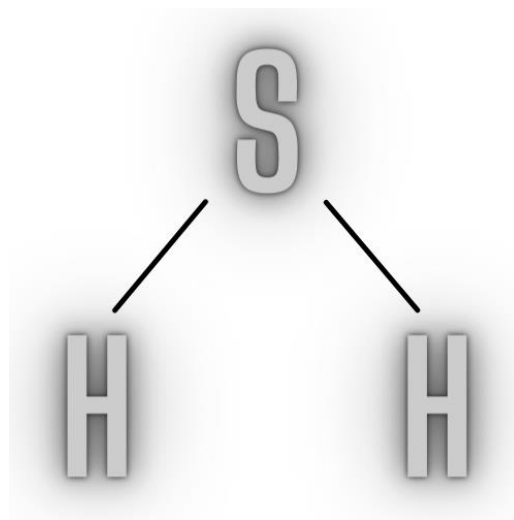


FMH606 Master's Thesis 2021

Process Technology

# Electrochemical Sulphide Oxidation – An Experimental Study



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**Summary:**

Hydrogen sulphide ( $H_2S$ ) is a problem that occurs everywhere in the industries. This has hazardous properties like high corrosive, hazardous when inhaling and high flammability. The gas is either produced naturally or as a by-product in the oil and gas industries.

Electrochemical oxidation was used for the electrochemical treatment of the hydrogen sulphide. This is a technique that requires small amount of energy to oxidise the pollutant. Hydrogen were oxidised to elemental sulphur and then to sulphate. The experiment was tested with different concentrations (300 ppm and 500 ppm) and different potentials (0.0 V, 0.3 V, 0.5 V and 0.7 V). The sulphide removal rate decreased as the potentials were increased and the current productions for the experiment increased in the beginning and started to stabilise towards the end of every experiment.

The oxidation process was studied and analysed using cyclic voltammetry as an electrochemical test. This technique demonstrates when the oxidation and the reduction of the species occurs. The anodic peaks for 300 ppm were  $E_{ox_1} = + 0.33$  V,  $E_{ox_2} = + 0.67$  V and  $E_{ox_3} = + 0.95$  V for the first cycle. The second and the third cycle were similar. In comparison to 500 ppm, one anodic peak was observed at  $E_{ox_1} = + 0.70$  V. The other cycles barely had any anodic peak but the cathodic peak for 300 ppm and 500 ppm were  $E_{red} = - 1.5$  V.

PBS was another test taken beside cyclic voltammetry to compare and study if any extra oxidation would happen or not. Both 300 ppm and 500 ppm had a tiny anodic peak at + 0.78 V for 300 ppm and + 0.22 V for 500 ppm.

# Preface

Writing the master's thesis has been both exciting, educational and challenging. It has given me the opportunity to immerse myself in the topic of electrochemical sulphide oxidation, but it has also been demanding for me to formulate such a large amount of written work in a relatively short time. Thus, I would also like to mention the tough situation among students in relation to the pandemic. In my case, it has affected the ability to concentrate, which led to the self-studying becoming challenging occasionally. Despite that, my friends, my family and fellow students have encouraged and supported me along the way, and I am very grateful for this.

I would like to thank my supervisor Carlos Dinamarca and co-supervisor Vibeke Bredvold Karlsen for giving me good professional advice and good guidance, and I really appreciate that both have always been available.

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Hudda Samir Abukar Muhidin

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# Nomenclature

Symbol	Description	SI units
$A$	Surface area of the electrodes	$cm^2$
$C^o$	Bulk concentration	$mol/cm^3$
$D^o$	Diffusion coefficient	$cm^2/s$
$E$	Potential of electrochemical cell	$mV$
$E^o$	Standard potential of a species	$mV$
$F$	Faraday's constant	—
$\Gamma^*$	Surface coverage of absorbed species	$mol/cm^2$
$i_p$	Peak current	$A$
$n$	Number of electrons that are transferred	—
$R$	Universal gas constant	$J/(K * mol)$
$T$	Temperature	$^{\circ}C$
$\nu$	Scan rate	$V/s$

# List of abbreviation

Abbreviations	Description
Ag	Silver
AgCl	Silver chloride
AOP	Advanced oxidation process
CV	Cyclic voltammetry
EAO	Electrochemical advanced oxidation
EO	Electrochemical oxidation
Fc	Ferrocene [Fe(Cp) <sub>2</sub> ]
Fc <sup>+</sup>	Ferrocenium [Fe(Cp) <sub>2</sub> ] <sup>+</sup>
HCl	Hydrogen chloride
H <sub>2</sub> S	Hydrogen sulphide
KH <sub>2</sub> PO <sub>4</sub>	Potassium dihydrogen phosphate
K <sub>2</sub> HPO <sub>4</sub>	Potassium hydrogen phosphate
NaOH	Sodium hydroxide
Na <sub>2</sub> S	Sodium sulphide
ORP	Oxidation reduction potential
PBS	Phosphate buffer solutions

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# 1 Introduction

## 1.1 Background

Hydrogen sulphide ( $\text{H}_2\text{S}$ ) or also known as hydrosulphuric acid, sewer gas and stink damp is a colourless gas with a strong rotten egg odour [1]. Inhaling hydrogen sulphide is hazardous, toxic and harm the human health.  $\text{H}_2\text{S}$  is produced naturally in natural gas, crude petroleum and volcanic gases. The gas can be produced and be a result of different causes like industrial activities at petroleum refineries or from bacterial breakdowns of organic matters [2].

Electrochemical treatment is a method that uses oxidation and reduction reactions to reduce the content of unwanted pollutants. This treatment contributes to a cleaner environment and is mostly used for wastewater [3]. The pollutants can be removed using electrochemical oxidation, electrochemical reduction and electrochemical advanced oxidation processes.

Cyclic voltammetry (CV) is a method that shows how a molecular species behaves in terms of oxidation and reduction reactions. This technique is useful and a great way of studying the oxidation and the reduction processes of the species [4]. Choosing the values for the parameters like scan rate, step size and potential limits are important. Thus, to capturing small oxidations happening in the CV is beneficial for this work.

There are several technologies that is developed to remove this gas and it has been existing for years. One of the known technologies to remove hydrogen sulphide is the electrochemical treatment.

## 1.2 Objective

The aim of this work is to investigate the behaviour of hydrogen sulphide in the reactor using electrolytic cell. Two different concentration has been done for this experiment and with different potentials, including zero potential to see if there are any oxidations.

To achieve the aim of this work, these following objectives are required to make it happen:

- Literature review on hydrogen sulphide and its characteristics including HMS evaluation before doing experiments.
- Literature review on electrochemical treatment.
- Literature review on cyclic voltammetry and PBS as the electrochemical test for this work.
- Experiment on the electrochemical reactor with two different concentrations (300ppm and 500 ppm) and four different potentials applied to the reactor (0 V, 0.3 V, 0.5 V and 0.7 V).
- Evaluate the sulphide oxidation over time, products formation and its distribution.
- Define the key parameters for the process and evaluate when changing one of the parameters.
- Evaluate the technical and economic feasibility of the systems.

### 1.3 Overview

This work is divided into four parts where each part is described in each chapter. Chapter 2 contains literature review on electrochemical treatment, characteristics of hydrogen sulphide and cyclic voltammetry. Chapter 3 contains electrochemical test, experimental setup for CV and electrochemical removal of hydrogen sulphide. The results of the experiments are described in chapter 4. The last part of the work is included in chapter 5 where the analysis and results from chapter 4 are discussed and presented.

## 2 Literature review

Chapter 2 is about the characteristics of hydrogen sulphide, the health effects and its HMS. This chapter includes overview of literature studies about cyclic voltammetry and electrochemical treatment.

### 2.1 Hydrogen sulphide

Hydrogen sulphide occurs everywhere as a gas and has a lot of hazardous characteristics. In industries this gas is produced as a by-product. However, it is dangerous in oil and gas reservoirs because of its highly corrosive property [5]. When H<sub>2</sub>S gets in contact with water, it would make the water become acidic, lower the pH and would make the carbon steel get exposed to corrosion [6]. The damages it brings is costly and can ruin pipelines etc [11].

#### 2.1.1 Characteristics

Hydrogen sulphide is a colourless gas that is heavier and denser than air. The gas would travel under the ground and stay in the areas where there is no exposure to oxygen. The places the gas would stay low and enclosed are the areas that are poorly ventilated such as sewer lines, manholes, manure pits etc [6]. Having hazardous properties, inhaling the gas would rapidly go to the human lungs and be absorbed quickly.

When the concentration of this gas is low, people would smell the rotten egg odour the gas has. However, at high concentration the people would lose the ability to smell the gas. Hydrogen sulphide has other properties like high flammability. It would produce sulphur dioxide when the gas is ignited and burns. Hydrogen sulphide can appear as a gas and as a liquid. Being in contact with a liquid hydrogen sulphide is hazardous because it can cause frostbite [6].

Table 2.1 gives an overview of the characteristics of the chemical.

Table 2.1: Physical and chemical characteristics of Hydrogen Sulphide [1] & [7]

<b>Molecular Formula</b>	H <sub>2</sub> S
<b>Molecular Weight</b>	34.08 g/mol
<b>Odour</b>	Rotten egg odour
<b>Boiling Point</b>	-60.2 °C
<b>Melting Point</b>	-85.49 °C
<b>Density</b>	1.1363g/L relative to air
<b>Viscosity</b>	0.0128 cP at 25 °C and 101.325 kPa

### 2.1.2 Health effects

The health effects of hydrogen sulphide exposure depend on how high the concentration is and how much the worker inhales the gas. When the concentration is low, several areas in the face would get irritated like the eyes, nose, and throat. As mentioned earlier in chapter 1, inhaling the gas can cause breathing difficulties as well as coughing and teary eyes. Workers or people with asthma would not be able to breathe properly and it can be dangerous. People would get headache, fatigue, weight loss and irritability [5] & [6].

When the concentration is moderate, the breathing difficulties would worsen. However, other symptoms would worsen and appear such as headaches, fatigue, dizziness, vomiting and more irritation in the eyes [6].

High concentration can cause more damage to the human health and even cause unconsciousness and death if the human is exposed and inhales the gas for a long period of time [5].

