CYCLIC POLARIZATION OF AA 3102 IN CORROSIVE ELECTROLYTES
CONTAINING SODIUM CHLORIDE AND AMMONIUM SULFATE

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Corrosion of all aluminum microchannel heat exchangers present a challenge in automotive and heating, ventilation, and air conditioning (HVAC) industries. Reproducibility of Salt Water Acetic Acid Test (SWAAT) has been questioned and a need to new corrosion tests with better reproducibility has risen. Cyclic polarization, that is an electrochemical test, was explored for its suitability for the assessment of AA 3102 tube material that is currently a popular aluminum alloy used in manufacturing of heat exchanger. Corrosive electrolytes containing 3.5% sodium chloride with 0.5% ammonium sulfate (high chloride) or 0.5% sodium chloride with 3.5% ammonium sulfate (high sulfate) at their pH or acidic (pH=4) were used to measure corrosion potential (Ecorr), protection potential (Epp), pitting potential (Epit), Tafel constants (βa and βc), corrosion rate (mpy). Corrosive electrolyte used in SWAAT test (4.2% Sea Salt at pH 2.9) was also used to compare corrosion resistance of AA 3102 in SWAAT electrolyte compared to the other electrolytes used in this research. Scanning electron microscopy (SEM) was used to observe and document sample surface corrosion damage after each electrochemical test on all samples. Results of the cyclic polarization tests indicated that SWAAT electrolytes was the most aggressive electrolyte resulting in highest corrosion rates compared to all other electrolytes used in this investigation. SEM results indicated AA 3102 alloy exhibited higher pitting tendency in electrolytes with high sodium chloride whereas high sulfate electrolytes cause appearance of uniform corrosion surface damage on this alloy. Both high sulfate and SWAAT electrolytes showed intergranular corrosion but high chloride electrolyte showed severe pitting of AA 3102.
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Heat exchanger is a device that transfers heat between fluids. A solid wall to prevent mixing may separate the fluids or they may be in direct contact [1]. One application of heat exchangers is in internal combustion engines. Engine coolant flows through radiator coils and air flows past the coils, which cools the coolant by heating up the air. Another application of heat exchangers is for air conditioning of buildings and vehicles, which is commonly called air coils or just coils but in vehicles heat coils are called heater cores. For cooling coils, chilled water and refrigerant are most common. Chilled water is supplied from a chiller that is potentially located very far away, but refrigerant must come from a nearby condensing unit.

1.1. Types of Heat Exchangers

- Shell and tube heat exchanger
- Plate heat exchanger
- Plate and shell heat exchanger
- Adiabatic Wheel heat exchanger
- Plate fin heat exchanger
- Pillow plate heat exchanger
- Fluid heat exchanger
- Waste heat recovery unit
- Dynamic scraped surface heat exchanger
- Phase change heat exchanger
- Direct contact heat exchanger
- Microchannel heat exchanger

Round Tube Plate Fin (RTPF) (Figure 1-1) heat exchanger is traditional Aluminum-Copper coils which has been in use for a century and the other types of heat exchangers are based on this design. However during the years the concept of heat exchangers enhanced to achieve higher level of heat transfer but it does not have impressive development in the performance. One of the
most important inherent problems, which associated with RTPF, is the presence of dissimilar alloys (Copper and Aluminum alloys) causing galvanic corrosion.

Figure 1-1: Round Tube Plate Fin Design [2].

Galvanic corrosion is an electrochemical process in which one metal corrodes preferentially over the other when both metals are in physical contact, in the presence of an electrolyte. Dissimilar metals and alloys have different electrode potentials, and when two or more come into contact in an electrolyte, one metal acts as anode and the other as cathode. The electro potential difference between the dissimilar metals is the driving force for an accelerated attack on the anode member of the galvanic couple. The anode metal dissolves into the electrolyte, and deposit collects on the cathodic metal. Therefore All Aluminum microchannel (MCHX) are designed to have better heat transfer performance and higher corrosion resistance (Figure 1-2).
Manufacturing a heat exchanger with reliable heat transfer and higher level of efficiency has been a constant challenge in air conditioning industry. Corrosion of heat exchangers due to environmental factors in both MCHX and RTPF designs is a major challenge in achieving the goals of heat exchanger manufacturers.

Corrosion in heat exchangers could be divided in two parts:

- Localized attack (pitting)
- Uniform oxidation (Atmospheric corrosion)

Corrosion of condenser coils causes heat exchanger performance degradation, poor aesthetics, and possible equipment failure. Atmospheric and pitting mechanisms of corrosion are dominant in heat exchangers that are the focus of this research. All-aluminum heat exchangers are used extensively therefore the following sections provide description of mechanisms and parameters involved in atmospheric and pitting forms of corrosion in Aluminum alloys used in manufacturing of MCHX.
1.2. Pitting Corrosion

Pitting corrosion is a localized form of corrosion which, tube perforation or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits. A small, narrow pit with minimal overall metal loss can lead to the failure of an entire engineering system. Pitting corrosion, which, for example, is almost a common denominator of all types of localized corrosion attack, may assume different shapes. Pitting corrosion can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped [4].

Types of pitting corrosion [4]:

- Through pits (Figure 1-3)
  1. Narrow, deep
  2. Shallow wide
  3. Elliptical
  4. Vertical grain attack

- Sideway Pits (Figure 1-4)
  1. Subsurface
  2. Undercutting
  3. Horizontal grain attack
The more conventional explanation for pitting corrosion is that it is an autocatalytic process. Metal oxidation results in localized acidity that is maintained by the spatial separation of the cathodic and anodic half-reactions, which creates a potential gradient and electro migration of aggressive anions into the pit [5].

This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages the deep structures of the metal. Corrosion products often obscure the pits on the surface. Pitting can be initiated by a small surface defect, being a scratch or a local change in composition, or damage to protective coating. Polished surfaces display higher resistance to pitting.

1.3. Atmospheric Corrosion

Atmospheric corrosion is the deterioration and destruction of a material and its vital properties due to electrochemical as well as the other reactions of its surface with the constituents of the atmosphere surrounding the material. Based on ISO 9223 [6], corrosivity of environments is divided to five categories, which are presented in Table 1-1. This standard classifies the corrosivity of atmosphere corrosion based on time of wetness and pollution.
categories which are only airborne chloride and sulfur oxide that give good coverage of rural, urban, industrial and marine atmospheres.

Table 1-1: Corrosivity of environments based on ISO 9223 standard for Aluminum Alloys [6].

<table>
<thead>
<tr>
<th>Category</th>
<th>Corrosion Rate (CR) of Aluminum (g/m²/year)</th>
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<tr>
<td>C1</td>
<td>Negligible</td>
</tr>
<tr>
<td>C2</td>
<td>CR &lt;= 0.6</td>
</tr>
<tr>
<td>C3</td>
<td>0.6 &lt; CR &lt;= 2</td>
</tr>
<tr>
<td>C4</td>
<td>2 &lt; CR &lt;= 5</td>
</tr>
<tr>
<td>C5</td>
<td>CR &gt; 5</td>
</tr>
</tbody>
</table>

In the past 20 years, most of the industrial companies use aluminum in automotive heat exchangers and it becomes a standard in all vehicles for automotive air conditioning and engine cooling. Using the aluminum is due to its lower cost, high durability, lightweight and ease of manufacturability. HVAC system manufactures are currently starting to use all-aluminum heat exchangers in home heating and cooling systems.

The all-aluminum heat exchanger consists of three parts (Figure 1-5):

- Fins
- Tubes
- Side supports
All Aluminum condensing coils significantly reduces refrigerant charge requirement (52% less compared with RTPF), 90 lbs. less weight for a 10-ton rooftop unit, 20% less brazed joints, decreased potential for leakage by increasing reliability. Aluminum brazing sheets make up these parts. The alloys that are used in this type of heat exchanger are Al 3003, Al 3102 and Al 4045 (Table 1-2). Al 3003 alloy is corrosion resistant and can be formed, welded and brazed. It can be purchased with a zinc sacrificial coating to the aluminum to extend the surface life of the tubes. As it is cited before, the issue with all aluminum heat exchangers is pitting corrosion in natural atmospheric conditions in different kind of environments like industrial, agricultural, marine, rural and urban. Corrosion of heat exchangers specially the condensers leads to performance degradation, poor aesthetics and possibly failure of equipment. The different parts of heat exchangers are brazed to each other with the use of a flux at temperature above 800 °F. There are three different methods to braze the parts together:

1. Flux-dip Brazing
2. Torch Brazing
3. Furnace and Vacuum Brazing
Table 1-2: Chemical Composition of Aluminum Alloy 3003, 4045 and 3102.

