Titanium Corrosion in Simulated Hydrometallurgical Leaching Solutions in the

Presence of Solids

by

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Abstract

This work comprehensively investigated the corrosion behaviour of titanium in the presence of the solids in simulated copper sulfide leaching solutions. The effect of inert solid deposits on the corrosion behaviour of titanium grade 2 (Ti-2) was investigated. The solid deposits effectively slowed the mass transfer of the corrosion process, thus resulted in a decreased corrosion rate of the underlying Ti-2 in sulfuric acid-chloride solution. This effect, however, resulted in an increased corrosion rate of Ti-2 in simulated leaching solution (acid plus dissolved metals) since its barrier effect slowed the formation and repair of the protective oxide film by passivating species from the bulk solution. The deposit-covered Ti-2 showed a significant increase in corrosion rate at high temperatures compared with the bare Ti-2. The barrier effect of the four deposits for the investigated condition was in the sequence of gypsum > S3 ($d_{0.5}$: 20.4 µm) > S2 ($d_{0.5}$: 193 µm) > S1 ($d_{0.5}$: 425 µm).

Titanium hydrides—important titanium acid corrosion products—were investigated due to their close relationship to titanium substrate cracking. Titanium hydrides generated by electrolysis catalysed the hydrogen evolution reaction and facilitated subsequent passivation of Ti-2. X-ray diffraction analysis revealed that these hydrides were primarily composed of TiH_{1.5}, with small amounts of TiH_{1.7} and TiH₂.

The effect was investigated of Fe(III) and Cu(II) species in leaching solutions on Ti-2 passivation. The critical concentrations of Fe (III) and Cu(II) species required to induce passivation increased linearly with temperature from 30 to 80°C. The mechanism associated with the passivation was acceleration of cathodic reactions due to the introduction of Ti-2 oxidants. Cu(II) was more effective than Fe(III) at passivating Ti-2 under experimental conditions.

Erosion-corrosion of Ti-2, which pertains to mineral slurries in acidic leaching conditions, was investigated using electrochemical techniques. Erosion-corrosion of Ti-2 was caused by solid particle impingement. Electrochemical noise revealed that solid particle impacts resulted in localised fracture of the passive film, and erosion-corrosion proceeded in the form of current transients. The investigation based on the current transients revealed that erosion-corrosion is a threat to titanium equipment exposed to acidic slurries.

Lay Summary

Mineral solids are always present in water-based metal extraction (*i.e.* leaching) processes. This work investigated the effects of these solids on the corrosion behaviour of titanium under solid deposits and when exposed to solid slurries. Results revealed that solid deposits on the surface of titanium can significantly affect the corrosion behaviour of the underlying titanium, and erosion-corrosion is a threat to titanium equipment exposed to acidic slurries. In addition, some corrosion products—titanium hydrides—were found to enhance hydrogen production at the titanium surface, and this may reduce titanium's ability to resist applied stresses. Titanium corrosion can be mitigated by adding soluble iron and copper ions, and the extent to which this is possible was demonstrated. This work revealed the detrimental effects of the solid phase of slurries on the integrity of titanium and provides data for industry guidance under metal leaching operations conditions.

Preface

This work was carried out in the Corrosion Laboratory in the Department of Materials Engineering, The University of British Columbia, under the supervision of Prof. Edouard Asselin. The journal articles and conference presentations produced from this dissertation are listed below. I am the primary contributor for all papers: I designed and executed all the experiments, conducted most of the data analysis, and wrote the first drafts. Prof. Asselin helped with data analysis, interpretation, and editing of the manuscripts. Dr. Rebecca Schaller extensively helped with the writing papers. Both Prof. Asselin and Dr. Schaller assisted with the revisions during the peerreview processes. Drs. Jing Liu and Zihe Ren contributed original ideas and methods discussed in article "1". Prof. Akram Alfantazi assisted in my Ph.D. study and completion of article "3".

Journal Articles

- 1. Yu Liu, Zihe Ren, Jing Liu, Rebecca Schaller, Edouard Asselin, "Electrochemical investigation and physical identification of titanium hydrides formed in simulated acidic leaching solution", *Journal of Electrochemical Society*, 166(11) C1–C10 (2019)
- Yu Liu, Rebecca Schaller, Edouard Asselin, "Effect of Fe(III) and Cu(II) on the passivation of Ti-2 in acidic chloride solutions", *Journal of Electrochemical Society*, 166(2) C76–C82 (2019)
- Yu Liu, Akram Alfantazi, Rebecca Filardo Schallera, Edouard Asselin, "Localised instability of titanium during its erosion-corrosion in acidic slurries", *Corrosion Science*, Volume 174, 108816 (2020)

Conference Presentations

- Yu Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in simulated leaching solutions", *Hydrochair Poster Session*, September (2018), The University of British Columbia, Vancouver, BC, Canada
- Yu Liu, Jing Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in the leaching solutions", *China-Canada Nonferrous Metallurgy Forum*, July (2018), Northeast University, Shenyang, China
- Yu Liu, Edouard Asselin, "Metastable pitting during the erosion-corrosion of titanium in acidic leaching slurries", 58th Annual Conference of Metallurgists (COM 2019) and International Copper Conference, August (2019), Vancouver Convention Center, Vancouver, BC, Canada

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List of Symbols

Symbol	Meaning	Common Units
В	Stern-Geary coefficient	V
СН	empirical coefficient	_
C_j	bulk solution concentration	М
CR	corrosion rate	$mm \cdot y^{-1}$
ΔC	concentration gradient	$mol \cdot m^{-3}$
$d_{0.1}$	maximum diameter of the finest 10% of the grains	cm
<i>d</i> _{0.5}	maximum diameter of the finest 50% of the grains	cm
D	diffusion coefficient	$\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
D_s	bulk sediment/solid diffusion coefficient	$\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
D_s	bulk sediment/solid diffusion coefficient	$\mathrm{cm}^2 \cdot \mathrm{s}^{-1}$
Ecorr	corrosion potential	V
Ecrit	critical potential for passivity	V
Erev	reversible potential	V
E^0	standard half-cell reduction potential	V
fn	characteristic frequency	s^{-1}
f_s	sampling frequency	s^{-1}
F	formation resistivity factor	_
F'	solution formation resistivity factor	_
İcorr	corrosion current density	$A \cdot cm^{-2}$
<i>i_{crit}</i>	critical current density for passivity	$A \cdot cm^{-2}$
<i>i</i> _L	limiting current density	$A \cdot cm^{-2}$

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İmean	mean coupling current	$A \cdot cm^{-2}$
J	diffusion flux	$mol{\cdot}m^{-2}{\cdot}s^{-1}$
k	permeability	$\mathrm{cm}\cdot\mathrm{s}^{-1}$
P_d	particle density	$g \cdot cm^{-3}$
P_b	particle bulk density	$g \cdot cm^{-3}$
q	characteristic charge	С
Q	constant phase element	_
R	universal gas constant	$J{\cdot}mol^{-1}{\cdot}K^{-1}$
R _{ct}	charge transfer resistance	$\Omega \cdot cm^2$
R _{film}	passive film resistance	$\Omega \cdot cm^2$
R_p	linear polarisation resistance	$\Omega \cdot cm^2$
S	specific surface area	$m^2{\cdot}g^{-1}$
Vs	deposit sample volume	ml
V_t	total volume	ml
Vwater	water volume	cm ³
Δx	position distance	m
Ζ	impedance	$\Omega \cdot cm^2$
а	chemical activity for the relevant species	_
a _{Rex}	activity of the reduced form	_
a_{Ox}	activity of the oxidised form	_
arphi	porosity	%
$arphi^T$	theoretical porosity	%
$arphi^E$	experimental porosity	%

arphi-average	average porosity	%
β	stability constant for ion complex	_
$ heta_{ads}$	surface coverage by adsorbed hydrogen	_
θ	tortuosity of the sediment or deposit	_
δ_i	standard deviation of current noise	А
δ_E	standard deviation of potential noise	V
δ	diffusion layer thickness	m
ρ	metal density	$g \cdot cm^{-3}$
$\Psi_{E,0}$	low frequency limit of potential PSD	$V^2 \cdot Hz^{-1}$
$\Psi_{i,0}$	low frequency limit of current PSD	$A^2 \cdot Hz^{-1}$
χ^2	chi-square value	_

List of Abbreviations

AA	anti-aliasing
AC	alternating current
A/D	analog-to-digital
CE	counter electrode
СР	commercially pure
CPE	constant phase element
DC	direct current
DI	deionised water
EBSD	electron backscatter diffraction
EN	electrochemical noise
EEC	electrical equivalent circuit
EIS	electrochemical impedance spectroscopy
EW	equivalent weight
FFT	fast Fourier transformation
HER	hydrogen evolution reaction
HIC	hydrogen-induced cracking
ICP-MS	inductively coupled plasma mass spectrometry
LPR	linear polarisation resistance
OCP	open circuit potential
ORP	oxidation-reduction potential
PD	potentiodynamic polarisation
PS	potentiostatic polarisation

PSD	power spectral density
PTFE	polytetrafluoroethylene
RE	reference electrode
SCC	stress-corrosion cracking
SCE	saturated calomel reference electrode
SEM	scanning electron microscope
SHE	standard hydrogen electrode
S1	silica particle sample 1
S2	silica particle sample 2
S3	silica particle sample 3
TGO	thermally grown titanium oxide
Ti	titanium
Ti-2	titanium grade 2
ToF-SIMS	time-of-flight secondary ion mass spectrometry
UDC	under-deposit corrosion
VA	voltage amplifier
WE	working electrode
XRD	X-ray diffraction
ZRA	zero-resistance ammeter
3D	three-dimensional

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Dedication

Dedicated to

my beloved parents

Chapter 1: Introduction

The use of metals directly or indirectly affects many aspects of our lives. The science and technology of extractive metallurgy determines the production, value, and use of metals. Of the two main branches of extractive metallurgy—pyrometallurgy and hydrometallurgy—the latter employs aqueous solution chemistry to extract, separate, and recover metals from ores. In recent decades, hydrometallurgy has figured prominently in the production of many base (Cu, Ni, Zn), precious (Au, Ag, Pt), and rare (Ge, In) metals, as well as by-product elements (As, Sb) [1].

One advantage of hydrometallurgy over traditional pyrometallurgy is that it allows for treatment of low-grade ores [2]. Over the years, ore grades have decreased for many metals as richer ores have been exploited. For example, copper has a long history of human use and is still among the biggest tonnage metals produced (ranking third after iron and aluminum). Mined copper ore grades have been decreasing since 2005 (Figure 1-1) [3], a trend that is expected to continue. Currently, copper is mainly extracted from low-grade oxide ores and some sulfide ores through leaching (solvent extraction) and electrowinning. Whereas solvent extraction-electrowinning production was virtually non-existent before the 1960s, increasingly low grades and dirty concentrates have made pyrometallurgical smelting less attractive. The International Copper Study Group reported that in 2018, refined copper production from hydrometallurgical processes represented approximately 16% (3.9 million tonnes) of total refined copper production [4]. Furthermore, hydrometallurgical processes provide a viable alternative to meet environmental challenges. Pyrometallurgical processes are often associated with toxic emissions, requiring the installation of equipment that has high capital and operating costs. In contrast, hydrometallurgy provides greater economic viability to deal with toxic emissions [2].





In view of ore grade and environmental challenges, hydrometallurgical methods have gained increasing popularity in the metals extraction industry. The model system studied herein is the hydrometallurgical leaching of chalcopyrite (CuFeS₂), the most abundant copper-bearing sulfide mineral. Cominco Engineering Services Ltd (CESL) has developed a proprietary hydrometallurgical process, *i.e.*, the CESL Process, with the express purpose of converting copper sulfide concentrates to copper metal. The CESL Process involves oxidation of the sulfide concentrates at elevated pressure and temperature in the aggressive sulfuric acid systems with the presence of moderate concentrations of catalytic chloride ions (sulfuric acid-chloride system) [5]. Sulfuric acid concentration may range from 20–55 g·L⁻¹, depending on the grade of concentrate. Concentrates subjected to leaching are ground and agitated in the acidic solutions for efficient particle/solution contact to accelerate copper extraction [6]. The addition of chloride ions is to accelerate the oxidation of copper sulfide—they promote the formation of a more porous sulfur product on the mineral surface, thus permitting the dissolution reaction to proceed at a reasonable

rate [7]. Ferric ions and dissolved oxygen are the most often used oxidants for the oxidation of chalcopyrite in leaching systems, and a faster leaching rate is generally observed with the increase of their concentration [2, 6-12].

In hydrometallurgical operations, titanium (Ti) and its alloys are often used to construct the liner and internal parts of autoclaves such as agitators, pumps, and piping, due to their excellent corrosion resistance under these aggressive leaching conditions [13, 14]. Unalloyed Ti, such as ASTM grades 1 and 2 (Ti-1, Ti-2), are most often used as the materials for autoclave internal liners. Grade 12 (Ti-12) is alloyed with 0.3% Mo and 0.8% Ni and stronger than unalloyed Ti. It is used in areas of high abrasion such as nozzles and valves. Grade 18 (Ti-18, Ti-3Al-2.5V-Pd), even stronger, is used in dynamic components such as agitator blades. Grade 7 (Ti-7, 0.15% Pd alloyed) is usually employed to repair any corrosion damage—it has superior resistance to crevice corrosion [15, 16].

Titanium suffers severe corrosion attack in hydrochloric or sulfuric acid solutions that do not contain metals or oxygen [17-19]. Oxidants like ferric or cupric ions or dissolved oxygen are reported to passivate titanium with a chemically inert and exceptionally stable protective oxide film formed on the metal surface, thus protecting titanium from corrosion [13, 14]. Therefore, these passivating species act as inhibitors for titanium corrosion in the acidic solution. Solid minerals are ubiquitous and integral to hydrometallurgical autoclaving processes. The presence of these solids, however, may significantly affect the corrosion behaviour of Ti.

First of all, solid minerals may deposit and accumulate on the internal surfaces of titanium autoclaves during normal operation or production shutdowns. Solid deposition may cause accelerated localised corrosion beneath or around deposits on a metal surface, which is termed under-deposit corrosion (UDC) [20]. UDC is frequently reported in oil & gas industries, where suspended solids are commonly present and accumulate along the interior of production or transmission equipment [21, 22], and it has frequently been cited as responsible for high corrosion rates and loss of containment of pipeline steels [22-26]. The deposition of solid minerals may also affect the corrosion behaviour of titanium substrates as reported with pipeline steels. However, related investigations on titanium corrosion in hydrometallurgical leaching conditions have yet to be reported.

Secondly, mineral slurries are vigorously agitated during leaching, and that may cause erosion-corrosion of titanium due to contact with the high-speed slurries in the autoclaves. Erosion-corrosion is a combined mechanism, where the electrochemical corrosion in the aggressive solution and the mechanical wear resulting from solid impingement occur simultaneously [27]. The interaction between these two processes may be self-reinforcing, enabling the overall erosion-corrosion rate to be greater. Previous work on passive metals—those that readily form a protective oxide film like stainless steel and nickel-based alloys—has shown that material loss rates can be significantly accelerated when a mechanical process is involved in the corrosion process [28]. Thus, the erosion-corrosion behaviour of titanium in aggressive leaching conditions needs to be evaluated to determine the limits of its safe use in industrial operations.

Thirdly, titanium acid corrosion involves the products of titanium hydrides, which are closely related to the mechanical degradation of the titanium substrate. Titanium hydrides may electrochemically catalyse the hydrogen evolution reaction (HER), and this catalysis in turn promotes the formation of titanium hydrides, further weakens the titanium substrate, thus jeopardizing the integrity of titanium equipment. In view of the relatively limited understanding of titanium hydrides, an investigation pertaining to their electrochemical properties and physical characterisation is required.

Lastly, ferric and cupric ions in acidic leaching solutions are known to promote the passivation of titanium and thus maintain its stability in aggressive acidic applications. However, their effectiveness with respect to titanium passivation has not been quantified, nor the associated mechanisms elucidated. The interaction between these cations and titanium is of vital importance and its clarification is of practical significance for titanium corrosion protection across a variety of industrial applications, including hydrometallurgical.

The corrosion behaviour of titanium in acid solutions and simulated leaching solutions has been investigated in the absence of solids [10, 16]. However, these data may not represent the corrosion behaviour of titanium when solid mineral particles are present. This thesis will clarify the effects of solids on the corrosion behaviour of Ti-2 in the high acidity and oxidation leaching solutions (the typical synthesised copper leaching solution: $30 \text{ g} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4 + 12 \text{ g} \cdot \text{L}^{-1} \text{ Cl}^- + 15 \text{ g} \cdot \text{L}^{-1} \text{ Cu}(\text{II}) + 1 \text{ g} \cdot \text{L}^{-1} \text{ Fe}(\text{III})$ and bubbled with O₂ [29]). The thesis is organised as follows.

Chapter 2 is a literature review of pertinent information about titanium corrosion in acid solutions (sulfuric acid and hydrochloric acid), titanium passivation by oxidising species, titanium hydrides, and two related forms of corrosion: UDC corresponding to solids deposition and erosion-corrosion corresponding to slurry movement. **Chapter 3** states the motivation and key objectives of this research work. The experimental design, electrode fabrication, solution preparation, and detailed experimental procedures are described in **Chapter 4**. **Chapter 5** presents the effects of solid deposition on corrosion behaviour of titanium and the detrimental effect of solid deposition on the corrosion resistance of titanium in the simulated leaching solution. The titanium hydride phases are characterised, and their electrochemical properties and extent to which they catalyse

the HER are investigated in **Chapter 6**. In **Chapter 7**, the passivation of Ti-2 by ferric and cupric ion species is investigated by electrochemical techniques, and the passivation mechanism is discussed. The erosion-corrosion behaviour of titanium subjected to slurry solutions during leaching is evaluated in **Chapter 8**. Current transients due to solid particle impingement are characterised and they are related to the fracture and repassivation of the protective film on the titanium surface. Finally, a summary of key findings, practical implications, and opportunities for future work are described in **Chapter 9**.
Chapter 2: Literature review

2.1 Titanium corrosion in sulfuric and chloride acid solutions

Titanium (Ti) is an important structural material in various applications, such as nuclear fuel waste containers, desalination plants, biological implants, chemical processing, and seawater treatment equipment [14, 16, 30, 31], because it combines low density with high strength and resistance to corrosion attack. Titanium is a typical passive metal. Pure titanium metal is very active, and it quickly reacts to form a layer of passive oxide film on the surface when exposed to air or water. This passive film layer is inert, compact, and mechanically stable, and it accounts for the excellent corrosion resistance of titanium [14]. However, the passive film can be destabilised and may dissolve rapidly. When this occurs, titanium suffers severe corrosion attack in sulfuric or hydrochloric acid solutions, especially in the absence of corrosion-inhibiting agents [10, 16, 32]. The passivation behaviour of titanium will be introduced in Section 2.3, and the corrosion of titanium will be the focus of this Section.

In the absence of corrosion inhibitors, the titanium corrosion rate in acid solutions is strongly influenced by factors such as acid concentration (solution pH), temperature, and the possible complexation reactions with anions (*i.e.*, sulfate and chloride ions) [33-38]. The relationship between the corrosion behaviour of titanium and these factors can be illustrated by phase diagrams based on thermodynamic calculations, and iso-corrosion diagrams based on kinetic evaluations.

2.1.1 Thermodynamic evaluation of titanium corrosion

The state of titanium can be predicted by phase diagrams, known as Pourbaix diagrams or E_h -pH diagrams, based on thermodynamic calculations. These diagrams indicate regions of "immunity", "passivity", and "corrosion", giving guidance as to the state of a particular metal in a

specific environment. The vertical axis is the potential, *E* (or E_h), which is commonly expressed versus the standard hydrogen reference electrode (SHE): by convention the hydrogen evolution reaction (HER) has a potential of 0 V (Figure 2-1). The effects of chemical species, temperature, and concentration of solvated ions and ligands shift the equilibrium lines in a Pourbaix diagram as calculated by the Nernst equation. In Figure 2-1, soluble titanium ions, such as Ti(III) and Ti(IV), show up in the acidic regions at pH < 2.5 [39], and this indicates that titanium would tend to corrode under these conditions. The hydrated titanium oxide, TiO₂·H₂O, represents the passivity of titanium. It is thermodynamically stable over a wide range of potential and pH—this accounts for the overall excellent corrosion resistance of titanium. When the potential is more negative than approximately –500 mV at pH = 0, the most stable phase is titanium hydride (TiH₂), an important product of the titanium corrosion process.



Figure 2-1 E_h -pH diagram for Ti-H₂O system (298K, Ti ion activity = 10⁻⁶) [15, 16]

Increasing temperature to 463 K significantly decreases the passive region of $TiO_2 \cdot H_2O$ (Figure 2-2). Instead, $HTiO_3^-$, the predominant phase in alkaline solution [40-42], expands into the passive region of $TiO_2 \cdot H_2O$. Thus, it is clear that the passive region of titanium significantly decreases as temperature increases in the E_h -pH diagram. This indicates that Ti's industrial use may be more limited at high temperatures.



Figure 2-2 E_h -pH diagram for Ti-H₂O system (463 K, Ti ion activity = 10⁻⁶) [15, 16]

The effect of complexation by sulfate and chloride anions on titanium corrosion can also be illustrated by E_h -pH diagrams [41, 43-45]. The equilibrium constants for Ti-SO₄²⁻ and Ti-Cl⁻ species are listed in Table 2-1 and Table 2-2, respectively. The E_h -pH diagrams for the Ti-Cl⁻-H₂O system and the Ti-SO₄²⁻-H₂O system are shown in Figure 2-3 and Figure 2-4, respectively.

Sulfate ions have a stronger ability to complex with soluble Ti(III) and Ti(IV) ions than chloride ions in acidic sulfuric and hydrochloric electrolytes. The complexation with Cl^- is significant only with Ti^{IV} ions, which results in the thermodynamic stability of $TiOCl_4^{2-}$ (Figure 2-3). In contrast, SO_4^{2-} complexes with both Ti^{III} and Ti^{IV} ions (Figure 2-4). In addition, SO_4^{2-} increases the solubility of Ti^{IV} ions to a greater extent than Cl^- .

Table 2-1 Ti-SO4²⁻ species equilibrium constants [15, 44, 46]

Reactions	Equilibrium Constant
$Ti^{3+} + SO_4^{2-} \rightleftharpoons TiSO_4^+$	24.3
$Ti^{3+} + 2SO_4^{2-} \rightleftharpoons Ti(SO_4)^-$	180
$Ti^{3+} + 3SO_4^{2-} \rightleftharpoons Ti(SO_4)_3^{3-}$	376
$TiO^{2+} + SO_4^{2-} = TiOSO_4$	169.5
$TiO^{2+} + 2SO_4^{2-} = TiO(SO_4)_2^{2-}$	13038

Reactions	Equilibrium Constant
$Ti^{3+} + Cl^{-} \rightleftharpoons TiCl^{2+}$	0.07/0.20*
$Ti^{3+} + 2Cl^{-} \leftrightarrows TiCl_{2}^{+}$	0.003/0.005*
$Ti^{3+} + 3Cl^{-} \rightleftharpoons TiCl_{3}$	0.001/0.0002*
$Ti^{3+} + 4Cl^{-} \rightleftharpoons TiCl_4^{-}$	0.0003/0.01*
$TiO^{2+} + Cl^{-} \rightleftharpoons TiOCl^{+}$	3.55
$TiO^{2+} + 2Cl^{-} \rightleftharpoons TiOCl_2$	1.42
$TiO^{2+} + 3Cl^{-} = TiOCl_{3}^{-}$	15.05
$TiO^{2+} + 4Cl^{-} \rightleftharpoons TiOCl_4^{2-}$	180.62
second set of data [47]	

Table 2-2 Ti-Cl⁻ species equilibrium constants [15, 47, 48]



Figure 2-3 E_h -pH diagram for Ti-Cl⁻-H₂O system (298 K, Ti ion activity = 10⁻⁶, Cl⁻ activity = 0.1) [15]



Figure 2-4 E_h -pH diagram for Ti-SO₄²⁻-H₂O system (298 K, Ti ion activity = 10⁻⁶, SO₄²⁻ activity = 0.1) [15]

 E_h -pH diagrams must identify the correct phases to be reliable. This is contingent on the use of correct thermodynamic data. Since the thermodynamic data for titanium phases continues to be developed, there is a case for updating the diagrams shown in Figures 2-1 to 2-4 [40, 41, 49-51]. However, in general, the picture is expected to remain consistent: titanium will corrode in acidic solutions and reducing conditions will result in hydride formation.

2.1.2 Kinetic evaluation of titanium corrosion

 E_h -pH diagrams provide a basic description of the stability regions under specific conditions but do not allow for reaction rate or kinetic effects to be considered. Iso-corrosion diagrams are commonly used to represent the uniform corrosion resistance of a given material. They provide a convenient method to relate the corrosion rate to environmental factors such as temperature and acid concentration. Figure 2-5 shows the 0.1, 0.5, and 1.0 mm·y⁻¹ iso-corrosion lines for titanium in sulfuric acid from Liu *et al.* [52], and Figure 2-6 shows the 1.0 mm·y⁻¹ isocorrosion line for titanium and its alloys in hydrochloric acid from Schutz and Covington [1]. These diagrams illustrate that for any fixed corrosion rate, the allowable operating temperature for titanium applications decreases with increasing acid concentration.

It is noticed that the presence of Fe^{3+} and Cu^{2+} ions significantly extends the operating area below the iso-corrosion line. These two species promote the passivity of titanium *via* the formation of the protective oxide film on the titanium surface (Figure 2-5). In addition, titanium shows a higher dissolution rate in sulfuric acid than in hydrochloric acid solution (Figure 2-6), which can be attributed to the larger extent of complexation of titanium ions with sulfate than chloride anions [41, 43-45], as illustrated in Figure 2-3 and Figure 2-4.



Figure 2-5 Iso-corrosion diagrams at (a) 0.1 mm·y⁻¹, (b) 0.5 mm·y⁻¹, and (c) 1.0 mm·y⁻¹, for titanium in



3 wt.% to 50 wt.% H₂SO₄ solutions [52]

Figure 2-6 Iso-corrosion diagrams for titanium and titanium alloys corrosion rate at 0.127 mm·y⁻¹ in (a) H₂SO₄, (b) HCl solutions [1]

2.2 Titanium hydride formation

Titanium is a hydride-forming metal: hydride phases are predicted in E_h -pH diagrams and widely observed to form on its surface [53-59]. Titanium hydrides are important product(s) of acidic corrosion of titanium. In aqueous conditions, titanium hydrides form simultaneously with the HER. Reducing conditions can occur in hydrometallurgical autoclaves during upset conditions (if the molten sulfur reaction product is allowed to pool at the bottom of an autoclave, for example [60, 61]), or possibly during normal operation when oxidation-reduction potential (ORP) is low for various process reasons [62]. The generally accepted reaction scheme for hydride formation can be written as Equation 2-1, steps (a)-(d) [63]. The adsorption of hydrogen starts with H⁺ discharge on the metal surface and the subsequent formation of adsorbed H species. Then, the interfacial H transfer from the adsorbed to the absorbed state occurs and is followed by hydride formation and H diffusion into the bulk metal [54, 59, 64].

$$H^+ + e^- + Ti \rightarrow TiH_{ads}$$
 E-step (or Volmer step) Equation (2-1a)

followed by either the chemical reaction:

$$2\text{Ti}\text{H}_{ads} \rightarrow 2\text{Ti} + \text{H}_2$$
 C-step (or Tafel step) Equation (2-1b)

or the electrochemical reaction:

$$TiH_{ads} + H^+ + e^- \rightarrow Ti + H_2(g)$$
 E-step (or Heyrovsky step) Equation (2-1c)

hydrogen absorption and hydride formation:

$$\Gamma i H_{ads} \rightarrow T i H_{abs} \rightarrow T i H_x$$
 Equation (2-1d)

The hydride formation can occur in sulfuric or hydrochloric acid solutions during natural corrosion processes or by cathodic polarisation (*i.e.*, cathodic galvanostatic polarisation, potentiostatic polarisation, or galvanic connection to a more active metal) [18, 64, 65]. Metallographic cross-sections have demonstrated that hydrides also form on crevice-corroded surfaces of freely corroding Ti-2 specimens in neutral NaCl solutions [58, 66]. In the crevice, a local acidic solution can develop and active corrosion can propagate [66-71]. Titanium hydrides have also been observed during tensile testing of Ti-2 and titanium grade 3 when the potential was held below -0.7 V versus a saturated calomel reference electrode (SCE) in 6% NaCl solution at pH 1 and 70°C [56]. Empirical observations suggest that hydrogen absorption by titanium starts

in the range -0.6 to -1 V vs. SCE [57, 64, 72, 73]. Recent work reveals that hydrogen absorption by titanium could occur at -0.37 or even -0.35 V vs. SCE [64, 74], where the capacitance and resistance of the titanium oxide films on the surface dramatically changed.

Titanium hydrides formed on Ti-2 by galvanostatic polarisation in acidic and deaerated NaCl solution at 95°C (absorbed hydrogen concentration: 0.53 mg·cm⁻²) had a needle-banded morphology, with the hydrides deeply penetrating the specimen at grain boundaries [55]. Further investigation showed that the titanium hydrides were unevenly distributed on the surface and preferentially located at iron-containing intermetallic particles along grain boundaries [63]. Titanium hydrides prepared by a gas-equilibration method (absorbed hydrogen concentration: 1– 3 at.%) had a thin platelet-like morphology with length up to several hundred micrometres [75]. From titanium samples charged with gaseous hydrogen, Briant et al. [76] noted that the hydrides became coarser and the outline of the grain boundaries became more complete when the hydrogen concentration increased from 600 to 3490 wppm (weight parts per million). At 3490 wppm hydrogen, the hydride microstructure changed from an equiaxed structure with hydrides along the grain boundaries to a lath or Widmanstatten-like structure [76]. Various factors, such as the overall electrode geometry, charging method, and charging conditions, can influence hydrogen absorption, hydride formation, and hydride morphology. In general, the preferential formation of hydrides along grain boundaries is consistently reported at low hydrogen concentrations, with similarly reported morphologies [55, 63, 75, 76].

2.2.1 Effects of titanium hydrides on titanium substrate

Titanium hydrides have been associated with stress-corrosion cracking and increased susceptibility toward hydrogen-induced cracking of titanium equipment [53, 77-80]. Numakura and Koiwa [75] found that the α -matrix titanium around the hydride was subject to high stress due

to the larger specific volume of the hydride. The compressive stress that developed in the hydride layer during hydrogen charging increased proportionally to the quantity of hydrides formed [79]. The induced stress is accommodated either elastically or plastically. Thus, the surface layers of hydrides were reported to cause embrittlement of titanium, and the loss of ductility increased with increasing hydride quantities [79]. Titanium hydrides were also found to form in the vicinity of crack tips, where crack propagation proceeded through the hydrides [53] or along the hydridematrix interface [53, 77, 80]. The mechanical properties of the hydrides are strongly related to degradation of titanium mechanical properties. Setoyama et al. [81] investigated bulk titanium hydrides prepared by gaseous hydrogen charging and found that the titanium hydrides had smaller elastic moduli than the titanium metal, and the elastic moduli depended on the hydrogen content. Xu et al. [82] prepared titanium hydride thin films by an electrolytic technique, and reported that the hydrides had approximately 30% higher hardness and 100% higher yield stress than pure Ti. In general, the inherent brittleness of hydrides plays a central role in premature cracking of hydride-forming metals: this could become an issue if titanium is used for pressure containment in acidic aqueous environments [83].

In addition to degrading the mechanical properties of titanium, hydrides may also accelerate HER, that is, an increased current density corresponding to HER has been observed when hydrides are present [38, 55, 58, 63, 84, 85]. Yan *et al.* [63] described the interaction between titanium hydrides and the HER with Equation 2-1 and Figure 2-7. After 5 h of galvanostatic polarisation, they observed a Tafel slope for proton reduction of -129 mV/decade. H adsorption (Equation 2-1, step (a)) was rapid and irreversible with a rate constant of k_l [86], while the H discharge rates of both steps (b) and (c) reactions were slow at this moment (Figure 2-7 (a)). However, after being polarised for 30–50 h, steady-state conditions were established, and a smaller

Tafel slope of -40 mV/decade was observed. They attributed the Tafel slope change to catalysis of proton reduction, which resulted from formation of titanium hydrides during cathodic polarisation. In addition, the formation of titanium hydrides suppressed H absorption into the metal, which led to increased adsorbed H coverage, θ_{ads} , and finally resulted in the steady state where the H adsorption reaction (step (a)) became reversible (Figure 2-7 (b)). In general, research associated with the catalysis properties of titanium hydrides is relatively limited, and information about hydride catalysis is insufficient.



Figure 2-7 Mechanisms for hydrogen evolution at 25°C in 0.27 M NaCl plus 0.60 M HCl for (a) 5 h polarisation and (b) 35 h polarisation [63]

2.2.2 Titanium hydride phases

Many allotropic forms of titanium hydrides (H/Ti atom ratio: 0–2) are predicted in the Ti-H phase diagram as a function of hydrogen concentration, system temperature, and applied pressure [87-90]. Phases such as α , β , and δ have been reported and illustrated in phase diagrams (*e.g.*, Figure 2-8) [75, 91-93]. The α and β phases are random solid solutions of hydrogen in the hexagonal close-packed and body-centered cubic forms of metal Ti, respectively. The δ phase is most common and shows a wide range of non-stoichiometry. Its crystal structure is the CaF₂-type belonging to the space group Fm–3m, in which the metal atoms form a face-centered cubic lattice, and hydrogen atoms are randomly located in tetrahedral interstitial sites [91, 94]. For high hydrogen concentrations approaching the limiting composition TiH₂ below room temperature, the hydride transforms into ε hydride, which is a tetragonally distorted modification of the δ phase [95, 96]. The γ phase has also been observed and is metastable, appears only with a low concentration of hydrogen, and is always the minor constituent in composites in which the equilibrium phase δ is dominant [75, 93].



For titanium hydrides formed by electrolysis, Phillips *et al.* [79] estimated that the mean H/Ti atom ratio of hydrides increased from 1.21 to 1.48 during galvanostatic polarisation as the cathodic current density increased from 0.05 to 3.0 mA·cm⁻² in 0.05 M H₂SO₄ at 25°C [79]. Millenbach and Givon [92] found that the hydrogen content increased from TiH_{1.62} to TiH_{1.78} as the cathodic current density increased from 5 to 20 mA·cm⁻² in 0.5 M H₂SO₄. This increase depended exclusively on the cathodic current density. Other researchers have generally referred to the hydride phase as TiH₂ in acidic conditions (0.1–5 A·cm⁻² for 10 min. in 1 M H₂SO₄ solution

at 25°C) [97], in 0.2 or 2.0% APF (2.0% NaF + 1.7% H₃PO₄, pH 5.0) at the corrosion potential [98], or in alkaline solutions (0.1 M NaOH, pH 11.8; 2 M NaOH, pH 13.5) [99]. The differences in the titanium hydride forms observed in these studies likely result from differing environmental factors (*i.e.*, solution composition, pH, electrode potential, temperature, and cathodic current densities) [18, 79, 85, 92, 100]. Also, determining titanium hydride forms is complicated by the difficulty in obtaining a uniform hydride layer with non-trivial thickness in comparison with gaseous-formed hydrides [92]. Understanding about the hydride phase formation by electrolysis and the subsequent electrochemical kinetics is still required.