### 2.1.3 Health precautions when exposed to H<sub>2</sub>S

Working around a hazardous chemical is dangerous and with a gas like hydrogen sulphide, there are some precautions that must be taken [6]:

- 1) The concentration of hydrogen sulphide should be less than 100 ppm, and if it is above then working under ventilation hood constantly.
- 2) The ventilation must be working all the time when the gas is presented. When working with the gas in a laboratory, it must not be exposed to oxygen as it can oxidise rapidly to thiosulphate.
- 3) If the gas is difficult to remove from the area then respiratory protection or any protection equipment should be used.
- 4) All waste containing high amount of hydrogen sulphide should not be disposed in the sink but in a waste disposal container.

## 2.2 Electrochemical treatment

Electrochemical treatment is an effective technique that removes toxic pollutants from wastewater. This treatment is a better technique for the environment and removing pollutants because there is a low risk happening when transporting or dosing of chemicals. They also offer a robust removal of this chemical in situ, meaning that everything happens in its original place [3].

There are different types of electrochemical treatments:

- 1) Electrochemical oxidation
- 2) Electrochemical reduction
- 3) Electrochemical advanced oxidation

### 2.2.1 Electrochemical oxidation

Electrochemical oxidation is a great technique of oxidizing pollutants from organic to inorganic compounds like water and carbon dioxide. This process requires a small amount of energy to activate the electrodes [8].

### 2.2.2 Electrochemical reduction

Electrochemical reduction is the opposite of EO, where the greenhouse gases are reduced to chemicals that are useful using electrical energy. This technique is common to use by reducing carbon dioxide to formic acid [9].

### 2.2.3 Electrochemical advanced oxidation

Electrochemical advanced oxidation, also known as EAO or AOP for advanced oxidation process uses an oxidation agent like hydroxyl radical ( $\cdot\text{OH}$ ) and generates in situ in a reaction medium [10].

## 2.3 Cyclic Voltammetry

Cyclic voltammetry (CV) is a unique electrochemical technique used for investigating the redox behaviour of different molecular species. This technique is popular and powerful because of the way the oxidations and the reductions processes are studied. Cyclic voltammetry can also be used to study how the electrons behave and move when they are transferred in chemical reactions including catalysis. The changes in potentials happen step wise with a constant scan rate from an outer limit to another along the x-axis. The changes in the current is observed along the y-axis [4].

There are two ways to present CV graphs; the US convention and the IUPAC convention. The main difference between these conventions is the units. In addition, the x-axis of the US convention moves from high potentials to low potentials. Figure 2-1 shows the US convention having the upper part of the graph as the reduction. For the IUPAC convention, it is the opposite of the US convention. The direction of the potentials goes from the lowest to the highest and oxidation being the top peak of the graph. Both conventions are common to use to find when the oxidations and the reductions happen for the molecular species.

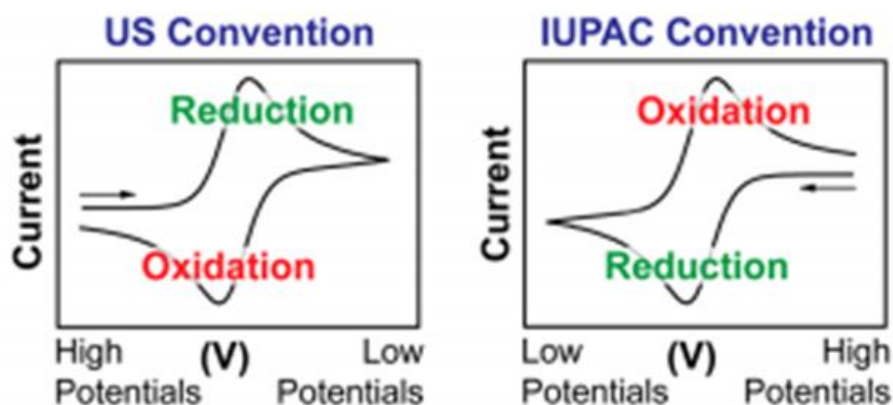


Figure 2-1 US Convention vs. IUPAC Convention [4]

In Figure 2-1, the main difference between both is how the trace is moving. In the US convention graph the trace starts moving negatively from the starting point to the switching point on the other side of the graph. This negative potential direction is called the cathodic trace. When the trace starts going back to the starting point, the direction of the potential is positive, and it's called the anodic trace. For the IUPAC convention graph, this is the opposite where it starts with an anodic trace and goes back with a cathodic trace [4].

### 2.3.1 The Nernst Equation

The Nernst equation is used to see how a system will behave when the concentration of the species or the electrode potential is changed. In addition to this, the equilibrium between the oxidation and the reduction reactions of the species are described by this equation. This equation is defined as [4].

$$E = E^0 + \frac{RT}{nF} \ln \frac{(Ox)}{(Red)} = E^0 + 2.3026 \frac{RT}{nF} \log_{10} \frac{(Ox)}{(Red)} \quad (2.1)$$

Where,  $E^0$  is the standard potential of a species

$F$  is the Faraday's constant

$n$  is the number of electrons that are transferred

$R$  is the universal gas constant

$T$  is the temperature

Although the Nernst equation shows how the system is behaving, it also predicts when a species will reduce. Using Figure 2-2 as an example, the Nernst equation would predict that the  $Fc^+$  would be reduced to  $Fc$  and the equilibrium being achieved. According to this equation, the concentrations of the species near the electrodes would change when a certain amount of time has passed. Each CV graph has a different shape depending on the electrode material. However, there are some factors involved that is dependent on this [4]:

- The concentrations of the  $Fc$  and the  $Fc^+$
- The distance from the surface to the electrodes
- The potential that is being applied to the system
- The movement of the species between the electrode surface and the bulk solution

These factors can influence how the graph would look by applying more potential, higher concentration and vice versa. If the concentration is low but the potential is high, then it would take less time until the oxidation peak would show on the graph. However, if the concentration were higher and same potential applied to the system, it would take more time to notice the oxidation peaks on the graph.

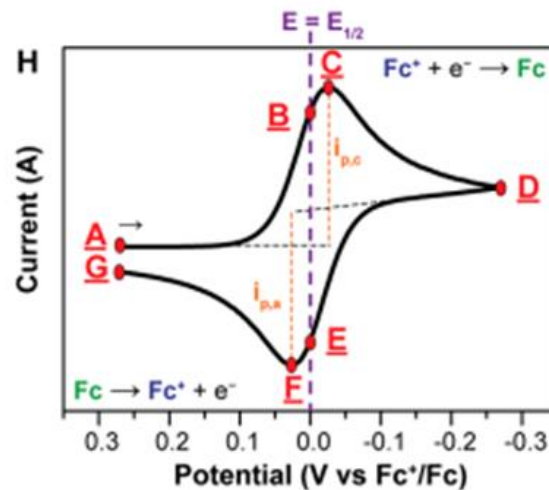


Figure 2-2 US Convention Graph for  $\text{Fc}^+/\text{Fc}$  [4]

From point A to point D, the potentials are moved in a negative direction (also called cathodically) where  $\text{Fc}^+$  is reduced to  $\text{Fc}$ . On the top peak at point C, the current is called the cathodic current ( $i_{p,c}$ ) because that's where the extra  $\text{Fc}^+$  is delivered from the bulk solution with the help of diffusion. From point C to D, the current would start decreasing slowly because of the diffusion layer would grow around the surface of the electrodes. This is because the remains of the  $\text{Fc}$  are still there and the diffusion rate of  $\text{Fc}^+$  would become slower. At point D, the switching potential would be reached, and the direction of the scan would reverse to a positive direction. The positive reversing direction is also called the anodic direction and the  $\text{Fc}$  concentration would start increasing as it would satisfy the Nernst equation. When the oxidation of the  $\text{Fc}$  to  $\text{Fc}^+$  happens, the potential would start growing more positively. Point B and point E is where the concentrations of the  $\text{Fc}$  and  $\text{Fc}^+$  would be at equilibrium. Meanwhile point C and F would be the two peaks that contributes to estimating the  $E^{0'}$  which is the formal potential [4].

### 2.3.2 Scan Rate – $\nu$

A crucial parameter in cyclic voltammetry is the scan rate. The scan rate controls how fast the potentials applied is scanned. In electrochemical processes, the Randles-Sevcik equation is used to describe and show how dependent the peak current is of the scan rate. The equation describes how the peak current is proportional to the square root of the scan rate. The Randles-Sevcik equation is defined as [4]:

$$i_p = 0.446nFAC^0 \left( \frac{nF\nu D^0}{RT} \right)^{1/2} \quad (2.2)$$

Where,  $i_p$  is the peak current [A]

$\nu$  is the scan rate [V/s]

$n$  is the number of electrons that are transferred

$A$  is the surface area of the electrodes [ $\text{cm}^2$ ]

$D^0$  is the diffusion coefficient [ $\text{cm}^2/\text{s}$ ]

$C^0$  is the bulk concentration [ $\text{mol}/\text{cm}^3$ ]



## 2 Literature review

If the equation is applicable to the process then the process is controlled by the diffusion. However, if the peak current is proportional to the scan rate linearly, then the process is controlled by adsorption. This equation indicates whether the analyte is diffused freely in the solution or absorbed on the electrode. The analyte tends to sometimes absorb on the surface of the electrode. It is important to get the access of knowing if the analyte is and has the same reactivity when it is analysed. To observe the current behaviour of an absorbed analyte, it is described as [4]:

$$i_p = \frac{n^2 F^2}{4RT} \nu \Gamma^* \quad (2.3)$$

Where,  $\Gamma^*$  is the surface coverage of the absorbed species [mol/cm<sup>2</sup>]

## 3 Materials and methods

### 3.1 Experimental setup

The experimental setup consists of a 1.5 L glass reactor connected to a potentiostat (Gamry Interface 1010E). The electrodes consist of a plastic frame around carbon steel material (Alfa Aesar, Fischer GmbH in Germany) with Titanium wires. Three wires are waved in and out of the material throughout the whole electrode for the anode and the cathode. The wires are made of Titanium, grade 5 with the diameter of 1 mm. The active size of the electrodes is 12 cm x 3 cm x 0.318 cm. When the plastic frame on the sides are included, the total size of the electrodes is 12.5 cm x 3.7 cm x 0.318 cm. The anode potential is controlled in reference to an Ag/AgCl electrode. The Ag/AgCl electrodes have a standard potential at 0.199 mV. The reactor is connected to a pump and to a water bath to keep the temperature on the reactor constant.

