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## LABORATORY SCALE EXPERIMENTAL ANALYSIS OF THE EFFECT OF SURFACTANTS ON ACID MIST SUPPRESSION DURING COPPER

## ELECTROWINNING

by

## THURMAN KOLLIE ELGIN JR

## A THESIS

Presented to the Graduate Faculty of the

## MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

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Approved by:

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## ABSTRACT

The reduction in acid mist generation is an industrial occupational objective in the electrowinning industry of base metals. The technology of electrowinning as an extractive metallurgical technique of metals proficiently contributed to the recovery of pure base metals. During the process of electrowinning, oxygen bubbles are generated on the anode of the electrowinning cell because of the over potential in the cell due to high voltage. The bubbles formed tend to contain sulfuric acid of the electrolyte in the form of liquid-gas ascending particles of the solution. As these bubbles ascend to the surface of the solution, they burst at the solution-air interface due to the surface tension effect, thus emitting acidic vapors (acid mist) into the atmosphere which poses health problems to workers in the electrowinning tankhouse.

To reduce the amount of acid mist produced during electrowinning, chemical additives (surfactants) are used to affect the surface tension of the electrolyte to suppress the bubbles bursting at the surface of the electrolyte. The most common surfactant used in the copper electrowinning industry was 3M Acid Mist Suppressant FC-1100. The manufacturing of this surfactant has been discontinued by the manufacturer due to environmental issues. As such, a replacement for FC – 1100 was keen through our study.

To find a replacement for FC - 1100, this study conducted a laboratory evaluation of several surfactants using aerosol sampling above an electrolyte sparged with oxygen, phase separation during solvent extraction, and electrowinning.

Results generated from the study showed a possible replacement for the FC - 1100 which is no longer available to the electrowinning industry.

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## NOMENCLATURE

Symbol	Description
Cu	Copper
Zn	Zinc
Ni	Nickel
CuSO <sub>4</sub>	Copper Sulfate
$H_2SO_4$	Sulfuric acid
°C	Degree Celsius
Pb	Lead
Ca	Calcium
L	Liter
OSHA	Occupational Safety and Health Administration
TWA	Time Weighted Average
mg/m <sup>3</sup>	milligram per cubic meter
cm	centimetres
mm/s	millimeter per second
g/L	gram per liter
L/min	Liter per minute
rpm	revolution per minute
Pb	Lead
Ca	Calcium
L	Liter

## **1. INTRODUCTION**

#### **1.1. OVERVIEW**

The trend in massive electrification (renewable energy, electric vehicles, etc.) requires rapid increase in the electrowinning operations for copper production. About 18 % of primary copper is produced from the hydrometallurgical process of leaching, solvent extraction (SX), and electrowinning (EW). Primary copper is generated from the crushing and grinding of copper ore. Leaching and SX produce rich copper sulfuric acid electrolyte, which is used in electrowinning to generate pure metallic copper [1]. The electrolyte is contained in polymer concrete cells with a multitude of anodes and cathodes. The copper that is present in the rich copper sulfuric acid electrolyte is electrodeposited on the cathodes when direct electric current is applied to the cells [2].

Figure 1.1 shows a schematics on how oxygen bubbles are formed on the anodes during electrowinning and how these bubbles moved to the surface of the electrolyte to produce droplets after bursting. The generated acid droplets can range from  $0.5 - 30 \,\mu\text{m}$  in size [3]. These droplets can remain suspended above the electrowinning cells for some time and then travel into the breathing space of workers by air flow. Sulfuric acid mist in the past and up to current was seen as a carcinogenic hazard. Exposure to sulfuric acid mist irritates the skin, eyes, nose, throat, and lungs; and long-term exposure to it causes larynx and lung cancer [2]. Acid mist also creates a corrosive atmosphere that is detrimental to the physical production facility [3]. Because the accumulation of acid mist over time is hazardous to humans' occupational health and equipment durability, efforts in reducing acid mists expulsion into the atmosphere during base metals electrowinning

need to be considered [15], [16]. Currently, there are some existing control methods that are being used in the industry which are discussed in section 2.5.

As a carcinogenic hazard, regulatory authorities—Occupational Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH)—have set restrictions on the permissible concentration of acid mist in electrowinning tankhouses. A concentration of 1.0 mg/m<sup>3</sup> as the Time Weighted Average (TWA) for employees' exposure on an 8-hour shift was instituted as the standard concentration by NIOSH and OSHA. With this concentration (1.0 mg/m<sup>3</sup>) required by regulatory authorities, more than 1.0 mg/m<sup>3</sup> of sulfuric acid mist is still being captured in the atmosphere of electrowinning tankhouse which violates the regulations [4].

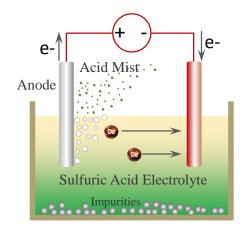


Figure 1.1: The EW process and acid mist formation.

Some existing methods available to control acid mist emission include the use of surfactants, ventilation, floating objects, bubbles coalescence, and hood [5]. Among these existing methods, the use of surfactants as a control method is widely used in copper electrowinning industry [6]. The other above-mentioned methods are applied in

controlling acid mist emission during tankhouse operations; they are used in combination. For example, floating heat retention balls as a suppression method is mostly used in combination with the surfactant method to enhance mist suppression efficiency. Several research studies proposed that the other methods when used alone, may be less effective [5], [7], [8]. Moreover, the cost of applying them is relatively high, and their usage provides tight space in handling cell anodes and cathodes during the unloading and loading process.

The current global transition from non-renewable energy to green energy influenced the mining and pure copper extraction (99.99 % Cu) from copper ore by the process of electrometallurgy. This transition caused the mining and extractive metallurgical industry of copper to dramatically stand out in the mineral industry in the last 35 – 40 years. Increase in the demand and growth of clean energy, projected a drastic increase in copper production [9]. During the extraction of pure copper from leach pads, solvent extraction and electrowinning are the electrometallurgical techniques used. Therefore, this makes electrowinning important in the copper production for green energy applications. As the renewable energy industry continues to expand considerably and become one of the key modes for the global economy, the demand for copper will eventually follow the uprising trend [10]. Renewable energy equipment like wind turbines require between 2.5 tonnes and 6.4 tonnes of copper per Megawatt (MW) for the generator, cabling, and transformers. Photovoltaic solar power systems use approximately 5.5 tonnes of copper per MW [11], [12].

The objective of this study was to evaluate different surfactants at a laboratory scale operation to find a possible replacement for the 3M Acid Mist Suppressant FC-

1100. Research studies about acid mists generation and control showed that the use of surfactant can significantly reduce acid mist during electrowinning operations [2], [6], [13]. As such, existing acid mist control methods continue to favor the use of surfactants, FC-1100, as the promising control method that is effective and cost-efficient. The evaluations from our studies were conducted in three phases: acid mist testing, phase separation analysis, and electrowinning. The acid mist sampling was achieved by collecting acid mist samples and performing laboratory titration analysis to acquire data. The phase separation was accomplished by mixing an aqueous and organic solution with surfactant being added and then observing the disengagement time. The electrowinning of copper in the study involved the use of laboratory electrowinning cells (beakers). Data generated from the three phases of the research study were synthesized into reasonable information to ascertain a sustainable replacement for the FC-1100 surfactant, which was achieved.

#### **1.2. RESEARCH FOCUS AND OBJECTIVES**

As mentioned earlier, the surfactant method is the widely used method of suppressing acid mist during copper electrowinning operations. With current restrictions being placed on the use of the favorable surfactant (FC - 1100) during copper electrowinning, our project focused on keeping the continuous use of the surfactant method in the electrowinning industry. Therefore, to achieve this, our study evaluated several surfactants simulating industrial parameters to find a possible replacement for the

FC - 1100 surfactant. The evaluation integrated industrial parameters (electrolyte temperature, solution acidity, etc.) that allow us to make recommendations to electrowinning tankhouses on the possible replacement of FC - 1100.

### **2. LITERATURE REVIEW**

#### **2.1. OVERVIEW**

The reduction in acid mist formation is an industrial occupational objective in the electrowinning industry of base metals. The technology of electrowinning, as an extractive metallurgical technique of metals, proficiently contributed to the recovery of pure base metals (copper). During the process of electrowinning, electrolysis is used by which electric current is passed through a copper bearing solution that contains cathodes and non-dissolving anodes (lead alloy). The goal of this is to extract soluble copper as pure metallic copper. During this process, bubbles are generated on the anodes of the electrowinning cell as a result of water molecules being oxidized. The oxygen bubbles that are formed on the anodes initially nucleate and grow into bigger bubbles. The difference in forces in the electrolyte causes these bubbles to get detached from the anodes and travel through the electrolyte bursting at the surface of the electrolyte [14]. The bursting of these bubbles produces acidic aerosols (mists) that are inhalable. The possibility of tankhouse workers inhaling these aerosols results in the need for engineering solutions to protect their health and safety.

Several parameters in the operational design of the tankhouse can influence the bubbles generated on cell anodes. These can include current density, temperature, solution acidity, etc. Therefore, the optimality of process parameters during electrowinning is still uncertain. Interestingly, these parameters mentioned also contribute to the overall productivity and efficiency of the electrowinning process in the tankhouse. Increasing or decreasing certain parameters will lead to high or low production but create a hazardous working environment from the generation of acid mist. This scenario is vice versa. Optimizing electrowinning tankhouse operational parameters is still being researched. A study researched that increasing the electrolyte temperature increases the quantity of acid mist generated but yields a higher recovery of copper [3]. Other studies also postulated that increasing the current density above 400 A/m<sup>2</sup> and lowering the acidic concentration of the electrolyte yields high production with more acid mist being generated [11], [17]. So, finding the optimum point of tankhouse operating variables for the electrowinning process remains unclear.

The objective of this review study was to analyze the effect of surfactant selection on acid mist suppression during copper electrowinning. The study also aimed to provide recommendations on the use and benefits of outstanding suppression methods arising from this review. To achieve these objectives, a review of past studies was conducted to propose measures for acid mists reduction. The theoretical analysis involved the process parameters consideration in the electrowinning process that contribute to the generation of acid mist. These parameters include temperature variations, current density, surface tension parameters, electrolyte concentration, and suppressants availability. The analysis of this review was geared toward controlling acid mist expulsion by proposing an optimized electrolyte solution process in the metallurgy industry of copper electrowinning.

