HIGH TEMPERATURE AND HIGH PRESSURE CORROSION OF Ni-BASED
ALLOYS AND STAINLESS STEELS IN AMMONIACAL SULPHATE
SOLUTION

by

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ABSTRACT

The corrosion characteristics of Alloy 625 (UNS 00625, Ni – 22 Cr – 10 Mo) in oxygenated ammoniacal sulphate environments are determined at room temperature and pressure and up to high temperatures and pressures (673 K, 250 bar) commensurate with the process of supercritical water oxidation (SCWO). Electrochemical methods such as linear polarization, potentiodynamic polarization and impedance spectroscopy are used.

It is found that the electrochemical and morphological response is dictated by the alloying element Cr and the formation of a Cr(III) oxide. Mo and, to a lesser extent Ni, are found to dissolve readily. Thermodynamic analysis of the Ni-NH₃-H₂O system, including new Pourbaix diagrams at temperatures as high as 653 K, has shown that Ni-ammine formation is possible at moderate temperatures but that the stability of these complexes decreases substantially with temperature. According to one of the models investigated, which is based on the only available high temperature equilibrium constant data, Ni-ammines become unstable above approximately 473 K.

Impedance spectroscopy has shown that transpassive dissolution of the alloy’s p-type, cation conducting, Cr(III) oxide occurs at temperatures as low as 373 K and total pressure (oxygen saturated) as low as 40 bar. As temperature and pressure are increased the corrosion process is increasingly diffusion controlled. Transpassive dissolution results in the thinning and eventual total removal of the alloy’s protective semiconductor barrier layer. Cation ejection from the barrier layer into the solution and porous outer layer phase results in precipitation of a Cr(III) scale (oxide or hydroxyl-oxide) at the alloy surface which acts as a diffusion barrier. It is hypothesized that the outer layer is either physically removed at supercritical conditions due to rapid dissolution and grain
boundary attack of the alloy or chemically removed by solution acidification due to the formation of sulphuric acid at high density supercritical conditions.

Alloys 625, 316 L, Ni – 20 Cr and pure Nb are tested at SCWO conditions and it is found that the corrosion resistance increases with Cr content and Nb is found to perform well in sulphate containing SCWO solutions at oxygen concentrations up to 4 m. It is also confirmed in this work that maximum material loss occurs in the high-density supercritical region of the reactor.

New Pourbaix diagrams for Nb at elevated temperatures (348 and 368 K) are calculated and compared to electrochemical and weight loss measurements performed in concentrated acids. Through electrochemical experiments in concentrated sulphuric and hydrochloric acids, Nb is found to be an ideal candidate for the high-density supercritical sections of SCWO reactors.
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DEDICATION

Pour mon père qui me manquera toujours.

Pour ma mère à qui je dois tout.

Pour mon frère qui poursuit son propre chemin.

And for my wife who is an inspiration.
1 INTRODUCTION

760 kg of iron has been corroded as you read this. This sentence was presented as a poster at a corrosion exhibition in Brussels in 1937 [Pourbaix 1973]. Undoubtedly, the rapid pace of the post Industrial Revolution development of corporate and national infrastructure required that attention be placed on the issue of corrosion and that a concerted effort be put towards understanding and mitigating it. The problem of corrosion is, however, not a modern preoccupation. Humans have been interested to varying degrees with the prevention of corrosion since the application of metals to practical purposes. The Greek Historian Herodotus (fifth century B.C.) and the Roman naturalist Pliny the Elder (first century B.C.) mention the use of tin for the protection of iron [Tomashov 1966]. It is likely that we have been studying this problem to an increasing degree since the Bronze Age, the earliest stages of which can be traced to southern Russia circa 3000 BC. Indeed, Chinese bronzes (weapons and mirrors) from the Shang and Chou dynasties (1600-221 B.C.) are known to have been intentionally coated with a glassy silicate which has resulted in corrosion protection despite three millennia of exposure to soil [Soto 1983]. Despite this impressive achievement in materials science, anti-corrosion technology remained entirely empirical until the 1920s [Crolet 2003].

The earliest documented corrosion experiments of a scientific nature date back to the mid 18th century. According to Tomashov, Lomosonov was the first to notice the passivation of iron in nitric acid (1743-1750). Later, in what is generally acknowledged as the first series of experiments on passivation (or "curious appearances"), Keir
observed that when he put “some pieces of clean fresh iron wire into a concentrated and red fuming nitrous acid (...) no apparent action ensued” and that “it was altered” and “rendered incapable of being attacked either by a phlogisticated solution of silver, or by dephlogisticated nitrous acid”. This altered iron was “acted on by a dilute phlogisticated nitrous acid; but not by a red concentrated acid, which is known to be highly phlogisticated” [Keir, 1790]. Simply stated, and without the benefit of phlogiston, Keir found that when immersed in concentrated nitric acid, iron does not readily corrode but that when immersed in dilute nitric acid, corrosion occurs quite readily. Keir stated at the end of his paper that “the explanation of these phenomena will be attempted in the subsequent Papers which I propose to present on this subject to the Society.” [Keir, 1790] Uhlig notes that this was never done and that “early attempts at explanation by others were vague and vacillating” [Uhlig 1978]. In a letter to Faraday in 1836, Professor Schoenbein from the University of Basel reported several experiments dealing with the passivation of iron and the galvanic effects between active and passive iron. In fact, the first use of the term “passive” is attributed to Schoenbein [Uhlig 1978]. At Schoenbein’s behest, Faraday performed some of the most interesting, perspicacious and now famous experiments on the passivation of iron. Aside from confirming the remarks by Keir with regards to strong and dilute nitric acid, he also noted that while Fe in 1.3 to 1.35 sg nitric acid corroded readily, if made to contact Pt wire immersed in the same solution, the corrosion stopped immediately [Faraday 1836]. Moreover, Faraday describes the most “valuable result” of this work as being the “proof that voltaic electricity is due to chemical action not to contact”. Through measurement of induced current in a Passive Fe || Nitric Acid || Pt | Active Fe || Nitric Acid || Pt cell he was able to demonstrate that the passive film was not an insulator [Faraday 1836]. With these
experiments and the associated analysis, the oxide film theory upon which we have based
the most modern aspects of corrosion science was born [Faraday 1836]:

“My strong impression is that the surface of the iron is
oxidized, or that the superficial particles of the metal are in
such relation to the oxygen of the electrolyte as to be
equivalent to an oxidation; and that having thus their affinity
for oxygen satisfied, and not being dissolved by the acid
under the circumstances, there is no renewal of the metallic
surface, no reiteration of the attraction of successive particles
of the iron on the elements of successive portions of the
electrolyte, and therefore not those successive chemical
actions by which the electric current (which is definite in its
production as well as its action) can be continued”

It is only recently through the work of Pourbaix in the 1960s, that science and the
study of corrosion have enabled a better understanding of the 18th and 19th century
observations [Macdonald 1999]. Through the use of electrochemical thermodynamic
calculations it is now known that the relative immunity of iron to concentrated nitric acid
is due to a metastable oxide phase forming on the surface of the metal, resulting in a
barrier layer, or passive film, between the bare metal and the solution [Macdonald 1999].

This explanation, on the surface is quite adequate but the reader will notice that it does
not add much to the discussion insofar as it very much resembles the Faraday analysis.
There is then a certain degree of obscurity which surrounds such an analysis and serves
to highlight the complexity of corrosion phenomena. For example, one might wonder
what the real stability limits for this oxide are (distinction made here between the
thermodynamic stability and the real observed meta-stability). Alternatively, the student
might be interested in the chemical versus electrochemical stability of the film. Or
perhaps, from a kinetic point of view: how fast does this passive film form? There is also
the question of steady-state behaviour – does the film grow infinitely? What about the
nature of the film? What exactly is it made of? What is its stoichiometry? How conductive is it? Is it porous? How does it form? How does it break down and how does it interact with the environment? Is it susceptible to certain species? What about the thermal and physical stability of the film? These are only some of the questions that have occupied the corrosion engineer and scientist for the last two centuries and they are of the greatest importance in designing and understanding the materials and processes we so heavily rely upon. They are extremely complicated questions which are highly dependent on the entire metal-environment system to which answers are more often than not unavailable. The consequence of these questions and of the phenomenon of passivation cannot be understated. Indeed, Macdonald has written that “humankind has been able to develop a metals-based civilization primarily because the reactive metals (Fe, Ni, Cr, Al, Ti, Zr, …) exhibit extraordinary kinetic stabilities in oxidizing environments” [Macdonald 1999].

Crolet has said that “corrosion is often qualified alternatively as an emerging science or a stabilized technology, which is quite obviously incompatible, but also equally wrong in each case” [Crolet 2003]. It is my opinion that these opposing views stem from two facts: (1) the science of corrosion is still largely empirical in nature and (2) corrosion is an obvious Second Law process. To illustrate this, Speller notes in 1951 in his introduction to the subject, that “the underlying facts which govern corrosion are now fairly well established” and that “all metals when exposed to the elements have a certain inherent tendency to revert back to one or another of the forms in which they were originally found in the earth”; but he goes on further to say that “much more remains to be learned as to the operation of many of the factors” [Speller 1951]. This is still the dilemma facing the corrosion community. Everyone understands corrosion to
the extent that everyone understands ageing, for example, but the underlying factors which drive the process are still not clear.

Nevertheless, the costs involved in corrosion losses cannot be ignored and warrant an increased effort into the development of corrosion science. A 1998 congressional study into corrosion costs and preventive strategies in the U.S. estimated that the impact of corrosion on the U.S economy was on the order of 3.1% of GDP or some $276 billion dollars [Koch 2001]. Estimates for the cost in Canada in 2004 were on the order of CAD $30 billion [Shipilov 2005]. While cost reduction is the largest driving factor for studying corrosion, from a scientific and socio-economic standpoint it is perhaps not the most important. In Speller’s book, a mining engineer turned depression-era President is quoted as saying:

“It is only through the elimination of waste and the increase in our national efficiency that we can hope to lower the cost of living, on the one hand, and raise our standards of living, on the other. The elimination of waste is a total asset. It has no liabilities.” Herbert Hoover, 1925.

Considering the energetic, environmental and human costs expended to make the materials that we use at ever increasing rates, the loss of these materials to corrosion is an inexcusable waste. With the impending issues related to climate change, resource and oil scarcity and a growing population, any improvements in the efficiency of our materials consumption is a positive step. This thesis does not purport to offer any substantive assuagement to the global problem of corrosion. Instead, I hope it might offer some insight into how best to preserve certain, industrially relevant materials under very specific conditions related to a technology called Supercritical Water Oxidation (SCWO).
SCWO [Modell 1989, 1993] uses supercritical water (T > 374°C, p > 221 bar) as a reaction medium to destroy many types of military and civilian waste which are environmentally harmful and typically difficult to dispose-of. Under SCWO conditions organics become entirely miscible with the solvent supercritical water which acts as a non polar dense gas. With the addition of oxygen or hydrogen peroxide the oxidation reaction proceeds rapidly. Products of the oxidation of hydrocarbons are H₂O and CO₂ while hetero-atoms are converted to inorganic compounds such as acids and salts. Specifically, compounds containing sulfur, chlorine or phosphorus, for example, will oxidize to sulfuric acid (H₂SO₄), hydrochloric acid (HCl) or phosphoric acid (H₃PO₄) within less than a minute. Under these conditions of high temperature and high pressure and low pH (often chemical feeds are acidic even before treatment), corrosion has become a major concern in the development of SCWO technology. SCWO has earned a reputation for an almost insurmountable materials challenge. It has been said that no one material currently exists which meets all the requirements of the different conditions under which a SCWO reactor might function [Mitton 2000]. From preheat to high subcritical, to supercritical, the aggressive nature of the SCWO environment differs quite dramatically. Traditionally Ni-Cr alloys, particularly alloy 625 (UNS NO6625), have seen widespread service in SCWO reactors due to their demonstrated corrosion resistance and mechanical properties at high temperature and pressure in other successful processes. As such, research has been mainly focused on the problem of corrosion of these materials. Furthermore, the overwhelming majority of work has focused on assessing the corrosion characteristics of SCWO systems under aggressive acidic feeds (HCl and H₂SO₄) [Mitton 2000], [Mitton 2002], [Gonzalez], [Boukis 1997], [Downey 1995], [Konys 1999], [Kritzer 2000], [Kritzer 1999], [Fodi 1997], [Kritzer 1998],
[Watanabe 2002]. This is of course in large part due to the phenomenon of acid formation but also because the few studies performed under neutral to alkaline conditions, have shown little or no corrosion (in Na$_2$SO$_4$ for instance [Kritzer 1998]). However, recently, the failure of two sections of alloy 625 tubing at the UBC/NORAM SCWO pilot plant has shown that severe material degradation can be caused by mildly alkaline ($pH_{298K} = 10$) ammoniacal sulphate solutions which were not anticipated to be corrosive. This solution has therefore been used as the main testing medium throughout the work presented below.

As there is very little information directly pertinent to the corrosion of Ni-based alloys or stainless steels in ammoniacal solutions, the following pages will endeavour to present some aspects of this problem with a particular emphasis on alloy 625. For reasons to be discussed later, Ni-based alloys are generally preferred at high temperatures and pressures, but there was some indication that stainless steels might outperform them in ammoniacal solutions. While corrosion studies under supercritical water conditions will eventually be presented, due to the paucity of information regarding the behaviour of these alloys in ammoniacal systems, this study will begin by characterizing their electrochemical response at room temperature and then follow with results from successively higher temperatures. The effects of oxygen were also identified as important so a parallel emphasis is placed on the effect of oxidant concentration on the corrosion characteristics of alloy 625.

The following section (Chapter 2) will discuss some of the pertinent literature and serve to frame the discussion as well as set out the objectives of the work. Chapter 3 will present the objectives of this work. Chapter 4 discusses the results of studies performed
at room temperature on alloy 625 and its constitutive elements at varying oxidative and pH conditions. Chapter 5 discusses the results of high temperature electrochemical work performed on alloy 625 to characterize the passive film and its response to oxygen concentration. Chapter 6 presents the results of thermodynamic calculations for the Ni-NH$_3$-H$_2$O system at high temperatures and Chapter 7 relates the results of SCWO corrosion experiments. Chapter 8 presents the results of work aimed at showing that Nb may constitute a viable alternative to Ni-Cr alloys under oxidative high temperature conditions. Finally, Chapter 9 presents the conclusions and recommendations for future work in this area.

There is no doubt that this contribution constitutes a “drop in the proverbial bucket” of engineering challenges which face the corrosion community. Notwithstanding, I have had the opportunity, through the course of the research presented here, to explore not only some aspects of corrosion science as it relates to high temperature, high pressure aqueous corrosion but also to apply this analysis to SCWO which provides considerable environmental benefits over traditional incineration for organic waste treatment. In so doing I hope to have taken up, in some small way, the challenge most aptly presented by Hoover some 81 years ago.
2 LITERATURE REVIEW

2.1 The Process of SCWO

2.1.1 The UBC reactor

The process of SCWO, as used in the UBC reactor, is roughly schematized in Figure 2-1, p.13. The waste feed stream is added to water and pumped into the reactor by a high pressure piston pump. The effluent end of the reactor is fitted with a back-pressure regulator which modulates pressure as required, usually between 220 and 300 bar. Oxygen is added to the mix by means of an oxygen pressure booster. Typically oxygen is added in large excess with respect to the organic to be degraded (ex: 200%) to ensure full oxidation of the influent. Hydrogen peroxide (H$_2$O$_2$) injection is an alternate route to adding oxidizing agent but some authors have reported that this method requires the use of a catalyst (platinum is one option) to decompose the peroxide as the kinetics of the hydrogen peroxide breakdown are slow. In general, the use of H$_2$O$_2$ is limited to laboratory scale units as it is more portable than direct oxygen injection but largely more expensive. Initially the feed passes through a recuperative heat exchanger and is then preheated up to the supercritical temperature (two preheater sections are employed to this end at UBC, PH1 and PH2). In the reactor, the spontaneous oxidation of the organic feed stream raises the temperature to levels well in excess of 773 K. This reaction takes place very quickly with typical residence times of one minute or less. Salts in the stream precipitate because their solubility above the supercritical temperature decreases
substantially. Problems with respect to reactor fouling ensue but that is an issue beyond the scope of this work. At the outlet of the reactor the effluent passes once again through the heat exchanger (RHX) and is then cooled to approximately 313 K in the process cooler. A gas separator is the last component of the system in Figure 2-1.

Other reactor schemes have been employed such as tank or transpiring wall designs. Both these designs reportedly have the advantage of reducing salt deposition. In the case of the tank reactor a cool zone is maintained at the bottom where salts are dissolved and then removed as brine. The transpiring wall reactors use a porous pipe which is rinsed with water to prevent salts from depositing and plugging the reactor [Schmieder 1999].

2.1.2 Advantages of SCWO

With temperatures in the reactor section between 773 and 873 K, residence times for 98% conversion efficiencies are on the order of less than 1 min [Dinjus 2004]. Unlike traditional incineration which is known to release dioxins and NO\(_x\), the temperatures used in SCWO are low enough to ensure that organic-bonded N is converted to mostly \(\text{N}_2\) and minor amounts of \(\text{N}_2\text{O}\) [Kritzer 2001].

One of the other major advantages to SCWO is that it can operate as a closed system such that reactants and products are easily isolated. With reported destruction efficiencies as high as 99.9999% it is then ideally suited for treating such wastes as radioactive sludge or military chemical agents such as VX or Sarin gas. The US Department of Defense has reportedly spent a significant amount of resources investigating the application of SCWO to such purposes through General Atomics and Sandia National Laboratory. Other investigated systems with high destruction efficiencies include ethanol, toluene, trichloroethylene and phenols. Particularly
refractory compounds include pyridine, urea, ammonia and acetic acid [Schmieder 1999]. The issue of ammonia destruction is relevant to this thesis and will be discussed in the following section.

2.1.3 Ammonia persistency

Many of the wastes potentially treatable by SCWO either include ammonia at the onset (municipal waste or organic sludge which could depend on ammonia for liquefaction), or result in its formation as a refractory and oxidation rate-determining step. For instance Goto et al. have found that ammonia decomposition in sewage sludge after 4 hours of reaction at 723 K at 300 bar was 30 % [Goto 1999]. Ding et al. have reported approximately 30-40 % NH$_3$ conversion over a MnO$_2$/CeO$_2$ catalyst at 723 K at 280 bar. Dell’Orco et al. have reported conversion of less than 10 % after exposure to SCWO environments at 723 K, 300 bar and 10 sec residence times [Dell’Orco 1997]. Helling and Tester have said that “ammonia is very difficult to oxidize below 813 K at residence times of 6-13s” and have reported conversions of ~ 6 % under such conditions [Helling 1988]. Perhaps the most cited work in this area is that of Webley et al. who have summarized by saying that the ammonia oxidation rate was mainly dependent on reactor wall catalysis and that ammonia oxidation occurred to a maximum of ~ 40 % at 973 K, 246 bar, 16 sec residence times over a packed-bed reactor with a high surface to volume ratio (S/V) of ~ 600. Conversions of ~ 10% were reported for a tubular reactor with S/V ~ 20 under the same P and T conditions but with 10 s residence times [Webley 1991]. Segond et al. found similar results with regards to the S/V ratio. Generally conversion rates of > 50% were obtained at residence times of ~ 30s at 873 K, 245 bar. Up to 95 % conversion was obtained at 1 min residence times for S/V = 4 [Segond
2002]. For purposes of comparison, the S/V ratio for the UBC reactor is roughly 6.5. As such, oxidation of NH\(_3\) is not expected to be fast until approximately 873 K.

It should also be noted, and this is important, that none of these authors have reported corrosion damage to their 316 L, Inconel 625 or Hastelloy C-276 reactors (cf. Table 2-1). This is one of the reasons why experiments performed at UBC in the presence of ammonia were not expected to result in significant corrosion. Discussion on this point will follow.

<table>
<thead>
<tr>
<th>Table 2-1 Alloy compositions (wt%)</th>
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<tbody>
<tr>
<td><strong>Cr</strong></td>
</tr>
<tr>
<td>625</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>C-276</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>C-22</td>
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<tr>
<td></td>
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<tr>
<td>316L - SS</td>
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Figure 2-1  SCWO flowsheet as implemented at the UBC/NORAM reactor
2.2 Properties of supercritical water

Upon heating water in a closed system, vapour density increases while liquid density decreases. If the pressure is allowed to reach $P > 221$ bar at a temperature of $T > 647$ K, the vapour density is equal to the liquid density and the result is supercritical water. This phase exhibits entirely different properties from the solid, liquid and gas phases. Supercritical water shows high gas-like diffusion rates along with high liquid-like collision rates. In a SCWO reactor, pressure is maintained constant from ambient temperature to supercritical temperatures. The change from high temperature water to supercritical water occurs quite rapidly and markedly at temperatures close to 647 K and pressures in excess of 221 bar. Figure 2-2 illustrates the variation in density with respect to temperature at 240 bar.

Figure 2-2 Properties of water at 240 bar. The property transition point is shown by the dashed line while the region of dense supercritical water is highlighted by the grey zone. After Kritzer 2001.
The temperature at which the properties of water make the sub- to supercritical transition is greatly affected by pressure [Kritzer 1999A]. For instance, while water at 647 K, 240 bar has clearly exceeded the critical point, it has not yet undergone the distinguishing drop in density associated with lower pressure supercritical water – conversely, water at 658 K, 240 bar has made what one might describe as the "property transition". This distinction is often referred-to in terms of high-density supercritical water, before the property transition, and low-density supercritical water, after the transition. As pressure is increased the property transition point of water moves to higher temperatures (at 250 bar it is closer to 673 K).

Fluid density at SCWO conditions is in the region of 0.1g/cm$^3$. Similarly, the dielectric constant of water drops from about 80 at room temperature to 1 or 2 at 250 bar and 723 K. The ion product of water also decreases from a value of $10^{-14}$ to $10^{-23}$ [Marshall 1981]. The result is that low density supercritical water resembles a non-polar dense gas in that it has a high solvency for hydrocarbons and organics whereas inorganics tend to precipitate [Mitton 2001]. In contrast, high density supercritical water displays less solvency for organics but a high solvency for inorganics. Most SCWO applications have operating pressures between 250 and 350 bar such that there are regions in the reactor exposed to high-density supercritical water which, due to its high solvency for salts, has been shown to be extremely corrosive [Macdonald 1993], [Kriksunov 1995]. In fact, it is generally acknowledged that corrosion rates reach a maximum in the high density supercritical region - between ~ 647 and 673 K from 221 to 250 bar [Liu 1994]. This maximum has been related to the competing effects of temperature on the corrosion rate constant and on the properties of the aqueous medium.
such as density and the dielectric constant [Macdonald 2001]. Thus, while reaction kinetics increase with temperature, the solvent water is less able to dissociate acids or accommodate inorganic reaction products. As a result, above the property transition temperature corrosion rates decrease substantially to the extent that they are generally acceptable in low-density supercritical water. An interesting discussion on this topic is presented by Macdonald who has shown that as temperatures increase to the critical point, the contribution of the activation energy to the total reaction rate loses in relative importance to the contributions from solution density and acid dissociation (dielectric) [Macdonald 2004].

High concentrations of oxygen are required for high waste destruction efficiencies in SCWO reactors. In general, oxygen solubility decreases in water to a minimum somewhere in the region of 363 K. Above this temperature there is an exponential increase in the gas’ solubility. Any corrosion process requires both an anodic and cathodic reaction to proceed. The cathodic reaction consumes the electrons generated at the anode (presumably corroding tubing) and is considered the driving force in corroding systems. In the absence of a stronger oxidant, oxygen reduction is the cathodic reaction most likely to occur in SCWO systems. The amount of available oxygen and its solubility in the reactor environment is then a very important consideration in SCWO corrosion investigations. In high density supercritical water oxygen is almost fully soluble and this is a further aggravator to the increased malignancy of this medium [Kritzer 2000B].

Any corrosion reaction can be limited by a build up of corrosion products such as salt films, oxides, or what some refer to as scales. In the case of Ni-Cr-Mo alloys a mixed oxide layer containing chromium oxide and nickel oxide is possible. The
thermodynamic stability of these “passive” layers is very much dependent on pH and temperature. However, thermodynamic stability is not the only factor which controls passivation. In low temperature solutions an oxide may not be thermodynamically stable but the kinetics of dissolution are such that the transformation from oxide to soluble species is slow – the corrosion process is then under kinetic control. With higher temperatures, chemical reaction rates increase and the importance of kinetic control decreases [Kritzer 1999A]. Under such circumstances diffusion control of the corrosion process is expected to take over through rate controlling delivery of oxygen to the reacting surface, particularly if oxides, salt films or scales build up on the surface as precipitates. Diffusion control is more easily modeled than kinetic control so that corrosion rates in the absence of oxides or scales might be predictable. This is one avenue which will be examined in this thesis because it reveals the importance of salt film/oxide/scale solubility to the study of SCWO materials degradation.

The apparent competition between kinetic control and thermodynamic stability is one of the limitations of Pourbaix diagrams and will be discussed in the following section which deals with the thermodynamics and passivation of Ni-Cr-Mo alloys.

2.3 **Thermodynamics and passivation**

Since the inception of Pourbaix diagrams corrosion scientists and engineers have had access to a phenomenal tool for the interpretation and prediction of metal stability. There are 3 major categories delineated by Pourbaix diagrams, 1- active corrosion, 2-immunity, 3- passivation [Pourbaix 1966]. This last category is the focus of the following discussion and indeed a very important theme in this work.
Perhaps the most persuasive description of passivation is that which is inferred from a look at the Evans diagram (potential-log current) for a passive metal, as seen in Figure 2-3 (a). A definition for this type of passivity is as follows:

“A metal is passive if, on increasing its potential to more positive values, the rate of dissolution decreases, exhibiting low rates at high potentials (also known as thin film passivity).”[Kelly 2003]

With reference to Figure 2-3, there is clearly some process by which the corrosion rate of the material is slowed. Typically, Ni, Cr or Mo would exhibit this type of behaviour in solutions of H₂SO₄. There is, however, another type of passivity in the electrochemical sense, which is referred to as “thick film passivity” by Kelly et al.(Figure 2-3(b)). The definition of which is:

![Figure 2-3 Schematic Evans diagrams (a) thin film passivation, (b) thick film passivation](image-url)
“A metal is passive if it substantially resists corrosion in an environment where there is a large thermodynamic driving force for its oxidation.” [Kelly 2003]

Mg or Al in water, or Pb in H₂SO₄ would behave according to this second definition. This issue of “thin film” or “thick film” is a bit misleading in some respect as it obfuscates the true underlying reason for the corrosion resistance which is likely due to the relative importance of one of the two sections which are known to constitute the passive film. Indeed, passive films are known to occur as bi-layer structures with a thin (1-3 nm) and homogeneous semiconductor-like film (barrier layer - bl) immediately adjacent to the metal (m) surface and a thicker precipitated, hydrated and porous mixed oxide-hydroxide layer (outer layer - ol) on the solution side [Macdonald 1992]. There is a substantial amount of experimental evidence to support this for the particular case of Ni-Cr alloys and also for other systems ([Bockris 1971] for iron, [Sato 1974] for nickel). Lloyd et al. and others ([Jabs 1997], [Maurice 1998] and [Machet 2002]) have effectively communicated that in Ni-Cr alloys the passive layers “can be roughly divided into two sub-layers: the inner oxide layer consisting of Ni(II) oxide, Cr(III) oxide and O²⁻, and the outer hydroxide layer consisting of Ni(II) hydroxide, Cr(III) hydroxide, Cr(VI), OH⁻, and H₂O” [Jabs 1997].

A schematic of the bi-layered structure is shown in Figure 2-4. The ejection of metal cations through the bl to the solution side results in precipitation of the ol which, if thick enough, can lead to the type of response shown in Figure 2-3 (b), often also referred to as “spontaneous passivation”.
Figure 2-4 Schematic of bi-layered film structure on metal surface. Modified from Macdonald 1992.

Whether passivation is "thick film" or "thin film", there is no doubt that it is the basis for the utility of most of today's technologically useful materials. Indeed, and quite paradoxically, we rely heavily on inherently reactive materials. For instance, Ni, Al and Ti will spontaneously ignite in air if ground into fine enough particles. Similarly, in a notable review on the subject of passivity entitled "Passivity – the key to our metals-based civilization", Macdonald has remarked that Al has an energy density of 22 kW.h.kg$^{-1}$ whereas decane, a simulant for gasoline, has an energy density of 10 kW.h.kg$^{-1}$ [Macdonald 1999].

Ni and Cr form barrier layers ~ 1 to 3 nm in thickness. At room temperature the electric field strength of these layers is somewhere in the region of $10^5$ V.cm$^{-1}$ enabling ion migration through the layer. This migration corresponds to current densities of some
μA/cm² or less at room temperatures [Strehblow 1995]. The chemical structure of oxide layers is not as straightforward or stoichiometric as “Cr₂O₃” or “NiO”. Barrier layers are highly doped semiconductors with multiple crystallographic defects while outer layers are a complicated configuration of oxides, hydroxides and hydroxy-oxides such that the stoichiometry usually used to describe these films is rarely observed. This is one of the many limitations of Pourbaix diagrams in that they require assuming the existence of a compound which, in reality, may differ from its ideal and assumed configuration.

Moreover, as discussed above, reaction kinetics are not a factor in Pourbaix calculations though they may greatly affect the real behaviour of the metal. For instance, in acidic electrolytes the passive layer on metals such as Ni, Fe and Cr is far from its domain of thermodynamic stability (well documented: [Pourbaix 1966], [Glasstone 1942]) and passivation in these cases is due to the slow dissolution kinetics of the metastable oxide. Furthermore, the issues of outer layer porosity and/or barrier layer adherence are not addressed in these diagrams. To illustrate the ambiguity associated with the label “passive” a quote from Pourbaix’s *Atlas of Electrochemical Equilibria in Aqueous Solutions* may prove to be helpful:

“...the metal then tends to become coated with this oxide, hydroxide, hydride or salt which can, according to the circumstances, form on the metal either a non-porous film practically preventing all direct contact between the metal itself and the solution (in which case protection against corrosion is perfect), or a porous deposit which only partially prevents contact between the metal and the solution (in which case the protection is only imperfect). Understood in this way, *passivation thus does not necessarily imply the absence of corrosion.*” (p. 71)
This final emphasis is not this author's but rather Pourbaix's - this point is paramount in understanding the discussion which follows because the surface of a metal may be both passive and corroding. For all the reasons stated, interpretation of electrochemical phenomena through reference to Pourbaix diagrams, especially for the Ni-H₂O system, is a notoriously challenging endeavour. The addition of high temperature uncertainties related to imperfect thermodynamic data for both solid and, more so, ionic species complicates the problem. However, these interpretations certainly give a direction toward which to pursue further study and it is here that we shall start with a look at the passivation in the Ni-H₂O and Cr-H₂O systems at high temperature.

Through the last 40 years there has been a large body of work presented on the subject of Pourbaix diagrams for both the Ni-H₂O and Cr-H₂O systems up to ~ 573 K. The largest problem surrounding this body of work is that the ionic chemical potential data at T > 298 K is estimated from a variety of sources and using a variety of methods. Generally, the work can be summarized in this way:

- There is a common movement of the diagrams to lower pH as temperature is increased,
- and reactions are depressed to more negative potentials as temperature is increased

With regards to the stability of ions, in 1972 Brook published the Pourbaix diagrams for Ni and Cr up to 423 K and stated that “since the domains of stability of (...) the lower valence oxides decrease with increasing temperature the domains for the oxyanions show a greatly enlarged range” [Brook 1972]. Macdonald came to a similar finding in 1979 in his work on the nickel-water system in geothermal brines (up to 523 K): “the stability
regions for cations at low pH values become more restricted as the temperature increases, whereas those for the anions (...) increase” [Macdonald 1979A]. It should be noted that Brook used some estimated entropy data and his high temperature data was calculated using temperature coefficients derived from these same estimated ionic entropies. Macdonald’s calculations used the linear ionic heat capacity approximation (LIHCA) based on Criss and Cobble’s correspondence principle, which has been shown to be remarkably accurate up to ~ 573 K [Criss 1964 A, B], [Taylor 1978]; although the general applicability of the LIHCA past 473 K is not without controversy [Liu 2005]. Lee has presented Pourbaix diagrams for Cr and Mo up to 573 K using the LIHCA and the main findings of pertinence to this work were (1) that the domain of stabilities of the oxides were generally reduced as temperature was increased, (2) that the domain of stability of chromium hydroxide (CrOOH or Cr(OH)₃) is wider than that of the anhydrous oxide (Cr₂O₃) and (3) that molybdenum dioxide is unstable above 523 K [Lee 1981].

