AN INVESTIGATION OF THE FAILURE MECHANISMS OF ALUMINUM CATHODES IN ZINC ELECTROWINNING CELLS

by

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ABSTRACT

Aluminum cathodes have long been used for the electrowinning of zinc from zinc sulfate-sulfuric acid electrolyte. Severe corrosion above the electrolyte/air interface limits the life of aluminum cathodes to ca. 18-24 months for a 6 mm thick plate. The failure characteristics of aluminum cathodes were analyzed using optical microscopy, scanning electron microscopy, energy dispersive x-ray analysis, and x-ray diffraction analysis. Three corrosion zones were identified: zone I below the electrolyte/air interface, zone II 0-40 mm above the electrolyte/air interface, and zone III 40-140 mm above the electrolyte/air interface. Zone II experienced maximum corrosion damage in the form of shallow, dense, cusp-like pitting. For a rejected aluminum plate, the corrosion damage in zone II was ca. 80% reduction in plate thickness. The corrosion damage in zones I and III was minor corresponding to ca. 10% reduction in plate thickness. The failure pattern of aluminum cathodes and the factors causing variation in corrosion rate in the different zones were studied.

Corrosion processes occurring under thin electrolyte film conditions limited the life of the cathode plate. The influence of microstructure, chloride, and fluoride on the corrosion susceptibility of aluminum cathodes was investigated in simulated and industrial electrolytes using cyclic polarization, potentiodynamic polarization, potentiostatic, galvanostatic, open circuit, and free immersion techniques. These techniques were coupled with electron metallography and chemical analysis of test solutions. The corrosion rate of the aluminum cathode plate decreased with increased pH and zinc concentration. Titanium addition to the cathode plate undermined its corrosion resistance in zone I by enhancing hydrogen evolution. In the presence of cathodic polarization, fluoride activated zone I corrosion but had minimal effect on zone II corrosion. Chloride had minimal effect on zone I corrosion; however, it strongly activated zone II corrosion and was the primary factor responsible for plate failure. A mechanism through which chloride acted on the aluminum cathode plate was proposed.
TABLE OF CONTENTS

Abstract ii
Table of Contents iii
List of Tables vii
List of Figures viii
List of Symbols and Abbreviations xviii
Acknowledgement xx

1.0 Introduction 1

2.0 Background 2

2.1 Zinc Hydrometallurgy: An Overview 2
  2.1.1 Roasting and Leaching 3
  2.1.2 Electrolyte Purification 4
  2.1.3 Zinc Electrowinning 6
  2.1.3.1 Design of Aluminum Cathode Plates 9

2.2 Aqueous Aluminum Corrosion 10
  2.2.1 Surface Oxide Film 11
  2.2.2 Effect of Ligands 15
  2.2.3 Pitting Corrosion 16
  2.2.3.1 Passive Film Breakdown 17
  2.2.3.1 A Ion Penetration Models 18
  2.2.3.1 B Adsorption Models 21
  2.2.3.2 Metastable Pitting 25
  2.2.3.3 Stable Pit Growth 27

2.3 Cathodic Corrosion of Aluminum 28
  2.3.1 Influence of Oxygen 32
  2.4 Corrosion Behavior of Al Cathode Plates 33
  2.4.1 Effect of Alloyed Elements 34
  2.4.2 Effect of Halides 36

2.5 Summary 38

2.6 Objectives 39
3.0 Experimental
3.1 Materials and Processing
3.1.1 Aluminum Alloys Processing
3.2 Microstructural Analysis
3.2.1 Metallographic Sample Preparation
3.2.2 Microetching
3.2.3 Microscopy
3.2.3.1 Transmission Electron Microscopy
3.2.4 Surface Analytical Methods
3.3 Failure Analysis
3.4 Electrochemical Testing
3.4.1 Electrode Preparation
3.4.2 Electrolytes
3.4.3 Instrumentation
3.4.4 Chemical Analytical Techniques
3.4.4.1 Quantitative Al Analysis
3.4.4.2 Chlorine Detection
3.4.5 Experimentation and Techniques
3.4.5.1 Potentiodynamic and Cyclic Polarization
3.4.5.2 Potentiostatic
3.4.5.3 Galvanostatic
3.4.5.4 Open Circuit
3.4.5.5 Free Immersion
3.4.5.5.A 200-day Test
3.4.5.5.B 83-day Test
3.4.5.5.C 4-day Test
3.4.5.5.D 1-day Test (Effect of pH)
4.0 Results and Discussion
4.1 Microstructural Analysis
4.2 Failure Analysis
4.3 Corrosion of Al Cathode Plates
<table>
<thead>
<tr>
<th>Appendix II: Al-Ti and Al-Mg Phase Diagrams</th>
<th>217</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix III: ICP-MS Spectrums for Cathode Plate Alloys</td>
<td>218</td>
</tr>
<tr>
<td>Appendix IV: Calculations of $E_{\text{red}}^\circ$ for AlCl$_3$ (aq) and AlF$_6^{3-}$ (aq)</td>
<td>219</td>
</tr>
<tr>
<td>Appendix V: Replated Cu in Zone II of a Monel Sample</td>
<td>220</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table I</td>
<td>Typical Electrolyte Composition after Purification [7]</td>
<td>5</td>
</tr>
<tr>
<td>Table II</td>
<td>Activation Energies and Reaction Orders for the Pit Initiation Reaction of Al 7075 with Different Halides [50]</td>
<td>24</td>
</tr>
<tr>
<td>Table III</td>
<td>Corrosion Potentials of Some Common Al Precipitates in 53 g dm(^{-3}) NaCl + 3 g dm(^{-3}) H(_2)O(_2) solutions that were open to air [116]</td>
<td>28</td>
</tr>
<tr>
<td>Table IV</td>
<td>Potentiostatic Weight Loss Measurement for 99.99% Al [118]</td>
<td>29</td>
</tr>
<tr>
<td>Table V</td>
<td>Intermetallics Presents in the Test Alloys [122]</td>
<td>32</td>
</tr>
<tr>
<td>Table VI</td>
<td>Composition of the 1070 and H1S Cathode Plates</td>
<td>40</td>
</tr>
<tr>
<td>Table VII</td>
<td>Cathode Plate Corrosion as a Function of Time in Different H(_2)SO(_4)-Halide Solutions</td>
<td>63</td>
</tr>
<tr>
<td>Table VIII</td>
<td>Variation of corrosion rate with F(^{-}) concentration for the H1S and 1070 alloys</td>
<td>73</td>
</tr>
<tr>
<td>Table IX</td>
<td>Potential measurements above and below solution line</td>
<td>82</td>
</tr>
<tr>
<td>Table X</td>
<td>Thermodynamic data for the formation of AlCl(_3) (aq) and AlF(_6)(^{3-})</td>
<td>218</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Typical flow sheet for hydrometallurgical zinc production.</td>
<td>2</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Schematic diagram showing the distribution of cell voltage and energy requirement of a zinc electrowinning cell.</td>
<td>7</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Schematic diagram showing a typical design of an Al cathode plate.</td>
<td>10</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Pourbaix diagram for aluminum in pure water at 298.15 K.</td>
<td>13</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Effect of pH on corrosion of Al 1100-H14 alloy by various chemical solutions [40].</td>
<td>14</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Pourbaix diagrams for the Al-F-H₂O system at 298.15 K and several F⁻ concentrations.</td>
<td>15</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Schematic illustration of the ion penetration model [74].</td>
<td>19</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Schematic illustration of the adsorption model [74].</td>
<td>22</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Variation of current with time at different potentials (SCE) in the vicinity of E₀ for Al - 4.5% Mg-0.8% Mn [61].</td>
<td>26</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Schematic diagram showing the Mechanism of cathodic Al corrosion in unstirred neutral environments.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Current-time transient for several Al alloys at -1.2 Vₘₜₜ in deaerated 3% NaCl [122].</td>
<td>31</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Variation of corrosion rate of H1S alloy with immersion time under open-circuit and at - 400 A m⁻² in 10 ppm F⁻-200 g dm⁻³ H₂SO₄ [139].</td>
<td>37</td>
</tr>
<tr>
<td>Figure 13</td>
<td>[a] Optical photomicrograph showing the microstructure of the H1S alloy (500 X): (1) primaryAl phase, (2) blade shape intermetallics, and (3) round rosettes; and [b] EDX analysis of the blade-shaped intermetallic particles.</td>
<td>109</td>
</tr>
<tr>
<td>Figure 14</td>
<td>SEM photomicrographs showing the morphology of the intermetallics at low and high magnifications and their alignment along the rolling direction.</td>
<td>110</td>
</tr>
<tr>
<td>Figure 15</td>
<td>[a] SEM photomicrograph showing clustering of angular particles near the edges of the H1S plate and [b] EDX spectra from these angular particles.</td>
<td>111</td>
</tr>
</tbody>
</table>
Figure 16: SEM photomicrograph showing the presence of Cu-containing particles in the H1S alloy.

Figure 17: EDX analysis from different regions of the photomicrograph in Figure 16.

Figure 18: TEM photomicrograph (60000 X) showing the alignment of Al-Fe intermetallics along the rolling direction.

Figure 19: TEM photomicrographs showing the two morphologies of Al-Fe intermetallic particles: [a] blade shape (80000 X) and [b] rectangular shape (30000 X).

Figure 20: [a] TEM photomicrograph (100000 X) showing nucleation of an Al-Cu precipitate on an Al-Fe intermetallic particle and [b] TEM photomicrograph (60000 X) showing the precipitation of Cu along the contour of an Al-Fe intermetallic particle.

Figure 21: Optical photomicrographs (100 X) showing the grain structure of the H1S alloy: [a] longitudinal section and [b] transverse section.

Figure 22: Optical photomicrographs (400 X) showing identical areas of a transverse section: [a] grain structure and [b] distribution of secondary particles.

Figure 23: TEM photomicrograph (70000 X) showing substructure in the H1S plate: (1) subboundary, (2) parallel dislocation array, and (3) intragranular dislocations.

Figure 24: Corrosion-distance plot for a failed Al H1S cathode plate after 24 months in service.

Figure 25: [a] SEM photomicrograph showing mud-crack sulfate deposit in zone III and [b] EDX spectra collected from the mud-crack deposit.

Figure 26: SEM photomicrograph showing crystallographic pitting underneath the mud-crack sulfate deposit of zone III.

Figure 27: SEM photomicrographs showing [a] cusp-like pitting in zone II and [b] minimal corrosion damage in zone I below the electrolyte level.

Figure 28: X-ray diffraction patterns from an Al H1S plate showing variance in diffraction peak intensity below and above the solution line: [a] zone II and [b] zone I.

Figure 29: Cross sectional view of two failed plates: (1) Cominco plate and (2) Kidd Creek plate. The photograph shows the characteristic hourglass
profile for the three corrosion zones and shows relatively more thinning in zone III of the Kidd Creek plate.

Figure 30  The effect of cathodic current density on the corrosion rate of fully immersed Al HIS cathode plate in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\).

Figure 31  Potential-time records for fully immersed Al HIS cathode plate in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\) at selected cathodic current densities.

Figure 32  SEM photomicrographs showing cusp-like pitting in the HIS alloy under open circuit conditions in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\).

Figure 33  Potential-time records for fully immersed Al HIS cathode plate at \(-400\) A m\(^{-2}\) in (1) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\) and (2) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\). Note the potential fluctuations in the halide-containing solution.

Figure 34  SEM photomicrographs of fully immersed HIS plate showing numerous micropits around the sites of the intermetallic particles in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\).

Figure 35  Potential-time records for fully immersed Al HIS cathode plate at \(-400\) A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halides.

Figure 36  Potential-time records for the Al cathode plate at \(-400\) A m\(^{-2}\) in (1) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\) and (2) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\).

Figure 37  Current density-time records for fully immersed Al HIS cathode plate at \(-1.574\) V\(_{MSE}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halides electrolytes.

Figure 38  SEM photomicrographs showing the corrosion morphology of the HIS alloy in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\) solution.

Figure 39  SEM photomicrographs showing the corrosion morphology of the HIS alloy in the 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-40 ppm F\(^{-}\) solution.

Figure 40  SEM photomicrographs showing the nucleation of pits near the intermetallic particles.

Figure 41  SEM photomicrograph showing the corrosion morphology of the HIS alloy in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\) solution. Note the minimal attack at the intermetallics.
Figure 42  Cyclic polarization curves for the H1S alloy exposed to 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halides. Scan rate is 1 mV s\(^{-1}\).

Figure 43  XPS survey spectra recorded from the Al H1S plate using AlK\(_\alpha\) radiation. The survey shows the incorporation of F\(^-\) in the oxide structure for a sample that was polarized at – 400 A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-1000 ppm F\(^-\) solution.

Figure 44  [a] SEM photomicrograph showing the precipitation of Al chloride salt particles in pits of zone I and [b] EDX analysis from these salt particles.

Figure 45  SEM photomicrograph showing a small batch with cusp-like pitting in relief, indicative of possible transformation of pit morphology from cusp-like to crystallographic morphology at advanced stages of the pitting process.

Figure 46  EDX spectra collected from zone III showing the presence of Cl\(^-\) anions.

Figure 47  Optical photomacrographs (12 X) showing the effect of Al dust addition on the corrosion morphology in zone II: [a] 50 ppm Al dust and [b] 200 ppm Al dust.

Figure 48  Optical photomacrographs (12 X) showing the corrosion morphology in zone II produced by the addition of 200 ppm Al in the form of Al sulfate.

Figure 49  Galvanostatic potential-time records comparing the effect of adding 200 ppm Al either as elemental Al dust or as Al sulfate.

Figure 50  Potentiostatic current density-time records at – 1.115 V\(_{MSE}\) for the H1S alloy showing the inhibitory effect of Zn\(^{2+}\) on Al dissolution in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl\(^-\)-x g dm\(^{-3}\) Zn\(^{2+}\) solutions.

Figure 51  Optical photomacrographs (10 X) showing the corrosion morphology corresponding to Figure 50: [a] no Zn\(^{2+}\) and [b] with 60 g dm\(^{-3}\) Zn\(^{2+}\).

Figure 52  Cyclic polarization curves for the H1S and 1070 alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl\(^-\)-60 g dm\(^{-3}\) Zn\(^{2+}\). Scan rate is 0.17 mV s\(^{-1}\).

Figure 53  Variation of corrosion rate with pH for cathode plate samples freely immersed in 1000 ppm F\(^-\).

Figure 54  Variation of corrosion rate with pH for cathode plate samples freely immersed in 1000 ppm Cl\(^-\).
Figure 55 SEM photomicrographs showing precipitation of solution products on cathode plate samples at pH = 3.5: [a] H1S alloy and [b] 1070 alloy.

Figure 56 Open circuit potential-time records for the H1S alloy and 99.9999 % Al in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\).

Figure 57 Mixed potential plot showing increased corrosion rate and a positive \(E_{\text{corr}}\) shift with increased exchange current density, \(j_0\).

Figure 58 Cyclic polarization curves for H1S and 99.9999 % Al samples exposed to 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halide electrolytes. Scan rate is 1 mV s\(^{-1}\).

Figure 59 Cyclic polarization curves for 99.9999% Al exposed to 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halides electrolytes. Scan rate is 1 mV s\(^{-1}\).

Figure 60 Open circuit potential-time record for Al-4 % Cu in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\).

Figure 61 SEM photomicrographs for Al-4 % Cu alloy showing the corrosion morphology after 10 hour free immersion in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\): [a] minimal surface damage and [b] precipitation of a bulky surface film.

Figure 62 Cyclic polarization curves comparing the pitting behavior of Al-4 % Cu alloy to that of the 1070 and H1S alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\). Scan rate is 0.2 mV s\(^{-1}\).

Figure 63 Close-up of the cyclic polarization curve for Al-4 % Cu around the primary passivation potential showing evidence of partial passive behavior. Scan rate is 0.2 mV/s.

Figure 64 Galvanostatic potential-time records for the H1S alloy at \(-400\ \text{A m}^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^{-}\) showing a positive potential shift with increased F\(^{-}\) concentration.

Figure 65 Galvanostatic potential-time records for the 1070 alloy at \(-400\ \text{A m}^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^{-}\) showing positive potential shift with increased F\(^{-}\) concentration.

Figure 66 SEM photomicrographs comparing the extent of corrosion damage at \(-400\ \text{A m}^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-15 ppm F\(^{-}\): [a] H1S alloy and [b] 1070 alloy.

Figure 67 Galvanostatic potential-time records comparing the 1070 and H1S alloys at \(-400\ \text{A m}^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^{-}\).
Figure 68 SEM photomicrographs showing the similarity in corrosion morphology observed in the H1S and 1070 alloys in F- containing solutions. Note the shallow, cusp-like pitting at 1000 ppm F-.

Figure 69 Galvanostatic potential-time records for partially immersed cathode plate samples held at – 400 A m² in 150 g dm⁻³ H₂SO₄–x ppm F⁻ solutions. Note the potential decay behavior in the absence of F⁻ anions.

Figure 70 SEM photomicrographs at – 400 A m² in 150 g dm⁻³ H₂SO₄–x ppm F⁻ solutions showing increased corrosion damage with increased F⁻ concentration: [a] 80 ppm F⁻ and [b] 1000 ppm F⁻.

Figure 71 SEM photomicrograph at – 400 A m² in 150 g dm⁻³ H₂SO₄–1000 ppm F⁻ solution showing extensive mud-crack deposit in zone III above the electrolyte level.

Figure 72 SEM photomicrographs at – 400 A m² in 150 g dm⁻³ H₂SO₄–x ppm F⁻ solutions showing the minor effect of F⁻ on zone II corrosion: [a] 0 ppm F⁻ and [b] 1000 ppm F⁻.

Figure 73 Optical photomacrographs comparing zone II corrosion at – 400 A m² in 150 g dm⁻³ H₂SO₄–x ppm F⁻ solutions: [a] 0 ppm F⁻ and [b] 80 ppm F⁻. Note the absence of zone II corrosion in both cases.

Figure 74 XPS survey spectra recorded from an Al H1S plate that was polarized at – 400 A m² in 150 g dm⁻³ H₂SO₄–1000 ppm F⁻ solution. The survey, recorded using AlKα radiation, shows the incorporation of F⁻ in the oxide structure in zone II and a strong F⁻ signal in the mud-crack deposit of zone III.

Figure 75 SEM photomicrographs at – 400 A m² in 150 g dm⁻³ H₂SO₄–x ppm Cl⁻ solutions showing superficial corrosion damage at high Cl⁻ concentrations: [a] 1500 ppm Cl⁻ and [b] 4000 ppm Cl⁻.

Figure 76 SEM photomicrographs showing the corrosion morphology after 6-hour immersion at open circuit in 150 g dm⁻³ H₂SO₄ solution: [a] H1S alloy and [b] 1070 alloy.

Figure 77 Open circuit potential-time records in 150 g dm⁻³ H₂SO₄ showing relatively high cathodic activity on the H1S alloy.

Figure 78 Open circuit potential-time records in 150 g dm⁻³ H₂SO₄–150 ppm Cl⁻ showing relatively high cathodic activity on the H1S alloy.
Figure 79  SEM photomicrographs comparing the extent of corrosion damage at open circuit in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–150 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 80  SEM photomicrographs showing pit nucleation around secondary phases at open circuit in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–150 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 81  SEM photomicrographs comparing the corrosion damage at open circuit in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy. Note the minimal damage in the 1070 alloy.

Figure 82  Open circuit potential-time records for several 1070 samples in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) showing good reproducibility.

Figure 83  Open circuit potential-time records comparing the 1070 and the H1S alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\).

Figure 84  Mixed potential plots showing the effects of H\(_2\) evolution kinetics on the appearance of the E\(_{corr}\) curves for the H1S and 1070 alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions.

Figure 85  Open circuit potential-time records in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–x ppm Cl\(^-\) solutions showing the effect of Cl\(^-\) concentration on the behavior of the H1S and the 1070 alloys.

Figure 86  Optical photomacrographs (6 X) showing the overall morphology of corrosion damage after 200-day free immersion in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 87  SEM photomicrographs showing cusp-like pitting after 200-day free immersion in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 88  SEM photomicrograph showing cusp-like pitting in zone II of a rejected plate that was in service for 24 months in Trail, Canada.

Figure 89  Optical photomacrograph (16 X) showing precipitation of aluminum sulfate on the 1070 alloy after 200-day free immersion in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions. Precipitation is still evident despite rinsing with deionized water and sample handling.

Figure 90  Optical photomacrographs (6 X) showing severe corrosion damage under thin electrolyte film conditions after 83-day free immersion in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 91  SEM photomicrographs showing superficial pitting in a 1070 alloy sample that was freely immersed in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solution for 92 hours.

Figure 92  EDX analysis of the white deposit formed on Al under thin H$_2$SO$_4$–Cl$^-$ electrolyte film. The chemical composition of the deposit is consistent with Al sulfate.

Figure 93  Optical photomacrographs (8 X) showing more voluminous Al sulfate deposit on the 1070 alloy relative to ultra pure Al under thin H$_2$SO$_4$–Cl$^-$ electrolyte films: [a] 1070 alloy and [b] 99.9999 % Al.

Figure 94  Optical photomacrographs (8 X) comparing the corrosion damage underneath the Al sulfate deposits: [a] 1070 alloy and [b] 99.9999 % Al. Note the minimal damage in the high purity Al.

Figure 95  SEM photomicrographs comparing the corrosion damage underneath the Al sulfate deposits: [a] 1070 alloy and [b] 99.9999 % Al.

Figure 96  Potentiodynamic cathodic polarization curves for the HIS alloy generated using a divided cell (H-cell) in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions. Argon-deaeration started 280 minutes prior to sample immersion.

Figure 97  SEM photomicrographs comparing the corrosion damage in deaerated and oxygenated solutions after 48-h open circuit immersion in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions: [a] Deaerated and [b] Oxygenated.

Figure 98  Variation of corrosion current density with applied potential for the HIS and 1070 alloys in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions. Each potential value was applied for 6 hours, then the corrosion rate was determined by chemical analysis.

Figure 99  Current density-time records for the HIS and 1070 alloys at $E = -1.115 \text{ V}_{\text{MSE}}$ in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions.

Figure 100  Current density-time records for the HIS and 1070 alloys at $E = -1.1 \text{ V}_{\text{MSE}}$ in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions.

Figure 101  Cyclic polarization curves comparing the pitting behavior of fully immersed 1070 and HIS alloys in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions. Scan rate is 0.17 mV s$^{-1}$.

Figure 102  Optical photomacrographs (8 X) showing the detrimental effect of Cl$^-$ anions on zone II corrosion in 150 g dm$^{-3}$ H$_2$SO$_4$–x ppm Cl$^-$ solutions: [a] no Cl$^-$ and [b] 150 ppm Cl$^-$.  

xv
Figure 103 [a] Optical photomacrograph (9 X) and [b] SEM photomicrograph showing increased corrosion damage in zone II with increased Cl\textsuperscript{\textendash} concentration. The sample was galvanostatically tested in 150 g dm\textsuperscript{3} H\textsubscript{2}SO\textsubscript{4}–1000 ppm Cl\textsuperscript{\textendash} solution.

Figure 104 Optical photomacrographs (8 X) comparing zone II corrosion in the 1070 and H1S alloys in 150 g dm\textsuperscript{3} H\textsubscript{2}SO\textsubscript{4}–150 ppm Cl\textsuperscript{\textendash} solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 105 SEM photomicrographs comparing zone II corrosion in the 1070 and H1S alloys in 150 g dm\textsuperscript{3} H\textsubscript{2}SO\textsubscript{4}–150 ppm Cl\textsuperscript{\textendash} solutions: [a] 1070 alloy and [b] H1S alloy.

Figure 106 [a] SEM photomicrograph showing Cl\textsuperscript{\textendash}rich deposit in zone II and [b] EDX spectra confirming the presence of Cl\textsuperscript{\textendash} anions in the deposit.

Figure 107 Optical photomacrographs (8 X) showing reduction in zone II corrosion due to sacrificial Mg anode: [a] without sacrificial protection and [b] with sacrificial protection.

Figure 108 X-ray diffraction analysis showing similar spectra recorded from the H1S and the 1070 cathode plates.

Figure 109 SEM photomicrographs showing the distribution of secondary phases in the H1S alloy before and after artificial aging for 28 hours at 200 \textdegree C: [a] before and [b] after.

Figure 110 SEM photomacrographs showing the distribution of secondary phases in the 1070 alloy before and after artificial aging for 28 hours at 200 \textdegree C: [a] before and [b] after.

Figure 111 XPS spectra recorded from the H1S and the 1070 cathode plates showing similar surface films and no Ti presence in the H1S protective film.

Figure 112 Current density-time records for the H1S and 1070 alloys at E = -1.130 V\textsubscript{MSE} in 150 g dm\textsuperscript{3} H\textsubscript{2}SO\textsubscript{4}–500 ppm Cl\textsuperscript{\textendash} solutions.

Figure 113 Potentiodynamic cathodic polarization curves comparing fully immersed pure Al and pure Ti in 150 g dm\textsuperscript{3} H\textsubscript{2}SO\textsubscript{4} solutions.

Figure 114 Three configurations of cathode plates examined in rectangular Zn electrowinning cells.

Figure 115 Optical photomacrographs (6 X) showing higher corrosion propensity near the cathode side containing the electrical contact notch: [a]
opposite side and [b] electrical contact side. The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$.  

**Figure 116** Optical photomacrographs (8 X) showing significantly lower corrosion damage on the modified plate of configuration C: [a] unmodified plate (configuration A) and [b] modified plate (configuration C). The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$.  

**Figure 117** Optical photomacrographs (8 X) showing significantly lower corrosion damage on the cathode plate tested in the presence of airflow: [a] with airflow (configuration A) and [b] without airflow (configuration A). The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$.  

**Figure 118** SEM photomicrographs showing minimal corrosion damage in zone II under an Ar atmosphere: [a] zone I of an unmodified plate (configuration A) and [b] zone II of the plate. The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$.  

**Figure 119** SEM photomicrographs from the test in Figure 118 at higher magnification.
LIST OF SYMBOLS AND ABBREVIATIONS

AA, Atomic Absorption
B, Tafel Slope
E_a, Apparent Activation Energy for the Pit Initiation process.
E_b, Breakdown Potential
E_{cell}, Equilibrium Cell Voltage
E_{corr}, Corrosion Potential
EDX, Energy Dispersive X-ray
E_{red}, Reduction Potential
\Delta E_b = E - E_b, Breakdown Overpotential.
F, Faraday’s Constant
H1S, Commercial Designation of an Al-Ti Alloy
ICP-MS, Induction Coupled Plasma Mass Spectroscopy
j_0, Exchange Current Density
j_a, Partial Anodic Current Density
j_c, Partial Cathodic Current Density
k, Specific Rate Constant
MPC, Metaparacresol
m, Reaction Order
MSE, Mercury Sulfate Electrode
PVC, Polyvinyl Chloride
R, Universal Gas Constant
SEM, Scanning Electron Microscopy
SIMS, Secondary Ion Mass Spectroscopy
STEM, Scanning Transmission Electron Microscopy
t_i, Induction Time to Pit Initiation
T, Temperature
[X], Concentration of Species X
XAS, X-ray Absorption Spectroscopy
XPS, X-ray Photoelectron Microscopy
XRD  X-ray Diffraction Analysis

$z$  Valence of Metal Cations

$\alpha$  Polarizability of the oxide/electrolyte interface,

$\alpha_a$  Anodic Transfer Coefficient

$\alpha_c$  Cathodic Transfer Coefficient

$\eta$  Overpotential
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1.0 INTRODUCTION

Electrolytic zinc extraction accounts for at least 75% of zinc production worldwide [1]. Zn is electrowon from an acidified zinc sulfate bath. An applied cathodic current density of ca. 400 A m$^{-2}$ deposits high purity Zn onto Al cathode plates and generates $\text{H}^+$ and $\text{O}_2$ at insoluble Pb anode plates. After plating for 16 to 72 hours, the Al cathode plates are removed from the cells and the deposited zinc is stripped and recovered.

