anaerobic conditions and at temperatures from ambient up to approximately 100 - 120°C. Information from studies performed outside this range of conditions has only been included if it provides insight into the behaviour for the conditions of interest.

3.1 Mechanism of the Anaerobic Corrosion of Carbon Steel
3.1.1 Uniform Corrosion
3.1.1.1 Electrochemical Reactions
Under anaerobic conditions, the electrochemical reactions of interest are the anodic dissolution of Fe

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1) \]

and the cathodic reaction of H₂O

\[ \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \quad (2) \]

The overall corrosion reaction can therefore be written as

\[ \text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2 \quad (3) \]

Under some conditions, Fe(OH)₂ is transformed to Fe₃O₄, via the Schikker reaction

\[ 3 \text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \quad (4) \]

Alternatively, the direct formation of Fe₃O₄ can be written as

\[ 3 \text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 \quad (5) \]

The formation of magnetite is generally considered to be favoured at higher temperatures. Linnenbom (1958) suggests that the transformation of Fe(OH)₂ to Fe₃O₄ is favoured at temperature above ~ 60°C.
The above reactions, in principle, are irreversible with a reversible potential of:

\[
E_{r, H^+/H_2} = E^\circ_{H^+/H_2} - \frac{RT}{F} \ln \frac{P_{H_2}}{a_{H^+}} \tag{6}
\]

In neutral solution or at the expected pH 8 in the repository, the concentration of hydrogen ions is too low to have the reaction proceed at a significant rate. Also no dependence of the corrosion rate or cathodic reaction on \( P_{H_2} \) has been reported (Smart et al. 2001, 2002a). Neither the cathodic Tafel slope nor the corrosion current density (determined by Tafel extrapolation) varied systematically with the hydrogen pressure for pressures between 0.1 MPa and 9 MPa at temperatures of 24°C and 80°C. Corrosion potential, \( E_{\text{CORR}} \), was also insensitive to hydrogen partial pressure under the same conditions indicating that the overall corrosion reaction is not cathodically limited by the rate of hydrogen evolution (Platts et al. 1994, Simpson 1989).

The mechanism of \( H_2 \) evolution has been the subject of extensive study, and useful reviews are given by Bockris and Reddy (1970) and Kaesche (1985). The overall reaction is a two-stage process, involving first the formation of adsorbed hydrogen atoms (H\(_{\text{ADS}}\))

\[
H_2O + M + e^- \rightarrow MH_{\text{ADS}} + OH^- \tag{7}
\]

where \( M \) is a surface metal site. The second stage may follow one of two routes depending on a number of factors, including the nature of the surface, potential, and the surface coverage by H\(_{\text{ADS}}\). The so-called Volmer-Tafel route involves the surface recombination of two MH\(_{\text{ADS}}\) species

\[
2MH_{\text{ADS}} \rightarrow H_2 + 2M \tag{8}
\]

whereas the Volmer-Heyrovsky mechanism involves reaction between MH\(_{\text{ADS}}\) and \( H_2O \)

\[
MH_{\text{ADS}} + H_2O + e^- \rightarrow H_2 + M + OH^- \tag{9}
\]

No detailed studies have been performed of the evolution of \( E_{\text{CORR}} \) for carbon steel in a deep geological repository. Compounding the complexity of the various processes described above is the fact that the repository environment evolves over time. An example of the evolution of \( E_{\text{CORR}} \) of film-covered carbon steel is shown in Figure 3 (Qin et al. 2004). In this example, the film is a layer of millscale comprising of Fe\(_2\)O\(_4\) and FeCO\(_3\), and \( \gamma \)-Fe\(_2\)O\(_3\) (magnetite). The data in Figure 3 are shown to illustrate the evolution of \( E_{\text{CORR}} \) of a carbon steel used fuel container in the repository. Various electrochemical processes occur during the course of the experiment. Initially, the potential appears to be determined by redox processes between the
Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ phases and dissolved Fe(II) in solution (Stage I). After a period of exposure, $E_{\text{CORR}}$ decreases precipitously before reaching a second steady-state value in Stage III. During Stage II, the study suggested that the reductive dissolution of Fe(III) in the millscale is galvanically coupled to dissolution of Fe in the underlying steel, which becomes possible as the pores and cracks in the film are opened by dissolution of the oxide. As the pores become increasingly larger, the dominant electrochemical reactions become the dissolution of Fe as Fe(II) coupled to the reduction of H$_2$O, with both occurring over the same surface area, presumably at the base of the pores now opened by further oxide dissolution (Stage III).

![Figure 3: Time dependence of the corrosion potential of a millscale-covered C-steel electrode in CO$_2$-containing solution (Qin et al. 2004)](image)

3.1.1.2 Gas Generation and Transport

Under anaerobic conditions, uniform corrosion of carbon steel is accompanied by the generation of hydrogen. The overall reaction for the corrosion of carbon steel is given by Equation (3), from which it can be seen that 1 mole of H$_2$ is produced for each mole of Fe oxidised. However, if the corrosion product from Reaction (3) (i.e. Fe(OH)$_2$) reacts further to produce Fe$_3$O$_4$ via the Schikkor reaction (Equation (4)), an additional 0.33 mole of H$_2$ is produced for each mole of Fe oxidised.

The hydrogen generated by corrosion will be transported away from the container surface via a number of mechanisms. Some will be absorbed by the carbon steel and diffuse through the container wall. The remainder will accumulate at the used fuel container / buffer interface and
be transported away from the container. Because of the limited solubility of H$_2$ in water and because of the restrictive mass-transport of dissolved species through compacted bentonite, the rate of diffusive transport of H$_2$ away from the container surface is expected to be limited. Based on the estimates reported by Nagra (2002), the maximum diffusive flux of H$_2$ away from the container surface is equivalent to a corrosion rate of $< 0.1 \, \mu m \cdot a^{-1}$. At higher corrosion rates a secondary H$_2$ gas phase will form. Transport of gaseous H$_2$ through compacted bentonite occurs above a threshold gas pressure approximately equal to the sum of the swelling and hydrostatic pressures (Nagra 2002). The exact mechanism of transport is uncertain, but may involve micro-fracturing and pathway dilation, although capillary flow is believed possible (Nagra 2002).

3.1.1.3 Film Structure and Composition

In considering the available information on the film structure and composition during the long-term anaerobic corrosion of a carbon steel container, it is important to take into account the evolution of environmental conditions within the repository. Prior to the establishment of cool anaerobic conditions, the container will have been exposed to a period of aerobic redox conditions and elevated temperature. Therefore, the nature of the film during the long-term anaerobic period will inevitably be affected by this preceding period of transitory conditions.

3.1.1.3.1 Aerobic Conditions

The nature of the film that forms under aerobic conditions is relevant here only in as much as the anaerobic phase in the repository is preceded by a period of aerobic corrosion. There are a large number of studies of the composition and structure of films formed on iron and steel under aerobic conditions. King and Stroes-Gascoyne (2000) reviewed the formation and transformation of Fe(II) and Fe(III) corrosion products on steel under conditions likely to exist in a deep geological repository.
Figure 4: General reaction scheme for the formation and transformation of corrosion product films on carbon steel (King and Stroes-Gascoyne 2000)

Figure 4 shows a general scheme for the formation of various green rusts, ferric oxyhydroxides, and oxides that could form, with the preferred products and reaction paths dependent on the environmental conditions (King and Stroes-Gascoyne 2000). Initial oxidation of Fe in neutral and slightly alkaline solutions generally leads to the formation of Fe(OH)\(_2\). Under aerobic conditions, Fe(OH)\(_2\) will be oxidized to produce Fe(III)-containing corrosion products. Various authors have studied the oxidation of Fe(OH)\(_2\) to α-, β- and γ-FeOOH and Fe\(_3\)O\(_4\). Rapid oxidation in aerated solutions tends to produce one or more of the ferric hydroxides (Domingo et al. 1994), whereas slower oxidation in deaerated solutions produces Fe\(_3\)O\(_4\) (Domingo et al. 1994, Odziemkowski et al. 1998). Slower oxidation is believed to allow time for incorporation of Fe\(^{2+}\) into the lattice, a process that is also supported by a slight excess of Fe(II) in solution. The stability of Fe\(_3\)O\(_4\) is also increased at higher temperatures (Domingo et al. 1994). Conversely, the opposite factors favour the formation of either α-FeOOH (goethite) or γ-FeOOH (lepidocrocite). The formation of β-FeOOH (akaganeite) is rarely reported.

In the presence of groundwater anions, oxidation of Fe(OH)\(_2\) to FeOOH and Fe\(_3\)O\(_4\) proceeds via intermediate compounds – green rusts. Green Rust 1 (GR1) is formed in solutions containing planar ligands, such as Cl\(^-\), Br\(^-\) and CO\(_3\)^{2-} (Refait and Génin 1993) and Green Rust 2 (GR2) is formed in solutions containing SO\(_4\)^{2-}. Green rusts are hydrated intermediate species containing various proportions of Fe(II), Fe(III) and the corresponding anion. The composition of Green Rust 1 formed in chloride solutions is reported to be
3Fe(OH)$_2$·Fe(OH)$_3$Cl·nH$_2$O (Refait and Génin 1993), consisting of two ferrous species for each ferric ion. In SO$_4^{2-}$ solutions, GR2 has a composition of 4Fe(OH)$_2$·2FeOOH·FeSO$_4$·nH$_2$O with a Fe(II):Fe(III) ratio of 5:2 (Olowe and Génin 1989). The proportion of FeOOH and Fe$_3$O$_4$ in the final oxidation product is a sensitive function of the pH and concentration of anion.

### 3.1.1.3.2 Film Transformation during the Aerobic-Anaerobic Transitions

At the end of the aerobic phase, the container surface will be covered by an Fe(III)-rich corrosion product layer that may contain various amounts of α-FeOOH, γ-FeOOH, Fe$_3$O$_4$ and GR1 and GR2. Corrosion product films formed in natural systems tend to be spatially inhomogeneous, with these species distributed over the surface rather than being present as uniform layers.

As redox conditions within the repository become anaerobic, the Fe(III) phases within the corrosion product film will become thermodynamically unstable and will be reduced to predominantly Fe(II) species. The reduction of Fe(III) in corrosion products on carbon steel surfaces has been studied in a number of systems. Corrosion products can be dissolved (transformed) both electrochemically (by reducing Fe(III) to Fe(II)) or chemically at acidic pH and in the presence of complexants for dissolved Fe. In repository expected environment, the electrochemical reduction process is more relevant as the solubility of the Fe(II) solids in neutral to slightly alkaline bentonite pore-water solutions will be low.

Electrochemical reduction of Fe(III) species can proceed by one of two mechanisms, namely: (i) coupling of the oxidation of the underlying steel to reduction of the corrosion product or (ii) reaction between dissolved Fe(II) and the Fe(III) corrosion product. Figure 5 shows the expected evolution of the corrosion potential, $E_{\text{CORR}}$, of a carbon steel container as the environment in the repository evolves from aerobic to anaerobic. The transition period is characterized by a rapid decrease in $E_{\text{CORR}}$. Prior to this decrease the corrosion potential is determined by the redox potential between the Fe(III) corrosion products and dissolved Fe(II) and Fe(III) species in solution. As the underlying steel surface is exposed to the environment, oxidation of Fe couples with reduction of Fe(III)

$$Fe + 2{^{\text{Fe(III)}}} \rightarrow 3 {^{\text{Fe(II)}}}$$

where “Fe(III)” represents the Fe(III)-rich corrosion product formed during the aerobic phase and “Fe(II)” represents either dissolved ferrous ions or a secondary precipitated Fe(II)
corrosion product. Eventually sufficient underlying steel is exposed that the potential is determined by the rates of Fe dissolution and H₂O reduction on the underlying surface and E_{CORR} attains a value representative of that in anaerobic solution. This type of transition has been observed not only for the reductive dissolution of Fe₂O₄ deposited in steam generators (Shoesmith et al. 1981) but also for the dissolution of millscale on pipeline steel (Qin et al. 2004).

Figure 5: Schematic of expected evolution of the corrosion potential of a carbon steel used fuel container (King 2005a)

Various studies of the reduction of FeOOH by Fe(II) have been reported. Ishikawa et al. (1998) studied the reduction of α-, β- and γ-FeOOH by Fe(II) in chloride solutions as a function of temperature and [OH⁻]:[Fe(II)] ratio. The reduction of γ-FeOOH by Fe(II) resulted in the complete conversion of the ferric species to Fe₃O₄ between 25°C and 100°C and pH 3-13. The reduction of β-FeOOH resulted in the formation of Fe₃O₄ and α–FeOOH, whilst the reduction of α–FeOOH was sluggish with little apparent conversion to Fe₃O₄. Increasing temperature increased the amount of Fe₃O₄ formed. Overall, the relative ease of conversion was β-FeOOH >γ-FeOOH >α –FeOOH. Reduction of the ferric phase was believed to proceed via dissolved Fe(II) and Fe(III) species, the relative ease of conversion being directly related to the solubility of the various FeOOH polymorphs. Tamaura et al. (1983) also studied the reaction between Fe(II) and γ–FeOOH

\[
\text{Fe}^{2+} + 2\gamma\text{–FeOOH} \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}^+ \quad (11)
\]

The reaction was believed to proceed via two distinct steps, each involving a de-protonation process. Stratmann and Hoffmann (1989) studied the reduction of α- and γ-FeOOH as a
function of potential at 25°C using in situ Mössbauer spectroscopy. At potentials between -0.2 and -0.4 V_SHE, γ-FeOOH is partially transformed to Fe_3O_4, although conversion appears complete towards the negative end of this potential range. At more negative potential α-FeOOH is reduced.

3.1.1.3.3 Anaerobic Conditions
Odziemkowski et al. (1998) studied the anaerobic oxidation of iron particles in simulated dilute groundwater solutions at ambient temperature using normal and enhanced Raman spectroscopy. Magnetite was formed from a precursor Fe(OH)_2 phase, with conversion proceeding within a matter of a few ten’s of hours even at room temperature. The study suggested the growth of the Fe_3O_4 phase resulted from a dissolution-precipitation process. To explain the increase in corrosion potential observed in the experiment, Odziemkowski et al. (1998) propose that the anodic and cathodic reactions are spatially separated, with anodic dissolution occurring at the base of pores in the porous Fe_3O_4 layer and H_2O reduction occurring at the film/water interface.

In the presence of Cl^-, studies have observed that Cl^- interferes with the formation of Fe(OH)_2 through a competition between OH^- and Cl^- ions in the initial oxidation of Fe (Ashley and Burstein 1991, MacFarlane and Smedley 1986). Ashley and Burstein (1991) reported a mixed Cl^-/OH^- layer was formed, which would be expected to interfere with the formation of a ‘passive’ Fe(OH)_2 layer or its transformation to Fe_3O_4. However, it is difficult to draw conclusions regarding the long-term effect of Cl^- on the passivity of carbon steel based on its impact on the composition of the first oxidized monolayer due to a lack of sufficient experimental data.

Carbonate species will also be present in the bentonite pore water because of the dissolution of calcite impurities in the clay. Iron carbonate is only reported to be formed in a limited range of pH and potential values. In moderately alkaline carbonate solutions (> pH 9.5), Fe(OH)_2, Fe_3O_4 and γ-FeOOH species are reported by surface-enhanced Raman spectroscopy (Gui and Devine 1995, Simpson and Melendres 1996). Simpson and Melendres (1996) report the formation of FeCO_3 only at lower pH, at temperatures < 50°C, and at potentials between -0.7 V_SCE and -0.5 V_SCE. Lee et al. (2006 a,b) report the formation of a porous FeCO_3 layer in carbonate-rich solutions. Open pores within the film were maintained by the complexation of Fe^{2+} by HCO_3^-, which prevented precipitation within the film. The formation of FeCO_3 films...
is of particular interest given the observation of this phase during corrosion experiments under simulated repository conditions in the presence of compacted bentonite (Papillon et al. 2003, Taniguchi et al. 2004).

Porous corrosion deposits are also associated with the formation of protective films on carbon steel exposed to high temperature water (Castle and Masterson 1966, Friggens and Holmes 1968, Park and MacDonald 1983). A duplex $\text{Fe}_3\text{O}_4$ layer is formed in this system, with a thin inner layer formed by a solid-state process and a porous layer formed by a dissolution / precipitation mechanism. Porosity in the outer layer is maintained by the hydrolysis of cations and the consequent decrease in pH which prevents precipitation within the pores.

### 3.1.1.4 Film Properties

The most common structure observed for films on carbon steel surfaces is a bi-layer structure, involving a thin compact interfacial layer with a thicker outer layer of deposited material (Blackwood et al. 1994, Castle and Masterson 1966, Mabuchi et al. 1991, Ohtsuka and Yamada 1998, Ramesh Kumar and Balasubramaniam 1998). The inner layer is usually an epitaxial layer (i.e. its structure conforms to that of the underlying substrate), and grows via a solid-state process involving a high-field ionic conduction mechanism (Ohtsuka and Yamada 1998). This interfacial layer is generally thin, with thicknesses varying between 1-5 nm in short-term electrochemical experiments (Ohtsuka and Yamada 1998) to fractions of a µm in longer-term or higher-temperature exposures (Blackwood et al. 1994, Castle and Masterson 1966, Ramesh Kumar and Balasubramaniam 1998). The outer layer is generally crystalline in nature and is formed by a dissolution-precipitation mechanism, in which Fe(II) diffuses through the inner barrier layer into solution, where it is subsequently oxidized to Fe(III) and/or precipitated as an Fe(II)-, Fe(III)- or mixed Fe(II)/Fe(III)-containing solid when the respective concentrations exceed the solubility for the given phase in the particular environment. This outer layer is more porous than the inner layer. The crystalline material may age with time due to Ostwald ripening (in which smaller crystals preferentially dissolve and larger crystals grow) or by transformation into secondary phases as the environment changes or as metastable phases formed initially transform into more thermodynamically stable phases (Shoesmith 1983). Typically, the inner barrier layer is composed of $\text{Fe}_3\text{O}_4$ with an outer layer composed of either $\text{Fe}_3\text{O}_4$ or ferric species ($\alpha$-, $\beta$-, $\gamma$-FeOOH or $\alpha$-, $\gamma$-Fe$_2$O$_3$), depending upon the degree of aeration of the environment in which the film was formed.
3.1.1.4.1 Effect of corrosion products

Kojima et al. (1995) simulated the long-term corrosion behaviour of carbon steel by contacting carbon steel coupons with compacted Fe₃O₄ powder (maintained in place by compacted bentonite) or by a compacted Fe₃O₄/bentonite mixture. In the case of a layer of compacted Fe₃O₄, the layer thickness was varied from 0 to 10 mm. For the Fe₃O₄/bentonite mixture, the magnetite content was varied from 0 to 50 wt. %. The compacted mixtures were saturated with a 3 wt. % NaCl solution. Two carbon steel electrodes were used and the coupling current between the electrodes and the coupled potential were recorded. The polarization resistance \( R_P \) was measured at the end of the tests by electrochemical impedance spectroscopy (EIS).

The presence of the Fe₃O₄ simulated corrosion product resulted in an increase in the corrosion rate and, in the case of the Fe₃O₄/bentonite mixture, the degree of localization of the attack. The corrosion rate increased with either increasing Fe₃O₄ content of the mixture or with the thickness of the Fe₃O₄ layer. In the latter case, the presence of the Fe₃O₄ layer ennobled the corrosion potential. This implies that for a corroding carbon steel used fuel container, corrosion rate could increase with time as corrosion product accumulates.

The reasons for the apparent increase in corrosion rate with Fe₃O₄ loading were not discussed by Kojima et al. (1995). However, it is possible that either (i) the reductive dissolution of the Fe₃O₄ powder was coupled to the oxidation of the carbon steel coupon, or (ii) the simulated Fe₃O₄ corrosion product is acting as a large surface area cathode. The first explanation suggests that a Fe₃O₄ covered system is only metastable under these conditions and would revert to an Fe²⁺ surface film. In this scenario this effect is transient and would not result in a permanently raised corrosion rate. However if the Fe₃O₄ is effectively a coupled cathode then the increase in corrosion rate might increase as corrosion proceeds as long as the Fe₃O₄ continues to accumulate. Taniguchi (2003) attempted to replicate the findings of Kojima et al. (1995) by immersing Fe wires in powdered magnetite in ampoules under strictly anaerobic conditions and measuring both the amount of H₂ produced and the change in Fe(III):Fe(II) ratio in the corrosion product. Experiments were conducted in distilled water, 0.5 mol·dm⁻³ NaCl, and 0.1 mol·dm⁻³ NaHCO₃ solutions at 80°C for periods of 30-90 days. The mass-loss corrosion rate was observed to increase with the loading of Fe₃O₄ powder, although not linearly (Figure 6). Also shown in Figure 6 is the equivalent corrosion rate based on the...
amount of H₂ found in the ampoule at the end of the test. The reduction of H₂O accounted for only about 30% of the total mass loss, with the remainder resulting from the reduction of Fe(III) to Fe(II) in the magnetite powder, as determined after the test by titration. However, it is apparent from Figure 6 that the presence of Fe₃O₄ did increase the amount of H₂ produced over that in the absence of the simulated corrosion product. Thus, it was concluded that much of the increase in corrosion rate reported by Kojima et al. (1995) was caused by the reduction of the Fe₃O₄ itself. Taniguchi (2003) also estimated the additional corrosion that might occur based on his measurements and concluded that the consequences would have a minimal impact on the used fuel container lifetime.

*Figure 6: Dependence of the mass-loss corrosion rate on the magnetite loading in 0.5 mol·dm⁻³ NaCl solution (Taniguchi 2003)*

Fushimi et al. (2002) used scanning electrochemical microscopy (SECM) to study the generation of H₂ from a galvanic couple between carbon steel and a Fe₃O₄ single crystal in pH 5.8 sulphate solution. The SECM was used to determine the amount of H₂ generated in solution above the Fe₃O₄ crystal, from which it was concluded that H₂O reduction on Fe₃O₄ accounted for ~ 50% of the couple current measured between the two electrodes. These measurements confirm, therefore, that H₂O is reduced on Fe₃O₄. The enhancement of the H₂ evolution reaction on Fe(III)/Fe(II) corrosion products has also been reported by Been et al. (2007). Figure 7 shows steady-state current-potential behaviour for three different steel surface conditions, namely: a polished and cathodically pre-cleaned surface, a polished surface pre-oxidized for 5 minutes at -0.7 V SCE, and millscale-covered surface comprising a mixture of FeCO₃ and Fe₃O₄. Experiments were performed in a dilute...
simulated groundwater purged with 5 vol.% CO₂/N₂ (~ pH 6.5). The rate of H₂O reduction is enhanced at moderately cathodic potentials (up to approximately -0.95 V SCE) on both the millscale and pre-oxidized surfaces, but this catalytic activity is lost on the pre-oxidized surface at more-negative potentials. Enhanced H₂ evolution is maintained on the millscale-covered electrodes. This enhanced H₂ evolution is believed to be catalyzed by Fe(III)/Fe(II) active sites on the surface which, on the pre-oxidized surface, are lost if the electrode is polarized too negatively. Large cathodic Tafel slopes (~ 200 mV) are observed which reflect not only the kinetics of H₂O reduction but also the potential dependence of the number of active Fe(III)/Fe(II) surface sites. However, even if such a mechanism is relevant to the compact Fe₃O₄ layer that might form on a used fuel container surface, the process is inherently self-stifling. As corrosion proceeds the Fe₃O₄ will be progressively reduced to an Fe(II)-dominant secondary phase which would ultimately shut down the process. Since Fe(III) reduction accounts for ~ 50-70% of the additional corrosion observed then the period of enhanced corrosion should be transitory.

Figure 7: Steady-state cathodic polarization curves for hydrogen evolution on various steel surfaces in dilute synthetic groundwater at pH ~6.5 (Been et al. 2007)

3.1.1.4.2 Mechanical and Physical Properties

The expansion of corrosion products is an important process both from the viewpoint of the generation of stresses in the container shell and the possibility of spalling of the protective oxide.
The Swedish nuclear waste management program has carried out many studies to determine the stresses that might arise between the outer copper shell and inner cast iron insert of a failed canister due to expansion of the iron corrosion products (Smart et al. 2006). Stacks of alternating copper and carbon steel or cast iron discs were confined under a compressive load representative of that expected in a repository and immersed in deaerated simulated groundwater at 69°C. The expansion of the stack was measured using displacement transducers. In separate experiments, carbon steel and cast iron coupons were corroded under anaerobic conditions at 50°C and 80°C and the mechanical properties and structure of the oxide measured using conventional atomic force microscopy (AFM). Chemical composition of the film was determined by Raman and XPS.

No expansion of the test cells was observed over periods of up to 380 days. Expansion of the stack of coupons was observed if a low compressive load, smaller than that expected in a repository, was applied under cyclic wet-dry conditions. This latter test confirmed that the experimental technique worked and that expansion of unconfined (or weakly confined) coupons does occur. Surface analysis of the samples indicated the presence of Fe₃O₄, although α–FeOOH (goethite) and Fe₂O₃ were also detected by XPS, possibly because of air exposure during transfer of the samples to the instrument.

The absence of any observed expansion under realistic confining loads may be explained by the mechanical properties of the oxide. The AFM data suggest that the oxide is compliant and has a low Young’s modulus in the range of 0.04 – 2 MPa, approximately 2-4 orders of magnitude lower than that for Fe₃O₄ formed at high temperatures (Smart et al. 2006), possibly as a result of the higher water content of the oxide formed at lower temperature. The study does not consider whether this more compliant Fe₃O₄ may affect its conversion to Fe₂O₃. In support of the absence of expansion effects observed experimentally, Smart and Adams (2006) examined a number of archaeological and industrial artifacts in which copper alloys in contact with steel or iron have been exposed to corrosive environments. In none of these cases was there any evidence for deformation caused by expansion of corrosion products.

Even if the growth and expansion of corrosion products is insufficient to induce strain in the canister shell, it is possible that such expansion will cause protective corrosion products to spall from the surface. This, in turn, might result in an increase in corrosion rate. No detailed
studies of the spalling of oxides under anaerobic conditions or the effect on the corrosion rate were found in the literature under repository-relevant conditions.

However, there are a number of indirect observations that suggest that, even if spalling should occur, the corrosion rate will not increase significantly. First, there were no indications of an increase in H₂ generation rate due to spalling of corrosion products during the experiments of Schenk (1988), Simpson et al. (1985), or Smart et al. (2001, 2002b). Schenk (1988) did observe spikes in the H₂ generation rate, but these were ascribed to localized corrosion in some solutions rather than the sudden loss of protectiveness of the oxide film. Furthermore, in one test Smart et al. (2001) mechanically removed the outer layer of oxide by rubbing the coupon with a paper tissue. When the sample was returned to the test solution, there was only a temporary modest increase in the H₂ generation rate, suggesting that removal of the outer part of the protective film did not affect the protectiveness of the inner layer. In addition, scratching electrode tests showed rapid re-passivation (Smart et al. 2001), again suggesting a rapid film repair mechanism.

3.1.1.5 Rate-Controlling Process

The nature of the rate-controlling process for the anaerobic corrosion of carbon steel can be inferred from the results of the above reported studies.

The anaerobic corrosion rate of carbon steel decreases with time due to the formation of a protective corrosion product layer. The exact nature and identity of this film is uncertain, but the most likely composition is either Fe₃O₄ (Smart et al. 2001) or, in the presence of high [HCO₃⁻/CO₃²⁻] and/or compacted bentonite, FeCO₃ (Lee et al. 2006a,b, Papillon et al. 2003, Taniguchi et al. 2004). A duplex structure has been inferred for the film possibly comprising an inner layer overlaid by a porous Fe(OH)₂, FeCO₃, or (with increasing temperature) Fe₃O₄ layer, but no direct surface analytical evidence has been provided for this duplex structure (Smart et al. 2001).

The observation that the corrosion rate decreases as the corrosion potential shifts to more-positive values (Smart et al. 2001, 2002a) is consistent with a combination of kinetically controlled H₂ evolution and anodic dissolution under passive conditions, in which the anodic reaction is rate-controlling. The rate-determining step, therefore, is likely the transport of a
species across the surface film, but whether it is the diffusion of anions to the metal/film interface or the diffusion of cations in the other direction is unknown. Smart et al. (2001, 2002a,b) concluded that the corrosion rate is anodically controlled by ion transport across the inner barrier layer of a duplex Fe$_3$O$_4$ film on the surface.

Further evidence of anodic control is the absence of any effect on $E_{\text{CORR}}$ or the corrosion rate of elevated H$_2$ partial pressures (Smart et al. 2001, 2002a). In addition, Simpson (1989) found that adsorption of Fe(II) by bentonite paste leads to an increase in corrosion rate by interfering with the formation of a precipitated protective layer. Although the presence of compacted bentonite will also lead to Fe(II) adsorption, the effect that this has on the rate of precipitation may be offset by the restrictive mass-transport conditions.

For Fe$_3$O$_4$ covered surfaces, there is some evidence that the cathodic reduction of H$_2$O occurs at the film/solution interface (Fushimi et al. 2002, Been et al. 2007). Hydrogen evolution may also occur on the carbon steel surface (or at least the surface of the inner layer of a duplex film). A similar effect would not be expected for non-conducting FeCO$_3$ films.

3.1.2 Localized Corrosion

By definition, localized corrosion results from the spatial separation of anodic and cathodic reactions, resulting in the localized dissolution of the metal. Classically, localized corrosion occurs as a result of the breakdown of a passive film, whereby the majority of the surface is protected from corrosion and dissolution occurs preferentially at defects in the passive layer (Szklarska-Smialowska 2005). It is uncertain whether the surface of a carbon steel used fuel container will be passive or not. Japanese studies in compacted bentonite (JNC 2000) suggest that the surface is active, an observation that is consistent with the expected pore-water pH value of pH 7-8 (King 2005b). As illustrated in Figure 8, carbon steel (or Fe) will passivate due to the formation of a Fe$_3$O$_4$ film in the pH range pH 7-9, depending upon potential (based on the equilibrium between Fe$_3$O$_4$ and a 10$^{-6}$ mol·dm$^{-3}$ Fe(II) solution). Under relatively oxidizing conditions (e.g. -0.25 V$_{\text{SHE}}$ or -0.5 V$_{\text{SCE}}$), Fe$_3$O$_4$ is thermodynamically stable at ~ pH 7. Conversely, under anaerobic conditions (e.g. -0.55 V$_{\text{SHE}}$ or -0.8 V$_{\text{SCE}}$), the equivalent pH is ~ pH 8.5.
Localized attack, however, can be induced by other processes, such as the inhomogeneous distribution of environmental conditions. For example, a non-uniform flux of O₂ to the container surface, or the presence of chemical gradients due to the inhomogeneous distribution of mineral impurities in the clay or local mass-transport gradients. Under such circumstances, however, if the surface is not inherently passive then attack tends to be in the form of ‘uneven’ but still classically uniform corrosion.

![Potential-pH diagram for the Fe-H₂O system at 25°C (Pourbaix 1974)](image-url)

**Figure 8:** Potential-pH diagram for the Fe-H₂O system at 25°C (Pourbaix 1974)

### 3.1.2.1 Mechanism of Localized (Pitting) Corrosion of Carbon Steel Used Fuel Container

A number of different mechanisms can be postulated under which a certain degree of localized attack of the surface could occur. The possible localized (pitting) corrosion mechanisms discussed here are: (i) non-uniform wetting of the surface during the initial cooling phase following the peak in used fuel container surface temperature, (ii) localized breakdown of a passive film, and (iii) reductive dissolution of an Fe(III)-rich film during the transition from aerobic to anaerobic conditions.

During the initial thermal transient, the used fuel container surface will first dry out and then re-wet as the temperature drops and the %RH in the bentonite pores increases. Wetting of the
used fuel container will first occur as a result of the deliquescence of (salt) impurities on the surface of the container (King 2006). Deliquescence of isolated salt crystals will cause the spatial separation of anodic and cathodic sites, with the anodic reaction located under the water droplet condensed on the salt particle and the cathodic reaction restricted to the periphery of the droplet and in satellite micro-droplets (Figure 9). The degree of localized corrosion will depend on a number of environmental factors, including:

(i). The areal density of contaminants, with less localized attack the greater the density of salt crystals;
(ii). The rate of increase in the %RH, and
(iii). The duration of the aerobic phase.

Figure 9: Proposed mechanism for the distribution of anodic and cathodic reactions for micro- and large droplets of water (Zhant et al. 2005)

The driving force for localized corrosion via this non-uniform surface wetting mechanism will diminish with time as the surface becomes more-evenly wetted. Separation of anodic and cathodic sites results from the greater access of O₂ to the carbon steel surface around the periphery of the droplets and to the micro-droplets and thin surface film connecting the micro-droplets to the main droplet (King 2006). As the %RH increases, the surface will become increasingly wetted and the solution in the droplet will become more dilute. More uniform
wetting results in uniform access of O\textsubscript{2} and the loss of the spatial separation of anodic and cathodic reactions. As the environment evolves, therefore, the natural tendency will be for this form of localized corrosion to be stifled.

