# Corrosion of Titanium and its Alloys at High Temperatures and Pressures

By

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# ABSTRACT

Selected Ti alloys (ASTM Grades 1, 12, and 18) were tested in sulfate media, simulating typical Ni laterite leach liquor. The investigation involved a thermodynamic analysis of the Ti–H<sub>2</sub>O, Ti–S–H<sub>2</sub>O, and Ti–Cl–H<sub>2</sub>O systems. Long–term immersion (ASTM G31), potentiodynamic polarization (ASTM G5), cyclic polarization, and potentiostatic tests were administered to investigate and quantify the corrosion. XRD, SEM, XPS, and AES were used to characterize the uncorroded and corroded surfaces and the nature of the corrosion products.

Long-term immersion tests provided real time corrosion rates. Two week moderate temperature immersion tests were implemented to compliment the long-term results. Ti corrosion increased with more acid and higher temperatures. The addition of chlorides led to higher corrosion rates while the addition of Fe, Cu and the presence of Ti ions inhibited the corrosion.

Polarization experiments were performed at intermediate temperatures (50–70 °C, 323–343 K) using a water bath and at elevated temperatures (150–250 °C, 423–523 K) using a 2L autoclave. Results from the polarization tests complement the immersion results. Corrosion rates calculated from the polarization tests exaggerated the rate of Ti-18 and underestimated the rate of Ti-12. The Ti-18 accelerated corrosion rates were inflated because there was insufficient time for Pd to become enriched on the surface.

Characterization of the samples exposed the different corrosion behaviour of the alloys and provided chemical and depth profile information regarding the thermally induced oxides at simulated HPAL conditions.

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# **1** INTRODUCTION

Increased a pplication of T i–alloys in extractive metallurgy and the chemical process industry has prompted further research into their high temperature aqueous corrosion. Ti has been the material of c hoice for u se in autoclave liners and internal components where it is subjected to severe conditions of acidity, temperature, and pressure. Although highly erosion and corrosion resistant, Ti–alloys are not completely immune to both local and general forms of corrosion, and occasionally, processes are interrupted to repair Ti corrosion damage.

The process conditions that are investigated in this thesis are those of the High Pressure and Temperature Acid Leaching (HPAL or HTAL) of Ni laterite ores in Ti lined autoclaves. The main issue in these autoclaves is that of localized corrosion. The presence of many oxidizing species in the bulk solution ensures a passive rest potential for the Ti liner and parts. Scales concentrated in Fe and Al formed during the leaching process provide the opportunity for localized corrosion systems to be established.

This investigation of Ti and Ti–alloy corrosion in sulphuric acid media was an attempt to understand the behaviour of these materials under variable conditions of temperature, pressure, and solution chemistry. The approach taken was to test the metals at room temperature and relate the findings to published results and current theory. After gaining an understanding of the corrosion mechanisms of Ti, the alloys were tested at higher temperatures to simulate industrial conditions. Immersion tests were administered to attain real time corrosion rates that complimented accelerated corrosion rates obtained from electrochemical polarization work. Extensive material characterization was also undertaken.

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This research is a continuation of the Ti corrosion effort at U.B.C. initiated by Jantje Been [1] with her PhD thesis *Titanium Corrosion in Alkaline Hydrogen Peroxide Environments*. This was followed up by Peter Reid [2] with his M.A.Sc. thesis, *Corrosion of Titanium and Titanium Alloys in Aqueous Acid Electrolyte*.

Specific objectives for the research are summarized as follows:

- Create E-pH stability diagrams to provide a theoretical map of the systems being tested.
- Investigate the corrosion resistance of selected Ti Alloys in sulfate media at various concentrations using immersion testing and polarization techniques.
- Calculate accelerated corrosion rates from the maximum current (i<sub>max</sub>) during potentiodynamic scanning and real time corrosion rates from the weight losses measured during immersion testing.
- Calculate and correct measured potential values for the TJP and LJP to relate results to the thermodynamic stability diagrams.
- ▶ Use XPS, AES, SEM and XRD to characterize the samples and corrosion products.
- > Observe the effects of select slurry constituents (Cl, Ti, Fe, and Cu).
- Test the metals at intermediate temperatures (< 373 K) in a water bath and elevated temperatures (> 373 K) and pressures using an autoclave.

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# 2 LITERATURE REVIEW

## 2.1 High Pressure Acid Leaching

The use of HPAL to process Ni laterite ore is recent, notably used by four Ni mining companies. The leaching takes place in autoclaves at temperatures of up to 523 K (250°C), pressures of 5 MPa (725 psi), and sulfuric acid concentrations of 30–100 gpL, injected as pure  $H_2SO_4$  [3]. The desired metals, Ni and Co, are dissolved along with Fe, Mn, Al, Cu, Mg, Sb, and Na. Chlorides are present in the leach liquor from the plant process water in concentrations from 500 to 200,000 ppm. The saline water usually contains Na, Mg and SO<sub>4</sub> [4]. Scale buildup on the autoclave liner and components provide the opportunity for localized corrosion.

Australian laterite ores generally contain the following elements: Si, Fe, Al, Mg, Ni, Co, Mn, Cr, Ca, S and have moisture contents ranging from 10–35% [4][5]. During the autoclave warm–up, Fe and Al (in the form of goethite and boehmite respectively), dissolve around 408–428 K (135–155 °C). Upon further heating, iron will precipitate as hematite and ferric sulfate, whereas aluminum will precipitate as alunite and aluminum sulfate thus regenerating the acid used to dissolve the metals in the first place [6]. The scales formed on the autoclave surfaces were found to be composed of mainly natrojarosite / natroalunite solid solutions or hydronium alunite, hematite, and amorphous silica, however, the exact composition depends on the original ore [7].

## 2.2 Autoclave Materials

Autoclaves used in the HPAL processes are constructed using Ti clad low carbon steel due to cost considerations in comparison with a solid Ti bomb. The Ti liner is joined to the steel shell using explosion bonding, a "cold welding" technique that "produces a mechanically induced fusion type weld with an extremely small fusion zone and extremely high cooling rates" [8]. The Ti liner contacts the hot acid slurry and resists corroding while the steel shell provides the structural support. The grade of Ti used can vary throughout the vessel to provide specific protection: alloys containing Pd or Ru where crevice corrosion might occur; abrasion resistant alloys where erosion is prevalent; ignition resistant alloys where oxygen or rubbing surfaces pose a threat of Ti fires [9]. Out of the six Ni HPAL autoclave built worldwide, the Ti alloys used for the liners have been Ti–1 (four autoclaves), Ti–11 (one autoclave), and Ti–17 (one autoclave) [1]. Autoclaves are shut down regularly to remove scales and inspect the parts and liner and, if localized corrosion is identified, the area is field weld–repaired. Pd bearing Ti is recommended for repaired areas to prevent further corrosion [1].

Typically, Ti-12 is used in sites of potential erosion such as for wear plates beneath the agitators and in piping components (tees and elbows), while weirs, baffles, flanges and nozzles are made of either Ti-2 or Ti-12 [1]. F inally, Ti-5 and Ti-18 have been the materials of choice for agitator blades that face the slurry and are abraded the most [1][10].

# 2.3 Titanium Alloys

Ti transforms phases from hexagonally close-packed (HCP or  $\alpha$ -phase) to bodycentered cubic (BCC or  $\beta$ -phase) at temperatures above 882 °C [11]. The alloys that were tested in this work, Ti-1, Ti-12, and Ti-18. T i-1 and Ti-18, are known to have  $\alpha$ -phase structures. The Ti-12 is considered to be a near- $\alpha$  structure as it contains only a small amount of  $\beta$ -phase.

ASTM Grade	1	2	12	18
UNS #	R50250	R50400	R53400	R56322
Description	Unalloyed (0.06%) O <sub>2</sub>	Unalloyed (0.12%) O <sub>2</sub>	Ti-0.3Mo-0.8Ni	Ti-3Al-2.5V-0.05Pd
Tensile/Yield Strength (MPa)	240 / 170	345 / 275	483 / 345	620 / 483
Grain Size (um)	20	20	4	7
Motivation	Most formable Low cost	Good strength and ductility	Added corrosion resistance over Ti-2	Cold formable, improved reducing acid/crevice resistance
Uses	Liner, parts	Liner, parts	Internals, nozzles and valves	Dynamic equipment components, high pressure service

 Table 1 Titanium and Ti-alloy information [1][10][12][13][14]

Alloy Ti-1 is slightly more pure, thus more formable than Ti-2, and is used in explosively clad plates and in complex parts that require deep drawing [15]. Ti-12 and Ti-18 have intermediate strength, good ductility, toughness, creep resistance and weldability. Ti-1 and Ti-12 were cold rolled to a > 50% reduction followed by annealing. Ti-18 was hot rolled at a sub-transus temperature (in the range of 760–930°C, 1033–1203 K) followed by a final alpha / beta anneal.

The Mo and Ni in Ti-12 can provide improved corrosion resistance in certain reducing acid environments [12]. Mo enrichment have been identified near pit sites on Ti-32 tested in HCl with a pH of 2 and temperature up to 373 K [16]. During studies of Ti-2 and Ti-12, samples were being strained while held at a cathodic potential of -730 mV SHE, at temperatures greater than 373 K. These conditions led to extensive hydride formation in Ti-12 while having no effect on Ti-2 samples [11]. On the other hand, Ti-12 had an increased resistance to crevice corrosion when tested in saline solutions up to 373 K [18][19].

Particles of Ti<sub>2</sub>Ni help the re-passivation of Ti by reducing the protons formed inside the crevice [19]. The intermetallics Ti<sub>2</sub>Ni, TiNi, and TiNi<sub>3</sub> have been identified on the surface of a Ni electrode after being cathodically polarized at high temperatures (680–850 °C, 953–1123 K) when Ti was present in a NaCl-KCl melt. Intermetallics were not detected on the surface of a Mo electrode at the same conditions [20]. Alloying Ti with metals such as Ni, Mo or Pd allows for cathodic depolarization of the surface by providing sites of low hydrogen overvoltage, thus shifting the potential to the noble direction and stabilizing the protective oxide layer. This is the same mechanism as Ti<sub>2</sub>Ni induced re-passivation [21]. Usually, the alloys that modify the exchange current density do not exist on the surface as pure metal but rather as intermetallic compounds with Ti. They also tend to precipitate as separate phases often at grain boundaries and triple points [1]. The Ti passive film is likely to be discontinuous around these intermetallic precipitates [1]. Robert S. Glass [22] attributed the corrosion of TiCODE12 (Ti-0.8Ni-0.3Mo) in boiling HCl to the breaking of the galvanic couple between the Ti matrix and the Ti<sub>2</sub>Ni particles.

Al was found to selectively leach from the surface of Ti-6Al-4V samples, into a solution of 0.05 M  $H_2SO_4$  and 0.05 M NaCl when held at potentials close to 0 V vs. Ag / AgCl. The V concentration on the surface of the samples remained unchanged [24].

Alloying additions are generally made to improve the mechanical properties, the exception being Pd "the electrochemists alloy" [12]. Ti-12 and Ti-18 are alloyed to maximize mechanical properties while minimizing the formation Ti  $\beta$ -phase. The presence of the  $\beta$ -phase is known to reduce the corrosion resistance of Ti, this is possibly a galvanic effect. Ni, Mo and V are  $\beta$ -phase stabilizers as seen in the following ternary phase diagrams and table (Figure 1 and Table 2).

6



Figure 1

Ti-Ni-Mo ternary phase diagram [21]



Figure 2

Ti-Al-V ternary phase diagram [21]

Table 2 Titanium α-phase limit of select alloy additions [21]

Alloy	Ni	Мо	Al	V
α–phase limit (atomic .%)	0.3	0.8	32	3

Small differences in interstitial elements (O, C, and N) do not have any significant effect on the corrosion rate when the rate is very low as the composition of the passive film is unaltered. The presence of dissolved oxygen in Ti increases the potential towards noble values [25] as it depolarizes the cathodic surface [26]. Fe and S have been shown to increase corrosion when the rate is greater than 0.13 mmpy [21]. However, when Fe is associated with Ni as an intermetallic particle it may assist in suppressing crevice corrosion of Ti [1].

Table 3 $E_{corr}$ and $i_{max}$ for select Ti–alloys,	0.9 M NaCl, 0.1 M HCl, 3	373 K [27]
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Elements alloyed with Ti (weight %)	E <sub>oc</sub> (V) vs SCE	$i_{max}$ ( $\mu$ A/cm <sup>2</sup> )
Unalloyed	-0.73	130
4V + 6 Al	-0.73	190
0.15 Pd	-0.34	Not available

÷

## 2.4 Titanium Corrosion

## 2.4.1 Oxygen

Ti is a very reactive metal. Its high corrosion resistance is due to a thin tenacious surface oxide layer that forms when exposed to air or water. The corrosion resistance of Al and Cr is also due to their protective oxide layers. Ti oxide film growth resembles that of metals such as Zr, Nb, Ta, Hf, but its ability to spontaneously activate in deoxygenated aqueous sulfate solution is a trait of active–passive metals (Fe, Co, Ni, Cr Al) [17]. The extent of surface oxidation is strongly influenced by the polarization procedure applied, electrolyte composition, temperature, and pH [28]. The Oxide layers properties dictate surface reaction kinetics. Some experimental techniques used to form oxides are potentiostatic polarization, galvanostatic polarization, and potential cycling. Techniques used to characterize the oxides include x–ray photoelectron spectroscopy (XPS), linear–sweep voltammetry, and cyclic voltammetry. The nature of the Ti oxide film remains the subject of some debate, the following summary of the three "distinct schools of thought" concerning the surface of Ti in active corrosion conditions was written by Eugene J. Kelly [17]:

Briefly stated, there are three distinct schools of thought. The first, one which might be referred to as the monolayer or two-dimensional school, maintains that only adsorbed species on the monolayer level are present on the surface of the metal in the active and transition states, a concept which was found to apply to the other metals of the active-passive group. The second school of thought, the phase-oxide or three-dimensional school, embraces a concept according to which a phase oxide, (as opposed to adsorbed monolayer species) exists on titanium not only in the passive states, but also in the active and transition states. Finally, it should be noted that, at one time, titanium hydride was considered to p lay the dominant role in d etermining the electrochemical b ehavior of the metal, and in fact, was assumed to be responsible for the passivity of titanium. Although this viewpoint has not been sustained, the exact role played by adsorbed hydrogen or hydride remains rather obscure.

More recently, a review of Ti oxide surfaces when submerged in a corrosive medium was described by Jantje Been and Jim Grauman [12]:

When the oxide is sufficiently thick and stable, electron exchange occurs p redominantly with the oxide film. The semiconductive properties of the oxide determine the current/potential behavior of the titanium/oxide system. When the oxide is sufficiently thin (0.4-3nm), electron exchange occurs between the redox electrolyte and the underlying metal by direct tunneling or resonance tunneling via intermediate states.

TiO<sub>2</sub> is an *n*-type semiconductor and thus has the ability to conduct electrons [21]. This semi-conducting property is attributed to O and Ti interstitials that function as donor sites [17]. TiO<sub>2</sub> is a known photocatalyst. When exposed to light and oxygen or water, electrons and holes are created causing hydroxyl and oxygen radicals that catalyze many reactions, notably breaking down organic material. This effect has a considerable ability to catalyze the decomposition of water to hydrogen gas on a Ti cathode or oxygen on a Ti anode. It has been recommended that immersion tests take place in a dark room to properly simulate underground environments [29].

The passive oxide film is mainly composed of Ti(IV). There are many reports of Ti(III) and Ti(II) in the film, however these results are subject to debate as Ti in a reduced state may be an artifact produced by Ar sputtering.

Name	Formula	Ti-O bond length (Å)	Density (g/cm <sup>3</sup> )	Colour
Anatase	TiO <sub>2</sub>	1.91	3.90	
Brookite	TiO <sub>2</sub>	1.84-2.03	4.13	
Rutile	TiO <sub>2</sub>	1.988	4.27	
Ti Sesquioxide	Ti <sub>2</sub> O <sub>3</sub>		4.486	Purple-Violet
Ti Oxide	TiO		4.888	Bronze

Table 4	Titanium	oxide	information	[30]
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Pang et al. [31] studied the anodically formed oxide films on Ti in 0.1 M sulphuric acid. They concluded that the scan rate has considerable influence on anodic polarization and the commencement and extent of oxygen evolution are indicative of film breakdown that occurs when the polarization rate is decreased. The composition of the film formed at different rates are the same, yet, the crystal structure differs. Polarized films (1 m V/s) consist of m ainly anatase TiO<sub>2</sub> as opposed to the slightly more stable rutile. Pang et al. also noted that most oxygen evolution occurs above 2 V vs. SCE.

