In-situ Chlorine Generation for Water Disinfection

by

HAIRUL AKMAL BIN MOHD YUSOFF

Dissertation report submitted
in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

JULY 2008

Universiti Teknologi Petronas
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

In-Situ Chlorine Generation for Water Disinfection

by

Hairul Akmal Bin Mohd Yusoff

A project dissertation submitted to the

Civil Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CIVIL ENGINEERING)

Approved by,

_____

(Assoc. Prof. Dr. Mohamed Hasnain Isa)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

_____
HAIRUL AKMAL BIN MOHD YUSOFF

ABSTRACT

An intimate knowledge of available disinfection processes is a prerequisite in selecting the most appropriate system. This report is to decide on an in-situ chlorine generation and its effectiveness to be use in water disinfection. This technology is to eliminate the hazards of transportation and storage. Also this alternative technology is to lower the probability of workers exposure to the potential discharge of a toxic vapor cloud resulting from an attack on chlorine storage room. There are several types of disinfection that could be generated on-site which are chlorine gas, chlorine dioxide and sodium hypochlorite. The suitable particular type of on-site generator in this report is sodium hypochlorite. The sodium hypochlorite was generated in an electrochemical cell. The electrodes used were MMO-coated titanium as the anode and titanium as the cathode. The results show that the MMO-coated titanium anode has better performance than graphite anode. The MMO-coated titanium anode was also better than Ti/RuO_2 anode. Under the following conditions, a concentration of as high as 45.42 g/l Cl_2 of Free Available Chlorine was obtained, surface area of the anode; 15 cm^2, inter-electrode gap, 0.5 cm; current density, 200 mA/cm^2; concentration of NaCl aqueous solution, 2M; and time, 120 minutes.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Disinfection technologies are improved and readily available. The differences of their common use are based on their strengths and weaknesses in treating municipal drinking and wastewater. Final decision on a disinfection process depends on its effectiveness concurrent with increasing regulations (*Fleming and Huebner, 2001*).

The most commonly used disinfectant in the drinking water treatment industry is chlorine. Today, chlorine is used as a primary disinfectant, more than 63 percent being used as a pre-disinfectant and as a post disinfectant in more than 67 percent of all surface water treatment plants. (*USEPA, 1999*)

In-site chlorine generation technologies include; chlorine gas, sodium hypochlorite, and chlorine dioxide with a few related treatment processes are covered briefly in this report.

Chlorine gas (Cl_2) is usually produced at a plant and shipped as a liquid in pressurized bulk containers to water treatment plants. These containers range in size from rail tank cars to road tank truck. Briefly, there are potential hazards present in transportation and storage. Chlorine dioxide (ClO_2) is one of the selective oxidizing agents widely used in pulp bleaching, water disinfection and numerous other applications. This chemical is also better in removing iron and manganese that exist.. Due to its inherent instability, it cannot be transported and, therefore, it is produced in-situ at the point of use. Unfortunately, in-situ chlorine dioxide generation needs skilled operators, additional chemical storage and need further laboratory analysis which increases the operation

1

cost. Sodium hypochlorite (NaOCl) is considered the second cheapest disinfectant after chlorine gas (bulk liquid). Commercially, it is used as disinfectant, oxidizing agent and residual disinfectant. Compared to chlorine gas, sodium hypochlorite does require being transported or stored and cause hazards but it tends to decompose in storage depending on storage temperature, its age, concentration and contaminants it may contain (*Fleming and Huebner, 2001*). Based on Table A.1 in the Appendix A, cost to have sodium hypochlorite (NaOCl) generated on-site is lower than Cl_2 on-site. The capital cost is little higher than Cl_2 but it saves on the operating and maintenance costs.

There are other disinfectants/oxidants that have been used such as chloramines, ozone peroxide blends, bromine chloride, ultraviolet (UV) radiation and potassium permanganate (*Spellman, 1999*). However, their current level of use is relatively minor due to cost or operational complexity. These disinfectants's effectiveness along with some related application process is shown in the Appendix A (Table A.2). Chlorination is the only method that persists long enough to keep water germ-free right up to the tap while other alternative disinfectants work barely for short term. Another distinct advantage is that it can be used with relatively simple techniques and at low costs, which makes chlorination a particularly appropriate disinfection technique for lesser-developed countries (*Wijk, 2002*).

1.2 Problem Statement

1.2.1 Problem Identification

The most commonly used disinfection process is chlorination. The conventional chlorination methods have their associated hazards. These include hazards present in transportation, storage and also the probability of workers exposure to the potential discharge of a toxic vapor cloud resulting from an attack or accident at a chlorine storage room.

2

1.2.2 Significance of the Project

The generation of chlorine on-site will minimize hazards present in its transportation, storage, use, high safety risk in plant and in reducing the maintenance and power cost. The effectiveness of disinfection depends on the type of disinfectants used.

An ideal in-situ disinfection technology (*USEPA, 1999*):

- Kills all potential pathogens in the water
- Adds no toxic compounds to the water
- For potable water, provides lasting residual disinfectant without excess chemicals
- Is safe, easy and inexpensive to use
- Meets current and upcoming regulations

1.3 Objectives of Study

The main objectives of this project are:

1. To determine the suitable in-situ chlorine generation method and its effectiveness in water disinfection.
2. To find the optimum operating conditions, i.e. concentration of electrolyte, reaction time and current density.
3. To treat the water in a safe and environment friendly manner.

1.3.1 Scope of Study

This study is focused on the in-situ hypochlorite ion generation with different electrodes and combination of different levels of current density, electrolyte concentration and reaction time (electrolysis). The scope of study is as follows:

1. The study was carried out in batch electrolytic cell (reactors).
2. Current density of 1 to 200 mA/cm^2 was tested for hypochlorite production efficiency.
3. The brine solution concentration used was 1, 2, and 3 g/l.
4. The effective area of anode and cathode used was 15 cm^2 each.
5. In the optimization, current density of 50 to 200 mA/cm^2 and electrolyte of 0.04, 1.02 and 2 M were used.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Theory of Disinfection

Disinfection process is applied to reduce the number of pathogenic microorganisms. Coagulation-flocculation-sedimentation and filtration (Fig. 2.1) of water treatment processes are not intentionally designed for pathogen reduction.
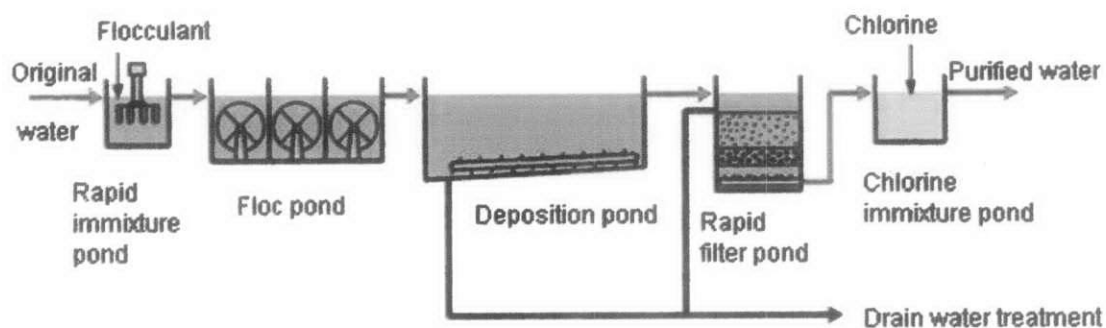
Figure 2.1: Conventional water system

2.2 Scenario

The transport of chlorine or hypochlorite by road (Figure A.1, Appendix A) or rail poses serious environmental hazard and legislation is now being introduced in many countries which would prohibit the transport of these materials (*Robertson and Gnehm, 1983*). The trend is therefore for on-site generation.

Chlorine is transported and stored as liquid under high pressure. If it was released in the atmosphere, it could quickly vaporize into a toxic gas cloud nearly 500 times its pressurized volume (*Gautrin et, al., 1999*)

The hazard presented by a toxic substance depends on the exposure conditions and on the chemical itself. It ranges from a sudden brief exposure at high concentration to prolonged exposure at low concentrations over a working life (*Lees, 1996*). Toxicity is a general term used to indicate the adverse effects (Table 2.1) produced by poisons. These adverse effects can range from slight symptoms like headaches or nausea to severe symptoms such as coma, convulsions and death. A few examples are the explosive rupture of a process vessel as a result of excessive pressure caused by a runaway reaction, the rupture of a pipeline containing toxic materials at high pressure, the rupture of a tank containing toxic material stored above its atmospheric boiling point, and the rupture of a train or truck transportation tank following an accident (*Crowl and Louvar, 2001*).

Table 2.1: Chronic Respiratory Symptoms in Workers at Risk of Chlorine Exposure

	At least one symptom		Wheezing		Shortness of breathe		Symptom on exercise	
	N	%	N	%	N	%	N	%
Absent on both assessments	159	75.4	178	84.4	197	93.4	191	90.5
Present in 1992 and absent in 1994	16	7.6	9	4.3	4	1.9	8	3.8
Absent in 1992 and present in 1994	19	9.0	14	6.6	5	2.4	9	4.3
Present on both assessments	17	8.1	10	4.7	5	2.4	3	1.4

(Source: Gautrin et, al., 1999)

On April 11, 1996, 19 cars from a Montana Rail Link (MRL) freight train derailed near Alberton, Montana. Six of the derailed cars contained hazardous materials. One derailed tank car containing chlorine (a poison gas) ruptured, releasing 130,000 pounds of chlorine into the atmosphere and another tank car containing potassium hydroxide solution (potassium cresylate, a corrosive liquid) also a covered hopper car containing sodium chlorate (an oxidizer) spilled 85 dry gallons onto the ground (Figure 2.2). This chlorine spill is the second largest in US history.

About 1,000 people from the surrounding area were evacuated. Approximately 350 people were treated for chlorine inhalation, 123 of whom sustained injury. Nine people, including both members of the train crew, were hospitalized. A transient riding the train died from acute chlorine toxicity. U.S. Interstate Highway 90 (I-90) is roughly parallel and about 150 yards north of the MRL tracks at the accident site. The hazardous material cloud drifted across I-90 resulting in multiple highway traffic accidents. Several motorists were stranded in the cloud after these accidents. I-90 was closed following the accident requiring an 81-mile detour. Monetary damage was estimated to be $3.9 million. The Governor of Montana declared a state of emergency in Missoula and Mineral Counties. After 3 days from the day of incident, the evacuation area was reduced to 15 squares (*NTSB 1998*).

Two separate incidents that occurred within one week are the only two state emergency declarations for hazardous material release which were the Alberton Chlorine Spill and derailment involving a chlorine tanker car near Dodson (Table 2.2). The Dodson derailment did not cause a release of the chlorine.

Table 2.2: State and Federal Declarations for Hazardous Materials in Montana, 1974 to 2003

Incident	Date	Spill	Cost
Train Derailment at Alberton, MT (EO 8-96)	4/11/96	3 Chlorine tank cars	State: $417
Train Derailment Philips County, Dodson (EO 9-96)	4/17/96	Chlorine tanker	State: $3,806

(Source: MDES, 2003)
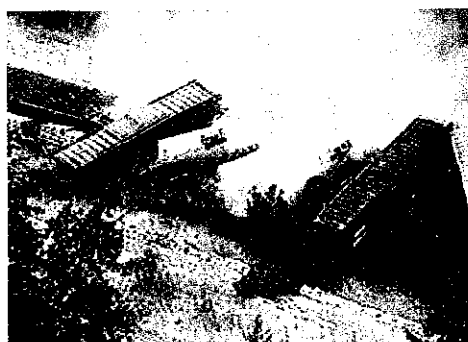
Figure 2.2: Alberton Derailment, Chlorine Gas Release

2.3 History of Chlorine and Technologies

In 1908, disinfection of water by chlorine first occurred at Bubbly Creek (Chicago) and the Jersey City Water Company. Chlorine was introduced as a disinfectant at many places and other smaller treatment plants within two years (*Haas, 1999*). Chlorine also prevents the growth of biofilm (algae in pipes and slime formation in storage tanks) (*Wijk, 2002*).

Chloramination is produced by the addition of both chlorine and ammonia either simultaneously or sequentially. Pre-reaction of two chemicals added to the full flow of water in their early application. Pre-ammoniation (the addition of ammonia prior to chlorine) was developed later. In both cases, the process was advocated and for its ability to prolong the stability of residual disinfectant during distribution and for diminished propensity to produce chlorophenolic taste and odor substances. Free chlorine recognized as disinfectant due to shortage of ammonia during World War II reduced the popularity of chlorimination (*Wolfe et, al., 1984*).

Large gaseous chlorination systems pose a health risk to facility operators and a potential risk to military personnel and the public due to chlorine's inherent toxicity. These systems are already required to have in place accidental release prevention and emergency response programs that Protection Agency (EPA), and state regulations to ensure safe water and protection of the environment. Numerous treatment plants established the conversion of water and wastewater treatment system from gaseous chlorine (bulk) to an alternative technology which is in-situ generation technology in corroboration of the requirement (*Leslie et, al., 1998*).

Chlorine is effective against all types of microbes, (including bacteria, viruses, moulds and spores). It is easy to use, low cost and widely available. Chlorine has been used for more than a century to disinfect water and with a promising world population will continue to play an essential role in protecting public health during the 21st century (*Wijk, 2002*).

2.3.1 Chlorine Gas

In the United States about 70 percent of the chlorine is produced from the electrolysis of salt brine and caustic solutions in a diaphragm cell. Chlorine is typically produced off-site by a chemical manufacturer because of its stability. Once produced, chlorine is packaged as a liquefied gas under pressure for delivery to the site in railcars, tanker trucks, or cylinders (*White, 1992*).