Classical localized corrosion due to the breakdown of a passive film requires that the used fuel container surface be passive. Japanese researchers have studied the passivity of carbon steel in compacted 70:30 bentonite : sand buffer as a function of pore-water pH and buffer density (Figure 10). In dense buffer material (dry density 1.8 Mg·m\textsuperscript{-3}), voltammetric scans suggest active behaviour in the range pH 9-11 (Figure 10a). At a constant pH 10, passivity is observed at dry densities of 1.2 Mg·m\textsuperscript{-3} and 1.8 Mg·m\textsuperscript{-3}, but not at 0.5 Mg·m\textsuperscript{-3}. No explanation was given for this latter effect, but it may reflect the lower pH-buffering capacity of the relatively unconsolidated buffer. Ion-exchange and equilibration with calcite impurities in the bentonite are likely to result in a decrease in the initial pore-water pH to values closer to the pH 7-8 range.

Fukuda and Akashi (1995) and Fukuda \textit{et al.} (1995) report a critical pH (in bulk solution) of \textasciitilde pH 9.5 at 20\degree C above which carbon steel is passive (Figure 11). This pH value is lower than the initial pore-water pH values in the compacted buffer tests in which only active behaviour was reported (Figure 10), further suggesting that the pore-water pH in these latter tests is
modified by interaction with the clay minerals. Fukuda et al. (1995) also determined the values of the re-passivation potential for creviced carbon steel sample ($E_{R,CREV}$, Figure 11a) and the value of $E_{CORR}$ in aerated and deaerated solution (Figure 11b), both as a function of pH.

Comparison of these data suggest that localized corrosion due to the breakdown of a passive film is unlikely to occur for a carbon steel used fuel container in compacted buffer material. The value of $E_{CORR}$ only exceeds $E_{R,CREV}$ at pH > 9.5 and then only in aerated solution. As with the deliquescence-induced localized corrosion mechanism described above, this mechanism also becomes less likely as the environment evolves and condition becomes anaerobic.

The third possible mechanism for localized corrosion occurs during the transition from aerobic to anaerobic conditions. Reductive dissolution of Fe(III) corrosion products could become coupled to the dissolution of the underlying carbon steel exposed at pores or cracks in the corrosion product layer (Figure 12a). This coupled process would occur during Stage II in the evolution of $E_{CORR}$ illustrated in Figure 3 or, during the transition from aerobic to anaerobic conditions in the repository. Evidence for such coupled processes is widespread in the literature (e.g. Shoesmith et al. 1981). By comparing Figures 8 and 11, the study (Fukuda et al. 1995) supports the view of localized corrosion via reductive dissolution of Fe(III) will not continue at the repository anticipated pH and as the environment becomes anaerobic.

(a). Crevice re-passivation potential

(b). Corrosion potential
Figure 11: Dependence of repassivation potentials for the pitting and crevice corrosion of carbon steel and pH (Fukuda et al. 1995)

Figure 12: Illustration of possible spatial locations for anodic and cathodic reactions on a film-covered carbon steel surface

The duration of this localized corrosion mechanism therefore depends on: (i) the quantity, exposed surface area and rate of reduction of Fe(III) corrosion product, (ii) the relative rates of Fe(III) reduction and the reduction of H$_2$O, and (iii) the rate of pore-opening and increasing surface area of exposed carbon steel. Rapid rates of localized penetration will only occur if the small anode:large cathode geometry is maintained. As the pores in the Fe(III) corrosion product layer increase in size due to dissolution of the layer, the overall cathodic current will
become increasingly dominated by the reduction of $\text{H}_2\text{O}$ on the exposed carbon steel layer at the base of the pores (Figure 12b). Under these circumstances, the anodic and cathodic reactions are occurring in the same location and corrosion becomes uniform in nature. This localized corrosion mechanism is transitory and again tends to stifle with time. For the catalysis of $\text{H}_2\text{O}$ reduction on areas of the surface covered by $\text{Fe}_3\text{O}_4$ coupled to Fe dissolution in pores or cracks in the film (Figure 12c), Jack et al. (2003) report evidence for faster $\text{H}_2\text{O}$ reduction kinetics on millscale-covered surfaces than on polished carbon steel.

Overall, the driving force for localized corrosion diminishes with increasing time. Localized corrosion is likely of concern during the initial period in the evolution of the repository environment. After the establishment of stable, long-term anaerobic conditions, corrosion is expected to be uniform in nature.

### 3.1.2.2 Initiation and Propagation

Many methods have been used for predicting the localized corrosion behaviour of carbon steel. They can be broadly classified as relating to either the initiation of localized corrosion or the propagation of damage following initiation. Predictions based on initiation are often used if it is expected that the carbon steel will be immune to localized corrosion, or only susceptible for a short period of time or under a limited set of conditions. Propagation models are used when initiation is assumed but the extent of damage is thought to be limited, either because of limitations of time or environment or because the material properties are such that the propagating pit or crevice will stifle. In the case of carbon steel UFC in a repository, both initiation and propagation arguments may be used.

Initiation of localized corrosion is typically predicted based on a comparison of the corrosion potential $E_{\text{CORR}}$ and the re-passivation potential $E_{\text{RP}}$. Localized corrosion is assumed to initiate if $E_{\text{CORR}} \geq E_{\text{RP}}$. This approach is considered conservative, since initiation actually occurs at the breakdown potential $E_{\text{B}}$, which is typically 50-200 mV more positive than $E_{\text{RP}}$. The re-passivation potential is actually the potential at which an already initiated pit ceases to grow (Szklarska-Smalowska 2005). The initiation approach has been extensively used in the U.S. Yucca Mountain Project for the prediction of localized corrosion of Alloy 22 (Gordon 2002) and has also been implicitly used for the prediction of the pitting of copper used fuel container (King 2002, 2004; King et al. 2001, 2002). This method requires knowledge of the
time-dependent $E_{\text{CORR}}$ of the carbon steel container and of the value(s) of $E_{\text{RP}}$ under a range of relevant environmental conditions. Re-passivation data for carbon steel are available in the compilation of Szkłarska-Smialowska (2005) and numerous other individual studies. A key role is played by the pH of the environment, with uniform corrosion observed below a critical pH ($pH_{\text{CRIT}}$) and localized corrosion possible at higher pH (Brossia and Cragnolino 2000). The value of $pH_{\text{CRIT}}$ depends on the temperature and the concentration of ions in solution, and has been reported to range from pH 8 to pH 10.5 (Bird et al. 1988, Fukuda and Akashi 1995, Makar and Tromans 1996, Marsh and Taylor 1988). Species such as Cl$^-$ and SO$_4^{2-}$ promote localized film breakdown, whereas HCO$_3^-$ / CO$_3^{2-}$ and increasing pH promote passivity. The long-term $E_{\text{CORR}}$ behaviour can be predicted using a mixed-potential model, as carried out by King and Kolar (2000).

Propagation of localized corrosion has been predicted in a number of ways (Turnbull 1993). They can be broadly classified as either empirical or mechanistic in nature. Empirical models make use of measured parameters, such as current transients from electrochemical experiments or direct measurements of damage from simple immersion tests, to extrapolate into the future. For empirical models, the key factor is whether the environments in which the measurements were made are representative of the service conditions for which the prediction is required. Mechanistic models are based on the mechanism of the pitting or crevice corrosion process. These models typically account for the electrochemical, chemical, mass transport, and precipitation/dissolution reactions inherent in the overall corrosion process. As such, the effects of many different environmental factors can be taken into account, provided the mechanism is sufficiently well understood.

In reviewing these modelling approaches, Turnbull (1993) concluded that the best approach to predicting localized corrosion propagation was through a combination of empirical and mechanistic modelling. Predictions of corrosion damage are best made using empirical techniques, but the understanding derived from mechanistic models is essential for assessing the robustness of the predictions and for providing insights into the empirical data.

The Japanese (JNC 2000) and Swiss (Johnson and King 2003) nuclear waste management programs have made use of an extensive database of pitting factors derived from a long-term underground corrosion study carried out by the U.S. National Bureau of Standards (Romanoff
1989). Similar databases exist in the pipeline industry (e.g., Katano et al. 2003, Martinsek 2003), although these latter sources have not yet been incorporated into predictions of UFC lifetimes.

3.1.3 Hydrogen Effects

3.1.3.1 Mechanism of Hydrogen Generation

As suggested in Equations (7), (8), and (9), the two-stage reaction involves the initial discharge reaction

\[ \text{H}_2\text{O} + \text{Fe} + e^- \rightarrow \text{FeH}_{\text{ADS}} + \text{OH}^- \quad (12) \]

followed by either chemical desorption

\[ \text{FeH}_{\text{ADS}} + \text{FeH}_{\text{ADS}} \rightarrow \text{H}_2 + 2\text{Fe} \quad (13a) \]

or an electrochemical desorption process

\[ \text{FeH}_{\text{ADS}} + \text{H}_2\text{O} + e^- \rightarrow \text{H}_2 + \text{Fe} + \text{OH}^- \quad (13b) \]

Regardless of Reaction (13a) or (13b), the overall reaction can be written as

\[ \text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (14) \]

Subramanyan (1981) suggests the mechanism of the hydrogen evolution reaction in Fe involves slow discharge, followed by fast electrochemical desorption or coupled discharge-desorption control with chemical desorption.

Most mechanistic studies of the evolution of hydrogen have been conducted on freshly polished and electrochemically cleaned electrode surfaces. The surface condition will clearly affect both the rate and, the mechanism of hydrogen evolution. Figure 13 shows the effect of the surface condition on the steady-state current for the reduction of H/H\textsubscript{2}O on carbon steel (Been et al. 2007). At potentials close to the corrosion potential (E\textsubscript{CORR}) in anaerobic solutions (-750 mV\textsubscript{SCE} to -800 mV\textsubscript{SCE}), the rate of water reduction is ca. one order of magnitude higher on oxidized surfaces than on a surface electrochemically cleaned at a potential of -1300 mV\textsubscript{SCE}. Catalysis of the hydrogen evolution reaction is observed for
surfaces either pre-oxidized in situ electrochemically or covered by a Fe₃O₄-containing millscale.

Figure 13: Steady-state cathodic polarization curves for the reduction of water on various steel surfaces in dilute synthetic groundwater at pH 6.5 (Been et al. 2007)

Of the amount of H₂ generated, the rate at which hydrogen is absorbed will be directly related to the rate at which it is generated. King (2008a) has reviewed the available literature on the anaerobic corrosion behaviour of carbon steel. A significant difference was found between the results of studies in bulk groundwater or pore-water solutions and those conducted in the presence of compacted clay. Corrosion rates were lower in bulk solution (steady-state rates of the order of 0.1 µm·a⁻¹) than in compacted clay (1-2 µm·a⁻¹ after 4 year exposure). Compact and protective Fe₃O₄ films were formed in bulk solution, whereas less protective carbonate-containing films are found in compacted bentonite. The higher corrosion rate and the formation of a less-protective film in compacted bentonite is associated with the transport in, and interaction of Fe(II) with, the bentonite.

3.1.3.2 Hydrogen Uptake and Transport

3.1.3.2.1 Hydrogen Uptake

Hydrogen can be absorbed into the carbon steel from both the gaseous and aqueous phases. Hydrogen absorption from the gas phase involves three processes as illustrated in Figure 14 (Wei and Gao 1985):
1. Physical adsorption (also referred to as physisorption)
2. Dissociative chemical adsorption (also referred to as chemisorption)
3. Hydrogen entry (or absorption)

Figure 14: Processes involved in the absorption of hydrogen from the gas phase and the subsequent embrittlement reaction (Wei and Gao 1985)

Physisorption is the result of Van der Waal’s forces between the adsorbate (H$_2$) and adsorbent (the oxide-covered steel). The reaction is generally fast and, hence, at or close to equilibrium and is accompanied by an enthalpy change of $< 20 \text{ kJ}\cdot\text{mol}^{-1}$ (Pasco and Ficalora 1985). The chemisorption step is typically slow and rate determining. Pasco and Ficalora (1985) have suggested the following mechanism:

\begin{align*}
\text{Fe} + \text{H}_2 (g) &\rightarrow \text{Fe} + \text{H}_2^+ (\text{ads}) + e^- \quad (15) \\
\text{H}_2^+ (\text{ads}) + \text{Fe} &\rightarrow \text{Fe} + 2\text{H}^- (\text{ads}) + e^- \quad (16) \\
2\text{H}^- (\text{ads}) + 2\text{Fe} + 4e^- &\rightarrow 2\text{Fe} + 2\text{H}_2 (\text{ads}) \quad (17)
\end{align*}

The nature of the final step and of the anionic adsorbed H species appears unusual, but Pasco and Ficalora (1985) indicate that the nature of the electron-transfer reactions has been confirmed by surface potential measurements. In contrast, Marcus and Oudar (1985) refer to adsorbed H atoms resulting from the interaction of Fe surfaces with gaseous H$_2$.

Hydrogen absorption from aqueous solution or from the discharge of protons involves the absorption of adsorbed hydrogen (FeH$_{\text{ads}}$). In general, any process that either increases the...
surface coverage of FeH$_{ads}$ or increases the rate of the adsorption process will increase the rate or extent of the absorption process. There are relatively few direct measurements of the hydrogen absorption efficiency as expressed by the ratio of the amount of FeH$_{ads}$(i.e. amount of Fe absorbed with adsorbed H) formed to the amount of H absorbed as FeH$_{abs}$, although various factors are known to either promote or inhibit H absorption. Gajek and Zakroczymski (2005) reported a value of between 0.0002 and 0.016 during aggressive cathodic charging (at a current density of 7.5 mA·cm$^{-2}$) under film-free conditions at pH 2.6. Studies performed in the Swedish radioactive waste management program (SKB 2010) has reported that among the various chemical species that are known to promote the absorption of hydrogen by steel, sulphur has the most detrimental effect and its content must be controlled in the bentonite surrounding the container. Flis (1991) presents compelling evidence that the active component is the molecular form of the hydride of these elements, i.e., H$_2$S in the case of sulphur. The enhancement of hydrogen absorption in environments containing H$_2$S/HS$^-$/S$^{2-}$ diminishes with increasing pH above pH 7, which corresponds to the pK of the H$_2$S/HS$^-$ dissociation reaction and, hence, decreasing fraction of the molecular species in solution. Various mechanisms have been proposed to explain the enhancement of hydrogen absorption by hydrogen sulphide (Flis 1991):

- Poisoning of the hydrogen recombination reaction, which would result in an increase in the surface coverage by FeH$_{ads}$;
- The adsorbed sulphide occupies surface sites reducing the surface concentration of FeH$_{ads}$ and reducing the probability of two FeH$_{ads}$ species combining to form H$_2$;
- A reduction in the FeH$_{ads}$ bond energy, which would promote the adsorption of adsorbed hydrogen;
- A reduction in the Fe-Fe bond energy, thereby promoting the absorption of hydrogen via the chemisorptions of H$_2$S, and / or;
- The dissociative chemisorptions of H$_2$S leading to an increase in [FeH$_{ads}$]

Any mechanism that results in an increase in [FeH$_{ads}$] would only result in an increase in hydrogen absorption if the subsequent chemical and electrochemical desorption steps are fast. If these latter reactions are slow, then the [FeH$_{ads}$] will remain high and increasing the concentration would have minimal impact on H absorption. Furthermore, promotion of hydrogen absorption by chemisorption of H$_2$S is only likely on clean Fe surface, i.e., not on oxide-covered surfaces (King 2009). Other promoters of H absorption include thiosulphate
(S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}) and, in acid solution, sulphite (SO\textsubscript{3}\textsuperscript{2-}) (Abd Elhamid et al. 2001), Ca(OH)\textsubscript{2} surface films (Lillard et al. 2000), and cement mortar (Lillard and Scully 1996). Chloride ions have also been reported to inhibit H entry in alkaline solutions (pH 13) at high cathodic polarization levels but to have no effect at low overpotentials (Allam et al. 1997). Conversely, Lillard and Scully (1996) report no effect at all of chloride ions on H pick up.

In addition to the above identified inhibitors, oxides and corrosion product film will also inhibit the absorption of hydrogen. Thus, although adsorbed H\textsubscript{2}S will promote hydrogen uptake, the FeS film formed as a consequence of the presence of sulphide in solution inhibits hydrogen adsorption. The effect of corrosion product films may be a result of several factors:

- Porous or defected insulating films may block the surface resulting in a decrease in the rate of H\textsuperscript{+} or H\textsubscript{2}O reduction and, consequently, of the surface coverage H\textsubscript{ads};
- Continuous surface films may act as a diffusion barrier or exhibit slow rates of H absorption at the electrolyte/film interface or of desorption at the oxide/metal interface; and

The rate of H\textsuperscript{+}/H\textsubscript{2}O reduction on continuous conducting films may be slower than on film-free surfaces, or the rate of FeH\textsubscript{ads} combination faster.

### 3.1.3.2.2 Hydrogen Trapping

Traps are locations in the metals that serve to locally concentrate hydrogen, leading to high local concentrations and the possible initiation of hydrogen damage. Once initiated as a crack, the flaw can grow to critical dimensions leading to unstable fast fracture. Trapping of hydrogen can occur at many microstructural sites in steel, including grain boundaries, phase boundaries, dislocations, interfaces between the matrix and inclusions and particles, vacancies and solute atoms. Certain traps, particularly voids associated with inclusions, can act as dynamic or non saturable traps as they increase in size as H is trapped and the pressure of precipitated H\textsubscript{2} increases (Turnbull 2009). Traps can be categorized as (i) attractive – H is attracted to the trap site due to a gradient in stress or temperature; (ii) physical – a metallurgical or microstructural feature; or (iii) mixed attractive – physical. The significance of the different trap sites for diffusion depends on the density and binding energy and in the case of voids, whether the threshold hydrogen content for void growth has been exceeded. Trap sites with lower binding energy trap H in a reversible manner, whilst those with higher binding energies lead to irreversibly trapped H. Various factors affect the number of trap sites.
within a material. Cold work introduces dislocations near the surface of the material resulting in high near-surface H concentrations. Cold-worked material therefore tends to undergo H cracking near the surface. Figure 15 shows the dependence of the number of trap sites on the degree of cold work for an initially hot-rolled type 1020 steel (Huang and Shaw 1995).

![Figure 15: Effect of Cold Work on the Density of Trap Sites (Huang, and Shaw 1995)](image)

Hydrogen absorbed by the carbon steel may exist in different forms (Flis, 1991): (i) as an interstitial species dissolved in the matrix in solid solution; (ii) associated with structural defects, such as dislocations, and (iii) as gaseous hydrogen accumulated in fissures, voids, or blister. These different forms exhibit different mobilities and affect the mechanical and physical properties of the material to different degrees. The amount of hydrogen associated with structural defects and present as gaseous H$_2$ depends on the properties and composition of the material. The amount of dissolved (lattice) hydrogen depends on the charging conditions and is related to the external environmental conditions.

Lattice hydrogen concentrated at the crack tip has been demonstrated both experimentally and theoretically. Razzini et al. (1999) have used photoelectrochemical techniques to image the distribution of lattice H around cracks in carbon steel. Although the technique is not quantitative, their study clearly shows the higher concentrations in the fracture process zone ahead of the crack tip. It is interesting to note the relative distribution of H (as illustrated by the degree of brightness of Figure 16) corresponds to the distribution of stress ahead of the crack tip. Yu et al. (1997) have used an ion microprobe to map the relative concentration of H ahead of a notch in carbon steel samples. Figure 17 shows the concentration of H ($C_{hi}$) relative to the bulk lattice concentration ($C_0$) as a function of distance from the notch for
different stress intensity factors. Two points from Figure 17 are noted: (i) there is no preferential accumulation of H in the absence of a stress (i.e. $K_I = 0$); and (ii) in the presence of stress, the maximum H concentration is located at the point of highest stress a few hundred microns ahead of the notch.

![Image of hydrogen concentrating at the locations of highest stress in the fracture process zone ahead of the crack tips](image)

**Figure 16**: Photoelectrochemical image of hydrogen concentrating at the locations of highest stress in the fracture process zone ahead of the crack tips (Razzini *et al.* 1999)

![Graph showing measured accumulation of hydrogen ahead of a notch](image)

**Figure 17**: Measured accumulation of hydrogen ahead of a notch in carbon steel as a function of stress intensity factor (Yue *et al.* 1997)

Interstitial (lattice) hydrogen dilates the Fe crystal lattice because the effective size of the hydrogen is greater than the free space at the interstitial site. Evidence suggests that the H occupies a tetrahedral site in the lattice (Hirth 1980). The extent to which the lattice is dilated
by H, and hence the degree to which the strain field is increased, can be assessed from the partial molar volume of H. Values for the partial molar volume of 2.0 cm$^3$mol$^{-1}$ for pure Fe and 2.6 cm$^3$mol$^{-1}$ for Armco iron have been reported (Hirth 1980). Because of its small size, lattice H diffuses rapidly through crystal lattices and, because it dilates the lattice, tends to diffuse to areas of high stress, especially to the region of crack tips or other sharp defects where the hydrostatic stress can be very high (greater than the yield stress). The microstructure also influences the trapping characteristics of the steel (Park et al. 2008). Park et al. (2008) studied the effect of various microstructure produced by thermomechanical controlled processing on the trapping characteristics of an X-65 grade steel pipe (0.05 wt. % C, 0.002 wt. % S). The trapping efficiency increased in the order degenerated pearlite < ferrite/bainite < acicular ferrite, with the total H concentration increasing by a factor of \( \sim 2 \) and the effective diffusivity decreasing by the same proportion over this range of microstructures.

It is known that MnS inclusions act as both traps and as crack initiation sites. The shape of the MnS inclusions plays a critical role in the severity of trapping, with elongated inclusions better trap sites than spherical inclusions. Calcium is added to steels to control the shape and limit the formation of elongated inclusions. Lowering the overall S content also aids in controlling the aspect ratio of the inclusion (length/thickness) (Bernstein and Pressouyre 1985). Yu et al. (1997) report accumulation factors (the ratio of the trapped to lattice H concentration) for various types of inclusion and particle. MnS inclusions exhibited accumulation factors of 10-17, whereas TiN, TiO, Al$_2$O$_3$, and CaO·Al$_2$O$_3$+CaS particles showed accumulation factors that ranged from 8 to 20.

Hydrogen is known to react to form H$_2$ within the crystal lattice. This precipitated H$_2$ behaves the same way as gaseous H$_2$ and, if constrained at voids or micro-cracks, can exert significant pressures within the material. In the absence of gaseous H$_2$ in voids and micro-cracks, the total H concentration in the steel \( (C_T) \) is equal to the sum of the concentrations of lattice H \( (C_o) \) and trapped H

\[
C_T = C_o + C_r + C_i
\]

where \( C_r \) and \( C_i \) are the concentrations of reversibly and irreversibly trapped H, respectively. Because the reversibly trapped H is labile and can contribute to the diffusion of hydrogen in the lattice, the sum of the lattice and reversibly trapped H is termed “diffusible” H, although the use of this term in the literature is not consistent.
At steady state the concentration of irreversibly trapped hydrogen is the density of trap sites whilst the reversibly tapped hydrogen content depends on the binding energy, density of traps, and lattice hydrogen concentration.

### 3.1.3.2.3 Hydrogen Transport

The diffusivity of hydrogen in steel is a function of the crystal structure. Alpha-ferrite (bcc microstructure) exhibits a H diffusivity of $1.6 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ at 25$^\circ$C (Warren 1987), whereas the H diffusivity in austenite (fcc) is 4-5 orders of magnitude lower ($5.4 \times 10^{-10} \text{ cm}^2\text{s}^{-1}$). Steel (a bcc mixture of $\alpha$–Fe and Fe$_3$C) has a H diffusivity of $3 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$ (Warren 1987).

The diffusivity of hydrogen in steel follows an Arrhenius relationship, of the form

$$D = D_o \cdot \exp\left(-\frac{\Delta E}{RT}\right) \quad (19)$$

where $D_o$ is a material dependent constant and $\Delta E$ is the activation energy for diffusion. Thus, the reported diffusivity of H in $\alpha$–Fe is $1.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, $3.5 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, $6.7 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ at temperatures of 20$^\circ$C, 100$^\circ$C, and 200$^\circ$C, respectively (Warren 1987), equivalent to an activation energy of 9.6 kJ·mol$^{-1}$. For Fe and steel, Hirth (1980) recommends a value of

$$D = 0.002 \cdot \exp\left(-\frac{6880}{RT}\right) \text{ cm}^2\text{s}^{-1} \quad (20)$$

Revie et al. (1993) report a higher value for the activation energy of the diffusion of H in pipeline steels of 21 kJ·mol$^{-1}$. The reported values of hydrogen diffusivity for steel at room temperature vary by several orders of magnitude because of variability in the degree of trapping in different materials. Figure 18 shows the variability of diffusivity based on compilations of Völkl and Alefeld (1978) (as reported by Hirth 1980) and Boellinghaus et al. (1995) (as reported by Turnbull 2009). The spread in reported values, especially at around room temperature, is a result of the different extent of trapping in the different samples used by various researches. Figure 18b also illustrates the dependence of diffusivity on microstructures, with higher diffusivity in austenite and $\delta$–ferrite than in the ferrite-pearlite microstructure.
The apparent diffusivity $D_{\text{app}}$ is related to the lattice diffusivity $D_o$ (Oriani 1970)

$$D_{\text{app}} = D_o \left( \frac{C_o}{C_o + C_t (1 - \Theta_t)} \right)$$  \hspace{1cm} (21)$$

where $D_o$ is the lattice diffusivity of hydrogen in the metal, $C_o$ is the hydrogen concentration in the lattice, $C_t$ and $\Theta_t$ are the concentration of trapped H and the fractional occupancy of trap sites, respectively. Trap sites, in the form of dislocations, can be introduced by cold work. Huang and Shaw (1995) reported a 5-fold decrease in $D_{\text{app}}$ after 40% cold work, but no further
decrease on increasing deformation (Figure 19). Particles and non-metallic inclusions also act as H trapping sites and the apparent diffusivity decreases with increasing fraction of particle formers (Figure 20) (Scully and Moran 1988). Tensile stress also increases the diffusivity of H in steel (Quan 1997). Thermodynamically, the presence of a tensile stress leads to a decrease in the chemical potential of lattice hydrogen under elastic conditions (and an increase in chemical potential under compressive loading). The decrease in chemical potential at locations of higher tensile stresses will cause hydrogen to diffuse preferentially down the chemical potential gradient to these locations. As a consequence, hydrogen accumulates in the higher stress regions. Quan (1997) reported that both the lattice and apparent diffusivities were proportional to the stress gradient \( (d\sigma/dx) \)

\[
D_{\text{app}} = D_{\text{app0}} \exp\left( k_{\text{app}} \frac{d\sigma}{dx} \right)
\]

(22)

where \( D_{\text{app0}} \) and \( k_{\text{app}} \) are fitting constants.

Figure 19: Relationship between cold work and the apparent diffusivity of hydrogen in 1020 carbon steel at 25°C (Huang and Shaw 1995)
Models have also been developed that can account for the accumulation of H in the fracture process zone (Gangloff 2009, Lufrano and Sofronic 1998). The concentration of H that accumulates in the fracture process zone is given by Gangloff (2009):

\[
C_H = \frac{c_0 \exp \left( \frac{E_B}{RT} \right) \exp \left( \frac{\sigma \bar{v}}{RT} \right)}{1 + c_0 \exp \left( \frac{E_B}{RT} \right) \exp \left( \frac{\sigma \bar{v}}{RT} \right)}
\]  

(23)

where \(\sigma\) is the stress in the fracture process zone, \(c_0\) is the lattice hydrogen concentration, \(E_B\) is the trap binding energy, and the \(\bar{v}\) is the partial molar volume of hydrogen in the metal. H can be redistributed from trap sites to the lattice, thus promoting crack growth (Scully 2004). Partitioning of the H from the trap sites to the lattice is possible if \(\sigma \bar{v} > E_B\), with the repartition probability, \(P_\sigma\) defined by:

\[
P_\sigma = \frac{\exp \left( \frac{\sigma \bar{v}}{RT} \right)}{\exp \left( \frac{E_B}{RT} \right) \exp \left( \frac{\sigma \bar{v}}{RT} \right)}
\]  

(24)
Figure 21 shows the H repartition probability for a carbon steel with a yield strength of 483 MPa as a function of trap binding energy for various assumed hydrostatic stresses between 2.5 times and 8 times the yield strength (Scully 2004). Also shown on the figure are the typical binding energies for various reversible and irreversible types of trap. Even for the highest assumed stress level (3860 MPa), the probability that H will repartition from even the weakest trap site (Fe/Fe₃C interface) is < 50%. At lower stress levels, the repartition probability is small, especially for dislocations, voids, and grain boundaries. Unlike high-strength steels, therefore, trap sites do not act as a “reservoir” of H that can be released under the action of an applied or residual stress and support crack growth.

Figure 21: Predicted hydrogen repartition probability for a carbon steel with a yield strength of 483 MPa as a function of trap binding energy (Scully 2004)

3.1.3.3 Hydrogen Degradation Modes in Carbon Steel

A number of hydrogen-related degradation modes have been identified for carbon steel (Craig 1987) including: (i) embrittlement during plastic deformation due to exposure to gaseous H₂; (ii) hydrogen stress cracking (or hydrogen-induced cracking, HIC and, in sulphide-containing environments, sulphide stress cracking); (iii) the loss of ductility during plastic deformation; (iv) high-temperature hydrogen attack; (v) blister formation; (vi) damage due to hydrogen picked up during casting and forging; (vii) hydrogen cracking of welds, and (viii) degradation of creep properties. The various failure modes will be discussed in more details in the
following sections, however, it is worth noting that amongst these mechanisms, a number of them are not relevant under repository conditions (Craig 1987). First, hydrogen embrittlement in gaseous $H_2$ or high temperature hydrogen attack will not occur at repository temperatures. Second, processes such as the loss of ductility during plastic deformation and the degradation of creep properties by hydrogen can be avoided through proper UFC design that limits plastic strain or creep due to external loading. Third, the unwanted absorption of hydrogen during casting/forging and welding can be avoided through proper specification of procedures and weld consumables. Consequently, the two hydrogen degradation mechanisms of most concern are: (i) hydrogen stress cracking in which hydrogen accumulates under a stress gradient leading to internal crack formation; and (ii) blister formation as a result of hydrogen accumulation at internal voids, laminations, or inclusions. These two failure modes have been extensively studied in the oil and gas industry. In general, the susceptibility of carbon steel to these failures increases with increasing strength of the material and increasing absorbed hydrogen concentration $[H]$ (Figure 22). For these reasons, both JNC (2000) and Johnson and King (2003) argued that both the use of a low strength steel container and the nature of the repository environment mitigated against hydrogen-related degradation mechanisms. Based on Figure 22, the maximum “allowable” $[H]$ to avoid hydrogen-related cracking mechanisms would be of the order of 2 $\mu g \cdot g^{-1}$ and 10 $\mu g \cdot g^{-1}$, respectively. Under the effect of various environmental parameters, King et al. (2005) reported, with the exception of HS⁻, the concentrations of $[H]$ on the sub-surface of the metal are of the order of 0.2-2 mol·m⁻³ (0.05-0.5 $\mu g \cdot g^{-1}$), approximately one order of magnitude below the “allowable” $[H]$ based on Figure 22. For the case of HS⁻, King et al. (2005) explained the sulphide results in higher $[H]$ because of the poisoning of the $H$ atom recombination reaction on the surface. The presence of a surface film reduces the concentration of absorbed hydrogen, possibly by blocking surface sites for $H$ formation and subsequent absorption as discussed above (Jack et al. 2003).
Figure 22: Schematic illustrating the zones of susceptibility of carbon steel to hydrogen-related degradation mechanisms based on the absorption hydrogen concentration and the material yield strength (JNC 2000)

(a). Effect of HCO$_3^-$

(b). Effect of pH
3.1.3.3.1 Hydrogen Embrittlement

Hydrogen embrittlement (HE) is defined as the deterioration in the mechanical properties of the material, such as the tensile strength, elongation to failure, and fracture toughness. Hirth and Johnson (1976) distinguished three forms of hydrogen embrittlement: (i) delayed failure; (ii) reduced plasticity; and (iii) brittleness in contact with gaseous hydrogen. These various forms of hydrogen embrittlement can be reversible if the source of hydrogen is removed or irreversible if micro-cracks develop during exposure.

Hydrogen embrittlement is more likely in steels with higher strength (tensile strength > 830 MPa or hardness > 22 HRC, Warren 1987) and at higher applied or residual stress (for those
forms of HE that require a pre-existing source of tensile stress). Severe cold working also increases the probability of hydrogen embrittlement. Hydrogen embrittlement is caused by lattice hydrogen interacting with the steel. The elastic properties are not affected but the lattice H greatly affects the plastic properties of the steel, particularly the capacity for plastic flow in the presence of stress or a stress raiser.

Hydrogen embrittlement of plastically deformed steel is most evident temperatures in the range -20°C to +40°C and at slow (tensile or bending) strain rates (Warren 1987). Under these conditions, which correspond to those expected in the DGR after a period of several thousands of years, hydrogen is able to diffuse to the location of plastic strain quickly enough to maintain a sufficient flux of H. Conversely, HE is rarely observed at temperature below 100°C, because the diffusivity of H is too low, or at temperatures greater than +125°C, because the higher diffusivity prevents the concentration of H in regions of plastic strain. Similarly, HE is not observed at high strain rates (e.g., under impact loading) because H cannot diffuse to the region of changing plastic strain fast enough.