Oxygen solubility in pure water and various electrolyte solutions (1.525 m CuSO<sub>4</sub>, 1.501 m NaOH and, 5.69 m NaCl) is at its minimum around 373 K (100°C). Its solubility is higher in pure water compared to the electrolytes [32].

#### 2.4.2 Hydrogen

When bare Ti metal interacts with aqueous environments, a highly cathodic potential is observed (-665 mV vs. SCE in 1N HCl) [17]. Generally, an oxide film will protect Ti, however, if this film is damaged or r emoved, the exposed m etal will a bsorb h ydrogen and produce Ti hydrides. Hydrides produced in association with corrosion can penetrate the metal to significant distances at temperatures above 130 °C (403 K). Minimal amounts of hydrides are formed in hot oxidizing halide media due to bulk solution cathodic depolarization [13]. However, hydrides are found in Ti crevices caused by crevice corrosion [21]. The Tafel slope for HER on Ti was found to be -120 mV / decade in H<sub>2</sub> saturated acidic sulfate media with pH ranging from 0–4 [33]. The HER pertaining to Ti corrosion is defined by Kelly as follows:

A cathodic behaviour that occurs in conjunction with active corrosion of Ti, or when Ti is polarized to sufficiently low potentials, either by an externally impressed current or through electrical contact with another actively corroding metal (*i.e.*, galvanic coupling) [17].

Since the exchange current of the HER in 1 M  $H_2SO_4$  is significantly higher for Pd and Ni compared with Ti; only a small amount of these metals on the surface is required to change the overall exchange current density for the Ti–alloy. TiH<sub>2</sub> has a lower overvoltage for

hydrogen evolution than Ti [27]. When alloyed with Mo, cathodic reactions on Ni-based alloys are enhanced. It is believed that Mo allows for a fast proton discharge that is thought to be the rate-determining step [35].

Metal	-log(i <sub>o</sub> )	$i_o (A/cm^2)$
Pd	3.0	$1.0 \cdot 10^{-3}$
Pt	3.1	$7.9 \cdot 10^{-4}$
Ni	5.2	$6.3 \cdot 10^{-6}$
Ti	8.2	6.3.10 <sup>-9</sup>

Table 5 Exchange current density (i<sub>0</sub>) for the HER in 1 M H<sub>2</sub>SO<sub>4</sub> [34]

A Ti-2 weight percent Ni alloy absorbs 10 times more hydrogen than unalloyed Ti when galvanically coupled to Al in an aerated solution [26]. Table 6 displays how hydrogen penetrated into Ti after being held at a potential of -0.4 or -1 V, a temperature of 363 K in 260 g/L NaCl solution saturated with Cl(g) [36].

No. Layers	Thickness of Layers (μm)	H/Ti Ratio (atomic) (E = -0.4 V)	Thickness of Layers (μm)	H/Ti Ratio (atomic) (E = -1 V)
1	0.66	0.12	0.56	0.98
2	0.56	0.10	0.62	0.92
3	0.93	0.088	1.23	0.86
4	0.23	0.046	0.73	0.32
5	1.64	0.021	0.62	0.11

 Table 6 Penetration of hydrogen into Ti specimens [36]

### 2.4.3 Mechanisms of Corrosion

In his review entitled *Electrochemical Behavior of Titanium*, [17] Eugene Kelly describes three states where the behavior of Ti is unique, the following are his conventions that will be used in this thesis:

- 1. An active state in which the metal is oxidized to form Ti(III) ions in solution.
- 2. A passive state in which the metal is covered with an oxide film (TiO<sub>2</sub>, although generally non-stoichiometric), and in which the substrate metal is oxidized to form additional film and/or Ti(IV) ions in solution.

3. An active-passive transition region corresponding to the passivation process, i.e., to the transformation of the metal from the active to the passive state.

Corrosion can be thought of as the destructive attack on metal by reaction with the environment. General corrosion occurs when the metal exposed to a corrosive solution dissolves evenly. Although Ti does not undergo general corrosion under Ni laterite leaching conditions, understanding the corrosion mechanisms is crucial to understanding localized corrosion. Ti will corrode (activate) in deoxygenated chloride or sulfate solutions ( $[CI^-] = 1M$  or  $[SO_4^{--}] = 0.5$ ) at pH values below 2.3 and 3.0 respectively [17][37]. The addition of NaCl has been found to increase the activity of the protons considerably [27]. The anodic and cathodic reaction is depicted in Equation 1 and Equation 2 respectively.

## Equation 1 Ti $\rightarrow$ Ti<sup>+++</sup> + 3 e<sup>-</sup>

# Equation 2 $3H^+ + 3 e^- \rightarrow {}^{3}/_{2}H_{2}(g)$

The stable active-state c orrosion p otential of T i is -665 mV vs. SCE (-425 mV vs NHE) [17][37][38]. Ti(III) in solution exhibits a characteristic violet color. Oxygen or other oxidizing species can convert the Ti(III) to the less soluble pale yellow Ti(IV) ion [21]. The surface of Ti that has undergone general corrosion often appears rough, resembling localized attack, this is due to variations in the reaction rates caused by corrosion products or gas bubbles. Passive corrosion rates are typically much lower than 0.04 mmpy [21].

### 2.4.4 Localized Corrosion

Many factors contribute to the susceptibility to localized attacks, among these are temperature, chemistry, alloys, metal surface condition, and potential [13]. Crevice corrosion is known to occur in tight crevices exposed to sulfate media at temperatures greater than 70 °C (343 K) [21]. The extent of crevice attack increases with salt concentration and was found to occur when chlorides, iodides, bromides or sulfates are present [27].

The corrosion issue that arises in HPAL processes is one of localized corrosion where the stagnant solution chemistry can deviate significantly from the bulk. Fe and Al based scales precipitate in the vessel and create the opportunity for stagnant pools of leach liquor to form (see High Pressure Acid Leaching). The chemistry of crevice corrosion of Ti has been described in many papers [2][13][14][19][27][39][40][41]. The following is a depiction of the reactions that may occur (Figure 3) and descriptions of the reactions (Equation 1– Equation 6).





Localized corrosion of titanium

#### **Equation 3**

 $3\text{Ti} + 2\text{H}_2\text{O} + 3\text{SO}_4^- + 4\text{Cl}^- \rightarrow \text{Ti}\text{O}\text{Cl}_4^- + \text{Ti}\text{O}(\text{SO4})_2^- + \text{Ti}\text{SO}_4^+ + 2\text{H}_2(g) + 7e^-$ 

## Equation 4 TiOCl<sub>4</sub><sup>--</sup> + H<sub>2</sub>O $\rightarrow$ TiO<sub>2</sub> + 2H<sup>+</sup> + 4Cl<sup>--</sup>

Equation 5  $O_2(dis) + 4H^+ + 4e^- \rightarrow 2H_2O$ 

#### Equation 6

 $Ti + 2H^+ + 2e^- \rightarrow TiH_2$ 

Ti inside the pit or crevice will actively dissolve if the potential is sufficiently reducing (Equation 1). Ti(III) and Ti(IV) form complexes in acid when  $Cl^{-}$  and  $SQ_{4}^{--}$  are present (See Equilibrium). Highly mobile Cl<sup>-</sup> electrically migrate up a concentration gradient into the crevice or pit to maintain electroneutrality, resulting in a high C1<sup>-</sup> concentration in the pit. Since the activity of HCl increases with concentrations above  $\sim 0.5 \text{ mol} \cdot \text{dm}^{-3}$  there is the possibility of a very aggressive pit solution [1]. The formation of Ti oxides within the crevice consumes dissolved oxygen and reacts with water to acidify the solution (Equation 4). If the kinetics of Ti dissolution are high enough, mass transfer limited oxygen diffusion into the pit will not suffice to passivate the localized corrosion. Depletion of oxygen causes the potential of Ti to decrease [27]. Electrons travel through the semi-conducting oxide film to be consumed by protons and dissolved oxygen, this depolarizes the cathodic surface exposed to the bulk solution (Equation 5). Protons and metal cations diffuse out of the pit. Proton reduction inside the pit accounts for more of the electron consumption than oxygen reduction at the cathodic surface [1]. Gas analysis of crevice corrosion systems have shown that oxygen is consumed and hydrogen is produced; bubbles exiting from the crevices are visible during experiments [27]. Ti hydrides are formed in the pit when the potentials are sufficiently low (Equation 6).

A special form of localized corrosion of unalloyed Ti has been identified in hot brines called "smeared surface iron pitting". As the name suggests, this occurs when iron, carbon steel or low-alloy steel breaches the Ti oxide surface and becomes embedded in the underlying metal [21].

Pitting can be induced on metals by polarizing samples to high potentials. The potential at which a metal's protective film breaks down is referred to as the pitting potential. The pitting potential for unalloyed Ti in 1N NaCl is between 9 and 11 V. When Ti is alloyed with Al and V (Ti-6Al-4V), the pitting potential in the same solution is reduced significantly (2.84 V) [42].

### 2.4.5 Inhibition

An inhibitor as it pertains to this research can be defined as "a substance which can be added in microgram quantities to an environment to retard corrosion" [27]. Ti is known to spontaneously activate in deoxygenated sulfate solutions, however, the presence of metal ions will stabilize the oxide film by depolarizing the cathodic surface reactions. This is the same mechanism as alloying to prevent corrosion [1][21]. Ti would not be suitable for HPAL if it were not for the inhibitor effect.

The following are some examples of the inhibitor effect beginning with Cu,: "the addition of 1000 ppm of Cu<sup>2+</sup> reduces the corrosion rate of grade 2 titanium by a factor of 1250 in 20% sulfuric acid at 100 degrees Celsius (from about 62.5 mm/yr to 0.05 mm/yr)" [1]. The addition of small amounts (<0.01 *m*) of CuCl<sub>2</sub> or CuCl to Ti in HCl solution at pH 0 with 1 *m* NaCl at 90 °C (363 K) has been shown to raise the  $E_{oc}$  from ~ -0.6 V to above 0.0 V vs.

SCE [40]. Finally, an experiment, performed by the Materials Technology Institute of the Chemical Process Industries showed that the addition of 100 ppm Ni<sup>++</sup> to a system where Ti-2 was under crevice attack reduced the corrosion current from  $4 \cdot 10^{-4}$  to  $1.5 \cdot 10^{-4}$ A [43].

Strength of Inhibition	Moderate	High	
Oxidizing metal cations	Ni <sup>++</sup> , Co <sup>++</sup>	Cu <sup>++</sup> , Fe <sup>3+</sup> , Ti <sup>4+</sup> , VO <sup>++</sup>	
Oxidizing anions	$NO_3^-$ , $NO_2^-$ , $S_2^-$ , $O_3^-$ , $ClO_3^-$ , $OCl^-$	ClO <sub>4</sub> <sup></sup> , Cr <sub>2</sub> O <sub>7</sub> <sup></sup> , MoO <sub>4</sub> <sup></sup> , MnO <sub>4</sub> <sup></sup> ,WO <sub>4</sub> <sup></sup> , VO <sub>4</sub> <sup>3-</sup> , VO <sub>3</sub> <sup></sup>	
Precious metal ions	Au <sup>3+</sup>	Pt <sup>++</sup> , Pt <sup>4+</sup> , Pd <sup>++</sup> , Ru <sup>3+</sup>	
Oxidizing organic compounds	Picric acid, o-dinitrobenzene, 8-nitroquinoline m-nitroacetanilide, trinitrobenzoic acid		
Others $O_2, H_2O_2$		$Cl_2, ClO_2$	

 Table 7 Select list of inhibitors and their relative potency [1][10][27]

Although oxidizing species such as Fe(III) and Cu(II) are excellent inhibitors of general corrosion, they can accelerate crevice corrosion by depolarizing the cathodic (outer) surface of the crevice. Other inhibitors such as  $NO_3^-$ ,  $ClO_3^-$ ,  $OCl^ CrO_3^-$ ,  $ClO_4^-$ , and  $MnO_4^-$  can migrate into the crevice and inhibit localized attack when present in halide solutions [21].

A notable fact concerning inhibition is that titanium's corrosion product, Ti(III), when oxidized to Ti(IV) acts as a strong inhibitor. This leads to the "autopassivation" of localized corrosion as small amounts of Ti(IV) can passivate a localized corroding surface. The autopassivation is less likely to happen in chloride media as the stability of Ti(IV) in chlorides is significantly less than in sulfate media [1][17]. Kelly found that it requires 10.5 times as much Ti(IV) to passivate Ti in 1.0 mol·dm<sup>-3</sup> HCl than in 0.5 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> [17].

### 2.4.6 Corrosion Rates

Metal	Medium	Concentration	Temperature	Corrosion Rate
		%	°C / K	mmpy
Unalloyed	Aerated H <sub>2</sub> SO <sub>4</sub>	3	60 / 333	0.013
Unalloyed	Aerated H <sub>2</sub> SO <sub>4</sub>	5	60 / 333	4.83
Unalloyed	Aerated H <sub>2</sub> SO <sub>4</sub>	1	100 / 373	7.16
Unalloyed	Aerated H <sub>2</sub> SO <sub>4</sub>	3	100 / 373	21.1
Unalloyed	$H_2SO_4$	1	Boiling	17.8
Unalloyed	$H_2SO_4 + 0.25\% CuSO_4$	30	95 / 368	0.088
Unalloyed	$H_2SO_4 + 0.5\% CrO_3$	30	95 / 368	0
Unalloyed	$H_2SO_4$ + Chlorine (sat.)	45	24 / 297	0.003
Unalloyed	$H_2SO_4 + 4 g/L Ti(IV)$	40	100 / 373	0
Ti-12	Aerated H <sub>2</sub> SO <sub>4</sub>	3	66 / 339	1.65
Ti-12	Aerated H <sub>2</sub> SO <sub>4</sub>	1	Boiling	0.91
Ti-12	Aerated H <sub>2</sub> SO <sub>4</sub>	1	204 / 477	0.91
Mo	De-aerated H <sub>2</sub> SO <sub>4</sub>	40	Boiling	1.5
Pd	$H_2SO_4$	Concentrated	100 / 373	1.6
Pd	FeCl <sub>3</sub>	10	100 / 373	rapid dissolution

Table 8 Corrosion rates of Ti, Mo and Pd [21]

## 2.5 Equilibrium

Ti stability at various conditions of potential and pH are depicted in the following EhpH diagrams based on select thermodynamic data. Many references were consulted for the free energy values and calculations [44]–[57] (refer to Appendix A for details and calculations). Stability diagrams can vary considerably depending on what species are chosen to be included. Chosen oxides include a passive hydrated rutile (TiO<sub>2</sub>·H<sub>2</sub>O) when E<sup>o</sup> > -90 mV and titanium hydroxide (Ti(OH)<sub>3</sub>) when E<sup>o</sup> < -90 mV. TiH<sub>2</sub> is the most stable solid at E<sup>o</sup> < -480 mV. The anodic behaviour of Ti below E<sub>max</sub> closely resembles the behavior of a TiH<sub>2</sub> electrode [57]. Ti(II) was not included as it is highly unstable in solution [17]. Ti(IV) ions are considered to be associated with water or o xygen to form either (Ti(OH)<sub>2</sub><sup>++</sup> or TiO<sup>++</sup>) [17]. TiO<sup>++</sup> was arbitrarily chosen for the diagrams. Ti<sup>+++</sup> is the stable ion species at lower potentials, at  $E^{\circ} > 101 \text{ mV}$  it is oxidized to  $TiO^{++}$  and > 1800 mV the ions are oxidized to the orange coloured pertitanyl ion  $(TiO_2^{++})$ . The solid Ti(VI) oxide, represented by dashed lines, was placed on the diagram where Pourbaix suggested that a solid hydrated trioxide  $(TiO_3 2H_2O)$  exists, he warned that its representation in acid is "grossly approximate" [52].



Figure 4 E-pH diagram, Ti-H<sub>2</sub>O, 298 K, Ti ion activity =1.10<sup>-6</sup>

The thermodynamic calculations were adjusted for high temperature exposure. This was done using empirical formulas for the heat capacity at high temperatures [55] and the Criss Cobble Entropy Correspondence Principle [46][47]. Entropy and heat capacity values for  $\text{TiO}^{++}$ ,  $\text{TiO}_2^{++}$ ,  $\text{HTiO}_3^{--}$ ,  $\text{TiO}_2 \cdot \text{H}_2\text{O}$ , and  $\text{Ti}(\text{OH})_3$  were estimated by Jantje B een u sing a summation of entropy and heat capacity contributions from the various parts of the compound [5]. With this information, stability diagrams were created for  $\text{Ti}-\text{H}_2\text{O}$  at 463 and 498 K (Figure 5 and Figure 6 respectively).