#### 2.2. COPPER ELECTROWINNING CHEMISTRY AND CELL ELECTRODES

The operating parameters of electrowinning tankhouses pretty much have the same flow of operations, but may vary in parameter (electrolyte concentration, electrodes

dimensions, tankhouse layout, etc.) specifications. The variation in these parameters can be skewed to the design, safety, and production target of the tankhouse.

**2.2.1. Copper Electrowinning Chemistry (Oxidation-Reduction Reaction).** In chemistry, there are two types of reactions that prevalently take place, oxidation, or reduction reaction. Interestingly, these two reactions take place concomitantly during an electrolysis process [18]. Using electrolysis to extract pure copper primarily involves two electrochemical techniques: electrorefining and electrowinning. In electrorefining, copper anodes are allowed to dissolve in the electrolyte and get deposited on the cathodes as pure copper through chemical reactions. During this method (electrorefining), floating slimes and anode passivation can affect the quality of copper recovered, which is a challenge to copper electrorefining [19]. Electrowinning involves the electrodeposition of leached copper present in a concentrated copper electrolyte onto a stainless plate (cathode) in an electrowinning cell, where oxygen gas evolution on the anodes is a concern [8] Interestingly, the chemical reactions taking place at the cathodes during the electrorefining of copper are similar to that of electrowinning. In these reactions, copper is being electrodeposited on the cathodes by an occurrence of a reduction reaction taking place in the solution [18], [20]. However, at the anodes, the reactions taking place during electrorefining and electrowinning are different. In electrorefining, copper anodes are oxidized into solution and then electroplated onto the cathodes by means of electrolysis. During electrowinning, there is an oxidation anodic reaction that takes place at the inert lead anodes that generates oxygen gas due to the dissociation of water molecules [21]. Equation 2.1 shows the chemical formation of oxygen bubbles produced on the anodes of an electrowinning cell.

$$H_2O_{(1)} \rightarrow 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} + 2e$$
-Equation 2.2

**2.2.2. Electrolytes.** Electrolytes used in electrowinning cells are one of the key components of the electrochemical process that takes place during copper electrometallurgy. These solutions are good conductors of electric current which make them important for the electrowinning and electrorefining of copper. Copper electrowinning electrolytes are primarily made of copper sulfate and sulfuric acid. Other minor elements and reagents can be added to the electrolyte to stabilize and contribute to the efficiency of the chemical reactions taking place in the system; elements like cobalt, iron, chlorine, etc. [2], [22]. Electrolytes used in different tankhouse operations will vary in chemistry, depending on the quality and production of copper to be produced as well as the design parameters of the tankhouse.

Conventionally, fresh commercial electrolytes that are used for the electrowinning of copper are made in the range of 30 - 50 g/L Cu<sup>2+</sup>, and 150 - 180 g/L H<sub>2</sub>SO<sub>4</sub>. As said earlier, the chemistry of tankhouse electrolyte can vary with operational designs [12], [16]. Operating electrolytes (based on the chosen chemistry) used in the tankhouse are blended with used (spent) electrolytes from the tankhouse to circulate through electrolyte in the cells [16].

**2.2.3. Anodes.** Industrial electrowinning operations are becoming more concerned about power consumption and material durability in the electrolyte, thereby making the selection of cell electrodes (anodes and cathodes) keen. Anodes used during copper electrowinning are positive inert lead steel plates (Pb-Sn or Pb-Sb alloys) placed

in the electrolyte cell that supports the transfer of electrons through the electrolyte during electrolysis. Like the cathodes, anodes are supported with metal bars (lead plated copper bars or copper bars) that allow them to be suspended in the electrolyte. In the history of copper electrowinning, Pb-Sn or Pb-Sb alloys were used as anodes [21]. These metal alloys are stable, efficient, and long lasting (~ 5 years) in industrial electrowinning operations. However, they have a high potential of faster corroding in the electrolyte which gives rise to the addition of cobalt to the electrolyte solution. Cobalt helps in minimizing the corrodibility of the anodes[15], [21].

Conversely, studies showed that these alloys (Pb-Sn or Pb-Sb alloys) that are used as anodes can contaminate the cathodes with their corroded particles. Such contamination may result from falling corroded particles settling onto the cathodes [11], [20]. As such, modern electrowinning operations are now transitioning to the use of cold-rolled anodes.

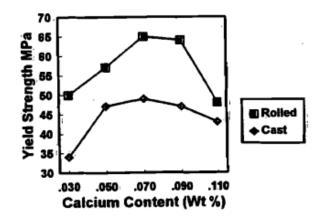


Figure 2.1: Calcium effect on the mechanical properties the of cathodes [11].

The cold-rolled anodes are made of Pb-Sn-Ca. The chemistry of this alloy contains about Sn 1.35 % while the Ca is about 0.08 %, with Pb being the dominant element. The

strength and anti-corrosivity of the cold-rolled anode are provided by Sn, while the Ca component enhances the anodes' mechanical properties and potential for low power consumption. Figure 2.1 illustrates how the mechanical strength of the cold-rolled anodes declines with increase in the wt. % of calcium [11], [16].

**2.2.4. Cathodes.** The advancements in the technology of the electrometallurgical industry saw new designs of cathodes being used in electrowinning tankhouses. Research showed that early electrowinning operations used starter sheets as cathodes in the electrowinning cells [21], [23]. Starter sheets cathodes are thin copper sheets (< 1 cm thick) obtained from copper electroplating. The duration of the electroplating is approximately 24 hours. The thin copper sheets obtained are looped with metal to hold hanging bars. The hanging bars can be I-beams or rectangular beams which support the starter sheet cathodes to be suspended in the electrolyte [15]. Making starter sheet cathodes is time and labor consumptive; therefore, most electrowinning tankhouse operations are now transitioning to the use of permanent cathodes, 316 L stainless steel blank. This technology (stainless steel blanks 316 L) is becoming lustrous in the electrowinning industry.

**2.2.4.1. Stater sheet cathodes.** The beginning of electrometallurgy operation started with the use of starter sheets as cathodes. These thin copper sheets are being used in the electrowinning industry as electrodes (cathodes) to produce copper cathodes. Starter sheets are made in separate sections of the tankhouse. As mentioned earlier, copper is allowed to be electrodeposited onto stainless titanium 316L blank sheets for about one day and then harvested. The harvested copper sheets are then moved to the commercial cells for copper plating. In smaller electrowinning tankhouses, starter sheets

are imported from bigger electrometallurgical facilities [20]. Because of the manual labor associated with the production of starter sheet cathodes, and their single usage in the industry, this technology is now becoming unpopular in the electrometallurgy industry [16]. However, electrowinning plants in North and South America, as well as Africa still use the starter sheet cathode technology to produce copper cathodes [17].

**2.2.4.2. Permanent cathodes.** The reusability of 316 L stainless steel as cathodes in tankhouses has favored the permanent cathodes technology in recent electrowinning operations. The technology has enhanced tankhouse productivity, cells current efficiency, high quality cathode copper, and low short circuits [16]. The planarity and excellent geometry of the steel plates make it easy to fit into the electrowinning cells. The planar property of the 316 L stainless steel has helped in reducing the time and energy consumption that is traditionally used in the starter sheets technology for pressing starter sheets. Permanent cathodes technology proved to be less labor intensive by eliminating the operation of starter sheets production [17]. Many electrowinning operations are now transitioning to the technology of permanent cathodes.

**2.2.5. Electrolyte Additives.** The addition of reagents (additives) to tankhouse electrolytes can enhance the purity of copper deposited on the cathodes. These additives can also improve the efficiency of the electrolysis process, yielding smooth cathodes plating. Electrolyte additives can foster the smoothening of copper cathodes by reducing the surface roughness of the cathodes [22]. Common electrolyte additives used in electrowinning tankhouse include the guar gum, chloride ion, cobalt sulfate, DXG-F7, HydroStar, and Cyquest-N900 [24].

#### 2.3. ACID MIST GENERATION

**2.3.1. Generic Formation of Acid Mists.** The electrolysis process of copper extraction from electrolytes involves the formation of oxygen gas ( $O_2$ ) and hydrogen ion ( $H^+$ ) at the anode surfaces. The generation of oxygen gas that has been mentioned in previous sections can be seen in the chemical reaction in Equation 2.1. The  $H^+$  in the equation stays in solution and reacts with the sulfate (SO<sub>4</sub>) to regenerate sulfuric acid ( $H_2SO_4$ ) [18]. See (Equation 2.2). At the end of the chemical reaction the final products in Equation 2.2 are pure metallic copper (99.99 % Cu), oxygen gas, and the regeneration of sulfuric acid.

$$CuSO_{4(l)} + H_2O_{(l)} \rightarrow Cu_{(s)} + \frac{1}{2}O_{2(g)} + H_2SO_{4(l)}$$
 Equation 2.3

The oxygen gas that evolves at the surface of the anode plates tends to form small bubbles. These bubbles exist in three phases: bubble nucleation, bubble growth, and bubble detachment. As electrons flow through the cell electrodes, the thermal energy of the electrodes starts to build, thus increasing the temperature of the electrolyte. Chemical and electrochemical reactions begin to take place in the solution. More oxygen gas bubbles start to form on the anode surface. Over time, bubbles nucleation starts to take place due to the extreme supersaturation of volatile gases in the cell electrolyte. As more gases are being produced at the anode, bubbles start to grow by attaching themselves to neighboring bubbles, forming bigger bubbles. These bigger bubbles tend to go through the third phase of bubble existence in the electrolyte solution, bubble detachment. This phase occurs when the force that attracts the bigger bubbles to the electrodes (anodes) becomes less than the pull-away force (bubble-surface detachment force) on the bubbles. When this happens, the bubbles detach from the anodes and make their way through the electrolyte bursting at the electrolyte surface [25]. The equilibrium state and duration of these bubbles in the electrolyte depend on several parameters in the electrowinning cell, including the suppressant concentration, electrolyte temperature, solution drainage rate, and surface tension [18], [26].

During the detaching of the gas bubbles from the anodes, there are fluid forces that impact the detachment, the buoyant and surface tension force. The buoyant force is the ascending force a fluid exerts on an object (i.e., the bubble), while the surface tension force tends to oppose other forces within the liquid. The stability of the bubbles detaching from the plates and bursting at the electrolyte interface occurs when the force of buoyancy is more than the force of surface tension. The difference in the magnitude of these forces gives rise to the bubbles bursting.

An interesting phenomenon to note is that after reaching the air-electrolyte interface, bubbles that are detached from the anodes in the cell, they do not shrink or burst at once. The bubbles form a film that gradually wears out as time progresses. The film continues to thin until a hole is developed. When this hole is developed, the force of surface tension lowers the film's surface area thus causing the bubble to burst which emits acidic aerosols [5], [18].