A large zinc plant uses around 25000 cathode plates, each weighing 25-35 kg. The useful life of a cathode plate is generally short, about 18-24 months for a 6 mm thick plate. Plate failure often results from intense localized pitting corrosion just above the electrolyte/air interface. Corrosion of the plate in this region undermines its mechanical integrity, and it subsequently fails under the stresses encountered during deposit stripping. Replacement of rejected plates represents a significant operating expenditure for the plant. Corrosion below the electrolyte/air interface is also problematic. It destroys the barrier Al oxide film, allowing direct contact between the deposited Zn and the Al substrate. When this occurs, the deposited Zn adheres firmly to Al and cannot be stripped easily. These problems arise even though the Al plate operates under cathodic potential control.

Cathodic Al corrosion is not only relevant to the zinc industry, but also important in other applications such as cathodically protected systems and integrated circuits [2-3]. Despite the scientific and industrial importance of cathodic corrosion, relatively few fundamental studies have explored its underlying mechanisms, especially in acidic environments. Previous Al cathode plate development for zinc electrowinning reactors involved a trial-and-error approach and focused on practical testing, which accounts for the sluggish improvement in the performance of cathode plates. This thesis investigates the basic corrosion mechanisms of Al cathode plates. Once these mechanisms have been identified, the corrosion resistance of the cathode plate can be optimized through judicious alloying additions and careful application of protective methods.
Zinc extraction from zinc concentrates can be attained either by a pyrometallurgical or hydrometallurgical route. Most zinc plants use the hydrometallurgical method since it offers the advantages of high production capacity, high efficiency, and high purity Zn metal. The hydrometallurgical method consists of four sequential stages: roasting, leaching, purification, and electrowinning [1]. A simplified flow sheet of the process is shown in Figure 1.

Figure 1. Typical flow sheet for hydrometallurgical zinc production.
2.1.1 ROASTING AND LEACHING

The feed to the process is a zinc concentrate consisting of zinc sulfide, iron sulfide, and several minor impurity elements. Zinc extraction begins by roasting the concentrate at ca. 925 °C in fluid bed roasters. Roasting converts zinc sulfide to acid-soluble zinc oxide, and converts iron sulfide to zinc ferrite. Two distinct sulfuric acid leaching stages are used to dissolve the calcine: neutral leach stage and hot acid leach stage. In the neutral leach stage, excess calcine is leached with spent electrolyte to dissolve zinc oxide and form zinc sulfate solution. The excess calcine maintains the pH of the leach solution around 5. At this pH, zinc ferrite is poorly soluble and remains undissolved. Ferric and aluminum ions precipitate as hydroxides, carrying with them, by adsorption, impurities such as antimony, arsenic, germanium, and silica. If iron is present as ferrous ions, it remains in solution and does not precipitate. The addition of manganese dioxide or air oxidizes the ferrous ions to ferric ions, thus completing the removal of iron as ferric hydroxide. The clarified neutral leach liquor passes to the purification stage and the residue passes to the hot acid leach stage.

The residue from the neutral leach stage contains zinc ferrite and hydroxide precipitates. It is releached with addition of concentrated sulfuric acid at 95 °C. Under these aggressive conditions, most of the iron and zinc dissolve. Iron is then rejected from solution by jarosite precipitation in the pH range 1 to 1.5:

\[
3 \text{Fe}_2(\text{SO}_4)_3 + 10 \text{H}_2\text{O} + 2 \text{NH}_4\text{OH} = (\text{NH}_4)_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12} \downarrow + 5 \text{H}_2\text{SO}_4 \quad (1)
\]

Sodium and potassium cations may be used, instead of ammonium, to complex and precipitate the basic iron sulfate. As jarosite precipitation progresses, the pH decreases due to acid generation. The addition of zinc oxide offsets this pH shift, maintaining the pH at the desired level. After separating the jarosite precipitate by thickening and filtering, the zinc-rich liquor returns to the neutral leach stage. Some zinc plants use alternative iron rejection methods such as goethite (FeOOH) [4] and hematite (Fe$_2$O$_3$) precipitation [5].
A relatively recent development in Zn plant practice was the introduction of oxidative pressure leaching. In this process, the Zn concentrate bypasses the roasting step. The concentrate is leached directly with dilute H\textsubscript{2}SO\textsubscript{4} at 150 °C under an oxygen pressure of 700 kPa [6]. The products of this process are a ZnSO\textsubscript{4} slurry and elemental sulfur. The Zn solution flows to the purification stage and the sulfur is recovered for subsequent sale. Pressure leaching has two main advantages over the roast-leach process: (i) it eliminates the gas and particulate emission problems of roasting and (ii) it provides flexibility by eliminating the need to couple Zn production with H\textsubscript{2}SO\textsubscript{4} production, which became necessary in order to keep emission of roasting gases (SO\textsubscript{2}) below the regulated level.

2.1.2 ELECTROLYTE PURIFICATION

During leaching, minor impurity elements present in the concentrate also enter the solution. Most impurity elements are detrimental to the Zn electrowinning process. They may corrode plant materials (Cl\textsuperscript{-} and F\textsuperscript{-}), contaminate the zinc deposit (Pb, Cd, and Cu), or decrease current efficiency (As, Sn, Ni, Se, Co, Sb, and Ge). As the reduction potential for zinc is more negative than that for hydrogen, zinc electrowinning is particularly sensitive to impurities that lower hydrogen overpotential: Sb and Ge can completely prevent zinc deposition if their concentration exceeds 0.05 ppm and 0.01 ppm, respectively [7-8]. Therefore, it is essential to lower the concentrations of detrimental elements to the necessary levels (Table I). This is accomplished by the purification stage.

Purification of the neutral leach liquor is conducted in agitated tanks using zinc powder. Metals that are more noble than zinc deposit on the zinc powder by a displacement process called cementation. Antimony and copper, in the form of Sb\textsubscript{2}O\textsubscript{3}, and CuSO\textsubscript{4}, are usually added to the purification stage to activate the zinc powder and improve its selectivity and efficiency. The amount of zinc powder required far exceeds that predicted by the reaction stoichiometry. The excess amount compensates for zinc particles lost due to deactivation by cemented coatings [1]. After Cu and Cd are cemented at low temperature, the liquor is heated to 90 °C to displace Co, Ge, and the remaining
impurities. The cementation cake is processed to recover valuable metals such as Cd and Cu. Table I shows a typical composition of a purified solution.

Table I
Typical Electrolyte Composition after Purification [7]

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration/10⁻⁴ g dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>[110 – 180] x 10⁴</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>&lt; 5 x 10⁴</td>
</tr>
<tr>
<td>Magnesium</td>
<td>[5 – 12] x 10⁴</td>
</tr>
<tr>
<td>Manganese</td>
<td>[0.5 – 20] x 10⁴</td>
</tr>
<tr>
<td>Chloride</td>
<td>500 - 3000</td>
</tr>
<tr>
<td>Fluoride</td>
<td>30 - 400</td>
</tr>
<tr>
<td>Iron</td>
<td>30 - 150</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1 - 4</td>
</tr>
<tr>
<td>Copper</td>
<td>1 - 4</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1 - 4</td>
</tr>
<tr>
<td>Nickel</td>
<td>1 - 5</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.1 – 0.5</td>
</tr>
<tr>
<td>Germanium</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

The purified solution contains chloride and fluoride anions. These anions are highly corrosive to cell materials. Chloride can oxidize at the anode evolving Cl₂, a toxic and corrosive gas. Fluoride is a powerful stimulator of Al corrosion because it forms many stable, soluble complexes with Al. Both halides are considered the primary culprits in the formation of firmly adherent zinc deposits [9-15]. Corrosion and strippability problems occur even though the Zn cell operates under cathodic potential control. In the Zn electrowinning environment (pH ≈ 0), the exact role of Cl⁻ and F⁻ anions in the corrosion mechanisms of Al cathode plates has received limited attention.

Morgan [1] stated that the Cl⁻ concentration can be reduced by precipitation with Ag sulfate, but this treatment is expensive without the complete recovery of the precipitated Ag. Fluoride ions are partially removed during neutral leaching by adsorption on the hydroxide precipitates. Further F⁻ control can be attained by the addition of Al sulfate to
form aluminum fluoride complexes [1]. Nonetheless, the corrosive effects of these halides occur even when their concentration in solution is only a few ppm. After the purification stage, the solution is filtered and passed on for electrowinning.

### 2.1.3 ZINC ELECTROWINNING

Zinc electrowinning practice varies somewhat from plant to plant. The following description relates mainly to the Cominco operation at Trail, Canada [16]. Electrowinning is carried out in a series arrangement of rectangular, multielectrode cells. In the Cominco cellhouse, each cell contains 51 Pb-0.75% Ag anodes alternating with 50 Al cathodes. The electrodes contact the busbars through a single inverted V-notch in the header bar. The electrical connection to the electrodes is monopolar: the anodes rest on the positive busbar; the cathodes rest on the negative busbar. The deposition area of each cathode is ca. 3 m$^2$. Anodes are slightly smaller than cathodes and equipped with plastic spacers to maintain a uniform interelectrode gap of 45 mm at the start of electrowinning.

The electrolyte circulates between the cells and cooling towers. The cooling towers extract part of the heat liberated during electrolysis, keeping the electrolyte temperature below 40 °C. This limits the H$_2$ evolution rate since the hydrogen overpotential decreases as temperature increases. The circulating electrolyte is usually maintained at ca. 35 °C with Zn and H$_2$SO$_4$ concentrations of 50 and 150 g dm$^{-3}$, respectively. The electrolyte contains surfactants such as glue and metaparacresol (MPC) at concentrations of 10 and 3 ppm, respectively. Glue improves deposit quality. MPC forms a stable foam layer at the electrolyte/air interface, reducing acid mist concentration below 1 mg H$_2$SO$_4$ per m$^3$ of air, a level required for a hygienic work environment.

An applied cathodic current density of ca. 400 A m$^{-2}$ deposits high purity Zn (> 99.99%) onto the Al cathodes and generates H$^+$ and O$_2$ at the Pb anodes. This current density corresponds to a cell voltage of ca. 3.3 V. Since the reversible cell voltage is about 2 V, the Zn electrowinning cell operates at a voltage efficiency of ca. 60%. Anodic polarization and ohmic drop in the electrolyte account for most of the additional energy.
Figure 2 summarizes the various components contributing to the voltage requirement in a typical zinc cell. Although Zn deposition and O$_2$ evolution reactions are the primary electrode processes, secondary reactions proceed at both the cathode and anode. An important secondary reaction at the cathode is H$_2$ evolution. This reaction decreases current efficiency since it uses approximately 10% of the applied cathodic current. Secondary reactions at the anode include Cl$^-$ and Mn$^{2+}$ oxidation, the products of which are Cl$_2$ gas and MnO$_2$, respectively:

\[
2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^{-} \tag{2}
\]
\[
E_{2}/\text{V}_{\text{SHE}} = 1.36 + 0.0296 \log (\text{Cl}_2) - 0.0296 \log [\text{Cl}^-]
\]
\[
\text{Mn}^{2+} + 2 \text{H}_2\text{O} = \text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \tag{3}
\]
\[
E_{3}/\text{V}_{\text{SHE}} = 1.23 - 0.12 \text{pH} - 0.0296 \log [\text{Mn}^{2+}]
\]

\[
2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- + Zn^{2+} + 2 \text{e}^- \rightarrow Zn
\]

Anode Overpotential = 0.72 V  
Anode Reversible Pot. = 1.23 V  
Resistance = 0.48 V  
(Hardware & Electrolyte IR Drop)  
Cathode Reversible Pot. = - 0.76 V  
Cathode Overpotential = - 0.11 V

\[i = 400 \text{ A m}^{-2}\]
Current Efficiency (CE) = 90%  
Electric Energy Requirement = 82 * V/ CE = 82 * 3.3/90 = 3.0 kWh/kg of Zn

Figure 2. Schematic diagram showing the distribution of cell voltage and energy requirement of a zinc electrowinning cell.
Corrosion at the anode can raise the amount of Pb\(^{2+}\) ions in the circulating electrolyte to levels that lead to contamination of the Zn deposit [16]. New anodes are usually pretreated to form a coating of lead dioxide that mitigates anode corrosion [16]. Initially, the anodes corrode and precipitate lead sulfate which then oxidizes to lead dioxide if the potential is \(\geq 1.9\) \(V_{\text{SHE}}\). The reactions occurring during anode treatment are as follows:

\[
Pb + SO_4^{2-} \rightarrow PbSO_4 (s) + 2 e^- \quad (4)
\]

\[
E_{\text{f}/V_{\text{SHE}}} = -0.356 - 0.0296 \log [SO_4^{2-}] 
\]

\[
PbSO_4 (s) + 2 H_2O \rightarrow PbO_2 + 4 H^+ + SO_4^{2-} + 2 e^- \quad (5)
\]

\[
E_{\text{f}/V_{\text{SHE}}} = 1.7 + 0.0296 \log [SO_4^{2-}] - 0.12 pH
\]

The formation of a MnO\(_2\) scale, due to Mn\(^{2+}\) oxidation at the anode, provides added control of anode corrosion [1, 8]. The presence of Ag in the Pb anode promotes the formation of an adherent MnO\(_2\) scale [8]. As the scale thickens, it falls to the bottom of the cell carrying with it adsorbed residual impurities such as Cu and Co [1]. Some Zn plants maintain a minimum Mn content because of these useful functions. However, excessive scale formation increases cell voltage and causes short-circuits. Cell tanks and anodes require periodic cleaning to remove MnO\(_2\). The addition of 250 to 2000 g SrCO\(_3\) tonne\(^{-1}\) of Zn to the circulating electrolyte reduces the concentration of Pb\(^{2+}\) in solution by coprecipitating PbSO\(_4\) with SrSO\(_4\) [7].

Stripping and handling of electrodes are automated operations in modern zinc plants. Cathodes and anodes can be removed individually or in groups by means of overhead cranes. At the end of the deposition cycle, the cathodes are removed from the cells, rinsed in water tanks, then conveyed to the stripping machines to recover the deposited zinc. The recovered zinc is washed, dried, then melted in low-frequency induction furnaces. The molten zinc is cast into various shapes, compositions, and sizes according to customer specifications. After stripping, the Al cathodes are inspected for damage and conditioned by automatic, cylindrical steel brushes to regenerate the surface and remove adherent zinc particles. The conditioned cathodes are returned to the cells for re-use.
2.1.3.1  Design of Aluminum Cathode Plates

A successful cathode plate must possess good corrosion resistance and high strength. The plate must have high electrical conductivity to minimize electric energy usage and high hydrogen overpotential to maximize current efficiency. It must also possess a stable, conductive, barrier coating. The coating prevents bonding between the Al substrate and the deposited Zn, thereby precluding alloy formation and facilitating Zn stripping.

The zinc industry has long used Al cathode plates because they offer the best compromise between the above criteria and cost. The particular Al alloy plate used in Zn extraction is a 1xxx series alloy containing at least 99.0% Al. Aluminum is thermodynamically unstable in low pH environments; however, slow dissolution kinetics and protection by the Zn deposit mitigate the corrosion damage below the electrolyte surface. Minor alloyed additions of Mg, Si, or Ti have been added to various cathode plates to improve corrosion resistance and strippability [17-19]. Despite these additions, the service life of Al plates remains limited to ca. 18 months owing to high corrosion susceptibility above the electrolyte/air interface.

Typically, the aluminum cathode plate is manufactured by hot rolling cast ingots, which are pre-heated then cold worked to a thickness of ca. 6.5 mm or 4.8 mm. Cold working increases the yield strength of the plate to ca. 140 MPa, a strength level necessary for the stripping operation [20]. Figure 3 shows a typical design of a cathode plate. The plate is welded to an aluminum header bar of sufficient cross-sectional area (length = 1540 mm x height = 90 mm x width = 25 mm) to carry the current used in electrolysis. The header bar contains two handling lugs and contacts the electrical DC system through an inverted copper V-notch. The Cu notch is welded to the header bar and especially designed to minimize contact resistance. Plastic materials mask the edges of the plate (edgesticks) to maintain a uniform current density and to prevent the zinc deposit on the two faces of the plate from bonding around the edges. A plastic flipper is attached to the side of the plate and can pivot upward during stripping to allow entry of the horizontal knives. The height
of the cathode plate protruding above the electrolyte surface is ca. 0.14 m, excluding the header bar.

![Schematic diagram showing a typical design of an Al cathode plate.](image)

**Figure 3.** Schematic diagram showing a typical design of an Al cathode plate.

### 2.2 AQUEOUS ALUMINUM CORROSION

Corrosion is defined as the degradation of a structure because of chemical or electrochemical interaction with the surrounding environment [21]. The driving force for metallic corrosion is the tendency of metals to release the excess internal free energy gained during the extraction of metals from their minerals [21]. Passivity refers to a state of diminutive corrosion current arising from the formation of a protective surface film under oxidizing conditions with marked anodic polarization [21]. Aluminum is a highly reactive metal: it is passivity that makes it a useful engineering material.
A fresh Al surface oxidizes spontaneously in air and passivates due to formation of a tenacious, transparent film of aluminum oxide. The film isolates the highly reactive Al substrate from the electrolyte environment and stifles the anodic process. The properties of the film control the corrosion behavior of Al [22-27]. The oxide film is compact, extremely thin (2-5 nm) and, if damaged, capable of self-healing in most near-neutral environments [28]. In aqueous solutions, the film has a two-layer structure: a thin, amorphous barrier layer adjacent to the metal surface and a porous, crystalline outer layer [23]. The thickness of the amorphous layer depends only on temperature [22]; it attains a limiting thickness of 1 nm and thickens at a rate of 1 nm/100 K [23]. Thick oxide films produced in aqueous solutions result mainly from growth in the outer crystalline layer.

At room temperature, oxide growth in water occurs according to the following sequence: 
\[ \text{Al(OH)}_3 \text{ (amorphous)} \rightarrow \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O (boehmite)} \rightarrow \beta-\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O (bayerite)} \rightarrow \alpha-\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O (gibbsite)} \]  
At ca. 200 °C, the trihydrated oxides transform to monohydrated oxides which in turn dehydrate to \( \gamma-\text{Al}_2\text{O}_3 \) in the temperature range 380-450 °C [30]. Although gibbsite is the equilibrium phase at room temperature, it has not been found in actual oxide films [28]. Altenpohl and Post [31] identified bayerite as the main constituent of the oxide film formed in water below 75 °C. Other investigators [22, 32-33] identified boehmite as the stable oxide polymorph at low temperatures. MacDonald and Butler [29] attributed this inconsistency to the propensity of the various oxide polymorphs to exist as metastable phases. Further, equilibrium conditions are difficult to attain because the transformations from boehmite \( \rightarrow \) bayerite \( \rightarrow \) gibbsite are extremely slow.

Environmental conditions prevailing during film formation determine the composition, structure, and thickness of the oxide film. These conditions include temperature, electrolyte composition and, in the case of anodizing, applied potential [26]. Substrate composition also can influence the properties of the passive film, as some alloyed elements partition into the oxide lattice. Godard [28] stated that passive films on Al-Mg...
alloys may contain MgO in an amount proportionately larger than the percentage of Mg in the alloy. Textor and Grauer [34] used x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) to assess the enrichment of alloyed Li and Mg in the oxide film on pure Al. During thermal treatment, pronounced enrichment of these elements occurred even at temperatures as low as 280 °C. Brock and Hein [35] observed the formation of MgO crystals in an alumina film at 350 °C in thermal oxidation of Al–3% Mg alloys. Magnesia formed according to the following solid-state reaction:

$$\text{Al}_2\text{O}_3 + 3 \text{Mg} \rightarrow 3 \text{MgO} + 2 \text{Al} \quad (6)$$

Under certain conditions, reaction (6) could proceed until the film consisted entirely of the less protective MgO. This deleterious modification of the passive film may occur during material fabrication or during subsequent thermomechanical processing.

Substantial improvement in corrosion resistance can be attained if beneficial elements (e.g., Ta, Zr, and Ti) are successfully incorporated within the oxide lattice. These elements may modify the electrical properties of the passive film so that adsorption of aggressive species is unfavorable or they may produce passive films that are intrinsically more resistant to corrosion attack. The inhibition of aggressive species adsorption arises from the concept of pH of zero charge, $\text{pH}_{\text{zch}}$, which determines the adsorption behavior of the surface [36-38]. The $\text{pH}_{\text{zch}}$ is the pH at which the oxide surface is electrically neutral. It is a characteristic parameter of the oxide film. If the pH of the solution is greater than the $\text{pH}_{\text{zch}}$, the surface is negatively charged and anion adsorption is unfavorable. Accordingly, a low $\text{pH}_{\text{zch}}$ improves corrosion resistance since it discourages $\text{Cl}^-$ adsorption, a necessary step in the corrosion process. McCafferty and Natishan [37] implanted an Al surface with species having $\text{pH}_{\text{zch}}$ values lower than that of $\text{Al}_2\text{O}_3$ to improve the pitting resistance. The authors showed that the Al breakdown potential, $E_b$, improved significantly when oxides of low $\text{pH}_{\text{zch}}$ were incorporated into the alumina film. Silicon and molybdenum shifted $E_b$ several hundred mV in the positive direction. Implantation of these elements imparted a more negative charge to $\text{Al}_2\text{O}_3$, thus reducing the tendency of the $\text{Cl}^-$ anions to adsorb at the surface.
The thermodynamic stability of Al in aqueous environments can be assessed using a Pourbaix diagram (Figure 4). The diagram displays the domains of stability for the various species involved in the electrochemical equilibria. The domains of stability for the oxide film, soluble ions, and the metal are termed passivation, corrosion, and immunity respectively. It can be seen from the Al–H$_2$O Pourbaix diagram that the oxide film is unstable in low and high pH environments. The film is stable in the pH range of approximately 4 to 10. In this range, Al passivates and exhibits a very low general corrosion rate. Outside this range, the protective film dissolves and Al corrodes uniformly. At sufficiently low potentials, the Al metal itself is stable and thermodynamically immune to corrosion.

![Pourbaix diagram for aluminum in pure water at 298.15 K.](image)

**Figure 4.** Pourbaix diagram for aluminum in pure water at 298.15 K.

---

1 The data used in constructing Pourbaix diagrams are listed in Appendix I. Unless specified, all dissolved species are at activities of 10$^{-6}$; gaseous species are at 101.3 kPa.
The Pourbaix diagram has some inherent limitations. It presents theoretical thermodynamic data but provides no kinetic information. Although the diagram predicts Al oxide dissolution in low-pH environments, the corrosion rate of Al in some acids (e.g., dilute H\(_2\)SO\(_4\)) remains low owing to slow oxide dissolution kinetics. Even when the underlying Al substrate becomes locally exposed, the corrosion rate of pure Al may still be low. This is because the oxide film possesses poor electronic conductivity, which prevents it from acting as an efficient cathode for the exposed site [39]. In practice, the stability of the passive film and its rate of dissolution depend more on the nature of the individual aqueous species than on the pH of the environment. For example, the corrosion rate of Al 1100-H14 alloy is very low in glacial CH\(_3\)COOH (pH = 5), concentrated HNO\(_3\) (pH = 1), and concentrated NH\(_4\)OH (pH = 13). However, NaOH, Na\(_2\)CO\(_3\), and HF acid accelerate the rate of dissolution in the same alloy (Figure 5).

\[\text{Figure 5. Effect of pH on corrosion of Al 1100-H14 alloy by various chemical solutions [40].}\]
2.2.2 **EFFECT OF LIGANDS**

A ligand is an atom or a group of atoms that bonds to the central element in a complex ion. Ligands enhance corrosion by stabilizing metal ions in solution. Halide anions are important ligands in Al corrosion because of their aggressiveness and ubiquity [41-48]. Their effect is particularly pronounced in acidic environments due to increased complex solubility. Fluoride, for example, forms a series of cationic and anionic complexes with Al that range from $\text{AlF}^{2+}$ to $\text{AlF}_6^{3-}$ depending on the $\text{F}^-$ activity and the pH of the environment [15, 49]. Figure 6 displays the Pourbaix diagrams for the Al-F-H$_2$O system at various fluoride concentrations.

![Pourbaix diagrams for the Al-F-H$_2$O system at 298.15 K and several F$^-$ concentrations.](image_url)

**Figure 6.** Pourbaix diagrams for the Al-F-H$_2$O system at 298.15 K and several F$^-$ concentrations.
The diagrams demonstrate that increased fluoride concentration expands the corrosion domain and contracts the passivity domain. Low fluoride concentration and low pH favor the formation of soluble cationic complexes such as AlF$_{2+}$ and AlF$_{22+}$. As the F$^-$ concentration increases ([F$^-$] $\geq$ 40 ppm F$^-$), anionic complexes begin to appear in the neutral regime. At 1000 ppm F$,^-$ anionic complexes ranging from AlF$_{4^-}$ to AlF$_{63^-}$ dominate the neutral and acidic regimes.

The formation of Al fluoride complexes can result in a quick and general loss of passivity even in environments with extremely low F$^-$ concentrations. Chloride ions also form several stable soluble complexes with Al (e.g., AlCl$_3$). In comparison to fluoro complexes, the chloro complexes are fewer in number, less stable, and less well defined. Chloride usually produces localized passivity breakdown at weak surface points, whereas F$^-$ produces general passivity breakdown.

2.2.3 PITTING CORROSION

Although Al passivates in the pH range 4 to 10, it can sustain severe localized corrosion if the electrolyte contains aggressive species such as Cl$^-$ anions. Loss of passivity occurs at selected surface sites through the formation of soluble Al chloride complexes [50-53]. Complex formation at these energetically preferred sites localizes the corrosion attack. The susceptible sites can be dislocations, grain boundaries, intermetallic particles, or flaws in the oxide film. According to Wood et al. [54], pure Al contains flaws at a population density of $10^4$ to $10^5$/cm$^2$. The addition of alloying elements (e.g., Cu) increases the density to ca. $10^{10}$ cm$^2$.

The selective corrosion attack at weak sites can result in many forms of localized corrosion, but pitting is the most common form in Al alloys. A stable pit develops on a passive surface in three sequential stages:

I. Passive film breakdown,
II. Metastable pitting, and
III. Stable pit growth.
2.2.3.1 **Passive Film Breakdown**

Passivity breakdown requires a critical threshold potential called the breakdown potential [55]. The breakdown potential ($E_b$) reflects a material's resistance to the nucleation of pits. The more positive $E_b$, the more resistant is the material to pit nucleation. Since Al is an amphoteric metal, the breakdown of its oxide film can also occur during cathodic polarization, which can shift the local pH upward into the domain of Al oxide instability (Figure 4). The effect of cathodic polarization is particularly pronounced in neutral solutions.

Knornschild and Kaesche [56] showed that $E_b$ depends on Cl$^-$ concentration and on the type and amount of alloyed elements present in solid solution with Al. The dependence of $E_b$ on Cl$^-$ concentration is semi-logarithmic with $E_b$ decreasing with increasing Cl$^-$ concentration. Varying the solute content in Al can increase or decrease $E_b$ depending on whether the solute is more noble or more active, respectively. For example, increasing the amount of Cu in solid solution increases $E_b$ while Zn addition decreases it. It should be emphasized that $E_b$ indicates a material's resistance to pit initiation, but it does not indicate the extent of damage that will result from the propagation of stable pits.