2.3 Titanium passivation

The exceptionally chemically inert and stable oxide passive film that forms on Ti's surface accounts for its excellent corrosion resistance [13, 14]. The oxide film effectively isolates the titanium substrate from the surounding aggresive environments, protects it from chemically corrosive and mechanically erosive attack, and thus enables its application in various highly corrosive environments [13, 101, 102]. Titanium passivity is predicted in the Pourbaix diagrams discussed in Section 2.1.1 [49, 50] and is also observed in a variety of experimental conditions [45]. The presence of oxidants, moderate pH, noble potentials, and galvanic coupling have all been reported to promote the passivation of titanium [45, 49, 50, 55].

For metals that exhibit passive behaviour like titanium, Figure 2-9 can schematically represent their polarisation behaviour. Although this figure is general in nature and, therefore, does not show all characteristics of real systems, it is sufficiently accurate to describe most experimental observations.



Figure 2-9 Typical anodic polarisation curve for metals which exhibit passivity, obtained by fixing the potential and measuring the current [35]

As the potential is shifted toward the noble direction, titanium goes through the active corrosion state (AB), active-passive state transition (BE), and finally enters the passive state (EF). Each state corresponds to different electrochemical reaction(s). In the potential range from A to B, titanium is in the active corrosion state and the primary oxidation reaction is solution of titanium metal to form soluble Ti(III) ions. In acid solutions where conditions do not allow for titanium passivation, it attains a corrosion potential of -0.7 to -0.9 V *vs*. SHE [45, 55].

As the potential increases, the anodic current density continues to increase along AB. The "nose" of the polarisation curve at point B corresponds to the maximum anodic current density, defined as the critical current density for passivity, i_{crit} , and its corresponding potential is the critical potential for passivity, E_{crit} [45, 103]. Above E_{crit} , the current density decreases abruptly as the potential increases from B to E. In EF, titanium achieves passivity, and the current density remains low, indicating a slow metal dissolution rate (low corrosion rate). Beyond EF, the

electrode processes depend on both the metal and the environment. Thus, it is not further discussed in the scope of titanium passivity studies.

 i_{crit} and E_{crit} are important parameters related to the passivity of metals and alloys [35]. A relatively low critical anodic current and active critical potential of the passive metals always favor passivity [35]. In a comparison investigation of the passivation of Fe and Fe-Cr alloys in sulfuric acid solutions by ferric ions, i_{crit} for Fe and for Fe-Cr alloy were 1 A·cm⁻² and 2.2 mA·cm⁻², respectively (note the 3 order of magnitude difference). Similar additions of ferric ions only resulted in passivity of the Fe-Cr alloy, which had the lower i_{crit} than that of Fe [104]. This result indicates that an increase in i_{crit} might be consistent with a requirement for higher concentrations of oxidative ions to achieve passivation.

The relationship between environmental conditions and titanium passivity can be demonstrated by their influence on the passivity parameters i_{crit} and E_{crit} . Increasing acid concentration is reported to increase the i_{crit} of Ti, that is, it makes it harder to passivate the metal [16, 35]. In 30 g·L⁻¹ H₂SO₄ solution at 21°C, Ti-2 remained passive; when the acid concentration was increased to 100 and 500 g L⁻¹, Ti-2 actively corroded and i_{crit} was 0.01 and 0.11 mA·cm⁻², respectively [16]. In boiling H₂SO₄ solution containing 500 g·L⁻¹ Na₂SO₄, when the H₂SO₄ concentration was increased from 1 to 5 g L⁻¹, the i_{crit} of commercially pure (CP) titanium increased from 0.05 to 1.8 mA·cm⁻² [35]. E_{crit} , however, is not significantly influenced in most conditions at temperatures below 100°C, such as in sulfuric acid solutions with chloride [105], HCl solution containing 5% Na₂SO₄ [35].

2.3.1 Titanium passivation by passivating species (oxidants)

Introducing oxidants or passivating species (sometimes also referred to as passivating inhibitors), into a corrosive environment is a simple method to induce titanium passivity and enhance titanium corrosion resistance by increasing the redox potential to a value that is commensurate with titanium being in zone E-F of Figure 2-9. In hydrometallurgical conditions, the passivating species commonly encountered are Fe(III), Cu(II) and dissolved O₂. Their presence plays an important role in maintaining the stability of Ti-lined autoclaves, which otherwise would rapidly corrode in sulfuric or hydrochloric acid solutions [10, 16]. The ability of oxygen to inhibit titanium corrosion was reported by Golden *et al.* [33]: titanium was fully resistant to up to 3% sulfuric acid solution when aerated, but corrosion attack was obvious when the solution was bubbled with nitrogen [33]. The oxygen may also influence the speciation of other oxidants in the system [103]. For example, in leaching solutions, oxygen is bubbled mainly to oxidise ferrous to ferric ions [106].

Cupric and ferric ions are reported to be effective at promoting the anodic passivity of titanium and maintaining its stability in aggressive mixed sulfuric acid-chloride systems. The presence of $1.0 \text{ g} \cdot \text{L}^{-1}$ ferric ions was observed to induce the most beneficial effect on increasing the corrosion resistance of titanium [10, 16]. The passivating effect of ferric and cupric ions was also reported by Levy and Stern [36, 103]. The weight loss tests conducted by Stern [103] showed corrosion inhibition by ferric and cupric ions of CP-Ti in 1% H₂SO₄ and 3% HCl solutions. Levy [36] investigated how ferric and cupric ions affected the polarisation behaviour of Ti-6A1-6V-2Sn alloy in 20% H₂SO₄. The critical current for passivity of titanium decreased with increasing ferric concentrations; the critical potential for passivity (defined in Section 2.2.3.1) also shifted in the more active (toward more negative potential) direction.

One frequently observed phenomenon is that there is a critical concentration of the passivating species that is necessary to promote titanium passivation [103, 107, 108]. The critical concentration depends on the passivation behaviour of the metal and the aggresiveness of the system, and depends strongly on intrinsic characteristics of the inhibiting species. Levy [36] reported that 0.03 M Fe(III) was effective in inhibiting the corrosion of Ti-6A1-6V-2Sn in 20% H_2SO_4 at 65°C. Stern [103] found that 0.01 M CuCl₂ or FeCl₃ was sufficient to inhibit the corrosion of CP-Ti to an undetectable rate in 1% H_2SO_4 and to 1 mg·dm⁻²·day⁻¹ in 3% HCl. They further stated that the critical Fe(III) required to passivate titanium in H_2SO_4 solutions increased with the aggressiveness of the H_2SO_4 solution [103]. Cobb and Uhlig [107] further pointed to the influence of Ti's surface state on the critical concentration of Fe(III) or Cu(II). The critical concentration required to inhibit the titanium corrosion reported by these authors is summarized in Table 2-3.

Solution	Surface condition	i_{crit} / mA·cm ⁻²	Fe(III) / M	Cu(II) / M	Ref.
Boiling 1% H ₂ SO ₄ + 5% Na ₂ SO ₄	Acid-activated*	0.05	0.000714	_	[103]
Boiling 2% H ₂ SO ₄ + 5% Na ₂ SO ₄	Acid-activated*	0.2	0.00152	_	[103]
Boiling 3% H ₂ SO ₄ + 5% Na ₂ SO ₄	Acid-activated*	0.4	0.00348	_	[103]
Boiling 5% H ₂ SO ₄ + 5% Na ₂ SO ₄	Acid-activated*	1.8	0.00446	_	[103]
Boiling 10% HCl or H ₂ SO ₄	Air-formed	_	0.005	0.005	[107]
Boiling 10% H ₂ SO ₄	Pickled (10% HNO ₃ + 0.25 HF solution for 40 s at 80°C)	_	0.03	0.03	[107]
Boiling 10% HCl	Pickled (as above)	_	0.02	0.02	[107]

Table 2-3 Critical concentration of Fe(III) or Cu(II) required to passivate titanium

* Ti was placed in the boiling acid solution until it was actively corroding *i*_{crit}: critical anodic current density for passivity

2.3.2 Interaction between titanium and passivating inhibitors

Mixed potential theory can explain the interaction between titanium and passivating inhibitors. The addition of an oxidising agent to the solution creates a reduction-oxidation (redox) system with a noble reversible potential. Anodic polarisation accompanies reduction of the oxidised species on the metal surface (Figure 2-10). The system will obtain a mixed potential, at which the sum of all reduction rates is equal to that of all oxidation reaction rates [35]. If the mixed potential is in the passive region, the metal achieves passivation and the dissolution rate of the metal is considerably lower than that observed at the active potential. A larger i_{crit} corresponds to more difficulty in creating passivation: the oxidising agents must provide greater polarisation to exceed i_{crit} .



Figure 2-10 Polarisation diagram for a metal passivated by an oxidising inhibitor [35]

The E_{crit} for titanium is approximately -0.7 V vs. SHE, which is 0.6 V more active than Fe and 0.1–0.2 V more active than stainless steel [103]. This unusually active critical potential contributes significantly to the ease with which titanium is passivated by many oxidising inhibitors and even by galvanic coupling. Strongly oxidising organic and inorganic compounds (HNO₃, K₂Cr₂O₇, KMnO₄, KIO₃) and cations of electropositive metals are effective in promoting titanium passivation at sufficient concentrations [17, 36, 103, 107, 109]. Pt, C, 18-8 stainless steel (AISI 304), and Hastelloy alloy F passivate titanium by galvanic connection in environments where they exhibit more noble potentials than titanium [35].

2.4 Under-deposit corrosion

2.4.1 Solid deposit compositions in hydrometallurgy

In hydrometallurgy, solids accumulate on process equipment surfaces to significant thicknesses. Figure 2-11 shows the interior of an autoclave from an oxidative leaching operation plant, belonging to a Canadian mining company. It is very clear that the solid deposits almost completely cover the autoclave wall and agitator blades. The layer is very thick (7–13 cm). Solids deposition occurs rapidly, and manual descaling with jack-hammers must be conducted at least twice a year to ensure normal operation of the autoclaves.

Chalcopyrite and other sulphide ores usually have a very complex composition, resulting in complex deposits on surface equipment during hydrometallurgical extraction (Figure 2-12 shows an example of a chalcopyrite ore, which was associated with multiple relatively inert minerals such quartz and feldspar [110]).



Figure 2-11 Solids deposition in process autoclaves in a Canadian oxidative leaching operation plant



(provided by the company)

Figure 2-12 Quantitative evaluation of materials by scanning electron microscopy (QEMSCAN) analysis of multiple blocks of chalcopyrite ore particle (> 7 mm, 0.7% Cu); chalcopyrite was primarily associated with pyrite and quartz/feldspar [110]

Since deposits can comprise leached (residue) as well as unleached ores (feed), the deposit composition lies on a spectrum between complex feed products, reaction intermediates, and complex residues. Residues characterised from several hydrometallurgical chalcopyrite leaching pilot plants showed that they contain mainly iron oxides/oxyhydroxide phases (*e.g.*, hematite, jarosite, goethite), sulfur, inert quartz, and gypsum (Table 2-4). The amount of iron oxide produced in the process depends on process conditions and feed mineralogy, varying from undetectable to 61 wt.% of the residue (Table 2-4). Quartz and gypsum are prevalent in residues (generally 4–30%) [111, 112]. Considering the complexity of the corrosion issues caused by solid deposits that may continue to react or leach, the following discussions will focus on the inert solids to demonstrate the effect of their presence on titanium corrosion. The data presented later are considered foundational to understanding the effects of these complicating factors on UDC.

Plant [reference]	Hematite (wt.%)	Jarosite (wt.%)	Goethite (wt.%)	Sulfur (wt.%)	Gypsum (wt.%)	Quartz (wt.%)	Leaching conditions
CESL S1[113]	_	14	_	16	3.2	4.2	150°C, 1300 kPa total pressure; mixed sulfate-chloride medium pH 2–3; solids loading 10.2%, retention time 91 min.
CESL S2 [113]	20.6	0.6	3.5	20	_	0.9	150°C, 1264 kPa total pressure; mixed sulfate-chloride medium; solids loading 23.2%; retention time 58 min.
Vale [113]	35	1	8	24	1.0	_	150°C, 1030 kPa total pressure; mixed sulfate-chloride system, solids loading 5%, retention time 80 min.
CESL [114]	16-58	0-32	0-10	19–44	2-21	3.1–8. 6	150°C, 1379 kPa total pressure; mixed sulfate-chloride system; leach time 60 min.
Anglo/UBC [115]	13-43	0-32	0-14	3-35	2-7	10-21	150°C, P(_{O2}) 700 kPa; of Quebracho or/and solidum lignosulfonate surfactant addition to sulfuric acid system
CESL [115]	7–27	0-12	0-37	19–30	3-5	8-18	150°C, P(_{O2}) 700 kPa; sulfate-chloride system
Phelps Dodge- Placer Dome [6]	29–61	0-10	_	0-15	6–22	2-6	220°C, P(₀₂) 700 kPa; sulfate-chloride system; solids loading 5%; reaction time 30–150 min.
Activox® [6]	_	0-37	0-27	20-37	9–12	<30	108°C, P(₀₂) 700 kPa, sulfate-chloride system pH 3–4; solids loading 10%
Anonymous	13-81	0-0.7	_	0	2.3-20	5-25	220°C; 35 g/L sulfuric acid

Table 2-4 Residue characterisation from medium-temperature leaching of chalcopyrite concentrates from hydrometallurgical pilot plants

2.4.2 Effects of solid deposition on the corrosion process

One important form of corrosion highly related to solid deposition is UDC, which is a localised corrosion that progresses around or underneath a deposited layer on a metal surface. UDC is considered to be a significant structural integrity risk for oil and gas production and transportation utilities [22]. UDC is highly influenced by the type and geometry (thickness, particle size) of deposits, the corrosive species in solution, the prevailing environmental conditions (temperature, pH), *etc.*, therefore, a single mechanism may not apply in all cases [116]. In this work, only inorganic inert deposits will be considered.

The deposition of inorganic solids may affect corrosion process in different ways. Solid deposits can act as a barrier to the transport of corrosive species (*e.g.*, protons and the chloride anion) and inhibitors between the bulk solution and the localised region under the deposits. By estimating the intrinsic or baseline corrosion rate of the underlying metal in comparison with an uncovered surface, the direct effect of solid deposition on the corrosion process may be ascertained. In addition, the electric connection between adjacent covered and uncovered regions of the same metal surface may give rise to a galvanic cell. Thus, two corrosion scenarios can be envisaged: (1) where the entire surface is covered with a deposit and mass transfer affects the corrosion process, and (2) only portions of the surface are covered but galvanic effects occur due to differential coverage. These two scenarios can be visualised in Figure 2-13: action 1 (switch off) corresponds to the first scenario that the metallic surface is fully covered by solid deposits; action 2 (switch on) corresponds to the second scenario of the partially covered metallic surface.



Figure 2-13 Illustration of under-deposit corrosion scenarios

2.4.2.1 In inhibited systems

It will be noted that discussions in this section are mainly based on steels research since they are widely used in the oil and gas transportation industry where solid deposition is an important challenge. Research surrounding titanium pertaining to solid deposition is very limited to the author's knowledge. Research results based on steels can still provide information on understanding the mechanisms associated with titanium corrosion under solid deposits.

UDC is a prominent issue in the pipeline industry where steels are often used in the presence of inhibitors [23, 24, 117-120]. The presence of solid deposits is widely reported to affect inhibitor performance and thus can result in the severe corrosion of pipeline steels. Imidazoline and phosphate ester are effective inhibitors for the corrosion of X65 steel in CO₂-saturated 10% NaCl solution, but they failed to inhibit the corrosion rate of X65 steel when it was under a 10 mm-thick sand deposit layer [121]. Similarly, a generic imidazoline-based inhibitor—imidazoline ($C_3H_6N_2$) is the most commonly used organic inhibitor in oil and gas pipelines—decreased the corrosion rate of X65 steel with 90% efficiency in CO₂-saturated 1 wt.% NaCl aqueous solutions at pH 5 and 25°C, but it failed to reduce the corrosion rate of the steel beneath a 2 cm-thick silica

layer [119]. Thus, an inhibitor that provides good protection when solid deposits are absent does not necessarily have satisfactory performance when solids are present.

The effect of solid deposits is manifested by slowing the mass transport of inhibitors from the bulk solution to the underlying region, or competitively adsorbing the inhibitors. The resultant insufficient inhibitor concentration at the underlying metal surface yields rapid corrosion rates for underlying steels: this is one common manifestation of UDC. Adsorption onto the solid deposits is common for the organic inhibitors since they generally contain specifically designed surface active compounds. Organic compounds containing N, O, P, and/or S (e.g., imidazolium) are often employed as corrosion inhibitors in the pipeline industry [122]. The organic inhibitors usually demonstrate Langmuir type adsorption behaviour, and the extent of adsorption can be determined by the steady state equilibrium of inhibitors in the aqueous phase, on the solids surface, and on the metal surface [23]. The loss of one organic inhibitor (MW 200) was as high as 85% due to adsorption on sand rather than on the metal surface (the initial inhibitor concentration was 10 ppmw and sand concentration was 10% with size of 1 µm) [23]. In the evaluation of four organic compounds on inhibiting UDC, Pandarinathan et al. [122] also found that sand deposits affected the inhibition performance for carbon steel by competitive adsorption onto sand particles. For inorganic species, however, no obvious competitive adsorption onto solid deposits has been reported, and solid deposits are more likely to affect the corrosion process by slowing the mass transfer process of the corrosion species and/or the inhibitors.

2.4.2.2 In uninhibited systems

The barrier effect of solid deposits on the corrosion process will be better understood in the absence of any complications that arise due to corrosion inhibitors. In an uninhibited system, corrosive species and corrosion by-products have to be transported through the deposit layer. When the corrosion rate is controlled by the diffusion of the reactants, it is expected that the corrosion rate under the deposits would be lower than for an uncovered area. In simulated sweet corrosion gas pipeline systems, De Reus *et al.* [23] reported that the corrosion rate of steel decreased from 1.0 to 0.45 mm·yr⁻¹ due to the presence of sand on the specimen. When X65 steel was covered by sand, its corrosion rate was also reduced from approximately 2.6 to 0.4 mm·yr⁻¹ in CO₂-saturated 10 wt.% NaCl solution [121]. In a study of UDC of carbon steel in a CO₂-saturated synthetic Forties brine under sand deposits, Turnbull *et al.* [120] also found a slowed corrosion rate for the steel due to the restricted mass transfer. Huang *et al.* [123] also investigated the internal CO₂ corrosion of X65 pipeline steel under solid deposits, and found that introduction of a deposit layer on the steel surface caused a sudden decrease in the corrosion rate by a factor of 2 to 4, with the corrosion potential increasing by approximately 10–20 mV compared with steel exposed to the bulk solution. Their results suggest that the lower the porosity or the thicker the deposit layer, the lower the resultant corrosion rate [123].

Electrochemical results have characterised the slowed mass transfer due to the presence of solid deposits. Polarisation curves reveal that the presence of sand deposits inhibited both anodic and cathodic processes and resulted in a positive shift in the overall open circuit potential relative to the uncovered condition [23, 120, 123]. Electrochemical impedance spectroscopy (EIS) revealed that solid deposits also resulted in increased solution-side resistance due to electrode surface blockage, which manifests as solution resistance in typical EIS equivalent circuits [124]. Indeed, the denser the deposits, the larger the solution resistance [123].

It is important to notice that, in general, the corrosive environment under deposits may change significantly with time and this may influence UDC damage evolution. pH is recognised as a key parameter that reflects solution chemistry changes and thus influences electrochemical reaction rates and mechanisms [123]. The pH change under deposits has been theoretically predicted based on thermodynamic, kinetic, and transport models, and directly measured in experiments using a specially designed pH probe [123, 125-129]. Han *et al.* [129] developed a mesh-capped surface pH probe and measured the surface pH of mild steel under silica deposits in a CO₂ purged 1% NaCl solution at 25°C. Higher surface pH (5.8–6.3) was consistently observed under deposits than in bulk solutions (pH 4–6). Increasing temperature (*e.g.*, to 80°C) or decreasing deposit porosity made the under deposit–bulk solution pH gap larger, in some cases reaching mildly alkaline surface conditions in acidic bulk solution [129]. A stable passive film forms on the surface of steel in relatively alkaline conditions was related to the limited transport of reacting species due to the deposit layer. In the local region under deposits, protons were consumed by electrochemical reactions, and a lower proton concentration (*i.e.*, higher pH) is expected on the surface as proton transfer from the bulk solution is limited by the deposit layer [123, 129].

The reports above reveal that in uninhibited systems, the solid deposits will not accelerate the corrosion rate of underlying metal, instead, they may slow the mass transfer and slow the corrosion rate. Thus, solid deposition is a more severe problem in systems that require inhibition (through the addition and mass transfer of passivating inhibitors) and accounts for the accelerated UDC attack of the underlying metals in such systems. However, the conclusion above does not always apply to other conditions. For example, active deposits (*e.g.*, sulfur-containing deposits) may participate-in and significantly influence the UDC process [25, 130]. Microorganism-containing deposits may result in severe UDC attack because microbial metabolism may generate substances (*e.g.*, acids) under the deposits.

2.4.3 Galvanic cell generated by solid deposits

The electrical connection between covered and uncovered portions of the same metal can result in the formation of a galvanic cell. In inhibited systems, the combined effect of inhibition and galvanic coupling is reported to be significant in initiating and accelerating the corrosion rate of the solid-covered portion, and becomes an important mechanism of UDC [23, 25, 116, 120, 121, 124].

Huang et al. [119] observed localised corrosion when a generic imidazoline inhibitor failed to inhibit the steel underneath individual sand particles. Neither limited mass transfer nor competitive adsorption of the inhibitor could explain their results. Instead, they found pits beneath individual sand particles that were related to the inability of the inhibitor to protect the steel surface in the crevices immediately beneath individual sand particles. The inhibitor molecules failed to adsorb and protect the steel surface in the crevices, while other more open access areas were inhibited. These pits propagated very quickly due to galvanic effects arising from connection to the bare steel surface exposed to the bulk solution, eventually merged, and caused a high rate of "general" attack underneath the sand deposits. Nyborg and Foss [124] mounted three carbon steel specimens in an apparatus: two were covered by sand and one was not covered. In 10% NaCl solution with CO₂ purging, the galvanic current was negligible. When inhibitor was added, however, a potential difference of approximately 20 mV was observed between the sand covered and uncovered specimens. The galvanic current was measured and galvanic corrosion attack was observed on the sand covered specimen. This galvanic effect on initiating UDC of X65 steel in an inhibited system was investigated by Barker et al. [121]. Four corrosion inhibitors caused an immediate increase in the galvanic current between a portion covered by 10 mm of silica layer and the bare steel. The under-deposit electrode became a net anode and began to corrode more quickly

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than its intrinsic corrosion rate (*i.e.*, when it was not coupled to the bare steel). Turnbull *et al.* [120] used a multi-electrode array consisting of 24 carbon steel electrodes to evaluate two inhibitors' ability to control UDC in a CO₂-saturated synthetic Forties brine. In the absence of inhibitors, the corrosion rate of the electrode under sand was $< 0.1 \text{ mm} \cdot \text{y}^{-1}$ when it was not galvanically coupled to the external bare electrode. After inhibitors were added, the connection to the external large electrode polarised the external electrode to nobler values than the under-deposit steel, that is, the galvanic effect resulting from the potential difference significantly accelerated corrosion of the underlying metal (a peak average corrosion rate of around 4 mm \cdot y⁻¹ was reached after about 1 day). Similar findings were reported for a deposit-covered carbon steel electrode and a bare electrode in CO₂-containing formation water (a strong chloride solution) [25]. In addition, as the area of bare electrode increased relative to the deposit-covered electrode, the galvanic current increased, resulting in accelerated corrosion of the deposit-covered steel. Tan et al. [116] investigated UDC of mild steel and its inhibition by imidazoline. They simulated partially sandcovered steel using a wire beam electrode method. When inhibitor was added to the CO₂-saturated brine solution, the sand-covered area became the corrosion anode and the uncovered area was the cathode, and they linked this separation to UDC initiation. Although increased inhibitor concentration decreased the overall corrosion rate of the wire beam electrode, it enhanced the corrosion rate of the sand-corvered area, *i.e.*, UDC.

In addition to the "differential inhibitor concentration cell" in the inhibited condition, solid deposition also caused a "differential aeration cell": a galvanic cell arising from the O_2 concentration difference between the bare and deposit-covered samples. Tan *et al.* [116] reported that in the absence of inhibitors, when O_2 was introduced to the saturated brine for the partially covered electrode, anodic corrosion attack was concentrated in an area covered by sand, while the

cathodic area that corresponded to the oxygen reduction reaction was distributed primarily outside the sand deposits [116].

The differential aeration cell observed in UDC is highly analogous to another form of localised corrosion, *i.e.*, crevice corrosion. Crevice corrosion is a form of occluded cell corrosion, where mass transport is limited most often in narrow fissures or gaps, restricting free exchange between the localised solution and the bulk solution. UDC can be considered a related phenomenon where the impediment is formed by one or more types of solid deposit (e.g., corrosion products, oxides, dust). Crevice corrosion exhibits an autocatalytic process. The initiation process can be explained by the deoxygenation-acidification theory illustrated by Figure 2-14 [131-137]. The initiation starts from the depletion of oxygen within the crevice. Due to the restricted oxygen mass transfer to the crevice, oxygen cannot replenish sufficiently, and oxygen reduction (cathodic reaction) occurs mainly outside the crevice where oxygen is more accessible. Consequently, inside the crevice, metal dissolution (anodic reaction) is the dominant reaction. The metal cations in the crevice solution hydrolyse and result in local solution acidification. The solution pH drop and Cl⁻ accumulation (to maintain electrical neutrality) lead to an increasingly aggressive solution in the crevice environment, until the "critical crevice solution" is reached, when the passive film breaks down and active corrosion take place [45, 133-135, 138, 139].

Crevice corrosion is one of the most insidious forms of metal failure, occurring in metals and alloys that are highly resistant to uniform corrosion, such as titanium and its alloys [131-133]. UDC shares fundamental characteristics in common with crevice corrosion, and it may display electrochemical behaviour consistent with crevice corrosion and initiated on titanium by the galvanic effect as a differential aeration cell. It appears that this similarity is understudied.



Figure 2-14 Schematic representation of the processes occurring during crevice corrosion of titanium

2.5 Erosion-corrosion

2.5.1 Erosion-corrosion concern of titanium in leaching conditions

Erosion-corrosion is a common problem in a wide range of industrial applications, including oil and gas, chemical processing, mining, hydraulic equipment, and extractive metallurgy, where components (*e.g.*, tubes, pipelines, pumps, valves, and agitators) handle slurries during normal operation [140, 141]. In hydrometallurgy, leaching process vessels or autoclaves, and their associated piping, pumps, agitators and other ancillary equipment contain or encounter high pressure and high temperature slurries. Solid mineral particles in the size range of 10–400 µm are suspended in aggressive leaching solutions to enhance metallic ion extraction [6]. Erosion-corrosion attack of these autoclave parts can be a safety concern.

Erosion-corrosion is a combined mechanism: electrochemical corrosion in aggressive solutions and mechanical wear from solid impingement occur simultaneously [27]. Investigations on a wide range of materials have shown that the material loss rates can be significantly increased when mechanical attrition contributes to corrosion, leading to premature failure of processing equipment due to the mechanical-electrochemical interactions [142-146]. The interaction between

electrochemical corrosion and mechanical erosion process may be self-reinforcing, enabling the overall erosion-corrosion rate to be greater than the simple sum of the rates from each process acting separately—there are synergistic effects between the two [140, 141, 147, 148]. That is, after the surface of the protective passive film is impacted in the erosion-corrosion conditions, the reaction between the activated area and corrosive media occurs more easily. Similarly, after flow-induced corrosion, the surface of the passive film may become porous and brittle, making material removal by the slurry impact easier and more effective. The synergistic effects on the erosion-corrosion rate of materials in erosion-corrosion conditions is represented in Equation 2-2 [148]:

$$E_{EC} = E_E + E_C + E_{S-E} + E_{S-C}$$
 Equation 2-2

where, E_{EC} is the erosion-corrosion rate; E_E is the erosive wear rate; E_C is the flow-induced corrosion rate; E_{S-E} and E_{S-C} are the synergistic effects of erosive wear on the flow-induced corrosion rate and flow-induced corrosion on the erosive wear rate, respectively.

As discussed in Section 2.3, the corrosion resistance of titanium is attributed to the extremely inert passive oxide film that spontaneously forms on its surface. The oxide film serves as a barrier to separate the metal from the corrosive environment and protects the substrate metal. The corrosion behaviour of titanium has been extensively investigated and its high corrosion resistance is widely acknowledged in stagnant simulated leaching solutions [10, 16, 50, 52]. However, the high stability of titanium exhibited in aggressive, but stagnant solutions does not guarantee satisfactory performance in dynamic slurry conditions; especially those that combine strong acid, solid particles in suspension, and high-speed circulating fluids [28, 143, 146]. These conditions may destabilise the titanium oxide film and accelerate material loss by the combined erosion-corrosion mechanism. Previous work on passive metals, such as stainless steels and nickel based alloys, has shown that material loss rates can be significantly accelerated when the passive

film on the material is mechanically breached, causing local damage to or removal of the passive film [28, 143]. This can drive up maintenance costs and cause production delays. For example, four autoclaves at an agitated leaching operation at a Canadian mining company operating at an acid concentration of approximately 35 g·L⁻¹ at approximately 220°C must be shut down twice per year to replace the worn titanium agitator blades and reconstruct corroded internal walls. Erosion-corrosion is a top concern in the leaching plants. This maintenance and replacement results in production delays and substantial financial costs. In some high temperature autoclave environments, the combination of particle erosion and impact on titanium surfaces has led to very dangerous fires in process equipment containing upwards of 500 m³ of slurry at nearly 2700 kPa [61]. Such fires have been seen in titanium vent lines, valves, weirs, and other equipment where the combination of particle impact and high oxygen partial pressure can be catastrophic.

2.5.2 Titanium erosion-corrosion investigation

There are reports of erosion-corrosion of titanium in other industries. For example, abnormal wall thinning of titanium tubes due to erosion and cavitation corrosion, and their synergetic effects, was observed in a nuclear power plant in China [146]. Based on experimental results measured using a jet-in-slit rig, severe erosion-corrosion of titanium was also predicted [28, 144, 148]. Tu [148] reported that the erosion-corrosion rate of α -Ti could reach 9.5 mg·h⁻¹ in 3.5% NaCl containing 100 g·L⁻¹ solids slurry at room temperature when the jet velocity increased to 12.8 m·s⁻¹. Neville and McDougall [28, 144] reported that the total weight loss rate of CP-Ti over 8 h reached 3.1 mg·h⁻¹ in 3.5% NaCl solution with 1 g·L⁻¹ solids slurry at 18°C at a velocity of 17 m·s⁻¹. The weight loss rate of titanium further increased significantly as the slurry velocity or the silica loading increased [28, 144, 148]. The weight loss component due to erosive wear is generally found to be dominant compared with pure electrochemical corrosion, and it becomes more

dominant as slurry velocity increases. Neville and McDougall [144] reported that erosive wear could account for 80% of metal loss in their experiment, and Tu [148] stated that it increased from 60 to almost 90% as slurry velocity increased from 4.8 to $12.8 \text{ m} \cdot \text{s}^{-1}$.

In contrast, Bermúdez *et al.* [142] conducted erosion-corrosion tests of CP-Ti in a glass vessel containing 10 wt% HCl in the presence of α -Al₂O₃ particles agitated at 1000 RPM for 168 h at room temperature using a magnetic stirrer. The weight loss due to erosion-corrosion was very small, and the erosion-corrosion attack was only confined to the oxide scale based on morphological observations, *i.e.*, the base metal was unaffected [142]. The excellent corrosion resistance of titanium to fluid impingement attack was confirmed by other researchers [149], who found titanium showed no measurable weight loss after either sea-spray tests or sea water jetting containing 2.4% by volume of entrained air. *In-situ* studies on the effects of sea-water velocity on titanium found that it was unaffected by seawater flow over test durations ranging from 30 days to 1 year [150, 151].

2.5.3 Erosion-corrosion investigation methods

The discrepant views on the erosion-corrosion resistance of titanium may be attributed to the various environmental parameters that influence its degradation rate [140, 143, 147, 152, 153]. However, one important and consistent observation is that, for a given material and environmental condition, erosion-corrosion rates generated from jet impingement tests are always orders of magnitude larger than those acquired from other test methods, *i.e.*, rotating disc tests, rotating spindle tests, or multivelocity jet tests [154]. That is because the thinner velocity boundary layer on the metal surface, the direct projection of all solids towards the metal surface, and the hydromechanical effects that are observed in a jet impingement test all result in increased corrosion rates [154]. Furthermore, the different corrosion states and wear patterns between the central

region, that is frequently impinged, and the region farther out from this central region, where impact occurs less frequently, are always observed and this complicates the analysis of jet impingement tests [28]. α -Ti jet impingement studies also show that the angle of a jet nozzle to the specimen surface makes a significant difference in the test results [148, 155]. Thus, the experimental results obtained from jet impingement tests may not represent an actual scenario. To increase the reliability of such experimental data for a given industrial application, the test should be conducted to mimic the operational situation.

A readily accessible measurement for assessing material performance under liquid-solid erosion-corrosion conditions is weight loss [28, 140, 141, 144, 147, 148]. Weight loss provides direct and intuitive results that reflect the effects of erosion condition on degrading materials, the dependence of erosion rate on the erosion parameters, and the material intrinsic properties. However, the weight loss method is slow and cumbersome: although it is suitable to short-term investigation of materials that are sensitive to erosion, long-term studies tend to produce large experimental errors.

