

CHAPTER 1

INTRODUCTION

In the oil and gas exploration/production, transportation, and processing industries, low-grade carbon steel represents the most commonly used construction material for pipelines. Depending upon the existing conditions, carbon steel corrosion may occur either as uniform or localized attack, the latter in the form of pitting corrosion, crevice corrosion, and stress corrosion cracking or corrosion fatigue. Pitting corrosion, rather than uniform corrosion, is the principal cause for failure of the producing and transporting equipment. In recent years, electrochemical noise (ECN) technique, due to its non-perturbation and simplicity, has been used to evaluate the pitting corrosion behavior of carbon steels. In the sweet oil and gas, the formation water contained many other cations such as Ca^{2+} , Mg^{2+} and so on, which lead to precipitation of scale deposits and may influence the susceptibility to pitting corrosion and/or uniform corrosion. Therefore, it was decided to add Ca^{2+} (usually in the form of CaCl_2) into NaCl solution in the laboratory to simulate the aqueous medium from the real field in order to improve the understanding of carbon steel corrosion in the presence of Ca^{2+} .

1.1 Project Background

In this project, the experiment was conducted by using the electrochemical noise analysis which is one of the current methods available in detecting the corrosion behaviour. The first experiment was conducted to study the temperature effect on the CO_2 corrosion rate, at the same time to determine the optimum environment in which CO_2 corrosion occur. The experiment was further extended to study the effect of changing the concentration of Cl^- ion and Ca^{2+} ion on CO_2 corrosion in NaCl environment. The result was analysed base on the electrochemical noise analysis principle. The result was then compared to give both the disadvantages and advantages of electrochemical analysis in evaluating the corrosion rate by referring to the other research paper.

1.2 Problem Statement

In the sweet oil and gas fields, the formation water contained many other cation such as Ca^{2+} , Mg^{2+} , and so on, which lead to the precipitation of scale deposits and may influence the susceptibility to pitting or uniform corrosion. For example, severe carbon dioxide corrosion of oil tubes was reported to occur in the Shengli oil field in Northern China where the stratum water is rich in calcium.

Although many studies in the laboratory have been carried out to simulate the CO_2 corrosion behaviour of pipeline steel in NaCl solution, less work has focused on corrosion problems of carbon steel in NaCl solution in the presence of Ca^{2+} .

In recent years Electrochemical Noise Technique due to its non perturbation and simplicity can be used to evaluate the pitting corrosion behaviour of carbon steel. By taking this advantage, this project is aimed to evaluate the result of the CO_2 corrosion by using ECN to study the effect of Ca^{2+} and Cl^- ion on the corrosion rate.

1.3 Objective and Scope of Study

The following are the main objectives of the project:

- To study the effect of different concentration of calcium ions (Ca^{2+}) on CO_2 corrosion.
- To evaluate the electrochemical noise analysis method in measuring the pitting corrosion in CO_2 environment with existence of Calcium ion.

The scope of study of this project includes conducting lab experiment to study the effect of calcium ions concentration on CO_2 corrosion by using electrochemical noise analysis. The study also includes measuring the accuracy of the ECN methods comparing to the other methods.

CHAPTER 2

LITERATURE REVIEW

In the oil and gas exploration/production, transportation and processing industries, grade carbon steel represents the most commonly used construction material for pipelines. The resistance of material to CO₂ corrosion is affected by the application of CO₂ injection for enhanced oil recovery and the active exploitation of deep natural gas reservoir containing CO₂[1]. Depending upon the existing conditions, carbon steel corrosion may occur either as uniform or localized attack, the latter in the form of pitting corrosion, crevice corrosion, and stress corrosion cracking or corrosion fatigue. Pitting corrosion rather than uniform corrosion is the principal cause for failure of the producing and transporting equipment.

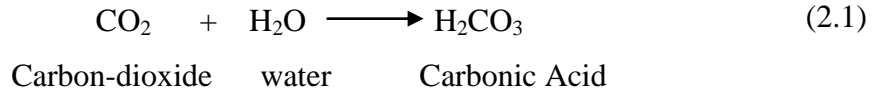
In laboratory experiment, Schmitt and Rothman [2] found that pitting corrosion appeared for several for several non-alloyed and low alloyed steels after prolonged exposure to oxygen free CO₂ containing distilled water at 25° C. According to Scmitt [3], the highest susceptibility to pitting corrosion occurred at 60-80 ° C.

In the sweet oil and gas fields, the formation water contained many other cation such as Ca⁺, Mg²⁺, and so on, which lead to the precipitation of scale deposits and may influence the susceptibility to pitting/uniform corrosion. For example, severe carbon dioxide corrosion of oil tubes was reported to occur in the Shengli oil field in Northern China where the stratum water is rich in calcium [4].

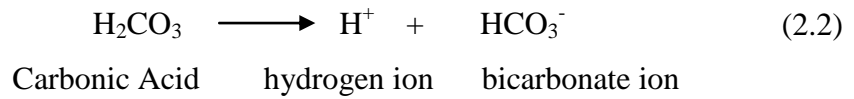
2.1 CO₂ Corrosion Mechanism

Carbon Dioxide (CO₂) corrosion is one the most studied form of corrosion in oil and gas industry. This is generally due to the fact that the crude oil and natural gas from the oil reservoir and gas well usually contains some level of CO₂ (and H₂S – hydrogen sulphide). The major concern with CO₂ corrosion in oil and gas industry is that CO₂ corrosion can cause failure on the equipment especially the main down hole tubing and transmission pipelines and thus can disrupt the oil and gas production.

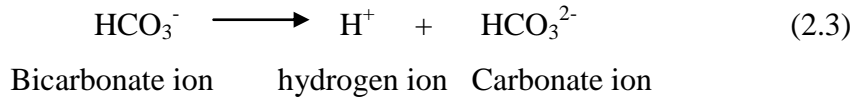
CO₂ gas can attack material in various mechanisms. One of the examples is through anodic and cathodic reaction. The anodic reaction is influenced by the amount of OH⁻ ions that formed during the reaction. On the other hand, the cathodic reaction depends on the solution composition and the reactivity of the chemical reaction. The CO₂ corrosion is explained by according to the following mechanism [5]:



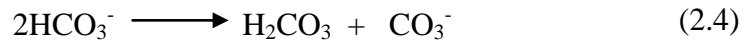
Carbonic acid will be ionized forming hydrogen ion and bicarbonate ion:



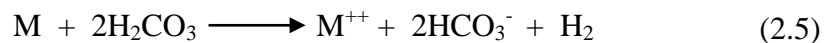
Bicarbonate ion will be further ionized into hydrogen ion and carbonate ion:



Bicarbonate ion will be able to produce more Carbonic acid that will form on the surface of the metal through the reaction of disproportionation and forming new hydrogen ions:



The overall reactions that occur are as follows:



CO₂ pitting corrosion is mainly caused by the presence of bicarbonate ions. Halide ions inhibit at low concentration. The efficiency increases with the ion mass and adsorption energy [6].

As stated before, CO₂ corrosion is one of the most common environments where corrosion occurs, and exists almost everywhere. Areas where CO₂ corrosion is most common include flowing wells, gas condensate wells, areas where water condenses, tanks filled with CO₂, saturated produced water and flow lines, which are generally corroded at a slower rate because of lower temperatures and pressures. Figure 2.1 shows the normal condition of CO₂ corrosion experience by metal surface.

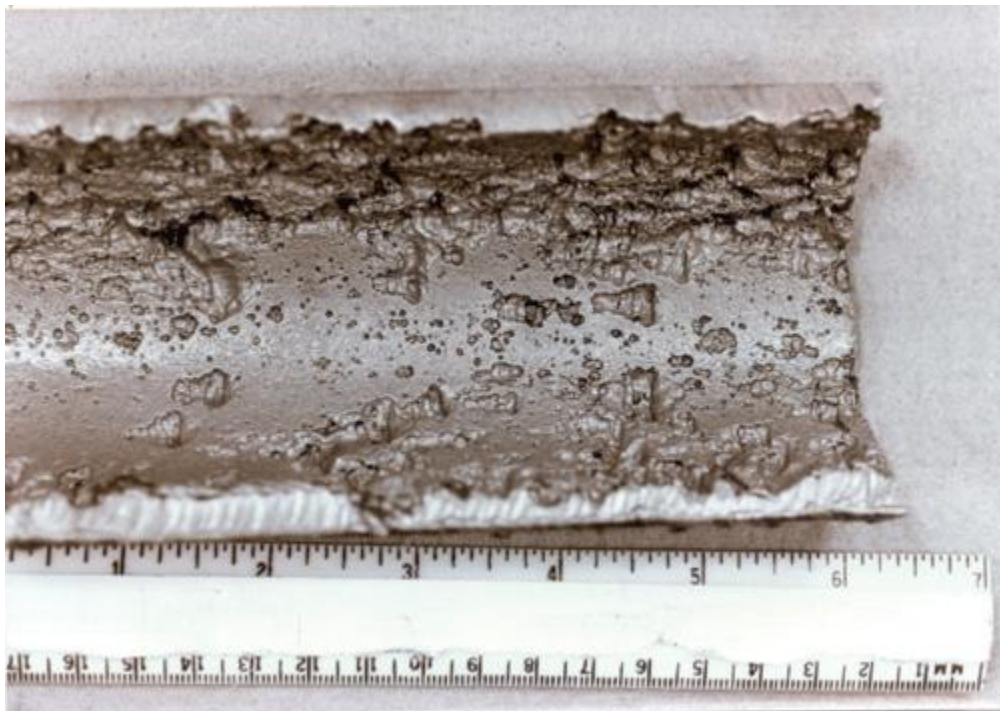


Figure 2.1: Localized thinning or pitting corrosion on carbon steel by CO₂ corrosion.

In the paper written by X. Jiang, Y.G. Zheng and D.R. Qu. on the effect of calcium ions on pitting corrosion and inhibition performance in CO₂ corrosion of N80 steel [7], he stated that the modelling of CO₂ corrosion mechanism is conducted at 57 ± 1 °C with pH value at was 3.85–3.87, and this was in accordance with the similar tests of other researchers [8]. In this paper the pH value at 57 °C was not monitored, but it should be constant during the tests with the same CO₂ purging process.

According to G. Schmitt and S. Feinen on his study of effect of anions and cations on the pit initiation in CO₂ corrosion of iron and steel [6] he mentioned that the temperature below 60°C, protectivity of carbonate layers is rather low. In this situation, metal will have higher tendency to corrode. This is best to represent the underwater model of CO₂ corrosion especially in lab session.

According the report by G. Schmitt and S. Feinen in effect of anions and cations on the pit initiation in CO₂ corrosion of iron and steel, this paper reports on fundamental model investigations on environmental effects (i.e. anion and cation effects, presence of corrosion inhibitors and temperature effects) on the pitting susceptibility of pure iron and low alloy steels under CO₂ corrosion conditions. The effect of anion in this experiment only consider several cations such as H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺, Zn²⁺, and Al³⁺. There is no effect of calcium ions studied in this paper. Figure 2.2 shows result of the effect of cation to the CO₂ corrosion:

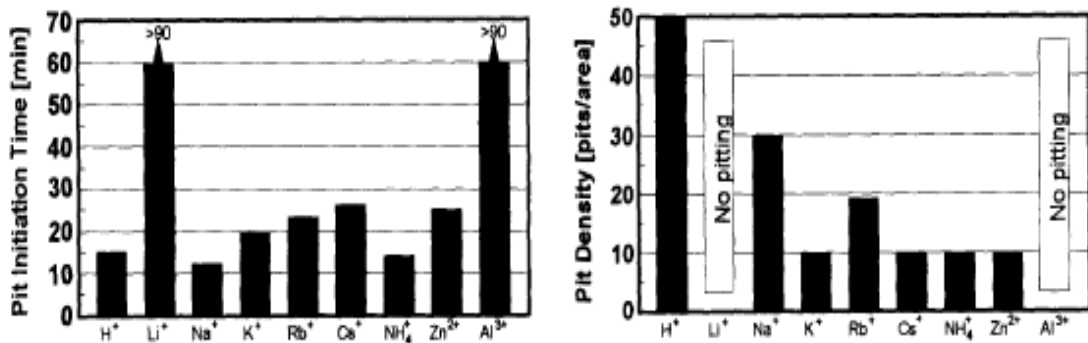


Figure 2.2: The effect of cation on CO₂ corrosion base on pitting initiation time.

In this paper the writer stated that in order to quantify the pitting susceptibility of the metal under given conditions, measurements were performed by using:

- i. On the time needed to produce the first visible pit (pit initiation time) and
- ii. The number of pits on a surface area of 1.3 mm z (pit density) produced within a time span of 90 minutes.