<table>
<thead>
<tr>
<th>Element</th>
<th>Aluminum %</th>
<th>Copper %</th>
<th>Iron %</th>
<th>Manganese %</th>
<th>Silicon %</th>
<th>Zinc %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA 3003</td>
<td>96.8-99</td>
<td>0.05-0.2</td>
<td>0.7 Max</td>
<td>1-1.5</td>
<td>0.6 Max</td>
<td>0.1 Max</td>
</tr>
<tr>
<td>AA4045</td>
<td>87.3-91</td>
<td>0.3 Max</td>
<td>0.8 Max</td>
<td>0.05</td>
<td>9-11</td>
<td>0.1 Max</td>
</tr>
<tr>
<td>AA 3102</td>
<td>97.85-99.95</td>
<td>0.1 Max</td>
<td>0.7 Max</td>
<td>0.05 – 0.4</td>
<td>0.4 Max</td>
<td>0.3 Max</td>
</tr>
</tbody>
</table>

In heat exchangers, materials are selected such that fins are more anodic compared to the tubes materials therefore in corrosion processes fins are designed to corrode and protect the tubes sacrificially. Figure 1-6 shows schematic of a typical fin-tube arrangement in an all-aluminum microchannel heat exchanger highlighting the site where damage is usually observed. This type of design is more vulnerable to crevice corrosion. Crevice corrosion is a localized attack which occurs on the sample surface or immediately adjacent to the gap or crevice between two joining surfaces. This gap or crevice which can be formed between two metals or a metal and non-metallic material causes severe corrosion because of trapping oxygen atoms in that area.

![Figure 1-6: Tube-Fin arrangement in all aluminum MCHX showing location of corrosion attack.](image)

Various accelerated corrosion test methods are used to test corrosion resistance assessment in light of part manufacture warranty by manufactures. Some of the methods of accelerated corrosion testing are proprietary to each individual manufacture. For example, the Calsonic corrosion test [7] that uses a clay-based slurry is derived from a worldwide field survey
carried out in 1979. The most popular tests are the ASTM B117 (Neutral Salt Fog), ASTM B368 (Copper Accelerated Acid Salt, CASS) and ASTM G85 (Salt Water Acetic Acid Test, SWAAT). A.C. Scott [8] used these three tests along with two other tests, ASTM G44 (Alternate Immersion, AI) and a modified ASTM G44 (Acidified, AI0, to study the corrosion resistance of a new aluminum alloy heat exchanger. A.C. Scott [8] suggested seven criteria for an acceptable corrosion test as follow:

1. The mode of attack—corrosion morphology—matched the corrosion observed in samples returned from field,

2. The accelerated test environment was a plausible analog of the field environment,

3. Similarly, the test specimen was an appropriate model of the material as used in the field,

4. The test performance criterion was an appropriate measure of corrosion resistance in the field,

5. The test gave objective, quantifiable results,

6. Test duration was reasonably short,

7. The test was an industry standard, and could be readily put into use by other aluminum producers, radiator manufacturers, etc.

The mode of attack that is observed in the field is pitting corrosion, but immersion of the sample in a corrosive solution is not a duplication of the corrosion mechanism in the field.
Electrochemical testing is another method to study pitting corrosion of engineering alloys. One of the chemical solutions used in these tests is SWAAT solution in which open circuit potential of the alloy is measured in the solution according to ASTM G69.

1.4. Problem Statement

The goal of this research is to define a test to satisfy the need of HVAC and automotive industry. This study will include an electrochemical testing method to characterize the pitting tendency of AA 3102 in different solutions. However there are various methods to test the aluminum alloy corrosion in fin and tube heat exchangers such as electrochemical testing, SWAAT, salt fog testing, etc. but unfortunately there is no standard universally accepted method for all aluminum heat exchangers. Although most manufactures have developed their own cabinet based test methods to estimate the life span of their products, but the results from cabinet style tests neither correlate with each other’s test nor correlate with actual field conditions. The test protocols, which are design to estimate the heat exchangers’ material performance, should duplicate failure mechanism observed in the field. Improper test procedures may alter the failure mechanism in heat exchangers results in invalid data leading to inaccurate conclusions.

1.5. Purpose of Research

The purpose of this research is to define a reproducible accelerated corrosion testing method based on electrochemical testing. The pitting tendency of Al 3102 has been studied. Also the mode of failure of Al 3102 in different solutions with different pH was investigated using Scanning Electron Microscopy (SEM). Fourier Transform Infrared Spectrophotometry (FTIR)
was used to characterize corrosion products formed on AA 3102 alloy after cyclic polarization tests.

1.6. Research Questions

1. Does electrochemical testing provide reliable information on corrosion susceptibility of Al 3102 alloy in different corrosive electrolytes?

2. Can mechanism of failure in all Aluminum MCHEX be duplicated in electrochemical testing?

3. How does the electrochemical test correlate to the service life of the heat exchanger?

4. How repeatable are the results for this test for the all-aluminum tube?

1.7. Statement of the Need

Manufacturers of all aluminum heat exchangers use different accelerated corrosion tests but still an accepted accelerated corrosion test, which simulates the corrosion of materials in real environment, does not exist. The American Society of Heating, Refrigerating, and Air-conditioning Engineers (ASHRAE) and its sponsoring Committee (TC 8.4, Air to-Refrigerant Heat Transfer Equipment) initiated this project in order to evaluate performance of all aluminum heat exchangers and investigating either to justify the utility of existing testing methods or develop new test(s) which are used to study pitting corrosion and pitting tendency of the tube and fins. These electrochemical tests help ASHRAE to determine if the tests meet the 7 criteria of AC Scott [8]. These tests help manufactures to present more accurate warranty for their products.
2.1 Aluminum Alloys for Heat Exchanger Design in Automotive Industry

In order to reduce the weight of the vehicles, which cause reduction in fuel consumption and consequently reduction in air pollution, there is a great demand for using aluminum alloys in automotive industries. One of the most use of aluminum alloys is in heat exchangers specially assembly of AA 4xxx/3xxx/4xxx [9]. Coils of aluminum alloys are delivered in industries and then they change them to sheets in different sizes [10]. AA3xxx series are aluminum manganese alloy and AA4xxx series are aluminum silicon alloys which their difference is in their melting points. During the brazing process in order to connect different parts to each other, clad will reach its melting point sooner than the core and ensures proper joining between different parts [11]. As mentioned before, application of aluminum alloys are demanding in automotive industries therefore companies must have an estimation of the life span of the products. Accelerated corrosion tests help industries to estimate the life span of their products. Next section provides a brief explain on accelerated corrosion test.

2.2 Accelerated Corrosion Test

Accelerate corrosion testing has three subset:

1. Cabinet Style Test
2. Electrochemical Test
3. Less common tests like Calsonic tests.
2.3 Cabinet Style Test

A symposium entitled “Cyclic Cabinet Corrosion Testing” [12] was sponsored by ASTM Committee G-1 in November 1995. The goal of that symposium by presented papers was promotion of standardization of cyclic cabinet tests. It has been found that the salt spray test (ASTM B-117) is not effective to predict actual service condition of the products [12]. Some parameters such as time of wetness, wetting and drying on corrosion rates and morphology of the corrosion products on engineering alloys were highlighted in STP 646 [13]. The test criterion is the number of days until the occurrence of perforation of the heat exchanger tube material. This cabinet based test method may take long time for a few days up to several weeks, however a minimum 20 days test is required by the industries. Although the cabinet test method simulates the service life of the products, but it has some drawbacks like its long duration and the low reproducibility.

2.4 Electrochemical Test

In the late 70’s and early 80’s electrochemical (ECHEM) instruments had been found as a valuable corrosion testing tools [14]. Corrosion involves electrochemical oxidation and reduction reactions therefore corrosion specialist use electrochemical instruments to do accelerated corrosion tests on different materials such as aluminum alloys which is the goal in ECHEM test in this thesis. The electrochemical test methods are based on electrochemical reactions that occur at the interface between the metal and an electrolyte.
2.5 Oxidation and Reduction Reactions

These reactions which are known as redox reaction is a chemical reaction which involves electron transfers between two metal [15]. Oxidation is the reaction involved in losing electrons by a metal in this case and reduction is a reaction involving gaining electrons.

2.6 Electrochemical Instrument

Redox reactions create an electrochemical potential at the surface of the metal, which is known as corrosion potential or the open circuit potential. This is measured in Volts and shown as \( E_{\text{CORR}} \). \( E_{\text{CORR}} \) is measurable only with respect to a reference electrode. Figure 2-1 shows schematic of an electrochemical three-electrode system used to perform electrochemical tests [14]. At \( E_{\text{CORR}} \) rate of oxidation reaction is equal to rate of reduction reaction.

![Figure 2-1: Measurement of \( E_{\text{CORR}} \) for a metal solution system.](image-url)
The most popular reference electrode among the corrosion specialist is Saturated Calomel Electrode (SCE), which is based on reaction between mercury and mercury (I) chloride. Theory of operation is as follow [16]:

Based on the redox reaction:

\[ \text{Hg}_2^{2+} + 2e^- \rightleftharpoons 2\text{Hg}(l) \]

Then the potential for the reduction is written [16-17]:

\[ E = E^0_{\text{Hg}_2^{2+}/\text{Hg}} - \frac{RT}{2F} \ln \frac{1}{a_{\text{Hg}_2^{2+}}} \]

Where \( E^0 \) stands for standard electrode potential for the reaction and \( a_{\text{Hg}} \) stands for activity for the mercury cation (Note: the activity for a liquid of 1 Molar is 1). The solubility product of the reaction will gives us the activity

\[ \text{Hg}_2^{2+} + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2(s), \quad K_{sp} = a_{\text{Hg}_2^{2+}}a_{\text{Cl}^-}^2 \]

Now if we replace the activity in the Nernst equation with the value which had been driven in the solubility equation [16]:

\[ E = E^0_{\text{Hg}_2^{2+}/\text{Hg}} + \frac{RT}{2F} \ln K_{sp} - \frac{RT}{2F} \ln a_{\text{Cl}^-}^2 \]

All potential measurements such as corrosion potential of the alloy in corrosive solutions (\( E_{\text{CORR}} \)) are measured with respect to the SCE. Complete basics of electrochemistry are covered in references [17-18].
2.7 Potential and Current in ECHEM Experiment

Figure 2-2 shows different directions in a change in potential in an ECHEM test. If one assumes the intersection of horizontal and vertical lines as an indicator of $E_{\text{CORR}}$, potentials more positive than $E_{\text{CORR}}$ will accelerate the oxidation reaction and the current of oxidation is called anodic current which is shown by positive polarity. On the other side potentials less than $E_{\text{CORR}}$ will accelerate the reduction reaction and the current of reduction is called cathodic current and is shown with negative polarity [14].