2.5.3.1 Electrochemical techniques and electrochemical noise

By comparison, electrochemical techniques are highly sensitive and efficient from a testing perspective, and, thus, may be advantageous for characterising the erosion-corrosion process of refractory metals. During slurry erosion-corrosion, monitoring the state of the oxide film, which warrants the integrity of titanium application, is important and significant. The fracture or breakdown of the protective passive film by the mechanical perturbation of small abrading particles generates transient corrosion phenomena, which can be recorded as electrochemical quantities, such as current noise or potential noise. It has been established that these current transients are the result of pit nucleation, and they are related to the repassivation of the freshly bared metal surface caused by localised instability and breakdown [133, 156-162]. Research on stainless steels suggests metastable pitting in the form of current transients at potentials below the pitting potential in chloride solutions. These current transients precede the formation of stable pits and reveal information on the early stages of pitting corrosion [133, 156-162]. Current transients are also widely observed on titanium at potentials well below its pitting potential [163, 164]. Burstein and Souto [163] reported the transient microscopic breakdown of passive titanium in acidic chloride solutions. Sharp anodic current spikes were observed at potentials well below the pitting potential, and a few propagated as metastable pits before they too, repassivated. In bromate solutions, current transients were observed at potential more than 1 V lower than the pitting potential [164]. The current transient activity (occurrence frequency) and transient size (height and lifetime) were qualitatively found to depend mainly on the bromate concentration and the purity of titanium, which are also the major factors influencing the stable pitting corrosion of titanium [164]. The breakdown of passivity may happen in a highly abrasive, at high acidic environment, or under high applied voltages [164]. Current transients, however, can occur more readily, and their occurrence indicates that microscopic fracture events can take place in the region of stable passivity. Thus, investigations of these current transients may be of diagnostic significance for film instability and macroscopic failure prediction.

Among the various electrochemical techniques, electrochemical noise (EN) has shown promise in monitoring surface state activity and reliably indicating localised corrosion. EN, recording the stochastic fluctuations of current and potential occurring at the electrode/solution interface [156, 157, 165-170], appears to be appropriate to detect the kinetics of the fracture and repair process of passive films in slurries. EN has been applied to characterise the erosioncorrosion process, and the kinetics of the breakdown and healing processes of passive films continuously abraded by impinging solid particles were characterised *via* EN transients [171-173].

EN was first leveraged for corrosion studies using potentiostatic or galvanostatic methods, but such measurements do not directly measure the corrosion rate. In the recent years, a group from Manchester, UK, proposed a new EN technique using two identical working electrodes (WEs) of the same material, same size, and same surface preparation, connected through a zeroresistance ammeter (ZRA), so as to have both WEs at the corrosion potential [174]. The current noise is measured by the ZRA, while the potential noise is measured with respect to a third electrode, either a true reference electrode (RE) or an electrode identical to the WEs. The state-ofthe-art methods of data interpretation based on this cell are rapidly developing [175-180]. A quantitative relationship between the corrosion rate and the fluctuation of both potential and current was found to exist [177, 179]. This cell also shows great potential to be a diagnostic tool to distinguish localised corrosion, possibly in real time, and perhaps also between various kinds of localised corrosion, such as pitting corrosion, crevice corrosion, intergranular corrosion, etc., on the basis of shape and amplitude of the current fluctuations [176, 177, 179, 181]. This information, however, cannot be provided by the classical deterministic techniques (linear polarisation, EIS, etc.), which average the signals in time. In addition, EN measurements based on ZRA mode demonstrate a suitability to *in situ* corrosion monitoring. EN data are collected from the freely corroding system without disturbing the corrosion process, while conventional electrochemical methods normally need to apply an external polarisation to the sample, which will introduce unavoidable changes in its surface chemistry. Applying in situ non-interference corrosion monitoring is important for the economical and safe operation of industrial plants. These advantages explain the increasing use of EN in corrosion investigations.
The problems associated with EN measurements can be divided into those concerning the detection of the noise signal above all undesirable influences, such as fluctuations induced by external sources and the intrinsic noise of the instrumentation, and the problems relative to the analysis of the EN measurements [180]. External sources of noise, such as mechanical vibrations and electromagnetic interference, have to be minimized, particularly if the EN level is low. Electromagnetic interference is often picked up from the alternating current (AC) power supplies, and it may also come from the switching on and off of electric equipment in the experiment or in the environment [180]. In practice, interference reduction can be challenging but practical solutions should be considered [182]. The instrumental noise in EN measurements, such as from a voltage amplifier (VA), the controlling device (the potentiostat and ZRA), has to be considered too. The noise of the RE can also be significant [183]. Because of the low amplitude of the EN signal and the difficulty in distinguishing it from the instrumental noise, it is important to use low-noise, highly sensitive instrumentation (amplifiers and ZRA), especially at frequencies above 1 Hz or at all frequencies for coated or passive electrodes where the current noise may be in the nanoampere range.

The measurement problems can be caused by nonstationary signals, instrumental noise, or aliasing in the analog-to-digital (A/D) conversion. The results obtained by a large number of groups in a round-robin experiment on EN measurement, showed significant deviations between participants because of these evident measurement problems [184]. Stationarity is a required property of the EN signal for second-order statistics to be valid. Therefore, drifting signals, that is, signals for which the direct current (DC) baseline appears to steadily change, have to be conditioned before any statistical calculation. These can be done on the analog signal by inserting an analog HP filter in the measurement channel before data

acquisition. In addition, the effect of discontinuities introduced by the amplitude difference between the first and the last data points also should be eliminated. A way to eliminate this is to multiply the time record by a "window", and this reduces the leakage of the low frequencies to the higher frequencies in the calculated PSD. Among several windows that have been developed for signal analysis, the Hann window is the one most commonly used [180].

Aliasing is another common problem. According to Nyquist theory, when sampling at frequency f_s , the maximum frequency that can be correctly analysed is $f_{max} = f_s/2$. Therefore, if the analog signal contains components at frequencies higher than $f_s/2$, these components will appear at frequencies lower than $f_s/2$. To avoid this phenomenon, called aliasing, all signal components at frequencies above $f_s/2$ have to be eliminated before the A/D conversion by using a low-pass analog filter. Without this filter, the signal power at high frequencies of more than $f_s/2$ is aliased at lower frequencies, therefore, all frequency-independent spectra will have a higher amplitude in both the frequency domain and digital time domain of the random signal [180]. In order to obtain valid EN data and take advantage of this technique, it is necessary to address and solve these problems.

Chapter 3: Objectives

3.1 Effects of solid deposits on the corrosion behaviour of titanium in simulated leaching conditions (Chapter 5)

Based on the literature review, it is clear that the corrosion behaviour of titanium in leaching conditions and in the presence of solid particles is very complex, involving multiple scenarios and processes. So far, the data about the effect of solid deposits on the corrosion process are mainly based on the steels, which are widely used in the oil and gas transportation industry where solid deposition is an important challenge. For titanium, condition-relevant studies have not yet been reported and the effects of solid deposits on its corrosion behaviour are still largely unknown. The significant differences between titanium and steel corrosion make the data based on steels irrelevant for titanium. Therefore, because titanium is used in hydrometallurgical processes where solids are present, an investigation of its response to deposits and particle-induced erosion-corrosion is required.

It's worth noting that titanium may show significantly different corrosion behaviour when oxidising species, *i.e.*, Fe(III), Cu(II) and/or O₂, are present. In the sulfuric acid-chloride leaching system in the absence of oxidising species, titanium is expected to actively corrode, while in the presence of the oxidising species, titanium will be passive.

Therefore, for the first objective to **investigate the effects of solid deposits on the corrosion behaviour of titanium in simulated leaching conditions,** the combination of solid deposition and the different leaching solutions that titanium may encounter divides the required investigation into two basic sets of conditions:

a. effect of solid deposits on the corrosion behaviour of Ti-2 in the sulfuric acid-chloride solution in the absence of oxidising species

 effect of solid deposits on the corrosion behaviour of Ti-2 in the simulated leaching solution in the presence of oxidising species

Condition (a) is a simpler system. The investigation of condition (a) aims to explore the effect of solid deposits on the corrosion process, that is, how the solid deposits influence the corrosion behaviour of underlying titanium. The properties of the solid deposit layer, such as the deposit particle size, deposit type, and deposit layer thickness, *etc.*, will be considered.

Condition (b) involves oxidising species, which strongly affect the corrosion state (active *vs.* passive) and corrosion resistance of titanium. Therefore, the two scenarios relating to the initial state of titanium, *i.e.*, active corrosion and passive state, corresponding to its sufficient inhibition and insufficient inhibition by the oxidising species, respectively, prior to solid deposition, will be investigated. Different from condition (a), condition (b) will then focus on the interaction between titanium and these oxidising species when solids are present. Therefore, the inhibition performance of individual passivating species on titanium in the solid deposition conditions will be evaluated by using titanium samples with an initially active state. For the initially passive titanium, how the solid deposits affect its stability/passive corrosion rate is also interesting. Therefore, the parameter of temperature is introduced since titanium's stability is closely related to the temperature. A comparison of corrosion rate between the solid deposit covered titanium and bare titanium will be conducted as a function of temperature. This series of studies will allow for an answer to the following questions:

- 1. Can active titanium be passivated through the action of oxidising agents when solids exist?
- 2. Can passive titanium be activated, potentially leading to catastrophic corrosion, when deposits exist?

In view of these multi-faceted corrosion scenarios, Figure 3-1 shows a schematic of the experimental design, demonstrating the different approaches and test solutions that are used to address this particular objective.



Figure 3-1 Schematic of the experimental design for the investigation of the effects of solid deposits on the corrosion behaviour of titanium in simulated leaching conditions (Chapter 5)

3.2 Electrochemical investigation of the catalytic effect of titanium hydrides on the HER and hydrides phase identification (Chapter 6)

Titanium corrosion in acidic conditions results in titanium hydride formation. Titanium hydrides are closely related to stress-corrosion cracking (SCC) and hydrogen-induced cracking (HIC), thus, their presence is a major concern for material integrity. Recent reports suggest that titanium hydrides may catalyse the hydrogen evolution reaction (HER). This property is of vital significance since it will accelerate the production of titanium hydrides that form along with the

HER, possibly resulting degradation and early failure from cracking phenomena. However, the catalytic effect of titanium hydrides on the HER is poorly understood. Thus, another objective of this project is to electrochemically investigate the catalytic effect of titanium hydrides on the HER and characterise the hydride phases that may be present.

In order to obtain a non-trivial layer thickness of titanium hydride(s), titanium hydrides will be genenrated by electrolysis in the sulfuric acid-chloride solution, consistent with the acidic leaching system. Various electrochemical techniques will be applied to investigate the electrochemical effect of titanium hydrides on the HER, by evaluating the change of corrosion behaviour of titanium due to the presence of hydrides (*i.e.*, corrosion potential, corrosion resistance, anodic polarisation, and cathodic polarisation). At last, the generated titanium hydrides will be characterised for a better understanding of their compositions and phases. The two important parameters for the generation of titanium hydrides—the magnitude of cathodic polarisation (*i.e.*, cathodic current density) and the duration of polarisation—will also be considered.

Figure 3-2 is the schematic of the experimental design for the electrochemical investigation and phase identification of titanium hydrides.



Figure 3-2 Schematic of the experimental design for the electrochemical investigation and phase identification of titanium hydrides (Chapter 6)

3.3 Effect of Fe(III) and Cu(II) species on titanium passivation in sulfuric acid-chloride solutions (Chapter 7)

Fe(III) and Cu(II) species are ubiquitously present in acidic hydrometallurgical leaching solutions. Previous research has shown that they are effective species for the passivation of titanium, and that their presence is vital to maintain the passivation and stability of titanium in aggressive acidic solutions. One frequently observed phenomenon in passivation studies of titanium is that there exists a critical concentration of the passivating inhibiting species that is necessary to promote the passivation. In the aggressive sulfuric acid-chloride systems for copper sulfide leaching, the ability of Fe(III) and Cu(II) species to passivate titanium is known, however, neither the quantitative effectiveness for inhibition nor the mechanism related to passivation are clear. Therefore, the third objective of this project is to **investigate the effect of Fe(III) and Cu(II) species on the passivation of titanium in the sulfuric acid-chloride solutions**.

It's worth noting that applications of titanium in hydrometallurgical extraction involve the use of the material in pressure vessels that operate at a generally higher temperature range (90–250°C). However, current studies do not account for the effects of temperature on inhibitor

effectiveness. Since temperature is an important and varying parameter in industrial leaching processes, and it can significantly influence the kinetics of reactions, it is important and necessary to take temperature into consideration in any titanium passivation study.

Thus, the first step of this work is to determine the critical concentration of Fe(III) and Cu(II), respectively, on the passivation of titanium in the sulfuric acid-chloride solutions at temperatures from 30 to 80°C. Based on the results, the mechanism of titanium passivation by these oxidising species will be explored; the effect of temperature will be analysed, and the effectiveness of Fe(III) and Cu(II) toward titanium passivation will be compared. The results will provide practical data for the corrosion prediction and protection of titanium vessels and equipment in the hydrometallurgical industry.

Figure 3-2 is the schematic of experimental design for the investigation about the effect of Fe(III) and Cu(II) species on the passivation of titanium in the acidic leaching solutions.





3.4 Localised instability of titanium during its erosion-corrosion in simulated acidic hydrometallurgical slurries (Chapter 8)

In hydrometallurgical leaching processes, solid minerals are mixed with aggressive leaching solution and are vigorously agitated as slurries in titanium-lined autoclaves. The solid mineral particles mechanically impact the autoclave walls and cause erosion-corrosion of Ti-liners and associated agitators, pumps, and piping. Erosion-corrosion is a top concern for autoclaves in industry. Up to now, the data related to the erosion-corrosion behaviour of titanium and its alloys in hydrometallurgical conditions are not publicly available. Existing studies about erosioncorrosion of titanium are in other conditions, commonly in reducing acid solutions without dissolved metals or brine solutions, which are quite different from the high acidity, high oxidisation hydrometallurgical leaching solutions, and the obtained data cannot be representative of what would be expected from leaching conditions.

Titanium erosion-corrosion is highly dependent on the passive oxide film formed on the surface, which serves as a barrier to separate the metal from the corrosive environment and protects the substrate metal. The stability of this oxide film accounts for the high corrosion and erosion-corrosion resistance of titanium. Thus, understanding the conditions that undermine this film layer is of vital significance for safe use of titanium equipment. Localised characterisation associated with the micro-fracture of this film will provide important information about erosion-corrosion attack in its early stages. Therefore, an effort of this work will be monitoring the activity of the oxide film by electrochemical noise technique, thus, exploring the mechanism of erosion-corrosion of titanium.

Therefore, the last objective of this project is to characterise the localised instability of titanium during its erosion-corrosion in the simulated leaching slurries.

To increase the reliability of experimental data, the test will be conducted in the glass cell equipped with an overhead agitator to mimic the operational situation of the copper sulfide leaching conditions. Inert silica particles will be used to model the impact of slurries in the leaching solutions, and the erosion-corrosion results in the slurry conditions will be compared with those in static and dynamic solutions, to demonstrate the effect of particle impacts. Effect of temperature and slurry speed on the erosion-corrosion behaviour of titanium will also be investigated.

Figure 3-4 is the schematic of experimental design for the investigation about the erosioncorrosion of titanium in the simulated leaching slurries.





the simulated leaching slurries (Chapter 8)

Chapter 4: Approach and methods

4.1 Materials and electrodes

Commercially pure titanium Grade 2 (Ti-2) sheets and bar (McMaster-Carr) were used to fabricate working electrodes (WE). All samples were cut directly from Ti-2 materials and tested in the as-received conditions. Three types of Ti-2 samples were prepared: disc, flat square, and erosion-corrosion samples (Table 4-1).

Table 4-1 Chemical composition of Ti-2 materials (wt.%, Ti balanced) used for sample fabrication and

Ti-2	С	N	0	Fe	Н	Thickness/mm	Samples	Chapter
Thick sheet	0.01	0.008	0.12	0.14	21ppm	3.2	Disc	5,6,7
Thin sheet	0.01	0.008	0.12	0.14	21ppm	0.51	Flat square	6
Ti-2 bar	0.006	0.008	0.11	0.08	20ppm	3.2	Erosion-corrosion	7

Chapters in which samples are used

Disc samples were used in tests outlined in Chapters 5–7. They were 15.9 mm in diameter and cut from the thick sheet. A copper wire was connected to the back of each disc with conductive silver epoxy (MG Chemicals 8331), and discs were mounted in a high-temperature epoxy resin (Duralco 4460) with one flat surface (1.98 cm²) exposed. In the study of solid deposition effects in Chapter 5, the disc sample was inserted into a piece of polytetrafluoroethylene (PTFE) tube with the bottom contact rim sealed by silicone. The PTFE tube created a receptacle for the solid deposits and enabled modification of deposit thickness and type (Figure 4-1). Similar methods have been used to investigate X65, mild, and carbon steel UDC in CO₂-saturated brine with sand receptacles created by pistons [24], rubber O rings [116], or PTFE cups [185].



Figure 4-1 Schematic of working electrode to evaluate effects of solid deposition on the corrosion behaviour of Ti-2 in simulated leaching solutions

Three types of laboratory-grade silica particles with different particle size ranges (Purity (SiO₂) = 99.8%, Mohs hardness 7, specific gravity 2.65, American Foundry Society (AFS) acid demand value (ADE, at pH 7) < 1.0) and calcium sulfate dihydrate (CaSO₄·2H₂O powder, 99%) purity, Alfa Aesar) were used as inert deposits. The morphology and size distribution of the silica particle sample 1(S1) are shown in Figure 4-2(a) and Figure 4-2(b), respectively. They are semiround, with very few sharp corners (S1, $d_{0.5}$: 425 µm, specific surface area: 0.017 m²·g⁻¹, VWR). The deposits characterisation for the silica particle sample 2 (S2, $d_{0.5}$: 193 µm, specific surface area: 0.039 m²·g⁻¹, VWR) and silica particle sample 3 (S3, $d_{0.5}$: 20.4 µm, specific surface area: 0.99 m²·g⁻¹, VWR) was shown in Figure 4-3 and Figure 4-4, respectively. Calcium sulfate dihydrate was used to represent gypsum scales that are known to occur in many process vessels. In view of the high-acidity, high-sulfate system under investigation, the silica and gypsum solubility was considered to be negligible: they were considered inert [186, 187]. The test solution pH was monitored and was not obviously affected by their presence. As discussed in Section 2.4.1, the deposit composition in hydrometallurgy is very complex, and varies widely with the nature of the input ores, process technologies and conditions. The inert deposits used here are not truly

representative of industrial deposits, but they are appropriate to start investigations into the complicated corrosion issues at interest here.

The solid particles were introduced through a funnel to the desired layer thickness into the PTFE receptacle, which was attached to the bare titanium sample (Figure 4-1), and the deposit's free surface was smoothened using a spatula. No added external pressure/treatment was applied, that is, the solid deposits were loosely and naturally packed. The solid deposits were then wetted by the test solution and the solid deposit-covered working electrode was immediately introduced to the test cell. For the deposits of S3 and gypsum, a quick stir with a spatula was required to thoroughly mix the deposits and the test solution. The solid deposit-covered samples were then stabilised in the test solution until reaching steady state and in preparation for the subsequent test. After an experiment, the wet deposits adhered to the PTFE receptacle and were not inclined to pour out; especially for S3 and gypsum, where removal from the receptacle became more difficult and always required scooping-out using a spatula.



Figure 4-2 (a) SEM micrograph and (b) size distribution of silica particle sample 1 (S1)



Figure 4-3 (a) SEM micrograph and (b) size distribution of silica particle sample 2 (S2)





The flat square samples were cut from the thin Ti-2 sheet and were 15×15 mm in dimension. They were used to generate titanium hydrides for phase characterisation.

The erosion-corrosion sample was cut from the Ti-2 bar and had the dimensions of $2.54 \times 1.27 \times 0.58$ cm. One 1.27×0.58 mm surface was drilled and taped to UNC 4-40 to enable attachment of a stainless-steel threaded rod, which was used for the potentiostat connection and insulated from the test solution *via* a PTFE sample holder. The exposed surface area of the WE was 10.13 cm². The schematic diagram for the erosion-corrosion WE and its connector is shown in Figure 4-5.



Figure 4-5 Schematic diagram of erosion-corrosion sample and its connector

Before the experiments, all samples were successively abraded up to 600 grit SiC paper, rinsed with deionised water (DI), and immediately connected to the sample holder or installed in test cells to maintain a fresh surface to the maximum extent.

4.2 Solutions

As noted above, the CESL process for medium-temperature copper sulfide leaching typically contain 20–55 g·L⁻¹ sulfuric acid, 8–12 g·L⁻¹ Cl⁻, 10–15 g·L⁻¹ Cu(II), and less than 1 g·L⁻¹ Fe(III) [10, 106]. In this work, a simulated leaching solution was used: 30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻ + 15 g·L⁻¹ Cu(II) + 1 g·L⁻¹ Fe(III), bubbled with O₂ [29]. It consists of two parts: the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) and three passivating species with different concentrations, *i.e.*, Fe (III) (1 g·L⁻¹), Cu(II) (15 g·L⁻¹) and O₂ (O₂ concentration of bubbled solutions was measured to be approximately 5.5 mg·L⁻¹ at 50°C).

For the effects of solid deposition on the corrosion behaviour of Ti-2 in simulated leaching solutions (Chapter 5): blank solution, concentrated leaching solution, concentrated cupric ion solution, and concentrated ferric ion solution were prepared as shown in Table 4-2. The blank solution refers to the absence of passivating species (Cu(II), Fe(III)) and was de-oxygenated by

bubbling with 99.9% N_2 for at least 30 min. (to remove O_2 in solution). The concentrated leaching solution, concentrated cupric ion solution, and concentrated ferric ion solution were prepared by dissolving ferric and/or cupric ions into the blank solution, and they were all deoxygenated by bubbled with N_2 . The concentrated leaching solution was used to adjust the blank solution to the simulated leaching solution (supplemented with O_2 bubbling). The concentrated cupric ion and concentrated ferric ion solutions were used to adjust the Fe(III) and Cu(II) concentration of the test solution, respectively.

Solutions	Composition				
Blank	$30 \ g \cdot L^{-1} \ H_2 SO_4 + 12 \ g \cdot L^{-1} \ Cl^- + N_2 \ bubbling$				
Concentrated leaching	60 g \cdot L ⁻¹ Cu(II) + 4 g \cdot L ⁻¹ Fe(III) + blank solution				
Concentrated cupric ion	60 g·L ^{-1} Cu(II) + blank solution				
Concentrated ferric ion	4 g·L ^{-1} Fe(III) + blank solution				

Table 4-2 Solutions used to investigate UDC of Ti-2 in simulated leaching solutions

For the electrochemical investigation and characterisation of titanium hydrides (Chapter 6): 30 g·L⁻¹ sulfuric acid solution was used. The acid solution was selected as it favored the formation of hydrides and its acid concentration was consistent with the simulated leaching solution. Solutions were deoxygenated by bubbling with 99.9% N₂ for at least 30 min. before testing; N₂ bubbling was maintained during the entire experiment at a constant flow rate.

For the effect of Fe(III) and Cu(II) on the passivation of Ti-2 (Chapter 7): in addition to the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻), a 0.15 M (8.4 g·L⁻¹) Fe(III) solution and a 0.075 M (4.8 g·L⁻¹) Cu(II) solution were prepared by dissolving ferric sulfate or cupric sulfate into blank solution. These solutions were used to adjust the Fe(III) and Cu(II) concentration of the test solution, when varying concentrations of these elements was required. Solutions were deoxygenated as aforementioned.

For assessment of the localised instability of titanium during its erosion-corrosion in acidic hydrometallurgical leaching slurries (Chapter 8): the simulated leaching solution ($30 \text{ g} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ + 12 g·L⁻¹ Cl⁻ + 15 g·L⁻¹ Cu(II) + 1 g·L⁻¹ Fe(III), bubbled with O₂) was used.

DI water, sulfuric acid (H₂SO₄, BDH, ACS 95–98%), sodium chloride (NaCl, Cryst./Certified ACS), cupric sulfate (CuSO₄·5H₂O, Cryst./Certified ACS) and ferric sulfate (Fe₂(SO₄)₃·5H₂O, 97%, Acros) were used to prepare experimental solutions. The temperature of the test solutions was controlled at 50–95°C by circulating water from a Cole-Parmer Polystat Heated Circulator with an accuracy of \pm 1°C. These temperatures are near the low end of the range used in hydrometallurgical processes (copper leaching, for example, takes place at a wide temperature range from room temperature up to 230°C [6, 188, 189].) The obtained results provide important data to inform future studies at higher temperatures.

4.3 Experimental procedures

4.3.1 Effects of solid deposition on corrosion behaviour of Ti-2 in simulated leaching solutions

4.3.1.1 Deposit-covered Ti-2 in the blank solutions

All Ti-2 samples were first introduced to the blank solution to eliminate the effect of the naturally formed oxide film on the surface and obtain a consistent surface state—this is referred to as an "activation process". After the completion of activation process, one of four types of solid deposit (S1, S2, S3, and gypsum) was placed on top of the samples to a thickness of 2.5 cm to simulate a solid deposition scenario. The sample's open circuit potential (OCP) was monitored until a stable corrosion potential, E_{corr} , was obtained. Then, the electrochemical impedance

spectroscopy (EIS), linear polarisation resistance (LPR), and potentiodynamic polarisation (PD) were sequentially measured (OCP measurement for a duration of 10 min. was done in between each of these test methods). EIS was conducted at E_{corr} after the sample became stable, as noted above. The perturbation voltage amplitude of the EIS was 10 mV over the frequency range from 10 kHz to 10 mHz with 10 points per decade sampled. LPR was scanned from -0.015 to +0.015 V vs. E_{corr} at a rate of 10 mV/min. The PD was scanned from -0.3 to +0.5 V vs. E_{corr} at a rate of 0.5 mV/s. The same tests were also conducted on a control sample that was not covered by solid deposits but exposed to the same bulk solution. Results from this control test were used to demonstrate the effects of deposit layers.

4.3.1.2 Under deposit passivation of active Ti-2 exposed to simulated leaching solutions

Two cases pertaining to the initial state of Ti-2 prior to solid deposition in the leaching solution were investigated. The first case, described in this subsection, pertains to solid deposition under conditions of insufficient inhibition, that is, solid deposition prior to inhibitors addition. This represents a worst-case scenario because the Ti-2 is not adequately passivated prior to being exposed to the corrosive environment. In effect, this is a passivation test—how effectively is Ti-2 passivated under a deposit? Ti-2 samples covered by the four different types of solid deposits with varying layer thickness were first activated in the deoxygenated blank solution, and their potential was monitored for up to 19 h as the test solution was adjusted to the simulated leaching solution (by adding concentrated leaching solution and changing from N₂ to O₂ bubbling). This procedure is schematically shown in Figure 4-6.



Figure 4-6 Experimental procedure to evaluate the UDC of Ti-2 in simulated leaching solution at 50°C

To evaluate the inhibition performance of each passivating species present in the leaching solution (i.e., Cu(II), Fe(III) and O₂) on solid-covered Ti, the electrochemical response of S1covered (2.5 cm thickness) Ti-2 in the presence of each individual passivating species, consistent with their in-service concentration in the simulated leaching solution was monitored. After S1covered Ti-2 was activated in 300 mL blank solution (30 $g \cdot L^{-1} H_2SO_4 + 12 g \cdot L^{-1} Cl^{-}$), 100 mL of concentrated cupric ion solution (60 g \cdot L⁻¹ Cu(II) + blank solution, Table 4-2) was introduced. The resulting solution was a Cu(II)-exclusive leaching solution: 15 $g \cdot L^{-1}$ Cu(II) + 30 $g \cdot L^{-1}$ H₂SO₄ + 12 g·L⁻¹ Cl⁻—the effect of Fe(III) and O₂ was eliminated. Similarly, when 100 mL concentrated ferric ion solution (4 $g \cdot L^{-1}$ Fe(III) + blank solution, Table 4-2) was introduced to 300 mL of the blank solution, the resulting solution was a Fe(III)-exclusive leaching solution: $1 \text{ g} \cdot \text{L}^{-1}$ Fe(III) + 30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻; when O₂ bubbling was introduced into the blank solution, the resulting solution was an O₂-exclusive leaching solution: 5.5 mg·L⁻¹ O₂ + 30 g·L⁻¹ H₂SO₄ + 12 $g \cdot L^{-1}$ Cl⁻. This procedure is illustrated as Test I in Figure 4-7. The corrosion behaviour of the control samples, which were not covered by solid deposits and represented the corrosion behaviour of titanium in the bulk solution, were also monitored for the same conditions.

Considering the concentration differences of the three types of passivating species in the simulated leaching solution, the effects of individual passivating species at comparable

concentrations on UDC inhibition were also evaluated. That is, 5.5 mg·L⁻¹ Cu(II) and Fe(III) separately, consistent with the O₂ concentration in the simulated leaching solution; $1 \text{ g} \cdot \text{L}^{-1}$ Cu(II), consistent with the Fe(III) concentration in the simulated leaching solution; $15 \text{ g} \cdot \text{L}^{-1}$ Fe(III), consistent with the Cu(II) concentration in the leaching solution. Since experiments were done at atmospheric pressure, it was impossible to obtain O₂ concentration of either 1 g·L⁻¹ or 15 g·L⁻¹ for the latter two cases. This testing procedure is illustrated as Test II in Figure 4-7.



Figure 4-7 Experimental procedure to evaluate the inhibition performance of individual passivating species at 50°C during the UDC of Ti-2

4.3.1.3 Under-deposit corrosion of passive Ti-2 in simulated leaching solutions

The second UDC case of interest is a scenario where solid deposition on titanium occurs in the presence of sufficient inhibitor concentration at bare surfaces. Ti-2 samples covered by S3 (2.5–6 cm), which were saturated with the simulated leaching solution before deposition on the sample surface, were stabilised in the leaching solution, and EIS and LPR tests were conducted as temperature was incrementally increased from 50 to 80°C (24 h per 10°C). PD was also conducted at the end of the test at 80°C. The measurement procedures were described as in Section 4.3.1.1. A control sample was also tested as a reference.

4.3.2 Electrochemical investigation of the titanium hydrides

Electrochemical investigation of titanium hydrides was conducted in a 1-L cell with a three-electrode configuration. Galvanostatic polarisation was applied to generate titanium hydrides: a cathodic current density in the range of $0.1-1 \text{ mA} \cdot \text{cm}^{-2}$ was applied on the disc sample for up to 60 h. To eliminate the effect of natural oxide film on the surface, all Ti-2 samples were first activated by exposing them to the test solution for at least 0.5 h to achieve a stable corrosion potential, *E*_{corr}. After cathodic galvanostatic polarisation, the potential of the sample with the generated hydrides was monitored for another 30 min. to measure the new stable corrosion potential, *E*'_{corr}, prior to investigation by EIS and anodic PD. The EIS spectra were recorded with the base potential set to the recorded *E*'_{corr}. The perturbation voltage amplitude of the EIS was 10 mV over the frequency range from 10 kHz to 10 mHz with 10 points per decade sampled. The PD was scanned from *E*'_{corr} to +0.5 V vs. *E*'_{corr} at a rate of 10 mV/min. A control sample that was not subjected to the galvanostatic polarisation for hydride generation was also investigated by EIS and PD, based on the control's *E*_{corr}.

The cathodic polarisation process of Ti-2 was investigated by comparison of the cathodic potentiostatic polarisation (PS) and cathodic PD results. These two electrochemical polarisation experiments were separately conducted on control disc samples (without galvanostatically-generated hydrides) in similar test solutions. PS was performed from E_{corr} to -1.0 V vs. Ag/AgCl with a potential step of 50 mV and 3 ks for each step. PD was scanned from the E_{corr} to -1.0 V vs. Ag/AgCl at the rate of 10 mV/min.

For physical characterisation, a series of titanium hydrides were generated on the flat square samples at cathodic galvanostatic current densities of 0.1, 0.3, 0.5, and 1 mA·cm⁻², for durations of 1, 5, 15, and 60 h. These cathodic current charging tests were conducted in a flat cell (total solution volume 300 mL). The flat square sample was mounted in the flat cell with the prepared surface exposed to the solution inside the cell. Copper tape was stuck to the back of the sample for electrical connection purposes. The cathodic galvanostatic polarisation was performed as described above.

4.3.3 Physical characterisation of the titanium hydrides

The crystallographic texture and microstructure of Ti-2 sheet material were characterised through electron backscatter diffraction (EBSD). The sample was successively ground to 800 grit SiC, polished using 1- and 0.5- μ m polishing cloth with the appropriate colloidal suspensions and ultrasonically cleaned in DI water before examination. The EBSD map was acquired from the center to the surface of the sample on the plane parallel to the extrusion direction and normal direction (*i.e.*, ED-ND plane). EBSD measurements were conducted with a Zeiss Σ igma scanning electron microscope (SEM) using a Nikon high-speed camera and EDAX/TSL-OIM data collection (6th edition) software.

Upon removal from the flat cell, flat samples with galvanostatically-generated titanium hydrides were examined by X-ray diffraction (XRD) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). XRD results were analysed by Rigaku MultiFlex with a 2 kW X-ray generator. Cu K α radiation was used as the X-ray source and operated at 40 kV and 40 mA. The step size was 0.01° and the scan rate was 0.5°/min. ToF-SIMS depth profiles and analysis were performed using a Trift V nanoToF-SIMS (Physical Electronics) instrument. The ion gun was operated at the accelerating voltage of 3 kV to sputter the sample. The sputter area was 400 × 400

 μ m. The DC current of Ar⁺ primary ions delivered to the sample was 400 nA. Each sputter cycle was 20 s in duration. The analysis was carried out using Au LMIG operated with bunched mode using the Ar⁺ primary ion. Each analytical cycle was 60 s in duration with the analysis area of 100 \times 100 μ m. Mass spectra were collected in the mass-to-charge (m/z) range of 0–1850 amu, in both the positive and negative polarities.

4.3.4 Effect of Fe(III) and Cu(II) on the passivation of Ti-2

Electrochemical tests were conducted in a 1-L water-jacketed three-electrode cell, containing 600 mL of test solution. The critical concentration of Fe(III) or Cu(II) required to passivate Ti-2 in the acidic leaching solution was determined as follows. To obtain a uniform fresh surface, the Ti-2 disc electrode was activated by exposing it to the blank solution at OCP for 30 min. (60–80°C) or by cathodic polarisation at -1.0 V vs. Ag/AgCl for 60 s (30–50°C, since it may take a long time to activate at OCP at temperatures below 60° C) to eliminate the effect of the airformed oxide film before subsequent testing. The cathodic polarisation step was aimed at dissolving the natural oxide film, which is reported to significantly affect titanium passivation by Fe(III) or Cu(II) [107]. This polarisation may result in hydride formation, but the hydride formation is not expected to be significant considering the duration of cathodic polarisation. To investigate Fe(III), 2 mL of 0.15 M Fe(III) solution was added to 600 mL of the blank test solution to achieve an Fe(III) concentration increment of 0.5 mM. To investigate Cu(II), 1 mL 0.075 M Cu(II) solution was added to 600 mL of the blank testing solution for a Cu(II) concentration increment of 0.125 mM. Smaller concentration increments were used for Cu(II) because it has a stronger passivating effect. During each incremental concentration increase, the potential transient of Ti-2 was monitored for 10 min., and LPR was measured thereafter from -0.012 to +0.012 V vs. E_{corr} at a rate of 10 mV/min.