(i). Delayed failure

Delayed failure is characterized by brittle cracks in H-containing material subject to stresses below the yield stress. Typically, delayed fracture follows an induction time and exhibits a critical stress level. The severity of delayed fracture increases with increasing hydrogen content, increasing overall stress, and with the presence of local stress concentrators. Terms used to describe delayed failure include hydrogen induced cracking (HIC), stress-oriented hydrogen induced cracking (SOHIC), stepwise cracking (SWC), hydrogen stress cracking (HSC), and, in sulphide environments, sulphide stress cracking (SSC). Table 1 further describes the various forms of delayed cracking of carbon steels. The source of H is typically corrosion, electrolysis (e.g. cathodic protection), or absorption of H or H₂O during thermal treatment or welding.
### Table 1: Forms of delayed cracking of carbon steels (based on NACE 2001)

<table>
<thead>
<tr>
<th>Form</th>
<th>Stress Condition</th>
<th>Mechanism</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>HIC</td>
<td>No externally applied stress</td>
<td>Cracking due to H(_2) pressurization at trap site</td>
<td>Lattice H diffuses to trap sites and precipitates as molecular H(_2). Cracks form in plane.</td>
</tr>
<tr>
<td>HSC</td>
<td>Applied and/or residual tensile stress</td>
<td>Crack formation due to embrittlement by lattice H</td>
<td>Typically occurs in metals galvanically coupled to more active material</td>
</tr>
<tr>
<td>SWC</td>
<td>No externally applied stress</td>
<td>Cracking due to H(_2) pressurization at trap site</td>
<td>SWC is often used to describe the crack appearance.</td>
</tr>
<tr>
<td>SOHIC</td>
<td>Applied and/or residual tensile stress</td>
<td>Crack formation due to embrittlement by lattice H or by H(_2) pressurization</td>
<td>Staggered small cracks, aligned perpendicular to principal tensile stress, resulting in “ladder-like” appearance.</td>
</tr>
<tr>
<td>SSC</td>
<td>Applied and/or residual tensile stress</td>
<td>Crack formation due to embrittlement by lattice H</td>
<td>In sulphide environments, lattice H reduces ductility and increases susceptibility to crack formation in presence of a tensile stress. Affects high strength grades and hard weld zones.</td>
</tr>
</tbody>
</table>

a) **Hydrogen-Induced Cracking (HIC)**

Hydrogen-induced cracking (HIC) is caused by the precipitation of molecular H\(_2\) at voids or microcracks in the steel (Craig 2005). As the internal pressure increases, these voids and microcracks grow and initiate further cracking. No pre-existing source of applied or residual stress is required for HIC. Cracking occurs in low-strength steels and typically is orientated parallel to the plate rolling direction. The rate of crack growth depends on the supply of H and is, therefore, dependent on the diffusivity of H and the lattice H concentration, with a critical value of C\(_0\) below which cracking is not observed. HIC is associated with lower temperatures, with a maximum sensitivity at \(~ 20^\circ\text{C}\) (Turnbull 2009). The incidence of HIC is strongly correlated with the microstructural properties of the steel, in particular the density, shape, and orientation of MnS inclusions (Domizzi *et al*. 2001, Elboujdaini *et al*. 2003, Revie *et al*. 1993b). Although reducing the overall S content is beneficial, the major factor is the
shape of the inclusion, with elongated inclusions primarily responsible for HIC. A banded microstructure (e.g., ferrite-pearlite banding) is particularly susceptible (Elboujdaini et al. 2003, Revie et al. 1993b), although if the banding micro-hardness is < 300Hv the influence of banding is minimal (Domizzi et al. 2001).

b) Hydrogen Stress Cracking / Sulphide Stress Cracking (HSS / SSC)

Both hydrogen stress cracking (HSS) and sulphide stress cracking (SSC) result from the interaction of lattice H and the subsequent reduction in ductility. Under an applied or residual stress, the material cannot accommodate the required strain and a crack initiates. This form of cracking is typically associated with either higher strength materials (tensile strength > 1030 MPa) or severe charging conditions (e.g. H₂S-containing, low pH solutions, the presence of cathodic polarization).

HSS and SSC are dependent on the microstructure (Koh et al. 2004). Ferrite-bainite and ferrite-pearlite microstructures are more susceptible than acicular ferrite as a result of more facile crack initiation at cementite at grain boundaries or hard martensite phases.

c) Stress-Oriented Hydrogen Induced Cracking (SOHIC)

Stress-oriented hydrogen induced cracking manifests itself as a “ladder-like” array of cracks orientated in the rolling direction, inter-connected by cracks in the perpendicular direction. There is some disagreement about the basic mechanism, with some researchers suggesting that the in-plane cracks are a result of internal pressurization of H₂ (Pargeter 2007, Turnbull 2009) and others suggesting a role for embrittlement by interstitial h (Hay 2003). If internal pressurization was responsible, then HIC-resistant steels would also be resistant to SOHIC, but this does not seem to be the case (Pargeter 2007). Regardless, an applied or residual tensile stress is a pre-requisite for SOHIC.

The applied stress may play a number of roles in the cracking mechanism, including:

- Formation of the inter-linking cracks normal to the in-plane cracks;
- Increasing the hydrogen solubility in strained material;
- Localization of H at inclusions, defects, and dislocations; and
- Facilitating void growth.
As with HIC, the rate of crack growth depends on the flux of H, with SOHIC associated with severe charging conditions and high stresses (Pargeter 2007). The threshold H concentration is stress-dependent (Turnbull 2009). Microstructurally, the factors associated with HIC (e.g., elongated inclusions and banded microstructures) are also associated with SOHIC. Locally hard spots in welds also promote SOHIC (Hay 2003).

(ii). Reduce Plasticity
Reduced plasticity is characterized by a decrease in the elongation and reduction-in-area (necking) under tensile loading (Craig 2005). The effect is most noticeable at slow strain rate.

(iii). Britteness
Britteness as defined by Hirth and Johnson (1976) occurs in plastically strained materials in gaseous H$_2$ atmosphere and, unlike delayed failure, exhibits neither an induction time nor a critical stress level. Somerday (2007) summarizes the tensile properties of smooth and notched carbon steel samples exposed to air and 6.9 MPa H$_2$ at room temperature. Whilst there is little effect on either the yield or tensile strength, the % elongation of smooth samples and the % reduction-in-area (%RA) of both smooth and notched samples decreases significantly (average decrease in %RA of 37% and 71% for smooth and notched samples, respectively). The fracture toughness also decreases significantly. Figure 24 shows the dependence of the fracture toughness on H$_2$ pressure for two low-strength carbon steels (yield strength 280 – 375 MPa). It is interesting to note that the fracture toughness reaches a minimum at a H$_2$ pressure approximately equal to the maximum expected in the repository (~8 MPa).
(iv). Hydrogen Embrittlement of Welds

Welds can be particularly susceptible to hydrogen embrittlement because of (i) the effects of temperature changes the solubility of H; (ii) the formation of susceptible microstructures; and (iii) the presence of residual stress and/or stress raisers. These factors can lead to the spontaneous cracking of the weld metal and/or the heat-affected zone (HAZ) due to the presence of the hard brittle martensite phase. Martensite has a body-centred tetragonal crystal structure and a much lower solubility for H than the face centre cubic (fcc) austenite, from which it forms as the material cools. Susceptible welds are typically those from material with a carbon content of 0.25 – 0.35 wt. % (Warren 1987).

The sources of H in the weld include moisture on coated electrodes, grease and fluxes, and a high humidity atmosphere. Note that all these factors are controllable. Other contributing factors are insufficient pre-heat (< 93°C) and the failure to stress relieve by post-weld heat treatment.

Somerday (2007) has summarized information on the tensile properties and fracture toughness of welded carbon steel in the presence of 6.9 MPa H2. The reduction in ductility (%RA) observed for the base metal was also determined in the welded samples. The least-ductile welds were electric resistance, gas tungsten arc, and gas metal arc welds. In terms of the resistance to cracking, the weld fusion zone exhibited a similar fracture toughness to the base metal, but the heat affected zone was significantly less resistant to cracking.
3.1.3.3.2 Blister Formation

Blister formation results from the accumulation of gaseous H$_2$ at voids, laminations, microcracks, inclusion interfaces, or other defects resulting in the formation of large discontinuities or “blister” within the material. Blister formation is more likely to occur at low applied stress and in materials of lower strength (yield strength of $< 480 – 550$ MPa) or hardness $< 22$ HRC (Warren 1987), but it does not cause embrittlement of the material as such. An applied stress is not required for blister formation, but if present, external stress affects the growth and stepwise interlinking of blisters (Iino 1985). As with other forms of H damage, the presence of sulphide inclusion is deleterious, both as trap sites that can concentrate H and as sites at which blisters can nucleate.

For a steel surface in contact with gaseous H$_2$, the pressure of gas in the blister cannot exceed that in the external environment (Louthan 2008). Corrosion is a more likely cause of blister formation than exposure to gaseous H$_2$. It should be noted that blisters in themselves are not necessarily of concern in the case of carbon steel container in a deep geological repository as they do not lead to a through-wall defect and loss of containment. However, cracks can initiate from blisters as the edges act as notches causing an increase in triaxial stress and the accumulation of lattice H.

3.1.3.3.3 Hydrogen Attack

Hydrogen attack involves the conversion of carbon in the steel to methane (CH$_4$) in a process known as decarburization involving the reaction of lattice H with cementite (Fe$_3$C)

$$4 \text{H} + \text{Fe}_3\text{C} \rightarrow \text{CH}_4 + 3 \text{Fe} \quad (25)$$

The resultant gas exerts an internal pressure, leading to voids, fissures, cracks, or flaking and a consequent loss of ductility and strength. This reaction is thermally activated and becomes increasingly severe with increasing temperature. As shown in Figure 25, the threshold temperature for H attack decreases with increasing exposure time because of the kinetics of the reaction. After 10,000 hours exposure (416 days), the threshold temperature at a H$_2$ pressure of 8 MPa is 260°C with no attack, regardless of the exposure period, the threshold temperature at a H$_2$ pressure of 8 MPa is 253°C with no attack (Maximum H$_2$ pressure of 8 MPa in the repository is equivalent to 1160 lb/in$^2$).
3.1.3.3.4 Other Effects of Hydrogen on Steels and their Oxides

Hydrogen can impact other properties of carbon steel that may be relevant to the long-term performance of the used fuel container. Absorbed H is known to promote the anodic dissolution of carbon steel, but extreme charging conditions are required to demonstrate the effect. For example, Figure 26 shows the enhanced dissolution for a pipeline steel (yield strength 359 MPa) following 24 hour cathodic charging at a current density of 3 mA·cm$^{-2}$ in a 1 mol·dm$^{-3}$ H$_2$SO$_4$ solution containing 250 µg·g$^{-1}$ As$_2$O$_3$ (a H absorption promoter) (Gu et al. 1999). These charging conditions would lead to a lattice H concentration of 10’s µg·g$^{-1}$ (two to three orders of magnitude higher than that expected for a used fuel container in the DGR) and would cause significant lattice dilation, as well as possible blister formation and micro-crack initiation. The effect of less aggressive charging conditions on H-enhanced anodic dissolution is unknown and, in all probability immeasurable.
Figure 26: Enhanced anodic dissolution of carbon steel in 0.005 mol·dm$^{-3}$ NaHCO$_3$ solution following hydrogen cathodic pre-charging for 24 hours in 1 mol·dm$^{-3}$H$_2$SO$_4$ + 250 μg·g$^{-1}$ As$_2$O$_3$ solution. (Gu et al. 1999)

Hydrogen is also reported to destabilize passive films on Fe; for example hydrogen leads to an increase in photocurrent as well as changes in other photochemical characteristics of the film (Zeng et al. 2004). Electrochemically, the Fe surface changes from passive to active-passive in moderately alkaline solutions in the presence of H charging (Yu et al. 2001, 2002). The magnitude of these effects increases with increasing cathodic charging current density. However, as noted previously, these studies are typically carried out at aggressive charging current densities (0.1 mA·cm$^{-2}$ to > 1 mA·cm$^{-2}$) and the relevance of the observations to less-aggressive charging conditions is unclear.

Oriani and Josephic (1981) showed that gaseous H$_2$ causes an increase in the ambient creep rate of a spheroidized carbon steel. The authors explained the observations in terms of the effect of H on the movement of dislocations and the softening effect of an increased number of micro-voids due to the presence of H.

Finally, H is also known to affect the corrosion fatigue properties of carbon steel (Gangloff 2009). However, since the UFC will not experience cyclic loads, this effect is not considered further in this review.
3.1.3.4 Hydrogen Degradation Mechanisms

There are different degradation mechanisms to account for the effect of hydrogen on carbon steel. These include (i) the development of internal pressure (i.e. hydrogen-induced cracking, HIC or stress oriented hydrogen-induced cracking, SOHIC); (ii) hydrogen enhanced decohesion (HEDE) of Fe-Fe bonds; (iii) hydrogen enhanced localized plasticity (HELP); and (iv) adsorption induced dislocation emission (AIDE). These mechanisms are not mutually exclusive in some cases. Hydride formation may be an issue in some alloys (Group 4 and Group 5 metals of the Periodic Table) such as titanium, but is not relevant to carbon steels as iron does not form hydrides.

3.1.3.4.1 Internal Pressure

The concept of the internal pressure mechanism is that hydrogen atoms recombine to form molecular hydrogen at internal voids or fissures. An increasing pressure develops as the concentration of hydrogen increases until the pressure increase is sufficient to either initiate a crack or to increase the volume of the void. The Griffith model for brittle fracture describes the critical stress ($\sigma_{\text{crit}}$) for the growth of an elliptical crack of length “a” under plane stress condition as:

$$\sigma_{\text{crit}} = \left(\frac{2E\gamma}{\Pi a}\right)^{1/2}$$

(26)

where $E$ is Young’s modulus and $\gamma$ is the surface energy of the crack. If the crack is considered to represent an interface between an inclusion at which a blister could initiate, the critical pressure for blister formation ($P_{\text{crit}}$) is given by Subramanyan 1981.

$$P_{\text{crit}} = \sigma_{\text{crit}} - \sigma_{\perp}$$

(27)

where $\sigma_{\perp}$ is the applied stress perpendicular to the length direction. In the absence of an external stress,

$$P_{\text{crit}} = \sigma_{\text{crit}} = \left(\frac{2E\gamma}{\Pi a}\right)^{1/2}$$

(28)
Internal pressurization is a plausible explanation for blister formation and hydrogen induced cracking, but cannot explain other forms of cracking or changes in mechanical properties.

3.1.3.4.2 Hydrogen Enhanced Decohesion
In the hydrogen enhanced decohesion mechanism, hydrogen accumulates under an external stress to a level that the interatomic force between adjacent Fe atoms in the lattice is lowered sufficiently that cracks may form (Birnbaum 1991, Oriani 1990, Gangloff, 2008). The applied stress not only serves to concentrate the lattice H but also overcomes the lowered Fe-Fe bond energy. Fracture may occur transgranularly along cleavage planes or intergranularly, depending upon the location of H accumulation. The decohesion mechanism is more important in high strength materials because a high stress is required (Gerberich et al. 1993, Turnbull 2009). Other contributing factors are high H concentrations, sharp crack tips, and high applied or residual stresses. In addition to lattice H, trapped H can also repartition to the crack tip if the hydrostatic stress is sufficient to overcome the binding energy of the trap.

3.1.3.4.3 Hydrogen Enhanced Local Plasticity (HELP)
In the hydrogen-enhanced local plasticity mechanism, hydrogen enhances dislocation motion and the formation of dislocations at surfaces or crack tips, resulting in localized softening (plasticity) of the material (Craig 2005). Much of the evidence for HELP is based on examination of fracture surfaces. Birnbaum (1991) observed the distribution of H ahead of the crack is non-uniform which leads to high localized plastic deformation and an apparently brittle fracture surface. Although there is local plastic deformation, the overall ductility is significantly reduced.

The HELP mechanism requires an applied or residual stress to promote H transport and solubility ahead of the crack tip. The interaction of H with dislocations causes dislocation motion, resulting in a decrease in the flow stress and the occurrence of slip at stresses below those required in the absence of H (Birnbaum 1991). The dislocation velocity is proposed to increase with increasing H$_2$ pressure (Turnbull 2009).

3.1.3.4.4 Adsorption Induced Dislocation Emission (AIDE)
In the adsorption-induced dislocation emission (AIDE) mechanism, hydrogen absorbed in the first few atomic layers weakens the Fe-Fe interaction and facilitates the emission of
dislocations at the crack tip. The fracture surface shows evidence of small voids at particles interconnected by a seemingly macroscopic brittle crack.

The AIDE mechanism shares similarities with the HELP mechanism, in that both are based on fractographic evidence for the presence of ductile features in an overall brittle fracture. However, the mechanisms differ in that (a) the AIDE mechanism involves the creation of dislocations rather than their movement (Turnbull 2009) and (b) AIDE involves surface concentration of H whereas the HELP mechanism also considers the effects on dislocation movement of H in the bulk of the material (Birnbaum 1991).

3.1.3.5 Threshold Conditions for Hydrogen Damage

Many forms of hydrogen degradation exhibit a threshold or critical condition below which damage is not observed. In general, these critical conditions take the form of either a critical H concentration ($H_{\text{crit}}$), for blister formation or HIC, or a critical stress intensity factor ($K_{\text{IH}}$) for crack growth.

3.1.3.5.1 Critical Hydrogen Concentration

The critical hydrogen concentration is often compared with the concentration of lattice hydrogen in order to predict whether the material will be susceptible to a given form of damage in a given environment. It should be noted that the susceptibility to damage is related to the concentration of lattice hydrogen, rather than the total H concentration in the steel (which includes the amounts of atomic or molecular H associated with dislocations, voids, blisters, etc.). The concentration of lattice hydrogen is affected by many factors including temperature, the number, size, shape, and distribution of inclusions, the degree of cold work (dislocations), the strength of the material, microstructure, and in the case of forms of hydrogen embrittlement that require an applied or residual stress, the stress level.

The susceptibility to hydrogen damage generally increases with increasing lattice H concentration and with increasing strength of the material. Figure 27 delineates hydrogen embrittlement immune and “cracking” zones as a function of the yield strength of the steel and the diffusible (lattice) hydrogen concentration (Okada 1977). Data for both a “mild” and a “severe” notch (the meaning of which was not defined by Okada (1977)) are given, which shows the stress-concentration effect of notches or discontinuities on the surface. The figure
also shows the approximate concentrations of lattice H generated in different environments, including liquid NH₃ and H₂S, both of which represent extreme service conditions. The environmental condition similar to the deep geological repository is that labelled “natural environment” which represents near-neutral pH conditions. Under these relatively benign conditions, the figure shows a lattice H concentration of ~ 0.05 µg·g⁻¹ (0.6 cm³ H₂ / 100 g Fe). Under such conditions, steels with yield strength of less than 1000 MPa would be immune to hydrogen embrittlement involving delayed failure.

Figure 27 also provides guidance on the critical lattice H concentration for blister information. As noted previously, blister formation is limited to lower strength materials in which the development of an internal H₂ pressure can exceed the yield strength. However, the critical lattice H concentrations are of the order of 10-100 µg·g⁻¹ (11-110 cm³ H₂ / 100 g Fe). Okada (1977) also describes a “peculiar” form of cracking that occurs in lower-strength materials, again at high lattice H concentrations, and which appears to be a form of delamination due to the development of internal H₂ pressure.

![Figure 27: Zones of susceptibility and immunity to cracking and blister formation as a function of the steel yield strength and diffusible (lattice) hydrogen concentration (Okada 1977)](image)

A yield strength of 100 kg/mm² is equivalent to 981 MPa and a diffusible H concentration of 1 ppm (µg·g⁻¹) is equivalent to 1.12 cm³ H₂ / 100 g Fe.
Other measurements of the critical H concentration for blister formation, HIC, SSC, and HE are summarized in Table 2. There is a wide range of lattice hydrogen concentration values and, in some cases, it is not clear whether the authors are reporting lattice H concentrations or whether the reported threshold “diffusible” H concentration also includes reversibly trapped H. Many studies also included tests at different temperatures. In all cases, the critical H concentration increases with increasing temperature regardless of whether the form of damage is blister formation (Beck et al. 1966) or SSC (Asahi et al. 1994).

**Table 2:** Critical hydrogen concentration for various forms of hydrogen damage

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt. %)</th>
<th>Temp.</th>
<th>Yield strength</th>
<th>( C_{\text{crit}} ) (( \mu g \cdot g^{-1} ))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armco Iron</td>
<td>Unknown</td>
<td>19 °C</td>
<td>Unknown</td>
<td>0.031</td>
<td>Beck et al. 1966</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26 °C</td>
<td>Unknown</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>43 °C</td>
<td>Unknown</td>
<td>0.047</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>66 °C</td>
<td>Unknown</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>80 °C</td>
<td>Unknown</td>
<td>0.100</td>
<td></td>
</tr>
<tr>
<td>API X46</td>
<td>0.10 C, 0.034 S</td>
<td>Room</td>
<td>310 MPa</td>
<td>0.36</td>
<td>Maccagno et al. 1998</td>
</tr>
<tr>
<td></td>
<td>0.11 C, 0.035 S</td>
<td>Temp</td>
<td>310 MPa</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.09 C, 0.014 S</td>
<td></td>
<td>310 MPa</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>API X52</td>
<td>0.20 C, 0.013 S</td>
<td>RT</td>
<td>359 MPa</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>API X56</td>
<td>0.09 C, 0.018 S</td>
<td>RT</td>
<td>389 MPa</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>API X70</td>
<td>0.07 C, 0.008 S</td>
<td>RT</td>
<td>483 MPa</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>API C90</td>
<td>0.26C, 0.002S, 1.06Cr,0.26Mo</td>
<td></td>
<td>668 MPa</td>
<td>8.5</td>
<td>Chu et al.1999a</td>
</tr>
<tr>
<td></td>
<td>0.026C, 0.003S, 0.98Cr,0.32Mo</td>
<td></td>
<td>658 MPa</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23C, 0.013S, 0.95Cr,0.21Mo</td>
<td></td>
<td>708 MPa</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26C, 0.010S, 0.91Cr,0.44Mo</td>
<td>RT</td>
<td>672 MPa</td>
<td>5.0</td>
<td>Yu et al. 1997</td>
</tr>
<tr>
<td></td>
<td>0.23C, 0.013S, 0.95Cr,0.21Mo</td>
<td></td>
<td>658 MPa</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26C, 0.010S, 0.91Cr,0.44Mo</td>
<td></td>
<td>706 MPa</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26C, 0.002S, 1.06Cr,0.26Mo</td>
<td></td>
<td>673 MPa</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>0.72 C, 0.010 S</td>
<td>RT</td>
<td>796 MPa</td>
<td>0.7</td>
<td>Chu et al.1999b</td>
</tr>
<tr>
<td>B</td>
<td>0.74 C, 0.014S, 0.09 V</td>
<td>RT</td>
<td>942 MPa</td>
<td>2.1</td>
<td>Chu et al.1999b</td>
</tr>
</tbody>
</table>
## Table 2b: Hydrogen induced cracking

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt. %)</th>
<th>Temp.</th>
<th>Yield strength</th>
<th>$C_{\text{crit}}$ (µg·g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>API X56</td>
<td>0.13 C, 0.0084 S, 1.09 Mn</td>
<td></td>
<td>386 MPa</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>API X42</td>
<td>0.22 C, 0.0054 S, 0.77 Mn</td>
<td></td>
<td>290 MPa</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>API X52/56</td>
<td>0.16 C, 0.001 S, 0.85 Mn</td>
<td></td>
<td>359 MPa/386</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>API X52/56</td>
<td>0.10 C, 0.0013 S, 0.84 Mn</td>
<td>25°C</td>
<td>359/386 MPa</td>
<td>&gt;1.8</td>
<td>Revie et al. 1993b</td>
</tr>
<tr>
<td>API X52</td>
<td>0.080 C, 0.0016 S, 0.80 Mn</td>
<td></td>
<td>359 MPa</td>
<td>&gt;1.8</td>
<td></td>
</tr>
<tr>
<td>Seamless</td>
<td>0.20 C, 0.0088 S, 0.96 Mn</td>
<td></td>
<td>Unknown</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Seamless</td>
<td>0.095 C, 0.0018 S, 0.73 Mn</td>
<td></td>
<td>Unknown</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>API X70</td>
<td>0.03 C, 0.25 Cr</td>
<td>RT</td>
<td>483 MPa</td>
<td>1.63</td>
<td>Kim et al. 2008</td>
</tr>
<tr>
<td></td>
<td>0.05 C, 0.25 Cr</td>
<td></td>
<td>483 MPa</td>
<td>1.3-1.8</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.74 C, 0.014 S, 0.09 V</td>
<td>RT</td>
<td>942 MPa</td>
<td>0.24</td>
<td>Chu et al. 1999b</td>
</tr>
</tbody>
</table>

## Table 2c: Sulphide stress cracking

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt. %)</th>
<th>Temp.</th>
<th>Yield strength</th>
<th>$C_{\text{crit}}$ (µg·g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>API C90</td>
<td>0.26C, 0.002S, 1.06Cr,0.26Mo</td>
<td>Room</td>
<td>668 MPa</td>
<td>0.82</td>
<td>Chu et al. 1999a</td>
</tr>
<tr>
<td></td>
<td>0.026C, 0.003S, 0.98Cr,0.32Mo</td>
<td>Temp</td>
<td>658 MPa</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.23C, 0.013S, 0.95Cr,0.21Mo</td>
<td></td>
<td>708 MPa</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.26C, 0.010S, 0.91Cr,0.44Mo</td>
<td></td>
<td>672 MPa</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>NS</td>
<td>0.24C, 0.002S, 0.91Cr,0.44Mo</td>
<td>25°C</td>
<td></td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50°C</td>
<td>705-1186 MPa</td>
<td>7.2</td>
<td>Asahi et al. 1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80°C</td>
<td>MPa</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>NP</td>
<td>0.16 C, 0.005 S</td>
<td>25°C</td>
<td></td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50°C</td>
<td>647-1098 MPa</td>
<td>13.5</td>
<td>Asahi et al. 1994</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80°C</td>
<td>MPa</td>
<td>25.0</td>
<td></td>
</tr>
</tbody>
</table>
Table 2d: Hydrogen embrittlement

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt. %)</th>
<th>Temp.</th>
<th>Yield strength</th>
<th>C_{crit} (µg·g^{-1})</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unknown</td>
<td>Unknown</td>
<td>45 °C</td>
<td>959 MPa</td>
<td>856 MPa</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>757 MPa</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>686 MPa</td>
<td>17.7</td>
</tr>
<tr>
<td>A</td>
<td>0.72 C, 0.010 S</td>
<td>RT</td>
<td>796 MPa</td>
<td>0.09</td>
<td>Chu et al. 1999b</td>
</tr>
<tr>
<td>B</td>
<td>0.74 C, 0.014 S, 0.09 V</td>
<td>RT</td>
<td>942 MPa</td>
<td>0.26</td>
<td>Chu et al. 1999b</td>
</tr>
</tbody>
</table>

3.1.3.5.2 Threshold Stress Intensity Factor

The threshold stress intensity factor for hydrogen enhanced crack growth (K_{th}) has been reported to be a function of (i) yield strength (Figure 28); (ii) severity of electrochemical (Figure 28) or gaseous H\textsubscript{2} charging (Figures 28 and 29); and (iii) temperature (Figure 30) (Gangloff and Turnbull 1986). The most susceptible materials are high strength alloys exposed to either extreme cathodic charging conditions or high pressure H\textsubscript{2} environments at ambient temperature as shown in Figures 28-30.

Table 3 summarizes additional values of K_{th} for various materials in various environments.

![Figure 28: Dependence of the threshold stress intensity factor for hydrogen embrittlement of alloy and C-Mn steels at 23°C (Gangloff 2009)](image-url)
Figure 29: Dependence of the threshold stress intensity factor for crack growth ($K_{IH}$) for ASTM A516 carbon steel and for crack arrest ($K_{TH}$) for three low-alloy steels on hydrogen pressure (Gangloff 2009)

Figure 30: Temperature dependence of the threshold stress intensity factor for crack arrest ($K_{TH}$) for various high-strength steels in gaseous hydrogen (Gangloff 2009)
### Table 3: Critical threshold stress intensity factors for hydrogen-assisted cracking

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition (wt. %)</th>
<th>Environment</th>
<th>Temp.</th>
<th>Yield strength</th>
<th>$C_{\text{crit}}$ (µg·g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM A516</td>
<td>Grade not given</td>
<td>69 MPa H$_2$</td>
<td>13 °C</td>
<td>290 MPa</td>
<td>82</td>
<td>Somerday 2007</td>
</tr>
<tr>
<td>ASTM A106</td>
<td>Grade C</td>
<td>97 MPa H$_2$</td>
<td>13 °C</td>
<td>345 MPa</td>
<td>55</td>
<td>Somerday 2007</td>
</tr>
<tr>
<td>API C90</td>
<td>0.26 C, 0.002 S, 1.06 Cr, 0.26 Mo</td>
<td>Cathodic charging in H$_2$SO$_4$ + As$_2$O$_3$</td>
<td>Room Temp</td>
<td>658MPa</td>
<td>46-12.5lnC$_0$*</td>
<td>Yu et al. 1997</td>
</tr>
<tr>
<td>690</td>
<td>0.15C, 0.001S, 0.49 Cr, 0.45 Mo</td>
<td>Biological active sea water</td>
<td>Room Temp</td>
<td>690MPa</td>
<td>43.1·e$^{-1.40 C_0}$</td>
<td>Robinson &amp; Kilgallon 1994</td>
</tr>
<tr>
<td>BS4360 Gr. 50D</td>
<td>0.20 C, 0.035 S</td>
<td>Artificial sea water</td>
<td>Room Temp</td>
<td>355MPa</td>
<td>91.2·e$^{-0.49 C_0}$</td>
<td>Lucas and Robinson 1986</td>
</tr>
</tbody>
</table>

*C$_0$ in units of µg·g$^{-1}$

#### 3.1.4 Stress Corrosion Cracking (SCC)

Stress corrosion cracking is a failure mechanism that occurs because of the simultaneous presence of tensile stresses (due to static or cyclic loading conditions), an environment, and a susceptible material. Carbon steel is susceptible to stress corrosion cracking in a number of environment, notably: caustic, nitrate, phosphate, CO-CO$_2$, high-temperature water (> 200°C), and HCO$_3^-$ / CO$_3^{2-}$ (Ciaraldi 1992). Of these causes, a number can be excluded from consideration because the environment will not form in the repository (Johnson and King 2003, King 2005a), particularly nitrate, phosphate, CO-CO$_2$, and high-temperature water. Because of the pH-buffering capacity of the bentonite clay, it is unlikely that the pH at the container surface will be high enough to cause caustic cracking, even if an alkaline plume reaches the container.

With these environmental considerations, the most likely forms of SCC are those in HCO$_3^-$ / CO$_3^{2-}$ environments. These forms of cracking have been observed on buried pipelines and are referred to as high-pH and low (or near-neutral) pH SCC, based on the range of pH of the electrolyte found in contact with patches of SCC in the field (Parkins 2000). High-pH SCC is observed in concentrated HCO$_3^-$ / CO$_3^{2-}$ solutions (of the order of 0.1-1 mol·dm$^{-3}$) at pH 9.5-
11.5 (Figure 31). A corrosion fatigue mechanism has been proposed (Been et al. 2004, 2005). It is reported that each form of SCC occurs at a pH corresponding to one of the pK’s for the $\text{H}_2\text{CO}_3 / \text{HCO}_3^- / \text{CO}_3^{2-}$ system (the $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$ equilibrium in the case of near-neutral pH SCC and the $\text{HCO}_3^- / \text{CO}_3^{2-}$ equilibrium for high-pH SCC), which can be expressed as:

$$pH = pK + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$  \hspace{1cm} (29)

In the repository, these forms of SCC are unlikely to affect a carbon steel container. The high-pH environment is unlikely to form on the UFC surface because of the need for a highly concentrated $\text{HCO}_3^- / \text{CO}_3^{2-}$ solution. Since the container surface temperature will likely not exceed 100°C, the only concentration mechanism that could generate such solutions involves the deliquescence of precipitated salts during the initial saturation of the repository. However, Cl$^-$ salts tend to deliquesce at a higher temperature (or lower relative humidity) than carbonate salts, so it is unlikely that concentrated $\text{HCO}_3^- / \text{CO}_3^{2-}$ solutions will form by deliquescence.

The environment for near-neutral pH SCC is possible, however, and it is difficult to exclude this form of cracking on environmental grounds.

Figure 31: Potential-pH diagram for iron showing the regions of susceptibility for the two forms of stress corrosion cracking of carbon steel pipelines (King 2005a)
Residual stress could result in superficial cracking of the used fuel container. Figure 32 shows the cross section through a crack in pipeline steel typical of the vast majority of cracks found in the field. Approximately 99% of the cracks observed are of the order of 0.5-1 mm deep and exhibit rounded crack tips and corroded crack walls. These cracks are dormant and are believed to have stopped growing as the crack penetrated beyond the surficial layer of tensile residual stress. Residual stresses can result from the fabrication welding process. However, suitable post-weld heat treatment (PWHT) at elevated temperature (i.e. > 600°C) can be employed to remove the residual stresses from welding, which also soften the hardened microstructure in the heat-affected zone. In cases where PWHT at an elevated temperature cannot be performed, other types of stress-relief treatment could be considered. For example Figure 33 shows the beneficial effect of shot peening on the distribution of residual stress on pipeline steel (Eadie et al. 2002). A net compressive stress of ~ 500 MPa was induced at the surface, with some benefit to depths of ~ 0.6 mm. Machining of the final weld bead will also reduce the stress magnification resulting from the shape of the weld (Eadie et al. 2002). Laser peening is being considered as a post-weld stress-relief treatment in the U.S. Yucca Mountain project. Figure 34 shows the magnitude of the reduction in residual tensile stress in Alloy 22 closure welds resulting from laser peening (BSC 2004). As with shot-peening, a net reduction in surface stress of ~ 500 MPa is possible which, in this case, was sufficient to produce a net surface compressive stress. Compressive stresses persisted for a depth of 2-4 mm in this case.