As temperatures are increased near the critical point of water, the LIHCA becomes unreliable so equations of state for the prediction of ionic standard partial molal thermodynamic properties have been developed by Helgeson, Kirkham and Flowers – known as the HKF model [Helgeson 1981]. Beverskog and Puigdomenech have calculated the Pourbaix diagram for Ni from 298 to 573 K and used the HKF model for the aqueous species. They concluded that NiO is the most stable solid compound formed above 473 K [Beverskog 1997]. Kriksunov and Macdonald have also published Pourbaix diagrams at temperatures up to 723 K, 500 bar for Ni which were generated using a computer program called Supcrt 92 and which employs the HKF model for its calculations. At 573 K, 500 bar their results are similar to those presented by Beverskog
although Kriksunov and Macdonald have chosen not to include “hydrated forms of oxides and complex oxyanions, because of the great uncertainty in the extrapolated thermodynamic functions for those species in the supercritical region, and because low water densities in near-critical and supercritical systems at pressures below 500 bars favors decomposition of hydrated oxides to oxides and also greatly decreases the stability of ionic species” [Kriksunov 1993]. Mitton et al. have also developed a recent E-pH diagram for Ni-Cr-Mo alloy systems without the oxyanions (such as HNiO₂⁻) [Mitton 2000] but based on experimental results from SCWO alloy 625 tubing exposed at 573 K. Their data is consistent with the previously cited literature and supports the following conclusions with regard to the thermodynamic stabilities of Ni, Cr and Mo at high subcritical temperatures:

- At neutral to high pH (approx. 5 to 14), NiO is stable.
- At neutral to low pH (approx. 2 to 5) some form of chromium oxide (Cr₂O₃ or CrOOH) is stable.
- Mo is unstable.

Based on these conclusions there is then a very wide pH range over which Ni-Cr and Ni-Cr-Mo alloys such as alloy 625 are expected to be passive. However, when in the presence of strong oxidant, Cr(III) oxide has a tendency to corrode transpassively which effectively removes any protection in acidic environments. This phenomenon is discussed in the next section.
2.4 The point defect model (PDM) and Transpassivity

Transpassive corrosion has been accepted as the leading contributor to severe and general degradation of Ni-Cr alloys and stainless steels in oxidizing environments such as SCWO [Kritzer 1998, 1999A, 2000A,B], [Hara 2002], [Laycock 1995], [Son 2002], [Wilson 2000]. Both classes of alloys rely on the stability of Cr(III) oxide for corrosion protection, particularly in the presence of acidic environments where NiO is not stable. The reaction proposed by Pourbaix is the following [Pourbaix 1966]:

\[ 2CrO_4^{2-} + 10H^+ + 6e^- = Cr_2O_3 + 5H_2O \]  

While this equation is adequate from an overall electrochemical standpoint, it does little to explain the mechanisms which lead to transpassive corrosion, particularly within the framework of the bi-layered structure mentioned earlier. These mechanisms could shed light on the expected corrosion morphology and electrochemical response of Ni-Cr alloys that are corroding in the transpassive region. This is one area of fundamental corrosion research which has the potential for a very direct impact on service life and process design. Bojinov has said that “transpassive dissolution is a complicated process including electron and ion transport through a surface film, multistep electrochemical reactions at the film/solution interface and transport of reaction products in the bulk solution” [Bojinov 2000]. To gain a more fundamental perspective it is necessary to deviate from the discussion a bit and introduce the point defect model (PDM). The PDM is the leading model to describe the kinetics of passivity. It was developed by Macdonald and co-workers in the early 1980s. There are three fundamental, well established, experimental observations which have framed the PDM and they are, very generally [Macdonald 1992]:
A. As already mentioned, passive films are bi-layered and passivity is attributed to the inner bl which is a highly defective, defect semiconductor in which vacancies act as the electronic dopants [Macdonald 1999]. These vacancies are annihilated and generated at the interfaces - the metal (m)/barrier layer (bl) interface and the bl/solution (s) interface which are separated by a few nanometers.

B. Under steady state conditions, the bl thickness and the logarithm of the currents both vary linearly with applied voltage.

C. The bl grows into the metal while the ol grows out from the metal surface. Figure 2-5 is a schematic of the process of film growth and dissolution as described by the PDM where $m =$ metal atom, $M_M =$ metal cation in a cation site, $O_O =$ oxygen ion in anion site, $V_M^x =$ cation vacancy, $V_O^z =$ anion vacancy, $V_M =$ vacancy in metal phase.
Figure 2-5 The PDM: (1) Injection of a lattice cation with elimination of a cation vacancy (2) Injection of a lattice cation and creation of an oxygen vacancy (3) Oxidative dissolution and creation of a cation vacancy (4) Elimination of an oxygen vacancy, anion injection (5) Chemical oxide dissolution. After Macdonald 1992.

At the m/bl interface, oxygen vacancies are generated and flow towards the bl/s interface. At the bl/s interface cation vacancies are generated and flow towards the m/bl interface. These statements are equivalent to saying that metal cations diffuse from the m/bl to the bl/s interface and that the diffusion of oxygen anion occurs in the opposite direction. After studying Figure 2-5, it becomes clear that the diffusion of $V_O^{-}$ results in oxide growth whereas the diffusion of $V_M^{\chi -}$ is solely the result of cation ejection. There are two equations, (2) and (5), that determine growth and dissolution of the barrier layer – these
are termed lattice non-conservative processes as they result in the movement of the barrier layer boundaries relative to a fixed reference frame. Thus when reaction rates for (2) and (5) are equal, a steady-state film thickness is reached. Reactions (1), (3) and (4) are termed lattice conservative as they do not result in barrier layer boundary shift.

Because the reactions presented in Figure 2-5 are not assumed but are in fact mandated by the widely accepted experimental observations (A through C), the PDM has the advantage of providing a clear interpretation of the mechanisms which determine the corrosion characteristics of a given film. One such mechanism is transpassive dissolution. Thus, according to Macdonald, if reaction (3) is so fast as to overwhelm the capacity for cation vacancy annihilation through reaction (1) then cation vacancies will condense at the m/bl interface. This in turn could lead to macroscopic de-cohesion of the bl from the metal and subsequent replacement of the bl by a salt film (or outer layer) whose protective properties are generally thought to be inferior [Macdonald 1999].

Bojinov et al. have shown, through extensive impedance studies of Ni-Cr alloys, that transpassive dissolution is in fact due to the oxidative ejection of hexavalent Cr from the bl to the ol through a two step process [Bojinov 2000, 2002, 2003], [Betova 2004]. To model the process they have employed a variant on the PDM called the “mixed conductor model” or MCM. Furthermore, Macdonald has shown that “the transpassive state is induced by the oxidative emission of cations from, and by the oxidative dissolution of, the barrier layer, with the latter resulting in a decrease in the barrier layer thickness as the voltage is increased” [Macdonald 2004B].

The issue of applied voltage is important because, from a thermodynamic standpoint, the equilibrium potential for equation 2-1 is ~ 0.23 V with respect to the standard hydrogen electrode (SHE – all further potentials will be referred to this scale) at
298 K, pH 10. When compared to the oxidation of Cr to Cr₂O₃ which occurs at ~ -1.18 V and the oxidation of Ni to NiO at ~ -0.46 V, under the same conditions, the transpassive potential for Ni-Cr alloys is high (cf. $E_{\text{tp}}$ - transpassive potential and $E_{\text{corr}}$ - corrosion potential in Figure 2-3). Thus in the laboratory, it is necessary (under most circumstances where oxidants have not been added) to apply high anodic overpotentials to study transpassive corrosion. From a practical engineering perspective, it is more interesting to know under what natural and un-simulated conditions one could expect to see transpassive corrosion because in a SCWO reactor the applied voltage is set by the chemical composition of the solution. Thus, if the equilibrium potential of the oxygen reduction reaction is high enough, transpassive dissolution could be expected to occur. Such a case could arise when the solubility of oxygen is high such as in a SCWO reactor. But the concentration of oxygen, $C_{O_2}$, (and thus temperature) at which the transpassive corrosion begins is largely unknown as it depends on the kinetics of both the anodic and cathodic reactions. This temperature which results in the transition from the passive state to the transpassive state is known as the “inversion temperature” [Kritzer 2000A].

Attempts have been made to determine the inversion temperature by morphological analysis of corroded tubing exposed to SCWO conditions. Kritzer et al. have extensively studied the issue and have come to the conclusion that the inversion temperature is ~ 523 K for alloy 625 when exposed to acidic solutions with ~ 0.48 m $C_{O_2}$. Schroer et al. have proposed a similar result (523 to 573 K) for various Ni-Cr alloys in 0.12 m HCl, 0.06 m $C_{O_2}$. The importance of this point is related to the interpretation of the corrosion process. Macdonald has argued that dissolution of the bl controls the process even up to high sub-critical temperatures [Macdonald 2001]. Kritzer
does not differentiate between a bl and ol but simply states that the corrosion rate depends strongly on the solubility of the oxides [Kritzer 1998]. These are the questions which arise:

- If at all, when does the bl fail i.e. when does the solubility of the ol control the corrosion process?
- What is the mechanism leading to failure? Is it dissolution of the bl first, then dissolution of the ol, or both at the same time?
- Can morphological observations alone account for a complex electrochemical process such as transpassive corrosion?
- If the dissolution of the ol controls the corrosion process, what are the morphological and electrochemical implications?

Simply put, these questions highlight the fact that the issue of transpassive corrosion and its relationship to oxygen concentration is largely unknown. With regards to the implementation of SCWO, it is clear that the increased solubility of oxygen at high temperatures combined with increased reaction kinetics is expected to lead to high corrosion rates. All the more so that oxidant feed concentrations are by process necessity high in SCWO reactors. Corrosion in SCWO reactors is generally found to reach a maximum in the high density sub- to supercritical region (623 < T < 660 K) where it is believed that near perfect oxygen solubility leads to high rates of transpassive dissolution [Kritzer 2000A, B]. While this observation is indicative of some measure of oxygen control over the corrosion process, it is unclear to what extent charge transfer of the cathodic reaction (oxygen reduction) plays a role in determining corrosion rates, particularly as temperatures are varied. Further to this, it is also unclear at which
temperature a diffusion controlled process might be expected to determine the rate of
corrosion. There have been some studies pertaining to the kinetics of oxygen reduction
on stainless steels [Babic 1993], [LeBozec 2001] and on alloy C-22 [Davydov 2005] at
room temperature. In general, the surface condition of the alloys is found to play a large
role on the cathodic process and, in particular, the passive film was found to suppress
both the diffusion limited current density and the charge transfer kinetics of the oxygen
reduction reaction.

Most corrosion studies tend to focus on the anodic processes and their kinetics.
From a corrosion rate standpoint it may be more practical to study the rate of cathodic
reaction as there is available data on the solubility of oxygen and its diffusivity.
Moreover, given that the limiting diffusion current can be modeled by the flux of oxygen
to the corroding surface, it may be possible to extrapolate room temperature corrosion
rates up to high temperatures and pressures with an adequate degree of certainty. Indeed,
such an analysis has been performed by Tromans for the corrosion of steels and the
leaching of sulphide concentrates [Tromans 1999, 2000]. However, besides the work
done by Speller [Speller 1951] there is little published data of an experimental nature
with which to validate the oxygen diffusion controlled model and, to this author’s
knowledge, no data on the mixed control scenario which may occur at low to moderate
temperatures. In particular, there does not appear to have been much work done of a
quantitative nature in regards to the effect of oxygen on the corrosion behaviour of Ni-
Cr-Mo alloys which were developed for- and are frequently employed in oxidative high
temperature media. Within the context of this discussion, the PDM is important as it
provides a framework and a powerful tool through which to investigate and interpret
these issues.
Finally, it should be reiterated that while transpassive dissolution leads to rapid corrosion in acidic solutions, it does not affect Ni-Cr alloys exposed to neutral solutions at SCWO conditions. This is because under such conditions NiO is able to passivate the alloy. A schematic E-pH diagram showing the regions of stability for NiO and Cr$_2$O$_3$ as well as their chemical or electrochemical dissolution is presented in Figure 2-6.

![Figure 2-6 Stability fields for NiO and Cr$_2$O$_3$ in SCWO. Transpassive dissolution (upwards arrow) only results in severe loss when pH is acidic. Modified from Kritzer 2000A.](image)

2.5 **Alternatives to Ni-based alloys or stainless steels**

Due to their tendency towards transpassive dissolution, alternatives to Ni-Cr alloys are required in the high-density region of SCWO reactors. Two of the more
reasonably priced valve metals which are often used in the chemical industry for aggressive acidic environments are Nb and Ti. It is generally accepted that these materials do not corrode transpassively and in fact remain passive over a wide range of oxidizing conditions. In fact, the breakdown potential of Nb is reportedly in the vicinity of 100V! Some conflicting work on their respective corrosion resistance has been published. For corrosion testing purposes researchers at General Atomics built a Pt lined SCWO reactor in which they placed coupons of such materials as Pt/Ir and Pt/Rh alloys, Hf, Ti, Zr, Mo, Nb, Ta, Al₂O₃, AlN, Sapphire, ZrO₂ and for good measure, alloys C22, C276 and 625. For various reasons, none of these materials performed well in all three of the tested solutions which were highly aggressive: 3.1wt% H₂SO₄, 2.3% HCl and 7.0% H₂O₂ is one example [Downey 1995]. Ti was found to perform adequately, and better than Nb, and has since been adopted as a sacrificial reactor liner for use in the SCWO testing programs at General Atomics. However, the use of Ti is generally not recommended in the presence of sulphates [Kritzer 1999A]. Moreover, Kritzer et al. have found that Nb was un-attacked (gained weight) up to 623 K, 240 bar in 0.05 m H₂SO₄ and 0.05 m HCl [Krtizer 1999C]. The next temperature increment for Kritzer’s work was 773 K so that the corrosion resistance in the 623 to 673 K range is unknown. Also, from a general corrosion rate perspective it is well documented that Nb outperforms Ti in both HCl and H₂SO₄ solutions up to at least 373 K [Brubaker 1987], [Degnan 1987], [Yau 1987]. Finally, there is the issue of Nb as an alloying element. Alloy 625 is alloyed up to ~ 4% (Table 2-1) with Nb to tie up carbon and prevent grain boundary carbide precipitation as well as to promote strength through solid solution and precipitation hardening mechanisms. This is unfortunately not enough to form a protective Nb₂O₅ film. It is conceivable that
adding Nb to Ni-Cr alloys could result in better resistance to transpassive attack. The study of Nb corrosion at high potentials and in oxidizing environments is not complete so it was deemed important to contribute in this area with a view to employing this metal as an alloying element in Ni-Cr alloys or unalloyed as a section of a SCWO reactor.

2.6 The issue of ammonia and Ni-based alloys

In the department of materials engineering at UBC there is sometimes a look of puzzlement on the faces of colleagues as I explain to them that I have undertaken the study of corrosion of Ni-based alloys in ammoniacal sulphate solutions in high temperature oxidative media. Perhaps this is due to the fact that the Sherritt process for the oxidative recovery of Ni from sulphide ores at ~ 423 K was invented by Frank Forward, the first head of our department and our building’s namesake [Forward 1951, 1953, 1955]. This process is based on the thermodynamic stability of some transition metal ammine complexes such as Ni, Cu, Zn and Co. For the case of Ni it is expected that $\text{Ni}(\text{NH}_3)_\nu^{2+}$, where $\nu$ is 1 to 6, would form in the presence of ammoniacal solution. Furthermore the leaching of oxide ores using ammonia was patented by Lance in 1904 [Lance 1904]. Hydrometallurgy is an expertise in the department such that most are not surprised that Ni corrodes readily under such exposure. In fact, the study of corrosion in ammoniacal solutions has historically been undertaken at UBC. For instance, Halpern published three papers on the dissolution kinetics of Cu and Cu-Au alloys in the presence of ammoniacal sulphate solution at $O_2$ pressures up to 7 bar [Halpern 1953, 1959], [Fisher 1956]. Of relevance to this work is the fact that oxygen availability was rate determining at low oxygen pressures and that this limitation was ascribed to diffusion
limited oxygen transport through the reaction product film [Fisher 1956]. Birley and Tromans have also studied the brass-NH₃ system with an emphasis on stress corrosion cracking [Birley 1971]. Generally these corrosion studies have shown that copper alloys exhibit unsatisfactory behaviour when in the presence of ammonia. Copper ammine complexes readily form and stress corrosion cracking is possible. The behaviour of nickel in ammoniacal solutions is less predictable. Corrosion studies of copper-nickel alloys in ammonia containing environments have shown that increasing the alloying content of nickel increases corrosion resistance [Caruso 1981], [Rajagopalan 1981]. Similarly, Rice found that atmospheric corrosion of nickel was inhibited by the presence of ammonia [Rice 1980]. However, Uhlig’s Corrosion Handbook makes a brief reference to the fact that nickel may be unsuitable for use in ammonium salt solutions [Revie 2000]. Electrodeposition studies have shown that nickel deposition increases by some 40 to 60% in high ammonia concentration baths at pH=10 (as compared to ammonium baths at pH=5). The reason for this was attributed to the predominance of a thermodynamically stable nickel ammine – Hexamminenickel (\(\text{Ni(NH}_3\text{)}_{6}^{2+}\)) and the complexing nature of ammonia. Indeed, Rodriguez-Torres developed speciation diagrams at 298 K for the Ni(II)-NH₃-H₂O system and found a large region of stability for \(\text{Ni(NH}_3\text{)}_{6}^{2+}\), even at low partial pressures of ammonia [Rodriguez-Torres 1999].

At 298 K, pH 10 it appears as though nickel should readily corrode in ammoniacal solutions. Whether this tendency is translatable to a Ni-Cr-Mo alloy such as alloy 625 at temperatures in excess of 647 K was one of the veins of pursuit for the study that follows.
3 OBJECTIVES

In view of the preceding discussion the following objectives were set-out.

A. To determine the corrosion resistance of Ni-Cr alloys, exemplified by alloy 625, to ammoniacal sulphate solution in the approximate temperature range of 298 to 673 K.

B. To determine the effect of pH on the corrosion characteristics of alloy 625 when exposed to ammoniacal sulphate solution.

C. To measure the effects of oxygen on the corrosion behaviour of alloy 625 in the same temperature range.

D. To identify the expected electrochemical and morphological response to naturally induced transpassive corrosion (i.e. not by applied potential)

E. To investigate the issue of diffusion control at high sub-critical temperatures with a view to possibly predicting corrosion rates.

F. To calculate the phase diagram for the Ni-NH₃-H₂O system throughout the temperature range of interest.

G. To explore the possibility of using Nb for the high density supercritical sections of the reactor.

H. To determine the corrosion rate of other related alloys under SCWO conditions.
4 POLARIZATION STUDY OF ALLOY 625, Ni, Cr AND Mo IN AMMONIA CAL SULPHATE SOLUTIONS

The effect of ammoniacal salt solutions on the corrosion of Ni-Cr alloys is of significant fundamental interest but has of yet not been studied. Given that these alloys are known to be protected by NiO in moderately alkaline solutions, any tendency toward the selective removal of Ni or instability of NiO due to Ni-ammne formation could result in unexpected degradation of the material. Since this is a baseline study into the corrosion characteristics of alloy 625 and its main constituents (Ni, Cr, Mo) in solutions of ammonium sulphate, all tests were performed at room temperature. High temperature studies will follow. Polarization results are related to Pourbaix diagrams and the effect of pH, oxidant and alloying elements on the overall alloy behavior is investigated.

4.1 Experimental

Electrochemical tests were performed using coupon samples lathe cut from 3/4” diameter alloy 625 (UNS N06625) bar stock. High purity (~99%) molybdenum, nickel and chromium were purchased as commercially available samples. Coupons were 16mm in diameter and 3 mm thick so as to fit in a pre-fabricated, commercially available, nylon sample holder complete with crevice free washers. A standard ASTM corrosion cell with two high-density graphite counter electrodes and saturated calomel (SCE, E = 0.241 V vs. SHE) reference electrode was used. The reference electrode was kept in contact with the solution through a salt bridge terminating in a Luggin-Haber probe. Solutions were prepared in distilled water using reagent grade H₂SO₄ and NH₄OH. To distinguish the
effect of ammonia from that of sulphate, some tests were also performed in solutions of
Na\textsubscript{2}SO\textsubscript{4} or H\textsubscript{2}SO\textsubscript{4} at adjusted pH. The results presented below which examine the effect
of oxidant and alloying elements are from tests performed at pH 10 (0.2 m H\textsubscript{2}SO\textsubscript{4} / 1.6 m
NH\textsubscript{4}OH) because, as demonstrated by the failure described in the introduction, alloy 625
has been shown to be susceptible to ammoniacal solutions at that pH.

The test samples were wet polished to 600 SiC, degreased in ethanol and
ultrasonically cleaned in acetone. They were then mounted in the sample holder,
immersed in solution and cathodically pre-treated at -2.46 V for 600 seconds to remove
any air formed oxide and create a consistent starting point. Potentiodynamic scans were
not performed subsequent to reaching steady-state. If allowed to sit at open circuit the
alloy 625/ammonium sulphate system would take roughly 8 hours to reach steady-state
(defined here as a change of less than 1 mV over a 10 minute period). Instead, most
scans were performed immediately after the cathodic pre-treatment, starting in the
cathodic range at -1.26 V and ending at 0.942 V. The potential scan rate was 0.8 mV/s.
The result of one polarization test performed at steady-state conditions is presented
below for comparison. To assess the influence of oxygen on alloy 625 some tests were
conducted under de-aerated or naturally aerated (open to the atmosphere) conditions
while one graph presents results from an oxygen saturated solution. In this last case
oxygen was sparged into a rapidly stirred solution for the duration of the experiment. In
the case where de-aeration was required, the solution was argon sparged and stirred one
hour prior to testing. At the onset of scans following argon sparging, stirring was
terminated while purging continued. Naturally aerated experiments were not stirred.
Experiments were controlled through the use of a potentiostat run by a computer.
The corrosion potential, $E_{corr}$, was taken as the point at which the cathodic current was equal to the anodic current on the polarization curves. The corrosion current density at $E_{corr}$ is $i_{corr}$. Points referred to as $E_1$ and $E_2$ are the potentials corresponding to the two anodic peaks (i₁ and i₂) observed on the polarization curves of alloy 625. $E_1$ is the lower potential point. The passive current density for all scans, $i_{pass}$, is taken as the current density corresponding to the potential which is 250 mV above $E_2$. This potential was chosen as it lies within the passive range between $E_2$ and $E_t$ (transpassive potential) and also because it roughly coincides with the corrosion potential achieved after 8 hours of immersion under open circuit. In other words it reflects the corrosion potential at steady state. The reader is referred to Figure 4-3 for an illustration of these points.

In order to relate polarization results presented in this work to theoretical, thermodynamically stable species, Pourbaix diagrams for the Ni-NH₃-H₂O and Cr-H₂O systems were calculated. Aside from the nickel ammines which were considered here, all species considered were those originally suggested by Pourbaix. To simplify the Ni-NH₃-H₂O diagram, complexation of Ni was considered only for the diammine, tetrammine and hexammine complexation groups. Free energy of formation values used to calculate the Pourbaix diagrams are largely from the Atlas [Pourbaix 1966] with the exception of the ammines which are derived from equilibrium constants presented in Osseo-Asare’s work on the Ni-NH₃-H₂O system [Osseo-Asare 1981].
4.2 Results and discussion

4.2.1 Pourbaix diagrams

The concentration of total ammonia was set at 1.6 molal (m) and dissolved metals were set at $10^{-6}$ m. Figure 4-1 and Figure 4-2 are the diagrams for the Ni-NH$_3$-H$_2$O and Cr-H$_2$O systems, respectively. Both diagrams are presented at 25°C. The addition of ammonia to the Ni-H$_2$O system removes any predicted field of stability for NiO or Ni(OH)$_2$. Nickel is therefore not expected to passivate in solutions of ammonia. Cr, however, will passivate between pH 4 and 12.6 under reducing and mildly oxidizing conditions. The transpassive oxidation of Cr(III) oxides to Cr(VI) soluble species is expected to occur above 0.25 V at pH 10.

Figure 4-1 Pourbaix diagram for the Ni-NH$_3$-H$_2$O system at 25°C.
The application of Pourbaix diagrams to the interpretation of electrochemical results is notoriously difficult. For example, under acidic conditions devoid of oxidant, such as in de-aerated 1M H₂SO₄, Gilli et al. reported passivation whereas the Pourbaix diagram for nickel predicts general corrosion [Gilli 1969]. Pourbaix’s Atlas also presents some contradictions between the predicted Ni-H₂O system and experimental results. There are two approaches to explain conflicting passive behavior and thermodynamic predictions: salt film precipitation or metastable oxide formation. At high concentrations of sulphate, passive-like behavior has been linked to salt film precipitation. Melendres and Tani have presented laser Raman spectroscopy results identifying a corrosion film in the passive region on nickel in 14 M H₂SO₄ as NiSO₄•SO₄ [Melendres 1986]. Similarly, under conditions of concentrated H₂SO₄, Gilli et al. were able to identify β-NiSO₄•6H₂O by X-ray diffraction powder patterns [Gilli 1969]. However, the experiments performed here were in solutions of 0.2 m SO₄²⁻ and concentrations of Ni were assumed to be 10⁻⁶ m. The solubility of NiSO₄ is reported to be roughly 2.6 m at 25°C [Linke 1965]. It is then unlikely that NiSO₄ precipitation could have occurred during the experiments conducted in this work. Metastable oxide formation is therefore a likely explanation for any passivation presented in this work which occurs outside the predicted fields of stability for NiO, Ni(OH)₂, or Cr₂O₃ [Macdonald 1999].

Recent surface analysis performed on Ni-Cr [Jabs 1997] and Ni-Cr-Mo [Lloyd 2003] alloys, in solutions of 0.5 M H₂SO₄ and 0.1 M H₂SO₄ + 1 M NaCl respectively, have shown that the passive film is almost entirely comprised of Cr(III) ions. Given this information and the thermodynamic predictions herein, it was expected that alloy 625 would show a similar polarization curve to that of elemental Cr as its oxide has a wider region of stability.
4.2.2 Effect of oxidant

Polarization curves of alloy 625 in 0.2 m H₂SO₄ / 1.6 m NH₄OH, pH 10, under de-aerated (argon sparged), aerated (naturally aerated) and oxygenated (O₂ sparged) conditions are shown in Figure 4-3.

In de-aerated solutions, two small oxidation peaks appear just below the passive region, the first is at \( E_1 = -0.539 \) V and the second is at \( E_2 = -0.213 \) V. Given the Pourbaix diagrams displayed in Figure 4-1 and Figure 4-2 and the good agreement between these peaks and those demonstrated by Ni and Cr (Figure 4-7) under the same
polarization conditions, it is hypothesized that $E_1$ is associated with the onset of chromium oxidation to chromium oxide ($\text{Cr}_2\text{O}_3$) and that $E_2$ corresponds to the solubilization of nickel as the hexavalent nickel ammine $\text{Ni(NH}_3\text{)}_6^{2+}$. It is likely that at $E_2$ both reactions are occurring.

Under aerated conditions, alloy 625 displays cathodic loop behavior between -0.33 and -0.13 V. This type of polarization curve is a result of the cathodic reaction rate exceeding the passive current density at a given potential range [Kelly 2003]. This range, which follows a “second” $E_{corr}$, exhibits a net cathodic current, or what is conventionally displayed as a negative current on a non-log graph.
Under oxygenated conditions the increased mass transfer of \( \text{O}_2 \) to the surface of the alloy caused a very high rate of oxygen reduction which exceeded the net anodic current and effectively raised the corrosion potential to approximately -100 mV. In fact, there is a much higher rate of oxygen reduction than one might expect for the oxygenated solution. Indeed, the bulk oxygen concentration of naturally aerated solutions is approximately 0.25 mM/L [Kelly 2003] whereas the solubility limit of \( \text{O}_2 \) is somewhere in the region of 0.7 mM/L in solutions of ammonium sulphate at 298K – a difference of only a factor of 2.8 [Tromans 2000]. In contrast, Figure 3 shows that the limiting current density of the oxygen reduction reaction (ORR) for the oxygenated solution is roughly 2 orders of magnitude larger than the current registered at the cathodic loop in the naturally aerated solution. This high rate of oxygen reduction can be explained by the vigorous stirring which took place throughout the experiment. This was done intentionally to maximize the corrosion potential. Despite a very high rate of oxygen reduction alloy 625 maintains a relatively low corrosion current in the presence of ammonia/ammonium sulphate and the corrosion potential remains within the passive region. However, the addition of one part 30\% \text{H}_2\text{O}_2 to five parts of ammonium sulphate solution at pH 10 (a concentration equivalent of 1.95 M \text{H}_2\text{O}_2) results in a much more aggressive environment. In this case the potential is raised to such an extent as to preclude passivation; the alloy then exhibits active behavior. Moreover, the corrosion current is an order of magnitude higher than the passive current density seen under less oxidizing conditions.
4.2.3 Effect of pH

The polarization curves for alloy 625 in selected de-aerated solutions are shown in Figure 4-4. There is a strong agreement between thermodynamic predictions and the results of the polarization experiments. The relationship between $E_{corr}$ and pH is linear and coincides almost exactly with the hydrogen evolution reaction (HER) (Figure 4-5). The slope of the line relating the first oxidation peak ($E_1$) to pH is also similar to that of the HER, only with a positive shift in ordinate of 70 mV. The data points obtained for $E_2$ are more scattered than $E_{corr}$ or $E_1$, particularly at pH 3.35 and 5.54, and for this reason the relationship between $E_2$ and pH is not obviously linear.

![Figure 4-4](image)

Figure 4-4 Potentiodynamic polarization curves in selected de-aerated environments.

Effect of pH.
Following the progression of these potentials as pH is varied across the Pourbaix diagrams for nickel and chromium, it is possible to identify the major reactions occurring at each oxidation peak as pH is modified. Thus, at higher pH (6.5 and above) nickel will dissolve at $E_2$ through a complexation process to form an ammine $Ni(NH_3)_2^{2+}$. The formation of ammines is important as it appears to remove one of the distinct advantages to the use of nickel in high pH solutions, particularly if the solution is mildly oxidizing.

As pH is lowered and the free ammonia concentration drops, nickel dissolves as a divalent ion without forming an ammine. It is likely that at all pH, alloy 625’s surface is depleted in Ni. This would result in a local enrichment in Cr and thus the formation of $Cr_2O_3$ can be identified as the main mode of passivation for alloy 625. However, and with reference to Figure 4-2, $Cr_2O_3$ is not thermodynamically stable above pH 12.6 and below pH 4. Furthermore, $i_2$ is larger with respect to $i_{pass}$ at pH levels lying outside or at the limit of the thermodynamic stability of $Cr_2O_3$ (for example 0.05 and 11.91). This indicates a higher rate of Ni dissolution and in turn a less protective surface film.

Passivation at pH 0.05, as seen in Figure 4-4, may then be explained by the formation of a metastable oxide as outlined earlier.

According to Shimakage and Morioka, nickel dissolves in ammonia through the following reaction,

$$Ni + \frac{1}{2}O_2 + nNH_3 + H_2O \rightarrow Ni(NH_3)_n^{2+} + 2OH^- \quad 4-1$$

and in order for the reaction to continue, the removal of $OH^-$ ions is necessary,

[Shimakage 1971] i.e.

$$OH^- + NH_4^+ \rightarrow NH_4OH \rightarrow NH_3 + H_2O \quad 4-2$$
Then, the dissolution of nickel in ammonia/ammonium salt solutions proceeds as shown below:

\[ Ni + \frac{1}{2}O_2 + (n-2)NH_3 + 2NH_4^+ \rightarrow Ni(NH_3)_n^{2+} + H_2O \]  

4-3

In view of equations 4-2 and 4-3, the ratio of ammonium ions to dissolved ammonia is an important consideration when looking at the corrosion of nickel (or Ni-base alloys) in ammoniacal solutions. This ratio is linked to pH due to the following equilibria:

\[ NH_4^+ \rightleftharpoons (NH_3)_{aq} + H^+ \]  

4-4

\[ (NH_3)_{aq} + H_2O \rightleftharpoons NH_4^+ + OH^- \]  

4-5

We can calculate the relative concentrations of ammonium and ammonia using the equilibrium constant for reaction 4-4 \( NH_4^+ \rightleftharpoons (NH_3)_{aq} + H^+ \)  

4-4:

\[ k_{NH_4} = [(NH_3)_{aq}][H^+]/[NH_4^+] = 5.628 \times 10^{-10} \]  

4-6

where, for the purposes of this work, the square brackets [ ] correspond to molalities, m, in mol.kgH_2O^{-1}. 

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We can calculate the ratio, $R = n/N$, of ammonium to total ammonia in the system, according to the following modification of equation 4-6:

$$n = (N - n)[H^+] / k_{NH_3} = N[H^+] / ([H^+] + k_{NH_3})$$ \hfill (4-7)

where $n = [NH_4^+]$ and $N = [NH_4^+] + [(NH_3)_{eq}]$ [Tromans 2000].

At 298 K the buffer point of ammonia (the point at which ammonium becomes more prevalent than ammonia as pH decreases) is pH 9.27. At equilibrium, the value of $R$ for the pH 10 solution which was predominantly used in this work is 15.7% i.e. the available ammonia is largely in the form of dissolved ammonia. An effort was made to determine a correlation between $R$ and the passive current density for various solutions between pH 11.91 and 0.05. No relationship was readily apparent. Instead, the
overriding variable appeared to be pH. This is another indication that \( \text{Cr}_2\text{O}_3 \) determines the polarization characteristics of the alloy as one would expect more fidelity to R if Ni was dominating the corrosion process. Passive current densities are plotted with respect to pH in Figure 4-6. There is clearly a trend of increased current densities with decreasing pH. Current densities obtained from polarization tests of alloy 625 in solutions of similar pH and at the same sulphate concentration (\( \text{H}_2\text{SO}_4 \) or \( \text{Na}_2\text{SO}_4 \) adjusted with \( \text{NaOH} \)) as in the ammonia experiments are also shown. Passive current densities obtained in solutions of sulphate alone are higher than in the ammoniacal solutions. This is probably related to the buffering action of the ammonium solution which would, according to reaction 3-7, resist local acidification at the bl-s interface during passivation. This is in fact a well understood phenomena which is linked to proton generation during film formation. If buffers are not present the enhanced proton concentration results in higher corrosion rates. The subject has been elegantly discussed by Tromans and Sun [Tromans 1992].
Figure 4-6 Passive current densities for alloy 625 in solutions of ammonium sulphate and solutions of sodium sulphate

4.2.4 Effect of alloying elements

Figure 4-7 presents the polarization curves for Ni, Cr, Mo and alloy 625 in de-aerated solution at pH 10. Alloy 625 adopts a very similar general polarization profile to that of chromium especially with respect to the passive region. Chromium spontaneously passivates and has the lowest corrosion potential of all three metals seen in Figure 4-7. Chromium also has a very similar passive current density to that observed on alloy 625. Nickel displays a prominent anodic nose (~ 5.5 mA at ~ -0.180 V) while its passive current density is twice that of the alloy and Cr. This is further weight to the argument
that the alloy's behavior is dictated by the formation of chromium oxide and that Ni is selectively removed from this oxide. Mo does not passivate and simply dissolves above $E_{corr} = -0.590$ V as molybdate ($\text{MoO}_4^{2-}$).

