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ELECTROCHEMICAL CHARACTERIZATION OF ANODE PASSIVATION MECHANISMS IN COPPER ELECTROREFINING

by

Michael Scott Moats

A Dissertation Submitted to the Faculty of the DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
In Partial Fulfillment of the Requirements For the Degree of DOCTOR OF PHILOSOPHY
In the Graduate College UNIVERSITY OF ARIZONA

1998
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Michael Scott Moats entitled ELECTROCHEMICAL CHARACTERIZATION OF ANODE PASSIVATION MECHANISMS IN COPPER ELECTROREFINING and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of DOCTOR OF PHILOSOPHY.

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SIGNED: [Signature]
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ABSTRACT

Anode passivation can decrease productivity and quality while increasing costs in modern copper electrorefineries. This investigation utilized electrochemical techniques to characterize the passivation behavior of anode samples from ten different operating companies. It is believed that this collection of anodes is the most diverse set ever to be assembled to study the effect of anode composition on passivation. Chronopotentiometry was the main electrochemical technique employing a current density of 3820 A m$^{-2}$. From statistical analysis of the passivation characteristics, increasing selenium, tellurium, silver, lead and nickel were shown to accelerate passivation. Arsenic was the only anode impurity that inhibited passivation. Oxygen was shown to accelerate passivation when increased from 500 to 1500 ppm, but further increases did not adversely affect passivation. Nine electrolyte variables were also examined. Increasing the copper, sulfuric acid or sulfate concentration of the electrolyte accelerated passivation. Arsenic in the electrolyte had no effect on passivation. Chloride and optimal concentrations of thiourea and glue delayed passivation. Linear sweep voltammetry, cyclic voltammetry, and impedance spectroscopy provided complementary information.

Analysis of the electrochemical results led to the development of a unified passivation mechanism. Anode passivation results from the formation of inhibiting films. Careful examination of the potential details, especially those found in the oscillations just prior to passivation, demonstrated the importance of slimes, copper sulfate and copper oxide. Slimes confine dissolution to their pores and inhibit diffusion. This can lead to copper
sulfate precipitation, which blocks more of the surface area. Copper oxide forms because of the resulting increase in potential at the interface between the copper sulfate and anode. Ultimate passivation occurs when the anode potential is high enough to stabilize the oxide film in the bulk electrolyte. The effect of anode impurities or electrolyte concentrations can be related to the formation one of these films.

Reactions occurring after passivation have also been examined. Post-passivation reactions are believed to include silver dissolution, transformation of lead sulfate to lead oxide, and oxygen evolution. Following the sharp potential increase caused by the passivation, silver that has accumulated on the anode surface will dissolve into the electrolyte at a potential between 1.0 and 1.3 V. After the silver has dissolved, the potential increases again at which point the oxidation of lead sulfate to lead oxide occurs. The formation of lead oxide provides a surface with a lower oxygen evolution overpotential. The presence of kupferglimmer also results in a stable lower oxygen evolution potential occurring at approximately 2.0 V.
1 INTRODUCTION

1.1 General Background

As human civilization advances into the twenty-first century, an increasing dependence on high purity materials abounds, particularly related to the manufacturing of electronic devices and wiring. An integral raw material for electronics is high purity copper. While copper has been mined and smelted for more than 5000 years, the requirements of modern technology are for the large-scale industrial production of copper with greater than 99.99% purity. Over the past 150 years, processes have been developed that can ensure a steady supply of low-cost high-purity copper for worldwide consumption. The processes can be categorized into two main commercially used methods. One method produces copper from primary sources (i.e. ores), while the other involves the recycling of copper scrap. The two major routes for recovering copper are conventional (or pyrometallurgical) and hydrometallurgical processing. Secondary copper production recovers copper from scrap using some of the same operations as conventional processing.

1.1.1 Conventional Copper Production

The production of copper by conventional or traditional methods is shown schematically in Figure 1.1. It begins with the mining of a copper sulfide ore, particularly ones with chalcopyrite as the predominant copper bearing mineral. Ore grades in the western United States have been decreasing over the past century. Current head grades for most
Figure 1.1 Schematic Diagram of Conventional Copper Processing. Biswas and Davenport [1].
mines are between 0.3% to 0.7% Cu [1]. In many instances the ores are very complex thus the ability to handle impurities is needed. The low-grade ore results in mines surviving on efficient processing and economy of size. The result is enormous open pit mines that excavate thousands of tons of ore daily.

1.1.1.1 Mineral Processing

Once mined, the ore is crushed and ground to liberate the copper-bearing mineral from the gangue material. Crushing typically involves a primary gyratory crusher in the pit. The reduced product is then conveyed to a crushing plant where the material passes through a secondary and/or a tertiary crushing cycle. Following crushing, the size of the ore is further reduced by milling. Traditionally, the first stage of milling is accomplished by a large number of rod mills or ball mills. A recent trend over the past twenty years is the development of huge semi-autogenous (SAG) mills (9-10 m in diameter) that allow the ore to grind itself with the help of a small amount of large (12.5 cm) steel balls. One SAG mill has replaced what was once done by dozens of rod or ball mills. Final grinding involves smaller ball mills, which produce a final product size of typically -100 microns.

During the final milling of the ore, reagents called collectors are added to the slurry which preferentially absorb onto copper sulfide minerals. These chemicals cause the sulfide particles to become hydrophobic. The copper minerals are then concentrated by flotation when air bubbles are introduced into the slurry. The hydrophobic particles attach themselves to the air bubbles and float to the surface of the slurry. Chemicals
called frothers are typically added to stabilize the particle laden bubbles at the top of the slurry thus creating a froth. The copper rich froth is then removed by an overflow mechanism. After de-watering, the resulting concentrate contains approximately 25-35% copper and is sent to a smelter for pyrometallurgical processing.

1.1.1.2 Pyrometallurgical Processing

Pyrometallurgical processing of the concentrate consists of smelting, converting, and fire refining. Smelting consists of melting the sulfide concentrate in an oxidizing atmosphere, which produces a copper rich (35-70% Cu) molten sulfide phase called matte, a low copper silicate slag, and offgas with SO₂. The capture of SO₂ is environmentally important and economically significant due to the production of H₂SO₄. Smelting is carried out either in a reverberatory or flash furnace. Flash furnaces are replacing older reverberatories and account for approximately 75% of the world's current smelting capacity [1].

Converting is a two step process in which matte is made into "blister" copper. The first stage of converting is the removal of iron in a slag and the generation of an SO₂ bearing offgas. The second stage involves the further oxidation of the remaining copper sulfide to liquid or "blister" copper. Converting has traditionally been performed batch style in a Peirce-Smith converter. Recent developments have led to continuous converting, but these technologies are not widely used.
The final pyrometallurgical step is fire refining. Fire refining consists of an oxidation step followed by reduction. The "blister" copper is oxidized to lower the sulfur content of the copper to approximately 0.001%. Following oxidation, oxygen is removed by the introduction of a reducing agent such as natural gas or ammonia. A traditional reducing agent was a tree trunk or pine pole giving this stage the common name of "poling". The final oxygen content is typically between 1500 and 3500 ppm.

The removal of sulfur and oxygen is imperative to ensure a flat, thin casting needed for the last process in the production of pure copper, electrorefining. Most industrial casting involves the use of an anode casting wheel. The molten copper from fire refining is poured into a tiltable tundish where the amount of copper is weighed to ensure proper anode weights. Upon achieving the desired weight, the copper is poured into an anode shaped mold on the casting wheel. There are twenty to thirty such molds on the wheel. The wheel is then rotated and copper is poured into the next mold. As the process continues, the copper anode is cooled within the mold due to water cooling of the wheel and water spray on top. After about a one-half rotation, the anodes are removed from the mold. This is achieved by an automatic raising pin and a lifting machine. The lifting machine places the anodes in a quench tank which lowers their temperature so they can be transported to the electrorefinery. The empty molds are sprayed with a barite-water wash to prevent sticking of the next anode.
A few smelters (four of the fifty-three in Schleon and Davenport's survey [2]) use a Hazelett continuous caster instead of a casting wheel. The continuous caster uses two water cooled steel belts (one on top, the other on the bottom) and stationary edge dams to contain the molten copper. As the belts rotate, the copper is moved through the caster and cooling occurs. When the copper leaves the caster, it is a solid continuous strip with the correct anode thickness. Anodes are made from the strip by shearing. If the reader desires more information on the pyrometallurgical processing of copper, Biswas and Davenport provide an excellent overview of the topic [1].

1.1.1.3 Electrorefining

Electrorefining is an age-old process. It was first demonstrated experimentally by von Leuchtenberg in 1847 [3]. Elkington, however, patented the process in 1865 and developed the first successful plant in Pembrey, Wales in 1869. The first commercial electrorefining plant in the United States was constructed by Balbach Smelting & Refining Co. in 1883. The Newark, New Jersey plant produced 2-3 tons of electrolytic copper per day during the first year.

Electrorefining utilizes the electrochemical dissolution of an impure copper anode in an electrolytic cell containing a copper sulfate-sulfuric acid solution. Copper ions are transported to the cathode where they are deposited with suitable purity. The basic electrochemical reactions involved are:

Anodic Reaction: \[ \text{Cu}_{\text{impure}} \rightarrow \text{Cu}^{2+} + 2e \]  \hspace{1cm} (Eq. 1)
Cathodic Reaction: \[ \text{Cu}^{2+} + 2e \rightarrow \text{Cu}_{\text{pure}} \]  
(Eq. 2)

Net Reaction: \[ \text{Cu}_{\text{impure}} \rightarrow \text{Cu}_{\text{pure}} \]  
(Eq. 3)

As dissolution occurs, impurities are released either as solid phases or as aqueous species. Purification results from differences in the oxidation/reduction potentials of the individual ions. First, more electrochemically noble impurities, such as gold and silver, will remain at or near the anode. The elements that are less noble than copper will dissolve along with copper into the bulk electrolyte. At the cathode, copper being the most noble element in solution will deposit preferentially. Careful control of the system's voltage, current density, temperature, electrolyte contamination, and deposit morphology ensures an extremely pure copper deposit.

In an industrial tankhouse, a constant current is utilized to control the production rate. Typical cathodic current densities in commercial electrorefining are between 200-300 A m\(^{-2}\). Higher current densities can cause problems such as anode passivation and/or cathode contamination. Theoretically, the net reaction (Eq. 3) for copper electrorefining is 0.0 V. In practice, overvoltages at the anode and cathode and the resistance in the electrolyte and electrical system result in the need for an applied voltage of approximately 0.3 V. Tseidler has indicated that 70-80% of the voltage is consumed by electrolyte resistance, approximately 5% by polarization, and the remainder in the resistance of the electrical system including the electrodes and electrical contacts [4]. If the voltage becomes too high, contamination can occur by the deposition of impurities.
such as the Group VB elements on the cathode. Contamination can also occur because of dendritic growth which traps impurity laden electrolyte within the deposit.

Electrolyte temperature is another important system parameter. Increased temperature reduces the resistance of the electrolyte, which lowers the cost of production. The temperature also controls the solubility of impurities in the solution. A decrease in temperature can cause precipitation of impurity phases. However, heating the electrolyte adds cost to the operation. Thus, most refineries compromise and have electrolyte temperatures between 60 and 65 °C.

Electrolyte impurity concentrations can lead to cathode contamination. Elements that typically accumulate in the electrolyte are nickel, arsenic, antimony, bismuth, and iron. The Group VB elements can be particularly problematic because their standard reduction potentials are very close to that of copper. Another concern that may arise from these elements is the formation of floating slimes. Floating slimes are composed of antimony arsenate, SbAsO₄, and bismuth arsenate, BiAsO₄. These phases form by precipitation away from the anode and can float to the cathode causing contamination. Impurities are typically maintained at acceptable levels in the electrolyte by removal in a bleed stream by electrolysis and crystallization. Recently, ion exchange and solvent exchange have been implemented in the removal of impurities, particularly the Group VB elements (As, Sb, and Bi).
Morphology is also extremely important in maintaining cathode purity. Nodules and dendrites are the most common surface defects that lead to impurities in the cathode. A nodule forms when a conductive particle remains on the cathode surface. The deposit will then grow around the particle encasing it. This results in a bump on the surface. The bump will then act as a ledge which other particles can come to rest on. Thus the nodule becomes larger with the growth of the copper case and more contaminated with slime particles.

Uninhibited growth of the copper electrodeposi t will typically lead to the formation of dendrites. These surface irregularities can lead to entrapment of electrolyte or colloidal particles into the deposit. Additives, such as, thiourea, glue, and chloride, are added to the electrolyte to inhibit the formation of dendrites. While the complete mechanism in which these additives interact with the cathodic surface is not fully understood, the results are reproducible. Thiourea and glue, which are usually added to maintain concentration of 1-3 mg l\(^{-1}\) (ppm), act as leveling agents. It is believed that these organic molecules adsorb onto high spots on the deposit. This blocks these sites, causing deposition to occur at the low areas, which result in a smooth deposit. Chloride is contained in the makeup water or added as NaCl with typical concentrations being 40-60 mg l\(^{-1}\) (ppm). Cl\(^-\) acts as a grain refiner for the deposit. Proper concentrations of these additives result in a smooth and dense cathode with suitable purity.
1.1.2 Hydrometallurgical Copper Processing

The leaching of copper from ores has been practiced for many centuries, but the large-scale recovery of high purity copper by hydrometallurgical processing has only recently been achieved. Leaching of copper from weathered pyrite was performed in Spain as early as the 1700's [1]. Recovery of copper was achieved primarily by cementation onto iron. Iron cementation produced a copper-iron sponge that required further processing. Cementation and precipitation were the main recovery methods until earlier this century and produced impure copper products. Electrolysis or electrowinning of 99.15 to 99.85 percent copper from vat leaching of high grade copper ore was proven feasible in the United States in 1914 [3]. However, the large-scale hydrometallurgical production of high purity copper from low-grade ores was still decades away.

In 1968, the first commercial plant to utilize solvent extraction to concentrate and purify leach solutions was operated in Miami, Arizona by Ranchers Exploration and Development Co. Ltd. Solvent extraction had been used for numerous years in analytical laboratories for the separation and concentration of compounds for subsequent analysis. The use of amine solvent extraction was proven for the recovery of uranium from leach liquors in 1956. The recovery of copper from leach solutions was not possible on a large scale basis until the development of hydroxyoximes. The first hydroxyoximes, such as LIX 63 and 64, had serious limitations. The second generation, LIX 64N, exhibited much higher selectivity of copper over iron, faster kinetics, and improved phase separation. Future generations have only improved upon these
characteristics. The development of these extractants has led to development of the solvent extraction electrowinning process (SX/EW).

SX/EW is shown schematically in Figure 1.2. The process starts with the blasting and crushing of the ore. The use of crushing is dependent on the head grade of the ore. Reducing the size usually increases the leaching rate and thus recovery occurs more rapidly. However, the cost of crushing must be overcome. Low grade ores are sometimes leached as run-of-mine product. Prior to the irrigation of heaps on prepared pads or stockpiles of waste and low-grade ore with dilute sulfuric acid, a cure will sometimes be used. The cure solution is typically higher strength acid which is allowed to react with the ore for several days. The result of the cure is a quicker recovery of copper with less total acid consumption.

Materials that are most amenable to leaching with sulfuric acid are oxides and secondary sulfides. Leaching of stockpiles (formerly called dump leaching) which contain primary sulfides usually involves bacterial assisted leaching and has leach times measured in years.
$H_2SO_4$ Leach Solution, recycle from solvent extraction

Make-up $H_2SO_4$

- Mine Waste 'Dumps' (~0.2% Cu)
- Oxidized ore 'Heaps' (0.5 - 2.0% Cu)

Sump pumps

1 to 5kg Cu m$^{-3}$

Sump pumps

Solvent Extraction

Electrolyte, 50 kg Cu m$^{-3}$

Electrowinning

Cathodes

Melting

Molten Copper, (20 ppm Impurities ~250 ppm Oxygen

Continuous Casting

Fabrication and Use

Figure 1.2 Schematic Diagram of Hydrometallurgical Processing of Copper. Biswas and Davenport [1].
After leaching, the pregnant leach solution (PLS) is collected and pumped to a solvent extraction plant. Solvent extraction usually involves several extraction and stripping stages. In extraction, the PLS is mixed intimately with an organic phase containing the copper extractant, HR. The copper is preferentially extracted into the organic phase according to the equation (Eq. 4).

\[
\text{Extraction: } \text{CuSO}_4 + 2 \text{HR} \rightarrow \text{CuR}_2 + \text{H}_2\text{SO}_4 \quad (\text{Eq. 4})
\]

The copper bearing organic phase separates from the copper depleted aqueous solution or raffinate because of the immiscibility and the density of the two solutions. The raffinate that has been replenished with acid is returned to the heap or waste stockpile to leach more copper. The organic phase is cycled to the stripping stage. In stripping, the organic phase is mixed with an aqueous solution of higher acidity to reverse the previous equation (Eq. 5). This causes the copper to leave the organic phase and re-enter the aqueous phase. This process results in conversion of the organic extractant into its acid form or regeneration. The regenerated organic is then recycled back to the extraction phase. The aqueous solution that is rich in copper and has very low concentrations of impurities is pumped to a tankhouse for copper recovery.

\[
\text{Stripping: } \text{CuR}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + 2 \text{HR} \quad (\text{Eq. 5})
\]

The recovery of copper from the rich electrolyte occurs by electrowinning. Electrowinning consists of the plating of copper onto the cathode and the evolution of oxygen at the anode. The chemical reactions involved with these processes are shown in equations 6 and 7, respectively. Plating of copper occurs on copper starter sheets,
titanium blanks or stainless steel blanks. To ensure suitable purity, morphology is critical and additives are sometimes included in the electrolyte to help produce a smooth and dense deposit. The anodes are typically alloys of Pb-Ca or Pb-Ca-Sn. Anodes are quasi-inert (i.e. dimensionally stable) in the electrolyte and provide an adequate surface for oxygen evolution. Purities of greater than 99.999% have been produced using the SX-EW process.

\[
\text{Cathode: } \quad \text{CuSO}_4 + 2 \text{e} \rightarrow \text{Cu}^+ + \text{SO}_4^{2-} \quad \text{(Eq. 6)}
\]

\[
\text{Anode: } \quad \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + 0.5 \text{O}_2 + 2 \text{e} \quad \text{(Eq. 7)}
\]

1.1.3 Secondary Copper Processing

The secondary processing of copper from scrap has many of the same processes as conventional processing except for the mineral processing steps. The process involved in recovering copper from scrap material depends on the grade. High-grade scrap is virtually pure copper, which needs only to be re-melted and cast into useful shapes. Lower grade material is processed by pyrometallurgical methods and electrorefining. A schematic flow sheet for treating low-grade scrap is given in Figure 1.3. While the furnaces are slightly different than those used to smelt sulfide concentrates, the processing is essential the same. A significant difference can occur in the resulting composition of the copper anode because scrap can contain large amounts of other metallic elements. This results in higher impurity loading in the anode than those produced from clean ores, which can aggravate problems during electrorefining. To illustrate this point two anode compositions are listed in Table 1.1. The two anodes were submitted by the same electrorefinery. The anode form ore was produced by the
Figure 1.3 Schematic Diagram of Secondary Copper Processing. Biswas and Davenport [1].
Table 1.1
Comparison of Anode Compositions from Ore and Scrap

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Anode from Ore</th>
<th>Anode from Scrap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>805</td>
<td>20</td>
</tr>
<tr>
<td>Te</td>
<td>133</td>
<td>16</td>
</tr>
<tr>
<td>As</td>
<td>402</td>
<td>654</td>
</tr>
<tr>
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<td>1069</td>
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<tr>
<td>Bi</td>
<td>195</td>
<td>274</td>
</tr>
<tr>
<td>Ni</td>
<td>1045</td>
<td>3456</td>
</tr>
<tr>
<td>Pb</td>
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<td>387</td>
</tr>
<tr>
<td>Sn</td>
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<td>153</td>
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</tr>
<tr>
<td>Zn</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>Ag</td>
<td>1589</td>
<td>352</td>
</tr>
<tr>
<td>Au</td>
<td>18</td>
<td>1</td>
</tr>
<tr>
<td>O</td>
<td>2124</td>
<td>1548</td>
</tr>
</tbody>
</table>

company's smelter. The other was being toll refined for a secondary copper producer. It should not be assumed that dirtier anodes come from a secondary producer. By blending different grades of scrap, secondary smelters can achieve anode impurity levels lower than anodes produced from complex ores.

1.2 Recent Development and Trends in Electrorefining

The production of copper by electrorefining has improved substantially since it was established in the late nineteenth century. Improvements in current efficiency, materials handling, electrolyte purification, and automation of process control have led to substantial production increases, particularly in the last several decades. According to Schloen and Davenport [2], the electrorefining capacity of 53 commercial tankhouses located throughout the world was 10.8 million metric tons in 1995. Some of the recent developments that have led to increases in production and cathode quality have been
reusable cathodes, improved electrolytic bleeds, monitoring of additives, periodic current reversal, and anode preparation machines.

1.2.1 Reusable Cathodes

From the early days of electrorefining, copper starter sheets have been used as the cathode. The sheets are electrowon from stripper cells usually within the refinery. These thin sheets can create difficulties due to warping or bending. In recent years, the use of reusable starter sheets of titanium and stainless steel have become prevalent. Copper is electrodeposited on the mother plate for a suitable time, typically 7-14 days. The copper is then removed, usually by a mechanical stripping machine. Following a visual inspection, the starter sheets are returned to electrorefining cells.

Stainless steel technology has been growing in popularity compared to titanium because of the significantly lower initial capital expenditure. There are two different stainless steel technologies, the ISA process [5] and the Kidd Process [6]. The major difference between the methods is on the bottom of the cathode. The ISA process uses wax to prevent copper deposition and thus produces two cathode sheets (one on each side of the stainless steel blank). The Kidd Process leaves the bottom exposed, which creates two sheets connected at the bottom. The major advantages of the stainless steel technology over traditional copper starter sheets are the avoidance of starter sheet manufacturing and improved verticality. Improvements to the verticality of the cathode have led to fewer shorts, greater current densities, and purer cathodes.
1.2.2 **Electrolyte Bleeds**

While the removal of impurities from the electrolyte has been practiced for many decades, there have been some recent changes in the removal method. Traditionally, the bleeding of impurities involves the use of liberator cells. In a liberator cell, there are several stages of electrowinning followed by crystallization. The electrowinning stages remove copper and the Group VB elements (As, Sb, and Bi). The first electrowinning step usually deposits a fairly pure copper product. The second and sometimes third electrowinning stage removes Cu, As, Sb, and Bi. Following electrowinning, the solution is heated to evaporate water and thus crystallize nickel, cobalt and iron as sulfates.

The removal of As, Sb, and Bi from the bleed streams using solvent extraction and chelating resins has received considerable attention within the last twenty five years. Hoey *et al.* [5] indicated that solvent extraction can be utilized for As removal with a final salable product of bicupric arsenate, which is a precursor for chrome copper arsenate, a lumber preservative. Rondas *et al.* [7] reviewed the solvent extraction of arsenic with TBP, which has been employed at Union Miniere since 1974. Ferric ions hinder the arsenic removal by TBP because of an undefined relationship between As$^{5+}$ and Fe$^{3+}$. Shibata *et al.* [7] related the ability of UR-3300, a chelating resin manufactured by Unitika Co., to remove Sb and Bi selectively from commercial electrolyte. A final product of antimony chloride and bismuth chloride is produced by stripping the resins with 6 N HCl. Dreisinger and Scholey [8] performed laboratory
studies on two phosphonic acid based resins, UR-3300 and C-467, indicating a process to minimize ferric loading on to the resins. Sasaki [9] reported using another chelating resin for Sb removal. The resin was EPORUS MX-2 produced by Miyoshi Oil and Fat Co. Ltd. and could be used with a 2-4 M HCl stripping solution. Toyabe et al. [10] demonstrated that activated carbon can also be used to absorb antimony from the electrolyte. The loaded activated carbon is used as a reducing agent in a furnace within the silver refinery attached to the copper refinery.

1.2.3 Additive Monitoring

Additives, such as chloride, thiourea, glue and Avitone, are used extensively in electrorefining as grain refiners and leveling agents for deposition. They allow the production of smooth dense cathodes which will not encapsulate impurities either in the electrolyte or secondary phases. While additives have been used for many decades, the monitoring of these has only recently been employed. The development of the Reatrol Process by Asarco to monitor thiourea [11] and the CollaMat system for glue by Norddeutsche Affiniere [12] have led to substantial improvements in deposition consistency and improved current efficiency. The Reatrol Process is a patented technique, which utilizes differential pulse polarography to ascertain the active concentration of thiourea by complexation with a dropping mercury electrode. It is said to be accurate to 100 ppb of thiourea. A disadvantage with the Reatrol Process is that it is an off-line measurement. The CollaMet system is a proprietary real-time glue monitoring apparatus. There has been no literature on the details of the system except that it is based on evaluation of potential.
1.2.4 Periodic Current Reversal

Periodic current reversal (PCR) is being employed in at least 11 refineries to increase the rate of cathode production by increasing the applied current density [2]. PCR is a method by which a forward current is applied for a length of time followed by a quick current reversal. The forward to reverse period ratio is typically between 20/1 to 30/1. The reversal of current allows for higher current densities to be employed without causing anode passivation. The advantage arises from the reversal current depleting the built up copper concentration within the anodic boundary layer. This helps avoid the precipitation of copper sulfate, which is one of the causes of passivation. Depleting the copper concentration also affects the localized pH, which can significantly affect the stability of copper oxide films, another cause of passivation. The major disadvantage of PCR is higher energy costs. This has limited the use of this technology.

1.2.5 Anode Preparation Machines

Anode preparation machines are growing in usage by allowing greater current densities, decreasing shorts, and decreasing damage to the electrolytic cells. This is caused by the improved verticality caused by pressing and lug machining and greater control of anode physical dimensions and weight. Anode preparation machines are now found in 23 of the 53 electrorefineries reported in Schloen and Davenport's most recent survey [2].

Anode preparation machines usually consist of at least five critical components: 1) receiving station, 2) anode weighing unit, 3) anode press, 4) lug press and milling and 5) spacing conveyor. The receiving station is where the anodes are loaded into the process
stream of the electrorefinery. This is typically done with a forklift or straddle car. The anodes are then weighed. Anodes with out-of-spec weight are returned for re-casting. By controlling the anode weight, shorts are minimized and post-refinery scrap is minimized. While the least amount of anode scrap is ideal, anodes that break apart in the electrolytic cell can cause damage to the liner and hinder production. After weighing, the anodes are pressed to ensure proper physical dimensions. Pressing can be associated with measuring of anode thickness. Anodes that are too thick or thin are rejected. The lug press and milling is performed to ensure that the anodes will hang straight in the tankhouse and have a proper electrical contact. The final stage is the spacing conveyor. From the conveyor, the anodes are picked up, typically with an overhead crane and placed in the electrorefining cells. Proper spacing is critical to ensure uniform dissolution and minimize shorts. Spacing between anode and cathode (center to center) ranges from 60 to 177.8 mm with most tankhouses operating around 100 mm [2].

1.3 Anode Passivation

Even with these technological advances, passivation of commercial copper anodes still occurs in most modern electrorefineries. Passivation is the inhibition of the dissolution reaction caused by the formation of non-dissolving films. Anode passivation results in lost production capacity, increased power costs, and decreased cathode quality. Thus, the minimization of anode passivation could ultimately improve worldwide copper quality and decrease production costs.
1.3.1 Copper Dissolution

Before the causes of passivation of impure commercial copper anodes can be addressed, an understanding of the mechanism of copper dissolution is needed. Copper appears to dissolve by a two-electron transfer (Eq. 1). However, the likelihood of this occurring is minimal based on statistical thermodynamics and a series of single electron reactions is more likely. Mattsson and Bockris [13] were the first to indicate that the reaction occurs by the two single electron steps with one being the rate-determining step. In a sulfate medium, the reactions occur as shown in (Eq. 8) and (Eq. 9).

\[
\text{Cu} \rightarrow \text{Cu}^+ + e \quad \text{(Eq. 8)}
\]

\[
\text{Cu}^+ \rightarrow \text{Cu}^{2+} + e \quad \text{(Eq. 9)}
\]

The reaction between the cuprous and cupric ions was declared as the rate determined step based on the anodic and cathodic transfer coefficients being asymmetric, 1.64 +/- 0.25 and 0.46, respectively. These transfer coefficients were more recently verified by Stankovic [14] in copper and sulfuric acid concentrations similar to those observed in commercial copper electrorefining.

Bockris and Enyo [15] and Bockris and Kita [16] proposed that the rate-determining step is controlled by charge transfer or surface diffusion at low current densities and only charge transfer at high current densities. Slaiman and Lorenz [17] used a double-pulse galvanostatic method to illustrate that at low current densities the overpotential causing the slowness of (Eq. 9) contains charge transfer and surface diffusion components. The
preference appeared to be related to the experimental conditions. De Agostini, Schmidt, and Lorenz [18] indicated that the oxidation of cuprous ions may be occurring between cuprous ad-ions on the surface and cupric ions in solution. The mechanism of the reaction was investigated as a function of current density by Jardy et al. [19] using a quartz crystal microbalance and rotating ring-disk electrode. It was shown that the dissolution valence was a function of current density and that the mechanism for copper dissolution in 0.1 M Na₂SO₄ acidified to pH 1.5 was:

\[
Cu \rightarrow Cu^+_{\text{(ads)}} + e^- \quad \text{(Eq. 10)}
\]

at current densities less than \(10^{-6} \text{ A/cm}^2\):

\[
Cu^+_{\text{(ads)}} \rightarrow Cu^+_{\text{(sol)}} \quad \text{(Eq. 11)}
\]

\[
Cu^+_{\text{(sol)}} \rightarrow Cu^{2+}_{\text{(sol)}} + e^- \quad \text{(Eq. 12)}
\]

at current densities greater than \(10^{-2} \text{ A/cm}^2\):

\[
Cu^+_{\text{(ads)}} \rightarrow Cu^{2+}_{\text{(sol)}} + e^- \quad \text{(Eq. 13)}
\]

It is readily observed that the complexity of the dissolution mechanism of pure copper leads to some inherent difficulties when discussing the passivation of impure copper anodes.

To further complicate the dissolution mechanism is the ability of copper to disproportionate. At high current densities, cuprous ions can be generated so quickly that they react with each other (Eq. 13). This provides yet another possible chemical or electrochemical route for copper dissolution.
\[ 2 \text{Cu}^{+}_{\text{(sol)}} \rightarrow \text{Cu}^{2+}_{\text{(sol)}} + \text{Cu}^{0} \]  
(Eq. 13)

1.3.2 Passivation of Pure Copper

The passivation of pure copper in a synthetic industrial electrolyte containing nickel at 65 °C was investigated by Ghali and others. Using potentiostatic and voltammetric techniques Garneau et al. [20] generated a passivating film and determined it to be mostly \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\) by X-ray photoelectron spectroscopy and scanning electron microscopy. \(\text{Cu}_2\text{O}\) was also detected after multiple sweeps using cyclic voltammetry. Jin and Ghali [21] found similar results using chronopotentiometry followed by X-ray induced Auger electron spectroscopy (XAES). Gauthier, Manzini and Ghali [22] found copper sulfate and copper oxides by SEM and XAES after passivation in linear sweep voltammetry.

These findings coincide with the discussion presented by Kortum [23] on film formation and growth. An oxide coating on metals is predominantly an ion conducting film which forms only after an increase in voltage caused by the formation of a non-conducting film. Therefore, it is believed for pure copper, a \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}\) (a non-conducting substance) film forms by precipitation from the saturation of the boundary layer. This results in an increase in potential, which allows the formation of \(\text{Cu}_2\text{O}\).

1.3.3 Passivation of Impure Copper Anodes

Under normal industrial electrorefining operating conditions, pure copper will not passivate. Therefore, the ultimate cause of passivation is the impurities contained within
the anode and electrolyte. Impurities in the anode are the result of the original ore or scrap feed. As the anode dissolves, some impurities report to the slimes; others to the electrolyte. Impurities in the electrolyte become concentrated over time in the closed electrolyte system.

The studying of anode impurities has been limited to specially alloyed copper samples and a few commercial copper anodes. The alloyed copper usually contains one or two metallic impurity elements and oxygen. The passivation results from alloys and the electrochemical method used are listed in Table 1.2. Minotas et al. [24] used cyclic voltammetry (CV) on alloys of Cu-Sb, Cu-As, Cu-O to conclude that arsenic and oxygen delay passivation and antimony increased the likelihood of passivation. Bounoughaz et al. [25] studied alloys of Cu-O, Cu-Ag, Cu-Se, and Cu-Ag-Se using CV, chronopotentiometry (CP) and impedance spectroscopy (EIS). It was found that tendency to passivate was Cu < Cu-O < Cu-Ag < Cu-Se < Cu-Ag-Se. Noguchi et al. [26] used copper samples alloyed individually with S, Se, Pb, Ag, Bi, Sn, Ni, and Sb in the range of 2000 to 50000 ppm. Using CP, anodes with sulfur (2000 ppm), arsenic (30000 ppm), bismuth (40000 ppm), and silver (30000 ppm) passivated (impurity level where passivation was first detected is within the parentheses) while samples with nickel, tin, lead, and selenium did not passivate. However, the impurity loading in the samples that did passivate is much higher than normally found in commercial copper anodes. Gumowska and Sedzimir [27] investigated copper alloyed with lead and oxygen
using CP. They concluded that lead contents up to 2 wt% (20000 ppm) did not influence passivation. Oxygen, on the other hand, was found to promote passivation.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Effect on Passivation</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>As, O, Sb</td>
<td>Inhibited Accelerated</td>
<td>CV</td>
<td>[24]</td>
</tr>
<tr>
<td>O, Ag, Se, Ag&amp;Se</td>
<td>Accelerated</td>
<td>CV, CP, EIS</td>
<td>[25]</td>
</tr>
<tr>
<td>S, As, Ag, Bi, Ni, Pb, Sb, Sn</td>
<td>Accelerated No Effect</td>
<td>CP</td>
<td>[26]</td>
</tr>
<tr>
<td>O, Pb</td>
<td>Accelerated No Effect (&lt;2%)</td>
<td>CP</td>
<td>[27]</td>
</tr>
</tbody>
</table>

It is apparent the results using specialty alloys are contradictory. Alloys with single elements also eliminate the possibility of interactions between impurities and may not have a microstructure similar to commercial copper anodes. Therefore, commercial copper anode samples have been studied as well. A summary of findings on passivation using commercial copper anodes is given in Table 1.3. Abe et al. [28] studied thirteen anodes using CP. They illustrated that time to passivation (tp) decreased with increasing oxygen and slimes. Abe and Goto [29], also using CP, illustrated that the susceptibility to passivate increased when nickel, oxygen, or silver levels were high in the anode. Baltazar et al. [30] investigated the effect of arsenic and antimony using twelve different anode samples with chronopotentiometry at near to industrial conditions. Anodes with a molar ratio of As to Sb greater than two resisted passivation. Cheng and Hiskey [31] revealed that increasing arsenic within commercial copper anodes inhibited passivation in CP experiments. Increasing oxygen in anodes with low arsenic (<400 ppm) decreased
tp. Hiskey et al. [32] studied thirteen commercial copper samples using CP and showed that tp decreased with increasing oxygen and antimony and decreasing arsenic.