2.3.2 On-site Generation of Chlorine Gas

The methods use electrolysis with membrane cells as in Fig. 2.3 and brine (sodium chloride). High capital cost problems as well as the cost for operation and maintenance leads to unsuccessful attempts of this method. One successful method that applies electrolysis of hydrochloric acid in an electrochemical cell is ElectroChlor process which produces chlorine gas on demand. Rate of chlorine gas produced controlled by automatic controls permit variation to suit the need of water treatment plants. Many treatment plants have turned into on-site chlorine gas generation to avoid the potential hazards of a chlorine gas leak (*Fleming and Huebner, 2001*).
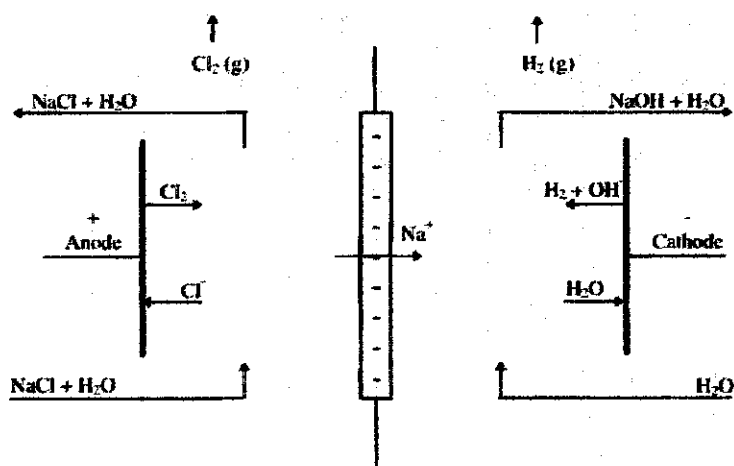
Figure 2.3: Schematic representation of a cell unit in the chlor-alkali process

9

An electrolytic chlorine gas generating system includes an electrolytic cell generating the chlorine gas, a brine tank supplying saturated brine to the anode compartment of the cell, and an acid feed tank containing hydrochloric acid at sufficient concentration to maintain the anolyte brine at less than about pH 4.0. In operation, the brine tank contains solid sodium chloride which dissolves in the brine and replenishes the anolyte brine solution as chloride ion (Cl⁻) is consumed during electrolysis (*Lynn et al., 1994*).

2.3.3 On-Site Generation of Sodium Hypochlorite

Sodium hypochlorite (NaOCl) offers an excellent alternative approach to disinfection. The active ingredient in the compounds is the hypochlorite ion (OCl⁻), which hydrolyzes to form hypochlorous acid (HOCl) (*Fleming and Huebner, 2001*). Dilute sodium hypochlorite solutions (less than 1 percent) can be generated electrochemically on-site from salt brine solution (*Gordon et al., 1995*). It uses the electrolysis of a dilute brine solution in a low voltage cell. This produces a 0.8 percent solution of sodium hypochlorite that is stored in a holding tank and fed into the process by a metering pump. The 0.8 percent solution is not subject to decomposition compared to12.5 percent chemical solution. However it can produce bromates if bromide impurities exist in the salt brine (*Fleming and Huebner, 2001*).

The cell which consists of an anode and a cathode without a separator or diaphragm as in Fig. 2.4 employed for this purpose are the same as those used in chlorine gas generation. The anodic and the cathodic reactions are the same as in chlor-alkali as in Fig 2.3, the difference being the pH of the electrolyte, which is maintained in the range of 10 to 12. The schematic electrolytic generated chlorine reacts with sodium hydroxide to form sodium hypochlorite is shown in Fig 2.4. The OCl⁻ formed in the bulk is easily reduced at the cathode to reform Cl⁻ (*Bommaraju et, al., 2001*). The stability of sodium hypochlorite solution depends on the hypochlorite concentration, the storage temperature, the

10

length of storage (time), the impurities of the solution, and exposure to light. Decomposition of hypochlorite over time can affect the feed rate and dosage, as well as produce undesirable byproducts such as chlorite ions or chlorate (*Gordon et al., 1995*).
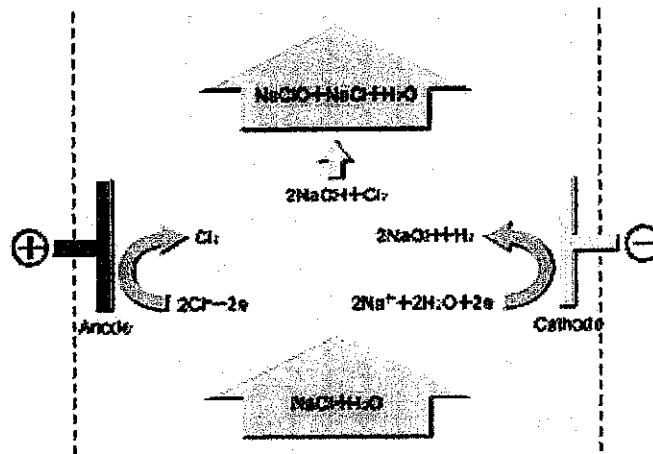
Figure 2.4: Schematic representing electrolysis in producing NaOCl

Equipment to produce sodium hypochlorite on site has a high initial capital cost and requires periodic replacement of electrodes as well as de-scaling of the cell. The approximate costs between the chlorine gas and sodium hypochlorite are in the appendix (Table A.1). Its generation on-site may be cheaper than bulk methods depending on brine and power costs impelling many municipalities in using this method of on-site generation (*Fleming and Huebner, 2001*).

Power stations are significant users of on-site generation systems; however the technology has not been as widely utilized in Water Treatment Plant (*Hooper, 2005*). The sodium hypochlorite usually safely stored in a day tank as in Fig. 2.5. The system automatically restarts to replenish its supply when hypochlorite in storage reaches the low-level set point (*Hopper, 2005*). Due of the storage problems, many systems are investigating on-site generation of hypochlorite in lieu of its purchase from a manufacturer or vendor (*USEPA, 1998b*)

11
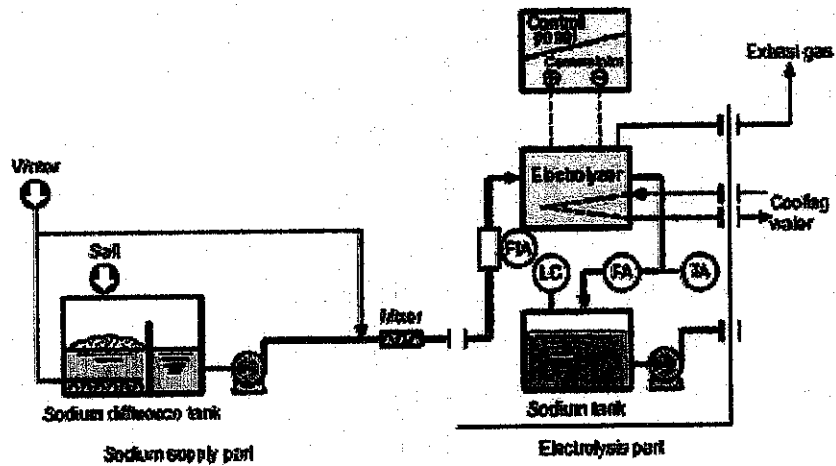
Figure 2.5: Schematic on flow of NaOCl production

2.3.4 Chlorine Dioxide

Chlorine dioxide (ClO_2) is usually produced on site by mixing chlorine gas with sodium chlorite ($NaClO_2$). It is recognized as an efficient oxidizer and a broad-spectrum, fast acting biocide. It also is used where only short contact time is available. One desirable characteristic of chlorine dioxide is it does not react with naturally occurring organic matter in the water to produce trihalomethanes (THMs) and haloacetic acids (HAAs) as chlorine does. It also does not react with bromides to form bromates as ozone does. The chemical also has a long track record in removing iron and manganese which exists in complex chemical compounds (*Fleming and Huebner, 2001*).

Chlorine dioxide can produce undesirable by-products like chlorites (ClO_2^-) and chlorates (ClO_3^-). Since, 80 percent of the chlorine dioxide is converted to chlorite; there is a limit of maximum practical dosage with this chemical. Chlorine dioxide as well cannot be transported as a compressed gas (*Fleming and Huebner, 2001*).

Chlorine dioxide must be generated on-site because it is an unstable compound in air at concentration above 10 percent by volume. Therefore it is always

12

generated on-site in an aqueous solution that could be stored up to seven days. This chemical decomposes if exposed to sunlight (*Leslie et, al., 1998*). The conventional chlorine dioxide generation process uses chlorine gas as feed to generate chlorine dioxide through the following reaction:

$$NaClO_2 + \frac{1}{2} Cl_2 \rightarrow ClO_2 + NaCl \qquad [1]$$
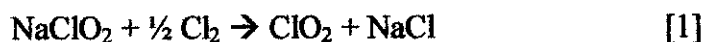
There is a chlorine dioxide system, which is very new to the market, employs an electrolytic cell, a gas pore membrane, and recirculation to produce pure chlorine dioxide from an aqueous solution of sodium chlorite. This new system has the advantage of having a single chemical feed and uses membrane separation to prevent any excess sodium chlorite and sodium chlorate (formed via side reactions) from contacting the resulting disinfected water (*Leslie et. al., 1998*). The chemical reaction involved in this process is:

$$NaClO_2 + H_2O \rightarrow ClO_2 + NaOH + \frac{1}{2} H_2 \qquad [2]$$

Findings and recommendation on chlorine dioxide (*Spellman, 1999*):

- Chlorine dioxide does not have significant of use treatment of municipal wastewater
- Chlorine dioxide generate on-site is much more expensive than elemental chlorine
- Chlorine dioxide has several safety-related problem; it is dangerous because two gases (chlorine and sodium chlorite) must be handled
- No one at the Authority has any experiences using chlorine dioxide

Based on the findings, chlorine dioxide is not a proven disinfectant alternative for wastewater. Chlorine dioxide is also not suitable for use in potable water and small drinking water plant in term of cost.

2.4 Salinity

Good indicators of NaCl concentration of electrolyzed oxidizing water (EOW) were conductivity and salinity. Study also had shown that 46 percent of Cl⁻ remained in the EOW after electrolysis (*Hsu, 2003*). High salt concentration of input solution resulted in high salt concentration and high conductivity of electrolysis. Figure 2.6 and 2.7 show that electrical conductivity and salinity of the EOW increased linearly with increases in salt concentration of the input (anode-side) solution (*Hsu, 2005*). The high conductivity and high salt concentration force extra OCl⁻ to be produced; therefore if the salt concentration in input solution is controlled then the required concentration of hypochlorite could be determined.
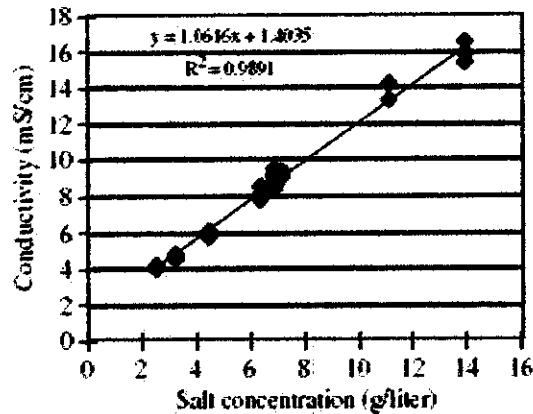
Figure 2.6: Changes of EO water conductivity with respect to salt concentration of input solution
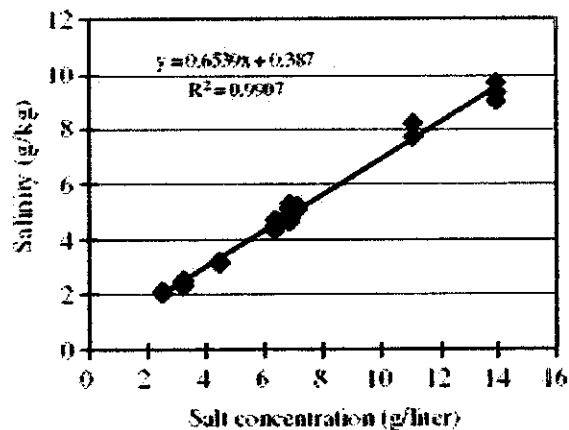
Figure 2.7: Changes of EO water salinity with respect to salt concentration of input solution

14

2.5 Water Temperature and pH

Electrolysis decrease pH probably due to generation of chlorine gas, hypochlorous acid and hydrochloric acid. Many of the EOW generators had been designed to control pH by direct control of the electric voltage of the electrolysis process (*Hsu, 2005*).