### 3.2 Experimental routine

Before the experiment starts, it is made sure that the water bath is filled with water almost all the way up. The temperature is set to 38.5 degrees Celcius because of the heat loss from the water bath to the reactor. A 3 L Erlenmeyer flask is filled with 1.25 L of distilled water. The water filled Erlenmeyer flask is placed on top of a mixer and is mixed constantly while the chemicals are being measured.

For the 300 ppm H<sub>2</sub>S experiment, 24.86 g K<sub>2</sub>HPO<sub>4</sub> and 0.993 g KH<sub>2</sub>PO<sub>4</sub> had been added to the water along with 0.25 L of distilled water. Once the buffer mixture is solved and mixed well, the pH was measured and few drops of NaOH were added into the buffer mixture to get the pH to 8.5. After getting the pH to 8.5, 300 mL of that buffer mixture was poured onto a 300 mL Erlenmeyer flask. For the 300 ppm, 3.9 g of Na<sub>2</sub>S has been mixed and solved with the 300 ml buffer mixture. Table 3-1 shows an overview of how much chemical was used for different concentrations and pH level.

Table 3-1 Overview of chemicals used for different concentrations

Concentration	300 ppm	500 ppm
Na <sub>2</sub> S	3.9 g	11.5 g
K <sub>2</sub> HPO <sub>4</sub>	24.86 g	4.08 g
KH <sub>2</sub> PO <sub>4</sub>	0.993 g	20.91 g
NaOH for 300 ppm   HCl for 500 ppm	Few drops until pH level is reached	6 mL
pH level	Approximately 8.5	Between 10 and 11

### 3 Materials and methods

For the 500 ppm, instead of getting the pH to 8.5 with the help of NaOH, 6 mL of hydrochloride acid also known as HCl was added. The reason was to have the pH level between 10-11 and never above 11. The buffer mixture would be well mixed with HCl before adding Na<sub>2</sub>S to the reactor.

This mixture was covered with a laboratory film to make sure no oxidation happened, and no gas was leaking out. The reactor was sealed tightly with a laboratory film to ensure that nothing will be leaking during the experiment. The buffer mixture and the mixture containing the Na<sub>2</sub>S were poured into the reactor and the mixer was set to 430 rpm. The potentiostat was connected to the reference electrodes and the pump was turned on with the setting at 110 rpm. The last step before starting the potentiostat was to connect the ORP and pH measure instrument and had it turned on.

The potentiostat is run by a program called Gamry Instruments Framework. When opening the program and everything was set to correct values, the first sample was taken out from the reactor before starting the experiment. The program was running for 4.5 hours and after every 45 minutes a sample was taken out from the reactor. When the sample is taken out, the mixture for both concentrations 300 ppm and 500 ppm were diluted. In Table 3-2, sulphide (S<sup>2-</sup>) and sulphate (SO<sub>4</sub><sup>2-</sup>) were diluted differently depending on which concentration was used.

Table 3-2 Dilutions for sulphide and sulphate at different concentrations

Concentration	300 ppm	500 ppm
Dilution for Sulphide	2 mL : 500 mL	2 mL : 1000 mL
Dilution for Sulphate	5 mL : 20 mL	5 mL : 50 mL

When the dilutions for sulphide and sulphate were done, 5 mL were taken out from each volumetric flask. For analysing the sulphide content, 5 mL was taken out from the 500 mL volumetric flask and the procedure for how to analyse this was followed. For the sulphate, the process was similar but this time it had to sit for approximately 2 minutes before analysing it. The dilution process was different for 500 ppm as shown in Table 3-2 but the analysing of the sulphide and sulphate was the same. A spectrometer was used to analyse these components. Three parallels were taken for the sulphide and two parallels for the sulphate. This process was done 7 times and the ORPs after every 45 minutes were noted. After the experiment was done, the file was created as a DTA-file and all the data were imported to the excel to make graphs.

## 3.3 Electrochemical test

### 3.3.1 Cyclic voltammetry

In this work, cyclic voltammetry was conducted to observe the redox behaviour of the molecular species and to select anode potentials for the potentiostatic experiments. Two

### 3 Materials and methods

different concentrations were used for the CV to study if there are any major or minor differences when the concentration is increased. The parameters that has been used for the CVs are shown in Table 3-3. The step size was chosen to gather as much information as possible between every step. The smaller the step size is the more would the chances be to see every small oxidation happening. The scan rate was chosen because in literature they would either use 5 mV/s or 10 mV/s [3] & [12]. Same reason for the potential range, and to capture the complete cycles in the graph.

Table 3-3 Parameters used for the cyclic voltammetry tests

Concentration of the buffer solution	300 ppm	500 ppm
Scan rate (v)	5 mV/s	5 mV/s
Number of cycles	3	3
Step size	2 mV	2 mV
Potential range	From – 1.5 V to + 1.5 V	From – 1.5 V to + 1.5 V

#### 3.3.2 PBS

PBS was conducted to observe any oxidation or reduction happening using only buffer solutions. The preparation and the experimental routine for the PBS test was the same as the CV and the other experiments except no other chemicals were used. The buffer solutions were prepared differently for both concentrations and Table 3-4 shows an overview of how much of each chemical were used for the buffer solution at different concentrations.

Table 3-4 Overview of chemicals used for the buffer mixture

Concentration	300 ppm	500 ppm
K <sub>2</sub> HPO <sub>4</sub>	24.86 g	4.08 g
KH <sub>2</sub> PO <sub>4</sub>	0.993 g	20.91 g

## 4 Results and discussion

Chapter 4 contains results from the electrochemical sulphide oxidation experiment at two concentrations (300 ppm and 500 ppm) and three different potentials including running the potentiostat with no potential. Two parallels were done for each concentration and comparison between them are presented in Chapter 4.3 and 4.6. The results from first and second parallel for 300 ppm are presented and analysed in Chapter 4.1 and 4.2, and the same for 500 ppm in Chapter 4.4 and 4.5. Cyclic voltammetry is the electrochemical test for this work and the results from the CV at different concentrations are presented, analysed and discussed in Chapter 4.7.1 and 4.7.2.

### 4.1 First parallel for 300 ppm

Figure 4-1 and Figure 4-2 are analysed to see how sulphide has been oxidised to sulphate in 4.5 hours for different potentials. Barely any oxidation was happening when no potential was applied. The sulphide concentration decreased from 200.83 mg/L to 185.83 mg/L. When the potential 0.3 V was applied, the concentration was decreasing slowly yet efficiently. Generally, the sulphide concentration would decrease as the potentials were increasing. With higher potential, the sulphide would oxidise to sulphate, sulphite etc. The concentration for sulphide was decreasing from 204.17 mg/L to 145 mg/L when the potential was 0.3 V. Looking at this graph the oxidation at 0.5 V decreased more than 0.7 V.

The reason for this could be the electrodes had to be replaced with a new one. Another reason could be the reactor being exposed to oxygen during the experiment. When the  $\text{H}_2\text{S}$  mixture in the reactor is exposed to oxygen, it would react and oxidise rapidly. For the 0.5 V, the concentration decreased from 212.5 mg/L to 98.33 mg/L. The potential at 0.7 V didn't decrease as expected and went from 196.67 mg/L to 145.83 mg/L.

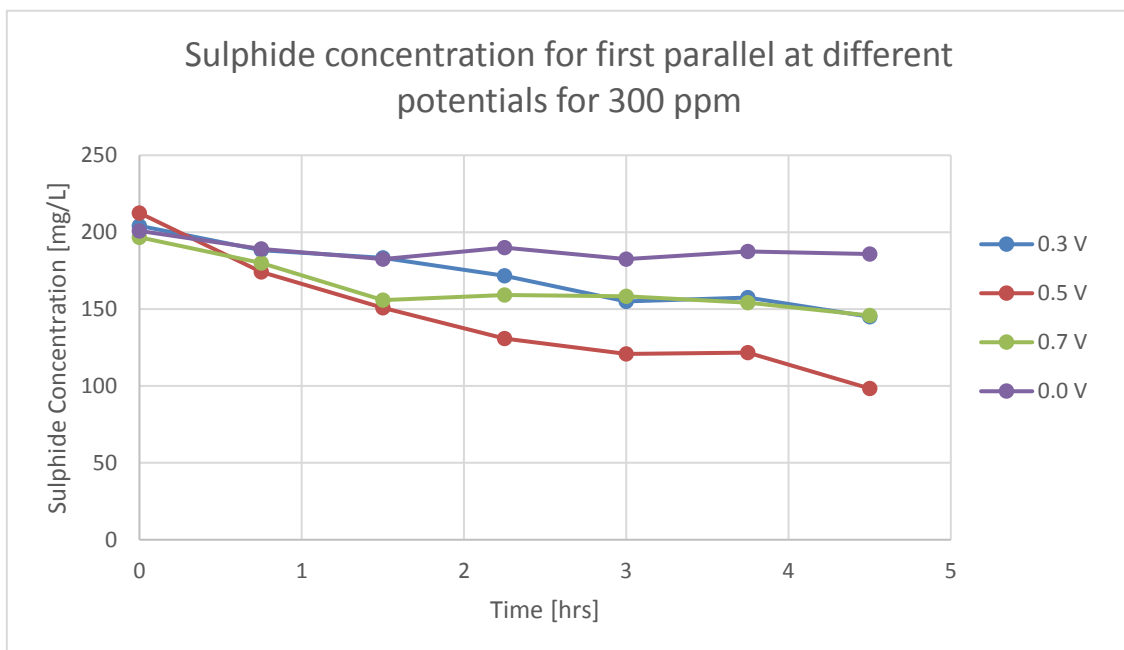


Figure 4-1 Sulphide concentration for first parallel at different potentials for 300 ppm

## 4 Results and discussion

For the sulphate, the biggest challenge to get the accurate concentration is to measure the concentration after approximately two minutes. The reason for this is because after the two minutes, the sulphate would oxidise rapidly. In addition, it is easy to analyse and observe when it has passed two minutes. For all the potentials, the sulphate concentration was increasing except for the last part at the potential 0.3 V and no added potential. As mentioned earlier the main reason is when the measurement in the spectrometer were taken. Another reason can also be when preparing the sulphate test, the powdered chemical added could've been less added compared to the other tests taken. When the potential is increasing, the oxidation to sulphate should happen quicker and the concentration would increase as well.