Although the critical concentration for passivation was usually lower, titanium was certain to passivate in the blank solution containing 6 mM Fe(III) or 2 mM Cu(II) at every temperature. Thus, these concentrations were used for detailed analysis of the electrochemical response after passivation. After stabilisation at these concentrations for 1.5 h, the passive film that formed on the Ti-2 disc sample was characterised by step-wise PS. PS started from the corrosion potential E_{corr} up to 1.6 V vs. Ag/AgCl, with a step increment of 0.2 V every 20 min. In addition, the cathodic process on Ti-2 in the presence of Fe(III) or Cu(II) was investigated by PD on similarly prepared samples at a scan rate of 0.5 mV/s, from E_{corr} to -1 V vs. Ag/AgCl.

4.3.5 Erosion-corrosion investigation

All the electrochemical tests were carried out in a 1 L water-jacketed cylindrical cell. E_{corr} , EIS and PD were conducted in static solution, dynamic solution, and slurry conditions (silicacontaining) at given temperatures. The dynamic solution and slurry conditions were to assess the effect of impacting liquid flows and solid particle impingement on the erosion-corrosion behaviour of titanium, respectively. For the dynamic solution and slurry conditions, the solutions were agitated at a rate of 1200 RPM with an overhead agitator to simulate a stirred tank reactor. The agitator was equipped with a PTFE four-pitched-blade turbine on a shaft of 6 mm in diameter.

The silica sample S1 (Figure 4-2) was used to simulate the solid particle in slurry conditions. The silica concentration in the slurry was 100 g·L⁻¹, and the silica particles were suspended in the slurry during the test. As shown in Figure 4-2 (a), the particles are semi-round, with very few sharp corners. In contrast, feed mineral particles in operations might be more angular in shape, that is, however, highly related to the ore type and the comminution operations that are employed. The more angular feed mineral particles can cause more significant mechanical perturbation during erosion-corrosion processes [190]. Thus, the particles used here provide a

conservative estimate of the impact of particles on erosion-corrosion. Silica particles used in this work were distributed between 300 and 620 μ m, 80% of the distribution having a particle size smaller than 520 μ m, as determined by sieve analysis by the supplier. These sizes are in reasonable agreement with operations where particles are typically less than 1 mm for agitated leaching [6, 191]. The influence of the shape and size of solid particles on the erosion-corrosion behaviour of titanium was not explored in the present work.

The WE was placed in the cell with the main surface area (2.54×1.27 cm) perpendicular to the radial direction of the cylinder cell. This type of setup has been adopted to study erosioncorrosion in previous work [150, 154], and simulates actual service conditions. Under each test condition, after the WE sample obtained a stable E_{corr} (typically about 1.5 h), EIS and PD were subsequently conducted. The EIS spectra were recorded with the base potential set to the recorded value of E_{corr} . The applied potential was varied sinusoidally at a series of single frequencies over the range of 10 mHz to 10 kHz with the root-mean-square (RMS) voltage amplitude of 10 mV and 10 points per decade. PD was performed after the EIS, and was scanned from -0.3 to +0.3 V vs. E_{corr} , with a rate of 0.5 mV/s. The jacketed cell was open to the atmosphere and no gases were added to the 600 mL of solution that was used for the tests. The temperatures investigated were 40° C, 60° C, 80° C, and 95° C.

For another set of experiments with similarly prepared WEs and fresh solutions, electrochemical noise (EN) measurement was conducted between two nominally identical WEs in the zero-resistance ammeter (ZRA) mode of the potentiostat. EN data were first collected in the static solution. They were then collected in the dynamic solution and, at last, conducted in the slurry conditions (silica concentration in the slurry was $100 \text{ g} \cdot \text{L}^{-1}$) as the rotation rate increased to 1200 RPM. This test sequence enabled the electrochemical response associated with each test

condition to be monitored. Before EN data collection, stable corrosion potentials, E_{corr} were attained. The schematic diagram for the EN experimental setup was shown in Figure 4-8, where the two WEs were symmetrically placed in the cell with the main surface area perpendicular to the radial direction of the cylindrical cell. ASTM G199-09: Standard guide for EN measurement was followed. The EN data were acquired at 100 Hz for 120 s at each condition. The coupled potential was also measured.

In order to characterise the morphology change on the surface of the titanium specimen after erosion-corrosion testing, SEM pictures were taken at the same area of the sample before and after testing. The sample was scratched with a diamond cutter, in a cross pattern, as an identifying mark. SEM pictures were taken at the same area of the sample surface before and after erosion testing *via* locating this cross mark. SEM was conducted by a Zeiss ∑igma scanning electron 236 microscope using a Nikon high-speed camera and EDAX/TSL237 OIM Data collection (6th edition) software.



Figure 4-8 Schematic diagram for electrochemical noise experimental setup

In all experiments with a three-electrode configuration, an Ag/AgCl electrode (potassium chloride [KCl] = 4 M) with a Luggin capillary was used as a reference electrode (RE), and potential 68

values are quoted with respect to this RE (0.197 V vs. SHE), unless otherwise stated. A 2 cm \times 1.5 cm platinum sheet was used as the counter electrode (CE). Thermal effects on the measured potentials for the investigated system are not considered since they were found to be insignificant at temperatures < 100°C (< 0.05 V) according to Yue and Asselin [192], Nickchi and Alfantazi [193] and Liu *et. al* [52]. All the electrochemical tests were operated by a Princeton Applied Research VersaSTAT 4 potentiostat, except EN measurement, which was performed by a Princeton Applied Research PARSTAT 4000 potentiostat. Data was captured with the VersaStudio software package. All the tests were repeated 3 times, separately, unless otherwise stated. The results are reported as the mean of the three data sets along with the standard deviation of the mean.

Chapter 5: Effects of solid deposition on the corrosion behaviour of Ti-2 in simulated leaching solutions^{1, 2}

Solid mineral deposition, also known as scaling, is widespread in various autoclave installations in hydrometallurgy. Titanium is widely used as the construction material for autoclave liners and various internal parts. Accumulation/deposition of minerals and reaction products during normal operation or production shutdowns results in corrosion concerns for the underlying titanium, that is, under-deposit corrosion (UDC). This chapter investigates the effects of solid deposition on the corrosion behaviour of titanium grade 2 (Ti-2) and illustrates the barrier effect of the deposit layer on mass transfer in the corrosion process. The passivation of deposit-covered Ti-2 by oxidising species (Cu(II), Fe(III), and O₂) present in the simulated leaching solution is also investigated. The results provide important information for the use of titanium in hydrometallurgical environments where deposits may be present.

5.1 Deposit-covered Ti-2 in the blank solution

5.1.1 Effect of solid deposits on the corrosion rate of Ti-2 in the blank solution

Figure 5-1 shows a typical potential change of a control Ti-2 sample (in the normal bare/uncovered condition) in the deoxygenated blank solution (30 $g \cdot L^{-1} H_2SO_4 + 12 g \cdot L^{-1} Cl^-$) and in the simulated leaching solution (blank solution + 15 $g \cdot L^{-1} Cu(II) + 1 g \cdot L^{-1}$ Fe(III), bubbled with O₂), respectively. In the blank solution, the sample had an initial decrease in potential, then

¹ Yu Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in simulated leaching solutions", *Hydrochair Poster Session*, September (2018), The University of British Columbia, Vancouver, BC, Canada

² Yu Liu, Jing Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in the leaching solutions", *China-Canada Nonferrous Metallurgy Forum*, July (2018), Northeast University, Shenyang, China

there was a sudden potential drop at approximately -0.3 V (the initial potential and the time duration varied with the pre-treatment processes). This sudden drop in potential is known as an activation process, and it corresponds to the destabilisation of the air-formed passive oxide film, which plays an important role in the corrosion behaviour of titanium [45]. After the complete breakdown of the air-formed film, the Ti-2 sample attained a stable corrosion potential of about -0.65 V, indicating active corrosion as predicted by the Pourbaix diagrams [15, 16]. In the simulated leaching solution, the Ti-2 sample had an immediate potential increase and was passivated (the Ti-H₂O Pourbaix diagrams predict passivation at approximately > -0.4 V, depending on the test condition [15, 16]). This passivation is attributed to the presence of the Cu(II), Fe(III), and/or O₂ in the simulated leaching solution, as reported in previous work [10, 52].



Figure 5-1 Potential change of a control (bare) Ti-2 sample in the blank solution and in the simulated leaching solutions

In order to understand the effect of solid deposits, titanium corrosion behaviour in the absence of inhibitors, *i.e.*, the blank solution was first assessed. Ti-2 samples covered by three types of silica particles with different size distribution, *i.e.*, S1 ($d_{0.5}$: 425 µm), S2 ($d_{0.5}$: 193 µm),

S3 ($d_{0.5}$: 20.4 µm), and gypsum with a thickness layer of 2.5 cm were investigated. Figure 5-2 shows the potentiodynamic polarisation measurements for each sample after stabilisation for 2 h in the blank solution. All samples had typical polarisation characteristics for passive metals such as Ti-2. In the anodic branch, as potential was swept more positive, the anodic current increased until the critical potential for passivity, E_{crit} . The magnitude of the current near E_{crit} for the deposit-covered samples was always smaller than the control, and the smaller the deposit particle size was, the smaller the anodic current appeared to be, as indicated by the arrow in Figure 5-2 near -0.5 V. In this potential region, the anodic current is attributed to the dissolution of the titanium substrate to soluble Ti^{III} ions [35, 45]. Lower anodic current snear E_{crit} suggest a slower dissolution rate due to the presence of the deposits. Above E_{crit} , the current rise, at E_2 , is associated with another oxidation process, *i.e.*, Ti^{III} to TiO₂, not related to the anodic dissolution of the titanium substrate [35, 45].

The cathodic branch shows the same trend, in terms of decreasing currents, as observed near E_{crit} . The cathodic reaction is also slowed by the presence of deposit layers and the barrier effect is in the sequence of gypsum > S3 > S2 > S1.

Figure 5-3 shows the linear polarisation resistance, R_p , for the same samples/conditions. An increased magnitude of R_p was observed for Ti-2 covered by a denser deposit layer. The corrosion current density, calculated from R_p and cathodic Tafel slope ($\beta_c= 0.22$ V/decade [35]), is also included in Figure 5-3. The presence of a deposit layer on the Ti-2 surface caused a decrease in the corrosion current density by a factor up to 5, in the sequence of gypsum > S3 > S2 > S1, consistent with the barrier effect revealed by the potentiodynamic polarisation results. However, even though a drop in the corrosion rate is seen with thicker deposits, it is important to note that corrosion rates shown in Figure 5-3, and throughout this Section 5.1, are high for Ti-2. This is because the Ti-2 was actively corroding and passivation was not possible in the blank solution.



Figure 5-2 Potentiodynamic polarisation measurements of Ti-2 samples in the bare condition (control) and covered by three types of silica particles, S1 ($d_{0.5}$: 425 µm), S2 ($d_{0.5}$: 193 µm), S3 ($d_{0.5}$: 20.4 µm), and gypsum with a layer thickness of 2.5 cm in the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) at 50°C (E_{crit} is critical

potential for passivity; *E*₂ is associated with the oxidation of Ti^{III} to TiO₂)



Figure 5-3 Linear polarisation resistance (*R_p*) and corrosion current density (*i_{corr}*) of Ti-2 samples in the bare condition (control) and covered by three types of silica particles, S1 (*d_{0.5}*: 425 μm), S2 (*d_{0.5}*: 193 μm), S3 (*d_{0.5}*: 20.4 μm), and gypsum with a layer thickness of 2.5 cm in the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) at

50°C

The slowed anodic and cathodic processes and decreased corrosion rate due to the presence of solid deposits have also been observed by other researchers, and these phenomena are attributed to the barrier effect of solid deposits on limiting the mass transfer of corrosive species [23, 120, 123]. For example, in the investigation of mild steel CO₂ corrosion in the presence of different inert solid deposits (SiO₂ powder, glass beads and sand), Huang *et al.* [123] observed a linear corrosion rate decrease with the decrease of deposit porosity.

The porosity of the deposits used in the current work was determined by both theoretical calculation and experimental measurement. Before determination of porosity, each type of deposit was oven dried at 105°C for 48 h. The following equation is used to calculate porosity, φ , theoretically:

$$\varphi = 1 - \frac{P_b}{P_d}$$
 Equation 5-1

where, P_d is the particle density, and it is assumed to be 2.65 and 2.96 g·cm⁻³ for silica and gypsum powder, respectively; P_b is the bulk density, and it is calculated by dividing the dry mass of the deposit sample by the deposit sample volume.

In the experimental measurement, a specific amount of DI water, V_{water} , was added to a deposit sample with a known volume (V_s). The water should fully saturate the sample and the water level should be as close to the surface level of the solid sample as possible. The porosity will then be the ratio of pore volume (*i.e.*, V_{water}) to the total volume V_t of deposit sample and water. The determined porosity φ for each type of deposit is listed in Table 5-1.

Table 5-1 Porosity φ for each type of deposit tested herein and determined by theoretical calculation (φ^T) and experimental measurement (φ^E)

Φ / %	S 1	S2	S 3	Gypsum
$arphi^T$	39.4±0.7	49.0±0.2	50.2±0.1	59.6±1.4
$\pmb{\varphi}^E$	37.2±1.8	42.1±0.4	47.4±1.9	44.3±0.5
$arphi_{-average}$	38.3	45.6	48.8	51.9

The corrosion rate (CR) in terms of penetration rate according to ASTM standard G 102-89 [194] was calculated by Equation 5-2:

$$CR = K_1 \frac{l_{corr}}{\rho} EW$$
 Equation 5-2

where, *CR* is given in mm·yr⁻¹; i_{corr} in uA·cm⁻²; $K_I = 3.27 \times 10^{-3}$ mm·g·(uA·cm·yr)⁻¹; ρ is the metal density, 4.5 g·cm⁻³ for titanium; *EW* is the equivalent weight, 15.97 for Ti^{III}, and considered dimensionless in this calculation.

The relationship between CR and the porosity of the deposit layer is shown in Figure 5-4.



Figure 5-4 Relationship between deposit porosity and corrosion rate of Ti-2 for the bare sample (control) and samples covered by three types of silica particles, S1 (*d*_{0.5}: 425 μm), S2 (*d*_{0.5}: 193 μm), S3 (*d*_{0.5}: 20.4 μm), and gypsum with a layer thickness of 2.5 cm in the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) at 50°C

Inconsistent with the observation of Huang *et al.* [123], high deposit porosity could not be positively correlated with high corrosion rates in this work. Suarez *et al.* [195] also claimed that deposit porosities could not be associated with higher corrosion rates in their study of carbon steel corrosion, where CaCO₃ had the highest porosity (80%) and yet it resulted in the least corrosion in comparison with the other two types of deposits (Al₂O₃: 67% and SiO₂: 27%).

Consistent with the results reported by Suarez *et al.* [195], Table 5-1 and Figure 5-4 revealed that the deposits with a smaller mean particle size had a higher porosity, and corresponded to a lower corrosion rate of underlying metals. In a permeability-porosity study based on nearly a thousand samples of natural deposit samples of river bars, beaches, and dunes, Pryor [196] reported that the relation of porosity versus mean size separated the data into two different groups: the group of beaches and dunes, which had smaller average grain size (mean grain size ranging from about 0.5 mm to less than 0.1mm), showed increased porosities with the decrease of mean grain size,

which was different from the group of the river bars, which had larger average grain size (mean grain size ranging from about 1 mm to 0.3 mm). Hamilton and Menard [197] also stated sands with median diameters of approximately 0.7 mm had porosities of about 40% and clays with median diameters of less than 20 µm had porosities of nearly 80%. In a study on the effect of grain size on porosity with sands obtained from the Niger Delta, Ogolo *et al.* [198] observed that porosity increased from about 26% to 42% as the sand grain sizes decreased from 1 mm to 45 µm. For porous core with a size range of 0.6 µm to 0.063 µm, Onuoha *et al.* [199] reported that the porosities were found to increase with decreasing grain size from 37% to 44%. Theoretically grain size should have no effect on porosity for well sorted grains. However, in natural assemblages, as grain size decreases, the sphericity of natural particles decreases and the subsequent packing becomes poorer. In addition, friction, adhesion, and bridging become important because of the higher specific surface area. These account for the increased porosity as grain size decreases [200].

The relationship between solid deposits and underlying metal corrosion rate can be demonstrated by its influence on the mass transfer of the involved corrosion species. In a corrosion process, the mass transfer of the solutes through a solid deposit layer is directly related to the concentration gradient of the solute, a solid deposit layer's intrinsic permeability, and the mass diffusivity of the solute. In the absence of bulk fluid movement, the mass transfer of the solute can be approximated by Fick's laws:

$$J = -D\frac{\Delta C}{\Delta x}$$
 Equation 5-3

where, *J* represents the diffusive flux, for which the dimension is amount of substance per unit area per unit time (mol·m⁻²·s⁻¹); *D* is the effective diffusion coefficient or diffusivity of the solute, for which the dimension is area per unit time (m²·s⁻¹); ΔC is the concentration gradient, for which

the dimension is amount of substance per unit volume (mol·m⁻³); Δx is position distance, the dimension of which is length (m).

The presence of solid particles causes the diffusion paths of species to deviate from straight lines. Due to the pores' tortuous nature and pore constrictions, the diffusivity in sediment/solid is corrected by tortuosity, and can be related to the diffusion coefficient in free solution as follows [201]:

$$D_s = \frac{D_0}{\theta^2}$$
 Equation 5-4

where, D_s is bulk sediment/solid diffusion coefficient; D_0 is free solution diffusion coefficient without the presence of the sediment; θ is tortuosity of the sediment or deposit.

Tortuosity is defined as the mean length of the path through the porous space between two points relative to a straight line between the same two points. It depends on the geometry of the sediment and is difficult to measure directly. The general requirements for θ are [202, 203]:

(1) $\theta^2 \ge 1$, which simply means that the actual (average) path traversed by the species while diffusing in a porous medium is longer than in the absence of the solid;

(2) $\lim_{\varphi \to 1} \theta = 1$, φ is solid porosity, ranging between 0 and 1. That is, there is no hindrance to diffusion in the absence of solids. $\lim_{\varphi \to 0} \theta = \infty$, indicating the tortuosity is finite for all nonzero values of porosity and hindrance is complete.

There are two approaches that lead to an indirect estimate of tortuosity—both of them relate θ^2 to solid porosity, φ [204, 205]. One approach relates the tortuosity to a quantity termed the formation resistivity factor and to porosity [202, 205, 206]:

$$\theta^2 = (F \cdot \varphi)^n$$
 Equation 5-5

where, n is an adjustable empirical parameter; F is the formation resistivity factor.
Another approach measures the diffusion coefficient of a chosen nonreactive species both in free solution and in a sediment of known porosity, which is a time-consuming process. Empirical relations based on experimental measurements, on the other hand, may better describe the observed data and these relations may contain various adjustable parameters.

The porous medium permeability, which represents the resistance to fluid flow passing through it, explains the different behaviour of the solid deposits. As the particle size decreases, the particle-wall interactions become more frequent, giving rise to additional wall friction, *i.e.*, viscous and Knudsen friction. At small characteristic dimensions (mm to μ m scale), one of the first proposed empirical relations, the Hazen relation, relates the permeability (or hydraulic conductivity) *k* in cm·s⁻¹ of a porous unit to the characteristic particle diameter *d*_{0.1} (the maximum diameter of the finest 10% of the grains in that sand) in cm [207]:

$$k = c_H d_{0.1}^2$$
 Equation 5-6

where, c_H is an empirical coefficient, typical values are around 100, although values from 1 to 1000 are possible [208]. The applicability of the Hazen relation is limited to 0.01 cm $< d_{0.1} < 0.3$ cm. The small range of characteristic particle diameters and the variability of c_H have limited its general use.

A second widely used approach is the Kozeny-Carman equation, which estimates the permeability, k, directly [208, 209]:

$$k_{KC} = \frac{\varphi^3}{\theta (1-\varphi)^2 S^2}$$
 Equation 5-7

The Kozeny-Carman equation uses parameters more relevant to natural porous media, *i.e.*, tortuosity θ and specific surface area S. It is worth noting that particle size has the most influence on the calculated S. The Kozeny-Carman equation may significantly overestimate the

permeability, especially for complex, tortuous, heterogeneous, or poorly connected porous media [210].

The discussions above suggest that the permeability of a porous medium is correlated with porosity, but that it is also significantly influenced by other parameters linked to pore geometry, such as the specific surface area, grain size distribution, or the tortuosity, especially for fine particles [202]. This explains why deposits with a smaller mean particle size have a more significant effect on slowing the mass transfer process of solute species, and thus the corrosion rate. Furthermore, chemical reactions between the species in the fluid phase and interaction between the species and solid medium may strongly affect the transport of a species, and further complicate this process. The mechanism of solute transfer through the solid pores is beyond the research scope of this work, and is not analysed further. Instead, the barrier effect of deposits on mass transfer of species is interpreted in the context of corrosion based on the electrochemical quantities.

5.1.2 EIS results

The corrosion processes for the deposit-covered and uncovered samples were also evaluated by EIS, and the results are shown in Figure 5-5. All samples displayed two time constants, *i.e.*, one in the high frequency range of 10–100 Hz (related to the surface layer—this could result from monolayer adsorbed species, a thin, porous, and unprotective surface oxide, or, perhaps, hydrides [45]) and a second one in the low frequency region around 10 mHz (related to charge transfer at the metal/oxide interface). For quantitative information, EIS spectra were fitted with electrical equivalent circuits (EECs). The two time-constant EEC, $R_{sol}(Q_{film}(R_{film}(R_{cl}Q_{l})))$, which is widely used for titanium to simulate EIS data, was adopted [10, 64, 134, 211-214]. This EEC represents the case when the oxide film is porous and the active electrochemical reaction,

i.e., anodic dissolution of the metal substrate, occurs through the pores. It is acknowledged that this EEC may not be physically appropriate for the covered samples, however, since these samples had similar kinetics to the control sample-in terms of the order-of-magnitude current densities, shape of the PD curves (Figure 5-2) and shape of the EIS curves (Figure 5-5)—it is a reasonable assumption that the deposit had a minor effect on changing the reaction kinetics. As a result, any mass transfer effects can be accounted for by implicit changes in R_{sol}. In this EEC, R_{sol} is the solution resistance; R_{film} is the surface oxide film resistance; the parallel constant phase element (CPE), Q_{film} , corresponds to the capacitive behaviour of the oxide film; the other R-CPE pair of R_{ct} and Q_i account for the charge transfer reaction and the capacitance of the electrical double layer, respectively. The constant phase element, Q, instead of a capacitor C, was adopted here to compensate for the non-ideal capacitive behaviour of the surface and the distribution of relaxation times resulting from different degrees of heterogeneities at the electrode surface [215, 216]. The fitting was conducted in ZsimpWin software, and the fitting quality was evaluated by the chisquared (χ^2) values. The fitting lines were included in the EIS spectra and the data are listed in Table 5-2.



Figure 5-5 EIS spectra of Ti-2 samples in the bare condition (control) and covered by three types of silica particles, S1 ($d_{0.5}$: 425 µm), S2 ($d_{0.5}$: 193 µm), S3 ($d_{0.5}$: 20.4 µm), and gypsum with a layer thickness of 2.5 cm in the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) at 50°C (a) Nyquist plots, (b) Bode magnitude and phase

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Table 5-2 Electrical parameters of the EEC obtained by fitting the EIS spectra in Figure 5-5

Species	R_{sol} $\Omega \cdot \mathrm{cm}^2$	$\begin{array}{c} Q_{\textit{film}}\text{-}\mathrm{Y}_{0} \\ \times 10^{-5} \\ \mathrm{S}{\cdot}\mathrm{s}^{\mathrm{n}}{\cdot}\mathrm{cm}^{-1} \end{array}$	<i>Q_{film}-n</i>	R_{film} $\Omega \cdot \mathrm{cm}^2$	Q_i -Y ₀ ×10 ⁻² S·s ⁿ ·cm ⁻²	Qi-n	$R_{ct} \Omega \cdot \mathrm{cm}^2$	$\chi^2 \times 10^{-3}$
Control	3.4±2	51±5	0.92±0.01	173±30	3.3±0.6	0.7±0.1	233±30	8.1
S1-covered	35±4	59±0.3	0.86±0.02	213±10	8.0±0.8	0.97±0.1	241±40	7.3
S2-covered	37±6	69±0.3	0.72±0.01	279±50	5.5±0.8	0.90±0.3	226±40	8.0
S3-covered	55±7	47±0.3	0.59±0.01	645±10	4.7±0.7	1±0.01	387±40	3.4
Gypsum- covered	61±6	50±0.3	0.66±0.00	690±10	4.7±0.8	1±0.01	480±40	9.3

The fitting results showed that the charge transfer resistance, R_{ct} , which is used to represent the corrosion resistance, is generally larger for the deposit-covered samples than the control sample as suggested by the R_p results.

As anticipated, the solution resistance R_{sol} of the control sample is lowest (about 3 $\Omega \cdot \text{cm}^2$). R_{sol} increases in the sequence of gypsum > S3 > S2 > S1, *i.e.*, the smaller the deposit particle size, the higher the solution resistance. R_{sol} represents the total resistance between the working electrode and the reference electrode in the corrosion circuit, consisting of the resistance of the electrolyte and the resistance resulting from the deposits (which may be very small in the case of thin deposits consisting of coarse particles). Thus, the increased R_{sol} for the deposit-covered samples is attributed to the mass transfer effects of the silica deposits [204, 206]. In the investigation of X65 steel UDC, Barker *et al.* [121] found that a 10 mm sand cover resulted in an increase of R_{sol} from 10 to 30 $\Omega \cdot \text{cm}^2$ for the underlying X65 steel in CO₂ saturated 10% NaCl solution, suggesting the sand acted as a diffusion barrier. Consistently, Huang *et al.* [123] investigated X65 pipeline steel under different solid deposits and found that all their R_{sol} values were larger than bare steel, and the more dense the deposit, the larger R_{sol} , therefore more obvious barrier to the diffusion process.

The relation expressed in Equation 5-5 comes from the observation that hindrance to electrical conduction and to solute diffusion are similar [217]. The formation resistivity factor F, is determined by measuring the resistivity of a porous medium, relative to that of the free solution [205]. The calculation of this factor usually requires specialised equipment, *i.e.*, resistivity probes. Here, a solution formation resistivity factor F' is defined based on the EIS measurements, which is the ratio of solution resistance R_{sol} in the presence of the solid deposit to that in the bulk solution. Its relation with *CR* is shown in Figure 5-6.



Figure 5-6 Solution formation resistivity factor F' (Rsol-deposits /Rsol-bulk solution) calculated from EIS spectra in Figure 5-5

CR appears to be inversely related to F', that was consistent with Equation 5-5 when n was 1, as has been reported for sand [205], and that suggests an inverse relationship between *CR* and *F*, consistent with the relation revealed in Figure 5-6. A higher value of F' represents a higher solution resistance in the corrosion process, thus a decreased corrosion rate is expected to occur.

5.2 Under deposit passivation of active Ti-2 in simulated leaching solutions

In order to simulate a scenario where insufficient inhibition under solid deposits might occur, the potential of the initially activated deposit-covered Ti-2 was recorded as the simulated leaching solution, containing passivating species, was added (Figure 5-7(a)-(d)). The potential values before the introduction of simulated leaching solution indicated a consistent surface condition for all samples. When simulated leaching solution was introduced, samples covered with deposit S1 achieved potentials > -0.4 V very soon, for example, 1 min. for the deposit layer thickness of 2.5 cm (Figure 5-7(a)). Samples covered by S2 showed obvious delay in passivation, *i.e.*, approximately a half-hour was needed for passivation for the deposit layer thickness of 2.5 cm (Figure 5-7(b)). Samples covered by S3 (Figure 5-7(c)) or gypsum (Figure 5-7 (d)), with a

deposit thickness of 0.5 cm, exhibited an obvious potential increase after approximately 1 h. There was an induction time associated with passivation for thicker deposits of fine silica and gypsum. For example, the time taken for a significant potential increase, *i.e.* to -0.4 V, was at least 5 h for the 1 cm S3 and at least 7 h for the 1 cm gypsum covered sample. When the thickness of S3 or gypsum deposits was 1.5 cm, the underlying Ti-2 remained in the active corrosion state for up to 19 h. Thus, no thicker deposits were tested.



Figure 5-7 Potential change of initial active Ti-2 samples covered by (a) S1 ($d_{0.5}$: 425 µm), (b) S2 ($d_{0.5}$: 193 µm), (c) S3 ($d_{0.5}$: 20.4 µm), and (d) gypsum with varying thickness during exposed to simulated leaching solutions solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻⁺ 15 g·L⁻¹ Cu(II) + 1 g·L⁻¹ Fe(III), bubbling with O₂) at 50°C

Passivation for the deposit-covered titanium is linked to mass transfer of the passivating species through the deposits as well as the related titanium passivation process itself (which is dependent on kinetics and thermodynamics). Titanium will be passivated immediately when a specific concentration of passivating species is accumulated on its surface (a more detailed investigation pertaining to titanium passivation will be discussed in Chapter 7). However, the mass transfer process is time-dependent. Thus, it appears that passivating species mass transfer is the rate controlling step for deposit-covered Ti-2 passivation. For the investigated conditions, Ti-2 passivation in the absence of solid deposits is rapidly achieved once passivating species are introduced (~ few seconds). On the other hand, the induction time associated with passivation of solid-covered Ti-2 samples reflects the barrier effect of solid deposits on the mass transfer of the passivating species. The induction time for Ti-2 passivation (to -0.4 V) in Figure 5-7 is summarised in Figure 5-8 (a). The ratio of the induction time to the passivation time of the solidcovered Ti-2 samples to that of the control sample in the bulk solution is shown in Figure 5-8(b). This ratio is analogous to the tortuosity factor, θ^2 (ratio of the diffusion coefficient in the solid layer, D_s , to that in the bulk solution, D_0), representing the slowed mass transfer process due to the presence of solid deposits.



Figure 5-8 (a) Induction time associated with the passivation of Ti-2 covered by solid deposits (time takes to reach -0.4 V) in Figure 5-7, (b) ratio of induction time to passivation of solid-covered Ti-2 samples (t) to that of the control sample in the bulk solution (t_0) (deposit layer thickness = 1 cm, t_0 = 1)

In addition to acting as a barrier to the transport of corrosive and passivating species, the deposit layer may demonstrate its effect *via* competitive adsorption of the passivating species. Adsorption onto the solid deposits is common for organic inhibitors, and it results in significant inhibitor loss, accounting for UDC in the pipeline industry. For inorganic species, including corrosive species (*i.e.*, H⁺) and passivating species (*i.e.*, Cu(II), Fe(III) or O₂), to the best of the author's understanding, there are no available reports suggesting adsorption onto untreated silica particles or gypsum. In this work, the adsorption of these passivating species onto the deposits does not appear to be an explanation. Indeed, the simulated leaching solution was analysed after each test and the residual concentrations of these species were not found to be significantly different than the initial concentrations. In addition, the adsorption behaviour of Cu(II) and Fe(III) by S1 was investigated by the thermostatic flask shaker method, and the experimental and results are shown in Appendix A. The adsorption was found to be negligible (less than 5% even when the initial Cu(II) and Fe(III) concentration was on the scale of mg·L⁻¹).

5.2.1 Inhibition performance of individual passivating species on the silica-covered Ti-2

5.2.1.1 Test I: individual passivating species at in-service concentrations

In view of the concomitant three types of passivating species in the simulated leaching solution, the inhibition performance of individual passivating species on the deposit-covered Ti-2 was not clear, thus, the related study was conducted and demonstrated in this section.

The introduction of O₂ bubbling (5.5 mg·L⁻¹, Figure 5-9(a)) or 1 g·L⁻¹ Fe(III) (Figure 5-9(c)), at the in-service concentrations did not affect the potential of Ti-2 covered by 2.5 cm of S1. The relatively negative potentials seen in Figure 5-9(a, c) indicates an active corrosion state for the test duration. In contrast, the introduction of 15 g·L⁻¹ Cu(II) resulted in a rapid potential increase from -0.7 up to 0.4 V, indicating passivation (Figure 5-9(b)). In contrast to the silica-covered samples, the control samples had an immediate increase in potential and achieved passivation upon the addition of O₂ (Figure 5-9(a)), Cu(II) (Figure 5-9(b)), or Fe(III) (Figure 5-9(c)). These results prove that in the absence of any surface deposits or scales, Ti-2 can be readily passivated by either O₂, Cu(II), or Fe(III) present in the leaching solution. This is consistent with previous reports [10, 105, 107].

When deposits are present, two conclusions can be drawn: (1) the leaching solution, which contains $15 \text{ g} \cdot \text{L}^{-1}$ Cu(II) is sufficient to induce passivation, and (2) relatively high concentrations of inhibitors are required. This is evident by the effect of $15 \text{ g} \cdot \text{L}^{-1}$ Cu(II) on the passivation of Ti-2 under the 2.5 cm S1, whereas the much lower concentrations of ferric and oxygen had no passivating effect. Since the concentrations of inhibitors in the leaching solution are so disparate, Test II will investigate the response of Ti-2 to comparable inhibitor concentrations. While these concentrations may not reflect industrial practice, it is important to understand their individual effects as industrial process concentrations vary significantly.



Figure 5-9 Potential change of deposit-covered (S1-2.5 cm) and control (no deposit) Ti-2 samples as exposed to (a) 5.5 mg·L⁻¹ O₂, (b) 15 g·L⁻¹ Cu(II), and (c) 1 g·L⁻¹ Fe(III) (at the same concentration as in the simulated leaching solution) at 50°C

5.2.1.2 Test II: individual passivating species at comparable concentrations

When Fe(III) concentration was 15 g·L⁻¹ (corresponding to the in-service concentration of Cu(II)), the potential of the silica-covered Ti-2 increased to > 0.35 V, corresponding to the passivation of Ti-2, as also observed with the 15 g·L⁻¹ Cu(II) concentration used in Test I (represented in Figure 5-10 for comparison). In contrast, neither Cu(II) or Fe(III) with concentrations of 5.5 mg·L⁻¹ (corresponding to the in-service concentration of O₂) or 1 g·L⁻¹ (corresponding to $\frac{89}{89}$

the in-service concentration of Fe(III)) was able to passivate the silica-covered Ti-2 and inhibit UDC. Clearly, as noted above, the passivation of silica-covered Ti-2 seen in Figure 5-7 was driven by the high concentration of Cu(II) in the leaching solution. In other words, higher inhibitor concentrations are needed when solid deposits are present in comparison with the control samples, as suggested from similar studies for steel in the pipeline industry [23, 24, 117, 118].

A more detailed investigation of the performance of Cu(II) and Fe(III) species toward the passivation of titanium and the associated mechanisms is provided in Chapter 7 [105].



Figure 5-10 Potential change of deposit-covered (S1-2.5 cm) Ti-2 samples at comparable inhibitor concentrations at 50°C

5.3 Under-deposit corrosion of passive Ti-2 in simulated leaching solutions

5.3.1 Effect of solid deposits and temperature on the corrosion behaviour of passivated Ti-

2: corrosion rate

It is clear from Figure 5-7 that passivation can be induced under thick deposits from an active state at 50°C, by adding sufficient concentrations of passivating species. However, one important question that arises is: can this deposit-covered, passivated, surface be activated when

temperature is increased? One way to answer this question is to increase temperature and monitor the sample corrosion behaviour and corrosion rate.

