

Efficiency Optimization of Copper Anode Treatment

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Abstract

This research was performed to study the electrochemistry of copper anode treatment of Coors beer, manufactured from Coors Brewing Company, to capture the trace amounts of sulfur. The relationship between electrode surface area, electrode separation or electrode gap, copper dissolution and current/voltage applied was investigated using small scale electrochemical cell. The optimum conditions, which limited the copper dose approximately 30–50 ppb in the beer stream for removing the trace amounts of H₂S and other sulfur compounds, were determined. The small scale electrochemical cell was designed and set up, as well as the continuously copper concentration analysis system by Ion Analyzer. The compositions of corrosion scale from Coors copper prototype electrode was analyzed by X-ray diffraction method. The data interpretation and analysis was accomplished via Microsoft Excel spreadsheet using desktop computer.

The experimental results showed that; 1) Electrode separation of ¾" to 1" was optimum for high current efficiency but the gap ¾" was more practical; 2) The minimum current was supposed to be 0.5 amperes, which maintained the copper dose in the range of 35–40 ppb; 3) The current density change was higher with the higher surface areas; 4) Electrode fouling was caused from both sulfides and oxides of copper, which were mixed together in corrosion scale; and 5) Formation of copper sulfide was preferred over copper hydroxide precipitation.

Keywords: copper dose, H₂S, sulfur capture, beer stream, electrochemistry.

1. Introduction

This research was performed in 2000–2001 in Department of Metallurgical and Materials Engineering (MME), Colorado School of Mines (CSM), CO, USA, as a project to support the beer manufacturing of Coors Brewing Company (Figure 1.1). It was aimed to study the electrochemistry of copper anode treatment of beer to capture the trace amounts of sulfur. The effects of electrode separation and electrode surface area on the efficiency of copper dosing of the beer stream were evaluated. The electrolytes, water and beer, were provided by Coors Brewing Co. The main objectives of this research were;

- 1) To determine the relationship between electrode surface area, electrode gap, copper dissolution and voltage applied using small scale electrochemical cell in order to apply to an existing copper anode prototype for scale up.

- 2) To investigate the optimum conditions that allow approximately 30–50 ppb [Cu] of copper dose to the beer stream for removing the trace amounts of H₂S and other sulfur compounds which contributed to an off-state.



Figure 1.1 Coors Brewing manufacturing plant, Golden, CO, USA

2. Experimental

2.1 Materials, chemicals, and analytical equipment

1. Copper sheet (Alfa Aesar), 20 x 20 cm², 1/4 " thickness, and some small copper strips
2. Spray paint and enamel paint
3. Storage tank, 20 x 40 x 26 and 20 x 30 x 28 cm³ for the electrochemical cell
4. DC power source, 1.5 A and 60 V maximum, and electrical wires
5. Metal strips and Plexiglas sheet for the cover
6. Circulation loop:
 - Old model Cole–Palmer thermoregulator
 - Rotameter for water
 - 1/2 " PVC pipe, nylon tubes 1/2 x 3/8", some nylon fittings and joints, and 1/4 " ball valve
7. Some tools, i.e. cutter, measuring tape, drill and hacksaw
8. Tap water, de-ionized water, Coors–A– water, and Coors Light beer
9. 1000–ppm copper standard solution and 5 M NaNO₃ ionic strength adjuster solution
10. Magnetic stirrer and some glass wares
11. Stopwatch (Sper Scientific)
12. Weight balances, Mettler AE 260 and old model of Denver Instrument Company
13. Omega PHI–40, Ion Analyzer, for pH, mV, and temperature measurement

14. Cole–Palmer selective–copper ion electrode for copper analysis using PHI–40
15. Rigaku X–ray diffraction analysis equipment
16. Desktop computer for data interpretation and analysis

2.2 Process equipment set-up

The electrochemical cell was designed for operating in both static and circulating modes [1]. The electrode holder racks were installed on the plexiglas cover where some holes were drilled for the pH/mV probe, temperature probe, and PVC pipes. Two PVC pipes were inserted through the holes on this cover to support the plastic tubes from the circulation pump and the small syphon pump.

The copper plate was cut into two copper electrodes, each of 10x20 cm². The hanging holes were drilled on the top and the paint was sprayed to coat all surfaces except 10x15 cm² area. To install the copper electrodes to the electrochemical cell, the copper electrodes were hooked with the electrical wires from the cover. The distance gap was adjusted from the holder racks and by bending electrical wires. The electrical wires length in the electrochemical cell was also adjusted, to maintain the immersion depth of both copper electrodes in the electrolyte.

The PHI-40, Ion Analyzer, was applied to measure pH/mV and temperature of the electrolyte continuously while the electrochemical cell was in operation. The solution output from the small circulation pump, using the old model of Cole–Palmer thermoregulator, was separated into two lines. One was by-passed back to the thermoregulator storage tank. The solution in another line flew through the rotameter to the electrochemical cell. The volume in the electrochemical cell was controlled from the rotameter, the electrolyte height, and the small syphon-pump that recycled solution back to the thermoregulator storage tank. The photograph of this equipment set-up is shown in Figure 2.1.

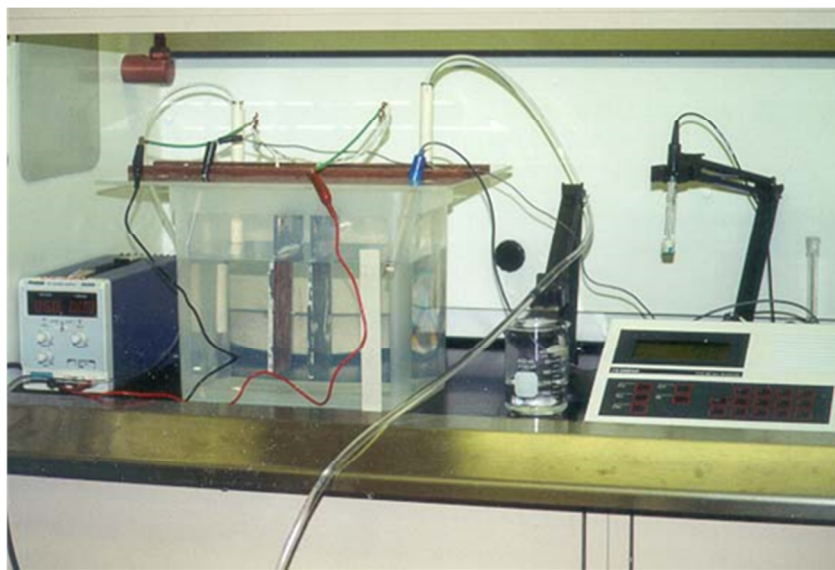


Figure 2.1 Electrochemical cell set-up

3. Preliminary Testing Procedures

3.1 Estimation of the voltages and the amperes applied

The small electrochemical cell, static mode, was set up using 500-ml beaker. The cathode and anode, which were the small copper strips coated one face with spray paint, were connected to the DC power source. The following steps were carried out;

a) Trial and error test was run using the tap water electrolyte and the high voltage of over 20 volts. The deep gelatinous blue precipitate [2] of $\text{Cu}(\text{OH})_2$ occurred on the anode rapidly and the gas bubbled on the cathode. The voltage was lowered to 5 volts and the electrochemical cell was operated for 1.5 hours. The blue precipitate occurred slightly and there was no appreciable weight loss.

b) The trial and error test was repeated using Coors-A-Light water with 5 volts (V) and 1.5 amperes (A) maximum. The weight loss was plotted as a function of power supplied in 1.5 hours. The experimental results are in Table 3.1 and the graphical presentation is illustrated as Figure 3.1. The photograph of the blue gelatinous $\text{Cu}(\text{OH})_2$ precipitate occurred, is shown in Figure 3.2.