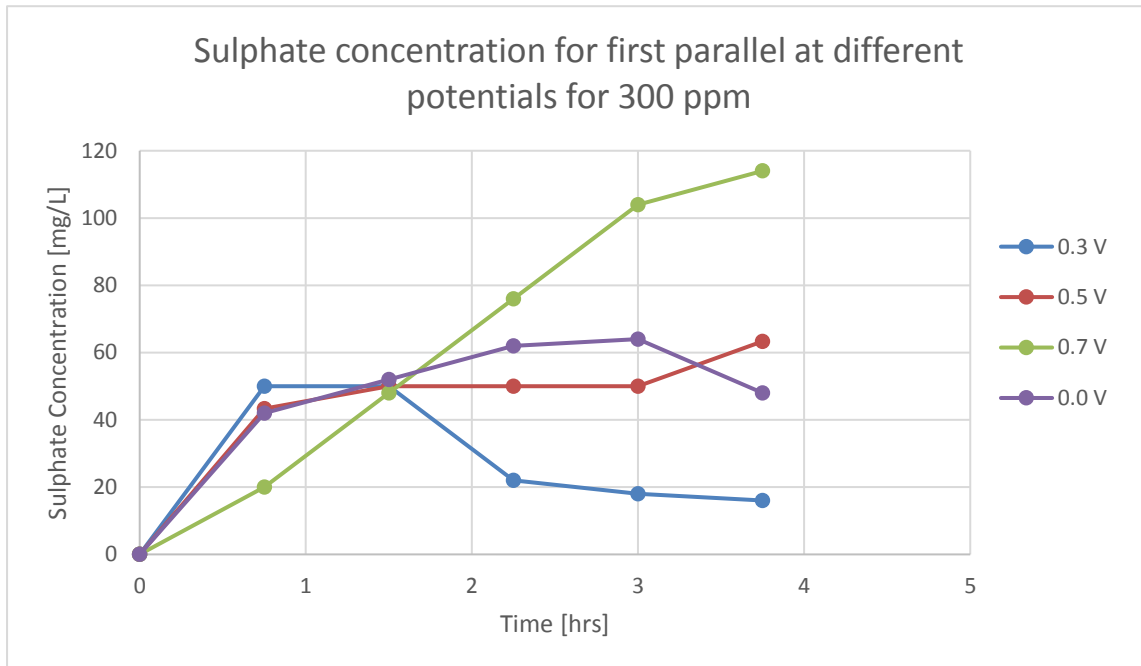


Figure 4-2 Sulphate concentration for first parallel at different potentials for 300 ppm

All the sulphate tests were taken at  $t = 0.75$  hrs because no sulphate was produced in the beginning of the experiment. The concentration at 0.0 V would go from 0 mg/L to 48 mg/L while the concentration for 0.3 V went from 0 mg/L to 16 mg/L. Another reason of why the results have major differences is because the dilution in the beginning for the sulphate was 5 mL : 50 mL but quickly changed to 5 mL : 20 mL. The change of the dilution is simply because when the spectrometer was measuring the concentration, it was outside the limit and the result would be negative. For the 0.5 V, the concentration went from 0 mg/L to 63.3 mg/L and 0 mg/L to 114 mg/L for the potential at 0.7 V.

The current production for all the potentials in Figure 4-3 would start with a low current and then increase before it stabilises. All the peaks in the graphs are when the samples from the reactor were taken out. With the experiment being sensitive to every touch on the reactor or the wires, the peaks would appear on the graph. The potential at 0.5 V had much higher current production than 0.3 V and 0.7 V. This can be because of exposure to oxygen, the necessity of changing the electrode material.

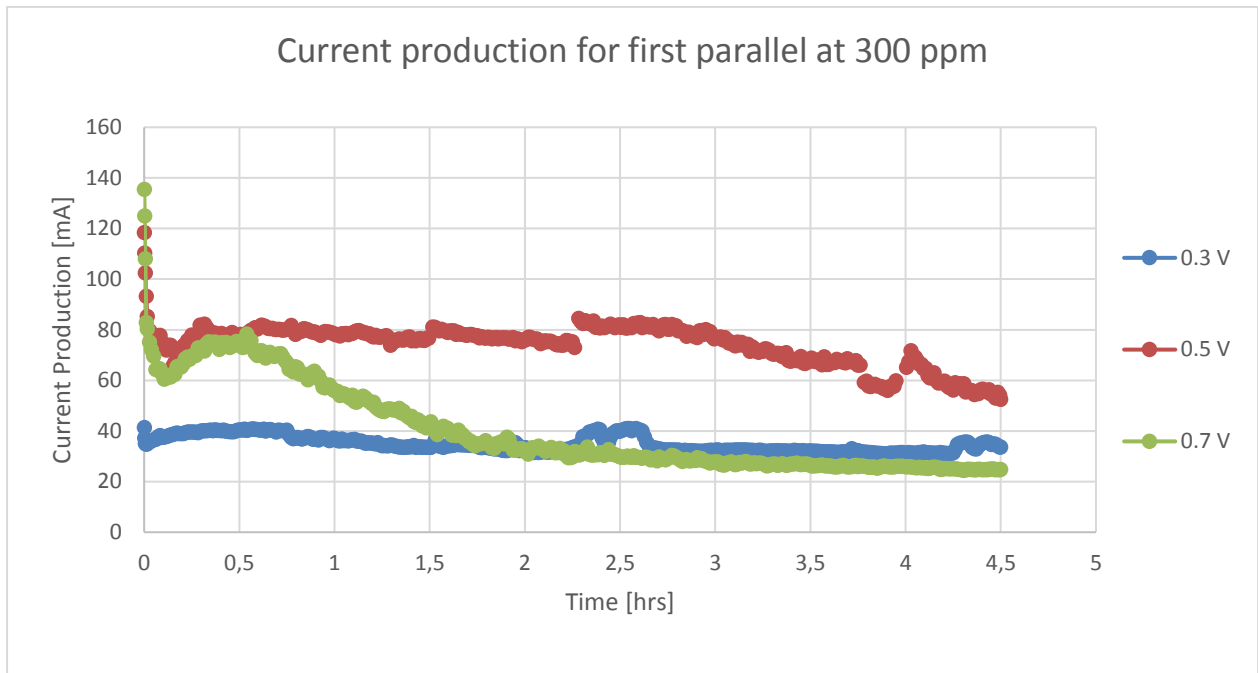


Figure 4-3 Current production for first parallel at 300 ppm

## 4.2 Second parallel for 300 ppm

A second parallel were taken for this experiment and this is to analyse and compare with the first parallel. In this experiment the decreasing of the sulphide concentration were slow. There wasn't a lot of decreasing happening for the potential at 0.5 V as shown in Figure 4-4. The zero potential experiment was done once, and it was assumed that it would be around the same area if it was one twice. The other potentials (0.3 V and 0.7 V) except for 0.5 V were decreasing efficiently.

The reason for this could be the same as for the first parallel. The electrodes had to be replaced with a new one. Another reason could be the potentiostat had to be replaced with a new one. During the first parallel, problems started to occur as the potentiostat were running. A newer model of this potentiostat was used during this experiment, which may be the cause of this standing out more than the other potentials.

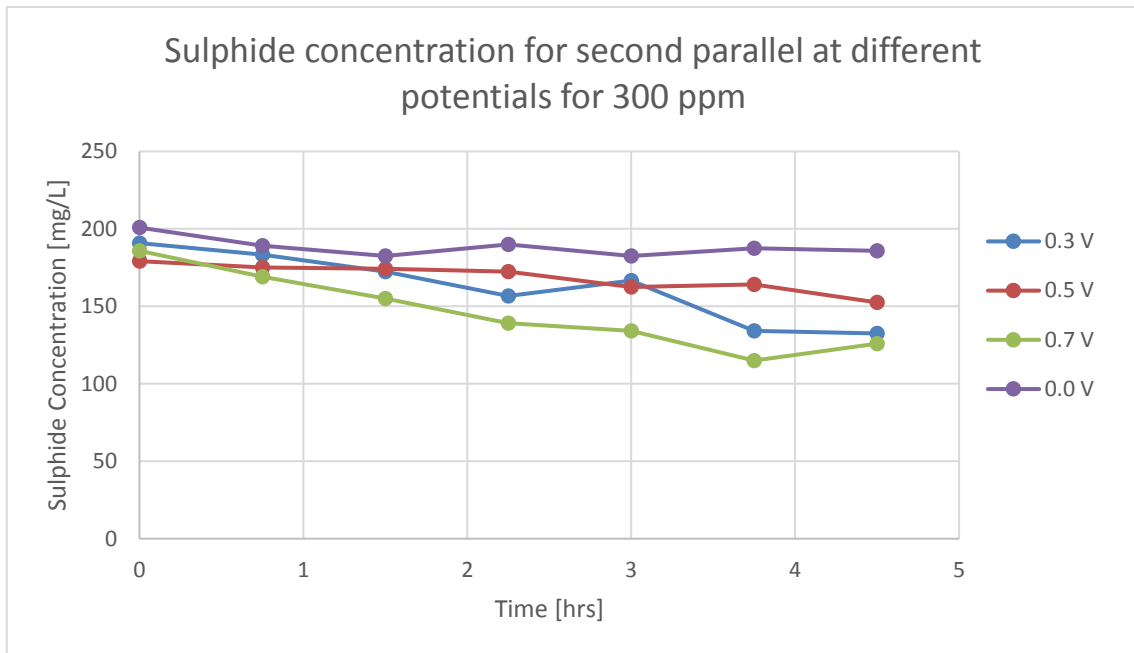


Figure 4-4 Sulphide concentration for second parallel at different potentials for 300 ppm

For the concentrations of sulphate in Figure 4-5, the results from zero potential is the same as the first parallel. All the concentrations are increasing for all potentials as expected. The only issue here is the production of sulphate for 0.5 V was not higher than 0.3 V and the reason is the same as mentioned above. For 0.3 V, the last test was taken and measured at  $t = 3.75$  hrs compared to 0.5 V and 0.7 V. When the new potentiostat was replaced, it was decided to measure the concentration at  $t = 4.5$  hrs.