Under aerated conditions Ni, Cr and 625 show a decrease of roughly 30% in their passive current densities as compared to those recorded under de-aerated conditions (Fig. 8). It is believed that this decrease is due to a higher rate of oxygen reduction which acts to suppress the total measured current. The increased rate of the ORR is also observed in both the positive shift in $E_{corr}$ for nickel, chromium and molybdenum as well as the clear cathodic transition between the HER and ORR on these same metals.

The curve for the transpassive region of 625 is remarkably similar in shape to the anodic dissolution of Mo, particularly in its limiting current behavior above 0.6 V. It is believed that although delayed to higher potential, the transpassive dissolution of 625 is in fact closely related to the dissolution of Mo. This finding is not unexpected as Sugimoto and Sawada have shown that Mo containing steels resist pitting attack through adsorption of $\text{MoO}_4^{2-}$ (molybdate ion) in pits at onset of pitting [Sugimoto 1976]. By analogy, alloy 625 may resist pitting attack through selective adsorption of $\text{MoO}_4^{2-}$. The theory surrounding the role played by Mo in the protection of corrosion resistant alloys is twofold. Firstly, it has been reported that Mo(VI), located at the outer layers of the oxide film, is stabilized as $\text{MoO}_4^{2-}$ by the high electric field at that location. Such stabilization would lead to the de-protonation of $\text{OH}^-$ within the oxide film, in turn supplying $\text{O}^{2-}$ for the formation of $\text{Cr}_2\text{O}_3$ [Brooks 1986], [Clayton 1986]. Secondly, $\text{MoO}_4^{2-}$ is also believed to confer a cation selective quality to the outer regions of the oxide. This would result in higher resistance to chloride induced pitting [Sakashita 1977].
Figure 4-7 Polarization curves for alloy 625, Ni, Cr and Mo in de-aerated solution at pH 10.
4.2.5 Steady State behavior and corrosion rate

It is customary to present data for polarization curves under steady-state conditions. However, the nature of alloy 625 in ammonium sulphate solution is such that steady state conditions require an impractical amount of time to be achieved. Furthermore, the free corroding potential is very difficult to duplicate given its dependency on the reproducibility of a passive film, particularly when in the presence of oxygen. Moreover, the real nature of the polarization curve is masked under these conditions. However, for the purposes of establishing a general idea of the steady state
behavior and corrosion rate of alloy 625 at pH 10, the alloy was allowed to rest in naturally aerated solution for 8 hours prior to running a polarization scan from -0.250 vs. open circuit to a maximum of 1.2 V. The result of this experiment is seen in Figure 4-9. The alloy exhibits Tafel behavior and active dissolution of the passive film is evident. 

\[ E_{corr} \] lies within the passive range of the aerated scan and it is clear that the steady state corrosion current density, \( i_{corr} = 1.1 \times 10^{-7} \text{ A/cm}^2 \), is less than the passive current density \( i_{pass} = 6 \times 10^{-6} \text{ A/cm}^2 \) recorded under direct scan conditions. Using the passive current density as an approximation to the corrosion rate, [Kelly 2003] the highest rate of attack occurs at the lowest pH values (Figure 4-4). By the same assumption Ni would corrode roughly twice as fast as the alloy itself. Thus, it is reasonable to expect selective dissolution of Ni from alloy 625 at pH 10.

At pH 10 in ammonium sulphate solution, the steady state corrosion rate for alloy 625 is calculated from \( i_{corr} \) to be \( \sim 1.2 \times 10^{-3} \text{ mmpy} \). This corrosion rate is acceptable and one can conclude that alloy 625 does not corrode to any appreciable extent in this solution. Even with a high rate of oxidant delivery, as in the case of the oxygenated solution, the alloy remains passive. The corrosion rate in the presence of hydrogen peroxide is however much higher (0.15 mmpy) and highlights this alloy’s susceptibility to transpassive corrosion.
Figure 4-9  Polarization curves for alloy 625 under direct scan and steady state scan conditions - naturally aerated.

4.3 Summary

Alloy 625, Ni, Cr and Mo were tested in various solutions of ammonium sulphate at different pH. The effect of oxidant on the polarization behaviour was also established. Alloy polarization curves were similar to curves obtained for Cr indicating that the alloy's behavior was dominated by formation of a passive Cr(III) film on its surface. Ni displayed the highest rate of passive dissolution and a large anodic nose. Mo readily dissolved.
Polarization curves were compared to Pourbaix diagrams. Passivation observed at acidic pH for Ni and Cr, and at pH 10 for Ni, could not be predicted thermodynamically. In fact Ni is not thermodynamically stable at any pH in the presence of ammonia at 298 K. It is believed that metastable oxides are responsible for the passive behavior observed.

Passive current densities increased with pH, pointing to the fact that proton concentration was the main determinant to the corrosion rate rather than ammine formation. Moreover, sulphate solutions alone were found to result in higher passive current densities than ammonium sulphate solutions at the same pH. The buffering effect of the ammonia system may explain this occurrence.

In general, corrosion rates for alloy 625 were found to be acceptable, even at high rates of O2 mass transfer. However, under heavily oxidizing conditions, such as in the presence of H2O2, alloy 625 is susceptible to transpassive dissolution in the presence of ammonium sulphate. This is particularly relevant in the context of SCWO where solutions are heavily oxidizing. As discussed throughout this work, while not necessarily an issue in the low temperature sections of a reactor, transpassive corrosion is a significant problem in SCWO reactors at higher temperatures. Moreover, there is ample evidence from these results that Ni would preferentially dissolve in solutions of ammonia. It is likely that at higher temperatures this selective dissolution would be aggravated.

The extent to which both the issue of de-alloying and transpassive dissolution affect the behaviour of alloy 625 at higher temperatures is addressed in the following pages.
5 EFFECT OF OXYGEN ON THE CORROSION BEHAVIOUR OF ALLOY 625 AT ELEVATED TEMPERATURES

While the presence of ammonium sulphate probably results in Ni de-alloying through ammine complexation (alkaline pH) or dissolution as Ni$^{2+}$ (acidic pH), it has been shown that corrosion rates at room temperature are low unless high concentrations of oxidant (H$_2$O$_2$) are present, at which point the transpassive potential of the alloy is exceeded.

To determine the effect of oxygen solubility and partial pressure on the corrosion behaviour of alloy 625 in ammoniacal sulphate solution, a series of potentiodynamic, linear polarization and impedance measurements were performed between 298 and 473 K at varying oxygen partial pressures. Potentiodynamic polarization data was used to glean information about the kinetics of the oxygen reduction reaction as well as to shed light on the transpassive potential of the alloy as a function of temperature. Impedance data gathered at open circuit was used to determine the corrosion process and nature of the oxide film. Lastly, the corrosion rates obtained by electrochemical testing were compared to an oxygen diffusion model similar to that proposed by Tromans.
5.1 Experimental

5.1.1 Safety considerations

It should first be noted that the work described below was performed in a titanium autoclave at high oxygen partial pressures. It is well known that Ti can auto ignite in such environments and that industrial autoclave fires have resulted from such occurrences of auto ignition. A good review is provided by Costa [Costa 2005]. Generally these fires have resulted from either frictional heating, impact or promoted combustion (nearby burning component). There have also been instances of oxygen sparger/feed line ignition due to rapid, sudden and high pressure injection of oxygen. In all instances the Ti-oxide which protected the underlying metal was caused to fail. Ti will not spontaneoulsy ignite at temperatures up to 250°C without having a freshly fractured, abraded or scratched surface exposed.

In an abundance of caution the following precautions were followed:

- Injection lines were made from 316 SS
- No dynamic motion occurred during the experiments (i.e. no stirring)
- Injection of O₂ was always performed cold
- The autoclave area was cordoned off during runs
- The partial pressure of O₂ and the total pressure were kept just below the “static” ignition curves as determined by Littman and Church [Littman 1961]

Static ignition curves generally describe a situation in which a freshly fractured Ti surface is exposed to static oxygenated environments. Dynamic ignition curves relate to motion of O₂ across the fractured surface and for this reason dynamic ignition curves delineate a more conservative area on the T and P plane. The reader will note that there
was never the possibility of a fractured Ti surface being exposed to the oxygenated environment in the work detailed below because no mechanical motion occurred during the experiments. Finally it might be mentioned that NH$_3$ is a fairly good fuel and as such any similar work undertaken in the future should be done very carefully.

**5.1.2 General considerations**

A 1.8 L glass-lined titanium autoclave was used for the electrochemical experiments. The alloy 625 working electrode (WE) was a cylindrical specimen and the holder was of the Stern-Makrides variation [Kelly 2003] - please refer to Appendix A for drawings and pictures. The counter electrode (CE) consisted of a Pt wire with approxiamtely 3 times the surface area of the WE. An external pressure balanced saturated Ag/AgCl reference electrode was used (EPBRE) and was bridged to the solution through a fiberglass wicked PTFE tube which contained the test solution. All potentials have been converted from Ag/AgCl to the SHE i.e.

\[ E_{SHE} (mV) = E_{Ag/AgCl} + 197 mV \]

and all further potentials are reported with respect to SHE. The thermal liquid junction potential (TLJP) across the electrolyte bridge was ignored in this work. This potential is difficult to accurately estimate and is only available in the literature for HCl, NaCl and KCl solutions [Lvov 1996][Macdonald 1979B]. As thermal diffusion phenomena are determinant in calculating the TLJP, it is generally expected that larger, less mobile ions will result in lower potential drops across the bridge. Thus a very qualitative estimate for the anticipated TLJP in the $NH_4^+$, $OH^-$ and $SO_4^{2-}$ containing bridge used here could be between 0 mV at 298 K and 30 mV at 473 K [Lvov 1996].
A 0.2 m sulphate and 1.6 m total ammonia solution at ~ pH 10 was prepared using de-ionized water and reagent grades of ammonium hydroxide and sulphuric acid. Prior to immersion in solution, the WE was wet ground to 600 SiC, rinsed in de-ionized water and ultrasonically cleaned in acetone. The solution volume poured into the autoclave at 298 K was 1.1 L allowing for a head space of 0.7 L. After assembly, the autoclave head space and solution were sparged with oxygen for at least 25 minutes and then, if required, oxygen was added to the system to increase the total pressure

\[ P_{\text{TOTAL},298\,K} = P_{O_2} + P_{H_2O} + P_{NH_3}. \]

Varying total gauge pressures at 298 K were used, from atmospheric (0 bar\textsubscript{g}) up to 27.58 bar\textsubscript{g} (400 PSIG). It should be noted here that unless otherwise specified, all further pressures in this section will be reported as gauge pressures. When the autoclave was fully sealed and therefore constituted a closed system at constant volume, it was brought incrementally to temperature (298, 323, 348, ..., 473 K) with electrochemical measurements performed at each increment. Three main types of electrochemical experiments were performed separately: potentiodynamic Tafel polarization, linear polarization and electrochemical impedance spectroscopy.

The entire set-up procedure was started anew for each set, or type of experiment i.e. the data for the potentiodynamic sets, linear polarization sets and EIS sets of experiments was collected separately with fresh solutions and fresh samples. However, within each set of experiments, spanning the entire temperature range, neither the sample nor the solution was changed as the behaviour of a single, consistent sample/system interface was of interest. For example, a scan having been run at 298 K, the same system was then brought to 323 K and a subsequent scan was performed, and so on, until the last scan performed at 473 K. To attenuate concerns pertaining to the steady-state condition
and electrode stability, following the 20 minute heat-up period a 30 minute rest at open circuit was performed for each temperature increment. Furthermore, the alloy's oxide film was never overly perturbed as potentials did not exceed ± 250 mV OC. The autoclave temperature was controlled to within 5 degrees during any experiment and pressures were recorded from a pressure transducer to ± 3 bar. The error band in the temperatures and pressures are limitations of the equipment. During an electrochemical experiment the temperature controller was turned off to ensure that cold water passed through the autoclave's cooling coil did not induce convection currents in the autoclave. The pressure transducer was separated from the autoclave head by an oil filled isolator/piston assembly to protect it from exposure to ammonia and oxygen which resulted in very little sensitivity at low pressures.

The potentiodynamic polarization experiments (PD) were performed in the anodic direction from -250 mV versus open circuit (OC) to +250 mV OC at 1 mV/s. These experiments were performed at $P_{\text{TOTAL, } 298K} = 0$ and at $P_{\text{TOTAL, } 298K} = 13.79$ bar (0 and 200 psig) and the entire sets were repeated at least twice. The results of these tests were used to calculate the cathodic Tafel slopes at each temperature and to estimate the corrosion current density by extrapolation of the linear portions of the cathodic curves to the corrosion potential.

Linear polarization (LP) experiments were performed at $P_{\text{TOTAL, } 298K} = 6.89$, 13.79 and 20.68 bar (100, 200 and 300 PSIG). Scan rate was 0.5 mV/s in the anodic direction through the range of ±20 mV OC. The polarization resistance ($R_p$) was determined by computer assisted linear least-squares fitting around the corrosion potential ($E_{\text{corr}}$) and also manually by calculating the slope of the tangent to the $E-i$ curves at $E_{\text{corr}}$. 
For the EIS measurements, the autoclave was loaded with oxygen to $P_{TOTAL,298K} = 27.58$ bar (400 PSIG). The WE was polarized at ±10 mV OC in the frequency range of 100 kHz to 10 mHz. Similarly to the linear polarization experiments, the goal of this work was to estimate the polarization resistance but with the added advantage of shedding light on the metal/oxide/solution interfaces. These experiments were repeated twice.

5.1.3 Oxygen diffusivity and concentration calculations

In order to fully explore the impact of oxygen on the corrosion characteristics of alloy 625, both its diffusivity and concentration are required. Tromans has developed a theoretical model for oxygen solubility which allows for the calculation of its concentration ([Tromans 1998, 2000B]). Generally, the relationship between $P_{O_2}$ (partial pressure of oxygen in atmospheres) and $C_{O_2}$ (dissolved oxygen in mol.kgH$_2$O$^{-1}$) is:

$$C_{O_2} = k \cdot \frac{\phi_{O_2}}{\gamma_{O_2}} \cdot P_{O_2}$$  \hspace{1cm} (5-1)

Where $k$ is the inverse of the Henry's Law constant and, for pressures below 60 bar (~880 PSI), is given by:

$$k = \exp \left( \frac{0.046T^2 + 203.35T \ln \left( \frac{T}{298} \right) - (299.378 + 0.092T)(T - 298) - (20.591 \times 10^3)}{8.31447} \right)$$ \hspace{1cm} (5-2)
The variable $\phi$ represents the fraction of water which is available to dissolve $O_2$; $(1 - \phi)$ being relegated to the interactions with dissolved ionic components. For the solution used here $\phi = 0.96401$ [Tromans 2000]. The variables $\gamma_{O_2}$ and $\varphi_{O_2}$ are the activity and fugacity coefficients of $O_2$, respectively. Oxygen is so sparingly soluble in water, even at high pressure and temperature that $\gamma_{O_2}$ is usually considered to be unity.

The initial volume of gas in the autoclave being known, we can calculate the partial pressure of oxygen at STP using the ideal gas law (equation 5-3). Knowing the concentration of ammonia we are able to calculate the partial pressures of ammonia and water according to Raoult’s law (equation 5-4).

$$P_{O_2}V = n_{O_2}RT \quad \text{(5-3)}$$

$$P_i = \gamma_i P = \gamma_i x_i P_{vpi} \Xi_i \quad \text{(5-4)}$$

Where $n_{O_2}$ is the number of moles of oxygen in the gas phase, $R$ is the gas constant, $P_i$ is the partial pressure of component $i$, $P$ is the total pressure, $\gamma_i$ is the mole fraction of component $i$ in the gas phase, $\gamma_i$ is the activity coefficient of $i$, $x_i$ is the mole fraction of $i$ in the liquid phase, $P_{vpi}$ is the vapour pressure of component $i$ and $\Xi_i$ is a correction relating to gas phase non ideality. For the purposes of the calculations performed here, it is safe to assume that $\Xi_i = 1$.

Given that total pressures between 298 and 473 K are less than 60 bar the assumption that the gas phase is ideal is adequate. Indeed, below 60 bar, Tromans has shown that the fugacity coefficient for the gas phase does not deviate substantially from unity [Tromans 1998]. The calculations for $P_{O_2}$ at $T + 298$ were performed using a Matlab algorithm which proceeded as follows. First, the pure liquid vapour pressures...
were obtained – a Matlab function based on the International Association for Properties of Water and Steam Industrial Formulation 1997 (IAPWS IF-97) was used to this end. The vapour pressure of ammonia was calculated using the Pitzer expansion of the Clausius-Clapeyron equation [Reid 1987]. Since experimental data for the partial pressure of ammonia over ammoniacal solutions is available up to 403 K [Perry 1997], it is possible to extrapolate activity coefficients for water, $\gamma_{H_2O}$ and ammonia, $\gamma_{NH_3}$ by calculating the excess Gibbs energy for the experimental data:

$$g^E = RT(x_{NH_3} \ln \gamma_{NH_3} + x_{H_2O} \ln \gamma_{H_2O})$$ \hspace{1cm} 5-5

and by calculating the Margules coefficient [Reid 1987], $A$, by linear approximation above 403 K such that:

$$g^E = Ax_{NH_3}x_{H_2O}$$ \hspace{1cm} 5-6

Activities are then given by:

$$\gamma_{NH_3} = \exp\left(\frac{A \cdot x_{H_2O}}{RT}\right)$$ \hspace{1cm} 5-7

and,

$$\gamma_{H_2O} = \exp\left(\frac{A \cdot x_{NH_3}}{RT}\right)$$ \hspace{1cm} 5-8

In this way we are able to estimate the ammonia and water partial pressures above the critical temperature of ammonia which lies at 403 K. An iterative process will then produce $P_{O_2}$:

1. initial $P_{O_2}$ and $C_{O_2}$ are calculated based on the volume of the gas phase at 298 K,
2. both the gas phase and liquid phase composition are re-calculated to account for the dissolved oxygen and evaporated ammonia and water
a mass balance is performed on the ammonia in liquid and gas phases using the
solubility data published by Kawazuishi and Prausnitz [Kawazuishi 1987]

the gas and liquid volumes are then re-calculated

$P_{O_2}$ is then re-calculated using the new volume

Oxygen diffusivity was calculated by assuming that it would be close to that of the self-
diffusivity of water (the results of these calculations are presented in Appendix B).

Tromans has suggested the following Arrhenius type equation [Tromans 2000A]:

$$D_{O_2} = k_D \exp(-Q_T / RT), \text{ in } cm^2.s^{-1}$$

where

$$k_D = 1.363 \times 10^{-2} \text{ cm}^2.s^{-1}$$

$$Q_T = 14.227 \times 10^3 + (4.661 \times 10^{19})(T)^{-6.8132}, \text{ in } J.mol^{-1}$$

5.2 Results and discussion

5.2.1 Potentiodynamic polarization experiments

Potentiodynamic polarization curves for initial oxygen loading of $P_{TOTAL,298K} = 0$
and 13.79 bar at each temperature increment are shown in Figure 5-1 and Figure 5-2,
respectively. The corrosion potential and the corrosion current density both increase
with temperature. At the higher temperatures (398 K to 473 K) and in the anodic range
the polarization plots begin to show the passive to transpassive transition within the
limited $+250 \text{ mV OC scan range}$. $E_{corr}$ for the experiments conducted at $P_{TOTAL,298K} =$
13.79 bar are very close to the transpassive potential. In fact there is little evidence of
passivation under these conditions. There is a distinct “active” appearance to the anodic
sections of the polarization plots, particularly at higher temperatures and pressures. As we have shown in chapter 4, it is assumed here that the anodic reaction corresponds to the oxidation of Cr to Cr$_2$O$_3$ and to the dissolution of Ni as Ni$^{2+}$. Moreover, this potentiodynamic response is indicative of at least quasi-steady state conditions (Figure 4-9, anodic Tafel slopes in ref. [Priyantha 2004]) in an oxygenated environment where the elevated oxygen concentration results in an elevated $E_{corr}$ within the passive range.
Figure 5-1  Polarization curves for alloy 625 in ammoniacal solution from 298 to 473 K at absolute initial autoclave loading of 1 ATM or $P_{TOTAL,298K} = 0$ bar.
Figure 5-2  Polarization curves for alloy 625 in ammoniacal solution from 298 to 473 K at initial autoclave loading $P_{TOTAL,298K} = 13.8$ bar.
Aside from the obvious conclusion that the passive region shrinks with increasing temperature and oxygen partial pressure, it is interesting to note that the transpassive potential (\( E_t \)) does not appear to vary to any significant degree with temperature. We have seen that it is widely accepted that the transpassive potential is determined by the onset of extensive Cr(III) to Cr(VI) oxidation, likely with the product in the form of chromate (\( CrO_4^{2-} \)), cf. equation 2-1 for the overall reaction.

Figure 5-3  Corrosion potentials (\( E_{corr} \)), theoretical (\( E_i \)) and measured (\( E_t \)) transpassive potential as a function of temperature at initial oxygen loading \( P_{TOTAL,298K} = 0 \) bar
Figure 5-3 and Figure 5-4 show the measured values of $E_t$, the theoretical calculated values of the reduction potential for reaction 2-1, $E_{Cr(VI)}$, and $E_{corr}$, with respect to temperature. $E_t$ was measured by selecting the potential at which the polarization curve departed from a linear fit to the anodic Tafel slope. $E_{Cr(VI)}$ was calculated using the Nernst equation ($[Cr] = 1 \times 10^{-6} \text{m}$) where the chemical potentials for each species were estimated at high temperature through the Criss-Cobble based linear ionic heat capacity approximation as suggested by Lewis [Lewis 1970], [Taylor 1978], [Criss 1964A, B] which is very reliable in the 298 to 473 K temperature range used here. It has been reported in the literature that the transpassive potential should monotonically decrease with temperature [Kritzer 1998]. This is shown in Table 5-1 where the results of calculations performed for $E_{Cr(VI)}$ at a constant pH = 9.92 and at various temperatures are shown.

Table 5-1 Theoretical reduction potential $E_t$ at constant pH, equilibrium constant $k_2$ for reaction 2, estimated pH as a function of temperature and $E_t = f(pH(T))$

<table>
<thead>
<tr>
<th>$T$</th>
<th>$E_{Cr(VI)} (V)$, pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$9.92$</td>
</tr>
<tr>
<td>25</td>
<td>0.27</td>
</tr>
<tr>
<td>50</td>
<td>0.18</td>
</tr>
<tr>
<td>75</td>
<td>0.09</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
</tr>
<tr>
<td>125</td>
<td>-0.09</td>
</tr>
<tr>
<td>150</td>
<td>-0.18</td>
</tr>
<tr>
<td>175</td>
<td>-0.27</td>
</tr>
<tr>
<td>200</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$k_2$</th>
<th>pH(T)</th>
<th>$E_{Cr(VI)} (V) = f(pH(T))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.56 \times 10^{-10}</td>
<td>9.92</td>
<td>0.26</td>
</tr>
<tr>
<td>5.10 \times 10^{-9}</td>
<td>9.42</td>
<td>0.23</td>
</tr>
<tr>
<td>7.40 \times 10^{-9}</td>
<td>8.92</td>
<td>0.21</td>
</tr>
<tr>
<td>3.55 \times 10^{-8}</td>
<td>8.42</td>
<td>0.20</td>
</tr>
<tr>
<td>6.36 \times 10^{-8}</td>
<td>7.92</td>
<td>0.18</td>
</tr>
<tr>
<td>3.51 \times 10^{-7}</td>
<td>7.42</td>
<td>0.18</td>
</tr>
<tr>
<td>5.82 \times 10^{-7}</td>
<td>6.92</td>
<td>0.18</td>
</tr>
<tr>
<td>1.54 \times 10^{-6}</td>
<td>6.42</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 5-4 Corrosion potentials ($E_{\text{corr}}$), theoretical ($E_{\text{t}}$) and measured ($E_{\text{m}}$) transpassive potential as a function of temperature at initial oxygen loading $P_{\text{TOTAL,298K}} = 13.8$ bar.

However, for the results presented in Figure 5-3 and Figure 5-4, the effect of pH has been included in the calculations. Solution pH is expected to decrease with temperature as the ionic product of water increases [Marshall 1981]. The case of ammoniacal solutions requires special consideration due to the ammonia buffer point. The equilibrium constant for reaction 4-7, $k_{NH_3}$, increases with temperature (cf. Table 5-1) and the buffer point of ammonia drops to lower pH. This results in a decrease in pH for the test solution (test solution here reached equilibrium at pH ~ 10, 298 K). The theoretical pH variation as a
function of temperature is also shown in and is the result of a series of equilibrium and charge balance calculations. In reality therefore, $E_{Cr(VI)}$ does not vary linearly with temperature as seen in the second column of Table 5-1 as it is both a function of pH and temperature.

Agreement between the predicted values of $E_{Cr(VI)}$ and measured values of $E_t$ is good. There is a fairly large standard deviation in both $E_t$ and $E_{corr}$ data of approximately ±100 mV. Corrosion potential measurements are generally extremely difficult to reproduce for passivating metals and alloys when in the presence of oxygen. This is one of the many reasons standardized tests are de-aerated. However, it is believed that the room temperature oxygen sparging time is the main contributor to this variation. Because the sparging was started immediately upon pouring the solution into the autoclave, several factors affected the total sparging time. These included but were not limited to the time required for the autoclave to be brought from room temperature to 298 K and the time required to seal the autoclave including the EPBRE. Thus sparging time was unintentionally varied from between 25 and 50 minutes. Interestingly this resulted in a high fidelity correlation between sparge time and initial $E_{corr}$ measurement at a given oxygen partial pressure. As expected, the higher sparge times resulted in higher $E_{corr}$ values with the inference that the passive film characteristics were altered or that the solution saturation in oxygen had not been complete for the lower sparge times. Another complicating factor when dealing with sparging oxygen through ammoniacal solutions is the slow evaporation of $NH_3$ which results in lower pH. In an interesting aside, as this issue has been a concern throughout this testing program, pH measurements as a function of time through oxygen sparged solutions were conducted in various cell
geometries. It was found that the pH varied at up to ~ 0.3 pH units per hour depending on stirring rates/methods and geometrical cell conditions. Wider mouthed flasks with larger exposed surface area (such as the autoclave) were, as expected, less able to retain ammonia even at the modest concentrations used here. The effect of lower pH is to raise both $E_{\text{corr}}$ and $E_t$ (cf. Figure 4-4, [Bojinov 2002]). Therefore, the variation in oxygen sparge times had a direct (oxygen concentration and film characteristics) and indirect (acidification through ammonia evaporation) effect on the measured values of $E_{\text{corr}}$ and $E_t$, but both of these effects resulted in higher potentials.

In Figure 5-3 and in Figure 5-4 it is clear that despite large standard deviation, the mean values are very close to the regression analysis line fit. One can estimate from this data, for the given pressure conditions, the temperature at which $E_t$ would be exceeded by $E_{\text{corr}}$, thus leading to transpassive corrosion i.e. the inversion temperature. Clearly the slope of $E_{\text{corr}}$ vs. T is higher for the $P_{\text{TOTAL}} = 13.79$ bar experiments such that the inversion temperature should be lower. It appears as though for the case of the lower pressure ($P_{\text{TOTAL}} = 0$ bar) the inversion temperature is ~ 585 K. For the higher pressure ($P_{\text{TOTAL}} = 13.79$ bar) condition some resistance to transpassive corrosion occurs near approximately 400 K as the transpassive potential is seen to increase upon increase in temperature and also deviates substantially in an upward direction from its predicted thermodynamic values. The inversion temperature in this case is difficult to predict and it is hypothesized that the passive film composition or quality may have been altered. In fact, as one might expect, $E_{\text{corr}}$ was higher for the $P_{\text{TOTAL}} = 13.79$ bar experiments due to the higher equilibrium potentials for the oxygen reduction reaction.
This resulted in higher rates of dissolution in the anodic sections of the plots which likely resulted in high rates of precipitated ol film formation (cf. below re. diffusion layer thickness and mixed control and also refer to Figure 2-4).

Table 5-2 Potential and kinetic data for the oxygen reduction reaction.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (A.cm$^{-2}$)</th>
<th>$\beta_C$ (mV)</th>
<th>$E_{O_2}$ (mV)</th>
<th>$i_O$ (A.cm$^{-2}$)</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (A.cm$^{-2}$)</th>
<th>$\beta_C$ (mV)</th>
<th>$E_{O_2}$ (mV)</th>
<th>$i_O$ (A.cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-61</td>
<td>$6.9 \times 10^{-7}$</td>
<td>101</td>
<td>645</td>
<td>$7.1 \times 10^{-14}$</td>
<td>-73</td>
<td>$7.0 \times 10^{-7}$</td>
<td>93</td>
<td>663</td>
<td>$8.6 \times 10^{-15}$</td>
</tr>
<tr>
<td>323</td>
<td>-28</td>
<td>$1.1 \times 10^{-6}$</td>
<td>93</td>
<td>608</td>
<td>$1.6 \times 10^{-13}$</td>
<td>-61</td>
<td>$1.0 \times 10^{-6}$</td>
<td>86</td>
<td>627</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>373</td>
<td>18</td>
<td>$1.3 \times 10^{-6}$</td>
<td>89</td>
<td>590</td>
<td>$4.8 \times 10^{-13}$</td>
<td>67</td>
<td>$1.2 \times 10^{-6}$</td>
<td>79</td>
<td>612</td>
<td>$1.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>423</td>
<td>104</td>
<td>$2.3 \times 10^{-6}$</td>
<td>94</td>
<td>567</td>
<td>$2.7 \times 10^{-11}$</td>
<td>180</td>
<td>$1.8 \times 10^{-6}$</td>
<td>99</td>
<td>592</td>
<td>$1.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>473</td>
<td>104</td>
<td>$6.3 \times 10^{-6}$</td>
<td>93</td>
<td>536</td>
<td>$1.4 \times 10^{-10}$</td>
<td>295</td>
<td>$1.5 \times 10^{-5}$</td>
<td>121</td>
<td>564</td>
<td>$8.8 \times 10^{-8}$</td>
</tr>
</tbody>
</table>

The Tafel slopes for the oxygen reduction reaction indicate that the corrosion process is mostly under charge transfer control, (Figure 5-1 and Figure 5-2). However, between 298 and 423 K the higher pressure condition resulted in smaller Tafel slopes which indicate that mixed control was occurring at the lower $O_2$ partial pressures. As temperatures reached the 423 to 473 K range, the Tafel slopes for the $P_{TOTAL,298K} = 13.79$ bar experiments were higher than those for the lower pressure experiments such that the situation of mixed control appears to have been reversed. This can be explained by the alloy’s surface condition. It is believed that the increased Tafel slopes for the higher pressure experiments are the result of a thicker or less porous ol resulting in larger diffusion lengths for $O_2$. Because the bl is almost entirely responsible for protecting the alloy from corrosion (Macdonald et al. have measured resistivities on the order of $10^{13}$ $\Omega$.cm for a 1-2 nm thick bl on Ni – [Macdonald 1990A]) the ol is usually assumed to be
porous and hydrated offering only little resistance to ionic motion. It does, however, stand to reason that this ol would provide some limitations on molecular oxygen ingress towards the bl/ol interface. This hypothesis is also further substantiated by the increasing currents observed for the higher pressure experiments, particularly as temperatures approached the 473 K mark (Table 5-2). Indeed, as the alloy corrodes it releases metal cations at the bl/ol interface which precipitate as hydroxides thus forming the ol. Higher corrosion rates imply more cation ejection which could result in either a thicker or denser (less porous) ol.

To confirm that the oxygen diffusion lengths were in fact increasing with temperature and pressure, a series of cathodic polarization experiments were performed to determine the limiting current density. These experiments were performed at a scan rate of 2 mV/s from $E_{corr}$ to -1.2 V under the same temperature and pressure conditions as the Tafel polarization experiments. Analytically, the limiting current density is obtained when all of the available oxygen is consumed at the bl/s interface such that:

$$\frac{i_L}{nF} = \tau_L = \frac{D_o \cdot C_{O_2}}{\delta}$$

where $\tau_L$ is the diffusion flux and $\delta$ (cm) is the diffusion layer thickness. It is possible to calculate $\delta$ by using equation 5-12 with the calculated data for $C_{O_2}$ (mol.cm$^{-3}$) and $D_{O_2}$ and the measured values of $i_L$. Results of these calculations are presented in Table 5-3 along with the $i_L$ data. There is a significant increase between the diffusion lengths calculated at $P_{TOTAL,298K} = 0$ bar (0.04 to 0.21 cm) and those calculated at $P_{TOTAL,298K} = 13.79$ bar (0.19 to 0.48 cm). It was originally expected that as a result of the autoclave head not being insulated, the diffusion layer thickness would actually decrease at $\sim 448$
to 473 K due to the settling-in of convection currents. Clearly this outcome was totally negated by the ol precipitation. The diffusion length is obviously not representative of a classical Nernstian fluid diffusion layer so as such it may be referred to as an effective diffusion layer thickness which is the result of ol pore size and tortuosity restrictions.