The experimental results indicated that in this cell, the limiting current of the electrochemical process was about 0.5 amperes under the conditions applied.

Table 3.1 Trial and error run in small static electrochemical cell with Coors-A-water as an electrolyte.

<i>Volts</i>	<i>Amperes</i>	<i>Power, watt-hr</i>	<i>Anode weight loss, g</i>	<i>Note</i>
5	1.5	11.25	0.0112	$\text{Cu}(\text{OH})_2$ precipitated.
5	0.5	3.75	0.0097	$\text{Cu}(\text{OH})_2$ precipitated.
3	0.5	2.25	0.0064	$\text{Cu}(\text{OH})_2$ precipitated.
2	0.5	1.5	0.0018	<i>Slightly $\text{Cu}(\text{OH})_2$ occurred.</i>
1	0.5	0.75	0.0009	No precipitate observed.

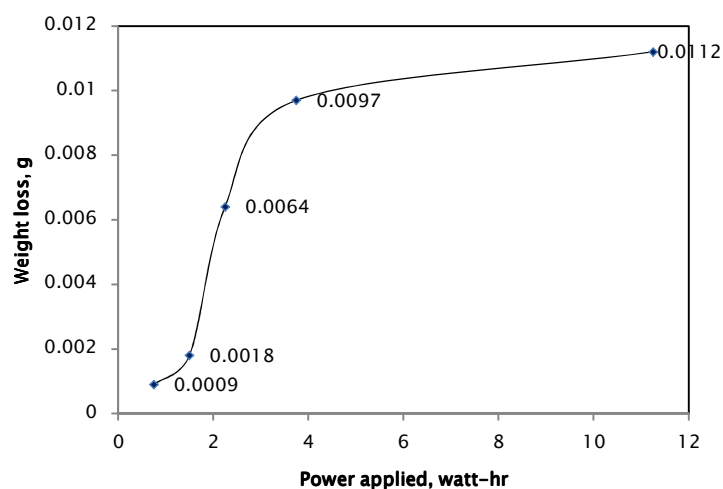


Figure 3.1 Plot of the anode weight loss as a function of the power applied.



Figure 3.2 The blue gelatinous $\text{Cu}(\text{OH})_2$ precipitate from different power applied

3.2 Estimation of the immersion depth and the distance gap

The copper electrodes were arranged in the electrochemical cell with Coors-A-water as an electrolyte. The experiments were carried out in static condition with two immersion depths of 13.5 cm and 7.0 cm. The electrode gaps tested were 3", 2", 1", and $\frac{3}{4}$ ". The current setting was 1 ampere maximum and the maximum voltage applied was 5 volts. The voltage applied was decreased and the cell current readings were recorded from DC power source. The current density was calculated by dividing the cell current with the electrode surface area. The relationship between

the current density, the voltage applied, the electrode gap, and the immersion depth are illustrated in Figures 3.3 and 3.4.

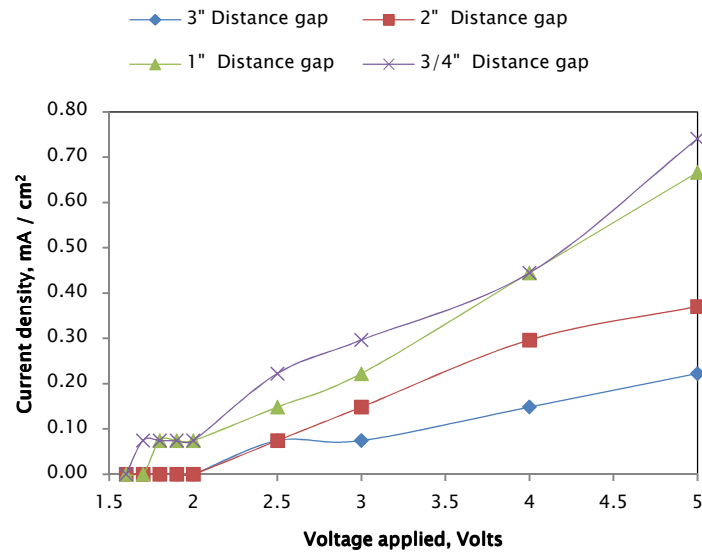


Figure 3.3 Plot of the current density as a function of voltage applied for the 135-cm² immersion surface area.

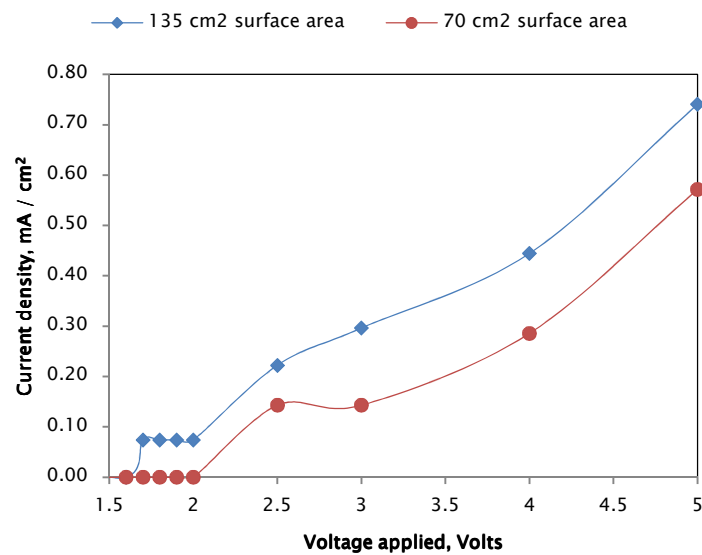


Figure 3.4 The current density changes with different surface areas at $\frac{3}{4}$ " electrode gap as a function of the voltages applied.

3.3 Investigation of the difference between tap water and Coors-A-water electrolyte

The electrochemical cell was operated with 150-cm² copper electrodes in static condition. The voltage was increased, from zero to 5 volts for Coors-A-water electrolyte, and from zero to 15 volts for tap water electrolyte. The electrode gap was 2.5" for Coors-A-water electrolyte and 2.75" for tap water electrolyte.

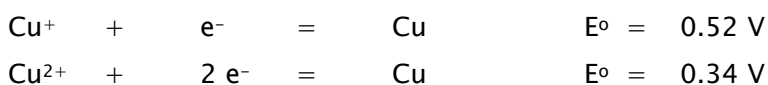
At the same voltage applied, 5 V, the cell current reading was 0.03 A for tap water electrolyte. It was lower than the cell current reading of 0.05 A for Coors-A-water electrolyte, although the electrode gap was ¼ " higher ($\Delta = 2.75" - 2.5" = 0.25"$ or ¼"). This was due to higher conductivity of Coors-A-water than the tap water.

3.4 Conclusions from preliminary tests

The anode in the electrochemical cell was expected to add approximately 30–50 ppb copper to the beer stream to remove trace amounts of H₂S and other sulfur compounds. Therefore, the blue gelatinous of Cu(OH)₂ (Figure 3.2) was not supposed to occur because of the low amount of copper ions in the electrolyte. The preliminary tests were concluded as the following;

a) From Table 3.1 and Figure 3.1, the power applied should be less than 1.5 watt-hr. Beyond this condition, 2 V and 0.5 A, in 1.5 hours, the anode weight loss increased rapidly.