![Figure 2-2: Convention of Corrosion for potential and current [14].](image)

2.8 Electrochemical Cell

Figure 2-3 depicts a schematic of electrochemical cell. The cell electrodes are connected to a power source that applies and controls potentials, which is called a potentiostat. Auxiliary electrode is the supplier of the current to the test specimen (working electrode) in order to polarize it. The system’s design only allows an extremely small current to be passed between the reference electrode and working electrode. ASM Metals Handbook volumes A through C provides results of electrochemical testing on various Engineering Alloys in different corrosive electrolytes [19]. Figure 2-3 shows different parts of an ECHEM cell [14]. Figure 2-4 shows a
A typical polarization plot showing measured $E$ in a cyclic polarization experiment. $E_{PI}T$ refers to the pitting potential where pits can start forming. In fact $E_{PI}T$ is the least positive potential, which creates the pits.

![Electrochemical corrosion test cell](image1)

*Figure 2-3: Electrochemical corrosion test cell [14].*

![Cyclic Polarization plot](image2)

*Figure 2-4: Cyclic Polarization plot of a typical engineering alloy in a corrosive environment depicting hysteresis loop [14].*

S.D. Meijers, et al. [20] used both cabinet style tests and electrochemical tests for corrosion performance assessment of heat exchangers made of Aluminum alloys. They used samples similar to what is shown in Figure 2-5 for cabinet test and the individual alloys of tube
and fins for electrochemical test. Table 2-1 shows the alloy system that they used and Figure 2-6 shows the results from tests on alloy A (AA3003). They performed experiments and measured open circuit potential of alloys in Sea Water Acetic Acid Test (SWAAT) solution according to ASTM G69 [21] results of which are given in Table 2-2. They also measured open circuit potential for different combination of tube and fin materials and the results are shown in Table 2-3. They plotted potential difference between fin and tube A as a function of the SWAAT performance with using of their results in electrochemical tests (Figure 2-7). Figure 2-7 shows tube A and fin A in 0 potential differences. Potential differences between tube A and fin D in negative which means tube A will corrode before fin D because tube A protected fin A galvanically and it is not desirable. Based on Figure 2-7 there is an optimal potential difference from 10 to 30 mV. If potential differences are too low the tube will corrode before fin. Also too large potential difference is not desirable as they suggested based on their researches. They stated that potential differences is only the measure of the driving force and it is not the indicator of kinetics of corrosion, therefore one may have difference of 100 mV with lower corrosion rate and another one may have 50 mV difference in potential with higher corrosion rate (Figure 2-8). S.D. Meijers et al. [20] concludes that maximum and minimum potential difference does not exist for a good system. Table 2-4 summarizes findings of other investigators.

Figure 2-5: Schematic presentation of the test sample [20].
Table 2-1: Sample codes used in S.D. Meijers et al. investigation [20].

<table>
<thead>
<tr>
<th>Code</th>
<th>Alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Tube</td>
</tr>
<tr>
<td></td>
<td>Hogal 4437/AA3003/Hogal4437</td>
</tr>
<tr>
<td>B</td>
<td>Tube</td>
</tr>
<tr>
<td></td>
<td>Hogal4101/LL/Hogal4101</td>
</tr>
<tr>
<td>C</td>
<td>Fin 2050</td>
</tr>
<tr>
<td>D</td>
<td>Fin AA3003</td>
</tr>
<tr>
<td>E</td>
<td>Fin AA3003 modified</td>
</tr>
<tr>
<td>F</td>
<td>Fin Hogal 3535</td>
</tr>
</tbody>
</table>

Figure 2-6: Corrosion performance in days till perforation in the SWAAT and CASS for tube alloy A (AA3003) [20].

Table 2-2: The open circuit potentials of the alloys measured in SWAAT solution [20].

<table>
<thead>
<tr>
<th></th>
<th>OCP [ mV_SCE]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube A</td>
<td>-781</td>
</tr>
<tr>
<td>Tube B</td>
<td>-724</td>
</tr>
<tr>
<td>Fin C</td>
<td>-827</td>
</tr>
<tr>
<td>Fin D</td>
<td>-740</td>
</tr>
<tr>
<td>Fin E</td>
<td>-996</td>
</tr>
<tr>
<td>Fin F</td>
<td>-794</td>
</tr>
</tbody>
</table>
Table 2-3: The system potential and corrosion current as taken from the polarization graphs [20].

<table>
<thead>
<tr>
<th>Fin</th>
<th>Tube A</th>
<th>Tube B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{system}}$ [mV$_{\text{SCE}}$]</td>
<td>$I_{\text{corr}}$ [mA/cm$^2$]</td>
</tr>
<tr>
<td>C</td>
<td>-809</td>
<td>0.11</td>
</tr>
<tr>
<td>D</td>
<td>Not Crossing</td>
<td>-</td>
</tr>
<tr>
<td>E</td>
<td>No Clear Crossing</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>-772</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Figure 2-7: Potential difference between fin and tube A as function of the SWAAT performance (positive difference means fin is less noble) [20].
Figure 2-8: Schematic presentation of polarization graph of a tube and two fins with different kinetic behaviors [20].

Table 2-4. Review of literature on heat exchanger materials laboratory testing and highlights

<table>
<thead>
<tr>
<th>Researcher(s)</th>
<th>Testing method(s)</th>
<th>Sample(s)</th>
<th>Finding(s)</th>
<th>Comment(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. Szala [22]</td>
<td>Scanning Electrode Vibration Technique (SEVT)</td>
<td>Similar to reference 20</td>
<td>Undesirable potentials at certain areas related to potential areas which are vulnerable to perforation and eventual pitting results</td>
<td>This test does not show the actual pitting of hole initiation, but results correlate with SWAAT results reasonably</td>
</tr>
<tr>
<td>S. Tierce [23]</td>
<td>Electrochemical Testing</td>
<td>Aluminum alloy 4343/3003/4043</td>
<td>Corrosion propagation through core material, BDP layer and cladding layer</td>
<td>Solution was neutral water-ethylene glycol mixtures with and without chlorides</td>
</tr>
<tr>
<td>Researcher(s)</td>
<td>Testing method(s)</td>
<td>Sample(s)</td>
<td>Finding(s)</td>
<td>Comment(s)</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-------------------</td>
<td>-------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Z. Dan [24]</td>
<td>Electrochemical</td>
<td>Al 1000, Al 6061</td>
<td>Sulfate ions cause changes of pitting potential from -0.4V to -0.64V</td>
<td>Solution was artificial sea water with and without sulfate ions</td>
</tr>
<tr>
<td></td>
<td>Testing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F.N. Afshar [25]</td>
<td>Electrochemical</td>
<td>Brazed Aluminum</td>
<td>Top layers are more susceptible to localized attack because of the intergranular and pitting corrosion mechanism of the clad layer.</td>
<td>Cathodic and anodic reactivity of top layers are higher than the bulk material.</td>
</tr>
<tr>
<td></td>
<td>testing, Glow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Discharge Optical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Emission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Spectroscopy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(GDOES)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F.N. Afshar [26]</td>
<td>Electrochemical</td>
<td>AA 4XXX, AA 3XXX</td>
<td>Brazing causes copper accumulation in the eutectic phase. Intergranular corrosion susceptibility of the re-solidification clad materials.</td>
<td>The Phenomena cause 50 mV increase in corrosion potential</td>
</tr>
<tr>
<td></td>
<td>Testing</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F.N. Afshar [27]</td>
<td>Electrochemical</td>
<td>AA 3XXX</td>
<td>Results of ECHEM test can predict the behavior of materials in SWWAT. In the presence of 100 mV and 150 mV potential, fluxed materials are shown an extra breakdown potential (Figure 2-15).</td>
<td>Behavior and performance of base line material (300 micro meter AA 3XXX) and material with 1 g/m² and 6 g/m² of flux loaded in brazing process</td>
</tr>
<tr>
<td></td>
<td>testing, SWAAT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y. Liu, G.Z. Meny,</td>
<td>Electrochemical</td>
<td>Al 3003</td>
<td>Film in chloride free solution is more stable. In the presence of chloride ions, pitting of AA 3003 passivated both in air and in aqueous solution</td>
<td></td>
</tr>
<tr>
<td>Y.F. Cheng [28]</td>
<td>Testing</td>
<td></td>
<td></td>
<td>E_pit = -0.6 V (SCE) in air. E_pit = -0.53 V (SCE) in chloride containing solution E_pit = -0.5 V (SCE) in Na₂SO₄ Solution Higher E_pit = Higher pitting resistance (Figure 2-10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Davodi [29]</td>
<td>Electrochemical</td>
<td>Brazed Aluminum alloys</td>
<td>Cyclic polarization can evaluate pitting vulnerability of brazed Aluminum alloys.</td>
<td>Pitting potential and cyclic loop areas are related to pitting tendencies of different alloys (Figure 2-11 (a-b))</td>
</tr>
</tbody>
</table>
Figure 2-9: Potentiodynamic polarization curves for the baseline and the 6 g/m² fluxed material [27].