E-pH diagram, Ti-H<sub>2</sub>O, 463 K, Ti ion activity =  $1 \cdot 10^{-6}$ 





The region of stability of passive  $TiO_2 \cdot H_2O$  increased slightly at lower pH values as the temperature is increased. Apparently the stability of the  $HTiO_3^-$  ion increased dramatically with increasing temperature. No attempt was made to verify this.



Figure 7 E-pH diagram, Ti-H<sub>2</sub>O, 498 K, Ti ion activity =  $1 \cdot 10^{-6}$ , close-up

The system in question involved sulfate media. Figure 8 is a combined  $Ti-H_2O$  and  $S-H_2O$  diagram at 298 K followed by a discussion of the stability of Ti sulfate species. TiS,  $TiS_2$  or any other solid titanium-sulfur compound is not thermodynamically stable at the conditions tested [59].



Figure 8 E-pH diagram, Ti-H<sub>2</sub>O and S-H<sub>2</sub>O, 298 K, Ti ion activity =  $1 \cdot 10^{-6}$ , S ion activity = 1

When sulfate ions are present in sufficient concentrations, the stable Ti species in solution is no longer  $TiO^{++}$  or  $Ti^{+++}$ , it is a  $Ti-SO_4^{--}$  complex. Figure 9 and Figure 10 show how the relative concentrations of Ti species vary with  $SO_4^{--}$  concentration.



Figure 9 Speciation diagram, [Ti(III)] vs. [SO<sub>4</sub><sup>-</sup>], 298 K



Figure 10 Speciation diagram, [Ti(IV)] vs. [SO<sub>4</sub><sup>-</sup>], 298 K

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The following E–pH diagram (Figure 11) has an SO<sub>4</sub><sup>--</sup> activity of 0.1. The calculated concentration of  $[SO_4^{--}]$  in 100 gpL H<sub>2</sub>SO<sub>4</sub> at 298 K is 0.1 M (Appendix B). The most thermodynamically stable Ti–SO<sub>4</sub><sup>--</sup> species at this SO<sub>4</sub><sup>--</sup> concentration are TiO(SO<sub>4</sub>)<sub>2</sub><sup>--</sup> and TiSO<sub>4</sub><sup>+</sup>. Equilibrium constants are only approximations as other authors have found different values [9]. In solutions containing both Ti(III) and Ti(IV) there is the possibility of mixed oxidation states such as (Ti(IV)O<sub>2</sub>Ti(III)SO<sub>4q</sub>H<sup>+</sup><sub>p</sub>)<sup>(2q-3-p)-</sup> [49].



Figure 11 E-pH diagram, Ti-SO<sub>4</sub><sup>-</sup>-H<sub>2</sub>O, 298 K, Ti ion activity =  $1 \cdot 10^{-6}$ , SO<sub>4</sub><sup>-</sup> activity = 0.1

Having  $SO_4^-$  present will increase the region of stability of aqueous Ti higher pH values, especially for the Ti(IV) ion as seen in Figure 11.

As for chlorides, Figure 12 and Figure 13 are the species diagrams for Ti(III) and Ti(IV) when Cl<sup>-</sup> is present. Average values of the equilibrium constants for the Ti(III)–Cl<sup>-</sup> stability diagram were used as the author published two sets of data found using different methods [51]. This average has a large uncertainty associated with it, as the values of equilibrium constants for the formation of TiCl<sup>++</sup> were 0.07 and 0.2 [51]. Regardless, a Cl<sup>-</sup>

activity of 1 results in a Ti(IV)–Cl complex being the most stable ion at higher potentials while Ti(III) does not significantly complex with Cl<sup>-</sup>. A considerably higher chloride activity (~ 8) is required before a Ti(III)–Cl complex predominates. The Cl<sup>-</sup> ion is stable throughout most of the E–pH diagram (Figure 14).



Figure 12 Speciation diagram, [Ti(III)] vs. [Cl<sup>-</sup>], 298 K



Figure 13 Speciation diagram, [Ti(IV)] vs. [Cl<sup>-</sup>], 298 K



Figure 14 E-pH diagram, Ti-H<sub>2</sub>O and Cl-H<sub>2</sub>O, 298 K, Ti ion activity = 1·10<sup>-6</sup>, Cl ion activity = 1

Despite the fact that  $Cl^-$  concentrations in the HPAL process solution probably do not get m uch h igher t han 0.2 m, an activity of 1 w as u sed in Figure 15 as  $Cl^-$  concentrates in localized corrosion solutions (See Localized Corrosion).





The effect of Cl<sup>-</sup> present in the solution will increase the thermodynamic stability of Ti(IV) ions (Figure 15) but not to the same extent as SO<sub>4</sub><sup>-</sup> (Figure 11).

## 2.6 Conversion to NHE

#### 2.6.1 Reference Electrodes

The SSE (Hg / Hg<sub>2</sub>SO<sub>4</sub>) electrode was used as the reference electrode for room and moderate temperature tests to avoid the possibility of unwanted Cl<sup>-</sup> from SCE (Hg / HgCl). The potential added to measured values to convert to the NHE scale was 639.2 mV calculated using the Nernst equation (Equation 7):

#### **Equation 7**

E vs. NHE (V) =  $E_0 - (RT/nF) \cdot \log(a_{\text{products}}/a_{\text{reactants}})$ 

Where,  $E_0$  for Hg/Hg<sub>2</sub>SO<sub>4</sub> = 0.6151 V, R = 8.314 J/ mol·K, T = 298 K, n = 2 electrons, F = 96500 C/mol, and  $a_{\text{products}}/a_{\text{reactants}} = [SO_4^-] \cdot \gamma = 0.61 * 0.241 = 0.153$ 

Values for  $[SO_4^-]$  and  $\gamma$  are from the CRC Handbook of Chemistry and Physics (online) [55]. The conversion to NHE (SHE(T)) for the Ag/AgCl electrode used in the high temperature experiments was included in the following section.
# 2.6.2 Thermal Junction Potential

A correction for the thermal junction potential that occurred in the high temperature experiments was made using potential values found by D.D. Macdonald, Table 9, [60].

Temperature	TJP $\Delta E_{SHE}(T) - \Delta E_{OBS}(mV)$
°C / K	Added to measured value E vs SHE(T)
150 / 423	87
200 / 473	14
225 / 498	-24
250 / 523	-71

Table 9 Thermal junction potentials added to high temperature values, 0.5 M KCl salt bridge

# 2.6.3 Liquid Junction Potential

The liquid junction potential is caused by a chemical or concentration difference between the test solution and reference electrode solution when the two come into contact. Potential measurements in this thesis are corrected using the Henderson equation [61]. The junction potential is mainly caused by the high mobility of  $H^+$  in the test solution compared to the  $K^+$  in the reference solution. The junction potential increased greatly with acid concentration. The concentration and mobility of the ions at higher temperatures were also estimated [32] (See Appendix B for the detailed calculations).

Solution 1	Solution 2	Temperature (°C / K)	LJP add to measured value (mV)
K <sub>2</sub> SO <sub>4</sub> (sat)	0.3 M H <sub>2</sub> SO <sub>4</sub>	25 / 298	-10.32
$K_2SO_4$ (sat)	0.3 M H <sub>2</sub> SO <sub>4</sub>	50 / 323	-10.38
$K_2SO_4$ (sat)	0.3 M H <sub>2</sub> SO <sub>4</sub>	70 / 343	-10.53
$K_2SO_4$ (sat)	1 M H <sub>2</sub> SO <sub>4</sub>	25 / 298	-25.02
$K_2SO_4$ (sat)	1 M H <sub>2</sub> SO <sub>4</sub>	50 / 323	-26.52
K <sub>2</sub> SO <sub>4</sub> (sat)	1 M H <sub>2</sub> SO <sub>4</sub>	70 / 343	-27.82
$K_2SO_4$ (sat)	5 M H <sub>2</sub> SO <sub>4</sub>	25 / 298	-49.47
$K_2SO_4$ (sat)	$5 \text{ M H}_2\text{SO}_4 + 16 \text{ gpL NaCl}$	25 / 298	-48.68
$K_2SO_4$ (sat)	$5 \text{ M H}_2\text{SO}_4 + 32 \text{ gpL NaCl}$	25 / 298	-47.91
$K_2SO_4$ (sat)	5 M H <sub>2</sub> SO <sub>4</sub>	50 / 323	-53.29
$K_2SO_4$ (sat)	5 M H <sub>2</sub> SO <sub>4</sub>	70 / 343	-56.41
1 M KCl	0.3 M H <sub>2</sub> SO <sub>4</sub>	150 / 423	-25.77
1 M KCl	0.3 M H <sub>2</sub> SO <sub>4</sub>	200 / 473	-28.56
1 M KCl	0.3 M H <sub>2</sub> SO <sub>4</sub>	225 / 498	-30.00
1 M KCl	0.3 M H <sub>2</sub> SO <sub>4</sub>	250 / 523	-31.48

 Table 10
 Liquid junction potentials added to measured values

# **3** Experimental Aspects

## 3.1 Materials Characterization

Etched samples were prepared for SEM analysis by mechanically grinding to 1200 grit using SiC paper, followed by polishing to 1  $\mu$ m using diamond paste, then, electrochemically etched at a temperature below -30 °C (243 K) in a solution of 300 ml methyl alcohol, 175 ml *n*-butyl alcohol, and 30 ml of 60% perchloric acid. Samples were cooled in a liquid nitrogen bath at low temperatures to avoid the formation of hydride precipitates at the grain boundaries. The potential of the sample was maintained at 20-30 V with a current density of approximately 0.1 A/cm<sup>2</sup> for 15 minutes until the samples showed visible signs of grain boundary etching [27].

# 3.2 Immersion Tests

### 3.2.1 Sample Preparation

Immersion tests were administered to attain real time corrosion rates by weighing the immersed specimens regularly during exposure to various sulphuric acid solutions. Test procedure was with reference to ASTM G31 standard practice [62]. Additions of Cl<sup>-</sup> (NaCl), Fe (Fe<sub>2</sub>O<sub>3</sub>), and Cu (CuO) were made to study the effect of other slurry constituents. Experiments at room temperature as well as 50°C (323 K) were also employed.

The thickness of the samples varied for the three grades of Ti sheets supplied by TIMET; 0.125 cm for Ti-2, 0.05 cm for Ti-12 and 0.15 cm for Ti-18. All samples were individually measured for length, width, and thickness using Vernier calipers prior to immersion. They were cleaned using de-ionized water and acetone then dried and weighed with a precision scale ( $^{+}/_{-}$  0.0005 g).



Figure 16 Room temperature immersion samples, 10 gpL H<sub>2</sub>SO<sub>4</sub>, 218 days

For the room temperature immersion tests, samples were cut into 2.5 X 1.3 cm rectangles (Figure 16) and a hole was drilled in the top of each sample to secure them to the experimental setup using nylon screws. Throughout the test, the samples were only partially immersed to about 1.7 cm lengthwise.



Figure 17 Moderate temperature immersion samples, 323 K, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 14 days

Immersion samples for the moderate temperature tests were cut into 1 X 1 cm squares (Figure 17). Because of degradation problems, Nylon screws were not used for the moderate temperature tests. Instead, the samples stood upright, half immersed in sand, and totally immersed in solution. They were held upright by a glass rod passing through a  $0.02 \text{ cm}^2$  hole located in the middle of the sample.

# 3.2.2 Experimental Setup

Immersion tests were carried out in a beaker with an airtight rubber stopper. A highdensity polyethylene sample tree held four samples while maintaining electrical isolation. Test solution 6 was a darker violet colour due to a high concentration of Ti(III) ions (Figure 18).



### Figure 18 Photograph of the immersion test cells, solutions 5 and 6 (left and right)

Test solution 8 was blue due to Cu ions and solution 9 was yellow due to Fe ions (Figure 19).



Figure 19 Photograph of the immersion test cells, solutions 7,8,9, (cells 1, 2 and 3 respectively)

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# 3.2.3 Test Conditions

The samples were cleaned, dried and weighed once a week for the highly concentrated solutions and less frequently for the less concentrated solutions. The immersion test conditions are summarized in Table 11.

Solution	H <sub>2</sub> SO <sub>4</sub> (gpL)	Cl <sup>-</sup> (gpL)	Temperature (°C / K)	Additional ions, (gpL)
1	10	0	25 / 298	
2	10	10	25 / 298	
3	100	0	25 / 298	
4	100	10	25 / 298	
5	500	0	25 / 298	
6	500	10	25 / 298	
7	100	10	50 / 323	
8	100	10	50 / 323	Cu, 1
9	100	10	50 / 323	Fe, 1

Table 11Immersion test conditions

### 3.2.4 Real Time Corrosion Rate Calculations

Corrosion rates were calculated using Equation 8.

### **Equation 8**

Corrosion rate (mmpy) =  $(8.76 \times 10^4 \cdot W)/(d \cdot A \cdot t)$ 

Where d is the alloy density in  $g/cm^3$ , A is the sample surface area exposed to the solution in  $cm^2$ , t is the exposure time in hours and W is the weight change in grams [21]. (See

.

Appendix C for a sample calculation)

# 3.3 Polarization Tests

### 3.3.1 Sample Preparation

Circular disks were punched from Ti sheet stock using a 5/8" diameter punch and were ground to 600 grit on SiC paper. The samples were then cleaned by rinsing with water, degreased with acetone, rinsed a second time, and ultrasonically cleaned in distilled water for 3 minutes. Testing took place within 20 minutes of ultrasonically cleaning unless otherwise indicated.

### 3.3.2 Apparatus (293–353 K)

The test cell used was the Model K47 Corrosion Cell System from Princeton Applied Research. The test electrode was a flat sample holder (K105) containing a circular Ti specimen, protected from crevice corrosion by a specially designed washer (PAR part no. MP1239). The two counter electrodes were high-density graphite. The reference electrode was a SSE (Hg / Hg<sub>2</sub>SO<sub>4</sub>, PAR part no. G0093). The final opening on the corrosion test cell was for an inert gas line for purging with N<sub>2</sub>.

The equipment can be seen in Figure 20. The high–density graphite counter electrodes were on either side of the working electrode sample holder. The SSE reference electrode was separated from the solution by an ion conducting glass frit located at the end of the glass bridge tube that extends to the working electrode surface. Nitrogen gas was introduced to the solution by a porous ceramic plug (behind the working electrode). The potentiostat used was the PAR model 273A with M352 analysis software.



Figure 20 Photograph of the assembled corrosion cell kit

# 3.3.3 Apparatus (423–523 K)

The high temperature experiments were performed at the CANMET Materials Technology Laboratory in Ottawa. The test cell used was a laboratory scale autoclave from PARR with a glass liner (Figure 1). Potential measurements were compared to the external reference electrode (ERE), a pressurized Ag/AgCl system mounted above the autoclave. This electrode operated at system pressure and at ambient temperature. The temperature was maintained by an external copper-cooling coil with coolant being passed at 283 K. Working electrode attachments were covered with Teflon tape and a coiled Pt wire served as the counter electrode.



The high temperature equipment can be seen in Figure 22. The furnace is located in the left foreground. The autoclave head is in its stand (center), it was attached to the refrigeration system (right) by tubes full of cooling solution.



Figure 22 Photograph of the high temperature test equipment

L. Altan

The autoclave head accessories can be seen in Figure 23. From left to right they are the rupture pipe (Cu tube), gas outlet, pressure gage, reference electrode port (with Cu cooling tube coiled), and the gas inlet.



Figure 23 Close–up photograph of the autoclave head

# 3.3.4 Open Circuit Potential Measurements

Open circuit potential measurements ( $E_{oc}$ ) were made between the working electrode and the reference electrode without current being passed to the counter electrodes. This measurement showed the potential at which the anodic and cathodic reaction currents at the working electrode / solution interface were balanced. In the case of Ti corrosion, these measurements are useful as qualitative information regarding the state of the working electrode surface.  $E_{oc}$  measurements were made to prior to electrochemical polarization experiments to ensure stability. They were also used to evaluate the effects of inhibitors and relative nobility of the samples.