The electrochemical reactions occurring on copper electrode are supposed to be [3]:



Cu²⁺ is preferred to occur from anodic reaction more than Cu⁺ because of the lower standard electrode potential. All the electrochemical reactions occurred are presented in the diagram of Figure 3.5.

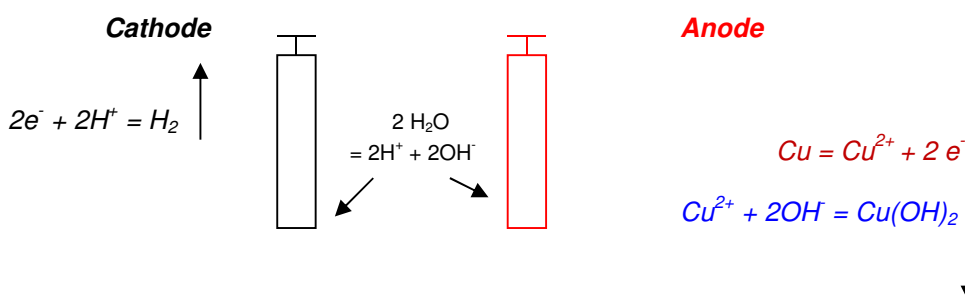


Figure 3.5 The electrochemical reactions occurring at copper electrodes

The old prototype electrode gap was $\frac{3}{4}$ " but the new electrode gap was modified to 1.5". Study was performed in the prepared electrochemical cell using the copper electrodes with the immersion surface areas of 70 and 135 cm². The electrode gaps were $\frac{3}{4}$ ", 1", 2", and 3".

b) From Figure 3.3, the closer the electrode gap, the higher the current density. The current density increasing of $\frac{3}{4}$ "-electrode gap was close to of 1"-electrode gap. Therefore, $\frac{3}{4}$ "-electrode gap was more practical.

c) The behavior of the current density increasing between 2"-electrode gap and 3"-electrode gap was the same with the applied voltage, which was lower than 2.5 volts (Figure 3.3).

d) For the same $\frac{3}{4}$ "-electrode gap (Figure 3.4), the current density change was higher with the higher surface area. However, the current density increasing rates of both surface areas applied were almost the same due to the parallel curves in this Figure.

e) Between Coors-A-water and tap water in the third preliminary test, Coors-A-water was the better electrolyte than the tap water because of its higher cell conductivity.

4. Analysis Procedure

4.1 Copper ion concentration analysis study using PHI-40 and Cu-ion selective electrode

Omega PHI-40 Ion Analyzer had the capability to measure pH, millivolts (mV), concentration, and temperature. The pH/mV mode and the ion-mode were applied for the ion concentration analysis. In order to analyze the copper ion concentration in the electrolyte, the Cole-Palmer copper ion selective electrode was connected to PHI-40.

The preliminary chemical analysis study was performed both in mV-mode and ion-mode following the operating procedures of PHI-40 and Cu-ion electrode. Despite of the low copper concentration in the process electrolyte, it was necessary to investigate the analysis method for copper concentration, which was lower than 0.6 ppm, for accuracy and precision.

The chemical analysis was achieved using 100-ml solution, and then ionic strength adjuster (ISA) or low level ISA was added, followed with uniform mixing by magnetic stirrer. The Cu-ion electrode and the temperature probe were put in the solution. It took 15 minutes to 1 hour for the stabilized millivolt reading depending on the concentration of copper in the solution.

The rough estimation of copper concentration was investigated using ion-mode. The actual concentration was measured with mV-mode from the calibration curve of the standard solutions in the same range of mV-readings. The solution matrix for the standards was needed to be the same as the sample solution matrix.

The accuracy from the low level copper concentration analysis was 14.34 ppb using 10-ppb standard solution, de-ionized water matrix. For Coors-A-water matrix, the accuracy was 0.1174 ppm from 0.1 ppm standard copper solution. For the low 10-ppb concentration, the deviation is 43.4%. For

the higher 0.1–ppm or 100–ppb concentration, the deviation is 17.4%. The higher the concentration, the more the accuracy.

The copper concentration in Coors–A–water after passing the current from the above preliminary test was measured by this procedure. Its concentration was 1378.69 ppb or 1.38 ppm.

4.2 X-ray diffraction analysis of corrosion scale from copper electrode

The black corrosion scale from Coors copper prototype electrode was scrubbed, filtrated, rinsed with de-ionized water and acetone. After drying, it was grounded with ceramic mortar. The scale analysis was achieved using Rigaku X-ray diffraction equipment with the following operating conditions.

<i>Voltage:</i>	<i>39</i>	<i>kV</i>	<i>Current:</i>	<i>90</i>	<i>mA</i>
<i>Selected axis</i>	<i>2 theta / theta</i>				
<i>Start angle (degrees)</i>	<i>20</i>				
<i>Stop angle (degrees)</i>	<i>80</i>				
<i>Step width (degrees)</i>	<i>0.02</i>				
<i>Maximum counts</i>	<i>800k</i>				
<i>Fixed time/step (sec)</i>	<i>2.0</i>				
<i>Chart speed (mm/min)</i>	<i>Stop</i>				
<i>Material name</i>	<i>Cu</i>				
<i>Radiation constant</i>	<i>1.540598</i>				
<i>Out of range data</i>	<i>Scale</i>				
<i>Programs debug mode</i>	<i>None</i>				
<i>Minimum d-space</i>	<i>1.199</i>		<i>Maximum d-space</i>	<i>4.436</i>	
<i>Minimum 2θ</i>	<i>20</i>		<i>Maximum 2 θ</i>	<i>79.98</i>	
<i>Minimum intensity</i>	<i>664.00</i>		<i>Maximum intensity</i>	<i>3021.00</i>	

The intensities of various peaks from the XRD results were compared with the theoretical intensity in JPDS–International Centre for Diffraction Data at the same d–spacing value. The analytical results showed that the oxide and sulfide compounds of copper and iron were mixed together. They were β-Cu₂S, CuS₂, CuS, Cu, CuO, Cu₂O, Fe₂O₃, FeO, and FeS.

The oxides occurred from the reactions of the ions of copper and irons with oxygen dissolved in the beer stream. The corrosion of the steel pipes caused the iron ions to the solution. The trace amounts of H₂S and other sulfur compounds in the beer stream formed sulfide compounds with ions of copper and iron.

From the anode reaction, the copper ion was supposed to be Cu²⁺ more than Cu¹⁺. Therefore, the main copper sulfide corrosion scale should be CuS₂ (black) and CuS (dark blue).

5. Experimental Runs and Results

The test runs were operated in both static and circulated–electrochemical cell. The electrolytes used in these experiment runs were;

- a) Spoiled Coors–Light beer;
- b) Fresh Coors–Light beer;
- c) The mixed beer from the fresh and used electrolyte; and
- d) The de–ionized water.

The copper electrodes were weighed before and after each electrochemical cell run. The total exposure time was 1 hour and the samples were taken every 15, 30, and 60 minutes. The voltage applied was 5 volts with 1 ampere current maximum. The electrode gap fixed was 1.5" and the immersion surface area was $9.5 \times 10 \text{ cm}^2$ for Experiment #1 and $10 \times 15 \text{ cm}^2$ for Experiments #2, 3, and 4.

Experiment 1

The immersion depth was only 9.5 cm and then the surface area was only 9.5×10 or 95 cm^2 . Three samples, 100 ml each, were pipetted at 15, 30, and 60 minutes. Assumed that the amount of the samples pipetted was neglected compared with the total volume of the electrolyte in the electrochemical cell.