2.1.1 Pitting Corrosion Model base on CO₂ Corrosion Mechanism

According to G. Schmitt and S. Feinen [6] during sweet gas production CO₂ corrosion can cause pitting in carbon steel production tubings. The pits can act as flow disturbances which, depending on the flow intensity, may initiate subsequent flow induced localized (erosion) corrosion. Although this problem is well known in service and documented in the literature, there is still considerable discussion on the mechanism of pit initiation. The understanding of the pit initiation steps is, however, a precondition to apply appropriate corrosion protection measures. Therefore, in this study the mechanism of pitting corrosion under influence of CO₂ corrosion is also study in this work. Figure 2.3 describe the process of pitting initiation [9]:

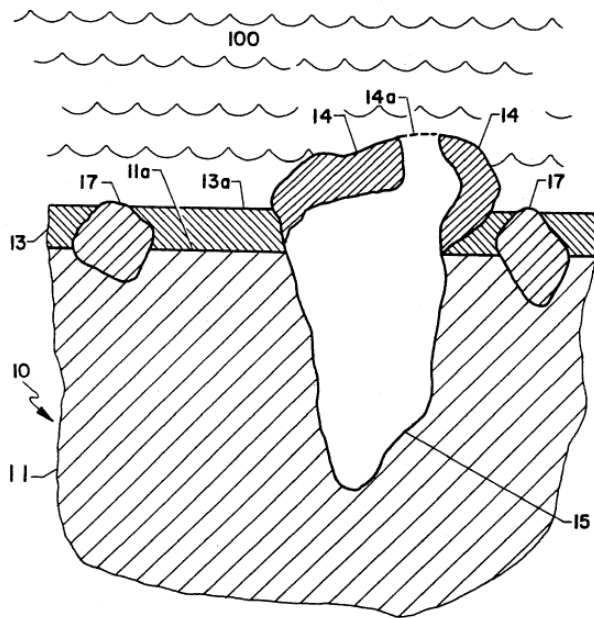


Figure 2.3: A Diagrammatic Diagram Of An Established Pitting Corrosion Of Metal Exposed To Aqueous Solution.

The figure shown is illustration of the well established pitting cell **15**. The metal is exposed to the aqueous chloride environment or solution. The metal **10** comprise of the interested metal (pipe) and a corrosive oxide layer film **13**. The film is naturally formed and is tightly adhere to the surface of the metal. The surface of oxide is exposed to the aqueous chloride environment. A crust **14** of is formed over the pit **15** restrict the solution to enter the interior of the pit. But the solution will enter the pit

thru the pore, designated generally by **14a** in the crust. The growth of the pit 15 involves the interaction between the metal bases directly with the solution **100**, within the pit [9].

2.2 Electrochemical Noise Analysis

Electrochemical Noise (ECN) is the generic term given to fluctuations of current and potential. When associated with corrosion is the result of stochastic pulses of current generated by sudden film rupture, crack propagation, discrete events involving metal dissolution and hydrogen discharge with gas bubble formation and detachment. The technique of measuring Electrochemical Noise uses no applied external signal for the collection of experimental data.

The ECN technique measures the signal perturbations which are low level fluctuations of the corrosion potential between two nominally identical electrodes which can be used in the mechanistic determination of corrosion type and speed. The fluctuations are usually of low amplitude, less than a millivolt and of low frequency bandpass filtered RMS value (DC and high frequency AC components removed).

The noise corresponds with the low level frequency noise (differential of the ZRA) signal but has much lower amplitude when general corrosion is involved. The technique considers the reactions occurring at the metal - solution interface and suggests two currents flowing on each electrode as a result of the anodic and cathodic reactions [10].

In recent years, electrochemical noise (ECN) technique, due to its non-perturbation and simplicity, has been used to evaluate the pitting corrosion behavior of carbon steels [11]. Figure 2.4 shows the basic principle of electrochemical noise analysis.

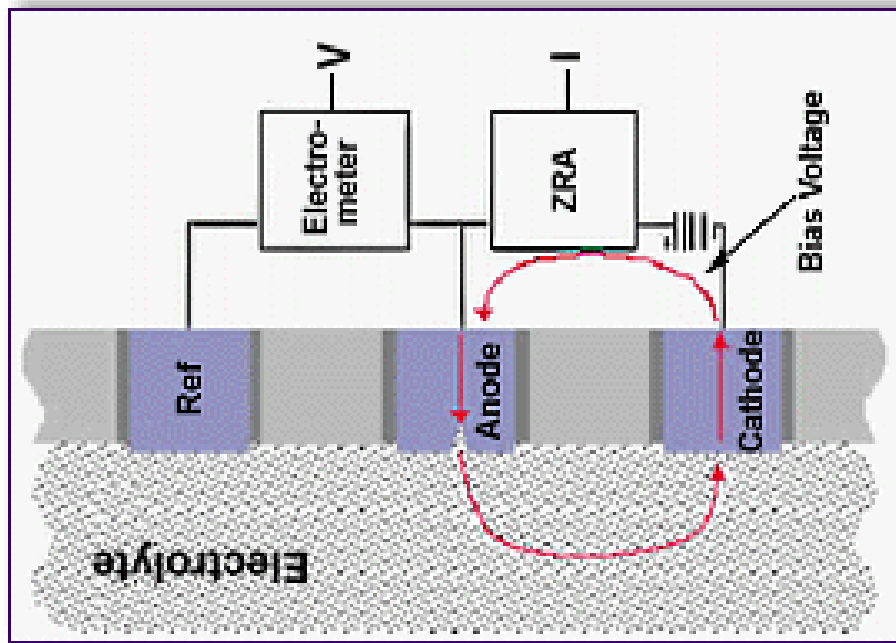


Figure 2.4: Representation of electrochemical noise analysis on the metal surface.

The source of noise is from the fluctuation of ion H^+ that exist on the electrode surface. Figure 2.5 shows sample of electrochemical pulse due to perturbation in the noise signal. Figure 2.5(a) is the noise current on pitting corrosion and figure 2.5(b) shows the noise polarization of rough surface of material. The potential change and disturbance on the current is what we define as electrochemical noise.

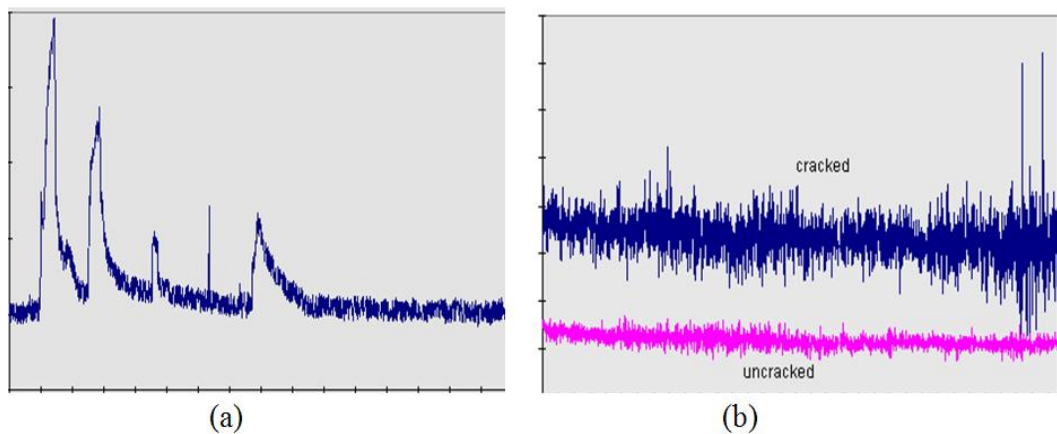


Figure 2.5: Noise Signal Measure by ECN: (a) Due to pitting corrosion. (b) Due to surface with crack (rough surface)

2.2.1 Basic Principle of Electrochemical Noise Analysis

Electrochemical noise signal is measured from the randomly moving electron in certain period of time. The movement of electron can be represented by noise current. Assuming I_n as a noise current happen on short period of time, thus the noise equation can be written as:

$$\overline{I_n^2} = 2elb \quad (2.6)$$

With $\overline{I_n^2}$: noise current
e : electron capacitance
I : current flowing
b : bandwidth measurement

Or can also be written as:

$$\overline{I_n^2} = 2qlb \quad (2.7)$$

With q: the solution charge capacitance in given time

From the data gain, we can calculate the polarization noise resistance using the following equation:

$$\sqrt{E_n^2} = \sqrt{I_n^2} \times R_p \quad (2.8)$$

With E_n : Noise Potential
 R_p : Noise polarization resistance

There are two ways to measure the electrochemical noise:

- Measurement using single electrode with reference electrode that having low noise measurement.
- Measuring the noise current between two identical electrodes. At the same time able to measure the potential between these two electrodes.

Beside this, ECN measurement can also be conducted by combination of the two above methods. In this case two identical electrodes are used to measure the current perturbation and one reference electrode is use and this electrode having low noise level. This working principle is illustrated in figure 2.6.

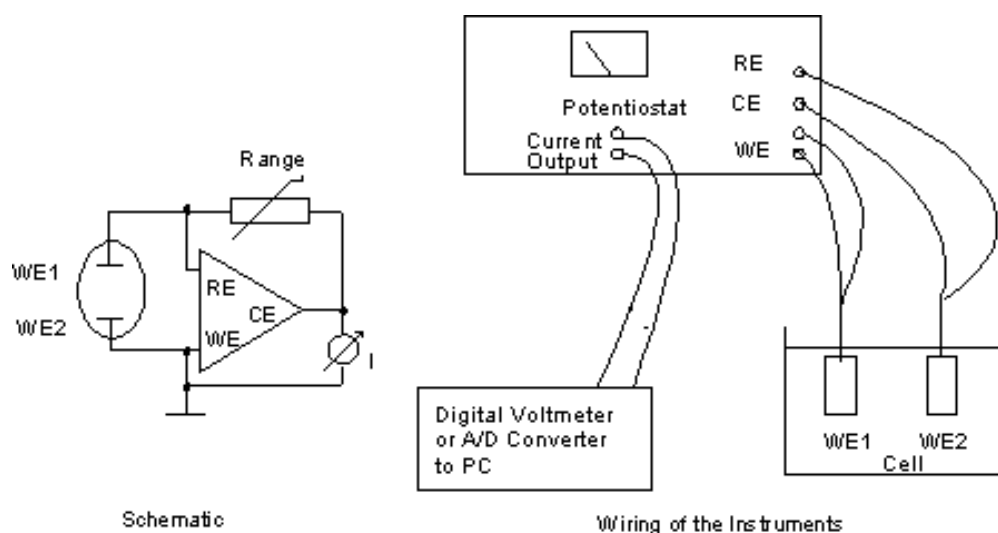


Figure 2.6: Electrochemical noise setup using 2 identical electrode methods.

CHAPTER 3 METHODOLOGY

3.1 Methodology Flow Chart

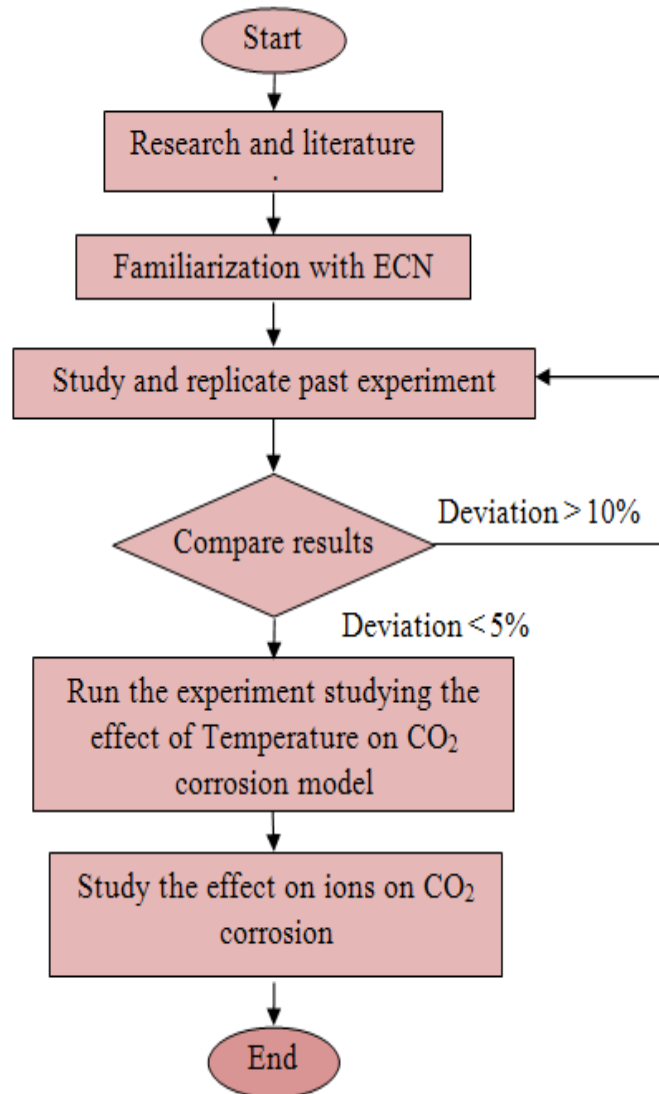


Figure 3.1: Project Methodology Flow chart

Figure 3.1 illustrate the project flow chart. A further research through available resources such as internet, journals, previous related FYP dissertation and discussion with fellow students and supervisor was conducted to have a clearer view of the topic. As this project required coordination with postgraduate student, there are a lot

of discussions held from time to time. Since this method (electrochemical noise analysis) required lot of practice to get familiar and better understanding, many resources from the internet need to be used. At the initial stage the main goal is to get familiar with this method, a duplicate of few past experiments were conducted to check the validity of the equipment in the laboratory. After that the set up is used to analyze the effect of calcium ions on CO₂ corrosion.

3.2 Key milestone and Gantt Chart

The key milestone in this project is reached when the effect of ions on CO₂ corrosion is recognised. By the temperature experiment that had been conducted earlier this temperature will be used to carry out the experiment.