Total residual chlorine was significantly affected by salt concentration and water temperature. In Fig 2.8, total residual chlorine increased with increase of salt concentration, while effects of temperature were small probably due to the small range that was tested in the study (*Hsu, 2005*). It is recommended to work at lower temperature than 40°C and at alkaline pH in order to prevent the formation of chlorates (*Khelifa et, al., 2004*).
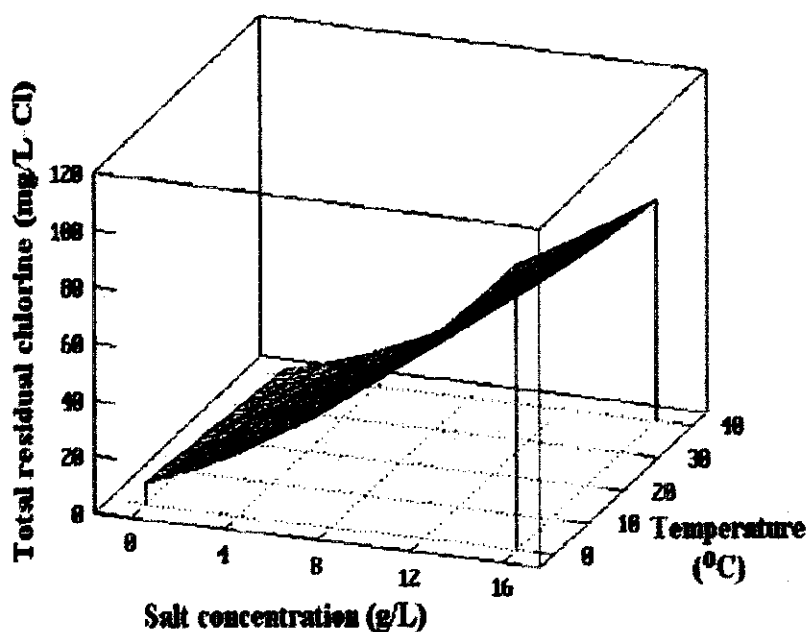
Figure 2.8: Total residual chlorine concentration of EO water with respect to salt concentration and temperature of input solution

2.6 Cell Parameters

2.6.1 Effects of S_a/S_c

The effects of the ratio of the surface areas of the electrodes on active chlorine production are shown in Fig 2.9. The electrodes were titanium oxide-coated titanium anode and titanium cathode. The active chlorine (AC) rose almost linearly by increasing S_a. An optimal ratio S_a/S_c of 1.33 was found for maximum values of AC. This proved that a larger S_a to a smaller S_c would enhance the AC because a larger S_a would promote the conversion of Cl⁻ into OCl⁻ (*Khelifa et, al., 2004*).
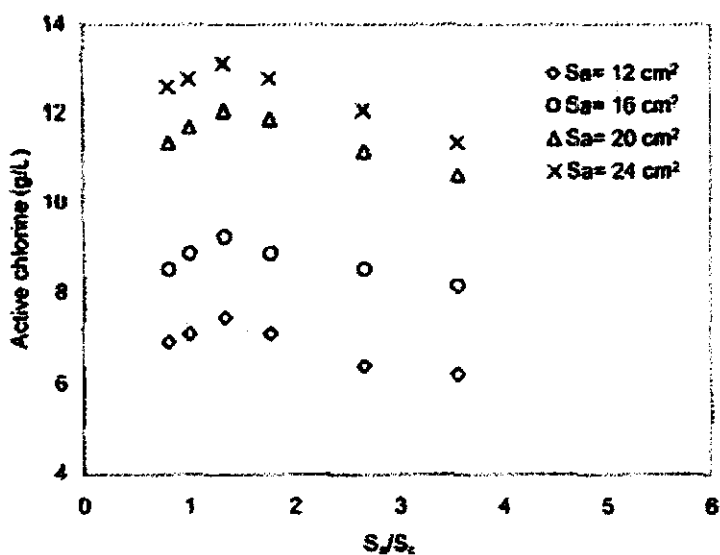
Figure 2.9: Effect of Sa/Sc ratio. Current density, 10 A/dm²; NaCl concentration, 2 M; temperature 20°C

16

2.6.2 Inter-Electrode Gap

Variations of AC as function of inter-electrode spacing for Sa/Sc equal to 1.33 are shown in Fig 2.10. The AC decreased as the inter-electrode distance increased. Shorter distance would favor the conversion of Cl⁻ into OCl⁻ and lead to higher current density. An inter-electrode gap shorter than 0.8 cm provided the optimal conversion of Cl⁻ into ClO⁻ (*Khelifa et, al., 2004*).
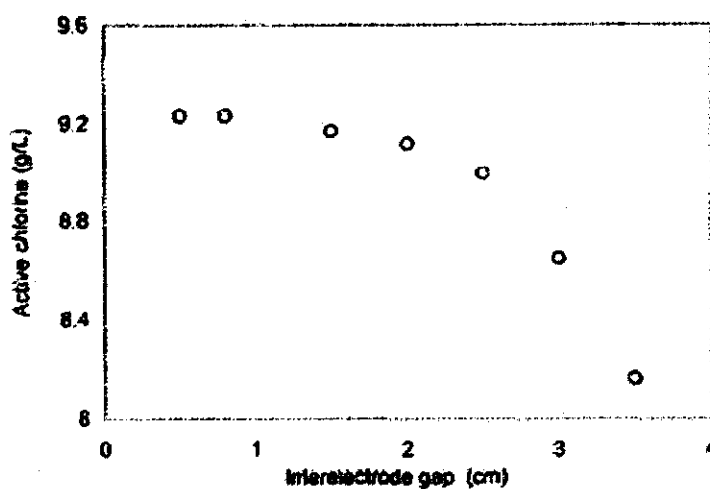
Figure 2.10: Effects of the inter-electrode gap. Current density, 10 A/dm^2; NaCl concentration, 2 M; temperature 20°C

2.6.3 Current Density

Variations of the AC production with current density by using different electrodes of anodes are shown Fig 2.11. The electrodes were tested using ruthenium oxide-coated titanium (Ti/RuO$_2$), platinum-coated titanium (Ti/Pt) and graphite. It shows that graphite anode could not tolerate a larger current density than 20A/dm^2. The AC production rose almost linearly with current density for the other two anodes. Both electrodes also could sustain higher current densities and increased the efficiency (*Khelifa et, al., 2004*).
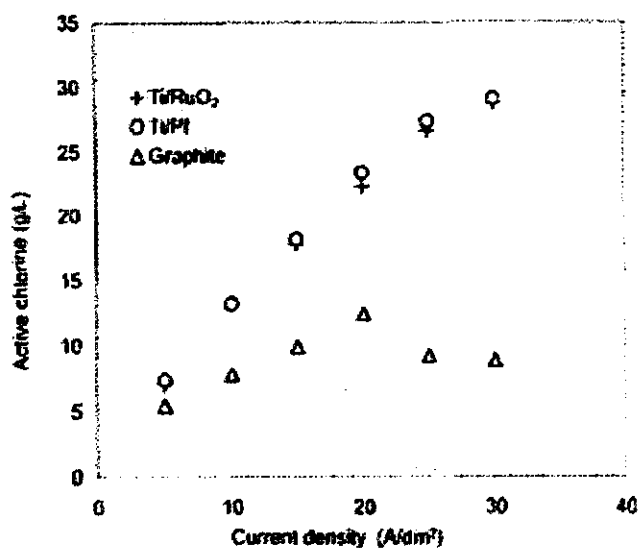
Figure 2.11: Effect of the current density as a function of the nature of the anode. NaCl concentration, 2 M; temperature 20°C; electrolysis time, 1h

2.6.4 Electrolysis Time

The result in the Fig 2.12 shows that the AC increased to reach maximum values and dropped negatively afterward. Ti/Pt and Ti/RuO$_2$ anodes were observed to have better performance in term of active chlorine production and current efficiency. Both electrodes produced additional AC as the time increased subsequently, the AC concentration decreased due to promoting the formation of chlorates (*Khelifa et, al., 2004*).
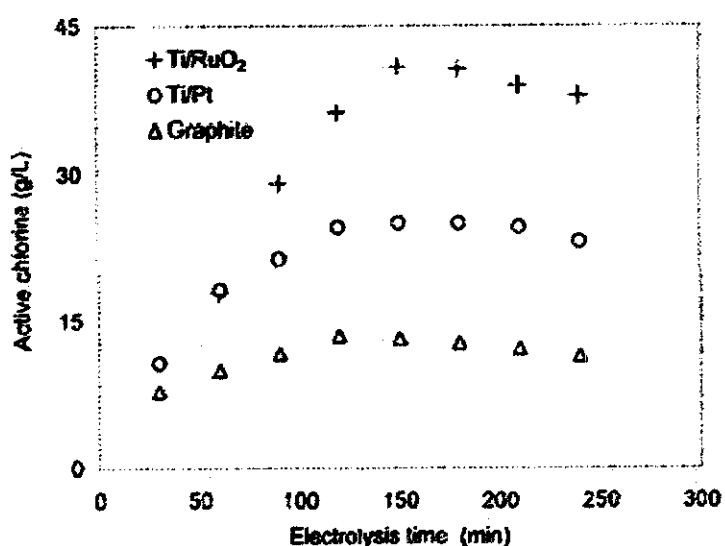
Figure 2.12: Effects of electrolysis time as a function of the nature of anode. Current density, 15 A/dm^2; NaCl concentration, 2 M; temperature 20°C

CHAPTER 3

METHODOLOGY

3.1 Materials

3.1.1 Sodium Chloride

The raw material used to produce chlorine which itself is required for the production of many modern materials including PVC and pesticides. Industrially, elemental chlorine is usually produced by the electrolysis of sodium chloride dissolved in water. The purity of sodium chloride used was 99 percent.

3.1.2 Electrodes

Experiments were carried out using different configurations of electrodes. Types of electrodes used were rod and plate Mixed Metal Oxide (MMO) coated-titanium anode (Appendix D), and rod and plate titanium cathode, plate graphite anode and rod titanium cathode. The effective surface area of each electrode was $15cm^2$. The advantages of using titanium electrodes were to resist corrosion, save power, reduce maintenance cost and also to avoid product contamination.

3.2 Methods

Basically, experimental setup for chlorine gas and sodium hypochlorite is identical (electrochemical or electrolysis) however the concentration of brine solution that would be used is poles apart. Weak brine solution is used for sodium hypochlorite generation whereas strong brine solution for chlorine gas. Free Available Chlorine (FAC) was determined by the DPD method (section 3.2.3).

3.2.1 Brine Solution

NaCl solutions of 1, 2 and 3 g/l were prepared by dissolving appropriate amounts of NaCl in distilled water.

3.2.2 Electrolytic Cell

1. Experiments were conducted with 1, 2 and 3 g/l NaCl solutions in a bench-top electrolysis cell with a working volume of 250 ml.

2. Experimental setup was connected with a regulated DC power supply and an ammeter using wire and crocodile clips (Figure 3.1).
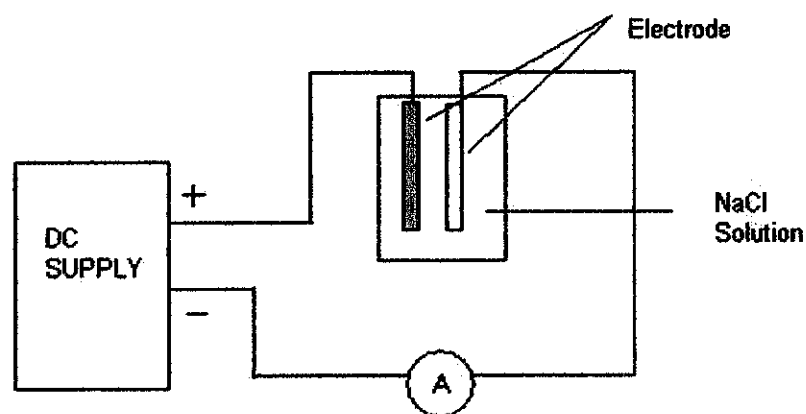
Figure 3.1: Schematic diagram of experiment setup

21

3. The MMO-coated titanium anode and titanium cathode were positioned vertically and parallel to each other with an inter electrode gap of 0.5 cm.

4. The DC power was switched on and the voltage was regulated to the required current densities of 1 to 200 mA/cm^2.

5. At the same time, a stopwatch was started to determine the electrolysis time.

6. 10ml samples were withdrawn at 20, 40 and 60 minutes for analysis. Analysis was done by the DPD method (section 3.1.3)

7. The above steps were repeated using different configurations of electrodes i.e. combination of MMO-coated titanium plate anode and graphite cathode; MMO-coated titanium plate anode and graphite plate cathode; and graphite anode and titanium cathode.

3.2.3 DPD Method

This method uses HACH Spectrophotometer (DR 2800) (Figure B.4 - Appendix B) for testing free chlorine (hypochlorous acid and hypochlorite ion) in water and treated water.

1. Program was stored.

2. Test number 80 chlorine, F&T PP was selected.

3. Blank preparation: A square sample cell was filled with 10ml sample

4. The blank was cleaned with tissue and inserted into the cell holder with the fill line facing right.

5. Zero buttons was pressed. The indicator had shown 0.00 mg/l Cl_2.

6. Second square cell was filled with 10ml of sample. The sample cell was added with the content of one DPD Free Chlorine Pillow.

7. The sample cell was swirled for 20 seconds to mix. A pink color developed.

8. The sample was inserted into the cell holder within 1 minute of adding the reagent. Read button was pressed.

9. Result was shown in mg/l Cl_2.

3.3 Design Expert 6.0

The Design Expert software requires a methodological approach, particularly in terms of the definition of a system response and of the factors affecting this response and their respective domains of variation. In the present case, the amount of Free Available Chlorine produced in mg/l Cl_2 was taken as the system response, and the considered variables were the most influencing parameters. The total numbers of 27 experiments per set combination of electrodes (Table 3.1) were carried out. Table 3.2 shows the different factor levels and combinations that were analyzed using the Design Expert software.

Table 3.1: Types of electrodes

Anode	Cathode
Graphite	Titanium
MMO-coated titanium	Titanium

Table 3.2: Data for operation

Variable	Factor	Level (-1)	Level (0)	Level (+1)
A	NaCl concentration, g/l	1	2	3
B	Current density, mA/cm^2	1	2	3
C	Electrolysis time, min	20	40	60

Three factors were considered, each having the low, medium and high levels designated by (-1), (0) and (+1), respectively, that defined the domains of variation. The two levels factorial appeared to be most appropriate for this particular study.

The Design Expert 6.0 software was used to design and optimize the experimental conditions. Features of the software were:

- Two-level factorial screening studies – Identify the vital factors that affect the process for the improvements.
- General factorial studies – Discover the ideal combination of categorical factors and identify the vital factors that affect the process or product.
- Response Surface Method (RSM) – Find the ideal process settings in order to achieve an optimal performance.
- Mixture Design Techniques – Discover the optimal formulation.
- Combination of process factors, mixture components, categorical factors – Tailor DOE to what information is required.

Design Expert software offers rotatable 3D plots for visualization of response surfaces. It cal also set the flags and explore the contours on interactive 2D graphs. The numerical optimization function finds maximum desirability for up to dozens of response simultaneously.