The pH and mV of this spoiled beer before passing the current was 3.899 at 21.6°C and 170.1 mV at 21.8°C , respectively. The pH increased from 4.157 at 21.2°C to 4.242 at 21.3°C in 60–min operating time. The cell current reading reduced from 0.11 A at starting to 0.10 A, in 60 minutes. The anode weight loss was 1 gram using rough weight balance.

The beer was spoiled by bacteria before and it looked deep yellow, high turbidity and viscosity. There was a problem analyzing with mV–mode because of the lower pH occurring from bacteria reactions. This experiment was implemented for the first trial and error test to continue for the next runs, # 2, 3, and 4 (Table 5.1).

Table 5.1 Experiments 2, 3, and 4

Operating conditions	Exp. Run # 2	Exp. Run # 3	Exp. Run # 4
<i>Run mode</i>	Static	Circulating	Circulating
<i>Starting electrolyte</i>	Fresh Coors beer	Fresh Coors beer mixed with Run # 2-used electrolyte	De-ionized water
<i>pH/mV and cell current reading of the starting electrolyte</i>	<ul style="list-style-type: none"> • pH = 4.335 at 21.0 °C • Conductivity 145.3 mV at 21.0 °C • Cell current = 0.13 A 	<ul style="list-style-type: none"> • pH = 4.406 at 22.0 °C • Conductivity 141.0 mV at 22.0 °C • Cell current = 0.14 A 	<ul style="list-style-type: none"> • pH = 5.949 at 21.3 °C • Conductivity 52.1 mV at 21.3 °C • Cell current < 0.01 A
<i>Operating conditions</i>	<ul style="list-style-type: none"> • 5 V, 1 A • 1.5" distance gap • 10x15 or 150 cm² immersion surface area • 1-hour exposure time • 10-liter approximate beer volume 	<ul style="list-style-type: none"> • 5 V, 1 A • 1.5" distance gap • 10x15 or 150 cm² immersion surface area • 1-hour exposure time • 12-liter approximate beer volume in electrochemical cell and circulator. • 6 ± 1 gph input flowrate 	<ul style="list-style-type: none"> • 5 V, 1 A • 1.5" distance gap • 10x15 or 150 cm² immersion surface area • 1-hour exposure time • 12-liter approximate beer volume in electrochemical cell and circulator. • 6 ± 1 gph input flowrate
<i>Anode weight loss (Same cathode weight)</i>	0.16 g	0.14 g	0.11 g
<i>pH/mV and cell current reading of 60-minute electrolyte</i>	<ul style="list-style-type: none"> • pH = 4.428 at 21.3 °C • Conductivity 138.6 mV at 21.3 °C • Cell current = 0.13 A 	<ul style="list-style-type: none"> • pH = 4.483 at 22.7 °C • Conductivity 137.3 mV at 22.7 °C • Cell current = 0.13 A 	<ul style="list-style-type: none"> • pH = 6.213 at 21.8 °C • Conductivity 37.4 mV at 21.8 °C • Cell current < 0.01 A

After shut down the current, pH/mV of the electrolyte from Exp. Run # 2 and Exp. Run # 3 were measured again. It was found that pH decreased but mV increased. The copper electrodes were pulled out, cleaned, and weighed. The photograph of the copper cathode and anode after experimental run is shown in Figure 5.1. The cathode surface was bright because of the hydrogen gas occurred but there were some dark dirty areas. They might be foul from some oxide or sulfide scales. The anode surface looked deep golden brown after elimination of Cu^{2+} to the electrolyte.

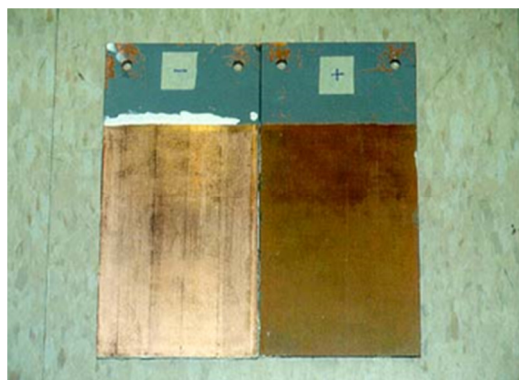


Figure 5.1 Copper electrode surfaces after passing the current

In order to investigate the phenomenon happened, pH/mV of the Exp. 4–solution electrolyte after shutting down the current was measured in half an hour. Plots of pH/mV of Exp. 2–4 vs exposure times were illustrated in Figure 5.2, 5.3, and 5.4. The concentrations of copper in the input, output, and every 15, 30, and 60 minutes were analyzed using PHI-40 with Cu–selective electrode in ion–mode and mV–mode. The copper concentration profiles of 60–min exposure time were illustrated as in Figure 5.5, 5.6, and 5.7.

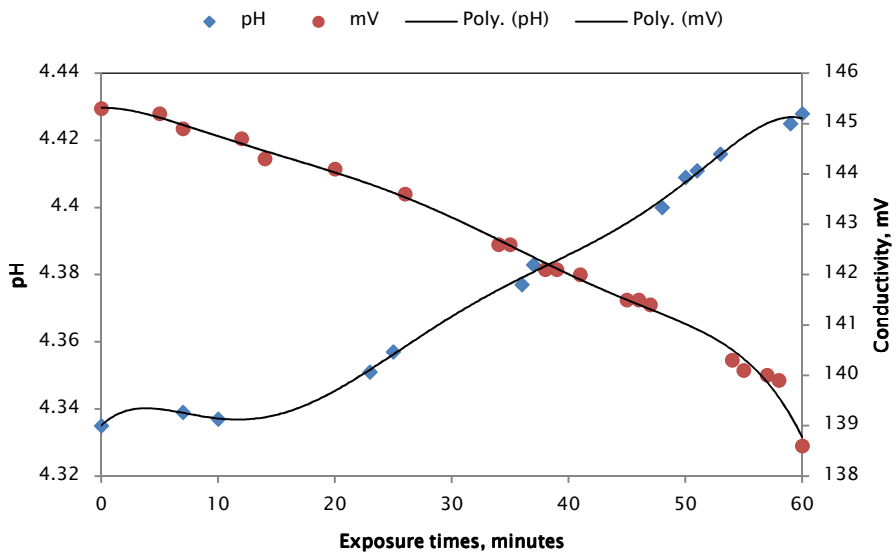


Figure 5.2 Plot of pH and conductivity as a function of exposure time in the static electrochemical cell using fresh Coors Light beer as an electrolyte.