The Gantt Charts for the project are shown in Figure 3.2. These Gantt chart shows the work planned and summarized the elements of the project. The Gantt chart is important to make sure that all the work load of the project is balance and comfortable.

3.2.1 Gantt Chart for FYP II

No.	Activities/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Literature review on research project topic	■	■	■	■	■	■	■	■	■	■				
2	Experiment Conducted to study the effect of temperature	■	■	■											
3	Analysis of all the result obtained			■	■										
4	Submission of progress report 1				*										
5	Compare the Temperature result				■	■	■	■							
6	Study the effect of ions in CO ₂ corrosion					■	■	■	■	■					
7	Submission of progress report 2								*						
8	Seminar								*						
9	Further analysis of final experiment result									■	■	■			
10	Poster Exhibition & Dissertation											*			
11	Preparation for oral presentation												■	■	
12	Hardbound dissertation													■	■

Figure 3.2: Gantt chart for FYP II

3.3 Test Medium

All experiments were carried out in NaCl background with different concentration of existing ions. The solution is saturated with CO₂ gas and O₂-free environment. Prior to tests, CO₂ was supplied continually to the solution for 1 hour throughout each experiment to keep it fully saturated; however, this was performed at a very slow rate to prevent solution flow effects during running process of the experiment.

The first test medium in studying the effect of temperature on the CO₂ corrosion was conducted by using 0.1M of NaCl and ranging the temperature of the environment. Table 3.1 shows the temperature use in studying the effect of temperature on CO₂ corrosion under average concentration of NaCl:

Table 3.1: Study of temperature effect on CO₂ corrosion

Environment	Temperature
0.1M NaCl + 1h of CO ₂ purging	25 °C
0.1M NaCl + 1h of CO ₂ purging	45 °C
0.1M NaCl + 1h of CO ₂ purging	85 °C - 115 °C
0.1M NaCl + 1h of CO ₂ purging	125 °C

Base on the experiment conducted above, the best medium is taken to be the environment in conducting an experiment of the study of ions on CO₂ corrosion. In this experiment the effect of Ca²⁺ ions and Cl⁻ ions is study. All experiments were conducted at 45 ± 1 °C. The pH value at 25 °C was 3.85–3.87, and this was in accordance with the similar tests of other researchers and the temperature effect that had been studied earlier. The pH value at 57 °C was not monitored, but it should be constant during the tests with the same CO₂ purging process. The surface of specimen was polished with silicon carbide paper up to 800-grit, rinsed with distilled water and degreased with acetone.

The basic of the experiment for the study of calcium ions is tabulated in table 3.2:

Table 3.2: The environment to study the CO₂ corrosion.

Material Use	Carbon Steel X52 carbon steel
Medium	1 litter distilled water + NaCl and independent variables
Culture temperature(°C)	45±1 ⁰ C
Duration of experiment	20-24 hours (reading every 1 hour)
Purging duration	1 hour supply with O ₂ – free CO ₂ gas. (deoxygenation) <i>**Perform at a very slow rate</i>
pH	≈3.9

The initial experiment was to study the effect Ca²⁺ ions on CO₂ corrosion. In this study, the concentration of Ca²⁺ ions is varied but at the same time we need to consider the effect of adding CaCl₂ ion since adding the CaCl₂ mean adding more chloride ion concentration. Thus a redundant experiment required to study the effect Cl⁻ ion when the amount of CaCl₂ is added to the experiment. Table 3.3 summarizes the test matrix in the study of calcium ion effect on CO₂ corrosion.

Table 3.3: To study the effect of Ca²⁺ ion on CO₂ corrosion

Condition (Stagnant)	3% NaCl of 1 liter distilled water	3% NaCl + 1.5% CaCl ₂ of 1 liter distilled water	4.6% NaCl of 1 liter distilled water
Presence of Ca ²⁺	No	Yes	No
Temperature	~45 ⁰ C	~45 ⁰ C	~45 ⁰ C
pH	~4.7	~4.7	~4.7
Experiment Duration	24 hours	24 hours	24hours

3.4 Test Apparatus

A standard three-electrode cell configuration was used for all electrochemical measurements under stagnant conditions. The schematic diagram of the electrochemical cell under stagnant conditions is shown in Figure 3.3. Under stagnant condition, copper wire was attached to the back of the specimen, which was mounted in an epoxy resin leaving an area of 1 cm^2 exposed to the solution. The five holes distributed on the cover of the container for CO_2 gas entry, working electrode, reference electrode (saturated Ag/AgCl), counter electrode (graphite) and condenser.

Two probes of salt bridge symmetrically distributed and connected with each other by using soft tubes and T-tube and then connected with saturated Ag/AgCl electrode. Two graphite electrodes were used as the counter electrode, which were mounted diametrically opposite with each other. The result is collected from ACM machine. The coupons were analyzed for the nature of the corrosion product morphology by using SEM.

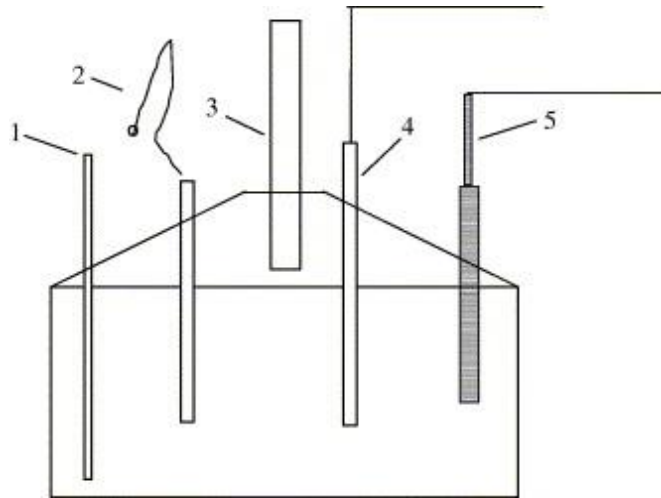


Figure 3.3: Schematic diagram of the experimental test cell under stagnant condition: 1. Gas inlet, 2. reference electrode, 3. condenser and gas outlet, 4. working electrode, 5. counter electrode.

3.4.1 Sample Preparation:

Before the experiment is conducted, the material needs to be prepared according to electrochemical noise requirement. This experiment is conducted by using the X52 carbon steel and the composition of the material are tabulated in table 3.4:

Table 3.4: Chemical composition of wt% of X52 steel

C	Si	Mn	P	S	Al	Cu	Nb	Ni
0.24	0.32	1.58	0.022	0.012	<0.01	0.006	<0.008	0.05

The material preparations include the following process:

- ✓ Cutting the material to desired size (diameter of 1.2cm)
- ✓ Polishing the material by grinder to get good surface finish
- ✓ Soldering the cuprum wire to the material
- ✓ Tubing the wire
- ✓ Raisin process to expose only one surface to the corrosion environment

Figure 3.4 shows the finish material that will be used as working electrode in electrochemical noise analysis. Two material are used as electrode, the other material is used to conduct the SEM process.



Figure 3.4: X52 complete with copper wire attach use as electrode and without raisin use for SEM analysis

After the specimen has been completed the setup of the experiment is developed. Figure 3.5 shows the experimental setup:

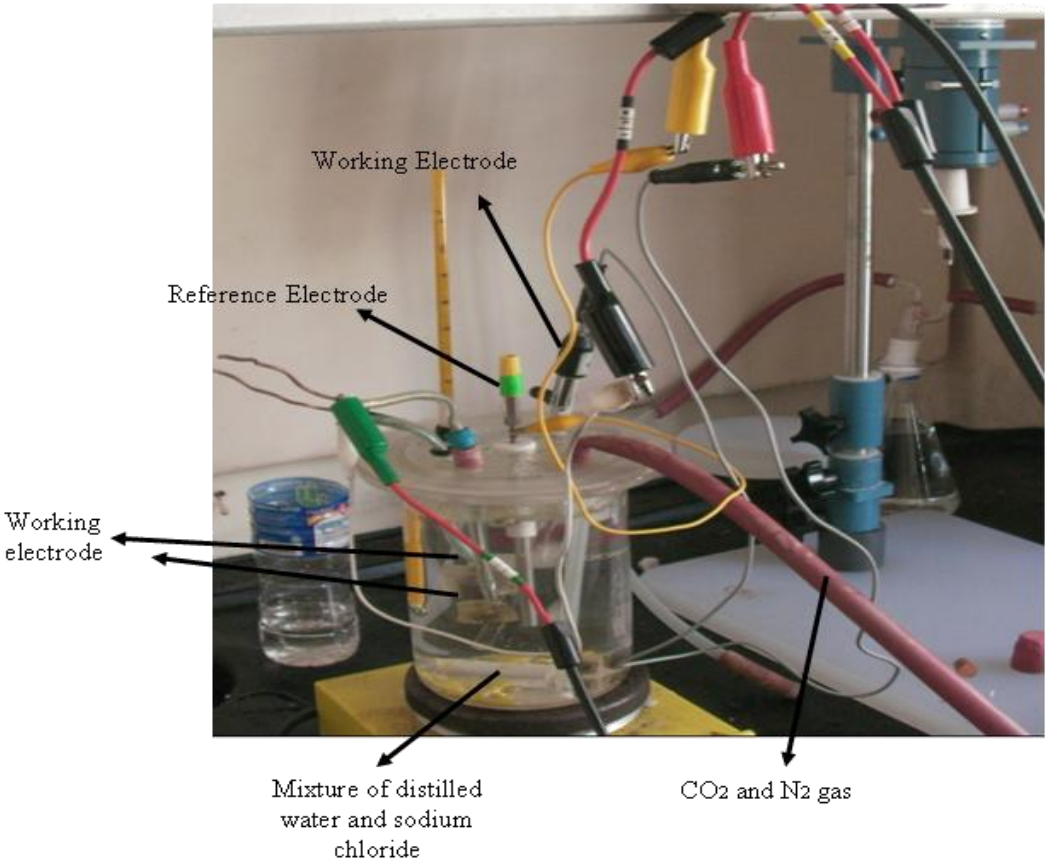


Figure 3.5: The setup equipment for studying the effect of CaCl₂ on CO₂ corrosion.

CHAPTER 4

RESULT AND DISCUSSION

Base on the methodology above, the experiment is basically divided into two parts, first to study the effect of temperature on the CO₂ corrosion. Base on the result of the first experiment, the data gathered will be used to study the effect of Ca²⁺ ions.

4.1 The effect of temperature in CO₂ corrosion

In CO₂ corrosion the temperature considerably influences the pitting susceptibility of metal. Below approx. 35 °C the protectivity of carbonate layers is rather low. Therefore, the pitting tendency is relatively low below 35 °C. Above approx. 35 °C the pitting tendency increases, and decreases again above approximately 130 °C. The temperature of maximum pitting susceptibility depends strongly on the alloy composition.

All low alloy steels used in sweet gas production experience pitting in the temperature range of 45 to 110 °C. The effect of temperature on the pitting susceptibility of pure iron was studied in 0.1 M NaCl solution. The results are tabulated in table 4.1:

Table 4.1: The temperature variation in 0.1M NaCl + 1h of CO₂ purging environment

Environment	Temperature	Pit Initiation Time Observe Thru ECN
0.1M NaCl + 1h of CO ₂ purging	35°C	-
	45 °C	18 th hour
	85 °C - 115 °C	12 th hour
	125 °C	-

Some of common data gain in these experiments are as followed:

4.1.1 35°C of temperature with 0.1M NaCl + 1h of CO₂ purging

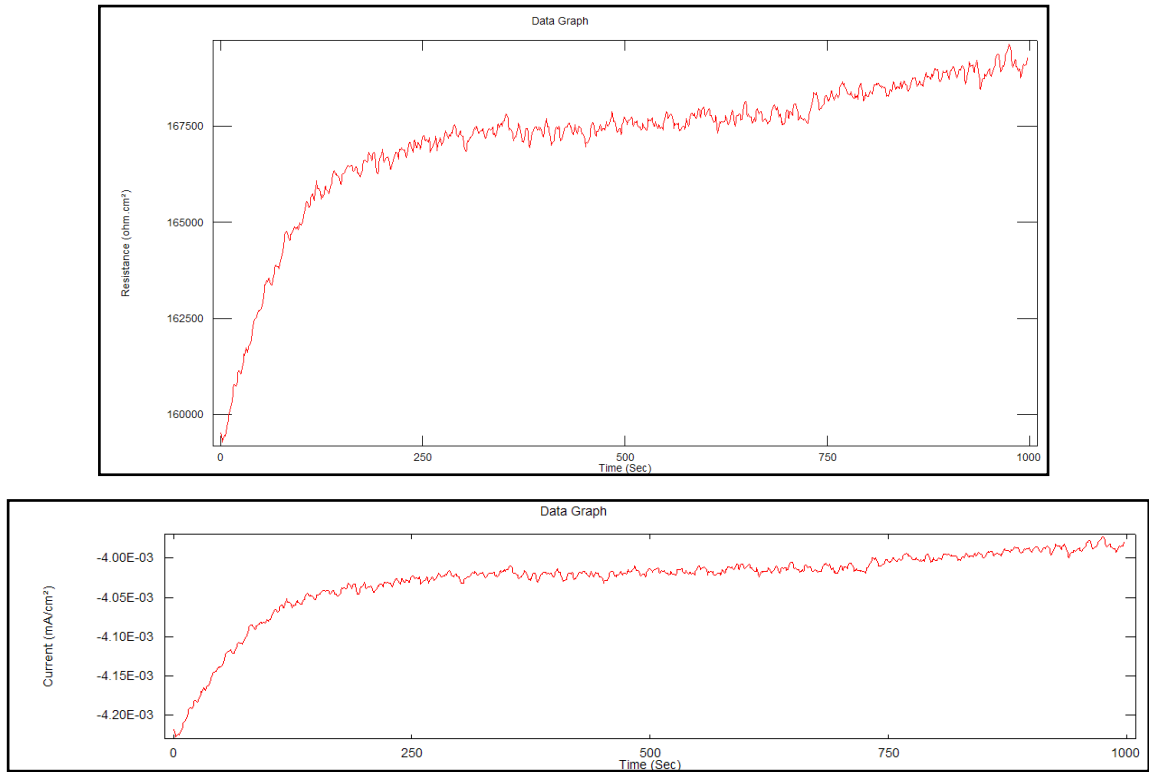
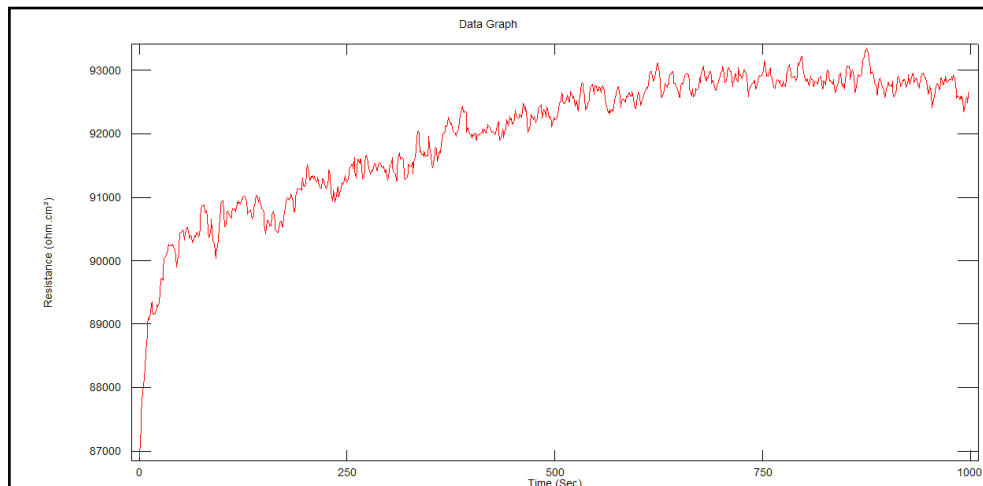


Figure 4.1: ECN data on 5th hour of CO₂ corrosion under temperature of 35 °C

In figure 4.1, data of first 5th hours of resistance vs. time and current vs. time for the temperature effect, the data showing no effect current perturbation in this situation mean no pitting occur at temperature around 35°C.



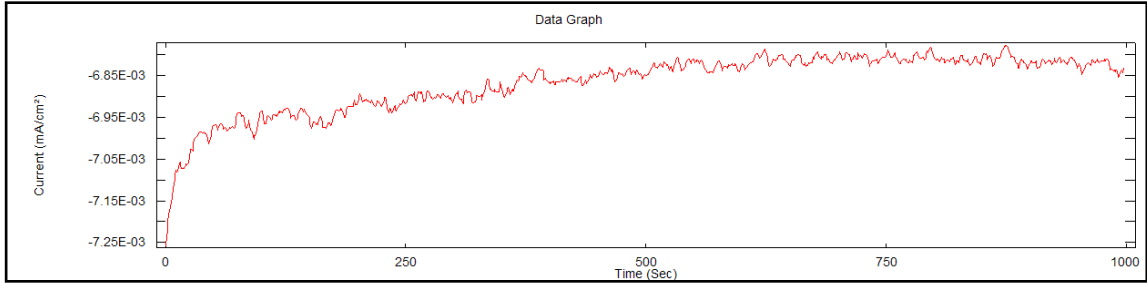
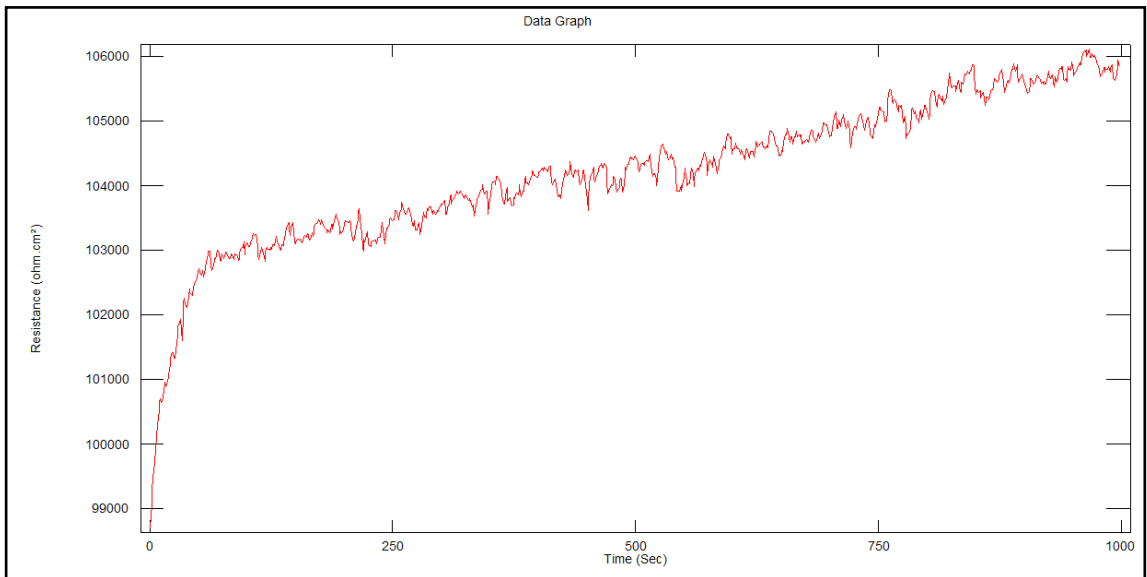


Figure 4.2: ECN data on 24th hour of CO₂ corrosion under temperature of 35 °C

Data of 24th hours of resistance vs. time and current vs. time for the temperature effect, the data in figure 4.2 showing no effect in current perturbation in this situation mean no pitting occur at temperature around 35°C up to 24hours, the pitting might be taking longer time for pitting to initiate.

4.1.2 45°C of temperature with 0.1M NaCl + 1h of CO₂ purging

The next experiments were conducted on the same environment but the temperature is increased in the range of 45°C. Some of the ECN data collected are shown in figure 4.3:



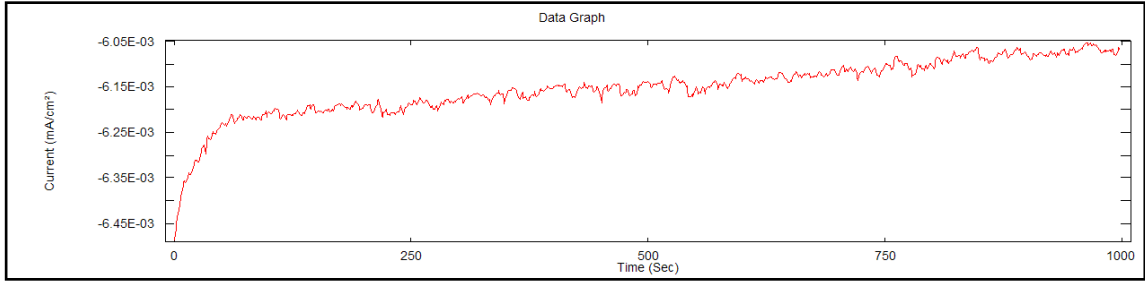


Figure 4.3: ECN data on 5th hour of CO₂ corrosion under temperature of 45 °C

Data of 5th hours of resistance vs. time and current vs. time for the temperature effect in figure 4.3 shows no effect on current perturbation in this situation mean no pitting occur at temperature around 45°C. But at the 19th hour data, current perturbation is observed. The following graph in figure 4.4 shows the current perturbation due to the pitting appearance on the 19th hour of exposure to 45°C environment.

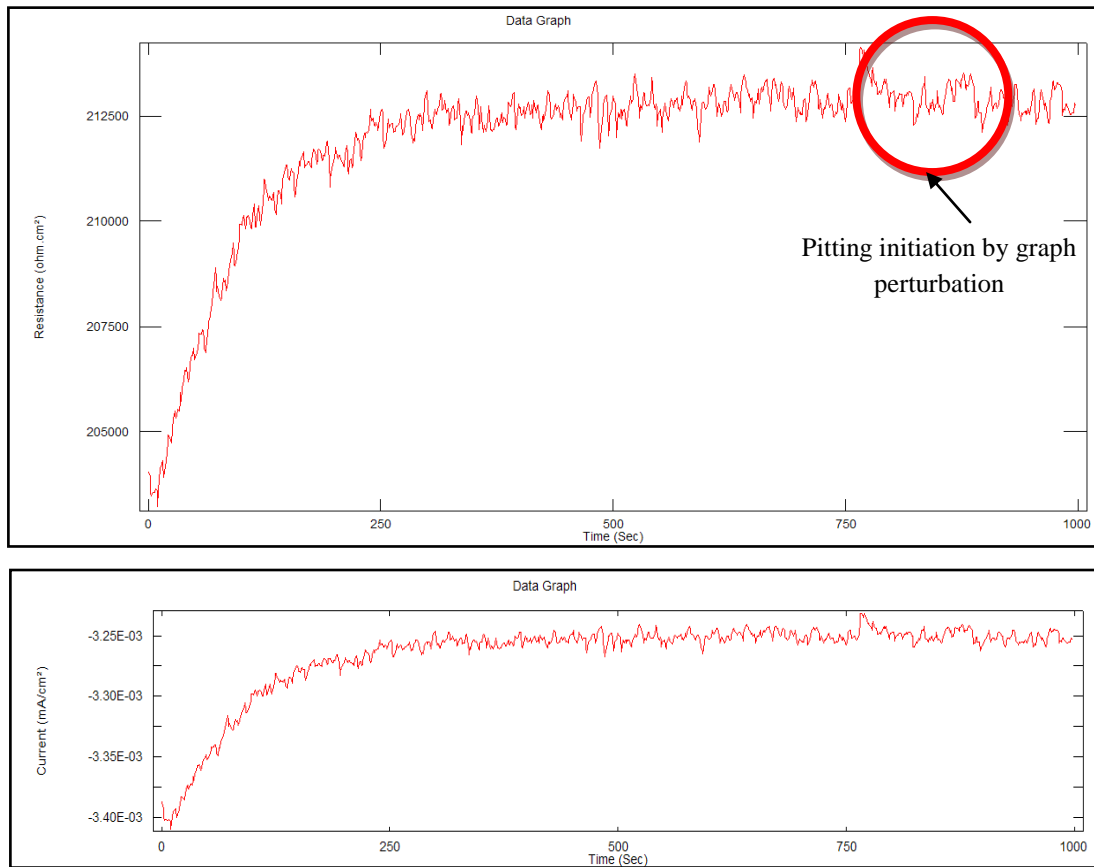


Figure 4.4: ECN data on 19th hour of CO₂ corrosion under temperature of 45 °C

In this data the first pitting is occur by detecting the current perturbation on the ECN data. The perturbation can be detected both in current and resistance vs. time graph plotted.