### 3.3.5 Potentiodynamic and Potentiostatic Tests

Potentiodynamic tests were employed with reference to ASTM G31 standard practice [66]. The polarization solution was  $H_2SO_4$  made with reagent grade acid and DI water. The following concentrations were employed: 30, 100, and 500 gpL  $H_2SO_4$ . Cl<sup>-</sup> ions were added in the form of NaCl. The room temperature experiments varied from 18 to 24 °C but were mostly between 20 and 22 °C. Moderate temperature tests (50 to 90 °C or 323 to 363 K) were conducted in an Oakton "Stabletemp" water bath. Room temperature experiments were performed in the absence of oxygen unless otherwise indicated. This was achieved by purging the electrolyte with nitrogen gas for a minimum of 15 minutes prior to testing. Moderate temperature tests were performed in naturally aerated solutions. The scan rate employed was 0.5 mV/sec. Following testing, samples were removed from the holder, rinsed with DI water and dried in a dessicator. Select samples were examined using SEM.

High temperature tests were conducted in a glass beaker that contained 1.2 Liters (1.1 Liters for temperatures greater than 498 K) of 30 gpL  $H_2SO_4$  solution. The solution was dearrated for 15 minutes by purging with N<sub>2</sub> prior to increasing the temperature. The open circuit potential was observed and recorded during the warm–up. After the temperature and open circuit potential stabilized, the sample was cyclically polarized with at a scan rate of 5 mV/s. The potentiostat used was PC internal, manufactured by Gamry. Corroded samples were prepared by exposing the metal to 30 gpL  $H_2SO_4$ , heating them at 473 K in the autoclave for 3 hours then allowing them to cool overnight. Quickly rinsing the samples and storing them in isopropanol after opening the autoclave minimized the corroded sample's contact with the air.

Potentiostatic tests were conducted to complement the potentiodynamic experiments and attain information pertaining to the measured currents at steady state. For Ti-1 the passive state test was conducted in fresh solution at E = 500 mV. The active state potentiostatic tests were implemented following a cyclic potentiodynamic scan and held at their E<sub>max</sub> values, -300 mV for Ti-1 and -250 mV for Ti-12 and Ti-18.

### 3.3.6 Accelerated Corrosion Rate Calculations

The accelerated corrosion rates were calculated using the following equation. Maximum anodic current values  $(i_{max})$  were used in the place of  $i_{corr}$  values.

#### **Equation 9**

Corrosion rate (mmpy) =  $(K \cdot i_{corr} \cdot EW)/(d \cdot F)$ 

Where K is a conversion factor  $(3.1536 \cdot 10^8 \text{ (mm/yr)/(cm/s)})$ ,  $i_{corr}$  is the measured corrosion current (A/cm<sup>2</sup>), d is the alloy density (g/cm<sup>3</sup>), EW is the equivalent weight of Ti (16 (g/mol e<sup>-</sup>) under reducing conditions and 12 (g/mol e<sup>-</sup>) under oxidizing conditions) and F is Faradays constant (96485 C/mol). (See Appendix C for a sample calculation)

## 3.4 Characterization

### 3.4.1 X–Ray Diffraction (XRD)

A SIEMENS (Bragg–Brentano) Diffraktometer D5000 was employed for the XRD analysis. The results were analyzed using the International Center for Diffraction Database (ICDD) and search and match software by SIEMENS (Bruker) with PDF2 data sets (1–49 plus 70–86). Radiation was provided by a CuK $\alpha$  source with a current of 40 mA and potential of 40kV. The diffraction angle ranged between 20–90 °2 $\Theta$ .

### 3.4.2 Scanning Electron Microscope (SEM)

SEM provided high-resolution micrographs of the corroded and uncorroded samples as well as information regarding elements present using BEI and EDS. The SEM used was a Hitachi S-3000N with an Energy Dispersive Spectroscopy (EDS) system and Quartz analysis software. The working distance for the EDS measurements was 15 mm.

### 3.4.3 X–Ray Photoelectron Spectroscopy (XPS)

XPS was utilized to characterize the outer surface of corroded and uncorroded samples. The technique involved irradiating the samples under high vacuum  $(1.10^{-9} \text{ torr})$  with mono-energetic soft x-rays. The emitted secondary electrons are then detected and measured for kinetic energy and frequency. The kinetic energy is subtracted from the x-ray energy to calculate the binding energy of the electron. Every element has a unique spectrum, whereby they can be identified from the intensity vs. binding energy plot. Identifying and measuring the area under specific peaks gives an approximation of the quantity of elements present. The area was multiplied by empirically based coefficients that relate intensities to actual composition. Information revealing the nature of the compounds was also seen in shifts of the peaks' positions. Upon testing the outermost surface (~10 Å deep), argon etching was used to perform depth profiling. The information yielded was an average of a large circular surface area (350 µm diameter) compared to the depth of analysis. A PHI model 5700 SXPS was used. It provided a direct, non-destructive semi-quantitative surface chemical analysis present at the outermost few atomic layers of the solid surfaces (< 0.1 mono-layer sensitivity or  $10^{-9}$  g/cm<sup>2</sup>). A very important feature of XPS was that it determined elemental speciation (chemical forms and oxidation states) at or near the surface of these materials.

# 3.4.4 Auger Electron Spectroscopy (AES)

A PHI model 600 Scanning Auger Multiprobe capable of very high–resolution Auger electron spectroscopy (AES) and Auger and secondary electron (SE) or back–scattered electron (BSE). Semi–quantitative surface elemental composition and elemental distributions on micron–sized regions (or features) could be determined. Typically an Auger spectrum indicates the presence of a specific element (and amount) but cannot yield chemical bonding (oxidation state, speciation) information. Elemental depth profiles were acquired using AES in conjunction with the computer controlled, rastered ion beam (etching) and were obtained on small features, <  $1.0 \mu m$ .

# 4 Results and Discussion

# 4.1 Materials Characterization

The Ti samples received from TIMET were characterized in the etched condition using the SEM (etched), the as received condition using XRD and freshly ground using AES and XPS (See Introduction and Experimental Aspects for alloy descriptions and techniques used).

The results of the XRD analysis revealed very similar crystal structure among the three alloys Ti-1, Ti-12, and Ti-18 (Figure 24). The spectrum for the three metals, as received, corresponded to an HCP ( $\alpha$ -phase) structure. The spectra for the annealed sample also shows a rutile peak (d=3.24) that was the result of the thermally induced thickening of the oxide layer.



Figure 24 XRD spectra on as received samples and the effect of annealing



Figure 25 Microstructure of electrochemically-etched samples

The average grain size was taken by making 7 random measurements of different areas from one micrograph. At least three grains were included in each measurement. The immersion test samples revealed the grain size of Ti–18 more clearly than the attempt at etching (Figure 25 vs. Figure 44). The grain size for Ti–12 was a rough approximation, as the grain boundaries were not clearly revealed.

Sample	Ti-1	Ti-12	Ti-18
Average grain size (µm)	23	4.5	11

International Plasma Laboratory LTD conducted the elemental analyses of the Ti samples. The technique used was Inductively Coupled Plasma Mass Emission Spectrometry (ICP-MS). The results shown exclude elements that were found to constitute less than 100 ppm. Ti-12 was specified to be Ti-0.3Mo-0.8Ni, and its composition was measured to be Ti-0.6Mo-0.86Ni. Ti-18 was specified to be Ti-3Al-2.5V-0.05Pd and its composition was measured to be Ti-1.76Al-2.64V. The samples were not tested for Pd. Co was found to be the impurity with the highest concentration in the Ti alloys at ~0.2 wt%.

Table 13

ICP elemental analysis of Ti-alloys, (atomic %)

Ti–Alloy	AI	Ca	Co	Cu	Pb	Mg	Hg	Мо	Ni	Ag	Na	Ti	V
1	0.02	0.05	0.17	0.04	0.07	0.06	0.01	0.00	0.00	0.01	0.02	99.49	0.06
2	0.03	0.06	0.17	0.04	0.07	0.06	0.02	0.00	0.01	0.01	0.04	99.41	0.07
12	0.02	0.04	0.17	0.04	0.07	0.06	0.02	0.30	0.71	0.01	0.00	98.49	0.06
18	3.10	0.04	0.15	0.05	0.06	0.05	0.01	0.01	0.00	0.01	0.02	94.03	2.46

Table 14	ICP elemental analysis of Ti-alloys, (weight %)
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Ti–Alloy	AI	Ca	Co	Cu	Pb	Mg	Hg	Мо	Ni	Ag	Na	Ti	V
1	0.01	0.04	0.21	0.05	0.29	0.03	0.06	0.00	0.00	0.03	0.01	99.20	0.07
2	0.02	0.05	0.21	0.05	0.32	0.03	0.07	0.00	0.01	0.03	0.02	99.11	0.07
12	0.01	0.04	0.21	0.05	0.32	0.03	0.08	0.60	0.86	0.03	0.00	97.71	0.07
18	1.76	0.04	0.19	0.07	0.27	0.03	0.04	0.01	0.00	0.02	0.01	94.91	2.64

The freshly ground sample surfaces of Ti-2 and Ti-12 were also analyzed using XPS (Table 15 and Table 16) and AES (Table 17 and Table 18) at the CANMET Materials Technology Laboratory. The XPS depth profiles show a gradual transition from the oxide to metal, this is due to the surface roughness incurred by grinding with 600 grit paper and having an analysis a rea of 350  $\mu$ m<sup>2</sup>. XPS analysis was taken from a circular area with a 350  $\mu$ m diameter. AES analysis were from smaller spots with areas of ~ 1  $\mu$ m<sup>2</sup>. Most of the C and Si found on ground Ti surfaces are from the SiC grinding paper.

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	XPS	analysis,	Ti-2 (	atomic	%)
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Etch Depth (Å)	0	Ti	С	N	Fe	CI	Si
0	47.3	19.8	28	2.3	0.8	0.2	1.6
25	38.4	51.9	6.8		1.4		1.5
100	38.4	50.4	8.5		0.9		1.9

Table 16XPS analysis, Ti-12 (atomic %)

Etch Depth (Å)	0	Ti	С	N	Fe	CI	Si
0	48.9	15.6	29.3	3.2	0.4	2.5	0
25	52.5	39.3	6.8		0.2	1.2	0
100 ·	36.9	55.1	5.8		0.9	1.3	0
200 <sup>·</sup>	27.3	62.1	7.4		0.3	1.5	1.3
500	14.5	75.8	6.2		0.2	1.4	1

Ti-2, Spot 1 (Table 17) was visible optically as discolouration was observed on the surface and it was found to be high in Fe. The source of this Fe contamination was not determined. Fe was also found in the weld–affected area on Ti-12, (Table 18, Spot 1) using AES. AES depth profiles taken on well–defined small spots reduced the error associated with surface roughness measured with the XPS, oxide thickness for the freshly ground samples were on the order of 250–300 Å for all of the alloys.

Table 17	AES analysis. Ti-2 (atomic %)
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Location	Etch Depth (Å)	0	Ti	С	Fe	Si	Ρ	Мо	N	S
Spot 1	0	38	4	24	28			0.5	5	0.2
Spot 2	0	36	12	40					12	
Spot 2	500	7.6	78.4	12.2		1.9				

Table 18	AES	analysis,	Ti-12	(atomic %	6)
				(	~ /

Location	Etch Depth (Å)	0	Ti	С	Fe	Si	P	Мо
Spot 1	0	42	12.2	33.5	12.3			
Spot 2	0	36.4	23.9	36	1.3	1.3	0.8	0.2
Spot 3	0	39	40	20.5		0.5		
Spot 3	680	6	89.6	4.4				

# 4.2 Immersion Tests

Real time corrosion rates obtained from the immersion samples are summarized in Table 19. The corrosion rates were calculated for the full 218 days for tests 1 to 4 (See Appendix C for the calculations). The corrosion rates were very low; in fact, in some cases the samples gained mass throughout the test (negative corrosion rates).

The test solutions 5 and 6 yielded higher corrosion rates (Table 19). The rates for these samples were taken for the time period before the samples passivated due to the increased concentration of inhibitor ions, mainly Ti(IV). The corrosion rates were calculated based on the first 42 days for samples Ti-2 solution 5, and Ti-12 solution 5; 28 days for samples Ti-2 solution 6, and Ti-12 solution 6; 14 days for samples Ti-18 solution 5, and Ti-18 solution 5. The passivation of the samples can be seen clearly in Figure 40 and Figure 43. Increasing the temperature to 50°C (323 K) resulted in high rates of corrosion for Ti-1 and Ti-12. The temperature increase did not affect the passive state of Ti-18. The addition of 1 gpL Cu and Fe inhibited corrosion.

Test	H <sub>2</sub> SO <sub>4</sub>	Addition ion		Addition ion		Duration	Temperature	Corros	sion Rate (n	nmpy)
Number	(gpL)	(gpL / ion)		(gpL / ion)		(days)	(°C / K)	Unalloyed	Ti-12	Ti-18
1	10			218	Room	$-8 \cdot 10^{-4}$	8·10 <sup>-5</sup>	$-9.10^{-4}$		
2	10	10	Cl	218	Room	$-8 \cdot 10^{-4}$	$-1.10^{-3}$	$-4 \cdot 10^{-4}$		
3	100			218	Room	$-1.10^{-3}$	$7.10^{-4}$	$9.10^{-4}$		
4	100	10	Cl	218	Room	$3 \cdot 10^{-2}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$		
5	500			129	Room	0.56	1.11	0.20		
6	500	10	Cl	129	Room	2.21	2.31	0.58		
7	100	10	Cl	14	50 /323	4.61	4.50	-0.22		
8	100	10,1	Cl, Cu	14	50 / 323	$-1.8 \cdot 10^{-2}$	$-2.6 \cdot 10^{-2}$	$-1.3 \cdot 10^{-2}$		
9	100	10,1	Cl, Fe	14	50 / 323	$-2.10^{-3}$	$-1.5 \cdot 10^{-2}$	$4 \cdot 10^{-3}$		

 Table 19
 Immersion test conditions and determined corrosion rates



Figure 26 % Change in mass vs. time, Ti-12, 10 and 100 gpL  $H_2SO_4$ , 0 and 10 gpL  $Cl^-$ 



Figure 27 SEM micrographs, Ti-12, 10 gpL H<sub>2</sub>SO<sub>4</sub>, 218 days



Figure 28 SEM micrographs, Ti-12, 10 gpL H<sub>2</sub>SO<sub>4</sub>, Cl<sup>-</sup>, 218 days



Figure 29 SEM micrographs, Ti-12, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 218 days



Figure 30 SEM micrographs, Ti-12, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 218 days



Figure 31 Cross-sections, Ti-12, 100 gpL H<sub>2</sub>SO<sub>4</sub>, no Cl<sup>-</sup> (left), 10 gpL Cl<sup>-</sup> (right)

The immersion tests at 10 and 100 gpL  $H_2SO_4$  did not induce significant corrosion on Ti-12 (less that 0.3 % mass loss in 7 months). In fact, the samples exposed to 10 gpL  $H_2SO_4$  gained mass initially for ~100 days before losing any.

An explanation is that the initial mass gain is a result of Ti oxide film thickening as the samples were weighed regularly and the oxygen content of the solution was refreshed. The final weigh–in was following 118 days without opening the test cell, the samples weights were lower than the previous measurement. Another factor was that the preferential pitting of the grain boundaries exposed and increasing surface area of the corroding material. The passive surface area remained more or less constant over the course of the 218 days.

Presence of  $CI^-$  lowered the final masses except in the case of Ti-12 at 10 gpL H<sub>2</sub>SO<sub>4</sub>. This extra d ecreased m ass is due to increased a ctivity of H<sup>+</sup> in the presence of N aCl [27]. Chlorides also assist in localized corrosion (See Localized Corrosion) and help stabilize Ti(IV) in solution (See Equilibrium). Increased mass when  $CI^-$  is present might be the result of Ni or Mo chloride formation (NiCl<sub>2</sub>, MoCl<sub>2</sub>, MoCl<sub>3</sub>, MoOcl<sub>3</sub>, MoO<sub>2</sub>Cl<sub>2</sub>.H<sub>2</sub>O). These chloride compounds would not be as stable at the lower pH of the 100 gpL H<sub>2</sub>SO<sub>4</sub> solution [59].