Ti-2 was passivated in the simulated leaching solution and was then covered with S3, which was previously saturated with the simulated leaching solution. The corrosion behaviour of the Ti-2 was compared with a control sample in the simulated leaching solution. Figure 5-11(a) shows the corrosion potential, E_{corr} , of the S3-covered and control Ti-2 samples at 50-80°C. All the samples have E_{corr} higher than 0.5 V, indicating that the Ti-2 samples are indeed passivated. The control sample has a slightly higher potential than that of the fine silica-covered samples. Figure 5-11(b) shows the potentiodynamic polarisation curves of all samples measured at the end of corrosion potential measurements: all of the Ti-2 samples show passivation behaviour in the anodic branch. In the cathodic branch, the magnitude of the cathodic current density was smaller as the S3 deposit thickness increased, indicating the increased barrier effect on limiting the mass transfer of cathodic reaction species, *i.e.*, Fe(III), Cu(II), H⁺. An important feature to note in these potentiodynamic curves is the increased current at anodic potentials when the deposits were thicker. This current is due to both the oxidation of titanium and the various species that were reduced in the preceding cathodic branch. These species would be confined to the surface of the titanium electrode (or near it) due to the presence of the deposit layer. Thus, the more significant the barrier effect, the higher the concentration of such species at the electrode surface and thus the higher the anodic current upon their oxidation.



Figure 5-11 (a) Corrosion potential (*E_{corr}*) of S3-covered and control Ti-2 samples in simulated leaching solutions at 50–80°C (24 h/10°C), and (b) potentiodynamic polarisation curves of S3-covered and control Ti-2 samples in simulated leaching solutions at 80°C

The polarisation resistance, R_p , which was measured *via* polarisation resistance and is commonly used to estimate the corrosion rate, is shown in Figure 5-12(a) for the S3-covered and control samples. The control sample had a higher value of R_p than the S3-covered samples at each temperature. With the increase of temperature, the values of R_p for both the control and S3-covered Ti-2 samples decreased. The corrosion current, *i*_{corr}, calculated from R_p is shown in Figure 5-12(b). For the initially passive Ti-2, solid deposits will result in an increased corrosion rate in comparison with the control sample, which is exposed to the bulk solution, especially at high temperatures. However, the relatively small value of *i*_{corr} (< 16.5 μ A·cm⁻²) still indicates an acceptable corrosion rate and relatively good corrosion resistance of Ti-2.



Figure 5-12 (a) Linear polarisation resistance (R_p), (b) corrosion current calculated based on R_p of S3-covered and control Ti-2 samples in simulated leaching solutions at 50–80°C (24 h/10°C)

The unfavorable effect of solid deposit on the corrosion rate of Ti-2 (Figure 5-12) may be interpreted in terms of the influence of mass transfer of oxidising species (*i.e.*, Fe(III), Cu(II), and O_2) on the corrosion behaviour of titanium [218]. Greater mass transfer of these passivating species to the titanium surface promotes passive film growth and repair, and thus inhibits corrosion. Therefore, the control sample exposed to the bulk solution had a higher value of E_{corr} and larger corrosion resistance because the passivating species were more accessible. In comparison, the solid deposits limited mass transfer of the passivating species to the underlying Ti-2 samples (as indicated by Figure 5-11(b)). At the corrosion potential, when a deposit is present, its thickness (from 2.5 to 6.5 cm) does not appear to play a significant role in the corrosion rate of the underlying Ti-2 samples, as they all experienced similar changes in corrosion potential and linear polarisation resistance.

It is also important to notice the effect of temperature. The value of i_{corr} increased as the temperature increased for both the control and S3-covered Ti-2 samples, while the difference in i_{corr} between them appears to increase. The protective oxide film on the surface of Ti-2 is reported

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to undergo a breakdown/crystallisation process at temperatures higher than 60°C in NaCl solution [55, 134]. This process is an important phenomenon for titanium oxide films in terms of the oxide growth rate, composition, structure, and corrosion resistance because it may create grain boundaries and cracks, and provide lower-resistance pathways for titanium ion transport through the film, thus resulting in a decreased corrosion resistance [219, 220]. This, along with increased Arrhenius kinetics, explained the increased corrosion rate of Ti-2 samples at higher temperatures. However, the repair of the passive film by the oxidising species will be slowed due to the presence of solid deposits, thus, the more obvious decreases in R_p , and increases in *i*_{corr} at higher temperatures. Thus, the presence of solid deposits is expected to be unfavorable for the integrity of titanium equipment at high temperatures, provided that leaching solution remains in physical contact with the underlying metal. For example, copper leaching takes place at temperatures up to 230°C, and unless deposits completely block the metal from solution access, one would expect significant corrosion rates under such deposits [6, 188, 189].

In order to have a better understanding of the corrosion rate of titanium at high temperatures, the corrosion current density, i_{corr} , obtained from 50 to 80°C, was calculated as a *CR* in terms of penetration rate (calculated by Equation 5-2) and extrapolated to higher temperatures. Figure 5-13 shows that $\ln(CR)$ can be represented as a straight-line function of 1/T, *i.e.*, Arrhenius behaviour. The Arrhenius type equation has been widely used as a model of the temperature effect on the chemical reaction rate constant [221, 222], and the temperature dependence of passive corrosion of titanium has been studied by the Arrhenius type equation over a temperature range of 60 to 90°C [134]. These provide the justification for adopting this model here:

$$\ln(CR) = -(E_a/RT) + \ln A$$
 Equation 5-8

where, E_a is the apparent activation energy in J·mol⁻¹; R is the universal gas constant in J·mol⁻¹·K⁻¹; T is temperature in K; A is the pre-exponential factor.

Arrhenius plots revealed a E_a value of 51.5 kJ·mol⁻¹ for the control sample, and 66.4 to 83.2 kJ·mol⁻¹ for the S3-covered Ti-2 samples. In corrosion inhibition studies of steels, a higher value of E_a for steels in the presence of inhibitors than that in the uninhibited acid solutions was observed [223, 224]. The higher value of E_a was explained to represent the increased difficulty in the diffusion through the film of corrosion products and inhibitors when inhibitors blocked the active sites of the metals [223, 224]. For the investigated condition, the higher values of E_a in the presence of the solid deposit layer when compared to the control sample might be attributed to the barrier effect of the deposit layer on the mass transfer process. It was obvious that the pre-exponential factors were also higher for the S3-covered samples, indicating the increased corrosion rate due to the presence of solid deposit layer. The kinetic parameters derived from Arrhenius plots in Figure 5-13 are listed in Table 5-3.

According to the conventional standards for relative corrosion resistance [225], corrosion rates below 0.5 and 5 mm·yr⁻¹ are defined as good and fair, respectively; corrosion rates above 5 mm·yr⁻¹ are defined as unacceptable (marked in Figure 5-13). As expected, it is predicted that the control Ti-2 would maintain a slower *CR* than that of the S3-covered sample at the same temperature. Its corrosion rate was expected to increase to 0.5 mm·yr⁻¹ as temperature increased to 127°C (as marked $1/T_{CR=0.5}$ in Figure 5-13), and it would retain this good corrosion rate up to 197°C ($1/T_{CR=5}$). The result of 127°C is consistent with titanium iso-corrosion diagrams constructed by Liu *et al.*[52], where *CR* = 0.5 mm·yr⁻¹ was observed to occur at about 125°C in a similar solution. In comparison, the S3-covered Ti-2 samples reached a *CR* of 0.5 mm·yr⁻¹ at lower temperatures of about 93°C, and attained 5 mm·yr⁻¹ when temperatures were higher than 127°C.

This higher corrosion rate suggests that titanium vessels and equipment may suffer from high corrosion rates at high temperatures due to solid deposition—it is acknowledged here that further experimental work is required to prove this.



Figure 5-13 Corrosion rate (CR) of S3-covered and control Ti-2 samples in simulated leaching solutions extrapolated to higher temperatures (inset is the measured CR data from 50 to 80°C)
Table 5-3 Kinetic parameters derived from Arrhenius plots for S3-covered and control Ti-2 samples in

	E_a (kJ·mol ⁻¹)	A	R-square
Control	51.54	2.70E6	0.9041
S3-2.5 cm	83.24	3.75E11	0.9697
S3-4 cm	82.10	2.25E11	0.9983
S3-6 cm	66.37	1.28E9	0.9996

simulated leaching solutions extrapolated to higher temperatures

5.3.2 Effect of solid deposits and temperature on the corrosion behaviour of passivated Ti-2: EIS results

EIS spectra for the S3-covered (2.5 cm) and the control samples at different temperatures are shown in Figure 5-14 and Figure 5-15, respectively. Different from that in the blank solution (with no passivating species, Figure 5-5), both the S3-covered and control Ti-2 samples show obvious passive behaviour in the simulated leaching conditions. Ti-2 has highly capacitive response in the Nyquist plot, the phase angles approaching -90° over a large frequency range of 10^{-1} to 10^{2} Hz, and large impedance magnitude of |Z| at a low frequency limit. These suggest the formation of a thin and compact passive oxide film on the metal surface [212]. It is noted that as the temperature is increased, all samples had decreased impedance, indicating decreased corrosion resistance. When the temperature increased to 70°C, the S3-covered Ti-2 (Figure 5-14) sample seemed to show a second time-constant at low frequencies, as demonstrated by the rising tail in the enlarged view. The control Ti-2 did not show this feature until the temperature was increased to 95°C (Figure 5-15).



Figure 5-14 EIS spectra of S3-covered (layer thickness = 2.5 cm) Ti-2 samples in simulated leaching solutions at 50–80°C (24 h/10°C) (a) Nyquist plots, (b) Bode magnitude and phase plots



Figure 5-15 EIS spectra of control Ti-2 samples (without deposit) in simulated leaching solutions at 50–80°C (24 h/10°C), and 95°C (1.5 h) (a) Nyquist plots, (b) Bode magnitude and phase plots

For the passive Ti-2 samples, a one time-constant EEC, $R_{sol}(R_{film}Q_{film})$ is commonly used (Figure 5-16)[10, 64]. It represents an unbroken film in which the pores are exceedingly fine or non-existent. In this case, R_{sol} is the solution resistance; R_{film} corresponds to the surface oxide film resistance; Q_{film} represents the capacitive behaviour of the oxide film. The two time-constant circuit $R_{sol}(Q_{film}(R_{film}(Q_{film}R_{film})))$ is used when the oxide film is porous and active electrochemical reactions occur (the meaning for each element is described in Section 5.1). The EIS spectra for the S3-covered Ti-2 at 70°C were fitted by both the one time-constant and two time-constant circuits, and the fitting is shown in Figure 5-17. Looking at the measured data and the fit of the Nyquist and phase plots, it is clear that the one time-constant circuit fit is not good at low frequencies. In comparison, the two time-constant circuit gives a near-perfect fit to the measured data. This indicates that faults or pores appear on the electrode surface at or near 70°C. Thus, the two timeconstant circuit was used to fit the EIS spectra of S3-covered Ti-2 at 70 and 80°C, and to fit the control Ti-2 at 95°C. The one time-constant circuit was used to fit the other EIS spectra. The fitting results are listed in Table 5-4.



One time-constant circuit Two time-constant circuit

Figure 5-16 Two electrical equivalent circuits (EECs) used to fit EIS spectra of Ti-2



Figure 5-17 Measured EIS spectra for S3-covered Ti-2 at 70°C in simulated leaching solutions and the fit by

using one time-constant circuit and two time-constant circuit

Species	R_{sol} $\Omega \cdot \mathrm{cm}^2$	Q_{film} -Y ₀ ×10 ⁻⁵ S·s ⁿ ·cm ⁻¹	<i>Q_{film}-n</i>	$R_{film} \ { m k} \Omega \cdot { m cm}^2$	Q_i -Y ₀ ×10 ⁻³ S·s ⁿ ·cm ⁻²	Q _i -n	R_{ct} k $\Omega \cdot c$ m ²	$\begin{array}{c} \chi^2 \\ \times 10^{-3} \end{array}$
50°C-control	5.4±2	4.4±0.1	$0.94{\pm}0.01$	91±10	_	—	_	4.0
50°C-S3-2.5cm	35±4	5.8±0.3	$0.91 {\pm} 0.02$	30±4	—	_	_	1.1
60°C-control	5.9±4	4.6±0.3	$0.94{\pm}0.01$	64±3	—	—	_	3.7
60°C-S3-2.5cm	29±7	4.6±0.3	$0.93{\pm}0.02$	13±0.3	_	_	_	0.8
70°C-control	9±6	5.8±0.3	$0.94{\pm}0.01$	17±2	—	—	_	1.4
70°C-S3-2.5cm	32±6	3.7±0.3	0.95 ± 0.01	3.1±0.5	1.1 ± 0.2	0.37±0.01	$1.7{\pm}0.1$	2.1
80°C-control	11±3	5.4±0.3	0.96 ± 0.02	6.1±0.5	—	—	_	_
80°C-S3-2.5cm	35±4	4.8 ± 0.2	$0.93{\pm}0.02$	1.3±0.2	4.0 ± 0.1	0.9 ± 0.04	1.2 ± 0.2	2.3
95°C-control	10±4	10±0.2	$0.90{\pm}0.05$	3.4±0.5	6.7±0.1	$0.50{\pm}0.2$	1.6 ± 0.4	1.7

T.I.I. # 4 El 4	· · · · · · · · · · · · · · · · · · ·	EEC. Lt I	L CAL TIC		E 1E
I able 5-4 Electrical	parameter values to	or EECs obtained	by fitting EIS	spectra in Figure 5-14,	2-12

As shown in Table 5-4 and Figure 5-18, the values of R_{film} decreased with increasing temperature for both the control and S3-covered Ti-2 samples, and the control sample always had a higher value than the S3-covered Ti-2 sample at a given temperature. This observation is consistent with that in Section 5.3.1, and confirmed that increasing temperature results in a decreased corrosion resistance of titanium, and the presence of solid deposits further deteriorates its corrosion-resistance.



Figure 5-18 Film resistance (R_{film}) obtained from EIS spectra of control and S3-covered (layer thickness = 2.5 cm) Ti-2 samples in simulated leaching solutions at 50–80°C (24 h/10°C) and 95°C (1.5 h)

5.4 Summary

Electrochemical investigations of Ti-2 covered by four types of inert solid deposits (S1 $(d_{0.5}: 425 \ \mu\text{m})$, S2 $(d_{0.5}: 193 \ \mu\text{m})$, S3 $(d_{0.5}: 20.4 \ \mu\text{m})$, and gypsum) in the deoxygenated blank solution $(30 \ g \cdot L^{-1} \ H_2 \text{SO}_4 + 12 \ g \cdot L^{-1} \ \text{Cl}^-)$ demonstrate that the presence of solid deposits effectively slowed the mass transfer in the corrosion process, resulted in an increased measurement of solution resistance, and slowed the corrosion rate of titanium. The barrier effect of the solid deposits on mass transfer is in the sequence of gypsum > S3 > S2 > S1. This barrier effect was mostly related

to parameters linked to pore geometry (*e.g.*, the specific surface area, grain size). It is also consistent with the solution formation resistivity factor F', which is represented by the ratio of the solution resistance in the presence of deposits to that in the absence of deposits. It is, however, important to reiterate here that the blank solution did not allow for the Ti-2 to passivate at the corrosion potential. The Ti-2 was actively corroding, whether deposits were present or not (and corrosion rates were all comparatively higher to cases where passivation was possible). This is in contrast to subsequent experiments where the effect of solids on passivated Ti-2 was evaluated.

The passivation of the initially active solid-covered Ti-2 in the simulated leaching solution was investigated in Section 5-2. The induction time associated with the passivation of Ti-2 covered by solid deposits was found to be dependent on the deposit type, and increased with increasing deposit layer thickness. The induction time was used to represent the barrier effect of the deposit layer on slowing the mass transfer of passivating species. The induction time increased in the order of gypsum > S3 > S2 > S1. Further study of individual passivating species revealed that it was the high concentration of Cu(II) present in the leaching solution, rather than any other intrinsic factor, that was responsible for the passivation of underlying Ti-2. These experiments revealed that, with few exceptions, initially active Ti-2 could be passivated even under deposits, as long as the inhibitor concentration was high enough.

The final series of experiments in Section 5-3, attempted to activate initially passive, and deposit-covered, Ti-2 by ramping up the temperature. Increasing temperature increased the corrosion rate and the covered Ti-2 appeared to show poorer performance than uncovered Ti-2. That said, Ti-2 could not be activated under the conditions tested here (up to 80°C). Extrapolation of results based on the data from 50 to 80°C suggested that increasing temperature to 127°C might result in activation of previously passive Ti-2 under deposits. Temperatures higher than 127°C and

solid deposition are commonly encountered in the hydrometallurgical industry—further experimental work would be required to confirm this.

Indirectly related to the above, galvanic cell corrosion resulting from the electrical connection between covered and uncovered portions of the same metal was investigated but not reported here. These experiments were done in neutral chloride solution, where titanium is passive and maintains stability in normal (un-deposited) conditions. This investigation demonstrated the autocatalytic characteristics of UDC due to the galvanic effect, and the results are included in Appendix B.

Chapter 6: Electrochemical investigation and identification of titanium hydrides³

Chapter 5 has demonstrated that reducing conditions can occur in hydrometallurgical autoclaves under solid deposition conditions (Section 5.2). Titanium hydrides are important corrosion products and commonly observed on the surface of titanium in reducing conditions. Titanium hydrides are closely related to the titanium stress-corrosion cracking (SCC) and hydrogen-induced cracking (HIC). They may accelerate the hydrogen evolution reaction (HER), which will further promote the production of titanium hydrides. These two processes are self-reinforcing, and the increased amount of titanium hydrides would jeopardise the titanium substrate's mechanical properties. The electrochemical effects of titanium hydrides on the HER are poorly understood. Considering the potential risks resulting from an accelerated HER, a better understanding of the electrochemical effects of titanium hydrides on the HER is critical and further investigation is required. In this chapter, titanium hydrides were generated on titanium grade 2 (Ti-2) by cathodic galvanostatic polarisation in sulfuric acid solution. The electrochemical effect of titanium hydrides on the HER is then investigated using various electrochemical techniques. Physical characterisation of the hydrides that are generated by electrolysis is also conducted.

6.1 Electrochemical results

6.1.1 Effect of galvanostatic polarisation on corrosion potential

Figure 6-1(a) depicts a typical potential transient of Ti-2 that successively underwent initial corrosion potential stabilisation after activation, cathodic galvanostatic polarisation and the

³ Yu Liu, Zihe Ren, Jing Liu, Rebecca Schaller, Edouard Asselin, "Electrochemical investigation and physical identification of titanium hydrides formed in simulated acidic leaching solution", *Journal of Electrochemical Society*, 166(11) C1–C10 (2019)

subsequent re-establishment of the stable corrosion potential in 30 $g \cdot L^{-1}$ H₂SO₄ solution at 60°C. When the sample was initially introduced into the solution, the large potential decrease of Ti-2 was due to the destabilisation of the naturally formed oxide film on the surface [45]. The initial corrosion potential values, E_{corr} , measured across all samples ranged from -0.5 to -0.6 V in the 30 $g \cdot L^{-1}$ H₂SO₄ solution at 60°C, and are illustrated in Figure 6-1(b). During the galvanostatic polarisation, after the momentary decrease in potential with the application of the cathodic current, the potential gradually increased over time, to about 0.1 V above E_{corr} over the 5 h polarisation as shown in Figure 6-1(a). The potential increase for Ti-2 during galvanostatic polarisation was also observed by other researchers in acidic solutions (15.8 g \cdot L⁻¹ NaCl + 21.9 g \cdot L⁻¹ HCl solution [63], 148 g·L⁻¹ tartrate buffer at pH 2.2) [85]. This potential increase indicates the decreased overpotential of the cathodic reduction reaction, which corresponds to the HER in the acidic solution investigated here [226, 227]. When the cathodic polarisation ceased, the potential of the Ti-2 with galvanostatically-generated hydrides rapidly increased and a new corrosion potential value, E'corr, was established. For the investigated condition, E'corr was consistently more positive than E_{corr} . The statistical distribution of E_{corr} and E'_{corr} from ten tests are displayed in the box and whisker chart in Figure 6-1(b). The average E_{corr} value was -0.55 V, while the average E'_{corr} was -0.29 V. The corrosion potential values indicated that prior to galvanostatic polarisation, the Ti-2 samples were in the active corrosion state, whereas post-polarisation, the Ti-2 samples were passivated [49, 50]. These potential measurements provided preliminary information indicating the state change of titanium due to the cathodic modifications, *i.e.*, hydride formation. For a better understanding of the surface state generated by the cathodic modifications imposed on the Ti-2, electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarisation were conducted.



Figure 6-1 (a) Potential transient of Ti-2 during cathodic galvanostatic polarisation (Note E_{corr} , E'_{corr} are the respective corrosion potentials pre and post cathodic galvanostatic polarisation), (b) statistical analysis of

*E*_{corr}, *E*'_{corr} (Max -, 99% ×, Mean \Box ,1%×, Min -) in 30 g·L⁻¹ H₂SO₄ solution at 60°C

6.1.2 Effect of galvanostatic polarisation on corrosion resistance

Representative EIS curves for the Ti-2 samples with galvanostatically-formed hydrides compared to a control sample which was without galvanostatically-generated hydrides are shown in Figure 6-2. The Ti-2 samples with hydrides formed at cathodic current densities of 0.1, 0.5, and 1 mA·cm⁻² displayed a single loop of capacitive behaviour, which was indicated by the phase angles approaching 90° over a large frequency range from medium to low frequencies (1–100 Hz). This behaviour suggested the formation of a thin and stable oxide film on the surface [134, 213]. In comparison, the control sample demonstrated two peaks on the phase angle plot, indicating two time constants. The magnitude of the impedance, |Z|, obtained at the low frequency limit represents the corrosion resistance of titanium in the investigated system [228, 229]. The |Z| of the samples with galvanostatically formed hydrides was significantly higher than that of the control sample, indicating the superior corrosion resistance of the former.

The electrical equivalent circuits (EECs), $R_{sol}(R_{film}Q_{film})$ and $R_{sol}(Q_{film}(R_{film}(R_{ct}Q_{i})))$, have previously been used to fit the impedance spectra of titanium [134, 211-214], and they were both used to fit the EIS results in this work. In the one time constant EEC, $R_{sol}(R_{film}Q_{film})$, represents an unbroken film in which the pores are exceedingly fine or non-existent. In this case, R_{sol} is the solution resistance; R_{film} corresponds to the surface oxide film resistance and the parallel constant phase element (CPE), Q_{film}, represents the capacitive behaviour of the oxide film. The two time constants EEC, $R_{sol}(Q_{film}(R_{film}(R_{ct}Q_i)))$ represents the case where the oxide film has pores where the active electrochemical reaction occurs. This model has been widely applied to interpret electrode kinetics for metals covered with porous films [230, 231]. In this EEC, R_{sol} is the solution resistance; R_{film} and Q_{film} correspond to the surface oxide film resistance and the capacitive behaviour of the oxide film, respectively; the other R-CPE pair of R_{ct} and Q_i account for the charge transfer kinetics and the capacitance of the electrical double layer, respectively [64]. In Figure 6-2, the two time constants (R-CPE pairs) were clearly observed on the control sample, which was actively corroding in the acidic solution. However, the two *R-CPE* pairs were not observed, or cannot be observed as distinct from one another, on the titanium with galvanostatically formed hydrides. Therefore, the two-time constant EEC was used to model the control sample, and the simple one-time constant EEC was used to model the titanium samples with hydrides formed at various galvanostatic values. The good fit of the models to data is evaluated by the chi-squared (χ^2) values and evident in Figure 6-2. The constant phase element, instead of a capacitor, was adopted here to compensate for the non-ideal capacitive behaviour of the surface and the distribution of relaxation times resulting from different degrees of heterogeneities at the electrode surface [64, 215, 216]. The fitting results from ZsimpWin are shown in Table 6-1.



current densities for 5 h compared to a control sample in 0.31 M H₂SO₄ solution at 60°C (a) Nyquist plots, (b) Bode magnitude and phase plots

The fitting results in Table 6-1 clearly show that the Ti-2 with galvanostatically formed hydrides demonstrated a significant increase of R_{film} in comparison with the control sample. That is, R_{film} for the Ti-2 samples with galvanostatically formed hydrides ranged from 4 to 5 k Ω ·cm², while R_{film} of the control sample was only 0.12 k Ω ·cm², indicating the porosity of the surface film. Combined with the small magnitude of the R_{ct} (0.14 k Ω ·cm²), the EIS results suggest an active corrosion state for the control sample. These results agree with the findings for corrosion potential in Figure 6-1. The protective oxide film identified *via* EIS, which formed after cathodic polarisation, corresponds to the passivation revealed by the corrosion potential measurements. In comparison, the control sample still displayed active corrosion and the lack of a protective film. The magnitude of the applied cathodic current density did not significantly affect the corrosion behaviour of Ti-2 post galvanostatic polarisation.

Galvanostatic polarisation (mA·cm ⁻²)	R_{sol} ($\Omega \cdot \mathrm{cm}^2$)	$\begin{array}{c} Q_{\mathit{film}} extsf{-} extsf{Y}_0 \ (imes 10^{-5} \ extsf{S} \cdot extsf{s}^n \cdot extsf{cm}^{-2}) \end{array}$	Q _{film} -n	R_{film} (k $\Omega \cdot \mathrm{cm}^2$)	Q_{i} -Y ₀ (×10 ⁻² S·s ⁿ ·cm ⁻²)	Q _i -n	R_{ct} (k Ω ·cm ²)	χ ² (×10 ⁻³)
Control Ti	9.3±0.05	45±3	0.92±0.01	0.12±0.003	3.1±0.2	0.91±0.01	0.14±0.02	1.8
-0.1	9.0±0.03	16±2	0.92±0.01	4.8±1.1	_	_	_	2.3
-0.5	9.6±0.01	20±1	0.90±0.01	4.9±0.4	_	_	_	1.6
-1.0	13±0.1	17±2	0.92±0.01	4.3±0.5	_	_	_	4.9

Table 6-1 Electrical parameters for the EECs used to fit the EIS impedance spectra

"±" represents the scatter from the replicated experiments

6.1.3 Effect of hydride formation on subsequent anodic polarisation

Representative potentiodynamic polarisation (PD) curves of the Ti-2 samples with galvanostatically formed hydrides compared to a control sample are shown in Figure 6-3. The control sample was initially in the active state and displayed an anodic current peak prior to passivation. The samples with galvanostatically formed hydrides, however, were spontaneously in the passive state or displayed an active-passive transition that was reduced by greater than an order of magnitude. There was no active region apparent from the polarisation measurements. The magnitude of the cathodic current densities was found to slightly influence the passivity of titanium. The titanium with the hydrides formed at larger cathodic current densities, displayed a more evidently reduced active-passive transition in the PD curve than that formed at smaller cathodic current densities. This indicates that the larger cathodic current densities may slightly enhance the passivity of titanium. This influence was relatively small, which was manifested by the small difference between the current densities in the transition region (< 3 μ A·cm⁻²), thus this finding is not conclusive.

As the potential shifted positively, the anodic reaction in the active corrosion region (< -0.3 V) for the control sample was [45, 63]:

$$Ti \rightarrow Ti^{III} + 3e^{-}$$
 Equation 6-1

in the passive region (> -0.2 V) it was:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$$
 Equation 6-2

and the following reaction, which may also be attributed to the observed current density in the transition region:

$$Ti^{III} \rightarrow Ti^{IV} + e^{-}$$
 Equation 6-3



Figure 6-3 Anodic PD for Ti-2 samples with hydrides galvanostatically formed at different cathodic current densities compared to a control sample in 30 g·L⁻¹ H₂SO₄ solution at 60°C

6.1.4 Effect of hydride formation on cathodic polarisation

Figure 6-4(a) displays the current density transients observed on the control sample during stepwise cathodic potentiostatic polarisation (PS). At each discrete potential, rather than maintaining a constant magnitude, the cathodic current density increased during the polarisation duration (3 ks). The inset in Figure 6-4(a) displays an example of the increasing current density

over time at -0.10 V vs. E_{corr} , *i.e.*, -0.65 V. As demonstrated in Figure 6-4(a), this increase in current became more obvious when the magnitude of the potential was greater than -0.35 V below E_{corr} . The increase in the magnitude of the current density over time during cathodic PS was previously observed by other researchers in low pH solution at negative potentials [63]. The current density increase at constant potential suggests an increasing cathodic reduction reaction rate, in this case corresponding to the HER.

The current density recorded at the end of each potential step is plotted versus applied potential in Figure 6-4(b) and compared to the current density versus potential relationship obtained from PD. The magnitudes of the current densities obtained from PS were larger than those obtained from PD at comparable potentials when the potential decreased below -0.7 V. This difference was accentuated as the potential became more negative.



Figure 6-4 (a) Current density transients for Ti-2 under cathodic PS, (b) current density versus potential relationship obtained from PS (terminal current densities are displayed) and from PD

6.2 Characterisation of the titanium hydrides

6.2.1 Characterisation of the Ti-2 substrate

Figure 6-5 displays the X-ray diffraction (XRD) spectra for the Ti-2 substrate examined in this work, compared to the titanium standard powder diffraction pattern (44-1294). The titanium examined in this work displayed a preferred orientation in the (002) direction. The presence of this preferred orientation (002) can be attributed to the manufacturing process, such as rolling [92], and is commonly observed among titanium materials.



Figure 6-5 Comparison of the XRD pattern for, (a) titanium standard powder, and (b) Ti-2 substrate examined in this work

Commercially pure titanium is α phase and has a hexagonal close packed (HCP) crystal structure at low temperatures [232]. Figure 6-6(a) shows the primary α grains [233]. There were noticeable particles/lamellae distributed across the whole surface, and these might be dislocations introduced during sample preparation, which are commonly observed on ductile metals. As shown in Figure 6-6(b), the Ti-2 material examined here had an average grain size of 30 µm and a split basal texture with most of the c-axes located at approximately ±25–35° away from the normal

direction (ND) toward the transverse direction (TD) (Figure 6-6(c)). This type of rolling texture is typical for commercially pure titanium [92]. This finding was consistent with the XRD pattern obtained over the θ -2 θ measurement, and confirmed the preferred orientation of the Ti-2 substrate.



Figure 6-6 Microstructure of Ti-2 substrate (a) SEM back scattered image, (b) EBSD micrograph of the mapped area along with the stereographic triangle and (c) (0001) pole figure

6.2.2 Effect of galvanostatic polarisation on the hydrogen distribution

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is widely used to study surface composition due to its high molecular specificity and surface sensitivity [234, 235]. In ToF-SIMS, a pulsed primary ion beam (Cs or microfocused Ga) is used, which generates secondary species. These secondary ions are extracted into an analyser by a high voltage potential and their mass is determined by measuring their time-of-flight from the sample to the detector. The mass spectrum and secondary ion images can then be used to obtain composition, distribution and molecular information of surface constituents [236]. The Ti-2 sample after cathodic galvanostatic polarisation was examined by ToF-SIMS. A representative three-dimensional (3D) image of hydrogen distribution in the Ti-2 sample after galvanostatic polarisation ($-0.1 \text{ mA} \cdot \text{cm}^{-2}$ for 5 h), compared with a control sample is shown in Figure 6-7. These images provide a visualisation of the hydrogen distribution (denoted as H, from all possible hydrogen species) at the surface of titanium. They were constructed from a depth of 0 nm (at the surface) to about 208 nm 112

into the hydrided surface. The 3D views show a higher concentration of H in the titanium samples after galvanostatic polarisation than in the control sample. The H in the control sample may be introduced during manufacturing processes or sample preparation, *i.e.*, grinding and polishing prior to testing [97]. The 3D view demonstrates that H is not evenly distributed in titanium, *i.e.*, it has a clustered and localised distribution. This finding is consistent with that reported by Yan *et al.* on the non-uniform characteristics of hydride layers [63]. Based on SIMS imaging results, they also found that the non-uniform distribution of hydrides was due to their preferential formation at iron-containing intermetallic particles located along grain boundaries.



Figure 6-7 Mass resolved 3D views of the hydrogen distribution on the surface of, (a) a Ti-2 sample after cathodic galvanostatic polarisation (-0.1 mA·cm⁻² for 5 h in 30 g·L⁻¹ H₂SO₄ solution at 60°C), and (b) a control sample (polished, but was not galvanostatically polarised)

Figure 6-8 shows the H concentration, in counts ratio versus depth, for the titanium sample after galvanostatic polarisation and the control sample shown in Figure 6-7. The detected H signal intensity was normalised with respect to the peak intensity of the substrate Ti-2, which was the dominant peak in the spectrum. The results clearly demonstrate the higher H concentration in the Ti-2 after cathodic galvanostatic polarisation than in the control sample over the test depth range. The concentration difference in counts ratio was about 0.013 at the surface, and 0.0075 with depth 113 below the surface. The origin for the observed slight drop in hydrogen concentration at about 50 nm is not yet known. For both the galvanostatically polarised and control samples, the H concentration was relatively higher on the surface and reached a constant concentration with depth into the sample. The results also indicate that the absorption of H into titanium may not be limited to the near surface region, but instead it penetrates the substrate over the depth tested here. Due to limited depth detection with this technique, the ultimate diffusion depth of H in the Ti-2 substrate was not obtained. Based on the reported hydrogen diffusion coefficient for α -Ti at 60°C, 1.7 × 10⁻⁶ $cm^2 \cdot s^{-1}$ [237, 238], and an assumption of constant-flux boundary conditions and steady state diffusion in an infinite plane, the diffusion depth of hydrogen over 60 h could reach up to 4 mm [237-239]. This assumes a constant H diffusivity in α -Ti over the entire charging period and does not account for the influence of hydrides on the diffusion coefficient. Hydrides have been reported at depths of 10 to 200 µm during cathodic galvanostatic polarisation [55, 56, 63, 79]. Although ToF-SIMS does not provide sufficient depth measurement to capture the diffused hydrogen concentration, it does provide pertinent information with regards to the near surface distribution of hydrogen.



Figure 6-8 ToF-SIMS depth profiles of normalised hydrogen intensity (I_H/I_{Ti})

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6.2.3 XRD characterisation of the titanium hydrides

Figure 6-9(a) shows the XRD spectra for Ti-2 samples after galvanostatic polarisation at different current densities for 2 h. The majority of the diffraction peaks displayed were from the Ti-2 substrate and compared well to the reference standard titanium powder data (44-1294). However, the peak at $2\theta = 35.9^{\circ}$, indicated with the triangular symbol in Figure 6-9(a), corresponds to the (111) plane of the TiH_{1.7} phase (78-2215). In addition, the peak at $2\theta = 41.0^{\circ}$ corresponds to the (200) plane of TiH_{1.5} (78-2216) and is indicated with the square symbol. Trace amounts of TiH₂ may also exist but this was difficult to resolve as the peak positions for TiH₂ are close to those for TiH_{1.5}. The peak at $2\theta = 59.5^{\circ}$ is the diffraction from all of the hydride phases present (TiH_{1.7}, TiH_{1.5} and TiH₂) without interference from the Ti-2 substrate, and it is marked with a circle. The XRD results demonstrate that the hydrides formed for this condition (galvanostatic polarisation with cathodic current densities between -0.1 and -0.5 mA·cm⁻² in 30 g·L⁻¹ H₂SO₄ solution at 60°C) consisted of TiH_{1.7}, TiH_{1.5}, and with possible trace amounts of TiH_{2.5}/TiH₂), instead of a single TiH₂ phase as some have reported previously [97-99].