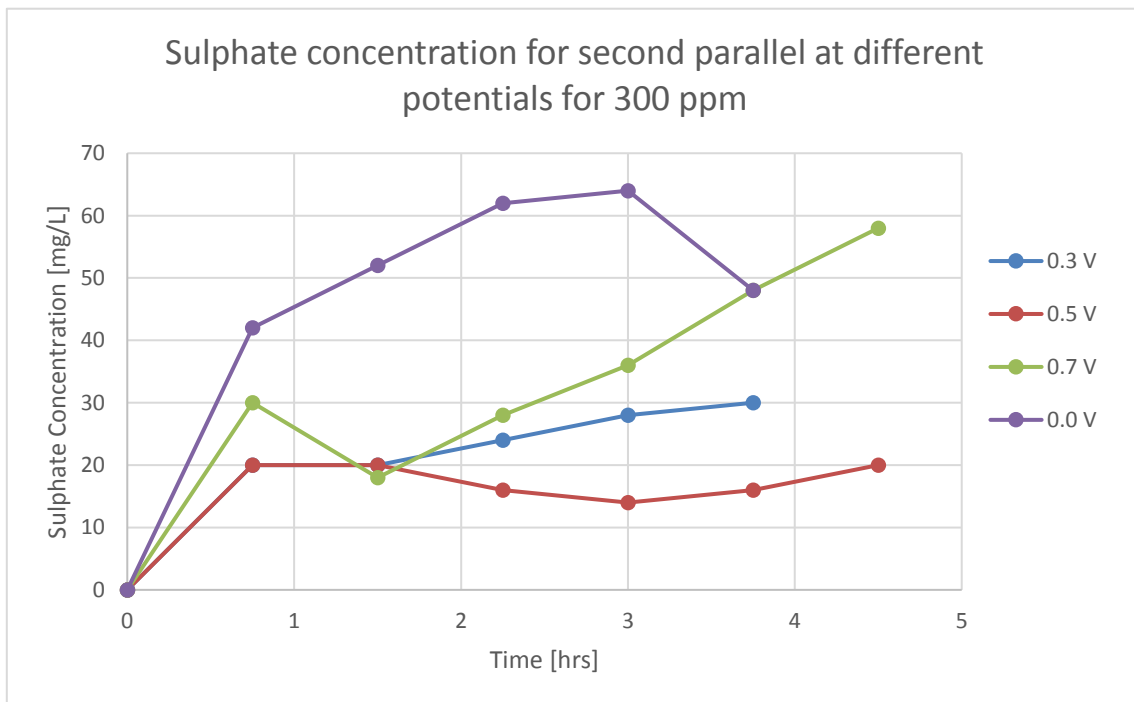


Figure 4-5 Sulphate concentration for second parallel at different potentials for 300 ppm



## 4 Results and discussion

In Figure 4-6, the current production here for 0.5 V has been stable and low during the experiment. As mentioned earlier, this may be because of the new potentiostat. The other potentials have higher current production and it took time before the production started to stabilise.

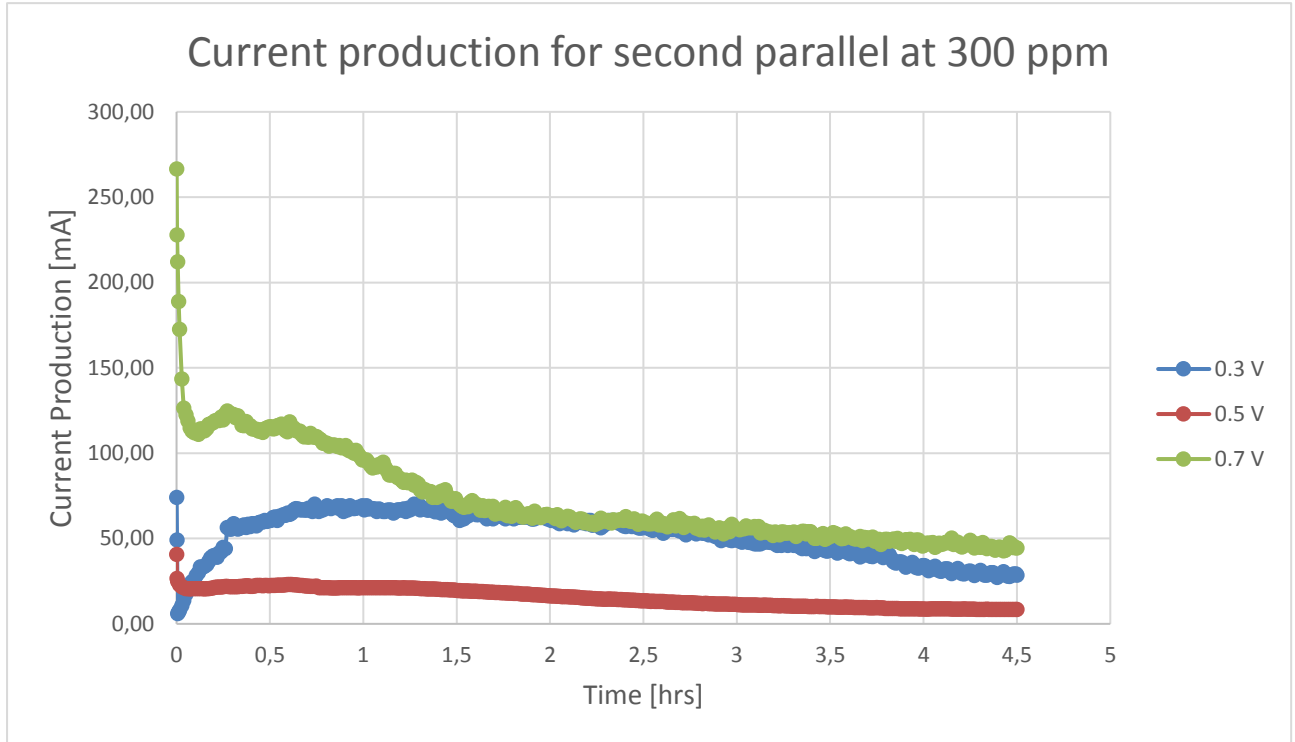


Figure 4-6 Current production for second parallel at 300 ppm

### 4.3 Comparison for 300 ppm

All the figures from chapter 4.1 and 4.2 were analysed and both parallels had similar results when the potentials were increased. The minor differences between the results were because of the replacement of the potentiostat. There was also replacement of the electrodes that may have affected the results from the figures in chapter 4.1 and 4.2. The current production was much lower during the second parallel compared to the first parallel. The major difference for the current production were for the potential 0.5 V.

### 4.4 First parallel for 500 ppm

At higher concentration the removal of sulphide would be a bit challenging depending on two parameters: the potential applied to the system and the time period. The potentials for obtaining promising results must be higher than 0.7 V. The reason is when the concentration is high the molecules expects more high potential so the oxidation can happen. This has been noticed on chapter 4.1 and 4.3.

In Figure 4-7, the sulphide concentrations are constant but decreasing very slow. This applies to all the potentials. The concentrations for no potential added were used for this chapter and

## 4 Results and discussion

chapter 4.5. The 0.5 V concentrations were higher than the concentrations for 0.3 V and 0.7 V.

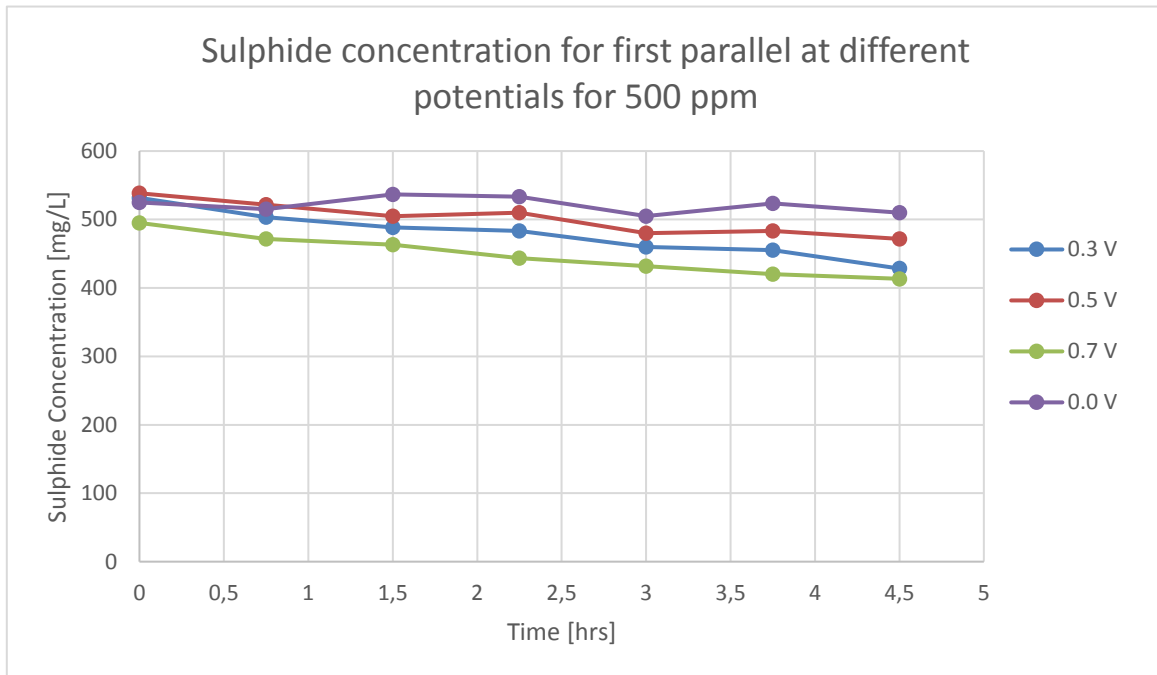


Figure 4-7 Sulphide concentration for first parallel at different potentials for 500 ppm

As for the sulphate concentration, all the potentials were increasing as expected except for 0.7 V. The sulphate concentration was supposed to increase and not the opposite because more potential was applied. There can be two reasons for this. One reason can be the sulphate sat less than two minutes or the second reason could be the dilution not being exactly 5 mL : 50 mL.