Table 1.3
Effects of Anode Impurities in Commercial Copper Anodes on Passivation

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Effect on Passivation</th>
<th>Technique</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O, Slimes</td>
<td>Accelerated</td>
<td>CP</td>
<td>[28]</td>
</tr>
<tr>
<td>Ni, O</td>
<td>Accelerated</td>
<td>CP</td>
<td>[29]</td>
</tr>
<tr>
<td>As, Sb</td>
<td>Inhibited if As/Sb &gt; 2</td>
<td>CP</td>
<td>[30]</td>
</tr>
<tr>
<td>As</td>
<td>Inhibited</td>
<td>Accelerated</td>
<td>CP</td>
</tr>
<tr>
<td>O</td>
<td>Inhibited</td>
<td>Accelerated</td>
<td>CP</td>
</tr>
<tr>
<td>As</td>
<td>Inhibited</td>
<td>Accelerated</td>
<td>CP</td>
</tr>
</tbody>
</table>

While all of the aforementioned information is critical in understanding the complex issues involved in anode passivation, none fully elucidates the cause of passivation in impure commercial copper anodes. Passivation is the result of something stopping the ability of copper to dissolve and thus the flow of current. Numerous authors [20-22, 24, 28, 34-40] have reported observations of passivating films, such CuSO₄·5H₂O, Cu₂O and CuO. Though no completely satisfactory passivation mechanism has been introduced, Abe and Gotoh [28] have presented the most complete model in describing oscillations during CP experiments. A schematic of the oscillations observed by these researchers is presented in Figure 1.4. This mechanism associates the oscillations with the precipitation and re-dissolution of CuSO₄·5H₂O. The oscillations are believed to be caused by the instability of a CuSO₄ phase. However, this mechanism is lacking because it disregarded copper oxide formation, which was noted by the authors during the oscillations.
Figure 1.4 Schematic Diagram of Oscillations in a Chronopotentiogram Detected by Abe and Gotoh Using Commercial Copper Anodes in 40 g l⁻¹ Cu, 200 g l⁻¹ H₂SO₄, 20 g l⁻¹ Ni, 50 °C, 400 A m⁻² (after 24 hours at 200 A m⁻²), no agitation, ambient atmosphere [28].

1.3.4 Secondary Phases Within the Anode

To fully realize the effect of each impurity within the electrorefining system, the behavior of that impurity during casting and electrorefining must be understood. With this in mind, the mineralogy and microstructure of anodes will be reviewed. The deportment of the impurities during electrorefining will then be discussed in terms of slimes, non-slime elements, and impurities in the electrolyte.

Chen and Dutrizac [35-37, 41-47], because of their numerous investigations concerning phases in commercial copper anodes, have greatly expanded the available information in this area. They primarily used scanning electron microscopy with an electron
microprobe for morphological and elemental analyses. Their finding are numerous. Some of the more significant ones will be listed here. Silver is mostly contained in solid solution (85% to 95%) with the remainder tied to oxidate and selenide phases [35-37, 46, 48]. Arsenic is also detected in solid solution between 30-60% of its original concentration with the rest occurring as arsenic oxide associated with complex lead-copper-oxide structures [37, 45, 48]. Nickel remains in solid solution up to 3000 pm; above which NiO and/or kupferglimmer forms [37, 42, 47]. The amount of nickel oxide increases toward the set side of the anode due to increased oxygen concentration from the atmosphere. Kupferglimmer, which is Cu$_3$Ni$_{2-x}$SbO$_{6-x}$ with x = 0.1-0.2, is detected when Sb is above 200 ppm. Tin can also substitute for antimony in the kupferglimmer structure. Cuprous oxide was the most abundant inclusion phase. Some of the Cu$_2$O particles are encased by Cu$_2$(Se,Te) shells [35, 37, 41, 48]. These result in selenide spheroids and tubular shape phases. Most tellurium is found in solid solution within the selenide phases except when tellurium is high. In high tellurium anodes, Te can be found in solid solution up to 2-8% of its original concentration and as copper tellurides [45, 46]. Lead is usually found as complex oxides involving copper and Group VB elements associated with Cu$_2$O and Cu$_2$(Se,Te) [35, 41, 43, 48]. Some lead is also found in solid solution. Silicates of various composition have been detected [41, 42, 44].

Research directed by Forsen [49-52] has greatly expanded the understanding of the deportment of nickel within copper anodes. Forsen and Tikkanen indicate that NiO and kupferglimmer will form when nickel is greater than 2500 ppm [52]. This is in
disagreement with the value reported by Chen and Dutrizac. Recent work at the University of Arizona indicates that 2500 ppm is more correct than 3000 ppm [53]. Forsen's group also discovered that both NiO morphology and the abundance of kupferglimmer depend on cooling rate [49, 50, 52]. The abundance of kupferglimmer was also determined as a function of nickel and oxygen concentrations within copper containing 1000 ppm Sb [51].

Finally, Miton [54] using optical and scanning electron microscopy with energy dispersive spectroscopy, studied ten of the same commercial anodes that were electrochemically investigated in this study. His findings were similar in many aspects to the work reported previously except for a focus on grain size. A correlation was made between the maximum average grain size of an anode and time to passivation. Also for a kupferglimmer containing anode, the appearance of kupferglimmer increased as the grain size increased within the anode.

Using this information, a list of the more common phases and elements within commercial copper anodes is given in Table 1.4 from Hiskey and Moats [32].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu, Ag, Au</th>
<th>O, S, Se, Te</th>
<th>As, Sb, Bi</th>
<th>Ni, Zn, Fe, Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phases</td>
<td>Cu\textsuperscript{0}, Ag\textsuperscript{+}, Au\textsuperscript{+}</td>
<td>Cu\textsubscript{2}O, CuO, Cu\textsubscript{2}S, CuS, Cu\textsubscript{2}Se, Cu\textsubscript{2}Te</td>
<td>As\textsuperscript{+}, As\textsubscript{2}O\textsubscript{3}, Cu\textsubscript{3}As, Sb\textsuperscript{+}, Sb\textsubscript{2}O\textsubscript{3}, Bi\textsuperscript{+}, Bi\textsubscript{2}O\textsubscript{3}</td>
<td>Ni\textsuperscript{+}, NiO, kupferglimmer</td>
</tr>
<tr>
<td></td>
<td>(Cu, Ag)Se, Ag\textsubscript{2}Se, Au\textsubscript{2}Te, Ag\textsubscript{2}Te</td>
<td>Cu\textsubscript{2}Te</td>
<td>Cu\textsubscript{2}Se</td>
<td>ZnO, Fe\textsuperscript{+}, Fe\textsubscript{2}O\textsubscript{3}, Pb\textsuperscript{+}, Pb\textsubscript{0}, PbO, Pb-(As, Sb, Bi)-oxides</td>
</tr>
</tbody>
</table>

* - denotes solid solution
It is important to understand for anode passivation which impurities are present and in what phases to predict which of these will not dissolve into the electrolyte. As the copper anode dissolves, refractory (i.e. do not dissolve) inclusions are released at the surface of the anode. After a time, the build up of these inclusions forms a porous barrier that inhibits diffusion of species to and from the surface. This porous barrier in industrial terminology is the anode slimes.

1.3.5 Slimes

Like anode secondary phases, the understanding of the phases present in the slimes layer has been greatly enhanced by Chen and Dutrizac [35-37, 41-48, 55-59]. The important phases that were detected were \((\text{Cu,Ag})_2\text{Se}\) rings, euhedral NiO crystals, \(\text{PbSO}_4\), silicates, kupferglimmer, and various complex oxides. Most of these phases were formed during prior pyrometallurgical processing. During dissolution they are released from the anode. Several phases, however, are formed or transformed during the electrorefining process. Selenium occurs predominantly as a metal deficient copper selenide \((\text{Cu}_{2-x}\text{Se})\) along the grain boundaries of the copper matrix. During electrorefining, silver ions have been shown by Scott [60] and Chen and Dutrizac [55, 58] to rapidly react with the selenides causing a transformation from \(\text{Cu}_2\text{Se}\) to \(\text{Ag}_2\text{Se}\). Hiskey et al. [61] illustrated that this reaction causes a 20% increase in the volume of the selenide phase. This would help to explain why Abe and Goto [29] noted that an anode with high silver exhibited a thicker and denser slimes layer than other anodes. The presence of lead sulfate is another indication of a reaction occurring within the slimes layer. Lead typically occurs as a complex lead oxide associated with various elements.
These inclusions usually dissolve upon exposure to the highly acidic electrolyte. The resulting lead ions precipitate with the sulfate contained within the electrolyte to form PbSO₄ within the slimes barrier.

An understanding of the slimes chemistry and morphology is imperative because the slimes layer can inhibit diffusion, which leads to passivation. Abe and Gotoh [34] illustrated that pure copper, which did not passivate, passivated when masked with an artificial slimes layer (Millipore filter paper). It was also demonstrated that the tendency to passivate increased with decreasing pore size. Thus, a slimes layer that is denser and thicker will increase the probability of passivation. This was perhaps shown more precisely by Abe, Burrows, and Ettel [28], who demonstrated that the time to passivation measured by chronopotentiometry decreased with increasing amounts of slime formers within commercial copper anodes. Petkova [62] performed a sedimentary study to determine that the particle sizes varied from 0-30 microns in diameter with most being between 10-30 microns.

1.3.6 Non-Slime Impurities

There are impurities in the anodes that are not usually involved with anode slime formation that can also affect passivation. These elements, even at low concentration, can affect the complex copper dissolution reaction. Stankovic, using pure copper, illustrated that Fe [63] slightly accelerated, As [64] significantly increased, and Sb [64] slightly hindered the dissolution reaction of copper when present in the electrolyte at concentrations ranging from 10⁻⁵ to 10⁻¹ M. In commercial anodes, the most significant
impurities appear to be oxygen and the Group VB elements (As, Sb, and Bi). Minotas, Djellab, and Ghali [24], using cyclic voltammetry, concluded that oxygen was beneficial in delaying passivation. However, Abe, Burrows, and Ettel [28] had previously indicated that oxygen content in commercial anodes was detrimental from chronopotentiometric results. This latter viewpoint of oxygen accelerating passivation was also concluded by Bounoughaz, Manzini, and Ghali [25] and Hiskey et al. [61].

Arsenic, antimony, and bismuth are very troublesome elements in copper electrowrefining. Their reduction occurs at nearly the same voltage as copper, which can cause cathode contamination during periods of passivation. Another problem caused by the Group VB elements is their accumulation in the electrolyte, which can lead to the formation of floating slimes. Floating slimes, which are SbAsO₄ and BiAsO₄ [65], form by precipitation typically away from the anode surface. In the electrolyte, they can float to the cathode where they can be entrapped; thus causing contamination. However, none of these reasons overtly affects anode passivation. Hiskey et al. [61] demonstrated using chronopotentiometry on commercial anodes, that arsenic inhibits passivation, antimony accelerates it, and bismuth has a complex interaction. Finally, arsenic has been reported by Demaeral [66] to cause a decrease in the adhesion of slimes, which would hinder passivation by the removal or sloughing of the diffusion barrier.

Hiskey et al. [61] proposed that the effect of Group VB elements and oxygen could be explained by using a bi-layer passivation model. It is theorized that the slimes layer,
because of its hindrance to diffusion, creates a substantial boundary layer adjacent to the anode surface. The concentrations of ions can be extremely different in this boundary layer than that in the bulk electrolyte. As oxides, particularly of As, Sb and Bi, dissolve, they either cause acid consumption or generation. Samples of possible reactions are as follows:

\[
\begin{align*}
\text{Cu}_2\text{O} + 2\text{H}^+ &\rightarrow \text{Cu}^{2+} + \text{Cu} + \text{H}_2\text{O} \quad \text{(Eq. 10)} \\
\text{As}_2\text{O}_3 + 3\text{H}_2\text{O} &\rightarrow \text{H}_2\text{AsO}_4 + 2\text{H}^+ + 2\text{e} \quad \text{(Eq. 11)} \\
\text{Sb}_2\text{O}_3 + 2\text{H}^+ &\rightarrow 2\text{SbO}^+ + \text{H}_2\text{O} \quad \text{(Eq. 12)} \\
\text{Bi}_2\text{O}_3 + 6\text{H}^+ &\rightarrow 2\text{Bi}^{3+} + 3\text{H}_2\text{O} \quad \text{(Eq. 13)}
\end{align*}
\]

The consumption of hydrogen ions can lead to a localized area of high pH at the anode surface. This can lead to the formation of cuprous oxide by several reactions including the reverse of (10) and cause passivation. It would appear that cuprous oxide would be unstable in the highly acidified electrolytes utilized, but due to the diffusion barrier caused by the slimes layer, localized pH conditions could be favorable for this phase to form. Arsenic, which is the only impurity to show an inhibiting effect on passivation, could generate acid by (11), which would hinder the formation of \( \text{Cu}_2\text{O} \).

1.3.7 Electrolyte

The electrolyte composition and temperature play a critical role in passivation. Numerous researchers have shown that passivation is aggravated by increasing the copper concentration, the acid concentration, or decreasing the temperature [28, 40, 67-]
Noguchi et al. showed that time to passivation decreased with increasing Sb\(^{3+}\), As\(^{3+}\), Bi\(^{3+}\) and dissolved O\(_2\) in the electrolyte [26]. Abe et al. demonstrated that passivation time decreased with increasing nickel added as nickel sulfate [28].

Several recent studies have focused on the effect of additives on passivation in laboratory experiments. Hiskey and Cheng illustrated that time to passivation is a function of thiourea [70]. For small addition, 1-5 ppm, thiourea improves the passivation behavior, but for large addition, greater than 15 ppm, passivation times decreased. Jin et al. showed that the addition of amino acid chelating agents can inhibit passivation. In particular ethylenediaminetetraacetic acid (EDTA), diethylenediaminepentaacetic acid (DTPA), and triethylenediaminehexaacetic acid (TTHA) show some benefit. All three exhibit an optimal concentration for extending passivation times [71]. Jin and Ghali studied the effects of several aromatic nitro compounds. The most beneficial to inhibiting passivation were 3, 5 - dinitrosalicylic acid and 3, 5 - dinitrobenzoic acid [66].

All of the additive compounds listed above have the ability to stabilize cuprous ions [71-73]. Therefore, it would appear that increasing the cuprous concentration increases the time to passivation. This coincides with the combined observations of Noguchi et al. [26] and Bombach et al. [74]. Recall that Noguchi showed that passivation time decreased with increasing dissolved O\(_2\). Bombach et al. demonstrated that Cu\(^+\) ion decreased with increasing dissolved O\(_2\). Combining these two observations would seem
to indicate that increasing the cuprous content might be beneficial to passivation. Therefore, cuprous stabilizing compounds might be interesting to study. Parker et al. [75] studied several copper(I) complexing ligands in aqueous solutions and ranked them by strength accordingly: \( \text{CN}^- \gg \text{S}_2\text{O}_3^{2-} > \text{Me}_2\text{NCHS} > \text{KI} > \text{NH}_3 > \text{C}_3\text{H}_5\text{N} > \text{KBr} > \text{KCl} > \text{C}_3\text{H}_5\text{OH} \geq \text{MeCN, CO, C}_2\text{H}_4 > \text{C}_3\text{H}_6 \). Steppan et al. [76] showed that poly(ethylene) glycol stabilizes cuprous ions. Yokoi et al. [77-79] indicated that cuprous ions increased with increasing chloride up to 106 ppm of chloride in de-aerated electrorefining solutions.

1.4 Electrochemical Techniques

Since electrorefining and passivation are electrochemical processes, the use of electrochemical techniques can be used to elucidate the mechanisms and reactions involved. Several common techniques were used in this investigation and these will be reviewed in the following sections.

1.4.1 Chronopotentiometry

The main electrochemical technique used was chronopotentiometry (CP). In this type of experiment, a constant current is applied as a step function and held for the duration of the test. Potential is then measured as a function of time. Constant current experiments are useful in that the boundary conditions are based on the known current or fluxes. A disadvantage is that double-layer charging occurs throughout the experiment. Another disadvantage is that stepwise reactions are difficult to identify. Even with these
disadvantages, Cheng and Hiskey have shown that using CP with 3820 A m\(^{-2}\) for commercial copper anodes provides sensitivity that other techniques can not [31].

A typically chronopotentiogram (also referred to as CP) for a commercial copper anode is presented in Figure 1.5. Each chronopotentiogram exhibits four characteristic regions - I active dissolution, II pre-passivation, III passivation on-set, IV passivation. Each region contains information that will be used to construct a passivation mechanism. The single most valuable and identifiable value from the plot is \(t_p\) or time to passivation which occurs between Region II and Region III. The time to passivation has been shown to be a function of anode chemistry [61].

![Chronopotentiogram Diagram](image)

Figure 1.5 A typical chronopotentiogram for a commercial copper anode in 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, ambient atmosphere.

1.4.2 Voltammetry

Voltammetry utilizes a potential scan to observe changes in current as a function of voltage. Two common voltammetries are linear sweep and cyclic. In linear sweep
voltammetry (LSV), the potential is increased at a constant rate from an initial to a final voltage. Cyclic voltammetry (CV) is like LSV in the use of a constant scan rate; however as the name implies, the potential is cycled between two values. The cycling process can be repeated numerous times to determine how the reaction is affected. The measured current is generated as a function of the potential versus the reversible potential of the reaction in question, the sweep rate, the surface area, diffusion coefficients of the reacting species, and concentration in certain cases. There are several important parameters that can be measured. Of these, the peak current, the peak potential, and the limiting current are usually quoted.

Kucharska-Giziewicz and MacKinnon identified five distinct regions using CV on commercial copper anodes, particularly those rich in silver [80-82]. The five regions were (1) initial dissolution, (2) 1st peak, (3) 2nd peak, (4) oscillations, and (5) second dissolution. While these authors indicated trends between these regions and anode composition, Cheng and Hiskey believed that neither LSV nor CV was sensitive enough to discern multiple elemental effects [31]. Because of this, LSV and CV will be used to provide only complementary data to CP in this investigation.

In particular, voltammetry was utilized to determine the apparent diffusion coefficient of Cu^{2+} in synthetic industrial electrolytes. LSV was used in conjunction with a rotating disc electrode. Rotating disc electrodes use the principal of forced convection to establish stabilized hydrodynamic conditions and laminar flow near the electrode
surface. These conditions are essential to maintain a constant diffusion or Nernst boundary layer. Under these conditions, the diffusion coefficient can be calculated from the limiting current by the Levich equation

\[ i_l = 0.620 \text{nFAD}_o^{2/3} \omega^{1/2} \nu^{-1/6} \]  
\[ \text{(Eq. 14)} \]

where \( i_l \) is the limiting current, \( n \) is the number of electrons involved in the reactions, \( F \) is Faraday's constant, \( A \) is the surface area, \( D_o \) is the diffusion coefficient, \( \omega \) is the rotational frequency in radians and \( \nu \) is the viscosity in \( \text{cm}^2 \text{sec}^{-1} \).

1.4.3 Electrical Impedance Spectroscopy

The last technique utilized in this investigation was electrical impedance spectroscopy (EIS). This electrochemical technique utilizes an AC signal of varying frequency and measures the impedance and phase of the resulting signal. Using this information, an equivalent circuit can be constructed to model the system. Dissolution and deposition of metals near their reversible potential can typically be modeled using a simple R(RC) circuit as shown in Figure 1.6. A schematic of the resulting Nernst plot from the EIS data is displayed in Figure 1.7. The modeling of EIS data has to be done carefully and in conjunction with other electrochemical techniques. This is because numerous equivalent circuits can be constructed to mathematically simulate the measured data.
Figure 1.6 Equivalent circuit for simple metal dissolution or deposition reaction near the reversible potential. \( R_s \) is the solution resistance, \( R_{CT} \) is the charge transfer resistance and \( C_d \) is the double layer capacitance.

Figure 1.7 A schematic of the Nernst or impedance plant plot for the equivalent circuit in Figure 1.6.

Compere et al. used EIS with potentiodynamic (LSV) and galvanostatic (CP) to study passivation of three commercial copper anodes and pure copper [83]. While the impedance spectra were useful, it appears that they are best used to study anode passivation in tandem with the above mentioned techniques.
Using the data generated by CP, LSV, CV, and EIS, a complete passivation mechanism that incorporates copper sulfate, copper oxide, and slimes generation will be presented. This mechanism will then be used to help explain trends and tendencies with respect to the effect of anode composition and electrolyte concentrations on passivation behavior. Finally, a model capable of indicating the tendencies of anodes to passivate will be developed.
2 EXPERIMENTAL

2.1 Commercial Copper Anodes

Seventy-three anode samples were received from ten companies with varying compositions and physical dimensions. This collection of specimens is believed to be the most diverse set of commercial copper anodes assembled for studying anode passivation. Chemical analyses were performed on chips either provided by the companies or cored from the anode samples. The chemical analyses were performed by BHP Copper personnel at their San Manuel, AZ facility using a Leco RO-16 oxygen analyzer and spark emission spectroscopy. The compositions for the anode samples are listed in Table 2.1. A few experiments were conducted with pure copper to elucidate some mechanistic aspects. The pure copper was electrowon cathode from BHP Copper - San Manuel. The supplied composition is also given in Table 2.1.
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Because of time constraints, about half of the samples were used for electrochemical testing. The selection criteria was based on generating the widest range possible for each impurity and using at least four anodes from each company. From these considerations, forty-four anodes were selected. They are listed in Table 2.2.

Table 2.2

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2.2 Electrode Preparation

A section of each selected commercial anode sample was carefully machined to produce a working electrode. Working electrodes were carefully machined from these sections into cylinders of 1.1 cm in diameter and at least 1 cm in height. If possible, each electrode was taken from the set side of each sample. Electrical contact was provided by soldering a copper or aluminum wire to the back surface (away from the set side) of the cylinder using a lead-tin low temperature melting alloy. The electrode was then mounted to a length of glass tubing (1.2 cm ID) with epoxy resin. The resin also protected the copper piece from electrolyte contact except for the circular face of the cylinder. This exposed face had a surface area of 1 cm². The glass tubing provided rigidity and
protection from the electrolyte for the contact wire. A schematic diagram of a working electrode is display in Figure 2.1.

Figure 2.1 Schematic Diagram of Working Electrode Used in Many of the Electrochemical Experiments.

2.3 Electrolyte

A synthetic electrolyte was utilized for all electrochemical testing. The electrolyte was prepared by using ACS reagent grade chemicals with no further treatments (except glue which was obtained from BHP Copper) and 18.2MΩcm deionized water. Unless otherwise noted, a standard electrolyte composition of 40 g l⁻¹ Cu (0.63 M) and 160 g l⁻¹ H₂SO₄ (1.66 M) was used at a temperature of 65 °C +/- 0.5 °C. The copper source chemical was CuSO₄·5H₂O. For the experiments where electrolyte composition was
studied, the following procedure was used. The copper and acid concentrations were 40 g l⁻¹ and 160 g l⁻¹, respectively, unless that was the variable being studied. Electrolytes with impurities were typically prepared by adding the desired concentration of contaminant to the standard electrolyte and allowing the solution to come to equilibrium. Additives that are known to decompose with time in the electrolyte, such as thiourea and glue, were added just prior to heating the electrolyte. The compounds used as sources for each impurity are listed in Table 2.3.

Table 2.3
Source Compounds for Impurities

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<tr>
<th>Impurity</th>
<th>Source Compound</th>
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<tr>
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<td>Thiourea</td>
<td>Thiourea</td>
</tr>
<tr>
<td>Glue</td>
<td>Glue</td>
</tr>
<tr>
<td>As</td>
<td>As₂O₅, As₂O₃, and NaH₂AsO₄</td>
</tr>
<tr>
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<td>NaBr</td>
</tr>
<tr>
<td>Polyethylene Glycol</td>
<td>Polyethylene Glycol</td>
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</table>

2.4 Electrochemical Techniques

2.4.1 Chronopotentiometry

Chronopotentiometry (CP) was performed to observe the effect of compositional and electrolyte variables on the passivation during anodic dissolution. The CP tests were performed in a one liter three-electrode cell, purchased from EG&G Instruments Inc. The working, auxiliary, and reference electrodes were a cylinder from an anode sample, a length of high purity copper rod and a saturated mercurous sulfate electrode (MSE), respectively. The working and counter electrodes were prepared by polishing with
silicon carbide paper from 180 grit to 600 grit and cleaning with 18 MΩcm deionized water in an ultrasonic bath for five minutes. The electrodes were rinsed with a copious amount of deionized water and transferred to the electrolytic cell containing one liter of synthetic electrolyte held at 65.0 °C +/- 0.5 °C.

2.4.1.1 Standard Procedure

The electrodes were allowed to equilibrate with the system by being held in the electrolyte at open circuit potential for five minutes. A constant current density of 3820 A m⁻² was then applied using an EG&G model 273 Potentiostat/Galvanostat controlled by HEADSTART software for the duration of the test. 3820 A m⁻² was selected based on previous work by Cheng and Hiskey [31] which illustrated that this current density results in the enough sensitivity to observe the effect of anode composition on passivation in an acceptable time frame. Other current densities were employed to study the effect of that parameter on passivation characteristics of anodes and pure copper. Potential-time (E-t) responses were collected as averages of two-second intervals by a 55Z IBM PS/2 computer. The experiments were typically run for 3600 seconds. All tests were conducted in air under static conditions.

During the initial testing, several anodes exhibited larger variability than expected. This variability seemed to be related to the first test of an anode or those anodes with long passivation times or significant porosity. Therefore, numerous (three to six) replications were conducted to ensure that accurate and dependable values were generated. Due to
time constraints during the testing of electrolyte variables, replications were only conducted if the results were in question.

2.4.1.2 Fast Scan Procedure

The fast scan chronopotentiometry experiments were conducted in a very similar manner to the standard procedure. The exceptions involved the control of the Potentiostat/Galvanostat and data acquisition. The EG&G model 273 Potentiostat/Galvanostat was programmed to apply 382 mA of current using the front face controls. Data was acquired through the external port, which was connected to a National Instruments Lab-PC-1200/AI data acquisition card with 12-bit resolution. The data was streamed from the card into a spreadsheet format by using LabView 4.0. Potential samples were taken at a rate of 500 per second compared to once every two seconds in the standard procedure.

2.4.2 Voltammetry

Voltammetry was also used to investigate the effect of impurities on the electrochemical response of commercial copper anodes. Linear sweep voltammetry and cyclic voltammetry were used primarily to investigate various details observed in the chronopotentiometry study.

2.4.2.1 Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) was conducted in a one-liter three-electrode cell with the electrodes arranged similar to the CP tests. The supporting electrolyte was again 40 g l⁻¹ Cu²⁺ and 160 g l⁻¹ H₂SO₄ made from ACS reagent grade chemicals. The electrodes
were prepared using the same technique as used in the CP study. The electrodes were allowed to equilibrate with the system for five minutes before a potential was applied. Polarization curves were generated for each anode by sweeping from the open circuit potential to 2.6 V at a scan rate of 0.1 mV/sec. A model 273 Potentiostat/Galvanostat, controlled by M352 SoftCorr II Corrosion Software (provided by EG&G Instruments, Inc.), was used for these measurements. Data was collected using an IBM 55Z PS/2 computer.

2.4.2.2 Cyclic Voltammetry

Cyclic voltammetry was performed to elucidate observations made in the CP tests. Again, the tests were conducted in a three-electrode cell with the electrodes prepared and arranged as discussed for the CP study. The electrolyte was 40 g l⁻¹ Cu²⁺ and 160 g l⁻¹ H₂SO₄ held at 65°C in air under static conditions. The potential was swept from the open circuit potential, approximately 0.26 V vs. NHE, to 3.14 V and then back to the open circuit potential at a scan rate of 20 mVs⁻¹. Five scans were performed successively with no delay time between scans. A model 273 Potentiostat/Galvanostat, controlled by M352 SoftCorr II Corrosion Software (provided by EG&G Instruments, Inc.), was used for these measurements. Data was collected using an IBM 55Z PS/2 computer.

2.4.2.3 Diffusion Measurements

The diffusivity of cupric ion was determined by depositing copper using linear sweep voltammetry in synthetic industrial electrolytes of various copper and acid concentrations and temperatures. A three-electrode setup was utilized with the working, auxiliary, and
reference electrodes being a high temperature rotating platinum disc electrode with a
diameter of 5 mm obtained from Pine Instruments, a section of copper starter sheet
obtained from BHP Copper, and a saturated mercurous sulfate electrode, respectively.
All tests were conducted in approximately 650 ml of electrolyte contained in a jacketed
reactor to maintain the desired temperature with +/- 0.5 °C precision. To de-oxygenate
the system, high purity N₂ was sparged into the electrolyte for one hour prior to each
experiment and used to blanket the electrolyte during the actual electrochemical
measurements.

Once the rotation speed of the working electrode was set, the system was allowed to
equilibrare for five minutes. This was done to ensure a constant hydrodynamic layer at
the electrode surface. The potential was then swept from +0.317 V (vs. the NHE) to -
0.583 V at a rate of 10 mV s⁻¹ to deposit copper on the working electrode. From the
deposit scan, the limiting current was determined at around -0.333 V. The copper deposit
was then removed by scanning from +0.317 to +1.817 V. The anodic scan was usually
stopped after the current had reached zero. Visual inspection of the working electrode
was used to ensure all the copper had dissolved prior to starting the next sweep. The
cathodic and anodic scans were then repeated at four other rotation speeds. A CS-2000
Potentiostat/Galvanostat system from Cyprus Systems Inc. was used to control the
experiment and collect the data. According to the Levich [84] equation:

\[ i_l = 0.620nFAD^{2/3} \omega^{1/2}v^{-1/6}C_o \]  

(Eq. 14)
a plot of the limiting current versus $\omega^{1/2}$ (rotation frequency) should yield a straight line with a slope of $0.620nFAD^{2/3}v^{-1/6}C_o$ where $n$ is the number of electrons transferred, $F$ is Faraday's constant, $D$ is the diffusion coefficient in cm$^2$ s$^{-1}$, $v$ is viscosity in cm$^2$ s$^{-1}$, and $C_o$ is the bulk electrolyte concentration of copper in moles cm$^{-3}$. Thus, from the slope the diffusion coefficient can be calculated.

2.4.3 Impedance Spectroscopy

A flat cell obtained from EG&G Instruments (Model K0235) was used for the impedance measurements. The working, counter and reference electrodes were similar to those used in the linear sweep experiments. For this test, 300 ml of the electrolyte at 65°C ± 0.5°C were used for each test.

An EG&G model 273 Potentiostat/Galvanostat and an EG&G model 5210 two-phase lock-in analyzer were controlled by M398 Electrical Impedance Software (provided by EG&G Instruments, Inc.), to perform the impedance spectroscopy. For the rest potential measurements, a single sine was used with an amplitude of 5 mV. The frequency was swept from 100 kHz to 100 mHz. The passive measurements were conducted after the voltage was stepped into the passive region as determined from each anode's voltammograms. This voltage was usually around 0.8 V. This voltage was maintained for 20 minutes prior to the impedance measurements. The passivated impedance spectra were obtained using the same perturbation and frequency range as the open circuit measurements.
3 RESULTS

3.1 Correlation Between Impurities

Since the anodes collected are believed to be the largest and most diverse set of anodes ever published, it provided a unique opportunity to determine if any correlations existed between impurity concentrations. It was somewhat surprising, given the very different sources of anodes, that a relationship was observed between the amounts of silver and selenium within an anode. The silver and selenium compositions of the seventy-three anode samples are plotted in Figure 3.1 along with other commercial copper anode compositions taken from the literature. Considering the extremely diverse sources, it would appear that silver and selenium content in anodes are closely related regardless of the prior source or processing.

3.2 Chronopotentiometry

The main electrochemical technique utilized in this investigation was chronopotentiometry. As shown in Section 1, CPs of commercial copper anodes typically exhibit four different regions with three unique values ($t_p$, $t_p'$, and $t_p''$). These regions and values will change depending on the impurities within the anode or the composition of the electrolyte. All of the CPs generated in this investigation are presented in Appendix 1. It is believed that this atlas of electrochemical data is the largest of its kind ever published investigating the effect of anode composition on passivation during copper electrorefining.
During the first part of this investigation, great caution was taken to determine reproducibility for each anode. That is why numerous experiments were performed for each anode sample. Examination of each anode's CPs indicates that variations occurred in passivation times from test to test. The most reasonable experiments were then used to determine average passivation values \((t_p, t'_p, t''_p)\), duration of Regions II and III \((\Delta t_{II} \text{ and} \ \Delta t_{III})\)
At $\Delta t_{III}$, respectively)) and standard deviation for each anode. The significant impurity concentrations for each anode along with the average and standard deviation for $t_p$ are listed in Table 3.1. All passivation values henceforth will be the average value.