Figure 2-10: Cyclic polarization curves of the passivated 3003 Al alloy electrode in 0.25M Na₂SO₄ + 0.5M NaCl solution (potential scanning rate: 0.333 mV/s) [28].
Figure 2-11 (a, b): (a) Schematic of a polarization curve showing critical potentials and metastable pitting region. $E_p$, pitting potential; $E_r$, repassivation potential; $E_{corr}$ corrosion potential [10]. (b) Cyclic Polarization curve of 0.1 mm thick EN AW-3003 alloy (Si 0.15%*, Fe 0.48%, Cu 0.12%, Mn 1.1%, Mg 0.03%, Zn <0.01%) in 10 mM NaCl solution (* wt%) [29].

Hernández F.J. [30] has done research on the atmospheric corrosion of aluminum alloys. They ran their tests in Tenerife (Canary Islands, Spain). They characterized localized attacks (pitting Corrosion) in terms of the depth and the density of the pits. They found that the pits sizes are greatly influenced by the concentration of pollutants and the wetness of the atmospheres. They defined a direct linear relationship between the pitting parameters and the chloride content. They proved with electrochemical tests that the addition of sulfate ions to chloride-containing solutions assists the growth of larger pits. [30]. Table 2-5 shows the chemical composition of their aluminum samples. They have done electrochemical tests on 99.5% purity aluminum plates in 20 mm X 40 mm X 2mm dimensions. They grinded the samples with 800 and 1000 grit emery paper and then they polished the samples with 0.3 micro meter size alumina powder until mirror appearance. Finally the samples were washed in acetone inside an ultrasonic bath, followed by rinsing with distilled water and dried in a glass container under vacuum. In order to remove any mechanical stresses, they heated the samples in 180-210 °C range for 4 hours.
Table 2-5 Chemical composition of aluminum plate used in Hernández’s work [30].

<table>
<thead>
<tr>
<th>Element</th>
<th>Base Al</th>
<th>Si</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Ti</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>Balance</td>
<td>0.30</td>
<td>0.40</td>
<td>0.05</td>
<td>0.10</td>
<td>0.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

They performed the potentiodynamic polarization measurements from -250 mV until +1500 mV with 0.5 mV/s for scan rates. They also purged the system under argon atmosphere for 3 hours until they attained stable open circuit (OCP) measurements. The solution for this experiment was 0.05 M NaCl+x M Na₂SO₄, with the following values of x: 0, 10⁻³, 10⁻² and 10⁻¹.

The result of the cyclic polarization curve is shown in Figure 2-12 which is the cyclic polarization curve of the given aluminum plate, immersed in 0.05 M (0.95%) NaCl + 0.1 M (4.28%) Na₂SO₄. They measured breakdown potential about -0.20 V vs. SCE.

Figure 2-12: cyclic polarization curve of aluminum alloy in 0.05 M NaCl + 0.1 M Na₂SO₄ solution with 0.5 mV/s for scan rate [30].
Figure 2-13 shows the SEM micrographs in order to assist the characterization of the advancement of localized attack (pitting corrosion). Figure 2-13 A and B depict the results of the experiments. A shows the pitting corrosion when chloride ions are the only pollutants. The result is the formation of big number of pits. B shows the pitting corrosion when they add sulfate to the solution. However, the number of pits are less than previous experiment, but sulfate ions cause bigger pits in depth and diameter.

Figure 2-13: SEM micrographs after electrochemical tests in 0.05 M NaCl (A), and 0.05 NaCl + 10⁻³ M Na₂SO₄ (B)[30].

Following are their conclusion for the experiments:

1. In general, longer exposures of aluminum samples to atmospheres in the island of Tenerife result in higher pit densities as well as the pits growing deeper from the surface, though the magnitude of the latter effect greatly depends on the composition of the local environments.

2. Linear relationships on pollutant concentrations, namely chloride ions and SO₂, could be established for both the pit densities and the pit depths.

3. Competitive adsorption of chloride and sulfate ions on the metal surface occurs when these species are simultaneously present in the
aqueous phase. The number of pits induced in an electrochemical cell decrease with the increase of sulfate concentration in the electrolyte, though the average pits grow to greater diameters and depths in the presence of sulfate ions. If this is a direct quote it should be placed in “quotation marks”.
CHAPTER 3
EXPERIMENTAL PROCEDURES

The alloy of this research is AA 3102. Table 1-2 presents chemical composition and properties of this alloy.

3.1 Surface Preparation

The first step of the experiments is to cut 1”x1” AA3102 samples for surface preparation. Polishing is used to make the surface of the sample smooth. Since the thickness of the clad layer is 0.5% of the sample thickness so grinding is not operated because grinding will remove the clad layer completely. Therefore plain sheets of AA 3102 alloy prior to brazing step in manufacturing is used to polish using polishing solutions containing 5, 1, and 0.05 micrometer Al$_2$O$_3$ particles. Then the polished sample will be rinsed with acetone or alcohol and then distilled water in order to remove any contamination from the sample surface. A flat cell with three-electrode system was utilized in this research. The electrolyte is made of corrosive agents. Samples will be tested with different solution in order to find their corrosion behavior in different solution environments including:

I. 0.5% NaCl + 3.5% (NH$_4$)$_4$SO$_2$ (At acidic pH and no change in pH)

II. 3.5% NaCl + 0.5% (NH$_4$)$_4$SO$_2$ (At acidic pH and no change in pH)

III. 4.2% NaCl + 1% Glacial Acetic Acid (SWAAT solution)

3.5% salt solution is used to imitate a coastal environment and 4.2% NaCl solution present the seawater environment which calls SWAAT solution. The solutions are prepared in different pH (Acidic to simulate industrial environment), Neutral (to represent urban environment) and
Basic to represent marine environments) in order to evaluate the corrosion behavior of the samples in various environments.

Cyclic polarization will be performed in this investigation as is described below.

3.2 Cyclic Polarization

Cyclic polarization [31], is used to investigate and study the corrosion behavior and pitting tendency of a material in an electrolyte, which is corrosive. Figure 3-1 shows the electrochemical cell with its parts.

![Electrochemical cell electrodes](image)

*Figure 3-1: Electrochemical cell electrodes.*

In cyclic polarization the potential starts in a potential below $E_{corr}$ and is moved toward the positive direction until it reaches the preselected potential or current and then it is reversed to more negative values to the beginning value of the potential. Figure 3-2 shows the sample geometry, which should be the same alloy as the one, used to make the heat exchangers. In order to avoid gathering invalid data, the test should be done based on standards and it should not be
altered in any way. For example SWAAT solution is consist of 4.2% NaCl in which the pH is decreased between 2.8 and 3.0 with glacial acetic acid. The solution should not cause unnatural corrosion by altering the material. Overall objective of the research is to identify and define a test procedure that can be used by manufacturer of all-aluminum heat exchangers and the optimum test can be one of the existing test methods, which needs modification or even a new test that can be standardized. Higher breakdown potentials (E_{br}) that are indicative of higher pitting resistance of Aluminum alloy are highly desirable. Cyclic polarization is an electrochemical test, which can measure the tendencies of Aluminum alloys toward pitting. For all kind of heat exchangers, pitting is the consequence of atmospheric corrosion in environments containing pitting agents such as chloride. The electrolytes of these tests are selected in a way to simulate the effects of pollutants, which exist in environment. These contaminants include Sulfur, Chloride, and Nitrogen. Parameters, which are measured in these tests are Passive potential (E_p), pitting potential (E_{PIT}) and pitting loop which is the area under the potential-current loop. Pitting loop measures the pitting tendencies of Aluminum alloys. Different corrosion products which, are the results of the different electrolytes on the electrode surface (Aluminum Alloy), will be analyzed with the use of FTIR. This helps to ensure the relevance of the test to the corrosion mechanism, which is observed.
3.3 Mechanism of Failure

In order to show similarity of corrosion product and failure of the material with what have been observed in marine, urban and industrial environments, it is needed to analyze corrosion products which are formed after the tests on the surface of the materials. To do this, the corrosion product on the surface of the samples in damaged regions will be gathered in powder form after electrochemical test. A KBr pellet made of the corrosion products will be utilized in Fourier Transformation Infrared Spectroscopy (FTIR). FTIR is a technique to obtain an infrared spectrum of emission or absorption of a gas, liquid or solid materials.

In FTIR, different frequencies of infrared radiation are passed through a sample such that some frequencies transmit through the sample and some frequencies are absorbed. This absorbed radiation creates a finger print spectrum of the corrosion product, which is formed on the samples. This provides information about phase(s) which, these information can be compared
with those from actual field samples. This, allow us to compare the data and make sure about the similarity between accelerated corrosion test results and those from actual field.