Figure 32

SEM micrographs, Ti-12, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 14 days, 323 K



Figure 33 SEM micrographs, Ti-1, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 14 days, 323 K



Figure 34 % Change in mass vs. time, Ti-18, 10 and 100 gpL H<sub>2</sub>SO<sub>4</sub>, 0 and 10 gpL Cl<sup>-</sup>



Figure 35 SEM micrographs, Ti-18, 10 gpL H<sub>2</sub>SO<sub>4</sub>, no Cl<sup>-</sup> (left), 10 gpL Cl<sup>-</sup> (right), 218 days



Figure 36 SEM micrographs, Ti-18, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 218 days



Figure 37 SEM micrographs, Ti-18, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 218 days



Figure 38 Cross-sections, Ti-18, 100 gpL H<sub>2</sub>SO<sub>4</sub>, no Cl<sup>-</sup> (left), 10 gpL Cl<sup>-</sup> (right), 218 days



Figure 39 SEM micrographs, Ti-18, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, 14 days, 323 K

Ti-18 exposed to 10 and 100 gpL H<sub>2</sub>SO<sub>4</sub> were corroded less than Ti-12 (< 0.2%). The 100 gpL H<sub>2</sub>SO<sub>4</sub> solution caused Ti-18 to form an oxide layer more quickly than the 10 gpL solution, however, the higher acid also shortened the time before the sample lost mass. The addition of chlorides was especially noticeable at 100 gpL H<sub>2</sub>SO<sub>4</sub> concentrations in terms of the sample losing more mass than the sample unexposed to chlorides. The mechanism of weight loss appears to be localized attack on the grain boundaries in the 100 gpL H<sub>2</sub>SO<sub>4</sub> solutions as seen in Figure 34 and Figure 35. Localized attack cannot be seen on Ti-18 samples exposed to 10 gpL H<sub>2</sub>SO<sub>4</sub>. Although our weight loss tests suggest that the penetration rate of Ti-18 in solution 6 is  $2 \cdot 10^{-3}$  mmpy (Table 19) as Figure 38 indicates, the depth of penetration due to localized attack can reach a height of 20 µm in 218 days or  $33 \cdot 10^{-3}$  mmpy.

The pH values were calculated and adjusted using the mean activity coefficients of  $H_2SO_4$  in aqueous solution at 25 °C [63]. Concentration calculations assumed full dissociation to  $HSO_4^-$  and partial second dissociation as indicated in Table 37 to Table 39 (Appendix B). The "final" pH of solutions 1 to 6 was taken after 63 days of immersion and solutions 7 to 9 were taken after 14 days of immersion. Measurements of the pH showed that the addition of NaCl increased the activity of H<sup>+</sup> (Table 20). The pH of tests 1 to 4 increased slightly over the first 63 days of testing while a decrease in pH was seen for solutions 5 and 6. The increased pH acid may be due to protons reacting with dissolved oxygen, Equation 5.

Immersion Test	1	2	3	4	5	6	7	8	9
Calculated	1.14	1.14	0.52	0.52	0.14	0.14	0.56	0.56	0.56
Measured (initial)	0.98	0.91	0.13	0.1	-0.56	-0.72	0.48	0.52	0.73
Measured (final)	1.1	0.96	0.17	0.04	-0.92	-1.12	0.68	0.64	0.60

 Table 20
 pH of immersion tests, measurements taken at room temperature

The lower pH levels during immersion testing at higher acid concentration may be caused by the hydrolysis of Ti ions. Once the limited supply of dissolved oxygen was used up, water dissociated to provide oxygen molecules. The HER consumed protons, however, the net reaction resulted in a production of protons. The second dissociation of sulphuric acid replaced  $SO_4^-$  and lowered the pH.

### **Equation 10**

 $Ti + H_2O + 2SO_4^- + 2H^+ \rightarrow TiO(SO_4)_2^- + 2H_2(g)$ 

Equation 11  $2HSO_4^- \rightarrow 2SO_4^- + 2H^+$ 



Figure 40

% Change in mass vs. time, Ti–12, 500 gpL  $H_2SO_4$ , 0 and 10 gpL  $Cl^-$ 



Figure 41 SEM micrographs, Ti-12 immersion sample, 500 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>

The Ti-12 sample experienced a great deal of corrosion damage in the highly acidic conditions. The corrosion was similar to that at higher pH (solutions 1 to 4) except here, the small holes have become larger. Figure 41 shows the surface near the end of the immersion test; there were divots in the surface and small white spherical particles. An EDS analysis on the particle revealed a Ni: Mo ratio of 6.04 : 1.18 wt. %, a similar analysis of the matrix yielded 1.60 : 1.03 wt. %. Figure 42 was taken using backscattered imaging where the precipitates showed up in a lighter colour, indicating a heavier element. The white particles are likely Ti<sub>2</sub>Ni or a similar Ni/Ti intermetallic and appeared to be more corrosion resistant than Ti under these conditions.



Figure 42 SEM micrograph, Ti-12 immersion sample, 500 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, BEI

At higher acid concentrations Ti-12 undergoes significant corrosion, especially when  $Cl^{-}$  is present. Prior to changing the solution on the  $121^{st}$  day, the Ti-12 samples had lost 40%

and 56% (solution 5 and 6 respectively) of their original weight. After changing the solution, the sample exposed to  $Cl^-$  lost significant mass (Figure 41). Both samples corroded at similar rates for approximately fourteen days when 15 ml of solution was removed from both test 5 and 6 to prevent the nylon screws from dissolving. The sample unexposed to  $Cl^-$  remained passive for the following twenty-one days then corroded for one week and remained passive until the solution was changed on the one hundred and twenty first day. The sample exposed to  $Cl^-$  corroded at a steady rate until the twenty-eighth day after which it ceased losing weight until the solution was refreshed (Figure 40).



Figure 43 % Change in mass vs. time, Ti-18, 500 gpL H<sub>2</sub>SO<sub>4</sub>, 0 and 10 gpL Cl<sup>-</sup>

The surface of Ti-18 exposed to solutions 5 and 6 were different from Ti-12 or T-18 from solutions 1 to 4. The morphology as seen in Figure 44 appeared to be bubbly as opposed to pitted. The creation of this bubbly morphology at higher acid concentrations could be caused by the selective precipitation of Ti salts from the ion rich solution to the part of the surface most concentrated in Pd. This, along with the corrosion of the areas that are of lowest Pd concentration eventually results in the high points of the bubbles where Pd was initially rich and low points where localized corrosion removed a layer of metal before the Pd

sufficiently concentrated. Corrosion was still possible on the bubbly samples as seen in Figure 43 when the solution was changed on the one hundred and twenty first day. The chlorides had a strong effect on the corrosion rate of Ti-18 in highly acidic media.



Figure 44 SEM micrographs, Ti-18 immersion sample, 500 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>

The Ti-12 sample was much thinner than the Ti-18, so its surface area to volume ratio was considerably higher than Ti-18, 42:15 cm<sup>-1</sup> (Ti-12 : Ti-18). However, even after taking the thickness into account, Ti-18 remained more corrosion resistant than Ti-12. Without chlorides in the solution, Ti-18 lost only ~1.25 % of its weight after one hundred and twenty-one days. When chlorides were added, 5.5 % of Ti-18 was lost in the same timeframe. When the solution was changed after one hundred and twenty-one days, Ti-18 unexposed to Cl<sup>-</sup> had only a moderate increase in corrosion while the sample exposed to Cl<sup>-</sup> lost a considerable portion of its mass.

Pitting on alloys tested at room temperature for 218 days was shallow and preferential to the grain boundaries. The largest pit found on the cross-sectioned samples was ~25 um deep (Ti-18, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 10 gpL Cl<sup>-</sup>, Figure 38). Reid [2] attributed pit initiation on unalloyed Ti to Fe impurities in the metal. While this is a possibility, Co impurities could initiate pitting by the same mechanism of preferentially dissolving and lowering the local

potential to the range of active Ti dissolution. There was a considerably higher amount of Co in the samples (~0.16 atomic % : Below detection limits, Co : Fe, Table 13)

Ti-Alloy	H <sub>2</sub> SO <sub>4</sub> / Cl <sup>-</sup> (gpL)	Temperature (°C / K)	Visible Pitting	Precipitates / size (μm)
12	10, 100 / 0, 10	25 / 298	Yes, GB prefered	No
18	10 / 0, 10	25 / 298	No	Yes, Pd rich flakes $/ < 1$
18	100 / 0	25 / 298	Yes, GB prefered	Yes, Pd rich flakes $/ < 1$
18	100 / 10	25 / 298	Yes, GB prefered	No
12	500 / 0, 10	25 / 298	Yes	Yes, Ni rich / < 1
18	500 / 0, 10	25 / 298	No	No
1	500 / 0, 10	25 / 298	Yes	No
12	100 / 10	50 / 323	No	No
18	100 / 10	50 / 323	No	Yes, Pd rich, < 1

Table 21Pitting and precipitates on immersion samples

Table 22

Analysis of immersion test solutions (mg/L)

H <sub>2</sub> SO <sub>4</sub> / Cl	Day	Ti	Mo	Ni	Al	V
10 / 0	49	0.5		0.03	0.3	
10/0	218				1.2	0.02
10 / 10	49	0.5		0.02		
10 / 10	218				1.1	
100 / 0	49	2.8			0.3	0.04
100 / 0	218				1.1	0.01
100 / 10	49	93.8		0.06	0.3	0.13
100 / 10	218				1.1	
500 / 0	49	836.8	1.29	2.98	1.2	1.44
500 / 0	128	922.6	1.54	3.83	2.3	1.67
500 / 10	49	1600	1.66	3.92	4	4.41
500 / 10	128	1700	2.01	5.10	6.3	5.19

### 4.3 Open Circuit Potential Measurements

#### 4.3.1 Room Temperature

The spontaneous activation of Ti-1 can be seen in Figure 45. The thinning of the air formed oxide layer (Equation 12) occurred during the first 3 or 4 hours of immersion. This is depicted by a slow decrease in potential [67].

#### **Equation 12**

 $TiO_2 + H_2O + H^+ \rightarrow Ti(OH)_3^+$ 

The sudden drop in potential at  $\sim -100$  mV is the result of the protective oxide film completely dissolving and the formation of TiH<sub>2</sub>. The potential dropped to a minimum where TiH<sub>2</sub> was the stable solid species. The potential then increased with time as the TiH<sub>2</sub> film thickened slightly. TiH<sub>2</sub> is not a passive film and is known to have a lower overvoltage for the HER. The final E<sub>oc</sub> when the potential stabilized is considered to be the active state dissolution potential (E<sub>corr</sub>). E<sub>corr</sub> was -427 and -442 mV vs. NHE at 30 and 100 gpL H<sub>2</sub>SO<sub>4</sub> respectively. The stable  $E_{corr}$  of Ti is reported to be -665 mV vs SCE (~ -425 mV vs. NHE) at 30°C in 1N HCl [17][37]. Results from Thomas and Nobe at 24 °C indicated a decrease in  $E_{corr}$  with increasing pH (-680 and -700 mV vs SCE at pH of 0.25 and 2 respectively) [38]. It is likely that Thomas and Nobe were actually noticing the increase in LJP. The LJP increases the observed potential with decreasing pH. Thomas and Nobe also reported that only a few of their specimens spontaneously activated or "self activated" while most of them settled to the passive region at potentials of 400 to 700 mV vs SCE. Many attempts to reproduce the spontaneous activation seen in Figure 45 were unsuccessful. The samples tended to exhibit passive behaviour with potentials in the order of 300 to 600 mV vs NHE (160-360 mV vs SCE). The passive potentials reported by Thomas and Nobe were for samples annealed under a vacuum at 700 °C before testing. This thermally induced oxide might account for the

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difference in passive potential when compared to the freshly ground surfaces used in this thesis. Thermally induced oxides promote the formation of the stable rutile  $TiO_2$  (See Materials Characterization, XRD).

At temperatures around 20 to 25 °C there was a balancing point between spontaneous activation and passivation. Increased acid concentration did not necessarily result in activation (Figure 46). Passivation of the metal can be influenced by trace impurities in the solution or in the Ti metal, excess oxygen and surface preparation. The critical factor was not determined from this work. It was found that a temperature increase to 50 °C (323 K) ensured spontaneous activation and also increased the rate of TiO<sub>2</sub> dissolution (Figure 47).



Figure 45 Open circuit potential vs. time, Ti-1, 30 and 100 gpL H<sub>2</sub>SO<sub>4</sub>

Since the protection against corrosion of a particular oxide film depends on its growth history [67], the effects of sample preparation were investigated. Figure 46 depicts two samples, one was freshly ground and the other sample was air dried for 24 hours.

The air-formed oxide had a higher potential initially. The potential dropped for about 10 hours then stabilized. The initial drop was probably a combination of the dissolution and hydration of the air formed  $TiO_2$ .

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The sample tested immediately after grinding (with minimal contact to air) had a lower potential initially but increased in potential for about 16 hours where it also stabilized. The increase in potential corresponded the thickening of the oxide. Notice that both samples appear to come to rest at passive potentials in strong sulphuric acid. Since the unalloyed immersion specimens at 500 gpL H<sub>2</sub>SO<sub>4</sub> experienced significant corrosion after the first week, it is likely that these samples would eventually drop back down to the active state corrosion potential (~ -450 mV vs NHE).



Figure 46 Open circuit potential vs. time, Ti-1, 500 gpL H<sub>2</sub>SO<sub>4</sub>

### 4.3.2 Moderate Temperature

The test at 343 K began at 323 K and was increased to 343 K after about 40 minutes (Figure 47) where the potential decreases a second time. The LJP correction applied in the 343 K test (Figure 47) was -27.8 mV. The kinetics of oxide film dissolution increased as temperatures were raised.  $E_{corr}$  values decreased with increasing temperatures due to the increase in Ti dissolution.



Figure 47 Open circuit potential vs. time, Ti-1, 100 gpL H<sub>2</sub>SO<sub>4</sub>

Minor alloy additions that differentiate Ti-1, Ti-12 and Ti-18 had a major effect on the  $E_{oc}$  vs. time plots. Figure 48 showed that Ti-1 settled to the lowest  $E_{corr}$  of the three alloys. Ti-12 spontaneously activated after 4 minutes while it took 13 minutes and 27 minutes for Ti-1 and Ti-18 respectively. Although the time to spontaneous activation relied partly on sample preparation, Ti-18 consistently took longer than Ti-12 and Ti-1. The potential of Ti-18 still increased after two hours of immersion. The reason that the potential of Ti-18 increased with time is that Pd on the surface concentrated and facilitated the HER by lowering its overvoltage. Ti-18 would have eventually passivated at these conditions (See Immersion Tests, Table 19, test number 7).





Table 23 summarizes the final  $E_{oc}$  values at low and moderate temperatures in 100 gpL  $H_2SO_4$  solutions. Increased temperature lowered the  $E_{oc}$ . Both Ti-12 and Ti-18 alloys had higher  $E_{oc}$  values than Ti-1.  $E_{oc}$  values for Ti-1 and Ti-12 stabilized while those for Ti-18 did not. The addition of Cu to the solution ensured a passive  $E_{oc}$ .

Ti-Alloy	Temperature	Eoc	Addition	Time (Hours)	Notor
	<u>(°C / K)</u>	(mV) vs NHE		1 mie (110u13)	rotes
1	22 / 295	442		12.5	
11	50/323	-569		3.1	
1	70 / 343	-622		1.9	
12	50/323	-323	· · · · · ·	3.3	
12	70/343	-330		0.8	
12	50/323	353	3 gpL Cu	3.3	
18	50 / 323	-355		2.2	E still increasing
18	70 / 343	-205		0.7	E still increasing
18	80 / 353	397	10 gpL Cu	2.2	
7	50 / 323	70		8	Reference [2]

Table 23 $E_{oc}$  at low and moderate temperatures, 100 gpL  $H_2SO_4$ 

### 4.3.3 High Temperature

The  $E_{oc}$  of the alloys at 498 K stabilized to values that were intermediate to active and passive potentials from low and moderate temperature measurements (Figure 49). It is interesting to note that the maximum potential Ti-12 and Ti-18 experienced occurred over the same temperature region that Fe is known to dissolve from goethite and boehmite in the HPAL process (408-428 K). Fe dissolved into solution from the autoclave walls as Fe(III) and drove the potential of the Ti upwards. Upon further heating the Fe precipitated as a ferric sulphate causing the potential to drop again. Ti-12 and Ti-18 settled to a similar  $E_{oc}$  while Ti-2 was ~50 mV lower. Ti-2 experienced some metastable pitting characterized by a sharp drop in potential at initiation, then slowly returned to the higher potential as the oxide was re-established. The samples were cyclically polarized following these measurements. No evidence of pitting was visible on the samples after being polarized.