The chronopotentiometric results will be presented in three subsections with the emphasis in each being: 1) correlation between the regions and values of the CPs, 2) the effect of individual impurities, and 3) the effect of electrolyte constituents.
### Table 3.1
Selected Chemical Analyses and Time to Passivation Values for Anode Samples

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<td>284</td>
<td>17.1</td>
<td>1544</td>
<td>1525</td>
<td>105</td>
</tr>
<tr>
<td>MCCA-53</td>
<td>523</td>
<td>116</td>
<td>223</td>
<td>649</td>
<td>876</td>
<td>855</td>
<td>1533</td>
<td>1036</td>
<td>34.3</td>
<td>1395</td>
<td>962</td>
<td>69</td>
</tr>
<tr>
<td>MCCA-54</td>
<td>577</td>
<td>133</td>
<td>76</td>
<td>467</td>
<td>2521</td>
<td>580</td>
<td>2834</td>
<td>511</td>
<td>25.5</td>
<td>3496</td>
<td>1233</td>
<td>9</td>
</tr>
<tr>
<td>MCCA-55</td>
<td>605</td>
<td>134</td>
<td>75</td>
<td>459</td>
<td>2478</td>
<td>606</td>
<td>2811</td>
<td>516</td>
<td>25.9</td>
<td>2632</td>
<td>1288</td>
<td>36</td>
</tr>
<tr>
<td>MCCA-57</td>
<td>538</td>
<td>121</td>
<td>71</td>
<td>440</td>
<td>2430</td>
<td>610</td>
<td>2884</td>
<td>520</td>
<td>27.6</td>
<td>2084</td>
<td>1221</td>
<td>22</td>
</tr>
<tr>
<td>MCCA-59</td>
<td>572</td>
<td>132</td>
<td>71</td>
<td>447</td>
<td>2440</td>
<td>588</td>
<td>2834</td>
<td>514</td>
<td>26.7</td>
<td>2305</td>
<td>1250</td>
<td>46</td>
</tr>
<tr>
<td>MCCA-64</td>
<td>299</td>
<td>61</td>
<td>23</td>
<td>181</td>
<td>803</td>
<td>84</td>
<td>73</td>
<td>328</td>
<td>19.5</td>
<td>3120</td>
<td>1977</td>
<td>114</td>
</tr>
<tr>
<td>MCCA-65</td>
<td>303</td>
<td>64</td>
<td>26</td>
<td>182</td>
<td>801</td>
<td>88</td>
<td>74</td>
<td>333</td>
<td>20.6</td>
<td>3046</td>
<td>1874</td>
<td>61</td>
</tr>
<tr>
<td>MCCA-67</td>
<td>299</td>
<td>53</td>
<td>22</td>
<td>125</td>
<td>616</td>
<td>45</td>
<td>56</td>
<td>343</td>
<td>18.2</td>
<td>2520</td>
<td>1778</td>
<td>152</td>
</tr>
<tr>
<td>MCCA-72</td>
<td>404</td>
<td>53</td>
<td>25</td>
<td>201</td>
<td>826</td>
<td>49</td>
<td>59</td>
<td>334</td>
<td>18</td>
<td>2995</td>
<td>1363</td>
<td>54</td>
</tr>
</tbody>
</table>

3.2.1 Correlation Between CP Values

The most significant correlations between values and regions were between $t_p$, $t_p''$, and the duration of Region II ($\Delta t_{II}$). These relationships are illustrated in Figures 3.2 and 3.3. The correlation of these values indicates that the same phenomena are probably responsible for each. Since $t_p$ is the most easily identifiable parameter, it will be used extensively to describe the passivation behavior of each anode using a single value. This will make the discussion of the passivation characteristics for each anode easier. Instead of having to relate several values, a single characteristic number, $t_p$, can be used.
Figure 3.2 The Correlation Between $t_p$ and $t_p''$ for Commercial Copper Anodes. 382 mAcm$^{-2}$ in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$ at 65 °C under static conditions open to the atmosphere.

Figure 3.3 The Correlation Between $t_p$ and $\Delta t_{II}$ for Commercial Copper Anodes. 382 mAcm$^{-2}$ in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$ at 65 °C under static conditions open to the atmosphere.
3.2.2 The Effect of Individual Anode Impurities

Since the forty-four samples tested were selected from commercial anodes, individual elements were not specifically controlled. By careful selection of the anodes, the effect of individual impurities was gleaned from the data using two methods. The first method was using statistical correlations from a multiple linear regression analysis. The second method was to examine subsets of anodes where certain elements were limited to a particular range. From these methods, the elements that were found to be most significant on passivation behavior were selenium, nickel, oxygen, tellurium, lead, arsenic and silver.

3.2.2.1 Multiple Linear Regression

Multiple linear regression was utilized to determine which elements had the most significant response on time to passivation. While the chemical analyses were performed for fourteen elements, it was determined that only nine of the elements were significantly different. These nine elements, selenium, tellurium, arsenic, bismuth, antimony, nickel, silver, oxygen, and lead were used in the regression analysis. The analysis was performed using two different inputs - the concentration in ppm and the logarithm of concentration in ppm. Summaries of the results of these regressions are shown in Tables 3.2 and 3.3, respectively. The values presented are the coefficient and t-value of each variable, and the intercept, the correlation coefficient (adjusted R^2) and the F-value of the complete regression. An empirical time to passivation can be calculated from an anode composition by using the listed coefficients. For example, using the values from Table 3.3
$t_p (\text{sec}) = 4750 - 404 \log [O] - 214 \log [\text{Ni}] - 278 \log [\text{Se}] - 179 \log [\text{Pb}]
- 139 \log [\text{Bi}] - 146 \log [\text{Te}] + 145 \log [\text{As}] - 88 \log [\text{Ag}] + 42 \log [\text{Sb}] \quad (3.1)$

The listed $t$-values show the statistical significance of each impurity to the regression with a higher absolute value indicating a greater importance. Again from Table 3.3, this regression indicates that oxygen, nickel, and selenium have the most significance and silver and antimony are the least significant. The correlation coefficient and F-value represent the statistical significance of the complete regression. Examination of these two values reveals that using the logarithm of the impurity concentrations provided a better mathematical fit. This is also seen when the measured times to passivation are compared visually to the calculated $t_p$ in Figures 3.4 and 3.5.

### Table 3.2
**Multiple Linear Regression Coefficients Using Nine Impurity Concentrations in PPM for the Prediction of Time to Passivation**

<table>
<thead>
<tr>
<th>Values</th>
<th>Intercept</th>
<th>Ni</th>
<th>Se</th>
<th>Bi</th>
<th>As</th>
<th>Te</th>
<th>Sb</th>
<th>O</th>
<th>Pb</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeff.</td>
<td>2090</td>
<td>-0.17</td>
<td>-0.50</td>
<td>-1.44</td>
<td>0.12</td>
<td>-1.08</td>
<td>0.20</td>
<td>-0.07</td>
<td>-0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>$t$-Value</td>
<td>11.9</td>
<td>-2.97</td>
<td>-2.48</td>
<td>-1.80</td>
<td>1.63</td>
<td>-1.35</td>
<td>1.25</td>
<td>-0.99</td>
<td>-0.68</td>
<td>0.23</td>
</tr>
<tr>
<td>Adjusted $R$ Squared</td>
<td>0.637</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.37</td>
</tr>
</tbody>
</table>

### Table 3.3
**Multiple Linear Regression Coefficients Using the Logarithm of Nine Impurity Concentrations in PPM for the Prediction of Time to Passivation**

<table>
<thead>
<tr>
<th>Values</th>
<th>Intercept</th>
<th>O</th>
<th>Ni</th>
<th>Se</th>
<th>Pb</th>
<th>Bi</th>
<th>Te</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeff.</td>
<td>4750</td>
<td>-404</td>
<td>-214</td>
<td>-278</td>
<td>-179</td>
<td>-139</td>
<td>-146</td>
<td>145</td>
<td>-88</td>
<td>42</td>
</tr>
<tr>
<td>$t$-Value</td>
<td>5.14</td>
<td>-1.61</td>
<td>-1.53</td>
<td>-1.48</td>
<td>-1.12</td>
<td>-0.95</td>
<td>-0.74</td>
<td>0.71</td>
<td>-0.29</td>
<td>0.20</td>
</tr>
<tr>
<td>$R$ Squared</td>
<td></td>
<td>0.671</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10.76</td>
</tr>
<tr>
<td>F-Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.4 Actual $t_p$ versus Calculated $t_p$ from Multiple Linear Regression using Nine Impurity Concentrations.

Figure 3.5 Actual $t_p$ versus Calculated $t_p$ from Multiple Linear Regression using the Logarithm of Nine Impurity Concentrations.

Focusing on the log concentration analysis, the t-values of each independent variable indicate that silver and antimony are not very statistically important. Removal of these two elements produces an even better correlation coefficient and F-Value as seen in Table 3.4. This new data reveals that bismuth is the least significant of the remaining elements. Eliminating bismuth from the regression generates the same correlation value with a higher F value as seen in Table 3.5. All other elements are considered significant.
because their removal causes the correlation coefficient and F-value to decrease. The remaining six elements will be investigated further in order of their significance from the regression analysis using the logarithm of the concentration in ppm. It should be emphasized that of these six elements only arsenic appears to prolong the time to passivation as seen by its positive coefficient.

Table 3.4
Multiple Linear Regression Coefficients Using the Logarithm of Seven Impurity Concentrations in PPM for Selected Elements to Predict Time to Passivation

<table>
<thead>
<tr>
<th>Values</th>
<th>Intercept</th>
<th>Se</th>
<th>Ni</th>
<th>O</th>
<th>Te</th>
<th>As</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeff.</td>
<td>4665</td>
<td>-316</td>
<td>-237</td>
<td>-410</td>
<td>-176</td>
<td>178</td>
<td>-155</td>
<td>-126</td>
</tr>
<tr>
<td>t-Value</td>
<td>5.48</td>
<td>-2.77</td>
<td>-2.13</td>
<td>-1.74</td>
<td>-1.27</td>
<td>1.25</td>
<td>-1.17</td>
<td>-0.98</td>
</tr>
<tr>
<td>R Squared</td>
<td>0.689</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-Value</td>
<td>14.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.5
Multiple Linear Regression Coefficients Using the Logarithm of Six Impurity Concentrations in PPM for the Most Significant Elements to Predict Time to Passivation

<table>
<thead>
<tr>
<th>Values</th>
<th>Intercept</th>
<th>Se</th>
<th>Ni</th>
<th>O</th>
<th>Te</th>
<th>Pb</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeff.</td>
<td>4617</td>
<td>-293</td>
<td>-264</td>
<td>-409</td>
<td>-220</td>
<td>-152</td>
<td>145</td>
</tr>
<tr>
<td>t-Value</td>
<td>5.43</td>
<td>-2.62</td>
<td>-2.44</td>
<td>-1.73</td>
<td>-1.68</td>
<td>-1.15</td>
<td>1.05</td>
</tr>
<tr>
<td>R Squared</td>
<td>0.689</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-Value</td>
<td>16.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2.2.2 Selenium

Selenium is present in copper anodes typically in the form of copper selenides. The most common copper selenide has the mineralogical form of berzelianite, Cu$_{2+n}$Se. Selenides form as complete and incomplete shells on copper oxide cores resulting in spheroidal shapes. During electrorefining, if the copper oxide core is exposed to acid it will dissolve leaving a selenide remnant. This can be seen from the field emission scanning electron (FESEM) photomicrograph displayed in Figure 3.6. In the figure, there are three
spheroids in different states of dissolution. Energy dispersive X-ray spectroscopy (EDS) of the shells and remnant identified copper and selenium as the predominant elements.

Figure 3.6 FESEM Photomicrograph of Copper Selenide Structures in Slimes Collected from MCCA-16 after a Standard Chronopotentiometry Experiment.

Figure 3.7 shows the average time to passivation of all of the anodes tested versus selenium. This plot reveals there is a general decline in $t_p$ with increasing selenium, but with some definite scatter. However, if ranges are set on nickel, oxygen, and tellurium, the correlation between selenium and time to passivation is readily seen in Figure 3.8.

Copper selenides are refractory phases and do not dissolve readily during electrorefining. Their presence at the surface of the anode can influence the dissolution process by blocking the active surface area or inhibiting diffusion by forming a porous layer. Both cases would lead to the increased probability of passivation seen in Figure 3.8.
Figure 3.7 The Effect of Selenium on Time to Passivation for All Anodes Tested. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.

Figure 3.8 The Effect of Selenium on Time to Passivation for a Selected Group of 17 Anodes. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
3.2.2.3 Nickel

Nickel forms a solid solution with copper up to about 2500-3000 ppm in the presence of oxygen. Then it will form nickel oxide or kupferglimmer depending on the oxygen, antimony, and tin content of the anode. The average $t_p$'s versus nickel for all of the anodes are shown in Figure 3.9. Times to passivation generally decrease with increasing nickel but with even more scatter than with selenium. By placing restrictions on selenium, oxygen, and tellurium, the trend becomes more obvious in Figure 3.10.

![Graph showing the effect of nickel on time to passivation for a selected group of anodes.](image)

**Figure 3.9 The Effect of Nickel on Time to Passivation for a Selected Group of Anodes.**

40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 3820 A m$^{-2}$, no agitation, atmospheric conditions.

Both nickel oxide and kupferglimmer are refractory in nature. Therefore, they can affect passivation in the same way as selenides. Kupferglimmer is particularly harmful because of its morphology as seen in Figure 3.11. Kupferglimmer forms platelets that can affect more surface area than crystallites of nickel oxide.
Figure 3.10 The Effect of Nickel on Time to Passivation for a Selected Group of 18 Anodes. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 3820 A m$^{-2}$, no agitation, atmospheric conditions.

Figure 3.11 FESEM Photomicrograph of a Large Kupferglimmer Platelet in Slimes Collected from MCCA-34. Photo courtesy of Mr. Scott Campin [53].

Kupferglimmer also has a significant impact on the CP behavior in Regions III and IV. CPs for three different samples are shown in Figure 3.12 illustrating this point. When kupferglimmer is present a more stable oscillation is observed around two volts. This behavior is believed to be associated with oxygen evolution. This is confirmed by
observations made at certain electrorefineries that show anodes containing kupferglimmer evolve oxygen after passivation, while those that are free of kupferglimmer do not [85].

![Figure 3.12 Region IV for Anodes with Kupferglimmer. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.](image)

3.2.2.4 Oxygen

Oxygen has been shown by Abe et al. [28, 66], Noguchi et al. [26], and Hiskey et al. [61] to adversely affect passivation. Interestingly, a plot of the times to passivation versus oxygen for all the samples tested, Figure 3.13, exhibits little trend amidst the scatter. Again by constraining selenium, nickel, and tellurium, the adverse affect of oxygen becomes present in Figure 3.14. For this particular subset, it appears that increasing the oxygen concentration greater than 1500 ppm has a minimal detrimental effect.
Copper has a very low solubility limit for oxygen. Thus, most oxygen occurs as copper oxides and as oxides with other impurities like lead, nickel, and the Group VB elements.
Copper oxides will typically dissolve chemically when exposed to the acidic electrolyte. This would result in a higher flux of copper from the anode than expected based on Faraday's Law and would consume acid at the anode surface. Oxygen does not appear to overtly affect slime formation.

3.2.2.5 Tellurium

Tellurium is very similar in its behavior to selenium. This is probably the result of tellurium being a substitutional element for selenium in the selenide phases. Increasing tellurium tends to decrease time to passivation as observed in Figure 3.15. This trend can be more easily seen in Figure 3.16 when ranges are placed on selenium and oxygen. Tellurium affects $t_p$ by decreasing the active surface area and creating a porous diffusion inhibiting layer with selenium in the form of $(\text{Cu,Ag}_2)_{(\text{Se,Te})}$.

Figure 3.15 The Effect of Tellurium on Time to Passivation for All Anodes Tested. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 3820 A m$^{-2}$, no agitation, atmospheric conditions.
Figure 3.16 The Effect of Tellurium on Time to Passivation for a Selected Group of 12 Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.

3.2.2.6 Lead

In copper anodes, lead is present in solid solution and as complex oxides. The oxides usually include copper, arsenic, antimony, and/or bismuth. Passivation times versus the lead content of each anode tested are shown in Figure 3.17. Figure 3.18 illustrates the detrimental effect of lead on tₚ by examining a specific set of anodes.

Lead oxides are not refractory like the other inclusion phases mentioned previously. As the lead containing phases dissolve, the lead reacts with the high sulfate concentration of the electrolyte. This causes the precipitation of lead sulfate at or near the anode surface. This can cause the same problems of inhibiting diffusion and/or decreasing the active surface area.
Figure 3.17 The Effect of Lead on Time to Passivation for All of the Anodes Tested. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.

Figure 3.18 The Effect of Lead on Time to Passivation for a Selected Group of 27 Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.
3.2.2.7 Arsenic

As noted previously by Hiskey et al. [61], arsenic is the only impurity element found to have a positive effect on passivation. This is difficult to see when examining all of the data from this study as seen in Figure 3.19. However, a subset reveals this trend better as displayed in Figure 3.20.

Arsenic is found in solid solution and complex oxides. There are currently two possible theories for the positive effect of arsenic. Demaerel indicated that with extremely high levels of arsenic in anodes, the slime adhesion to the anode surface decreased [66]. In the current experiments, several anodes exhibited reactivation in Region IV as observed in Figure 3.21. The reactivation occurred after a substantial portion of slimes generated fell from the anode surface. This behavior was not reproducible for most anodes, but for those that did experience it, all had high levels of arsenic. Therefore, arsenic may help in the sloughing of slimes from the anode surface. The second theory concerning arsenic involves acid generation and localized electrolyte conditions [61]. This second theory will be discussed more thoroughly in Section 4.
Figure 3.19 The Effect of Arsenic on Time to Passivation for All Anodes Tested. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.

Figure 3.20 The Effect of Arsenic on Time to Passivation for a Selected Group of 11 Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.
Figure 3.21 Re-activation in Region IV noted for Anodes with High Arsenic. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², Anode MCCA-54, no agitation, atmospheric conditions.

3.2.2.8 Silver

While the multiple linear regression analyses did not indicate silver was statistically significant, other researchers have shown that silver can affect anode passivation [26]. It is believed that the effect of silver was masked in the multiple linear regression analysis by selenium since anode selenium and silver concentrations are related (see Figure 3.1). A plot of average passivation time versus silver, Figure 3.22, reveals a similar trend to selenium.
From previous investigations, it would appear that both selenium and silver affect passivation. Silver has been shown to locally dissolve and then re-cement on to the anode surface as small crystallites [54]. Silver can also cause the transformation of copper selenides and tellurides into copper-silver selenides and tellurides [55, 58, 60]. Hiskey et al. [61] have calculated that the transformation would result in a volume expansion. Thus, silver can decrease the active surface area of the copper anodes and inhibit diffusion from the anode surface.

Besides affecting passivation times, silver appears to affect the CP response in Region III when greater than 800 ppm. This can be seen in Figure 3.23. Anodes with less than 800 ppm exhibit a short Region III, while those with more silver have a protracted one. Possible causes for this will be discussed in Section 4.
Figure 3.23 Extended Region III for Anodes with High Silver. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.

3.2.3 The Effect of Electrolyte Constituents

The effects of seven electrolyte parameters were investigated in a controlled laboratory setting. The parameters are divided into three sub-categories: base constituents (copper and acid), major impurities (nickel and arsenic), and common additives (chloride, thiourea, and glue). Each component was evaluated at several concentrations using selected commercial copper anodes. A simulated electrolyte of copper, acid, chloride, thiourea, and glue was also tested using twenty anodes of varying compositions. Two factorial designs were employed to observe the effect and interactions between the three
additives studied on two different anodes. Finally, bromide and polyethylene glycol were investigated because of their ability to complex cuprous ions.

3.2.3.1 Base Constituents

The principal components of all electrorefining electrolytes are copper and sulfuric acid. From Schloen and Davenport's survey of world tankhouse data, the range of industrial concentrations for these two compounds is 37 to 60 g l⁻¹ copper and 140 to 220 g l⁻¹ acid [2]. Based on this information and guidance from the project sponsors, three levels of copper and four of acid were tested using two different anodes, MCCA-23 and MCCA-25. MCCA-23 and MCCA-25 were selected based on their long (2675 sec) and short (1015 sec) times to passivation in the standard electrolyte (40 g l⁻¹ Cu and 160 g l⁻¹ H₂SO₄), respectively.

3.2.3.1.1 Copper

Increasing the copper concentration of the electrolyte decreased the time to passivation for both anodes as observed in Figure 3.24. MCCA-25 reacted much more significantly than MCCA-23. As previously indicated by other investigations, copper sulfate precipitation could cause passivation. Thus, increasing the copper concentration closer to saturation level would lead to quicker passivation.

3.2.3.1.2 Sulfuric Acid

Figure 3.25 illustrates the adverse effect of increased acid concentration on t_p. The same rationale used for copper can be applied to adding more sulfate in the form of sulfuric
acid. As the acid concentration increases, the electrolyte approaches the saturation level, increasing the likelihood of copper sulfate formation.

Figure 3.24 The Effect of Copper Concentration on Time to Passivation for Two Selected Anodes. 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.

Figure 3.25 The Effect of Acid Concentration on Time to Passivation for Two Selected Anodes. 40 g l\(^{-1}\) Cu, 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
The $t_p$ results for MCCA-25 are plotted on a grid of copper and sulfuric acid concentration in Figure 3.26. The saturation limit interpolated from Linke's data [86] is also shown. It becomes obvious that as the electrolyte concentration starts closer to the saturation limit, the times to passivation decrease.

![Figure 3.26 The Time to Passivation of MCCA-25 Plotted as a Function of the Starting Electrolyte Composition. (The saturation limit is interpolated from data gathered by Linke [86].)](image)

3.2.3.2 Major Impurities

Industrial electrolytes contain numerous inorganic impurities. Schloen and Davenport's data [2] indicate the most common impurities with high concentrations were nickel and arsenic. Therefore, these two impurities were investigated using MCCA-23 and MCCA-25.
3.2.3.2.1 Nickel

Times to passivation for MCCA-23 and MCCA-25 versus nickel are shown in Figure 3.27. Notice that the trend is very similar to that seen with copper and sulfuric acid. The decrease in \( t_p \) is not believed to be caused by nickel, but by the added sulfate that was introduced with the nickel. To confirm this, sodium sulfate was added to give the same total sulfate content as each of the nickel experiments. The results are exhibited in Figure 3.28 and tabulated in Table 3.6. It becomes apparent that the sulfate controls the observed behavior. To further elucidate the effect of nickel, several constant sulfate experiments were performed and those results are listed in Table 3.7. From these experiments, nickel may have some effect on passivation, but it is uncertain if the decreasing acid content affected the results.
Figure 3.27 The Effect of Nickel Concentration on Time to Passivation for Two Selected Anodes. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) \(\text{H}_2\text{SO}_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.

Figure 3.28 The Effect of Sulfate Concentration on Time to Passivation for Two Selected Anodes. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) \(\text{H}_2\text{SO}_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
Table 3.6
Time to Passivation in Seconds as a Function of Added Sulfate in 40 g l⁻¹ Cu and 160 g l⁻¹ H₂SO₄ at 65 °C under no agitation and atmospheric conditions

<table>
<thead>
<tr>
<th>Anode</th>
<th>40 g l⁻¹ Cu</th>
<th>Sulfate added as NiSO₄</th>
<th>Sulfate added as Na₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCCA-23</td>
<td>1015</td>
<td>1094</td>
<td>458</td>
</tr>
<tr>
<td>MCCA-25</td>
<td>2675</td>
<td>1580</td>
<td>860</td>
</tr>
</tbody>
</table>

Table 3.7
Summary of Times to Passivation in Seconds for the Constant Sulfate Experiments

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>MCCA-23</th>
<th>MCCA-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄</td>
<td>1015</td>
<td>2675</td>
</tr>
<tr>
<td>40 g l⁻¹ Cu, 140 g l⁻¹ H₂SO₄, 12 g l⁻¹ Ni²⁺</td>
<td>728</td>
<td>2361</td>
</tr>
<tr>
<td>40 g l⁻¹ Cu, 120 g l⁻¹ H₂SO₄, 24 g l⁻¹ Ni²⁺</td>
<td>887</td>
<td>688</td>
</tr>
</tbody>
</table>

3.2.3.2.2 Arsenic

The addition of arsenic to the electrolyte decreased tₚ for both MCCA-23 and MCCA-25 as seen in Figure 3.29. At first, this would seem to contradict the finding that arsenic in the anode extends the time to passivation. However, an industrial observation supports the fact that arsenic added to the electrolyte does not alleviate a passivation problem, but arsenic in the anode does [87]. Different sources of arsenic were tried to determine if that may cause some positive effect, but as Figure 3.30 illustrates, it did not. This indicates that arsenic must be added to the anode, and not the electrolyte, for a positive effect to be observed.
Figure 3.29 The Effect of Arsenic Concentration in the Electrolyte on Time to Passivation for Two Selected Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions, arsenic added as As₂O₅.

Figure 3.30 The Effect of Different Sources of Arsenic in the Electrolyte on Time to Passivation for Two Selected Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions. Anode MCCA-23.

The negative effect of arsenic in the electrolyte on time to passivation may be related to the increased likelihood of copper sulfate formation. The dissolution of arsenic oxide would consume acid and disturb the equilibrium between SO₄²⁻ and HSO₄⁻. The result
would be more free sulfate in solution which would cause precipitation of CuSO₄•5H₂O at a lower cupric concentration. Since copper sulfate is thought to be a passivation film, this would explain the decrease in $t_p$ observed for increasing arsenic.

3.2.3.3 Additives

Additives are commonly introduced to electrolyte to control the cathode deposit characteristics. The most common additives are chloride, thiourea, and glue [2]. These reagents were evaluated at various concentrations. For chloride and thiourea, other anodes were examined besides MCCA-23 and MCCA-25.

3.2.3.3.1 Chloride

Chloride is typically the only non-organic electrolyte additive used in electrorefining. Figure 3.31 illustrates the positive effect of chloride on time to passivation for MCCA-23 and MCCA-25. Experiments were performed with MCCA-25 in electrolyte containing 30, 50, and 75 ppm chloride. These tests did not passivate in the one hour time frame of a normal chronopotentiogram. To conserve the working electrode from MCCA-25, the 30, 50, and 75 ppm chloride experiments were not repeated.
Several other anodes were tested with electrolyte containing chloride. These results are plotted in Figures 3.32 and 3.33. The anodes in Figure 3.32 exhibit a positive effect, while those in Figure 3.33 show little or no effect.

Figure 3.31 The Effect of Chloride in the Electrolyte on Time to Passivation for Two Selected Anodes. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, atmospheric conditions.
Figure 3.32 Anodes Exhibiting a Positive Effect to Chloride in the Electrolyte. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.

Figure 3.33 Anodes Exhibiting a Neutral to Negative Effect to Chloride in the Electrolyte. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
3.2.3.3.2 Thiourea

The effect of thiourea on $t_p$ for MCCA-23 and MCCA-25 is displayed in Figure 3.34. Thiourea appears to have a positive effect at low concentrations and a negative effect at high concentrations. This phenomenon was tested using two other anodes, MCCA-35 and MCCA-28. Those results are plotted in Figure 3.35. The same trend is observed for these two anodes as with MCCA-23 and MCCA-25.

Previously Hiskey and Cheng [70], using the same procedure as the current investigation, detected re-activation during Region IV of chronopotentiograms of a commercial copper anode in synthetic electrolytes containing 15, 50, or 100 ppm of thiourea. This behavior was not detected for any of the four anodes tested at any of the thiourea concentrations utilized. The role of thiourea in re-activation is not fully understood. A dependence on anode composition may cause the lack of re-activation in this investigation.
Figure 3.34 The Effect of Thiourea in the Electrolyte on Time to Passivation for Two Selected Anodes. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.

Figure 3.35 The Effect of Thiourea in the Electrolyte on Time to Passivation for MCCA-35 and MCCA-28. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
3.2.3.3.3 Glue

The influence of glue concentration on passivation time for anodes MCCA-23 and MCCA-25 is summarized in Table 3.8. While both anodes appear to exhibit a maximum \( t_p \) around one ppm, the value for MCCA-23 may not be statistically significant. Higher concentrations appear to have little or no effect. Interestingly, both anodes exhibit a periodic re-activation/passivation within Region IV of the CPs with 20 ppm glue as observed in Figure 3.36.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Glue Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>MCCA-23</td>
<td>1015</td>
</tr>
<tr>
<td>MCCA-25</td>
<td>2675</td>
</tr>
</tbody>
</table>

Figure 3.36 Reactivation Detected in Region IV in the Presence of 20 ppm Glue in the Electrolyte for MCCA-23. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^{-2}\), no agitation, atmospheric conditions.
3.2.3.3.4 Simulated Industrial Electrolyte

An electrolyte of 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 30 ppm Cl\(^-\), 1 ppm thiourea, and 1 ppm glue was used to study the effect of a simulated industrial electrolyte on twenty different anodes. The times to passivation for each anode in standard electrolyte (40 g l\(^{-1}\) Cu and 160 g l\(^{-1}\) H\(_2\)SO\(_4\)) and simulated electrolyte are listed in Table 3.9. Of the twenty anodes tested, 10 indicated a definitive increase in passivation time, eight remained about the same, and two exhibited a significant decrease.

Table 3.9
Time to Passivation for Selected Anodes in Standard and Simulated Electrolyte at 65 °C with a Current Density of 3820 A m\(^{-2}\)

<table>
<thead>
<tr>
<th>Response to Additives</th>
<th>Anode</th>
<th>Standard (t_p) (sec)</th>
<th>Simulated (t_p) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Increase</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCA-17</td>
<td>2253</td>
<td>4111</td>
<td></td>
</tr>
<tr>
<td>MCCA-18</td>
<td>1846</td>
<td>2463</td>
<td></td>
</tr>
<tr>
<td>MCCA-23</td>
<td>1015</td>
<td>3015</td>
<td></td>
</tr>
<tr>
<td>MCCA-28</td>
<td>770</td>
<td>1154</td>
<td></td>
</tr>
<tr>
<td>MCCA-45</td>
<td>846</td>
<td>1044</td>
<td></td>
</tr>
<tr>
<td>MCCA-50</td>
<td>1525</td>
<td>1828</td>
<td></td>
</tr>
<tr>
<td>MCCA-54</td>
<td>1233</td>
<td>1804</td>
<td></td>
</tr>
<tr>
<td>MCCA-57</td>
<td>1221</td>
<td>2229</td>
<td></td>
</tr>
<tr>
<td>MCCA-65</td>
<td>1874</td>
<td>2839</td>
<td></td>
</tr>
<tr>
<td>MCCA-72</td>
<td>1363</td>
<td>1648</td>
<td></td>
</tr>
<tr>
<td><strong>No Measurable Difference</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCA-2</td>
<td>977</td>
<td>956</td>
<td></td>
</tr>
<tr>
<td>MCCA-5</td>
<td>1014</td>
<td>1148</td>
<td></td>
</tr>
<tr>
<td>MCCA-9</td>
<td>939</td>
<td>1174</td>
<td></td>
</tr>
<tr>
<td>MCCA-21</td>
<td>1034</td>
<td>1036</td>
<td></td>
</tr>
<tr>
<td>MCCA-25</td>
<td>2675</td>
<td>2480</td>
<td></td>
</tr>
<tr>
<td>MCCA-35</td>
<td>1358</td>
<td>1422</td>
<td></td>
</tr>
<tr>
<td>MCCA-40</td>
<td>2120</td>
<td>1924</td>
<td></td>
</tr>
<tr>
<td>MCCA-48</td>
<td>1128</td>
<td>1108</td>
<td></td>
</tr>
<tr>
<td><strong>Decrease</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCCA-3</td>
<td>1673</td>
<td>1044</td>
<td></td>
</tr>
<tr>
<td>MCCA-42</td>
<td>1319</td>
<td>1020</td>
<td></td>
</tr>
</tbody>
</table>
The effect of anode composition interacting with the additives in the electrolyte was examined. The fractional change was calculated according to the following formula

\[(\text{SIM} - \text{STD}) / \text{STD}\]  

(Eq 3.1)

where SIM is the tp in the simulated electrolyte (40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 30 ppm Cl\(^{-}\), 1 ppm thiourea, and 1 ppm glue) and STD is the tp in the standard electrolyte (40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\)). The fractional change was compared to each significant impurity identified by multiple linear regression for STD. The best correlation between fractional change and composition for all of the data was found with arsenic. That trend is plotted in Figure 3.37. The most significant observation from this trend is that anodes with high As (>1200) experienced large increases in tp. If the high arsenic and high nickel (>2800) anodes are removed from consideration, the remaining data reveals a negative trend with increasing silver as shown in Figure 3.38.
Figure 3.37 The Effect of Arsenic Concentration of the Anode on the Change of Time to Passivation with the Introduction of 30 ppm Cl\(^-\), 1 ppm Thiourea and 1 ppm Glue to the Electrolyte. 40 g l\(^-1\) Cu, 160 g l\(^-1\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^2\), no agitation, atmospheric conditions.

Figure 3.38 The Effect of Silver Concentration of Anodes with Low Arsenic and Nickel on the Change of Time to Passivation with the Introduction of 30 ppm Cl\(^-\), 1 ppm Thiourea and 1 ppm Glue to the Electrolyte. 40 g l\(^-1\) Cu, 160 g l\(^-1\) H\(_2\)SO\(_4\), 65 °C, 3820 A m\(^2\), no agitation, atmospheric conditions.
3.2.3.3.5 Factorial Design

Factorial designs were performed to statistically determine the effect of additives and the interactions between them. A $2^3$ factorial design was utilized with the variables and levels being chloride (20 and 40 ppm), thiourea (1 and 5 ppm) and glue (0.5 and 2 ppm). The experimental design was implemented with three different anodes, MCCA-21, MCCA-57, and MCCA-42. The responses for each anode are summarized in Tables 3.10, 3.11, and 3.12. The analysis of variance (ANOVA) for each factorial design was performed. Responses that were examined are $t_p''$ (start of Region II), $t_p$, $t_p'$ (start of Region IV), $\Delta t_{II}$ (duration of Region II) and $\Delta t_{III}$ (duration of Region III). The variables and interactions that illustrated significance of at least 85% are shown in Tables 3.13, 3.14, and 3.15 for anodes MCCA-21, MCCA-57, and MCCA-42, respectively.