The hydrides (TiH_{1.7}, TiH_{1.5}/TiH₂) formed at different cathodic current densities were semi-quantitatively analysed based on the XRD results. The strongest intensity peak for each hydride phase was normalised with respect to the strongest titanium substrate peak ($2\theta = 40.2^{\circ}$) in each spectrum and the results are displayed in Figure 6-9(b). Figure 6-9(b) demonstrates the relative amount of the two hydride phases, *i.e.*, TiH_{1.7} *vs*. TiH_{1.5}/TiH₂. As shown in Figure 6-9(b), TiH_{1.7} was only a small percentage of the total hydrides, whereas the TiH_{1.5}/TiH₂ phases were dominant. Information on the hydride formation behaviour can also be inferred from Figure 6-9(b). The formation of TiH_{1.7} was only slightly influenced with increasing cathodic current density. The amount of TiH_{1.5}/TiH₂ increased when the magnitude of the cathodic current density was increased from 0.1 to 0.5 mA·cm⁻², while further increase of the cathodic current density to 1 mA·cm⁻² did not result in significant formation. The reduced production of titanium hydrides at higher cathodic current densities could be related to the saturation of the surface hydrogen concentration as current density increased [240], as well as increased diffusion resistance for hydrogen through the surface hydride layer to the metal/TiH_x interface upon hydride formation [59, 64, 79, 100]. This is consistent with previous work that reported hydrogen absorption efficiency decreased and hydride layer thickness was independent of the applied cathodic current density when it was larger than 0.5 mA·cm^{-2} [63]. However, the limitations of XRD makes quantitative analysis difficult, and the information provided here can be regarded as a general understanding of the trend of hydride formation under the investigated condition.



Figure 6-9 (a) XRD spectra of Ti-2 hydrides formed at various cathodic current densities for 2 h in 30 g·L⁻¹ H₂SO₄ solution at 60°C, and (b) the normalised intensities of TiH_{1.7} and TiH_{1.5}/TiH₂ versus the cathodic

current density applied for formation

The dependence of titanium hydride formation on the charging duration was also analysed *via* XRD and these results are shown in Figure 6-10(a). For Ti-2 samples after cathodic polarisation at a cathodic current density of 0.1 mA·cm⁻², the titanium hydrides formed were TiH_{1.7} and

TiH_{1.5}/TiH₂, and they were present during the full course of polarisation up to 60 h. Semiquantitative normalised intensities of TiH_{1.7} and TiH_{1.5}/TiH₂ are shown in Figure 6-10(b). TiH_{1.5}/TiH₂ remained the dominant phases. The formation of TiH_{1.5}/TiH₂ increased with time during the test duration. The overall amount of TiH_{1.7} increased when the charging duration increased from 2 h to 5 h, and no obvious increase was found with further increase of charging duration. The linear increase of TiH_{1.5}/TiH₂ formation with time (up to 60 h) may represent the trend of overall production of hydrides over time. The hydride production *vs.* time results are consistent with previous observations from Phillips *et al.* (in 4.9 g·L⁻¹ H₂SO₄ solution at 25°C in the cathodic current range of 0.05–3.0 mA·cm⁻²)[79], who found a linear increase in hydride production with time and a parabolic increase with time when the charging duration exceeded those studied here (from 60–160 h).



Figure 6-10 (a) XRD spectra of Ti-2 cathodically polarised at 0.1 mA·cm⁻² for different durations in 30 g·L⁻¹ H₂SO₄ solution at 60°C, and (b) the normalised intensities of TiH_{1.7} and TiH_{1.5}/TiH₂ versus the charging

duration

6.3 Discussion

6.3.1 Effect of titanium hydrides on the hydrogen evolution reaction

Figure 6-4(a) demonstrates the unsteady-state current density obtained during cathodic potentiostatic polarisation, *i.e.*, the increasing cathodic current density at each potential over the time duration of the step. The cathodic current corresponds to the HER. Thus, the increasing current density indicates an accelerating HER rate. One possible explanation for the enhanced rate of HER is the formation of titanium hydrides. The formation of titanium hydride phases has been thermodynamically elucidated by previous researchers, and demonstrated in the E_h -pH diagram of titanium [16, 45]. The electrochemical reaction pertaining to the formation of the titanium hydride phase TiH₂, the only one for which the thermodynamic data are available in the standard reference works [241], is shown in Equation 6-4. For the investigated condition, *i.e.*, 30 g·L⁻¹ H₂SO₄, at 60°C, the thermodynamically stable region of titanium hydride phases was calculated to be below 0.21 V vs. Ag/AgCl. This value is consistent with a previous report [16].

$$Ti + 2H^+ + 2e^- \rightarrow TiH_2$$
 Equation 6-4

Titanium hydrides formed simultaneously with the HER during the cathodic polarisation. Their presence may provide active sites for the HER to occur at, and account for the increasing current density [63]. This accelerating HER in the presence of hydrides has been suggested by other researchers [35, 38, 55, 58, 63, 65, 84, 85, 227, 242-244]. The increased HER indicates more hydrogen will be reduced, resulting in the formation of more titanium hydrides, which further catalyse the HER. This self-catalytic process leads to the current increase observed here.

ToF-SIMS gave evidence of enhanced near surface hydrogen concentrations after cathodic polarisation, which in part could be attributed to hydride formation. Additionally, evidence of

hydrogen clustering was observed (Figure 6-7), which may be due to enhanced grain boundary diffusion of H or preferential formation of hydrides at the grain boundaries [63, 238].

The oxide film on the surface of the electrode may also influence this process through film removal and/or redox transformation [63, 227]. In the present work, the titanium sample was initially activated to eliminate the effect of the naturally formed oxide film on the surface. Even if some oxide film residue remained post-activation, the oxide film would quickly reduce to Ti^{III} species in the acidic solution when the potential decreased below -0.55 V [245]. Thus, the residual oxide film on the surface cannot account for the increasing current density during polarisation.

Based on the hydride catalysis mechanism, the larger current density observed during cathodic PS than PD would be expected (Figure 6-4(b)). The long-term cathodic potentiostatic polarisation promoted the formation of titanium hydrides, which accounted for the increased cathodic current density by the self-catalytic increase in the reaction rate of the HER. In comparison, due to the rapid scan rate, the amount of hydrides formed during potentiodynamic polarisation was negligible. Thus, the higher cathodic current density observed during potentiostatic polarisation versus potentiodynamic polarisation was due to the increased formation of hydrides. The increased magnitude of cathodic current obtained from cathodic PS as compared to PD could be interpreted as being due to the increase of the cathodic current magnitude over the whole suface, however, it cannot explain the results of corrosion potential (Figure 6-1), EIS (Figure 6-2), and anodic polarisation (Figure 6-3)), which demonstrated the passivation of Ti-2 with hydrides formed on the surface. The passivation of titanium can be facilitated *via* the acceleration of cathodic current per unit area, *i.e.*, current density.

The mechanism of titanium passivation can be explained by the schematic diagram in Figure 6-11 based on mixed potential theory [246]. In Figure 6-11, A represents the anodic polarisation curve corresponding to the oxidation of titanium; curves marked C represent the cathodic reaction, which corresponds to the HER under the conditions investigated here. Initially, the cathodic reaction proceeded as C_I , and the corrosion potential of the system obtained was E_{corrI} . When the cathodic reaction was accelerated and moved to C_2 , multiple corrosion potential points could be observed in the system (as the control sample in Figure 6-3). As the cathodic reaction moved to C_3 , where the cathodic current exceeded the critical current for the passivity of titanium, i_{crit} , the titanium was successfully passivated. This last scenario is believed to have occurred after the formation of surface hydrides in the investigated condition. The hydrides self-catalysed and enhanced the HER, thus increasing the cathodic current density, and passivating titanium. This explains the passivation of Ti-2 samples as demonstrated by the corrosion potential, EIS and PD results when titanium hydrides were generated *via* the galvanostatic polarisation.



Figure 6-11 Schematic diagram of titanium passivation by the accelerated cathodic reaction

6.3.2 Parameters influencing titanium hydride phase formation

The phase characterisation results revealed that the hydrides formed in this work were a mixture of TiH_{1.7}, TiH_{1.5}, and/or TiH₂ (trace), with the TiH_{1.5} being the main constituent for the investigated conditions. Due to the large disparities in the ionic radii between titanium (0.86 Å [247]) and H (1.0–1.4 Å [248]) atoms and the high compressibility of H⁻ ions, metastable (amorphous) Ti-H phases may occur at the interface between the hydride and substrate to accommodate the strain between the titanium and TiH_x crystals. This may give rise to several different allotropic forms of titanium hydrides. In this work, however, TiH_{1.5} was the main constituent under all magnitudes of the cathodic charging current density and charging durations. The hydride phase of TiH_{1.5} observed here is consistent with Numakura and Koiwa [75] based on their electron diffraction and electron microscopy results. In their work, the hydrides were formed by gas-equilibration method in the concentration range between 1 and 3 at.% hydrogen or deuterium at high temperatures (773 K for about 10 h, and then furnace cooled at a rate of 1 K·min⁻¹).

The preferential formation of TiH_{1.5} to other hydrides with higher hydrogen concentration, *i.e.*, TiH_{1.7} and TiH₂, may be associated with volume misfit, substrate texture, solid solution formation, and/or preferred orientation, *etc.* Numakura and Koiwa [75] related the formation of TiH_{1.5} to the volume misfit between the hydrides and matrix. The formation of TiH_{1.5} resulted in a smaller relative volume increase than other hydrides with higher H concentrations [75]. Additionally, the substrate properties, such as the texture or microstructure *etc.*, are believed to influence the surface product formation [87-90, 249], *i.e.*, hydrides in this case. Ti-2 substrate used here is an α -matrix hexagonal close-packed structure. TiH_{1.5} is a δ phase with cubic close packed structure (space group = Fm-3m) and TiH_{1.7} is a base-centered orthorhombic structure (space group = Cccm) [93]. According to the phase diagram [75, 93], the α -matrix titanium can form a solid solution with δ phase titanium hydrides, *i.e.*, TiH_{1.5}, but not with TiH_{1.7} or TiH₂. That may be another reason for the preferential formation of TiH_{1.5}. Lastly, it was noticed that TiH_{1.5} showed preferred orientation. By subtracting the substrate titanium pattern from the measured pattern, the preferred orientation of TiH_{1.5} for the investigated conditions can be estimated and is shown in Figure 6-12. For the standard (randomised) TiH_{1.5}, the relative intensity of I₍₂₀₀₎ (the ratio of I₍₂₀₀₎/to the strongest peak I₍₁₁₁₎, I₍₂₀₀₎/I₍₁₁₁₎) is 0.426. For the results presented here, the relative intensity of I₍₂₀₀₎ was 0.875, which suggested that the (200) plane was the preferred plane in TiH_{1.5}. The preferred orientation of TiH_{1.5} might be related to the titanium substrate. Millenbach and Givon [92] suggested the close relation of the titanium (002) plane to the hydride (200) plane and this became the initial point for the cubic hydride lattice, TiH_{1.5}, to grow from. Further calculation and investigation is needed to relate the development of TiH_{1.5} from the Ti-2 substrate.



Figure 6-12 Ti_{1.5} phase obtained by subtracting substrate pattern from the overall pattern

6.4 Summary

Titanium hydrides were generated by galvanostatic polarisation of Ti-2 in acidic solutions. Titanium hydrides may catalyse the HER, increase the cathodic current densities, and therefore result in the passivation of Ti-2. In comparison with a control Ti-2 sample, the Ti-2 with galvanostatically formed hydrides showed an increased E_{corr} (from -0.55 V to -0.29 V), and a significant oxide film resistance of 4 to 5 k Ω ·cm².

ToF-SIMS measurements revealed increased H concentrations in the galvanostatically polarised sample with a clustered distribution of H in the near surface region of the titanium substrate. The XRD results demonstrate that the generated hydride phases were mainly TiH_{1.5}, and small amounts of TiH_{1.7} and/or TiH₂ (trace). The preferential formation of TiH_{1.5} may be due to its smaller volume misfit between the hydrides and matrix, ability to form solid solution with the α matrix titanium, and association with the texture of the underlying Ti-substrate. However, further research regarding the correlation between the Ti-substrate and the preferred TiH_{1.5} hydride formation is necessary. If established, this relationship could increase the understanding of hydride formation and develop the potential for tuning the corrosion resistance behaviour of titanium. Reducing conditions can occur in hydrometallurgical Ti-lined autoclaves during upset conditions or possibly during normal operation when oxidation-reduction potential (ORP) is low for various process reasons, and titanium hydrides are expected to form in these conditions. The investigation and understanding of titanium hydrides is important for maintaining the integrity of these titanium vessels and equipment.

Chapter 7: Effect of Fe(III) and Cu(II) on the passivation of Ti-2^{4, 5, 6}

Fe(III) and Cu(II) species are commonly present in aggressive leaching solutions, and, as shown in Chapter 5, they can passivate Ti-2 and maintain its passivity even when the metal surface is covered with deposits. However, the quantitative effectiveness of Fe(III) and Cu(II) species on titanium passivation is unclear. Furthermore, the influence of temperature on their effectiveness, which commonly varies over a broad range in hydrometallurgical extraction also goes unreported. This chapter quantitatively identifies, by electrochemical techniques, the passivation of titanium grade 2 (Ti-2) *via* the addition of Fe(III) and Cu(II) species to the blank solution (sulfuric acid-chloride). The effect of temperature on the critical concentrations of Fe (III) and Cu(II) species required to induce passivation is also determined from 30 to 80°C. The results provide practical data for the corrosion prediction and protection of titanium vessels and equipment in the hydrometallurgical industry.

7.1 Electrochemical results

7.1.1 Critical concentration of Fe(III) and Cu(II) species to passivate Ti-2

Figure 7-1(a) shows the corrosion potential, E_{corr} , of Ti-2 as a function of the Fe(III) concentration in the blank solutions from 30 to 80°C. At a given temperature, incrementally

⁴ Yu Liu, Rebecca Schaller, Edouard Asselin, "Effect of Fe(III) and Cu(II) on the passivation of Ti-2 in acidic chloride solutions", *Journal of Electrochemical Society*, 166(2) C76–C82 (2019)

⁵ Yu Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in simulated leaching solutions", *Hydrochair Poster Session*, September (2018), The University of British Columbia, Vancouver, BC, Canada

⁶ Yu Liu, Jing Liu, Rebecca Schaller, Edouard Asselin, "Effect of solid deposits on the corrosion behaviour of titanium in the leaching solutions", *China-Canada Nonferrous Metallurgy Forum*, July (2018), Northeast University, Shenyang, China

increasing Fe(III) concentration resulted in an immediate increase of E_{corr} of about 20 mV, which eventually leveled off to the values shown in Figure 7-1(a) (the representative potential change as function of time was shown in the insert graph). Once the Fe(III) concentration reached a certain value, an abrupt potential increase was observed, indicating the passivation of Ti-2. This value therefore corresponded to the critical Fe(III) concentration required to passivate Ti-2 for the indicated temperature. Above the critical Fe(III) concentration, the potential increase with incremental Fe(III) was again small. The linear polarisation resistance, R_p , of Ti-2 as a function of the Fe(III) concentration is shown in Figure 7-1(b). At a given temperature, the Ti-2 had a low R_p value (100–1000 $\Omega \cdot \text{cm}^2$ in the investigated condition) when the concentration of Fe(III) was below the critical value. However, R_p increased significantly when the Fe(III) concentration attained the critical value. The critical Fe(III) concentration identified by the R_p measurements was consistent with the potential transients in Figure 7-1(a). Above the critical concentration, R_p leveled off.

The critical Fe(III) concentration, which was determined from E_{corr} and R_p results, was highly dependent on temperature. Figure 7-1 shows that both the E_{corr} and R_p curves shifted to the right, *i.e.*, the critical Fe(III) concentration increased with temperature.

The passivation of Ti-2 by Cu(II) is shown in Figure 7-2. E_{corr} in Figure 7-2(a) and the R_p data in Figure 7-2(b) reveal the critical Cu(II) concentration required for passivation at various temperatures. The trends are similar to those observed for Fe(III), but the Cu(II) concentration required for passivation is less than for Fe(III). However, the addition of Cu(II) generally resulted in lower R_p values than Fe(III) once passivation had been attained when the temperature was higher than 30°C, indicating the slightly smaller corrosion resistance of titanium in the indicated condition. A similar phenomenon was also reported by Liu *et al.*[10], where the modest addition of Fe(III) (1.0 g·L⁻¹) enhanced the corrosion resistance of titanium more significantly than Cu(II)

(15 g·L⁻¹). The higher corrosion resistance of Ti-2 achieved by Fe(III) than that of Cu(II) was further verified in the following parts.



Figure 7-1 (a) E_{corr} of Ti-2 with the incremental increase of Fe(III) concentration, (b) R_p of Ti-2 with the incremental increase of Fe(III) concentration in blank solutions (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻)



Figure 7-2 (a) E_{corr} of Ti-2 with the incremental increase of Cu(II) concentration, (b) R_p of Ti-2 with the

incremental increase of Cu(II) concentration in blank solutions (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻)

The critical concentration of Fe(III) and Cu(II) required to passivate Ti-2 at various temperatures is shown in Figure 7-3. The minimum concentration of Fe(III) and Cu(II) required to passivate Ti-2 increased with temperature. The critical concentration of Fe(III) increased from 1.0

 \pm 0 to 6.0 \pm 0 mM, and Cu(II) from 0.25 \pm 0 to 1.15 \pm 0.23 mM, when temperature increased from 30 to 80°C. Figure 7-3 shows again that Cu(II) was more effective in promoting the passivation Ti-2 even though Fe(III)/Fe(II) results in a higher oxidation reduction potential [250]. Specifically, at the same temperature, 4 times more Fe(III) than Cu(II) was needed to passivate the Ti-2.

It is also noticed that R_p values recorded in the presence of both cations decreased as the temperature increased in particular when the temperature was higher than 50°C (Figure 7-1(b), Figure 7-2(b)). The decrease of R_p indicated a degradation of the titanium oxide film's protective properties at higher temperatures, which may be attributed to the film breakdown and/or a crystallisation process. Titanium oxide films are reported to undergo a breakdown crystallisation process at temperatures higher than 60°C, or at applied potentials in the 4–8 V range [251, 252]. Breakdown crystallisation is an important phenomenon for titanium oxide films in terms of the oxide growth rate, composition, structure, and corrosion resistance because it may create grain boundaries and cracks, thus resulting in a decreased corrosion resistance [219, 220]. Noël [55] and He et al. [134] observed a significant corrosion resistance drop for Ti-2 in the temperature range 40–60°C, and at temperatures higher than 65°C, respectively, in 15.8g·L⁻¹ NaCl. The observed R_p decrease at high temperature in the present work is consistent with their results and the oxide film breakdown recrystallisation mechanism. The slight variation of the critical temperatures reported among various researchers may be caused by differing environmental factors, such as solution composition, oxide film formation time, test methods, etc.[253].

 E_{corr} did not change obviously when the oxide film appeared to suffer breakdown crystallisation. During the breakdown crystallisation process, the oxide film continues to demonstrate corrosion resistance (as high as $10^4 \ \Omega \cdot cm$ [55, 134]) and titanium remains in the passive state. Within the broad, low-current passive region, the value of E_{corr} is subject to the influence of various redox couples present in the solution, *i.e.*, Fe(III)/Fe(II) or Cu(II)/Cu(I) reactions, and may also occur from reactions occurring at localised sites that do not represent the state of the vast majority of the surface. The value of E_{corr} may then settle at an appropriate potential anywhere in this region [55]. Thus the E_{corr} results do not show any meaningful trend with increasing temperature, as suggested by Noël [55]. In addition, the E_{corr} values reported in our work may not always reach a steady state because of the relatively short test duration. Thus, the diagnostic significance of the E_{corr} values is relatively low in comparison to the R_p values.



Figure 7-3 Critical concentrations of Fe(III) and Cu(II) to passivate Ti-2 with temperatures in blank solutions $(30 \text{ g}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4 + 12 \text{ g}\cdot\text{L}^{-1} \text{ Cl}^-)$

7.1.2 The critical current for the passivity of Ti-2

Anodic potentiodynamic polarisation (PD) was conducted to measure the critical current density for passivity of titanium in the blank solution at different temperatures, and the results are shown in Figure 7-4. It is clear that as temperature was increased, the critical potential for passivity of Ti-2, E_{crit} , remained constant (-0.54 V), however, the critical current density for pasivity of titanium, i_{crit} , increased from 0.114 mA·cm⁻² at 40°C to 1.17 mA·cm⁻² at 80°C. The temperature independence of $E_{passive}$ and the temperature dependence of $i_{passive}$ agree with other studies, such as

in 1 N HCl [18], 4.9 g·L⁻¹ H₂SO₄ containing 7.1 g·L⁻¹ Na₂SO₄ [35], 6 N H₂SO₄ [254], and 19.6 g·L⁻¹ H₂SO₄ [36].



Figure 7-4 Anodic PD curves of Ti-2 in blank solutions (30 $g \cdot L^{-1} H_2 SO_4 + 12 g \cdot L^{-1} CI^-$) at 40°C, 60°C, and 80°C. *C* represent the cathodic polarisation curves

7.1.3 Cathodic process of Ti-2 in the presence of Fe(III) and Cu(II) species

The cathodic process when Fe(III) species were present was analysed *via* cathodic PD. Figure 7-5 shows the cathodic polarisation curves for passive Ti-2 in the presence of 6 mM Fe(III) at 40, 60, and 80°C. The polarisation curves in the absence of Fe(III) are also presented. In the presence of 6 mM Fe(III) species, Ti-2 was well passivated and showed significantly higher cathodic current density than Ti-2 in the blank solution with the absence of Fe(III) species. According to the characteristics of the cathodic polarisation curves, the polarisation curves of Ti-2 in the presence of Fe(III) can be divided into three potential regions, I, II, and III as shown in Figure 7-5.

When 6 mM Fe(III) was added to the blank solution (30 $g \cdot L^{-1} H_2 SO_4 + 12 g \cdot L^{-1} Cl^-$), the redox potential of the Fe(III)-SO₄²⁻-Cl⁻ system was reported to be solely determined by the Fe³⁺/Fe²⁺ couple as shown below [192, 255, 256]:

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$$Fe^{3+} + e^{-} = Fe^{2+}$$
 Equation 7-1

The Fe³⁺/Fe²⁺ couple has rapid reaction kinetics and a high reversible potential (E_{rev}) [12]. Based on previous investigations [192, 255], the E_{rev} of the Fe³⁺/Fe²⁺ couple for the investigated conditions was calculated by assuming equimolar concentration of Fe³⁺ and Fe²⁺, *i.e.*, both 3 mM. That is, 0.56 V at 25°C, 0.58 V at 40°C, 0.61 V at 60°C, and 0.64 V at 80°C (refer to Appendix C for details and calculations).

Figure 7-5 shows that the reduction of Fe(III) species on the surface of Ti-2 started from the beginning of the cathodic polarisation and significantly enhanced the cathodic current density throughout the entire potential region I. When the potential decreased to about -0.2 V, entering region II, the polarisation resulted in a limiting current for Fe(III) reduction (from -0.5 to -1.2mA·cm⁻² when the temperature increased from 40 to 80°C). As the potential was decreased to about -0.58 V, entering region III, the current density increased significantly, which corresponds to the hydrogen evolution reaction (HER) [226, 227]:

$$2H^+ + 2e^- = H_2$$
 Equation 7-2

Hydrogen evolution was also observed on the Ti-2 exposed to the blank solution, and it was the driving force for the corrosion of Ti-2 in this condition. E_{rev} for this reaction was also calculated for the investigated conditions, where the pH of the blank solution slightly decreased from 1.77 at 25°C to 1.42 at 80°C. The thermodynamic data used for the E° calculation, *i.e.*, the standard Gibbs free energies of formation and the entropies are from handbook [257]; equations for the temperature dependency of the standard molar heat capacity are from handbook [258]; extrapolation of thermodynamic data to elevated temperatures followed the Criss and Cobble method [259, 260]. The E_{rev} for HER was -0.30 V at 25°C, -0.29 V at 40°C, -0.28V at 60°C, and -0.27 V at 80°C (refer to Appendix C).

During cathodic polarisation, the passive oxide film formed on the surface of Ti-2 in the presence of Fe(III) is also expected to change in respect to its properties and composition [64, 245]. At -0.32 V, titanium oxide is reported to show a significant decrease in film resistance and increase in film capacitance [64]. These changes enabled the onset of underpotential deposition of hydrogen atoms on the titanium electrode through the oxide film, while not necessarily leading to significant hydrogen evolution [64]. These oxide film property changes are supposed to occur in potential region II in the present work. By comparison with the cathodic polarisation curves in the blank solution, the cathodic current density observed in potential regions I and II appeared to be mainly due to Fe(III) reduction. The cation reduction rate might be slowed by the presence of an oxide film via slowed electron transfer through the oxide film, but such a change is difficult to quantify. When the potential was decreased to -0.55 V, the oxide film was expected to undergo redox transformation from Ti(IV) to Ti(III). Ti(III) species is said to be ineffective in obstructing the HER [64, 245]. This phenomenon is consistent with the observed increase in cathodic current density for Fe(III) reduction and the HER at this potential. However, the current corresponding to the Ti(IV)/Ti(III) reduction was very difficult to distinguish from the other cathodic processes. In addition, the oxide film is reportedly very thin at this potential (several nanometers [245]). The current density corresponding to the redox transformation of the oxide film is expected to be insignificant in comparison with the Fe(III) reduction and HER. Thus, the cathodic polarisation curves shown here can be seen to represent cation reduction and/or HER, without comprising any significant contribution from oxide film redox transformation. As aforementioned, region I is largely the reduction of Fe(III) to Fe(II). This reaction accounts for the accelerated cathodic current density. Region II showed the limiting current density of Fe(III) reduction, from the bulk solution to the oxide film/electrolyte interface when the applied potential was less than -0.2 V. Region III,

at still lower potentials, is the onset of the HER [226, 227]. In addition, as far as we know, the cathodic reduction mechanism of cations, has not been reported to be influenced by the properties and composition changes of titanium oxide films.

Figure 7-3 demonstrated that 2 mM Cu(II) was always more than sufficient to passivate Ti-2 in the investigated conditions. Therefore, the cathodic polarisation curves of Ti-2 in the presence of 2 mM Cu(II) were measured and they are shown in Figure 7-6. The polarisation curves indicate that Cu(II) is reduced in two stages, *i.e.*, from Cu(II) to Cu(I), and from Cu(I) to Cu(0). Copper species are known to complex with Cl⁻. The predominant forms of Cu(II) and Cu(I) in the investigated solutions are CuCl⁺ and CuCl₂⁻ according to previous work [256, 261]. The half-cell reaction for Cu(II)/Cu(I) is shown in Equation 7-3, and this reaction corresponds to the increased cathodic current at the beginning of cathodic polarisation. Then the CuCl₂⁻ species would be further reduced to copper (as shown in Equation 7-4) on the surface of Ti-2 as the negative shift of potential. This reaction corresponds to the current increase in the polarisation curves (indicated by A in Figure 7-6) when the potential decreased to -0.3 V. For the investigated condition, the E_{rev} was calculated for each reaction couple by invoking the Nernst equation and existing thermodynamic data [256, 261-263]. Erev obtained for Equation 7-3 by considering the equimolar concentrations of CuCl⁺ and CuCl₂⁻, *i.e.* 1 mM, was 0.23 V at 25°C, 0.25 V at 40°C, 0.28 V at 60° C, and 0.30 V at 80°C. The E_{rev} obtained for Equation 7-4 based on the concentration of 2 mM for CuCl₂⁻ was -0.15 V at 25°C, -0.17 V at 40°C, -0.19 V at 60°C, and -0.22 V at 80°C (Appendix C).

$$CuCl^+(aq) + Cl^- + e^- = CuCl_2^-(aq)$$
Equation 7-3

 $CuCl_2^-(aq) + e^- = Cu(s) + 2Cl^-$
Equation 7-4

Visual observation during the critical concentration determination tests (Figure 7-2) was consistent with the cathodic reduction process of Cu(II) discussed above. At the beginning of the test, the Ti-2 was in the active state with a negative corrosion potential (E_{corr}) ranging from -0.7 to -0.6 V in the blank solution (Figure 7-1 and Figure 7-2). The addition of Cu(II) resulted in an increase of the Ti-2 E_{corr} . If the E_{corr} of the sample remained sufficiently negative ($< E_{rev}$ for the Cu(I)/Cu(0) couple), the sample surface was observed to turn red and the red colour became more intense upon the incremental addition of Cu(II). This colour change indicates the deposition and accumulation of copper as a result of the reduction reactions in Equation 7-3 and Equation 7-4. However, with further addition of Cu(II) and a resultant increase of $E_{corr} (> E_{rev}$ for the Cu(I)/Cu(0) couple), the red colour became lighter until it completely disappeared, indicating the oxidation of the deposited copper. The observed copper deposition and disappearance provided additional proof for the two separate steps for Cu(II) reduction predicted in Equation 7-3 and Equation 7-4. The observed Cu(II) reduction process was consistent with previous reports [256, 261, 262].



Figure 7-5 Cathodic PD of Ti-2 in blank solutions (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) with or without the addition of 6 mM Fe(III) at 40°C, 60°C, and 80°C



Figure 7-6 Cathodic polarisation of Ti-2 in blank solutions (30 $g \cdot L^{-1} H_2 SO_4 + 12 g \cdot L^{-1} CI^-$) with or without the presence of 2 mM Cu(II) at 40°C, 60°C, and 80°C

7.1.4 Effect of Fe(III) and Cu(II) species on the passive film of Ti-2

The passive film on Ti-2 formed by the introduction of either Fe(III) or Cu(II) species was compared with an equivalent passive film that was generated *via* the application of an external DC potential in the blank solution. The detailed procedures for the passive film generated by Fe(III) introduction are described as follows. 6 mM Fe(III) was added to the blank solution to passivate the Ti-2 sample without any external DC polarisation. The sample then stabilised at E_{corr} for 1.5 h until a stable E_{corr} of 0.3 V at 40°C was observed. The passive film formed by this procedure (*i.e.*, the simple addition of Fe(III)) was then investigated by step-wise potentiostatic polarisation (PS) in the same solution, *i.e.*, in the 6 mM Fe(III) + blank solution. The detailed procedure for the stepwise PS was described in Section 4.3.4.

In contrast to the Fe(III)-containing sample, the passive film on the control sample was generated by an applied potential of 0.3 V (with a potentiostat) for 1.5 h in the blank solution. Then

the step-wise PS was immediately applied to investigate the PS-formed passive film in the same solution.

The procedures for Ti-2 exposed to Cu(II) solutions and for the corresponding control were the same as above except that the potential (corresponding to E_{corr} in the presence of Cu(II)) was 0.15 V. The two films formed by (1) Cu(II) introduction and (2) external potential polarisation at 0.15 V were also subsequently investigated, separately, by the step-wise PS in their respective solutions. Thus, this study compares the oxide films formed at these potentials (at 0.3 V and 0.15 V) but using two different routes to obtain said potentials, *i.e.*, by cation introduction or external DC polarisation. Therefore, the effect of cations on the oxide film formation was elucidated.

The passive current densities $i_{passive}$ recorded from the step-wise PS for the case of Fe(III) and Cu(II) species at 40°C are shown in Figure 7-7, bottom and top, respectively. During PS up to 1.6 V, the magnitude of $i_{passive}$ was generally less than 10 μ A·cm⁻², which indicates the good corrosion resistance of the films. The $i_{passive}$ registered on the passive film formed by Fe(III) introduction were comparable with those formed by anodic PS with the equivalent potential. The same is true for the case of Cu(II). The difference between the $i_{passive}$ of the passive films generated by these two methods was too small to attach any significance.

The PS results suggest that these cations may not significantly affect the property of the passive films, nor the anodic process of titanium in the investigated condition. The effect of oxidising cations on the corrosion of nickel [264] and iron [265] under similar experimental conditions has previously been reported. In 1 N sulfuric acid solutions, nickel dissolution rates in solutions containing various electropositive cations agreed well with those predicted from PS at the same potential [264]. Identical corrosion rates were also observed on iron in the passive region

regardless of whether the shift in potential was caused by external anodic polarisation or through introduction of Ce^{4+} or quinone ions into solution [264].



Figure 7-7 Passive current density of Ti-2 with passive film formed by introducing either 2 mM Cu(II) or 6 mM M Fe(III). Each cation-passivated film is compared with a film obtained *via* anodic DC polarisation in the blank solutions at 40°C

7.2 Discussion

7.2.1 Mechanism of Ti-2 passivation by Fe(III) and Cu(II) species

The results given in 7.1.3 and 7.1.4 show that the passivation of Ti-2 by Fe(III) and Cu(II) species was mainly achieved by enhancing the cathodic process, *i.e.*, increasing the cathodic current density. This is well described by the polarisation diagram in Figure 7-8 [103, 244, 264].

In Figure 7-8, curve *A* represents the anodic polarisation curve of Ti-2, which was initially in the active state when it was exposed to the blank solution. The curve marked *C* represents the cathodic reduction reaction of Fe(III) or Cu(II) species, which have a more noble reversible potential than titanium and are expected to be reduced on the surface of Ti-2. Since the HER was not significant at the corrosion potential of Ti-2, it is not shown in Figure 7-8. As the concentration

of Fe(III) or Cu(II) species was increased from C_1 to C_5 , the reversible potential of these electropositive cations became more noble and the cathodic current density increased. Therefore, the corrosion potential of the system was shifted towards the positive direction from Ecorr1 to Ecorr5 as indicated in Figure 7-8. Concentration C_3 in Figure 7-8 produces an interesting situation where two possible mixed potentials, *i.e.*, E_{corr3} and E_{corr3} , to are present, and the Ti-2 will oscillate between the passive and active state depending on the surface condition. For the initially active Ti-2 sample adopted here, it is most likely that E_{corr3} , instead of E_{corr3} , would be obtained. That is, at concentration C_3 , the Ti-2 was still in the active state, and stable passivation would only be created with further addition of oxidising species to a concentration of C_4 , as marked in Figure 7-8. In contrast, other authors have reported that passivated samples may be maintained in the passive state at lower concentrations (schematically represented here by C_3) [103, 107]. Thus, the pre-activation of the Ti-2 sample adopted in this work results in the most difficult scenario for titanium passivation. As a result, the data provided here is conservative for the investigated conditions. When the concentration of Fe(III) or Cu(II) species increased to C_4 , the cathodic current density was larger than the critical current density for passivity of titanium, icrit, the titanium became passive, and the system then obtained a new corrosion potential E_{corr4} . Further concentration increase to C_5 caused a slight increase of the corrosion potential to E_{corr5} . This slight increase in the corrosion potential is consistent with Figure 7-1 and Figure 7-2. At sufficient concentrations, Fe(III) and Cu(II) created a stable mixed potential that was noble enough to cause Ti-2 passivation [103].