Although $E_b$ for 2024 Al (Al-Cu alloy) is more noble than $E_b$ for 7075 Al (Al-Zn-Mg alloy), the former alloy suffers greater pitting damage in Cl$^-$ environments. Bond et al. [57] noted that the pitting susceptibility of Al is determined primarily by the distribution of cathodic phases and this distribution has no effect on $E_b$. Moreover, $E_b$ for Al is generally insensitive to variation in alloy composition [58-61]. For these reasons, the utility of $E_b$ as a parameter for alloy evaluation is rather limited [54]. However, $E_b$ is useful when augmented with knowledge of cathodic polarization behavior [62].

The exact role of halides in passivity breakdown is not well understood: it is unclear whether halides initiate the local breakdown of the passive film or simply impede film self-healing at sites bared by chemical dissolution [63-68]. Many models have been put forward to explain the mechanisms of passivity breakdown; there is still no single model that is consistent with all experimental observations. The proposed models may be
classified into two groups according to the location of pit initiation [69]: (1) ion penetration models which assume pit initiation at the metal/oxide interface and (2) adsorption models which assume pit initiation at the oxide/electrolyte interface. Both groups consider adsorption as the first step in the pitting process.

2.2.3.1.A Ion Penetration Models

Penetration models require the direct interaction of aggressive anions with the metal substrate. The interaction may be facilitated by physical defects in the oxide film such as pores, flaws, and mechanically induced cracks [70-74]. Hoar [71] suggested that Cl\textsuperscript{-} adsorption at the oxide/electrolyte interface gradually lowers interfacial tension through mutual repulsion of the adsorbed anions. When the interfacial tension is sufficiently low, the concentrated surface charge produces a kind of peptization. Because the anions are strongly attached to the oxide film, the repulsive forces between them produce cracks in the protective film exposing the underlying substrate to direct interaction with the aggressive anions.

Hoar et al. [75] proposed another model that emphasized the role of the large electric field across the passive film. According to this model, the adsorbed aggressive anions penetrate the film when the electric field reaches a critical value corresponding to $E_b$. (Figure 7). Incorporation of the aggressive anions within the film increases its ionic conductivity. Consequently, the rate of cation transport through the film accelerates and pitting proceeds rapidly. The main role of the anions is to prevent repassivation of activated sites.

Pryor [76] presented a similar model. The anions adsorbed at the oxide/electrolyte interface generate a high electric field that enhances the diffusion of Cl\textsuperscript{-} through the defect structure of a thin, uniform $\gamma$-Al\textsubscript{2}O\textsubscript{3} film. In contrast to the previous model [75], the diffusing ions undergo a substitution reaction in the oxide lattice; three Cl\textsuperscript{-} anions replace three oxygen ions which migrate in the reverse direction. This anion exchange process upsets electrical neutrality. To restore neutrality, a single Al ion diffuses through
the film via vacancies and enters the solution. The authors postulated that the ion exchange process creates additional neutral cation vacancies, which further enhances the diffusion of Al ions through the oxide film. These conclusions were inferred from impedance measurements that indicated a drop in the ionic resistivity of the anodized $\gamma$-Al$_2$O$_3$ film without a change in its electronic resistance. This model has been widely criticized. Vetter [77] remarked that the model required oxygen ion migration against the high electric field. Wood [78] questioned the experimental technique and interpretation of results. Foley [68] commented that, contrary to experimental evidence, the model assumed a uniform anhydrous oxide film and neglected the existence of flaws in the film. Foley cited the work of Konno et al. [79] and Bernard et al. [80] and suggested that changes in the electrical properties of the oxide film can be explained simply by the hydration of the anhydrous oxide film.

Figure 7. Schematic illustration of the ion penetration model [74].
Experimental evidence does not support models requiring diffusion of aggressive anions through the lattice structure of the oxide film. The experimentally observed induction time ($t_i$) to pit nucleation is very short, less than 1 ms [81]. The diffusion rate of anions through the oxide lattice would be much too slow to account for the observed induction time [82]. In particular, the penetration model cannot explain the corrosion of Al in NO$_3^-$ containing solutions. The diffusion of these large polyatomic ions through the oxide lattice is unlikely or at best very slow, yet small induction times have been observed [83]. The penetration model is also contradicted by some surface analytical studies, which found no evidence of Cl$^-$ incorporation within the Al$_2$O$_3$ film [84-85]. Models based on mechanical film breakdown, due to built-in film stresses, lack supportive experimental evidence.

Lin, Chao, and Macdonald [86] proposed a theoretical model to predict the nucleation of corrosion pits at the metal/oxide interface. According to this model, called the point defect model, the aggressive halide ions become incorporated into the oxide lattice by occupying the oxygen anion vacancies at the oxide/electrolyte interface. The film responds by generating ion-pair vacancies (Schottky imperfections) which raise the concentration of cation vacancies at the oxide/electrolyte interface. This enhances the flux of cation vacancies to the metal/oxide interface where they coalesce and form voids. When a void reaches a critical size, it stresses and destabilizes the passive film. The film ruptures and rapid localized attack ensues.

The authors derived the following mathematical expressions for $E_b$ and $t_i$:

$$E_b = A - B \log a_{Cl^-}$$  \hspace{1cm} (7)

$$t_i = B \exp \left( -\frac{zF \alpha \Delta E_b}{2RT} \right) + C$$ \hspace{1cm} (8)

Where:

$A$, $B$, and $C$ are constants,

$a_{Cl^-}$ is the chloride activity,
F is Faraday's constant,
z is the valence of metal cations in the film,
α is the polarizability of the oxide/electrolyte interface,
RT is the thermal energy, and
ΔE_b = E - E_b is the breakdown overpotential.

Equations (7) and (8) are in qualitative agreement with experimentally observed behavior. Equation (7) predicts the observed semi-logarithmic dependence of E_b on Cl\(^-\) concentration. Equation (8) is consistent with the fact that t_i increases with film thickness. However, some of the model's parameters are unknown and, hence, verification is not possible. Also, the model requires the occurrence of a threshold initiation potential, the existence of which is questionable in many metallic systems.

2.2.3.1.B Adsorption Models

Adsorption models assume pit nucleation at the oxide/electrolyte interface. Considerable experimental evidence points to halide adsorption as the initial step in the pitting process [87-90]. Anions adsorb spontaneously on a passive film exposed to an aqueous electrolyte. Wood et al. [89] immersed pure Al (99.99%) for 6 hours in a KCl solution under free corrosion conditions. Using SIMS, the authors observed a significant Cl\(^-\) adsorption at the oxide/electrolyte interface. Augustynski [90] reported similar results using XPS with pure Al (99.99%) exposed to various anion-containing environments (e.g., Cl\(^-\), SO\(_4^{2-}\), ClO\(_4^-\)). Augustynski also noted that anion adsorption was proportional to the applied potential. The surface concentration of Cl\(^-\) increased from 3 to 12% (atomic) when the applied potential was shifted from E_cor to E_b. These studies demonstrate that Cl\(^-\) adsorption is necessary, but not sufficient condition for pit nucleation, as adsorption occurs even at E_cor, but stable pitting will not ensue until the potential exceeds E_b.

Bohni and Uhlig [59] proposed the concept of competitive adsorption. According to this concept, Cl\(^-\) and passivating anions adsorb simultaneously on the passive surface. Above E_b, Cl\(^-\) adsorption is favored and a loss of passivity occurs. This mechanism explains the
nonuniform distribution of localized corrosion since adsorption is likely to occur at discrete surface defects such as edge dislocations emerging to the surface. The mechanism, however, cannot explain the dependence of $t_i$ on film thickness [91].

Hoar and Jacob [92] postulated that Cl\textsuperscript{-} anions adsorb at the oxide/electrolyte interface and form highly soluble transitional complexes with the metal cations. Once formed, a complex can readily leave the surface. When another cation moves to the surface to replace the dissolved cation, it complexes with other adsorbed Cl\textsuperscript{-} anions and the process repeats itself. The net effect is an autocatalytic local thinning of the passive film. The electrostatic field in the thinned region continuously increases, further enhancing the oxide dissolution process (Figure 8).

\[ \frac{d\delta}{dt} = \frac{V_m}{Z F} (i_i - i_c) \]

\[ i_c \gg i_{cp} \]

(by ads. aggr. ions)

\[ i_i (= i_{cp}) \]

\[ i_i \]

\[ i_i (= i_{ch}) \]

$i_c =$ corrosion current density; $i_{cp} =$ passive current density; $i_{ch} =$ free corrosion current density

**Figure 8.** Schematic illustration of the adsorption model [74].
Foroulis and Thubrikar [93] extended this concept to passivity breakdown in Al. They proposed two stages for passivity breakdown in near-neutral solutions:

1. The competitive adsorption of Cl\(^-\) anions on the oxide/electrolyte interface in preference to the adsorption of OH\(^-\) anions or H\(_2\)O molecules;
2. The adsorbed Cl\(^-\) anions form a soluble Al(OH\(_2\)Cl salt:

\[
\begin{align*}
\text{Al(OH)}_3 & \quad \leftrightarrow \text{Al(OH)}_2^+ + \text{OH}^- & (9) \\
\text{Al(OH)}_2^+ + \text{Cl}^- & \rightarrow \text{Al(OH)}_2\text{Cl} & (10)
\end{align*}
\]

Reaction (9) ionizes the hydrated surface film imparting a positive character that promotes Cl\(^-\) adsorption. The above reactions proceed autocatalytically until the oxide film is locally removed. Cl\(^-\) anions attack the exposed metal substrate and metal dissolution ensues. The induction time in the above model is related to the rate of localized oxide dissolution. It increases with an increase in film thickness. Foroulis [93] observed that E\(_b\) became more noble as the film thickness increased. He interpreted E\(_b\) as the minimum potential across the oxide/electrolyte interface at which Cl\(^-\) anions could penetrate the electric double layer and adsorb on the hydrated oxide surface. The thicker the film, the greater was E\(_b\) due to potential drop within the film. As noted before, significant anion adsorption occurs even under open circuit conditions.

Foley et al. [50-52] studied the nature of compounds formed between adsorbed halide anions and the passive film as a function of pH. The authors considered the reciprocal of the induction time (1/t\(_i\)) to approximate to the rate of pit initiation. The rate law and Arrhenius expressions for the pit initiation process have the following logarithmic forms, respectively:

\[
\begin{align*}
\ln (1/t_i) &= \ln k + m \ln [\text{Al}^{3+}] + n \ln [X] & (11) \\
\ln (1/t_i) &= \ln A - E_a/RT & (12)
\end{align*}
\]

Where:
k is the specific rate constant,
[X'] is the halide concentration,
[Al^{3+}] is the Al concentration,
m, n are the respective reaction orders,
A is a constant having the same units as k,
RT is the thermal energy, and
\(E_a\) is the apparent activation energy for the initiation process.

The reaction order \(n\) represents the number of halide anions coordinated to a single Al atom. Assuming \(m, k, \text{ and } [\text{Al}^{3+}]\) are constant, a logarithmic plot of \(1/t\) versus \([X']\) yields the value of \(n\). Activation energy, \(E_a\), was determined from the usual Arrhenius plot. Table II summarizes the experimentally determined \(n\) and \(E_a\) values for different halides. It can be seen that acidic solutions favor high \(n\) and \(E_a\) values, especially for Cl\(^-\) and Br\(^-\) anions. According to the authors, the high \(E_a\) values are evidence of the direct chemical interaction between these two halides and the Al surface. The authors postulated that in H\(_2\)SO\(_4\)/Cl\(^-\) environments the initial dissolution occurs via the formation of Al\(_2\)Cl\(_8\)^{-2} [50].

<table>
<thead>
<tr>
<th>Halide</th>
<th>(E_a / \text{kJ mol}^{-1})</th>
<th>Halide Reaction Order (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH = 0.3</td>
<td>pH = 5.8</td>
</tr>
<tr>
<td>F(^-)</td>
<td>-</td>
<td>19.3</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>75.3</td>
<td>50.2</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>108.8</td>
<td>41.9</td>
</tr>
<tr>
<td>I(^-)</td>
<td>27.6</td>
<td>-</td>
</tr>
</tbody>
</table>

Solutions: 0.5 M H\(_2\)SO\(_4\) (pH = 0.3) and 0.1 M Na\(_2\)SO\(_4\) (pH = 5.8)

Foley [68] reviewed the literature on localized Al corrosion. He suggested that localized corrosion can be logically organized in four sequential steps: (1) adsorption of aggressive anions, (2) chemical interaction between the anions and Al in the surface film to form
stoichiometric compounds, (3) thinning of the surface film by dissolution at weak sites, and (4) direct interaction between the substrate and the anions. Foley argued that the different opinions on localized corrosion originate from emphasizing a particular step in this multi-step pitting process. Step (4) marks the onset of pit growth, which is initially unstable.

2.2.3.2 Metastable Pitting

When passivity is lost and a pit nucleates on the substrate, the pit may either repassivate or it may survive long enough to propagate and grow into a stable pit. The survival of a newly nucleated pit depends on the local electrolyte composition. Aziz [94] investigated pit initiation on an Al sheet immersed in water by a radioactive-tracer technique. He noted that an infinite number of surface sites developed local cells. Most of the local cells polarized and passivated without forming a visible pit. The most highly active sites did not immediately passivate, and developed increased acidity which raised the driving potential and hindered repassivation. Wright and Godard [95] showed that although AA-1100 Al pitted in stagnant tap water, a small amount of agitation was sufficient to prevent pitting. Agitation prevented the formation of strongly acidic sites which were necessary for the survival of local cells.

Galvele [96] proposed that a transition from metastable to stable pitting occurred when a critical combination of pit depth (d) and current density (i) was achieved at the nucleation site. The agglomeration of adsorbed Cl\(^-\) anions at weak spots produced chloride islands. The islands generated concentrated acid chloride microenvironmements that provided suitable conditions for pit propagation. The remnant of the oxide film might cover the pit mouth and help maintain the concentrated microenvironment. The propagation at this early stage was unstable and the critical microenvironment could be disrupted by external factors such as agitation. If the microenvironment remained undisturbed, metal dissolution continued and the critical pit depth (d) was attained. The rapid attack beneath a salt island produced a surface cavity that protected and shielded the microenvironment, further reducing the probability of repassivation.
The initiation rate for metastable pits increases as the applied potential approaches $E_b$. This is illustrated in Figure 9 which shows current records at three different potentials for Al-4.5 Mg-0.8% Mn alloy ($E_b = -740 \text{ mV}_{\text{SCE}}$). For a low pitting driving force, the current increases rapidly in the first 100 s, but quickly decays to a low value. This indicates the formation and repassivation of a large number of metastable pits. The low driving force is unable to sustain a sufficiently low pH to prevent repassivation. At the highest potential, the current stabilizes at a high level and many pits continue to grow since critical acidification is more readily attained at high anodic potentials above $E_b$. At potentials more active than $E_b$, metastable pits still nucleate but are unable to grow to more than 1 μm in diameter.

Figure 9. Variation of current with time at different potentials (SCE) in the vicinity of $E_b$ for Al - 4.5% Mg-0.8% Mn [61].
2.2.3.3 Stable Pit Growth

After the critical conditions for pit stability are established, the anodic dissolution of Al steadily raises the concentration of Al\(^{3+}\) in the base of the pit. Because of diffusional limitations between the pit and the bulk solutions, excess positive charge accumulates at the base of the pit. Chloride anions enter the pit to maintain electroneutrality [97]. The pH within the pit tends to decrease owing to hydrolysis:

\[
\text{Al}^{3+} + 2 \text{H}_2\text{O} = \text{Al} (\text{OH})^{2+} + \text{H}_3\text{O}^+ \quad (13)
\]

Aluminum dissolution continuously increases the concentration of H\(^+\) and Cl\(^-\) within the confines of the pit, and the dissolution process accelerates autocatalytically since both of these ions stimulate dissolution [98]. Some pits may propagate in a stable manner for a long time, then terminate. Termination of pitting appears to result from the accumulation of corrosion products within the pit cavity. Godard [28] stated that corrosion products terminate pitting by raising the internal resistance of the cell. Moore et al. [99] attributed pit termination to water migration through the precipitated salt layer as the layer reaches a certain thickness.

Impurities and alloying elements generally reduce the pitting resistance of Al [100-103]. The increased pitting susceptibility arises from the relatively high chemical reactivity of Al and from the limited solid solubility of other elements in Al [28]. The high chemical reactivity renders Al anodic to almost all the principal alloying elements. The limited solubility results in the formation of microstructural heterogeneities in the form of intermetallic particles. Intermetallic particles can increase the pitting susceptibility of Al in several ways [104-110]. They can establish local galvanic couples with the adjoining matrix, they can disrupt the continuity of the protective film, and they can catalyze the cathodic reaction. Intermetallic phases such as FeAl\(_3\) and CuAl\(_2\) markedly increase corrosion damage in Al by catalyzing the cathodic reaction kinetics [111-115]. Reducible ions (e.g., Cu\(^{2+}\)) plated on the passive film have a similar effect. Intermetallics can be cathodic or anodic to the Al matrix depending on their chemical composition and
structure. Table III displays the corrosion potentials of several intermetallics in Al alloys and the driving force for microgalvanic corrosion; the greater the potential difference $E_{\text{phase}} - E_{\text{Al}}$, the greater is the thermodynamic strength of the microgalvanic couple.

### Table III

Corrosion Potentials of Some Common Al Precipitates in 53 g dm$^{-3}$ NaCl + 3 g dm$^{-3}$ H$_2$O$_2$ solutions that were open to air [116]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Potential/mV$_{\text{SCE}}$</th>
<th>$E_{\text{phase}} - E_{\text{Al}}$/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (99.95 %)</td>
<td>-760</td>
<td>--</td>
</tr>
<tr>
<td>Si</td>
<td>-170</td>
<td>590</td>
</tr>
<tr>
<td>NiAl$_3$</td>
<td>-430</td>
<td>330</td>
</tr>
<tr>
<td>FeAl$_3$</td>
<td>-470</td>
<td>290</td>
</tr>
<tr>
<td>CuAl$_2$</td>
<td>-640</td>
<td>120</td>
</tr>
<tr>
<td>MnAl$_6$</td>
<td>-760</td>
<td>0</td>
</tr>
<tr>
<td>Mg$_2$Al$_3$</td>
<td>-1150</td>
<td>-390</td>
</tr>
</tbody>
</table>

Manganese is a notable exception to the deleterious influence of other elements on Al. It has relatively high solid solubility in Al, and Al-Mn intermetallics exhibit limited tendency to catalyze cathodic processes. The intermetallics develop corrosion potentials close to that of the matrix, thereby minimizing microgalvanic action [117]. They also tend to tie up residual Fe in (Fe, Mn)Al$_6$ particles. The incorporation of Fe in the lattice structure of these particles restricts the formation of the harmful FeAl$_3$ phase.

### 2.3 CATHODIC CORROSION OF ALUMINUM

Cathodic corrosion refers to corrosion damage during cathodic polarization. As the Pourbaix diagram in Figure 4 shows, Al oxide is thermodynamically soluble in both strong acid and strong alkali environments. DiBari and Read [118] demonstrated the amphoteric character of the Al oxide film through potential-controlled weight loss experiments on 99.99% Al. The electrolyte was aerated 0.5 N NaCl solution at 30 °C; the initial pH was 4.0. Their results are summarized in Table IV. As the applied potential shifted away from the corrosion potential ($E_{\text{corr}} = -1.24$ V$_{\text{SCE}}$), the corrosion rate climbed
for both cathodic and anodic overpotentials ($\eta = E - E_{corr}$). Relatively higher corrosion rates and higher alkalinity were associated with cathodic overpotentials. For example, the corrosion rate and the pH rise were much higher at $E = -1.5\ V_{SCE}$ ($|\eta| = 0.26\ V$) compared to the values at $E = -0.8\ V_{SCE}$ ($|\eta| = 0.44\ V$). For a constant cathodic overpotential (e.g., - 0.26 V), increasing the exposure time produced higher alkalinity and, consequently, a substantial increase in corrosion rate.

Table IV
Potentiostatic Weight Loss Measurement for 99.99% Al [118]

<table>
<thead>
<tr>
<th>$\eta$/V</th>
<th>Final pH</th>
<th>Test Time/10^3 s</th>
<th>Corr. Rate/A m^-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.26</td>
<td>8.6</td>
<td>95.4</td>
<td>4.10</td>
</tr>
<tr>
<td>-0.26</td>
<td>9.6</td>
<td>161.3</td>
<td>9.90</td>
</tr>
<tr>
<td>-0.16</td>
<td>4.2</td>
<td>242.6</td>
<td>0.40</td>
</tr>
<tr>
<td>-0.06</td>
<td>4.1</td>
<td>230.4</td>
<td>0.10</td>
</tr>
<tr>
<td>+0.44</td>
<td>7.0</td>
<td>89.3</td>
<td>1.13</td>
</tr>
</tbody>
</table>

Even in environments where the thermodynamic tendency for Al dissolution is high, the corrosion damage of ultra pure Al can be minimal owing to the high electronic resistance of the Al oxide film [39]. This resistance hinders the kinetics of cathodic processes and thus limits corrosion damage. As the purity of Al decreases, intermetallic particles form in the microstructure. Cathodic activity concentrates around these particles because they provide low-resistance paths for the migration of electrons to the film/solution interface, i.e. the particles are better catalysts for cathodic reactions. Since the common cathodic processes usually consume H\(^+\) or generate OH\(^-\), the local pH of the solution tends to rise. If the pH rises above ca. 10, the oxide film dissolves and Al oxidation is controlled by the aluminate reaction. Critical alkalinity and subsequent oxide dissolution are more likely to develop around intermetallic particles due to their high cathodic activity [119-124, 57]. Aggressive anions (e.g., Cl\(^-\) and F\(^-\)) in the environment can lead to further instability and intensification of the corrosion attack. Figure 10 illustrates the mechanisms of cathodic Al corrosion in neutral environments.
Figure 10. Schematic diagram showing the mechanism of cathodic Al corrosion in unstirred neutral environments.

Nisancioglu and Holtan [121] stated that an electrode surface subjected to high cathodic overpotential in a neutral solution readily develops an alkaline solution layer that may extend up to 1 mm into the bulk of an unstirred solution. The increased alkalinity, coupled with aggressive anions, dissolves the oxide film surrounding the cathodic particles causing pits to develop near the particle/matrix interface. Hydrogen bubbles block the pit mouth and help maintain the local alkalinity by minimizing intermixing between the pit solution and the bulk. Thus, the matrix dissolution accelerates and ultimately results in particle drop-out. After a particle falls out of the matrix, the cathodic activity declines and alkalinity gradually drops, allowing the reaction site to repassivate upon reaching the stability domain for the oxide film.

In a later study, Nisancioglu et al. [122] presented electrochemical measurements that supported the above mechanism. Current-time transients generated during the cathodic polarization of several Al alloys displayed a consistent trend (Figure 11). The cathodic
current initially rose to a maximum value that depended on the cathodic activity of the intermetallic particles, then the current decayed exponentially to a low value indicative of decreased cathodic activity due to particle drop-out. The variation in curve shape between different alloys reflected differences in structure, composition, size, and distribution of the intermetallic particles. For example, the 6081 alloy showed relatively small, constant current owing to the polarization of the cathodic reaction by Mn and Si. On the other hand, Fe-rich secondary phases displayed a strong catalytic effect on the cathodic reaction. Table V shows the intermetallic particles predominant in each alloy.

Figure 11. Current-time transient for several Al alloys at -1.2 V SCE in deaerated 3% NaCl [122].
The above behavior of current-time transients was observed in the potential range -1 to -1.3 V_{SCE}. At potentials more negative than -1.3 V_{SCE}, cathodic breakdown of the passive film occurred and the current increased continuously to a large steady-state value. The surface developed a high pit density and appeared uniformly etched. Above -1 V_{SCE} the net current was very low and often anodic [121]. The presence of dissolved oxygen increased the net cathodic current, but the current decay behavior was unchanged.

The mechanisms of Al cathode corrosion described above were inferred from experimentation in neutral Cl⁻ solutions. Mechanistic studies of Al cathode corrosion in F⁻-containing solutions could not be found in the literature survey. The behavior of Al in acid halide solutions may be quite different because the composition and structure of the protective oxide film depend on the electrolyte environment. Cathodic corrosion of Al in the Zn electrowinning cell (pH ≈ 0) has received limited attention.

2.3.1 **INFLUENCE OF OXYGEN**

Conflicting results have been reported with regard to the influence of dissolved O₂ on the cathodic corrosion of pure Al in neutral electrolytes [125-127]. Haynie and Ketcham [126] reported a lower corrosion rate for cathodically polarized pure Al in the presence of O₂. DiBari and Read [118] observed that the presence of O₂ raised the cathodic activity and increased the pitting tendency of high purity Al. However, Beck et al. [127] concluded that the corrosion rate of pure Al was unaffected by dissolved O₂ concentration.
The corrosion rate in commercially pure aluminum is said to increase with increased dissolved oxygen concentration, as observed with Fe, Ni, and Al alloys [128-129]. Nisancioglu and Holtan [130-131] detected no pitting on commercially pure Al in deaerated, acetate-buffered NaCl solution of pH 4.5 despite a high rate of H₂ evolution. The addition of the acetate buffer prevented corrosion attack even at -1.5 $V_{SCE}$. In an unbuffered solution, the same material pitted during cathodic polarization independent of whether oxygen was present or not. These observations suggested that pH change was more important than oxygen concentration.

The Zn electrowinning bath is saturated with oxygen, the evolution of which is the anode reaction. The influence of oxygen on the intense corrosion attack seen above the solution level in Al cathode plates has not been investigated. Cole et al. [13, 132] examined solution-level corrosion in Zn starter sheets. They concluded that the corrosion damage resulted from the action of dissolved oxygen. According to the authors, the sheet corroded at the solution line because oxygen diffused to the cathode and oxidized the Zn to ZnO which readily dissolved in the Zn bath. The authors claimed that an interelectrode barrier of Plexiglas could prevent oxygen transport to the cathode and eliminate cathode dissolution. The barrier extended across the width of the cell and dipped 10 to 100 mm below and protruded 10 to 100 mm above the electrolyte surface. Oxygen transport to, and reduction at, the cathode has been reported to affect current efficiency [133]. However, it is difficult to see how the above barrier could block oxygen transport to the cathode; oxygen evolution occurs over the entire surface of the anode, not just the top portion of it. Zn starter sheets are not used industrially for Zn recovery.

### 2.4 CORROSION BEHAVIOR OF Al CATHODE PLATES

Aluminum cathode plates fail in service partially as a result of severe pitting corrosion in a narrow band above the electrolyte/air interface. Little is known about the mechanisms of this corrosion failure or the characteristics of the pitting process, i.e., morphology, structure, and distribution of the corrosion pits. Systematic and
fundamental characterization of Al plate corrosion is lacking. Previous efforts to improve the corrosion resistance of Al cathode plates tended to involve a trial-and-error approach.

2.4.1 EFFECT OF ALLOYED ELEMENTS

Various alloyed elements have been added to commercial purity Al to improve the performance of the Al cathode plate. Krauss and Perri [17] patented Al-Ti and Al-Mg cathode plates claiming improved strippability and corrosion resistance. For Ti, the improvement was optimum in the concentration range 0.02 to 0.05 wt. % Ti. A similar improvement was observed with Mg addition, and the effective range for Mg was 0.7 to 2 wt. %. The benefits were achieved when Mg and Ti were alloyed either singly or in combination, provided that the level of alloy purity was at least 98% Al. The authors presented no explanation for the beneficial effect of these two elements. The cathode plate used by Cominco Limited is based on this patent and designated as HIS alloy. It contains 500 ppm Ti. The Al-Ti and Al-Mg phase diagrams are included in Appendix II.