Figure 32: Cross-section of dormant crack in pipeline steel (Chen et al. 2002)
Figure 33: Effect of shot peening on the distribution of residual stress on pipeline steels (Eadie et al. 2002)

Figure 34: Depth dependence of the residual stress in the hoop and radial directions for the laser-peened outer closure lid and the middle closure lid welds for an alloy-22 waste package (after BSC 2004)
3.1.5 Microbiologically Influenced Corrosion (MIC)

Microorganisms including bacteria, algae and fungi play a critical role in metal corrosion. Bacteria do not directly react with metals but affect corrosion in a variety of ways because their metabolism can change the chemical composition and physical properties of the environment in contact with the metal surface. This in turn affects the thermodynamics and kinetics of the electrochemical reactions that determine the corrosion rate. Microbiologically influenced corrosion of carbon steel is often associated with sulphate-reducing bacteria (SRB) and the formation of sulphide. SRB oxidize organic nutrients using sulphate as a terminal electron acceptor for respiration, thereby generating sulphide. SRB thrive in anaerobic environments in the presence of organic carbon and sulphate, both substances being present in bentonite. However, several factors combine to make saturated bentonite an inhospitable environment for SRB: a small pore size compared to bacterial dimensions, a low water activity, a limited availability of nutrients and an uncertain survival probability of SRB during the initial aerobic high temperature phase (Stroes-Gascoyne 2005, Stroes-Gascoyne et al. 2006, King 2008b). Under expected repository conditions, the water activity is expected to be equal or lower than 0.96 (Stroes-Gascoyne et al. 2006). Such a low water activity is expected to severely limit the growth of active SRB strains. The population of different strains of SRB in saturated bentonite was found to decrease during swelling (Pedersen et al. 2000a, 2000b) and very few cells were expected to be presented in bentonite at full compaction. Consistent with these results, a study using a radioactive labelling technique found that the rate of copper sulphide formation due to MIC of copper decreased with increasing swelling pressure (Masurat et al. 2008). At the highest swelling pressure corresponding to a water activity of 0.96, the corrosion rate was within the scatter band for corrosion in the absence of SRB and two to three orders of magnitude lower than the rate required to reduce the copper container lifetime to 100,000 years (Masurat et al. 2008). Groundwater was considered the main source of SRB but some SRB were thought to originate from the original bentonite and seemed to have survived at 120°C.

There are other forms of MIC associated with acid-producing bacteria. In addition, any form of microbial activity that produces a biofilm can potentially induce localized corrosion. Little et al. (1991) have reported the most aggressive forms of MIC occur underneath biofilms. Biofilms typically contain water, bacteria, and extracellular polymeric substances together
with material from the environment. The area underneath the film becomes anodic with respect to the adjacent surface which acts as the cathode for oxygen reduction. Many scientific reports have presented credible arguments that due to a combination of factors, the risk of bacterial activity and resulting MIC in saturated bentonite under anaerobic conditions is very low. However, a definite proof for the total absence of bacterial activity cannot be given. Rather than trying to demonstrate the total absence of SRB activity in unsaturated bentonite, a different approach which bases on mass balance considerations involving the amounts of available nutrients and sulphate and on mass transport rates of metabolic products to and from the canister surface was considered.

A mass balance approach to microbiologically influenced corrosion of carbon steel containers for nuclear waste disposal was first proposed by Marsh and Taylor (1988), who assumed that the maximum metal loss due to MIC is limited by the total amount of organic nutrients available in the backfill. Sulphate-reducing bacteria oxidize organic carbon compounds to CO₂ or carbonate and reduce sulphates to hydrogen sulphide in stoichiometric proportion. The total amount of material that reacts in a given volume of bentonite is limited by the amount of organic matter or of sulphate present. Marsh and Taylor assumed that the hydrogen sulphide produced by the bacteria reacts with iron as follows:

\[
Fe + H_2S \rightarrow FeS + 2H_2 \tag{30}
\]

or

\[
Fe + HS^- + H_2O \rightarrow FeS + H_2 + OH^- \tag{31}
\]

According to these reactions the reduction of one mole of sulphate by SRB leads to the reaction of one mole of Fe, liberating one mole of hydrogen gas. Each mole of sulphate reduced requires the oxidation of a distinct number of moles of organics that depends on the type of molecules reacting. The maximum depth of corrosion due to SRB which is limited by the availability of nutrients and sulphate can thus be calculated, subject to two conditions. Firstly, for the calculation of corroded depth from the total amount of transformed material, the corroding surface area is required. For corrosion of carbon steel containers in saturated bentonite, it is reasonable to assume that the entire container surface corrodes uniformly and the corroded area is equal to the container surface. Secondly, according to the Equations (28) and (29), the increase in steel corrosion due to MIC is proportional to the amount of hydrogen sulphide generated by SRB. It cannot be entirely ruled out that hydrogen sulphide affects the kinetics of other corrosion reactions involving reduction of water.
Mass balance models give a conservative estimate of the possible corrosion damage due to MIC because they consider that all sulphate present in the bentonite backfill is transformed to hydrogen sulphide that then reacts with the container surface over a specified time period. However, transport processes may be too slow for this to occur. Indeed, to affect corrosion, metabolic products must be present in the immediate vicinity of the container surface. They must either be generated there or reach the container surface by diffusion. The metabolic activity of SRB at the metal surface, and hence the rate of sulphide generation there, is limited by the rate of supply of organic nutrients and of sulphate. Transport of either one of these species may be rate limiting. Bacteria, on the other hand, are much larger and unlikely to diffuse in bentonite. In transport models SRB may therefore be considered as a stationary volume source of metabolic products. Diffusion coefficients of ions in saturated bentonite are two orders of magnitude lower than in aqueous solution, so diffusion is a slow process and one expects a marked decrease of reaction rate with time (Landolt et al. 2009). While a number of studies present credible arguments that SRB are unlikely to metabolize in saturated bentonite and therefore the risk is small, the presence of active SRB in saturated bentonite cannot be ruled out conclusively.

3.1.6 Corrosion Behaviour of Welds
Sealing of the used fuel container will be accompanied by welding the closure lid to the body of the container. Welds are often preferential locations for corrosion and cracking to occur, and special attention must be paid to the design, fabrication, post-weld stress relief (if any), and inspection of the weld in order to ensure sufficient long-term integrity.
Weld development studies for carbon steel containers have been performed in Japan (Asano and Aritomi 2005; Asano et al. 2005, 2006a,b). Tungsten inert gas (TIG) and electron beam (EB) welds have been produced in carbon steel plates with a thickness of 40-190 mm, the upper end of the range corresponding to the proposed thickness of the carbon steel overpack in the Japanese program. High quality TIG welds were produced, with no significant weld flaws (Asano et al. 2005). Electron-beam welding produced welds that were less satisfactory, primarily because of the surface protrusions and porosity at the start and end of the weld (Asano et al. 2006a), and it was concluded that further work was necessary. Residual stress measurements were also made on the completed welds. Tensile stress levels were lower for the EB welds (of the order of 200-300 MPa) than for the TIG welds (300-400
MPa), compared with the yield and ultimate strengths of the base material of 176-310 MPa and 378-430 MPa, respectively. For TIG welds, the maximum tensile residual stress was located at a depth of 10-20 mm below the surface and, in terms of the surface stress, at a distance of 15-30 mm away from the centre of the weld (Asano et al. 2005). For EB welds, the maximum tensile residual stress was located at a depth of ~ 30 mm and 30-50 mm away from the centre of the weld for the maximum surface tensile stress (Asano et al. 2006a). Post-weld stress relief through shot-or laser-peening is expected to be capable of imparting a net compressive residual stress on the closure weld without the need to heat the container and its content. Corrosion tests of TIG, EB, and gas-metal arc welds (MAG) have been performed in aerobic synthetic seawater and a dilute groundwater solutions at 80°C for a period of 90 days (Yokoyama et al. 2007). These environments were selected to represent the early transient conditions in the repository. Preferential attack of the weld metal was observed for TIG- and MAG-welded specimens, but no preferential attack occurred on EB-welded samples. Weight-losses were higher in the dilute groundwater, possibly because of the lower [O₂] in the synthetic seawater due to salting-out effects. Less corrosion was observed in synthetic seawater if bentonite was added to make a stiff slurry (solid:solution ratio 1Mg:1 m⁻³), again possibly because of mass-transport limitations on the supply of O₂ to the surface. Plans are in place for long-term (> 1 year) immersion tests and for tests in anaerobic environments, as well as SCC testing. Conventional arc welding processes for fabricating the steel container will result in the development of hardened microstructures in the heat-affected zone, which will be more susceptible to SCC than the base metal. Elevated-temperature post-weld heat treatment can be used to temper and reduce the hardness of the heat-affected zone, which will also reduce residual stresses and the hydrogen content in the weld metal and heat-affected zone. However, if PWHT cannot be performed due to the concern over thermal damage to the used nuclear fuel, the temper bead welding technique may be considered to produce a tempered heat-affected zone with acceptable hardness without the need for PWHT at high temperatures. Other types of stress relief processes may also be used to reduce the residual stresses of the final closure weld.
3.2 Formation and Structure of Iron Oxides

The structures of iron corrosion products depend on the composition of the layer and the morphology of the individual crystallites. There are sixteen known iron oxides and these compounds may exist as oxides, hydroxides or oxide-hydroxides as listed in Table 4. The iron oxides are composed of Fe together with O and/or OH. In essence, iron oxides formation involves two basic mechanisms:

1. Direct precipitation from Fe(II) or Fe(III)-containing solutions; and
2. Transformation of an Fe oxide precursor, either by a dissolution / reprecipitation process or via a solid state transformation involving internal rearrangements within the structure of the solid precursor.

Table 4: Various forms of iron oxides

<table>
<thead>
<tr>
<th>Oxide-hydroxides and hydroxides</th>
<th>Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite, $\alpha$-FeOOH</td>
<td>Hematite, $\alpha$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Lepidocrocite $\gamma$-FeOOH</td>
<td>Magnetite, Fe$_3$O$_4$ (Fe$^{II}$Fe$^{III}$O$_4$)</td>
</tr>
<tr>
<td>Akaganéite $\beta$-FeOOH</td>
<td>Maghemite, $\gamma$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Schwertmannite Fe$<em>{16}$O$</em>{16}$(OH)$_y$(SO$_4$)$_z$·nH$_2$O</td>
<td>$\beta$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Feroxyhyte, $\delta$-FeOOH</td>
<td>$\varepsilon$-Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Feroxyhyte, $\delta'$-FeOOH</td>
<td>Wüstite FeO</td>
</tr>
<tr>
<td>High pressure FeOOH</td>
<td></td>
</tr>
<tr>
<td>Ferrihydrite Fe$_5$HO$_8$·4H$_2$O</td>
<td></td>
</tr>
<tr>
<td>Bernalite Fe(OH)$_3$</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td></td>
</tr>
<tr>
<td>Green rusts Fe$_x$($III$Fe$<em>y$($II$)(OH)$</em>{3x+2y}$($A$)$_z$; $A^-$ = Cl$^-$; SO$_4^{2-}$)</td>
<td></td>
</tr>
</tbody>
</table>

3.2.1 Formation of Iron Oxides in Aqueous Solution

In Fe(II) solution, goethite, lepidocrocite and akaganéite, magnetite, maghemite, ferrihydrite, feroxyhyte and hematite can be formed by oxidation followed by hydrolysis. Oxidation of Fe(II) salt solutions has been investigated intensively (Davidson and Seed 1983, Roekens and Van Grieken 1983, Millero et al. 1987; von Gunten and Schneider 1991, Vracaer and Cerovic 1997, Rose and Waite 2002). The oxidation reaction of Fe$^{2+}$ with oxygen is:

$$2 \text{Fe}^{2+} + 3 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2 \text{FeOOH} + 4 \text{H}^+ \quad (32)$$

In the neutral pH region, the rate of oxidation of Fe$^{2+}$ with oxygen is first order with respect to [Fe$^{2+}$] and dissolved oxygen, and second order with respect to pH (Stumm and Lee 1961):

$$\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{Fe}^{2+}] \cdot P_{\text{O}_2} \cdot [\text{OH}^-]^2 \quad (33)$$

- 69 -
In Fe(III) solution, Fe$^{3+}$ dissociates in the presence to form the hexa-aquo ion and the electropositive ion induces deprotonation and complete hydrolysis corresponds to formation of an Fe(III) oxide or oxide hydroxide:

\[
\begin{align*}
\text{Fe}^{3+} + 6 \text{H}_2\text{O} & \rightarrow \text{FeOH}^{2+} + \text{H}^+ \\
\text{FeOH}^{2+} + \text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2^+ + \text{H}^+
\end{align*}
\]

As indicates above, the rate of oxidation increases one hundredfold per pH unit. Studies have reported oxidation to be extremely slow below pH 6 and rises sharply above pH 6 (Sung and Morgan 1980; Millero et al. 1987). Increasing the ionic strength of the system also retards oxidation (Sung and Morgan 1980; Millero et al. 1987) but oxidation is accelerated by increasing the stirrer speed (Perez et al. 1998; Perez and Umitsu 2000). Oxidation is accelerated by anions such as $\text{F}^-$, $\text{H}_2\text{PO}_4$ and $\text{HPO}_4^{2-}$ and lowered by others in the order, $\text{ClO}_4^->\text{NO}_3^->\text{Cl}^->\text{H}_3\text{SiO}_4^>\text{Br}^->\text{I}^->\text{SO}_4^{2-}$ (Tamura et al. 1976). Small amounts of Cu, Mn, Co and anions which complex Fe(III) have a catalytic accelerating effect (Stumm and Lee 1961), whereas organic ligands, particularly those found in natural waters, may retard oxidation (Stumm and Singer 1966).

### 3.2.2 Formation of Fe(OH)$_2$ and Fe$_3$O$_4$

As illustrated in Figure 4, various possible oxides, hydroxides and oxyhydroxides of Fe(II) and Fe(III) may be formed on the carbon steel container surface. Which oxide forms is governed by the pH, the rate of oxidation, the temperature, [$\text{Fe}^{2+}$] and also by foreign compounds in the environment. As shown in Reactions 3-5, initial oxidation of Fe in neutral and slightly alkaline environment generally leads to the formation of Fe(OH)$_2$. Ferrous hydroxide is not generally considered to be either kinetically or thermodynamically stable, especially at temperatures $> 100^\circ\text{C}$ and in the presence of O$_2$. The thermodynamic stability of Fe(OH)$_2$ with respect to Fe$_3$O$_4$ decreases with increasing temperature and [O$_2$] (or decreasing [H$_2$]). Venderbosch (1985) suggests Fe(OH)$_2$ is stable at temperatures up to 67$^\circ\text{C}$ in the presence of 100 MPa H$_2$. Thus Fe(OH)$_2$ could be stable inside the used fuel container if formed at a later time (i.e. temperature $<\sim 67^\circ\text{C}$) and if high H$_2$ partial pressures are present. Fe(OH)$_2$ will be oxidized to produce Fe(III)-containing oxides. Various authors have studied the oxidation of Fe(OH)$_2$ to $\alpha$-, $\beta$-, and $\gamma$-FeOOH and Fe$_3$O$_4$. Rapid oxidation in aerated solutions tends to produce one or more of the ferric hydroxides (Domingo et al. 1994), whereas slower oxidation in deaerated solutions produces Fe$_3$O$_4$ (Domingo et al. 1994,
Slower oxidation is believed to allow time for incorporation of Fe$^{2+}$ into the lattice, a process that is also supported by a slight excess of Fe(II) in solution. Other factors that increase the stability of Fe$_3$O$_4$ are higher temperatures (Domingo et al. 1994) and the presence of Cu$^{2+}$ (Ishikawa et al. 1999). Conversely, the opposite factors favour the formation of either α-FeOOH (goethite) or γ-FeOOH (lepidocrocite).

### 3.2.2.1 Effect of pH

Tamura et al. (1981) monitored the transformation of Fe(OH)$_2$ at pH 11 and 65°C. Initially both goethite and magnetite formed, but goethite formation ceased at an early stage of the reaction. It was suggested that the Fe$^{2+}$ ions in solution interact with the goethite or any other Fe(III) oxide such as lepidocrocite to form magnetite (Tamura et al. 1983). Domingo et al. (1994) also reported goethite and lepidocrocite are formed in acidic solutions with large excesses of Fe$^{2+}$, particularly in aerated solutions at temperatures below 90°C. Feitknecht (1959) used Transmission Electron Microscopy (TEM) to monitor magnetite formation from Fe(OH)$_2$ in strongly alkaline media. The hexagonal flakes of Fe(OH)$_2$ were gradually oxidized to thicker plates of green rust which in turn were converted to smaller, thick crystals of magnetite. Feitknecht considered that a topotactic transformation was involved, but subsequently, Sugimoto and Matijevic (1980) showed with TEM that magnetite nucleated on the surface of platy Fe(OH)$_2$ crystals. This growth involved soluble species. The small magnetite crystals aggregated and underwent recrystallization to form larger, single crystals. Once the local supply of neighbouring particles was exhausted, crystal growth ceased and this limited the size of the final crystals.

In 1973, Misawa et al. reported that addition of base to a solution with Fe$^{3+}$/Fe$^{2+}$ ~2 (ratio of magnetite) led first to formation of green rust complexes and then to a dark red complex with the formula, Fe$^{II}$Fe$^{III}$O$_x$(OH)$_{2(3-x)}$xH$_2$O from which magnetite precipitated. Other authors, however, suggested that magnetite formation involved interaction of Fe$^{2+}$ ions with some ferrihydrite that had precipitated initially (Regazzoni et al. 1983, Blesa & Matijevic 1989, Mann et al. 1989, Schwertmann & Fechter 1994).

### 3.2.2.2 Effect of Oxidation Rate

The rate of oxidation depends on the pH and temperature on the container surface, O$_2$ solubility, and other geometry factors. Low oxidation rates appear to promote magnetite and
goethite, whereas high rates favour lepidocrocite. Magnetite formation probably requires slow oxidation because complete dehydroxylation of the precursor (green rust) prior to complete oxidation is only possible if sufficient is available; if, on the other hand, complete oxidation is fast and precedes dehydroxylation, lepidocrocite forms in preference to magnetite (Schwertmann & Taylor 1977). Dehydroxylation and oxidation appear to completing reaction steps.

### 3.2.2.3 Effect of Foreign Compounds

Foreign compounds affect the formation of Fe oxides. A particularly strong effect was found with the various anions. Chloride and other halogenides promote lepidocrocite (Detournay et al. 1976, Taylor 1984). It has been suggested that Cl\(^-\) retards magnetite formation by hindering the condensation of neighbouring OH groups to form Fe-O-Fe linkages. Sulphate had a goethite promoting effect. Whereas the oxidation of Fe(OH)\(_2\) at [SO\(_4^{2-}\)] = 0.03 M and pH 11 leads to magnetite, only goethite is formed at [SO\(_4^{2-}\)] = 0.1 M (Tamaura et al. 1981).

The effect of carbonate has been investigated by oxidizing green rust with a gas mixture containing varying proportions of O\(_2\) and CO\(_2\). Mixtures of goethite and lepidocrocite formed with the proportion of goethite rising as the CO\(_2\)/O\(_2\) ratio increased (Frey & Dixon 1981, Carlson & Schwertmann 1990). The presence of IR adsorption bands at 1300 and 1500 cm\(^{-1}\) indicate that the goethite always contains some perturbed and tightly bound carbonate anions. Alternatively, TEM observations have suggested that carbonate ions may suppress nucleation lepidocrocite (Cornell et al. 1989a). Phosphate suppressed the goethite-favouring effect of carbonate (Torrent and Barron 2000). Goethite only formed if CO\(_2\) were present. Carbonate found in calcite (CaCO\(_3\)) does not induce goethite formation due to the low solubility of CaCO\(_3\). In considering the effect of the anion on the product, studies reported the stability of the green rust precursor depends on the interlayer cation and increases in the order Cl\(^-\)< SO\(_4^{2-}\)< CO\(_3^{2-}\) (Taylor & McKenzie 1980).

### 3.2.3 Transformation

Under the appropriate conditions, iron oxides can be converted between the different forms and these interconversions have an important role in corrosion processes. These interconversions are classified both on the basis of the chemical processes that occur in terms of their structural features. Transformations without chemical changes are term *isochemical*. 
Transformations that involve chemical modification are *dehydration* (loss of H₂O), *dehydroxylation* (loss of OH) and *oxidation / reduction* (a turnover of electrons). Structurally, the transformation processes are either topotactic or reconstructive (Mackay 1961). A topotactic transformation takes place within the solid phase. It involves internal atomic rearrangement with a single crystal of the initial phase being transformed into a single crystal of another phase, i.e. the initial and final crystals have similar 3 dimensional structures. Other solid state reactions in which the end product is not a single crystal are termed *pseudomorphic*. Because a solid-state transformation in the dry state requires a certain mobility of the atoms, it usually takes place only at elevated temperatures.

The reconstructive transformation involves dissolution / reprecipitation; the initial phase breaks down completely (dissolves) and the new phase precipitates from solution (Blesa and Matijevic 1989). There is no structural relationship between the precursor and the product. In contrast to the solid-state transformation, the reconstructive process is driven by an energy gradient and depends on the solubility and dissolution rate of the precursor and therefore, can take place under ambient conditions.

### 3.2.3.1 Solution Transformations

Figure 35 shows a schematic diagram of formation and transformation pathways of ferric and ferrous oxides in aqueous solution (Cornell and Schwertmann 2003). As noted in Figure 35, intermediate oxides which may be precursors of final corrosion products are formed. For instance, ferrous hydroxide Fe(OH)₂ is likely to be converted to green rust by oxidation as oxides containing ferrous ions are easily oxidized under ambient conditions. As anions are intercalated among the atomic layers structures of Fe(OH)₂ and green rust, the anions may play a crucial role in the formation of resultant corrosion products. Magnetite can be obtained in aqueous, alkaline systems by precipitation from a mixed Fe(II) / Fe(III) solution, by oxidation of Fe(II) solution via green rust of Fe(OH)₂, or by interaction of Fe²⁺ with ferrihydrite.
3.2.4 Morphology and Size

The morphology is the external shape of the crystal. Morphology comprises such characteristics as crystal system, cleavage, twinning and specific crystal faces present and shape. The faces which enclose a crystal and give it its characteristic habit can be grouped into forms, i.e. sets of crystal faces which are underlain by ions or atoms in the same geometrical relationship and which have, therefore, the same relationship to the crystal symmetry elements.

Properties of iron oxides and magnetic and dissolution behaviour may be influenced by crystal morphology and crystal size. The range of shapes and sizes displayed by iron oxides reflects the growth environment. Such a set of planes is enclosed in curly brackets. The general form
of a crystal corresponds to a group of faces which intersects all the crystal axes. All other forms present in a crystal are termed special forms. For example, hematite has a number of forms (i.e. \{100\}, \{101\}, \{201\}, etc), whereas magnetite octahedral display only one form, viz \{111\}. A single form is permissible for magnetite because the \{111\} planes enclose all space. Forms are frequently denoted by letters. By convention, the pinacoids that cut the a-, b- and c-axes are referred as a, b and c forms, respectively, and the \{111\} and \{101\} forms are p and m, respectively.

3.2.5 Oxide Structure

Iron oxides and hydroxides consist of arrays of Fe ions and O$^{2-}$ or OH$^{-}$ ions. As the anions are much larger than the cations (the radius of the O$^{2-}$ ion is 0.14 nm, whereas those of Fe(III) and Fe(II) are 0.065 and 0.082 nm, respectively), the arrangement of anions governs the crystal structure and the ease of topological inter-conversion between different iron oxides.

3.2.5.1 Fe(OH)$_2$

Fe(OH)$_2$ is isostructural with brucite (Mg(OH)$_2$) and CdI$_2$. The unit cell is hexagonal with $a = 0.3258$ nm and $c = 0.4605$ nm. The structure consists of sheets of corner-sharing, trigonally distorted Fe(OH)$_6$ octahedra stacked along the \{001\} direction. The Fe(II) ions occupy only half the available octahedral interstices and this results in a structure in which each filled layer of sites alternates with an empty layer of sites. The OH radical behaves as a single entity. Fe(OH)$_2$ is readily oxidized by air and even by water, upon which the colour changes from white to brownish. The structure can be maintained up to a replacement of one tenth Fe(II) by Fe(III). (Bernal et al. 1959).

3.2.5.2 Magnetite Fe$_3$O$_4$

Magnetite has a face-centered cubic unit cell based on 32 O ions which are regularly cubic close packed along the \{111\}. The unit cell edge length is $a = 0.839$ nm. There are eight formula units per unit cell. Magnetite differs from most other iron oxides in that it contains both divalent and trivalent iron. Its formula is written as Y[XY]O$_4$ where X = Fe(II), Y = Fe(III) and the brackets denote octahedral sites (M sites). Eight tetrahedral sites (T sites) are distributed between Fe(II) and Fe(III), i.e. the trivalent ions occupy both tetrahedral and octahedral sites. The structure consists of octahedral and mixed tetrahedral / octahedral layers stacked along \{111\}.
Magnetite is frequently non-stoichiometric in which case it has a cation deficient Fe(III) sublattice. In stoichiometric magnetite Fe(II)/Fe(III) = 0.5, the divalent iron may also be partly or fully replaced by other divalent ions (e.g. Mn(II) to Zn(II)). Fitting of guest ions into the structure is assisted by the flexibility of the oxygen framework which can expand or contract to accommodate cations which differ in size from Fe(II). Cation substitution is accompanied by changes in the unit cell edge length.

3.2.6 Characterization of Metal Surfaces Post-Corrosion

Non destructive characterization methods including X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, infrared spectroscopy and scanning electron microscopy have been used in this study to examine the corrosion products. A brief description of the basic concept of each technique is provided below.

3.2.6.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy involves irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. The spectrometer measures the kinetic energy and the number of electrons escaping from the material surface. From the kinetic energy (KE), the binding energy (BE) of the electrons to the surface atoms can be calculated.

\[ E_k = h\nu - E_B - \phi_{sp} \]  \hspace{1cm} (36)

where \( E_k \) is the kinetic energy of the emitted electron as measured, \( E_B \) is the binding energy of the ejected electron, \( h\nu \) is the energy of the x-ray photons being used, and \( \phi_{sp} \) is the work function of the spectrophotometer. The kinetic energy of the emitted photoelectrons is measured by the spectrophotometer and the data presented as a photoelectron spectrum of the measured photoelectron intensity as a function of the binding energy. Those electrons which are excited and escape without energy loss contribute to the characteristic peaks in the spectrum; those which undergo inelastic scattering and suffer energy loss contribute to the background of the spectrum. XPS measures the elemental composition, chemical state and electronic state of the elements that exist within a material. It detects all elements with an atomic number of 3 (i.e. lithium) and above but cannot detect hydrogen or helium.
The X-ray photoelectron spectroscopy (XPS) analyses performed in this study used a Kratos AXIS Ultra X-ray photoelectron spectrometer. The AXIS Ultra spectrometer is equipped with an integrated magnetic immersion lens and charge neutralization system with a spherical mirror analyser. The ultra high vacuum (UHV) environment required to minimize surface contamination is provided by two reaction chambers – (i) sample treatment chamber (STC); and (ii) sample analysis chamber (SAC). The vacuum chambers are manufactured from 316 non magnetic stainless steel and all materials are UHV compatible materials allowing a base pressure of $5 \times 10^{-10}$ torr to be achieved. UHV pumping and gauging provided in the STC is a turbomolecular pump backed by an oil filled rotary pump. The SAC is pumped by an ion pump equipped with an additional titanium sublimation pump (TSP). The ion pump is fitted with a cryobaffle which may be filled with liquid nitrogen to increase the pump efficiency of the pump. Specimens were analyzed in the analysis chamber of $10^{-6} - 10^{-7}$ Pa (we note that for redox sensitive samples UHV analysis may induce some changes to the material). The STC is isolated from the SAC by an electrically operated flap valve allowing the STC to be vented to dry gas in order to introduce sample to the vacuum system. The magnetic immersion lens is positioned below the specimen and comprises an iron circuit with a gap through which extends an iron pole piece. A water cooled solenoid energises the circuit to produce an intense magnetic field between the pole piece and the outer body of the lens. The magnetic immersion lens has a low spherical aberration coefficient and so enables a large angle of acceptance (a collection angle of 90°) which increases the count rates and also provides good spatial resolution (~ 3 µm). To control charging of the specimens, the charge neutralization system was used to neutralize the (+)ve charging with an excess of low energy electrons. The spherical mirror analyzer provides real-time chemical state and elemental imaging using a full range of pass energy. A micro-channel plate and phosphor detection system are incorporated into the system to provide parallel imaging capability. The parallel imaging technique enhances the speed of data collection by performing simultaneous detection of photoelectrons of the entire analysis area. This method also provides good image resolution (~ 3 µm) as spatial resolution is limited only by the aberrations in the lens system. Limiting the angular acceptance of the lens can reduce the effect of the aberrations and so resolution can be further improved at the expense of sensitivity.
Monochromatic X-rays produced by an AlKα source (15 mA, 14 kV) were bombarded on the specimen and the resulting photoelectrons were collected by the analyzer. Diffraction of AlKα in the quartz crystal provides first-order reflection to produce a narrow X-ray line (reduction in X-ray line width from 0.9 eV to 0.26 eV) and also to remove the unwanted spectrum such as the Bremsstrahlung continuum and satellite peaks. The removal of x-ray satellites and Bremsstrahlung radiation leads to lower background levels and better signal to noise ratios from monochromatic sources. Survey scan spectra were collected at an energy range of 1100 – 0 eV with a pass energy of 160 eV, from an analysis area of 300 x 700 microns. High-resolution analyses were carried out on an analysis area of 300 x 700 microns with a pass energy of 20 eV, 0.05 eV step and 60-s sweep intervals in order to establish the chemical states of the elements present and for quantification purposes.

The obtained spectra and imaging were analyzed using CasaXPS processing software (version 2.3.14). Gaussian (70%)-Lorentzian (30%), defined in CasaXPS as GL(30), profiles were used for each component. Asymmetry of the main metal peak was defined in the form of LA (α, β, m) where α and β define the spread of the tail on either side of the Lorentzian component. The parameter m specifies the width of the Gaussian used to convolute the Lorentzian curve. If values of α and β greater than unity are used, this line shape will correct a problem with previous asymmetric line shapes (Biesinger et al. 2004; Grosvenor et al. 2004; Grosvenor et al. 2006) that tend to incorrectly estimate the peak area by incorporating area under the curve from binding energies well above the peak profile (Fairley 2005). To correct for the inelastically scattered electron background, a standard Shirley background subtraction was used as this subtraction method is generally good for metal XPS peaks. The underlying assumption for the Shirley algorithm is that the background caused by inelastic scattering processes at an energy, E, is proportional to the number of electrons with kinetic energies higher than E. The background, at a given point beneath a peak, is computed from a weighted average of the intensities at the points used to define the extend of a peak within a spectrum, where the end points are weighted with respect to the integrated background-subtracted spectrum to the left and right of the current point. Since the background-subtracted intensity used to calculate the background requires the background as part of the calculation, a Shirley background computed from the data is iteratively determined.
All spectra were calibrated using the adventitious C 1s peak with a fixed value of 284.8 eV. After calibration, the background from each spectrum was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. All survey scans were analyzed to determine the stoichiometry of the compound by using the appropriate sensitivity factors.

3.2.6.2 Raman Spectroscopy

Laser Raman spectroscopy measurements in this study were performed using a Renishaw Model 2000 Raman Spectrometer equipped with a Leica microscope and a thermoelectronically cooled CCD detector. The 632.8 nm line of a HeNe laser was used as the excitation source with an average power of several milliwatts at the steel sample. The measurements were made using a 633 nm laser. The sampling area for this analysis is approximately 2 µm in diameter. The Raman process begins with the laser beam travels through a transmission grating to spread out the outlying light of slightly different wavelengths while reflecting the light beam 90°. Through the collimating lens, the laser light is straightened and concentrated into a point. The light then passes through an iris that only permits the central light at 632.8 nm, the outlying light is absorbed by the iris. The test specimen is irradiated. To block Rayleigh scattering, holographic notch filters are provided to take out the small range of flight near the 632.8 nm range. Following the filters, the focusing lens focuses the light into the CCD where Raman scattering is detected and converted to detectable spectra of light wavelengths, the light signal is converted to electric signal.

Raman spectroscopy is a light scattering technique based on inelastic scattering of monochromatic light. The Raman effect occurs as light impinges upon a molecule, it interacts with the electron cloud causes a change in the molecular polarization potential. A light photon excites the molecule from ground state to a virtual energy state. When the molecule relaxes it emits a photon and it returns to a different rotational or vibrational state. The difference in energy between the original state and its new state leads to a shift in the emitted photon’s frequency. Active Raman vibrations are those that produce a change in the polarization of the system. The Raman effect is based on molecular deformations in electric field, E, determined by molecular polarizability, α. Upon interaction with the sample, the electric field induces electric dipole moment, µ, which deforms molecules of the sample

\[ \mu = \alpha \cdot E \] (37)
Due to the periodical deformation, molecules start vibrating with characteristic frequency $\nu_m$. Raman scattering phenomena are two-photon processes, where an incident photon is momentarily absorbed into a virtual state, a new photon is created and scattered from this virtual level at 3 possible frequencies:

(i). **Rayleigh scattering** – a molecule with no Raman-active modes absorbs a photon with the frequency $\nu_o$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\nu_o$ as an excitation source.