Figure 49 Open circuit potential vs. time, 30 gpL H<sub>2</sub>SO<sub>4</sub>, temperature increasing to 498 K

Table 24 indicates that even at high temperatures and pressures  $E_{oc}$  values lowered with increased temperatures. Ti-12 and Ti-18 have higher rest potentials than Ti-2, similar
to low and moderate temperature results (Figure 48). The pH of the solution was  $\sim 2$  and potentials were the range of -100 to -150 mV at 498 K [69]. The corresponding E–pH diagram (Figure 7) indicated that the Ti metal was in the passive region. AES results showed that the oxide of the samples exposed to these conditions thickened dramatically (Figure 69 and Figure 70). Polarization scans of the samples did not reveal any signs of active corrosion under these conditions (Figure 61 and Figure 62).

Ti–Alloy	Temperature (°C / K)	Pressure (Mpa / psi)	Eoc (mV) vs NHE	Notes
1	150 / 423	0.67 / 100	-102	Potential increasing
2	225 / 498	2.76 / 400	-143	
12	225 / 498	2.76 / 400	-107	
18	225 / 498	2.76 / 400	-105	
18	250 / 523	4.24 / 615	-152	
12	200 / 473	1.93 / 280	-112	Potential decreasing
12	200 / 473	1.93 / 280	-47	Previously polarized sample

Table 24E<sub>oc</sub> at high temperatures and pressures

# 4.4 Potentiodynamic Tests

### 4.4.1 Room Temperature

Typical polarization behaviour of Ti in H<sub>2</sub>SO<sub>4</sub> solution can be seen in Figure 50. The potentiodynamic scan began at a cathodic potential (-800 mV) and increased to an anodic potential at a scan rate of 5 mV / s. The current in Region I, shown on a logarithmic scale corresponds to the HER. Region II was the active dissolution of Ti, a thin rapidly dissolving layer of Ti(OH)<sub>3</sub> probably existed between the metal and the solution. Region II changed to Region III at the point of maximum current ( $i_{max}$ ,  $E_{max} = -300$  mV). The  $i_{max}$  taken from this plot was an underestimate of the dissolution of Ti as it was necessary to add the HER current to attain the correct value. The point of maximum current in between regions II and III ( $i_{max}$ ) was used to calculate accelerated corrosion rates. Above  $i_{max}$  (region III), Ti(OH)<sub>3</sub> was sufficiently stable to begin passivating the sample. Finally, region IV is considered the

passive region. The "passive current" seen in region IV was due mainly to the oxidation of Ti(III) ions in solution to Ti(IV). Oxide film thickening and dissolution has been shown to represent only a small fraction of the current in region IV [17]. See Figure 67 for a potentiostatic test at E = 500 mV.





Purging with  $N_2(g)$  (Figure 51) impeded one of the cathodic oxygen reduction reactions, oxygen reduction. The oxygen in solution in the naturally aerated test increased at which the cathodic and anodic currents were balanced.



Figure 51 The effect of purging, Ti-1, RDE (1200 rpm), 40 gpL  $H_2SO_4$ , SR = 5mV / s

Room temperature tests began with a cathodic polarization because the samples would not necessarily activate at 25 °C (See Open Circuit Potential Measurements). Since moderate temperature tests activated consistently and generally stabilized within a few hours, an anodic polarization was sufficient. The scan rate heavily influenced the polarization behaviour, especially at higher potentials. A scan rate of 0.5 mV / s was chosen for most of the experiments as the best compromise between achieving steady state values and, testing an adequate number of conditions within the time available.

Figure 52 depicts potentiodynamic scans on fresh samples. The first scan was using a fresh solution while the second was recycled solution from the first experiment. There were many differences in the results. At the beginning of the first scan, the corrosion potential was a normal value of -450 mV while the sample in the re-used solution was closer to -366 mV. The  $E_{max}$  values were very close  $\sim -280 \text{ mV}$  with the  $i_{max}$  being much higher for in fresh solution (280  $\mu$ A/cm<sup>2</sup> compared to 150  $\mu$ A/cm<sup>2</sup>). The sample in the re-used solution had a higher passive current with increasing potential.

A possible explanation is that the first sample corroded at low potentials and a considerable amount of Ti(III) dissolved into the solution. The high passive current resulted mainly from the oxidation from Ti(III) to Ti(IV), there was also a small contribution from Mo to Mo(IV) (E > -150 mV, Figure 53) and Ni to Ni(II) (E > -300 mV, Figure 55). Dealloying of Mo from Ti-Mo alloys is known to occur in the trans-passive region with respect to Mo in 1N boiling H<sub>2</sub>SO<sub>4</sub> [23]. The increased current at ~1750 mV was mainly caused by the oxidation of Ti(III) and Ti(IV) to Ti(VI) and Mo and Mo(IV) to Mo(VIII) (E > 1.6 V). When the second sample was immersed, Mo and possibly Ni reduced onto its surface, greatly enhancing the HER. This, along with the presence of Ti(IV) inhibitor ions, reduced the corrosion rate of the second sample, limiting the production of fresh Ti(III). The second anodic peak at ~150 mV was the oxidation of Mo to MoO<sub>2</sub> ( $i_{max2} = 12.6 \mu A/cm^2$ ). John Griess Jr. made similar observations when he polarized Ti–Mo alloys of varying Mo concentration [54]. The passive current was lower on the second sample because the limited Ti(III) ions were available for oxidation.



Figure 52 The effect of re–using the solution, Ti-12, 500 gpL  $H_2SO_4$ , SR = 0.5 mV / s

















The increased current at potentials above ~2200 mV seen in Figure 57 for Ti-12 and to a lesser extent Ti-18 is not the result of Ti oxide thickening, breakdown or Ni de-alloying. A.J. Sedriks *et al.* have demonstrated this with Ti-Ni alloys using an ellipsometric technique [26]. They attributed this to  $Cl_2(g)$  evolution. Since there was no  $Cl^-$  in these tests, the only possible reactions are  $O_2(g)$  evolution and acid decomposition. The oxygen overvoltage for a Pd electrode is approximately 250 mV while it is only 60 mV for Ni [63]. The acid decomposition potential is 1.67 V for H<sub>2</sub>SO<sub>4</sub> [63].



Figure 57 The effect of the alloy (high potentials), 100 gpL  $H_2SO_4$ , SR = 0.5 mV / s

The addition of NaCl increased the H<sup>+</sup> activity (Figure 58). The slope of the HER and  $E_{corr}$  for Ti also increased. Cl<sup>-</sup> is known to aggravate crevice corrosion by increasing H<sup>+</sup> activity and forming complexes with Ti ions (Figure 15). It plays a dual role by inhibiting the active dissolution of Ti when complexing with oxygen, e.g.  $ClO_4^-$  (See Table 7). The corrosion behavior of Ti in Cl<sup>-</sup> containing solutions depends on the concentration of the oxygen–chloride compounds [36]. The increased anodic current at higher potentials (E > 1500 mV) most likely correspond to the formation of Cl(g), (E<sup>o</sup> > 1.31 V) and ClO<sub>4</sub><sup>-</sup> (E<sup>o</sup> > 1.40 V, See Figure 14).



Figure 58 The effect of Cl<sup>-</sup>, Ti-1, RDE (1200 rpm), 500 gpL H<sub>2</sub>SO<sub>4</sub>, SR = 0.5 mV / s

# 4.4.2 Moderate Temperature

The effect of acidity and temperature are depicted in Figure 59. Higher temperature and acidity increased the rate of Ti dissolution. The  $E_{oc}$  decreased with increasing temperature and acidity while  $E_{max}$  remained relatively stable at ~ -330 mV. The passive current was proportional to the amount of Ti dissolution that took place. Room temperature tests were deaerated while the elevated temperature tests were naturally aerated.

Contra-



Figure 59 The effect of acidity and temperature, Ti-1, SR = 0.5 mV / s

The anodic scans in Figure 60, were initiated following the  $E_{oc}$  measurements in Figure 48. The  $i_{max}$  values of Ti-12 and Ti-18 were less than Ti-12. The passive current was slightly erratic for Ti-12. This is likely due to the Ti<sub>2</sub>Ni particles on the surface as seen in Figure 65.



Figure 60 The effect of the alloy, 100 gpL  $H_2SO_4$ , 323 K, SR = 0.5 mV / s

The corrosion rates in Table 25 were calculated using  $i_{corr}$  values from potentiodynamic scans (SR = 0.5 mV / s). The  $i_{corr}$  values used are the  $i_{max}$  values that were corrected for the HER using Equation 18 (See Appendix C for the details).

· · · · ·

Ti-Alloy	H₂SO₄ (gpL)	Temperature (°C / K)	Corrosion Rate (mmpy)
1	100	25 / 298	0.30
12	100	25 / 298	0.28
18	100	25 / 298	0.19
1	500	25 / 298	3.78
12	500	25 / 298	3.89
18	500	25 / 298	4.52
1	100	50 / 323	5.75
1	100	70 / 343	18.08
12	100	50 / 323	1.28
18	100	50 / 323	1.57

 Table 25
 Accelerated corrosion rates, calculated from imax, corrected for HER current

The accelerated corrosion rates attained do not necessarily translate to real time corrosion rates. However, they do provide reliable information concerning the dissolution kinetics of the alloys at different conditions of temperature and acid. It should be noted that while Ti-18 had accelerated corrosion rates similar to Ti-12. Immersion tests results prove that Ti-18 passivated (Table 19, solution 7, Ti-18).

The apparent activation energy was estimated to quantify the temperature–dependence of the corrosion at  $i_{max}$  using the Arrhenius Law (Equation 13 and Table 26). The apparent activation energies were estimated using only two values (294 K and 323 K). 294 K was used to more closely represent the actual room temperature (as opposed to 298 K). Ti-12 and Ti-18 did not exhibit linear behaviour on the Arrhenius plot (ln(A) vs 1/Temperature) above 323 K due to surface enrichment of Ti-Ni and Ti-Pd intermetallics. Ti-12 had the lowest activation energy followed by Ti-18 and Ti-1. The activation energy for Ti-1 was considerably higher than published steady state values, 80.3 kJ/mol compared with 59.9 kJ/mol [17]. 59.9 kJ/mol was for steady state conditions and the corrosive media was 0.5 mol·dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

#### **Equation 13**

 $k = Ae^{(-Ea/RT)}$ 

Where, k is the rate constant (moles of Ti  $\rightarrow$  Ti<sup>+++</sup>/ s), Ea is the activation energy (J/mol), R is the rate constant 8.314 J / mol·K, and A is a constant

Table 26The activation energy of Ti-1, Ti-12, and Ti-1, 100 gpL H2SO4, (294-323 K)

Ti-Alloy	ln(A)	Ea (kJ/mol)
1	21.2	80.3
12	5.1	41.2
. 18	11.5	57.8

### 4.4.3 High Temperature

Figure 61 and Figure 62 are cyclic polarization curves for Ti-12 and Ti-18 respectively. T he arrows on the plots indicate the scan direction beginning with a forward sweep (cathodic to anodic) followed by a reverse sweep (anodic to cathodic). High scan rates, such as the one used for these experiments, are known to exaggerate the passive currents when the potential is increased [12].

The low value of  $E_{corr}$  for Ti-12 on the reverse scan at 498 K suggests that the surface oxide was less stable than at 473 K. The negative hysteresis is not indicative of pitting corrosion. No pitting was found on the sample after testing. Even though the current increased considerably with potential, the maximum anodic current measured remained lower than passive currents seen at low and moderate temperature experiments.

Ti-18 was exposed to a higher temperature (523 K) and pressure (4240 kPa) than Ti-12. The scans in Figure 62 were almost identical, suggesting that the surface of Ti-18 was quite stable under these autoclave conditions. A deviation from the passive current was identified on all of the forward scans. Table 27 is a tabulation of the potentials at which the current began to deviate (apparent trans-passive potential).



Figure 61 Cyclic polarization, Ti-12, 30 gpL  $H_2SO_4$ , SR = 5 mV / s



Figure 62 Cyclic polarization, Ti–18, 30 gpL  $H_2SO_4$ , SR = 5 mV / s

The deviation from a passive current on the forward scan was likely due to the oxidation of metal species that dissolved from the autoclave walls. The ions reduced on or by the Ti surface during the cathodic portion of the sweep. A rough integration of these areas of current deviation from the Ti-12 plot revealed the charge passed was on the order of 600  $\mu$ C at 473 K and 1500  $\mu$ C at 498 K. The concentration of Fe in the solution after the tests was measured to be 100 ppm, the Ni content was 500 ppm. Other elements that were found on the

surface of the corroded sample using XPS, were W, Mo, Mg S, Ca, Na, Si, and C. The autoclave body was made of Hastelloy–C containing high amounts of Ni, Cr, and Mo as well as some Fe, W, Co, Mn, and Si. Likely oxidation reactions with these constituents are Mo to Mo(IV), Cr(II) to Cr(III) and Fe(II) to Fe(III) [59].

Sample, Temperature / Pressure (K / kPa)	Apparent trans–passive Potential (mV vs NHE)
Ti-12, (473 / 1930)	190
Ti-12, (498 / 2760)	35
Ti–18, (498 / 2760)	535
Ti-18, (523 / 4240)	535

 Table 27
 Apparent trans-passive potentials for high temperature polarization tests

The pH of  $H_2SO_4$  solutions increased with increasing temperature, the initial pH of the solution was about 0.55 at 298 K. This would correspond to a pH of 1 at 423 K and nearly 2 at 523 K [69].

# 4.5 Potentiostatic Tests

Current was measured while the potential was held in the active region (Figure 63) and passive region (Figure 67). The initial peak in current at  $\sim$ 300 seconds in the active region is the dissolution of the surface oxide film, followed by a relatively steady dissolution of Ti for Ti–1 and Ti–12. The current from the Ti–18 sample steadily dropped into the cathodic region as the Pd was exposed, allowing for the HER to take place at high rates. Ti–18 suffered less corrosion than Ti–1 or Ti–12. The scratches from grinding remained visible (Figure 66)



Figure 63 Active region, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 343 K



Figure 64 SEM micrographs, Ti-1, E = -300 mV vs NHE, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 343 K, 8000 seconds



Figure 65 SEM micrograph, Ti-12, E = -250 mV vs NHE, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 343 K, 8000 seconds



Figure 66 SEM micrograph, Ti-18, E = -250 mV vs NHE, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 343 K, 8000 seconds

Figure 67 depicts the behavior of Ti–1 being held at a passive potential (500 mV). The current is due to a combination of oxide thickening and oxidation of Ti(III) ions to Ti(IV). Current v alues on the potentiodynamic s cans at 0.5 mV/s were orders of m agnitude higher than 2  $\mu$ A/cm<sup>2</sup> (the current after ~17 hours).



Figure 67 Passive region, E = 500 mV, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 323 K

# 4.6 Surface Analysis

Corroded samples were prepared by exposing the metal to 30 gpL  $H_2SO_4$ , heating them at 473 K in the autoclave for 3 hours then allowing them to cool overnight. Samples were rinsed quickly and stored in isopropanol after the autoclave was opened to minimize their contact with air.

XPS analyses showed that the oxide thickness of the uncorroded samples was 300-500 Å while samples exposed to conditions of high temperature acid had a much greater oxide thickness, 5,000-10,000 Å (Table 28 and Table 29). Surface roughness lead to the large error associated with these values. The values represent the depth at which the concentration of Ti was 67–75 atomic percent. The chemistry of the oxide film at the surface of freshly ground samples was found to be composed of mainly Ti(OH)<sub>4</sub>. Ti(OH)<sub>4</sub> is an unstable precipitate of orthotitanic acid [52]. A sample of the XPS spectra is seen in Figure 68.