Figure 7-8 Schematic representation of titanium passivation by Fe(III) or Cu(II)

7.2.2 Effect of temperature

Figure 7-3 demonstrates the relationship between temperature and critical inhibitor concentration. Higher Fe(III) or Cu(II) concentrations were needed to passivate Ti-2 and to maintain its stability at higher temperatures. These results point to increased corrosion risk for titanium vessels used in higher temperature processes, especially if oxidising conditions cannot be maintained.

Figure 7-4 clearly shows that i_{crit} increases with temperature, which suggests the increased difficulty for titanium to achieve stable passivation, resulting in an increased critical inhibitor concentration necessary for passivation. In addition to increasing i_{crit} , temperature increases also gave rise to increases for the cathodic current density corresponding to the reduction of Fe(III) and Cu(II) at a given concentration. This phenomenon is shown in Figure 7-5 and Figure 7-6 when the temperature was increased from 40 to 80°C. Therefore, the effect of temperature on Ti-2 passivation by Fe(III) and Cu(II) reveals a competition between the i_{crit} and cathodic current density. Although the increase of temperature promotes both cathodic reduction current density

and critical current density for passivity of titanium, the increase of the latter is more significant. As demonstrated in Figure 7-4, the increase of temperature from 40 to 60°C resulted in an i_{crit} increase by 0.338 mA·cm⁻², and an even further increase of 0.718 mA·cm⁻² when temperature increased to 80°C. The change of cathodic current density corresponding to the reduction of Fe(III) and Cu(II) change in temperature was not quantified here because of the various parameters, such as potential and concentration. In brief, the effect of temperature can be illustrated by Figure 7-4, which displays how the temperature affects the passivation of titanium by Fe(III) or Cu(II) species. In Figure 7-4, the cathodic polarisation curves corresponding to the reduction of Fe(III) or Cu(II) species are schematically represented by the lines $C_{60^{\circ}C}$, $C_{80^{\circ}C}$, and $C'_{80^{\circ}C}$. At 60°C, $C_{60^{\circ}C}$ represents the critical concentration of Fe(III) or Cu(II) species required to passivate Ti-2. When the temperature was increased to 80°C, the cathodic current density increased to $C_{80^{\circ}C}$, however, the critical current density for the passivity of Ti-2 increased to $i_{crit-80^{\circ}C}$. The magnitude of $i_{crit-80^{\circ}C}$ was larger than what $C_{80^{\circ}C}$ could provide, therefore an increase of Fe(III) or Cu(II) concentration to $C'_{80^{\circ}C}$ was required to passivate Ti-2 at 80°C.

7.2.3 Effectiveness of Fe(III) and Cu(II) toward Ti-2 passivation

Figure 7-3 demonstrates the higher effectiveness of Cu(II) toward the passivation of Ti-2 for the investigated conditions, specifically, Cu(II) species exhibited a more than 4 times higher effectiveness than Fe(III) species. The double-electron transfer process of Cu(II) reduction shown in 7.1.3 (Equation 7-3 and 7-4) was one important reason for this positive comparison with respect to Fe(III) reduction (Equation 7-1). In addition, the metallic copper deposition, which occurs during the Cu(II) reduction reaction, may also be related to the high effectiveness of Cu(II). In fact, the deposition of metallic copper may exert a significant influence by facilitating the HER kinetics. In acidic solutions, titanium was reported to exhibit a particularly low exchange current

density (approximately $1.9 \times 10^{-12} \text{ A} \cdot \text{cm}^{-2}$) and a high hydrogen overvoltage (about 0.6 V) in hydrogen-saturated 20% H₂SO₄ at room temperature [35]. These current densities and potentials are not conducive to the establishment of passivity. The noble metals, however, are known to have a lower overvoltage for the HER, therefore facilitating the cathodic kinetics [103, 244, 266, 267]. For titanium, the effect of the noble metals, such as Pt, Pd, Ni, Fe, etc., as alloying additions, on its electrochemical and corrosion behaviour has been reported [35, 67, 70, 243]. Palladium, nickel and iron exist as the intermetallics Ti₂Pd [268], Ti₂Ni [243] and Ti_xFe, respectively, in titanium alloys. These intermetallic regions had high exchange currents for the HER and created a noble mixed potential for passivation of titanium. This explains the enhanced corrosion resistance of such alloys. A similar explanation may be offered for the passivation of Ti-2 in the presence of Cu(II) species. As demonstrated in Figure 7-5 and Figure 7-6, the cathodic HER exhibits an obvious smaller Tafel slope on titanium with Cu(II) present (to 0.07 V /decade) than that in the blank solution or with Fe(III) present (approximately 0.3 V/decade), indicating the accelerated HER. Specifically, when the potential was -0.6 V, the cathodic current density with Fe(III) present was 6.52×10^{-4} A·cm⁻² at 40°C, 1.43×10^{-3} A·cm⁻² at 60°C, and 2.12×10^{-3} A·cm⁻² at 80°C; while it was 1.3×10^{-3} A·cm⁻² at 40°C, 7.4×10^{-3} A·cm⁻² at 60°C and larger than 0.5 A·cm⁻² (exceeding the current detection limit) at 80°C in the case of Cu(II). Thus, the reduction of Cu(II) to copper and the accelerated HER led to a significantly increased cathodic current density, which effectively passivated Ti-2. This explains the higher effectiveness of Cu(II) versus Fe(III) for Ti-2 passivation.

Furthermore, Figure 7-5 and Figure 7-6 demonstrate the difference in the limiting current density i_L of Fe(III) and Cu(II) reduction reactions in potential region II. This difference can be

used to reveal the influence of the diffusion coefficient of these cations on the kinetic response of these reduction reactions.

The limiting current density i_L can be expressed using the following Equation 7-5 [269]:

$$i_L = \frac{nF}{S_j} \cdot \frac{D_j}{\delta} \cdot C_j \qquad \qquad \text{Equation 7-5}$$

where, D_j is the diffusion coefficient of the electroactive species Fe(III) or Cu(II) investigated here; C_j is their bulk solution concentration; δ is the diffusion layer thickness, here we assume a value of 0.3 mm for natural convection [270]; s_j is stoichiometric coefficient, which is 1 here; n is the electrons transferred in the reaction, which is 1 for both Fe(III)/Fe(II) and Cu(II)/Cu(I) reduction; F is Faraday's constant.

Therefore, higher concentrations and larger diffusion coefficients for the cations will lead to an increased limiting current density. Take the results in the present work at 40°C, for example. The limiting current density, i_L , in the presence of 6 mM Fe(III) was 0.6 mA·cm⁻²; whereas i_L in the presence of 2 mM Cu(II) was 0.7 mA·cm⁻². Therefore, the *D* for Fe(III) can be estimated as 3.1×10^{-6} cm²·s⁻¹, and for Cu(II) an estimate of 1.1×10^{-5} cm²·s⁻¹ can be calculated. These values are comparable with the results reported by other researchers [271, 272]. A one order of magnitude higher *D* for Cu(II) compared to Fe(III) effectively improves the kinetic response of the Cu(II) reduction reaction. This may be another reason for the higher effectiveness of Cu(II) versus Fe(III) for Ti-2 passivation.

7.3 Summary

The passivation of Ti-2 in blank solutions (30 $g \cdot L^{-1} H_2SO_4$ and 12 $g \cdot L^{-1} Cl^{-}$) by Fe(III) and Cu(II) species was investigated *via* electrochemical techniques, and the conclusions are:

(1) A critical concentration of Fe(III) and Cu(II) species was required to passivate Ti-2. The critical concentration of these two species both increased with temperature. The required Fe(III) addition increased from 1.0 ± 0 to 6.0 ± 0 mM between 30 and 80°C. The critical concentration of Cu(II) increased from 0.25 ± 0 to 1.15 ± 0.23 mM between 30 and 80°C.

(2) Fe(III) and Cu(II) species passivated Ti-2 by accelerating the cathodic current density, and polarising the Ti-2 into the passive state. Fe(III) and Cu(II) species did not affect the anodic process of Ti-2.

(3) Cu(II) was more effective at inducing passivation than Fe(III). Fe(III) accelerated the cathodic current density by the direct reduction to Fe(II). The two-stage reduction of Cu(II) to copper, the facilitated kinetics of the HER on the precipitated copper, and the higher diffusion coefficient for Cu(II) species, accounted for the higher effectiveness of Cu(II) for initiating the passivation of Ti-2.

Chapter 8: Localised instability of titanium during its erosion-corrosion in simulated leaching slurries^{7, 8}

Chapter 5 has demonstrated that the solid deposits can alter the kinetics of titanium corrosion, and that oxidising species are necessary to passivate this metal and maintain its stability in stagnant leaching solutions. However, hydrometallurgical systems are dynamic. Indeed, in leaching processes, the vigorous agitation of solid minerals in the aggressive leaching solution may cause erosion-corrosion of the internal parts of titanium autoclaves. The erosion-corrosion behaviour of titanium in hydrometallurgical conditions is not well understood and related data are not publicly available. By using appropriate methods, *i.e.*, electrochemical techniques, this chapter monitors the state of the titanium oxide film and investigates the erosion-corrosion of titanium in simulated hydrometallurgical leaching conditions. Potentiodynamic polarisation, linear polarisation resistance and electrochemical noise (EN) are applied to explore the mechanism of titanium erosion-corrosion. The influence of temperature and slurry agitation rate on the erosion behaviour of titanium is also demonstrated.

8.1 Electrochemical results

8.1.1 EIS results

Electrochemical impedance spectroscopy (EIS) data for Ti-2 in the three conditions, *i.e.*, static solution, dynamic solution, and agitated slurry at 40, 60, 80, and 95°C are shown in Figure

⁷ Yu Liu, Akram Alfantazi, Rebecca Filardo Schallera, Edouard Asselin, "Localised instability of titanium during its erosion-corrosion in acidic slurries", *In Press* at *Corrosion Science* (2020)

⁸ Yu Liu, Edouard Asselin, "Metastable pitting during the erosion-corrosion of titanium in acidic leaching slurries", *58th Annual Conference of Metallurgists (COM 2019) and International Copper Conference,* August (2019), Vancouver Convention Center, Vancouver, BC, Canada

8-1. Titanium grade 2 (Ti-2) has a similar impedance response in the various test environments, indicating that the same controlling electrochemical process occurs on the electrode surface [273]. Nyquist plots show the capacitive behaviour of the investigated samples, and the phase angles approach 90° over a large frequency range from medium to low frequencies (1–1000 Hz). This suggests the formation of a thin and relatively stable oxide film on the surface of the samples, despite the fluid motion and silica particle impacts [134, 213]. The impedance magnitude |Z| at the low frequency limit, which is a proxy for the corrosion resistance [228, 229], is consistently larger for the samples in the static and dynamic solutions than in the slurry, indicating the degraded performance of the titanium oxide film in the latter conditions.

An electrical equivalent circuit (EEC), $R_{sol}(R_{film}Q_{film})$, was adopted to fit the impedance spectra. This circuit is also known as the Randle's circuit. It is valid for the presence of a compact passive film on titanium, in which the pores are exceedingly fine or non-existent [274]. It consists of the solution resistance (R_{sol}), a constant phase element (Q_{film}), which represents the capacitance behaviour of the titanium oxide films, and the passive film resistance (R_{film}) which is in parallel with Q_{film} . The fitting was conducted with ZSimpWin, and the fitting results are included in Figure 8-1, indicating the satisfactory fitting. The passive film resistance, R_{film} , is also shown in Figure 8-2 and shown in Table 8-1. The R_{film} in the dynamic solution was comparable or even slightly larger than that in the static solution (Figure 8-2). This indicates that the fluid flow did not significantly affect the passive oxide film on the surface. The slight increase of R_{film} may be interpreted in terms of the influence of fluid flow on the corrosion reaction, that is, the greater mass transfer of oxidising species (*i.e.*, oxygen, ferric ions and cupric ions) to the titanium surface promoted passive film growth and inhibition of corrosion [218]. A similar phenomenon was also observed for stainless steel [275]. Insignificant effects from fluid flow are commonly observed for nonporous and protective films since the resultant mechanical effects are not sufficient to remove the surface oxide film [154]. However, the introduction of the solids obviously affected the integrity of the oxide film. R_{film} in the slurry was always lower than that in the static and dynamic solutions; specifically at temperatures $\geq 80^{\circ}$ C, the film resistance decreased to $\leq 10 \text{ k}\Omega \cdot \text{cm}^2$. It was also noticed that as the conditions became more abrasive (the agitation rate was increased to 2400 RPM and the silica particle concentration was increased to 150 g·L⁻¹—labelled as "slurry⁺"—), the passive film was further degraded with its resistance decreasing to 5.7 k $\Omega \cdot \text{cm}^2$.



Figure 8-1 EIS spectra of Ti-2 in simulated sulfide leaching solutions in static, dynamic and suspended silica slurry conditions at (a) 40°C, (b) 60°C, (c) 80°C, and (d) 95°C (slurry⁺:2400 RPM + 150 g·L⁻¹ silica)

	Conditions	R_{sol} ($\Omega \cdot \mathrm{cm}^2$)	Q_{film} -Y ₀ (×10 ⁻⁵ S·s ⁿ ·cm ⁻²)	<i>Q_{film}-n</i>	R_{film} (k $\Omega \cdot \mathrm{cm}^2$)	χ ² (×10 ⁻³)
40°C	Static solution	14±0.5	3.0±0.5	0.98±0.05	22±1	1.4
	Flow solution	13±0.9	2.9±0.2	0.98 ± 0.03	25±3	1.5
	Slurry	12±0.7	2.7±0.5	0.98 ± 0.04	15±0.9	1.2
60°C	Static solution	12±0.4	3±0.7	0.98 ± 0.02	27±0.3	0.8
	Flow solution	9±0.3	2.8±0.9	0.98 ± 0.01	27±0.5	0.8
	Slurry	17±0.5	2.7±0.2	0.98 ± 0.03	18±0.7	2.2
80°C	Static solution	9.8±0.1	2.6±0.5	0.99±0.03	15±1	1.5
	Flow solution	15±0.3	2.5±0.4	0.99 ± 0.02	15±0.8	1.6
	Slurry	18±0.3	2.6±0.8	0.99 ± 0.02	9.2±0.7	2.3
95°C	Static solution	5.8±0.2	2.7±0.5	0.98±0.01	15±0.9	1.0
	Flow solution	6.1±0.3	2.7±0.6	0.98 ± 0.03	15±0.8	1.0
	Slurry	7.5±0.5	2.8±0.5	0.98 ± 0.02	$7.0{\pm}0.4$	1.4
	Slurry ⁺	6.7±0.4	2.7±0.6	0.97±0.02	5.7±0.5	2.0

Table 8-1 Electrical parameters for the EEC ($R_{sol}(R_{film}Q_{film})$) used to fit the EIS impedance spectra (slurry⁺ is the 2400 RPM + 150 g·L⁻¹ silica test)

"±" represents the scatter from the replicated experiments

In addition, the temperature was also noticed to influence the passive film resistance, R_{film} . Under the same conditions of static or dynamic solution, the passive film first showed an increase in R_{film} from 40 to 60°C, which might be due to an increased amount of bound water in the film. Bound water has been reported to play an important role in improving the corrosion resistance of titanium [276]. However, at 80°C an obvious drop of 6 to 10 k $\Omega \cdot \text{cm}^2$ was observed. This indicates a degradation of the titanium oxide film's protective properties at T \geq 80°C. The passive film resistance further decreased in the slurry, and, thus, the lowest magnitude of R_{film} was observed herein. Previous reports also observed a significant corrosion resistance drop of titanium for T > 70°C [55, 105, 134], and this may be attributed to the breakdown/crystallisation process of the oxide film [251]. Breakdown/crystallisation is an important phenomenon for titanium oxide films 147 in terms of the oxide growth rate, composition, structure, and corrosion resistance. It may create grain boundaries and cracks, provide lower-resistance pathways for ion transport through the film, thus resulting in a decreased corrosion resistance [219, 220]. Breakdown/crystallisation did not result in the formation of open, active cracks and pores in the experiments performed here, since the titanium remained passive and still showed relatively high resistance. However, crevice corrosion becomes possible when breakdown/crystallisation occurs, as observed by previous reports [55, 105, 134].



Figure 8-2 *R_{film}* from EIS spectra fitting of Ti-2 in simulated sulfide leaching solutions in static, dynamic, and suspended silica slurry conditions (slurry⁺ is the 2400 RPM test)

8.1.2 Potentiodynamic polarisation results

PD curves for Ti-2 at different conditions are shown in Figure 8-3. All the Ti-2 samples have passive behaviour, which is characterised by low passive current densities, $i_{passive}$, (< 10 μ A·cm⁻²) as the potential was scanned from E_{corr} in the positive direction. PD curves show that the fluid flow or the suspended solids did not significantly affect the cathodic polarisation behaviour of Ti-2. However, the anodic current, which is a measure of the electrochemical dissolution rate was affected. Ti-2 had similar anodic current densities in the static and dynamic 148 solutions, while an apparent current increase was observed for the slurry condition. When the temperature was increased to 80°C, the anodic current density in the slurry condition was almost two times larger (~ 10 μ A·cm⁻²) than that in the other two conditions. This is further evidence for the detrimental effect of silica impingement on the integrity of the titanium oxide surface film. As shown in Figure 8-3 (c), a further temperature increase to 95°C did not result in a significant increase of anodic polarisation current density compared with that at 80°C. As the condition became more abrasive (*i.e.*, "slurry⁺"), the anodic polarisation current density of Ti-2 showed an apparent increase (by about 3 μ A·cm⁻²), as indicated by the arrow near 1 V in Figure 8-3 (c).



Figure 8-3 Potentiodynamic polarisation curves of Ti-2 in simulated sulfide leaching solutions in static, dynamic and suspended silica slurry conditions at (a) 40°C, (b) 60°C, and (c) 80°C and 95°C

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PD results are consistent with the EIS results, and suggest a decreased corrosion resistance of titanium during silica impingement. It is likely that the oxide film is periodically damaged (and perhaps broken) by the silica impingement and that the underlying metal surface is instantaneously exposed. The resultant oxidation of the underlying titanium substrate at a damaged zone would result in increased current. The increased current would occur across the exposed surface area as different localised film breakdown points were exposed to solution, and thus the increased current represents an aggregate increase in anodic activity. However, localised characterisation pertaining to titanium erosion-corrosion is needed. Therefore, EN was conducted to further explore the erosion-corrosion mechanism of titanium. In the following section, the erosion-corrosion behaviour of titanium at 80°C was investigated *via* the EN technique, and it was analysed as a function of the increase of slurry rate, *i.e.*, abrasive level.

8.1.3 Electrochemical noise results

Figure 8-4 shows time recorded current and potential noise for Ti-2 in static solution (Figure 8-4(a)), dynamic solution (Figure 8-4(b)), and slurry conditions as impeller rotation rate increased to 1200 RPM (Figure 8-4(c)–(e)) at 80°C. It is clear that the current noise was background noise, showing no transients for titanium in the static and dynamic solutions (Figure 8-4(a), Figure 8-4(b)). However, when titanium was exposed to slurry conditions, sharp current transients with peak amplitudes of almost 10 μ A showed up at 600 RPM (Figure 8-4(c)). As rotation rate increased in the slurry, the current transients were intensified, as indicated by the increased occurrence frequency and magnitude of the transients (Figure 8-4(d)). When the slurry agitation rate was 1200 RPM, for which EIS and PD results revealed an obvious decrease of corrosion resistance (Section 8.1.1 and 8.1.2), the current transients have been observed on passive
metals under potential control conditions [133, 156-164], and in the erosive conditions under particle impacts [171, 277]. These current transients represent the pit nucleation events, corresponding to the microscopic/localised fracture of the passive film [156, 157, 165-170, 172]. Current transients observed in slurry conditions (Figure 8-4(c)–(e)) suggested that the localised film rupture was mechanically triggered by silica particle impingement [147, 278, 279].

The "fluctuation" level of the current noise can be described by the standard deviation values, δ_{i} , which were computed from Equation 8-1 after linear detrending of the raw data:

$$\delta^2 = \frac{\sum_{1}^{N} (x_i - \bar{x})^2}{N - 1}$$
 Equation 8-1

where, $\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$, is the mean of the noise; *N* is the number of points in the calculation. The standard deviation of electrochemical current noise δ_i was 2.1×10^{-7} , 3.1×10^{-6} and 4.4×10^{-7} A for slurry agitation rates of 600, 800, and 1200 RPM, respectively. Pistorius [280] had suggested δ_i was positively correlated to the corrosion current density (*i*_{corr}) (proportional to *i*_{corr} or to the square-root of *i*_{corr}, depending upon whether the current transients were superimposed or temporally separated). Thus, the obvious increase of δ_i indicates an increase of the corrosion rate of titanium as the mineral slurry agitation rate increases. In comparison, the potential fluctuation pertaining to the transient events was not as obvious as the current fluctuation. The damped potential response was due to its larger time constant than that of the current transient in EN measurement, and this has also been observed by other researchers [173, 280]. The potential noise showed quantisation noise due to the relatively low-resolution data acquisition system of the potentiostat, and that also decreased the diagnostic significance of potential response in the time domain.



Figure 8-4 EN current and potential records for Ti-2 in simulated leaching solutions in (a) static solution, (b) dynamic solution, and silica slurry conditions with different impeller rotation rate of 600 RPM (c), 800 RPM (d), and 1200 RPM (e)

The potential and current noise data were transformed into the frequency domain with the fast Fourier transformation (FFT) method, and the power spectral densities (PSD) of the EN data were calculated by a programme provided by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (available for free at <u>www.ecg-comon.org</u>). A section of N = 2048 data points for 5 sets was calculated and averaged. Before transformation, a linear trend removal was applied and the Hann window was used in each section. The calculations were described by Ritter, Huet and Cottis [178]. As shown in Figure 8-5(a), potential PSD curves for titanium in static and dynamic solutions are comparable and show the lowest noise level. In slurry conditions, the magnitudes of potential PSD are obviously larger, and increase as conditions become more abrasive at the low frequencies (< 2 Hz). In addition, the PSD curves show a linear decrease with a slope of approximately -2 on the log-log scale at frequencies < 2 Hz, and that is typically found for passive surfaces undergoing pitting corrosion [172]. Consistently, the magnitudes of the current PSD plots increase as the slurry rotation rate increases (Figure 8-5(b)). The increased current power is reported to indicate an accelerated corrosion process [281-287].

It is worth noting that there is no anti-aliasing (AA) filter in the data acquisition system of the potentiostat used here, which is indicated by the absence of a rapid decrease of PSD curves close to the maximum frequency, $f_s/2$ ($f_s = 100$ Hz is the sampling frequency). Therefore aliasing noise can occur in the time records and result in overestimation of current and potential PSD values [288], especially for the relatively flat PSDs, *i.e.*, in the static and dynamic solutions. Specifically, the potential fluctuations corresponding to a PSD value of 10^{-10} V²·Hz⁻¹ cannot be attributed to corrosion because of the presence of aliasing and quantisation noise: only the potential PSD curves in the slurry conditions at low frequencies (< 2 Hz) are due to corrosion. For the current noise, it is also impossible to conclude for the PSD curves corresponding to the static and dynamic solutions

due to the absence of AA filters, and aliasing of impeller rotation and the mains explains the peaks at 20 and 40 Hz [180]. The current PSD curves for slurry conditions (600–1200 RPM) are decreasing at frequencies close to $f_s/2$, indicating that aliasing was not significant, therefore, they are due to corrosion at frequencies < 10 Hz. Electrochemical noise impedance (Z_n) is defined as the square root of the ratio of the potential PSD and the current PSD. Because of the presence of aliasing and quantisation noise, only the Z_n values for the slurry conditions at frequencies below 2 Hz can be attributed to corrosion, and are plotted in Figure 8-5(c). For two identical electrodes having the same impedance in ZRA mode, and with a noiseless reference electrode, Z_n is expected to be equal to the impedance of Ti-2 at the 1200 RPM slurry condition, |Z|, measured from EIS has been added on Figure 8-5(c). Z_n corresponded well to |Z| at the low-frequency plateau for this condition, which validates the EN measurements for the slurry conditions at low frequencies where aliasing was not significant. Assessment of the EN measurements from various potentiostats and validation of the EN data is added in Appendix D.

To have a closer look, the typical current transients observed in the time records from 600 to 1200 RPM are shown in Figure 8-6. The current transients show an extremely sharp rise followed by a relatively slow fall back to the background level, indicating pit nucleation and its termination *via* a repassivation process. This kind of current transient is commonly observed on titanium and its alloys upon thin film fracture [289] and during anodic polarisation [163, 164, 290], and is also a characteristic transient for carbon steel, pure iron and aluminium [167, 171, 291], while different from that found on stainless steels (slow rise in current followed by a quick drop) [183]. In addition, this current transient shape is commonly observed in cases associated with the mechanical fracture of a surface film, such as *via* abrasion, scratching or laser illumination [133,

292, 293]. The current transient shape is clearly associated with the growth and repassivation kinetics of metastable pits generated on a particular metal, but the reasons for the different shapes are not known at this time.



Figure 8-5 Potential power spectral density (a), current power spectral density (b), and noise impedance (c) as a function of frequency (calculated from data in Figure 8-4)

As the conditions became more abrasive, the peak magnitude of the current transient shows an obvious increase. Each current transient event corresponds to a relatively short period of anodic dissolution upon the localised fracture of the passive film: the increase of the transient peak then indicates increased charge loss *via* an electrochemical oxidation reaction for each event. The 155 erosion-corrosion of titanium, therefore, proceeds in the form of current transients. In agreement with earlier findings from stainless steels and iron studies in abrasive conditions [171, 277], the current transients represent the instability of the passive film, which is continuously fractured locally due to silica particle impacts.

For the investigated conditions, the passive oxide film remained corrosion resistant to some extent, as indicated by the EIS and PD results. This is attributed to the rapid repassivation process of titanium when the protective oxide film is immediately regenerated. Figure 8-6 shows that the lifetime of the current transients, corresponding to its rise and decay back to the background [293, 294], was about 0.05 s in general (shorter than that of titanium under anodic polarisation, whose lifetime was observed to vary between tenths of a second up to about 3 s [163, 164, 290]). Whilst there is a variation of the experimental conditions, there is a common observation that titanium demonstrates a much shorter repassivation time in comparison with carbon steel (larger than 5 s in sodium chloride solutions at room temperature [167]) and aluminium (larger than 8 s in 0.075 M ClO⁻ solution at 25°C [291]), indicating relatively good repassivation behaviour. The competition between the film instability and repassivation determines the protective property of the film and erosion-corrosion rate of titanium [295]. A consistent observation from the previous titanium erosion-corrosion investigations was that the increased total mass loss was observed when the abrasive level increased [28, 144, 148].

In addition to characterising the erosion-corrosion behaviour of titanium in the various abrasive slurry conditions and evaluating the localised instability of the passive film, EN measurements demonstrate a suitability to *in situ* corrosion monitoring. EN data are collected from the freely corroding system, which avoids disturbing the corrosion process. The current transients, which indicate the erosion-corrosion phenomenon, are well-defined and distinguishable in EN measurements. Their detection sets an early warning of corrosive attack, and could permit remedial action before significant damage occurs to process equipment. As pro-active ageing management is becoming more and more important for the economical and safe operation of industrial plants, applying *in situ* non-interference corrosion monitoring is a key element. The EN measurements allowed for a more in-depth interpretation by characterising the localised fracture events of the oxide film in slurry conditions.



Figure 8-6 Typical current transients for titanium oxide film rupture in simulated sulfide leaching conditions in various silica slurry conditions

Figure 8-7 shows the morphological change of the specimen surface after erosion-corrosion testing. Figure 8-7 (a) is the initial surface after preparation. It is clear that the features produced from sample preparation were worn down after erosion-corrosion testing as a result of particle impacts. Film fracture scars cannot be identified as shown in Figure 8-7(b). The plastic deformation due to mechanical attack of solid particles in the erosion-corrosion conditions is

commonly observed on ductile materials, such as copper, aluminium and titanium, and thus, a relatively "flat", "smooth" surface is observed [144, 190, 296-298].

The titanium oxide film that forms on the surface of titanium is supposed to provide protection from both corrosive and erosive attack. Therefore, in addition to being chemically inert and stable, the titanium oxide film should adhere well to the substrate and have reasonable elasticity and plasticity to resist fracture. In slurry conditions, the stress on titanium oxide film caused by a single particle impact was theoretically estimated to be very high by Wang et al. [299]. In an erosion-corrosion study, Zhou *et.al* [300] reported that the titanium oxide films ($\leq 1 \mu m$) are relatively brittle in comparison with the titanium substrate (the elastic modulus for titanium oxide is 230 GPa, while it is 115 GPa for titanium). The high stress caused by a particle impacts can lead to a more severe plastic deformation of the titanium substrate than of the oxide film. As a result, the surface film will rupture because it is too brittle to deform together with the substrate. The deformation of the titanium oxide film was also experimentally studied by indentation tests [300]. Under external compressive deformation, the oxide film cracked along the indentation boundaries, indicating the poor adherence between the oxide and its substrate even during static loading. The adhesion of a 180 nm thermally grown titanium oxide (TGO) on pure titanium has also been examined. Tensile loading resulted in multiple cracks in the TGO layer along with distinctive inclined cracking driven by shear band deformation in the titanium substrate, and localised delamination of the TGO was observed when the titanium substrate was strained well within the plastic deformation region by more than about 2.5% [301]. Investigations on the brittleness and adhesion of oxide films on the order of several nm thick, consistent with those formed in this thesis, are not reported and thus no scientific consensus exists on what failure mechanism would be anticipated. Such layers may have a relatively high adhesion and ductility because of their very small thickness, however, in general the oxide film is believed to be brittle compared to the ductile titanium substrate, and this inherent brittleness can limit its lifetime under localised contact stresses and external loading [301]. Thus, in addition to the direct rupture by solid particle impacts, the indirect rupture due to the separation and dislocation from substrate deformation is also believed to contribute to the mechanical rupture of the titanium oxide film. This film rupture resulted in the exposure of the active titanium substrate, which was then immediately re-oxidised as demonstrated by the current transients observed in this work.



Figure 8-7 Surface morphology of the Ti-2 sample (a) before erosion testing and (b) worn surface after erosion testing in simulated leaching conditions in suspended silica slurry at 80°C for 30 min.

Surface roughness, that is, the amount of asperities and irregularities on the surface of samples is known to be important for erosion-corrosion behaviour. Change in the surface roughness causes changes in the degree to which the surface is being influenced by the erodent

particles. Bowden and Brunton [302] proposed that the actual damage occurring for a surface with pre-existing miniscule steps results from the shear stresses induced by the impacts. Similarly, Heymann [303] described erosion as a fatigue-like phenomenon, and the surface irregularities would be very important in initiating fatigue cracks, as they may act as raisers for the impactinduced shear stresses. From a tribological perspective, if the surface was (theoretically) perfectly flat, with no irregularities, the erodent particles would smoothly slide on it. However, as the amount of irregularities is more abundant, in the case of rougher surfaces, they will tend to entrap the particles, hence, more damage occurs. In addition, the response of different surface conditions to erosion impacts also depends on the material's mechanical properties. Abrasive particles impact the material's surface and result in particle dis-bonding, micro-cutting, and micro-ploughing, *etc.* When compared with other materials, titanium undergoes more plastic deformation than microfracture due to its relatively lower hardness [304]. This explains why a relatively "flat" and "smooth" surface, instead of a "pitted" and "scratched" surface was observed in Figure 8-7.

8.2 Summary

Erosion-corrosion behaviour of titanium in hydrometallurgical leaching slurry conditions was investigated by electrochemical methods. EIS and PD results demonstrated an obvious corrosion resistance drop for titanium in slurries, and suggested erosion-corrosion of titanium was attributed to silica particle impingement. EN measurements revealed the erosion-corrosion of titanium originated from mechanical localised fracture of the passive film due to solid particle impingement, which proceeded in the form of electrochemical current transients. EN measurements revealed increased localised instability of the passive film as the slurry mixing rate increased. This suggests that erosion-corrosion may be an important threat to titanium in acidic slurries and thus further study of this phenomenon, especially at elevated temperatures, is warranted.

Chapter 9: Conclusions

9.1 Key findings

This thesis is the first report on the effects of solids on the corrosion behaviour of titanium grade 2 (Ti-2) in acidic oxidising hydrometallurgical leaching solution ($30 \text{ g} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4 + 12 \text{ g} \cdot \text{L}^{-1}$ Cl⁻ + 15 g·L⁻¹ Cu(II) + 1 g·L⁻¹ Fe(III), bubbled with O₂). Although previous investigations on the corrosion behaviour of titanium (Ti) in bulk solutions have been published, these data cannot be used to predict the metal's response to the presence of solids. Other issues that are closely related to titanium corrosion in acidic hydrometallurgical systems, that is, titanium hydride formation and titanium passivation are also investigated in this work. Following are the conclusions from the experimental results presented in the preceding chapters.

Chapter 5 investigated the corrosion behaviour of Ti-2 under solid deposits. Three scenarios related to the bulk solution, S_b , and localised solution under deposits, S_l , which are directly in contact with Ti-2 samples, are illustrated in Figure 9-1:



Figure 9-1 Schematic illustration of scenarios pertaining to the effect of solid deposits on the corrosion behaviour of underlying titanium

- 1. when both S_b and S_l were blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻): Ti-2 actively corroded in this acidic reducing condition. The presence of solid deposits was found to have a barrier effect on the mass transfer in the corrosion process of underlying actively corroding Ti-2, and resulted in decreased corrosion rate of underlying Ti-2 (though all corrosion rates remained high in comparison to all other experiments in this thesis, $i_{corr} >$ 0.05 mA·cm⁻²). The barrier effect of the four deposits for the investigated conditions decreased in the sequence of gypsum > S3 ($d_{0.5}$: 20.4 µm) > S2 ($d_{0.5}$: 193 µm) > S1 ($d_{0.5}$: 425 µm)
- 2. when S_l was the blank solution and S_b was the simulated leaching solution (blank solution + 15 g·L⁻¹ Cu(II) + 1 g·L⁻¹ Fe(III), bubbled with O₂)—a scenario of insufficient inhibition under solid deposits: when passivating species were added to the system (Fe(III), Cu(II), or O₂), the presence of solid deposits slowed the mass transfer of the passivating species to the surface of initially active Ti-2 under deposits and resulted in an increased induction time associated with its passivation. The induction time, which represented the difficulty in passivating the active Ti-2 under deposits, increased in the sequence of gypsum > S3 ($d_{0.5}$: 20.4 µm) > S2 ($d_{0.5}$: 193 µm) > S1 ($d_{0.5}$: 425 µm), and also increased with increasing deposit layer thickness. When the thickness of S3 or gypsum deposits was 1.5 cm, the underlying Ti-2 remained in the active corrosion state for the test duration up to 19 h
- 3. when both S_b and S_l were simulated leaching solution—a scenario of sufficient inhibition by passivation under solid deposits: for the initially passive Ti-2, the presence of solid deposits resulted in a decreased corrosion resistance and increased corrosion rate in comparison with the control sample in the bulk solution. This is attributed to the barrier effect of the solid deposit on the mass transfer of passivating species, which play an

important role on the growth and repair of the oxide passive film of Ti. Increasing temperature resulted in an increased corrosion rate for both control and deposit-covered Ti-2 samples. The combination of solid deposits and high temperature resulted in an accelerated passive corrosion rate of Ti-2. Further elevation in temperature to 127°C may activate the Ti-2 and result in unacceptably high corrosion rate, but more work is required to verify this.