4.1.3 85°C - 105 °C of temperature with 0.1M NaCl + 1h of CO₂ purging

The next experiments were conducted on the same environment but the temperature is increased in the range of 85°C - 105°C. Some of the ECN data collected are shown in figure 4.5 and 4.6:

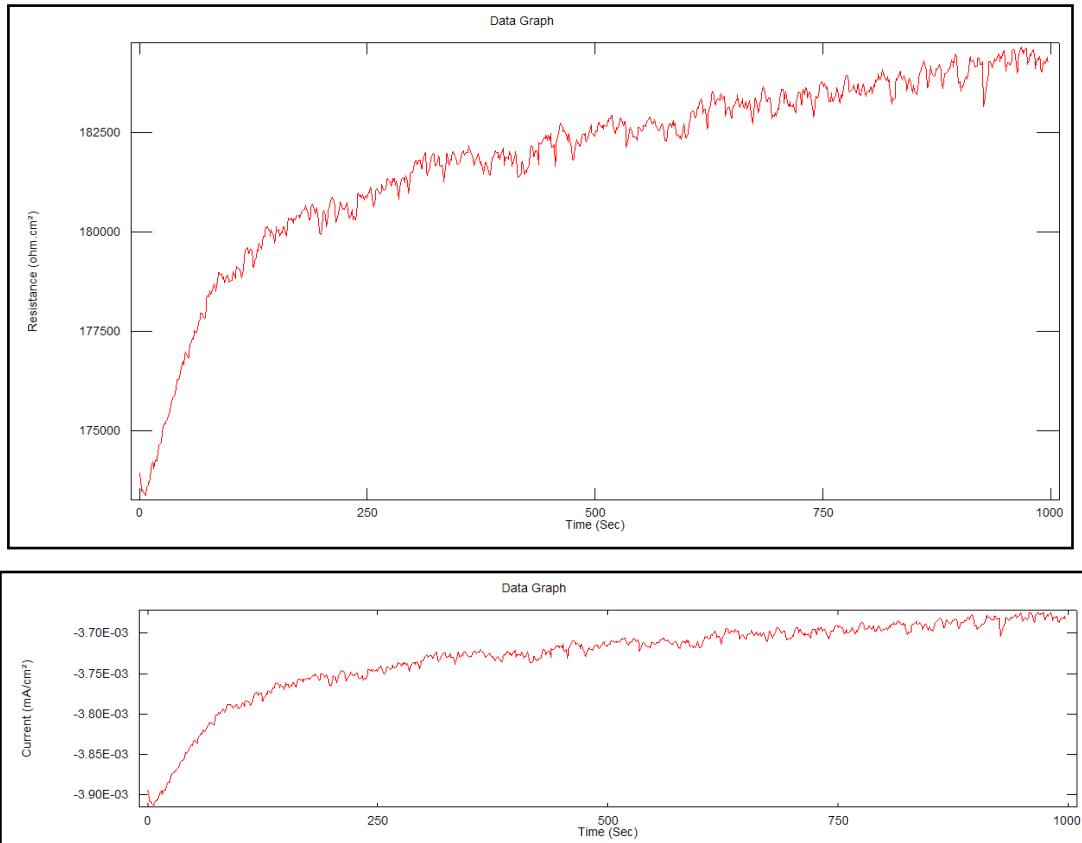


Figure 4.5: ECN data on 5th hour of CO₂ corrosion under temperature of 85°C - 105 °C

The data in figure 4.5 shows no pitting initiation occurs. After few hours the first current perturbation is observed in the 13th data which is the 12 hours after the experiment conducted. The following graph in figure 4.6 shows the current perturbation on the data:

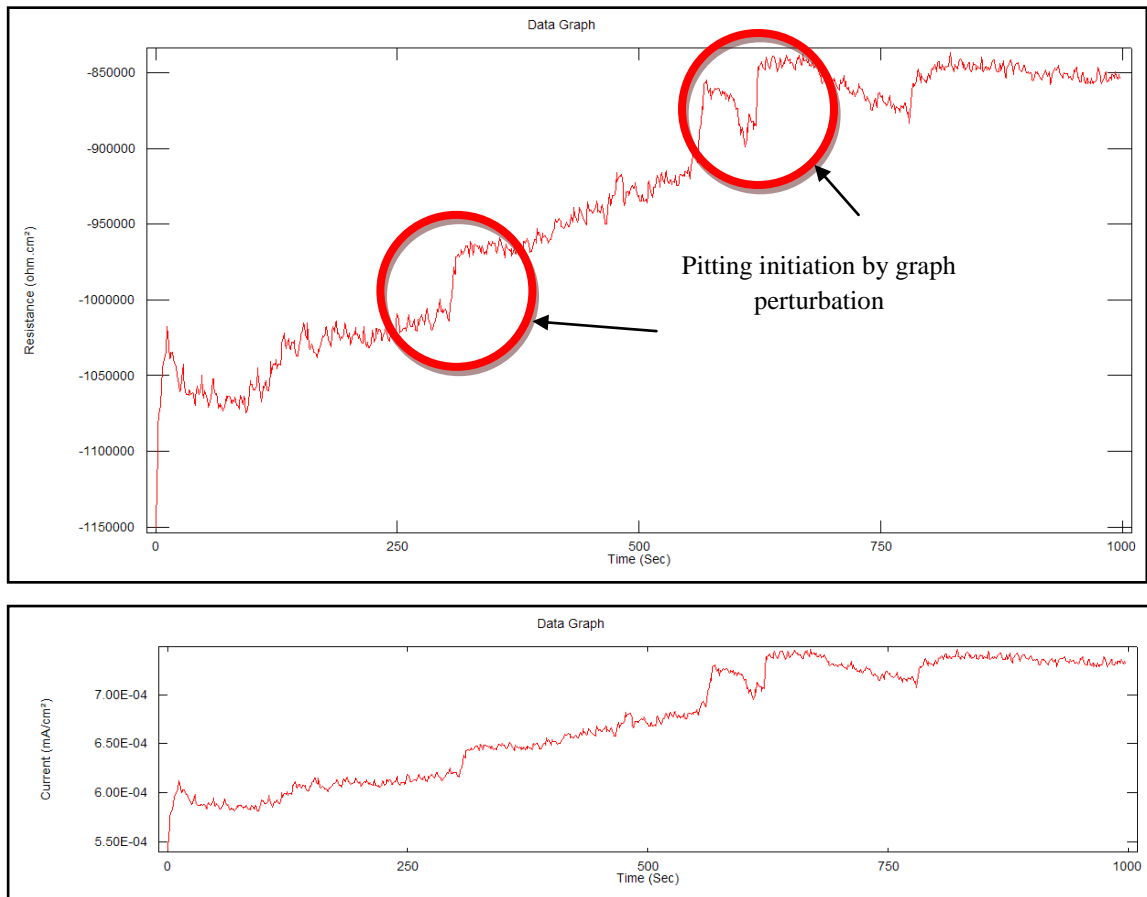


Figure 4.6: ECN data on 12th hour of CO₂ corrosion under temperature of 85°C - 105 °C

Clearly in this graph the pitting initiations occur several time and more rapid compare to 45°C. The current perturbation is observed in the 12th hours meaning that it takes 12 hours for pitting corrosion to occur in 85°C - 105°C environments.

4.2 Discussion on the Effect of Temperature on CO₂ Corrosion by the Pit Initiation Time

The effect of temperature on the pitting susceptibility of pure iron was studied in 0.1 M NaCl solution. While no pitting was observed at 35°C within an exposure time of 24 hours the first visible pit needed only 18 hours to form pitting corrosion. In the temperature range of 85 to 115°C the pit initiation time was about 12 hours. Above 115°C the pit initiation time tended to increase. Above 125°C it became extremely difficult to keep the experimental conditions constant for more than 30 min due to slow

evaporation of water from the drop positioned on the metal surface causing an increase of the chloride concentration in the test solution.

The pit density after 18 hours of exposure increased with the temperature from zero at 35 °C to 7 at 55°C, 22 at 65 °C and 30 at 85 °C. In accordance with the known temperature effects on the pitting tendency of low alloy steels the slope of the pit density vs. time curve increases significantly above 55 °C. Between 85 °C and 115 °C the pit density remained approx, constant.

These results showed, that pit initiation can occur within hours and that temperature effects observed for CO₂ pitting corrosion at low alloy steels also apply for pure iron. Therefore, further model investigations could be performed with pure. Iron without significant loss of relevance to the performance of low alloy steels under CO₂ corrosion conditions.

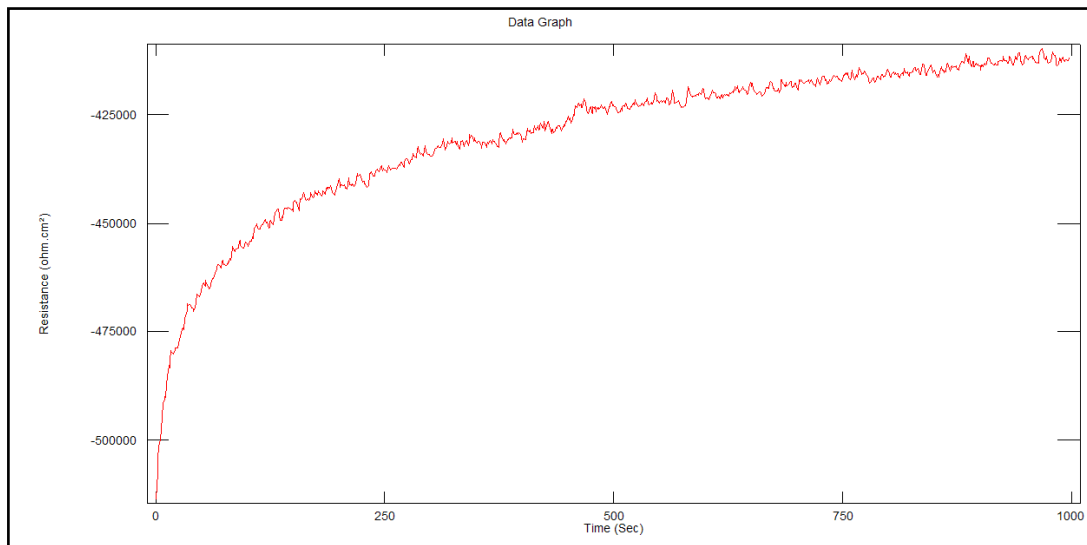
As maximum pit susceptibility had been found at 85 °C, but due to lab purposes this temperature is not being considered since it is not suitable for lab experiment and maintaining high temperature for experiment can be tedious. In this experiment the pit initiation occur the at lowest temperature approximately around 45°C, this data is suitable for 24 hours taking data that will be conducted for the next experiment to study the salt ions effect on CO₂ corrosion.

4.3 Effect of Calcium Ion on CO₂ Corrosion

In this chapter the effect of calcium ion as well as chloride ions on CO₂ corrosion is considered. The first step of this experiment is by taking one of the concentrations of NaCl which represent the underwater saltwater environment as a reference point. By adding certain amount of ion calcium Ca²⁺ in the form of CaCl₂, the effect of calcium ion is investigated. By adding CaCl₂ in the second experiment we are actually adding more concentration of Cl⁻ ions. The effect on the second experiment might be due to the adding more chloride ions or adding calcium ions. The third experiment needs to be carried out by examining the effect of chloride ion by the same chloride ions concentration as in second experiment.

4.3.1 3% NaCl in 1 Liter Distilled Water.

The ECN data was collected for 24 hours in this environment. The first data showing the current perturbation in the signal is assumed to be the pitting initiation times same like in the temperature analysis. The following figure 4.7 are the data for 5th hours showing that constant current without obvious perturbation which refers to no pitting appearance.



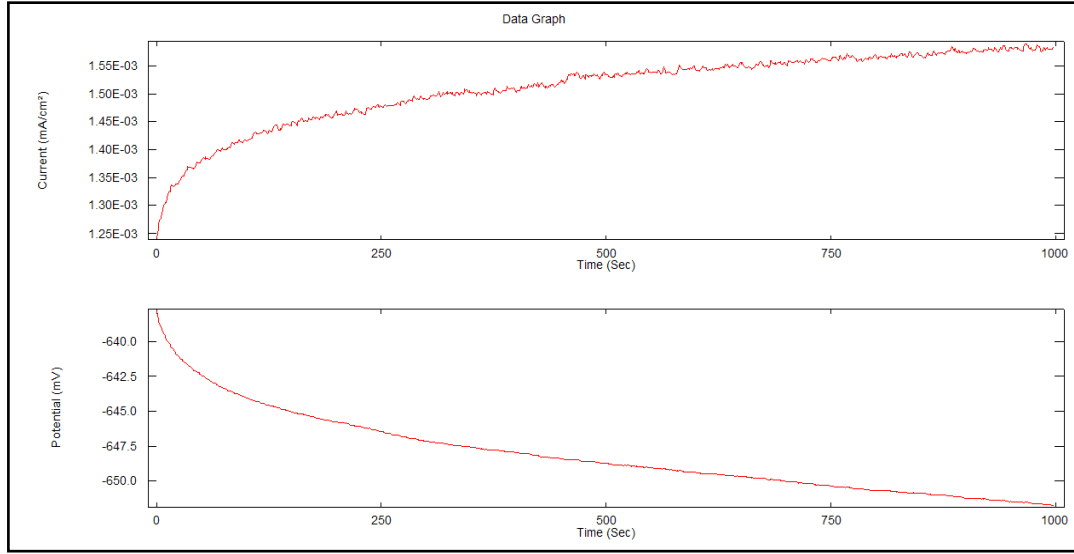
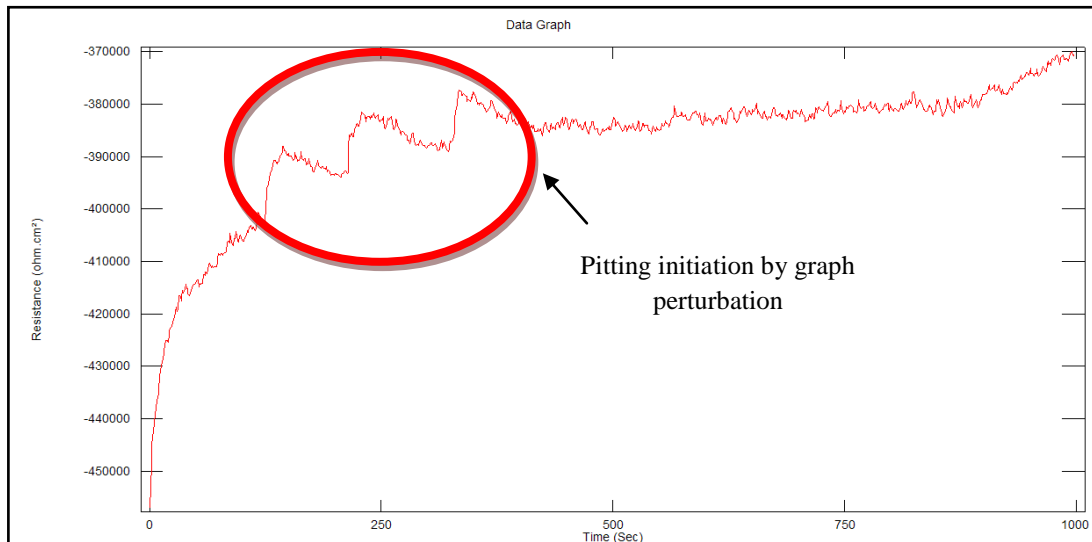


Figure 4.7: 5th hour data for 3% NaCl in distilled water.