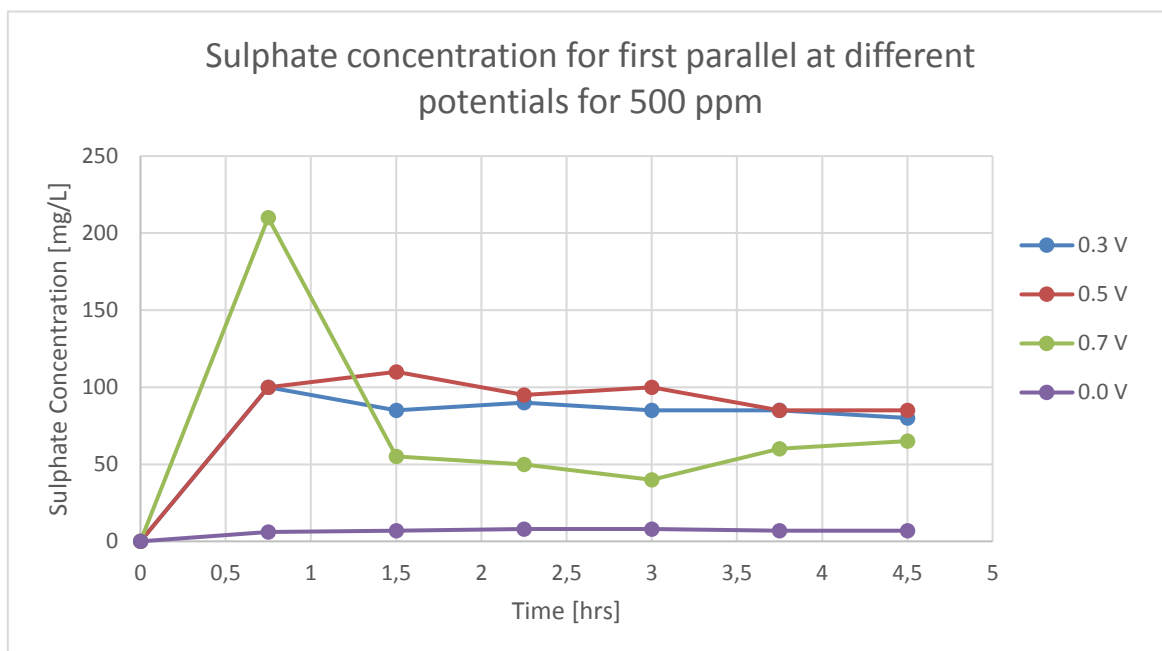


Figure 4-8 Sulphate concentration for first parallel at different potentials for 500 ppm

## 4 Results and discussion

In Figure 4-9, the current production for 0.7 V is lower than 0.3 V and 0.7 V during the experiment. This figure also shows three different points in the x-axis with the current production decreasing rapidly. These points were when the sample were taken out and when the wires were moved by accident. All the potentials after the decreasing points started to stabilise.

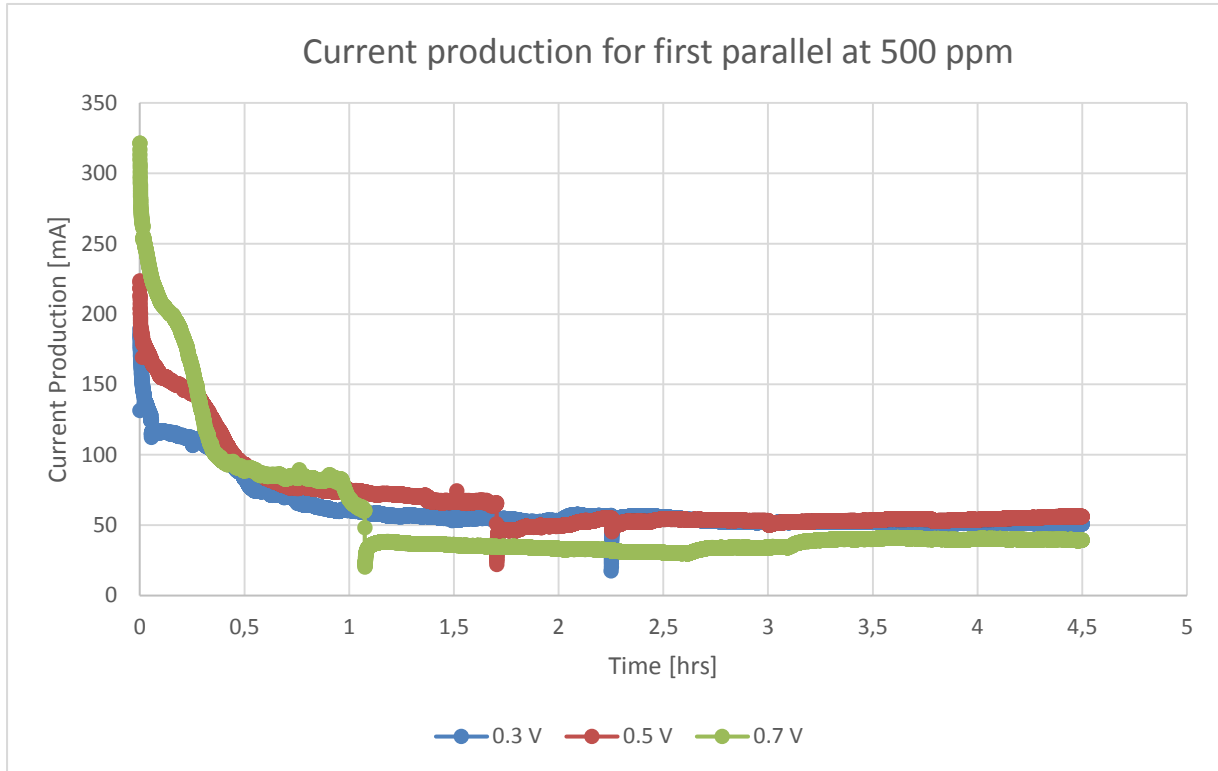


Figure 4-9 Current production for first parallel at 500 ppm

### 4.5 Second parallel for 500 ppm

Second parallel were done for this experiment to compare the results from the first parallel. The results from removing the sulphide in Figure 4-10 has been similar for all the potentials. The difference from the start concentration to the end concentration for each potential is approximately 100 mg/L. For potential 0.7 V, the concentration is decreasing more than the other potentials as expected. As for 0.5 V, the removal rate has been almost constant and stable throughout the experiment.

## 4 Results and discussion

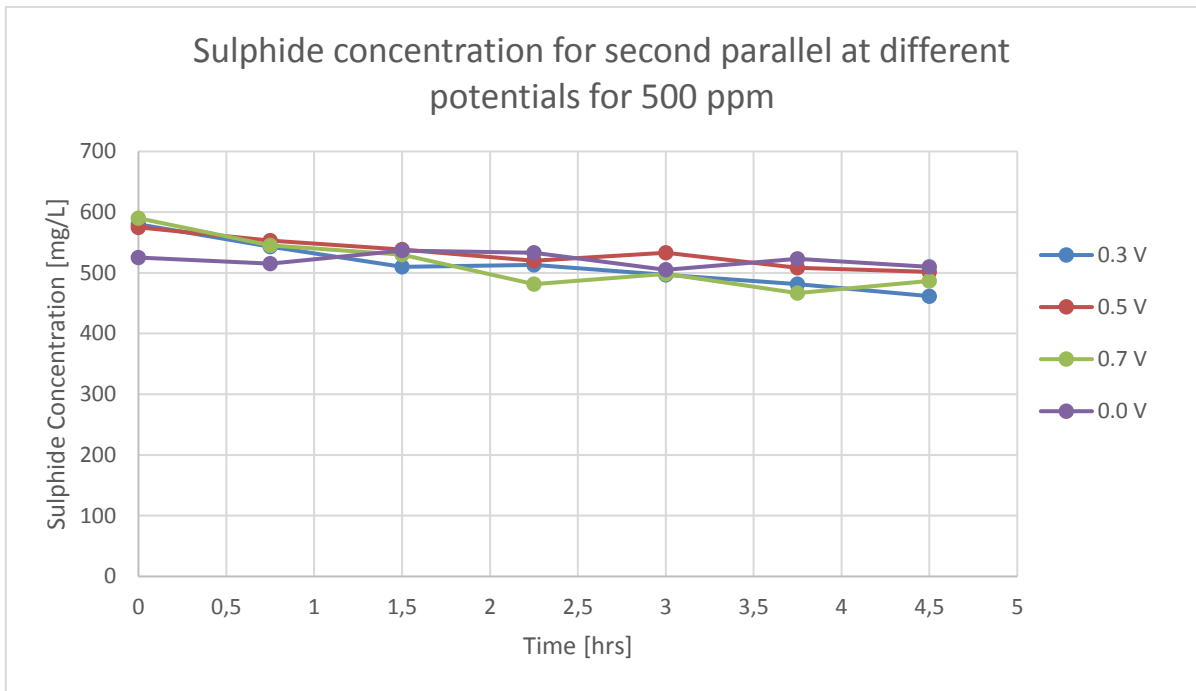


Figure 4-10 Sulphide concentration for second parallel at different potentials for 500 ppm

The sulphate rate in Figure 4-11 would increase as the potentials were increasing except for 0.5 V. However, the rate was increasing for 0.5 V and 0.7 V, but both had lower concentration rate than 0.3 V. This could be because of the oxidation process during the two minutes it has been sitting before it gets measured. The results from zero potential is the same as the one from Figure 4-8 because this was done once and not twice.