First step is cleaning the pellet making tools for sample preparation. In this step all the mortar and pestle should be washed and rinsed with acetone and distilled water to make sure there is no contaminant on their surfaces. Then about 100 mg of KBr is measured and is poured into the pestle. About 2 mg of the corrosion product (on the surface of the sample) should be scraped and added to the KBr. Then with the use of the mortar and pestle two substances must be homogenized. An acceptable amount of the final product, which is not too thick or thin, should be poured in the assembled pellet press stainless steel die. A hydraulic jack should be used to press the mixture in the die to 4000 psi. Next is to locate the prepared pellet sample in FTIR holder with the use of tweezers. Before collecting the sample spectrum, the room ambient background spectrum must be collected in order to get the accurate results.

FTIR instrumentation:

- Spatula
- Mortar and pestle
- KBr (Potassium Bromide)
- Die set
- Pellet press
- Vacuum pump
- Tweezers
- FTIR
- Computer

3.4 Morphological Characterization of Damaged Aluminum Surfaces Using SEM

Previous investigators indicated intergranular corrosion mechanism as the cause of pitting corrosion of heat exchangers. To characterize corrosion mechanism and chemical analysis of corrosion products, Scanning Electron Microscopy (SEM) is used.
SEM is a method used for imaging of surfaces in high resolution. While ordinary microscope uses visible light beam, SEM uses electrons for imaging. The advantage of SEM over light microscopy is higher magnification (>100,000X) and greater depth of field up to 100 times deeper than light microscopy. The SEM generates an electron beam above the sample surface. These electrons are produces by a thermal emission source like heated tungsten filament. Energy of electrons varies from 100 eV to 30 KeV. With the use of electromagnetic lenses the beam is focused on the surface of the sample. When the electron’s beam hits the surface, it interacts with the atoms in the sample. The secondary electrons are produced by elastic interaction between beam electrons and valence electrons of the sample. Also backscattered electrons that are produced by inelastic collision between beam electrons and the nuclei of sample atoms and reflected from deeper sections of the sample.

3.5 Design of Experiment

Scope of this part is to focus on analysis of Aluminum alloy 3102 which is tube material. All these samples will be tested in different electrolytes, which their chart is presented in Table 3-1.

<table>
<thead>
<tr>
<th>Electrochemical Test</th>
<th>Solutions</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclic Polarization</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>Acidic</td>
</tr>
<tr>
<td>Cyclic Polarization</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>No Change in pH</td>
</tr>
<tr>
<td>Cyclic Polarization</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>Acidic</td>
</tr>
<tr>
<td>Cyclic Polarization</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>No Change in pH</td>
</tr>
<tr>
<td>Cyclic Polarization</td>
<td>SWAAT</td>
<td>Acidic</td>
</tr>
</tbody>
</table>
3.6 Corrosion Rate Calculations

Results from EC tests provides a diagram which shows the relation between potential and log current density and Tafel slopes are the keys to calculate corrosion rate. In order to draw $\beta_A$ which stands for anodic Tafel slope and $\beta_C$ which stands for cathodic Tafel slope, a potential ± 50 mV from $E_{CORR}$ must be define and a tangent line must be drawn. A line passed from this point linear to X axis defines $E_{CORR}$ and a line passed from this point linear to Y axis defines $i_{CORR}$ (Corrosion Current). Calculations for Corrosion Rate follow as:

$$\frac{\Delta E}{\Delta i} = R_p = (\beta_a \beta_c) / (2.3 \ (i_{corr}) \ (\beta_a + \beta_c)) \quad \text{I}$$

- $\Delta E/\Delta i = R_p$ = the slope of the linear region.
- $\Delta E$ is expressed in volts (V).
- $\Delta i$ is expressed in microamps ($\mu$A).
- $\beta_a$ = anodic Tafel constant expressed in volts per decade of current.
- $\beta_c$ = cathodic Tafel constant expressed in volts per decade of current.
- 2.3 = natural log of 10 $i_{CORR}$ = corrosion current ($\mu$A).

Based on equation “I”, $i_{corr}$ is driven as:

$$i_{corr} = (\beta_a \beta_c) / (2.3 \ (R_p) \ (\beta_a + \beta_c)) \quad \text{II}$$

Corrosion Rate (mpy) = (0.13 $i_{corr}$ (E.W.)) / (Axd) \quad \text{III}

- E.W. = equivalent weight (in g/eq.)
- A = area (in cm²)
- d = density (in g/cm³)
- 0.13 = metric and time conversion factor
CHAPTER 4
RESULTS AND DISCUSSION

4.1 Electrochemical Testing

Cyclic polarization was performed on Aluminum alloy 3102 in various corrosive electrolytes. Samples from a tube sheet of multiport AA3102 alloy with dimensions 1” x 1” size were prepared and then polished with Al₂O₃ particles in order to achieve a shiny surface with no significant scratches on the surface. Next step, the sample was rinsed with acetone and DI water in order to remove any contamination on its surface. Cyclic polarization tests were then performed according to test parameters indicated in the legend of each test output. Figure 4-1 shows the cyclic polarization on AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with no change in pH (pH=5.57). Upon the completion of each test, several measured parameters of interest including corrosion potential ($E_{corr}$), primary passive potential ($E_{pp}$), protection potential ($E_{PR}$), and transpassive potential ($E_{TRANSPASSIVE}$) were identified and tabulated. Table 4-1 presents measured parameters of interest in duplicate measurements and the average values of the parameters are presented in Table 2. Data presented in Tables 4-1 and 4-2 shows SWAAT solution shows a more positive corrosion potentials compared to all other electrolytes used in this investigation. However, due to the fact that pH of the SWAAT electrolyte is lowest meaning the SWAAT electrolyte is the most acidic electrolyte used in this research and therefore, it is expected that this electrolyte result in highest corrosion rate of AA 3102 alloy. Passive potential in all electrolytes did not vary tremendously whereas protection potential for AA 3102 in SWAAT solution was more positive than those in other electrolytes. Transpassive potentials of AA 3102 in both SWAAT and the electrolyte containing high sodium chloride solutions were the most negative indicating vulnerability of AA 3102 to pitting in these
electrolytes. Low sodium chloride electrolyte (0.5% NaCl containing electrolytes) resulted in the most positive transpassive potential of about -0.78 V vs. SCE.

**Table 4-1: Corrosion Potential ($E_{CORR}$), Primary Passive Potential ($E_{PP}$), Protection Potential ($E_{PR}$), Transpassive Potential ($E_{TRANSPASSIVE}$) and Breakdown Potential ($E_{BREAKDOWN}$) of different samples in different solutions are presented.**

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>$E_{CORR}$ (mV)</th>
<th>$E_{PP}$ (mV)</th>
<th>$E_{PR}$ (mV)</th>
<th>$E_{TRANSPASSIVE}$ (mV)</th>
<th>$E_{BREAKDOWN}$ (mV)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWAAT</td>
<td>2.9</td>
<td>-1.034</td>
<td>-0.947</td>
<td>-0.759</td>
<td>-0.921</td>
<td>_</td>
<td>99.9</td>
</tr>
<tr>
<td>SWAAT</td>
<td>2.9</td>
<td>-1.037</td>
<td>-0.958</td>
<td>-0.760</td>
<td>-0.928</td>
<td>_</td>
<td>72.3</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.166</td>
<td>-0.979</td>
<td>-0.900</td>
<td>-0.926</td>
<td>-1.117</td>
<td>9.3</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.185</td>
<td>-0.979</td>
<td>-0.856</td>
<td>-0.926</td>
<td>-1.139</td>
<td>28</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.132</td>
<td>-0.975</td>
<td>-0.938</td>
<td>-0.815</td>
<td>_</td>
<td>13.7</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.107</td>
<td>-0.967</td>
<td>-0.917</td>
<td>-0.810</td>
<td>_</td>
<td>25.3</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.8</td>
<td>-1.172</td>
<td>-0.970</td>
<td>-0.852</td>
<td>-0.923</td>
<td>-1.105</td>
<td>35.3</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.8</td>
<td>-1.185</td>
<td>-0.976</td>
<td>-0.848</td>
<td>-0.923</td>
<td>-1.110</td>
<td>52.9</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.57</td>
<td>-1.132</td>
<td>-0.973</td>
<td>-0.933</td>
<td>-0.781</td>
<td>_</td>
<td>11.9</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.57</td>
<td>-1.135</td>
<td>-0.982</td>
<td>-0.916</td>
<td>-0.786</td>
<td>_</td>
<td>14.6</td>
</tr>
</tbody>
</table>

**Table 4-2: Average of the results of data presented in Table 4-1.**

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>$E_{CORR}$ (mV)</th>
<th>$E_{PP}$ (mV)</th>
<th>$E_{PR}$ (mV)</th>
<th>$E_{TRANSPASSIVE}$ (mV)</th>
<th>$E_{BREAKDOWN}$ (mV)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWAAT</td>
<td>2.9</td>
<td>-1.035</td>
<td>-0.952</td>
<td>-0.760</td>
<td>-0.924</td>
<td>_</td>
<td>86.1</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.175</td>
<td>-0.979</td>
<td>-0.878</td>
<td>-0.926</td>
<td>-1.128</td>
<td>18.7</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>4.0</td>
<td>-1.119</td>
<td>-0.971</td>
<td>-0.927</td>
<td>-0.812</td>
<td>_</td>
<td>19.5</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.8</td>
<td>-1.178</td>
<td>-0.973</td>
<td>-0.850</td>
<td>-0.923</td>
<td>-1.108</td>
<td>44.1</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH$_4$)$_2$SO$_4$</td>
<td>5.57</td>
<td>-1.133</td>
<td>-0.975</td>
<td>-0.924</td>
<td>-0.784</td>
<td>_</td>
<td>13.3</td>
</tr>
</tbody>
</table>

Cyclic polarization plots are commonly used to assess pitting tendency of engineering alloys in corrosive environments most of which containing chloride ions. In cyclic polarization,
potential sweep starts at a potential below $E_{\text{corr}}$ and proceeds in the anodic direction (more positive direction) and is reversed based on preselected potential or current. If the reverse path results in higher currents compared to forward path for any given potential, then a hysteresis loop is generated in the potential-current plot. The size of the generated loop indicates the pitting tendency of the alloy in a given corrosive electrolyte. A larger loop area is indicative of higher pitting tendency of the alloy in the corrosive electrolyte. If the reverse path results in lower currents compared to its forward counter path, then the alloy is not vulnerable to pitting in that corrosive electrolyte. In addition, when protection potential is more positive than passive potential the alloy is not expected to undergo pitting in that electrolyte.