Location	Depth (Å)	С	0	Ti	Fe	Si	S	Na	Мо	Ni	Ca	Zn
Area-2	0	21.9	54.9	21.2			0.5		0.2		0.8	0.4
Area-3	0	19.5	57.3	21.3			0.3		0.6		0.8	0.3
Area-1	0	27.6	48.3	17.2	0.3		0.3	3.9	0.2		1.7	0.3
Area-1	30	6.4	64.2	27.8					0.1		1.5	0.1
Area-1	100	3.9	64.5	30					0.1		1.1	0.3
Area-1	500	2.4	63.2	32.7			0.4		0.1		0.7	0.5
Area-1	1000	2.4	62.8	34			0.2		0.1		0.5	
Area-1	5000	1.9	43	53.9		0.5	0.4		0.1		0.1	
Area-1	10000	3.8	27.3	67.2		1.3				0.3	0.1	

Table 28XPS analysis of corroded surface, Ti-12, 30 gpL H2SO4, 3 hours, 473 K

Table 29XPS analysis of corroded surface, Ti-18, 30 gpL H2SO4, 3 hours, 473 K

Location	Depth (Å)	С	0	Ti	Si	V	AI	S	Na	W	Мо	Mg	Ca
Area-2	0	54.5	34.1	5.0				1.7	1.7	1.0	2.0		
Area-3	0	55.3	32.7	5.3				1.9	1.5	1.0	2.0	0.1	0.3
Area-1	25	40.5	35.7	12.4				2.1	3.9	1.6	3.2	0.2	0.4
Area-1	100	21.8	49.3	21.7				1.3		2.3	3.4		0.3
Area-1	500	7.5	58.3	30.3				.1.1		0.7	1.9		0.2
Area-1	1000	6.1	59.5	31.6				1.2	•		1.6		
Area-1	5000	5.1	39.2	55.2							0.5		
Area-1	10000	6.1	20.4	70.0	1.8	1.2	0.6						
Area-1	0	47.3	35.5	8.9	0.3	. ·		1.9	2.3	1.2	2.3		0.4





XPS spectra, Ti-12, freshly ground

AES chemical depth profiling (Figure 69 and Figure 70) was also used to measure the thickness of the oxide exposed to  $H_2SO_4$  at high temperature (498 K) and pressure (2760 kPa). The spot size was < 1 $\mu$ m in diameter minimizing the error associated with surface roughness. The corroded oxide thickness for Ti–18 was found to be less than that of Ti–12, approximately 2200 Å and 4500 Å respectively. These values represent the depth at which the concentration of Ti is 90 atomic percent. Oxygen associated with Ti and carbon was found near the surface.

Table 30

AES analysis of corroded surface, Ti–12, 30 gpL H<sub>2</sub>SO<sub>4</sub>, 3 hours, 473 K

Location	Etch Depth (Å)	0	Ti	N	Ca	С	S	CI	Р
1515 µm²	0	40	11	8	1	36	<0.5	<0.5	
66 µm²	0	52	14	11	1	21	<0.5		
66 µm² (2)	0	52	14	10	2	23	<0.5		
Spot 1	0	51	18	10	1	18	1		<0.5
Spot 1	100	55	30	<5		7	<2		
Spot 2	0	45	23	10	1	18	3		<0.5
Spot 2 (2)	0	45	23	10	1	18	3		
Spot 2	10,000	1.4	97.6			<1			

Table 31AES analysis of corroded surface, Ti-18, 30 gpL H2SO4, 3 hours, 473 K

Location	Etch Depth (Å)	0	Ti	N	Ca	С	Мо	S
1515 µm²	0	17	0.7	2.5		79	0.5	0.4
66 µm²	0	14	1.2	3		75	1.5	4.2
66 µm² (2)	0	15	1.2	2.5		76	1.4	4
Spot 1	0	11	4.2	3.5		68	3.7	9.5
Spot 1	10,000	1.1	97.4			1.5		
Spot 1b	0	11	5	3.5		72	2.1	7
Spot 1b	10,000	4.4	72.8			19.4	1.5	1.9
1b 2.5 µm²	10,000	4.7	70.3			21.1	1.4	2.4
Spot 2	0	8	1.4	2.5		83	1.3	4.2



Figure 69 AES depth–profile, Ti-12, 498 K, 30 gpL  $H_2SO_4$ , 3 hours, PR = 300 Å / min





AES depth–profile, Ti-18, 498 K, 30 gpL  $H_2SO_4$ , 3 hours, PR = 300 Å / min

# 5 Conclusions and Recommendations

# 5.1 Thermodynamic Considerations

Specialized E-pH stability diagrams were created to describe the possible corrosion scenarios and to help interpret polarization behaviour. The Ti-H<sub>2</sub>O and Ti-SO<sub>4</sub><sup>--</sup>-H<sub>2</sub>O diagrams described Ti interaction with bulk HPAL solution while the Ti-Cl<sup>-</sup>-H<sub>2</sub>O diagram was designed to help understand the role of Cl<sup>-</sup> in localized corrosion systems. Ti-H<sub>2</sub>O diagrams were extrapolated to the process temperatures of 463 K and 498 K.

Although these diagrams were adequate for predicting the electrochemistry of the system, many improvements are still possible. For example, the passive oxide might not be composed  $TiO_2 \cdot H_2O$  as  $Ti(OH)_4$  was the most prominent species identified using XPS. Utilizing the  $Ti(OH)_2^{++}$  species as opposed to  $TiO^{++}$  would also best to describe the system as it is the most stable oxidized Ti(IV) ion. Finally, it has been discovered that Ti(IV) ions complex with  $HSO_4^-$ , the most dominant species being  $Ti(OH)_3HSO_4$ . Since leach liquor in the HPAL processes has a considerably higher concentration of  $HSO_4^-$  than  $SO_4^-$ , it is recommended that the  $Ti(OH)_3HSO_4$  species be represented as opposed to  $TiO(SO_4)_2^-$ .

### 5.2 Corrosion Behaviour

A great deal of information was derived from the polarization measurements. Open circuit measurements indicated whether the sample was active or passive and also showed the relative nobility of the alloys in solution. Polarization experiments provided maximum current values that were used to calculate accelerated corrosion rates. Knowing the kinetics of anodic dissolution clearly revealed the relative aggressiveness of the solutions and complimented the corrosion rates calculated from the immersion test results.

The open circuit measurements were the primary method of evaluating the alloys behaviour in solution. Ti–1 settled to the lowest  $E_{oc}$  of the three alloys at any given condition. Increased temperature or acid concentration further lowered the  $E_{oc}$  of the unalloyed sample. Ti-12 and Ti-18 tended to have similar  $E_{oc}$  values that were higher than Ti-1. The presence of alloys that with lower hydrogen over-potentials than Ti (Ni and Mo for Ti-12 and Pd for Ti-18) increased the  $E_{oc}$ . While Ti-12 usually stabilized quickly, the  $E_{oc}$  of Ti-18 continued to increase with time, this was attributed to Pd enrichment of the Ti surface, which eventually led to the passivation of the sample. The addition of a sufficient amount of Fe or Cu resulted in a large increase in the  $E_{oc}$ . These oxidizing metals inhibited the corrosion by polarizing the sample to a potential region where the passive TiO<sub>2</sub>·H<sub>2</sub>O was thermodynamically stable.

Accelerated corrosion rates that were measured from potentiodynamic scans revealed the Ti-18 to be more acid sensitive compared to the other alloys. Ti-1 was more temperature sensitive than the other alloys. Ti-1 corrosion increased significantly with increases in temperature or acid as was indicated by  $E_{oc}$  measurements.

Real time corrosion rates calculated from weight loss experiments confirmed that temperature and acidity increased corrosion rates, with a temperature increase of 298 to 323 K

having a greater effect than an acid concentration increase of 100 to 500 gpL. The corrosion rates of Ti-1 and Ti-12 were very similar while Ti-18 exhibited significantly lower corrosion rates under all aggressive conditions. In conclusion, the higher corrosion rates from accelerated calculations do not properly indicate the corrosion behaviour of Ti-18. The "enhanced corrosion resistance" of Ti-12 at higher acid concentrations and elevated temperatures did not materialize. This lack of corrosion resistance was attributed to the break—up of the galvanic couple between the noble  $Ti_2Ni$  particles and the Ti matrix. This occurred by corrosion of the area surrounding the particles leading to a mechanical separation. Also, if the increased potential caused by the alloying was not sufficient to stabilize the passive film, it served to aggravate the corrosion as seen at 500 gpL H<sub>2</sub>SO<sub>4</sub>, where the corrosion rate of Ti-12 was nearly twice as high as Ti-1.

All the immersion samples eventually passivated. Increased Ti(IV) concentration from oxidation of the corrosion product (Ti(III)) inhibited corrosion in the same manner as Fe and Cu ion addition during the  $E_{oc}$  measurements. The presence of Cl<sup>-</sup> in immersion tests led to an increase in corrosion rates in the more aggressive solutions. Although ClO<sub>4</sub><sup>--</sup> inhibits corrosion in certain situations, Cl<sup>-</sup> amplified corrosion by increasing the activity of H<sup>+</sup>, lowering the oxygen solubility in the solution and promoting localized corrosion.

## 5.3 Recommendations

When localized c orrosion o ccurs d uring HPAL p rocessing, o nly n oble a lloy a dditions should be considered in providing extra protection. If the mechanical properties of Ti-12 are desirable, a new Ti-12 alloy with a lean addition of noble metals should be developed. The heat treatment of Ti-12 should be carried out to minimize the agglomeration of  $Ti_2Ni$  particles. Since the lean Pd content (0.05 at. %) of Ti-18 resulted in improved corrosion resistance at all aggressive conditions, the creation of a leaner Pd alloy is highly recommended when the metal price is a priority. Accelerated corrosion tests can provide reliable corrosion rate information for unalloyed Ti. Real time weight loss experiments should be implemented when considering Ti-12 or Ti-18 for service in corrosive environments.

# 5.4 Future Work

To investigate this issue further, future work should incorporate the development of a high temperature / pressure electrochemical reactor. Interference by dissolved species from the autoclave walls must be minimized. More aggressive solutions should be tested at high temperatures. Crevice corrosion tests at low temperatures and at HPAL conditions are necessary to fully understand the localized corrosion problem. It would be beneficial to evaluate the corrosion properties of lean alloys as described in the recommendations.

# 6 SYMBOLS AND ABBREVIATIONS

AES	Auger Electron Spectroscopy
γ	Activity coefficient
BCC	Body-centered Cubic
BEI	Backscattered Electron Image
С	Electrical charge (Coulombs)
(dis)	Dissolved species
e	Electron
E	Potential (Volts)
E <sub>corr</sub>	Stable active state dissolution potential
E <sub>oc</sub>	Open circuit potential
E°	Standard reduction potential
E <sub>max</sub>	Potential corresponding to imax
GB	Grain boundary
gpL	Grams per Liter (g/L)
HCP	Hexagonal Close–packed
HER	Hydrogen Evolution Reaction
HPAL	High Pressure Acid Leaching
HTAL	High Temperature Acid Leaching
i <sub>H</sub>	Current density for the HER $(A/cm^2)$
i <sub>max</sub>	Current density maximum (A/cm <sup>2</sup> )
M	Molar (mol/L)
m	Molal (mol/kg of water)
mmpy	Corrosion rate (millimeters per year)
PR	Profiling rate
RDE	Rotating disc electrode
(sat)	Saturated
SEM	Scanning Electron Microscope
SCE	Standard Calomel Electrode
SSE	Saturated Sulfate Electrode
SR	Scan rate
Ti-1	ASTM Grade-1 Titanium (Commercial Purity)
Ti-2	ASTM Grade-2 Titanium (Commercial Purity)
Ti-5	ASTM Grade-5 Titanium (Ti-6Al-4V)
Ti-7	ASTM Grade-7 Titanium (Ti-0.15Pd)
Ti-12	ASTM Grade-12 Titanium (Ti-0.8Ni-0.3Mo)
Ti-18	ASTM Grade-18 Titanium (Ti-4Al-V-0.05Pd)
Ti–32	ASTM Gr32 Titanium (Ti-5Al-1Sn-1V-1Zr-1Mo)
um or µm	Micrometer $(1 \cdot 10^{-6} \text{ meters})$
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
	-

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# 8 Appendix A Determination of Thermodynamic Data

Species	State	Go (298 K)	Go (463 K)	Go (498 K)	References
H	aq	0.0	-2.2	-4.2	[1][46][47]
H₂O(I)	1	-237.1	-251.7	-255.4	[55]
O <sub>2</sub> (g)	g	0.0	-35.0	-42.7	[55]
H₂(g)	g	0.0	-22.7	-27.9	[55]
Ti	c	0.0	-6.0	-7.5	[55]
TiO	c	-513.3	-520.9	-523.0	[55]
TiO₂	c	-888.4	-899.5	-902.5	[55]
TiO <sub>2</sub> .H <sub>2</sub> O	c	-1058.5	-1078.4	-1083.7	[1][46][47]
Ti₂O <sub>3</sub>	С	-1432.2	-1449.2	-1453.8	[55]
Ti(OH)₃	c	-1049.8	-1069.3	-1074.9	[1][46][47]
	aq	-314.0	-307.9	-309.7	[1][46][47]
	aq	-350.0	-318.0	-315.6	[1][46][47]
TiO <sup>++</sup>	aq	-577.4	-560.5	-560.5	[1][46][47]
TiO <sub>2</sub> <sup>++</sup>	aq	-467.2	-451.9	-452.2	[1][46][47]
TiH₂	c	-105.16	-111.51	-113.26	[56][46][47]
HTiO₃ <sup>−</sup>	aq	-955.9	-976.1	-981.0	[1][46][47]
HSO₄¯	aq	-756.2			[59]
SO4	aq	-744.9			[59]
HS⁻	aq	12.1			[59]
S <sup></sup>	aq	85.8			[59]
S	c	0.0			[59]
H₂S	aq	-28.6			[59]
TiO(SO <sub>4</sub> )2 <sup></sup>	aq	-2090.68			[49][50]
TiSO₄⁺	aq	-1102.77			[49][50]
TiOCl₄"	aq	-1115.69	J		[54]

Table 32

Gibbs free energy used to calculate the E-pH diagrams

The Gibbs energy at high temperature was calculated using the Criss Cobble Entropy Correspondence Principle [46][47]as follows:

### **Equation 14**

 $G_{0T} = \Delta G_{0298} + AvC_{PT} \cdot \Theta - (T - 298)\Delta S_{0298} (A-1)$ 

 $\Delta G_{0,T}$  – Gibbs free energy at 463 or 498 K, kJ/mol

AvC<sub>P,T</sub> – Approximated average heat capacity between 298 K and T

 $\Theta$  – function of temperature (T–298–T·ln(T/298))

 $abs\Delta S_{0.298}$  - standard entropy (absolute scale), J/mol·K

### **Example:**

For H<sup>+</sup> at 498 K,  $\Theta = (498 - 298 - T \cdot \ln(498 / 298)) = -55.7$ 

 $\Delta G_{0T} = 0 + 150.72 \cdot (-55.7) - (498 - 298) \cdot (-20.92) = -4211 \text{ J/mol} = -4.2 \text{ J/mol}$ 

The absolute scale  $\Delta S_{0,298}$  values are required to establish linear relationship between entropies. These values are determined by adding  $S_0(H^+)z$  where  $S_0(H^+) = -20.92$  J/mol·K and z is the ionic charge.