Design Expert software also provides various graphs to help interpret the model selected. In the Response Surface Method, the primary graph will be the contour and 3D surface. Both methods show any two factors affect the response and focus on the effects of the significant terms.

The optimization module in the Design Expert searches for a combination of factor levels that simultaneously satisfy the requirement placed on each of the response and factors. Optimization of one response or the simultaneously optimization of multiple response can be performed graphically or numerically. Usually graphical optimization was used to display the area of feasible response values in the factor space according to the setting of graphical optimization criteria limits. Regions that do not fit the optimization criteria are shaded and else that satisfied the multiple constraints on the responses.

24

3.4 Health, Safety and Environment

Chlorination reactions are part of various processes in the chemical industry, to manufacture heavy chemicals, specialty chemicals, pesticides and pharmaceuticals, in inorganic and organic chemistry.

In each laboratory, additional hazards need to be addressed. Special attention to the proper storage must be taken care of in safety practices. First aid plays main role in treating minor accidents such as burns. In terms of fire, do not run because this only fans the flames. The drop and roll technique is the finest way to get free from fire in case fire blankets are unavailable (*Buzzi, 1992*).

Gas phase explosion hazard with chlorine as an oxidizer is present in the production of chlorine by electrolysis, in gas phase chlorination processes and in chlorination reactions carried out in the condensed phase. When chlorination is carried out by chlorine injection in the liquid phase, gas phase explosion hazard is related to chlorine evolution in the vapour phase, giving a flammable mixture with the solvent or reaction mixture vapour. Hazard assessment is achieved by comparing the gas phase composition with the flammable area of the gaseous mixture. Self-ignition is also considered because the self-ignition temperature of gaseous fuels in chlorine atmosphere is lower than in air or oxygen and often close to the ambient temperature (*Gustin, 2005*).

3.5 Hazard Analysis

3.5.1 Sodium Chloride

1. Physical data
   - Molecular weight: 58.44g
   - Chemical formula: NaCl
   - Colour: White
   - Physical form: Powder
   - Common synonyms: Salt; Rock Salt; Saline; Table Salt

2. Toxicology
   - May cause mild irritation to the respiratory tract if inhaled
   - Very large doses can cause vomiting, diarrhea, and prostration if ingested.
   - May irritate damaged skin; absorption can occur with effects similar to those via ingestion.
   - Causes irritation, redness, and pain to eyes.

3. Personal protection
   - Wears safety glass and lab coat

4. Occupational release
   - Keep in a tightly closed container, stored in a cool, dry, ventilated area.
   - Protect against physical damage.
   - Containers of this material may be hazardous when empty since they retain product residues.
   - Observe all warnings and precautions listed for the product.
   - Keep unnecessary people away, isolate hazard area and deny entry.

3.5.2 Sodium Hypochlorite

1. Physical data
   - Formula weight: 74.44g
   - pH: 9 for 0.8% NaOCl, 13 for 12.5% NaOCl
   - Common synonyms: Hypochlorous acid, Sodium salt or Clorox
   - Flammability: Slight
   - Reactivity: Slight

2. Toxicology
   - Warning causes burns
   - Harmful if swallowed
   - Irritating to eyes
   - Irritating to respiratory system

3. Personal protection
   - Wears safety glass and lab coat
   - Adequate ventilation
   - Keep in tightly closed container
   - Wash hand thoroughly after handling

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Graphite Anode

4.1.1 Analysis of Variance (ANOVA)

The ANOVA includes a full analysis of variance, prediction equations, and case statistics. Table 4.1 shows the analysis of variance for the electrode combination of graphite anode and titanium cathode. The Model F-value of 8.49 implies the model is significant. There is only a 0.25% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, C, are significant model terms.

Table 4.1: Analysis of Variance (Partial sum of squares)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Block	30.97	5	6.19		
Model	47.69	2	23.85	8.49	0.0025
A	17.01	1	17.01	6.06	0.0242
C	30.68	1	30.68	10.92	0.0039
Curvature	2.11	1	2.11	0.75	0.3974
Residual	50.58	18	2.81		
Cor Total	131.35	26			

Std. Dev.	1.68
Mean	4.57
C.V.	36.65

R-Squared	0.4853
Adj R-Squared	0.4281
Adeq Precision	7.5200

The "Curvature F-value" of 0.75 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 39.74% chance that a "Curvature F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 7.520 in the above table indicates an adequate signal.

The ANOVA also simulated equation for the response surface correlation with all model terms. The final equation in terms of coded factors is shown in Eq.[3]:

Free Available Chlorine = $4.52 + 0.97A + 1.31C$ [3]

4.1.2 Model Diagnostic Plots

Table 4.2 shows the diagnostics case statistics for the electrode combination of graphite anode and titanium cathode. The value predicted from the model, generated by using the prediction equation. It includes block and center point corrections, if present. "Residual" is the difference between Actual and Predicted values of each point.

Table 4.2: Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	1.50	2.26	-0.76	0.580	-0.702	0.076	-0.692
2	2.00	2.08	-0.08	0.580	-0.075	0.001	-0.073
3	2.00	3.17	-1.17	0.233	-0.798	0.021	-0.790
4	4.00	3.94	0.06	0.094	0.040	0.000	0.039
5	5.00	5.58	-0.58	0.580	-0.536	0.044	-0.525
6	6.00	5.70	0.30	0.233	0.204	0.001	0.199
7	2.00	2.17	-0.17	0.233	-0.117	0.000	-0.114
8	4.00	5.95	-1.95	0.233	-1.328	0.060	-1.359
9	5.00	3.03	1.97	0.233	1.340	0.061	1.372
10	6.00	3.95	2.05	0.233	1.396	0.066	1.437
11	2.00	3.80	-1.80	0.580	-1.661	0.423	-1.754
12	5.00	4.71	0.29	0.580	0.270	0.011	0.263
13	2.00	3.92	-1.92	0.233	-1.309	0.058	-1.338
14	5.00	5.82	-0.82	0.580	-0.753	0.087	-0.744
15	2.00	2.54	-0.54	0.580	-0.497	0.038	-0.487
16	5.00	4.06	0.94	0.233	0.640	0.014	0.629
17	7.00	7.59	-0.59	0.233	-0.401	0.005	-0.391
18	7.00	7.03	-0.03	0.233	-0.023	0.000	-0.022
19	5.00	3.21	1.79	0.094	1.120	0.014	1.128
20	6.00	6.00	0.00	1.000 #			
21	5.00	3.55	1.45	0.094	0.911	0.010	0.906
22	8.00	5.82	2.18	0.094	1.363	0.021	1.399
23	3.00	5.49	-2.49	0.094	-1.562	0.028	-1.632
24	8.00	5.10	2.90	0.094	1.816	0.038	1.953
25	2.00	3.39	-1.39	0.233	-0.950	0.030	-0.947
26	4.00	4.26	-0.26	0.233	-0.174	0.001	-0.169
27	10.00	9.36	0.64	0.580	0.590	0.053	0.579

Note: Predicted values of center points include center point coefficient.

Case(s) with leverage of 1.0000: Student Residuals, Cooks Distance & Outlier T undefined.

* Case(s) with |Outlier T| > 3.00

Obs with Leverage > 2.00 *(average leverage)

Numerical value between zero and one that indicates the potential for a design point to influence the model fit is called "Leverage". A value of one means that the predicted value will be forced to be exactly equal to the actual value, with zero residual. The sum of the leverage values across all cases equals the number of parameters fit by the model. The maximum leverage an experiment can have is 1/k, where k is the number of times the experiment is replicated. The standard order 20 have values larger than 2 times the average leverage, therefore it was flagged.

Studentized Residual is the residual divided by the estimated standard deviation (Std Dev) of that residual. It measures the number of standard deviations separating tha actual and predicted values.

Cook's distance is a measure of how much the regression changes if the case is deleted. The regression does not changes much since the statistics is in average region. Relatively large values are associated with cases with high leverage and large studentized residuals.

The outlier t statistic is the number of standard deviations between an actual data point and the predicted value at that point using a model based on all of the data except this point. The statistic shows that data point fits in with the other points for this mode, therefore there are no outliers.

4.1.2.1 Normal Plots of Residuals

Figure 4.1 shows that the residuals were normally distributed as they yielded a straight line plot. Some scatter shown with normal data. It also looks definite patterns more like a straight line curve, which indicates that only minor transformation of the response to provide a better analysis.
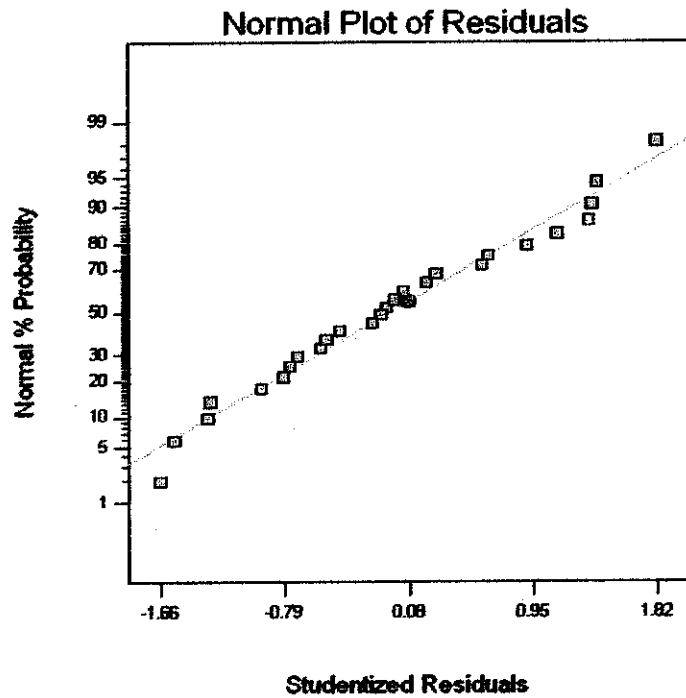
Figure 4.1: Normal Probability versus Studentized Residuals

4.1.2.2 Residuals vs. Predicted

Figure 4.2 shows the plot of the residuals versus the predicted response values for graphite anode. In the above plot, there are some points have the same predicted value within the constant range. All data were in the between constant range of residuals and evenly scattered. This plot implies that the residuals were distributed within constant variance and the expanding in the variance need for a transformation.
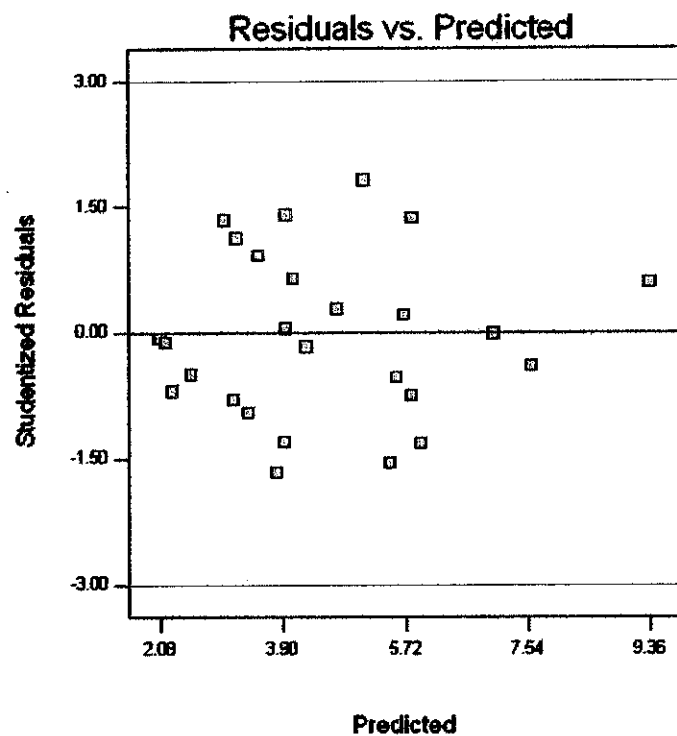
Figure 4.2: Residuals versus Predicted

4.1.2.3 Residuals vs. Run Numbers

Figure 4.3 shows the plot of the residuals versus the experimental run order. It also checks for lurking variables that may have influenced the response during the experiment. The plot shows a random scatter. It can be noticed that all data were scattered within the constant range of residuals.
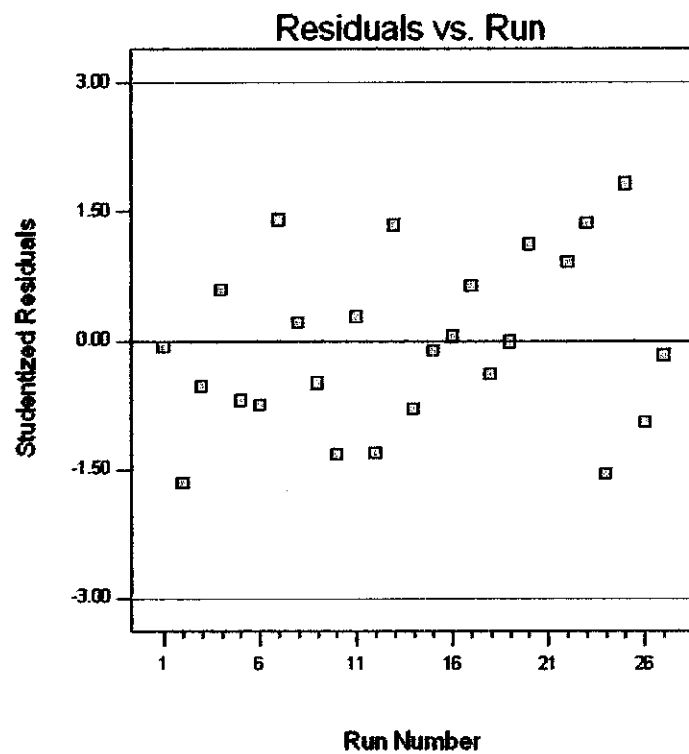
Figure 4.3: Residuals versus Run Numbers