The graph shows no current perturbation in the current measure. The first pitting occurs in the 17th hour of the experiment which is on the 18 data. The following graph in figure 4.8 showing the graph of pitting initiation for 3% NaCl:



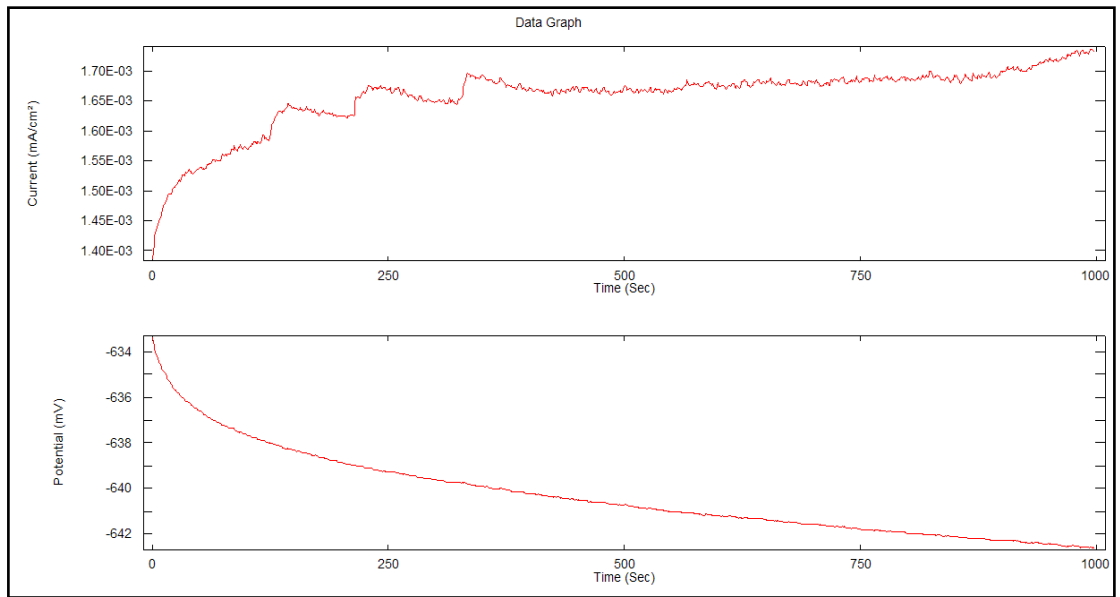


Figure 4.8: 17th hour data for 3% NaCl in distilled water.

The graph in figure 4.8 shows that three pitting occur on the surface of the material on the 17th hour. The corrosion rate of the material is increased with increasing time. Table 4.2 shows the corrosion rate of material taken for certain hours along the 24 hours data taken:

Table 4.2: The corrosion rate of metal in 3% nacl in distilled water.

Time (hour)	Corrosion Rate(mm/yr)
1	0.6155
4	0.0976
8	0.0859
12	0.0693
16	0.0534
20	0.0511
24	0.0611

4.3.2 3% NaCl + 1.5%CaCl₂ in 1 Liter Distilled Water.

The ECN data was collected for 24 hours in this environment. The first data showing the current perturbation in the signal is assumed to be the pitting initiation times same like in the temperature analysis. The following graph in figure 4.9 are the data for 5th hours showing that constant current without obvious perturbation which refers to no pitting appearance.

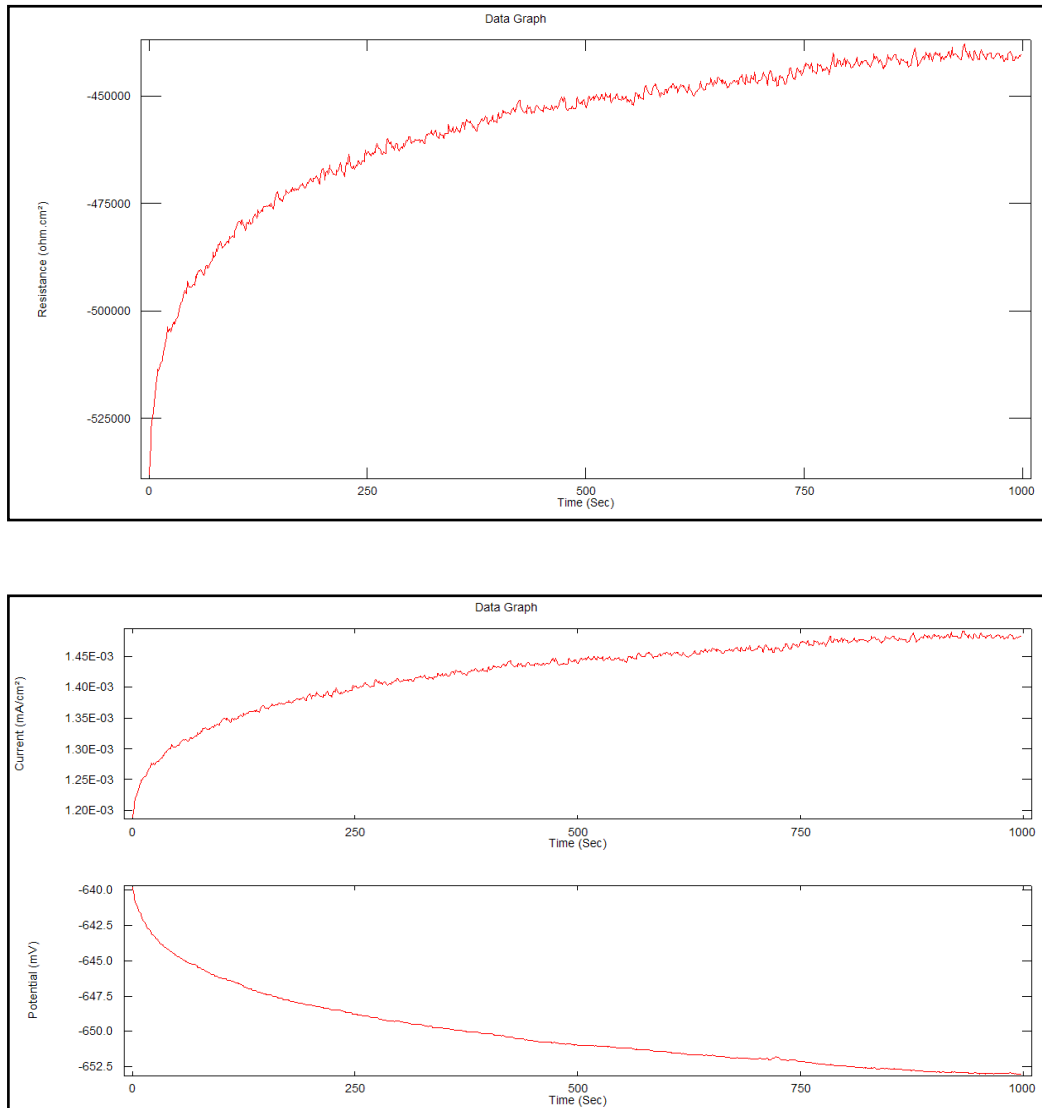


Figure 4.9: 5th hour data for 3% NaCl+1.5% CaCl₂ in distilled water.

While no pitting is appeared the first data perturbation is observed in the 15th hour of the experiment:

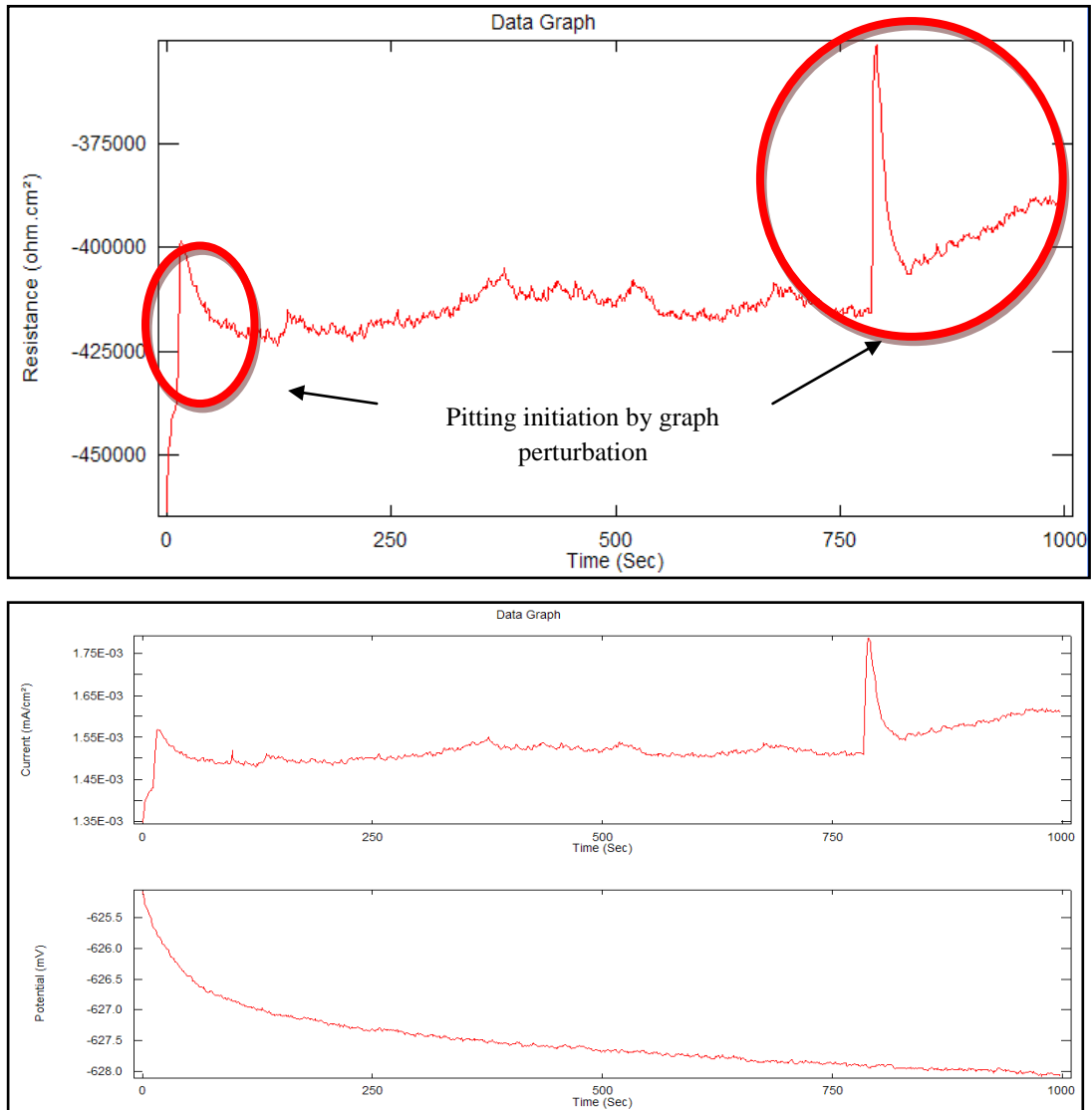


Figure 4.10: 15th hour data for 3% NaCl+1.5% CaCl₂ in distilled water.

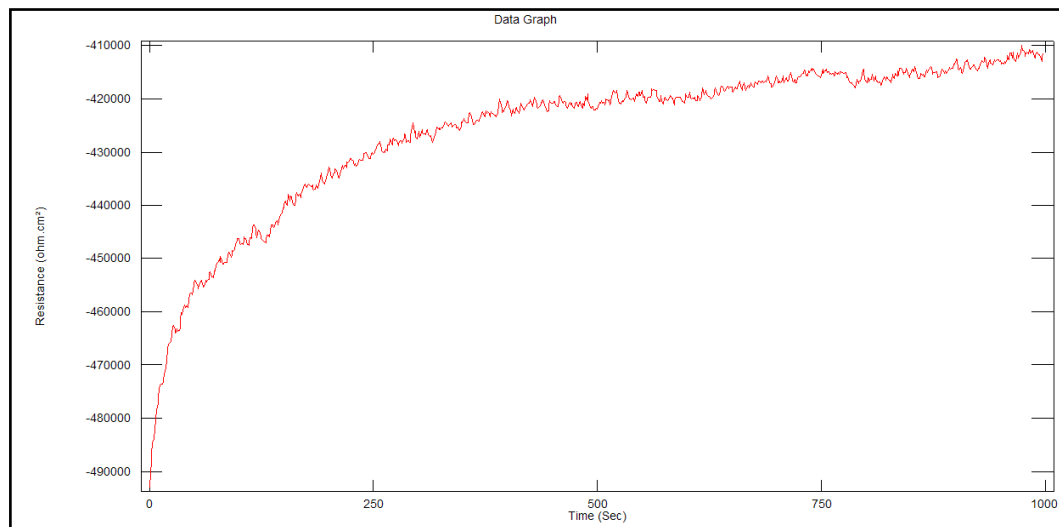
The graph show that two pitting occur on the surface of the material on the 15th hour. The graph perturbation is high showing that pitting occur might be severe. The corrosion rate of the material is increased with increasing time. Table 4.3 shows the corrosion rate of material taken for certain hours along the 24 hours data taken:

Table 4.3: The corrosion rate of metal in 3% NaCl + 1.5% CaCl₂ in distilled water.