(ii). **Stokes frequency** – a photon with frequency $\nu_o$ is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon’s energy is transferred to the Raman-active mode with frequency $\nu_m$ and the resulting frequency of scattered light is reduced to $\nu_o - \nu_m$.

(iii). **Anti-Stokes frequency** – a photon with frequency $\nu_o$ is absorbed by Raman-active molecule, which at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman-active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_o + \nu_m$.

The Renishaw Raman Spectroscopy Model 2000 used in this study is a Raman spectrometer coupled with an optical microscope. Advantages of such instrumental setup include: (i) confocal light collection, high lateral spatial resolution, good depth resolution, and large solid collection angle for the Raman light. The use of 633 nm wavelength does not promote the electronic transition (i.e. fluorescence) and so the Raman scattering may be easier to detect.

The main difficulty of Raman spectroscopy is to separate the usually weak spontaneous Raman scattering from the intense Rayleigh scattering. More precisely, it is not the Rayleigh scattering that is causing the problem but the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the Raman signal. Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. The holographic grating equipped in the Raman spectrometer exhibits less scattered light than ruled gratings. Other ways to improve Raman signal intensity include the following (Diem 1993):

(i). **Stimulated Raman**: this method irradiates sample with a very strong laser pulse with electric field strength $> 10^9$ V·cm$^{-1}$ (as compare to typical continuous wave lasers with electric field of about only $10^4$ V·cm$^{-1}$), a much larger portion of incident light is transformed into useful Raman scattering and substantially improve signal-to-noise ratio.
Up to 50% of the laser pulse energy can be transformed into coherent beam at Stokes frequency \((\nu_o - \nu_m)\). The Stokes frequency is so strong it acts as a secondary excitation source and generates the second Stokes line with frequency \(\nu_o - 2\nu_m\). The second Stokes line generates the third one with the frequency \(\nu_o - 3\nu_m\), etc. Stimulated Raman technique enjoys 4-5 order of magnitude enhancement of Raman signal as compared to the spontaneous Raman scattering.

(ii). Coherent Anti-Stokes Raman Spectroscopy: this type of spectroscopy uses two very strong collinear lasers to irradiate a sample. Typically, the frequency of the first laser \((\nu_1)\) is constant while the frequency of the second one \((\nu_2)\) is tuned so that the frequency difference between the two lasers equals exactly the frequency of the Raman-active mode of interest (i.e. \(\nu_1 - \nu_2 = \nu_m\)). The frequency of strong scattered light will be \(\nu_1 + \nu_m\), Anti-Stokes frequency. This method only yields one strong Raman peak of interest.

(iii). Resonance Raman (RR): this technique uses an excitation laser frequency at the first or second electronic state which causes the molecules to produce strong Raman scattering (not fluorescence) – Resonance Raman. Note that not all the bands of spontaneous Raman spectrum are enhanced, the chromophoric group which is responsible for the molecule’s coloration typically experience the highest level of enhancement. Tunable lasers are typically used for the Resonance Raman technique.

(iv). Surface-Enhance Raman Spectroscopy & Surface-Enhanced Resonance Raman Spectroscopy (SERS & SERRS): Raman signal from molecules adsorbed on some metal surfaces can be 5-6 orders of magnitude stronger than the Raman signal from the same molecule in bulk volume. The first enhancement may occur because of chemical enhancement which is a charge-transfer effect or chemical bond formation between metal surface and molecules being studied. A second enhancement may be due to electromagnetic enhancement which is the interaction of the laser beam with irregularities on the metal surface. Laser light excites conduction electrons at the metal surface leading to a surface plasma resonance and strong enhancement of electric field. A disadvantage of SERS is the difficulty of spectra interpretation. The signal enhancement may end up enhancing the weak Raman bands that normally would be unnoticed in spontaneous Raman spectra. Trace contaminants can also contribute additional peaks. The main advantage of SERRS is its spectra resemble regular RR
spectra, i.e. easier to interpret. The magnetite spectrum has two peaks at 532 and 667 cm\(^{-1}\) (Oh et al. 1998)

### 3.2.6.3 Infrared Spectroscopy

This study uses Fourier Transform Infrared Spectroscopy (FTIR) to study the chemical bonds present in the corrosion products. FTIR measurements were performed using Bruker IFS 55 instrument under reflection mode with microscope attachment.

Infrared spectroscopy studies the interaction of infrared light with matter as molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. For molecules to absorb infrared radiation, two conditions are required to be fulfilled:

(i) the molecule must have a vibration during which the change in dipole moment with respect to distance is non-zero, i.e.

\[
\frac{\delta \mu}{\delta x} \neq 0
\]  

where \(\delta \mu\) = change in dipole moment, \(\delta x\) = change in bond distance. For molecules without a permanent dipole moment, if the molecule interacts with an electric vector, a temporary induced dipole moment may form and infrared absorption can occur.

(ii) The energy of the light deposited on the molecule must equal a vibrational energy level difference within the molecule, i.e.

\[
\Delta E_{\text{vib}} = \hbar c W
\]

where \(\Delta E_{\text{vib}}\) = vibrational energy level difference in a molecule, \(\hbar =\) Planck’s constant, \(c =\) speed of light, \(W =\) wavenumber in cm\(^{-1}\). Photon energies associated with IR radiation does not have enough energy to excite electrons, but may only induce vibrational excitation of atoms and groups. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states. The main factors determining where absorption will occur are the bond order and the types of atoms joined by the chemical bond. Therefore the same or similar functional groups will absorb within the same, specific frequency ranges. If the energy does not equal to a vibrational energy, level, the energy will be transmitted by the sample. The vibrational energy of a molecule is essentially determined by the shape of the molecule, the masses of the atoms and the associated vibronic coupling. In
molecular vibrations, the position of each atom can be defined by the x, y, and z coordinates as in a Cartesian coordinate system. This results with three independent degrees of freedom of motion. If there are N atoms in the molecule, there will be a total of 3N degrees of freedom of motion for all the nuclear masses in the molecule. After subtracting the 3 translational, 2 rotational and 1 vibrational degrees of freedom from the total 3N degrees of freedom, there are 3N-6 internal degrees of freedom (or normal modes of vibration) for a nonlinear molecule and 3N-5 internal degrees of freedom for a linear molecule. Vibrations can involve either a change in bond strength (stretching) or bond angle (bending) as illustrated in Figure 36.

![Different types of stretching and bending vibrations](image1)

**Stretching and bending vibrations**  **Symmetric and asymmetric stretching vibrations**

![Different types of bending vibrations](image2)

**Different types of bending vibrations**  **Out-of-plane & In-plane bending vibrations**

**Figure 36: Different types of stretching and bending vibrations**

Some bonds can stretch in-phase (symmetrical stretching) or out-of-phase (asymmetric stretching). According to Hooke’s Law when a bond is stretched:

\[ F = -kx \quad (40) \]

where \( F \) = the restoring force of the spring in Newton, \( k \) = force constant in Newton / cm, \( x \) = the displacement from its equilibrium position in cm. And from Newton’s 2\(^{nd} \) Law:

\[ F = ma = -kx = m \cdot \ddot{x} \quad (41) \]

where \( F \) = force [Newton], \( m \) = mass [kg], \( a \) = acceleration [m/s\(^2\)], \( \ddot{x} \) = 2\(^{nd} \) derivative of displacement (x) with respect to time (t).

Thus for harmonic vibrations,
\[ W = \frac{1}{2\pi c} \left( \frac{k}{\mu} \right)^{1/2} \]  
(42)

or

\[ \nu = \frac{1}{2\pi} \left( \frac{k}{\mu} \right)^{1/2} \]  
(43)

where \( W \) = wavenumber [cm\(^{-1}\)], \( c \) = speed of light; \( k \) = force constant in [Newton/cm], \( \mu \) = reduced mass [kg], \( \nu \) = frequency [Hertz]. Equation (41) shows that the chemical bond’s force constant and reduced mass determine the wavenumber at which a molecule will absorb infrared light. A molecule with a large force constant (i.e. a stiff chemical bond) will absorb at a high wavenumber, and a molecule with heavy atoms (a large reduced mass) will absorb at a low wavenumber.

In reality, atoms of different masses do not move with the same amplitude nor move in phase with each other, light atom moves vigorously while the massive atom hardly moves. Exciting one bond often leads to partial excitation of another bond and anharmonicity causes the vibrational energy levels to be unevenly spaced, i.e. vibrational interaction. Some vibrations that normally do not have enough intensity to appear in a spectrum may “take intensity” from another vibration of similar wavenumber and appear in the spectrum – Fermi resonance. The Fermi resonance effect usually leads to two bands appearing close together when only one is expected. The two vibrations “repel” each other, appearing at wavenumbers above and below where they are normally expected – Fermi doublet.

Molecules consisting of different functional groups vibrate differently, causing different dipole moment and therefore give rise to bands of differing intensity. The larger the change of dipole moment, the more intense the absorption band will be. The intensity of absorption peak is also affected by the concentration of the molecules. Beer’s Law relates concentration to absorbance:

\[ A = \varepsilon \cdot l \cdot c \]  
(44)

where \( A \) = absorbance, \( \varepsilon \) = absorptivity (an absolute measure of infrared absorbance intensity for a specific molecule at a specific wavenumber), \( l \) = pathlength, \( c \) = concentration.

The presence of different functional groups also gives rise to absorption bands with different peak widths. Intermolecular interaction affects the electronic structure and hence the force constant of the molecule. Strong intermolecular interactions often give more broad infrared bands due to the presence of more chemical environments or peak widths may also be
widened due to band overlap. Band overlapping may form complex band which may lead to
difficult spectrum interpretation. Regardless of the structure of the molecule, many functional
groups absorb infrared radiation at about the same wavenumber despite the effects of
temperature, pressure, and other environmental factors. These bands or “group wavenumber”
act as diagnostic markers for specific functional groups and may be broadly described as
follows:

**Table 5: Group Wavenumbers**

<table>
<thead>
<tr>
<th>Band position in cm(^{-1})</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3700 – 2500 cm(^{-1})</td>
<td>hydrogen stretching region, C-H, O-H, N-H</td>
</tr>
<tr>
<td>2300 – 2000 cm(^{-1})</td>
<td>triple bond stretching region, C ≡ C, C ≡ N</td>
</tr>
<tr>
<td>2000 – 1600 cm(^{-1})</td>
<td>double bond stretching region, C=C, C=O, C=N</td>
</tr>
<tr>
<td>1600 – 1000 cm(^{-1})</td>
<td>fingerprint region, large # of bands in this region including C-O, C-C, C-N, C-H bending. Most complex region to interpret.</td>
</tr>
<tr>
<td>1000 - 400 cm(^{-1})</td>
<td>aromatic region, bands due to rings such as benzene ring</td>
</tr>
</tbody>
</table>

FTIR is based on the concept of the interference of infrared radiation between two beams to
yield an interferogram. The most common interferometer used in FTIR spectrometry is a
Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which
can travel in a direction perpendicular to the plane (Figure 37).

**Figure 37: Schematic of a Michelson interferometer**

At the interferometer, the incoming infrared light strikes a beam splitter which passes 50% of
the light to a moving mirror that oscillates back and forth and 50% of the light to a fixed
mirror. On reflection from these mirrors, the beam splitter recombines the light which is then guided on towards the specimen where absorption occurs, and further to the detector. As the distance of the moving mirror from the beam splitter changes, different wavelengths of radiation are in-phase and out-of-phase at a frequency that is dependent upon both the rate at which the mirror moves and the frequency of radiation. The moving mirror produces an optical path difference (OPD) between the two arms of the interferometer. OPD can be expressed as the product of the physical distance travelled and \( n \), the index of refraction of the medium filling the interferometer:

\[ \text{OPD} = \Delta \lambda \cdot n \]  

(45)

As the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams “interfering” with each other. The moving mirror displacement, \( \Delta \lambda \), is measured from the zero path difference (ZPD) which is the point when the moving and fixed mirrors are at the same distance from the beamsplitter. The measured interferogram signal produced as a function of the change of pathlength between the two beams is often “decoded” to a frequency spectrum via Fourier Transformation. To determine the absorption intensity and to remove instrumental characteristics, a background spectrum was measured separately without the test sample in the measurement. To ensure the background and sample frequencies are identical, a laser (HeNe) at 632 nm was used.

The FTIR measurements of the steel wires were conducted using the attenuated total reflection (ATR) technique. ATR utilizes the phenomenon of total internal reflection in which an infrared beam is directed onto an optically dense crystal with a high refractive index at an incident angle. A diamond crystal was used in this study due to its robustness. The other two crystals commonly used for horizontal ATR – zinc selenide and germanium were not chosen due to (i) zinc selenide does not work effectively in pH 5-9 environment and the ZnSe crystal scratches easily; and (ii) germanium typically has an effective penetration depth of ~ 1 µm which may result in a weak spectrum for iron oxides on the steel wires.

The ATR concept originates from the fact that radiation propagating in an optically dense medium of refractive index \( n_1 \) undergoes total internal reflection at an interface of an adjacent medium of lower optical density (refractive index \( n_2 < n_1 \)). This “evanescent” wave occurs
only when the angle of incidence exceeds a critical angle, $\theta_c$, as illustrated in Figure 38. $\theta_c$ can be determined by:

$$\sin \theta_c = n_2 / n_1$$  \hspace{1cm} (46)

**Figure 38:** Schematic of the evanescent wave formed at the internal reflection element-sample surface

The depth of penetration, $d_p$, is a function of the wavelength, the refractive index of the crystal, $n_1$, and the angle of incidence, $\theta$.

$$d_p = \frac{1}{\left(2\pi \sin \theta - \left(\frac{n_2}{n_2} \right)^2 \right)^{1/2}}$$  \hspace{1cm} (47)

where $n_2$ is the refractive index of the sample.

Infrared spectra arise as a result of interactions of iron oxides with electromagnetic radiation (photons) in the wavelength range 1-300 µm (i.e. wave numbers of 10,000 – 33 cm$^{-1}$). These interactions involve excitation of vibrations or rotation of molecules in their ground electronic state and are associated with stretching deformations of the interatomic bonds and bending deformations of the interbond angles. The frequency of radiation absorbed depends upon the vibrational energy levels and the force constants of the interatomic bonds. An infrared spectrum is a plot of percent radiation absorbed versus the frequency of the incident radiation given in wavenumbers (cm$^{-1}$) or in wavelength (µm). Increased resolution and sensitivity as
well as more rapid collection of data is provided by Fourier-transform-IT (FTIR), which averages a large number of spectra.

3.2.6.4 Scanning Electron Microscopy Coupled with Energy Dispersive X-Ray (SEM/EDX)

The scanning electron microscope captures images of the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. High resolution images of surface topography are produced using a highly-focused, scanning (primary) electron beam. The primary electron beam interacts with the sample with an energy of 0.5 – 30 kV and generate many low energy secondary electrons. The intensity of these secondary electrons is largely governed by the surface topography of the sample. An image of the sample surface can thus be constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (< 5nm) is achieved when using a primary electron beam with an energy of < 1 kV.

In addition to low energy secondary electrons, backscattered electrons and X-rays are generated by primary electron bombardment. The intensity of backscattered electrons can be correlated to the atomic number of the element within the sampling volume. Hence, some qualitative elemental information can be obtained. The analysis of characteristic X-rays emitted from the sample gives more quantitative elemental information. Such X-ray analysis can be confined to analytical volumes as small as 1 cubic micron. The Hitachi X-4500 field emission SEM with a Quartz XOne EDX system has the following capabilities:

- < 2 nm spatial resolution at higher electron beam voltages (> 15 kV);
- Useful images at 100 KX magnification, or greater, can be obtained;
- Superb low voltage capability with < 5 nm resolution available at 1 kV beam voltage;
- The low voltage capability allows samples that normally require coating to reduce charging problems to be examined without coating;
- Elemental analysis from carbon to uranium;
- Semi-quantitative analysis with detection limits of ~ 0.5 weight % for most elements;
- EDX elemental mapping and backscatter electron imaging;
- The system uses full spectral imaging which allows for live and post-collection data analysis.

4.0 Corrosion Experiments and Hydrogen Gas Experiments

4.1 Overall Design of Corrosion Experiment

Hydrogen generation from a large surface area of carbon steel wires has been the primary means to monitor the corrosion behaviour of carbon steel under anaerobic unsaturated conditions. An initial glass-cell setup, measuring hydrogen using fluid displacement, was unsuccessful, owing to the imprecise response of the mercury manometer to very small pressure changes. Pressure monitoring was then pursued in a similar glass system, but using a high-sensitivity digital pressure gauge. After a series of evaluations, this setup was concluded to have satisfactory sensitivity and leak tightness, and has provided a controlled atmosphere for use in this atmospheric corrosion study. The effects of fundamental variables such as relative humidity (RH), surface condition including salt deposition, and temperature have been studied. Table 6 summarizes the test conditions studied in the series of corrosion experiments.
Table 6:  Test conditions evaluated in the glass cell – pressure gauge system

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Duration (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wires precorroded with 0.5M NaCl then dried</strong></td>
<td></td>
</tr>
<tr>
<td>Test #1 68% RH, 32°C</td>
<td>1347</td>
</tr>
<tr>
<td>Test #2 71% RH, 32°C</td>
<td>935</td>
</tr>
<tr>
<td>Test #3 75% RH, 32°C</td>
<td>1730</td>
</tr>
<tr>
<td>Test #4 100% RH, 32°C</td>
<td>1270</td>
</tr>
<tr>
<td>Test #5 30% RH, 50°C</td>
<td>1962</td>
</tr>
<tr>
<td>Test #6 51% RH, 50°C</td>
<td>1053</td>
</tr>
<tr>
<td>Test #7 75% RH, 50°C</td>
<td>450</td>
</tr>
<tr>
<td>Test #8 100% RH, 50°C (I)</td>
<td>237</td>
</tr>
<tr>
<td>Test #9 100% RH, 50°C (II)</td>
<td>1725</td>
</tr>
<tr>
<td>Test #10 100% RH, 70°C</td>
<td>213</td>
</tr>
<tr>
<td><strong>Wires pre-corroded with 0.05M NaCl then dried</strong></td>
<td></td>
</tr>
<tr>
<td>Test #11 51% RH, 50°C</td>
<td>1867</td>
</tr>
<tr>
<td>Test #12 75% RH, 50°C</td>
<td>2326</td>
</tr>
<tr>
<td>Test #13 75% RH, 32°C</td>
<td>3355</td>
</tr>
<tr>
<td><strong>As-cleaned surfaces</strong></td>
<td></td>
</tr>
<tr>
<td>Test #14 100% RH, 32°C</td>
<td>379</td>
</tr>
<tr>
<td>Test #15 100% RH, 50°C (deaerated with N₂ / H₂)</td>
<td>591</td>
</tr>
<tr>
<td>Test #16 100% RH, 50°C (deaerated with N₂)</td>
<td>615</td>
</tr>
<tr>
<td>Test #17 100% RH, 50°C (reused wires from pickled test at 74.1% RH, 70°C)</td>
<td>309</td>
</tr>
<tr>
<td><strong>Pickled surfaces</strong></td>
<td></td>
</tr>
<tr>
<td>Test #18 75% RH, 32°C</td>
<td>1171</td>
</tr>
<tr>
<td>Test #19 75% RH, 50°C</td>
<td>331</td>
</tr>
<tr>
<td>Test #20 74.1% RH, 70°C</td>
<td>1121</td>
</tr>
<tr>
<td>Test #21 100% RH, 32°C</td>
<td>1337</td>
</tr>
<tr>
<td>Test #22 100% RH, 50°C</td>
<td>1002</td>
</tr>
<tr>
<td>Test #23 100% RH, 50°C (reused wires from 75% RH, 50°C test)</td>
<td>688</td>
</tr>
<tr>
<td>Test #24 100% RH, 70°C</td>
<td>1006</td>
</tr>
</tbody>
</table>

4.2 Material

“Iron” wire of 0.25 mm diameter and 99.5% purity, supplied by Goodfellow Cambridge, was used in this study. Its nominal composition is listed in Table 7.

Table 7:  Nominal composition of iron wire [ppm]

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Sn</th>
<th>C</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>balance</td>
<td>30</td>
<td>30</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>4000</td>
<td>200</td>
<td>50</td>
<td>&lt;800</td>
<td>&lt;600</td>
<td>&lt;600</td>
</tr>
</tbody>
</table>

For comparison, SA516 Gr. 70 has the following nominal composition: C: max 0.28%, Mn: 0.85 to 1.2%, P: max 0.035%, S: max. 0.035%, Si: 0.15 to 0.4%.
Although the supplier refers to the wire as ‘iron’, it is a low-carbon steel, and as such should represent the corrosion performance of any fairly similar steel

4.3 Preparation of Wire Bundles

A total length of 130 m of steel wire, corresponding to 0.102 m² surface area (the same exposed surface area as the UK anaerobic corrosion experiment - Peat et al. 2001) was used for each exposure. The wire was cut into 50 mm lengths and 100 pieces of the cut wires were tied with two PTFE rings to form a bundle. A total of 26 bundles were placed into the glass cell.

Tied bundles were then degreased in acetone ultrasonically for 30 minutes, followed by a thorough rinse with water. The bundles were then further ultrasonically rinsed in deionized water three more times, each time for 3 minutes.

Following rinsing, one of three surface finishes was applied, namely (i) salt deposit or pre-corroded with NaCl; (ii) as-cleaned; and (iii) pickled; the corresponding preparation procedures are described below:

(i) Pre-corroded with NaCl (Tests #1 to #13): after rinsing with de-ionized water, the wires were ultrasonically soaked in 250 mL of 0.5M (Tests #1 to #10) or 0.05M NaCl solution (Tests #11-13) for 10 minutes at room temperature. NaCl soaked wires were then dried in a vertical position in an oven at 50°C for 12 hours or more. The weight gains of the wires after drying in each test are tabulated in Table 8. It should be noted that each weight gain includes both NaCl deposited and corrosion product produced during immersion and drying. The similar weight gains between samples soaked in different concentration solutions suggest that the corrosion products formed during the preparation process account for a large portion of the weight increase. During the wire preparation, there was some loss of corrosion product during drying, which could have introduced some minor differences from the expected 10 times ratio.

(ii) As-cleaned (Tests #14 to #17): after the rinsing with de-ionized water, the wire bundles were placed in anhydrous ethanol and then dried with ambient-temperature flowing air.

(iii) Pickled (Tests #18 to #24): after the rinsing in de-ionized water, the wire bundles were soaked in 10% HCl solution for 5 minutes, then ultrasonically rinsed using de-ionized
water three more times, each time for 3 minutes. After that, the bundles were rinsed in anhydrous ethanol and then dried with flowing air.

Table 8: Weight gained after NaCl deposition

<table>
<thead>
<tr>
<th>Test #</th>
<th>Test Conditions</th>
<th>Weight gained</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre-corroded with 0.5M NaCl</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>68% RH, 32°C</td>
<td>0.81 g</td>
</tr>
<tr>
<td>2</td>
<td>71% RH, 32°C</td>
<td>0.66 g</td>
</tr>
<tr>
<td>3</td>
<td>75% RH, 32°C</td>
<td>0.62 g</td>
</tr>
<tr>
<td>4</td>
<td>100% RH, 32°C</td>
<td>0.74 g</td>
</tr>
<tr>
<td>5</td>
<td>30% RH, 50°C</td>
<td>0.62 g</td>
</tr>
<tr>
<td>6</td>
<td>51% RH, 50°C</td>
<td>0.68 g</td>
</tr>
<tr>
<td>7</td>
<td>75% RH, 50°C</td>
<td>0.74 g</td>
</tr>
<tr>
<td>8</td>
<td>100% RH, 50°C</td>
<td>0.74 g</td>
</tr>
<tr>
<td>9</td>
<td>100% RH, 50°C(II)</td>
<td>0.67 g</td>
</tr>
<tr>
<td>10</td>
<td>100% RH, 70°C</td>
<td>1.14 g</td>
</tr>
</tbody>
</table>

|        | Pre-corroded with 0.05M NaCl |               |
| 11     | 51% RH, 50°C             | 0.75 g        |
| 12     | 75% RH, 50°C             | 0.68 g        |
| 13     | 75% RH, 32°C             | 0.18 g        |

4.4 Design of the Glass Cell – Pressure Gauge System

Photographs of the assembled corrosion cell/pressure gauge system are shown in Figures 39a and 39b. The cell has an inner volume of 170 mL and is equipped with 3 openings, Openings 1 and 2, with an inside diameter of 1 mm, are provided for cell deaeration and pressure relief. Opening 3 connects the digital pressure gauge to the corrosion cell using 2 mm diameter stainless steel tubing about 500 mm long. The connection of the pressure gauge to Opening 3 was sealed with a rubber ring, PTFE tape, and Dow Corning high vacuum grease. Two models of digital pressure gauges were used in the experiments: (i) GE Druck DPI 104 – a micro-processor controlled digital pressure gauge with 0.01 kPa resolution and 0.05% full scale accuracy; and (ii) Accu-Cal Plus digital precision test gauge - supplied by 3D Instruments, with 0.04% full scale accuracy. Both pressure gauges have an operation pressure range of 5-30 psig.

The wire bundles rested on a PTFE screen above the solution used for humidity control. Different solutions were used for humidity control. They are listed, along with their literature values of equilibrium relative humidity, in Table 9. Temperatures were controlled through the use of a water bath. A HH41 thermistor thermometer equipped with ON-403-PP immersion
thermistor probe (manufactured by Omega Engineering Inc.) was used to provide continuous monitoring of temperature of the water bath. The thermistor has a resolution of 0.01°C, with an overall accuracy of ± 0.2°C.

Three temperatures 32 °C, 50°C, and 70 °C, were studied. Pressure data was recorded at the set test temperature within a ± 0.05 °C range and later temperature corrected to the exact set temperature based on vapour pressure of water (Lide 2008).

<table>
<thead>
<tr>
<th>Saturated salt solution</th>
<th>30 °C</th>
<th>50 °C</th>
<th>70 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td></td>
<td>85.0 % RH</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>75.1 % RH</td>
<td>74.5 % RH</td>
<td>74.1 % RH</td>
</tr>
<tr>
<td>NaCl + KCl*</td>
<td>71.0 % RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>67.9 % RH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBr</td>
<td></td>
<td>50.9 % RH</td>
<td></td>
</tr>
<tr>
<td>MgCl₂</td>
<td></td>
<td>30.5 % RH</td>
<td></td>
</tr>
</tbody>
</table>

* Saturated NaCl and KCl solutions were prepared separately and equal amounts of the two solutions were mixed. Crystals of both NaCl and KCl were present in the mixed solution as suggested in Winston and Bates 1960.

A hygrometer, supplied by Omega Engineering, was used to confirm the relative humidity of the different saturated salt solutions. The hygrometer, with a resolution of 0.1 % RH, has a reported accuracy of +/- 2%RH in the range of 0 – 90% RH or +/- 3% RH at higher humidity (90-100% RH).

![Wire bundles in a glass cell](image1)

![Pressure gauge setup](image2)

**Figure 39:** Glass cell – pressure gauge system
4.4.1 Experimental Procedure – Pressure Gauge System

The test conditions studied in the series of corrosion experiments are tabulated in Table 6. The procedure for setting up and running the experiments was as follows:

1. Prepare test specimens by cleaning and pickling or NaCl depositing as required by the test conditions.
2. Assemble the components of the test cell in the open atmosphere.
3. Place a saturated salt solution (for humidity control) into the lower compartment of the cell with plenty of excess crystals; mount the test specimens on top of the PTFE screen inside the cell.
4. Deaerate the saturated salt solution by purging with high purity nitrogen for 2½ hours (estimated residual oxygen: 0.05 ppm from similar studies in the laboratory).
5. Continue deaeration of the remaining volume of the cell for another 30 minutes.
6. Close Openings 1 and 2 with rubber sheet and seal with Dow Corning high vacuum grease.
7. Close Opening 3 with a rubber ring and PTFE tape and seal with Dow Corning high vacuum grease.
8. Place the assembled test cell in the water bath to increase its temperature to the desired level.
9. Monitor pressure and temperature of the test cell. The maximum pressure allowed within the test cell was restricted to 110 kPa by pressure relief. The 110 kPa pressure level was chosen based on a leak test which had confirmed that the test cell was leak-tight with an internal hydrogen pressure of 110 kPa.
10. At the end of an experiment, dismantle the cell, measure the accumulated hydrogen concentration with the electrochemical sensor where necessary, and examine the specimens to determine the characteristics of any corrosion products

4.4.2 Leak Test

Several leak tests were carried out to evaluate possible H₂ leakage, or losses due to H₂ adsorption on components of the test setup, or diffusion into the humidity controlling solution. Results showing the leak tightness of the glass cell are presented in Appendix A. The procedure of the leak test was as follows:

1. Place ~ 25 mL of deionized water into the lower compartment of an assembled test cell.
2. Deaerate the deionized water by purging with high purity nitrogen (99.999%) for 2 hours.

3. Continue deoxygenation of the vapour space of the glass cell using N₂-5%H₂ for another 30 minutes.

4. Seal all openings with vacuum grease.

5. Place the assembled cell in the water bath set at 32°C.

6. Monitor pressure and temperature of the glass cell.

Figure 40 shows the result of one of the leak tests confirming the glass cell is air-leak tight and able to maintain a stable pressure for more than a month.

Figure 40: Typical leak test results (1 month period)

The outcome of the leak testing, calibration and initial corrosion testing gave a good degree of confidence that the glass cell – pressure gauge system could detect meaningful temperature-corrected pressure changes down to 0.1 kPa, and perhaps less, in tests lasting hundreds of hours. The real limits of the system became evident in the less aggressive environmental conditions. The incremental depth of corrosion corresponding to a pressure change of 0.1 kPa in a cell volume of 170 mL is estimated to be ~ 0.53 nm as shown in Appendix B. This
confirms that we have almost monolayer resolution on the amount of iron corroded over periods of hundreds of hours, even with a simple pressure gauge system.

4.5 Measurements of Low Rates of Hydrogen Generation Using a Solid-State Electrochemical Hydrogen Sensor in a Copper Corrosion Chamber

Since about 1983, a technology has existed for hydrogen monitoring in the gas phase, using a solid-state sensor containing a ceramic proton-conducting electrolyte (protic salt), of which the prototype was hydrogen uranyl phosphate (HUP) (Lyon and Fray, 1983). Originally the inventors and others were excited by the extraordinary sensitivity of this device, which can operate as a Nernstian potentiometric sensor and detect hydrogen partial pressures down to the $10^{-6}$ bar range. But this mode was never very successful, and recently similar probes have been marketed that operate as unpowered amperometric sensors (like miniature fuel cells) in a more restricted range of $p_{H_2}$, that is of interest to the oil and gas industry. A new ceramic electrolyte is used in the new probes, which does not suffer from problems with the HUP involving its oxidizing nature. The device functions as a powered amperometric sensor, giving both high sensitivity to hydrogen and good selectivity regarding other gaseous species. The hydrogen probe used in this study was manufactured by Ion Science Ltd, model Hydrosteel 6000 (serial number 08-01919). The feed gas is drawn into the probe at a flow rate of $30 \pm 1$ mL/min, and passed over an anodically charged catalyst that is incorporated into the proton conducting ceramic. The hydrogen is oxidised on the anode and the protons diffuse into the ceramic. At the cathodic side, protons are reduced and recombined to hydrogen gas. The current is proton-diffusion limited and scaled to a flux output reading measured in pl/cm$^2$/s (the cm$^2$ referring to a barnacle-type collection plate used to collect hydrogen emanating from cracked steel pipes – the original purpose of the probe). The sample gas flow path is linear; passing firstly over the anodic electrode, then through the pump, over the cathode, and exiting the pump at an exhaust port located at the base. The pump acts not only to prevent back-flow of the recombined hydrogen to the anode, but also introduces a second stream of ambient gas, which washes the cathode surface clear of accumulating hydrogen. Another important element to the pump design is that there is a bypass valve, connected to the pump in parallel to the source gas tube (likely connecting after the anode). Because the pump is designed to operate at a given flow rate, and is rather fragile due to its size, any blockage in
the inlet pipe could damage the pump. Should a blockage occur, the bypass is proportionally opened to permit ingress of ambient air, maintaining the flow rate at 30 ml/min.

For the less aggressive environments used in the pressure-gauge study, corrosion was undetectable, or became so after some time of exposure. In such cases the hydrogen sensor was used to obtain the necessary sensitivity. The original purpose of the copper chamber was to allow effusion of hydrogen through a palladium membrane, accumulating it in a second chamber where its concentration could be measured in a semi-continuous way by the solid-state hydrogen sensor. But after extensive studies it was concluded that this effusion method did not work. It is true that the use of palladium in such applications is rare at near-ambient temperatures. However, there is no theoretical objection to the method on grounds of permeability of palladium to hydrogen; the difficulties that we experienced have to do with surface poisoning of hydrogen entry into, and exit from, the palladium membrane (Lewis, 1967). Appendix D lists the conditions attempted.