34

4.1.2.4 Outlier T vs. Run Numbers

Figure 4.4 shows the plot of outlier T versus the experiment run order. It indicates measurement of how many standard deviations the actual value deviates from the value predicted after deleting the point in question. In order to make identification of abnormal runs easier, Design-Expert puts "control limits" at plus or minus 3.5 on the outlier t plot.
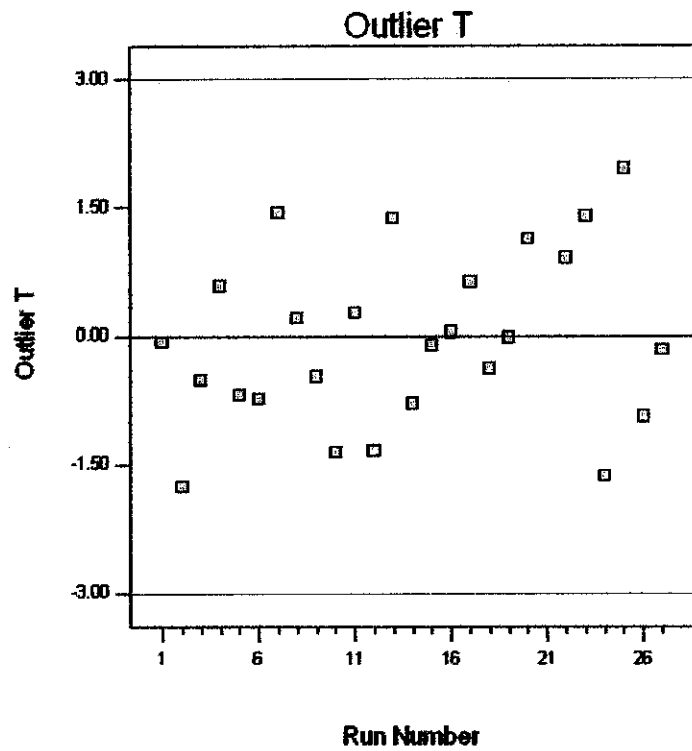
Figure 4.4: Outlier T versus Run Numbers

4.1.2.5 Predicted vs. Actual

Figure 4.5 shows a graph of the actual response values versus the predicted response values for the graphite anode. Most data were evenly dispersed from the straight line. In the ANOVA plot analysis the square of the correlation coefficient, R^2, always indicates the proportion of total variance in one variable that is predictable from its relationship with the other variables. The R-Squared value is 0.4853. The higher the R-Squared values (close to 1) mean the better will be the goodness of fit. The adjusted R-Squared value was 0.4281 which is slightly farther from 1.
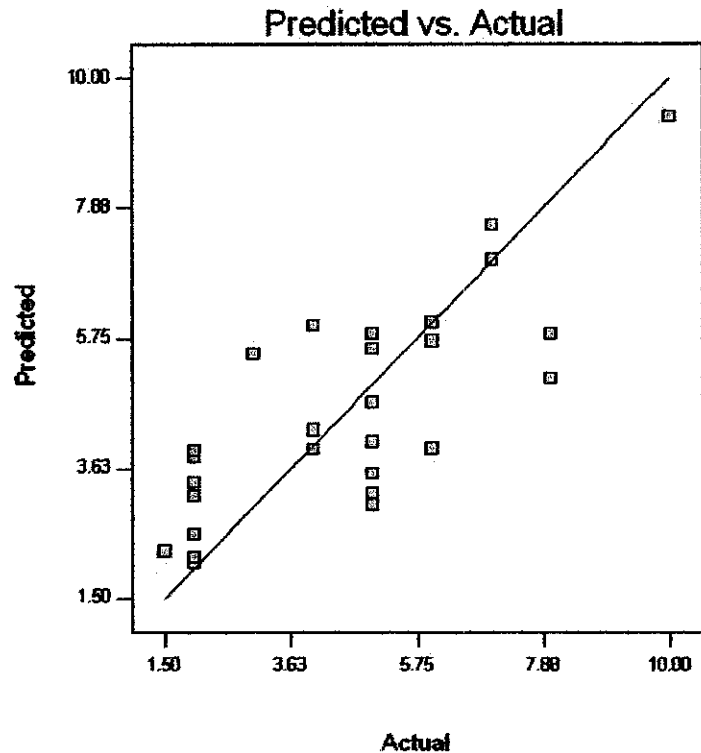
Figure 4.5: Predicted versus Actual

4.1.3 3D Surface Plots

The 3D surface model can be displayed in 3 dimensions and provide visual effect on the response. However the contour plot is more useful for establishing response values and coordinates.

Figure 4.6 shows that Free Available Chlorine was obtained as 4.76 mg/l Cl_2 at the maximum current density of 3 mA/cm^2 and NaCl concentration of 3g/l.

DESIGN-EXPERT Plot

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current Density

Actual Factor
C: Time = 20.0
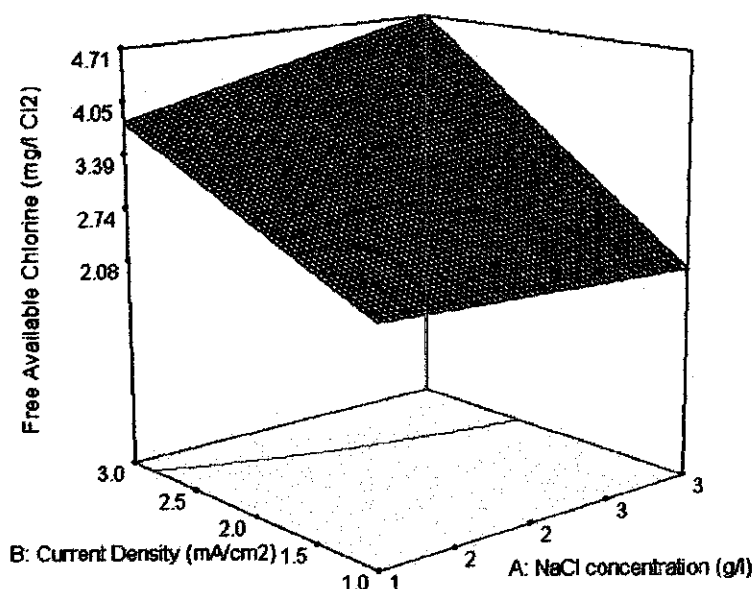
Figure 4.6: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 20 minutes

In Figure 4.7, the Free Available Chlorine was obtained as 7.08 mg/l Cl_2, also at the current density of 3 mA/cm^2 and NaCl concentration of 3 g/. The maximum Free Available Chlorine was obtained at 60 minutes of reaction time. Figure 4.8 shows that maximum Free Available Chlorine was obtained as 9.36 mg/l Cl_2 at the maximum current density and NaCl used which were 3 g/l.
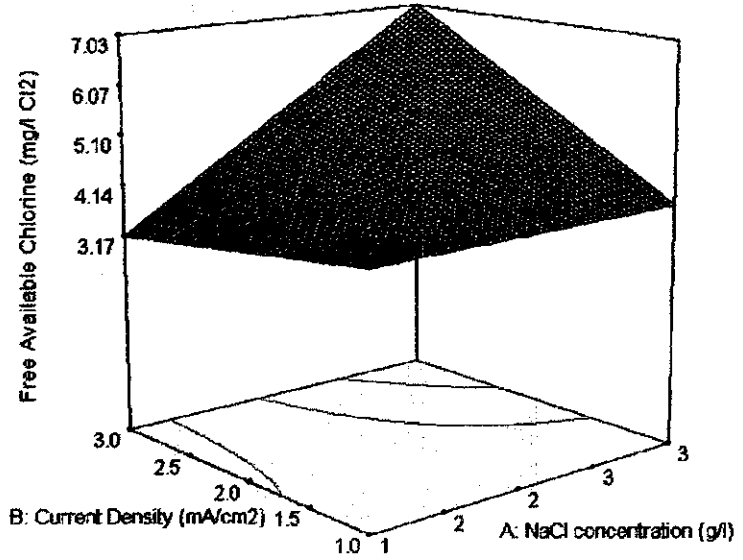
Figure 4.7: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 40 minutes
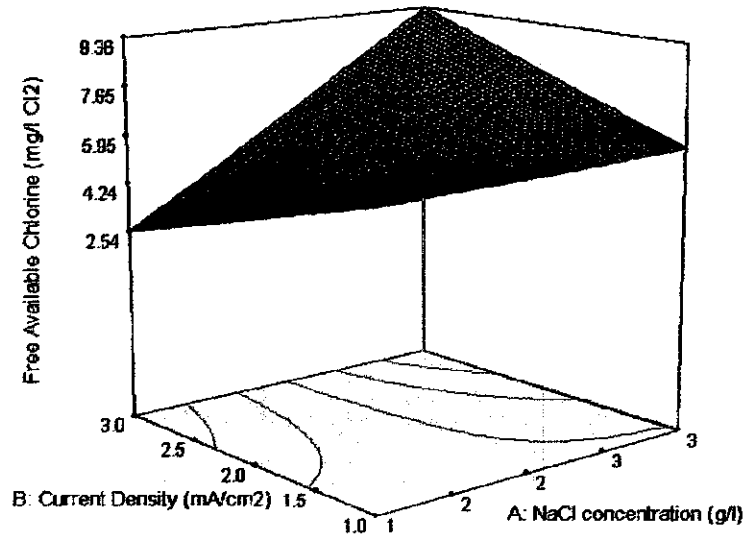
Figure 4.8: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 60 minutes

38

4.1.4 Effect of Sodium Chloride on the Formation of Hypochlorite

The effect of sodium chloride concentration used in range from 1 to 3 g/l. Figure 4.9 shows the effect of 20 minutes reaction time on the production of hypochlorite with respect to NaCl concentration and current density. Based on the contour lines, the Free Available Chlorine was predicted to increase as the current density and NaCl concentration increase.
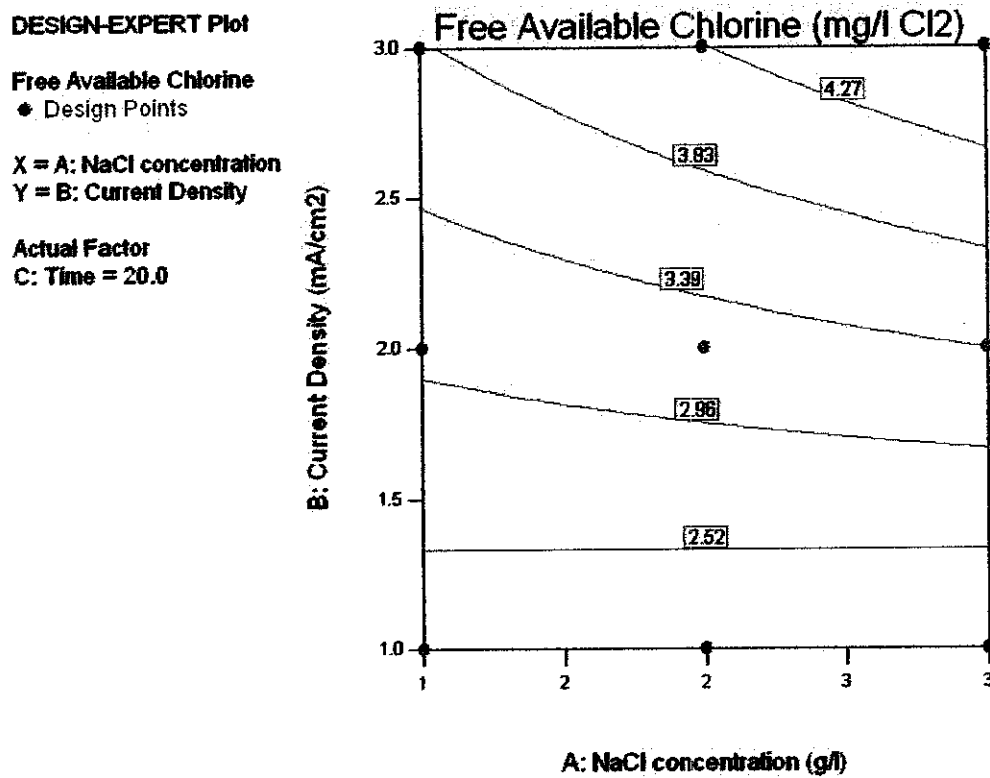
Figure 4.9: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density