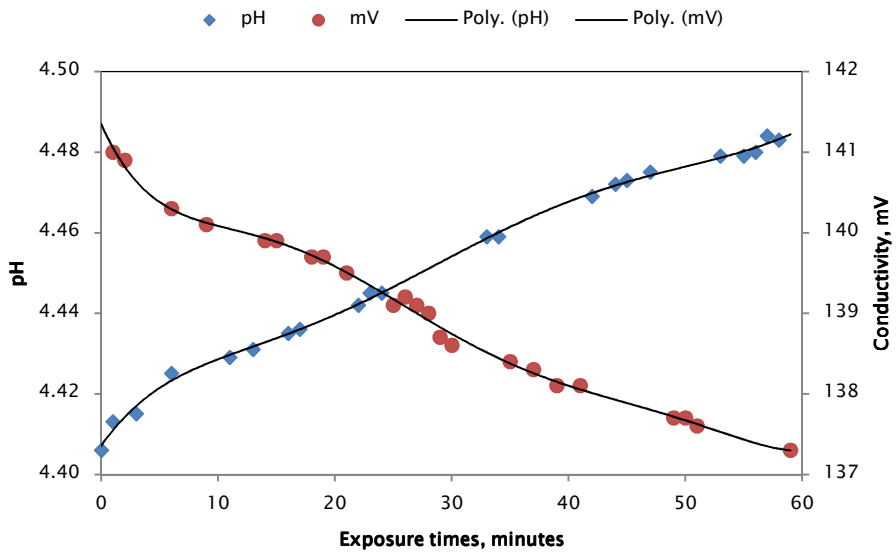


Figure 5.3 Plot of pH and conductivity as a function of exposure time in the circulated–electrochemical cell using mixed electrolyte from fresh Coors Light beer and Exp.2–used Coors Light beer electrolyte

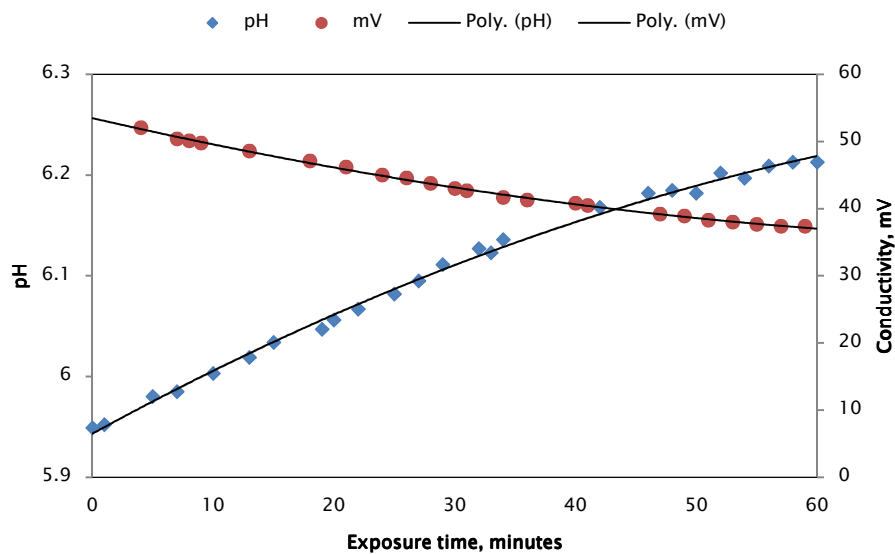


Figure 5.4 Plot of pH and conductivity as a function of exposure time in a circulated-electrochemical cell using de-ionized water as an electrolyte

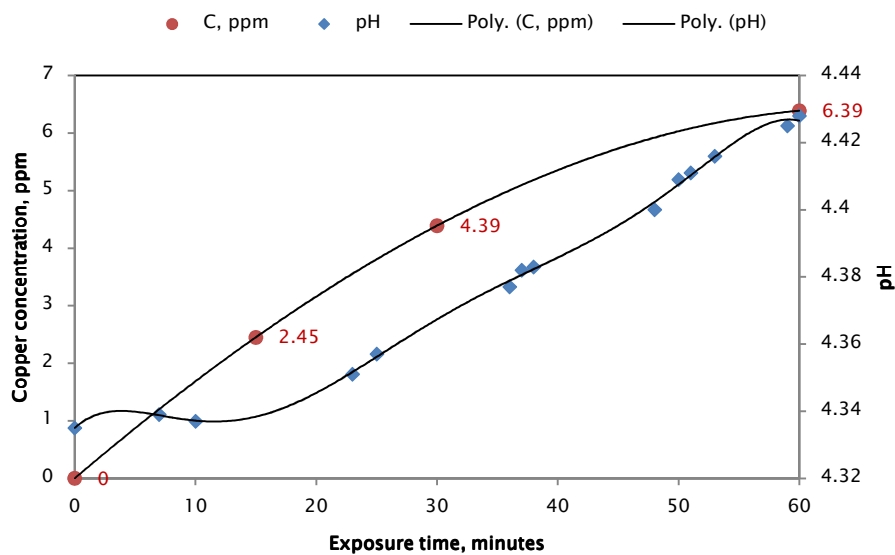


Figure 5.5 Plot of copper concentration profile and pH as a function of exposure time in static electrochemical cell using fresh Coors Light beer as an electrolyte

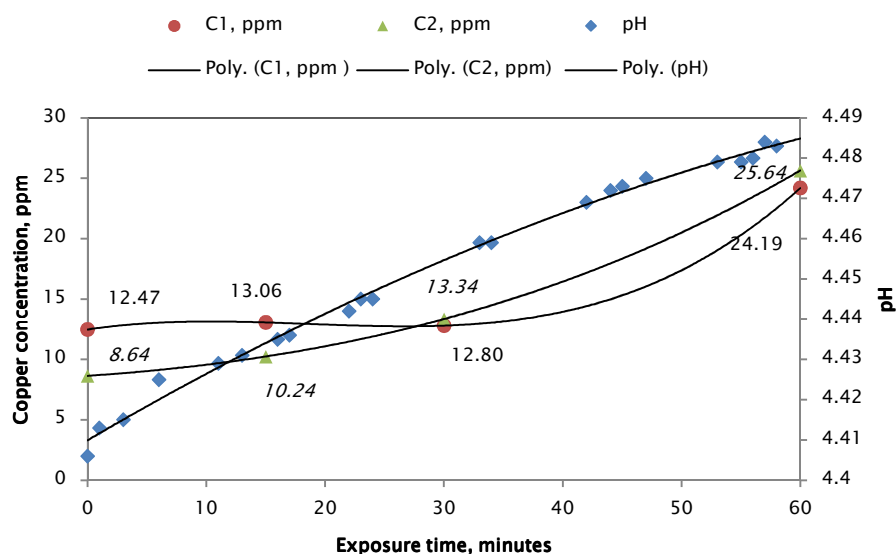


Figure 5.6 Plot of copper concentration profiles (2 inputs) and pH as a function of exposure time in circulated electrochemical cell using mixed electrolyte from fresh Coors Light beer and Exp.2-used Coors Light beer electrolyte

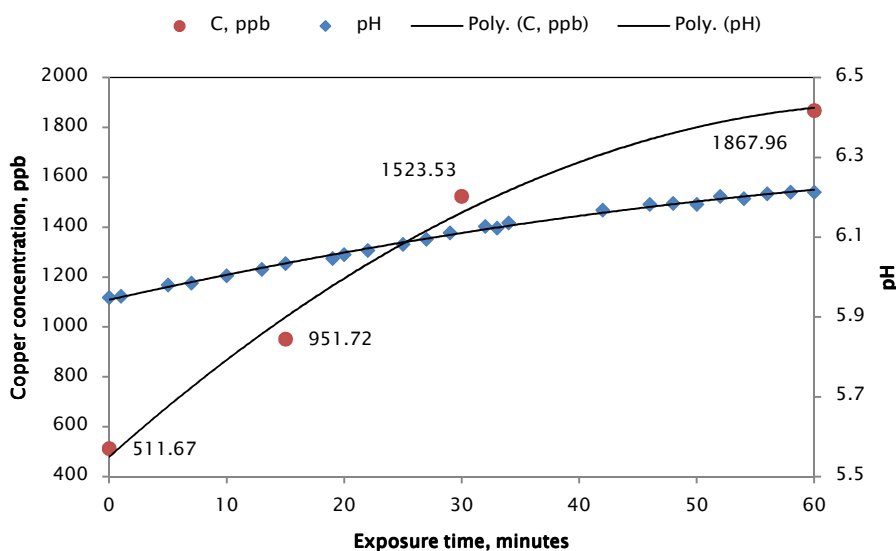


Figure 5.7 Plot of copper concentration profile and pH as a function of exposure time in circulated-electrochemical cell using de-ionized water as an electrolyte

6. Discussions

6.1 Copper mass balance

From experimental runs # 2, 3, and 4, the copper weights corroded in an electrolyte in 60 minutes were calculated using Faraday's equation [5], as shown in Table 6.1.