In view of the active corrosion of Ti-2 in the reducing acidic conditions, one important corrosion product(s), titanium hydrides, was investigated in Chapter 6. Key findings related to titanium hydrides are:

- 4. titanium hydrides were found to catalyse the hydrogen evolution reaction (HER), increase the cathodic current densities, and therefore result in a more facile passivation of Ti-2. The catalysis effect of titanium hydrides on HER may result in premature cracking of the titanium substrates as shown in the literature.
- 5. time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements revealed increased H concentrations in the galvanostatically polarised Ti-2, with a clustered distribution of H in the near surface region of the Ti-2 substrate. X-ray diffraction (XRD) results demonstrated that the generated hydride phases were mainly TiH_{1.5}, with small amounts of TiH_{1.7} and/or TiH₂ (trace). The preferential formation of TiH_{1.5} may be due to the smaller volume misfit between the hydrides and matrix, the ability to form solid solution with the α -matrix Ti, and association with the texture of the underlying Ti-2 substrate

As shown in Chapter 5, Fe(III) and Cu(II) species are commonly present in aggressive leaching solutions and they can passivate Ti-2 and maintain its passivity even when the metal

surface is covered with deposits. Chapter 7 quantitatively investigated the effectiveness of Fe(III) and Cu(II) species on Ti-2 passivation, and the key findings are:

- 6. a critical concentration of Fe(III) and Cu(II) species was required to passivate Ti-2 in acidic leaching solutions, which increased with temperature for both species. The critical concentration increased from 1.0 ± 0 to 6.0 ± 0 mM between 30 and 80°C for Fe(III) and from 0.25 ± 0 to 1.15 ± 0.23 mM between 30 and 80°C for Cu(II)
- 7. Fe(III) and Cu(II) species passivated Ti-2 by accelerating the cathodic current density and polarising the Ti-2 into the passive state. Cu(II) was more effective at inducing passivation than Fe(III) due to the two-stage reduction of Cu(II) to copper, the facilitated kinetics of the HER on the precipitated copper, and the higher diffusion coefficient for Cu(II) species

Hydrometallurgical systems are generally dynamic and the vigorously agitated solid minerals slurries continuously impact the Ti-lined vessels in leaching processes, the erosioncorrosion behaviour of titanium in hydrometallurgical conditions was investigated in Chapter 8. The electrochemical results show that:

- 8. the erosion-corrosion behaviour of titanium in hydrometallurgical leaching slurry conditions was caused by solid particle impingement originating from mechanical fracture of the passive film, and it proceeded in the form of current transients. The fluid flow alone did not exert a significant effect on the erosion-corrosion rate of titanium compared with the static solution
- 9. the erosion-corrosion behaviour of titanium was characterised by electrochemical noise (EN). EN detected the current transients and revealed the increased localised instability of the passive film as the slurry mixing rate increased from 600 to 1200 RPM. EN

measurements demonstrated the increased erosion-corrosion threat with increasing slurry agitation rate

9.2 Practical implications and future recommendations

This work revealed the detrimental effects of solids on the corrosion behaviour of titanium and identified conditions under which titanium corrosion may be an issue in practical applications:

1. Titanium in acidic reducing conditions

Two aspects related to titanium degradation in reducing conditions that merit attention:

- a. titanium actively corrodes and cannot create passivation in acidic reducing conditions. The corrosion rate can be very high ($CR = 3.6 \text{ mm} \cdot \text{yr}^{-1}$ in 30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻ solution at 50°C)
- b. the corrosion products, titanium hydrides, can jeopardise the titanium substrate's mechanical properties according to literature. Titanium hydrides are shown to accelerate the HER, which will further promote the production of titanium hydrides. These two processes are self-reinforcing, and the increased amount of titanium hydrides may result in premature cracking of the titanium substrate.

2. Titanium in solid deposition conditions

In general, leaching solutions are highly oxidising with high concentrations of passivating/oxidising species (*i.e.*, (Fe(III), Cu(II), or O_2)), and titanium is passivated and maintains stability in the normal (uncovered) condition. However, solid deposits adversely affect the corrosion resistance of titanium in both cases that may be encountered:

a. titanium with insufficient inhibition, *i.e.*, active corrosion state, before solid deposition.
 The presence of solid deposits can effectively limit the mass transfer of the

passivating/oxidising species from the bulk solution to the surface of underlying Ti. Thus, the underlying titanium would not passivate and rapid corrosion would continue.

b. titanium with sufficient inhibition, *i.e.*, is passivated, before solid deposition. The passivating/oxidising species play an important role in repair and maintaining the integrity of the passive oxide film on the surface of titanium metal. As solid deposits limit the accessibility of these species in the bulk solution to the underlying Ti, the passive corrosion rate of Ti-2 under deposits will be larger than normal. The corrosion issue will become more severe at high temperatures and may limit the use of titanium in vessels and hydrometallurgical equipment.

3. Titanium in aggressive erosion corrosion conditions

Mineral slurries impact can cause localised rupture of the protective oxide film on the surface of titanium. This film rupture results in the exposure of the active titanium substrate to the corrosive solution. The combination of mechanical erosion and electrochemical corrosion processes can be very significant, and the resultant erosion-corrosion is a top concern in many leaching plants

The results produced in this work supplement the existing data for titanium corrosion and contribute further to our understanding of titanium corrosion in acidic hydrometallurgical systems. A few points may be considered for further investigation:

In view of the variety of deposit compositions that occur in practice, active deposits (*i.e.*, those that react with the surrounding environment) should be considered in addition to inert deposits. Thus, the effects of sulfur-, iron oxide-, and pyrite-containing deposits on the UDC of titanium should be investigated.

- 2. Titanium hydride formation can be predicted from *E_h*-pH diagrams, but the reliability of this prediction is contingent on correct thermodynamic data. Updating the *E_h*-pH diagrams for Ti, based on the recent developments in thermodynamic data of titanium phases is necessary. In addition, reaction rate or kinetic information associated with titanium hydride(s) formation relates their occurrence and production to environmental factors, *e.g.*, temperature, acid concentration, and potential. Development of this kinetic information for titanium hydrides may be of practical significance for industrial guidance.
- 3. Further research regarding the relation between the Ti-substrate and preferred hydride phase formation (*i.e.*, TiH_{1.5} in this work) on its surface is necessary. If established, this relationship could increase the understanding of hydride formation and develop the potential for fine tuning the corrosion resistance behaviour of titanium.
- 4. Quantitative determination of titanium passivation by Fe(III) and Cu(II) was limited to low temperatures because of experimental limitations and time constraints. However, hightemperature leaching is common and therefore investigation at higher temperatures (> 95°C) is needed.
- 5. The dependence of titanium erosion-corrosion behaviour on environmental conditions should be further investigated and quantified. The corrosion resistance of the protective oxide film on the surface of titanium is significantly influenced by solution pH, solution composition, temperature, and the presence and concentration of various oxidising species. The stability of the oxide film strongly depends on mechanical interference from solid particles, which involves the variables of particle size, shape, concentration, as well as slurry rate. Interactions among these many variables need to be studied to gain a

comprehensive understanding of erosion-corrosion of titanium and to build predictive relationships between oxide film stability and the solution and mechanical variables.

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Appendices

Appendix A Adsorption investigation of Cu(II) and Fe(III) onto silica particles

The adsorption behaviour of Cu(II) and Fe(III) onto coarse silica particles, which were used as the solid deposit model in this work, was investigated *via* thermostatic flask shaker, at 200 RPM for 1 h. The experimental conditions are listed in Table A-1. The species adsorption onto the silica were determined by measuring the extent of depletion of species concentrations in solution. Solution species concentration was determined by inductively coupled plasma mass spectrometry (ICP-MS) with a Quadrupole ICP-MS Agilent 7700X.

Parameter	Conditions
Adsorbent	S1 (specific surface area: 0.017 m ² ·g ⁻¹ , $d_{0.5}$: 425 µm)
Base solution	Blank solution (30 g \cdot L ⁻¹ H ₂ SO ₄ + 12 g \cdot L ⁻¹ Cl ⁻)
Concentration of Cu(II), Fe(III)	$1{-}10 \text{ mg}{\cdot}\text{L}^{-1}$
Solution volume	50 mL
Solid concentration	$10-160 \text{ g} \cdot \text{L}^{-1}$
Temperature	50°C

Table A-1 Experimental conditions of adsorption tests

The adsorption behaviour of Cu(II) onto the coarse silica particles is shown in Figure A-1, Figure A-2 and Figure A-3. Since agents adsorption is more obvious in the lower concentration, the original Cu(II) concentration ranging from 1 to10 mg \cdot L⁻¹, which is much lower than that in the simulated leaching solution (15 g \cdot L⁻¹) was used, so does for Fe(III) adsorption study.


Figure A-1 Dependence of Cu(II) adsorption percentage on the original Cu(II) concentration in the blank





Figure A-2 Dependence of Cu(II) adsorption percentage on the silica concentration in the blank solution (5 $mg \cdot L^{-1}$ Cu(II), 50 mL solution, pH 1.5, 50°C)



Figure A-3 Dependence of Cu(II) adsorption percentage on pH of the blank solution (pH was adjusted by adding NaOH or H₂SO₄ to the basic solution, 5 mg·L⁻¹ Cu(II), 40 g·L⁻¹ silica concentration, 50 mL solution, 50°C)

The absorption behaviour of Fe(III) onto the coarse silica particles is demonstrated by Figure A-4 and Figure A-5.



Figure A-4 Dependence of Fe(III) adsorption percentage on the original Fe(III) concentration in the blank solution (40 g·L⁻¹ silica concentration, 50 mL solution, pH 1.5, 50°C)



Figure A-5 Dependence of Fe(III) adsorption percentage on the silica concentration in the blank solution (5 mg·L⁻¹ Fe(III), 50 mL solution, pH 1.5, 50°C)

The adsorption tests results show that Cu(II) adsorption by S1 is less than 5%, regardless of the original species concentration, silica concentration and solution pH. For Fe(III), the adsorption is less than 2%. The results suggest that Cu(II) and Fe(III) adsorption by the coarse silica particles is insignificant, and Cu(II) and Fe(III) loss by adsorption is negligible in the investigated condition.

Appendix B Galvanic effect on UDC of Ti-2 in solid deposition conditions

The deposition of solid particles on metallic surfaces may cause or accelerate corrosion of the underlying metals. This under-deposit corrosion (UDC) generally develops beneath or around deposits on a metal surface [20]. In practice, the deposits can give rise to coupling between regions covered with deposits and the uncovered adjacent regions. The solid deposits covered and noncovered portions may form a galvanic cell, and the resultant galvanic effect may be significant on the corrosion behaviour of the under-deposit corrosion (UDC). Crevice corrosion is a common form of occluded cell corrosion, where mass transport is limited most often in narrow fissures or gaps, restricting free exchange between the localised solution and the bulk solution. The localised solution may then acidify and corrosion initiates in the occluded region [131-133]. UDC can be considered a related phenomenon where the impediment is formed by one or more types of solid deposit (e.g., corrosion products, oxides, dust). UDC may display electrochemical behaviour consistent with the occluded cell effect. Both crevices and deposits are factors in industrial applications of titanium. However, investigations about the occluded cell nature of UDC have not been published. This work aims to improve our understanding of titanium UDC. The occluded cell characteristics of UDC in a neutral chloride solution were compared with well-documented findings for crevice corrosion.

B.1 Experimental

A conventional galvanic coupling technique was employed, where a small working electrode (WE) in the internal occluded region and a large counter electrode (CE) exposed to external environment are separated. A WE and CE of the same composition were cut from Ti-2 (C 0.012, N 0.008, O 0.120, and Fe 0.120 wt.%; H 17 ppm; and Ti as the balance) shim stock with 0.13 mm thickness. The WE was cut into a 1×1 cm flag shape and the CE was 10×5 cm (shown

in Figure A-6(a)). The flagpoles of the flag electrodes were electrically connected to the potentiostat lead. The area ratio of the CE to the WE was approximately 50:1. The use of flag samples avoided possible crevice corrosion that may have arisen from the gap between the epoxy sealant and the Ti-2 substrate.

A laboratory-grade fine silica particles (S3, specific surface area: 0.99 m²·g⁻¹, $d_{0.5}$: 20.4 µm, VWR) was used to prepare deposits in this work. The WE was inserted into fine silica deposits to depth of 2, 4, or 6 cm (from the center line of the flag). The large counter electrode was exposed outside the deposits.

Since local solution acidification is known to be a precursor for occluded cell corrosion initiation [55], a neutral 15.8 g·L⁻¹ NaCl (0.27 M) solution was prepared with DI water and Cryst./Certified ACS NaCl to investigate UDC attack caused by the galvanic cell effect. The test solution was vigorously aerated by transferring it between two beakers in air five times.



Figure A-6 Schematic of Ti-2 electrodes (a), and setup (b) to study the initiation of titanium UDC in 15.8 $g \cdot L^{-1}$ NaCl solution

A 1-L, cylindrical cell with a separate lid and a water jacket was used for the experiments; electrodes could be secured to ground glass joints on the lid (Figure A-6(b)). The lid and the vessel

were tightly connected by a clamp to seal the cell from the ambient air. The WE and CE were connected *via* the zero-resistance ammeter mode of the potentiostat. The current flowing between the deposit-covered WE and the CE was measured as the increase of temperature. The temperature was set initially to 55°C and then increased in stepwise (5°C/48 h) until reaching the initiation temperature or up to 90°C. The potential of the coupled electrodes was also measured simultaneously. Before the test, the WE and CE were immersed in 30 g·L⁻¹ sulfuric acid solution at 70°C for at least 30 min. to dissolve the oxide film, then rinsed with DI water for 30 seconds and immediately introduced to the test solution. The tests in this section were repeated twice due to the long test duration (>20 days).

An Ag/AgCl electrode (4 M KCl) with a Luggin capillary was used as a reference electrode; all potentials are quoted with respect to this reference electrode (0.197 V *vs.* standard hydrogen electrode (SHE)). All electrochemical experiments were conducted with a Potentiostat/Galvanostat VersaSTAT 4 from Princeton Applied Research.

B.2 Results

As the temperature was increased from 55 to 90°C, the potential of Ti-2 covered by 2 cm thick layer of fine silica showed a slight increase and then slowly leveled off toward a potential of approximately 0.35 V after 50 h (Figure A-7(a)). Simultaneously, the current between the deposit-covered Ti-2 WE and a large uncovered CE was initially negative, with current oscillations of $< 0.2 \ \mu$ A, then the current flattened out and its magnitude gradually decreased to a few nA. This initial negative current value and current oscillation can be attributed to anodic dissolution and passivation of the large CE as reported in previous work [305]. The current and potential did not appear to be significantly influenced by temperatures up to 90°C. The small current magnitude and relatively high potential indicate that UDC was not initiated on Ti-2 when the fine silica deposit

thickness was 2 cm. Moreover, visual examination of the sample surfaces did not show any corrosion attack morphology (data not shown).

When fine silica deposit thickness was 4 cm, the potential increased and reached approximately 0.23 V (Figure A-7(b)). The current leveled off to a negligible amount (~ nA) as the temperature was increased from 55 to 85°C. However, at 90°C, the potential showed an obvious decrease, and the current simultaneously increased—this signified the initiation of UDC. The potential decreased to a local minimum of approximately 0.16 V, and the current increased to a maximum of 0.58 μ A. The propagation did not last long (approximately 24 h) before the potential started to increase and the current decrease, indicating the repassivation process.

Under a 6 cm fine silica deposit, it was clear that UDC was initiated when the temperature was increased to 75°C (Figure A-7(c)). The potential showed an obvious drop to 0.1 V, and the current increased to 0.7 μ A. Although the propagation lasted only 24 h, the repassivation rate, demonstrated by the current decrease rate and potential increase rate, was much slower than in the case of the 4-cm layer (Figure A-7(b)). The current also showed oscillation for approximately 250 h during the repassivation process. Thus, UDC attack under a 6-cm layer should be more severe than under a 4-cm layer.

When the deposit layer thickness was increased to 8 cm, the critical temperature for UDC initiation was still at 75°C, as indicated by the galvanic potential drop (Figure A-7(d)). The galvanic current remained a very limiting value (\sim nA).

Charge Q during the propagation and repassivation process represented titanium loss during the UDC attack supported by the coupled external large CE where O₂ reduction took place. It was calculated by integrating the current vs time plots. Q was 0.19 C for titanium covered by 4-



cm layer; 0.33 C for titanium covered by 6-cm layer, and negligible for titanium covered by 8-cm layer.

Figure A-7 Current and potential during UDC initiation tests as a function of temperature for Ti-2 in 15.8 $g \cdot L^{-1}$ NaCl solution covered by S3 with thicknesses of (a) 2 cm, (b) 4 cm, (c) 6 cm, and (d) 8 cm

Figure A-8 shows the surface photos of Ti-2 samples beneath deposits before and after test. Metallic titanium is very active and reacts to form oxide film instantly when it is exposed to air. This layer of native oxide is very thin (~ 10 nm), and protective [306]. After test, titanium samples changed color. The color of the oxide has been explained by multiple-beam interference theory, and it is well established that the thickness of the oxide formed dictates the film color [307-310]. Ti-2 under 4 cm deposit layer had an overall brown color, suggesting an oxide layer thickness of approximately 36 nm; whereas the oxide formed under 6 cm deposit layer demonstrated various colors (*e.g.*, blue, purple, pink, bronze), indicating a thickness of 50–200 nm; the oxide formed under 8 cm deposit layer was expected to slightly thinner than that under 6 cm deposit layer.

The deposit-covered Ti-2 samples did not show obvious corrosion etching, nor did they show significant weight loss in the galvanic cell. The use of the term "corrosion" might be subject to controversy based on the conventional understanding of corrosion. However, the oxidation of metallic titanium to titanium oxide represents the degradation of the titanium substrate, and the thickness of oxide product can reflect the degradation level. The driving force for this oxidation is the galvanic effect that appears due to the solid deposit-formed galvanic cell.



Figure A-8 Surface morphologies of Ti-2 covered by (a) 4-cm layer silica deposits, (b) 6-cm layer silica deposits, and (c) 8-cm layer silica deposits after tests in 15.8 g·L⁻¹ NaCl solution

The degradation of Ti-2 under deposits in the neutral chloride solution can be explained by the deoxygenation-acidification theory based on crevice corrosion studies [131-137]. As oxygen depletes within the crevice, oxygen reduction (cathodic reaction) occurs mainly outside the crevice, and metal dissolution (anodic reaction) is the dominant reaction inside the crevice. This results in an increase in metal cation concentrations in the crevice solution and local acidification due to cation hydrolysis. The drop in solution pH and Cl⁻ accumulation (to maintain electrical neutrality) lead to an increasingly aggressive solution in the crevice environment, until the "critical

crevice solution" is reached, when the passive film breaks down and active corrosion take place [131-134].

Under occluded conditions, the occurrence of titanium film flaws is the key process leading to the localised solution aggressiveness and the corrosion initiation [134]. Titanium oxide film is reported to experience breakdown/crystallisation at approximately 70°C [55, 67, 134, 253]. During this process, the surface passive film becomes more "active", and grain boundaries or other more open pathways are introduced, which leads to a measurable film resistance drop and increased metal dissolution.

The degradation of Ti-2 under deposits in the neutral chloride solution, where degradation is not normally expected manifests the autocatalytic process of occluded cell corrosion. Ti-2 degradation under deposits showed dependence on the thickness of deposit layer. Corrosion attack became possible as the thickness of deposit layer increased to 4 cm; corrosion attack became severer and corrosion initiation temperature decreased as the thickness of deposit layer increased from 4 cm to 6 cm. Crevice corrosion study revealed that the severe crevice corrosion attack is always observed in a narrow and deep crevice since oxygen depletion and local solution chemistry change is more rapid and significant in the more occluded region [136]. Consistently, the thicker deposit layer is believed to make for a more occluded region, thus initiating under-deposit corrosion. However, the increase of deposit layer thickness also results in an increased mass transfer resistance in corrosion process, thus inhibits corrosion initiation, as shown in Figure A-7(d). Thus, the initiation of under-deposit corrosion should consider both the occluded effect and the mass transfer resistance in the galvanic cell.

Appendix C Reversible potential *E_{rev}* calculation

The reversible potential, *E_{rev}*, was calculated by invoking the Nernst equation as follows:

$$E_{rev} = E^0 + \frac{RT}{nF} ln \frac{a_{OX}}{a_{Red}}$$
 Equation A-1

where,

 E^{0} : standard half-cell reduction potential, and can be obtained from Gibbs free energies for the reaction;

R: universal gas constant, 8.314 J·K⁻¹·mol⁻¹;

T: temperature in kelvin, K;

F: Faraday constant, the number of coulombs per mole of electrons, 96485 $C \cdot \text{mol}^{-1}$;

n: the number of electrons transferred in the cell reaction;

a: the chemical activity for the relevant species. a_{Rex} is the activity of the reduced form and a_{Ox} is the activity of the oxidised form. The activity of species *i*, a_i , can be related to the physical concentrations c_i via $a_i = \gamma_i \cdot c_i$. γ_i is activity coefficient of species *i*.

C.1 Fe(III)/Fe(II) couple

When 6 mM Fe(III) was added to the blank solution (30 $g \cdot L^{-1} H_2 SO_4 + 12 g \cdot L^{-1} Cl^-$), the redox potential of the Fe(III)-SO₄²⁻-Cl⁻ system was reported to be solely determined by the Fe³⁺/Fe²⁺ couple as Equation A-2 shown below [192, 255, 256]:

$$Fe^{3+} + e^- = Fe^{2+}$$
 Equation A-2

 E_{rev} for Fe³⁺/Fe²⁺ couple can be written as:

$$E_{rev} = E^0 + \frac{2.303RT}{nF} \log \frac{\gamma_{ferric}}{\gamma_{ferrous}} + \frac{2.303RT}{nF} \log \frac{C_{ferric}}{C_{ferrous}}$$
Equation A-3

The E_{rev} calculation above required the standard half-cell reduction potential, E^0 , and the activity coefficient for ferric and ferrous, *i.e.*, γ_{ferric} and $\gamma_{ferrous}$. This reaction has been extensively

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investigated, and both the E^0 and the activity coefficient ratio of γ_{ferric} to $\gamma_{ferrous}$ can be obtained by the model proposed by Yue *et al.* [192, 255]. Thus, for the investigated condition (6 mM Fe(III), at 40, 60 and 80°C):

- > E^0 (vs. Ag/Ag/Cl) is: 0.580 V at 25°C, 0.604 V at 40°C, 0.636 V at 60°C, 0.668 V at 80°C.
- The term that includes the ratio of activity coefficients, $\frac{2.303RT}{nF} \log \frac{\gamma_{ferric}}{\gamma_{ferrous}}$ is: -0.021 V at 25°C, -0.022 V at 40°C, -0.024 V at 60°C, and -0.026 V at 80°C.
- Since the ferric concentration likely changes with time in the presence of Ti (*i.e.*, it is reduced to ferrous), we have assumed that equimolar concentration of Fe³⁺ and Fe²⁺, *i.e.*, both 3 mM. Therefore, the last term in Equation A-3 was assumed to be 0 at any temperature.

In summary, the calculated E_{rev} (vs. Ag/Ag/Cl) is for the investigated condition is: 0.56 V at 25°C, 0.58 V at 40°C, 0.61 V at 60°C, and 0.64 V at 80°C.

C.2 Hydrogen evolution reaction

Hydrogen evolution reaction (HER) is illustrated as Equation A-4:

$$2H^+ + 2e^- = H_2$$
 Equation A-4

The thermodynamic data used for the E^0 calculation, *i.e.*, the standard Gibbs free energies of formation and the entropies are from handbook [241]; equations for the temperature dependency of the standard molar heat capacity are from handbook [258]; extrapolation of thermodynamic data to elevated temperatures followed the Criss and Cobble method [259, 260].

- E⁰ vs. Ag/Ag/Cl calculated based on the thermodynamic data is: -0.197 V at 25°C, -0.187
 V at 40°C, -0.177 V at 60°C, and -0.167 V at 80°C.
- > The activity/gas pressure for H_2 is considered to be 1 in the calculation.

The pH values were measured in the blank solution, that is, 1.77 at 25°C, 1.62 at 40°C, 1.50 at 60°C, and 1.42 at 80°C.

In summary, the calculated E_{rev} for the HER vs. Ag/Ag/Cl is: -0.30 V at 25°C, -0.29 V at 40°C, -0.28 V at 60°C, and -0.27 V at 80°C.

C.3 Cu(II)/Cu(I), and Cu(I)/Cu couples

As the addition of 2 mM Cu(II) to the blank solution (30 g·L⁻¹ H₂SO₄ + 12 g·L⁻¹ Cl⁻) in the titanium corrosion system, Cu(II) was found to be reduced through two stages, *i.e.*, from Cu(II) to Cu(I), and from Cu(I) to Cu(0). Copper species are known to complex with the Cl⁻ in this type of solution. The predominant forms of Cu(II) and Cu(I) in the investigated solution are suggested to be CuCl⁺ and CuCl₂⁻ respectively according to previous work [256, 261]. The half-cell reactions for Cu(II)/Cu(I) and Cu(I)/Cu couples are illustrated as Equation A-5 and Equation A-6:

$$CuCl^+ + Cl^- + e^- = CuCl_2^-$$
 Equation A-5

$$CuCl_2^- + e^- = Cu(s) + 2Cl^-$$
 Equation A-6

For the E_{rev} calculation, the activity coefficients, γ_i , have been approximated by a slight modification of previous models [262]:

$$\log \gamma_{i} = -\frac{z_{i}^{2} A \sqrt{I}}{1 + B_{a}^{a} \sqrt{I}} - \log(1 + 0.018015I) + bI$$
 Equation A-7

Equation A-7 offers the advantage of simplicity as compared with that used for previous models, and gives similar results. This makes it appropriate for model simulations where ionic medium effects of moderate accuracy may be sufficient [262]. In Equation A-7, *I* is the ionic strength; *A*, *B* and *b* are temperature-dependent parameters; z_i is the electrical charge of the species *i*; *å* is a "distance of closest approach", which may be taken to be equal to that of NaCl (3.72 ×

 10^{-10} m). The calculated values of *A*, *B* and *b* as a function of temperatures, and the activity coefficients of each species are listed in Table A-2.

For the Cu(II)/Cu(I) couple shown in Equation A-3, the E_{rev} was calculated based on the same concentration of CuCl⁺ and CuCl₂⁻, *i.e.*, 1 mM. For the Cu(I)/Cu(0) couple shown in Equation A-4, the activity of solid copper is considered 1, and the concentration of CuCl₂⁻ was considered 2 mM for the E_{rev} calculation. The thermodynamic data for each species are obtained from [241, 256, 261, 262]

Table A-2 Activity coefficients of species for the cupric reduction reactions

T∕°C	A	<i>B</i> ×10 ⁻¹⁰	b -	Cu(II)/Cu(I) couple			Cu(I)/Cu(0) couple	
				γ-CuCl+	γ -Cl ⁻	γ -CuCl ₂ ⁻	γ -CuCl ₂ ⁻	γ-Cl⁻
25	0.509	0.328	0.064	0.659	0.659	0.659	0.659	0.659
40	0.531	0.332	0.060	0.655	0.655	0.655	0.655	0.655
60	0.553	0.336	0.066	0.651	0.651	0.651	0.651	0.651
80	0.575	0.340	0.072	0.646	0.646	0.646	0.646	0.646

The calculated E_{rev} for the reactions of interest in the investigated condition are all included

in Table A-3.

Table A-3 Calculated Erev for the reaction couples at different temperatures

<i>T</i> / °C	Fe(III)/Fe(II)	HER	Cu(II)/Cu(I)	Cu(I)/Cu(0)
25	0.56	-0.30	0.23	-0.15
40	0.58	-0.29	0.25	-0.17
60	0.61	-0.28	0.28	-0.19
80	0.64	-0.27	0.30	-0.22

Appendix D Assessment of electrochemical noise measurement potentiostats and validation of the electrochemical noise data

Assessment of electrochemical noise measurement potentiostats and validation of the electrochemical noise (EN) data is performed by following the guideline described by Ritter, Huet and Cottis [178] with a dummy cell. EN data are validated in the frequency domain by calculating the power spectral densities (PSDs) of the potential and current fluctuations for time records sampled at different sampling rates f_s . It includes: check whether an anti-aliasing (AA) filter is included in the data acquisition system before the analogue-to-digital converter; check the good overlap of PSDs sampled at different f_s ; compare the experimental PSD to the theoretical PSD of the thermal noise.

D.1 Assessment of the baseline noise

A dummy cell consists of a "star"-arrangement of resistors is used, which provides a welldefined source impedance and noise level, thereby allowing the testing of the noise level and sensitivity of the measuring instruments. The dummy cell is constructed of three resistors of equal value of 10 k Ω , connected in a star-arrangement (Figure A-9). The theoretical PSD of the thermal noise for this dummy cell is 2.47 × 10⁻¹⁶ (*6kTR*) for the potential thermal noise and 8.23 × 10⁻²⁵ (2*kT/R*) for the current thermal noise [178].



Figure A-9 Dummy cell configuration (all resistor values *R* are equal) [178]

All the potentiostats in our lab: Princeton Applied Research VersaSTAT 4, Princeton Applied Research PARSTAT 4000, and Gamry Reference 600 (software EN120), are checked by 201

performing EN measurements with this dummy cell (Figure A-10, A-11, A-12). PSDs of the potential and current fluctuations for time records sampled were calculated by using a programme provided by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON), which performs the calculation with the fast Fourier transformation (FFT) method. A section of 2048 data points for 2~9 sets was calculated and averaged. Before transformation, a linear trend removal was applied and the Hann window was used in each section.



Figure A-10 (a) Potential PSD and (b) current PSD measured on a dummy cell of 10 k Ω by Princeton Applied



Research VersaSTAT 4

Figure A-11 (a) Potential PSD and (b) current PSD measured on a dummy cell of 10 k Ω by Princeton Applied

Research PARSTAT 4000



Figure A-12 (a) Potential PSD and (b) current PSD measured on a dummy cell of 10 kΩ by Gamry Reference 600 (software EN120)

The PSD curves suggested that none of the potentiostats includes an AA filter in the data acquisition system: no PSDs show a decrease at frequencies close to the maximum frequency (or Nyquist frequency, $f_s/2$). Because of the absence of anti-aliasing filter, potential PSDs sampling at different f_s measured with VersaSTAT 4 (Figure A-10) and PARSTAT 4000 (Figure A-11) did not show good overlap. The aliasing became severer as the decrease of sampling frequencies, which was indicated by the increasing potential PSD levels. The peaks at 40 and 60 Hz in the current PSD curves can be explained by aliasing of the 60 Hz frequency of the mains. In general, PARSTAT 4000 shows a lower noise level than VersaSTAT 4: an approximate one order of magnitude lower noise at sampling rate of 100 Hz.

In comparison, PSDs sampled at different f_s show a good overlap measured with Gamry Reference 600 (software EN 120) (Figure A-12). In the measurement of the Gamry Reference 600 (EN 120), short blocks of current data are analysed periodically (where the block length, the data acquisition rate within the block, and the time between blocks are chosen, the noise data are "detrended" in each block, and the mean value and deviation of this data block is reported). To the authors' understanding, this procedure may correspond to a data-averaging AA filter as explained 203 in [288]. As pointed out by reference [288], this data-averaging AA filter might not be able to completely eliminate aliasing. Furthermore, this potentiostat reports a highest sampling rate limit of 10 Hz, which might be too low to record the fast corrosion transients information in some conditions, for example, the erosion-corrosion of titanium in slurries described in Chapter 8.

Compared with the thermal noise of the dummy cell, all three potentiostats show higher baseline noise levels. The baseline noise of the instruments depends on the resistors used, and it is not expected that it will always to be possible to measure the thermal noise of the resistors. The objective of the experiment is to determine the instrument noise levels.

The absence of AA filters and high level of instrument noise obviously leads to an increase in their measured PSD levels, especially when the sampling rate f_s is lower. This is, however, not rare for the commercially available potentiostats in view of the round-robin (RR) experiments results organized by the European Cooperative Group on Corrosion Monitoring of Nuclear Materials (ECG-COMON) [184]. Despite the aliasing problem and less than satisfactory system noise level, most of the commercially available potentiostats may still have the ability to generate valid EN data that provide insightful information.

D.2 Validation of electrochemical noise data in the investigated conditions

For the conditions under investigation of Chapter 8, EN measurements have been performed with VersaSTAT 4 and PARSTAT 4000 as shown in Figure A-13.



Figure A-13 Potential PSD of Ti-2 in the investigated conditions measured with VersaSTAT 4 (a), PSDs measured with PARSTAT 4000 (b)

Figure A-13 shows that VersaSTAT 4 shows a higher white noise level (flat potential PSD, $\sim 10^{-9} \text{ V}^2 \cdot \text{Hz}^{-1}$) than PARSTAT 4000 ($\sim 10^{-10} \text{ V}^2 \cdot \text{Hz}^{-1}$) as indicated at high frequencies ($\sim >3 \text{ Hz}$). Therefore, the potential fluctuations corresponding to a PSD value of $10^{-9} \text{ V}^2 \cdot \text{Hz}^{-1}$ measured with VersaSTAT 4 cannot be attributed to corrosion: only the three potential PSDs at highest slurry rates (600 RPM, 800 RPM and 1200 RPM) below 3 Hz are due to corrosion. In comparison, the potential PSDs measured with PARSTAT 4000 decreased with the increase of frequency even in static and dynamic solutions, indicating the aliasing was not significant at low frequencies for the investigated conditions. In the higher slurry rates conditions (> 400 RPM), the potential PSD levels measured with the two potentiostats were comparable, reflecting the corrosion activities. Therefore, VersaSTAT 4 is appropriate to conduct EN measurement for the slurry conditions with rotation rate higher than 400 RPM; PARSTAT 4000 is capable for EN measurements in all the conditions (static solution, dynamic solution, and slurry conditions) investigated in Chapter 8.