The work of Krauss particularly emphasized the positive effect of Ti on strippability. However, strippability and corrosion are closely linked because "sticky" deposits arise from destruction of the passive oxide film [134-135, 10]. As the stability of the oxide film increases, the corrosion resistance also increases and, hence, the tendency for firmly adherent deposit should decrease. In other words, improving corrosion resistance should minimize strippability problems. It is not yet clear if strippability can be improved independently and without adversely affecting corrosion resistance. A simultaneous improvement in strippability and corrosion resistance of the Al-Ti cathode plate could result from the partition of Ti into the oxide film. If Ti is not incorporated into the Al oxide lattice, two important questions arise: How does Ti improve strippability and how does it influence the corrosion resistance? These questions have not been addressed. No information is available on the microstructure of the Al-Ti cathode plate or on the properties of its oxide film. XPS can detect Ti partition into the oxide lattice.
Several workers [136-137, 18] determined the influence of Ti on the corrosion rate of the H1S alloy plate in Zn bath electrolytes. The H1S alloy was compared to the 1070 alloy, a standard Al cathode plate similar to the H1S plate except for the Ti content. Conflicting results were reported. Sanders [136] concluded that Ti addition slightly increased or at best had a minimal effect on corrosion rate. Byrne [18] reported 44% higher corrosion rate in the H1S alloy relative to the 1070 alloy. On the other hand, Arthur [137] reported that Ti addition significantly reduced pit density on the H1S cathode plate; the 1070 Al plate showed a pit density about 3 times higher than the H1S alloy.

Byrne [18] claimed that low Mg (0.3-0.5%) or Si (0.1-0.2%) additions to Al produced cathode plates with much improved strength and corrosion resistance. The author arrived at these conclusions by weight loss testing in zinc sulfate-sulfuric acid electrolytes. He did not elucidate how these alloyed additions improved the corrosion resistance. Magnesium is known to improve the corrosion resistance of Al only in marine and alkaline environments owing to the precipitation of an insoluble Mg(OH)$_2$ coating [138].

As the purity of Al decreases, its corrosion resistance weakens due to an increase in the concentration of structural and compositional heterogeneities on the oxide surface. Heterogeneities are prone to localized corrosion attack. Gonzalez and Ball [139] compared the corrosion behavior of high purity Al (99.999%) and the H1S alloy in synthetic and return acid electrolytes. The corrosion rate of pure Al was 50% lower than that of the H1S alloy. Pure Al developed uniform corrosion attack while the H1S alloy suffered pitting attack.

Xue et al. [15] reported similar results using immersion tests on pure Al and Al-Fe alloy. The presence of Fe in the microstructure increased the extent of corrosion damage and pits formed even in the absence of aggressive anions. The detrimental effect of Fe was related to its low solubility in the Al matrix. Iron formed noble intermetallics that catalyzed the kinetics of the cathodic process. The catalytic effect of Fe was manifested in the much greater H$_2$ evolution on the Al-Fe alloy in
comparison to evolution on the pure Al surface. The dissolution rate of the adjoining Al matrix accelerated in order to support the enhanced cathodic activity.

2.4.2 EFFECT OF HALIDES

It is generally accepted that Cl\(^-\) and F\(^-\) anions are the primary stimulants of the strippability and corrosion problems [140-141, 9-15]. The mechanisms and exact contribution of these halides to the corrosion pattern seen in cathode plates remain unclear. Gonzalez and Ball [139] assessed the corrosion of the H1S alloy in Cl\(^-\) and F\(^-\) solutions under full immersion conditions. The testing was conducted under open circuit and under cathodic current density of \(-400 \text{ A m}^{-2}\) in \(200 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4\) at 40 °C. At a fixed F\(^-\) concentration of 10 ppm, the corrosion rate decreased with time for both conditions and became constant after a 71-hour immersion (Figure 12). The H1S alloy corroded faster under open circuit conditions. The authors attributed the decrease in corrosion rate with time to the removal of either the cathodic phases or the deformation zone generated during the rolling operation.

According to Gonzalez [139], the corrosion damage was strongly dependent on F\(^-\) concentration; the higher the F\(^-\) concentration, the greater the corrosion rate. Chloride had little effect on Al cathode corrosion. In a mixed electrolyte containing Cl\(^-\), F\(^-\), and ClO\(_4\)^{-}, F\(^-\) was the predominant contributor to cathode plate corrosion. Other authors [45-46] reported that the halides acted synergistically to increase the corrosion rate of Al in neutral environments. Gonzalez [139] noted that the addition of Mn, as MnSO\(_4\), to minimize Cl\(_2\) losses during Cl\(^-\) tests, increased the corrosion rate of the H1S plate. The effect of Mn was more pronounced under cathodic potential control. It was unclear how Mn affected the corrosion rate. This work provided useful data and was one of the few efforts in the open literature to directly address the corrosion of Al cathodes under Zn electrowinning conditions. However, the authors presented no morphological data. More importantly, their results were applicable to corrosion below the solution line and did not directly relate to the corrosion taking place above the solution line in zinc electrowinning practice. Aluminum cathodes fail primarily
due to corrosion above the solution line under thin electrolyte film conditions. Thin electrolyte films are usually much more aggressive than bulk electrolytes. They are particularly damaging to coatings, which could explain the continual lack of success in finding an adequate protective coating for the solution line region. The mechanisms and fundamental laws governing thin and bulk electrolytes are not identical and extrapolation from one process to the other can be misleading.

Figure 12. Variation of corrosion rate of H1S alloy with immersion time under open circuit and at \(-400 \text{ A m}^{-2}\) in 10 ppm F\(^{-}\)-200 g dm\(^{-3}\) H\(_2\)SO\(_4\) [139].

37
2.5 SUMMARY

The corrosion resistance of Al relies on the stability of the Al oxide surface film. Aggressive anions such as Cl\(^-\) and F\(^-\) aggravate Al corrosion by destroying the protective oxide film through the formation of soluble complexes with Al. The complexes form at energetically favorable sites or "weak points" on the surface, resulting in pitting attack.

Corrosion processes in the zinc electrowinning electrolyte limit the useful life of Al cathode plates. The plates fail from intense pitting corrosion above the electrolyte/air interface. Chloride and fluoride anions are believed to cause this effect, but the precise mechanisms by which they operate are unknown. Little information is available on the corrosion pattern and failure characteristics in cathode plates. There is also a lack of data on pitting characteristics such as structure, morphology, and distribution of Al pits. More importantly, previous work examined cathode plate corrosion mostly under full immersion conditions and overlooked the significance of the thin electrolyte film present above the solution line. Plate failure results mostly from thin electrolyte film corrosion. Since electrochemical and mass transport processes depend on the immersion conditions of the surface, extrapolation of bulk electrolyte results to thin electrolyte film conditions can be misleading.

In near-neutral halide solutions, cathodic reactions on surface heterogeneities may generate high local alkalinity that destabilizes the protective Al oxide film. Critical alkalinity levels are unlikely to develop in the Zn bath due to low initial pH and continual bath agitation by O\(_2\) evolution. The mechanisms of cathodic corrosion in sulfuric acid-halide solutions remain unclear despite the scientific and industrial importance of this problem.

Alloy composition and microstructure are critical factors in cathode plate corrosion. A detailed analysis of plate microstructure and microstructure-corrosion relationship is needed in order to design an optimum alloy composition. The notable variation in
corrosion resistance between different Al systems in the Zn bath suggests that
improvement in cathode plate performance could be possible by careful and systematic
microstructural investigation and judicious choice and engineering of alloy and
microstructure. What follows is an effort to address these issues, increase the
knowledge base of Al cathode plate corrosion, and promote further systematic research
of this industrially important problem.

2.6 OBJECTIVES

The present investigation is a fundamental, systematic study of the corrosion behavior of
aluminum cathode plates. It has several objectives:

1. To analyze corrosion failure in cathode plates and develop an appropriate
   experimental methodology.
2. To analyze the microstructure of the plates and correlate microstructural features with
corrosion sites.
3. To quantify the aluminum dissolution processes and clarify the role of pH and halide
   anions (Cl\(^-\) and F\(^-\)).
4. To assess the influence of several alloying elements (Ag, Fe, Cu, Sb, and Ti) on the
corrosion resistance of Al cathode plates.
5. To determine the effect of cathode potential distribution on solution line corrosion.
6. To elucidate the basic corrosion mechanisms responsible for plate failure below and
   above the electrolyte/air interface.
7. To recommend countermeasures to mitigate cathode plate corrosion.

These objectives were achieved using electrochemical and corrosion techniques in
conjunction with chemical, metallographic, and surface analytical methods, as detailed in
the next section.
3.0 EXPERIMENTAL

3.1 MATERIALS AND PROCESSING

Four commercial materials were investigated in this work: high purity Al (99.9999%), 1070 cathode plate, and two H1S cathode plates with different gauges. Capral Aluminum (Australia) supplied the H1S and 1070 alloys. The chemical compositions of these alloys were analyzed using inductively coupled plasma-mass spectroscopy (ICP-MS). Table VI presents the nominal chemical composition and thicknesses for the H1S and 1070 plates. The full ICP-MS spectrum is included in Appendix III. The H1S and 1070 cathode plates had an identical metallurgical history and differed only in Ti content. Titanium in the H1S alloy was the only deliberate addition to these plates; the other elements were unavoidable impurities originating from the smelting process. The H1S and 1070 plates were investigated in parallel to assess the influence of Ti on the corrosion behavior of the cathode plate. The high purity Al acted as a control material for the research program. Aluminum-Cu alloys containing 1, 2, and 4% Cu, supplied by Dr. D. Tromans, were also examined.

<table>
<thead>
<tr>
<th>Cathode Plate</th>
<th>Alloying Element Concentration/PPM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
</tr>
<tr>
<td>1070 (4.8 mm)</td>
<td>67</td>
</tr>
<tr>
<td>H1S (4.8 mm)</td>
<td>456</td>
</tr>
<tr>
<td>H1S (6.4 mm)</td>
<td>419</td>
</tr>
</tbody>
</table>

3.1.1 ALUMINUM ALLOYS PROCESSING

Several binary Al alloys were processed to assess the influence of Ta, Ag, Ti, and Sb on the corrosion behavior of the cathode plate. The attempt to produce Al-Ta alloys
by traditional metallurgical methods was unsuccessful. The Al-Ag and Al-Sb alloys were produced by combining appropriate quantities of the pure individual components to give 1 and 10% Ag and 1% Sb. The Al-Ti alloys were produced from pure Al and an Al-6% Ti master alloy to give 0.08, 0.3, and 1% Ti.

Casting was carried out in a cylindrical graphite mold fitted with a movable graphite piston for stirring. The mold was 50 mm in diameter and 180 mm in height. The graphite stirrer was fabricated as follows. A graphite disk 10 mm thick and 45 mm in diameter was sliced from a solid graphite cylinder. A tapped hole 10 mm in diameter was created in the center of the disk. The remaining surface area was perforated with small holes. A graphite rod 200 mm long was manually threaded using a die, then screwed to the tapped hole. This stirrer design minimized gas entrainment and ensured a homogenous melt [142].

The required amounts for each casting were combined in the mold, placed in an induction furnace, then melted under an Ar atmosphere. Enough starting materials were mixed to give 60 mm high castings. The furnace cover contained an inlet for the stirrer which was positioned at 10 mm above the casting. This arrangement allowed stirring without removing the furnace cover and exposing the molten metal to the room atmosphere. When the molten metal reached the desired temperature, ca. 700 °C, the stirrer was lowered and the melt was agitated vigorously by the vertical movement of the stirrer. After stirring, the furnace was turned off and the melt was cast by resting the graphite mold on a chilled Cu cylinder which entered the furnace through an opening at the bottom. Each casting was homogenized for 24 hours at 550 °C.

3.2 MICROSTRUCTURAL ANALYSIS

3.2.1 METALLOGRAPHIC SAMPLE PREPARATION

Sample preparation followed standard metallographic practices for Al and its alloys [143]. Small samples each having a surface area of about 100 mm² were sectioned
from the bulk plate using a low-speed diamond wheel to minimize deformation. Each sample was cold-mounted in a matrix of an epoxy resin. Some samples were hot-mounted using pre-molded Bakelite preforms. After mounting, the samples were polished mechanically. Fine grinding was performed in successive steps using progressively finer SiC abrasives of 240, 320, 400, and 600 grit. Grinding was carried out under running water to prevent overheating. It was followed by rough polishing with 6 μm oil-base diamond suspension, then final polishing with 1 μm diamond suspension. Napless PVC (polyvinyl chloride) cloths were used for diamond polishing, and an oil-base lubricant was periodically added to prevent deep scratching of the soft Al samples.

Although a 1 μm diamond finish was sufficient to reveal secondary phases, some samples received a brief chemi-mechanical polishing using colloidal silica in a basic slurry. Silica was used on a wetted medium nap cloth. With an 8 nm particle size and high pH activation, the silica produced an etched mirror-like surface. After polishing, the samples were rinsed with deionized water, degreased in acetone for 5 minutes, rinsed in ethanol, then dried in a stream of hot air. The samples were usually examined immediately after preparation.

**3.2.2 MICROETCHING**

Intermetallic particles were visible in the optical microscope without etching. Samples that were polished finally with colloidal silica received incidental etching and showed a greater clarity of details. To ensure observation of all microconstituents, some samples were etched for 10–20 seconds in a 0.5% HF solution. This etchant distinguished between α-AlFeSi and FeAl₃, the principal intermetallics in commercial purity Al. The α-AlFeSi acquired a light tan color; the FeAl₃ particles became outlined, but their color remained unchanged.

Grain size and structure of many samples were readily revealed by a 60 second immersion in a solution composed of 3% HF and 6% HCl at room temperature.
Immersion time required trial-and-error adjustment to get optimum results. If the etching time was set improperly, many unetched grain boundaries remained in the microstructure leading to an overestimation of grain size.

A better method for revealing grain structure was anodizing. To prepare an Al electrode for anodization, a polished sample was soldered to a stripped end of an insulated Cu wire. Three successive insulating coatings (Microstop) were applied to the soldered sample insulating it entirely except for a 10 x 10 mm² window left for examination. A drying period of 4 hours was allowed after each coating to ensure complete drying before the next application. The samples were anodized in a stainless steel container using a Baker's reagent, an aqueous solution of 2.3% fluoboric acid (48% HBF₄) [144]. The steel container and the sample formed the electrodes of an electrolytic cell. The sample was connected to the positive terminal of a DC power supply and the steel container was connected to the negative terminal. A cell voltage of 20 V was applied between the electrodes for 80 s. The applied voltage anodically thickened the air-formed Al oxide film. When viewed with a polarizing microscope, the optical properties of the film revealed excellent grain contrast in the underlying substrate.

3.2.3 MICROSCOPY

Optical, scanning, and transmission electron microscopies were used to investigate the microstructure. Optical photomicrographs were generated with a standard metallograph, Model Unitron 9180, under either polarized illumination or bright-field illumination. For low-power photography under 20 X magnification, a Zeiss stereomicroscope was used. Scanning electron microscopy (SEM) was used to analyze the microstructure and to assess the extent and morphology of the corrosion attack. Energy dispersive x-ray analysis (EDX) supplemented the SEM results and was used to estimate the chemical composition of microstructural phases and corrosion products. The SEM, Hitachi Model S-570, was operated at 20 kV.
3.2.3.1 Transmission Electron Microscopy

The transmission electron microscope (TEM) was used to resolve fine structural details beyond the SEM capability. In particular, the TEM, Hitachi Model H-800, was used to search for fine precipitates of alloyed and impurity elements. The TEM was also used to produce electron diffraction patterns, EDX spectra, and photomicrographs. The microscope operated at 200 kV.

The TEM has high resolution (ca. 1 nm) but requires tedious, exact sample preparation owing to the restricted geometrical requirement of the specimen and the necessity for electron transparency. Electron transparency required samples less than 100 nm thick. Over 50 TEM samples from the 1070 and H1S alloys were prepared for this investigation. The samples were prepared as follows. Square samples 40 x 40 mm$^2$ (4-7 mm thick) were sectioned from each alloy. The rolled surface of each sample was mechanically ground under water using 240-grit SiC papers. This coarse grinding reduced sample thickness to 1000 μm. Disks of 3 mm diameter were spark machined from each sample; spark machining was conducted in a paraffin bath to prevent continuous arc build-up and to stabilize the spark. After ultrasonic degreasing in acetone for 5 minutes, each disk was placed in a special disk grinder, then mechanically ground under water with a 600-grit SiC paper until the thickness decreased from 1000 μm to 100 μm. Grinding was performed on both sides of the disk to ensure flatness, which was necessary for the success of the subsequent electropolishing operation. The ground disks were cleaned in acetone, then transferred to the electropolishing stage.

Electropolishing was carried out in a TENUPOL-2 double jet polisher using a solution composed of 100 cm$^3$ perchloric acid, 200 cm$^3$ glycerol, and 700 cm$^3$ methanol. The polisher was equipped with a photocell arrangement for automatic termination of polishing immediately after sample perforation. A methanol coolant, which circulated passed an assembly of heat exchanger tubes immersed in a liquid N$_2$ bath, regulated the electrolyte temperature. When the electrolyte temperature decreased below -5 °C,
electropolishing commenced at an applied cell voltage of 12 V. After perforation, the samples were cleaned in three successive ethanol solutions. Some samples received an additional 15 minute cleaning in an ion beam milling machine. The machine operated with a beam of Ar ions at 6 keV ion energy and 20° incidence angle.

3.2.4 SURFACE ANALYTICAL METHODS

X-ray photoelectron spectroscopy (XPS) is a highly surface sensitive technique. It generates a fingerprint from the first few atomic layers in the surface. It was used to characterize the nature of the passive surface layer and corrosion products. Monochromatic Mg K$_\alpha$ radiation (hv = 1253.6 eV) or Al K$_\alpha$ radiation (hv = 1486.6 eV) excited the photoemission process. Narrow scans were recorded at 96 eV pass energy of the analyzer. The wide scans were recorded at 192 eV pass energy in order to increase the sensitivity of the spectrometer. The spectra were corrected for static charging by reference to the C 1s peak at a binding energy of 285 eV.

X-ray diffraction analysis (XRD) was conducted using a Philips x-ray system with a vertical diffractometer. Monochromatic Cu K$_\alpha$ radiation ($\lambda = 1.5405 \text{ Å}$) filtered with Ni generated the diffraction peaks. The sample, the x-ray source, and the counter were coplanar. The sample and the counter rotated about an axis orthogonal to their plane and were mechanically coupled so that a sample rotation through $\theta$ corresponded to a 20° rotation of the counter. This coupling ensured that the incident and reflected angles remained equal. The intensity of the diffracted beam was recorded as a function of the diffraction angle 20, which was measured in the angular range 10° to 90° at an angular velocity of 2° minute$^{-1}$. The XRD technique was used to assess plate texture and to identify corrosion products.

3.3 FAILURE ANALYSIS

A two-week visit to the zinc plant of Cominco at Trail, Canada was arranged. During this period, cathode plates were monitored in service and many samples were collected
for macro and microscopic examination. Several rejected cathode plates were also received from Cominco and Kidd Creek at Timmins, Canada. Samples were sectioned from these plates and analyzed using optical microscopy, SEM, and XRD techniques.

The extent of corrosion in rejected plates (service life ca. 24 months) was assessed using the reduction in plate thickness as a corrosion index. The average reduction in thickness was determined as a function of distance from the electrolyte/air interface. This generated concise and characteristic corrosion plots for the corrosion behavior of the cathode plate. Corrosion products were collected from cathode plates for EDX and XRD analyses. Other samples from various regions of the cathode plate were cleaned in 80% nitric acid, then examined in the SEM to compare the corrosion morphology below and above the electrolyte surface. Plate texture below and above the liquid level was compared by XRD.

3.4 ELECTROCHEMICAL TESTING

3.4.1 ELECTRODE PREPARATION

Electrode samples 10 x 30 mm² were sectioned from bulk plates using a low-speed diamond saw to minimize deformation. A hacksaw created a centered groove at the end of each electrode. The electrode surface was ground mechanically to a 600-grit finish using conventional metallographic procedure, as described in Section 3.2.1. Some samples received a 1 μm diamond finish to facilitate the assessment of the most susceptible microstructural features. Samples for partial immersion testing had larger surface areas ranging from 500-1000 mm².

After polishing, the samples were rinsed with deionized water, then dried in a stream of hot air. Each sample was mechanically bonded to an insulated 14 gauge (American Wire Gauge, AWG) solid conductor Cu wire 0.25 m long. Bonding was attained by placing the grooved end of the sample in a vise, inserting a stripped end of the Cu wire (5 mm in length) in the groove, then tightly clamping the groove. The joint was
cleaned ultrasonically with acetone and the resistance of the electrode was measured to ensure intimate contact between the Cu lead and the sample. Three consecutive Microstop coatings were applied to the sample at 4-hour intervals to fully mask the unwanted area. The final electrode area was sufficiently remote from the mechanical joint to eliminate adventitious cold working effects.

Immediately before testing, the surface area of each electrode was measured and examined optically to ensure the attainment of a defect-free test area. Prior to introduction into the solution, the test electrode was rinsed with deionized water, then dried in a stream of hot air.

3.4.2 ELECTROLYTES

The electrolyte composition was selected to simulate plant conditions and was prepared by mixing appropriate quantities of analytical grade chemicals with Type I deionized water. Deionization was performed by passing water through a four-column Barnstead ion exchange unit. Unless otherwise specified, the base electrolyte for all tests contained 150 g dm\(^{-3}\) H\(_2\)SO\(_4\). Other components were added to the base electrolyte singly or in combinations to assess the individual and combined effect of electrolyte constituents. Chloride and Fluoride were added in the form of NaCl and NaF, respectively. Zinc was added in the form of ZnSO\(_4\) • 7 H\(_2\)O. Testing was also conducted with an actual plant electrolyte for comparison purposes.

Sparkleen detergent was used to clean the glassware. Before each test, the cell compartment and the salt bridge were rinsed thoroughly with deionized water and test electrolyte, then filled with fresh electrolyte and placed in a controlled-temperature water bath maintained at 35 ± 0.1 °C. Approximately 550 cm\(^3\) of electrolyte was used for each electrochemical test. Most testing was performed in oxygenated electrolytes. Oxygenation started 45 minutes prior to sample immersion and continued during the test. Unless stated otherwise, all discussion of results refers to testing in oxygenated electrolytes at 35 °C.
3.4.3 INSTRUMENTATION

The electrochemical instrumentation consisted of an EG&G 273A potentiostat/galvanostat with a built-in function generator. This was interfaced to a personal computer for remote operation and data acquisition. The instrumentation was used in conjunction with a three-electrode round-bottom glass cell. The test cell contained several openings to allow the insertion of a test electrode, a platinum auxiliary electrode, a reference electrode, a gas sparger, and a thermometer.

The reference electrode was mercury/mercury (I) sulfate (+ 0.616 V SHE). The conducting electrolyte in the mercury (I) sulfate electrode (MSE) was saturated K₂SO₄: Hg, Hg₂SO₄(s)/K₂SO₄(saturated). This reference electrode was selected because it minimized liquid junction potentials and avoided Cl⁻ contamination. The MSE contacted the solution chamber via a salt bridge and a Luggin capillary. The capillary tip was placed 1-2 mm from the test electrode. This arrangement, coupled with a base electrolyte (150 g dm⁻³ H₂SO₄) conductivity of ca. 60 S m⁻¹, minimized IR drop in the electrolyte. The auxiliary electrode was made of platinum foil spot-welded to a platinum lead. The foil geometrical area was 10⁻³ m². Deviations from the above description will be mentioned in connection with the particular set of experiments.

3.4.4 CHEMICAL ANALYTICAL TECHNIQUES

3.4.4.1 Quantitative Al Analysis

The chemical analytical techniques used were ICP-MS and graphite atomic absorption (AA) analysis. ICP-MS was used to determine the chemical composition of the cathode plates. It was also used together with AA to evaluate the extent of Al dissolution under various testing conditions. After vigorous stirring of a test electrolyte, a minimum sample volume of 15 cm³ was collected for analysis. The detection limit depended on the extent of sample dilution and was usually around 0.2 ppm Al. Samples of known
concentrations were occasionally analyzed together with the test samples to ensure accurate assays.

The measured amount of dissolved Al was converted to either a corrosion current density (A m$^{-2}$) or to an average penetration rate (mm year$^{-1}$) using Faraday’s law of electrolysis. All reported corrosion rates were determined by chemical analysis of test solutions.

3.4.4.2 Chlorine Detection

The evolution of Cl$_2$ was detected using a starch-iodide paper. A strip of the paper was placed across the electrodes of a running Zn electrowinning cell. The paper near the anode changed from light blue to deep blue signaling the presence of Cl$_2$. The reaction of Cl$_2$ with iodide formed iodine. Subsequently, iodine reacted with the starch and produced the observed color in the presence of iodide.

3.4.5 EXPERIMENTATION AND TECHNIQUES

The study of cathode plate corrosion above the electrolyte/air interface required the attainment of consistent wetting conditions in order to allow meaningful comparison of results. This was achieved provided that gas sparging did not disturb the meniscus zone.

In Zn-free electrolytes, numerous small H$_2$ bubbles evolved from the Al cathode surface and coalesced into a single large bubble at the meniscus. As this bubble grew in size, it pushed the meniscus line slowly upwards until the bubble finally burst, releasing a visible mist into the region above the solution level. This was recorded on video. The growth/collapse cycle of this bubble occurred regularly every few seconds and produced consistent wetting conditions above the electrolyte/air interface. The same processes occurred in Zn solutions, but at a slower rate owing to the lower hydrogen current.

The experimental set-up was redesigned to better characterize and study the meniscus corrosion behavior above the electrolyte level. It incorporated a traveling microscope.
and a new electrochemical cell with an optical window. This modification allowed accurate observation of bubbles and their range of movement. The events at the meniscus were videotaped. Also, a separate reference electrode circuit monitored the potential of the thin electrolyte film above the solution level. A fine-tip salt bridge/Luggin capillary assembly was built in-house for this purpose.

A variety of electrochemical and corrosion techniques were used. Unless otherwise stated, external control of the metal/solution interface was applied immediately after sample immersion. After each test, the sample was rinsed with deionized water and dried in a stream of hot air, then stored in a desiccator for subsequent examination and analysis. The corrosion techniques used in this work were potentiodynamic and cyclic polarization, potentiostatic, galvanostatic, open circuit, and free immersion.

3.4.5.1 *Potentiodynamic and Cyclic Polarization*

Potentiodynamic polarization was obtained by applying a linear potential scan \( E = f(t) \) to the test electrode at a selected sweep rate \( \frac{dE}{dt} \). Cyclic polarization was obtained when the scan direction was reversed so that it proceeded towards the starting point at the same sweep rate (triangular waveform). The corresponding current density was recorded continuously. This method provided valuable information on passivity and electrode processes such as information on the critical breakdown potential of the passive film. Also, the extent of pit nucleation and propagation was assessed from the magnitude of the corrosion hysteresis loop that was generated during cyclic polarization experiments.

The potential scan was usually started at \(-0.250\ V\) vs. \( E_{\text{cor}} \) and swept to \(-0.374\ V_{\text{MSE}}\), then reversed and scanned to \( E_{\text{cor}} \) at \(0.17\) or \(1\ mV\ s^{-1}\).

3.4.5.2 *Potentiostatic*

This technique involved the application of a constant potential and monitoring the resultant current as a function of time. Current-time transients provided data that could
be related to film quality and stability at various stages of exposure to the corrosive environment. By studying the frequency and intensity of oscillations observed on the current decay profiles, important information about pit initiation/repassivation events were revealed under a variety of test conditions. Moreover, processes occurring on the electrode surface and mechanistic details were inferred from the shape of the current decay profile. The potentiostatic technique was used to determine the breakdown potential \( E_b \) for the H1S and 1070 alloys. It was also used to generate current density-time records for the H1S alloy as a function of halide concentration. These polarization curves were generated at \(-1.574 \, V_{MSE}\).