W	=	MIt/nF
W	=	the copper weight corroded in an electrolyte, g
t	=	exposure time = 60x60 seconds
M	=	atomic mass of copper = 63.546 g/mol
n	=	number of electrons produced or consumed in the process = 2
F	=	Faraday's constant = 96,500 C/mol or A.s/mol
I	=	cell current flow, A
<i>Note: the accuracy of the current measurement was in the 2nd decimal.</i>		

Table 6.1 Calculated anode weight loss in an electrolyte in 60 minutes

<i>Operating conditions</i>	Exp. Run # 2 Static, fresh Coors Light beer	Exp. Run # 3 Circulation, mixed fresh Coors Light beer and Exp.2-used electrolyte	Exp. Run # 4 Circulation, de-ionized water
Cell current reading (I)	0.13 A	0.13 A	0.00 A
Anode weight loss (Table 5.1)	0.16 g	0.14 g	0.11 g
Calculated anode weight loss ($W = MIt/nF$)	0.1541 g	0.1541 g	0.01 g (using max. value of 0.005 A)
Comparison of anode weights loss between the experimental and the calculated values by the deviation, Δ : $\Delta = \frac{(Exp. - Cal.) \times 100}{Exp.}$	+3.69 % deviation Look the same.	-10.07 % deviation 10.07 % copper ions absence might form precipitates of sulfides, oxides, and hydroxide.	+90.9 % deviation • The high weight loss came from the golden brown precipitate coated on anode surface area. • The low, 0.00 A-cell current, means that there are trace ions diffusing to the electrolyte.

In the electrochemical cell operation, the copper concentration was measured as a function of exposure time, 15, 30, and 60 minutes. The copper weights gained (Table 6.2) in the electrolyte were calculated from the total electrochemical cell volume and the difference between the concentration input and output.

Table 6.2 Copper weights gained in the electrolyte

Exposure time, minutes	Exp. Run # 2 Copper concentration, ppm	Exp. Run # 3 Copper concentration, ppm	Exp. Run # 4 Copper concentration, ppb
0	0	12.47 8.64	511.67
15	2.45	13.06 10.24	951.72
30	4.39	12.80 13.34	1523.53
60	6.39	24.19 25.64	1867.96
¹ 15-min circulation after current shut down		¹ 15.48	
² 30-min circulation after current shut down		Note: Comparison between 2 test runs	² 1156.26
Output-Input	6.39-0 = 6.39	24.19-12.47 = 11.72 25.64-8.64 = 17.0	1867.96-511.67 = 1356.29
Total volume (liters)	10	12	12
Copper weight gained (g)	6.39x10 = 63.9 mg = <i>0.0639 g</i>	11.72 x12 = 140.64 mg = 0.1406 g 17.0 x12 = 204.0 mg = 0.2040 g	1.3563x12 = 16.2755 mg = 0.0163 g

The data from Table 6.1 and Table 6.2 was used to calculate approximated weight gained and copper concentration, which were summarized as Table 6.3. The comparison of the theoretical and the experimental results between copper weight loss and weight gained was also shown in this Table.

Exp. Run # 2 Calculation of approximated weight gained

The new output copper concentration from the input concentration of Run # 3 was estimated to be 12.47 ppm. Approximated one third of fresh beer was mixed with approximated two third of Exp. Run # 2 electrolyte.

$$\text{Therefore, } (1/3)(0 \text{ ppm}) + (2/3)(y \text{ ppm}) = (12.47 \text{ ppm})(1/3 + 2/3)$$

$$y = 12.47 \times (3/2) \quad \text{ppm}$$

$$\text{Run \# 2 estimated output concentration} = 18.705 \quad \text{ppm}$$

$$\text{Output - Input} = 18.705 - 0 = 18.705 \quad \text{ppm}$$

$$\text{Weight gained in 10-l electrolyte} = (18.705 \times 10) / 1000 \quad \text{g}$$

$$\text{Approximated copper weight gained in Run \# 2 electrolyte} = \mathbf{0.1871} \quad \text{g}$$

The approximated copper weight gained of 0.1871 g was closer to the weight loss of 0.16 g and the calculated weight loss of 0.1541 g.

Exp. Run # 3 Calculation of copper concentration

Let the maximum copper anode dissolution was equal to 0.20 g/hr. From the actual continuous beer flowrate of 4.75 l/sec (1.25 gallon/sec), the concentration of copper in the beer stream was calculated as the following.

$$\begin{aligned}\text{Copper concentration in 4.75 l/sec-beer stream} &= (0.20 \times 1000 \times 1000) / (4.75 \times 3600) \quad \text{ppb} \\ &= 11.70 \quad \text{ppb}\end{aligned}$$

Table 6.3 Comparison between the theoretical and experimental results of copper weights

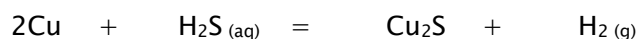
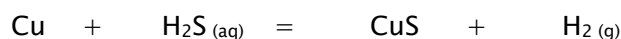
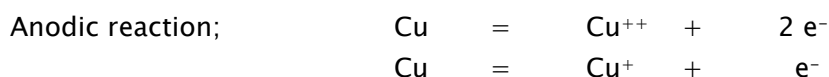
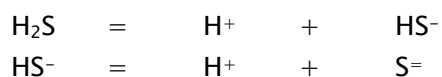
<i>Operating conditions</i>	Exp. Run # 2 Static, fresh Coors Light beer	Exp. Run # 3 Circulation, mixed fresh Coors Light beer and Exp.2-electrolyte	Exp. Run # 4 Circulation, de-ionized water
Anode weight loss (Table 6.1)	0.16 g	0.14 g	0.11 g
Calculated anode weight loss ($W = MIt/nF$) (Table 6.1)	0.1541 g	0.1541 g	0.01 g (using max. value of 0.005 A)
Copper weight gained (g) (Table 6.2)	$6.39 \times 10 = 63.9 \text{ mg}$ $= 0.0639 \text{ g}$	$11.72 \times 12 = 140.64 \text{ mg}$ $= 0.1406 \text{ g}$ $17.0 \times 12 = 204.0 \text{ mg}$ $= 0.2040 \text{ g}$	$1.3563 \times 12 = 16.2755 \text{ mg}$ $= 0.0163 \text{ g}$
Results comparison and analysis	<ul style="list-style-type: none"> The 60-min sample was not well-mixed because of the static condition. Approximated copper weight gained from the <i>Exp. Run # 2 calculation</i> = 0.1871 g 	<ul style="list-style-type: none"> Copper gained was equivalent to copper loss If let 0.20 g/hr. be the maximum copper anode weight loss, copper concentration from <i>Exp. Run # 3 calculation</i> = 11.7 ppb in 4.75 l/sec beer stream flowrate. 	<ul style="list-style-type: none"> Copper gained was equivalent to calculated copper loss More weight loss came from the scrubbed golden brown compound on anode surface.
<i>Current efficiency</i> = actual copper loss or gained / theoretical copper loss or gained	$= 0.16 / 0.1541 = 1.04$ <i>100 % of the current was effective in anode reaction.</i>	$= 0.14 / 0.1541 = 0.91$ <i>91 % current efficiency on anode reaction.</i>	$= 0.0163 / 0.01 = 1.63$ <i>100 % current efficiency</i>

From the operating conditions of Exp. Run # 3, cell current reading after 60-min. operation was 0.13 amperes (Table 6.1). From the results of Exp.3 and Exp.4, cell current varied with the concentration of copper in the electrolyte.