Table 5-3 Calculated values of $\delta$ based on measured $i_L$ data.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$i_L$ (A cm$^{-2}$)</th>
<th>$\delta$ (cm)</th>
<th>$i_L$ (A cm$^{-2}$)</th>
<th>$\delta$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$4.6 \times 10^{-4} \pm 1.1 \times 10^{-4}$</td>
<td>$0.04 \pm 0.01$</td>
<td>$1.3 \times 10^{-3} \pm 2.4 \times 10^{-4}$</td>
<td>$0.19 \pm 0.04$</td>
</tr>
<tr>
<td>323</td>
<td>$6.9 \times 10^{-4} \pm 1.8 \times 10^{-4}$</td>
<td>$0.03 \pm 0.01$</td>
<td>$3.7 \times 10^{-3} \pm 8.1 \times 10^{-4}$</td>
<td>$0.10 \pm 0.02$</td>
</tr>
<tr>
<td>348</td>
<td>$7.8 \times 10^{-4} \pm 1.2 \times 10^{-4}$</td>
<td>$0.05 \pm 0.01$</td>
<td>$5.2 \times 10^{-3} \pm 2.4 \times 10^{-3}$</td>
<td>$0.10 \pm 0.06$</td>
</tr>
<tr>
<td>373</td>
<td>$1.1 \times 10^{-3} \pm 2.6 \times 10^{-4}$</td>
<td>$0.05 \pm 0.01$</td>
<td>$6.7 \times 10^{-3} \pm 2.3 \times 10^{-3}$</td>
<td>$0.12 \pm 0.05$</td>
</tr>
<tr>
<td>398</td>
<td>$1.5 \times 10^{-3} \pm 2.5 \times 10^{-4}$</td>
<td>$0.06 \pm 0.01$</td>
<td>$8.0 \times 10^{-3} \pm 2.1 \times 10^{-3}$</td>
<td>$0.16 \pm 0.05$</td>
</tr>
<tr>
<td>423</td>
<td>$2.2 \times 10^{-3} \pm 2.6 \times 10^{-4}$</td>
<td>$0.06 \pm 0.01$</td>
<td>$1.2 \times 10^{-2} \pm 4.3 \times 10^{-3}$</td>
<td>$0.17 \pm 0.07$</td>
</tr>
<tr>
<td>448</td>
<td>$2.5 \times 10^{-3} \pm 6.2 \times 10^{-4}$</td>
<td>$0.09 \pm 0.02$</td>
<td>$1.3 \times 10^{-2} \pm 3.8 \times 10^{-3}$</td>
<td>$0.26 \pm 0.08$</td>
</tr>
<tr>
<td>473</td>
<td>$1.8 \times 10^{-3} \pm 4.7 \times 10^{-4}$</td>
<td>$0.21 \pm 0.06$</td>
<td>$1.2 \times 10^{-2} \pm 1.8 \times 10^{-3}$</td>
<td>$0.48 \pm 0.07$</td>
</tr>
</tbody>
</table>

To determine the general kinetics of the oxygen reduction reaction, the cathodic Tafel slopes were extrapolated to its equilibrium potential. The equilibrium potential was calculated using the Nernst equation, with the oxygen partial pressures listed in Appendix B (the Lewis method was used again here to calculate the Gibbs energy at $T > 298$ K). The calculated equilibrium potentials, corrosion potentials and extrapolated exchange current density are also shown in Table 5-2. Due to the differences in the effective diffusion layer thickness depending on the test conditions, the calculated values of $i_o$ at a given temperature varied sometimes up to 4 orders of magnitude. The oxygen sparge time was also found to play a role here. In Figure 5-5, $i_o$ is plotted against the pressure and sparge time conditions. The longer sparge times correlated well with larger
Tafel slope values: implying smaller limiting currents; this is an indication that the increased time of heightened mass transfer to the electrode resulted in larger effective diffusion layer thicknesses (probably because $E_{\text{corr}}$ was raised nearer to the transpassive range for longer periods of time). Other authors have also found that the oxygen reduction reaction has a very high dependence on alloy pre-treatment [LeBozec 2001].

Figure 5-5 Exchange current density as a function of temperature, pressure and sparge time. Circled values are considered most accurate due to smaller Tafel slopes.
5.2.2 Linear polarization experiments

The linear polarization experiments were performed to measure the effect of oxygen pressure on the corrosion rate without overly polarizing the alloy. The results of these experiments conducted at initial 298 K total pressures of 6.89, 13.79 and 20.68 bar are shown in Figure 5-6, Figure 5-7 and Figure 5-8, respectively. The overpotential, $\eta$, is plotted in abscissa and is given by the formula: $\eta = E - E_{corr}$ where $E$ is the applied potential. It is clear that the anodic sections of the curves, in particular, have progressively increasing slopes as temperature is increased which indicates a progressively smaller polarization resistance ($R_p$). Linearity is restricted to $\Delta E \sim 10$ mV, however some degree of curvature is expected away from OC [Kelly 2003].
Figure 5-6  Linear polarization as a function of temperature at initial oxygen loading

\[ P_{TOTAL,298K} = 6.89 \text{ bar} \]
Figure 5-7  Linear polarization as a function of temperature at initial oxygen loading

\[ P_{\text{TOTAL,298\,K}} = 13.79 \text{ bar} \]
Figure 5-8  Linear polarization as a function of temperature at initial oxygen loading

\[ P_{TOTAL,298K} = 20.68 \text{ bar} \]
There were three main issues of concern in this work with regards to the applicability of the linear polarization resistance method for corrosion rate measurement. The first was whether or not $\Delta E / \beta \ll 1$ to ensure that the Stern-Geary equation would hold:

$$i_{\text{corr}} = \frac{B}{R_p}$$

$$B = \frac{1}{2.3} \left( \frac{\beta_a \beta_c}{\beta_a + \beta_c} \right)$$

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively, and $B$ is a proportionality constant known as the Stern-Geary coefficient. With $\beta_a$ and $\beta_c$ values in the region of 90 and 180 mV/decade respectively, it was deemed safe to apply equation 5-14. Also, it was necessary to assume that $B$ would not change significantly over the temperature range tested. Due to the increased oxygen partial pressure used for the LP experiments it was found that $B$ did not, in fact, vary substantially ($\pm$ 3 mV) from the normal Stern-Geary coefficient of 26 mV i.e. both the anodic and cathodic curves were sufficiently removed from pure diffusion control to allow for charge transfer based estimations of $R_p$. Finally, due to experimental necessity, the hold-time at temperature (30 min) and voltage scan rate (0.5 mV/s) were respectively shorter and faster than is recommended for this type of experiment. This can lead to large capacitive effects and thus underestimates of $R_p$ [Kelly 2003], particularly when mass transfer such as oxygen diffusion is playing a role in the corrosion process. To verify that the scan rate was adequate a few small amplitude cyclic voltametry experiments were performed at 298, 398 and 448 K to check for hysteresis. No significant capacitive response was detected.
The corrosion rates obtained at various $P_{\text{TOTAL,298K}}$ and by various methods of measurement are shown in Figure 5-9. There is little discernible effect of pressure on the corrosion rate between ~ 298 to 398 K. There does appear to be some separation in the data as temperatures increased above 398 K suggesting that the corrosion rates were increased by higher pressures. For example, the corrosion rate at 473 K, $P_{\text{TOTAL,298K}} = 20.68$ bar is roughly 2.5 times the corrosion rate at $P_{\text{TOTAL,298K}} = 0$ bar. This is likely the result of $E_{\text{corr}}$ approaching $E_t$ at the higher oxygen partial pressures and is also a sign of an increasingly diffusion controlled corrosion process.

![Graph showing corrosion rates at various pressures and temperatures](image)

Figure 5-9 Corrosion rates as measured by various methods (PD – Potentiodynamic, LP – Linear Polarization, EIS – Electrochemical Impedance Spectroscopy) and at various $P_{\text{TOTAL,298K}}$. 
5.2.3 Electrochemical impedance measurements

Nyquist and Bode plots generated at temperatures up to 448 K at $P_{\text{TOTAL},298K} = 27.58$ bar are shown in Figure 5-10 and Figure 5-11, respectively. From these figures it is clear that the total impedance and thus $R_p$ decreases with temperature as was seen in the LP experiments. The Nyquist plots show a partially resolved semicircle at high frequencies and a Warburg-type response at low frequencies. Warburg impedance is normally associated with a semi-infinite diffusion controlled process (such as through the solution) and is characterized by linear 45° sections on a Nyquist plot. Normally semi-infinite diffusion is measured at very low frequencies (<1 mHz) [Macak 2006]. The frequency range tested in this work is not low enough to capture solution phase diffusion. The general shape of the curve at 298 K is very similar to the one found by Chao et al. on passivated Ni in a phosphate buffer solution [Chao 1982] and Macdonald and Smedley for the same system [Macdonald 1990A, B]. In the case of the Ni electrode and under the assumption that most of the current was carried by oxygen vacancy transport, Chao et al. attributed the observed Warburg-like diffusion to oxygen vacancy transport across the bl in accordance with the PDM [Chao 1982], [Macdonald 1990C, 1992A, B, 1999, 2004, 2005]. The PDM describes film growth in terms of oxygen anion or metal cation vacancy transport within the thin (1 to 3 nm) semiconductor-like bl. Cation vacancies diffuse from the bl/ol interface to the m/bl interface while oxygen anion vacancies diffuse in the opposite direction. A consequence of this model is that the “primary passive film (i.e. that which is not precipitated from solution) can only grow by the diffusion of oxygen anion vacancies” (cf. Figure 2-5) [Chao 1982]. The movement of cation vacancies does not result in film growth but does result in cation ejection from the
bl [Macdonald 1990C]. For most practical purposes this results in overall impedance
\((Z_T)\) of the form [Macdonald 2005]:

\[ Z_T = \sigma_M \omega^{-1/2} (1 - j) \]  

This is formally identical to Warburg impedance, where the Warburg coefficient is
\(\sigma_M\) and \(\omega\) is the angular frequency in rad.s\(^{-1}\). It is assumed in this work that the current is
due to cation vacancy transport rather than anion (oxygen) vacancy transport. Discussion
of this point will follow. To analyze the effect of temperature on the Warburg coefficient
for alloy 625 a Randles plot is shown in Figure 5-12 where

\[ \sigma_M = \frac{\partial Z'}{\partial \omega^{-1/2}} \]  

and \(Z'\) represents the real impedance. The decreasing slope of the Randles plots in Figure
5-12 with respect to temperature and thus the decreasing Warburg coefficient, implies
that \(i_{corr}\) should increase with temperature because according to the PDM, \(\sigma_M\) is
inversely proportional to the measured current. Moreover it is predicted in the PDM that
the product, \(i_{corr} \cdot \sigma_M\), should be constant. This was confirmed here.
Figure 5-10  Nyquist plots taken at peak-to-peak voltage excitation amplitude of 10 mV vs. $E_{\text{corr}}$ (100 kHz, left most point – 10 mHz, right most point), and at various temperatures. $P_{\text{TOTAL,298K}} = 27.58$ bar.
Figure 5.11 Bode plots at $E_{corr}$, $P_{TOTAL,298K} = 27.58$ bar. (A) Magnitude and (B) Phase angle.
Figure 5-12 Randles plot showing the real impedance as a function of $\omega^{-1/2}$ and temperature - the Warburg coefficient for cation vacancy transport was calculated by linear regression and is shown in the legend.
To estimate $i_{corr}$ equation 5-14 was used where $R_p$ was obtained by fitting a circuit model to the EIS results. Of course, the assumption that the Stern-Geary coefficient did not vary between the temperatures within the data set was again made. The model used was a simplified interfacial circuit model suggested by Priyantha et al. for alloy 22, which is presented in Figure 5-13 and where $R_p = R_1 + R_b + R_2$ [Priyantha 2004]. To account for capacitance dispersion across a rough barrier layer/solution interface, the model includes a constant phase element: $Q_2$ where $n$ can be treated as a coefficient of roughness for the bl/s interface. Representative model fit parameters are shown in Table 5-4. Agreement between the model and the experimental data was judged to be good and the reader is referred to Appendix C for examples. The corrosion rates obtained in this way are presented in Figure 5-9 and are consistent with those obtained by other methods.

![Circuit scheme used for fit to experimental data. Interfaces 1 and 2 represent the m/bl and bl/s interfaces respectively.](image)
Table 5-4 Model fit parameters for the simplified circuit model assumed (Figure 5-13) to represent the passive film and interfacial behaviour.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$R_1/\Omega\cdot\text{cm}^2$</th>
<th>$C_1 \times 10^5/F\cdot\text{cm}^{-2}$</th>
<th>$R_2/\Omega\cdot\text{cm}^2$</th>
<th>$C_2 \times 10^5/F\cdot\text{cm}^{-2}$</th>
<th>$n$</th>
<th>$Q_2/\times 10^5/F\cdot\text{cm}^{-2}$</th>
<th>$R_r/\Omega\cdot\text{cm}^2$</th>
<th>$R_p/\times 10^{-2}/\Omega\cdot\text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.853</td>
<td>0.007</td>
<td>712.84</td>
<td>27.49</td>
<td>0.86</td>
<td>141.65</td>
<td>9.52</td>
<td>5.57</td>
</tr>
<tr>
<td>323</td>
<td>0.006</td>
<td>0.004</td>
<td>424.72</td>
<td>24.82</td>
<td>0.85</td>
<td>107.28</td>
<td>10.20</td>
<td>4.46</td>
</tr>
<tr>
<td>348</td>
<td>298.62</td>
<td>53.634</td>
<td>357.56</td>
<td>23.21</td>
<td>0.84</td>
<td>163.73</td>
<td>12.06</td>
<td>3.85</td>
</tr>
<tr>
<td>373</td>
<td>184.24</td>
<td>23.944</td>
<td>157.05</td>
<td>82.70</td>
<td>0.84</td>
<td>89.11</td>
<td>13.56</td>
<td>3.26</td>
</tr>
<tr>
<td>398</td>
<td>145.62</td>
<td>96.704</td>
<td>59.95</td>
<td>23.49</td>
<td>0.84</td>
<td>51.81</td>
<td>16.24</td>
<td>2.93</td>
</tr>
<tr>
<td>423</td>
<td>1896.41</td>
<td>23.803</td>
<td>40.87</td>
<td>62.90</td>
<td>0.83</td>
<td>5.92</td>
<td>21.32</td>
<td>2.74</td>
</tr>
<tr>
<td>448</td>
<td>78.17</td>
<td>172.535</td>
<td>8.32</td>
<td>33.56</td>
<td>0.84</td>
<td>17.76</td>
<td>21.62</td>
<td>2.60</td>
</tr>
</tbody>
</table>

It was also of interest to estimate both the barrier layer thickness and electric field strength as a function of temperature. The former can be estimated by applying the formula for the parallel plate capacitor [Macak 2006] at high frequency:

\[
L_{ss} = \frac{\varepsilon_r \varepsilon_0 A}{C_\infty}
\]

5-17

where $L_{ss}$ is the steady-state barrier layer thickness, $\varepsilon_r$ is the relative permittivity of the oxide and $\varepsilon_0 = 8.85 \times 10^{-14} F\cdot\text{cm}^{-1}$ is the vacuum permittivity and $A$ is the electrode area which was 0.71 cm$^2$ in this work. Macdonald et al. have estimated that $\varepsilon_r \sim 30$ for alloy 22. This value was retained here as the composition of the oxide formed on alloy 22 is known to be mostly Cr$_2$O$_3$ and therefore similar to that formed on alloy 625. The geometric capacitance, $C_\infty$, is a parameter usually estimated from the intercept of the linearly extrapolated low frequency capacitive response and the real axis of the complex capacitance [Macak 2006]. To eliminate the error involved in line fitting and extrapolation the measured capacitance at 6 kHz was used here. This practice has been employed by other authors [Macdonald 2004B, 2005], [Raja 2006]. The calculated data
for $L_{ss}$ and $R_b$ (the barrier layer resistance) is shown in Figure 5-14. The calculations suggest that that the barrier layer is being destroyed as temperature is increased: it thins linearly by roughly one half between 298 (1.4 nm) and 473 K (0.7 nm) and $R_b$ decreases exponentially over the same temperature range. The values of $L_{ss}$ calculated by Macdonald et al. for alloy C-22 are similar: ~0.8 to 2.0 nm depending on applied voltage at 353 K. Lloyd et al. have measured oxide thickness on alloys 22 and C-276 by time of flight secondary ion mass spectroscopy after up to 60 hours of potentiostatic treatment at temperatures ranging from 298 to 358 K and found values ranging from 2.0 to 2.8 and 1.5 to 3.2 nm, respectively with NiO concentrations in the region of 10 to 40 at% [Lloyd 2003]. Also, From XPS measurements after exposure to sulphuric acid at 338 K, Wallinder et al. found that the passive film on stainless steel 316 L was ~2nm [Wallinder 1999]. Both Macdonald and Lloyd found that the oxides generally thickened up to ~450 mV. Above 450 mV, Macdonald et al. found that the oxide thinned linearly with increasing potential and it was concluded that this corresponded to transpassive dissolution [Macdonald 2004B]. While voltage was not varied explicitly in this work it was indirectly affected by the increasing temperature and oxygen partial pressures. Considering the fact that $E_{corr}$ was close to the transpassive potential for alloy 625 at $P_{TOTAL,298K} = 13.79$ bar and 473 K it seems reasonable to assume that within the tested temperature range at $P_{TOTAL,298K} = 27.58$ bar one might encounter transpassive dissolution.
Figure 5-14 Calculated values of the steady-state barrier layer thickness ($L_{ss}$) and film (bl + ol) resistance ($R_b$) as a function of temperature. $L_{ss}$ was calculated using the parallel plate formula, equation 4-17.

Table 5-5 Parameters derived from EIS measurements, according to equations 5-13 and 5-19 ($B = 0.026$, $\varepsilon = 1.10 \times 10^6 \, V.cm^{-1}$, $\alpha = 0.878$). $\Sigma$ is the standard deviation for $R_p$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$10^{-2} \times R_p , \Omega.cm^2$</th>
<th>$10^{-2} \times \Sigma , \Omega.cm^2$</th>
<th>$\sigma_M , \text{rad}^{-1/2}$</th>
<th>$10^6 \times i_{corr} , A.cm^{-2}$</th>
<th>$10^6 \times \varepsilon , cm^2.s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>854.50</td>
<td>185.94</td>
<td>7880</td>
<td>0.30</td>
<td>1.90</td>
</tr>
<tr>
<td>323</td>
<td>532.00</td>
<td>637.96</td>
<td>5140</td>
<td>0.49</td>
<td>1.95</td>
</tr>
<tr>
<td>348</td>
<td>524.27</td>
<td>66.36</td>
<td>3660</td>
<td>0.50</td>
<td>2.73</td>
</tr>
<tr>
<td>373</td>
<td>248.00</td>
<td>72.45</td>
<td>3010</td>
<td>1.05</td>
<td>4.17</td>
</tr>
<tr>
<td>398</td>
<td>113.22</td>
<td>46.06</td>
<td>2160</td>
<td>2.30</td>
<td>4.07</td>
</tr>
<tr>
<td>423</td>
<td>65.76</td>
<td>1.47</td>
<td>490</td>
<td>3.95</td>
<td>5.49</td>
</tr>
<tr>
<td>448</td>
<td>26.86</td>
<td>10.60</td>
<td>350</td>
<td>9.68</td>
<td>6.76</td>
</tr>
</tbody>
</table>
The advantage gained by the variance in initial oxygen sparge time is that it
allowed for a spectrum of $E_{\text{corr}}$ data at a given temperature. This advantage was used to
generate a Mott-Schottky plot for alloy 625 as a function of temperature and the result is
shown in Figure 5-15. It appears as though the passive film formed under the conditions
tested here is a p-type semiconductor. The slope for the Mott-Schottky relationship

\[
(1/C^2 = f(V))
\]

for a p-type semiconductor is given by,

\[
\frac{\partial C^{-2}}{\partial V} = \frac{-2}{\varepsilon_0 \varepsilon_r e N_A}
\]

where the electronic charge $e$ is $1.6 \times 10^{-19}$ C. Assuming a good estimate of $\varepsilon_r \sim 30$, we
can calculate the film’s acceptor (cation vacancy) concentration, $N_A$ as a function of
temperature. This yields values of $\sim 2.26 \times 10^{20} \text{cm}^{-3}$ at 298 K, $2.96 \times 10^{20} \text{cm}^{-3}$ at 348 K
and $1.69 \times 10^{21} \text{cm}^{-3}$ at 448 K. Macdonald et al. have calculated values of

$\sim 3 \times 10^{20} \text{cm}^{-3}$ for alloy 22 at 353 K in the transpassive range (>0.6 V SHE). At
potentials below the transpassive region the barrier layer on alloy 22 is apparently n-type.
The increased acceptor concentration and transition to a p-type film indicates, according
to Macdonald et al., a high rate of cation vacancy generation at the bl/s interface due to
ejection of high valence Cr(VI) cations through transpassive dissolution [Macdonald
2004B]. These vacancies diffuse to the m/bl interface and if they are not annihilated
eventually condense leading to bl separation and eventual film breakdown. Such an
analysis, applied here, would indicate that even at 298 K alloy 625 was corroding
transpassively. However, while in the case of alloy 22 the transition from n-type to p-
type is clearly an indication of transpassive corrosion, the case presented here is less
clear.
Figure 5-15 Mott-Schottky plot for alloy 625 as a function of temperature at various $E_{\text{corr}}$ values which were varied according to oxygen sparge time at 298 K.

It is possible that the barrier layer on alloy 625 is a cation conductor throughout its passive range. Films on Ni in borate buffer solutions, for example, are p-type in both the passive and transpassive range [Sikora 2002], [Macdonald 1992A]. Furthermore, it is well known that Cr$_2$O$_3$ is a p-type semiconductor [Hakiki 1995, 1998], [Kofstad 1980], [Sunseri 1990] and Hakiki et al. have found that pure chromium oxide is expressly p-type over the range $\sim$ 0 to 0.5 V which is close to the observed range here (-0.050 to 0.25 V). The fact that alloy 625 is a highly doped cation conductor in ammoniacal solution may
also be a reflection of the fact that high rates of Ni$^{2+}$ expulsion from the bl are occurring within the passive range and as a result of the instability of NiO which could be associated with ammine formation or solution acidification. Interestingly, Table 5-5 shows that the corrosion current densities for these experiments were low and not commensurate with what one would normally expect for transpassive corrosion i.e. $i_{corr}$ values larger than $\sim 10^5$ A.cm$^{-2}$ at 298 K, for example (cf. Figure 4-4). Though, Lloyd et al. have found that despite expulsion of Cr(VI) species from the passive film on alloy 22 at high potentials (up to 0.9 V) at 353 K, this film was able to concentrate Cr within its oxide and only corroded at $\sim 1x10^{-6}$ A.cm$^{-2}$ [Lloyd 2003]; so the corrosion current is not necessarily a good diagnostic criterion for transpassive corrosion either.

Perhaps the best way to make the determination of passive versus transpassive corrosion is the $E_{corr}$ data. During the course of the EIS experiments, $E_{corr}$ was generally higher than for all other experimental conditions - a result of the elevated equilibrium potential for the oxygen reduction reaction due to the higher pressures used (cf. Appendix B). However, Figure 5-16 shows that above $\sim$ 40 bar (373 K), $E_{corr}$ actually slightly decreased (125 to 57 mV) as pressure and temperature were increased. A simplified Evans diagram is shown in Figure 5-17 and it graphically represents the scenario believed to have taken place. Figure 5-1 and Figure 5-2 show that the anodic Tafel slopes tend to zero as $E_i$ is approached and the effect of higher pressure and temperature on the oxygen reduction reaction has already been discussed. In Figure 5-17 it is assumed that $i_L$ continues to increase with temperature. This is perhaps not the case due to a thickening diffusion layer, as shown in Table 5-3 ($i_{L,473K} \sim 0.9i_{L,448K}$ for the
$P_{\text{TOTAL,}298^K}=13.79$ bar experiments), however, a decrease in $i_L$ would only result in the observed decrease in $E_{\text{corr}}$ and concomitant increase in corrosion rate if $E_t$ had been reached. Thus either explanation leads to the conclusion that the corrosion reaction is approaching limiting cathodic currents at $\sim 373$ K, 40 bar and that this temperature/pressure combination leads to transpassive corrosion. Therefore, it is very likely that at 40 bar and, in an oxygen saturated ammoniacal environment, the inversion temperature for alloy 625 is $\sim 373$ K.

![Figure 5-16 Dependence of $E_{\text{corr}}$ on total pressure for all EIS data- decreasing $E_{\text{corr}}$ values above $\sim 40$ bar substantiate the assumption of diffusion control at high temperature.](image)

Figure 5-16 Dependence of $E_{\text{corr}}$ on total pressure for all EIS data- decreasing $E_{\text{corr}}$ values above $\sim 40$ bar substantiate the assumption of diffusion control at high temperature.
Figure 5-17 Predicted effect of pressure and temperature on $E_{corr}$ at $P_{TOTAL.T} > 40$ bar - $T_3 > T_2 > T_1$ and $P_3 > P_2 > P_1$ - it is expected that transpassive corrosion occurs readily at this pressure.

One final corroborating factor that the inversion temperature is $373 \, K$ is the general shape of the Nyquist plots shown in Figure 5-10. For $T \leq 373 \, K$ the curves are nearly linear and the imaginary and real components are almost equal. At $T \geq 373 \, K$ the imaginary component is suppressed and the curve takes the shape of a semi-circle. This behaviour has also been observed by Sikora and Macdonald for Ni in the transpassive region [Sikora 2002]. The preceding discussions regarding the inversion temperature
have been emphasized because for significantly harsher conditions (P = 240 bar, 

\[ [\text{H}_2\text{SO}_4]^+ = 0.1 \text{ m}, \ C_{\text{aq}} = 0.48 \text{ m} \]), Kritzer et al. have argued that an inversion temperature of \( \sim 523 \text{ K} \) could be justified through morphological analysis of SCWO reactor tubing which showed generalized pitting [Kritzer 1998]. Given the findings presented here, it seems reasonable to suggest that morphological examination alone may not adequately estimate the inversion temperature; particularly as the corrosion rates found here were still quite low despite onset transpassive attack, meaning that the morphology may not be well developed. Figure 5-18 shows the surface of alloy 625 after the EIS experiments. There is a definite appearance of intergranular attack but it should be emphasized that this coupon was subjected to temperatures of up to 473 K therefore it is not clear at which temperature the morphology was developed.

With the film thickness and voltage data (Figure 5-14 and Figure 5-15) the electric field strengths were calculated as a function of temperature for a cation conducting film:

\[
\varepsilon = \frac{(\alpha - 1)}{(\frac{\partial L_{\text{ss}}}{\partial V})_{\text{pH}, \varepsilon^{\text{ds}}_M}}
\]

where \( \alpha \) is the polarizability of the bl/ol interface. The field strength was found to increase from a value of \( \sim 2 \times 10^6 \text{ V.cm}^{-1} \) at 298 K to \( \sim 7 \times 10^6 \text{ V.cm}^{-1} \) at 448 K (Table 5-5). Both the value for \( \alpha = 0.5 \) which was used for the calculations and the values obtained for the field strengths themselves are typical of those found by others [Macdonald 1990C]. Moreover, Sato and Noda have found that the field strength increases with decreasing pH. This is consistent with the results presented here which show the pH decrease as temperature is increased.
Figure 5-18 SEM micrograph showing corrosion morphology after EIS testing through the temperature range 298 to 473 K, $P_{TOTAL,298K} = 27.89$ bar. IGA is apparent.

5.2.4 Corrosion rate and mixed control

It has been have shown that the pressure and temperature conditions examined in this work lead to a complex scenario of mixed control. Generally, there are a few conclusions which are consistent with all of the data: the corrosion rate increases with temperature, the effective diffusion layer thickness increases with temperature, the bl film is p-type in nature and the ejection of cations through the bl leads to the “lengthening” of this diffusion layer due to ol precipitation and, finally, as temperature and pressure are increased $E_{corr}$ tends to $E_i$ which results in the rate control scenario
being more diffusional in nature. It is also clear that the oxygen partial pressure and thus solubility are linked (at least in part) to the degree of mixed control. Qualitatively this observation is confirmed by the isothermal Tafel slopes observed at different pressures.

Macák et al. have observed oxygen diffusion controlled corrosion for stainless steel in high temperature water but the concentrations of $O_2$ used in their work was on the order of $5 - 30$ ppb [Macak 2006]. In this work $O_2$ concentrations are on the order of 40 ppm (0 bar, 298 K) to 2000 ppm (62.5 bar, 448 K) meaning that the limiting current densities are theoretically much higher (assuming no change in $\delta$ cf. equation 5-13). Moreover, Macák et al.’s findings were also supported by semi-infinite Warburg diffusion at low frequency ($< 1$ mHz). The Warburg behaviour observed here is more consistent with vacancy diffusion through the bl. It is therefore of interest to explore the equations governing the corrosion rates as they relate to oxygen concentration, diffusivity and diffusion layer thickness.

Under steady state conditions all steps in a consecutive corrosion reaction are proceeding at the same rate regardless of whether they are charge transfer or transport related. Therefore, according to Kirchhoff’s first law we have:

$$i_{\text{corr}} = i_{\text{ct}} = i_{\text{trans}}$$  

which can be restated as the flux equality condition [Bockris 1970],

$$i_{\text{corr}} = \frac{i_{\alpha}}{nF} = \tau = \frac{D_{O_2}}{\delta} \left( C_{O_2}^b - C_{O_2}^{\text{bl/ol}} \right)$$  

where $\tau$ is the diffusion flux, $C_{O_2}^b$ is the oxygen concentration in the bulk solution, $C_{O_2}^{\text{bl/ol}}$ is the oxygen concentration at the bl/ol interface, $D_{O_2}$ is the oxygen diffusivity and $\delta$ is the diffusion layer thickness. It is convenient now, to express the corrosion rate as a
function of temperature in terms of the normalized corrosion rate \( \left( \frac{i_{corr}}{i_{corr}} \right)_{298} \). Such a procedure yields:

\[
\left( \frac{i_{corr}}{i_{corr}} \right)_{298} = \left( \frac{D_{O_2}}{D_{O_2}} \right)_{298} \times \left( \frac{C_{O_2}^B}{C_{O_2}^B} \right)_{298} \times \left( \frac{C_{O_2}^{bl/d}}{C_{O_2}^{bl/d}} \right)_{298} \times \left( \delta \right)_{298}
\]

Equation 5-22

The first term on the right-hand side of equation 5-22 can be estimated and is known to increase exponentially with temperature (cf. Table A1). The third term has been observed to generally decrease monotonically with temperature (Table 5-3). The second term in equation 5-22 has the most potential to affect the normalized corrosion rate because we have shown that at 298 K the corrosion reaction is mostly under charge transfer control which implies that \( \left( C_{O_2}^B \right)_{298} - \left( C_{O_2}^{bl/d} \right)_{298} \sim 0 \). In Figure 5-19 the normalized corrosion rate is plotted as a function of temperature for each type of experiment. The purely diffusion controlled scenario is also plotted in Figure 5-19 and was obtained through calculations performed according to a method outlined elsewhere and in detail by Tromans. Central to this method is of course the assumption that the corrosion rate is under oxygen control. The principal equations for determining the maximum limiting diffusion flux of oxygen at temperature \( T \) \( \left( \tau_t \right)_T \) are [Tromans 2000A]:

\[
\left( \frac{i_{corr}}{i_{corr}} \right)_{298} = \left( \frac{\tau_t}{\tau_t} \right)_{298}
\]

Equation 5-23

\[
\left( \tau_t \right)_T = \left( \frac{C_{O_2}}{D_{O_2}} \left( \rho \right)_{T} \right) \times \left( \delta \right)_{T}, \text{ mol.cm}^{-2}.\text{s}^{-1}
\]

Equation 5-24
Where the solution density, \( \rho \), is in kg cm\(^{-3}\) and can be calculated with the volumetric data generated by equations 5-1 through 5-8. \( \sigma \), for this model was assumed to be constant.

![Diagram showing normalized corrosion rate as a function of temperature, pressure, and method of measurement.](image)

Figure 5-19 Normalized corrosion rate as a function of temperature, pressure and method of measurement

At \( P_{TOTAL,298K} = 0 \) bar the data presented in Figure 5-19 diverges from the diffusion limited case in a downward direction because the third term in equation 5-22 is dominant. At \( P_{TOTAL,298K} = 6.89 \) and 13.79 bar the data is fortuitously aligned with the diffusion limited calculations. This could only be the result of the difference

\[
\left( C_{O_2}^8 \right)_T - \left( C_{O_2}^{bl/d} \right)_T
\]

going larger meaning that the corrosion reaction is increasingly
diffusion controlled as pressure is increased. This trend is confirmed by the data for the $P_{TOTAL,298K} = 20.68$ and $27.58$ bar experiments which depart exponentially from the theoretical diffusion controlled model.