Figures 4.10 and 4.11 below show the effect of 40 and 60 minutes reaction time on the production of hypochlorite with respect to NaCl concentration and current density. Based on the contour lines, the Free Available Chlorine was also predicted to increase as the current density and NaCl concentration increase.
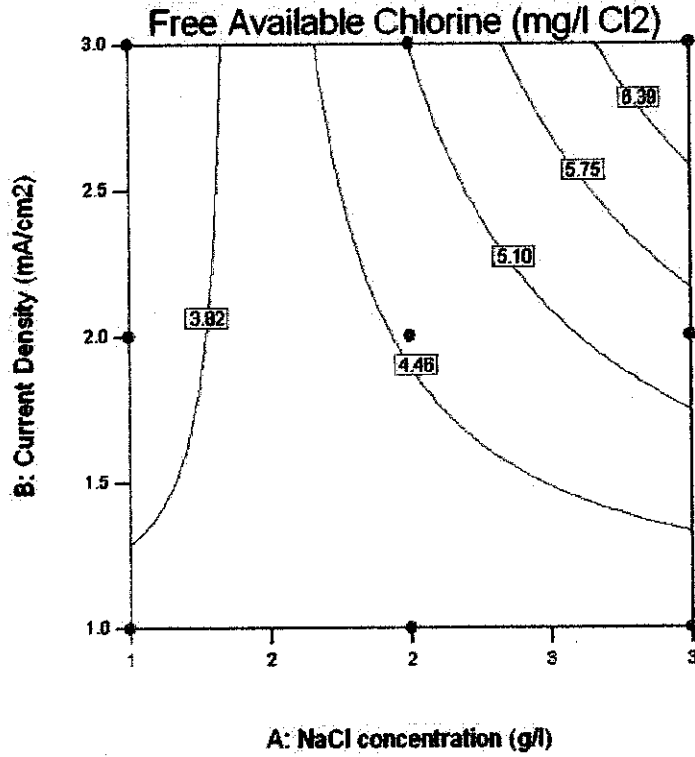
Figure 4.10: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density
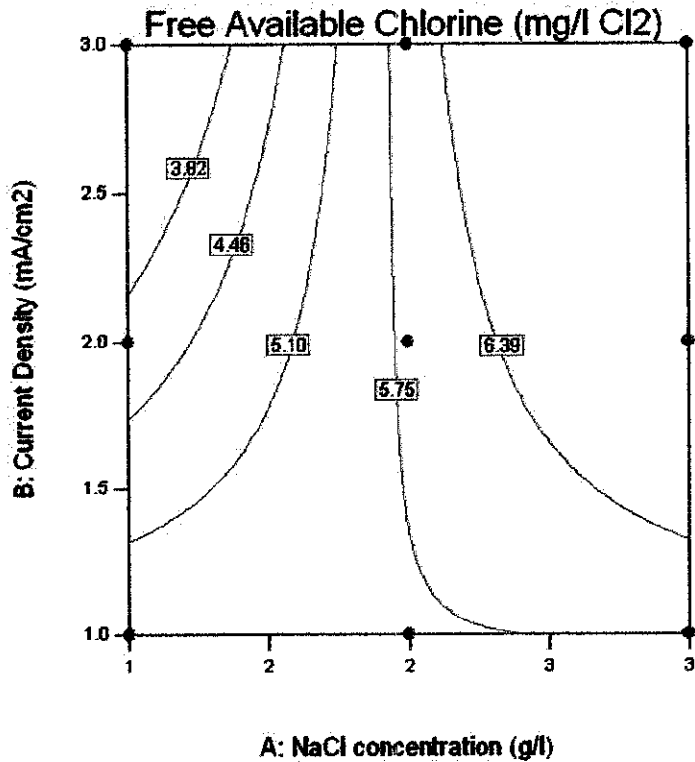
Figure 4.11: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density

40

4.2 MMO-coated Titanium Anode

4.2.1 Analysis of Variance (ANOVA)

The ANOVA includes a full analysis of variance, prediction equations, and case statistics. Table 4.3 shows the analysis of variance for the electrode combination of MMO-coated anode and titanium cathode. The Model F-value of 22.60 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, ABC are significant model terms.

Table 4.3: Analysis of Variance (Partial sum of squares)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Block	215.56	2	107.78		
Model	6225.56	5	1245.11	22.60	< 0.0001
A	867.43	1	867.43	15.75	0.0010
B	2655.32	1	2655.32	48.21	< 0.0001
C	1859.69	1	1859.69	33.76	< 0.0001
AB	699.70	1	699.70	12.70	0.0024
ABC	629.42	1	629.42	11.43	0.0036
Curvature	42.30	1	42.30	0.77	0.3931
Residual	936.42	17	55.08		
Cor. Total	7419.84	25			

Std. Dev.	7.42	R-Squared	0.8693
Mean	21.31	Adj R-Squared	0.8308
C.V.	34.83	Adeq Precision	17.772

The "Curvature F-value" of 0.77 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 39.31% chance that a "Curvature F-value" this large could occur due to noise. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 17.772 in the above table indicates an adequate signal.

The ANOVA also simulated equation for the response surface correlation with all model terms. The final equation in terms of coded factors is shown in Eq.[4]:

$$Free\ Available\ Chlorine = 23.62 + 7.19A + 12.58B + 10.16C + 0.804AB$$
$$+ 8.87ABC \qquad [4]$$

4.2.2 Model Diagnostic Plots

Table 4.4 shows the diagnostics case statistics for the electrode combination of MMO-coated titanium anode and titanium cathode. The value predicted from the model, generated by using the prediction equation. It includes block and center point corrections, if present. "Residual" is the difference between Actual and Predicted values of each point.

Numerical value between zero and one that indicates the potential for a design point to influence the model fit is called "Leverage". A value of one means that the predicted value will be forced to be exactly equal to the actual value, with zero residual. The sum of the leverage values across all cases equals the number of parameters fit by the model. The maximum leverage an experiment can have is $1/k$, where k is the number of times the experiment is replicated. The standard order 14 have values larger than 2 times the average leverage, therefore it was flagged.

The outlier t statistic is the number of standard deviations between an actual data point and the predicted value at that point using a model based on all of the data except this point. The statistic shows that data point fits in with the other points for this model. But extreme values for standard order 24 (t=3.5 or larger) should be considered outliers. Sometimes also called externally studentized residual.

Table 4.4: Diagnostics Case Statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t
1	0.04	-1.93	1.97	0.580	0.340	0.018	0.332
2	13.00	7.35	5.65	0.233	0.722	0.018	0.712
3	16.00	16.62	-0.62	0.580	-0.108	0.002	-0.105
4	30.00	24.29	5.71	0.580	0.986	0.149	0.985
5	3.00	11.18	-8.18	0.233	-1.045	0.037	-1.048
6	18.00	15.01	2.99	0.094	0.352	0.001	0.343
7	25.00	22.67	2.33	0.233	0.298	0.003	0.290
8	22.00	18.84	3.16	0.233	0.404	0.006	0.395
9	26.00	21.05	4.95	0.580	0.855	0.112	0.849
10	2.00	2.87	-0.87	0.233	-0.112	0.000	-0.109
11	10.00	13.45	-3.45	0.094	-0.406	0.002	-0.396
12	17.00	24.03	-7.03	0.233	-0.898	0.027	-0.893
13	9.00	9.62	-0.62	0.094	-0.073	0.000	-0.071
14	16.00	16.00	0.00	1.000 #			
15	37.00	37.61	-0.61	0.094	-0.072	0.000	-0.070
16	15.00	16.36	-1.36	0.233	-0.174	0.001	-0.169
17	23.00	33.78	-10.78	0.094	-1.267	0.019	-1.291
18	40.00	51.20	-11.20	0.233	-1.431	0.069	-1.477
19	10.00	7.68	2.32	0.580	0.401	0.025	0.391
20	17.00	19.56	-2.56	0.233	-0.327	0.004	-0.319
21	30.00	31.44	-1.44	0.580	-0.248	0.009	-0.241
22	14.00	8.06	5.94	0.233	0.759	0.019	0.750
23	22.00	32.23	-10.23	0.094	-1.202	0.017	-1.218
24	76.00	56.39	19.61	0.233	2.505	0.212	3.016 *
25	19.00	8.44	10.56	0.580	1.824	0.511	1.964
26	30.00	44.89	-14.89	0.233	-1.903	0.122	-2.069
27	90.00	81.35	8.65	0.580	1.494	0.342	1.551

Note: Predicted values of center points include center point coefficient.

Case(s) with leverage of 1.0000: Student Residuals, Cooks Distance & Outlier T undefined.

* Case(s) with |Outlier T| > 3.00

Obs with Leverage > 2.00 *(average leverage)

4.2.2.1 Normal Plots of Residuals

Studentized Residual is a rescaling that reflects the number of standard deviations between the actual and predicted response values. It is the residual divided by the estimated standard deviation of that residual which refers to the difference between observed response (actual) and the predicted value by the model for a particular design point.

Probability refers to the proportion, or fraction, of times that a particular outcome is likely to occur. Figure 4.12 shows that the residuals were normally distributed as they yielded a straight line plot. The normal probability plot indicates whether the residuals follow a normal distribution, in which case the points will follow a straight line. Some scatter is shown with normal data in the plot. It also looks definite patterns like an "S-shaped" curve, which indicates that a transformation of the response may provide a better analysis.

DESIGN-EXPERT Plot
Free Available Chlorine

Normal Plot of Residuals

Normal % Probability

Studentized Residuals
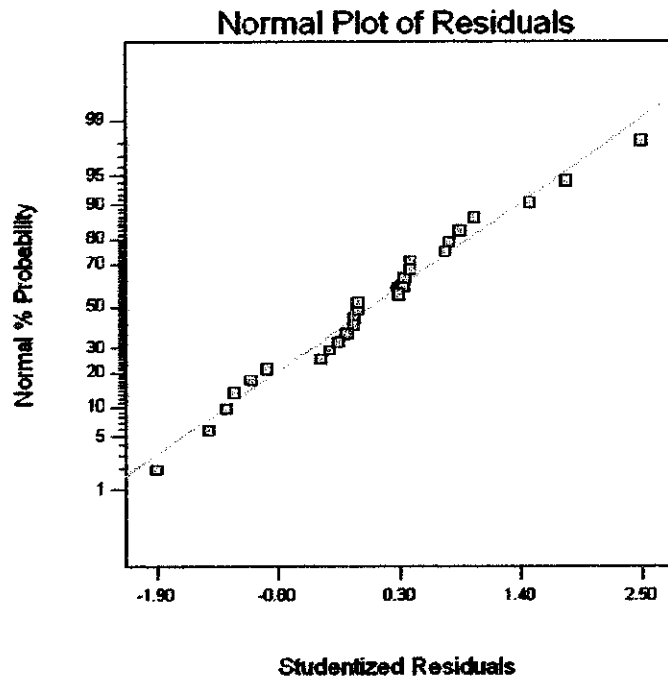
Figure 4.12: Normal Probability versus Studentized Residuals

45

4.2.2.2 Residuals vs. Predicted

Figure 4.13 indicates a plot of the residuals versus the ascending predicted response values. The predicted values were generated by using the model prediction equation. This plot tests the assumption of constant variance and should be a random scattered in between the constant range of residuals across the graph.
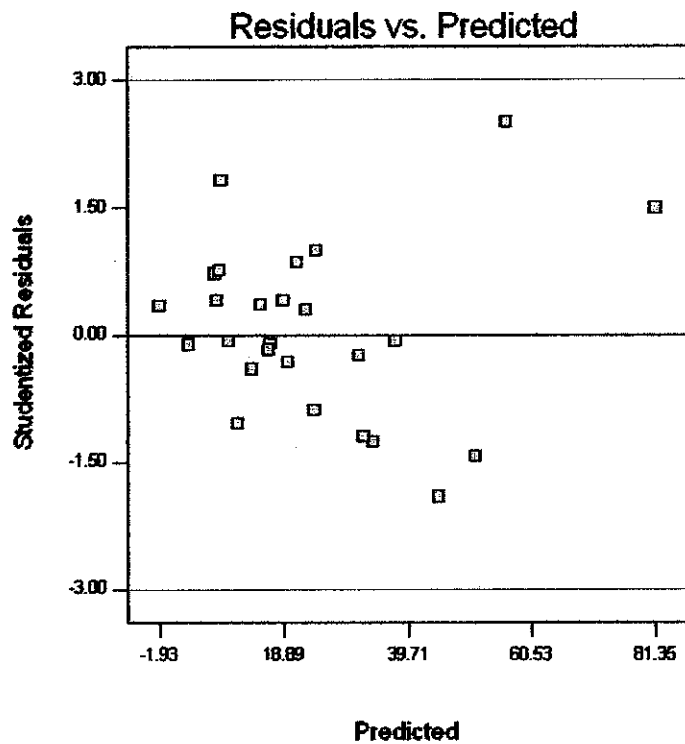
Figure 4.13: Residuals versus Predicted

In the above plot, some points have the same predicted value within the constant range. All data were within the constant range of residuals. This plot implies that the residuals were distributed within constant variance.

4.2.2.3 Residuals vs. Run Numbers

Figure 4.14 indicates plot of the residuals versus the experimental run order. The plot shows a random scatter. It can be noticed that all data were scattered within the constant range of residuals however there some data were randomized which provide insurance against trends that ruin the analysis.

Figure 4.14: Residuals versus Run Numbers

4.2.2.4 Outlier T vs. Run Numbers

Figure 4.15 shows the plot of outlier T versus the experiment run order. The measure could be referred as an "externally studentized residual" since the individual case is not used in computing the estimate of variance. In order to make identification of abnormal runs easier, Design-Expert puts "control limits" at plus or minus 3.5 on the outlier t plot. All data were in the range, therefore there are no outliers for this section.
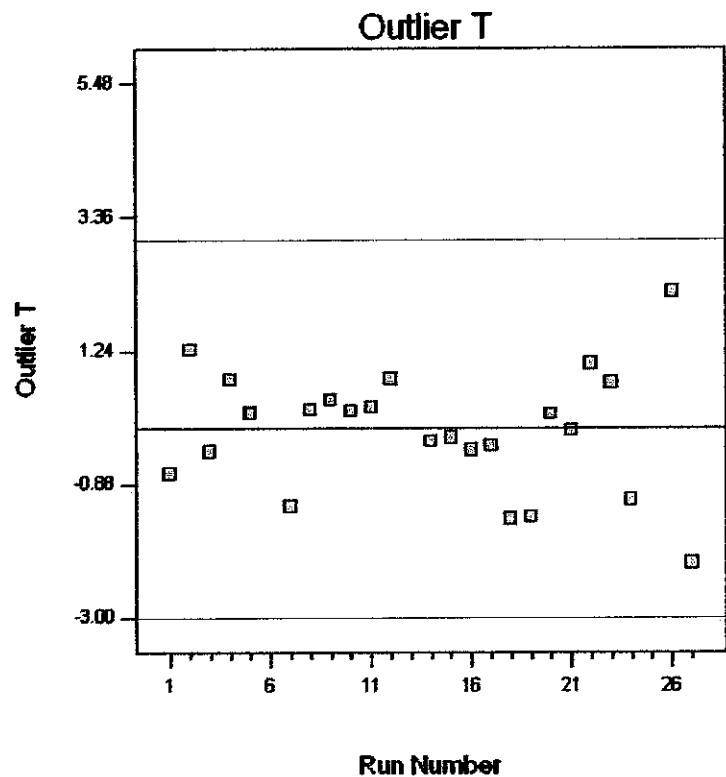
Figure 4.15: Outlier T versus Run Numbers

48

4.2.2.5 Predicted vs. Actual

Figure 4.16 shows the actual response values versus the predicted response values. It shows good agreement between actual and predicted values. In the ANOVA plot analysis the square of the correlation coefficient, the R-Squared value obtained was 0.8693. The higher the R-squared value means the better will be the goodness of fit. The adjusted R-squared value was 0.8308 which is slightly lower but still close to 1. Based on the figure above also could be observed that the MMO-coated titanium anode is much better compared to the graphite.