Figure 4-1: Cyclic Polarization plot of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution ($pH = 5.57$).

Duplicate runs were performed for each test to ensure reproducibility of the test results. (Figure 4-2).
Figure 4-2: Cyclic Polarization plot of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution (pH = 5.57).

Figures 4-3 and 4-4 shows the cyclic polarization of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with the pH of 4.0.

Figure 4-3: Cyclic Polarization plot of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution (pH = 4.0).
In addition to collection of measured parameters of interest such as corrosion potential ($E_{\text{corr}}$), primary passive potential ($E_{\text{pp}}$), protection potential ($E_{\text{PR}}$), and transpassive potential ($E_{\text{TRANSPASSIVE}}$), anodic and cathodic Tafel slopes for each polarization data was measured and used to calculate corrosion rate of AA 3102 in different corrosive solutions. Corrosion rates of AA 3102 in 0.5 % NaCl + 3.5 % (NH$_4$)$_2$SO$_4$ electrolyte at pH 5.58 and 4.0 were 13.3 mpy and 19.5 mpy respectively. Lower pH electrolyte is responsible for higher corrosion rate of AA 3102 alloy.
Scanning electron micrographs of representative samples tested in 0.5 % NaCl + 3.5 % (NH₄)₂SO₄ electrolyte at pH 5.58 and 4.0 are shown in Figure 4-5 a and b respectively. Both images show intergranular attack by the acidic electrolyte on the AA 3102.

Figure 4-5: SEM micrograph of AA 3102 surface after cyclic polarization test in 0.5 % NaCl + 3.5 % (NH₄)₂SO₄ showing intergranular attack.
Figure 4-6 and 4-7 shows cyclic polarization which is performed on AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate with no change in pH (pH=5.8).

**Figure 4-6:** Cyclic Polarization plot of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution (pH = 5.8).

**Figure 4-7:** Cyclic Polarization plot of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution (pH = 5.8).
High salt content in the electrolyte and lower sulfate content has been selected to indicate the effect of salt domination on both corrosion rate and corrosion morphology of AA 3102 alloy. Higher concentration of sodium chloride is expected to increase probability of pitting corrosion in AA 3102. Figure 4.8 (a, b) shows SEM micrographs for AA 3102 surface after cyclic polarization in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate with pH of 5.8 (a) and pH of 4.0 (b).

Figure 4.8: SEM micrographs of AA 3102 surface after cyclic polarization in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate with pH = 5.8 (a) and pH = 4.0 (b).
Figures 4-9 and 4-10 show cyclic polarization performed on AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate with the pH of 4.0. Corrosion rates of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate at pH = 5.8 and pH = 4.0 were 18.67 mpy and 44 mpy respectively. As expected, electrolyte with lower pH resulted in higher corrosion rate.

Figure 4-9: Cyclic Polarization plot of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution (pH = 4.0).

Figure 4-10: Cyclic Polarization plot of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution (pH = 4.0).
Also Figures 4-11 and 4-12 show cyclic polarization plots for AA 3102 in SWAAT solution.

**Figure 4-11:** Cyclic Polarization plot of AA 3102 in SWAAT solution.

**Figure 4-12:** Cyclic Polarization plot of AA3102 in SWAAT solution.
SWAAT solution is a solution used for cabinet style corrosion tests, which is based on ASTM G85.A3 standards [31] and is a mixture of 42 g sea salt, 10 ml Glacial Acetic Acid and DI water in total amount of 1000 ml solution. Corrosion rate of AA 3102 in SWAAT solution is 86 mpy that is higher than all previous electrolytes indicating lowest solution acidity results in the highest corrosion rates as expected. Therefore, all chosen electrolytes containing sodium chloride and ammonium sulfate were milder than SWAAT electrolyte that appears to be more aggressive than the electrolytes used in this investigation. SEM micrograph of AA 3102 surface after cyclic polarization showed severe grain boundary attack and regions with deep anodic dissolution of the alloy (Figure 4-13).

Figure 4-13: SEM micrograph of AA 3102 surface after cyclic polarization test in SWAAT electrolyte.
4.2 Metallography of AA 3102 Before and After Cyclic Polarization

In order to observe microstructural features of AA 3102 including its grain boundaries and grain structure, sheets of the alloy were polished (Figure 4-14, a) and etched with Weck’s reagent (Figure 4-14, b). As polished, un-etched sample almost showed the microstructure of the alloy however, etching the sample with Weck’s solution exhibited clearer microstructure and grain boundaries of the alloy. Aluminum alloy 3102, the sample surface polished with Al₂O₃ particles (5, 1, and 0.05 μm) and etched with Keller’s solution for 4 seconds resulted in optical microscopy images presented in Figure 4-15 showing similar microstructure of AA 3102 surface.

![Figure 4-14: Optical micrographs of AA 3102 polished-unetched (a) and etched with Weck’s etchant (b).](image-url)
It must be noted that these micrographs represent AA 3102 microstructure before the brazing stage of the heat exchanger manufacturing. Brazing process and other thermal treatment of the alloy in the heat exchanger manufacturing processing steps will affect the microstructure of the AA 3102.

Optical microscopy is performed on corroded area of the samples after cyclic polarization. Figure 4-16 shows intergranular attack on AA 3102 surface after cyclic polarization in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 5.57. Also Figure 4-17 shows uniform corrosion on the sample surface after cyclic polarization test. Other salt solutions with different pH showed almost the same effect on the surface of the sample after the electrochemical test.
Figure 4-16: Intergranular attack on AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 5.57.

Figure 4-17: Uniform corrosion of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 5.57.

Figure 4-18 shows uniform corrosion on AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 4.0. Shiny areas did not corrode and darker areas show extensive uniform corrosion.
Figure 4-18: Uniform corrosion of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 4.0.

Figure 4-19 depicts intergranular attack on AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with pH of 4.0.

Figure 4-19: Intergranular attack on AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with pH of 4.0.
Also the result of the electrochemical testing on AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate with the pH of 4.0 (Figure 4-20).

Figure 4-20: Intergranular attack on AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with pH of 4.0.

In this research attempts were made to measure thickness loss of the micro channel tube’s wall using optical microscope. Figure 4-21 shows the schematic of the cross section of a multiport micro channel tube arrangement. Total thickness of the tube sheet is 1.5 mm. Thickness of the each wall is 0.5 mm and the diameter of the micro channels is 0.5 mm.

Figure 4-21: Schematic of the cross section of tubes. Black circles are indicator of micro channels.
For AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 5.8 thickness loss measured 120.04 μm. Figure 4-22 shows the thickness of the thinnest section of the corroded wall and Figure 4-23 shows original un-corroded wall of the tube thickness. The difference in the two thicknesses (470.27 μm - 350.23 μm) = 120.04 μm.

**Figure 4-22: Corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 5.8.**

**Figure 4-23: Un-corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 5.8.**
Figure 4-24 and 4-25 show the difference between the thicknesses of the tube’s wall of AA 3102 in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 4.0. Thickness loss measured 250.14 μm.

*Figure 4-24: Corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 4.0.*

*Figure 4-25: Un-corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution (pH of 4.0).*
Figure 4-26 and 4-27 show the difference between the thicknesses of the tube’s wall of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with the pH of 5.57. Thickness loss measured 108.74 μm.

Figure 4-26: Corroded wall of the tube in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with the pH of 5.57.

Figure 4-27: Un-corroded wall of the tube in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution (pH of 5.57).
Also Figure 4-28 and 4-29 show the difference between the thicknesses of the tube’s wall of AA 3102 in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution with the pH of 4.0. Thickness loss measured 101.3 μm.

Figure 4-28: Corroded wall of the tube in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution (pH of 4.0).

Figure 4-29: Un-corroded wall of the tube in 0.5% Sodium Chloride and 3.5% Ammonium Sulfate solution (pH of 4.0).
Figure 4-30 and 4-31 show the difference between the thicknesses of the tube’s wall of AA 3102 in SWAAT solution with the pH of 2.9. Thickness loss measured 22.52 μm.

**Figure 4-30:** Corroded wall of the tube in SWAAT solution with the pH of 2.9.

**Figure 4-31:** Un-corroded wall of the tube in SWAAT solution with the pH of 2.9.
Duplicate thickness loss measurements were made to assess reproducibility of these measurements. Figure 4-32 to 4-33 shows the thickness loss of AA 3102 tube’s walls after cyclic polarization in the same solutions and conditions as the previous measurements.