Table 3.10
Factorial Design Results Using MCCA-21 in Electrolytes Containing Additives

<table>
<thead>
<tr>
<th>Glue (ppm)</th>
<th>[Tu] (ppm)</th>
<th>[Cl] (ppm)</th>
<th>$t_p''$ (sec)</th>
<th>$t_p$ (sec)</th>
<th>$t_p'$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1st test</td>
<td>2nd test</td>
<td>1st test</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>20</td>
<td>906</td>
<td>724</td>
<td>1094</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>20</td>
<td>980</td>
<td>792</td>
<td>1126</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>20</td>
<td>788</td>
<td>460</td>
<td>910</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>20</td>
<td>944</td>
<td>700</td>
<td>1044</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>40</td>
<td>954</td>
<td>758</td>
<td>966</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>40</td>
<td>762</td>
<td>1410</td>
<td>910</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>40</td>
<td>610</td>
<td>934</td>
<td>634</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>40</td>
<td>770</td>
<td>530</td>
<td>904</td>
</tr>
</tbody>
</table>
### Table 3.11
Factorial Design Results Using MCCA-57 in Electrolytes Containing Additives

<table>
<thead>
<tr>
<th>Glue (ppm)</th>
<th>[Tu] (ppm)</th>
<th>[Cl] (ppm)</th>
<th>$t_p''$ (sec)</th>
<th>$t_p$ (sec)</th>
<th>$t_p'$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1st test</td>
<td>2nd test</td>
<td>1st test</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>20</td>
<td>1352</td>
<td>1308</td>
<td>1530</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>20</td>
<td>1376</td>
<td>2363</td>
<td>1510</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>20</td>
<td>1234</td>
<td>1630</td>
<td>1296</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>20</td>
<td>1338</td>
<td>1204</td>
<td>1464</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>40</td>
<td>2245</td>
<td>2003</td>
<td>2353</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>40</td>
<td>2499</td>
<td>1824</td>
<td>2611</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>40</td>
<td>1782</td>
<td>1626</td>
<td>1924</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>40</td>
<td>1130</td>
<td>1788</td>
<td>1228</td>
</tr>
</tbody>
</table>

### Table 3.12
Factorial Design Results Using MCCA-42 in Electrolytes Containing Additives

<table>
<thead>
<tr>
<th>Glue (ppm)</th>
<th>[Tu] (ppm)</th>
<th>[Cl] (ppm)</th>
<th>$t_p''$ (sec)</th>
<th>$t_p$ (sec)</th>
<th>$t_p'$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1st test</td>
<td>2nd test</td>
<td>1st test</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>20</td>
<td>906</td>
<td>898</td>
<td>1346</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>20</td>
<td>910</td>
<td>984</td>
<td>1360</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>20</td>
<td>722</td>
<td>716</td>
<td>934</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>20</td>
<td>1126</td>
<td>1178</td>
<td>1232</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>40</td>
<td>848</td>
<td>892</td>
<td>1182</td>
</tr>
<tr>
<td>2.0</td>
<td>1.0</td>
<td>40</td>
<td>886</td>
<td>1076</td>
<td>1166</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0</td>
<td>40</td>
<td>828</td>
<td>948</td>
<td>1018</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>40</td>
<td>890</td>
<td>968</td>
<td>1016</td>
</tr>
</tbody>
</table>

### Table 3.13
Significant Parameters or Interactions on Factorial Responses for MCCA-21

<table>
<thead>
<tr>
<th>Response</th>
<th>Variable</th>
<th>Effect</th>
<th>F</th>
<th>% Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_p''$</td>
<td>Thiourea</td>
<td>-195</td>
<td>2.81</td>
<td>86.2</td>
</tr>
<tr>
<td>$t_p$</td>
<td>Thiourea</td>
<td>-230</td>
<td>4.11</td>
<td>91.8</td>
</tr>
<tr>
<td>$t_p'$</td>
<td>Thiourea</td>
<td>-253</td>
<td>5.11</td>
<td>94.2</td>
</tr>
<tr>
<td>$\Delta t_{II}$</td>
<td>Chloride</td>
<td>-57</td>
<td>4.43</td>
<td>92.6</td>
</tr>
<tr>
<td>$\Delta t_{III}$</td>
<td>All - very short Region III's</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.14

Significant Parameters or Interactions on Factorial Responses for MCCA-57

<table>
<thead>
<tr>
<th>Response</th>
<th>Variable</th>
<th>Effect</th>
<th>F</th>
<th>% Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_p''$</td>
<td>Thiourea</td>
<td>-405</td>
<td>4.94</td>
<td>93.8</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>387</td>
<td>4.50</td>
<td>92.8</td>
</tr>
<tr>
<td>$t_p$</td>
<td>Thiourea</td>
<td>-407</td>
<td>5.09</td>
<td>94.1</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>400</td>
<td>4.90</td>
<td>93.8</td>
</tr>
<tr>
<td>$t_p'$</td>
<td>Thiourea</td>
<td>-445</td>
<td>7.04</td>
<td>96.7</td>
</tr>
<tr>
<td></td>
<td>Chloride</td>
<td>378</td>
<td>5.07</td>
<td>94.1</td>
</tr>
<tr>
<td>$\Delta t_{II}$</td>
<td>None</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta t_{III}$</td>
<td>None</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.15

Significant Parameters or Interactions on Factorial Responses for MCCA-42

<table>
<thead>
<tr>
<th>Response</th>
<th>Variable</th>
<th>Effect</th>
<th>F</th>
<th>% Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_p''$</td>
<td>Glue</td>
<td>158</td>
<td>23.8</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>Glue + Thiourea</td>
<td>80</td>
<td>6.06</td>
<td>95.7</td>
</tr>
<tr>
<td></td>
<td>Glue + Chloride</td>
<td>-82</td>
<td>6.36</td>
<td>96.0</td>
</tr>
<tr>
<td></td>
<td>Glue + Thiourea + Chloride</td>
<td>-115</td>
<td>12.6</td>
<td>99.1</td>
</tr>
<tr>
<td>$t_p$</td>
<td>Thiourea</td>
<td>-173</td>
<td>19.0</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>Glue</td>
<td>120</td>
<td>9.18</td>
<td>98.1</td>
</tr>
<tr>
<td></td>
<td>Glue + Chloride</td>
<td>-81</td>
<td>4.18</td>
<td>92.0</td>
</tr>
<tr>
<td></td>
<td>Glue + Thiourea + Chloride</td>
<td>-80</td>
<td>4.08</td>
<td>91.7</td>
</tr>
<tr>
<td>$t_p'$</td>
<td>Thiourea</td>
<td>-235</td>
<td>22.5</td>
<td>99.8</td>
</tr>
<tr>
<td></td>
<td>Glue</td>
<td>93</td>
<td>3.51</td>
<td>89.7</td>
</tr>
<tr>
<td></td>
<td>Glue + Chloride</td>
<td>-90</td>
<td>3.32</td>
<td>88.9</td>
</tr>
<tr>
<td>$\Delta t_{II}$</td>
<td>Thiourea</td>
<td>-170</td>
<td>27.2</td>
<td>99.9</td>
</tr>
<tr>
<td>$\Delta t_{III}$</td>
<td>Thiourea</td>
<td>-62</td>
<td>19.4</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>Glue</td>
<td>-28</td>
<td>3.81</td>
<td>90.8</td>
</tr>
<tr>
<td></td>
<td>Glue + Thiourea</td>
<td>26</td>
<td>3.41</td>
<td>89.3</td>
</tr>
<tr>
<td></td>
<td>Thiourea + Chloride</td>
<td>-27</td>
<td>3.54</td>
<td>89.8</td>
</tr>
</tbody>
</table>
3.2.3.4 Cuprous Complexing Reagents

Based on the results from the additives, several other compounds were selected to observe their effect on passivation behavior. The most encouraging results from the additives studied were from chloride and small additions of thiourea and glue. Both chloride and thiourea are known cuprous ion complexing reagents. Therefore, reagents, such as bromide and polyethylene glycol, which have exhibited an ability to complex cuprous ions, were investigated.

3.2.3.4.1 Bromide

The negative effect of bromide on time to passivation of MCCA-25 can be seen in Figure 3.39. This is in severe contrast to the positive effect observed with chloride ion. The bromide concentrations used were much lower than those for chloride because of the difference in the solubility constants of CuBr and CuCl, respectively. As shown by the calculation in Appendix II, the theoretical cuprous concentration caused by the addition of 10 ppm chloride is equivalent to that of 0.6 ppm bromide. It is believed the negative effect, however, is caused by the precipitation of CuBr on to the anode surface.
3.2.3.4.2 Polyethylene Glycol

The effect of polyethylene glycol (PEG) on $t_p$ for MCCA-25 and MCCA-57 is illustrated in Figure 3.38. The data indicate that an optimal concentration of 200 molecular weight (MW) PEG exists that increases the time to passivation for both MCCA-25 and MCCA-57. The optimal concentration appears to vary depending on anode composition. 1500 MW PEG was tested using MCCA-25. The higher molecular weight PEG eliminated the positive effect of the additive and in certain experiments decreased the time to passivation relative to the standard additive free electrolyte.

Figure 3.39 The Effect of Bromide in the Electrolyte on Time to Passivation. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 3820 A m$^{-2}$, no agitation, atmospheric conditions.
3.2.4 The Effect of Current Density

One of the differences between this laboratory study and industrial electrorefining is the current density employed. To accelerate passivation into a manageable time frame, 3820 A m\(^{-2}\) was utilized. In industrial electrorefining, current densities at the cathode range between 176 and 400 A m\(^{-2}\) with typical values between 200 and 300 A m\(^{-2}\) [2]. Since the majority of this investigation utilized a current density at one order of magnitude larger than industrial practice, the effect of current density on time to passivation was studied for several selected anodes. The results at three different current densities for six different anodes are listed in Table 3.16. Reducing the current density greatly reduces the likelihood of passivation. It should be noted that the 2500 A m\(^{-2}\) experiment involving MCCA-67 passivated because of a decrease in surface area and the electrolyte reaching the solder/contact wire; therefore, the \(t_p\) is reported as greater than the value recorded.
Table 3.16
Time to Passivation as a Function of Current Density

<table>
<thead>
<tr>
<th>Anode</th>
<th>Passivation Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2500 A m⁻²</td>
</tr>
<tr>
<td>MCCA-1</td>
<td>1692</td>
</tr>
<tr>
<td>MCCA-2</td>
<td>3762</td>
</tr>
<tr>
<td>MCCA-3</td>
<td>31374</td>
</tr>
<tr>
<td>MCCA-22</td>
<td>4896</td>
</tr>
<tr>
<td>MCCA-57</td>
<td>10680</td>
</tr>
<tr>
<td>MCCA-67</td>
<td>&gt;42696</td>
</tr>
</tbody>
</table>

An attempt was made to passivate anode samples MCCA-23 and MCCA-55 at 1000 A m⁻², but each experiment resulted in the complete consumption of the sample. MCCA-23 ran 23.2 hrs (83,640 sec) and MCCA-55 ran 32.2 hrs (115,980 sec). By comparison, MCCA-23 and MCCA-55 passivated at 1015 and 1288 seconds at 3820 A m⁻², respectively.

3.2.5 Fast Scan Chronopotentiometry

The majority of the chronopotentiometry data was collected using a method that averages the potential over a two second interval. This was done to keep the data to a manageable size. However, with the speed of computers and the size of hard drive memory increasing, several experiments were conducted using the same experimental setup but a data point was taken every two milliseconds (500 scans per second). This was done to investigate the oscillations that are usually seen in Region II.

The fast scan chronopotentiometry (FSCP) produced significantly more detail than the previous CPs. All of the Region II's produced by FSCP are shown in Appendix III.
Samples of those are shown in Figures 3.41, 3.42, and 3.43. One of the most interesting revelations using FSCP was that MCCA-28, which demonstrated little or no oscillations in the standard tests, had a very periodic oscillatory behavior. The details generated from FSCP in Region II will be used to discuss the meaning of these oscillations in Section 4.

Figure 3.41 Region II from a fast scan chronopotentiogram for MCCA-21 in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 1 cm$^2$ surface area, 3820 A m$^{-2}$, no agitation, ambient atmosphere.
Figure 3.42 Region II from a fast scan chronopotentiogram for MCCA-25 in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 1 cm$^2$ surface area, 3820 A m$^{-2}$, no agitation, ambient atmosphere.

Figure 3.43 Region II from a fast scan chronopotentiogram for MCCA-42 in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 1 cm$^2$ surface area, 3820 A m$^{-2}$, no agitation, ambient atmosphere.
3.2.6 Pure Copper

Chronopotentiograms using pure copper as the working electrode were generated to help in elucidation of a passivation mechanism. Cheng and Hiskey [31] showed that pure copper will not passivate in one hour with the conditions of a standard CP (382 mA cm$^{-2}$ in 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$ at 65 °C under static conditions open to the atmosphere).

To determine values for pure copper, chronopotentiometry was performed at 478, 573 and 764 mA cm$^{-2}$ with the other conditions held constant. The resulting chronopotentiograms are shown in Figures 3.44 and 3.45. In Figure 3.44, the data generated by Cheng and Hiskey [31] is displayed for comparison purposes. It is interesting that the potentials at 478 mA cm$^{-2}$ show extended oscillations but not a characteristic potential spike associated with complete passivation. Figure 3.45 has the time scale expanded to illustrate the passivation characteristics at 573 and 764 mA cm$^{-2}$.

Figure 3.44 Chronopotentiogram of Pure Copper at 191, 382 and 478 mA cm$^{-2}$. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$ at 65 °C under static conditions open to the atmosphere.
3.3 Voltammetry

Voltammetry was used to complement the data generated by chronopotentiometry. Two types of voltammetry, linear sweep and cyclic, were used in this investigation. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were utilized to identify reactions involving commercial copper anodes. LSV was also used in conjunction with a rotating platinum disc electrode to determine the diffusivity of the cupric ion in synthetic industrial electrolytes.

3.3.1 Commercial Copper Anodes

The focus of using LSV and CV with commercial copper anodes was to investigate secondary reactions occurring in Region III and IV of the chronopotentiograms. As previously noted, Region III and Region IV appear to be affected by the silver and nickel contents of the anode, respectively. The linear sweep and cyclic voltammograms of
selected commercial copper anodes are shown in Appendix IV. Anodes were selected based on their compositions to elucidate post-passivation reactions.

3.3.1.1 Linear Sweep Voltammetry

The pertinent data typically used to evaluate LSV's are listed in Table 3.17. The open circuit potential was very consistent for all of the anodes tested ranging from 0.256 V to 0.260 V vs NHE. The peak voltage varied from 0.465 V to 0.660 V. The peak current exhibited values from 333 to 490 mA cm^-2. Representative LSVs are shown in Figures 3.46, 3.47, and 3.48. Figure 3.46 exhibits typical LSV behavior in that a peak is generated with an active to passive transition and the current approaches a limiting current with increasing time. Secondary reactions can be observed in Figures 3.47 and 3.48. The secondary peak around 0.8 V as seen in Figure 3.47 would seem to coincide with the dissolution of silver given the high silver content of MCCA-6. Three of the twelve anodes tested exhibited a secondary peak around 0.8 V. These anodes all had high silver content relative to the other anodes except for MCCA-15. A peak around 1.6 V was also detected as depicted in Figure 3.48 A similar peak was observed by Bounoughaz et al. [25] and was attributed to slime fall allowing for re-activation. While this is possible, this author is cautious about assigning such a reason to the peak.
Table 3.17
Selected Data from Linear Sweep Voltammograms

<table>
<thead>
<tr>
<th>Anode</th>
<th>$E_{oc}$ (V vs. NHE)</th>
<th>$E_p$ (V vs. NHE)</th>
<th>$i_p$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCCA-6</td>
<td>0.257</td>
<td>0.544</td>
<td>386</td>
</tr>
<tr>
<td>MCCA-15</td>
<td>0.256</td>
<td>0.465</td>
<td>388</td>
</tr>
<tr>
<td>MCCA-25</td>
<td>0.259</td>
<td>0.660</td>
<td>467</td>
</tr>
<tr>
<td>MCCA-28</td>
<td>0.260</td>
<td>0.470</td>
<td>344</td>
</tr>
<tr>
<td>MCCA-29</td>
<td>0.256</td>
<td>0.521</td>
<td>423</td>
</tr>
<tr>
<td>MCCA-34</td>
<td>0.256</td>
<td>0.475</td>
<td>389</td>
</tr>
<tr>
<td>MCCA-35</td>
<td>0.256</td>
<td>0.493</td>
<td>401</td>
</tr>
<tr>
<td>MCCA-40</td>
<td>0.257</td>
<td>0.551</td>
<td>490</td>
</tr>
<tr>
<td>MCCA-45</td>
<td>0.256</td>
<td>0.496</td>
<td>333</td>
</tr>
<tr>
<td>MCCA-46</td>
<td>0.258</td>
<td>0.507</td>
<td>446</td>
</tr>
<tr>
<td>MCCA-54</td>
<td>0.260</td>
<td>0.503</td>
<td>361</td>
</tr>
<tr>
<td>MCCA-64</td>
<td>0.257</td>
<td>0.534</td>
<td>434</td>
</tr>
</tbody>
</table>

Figure 3.46 Linear Sweep Voltammogram for MCCA-25. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 1 cm$^2$ surface area, 0.1 mV s$^{-1}$, no agitation, ambient atmosphere.
Figure 3.47 Linear Sweep Voltammogram for MCCA-6. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 1 cm\(^2\) surface area, 0.1 mV s\(^{-1}\), no agitation, ambient atmosphere.

Figure 3.48 Linear Sweep Voltammogram for MCCA-5. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 1 cm\(^2\) surface area, 0.1 mV s\(^{-1}\), no agitation, ambient atmosphere.

3.3.1.2 Cyclic Voltammetry

Representative samples of CVs are given in Figures 3.49, 3.50, and 3.51. Figure 3.49 displays the 1\(^{st}\) and 4\(^{th}\) scans on MCCA-25. It is readily seen that the peak voltage and
current decrease between scans. No secondary reactions are seen, except oscillations are detected between 0.5 and 0.7 V on the reverse sweep. The voltammogram of MCCA-15 is shown in Figure 3.50. Between the first and fourth scans a decrease in peak current is detected, but there is little change in peak voltage. A secondary reaction is detected on MCCA-15 around 1.7 V, which appears to lead to oxygen evolution, especially on the reverse sweep. The secondary reaction that occurs around 1.7 V is observed on all anodes with greater than 800 ppm of silver. Oscillations are observed between 0.5 and 0.7 V, but not consistently on the forward or reverse sweep. Finally, the CV of MCCA-34 is exhibited in Figure 3.51. The voltammogram reveals a shift in peak voltage but not peak current. A significant rise in current can be observed after 2.1 V. This is thought to be caused by oxygen evolution. Oscillations were detected again between 0.5 and 0.7 V. Not all anodes exhibit oscillations between 0.5 and 0.7 V, but when their occurrence is observed it is in this potential range.
Figure 3.49 Cyclic Voltammogram for MCCA-25. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 1 cm² surface area, 20 mV s⁻¹, no agitation, ambient atmosphere.

Figure 3.50 Cyclic Voltammogram for MCCA-15 in 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 1 cm² surface area, 20 mV s⁻¹, no agitation, ambient atmosphere.
Figure 3.51 Cyclic Voltammogram for MCCA-34. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 1 cm² surface area, 20 mV s⁻¹, no agitation, ambient atmosphere.

3.3.2 Diffusivity of Copper

The last type of voltammetry performed was with a platinum rotating disc electrode to measure the diffusivity of cupric ion in electrolytes similar to those observed in industry. The diffusion coefficient was calculated from a measured limiting current when copper was deposited onto the platinum disc electrode at varying rotating speeds. The voltammograms for each condition are displayed in Appendix V. A sample is given in Figure 3.52. The limiting current (i_l) was taken around -1.05 V vs MSE (-0.433 V vs. NHE) for each rotation speed. A plot of i_l vs. ω¹⁄² was constructed to determine D.

According to the Levich equation (14) this should yield a straight line with a slope containing D. A sample of a i_l vs. ω¹⁄² plot is given in Figure 3.53 with the remaining contained in Appendix V. All of the plots exhibited extremely good correlation
coefficients. Using these voltammograms, the effect of copper, acid, and temperature on copper diffusion was measured.

![Figure 3.52 Linear Sweep Voltammogram with Platinum Rotating Disc Electrode. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 0.196 cm² surface area, 10 mV s⁻¹, N₂ sparged 30 minutes prior to and blanketed during each voltammogram.](image)

3.3.2.1 The Effect of Copper Concentration

Increasing the copper concentration from 35 to 70 g l⁻¹ with 160 g l⁻¹ H₂SO₄ at 65 °C decreases the diffusivity of cupric ion as observed in Figure 3.54. The diffusion coefficient for each condition is also listed in Table 3.18. It appears that D tends to decrease logarithmically with increasing copper concentration.
Figure 3.53 Limiting Current as a Function of Rotation. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 ºC, 0.196 cm² surface area, 10 mV s⁻¹, N₂ sparged 30 minutes prior to and blanketed during each voltammogram.

Figure 3.54 The Effect of Copper Concentration on the Diffusion Coefficient of Copper Ions. 160 g l⁻¹ H₂SO₄, 65 ºC.
Table 3.18
The Effect of Copper Concentration on the Diffusivity of Cupric Ion in Electrolyte with 160 g l^{-1} H_2SO_4 at 65 °C

<table>
<thead>
<tr>
<th>Copper (g l^{-1})</th>
<th>D (x 10^{-6} cm^2 s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>13.7</td>
</tr>
<tr>
<td>40</td>
<td>13.5</td>
</tr>
<tr>
<td>44</td>
<td>12.5</td>
</tr>
<tr>
<td>45</td>
<td>11.5</td>
</tr>
<tr>
<td>50</td>
<td>11.6</td>
</tr>
<tr>
<td>50</td>
<td>11.3</td>
</tr>
<tr>
<td>60</td>
<td>10.9</td>
</tr>
<tr>
<td>70</td>
<td>10.0</td>
</tr>
</tbody>
</table>

3.3.2.2 The Effect of Acid Concentration

The diffusion coefficient of cupric ion decreases with increasing acid concentration. This is seen in Figure 3.55 with the values summarized in Table 3.19. It is common to find tankhouse electrolytes with 160 to 200 g l^{-1} acid. At an equivalent copper concentration, these electrolytes could experience different diffusivities of the cupric ion by 20%.

Figure 3.55 The Effect of Acid Concentration on the Diffusion Coefficient of Copper Ions. 40 g l^{-1} Cu, 65 °C.
### Table 3.19
The Effect of H₂SO₄ Concentration on the Diffusivity of Cupric Ion in Electrolyte with 40 g l⁻¹ Cu at 65 °C

<table>
<thead>
<tr>
<th>H₂SO₄ (g l⁻¹)</th>
<th>D (x 10⁻⁶ cm²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>13.7</td>
</tr>
<tr>
<td>160</td>
<td>13.5</td>
</tr>
<tr>
<td>180</td>
<td>12.1</td>
</tr>
<tr>
<td>198</td>
<td>11.5</td>
</tr>
<tr>
<td>250</td>
<td>11.2</td>
</tr>
</tbody>
</table>

3.3.2.3 The Effect of Temperature

The effect of temperature on the diffusion coefficient typically adheres to an Arrhenius type relationship.

$$D = D_0 e^{-(Q/R)T}$$  \hspace{1cm} (3.2)

where D is the diffusion coefficient, D₀ is a pre-exponential factor, Q is the activation energy, R is the gas constant, T is temperature in K. The data generated in this study is no different. The results at several temperature are tabulated in Table 3.20. A plot of ln D vs. 1/T is contained in Figure 3.56 and yields a good linear relationship. From the slope of the Arrhenius plot, an activation energy, Eₐ, of 29.0 kJ/mole is calculated.
Table 3.20
The Effect of Temperature on the Diffusivity of Cupric Ion
in 40 g l⁻¹ Cu and 160 g l⁻¹ H₂SO₄ Electrolyte

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>D (x 10⁻⁶ cm²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>5.79</td>
</tr>
<tr>
<td>45</td>
<td>7.14</td>
</tr>
<tr>
<td>45</td>
<td>7.52</td>
</tr>
<tr>
<td>50</td>
<td>8.57</td>
</tr>
<tr>
<td>51</td>
<td>11.2</td>
</tr>
<tr>
<td>55</td>
<td>10.7</td>
</tr>
<tr>
<td>55</td>
<td>10.5</td>
</tr>
<tr>
<td>60</td>
<td>12.1</td>
</tr>
<tr>
<td>61</td>
<td>12.1</td>
</tr>
<tr>
<td>65</td>
<td>13.5</td>
</tr>
<tr>
<td>65</td>
<td>13.7</td>
</tr>
</tbody>
</table>

Figure 3.56 Arrenhius plot of ln Dₐ₁ vs 1/T for 40 g l⁻¹ Cu and 160 g l⁻¹ H₂SO₄ Electrolyte.

3.4 Impedance Spectroscopy

Impedance spectroscopy was performed on several commercial copper anodes to determine if any useful information could be generated that might help in interpreting
anode passivation. The impedance spectra were obtained for an active and passive surface in standard electrolyte and the passive surface in an electrolyte containing chloride. All of the impedance spectroscopy data are shown in Appendix VI.

3.4.1 Active Surface

A typical Nyquist plot of the impedance data for the active surface is shown in Figure 3.57. Analysis of the impedance data using a complex nonlinear least-squared fitting program as described by Boukamp [88, 89] led to an equivalent circuit model. The active electrode exhibited a parallel RC component in series with a resistor as depicted in Figure 3.58. The values of the components for this equivalent circuit are presented in Table 3.21. The components are the solution resistance (Rs), the charge transfer resistance (Rt), and the double layer capacitance as depicted by a constant phase element to include surface roughness (Q_{dl}, n). Regression analysis of the components of the active equivalent circuit indicated no obvious relationships with anode composition.
Figure 3.57 Nyquist Plot of MCCA-25 at the Open Circuit Potential with the Equivalent Circuit Calculated Values Plotted. 40 g l\(^{-1}\) Cu, 160 g l\(^{-1}\) H\(_2\)SO\(_4\), 65 °C, 1 cm\(^2\) surface area.

Figure 3.58 Equivalent Circuit for the Active Surface of a Commercial Copper Anode.
Table 3.21
Equivalent Circuit Parameters for the Active Surface

<table>
<thead>
<tr>
<th>Anode</th>
<th>$R_s$ (ohm)</th>
<th>$R_t$ (ohm)</th>
<th>$Q_{dl}$ (mF)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCCA-25</td>
<td>2.90</td>
<td>7.43</td>
<td>82.6</td>
<td>0.518</td>
</tr>
<tr>
<td>MCCA-28</td>
<td>2.96</td>
<td>3.53</td>
<td>139.7</td>
<td>0.557</td>
</tr>
<tr>
<td>MCCA-29</td>
<td>2.93</td>
<td>4.81</td>
<td>146.3</td>
<td>0.434</td>
</tr>
<tr>
<td>MCCA-34</td>
<td>2.93</td>
<td>8.33</td>
<td>98.4</td>
<td>0.494</td>
</tr>
<tr>
<td>MCCA-35</td>
<td>3.17</td>
<td>3.09</td>
<td>149.8</td>
<td>0.462</td>
</tr>
<tr>
<td>MCCA-40</td>
<td>2.85</td>
<td>5.38</td>
<td>78.0</td>
<td>0.545</td>
</tr>
<tr>
<td>MCCA-54</td>
<td>3.18</td>
<td>9.08</td>
<td>37.4</td>
<td>0.661</td>
</tr>
<tr>
<td>MCCA-64</td>
<td>2.74</td>
<td>5.98</td>
<td>51.4</td>
<td>0.596</td>
</tr>
</tbody>
</table>

3.4.2 Passive Surface

A sample Nyquist plot for a passivated copper surface is shown in Figure 3.59. From the data, an equivalent circuit was developed using the same method described previously. The equivalent circuit, shown in Figure 3.60, is similar to that presented by Compere, Frechette and Ghali [83] for a passivated impure copper surface. The appearance of a small capacitive loop at high frequencies indicates that another reaction step is occurring. In the case of copper, this would appear to be the cuprous dissolution reaction. The components of the circuit are solution resistance ($R_s$), the charge transfer resistance ($R_t$), the double layer capacitance as a capacitor ($C_{dl}$) and as depicted by a constant phase element to include surface roughness ($Q_{dl}$, $n$) for the first and second reaction, respectively and the resistance and inductance caused by an adsorbed intermediate on the surface ($R_{ads}$ and $L_{ads}$). The values of the components of the passive equivalent circuits are presented in Table 3.22.
Figure 3.59 Nyquist Plot of a Passive Surface of MCCA-25 with the Equivalent Circuit Calculated Values Plotted. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 1 cm² surface area, 0.8 V vs NHE.

Figure 3.60 Equivalent Circuit for the Passive Surface of a Commercial Copper Anode.
Table 3.22
Passive Surface Equivalent Circuit Model Components for 40 g/l Cu, 160 g/l acid, 0 ppm Cl at 65 C

<table>
<thead>
<tr>
<th>Anode</th>
<th>$R_s$ (ohms)</th>
<th>$R_t$ (ohms)</th>
<th>$C_{dl}$ (uF)</th>
<th>$R_i$ (ohms)</th>
<th>$Q_{dl}$ (mF)</th>
<th>$n(II)$</th>
<th>$R_{ads}$ (ohms)</th>
<th>$L_{ads}(I)$ (H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCCA-25</td>
<td>3.57</td>
<td>1.65</td>
<td>4.74</td>
<td>73.1</td>
<td>1.02</td>
<td>0.64</td>
<td>36.4</td>
<td>22.7</td>
</tr>
<tr>
<td>MCCA-28</td>
<td>3.38</td>
<td>0.51</td>
<td>4.06</td>
<td>67.0</td>
<td>3.44</td>
<td>0.53</td>
<td>25.6</td>
<td>9.0</td>
</tr>
<tr>
<td>MCCA-29</td>
<td>3.31</td>
<td>0.62</td>
<td>2.56</td>
<td>47.9</td>
<td>2.73</td>
<td>0.53</td>
<td>53.0</td>
<td>29.9</td>
</tr>
<tr>
<td>MCCA-34</td>
<td>3.50</td>
<td>0.91</td>
<td>2.16</td>
<td>47.1</td>
<td>1.62</td>
<td>0.59</td>
<td>44.3</td>
<td>24.1</td>
</tr>
<tr>
<td>MCCA-35</td>
<td>3.50</td>
<td>0.85</td>
<td>2.73</td>
<td>60.1</td>
<td>1.87</td>
<td>0.58</td>
<td>45.2</td>
<td>19.5</td>
</tr>
<tr>
<td>MCCA-40</td>
<td>3.83</td>
<td>1.11</td>
<td>2.20</td>
<td>74.7</td>
<td>1.36</td>
<td>0.61</td>
<td>35.9</td>
<td>16.6</td>
</tr>
<tr>
<td>MCCA-54</td>
<td>3.50</td>
<td>0.88</td>
<td>2.69</td>
<td>64.1</td>
<td>2.02</td>
<td>0.57</td>
<td>30.5</td>
<td>16.1</td>
</tr>
<tr>
<td>MCCA-64</td>
<td>3.57</td>
<td>1.80</td>
<td>1.29</td>
<td>95.0</td>
<td>1.09</td>
<td>0.61</td>
<td>49.7</td>
<td>22.6</td>
</tr>
</tbody>
</table>

Regression analysis of the passivated equivalent circuit in relation to anode chemistry exhibited several correlations. Comparing the charge transfer resistance ($II$) of anodes MCCA-40 and MCCA-64 show an increase with increasing oxygen which is in agreement with the findings of Bounoughaz, Manzini, and Ghali [25]. It is interesting to note that anodes MCCA-29 and MCCA-34 have compositions typical of anodes containing kupferglimmer and exhibit the lowest $R_t$. The double layer capacitance generally increases with increasing lead and selenium. Finally, the resistance and inductance due to the build up of adsorbed intermediate species decreases with increasing silver and selenium, as shown in Figures 3.61 and 3.62.
Figure 3.61 The Effect of Silver on the Resistance and Inductance Caused by Adsorbed Species on the Anode Surface.

Figure 3.62 The Effect of Selenium on the Resistance and Inductance Caused by Adsorbed Species on the Anode Surface.
3.4.3 The Effect of Chloride on the Passive Surface

After the positive response of chloride ion on passivation time as determined by chronopotentiometry, impedance spectroscopy was performed in an attempt to ascertain a possible mechanism. A typical complex plane plot of the impedance data generated by a passivated commercial copper anode in electrolyte containing 75 ppm chloride is shown in Figure 3.63. The results are similar in shape to the data generated in the absence of chloride and can be modeled with the same equivalent circuit, see Figure 3.58. The calculated component values for each of the eight anodes tested are summarized in Table 3.23. While changes in some values occurred with the introduction of chloride into the electrolyte, no obvious trends exist. Chloride also does not appear to counteract the effect of silver on the adsorbed species components as seen in Figure 3.64.

![Nyquist Plot](image)

Figure 3.63 Nyquist Plot of a Passive Surface of MCCA-64 with the Equivalent Circuit Calculated Values Plotted. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 75 ppm Cl⁻, 65 °C, 1 cm² surface area, 0.8 V vs NHE.
### Table 3.23
Passive Surface Equivalent Circuit Model Components for 40 g/l Cu, 160 g/l acid, 75 ppm Cl at 65 °C

<table>
<thead>
<tr>
<th>Anode</th>
<th>$R_s$ (ohms)</th>
<th>(I)</th>
<th></th>
<th>(II)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R_t$ (ohms)</td>
<td>$C_{dl}$ (uF)</td>
<td>$R_t$ (ohms)</td>
<td>$Q_{dl}$ (mF)</td>
<td>$n$ (II)</td>
<td>$R_{ads}$ (ohms)</td>
<td>$L_{ads(I)}$ (H)</td>
</tr>
<tr>
<td>MCCA-25</td>
<td>3.98</td>
<td>1.55</td>
<td>1.27</td>
<td>71.3</td>
<td>1.13</td>
<td>0.62</td>
<td>40.1</td>
<td>19.1</td>
</tr>
<tr>
<td>MCCA-28</td>
<td>3.70</td>
<td>1.04</td>
<td>1.60</td>
<td>60.9</td>
<td>1.78</td>
<td>0.58</td>
<td>28.5</td>
<td>18.0</td>
</tr>
<tr>
<td>MCCA-29</td>
<td>3.86</td>
<td>0.66</td>
<td>2.18</td>
<td>47.9</td>
<td>2.49</td>
<td>0.54</td>
<td>36.6</td>
<td>17.0</td>
</tr>
<tr>
<td>MCCA-34</td>
<td>4.04</td>
<td>1.42</td>
<td>1.38</td>
<td>63.3</td>
<td>1.40</td>
<td>0.59</td>
<td>52.4</td>
<td>26.1</td>
</tr>
<tr>
<td>MCCA-35</td>
<td>3.94</td>
<td>1.23</td>
<td>1.53</td>
<td>70.8</td>
<td>1.54</td>
<td>0.58</td>
<td>42.5</td>
<td>23.7</td>
</tr>
<tr>
<td>MCCA-40</td>
<td>3.66</td>
<td>0.96</td>
<td>1.79</td>
<td>59.1</td>
<td>2.46</td>
<td>0.54</td>
<td>37.7</td>
<td>16.3</td>
</tr>
<tr>
<td>MCCA-54</td>
<td>3.63</td>
<td>1.28</td>
<td>1.27</td>
<td>69.0</td>
<td>1.56</td>
<td>0.59</td>
<td>36.7</td>
<td>19.1</td>
</tr>
<tr>
<td>MCCA-64</td>
<td>4.10</td>
<td>1.39</td>
<td>1.30</td>
<td>73.6</td>
<td>1.21</td>
<td>0.60</td>
<td>49.2</td>
<td>23.8</td>
</tr>
</tbody>
</table>

![Figure 3.64](image_url)

**Figure 3.64** The Effect of Silver and Chloride on the Resistance Caused by Adsorbed Species on the Anode Surface.
4 PASSIVATION MECHANISM AND PREDICTIVE MODELING

4.1 Mechanistic Approach to Passivation

The predominant focus of this investigation has been the use of chronopotentiometry to elucidate the passivation characteristics of commercial copper anodes. Therefore, the four distinct regions typically observed in each chronopotentiogram will be thoroughly analyzed and discussed. Particular emphasis will be placed on developing a comprehensive mechanism for anode passivation. Supporting information from other electrochemical techniques will be introduced as clarifying or supporting evidence.

4.1.1 Active Dissolution (Region I)

The initiation of the applied current causes the dissolution of the commercial copper anode to commence, resulting in the first region of the chronopotentiogram. At first glance, the potential seems reasonably stable while slightly increasing. Compared to the large potential anomalies found in subsequent regions, this region appears to be rather well behaved and uneventful. However, the evidence deduced within the active dissolution region clearly foretells of the passivation that will eventually occur.