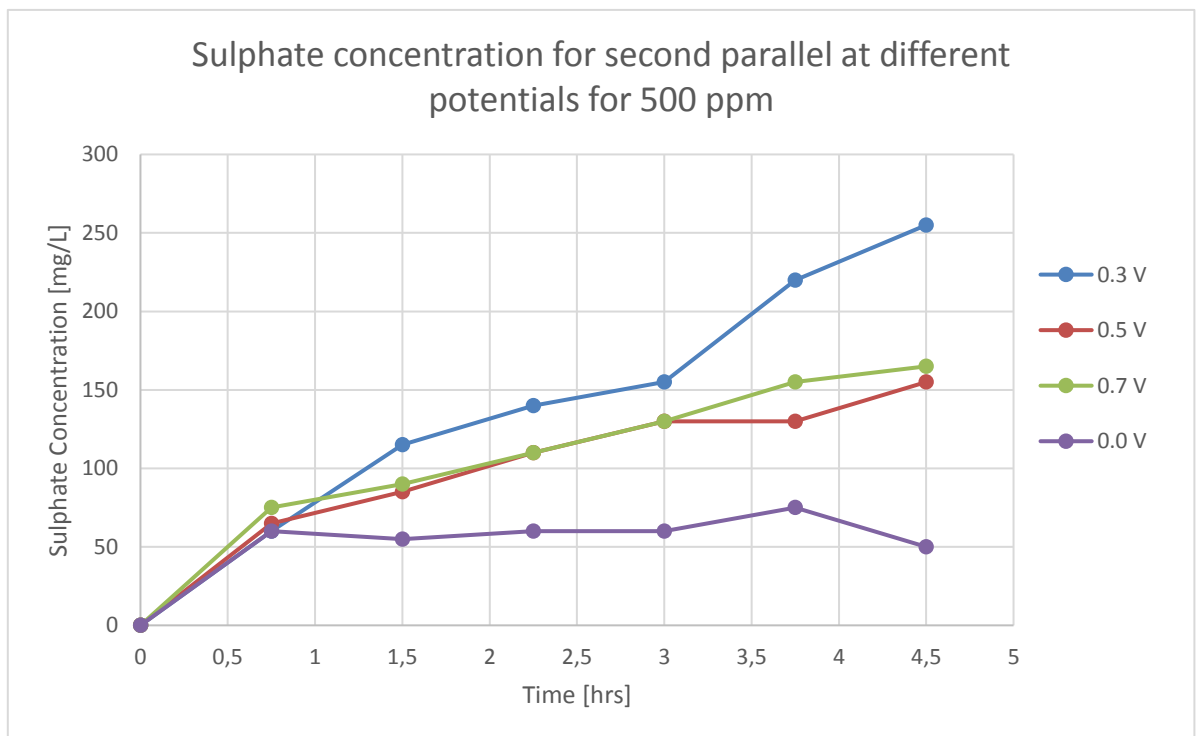


Figure 4-11 Sulphate concentration for second parallel at different potentials for 500 ppm

## 4 Results and discussion

The current production in Figure 4-12, all the current starts to stabilise earlier. The current production for 0.7 V started at 231 mV but decreased to 69 mV while 0.3 V started at 159 mV and decreased to 100 mV. The production for 0.3 V was more stable compared to 0.7 V and 0.5 V. This graph had one decreasing point and one low point in the x-axis. This can be concluded with the same reason as mentioned in chapter 4.4.

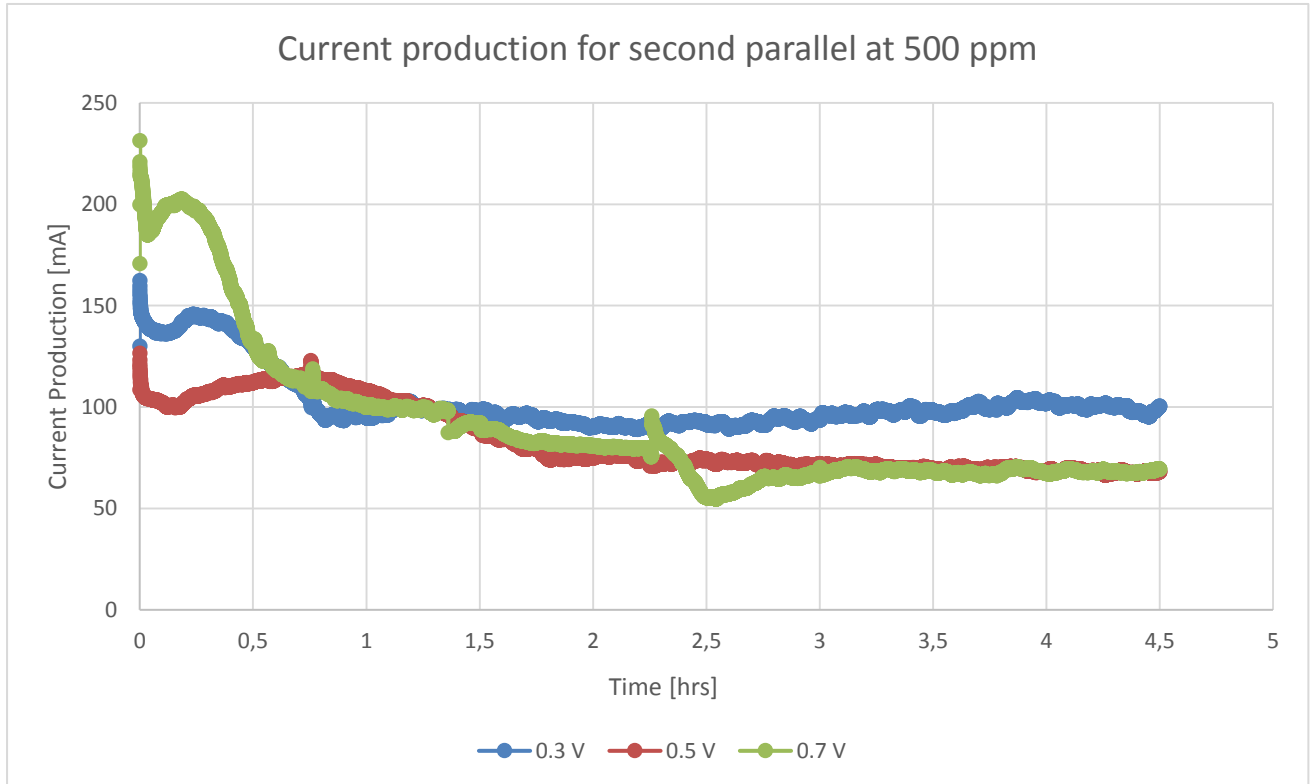


Figure 4-12 Current production for second parallel at 500 ppm

### 4.6 Comparison for 500 ppm

As the same as chapter 4.3, all figures from chapter 4.5 and 4.6 were analysed. After changing the potentiostat, the concentration results for the sulphide is very similar for the first and second parallel. Both parallels barely had any oxidation of the sulphide and it was stable during the experiment. The current production for the second parallel were lower compared to the first parallel. Both current productions took time to stabilise, but it took longer for the second parallel.

### 4.7 Cyclic voltammetry

#### 4.7.1 For 300 ppm

Figure 4-13 can be analysed to find anodic peaks and the reduction peak and identify the behaviour of hydrogen sulphide and its oxidation process. The potentiostat run the cyclic voltammetry cycle three times. Starting from the first cycle, there are three anodic peaks that were obtained. The potentials for the three peaks obtained are  $E_{ox\_1} = + 0.33$  V,  $E_{ox\_2} = + 0.67$

## 4 Results and discussion

V and  $E_{ox\_3} = + 0.95$  V. The first and the second anodic peak ( $E_{ox\_1}$  and  $E_{ox\_2}$ ) is assumed to be showing the oxidation from sulphide to elemental sulphur. The last anodic peak is the oxidation from sulphide to sulphate. During the cathodic trace, the cathodic peak would end at  $E_{red} = - 1.5$  V and reduce from sulphate to sulphide.

The potentials for the anodic peaks start to decrease slowly as the potentiostat runs for the second and third cycle. As the current were decreasing from the first to the third cycle, the oxidation and the concentration of sulphide would decrease. Thus, the graph would not show any major oxidations. However, in this case the opposite happened. The current from the first to the third cycle started to increase slowly but the anodic peaks were lower.

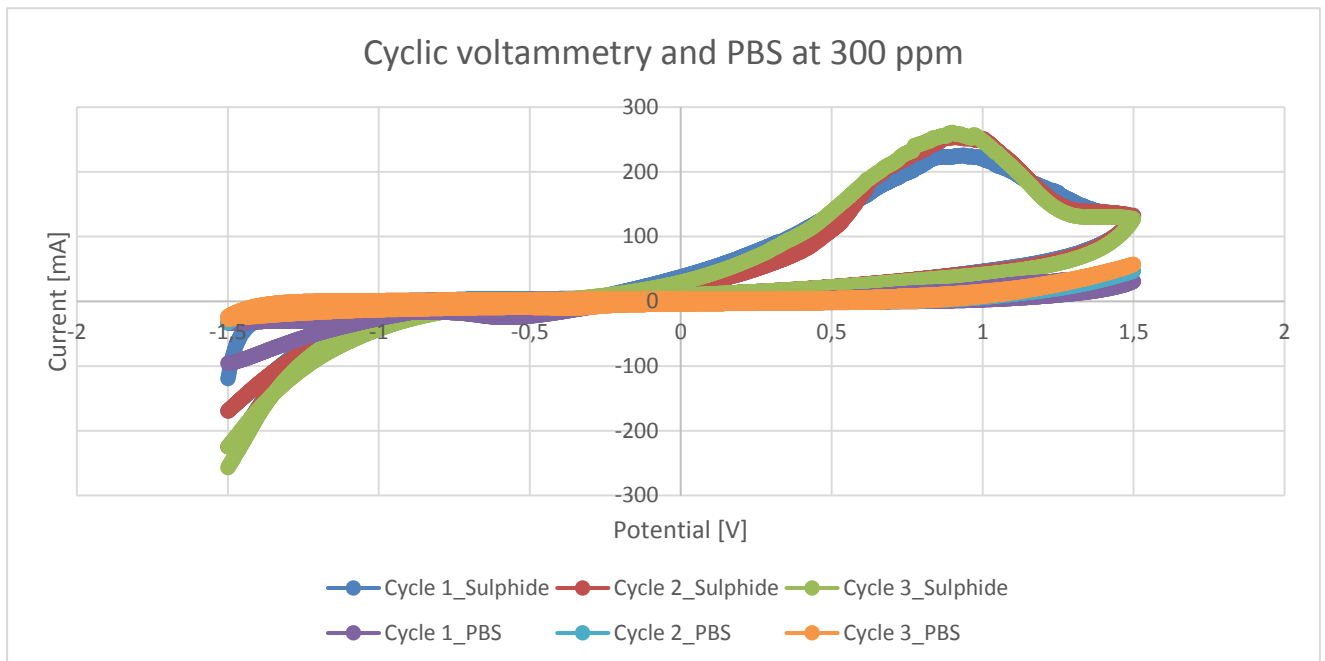


Figure 4-13 Cyclic voltammetry and PBS at 300 ppm

The reason behind the increase of the current can be that the mixture was exposed to air and everything wasn't sealed well. When pouring the sulphide in the volumetric flask with the buffer mixture, some of the oxidation may have happened sooner which led to the oxidation peak for the sulphide to be lower. Another reason may be the electrodes have slightly moved, which made the current to react. Thus, this can be concluded that the current would increase slowly with the anodic peaks being decreased.