**2.3.2. Types of Droplets (Mists) Produced from the Bursting of Bubbles.** As bubbles travel through the solution and reach the air-solution interface, they burst. Upon bursting, there are two types of droplets (mists) formed: film drops and jet drops. The formation and emission of these two types of drops are dependent on the size and genetics of the parent bubbles that grow at the anode surfaces. It is these parent bubbles

that burst at the surface of the liquid. These droplets (film and jet drops) tend to have their own intrinsic characteristics because of their mode of formation. It can be postulated that small parent bubbles most of the time give rise to jet drops, while on the other hand, big parent bubbles give rise to film drops. However, film drops can also descend from jet drops [27]. Figure 2.2 shows the bursting mechanism of bubbles at the surface of the solution. In the right-hand corner of the figure, a magnification of how the parent bubbles burst at the surface producing film drops is shown. These parent bubbles for example are bubbles that detach from the anode in the electrolyte. As the parent bubbles burst, film drops are formed because the bubble film ruptures. The quantity of film drops produced depends on the time interval that parent bubbles stay at the surface of the electrolyte. Longer time of rest at the surface will produce smaller amount of film drops [2]. In furtherance of the bubble bursting process, smaller jet drops (like spray) are further produced when the film drops burst [18]. This is shown in Figure 2.3. The tiny jet drops burst and produce airborne particles (mists, between  $0.5 - 30 \mu$ m) that are inhalable [3].

More studies on aerosols generated from bubbles considered seawater and freshwater as experimental solvents. Intrinsically, these two solvents have different compositions. However, data generated by researchers relative to the type and size of droplets produced are objectively parallel [28]. It was observed from research that there are similarities in the surface tension and viscosity property of copper electrolyte and seawater. As such, an inference can be made that the behavior of bubbles collapsing in a copper electrolyte is considerably the same for seawater [29]. This assumption is proposed due to the similarity in results generated from research studies conducted using these two solutions.

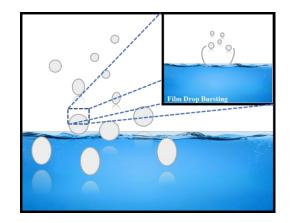


Figure 2.2: Mechanism of bubble bursting at a free surface.

In the electrowinning industry, jet droplets (mists) are the common mists (droplets) generated from the busting of the parent bubbles that are formed on the cell plates (anodes) within the electrolyte tanks. As bubbles generation during the electrowinning of copper continues to be inevitable, it is practical to understand the dimension of these bubbles that are generated. However, it is approximated that during copper electrowinning the dimensions of most bubbles bursting at the air-electrolyte interface fall within the range of 20 to 180  $\mu$ m which places them (bubbles) in the generic category of being parent bubbles that will produce film drops and then jet drops [2], [30]. Jet drops arising from the film bubbles rupture become further small in diameter qualifying them to be airborne which can be inhalable as airborne particles [3]. Figure 2.3 shows the bursting of film drop producing jet drops (sprays) into the atmosphere.

The rate of ascension of the detached bubbles from the anode to the surface of the electrolyte can be influenced by fluid velocity. Electrolytes are circulated into tanks by the influence of convection (upward-downward movement). The convectional movement creates velocity in the electrolyte which is capable of bringing bubbles to the top.

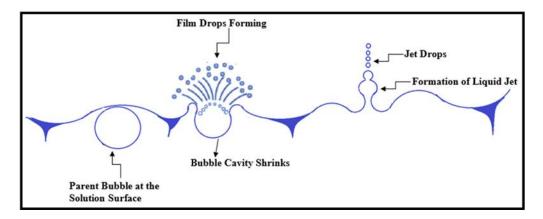


Figure 2.3: Jet drops formed from the bursting of film drops.

A high fluid velocity will create turbulence in the electrolyte which can rupture ascending bubbles. This lowers the quantity of bubbles reaching the surface. These bubbles contain oxygen gas that can burst at the electrolyte surface and emit air borne particles (mists) into the atmosphere. It is important to note that high fluid velocity is not considered a method to suppress acid mist but helps in transporting detached bubbles to the surface. However, fluid velocity is a variable parameter that can be controlled based on the operational parameter (tank size, electrolyte flow rate, dimensions of cell plates and temperature) of the tankhouse. A study proposed that in the electrolyte bath, the velocity at which bubbles detached from the anodes ascend through the electrolyte is key. It was postulated that the size, coalescence, and rate at which bubbles are generated and reach the surface of the electrolyte can potentially influence the quantity of bubbles bursting at the surface of the electrolyte [31]. This phenomenon was observed in the difference in two velocities: the fluid (electrolyte) velocity and the surrounding air velocity. Improving the air quality by ventilating (secondary acid mist control method) an electrowinning tankhouse has helped in the dilution of the contaminated air present in the tankhouse. It

was noted that high surrounding air velocity will contribute to bubbles ascending to the electrolyte surface by adding up to the velocity that brings the bubbles to top. Essentially, this is most likely to occur in small electrowinning tankhouses with tight space where mechanical ventilation is used [4], [5].

The working principle of this technique can be hypothesized that if the surrounding air velocity is high in magnitude than the fluid velocity that brings bubbles to the surface of the electrolyte, more bubbles may possibly be pulled in an upward air flow direction toward the surface of the electrolyte. Therefore, a higher fluid velocity in the electrolyte is essential. This will overcome the upward velocity in the tankhouse thus reducing the number of bubbles reaching and bursting at the solution surface. However, tankhouse operations are skeptical about applying this technique. This is because increasing the fluid velocity in the cells and lowering the surrounding air velocity in the tankhouse can contribute to temperature rise in the tankhouse, dehydration of employees, and other heat related problems. Therefore, it is important to keep the flow of electrolyte recirculation at 53 gallons per minute in the tanks. This velocity transports less bubbles to the electrolyte surface and does not require detailed attention to the surrounding air velocity [12].

#### 2.4. ACID MIST SAMPLING AND ANALYSIS

The quantifying of acid mists in electrowinning facilities can be realized by air sampling methods instituted by NIOSH (NIOSH Manual of Analytical Methods – method 7908). NIOSH in recent years (2020) has proposed a standard method for sampling and analyzing non-volatile acids (sulfuric and phosphoric acids) for acid mist

testing. In these methods, the equipment used in collecting samples during acid mist sampling includes but are not limited to an air sampling cassette, air filter membrane, and a sampling pump. After the air sampling, the examination of the collected samples is executed in a separate unit using deionized water and ion chromatography method to determine the quantity of acidic aerosols absorbed on the filter. In some instances, laboratory titration method [32]. This examination allows the proposition of quantifiable and statistical inferences of the samples collected.

**2.4.1. Acid Mist Sampling.** Figure 2.4 shows the schematics of the predominant experimental approach used for simulating industrial electrowinning process for sampling acid mist. Most research experiments on acid mist generation and control have used this approach since it falls within the experimental design instituted by NIOSH. In this approach, air samples are collected at a fixed elevation above the electrolyte solution. A constant elevation is used to avoid variations in the amount of acid mist absorbed on the filter as the mist reach the sampling point. For samples collection, the membrane filter is inserted into the air sampling cassette and the cassette is connected to a sampling pump via a plastic tube. The sampling pump is calibrated to the desired flow rate of the experimental design and samples are taken for a definite period for each experiment. Normally, the sampling time in acid mist experiments ranges from 20 - 30 minutes per sample [32]. This time allows good absorption of acidic aerosols onto the filter [2], [33]. Acid mists passing the sampling point are discharged by a natural or a forcing ventilation system.

Another method that is used to test for acid mist is the use of digital equipment. Let it be noted that this method is not a standard sampling method proposed by NIOSH.

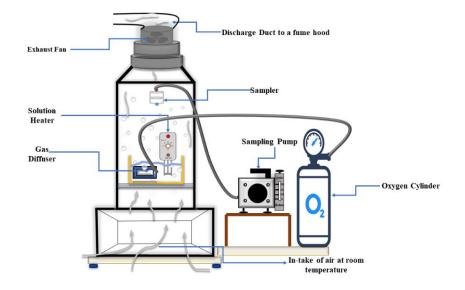


Figure 2.4: Acid mist sampling setup.

However, this method involves the use of a digital aerosols monitoring device that is used to ascertain the concentration of acid mist about 1.5 m above the electrolyte cells. This distance above the electrolyte is considered the active zone of acid mist occurrence [34]. An example of this device is the MIE aerosol monitor, model pDR-1200. During acid mist testing, the device automatically gives the mist concentration (mg/m<sup>3</sup>) at the tested height (1.5 m) above the electrolyte. Using this method to test for acid mist implies that the activity of laboratory titration or spectrometry are skipped.

**2.4.2.** Acid Mist Analysis. After the sampling of acid mist, chemical analysis instituted in the NIOSH Manual of Analytical Method – method 7908 can be used to aid in the analytical procedures to ascertain the acid mist concentration during sampling. This analysis was the Ion Chromatography (IC) method which used the charge properties of the desired compounds (SO<sub>4</sub>). During the analysis, the sampled filter papers from the acid mist sampling are submerged into deionized water. The deionized water containing the filters are analyzed for sulfate (SO<sub>4</sub>) concentration using an IC machine. The

concentration of sulfuric acid mist (mg/m<sup>3</sup>) during the experiment can be calculated using Equation 2.3 [35].

$$H_2SO_4 (mg \text{ per cu. m}) = (C \times V \times Y^{-1}) (1.02) (10^6)$$
 Equation 2.4

where C is the concentration of SO<sub>4</sub> in sampled solution, ( $\mu$ g/mL)

V is the volume of DI water containing the sampled filter, (mL) Y is the sampled air volume, (L)

and, 1.02 is the conversion factor for sulfuric acid mist,  $[(mg L)/(\mu g mL)]$ 

Aside from the IC analytical method, laboratory facilities that do not have IC machines tend to use laboratory titration method. In these analytical techniques, the sampled filter papers are submerged into a fixed volume of deionized water and then sonicated (agitated) to release the acidic particles on the filter into the deionized water. Titration process was done which allowed the calculation of the amount of acid deposited onto the filter. The analyses further provide the concentration of acid mist in the sampling environment considering the experimental setup [2], [6]. In these analyses, the titration process can be acid-base titration.