3.4.5.3 \textit{Galvanostatic}

The galvanostatic technique involved the application of a constant current to the metal solution/interface and recording the potential changes as a function of time. This technique provided information on the effect of halides on corrosion and passive film properties. The effect of cathodic current density on the corrosion of the cathode plate was investigated at -50, -150, -400, and -500 A m\(^2\). In industry, the Zn electrowinning cell operates at ca. -400 A m\(^2\).

3.4.5.4 \textit{Open Circuit}

Monitoring the open circuit potential with time was a useful guide to the corrosion mechanism because \( E_{corr} \) reflected the electrochemical processes that occurred at the metal/solution interface. \( E_{corr} \) indicated the influence of a particular parameter on electrode processes. In general, a parameter change that shifted the free corrosion potential in the active direction indicated enhanced anodic activity. Similarly, a shift in the noble direction indicated either enhanced cathodic activity or stifling of corrosion processes. Additionally, the extent and morphology of corrosion attack was determined under full or partial immersion conditions without interference from an external potential.
3.4.5.5  **Free Immersion**

Several sets of experiments were conducted under free immersion conditions. Samples were sectioned from cathode plates, cold-mounted in epoxy resin, then mechanically polished to a 600-grit finish, as described in Section 3.2.1. After sample cleaning, the epoxy matrix/sample interface was masked with a Microstop insulating paint to eliminate crevice effects.

3.4.5.5.A  **200-day Test**

The difference in corrosion behavior between the H1S and 1070 alloys was investigated by immersing samples for 4755.5 hours (ca. 200 days) in $\text{H}_2\text{SO}_4$-500 ppm Cl$^-$ electrolytes. The samples were immersed individually. The beakers containing the test samples were covered, to prevent contamination, and left at room temperature for the duration of the test. After 200 days, the corrosion morphology was examined in the SEM and the extent of corrosion assessed using chemical analysis of test solutions.

3.4.5.5.B  **83-day Test**

Another set of H1S and 1070 samples were immersed for 83 days under the same conditions as the previous 200-day test. However, the beakers in this set of experiments were loosely covered.

3.4.5.5.C  **4-day Test**

High purity Al and 1070 alloy samples were immersed in 500 ppm Cl$^-$ for 92 h at 35 °C. The goal of this experiment was to examine the effect of altering immersion conditions. Some samples received full immersion, other samples started with a thin electrolyte film. At the end of the test, the samples were examined optically and in the SEM. Their corrosion behavior was recorded.
3.4.5.5.D 1-day Test (Effect of pH)

The purpose of this test was to study the effect of pH on cathode plate corrosion in halide solutions. HIS and 1070 samples were immersed individually for 31 hours in 247 g dm$^{-3}$ zinc sulfate solution containing either 1000 ppm Cl$^{-}$ or 1000 ppm F$^{-}$. Zinc sulfate was selected for base electrolyte in order to avoid adjusting the pH with excessive amounts of NaOH. At a concentration of 247 g dm$^{-3}$ ZnSO$_4$, the SO$_4^{2-}$ concentration in the above electrolyte was equivalent to that in the standard 150 g dm$^{-3}$ H$_2$SO$_4$ base electrolyte.

The initial pH of the ZnSO$_4$ solution was approximately 4.65. The pH was adjusted by the addition of concentrated H$_2$SO$_4$ to produce additional test solutions of pH 3.5, 2.5, and 0. The test solutions were open to air and maintained at 35 °C for the duration of the test. After 31 hours, the samples were removed, rinsed with deionized water, then dried. Chemical analysis was used to determine the amount of dissolved Al and SEM/EDX analysis was used to assess the nature of the solid substances that formed.
4.0 RESULTS AND DISCUSSION

4.1 MICROSTRUCTURAL ANALYSIS

The cast microstructure of the cathode plate alloy consisted of three principal microconstituents: dendritic primary Al, script-shaped α-AlFeSi, and dispersed round rosettes. The primary Al dendrites solidified first at ca. 659 °C. Iron and silicon, the two main impurities in the alloy, formed the α-AlFeSi phase, which precipitated along grain and cell boundaries in the temperature range 649 to 654 °C. These precipitates formed immediately after the solidification of the primary Al dendrites. The round rosettes appeared at 649 °C towards the end of solidification; they represented solidification of the remaining pools of molten metal.

During the subsequent hot rolling operation, the α-FeAlSi particles fragmented and underwent a peritectoid transformation to FeAl$_3$ and Si. This transformation marked the transition from a cast to a wrought structure. The wrought structure of the cathode plate consisted of three principal phases: primary Al, uniformly distributed intermetallic particles, and round rosettes. The round rosettes in the ingot structure appeared unchanged in the wrought structure. The intermetallic particles exhibited blade shape morphology and light gray color, characteristics of FeAl$_3$ intermetallics. EDX analysis confirmed that their chemical composition was consistent with FeAl$_3$ (Figure 13). The intermetallic particles tended to align along the rolling direction (Figure 14). Iron formed a large number of these finely distributed particles because it was practically insoluble in Al; its solid solubility limit in Al is only 30 ppm at 400 °C [145]. Silicon also has limited solid solubility in Al of about 500 ppm at 200 °C [145]. However, it does not form binary intermetallics with Al. Elemental Si precipitated and formed angular particles. In one sample the Si particles tended to cluster in a narrow band along the edges of the plate (Figure 15).

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2 All figures are grouped at the end of the thesis starting on page 108.
Although the features described above dominated the microstructure of the cathode alloys, copper-containing particles were also detected in some samples, but their occurrence was rare (Figure 16). Compositional analysis by EDX indicated that these particles were composed of Al, Fe, and Cu in various proportions (Figure 17).

The H1S alloy contained ca. 500 ppm Ti. According to Mondolfo [145], the Ti solid solubility limit in Al at 400 °C is 300 ppm and decreases rapidly with decreasing temperature. Even though the alloyed Ti addition far exceeded the solubility limit, SEM examination detected no Ti-containing particles in the microstructure. In order to determine if Ti formed fine precipitates beyond the resolving power of the SEM, many H1S microsamples were prepared for TEM examination. The microstructure of the 1070 alloy was examined in parallel with that of the H1S alloy. Both alloys had an identical metallurgical history and differed only in Ti content (Table VI). No Ti particles could be found in the H1S microstructure and the two alloys exhibited similar microstructural features. The alloyed Ti formed an Al-Ti solid solution.

The TEM work confirmed the blade shape morphology of the FeAl3 particles and their alignment in the rolling direction (Figure 18). Some Fe-containing particles exhibited rectangular configuration (Figure 19). Significant amounts of fine Cu precipitates were observed. These precipitates were round and tended to occur in scattered clusters. Some Cu precipitates nucleated on the Fe-containing intermetallics and some decorated the contours of the FeAl3 particles (Figure 20).

The grain size and structure of the cathode alloy were evaluated by anodizing polished samples and examining them under polarized light. Anodizing produced a thick anisotropic oxide film. A reflected plain-polarized light passed through an analyzer in a crossed polars position, produced marked grain contrast. The anisotropic optical properties of the film and its epitaxial growth unveiled the grain structure of the underlying Al substrate. Variation in polarization direction from grain to grain generated a colorful grain structure whose various shades depended on differences in
grain size, shape, and orientation. Figure 21 displays the grain structure in the transverse and longitudinal sections.

The grain structure revealed features characteristic of a heavily worked plate. Deformation bands could be seen within the grains of the longitudinal section. The transverse section exhibited elongated grains. To assess the tendency of secondary phases to precipitate along grain boundaries, a selected area of a transverse section was examined by altering the lighting conditions to emphasize either grain boundaries or secondary phases (Figure 22). Precipitation of secondary phases occurred preferentially along grain boundaries.

Substructure refers to size, shape, and arrangement of subgrains inside ordinary grains. The driving force for the formation of a substructure is the reduction in internal energy of a heavily worked material. In order to lower strain energy and remove lattice curvature, dislocations migrate and form subboundaries that separate the original grain into numerous strain-free crystallites, called subgrains [146]. This rearrangement of dislocations occurs during recovery processes in the cold-worked plate. The misorientation between adjacent subgrains increases as the number of dislocations in the subboundary increases. It is up to 2° in the cold-worked state and disappears upon recrystallization.

Figure 23 shows the substructure of the cathode plate, as seen in the TEM. A prominent feature of the photomicrograph is the clearly delineated subboundaries and the presence of only few intragranular dislocations. The migration of nearly all the dislocations to the subboundaries suggested advanced recovery. Although these alloys did not receive a deliberate recovery treatment, the migration rate for dislocations at room temperature was sufficient for substructure formation. A noticeable tilt subboundary could be seen in the lower right corner of the photomicrograph. It consisted of a vertical array of parallel, uniformly spaced edge dislocations.
4.2 FAILURE ANALYSIS

The objective of this task was to determine the corrosion characteristics of Al cathodes that failed in service. This information highlighted the failure pattern in cathode plates and assisted in the design of laboratory tests that simulated service damage. It also provided some insight into the underlying failure mechanisms of the Al plates.

Corrosion plots expressing the extent of corrosion damage as a function of distance from the electrolyte/air interface were generated from plates that failed after 24 months in service. The decrease in plate thickness was taken as an index of corrosion damage. Rejected cathode plates always produced a characteristic corrosion-distance plot that displayed a quantitative as well as a qualitative summary of the average behavior of a failed plate. Figure 24 shows a typical corrosion-distance plot. Three distinct corrosion zones could be identified on the plot: zone I below the electrolyte/air interface, zone II 0–40 mm above the electrolyte/air interface, and zone III 40–140 mm above the electrolyte/air interface. The extent of corrosion in zone I was equivalent to 10% reduction in thickness. Some additional mechanical thinning occurred in zone I due to the scalping action of the horizontal stripping knives. The corrosion damage of zone III decreased gradually with distance from the electrolyte surface. It became equivalent to zone I corrosion (10%) at a distance ≥ 120 mm from the electrolyte level. Zone II experienced the greatest corrosion damage. The maximum damage occurred at 30 mm above the electrolyte surface and extended across the width of the plate. The reduction in thickness was around 80%. Some plates exhibited severe thinning and perforation, which often occurred near the electrical contact edge. Plates usually fail in service by fracture in zone II because the intense thinning makes the plates unable to withstand the stresses generated by the stripping operation.

The corrosion morphology differed in the three corrosion zones. A strongly adherent mud-crack deposit dominated zone III. Ultrasonic cleaning in acetone and ethanol was insufficient to remove the hardened deposit. It was removed only by immersion
in 80% nitric acid. XRD analysis of the deposit produced numerous spectral peaks in each sample. The peak intensity varied from sample to sample suggesting complex, non-uniform chemical composition. EDX analysis produced spectral peaks for S, Al, and Zn (Figure 25). These analyses indicated that the chemical composition of the deposit consisted of Zn sulfate-Al sulfate mixture. Underneath the deposit, the cathode plate exhibited crystallographic pits of square cross-section, as shown in Figure 26. This form of corrosion, called tunneling corrosion, predominates at potentials in the vicinity of the breakdown potential, $E_b$, especially in acid chloride solutions [147-148]. Yasuda et al. [149] analyzed pit structure on Al single crystals in Cl\textsuperscript{-} solutions; they showed that the pits were bounded by {100} planes. Measurement of $E_b$ on different low index planes revealed that the {100} planes were the most resistant to pit nucleation. Newman [150] noted that salt precipitation could terminate tunnel growth. It appears that tunnel corrosion proceeded in zone III until Al sulfate precipitation halted its progress. Laboratory testing proved that the sulfate deposit originated from the precipitation of corrosion products in the Al cathode plate. The deposit did not form in partially immersed materials that resisted corrosion in the Zn bath. Unlike Al cathodes, dimensionally stabilized Ti samples consistently displayed clean shiny surfaces above the electrolyte/air interface, signifying little chemical interaction with the environment.

Zone II exhibited a high density of shallow cusp-like pits. Some Fe-bearing intermetallics were observed inside the pits (Figure 27a). Pits often contained an adherent white deposit, which was analyzed by EDX, revealing that the pit deposit was identical with the mud-crack deposit collected from zone III. The sulfate deposit precipitated in zone II was not protective due to zone II proximity to the electrolyte surface, which permitted periodic wetting and deposit dissolution. The farther away the deposit from the electrolyte surface, the greater was its protective ability, as reflected in the progressive decrease in zone III corrosion with distance from the electrolyte surface. Although microscopically zone II was pitted, the overall deterioration within the zone II layer appeared uniform.
Corrosion in zone I was minimal (Figure 27b). The combination of cathodic protection and Zn deposit protected zone I. The Zn coating formed immediately after the plate entered the solution, curtailing the direct interaction between the oxide film and the electrolyte.

X-ray diffraction patterns from the failed plates indicated variations in x-ray diffraction peak intensity between regions below and above the electrolyte surface. The (111) and the (200) sets of crystallographic planes generated relatively more intense spectra in zone I. For example, the (111) peak was intense and prominent in zone I but barely visible in zone II (Figure 28). This reflected variations in preferred orientation across the thickness of the original H1S plate.

Figure 29 shows a cross-sectional view of two failed plates that were in service at Cominco and Kidd Creek (Canada). Even though these plates came from different cathode plate manufacturers and operated in different Zn plants, they displayed identical failure pattern and corrosion morphology. The only notable difference was the extent of corrosion damage in zone III. The plate from the Kidd Creek plant exhibited relatively more thinning in zone III: this difference confirmed the protective role of the sulfate deposit in zone III. The Kidd Creek plant uses pressurized water (ca. 690 kPa) to deliberately remove the sulfate deposit after each plating cycle. It is believed that such an effort minimizes the corrosive effect of the hygroscopic sulfate deposit. In fact, this practice accelerates zone III corrosion; however, its overall impact is minimal because the critical processes causing plate failure occur in zone II.

4.3 CORROSION OF ALUMINUM CATHODE PLATES

4.3.1 INHIBITIVE EFFECT OF CATHODIC POLARIZATION

The Al oxide film is amphoteric, being unstable in low and high pH environments (Figure 4). Cathodic polarization in neutral solutions can substantially increase Al corrosion because the resulting proton reduction tends to shift the local pH into the
domain of oxide instability [118-124]. Van de Ven and Koelmans [2] stated that even in HCl solutions (pH ≈ 3 and j = -191 A m⁻²) the local pH can rise to the alkaline range.

Cathodic polarization of H1S samples in 150 ppm Cl⁻-40 ppm F⁻ solutions (pH ≈ 0) indicated that the rate of cathodic corrosion decreased with increased cathodic polarization (Figure 30). In these solutions, the initial pH was sufficiently low that any pH rise tended to stabilize the surface film. This pH effect coupled with cathodic potential control lowered the corrosion rate. Figure 31 compares the potential-time curves at 0, -50, -150, and -400 A m⁻². These curves shifted negatively with rising cathodic current density. Excepting the open circuit curve, each curve approached a steady state potential within 10000 s. The open circuit curve rose steadily and stabilized only after 60000 s. It displayed slightly more noise, indicative of surface instability and passive film breakdown. Surface examination in the SEM showed a high density of shallow cusp-like pits at open circuit (Figure 32). Although the extent of pitting damage decreased as the applied current density increased, the cusp-like pitting morphology persisted at all current densities.

In the absence of halides, the H1S corrosion rate at -400 A m⁻² was considerably lower than that observed in mixed F⁻-Cl⁻ solutions (0.82 vs. 8.26 mm year⁻¹). This enhanced oxide film stability could also be inferred from the relatively smooth appearance of the electrochemical potential-time curve in the halide-free electrolyte (Figure 33). Halide-free electrolytes caused only superficial surface damage near the intermetallics, which were the most corrosion susceptible features in the microstructure. The sample surface contained a large number of micropits that were associated with the excavation of the intermetallic particles from the surface (Figure 34). Particle removal resulted from the formation of microgalvanic couples between the particles and the adjoining Al matrix. As the intermetallics in this alloy were predominately FeAl₃, the driving force for each microcell was ca. 300 mV (Table III).

Galvanic corrosion usually concentrates at the interface of a galvanic couple [97]. The corrosion attack declines with increasing distance from the interface owing to the IR
potential drop in the current path. The intermetallic particles fell out of the surface because the maximum driving force prevailed at the particle/matrix interface, thus weakening the interfacial bond. Once the intermetallics dropped out of the surface, the local microcells terminated, and the selected cathodic conditions were able to mitigate corrosion damage in the remaining Al matrix. Although local alkalization in acid environments has been reported [2], particle removal by such mechanism could be excluded in this case: the attainment of sufficiently aggressive alkalinity required a drastic pH shift of ca. 10 pH units, a highly improbable event.

At a constant cathodic current density, halide addition shifted the potential-time records in the positive direction. The greatest shift occurred in the mixed F\textsuperscript{-}/Cl\textsuperscript{-} electrolyte (Figure 35). The addition of 150 ppm Cl\textsuperscript{-} to the H\textsubscript{2}SO\textsubscript{4} base electrolyte produced a positive shift without an attendant increase in Al dissolution. These results suggested enhanced cathodic activity in the halide-containing electrolytes. The shape of the potential-time record in the F\textsuperscript{-}-containing electrolyte differed from that in other electrolytes. Immediately after the current density was applied, the potential in the F\textsuperscript{-} electrolyte moved positively to a maximum value and remained constant for the duration of the experiment. In F\textsuperscript{-}-free solutions, the potential moved positively to a maximum value, then decayed to a lower value (Figure 35). The initial movement of potential in the positive direction reflected increased cathodic activity on the intermetallic particles. The potential decayed as the particles dropped out of the surface. The lack of a pronounced decay behavior in F\textsuperscript{-} solutions was caused by corrosion processes which continually exposed new subsurface intermetallic particles. Close comparison of the potential-time records showed that the curve in the F\textsuperscript{-} solution did attempt to decay around the same potential as in the halide-free sample; however, it rose again as more particles became exposed (Figure 36).

4.3.2 EFFECT OF HALIDES ON CATHODIC ACTIVITY

The effect of halide anions on the cathodic activity of the H1S alloy was investigated potentiostatically in deaerated solutions. Argon deaeration started 45 minutes prior to
sample immersion and continued throughout the experiment. Each fully immersed sample was potentiostated for 4 hours at \(-1.574\ \text{V}_{\text{MSE}}\). The test solutions were sampled periodically to determine the extent of Al dissolution.

As seen in Figure 37, the least cathodic activity occurred in the halide-free electrolyte. The cathodic current density increased at a constant rate without reaching a steady-state value in the time scale of the experiment. Halide addition to the base electrolyte (150 g dm\(^{-3}\) H\(_2\)SO\(_4\)) produced high cathodic activity and the samples approached stationary conditions after ca. 2 hours. Comparison of the individual effect of Cl\(^-\) and F\(^-\) anions showed that initially the electrolyte containing F\(^-\) produced slightly higher cathodic activity than the Cl\(^-\)-containing electrolyte. The situation reversed after ca. 1 hour of immersion. The mixed F\(^-\)-Cl\(^-\) electrolyte displayed the highest cathodic activity.

Periodic solution sampling during each test confirmed the detrimental effect of F\(^-\) on Al corrosion. In F\(^-\)-containing solutions the level of dissolved Al increased with exposure time. The greatest Al dissolution occurred in the mixed F\(^-\)-Cl\(^-\) electrolyte, suggesting a synergistic effect between the halides. For fluoride-free electrolytes, Al\(^{3+}\) could not be detected in these 4-hour tests (Table VII); the detection limit of the ICP-MS technique was 0.2 ppm. It should be noted that even though the applied potential of \(-1.574\ \text{V}_{\text{MSE}}\) did not stop pitting in F\(^-\) or F\(^-\)-Cl\(^-\) electrolytes, the extent of corrosion damage was consistent with the galvanostatic testing described in Section 4.3.1: corrosion damage decreased as cathodic polarization increased. The above results suggest that Zn cell operation at the maximum practicable cathodic current density will minimize corrosion attack below the solution level by increasing the oxide (barrier) film stability.

SEM analysis of corrosion morphology in the different halide electrolytes supported the chemical analysis results. The sample from the mixed F\(^-\)-Cl\(^-\) electrolyte showed the greatest pitting damage. The pits were round and shallow (Figure 38). The attack concentrated around the intermetallic particles, resulting in the loss of almost all of them. Some corrosion appeared to follow the flow lines in the matrix, producing elongated shallow ditches. The electrolyte containing only F\(^-\) anions produced a pitting
morphology that was similar to that of the mixed electrolyte; however, the extent of
damage was less severe (Figure 39). Thus, the halides acted synergistically. Pit
nucleation near the intermetallics was ascertained as some pits could be observed at
intermetallics that remained in the matrix (Figure 40).

Table VII
Cathode Plate Corrosion as a Function of Time in Different H₂SO₄-Halide Solutions

<table>
<thead>
<tr>
<th>Time/10³ s</th>
<th>Aluminum Corrosion/10⁴ ppm m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No halides</td>
</tr>
<tr>
<td>5</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>11</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>13.5</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>14.4</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>

The halide-free and the Cl⁻-containing electrolytes produced minimal pitting damage.
Most of the intermetallic particles remained intact (Figure 41). This was another
indication that the intermetallics influenced corrosion through the formation of
microgalvanic couples with the Al matrix. If local alkalization was the operative
mechanism, even more particle drop-out should have occurred in this case due to the
higher cathodic polarization. Instead, the particles remained mostly intact because the
externally applied cathodic potential was large enough to suppress the local
microgalvanic cells.

Regardless of the cathodic potential, the Al matrix corroded in F⁻-containing solutions
because of the strong tendency of HF to form soluble complexes with Al. The Cl⁻ anions
were inactive possibly because the applied cathodic potential of −1.574 V_MSE inhibited
Cl⁻ adsorption at the oxide/electrolyte interface. It is known [93] that a minimum driving
force is necessary before Cl⁻ anions can destabilize the passive layer. The higher affinity
of F⁻ for Al could be seen from the thermodynamic tendency for complex formation:

\[ \text{AlCl}_3 (aq) + 3 \text{e}^- \rightarrow \text{Al} + 3 \text{Cl}^- \quad E_{\text{red}}^\circ = -1.7 \text{ V} \]  (14)
\[
\text{AlF}_6^{3-} (aq) + 3 \, \text{e}^- \rightarrow \text{Al} + 6 \, \text{F}^- \quad \quad E_{\text{red}}^0 = -2.1 \, \text{V} \quad \quad (15)
\]

The propensity for the above reactions to proceed in the anodic direction is significantly higher with the F\(^-\) anion, as reflected in its very large negative potential. Appendix IV contains the thermodynamic data and calculations of the above reduction potentials.

Cyclic polarization testing in deaerated solutions of varying halide concentrations corroborated the potentiostatic results. The polarization scan started 1 hour after sample immersion. It can be seen from Figure 42 that in the cathodic regime the behavior was consistent with the results of the potentiostatic tests. Increasing the Cl\(^-\) concentration from 0 to 40 to 150 ppm progressively increased the cathodic activity but had little effect on the anodic activity. During anodic polarization, all curves exhibited limiting current behavior due to ohmic polarization in the oxide film. The curve measured in 40 ppm F\(^-\) displayed the highest passive current density at 10 A m\(^{-2}\). In the F\(^-\)-free electrolytes, the passive current density was in the range 6-7 A m\(^{-2}\). The presence of F\(^-\) in the electrolyte produced a high frequency noise on the anodic branch, suggesting more nucleation and propagation of metastable pits. The reverse scan in each test traced the upward anodic branch, indicating minimal pit propagation and rapid repassivation.

These results implied the participation of halides in both the cathodic and anodic processes. Valand and Nilsson [43] noted increased cathodic activity on Al in F\(^-\) solutions. The authors presented kinetic and thermodynamic results which attributed this phenomenon to modification of the electrical properties of the oxide film. The F\(^-\) anions became incorporated into the oxide lattice by replacing the O\(^{2-}\) anions. The incorporation of F\(^-\) anions within the oxide lattice structure increased the electronic and ionic conductivity of the film and, hence, the cathodic reaction kinetics. Valand [43] stated that cathodic potentials and similarity in ionic radii between F\(^-\) and O\(^{2-}\) promoted this oxide structure modification.

The considerable rise of cathodic activity in Cl\(^-\) solutions (150 ppm Cl\(^-\)) without a commensurate rise in Al dissolution (Figure 37) suggested catalysis of the H\(_2\) evolution
reaction. The incorporation of Cl\textsuperscript{-} anions within the oxide lattice structure probably enhanced the electrical conductivity of the oxide film. In the mixed F\textsuperscript{-}-Cl\textsuperscript{-} electrolyte, this increased conductivity coupled with the aggressiveness of the F\textsuperscript{-} anions produced the observed synergistic effect between these halides. Although XPS analysis was not performed on the above potentiostatic samples, XPS analysis of HIS samples cathodically polarized in H\textsubscript{2}SO\textsubscript{4}-1000 ppm F\textsuperscript{-} confirmed the incorporation of F\textsuperscript{-} anions within the Al oxide film (Figure 43). Recently, Natishan et al. [151] examined the ability of Cl\textsuperscript{-} to enter the oxide lattice structure of pure Al using XPS and X-ray absorption spectroscopy (XAS). The authors reported the absorption of Cl\textsuperscript{-} within the oxide lattice at potentials below E\textsubscript{b}.

4.3.2.1 Control of Fluoride Concentration

The results in Section 4.3.2 proved the deleterious contribution of F\textsuperscript{-} anions to cathode plate corrosion under full immersion conditions. It could be inferred that reduction of F\textsuperscript{-} concentration should increase the useful life of the cathode plate. However, the useful life of the plate is affected primarily by corrosion processes under partial immersion conditions. It is shown below that extrapolation of results from full immersion to partial immersion conditions is not only misleading but can also aggravate the problem.

Partial immersion testing of HIS samples at \(-400\ \text{A m}^{-2}\) in 40 ppm F\textsuperscript{-}-150 ppm Cl\textsuperscript{-} solutions generated morphological attack identical to that seen in rejected plant plates. Although zone I exhibited a large number of shallow, round pits that roughened the surface, the extent of overall damage was minimal. Chloride-containing deposit was found at the bottom of some pits (Figure 44). This deposit was probably produced by the precipitation of AlCl\textsubscript{3} during pit growth. Zone II suffered the maximum amount of damage and the morphology of pitting was similar to that seen below the solution line; however, the pitting morphology appeared crystallographic at later stages of the pitting process (Figure 45). Crystallographic pitting and a strongly adherent sulfate deposit, often in the form of mud-cracks, characterized zone III. EDX analysis detected Cl\textsuperscript{-} anions in this zone (Figure 46). The presence of F\textsuperscript{-} anions in zone III was uncertain.
because the EDX unit used in this analysis was not equipped with a light element detector and, hence, could not detect elements below sodium.

In order to complex F\(^-\), the electrolyte environment was modified by the addition of 50 to 200 ppm Al either as elemental Al dust or Al sulfate. Increasing the Al dust content decreased the extent of corrosion damage in zone I. The situation in zone II was surprisingly different. The intensity of corrosion damage in zone II increased with increased Al dust concentration (Figure 47). At an Al dust concentration of 200 ppm, zone II suffered severe corrosion that nearly perforated the thickness of the plate during the 24-hour test. The addition of Al sulfate produced a similar behavior, but the damage was less severe (Figure 48).

Figure 49 compares the electrochemical plots produced by the addition of 200 ppm Al in the form of Al sulfate and Al dust. The potential-time curve for the dust addition rose smoothly and gradually to a noble, steady state potential value of ca. \(-1.124 \text{ V}_\text{MSE}\). This pattern suggested the spontaneous formation and growth of a protective surface film. Presumably when all the F\(^-\) anions were participating in complex formation, the oxide film was able to self-heal. In contrast, the potential-time curve for the Al sulfate addition shifted slightly in the positive direction and remained smooth and constant. The steady-state potential value attained with the sulfate addition was ca. 200 mV more negative than that attained with the Al dust addition.