Instead of the semi-continuous monitoring of hydrogen effusion, the hydrogen sensor was used in a batch mode to monitor cells in which the wires were corroding too slowly for any meaningful signal to be detected by pressure increase. An overview of the method is as follows: Having left the cell to accumulate hydrogen over a known time period, the sealed cell and necessary equipment is transferred into a glove box, which is deoxygenated with high purity nitrogen. To record the hydrogen reading, the hydrogen sensor is connected to the cell and draws the gas out. The probe response is not instantaneous, and takes several seconds to equilibrate with the gas concentration of the sample. As the gas is being drawn, a partial vacuum forms, causing a reduction in the flow rate from the cell. The bypass partially opens and the recorded hydrogen flux exponentially decreases as the probe is starved of cell gas (hydrogen). The highest flux reading is recorded and compared to the calibration peak to determine the concentration of hydrogen within the cell. Following sampling, the cell is purged with nitrogen to remove any accumulated hydrogen, in advance of the next sampling period.

The test conditions evaluated in this series of experiments are summarized in Table 10.
Table 10: Test conditions evaluated in the copper cell – H₂ sensor arrangement

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Duration (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pickled wires, 75% RH, 50°C</td>
<td>864</td>
</tr>
<tr>
<td>Pickled wires, 85% RH, 50°C</td>
<td>1826</td>
</tr>
<tr>
<td>Pickled wires, 75% RH, 50°C (II)</td>
<td>2733</td>
</tr>
<tr>
<td>Pickled wires, 100% RH, 50°C</td>
<td>385</td>
</tr>
</tbody>
</table>

The hydrogen probe was designed to identify sites of cracking in steels. This is done by attaching a barnacle probe to the steel structure being tested, and drawing ambient air over the surface. The air being drawn into the probe carries with it the hydrogen emanating from the steel, permitting the user to determine whether cracks are present or not. For the current work, the probe was used without the barnacle fitting, and the anoxic cell gas was drawn directly into the probe. It was deemed necessary to prove that the probe did not require oxygen in the input gas in order to operate correctly.

To show the hydrogen probe functions without input oxygen, the hydrogen probe (serial 07-01627 – a different probe to that used in the body of the work, which was 08-01919) was connected to a tedlar sample bag, which had been manually evacuated using a gas syringe and filled with one of the two following gas compositions:
1. 600 ml of 97.47 ppm (certified) H₂ gas with residual N₂ + 300 ml unfiltered laboratory air
2. 1 L of 97.47 ppm (certified) H₂ gas with residual N₂

The hydrogen probe response to the 2 gases is shown in Figure 41. The hydrogen concentration for the oxygen-containing gas has also been normalized to compensate for the dilution effect of adding air to the sample bag, for easier comparison.

The results demonstrate similar decay profiles. A linear fit of the data, from between 5 and 25 minutes, yielded the following gradients:

1. -0.827 pl/cm²/s/minute (O₂-containing gas)
2. -0.568 pl/cm²/s/minute (anoxic gas)
Both sets of data demonstrate a significant reduction in the sensitivity of the probe over the time scale tested. The differences in decay gradient could be due to a variety of factors, including the hydrogen gas concentration, ambient temperature, and sensor temperature (a function of operating time). No significant differences in probe response, due to the presence or absence of oxygen, were found, as would be expected of this type of amperometric device. Hydrogen is oxidised, is absorbed by the proton conducting ceramic, and is subsequently reduced and recombined at the outlet. The recorded current is proportional to the hydrogen concentration.

4.5.1 Experimental Procedure – H₂ Sensor

The procedure for carrying out the H₂ measurements was as follows:

1. Clean all components of the copper cell with acetone and rinse thoroughly with de-ionized water.

2. Assemble the internal components of the copper cell by placing a PTFE plate in a 50 mL beaker and putting the 50 mL beaker into a 100 mL beaker. The PTFE plate is provided...
to drain off condensation from the wire surfaces. Put both beakers into the copper cell (Figure 43).

3. Deaerate 20 mL of saturated salt solution with N₂ for 2 hours and pour the deaerated salt solution into the 100 mL beaker (inside the copper cell). Based on similar studies performed in the laboratory, residual oxygen is estimated to be about 0.05 ppm.

4. Prepare the test wires by cleaning and pickling as required by the test conditions.

5. Place the prepared wire bundles into the 50 mL beaker, on top of the PTFE screen (Figure 42).

6. Continue deaeration for another 30 minutes before closing the valve of the cell and sealing the cell using PTFE tape and vacuum grease.

7. Place the copper cell into the water bath at a pre-set temperature.

8. In initial trials where a palladium membrane was used (Figure 44), the palladium foil was pretreated separately. Various pre-treatment conditions were tried, including (i) heating the foil in an oven at 720-900°C for 30 – 60 minutes, then at 500°C for another 30 minutes; (ii) reducing any surface oxide on the Pd surface by flushing the foil with Ar + 2.5% H₂ mixture in a tube furnace for 5 minutes at 200°C; (iii) coating the Pd foil exit surface with 0.1M NaOH. After the pretreatment, the Pd foil was mounted between the upper and lower compartments of the copper cell and a mixture of N₂ and 100 ppm H₂ was then introduced into the copper cell for 30 minutes. The valve of the cell was then closed and the copper cell was sealed with PTFE tape and vacuum grease. H₂ measurements were carried out at various time intervals using the H₂ probe but none of these pre-treatments were found effective in resolving the surface poisoning problem encountered on the palladium membrane.

The procedure for monitoring H₂ in a batch mode is as follows:

9. Prepare the test wires and assemble the copper cell as described above.

10. At various time intervals (typically about 8-10 days), measure the accumulated H₂ in the copper cell by placing it into a glove box, along with the hydrogen sensor and other accessories required for H₂ measurement (e.g. thermometer and pressure gauge).

11. Deaerate the glove box with high purity nitrogen gas for 1 hour.

12. Seal the glove box, record the temperature and pressure of the glove box and the temperature of the copper cell.
13. Connect the H$_2$ probe to the copper cell valve and begin H$_2$ recording until H$_2$ detection is complete. Disconnect the H$_2$ probe from the copper cell.
14. Unseal the glove box and repeat deaeration of the cell and glove box with N$_2$ for 1 hour.
15. Reseal the glove box, close the copper cell valve.
16. Return the copper cell to the water bath until the next measurement.

Figure 42: Prepared wires in beaker, on top of PTFE ring

Figure 43: Prepared wires in beaker, placed in the copper cell
4.5.2 \textbf{H}_2 \textbf{Sensor Calibration Procedure}

The hydrogen sensor was calibrated with a known concentration hydrogen gas (balanced with N\textsubscript{2}) as follows:

1. Place the copper cell (cell valve opened), H\textsubscript{2} probe and other measurement accessories in the glove box.
2. Deaerate the glove box with N\textsubscript{2} for 1 hour, follow by another hour of N\textsubscript{2}/H\textsubscript{2} flushing (97 ppm H\textsubscript{2}).
3. Close the copper cell valve and record the temperature and gas pressure of the glove box.
4. Release H\textsubscript{2} from the glove box.
5. Connect the H\textsubscript{2} probe to the copper cell valve and begin H\textsubscript{2} measurement by opening the copper cell valve.
6. The maximum probe reading is used to determine the hydrogen concentration accumulated in the copper cell.

To further illustrate how a sample reading is typically analyzed, calibration curves and a recorded sample curve are presented in Figure 45. Both calibration curves were recorded for 97 ppm hydrogen (remainder nitrogen), as described by the procedure above.

The two calibration curves, recorded on different days, show the reproducibility of the method. The hydrogen concentration of the sample is calculated based on the ratio of the peak maxima, knowing the hydrogen concentration of the calibration samples. For instance, the readings of
240 pl/cm²/s correspond to 97 ppm hydrogen, therefore a peak of 20 pl/cm²/s is due to a hydrogen concentration of 8.1 ppm.

Figure 45: Calibration curves (for 97 ppm hydrogen) and a typical sample curve for comparison.

4.6 Analysis of Corrosion Products

4.6.1 Surface Analysis and Microscopy

The following surface analytical measurements were carried out at Surface Science Western, University of Western Ontario, to determine the surface oxide morphology, composition and where possible, chemical state, as a result of exposure to various environmental conditions:

1. Preliminary optical microscopy examinations were performed using a low power (10X – 80X) Zeiss Discovery V8 stereozoom microscope and a high power Zeiss Axioplan optical microscope.
2. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis (SEM/EDX) was performed using a Leo 440 conventional SEM equipped with a Quartz Xone EDX system. Secondary electron micrographs and EDX spectra were obtained from two different areas of interest per sample.

3. X-ray Photoelectron Spectroscopy (XPS) analyses were performed using a Kratos AXIS Ultra X-ray photoelectron spectrometer. Monochromatic X-rays produced by an Al (Kα) source were bombarded on the specimen and the resulting photoelectrons were collected using a spherical mirror analyser. Survey scan spectra were collected from an analysis area of 300 x 700 microns with a pass energy of 160 eV. High resolution XPS analyses were carried out on an analysis area of 300 x 700 microns with a pass energy of 20 eV. Spectra were corrected for charging by reference to the C 1s peak.

4. Laser Raman Spectroscopy measurements were performed using a Renishaw Model 2000 Raman Spectrometer. The measurements were made using a 633 nm laser. The sampling area for this analysis is approximately 2 μm in diameter.

5. Finally Fourier Transform Infrared Spectroscopy (FTIR) was performed to give further information on bonding. FTIR measurements were performed using a Bruker IFS55 instrument under reflection mode using a microscope attachment.

4.6.1.1 X-Ray Photoelectron Spectroscopy

Steel specimens, following exposures to various humidity and temperature conditions, were sealed in NMR glass tubes under anaerobic conditions and transferred to Surface Science Western (SSW) for surface analytical examination.

To begin the analysis, the NMR tube containing the steel specimens was placed in a glove box attached to the XPS instrument. The glove box was deaerated by purging with high purity dry argon gas for 1.5 to 2 hours. The NMR tube was then broken open and the steel wires were removed from the NMR tubing under the anoxic conditions. Small representative sections of the wire were then cut and placed on a XPS sample holder. Due to the small diameter of the steel wires (0.25 mm), the cut wire segments were placed across an opening in the holder so that the background of the sample holder was not analyzed. The sample holder was then transferred into the XPS instrument under vacuum for XPS survey scans, and high-resolution spectra were collected from selected locations of interest.
As wet-oxidized steel surfaces are expected to be highly oxygen-sensitive, it was expected that some formation of trace Fe III oxide or oxyhydroxide might be formed after emersion even after these precautions.

4.6.1.2 Scanning Electron Microscopy
After XPS analysis, wire samples were removed from the sample holder and transferred to the SEM chamber as quickly as possible in order to minimize air exposure. After SEM/EDX analysis, the wire samples were stored in a vacuum desiccator until other surface analyses were available.

4.6.1.3 Raman Spectroscopy
Bonding information on the corrosion products formed on the steel wires was determined using Raman spectroscopy, an optical technique with which chemical and phase-specific information can be obtained non-destructively. Several procedures were assessed. Initial Raman measurements were conducted on the steel wire samples inside their NMR tubes. The wires sat at the bottom of the tube which increased the distance between the objective lens and the steel wire surface. This resulted in exceptionally long acquisition times with very weak Raman response. To attempt to resolve this problem, the steel wire sample was bent prior to encapsulation into the NMR tube so that a portion of the wire surface was closer to the wall of the NMR tube and hence to the objective lens. This procedure did not provide satisfactory improvement of the signal intensity. Finally, comparative Raman measurements were performed on steel wire samples in the as-encapsulated condition and on the wire surface removed from the NMR tubing. The positions of features on Raman spectra from both measurements were comparable and brief exposure to the atmosphere did not seem to cause any significant differences.

4.6.1.4 Fourier Transform Infrared Spectroscopy (FTIR)
In addition to the specific vibrational information of the iron oxides present on the wire surface obtained in the Raman spectroscopy, FTIR was performed to provide further characterization information of the formed oxides. To minimize air exposure, FTIR measurements were performed immediately after Raman imaging.
4.7 Quartz Crystal Microbalance (QCM)

The quartz crystal microbalance has been used to quantify mass gain or loss resulting from dissolution or thin-film growth in metal corrosion studies. The QCM is based on the principle that when the mass of a vibrating cantilever changes, so does its frequency of vibration (Sullivan and Guilbault, 1999; Henry, 1996). A QCM measures a mass per unit area by measuring the change in frequency of a quartz crystal resonator. The resonance is disturbed by the addition or removal of a small mass due to oxide growth/decay or film deposition at the surface of the acoustic resonator. In electrochemistry and vacuum technology, it is well recognized that the QCM has sub-monolayer sensitivity, and at the outset of this project we believed it had very good potential for measuring the kinetics of iron oxidation. This turned out not to be the case, and the reasons are provided in Appendix C.

5.0 Results

5.1 Glass Cell – Pressure Gauge Experiments

All the glass-cell testing has been graphed as raw, temperature-corrected pressure data and as “corrosion rates” derived from differentiation of those data. In tests showing high corrosion rates, the raw data show discontinuities due to occasional pressure relief. Earlier it was discussed that a measurable pressure increase of 0.1 kPa corresponded, with our standard testing conditions such as metal surface area to 0.53 nm of corroded iron, assuming that the corrosion product is Fe(OH)\textsubscript{2}(the calculation is shown in Appendix B). This assumption gives a conservatively high corrosion rate compared with the assumption of Fe\textsubscript{3}O\textsubscript{4} as corrosion product, although later we observe evidence that the latter is formed in our test conditions. So a corrosion rate of 1 µm·y\textsuperscript{-1} would correspond to 189 kPa·y\textsuperscript{-1}, or 0.022 kPa·h\textsuperscript{-1}. Such corrosion rates can be easily monitored daily. On the other hand, a corrosion rate of 0.01 µm·y\textsuperscript{-1} corresponds to 0.005 kPa·d\textsuperscript{-1}. In that case, some weeks might be required to track a corrosion rate reliably. Corrosion rates of less than 0.01 µm·y\textsuperscript{-1} are difficult to infer from the pressure data due to variability in the readings that are caused by changes in room and waterbath temperature. For instance, in Figure 50, the pressure readings after 1000 hours have reached stability when viewed as a trend, but with daily scatter that is an experimental artefact. This causes the calculated corrosion rate to become scattered. Therefore, the corrosion rate of 0.01 µm·y\textsuperscript{-1} has been identified as the lowest reliable and accurate corrosion rate that can be determined using the pressure monitoring method. While this uncertainty may lead to
noticeable different corrosion rate results, the consequent results will provide added conservatism to the design of the used fuel container. Table 11 summarizes the results obtained from the glass cell-pressure gauge experiments.

5.1.1 Glass Cell – Pressure Gauge Experiments
The estimated corrosion rates and kinetic data for tests conducted using wire samples coated with NaCl are shown in Figures 46 to 57. The NaCl coat on these wire samples were deposited by first soaking in either a 0.05 M or a 0.5M NaCl solution. They were then dried and during the test, these wires were exposed to various relative humidities and temperatures. The estimated corrosion rates at the end of the tests were estimated to be in the range of 0.01 to 0.8 µm·y⁻¹ in test durations vary from 935 to 1725 hours. Higher transient corrosion rates in the range of 1 to 5 µm·y⁻¹ were observed in tests with shorter durations, ranged from 213 to 450 hours.

At 32 °C, the final corrosion rates were estimated to be about 0.15 to 0.45 µm·y⁻¹ for RH in the range of 68% to 100% (Table 11). The corrosion rates appear to be slightly higher at lower (68 to 75%) RH than at 100% RH (Figure 58), which may be explained by a more concentrated thin-film electrolyte at lower RH. This was, however, not a general result, as testing at 50°C showed the reverse trend.
<table>
<thead>
<tr>
<th>Test Conditions</th>
<th>Duration</th>
<th>Estimated Corrosion Rate (final)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.5M NaCl dipped wires</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 68% RH, 32°C</td>
<td>1347 hrs</td>
<td>0.15 µm·y⁻¹</td>
</tr>
<tr>
<td>- 71% RH, 32°C</td>
<td>935 hrs</td>
<td>0.2 µm·y⁻¹</td>
</tr>
<tr>
<td>- 75% RH, 32°C</td>
<td>1730 hrs</td>
<td>0.4 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 32°C</td>
<td>1269 hrs</td>
<td>0.4 µm·y⁻¹</td>
</tr>
<tr>
<td>- 30% RH, 50°C</td>
<td>1962 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 51% RH, 50°C</td>
<td>1053 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 75% RH, 50°C</td>
<td>450 hrs</td>
<td>1 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 50°C</td>
<td>237 hrs</td>
<td>3 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 50°C (II)</td>
<td>1725 hrs</td>
<td>0.8 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 70°C</td>
<td>213 hrs</td>
<td>5 µm·y⁻¹</td>
</tr>
<tr>
<td><strong>0.05M NaCl dipped wires</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 51% RH, 50°C</td>
<td>1867 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 75% RH, 50°C</td>
<td>2326 hrs</td>
<td>~ 0.08 µm·y⁻¹</td>
</tr>
<tr>
<td>- 75% RH, 32°C</td>
<td>3355 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td><strong>Degreased wires</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 100% RH, 32°C (deaerated with N₂)</td>
<td>379 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 50°C (deaerated with N₂ &amp; H₂)</td>
<td>615 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td><strong>Pickled wires</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- 75% RH, 32°C</td>
<td>1171 hrs</td>
<td>---</td>
</tr>
<tr>
<td>- 100% RH, 32°C</td>
<td>1337 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 75% RH, 50°C</td>
<td>331 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 50°C</td>
<td>1002 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 50°C (reused wires from 75% RH)</td>
<td>688 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 74.1% RH, 70°C</td>
<td>1121 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
<tr>
<td>- 100% RH, 70°C</td>
<td>1006 hrs</td>
<td>&lt;0.01 µm·y⁻¹</td>
</tr>
</tbody>
</table>
Figure 46: Corrosion behaviour of 0.5M NaCl dipped wires tested at 32°C and 68% RH

Figure 47: Corrosion behaviour of 0.5M NaCl dipped wires tested at 32°C and 71% RH
Figure 48: Corrosion behaviour of 0.5M NaCl dipped wires tested at 32°C and 75% RH

Figure 49: Corrosion behaviour of 0.5M NaCl dipped wires tested at 32°C and 100% RH
Figure 50: Corrosion behaviour of 0.5M NaCl dipped wires tested at 50°C and 30.5% RH
Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.

Figure 51: Corrosion behaviour of 0.5M NaCl dipped wires tested at 50°C and 51% RH
Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.
Figure 52: Corrosion behaviour of 0.5M NaCl dipped wires tested at 50°C and 75% RH

Figure 53: Corrosion behaviour of 0.5M NaCl dipped wires tested at 50°C and 100% RH
Figure 54: Corrosion behaviour of 0.5M NaCl dipped wires tested at 70°C and 100% RH

Figure 55: Corrosion behaviour of 0.05M NaCl dipped wires tested at 50°C and 51% RH

Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.
Figure 56: Corrosion behaviour of 0.05M NaCl dipped wires tested at 50°C and 75% RH

Corrosion rates of 0.01 µm·y\(^{-1}\) has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.

Figure 57: Corrosion behaviour of 0.05M NaCl dipped wires tested at 32°C and 75% RH
Figure 58: Corrosion behaviour of 0.5M NaCl dipped wires tested at 32°C and various RH
Figure 59: Corrosion behaviour of 0.5M NaCl dipped wires tested at 50°C and various RH

The long duration of these corrosion experiments prohibited test runs to be repeated multiple times to confirm their reproducibility. However, a careful interpretation of the obtained results shows clear consistency with the anticipated corrosion behaviour of steel (Kaesche 1985, King, 2008a). For instance, for 0.5M NaCl dipped wires exposed to 32°C, at various relative humidity (i.e. 68%, 71%, 75%, 100%), corrosion rates estimated range from 0.15 – 0.4 μm/yr. Results clearly indicate that corrosion rate increases with relative humidity, i.e. at higher relative humidity, more water is available to support the cathodic reaction of water. Another observation noted from this set of experiment is 68% RH is above the critical level
for aqueous corrosion to be possible. This is consistent with findings in King (2006) that contaminated metal surface can lower the critical RH to 60-70%. Similar results, ~0.4 μm/yr, are obtained in the case of 75% RH and 100% RH which indicate the amount of water available is no longer the determining factor in sustaining corrosion.

At a higher temperature 50°C, results obtained from the two low relative humidity cases (i.e. 30% and 51% RH) showed significantly lower corrosion rates than at higher relative humidity (75% and 100%) or at a lower temperature of 32°C. This indicates that corrosion rate could be limited by the supply of H₂O in which case, water acts not only as the electrolyte but also an oxidant. Despite the fact that the wire surfaces were salt contaminated, relative humidity at 51% has not reached the critical level for aqueous corrosion.

The effect of temperature is more pronounced when relative humidity was increased to 75% RH or 100% RH. At 75% and 100% RH, 50°C, corrosion rates are estimated to be ~1 μm/yr, and ~3 μm/yr, respectively. At 100%RH and 70°C, initial corrosion rate is as high as ~5 μm/yr. These results show that corrosion rates increase with temperature, albeit the dependence may be weak as reported in many studies (e.g. Honda et al. 1991). Nevertheless, the significant increase in the initial corrosion rate with increasing temperature is indicative of an activation-controlled process. For the 100% RH, 50°C and 70°C test trials, both conducted for ~200 hours, exhibit only the initial, short-term corrosion behaviour of the iron wires. To better understand the temperature dependence, a longer test period (> 1700 hours) was carried out using the 100% RH and 50°C test condition. Results from this 2nd trial showed similar high corrosion rate at the onset of the experiment (~3 – 5 μm/yr in ~250 hrs) but corrosion rates slowed down over time and remained stable at ~0.8 μm/yr after ~600 hours of exposure as the oxide film develops (Figure 53). Results from this 2nd test trial also suggest that as the oxide film develops, the corrosion rate becomes determined by the diffusion of various species through the oxide film, a process which is considerably less sensitive to increasing temperature.

Test results of the 0.05M NaCl dipped wires are consistent with those observed in tests using 0.5M NaCl dipped wires. Similar and slow corrosion rates (~<0.01 μm/yr) were noticed in both 0.5M and 0.05M NaCl dipped wires, 51% RH and 50°C tests. These tests support the
argument that even water condensation may be driven by the deliquescence of surface impurities, at 51% RH, there is insufficient moisture to support electrochemical reactions.

Further comparison of results of the 0.5M and 0.05M NaCl dipped wires showed that with sufficient moisture (i.e. 75% RH), both 50°C and 70°C tests illustrated not only the apparent corrosion reactions occurred, but also the influence of surface contaminant concentration on corrosion rates. The 0.05M NaCl dipped wires, when exposed to both 32°C and 50°C, 75% RH test conditions, exhibited an order of magnitude lower corrosion rate (i.e. ~0.01 μm/yr and ~0.08 μm/yr, for 32°C and 50°C, respectively) than the 0.5M NaCl dipped wires (~0.4 μm/yr and 1 μm/yr, for 32°C and 50°C, respectively).

As mentioned, results collected in these “slow” corrosion tests show fluctuation caused by changes in room and water bath temperatures which resulted with scattered estimated corrosion rates. For this reason, a careful review of the results has determined the corrosion rate of 0.01 μm·y⁻¹ as the lowest reliable and accurate corrosion rate that can be determined using the pressure monitoring method.

Whilst it would be valuable to provide repeat test runs under the same environment conditions in this study; this does not limit our investigation on anaerobic corrosion of steel. On the contrary, the test results, maintaining their consistency, have allowed additional test runs to be performed in order to further explore the corrosion phenomenon of steel, rather than repeating tests under the same environmental conditions. It was also determined to dedicate the more sensitive detection method to study the less aggressive test conditions.
Interestingly, the tests at 32 °C and 75% RH indicate that soaking the wires in 0.05M NaCl solution was much less aggressive than soaking in 0.5M NaCl solution (Figure 61). With 0.05M NaCl soaking, the metal loss tended to level out with time, indicating that chloride is more than just a catalyst for corrosion – i) the thickness of liquid layer and ii) absolute quantity of chloride in that layer are important. Corrosion rates observed on the 0.05M NaCl soaked wire surface are significantly slower, almost an order of magnitude, than the rates observed on the 0.5M NaCl soaked wire surfaces. It is believed that in the presence of chloride, the Cl\(^-\) ions compete with the OH\(^-\) and adsorb on the wire surface to

**Figure 60: Corrosion behaviour of 0.5M NaCl dipped wires exposed to 100% RH and various temperatures**
form ferrous-chloride complexes, such as FeCl+ or FeCl₂, FeCl₃⁻. The resulting species depend on the relative concentration of [Cl⁻] and [OH⁻] ions. The competition between OH⁻ and Cl⁻ ions is assumed as follow:

\[
\text{FeOH}^+ + \text{Cl}^- \rightarrow \text{FeCl}^+ + \text{OH}^- \quad (48)
\]

Significantly higher corrosion rates were observed in the experiments using stronger NaCl solution may be explained by in Cl⁻ dominated solution, FeOH⁺ is more likely to transform into a FeCl⁺ rather than precipitate as Fe(OH)₂.

Over time, the abundant OH⁻ in the liquid layer stifled corrosion as Fe(OH)₂ is formed on the wire surface, i.e.

\[
\text{FeCl}_2 + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 + 2\text{Cl}^- \quad (49)
\]

This effect is particularly apparent in the case of the wires soaked in weak NaCl solution.
These test results appear to show that steel corrosion would not stop as the relative humidity was reduced to, or slightly below, the value that is in equilibrium with saturated NaCl (i.e. 75.5%RH at 30°C and 74.5%RH at 50°C) (Figure 62). This is a well-known finding for atmospheric corrosion in ordinary aerated environments - that 60-70% RH provides sufficient moisture to support electrochemical reactions - but to our knowledge this is the first such study in anoxic environments. Various explanations for this are possible, including simple gas-phase reaction with water vapor, reaction with multilayer adsorption of water, hydrous corrosion products (hydroxides, oxyhydroxides), capillary condensation, and involvement of
hygroscopic iron salts (FeCl$_2$·xH$_2$O). Nevertheless, there was a steep decline in corrosion rate as the RH was reduced to 30% and 51% (Figure 62). At these low RH values, corrosion is not well sustained.

Figure 62: Corrosion behaviour of 0.5M NaCl dipped wires exposed to RH < equilibrium RH

The time dependence of corrosion rate for the tests that showed sustained corrosion in Figures 46 to 62 was not easy to fit to any rational law that might enable extrapolation to longer times. However it is evident, even from visual observation of the curves, that some corrosion rate decays approximate to exponentials with rather long time constants, e.g. the 68% RH data in Figure 62. Extrapolating such curves for predictive purposes would not suitable, as both kinds
of deviation – positive and negative – from such initially well-behaved lines have been observed. For illustrative purposes, the straight-line decay in Figure 63 approximates to the following:

\[ R = R_0 \exp \left( -\frac{t}{\tau} \right) \]

(50)

with \( R_0 \approx 6 \mu m.y^{-1} \) and \( \tau \approx 870 \) h. \( R, R_0 \) and \( \tau \) are defined as corrosion rate at time \( t \), “initial” corrosion rate (after curve fitting) and decay time constant, respectively. The assumption of this decay law would result with corrosion rate of less than 0.5 nm y\(^{-1}\) after only 1 year. Further attempts to better fit the curves using other power laws were made and resulted with more pessimistic predictions for long-term corrosion rates. Figure 63 shows a reasonable \( t^{-0.6} \) fit for the data of Figure 54, but may be too conservative as the corrosion rate shows a dip towards the end of the test. While the present curve fitting outcomes may be somewhat inadequate (the goodness of fit parameter is only 0.45), a preliminary observation of the corrosion rate would fall to 0.24 \( \mu m.y^{-1} \) after 1 year, and 3.7 nm y\(^{-1}\) after 1000 years may still be drawn. It is recognized that such an extrapolation would require more testing to demonstrate that this is an upper limit on the corrosion rate considering the dip seen at the end of the limited dataset and the variation from the fit at short time frames.

Figure 63: Power curve fit of corrosion rates – 0.5M NaCl dipped wires, exposed to 70 °C and 100% RH
5.1.2 Surfaces with No Salt Deposit

When wires were exposed without any salt deposit, the pressure gauge method again began to approach its limit of sensitivity for the detection of hydrogen, and when it did occur detectably, the hydrogen generation was mostly transient in nature. It is actually these tests that form the basis for the use of the hydrogen sensor in the next stage.

While similar behaviour was noticed for the pickled wires at 32, 50 and 70°C, 100% RH, these tests (Figures 64-67) did not show conclusive indication of long-term sustained corrosion, as the pressure changes became too difficult to detect shortly after the experiments started. A key application of the hydrogen sensor is to determine whether corrosion has really “stopped” after this sequence. The potential of whether hydrogen might have been absorbed, for the pickled-wire testing, during the pickling process and later effused during the test, i.e. affected the hydrogen measurements was considered. The speculation was subsequently eliminated as such effect was not observed in every test.

In Figures 65 and 66, the linear pressure versus time plots show the pressure becoming more stable at ~500 hrs (Fig 65) and ~900 hrs (Fig 66). As we assumed pressure increase is due to the evolution of hydrogen from anaerobic corrosion of steel within an air tight chamber, increasing pressure indicates that corrosion is ongoing and stable pressure implies corrosion has stopped or more likely that corrosion is so slow that the detection limit of the pressure gauges has been reached. The decreasing corrosion rates, as shown in Figures 65 and 66, may initially seem contradictory with the increasing pressure. However, a closer evaluation in fact indicates that the results correspond. It should be clearly noted that the increasing pressure as the upward trend of the pressure curve only indicates the presence of corrosion. The gradient of the pressure curve indeed shows the trend of the corrosion rates, i.e. increasing corrosion rates when the gradient is steep while decreasing corrosion when the pressure curve is more “flat”. Note that the corrosion rate versus time plots are on log scales. In this case, the downward trend of the corrosion rates indicates that the pressure increase is slowing down (but corrosion has not stopped and pressure continues to increase, although more gradually) until corrosion is slowing down to a level that could not be measured by the pressure gauge. Overall, the method used to calculate the corrosion rates based on the pressure data can be summarized as: first plot the pressure-time graph using raw pressure data; the plotted curve is
then curve fitted to obtain the best fit. With this fitted curve, pressure at each time point is corrected and pressure changes between 2 time points are used to calculate the corrosion rate.

With respect to the influence of pre-existing rust on corrosion and the subsequent formation of magnetite, as illustrated in Figure 4 and Equation (3), in the presence of oxygen or water (during the wire preparation step), initial oxidation of Fe in neutral and slightly alkaline solutions generally leads to the formation of Fe(OH)$_2$. Under aerobic condition, Fe(OH)$_2$ will be oxidized to Fe(III) containing corrosion products. Various authors have studied the oxidation of Fe(OH)$_2$ to α-, β-, γ-FeOOH and Fe$_3$O$_4$. Domingo et al (1994) have reported rapid oxidation in aerated solutions tends to produce one or more of the ferric hydroxides, whereas slower oxidation in deaerated solutions produces Fe$_3$O$_4$ (Domingo et al. 1994, Odziemkowski et al. 1998). Slower oxidation is believed to allow time for incorporation of Fe$^{2+}$ into the lattice, a process that is also supported by a slight excess of Fe(II) in solution. For wires that were dipped in NaCl solution, oxidation of Fe(OH)$_2$ to FeOOH and Fe$_3$O$_4$ may proceed via an intermediate compound - green rust. Refait and Génin (1993) has reported the composition of green rust formed in chloride solution to be 3 Fe(OH)$_2$·Fe(OH)$_2$Cl·nH$_2$O, consisting of two ferrous species for each ferric ion.

When the wires are placed in the deaerated corrosion cell, the wire surfaces are likely to have a Fe(III)-rich corrosion product layer that may contain various amounts of α-FeOOH, γ-FeOOH and Fe$_3$O$_4$ and green rust (for the NaCl soaked wires). Under anaerobic environment, the Fe(III) within the corrosion product film will become thermodynamically unstable and will be reduced to Fe(II) species. Electrochemical reduction of Fe(III) species can proceed by (i) coupling of the oxidation of the underlying Fe to reduction of the corrosion product or (ii) reaction between dissolved Fe(II) and the Fe(III) corrosion product. As the underlying steel surface is exposed, oxidation of Fe couples with reduction of Fe(III)

$$\text{Fe} + 2 \text{“Fe(III)”} \rightarrow 3 \text{“Fe(II)”} \quad (51)$$

where “Fe(III)” represents the Fe(III)-rich corrosion product formed during the aerobic phase and “Fe(II)” represents either dissolved ferrous ions or a secondary precipitated Fe(II) corrosion product. Various studies of the reduction of FeOOH by Fe(II) have been reported. Ishikawa et al. (1998) studied the reduction of α-, β-, γ-FeOOH by Fe(II) in chloride solutions
as a function of temperature and [OH]: [Fe(II)] ratio. The reduction of \( \gamma \)-FeOOH by Fe(II) resulted in the complete conversion of the ferrie species to Fe\(_3\)O\(_4\) between 25\(^\circ\)C and 100\(^\circ\)C. The reduction of \( \beta \)-FeOOH resulted in the formation of Fe\(_3\)O\(_4\) and \( \alpha \)-FeOOH, whilst the reduction of \( \alpha \)-FeOOH was sluggish with little apparent conversion to Fe\(_3\)O\(_4\). Reduction of the ferric phase was believed to proceed via dissolved Fe(II) and Fe(III) species, the relative ease of conversion being directly related to the solubility of the various FeOOH polymorphs. Tamaura et al (1983) also studied the reaction between Fe(II) and \( \gamma \)-FeOOH

\[
\text{Fe}^{+2} + 8\text{FeOOH} + 2e^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \tag{52}
\]

The reaction was believed to proceed via two distinct steps, each involving a de-protonation process. As Fe(III) corrosion products can be reduced to magnetite, driving oxidation of the steel without water reduction, it was noted the hydrogen measurements in this study may not indicate the actual corrosion rate as hydrogen is not evolved in the above reduction reaction. Nevertheless, it should be noted that this study was designed to assess the long-term corrosion behaviour of carbon steel used fuel container, and hydrogen is more of a concern than the short-term reduction of corrosion products.