Assumed that 0.15 amperes was the maximum cell current reading, *and if the current was set as 0.50 amperes, copper concentration became $(0.5/0.15) \times 11.7$, or 39 ppb. It was in the range of 30–50 ppb of expected copper concentration in the beer stream.*

6.2 Electrochemical Reactions

Because of the low pH, the trace amount of H_2S can dissociate to sulfide ion.



The more copper ions dissolved from anode reaction, the more sulfide ions eliminated from H_2S to form copper sulfides. From the diagram in Figure 6.1 [6], the more HS^- produced, the less H_2S in the beer stream. The reaction shifts to the right. As a result, H_2S is eliminated from the beer stream.

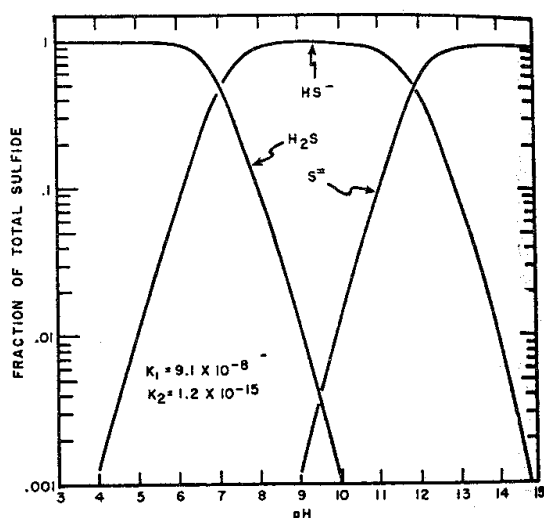
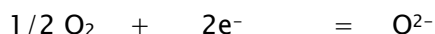


Figure 6.1 Approximate distributions of H_2S , HS^- , and $\text{S}^{=2}$

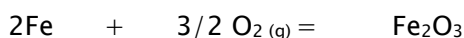
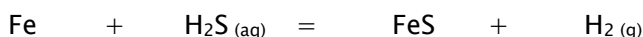
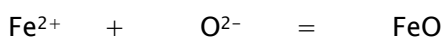
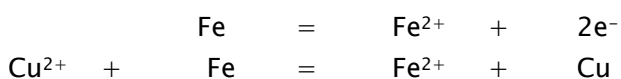
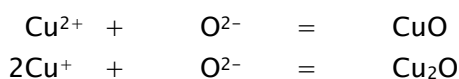
Because pH of the Coors Light beer is lower than 7, at pH values of around 4–5, oxygen dissolved in the beer electrolyte performs the cathodic reaction.



This reaction accepts electrons from anodic reaction and it causes higher rate of copper dissolution from anode. The protons from H_2S dissociation are supposed to be the small amount compared with the electrons from copper dissolution because of the trace amount of H_2S in the beer. As a result, it is possible that oxygen might have another cathodic reaction.



Therefore, except the sulfide compounds of copper, some oxides of iron and copper could be formed and deposited on cathode surface.



From the X-ray diffraction analysis results, the rust compounds fouling on cathode surface were Cu_2S , CuS_2 , CuS , Cu , CuO , Cu_2O , Fe_2O_3 , FeO , and FeS . Their formations are explained by these electrochemical reactions. The excess copper ion forms copper oxide with dissolved oxygen. Some accepts electrons from iron and causes copper metal deposit on cathode, too.

6.3 Electrode fouling

For 12 liter-total volume of circulated-electrochemical cell, 1-hr operation;

$$\begin{aligned} \text{copper weight} &= (50/1000)\text{mg/l} \times 12 \text{ liters} && \text{for minimum 50 ppb Cu/electrolyte} \\ &= 0.6 \text{ mg} \\ &= 6 \times 10^{-4} \text{ g} \\ &= 6 \times 10^{-4} / 63.546 = 9.44 \times 10^{-6} \text{ g-mole} \end{aligned}$$

The sulfides of copper were supposed to be Cu_2S , CuS , or CuS_2 . The maximum g-mole of H_2S needed is 2 g-moles per 1 g-mole of Cu for CuS_2 . That is equal to $2 \times 9.44 \times 10^{-6} \times 34.064$ or 6.4313×10^{-4} g or 53.59 ppb of H_2S in 12-liter electrolyte volume.

The amount of sulfide precipitate gained depended on the trace concentration of H_2S or sulfur compound in the beer stream.

Consider CuS, which consumed half of 53.59 ppb or 26.80 ppb of H₂S in 12-liter electrolyte volume.

Assumed that the rate of copper ion eliminated was 9.44×10^{-6} g-mole/hour

$$\begin{aligned}\text{The rate of CuS produced} &= 9.44 \times 10^{-6} \text{ g-mole/hour} \\ &= 9.44 \times (63.546 + 32.064) \times 10^{-6} \times 1000 = 0.9026 \text{ mg/hour}\end{aligned}$$

For 120 hours of operating time,

$$\begin{aligned}\text{CuS produced} &= 0.9026 \times 120 = 108.31 \text{ mg} \\ &= 108.31 \text{ mg} / 150 \text{ cm}^2 \text{ of cathode surface area}\end{aligned}$$

$$\text{CuS density [2]} = 4.6 \text{ g/cm}^3$$

$$\begin{aligned}\text{Then, CuS thickness} &= (108.31 \times 10^{-3} / 4.6) \text{ cm}^3 / 150 \text{ cm}^2 \\ &= (1.5697 \times 10^{-4} \text{ cm}) \times (10 \frac{\text{mm}}{\text{cm}}) \\ &= \mathbf{0.0016 \text{ mm}}\end{aligned}$$

The CuS calculated thickness on cathode surface was not high. However, the electrode fouling was caused from both sulfides and oxides.

Assumed that the maximum g-mole of the corrosion products occurred was approximately 100 times of CuS produced, therefore the scale thickness was approximately 0.16 mm or 0.2 mm.

$$[\text{Cu}] = 100 \times 50 = 5,000 \text{ ppb (ppm)}$$

Operating time of 120 hours was possible before electrode cleaning. However, the efficiency for the formation of oxides and sulfides of copper and iron was not 100%. That caused the amount of copper, which dissolved from anode, was higher than 50 ppb.

If the rate of anode copper dissolution was equal to the rates of formation of the oxide and sulfide scale on cathode, the copper ions should not be detected from an electrolyte.