*Figure 4-32: Corroded wall of the tube in SWAAT solution with the pH of 2.9.*

*Figure 4-33: Un-corroded wall of the tube in SWAAT solution with the pH of 2.9.*
Figure 4-34: Corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 4.0.

Figure 4-35: Un-corroded wall of the tube in 3.5% Sodium Chloride and 0.5% Ammonium Sulfate solution with the pH of 4.0.
Table 4-3 presents data for thickness loss of the AA 3102 tube’s walls in different corrosive solutions.
Table 4-3: Thickness loss (along with their averages) of AA 3102 samples after cyclic polarization in different corrosive solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>pH</th>
<th>Thickness Loss (μm)</th>
<th>Average Thickness Loss (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWAAT</td>
<td>2.9</td>
<td>22.52, 61.93</td>
<td>42</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>5.8</td>
<td>120.04</td>
<td>120</td>
</tr>
<tr>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>5.57</td>
<td>108.74</td>
<td>108</td>
</tr>
<tr>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>250.14, 67.54</td>
<td>159</td>
</tr>
<tr>
<td>0.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>101.03, 58.87</td>
<td>85</td>
</tr>
</tbody>
</table>

4.3 Fourier Transform Infrared Spectrophotometry (FTIR)

Accelerated corrosion testing procedures are only useful in assessing performance of engineering alloys if and only if the modeled corrosion mechanism in the accelerated corrosion test successfully simulates the corrosion process and pathway that takes place in natural atmospheres. In this regard, one of the commonly used methods by researchers is to characterize the corrosion products formed on alloy surface during accelerated corrosion test and compare phase formation/transformation and with those events during alloy exposure in natural corrosive environments. FTIR technique is proven to be a fast, inexpensive, and highly reliable analytical method that is used in characterization of corrosion products formed on alloy surfaces during corrosion processes. KBr pellets containing a few milligrams of the corrosion product is produced using standard procedure and FTIR spectra were collected according instrument manufacturer guidelines. Figures 4-38, 39, and 40 show the spectra of corrosion products formed on AA 3102 in 3.5% Sodium Chloride + 0.5% Ammonium Sulfate (pH=4), 0.5% Ammonium Sulfate + 3.5% Sodium Chloride (pH=4), and SWAAT solution respectively.
Figure 4-38: FTIR Spectrum of AA3102 tested in 3.5% Sodium Chloride + 0.5% Ammonium Sulfate (pH=4).

Figure 4-39: FTIR Spectrum of AA3102 tested in 0.5% Sodium Chloride + 3.5% Ammonium Sulfate (pH=4).
Comparing the spectra for corrosion products formed on AA 3102 after cyclic polarization with the available literature information, one can assign absorption bands around 3434 and 1630 cm\(^{-1}\) to water bands, which are resulted from the absorbed moisture on the sample. Wavenumbers around 2922, 2360 and also 2342 cm\(^{-1}\) band is coming from atmosphere CO\(_2\) present in the atmosphere. Based on available literature data, Aluminum alloys exposed to sulfate containing aqueous environments are expected to form Al\(_x\)(OH)\(_y\) SO\(_4\)\(_m\)H\(_2\)O that exhibit an FTIR absorption band in the wavenumber range of 1000 cm\(^{-1}\) to 1300 cm\(^{-1}\) [34]. Figures 4-38 and 4-39 do show a band in the indicated range that is possibly due to sulfate complex formation. The bands at about 1050 cm\(^{-1}\) and one around 600 cm\(^{-1}\) wavenumber appears to belong to Al-O bond and is observed in all three FTIR spectra. Therefore, the phases formed on AA 3102 during cyclic polarization appears to corroborate well with expected corrosion products formed in natural atmospheres containing sulfate and chloride containing anions.
4.4 Corrosion Mechanism Identification Based on SEM Results

SEM microscopy was performed to identify the mode of attack by corrosive electrolyte on the AA3102. Figure 4-41 (a-c) show SEM micrograph of AA 3102 alloy after cyclic polarization in 3.5% ammonium sulfate plus 0.5% sodium chloride (a), 3.5% sodium chloride plus 0.5% ammonium sulfate (b), and SWAAT solution (c). SEM images corresponding to AA 3102 tested in high sulfate containing electrolyte and SWAAT electrolyte show general dissolution of the alloy leading to what appears to be uniform corrosion (Figure 4-41 a and c). However, SEM image corresponding to the AA 3102 tested in high chloride solution shows severe pitting in localized regions of the surface (Figure 4-41 c). Figure 4-42 (a-f) show SEM micrographs of AA 3102 after cyclic polarization in 3.5% ammonium sulfate plus 0.5% sodium chloride (a, b), 3.5% sodium chloride plus 0.5% ammonium sulfate (c, d), and SWAAT solution (e, f). SEM micrographs show all corrosive electrolytes attack AA 3102 with intergranular mode of corrosion. Dissolution of metallic atoms appears to initiate from the grain boundary regions and propagate along the grain boundaries (Figure 4-42 a, b). Figure 4-42 c, and d show a surface of the alloy with localized attack due to possibly chloride interaction with the surface. Highly localized attack is observes in the samples tested in high sodium chloride containing electrolyte. The morphology of the surface damage due to corrosion is completely different in high sodium chloride solution compare to those of either high sulfate containing electrolyte or SWAAT solution (Figure 4-42 c, d and Figure 4-42 e, f). AA 3102 sample after cyclic polarization in SWAAT solution showed severe metal dissolution due to low pH (2.9) that is more aggressive than the other two corrosive electrolytes used in this investigation (Figure 4-42 e, f).
Figure 4-4: SEM micrographs of AA 3102 after cyclic polarization test in 3.5% ammonium sulfate plus 0.5% sodium chloride (a), 3.5% sodium chloride plus 0.5% ammonium sulfate (b), and SWAAT solution (c).
Figure 4-42: SEM micrograph of AA 3102 surface after cyclic polarization in 3.5% ammonium sulfate plus 0.5% sodium chloride (a, b); 3.5% sodium chloride plus 0.5% ammonium sulfate (c, d); and SWAAT solution (e, f).
CHAPTER 5

CONCLUSION

As it has been discussed in chapter 1, the main purpose of this research is to define a reproducible accelerated corrosion testing method based on electrochemical testing for characterization corrosion resistance of AA 3102. In order to find out the reproducibility of electrochemical testing, each test has been conducted two times on the same material, with the same surface preparation, same solution, same pH and also same potential limits. As it is shown in chapter 4, researchers observe results that were reasonably reproducible as indicated by data provided in Tables 4-1 and 4-2.

SEM micrographs of AA 3102 after cyclic polarization in high sulfate solution (Figure 4-5) and that of high chloride (Figure 4-8) clearly show grain boundary attack by corrosive electrolytes. This mode of corrosion is known as intergranular corrosion and one can see great corroboration between results of this research and corrosion morphology and mechanism observed on field samples. Optical micrographs of all AA 3102 samples taken after cyclic polarization tests confirmed grain boundary attack as shown in Figures 4-16, 4-19, and 4-20. Cyclic polarization data has effectively used in this research to measure corrosion rates of AA 3102 alloy in various corrosive electrolytes with different pHs. Corrosion rates in terms of corrosion current (μA/cm²) or thickness loss (mpy) are measurable parameters that can be used to differentiate alloy resistance in a corrosive environment.

Cyclic polarization of AA 3102 in low NaCl plus high sulfate containing electrolyte showed less pitting tendency compared to the same alloy in an electrolyte containing high NaCl and low sulfate environment (Figures 4-1 through 4-10). Similar observations were made in a parallel corrosion chamber study in our research laboratory (data not presented in this thesis).
High sulfate environments result in uniform corrosion mechanism and high chloride environments cause more severe pitting mechanism. SWAAT solution that is commonly used in corrosion chamber studies appear to be more aggressive due to its lower pH and produced more severe damage to AA 3102 surfaces as evidence in Figures 4-11 through 4-13. The required time to complete an EC test is extremely short rather than weeks required by SWAAT. Table 5-1 provides degree of satisfaction of cyclic polarization procedures and outcomes.

As it has been discussed in chapter 2, when $E_{PR}$ is higher than $E_{corr}$ it shows less pitting tendency of the material. Results from cyclic polarization tests for the materials in all solutions shows that the reverse path has more positive $E_{PR}$ potentials than those for the forward path. This means lower current on reverse path for the same potential, which means higher alloy resistance. This is because of uniform corrosion of AA 3102 surfaces. Aluminum oxide (Al$_2$O$_3$) is more resistant that the Aluminum itself, therefor one can expect formation of a passive layer on the surface of Aluminum after corrosion which protects it against faster corrosion.

As it has been said before, A.C. Scott [8] suggested seven criteria for an acceptable corrosion test as follows:

1. The mode of attack-corrosion morphology- matched the corrosion observed in samples returned from field,
2. The accelerated test environment was a plausible analog of the field environment,
3. Similarly, the test specimen was an appropriate model of the material as used in the field,
4. The test performance criterion was an appropriate measure of corrosion resistance in the field,
5. The test gave objective, quantifiable results,
6. Test duration was reasonably short,
7. The test was an industry standard, and could be readily put into use by other aluminum producers, radiator manufacturers, etc.
Table 5-1: Degree of satisfaction of cyclic polarization testing based on A.C. Scott [8] seven criteria.