In anaerobic condition, magnetite can be formed from a precursor Fe(OH)\(_2\) with conversion proceeding within a matter of a few ten’s of hours even at room temperature (Odziemkowski et al. 1998). The study suggested the growth of the Fe\(_3\)O\(_4\) phase resulted from a dissolution-precipitation process.

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2 \tag{53}
\]

\[
3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \tag{54}
\]

In the presence of Cl\(^-\), studies have observed that Cl\(^-\) interferes with the formation of Fe(OH)\(_2\) through a competition between OH\(^-\) and Cl\(^-\) ions in the initial oxidation of Fe (Ashley and Burstein 1991, MacFarlane and Smedley 1986). Ashley and Burstein (1991) reported a mixed Cl\(^-\)/OH\(^-\) layer was formed, which would be expected to interfere with the formation of a “passive” Fe(OH)\(_2\) layer or its transformation to Fe\(_3\)O\(_4\). This also supports the higher corrosion rates observed in the NaCl soaked wires test runs. However, it is difficult to draw conclusions regarding the long-term effect of Cl\(^-\) on the passivity of steel based on its impact.
on the composition of the first oxidized monolayer due to a lack of sufficient experimental data.

Studies have also reported the presence of Fe$_3$O$_4$ resulted in an increase in the corrosion rate (Kojima et al. 1995) although the reasons for the apparent increase in corrosion rate with Fe$_3$O$_4$ were not discussed in the study. However, it is possible that the reductive dissolution of the Fe$_3$O$_4$ was coupled to the oxidation of the iron wires. Taniguchi (2003) attempted to replicate the findings of Kojima et al (1995) and confirmed the presence of Fe$_3$O$_4$ did increase the amount of H$_2$ produced. The enhancement of the H$_2$ evolution reaction on Fe(III)/Fe(II) corrosion products has also been reported by Been et al. (2007). This enhanced H$_2$ evolution is believed to be catalyzed by Fe(III)/Fe(II) active sites on the surface but this catalytic activity is lost if the electrode is polarized too negatively (up to approximately -0.95 V$_{SCE}$). Due to the potential effect of corrosion products on hydrogen evolution, it was therefore decided the direct hydrogen measurements using the hydrogen sensor will focus on test runs using pickled wires. The potential of whether hydrogen might have been absorbed, for the pickled-wire testing, during the pickling process and later effused during the test, i.e. affected the hydrogen measurements was also considered. This speculation was subsequently eliminated as such an effect was not observed in every test.
Figure 64: Corrosion behaviour of pickled wires exposed to 32 °C, 100% RH

Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.
Figure 65: Corrosion behaviour of pickled wires exposed to 50 °C, 100% RH
Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.
Figure 66: Corrosion behaviour of pickled wires exposed to 70 °C, 100% RH
Corrosion rates of 0.01 μm·y⁻¹ has been considered as the lowest reliable corrosion rate that can be detected using the pressure monitoring method.

Figure 67: Corrosion behaviour of pickled wires exposed to 100% RH
Testing with degreased wires showed less corrosion, as expected. These wires have a well-formed air oxide prior to exposure.

Some attempts were made to fit decay functions to the corrosion transients obtained in these tests. For the pickled wires at 32°C and 100% RH (data of Figure 64), the corrosion rate appeared to decay linearly to zero – not a normal functional form for a corrosion-rate decay, but perhaps informative – Figure 68. At 50°C, the decay took on a definite exponential form – Figure 69. At 70°C, the fit was less impressive but as indicated, the time constant was shorter – close to 10 hours - Figure 70.

Figure 68: Linear curve fit of corrosion rates, pickled wires exposed to 32 °C and 100% RH
Figure 69: Exponential curve fit of corrosion rates, pickled wires exposed to 50 °C and 100% RH
Figure 70: Power curve fit of corrosion rates, pickled wires exposed to 70 °C and 100% RH

The faster corrosion-rate decay at 70°C than at 50°C is perhaps to be expected, as magnetite can more easily form at higher temperatures and is expected to be more protective than Fe(OH)$_2$.

5.2 Copper Cell – H$_2$ Sensor Experiments
Table 12 shows the results obtained with the hydrogen sensor, selected from a large number of tests. Where a corrosion rate is mentioned, it is the average over the mentioned interval; then the cell is flushed with nitrogen and the pH$_2$ is reset to zero (but the metal samples are not replaced).
<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Interval between Measurement time increment</th>
<th>Estimated Corrosion Rate (average over increment)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pickled wires, 85% RH, 50°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; measurement 164 hrs</td>
<td>1.0 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; measurement 259 hrs</td>
<td>1.0 x 10&lt;sup&gt;-3&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; measurement 313 hrs</td>
<td>1.6 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; measurement 235 hrs</td>
<td>2.5 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt; measurement 262 hrs</td>
<td>2.0 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
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<tr>
<td>6&lt;sup&gt;th&lt;/sup&gt; measurement 332 hrs</td>
<td></td>
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<td>7&lt;sup&gt;th&lt;/sup&gt; measurement 221 hrs</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Pickled wires, 75% RH, 50°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; measurement 353 hrs</td>
<td>7.0 x 10&lt;sup&gt;-5&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; measurement 359 hrs</td>
<td>1.8 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; measurement 310 hrs</td>
<td>3.0 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt; measurement 216 hrs</td>
<td>4.8 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt; measurement 283 hrs</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>6&lt;sup&gt;th&lt;/sup&gt; measurement 260 hrs</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>7&lt;sup&gt;th&lt;/sup&gt; measurement 408 hrs</td>
<td>3.3 x 10&lt;sup&gt;-3&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
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</tr>
<tr>
<td>8&lt;sup&gt;th&lt;/sup&gt; measurement 212 hrs</td>
<td>6.3 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>9&lt;sup&gt;th&lt;/sup&gt; measurement 218 hrs</td>
<td>4.9 x 10&lt;sup&gt;-4&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>10&lt;sup&gt;th&lt;/sup&gt; measurement 91 hrs</td>
<td>1.0 x 10&lt;sup&gt;-3&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>Pickled wires, 100% RH, 50°C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt; measurement 473 hrs</td>
<td>---</td>
<td></td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt; measurement 93 hrs</td>
<td>6.7 x 10&lt;sup&gt;-3&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt; measurement 93 hrs</td>
<td>2.5 x 10&lt;sup&gt;-3&lt;/sup&gt; µm·y&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

These tests are important, but considered preliminary, as the results are the lowest corrosion rate that has been reported in such an environment. While the apparent reason for the increase in corrosion rate with time is not apparent at present, it is evident that such rates would not pose a threat to repository disposal.

According to Ion Science, manufacturer of the hydrogen sensor, the sensor functions by drawing a stream of ambient air using a high performance pump. Hydrogen content in the test-gas stream is then measured by a sensitive amperometric detector. In anaerobic environment, hydrogen entering the proton conducting ceramic probe, which has a catalyst coated on both sides of the probe, reaches the anode and is oxidized to H<sup>+</sup> through the combination of catalyst and applied voltage. As proton exists within the ceramic, for each proton entering the ceramic, another exits and at the other side hydrogen is formed at the
Several attempts had been made to obtain design details of the hydrogen probe from Ion Science in order to better understand the operating principle of the probe but to no avail. The type of catalyst on the probe remains unknown at present. However, assuming hydrogen formation is kinetically faster than water formation, it is believed that the hydrogen sensor is not a fuel cell but functions as a driven proton pump. To verify the presumed operating principle of the sensor as well as to confirm oxygen on the inlet side is irrelevant in detecting hydrogen under anaerobic condition, a separate experiment, with details and results as described in Section 4.5, was conducted. Figure 41 shows almost identical response in both aerobic and anaerobic environments. Testing the probe’s function under normal operation mode has noticed that for every 1 mL of air entering the sensor, approximately 10 mL of exhaust gas is produced. It is suspected that the additional 9 mL is drawn in at the cathode side with the intention of removing accumulated adsorbed hydrogen, which would otherwise inhibit the sensor activity. A 100 ppm hydrogen input was used in the test and the hydrogen exiting was found to be approximately a tenth of the inlet concentration. The fact that hydrogen was found exiting the probe suggests that the probe is based upon a proton-exchange ceramic, which requires oxidation of the H\textsubscript{2} at the anode first and then proton reduction being the cathodic reactions. For a proton-exchange ceramic probe which requires oxidation of hydrogen at the anode first, hydrogen exiting the probe implies proton reduction is the cathodic reaction. To further understand whether oxygen is required in hydrogen measurements of our study, additional test, although rather crude, was conducted by connecting the probe to nitrogen, with isolated air inlet on the cathode side of the probe. No difference in probe function was observed when the cathode flow loop was full of nitrogen (instead of air). Based on the performed tests, it is therefore concluded that the hydrogen sensor is a driven proton device in which the output current is limited by diffusion of protons through the ceramic electrolyte under an applied voltage. The anodic reaction is therefore oxidation of hydrogen and the cathodic reaction is reduction of protons.

Due to the “mild” environment anticipated in the geological repository, the glass-cell testing method was used in initial testing to illustrate the general corrosion behaviour of steel under the expected repository environment. Results obtained from the glass-cell method guided the hydrogen sensor tests, i.e. by focusing on the need to study the relatively “mild” conditions
(e.g. pickled wires exposed to higher RH and temperature). This strategy was essentially owing to the long duration of the test runs.

It was realized, even at the onset of the study, that pressure monitoring using pressure gauges is a less accurate method than direct hydrogen detection using the hydrogen sensor. The digital pressure gauges used in the glass-cell technique, despite their relatively good full scale accuracy of 0.04% - 0.05%, monitored pressure changes within a sealed chamber taking into account the temperature fluctuations of the water bath. The hydrogen sensor method, on the contrary, measured hydrogen accumulated from anaerobic corrosion of iron directly and results suffered a lesser influence from temperature fluctuations.

In order to obtain meaningful results within the project timeframe, it was therefore decided that the hydrogen sensor should focus on the less aggressive conditions to obtain the necessary sensitivity. The relatively “slow” corrosion process under the less aggressive environment, along with perhaps inadequate operating experience of the hydrogen sensor, had resulted with some unstable / unreliable data. Despite these potential negative factors, results obtained are consistent. For instance, for the pickled wires under the condition of 75% RH and 50°C, the glass-cell testing method did not detect reliable pressure changes and can only conclude a corrosion rate of less than 0.01 μm/yr (Figure 71). Eight measurements using the hydrogen sensor, under the same test condition, persistently showed corrosion rates to range from $7.0 \times 10^{-5}$ μm/yr to $1.0 \times 10^{-3}$ μm/yr (Table 12), which confirmed the estimation observed in the glass-cell method. The same is observed for the pickled wires exposed to 100%RH and 50°C, 2 measurements using the glass-cell testing method observed the same result of less than 0.01 μm/yr (Table 11). The hydrogen sensor, under the same test condition, again verified the observation illustrated in the glass-cell test method and estimated corrosion rates to range from $2.5 \times 10^{-3}$ μm/yr to $6.7 \times 10^{-3}$ μm/yr (Table 12).

In reporting the experimental results, all obtained test data are reported in revised version of the thesis. Some unstable readings collected in the hydrogen sensor measurements were omitted in the previous version due to their unreliability and uncertainty. However, these readings have now been included in order to report all obtained results. While the unstable readings may lead to more complicated and/or inaccurate result interpretation, nevertheless,
all collected data are treated equally without some being treated with more significance than others. All data collected using the hydrogen sensor are presented in Appendix G.

Figure 71: Pressure measurements, pickled wires exposed to 50 °C and 75% RH
### 5.3 Surface Analyses

Surface analyses were conducted at the Surface Science Western facility at the University of Western Ontario. Table 13 lists the samples selected for surface analysis and microscopy.

#### Table 13: 15 samples examined by surface analyses

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Condition</th>
<th>RH</th>
<th>Temp</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control, no previous exposure, wires degreased in acetone</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>Control, no previous exposure, wires coated with 0.5M NaCl (no rinse before analyses)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>Degreased wires (w/ acetone), exposed to deaerated environment (using N₂)</td>
<td>100%</td>
<td>50°C</td>
<td>615 hrs</td>
</tr>
<tr>
<td>4</td>
<td>Pickled wires (w/ HCl)</td>
<td>100%</td>
<td>50°C</td>
<td>1001 hrs</td>
</tr>
<tr>
<td>5</td>
<td>Pickled wires (II)</td>
<td>100%</td>
<td>50°C</td>
<td>688 hrs</td>
</tr>
<tr>
<td>6</td>
<td>0.5M NaCl dipped wires, no rinse before analyses</td>
<td>75%</td>
<td>50°C</td>
<td>370 hrs</td>
</tr>
<tr>
<td>7</td>
<td>0.5M NaCl dipped wires, rinsed before analyses</td>
<td>75%</td>
<td>50°C</td>
<td>370 hrs</td>
</tr>
<tr>
<td>8</td>
<td>Degreased wires, exposed to anoxic environment (deaerated w/ N₂ / H₂)</td>
<td>100%</td>
<td>50°C</td>
<td>591 hrs</td>
</tr>
<tr>
<td>9</td>
<td>0.5M NaCl dipped wires, no rinse before analyses</td>
<td>100%</td>
<td>50°C</td>
<td>237 hrs</td>
</tr>
<tr>
<td>10</td>
<td>0.5M NaCl dipped wires, rinsed before analyses</td>
<td>100%</td>
<td>50°C</td>
<td>237 hrs</td>
</tr>
<tr>
<td>11</td>
<td>Pickled wires</td>
<td>100%</td>
<td>70°C</td>
<td>1006 hrs</td>
</tr>
<tr>
<td>12</td>
<td>Pickled wires</td>
<td>74.1%</td>
<td>70°C</td>
<td>1121 hrs</td>
</tr>
<tr>
<td>13</td>
<td>Raw steel wires for XPS sputtering experiment</td>
<td>--</td>
<td>400°C</td>
<td>Heated in air, 3 hrs</td>
</tr>
<tr>
<td>14</td>
<td>0.5M NaCl dipped wires, no rinse before analyses</td>
<td>100%</td>
<td>50°C</td>
<td>1725 hrs</td>
</tr>
<tr>
<td>15</td>
<td>0.5M NaCl dipped wires, rinsed before analyses</td>
<td>100%</td>
<td>50°C</td>
<td>1725 hrs</td>
</tr>
</tbody>
</table>

#### 5.3.1 XPS

Table 14 lists the apparent near-surface atomic compositions obtained from XPS survey spectra of all the samples, without any sputter etching except for sample 13. This sample was used to determine the elemental ratios that would exist on a well-characterized, oxidized iron surface after sputter etching – evidently a good 2:3 Fe:O ratio is found after 1 minute sputtering, but after 5 minutes there is evidence of film reduction.
Table 14: Composition data from XPS survey scan spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
<th>F</th>
<th>Mn</th>
<th>Si</th>
<th>N</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>42.4</td>
<td>40.6</td>
<td>0.3</td>
<td>0.5</td>
<td>0.5</td>
<td>1.2</td>
<td>0.7</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>22.4</td>
<td>19.8</td>
<td>49.1</td>
<td>3.0</td>
<td>4.5</td>
<td>0.9</td>
<td>0.3</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.3</td>
<td>48.6</td>
<td>39.9</td>
<td>0.5</td>
<td>0.9</td>
<td>3.9</td>
<td>0.9</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10.8</td>
<td>39.3</td>
<td>44.7</td>
<td>0.2</td>
<td>3.9</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>12.2</td>
<td>42.1</td>
<td>43.2</td>
<td>0.7</td>
<td>1.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>20.5</td>
<td>27.0</td>
<td>49.5</td>
<td>0.8</td>
<td>0.9</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>18.1</td>
<td>27.6</td>
<td>51.8</td>
<td>1.1</td>
<td>0.8</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.4</td>
<td>49.4</td>
<td>40.3</td>
<td>6.1</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>13.7</td>
<td>34.0</td>
<td>47.5</td>
<td>3.0</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>18.1</td>
<td>28.8</td>
<td>51.1</td>
<td>0.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>12.5</td>
<td>40.7</td>
<td>44.6</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>13.2</td>
<td>40.0</td>
<td>41.3</td>
<td>0.6</td>
<td>3.7</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>14.0</td>
<td>42.2</td>
<td>43.3</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 1 min sputtering</td>
<td>36.3</td>
<td>11.5</td>
<td>51.8</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>After 5 min sputtering</td>
<td>31.9</td>
<td>7.9</td>
<td>59.9</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>20.4</td>
<td>29.3</td>
<td>42.8</td>
<td>0.3</td>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>15.0</td>
<td>40.8</td>
<td>43.9</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 15 lists the results of fitting of high-resolution XPS spectra. This information is not all useful, but indicates the following broad findings –

- A Fe metal peak is found in a number of spectra, indicative of a thin oxide film, a few nm at most, with lower apparent Fe metal content corresponding to thicker films.
- Fe III species are found in many surfaces, which indicate (for samples previously exposed to anoxic conditions) that the precautions taken to avoid air exposure were not wholly successful.
- FeO is sometimes found according to the peak fitting; this assignation is not consistent with thermodynamic predictions and should be viewed with caution.
- Carbonate species are again indicative of an interaction with the atmosphere after anoxic exposure.
### Table 15: Summary of XPS high-resolution spectra data

<table>
<thead>
<tr>
<th>Sample</th>
<th>XPS Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe metal 4.3%, Fe₂O₃: 70.4%; FeO: 25.3%; film thickness: ~ 6 nm</td>
</tr>
<tr>
<td>2</td>
<td>Fe₂O₃: 60.6%; Fe₃O₄: 2.3%; FeOOH: 37.1%</td>
</tr>
<tr>
<td>3</td>
<td>Fe metal: 6.1%; Fe₂O₃: 47.9%; Fe₃O₄: 19.5%; FeOOH: 26.4%; film thickness: ~ 5.7 nm</td>
</tr>
<tr>
<td>4</td>
<td>Fe metal: 2.1%; Fe₂O₃: 30.6%; Fe₃O₄: 48.6%; FeOOH: 18.7%; film thickness: ~ 7.5 nm</td>
</tr>
<tr>
<td>5</td>
<td>Fe metal: 1.8%; Fe₂O₃: 29.6%; Fe₃O₄: 41.8%; FeOOH: 26.9%; film thickness: ~ 7.8 nm</td>
</tr>
<tr>
<td>6</td>
<td>FeCO₃: 63.9%; Fe₂O₃: 11.2%; FeO: 24.7%</td>
</tr>
<tr>
<td>7</td>
<td>FeCO₃: 64.6%; Fe₂O₃: 15.7%; FeO: 19.7%</td>
</tr>
<tr>
<td>8</td>
<td>Fe metal: 4.8%; Fe₃O₄: 26.2%; FeOOH: 10.3%; Fe₂O₃: 58.9%</td>
</tr>
<tr>
<td>9</td>
<td>FeCO₃: 60.1%; Fe₂O₃: 3.9%; FeO: 35.9%</td>
</tr>
<tr>
<td>10</td>
<td>Fe metal: 1.9%; Fe₃O₄: 50.4%; FeOOH: 5.2%; Fe₂O₃: 42.6%</td>
</tr>
<tr>
<td>11</td>
<td>Fe₃O₄: 60.9%; Fe₂O₃: 39.1%</td>
</tr>
<tr>
<td>12</td>
<td>Fe₂O₃: 49.3%; FeOOH: 29.4%; Fe₃O₄: 21.5%</td>
</tr>
<tr>
<td>13</td>
<td>Steel wire oxidized in air at 400°C and found to contain a mixture of Fe₂O₃/Fe₃O₄ in XPS analysis. Upon sputtering, the well-defined oxide (mixture) is reduced and is sufficiently damaged to make curve-fitting of the resulting spectra difficult. Peak widths are broadened significantly and metallic iron is formed.</td>
</tr>
<tr>
<td>14</td>
<td>Appears to be a mixture of Fe₂O₃, Fe₃O₄ and FeCO₃. FeOOH may also be present.</td>
</tr>
<tr>
<td>15</td>
<td>Appears to be a mixture of Fe₂O₃, Fe₃O₄ and FeCO₃. FeCO₃ levels are much lower than sample 14. FeOOH may also be present.</td>
</tr>
</tbody>
</table>

#### 5.3.2 SEM / EDX

Table 16 gives the results of EDX analysis, with some indication of the spatial variability of average composition within the analysis depth, which is much greater than that of XPS. Oxygen levels give a broad indication of which films have substantial thickness, of the order of at least 0.1 micron. These correspond, as expected, to the more aggressive conditions.
Table 16: Composition data from EDX analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1 Area 1</td>
<td>100</td>
</tr>
<tr>
<td>Area 2</td>
<td>100</td>
</tr>
<tr>
<td>2 Area 1</td>
<td>60.7</td>
</tr>
<tr>
<td>Area 2</td>
<td>62.3</td>
</tr>
<tr>
<td>Area 3</td>
<td>71.3</td>
</tr>
<tr>
<td>Area 4</td>
<td>71.8</td>
</tr>
<tr>
<td>3 Area 1</td>
<td>71.4</td>
</tr>
<tr>
<td>Area 2</td>
<td>86.7</td>
</tr>
<tr>
<td>4 Area 1</td>
<td>83.1</td>
</tr>
<tr>
<td>Area 2</td>
<td>60.3</td>
</tr>
<tr>
<td>5 Area 1</td>
<td>55.7</td>
</tr>
<tr>
<td>Area 2</td>
<td>81.8</td>
</tr>
<tr>
<td>6 Area 1</td>
<td>46.5</td>
</tr>
<tr>
<td>Area 2</td>
<td>64.6</td>
</tr>
<tr>
<td>7 Area 1</td>
<td>64.0</td>
</tr>
<tr>
<td>Area 2</td>
<td>49.5</td>
</tr>
<tr>
<td>8 Area 1</td>
<td>89.5</td>
</tr>
<tr>
<td>Area 2</td>
<td>88.0</td>
</tr>
<tr>
<td>9 Area 1</td>
<td>64.9</td>
</tr>
<tr>
<td>Area 2</td>
<td>64.9</td>
</tr>
<tr>
<td>10 Area 1</td>
<td>60.2</td>
</tr>
<tr>
<td>Area 2</td>
<td>80.1</td>
</tr>
<tr>
<td>11 Area 1</td>
<td>86.2</td>
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<tr>
<td>Area 2</td>
<td>81.7</td>
</tr>
<tr>
<td>12 Area 1</td>
<td>82.3</td>
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<tr>
<td>Area 2</td>
<td>72.0</td>
</tr>
<tr>
<td>13 Area 1</td>
<td>62.2</td>
</tr>
<tr>
<td>Area 2</td>
<td>61.2</td>
</tr>
<tr>
<td>14 Area 1</td>
<td>58.7</td>
</tr>
<tr>
<td>Area 2</td>
<td>57.5</td>
</tr>
</tbody>
</table>

5.3.3 Raman Spectroscopy and Fourier Transform Infrared (FTIR) Spectroscopy

Table 17 lists the findings of Raman spectroscopy analysis. It should be noted that this technique is not sensitive to Fe(OH)$_2$ (Odziemkowski et al. 1998). However, to the extent that Fe$_3$O$_4$ is positively identified, this clarifies the nature of the films formed in anoxic conditions. The formation of some Fe III oxide or oxyhydroxide, or carbonates, by exposure to traces of oxygen does not invalidate this basic finding. Yet we cannot say, at this point, what are the relative amounts of Fe$_3$O$_4$ and Fe(OH)$_2$ in these products, and diffraction would not necessarily help, as many of the films are thin and Fe(OH)$_2$ is always poorly crystalline. Some evidence towards a
preponderance of Fe$_3$O$_4$ is the lack of positive evidence for OH in the FTIR data, but these spectra were weak.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spectra data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$_3$O$_4$, could be FeO and amorphous carbon</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_3$O$_4$, α-FeOOH, likely carbonate species, amorphous carbon and other iron species such as maghemite (γ-Fe$_2$O$_3$) and ferrihydrite (generally presented as Fe$_2$HOOH·4H$_2$O, also written as 5 Fe$_2$O$_3$·9H$_2$O or as Fe$_2$O$_3$·2FeOOH·2.6H$_2$O.</td>
</tr>
<tr>
<td>3</td>
<td>Raman analysis did not find any evidence of oxide species on this sample.</td>
</tr>
<tr>
<td>4</td>
<td>Typical of Fe$_3$O$_4$.</td>
</tr>
<tr>
<td>5</td>
<td>Typical of Fe$_3$O$_4$. No other oxide species were detected.</td>
</tr>
<tr>
<td>6</td>
<td>Amorphous carbon, Fe$_3$O$_4$, Fe$_2$O$_3$, and gamma and alpha Fe$_2$O$_3$.</td>
</tr>
<tr>
<td>7</td>
<td>Fe$_3$O$_4$, carbonate, beta-FeOOH(Cl), and gamma-Fe$_2$O$_3$.</td>
</tr>
<tr>
<td>8</td>
<td>Raman: Amorphous carbon and Fe$_3$O$_4$. FTIR: Weak with no assignable peaks</td>
</tr>
<tr>
<td>10</td>
<td>Raman: Fe$_3$O$_4$, amorphous carbon, alpha FeOOH, Fe$_2$O$_3$, gamma-Fe$_2$O$_3$ and carbonate. FTIR: Likely mixed carbonate/hydroxide species.</td>
</tr>
<tr>
<td>11</td>
<td>Raman: spectra are consistent with Fe$_3$O$_4$ with some contribution from amorphous carbon. FTIR: spectra are very weak and undifferentiated. No evidence of hydroxide.</td>
</tr>
<tr>
<td>12</td>
<td>Raman: spectra are consistent with Fe$_3$O$_4$ with some contribution from amorphous carbon. FTIR: No evidence of hydroxide in the FTIR spectra.</td>
</tr>
<tr>
<td>13</td>
<td>Sample not examined using Raman</td>
</tr>
<tr>
<td>14</td>
<td>Raman: presence of mainly Fe$_3$O$_4$ with some areas showing the presence of gamma-Fe$_2$O$_3$ (maghemite). FTIR: mainly showed the presence of broad undifferentiated peaks which were not assigned.</td>
</tr>
<tr>
<td>15</td>
<td>Raman: presence of Fe$_3$O$_4$, with some areas also showing the presence of a peak likely arising from carbonates. FTIR: spectra were weak in some areas and strong in others. The strong spectra were consistent with the spectra observed previously and proposed as arising from a mixed carbonate/hydroxide species.</td>
</tr>
</tbody>
</table>

### 6.0 Discussion of Surface Analysis Results

Figure 72 shows the mixture of salt deposit and corrosion product that was the starting point for the NaCl 'coated' or 'precorroded' tests (images of Sample 2). Heavy deposits are found on wires surfaces.
Figure 72: SEM images of Sample 2 (3rd and 4th wires) – 0.5M NaCl coated wires

Figure 73 shows roughly circular patches that were found on some samples exposed to 100% RH without salt coating; these are possibly centred on manganese sulfide inclusions.
Figure 73: SEM images of Sample 3 – degreased wires, exposed to 615 hrs at 50 °C, 100% RH

Figure 74 shows isolated regions on a salt-coated surface that contain salt crystals, regions were composed purely of corrosion product. It should be noted that the use of ordinary air and water exposure for this NaCl pretreatment could account for the presence of Fe III species or carbonates in the corrosion products after anoxic exposure, but examination of the full range of data reveals that there must have been some post-air exposure as well. Regarding the fully Fe III species, it would be expected that hydrogen from anoxic corrosion would reduce these to magnetite or Fe II species, but such reactions may be slow.
EDX results in weight percent

<table>
<thead>
<tr>
<th>Analysis</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis 1</td>
<td>27.7</td>
<td>8.5</td>
<td>3.2</td>
<td>60.7</td>
</tr>
<tr>
<td>Analysis 2</td>
<td>30.7</td>
<td>8.5</td>
<td>6.9</td>
<td>62.4</td>
</tr>
<tr>
<td>Analysis 3</td>
<td>11.7</td>
<td>11.0</td>
<td>6.1</td>
<td>71.3</td>
</tr>
<tr>
<td>Analysis 4</td>
<td>19.7</td>
<td>8.5</td>
<td>71.8</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 74:** EDX spectra of Sample 2 – control, 0.5M NaCl coated wires

Generally EDX did not give much information on samples that were exposed to anoxic conditions without a salt deposit, but oxygen was detectable in some cases, as shown in Figure 75. This was expected considering the thin surface films formed and the lack of surface sensitivity of EDX.
EDX results in weight percent

<table>
<thead>
<tr>
<th>Analysis</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>S</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis 1</td>
<td>25.3</td>
<td>18.9</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
<td>55.7</td>
</tr>
<tr>
<td>Analysis 2</td>
<td>11.6</td>
<td>6.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>81.8</td>
</tr>
</tbody>
</table>

Figure 75: EDX spectra of Sample 5 – pickled wires (II), 50 °C and 100% RH

Figure 76 is included as an example of a high-resolution XPS spectrum for one of the thinner films formed under anoxic conditions. The take-off angle was large (90 degrees), so the analysis depth is maximized. The number of species to which the iron spectrum is fitted is at the limit of our ability to deconvolute such spectra; however the presence and approximate quantity of the different formal oxidation states (0, 2.66 and 3) should be fairly reliable (i.e. 1-2% Fe metal, 42% Fe$_3$O$_4$, 30% Fe$_2$O$_3$, and 27% FeOOH). The Fe III species indicate some effect of air exposure despite the precautions taken. The presence of a signal from Fe metal shows that the oxide layer is thin. Purely Fe II species such as Fe(OH)$_2$ was not observed. The approximate film thickness (7.8 nm) can be used for comparison with the integrated hydrogen production in the anoxic exposure in which case 27 nm of Fe$_3$O$_4$ was estimated to be formed according to the pressure measurements (the calculation is presented in Appendix E). The film thickness of Fe$_3$O$_4$ estimated based on the pressure data is significantly thicker than the XPS result, but the amount of metallic Fe deduced from XPS is very low and subject to uncertainties in deconvolution. Possible explanations for the discrepancy in the two
thicknesses are that the mass of the film is dominated by locally thicker areas, or (most likely) that the metallic Fe signal is only roughly estimated.

Sample 5 - Pickled wires, 50°C, 100%RH, Fe(2p) high resolution spectrum

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L.Sh.</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe metal</td>
<td>706.79</td>
<td>0.95</td>
<td>LA(1,2,4,8,3)</td>
<td>161.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Gamma Fe₂O₃ 1</td>
<td>709.78</td>
<td>1.20</td>
<td>GL(30)</td>
<td>828.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Gamma Fe₂O₃ 2</td>
<td>710.78</td>
<td>1.30</td>
<td>GL(30)</td>
<td>828.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Gamma Fe₂O₃ 3</td>
<td>711.78</td>
<td>1.40</td>
<td>GL(30)</td>
<td>613.9</td>
<td>6.7</td>
</tr>
<tr>
<td>Gamma Fe₂O₃ 4</td>
<td>712.98</td>
<td>1.40</td>
<td>GL(30)</td>
<td>275.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Gamma Fe₂O₃ 5</td>
<td>714.08</td>
<td>1.70</td>
<td>GL(30)</td>
<td>154.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe₃O₄ 2+1</td>
<td>708.35</td>
<td>1.20</td>
<td>GL(30)</td>
<td>631.6</td>
<td>6.9</td>
</tr>
<tr>
<td>Fe₃O₄ 2+2</td>
<td>709.15</td>
<td>1.20</td>
<td>GL(30)</td>
<td>563.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Fe₃O₄ 3+1</td>
<td>710.15</td>
<td>1.40</td>
<td>GL(30)</td>
<td>901.7</td>
<td>9.9</td>
</tr>
<tr>
<td>Fe₃O₄ 3+2</td>
<td>711.15</td>
<td>1.40</td>
<td>GL(30)</td>
<td>677.2</td>
<td>7.4</td>
</tr>
<tr>
<td>Fe₃O₄ 3+3</td>
<td>712.25</td>
<td>1.40</td>
<td>GL(30)</td>
<td>464.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe₃O₄ 3+4</td>
<td>713.35</td>
<td>1.40</td>
<td>GL(30)</td>
<td>216.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe₃O₄ 3+5</td>
<td>714.45</td>
<td>3.30</td>
<td>GL(30)</td>
<td>346.2</td>
<td>3.8</td>
</tr>
<tr>
<td>FeOOH 1</td>
<td>710.30</td>
<td>1.40</td>
<td>GL(30)</td>
<td>720.2</td>
<td>7.9</td>
</tr>
<tr>
<td>FeOOH 2</td>
<td>711.30</td>
<td>1.30</td>
<td>GL(30)</td>
<td>706.8</td>
<td>7.8</td>
</tr>
<tr>
<td>FeOOH 3</td>
<td>712.20</td>
<td>1.40</td>
<td>GL(30)</td>
<td>549.5</td>
<td>6.0</td>
</tr>
<tr>
<td>FeOOH 4</td>
<td>713.3</td>
<td>1.40</td>
<td>GL(30)</td>
<td>308.6</td>
<td>3.4</td>
</tr>
<tr>
<td>FeOOH 5</td>
<td>714.40</td>
<td>1.80</td>
<td>GL(30)</td>
<td>168.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe metal</td>
<td>714.40</td>
<td>1.80</td>
<td>GL(30)</td>
<td>168.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>714.40</td>
<td>1.80</td>
<td>GL(30)</td>
<td>168.0</td>
<td>1.8</td>
</tr>
<tr>
<td>FeOOH</td>
<td>29.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>41.8%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Film thickness</td>
<td>~7.8 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 76: XPS high resolution spectra of Sample 5 – pickled wires (II), 50 °C and 100% RH
High-resolution XPS spectrum of the iron wire heated at 400°C, before and after sputter etching, are shown in Figure 77. No metallic Fe is found on the outer surface, but partial film reduction occurs during sputtering. These spectra are useful for interpretation of the spectra of the corroded surfaces.