Cathode testing in H\(_2\)SO\(_4\)-Halides-Al was not pursued further in this work because the test conditions were not typical of Zn electrowinning practice. However, the above results stressed the importance of exercising caution when extrapolating between apparently similar experimental conditions. An apparent improvement in one zone of the plate could cause serious deterioration in another. When necessary, modification of the electrolyte chemistry should be carried out prior to electrolysis and its effect verified under partial immersion conditions. Most commercial evaluation of cathode plate corrosion is carried out using weight loss techniques under full immersion conditions. This methodology
neglects the electrochemical changes that arise from the protrusion of the cathode plate above the electrolyte surface.

4.3.3 **INHIBITIVE EFFECT OF ZINC IONS**

The ability of Zn$^{2+}$ to inhibit Al corrosion was seen in potentiostatic testing. Figure 50 compares the current density-time records for two fully immersed H1S samples held at $-1.115 \text{ V}_{\text{MSE}}$ in 500 ppm Cl$^-$. This potential was selected based on preliminary testing which indicated that the H1S surface suffered breakdown around this potential. It was also thermodynamically unfavorable to Zn deposition, thus allowing morphological examination of the corroded surfaces. In the absence of Zn ions, extensive anodic dissolution ensued within two hours of sample immersion. The dissolution rate climbed rapidly and stabilized at ca. 40 A m$^{-2}$ after 3.3 hours. In contrast, the sample immersed in a similar electrolyte that contained 60 g dm$^{-3}$ Zn showed no evidence of anodic dissolution; the observed current density remained cathodic for the 6-hour duration of the test. Morphological examination of the tested surfaces substantiated the electrochemical results. The sample tested in the Zn-free electrolyte suffered severe surface damage and only few isolated areas remained intact. The sample exposed to the Zn electrolyte sustained little damage (Figure 51). Both alloy surfaces were free of Zn deposit. Zinc addition probably reduced the Cl$^-$ activity by forming zinc-chloride complexes such as ZnCl$_2$, precluding the formation of a critical Cl$^-$ concentration. The Zn sulfate addition could also reduce the H$^+$ activity, decreasing the rate of the hydrogen evolution reaction, the reaction driving the corrosion process in zone I.

Cyclic potentiodynamic polarization showed that when the driving force for anodic dissolution was sufficiently high, the presence of Zn was ineffective in preventing corrosion damage. Figure 52 compares the cyclic polarization curves for fully immersed H1S and 1070 alloys in the above Zn-containing electrolytes. Both alloys suffered extensive damage; the relative shift of the H1S curve to the right was indicative of higher corrosion susceptibility in the H1S alloy.
The influence of Cl\textsuperscript{−} and F\textsuperscript{−} anions on Zn deposition was examined using partially immersed H1S samples. The electrolyte contained 60 g dm\textsuperscript{−3} Zn and either 500 ppm Cl\textsuperscript{−} or 500 ppm F\textsuperscript{−}. Both solutions produced readily strippable deposits; it is known that F\textsuperscript{−} produces “sticky” deposits but this effect may require many deposition cycles before it becomes evident [11]. The appearance of the Zn deposit changed with the type of anion in solution. In Cl\textsuperscript{−}-containing solutions, the deposit surface contacting the solution appeared relatively dark. The deposit surface contacting the Al plate exhibited the same surface roughness as the substrate. In other words, the Zn deposit surface was a replica of the original plate surface, duplicating the features left by the 600-grit mechanical grinding operation. In contrast, the F\textsuperscript{−}-containing solutions produced a shiny deposit on the solution side and a sparsely pitted (indented) surface on the other side. Hydrogen bubbles probably caused the spherical indentations at the Al/Zn side of the deposit.

4.3.4 EFFECT OF pH

The effect of pH was studied in 1000 ppm halide-ZnSO\textsubscript{4} solutions using freely, fully immersed samples. Figure 53 compares the variation of corrosion rate with pH for the H1S and 1070 alloys in the F\textsuperscript{−} environment. The corrosion rate in the 1070 alloy varied linearly with pH over the entire range. For pH values ≤ 2.5, the slopes for both alloys were nearly identical, but the extent of dissolution was higher in the H1S alloy. At pH > 2.5, the H1S alloy changed slope and displayed a lower dissolution rate. A similar trend occurred in the Cl\textsuperscript{−} environment with the H1S alloy changing slope at pH > 2.5 (Figure 54). The dissolution pattern of the H1S alloy suggested a change in the corrosion mechanism at higher pH values. High pH values favored increased precipitation of Zn compounds (Figure 55). As corrosion rates were determined by chemical analysis of test solutions, any Al\textsuperscript{3+} ions that entered the precipitated products were undetected. This effect introduced uncertainty in the measured corrosion rates at pH > 2.5.

The general trend was similar in both alloys; the corrosion rate decreased with rise in pH. In comparison to F\textsuperscript{−} solutions, both alloys exhibited significantly lower corrosion rates in Cl\textsuperscript{−} solutions over the entire pH range. Even at these relatively high halide concentrations
(1000 ppm), the extent of Al corrosion was low owing to the presence of Zn\(^{2+}\) in solution. As mentioned before, Zn\(^{2+}\) inhibited Al corrosion probably by reducing halide activity through complex formation. Also, a spontaneous Zn cementation at breached oxide sites could block incipient corrosion sites. Although the driving force for Zn cementation was high, the cemented Zn was unstable in the absence of cathodic potential. Consequently, continuous Zn deposition/dissolution cycles occurred over the corroding surface. These cycles hindered Al corrosion, but could not prevent it. The dissolution of Zn deposit depended on pH. The lower the pH, the higher was the dissolution rate. At higher pH, Zn was less prone to dissolution, which explained why corrosion inhibition was particularly effective at high pH.

4.3.5 EFFECT OF ALLOY COMPOSITION

The detrimental effect of alloy impurity can be readily seen in Figure 56, which compares the \(E_{\text{corr}}\) behavior of fully immersed H1S alloy and 99.9999% Al in 40 ppm F\(^{-}\)-150 ppm Cl\(^{-}\) solutions. \(E_{\text{corr}}\) for the high purity Al was ca. 650 mV less positive than that of the H1S alloy. High hydrogen overpotential on ultra pure Al, owing to the high electronic resistivity of the Al oxide film, shifted \(E_{\text{corr}}\) in the active direction. In contrast, \(\text{H}_2\) evolution occurred readily on the H1S alloy due to the catalytic effect of the intermetallic particles. The H1S alloy exhibited a higher exchange current density (\(j_0\)) for \(\text{H}_2\) evolution. The measured corrosion rate for the high purity Al was much lower than that of the H1S alloy. The displacement of \(E_{\text{corr}}\) in the positive direction and the increased corrosion rate with increased impurity content can be seen schematically in Figure 57.

Cyclic polarization testing in deaerated Cl\(^{-}\) and F\(^{-}\) solutions indicated that the anodic polarization behavior of the high purity Al and the H1S alloy was similar. The anodic branches for both materials in a particular environment were coincident and the passive current density approached a limiting value associated with IR drop across the passive oxide film. The passive current densities in Cl\(^{-}\) and F\(^{-}\) solutions were ca. 6 and 10 A m\(^{-2}\), respectively. Chloride addition (150 ppm) to the base electrolyte had little effect on the polarization curves. Fluoride displaced the polarization curves downward and to the
right, indicative of easing Al dissolution (Figure 58). High-frequency noise on the anodic branches in F⁻ solutions signified pit nucleation/repassivation events on the oxide-covered surface. Fluoride-free solutions produced smooth curves (Figure 58). The absence of hysteresis loops in all solutions was indicative of low pit propagation rates as reflected in the observed shallow pitting. Relative to the HIS alloy, the cyclic polarization curves of the pure Al samples were displaced significantly downward due to retardation of the H₂ evolution reaction on ultra pure Al. Impurity elements in the HIS alloy increased the electronic conductivity of the oxide film, thereby catalyzing the H₂ evolution reaction. The addition of 150 ppm Cl⁻ to the 40 ppm F⁻ environment had minimal effect on the polarization curve of pure Al in H₂SO₄-40 ppm F⁻ solutions (Figure 59).

4.3.5.1 Binary Cast Al Alloys

Several Al alloys were screened by comparing their corrosion resistance to that of commercial cathode plates. Wernick and Pinner [138] cited German literature that suggested Ti addition to Al in the range 0.16-1.37% Ti could be beneficial in acid solutions. Al-0.08% Ti, Al-0.3% Ti, and Al-1% Ti were fabricated and tested in H₂SO₄-Cl⁻ solutions. The corrosion resistance of these alloys was inferior to that of the commercial purity Al plates. Other binary alloys that were screened included Al-Sb, Al-Ag, Al-Mn, and Al-Mg. These alloys showed poor corrosion resistance relative to the commercial cathode plates. The Al-Mn and Al-Mg alloys were standard 3xxx and 5xxx commercial sheet alloys, respectively.

The effect of Cu on the corrosion behavior of Al was investigated using fully immersed Al-x% Cu alloys, where x was 1, 2, and 4. The Eₜₐₜₖ-time record was monitored for ca. 10 hours in 150 ppm Cl⁻. Figure 60 demonstrates a typical result for Al-4% Cu. The curve displayed marked potential fluctuations, but the surface suffered little corrosion damage. A reddish film that was visible to the unaided eye formed on the surface and stifled the dissolution process (Figure 61).
Cyclic potentiodynamic polarization testing in various Cl⁻ concentrations indicated that the Al-Cu alloys displayed a lower passive current density relative to the 1070 and HIS alloys (Figure 62). In addition, the hysteresis loop was absent in the Al-Cu alloys, indicative of low pit growth rate. The tendency of the Al-Cu alloys to passivate can be readily seen if the region around the primary passivation potential is enlarged (Figure 63). Unfortunately, the apparent passive behavior was lost, as the applied potential became sufficiently positive. It is known from Cu electrorefining that Cu anodes show a strong passivation tendency in H₂SO₄ electrolytes. Partially immersed Al-Cu alloy samples experienced extensive intergranular corrosion in zone II.

Unlike the results of Figure 58, the HIS alloy in this 150 ppm Cl⁻ environment displayed passive film breakdown and significant dissolution as evidenced from its large hysteresis loop. This difference was due to different surface finish and scan rates. The samples from Figure 58 had a 1 μm diamond finish and were scanned at 1 mV s⁻¹. The present samples had a 600 grit SiC finish and a scan rate of 0.17 mV s⁻¹. Slower scan rate and coarser surface finish made the present samples more susceptible to surface breakdown. At a fast scan rate, the pit formation rate lags behind the potential scan. The finer the surface finish, the more protective the oxide film.

4.3.6 ROLE OF FLUORIDE ANIONS

4.3.6.1 Corrosion of Fully Immersed Plates

The influence of F⁻ anions on the corrosion susceptibility of the Al cathode plates was investigated galvanostatically in oxygenated H₂SO₄ solutions containing 0, 15, 500, and 1000 ppm F⁻. Within seconds of sample immersion in a fluoride solution and prior to the application of the cathodic current density (- 400 A m⁻²), vigorous H₂ evolution could be seen over the Al surface. The higher the F⁻ concentration, the quicker was the onset of visible H₂ evolution. This was a manifestation of the high corrosion susceptibility of Al in acid fluoride environments; under open-circuit conditions, Al dissolution provided the
electronic current that sustained the H₂ evolution reaction. The two partial reactions were coupled, proceeding simultaneously at the same rate.

Figure 64 presents the influence of F⁻ concentration on the galvanostatic curves of the HIS alloy. At each F⁻ concentration, the potential approached a constant steady-state value. The stationary potential values varied little from one concentration to another. For example, raising the F⁻ concentration from 15 to 1000 ppm shifted the potential only 20 mV in the noble direction. The dominance of the H₂ evolution reaction in this system and its fast kinetics probably produced the similarity between the curves in all solutions. Even at 1000 ppm F⁻, the corrosion current density was ca. 50 A m⁻², which was only 12% of the applied cathodic current density (~ 400 A m⁻²). The electrochemical curves for the 1070 alloy behaved similarly (Figure 65). The only notable difference was their clearer separation with changing F⁻ concentration. When the F⁻ concentration was increased from 15 to 1000 ppm, the potential-time curve shifted positively by ca. 40 mV.

The Al dissolution rate increased as the F⁻ concentration increased (Table VIII). The corrosion rate of the HIS alloy was consistently higher than that of the 1070 alloy at each F⁻ concentration; however, the difference in the measured corrosion rates was small, especially in the low fluoride range. For example, at 15 ppm F⁻ the corrosion current densities, determined by chemical analysis, for the HIS and 1070 alloys were 3.55 and 3.37 A m⁻², respectively. SEM examination revealed slightly more damage in the HIS alloy (Figure 66), thus supporting the chemical analysis results. Comparison of the electrochemical curves for the two alloys indicated the development of a slightly more noble potential in the HIS alloy, indicative of higher cathodic activity on the HIS alloy (Figure 67). The difference between the curves for the two alloys became less noticeable at higher F⁻ concentrations. The corrosion morphology observed in the HIS and 1070 alloys was similar. Both alloys exhibited a high density of shallow, cusp-like pitting. The cusp-like pits were particularly evident at high F⁻ concentrations (Figure 68).
Table VIII
Variation of corrosion rate with F⁻ concentration for the HIS and 1070 alloys

<table>
<thead>
<tr>
<th>F⁻ Concentration/ppm</th>
<th>Corrosion Current Density/A m⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1070 Alloy</td>
</tr>
<tr>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>15</td>
<td>3.37</td>
</tr>
<tr>
<td>500</td>
<td>31.40</td>
</tr>
<tr>
<td>1000</td>
<td>49.64</td>
</tr>
</tbody>
</table>

4.3.6.2 Corrosion of partially Immersed Plates

To assess the influence of F⁻ anions on zone II corrosion, galvanostatic testing was performed under partial immersion conditions. The samples were held at -400 A m⁻² in 0, 80, and 1000 ppm F⁻ solutions. F⁻ addition shifted the potential-time curves in the positive direction (Figure 69). The addition of 80 ppm F⁻ to the H₂SO₄ base electrolyte produced a pronounced potential shift of ca. 50 mV. Increasing the F⁻ concentration from 80 to 1000 ppm, produced relatively minor potential shift (ca. 10 mV). The movement of potential in the positive direction signified increased cathodic activity. Upon the application of the cathodic current density, the potentials in the F⁻ solutions approached a constant value of ca. -1.280 V_MSE within 2000 s. In the absence of F⁻, the potential reached a maximum value of -1.275 V_MSE within 6000 s, then decayed slowly and stabilized around -1.335 V_MSE. As mentioned in Section 4.3.1, the initial movement of potential in the positive direction was due increased cathodic activity on the intermetallic particles. The potential decayed as particles dropped out of the surface due to microgalvanic corrosion. The higher corrosion rate in the F⁻ solutions continually exposed subsurface intermetallic particles, preventing potential decay.

Zone I exhibited shallow, cusp-like pitting morphology and the extent of pitting intensified with increased F⁻ concentration (Figure 70). Zone III exhibited hardened mud-crack sulfate deposit (Figure 71). Zone II, the most susceptible corrosion zone, showed negligible corrosion attack even at 1000 ppm F⁻ (Figure 72). The negligible zone II corrosion could also be seen in Figure 73, which shows a broad view comparison of
zone II corrosion at 0 and 80 ppm $F^-$. A rapid, but uniform, corrosion could conceivably mask the severity of surface damage in zone II, producing seemingly minimal corrosion. To rule out this possibility, a polished sample was marked with three microhardness indentations in zone II, then tested as before at 1000 ppm $F^-$. The indentation marks were clearly visible after the test, confirming the minor effect of $F^-$ above the electrolyte level.

Previous testing in Cl$^-\cdot$F$^-$ solutions detected only Cl$^-$ on the cathode surface above the electrolyte/air interface. The ability of F$^-$ anions to reach this region of the plate was uncertain because of EDX limitations. This ability was explored using the XPS technique. XPS spectra were collected from zones I, II, and III. Fluoride anions were detected in all the zones. They appeared to enter the oxide lattice structure of zones I and II. A much stronger F$^-$ peak was detected in the mud-crack deposit of zone III (Figure 74). The increased F$^-$ transport to zone III originated from the growth/collapse cycle of gas bubbles at the solution line. As gas bubbles collapsed, they released electrolyte mist directly into zone III; this was recorded on video.

The above results suggest that the aggressive F$^-$ anions play a major role only in zone I below the solution line. As seen in Section 4.2, the corrosion damage in zone I is minor relative to zone II: failure in industrial cathode plates often results from intense thinning above the electrolyte level. Zone I corrosion is relatively minor because industrial electrolytes usually contain low F$^-$ concentrations (e.g., ca. 10 ppm $F^-$ at Cominco), and a protective zinc coating covers the Al cathode plate immediately after immersion. Fluoride is probably the main culprit in the formation of a firmly adherent Zn deposit. However, its influence on plate service life can be considered insignificant.

4.3.7 ROLE OF CHLORIDE ANIONS

4.3.7.1 Corrosion of Fully Immersed Plates

The effect of Cl$^-$ anions on the corrosion behavior of cathode plates was investigated at Cl$^-$ concentrations of 150, 500, 1000, 1500, 2000, 3000, and 4000 ppm. When the Al
samples were cathodically held at -400 A m\(^{-2}\) for 6 hours, the corrosion rate in zone I was small and the damage was superficial at all concentrations (Figure 75). For example, the average measured corrosion rate at 2000 ppm Cl\(^-\) was 0.84 ± 0.01 mm year\(^{-1}\). Under the selected cathodic conditions, the Cl\(^-\) anions were unable to block the self-healing processes in the protective oxide film. Even though several workers [9-10, 12-14] associated Cl\(^-\) anions with strippability problems, the above results indicated that F\(^-\) anions were the primary cause of the problem. Chloride anions would be mostly inactive under the cathodic protection conditions encountered during Zn electrolysis.

Without cathodic protection (under open circuit conditions), the H1S and 1070 alloys corroded even in halide-free solutions. Figure 76 shows that slow dissolution occurred in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\) solutions. The E\(_{corr}\)-time curve for the H1S alloy was relatively more noble than that of the 1070 alloy, indicative of higher H\(_2\) evolution on the H1S surface and, hence, greater H1S dissolution. The H\(_2\) evolution reaction was strongly polarized on the surface of high purity Al (99.9999%), as reflected in the pronounced active shift of its E\(_{corr}\) curve (Figure 77). The H1S alloy also developed a significantly more noble E\(_{corr}\) in 150 ppm Cl\(^-\) (Figure 78). The measured corrosion rates were 1.74 and 2.45 mm year\(^{-1}\) for the 1070 and H1S alloys, respectively. SEM examination detected the higher dissolution rate in the H1S alloy (Figure 79) and the pits in both alloys tended to nucleate around secondary phases (Figure 80).

The extent of corrosion was always higher in the H1S alloy than in the 1070 alloy and this became progressively more noticeable with higher Cl\(^-\) concentration. Whereas the H1S alloy was unstable at 500 ppm Cl\(^-\) and displayed extensive surface damage, the 1070 alloy consistently resisted gross corrosion attack (Figure 81). The damage in the H1S alloy was equivalent to an average penetration rate of 43.6 mm year\(^{-1}\). The corresponding value for the 1070 alloy was only 1.7 mm year\(^{-1}\), which was close to the rate observed at 150 ppm Cl\(^-\). Many samples were tested in 500 ppm Cl\(^-\): the reproducibility of E\(_{corr}\) measurements was quite good (Figure 82). Figure 83 compares the E\(_{corr}\)-time curves for the H1S and 1070 alloys in 500 ppm Cl\(^-\). Two features of these curves deserve further elaboration: the potential fluctuations (noise) on the 1070 alloy and its relatively negative
corrosion potential, despite its low corrosion rate. These features are explained in the subsequent paragraphs.

\( E_{\text{corr}} \) is the mixed potential that results from the intersection of the anodic (Al dissolution) and cathodic (\( \text{H}_2 \) evolution) polarization curves, as seen schematically in Figure 84a. The anodic polarization curve for Al shows that Al is passive up to \( E_b \), the breakdown potential. At potentials more noble than \( E_b \), the protective film on Al is unstable and Al corrodes rapidly.

The nobility of \( E_{\text{corr}} \) in the HIS alloy placed this alloy in a potential range above \( E_b \), leading to a significant corrosion damage (Figure 84b). The alloy was polarized above its breakdown potential. The noble \( E_{\text{corr}} \) value for the HIS alloy was the result of increased cathodic activity over its surface. \( E_{\text{corr}} \) for the 1070 alloy stabilized in the passive range, as confirmed from the minimal corrosion damage seen in this alloy. Hence, the 1070 alloy exhibited a relatively more negative corrosion potential (Figure 84b). Differences between the HIS and 1070 alloys in such factors as alloy composition and/or metallurgical history altered the electrochemical kinetics (e.g., kinetics of the cathodic process) and produced the above \( E_{\text{corr}} \) shifts.

The appearance of potential fluctuations on the \( E_{\text{corr}} \) - time curve of the 1070 alloy can be readily explained by reference to Figures 84c and 84d. As \( E_{\text{corr}} \) for the 1070 alloy occurred on the steep passive portion of the anodic polarization curve, any small change in dissolution kinetics (e.g., arising from bubble formation or polarization/depolarization of the cathodic reaction) would produce pronounced potential fluctuations (Figure 84c). In contrast, \( E_{\text{corr}} \) for the HIS alloy intersected the horizontal transpassive portion of the curve; hence even an order of magnitude change in dissolution kinetics caused little change in the recorded potential (Figure 84d). In effect, the HIS alloy displayed the characteristics of a nonpolarizable interphase with little resistance to current flow, as evidenced in the appearance of its corroded surface.
An increase of Cl' concentration from 150 to 500 ppm, slightly shifted $E_{\text{cor}}$ for the 1070 alloy to a more noble value. For the H1S alloy, which suffered a pronounced rise in corrosion rate as the Cl' content increased from 150 to 500 ppm, $E_{\text{cor}}$ shifted markedly in the negative direction (Figure 85). The H1S shift signified the depolarization of the anodic dissolution reaction owing to the difficulty of maintaining passivity at high Cl' concentrations. The slight positive $E_{\text{cor}}$ displacement in the 1070 alloy with increased Cl' concentration could be attributed to improved passivity. Carroll and Breslin [46] noted that holding Al samples in the passive range in Cl'-containing solutions improved passive film quality. This improvement was linked to the incorporation of hydroxychloride complexes within the passive film, which later converted to hydrated alumina [152]. Arthur [137] used XPS to investigate the composition of the surface film of cathode plate samples corroded in H$_2$SO$_4$-Cl' solutions. As the exposure time increased, the author observed an increase in the oxide thickness and in the proportion of Al(OH)$_3$ in the film.

The discussion in this section highlighted two important points. First, under full immersion conditions in sulfuric acid-Cl' solutions the H1S alloy, which contained 500 ppm Ti, displayed a consistently higher corrosion rate than the 1070 alloy. Second, the effect of a particular variable on corrosion behavior cannot be determined solely from the direction of electrode potential displacement. To provide a useful guide for the corrosion behavior, $E_{\text{cor}}$ measurements must be coupled with knowledge of system kinetics and the types of corrosion control.

4.3.7.1.A Free Immersion Testing

The difference in corrosion behavior between the H1S and 1070 alloys was investigated at room temperature by immersing samples for 4755.5 hours (ca. 200 days) in 500 ppm Cl'. At the conclusion of the test, the H1S surface contained two massive pits that penetrated to a depth of 3000 μm, nearly half the thickness of the H1S plate. The remainder of the surface receded uniformly to a depth of 475 μm. The surface of the
1070 alloy receded uniformly to a depth of 400 μm and exhibited no macroscopic pitting (Figure 86). The corrosion attack was in the form of cusp-like pitting in both alloys (Figure 87). This corrosion morphology was identical to zone II corrosion seen in plant plates (Figure 88). The average penetration rate was 0.394 mm year$^{-1}$ for the 1070 alloy and 1.93 mm year$^{-1}$ for the HIS alloy. Dissolution was somewhat hindered in both alloys by the precipitation of insoluble corrosion products, mainly Al sulfate (Figure 89). The horizontal orientation of samples and the stagnant solutions promoted the precipitation of adherent corrosion products.

Additional HIS and 1070 samples were freely immersed in 500 ppm Cl$^{-}$ for 83 days at room temperature. Under full immersion conditions, the alloys behaved as before. In some beakers, the solution level gradually declined through evaporation until it fell below the plane of the sample. This led to severe dissolution that exposed the base of the epoxy matrix in both alloys (Figure 90). The extent of dissolution was still higher in the HIS alloy. As seen in the lower left corner of the HIS photograph, only a small area remained of the original rectangular HIS surface. Bulky moist Al sulfate nests developed on both alloys. A remnant of this sulfate corrosion product could be seen firmly adhering to the wall of the HIS cavity. This experiment provided the first indication that under thin electrolyte film conditions the corrosion susceptibility of the 1070 alloy was equivalent to that of the HIS alloy. The 1070 alloy was superior to the HIS alloy only under full immersion conditions.

4.3.7.1.B Influence of Oxygen

The free immersion tests in Section 4.3.7.1.A implied a possible transformation in corrosion mechanism as the immersion conditions changed from bulk electrolyte to thin film electrolyte. This possibility was explored in 500 ppm Cl$^{-}$. Four 1070 samples and two high purity Al (99.9999%) samples were tested for 92 hours at 35 °C under different immersion conditions. Under full immersion, the corrosion damage in both materials was minimal. As before, the 1070 alloy displayed dense superficial micropitting (Figure 91).
Some white Al sulfate flakes floated in the solution. Macroscopically, the surface corroded uniformly.

All samples that were exposed to thin electrolyte films developed a bulky white deposit. Quantitative EDX analysis of the deposit indicated that its chemical composition was consistent with $\text{Al}_2(\text{SO}_4)_3 \cdot 6 \text{H}_2\text{O}$ (Figure 92). The deposit on the 1070 alloy was more voluminous than the deposit on high purity Al (Figure 93), indicative of the higher dissolution rate in the 1070 alloy. Underneath the deposit, the 1070 alloy suffered intense pitting while high purity Al resisted corrosion attack and displayed only superficial damage (Figures 94 and 95).

The main cathodic processes in this system were $\text{O}_2$ reduction and $\text{H}^+$ discharge. The contribution from each process depended on the immersion conditions. Discharge of $\text{H}^+$ dominated the system in bulk electrolytes owing to fast kinetics and high $[\text{H}^+]$. Compared to the HIS, the 1070 substrate was a poor electrocatalyst for $\text{H}_2$ evolution, as reflected in its consistently lower corrosion rate in bulk electrolytes. Under thin electrolyte films, the $\text{O}_2$ reduction reaction dominated the cathodic process owing to a large increase in $\text{O}_2$ transport to the corroding surface. Tomashov and Matveeva [153] found that even in strongly acid electrolyte films, the $\text{O}_2$ contribution to the cathodic process could be orders of magnitude greater than that of $\text{H}_2$. A rising contribution from $\text{O}_2$ depolarization caused the increased corrosion susceptibility seen in the 1070 alloy upon a switch from bulk electrolytes to thin electrolyte films.