### 2.4.3. Example of Acid Mist Sampling and Analysis (NIOSH 7908 Method).

The generation of bubbles during electrowinning operations inevitably leads to the emission of acid mist in the electrowinning tankhouse. To simulate industrial generation of bubbles in laboratory scale research projects, a study used the standard NIOSH Manual of Analytical Methods (Method 7908) to test for acid mist. In the study, an electrolyte that contained 1 M H<sub>2</sub>SO<sub>4</sub> and 0.857 M of CuSO<sub>4</sub> and the electrolyte was placed in a bath. The electrolyte was heated to 27 °C. A 5 cm in diameter circular gas diffuser was

used to generate bubbles. In this study, a mean oxygen gas flow rate of 110 mL/min was passed through the bubbler to sparge bubbles. Bubbles were generated in a gas flow rate range of 45 - 175 mL/min and samples were collected for 30 min on a 37-mm membrane filter. Sampling flow rate was unknow in this study [6]. However conventional sampling flow rates stipulated by regulatory authorities range from 1 - 5 L/min [32].

The surfactant used during the study was the Pluronic F68 surfactant. Ethylene oxide was added to the electrolyte to yield good recovery during the tests. The F68 surfactant was tested at a concentration ranging of 0.5 - 2 g/L. Three sampling points (36 cm, 49 cm, and 67 cm) were set above the bubbler. The collected sample papers were analyzed using spectrometric analysis, one of the analytical methods mentioned earlier.

2.4.4. Example of Acid Mist Testing Non-standard Method. Another study also conducted a 6-month SX/EW pilot research project on the interaction between F3-A surfactant and SX/EW process. This study was carried out at the Radomiro Tomic (RT) SX/ EW pilot plant in Chile. The study was aimed at ascertaining if the periodic addition of F3-A surfactant will adversely affect the SX/EW process, which was proven it does not. The F3-A surfactant is a quillaja Saponaria wood extract that is manufactured into surfactant to help reduce acid mist during copper electrowinning. The study was also concerned about the suppression of acid mist by the surfactant over time as the concentration increases. During this research, 40 g/L Cu<sup>+2</sup> and 180 g/L H<sub>2</sub>SO<sub>4</sub> electrolyte was used for the experiments.

Bubbles were generated on the Pb-Ca-Sn anode by the process of electrolysis. Industrial grade of the cell electrodes were used, Pb-Ca-Sn anode plates, and 316 L stainless steel cathodes. The experimental concentration range of the surfactant was 5 – 32 ppm. Mean current density and temperature were 260  $A/m^2$  and 45 °C respectively. The acid mist concentration generated from the bursting bubbles at the surface of the electrolyte was measured using an aerosol monitor mentioned in section 2.4 [36].

#### 2.5. EXISTING ACID MIST CONTROL METHODS

Efforts to considerably reduce acid mist emission during the copper electrowinning process are still evolving as more techniques are being studied. In the base metals recovery industry where acid mist generation is prominent, current methods used for the suppression of acid mist include the use of surfactants, ventilation, hood, floating objects (beads, balls), and bubbles coalescence [5]. Majority of the tankhouses in the USA, Africa, South America and Asia use the surfactant method for acid mist suppression [17].

**2.5.1. Surfactant Method.** The cost effectiveness and efficiency of this method made it tramped over other existing acid mist control methods. The surfactant method was proven from several research studies to be expedient in suppressing acid mist during electrowinning [35], [37]. The reduction efficiency of this method is as high as above 90 % [2], [6], [13]. The use of this method can considerably suppress most of the acid mist that is generated during the electrowinning process.

During the electrowinning process, the cells electrolyte surfaces are aligned with air. So, reduction in the electrolyte surface tension by surfactants can cause strong bonding of the solution molecules. When absorbed at the surface, the surfactant forms a single layer at the surface of the electrolyte which reduces the force of cohesion between the molecules in the electrolyte. The reduction in the cohesive force among molecules is what affects the surface tension of the electrolyte. Surfactants can also exist in their undissolved state in electrolytes. Therefore, this allows them to have both hydrophobic (water-repelling) and hydrophilic (water-loving) properties. In other words, surfactants as a chemical compound have a non-dissolving component as well as a dissolving component when placed in a solvent [24]. Based on the operational parameters of the tankhouse, at a certain concentration (Critical Micelles Concentration-CMC) of the surfactant in the electrolyte, the surfactant starts to form micelles. These are sphereshaped foaming structures that have both hydrophobic and hydrophilic properties. They are essentially foaming blankets formed at the surface of the electrolyte. Micelles traps hydrophobic materials in the electrolyte (i.e., escaping bubbles from the anode faces) [12]. The trapped bubbles burst under the foam blanket and stay in the solution. For the surfactant to achieve this mechanism, the surface tension of the solution is reduced.

Based on the operational parameter and product availability, electrowinning plants used various surfactants for acid mist suppression. Some of these surfactants include Fluoro-surfactants (FC-1100, FC-5120), F3-A, Dowfroth 250, Licorice, Saponin, etc. Surfactant has shown an observable impact on acid mist reduction [37]. Most surfactants used in aqueous solutions as forming agents can be classified into one of the following groups based on the polarity of their hydrophilicity: anionic, cationic, nonionic, and amphoteric. The characteristics of the work done depict the kind of surfactants to be used. The principal surfactant used in copper electrowinning is an amphoteric type of surfactant, the FC-1100. This surfactant has an excellent state of chemical equilibrium that makes it suitable for workings involved with acid and high temperatures environments [16].

**2.5.1.1. FC – 1100 operational mechanism.** To achieve permissible acid mist levels, the 3M Acid Mist Suppressant FC-1100 was commonly used as a suppressant additive in electrolyte. The suppressant is influential at the electrolyte-air interface. As the bubbles encounter the electrolyte interface the suppressant is incorporated into the film of solution surrounding the oxygen bubble. The electrolyte surface tension is reduced by FC-1100, and thus the gas bubble wall becomes thinner when it reaches and protrudes above the electrolyte surface. The electrolyte drains from the walls of the bubbles when they arrive at the surface of the electrolyte, thus preventing the bubbles from bursting and forming mist. Interestingly, how FC-1100 reduces acid mist is still unclear [18]. However, two assertions were made in providing clarity on this. It was postulated that electrolyte surface tension that was reduced by the FC-1100 surfactant also decreases the velocity and activation energy of detached bubbles bursting at the airelectrolyte surface. Assertion two to the mechanism of FC - 1100 integrated other process parameters like temperature and solution viscosity to complement the effectiveness of FC - 1100. To support this, other variable parameters (current density, solution flow rate, etc.) were studied, and it was observed that the electrolyte temperature coupled with the surfactant concentration has a high impact on the generation of acid mist [18], [39].

**2.5.1.2. Potential drawdowns of the surfactant method.** Conversely, the addition of surfactants in high concentration to the electrolyte affects the depositional behavior of copper on the cell plates (by forming coatings of the insoluble components) as well as the potential risk of fire. This affects the rate of metal extraction during the electrowinning process. The risk of fire ignition may arise from the increment in trapped

oxygen present in the bubbles at the surface of the electrolyte which can combine with organic floats from the upstream SX plant. In the presence of these oxygen and organic materials if short circuits occur, it can lead to possible fire. Therefore, understanding the foaming behavior of surfactants to be used in an SX/EW plant is important [38]. The effectiveness of the current density of the electrolyte can also be affected by the presence of a high concentration of the surfactant in the electrolyte. Increasing the current density makes it difficult in keeping a steady state of the foam layer at the electrolyte surface [3], [38].

**2.5.2. Ventilation Method.** In electrowinning tankhouses, the improvement in the quality of the surrounding air lowers the rate of equipment corrosion as well as the intensity of hazards posed to tankhouse employees by the emission of acid mist. This is achieved by ventilating the tankhouse to dilute contaminated air containing acidic aerosols evolving from the bursting of bubbles that are generated on the anodes in the tanks. This approach in combination with other suppression methods tends to keep the concentration of acidic aerosols at an acceptable exposure limit—1.0 mg/m<sup>3</sup>. Practically, the ventilation approach aims at improving the air quality in a manageable space, but not necessarily preventing the bursting from bubbles at the electrolyte-air interface during the electrowinning process [2]. Air is forced into the electrowinning system and contaminated air from the system is expelled using an exhaust fan [26]. The dilution of acid mists in electrowinning tankhouses by the ventilation method has seen some success as a viable approach in controlling acid mist [5]. However, during cold weather, the ventilation method contributes to lowering the operating temperature of the tankhouse electrolyte which in turn requires excess energy to maintain the desired temperature of

the electrolyte [38]. The quantity of air to be treated in relation to the cost of power to be used is unfeasible. The required power needed to ventilate the tankhouse is estimated at 20 % of the power needed for the electrowinning process [5]. The inability of this method to prevent acid mist emission and the high-power consumption makes this method rarely or singly used as an acid mists control method in electrowinning [5], [40]. The system of ventilation involved in this approach includes forced ventilation. This method is more like a secondary control method.

**2.5.3. Hooding Method.** The hooding of copper electrowinning tankhouse sections has been proposed as one of the methods of controlling the emission of acid mist. In this method, acid mist is eliminated from electrowinning tankhouses by exhaust hoods and sent to a gas cleaning facility. This is mostly done by hooding each electrowinning tank or section. The gas cleaning facility detoxifies the collected gas containing sulfuric acid mist by a gas-scrubbing system and then discharges it into the surrounding outside the plant facility. New tankhouses that are currently being built, and emerging electrowinning facilities are incorporating the use of hooding in their operational designs to control acid mist [12], [38]. Treating electrowinning tankhouses as an isolated unit from the environment system prevents environmental threats posed to workers and equipment. The hooding of each electrowinning tank or section has resulted in an environmentally friendly operation [5]. However, it showed some high ridge in the capital involved in using this method as well as reducing the operational space for crane operators and tankhouse employees. Studies suggested that the hooding technique is not favorable for electrowinning tankhouses because there is a frequent removal of electrowinning cell plates being done daily [2], [5]. This restriction as well as the cost

intensiveness of the process is still being studied as electrowinning plants are considering a transition to this method.

2.5.4. Floating Objects (Beads and Balls) Method. In this method, heat retention balls (plastic balls) and beads are placed in the electrolyte container to cover the surface area of the solution as they float. This method is mostly used in combination with the surfactant method and is successful in reducing acid mist during copper electrowinning. Small concentration of surfactant is used together with beads and balls to avoid the production of massive foam and potential hazards that may be caused by a high surfactant concentration [2], [38]. The common effect of using floating objects is to minimize the surface area where bubbles will burst [4], [41]. When the heat retention balls are placed in the electrowinning cell to float at the surface of the electrolyte, they create a layer of floating balls that prevent ascending bubbles from reaching the surface of the electrolyte. However, removing the floating objects during cathodes harvesting makes this method time and labor consumptive [5], [7].