<table>
<thead>
<tr>
<th>Name</th>
<th>Pos.</th>
<th>FWHM</th>
<th>L.Sh.</th>
<th>Area</th>
<th>% Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃ 1</td>
<td>709.75</td>
<td>1.20</td>
<td>GL(30)</td>
<td>457.3</td>
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<tr>
<td>Fe₂O₃ 2</td>
<td>710.75</td>
<td>1.30</td>
<td>GL(30)</td>
<td>457.3</td>
<td>24.8</td>
</tr>
<tr>
<td>Fe₂O₃ 3</td>
<td>711.75</td>
<td>1.40</td>
<td>GL(30)</td>
<td>338.8</td>
<td>18.4</td>
</tr>
<tr>
<td>Fe₂O₃ 4</td>
<td>712.95</td>
<td>1.20</td>
<td>GL(30)</td>
<td>151.9</td>
<td>8.2</td>
</tr>
<tr>
<td>Fe₂O₃ 5</td>
<td>714.05</td>
<td>1.70</td>
<td>GL(30)</td>
<td>85.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe₃O₄ 2+1</td>
<td>708.45</td>
<td>1.20</td>
<td>GL(30)</td>
<td>58.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe₃O₄ 2+2</td>
<td>709.25</td>
<td>1.20</td>
<td>GL(30)</td>
<td>52.4</td>
<td>2.8</td>
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<tr>
<td>Fe₃O₄ 3+1</td>
<td>710.25</td>
<td>1.40</td>
<td>GL(30)</td>
<td>84.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Fe₃O₄ 3+2</td>
<td>711.25</td>
<td>1.40</td>
<td>GL(30)</td>
<td>63.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Fe₃O₄ 3+3</td>
<td>712.35</td>
<td>1.40</td>
<td>GL(30)</td>
<td>43.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Fe₃O₄ 3+4</td>
<td>713.45</td>
<td>1.40</td>
<td>GL(30)</td>
<td>20.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Fe₃O₄ 3+5</td>
<td>714.55</td>
<td>3.30</td>
<td>GL(30)</td>
<td>32.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>
Figure 78a shows an example of a Raman spectrum for an anoxic test without salt coating that gave a relatively thin oxide film, showing a well-resolved feature ascribed to Fe$_3$O$_4$. A total of 5 areas on different wires were analyzed. All spectra consistently show a peak near 667 cm$^{-1}$, typical of Fe$_3$O$_4$. The broad undifferentiated feature around 450 cm$^{-1}$ comes from the NMR tube in which the sample was encapsulated. Another area of the same sample showed a more intense peak typical of Fe$_3$O$_4$ – Figure 78b. More representative spectra were obtained by subtracting the spectrum of the NMR tube – Figure 78c.
(a) Raman spectrum of one area of Sample 4 – pickled wires, 50 °C, 100% RH

(b) Raman spectrum of another area of Sample 4 – pickled wires, 50 °C, 100% RH

(c) Raman spectrum of Sample 4 – pickled wires, 50 °C, 100% RH (with the spectrum of the NMR tube subtracted)

Figure 78: Raman spectrum of Sample 4 – pickled wires, 50 °C, 100% RH
Figure 79a shows the SEM images of Sample 7 – 0.5M NaCl coated wires, exposed to 75% RH and 50°C for ~ 370 hours. Samples rinsed after anoxic testing with a salt coating showed significant development of corrosion products compared with their condition before exposure, consistent with the amount of metal oxidized as deduced from hydrogen pressure increase. Large oxygen peaks are shown in EDX spectra, Figure 79b.

(a) SEM images of Sample 7 – 0.5M NaCl coated wires exposed to 50 °C, 75% RH
EDX results in weight percent

<table>
<thead>
<tr>
<th>Analysis</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>Ca</th>
<th>Fe</th>
</tr>
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<tbody>
<tr>
<td>Analysis 1</td>
<td>33.5</td>
<td>1.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td>64.0</td>
<td></td>
</tr>
<tr>
<td>Analysis 2</td>
<td>14.4</td>
<td>35.1</td>
<td>0.4</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 79: SEM images and EDX spectra of Sample 7 – 0.5M NaCl coated wires, 50 °C, 75% RH

Raman spectra from samples tested in anoxic conditions with salt coating showed intense peaks indicative of various iron oxides or oxyhydroxides – Figures 80a & 80b. Some areas showed mostly Fe$_3$O$_4$, while others showed complex mixtures, leading to the speculation that some products fell off the surface during rinsing, although this was done as gently as possible. We believe that the new corrosion product formed during anoxic exposure was nearly all Fe$_3$O$_4$. A total of 7 areas on different wires were analyzed. All spectra show the most common species observed were Fe$_2$O$_3$ and Fe$_3$O$_4$. Three areas analyzed showed amorphous carbon.
FTIR gave useful information on the thicker films formed on salt-coated samples. As shown in Figure 81, FTIR indicated the likely presence of a mixed carbonate / hydroxide species on the surface.
Films formed at higher temperatures in anoxic conditions without a salt coating showed very well-resolved magnetite Raman spectrum – Figure 82a. A total of six (6) areas were analyzed and all analyzed areas overlay nicely which showed significant consistency between the spectra. All spectra indicate the presence of Fe$_3$O$_4$ with some contribution from amorphous carbon. The six (6) spectra were averaged and the averaged spectrum is shown in Figure 82b, which clearly shows the dominance of magnetite.

Figure 81: FTIR spectrum of Sample 10 – 0.5M NaCl coated wires, 50 °C, 100% RH (rinsed)
(a) Raman spectrum of Sample 11 – pickled wires, 70 °C, 100 % RH

(b) Raman spectrum (average) of Sample 11 – pickled wires, 70 °C, 100 % RH

**Figure 82: Raman spectra of Sample 11 – pickled wires, 70 °C, 100% RH**

**7.0 Further Discussion and Conclusions**

The experiments show that corrosion is persistent with massive salt deposition, likely to stabilize in the range 0.01 – 0.1 μm·y⁻¹ but becomes extremely slow without salt deposition, even at 75-100% RH and 50-70 °C. While the present results obtained in the pre-corroded sample testing cannot accurately indicate how much corrosion has occurred, it is anticipated
that future research using longer-term testing and further improved test procedures shall reveal more corrosion mechanism details. This shall be important in confirming the required performance of the used fuel container under anticipated repository environment.

The effect of the amount of salt deposit on the long-term corrosion rate was unable to be further explored in this study due to the limited project budget. However, the mechanism of this effect or the phenomena such as filiform corrosion of coated steel shall be further investigated in the future.

The Raman spectroscopy results have detected magnetite as the predominant low-temperature product. The crystallization of magnetite on the wire surface, analogous to protective films formed in hot water environments, is a favorable outcome for the protection of the metal. This finding is encouraging particularly when compared with the looser Fe(OH)$_2$ type of film, despite the Raman inactivity of the latter, together with imperfect air exclusion during sample transfers, might have affected the interpretation. XPS analysis supports the presence of significant hydroxide in the products, noting that this can be ambiguous as the outer surface is always hydroxylated and contaminated with carbon. Generally, XPS reveals more useful information for thin, invisible films as formed in some of the milder environments. In future studies, better sample transfer protocols shall be developed to minimize potential contamination on the sample surfaces. Further combined use of Raman and XPS (with sputter etch profiling) is recommended, including spatially resolved studies such as examination of corrosion at sulfide inclusion.

In addition to the current results showing the promising performance of the carbon steel container for the disposal of used nuclear fuel, significant technical advances have been achieved in this study. Particularly, the ability of a pressure gauge system to measure corrosion rates as low as 0.01 μm·y$^{-1}$ is encouraging. The electrochemical hydrogen sensor has also revealed important potential for even lower corrosion rates in future studies.
8.0 References


Pedersen, K., M. Motamedi, O. Karnland and T. Sandén. 2000a: Cultivability of microorganisms introduced into a compacted bentonite clay buffer under high-level radioactive waste repository conditions, Engineering Geology Vol. 58, pg. 149.


SSW, University of Western Ontario. 2010. Surface analysis of carbon steel wire specimens (not issued).


APPENDIX A: Leak Test Results

Leak Test (I)

Volume of test cell: 168 mL
Volume of deionized water 23 mL
Test temperature 32°C

Note: steady pressure increase observed in the first leak test which was likely caused by unsteady temperature control. To improve temperature control, the water bath was covered with foam board to reduce evaporation and additional leak tests were performed to verify the suspected error.
Leak Test (II)

Volume of test cell: 166 mL

Volume of deionized water 26 mL

Test temperature 37°C

Note: Relatively stable pressure indications were obtained in the second leak test, suggesting proper sealing and air tightness of the glass cell.
Leak Test (III)

Volume of test cell: 167 mL
Volume of deionized water 27 mL
Test temperature 32°C

Note: Similar to leak test (II), pressure was stable for over 800 hours, confirming the glass cell was sealed and gas leak tight.
APPENDIX B: Estimate of Corrosion Depth Corresponding to a Pressure Change of 0.1 kPA

Moles of hydrogen produced = \( \frac{0.1\text{kPa} \times 0.17L}{101.3\text{kPa} \times 22.4L} = 7.5 \times 10^{-6} \) moles

Moles of iron corroded per mole of hydrogen produced: 7.5 \times 10^{-6} \) moles

(assuming corrosion product is Fe(OH)\(_2\))

Moles of iron corroded per cm\(^2\) = 7.5 \times 10^{-9} \) moles

Molecular weight of iron = 55.8 g/mol

Grams of iron corroded per cm\(^2\) = 4.2 \times 10^{-7} \) g·cm\(^{-2}\)

Density of iron = 7.9 g·cm\(^{-3}\)

Depth of iron corroded = 4.2 \times 10^{-7} \) g·cm\(^{-2}\) / 7.9 g·cm\(^{-3}\) = 0.53 nm
APPENDIX C: Quartz Crystal Microbalance (QCM) Testing

In an attempt to monitor changes of mass of the steel wires during the corrosion tests, a QCM200 Quartz Crystal Microbalance manufactured by Stanford Research Systems was used. The QCM200 measures mass and viscosity in processes occurring at or near surfaces, or within thin films. It is a stand-alone instrument with a built-in frequency counter and resistance meter. The instrument reads the resonant frequency and resistance of a 5 MHz, AT-cut quartz crystal.

The planned method for using the QCM200 was as follows:

1. Expose the crystal, coated with iron by vacuum deposition or electroplating, to a gaseous environment of particular relative humidity.

2. Measure the change of the crystal frequency with time, for which a meaningful duration would be 1-3 days. Superficial corrosion of the iron film will produce some corrosion product like Fe(OH)$_2$, along with hydrogen, and cause mass change of the iron film.

3. QCM can measure the mass change on the crystal surface by the equation:

\[ \Delta f = -C_f \Delta m \quad [C-1] \]

where

- $\Delta f$ – the observed frequency change in Hz;
- $\Delta m$ – the change in mass per unit area
- $C_f$ - the sensitivity factor for the crystal

$C_f$ is 56.6 Hz·µg$^{-1}$·cm$^2$ in a dry gas environment for the crystal we used at room temperature, but its value is affected by the environment and appropriate calibration is required. For our testing at 30$^\circ$C, and relatively high humidity, $C_f$ needs to be re-calibrated, using for example a silver or copper thin film.

It turns out that for a corrosion rate of ca. 0.01µm·y$^{-1}$, the QCM is adequately sensitive if well calibrated, but (omitting the details of many tedious investigations) has a day-to-day
drift, especially in humid conditions, that swamps the signal from the corrosion reaction, far beyond any possible effect (1 Hz or so) of temperature fluctuation – Figure C1.

Figure C1: Change of the frequency of the crystal without any deposit in an environment of 100% RH at 30°C
APPENDIX D: Preparation of the Palladium Membrane

<table>
<thead>
<tr>
<th>Date</th>
<th>Conditions Evaluated</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Jun 04, 09 | - Mounted a 100 µm thick Pd foil between the upper and lower compartment.  
- Filled the lower compartment with a H<sub>2</sub> / N<sub>2</sub> mixture for 20 minutes and measured H<sub>2</sub> via the outlet valve of the copper cell using the H<sub>2</sub> sensor at different time intervals.                                                                                                                                         | - 2 hours after the injection, no H<sub>2</sub> was detected in the upper compartment of the Cu cell.  
- 20 hours after the injection, no H<sub>2</sub> was detected.                                                                                                                                                                                                                      |
| Jun 05, 09 | Repeated above test at 50°C                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | No H<sub>2</sub> was detected.                                                                                                                                                                                                                                                  |
| Jun 12, 09 | - Heat treated the Pd membrane (prior to mounting inside the copper cell) by baking the Pd membrane at 600°C for 1 hour and allowed to cool to room temperature  
- The assembled copper cell was then placed in the water bath set at 50°C.                                                                                                                                                                                                                                                                                                                                                          | H<sub>2</sub> was measured after 18 hours, no H<sub>2</sub> was detected in the upper compartment of the Cu cell.                                                                                                                                                                   |
| Jun 21, 09 | - Heat treated the Pd membrane at 720°C for ½ hour and left in oven set at 500°C for several hours, and then allowed to cool to room temperature inside a crucible (the crucible was pre-filled with 100 ppm H<sub>2</sub> / N<sub>2</sub> mixture).  
- The assembled copper cell was then placed in the water bath set at 50°C.                                                                                                                                                                                                                                                                                             | H<sub>2</sub> was measured after 17 hours, no H<sub>2</sub> was detected in the upper compartment of the Cu cell.                                                                                                                                                        |
| Jun 24, 09 | - Heat treated the Pd membrane at 720°C for ½ hour and left in oven set at 500°C for several hours, and then allowed to cool to room temperature in air for another several hours.  
- The foil was then placed in a tube furnace set at 200°C for 30 minutes. During this period, the tube furnace continued to be flushed with Ar + 2.5% H<sub>2</sub>.  
- The assembled copper cell was then placed in the water bath set at 50°C.                                                                                                                                                                                                                                                                                       | The Pd foil showed a greenish dark colour during the cooling in air period.  
The membrane showed a silvery white colour after heated in the tube furnace at 200°C.  
H<sub>2</sub> was measured after 17 hours, no H<sub>2</sub> was detected in the upper compartment of the Cu cell.                                                                                                                                                                                                  |
| Jul 24   | - Annealed the Pd membrane in a crucible at 900°C for 1 hour  
- Cooled in an oven set at 500°C for several hours, and then further cooling to room temperature in air.                                                                                                                                                                                                                                                                                                                                                      | H<sub>2</sub> was measured 70 hours later, no H<sub>2</sub> was detected in the upper compartment of the Cu cell.                                                                                                                                                                   |
<table>
<thead>
<tr>
<th>Date</th>
<th>Conditions Evaluated</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Coated the exit side of the Pd foil with 0.1M NaOH.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Mounted the Pd membrane between the 2 compartments of the copper cell.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Flushed the lower compartment with 100 ppm H₂ (balance with N₂) mixture for 30 minutes.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Placed the assembled copper cell into a 50°C water bath.</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX E: Sample Calculation of Film Thickness Estimation of Fe₃O₄ based on Pressure Measurement

Pressure data for Sample 5 – Pickled wires exposed to 50°C, 100%RH is used to illustrate how the film thickness of Fe₃O₄ is estimated

Pressure detected: 4.8 kPa (from Figure 26)
Assume pressure measured = amount of hydrogen evolved, no. of moles of hydrogen is calculated using the ideal gas law.

No. of moles of H₂ in 0.14 L corrosion cell at 50°C = 2.45 x 10⁻⁴ moles

H₂ is generated in the following reaction:

\[ 3 \text{ Fe} + 4 \text{ H}_2\text{O} \rightarrow \text{ Fe}_3\text{O}_4 + 4\text{H}_2 \]

No. of moles of Fe₃O₄: 6.1 x 10⁻⁵ moles

Mass of Fe₃O₄ = 0.014 g (MW Fe₃O₄= 231.4 g/mol)

Volume of = 0.0027 cm³ with assumed density Fe₃O₄= 5.1 g/cm³

For surface area of 0.1 m², film thickness of Fe₃O₄= 27 nm
APPENDIX F: Converting Probe Flux Units to hydrogen concentration and calculation of corrosion rates

Conversion of probe readings to ppm

The hydrogen sensor records hydrogen concentration in pl/cm$^2$/s. The sensor was calibrated in each corrosion test. The calibration procedure is described in Section 4.5.2. To convert probe reading to hydrogen concentration, the measured reading was simply compared with the calibration reading. For instance, if the reading of 240 pl/cm$^2$/s was obtained in a calibration run using 97 ppm hydrogen, a peak of 20 pl/cm$^2$/s measured in a measurement will give a hydrogen concentration of 8.1 ppm.

Sample Calculation (using result of pickled wires exposed to 50°C, 100%RH, 92.7 hrs)

H$_2$ of 104 ppm (balanced N$_2$) was used in this calibration, max reading = 234 pl/cm$^2$/s

H$_2$ measurement = 256 pl/cm$^2$/s $\Rightarrow$ C$_{H_2}$ = 113.8 ppm H$_2$

Pressure in glove box = 100.7 kPa,

Temperature in glove box = 23.0°C,

Temperature in copper cell before H$_2$ measurement = 23.5°C

Gas volume in copper cell = 213.8 cm$^3$

C$_{H_2}$ = n$_0$ / (n$_1$ + n$_2$)

n$_1$ = PV/RT$_0$, 100,700 Pa * 213.8 x 10$^{-6}$ m$^3$ / 8.314 * 296 K = 8.75 x 10$^{-3}$ mol

n$_2$ = P$_w$V/RT$_{cell}$, 2900 Pa * 213.8 x 10$^{-6}$ m$^3$ / 8.314 * 296.5 K = 0.25 x 10$^{-3}$ mol

n$_0$ = (n$_1$ + n$_2$)C$_{H_2}$, (8.75 x 10$^{-3}$ + 0.25 x 10$^{-3}$) * 113.8 / 10$^6$ = 1.024 x 10$^{-6}$ mol, generated in 92.7 hrs

H$_2$ generation rate = 1.024 x 10$^{-6}$ mol / 92.7 hrs * 8760 hr.yr$^{-1}$ = 9.677 x 10$^{-5}$ mol.yr$^{-1}$

Fe + 2 H$_2$O $\rightarrow$ Fe(OH)$_2$ + H$_2$

Rate of Fe consumed = 9.677 x 10$^{-5}$ mol.yr$^{-1}$

Corrosion rate = 9.677 x 10$^{-5}$ mol.yr$^{-1}$ * 55.8 g.mol$^{-1}$ / 7.9 g.cm$^{-3}$ / 0.1 m$^2$ = 6.7 x 10$^{-3}$ µm.yr$^{-1}$

P – pressure in the glove box when the copper cell was sealed;

V – effective gas volume in the copper cell;

T$_0$ – temperature in the glove box when the glove box was sealed;

R – gas constant;

P$_w$ – water vapor pressure in copper cell just before the hydrogen measurement;

V – effective gas volume in the copper cell;

T$_{cell}$ – temperature in the copper cell just before the hydrogen measurement;

n$_0$, n$_1$, n$_2$ = no. of moles of H$_2$, N$_2$, and water vapor, respectively
**APPENDIX G:  Data collected using the hydrogen sensor**

Table G1.  Calibration results for H\textsubscript{2} measurements, for pickled wires at 50°C, 100%RH

<table>
<thead>
<tr>
<th>Hydrogen concentration in gas mixture (balance N\textsubscript{2})</th>
<th>Gas filling and measurement condition</th>
<th>Maximum probe reading by direct sucking the copper cell (pl.cm\textsuperscript{-2}.s\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>104 ppm</td>
<td>Glove box</td>
<td>104 ppm</td>
</tr>
<tr>
<td></td>
<td>Copper cell</td>
<td>104 ppm</td>
</tr>
</tbody>
</table>

P = 100.6 kPa  
T\textsubscript{0} = 23.0°C

Table G2.  H\textsubscript{2} measurements and estimated corrosion rates of pickled wires, at 50°C, 100%RH

<table>
<thead>
<tr>
<th></th>
<th>Maxreading (pl.cm\textsuperscript{-2}.s\textsuperscript{-1})</th>
<th>H\textsubscript{2} conc. C\textsubscript{H\textsubscript{2}} (ppm)</th>
<th>N\textsubscript{2} gas in copper cell</th>
<th>H\textsubscript{2}O vapor in copper cell</th>
<th>H\textsubscript{2} in copper cell</th>
<th>Time interval (between measurements) (hours)</th>
<th>Estimated corrosion rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st}</td>
<td>-*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>473.3</td>
</tr>
</tbody>
</table>
| 2\textsuperscript{nd} | 256 | 113.8 | P = 100.7 kPa  
V = 213.8 cm\textsuperscript{3}  
T\textsubscript{0} = 23.0°C | n\textsubscript{1} = 8.75 x 10\textsuperscript{-3} mol | P\textsubscript{w} = 2.90 kPa  
V = 213.8 cm\textsuperscript{3}  
T\textsubscript{cell} = 23.5°C | n\textsubscript{2} = 0.25 x 10\textsuperscript{-3} mol | 1024.2 \times 10\textsuperscript{-9} | 92.7 | 6.7 \times 10\textsuperscript{-3} |
| 3\textsuperscript{rd} | 96 | 42.7 | P = 100.9 kPa  
V = 213.8 cm\textsuperscript{3}  
T\textsubscript{0} = 24.0°C | n\textsubscript{1} = 8.74 x 10\textsuperscript{-3} mol | P\textsubscript{w} = 2.99 kPa  
V = 213.8 cm\textsuperscript{3}  
T\textsubscript{cell} = 24.0°C | n\textsubscript{2} = 0.26 x 10\textsuperscript{-3} mol | 384.3 \times 10\textsuperscript{-9} | 92.5 | 2.5 \times 10\textsuperscript{-3} |

* There was no hydrogen measurement during the first 473.3 hours, since the corrosion rate according to the pressure gauge test (Figure 1) was too high for the hydrogen probe to measure.

P – pressure in the glove box when the copper cell was sealed after hydrogen measurement;  
V – effective gas volume in the copper cell;  
T\textsubscript{0} – temperature in the glove box when the glove box was sealed;  
R – gas constant;  
P\textsubscript{w} – water vapor pressure in copper cell just before the hydrogen measurement;  
V – effective gas volume in the copper cell;  
T\textsubscript{cell} – temperature in the copper cell just before the hydrogen measurement;  
n\textsubscript{0}, n\textsubscript{1}, n\textsubscript{2} = no. of moles of H\textsubscript{2}, N\textsubscript{2}, and water vapour, respectively
Table G3. Calibration results for H₂ measurements using the copper cell, with pickled-50°C-75%RH

<table>
<thead>
<tr>
<th>Hydrogen concentration (balance N₂)</th>
<th>Pressure, temperature measurements</th>
<th>Maximum probe reading by direct sucking the copper cell (pl.cm⁻².s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>104 ppm</td>
<td>Glove box</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>T₀ = 23.5°C</td>
<td></td>
</tr>
<tr>
<td>copper cell</td>
<td>Tcell = 23.5°C</td>
<td></td>
</tr>
<tr>
<td>104 ppm</td>
<td>Glove box</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>T₀ = 24.0°C</td>
<td></td>
</tr>
<tr>
<td>copper cell</td>
<td>Tcell = 24.0°C</td>
<td></td>
</tr>
</tbody>
</table>

Average maximum probe reading: 241

Table G4. H₂ measurements and estimated corrosion rates of pickled wires at 50°C, 75%RH test (Copper cell)

<table>
<thead>
<tr>
<th>Maxreading (pl.cm⁻².s⁻¹)</th>
<th>H₂ conc., Cₘ (ppm)</th>
<th>N₂ gas in copper cell n₁=PV/RT₀</th>
<th>H₂O vapor in copper cell n₂=PᵦV/RTₜ₉</th>
<th>H₂ in copper cell n₀= (n₁+n₂)Cₘ</th>
<th>Time interval (between measurements) (hours)</th>
<th>Estimated corrosion rate (µm.yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>8</td>
<td>3.5</td>
<td>10.88x10⁻⁵ mol</td>
<td>1.75kPa V=266.8 ml T₀=20.0°C</td>
<td>38.7 x10⁻⁹ mol</td>
<td>352.5</td>
</tr>
<tr>
<td>2nd</td>
<td>21</td>
<td>9.1</td>
<td>10.98x10⁻⁵ mol</td>
<td>1.55kPa V=266.8 ml T₀=18.0°C</td>
<td>101.5 x10⁻⁹ mol</td>
<td>335.3</td>
</tr>
<tr>
<td>3rd</td>
<td>31</td>
<td>13.4</td>
<td>11.10x10⁻⁵ mol</td>
<td>1.75kPa V=266.8 ml T₀=20.0°C</td>
<td>151.3 x10⁻⁹ mol</td>
<td>309.7</td>
</tr>
<tr>
<td>4th</td>
<td>35</td>
<td>15.1</td>
<td>10.93x10⁻⁵ mol</td>
<td>2.05kPa V=266.8 ml T₀=22.5°C</td>
<td>168.4 x10⁻⁹ mol</td>
<td>215.9</td>
</tr>
<tr>
<td>5th*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6th*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T₀ = 25.0 °C</td>
<td>T₀ = 21.0 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>-------------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7&lt;sup&gt;th&lt;/sup&gt;</td>
<td>46</td>
<td>19.9</td>
<td>P = 100.7kPa V = 266.8 ml T₀ = 25.0 °C n₁ = 10.85 x10⁻³ mol</td>
<td>Pₚ = 1.87kPa V = 266.8 ml T₉ = 21.0 °C n₂ = 0.20 x10⁻³ mol</td>
<td>219.9 x10⁻⁹ mol</td>
<td>407.6</td>
</tr>
<tr>
<td>8&lt;sup&gt;th&lt;/sup&gt;</td>
<td>46</td>
<td>19.9</td>
<td>P = 100.8kPa V = 266.8 ml T₀ = 24.5 °C n₁ = 10.88 x10⁻³ mol</td>
<td>Pₚ = 1.75 kPa V = 266.8 ml T₉ = 20.0 °C n₂ = 0.19 x10⁻³ mol</td>
<td>219.9 x10⁻⁹ mol</td>
<td>212.3</td>
</tr>
<tr>
<td>9&lt;sup&gt;th&lt;/sup&gt;</td>
<td>37</td>
<td>16.0</td>
<td>P = 99.0kPa V = 266.8 ml T₀ = 22.5 °C n₁ = 10.76 x10⁻³ mol</td>
<td>Pₚ = 1.81kPa V = 266.8 ml T₉ = 20.5 °C n₂ = 0.20 x10⁻³ mol</td>
<td>175.4 x10⁻⁹ mol</td>
<td>217.9</td>
</tr>
<tr>
<td>10&lt;sup&gt;th&lt;/sup&gt;</td>
<td>32</td>
<td>13.8</td>
<td>P = 99.0kPa V = 266.8 ml T₀ = 24.0 °C n₁ = 10.70 x10⁻³ mol</td>
<td>Pₚ = 1.70kPa V = 266.8 ml T₉ = 19.5 °C n₂ = 0.19 x10⁻³ mol</td>
<td>150.3 x10⁻⁹ mol</td>
<td>90.7</td>
</tr>
</tbody>
</table>

* The 5<sup>th</sup> and 6<sup>th</sup> measurements were not successful.
Table G5. Calibration results for $\text{H}_2$ measurements using the copper cell, with pickled wires, at 50°C, 85%RH

<table>
<thead>
<tr>
<th>Hydrogen concentration of the gas mixture (balance $\text{N}_2$ filled)</th>
<th>Gas filling and measurement condition</th>
<th>Maximum probe reading by direct sucking the copper cell (plcm$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
</table>
| 97 ppm | Glove box | $P = 101.6kPa$  
$T_0 = 24.5^\circ\text{C}$ | 218 |
| Copper cell | $T_{\text{cell}} = 23.0^\circ\text{C}$ | |
| 97 ppm | Glove box | $P = 101.3kPa$  
$T_0 = 23.0^\circ\text{C}$ | 218 |
| Copper cell | $T_{\text{cell}} = 23.0^\circ\text{C}$ | |

Average maximum probe reading | 218 |

Table G6. $\text{H}_2$ measurements and estimated corrosion rates of pickled wires, at 50°C, 85%RH (copper cell)

<table>
<thead>
<tr>
<th>Maxreading (plcm$^{-2}$s$^{-1}$)</th>
<th>$\text{H}_2$ conc. $C_H$ (ppm)</th>
<th>$\text{N}_2$ gas in copper cell $n_1=PV/RT_0$</th>
<th>$\text{H}<em>2\text{O}$ vapor in copper cell $n_2=P_v/RT</em>{\text{cell}}$</th>
<th>$\text{H}_2$ in copper cell $n_0= (n_1+n_2)C_H$</th>
<th>Time interval (between measurements) (hours)</th>
<th>Average corrosion rate (µm.yr$^{-1}$)</th>
</tr>
</thead>
</table>
| 1$^{st}$ | 7 | 3.1 | $P = 100.8kPa$  
$V = 213.8$ ml  
$T_0 = 22.5^\circ\text{C}$ | $n_1 = 8.78 \times 10^9$ mol | $P_v = 22.5kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 22.0^\circ\text{C}$ | $n_2 = 0.20 \times 10^9$ mol | 27.8 x 10$^{-9}$ | 164.3 | 1.0 x 10$^{-4}$ |
| 2$^{nd}$ | 11 | 4.9 | $P = 100.0kPa$  
$V = 213.8$ ml  
$T_0 = 22.0^\circ\text{C}$ | $n_1 = 8.72 \times 10^9$ mol | $P_v = 22.5kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 22.0^\circ\text{C}$ | $n_2 = 0.20 \times 10^9$ mol | 43.7 x 10$^{-9}$ | 258.5 | 1.0 x 10$^{-4}$ |
| 3$^{rd}$ | 20 | 8.9 | $P = 100.9kPa$  
$V = 213.8$ ml  
$T_0 = 22.5^\circ\text{C}$ | $n_1 = 8.78 \times 10^9$ mol | $P_v = 23.9kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 23.0^\circ\text{C}$ | $n_2 = 0.21 \times 10^9$ mol | 80.0 x 10$^{-9}$ | 312.7 | 1.6 x 10$^{-4}$ |
| 4$^{th}$ | 24 | 10.7 | $P = 101.3kPa$  
$V = 213.8$ ml  
$T_0 = 23.0^\circ\text{C}$ | $n_1 = 8.82 \times 10^9$ mol | $P_v = 22.5kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 22.0^\circ\text{C}$ | $n_2 = 0.20 \times 10^9$ mol | 96.5 x 10$^{-9}$ | 234.5 | 2.5 x 10$^{-4}$ |
| 5$^{th}$ | 22 | 9.8 | $P = 99.7kPa$  
$V = 213.8$ ml  
$T_0 = 23.0^\circ\text{C}$ | $n_1 = 8.67 \times 10^9$ mol | $P_v = 1.99kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 20.0^\circ\text{C}$ | $n_2 = 0.17 \times 10^9$ mol | 86.6 x 10$^{-9}$ | 261.6 | 2.0 x 10$^{-4}$ |
| 6$^{th}$ | 32 | 14.2 | $P = 100.8kPa$  
$V = 213.8$ ml | $n_1 = 8.84 \times 10^9$ mol | $P_v = 2.11kPa$  
$V = 213.8$ ml  
$T_{\text{cell}} = 23.0^\circ\text{C}$ | $n_2 = 0.18 \times 10^9$ mol | 128.1 x 10$^{-9}$ | 331.5 | 2.4 x 10$^{-4}$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th>( T_0 = 20.5 , ^\circ C )</th>
<th>( T_{cell} = 21.0 , ^\circ C )</th>
</tr>
</thead>
</table>
| 7^th | 28 | 12.5 | \( P = 100.7 \, kPa \)  
\( V = 213.8 \, ml \)  
\( T_0 = 23.0 \, ^\circ C \) | \( n_1 = 8.75 \times 10^{-3} \, mol \)  
\( P_w = 2.11 \, kPa \)  
\( V = 213.8 \, ml \)  
\( T_{cell} = 21.0 \, ^\circ C \) | \( n_2 = 0.18 \times 10^{-3} \, mol \)  
\( 111.6 \times 10^{-9} \)  
\( 220.9 \)  
\( 3.1 \times 10^{-4} \) |