Potentiodynamic cathodic polarization proved the predominance of the $\text{H}_2$ evolution reaction in bulk $\text{H}_2\text{SO}_4$ environments. As seen in Figure 96, the polarization curves with and without $\text{O}_2$ were similar, reflecting the predominance of the $\text{H}_2$ evolution reaction. However, a minor contribution to the total cathodic activity from the $\text{O}_2$ reduction reaction was detected in open circuit testing. Compared to deaerated solutions, $E_{\text{corr}}$ was relatively more positive in oxygenated solutions, but the attendant increase in corrosion damage was small (Figure 97). Biegler and Swift [133] reported that the $\text{O}_2$ reduction rate during Zn electrolysis was $3.8 \text{ A m}^{-2}$, around 1% of the total cathodic current.
4.3.7.1.C Breakdown Potentials in the 1070 and H1S Plates

The determination of $E_b$ was conducted in oxygenated 500 ppm Cl$^-$ solutions. Figure 98 demonstrates the variation of corrosion current density with the applied potential for the H1S and 1070 alloys. Each alloy displayed a potential range in which it suffered little corrosion damage. A characteristic breakdown potential ($E_b$) was observed for each alloy. At potentials more positive than $E_b$, severe surface damage occurred. The breakdown potential for the 1070 alloy was relatively more noble, confirming the superiority of this alloy under these test conditions.

The higher corrosion resistance of the 1070 alloy can be seen in Figure 99 which compares the current density-time curves for the two alloys at $E = -1.115$ V$_{MSE}$. Since this potential was more positive than $E_b$ for the H1S alloy, extensive anodic dissolution ensued after about 2 hours of immersion. Only cathodic current passed over the 1070 surface which remained intact after 6 hours of immersion. Testing at $E = -1.1$ V$_{MSE}$ presented another indication of the superiority of the 1070 alloy. Although both alloys were severely damaged, corrosion in the 1070 alloy was lower by ca. 40%. This could also be inferred from the electrochemical curves which showed that the 1070 alloy remained cathodic much longer and dissolved slower than the H1S alloy (Figure 100). For example, anodic dissolution at a rate of 400 A m$^{-2}$ occurred after 6000 s in the H1S alloy while it took 18000 s to observe that level of dissolution in the 1070 alloy.

Potentiodynamic anodic polarization testing in acid chloride environments also indicated the higher corrosion resistance of the 1070 alloy. For example, potentiodynamic testing in 150 ppm Cl$^-$ produced the curves presented in Figure 101. The 1070 alloy exhibited only a limiting passive current density on the upward scan; the H1S alloy exhibited surface breakdown early in the upward scan, ca. 400 mV below the final anodic potential. The hysteresis loops indicated that pits nucleated and grew on both alloy surfaces. The extent of dissolution was substantially higher in the H1S alloy, as evident in its larger hysteresis loop. This conclusion was further supported by chemical analysis of test
solutions, which predicted penetration rates of 18.6 and 369.6 mm year\textsuperscript{-1} for the 1070 and H1S alloys, respectively.

4.3.7.2 Corrosion of Partially Immersed Plates

To ascertain the influence of Cl\textsuperscript{-} on zone II corrosion, partially immersed samples were tested in H\textsubscript{2}SO\textsubscript{4} solutions containing 0, 150, 500, 750, and 1000 ppm Cl\textsuperscript{-}. The samples were cathodically polarized at \(-400\) A m\textsuperscript{-2} for 6 hours. In cathodically protected samples, zone I suffered little corrosion damage. Zone II, which corroded under thin electrolyte film conditions, experienced extensive pitting corrosion (Figure 102). The damage intensified with increased Cl\textsuperscript{-} content (Figure 103). Both the H1S and 1070 alloys were susceptible to corrosion attack in zone II although the extent of damage was slightly higher in the H1S alloy (Figures 104 and 105). The higher corrosion rate in the H1S alloy suggested that thin electrolyte films diminished the H\textsubscript{2} contribution to the total cathodic activity but did not stop it. Chloride-rich deposits were detected in zone II (Figure 106). Since previous testing showed that Cl\textsuperscript{-} anions were inactive under cathodic conditions, the above results implied that the potential of zone II had to be positive with respect to zone I. This was verified by potential measurement in zone II.

4.3.7.2.A Potential Measurements in Zone II

Partially immersed samples were held galvanostatically or potentiostatically in 500 ppm Cl\textsuperscript{-} for 6 h. A separate reference electrode circuit monitored the potential of zone II. The reference electrode was connected to the test solution via a fine-tip Luggin probe that made a gentle contact with the working surface. The electrolyte film covering zone II was visible and in continuous contact with the bulk electrolyte.

Testing revealed that the potential of zone II was around 200 mV more positive than that of zone I. Typical potential measurements on the H1S alloy are given in Table IX. Extensive corrosion damage appeared after 3 hours of immersion. It should be noted that the potentials recorded in zone II after 3 hours were positive of E\textsubscript{b} (Figure 98). Chloride
accumulation in zone II coupled with an insufficient cathodic protection, due to IR potential drop in the thin electrolyte film, made zone II highly prone to corrosion attack. The potential increased exponentially with distance from the electrolyte/air interface. Correspondingly, the Al plate thinned gradually with distance reaching a maximum at the maximum IR drop, 30 mm above the interface (Figure 24). Beyond this limit, the corrosion rate gradually declined with distance because the precipitated Al sulfate became increasingly more stable. Also, as the distance from the electrolyte/air interface increased, the thickness of the electrolyte film decreased, hindering the ionic current. Potential gradation above the electrolyte/air interface was clearly illustrated with Monel samples, which developed three corrosion zones: reddish zone, metallic zone, and green zone. The reddish zone consisted of replated Cu (Appendix V). In the metallic zone, dissolution occurred, but the potential was insufficient to plate Cu. The green deposit developed the furthest away from the electrolyte; it was probably Ni sulfate.

| Table IX |
| Potential measurements below and above solution line for the H1S alloy in 500 ppm Cl\(^-\) at j = -500 A m\(^{-2}\) |

| Time (h) | Potential (mV\(_{MSE}\)) |
| --- | --- | --- |
| Zone I | Zone II | \(E_{II} - E_i\) |
| 1 | -1274 | -1120 | 154 |
| 2 | -1290 | -1130 | 160 |
| 3 | -1305 | -1104 | 201 |
| 5 | -1315 | -1114 | 201 |
| 6 | -1293 | -1085 | 208 |

Potential measurements suggested that depressing the potential of zone II into the negative direction might minimize the corrosion damage. Such potential displacement was achieved using sacrificial anodes. The test in Table IX was repeated using an identical sample, but with a thin Mg ribbon attached to zone II. The Mg ribbon minimized the potential difference (\(E_{II} - E_i\)), especially early in the experiment: The potential difference was only 36 mV after 1.5 hours of immersion. It rose steadily as the Mg ribbon receded owing to gradual consumption by the acid environment. After 6
hours of immersion, the maximum potential difference was 210 mV. Despite this increase in potential difference, the extent of corrosion damage was significantly less in the ribbon-containing sample (Figure 107). Similar results were obtained using a sacrificial Zn anode. Sacrificial anode protection appeared promising in mitigating corrosion damage above the electrolyte/air interface.

4.3.8 ROLE OF TITANIUM

Under the testing conditions outlined in this work, the corrosion resistance of the cathode plate decreased as the Ti content increased. The H1S alloy appeared inferior to the 1070 alloy. The difference was particularly pronounced in bulk electrolytes. Since these two alloys had an identical metallurgical history and differed only in Ti content, it was necessary to establish how the Ti addition influenced the microstructure and, hence, the electrochemical dissolution kinetics.

The effect of Ti on microstructure was investigated using TEM, XPS, and XRD methods. The XRD analysis showed no textural difference between the H1S and 1070 alloys (Figure 108). As reported in Section 4.1, microstructural analysis indicated that Ti in the H1S alloy was present in solid solution. The maximum solid solubility of Ti in Al is 1% at 665 °C, the peritectic temperature, but it decreases rapidly with decreasing temperature [145]. At 400 °C, the equilibrium Ti solubility in Al is 300 ppm. The solubility at room temperature is even lower. The Ti content of the H1S alloy was ca. 500 ppm, exceeding the solubility limit by at least 67%. If Ti formed a super-saturated solid solution with Al owing to nonequilibrium solidification of the alloy, a prolonged artificial aging could precipitate Ti.

To explore this possibility, H1S and 1070 samples were polished to a mirror-like finish, marked with a microhardness indenter, then photographed using the SEM. The samples were placed in a furnace and heat-treated for 28 hours at 200 °C. After heat treatment, the samples were re-examined for microstructural changes. As seen in Figures 109 and 110, the heat treatment had little effect on the microstructure. No new precipitates could
be detected. The only noticeable change was the appearance of some calcium-
contaminated porosity around the indentation marks. Thus, at room temperature the solid
solubility limit of Ti in Al is > 400 ppm.

The resistance of TiO₂ to corrosion attack is superior to that of Al₂O₃, especially in Cl⁻
solutions. The presence of TiO₂ in the Al oxide lattice can substantially improve the
corrosion resistance of Al. The higher the proportion of TiO₂ in the film, the better the
corrosion resistance. This improvement arises from the concept of pH of zero charge,
pHₜₜh, which determines the adsorption behavior of the surface [36-38]. The pHₜₜh is the
pH at which the oxide surface is electrically neutral. It is a characteristic parameter of the
oxide film. If the pH of the solution is greater than the pHₜₜh, the surface is negatively
charged and anion adsorption is unfavorable. Accordingly, a low pHₜₜh improves
corrosion resistance because it discourages Cl⁻ adsorption, a necessary step in the
corrosion process. Roy and Fuerstenau [154] showed that doping Al₂O₃ (pHₜₜh = 9.1)
with 0.5 at % TiO₂ (pHₜₜh = 5.3) produced a composite film with pHₜₜh = 7.5.

XPS analysis of the H1S alloy found no Ti incorporation into the oxide film. The XPS
spectra collected from the H1S and 1070 alloys were nearly identical. Both indicated the
presence of a very thin Al oxide film (Figure 111). The spectral peaks at Al 2p, Al 2s,
and O 1s emanated from photoelectron emission in the core levels of Al and O in the
oxide film. The O 1s peak was slightly more intense in the 1070 alloy. Adventitious
surface contaminants produced the C 1s peak. Since Ti was not absorbed into the
protective oxide film of the H1S alloy, it is not surprising that Ti addition had no positive
effect on the corrosion resistance of the alloy.

The formation of TiO₂ in Al is thermodynamically unfavorable. For instance, at 100 °C
the Ellingham diagram shows that Al reduces TiO₂ to Ti as follows:

\[
\begin{align*}
\frac{4}{3} \text{Al (s)} + \text{O}_2 (g, 1 \text{ atm}) &= \frac{2}{3} \text{Al}_2\text{O}_3 (s) \quad \Delta G^\circ = -1030 \text{ kJ} \\
\text{TiO}_2 (s) &= \text{Ti (s)} + \text{O}_2 (g, 1 \text{ atm}) \quad \Delta G^\circ = 837 \text{ kJ} \\
\frac{4}{3} \text{Al (s)} + \text{TiO}_2 (s) &= \text{Ti (s)} + \frac{2}{3} \text{Al}_2\text{O}_3 (s) \quad \Delta G^\circ = -193 \text{ kJ}
\end{align*}
\]
The driving force for the reduction of TiO$_2$ by Al is high and remains so in the temperature range 0-600 °C.

4.3.8.1 **Catalytic Effect of Ti**

Al is thermodynamically unstable in low-pH electrolytes. Its use in such environments is possible only because of the slow kinetics of the H$_2$ evolution reaction. As Al purity decreases, the H$_2$ evolution rate increases with an attendant rise in Al corrosion [111-115]. The H1S alloy displayed greater corrosion susceptibility because the incorporation of Ti in solid solution catalyzed the H$_2$ evolution process. Titanium was not dissolved from the solid solution, as chemical analysis of test solutions detected no Ti. Cathodic polarization, e.g. at -1.130 V$_{\text{MSE}}$, confirmed the enhanced H$_2$ evolution kinetics on the H1S alloy in comparison to the 1070 alloy (Figure 112). The discontinuities seen in the curves resulted from increasing partial anodic current density. Again, the higher corrosion resistance of the 1070 alloy is reflected in the shape of the curves: the H1S alloy exhibited a significant anodic current much sooner than the 1070 alloy.

The kinetics of H$_2$ evolution on Ti/TiH$_2$ are faster than on Al. Figure 113 compares the cathodic polarization curves for pure Ti and pure Al in H$_2$SO$_4$ solutions. It can be seen that at any potential, the cathodic current density on Ti was appreciably higher than that on Al. The exchange current density, $j_0$, is a measure of the intrinsic rate of a reaction at equilibrium when the net reaction rate is zero. It reflects the catalytic activity of a substrate. According to Bockris [155-156], $j_0$ for the H$_2$ evolution reaction on Ti in 1 M H$_2$SO$_4$ is 10$^{-4.2}$ A m$^{-2}$, two orders of magnitude higher than that of Al (10$^{-6}$ A m$^{-2}$). Consequently, the effect of Ti was particularly evident at low pH values where H$_2$ evolution was the primary cathodic reaction. At high pH values or under thin electrolyte films, the contribution from O$_2$ reduction became important and the effect of Ti became less noticeable. The dominance of O$_2$ reduction on the cathodic process was probably the reason the H1S changed slope and displayed lower corrosion rates at pH > 2.5, discussed in Section 4.3.4.
The important influence of \( j_0 \) on the corrosion process can be highlighted by deriving the relationship between the corrosion rate and \( j_0 \) [155]. Assuming Tafel kinetics, negligible mass transport effects, and negligible solution resistance,

\[
E_{\text{cell}} = \eta_c = \eta_a = 0
\]

\[
\eta_c = B_c \ln \frac{j_c}{j_{oc}}
\]

\[
\eta_a = B_a \ln \frac{j_a}{j_{oa}}
\]

\[
B = \frac{\partial \eta}{\partial \ln j} = \frac{RT}{\alpha F}
\]

Where:

- \( E_{\text{cell}} \) is the equilibrium cell voltage,
- \( \eta \) is the overvoltage,
- \( B \) is the Tafel slope,
- \( RT \) is the thermal energy,
- \( F \) is the Faraday constant,
- \( \alpha_a \) is the anodic transfer coefficient,
- \( \alpha_c \) is the cathodic transfer coefficient,
- \( j_a \) is the partial anodic current density,
- \( j_c \) is the partial cathodic current density,
- \( j_o \) is the exchange current density, and

In a freely corroding cell, \( j_a = j_c = j = \) the corrosion rate

Substituting equations (20) and (21) in equation (19) yields

\[
E_{\text{cell}} = B_c \ln \frac{j}{j_{oc}} + B_a \ln \frac{j}{j_{oa}}
\]

\[
j = \left( j_{oc} \right)^{B_c/B_t} \left( j_{oa} \right)^{B_a/B_t} \exp \left( E_{\text{cell}}/B_t \right)
\]

Where:

\[
B_t = B_c + B_a = \left[ \frac{RT}{F} \right] \left[ 1/\alpha_a + 1/\alpha_c \right] = R T \left( \alpha_a + \alpha_c \right)/F \alpha_a \alpha_c
\]

\[
B_c/B_t = \alpha_a/\left( \alpha_a + \alpha_c \right) = x
\]

\[
B_a/B_t = \alpha_c/\left( \alpha_a + \alpha_c \right) = y
\]

Hence, the relationship between the corrosion rate and \( j_o \) is given by
Corrosion Rate \( j = (j_{oc})^x (j_{oa})^y \exp \{\alpha_a \alpha_c F E_{cell}/R T [\alpha_a + \alpha_c]\} \) \hspace{1cm} (25)

The corrosion rate depends on cell voltage, reaction mechanism through \( \alpha \), and exchange current density, \( j_0 \). As \( j_0 \) is a pure kinetic parameter, it is a very important parameter in the corrosion system.

The corrosion potential of Al-base alloys varies with the concentration of the alloying addition up to the solubility limit of the added element. When the added element exceeds its solubility limit in Al, it forms secondary phases and it no longer affects the corrosion potential [143]. Generally, relatively noble elements (e.g., Cu, Si) shift \( E_{corr} \) in the positive direction while active elements (e.g., Zn, Mg) shift it in the negative direction. \( E_{corr} \) for the H1S alloy was consistently more noble than that of the 1070 alloy. The presence of Ti in solid solution increased the cathodic activity of the H1S alloy, displacing its \( E_{corr} \) in the positive direction.

The relationship between \( E_{corr} \) and \( j_0 \) is also useful in analyzing the open circuit results [155]. Under open circuit conditions, the oxidation reaction rate \( (j_a) \) equals the reduction reaction rate \( (j_c) \). Hence, equations (20) and (21) give

\[ j_{oc} \exp \{- \eta_{c}/B_c\} = j_c = j_{oa} \exp \{\eta_{a}/B_a\} = j_a \] \hspace{1cm} (26)

Where:

\[ \eta_c = E_{corr} - E_c \] \hspace{1cm} \[ \eta_a = E_{corr} - E_a \]

Substituting the \( \eta \) expressions in (26) and solving for \( E_{corr} \) gives

\[ E_{corr} = \{B_a B_c \ln (j_{oc}/j_{oa})\}/B_t + B_c E_0/B_t + B_a E_c/B_t \] \hspace{1cm} (27)

Equation 27 shows why the corrosion potential of the H1S alloy assumed a positive value relative to that of the 1070 alloy. The exchange current density determines the value of \( E_{corr} \). The higher the \( j_{oc} \) value, the higher is the corrosion potential. The increase in \( j_0 \) with the addition of 500 ppm Ti may not have been substantial. The difference in \( E_{corr} \)
values between the H1S and 1070 alloys was in the range 20-60 mV, depending on the environment. Nonetheless, in some electrolytes the $j_0$ increase was just enough to place the H1S alloy above $E_b$, the breakdown potential.

Although this work indicated that Ti addition was detrimental to the corrosion resistance of the cathode plate, industrial experience found little difference between the H1S and 1070 alloys; each alloy lasted 18-24 months for a 6-mm gauge. This can be readily explained. In the plant environment, the plates failed because of zone II corrosion under thin electrolyte films. The present work showed that under such films, H$_2$ evolution did not drive the corrosion process. Consequently, the presence of Ti contributed little to the failure process and the difference between the two alloys was inconsequential.

The patent for the H1S alloy [17] claimed improved strippability, and this claim has been supported by plant experience at Cominco [7]. Although strippability was not investigated in this work, improved strippability with the H1S alloy could be inferred from the above results. It was found that Ti formed a solid solution with Al and did not partition into the oxide lattice structure; therefore Ti had little influence on oxide film stability. Consequently, improvement in strippability could arise only from increased catalytic activity owing to the presence of Ti in solid solution. The enhanced H$_2$ evolution kinetics probably promoted the dissolution of any Zn deposit that bonded directly to the Al substrate. In effect, Ti opposed the ingress of Zn atoms into the Al lattice structure. By a galvanic action, Ti made the Al lattice less hospitable for the diffusing Zn atoms. Han and O’Keefe [11, 141] observed a similar effect with antimony: Sb addition improved the strippability of the Zn deposit. The authors speculated that the H$_2$ evolution reaction, catalyzed by Sb, corroded the Zn from the Al substrate preventing the formation of a firmly adherent deposit. The comparable effects of Ti and Sb on Zn adherence could be attributed to their similar electrocatalytic activity. The $j_{oc}$ values for H$_2$ evolution on Ti and Sb in 1 M H$_2$SO$_4$ are nearly identical, $10^{-4.2}$ and $10^{-4}$ A m$^{-2}$, respectively [155-157]. Based on these considerations the overall effect of Ti on the Al cathode plate is positive. Titanium improves strippability and has little influence on corrosion in zone II, the zone that determines cathode longevity.
4.3.9 MECHANISMS OF CATHODE PLATE CORROSION

4.3.9.1 Zone I Corrosion

The corrosion of zone I has already been discussed in detail. Hydrogen evolution chiefly drove the corrosion process. Oxygen reduction contributed slightly to the total cathodic process. Factors that enhanced the kinetics of \( \text{H}_2 \) evolution intensified zone I corrosion. Cathodic protection mitigated the corrosion damage but was unable to prevent \( \text{F}^- \) anions from attacking the Al plate even at \( \text{F}^- \) concentrations as low as 15 ppm. The dissolution rate depended strongly on \([\text{F}^-]\), higher values increasing the dissolution rate. On the other hand, \( \text{Cl}^- \) was found mostly inactive under cathodic protection even at \([\text{Cl}^-]\) concentrations as high as 4000 ppm. Without cathodic protection, the influence of \( \text{Cl}^- \) anions depended on the level of cathodic activity in the plate alloy. High cathodic activity led to severe corrosion damage, as was seen from comparing the H1S and 1070 alloys. When both halides were present in the electrolyte, they exerted a synergistic effect that accelerated the corrosion process. Zinc cations reduced Al dissolution in all electrolytes by lowering halide activity and by spontaneous cementation at pit sites.

4.3.9.2 Zone II Corrosion

Zone II corrosion was investigated by accelerated testing at \(-400 \text{ A m}^{-2}\) in rectangular Zn electrowinning cells using Pb-Ag anodes and Al cathodes. These electrodes were relatively large, each having a surface area of ca. 0.005 m\(^2\). Six-hour tests were conducted in \( \text{H}_2\text{SO}_4\)-500 ppm \( \text{Cl}^- \) electrolytes. Two electrodes were used in each run. The geometry of zone II was modified in some tests to gain an insight into the corrosion mechanism. Three configurations were investigated (Figure 114): Configuration B confirmed the propensity of the cathode plate for corrosion near the electrical contact side (Figure 115). Comparison of configuration C with the unmodified plate indicated that the extent of zone II corrosion was much less on the modified plate (Figure 116). Zone II corrosion was also hindered by forced airflow over the Zn cell or by placing a ventilation tube 150 mm above the cell (Figure 117).
When the vapor phase surrounding a partially immersed Al cathode plate was saturated with Ar gas, zone II experienced superficial corrosion damage; the corrosion morphology was similar to that seen in the submerged portion of the plate (Figures 118 and 119). When the experiment was repeated with O₂ gas, again little corrosion could be detected in zone II. At first, this might seem inconsistent, for if O₂ reduction really drove the corrosion cell in zone II, an intensification of the corrosion damage should have ensued. However, these results were not only consistent with the results reported earlier, but also reinforced them. The reduced corrosion attack in the presence of O₂ highlighted the critical role played by Cl⁻ in zone II corrosion. It was shown earlier that when zone I was cathodically controlled, Cl⁻ was the main activator of zone II corrosion. The mechanism by which Cl⁻ activated zone II should reconcile these observations.

The above observations hinted that a gaseous species stimulated zone II corrosion. The corrosion damage decreased in the airflow experiments because the forced convection swept away the aggressive species from the vapor phase, precluding its adsorption on the Al surface. The lower corrosion attack on the modified plate C could be attributed to a reduction in the probability of aggressive species adsorbing on the smaller area. The unmodified plate presented a relatively large hydrophilic area, which increased the chances of interaction between zone II and the corrosive species. The greater the interaction, the greater the corrosion attack. Previous findings on the role of Cl⁻ in the corrosion process, coupled with the above observations, suggested that Cl₂ was the most likely culprit in zone II corrosion. The presence of Cl₂ in the vapor phase above the Zn cell was confirmed by standard chemical detection methods described in Section 3.4.4.2. Also, Cl⁻-containing corrosion products were detected using EDX analysis (Figure 106).

In the Zn electrowinning cell, the anode operates at ca. 2 V_SHE. At this potential, Cl⁻ and H₂O oxidize simultaneously at the anode evolving O₂ and Cl₂:

\[
\begin{align*}
2 \text{Cl}^- & \rightarrow \text{Cl}_2 \uparrow + 2 \text{e}^- & E_{\text{red}} &= +1.36 \text{ V}_{\text{SHE}} \\
\text{H}_2\text{O} & \rightarrow \text{O}_2 \uparrow + 4 \text{H}^+ + 4 \text{e}^- & E_{\text{red}} &= +1.23 \text{ V}_{\text{SHE}}
\end{align*}
\]  

(28)  

(29)
Kinetic factors favor the Cl$_2$ evolution reaction. For example, in acid solutions the $j_0$ values for Cl$_2$ and O$_2$ evolution on platinum are $10$ and $10^{-7}$ A m$^{-2}$, respectively [157]. Chlorine evolution is well documented in plant practice despite low [Cl$^-$] in the Zn electrolyte (50-300 ppm). The presence of Cl$_2$ in the Zn plant atmosphere is particularly noticeable when new anodes are introduced into the cells [7]. Measures are usually taken to minimize Cl$_2$ evolution because of the toxicity and ensuing hygienic problems. Surfactants are used to form a foam layer that suppresses bath mist. Some plants maintain a minimum [Mn$^{2+}$], which reacts with Cl$_2$ according to the following reaction:

$$\text{Cl}_2 (g) + \text{Mn}^{2+} + 2 \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2 \text{Cl}^- + 4 \text{H}^+$$ (30)

The equilibrium position in reaction (30) depends strongly on pH. Although these measures minimize Cl$_2$ generation, they do not entirely prevent it.

In Industrial Zn electrowinning cells, zone II experiences minimal electrolyte turbulence and splashing. Wetting of zone II occurs mostly by condensation and by capillary action (high adhesive forces), resulting in thin electrolyte film corrosion. It is known [153] that in thin electrolyte films, even acid films, the contribution of H$_2$ evolution to the cathodic process is small. Unless a kinetically more favorable cathodic reaction is available, the O$_2$ reduction reaction would dominate the cathodic process in zone II due to a pronounced rise in O$_2$ transport to the corroding surface. However, because of the passivation tendency of Al, zone II corrosion probably proceeds under anodic control, making zone II more sensitive to stimulants of the anodic dissolution process. For this reason, O$_2$ saturation in the vapor phase did not produce a substantial rise in Al dissolution in the time scale of the experiment (6 hours).

The reduction of Cl$_2$ is an alternative cathodic reaction with fast reduction kinetics. The oxidizing strength of Cl$_2$ is far greater than that of O$_2$, and it is certain that the potential of zone II was conducive to the cathodic reduction of Cl$_2$. The solubility of Cl$_2$ is also significantly higher than that of O$_2$. The high surface area of the thin electrolyte film in zone II promotes the absorption of substantial amounts of Cl$_2$ from the vapor phase.
Saturation of the zone II layer with Cl₂ strongly depolarizes the anodic dissolution reaction. If the local pH exceeds ca. 3 [158], Cl₂ could hydrolyze according to the following reaction:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \] (31)

This reaction would tend to concentrate Cl⁻ in zone II. Chloride accumulation in zone II also occurs through direct transport from the electrolyte.

Chlorine may affect the corrosion process in another way. When an operating Zn cell is carefully monitored, it can be seen that the O₂ bubbles formed at the anode do not simply rise to the electrolyte surface near the anode. Rather, clouds of small bubbles vigorously spurt away from the anode surface towards the Al cathode. This convective action further increases the concentration of Cl₂ in the vicinity of the cathode. Because of the high reactivity of Cl₂ and the relatively high H₂ concentration near the cathode, HCl (g) can form by the following photochemical chain reaction:

\[ \text{H}_2 + \text{Cl}_2 \rightarrow 2 \text{HCl (g)} \] (32)

Laubusch [159] stated that the presence of O₂ increases markedly the rate of reaction (32). In the presence of moisture, the above reaction produces very pure HCl acid. Reaction (32) was probably the reason for the tendency of the plates to thin faster near the edge containing the electrical contact notch. The current density distribution should lead to relatively higher H₂ production on the electrical contact side; hence more Cl⁻ anions.

Although Cl₂ probably contributed to the corrosion process by increasing the cathodic activity, it should not be inferred that zone II corrosion was driven only by Cl₂ reduction. In plant environment, the Cl₂ concentration is much lower than that used in this accelerated testing program, and the contribution of O₂ reduction should still be
significant in the thin electrolyte film of zone II. The most critical contribution of Cl₂ was the depolarization of the anodic dissolution process.