4.1.1.1 Increased Copper Concentration at the Anode Surface

At the very beginning of each chronopotentiogram the potential jumps in response to the overpotentials generated as the current is applied. Figure 4.1 illustrates the potential response for anode MCCA-42 during the first 60 seconds of an experiment with a data acquisition rate of 500 samples s$^{-1}$. During the initial phases of this investigation, data
were collected at an acquisition rate of two samples s\(^{-1}\). Upgrades to computer interfaces and galvanostat control allowed for a more detailed examination of features present throughout the chronopotentiogram by measuring more points per second. For example, using the older method a 40 minute experiment would yield 1200 data points compared to the new system's 1.2 million data points. Needless to say, the increase in data acquisition gives better resolution to oscillations and other electrochemical phenomena.

After the initial sudden potential increase, there is a more gradual increase for approximately eight seconds. This is believed to be the result of increasing copper concentration in the electrolyte directly at the anode surface. Mass transfer of copper from the anode predominantly occurs by diffusion because convection is limited in the Nernst boundary layer and migration is hindered by copper's small transport number in these solutions [90].
A one-dimensional finite difference approach was used to calculate the copper concentration versus time caused by the dissolution of pure copper. A constant diffusion coefficient of $1.37 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, which was generated using linear sweep voltammetry with a platinum rotating disk electrode, was assumed for ease of calculation. The Nernst boundary thickness was taken to be 0.02 cm thick based on data from Schab and Hein [90]. The incremental distance and time were chosen to be 2.7 microns and 2.2 milliseconds, respectively. Using these parameters, the time dependence of the surface concentration of copper was calculated. The data is presented in Figure 4.2. Interestingly, saturation of CuSO$_4$·5H$_2$O based on data from Linke [86] should be achieved at approximately 6.8 seconds, which correlates well with the eight seconds of gradually increasing potential increased observed at the start of the chronopotentiogram.
Figure 4.2 The Time Dependence of Copper Concentration by Dissolving Pure Copper Calculated Using a Finite Difference Method.

4.1.1.2 Potential Response to the Formation of a Non-Conducting Film

From the finite difference calculations, it appears that for a pure copper sample that copper sulfate formation would occur rapidly. Copper sulfate would start to form a non-conducting barrier on the anode surface effectively blocking some of the surface area. This would result in an increase in the current density on the remaining active surface; thus causing a higher potential.

Kortum [23] illustrated the mathematical derivation for the potential-time response when a non-conducting film forms on the electrode due to the sudden application of a constant current. In the derivation, two assumptions are made. The first is that the formation of the film obeys Faraday's Law. The second assumption is that potential is linear with current (small field approximation), which fails when a high current density is applied as
in the current investigation. Therefore, the potential-time response has been re-derived assuming a Tafel relationship between the overpotential and the applied current density.

Potential is a function of the true current density, \( i_w \), not the apparent (geometric) current density, \( i_s \). The relationship between the two current densities is as follows:

\[
i_s = i_w (1-\theta)
\]

(4.1)

where \( \theta \) is the fraction of coverage on the electrode. Recalling that the film coverage is assumed to obey Faraday's Law thus

\[
d\theta/dt = k \ i_s
\]

(4.2)

where \( t \) is time, and \( k \) is a constant (the surface fraction covered due to one coulomb of charge passed). As indicated by Kortum, the film can also dissolve at a constant rate independent of surface coverage or potential provided the conditions of convection are fixed. This rate of dissolution can be expressed as an apparent dissolution current density, \( i_k \). Hence, the change in surface coverage can be re-written as

\[
d\theta/dt = k \ (i_s-i_k)
\]

(4.3)

Integration of (4.3) is trivial given that for a chronopotentiometric experiment, the applied current density is constant.

\[
\theta = k \ (i_s-i_k) \ t
\]

(4.4)

It is important to recall that time to passivation, \( \tau \), occurs when the surface is completely blocked by the non-conducting film or when \( \theta = 1 \). Therefore, at passivation the following is true:

\[
\tau = [k \ (i_s-i_k)]^{-1} \text{ or } 1 = k \ (i_s-i_k) \ \tau
\]

(4.5)
Combining equations (4.1), (4.4), and (4.5) yields the following equation for the true current density:

\[ i_w = i_o/(1-\theta) = i_o/[k (i_o-i_k) (\tau-t)] = k'/(\tau-t) \] (4.6)

where \( k' \) is a constant equal to \( i_o/[k (i_o-i_k)] \).

Now that a function has been derived for the actual current density as a function of time, the potential response caused by a large current density can be determined. Assuming a Tafel relationship, the overpotential is a function of the logarithm of the true current density or:

\[ \eta = a + b \log i_w \] (4.7)

where \( \eta \) is the overpotential and \( a \) and \( b \) are the Tafel constants.

From basic electrochemistry, the measured potential, \( E \), is the sum of the overpotentials and the reversible potential of the reaction, \( E_{\text{rev}} \).

\[ E = E_{\text{rev}} + \eta \] (4.8)

Rearranging (4.6), (4.7), and (4.8) yields the following relationship:

\[ E = E_{\text{rev}} + a + b \log k' + b \log [1/(\tau-t)] \] (4.9)

4.1.1.3 Film Formation for Commercial Copper Anodes

The previous derivation assumes that the formation of the blocking film is related to Faraday's Law. For pure copper, this film would be caused by the precipitation of copper sulfate. Thus, the surface coverage constant, \( k \), would be directly related to the
dissolution rate and the ability of diffusion to move the copper ionic species away from the surface.

For commercial copper anodes, other factors will affect the surface coverage constant. In particular, the formation of slimes at the anode surface will block active surface area just as copper sulfate or copper oxide will. Therefore in commercial copper anodes, the total surface coverage constant will be the sum of that caused by copper sulfate, copper oxide and slimes, which can be mathematically represented as:

\[ k_{\text{total}} = k_{\text{slimes}} + k_{\text{sulfate}} + k_{\text{oxide}} \]  

(4.10)

Assuming that during any individual experiment, the slime generation of an anode is constant, then the derivation of potential versus time still holds true. Also, since the predominant reaction involved is the dissolution of copper during Region I, the variables \( E_{\text{rev}}, a, \) and \( b \) should be constant. Therefore, a plot of \( E_t \) versus \( \log \left[ 1/(\tau-t) \right] \) should yield a straight line with a slope equivalent to the Tafel slope, \( b \), and the intercept equaling \( E_{\text{rev}} + a + b \log k' \).

Data from CP experiments using pure copper, MCCA-64 MCCA-39, and MCCA-44, are plotted in Figures 4.3-4.6, respectively. In the case of the impure anodes, it is readily seen that a linear relationship is present after some initial instability. The instability seen at the beginning of each experiment is thought to be a result of the experimental software utilized. The data for pure copper exhibit less of a correlation than those of the
commercial copper anodes. This may be caused by extremely short times to passivation that amplify any discrepancy. Regardless, it is believed that all of the plots exhibit enough linearity to indicate that non-conducting films are forming on the anode surface. The discussion of the identity of these films and a method to predict them will be presented in later sections.

All Region I potential data from the forty-four commercial copper anodes tested were plotted versus log \([1/(\tau-t)]\). Almost all of the data exhibited to a linear relationship with greater than 95% correlation. However, some individual experiments did not, and these were removed from the subsequent analysis. These non-compliances are probably a result of heterogeneities in the anode microstructure since most of the data experiments for each anode did adhere to the relationship.
Figure 4.4 Region I Potentials for MCCA-64 from Chronopotentiograms Plotted Versus Log \([1/(\tau-t)]\). A, B, C and D designate different experiments with the same anode.

Figure 4.5 Region I Potentials for MCCA-44 from Chronopotentiograms Plotted Versus Log \([1/(\tau-t)]\). A, B, C and D designate different experiments with the same anode.
Figure 4.6 Region I Potentials for MCCA-39 from Chronopotentiograms Plotted Versus Log \([1/(\tau-t)]\). A, B, C and D designate different experiments with the same anode.

4.1.1.4 Tafel Slope Determination

The average slope of each commercial anode determined from the potential vs log \([1/(\tau-t)]\) or Tafel slope is plotted as a histogram in Figure 4.7. It is readily seen that a normal distribution occurs with the exception of a few anodes with high values. All of these anodes are from one particular company, which provided samples from the ear of the anode instead of the main body. The mean slope of the entire population is 0.100 V/decade with a standard deviation of 0.025. Excluding of the data from the aforementioned company changes the mean to 0.094 V/decade and the standard deviation to 0.015. The average of the two slopes from the pure copper data is 0.134 V/decade.
The Tafel equation is a simplified form of the more complete Butler-Volmer equation that expresses the kinetics of electrochemical reaction from transition state theory. The Butler-Volmer equation can be expressed for anodic reactions as:

\[
i = i_o \left( \exp \left[ -\alpha_c F \eta / RT \right] - \exp \left[ \alpha_a F \eta / RT \right] \right)
\]  
(4.11)

where \( R \) is the gas constant, \( T \) is absolute temperature, \( F \) is Faraday's constant, \( i_o \) is the exchange current density, and \( \alpha_c \) and \( \alpha_a \) are the cathodic and anodic transfer coefficients, respectively. Rearranging (4.11) for conditions occurring at high anodic current densities reveals the Tafel equation where the constants \( a \) and \( b \) are explicitly stated:

\[
\eta = -(2.303 RT / \alpha_a F) \log i_o + (2.303 RT / \alpha_a F) \log i
\]

Comparing (4.7) and (4.12) reveals that:
From this work, the mean anodic transfer coefficient of the commercial copper anodes is calculated to be 0.67. This is extremely different than the values of 1.50 to 1.65 found by other researchers for the anodic transfer coefficient of pure copper [14-16]. However, the chronopotentiograms of pure copper in the current system exhibit an anodic transfer coefficient of 0.50. The difference is thought to result from the extremely high current densities employed in the current investigation. This may have resulted in the disproportionation reaction of the cuprous ions occurring to a greater extent than in the other studies. This changes the rate determining step from the electron transfer associated with the oxidation of cuprous to cupric. The resulting rate determining step is believed to be the dissolution of copper to cuprous. The disproportionation reaction then converts the large amounts of cuprous ion to solid copper and cupric ion. This seems to be confirmed by the observation of a significant quantity of fine copper powder that accumulated in the experimental vessel during the dissolution of pure copper.

4.1.1.5 Calculating Surface Coverage

From the previous sections, it is obvious that the increase in potential detected in Region I of the chronopotentiograms is related to the surface becoming covered with passivating films. Using the change in potential from the beginning of the active dissolution region to the end, the amount of surface blockage can be determined. The initial potential, $E_i$ is defined as the potential increase after the initial concentration build-up at the anode surface. The final voltage, $E_f$, is the value just before oscillations are detected or $t_p"$. The
difference between these values is the change in overpotential related to the decreasing surface area.

\[ E_f - E_i = \Delta \eta \]  \hspace{1cm} (4.14)

Recalling that the overpotential in the region can be expressed by the Tafel relationship, \( \Delta \eta \) can be rewritten as

\[ \Delta \eta = b \log \left( \frac{i_f}{i_i} \right) \]  \hspace{1cm} (4.15)

where \( i_f \) is the final actual current density and \( i_i \) is the initial actual current density. Since the applied current is constant and \( b \) has been determined for each anode, the relative change in surface area can be calculated using:

\[ \frac{A_f}{A_i} = 10^{-\Delta \eta/b} \]  \hspace{1cm} (4.16)

where \( A_f \) is the final active surface area and \( A_i \) is the initial active surface area. Obviously, the fraction of surface coverage is

\[ 1 - \frac{A_f}{A_i} = \theta_{\text{covered}} \]  \hspace{1cm} (4.17)

For the 44 anodes studied, the calculated surface coverage at the beginning of the potential oscillations (i.e. \( t_p" \)) was usually between 85% and 95%.

4.1.1.6 Fractional Surface Coverage Constants

The total fractional surface coverage constant, \( k_{\text{total}} \), can be determined for each anode by two different methods; the calculated surface coverage at \( t_p" \) and the time to passivation, \( t_p \). Recall that \( k_{\text{total}} \) is the fractional surface coverage per coulomb of current passed. Using the calculated surface coverage, \( k_{\text{total}} \) can be calculated by:

\[ k_{\text{total}} = \theta_{\text{covered}} / (t_p" i_{\text{applied}}) \]  \hspace{1cm} (4.18)
$k_{\text{total}}$ can also be derived from $t_p$, if surface coverage is assumed to be complete (or $\theta_{\text{covered}} = 1$) at the time of passivation.

$$k_{\text{total}} = \frac{1}{(t_p \text{ applied})}$$  \hspace{1cm} (4.19)

$k_{\text{total}}$ values were calculated for each anode using both methods. The average for each anode is graphically shown in Figure 4.8. The two different methods produced very similar values for the surface coverage constants for all forty-four anodes. Since the time to passivation is directly related to $k_{\text{total}}$, all of the previously mentioned trends with $t_p$ are directly applicable to the total surface coverage constant. This will be important when developing a model to predict $k_{\text{total}}$ and subsequently, time to passivation.

4.1.2 Pre-Passivation (Region II)

Usually between active dissolution and passivation is a region of potential oscillations. At first, these fluctuations appear very chaotic and random in the chronopotentiograms performed with potentials averaged every two seconds as shown in Figure 4.9. By
significantly increasing the number of data points taken per second, critical observations can be made about these oscillations. Before discussing the oscillations in the current system, a review of the work performed in the Fe/H₂SO₄ system will be given and then related to the Cu/H₂SO₄ system.

![Graph](image)

**Figure 4.9 Chaotic Oscillations Detected in Region II for Anode MCCA-64 using Standard Chronopotentiometric Procedure of 1 Sample per 2 sec.**

4.1.2.1 Oscillations in Fe/H₂SO₄ System

The electrochemistry of iron has probably received more attention than other metals because of the economic importance of the corrosion of iron, steel, and related ferrous materials. Oscillations during the anodic dissolution of iron in 1 N H₂SO₄ using constant potential control were first documented in the 1950's [91, 92]. Since then several different theories have been used to explain this phenomena [93-96]. Until recently, none have been able to adequately predict reasonable time constants and behavior. In 1995, Rush and Newman [97] showed that by using physical constants and a few assumptions,
they could generate oscillations using a computer model similar to those generated experimentally. Figure 4.10 illustrates this point by plotting the oscillation period versus potential for experimental and simulated data. The difference between the curves shown in Figure 4.10 is a physical parameter related to the experimental setup, which the authors claim can be modeled accurately.

The mechanism proposed by Rush and Newman involves several concepts, which can be directly applied to the oscillations observed in the Cu/H₂SO₄ system. In the discussion of the mechanism, comments will be made referring to what would be observed in a potentiostatic experiment (PS) and in a galvanostatic experiment or chronopotentiogram (CP). First, no oxide or salt is present on the surface when it is most active (maximum current (PS) or lowest potential (CP)). As the dissolution continues, the bordering electrolyte becomes concentrated with metal ion. This results in the removal of protons and the addition of sulfate to maintain electroneutrality. When the electrolyte next to the
anode becomes sufficiently supersaturated with a metallic ion, the nucleation of a non-porous sulfate salt occurs until the surface is covered (decreasing current (PS) or increasing potential (CP)). Once the surface is covered, metallic oxide will form at the interface between the sulfate salt and metal surface. The oxide can form due to the decreased presence of protons, the elevated potentials, and the presence of water hydrated in the sulfate salt. The salt film will continue to grow until the electrolyte decreases to the saturation concentration of the metal sulfate. The decrease in concentration occurs because of precipitation and the passivation of the anodic surface, which ceases to generate metal ions. Continued precipitation and diffusion depletes the adjoining electrolyte until the saturation concentration is achieved. Once the localized electrolyte reaches the saturation concentration, further reduction of the concentration by diffusion initiates salt dissolution. This will eventually expose the underlying oxide. The oxide still maintains the passivation of the metal surface. This continues to lower the metal ion concentration, which allows the transfer of protons toward the anodic surface. Once the pH of the adjacent electrolyte becomes sufficiently acidity, the thin oxide dissolves very rapidly. This results in the surface becoming active again (maximum current (PS) or minimum potential (CP)). At this point, one oscillation cycle is complete.

Before returning to the Cu/H₂SO₄ system, two more observations need should be noted from Rush and Newman's work. First, in a linear sweep experiment, as shown in Figure 4.11, a steady state current is observed before oscillations occur. The authors indicate that this is a result of periodic and random formation and subsequent dissolution of
ferrous sulfate on localized areas of the electrode. Oscillations will not occur until the precipitation of the salt becomes synchronized over most of the surface. The second observation is that two electrodes in the same electrolyte, but separated by a partition of insulating wax, oscillated out of phase with each other. However, the oscillations, became in phase once the partition was removed as shown in Figure 4.12.

Figure 4.11 Current-Potential Behavior for the Iron/Sulfuric Acid System at a Scan Rate of 0.2 mV/s. Rush and Newman [97]

Figure 4.12 Experimental Periodic Current-Time Curve for an Electrode Divided into Two Areas. Partition is removed during the experiment. Rush and Newman [97]
4.1.2.2 Preliminary Oscillations of Commercial Anodes

The fast scan chronopotentiograms of commercial copper anodes reveal two distinct regions of oscillations. Coming out of Region I, chaotic small amplitude oscillations are observed as seen in Figure 4.13. The amplitude of the oscillations seem dependent on the anode with values ranging from 10-40 mV. It is believed that the oscillations are the first sign that the anode is nearing passivation. The anode surface is partially covered with slimes and dissolution occurs in the pores. It is in these pores and on the surface that CuSO₄•5H₂O is forming. This is happening in an unsynchronized manner. Therefore, parts of the surface are being blocked and then unblocked as precipitation and dissolution of the salt occurs. The small scale chaotic oscillations seen in the first part of Region II are the first sign that synchronization is beginning. It should be noted that the potential is gradually increasing throughout these small oscillations, which indicates that the surface coverage caused by slimes, copper sulfate, and copper oxide is increasing.
4.1.2.3 Periodic Oscillations

The second set of oscillations in Region II is larger and periodic as seen at time greater than 1059 seconds in Figure 4.14. This is especially true for MCCA-28. Note that the potential scale (y-axis) and the time scale (x-axis) are not the same in Figures 4.13 and 4.14. The scales have been changed to accentuate the features of interest.

Further examination of Figure 4.14 reveals several interesting observations. The large-amplitude is predominantly the result of activation events. The activation is believed to be a result of the synchronization of the sulfate dissolution over a large fraction of the anode surface. The electrolyte in those areas can then be concentrated with copper ion from the recently activated surface. Eventually the increasing copper concentration will yield copper sulfate precipitation. The growth of the sulfate film causes a potential
increase and can eventually lead to a small passivation peak. The potential increase occurs over a longer period for MCCA-42 and MCCA-21 than MCCA-28. This causes a faster potential increase after activation of the surface. Regardless of the anode tested, during the larger oscillations, small oscillations are still detected as noted by the arrow in Figure 4.14. This indicates that the surface is fluctuating between unsynchronized and synchronized dissolution and formation of the sulfate/oxide film.

Once the anode becomes synchronized, then the oscillations exhibit a more uniform appearance; however, MCCA-28 is the only anode that truly exhibits a periodic behavior. Regardless, the same type of oscillation can be observed for each anode. An expanded view of this behavior is shown in Figure 4.15 (Reader: please note that the potential and time scales have been changed again to accentuate the discussed features). This plot represents only 0.45 seconds of chronopotentiometric data. A description of this
potential behavior can be generated by an analogous comparison to the model developed for the Fe/H₂SO₄ system. The cycle starts with minimum potential corresponding to the maximum active surface area. In the case of an impure copper anode, this surface area is still partially blocked by slimes, but most of the sulfate and oxide have been removed. This allows copper dissolution, which in turn causes copper sulfate formation. Copper sulfate nucleation and growth on the anode within the pores of the slimes increases from approximately 0.10 seconds at the start of the large oscillations to 0.35 seconds when the anode approaches passivation. The longer time seems to correspond with more of the surface becoming synchronized. At the interface of the sulfate and anode surface, oxide starts to form. Once the anode has passivated, the sulfate will eventually dissolve, exposing the oxide. Then the oxide may dissolve depending on the acidity of the electrolyte in each pore. Over time, the oxide will start dissolving until finally a massive dissolution occurs resulting in the activation of the surface. One cycle has been completed and another commences. These cycles will continue with ever increasing potentials until a point is reached where the potential needed to push the constant current is enough to stabilize the oxide in bulk electrolyte. The potential at which this occurred was not consistent between the three anodes examined with the fast scan chronopotentiometry. However, all of the values were greater than 0.8 V vs NHE. Once the oxide is stable, complete passivation of copper dissolution occurs.
This qualitative description of the observed oscillations relies on the formation and removal of copper sulfate and copper oxide. Abe and Gotoh [28, 34] showed that CuSO$_4$·5H$_2$O is present during potential oscillations. Cheng, Hiskey, and Krusmark [38] observed copper oxide films on an anode during the oscillations. More importantly Chen and Dutrizac displayed a photomicrograph in which a layer of CuSO$_4$·5H$_2$O is on top of a layer of copper oxide, which is in turn on top of the copper anode surface [36]. This is the configuration depicted in the previous mechanism discussion. Therefore the unified mechanism seems plausible.

### 4.1.3 Passivation Mechanism

From the analyses of Regions I and II, a mechanism for the passivation of commercial copper anodes can be developed. When the dissolution of an impure copper anode
commences, two important events occur. First, the copper concentration of the electrolyte at the anode surface increases. Secondly, refractory secondary phases (slimes) begin to release from the anode. The slimes will immediately reduce the active surface area of the electrode. This causes an increase in the current density and a subsequent increase in the copper concentration in the electrolyte within the pores of the slimes. Depending on the current density, amount of slimes, electrolyte composition and rate of diffusion, the copper concentration at the anode surface can reach the saturation limit of copper sulfate. The electrolyte will probably become supersaturated before the formation of CuSO₄•5H₂O nuclei occur in the pores of the growing slime film. At this point, the surface is coated with slimes and copper sulfate. The formation of the CuSO₄•5H₂O leads to a decrease in the copper concentration in the pores where it forms. This will eventually cause the copper sulfate to re-dissolve. Until that occurs, the sulfate layer will allow the formation of copper oxide between the sulfate and anode. When the sulfate does dissolve, if the potential and electrolyte conditions are not sufficient to sustain the oxide film, then it will also dissolve.

The slimes layer and sulfate/oxide films continue to grow with time, which causes the rise in potential noted in Region I. When the surface becomes increasingly covered, oscillations are detected as the dissolution/formation of the sulfate/oxide film become synchronized. The oscillations will continue until the electrode becomes suitably covered with slimes and oxide. This results in a high enough potential that a return to bulk
electrolyte conditions at the anode surface will not dissolve the oxide. Passivation is complete.

Simply stated, passivation occurs when the anode surface is completely covered with non-conducting or weakly conducting films. This causes the anode to stop dissolving copper. During the electrorefining of impure copper anodes, it has been shown that films of copper sulfate, copper oxide, and secondary phases or slimes can form at the anode surface. Thus, the formation rates of these film components will cause differences in passivation times.

4.1.3.1 Factors Affecting the Formation of Copper Sulfate

The formation of CuSO₄•5H₂O is dependent on the ability of the electrorefining system to supersaturate the electrolyte adjacent to the anode. Supersaturation is caused by the copper anode dissolving at a rate faster than the copper ions can diffuse away from the anode surface. Thus, anything that increases the dissolution rate or hinders diffusion will increase the formation rate of copper sulfate. This indicates that current density, electrolyte temperature and composition, and anode impurities will significantly affect CuSO₄•5H₂O formation and time to passivation.

4.1.3.2 Factors Affecting the Formation of Copper Oxide

From the qualitative analysis of Region II, the formation of copper oxide is dependent on the formation of CuSO₄•5H₂O. Copper oxide only forms after copper sulfate has blocked the surface. However, the stability of copper oxide after the copper sulfate is removed is
dependent on the potential and pH at the anode surface. Copper oxides will not dissolve until the potential and pH are low enough so that it is thermodynamically feasible.

4.1.3.3 Factors Affecting the Formation of Slimes

The formation of refractory secondary phases or slimes is completely dependent on anode chemistry and prior pyrometallurgical history. The amount of slime formers is not greatly affected by electrorefining conditions. The formation rate of slimes on the anode surface is related to the applied current because the release of slime components occurs as copper dissolves. Homogeneity of the anode structure and chemistry will affect the reproducibility of the formation rate of the slimes.

4.1.4 The Effect of Anode Composition on Passivation

Impurities in commercial anodes affect passivation by helping or hindering the formation of the three films. Therefore, contaminants can be categorized by their effect on each film. Those impurities that accelerate cupric ion generation lead to faster CuSO₄·5H₂O precipitation. Elements that affect localized pH influence the stability of copper oxide. Finally, elements that lead to slime formation by the phases that occur in the anode or reactions with the electrolyte. Each element that was shown to significantly affect time to passivation in Section 4.1 falls into at least one of these categories.

4.1.4.1 Copper Generators

The only element that can cause an increase in cupric ion generation is oxygen. Oxygen has a low solubility in copper and will form numerous oxides. The most common oxide is cuprous oxide. This oxide will dissolve chemically when exposed to the electrolyte.
That means the copper dissolution rate is the sum of the electrochemical reaction driven by the applied current and the chemical dissolution of copper oxide. Therefore, the formation of CuSO$_4$.5H$_2$O will occur more rapidly with increasing oxygen content. This should lead to a decrease in $t_p$, which is the observed trend from the data.

4.1.4.2 Acid Generators/Consumers

Elements that can affect the localized acidity of the electrolyte are Group VB (arsenic, antimony, and bismuth) and oxygen. This was theorized by Hiskey et al. [61] to describe the effect of oxygen, arsenic, and antimony on time to passivation of impure copper samples. The current investigation and data continues to follows this theory and advance it. The oscillations seen in Region II are extremely similar to those seen in the Fe/H$_2$SO$_4$ system. The Fe/H$_2$SO$_4$ oscillations can be explained by the formation of an iron oxide that dissolves when the localized pH is low enough. If copper passivation follows this type of behavior, then impurities that affect the adjacent electrolyte acidity must affect passivation.

Examination of the chemistries of each of these impurity elements indicates that oxygen, antimony, and bismuth should be acid consumers and arsenic should generate acid. This would cause oxygen, antimony, and bismuth to lead to passivation and arsenic to hinder it. In this investigation, increasing oxygen did lead to decreased passivation times (see Figure 3.12) and anodes with higher arsenic exhibited longer time to passivation (see Figure 3.18). Because of experimental scatter and the extreme variation in anode
chemistry, the effect of antimony and bismuth was not observed in this study. However, as stated earlier, the effect of antimony to decrease \( t_p \) was shown by Hiskey \textit{et al.} \cite{61}.

4.1.4.3 Slime Formers

Most of the elements shown to affect passivation in this study can be classified as slime formers. Slime-forming elements include selenium, tellurium, nickel, lead and silver. Selenium and tellurium has been shown by several researchers to occur in copper anodes predominantly as copper selenide and copper telluride. These phases dissolve very slowly in the electrolyte and thus form a portion of the slime film/layer. Therefore, increasing the selenium and tellurium should decrease the time to passivation, as seen in Figures 3.7 and 3.14. Nickel will be contained as a solute element in copper up to 2500 ppm. Above that, nickel will form two different oxides, NiO and kupferglimmer. Kupferglimmer will only form in the presence of antimony or tin \cite{47, 49-52}. Both of these oxides are corrosion resistant to the electrolyte and will block the active surface causing a decrease in \( t_p \) as seen in Figure 3.9. Kupferglimmer is believed to be especially troublesome because of its platelet morphology. Lead is usually found as a complex oxide with copper and the Group VB elements. These oxides typically dissolve into the electrolyte. Lead ion, however, is extremely insoluble because of the high sulfate concentration in the electrolyte. This causes PbSO\(_4\) to precipitate at and near to the surface, which will block the surface of the electrode. Lastly, silver is typically found in solid solution within the copper matrix. As the copper grains dissolve, the silver releases as an ion. The Ag\(^+\) then reacts in three ways: 1) it will cement on to the anode and/or selenide features as small crystallites by reacting with cuprous ions, 2) cementation with
occur will small copper crystallites which formed due to the disproportionation of cuprous ions or 3) the silver will react with the copper selenides and tellurides resulting in silver enrichment of these features [36, 60]. Obviously, the silver crystallites, which occupy surface sites, will block the dissolution of copper. The transformation of selenides and tellurides has been shown to result in a volume increase, thus covering more surface area.

4.1.5 The Effect of Electrolyte Concentrations on Passivation

Electrolyte composition affects anode passivation by its influence on the formation of blocking films. Films that can inhibit dissolution are copper sulfate, copper oxide, and adsorbed species. Since CuSO₄•5H₂O films occur by precipitation, electrolyte components that affect the solubility of copper sulfate will alter times to passivation. Copper oxide formation and stability is much more complex than that governing copper sulfate. Electrolyte parameters that alter pH and/or cuprous ion concentration can affect copper oxide formation. A film of adsorbed molecules can occur, particularly with the addition of organic compounds like glue. The adsorbed molecules would block the active surface area. Therefore, the effect of each electrolyte component can be characterized by its influence on copper sulfate solubility, pH, cuprous ion stability, and adsorbed species production.

4.1.5.1 Copper Sulfate Solubility

Copper sulfate will form on impure anodes after the concentration at the anode surface exceeds the solution's solubility with enough supersaturation to overcome any nucleation
barriers. Supersaturation occurs more rapidly when the bulk electrolyte content is closer to the saturation limit and the rate of concentration build-up at the anode increases. The increase in concentration at the surface occurs because the dissolution rate is greater than the rate of diffusion and migration. Anything that hinders diffusion will decrease the time to saturation. The copper and acid concentrations in the electrolyte affect both the proximity to the solubility limit and the rate of diffusion. Since the solubility of CuSO₄•5H₂O is controlled by the copper and sulfate concentrations in the electrolyte, increasing these would move the solution closer to the saturation limit. The diffusion rate of copper is also adversely affected by increasing the copper and acid concentrations of the electrolyte. Thus, increasing the copper and acid concentrations will lead to faster precipitation of CuSO₄•5H₂O on the anode surface. Any compound that adds more sulfate (NiSO₄, Na₂SO₄) to the total sulfate content of the electrolyte will have a similar effect, at least on the initial proximity to the saturation limit.

4.1.5.2 Acidity

Copper oxide formation and stability is governed by the potential and the acidity of the electrolyte at the anode surface. To visualize this, the Eₚ-pH diagram for the Cu-O-H₂O system is displayed in Figure 4.16 at 65 °C with a cupric ion activity of 3.97 x 10⁻³. This activity was calculated from the rest potential of 0.259 V in the linear sweep voltammetry. It is readily seen that the equilibrium between Cu²⁺ and Cu₂O or between Cu and Cu₂O is governed by a function that involves both potential and pH. The formation of the copper oxide, as theorized in section 4.2.2, occurs at the interface between the copper and precipitated CuSO₄•5H₂O as potential is elevated. The copper
sulfate will eventually dissolve thus exposing the copper oxide. The localized acidity and potential of the electrolyte will determine the stability of the copper oxide. The localized acidity will be affected by the initial concentrations of copper and acid in the electrolyte. The localized pH will increase as copper dissolution occurs to help maintain electroneutrality. The pH increase will be greater in electrolytes with lower copper and acid contents prior to copper sulfate precipitation. Thus, to minimize copper oxide stability, the concentrations of copper and acid in the electrolyte should be higher. However, this would lead to a greater likelihood of CuSO₄•5H₂O precipitation, leading to more oxide formation.

Figure 4.16 Eh-pH Diagram for the Cu-O-H₂O System at 65 °C with a cupric ion activity of 3.97 x 10⁻³.
4.1.5.3 Cuprous Ion Stability

Examination of the effect of the additives reveals that most compounds that extended the time to passivation exhibit an ability to complex cuprous ions. Complexation of cuprous ions could be beneficial by: 1) inhibiting the generation of copper particulates within the slimes resulting from the disproportionation reaction, 2) slowing the cupric concentration build-up at the anode and 3) decreasing the stability of Cu$_2$O. The dissolution of copper at the current density utilized in this investigation will involve the disproportionation reaction of the cuprous ion. With this reaction, copper particulates are formed which can join the second phase particles in the slimes. By complexing cuprous ions, this reaction will be hindered causing a decrease in the amount of slimes generation. Reduced slime quantities have been shown to result in longer times to passivation. The disproportionation reaction also generates cupric ions which lead to the saturation and precipitation of copper sulfate. By inhibiting the reaction, the formation of CuSO$_4$•5H$_2$O will occur less rapidly. Finally, the stability of Cu$_2$O can be influenced by complexing cuprous ions. The dissolution of cuprous oxide in acid can occur by the following reactions:

\[
\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0 + \text{H}_2\text{O} \quad (4.20)
\]

\[
\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e} \quad (4.21)
\]

The effect of stabilizing the cuprous ion is not easily seen in either (4.20) or (4.21). The chemical dissolution of the copper oxide (4.20) becomes more favorable with Cu$^+$ stabilization because the reaction implicitly involves the disproportionation reaction of cuprous. The electrochemical dissolution (4.21) of Cu$_2$O also involves the cuprous ion.
Reactions rarely involve a simultaneous two-electron transfer as indicated in (4.21). Therefore, an intermediate step could include the cuprous ion, which would be affected by the presence of a complexing agent. A theoretical sequence of reactions could be as follows:

\[ \text{Cu}_2\text{O} + \text{H}^+ \rightarrow \text{Cu}^+ + \text{CuOH} \]  \hspace{1cm} (4.22)

\[ \text{CuOH} + \text{H}^+ \rightarrow \text{Cu}^+ + \text{H}_2\text{O} \]  \hspace{1cm} (4.23)

\[ 2(\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{e}^-) \]  \hspace{1cm} (4.24)

Reactions (4.22) and (4.23) would favor the dissolution of cuprous oxide if the stability of the cuprous ion was increased. Regardless of the mechanism, the complexation of cuprous ions appears to extend the time to passivation.

4.1.5.4 Adsorbed Species

While organic additives, such as thiourea and glue, exhibited a positive effect at low levels, at higher concentrations these same compounds accelerated passivation. This phenomenon is thought to be caused by the adsorption of these compounds or their degradation products on the anode surface. The adsorbed film would block active surface sites just like slimes or copper sulfate, leading to passivation. In the case of thiourea, it is believed that formamidine disulfide (FDS), and ultimately elemental sulfur, act as the blocking species. However, for glue and its degradation products, it is unclear at this time how the adsorption occurs or what species are responsible for the passivating effect. There does appear to be an optimal concentration at which passivation is hindered for both glue and thiourea, but exceeding that level can be detrimental.
4.1.6 Interactions Between Anode and Electrolyte Compositions

The experiments conducted with twenty different anode samples in simulated electrolyte illustrated that interactions occur between anode composition and electrolyte additives. This was shown in Table 3.9 by the fact that some anodes experienced an increase in time to passivation while others decreased. The fractional change in $t_p$ ($\text{SIM-STD}/\text{STD}$) was compared to each impurity element. The strongest correlation was found for arsenic. High arsenic anodes, MCCA-17, MCCA-54, and MCCA-57, exhibited the largest normalized increase. This seems to indicate that anodes with arsenic respond favorably to additives in the electrolyte. Excluding these anodes high in arsenic, most of the remaining anodes show a decreasing trend in time to passivation with increasing silver. The few anodes that do not exhibit this behavior are those with high nickel.