<table>
<thead>
<tr>
<th>#</th>
<th>Criteria</th>
<th>Degree of Satisfaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The mode of attack matched to the samples of the material found in the field</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>2</td>
<td>The test environment is a credible match of the field environment</td>
<td>Somewhat Satisfactory</td>
</tr>
<tr>
<td>3</td>
<td>The test specimen is a suitable model for of the material used in the field environment</td>
<td>Somewhat Satisfactory</td>
</tr>
<tr>
<td>4</td>
<td>The criteria for the test was the applicable degree of the corrosion resistance in the field</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>5</td>
<td>The test gave measureable, impartial results</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>6</td>
<td>The test span is fairly short</td>
<td>Very Satisfactory</td>
</tr>
<tr>
<td>7</td>
<td>The test is a standard for the industry and could be put into use readily by aluminum producers and radiator manufactures</td>
<td>Satisfactory</td>
</tr>
</tbody>
</table>

In summary

- Cyclic polarization that is an electrochemical test can reliably provide insight into the corrosion rate and corrosion mechanism characteristics of AA 3102 in different corrosive environments. Good reproducibility in cyclic polarization results was attained.

- Based on SEM micrographs of AA 3102 surface after exposure to various corrosive electrolytes, one may conclude the mode of attack is intergranular. Therefore, cyclic polarization was successfully used to duplicate the mode of attack observed in field samples.

- Cyclic polarization plots for all AA 3102 samples tested in various corrosive electrolytes exhibited higher protection potential (Epp) than corrosion potential ($E_{corr}$) which means AA3102 is not highly vulnerable to pitting corrosion.

- SEM micrographs of AA 3102 surfaces after cyclic polarization test uniform metal dissolution leading to uniform corrosion of the alloy.

- Reverse path exhibited in all cyclic polarization test results was seen to be above forward path, which means lower current densities for the reverse path for a same potential.
• Cyclic polarization of AA 3102 in low NaCl and high sulfate containing electrolyte showed less pitting tendency compared to the same alloy in an electrolyte containing high NaCl and low sulfate environment and also similar observations were made in a parallel corrosion chamber study performed at our laboratory.

• High sulfate environments result in uniform corrosion mechanism and high chloride environments cause more severe pitting mechanism.

• SWAAT solution appears to be more aggressive due to its lower pH and produced more severe damage to AA 3102 surfaces.
APPENDIX A

TAFEL SLOPE CALCULATIONS
Figure A-1 to A-10 shows Tafel fits which are drawn on the EC test’s results on AA 3102 in different solutions.

*Figure A-1: Tafel fits on electrochemical test result of AA 3102 in SWAAT solution.*

*Figure A-2: Tafel fits on electrochemical test result of AA 3102 in SWAAT solution.*
Figure A-3: Tafel fits on electrochemical test result of AA 3102 in (3.5% NaCl + 0.5% \((NH_4)_2SO_4\) solution (pH=4.0).

Figure A-4: Tafel fits on electrochemical test result of AA 3102 in (3.5% NaCl + 0.5% \((NH_4)_2SO_4\) solution (pH=4.0).
Figure A-5: Tafel fits on electrochemical test result of AA 3102 in (0.5% NaCl + 3.5% (NH₄)₂SO₄) solution (pH=4.0).

Figure A-6: Tafel fits on electrochemical test result of AA 3102 in (0.5% NaCl + 3.5% (NH₄)₂SO₄) solution (pH=4.0).
Figure A-7: Tafel fits on electrochemical test result of AA 3102 in (3.5% NaCl + 0.5% (NH₄)₂SO₄) solution (pH=5.8).

Figure A-8: Tafel fits on electrochemical test result of AA 3102 in (3.5% NaCl + 0.5% (NH₄)₂SO₄) solution (pH=5.8.)
Figure A-9: Tafel fits on electrochemical test result of AA 3102 in (0.5% NaCl + 3.5% (NH₄)₂SO₄ solution (pH=5.57).

Figure A-10: Tafel fits on electrochemical test result of AA 3102 in (0.5% NaCl + 3.5% (NH₄)₂SO₄ solution (pH=5.57).
Table A-1 shows the results of Tafel fits on AA 3102 in different solutions. Also Table A-2 shows the average amount for each set of data for a particular solution.

### Table A-1. Data from Tafel fits

<table>
<thead>
<tr>
<th>#</th>
<th>Material</th>
<th>Solution</th>
<th>pH</th>
<th>E\text{corr} (mV)</th>
<th>I\text{corr}(μA)</th>
<th>B_a(mV)</th>
<th>B_c(mV)</th>
<th>Corrosion Rate (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AA 3102</td>
<td>SWAAT</td>
<td>2.9</td>
<td>-1034</td>
<td>2.355e2</td>
<td>233</td>
<td>57</td>
<td>99.9</td>
</tr>
<tr>
<td>2</td>
<td>AA 3102</td>
<td>SWAAT</td>
<td>2.9</td>
<td>-1038</td>
<td>1.704e2</td>
<td>219</td>
<td>60</td>
<td>72.3</td>
</tr>
<tr>
<td>3</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1166</td>
<td>2.119e1</td>
<td>47</td>
<td>77</td>
<td>93.3</td>
</tr>
<tr>
<td>4</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1181</td>
<td>6.6e1</td>
<td>82</td>
<td>288</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1132</td>
<td>3.221e1</td>
<td>91</td>
<td>54</td>
<td>13.7</td>
</tr>
<tr>
<td>6</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1106</td>
<td>5.961e1</td>
<td>173</td>
<td>59</td>
<td>25.3</td>
</tr>
<tr>
<td>7</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>5.8</td>
<td>-1168</td>
<td>8.33e1</td>
<td>79</td>
<td>166</td>
<td>35.3</td>
</tr>
<tr>
<td>8</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>5.8</td>
<td>-1185</td>
<td>1.246e2</td>
<td>115</td>
<td>207</td>
<td>52.8</td>
</tr>
<tr>
<td>9</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>5.57</td>
<td>-1132</td>
<td>2.817e1</td>
<td>74</td>
<td>54</td>
<td>11.9</td>
</tr>
<tr>
<td>10</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>5.57</td>
<td>-1134</td>
<td>3.445e1</td>
<td>76</td>
<td>61</td>
<td>14.6</td>
</tr>
<tr>
<td>#</td>
<td>Material</td>
<td>Solution</td>
<td>pH</td>
<td>$E_{corr}$ (mV)</td>
<td>$I_{corr}$ (μA)</td>
<td>$V_c$ (mV)</td>
<td>$V_a$ (mV)</td>
<td>Corrosion Rate (mpy)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>AA 3102</td>
<td>SWAAT</td>
<td>2.9</td>
<td>-1036</td>
<td>2.029 e2</td>
<td>226</td>
<td>58.5</td>
<td>86.1</td>
</tr>
<tr>
<td>2</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>5.8</td>
<td>-1173</td>
<td>4.36 e1</td>
<td>64.5</td>
<td>182.5</td>
<td>18.7</td>
</tr>
<tr>
<td>3</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1119</td>
<td>4.59 e1</td>
<td>132</td>
<td>56.5</td>
<td>19.5</td>
</tr>
<tr>
<td>4</td>
<td>AA 3102</td>
<td>3.5% NaCl + 0.5% (NH₄)₂SO₄</td>
<td>4.0</td>
<td>-1176</td>
<td>10.39 e1</td>
<td>97</td>
<td>186.5</td>
<td>44.1</td>
</tr>
<tr>
<td>5</td>
<td>AA 3102</td>
<td>0.5% NaCl + 3.5% (NH₄)₂SO₄</td>
<td>5.57</td>
<td>-1133</td>
<td>3.13 e1</td>
<td>75</td>
<td>57.5</td>
<td>13.3</td>
</tr>
</tbody>
</table>
APPENDIX B

CALIBRATION PROCEDURE FOR THE OPTICAL MICROSCOPE
Place the Calibration Glass on Objective lens.

On desktop, open program folder

Open Toup Tek folder

Wright click on software icon and choose “Pin to Taskbar” in order to have easy access for next times.
Open the program and click on UCM under Camera list tab to activate the camera.
In capture and resolution tab, click on Live and Snap and choose the highest magnitude.

Change the zoom to 100%.
Make sure magnification bar is on “NA”

Click on option then calibrate.

Click on “End Point” and choose “H Style”.

Enter the magnification which is “(Objective Lens Magnification)*(Eyepiece Magnification)”

For this setup Magnification is, 5*10=50X
In “Actual Length” tab, enter the actual distance between two lines on calibration glass.

Tangent the “H Style” to the lines and hit “OK”.

---

82
In order to make sure that calibration is done correctly, change the zoom to any other magnitude.

Click on magnification tab and choose 50X.
Click on Measurement Tab and chose one.

Click on Line tool and draw a line.
In order to have scale bar click on “Measurements” then “Scale bar”.

Set Up the properties and click on OK.
In order to remove a calibration set up, click on “Option”, then “Magnification”.

Select the magnification that you want to remove, and click on delete.

In order to save your images, using snipping tool is a better way because it save the image quality.
REFERENCES

4. https://www.nace.org/Pitting-Corrosion/
6. ISO 9223, "Corrosion of metals and alloys - Classification of corrosivity of atmospheres."