**2.5.5. Bubble Coalescence.** Coalescence of bubbles has been a promising method that can be supported by using floating objects in the electrolyte to suppress acid mist. The layer of floating objects (beads and balls) can reduce the space for bubbles reaching the surface of the electrolyte; thus, forcing bubbles to coalesce and burst in the electrolyte. This suggests that the bubble coalescence method favors the use of floating objects [5], [38]. The coalescence process occurs when more than one bubble (bubbles that are formed on the anodes) in the electrolyte collides and form a bigger bubble. The collision of these bubbles may occur in three stages: particle (small bubbles) collision, electrolyte drainage from bubble films when the bubbles are colliding, and film rupturing

[42]. The last phase, film rupturing will occur when the coalesced bubbles burst inward due to the overlying pressure of the floating objects.

#### 2.6. IMPACTING FACTORS OF ACID MIST GENERATION

The generation of acid mists during electrowinning process is attributed to the bursting of bubbles of variable sizes at the electrolyte surface. As is known, these bubbles are formed because of the oxidation of water molecules which form oxygen gas on the anodes of the cell plates. The emergence, growth, and detachment of these bubbles are characterized by several varying factors involved in the process; these factors include solution temperature, current density, and solution acidity [31] [12]. The variation in these process parameters impacts the generation of acid mist. A study claimed that these parameters affect the behavior of the electrowinning process [6].

**2.6.1. Temperature Impact.** The thermal property of an electrolyte solution plays an important role in the generation of bubbles at the anode as well as the foaming behavior of the surfactant added to the electrolyte. Controlling electrolyte temperature between 30 - 50 °C is important during electrowinning because this is the temperature range used in the industry [16]. Increase in electrolyte temperature above this range can foster the oxidation of water molecules at the anode which will lead to bubbles nucleation on the anode face [25]. The impact of this process parameter during electrowinning can also affect the surfactant presence in the electrolyte. Various surfactants will perform effectively in an electrolyte at different temperatures. A research study proposed that surfactant (FC – 1100) effectiveness can be influenced by electrolyte temperature. The study showed that an electrolyte containing the concentration of FC – 1100 at 30 ppm at

30 °C will produce a 0.2 mg/m<sup>3</sup> of acid mist in the atmosphere, while the same electrolyte at a temperature of 60 °C and the same concentration (30 ppm) of the surfactant in the solution will yield an atmospheric mist concentration of 14.5 mg/m<sup>3</sup> [31]. This assertion can be seen in Figure 2.5. The figure illustrates the difference in the concentration of acid mist at a 30 °C increment in the temperature of the electrolyte. The figure experimentally shows the difference in mist concentrations generated with the increase in temperature.

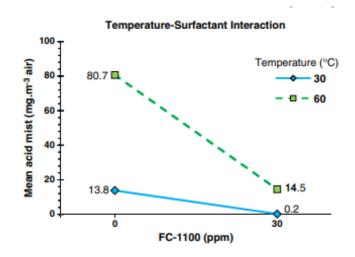


Figure 2.5: Temperature - FC-1100 curve [31].

**2.6.2. Current Density Impact.** High current density is essential for quality production, but on the other hand it increases the amount of acid mist generated during electrowinning. The impact of current density can be controlled by the influx of the rectifier current and the rate of production. Because the cost of running electrowinning cells at a high current density is economically intensive, low production of copper ore from mining facilities will require low influx of current, and vice versa. In the research

of acid mist reduction during copper electrowinning, the current density was observed as one of the process parameters that influences the generation of acid mist. This property of an electrowinning process is the quantity of electric current flowing in an electrolyte per unit cross-sectional area of electrolyte cell plates. Current density above 400 A/m<sup>2</sup> yields high production of copper, but in turn generates more acid mist [20], [31]. The effect of current density on the generation of acid mist also depends on the presence of surfactants. Increasing the current density and the surfactants can potentially generate more acid mist.

2.6.3. Surfactant Concentration. The surfactant concentration in tankhouse electrolyte plays an important role in the effectiveness of the surfactant to suppress acid mist. This concentration can vary with the chemistry of the surfactant and the size of the electrolyte tanks. Interestingly, different surfactants will show different suppression efficiencies at different concentrations. This allows flexibility in the use of surfactant. However, with the flexibility in the use of surfactant, a low concentration of surfactant during electrowinning is advisable. Low concentration of surfactant combined with other suppression methods can effectively suppress acid mist. More explanation on this can be found in section 2.5.1.1 The concentration at which a surfactant starts to be effective in the electrolyte solution is called the Critical Micelle Concentration (CMC) [43]. It is at this concentration that the surfactant affects the surface tension of the electrolyte. Since different surfactants will perform at different concentrations, it is important to know the surfactant's CMC in a particular amount of electrolyte due to the varying size of electrolyte tanks. To determine the CMC of surfactant, different concentrations (preferrable starting with 4g/L) are tried in samples solutions with the same chemistry as the tankhouse electrolyte. At each concentration, a tensiometer is used to measure the

surface tension of the electrolyte. These two parameters (surface tension and surfactant concentration) are plotted [43]. The concentration at which the slope deviates from linearity, is the feasible surfactant concentration. At this concentration the surfactant can reduce the surface tension of the electrolyte and suppress bubbles from bursting at the surface [31]. This helps in determining the CMC of surfactants because these chemical reagents have diverse chemistry.

Surfactants are diverse and have many types and can be used for different purposes. As mentioned in section 2.5.1, surfactants can be emulsifiers, detergents, depressants, or foaming agents. Surfactants in general will affect the surface chemistry of liquid or gaseous fluids when in contact with it. Their chemistry is usually amphiphilic. This property (amphiphilicity) allows them to be soluble (hydrophilic), or non-soluble (hydrophobic) in solutions. Because these reagents are of different types, they can be categorized into one of the following: anionic, cationic, non-ionic, and amphoteric surfactants based on their ability of affecting the surface tension of a fluid.

**2.6.3.1. Anionic surfactants.** These are the most common surfactants that are widely used. They can be used in industrial activities, scientific research studies, and everyday home activities. Anionic surfactants are cleaning agents. These surfactants have foaming properties that make them to be found in soap, shampoos, and gels. Their poor performance in harsh environments has made them unfavorable in the electrowinning industry where acid (180 g/L), high temperature (40 °C), and high power are used for metal extraction. They are workable in homes for house cleaning and hygiene products. Some examples of anionic surfactants include ammonium lauryl sulfate, sodium lauryl sulfate, and potassium lauryl sulfate [44].

**2.6.3.2. Cationic surfactants.** These surfactants exist mostly in hydrophilic states in solutions. Cationic solutions are most often mixed with other surfactants to affect solutions surface chemistry. Their complexity in chemistry when mixed with other surfactants make them limited in the extractive metallurgy of copper [45]. Cationic surfactants are mostly fatty acid, fatty amine salts, and quaternary ammoniums.

**2.6.3.3.** Non-ionic surfactants. These are surfactants that are the second most common in industrial usage. They are made of synthetic chemicals that are readily ionized in solutions but have good foaming properties. These surfactants tend to underperform when used in harsh temperature environments. However, they have a good effect on the surface tension of solutions [44]. A study investigated the use of non-ionic surfactants to reduce acid mist in copper electrowinning and found that these surfactants are good suppressants of bubbles bursting at the air-electrolyte interface. In the study, the surfactants showed a suppression efficiency of more than 95 %, but at a temperature less than 30 °C [6]. Conversely, the inability of non-ionic surfactants to be effective in high temperatures environments makes them unfavorable in tankhouse operations. Surfactant of this class include alkyl phenol ethoxylate, fatty alcohol ethoxylate.

**2.6.3.4. Amphoteric surfactants.** Chemical reagents that have both the characteristics of anionic and cationic surfactants. Amphoteric surfactants are widely used in harsh industrial operations because of their ability to exist and be effective in these terrains; industrial operations like copper electrowinning. These surfactants have high suppression efficiency and are applicable in almost everywhere [45]. The majority of the surfactants used in the electrowinning industry fall within this class of surfactant. They are low in toxicity, cause less irritation, and are a good surface tension reducer.

Like the FC - 1100 surfactant that is used to suppress acid mist during electrowinning is an amphoteric surfactant.

**2.6.4.** Solution Acidity. The impact of solution acidity does not have a greater effect on the generation of acid mist, yet it contributes. The contribution of solution acidity to the generation of acid mist has led to a continuous monitoring of the acid content in electrowinning electrolyte. Analytical data and analysis are continuously provided by onsite laboratories to ascertain the chemistry of the electrolytes [31]. The acidic range of electrowinning tankhouse electrolytes is between  $150 - 180 \text{ g/L H}_2\text{SO}_4$  [16]. Acid concentration below this range can potentially lead to the generation of acid mist. A research study showed that neglecting the existing current density and temperature in an electrolyte, high amount of acid mist can still be generated at low acid concentration in the electrolyte [31].

### 2.7. SUMMARY

The generation and emission of acid mist from the electrowinning process into tankhouse environments remains a challenge within the electrowinning industry. This challenge continues to endanger the life of tankhouse employees and shorten the life span of equipment and structures. With such a challenge, various acid mist reduction techniques were researched and employed in the electrowinning industry to minimize the quantity of mist generated and emitted during electrowinning. So far, the existing acid mist control methods include suppressants, ventilation, hood, floating objects (beads, balls), bubble coalescence [38]. Among these methods, the suppressant or surfactant method proven to be economically viable and efficient in reducing acid mist by 90 % [6], [8], [34]. The other methods of acid mist suppression are rarely used singly because of cost, labor intensiveness, and operational constraints that are associated with them. For example, the cost of using the ventilation method is equivalent to 20 % of the entire cost of the electrowinning process [40]. This cost added to the operational cost makes the ventilation method economical unfeasible in the electrowinning industry. The floating objects (plastic balls) method is mostly used together with the surfactant method. Therefore, with the cost and operational constraints associated with these methods, the surfactant method is favored for its simplicity of use and cost.