### **Example:**

For H<sup>+</sup>,  $abs\Delta S_{0,298} = \Delta S_{0,298} + S_0(H^+)z = 0 + (-20.92) \cdot 1 = -20.92$ 

							,	T, (K)	_	T <sub>2</sub> (K)	Θ	T <sub>3</sub> (K)	۲
								298.15		463.00	-38.93	498.00	-55.63
Sneriae	Ctate	$\Delta G_{0,298}$	$\Delta S_{0,298}$	Cp = A	+ BT + C	;/T^2 + DT	^2 (J/gmol-K)	ပံ	$abs\Delta S_{0.298}$	$AvC_{P}$	$\Delta G_{0.463}$	$AvC_{P,T}$	$\Delta G_{0,498}$
obcolco	Orare	(KJ/gmol)	(J-lomo/L)	۷	BX10^3	CX10^-5	DX10^6	(J/gmol-K)	(J/gmol-K)	463/298	(KJ/gmol)	498/298	(KJ/gmol)
Ť	aq	0.00	0.00						-20.92	144.44	-2.17	150.72	-4.20
H <sub>2</sub> O(I)	-	-237.14	69.95	59.69	23.01	5.87	24.76	75.35	69.95	76.87	-251.66	77.51	-255.43
$O_2(g)$	g	0.00	205.15	29.43	-4.02	0.00	12.82	29.37	205.15	29.84	-34.98	29.99	-42.67
$H_2(g)$	g	00.0	130.68	22.50	17.04	0.37	11.12	28.98	130.68	30.96	-22.75	31.43	-27.86
F	ს	0.00	30.29	5.25	2.52			25.13	30.29	26.00	-6.01	26.18	-7.51
Tio	ა	-513.30	34.77	10.57	3.60		-1.86	48.06	34.77	48.81	-520.93	48.94	-522.97
TiO <sub>2</sub> .H <sub>2</sub> O	ပ	-1058.50	90.06						90.06	130.00	-1078.40	130.00	-1083.72
Ti <sub>2</sub> O <sub>3</sub>	ပ	-1432.20	78.78	23.00	5.00			102.54	78.78	104.26	-1449.25	104.63	-1453.76
Ti(OH) <sub>3</sub>	ა	-1049.80	80.00			-			80.00	163.00	-1069.33	163.00	-1074.85
Ti <sup>++</sup>	aq	-314.00	-58.40						-100.24	267.30	-307.88	282.87	-309.70
ті***	aq	-350.00	-242.00						-283.84	381.13	-318.05	402.21	-315.65
Ti0 <sup>±+</sup>	aq	-577.40	-135.20						-177.04	314.92	-560.47	332.79	-560.53
TiO <sub>2</sub> <sup>±</sup>	aq	-467.20	-123.50						-165.34	307.66	-451.92	325.18	-452.25
TiH <sub>2</sub>	ა	-105.16	29.70					30.28	29.70	37.39	-111.51	38.89	-113.26
HTIO <sub>3</sub> <sup>-</sup>	aq	-955.90	116.00						136.92	-59.80	-976.14	-41.19	-980.97
<sup>r</sup> ahle 34	Ċ	-ies Cobhle h	iiah temnerati	ura avtre	anolation .	oonetante [/	ואלו						

Criss Cobble high temperature extrapolation constants [46][47] Table 34

		1				Extrapolated	1	Extrapolated
CpAv H <sup>+</sup>	4	28	23	31	33	34.5	35	36
/ Anions	В	3.07	3.44	3.97	3.95	4.15	4.24	4.5
Acid Oxy	V	-136	-122	-135	-143	-150	-152	-157
ions	В	2.2	1.96	2.24	2.27		2.53	
Oxy An	Α	-145	-127	-138	-133		-145	
Anions	В	0.179	-0.28	0	-0.03		-0.04	,
OH <sup>-</sup> and	А	-56.5	46	-58	-61		-65	
tions	В	-0.523	-0.41	-0.55	-0.59	-0.62	-0.63	-0.65
Ca	A	41.6	35	46	46	49	50	52
Temperature	(°C / K)	25 / 298	60 / 333	100/373	150/423	190 / 463	200 / 473	225 / 498

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Table 33

Calculation of high temperature thermodynamic data

Reactions	Equilibrium Constant
$TiO^{++} + SO_4^{}> TiOSO_4$	169.5
$TiOSO4 + SO_4^{} \rightarrow TiO(SO_4)_2^{}$	79.62
$Ti^{+++} + SO_4^{}> TiSO_4^+$	24.3
$Ti^{+++} + 2SO_4^{} -> Ti(SO_4)_2^{}$	180
$Ti^{+++} + 3SO_4^{}> Ti(SO_4)_3^{}$	376

Table 35Ti-SO4<sup>--</sup> species equilibrium constants [49][50]

### Table 36 Ti-Cl<sup>-</sup> species equilibrium constants [51][54]

Reactions	Equilibrium Constant		
$TiO^{++} + Cl^{-}> TiOCl^{+}$	3.55		
$TiOCl^+ + Cl^> TiOCl_2$	0.4		
$TiOCl_2 + Cl^> TiOCl_3^-$	10.6		
$TiOCl_3^- + Cl^> TiOCl_4^-$	12		
	Average (Methods A and B)	Method A	Method B
$Ti^{+++} + Cl^> TiCl^{++}$	0.1350	7.00E-02	0.200
$Ti^{+++} + 2Cl^{-} - > TiCl_2^{+}$	0.0040	3.00E-03	0.005
$Ti^{+++} + 3Cl^{-}> TiCl_3$	0.0006	1.00E-03	0.0002
$Ti^{+++} + 4Cl^{-}> TiCl_{4}^{-}$	0.0052	3.00E-04	0.010

# 9 Appendix B Determination of LJP and TJP

Table 37

Ion equilibrium for the  $2^{nd}$  dissociation constant of  $H_2SO_4$ , 30 gpL [69]

Temp (°C / K)	lnK	K	HSO4 <sup>-</sup>	$\mathbf{H}^+$	SO4 <sup></sup>
25 / 298	-4.2	1.5E-02	0.25	0.06	0.06
50 / 323	-5.2	5.5E-03	0.27	0.04	0.04
70 / 343	-6	2.5E-03	0.28	0.03	0.03
80 / 353	-6.4	1.7E-03	0.28	0.02	0.02
90 / 363	-6.8	1.1E-03	0.29	0.02	0.02
150 / 423	-8.2	2.7E-04	0.30	0.01	0.01
200 / 473	-10.2	3.7E-05	0.30	0.00	0.00
225 / 498	-11.5	1.0E-05	0.30	0.00	0.00
250 / 523	-12	6.1E-06	0.30	0.00	0.00

Table 38Ion equilibrium for the 2<sup>nd</sup> dissociation constant of H2SO4, 100 gpL [69]

Temp (°C / K)	lnK	K	HSO4 <sup>-</sup>	$\mathbf{H}^{+}$	SO4 <sup>-</sup>
25 / 298	-4.2	1.5E-02	0.90	0.12	0.12
50 / 323	-5.2	5.5E-03	0.95	0.07	0.07
70 / 343	-6	2.5E-03	0.97	0.05	0.05
80 / 353	-6.4	1.7E-03	0.98	0.04	0.04
90 / 363	-6.8	1.1E-03	0.99	0.03	0.03
150 / 423	-8.2	2.7E-04	1.00	0.02	0.02
200 / 473	-10.2	3.7E-05	1.01	0.01	0.01
225 / 498	-11.5	1.0E-05	1.02	0.00	0.00
250 / 523	-12.10	6.1E-06	1.02	0.00	0.00

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Ion equilibrium for the 2<sup>nd</sup> dissociation constant of H<sub>2</sub>SO<sub>4</sub>, 500 gpL [69]

Temp (°C / K)	lnK	K	HSO4 <sup>–</sup>	$\mathbf{H}^+$	SO4 <sup></sup>
25 / 298	-4.2	1.5E-02	4.83	0.27	0.27
50 / 323	-5.2	5.5E-03	4.93	0.16	0.16
70 / 343	-6	2.5E-03	4.99	0.11	0.11
80 / 353	-6.4	1.7E-03	5.01	0.09	0.09
90 / 363	-6.8	1.1E-03	5.02	0.07	0.07
150 / 423	-8.2	2.7E-04	5.06	0.04	0.04
200 / 473	-10.2	3.7E-05	5.09	0.01	0.01
225 / 498	-11.5	1.0E-05	5.09	0.01	0.01
250 / 523	-12	6.1E-06	5.09	0.01	0.01

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					·	·	· · · ·	
Temp (°C / K)	Ag <sup>+</sup>	CΓ	K⁺	SO <sub>4</sub>	HSO4	$\mathbf{H}^{+}$	OH <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>
25 / 298	1.6E-05	2.0E-05	2.0E-05	1.1E-05	1.3E-05	9.3E-05	5.3E-05	1.8E-05
50 / 323	2.9E-05	3.6E-05	3.4E-05	1.9E-05	2.3E-05	1.6E-04	9.3E-05	3.2E-05
70 / 343	4.2E-05	5.1E-05	4.9E-05	2.7E-05	3.4E-05	2.4E-04	1.3E-04	4.5E-05
80 / 353	4.9E-05	6.0E-05	5.8E-05	3.2E-05	3.9E-05	2.8E-04	1.6E-04	5.3E-05
90 / 363	5.7E-05	7.0E-05	6.7E-05	3.7E-05	4.6E-05	3.2E-04	1.8E-04	6.2E-05
150 / 423	1.1E-04	1.4E-04	1.4E-04	7.4E-05	9.3E-05	6.5E-04	3.7E-04	1.2E-04
200 / 473	1.8E-04	2.2E-04	2.1E-04	1.1E-04	1.4E-04	1.0E-03	5.7E-04	1.9E-04
225 / 498	2.1E-04	2.6E-04	2.5E-04	1.4E-04	1.7E-04	1.2E-03	6.8E-04	2.3E-04
250 / 523	2.5E-04	3.1E-04	3.0E-04	1.6E-04	2.0E-04	1.4E-03	8.1E-04	2.7E-04

Table 40Diffusion coefficients of select ions in water at infinite dilution [61][32]

Diffusivities at 25 °C (298 K) were taken from Newman [61]. High temperature values approximated using the T-dependent activation energy for self-diffusion of water as follows [32]:

#### **Equation 15**

 $D=A \cdot e^{-\Delta H/RT}$ ,  $\Delta H=14227 + 4.661 \cdot 10^{19} \cdot T^{-6.8132}$ 

- D Diffusion of the ions  $(cm^2/sec)$
- A Constant
- $\Delta H$  Enthalpy (J/mol)
- R Rate constant (8.341 J/(mol K))
- T Temperature (K)

Solve for A using the known values at 298 K and use A to calculate D at the higher temperatures.

#### **Example:**

At 298 K for  $H^+$ ,

 $\Delta H = 14227 + 4.661e19 \cdot 298^{-6.8132} = 14874.2 \text{ J/mol}$ 

 $A = D / exp(-\Delta H/RT) = 9.3e-05 / exp(-14874.2/8.314.298) = 0.038 cm^{2}/sec$ 

$$\Delta H = 14227 + 4.661e19 \cdot 498^{-6.8132} = 14246.57 \text{ J/mol}$$

 $D = 0.038 \exp(-14246.57/(8.314 \cdot 498)) = 0.0012 \text{ cm}^2/\text{sec}$ 

Liquid junction potentials were calculated to correct for the potential of the solution interface between the bulk solution and the reference electrode or salt bridge. The calculation of concentration of ions in the solution ( $c_i$ ) included the temperature effect on the second dissociation constant of sulphuric acid, Equation 16 [69].

### **Equation 16**

 $HSO_4^- \rightarrow SO_4^{--} + H^+$ 

The values of ion mobility  $(u_i)$  were replaced by ion diffusivities at infinite dilution [32] with a high temperature approximation using the T-dependent activation energy for selfdiffusion of water [47]. The LJP between solution–I and solution–II were calculated using the Henderson equation as follows [61]:

# Equation 17 $\Phi^{I} - \Phi^{II} = -(RT/F)*A*(ln(B^{I}/B^{II})/(B^{I}-B^{II}))$

Where, summations with respect to *i* and  $z_i$  being the ionic charge, R=8.314 J/mol·K, T is the temperature in K, F is 96500 C/mol, A =  $\sum z_i u_i (c_i^{I} - c_i^{II})$ , B<sup>I</sup> =  $\sum z_i^{2} u_i c_i^{I}$ , B<sup>II</sup> =  $\sum z_i^{2} u_i c_i^{II}$ 

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### Example:

At 225 °C (498 K), the LJP between  $30 \text{ gpL H}_2\text{SO}_4$  and 1 M K Cl (salt bridge to A g/AgCl ERE),

R=	8.314	J/(mol·K)		
T=	498	K		
F=	96500	C/mole		
zi,iv	1	$H^+, K^+$		
zii,v	-1	$HSO_4^-, Cl^-$		
ziii	-2	SO4		
ci	0.308	$\mathbf{H}^{+}$		
cii	0.304	HSO <sub>4</sub>		
ciii	0.002	SO4		
civ	1	$K^+, Cl^-$		
ui	1.2E-03	$H^+$		
uii	1.7E-04	HSO <sub>4</sub>		
uiii	1.4E-04	SO <sub>4</sub>		
uiv	2.5E-04	K <sup>+</sup>		
uv	2.6E-04	Cl		
Solution I is H <sub>2</sub> SO <sub>4</sub>		Solution II is KCl		
BI=	4.25E-04			
BII=	5.17E-04			
A=	3.28E-04			
-RT/F*A=	1.41E-05			
(ln(BI/BII))/(BI-BII)=	2128.8			
Potential=	0.030	V		
	30.00	mV		

Table 41Liquid junction potential calculation, 30 gpL H2SO4 / 1M KCl interface, 498 K

# Example:

At 50 °C (323 K), the LJP between 100 gpL H<sub>2</sub>SO<sub>4</sub> and saturated K<sub>2</sub>SO<sub>4</sub> (SSE),

		<b>1</b>
R=	8.314	J/(mol·K)
T=	323	K
F=	96500	C/mol
zi,iv	1	$H^+, K^+$
zii,v	-1	HSO <sub>4</sub>
ziii	-2	SO <sub>4</sub>
ci	1.092	H <sup>+</sup>
cii	0.947	HSO <sub>4</sub>
ciii	0.072	SO4
civ	1.263	K <sup>+</sup>
cv	0.631	SO4 <sup>—</sup>
ui	1.6E-04	$\mathrm{H}^+$
uii	2.3E-05	HSO4
uiii	1.9E-05	SO4
uiv	3.4E-05	$K^+$
Solution I is H <sub>2</sub> SO <sub>4</sub>		Solution II is K <sub>2</sub> SO <sub>4</sub>
BI=	2.1E-04	
BII=	9.1E-05	
A=	1.3E-04	
-RT/F*A=	3.7E-06	
(ln(BI/BII))/(BI-BII)		
=	7090.0	
Potential=	0.027	V
	26.5	mV

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Table 42Liquid junction potential calculation, 100 gpL H2SO4 / saturated K2SO4 interface, 323 K

# **10** Appendix C Corrosion Rate Calculations

**Example of real time corrosion rate calculations (Equation 8):** 

Corrosion rate (mmpy) =  $(8.76 \cdot 10^4 \cdot W)/(d \cdot A \cdot t)$ 

$$W = (0.6589 - 0.3949) = 0.264 g$$

 $d = 4.5 \text{ g/cm}^2$ 

 $A = 2*1.7(1.28+0.05)+1.28*0.05 = 4.586 \text{ cm}^2$ 

t = 42\*24 = 1008 hours

Corrosion rate = 1.11 mmpy (Table 19, solution 5, Ti-12)

#### **Example of accelerated corrosion rate calculations (Equation 9):**

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Corrosion rate (mmpy) = 
$$(K \cdot i_{corr} \cdot EW)/(d \cdot F)$$

$$K = 3.1536 \cdot 10^8 \text{ (mm/yr)/(cm/s)}$$

 $i_{corr} = 2.46 \cdot 10^{-5}$ 

$$EW = 16 \text{ g/mol e}^-$$

$$d = 4.51 \text{ g/cm}^3$$

F = 96485 C /mol

Corrosion rate = 0.28 mmpy (Table 43 and Table 25, Ti-1, 100 gpL H<sub>2</sub>SO<sub>4</sub>, 298 K)

 $i_{corr}$  values are corrected for the HER occurring simultaneously by adding HER current to the  $i_{max}$  observed.

#### **Equation 18**

 $i_{\rm H} = 10^{(-E \cdot F/(2 \cdot 2.303 \cdot R \cdot T))}$ 

 $i_H$  is the current (mV) due to the HER on Ti surface

E is the potential (V) vs SCE

F is Faradays constant (96485 C/mol)

R is 8.314 J/(mol·K)

T is the temperature (K)

### **Example of HER correction calculation:**

 $i_{\rm H} = 10^{-E \cdot F/(2 \cdot 2.303 \cdot R \cdot T)}$ 

E at  $i_{max} = -221 \text{ mV vs NHE} = -221-241 = -0.462 \text{ V vs SCE}$ 

F = 96485 C/mol

R = 8.314 J/(mol·K)

T = 298 K

 $i_{\rm H} = 8.1 \ \mu A$ 

Table 43

Accelerated corrosion rate calculation details

Ti–Alloy	H <sub>2</sub> SO <sub>4</sub> (gpL)	Temperature (°C / K)	i <sub>max</sub> (A/cm <sup>2</sup> )	E at i <sub>max</sub> (mV vs NHE)	i <sub>H</sub> (μA)	I <sub>corr</sub> (A/cm <sup>2</sup> )	Corrosion rate (mmpy)
1	100	25 / 298	1.79E-05	-221	8.1	2.60E-05	0.30
12	100	25 / 298	1.58E-05	-223	8.4	2.42E-05	0.28
18	100	25 / 298	9.81E-06	-209	6.4	1.62E-05	0.19
1	500	25 / 298	2.87E-04	-302	38.8	3.26E-04	3.78
12	500	25 / 298	2.89E-04	-310	45.3	3.35E-04	3.89
18	500	25 / 298	3.06E-04	-342	84.4	3.91E-04	4.52
1	100	50 / 323	4.63E-04	-355	33.1	4.96E-04	5.75
1	100	70 / 343	1.54E-03	-348	16.1	1.56E-03	18.08
12	100	50/323	1.03E-04	-268	6.9	1.10E-04	1.28
18	100	50 / 323	1.27E-04	-277	8.2	1.35E-04	1.57

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