DESIGN-EXPERT Plot
Free Available Chlorine
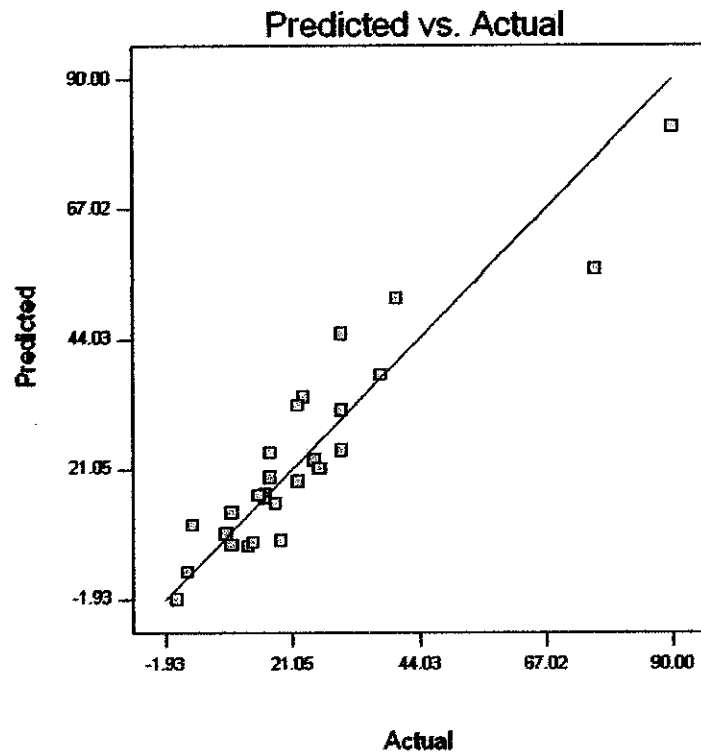
Figure 4.16: Predicted versus Actual

4.2.3 3D Surface Plots

All of the figures below show that concentration of Free Available Chlorine increased with the increases in current density and NaCl concentration. The maximum Free Available Chlorine was obtained at 60 minutes of reaction time. The maximum Free Available Chlorine was obtained as 81.35 mg/l Cl_2 as shown in Figure 4.19 at the maximum current density and NaCl used which were 3 g/l.

DESIGN-EXPERT Plot

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current density

Actual Factor
C: Time = 20
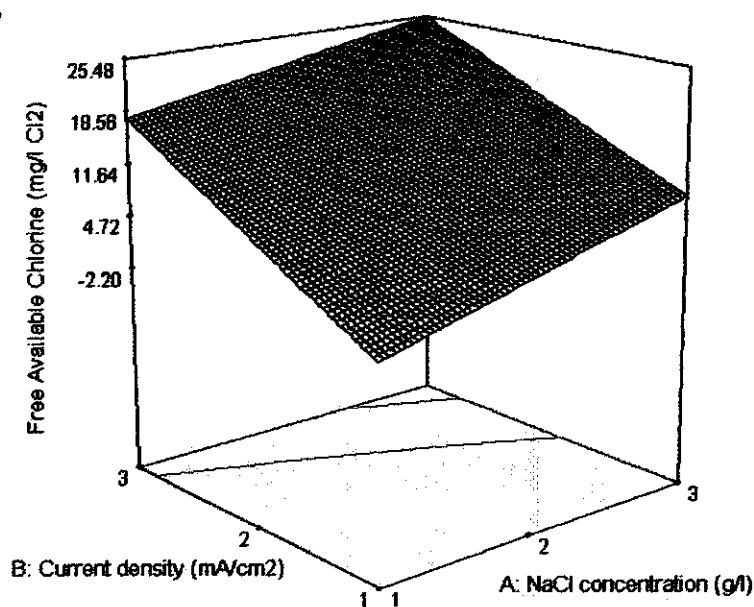
Figure 4.17: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 20 minutes

DESIGN-EXPERT Plot

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current density

Actual Factor
C: Time = 40
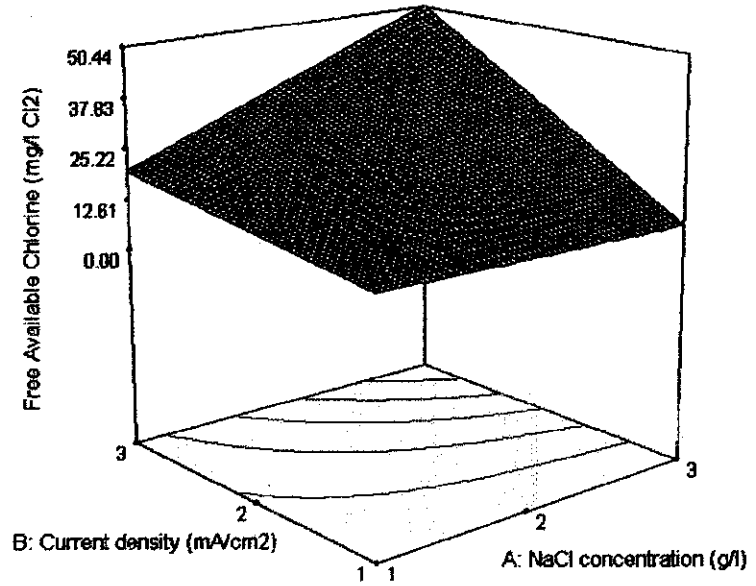
Figure 4.18: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 40 minutes

DESIGN-EXPERT Plot

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current density

Actual Factor
C: Time = 60
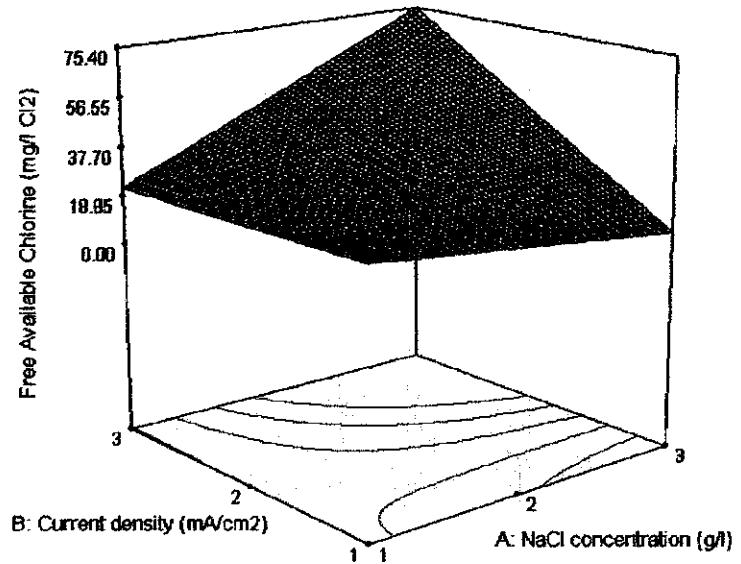
Figure 4.19: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 60 minutes

51

4.2.4 Effect of Sodium Chloride on the Formation of Hypochlorite

The effect of sodium chloride concentration used in range from 1 to 3 g/l. Figure 4.20 shows the effect of 20 minutes reaction time on the production of hypochlorite with respect to NaCl concentration and current density. Based on the contour line, the Free Available Chlorine was predicted to increase as the current density and NaCl concentration increases.
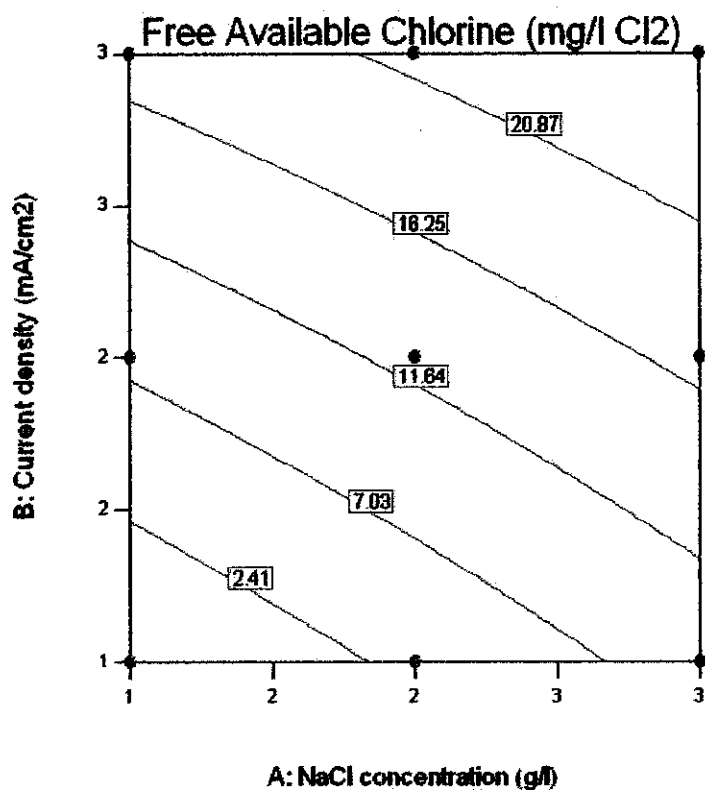
Figure 4.20: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density

Figures 4.21 and 4.22 show the effect of 40 and 60 minutes reaction time on the production of hypochlorite with respect to NaCl concentration and current density. Based on the contour line, the Free Available Chlorine also was also predicted to increase as the current density and NaCl concentration increases.
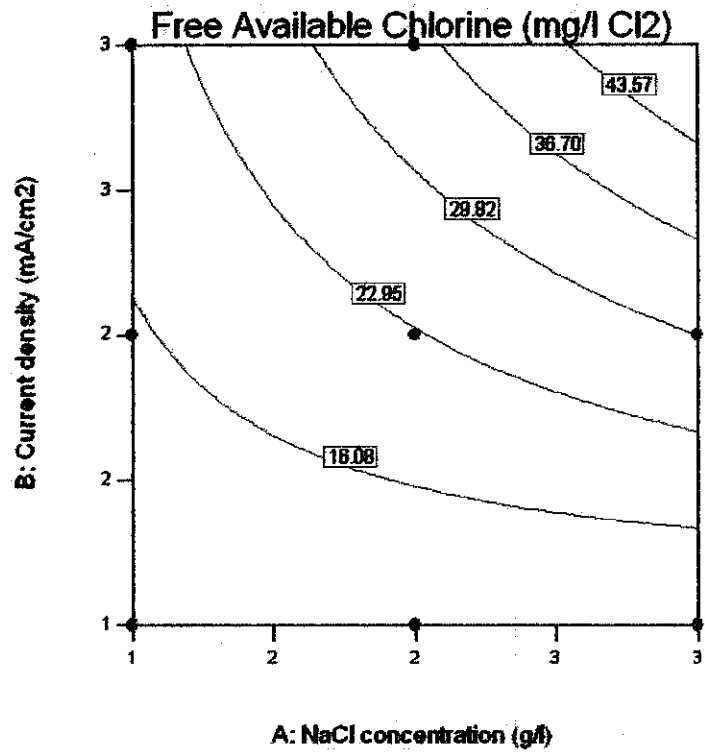
Figure 4.21: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density
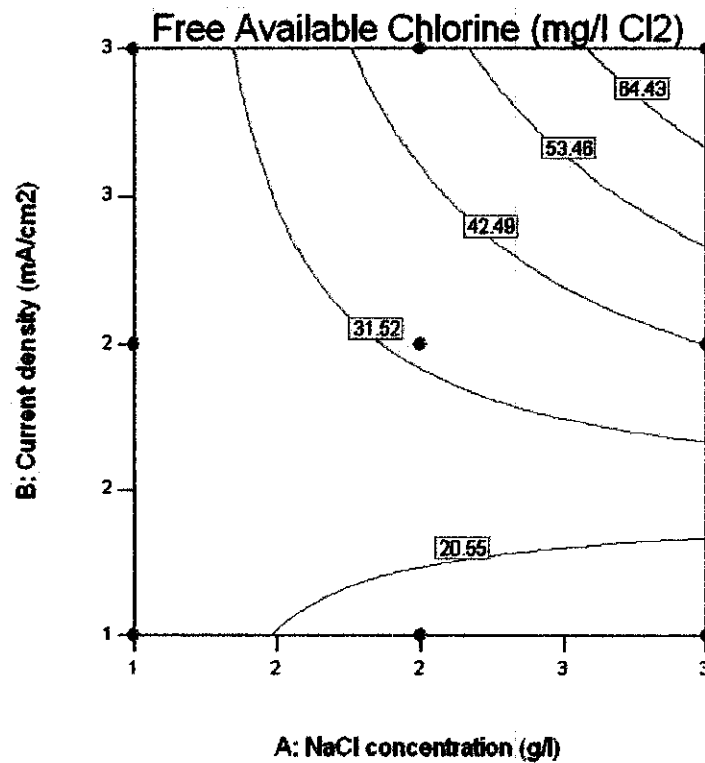
Figure 4.22: Contour plots of Free Available Chlorine with respect to NaCl concentration and current density

53

4.3 Performance and Comparison between Ti/MMO and Ti/RuO₂ Electrodes

A set of experiments were conducted to compare the performance of Ti/MMO with Ti/RuO2 (*Khelifa et, al., 2004*) found in literature. For this purpose, the experimental conditions were kept similar to those as adopted by Khelifa, et, al., (2004). Table 4.5 shows the experimental conditions used for this set of experiments.