The first PBS cycle had one peak at approximately + 0.78 V and no peaks after that. For the second and the third cycle there was no anodic peaks happening and can be concluded that the PBS was working properly and no other chemical or error occurred.

### 4.7.2 For 500 ppm

In Figure 4-14 the process for the cyclic voltammetry is the same but the concentration is higher. This figure has no obvious peaks that can be obtained from the graph and there may be few reasons behind this. The first cycle has a tiny anodic peak at  $E_{ox\_1} = + 0.70$  V. This could be the sulphide oxidation to elemental sulphur. The second anodic peak is closer to + 1.5 V but the possibility of all the sulphide and sulphur to oxidise to sulphate is small. As

## 4 Results and discussion

shown in Figure 4-14, there was barely any oxidation happening and the same for the second and the third cycle. The cathodic peak for this is also the same as the cathodic peak for 300 ppm. As the potentiostat would start running for the second and the third cycle the anodic peaks would be obtained earlier compared to the first cycle. The current would decrease, and the reason would be the decreasing of the sulphide concentration.

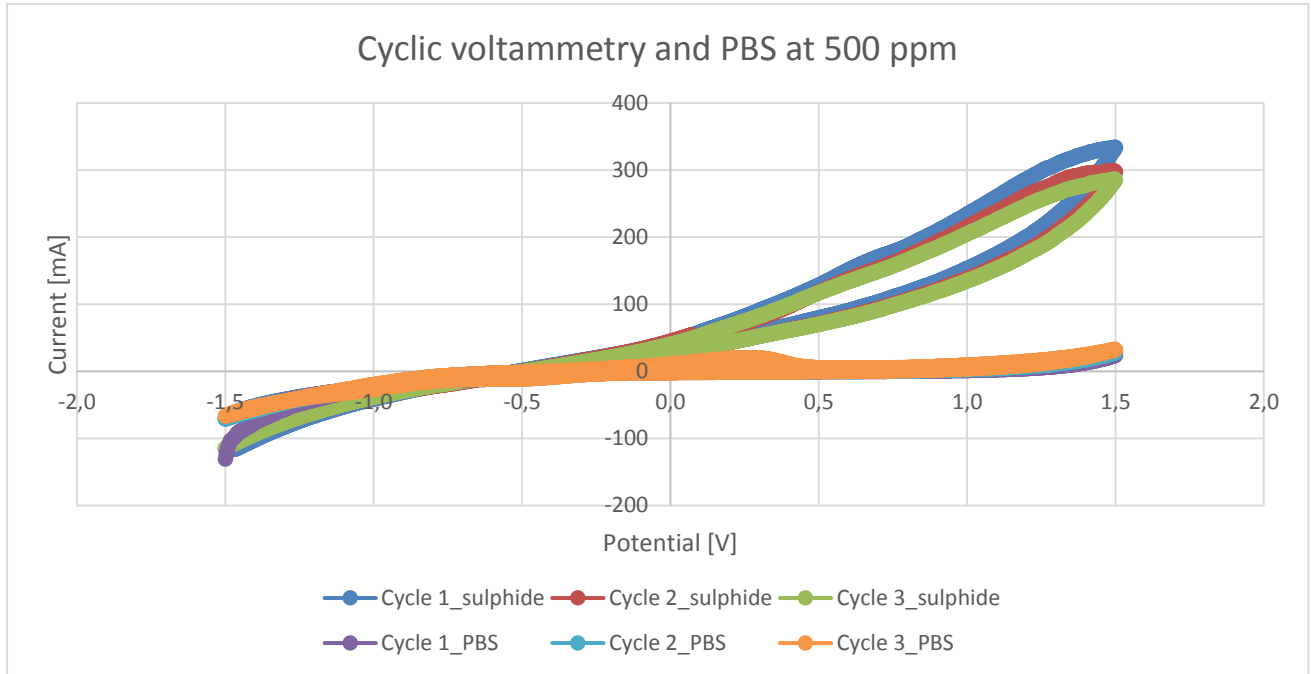


Figure 4-14 Cyclic voltammetry and PBS at 500 ppm

Another reason of why there aren't any obvious anodic peaks can be the time period not being large enough. The step size should've been smaller, so every possible oxidation peak could've been analysed and obtained. However, the time period should've been large because with a high concentration like 500 ppm it needed more time to oxidise. When the time period is small, regardless of how high the potential is, the oxidation wouldn't be as efficient as the oxidation for a longer time period.

For the PBS, it has an anodic peak at + 0.22 V on the first cycle. This peak would increase for the second and the third cycle and the current would decrease. Thus, the results from Figure 4-14 can be concluded with the same conclusion as the conclusion from Figure 4-13.

## 5 Conclusion

This work was done to understand why the hydrogen sulphide is an unwanted chemical and why it had to be removed. Literature review of hydrogen sulphide, electrochemical treatment and cyclic voltammetry was the initial step to understand how the electrochemical removal of hydrogen sulphide worked.

The experiment was performed on an electrochemical reactor to understand and evaluate the sulphide oxidation and its formation over time. Several tests were taken with different concentrations (300 ppm and 500 ppm) and different potentials (0.0 V, 0.3 V, 0.5 V and 0.7 V). The results from 300 ppm were decreasing as expected but some of the potentials failed to decrease how it was supposed to. The same happened for the first and the second parallels. However, the results from 500 ppm were better regardless of how slow it was decreasing. All the potentials were decreasing as expected for the removal rate of sulphide.

There were some results from sulphate for both 300 ppm and 500 ppm that oxidised rapidly compared to other results. The approximation of waiting two minutes of the test can be the main reason for why the results were different.

Cyclic voltammetry was the electrochemical test for this experiment. The potentiostat run the test for three times where three cycles were to analyse. The anodic peaks for the concentration 300 ppm were  $E_{ox\_1} = + 0.33$  V,  $E_{ox\_2} = + 0.67$  V and  $E_{ox\_3} = + 0.95$  V for the first cycle. The anodic peaks for the second and the third cycles were lower than the first and the cathodic peak for all the cycles were  $E_{red} = - 1.5$  V.

However, for the concentration 500 ppm the results differed, and the anodic peaks weren't visible to obtain. One tiny anodic peak was found at  $E_{ox\_1} = + 0.70$  V. The other anodic peak was closer to + 1.5 V. This was for all the cycles and the same with the cathodic peak. The cathodic peak was the same as the peak for 300 ppm  $E_{red} = - 1.5$  V.

Another electrochemical test was done for this experiment but with no sulphide and PBS only. The PBS only contained the phosphate buffer solution and were prepared the same way as for cyclic voltammetry. No anodic peak was to obtain from the PBS at 300 ppm, except for a tiny anodic peak noticed at + 0.78 V and no peaks were to obtain on the second or third cycle.

The PBS for concentration 500 ppm had one anodic peak at + 0.22 V on the first cycle. The current was decreasing for the second and third cycle and the anodic peaks would slowly increase.



## 6 Recommendation

The electrochemical reactor was a 1.5 L glass reactor connected to a pump and water bath. From the results in chapter 4, the oxidation of sulphide rate was not good enough. This experiment should be done with higher potential and more than 4.5 hours. Higher concentration is not necessary to use because if the time period and the potential were to increase, the results would be much easier to observe.

Moreover, these parameters would be costly because more energy is being applied to remove the hydrogen sulphide. The carbon material for this experiment is good but it should either be cleaned well or change the electrode with the wires and the material.

In the beginning of this work, sulphite and the potential 0.9 V were measured and applied to the reactor but not included in this work. No major changes were observed because of the electrode and the previous potentiostat. Thus, it is recommended to change the electrode as soon as possible. At the same time, it is important to consider when to change it because the material and the wire can be costly.

Finally, sealing the reactor and electrodes properly. With the reactor, electrodes and the wires being sensitive, the possibility of the reactor is exposed to oxygen can affect the results. The electrodes would move when samples are taken out which can affect it all.

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# Appendices

## Appendix A: FMH606 Master's Thesis – Task Description



Faculty of Technology, Natural Sciences and Maritime Sciences, Campus Porsgrunn

### FMH606 Master's Thesis

**Title:** Electrochemical sulphide oxidation: -An Experimental Study.

**USN supervisor:** Carlos Dinamarca (carlos.dinamarca@usn.no)

**Task background:**

Sulphides ( $\text{HS}^-/\text{HS}^2-$ ) are corrosive and toxic chemicals, waste products in numerous chemical process as in food and energy industries. Their removal from gas and liquid waste streams is compulsory due to their hazard nature. Often oxidation methods are expensive to operate, high energy-consuming and require chemicals, which in turn results in the downstream waste disposal. Sulphides could also be removed with the use of relative low voltages, in electrolytical cells, further lower potentials can be achieved with the help of bioelectrodes.

**Task description:**

The student will perform an experimental work with an electrolytic cell and evaluate:

- Sulphide oxidation over time,
- Products formation and distribution,
- Defining key process parameters and evaluate the effect of changing a selection of these parameters,
- Based on experimental results, the student needs to conclude on the technical and economic feasibility of such systems,
- The research may include simulations, depending on the student own interest.

**Student category:** EET, PT students

**The task is suitable for online students (not present at the campus):** No

**Practical arrangements:**

The student will work at USN laboratories, Campus Porsgrunn.

**Supervision:**

As a general rule, the student is entitled to 15-20 hours of supervision, which includes the necessary time for the supervisor to prepare for supervision meetings (reading material to be discussed, etc.).

**Signatures:**

Supervisor: *Carlos Dinamarca* 22.01.2021

Student: *Madeha Samir Ali* 22.01.2021