At this time, it is not fully understood why anodes with higher arsenic respond so favorably to the introduction of additives to the electrolyte. In pure electrolyte, the effect of arsenic has been related to possible changes in localized pH at the anode surface. While the change in pH could affect the complexing equilibrium between the additives and cuprous ions, arsenic could also have an effect by providing a beneficial redox couple. Thiourea (Tu) which complexes cuprous ion according to the following reaction

$$\text{Cu}^+ + 4 \text{Tu} \rightarrow [\text{Cu(Tu)}_4]^+ \quad K_f = 2.44 \times 10^{15} \quad (4.25)$$

can also oxidize and form formamidine disulfide (FDS) around 0.5 V vs NHE.

$$2 \text{Tu} \rightarrow [\text{FDS}]^{2+} + 2 e^- \quad E^0 \approx 0.5 \text{ V} \quad (4.26)$$

The structures of thiourea and FDS in the fully protonated form is shown in Table 4.1.
Table 4.1
The Structures of Thiourea and Fully Protonated Formamidine Disulfide

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea</td>
<td><img src="image" alt="Thiourea Structure" /></td>
</tr>
<tr>
<td>Formamidine Disulfide</td>
<td><img src="image" alt="Formamidine Structure" /></td>
</tr>
<tr>
<td>Fully Protonated Form</td>
<td><img src="image" alt="Protonated Form Structure" /></td>
</tr>
</tbody>
</table>

The dissolution of arsenic involves several reactions depending on the phase present within the anode. Regardless, the terminal species of arsenic in the highly acidic electrolyte will be arsenate in the form of $\text{H}_3\text{AsO}_4$, which is generated from arsenite with a reduction standard potential of 0.575 V.

$$\text{H}_3\text{AsO}_4 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \quad E^0 = 0.575 \text{ V} \quad (4.27)$$

The arsenic oxidation coupled with the reduction of FDS could result in more Tu present at the anode. This would increase the amount of cuprous ion complexed by thiourea and extend the time to passivation.

$$[\text{FDS}]^{2+} + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2 \text{Tu} + 2 \text{H}^+ \quad (4.28)$$

The detrimental effect of silver on the response to additives in the electrolyte is believed to be related to its influence on the cuprous ion concentration. Impedance spectroscopy of the passive surface indicated that the resistance of the adsorbed intermediate (cuprous ions) decreased with increasing silver content within the anode. The addition of 75 ppm chloride to the electrolyte had minimal effect on this resistance value for the anodes tested. Since the impedance spectroscopy was performed on a passivated surface at a
potential of 0.8 V, direct comparison to mechanisms occurring at active dissolution potentials can not be made. However, it seems clear that if increasing the cuprous ion concentration at the anode surface is beneficial, then silver interferes with the ability of chloride to promote \( \text{Cu}^+ \) stability. Another explanation for the effect of silver could be the precipitation of AgCl. Silver chloride would act as another passivating film on the anode surface.

4.1.7 Interactions Between Additives

While most of the electrolyte experiments conducted during this investigation focused on a single variable, experiments conducted in factorial designs allowed for interactions between variables to be analyzed. Two-level three-factor \( (2^3) \) design was utilized with three different samples (MCCA-57, MCCA-21 and MCCA-42). These anodes were selected based on their responses to the simulated electrolyte \( (40 \text{ g l}^{-1} \text{ Cu}, 160 \text{ g l}^{-1} \text{ H}_2\text{SO}_4, 30 \text{ ppm Cl}^-, 1 \text{ ppm thiourea, and 1 ppm glue}) \). MCCA-57 demonstrated an increase in \( t_p \) with the introduction of additives; MCCA-21 remained the same; MCCA-42 decreased. The results of the factorial designs will be discussed with emphasis placed on observed interactions between the additives.

In the factorial design using MCCA-57, thiourea and chloride were found to statistically affect \( t_p'' \), \( t_p \) and \( t_p' \). Thiourea decreased all of the values by approximately 400 seconds when the concentration was increased from one to five ppm in the electrolyte. Chloride, on the other hand, increased the \( t_p \) values by about 400 seconds when increased from 20 to 40 ppm. These results were consistent with the results found using single variable
experiments with other anode samples. No significant interactions between thiourea, chloride and glue were detected for MCCA-57.

The factorial design of MCCA-21 revealed a negative influence of thiourea on $t_p''$, $t_p$ and $t_p'$. Increasing thiourea from 1 to 5 ppm decreased these values on average by 195, 230, and 253 seconds, respectively. This is again consistent with the observed results from the single variable experiments. Chloride, unlike with MCCA-57, showed no affect on the $t_p$ values, but did decrease the duration of Region II by 57 seconds. Decreasing $A_{\text{II}}$ would indicate a shorter time to stabilize the oxide film on the anode. It is unclear how this would occur. Statistically, all variables and interactions affect the duration of Region III. It is believed that this is a statistical anomaly because $A_{\text{III}}$ was extremely small for all of the experiments in this factorial design except for one condition. Besides $A_{\text{III}}$, no interactions were found to be statistically significant.

The final factorial design using MCCA-42 demonstrated many more significant effects by individual variables and interactions than those with MCCA-57 and MCCA-21. This is most likely the result of better reproducibility between similar experiments. It is believed that MCCA-42 exhibited less scatter in its data because it is less sensitive to the additives being tested. This becomes obvious when the magnitude of the effects are compared between the factorial designs. MCCA-57 is most affected, followed by MCCA-21 and then MCCA-42.
Unlike anodes MCCA-21 and MCCA-57, the results for MCCA-42 show glue is an important variable with regards to passivation. This was observed for both individual effects and interactions. Increasing the glue content from 0.5 to 2.0 ppm caused an increase in the average $t_p''$, $t_p$ and $t_p'$ of 158, 120, and 93 seconds, respectively. Thiourea again demonstrated a negative effect on $t_p$ and $t_p'$ by decreasing these values by 173 and 235 seconds, respectively. Interestingly, chloride did not exhibit any significant effects by itself for anode MCCA-42.

MCCA-42 was the only anode to display statistically significant effects due to interactions between these additives. Perhaps the easiest way to examine these effects is by looking at the interaction plots shown in Figures 4.17 through 4.20.

In Figure 4.17, an interaction between chloride and glue is observed. At the low chloride concentration, glue is observed to increase the time to passivation by 200 seconds. Whereas at the higher chloride concentration glue has little effect. Similar trends were observed for the interaction between glue and chloride for $t_p''$ and $t_p'$. It may be that increased chloride speeds the degradation of glue, which inhibits the ability of the organic molecule to extend passivation.

The interaction plot between glue and thiourea on $t_p''$ is shown in Figure 4.18. At the low glue concentration, increasing thiourea from 1 ppm to 5 ppm has a detrimental effect on $t_p''$. Increasing the glue concentration overcomes the adverse effect of thiourea. The
interaction may result from a competition for adsorption sites on the anode surface. By increasing the amounts of the long complex animal proteins, glue, within the electrolyte, the thiourea or its degradation products may be inhibited from adsorbing on the surface. Thus, the effect of excessive thiourea may be overcome by the addition of higher levels of glue.

Figure 4.17 The Interaction of Glue and Chloride on Time to Passivation for Anode MCCA-42. 40 g l⁻¹ Cu, 160 g l⁻¹ H₂SO₄, 65 °C, 3820 A m⁻², no agitation, ambient atmosphere.
The effect of the interaction between glue and thiourea on the duration of Region III is illustrated in Figure 4.19. At the high thiourea concentration, glue has no effect on $\Delta t_{III}$. On the other hand, glue has a pronounced effect at 1 ppm thiourea. Region III will be shown to be significantly affected by silver (See Section 4.1.9). Extended Region III are believed to occur when oxygen evolution occurs on lead oxide assisted by silver. Thiourea is a known complexing agent for silver. By complexing silver, thiourea probably decreases the duration of Region III. With the decreased level of thiourea, a higher concentration of glue may be aiding the complexing ability of thiourea, thus decreasing $\Delta t_{III}$. 

Figure 4.18 The Interaction of Glue and Thiourea on $t_p''$ for Anode MCCA-42. 40 g l$^{-1}$ Cu, 160 g l$^{-1}$ H$_2$SO$_4$, 65 °C, 3820 A m$^{-2}$, no agitation, ambient atmosphere.
The final interaction plot, Figure 4.20, shows the interplay between thiourea and chloride on $\Delta t_{III}$. Once again, it is evident that increasing thiourea compresses the duration of Region III. At the higher thiourea concentration, increasing the chloride content appears to reduce $\Delta t_{III}$, but at the low thiourea concentration it does not. It is believed that chloride will remove silver ion from solution by forming silver chloride, AgCl. This would appear to decrease $\Delta t_{III}$ similar to the complexing action of thiourea. Therefore, it is not understood why increasing chloride at 1 ppm thiourea expands Region III.
The factorial designs helped confirm many trends observed in the single variable experiments. Interactions between the additives were only found to be statistically significant for one of the three anodes tested (MCCA-42). However, since interactions were detected, caution should be used in tankhouses when altering the concentration of one of the additives because passivation may be affected.

4.1.8 The Effect of Current Density on Passivation

It has been well known in industry for some time that the likelihood of anode passivation decreases with decreasing current density. This is caused by a slower dissolution rate at the anode surface. The decreased rate causes two important occurrences. Slimes are released more slowly because the impurity phases are only exposed as the surrounding copper dissolves away. Secondly, a slower dissolution rate allows diffusion to remove
copper ions from the vicinity of the anode surface. This decreases the rate of surface concentration build-up and may cause a steady state cupric concentration lower than that needed to form copper sulfate. Therefore, a slower rate of slime coverage and copper sulfate formation is why lower current densities result in longer times to passivation.

4.1.9 Post-Passivation Reactions

While $t_p$ represents the passivation of copper dissolution, the resulting higher potentials cause other reactions to occur. These post-passivation reactions can be interpreted from the data in Regions III and IV of the CPs. Voltammetry and impedance spectroscopy provide additional information to aid in the interpretation.

4.1.9.1 Region III

There are two occurrences found in Region III. Data extracted from the Region III's of chronopotentiograms for MCCA-43 and MCCA-40 illustrating these are displayed in Figures 4.21 and 4.22. The Region III for MCCA-43 displays evidence that at least two reactions are occurring after passivation. This is noted by the fact that two potential plateaus can be observed in Figure 4.21. The first plateau occurs between 1.0 to 1.3 V, while the second plateau is seen between 1.7 and 2.1 V. The second plateau can be rather extended, especially for high silver anodes like MCCA-43. In Figure 4.21, the second plateau extends for approximately 500 seconds.
Figure 4.21 Expanded View of Region III for Anode MCCA-43. Standard CP Experiment.

At first, the Region III for MCCA-40 appears to be significantly different than that observed for MCCA-43. The first plateau is not observed in Figure 4.22. In fact, the minimum potential in the figure is approximately 2.0 V vs NHE. Also, the ΔtIII for MCCA-40 is only 130 seconds. Careful examination, however, reveals that Region III of MCCA-40 appears very similar to the last 130 seconds of the same region for MCCA-43. Therefore, it is believed that MCCA-40 does not have an the composition necessary to generate the first plateau as in MCCA-43, but that the second plateau is present for both anodes to a certain degree.
Figure 4.22 Expanded View of Region III for Anode MCCA-40. Standard CP Experiment.

A potential plateau is observed when a predominant reaction is occurring at the anode surface. Region I can be considered as a plateau with the dominant reaction being copper dissolution. Therefore, there are two reactions in Region III, which will be identified and discussed.

4.1.9.1.1 Silver Dissolution

The first post-passivation reaction that occurs is believed to be the dissolution of silver. At first, the potential of the plateau (1.0-1.3 V) appears to be 200-500 mV above the standard potential of silver dissolution. This would appear to be confirmed by a silver dissolution peak detected between 0.8 and 1.0 V for several anodes using LSV. However, considering the current densities involved, several hundred millivolts
overpotential is not beyond the realm of reason. In fact, the potential increase at the start of each experiment when the current is first applied is between 200 and 300 mV.

Impedance spectroscopy of a passivated surface around 0.8 V indicates that silver in the anode affects an adsorbed intermediate on the anode surface. It is most likely that the intermediate species present is Cu$^+$. Previously it has been theorized [55, 60] that silver ions react with cuprous ions causing the formation of silver particulates and cupric ions as shown by the following reaction:

$$\text{Cu}^+ + \text{Ag}^+ \rightarrow \text{Cu}^{2+} + \text{Ag}^0$$

(4.29)

The decrease in the resistance ($R_{ads}$) and inductance ($L_{ads}$) of an adsorbed intermediate (determined by impedance spectroscopy) indicates the depletion of Cu$^+$ ions with increasing silver [98]. This confirms that this reaction is indeed occurring. The impedance data also indicated that selenium might have an effect on these equivalent circuit components. Careful examination of the anode chemistries indicates that for many of these samples silver increases with increasing selenium. Therefore, the effect of selenium may only be the effect of silver. On the other hand, selenium may be providing a substrate for a reaction between copper and silver. A possible reaction sequence involving silver, selenium, and the depletion of cuprous ions could be related to the transformation of copper selenides to silver selenides [55, 60]. The reactions would be as follows:

$$x \text{ Ag}^+ + \text{Cu}_2\text{Se} \rightarrow (\text{Cu}_{2-x}\text{Ag}_x)\text{Se} + x \text{ Cu}^+$$

(4.30)

$$2 \text{ Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}^0$$

(4.31)
Finally, if this first plateau is silver dissolution, then the length of the plateau should be a reflection of the amount of silver available to dissolve from the anode surface after passivation occurs. Of course, the available silver would be a function of the silver content of the anode. Time to passivation will also be a factor because longer times would release more silver from the anode. As indicated previously, silver can react with selenides and tellurides. If silver reacts with these phases prior to passivation then it would be unavailable for dissolution. Therefore, anodes with a higher molar ratio of silver to the sum of selenium and tellurium should have a longer plateau. Using these theories, the time where the potential is less than 1.3 V in Region III is plotted versus the product of silver content (ppm), $t_p$ (sec) and molar ratio of $\text{Ag}/(\text{Se}+\text{Te})$ in Figure 4.23. While there is some scatter, a positive trend does appear to exist between these factors and the plateau time. Hence, silver dissolution is believed to be responsible for the first potential plateau observed after passivation.
Figure 4.23 Duration of First Plateau in Region III versus Ag, t_p, and Ag/(Se+Te) molar ratio.

4.1.9.1.2 Lead Oxide Formation

The second plateau occurring between 1.7 to 2.1 V is detected in the CPs of almost every anode. The duration of this plateau can be quite extended as seen in Figure 4.21. The extended Region III's appear when silver is high in the anode. Possible anodic reactions involving silver within this potential range could involve the formation of Ag^{2+}, which has a standard potential of 1.8 V vs NHE. However, the formation of the argentie ion is very uncommon in these electrolytes.

The cyclic voltammograms with a sweep rate of 20 mV s\(^{-1}\) reveal that anodes with silver contents greater than 800 ppm have a reaction commencing between 1.67 V and 1.90 V. The reaction is always followed by an increased current for the remainder of the forward sweep and part of the return sweep. It is believed that most of this increased current is
generated by oxygen evolution. Therefore, it is thought that the second plateau is oxygen evolution at a lower potential than that seen in Region IV.

The question that arises is what is causing the potential stability between 1.7 to 2.1 V for only a limited period. It is theorized that the formation of lead oxide from lead sulfate allows the second plateau in Region III. The standard potential of PbSO₄ oxidizing to PbO₂ is 1.69 V. This reaction could occur within the potential region of interest. The first drawback to predicting this reaction is that several of the anodes exhibited extremely long second plateaus. None of the anodes appear to have enough lead to indicate PbO₂ formation occurring for that duration. However, it is well known from the use of lead anodes in electrowinning and lead-acid batteries that oxygen evolution occurs fairly readily on PbO₂. Thus, oxygen evolution could be causing the extended plateaus. If this was true, then one must ask what determines the length of the plateau and why is a dependence on silver observed. A review of some research dealing with lead anodes in sulfuric acid will answer these questions.

Given the volume of research conducted on the Pb/PbSO₄/PbO₂/H₂SO₄ system, only a cursory review will be presented here that highlights the areas of importance for this discussion. It is well documented that lead and lead alloys polarized beyond 0.95 V vs Hg/Hg₂SO₄ (1.57 vs NHE) form an oxide layer. This results in a two interface electrode: the Pb/oxide layer interface where metal dissolution occurs and the oxide layer/solution interface where oxygen evolution occurs. The complexity of the reactions involved was
discussed recently by Pavlov and Monahav [99]. The most relevant aspect of that discussion to the current work is that the stoichiometry of the anodic oxide layer significantly affects oxygen evolution.

The effect of silver on lead anode behavior was investigated by Pavlov and Rogachev [100]. They showed that silver in the electrolyte reduces the oxygen evolution overpotential. Silver affected the stoichiometry of the anodic layer, which lowered the oxygen overpotential. Silver was believed to be consumed during the reactions involved.

Concerning the second plateau in Region III, the effect of silver becomes fairly obvious. The oxidation of \( \text{PbO}_2 \) causes a surface for oxygen evolution, but the presence of \( \text{Ag}^+ \) caused by the first reaction in Region III lowers the oxygen evolution potential. This results in a plateau which will have a duration related to the amount of \( \text{Ag} \) present at the anode surface upon passivation. Thus, the duration of time for the second plateau will be related to the accumulated lead and silver. This trend is shown in Figure 4.24. The plateau finally ends when the \( \text{Ag}^+ \) is consumed resulting in a higher potential needed for oxygen evolution.
Figure 4.24 Duration of Second Plateau in Region III as a Function of Silver and Lead.

4.1.9.2 Region IV

In Region IV, there are three different types of observed behavior. These are shown in Figures 4.25, 4.26, and 4.27. Figure 4.25 is data taken from a chronopotentiogram of MCCA-25. This behavior is typical of most of the Region IVs observed for the commercial copper anodes. Several anodes with high nickel exhibited a different Region IV as seen in Figure 4.26. Finally, reactivation was sometimes detected as shown in Figure 4.27. The events causing these behaviors will now be discussed.
Figure 4.25 Typical Region IV for Most Anodes. Anode MCCA-25.

Figure 4.26 Typical Region IV for Anodes Containing Kupferglimmer. Anode MCCA-34.
4.1.9.2.1 Typical Anode

The typical Region IV is marked by high potentials and sporadic oscillations as shown in Figure 4.25. It should be noted that the maximum potential recorded by the standard experimental setup was 2.66 V. Hence, flat lines at 2.66 V should not be interpreted as a plateau. In addition, a value of 2.66 V resulted in an "overload" of the potentiostat that caused no current to flow.

The fast scan chronopotentiometry utilized a different experimental procedure. This allowed the recording of potentials up to 5 V, revealing potential oscillations that were caused by oxygen evolution. Therefore, Region IV can be interpreted as oxygen evolution on the commercial copper anode.
4.1.9.2.2 The Effect of Kupferglimmer

Anodes with high enough nickel and antimony to contain kupferglimmer produce a unique Region IV as demonstrated in Figure 4.26. A relatively stable small amplitude oscillation was detected at potentials between 2.0 and 2.2 V. Using LSV and CV, oxygen evolution was detected in this same potential range. It is believed that kupferglimmer provides a much lower oxygen evolution overpotential then the other surfaces in the slimes. In addition, kupferglimmer appears to be involved as a non-consumable, unlike silver in the oxygen evolution on lead oxide. This allows the evolution of oxygen to carry the applied current without increasing potential for a prolonged period. The belief that oxygen evolution is occurring on the kupferglimmer seems to be confirmed by an industrial observation detecting oxygen evolution when anodes with kupferglimmer passivate in an industrial tankhouse [85].

The Region IV behavior of kupferglimmer in commercial copper anodes seems to be an easy way to determine if kupferglimmer is present within the anode. In Figure 4.28, the copper-nickel-oxygen phase diagram from Forsen and Lilius [51] is shown with compositions where kupferglimmer was detected and in what abundance in the presence of 1000 ppm of antimony in the anode. Overlaid on the phase diagram are points which represent the nickel and oxygen content of several anodes tested during this investigation. The anodes are grouped based on the appearance of Region IV. A good correlation exists between the phase diagram and the type of appearance of Region IV. Thus, it would
appear that an easy way to detect the presence of kupferglimmer within an anode would be to measure the oxygen evolution potential.

Figure 4.28 Cu-Ni-O Phase Diagram with Schematic Indications of the Appearance of Kupferglimmer [51]. Superimposed upon the Plot are Data for High Nickel Anodes from this Study and which Region IV was Observed.

4.1.9.2.3 Slime Detachment

In the standard electrolyte experiments, several anodes displayed reactivation during Region IV in one or more of the replications. While reactivation was not always reproducible, it was observed visually that the sudden decrease in potential corresponded to the detachment of slimes from part of the anode surface. This phenomenon was detected for MCCA-1, all of the C-Series, and all of the O-Series. The reasons for
detachment are not fully understood at this time. Demaerel [66] indicated that slimes adhesion decreased with increasing arsenic. Higher levels of arsenic could explain the behavior of the O-series and MCCA-18, but not the other four anodes.

4.2 *Passivation Modeling*

From this investigation, it has been concluded that anode passivation occurs due to the appearance of films on the anode surface. These films include slimes, copper sulfate, and copper oxide. If one could predict the formation of these films at conditions similar to industrial conditions, then changes could be made either in tankhouse operation or upstream in the feed mix to the smelter to inhibit passivation. This section is dedicated to the modeling of the film formation under laboratory conditions. Qualitative descriptions will be given on how the model may be applied to industrial practices.

4.2.1 *Prediction of Slime Formation*

The most important part of the modeling effort was the development of a method to accurately predict the amounts, types, and morphology of phases present in the slimes. The abundance of information in the literature concerning secondary phases within the copper anode structure and those reporting to the slimes was extensively used. Particular reference was given to the outstanding papers by Chen and Dutrizac [35-37, 41-48, 55-59] and those coordinated by Forsen [49-52].

4.2.1.1 Modeling of Phases

From the literature, the most common slime phases are listed in Table 4.2 with several physical properties, which will be utilized in the model. Using several simple
 assumptions, the amount of slimes generated from an anode can be calculated. All calculations are done on a basis of one metric ton of anode. The assumptions used to predict the amount of each phase are as follows:

1. **Selenides and Tellurides** - Many researchers have reported that selenium and tellurium in the as-cast anode are found predominantly as Cu$_2$Se and Cu$_2$Te. Tellurium is typically found in solid solution within the selenide phase. However, when tellurium levels are high relative to the selenium content, tellurides have been detected. Upon dissolution, these phases react with silver as the metal is released from its solid solution with copper. The amount of silver that reacts with the selenides/tellurides appears to be dependent on the quantity of silver present in the anode, the morphology, and the Ag/(Se+Te) molar ratio. In this model, all silver is allowed to react with selenium and
tellurium. This results in a phase of Cu$_{2-x}$Ag$_x$Se$_{1-y}$Te$_y$. The subscripts $x$ and $y$ are calculated from molar ratios of Ag/(Se+Te) and Se/(Se+Te), respectively. For Ag/(Se+Te) ratios greater than two, $x$ is assumed to be two with the remaining silver generating elemental silver crystallites. The molar weight and volume of the selenide/telluride phase will be slightly different for each anode and is calculated by interpolation from the pure compounds of Cu$_2$Se, Cu$_2$Te, Ag$_2$Se and Ag$_2$Te.

2. *Silver and Gold* - Based on the assumption for the selenide and telluride phases, silver reacts with these phases. If the Ag/(Se+Te) ratio is greater than two, then silver is present as small crystallites of pure silver. Silver crystallites are observable on many anodes, but Chen and Dutrizac [35, 36] have indicated that most of the silver is tied up within the selenide/telluride structures. Gold will also form crystallites and report to the selenide/telluride phase [101]. In this model, gold is not included because it is an extremely small component (but an extremely important economical one). In the anodes tested, the Ag/Au is typically at least 20:1. Therefore, it is believed that the gold will not greatly affect the molar volumes or weights.

3. *Nickel Oxide and Kupferglimmer* - Chen and Dutrizac [42, 47] disagree with Forsen [52] on the nickel solubility limit in copper at which NiO and kupferglimmer will form. Based on the literature and the microscopic and electrochemical data generated at the University of Arizona [53, 54], the following rules were used to calculate NiO and kupferglimmer (Cu$_3$Ni$_{2-x}$SbO$_6$).
Nickel oxide will form when nickel is greater than 2500 ppm. Kupferglimmer will form if nickel is greater than 3000 ppm and the antimony and tin contents are high enough. It has been shown that kupferglimmer will form when the antimony content is above 300 ppm in the absence of tin. For a metric ton of anode, 300 ppm of Sb is equivalent to 2.464 moles. Therefore, if the sum of tin and antimony concentrations is greater than 2.464 moles, it is assumed kupferglimmer will form with the available nickel above the 3000 ppm limit. If the nickel content drops below 3000 ppm prior to the depletion of antimony and tin to the 2.464 moles level, then tin oxide will form with the remaining tin.

4. *Lead Sulfate* - Lead is predominantly contained in complex lead-copper-Group VB oxides within the anode microstructure. These typically dissolve quickly and cause the formation of lead sulfate. Therefore, all lead is predicted to become lead sulfate.

5. *Tin Oxide* - Tin oxide has been shown as a secondary phase in anodes. Tin oxide has a higher melting point than copper and cuprous oxide and thus will form in the melt. Tin oxide is a refractory phase and will report to the slimes. It is assumed that all tin will form SnO₂ unless kupferglimmer is present.

6. *Copper* - A major component of industrial slimes is copper and copper oxide particles. The source of copper is believed to be individual grains released by intergranular corrosion and/or the result of the disproportionation of copper and cuprous oxide. Copper oxide can form electrochemically during
dissolution. Typical industrial slimes contain 10-40% copper. In this model, no copper is added to the predicted slime weight. This is done because of the extremely short times of electrolysis within the laboratory. If applying this model to industrial applications, a copper component must be included.

Using these assumptions, the weight of slimes in grams per tonne of anode dissolved can be calculated. Verification of the model was first attempted using survey data from Shloen and Davenport [2]. The worldwide tankhouse information included typical anode compositions and the amount of slimes generated. Using only the anode compositions with complete analyses, a slime weight was calculated for each tankhouse and compared to its reported slimes weight. A sample calculation illustrating how the amount of slimes is calculated is contained in Appendix VII. Contained also within Appendix VII is the tabulation of each refineries' typical anode composition, the total calculated slimes weight and the reported slimes weight.

Linear regression between the calculated values and the reported values yielded a slope of 0.57 with a correlation coefficient of 0.52. For most of the reported slime weights, the conditions of the slimes were not indicated. Therefore, errors may occur because it is unknown whether the slimes were decopperized or not, which would result in the calculated values being too low. Assuming that most of the reported slimes, unless otherwise indicated, are not decopperized and that the weight of copper and copper oxides in the slimes is 35% yields the results shown in Figure 4.29. Considering the use
of a "typical" anode composition and slime weight, the correlation between the prediction model and the actual data is considered to be satisfactory.

![Graph](image)

Figure 4.29 Reported Slimes versus Calculated Slimes Assuming Reported Values Contained Copper Unless Specifically Noted.

Verification of the slimes prediction model was also conducted using slimes collected from eleven anode samples that were dissolved at the University of Arizona [53]. The amount of anode dissolved, the weight of slimes generated, the predicted weight, and the percent differences are listed in Table 4.3 for each anode. The calculated amounts of each phase and the total slimes are tabulated for all of the forty four anodes tested in this investigation in Appendix VIII.
### Table 4.3

Slime Weights - Actual versus Calculated for Laboratory Dissolved Anodes

<table>
<thead>
<tr>
<th>Anode</th>
<th>Slime Weight (g slimes/tonne anode)</th>
<th>Amount of Anode Dissolved (g)</th>
<th>Predicted Wt (g)</th>
<th>Actual Wt (g)</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCCA-2</td>
<td>5228</td>
<td>181.2</td>
<td>0.95</td>
<td>0.5</td>
<td>89%</td>
</tr>
<tr>
<td>MCCA-8</td>
<td>4279</td>
<td>8.09</td>
<td>0.035</td>
<td>0.06</td>
<td>-42%</td>
</tr>
<tr>
<td>MCCA-17</td>
<td>640</td>
<td>764.3</td>
<td>0.5</td>
<td>2.0</td>
<td>-67%</td>
</tr>
<tr>
<td>MCCA-18</td>
<td>1432</td>
<td>353</td>
<td>0.5</td>
<td>0.6</td>
<td>-7%</td>
</tr>
<tr>
<td>MCCA-22</td>
<td>4324</td>
<td>112.7</td>
<td>0.5</td>
<td>0.5</td>
<td>-2%</td>
</tr>
<tr>
<td>MCCA-22</td>
<td>4324</td>
<td>183.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0%</td>
</tr>
<tr>
<td>MCCA-28</td>
<td>11170</td>
<td>168.6</td>
<td>1.88</td>
<td>2.2</td>
<td>-14%</td>
</tr>
<tr>
<td>MCCA-34</td>
<td>7420</td>
<td>384</td>
<td>2.85</td>
<td>1.9</td>
<td>50%</td>
</tr>
<tr>
<td>MCCA-40</td>
<td>1637</td>
<td>594.1</td>
<td>1.0</td>
<td>1.3</td>
<td>-17%</td>
</tr>
<tr>
<td>MCCA-45</td>
<td>6602</td>
<td>430</td>
<td>2.8</td>
<td>3.2</td>
<td>0%</td>
</tr>
<tr>
<td>MCCA-46</td>
<td>4090</td>
<td>493.8</td>
<td>2.0</td>
<td>2.5</td>
<td>-10%</td>
</tr>
<tr>
<td>MCCA-56</td>
<td>3545</td>
<td>84.2</td>
<td>0.30</td>
<td>0.3</td>
<td>19%</td>
</tr>
<tr>
<td>MCCA-72</td>
<td>1360</td>
<td>522.8</td>
<td>0.7</td>
<td>1.3</td>
<td>-45%</td>
</tr>
</tbody>
</table>

Considering the small amount of anode dissolved and the much smaller weight of slimes collected, the correlation between the calculated and actual slimes weight is reasonable.

A plot comparing the actual weights to the predicted weights is shown in Figure 4.30. Linear regression analysis of the data yields a 72.0% correlation with a slope of 0.95. The error between the predicted and actual amounts is believed to be the result of the small amount of slimes generated and the lack of a copper/copper oxide component within the model. The dissolution times for these experiments were several days instead of one hour as in the standard CP experiments. A plot of the percent difference versus the amount of copper dissolved excluding MCCA-8, which had an extremely short dissolution time, is shown in Figure 4.31. The trend indicates that as the dissolution
weight increases (i.e. time) the percent difference decreases. This is believed to be the result of an increasing amount of copper and/or Cu$_2$O within the slime layer.

4.2.1.2 Time to Passivation versus Slimes Prediction Model

Other researchers [25, 26, 28] as well as the current study have illustrated that the slime forming elements (Se, Te, Pb, Ag and Ni) adversely affect time to passivation. The slimes prediction model was devised to see if $t_p$ could be correlated to the predicted amount of slimes. The average passivation time is plotted versus the calculated slime weight for each anode tested in Figure 4.32. While the trend of decreasing passivation time with increasing slimes weight is observed, the correlation between the two is no better than the multiple linear regression of the most statistically significant anode impurities.
Figure 4.30 Actual Slime Weight versus Calculated Slime Weight for Laboratory Experiments.

Figure 4.31 Percent Difference Between Actual and Calculated Slime Weight as a Function of Amount of Dissolution.
As discussed previously, passivating films such as slimes and copper sulfate led to the potential increase in Region I, the oscillations in Region II, and ultimately passivation. A total surface coverage constant, $k_{\text{total}}$, was calculated using $t_p$ and the increase in overpotential in Region I. This constant, however, is really the sum of the surface coverage constants of the individual films, $k_{\text{slimes}}$, $k_{\text{sulfate}}$, and $k_{\text{oxide}}$. Therefore, the ability to calculate $k_{\text{slimes}}$ from the slimes prediction model would be beneficial in the prediction of passivation.

To calculate $k_{\text{slimes}}$, which is the fractional surface coverage of slimes per coulomb, a few more assumptions are needed about the size and morphology of the phases in the slimes. These assumptions are based on microscopy and observations by Chen and Dutrizac [35-37, 41-48, 55-59], Mitan [54], Scott [60], and unpublished results [53]. The physical
descriptions of the phases used in these calculations are included in Table 4.2. For phases that form small crystallites (<1 micron), an ideal spherical shape is used to estimate the volume and surface area. NiO crystals were estimated using an octahedral shape. The selenide and telluride are represented by a ring with a circular cross section.

Using these assumptions with the slime prediction model, \( k_{\text{slimes}} \) was calculated for each anode tested. \( k_{\text{total}} \) calculated from \( t_p \) is compared to the calculated \( k_{\text{slimes}} \) in Figure 4.33. In general, \( k_{\text{total}} \) increases with increasing \( k_{\text{slimes}} \) as expected. While the correlation coefficient is approximately the same as the linear regression model and the natural logarithm fit to \( t_p \) versus slime weight, it is believed that this represents a better understanding of the passivation behavior and causes.

4.2.2 Copper Sulfate and Copper Oxide Coverage

As previously stated, surface coverage can result from slimes, copper sulfate and copper oxide. The sum of these coverages results in passivation. Prediction of sulfate and oxide formation and stability is extremely complex. It would involve accurate knowledge of the concentration of ionic species within the boundary layer at extremely high ionic strengths while the dynamic processes of diffusion, migration, dissolution, convection and chemical reactions are occurring within the porous structure of the slimes layer. The detailed and complex calculations needed to predict the ionic concentrations and activity coefficients are unavailable and beyond the scope of the present work.
With that understanding, several points can be noted about predicting the formation of copper sulfate and copper oxide. These constants should be related to the current density and the bulk electrolyte concentrations. The fractional coverage due to sulfate and oxide can be calculated by subtracting $k_{\text{slimes}}$ from $k_{\text{total}}$. The remaining value, which will be referred to as $k_{\text{other}}$, represents the sum of $k_{\text{sulfate}}$ and $k_{\text{oxide}}$.

4.2.2.1 The Effect of Current Density

The effect of current density on $k_{\text{other}}$ is shown in Figure 4.34. Changes in current density do not affect $k_{\text{slimes}}$ because it is the fractional surface coverage of slimes per coulomb not per second. For all of the anodes tested, $k_{\text{other}}$ decreases with decreasing current density. This is expected since lower current densities would cause a decrease in the dissolution rate, which allows diffusion to lower the cupric ion concentration at the anode surface.
This results in slower copper sulfate formation and quicker dissolution once the sulfate forms. Oxide stability will also be affected since the changing cupric ion concentration has a substantial control on the localized pH.