Several process parameters contribute to the generation of acid mist during the electrowinning process. These parameters include electrolyte temperature, current density, and electrolyte acidity [16], [17], [31]. Variation in these parameters leads to high production of copper as well as high generation of acid mist which can be vice versa. Optimizing these parameters to yield high production and at the same time reduce acid mist is still being studied. A study proposed that high generation of acid mist will exist if the temperature of the electrolyte solution is increased. The study also claimed that disregarding temperature and current density in the cell, if the acid concentration of the electrolyte is lower, more acid mist will be generated [31]. The increase and decrease in these parameters are still challenging for electrowinning plants.

While it is true that production is keen for electrowinning plant operations, the safety and healthy working environment is more important for tankhouse employees. This study conducted a critical review on the suppression methods of acid mist generation during copper electrowinning. Through the review, industrial regulations and compliance threshold limits for acid mist concentration emitted in electrowinning

tankhouses were considered. Our study also concluded with recommendations on optimizing electrowinning operations. Of all the acid mist suppression methods reviewed, it can be proposed by this study in which the surfactant method remains economically viable and operationally efficient in the electrowinning industry with 90 % or above acid mist suppression. Our study found that the reviewed process parameters (temperature, surfactant concentration, current density, solution acidity) remain investigative in finding an optimum point. For example, an electrolyte containing 40 g/L Cu and 10 g/L H<sub>2</sub>SO<sub>4</sub> does not reduce the amount of acid mist emitted into the atmosphere but shows a decrease in the acid concentration of the mist emitted into the atmosphere. However, for good production and tankhouse safety measures, it is important to keep the electrolyte temperature at 40 °C, the current density at 400 A/m<sup>2</sup>, and the electrolyte acid concentration at 180 g/L H<sub>2</sub>SO<sub>4</sub>. These values yield quality production of copper and at the same time reduce potential threats posed by the emission of acid mist.

#### **3. METHODOLOGY**

#### **3.1. ACID MIST SAMPLING EXPERIMENT**

As can be seen in Figure 2.4, an acid mist testing chamber was used to perform the acid mist sampling experiment. The cross section of the chamber was 50 cm x 50 cm, and the height was 170 cm. Air entered the chamber from the bottom and an exhaust fan at the top of the chamber pulls air upward providing an average flow velocity of 2.8 mm/s in the chamber (considering the geometry). A polypropylene tank (12.5 in x 6.5 in x 8.75) was placed on top of a perforated plastic sheet. The sheet was used to support the polypropylene tank that contained 5 L of electrolyte. The electrolyte was made of Cu 40 g/L and  $H_2SO_4 180 g/L$ . The surfactants tested during the research study are listed in Table 3.1 with the testing concentrations of 4 mg/L, 10 mg/L, and 20 mg/L. The temperature of the electrolyte was thermostatically controlled at 40 °C by a water heater. During the sampling process, bubbles were generated by disparaging industrial oxygen gas through the gas diffuser that was submerged in the electrolyte bath. The gas was discharged at a flow rate of 1.5 L/min. Essentially, this flow rate was chosen to simulate the amount of oxygen gas generated on a typical industrial anode (1 m x 1.2 m x 0.00125 m) per minute in an electrowinning tankhouse. A gas flow meter was used to control the flow of oxygen.

As gas was infused into the electrolyte solution, bubbles were generated, and then traveled through the solution up to the surface. These bubbles burst at the air-electrolyte interface emitting droplets of acidic aerosols (acid mist) into the air of the experimental chamber. The droplets containing acid were transported to the sampling point by the inlet air flow and the exhaust fan. Air samples were collected using the Open-face sampling cassette with a 37 mm diameter quartz fiber filter (Whatman QMA). Each sample was taken for 30 minutes at the sampling rate of 5 L/min to allow a reasonable number of vaporized aerosols to be absorbed onto the quartz fiber filter.

After samples were collected, the filters were removed from the sampling cassettes and placed in a 50 mL volumetric flask containing deionized water filled to the mark (50 mL). The volumetric flask containing the filters were sonicated for 15 minutes in a sonication bath. The sonication process was used to agitate the deionized water to wash off all the acid mists absorbed into the filter. After the sonication process, the titration analysis was the next step to be followed. This step led to understanding the performance of the surfactants in terms of mist suppression efficiency at the tested concentrations (4 mg/L, 10 mg/L, and 20 mg/L). The titration process was repeated three times per tested concentration (say 10 g/L). Therefore, a total of 30 mL (10 mL per titration) of the sonicated solution was pipetted out using a glass pipette. Every 10 mL of the sonicated solution was added to 40 mL of deionized water for titration. A Metroholm auto titrator (862 Compact Titrosampler) was used to determine the acid in the solution.

The F3-A surfactant was initially tested at a concentration of 1.5 mg/L and 8 mg/L considering the degradation of the surfactant as the surfactant potentially degrades over time. A 7.5 mg and 40 mg of the F3-A surfactant was weighted using a laboratory scale to account for the concentration of 1.5 mg/L and 8 mg/L respectively. The weighed surfactant was added to the electrolyte at time T0. The electrolyte bath was stirred for one minute to disperse the surfactant in the solution (Cu 40 g/L and H<sub>2</sub>SO<sub>4</sub> 180 g/L).

No.	Surfactants family	Sub-Product	Chemistry	
1	FC - 1100	N/A	Floroalkyl	
2	Family 1 (F1)	F1-A		
		F1-B	Lauryl Alcohol Ethoxylate (LAE)	
		F1-C		
	Family 2 (F2)	F2-A	Lauryl sulfate	
3		F2-B		
		F2-C		
4	Family 3 (F3)	F3-A	Saponified compounds	
		F3-B		
5	Family 4 (F4)	F4-A	Polypropylene glycol	
6	Family 5 (F5)	F5-A	Fluroalkyl acrylate adduct	
7	Family 6 (F6)	F6-A	Hydrotreated light petroleum distillate	
8	Family 7 (F7)	F7-A	Not available	
		F7-B		
		F7-C		
		F7-D		

Table 3.1: List of surfactants tested.

After dispersing the surfactant in the electrolyte by the stirring process, the acid mist chamber was sealed with an adhesive tape to avoid the inflow of air through the corners of the chamber. The airflow in the chamber was allowed to be stable for two minutes with acid mist sampling taking place immediately after the 2 minutes when the sampling pump was turned on (approximately 4 min). The sample was collected for 30

min at a sampling flow rate of 5 L/min and an oxygen flow rate of 1.5 L/min. The sampling start time was recorded as T1.

After the 30 minutes of sampling, another 30 min was allowed to observe the surfactant degradation over this time. Another sample was taken after 60 min from the initial time (T0). At the start of the sampling (starting the pump) the time was recorded as time two (T2). A third sample was taken 120 min after T0. Three samples were collected for the concentration of 1.5 L/min amounting to a total time of 120 min from time zero (T0); while four samples were collected for the concentration of 8 mg/L amounting to a total time 180 min from time zero (T0).

## **3.2. PHASE BREAK EXPERIMENT**

The phase break analysis was conducted in a 1000 mL glass beaker with stainless steel baffles. A 200 mL of aqueous—copper sulfate electrolyte (Cu 45 g/L and H<sub>2</sub>SO<sub>4</sub> 180 g/L) and 200 mL of organic—85 vol% SX-12 and 15% vol LIX 648—were mixed using a Cole-Parmer Ultra-compact Digital Mixer (model # 50006-01) with a 3.2 cm diameter plastic impeller at a speed of 1,750 rpm. The impeller was placed in the middle of the glass beaker 0.5 in above the bottom of the 1,000 mL beaker. The emulsion was mixed for 30 s after the mixer reached full speed (1,750 rpm). At a full stop after spinning, the impeller was removed from the emulsion. The disengagement time was measured from when the mixer was turned off until a clear visual boundary was formed between the two phases (the organic and aqueous phases). See Figure 3.1. The reported values were the average of three experiments conducted per surfactant. The phase break sampling for each surfactant was tested at 20 mg/L. As such, a mass of 4 mg of a

particular surfactant was added to the emulsion solution containing the organic and aqueous to conduct the phase break.



Figure 3.1: Phase break experimental setup.

# **3.3. LABORATORY COPPER ELECTROWINNING EXPERIMENT**

Pb plates (15 cm x 4.5 cm x 0.7 cm) were used as anodes and 316 L stainless steels (15.2 cm x 7.1 cm x 0.4 cm) were used as cathodes. The stainless steels were weighed on an analytical balance (scale) before the electroplating experiment to know the initial weights. Each plate was labeled to keep track of the weight of copper deposition after the experiment. Electrolyte (45 Cu g/L, 180 H<sub>2</sub>SO<sub>4</sub>) of volume 700 mL was poured into three (3) 1000 mL beakers and covered with a plastic lid. The anode and cathode were slotted through the rubber lid. The three (3) 1000 mL beakers were placed on separate laboratory hot plates to be heated at 40 °C. A thermometer was used to ascertain the temperature of the electrolyte. When the electrolytes were brought to temperature (40 °C), a smoothing agent (DXG - F7) was added at a volume of 3.5 mL per beaker to aid in smoothing the surface of deposited copper on the stainless plate during the plating. After another 30 min, different surfactants were added to each beaker at a mass of 14 mg per beaker. The 14 mg of various surfactants added to each beaker was derived using ratio and proportion analysis of surfactants added to the phase break solution (Cu 45 g/L and H<sub>2</sub>SO<sub>4</sub> 180 g/L), 200 mL.

DC current of 1.8 amp was supplied from a mini rectifier through a complete electric circuit (series connection) including the electrowinning cells for four hours. The time was monitored using a stopwatch.

After four hours, the rectifier and hot plates were turned off from operating and the stainless steel plates (cathodes) with the deposited copper were rinsed with deionized water and allowed to cool overnight to be weighed and analyzed the next day.

The deposition of metal on the stainless steel (cathode plate) was excellent relative to the theoretical mass (8.54 g) of copper calculated. The calculated mass gave a presumptive amount to be recovered within the designated platting time and current. The theoretical mass of copper,  $M_{Cu}$ , was calculated using Faraday's equation of electrolysis, Equation 3.1.

$$M_{Cu} = \frac{(I)(t)(A_{wt})}{(n)(F)}$$
Equation 3.1

where:

I is the current applied through the circuit (amps),

t is the electroplating time (s),

Awt is the atomic weight of the substance, copper (kg)

n is the number of charge of copper,

and F is Faraday's constant.

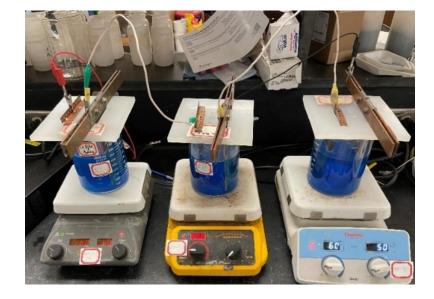


Figure 3.2: Electroplating experimental setup.