From the standpoint of corrosion in SCWO reactors, these findings are substantive only in that they point to a rationale for employing equation 5-12 to predict corrosion rates at pressures and temperatures near the critical point of water where corrosion rates are seen to be the highest. Of course, from the perspective of corrosion engineering a conservative corrosion rate estimate must always rely on limiting currents. However, the data presented here is important in that it effectively says that the precipitated ol is responsible for limiting the corrosion rate at high temperatures and pressures and that the barrier layer itself plays very little role. In fact, it is probably nonexistent near the critical point of water. Extension of the linear fit to the $L_{ss}$ data in Figure 5-14 gives zero thickness at $580$ K and the reader is reminded that this result is for pressures not exceeding $60$ bar so that the situation is expected to be worse in a SCWO reactor at $P > 221$ bar.

Under transpassive conditions the solubility of the precipitated ol is then the determining factor of corrosion rate. Studies have found that the precipitated corrosion products (ol) or scales at SCWO conditions are mostly $\text{Cr}_2\text{O}_3$ or $\text{CrOOH}$ [Schroer 2002], [Watanabe 2002]. Kritzer et al. found that scales formed in the transpassive region ($T > 523$ K) had high atomic oxygen to chromium ratios of ~ 2.2, indicating that higher valence Cr-oxides could be present [Kritzer 1998]. Indeed, as alloy 625 corrodes in the transpassive range it is expected to release $\text{Cr(VI)}$, $\text{Cr(III)}$, $\text{Ni(II)}$ and possibly $\text{Cr(IV)}$ ions (other alloying elements such as Nb and Mo are ignored here but are also factors).
Because the corrosion process occurs within the transpassive range, the ol can only be characterized as thermodynamically unstable but kinetically protected. This brings up the question: what prompts a sudden dissolution or removal of the ol and consequently high rates of corrosion ca. 650 K? It could be postulated that the precipitated Cr(III) oxide is ultimately removed by solution acidification, i.e. chemically rather than electrochemically. While the data with regards to solution pH is not fully born-out [Kriksunov 1995], this scenario seems probable and will be discussed later.

Should the ol become entirely soluble, alloy 625 would be expected to corrode at its limiting current density. Because the corrosion rates under limiting currents are so high, this analysis suggests that Pourbaix diagrams at SCWO conditions are even more relevant than those at room temperature.

It may be useful for future reference and corrosion rate estimation to obtain some data for the effective diffusion layer thickness in a SCWO reactor at temperatures where (a) the ol is present and (b) the ol is soluble. The concentration of O$_2$ at temperatures near the critical point must first be obtained. This is done in the following section.

### 5.2.5 Oxygen solubility at SCWO conditions

SCWO reactors typically operate at P > 250 bar and the temperature region of particular interest to corrosion studies is that which is near the critical point (623 < T < 660 K). Ideal gas assumptions are no longer valid under these conditions as the compressibility of the gas phase deviates substantially from unity. Non-ideal volumetric and phase data can be modeled using cubic equations of state (equation 5-25), such as the Redlich-Kwong-Soave (RKS) equation [Soave 1984]:
\[ P = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + wb^2} \]  
\[ 5-25 \]

For the RKS \( u = 1, w = 0, b = \frac{0.08664RT_C}{P_c}, \quad a = \frac{0.42748R^2T_C^2}{P_c} \left[ 1 + f\omega \left( 1 - T_r^{1/2} \right) \right]^3 \]

and \( f\omega = 0.48 + 1.574\omega - 0.176\omega^2 \). In the above equations, \( T_C \) and \( P_c \) are the critical temperature and pressure, \( T_r = T / T_C \) is the reduced temperature and \( \omega \) is the accentric factor which is a reflection of the non-sphericity of a molecule. The algorithm required to obtain convergence of equation 5-25 is beyond the scope of this work and the reader is referred to the manuscript by Reid, Prausnitz and Poling [Reid 1987] and to the Matlab code listed in Appendix E, p. 227. A few points are however important to make. A mixing rule is required to obtain parameters \( a \) and \( b \) for the mixture as they depend on the critical pressure and temperature of each component. Soave suggests the use of a quadratic mixing rule for mixtures containing a polar solvent [Soave 1984]:

\[ a = \sum_i \sum_j x_i x_j a_{ij} \text{ with } a_{ij} = (1 - K_{ij})(a_i a_j)^{0.5} \]  
\[ 5-26 \]

\[ b = \sum_i \sum_j x_i x_j b_{ij} \text{ with } b_{ij} = \left( 1 - h_{ij} \right) \left( b_i + b_j \right) / 2 \]  
\[ 5-27 \]

Here, \( i \) and \( j \) represent the two species present in the system i.e. water and oxygen and \( x_i \) is the mole fraction of species \( i \) (ideally, a ternary H_2O-O_2-NH_3 system should have been considered here but the mathematical implications were such that a purpose-built software package would be required). For the liquid calculations \( x_i \) is the mole fraction in the liquid phase and for the vapour calculations \( x_i \) is replaced by \( y_i \), the mole fraction in the vapour phase. \( K_{ij} \) and \( h_{ij} \) are the only adjustable parameters in the model and are meant to reflect the interaction between the two elements of the mixture. With the
assumptions of an initial mole fraction of O\textsubscript{2} as well as a system pressure, the model will yield specific volume, compressibility and fugacity coefficients. Shown here are results for a 95 mol\% water, 5 mol\% oxygen mixture at 250 bar. This mol distribution was chosen as it is similar to the one employed for SCWO experiments at UBC. The densities of the liquid and vapour phases are plotted with respect to temperature in Figure 5-20 as calculated by the model. The dense supercritical region is also pointed out in Figure 5-20. According to this model the property transition does not occur until ~ 673 K.

Figure 5-20  Liquid and gas phase densities at 250 bar as calculated by the RKS for a 95 mol\% H\textsubscript{2}O, 5 mol\% O\textsubscript{2} solution.
Figure 5-21 shows the Henry’s law constant as obtained from the ideal gas Tromans model (modified to mol% and GPa) and as obtained from the RKS calculations where,

\[
H = \frac{f_{o_1}}{x_{o_1}}
\]

5-28

\(f_{o_1}\) is the fugacity of oxygen (notice that \(H = 1/k\) from equation 5-1). There is obviously a difference between the RKS model and the Tromans model for temperatures below 500 K. Up to \(~500\) K at 250 bar the compressibility of the gas phase (1.0342 at 500 K) and the fugacity coefficient of oxygen (1.0775 at 500 K) do not actually differ much from unity. Therefore, phase data garnered from Tromans’ quantitative model is expected to be more accurate than the RKS in this temperature range. Furthermore, the Tromans model is in good agreement with the data presented by Himmelblau who also assumes ideal gas behaviour [Himmelblau 1960]. The only available experimental data at high pressure for the oxygen-water system is that of Japas and Franck (P > 300 bar) and this data is re-plotted in Figure 5-21 along with two estimates near the critical point which they have calculated using second virial coefficients to obtain the fugacity coefficient [Japas 1985]. Japas and Franck have also presented data similar to the Himmelblau data for \(T < 573\) K. The RKS model is reasonably accurate near the critical point and reproduces the experimental data to within 2% - a value which matches the uncertainty associated with the data itself. There is a remarkably good agreement between the Tromans model and the experimental data up to about 625 K – Tromans himself has stated that his model is valid up to 616 K but not above 61 bar [Tromans 1998]. Clearly this model is appropriate to at least 300 bar, ~ 616 K. Oxygen concentrations as well as other data calculated by the RKS are listed in Appendix D. An
interesting observation from this data (p.216) is that the concentration of oxygen actually decreases between 643 and 673 K and then dramatically increases at 673 K. This decrease is associated with the falling fugacity of oxygen above 473 K. The dramatic increase of oxygen concentration above 673 K is due to the supercritical transition where oxygen becomes entirely soluble. The local maximum in the oxygen concentration generally agrees well with peak corrosion rates being measured between 623 and 660 K, which is a further indication that the corrosion rate is oxygen diffusion controlled in this temperature range. This analysis also provides an explanation as to why experimental data overwhelmingly points to increased corrosion rates just below the critical point of water.

Figure 5-21 Oxygen solubility – Henry’s Law constant as a function of temperature and method of calculation
5.2.6 Effective diffusion layer thickness

During experiments into the feasibility of treating 2,4 dinitrophenolate with ammonium sulphate, the University of British Columbia's SCWO reactor corroded to failure at ~ 655 K, 250 bar in about 1 hour [Vera-Perez 2002]. Under the assumption that the corrosion process was diffusion controlled and with the corrosion rates measured from SCWO reactor tubing penetration depths, the \((C_{Oi})_T\) data as calculated above was used to estimate \((\delta)_T\) through equation 5-12. SEM micrographs of the corroded sections of alloy 625 tubing subjected to ammoniacal solution (same concentrations as those used in this work) at \(P_{TOTAL} = 250\) bar are shown in Figure 5-22 and Figure 5-23. Figure 5-22 presents the case where the ol was present and the temperature was ~ 633 K while Figure 5-23 represents an area immediately adjacent to the locus of tubing failure where it is apparent that no ol is present, ~653 K. After the failure, tube wall thicknesses were measured using ultrasound. At 653 K the normally 1.7 mm thick tube wall (3/8" tube with 0.065" wall thickness) was reduced to approximately 0.3 mm in thickness. The ultrasound was not sensitive enough to measure a difference in wall thickness at 633 K - thus it was estimated using Figure 5-22 to be approximately 15 \(\mu\)m. Using equation 5-29 the penetration depths were converted to current densities and are equivalent to corrosion rates of \(1.63 \times 10^{-2} \text{ A.cm}^{-2}\) at 633 K and \(1.52 \text{ A.cm}^{-2}\) at 653 K if \(n\) is set to an average (based on alloy composition - Table 2-1) and approximate value of 3 considering Ni dissolution as Ni\(^{2+}\) and Cr dissolution as a Cr(VI) species. The effective diffusion layer thickness at 633 K was then 14.32 cm at 633 K (!!!) and 1.5 mm at 653 K.

\[
rate(A\cdot cm^{-2}) = \frac{rate(mm/yr) \times nP_{alloy} \times 3.06 \times 10^{-4}}{M_{alloy}}
\]

5-29
At 633 K, an effective diffusion length of 14.32 cm points to the formation of a low void fraction and high tortuosity precipitate. This can be explained by introducing the effective inter-diffusivity, $D_{O_2, \text{eff}}$, which accounts for the void fraction in the material, $\omega$ (here the porous outer layer) and the tortuosity, $\tau$ [Poirier 1994]:

$$D_{O_2, \text{eff}} = D_{O_2} \left( \frac{\omega}{\tau} \right)$$  \hspace{1cm} 5-30

With $D_{O_2} = 9.13 \times 10^{-4} \text{ cm}^2.\text{s}^{-1}$ (Appendix D) at 633 K, $\omega = 0.001$ - approximately one one hundredth the porosity given for piled glass spheres - and $\tau = 8$, a value often used for compacted particles, $D_{O_2, \text{eff}} = 1.14 \times 10^{-7} \text{ cm}^2.\text{s}^{-1}$. If equation 5-12 is once again used to calculate the diffusion layer thickness with the new value for the effective inter-diffusivity, one obtains $(\delta)_T \sim 15 \mu\text{m}$ which is the thickness of the precipitated ol as measured from the micrograph. In other words, the available area for oxygen diffusion can be accounted for by either a large effective diffusion length or a decreased effective inter-diffusivity.

The value obtained at 653 K can be compared to an estimated value of the mass transfer coefficient obtained from analogy to the heat transfer coefficient as proposed by Rogak and Teshima [Rogak 1999] and based on the correlation proposed by Swenson et al. for the Nusselt number in supercritical water [Swenson 1965]:

$$\frac{2V_D r}{D_{O_2}} = 0.00459 \left( \frac{2Gr}{\mu_w} \right)^{0.923} \left( \frac{\mu_w}{\rho_w D_{O_2}} \right)^{0.613} \left( \frac{\rho_w}{\rho_b} \right)^{0.231}$$  \hspace{1cm} 5-31

where $V_D = D_{O_2} / \delta$ is the mass transfer coefficient in m.s$^{-1}$, $r$ is the tube radius in m, $G$ is the mass flow rate per unit area in kg.s$^{-1}$.m$^{-2}$ (270 kg.s$^{-1}$.m$^{-2}$), $\mu_w$ is the viscosity of
water at the wall of the tube in Pa.s ($5.24 \times 10^{-5}$ Pa.s) and, $\rho_w$ and $\rho_b$ are the density of water at the wall and in the bulk in kg.m$^{-3}$ (340 and 380 kg.m$^{-3}$), respectively. For the purposes of the calculations performed here it is assumed that the difference between the bulk and wall temperatures is ~ 10 K in agreement with findings by Rogak and Teshima [Rogak 1999]. Solving equation 5-30 for $\delta = D_{o_2}/V_D$ yields a value of ~ 0.08 mm, or a factor of 18 smaller than the value (1.5 mm) calculated according to the diffusion limited corrosion rate. This observed difference is likely due to the fact that at 653 K the corrosion reaction is still somewhat impeded by a very thin oxide film precipitate which was either lost during sample preparation or undetectable by SEM. However, factors such as viscosity and density which were used in equation 5-30 can only be considered rough estimates in that they do not account for dissolved metals, precipitates in solution, organic phase solubility etc. Thus the difference between the two values is judged to be acceptable and certainly points to a range of diffusion layer thicknesses which might be used for further corrosion rate estimations: ~ 0.1 to 1.5 mm.
Figure 5-22  SEM micrograph of outer chromium oxide layer (precipitated) on the surface of alloy 625 exposed to ammoniacal sulphate solution at 250 bar, ~633 K.
Figure 5-23  SEM micrograph of inner surface of alloy 625 tubing exposed to ammoniacal sulphate solution at 250 bar, ~ 653 K.

5.3 Summary

The results of the electrochemical work into the effect of oxygen concentration on the corrosion of alloy 625 in ammoniacal solution between 298 and 473 K can be summarized as follows:

1. As temperature and pressure are increased, $E_{corr}$ and $i_{corr}$ both also increase while the passive region for alloy 625 gets smaller.

2. $E_t$ does not vary much in the tested temperature range because pH is seen to decrease with increasing temperature.
3. O$_2$ sparging time played a significant role in determining $E_{\text{corr}}$ and $E$, by increasing the equilibrium potential for the oxygen reduction reaction and by displacing dissolved ammonia and acidifying the solution.

4. Limiting current measurements confirmed that O$_2$ diffusion lengths were considerably affected by the precipitation of the ol which is in turn believed to be thickened by increased corrosion rates (cation ejection) resulting from $E_{\text{corr}}$ values near $E_r$.

5. Exchange current densities for the oxygen reduction reaction were found to increase from $\sim 1 \times 10^{-16}$ at 298 K to $\sim 1 \times 10^{-9}$ A.cm$^{-2}$ at 473 K.

6. At 398 K and above, corrosion rates increased with increasing pressure due to the proximity of $E_{\text{corr}}$ to $E_r$, and in one case ($P_{\text{TOTAL}} > 40$ bar, $T \sim 373$ K) it is believed that the inversion temperature was actually exceeded.

7. Mott-Schottky analysis showed that the bl on alloy 625 is p-type i.e. cation conducting. Field strengths were estimated at between $2 \times 10^6$ and $7 \times 10^6$ V.cm$^{-1}$ and this increase was commensurate with decreasing solution pH as temperature was increased.

8. The corrosion rate was shown to be increasingly diffusion controlled as temperature and pressure were increased such that corrosion rates under SCWO conditions are probably controlled by the precipitated ol and can be safely modeled by limiting currents due to oxygen diffusion. The barrier layer is likely not present on alloy 625 in a SCWO reactor.

9. Oxygen concentrations at 250 bar and at high-subcritical temperatures were calculated in order to estimate diffusion lengths near the sub- to supercritical
transition. At 633 K we have estimated a diffusion length of ~14 cm due to the presence of a thick and tortuous ol while at 653 K the diffusion length was found to be in the range of ~0.1 to 1.5 mm.
6 THERMODYNAMICS OF THE Ni-H2O-NH3 SYSTEM

Under circumstances where the Cr₂O₃ passive film (bl or ol) is not expected to be stable Ni-Cr alloys rely on the formation of a NiO film. In the presence of ammonia, alloy 625 appears to be susceptible to preferential Ni dissolution, even at neutral pH. It is also of considerable interest to explore the influence of sulphate on the Ni-H₂O-NH₃ system as it may affect the solution pH at near critical temperatures. Lastly, as previously discussed, Pourbaix diagrams are increasingly important as the critical point is approached due to the onset of diffusion limited corrosion. This section will address the issue of NiO stability at high temperatures and delve into the issue of pH.

6.1 Calculations

Speciation and Pourbaix diagrams were constructed for the Ni-NH₃-H₂O system at 373, 473, 573 and 653 K. The method used for calculating high temperature Pourbaix diagrams is described in detail elsewhere [Cowan 1971], [Lee 1981], [Taylor 1978]. Generally, the standard chemical potential of species i at temperature T, \( \mu_{i,T} \), was determined through the use of equation 6-1:

\[
\mu_{i,T} = \mu_{i,298} + \int_{298}^{T} C_i \, dT - T \int_{298}^{T} \frac{C_i}{T} \, dT - \Delta T S_{298} \quad \text{(6-1)}
\]
Where $\mu_{i,298}$ is the absolute chemical potential of species $i$ at 298 K, $\overline{C_p}$ is the average partial molal heat capacity over the temperature increment $T - 298$ K, and $S^0_{298}$ is the standard partial molal entropy at 298 K. A literature search was undertaken for each species considered in this work to find the best ways of estimating $\mu_{i,T}$ either directly, or through eqn. 6-1, in which case the estimation of $\overline{C_p}$ was required. Table 6-1 lists all of the relevant $C_p$ equations, $\mu_{i,298}$ and $S^0_{298}$ used in this work while the reactions identified as relevant through the speciation study are listed in Table 6-2. The following sections will describe the methodology used in the calculation of the Pourbaix diagrams.
Table 6-1 Thermodynamic data used for Pourbaix diagram calculations

<table>
<thead>
<tr>
<th>Species</th>
<th>$\mu_{i,298}^0$, kJ.gmol$^{-1}$</th>
<th>$C_p(T)$, J.K$^{-1}$</th>
<th>$S_{i,298}^0$, J.(gmol.k)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0</td>
<td>22.496 + 17.044x10$^{-3}$T + 0.365x10$^3$T$^{-2}$ + 11.122x10$^{-6}$T$^2$</td>
<td>130.68</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>22.06 + 20.887x10$^{-3}$T + 1.621x10$^3$T$^{-2}$ - 8.207x10$^{-6}$T$^2$</td>
<td>205.15</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>237.14</td>
<td>186.88 - 464.25x10$^{-3}$T - 19.57x10$^5$T$^{-2}$ + 548.63x10$^{-6}$T$^2$</td>
<td>69.95</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>157.40</td>
<td>-</td>
<td>-10.71</td>
</tr>
<tr>
<td>H$^+$</td>
<td>0</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>16.27 + 36.758x10$^{-3}$T + 0.167x10$^5$T$^{-2}$ - 16.154x10$^{-6}$T$^2$</td>
<td>29.80</td>
</tr>
<tr>
<td>NiO</td>
<td>211.75$^d$</td>
<td>-</td>
<td>37.99$^f$</td>
</tr>
<tr>
<td>Ni$_3$O$_4$</td>
<td>-713.36$^e$</td>
<td>$^a$140.838 + 17.177x10$^{-3}$T - 24.38x10$^5$T$^{-2}$ + 54.02x10$^{-6}$T$^2$</td>
<td>114.27$^b$</td>
</tr>
<tr>
<td>Ni$_2$O$_3$</td>
<td>-470.51$^e$</td>
<td>$^a$143.566 - 36.323x10$^{-3}$T - 31.433x10$^5$T$^{-2}$ + 71.792x10$^{-6}$T$^2$</td>
<td>87.84$^b$</td>
</tr>
<tr>
<td>NiO$_2$</td>
<td>-215.75$^e$</td>
<td>$^a$69.454 + 10.209x10$^{-3}$T - 16.234x10$^5$T$^{-2}$ + 0x10$^{-6}$T$^2$</td>
<td>58.73$^b$</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>-45.72$^f$</td>
<td>LIHCA: $C_p = 0.84T$</td>
<td>-128.9$^f$</td>
</tr>
<tr>
<td>HNiO$_2$</td>
<td>-343.23$^d$</td>
<td>-</td>
<td>-150.72$^h$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_2$</td>
<td>-85.90$^g$</td>
<td>LIHCA: $C_p = 0.61T$ and Ni model: $C_p = 0.23T$</td>
<td>11.31$^f$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_2$</td>
<td>-127.90$^f$</td>
<td>LIHCA: $C_p = 0.49T$ and Ni model: $C_p = 0.12T$</td>
<td>85.40$^f$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_3$</td>
<td>-160.70$^g$</td>
<td>LIHCA: $C_p = 0.30T$ and Ni model: $C_p = -0.047$</td>
<td>199.07$^e$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_4$</td>
<td>-193.61$^g$</td>
<td>LIHCA: $C_p = 0.20T$ and Ni model: $C_p = -0.137$</td>
<td>258.60$^f$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_5$</td>
<td>-223.90$^g$</td>
<td>LIHCA: $C_p = 0.07T$ and Ni model: $C_p = -0.247$</td>
<td>335.50$^g$</td>
</tr>
<tr>
<td>Ni(NH$_3$)$_6$</td>
<td>-255.70$^f$</td>
<td>LIHCA: $C_p = -0.03T$ and Ni model: $C_p = -0.337$</td>
<td>394.64$^f$</td>
</tr>
</tbody>
</table>
From the database assembled by Roine unless otherwise specified [Roine 2002]; a $C_p(T)$ functions for Ni$_3$O$_4$, Ni$_2$O$_3$ and NiO$_2$ were not available so they were assigned the function for Co$_3$O$_4$, Fe$_2$O$_3$ and MnO$_2$, respectively; b $S_{i,298}^0$ values for Ni$_3$O$_4$, Ni$_2$O$_3$ and NiO$_2$ were not available so they were estimated using equation 6-3 and the entropy data for [Roine 2002] Co$_3$O$_4$, Fe$_2$O$_3$ and MnO$_2$, respectively; c $S_{i,298}^0$ for Ni(NH$_3$)$_2^{2+}$ and Ni(NH$_3$)$_3^{2+}$ was not available so it was estimated using equation 8-2 and the entropy value$^{38}$ for Cu(NH$_3$)$_2^{2+}$ and Cu(NH$_3$)$_3^{2+}$; d Calculated from Tremaine and Leblanc [Tremaine 1980]; e Data taken from the Pourbaix Atlas; f Data taken from the NBS Tables [Wagman 1982]; g Calculated from Smith and Martell, eqns. 10-11 [Smith 1977]; h From Shock [Shock 1997].
Table 6-2 Some of the reactions considered and their calculated standard electrode potentials.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$E^0_{\text{r}, V_{\text{SHE}}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>298 K</td>
</tr>
<tr>
<td>a)</td>
<td>$2H^+ + 2e^- = H_2$</td>
<td>0</td>
</tr>
<tr>
<td>b)</td>
<td>$O_2 + 4H^+ + 4e^- = 2H_2O$</td>
<td>1.23</td>
</tr>
<tr>
<td>1</td>
<td>$Ni^{2+} + 2e^- = Ni$</td>
<td>-0.23</td>
</tr>
<tr>
<td>2</td>
<td>$Ni(NH_3)_2^{2+} + H^+ + 2e^- = Ni + NH_4^+$</td>
<td>-0.03</td>
</tr>
<tr>
<td>3</td>
<td>$Ni(NH_3)_2^{2+} + 2H^+ + 2e^- = Ni + 2NH_4^+$</td>
<td>0.16</td>
</tr>
<tr>
<td>4</td>
<td>$Ni(NH_3)_4^{2+} + 4H^+ + 2e^- = Ni + 4NH_4^+$</td>
<td>0.64</td>
</tr>
<tr>
<td>5</td>
<td>$Ni(NH_3)_6^{2+} + 6H^+ + 2e^- = Ni + 6NH_4^+$</td>
<td>1.14</td>
</tr>
<tr>
<td>6</td>
<td>$Ni(NH_3)_2^{2+} + 2e^- = Ni + 2NH_3$</td>
<td>-0.39</td>
</tr>
<tr>
<td>7</td>
<td>$Ni(NH_3)_6^{2+} + 2e^- = Ni + 6NH_3$</td>
<td>-0.5</td>
</tr>
<tr>
<td>8</td>
<td>$NiO + 2H^+ + 2e^- = Ni + 2H_2O$</td>
<td>0.13</td>
</tr>
<tr>
<td>9</td>
<td>$HNiO_2$ + $3H^+ + 2e^- = Ni + 2H_2O$</td>
<td>0.68</td>
</tr>
<tr>
<td>10</td>
<td>$NiO_2 + H^+ + 2e^- = HNiO_2^+$</td>
<td>0.66</td>
</tr>
<tr>
<td>11</td>
<td>$Ni_2O_3 + H_2O + 2e^- = 2HNiO_2^+$</td>
<td>-0.11</td>
</tr>
<tr>
<td>12</td>
<td>$Ni_3O_4 + 2H_2O + 2e^- = 3HNiO_2^ + H^+$</td>
<td>-0.81</td>
</tr>
<tr>
<td>13</td>
<td>$Ni_3O_4 + 18NH_3 + 8H^+ + 2e^- = 3Ni(NH_3)_6^{2+} + 4H_2O$</td>
<td>2.73</td>
</tr>
<tr>
<td>14</td>
<td>$Ni_3O_4 + 6NH_3 + 8H^+ + 2e^- = 3Ni(NH_3)_2^{2+} + 4H_2O$</td>
<td>2.39</td>
</tr>
<tr>
<td>15</td>
<td>$Ni_3O_4 + 2H^+ + 2e^- = 3NiO + H_2O$</td>
<td>0.83</td>
</tr>
<tr>
<td>16</td>
<td>$Ni_3O_4 + 6NH_4^ + 2H^+ + 2e^- = 3Ni(NH_3)_2^{2+} + 4H_2O$</td>
<td>0.75</td>
</tr>
<tr>
<td>Reaction</td>
<td>$\Delta G$ (kJ/mol)</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>---------------------</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 3NH_4^+ + 5H^+ + 2e^- = 3Ni(NH_3)^{2+} + 4H_2O$</td>
<td>1.33 1.26 0.97 0.46 0.64</td>
<td></td>
</tr>
<tr>
<td>$NiO_4 + 8H^+ + 2e^- = 3Ni^{2+} + 4H_2O$</td>
<td>1.91 1.80 1.58 1.30 1.24</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 12NH_4^+ + 2e^- = 2Ni(NH_3)_6^{2+} + 3H_2O + 6H^+$</td>
<td>-1.03 -1.26 -1.88 -2.84 -4.26</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 8NH_4^+ + 2e^- = 2Ni(NH_3)_4^{2+} + 3H_2O + 2H^+$</td>
<td>-0.03 -0.18 -0.62 -1.34 -1.47</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 4NH_4^+ + 2H^+ + 2e^- = 2Ni(NH_3)_2^{2+} + 3H_2O$</td>
<td>0.93 0.84 0.54 0.05 0.25</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 2NH_4^+ + 4H^+ + 2e^- = 2Ni(NH_3)_2^{2+} + 3H_2O$</td>
<td>1.32 1.28 1.07 0.69 0.75</td>
<td></td>
</tr>
<tr>
<td>$NiO_3 + 6H^+ + 2e^- = 2Ni^{2+} + 3H_2O$</td>
<td>1.71 1.63 1.47 1.24 1.15</td>
<td></td>
</tr>
<tr>
<td>$2NiO_2 + 2H^+ + 2e^- = NiO_3 + H_2O$</td>
<td>1.43 1.44 1.40 1.31 1.18</td>
<td></td>
</tr>
<tr>
<td>$NiO_2 + 6NH_3 + 4H^+ + 2e^- = Ni(NH_3)_6^{2+} + 2H_2O$</td>
<td>1.84 1.75 1.40 0.82 -0.09</td>
<td></td>
</tr>
<tr>
<td>$NiO_2 + 6NH_4^+ + 2e^- = Ni(NH_3)_6^{2+} + 2H_2O + 2H^+$</td>
<td>0.20 0.09 -0.24 -0.77 -1.54</td>
<td></td>
</tr>
<tr>
<td>$NiO_2 + 4H^+ + 2e^- = Ni^{2+} + 2H_2O$</td>
<td>1.57 1.54 1.44 1.27 1.17</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$pH_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 6.09 5.58 5.57 7.59</td>
</tr>
<tr>
<td>9.27 7.46 5.82 4.64 3.72</td>
</tr>
<tr>
<td>6.37 4.87 4.35 4.89 2.91</td>
</tr>
<tr>
<td>6.37 5.53 5.22 5.31 3.68</td>
</tr>
<tr>
<td>7.98 6.69 6.03 5.92 6.47</td>
</tr>
<tr>
<td>8.29 7.13 6.53 6.41 10.61</td>
</tr>
<tr>
<td>13.67 10.69 9.92 5.66 -1.92</td>
</tr>
<tr>
<td>9.08 7.28 5.68 4.55 4.56</td>
</tr>
<tr>
<td>11.98 9.54 6.71 4.10 4.98</td>
</tr>
</tbody>
</table>
6.1.1 Condensed Ni phases

The experimentally determined solubility constants, \( K_{sp} \), by Tremaine and LeBlanc [Tremaine 1980] were used to determine the chemical potentials of NiO at all temperatures, \( \mu_{NiO,T} \), according to equation 6-2:

\[
\Delta G^\circ_T = -RT \ln K_{sp} = \mu_{Ni^{2+},T} + \mu_{H_2O,T} - \mu_{NiO,T} - 2\mu_{H^+,T}
\]

Standard chemical potentials at 298 K for \( Ni_3O_4 \), \( Ni_2O_3 \) and \( NiO_2 \) were found in the Pourbaix Atlas. Because the heat capacity as a function of temperature was not readily available for these species, Kelley functions [Kelley 1934] for species with similar molecular weights and chemical formulas (Table 6-1) were relied on to obtain the average heat capacity. Similarly, where \( S^0_{298} \) data were not available, they were estimated using a method suggested by Latimer [Latimer 1938]:

\[
S^0_{298,A} - S^0_{298,B} = \frac{3}{2} R \ln \frac{M_A}{M_B}
\]

Where \( M_X \) is the atomic weight of species \( X = A \) or \( B \) and \( R \) is the gas constant. The Kelley function for the heat capacity of Ni is available in the extensive thermochemical database compiled by Roine [Roine 2002].

6.1.2 Ionic Ni species

Conventional partial molal properties for many aqueous Ni species at room temperature are available in the NBS tables [Wagman 1982]. The Criss-Cobble ionic entropy correspondence principle is generally used to estimate the average heat
capacities for ionic species at high temperatures [Criss 1964A, B]. Cowan and Staehle as well as Taylor have shown that this method is valid up to 573 K [Cowan 1971], [Taylor 1978]. They used the Criss-Cobble theory to calculate standard electrode potentials for the Ag/AgCl $H^+/H_2$ cell between 298 and 573 K and compared these results to the experimentally measured values of Greeley [Greeley 1960]. Theoretical values for $E^0$ were within $\pm 20\%$ of experimentally determined values as calculated by Cowan and Staehle and within $\pm 10\%$ as calculated by Taylor with smoothed experimental data. Clearly, thermodynamic estimations of this nature will ignore activity changes and partial molal volume changes which undoubtedly result in errors; however Criss and Cobble have shown that these effects can be ignored up to 573 K [Criss 1964B]. In this work, three separate methods were used to estimate the partial molal chemical potential of Ni$^{2+}$: the Lewis linearization of the Criss-Cobble method [Lewis 1970], the revised Helgeson-Kirkham-Flowers model (HKF) [Shock 1988, 1997], [Tanger 1988] and the experimentally derived conventional Gibbs energy increments proposed by Tremaine and Leblanc [Tremaine 1980].

The Lewis linearization of the Criss-Cobble theory for heat capacity has also been referred to as the Linear Ionic Heat Capacity Approximation (LIHCA) [Taylor 1978] and is given by the following equations (Table 6-1):

$$C_p(T) = b_1 T$$  

$$b_1 = e + gS^{0,abs}_{298}, \text{ in J.mol}^{-1}.K^{-1}$$  

$$S^{0,abs}_{298} = S^0_{298} - 20.92Z$$
Where \( e \) and \( g \) depend on the ion type (simple cation, simple anion, oxy-anion etc.) and have the units J.mol\(^{-1}\).K\(^{-2}\) and K\(^{-1}\), respectively. The number -20.92 represents the absolute entropy of the H\(^+\) ion in J.mol\(^{-1}\).K\(^{-1}\) at 298 K.