6.4 The relation between the electrode surface and the cell current

For the copper electrodes in the electrolyte, the resistance of the electrolyte is defined as [7, 8]:

$$R = V / I \quad (\text{Ohm's law}) \dots\dots\dots (1)$$

$$R = L / \kappa A \quad \dots\dots\dots (2)$$

$$\begin{aligned}\text{Where, } V &= \text{Volts applied} \\ I &= \text{Cell current reading, amperes} \\ L &= \text{Average length of flow path or distance gap between both electrodes, cm.} \\ A &= \text{Copper electrode cross-sectional area, cm}^2 \\ \kappa &= \text{Conductivity of the electrolyte, ohm}^{-1}\text{cm}^{-1} \\ \kappa &= \Lambda c^* \quad \dots\dots\dots (3)\end{aligned}$$

$$\text{Where, } \Lambda = \text{Equivalent conductivity, ohm}^{-1}\text{cm}^2\text{eq}^{-1}$$

Let

$$\begin{aligned}
 c^* &= \text{Copper concentration in the electrolyte, equivalents cm}^{-3} \\
 x &= \text{g-moles or equivalents of copper dissolution to the electrolyte from anode} \\
 z &= \text{g-moles or equivalents of copper oxides and sulfides fouled on cathode surface} \\
 &= x \quad (\text{if rate of anode copper dissolution is equal to cathode oxides and sulfides formation}) \\
 c &= \text{g-moles or equivalents of copper in the electrolyte} \\
 &= x - z \quad (\text{If } z = 0, c = x) \quad \dots\dots\dots (4) \\
 y &= \text{g-moles or equivalents of theoretical copper dissolution} \\
 \text{If } \varepsilon &= \text{Cell current efficiency} = x / y \quad \dots\dots\dots (5) \\
 v &= \text{Total volume of electrolyte in the electrochemical cell, cu cm} \\
 \text{Then, } c^* &= c / v = (x - z) / v = (\varepsilon y - z) / v \quad \dots\dots\dots (6)
 \end{aligned}$$

Combination of (1), (2), (3), and (6),

$$\begin{aligned}
 V / I &= L / \kappa A = L / \Lambda c^* A \\
 &= L / [\Lambda A (\varepsilon y - z) / v] \\
 &= (L v / \Lambda A) / (\varepsilon y - z) \\
 (\varepsilon y - z) &= I (L v / \Lambda V A) \\
 z &= \varepsilon y - I (L v / \Lambda V A) \quad \dots\dots\dots (7.1) \\
 \text{or } z &= x - I (L v / \Lambda V A) \quad \dots\dots\dots (7.2) \\
 \text{or } c &= I (L v / \Lambda V A) \quad \dots\dots\dots (7.3)
 \end{aligned}$$

The distance gap (L), the electrolyte volume (v), the voltage applied (V), and the electrode surface area (A) are known. The cell current reading (I) and the copper concentration in the beer electrolyte (c) can be measured from the experiment runs. The equivalent conductivity (Λ) at each copper concentration in the beer electrolyte can be calculated from equation (7.3).

From the correlations of Eq. 6 and Eq. 7.3, the equivalent conductivity depends on the ion concentration in the electrolyte. The higher the concentration, the lower the equivalent conductivity.

Note: Some experiments might be performed to investigate the correlation between the equivalent conductivity and the copper ion concentration in the beer stream. The expected equivalent conductivity is supposed to input in equation (7.1) or (7.2) to calculate " z " or g-moles of oxides or sulfides of copper fouled on cathode surface.

Consider the voltage applied and the cell current reading (Eq. 4 and Eq. 7.3),

$$\begin{aligned}
 c &= I (L v / \Lambda V A) = (I / V) (L v / \Lambda A) \\
 \text{or } c &= x - z = (I / V) (L v / \Lambda A) = (1 / R) (L v / \Lambda A)
 \end{aligned}$$

The relations can be compared as the diagram in Figure 6.2 below.

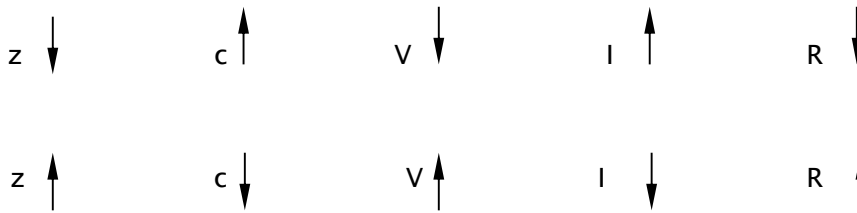


Figure 6.2 Comparison between various critical functions

The fouling (z) will be reduced with the reduced voltage (V) applied. The lower electrolyte resistance (R) will increase the cell ampere reading (I) and that causes more copper ions (c) in the beer electrolyte.

By conclusion, to reduce the copper ion concentration in the beer electrolyte means the fouling scale increases with the decreasing of the cell current. The voltage applied should be higher.

7. Conclusions

This corrosion research program was performed at Corrosion laboratory, MME Department, CSM, CO, USA, to investigate the electrochemistry of copper anode treatment of beer to capture trace amounts of sulfur.

Two electrolytes, water and beer, were provided by Coors Brewing Company. The data obtained was compared with the actual plant parameters of 25 volts and 1.4 amperes on an anode surface area of 260 cm². This Coors process, of year 2000–2001, was operated at 5–6 amps/cm² at an applied voltage of 25 V. The actual continuous beer flow rate was 4.75 l/sec (1.25 gallon/sec). The electrode gap of old prototype was ¾" but it was modified to 1.5" for the new prototype.

Two factors were departure from the actual process, which maintained 1.25 gallon/sec continuous high beer electrolyte flow rate. Both were; 1) The sulfide ion-bearing electrolyte was not applied to the simulated process; and 2) The flow condition of the electrolyte was restricted to the recirculation type only.

The effects of electrode separation and electrode surface area on the efficiency of copper dosing of the beer stream were evaluated from the experimental results.

Following conclusions were drawn from this work:

- a) Under static condition at room temperature;
 - The process was current limited at 0.5 amperes in the cell configuration used. This limiting current increased with flow of electrolyte and temperature (Table 3.2).
 - Local buildup of copper ions along the anode surface caused the precipitation of copper hydroxide at higher voltages as well as higher current density, i.e. fast rate of copper ion formation (Table 3.1 and Figure 3.5).

b) Under circulated condition at room temperature;

- The amount of copper ions added to the homogeneous recirculated beer, at a maximum process current of 0.15 amperes and 150 cm² anode areas, was 11–12 ppb per second. This was equivalent to 0.15–0.20 g of copper in one hour (Figure 5.6).
- In a flowing system, no buildup of local copper ion concentration to cause copper hydroxide precipitation.

c) Other investigation results;

- Under identical conditions of electrode separation, surface area and cell voltage, higher current was preferred to achieve in the beer than in the water due to higher electrical conductivity and lower pH of the electrolyte.
- The 60-minute duration experiments illustrated that over 95% current efficiency, the copper material balance was matched by anode weight loss and electrolyte ion concentration.
- At the calculated rate of copper dosing to the stream, no cathodic deposition of copper was expected.
- Formation of copper sulfide was a highly preferred reaction over copper hydroxide precipitation and sulfide formation was the most desired reaction for copper ions in the system.
- Electrode fouling was caused from both sulfides and oxides. From Figure 6.2, [Cu] or “c” decreased with decreasing cell current (I) and increasing voltage (V), which caused increasing of fouling scale (z).

d) Recommendations;

- Electrode gap of $\frac{3}{4}$ ” to 1” was optimum for high current efficiency (Figure 3.3). If possible, the electrode gap should be maintained at $\frac{3}{4}$ ” (figure 3.3 and Figure 3.4).
- Good electrolyte–electrode contact was desired in the flowing system to add the copper ions doses effectively for sulfur capture.
- The electrode surface area should be adjusted to achieve a minimum **current of 0.5 amperes**. At this current the copper dose was in the range of 35–40 ppb (Exp. Run # 3 Calculation of copper concentration). This range was the limited [Cu] in the beer stream for removing trace H₂S and other sulfur compounds.
- For the same electrode separation, the current density change was higher with the higher surface areas (Figure 3.4).
- The voltage should be adjusted to achieve the desired current, as well as lowering by decreasing the cell resistance.

8. Acknowledgements

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