![Graph](image)

Figure 4.34 The Effect of Current Density on $k_{\text{other}}$.

4.2.2.2 The Effect of Electrolyte Concentrations

Since localized electrolyte concentrations affect $k_{\text{other}}$, then the bulk electrolyte should have an effect on $k_{\text{other}}$. Figures 4.35 and 4.36 illustrate the dependence of $k_{\text{other}}$ on the copper and acid concentrations of the electrolyte, respectively. In general, $k_{\text{other}}$ increases with increasing copper and acid content in the bulk electrolyte. Increasing either of these electrolyte parameters would accelerate the formation of copper sulfate, thus increasing $k_{\text{other}}$. 

![Graph](image)
Figure 4.35 The Effect of Electrolyte Copper Concentration on $k_{(other)}$.

Figure 4.36 The Effect of Electrolyte Acid Concentration on $k_{(other)}$. 
4.3 Practical Implications of Work

The passivation modeling was performed to fit the data generated in accelerated laboratory experiments. Because of the higher current densities employed in this study, some of the assumptions used are probably not directly applicable to commercial tankhouses. However, there are trends and tendencies that have been identified that can be used by tankhouse personnel. The results with arsenic show that As is only beneficial if added to the anode, not to the electrolyte, which has been a topic of recent debate in the electrorefining community. Examining the effect of oxygen indicates that if decreasing oxygen of an anode below 1700 ppm is uneconomical then higher concentrations of oxygen may not adversely affect passivation characteristics. However, care should be taken because higher oxygen can lead to the creation of voids and might compromise the anode's structural integrity. The effect of common electrolyte additives and their interactions on anode passivation has not received much attention. The results indicate that there are complex relationships between the additives. Caution should be taken when changing the concentration of one of a tankhouse's additives. Also, there appears to be interactions between an anode's chemistry and electrolyte additives. Anodes with high arsenic responded well to the introduction of additives. Anodes with high silver reacted negatively to additives. Therefore, care should be taken when comparing the results of an additive between tankhouses or different periods within a refinery if the anode compositions are not comparable. Finally, the slimes generation model was shown to be a good predictor of the presence and amount of slimes generated. The ability to
predict slime generation prior to melting may allow for choices in ore or scrap blending to minimize passivation by heavy slimes.

The topics that are the less applicable to industrial tankhouses are the determination of the fractional surface coverage constants of the passivating films (i.e. $k_{\text{slimes}}$, $k_{\text{sulfate}}$, $k_{\text{oxide}}$). The calculation of $k_{\text{slimes}}$ assumes the slimes prediction model is completely accurate and all of the slimes remain on the surface of the anode, which is not an accurate portrayal of industrial conditions. It is well known that a distribution of sizes occur for each phase and that the selenide/telluride phase in particular have a distribution in composition. It is also well known that slimes fall during electrorefining. These discrepancies in the $k_{\text{slimes}}$ become obvious in the negative values calculated for $k_{\text{other}}$ at lower current densities. A negative $k_{\text{other}}$ value has no physical meaning, but it represents that not all of the slimes are blocking the surface as predicted. An accurate calculation of $k_{\text{slimes}}$ would involve a model that can accurately predict the microstructure of an anode, the distribution of shapes and compositions of phases and the location of the resulting slimes formation on the anode surface. The amount and rate of slime fall would then have to be determined and modeled. Any of these would not be trivial.

The difficulty of calculating an accurate $k_{\text{slimes}}$ is matched by the complexity of calculating $k_{\text{sulfate}}$ and $k_{\text{oxide}}$. It would be necessary to determine the concentration of each ionic species at high ionic strengths as a time dependent function while the dynamic processes of dissolution, diffusion, migration and convection are occurring. Also, the
structure of the slurries would have to be considered since the electrolyte concentrations will depend on the pore structure, which influences current density and the rate of diffusion by creating tortuous paths. The apparent randomness of the processes involved can be seen in Figure 4.37. The histogram of $k_{\text{other}}$ for the forty-four anodes tested at a constant current density and electrolyte concentration exhibits a fairly normal distribution. This indicates that parameters that affect $k_{\text{sulfate}}$ and $k_{\text{oxide}}$ are varying randomly even in a laboratory setting where experimental conditions are more reproducible than in an industrial refinery.

![Figure 4.37](image)

Figure 4.37 Histogram of Average $k_{\text{other}}$ for all 44 Anodes for Standard Chronopotentiometric Conditions.
5 CONCLUSIONS

The electrochemical characterization of the passivation behavior of commercial copper anodes in synthetic industrial electrolyte was performed. Chronopotentiometry was used extensively to measure the effect of anode composition and electrolyte concentrations. Voltammetry and impedance spectroscopy provided complementary data.

Chronopotentiograms exhibited four characteristic regions which correspond to: I - active dissolution, II - pre-passivation, III - post-passivation reactions, IV - passivation and oxygen evolution. Each of the four regions hold information concerning the mechanism of passivation or post-passivation occurrences. Time to passivation, \( t_p \), is a fundamentally important value and is extremely sensitive to changes in anode or electrolyte composition. It was determined that \( t_p \), \( t_p'' \) (the time at which oscillations are first detected), and the duration of the oscillations (Region II) are correlated. It is believed that a common mechanism determines all three values. This mechanism is responsible for passivation.

The extremely diverse set of forty-four commercial anodes allowed for a statistical evaluation of the effect of each impurity. Selenium, tellurium, lead, oxygen, nickel, and silver were all shown to negatively affect the time to passivation. Interestingly, as the oxygen content within an anode increased above approximately 1700 ppm, no further decrease in \( t_p \) was observed. Arsenic within the range of 103 to 2521 ppm was the only
impurity to exhibit a positive effect on $t_p$. Silver and lead were shown to be extensively involved with post-passivation reactions observed in Region III. After passivation, the dissolution of silver was observed followed by oxygen evolution. The evolution of oxygen is thought to first occur on a lead oxide which is present due to the transformation of lead sulfate. It is believed that the lead oxide's oxygen overpotential is decreased by the presence of silver, which is consumed in the process. Eventually oxygen evolution occurs on the copper oxide at a much higher potential. Anodes containing significant amounts of kupferglimmer revealed lower oxygen overpotential than the other anodes.

The response of time to passivation to eight electrolyte variables was determined. Increasing the concentration of copper, sulfuric acid and sulfate decreased $t_p$. Arsenic in the electrolyte was shown to have a minimal effect. Additives, such as chloride, glue, thiourea and polyethylene glycol, displayed an ability to delay passivation; however high levels of the organic molecules did accelerate passivation. Interactions between glue, thiourea and chloride were shown to be statistically significant in one of the three factorial designs performed. Anodes with high arsenic (>1200 ppm) responded most favorably to the introduction of chloride, glue and silver. Anodes with lower arsenic and low nickel (<2800 ppm) reacted negatively to these three additives with increasing silver content.

From a thorough analysis of the chronopotentiograms, a unified passivation mechanism was developed. The mechanism is based on the formation of inhibiting films, the most
important of which are slimes, copper sulfate, and copper oxide. Slimes limit the
dissolution process to their pore areas and inhibit diffusion by forming tortuous paths.
Copper sulfate precipitates within the slime pores and at the anode surface due to
supersaturation. Supersaturation occurs because copper diffuses at a rate slower than
dissolution within the pores. Slime formation and CuSO₄·5H₂O precipitation increases
the anode potential by decreasing the active surface area, which elevates the current
density. The higher potential results in the formation of copper oxide between the
CuSO₄·5H₂O and the anode surface. Oscillations in potential are detected because of the
instability of copper sulfate and copper oxide. Ultimate passivation occurs when the
anode potential becomes high enough to stabilize the copper oxide film in the bulk
electrolyte. All of the previous effects of anode composition and electrolyte chemistry
can be explained based on their influence on slime formation, copper sulfate
precipitation, and copper oxide stability.
APPENDIX I

Chronopotentiograms

All of the chronopotentiograms generated during this investigation are contained within this appendix. It is believed that this atlas of electrochemical data will be beneficial to future workers in the area of anode passivation during copper electrorefining. Unless otherwise stated the conditions for each experiment was 40 g l⁻¹ copper and 160 g l⁻¹ H₂SO₄ at 65 °C with a current density of 3820 A m⁻².
MCCA-3

A

B

C

D

Potential (V, vs. SHE)

Time (second)
MCCA-15

A

B

C

Potential (V, vs. SHE)

Time (second)
MCCA-20

Potential (V, vs. SHE)

Time (second)
MCCA-24

Potential (V, vs. SHE)

Time (second)
MCCA-34

**Graph D**

- **Y-axis**: Potential (V, vs. SHE)
- **X-axis**: Time (second)

**Graph E**

- **Y-axis**: Potential (V, vs. SHE)
- **X-axis**: Time (second)
MCCA-35

Potential (V, vs. SHE)

Time (second)
MCCA-44

A

B

C

D

Potential (V, vs. SHE)

Time (second)
Various Acid Concentrations with MCCA-23

- 160 g/l H₂SO₄
- 180 g/l H₂SO₄
- 200 g/l H₂SO₄
- 250 g/l H₂SO₄

Potential (V, vs. SHE)

Time (second)
Various Acid Concentrations with MCCA-25

Potential (V, vs. SHE)

Time (second)

- 160 g/l H₂SO₄
- 180 g/l H₂SO₄
- 200 g/l H₂SO₄
- 250 g/l H₂SO₄
Various Cu Concentrations with MCCA-23

Potential (V, vs. SHE)

Time (second)
Various Cu Concentrations with MCCA-25

Potentials (V, vs. SHE) vs. Time (seconds)

- **35 gpl Cu**
- **40 gpl Cu**
- **55 gpl Cu**
Various Ni Concentrations with MCCA-23

0 gpl Ni

1 gpl Ni

5 gpl Ni

20 gpl Ni

Potential (V, vs. SHE) vs. Time (second)
Various Ni Concentrations with MCCA-25

Potential (V, vs. SHE)

Time (second)
Added Sulfate as Na$_2$SO$_4$ with MCCA-23

Potential (V vs. SHE)

Time (second)
Added Sulfate as $\text{Na}_2\text{SO}_4$ with MCCA-25

<table>
<thead>
<tr>
<th>Time (second)</th>
<th>Potential (V, vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 gpl $\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>0</td>
<td>8.2 gpl $\text{SO}_4^{2-}$</td>
</tr>
<tr>
<td>0</td>
<td>32.7 gpl $\text{SO}_4^{2-}$</td>
</tr>
</tbody>
</table>
Constant Total Sulfate Experiments with MCCA-23

40 g/l Cu, 160 g/l H₂SO₄, 0 g/l Ni

40 g/l Cu, 140 g/l H₂SO₄, 12 g/l Ni

40 g/l Cu, 120 g/l H₂SO₄, 24 g/l Ni
Constant Total Sulfate Experiments with MCCA-25

- 40 g/l Cu, 160 g/l H₂SO₄, 0 g/l Ni
- 40 g/l Cu, 140 g/l H₂SO₄, 12 g/l Ni
- 40 g/l Cu, 120 g/l H₂SO₄, 24 g/l Ni

Time (second) vs. Potential (V, vs. SHE)
Arsenic added to Electrolyte as \( \text{As}_2\text{O}_5 \) with MCCA-23

<table>
<thead>
<tr>
<th>Concentration (gpl As)</th>
<th>0 gpl As</th>
<th>1 gpl As</th>
<th>5 gpl As</th>
<th>20 gpl As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (second)</td>
<td>0 600 1200 1800 2400 3000 3600</td>
<td>0 600 1200 1800 2400 3000 3600</td>
<td>0 600 1200 1800 2400 3000 3600</td>
<td>0 600 1200 1800 2400 3000 3600</td>
</tr>
</tbody>
</table>

Potential (V, vs. SHE)

Time (second)
Arsenic added to the Electrolyte as As$_2$O$_3$ with MCCA-23

![Graph showing potential (V, vs. SHE) over time (second) for 0 gpl As, 1 gpl As, and 5 gpl As.](image-url)
Arsenic added to the Electrolyte as NaH₂AsO₄ with MCCA-23
Arsenic added to the Electrolyte as $\text{As}_2\text{O}_3$ with MCCA-25

![Graph showing the effect of arsenic concentration on potential over time.](image)
Various Cl⁺ Concentrations with MCCA-23

- 10 ppm Cl⁺
- 30 ppm Cr⁺
- 50 ppm Cr⁺
- 75 ppm Cl⁺
Various Cl⁻ Concentrations with MCCA-25

Potential (V, vs. SHE)

Time (second)
Various Cl⁻ Concentrations with MCCA-42

Potential (V vs. SHE)

0 ppm Cl

20 ppm Cl

40 ppm Cl

75 ppm Cl

Time (second)
Various Cl\textsuperscript{-} Concentrations with MCCA-57

0 ppm Cl

20 ppm Cl

40 ppm Cl

75 ppm Cl

Potential (V, vs. SHE)

Time (second)
Various Thiourea Concentrations with MCCA-23

Potential (V, vs. SHE)

Time (second)
Various Thiourea Concentrations with MCCA-25

- 0 ppm Thiourea
- 0.5 ppm Thiourea
- 1 ppm Thiourea
- 3 ppm Thiourea

Potential (V, vs. SHE)

Time (second)
Various Thiourea Concentration with MCCA-42

0 ppm

0.5 ppm

1 ppm

5 ppm

Potential (V, vs. SHE)

Time (second)
Various Thiourea Concentrations with MCCA-57
Various Glue Concentrations with MCCA-23

Potential (V, vs. SHE)

Time (second)
Various Glue Concentrations with MCCA-25

Potential (V, vs. SHE)

Time (second)
MCCA-2 with Standard Electrolyte

MCCA-2 with Simulated Electrolyte

Potential (V, vs. SHE)

Time (second)
MCCA-3 with Standard Electrolyte

MCCA-3 with Simulated Electrolyte

Time (second)

Potential (V, vs. SHE)
Standard Electrolyte with MCCA-9

Simulated Electrolyte with MCCA-9
MCCA-17 with Standard Electrolyte

MCCA-17 with Simulated Electrolyte

Time (second)
MCCA-18 with Standard Electrolyte

MCCA-18 with Simulated Electrolyte
MCCA-21 with Standard Electrolyte

MCCA-21 with Simulated Electrolyte

Potential (V, vs. SHE)

Time (second)
MCCA-25 with Standard Electrolyte

MCCA-25 with Simulated Electrolyte

Potential (V, vs. SHE)

Time (second)
Standard Electrolyte with MCCA-28

Simulated Electrolyte with MCCA-28
Standard Electrolyte with MCCA-35

Simulated Electrolyte with MCCA-35

Potential (V, vs. SHE)

Time (second)
Standard Electrolyte with MCCA-40

Simulated Electrolyte with MCCA-40
Standard Electrolyte with MCCA-42

Simulated Electrolyte with MCCA-42

Potential (V, vs. SHE)

Time (second)
MCCA-45 with Standard Electrolyte

MCCA-45 with Simulated Electrolyte
Standard Electrolyte with MCCA-48

Simulated Electrolyte with MCCA-48

Potential (V, vs. SHE)

Time (second)
Standard Electrolyte with MCCA-50

Simulated Electrolyte with MCCA-50

Potential (V, vs. SHE)

Time (second)
Standard Electrolyte with MCCA-54

Simulated Electrolyte with MCCA-54
Standard Electrolyte with MCCA-57

Simulated Electrolyte with MCCA-57

Potential (V, vs. SHE)

Time (second)
Standard Electrolyte with MCCA-65

Simulated Electrolyte with MCCA-65
MCCA-21 Factorial Design

Potential (V, vs. SHE)

0.5 ppm glue, 1 ppm Thiourea, 20 ppm Cl

2 ppm glue, 1 ppm Thiourea, 20 ppm Cl

Time (second)
MCCA-21 Factorial Design

- 0.5 ppm glue, 1 ppm Thiourea, 40 ppm Cl
- 2 ppm glue, 1 ppm Thiourea, 40 ppm Cl

Potential (V, vs. SHE)

Time (second)
MCCA-21 Factorial Design

Potential (V, vs. SHE)

0.5 ppm glue, 5 ppm Thiourea, 40 ppm Cl

Time (second)

2 ppm glue, 5 ppm Thiourea, 40 ppm Cl
MCCA-42 Factorial Design

Potential (V, vs. SHE)

Time (second)

0.5 ppm glue, 1 ppm Thiourea, 20 ppm Cl

2 ppm glue, 1 ppm Thiourea, 20 ppm Cl

2 ppm glue, 1 ppm Thiourea, 20 ppm Cl
MCCA-42 Factorial Design

0.5 ppm glue, 5 ppm Thiourea, 20 ppm Cl

2 ppm glue, 5 ppm Thiourea, 20 ppm Cl

Potential (V, vs. SHE)

Time (second)
MCCA-42 Factorial Design

Potential (V, vs. SHE)

Time (second)

0.5 ppm glue, 1 ppm Thiourea, 40 ppm Cl

2 ppm glue, 1 ppm Thiourea, 40 ppm Cl
MCCA-42 Factorial Design

Potential (V, vs. SHE)

Time (second)

0.5 ppm glue, 5 ppm Thiourea, 40 ppm Cl

2 ppm glue, 5 ppm Thiourea, 40 ppm Cl
MCCA-57 Factorial Design

0.5 ppm glue, 1 ppm Thiourea, 20 ppm Cl

2 ppm glue, 1 ppm Thiourea, 20 ppm Cl

Time (second)
MCCA-57 Factorial Design

Potential (V, vs. SHE)

Time (second)

0.5 ppm glue, 5 ppm Thiourea, 20 ppm Cl

2 ppm glue, 5 ppm Thiourea, 20 ppm Cl
MCCA-57 Factorial Design

Potential (V, vs. SHE)

Time (second)

0.5 ppm glue, 1 ppm Thiourea, 40 ppm Cl

2 ppm glue, 1 ppm Thiourea, 40 ppm Cl

2 ppm glue, 1 ppm Thiourea, 40 ppm Cl
MCCA-57 Factorial Design

Potential (V, vs. SHE)

Time (second)

0 ppm glue, 5 ppm Thiourea, 40 ppm Cl

0.5 ppm glue, 5 ppm Thiourea, 40 ppm Cl

2 ppm glue, 5 ppm Thiourea, 40 ppm Cl
MCCA-25 with Bromide Added to the Electrolyte

Potential (V, vs. SHE)

Time (second)

0.2 ppm Br

0.4 ppm Br

0.6 ppm Br

1 ppm Br

0 600 1200 1800 2400 3000 3600

0 600 1200 1800 2400 3000 3600

0 600 1200 1800 2400 3000 3600

0 600 1200 1800 2400 3000 3600
MCCA-57 with Polyethylene Glycol

0 ppm PEG

25 ppm PEG

100 ppm PEG

200 ppm PEG

Potential (V, vs. SHE)

Time (second)
APPENDIX II

The calculation of cuprous concentration in equilibrium with 10 ppm chloride ion at 65 °C follows.

\[
\text{Cu}^{+}(_{\text{aq}}) + \text{Cl}^{-}(_{\text{aq}}) = \text{CuCl}(_{\text{s}})
\]

\[
\Delta G^\circ = \Delta G_{f,\text{CuCl}} - (\Delta G_{f,\text{Cu}} + \Delta G_{f,\text{Cl}^-})
\]

\[
\Delta G^\circ = -28.2 \text{ kcal mole}^{-1} - (12.0 \text{ kcal mole}^{-1} + -31.35 \text{ kcal mole}^{-1})
\]

\[
\Delta G^\circ = -8.85 \text{ kcal mole}^{-1}
\]

\[
\Delta G = \Delta G^\circ + RT \ln (1/K_{sp})
\]

at equilibrium \(\Delta G = 0\), so

\[
0 = -8850 \text{ cal mole}^{-1} + 1.987 \text{ cal K}^{-1} \text{ mole}^{-1} * 338.15 \text{ K} \ln (1/K_{sp})
\]

\[
K_{sp} = 1.90 \times 10^{-6} = a_{\text{Cu(I)}} a_{\text{Cl}^-}
\]

Assuming an activity coefficient of one for each specie then

\[
K_{sp} = 1.90 \times 10^{-6} = [\text{Cu(I)}] [\text{Cl}^-]
\]

10 ppm chloride ion is equivalent to \(2.82 \times 10^{-4}\) M.

\[
[\text{Cu(I)}] = 6.74 \times 10^{-3} \text{ M or 428 ppm}
\]

The calculation of the concentration of bromide ion that will be equivalent to 10 ppm chloride ion in terms of equilibrium with cuprous ions.

\[
\text{Cu}^{+}(_{\text{aq}}) + \text{Br}^{-}(_{\text{aq}}) = \text{CuBr}(_{\text{s}})
\]

\[
\Delta G^\circ = \Delta G_{f,\text{CuBr}} - (\Delta G_{f,\text{Cu}} + \Delta G_{f,\text{Br}^-})
\]

\[
\Delta G^\circ = -23.81 \text{ kcal mole}^{-1} - (12.0 \text{ kcal mole}^{-1} + -24.57 \text{ kcal mole}^{-1})
\]
\[ \Delta G^0 = -11.24 \text{ kcal mole}^{-1} \]

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{1}{K_{sp}} \right) \]

at equilibrium \( \Delta G = 0 \), so

\[ 0 = -11240 \text{ cal mole}^{-1} + 1.987 \text{ cal K}^{-1} \text{ mole}^{-1} \times 338.15 \text{ K} \ln \left( \frac{1}{K_{sp}} \right) \]

\[ K_{sp} = 5.43 \times 10^{-8} = a_{\text{Cu(I)}} a_{\text{Br}^-} \]

Assuming an activity coefficient of one for each specie then

\[ K_{sp} = 5.43 \times 10^{-8} = [\text{Cu(I)}] [\text{Br}^-] \]

The cuprous ion concentration from the calculation with chloride is \( 6.74 \times 10^{-3} \text{ M} \).

\[ [\text{Br}^-] = 8.06 \times 10^{-6} \text{ M} \text{ or } 0.64 \text{ ppm} \]
APPENDIX III

Fast Scan Chronopotentiograms

Fast scan chronopotentiometry (FSCP) was conducted to elucidate passivation mechanisms from the oscillations present in Region II. All experiments were conducted in 40 g l⁻¹ copper and 160 g l⁻¹ H₂SO₄ at 65 °C with a current density of 3820 A m⁻² at an acquisition rate of 500 samples per second. The Region II's from each FSCP is given in this appendix. The anode tested is given at the top of each plot.
FSCP with MCCA-21

Potential (V vs NHE)

time (sec)
FSCP with MCCA-21

Potential (V vs NHE)

time (sec)
FSCP with MCCA-28

Potential (V vs NHE) vs time (sec)
FSCP with MCCA-42

Potential (V vs NHE)

675 725 775 825 875 925 975

time (sec)
FSCP with MCCCA-42

Potential (V vs NHE) vs time (sec)
FSCP with MCCA-42

Potential (V vs NHE)

time (sec)
APPENDIX IV

Linear Sweep and Cyclic Anodic Voltammetry

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were utilized to complement the electrochemical data generated by chronopotentiometry. All experiments were conducted in 40 g l⁻¹ copper and 160 g l⁻¹ H₂SO₄ at 65 °C. LSV scan rate was 0.1 mV s⁻¹, while the CV scan rate was 20 mV s⁻¹. Results from LSV are shown first in the appendix with the anode designation in the upper right of each plot. For the CV data, all of the performed scans are displayed and the anode designation is located at the top of each plot.
MCCA-6

Current Density (A/m²)

Potential (V, vs. SHE)

$E_p = 0.544 \text{ V}$

$E_1 = 0.400 \text{ V}$

$E_2 = 0.800 \text{ V}$

0.257 V

0.0

0.5

1.0

1.5
MCCA-15

Current Density (A/m²)

Potential (V, vs. SHE)

E_p = 0.465 V
E_1 = 0.361 V
E_2 = 0.800 V

0.0 0.5 1.0 1.5

0 1000 2000 3000 4000 5000 6000
$E_p = 0.467 \text{ V}$

$E_2 = 0.900 \text{ V}$

$0.261 \text{ V}$
Potential (V, vs. SHE):

- $E_p = 0.471 \text{ V}$
- $E_2 = 0.800 \text{ V}$
- $0.261 \text{ V}$
The graph shows the current density (A/m²) as a function of potential (V, vs. SHE). The key potentials and values are:

- $E_p = 0.521 \text{ V}$
- $E_2 = 0.800 \text{ V}$
- $0.257 \text{ V}$

The graph is labeled with MCCA-29.
MCCA-34

Current Density (A/m²)

E_p = 0.475 V

E_2 = 0.800 V

0.257 V

Potential (V, vs. SHE)
MCCA-35

\[ E_p = 0.494 \text{ V} \]

\[ E_2 = 0.800 \text{ V} \]

\[ 0.257 \text{ V} \]

Current Density (A/m²)

Potential (V, vs. SHE)
MCCA-45

Current Density (A/m²)

Potential (V, vs. SHE)

Ep = 0.496 V
E₁ = 0.376 V
E₂ = 0.800 V

0.256 V
Potential (V, vs. SHE)

Current Density (A/m²)

Ep = 0.507 V
E1 = 0.383 V
E2 = 0.700 V
0.258 V
MCCA-54

Current Density (A/m²)

Potential (V, vs. SHE)

E_p = 0.504 V

E_2 = 0.800 V

0.261 V
Current Density (A/m²)

Potential (V, vs. SHE)

MCCA-64

$E_p = 0.534 \text{ V}$

$E_2 = 0.800 \text{ V}$

$0.257 \text{ V}$
MCCA-35

Current Density (A/cm²)

E vs. NHE (V)
MCCA-45

Current Density (A/cm²)

E vs. NHE (V)
MCCA-46

Current Density (A/cm²)

E vs. NHE (V)

1st Scan
2nd Scan
3rd Scan
4th Scan
5th Scan
MCCA-57

Current Density (A/cm²) vs. E vs. NHE (V)
APPENDIX V

Linear Sweep Cathodic Voltammetry

Linear sweep voltammetry (LSV) in conjunction with a rotating platinum electrode was utilized to determine the apparent diffusion coefficient of copper as a function of copper concentration, sulfuric acid concentration, and temperature of the electrolyte. All experiments were conducted by sweep the potential from -300 mV to -1200 mV vs the MSE using a scan rate of 10 mV s\(^{-1}\). This appendix contains the cathodic linear sweeps and the resulting plots of limiting current versus the square root of the rotational frequency. Using the Levich equation, the diffusion coefficient was calculated from the slope of the latter plots.
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 65 °C

Potential (V vs MSE)

mA

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200

700 rpm
500 rpm
400 rpm
300 rpm
200 rpm
Levich Equation:

\[ i_{lc} = 0.620nFAD_0^{2/3} \omega^{1/2} V^{-1/6} C_0 \]

Calculated Value:

- \[ D = 1.35 \times 10^{-5} \text{ cm}^2/\text{s} \]
- \[ y = 9.715E-02x - 3.798E-02 \]
- \[ R^2 = 9.539E-01 \]
LSV w/ RDE

40 g/l Cu, 160 g/l H$_2$SO$_4$, 65 °C

Potential (V vs MSE)

mA
Levich Equation:
\[ i_c = 0.620nFAD_o^{2/3} \omega^{1/2} \nu^{-1/6}C_o \]

Calculated Value:
\[ D = 1.37 \times 10^{-5} \text{ cm}^2/\text{s} \]

Graph:
- Linear relationship between \( \omega^{1/2} \) and \( i_{\text{lim}} \) with data points fitting the line:
  \[ y = 9.814 \times 10^{-2}x - 5.581 \times 10^{-2} \]
  \( R^2 = 9.953 \times 10^{-1} \)
LSV w/ RDE
44 g/l Cu, 160 g/l H₂SO₄, 65 °C

Potential (V vs MSE)

mA

700 rpm
600 rpm
500 rpm
400 rpm
300 rpm
200 rpm

0 50 100 150 200 250

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200
Levich Equation:
\[ i_{\text{lim}} = 0.620nFAD_0^{2/3}\omega^{1/2}V^{-1/6}C_0 \]

Calculated Value:
\[ D = 1.25 \times 10^{-5} \text{ cm}^2/\text{s} \]

**Graph:**
- Y-axis: \( i_{\text{lim}} \) (A/cm²)
- X-axis: \( \omega^{1/2} \)
- Points on the graph
- Equation of the line:
  \[ y = 1.022E-01x - 3.597E-02 \]
  \[ R^2 = 9.999E-01 \]
LSV w/ RDE
45 g/l Cu, 160 g/l H₂SO₄, 65 °C

Potential (V vs MSE)

mA

500 rpm
400 rpm
300 rpm
200 rpm
100 rpm

Potential (V vs MSE)
LSV w/ RDE
45 g/l Cu, 160 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lim} = 0.620 n F A D_o^{2/3} \omega^{1/2} v^{-1/6} C_o \]

Calculated Value:
\[ D = 1.15 \times 10^{-9} \text{ cm}^2/\text{s} \]

Calculated Line:
\[ y = 9.799 \times 10^{-2} x + 9.995 \times 10^{-3} \]

\[ R^2 = 9.953 \times 10^{-1} \]
LSV w/ RDE
50 g/l Cu, 160 g/l H$_2$SO$_4$, 65 °C

Potential (V vs MSE)

mA

0 50 100 150 200

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200

500 rpm
400 rpm
300 rpm
200 rpm
100 rpm
LSV w/ RDE
50 g/l Cu, 160 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lc} = 0.620nFAD_0^{2/3}ω^{1/2}v^{-1/6}C_0 \]

Calculated Value:
\[ D = 1.16 \times 10^{-5} \text{ cm}^2/\text{s} \]

Graph:
- Line equation: \( y = 1.095E-01x - 7.081E-03 \)
- \( R^2 = 9.970E-01 \)
LSV w/ RDE
50 g/l Cu, 160 g/l H₂SO₄, 65 °C
LSV w/ RDE
50 g/l Cu, 160 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lc} = 0.620nFAD_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
D = 1.13 x 10⁻⁵ cm²/s

\[ y = 1.073E-01x + 1.780E-02 \]
\[ R^2 = 9.939E-01 \]
LSV w/ RDE
60 g/l Cu, 160 g/l H₂SO₄, 65 °C

Potential (V vs MSE)

mA

500 rpm
400 rpm
300 rpm
200 rpm
100 rpm
LSV w/ RDE
60 g/l Cu, 160 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lc} = 0.620nFAD_o^{2/3} \omega^{1/2} v^{-1/6} C_o \]

Calculated Value:
\[ D = 1.09 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ y = 1.241E-01x + 1.720E-02 \]
\[ R^2 = 9.955E-01 \]
LSV w/ RDE
70 g/l Cu, 160 g/l H₂SO₄, 65 °C

Potential (V vs MSE)

mA

0 50 100 150 200 250 300

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200

100 rpm
200 rpm
300 rpm
400 rpm
700 rpm
LSV w/ RDE

70 g/l Cu, 160 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lim} = 0.620nFAD_o^{2/3} \omega^{1/2}V^{-1/6}C_o \]

Calculated Value:
\[ D = 1.00 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ y = 1.341E-01x + 7.262E-02 \]
\[ R^2 = 9.930E-01 \]
LSV w/ RDE
40 g/l Cu, 180 g/l H₂SO₄, 65 °C

Potential (V vs MSE)
LSV w/ RDE
40 g/l Cu, 180 g/l H₂SO₄, 65 °C

Levich Equation:
\[ i_{lc} = 0.620 n F A D_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
\[ D = 1.21 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ y = 9.035 \times 10^{-2} x - 3.621 \times 10^{-2} \]
\[ R^2 = 9.988 \times 10^{-1} \]
LSV w/ RDE
40 g/l Cu, 198 g/l H₂SO₄, 65 °C
Levich Equation:
\[ i_c = 0.620nFAD_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
\[ D = 1.15 \times 10^{-5} \text{ cm}^2/\text{s} \]

Regression Equation:
\[ y = 8.671E-02x - 2.632E-02 \]
\[ R^2 = 9.997E-01 \]
LSV w/ RDE

40 g/l Cu, 250 g/l H$_2$SO$_4$, 65 °C

Potential (V vs MSE)
Levich Equation:
\[ i_{lim} = 0.620nFAD_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
\[ D = 1.12 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ y = 8.447E-02x - 4.715E-02 \]
\[ R^2 = 9.980E-01 \]
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 40 °C
Levich Equation:

\[ i_{\lim} = 0.620nFAD_0^{2/3}\omega^{1/2}v^{-1/6}C_0 \]

Calculated Value:

\[ D = 5.79 \times 10^{-6} \text{ cm}^2/\text{s} \]

Regression Equation:

\[ y = 5.259 \times 10^{-2}x + 4.148 \times 10^{-2} \]

\[ R^2 = 9.979 \times 10^{-1} \]
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 45 °C

Potential (V vs MSE)

mA

500 rpm
400 rpm
300 rpm
200 rpm
100 rpm

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 45 °C

Levich Equation:
\[ i_c = 0.620n FAD_c^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
\[ D = 7.14 \times 10^{-6} \text{ cm}^2/\text{s} \]

\[ y = 6.099E-02x + 2.622E-02 \]
\[ R^2 = 9.816E-01 \]
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 45 °C

Potential (V vs MSE)
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 45 °C

Levich Equation:
\[ i_{lc} = 0.620 n F A D_o^{2/3} \omega^{1/2} v^{-1/6} C_o \]

Calculated Value:
\[ D = 7.52 \times 10^{-6} \text{ cm}^2/\text{s} \]

Graph:
- Equation: \( y = 6.315E-02x + 5.524E-03 \)
- \( R^2 = 9.936E-01 \)
LSV w/ RDE

40 g/l Cu, 160 g/l H₂SO₄, 50 °C
Levich Equation:

\[ i_{lc} = 0.620nFAD_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:

\[ D = 0.86 \times 10^{-5} \text{ cm}^2/\text{s} \]

Linear Fit:

\[ y = 6.960E-02x - 1.896E-02 \]

\[ R^2 = 9.999E-01 \]

\( \omega^{1/2} \) vs. \( i_{lim} \) (A/cm²)
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 51 °C

Potential (V vs MSE) vs mA

700 rpm
500 rpm
400 rpm
300 rpm
200 rpm

0 - 300 - 400 - 500 - 600 - 700 - 800 - 900 - 1000 - 1100 - 1200
Levich Equation:

\[ i_{\text{lim}} = 0.620n FAD_0^{2/3}\omega^{1/2} v^{-1/6}C_0 \]

Calculated Value:

\[ D = 1.12 \times 10^{-5} \text{ cm}^2/\text{s} \]

\[ y = 8.357 \times 10^{-2}x - 4.844 \times 10^{-2} \]

\[ R^2 = 9.709 \times 10^{-1} \]
LSV w/ RDE
40 g/l Cu, 160 g/l H$_2$SO$_4$, 55 °C