The HKF model has the advantage of being an equation of state which can account for partial molal volume changes and is reported to be accurate up to 1273 K, 5 kBar. The model is comprehensive and allows for the calculation of all relevant ionic partial molal properties. In the HKF, the conventional Gibbs energy is given by

\[
\Delta G_{p,T}^0 = \Delta G_f^0 - S_{p,T}^0 (T - T_r) - c_1 \left[ T \ln \left( \frac{T}{T_r} \right) - T + T_r \right] + a_1 (P - P_r) + a_2 \ln \left( \frac{\psi + P}{\psi + P_r} \right)
\]

\[
+ a_3 (P - P_r) + a_4 \ln \left( \frac{\psi + P}{\psi + P_r} \right) \left( \frac{1}{T - \theta} \right)
\]

\[
- c_2 \left[ \left( \frac{1}{T - \theta} \right) - \left( \frac{1}{T_r - \theta} \right) \right] \left( \frac{\theta - T}{\theta} \right) - \frac{T}{T_r} \ln \left( \frac{T_r (T - \theta)}{T (T_r - \theta)} \right)
\]

\[
+ \omega \left( \frac{1}{\varepsilon} - 1 \right) + \omega_{p,T} \left( \frac{1}{\varepsilon_{p,T}} - 1 \right) + \omega_{p,T} Y_{p,T} (T - T_r)
\]

...6-7

where \( \Delta G_{p,T}^0 = \mu_{i,T}^{0,abs} \), \( \Delta G_f^0 = \mu_{i,298}^0 \) and \( T_r \) and \( P_r \) are the reference temperature and pressure (298 K, 1 bar). The pressure independent parameters \( a_1, a_2, a_3, a_4 \), the temperature independent parameters \( c_1, c_2 \) and the reference Born coefficient \( \omega_{p,T} \) are available in the literature for a great many ionic species [Shock 1988, 1997]. The conventional species dependent Born coefficient \( \omega \) must be calculated at the desired temperature and pressure and is based on the effective electrostatic radius of the ionic species under those conditions [Shock 1988]. The solvent-dependent parameters \( \psi \) and \( \theta \) are equal to 2600 bar and 228 K, respectively, for water. The dielectric constant of water, \( \varepsilon \), is available in the literature. In this work, the tabulated data by Archer and
Wang was used for $\varepsilon$ [Archer 1990]. $Y$ is a Born function given by \( \frac{1}{\varepsilon} \left( \frac{\partial \ln \varepsilon}{\partial T} \right) \) and is equal to \(-5.8 \times 10^{-5} \text{K}^{-1}\) at $T_r$ and $P_r$.

The Tremaine and Leblanc data for Ni$^{2+}$ is available up to 573 K and was considered the most accurate so it was used to calculate the absolute (or standard) chemical potential of this species up to 573 K. It should be noted that because all reaction potentials (or electrode potentials: $E^0$) at a given temperature $T$ are usually reported with respect to the hydrogen evolution reaction (itself set to zero), equation 6-8 was employed to convert partial molal chemical potentials obtained from Tremaine and Leblanc from the conventional scale to the “absolute” scale:

\[
\mu_{i,T}^0 = \mu_{i,T}^{0,\text{abs}} - Z_i \mu_{H^+T}^0
\]

Where $\mu_{H^+T}^0$ refers to the absolute standard partial molal chemical potential of the hydrogen ion at temperature $T$, and $Z_i$ represents the charge of the $i^{th}$ aqueous ion [Tanger 1988]. It might also be mentioned that this equation is valid for all conventional standard partial molal properties such as entropy (eqn. 6-6) or enthalpy, for example. For the calculations at 653 K it was necessary to use the HKF model to estimate $\mu_{Ni^{2+},653K}^0$. In this instance the pressure term in eqn. 6-7 was set to 250 bar. Sensitivity trials were run to evaluate the effect of pressure between 250 and 300 bar on the calculated $\mu_{Ni^{2+},653K}^0$ and it was found that this pressure variation resulted in an approximately 5 kJ difference. Translated to the Pourbaix diagram at 653 K this is equivalent to a pH shift for reaction 33 (Table 6-2) of 0.2.
Until recently it has been standard procedure to use the Criss-Cobble method or its variant, the LIHCA, to calculate the heat capacities of the ammines of Ni to high temperatures. Unfortunately, the use of the original LIHCA for this purpose is predicated on the assumption that these complex ions behave as simple cations. The LIHCA constants for simple cations are then used in the heat capacity calculations. There is a good degree of validity to this argument as ammonia is entirely miscible with water in all proportions and is similarly a protonated solvent. Thus \( Ni(NH_3)_2^{2+} \) is analogous to \( Ni(H_2O)_2^{2+} \). However, to circumvent this assumption the so-called “Ni model” was developed by Osseo-Asare and Asihene and it has fit the equilibrium constants \( K \) measured by Letowski [Letowski 1970] to the LIHCA, thus generating a separate set of constants, cf. Table 6-1 [Osseo-Asare 1981, 2004]. It should be emphasized that this model is solely based on the only available experimental high temperature equilibrium constant data for Ni-ammines and that the temperature of the experimental work was limited to 453 K [Letowski 1970]. Furthermore, the experimental method used in Letowski’s work was EMF measurement. Briefly described, this method used an induced potential difference between two identical electrochemical cells containing ammonium nitrate when a known amount of Ni\(^{2+}\) ions were introduced into one of the cells. However, the use of EMF measurements to calculate \( K \) data relies on an accurate knowledge of the concentration of free \( NH_3 \) at high temperature. Indeed, as Muendel et al. have pointed out, considerable uncertainty about the state of ammonia in solution exists and some means of distinguishing between ammonia \( (NH_3) \) and ammonium \( (NH_4^+) \) should be found when trying to determine equilibrium constants based on EMF measurements [Muendel 1961]. To this end, the
ammoniacal solution from the liquid phase of the autoclave employed by Letowski was sampled at high temperature, condensed to room temperature and then titrated to measure the free NH₃ concentration. Ammonia losses to evaporation are likely. Therefore, due to the sampling procedure, it is probable that the free NH₃ concentration was underestimated. As a result, the Ni model probably underestimates $K$ values.

Thus, while this model is still considered to be the most accurate for the prediction of Ni-ammine heat capacity up to 573 K (it has been used in this work), the stability fields for the Ni-ammines, shown in Figure 6-6 through Figure 6-9 are likely smaller than they ought to be. According to calculations using the Ni model, ammine stability is basically nil at temperatures above ~523 K. The results of the calculations from the Ni model were compared to results using the simple cation constants from the LIHCA and the original Helgeson formula for complex dissociation (Figure 5, eqn. 9) [Helgeson 1967]. This last method was employed because the revised HKF parameters are not available for ammines.

\[
\log K_T = \frac{\Delta S_{298}^0(T_r)}{2.303RT} \left\{ T_r - \theta \left[ 1 - \exp \left( \frac{\exp(b + aT) - c + \frac{T - T_r}{\theta}}{\theta} \right) \right] \right\} - \frac{\Delta H_{298}^0(T_r)}{2.303RT}
\]

The standard reaction enthalpy change, $\Delta H_{298}^0$, and the standard entropy reaction change, $\Delta S_{298}^0$, were taken from the data collected by Smith and Martell at zero ionic strength [Smith 1977]. $\log K_T$ data calculated in this way was then used to calculate $\mu_{Ni(NH_3)}^{0,T}$ (eqn. 6-11). Unfortunately $\mu_{t_{298}}^{0}$ data for some of the ammines, necessary for eqn. 6-1, were not available so they were calculated from $\log K_{298}$ values, also published by Smith and Martell, also through the use of equations 6-10 and 6-11.
\[ Ni(NH_3)_v^{2+} = Ni^{2+} + vNH_3 \]  

\[ \Delta G^0_T = -2.3RT \log K_T = (\mu_{Ni^{2+},T}^0 + v\mu_{NH_3,T}^0) - \mu_{Ni(NH_3)_v^{2+},T}^0 \]

The chemical potential of the dinickelate ion, \( \mu_{HNiO_2^-,T} \), was calculated at all temperatures through the use of the revised HKF model [Shock 1997]. The dinickelate ion (\( HNiO_2^- \)) is the traditional notation for the hydrolyzed anionic Ni(II) complex and is generally used in Pourbaix diagrams; this is the notation we have conserved here. It should be mentioned that Beverskog and Puigdomenech, Beas and Mesmer and Tremaine and Leblanc have preferred to use \( Ni(OH)_3^- \), which results in smaller stability regions for this species [Beverskog 1997], [Beas 1976]. Furthermore, this species was omitted from the diagram at 653 K. This was deemed prudent as there is a great degree of uncertainty involved in the prediction of complex oxyanions at supercritical conditions [Kriksunov 1993, 1995].

### 6.1.3 Ammonia

The chemical potentials of ammonia (\( \mu_{NH_3,T} \)) and ammonium (\( \mu_{NH_4^+,T} \)) were calculated using the HKF [Plyasunov 2001]. Because the Born coefficient, \( \omega \), is independent of temperature and pressure for aqueous neutrals, it can be replaced in eqn. 6-7 by \( \omega_{H,T} \), which is \(-6.5 \times 10^5 \) J/mol for NH\(_3\) [Shock 1997].
6.2 Pourbaix diagrams

Speciation results used for the Pourbaix diagrams are presented in Figure 6-1 through Figure 6-4. The speciation at 653 K, according to the Ni model for ammine stability (Figure 6-4) is contrasted to the results from the original Helgeson equation for complex dissociation (eqn. 6-9) in Figure 6-5. Pourbaix diagrams for the Ni-NH$_3$-H$_2$O system at 373, 473, 573 and 653 K are presented in Figure 6-6 through Figure 6-9. To simplify the diagrams only the ammine-, diammine-, tetraammine- and hexaammine-nickel species are presented. Their regions of stability are numbered on the diagrams as 1, 2, 4 and 6, referring to the number of NH$_3$ ligands associated with each Ni$^{2+}$ ion. Oblique hatched lines labelled $a$ and $b$ refer to the hydrogen evolution and oxygen reduction lines, respectively. There are also two vertical hatched lines on each diagram, labelled $c$ and $d$ which represent the neutral pH at temperature $T$ and the ammonia buffer point at temperature $T$, respectively. The neutral pH ($pH_T = -\frac{1}{2} \log K_w$) was determined with the ion product of water ($K_w$) data published by Marshall and Franck [Marshall 1981]. For all diagrams the total ionic nickel concentration, $[Ni(aq)]_{tot}$, was $10^{-6}$ m and the total ammonia concentration: $[NH_3]_{tot} = 1.5$ m. The ammonia buffer point corresponds to the equilibrium between $NH_4^+$ and $NH_3$:

$$NH_3 + H^+ = NH_4^+ \tag{6-12}$$
Figure 6-1  Aqueous Ni speciation at 373 K, using Osseo-Asare Ni model.

\[ [Ni^{2+}] = 1 \times 10^{-6} \, m, \quad [NH_3]^\ominus = 1.5 \, m. \]
Figure 6-2  Aqueous Ni speciation at 473 K, using Osseo-Asare Ni model.

\[[\text{Ni}^{2+}]_r = 1 \times 10^{-6} \text{ m}, \ [\text{NH}_3]_r = 1.5 \text{ m} \].
Figure 6-3  Aqueous Ni speciation at 573 K, using Osseo-Asare Ni model.

\[ [Ni^{2+}]_T = 1 \times 10^{-6} m, [NH_3]_T = 1.5 m. \]
Figure 6-4 Aqueous Ni speciation at 653 K, using Osseo-Asare Ni model.

\[ [Ni^{2+}]_r = 1 \times 10^{-6} \, m, \quad [NH_3]_r = 1.5 \, m. \]
Figure 6-5  Aqueous Ni speciation at 653 K, using original Helgeson model (eqn.6-9).

\[
[Ni^{2+}]_r = 1 \times 10^{-6} \text{ m}, \ [NH_3]_r = 1.5 \text{ m}.
\]
Figure 6-6 Pourbaix diagram for the Ni-H₂O-NH₃ system, 373 K. \([Ni^{2+}] = 1 \times 10^{-6} m\), \([NH_3] = 1.5 m\). Line c represents the neutral pH for water while line d represents the \(NH_3 / NH_4^+\) equilibrium.
Figure 6-7 Pourbaix diagram for the Ni-H$_2$O-NH$_3$ system, 473 K.. $[\text{Ni}^{2+}] = 1 \times 10^{-6} \, \text{m}$, $[\text{NH}_3] = 1.5 \, \text{m}$. Line c represents the neutral pH for water while line d represents the $\text{NH}_3 / \text{NH}_4^+$ equilibrium.
Figure 6-8 Pourbaix diagram for the Ni-H₂O-NH₃ system, 573 K. \([Ni^{2+}]_T = 1 \times 10^{-6} \text{ m}, [NH_3]_T = 1.5 \text{ m}\). Line \(c\) represents the neutral \(pH\) for water while line \(d\) represents the \(NH_3/NH_4^+\) equilibrium.
Figure 6-9 Pourbaix diagram for the Ni-H₂O-NH₃ system, 653 K. \([Ni^{2+}]_T = 1 \times 10^{-6} \text{ m}\), \([NH_3]_T = 1.5 \text{ m}\). Line e represents the neutral pH for water while line d represents the \(NH_3 / NH_4^+\) equilibrium.

It is important to note that the diagrams presented here are valid for ideal systems of pure substances and take no account of the kinetics of reaction (for instance rate of oxide growth versus dissolution), activity coefficients, and localized phenomena which may affect the corrosion morphology and behaviour. Furthermore, the potential/pH behaviour of alloy 625 is certainly different from that of nickel. These diagrams do, however, offer a good guideline for the study of alloy 625 as nickel is its main constituent.
There is a marked shrinking of the region of immunity for Ni as temperature is increased; this enlargement of the metal cation stability field has also been noticed by Kriksunov and Macdonald for Ni and Fe [Kriksunov 1993, 1997]. In contrast, the regions of stability for NiO and complex oxyanion increase with temperature. A large region of stability exists for nickel ammines between approximately pH 5 and 11 at 373 K and pH 4 and 7 at 473 K (Figure 6-6 and Figure 6-7). At the temperature increments considered in this work, and according to the Ni-model calculations, the stability field for the ammines disappears between 473 and 573 K. This is a finding which is consistent with the current published literature as ammine stability constants are known to decrease in aqueous solutions [Isaev, 1990], [Letowski 1970], [Osseo-Asare 1981, 2004]. Figure 6-10 presents the stability constants of the ammine-nickel species as a function of temperature and method of calculation. Clearly there is a wide variation in the predicted stability depending on the method used to extrapolate chemical potentials. Generally the calculations are in trend agreement with those presented by Osseo-Asare, in that the Helgeson complex dissociation method (equation 6-9) predicts higher stability for ammines than both the LIHCA and the Ni-model [Osseo-Asare 2004]. There is, however, a surprising disagreement between the Ni-model as calculated here and the original Letowski stability constants on which this model is based. This is clearly a reflection on the differences between the thermodynamic data which was used to derive the Ni-model and that used in this work. For instance, the Ni-model is based on Letowski’s experimental reference data (\( \Delta H_{298}^0 \) and \( \Delta S_{298}^0 \)) whereas the data provided by Smith and Martell was used here. It is interesting to note that even Letowski’s \( \log K_{298} \) data is consistently lower than the Smith and Martell data - which lends further weight to
the argument that the Ni-model represents a lower bound on the stability limits of the Ni ammines. As such, the Pourbaix diagrams presented here can be considered a conservative estimate for the stability of these species. Referring to Figure 6-4 and Figure 6-5 it is clear that the use of the original Helgeson model (eqn. 6-9) for complex dissociation would lead to regions of stability on the Pourbaix diagram at 653 K for mono- and diammine-nickel between approximately pH 3 and 5.

![Stability constants as a function of temperature and method of calculation](image)

Figure 6-10 Stability constants as a function of temperature ($\log K_{1,T}$) and method of calculation. Letowski’s data has been superimposed:

\[ \log K_{1,T} = -558.42 / T + 9.6953 - 0.0175T \]

Upon closer inspection of Figure 6-9, the issue of ammine stability at 653 K becomes irrelevant. Indeed, the ammonia/ammonium hydrolysis line (line $d$) lies well within the boundary of the $Ni^{2+}$ stability field. If one assumes that the pH at 653 K is
buffered by the ammonia/ammonium equilibrium in the same way as the pH at 298 K
then a solution at pH$_{298K}$ = 10 should be at roughly pH$_{653K}$ = 4, indicating that Ni would
not passivate. This assumption is in fact not baseless. The issue of the significance of
pH under SCWO conditions is somewhat arcane and directly measuring it is difficult
[Macdonald 2001], [Lvov 1998]. There are three interrelated components which must be
considered when estimating pH at high temperature in the NH$_3$-H$_2$O-O$_2$ system
encountered in SCWO reactors: chemical equilibria, gas solubility and phase equilibria
i.e. partial pressures. The three equations determining the chemical equilibria are the
ammonia/ammonium stability (eqn. 6-13), the electroneutrality condition (eqn. 6-14) and
the ion product of water (eqn. 6-15). In the particular case of the experiments conducted
for this work there is also dissolved sulphate which has been included in eqn. 6-14.

\[
[NH_4^+] = \frac{[NH_3]_{tot}[H^+]}{([H^+] + \text{K}_a)} \quad 6-13
\]

\[
[NH_4^+] + [H^+] = [OH^-] + 2[SO_4^{2-}] \quad 6-14
\]

\[
\text{K}_w = [OH^-][H^+] \quad 6-15
\]

Where \( \text{K}_a \) is the ammonia/ammonium equilibrium constant and [ ] designates molal
concentration. Activities have not been considered because they were not considered in
the Pourbaix diagrams. Solving equations 6-13 through 6-15 at 653 K using the
calculated value for \( \text{K}_a = 1.92 \times 10^{-4} \), the ion product of water at 250 bar \( \text{K}_w = 1.67 \times 10^{13} \)
from Marshall and Franck, the concentration of sulphate \( [SO_4^{2-}] = 0.25 \text{ m} \) and \( [NH_3]_{tot} = 1.5 \text{ m} \), one gets a pH$_{653K}$ of 4.04. The solubility and partial pressures of ammonia affect
the available total aqueous ammonia concentration,\( [NH_3]_{tot} \), as determined by Henry's
Law:
As seen previously, SCWO reactors operating at 250 bar maintain a dual phase regime well into the supercritical temperature range (Figure 5-20) because oxygen is only fully miscible with low density/low polarity supercritical water (~ 0.15 g.cm\(^{-3}\)). At 250 bar / 653 K water/oxygen mixture density is approximately 0.4 g.cm\(^{-3}\) and only drops to the process required densities at temperatures close to 873 K. It is well known that ammonia solubility decreases with increasing temperature [Kawazuishi 1987]. As such, ammonia evaporation is possible well into the supercritical region. Using a volumetric equation of state to estimate the infinite dilution Gibbs energy of hydration, Plyasunov et al. have estimated Henry’s constant for NH\(_3\) in the binary NH\(_3\)-H\(_2\)O system up to the critical point and it was found to be ~ 5 bar.kg.mol\(^{-1}\) [Plyasunov 2000]. A thorough discussion of the phase equilibria in the NH\(_3\)-H\(_2\)O-O\(_2\) system is well beyond the scope of this work, however, to get an idea of the effect of varying \(P_{NH_3}\) and [SO\(_4^{2-}\)] at 653 K, equations 6-13 to 6-16 were simultaneously solved for \(pH\) using \(H_{NH_3} = 5\) bar.kg.mol\(^{-1}\). The results are presented in Figure 6-11 where the vertical line represents the pH above which NiO precipitates. In order to keep Ni from corroding (i.e. \(pH > 4.69\)) in the presence of NH\(_3\) and SO\(_4^{2-}\) at 653 K, high values of \(P_{NH_3}\) are required. With the concentration of SO\(_4^{2-}\) used in the SCWO tests at UBC, even \(P_{NH_3} = 20\) bar ([NH\(_3\)]\(_{tot}\) ~ 4 m) is not high enough to ensure Ni passivity. The \(P_{NH_3}\) which led to corrosion in the UBC SCWO reactor was definitely in the range of ~ 0 to 7.5 bar because [NH\(_3\)]\(_{tot}\) could not exceed 1.5 m.

\[
[NH_3]_{tot} = \frac{P_{NH_3}}{H_{NH_3}}
\]
Figure 6-11 Effect of ammonia partial pressure at 653 K, 250 bar. Partial pressures are in bar and $H_{NH_3} = 5$ bar.kg.mol$^{-1}$. Equations 6-13 through 6-16.

Clearly, from a charge balance perspective, if enough ammonia evaporates such that the concentration of ammonium is lower than twice the concentration of sulphate, ~0.5 m, then sulphuric acid would likely form. This is analogous to one of the perennial problems which is known to occur in SCWO reactors when halogenated organics are destroyed: the halogens combine with water to form the corresponding acid. This issue is, however, somewhat besides the point as Figure 6-11 shows that even if all of the available ammonia was in solution, the pH would still be too low to ensure passivation. Alternatively, the scenario represented by $P_{NH_3} = 0$ could be the result of $NH_3$ conversion to $N_2$ however, as mentioned earlier (p. 11), the literature indicates that this is
impossible at 653 K and that even after high residency times at 873 K, \( NH_3 \) is difficult to convert. It appears as though the presence of both \( NH_3 \) at low enough concentrations and \( SO_4^{2-} \) at high enough concentrations will in most cases result in high rates of Ni corrosion in and around the high density supercritical region. These findings are new but entirely in keeping with the literature which has never reported corrosion problems in SCWO experiments containing ammonia alone and has also found that Na\(_2\)SO\(_4\) solutions, for example, result in negligible corrosion rates. In other words, solutions containing \( NH_3 \) alone will maintain a high pH at 653 K (~ 8.5 at \( P_{NH_3} = 7.5 \) bar) due to NH\(_4\)OH stability and thus will ensure that the Ni is kept in its passive range. Similarly, solutions containing \( SO_4^{2-} \) alone in the form of a non-volatile inorganic salt will maintain a neutral pH.

It is clear from the literature and the work shown here that oxygenated SCWO solutions will invariably lead to transpassive corrosion of Ni-Cr alloys. A resolution to this problem could be to inject oxygen in the low-density region of the reactor, thus removing the oxidative conditions to temperatures where oxides are insoluble. Maintaining the stability of NiO would also help in maintaining reactor integrity and it seems as though pH adjustments would be required to this end. Ammonia at high concentrations appears to be somewhat benign from a corrosion standpoint and could easily be recovered at the effluent end of the reactor. Ironically, the injection of \( NH_3 \) to high partial pressures (\( P_{NH_3} > 20 \) bar, figure 7) could therefore be an ideal buffer for mitigating the acidifying effect of \( SO_4^{2-} \) originating from ammoniacal salts or even organic feed stock.
Finally, it should be reiterated here that the definitive stability of Ni-ammines (as discussed on page 128) at ~ 653 K has not been determined as the equilibrium constants employed here may in fact underestimate them. As a result any attempt to regulate pH by ammonia should be preceded by the determination of newer more reliable (at least in this author’s estimation) equilibrium data.

### 6.3 Summary

- Pourbaix diagrams confirm that ammoniacal sulphate solutions can lead to preferential Ni dissolution through the formation of ammines up to approximately 473 K. The Osseo-Assare Ni-model, which is the only published model based on high temperature equilibrium data, predicts that Ni-ammines should become unstable between 473 and 573 K.
- Analysis of Pourbaix diagrams showed that the low ammonia concentration and partial pressures (~ 1.5 m) led to acidification of the feed solution and the dissolution of Ni as Ni\(^{2+}\), thus obviating the formation of NiO.
- The low solubility of ammonia at low supercritical temperatures could also lead to the formation of sulphuric acid when sulphates are present.
- Higher concentrations of ammonia (\(P_{NH_3} > 20\) bar) may result in better materials performance through pH adjustment.
7 CORROSION AT SCWO CONDITIONS

7.1 Failure analysis

During the warm up phase of a test following a run simulating “red water” discharge from a dinitro benzene plant (2,4DNP with ammonium sulphate and free ammonia at pH_{298K} \sim 10, 250 bar), a failure occurred in the first preheater (PH1) of the UBC SCWO reactor at temperatures not exceeding 570 K. On a later cold static pressure test at 500 bar the tube side of the recuperative heat exchanger (RHX) burst. Solutions collected at the sampling ports during the treatment of only 58 litres of the red water solution were blackish in colour and contained a visible particulate which could only be metal precipitates [Vera-Perez 2002]. The highest levels of metals were collected from the PH2 sampling port, immediately down-stream of PH1. In all cases high contents of dissolved nickel, chromium, molybdenum and iron were found (Table 7-1). A wall thickness and SEM/EDX analysis of the failed portions of tubing follows.

Wall thickness measurements were taken using an ultrasound at locations adjacent to the corroded section as well as at the corroded section itself. Four sets of measurements 90° apart were taken every one inch along the tube. Figure 7-1 shows the tube wall thickness and the estimated bulk temperature profiles for PH1 [Vera-Perez 2002]. Material loss was highest in the high density supercritical region, approximately 650 to 655K. Moreover, little to no change in wall thickness occurred within a maximum distance of 0.8m from the failure site. Corrosion below temperatures of 640K and above temperatures of 660K was then not significant.
Figure 7-1  Wall thickness measurements and temperature profile near failed tubing location for PH1 [Vera-Perez 2002]

Table 7-1  Metals content in feed, in sampling ports throughout the reactor (distance from failure) and in the effluent (Eff.), in μg/g [Vera-Perez 2002]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Feed μg/g</th>
<th>5 m</th>
<th>10 m</th>
<th>30 m</th>
<th>55 m</th>
<th>Eff.</th>
<th>Total</th>
<th>% total dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>&lt;0.05</td>
<td>2640</td>
<td>891</td>
<td>437</td>
<td>836</td>
<td>5</td>
<td>4809</td>
<td>14.4</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt;0.2</td>
<td>1020</td>
<td>351</td>
<td>134</td>
<td>1190</td>
<td>&lt;0.2</td>
<td>2695</td>
<td>8.1</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>&lt;0.1</td>
<td>1400</td>
<td>800</td>
<td>344</td>
<td>1120</td>
<td>231</td>
<td>3895</td>
<td>11.7</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;0.05</td>
<td>9520</td>
<td>4710</td>
<td>2230</td>
<td>5350</td>
<td>81</td>
<td>21891</td>
<td>65.8</td>
</tr>
<tr>
<td>Total</td>
<td>&lt;0.4</td>
<td>14580</td>
<td>6752</td>
<td>3145</td>
<td>8496</td>
<td>317</td>
<td>33290</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 7-2  (a) SEM micrograph of epoxy mounted alloy 625 tube section exposed to ammoniacal sulphate solution at ~ 635 K, 250 bar (b) EDX map showing alloy (pink) and Cr enriched ol (blue) and (c) Cr enriched ol (d) line scan showing Ni depletion and Cr enrichment in ol, slight Mo enrichment is also apparent.
Cross sections of the tubing were analyzed using SEM and EDX. Selected samples were etched using a mixture of hydrochloric, acetic and nitric acid to check for sensitization. One of the main reasons alloy 625 is routinely used in high temperature processes is that it is known to have excellent sensitization resistance. Precipitates (niobium carbide and titanium nitride) found at the grain boundaries in the corroded material were similar both quantitatively and qualitatively to the ones found in the drawn condition.

Figure 7-2 shows SEM micrographs and EDX maps of a section of alloy 625 taken from PH1. All the samples shown here were carefully cut from the tubing, epoxy mounted and polished prior to study under the SEM. The sample shown in Figure 7-2 was exposed to temperatures of approximately 635 K in the SCWO reactor i.e. just before the temperature at which the wall thickness measurements started to show thinning (640 K). There is clearly Cr enrichment in the oxide (“oxide” is used here to describe the outer layer, “scale” may also be used) which is some 15 µm thick. Perhaps of most interest is the fact that almost no Ni was found in the oxide. According to these observations and to the calculations presented in Chapter 6, this is indicative of an acidic pH. This finding also echoes, from a qualitative standpoint, the morphology and surface characteristics found by other authors [Schroer2002], [Kritzer 1998]. Moreover, the oxide appears to be defective and the metal/oxide (outer-layer) interface is rough. This is consistent with the idea that the outer layer is formed by precipitation of ejected cations and that it is therefore inherently porous.

In Figure 7-3 and Figure 7-4 morphological evidence of the outer layer’s dissolution is shown. As temperature was increased by only ~ 5 degrees between Figure 7-2 at ~ 635 K and Figure 7-3 at ~ 640 K, oxide heterogeneity including cracks and
macro-porosity were developed. At 645 K (Figure 7-3 (c)) the oxide was even more degraded and magnification reveals what appears to be inter-granular attack (IGA)(Figure 7-3 (d)).

Figure 7-4 shows macroscopically visible surface roughening and wall thinning and confirms that the outer layer was removed between 645 and 660 K. As discussed in Chapter 5, p. 102, it is possible that chemical dissolution of the oxides occurs near ~ 650 K. However, given the current observations with regard to the precipitation of the outer layer and obvious stability of Fe and Cr oxides at SCWO conditions, it seems more likely that a mechanical process occurs to remove the oxide. It is hypothesized that the rate of metal corrosion and grain boundary attack at ~ 658 K (Figure 7-4 (c)) is such that the porous and agglomerated scale (or outer layer) is undermined by the removal of its support (the alloy below it). This would result in precipitates being “let loose” in the reactor and is a probable explanation for the “murky” blackish water observed during the experiment.
Figure 7-3 (a) EDX map overlaid on an SEM micrograph of the oxide layer on the inside surface of alloy 625 tubing exposed to ammoniacal sulphate solution at ~ 640 K, 250 bar. The oxide is visibly cracked. (b) ~ 642 K (c) ~ 645 K (d) ~ 645 K (magnified) showing intergranular attack and Mo enrichment at the oI/s interface (yellow colour)
Figure 7-4 (a) Macroscopically visible surface roughening and only patches of oxide (circled area) are visible at ~ 650 K. (b) 20X optical microscope picture of the bakelite mounted cross section ~ 650 K. Wall thinning is obvious. (c) Approximately 658 K: point of failure. Oxide is either completely removed (not shown here) or deep IGA is apparent. (d) ~ 658 K obvious wall thinning and ductile elongation are visible.
7.2 316 L Stainless steel reactor experiment

7.2.1 Experimental

To determine the effect of ammoniacal sulphate solution on the corrosion characteristics of a commonly used austenitic stainless steel (316 L - Table 2-1) at SCWO conditions, a bench-top SCWO reactor was built. The reactor consisted of a 20 ft (6 m) length of seamless ¼” (6.35 mm) 316 L tubing which was fed by two high pressure piston pumps and heated throughout its length by ceramic heaters. The system was also fitted with an in-line test cell which housed coupons for weight loss measurements on two alloys and two metals (Nb, Ni, Ni - 20 Cr, 625) of interest to this study. A schematic of the apparatus is provided in Figure 7-5 where the test conditions used for the experiment are also shown.

Figure 7-5 Schematic of bench-top SCWO apparatus
The solution used for this experiment was the standard 1.6 m \( NH_3 \), 0.2 m \( SO_4^{2-} \), pH \( \sim 10 \) solution used throughout most of this work. Oxidant was delivered in the form of hydrogen peroxide (H\(_2\)O\(_2\)). Several H\(_2\)O\(_2\) decomposition runs were made prior to the corrosion experiment to ensure that it decomposed to O\(_2\) in an adequately fast manor, so as to provide the desired O\(_2\) concentration in the temperature range of interest \( \sim 653 \) to 673 K and in the test cell. Decomposition rates of up to 50 % were measured at 583 K in distilled water, and a total flow rate (fast) of 170 ml/min. Considering that peroxide decomposition is catalyzed by the reactor tube wall and that the flow rate for the corrosion experiment presented here was roughly 25 mL/min and also that temperatures reached 753 K at the outlet of heater bank 3, it is qualitatively estimated that all of the peroxide was decomposed prior to reaching the test cell which contained the coupons (Figure 7-5). This would yield a concentration of roughly \( C_{oi} = 3 \) m in the supercritical region. This concentration is similar to the one employed in the larger SCWO reactor and which led to failure (\( \sim C_{oi} = 4 \) m, section 7.1, p.146).

The test cell consisted of a 316 L cylindrical vessel mounted in-line with the direction of solution flow. The solution was made to pass through tubular glass sample holders that were designed to stack (horizontally) in the test cell. The sample holders had an inlet diameter which was larger than the outlet diameter. Test coupons were rectangular and approximately 1 cm x 0.5 cm x 1.5 mm so as to fit inside the larger diameter section of the glass holders, but also so as not to fit through the smaller diameter section. A schematic of the test cell is given in Figure 7-6. The glass holders were necessary to remove any possibility of galvanic interaction.
The tested coupons were ground to 600 SiC, cleaned, dried and weighed prior to being put in the test cell.

The bench-top system was brought to temperature with distilled water over a period of approximately 1 hour such that the temperature at the exit of heater bank 4 was ~ 673 K. The temperature profile was also arranged so that high-density supercritical fluid was obtained within the 316 L tubing, i.e. the fluid was low- density supercritical in bank 4 and high-density supercritical in bank 3 and in the test cell (Figure 7-5). Temperature was measured by thermocouples on the outside of the tubing and the whole system was well insulated. The temperature inside the tube was assumed to be roughly the same as that of the thermocouples. As the hot fluid exited heater bank 4 it went directly into the test cell (Figure 7-5). Because the test cell was insulated but not heated, the incoming fluid was cooled as it passed the samples. The test cell was thermocoupled in six locations and temperatures measured on the surface of the cell and at the solution exit did not go below 653 K. It can then be safely assumed that the temperature in the cell was between 653 and 673 K – exactly the temperature range of interest.
7.2.2 Results and discussion

After the ~1 hour heat-up period, the influent feed stream was switched from distilled water to the ammoniacal sulphate solution and hydrogen peroxide mixture. Within approximately 10 minutes oxygen bubbles were visible in the G/L separator (made from transparent acrylic). Approximately 35 minutes later the reactor effluent became dark brown in colour and contained suspended solids. Moreover, the system became unstable; temperatures decreased and pressure rose. The experiment was terminated and the system was flushed with distilled water and allowed to cool for 40 minutes.