Figure 3.2 shows the experimental setup of what is described in section 3.3. The image illustrates the connection of a complete circuit between laboratory copper electrowinning cells. The connection starts from the electric current supply box or rectifier to the anode (positive plate), and with a neutral alligator cable connected from the cathode (negative plate) of the first cell to the anode of the second cell considering polarity. With the three laboratory copper electrowinning cells, the connections go through the cells and end at the last plate completing the circuit.

### **4. RESULTS**

### 4.1. ANALYSIS OF ACID MIST GENERATION

Analyses and explanations of the acid mist testing experiments were discussed in section 4. The presentation of the figures in this section was based on a grouping of surfactants having the same chemistry. Other surfactants individually supplied by the vendors that had different chemistry were plotted together into one graph. Four repetitive tests were conducted with FC – 1100 on different days to validate the setup and establish a baseline. Figure 4.1 illustrates the mist concentration and the suppression efficiency of FC 1100 at varying surfactant concentrations. The FC – 1100 surfactant is floroalkyl chemical that can reduce the surface tension of solutions; but has the potential of posing environmental threats due to its chemical characteristics of wearing away from the environment easily. Suppression efficiency for each surfactant was calculated considering the average mist concentration of no surfactant in the electrolyte. Equation 4.1 illustrates how the mist suppression efficiency was calculated.

$$SE = \left(1 - \frac{B}{b}\right) X \, 100$$
 Equation 4.1

where:

SE is the suppression efficiency (%)

B is the average mist concentration  $(mg/m^3)$  at the 4, 10, and 20 mg/L b is the average mist concentration  $(mg/m^3)$  at no surfactant

Based on the results, the baseline acid mist concentration (0 mg/L or no surfactant) varied between tests during the experimental study. The first test (labeled FC1100-1) in Figure 4.1 had the highest acid mist concentration at no surfactant, and the suppression efficiencies were unfavorable. There were a high variance in the first test relative to the other three tests. This may be due to experimental error, operational error, and/or the impact of ambient conditions (temperature, humidity, etc.), requiring further investigation. Generally, minimum suppression efficiencies were achieved at 4 mg/L. More than 58 % efficiency was seen at 10 mg/L, and the maximum efficiencies were 77 % to approximately 80 % at 20 mg/L. Results presented in Figure 4.1 also illustrate that FC – 1100 at 20 mg/L showed a suppression in acid mist generation of about 80 % which mirrors the results generated from other study [31].

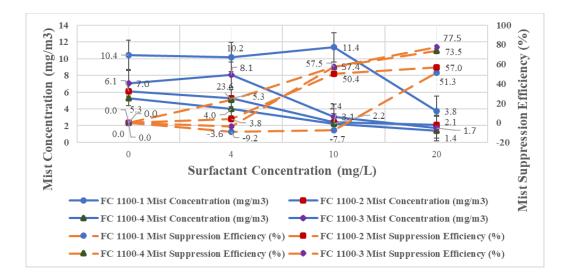


Figure 4.1: Repetition plots of FC-1100.

The results for the Family 1 surfactants (F1-A, F1-B, and F1-C) can be seen in Figure 4.2. The surfactants did not show tremendous suppression of acid mist through the experimental studies. The ability of the Family 1 surfactant to suppress acid mist was moderately frail and may be required to be used in combination with other acid mist suppression methods. As shown in the figure, the plot displayed that the F1-A demonstrated the maximum acid mist suppression efficiency of the Family 1 at 20 g/L with a 46.1 % suppression efficiency. This percentage was approximately 59 % effective as the baseline surfactant, the FC – 1100 (77.5 % mist suppression efficiency) which showed an under performance relative to the FC – 1100. The plot in Figure 4.2 also illustrate that the performance of the F1-B and F1-C showed an 11 % and 34 % respectively in suppressing acid mist relative to the baseline surfactant, FC 1100. Therefore, an inference can be made that the surfactants of the Family 1 were not favourable to be used alone for the suppression of acid mist considering the parameters used in the research studies.

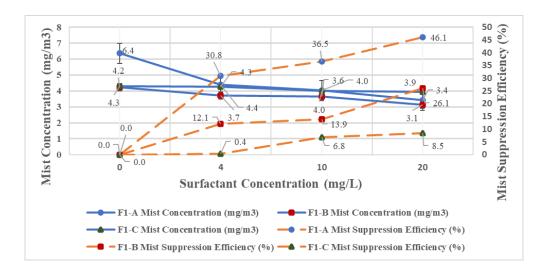


Figure 4.2: Results of the family 1 surfactants.

Another family of surfactants that was tested was the Family 2 surfactants (F2-A, F2-B, F2-C). Surfactants found in Family 2 are made of lauryl sulfate. These chemicals can reduce the surface tension of solutions which make them available for industrial use. The results of the Family 2 surfactant can be seen in Figure 4.3. As can be seen, this family of surfactant did not reduce acid mist concentration at the tested concentrations, thus, making the Family 2 surfactant family usage effective in the electrowinning industry. The maximum suppression efficiency of the surfactant at the tested concentration did not exceed 50 %.

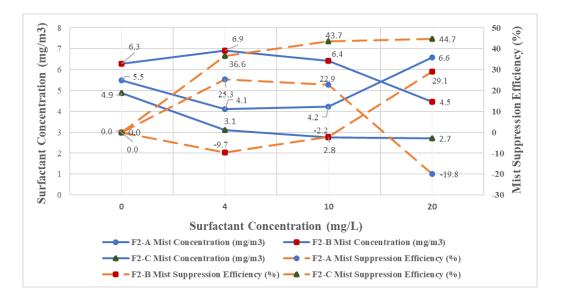


Figure 4.3: Results of the family 2 surfactants.

The results of the Family 3 (F3-A and F3-B) surfactants are presented in Figure 4.4. These surfactants are wood extracts that are further processed to produce surfactants for various applications to include copper electrowinning, etc. As shown, the F3-A surfactant demonstrated linearity in increment of surfactant concentration and

suppression strength. Maximum suppression efficiency (95 %) and mist concentration  $(0.2 \text{ mg/m}^3)$  of the surfactant was seen at the highest concentration tested (20 g/L). Results obtained from the experiment of the F3-A surfactant demonstrated an excellent suppression performance of the surfactant—a 93 % average suppression. The results also analytically showed that at the concentration of 20 g/L, the F3-A surfactant showed 18 % more suppression efficiency than the FC – 1100 surfactant.

The F3-B surfactant plots shown in the figure demonstrated an ineffective suppression of acid mist. The surfactant showed less than 25 % suppression with 5.3 mg/m<sup>3</sup> of acid concentration. This result rendered the F3-A surfactant not very effective in acid mist suppression when singly used in the electrowinning industry.

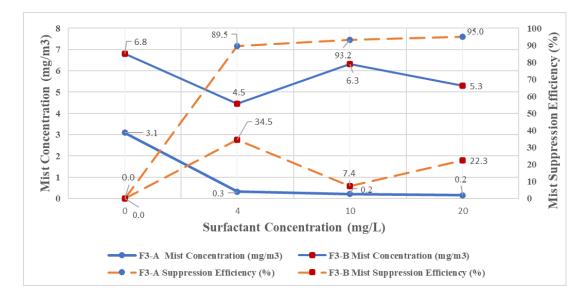


Figure 4.4: Results of the family 3 surfactants.

The F3-A degradation test results are shown in Figure 4.5. The surfactant was tested for 120 minutes based on the method described in Section 3.1. Experimental

results for the F3-A surfactant at 1.5 mg/L showed an increase in acid mist suppression over time from 13 to 56 %. At 8 mg/L, there was a decrease in mists suppression at longer time intervals as can be seen in Figure 4.5. It was hypothesized that the result obtained at 8 mg/L was influenced by the bio-degradable characteristic of the surfactant, which over time reduces the suppression strength of the surfactant.

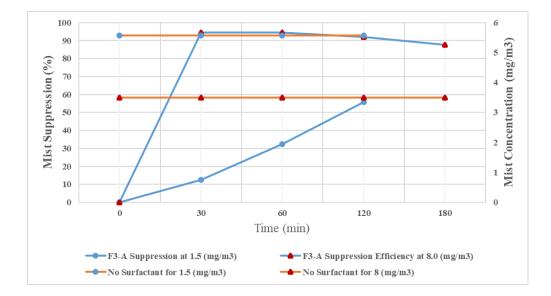


Figure 4.5: F3-A mist suppression at 1.5 mg/L and 8 mg/L.

The results of F4-A, F5-A and the F6-A surfactants are presented in Figure 4.6 illustrating a good performance of the F4-A and F5-A surfactants in suppressing acid mist. The F4-A surfactant showed an average suppression efficiency above 80 % at any concentrations above 4 mg/L. This efficiency was noticeably above the maximum suppression efficiency of the FC – 1100 as shown in Figure 4.1. The F5-A surfactant showed an increased performance with the increase in surfactant concentration. The surfactant can be presented as one of the outstanding surfactants that can be

recommended for use in the EW industry to suppress acid mist. The surfactant showed more than 80 % suppression efficiency which reflected a suppression efficiency more the baseline surfactant, FC - 1100. The results from the F6-A surfactant showed a slight increase in mist suppression as surfactant concentration increased. Above 10 mg/L, the suppression efficiency of the surfactant dropped. It was suggested that the maximum suppression of the F6-A surfactant can be seen at a concentration of 10 mg/L. However, this surfactant when used with other suppression methods can be effective in reducing acid mist.

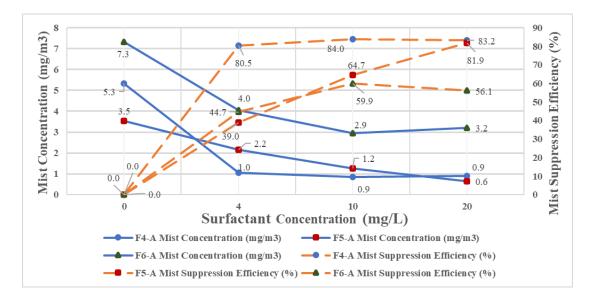


Figure 4.6: Results of the family 4, 5, and 6 surfactants.