Potential (V vs MSE)
Levich Equation:
\[ i_c = 0.620nFAD_0^{2/3} \omega^{1/2} V^{-1/5} C_0 \]

Calculated Value:
\[ D = 1.07 \times 10^{-5} \text{ cm}^2/\text{s} \]

Graph:
- \( y = 8.165 \times 10^{-2}x - 2.393 \times 10^{-2} \)
- \( R^2 = 9.991 \times 10^{-1} \)
Levich Equation:
\[ i_{\text{lim}} = 0.620nFAD_0^{2/3} \omega^{1/2} v^{-1/6} C_0 \]

Calculated Value:
\[ D = 1.05 \times 10^{-5} \text{ cm}^2/\text{s} \]

Graph:
- Plot of \( i_{\text{lim}} \) (A/cm²) vs. \( \omega^{1/2} \)
- Line with equation \[ y = 8.047E-02x - 2.296E-02 \]
- \( R^2 = 9.986E-01 \)
LSV w/ RDE

40 g/l Cu, 160 g/l H2SO4, 60 °C

Potential (V vs MSE)

mA
0 50 100 150 200

-300 -400 -500 -600 -700 -800 -900 -1000 -1100 -1200

700 rpm
500 rpm
400 rpm
300 rpm
200 rpm
Levich Equation:
\[ i_{lc} = 0.620nFAD_o^{2/3} \omega^{1/2} \nu^{-1/6} C_o \]

Calculated Value:
\[ D = 1.21 \times 10^{-5} \text{ cm}^2/\text{s} \]

Equation:
\[ y = 8.958E-02x - 4.940E-02 \]

\[ R^2 = 9.982E-01 \]
LSV w/ RDE
40 g/l Cu, 160 g/l H₂SO₄, 61 °C
Levich Equation:
\[ i_{lc} = 0.620nFA_0^{2/3} \sigma^{1/2} \nu^{-1/8}C_0 \]

Calculated Value:
\[ D = 1.21 \times 10^{-5} \text{cm}^2/\text{s} \]

\[ y = 8.957E-02x - 4.518E-02 \]
\[ R^2 = 1.000E+00 \]
APPENDIX VI

Electronic Impedance Spectroscopy

Electronic impedance spectroscopy (EIS) was conducted to complement the electrochemical data generated by the other techniques. Eight anode samples were investigated at their open circuit potential (active surface), after holding for 20 minutes at an elevated potential (passive surface), and the passive surface in the presence of 75 ppm chloride added to the electrolyte. The base electrolyte was 40 g l\(^{-1}\) copper and 160 g l\(^{-1}\) H\(_2\)SO\(_4\) at 65 °C. All of the EIS data generated are contained in this appendix.
MCCA-25
Potential: Open Circuit

- $Z''$ (ohm)

- $Z'$ (ohm)

- $|Z|$ (ohm)

- Phase (deg)

- Frequency (Hz)
MCCA-25
Potential: 0.900 V vs. NHE (75 ppm Cl')

- \( Z'' \) (ohm)

\[ \begin{array}{c}
4 & 5 & 6 & 7 & 8 \\
0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 & 1.2 & 1.4
\end{array} \]

\( Z' \) (ohm)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
</tr>
</tbody>
</table>

\( |Z| \) (ohm)

\[ \begin{array}{c}
-1 & 0 & 1 & 2 & 3 & 4 \\
1 & 0.8 & 0.6 & 0.4 & 0.2 & 0
\end{array} \]

Phase (deg)

\[ \begin{array}{c}
-1 & 0 & 1 & 2 & 3 & 4 \\
0 & 2 & 4 & 6 & 8 & 10 & 12 & 14 & 16
\end{array} \]

\[ \begin{array}{c}
-2 & 0 & 2 & 4 & 6 & 8 & 10 & 12 & 14 & 16
\end{array} \]

Frequency (Hz)
MCCA-28
Potential: Open Circuit

-\text{Z}'' (\text{ohm})

\text{Z}' (\text{ohm})

\text{Z} (\text{ohm})

|\text{Z}| (\text{ohm})

\text{Frequency (Hz)}

\text{Phase (deg)}

\text{Frequency (Hz)}
MCCA-28
Potential: 0.800 V vs. NHE

\[ \begin{align*}
Z'(\text{ohm}) \\
-15 &\quad 10 &\quad 20 &\quad 30 &\quad 40 \\
-15 &\quad -10 &\quad 0 &\quad 5 &\quad 10 \\
\end{align*} \]

\[ \begin{align*}
|Z| (\text{ohm}) \\
1 &\quad 2 &\quad 3 &\quad 4 \\
1 &\quad 1 &\quad 1 &\quad 1 \\
\end{align*} \]

\[ \begin{align*}
\text{Phase (deg)} \\
-30 &\quad -20 &\quad -10 &\quad 0 &\quad 10 &\quad 20 &\quad 30 \\
-30 &\quad -20 &\quad -10 &\quad 0 &\quad 10 &\quad 20 &\quad 30 \\
\end{align*} \]

Frequency (Hz)
MCCA-28
Potential: 0.800 V vs. NHE (75 ppm Cl⁻)

[Graph of -Z'' (ohm) vs. Z' (ohm)]

[Graph of |Z| (ohm) vs. Frequency (Hz)]

[Graph of Phase (deg) vs. Frequency (Hz)]
MCCA-29
Potential: Open Circuit

- $Z''$ (ohm)
- $Z'$ (ohm)
- $|Z|$ (ohm)
- Phase (deg)

Frequency (Hz)
MCCA-29
Potential: 0.700 V vs. NHE

$-Z''$ (ohm)

$Z'$ (ohm)

$|Z|$ (ohm)

Frequency (Hz)

Phase (deg)

Frequency (Hz)
MCCA-29
Potential: 0.700 V vs. NHE (75 ppm Cl⁻)

\begin{align*}
\text{Frequency (Hz)} & \\
-1 & 0 & 1 & 2 & 3 & 4 \\
|Z| (\text{ohm}) & \\
1 & & & & & \\
\text{Phase (deg)} & \\
-30 & -20 & -10 & 0 & 10 & 20 & 30 \\
\text{Frequency (Hz)} & \\
-1 & 0 & 1 & 2 & 3 & 4 \\
\end{align*}
MCCA-34
Potential: Open Circuit

\(-Z''\) (ohm)

\(Z'(\text{ohm})\)

\(|Z|\) (ohm)

Frequency (Hz)

Phase (deg)

Frequency (Hz)
MCCA-34
Potential: 0.800 V vs. NHE

- $Z''$ (ohm)

- $Z'$ (ohm)

- $|Z|$ (ohm)

- Phase (deg)

- Frequency (Hz)
MCCA-34
Potential: 0.800 V vs. NHE (75 ppm Cl⁻)
MCCA-35
Potential: Open Circuit

\[ -Z'' \text{ (ohm)} \]

\[ Z' \text{ (ohm)} \]

\[ |Z| \text{ (ohm)} \]

\[ \text{Frequency (Hz)} \]

\[ \text{Phase (deg)} \]

\[ \text{Frequency (Hz)} \]
MCCA-35
Potential: 0.800 V vs. NHE

\[ Z'(\text{ohm}) \]

\[ Z''(\text{ohm}) \]

\[ |Z| (\text{ohm}) \]

\[ \text{Phase (deg)} \]

\[ \text{Frequency (Hz)} \]
MCCA-35
Potential: 0.800 V vs. NHE (75 ppm Cl\textsuperscript{-})

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Frequency dependence of the EIS for MCCA-35 at 0.800 V vs. NHE (75 ppm Cl\textsuperscript{-}).}
\end{figure}
MCCA-40
Potential: Open Circuit

\[ Z'(\text{ohm}) \]

\[ Z''(\text{ohm}) \]

\[ |Z|(\text{ohm}) \]

\[ \text{Phase (deg)} \]

\[ \text{Frequency (Hz)} \]
MCCA-40
Potential: 0.950 V vs. NHE

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    title={MCCA-40 Potential: 0.950 V vs. NHE},
    xlabel={$Z'$ (ohm)},
    ylabel={$-Z''$ (ohm)},
    xmin=0, xmax=70,
    ymin=-25, ymax=20,
    xtick={0,10,...,70},
    ytick={-25,-20,-15,-10,-5,0,5,10,15,20},
    grid=major,
    legend pos=north east,
]
\addplot[only marks, mark options={draw=black, fill=black}]
    coordinates { (0,10) (10,15) (20,20) (30,15) (40,10) (50,5) (60,0) (70,5) };
\end{axis}
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    title={MCCA-40 Frequency (Hz)},
    xlabel={Frequency (Hz)},
    ylabel={$|Z|$ (ohm)},
    xmin=-1, xmax=4,
    ymin=0, ymax=2,
    xtick={-1,0,1,2,3,4},
    ytick={0,1,2},
    grid=major,
    legend pos=north east,
]
\addplot[only marks, mark options={draw=black, fill=black}]
    coordinates { (-1,2) (0,1) (1,0) (2,0) (3,1) (4,2) };
\end{axis}
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\begin{axis}[
    title={MCCA-40 Frequency (Hz)},
    xlabel={Frequency (Hz)},
    ylabel={Phase (deg)},
    xmin=-1, xmax=4,
    ymin=-40, ymax=40,
    xtick={-1,0,1,2,3,4},
    ytick={-40,-30,-20,-10,0,10,20,30,40},
    grid=major,
    legend pos=north east,
]
\addplot[only marks, mark options={draw=black, fill=black}]
    coordinates { (-1,-40) (0,-30) (1,0) (2,30) (3,20) (4,-10) };
\end{axis}
\end{tikzpicture}
\end{center}
MCCA-40
Potential: 0.950 V vs. NHE (75 ppm Cl⁻)

- $Z''$ (ohm)

$Z'$ (ohm)

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
</tr>
</tbody>
</table>

| $|Z|$ (ohm) |
|----------|
| 1.0      |
| 1.0      |
| 1.0      |
| 1.0      |
| 1.0      |

<table>
<thead>
<tr>
<th>Phase (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
</tr>
<tr>
<td>-10</td>
</tr>
<tr>
<td>-10</td>
</tr>
<tr>
<td>-10</td>
</tr>
<tr>
<td>-10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
</tr>
<tr>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
</tr>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>4.0</td>
</tr>
</tbody>
</table>
MCCA-54
Potential: Open Circuit

\[ \text{Z'} \text{ (ohm)} \]

\[ \text{Z'' (ohm)} \]

\[ |Z| \text{ (ohm)} \]

\[ \text{Frequency (Hz)} \]

\[ \text{Phase (deg)} \]

\[ \text{Frequency (Hz)} \]
MCCA-54
Potential: 0.800 V vs. NHE

- $Z''$ (ohm)

$Z'$ (ohm)

- $|Z|$ (ohm)

Frequency (Hz)

- Phase (deg)

Frequency (Hz)
MCCA-54
Potential: 0.800 V vs. NHE (75 ppm Cl\textsuperscript{-})

\begin{align*}
\text{Frequency (Hz)} & \quad \text{\(Z'(\text{ohm})\)} \\
20 & \quad 18 \\
16 & \quad 14 \\
12 & \quad 10 \\
8 & \quad 6 \\
4 & \quad 2 \\
0 & \quad -2 \\
\end{align*}
MCCA-64
Potential: Open Circuit

-2 -1 0 1 2 3 4 5
Frequency (Hz)

|Z| (ohm)

-2 -1 0 1 2 3 4 5
Frequency (Hz)

Phase (deg)

-2 -1 0 1 2 3 4 5
Frequency (Hz)
MCCA-64
Potential: 0.700 vs. NHE

\[ -Z'' \text{ (ohm)} \]
\[ Z' \text{ (ohm)} \]

\[ |Z| \text{ (ohm)} \]
\[ \text{Frequency (Hz)} \]

\[ \text{Phase (deg)} \]
\[ \text{Frequency (Hz)} \]
MCCA-64
Potential: 0.700 vs. NHE (75 ppm Cl⁻)

- $Z''$ (ohm)

- $Z'$ (ohm)

- $|Z|$ (ohm)

- Phase (deg)

- Frequency (Hz)

- Frequency (Hz)
APPENDIX VII

Slime Weight from Reported Anode Compositions and Sample Calculation

The slimes weights were calculated from reported "typical" anode compositions of several commercial refineries [2] using the slimes prediction model. All calculated values are listed in Table VII.1. Only compositions with all of the necessary composition information were utilized with the exception of tin, which was not reported for any of the refineries. Table VII.1 also contains the reported slimes weight of each refinery.

A sample calculation of slimes weight from anode composition is shown to illustrate more completely the slimes prediction model. The example will use the "typical" anode composition listed for ASARCO Inc. in Schleon and Davenport [2] which is shown in Table VII.1. The basis is taken to be for metric tonne of anode. This converts all ppm impurity concentrations into grams.

Selenium and Tellurium: all selenium and tellurium is assumed to report to the slime phase as a Cu$_{2-x}$Ag$_x$Se$_{1-y}$Te$_y$ phase. First, the molar ratio of Ag to Se + Te is calculated.

\[
\frac{Ag}{(Se+Te)} = \frac{(1500 \text{ g Ag}/107.28 \text{ g mole}^{-1} \text{ Ag})}{((850 \text{ g Se}/78.96 \text{ g mole}^{-1} \text{ Se}) + (90 \text{ g Te}/127.6 \text{ g mole}^{-1} \text{ Te}))}
\]

\[
\frac{Ag}{(Se+Te)} = 1.22
\]

Since this number is less than two, it is assumed that all of the silver reports to this phase.
Therefore $x = 1.22$ in the above phase formula. The next step is to calculate the \( \frac{Te}{(Se+Te)} \) ratio to determine $y$.

\[
\frac{Te}{(Se+Te)} = \frac{90 \text{ g Te}/127.6 \text{ g mole}^{-1} \text{ Te}}{(850 \text{ g Se}/78.96 \text{ g mole}^{-1} \text{ Se}) + (90 \text{ g Te}/127.6 \text{ g mole}^{-1} \text{ Te})}
\]

\[
\frac{Te}{(Se+Te)} = 0.06 = y.
\]

This determines the selenide/telluride phase as Cu$_{0.78}$Ag$_{1.22}$Se$_{0.94}$Te$_{0.06}$. It should be stressed that the selenide/telluride phase in the actual slimes will have a distribution of concentrations. However, for the sake of ease of calculation it is assumed all of the selenide/telluride phase has this composition. The molecular weight of this compound is calculated by:

\[
\text{M. W. of Cu}_{0.78}\text{Ag}_{1.22}\text{Se}_{0.94}\text{Te}_{0.06} = 0.78 \text{ mole Cu} \cdot 63.54 \text{ g mole}^{-1} \text{ Cu} + 1.22 \text{ mole Ag} \cdot 107.868 \text{ g mole}^{-1} \text{ Ag}
\]
\[
+ 0.94 \text{ mole Se} \cdot 78.96 \text{ g mole}^{-1} \text{ Se} + 0.06 \text{ mole Te} \cdot 127.6 \text{ g mole}^{-1} \text{ Te}
\]

\[
\text{M. W. of Cu}_{0.78}\text{Ag}_{1.22}\text{Se}_{0.94}\text{Te}_{0.06} = 263.04 \text{ g mole}^{-1}
\]

Thus the weight of the selenide/telluride phase is:

\[
\text{Weight of Cu}_{0.78}\text{Ag}_{1.22}\text{Se}_{0.94}\text{Te}_{0.06} = (850 \text{ g Se}/78.96 \text{ g mole}^{-1} \text{ Se}) + (90 \text{ g Te}/127.6 \text{ g mole}^{-1} \text{ Te}) \cdot 263.04 \text{ g mole}^{-1} = 3017 \text{ g per tonne of anode} = 3.0 \text{ kg per tonne of anode}
\]

**Lead:** all lead is assumed to be converted to PbSO$_4$.

\[
\text{Weight of PbSO}_4 = 280 \text{ g Pb}/207.19 \text{ g mole}^{-1} \text{ Pb} \cdot 303.26 \text{ g mole}^{-1} \text{ PbSO}_4
\]
\[
= 410 \text{ g per tonne of anode} = 0.4 \text{ kg per anode tonne}
\]
**Tin**: tin is not given in the "typical" composition. This component is ignored in this calculation. It is included the calculations with the anodes tested in this investigation. See Appendix VIII.

**Nickel**: The nickel composition of the ASARCO anode is listed as 910 ppm. This concentration is below the level at which nickel oxide or kupferglimmer will form. Therefore, no nickel phase are expected in the slimes. Contained within Appendix VIII is a calculation of nickel oxide and kupferglimmer weights.

**Total Slimes Weight**: the addition of the individual components yield the total weight.

\[
\text{Total Slimes} = \text{Wt of } Cu_{2,x}Ag_{x}Se_{1,y}Te_{y} + \text{Wt of } PbSO_{4} + \text{Wt of } SnO_{2} + \text{Wt of } NiO + \text{Wt of } Cu_{3}Ni_{2-x}SbO_{6-x}
\]

\[
= 3.0 + 0.4 + 0 + 0 + 0 = 3.4 \text{ kg slimes per anode tonne}
\]
Table VII.1

Typical Anode Composition of Thirty-two Electrorefineries, Their Calculated Slime Weight and Reported Slime Weight

<table>
<thead>
<tr>
<th>Company</th>
<th>Ag</th>
<th>Au</th>
<th>Ni</th>
<th>Pb</th>
<th>Sb</th>
<th>As</th>
<th>Se</th>
<th>Te</th>
<th>Slime Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asarco Inc.</td>
<td>1500</td>
<td>10</td>
<td>910</td>
<td>280</td>
<td>430</td>
<td>460</td>
<td>850</td>
<td>90</td>
<td>3.4</td>
</tr>
<tr>
<td>Atlantic Copper</td>
<td>200</td>
<td>30</td>
<td>30</td>
<td>50</td>
<td>130</td>
<td>150</td>
<td>200</td>
<td>20</td>
<td>0.7</td>
</tr>
<tr>
<td>BHP Copper (San Manuel)</td>
<td>375</td>
<td>8</td>
<td>120</td>
<td>50</td>
<td>170</td>
<td>320</td>
<td>450</td>
<td>40</td>
<td>1.5</td>
</tr>
<tr>
<td>Boliden Mineral AB</td>
<td>3500</td>
<td>100</td>
<td>4000</td>
<td>1000</td>
<td>1500</td>
<td>3500</td>
<td>650</td>
<td>300</td>
<td>8.0</td>
</tr>
<tr>
<td>Cerro Copper Products</td>
<td>270</td>
<td>0.7</td>
<td>400</td>
<td>1200</td>
<td>150</td>
<td>15</td>
<td>10</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>CODELCO (Chuquicamata)</td>
<td>385</td>
<td>1.3</td>
<td>57.5</td>
<td>12</td>
<td>183</td>
<td>1720</td>
<td>121</td>
<td>45</td>
<td>0.6</td>
</tr>
<tr>
<td>Companie General d'Electrolyse du Palais</td>
<td>407</td>
<td>7.1</td>
<td>2990</td>
<td>2571</td>
<td>347</td>
<td>133</td>
<td>61</td>
<td>53</td>
<td>4.9</td>
</tr>
<tr>
<td>Copper Range Co.</td>
<td>700</td>
<td>3.5</td>
<td>110</td>
<td>15</td>
<td>15</td>
<td>10</td>
<td>50</td>
<td>30</td>
<td>1.0</td>
</tr>
<tr>
<td>Copper Refineries Pty</td>
<td>125</td>
<td>9</td>
<td>250</td>
<td>80</td>
<td>30</td>
<td>390</td>
<td>25</td>
<td>8</td>
<td>0.3</td>
</tr>
<tr>
<td>Cyprus Miami Mining</td>
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<td>2500</td>
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<td>850</td>
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<td>1800</td>
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<td>Company</td>
<td>Ag</td>
<td>Au</td>
<td>Ni</td>
<td>Pb</td>
<td>Sb</td>
<td>As</td>
<td>Se</td>
<td>Te</td>
<td>Slime Wt Calculated (kg slimes/tonne of anode)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
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APPENDIX VIII

Slime Weights and $k_{\text{slimes}}$ for this Investigation's Anodes and Sample Calculation

The slimes weights were calculated using the slimes prediction model from the composition of each of the forty four anode tested with chronopotentiometry. All of the necessary compositions and calculated slimes weights are listed in Table VIII.1.

To better understand the slimes prediction model, a sample calculation of slimes weight and $k_{\text{slimes}}$ will be given. The example will use principally use the anode composition of MCCA-34. Other anode compositions will be introduces to illustrate more subtle points. Again the basis of the calculation will be for one metric tonne of the anode of question. This converts all impurity concentrations from ppm to grams.

Slimes Weight Calculation

Selenium and Tellurium: all selenium and tellurium is assumed to report to the slime phase as a $\text{Cu}_{2-x}\text{Ag}_x\text{Se}_{1-y}\text{Te}_y$ phase. First, the molar ratio of Ag to Se + Te is calculated.

$$\frac{\text{Ag}}{\text{Se+Te}} = \frac{(289 \text{ g Ag} / 107.28 \text{ g mole}^{-1} \text{ Ag})}{((12 \text{ g Se} / 78.96 \text{ g mole}^{-1} \text{ Se}) + (20 \text{ g Te} / 127.6 \text{ g mole}^{-1} \text{ Te}))}$$

$$\frac{\text{Ag}}{\text{Se+Te}} = 8.72$$

Since this number is greater than two, it is assumed that the silver completely replaces copper in the phase. The remaining silver will form small crystallites. Therefore $x = 2$ in the above phase formula. The next step is to calculated the $\text{Te}/(\text{Se+Te})$ ratio to determine $y$. 


\[
\frac{\text{Te/(Se+Te)}}{\text{(20 g Te/127.6 g mole}^{-1}\text{ Te})} = \frac{\text{((12 g Se/78.96 g mole}^{-1}\text{ Se}) + (20 g \text{ Te/127.6 g mole}^{-1}\text{ Te})}}{\text{((12 g Se/78.96 g mole}^{-1}\text{ Se}) + (20 g \text{ Te/127.6 g mole}^{-1}\text{ Te})}}
\]

\[
\text{Te/(Se+Te)} = 0.51 = y.
\]

This determines the selenide/telluride phase as \(\text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51}\). It should be stressed that the selenide/telluride phase in the actual slimes will have a distribution of concentrations. However, for the sake of ease of calculation it is assumed all of the selenide/telluride phase has this composition. The molecular weight of this compound is calculated by:

M. W. of \(\text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51}\) =

\[
2 \text{ mole Ag} \times 107.868 \text{ g mole}^{-1}\text{ Ag} + 0.49 \text{ mole Se} \times 78.96 \text{ g mole}^{-1}\text{ Se} + 0.51 \text{ mole Te} \times 127.6 \text{ g mole}^{-1}\text{ Te}
\]

M. W. of \(\text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51}\) = 319.40 g mole\(^{-1}\)

Thus the weight of the selenide/telluride phase is:

Weight of \(\text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51}\) = \((12 \text{ g Se/78.96 g mole}^{-1}\text{ Se}) + (20 \text{ g Te/127.6 g mole}^{-1}\text{ Te})\) * 319.40 g mole\(^{-1}\) = 99 g per tonne of anode = 0.1 kg per tonne of anode

**Silver:** since there was excessive silver after the transformation of the selenide/telluride phase, the remaining silver is assumed to be elemental silver as small crystallite. This weight is calculated by

Wt of Silver = Total Silver - Silver Consumed by Selenide/Telluride

\[
= 289 \text{ g Ag} - ((12 \text{ g Se/78.96 g mole}^{-1}\text{ Se}) + (20 \text{ g Te/127.6 g mole}^{-1}\text{ Te})) \times 2 \text{ moles Ag} \times 107.868 \text{ g mole}^{-1}\text{ Ag}
\]
454

= 222 g Ag per anode tonne = 0.2 kg per anode tonne

For anodes with a Ag/Se+Te ratio less than two, it is assumed no elemental silver is formed. This assumption is in conflict of what has been observed. However, it is believed to be an acceptable first approximation.

**Lead:** all lead is assumed to be converted to PbSO₄.

Weight of PbSO₄ = 737 g Pb/207.19 g mole⁻¹ Pb = 303.26 g mole⁻¹ PbSO₄

= 1079 g per tonne of anode = 1.1 kg per anode tonne

**Nickel:** The nickel composition of MCCA-34 is 4417 ppm. This indicates that nickel oxide will form since the value is greater than 2500 ppm. To determine if kupferglimmer will form, the moles of antimony and tin must be calculated.

Sb+Sn moles = 1318 g Sb/121.75 g mole⁻¹ Sb + 137 g Sn/118.69 g mole⁻¹ Sn

= 11.98 moles

Since this number is greater than 2.464, kupferglimmer is formed. The model assumes that kupferglimmer will form with all nickel above 3000 ppm unless the Sb+Sn moles drops below 2.464 in process.

Nickel above 3000 ppm = 4417 ppm - 3000 ppm = 1417 ppm.

moles of theoretical Kupferglimmer = 1417 g Ni/58.71 g mole⁻¹ Ni = 24.1 moles Ni

= 24.1 moles Ni/1.85 mole Ni mole⁻¹ kupferglimmer

= 13.05 moles of kupferglimmer (based on Ni)
Kupferglimmer contains one mole of Sb+Sn per mole. Therefore if 13.05 moles of kupferglimmer were to form then the Sb+Sn moles would drop below 2.464. (Note 13.05 - 11.98 = 1.07. Thus in the case of MCCA-34, the amount of antimony and tin control the amount of kupferglimmer.

moles of kupferglimmer = 11.98 - 2.464 = 9.52 moles kupferglimmer

Wt of Kupferglimmer = 9.52 moles \* 514.58 g mole\(^{-1}\) = 4899 g/anode tonne

= 4.9 kg per anode tonne

The remaining nickel above 2500 ppm will form NiO.

Consumed Nickel = 9.52 moles kupfer \* 1.85 moles Ni/mole kupfer \* 58.71 g mole\(^{-1}\)Ni

= 1034 g Ni

Remaining Nickel = 4417 g - 1034 g = 3383 g

Remaining Nickel above 2500 ppm = 3383 g - 2500 g = 883 g Ni

Wt of Nickel Oxide = 883 g Ni/58.71 g mole\(^{-1}\) Ni \* 74.71 g mole\(^{-1}\) NiO

= 1123.6 g NiO per anode tonne = 1.1 kg NiO per anode tonne

Another other case should be noted. This is when the nickel content of the anode is between 2500 and 3000 ppm. In this case only NiO will form with all of the nickel above 2500 ppm.

Tin: for the case of MCCA-34 since kupferglimmer consumes the Sn+Sb moles to 2.464, the model assumes no tin oxide will form. Two other cases can occur on anodes. The more common case is when nickel is below 3000 ppm and no kupferglimmer will
form. In this case, all tin is assumed to go to SnO₂. A sample calculation for 150 ppm Sn is as follows:

\[ \text{Wt of SnO}_2 = \frac{150 \text{ g Sn}}{118.69 \text{ g mole}^{-1} \text{ Sn}} \times 150.69 \text{ g mole}^{-1} \text{ SnO}_2 \]

\[ = 190.4 \text{ g per anode tonne} \]

The second case is when kupferglimmer forms, but does not deplete Sb+Sn to the 2.464 mole level. MCCA-2 falls into this category with nickel, antimony and tin concentration of 3456 ppm, 1069 ppm and 153 ppm, respectively. This means that a tonne of MCCA-2 has 10.07 moles of Sb+Sn (8.78 moles Sb and 1.29 moles Sn) but can only form 4.31 moles of kupferglimmer with 456 ppm of nickel above the 3000 ppm level. It is unclear from the literature as to the percentage of tin that will report to tin oxide versus kupferglimmer. Therefore it is assumed antimony will report first to kupferglimmer then tin. In the case of MCCA-2, there is more than enough antimony to fulfill the requirement of 4.31 moles of kupferglimmer. This results in all of the 153 g of Sn to be SnO₂, which is calculated similar the case where nickel is less than 3000 ppm.

**Total Slimes Weight:** the addition of the individual components yield the total weight.

For MCCA-34:

Total Slimes = Wt of Cu₂₋ₓAgₓSe₁₋ₓTe₇ + Wt of Ag + Wt of PbSO₄ + Wt of SnO₂ + Wt of NiO + Wt of Cu₃Ni₂₋ₓSbO₆₋ₓ

\[ = 0.1 + 0.2 + 1.1 + 0 + 1.1 + 4.9 = 7.4 \text{ kg slimes per anode tonne} \]
**k_{slime} Calculation**

The calculation of $k_{slimes}$ utilizing the amount of each phase generated by the slimes prediction model. These amounts are converted into volumes. Then the volumes are transformed into surface area covered. The volume calculation is simply multiplying the number of moles of a phase from the slimes prediction model by the phase's molar volume. The area of surface coverage is determined by multiplying the volume by the ratio of projected area to volume based on a phase's morphology. The shape used for each phase is listed in Table 4.3

From the slimes prediction model, the amount of each phase for one tonne of MCCA-34 dissolved is 0.31 moles $\text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51}$, 2.06 moles $\text{Ag}$, 3.56 moles $\text{PbSO}_4$, 9.52 moles kupferglimmer, 15.04 moles of $\text{NiO}$ and 0 moles of $\text{SnO}_2$.

**Selenide/Telluride:** The selenide/telluride phase is the most difficult to determine its molar volume since it has non-integer stoichiometry. However, a molar volume can be calculated by interpolation from the values listed in Table 4.3. In this case, the molar volume is calculated by:

\[
\text{Molar Volume of } \text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51} = 0.49 \times 36.84 \text{ cm}^3 \text{ mole}^{-1} + 0.51 \times 40.39 \text{ cm}^3 \text{ mole}^{-1} = 38.65 \text{ cm}^3 \text{ mole}^{-1}
\]

\[
\text{Volume of } \text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51} = 0.31 \text{ moles } \text{Ag}_2\text{Se}_{0.49}\text{Te}_{0.51} \times 38.65 \text{ cm}^3 \text{ mole}^{-1} = 11.98 \text{ cm}^3
\]
The shape of the selenide/telluride phase is assumed to a ring with a circular cross section with an outer diameter of 5 microns and an inner diameter of 3 microns. This results in a ratio of projected area in square centimeters to the volume in cubic centimeters of 3180.

Area Covered per Tonne = $11.98 \text{ cm}^3 \times 3180 \text{ cm}^2/\text{cm}^3 = 38096 \text{ cm}^2 \text{ tonne}^{-1}$

**Silver**: the molar volume of silver calculated from the density and atomic weight is 10.28 cm$^3$ mole$^{-1}$. The anode coverage per volume is 7500 cm$^{-1}$.

Volume of silver: $2.06 \text{ moles} \times 10.28 \text{ cm}^3 \text{ mole}^{-1} = 21.18 \text{ cm}^3$

Area Covered per Tonne = $21.18 \text{ cm}^3 \times 7500 \text{ cm}^{-1} = 158850 \text{ cm}^2 \text{ tonne}^{-1}$

**Lead Sulfate**: the molar volume of PbSO$_4$ calculated from the density and molecular weight is 48.91 cm$^3$ mole$^{-1}$. The anode coverage per volume is 3333 cm$^{-1}$.

Volume of PbSO$_4$ = $3.56 \text{ moles} \times 48.91 \text{ cm}^3 \text{ mole}^{-1} = 174.12 \text{ cm}^3$

Area Covered per Tonne = $174.12 \text{ cm}^3 \times 3333 \text{ cm}^{-1} = 580342 \text{ cm}^2 \text{ tonne}^{-1}$

**Kupferglimmer**: the molar volume of Cu$_3$Ni$_{2-x}$SbO$_{6-x}$ calculated from the density and molecular weight is 84.36 cm$^3$ mole$^{-1}$. The anode coverage per volume is 6667 cm$^{-1}$.

Volume of Cu$_3$Ni$_{2-x}$SbO$_{6-x}$ = $9.52 \text{ moles} \times 84.36 \text{ cm}^3 \text{ mole}^{-1} = 803.11 \text{ cm}^3$

Area Covered per Tonne = $803.11 \text{ cm}^3 \times 6667 \text{ cm}^{-1} = 5354334 \text{ cm}^2 \text{ tonne}^{-1}$

**Nickel Oxide**: the molar volume of NiO calculated from the density and molecular weight is 11.20 cm$^3$ mole$^{-1}$. The anode coverage per volume is 1590 cm$^{-1}$.
Volume of NiO = 15.04 moles * 11.20 cm³ mole⁻¹ = 168.45 cm³

Area Covered per Tonne = 168.45 cm³ * 1590 cm⁻¹ = 267836 cm² tonne⁻¹

**Tin Oxide:** the molar volume of SnO₂ calculated from the density and molecular weight is 21.68 cm³ mole⁻¹. The anode coverage per volume is 2500 cm⁻¹.

Volume of SnO₂ = 0 moles * 21.68 cm³ mole⁻¹ = 0 cm³

Area Covered per Tonne = 0 cm³ * 8500 cm⁻¹ = 0 cm² tonne⁻¹

**Total Surface Coverage:** the addition of the individual components yield the total surface coverage. For MCCA-34:

Total Surface Coverage = Area of Cu₂₋ₓAgₓSe₁₋ₓTeₓ + Area of Ag + Area of PbSO₄ + Area of SnO₂ + Area of NiO + Area of Cu₃Ni₂₋ₓSbO₆₋ₓ

= 38096 + 158850 + 580342 + 0 + 267836 + 5354334

= 6399458 cm² slimes per anode tonne

k_{slimes}: the fractional surface coverage per coulomb is calculated by converting cm² tonne⁻¹ to cm² C⁻¹ by utilizing Faraday's law. Since the current experiments utilize a 1 cm² working electrode, this value become k_{slimes}.

Number of Coulomb to Dissolve One Tonne of Copper

= \(10^6 \, \text{g}/63.54 \, \text{g mole}^{-1} \times 2 \, \text{moles electrons mole}^{-1} \times 96485 \, \text{C mole}^{-1} \) electrons

= \(3.04 \times 10^9 \, \text{C per tonne Cu}\)

k_{slimes} = \(6399458 \, \text{cm}^2 \, \text{slimes per anode tonne} / 3.04 \times 10^9 \, \text{C per tonne Cu}\)

= \(2.11 \times 10^{-3} \, \text{cm}^2 \, \text{C}^{-1}\)
Table VIII.1
Selected Chemical Analyzes, Calculated Slime Weight and \( k_{slime} \) of Tested Anodes

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<th>Anode</th>
<th>Se ppm</th>
<th>Bi ppm</th>
<th>Te ppm</th>
<th>Sb ppm</th>
<th>As ppm</th>
<th>Pb ppm</th>
<th>Sn ppm</th>
<th>Ni ppm</th>
<th>Ag ppm</th>
<th>Slime Wt kg/anode</th>
<th>( k_{slime} )</th>
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<td>805</td>
<td>195</td>
<td>133</td>
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6 REFERENCES