The effluent was collected and filtered to remove suspended solids. The filtrate was sent for inductively coupled plasma analysis to determine dissolved metals. The filtered cake was dried and weighed and it was found that 11.1 grams of solids had been removed from the reactor. The solids were analyzed by EDX and found to contain approximately 33 wt% O₂, 26 wt% Fe, 22 wt% Cr, 8 wt% Ni, 5 wt% S and 4.3 wt% Mo. It was thus determined that roughly 6.9 grams of stainless alloy had been corroded in the 45 minute time period for which it was exposed to the ammoniacal solution. If the entire surface area of the 6 m tube had corroded evenly this would mean a corrosion rate of approximately 140 mm.yr⁻¹ or complete tube dissolution in roughly 78 hours. If the 1.5 m length of tube exposed to the high-density supercritical solution is considered, the corrosion rate becomes 560 mm.yr⁻¹, or wall thickness penetration in 20 hours. Of course, in reality the length of tube affected is likely smaller than either of these
calculations would suggest such that the corrosion rate is obviously completely unacceptable. The dissolved metals concentrations are presented in Table 7-2.

Table 7-2  Concentrations of dissolved metal after SCWO experiment in 316 L tube

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg.L⁻¹</td>
<td>0.5 ± 0.11</td>
<td>0.17 ± 0.05</td>
<td>1.18 ± 0.03</td>
<td>1.28 ± 0.01</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

The order of solubility was Mo > Ni > Fe > Cr > Nb. This is similar to the order for the effluent concentrations collected from the tubing failure presented in section 7.1, Mo > Ni > Cr. This finding is also consistent with the room temperature polarization experiments which showed that Mo corroded readily in ammoniacal sulphate solution while the passive current on Ni was higher than that on Cr (Figure 4-7). The high rate of Ni and Mo dissolution (mostly as compared to Fe) is surprising given that the alloy concentrations are so minor: for 316 L Ni ~ 12 wt%, Mo ~ 2.5 wt%.

The alloy 625, Ni-20Cr, Nb and Ni samples were removed from the test cell with great difficulty. It was found that the glass sample holders had expanded within the cell and fused themselves to its wall. Also, it was observed that the glass had either fragmented under the expansion pressure or reacted with the solutions to form compact and sand-like powder. To extract the coupons the test cell was carefully face milled until the exposed glass holders were visible. The sand like product was then removed with an acid brush and the samples were collected.

The exposed coupons were all covered with a black scale (Figure 7-7 and Figure 7-8). They were first weighed after exposure without cleaning, and then were cleaned using a dilute HCl solution with an inhibitor to remove the scale and subsequently re-
weighed. The scale morphology is interesting as it appears to be the result of an agglomeration of spherical deposits. These deposits were analyzed with EDX and found to be roughly of the same composition as the dried solids filtered out from the effluent. Thus it would appear as though the Fe and Cr oxides, while insoluble, were removed from the 316L alloy surface by fluid motion. The implication is that they do not form a solid and adherent oxide, rather that the reaction products are loosely released into the solution. This substantiates the idea that rapid dissolution at the m/ol interface leads to the complete removal of the ol through physical means rather than chemical means. This also adds further weight to the diffusion limited corrosion theory proposed in this work.

Figure 7-7 High magnification morphology of deposits on the surface of coupons exposed to 653-673 K SCWO environment. EDX spectra reveal that the porous scale is mostly Fe oxide and Cr oxide removed from the 316 L reactor tube.
The measured corrosion rates for the cleaned, de-scaled coupons are presented in Table 7-3 and they reveal a very consistent picture of the corrosion behaviour of Ni-Cr alloys at SCWO conditions. The corrosion rates decreased with increasing Cr content. The decrease in corrosion rate can be attributed to the precipitation of an insoluble Cr(III) oxide. Furthermore, and perhaps most interestingly, Nb showed no attack up to at least 653 K. This is an entirely new result which provides extra incentive for examining the possibility of utilizing Nb in SCWO reactors.
Table 7-3  Coupon corrosion rates after exposure to ammoniacal sulphate solution at 653-673 K, $C_{\text{O}_2} \sim 3$ m.

<table>
<thead>
<tr>
<th>mm/yr</th>
<th>625</th>
<th>Ni, 20 wt% Cr</th>
<th>Ni</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(# coupons)</td>
<td>18 (3)</td>
<td>29 (1)</td>
<td>35 (2)</td>
<td>no change (2)</td>
</tr>
</tbody>
</table>

7.3 **Summary**

- Ni-Cr alloys experience unacceptable corrosion rates when exposed to heavily oxygenated ammoniacal sulphate solutions in the high density supercritical region. The morphological evidence suggests that a porous agglomerate of spherical Cr(III) oxide particles is formed on the surface of these alloys. Ni and Mo (for Ni-Cr-Mo alloys) dissolve readily. This morphology is consistent with the electrochemical measurements performed at 473 K which predict the formation of a diffusion limiting outer layer.

- Deep inter-granular attack is likely the mode of failure for alloy 625.

- Higher Cr content results in lower corrosion rates.

- Nb was not attacked under the conditions tested here.
8 CORROSION OF NIOBIUM IN CONCENTRATED SULFURIC AND HYDROCHLORIC ACID AT ELEVATED TEMPERATURES

Niobium (Nb) has received a great deal of attention in the chemical industry owing to its corrosion resistance in low concentration acidic solutions and at moderate temperatures. Many corrosion studies have been undertaken on pure niobium in sulphuric acid and hydrochloric acid solutions, however most have focused on corrosion rate measurements by gravimetric means only and have not included thermodynamic considerations, micro-structural corrosion morphology or polarization data. Moreover, there has been an emphasis on test conditions at temperatures at or above the boiling point of the acid solutions. For instance, Lupton et al. exposed Nb to boiling 70 and 75 wt% (%) H\textsubscript{2}SO\textsubscript{4} (boiling points of 165 and 185°C respectively) [Lupton 1981]. Burns et al. have published corrosion rates for Nb in boiling 10 to 70 % H\textsubscript{2}SO\textsubscript{4} and 10 to 36 % hydrochloric acid (HCl) with various salt additives (up to 15 % AlCl\textsubscript{3}, 10 % NaCl and 0.01 % FeCl\textsubscript{3}) [Burns 1984]. Bishop tested several refractory metals including niobium in H\textsubscript{2}SO\textsubscript{4} and HCl solutions at and above their boiling point (notably at temperatures up to 250°C) [Bishop 1963]. Robin and Rosa also determined iso-corrosion curves for Nb and Nb-Ta alloys in HCl solutions with concentrations ranging from 5 to 20 % HCl and at solution boiling point, 150°C and 200°C [Robin 2000]. Exposure time was between 3 and 14 days. MacLeary presented corrosion rates for Nb under a variety of conditions and acid type/concentration also mostly at the boiling point [MacLeary 1962].
On the lower end of the temperature scale, Covino et al. have presented results for the corrosion rate of Nb in HCl at temperature ranging from 35 to 100°C and concentrations of HCl of 1, 5 and 10 N (equivalent to roughly 4.8, 21.2 and 38.1 %) [Covino 1980]. Robin et al. have tested Nb and Nb-Ta alloys over a wide range of sulphuric acid concentrations (10 to 98 %), between room temperature and 175°C and at exposure times varying from 1 to 19 days [Robin 1991, 1997]. Bulhøes and Joanni have also studied the effect of temperature up to 40°C on Nb in a 96 % solution of H₂SO₄ and corrosion rates were given as current densities [Bulhøes 1984]. These low temperature data are summarized in Figure 8-1 and Figure 8-2 for H₂SO₄ and HCl solutions, respectively.

Figure 8-1 Corrosion rates in μm/yr for Nb in H₂SO₄ solutions at temperatures below the boiling point. Circle diameter reflects corrosion rate value rather than an area on the graph i.e. each corrosion rate value sits on a discreet point in the concentration-temperature plane.
The main objective of the present work was to investigate the corrosion behaviours of Nb in solutions of H₂SO₄ and HCl at 75 and 95°C by evaluating its corrosion resistance, corrosion morphology, thermodynamic tendencies and polarization behaviour. It was hoped that investigation of the polarization response, in particular, may shed light on its resistance to high temperature oxidative media. Furthermore, resistance to acidic conditions is one of the important criteria for selecting SCWO materials.

A metal's resistance to oxidative media can be tested by exposure (high temperature with high oxidant concentration) or by electrochemical polarization at potentials sufficiently removed from $E_{\text{corr}}$. The exposure route was investigated in the last section and the results were encouraging though the sample size was small. The
autoclave used in section 5 for electrochemical measurements is currently not capable of exceeding temperatures of ~498 K; nor is it advisable to expose it to strong acids and high, SCWO-like, oxygen concentrations. Therefore, in an effort to simulate electrochemical measurements at high temperature and to a lesser degree a SCWO environment, a balance was struck by exposing the Nb samples to exceedingly high concentrations of acid but at moderate temperatures.

8.1 Experimental

8.1.1 Immersion tests

Niobium ingots weighing about 0.9 kg each were cut into halves and cold worked to about 85 % rolling reduction and a thickness of 0.5 mm, suitable for immersion testing. They were then annealed at 1100°C for 1 hr under vacuum. The average grain size after annealing was ~77 μm as measured by the mean intercept method. Figure 8-3 shows an optical micrograph of the microstructure after etching.

Immersion tests were conducted in 20, 40 and 80 % H₂SO₄ and in 20 and 38 % HCl at 75 and 95°C. Reagent grade chemicals were used to make the solutions. Rectangular specimens approximately 25 mm × 50 mm × 0.5 mm were cut from the rolled sheets, and cleaned and degreased ultrasonically in acetone. After cleaning, the samples were thoroughly washed with de-ionized water, rinsed in ethanol, dried and weighed to an accuracy of 0.1 mg.

In the case of the H₂SO₄ solutions, the specimens were immersed in 300 mL beakers. The beakers were then sealed with rubber stoppers and placed in a water bath.
In the case of the HCl solutions, which had low boiling points of ~ 106°C for the 20 % HCl and ~ 48°C for the 38 % HCl [Degnan 1987], the samples were immersed in a 2000 ml beaker connected to a glass condenser to reflux vapors back into the solution. The specimens were physically separated and hung using a Teflon-coated wire. The beaker was then placed on a hot plate. Testing was carried out for a period of two weeks. Two or three coupons were immersed for some temperature and concentration conditions (c.f. Table 8-4) and the reproducibility was within 20%.

![Figure 8-3 Optical micrograph of the Nb microstructure after etching.](image)

Upon completion of each test, the samples were rinsed with water then ethanol and then dried with warm air. Specimens were re-weighed to determine the corrosion and the weight losses were converted into an average corrosion rate \( r \) in \( \mu \text{m/yr} \) using the relationship:

\[
r = 8.76 \times 10^7 \left( \frac{W}{AT \rho} \right)
\]  
8-1
Where $W$ is the weight loss in grams, $A$ is specimen area (cm$^2$), $T$ is the exposure time in hours, and $\rho$ is the density of Nb (8.57 g/cm$^3$).

### 8.1.2 Polarization experiments

Potentiodynamic polarization tests were carried out in a conventional three-electrode cell using an electrochemical interface. Test solution and temperature conditions were the same as those used for the immersion tests. The electrochemical cell consisted of a commercially available one-liter glass cell, a graphite counter electrode, an external Ag/AgCl reference electrode (saturated KCl fill solution), and the working electrode (WE).

Determination of the corrosion current density, $i_{corr}$, was done by back-extrapolation of the cathodic Tafel slope to the corrosion potential using a non-linear least squares fitting routine. The Tafel extrapolation was always initiated at least 0.1 V away from the corrosion potential, $E_{corr}$. Chi-squared values were generally less than 10 and always less than 50, indicating a good fit to the polarization data. The passive current, $i_{pass}$, at +1 V versus $E_{corr}$ was also registered for comparison. Experiments were reproducible to within 30 mV of $E_{corr}$, 7 $\mu$A of $i_{corr}$ and 50 $\mu$A of $i_{pass}$. The corrosion rate ($r$) in $\mu$m.yr$^{-1}$ can be related to $i_{corr}$ ($\mu$m.cm$^{-2}$) through Faraday’s law:

$$r = 3.28 \frac{M \times i_{corr}}{n \rho}$$  \hspace{2cm} (8-2)

Where $M$ is the atomic weight of the metal (for Nb, $M = 92.91$ g/mole), $n$ is the number of electrons exchanged for the reaction ($n = 5$ here, discussion follows in the results section), and $\rho$ is the density of the metal (for Nb, $\rho = 8.57$ g/cm$^3$).
Tests were performed after 1 hour of exposure to the solution at a sweep rate of 0.166 mV/s between -0.25 V vs. $E_{corr}$ and 1.8 V. Because of the concentrated solutions used in these experiments the liquid junction potential (LJP) between the reference electrode and the test solution was calculated at higher temperatures in a method described elsewhere, by Vaughan et al. [Vaughan 2003], and which was based on the Henderson equation [Newman 1973].

### 8.1.3 Pourbaix diagrams and thermodynamic calculations

New Pourbaix diagrams were constructed using the standard chemical potentials, $\mu^\circ$ for the relevant species from the Bard, Parsons and Jordan text [Bard 1985]. Kelley equation coefficients for condensed phase species were used to calculate heat capacities at 75 and 95°C and were obtained from the HSC thermo-chemical database [Roine 2002]. For all ionic species considered in this work, the chemical potentials at 75 and 95°C were calculated using the Criss and Cobble entropy correspondence principle and ionic heat capacity constants [Criss 1964A, B].

Estimated activities of species (represented by [ ]) in the H$_2$SO$_4$ solutions at 25, 75 and 95°C were calculated using the first and second dissociation equilibrium constants according to a method described by Tromans [Tromans 1998B]. This was done to situate pH values for use with the Pourbaix diagrams and to calculate the liquid junction potential between the reference electrode and the solution for the potentiodynamic experiments. Briefly, the standard chemical potentials for aqueous H$_2$SO$_4$, hydrogen sulphate (HSO$_4^-$) and sulphate (SO$_4^{2-}$) at 25°C were obtained from
published data [Bard 1985]. The dissociation constant was calculated by evaluating the
reaction free energy change:

\[ \Delta G^\circ = \sum (v \mu^c)_{\text{products}} - \sum (v \mu^c)_{\text{reactants}} = -RT \ln k_i \] 8-3

Where \( v \) is the stoichiometric coefficient of the corresponding reactant or product species
and \( k_i \) is the equilibrium constant for the following reactions:

\[ \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^- \quad k_1 = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} = 99 \text{ at } 25^\circ\text{C} \] 8-4

\[ \text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad k_2 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1 \times 10^{-2} \text{ at } 25^\circ\text{C} \] 8-5

Given a total molal concentration \( N \) then:

\[ N = [\text{H}_2\text{SO}_4] + [\text{HSO}_4^-] + [\text{SO}_4^{2-}] \] 8-6

\[ 2N = 2[\text{H}_2\text{SO}_4] + [\text{HSO}_4^-] + [\text{H}^+] \] 8-7

By simultaneously solving equations 8-4 through 8-7 it was possible to obtain
approximate values for proton activity in the sulphuric acid solutions. Unit activity
coefficients were assumed throughout this process which undoubtedly resulted in activity
errors. Nevertheless, Tromans indicates that the results obtained in this way are adequate
for order of magnitude estimates [Tromans 1998B].

Mean activity coefficients, \( \gamma_x \), for the hydrochloric acid solutions were
extrapolated from data published by Marsh and McElroy [Marsh 1985]. Estimates for
the individual ionic activity coefficients (\( \gamma_{\text{H}^+} \) and \( \gamma_{\text{Cl}^-} \)) were made according to the Bates
equations [Bates 1970]. These equations rely on the fact that salt hydration numbers are
dominated by the Lewis-Acid type interaction with cations whilst hydrogen bonding with
anions is typically weak [Muir 1985]. Thus it is a reasonable thermodynamic assumption
that the Cl\(^-\) ion is not hydrated in concentrated solutions of HCl and that measured values of \(\gamma_z\) can be separated as such:

\[
\log \gamma_H^+ = \log \gamma_z + 0.00782hm\phi \quad 8-8
\]

\[
\log \gamma_{Cl^-} = \log \gamma_z - 0.00782hm\phi \quad 8-9
\]

Where \(h\) is the hydration number for HCl (\(h = 8\)) [Robinson 1959], \(m\) is the molarity of the solution and \(\phi\) is the osmotic coefficient which is given by equation 10.

\[
\phi = \frac{-1000\ln[H_2O]}{18\sum_i \nu_im_i} \quad 8-10
\]

The osmotic coefficient is simply another way of expressing the activity of water, \([H_2O]\), while \(\nu_i\) is the stoichiometric coefficient and \(m_i\) is the molality of the dissociated species \(i\).

Activities of water were calculated using Raoult’s law: water vapour pressure over a solution of sulphuric (or hydrochloric) acid divided by water vapour pressure over pure water. The former are tabulated in Perry’s Handbook for Chemical Engineers [Perry 1997]. Table 8-1 presents the concentrations, estimated activities, pH and calculated equilibrium constants \((k_1\) and \(k_2\)) for the sulphuric acid solutions used in this work while Table 8-2 presents the concentrations, estimated activities and pH for the hydrochloric acid solutions.
Table 8-1  Estimated activities of H$_2$SO$_4$ solutions at 25, 75 and 95°C.

<table>
<thead>
<tr>
<th>$Wt%$</th>
<th>$M$</th>
<th>$m$</th>
<th>$\rho$, kg/L</th>
<th>$[H^+]$</th>
<th>$[HSO_4^-]$</th>
<th>$[H_2SO_4]$</th>
<th>$[SO_4^{2-}]$</th>
<th>pH</th>
<th>$[H_2O]$</th>
<th>$k_1$</th>
<th>$k_2$</th>
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<tr>
<td>20</td>
<td>2.32</td>
<td>2.55</td>
<td>1.14</td>
<td>2.50</td>
<td>2.48</td>
<td>0.06</td>
<td>0.01</td>
<td>-0.40</td>
<td>0.912</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5.31</td>
<td>6.80</td>
<td>1.30</td>
<td>6.40</td>
<td>6.38</td>
<td>0.41</td>
<td>0.01</td>
<td>-0.81</td>
<td>0.585</td>
<td>98.789</td>
<td>1.0123×10$^{-2}$</td>
</tr>
<tr>
<td>80</td>
<td>14.09</td>
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<td>1.72</td>
<td>31.04</td>
<td>31.02</td>
<td>9.75</td>
<td>0.01</td>
<td>-1.49</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.32</td>
<td>2.55</td>
<td>1.10</td>
<td>2.37</td>
<td>2.36</td>
<td>0.19</td>
<td>0.00</td>
<td>-0.37</td>
<td>0.897</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>5.31</td>
<td>6.80</td>
<td>1.26</td>
<td>5.72</td>
<td>5.71</td>
<td>1.08</td>
<td>0.00</td>
<td>-0.76</td>
<td>0.619</td>
<td>30.197</td>
<td>2.6111×10$^{-3}$</td>
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<tr>
<td>80</td>
<td>14.09</td>
<td>40.78</td>
<td>1.67</td>
<td>23.11</td>
<td>23.10</td>
<td>17.68</td>
<td>0.00</td>
<td>-1.36</td>
<td>0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>2.32</td>
<td>2.55</td>
<td>1.09</td>
<td>2.31</td>
<td>2.30</td>
<td>0.25</td>
<td>0.00</td>
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<td>0.892</td>
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<td>6.80</td>
<td>1.24</td>
<td>5.43</td>
<td>5.43</td>
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<td>21.589</td>
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<td>14.09</td>
<td>40.78</td>
<td>1.65</td>
<td>20.78</td>
<td>20.78</td>
<td>20.00</td>
<td>0.00</td>
<td>-1.32</td>
<td>0.018</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8-2 Estimated activities of HCl solutions at 25, 75 and 95°C.

<table>
<thead>
<tr>
<th>HCl concentration</th>
<th>Wt%</th>
<th>M</th>
<th>m</th>
<th>ρ, kg/L</th>
<th>γ⁺</th>
<th>γ⁻ Cl⁻</th>
<th>[Cl]</th>
<th>γ⁺ H⁺</th>
<th>[H⁺]</th>
<th>pH</th>
<th>[H₂O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>20</td>
<td>6.02</td>
<td>6.85</td>
<td>1.098</td>
<td>4.15</td>
<td>0.52</td>
<td>3.56</td>
<td>33.16</td>
<td>227.14</td>
<td>-2.36</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>12.39</td>
<td>16.81</td>
<td>1.189</td>
<td>47.82</td>
<td>0.03</td>
<td>0.43</td>
<td>8.95 x 10⁴</td>
<td>1.51 x 10⁶</td>
<td>-6.18</td>
<td>0.15</td>
</tr>
<tr>
<td>75°C</td>
<td>20</td>
<td>5.87</td>
<td>6.85</td>
<td>1.071</td>
<td>2.59</td>
<td>0.47</td>
<td>3.19</td>
<td>14.47</td>
<td>99.11</td>
<td>-2.00</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>38</td>
<td>12.04</td>
<td>16.81</td>
<td>1.156</td>
<td>14.62</td>
<td>0.03</td>
<td>0.56</td>
<td>6.44 x 10³</td>
<td>1.08 x 10⁵</td>
<td>-5.03</td>
<td>0.22</td>
</tr>
<tr>
<td>95°C</td>
<td>20</td>
<td>5.81</td>
<td>6.85</td>
<td>1.060</td>
<td>2.15</td>
<td>0.48</td>
<td>3.28</td>
<td>9.66</td>
<td>66.18</td>
<td>-1.82</td>
<td>0.69</td>
</tr>
<tr>
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<td>38</td>
<td>11.91</td>
<td>16.81</td>
<td>1.143</td>
<td>9.10</td>
<td>0.04</td>
<td>0.61</td>
<td>2.27 x 10³</td>
<td>3.82 x 10⁴</td>
<td>-4.58</td>
<td>0.25</td>
</tr>
</tbody>
</table>
8.2 Results and discussion

8.2.1 Pourbaix diagrams

Figure 8-4 presents all three Pourbaix diagrams for the Nb-H₂O system at the temperatures considered in this work i.e. 25, 75 and 95°C. The chemical potentials used to calculate the reactions' Gibbs free energy are presented Table 8-3. The original Pourbaix diagram was updated to include the stability regions for NbCV (metaniobate) and Nb(OH)₄⁺ (niobium tetrahydroxide). Both species were not considered in the original Pourbaix Atlas as at the time, the thermodynamic data was not available.

Table 8-3 Chemical potentials, $\mu$, of species at 25, 75 and 95°C

<table>
<thead>
<tr>
<th>Species</th>
<th>State</th>
<th>$\mu$ (kJ/mol), 25°C</th>
<th>$\mu$ (kJ/mol), 75°C</th>
<th>$\mu$ (kJ/mol), 95°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>l</td>
<td>-237.18</td>
<td>-240.97</td>
<td>-242.65</td>
</tr>
<tr>
<td>O₂</td>
<td>g</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>g</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁺</td>
<td>aq</td>
<td>0</td>
<td>-0.52</td>
<td>-1.05</td>
</tr>
<tr>
<td>NbO₅⁻</td>
<td>aq</td>
<td>-932.10</td>
<td>-930.25</td>
<td>-928.51</td>
</tr>
<tr>
<td>Nb(OH)₄⁺</td>
<td>aq</td>
<td>-1208.6</td>
<td>-1211.63</td>
<td>-1215.27</td>
</tr>
<tr>
<td>Nb</td>
<td>s</td>
<td>0</td>
<td>-1.92</td>
<td>-2.74</td>
</tr>
<tr>
<td>NbO</td>
<td>s</td>
<td>-378.60</td>
<td>-381.17</td>
<td>-382.29</td>
</tr>
<tr>
<td>NbO₂</td>
<td>s</td>
<td>-740.90</td>
<td>-743.86</td>
<td>-745.17</td>
</tr>
<tr>
<td>Nb₂O₅</td>
<td>s</td>
<td>-1768.10</td>
<td>-1775.50</td>
<td>-1778.75</td>
</tr>
</tbody>
</table>

$^a$ s = solid, l = liquid, g = gas, aq = aqueous

It is unlikely that metaniobate would actually form under most conditions but there is evidence that niobium pentoxide (Nb₂O₅) is soluble in strongly alkaline solutions [Bard 1985]. As temperature is increased, the stability plane of metaniobate increases in size and the chemical equilibrium between Nb₂O₅ and NbO₅⁻ shifts to more acidic values.
In his work on the corrosion of Nb in sodium hydroxide solutions, Robin states that the corrosion of Nb in alkaline solutions could occur through a chemical dissolution-precipitation mechanism: Nb dissolves as $\text{Nb}_6\text{O}_{19}^{9+}$ (hexaniobate) that precipitates as a sodium niobium oxide such as $\text{Na}_8\text{Nb}_6\text{O}_{19}$ [Robin 2004A, B]. Unfortunately a thorough literature search did not result in any thermodynamic data for hexaniobate.

![Pourbaix diagram](image)

Figure 8-4 Pourbaix diagram for the Nb-H$_2$O system at 25, 75 and 95°C. • represents the corrosion potential for the 75°C polarization tests and ○ represents 95°C tests. Lines $a$ and $b$ represent hydrogen evolution and oxygen reduction, respectively.

Niobium tetrahydroxide has not seen much attention in the literature. In fact, the only text in which I was able to find reference to it was that of Bard, Parsons and Jordan [Bard 1985]. Upon study of the Pourbaix diagram presented here, the formation of $\text{Nb(OH)}_4^{+}$ seems a likely explanation for the dissolution of $\text{Nb}_2\text{O}_5$ in strongly acidic
solutions. Robin has proposed that steady state corrosion, which in the case of Nb in concentrated acid solutions is observed after roughly 200 hours, is due to film dissolution [Robin 1991]:

\[ \text{Nb}_2\text{O}_5 + 10H^+ = 2\text{Nb}^{5+} + 5H_2O \] 8-11

There are little thermodynamic data to suggest that pentavalent Nb ions exist as hydrated ions, however there is at least some data to suggest that Nb(OH)_4^+ could form [Bard 1985]. The dissolution reaction in acidic solutions (below pH 0.5 at 25°C), could then proceed as either a chemical dissolution of metastable niobium pentoxide or an electrochemical dissolution of niobium dioxide.

\[ \text{Nb}_2\text{O}_5 + 3H_2O + 2H^+ = 2\text{Nb(OH)}_4^+ \] 8-12

\[ \text{NbO}_2 + 2H_2O = \text{Nb(OH)}_4^+ + e^- \] 8-13

8.2.2 Immersion tests

Corrosion rates for the Nb samples after two-weeks of exposure to the H_2SO_4 and HCl solutions are shown in Table 8-4. For the sulphuric acid solutions, corrosion rates were the lowest at 75°C (below ~ 34 μm/yr). In fact, specimens exposed to the 20 and 80 % concentrations did not show any macroscopically visible signs of attack after two weeks of immersion. The surfaces of the coupons exposed to the 40 % concentration were visibly pitted after exposure and corrosion rates were highest at this concentration for both temperatures. This was a surprising finding as it is generally found that corrosion rates increase with temperature and acid concentration. However, it is well documented that certain alloys perform well under concentrated sulphuric acid solutions.
Carbon steel, for example, is successfully used to handle concentrated \( \text{H}_2\text{SO}_4 \) (65 to 100 %) at ambient temperature and austenitic stainless steels can be used at concentrations above 93 % at ambient temperature and above 98.5 % at 70°C [Brubaker 1987]. While the mechanism of protection for carbon steel is believed to be by sulphate film, the use of austenitic stainless steels relies on passivation [Brubaker 1987]. The analogy to Nb is therefore not far fetched. In fact, alloying stainless steels with molybdenum broadens the applicable concentration range to 90 % and above at ambient temperature [Brubaker 1987]. It is therefore conceivable that Nb be well suited to applications in the 80 % range. Indeed, with reference to equation 8-14 below, it is clear that the rate of niobium oxidation should increase with increasing \( \text{H}_2\text{O} \) in solution. The cathodic reaction rate and therefore the overall corrosion rate will depend highly on the concentration of \( \text{H}^+ \) (assuming that hydrogen evolution is the dominant cathodic reaction). Thus, the corrosion rate is determined by both the available water in solution and the number of \( \text{H}^+ \) ions at the electrode interface. shows that while proton activity is increased on the order of 4x between 40 and 80 % \( \text{H}_2\text{SO}_4 \), water activity is actually decreased by roughly 44x. The lack of available water may limit the solubility of Nb at the 80 % concentration. A similar finding was observed by Smart and Bockris for iron in solutions of high ionic strength [Smart 1992]. It should however be noted that Robin et al. have reported corrosion rates for Nb at 100°C in 20, 50 and 80 % \( \text{H}_2\text{SO}_4 \) at 40, 95 and 250 \( \mu \text{m/yr} \), respectively [Robin 1991]. Clearly, these observations require more study; however, the gravimetric results are corroborated by the polarization data discussed below.

Raising the temperature to 95°C for the \( \text{H}_2\text{SO}_4 \) solutions resulted in larger corrosion rate increases as concentration was increased i.e. the corrosion rate in the 20 wt
% solution was ~ 1.5 times higher at 95°C than at 75°C while this multiple was ~ 2.5 and
~ 3.75 at 40 and 80 %, respectively.

Table 8-4 Corrosion rates for Nb in μm/yr from immersion tests

<table>
<thead>
<tr>
<th>T</th>
<th>wt% H2SO4</th>
<th>wt% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>75°C</td>
<td>10.4</td>
<td>33.6 ± 6.3 b</td>
</tr>
<tr>
<td>95°C</td>
<td>15.2 a</td>
<td>87.4</td>
</tr>
</tbody>
</table>

a mean of 13.6 and 16.8 μm/yr  
b mean and standard deviation for 3 coupons  
c mean of 46.5 and 50.3 μm/yr

For the HCl solutions, corrosion rates at 75°C were relatively low, particularly for
the 20% solutions. As was expected, increasing the concentration generally led to higher
corrosion rates. A significant increase in corrosion rates was observed upon increasing
the temperature from 75 °C to 95 °C. Corrosion rates in the 38% concentration HCl at
95°C were seven times higher than those observed at 75 °C.

Aside from the disagreement with Robin’s data at the 80 % H2SO4 concentration,
the results presented here are generally consistent with those presented by other authors.
There is one other small point of disagreement (less than a factor of 4): at 95°C and 38%
HCl our sample corroded at 306 μm/yr whereas Covino et al. report 90.5 μm/yr [Covino
1980].

Scanning electron micrographs of niobium samples after two weeks of immersion
are shown in Figure 8-5. Generalized pitting is evident on the samples exposed to 20 %
H2SO4 (95°C) and 40 % H2SO4 (75 and 95°C) (Figure 8-5, (a), (c) and (d)). In contrast,
only traces of localized attack are visible on the surfaces of the samples exposed to 80 \% H_2SO_4 and 20 and 38 \% HCl (Figure 8-5 (b), (e) and (f)). These latter samples showed more regular surface removal with patches of roughness in a preferred crystallization direction normal to the surface. This morphology was observed by Lupton et al. on Nb in boiling 75\% H_2SO_4 [Lupton 1981] and by Vehlow on tantalum in 98\% H_2SO_4 at 230\°C [Vehlow 1981]. According to Vehlow this effect is due to the different binding energies between different lattice planes in the BCC lattice.