In short, Cl⁻ was the primary stimulant for Al cathode corrosion above the electrolyte/air interface. It accumulated in zone II through direct transport from the bath (wetting) and through Cl₂ evolution. Its action was halted in zone III by the precipitation of an adherent Al sulfate-Zn sulfate deposit and possibly by diffusional limitation due to the remoteness of zone III. A further evidence for Cl⁻-induced corrosion above the electrolyte/air interface could be found in the failure analysis results of Section 4.2, which revealed the predominance of crystallographic etching. Crystallographic etching is characteristic of Al corrosion in acidic Cl⁻ solutions. In fact, HCl has long been used commercially to produce crystallographic etching in electrolytic Al capacitors, in order to maximize their capacitance per unit volume. The prevailing potential and electrolyte conditions in zone III were particularly suitable for crystallographic etching. Zone III remained relatively undisturbed by potential fluctuations, allowing pure crystallographic pitting to proceed until it was halted by salt precipitation. As was seen earlier, only a small acid halide concentration was necessary for depolarizing the Al dissolution reaction. For a single industrial Zn plating cycle, at least 1000 kg of Cl⁻ enters the cellhouse. The accumulation of a critical Cl⁻ concentration in the zone II layer should be readily attained.

4.3.10 COUNTERMEASURES FOR ZONE II CORROSION

Mitigating zone II corrosion in Al plates requires careful control of Cl⁻ concentration in the electrolyte environment. Pre-electrolysis measures for reducing [Cl⁻] should improve considerably the longevity of Al cathode plates. In the absence of a satisfactory method for Cl⁻ removal from the Zn electrolyte, several measures could be adopted based on the results of this work. The methods that were alluded to in the previous section, such as effective ventilation, could be optimized to reduce the harmful effect of Cl₂. Two additional measures appear promising:
4.3.10.1  *Al-Mn alloys*

High purity Al showed good resistance to corrosion under thin electrolyte films even at 500 ppm Cl⁻. Pure Al, however, lacks the strength necessary to withstand the stripping operation. As discussed before, most alloying additions that strengthen Al also undermine its corrosion resistance. An exception is Mn. Manganese has a relatively high solid solubility in Al and its intermetallics with Al have little thermodynamic tendency for microgalvanic corrosion (Table III). Also, Mn intermetallics tend to scavenge Fe, preventing it from forming the detrimental FeAl₃ particles. Manganese increases the work hardening rate of Al; it is extensively used as a hardener for Al alloys [145]. The improvement in strength and hardness of Al is most pronounced when Mn is present in solid solution. The hardening effect of Mn is highly desirable in the heavily cold-worked Al cathode plate. In addition to these advantages, Mn has a positive effect on Zn electrowinning, a process that is very sensitive to impurities in the Zn electrolyte. Therefore, a small Mn addition should strengthen pure Al without adversely affecting corrosion resistance or Zn recovery.

4.3.10.2  *Zone II Coating*

Potential measurements in zone II indicated that sacrificial anodes could suppress the potential difference between zones I and II, thereby arresting Cl⁻ attack. Thus, a Zn coat of zone II provides a physical corrosion barrier and cathodic protection at breached sites. In the past, some Zn plants attempted to introduce protective Zn coatings by submerging the plates in the Zn bath until zone II received Zn coverage. This was unsuccessful because in the absence of cathodic potential, the Zn coating dissolved easily.

It is well known from plant practice that halides, especially F⁻, in the Zn bath produce a strongly adherent Zn deposit that is difficult or impossible to strip. The protective Zn coating should be developed under such conditions. For example, a pretreatment of Al cathodes in a high F⁻ solution could generate a protective Zn coating in zone II.
5.0 CONCLUSIONS

(1) The corrosion susceptibility of Al cathode plates should be assessed using techniques that are appropriate for thin electrolyte film corrosion.

(2) Aluminum cathode plates exhibited three distinct corrosion zones. Extensive corrosion attack occurred in zone II, 0-40 mm above the electrolyte/air interface.

(3) Cathodic polarization diminished the extent of cathode plate corrosion in zone I in Cl\textsuperscript{-} and F\textsuperscript{-} environments. Thus, utilization of the maximum feasible current density should lessen zone I corrosion and, hence, strippability problems.

(4) Chloride and Fluoride anions increased the cathodic activity of the Al cathode plate by becoming incorporated into the oxide lattice structure.

(5) The presence of Zn\textsuperscript{2+} cations in solution inhibited cathode plate corrosion in zone I probably by reducing halide activity and by increasing the H\textsubscript{2} overpotential.

(6) The extent of corrosion attack in cathode plates declined as pH increased.

(7) Impurity elements in the cathode plate alloy increased its corrosion susceptibility.

(8) Hydrogen evolution drove zone I corrosion. Oxygen and chlorine reduction dominated zone II corrosion.

(9) The presence of Ti in the cathode plate alloy undermined the corrosion resistance in zone I by catalyzing the H\textsubscript{2} evolution reaction.

(10) The F\textsuperscript{-} anion acted on the cathode plate primarily in zone I. Thus, it was the main culprit in the formation of a firmly Zn adherent deposits. Fluoride had little effect on zone II corrosion.
(11) Under cathodic potential control, the Cl\(^-\) anion was mostly inactive in zone I but caused severe corrosion damage in zone II.

(12) The potential of zone II was ca. 200 mV more positive than that of zone I.

(13) Chloride accumulated above the electrolyte/air interface through direct electrolyte wetting and through Cl\(_2\) evolution. It was the primary contributor to the failure of cathode plates.
6.0 RECOMMENDATIONS

(1) Zone II corrosion in Al cathodes should be investigated only under well-characterized thin electrolyte films; bulk electrolyte conditions are not applicable in zone II.

(2) Surface analytical methods such as infrared reflection absorption spectroscopy (IRAS) should be used to identify the chemical species participating in zone II corrosion.

(3) The pronounced increase in zone II corrosion with the addition of Al dust should be investigated to determine its underlying cause.

(4) Testing should be carried out in a controlled Cl₂ atmosphere to quantify the effect of Cl₂ concentration on zone II corrosion.

(5) Measures to mitigate zone II corrosion suggested in this work should be further investigated and developed.
7.0 REFERENCES


Figure 13. [a] Optical photomicrograph showing the microstructure of the H1S alloy (500 X): (1) primary Al phase, (2) blade shape intermetallics, and (3) round rosettes; and [b] EDX analysis of the blade-shaped intermetallic particles.
Figure 14. SEM photomicrographs showing the morphology of the intermetallics at low and high magnifications and their alignment along the rolling direction.
Figure 15. [a] SEM photomicrograph showing clustering of angular particles near the edges of the H1S plate and [b] EDX spectra from these angular particles.
Figure 16. SEM photomicrograph showing the presence of Cu-containing particles in the H1S alloy.
Figure 17. EDX analysis from different regions of the photomicrograph in Figure 16.
Figure 18  TEM photomicrograph (60000 X) showing the alignment of Al-Fe intermetallics along the rolling direction.
Figure 19 TEM photomicrographs showing the two morphologies of Al-Fe intermetallic particles: [a] blade shape (80000 X) and [b] rectangular shape (30000 X).
Figure 20  [a] TEM photomicrograph (100000 X) showing nucleation of an Al-Cu precipitate on an Al-Fe intermetallic particle and [b] TEM photomicrograph (60000 X) showing the precipitation of Cu along the contour of an Al-Fe intermetallic particle.
Figure 21. Optical photomicrographs (100 X) showing the grain structure of the H1S alloy: [a] longitudinal section and [b] transverse section.
Figure 22. Optical photomicrographs (400 X) showing identical areas of a transverse section: [a] grain structure and [b] distribution of secondary particles.
Figure 23  TEM photomicrograph (70000 X) showing substructure in the H1S plate: (1) subboundary, (2) parallel dislocation array, and (3) intragranular dislocations.
Figure 24. Corrosion-distance plot for a failed A118S cathode plate after 24 months in service.
Figure 25.  [a] SEM photomicrograph showing mud-crack sulfate deposit in zone III and [b] EDX spectra collected from the mud-crack deposit.
Figure 27. SEM photomicrographs showing [a] cusp-like pitting in zone II and [b] minimal corrosion damage in zone I below the electrolyte level.
Figure 28. X-ray diffraction patterns from an Al H1S plate showing variance in diffraction peak intensity below and above the solution line: [a] zone II and [b] zone I.
Figure 29. Cross sectional view of two failed plates: (1) Cominco plate and (2) Kidd Creek plate. The photographs show the characteristic hourglass profile for the three corrosion zones and relatively more thinning in zone III of the Kidd Creek plate.
Figure 30. The effect of cathodic current density on the corrosion rate of fully immersed Al H1S cathode plate in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^{-}\)-40 ppm F\(^{-}\).
Figure 31: Potential-time records for fully immersed Al H13 cathode plate in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl$^-$ at selected cathodic current densities.
Figure 32. SEM photomicrographs showing cusp-like pitting in the H1S alloy under open circuit conditions in 150 g dm⁻³ H₂SO₄-150 ppm Cl⁻-40 ppm F⁻.
Figure 33. Potential-time records for fully immersed Al H1S cathode plate at \(-400\) A \(m^{-2}\) in (1) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^-\)-40 ppm F\(^-\) and (2) 150 g dm\(^{-3}\) H\(_2\)SO\(_4\). Note the potential fluctuations in the halide-containing solution.
Figure 34. SEM photomicrographs of fully immersed H1S plate showing numerous micropits around the sites of the intermetallic particles in 150 g dm$^{-3}$ H$_2$SO$_4$. 
Figure 35. Potential-time records for fully immersed Al H1S cathode plate at $-400 \, \text{A m}^{-2}$ in 150 g dm$^{-3}$ H$_2$SO$_4$-$x$ ppm halides.
Figure 36. Potential-time records for the Al cathode plate at $-400 \text{ A m}^{-2}$ in (1) 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl$^{-}$-40 ppm F$^{-}$ and (2) 150 g dm$^{-3}$ H$_2$SO$_4$. 
Figure 37  Current density-time records for fully immersed Al H1S cathode plate at –1.574 V_{ME} in 150 g dm$^{-3}$ H$_2$SO$_4$-x ppm halides electrolytes.
Figure 38  SEM photomicrographs showing the corrosion morphology of the H1S alloy in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl-40 ppm F$^-$ solution.
Figure 39. SEM photomicrographs showing the corrosion morphology of the H1S alloy in the 150 g dm⁻³ H₂SO₄-40 ppm F solution.
Figure 40. SEM photomicrographs showing the nucleation of pits near the intermetallic particles.
Figure 41. SEM photomicrograph showing the corrosion morphology of the H1S alloy in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl$^-$ solution. Note the minimal attack at the intermetallics.
Figure 42. Cyclic polarization curves for fully immersed H1S samples exposed to 150 g dm⁻³ H₂SO₄-x ppm halides. Scan rate is 1 mV s⁻¹.
Figure 43. XPS survey spectra recorded from the Al H1S plate using AlK$_\alpha$ radiation. The survey shows the incorporation of F$^-$ in the oxide structure for a sample that was polarized at $-400$ A m$^{-2}$ in 150 g dm$^{-3}$ H$_2$SO$_4$-1000 ppm F$^-$ solution.
Figure 44. [a] SEM photomicrograph showing the precipitation of Al chloride salt particles in pits of zone I and [b] EDX analysis from these salt particles.
Figure 45. SEM photomicrograph showing a small batch with cusp-like pitting in relief, indicative of possible transformation of pit morphology from cusp-like to crystallographic morphology at advanced stages of the pitting process.
Figure 46. EDX spectra collected from zone III showing the presence of Cl\(^-\) anions.
Figure 47. Optical photomacrographs (12 X) showing the effect of Al dust addition on the corrosion morphology in zone II: [a] 50 ppm Al dust and [b] 200 ppm Al dust.
Figure 48. Optical photomicrograph (12 X) showing the corrosion morphology in zone II produced by the addition of 200 ppm Al in the form of Al sulfate.
Figure 49. Galvanostatic potential-time records comparing the effect of adding 200 ppm Al either as elemental Al dust or as Al sulfate.
Figure 50. Potentiostatic current density-time records at $-1.115 \ \text{V}_{\text{MSE}}$ for the HIS alloy showing the inhibitory effect of $\text{Zn}^{2+}$ on Al dissolution in 150 g dm$^{-3}$ $\text{H}_2\text{SO}_4$-500 ppm Cl$^{-}$-x g dm$^{-3}$ Zn$^{2+}$ solutions.
Figure 51. Optical photomacrographs (10 X) showing the corrosion morphology corresponding to Figure 50: [a] no Zn$^{2+}$ and [b] with 60 g dm$^{-3}$ Zn$^{2+}$. 
Figure 52. Cyclic polarization curves for the H1S and 1070 alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl-60 g dm\(^{-3}\) Zn\(^{2+}\). Scan rate is 0.17 mV s\(^{-1}\).
Figure 53  Variation of corrosion rate with pH for cathode plate samples freely immersed in 1000 ppm F⁻.
Figure 54  Variation of corrosion rate with pH for cathode plate samples freely immersed in 1000 ppm Cl⁻.
Figure 55  SEM photomicrographs showing precipitation of solution products on cathode plate samples at pH = 3.5: (a) H11 alloy and (b) 1070 alloy.
Figure 56  Open circuit potential-time records for the H1S alloy and 99.9999 % Al in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-150 ppm Cl\(^-\)-40 ppm F\(^-\).
Figure 57  Mixed potential plot showing increased corrosion rate and a positive $E_{corr}$ shift with increased exchange current density, $j_o$. 

153
Figure 58. Cyclic polarization curves for fully immersed H1S and 99.9999 % Al samples exposed to 150 g dm⁻³ H₂SO₄-x ppm halide electrolytes. Scan rate is 1 mV s⁻¹.
Figure 59. Cyclic polarization curves for 99.9999% Al exposed to 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm halides electrolytes. Scan rate is 1 mV s\(^{-1}\).
Figure 61  SEM photomicrographs for Al-4 % Cu alloy showing the corrosion morphology after 10 hour free immersion in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl: [a] minimal surface damage and [b] precipitation of a bulky surface film.
Figure 62. Cyclic polarization curves comparing the pitting behavior of Al-4 % Cu alloy to that of the 1070 and H1S alloys in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm CT. Scan rate is 0.17 mV s$^{-1}$. 
Figure 63. Close-up of the cyclic polarization curve for Al-4 % Cu around the primary passivation potential showing evidence of partial passive behavior. Scan rate is 0.17 mV/s.
Figure 64. Galvanostatic potential-time records for the H1S alloy at $-400 \text{ A m}^{-2}$ in $150 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$-$x \text{ ppm F}^-$ showing a positive potential shift with increased F$^-$ concentration.
Figure 65. Galvanostatic potential-time records for the 1070 alloy at \(-400\) A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^-\) showing positive potential shift with increased F\(^-\) concentration.
Figure 66. SEM photomicrographs comparing the extent of corrosion damage at $-400 \text{ A m}^{-2}$ in $150 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$-15 ppm F: [a] H1S alloy and [b] 1070 alloy.
Figure 67. Galvanostatic potential-time records comparing fully immersed 1070 and H1S samples at – 400 A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^{-}\).
Figure 68. SEM photomicrographs showing similarity in corrosion morphology in the H1S and 1070 alloys in F-containing solutions. Note the shallow, cusp-like pitting at 1000 ppm: [a] H1S alloy and [b] 1070 alloy.
Figure 69. Galvanostatic potential-time records for partially immersed cathode plate samples held at -400 A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-x ppm F\(^{-}\) solutions. Note the potential decay behavior in the absence of F\(^{-}\) anions.
Figure 70. SEM photomicrographs at $-400 \text{ A m}^{-2}$ in 150 g dm$^{-3}$ H$_2$SO$_4$-x ppm F$^-$ solutions showing increased corrosion damage with increased F$^-$ concentration: [a] 80 ppm F$^-$ and [b] 1000 ppm F$^-$. 
Figure 71. SEM photomicrograph at – 400 A m\(^{-2}\) in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-1000 ppm F\(^-\) solution showing extensive mud-crack deposit in zone III above the electrolyte level.
Figure 72. SEM photomicrographs at –400 A m⁻² in 150 g dm⁻³ H₂SO₄-x ppm F⁻ solutions showing the minor effect of F⁻ on zone II corrosion: [a] 0 ppm F⁻ and [b] 1000 ppm F⁻.
Figure 73. Optical photomicrographs comparing zone II corrosion at $-400$ A m$^{-2}$ in $150$ g dm$^{-3}$ H$_2$SO$_4$, $x$ ppm F$^-$ solutions: [a] 0 ppm F$^-$ and [b] 80 ppm F$^-$. Note the absence of zone II corrosion in both cases.
Figure 74. XPS survey spectra recorded from an Al H1S plate that was polarized at $-400$ A m$^{-2}$ in 150 g dm$^{-3}$ H$_2$SO$_4$-1000 ppm F$^-$ solution. The survey, recorded using AlK$\alpha$ radiation, shows the incorporation of F$^-$ in the oxide structure in zone II and a strong F$^-$ signal in the mud-crack deposit of zone III.
Figure 75. SEM photomicrographs at $-400 \text{ A m}^{-2}$ in 150 g dm$^{-3}$ H$_2$SO$_4$-x ppm Cl$^-$ solutions showing superficial corrosion damage at high Cl$^-$ concentrations: [a] 1500 ppm Cl$^-$ and [b] 4000 ppm Cl$^-$. 
Figure 76. SEM photomicrographs showing the corrosion morphology after 6-hour immersion at open circuit in 150 g dm$^{-3}$ H$_2$SO$_4$ solution: [a] H1S alloy and [b] 1070 alloy.
Figure 77. Open circuit potential-time records in 150 g dm$^{-3}$ H$_2$SO$_4$ showing relatively high cathodic activity on the H1S alloy.
Figure 78. Open circuit potential-time records in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ showing relatively high cathodic activity on the H1S alloy.
Figure 79. SEM photomicrographs comparing the extent of corrosion damage at open circuit in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 80. SEM photomicrographs showing pit nucleation around secondary phases at open circuit in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 81. SEM photomicrographs comparing the corrosion damage at open circuit in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy. Note the minimal damage in the 1070 alloy.
Figure 82. Open circuit potential-time records for several 1070 samples in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl\(^-\) showing good reproducibility.
Figure 83. Open circuit potential-time records comparing the 1070 and the H1S alloys in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl\(^-\).
Figure 84. Mixed potential plots showing the effects of H₂ evolution kinetics on the appearance of the E\text{corr} curves for the H1S and 1070 alloys in 150 g dm⁻³ H₂SO₄–500 ppm Cl⁻ solutions.
Figure 85. Open circuit potential-time records in 150 g dm$^{-3}$ H$_2$SO$_4$–x ppm Cl$^-$ solutions showing the effect of Cl$^-$ concentration on the behavior of fully immersed H1S and 1070 alloys.
Figure 86. Optical photomacrographs (6 X) showing the overall morphology of corrosion damage after 200-day free immersion in 150 g dm\(^{-3}\) \(\text{H}_2\text{SO}_4\)-500 ppm Cl\(^-\) solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 87. SEM photomicrographs showing cusp-like pitting after 200-day free immersion in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 88. SEM photomicrograph showing cusp-like pitting in zone II of a rejected plate that was in service for 24 months in Trail, Canada.
Figure 89. Optical photomacrograph (16 X) showing precipitation of aluminum sulfate on the 1070 alloy after 200-day free immersion in 150 g dm⁻³ H₂SO₄–500 ppm Cl⁻ solutions. Precipitation is still evident despite rinsing with deionized water and sample handling.
Figure 90. Optical photomacrographs (6 X) showing severe corrosion damage under thin electrolyte film conditions after 83-day free immersion in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 91. SEM photomicrographs showing superficial pitting in a 1070 alloy sample that was freely immersed in 150 g dm$^{-3}$ H$_2$SO$_4$-500 ppm Cl$^-$ solution for 92 hours.
Figure 92. EDX analysis of the white deposit formed on Al under thin $\text{H}_2\text{SO}_4-\text{Cl}^-$ electrolyte film. The chemical composition of the deposit is consistent with Al sulfate.
Figure 93. Optical photomacrographs (8 X) showing more voluminous Al sulfate deposit on the 1070 alloy relative to ultra pure Al under thin $\text{H}_2\text{SO}_4-\text{Cl}^-$ electrolyte films: [a] 1070 alloy and [b] 99.9999 % Al.
Figure 94. Optical photomacrographs (8 X) comparing the corrosion damage underneath the Al sulfate deposits: [a] 1070 alloy and [b] 99.9999 % Al. Note the minimal damage in the high purity Al.
Figure 95. SEM photomicrographs comparing the corrosion damage underneath the Al sulfate deposits: [a] 1070 alloy and [b] 99.9999 % Al.
Figure 96. Potentiodynamic cathodic polarization curves for the H1S alloy generated using a divided cell (H-cell) in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions. Argon-deaeration started 280 minutes prior to sample immersion.
Figure 97. SEM photomicrographs comparing the corrosion damage in deaerated and oxygenated solutions after 48-h open circuit immersion in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl solutions: 

(a) Deaerated and (b) Oxygenated.
Figure 98. Variation of corrosion current density with applied potential for the H1S and 1070 alloys in 150 g dm$^{-3}$ H$_2$SO$_4$-500 ppm Cl$^-$ solutions. Each potential value was applied for 6 hours, then the corrosion rate was determined by chemical analysis.
Figure 99. Current density-time records for the H1S and 1070 alloys at $E = -1.115 \text{ V}_{\text{MSE}}$ in 150 g dm$^{-3}$ \( \text{H}_2\text{SO}_4 \)-500 ppm Cl$^-$ solutions.
Figure 100  Current density-time records for the H1S and 1070 alloys at $E = -1.1 \text{ V}_{\text{MSE}}$ in 150 g dm$^{-3}$ $\text{H}_2\text{SO}_4$–500 ppm Cl$^{-}$ solutions.
Figure 101. Cyclic polarization curves comparing the pitting behavior of fully immersed 1070 and H1S alloys in 150 g dm$^{-3}$ H$_2$SO$_4$-150 ppm Cl$^-$. Scan rate is 0.17 mV s$^{-1}$. 
Figure 102. Optical photomacrographs (8 X) showing the detrimental effect of Cl\textsuperscript{-} anions on zone II corrosion in 150 g dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4}–x ppm Cl\textsuperscript{-} solutions: [a] no Cl\textsuperscript{-} and [b] 150 ppm Cl\textsuperscript{-}.
Figure 103. [a] Optical photomacrograph (9 X) and [b] SEM photomicrograph showing increased corrosion damage in zone II with increased Cl\(^-\) concentration. The sample was galvanostatically tested in 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–1000 ppm Cl\(^-\) solution.
Figure 104. Optical photomacrographs (8 X) comparing zone II corrosion in the 1070 and H1S alloys in 150 g dm$^{-3}$ H$_2$SO$_4$–150 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 105. SEM photomicrographs comparing zone II corrosion in the 1070 and H1S alloys in 150 g dm$^{-3}$ $\text{H}_2\text{SO}_4$–150 ppm Cl$^-$ solutions: [a] 1070 alloy and [b] H1S alloy.
Figure 106.  [a] SEM photomicrograph showing Cl'-rich deposit in zone II and [b] EDX spectra confirming the presence of Cl' anions in the deposit.
Optical photomicrographs (8 X) showing reduction in zone II corrosion due to sacrificial Mg anode: [a] without sacrificial protection and [b] with sacrificial protection.

Figure 107.
Figure 108.  X-ray diffraction analysis showing similar spectra recorded from the H1S and the 1070 cathode plates.
Figure 109. SEM photomicrographs showing the distribution of secondary phases in the H1S alloy before and after artificial aging for 28 hours at 200 °C: [a] before and [b] after.
Figure 110. SEM photomicrographs showing the distribution of secondary phases in the 1070 alloy before and after artificial aging for 28 hours at 200 °C: [a] before and [b] after.
Figure 111. XPS spectra recorded from the H1S and the 1070 cathode plates showing similar surface films and no Ti presence in the H1S protective film.
Figure 112. Current density-time records for the H1S and 1070 alloys at $E = -1.130\ V_{\text{MSE}}$ in 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$ solutions.
Figure 113. Potentiodynamic cathodic polarization curves comparing fully immersed pure Al and pure Ti in 150 g dm⁻³ H₂SO₄ solutions.
Three configurations of cathode plates examined in rectangular Zn electrowinning cells.

Figure 11.4.
Figure 115. Optical photomacrographs (6 X) showing higher corrosion propensity near the cathode side containing the electrical contact notch: [a] opposite side and [b] electrical contact side. The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$–500 ppm Cl$^-$. 
Figure 116. Optical photomacrographs (8 X) showing significantly lower corrosion damage on the modified plate of configuration C: [a] unmodified plate (configuration A) and [b] modified plate (configuration C). The test solution was 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)–500 ppm Cl\(^-\).
Figure 117. Optical photomacrographs (8 X) showing significantly lower corrosion damage on the cathode plate tested in the presence of airflow: [a] with airflow (configuration A) and [b] without airflow (configuration A). The test solution was 150 g dm$^{-3}$ H$_2$SO$_4$—500 ppm Cl$^-$. 
Figure 118. SEM photomicrographs showing minimal corrosion damage in zone II under an Ar atmosphere: [a] zone I of an unmodified plate (configuration A) and [b] zone II of the plate. The test solution was 150 g dm\(^{-3}\) H\(_2\)SO\(_4\)-500 ppm Cl\(^-\).
Figure 119. SEM photomicrographs from the test in Figure 118 at higher magnification.
### APPENDIX I: Thermodynamic Data Used in Pourbaix Diagrams

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*Source of Thermodynamic data:*

APPENDIX II: Al-Ti and Al-Mg Phase Diagrams [145]
### APPENDIX III: ICP-MS Spectrums for Cathode Plate Alloys

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<td>&lt; 0.1</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Terbium</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>
APPENDIX IV: Calculations of $E^\circ_{\text{red}}$ for $\text{AlCl}_3\text{(aq)}$ and $\text{AlF}_6^{3-}\text{(aq)}$

Table X
Thermodynamic data for the formation of $\text{AlCl}_3\text{(aq)}$ and $\text{AlF}_6^{3-}$

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>-131.1</td>
</tr>
<tr>
<td>F$^-$</td>
<td>-279</td>
</tr>
<tr>
<td>$\text{AlCl}_3\text{(aq)}$</td>
<td>-878</td>
</tr>
<tr>
<td>$\text{AlF}_6^{3-}$</td>
<td>-2271.2</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\text{AlCl}_3\text{(aq)} + 3 \text{e}^- & \rightarrow \text{Al} + 3 \text{Cl}^- & E^\circ_{\text{red}} = -1.7 \text{ V} \\
\text{AlF}_6^{3-}\text{(aq)} + 3 \text{e}^- & \rightarrow \text{Al} + 6 \text{F}^- & E^\circ_{\text{red}} = -2.1 \text{ V}
\end{align*}
\]

$\Delta G^\circ_{\text{rxn}} = \Sigma n \Delta G^\circ_{\text{products}} - \Sigma n \Delta G^\circ_{\text{reactants}}$

(1 atm and 298 K)

$\Delta G^\circ (12) = 3 (-131.1) + 878 = 484.7 \text{ kJ mol}^{-1}$

$\Delta G^\circ (13) = 6 (-279) + 2271.2 = 597.2 \text{ kJ mol}^{-1}$

$\Delta G^\circ = - nF E^\circ$

$E^\circ (12) = - \frac{(484.7 \times 1000)(3 \times 96500)}{(3 \times 96500)} = -1.7 \text{ V}$

$E^\circ (13) = - \frac{(597.2 \times 1000)(3 \times 96500)}{(3 \times 96500)} = -2.1 \text{ V}$

#Source of Thermodynamic data:

APPENDIX V: Replated Cu in Zone II of a Monel Sample