The plot present in Figure 4.7 illustrates the results of the Family 7 surfactants (F7-A, F7-B, F7-C, and F7-D). Generally, Family 7 surfactants were shown to be effective at the concentration of 20 mg/L during the study. At 20 mg/L, the F7-A and F7-C surfactants showed an equal suppression efficiency as the FC – 1100 surfactant. At the

same concentration, the F7-D surfactant demonstrated an efficiency of 83.5 % mist suppression which proved its suppression strength over the baseline surfactant. From the plot, the F7-C surfactant showed a potential of being used in the electrowinning industry after suppressing acid mist by 66 %. Another thing that was observed from Family 7 surfactants in the plot was the suppression efficiency of the surfactants increased with an increase in surfactant concentration.

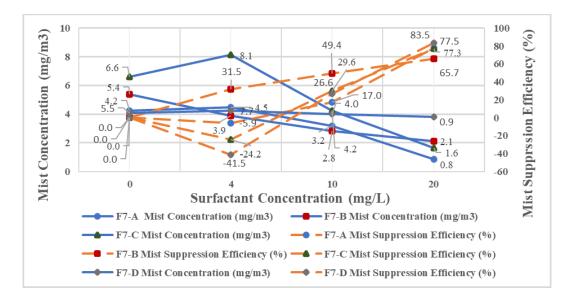


Figure 4.7: Results of the family 7 surfactants.

Figure 4.8 (a) shows the results of the different surfactants that demonstrated suppression strength equal to or greater than the FC – 1100 surfactant. As seen in the figure, the baseline surfactant showed a maximum suppression efficiency of 78 % which was also seen in the performance of the F7-A surfactant. The remaining surfactants in the plot showed more suppression relative to the FC – 1100 surfactant by 5 – 17 % increment in suppression on acid mist during the experiments. In Figure 4.8 (b), all the surfactants

showed less acid mist concentration than the FC – 1100 surfactant. The F3-A surfactant demonstrated the least mist concentration showing less than 0.3 mg/m<sup>3</sup> of mist concentration in the tested environment. The results of the F3-A surfactant suggested that the surfactant exhibited about 88 % less mist concentration relative to the FC – 1100 surfactant. It is important to note that mentioned results were results taken at 20 mg/L; the concentration at which the FC – 1100 showed its maximum suppression.

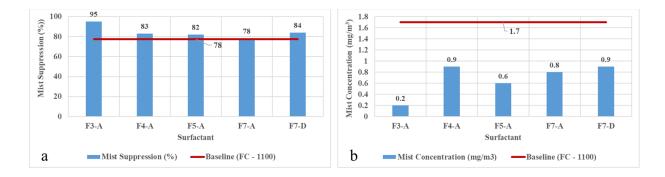


Figure 4.8: Results of surfactants that performed better than FC - 1100.

### 4.2. PHASE BREAK ANALYSIS

Phase break analysis is a quality control technique that is used in the extractive metallurgy industry to examine the disengagement time of the foam layer between an aqueous and an organic compound that is used for solvent extraction. In the industrial scale operations of copper electrowinning, the technique of phase break contributed to the success of minimizing the amount of impurities present in the aqueous solution. The PLS from upstream is mixed with the organic solution and then stripped off by solvent extraction as a more concentrated copper electrolyte for supply to the electrowinning tankhouse. At the mixing stage, longer foam disengagement time can cause entrainments

and settlings in the aqueous phase which can be carried downstream to the tankhouse. So, the control mechanism of phase separation matters at this point to observe the disengagement time of foam produced by the mixing process. As such, the application of various surfactants to a phase break experiment in our study produced different quantity of foam. With the variation in foam quantity produced by different surfactants, the time taken for the foam to wear away becomes a paramount factor in the use of the surfactant. Longer foam disappearance times indicate that the surfactant may pose issues in industrial solvent extraction settlers driving to expanded entrainment.

The experimental data presented in Figure 4.9 illustrates the results of the phase break experiments conducted during the research studies. The results show that the F9-A surfactant demonstrated an outstanding average disengagement time of 35 seconds which suggests that the surfactant was favorable for the set parameters of the laboratory studies. FC 1100 as the baseline of the laboratory testing showed 51.7 seconds for the average disengagement time. However, on an industrial scale, all the surfactants tested can be considered effective for solvent extraction operations. The average disengagement time in the industry takes about ten minutes which is significantly more than the highest time of the surfactants that were evaluated. Therefore, with 71.7 seconds being the highest disengagement time through the experiment, it can be inferred that all the surfactants tested can be used in the industry for solvent extraction.

### 4.3. LABORATORY COPPER ELECTROWINNING

Table 4.1 summarizes the test results for surfactants tested during the electrowinning phase of the study. From the results generated, it was seen that the current

efficiency during the rate of recovery of copper was excellent, ranging from 97 to 104 %. With a such current efficiency, it can be inferred that the amount of copper to be recovered from the theoretical calculation was achieved. Of 16 surfactants that were evaluated through the entire study, six surfactants were further evaluated through the electrowinning phase of the research study.

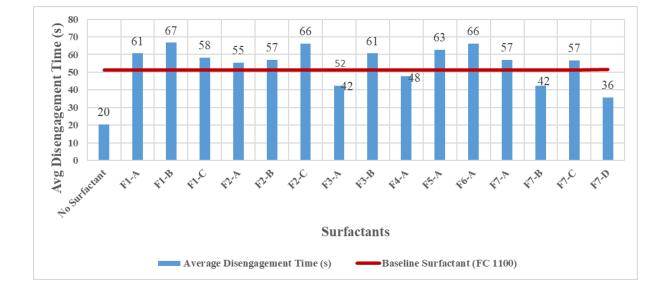


Figure 4.9 : Graphical representation of the results of phase break experiments.

These surfactants were selected based on their potential performance from the first two phases of the experiment (acid mist testing and phase separation). In furtherance, the observation of the impact of those selected surfactants on smooth plating and nodulations on the cathodes during the electrowinning experiments was also considered for their selection. In the electrowinning tests, the issue of anodes sludges was observed. Anode sludge, lead oxide (PbO), was produced when the lead anode oxidized in the cells. These oxidized particles may get deposited onto the cathode face while falling to the bottom of the cell and contaminating the cathode with coarse lead nuggets. These nuggets also roughen the surface of the cathode, indicating poor copper plating. However, in our research study, lead nuggets contamination was not observed. Figure 4.10 (a) and (b) show the morphology of the cathodes with and without surfactants respectively. In the presence of surfactants, bubbles generated on the anode faces were moderately controlled. There was no nodulation and massive surface roughness seen when no surfactants were used; see Figure 4.10 (b). This can be postulated surfactant (at low concentration) in the presence of smoothing agent (DXG-F7) enhances the electrowinning process and contributes to smooth copper plating.

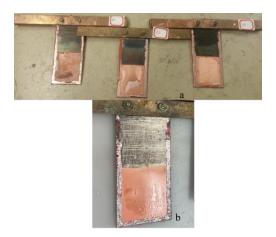


Figure 4.10 : (a) and (b) Electrowinning with surfactant and no surfactant respectively.

Figure 4.10 (a) also shows the stainless sheet blank cathodes with deposited copper after four hours plating time. The first plate in the figure shows a little dark stain on the harvested copper cathode. It was hypothesized that the stain was a result of existing surface mark of the stainless plate or extreme heat deriving from the slight increase in the current density. Current density will become uneven between electrodes

when the planarity of electrodes is not parallel. Due to the unparalleled position of the electrodes, areas with less resistance (much closer) experienced high current density as well as heat increase like seen in Figure 4.10.

Surfactant Added	Amount of Copper Deposited (g)	Recovery Rate (%)	Current Density (Amp/sq. m)
No Surfactant	8.37	98	
F2-A	8.46	99.1	383.8
F2-B	8.49	99.4	399.4
F3-A	8.88	104	395.3
F4-A	8.32	97.4	382.7
F7-A	8.41	98.5	396.4
F7-C	8.44	99	367.9

Table 4.1 : Electrowinning results of various surfactants tested.

#### **5. CONCLUSION**

Research efforts to control sulfuric acid mist during electrowinning in the electrometallurgical industry are still being pursued. Several methods to suppress the amount of acid mist generated during electrowinning were investigated in previous studies, but the problem can still be seen in the extractive metallurgy industry of base metals [5], [26], [47]. Studies found the surfactant method more effective in reducing acid mist as high as 90 % [36], [41]. This method has been used in the industry for more than 40 years because of its efficiency and ubiquity [35]. However, the manufacturer of the FC – 1100 has stopped producing the surfactant due to the prohibition placed on it by regulatory authorities, OSHA, NIOSH. Therefore, the purpose of this study was to find a possible replacement for the FC – 1100 surfactant.

To achieve finding a possible replacement for FC - 1100, our study have evaluated different surfactants during which laboratory data were obtained. The data generated from our study were processed into reasonable conclusions from which the suppression efficiency of the tested surfactants were obtained. Through the study, surfactant evaluations were conducted in three phases: acid mist sampling, phase separation during solvent extraction, and electrowinning.

Through the three phases of our study, the F3-A surfactant showed an excellent suppression of sulfuric acid mist. The exceptional performance of the surfactant was at the concentration of 20 g/L suppressing acid mist to about 95 %. In phase two and three of the study, a disengagement time under 40 seconds and a recovery over 100 % respectively was observed from the F3-A surfactant. These results rendered the surfactant

effective for electrowinning operations. However, other surfactants that were tested suppressed acid mist at different concentrations, which implies their effectiveness at those concentrations. F7-D showed the minimum phase separation time (36 sec) during the phase break experiments. The result suggested that the F7-D surfactant was an effective surfactant during solvent extraction relative to the research studies. For the phase break experiments, it can be inferred that all the surfactants evaluated were feasible for industrial operations, since their disengagement times were less than the industrial disengagement times, ten minutes.

Result generated from the evaluation of the F3-A surfactant was consistent with previous study [36]. Our study and another study confirmed that F3-A surfactant can suppress sulfuric acid mist above 90 % during the electrowinning process, and it can be feasibly used in the electrometallurgical industry of copper electrowinning [36]. In conclusion, as the usage of the FC-1100 surfactant has stopped in the extractive metallurgy industry (copper electrowinning), a potential replacement surfactant was discovered from this research study. The research study was geared toward evaluating different surfactants and proposing a possible replacement for the FC 1100 surfactant which was achieved. Therefore, a possible alternative in the absence of FC – 1100 can be recommended by this study.

Further research investigations need to be considered to understand why some surfactants will demonstrate good suppression at a low concentration rather than a high concentration. Understanding the degradability of the F7-A surfactant and how to prevent it to reduce purchase cost can be looked into as well.

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### VITA

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