### 8.2.3 Polarization experiments

Figure 8-6 and Figure 8-7 show the polarization curves for Nb in H_2SO_4 solutions at 75 and 95\°C, respectively. Figure 8-8 shows the polarization curves for Nb in the HCl solutions at 75 and 95\°C. Corrected corrosion potential (corrected for the liquid junction potential i.e. \( E_{corr} = E_{measured} + E_{LJP} \)), corrosion current density, passive current density, corrosion rate in \( \mu \text{m/yr} \), liquid junction potential correction \( (E_{LJP}) \) and the immersion test corrosion rates are listed in Table 8-5 and Table 8-6 for the H_2SO_4 and HCl solutions, respectively. The potentiodynamic (PD) corrosion rates were calculated with equation 8-2 where \( n \) was assumed to be equal to 5. This is consistent with the oxidation of niobium to niobium pentoxide:

\[
2Nb + 5H_2O = Nb_2O_5 + 10H^+ + 10e^- \quad 8-14
\]
Figure 8-5 Nb after two weeks immersion at (a) 95°C in 20% H₂SO₄, (b) 95°C, 80% H₂SO₄, (c) 75°C, 40% H₂SO₄, (d) 95°C, 40% H₂SO₄, (e) 95°C, 20% HCl and (f) 95°C, 38% HCl.
Estimated test solution pH and corrosion potential for the PD tests in H$_2$SO$_4$ solutions are reported on the Pourbaix diagrams (Figure 8-4) where • represents the 75°C tests and ○ represents the 95°C tests. While the potentials in the 20 and 40% solutions are, from a strictly theoretical standpoint, more representative of NbO$_2$ to Nb(OH)$_4^+$ oxidation, it is unlikely that NbO$_2$ (or for that matter NbO) would form as they are known to be thermodynamically unstable species. Furthermore, given that the PD behaviour is indicative of at least a metastable oxide formation, it is likely that Nb$_2$O$_5$ formation (equation 8-14) and dissolution (equation 8-12) are the competing processes giving rise to the measured corrosion rates. E-pH data for the HCl solutions is not plotted on the Pourbaix diagram, however Table 8-2 (pH) and Table 8-6 (E) list the data and it is apparent they would also lie along the NbO$_2$ to Nb(OH)$_4^+$ stability line. It is interesting to note that in the H$_2$SO$_4$ solutions the corrosion potentials for the 20 and 40% solutions are within 20 mV of each other at both temperatures while the corrosion potential in the 80% solution is generally ~ 120 to 170 mV higher, also at both temperatures. In contrast the corrosion potential in hydrochloric acid solutions decreases (~ 200 mV) upon an increase in concentration and does not seem to be overly affected by temperature. From a qualitative standpoint this is explained by the mildly oxidizing nature of sulphuric acid solutions whilst hydrochloric acid solutions are reducing in nature. Thus an increase in the former’s concentration would result in higher corrosion potentials and an increase in the latter’s would yield the opposite effect.
Figure 8-6  Polarization curves for Nb in 20, 40 and 80 % H₂SO₄ at 75°C

Figure 8-7  Polarization curves for Nb in 20, 40 and 80 % H₂SO₄ at 95°C
Table 8-5  Potentiodynamic polarization data in sulphuric acid solutions
(corrosion potential includes correction for liquid junction)

<table>
<thead>
<tr>
<th></th>
<th>20 wt% H\textsubscript{2}SO\textsubscript{4}</th>
<th>40 wt% H\textsubscript{2}SO\textsubscript{4}</th>
<th>80 wt% H\textsubscript{2}SO\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75°C</td>
<td>95°C</td>
<td>75°C</td>
</tr>
<tr>
<td>(i_\text{corr} \text{ (\mu A.cm}^{-2}\text{)})</td>
<td>17.40</td>
<td>50.46</td>
<td>26.92</td>
</tr>
<tr>
<td>(i_\text{pass} \text{ (\mu A.cm}^{-2}\text{)})</td>
<td>9.13</td>
<td>40.42</td>
<td>9.62</td>
</tr>
<tr>
<td>(E_\text{corr} \text{ (mV, SHE)})</td>
<td>-92</td>
<td>-140</td>
<td>-108</td>
</tr>
<tr>
<td>(E_{LJP} \text{ (mV)})</td>
<td>-27</td>
<td>-28</td>
<td>-39</td>
</tr>
<tr>
<td>Corr. Rate (\mu m/yr) – Potentiodynamic</td>
<td>123.8</td>
<td>358.9</td>
<td>191.5</td>
</tr>
<tr>
<td>Corr. Rate (\mu m/yr) - Immersion</td>
<td>10.4</td>
<td>15.2</td>
<td>33.6</td>
</tr>
</tbody>
</table>

Table 8-6  Potentiodynamic polarization data in hydrochloric acid solutions
(corrosion potential includes correction for liquid junction)

<table>
<thead>
<tr>
<th></th>
<th>20 wt% HCl</th>
<th>38 wt% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>75°C</td>
<td>95°C</td>
</tr>
<tr>
<td>(i_\text{corr} \text{ (\mu A.cm}^{-2}\text{)})</td>
<td>35.39</td>
<td>39.11</td>
</tr>
<tr>
<td>(i_\text{pass} \text{ (\mu A.cm}^{-2}\text{)})</td>
<td>28.25</td>
<td>87.89</td>
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<tr>
<td>(E_\text{corr} \text{ (mV, SHE)})</td>
<td>-216.30</td>
<td>-257.43</td>
</tr>
<tr>
<td>(E_{LJP} \text{ (mV)})</td>
<td>-115</td>
<td>-107</td>
</tr>
<tr>
<td>Corr. Rate (\mu m/yr) – Potentiodynamic</td>
<td>251.7</td>
<td>278.2</td>
</tr>
<tr>
<td>Corr. Rate (\mu m/yr) - Immersion</td>
<td>9.0</td>
<td>25.1</td>
</tr>
</tbody>
</table>

Nb polarization curves exhibited typical passive behaviour over a wide potential range in all solutions. However, current fluctuations were observed in the passive region.
for the samples exposed to the 20 % H$_2$SO$_4$ and 40 % H$_2$SO$_4$ solutions at 95°C and the 20 % HCl solution at 75 and 95°C. It is assumed that these fluctuations are due to the initiation of metastable pits followed by repassivation. This finding is substantiated by the generalized pitting observed in the 20 and 40 % H$_2$SO$_4$ solutions after immersion testing (Figure 8-5 (a)-(d)), and to a lesser extent by the few pits observed on the samples exposed to the 20 % HCl solution. It is expected that potentiodynamic polarization experiments are a better gauge of metastable pit initiation than simple observation of the corrosion morphology after immersion testing. However, it should be noted that polarization experiments performed under the conditions used for this work are difficult. The primary difficulty lies in the stability of the working electrode holder. Most experiments were performed using an epoxy resin mount and insulating paint was used to cover the epoxy/Nb interface. It was noticed, however, that in the H$_2$SO$_4$ solutions at 95°C the epoxy became unstable, and so flag electrodes were used at this temperature. While we were careful to inspect all electrodes for stability and to repeat all experiments at least once, it is within the realm of possibility that crevice effects for the epoxy held samples or increased localized attack at the water line for the flag electrodes played a role in the measured fluctuations.
Corrosion current densities were estimated by Tafel extrapolation to the corrosion potential and Tafel slopes ($\beta_c$) are reported in Table 8-7. There was no apparent pattern to the Tafel slopes other than a general decrease as temperature was increased. Under the high field conditions for which Tafel kinetics are valid ($|\eta| >> RT/F$, where $\eta$ is overpotential and R and F have their usual meaning), $\beta_c$ is given by equation 8-15.

$$\beta_c = \frac{2.03RT}{\alpha_c n F}$$  \hspace{1cm} 8-15

where $\alpha_c$ is the cathodic transfer coefficient and is usually assumed to be $\sim 0.5$ [Bockris 1970], [Vetter 1967] and $n$ is the number of electrons taking place in the charge transfer limited reaction. Clearly, and in contradiction to the results presented in Table 8-7, one would expect an increase in Tafel slopes as temperature is increased. Furthermore, aside
from the values for the 38% HCl solution, the $\beta_c$ values measured in this work are very high despite the elevated temperatures, usually a sign of concentration polarization. It is then likely that the observed Tafel slopes are a result of the natural aeration conditions under which the experiments were performed. Such conditions would lead to two cathodic processes occurring on the WE: oxygen reduction and hydrogen evolution, shown in equations 14 and 15, respectively.

\[ O_2 + 4e^- + 4H^+ = 2H_2O \]  
\[ 2H^+ + 2e^- = H_2 \]

Table 8-7 Cathodic Tafel slopes, $\beta_c$, in H$_2$SO$_4$ and HCl solutions (mV/dec).

<table>
<thead>
<tr>
<th>$T$</th>
<th>H$_2$SO$_4$</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>75</td>
<td>291 287 295 255</td>
</tr>
<tr>
<td>40</td>
<td>226</td>
<td>276 268 125 136</td>
</tr>
<tr>
<td>80</td>
<td>95</td>
<td>184</td>
</tr>
</tbody>
</table>
corrosion potential and Tafel slopes observed at 95°C in both HCl solutions (125, 20% and 136, 38%) where the values are closer to what one might expect for pure charge transfer control over the hydrogen evolution reaction. While these findings do not invalidate the corrosion rates obtained from the polarization experiments, they do suggest that de-aeration prior to polarization would yield more valid cathodic Tafel information. In this study however, a comparison of corrosion rates measured by both immersion and potentiodynamic polarization was of interest and this is why the solutions were not de-aerated. Passive current densities, $i_{pass}$ (Table 8-5 and Table 8-6) are also reported for comparison and are generally trend consistent with $i_{corr}$ and within the same order of magnitude. In the H$_2$SO$_4$ solutions $i_{pass}$ is an average of 81% lower than $i_{corr}$ while in the HCl solutions, $i_{pass}$ is an average of 286% higher than $i_{corr}$. This is an indication that Nb is better suited to service in sulphuric acid, and in particular, that oxidizing conditions are to be avoided in HCl solutions.

The corrosion rates from the immersion tests are, of course, lower. This is normal as corrosion current estimates based on PD tests are generally higher than those collected through weight loss experiments. In this work, samples were held at open circuit in solution for one hour prior to polarization and potential sweep rates were low (0.166 mV/s). Notwithstanding, the accelerated nature of the PD tests still did not account for the time necessary to achieve steady state corrosion. It is known that corrosion rates for Nb in acid solutions decrease with time. Such a decrease is typical of the thickening oxide film formed on the metal’s surface and the increasingly protective nature of the film as time elapses. Robin et al. have presented gravimetric data for corrosion rates in boiling (~100°C) 20 % H$_2$SO$_4$ as a function of time at 1, 2, 4, 10 and
18 day intervals [Robin 1991]. Their data were fitted to a logarithmic function giving the corrosion rate as a function of time:

\[ r = -19.805 \ln t + 225.64 \quad 8-18 \]

Where \( r \) is the corrosion rate in \( \mu \text{m/yr} \) and \( t \) is the time in minutes. Considering the one hour immersion at open circuit, and 0.25 V at 0.166 mV/s for the potentiodynamic polarization between the start potential and corrosion potential, \( t \) is roughly 85 min for our polarization experiments. According to equation 8-16, \( r \) should then be approximately 138 \( \mu \text{m/yr} \) which is within the same order of magnitude as that obtained in this work by potentiodynamic means (358.85 \( \mu \text{m/yr} \)) and differs only by a factor of \( \sim 2.6 \).

Similarly, Covino et al. have presented gravimetric corrosion rates as a function of time in 38 % HCl at 85°C and the data was fitted to \( r(t) \) given by equation 8-17.

\[ r = -40.563 \ln t + 671.39 \quad 8-19 \]

According to equation 8-17, \( r = 491 \ \mu \text{m/yr} \) after 85 minutes which lies well between the values obtained in this work for the 38 % HCl solutions at 75°C (286.87 \( \mu \text{m/yr} \)) and 95°C (544.12 \( \mu \text{m/yr} \)).

### 8.3 Summary

\( \text{Nb forms a passive film in concentrated sulphuric and hydrochloric acid and at temperatures below 95°C. New Pourbaix diagrams for the Nb-H}_2\text{O system, weight loss experiments and potentiodynamic polarization have shown that Nb exposed to concentrated HCl or H}_2\text{SO}_4 \text{ solutions likely corrodes through a competing process involving the oxidation of Nb to Nb}_2\text{O}_5 \) and the chemical dissolution of this oxide to \( \text{Nb(OH)}_4^+ \). Corrosion rates for Nb in 20 and 38 % HCl at 75 and 95°C increase with HCl.
concentration and temperature. In the H$_2$SO$_4$ solutions, corrosion rates increased from the 20 to 40% concentrations but decreased between the 40 and 80% concentrations at both temperatures. More study is required to determine an exact corrosion rate/concentration profile for Nb in H$_2$SO$_4$ solutions. SEM micrographs revealed generalized pitting at the 20 (95°C) and 40% (75 and 95°C) H$_2$SO$_4$ concentrations while the remaining test conditions resulted in preferential dissolution along certain crystallographic planes. Results of the polarization tests are consistent with the timescale involved in oxide thickening. The corrosion rates presented here are generally in good agreement with the literature.

With regards to SCWO, it is apparent that Nb is better suited to service in sulphuric acid than in hydrochloric acid solutions. Also, despite metastable pitting at high anodic potentials, wholesale film breakdown did not occur. Most of the SCWO research to date involving H$_2$SO$_4$ has tested solutions in the 0.2-0.5 m range. If this is representative of the concentration under SCWO conditions then the concentrations tested here are approximately an order of magnitude higher. Implications of this research are threefold:

- Nb is likely to outperform Ti in acidic sulphate bearing solutions

- Nb is likely to outperform Ni-Cr alloys in high density solutions due to superior resistance to corrosion at high anodic potentials

- Nb as a major alloying element to Ni (~12% range) should be investigated as it may provide superior resistance to transpassive corrosion.
9 CONCLUSIONS AND RECOMMENDATIONS

The electrochemical and thermodynamic analysis undertaken in this work to study the effects of oxygenated ammoniacal sulphate solution on the corrosion of Ni-Cr and stainless alloys has generated the following conclusions, tentative findings and recommendations.

9.1 Conclusions

- Potentiodynamic, morphological and solution analyses have shown that the corrosion behaviour of alloy 625 is dominated by Cr in ammoniacal sulphate solutions between 298 and 673 K. Cr(III) oxides are responsible for passivating the alloy, while Ni and Mo dissolve readily.

- Corrosion potential and impedance data have shown that transpassive corrosion of the cation conducting barrier layer on alloy 625 occurs at $T > 373$ K, $P > 40$ bar in oxygen saturated solutions. Furthermore, linear polarization, potentiodynamic and impedance experiments have shown that corrosion rates increase exponentially with temperature and become increasingly diffusion controlled, particularly as the barrier layer is transpassively attacked. This transpassive attack of the barrier layer results in cation emission to the barrier layer / outer layer interface and subsequent precipitation of mostly Cr(III) oxides which then reduce the ingress of oxygen to the barrier layer surface. The removal of this precipitate appears to occur in the 653 to 673 K range at which point the alloy becomes completely unprotected.
• Due to transpassive corrosion and solution acidification, Ni-Cr, Ni-Cr-Mo and stainless 316 L are not adequate materials for use in SCWO under high-density supercritical conditions. Nb is a good candidate material for this temperature range, particularly in the presence of sulphates.

9.2 Tentative findings

This work has also produced some results which require further investigation:

• The process leading to final removal of the Cr(III) oxide precipitates from the alloy surface at T > 653K is not clear. It is hypothesized that as temperature is increased near the critical point, failure is induced by either solution acidification leading to chemical dissolution of Cr(III) oxide precipitates or physical undermining of these precipitates due to rapid intergranular attack occurring at the metal / outer layer interface. To estimate solution pH at high density supercritical temperatures and rule out the former, a thorough set of H₂O-NH₃-O₂ phase equilibrium calculations should be performed.

• Thermodynamic analysis of the Ni-NH₃-H₂O system based on the only available experimental equilibrium constants measured by Letowski in 1970 has shown that nickel-ammines become unstable at T > 473 K which means that Ni-Cr alloys are probably not directly affected by ammonia under SCWO conditions. This is a tentative finding in that the equilibrium constants employed appear to underestimate the stability of the ammines. New empirical equilibrium constant data is required to substantiate this claim. A new series of carefully performed EMF measurements should be undertaken to this end.
9.3 Recommendations

The preceding discussions have also highlighted further areas of interest for future work:

- **Time.** The effect of time is always an issue for electrochemical corrosion measurements as they have been conceived specifically to accelerate data collection and estimate long term corrosion rates. We have seen in Chapter 4 that "steady-state" conditions are difficult to attain from a practical standpoint as they require ~ 8 hours to develop. As a result, the effect of time should be investigated on the isothermal and isobaric response of Ni-Cr alloys to oxygenated solutions.

- **473 - 623 K.** The temperature ranges investigated in this work did not include the 473 to 623 K range. From a SCWO standpoint this may not be the most interesting temperature range but it may yield very interesting scientific data, particularly if it is investigated electrochemically.

- **Ammine stability constants.** These should be re-measured as discussed in section 9.2.

- **Critical concentration.** The critical concentration of ammonium sulphate which leads to severe corrosion at a given total ammonia concentration should be investigated to confirm the predictions with regard to Ni^{2+}/NiO stability and solution acidity at high temperatures. In this regard, the effect of excess ammonia addition could be an effective way of mitigating corrosion by maintaining a constant concentration of ammonium ions to "tie up" anions such as sulphate or chloride.
• **Phase equilibria.** Ternary phase equilibria for the H₂O-O₂-NH₃ system should be calculated to confirm NH₃ solubility. This would also shed light on the failure mechanism.

• **SCWO experiments.** The experiments conducted here at SCWO conditions are certainly not exhaustive and more work should be performed in this area. Electrochemical analysis would be preferable.

• **Niobium.** Alloying Nb with Ni at levels higher than 5% should be investigated. More data for the electrochemical response of Nb is required, particularly at high temperatures.
REFERENCES


Criss, C.M., Cobble, J.W., 1964A. The thermodynamic properties of high temperature aqueous solutions. IV. Entropies of the ions up to 200° and the correspondence principle. Journal of the American Chemical Society 86, 5385-5390.


Gonzalez, V., et al., Corrosion of nickel-base alloys under the conditions of supercritical water oxidation (SCWO).


Kritzer, P., Schacht, M., Dinjus, E., 1999B. The corrosion behaviour of nickel-base alloy 625 (NiCr22Mo9Nb; 2.4856) and ceria stabilized tetragonal zirconia polycrystal (Ce-TZP) against oxidizing aqueous solutions of hydrofluoric acid (HF), hydrobromic acid (HBr), and hydriodic acid (HI) at sub- and supercritical temperatures. Materials and Corrosion 50.


Lance, D., 1904. French Patent 342865 (1904); see Moniteur Scientifique 64-65 Patent Section 53 (1906).


Appendix A - High temperature electrochemical apparatus

Figure A-1 Working electrode
Figure A-2  Working electrode sample detail
Figure A-3  Autoclave and working electrode assembly.
Figure A-4  Autoclave head and detail of electrodes.
Figure A-5 Autoclave Assembly
Figure A-6 Working electrode sample showing relative size (Staedler felt tip pen) and internal thread (small hole).

Figure A-7 Working electrode showing used PTFE seal, connecting rod and sample.
Figure A-8  External pressure balanced working electrode assembly.
Figure A-9  Assembled autoclave at work.
Appendix B - Concentrations and diffusivities of $O_2$ in the autoclave.

<table>
<thead>
<tr>
<th>$P_{\text{TOTAL, 298K}}$ bar</th>
<th>$T$ K</th>
<th>$D_{O_2}$ cm$^2$.s$^{-1}$</th>
<th>$\alpha_{NH_3}$</th>
<th>$\alpha_{H_2O}$</th>
<th>$P_{NH_3}$ bar$_{\text{abs}}$</th>
<th>$P_{H_2O}$ bar$_{\text{abs}}$</th>
<th>$P_{\text{TOTAL, T}}$ bar$_{\text{abs}}$</th>
<th>$P_{O_2}$ bar$_{\text{abs}}$</th>
<th>$C_{O_2}$ mol.$/kgH_2O$</th>
<th>$V_{gas}$ cm$^3$</th>
</tr>
</thead>
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<td>298</td>
<td>3.38 x $10^{-5}$</td>
<td>0.086</td>
<td>0.999</td>
<td>0.02</td>
<td>0.03</td>
<td>1.01</td>
<td>0.96</td>
<td>0.0012</td>
<td>699.98</td>
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<tr>
<td>323</td>
<td>5.95 x $10^{-5}$</td>
<td>0.102</td>
<td>0.999</td>
<td>0.09</td>
<td>0.12</td>
<td>1.27</td>
<td>1.06</td>
<td>0.001</td>
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<td>348</td>
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<td>0.119</td>
<td>0.999</td>
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<td>1.16</td>
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Appendix C – Examples of EIS curve fitting results

Table C-1 Calculated data at 298 K

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Figure C-10 Complex capacitance plot showing measured and calculated capacitance at 298 K.
Figure C-11  Bode plot showing the measured and model calculated data for the EIS spectrum at 373 K
Figure C-12 Nyquist plot showing the measured and model calculated data for the EIS spectrum at 448 K.
Appendix D - Oxygen concentration and fugacity at SCWO temperatures and at constant pressure: $P_{\text{TOTAL}} = 250$ bar

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<th>$\gamma_{O_2}$</th>
<th>$\rho_L$ kg.L$^{-1}$</th>
<th>$C_{O_2}$ mol. kgH$_2$O$^{-1}$</th>
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Appendix E - Matlab code used to generate RKS results

clear
% T = input('T in Celcius ') + 273.15;
T = 473.15;
P = 250;
R = 83.144;
L = 0.95;

% mole percent Water component 1
zl = 0.95;
% mole percent Oxygen component 2
z2 = 0.05;
% Liquid phase initial guesses
xl = 0.95;
x2 = 1 - xl;
% Vapour phase
yl = 0.05;
y2 = 1 - yl;
dont = 100;
cnt = 1;
sumxy = 1;

total = x2 * 31.25 + x1 * 55.56;
molesH2O = 55.56;

while T <= 698

   sumxy = 1;

   while abs(sumxy) >= le-9

      % Component 1, water
      Tc1 = 647.3; % K, critical point
      Pc1 = 221.2; % Bar, cr
      w1 = 0.344;
      f1 = 0.48 + 1.574 .* w1 - 0.176 .* w1 .^ 2;
      Tr1 = T / Tc1;
      % Y1 = 1 - Tr1 .^ 0.5;
      if Tr1 > 1
         f1 = (1 + 1.0873 .* Y1) .^ 2;
      else
         f1 = (1 + 1.0873 .* Y1 - 0.6377 .* Y1 .^ 2 + 0.6345 .* Y1 .^ 3) .^ 2;
      end
      a1 = 0.42748 * R * Tc1 .^ 2 / Pc1 .* (1 + f1 .* (1 - Tr1 .^ 0.5)) .^ 2;
      b1 = 0.08684 * R * Tc1 / Pc1;

   % Component 2, oxygen
   Tc2 = 154.6; % K, critical point
   Pc2 = 50.4; % Bar, cr
   w2 = 0.025;
\[ f_2 = 0.48 + 1.574 \ast w_2 - 0.176 \ast w_2 \ast 2; \]
\[ Tr_2 = T / T_c; \]
\[ Y_2 = 1 - Tr_2 \ast 0.5; \]
\[ f_2 = (1 + 0.8252 \ast Y_2) \ast w_2 \ast 2; \]
\[ \text{if } Tr_2 > 1 \]
\[ f_2 = (1 + 0.8252 \ast Y_2 + 0.2512 \ast Y_2 \ast w_2 - 1.7039 \ast Y_2 \ast 3) \ast w_2; \]
\[ a_2 = 0.42748 \ast R \ast T_c / \ast P_c \ast (1 + f_2 \ast (1 - Tr_2 \ast 0.5)); \]
\[ b_2 = 0.08664 \ast R \ast T_c / \ast P_c ; \]

%mixing rule for cubic EOS; x is for component 1

\[ k_{ij} = -0.11264; \% \text{estimated using Vcl and Vc2-0.11264} \]
\[ L_{ij} = -0.0066; \% \text{estimated using Yc1 and Vc2-0.0066} \]
\[ \text{if } dont > 1 \]
\[ \% \text{Liquid calculation} \]
\[ a = x_1 \ast 2 \ast a_1 \ast (1-k_{ij}) + 2 \ast x_1 \ast x_2 \ast (a_1 \ast a_2) \ast 0.5 \ast (1-k_{ij}) + x_2 \ast 2 \ast a_2 \ast (1-k_{ij}); \]
\[ b = b_1 \ast x_1 \ast 2 \ast (1-L_{ij}) + x_1 \ast x_2 \ast (b_1 + b_2) \ast (1-L_{ij}) + b_2 \ast x_2 \ast 2 \ast (1-L_{ij}); \]
\[ A = a \ast P / (R \ast T \ast 2); \]
\[ B = b \ast P \ast x_1 \ast 2 \ast (1-L_{ij}) + x_1 \ast x_2 \ast (bl + b2) \ast (1-L_{ij}) + b2 \ast x_2 \ast 2; \]
\[ A = a \ast P / (R \ast T \ast 2); \]
\[ B = b \ast P \ast x_1 \ast 2 \ast (1-L_{ij}) + x_1 \ast x_2 \ast (bl + b2) \ast (1-L_{ij}) + b2 \ast x_2 \ast 2; \]
\[ 2l = 1.1264; \% \text{mixing rule for cubic EOS} \]
\[ u = -A \ast B; \]

222
\[
3*t*x+s^2)/r/(36*t*s*r-108*u*r^2-8*s^3+12*t^3+1/2)/(4*t^3+r^2+s^2-18*t*s*r+u+27*u^2*r^2+4*u*s^3)/(1/2)*r)^{(1/3)}
\]

\[
\text{delta11} = (2.*a1.*0.5)/a.*((x1.*a1.*0.5.*a2.*b2.*x2.*a1.*a2.*0.5).*a2.*b2;\]
\[
\text{delta2} = (2.*a2.*0.5)/a.*((x1.*a1.*0.5.*x2.*a1.*a2.*0.5).*a1.*b1;\]
\[
\text{phill} = \exp(b1./b.*((\text{real}(Zl) - 1) - \log(\text{real}(Zl) - B) + A./B .*\text{(delta11)} .* \log((2.*\text{real}(Zl) + 2.*B)/(2.*\text{real}(Zl))));\]
\[
\text{phil2} = \exp(b2./b.*((\text{real}(Zl) - 1) - \log(\text{real}(Zl) - B) + A./B .*\text{(delta2)} .* \log((2.*\text{real}(Zl) + 2.*B)/(2.*\text{real}(Zl))));\]
\[
\text{end}\]

\% Vapour calculation
\[
a = y1.^2.*a1.*y1.*y2.*(al.*a2).^0.5.*y2.*(1-kij) + y2.*a2.*(1-kij);\]
\[
b = y1.*y2.*(1-Lij) + y1.*y2.*(b1 + b2).*(1-Lij) + b2.*y2.^2.*(1-Lij);\]
\[
A = a.*P./(R^2.*T.^2);\]
\[
B = b.*P./(R.*T);\]
\[r = 1;\]
\[s = -1;\]
\[t = A - B - B.^2;\]
\[u = A .* B;\]

\[
\text{delta1} = (2.*a1.*0.5)/a.*((y1.*a1.*0.5.*(1-kij)) + (y2.*a2.*0.5.*(1-kij));\]
\[
\text{delta2} = (2.*a2.*0.5)/a.*((y1.*a1.*0.5.*(1-kij)) + (y2.*a2.*0.5.*(1-kij));\]
\[
Zv = 1./6./r.*(36.*t.*s.*r-108.*u.*r.^2-8.*s.^3+12.*t^3+1/2)/(4.*t^3+r^2+s^2-18.*t.*s.*r+u+27.*u^2.*r^2+4.*u.*s.^3)/(1/2).*r)^{(1/3)}+2./3.*((-3.*t.*r+s.^2)/r./(36.*t.*s.*r-108.*u.*r.^2-8.*s.^3+12.*t^3+1/2)/(4.*t^3+r^2+s^2-18.*t.*s.*r+u+27.*u^2.*r^2+4.*u.*s.^3)/(1/2).*r)^{(1/3)}-1/3.*s./r;\]
\[
\text{phiv1} = \exp(b1./b.*(Zv - 1) - \log(Zv - B) + A./B .*\text{(delta1)} .* \log((2.*Zv + 2.*B)/(2.*Zv));\]
\[
\text{phiv2} = \exp(b2./b.*(Zv - 1) - \log(Zv - B) + A./B .*\text{(delta2)} .* \log((2.*Zv + 2.*B)/(2.*Zv));\]
\[
\text{if dont <= 1}\]
\[
\text{K1 = 1 .}/. \text{phiv1;}\]
\[
\text{K2 = 1 .}/. \text{phiv2;}\]
\[
\text{else}\]
\[
\text{K1 = phill .}/. \text{phiv1;}\]
\[
\text{K2 = phill .}/. \text{phiv2;}\]
\[
\text{x1 = z1 .}/. (K1 + L .* (1-K1));\]
\[
\text{y1 = K1 .* x1;\]
\[
\text{x2 = z2 .}/. (K2 + L .* (1-K2));\]
\[
\text{y2 = K2 .* x2;\]
\[
\text{sumxy = (x1 - y1) + (x2 - y2);}\]
\[
\text{end}\]
\[
\text{if sumxy} \sim 0;\]
\[ L = L - ((z_1 \cdot (K_1 - 1) \cdot (1 - K_1 \cdot L) + (z_2 \cdot (K_2 - 1)) \cdot (1 - K_2 \cdot L)) \cdot ((z_1 \cdot (K_1 - 1) \cdot ^2) \cdot (1 - K_1 \cdot L) \cdot ^2 + (z_2 \cdot (K_2 - 1) \cdot ^2) \cdot (1 - K_2 \cdot L) \cdot ^2)); \]

end

if \( L < 0 \)
\[
dont = 1;
\]
\[
L = 0;
\]
\[
y_1 = z_1;
\]
\[
y_2 = z_2;
\]
\[
x_1 = 0;
\]
\[
x_2 = 0;
\]
\[
sumxy = 0;
\]
break
end

end

if dont > 1
\[
V_1 = Z_1 \cdot R \cdot T \div P;
\]
\[
V_v = Z_v \cdot R \cdot T \div P;
\]
\[
d_1 = (x_1 \cdot 18 + x_2 \cdot 32) \div V_1; \quad \text{%must be in kg/L}
\]
\[
d_v = ((y_1 \cdot 18 + y_2 \cdot 32)) \div V_v;
\]
else
\[
V_v = Z_v \cdot T \cdot R \div P;
\]
\[
V_1 = NaN;
\]
\[
d_v = ((y_1 \cdot 18 + y_2 \cdot 32)) \div V_v;
\]
\[
d_1 = NaN;
\]
end
\[
Lprime(1, cnt) = L;
\]
\[
phi1prime(1, cnt) = phi12;
\]
\[
phi2prime(1, cnt) = phi2v;
\]
\[
K2prime(1, cnt) = K2;
\]
\[
dvprime(1, cnt) = dv;
\]
\[
dlprime(1, cnt) = dl;
\]
\[
Zvprime(1, cnt) = Zv;
\]
\[
Zlprime(1, cnt) = Zl;
\]
\[
Vvprime(1, cnt) = Vv;
\]
\[
Vlprime(1, cnt) = Vl;
\]
\[
Tprime(1, cnt) = T;
\]
\[
ylprime(1, cnt) = y1;
\]
\[
y2prime(1, cnt) = y2;
\]
\[
x1prime(1, cnt) = x1;
\]
\[
x2prime(1, cnt) = x2;
\]

if x2prime(1, cnt) >= 0.05, break, end
\[
T = T + 0.1;
\]
\[
cnt = cnt + 1;
\]
\[
PO2 = y2prime \cdot P;
\]

\$Tromans solubility model$
\[ kT = \exp\left(0.046 \cdot T' \cdot T' + 203.35 \cdot \log\left(\frac{T'}{298.15}\right) - (299.378 + 0.092 \cdot T') \cdot (T' - 298.15) - (20591)\right) / \left(8.3144 \cdot T'\right); \]
\[ gf = 1.016275 \cdot 0.901725753; \]
\[ Co = \text{phiv2prime} \cdot kT \cdot P02 \cdot 0.9869233; \]

In these formulas, the pressure in atmospheres gives moles per kg H₂O.

Calculating the ratio of corrosion rate at T to corrosion rate at 298
\[ Qt = 14227 + 46610000000000000000 \cdot T' \cdot (-6.8132); \]

%Activation energy
\[ T_{\text{final}}(1, \text{cnt } -1) = T; \]
\[ r25 = Co(1) \cdot dlprime(1) \cdot \exp\left(-Qt(1) / (8.3145 \cdot 298.15)\right); \]
\[ \text{ratio1} = Co \cdot dlprime \cdot \exp\left(-Qt / (8.3145 \cdot T')\right) / r25; \]
\[ \text{ratioRKS} = (x2prime \cdot 55.556 / (1 - x2prime)) \cdot dlprime \cdot \exp\left(-Qt / (8.3145 \cdot T')\right) / r25; \]

\[% \text{sigma12} = 0.5 \cdot (34.33 + 26.41); \%
\[ \text{omegaD} = 5e-12 \cdot T' \cdot T' \cdot 4 - 1e-8 \cdot T' \cdot T' \cdot 3 + 2e-5 \]
\[ \cdot T' \cdot T' \cdot 2 - 0.0084 \cdot T' + 2.8955; \]
\[ 3D12 = 1.8824e-3 \cdot \sqrt{(T' \cdot T' \cdot 3 \cdot (1 / 18 + 1 / 32)) / (P \cdot 100 \cdot \text{sigma12} \cdot \text{omegaD})}; \%
\[ \text{sigma12} = 0.5 \cdot (34.33 + 26.41); \%
\[ \text{omegaD} = 5e-12 \cdot T' \cdot T' \cdot 4 - 1e-8 \cdot T' \cdot T' \cdot 3 + 2e-5 \]
\[ \cdot T' \cdot T' \cdot 2 - 0.0084 \cdot T' + 2.8955; \]
\[ D12 = 1.8824e-3 \cdot \sqrt{(T' \cdot T' \cdot 3 \cdot (1 / 18 + 1 / 32)) / (P \cdot 100 \cdot \text{sigma12} \cdot \text{omegaD})}; \%
\]

end

\[ F2 = y2prime \cdot P \cdot \text{phiv2prime}; \%
\[ H21 = F2 / x2prime \cdot 1e-4; \%
\[ H21 = \log(H21); \%
\[ Tf = 1000 \cdot (1 / Tprime); \%
\[ \text{FranckH} = [-2.06 -1.59 -0.53 -0.35 -0.18 -0.03 0.15 0.30 0.62 0.82]; \%
\[ \text{FranckT} = [1.54 1.55 1.61 1.63 1.66 1.70 1.73 1.75 1.82 1.93]; \%
\]

plot(Tprime, y2prime)
%Coprime = x2prime \cdot total \cdot (total \cdot (1 - x2prime) \cdot molesH2O); \%
Coprime = x2prime \cdot x1prime \cdot 55.56; \%
plot(x2prime, Tprime, y2prime, Tprime)