Time (hour)	Corrosion Rate(mm/yr)
1	0.9155
4	0.3976
8	0.3859
12	0.3693
16	0.2534
20	0.2511
24	0.1611

4.3.3 4.6% NaCl in 1 Liter Distilled Water.

This experiment contains the same amount of chloride ions as in experiment two. The purpose of this experiment is to study the effect of chloride ions by having the same concentration; either the major effect is the chloride ions or the calcium ions. The further result will be discussed in the discussion topic. In figure 4.2 the first five hours data show no sign of pitting corrosion:



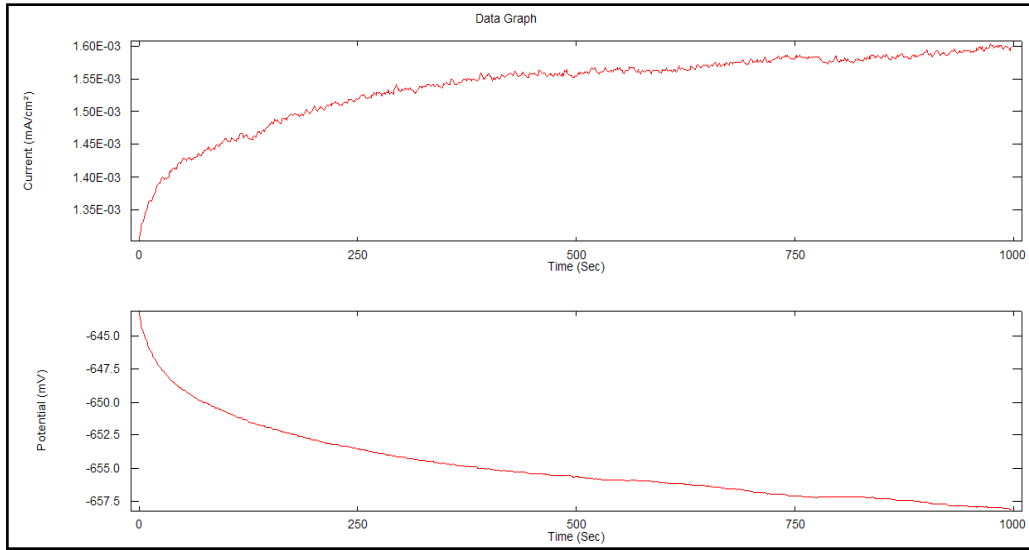
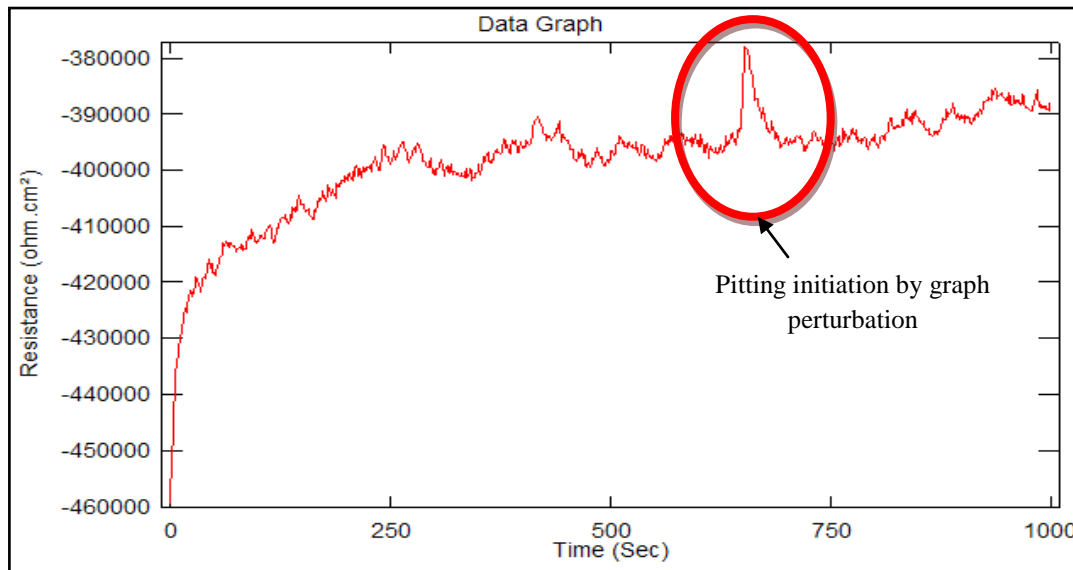


Figure 4.10: 5th hour data for 4.6% NaCl in distilled water.

The current perturbations appear on the 8th hour of the experiment, figure 4.11 illustrates the graph showing pitting appears at 8th hour of the experiment:



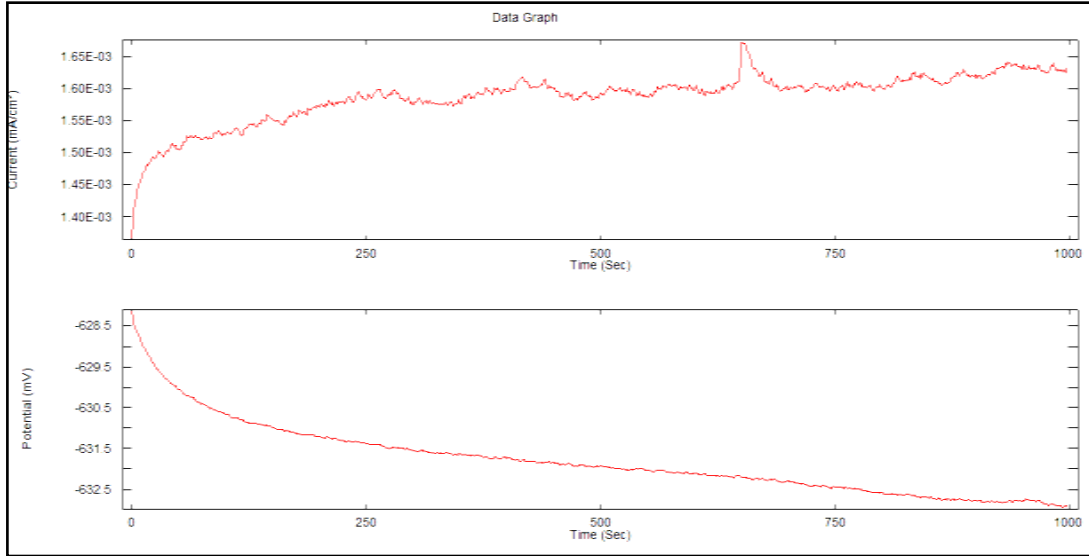


Figure 4.12: 8th hour data for 4.6% NaCl in distilled water.

The pit initiation time in this experiment is on the 8th hour, show the shortest time for the pitting to occur. The pitting characteristic at the end of 24 hours in this condition is quite critical, figure 4.13 shows the resistivity graph at the data taken at 24th hour:

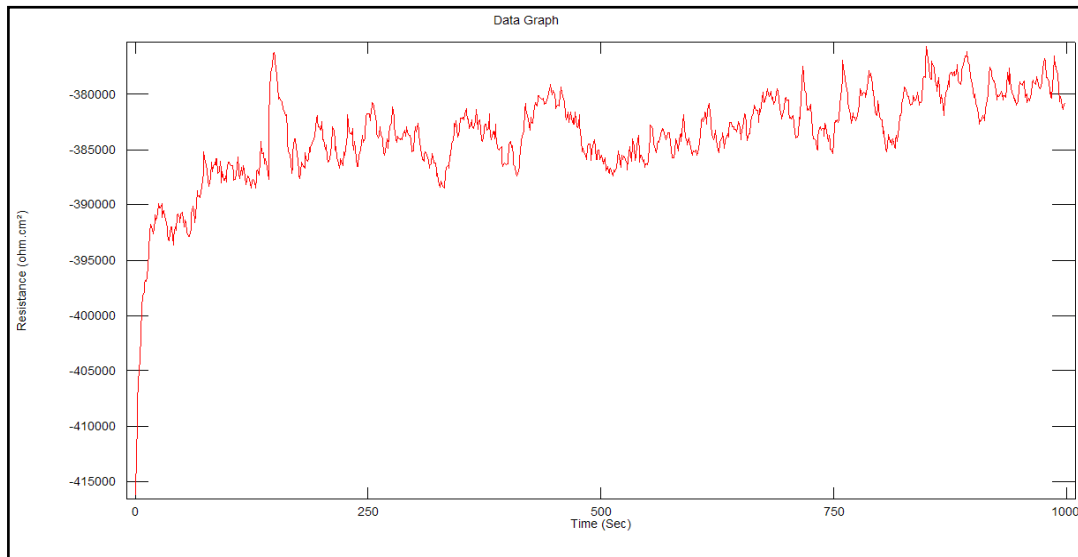


Figure 4.13: 24th hour data for 4.6% NaCl in distilled water.

Several pitting occurs on the metal surface and quite severe. The corrosion rate of metal under this condition increase with increasing time and showing the highest rate compare

to the other two conditions. The following table 4.4 shows the corrosion rate of material taken for certain hours along the 24 hours data taken:

Table 4.4: The corrosion rate of metal in 4.6% nacl in distilled water.

Time (hour)	Corrosion Rate(mm/yr)
1	1.641
4	1.24
8	1.19
12	1.392
16	1.188
20	1.233
24	1.225

4.4 Discussion on the Calcium Ion Effect of CO₂ Corrosion.

Pitting corrosion usually can take a few minutes or sometimes required a long initiation period before visible pits appeared. According to the results, the initiation period in 3% NaCl solution was 17 hours, but it decreased to 15 h in 3% NaCl + 1.5% CaCl₂ solution. However, because Ca²⁺ and Cl⁻ were simultaneously added by the addition of CaCl₂ into NaCl solution to simulate the real medium, it was not known which one caused the decrease of initiation period, Ca²⁺ or Cl⁻?

Chloride ions, Cl⁻ was widely thought as an aggressive pitting agent in the aqueous solutions. When the Cl⁻ concentration increased, the frequency of Cl⁻ attacks on the corrosion product film increased. Therefore, the initiation period decreased with the increase in the chloride ion concentration because of the addition of CaCl₂ into NaCl solution.

In order to further verify if Ca²⁺ also influenced the pitting corrosion, immersion test under stagnant condition in 4.6% NaCl solution, which had the same Cl⁻ concentration as 3% NaCl + 1.5% CaCl₂ solution, was carried out. Current and resistive plots vs. time

in 4.6% NaCl solution saturated by CO₂ under stagnant condition has shown that the pitting initiation time increased with exposure time of electrode up to 8th hours. Therefore, the initiation period in 4.6% NaCl solution was 8 hours. Namely the initiation period shifted from 17 hours in 3% NaCl solution to 8 hours in 4.6% NaCl solution and 15 hours in 3% NaCl + 1.5% CaCl₂ solution. This indicated that the initiation period decreased with increasing Cl⁻ concentration, and at the same Cl⁻ concentration, Ca²⁺ added into NaCl solution increased the initiation period of pitting corrosion. Table 4.5 summarizes the pitting initiation time for the three conditions:

Table 4.5: The pitting initiation time for three different conditions.

Conditions	Pitting Initiation Time (X th hours)
4.6% NaCl	8
3.0% NaCl + 1.5% CaCl ₂	15
3.0% NaCl	17

The following table 4.6 and graph in figure 4.14 summarizes the effect on CaCl₂ and Cl⁻ on the corrosion rate of CO₂:

Table 4.6: The corrosion rate recorded by ECN for three different conditions.

Time (hour)	Corrosion Rate(mm/yr)		
	4.6% NaCl	3%NaCl + 1.5%CaCl ₂	3% NaCl
1	1.641	0.9155	0.6155
4	1.24	0.3976	0.0976
8	1.19	0.3859	0.0859
12	1.392	0.3693	0.0693
16	1.188	0.2534	0.0534
20	1.233	0.2511	0.0511
24	1.225	0.1611	0.0611

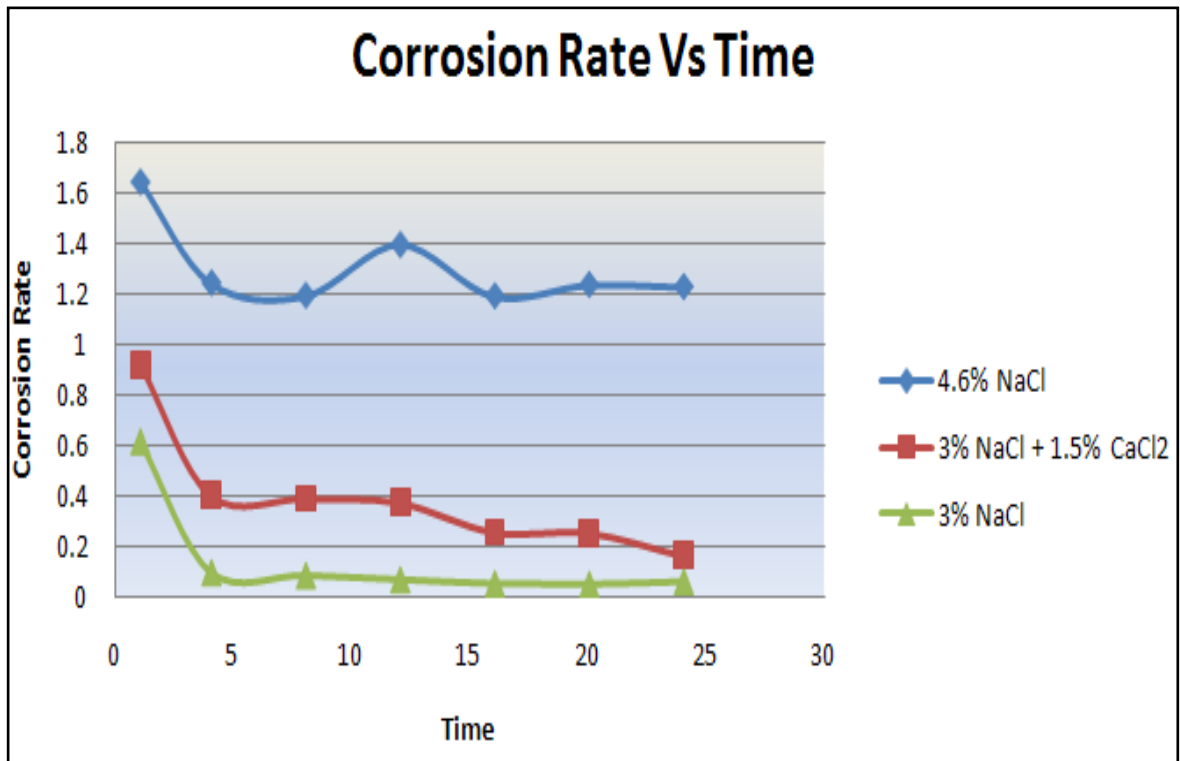


Figure 4.14: The corrosion rate vs. time graph recorded by ECN for three different conditions

CHAPTER 5

CONCLUSION AND RECOMENDATION

The pitting susceptibility of both metals increases with increasing temperature. Below 35°C the pitting initiation take more than 24 hours to occur. Above 45°C the pit initiation time is approximately 18 hour. In the temperature range of 85°C to 110°C pitting is likely to occur at both pure iron and low alloy steels. For underwater pipeline, the temperature of 45°C is taken to conduct the experiment.

The objectives of this project are:

- To study the effect of different concentration of Calcium ions (Ca^{2+}) on CO_2 corrosion.
- To evaluate the Electrochemical Analysis method in measuring the pitting corrosion in CO_2 environment.

Base on the objective given above, it can be concluded that under stagnant condition, the corrosion rate in the blank solution increased with the increase of Cl^- concentration from 3% NaCl solution to 4.6% NaCl solution. For the solutions with the same Cl^- concentration, the corrosion rate decreased due to the addition of Ca^{2+} . The initiation period of pitting corrosion decreased with increasing Cl^- concentration, but at the same Cl^- concentration, the initiation period increased because of the addition of Ca^{2+} .

ECN is a proper tool to measure corrosion rate of steels and more sensitive then conventional electrochemical noise approach. This can be seen in measuring the corrosion, by using electrochemical noise analysis, the precise time of pitting initiation time can be detected. Comparing to other method such as EIS, the pitting initiation time

is study by studying the curve of the result. ECN is a simple method where corrosion rate and pitting initiation of corrosion can be determined.

5.1 Recommendations

Through the entire project the following recommendations can be implemented to improvise the result:

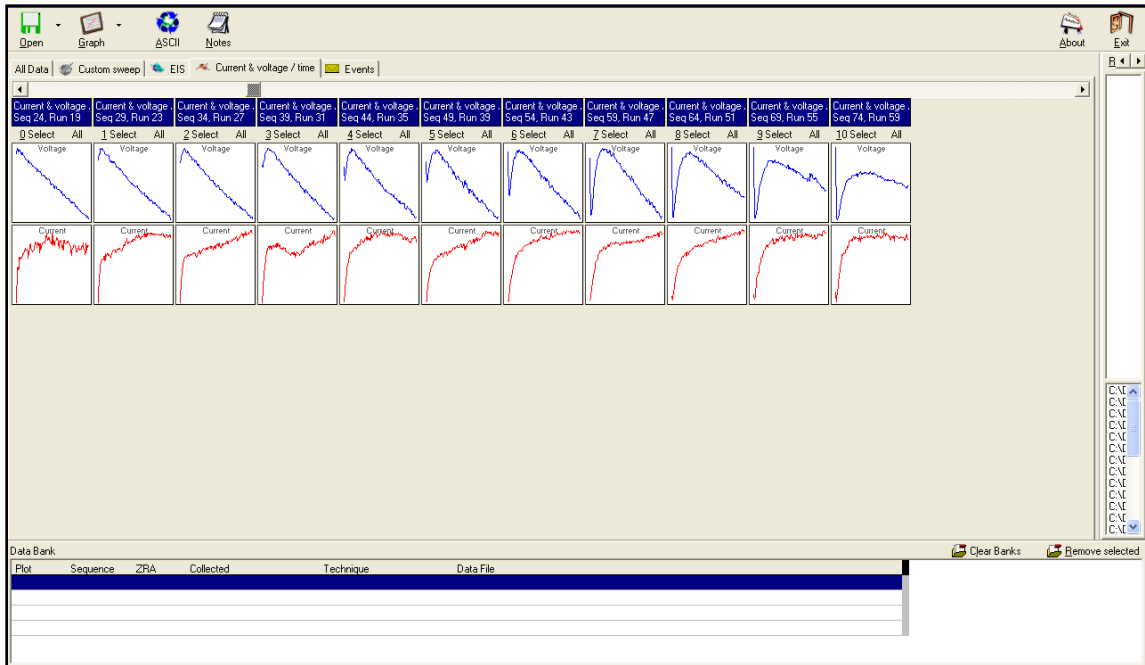
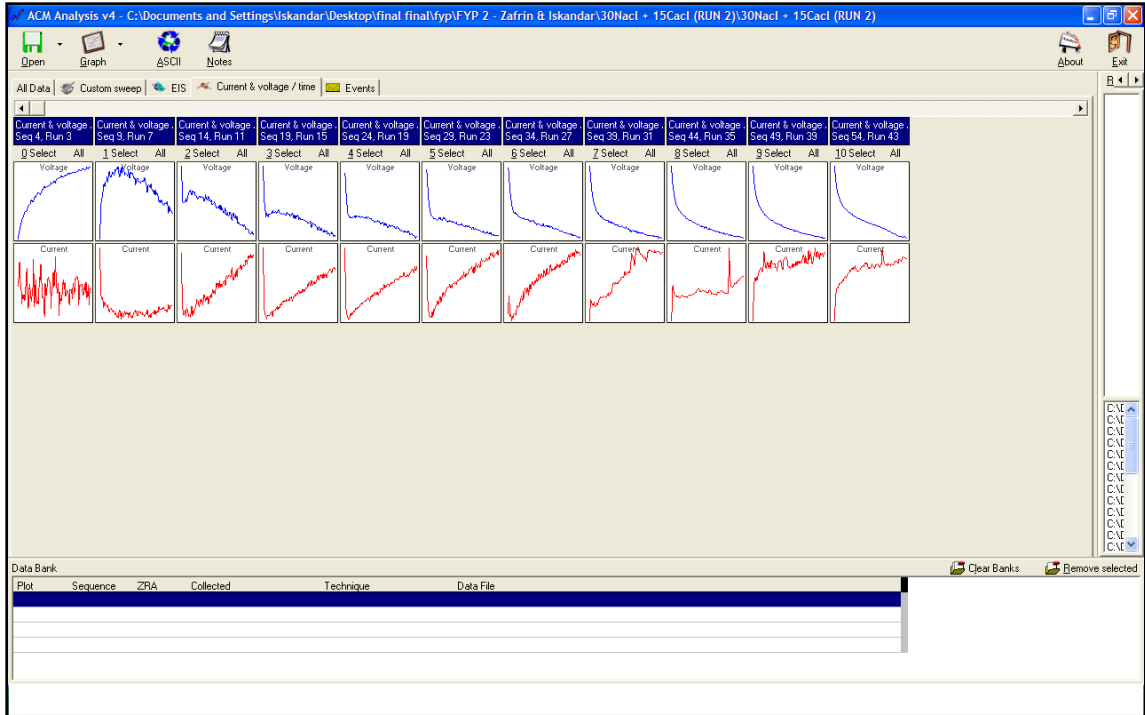
- i. SEM analysis is required to verify the existence of coating layer by CaCO_3 and the pitting form on the metal surface. In this situation the formation of pitting corrosion can be observed physically.
- ii. More lab work required to verify the result - this can be conducted by running using another approach such as EIS and LPR.
- iii. The studies need to be expanded to other elements such as Mg^+ :in real environment situation, Ca^{2+} is not the only type of ions exist in the environment.
- iv. The result can also be proved analytically and chemically for further research.

REFERENCES

- [1] A. Ikeda, M. Ueda, S. Mukai, Corrosion/85, paper No. 29, NACE, Houston, TX, 1985.
- [2] G. Schmitt and B. Rothmann, *Werkstoffe und Korrosion* 29 (1978), p. 167.
- [3] G. Schmitt, *Advances in CO₂ Corrosion* 1, NACE, Houston, TX (1985) p. 1.
- [4] S.L. Wu, Z.D. Cui, G.X. Zhao, M.L. Yan, S.L. Zhu and X.J. Yang, *Applied Surface Science* 228 (2004) (1–4), p. 17.
- [5] Kewei Gao *, Fang Yu, Xiaolu Pang, Guoan Zhang, Lijie Qiao, Wuyang Chu, Minxu Lu *Mechanical properties of CO₂ corrosion product scales and their relationship to corrosion rates*_Volume 50, Issue 10, October 2008, Pages 2796-2803
- [6] G. Schmitt and S. Feinen, *Effect of Anions and Cations on the Pit Initiation in CO₂ Corrosion of Iron and Steel*, Naces 2000
- [7] X. Jiang, Y.G. Zheng and D.R. Qu., *The Effect of Calcium Ions on Pitting Corrosion and Inhibition Performance in CO₂ Corrosion Of N80 Steel*. *Corrosion Science* 48 (2006) 3091–3108
- [8] Z. Xia, K.-C. Chou and Z. Szklarska-Smialowska, *Corrosion* 45 (1989) (8), p. 636
- [9] James E Miller, *Electrochemical Noise Measurement Techniques for the Determination of Aluminium Alloy Pit Initiation Rates*, Sept 29, 1992.\
- [10] Dawson J L "*Electrochemical Noise Measurements:ASTM STP 1277* (2) Mansfield F and Xiao H *Electrochemical Noise Impedance Analysis of Iron in Chloride media*
- [11] Y.F. Cheng and J.L. Luo, *Journal of the Electrochemical Society* 146 (1999) (3), p. 970.

APPENDICES

Common Result on ECN Data



Data taken on ECN for corrosion by influence of Ca^{2+} ion.

Time (Sec)	Current (mA/cm ²)	Potential (mV)	Resistance (ohm.cm ²)	Potential FFT (mV Hz ^{-½})	Current FFT (mA/cm ² Hz ^{-½})	Frequency (Hz)
0	-0.0073323	-605.79	82620	15826	0.6160962	0.0019531
1	-0.0072827	-605.63	83160	6310.6	0.4253516	0.0039063
2	-0.0072802	-605.47	83168	3360.5	0.3810656	0.0058594
3	-0.0072297	-605.39	83736	2387.2	0.1907628	0.0078125
4	-0.0073084	-605.3	82823	1818.3	0.6272869	0.0097656
5	-0.0073056	-605.18	82838	1289.2	0.2774056	0.0117188
6	-0.0071875	-604.98	84172	1093.5	0.2090155	0.0136719
7	-0.0069919	-604.87	86511	817.68	0.1451188	0.015625
8	-0.0068344	-604.87	88504	812.21	0.0727092	0.0175781
9	-0.0067442	-604.85	89685	663.59	0.2089019	0.0195313
10	-0.0069507	-604.8	87013	559.47	0.2648699	0.0214844
11	-0.0073287	-604.57	82494	404.46	0.1558737	0.0234375
12	-0.0073786	-604.49	81924	383.3	0.0879219	0.0253906
13	-0.0074104	-604.46	81569	332.41	0.1110007	0.0273438
14	-0.0073059	-604.42	82730	293.52	0.1527895	0.0292969
15	-0.007124	-604.35	84833	237.36	0.1540639	0.03125
16	-0.0070293	-604.32	85972	298.53	0.0654984	0.0332031
17	-0.0070341	-604.31	85911	270.03	0.0582078	0.0351563
18	-0.0068046	-604.32	88811	199.18	0.1074747	0.0371094
19	-0.0066458	-604.34	90936	225.17	0.0827378	0.0390625
20	-0.0065738	-604.29	91924	199.99	0.0653635	0.0410156
21	-0.0062713	-604.28	96358	227.97	0.0782516	0.0429688
22	-0.0061553	-604.26	98170	150.7	0.0448435	0.0449219
23	-0.0063474	-604.06	95167	142.56	0.1014881	0.046875
24	-0.0065757	-603.78	91821	149.46	0.0321921	0.0488281
25	-0.0067073	-603.72	90011	135.32	0.0943055	0.0507813
26	-0.0068421	-603.72	88236	146.38	0.0250449	0.0527344

Some data extracted for the ECN graph to be analysed by using Microsoft Excell