Table 4.5: Data for optimization operation

Variable	Factor	Level (-1)	Level (0)	Level (+1)
A	NaCl concentration, M	0.04	1.02	2
B	Current density, mA/cm²	50	150	200
C	Electrolysis time, min	10	120	120

4.3.1 Analysis of Variance (ANOVA)

The preliminary results indicated that better performance in term of FAC production and current efficiency was observed with MMO-coated titanium anode. In the present case, the amount of FAC was taken as the system response. The current density, the electrolyte solution concentration, and the electrolysis time are the most important electro-chlorination process variables (parameters). The two level factorials were used for this particular study.

In Table 4.6, the Model F-value of 53.55 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

54

Table 4. 6: Analysis of Variance (Partial sum of squares)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F
Block	49.65	2	24.83		
Model	3496.07	5	699.21	53.55	< 0.0001
A	952.88	1	952.88	72.97	< 0.0001
B	194.87	1	194.87	14.92	0.0011
C	1886.31	1	1886.31	144.46	< 0.0001
AC	400.38	1	400.38	30.66	< 0.0001
BC	61.63	1	61.63	4.72	0.0434
Curvature	22.27	1	22.27	1.71	0.2080
Residual	235.04	18	13.06		
Cor Total	3803.04	26			

Std. Dev.	3.61	R-Squared	0.9370
Mean	13.67	Adj R-Squared	0.9195
C.V.	26.44	Adeq Precision	21.277

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AC, BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The "Curvature F-value" of 1.71 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 20.80% chance that a "Curvature F-value" this large could occur due to noise.

The final equation in terms of coded factors is shown in Eq.[5]:

Free Available Chlorine = 13.49 + 7.28A + 3.29B +10.24C + 5.78AC

$$+ 2.27BC \qquad\qquad [5]$$

4.3.2 Model Diagnostic Plots

Figure 4.23 shows the actual response values versus the predicted response values. It shows good agreement between actual and predicted values. In the ANOVA plot analysis the square of the correlation coefficient, the R-Squared value obtained was 0.9370. Therefore the results were good as they were very close to 1. The adjusted R-squared value was 0.9195 which is slightly lower but still close to 1.
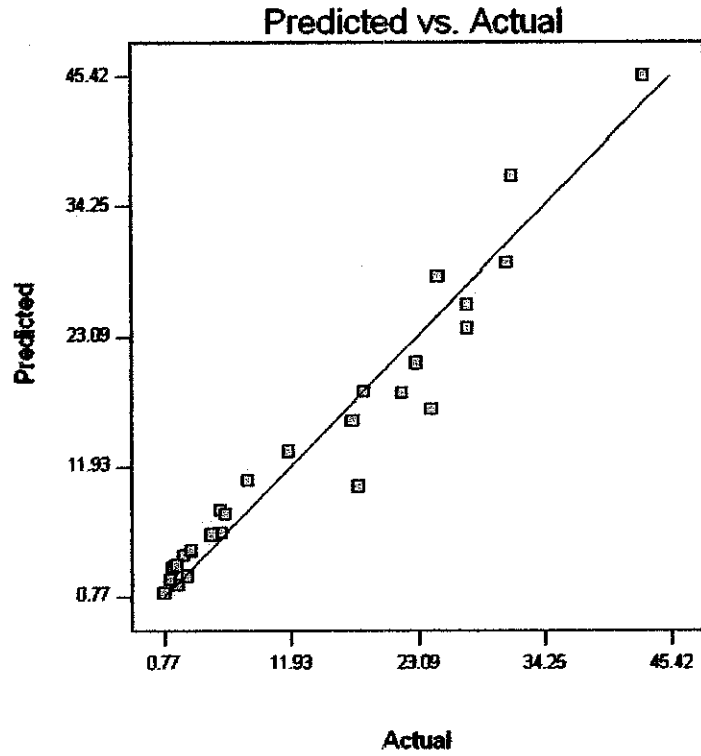
Figure 4.23: Predicted vs. Actual

4.3.3 3D Surface Plots and Comparison

Figures 4.24 and 4.25 show the Free Available Chlorine increased with the increases in current density and NaCl concentration. They were also having the same pattern than before the optimization. The maximum Free Available Chlorine was obtained at 120 minutes of the reaction time. The 3D plot shows that maximum Free Available Chlorine was obtained as 45.42 g/l Cl_2 at the maximum current density, 200 mA/cm^2 and NaCl, 117 g/l or 2 M.

DESIGN-EXPERT Plot

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current density

Actual Factor
C: Time = 60
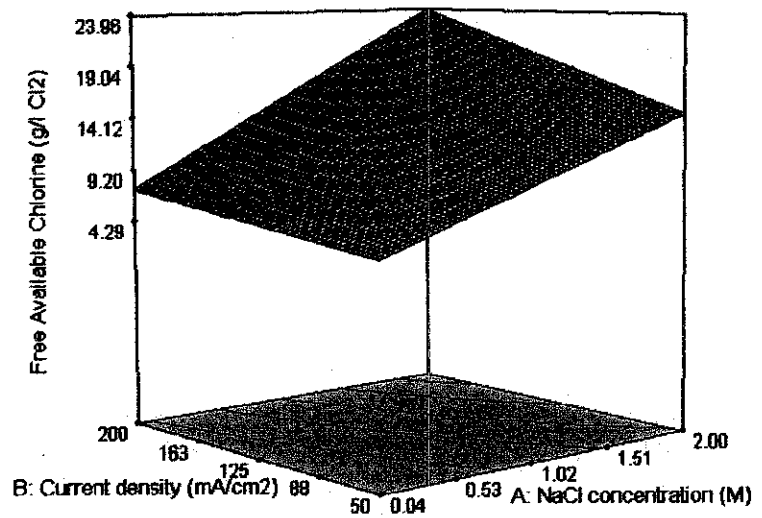
Figure 4.24: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 60 minutes

Free Available Chlorine
X = A: NaCl concentration
Y = B: Current density

Actual Factor
C: Time = 120
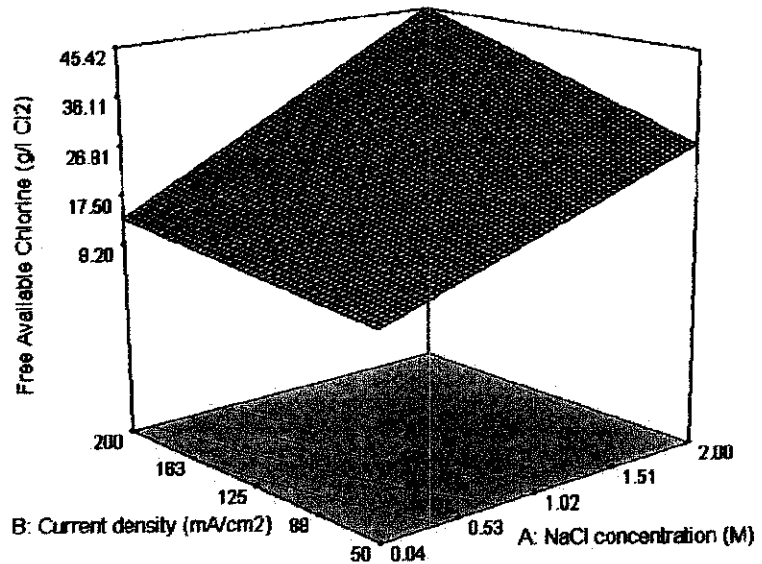
Figure 4.25: 3D Plot of Free Available Chlorine with respect to current density and NaCl concentration. Time: 120 minutes

The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. Optimization of one response or the simultaneous optimization of multiple responses was performed graphically.

The maximum criteria were selected for all of the factors. The results were in the Table 4.7.

Table 4.7: Solution for Optimization

Number	NaCl concentration	Current density	Time	Desirability
1	2.00	200	120	1.000
2	2.00	199	120	0.998
3	2.00	198	120	0.996
4	1.92	200	120	0.986
5	2.00	200	112	0.977

The solution shows that NaCl concentration of 2 M, 200 mA/cm^2 of current density and the 2 hours of reaction time had desirability of 1. Therefore it was the only solution that selected. The 3D plot for this solution was shown in Figure 4.25.

58

Figure 4.26 shows the comparison between the two anodes on terms of current density and available chlorine production. Data of Ti/RuO$_2$ were obtained from Khelifa, et, al., (2004). At the 200 mA/cm^2 of current density, the MMO-coated anodes had generated 43 g/l while the Ti/RuO$_2$ anode only generated 18.3 g/l of available chlorine
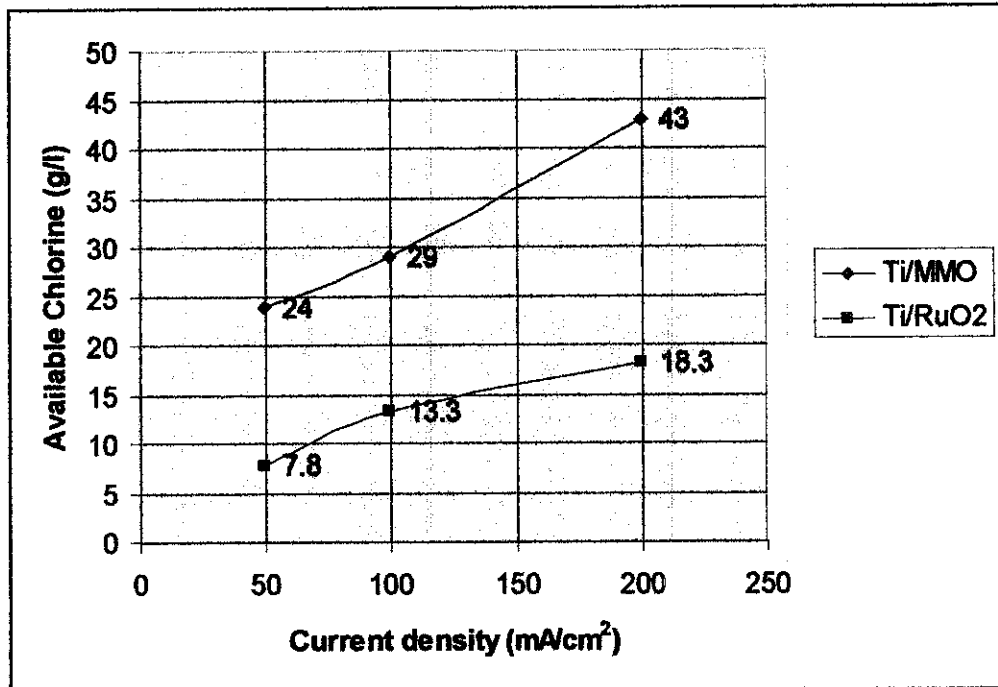
Figure 4.26: Comparison between Ti/MMO and Ti/RuO2. Ti cathode; time, 1 hour, NaCl concentration, 2 M

Figure 4.27 shows the comparison between the two anodes in terms of electrolysis time and available chlorine production. Data of Ti/RuO₂ was obtained from Khelifa, et, al., (2004). At the 2 hours of reaction time, the MMO-coated anodes had generated 37 g/l while the Ti/RuO₂ only generated 36 g/l of available chlorine. The MMO-coated titanium anodes were also having better performance than Ti/RuO₂ anode in term of reaction time.
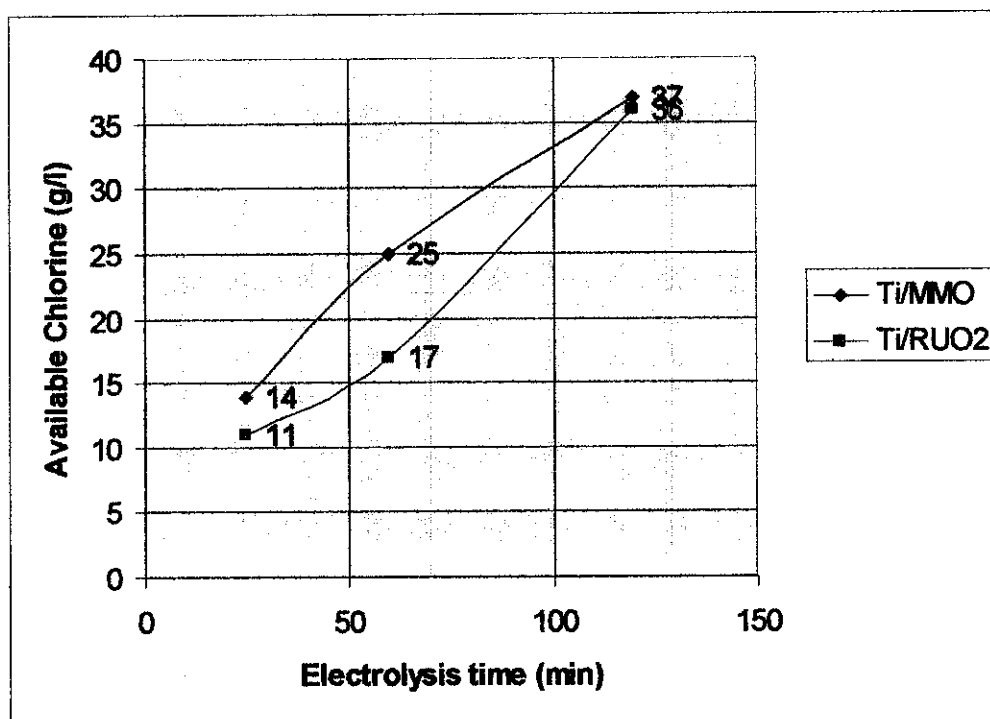
Figure 4.27: Comparison between Ti/MMO and Ti/RuO₂. Ti cathode; current density 150 mA/cm² ; NaCl concentration, 2 M

Therefore, the MMO-coated titanium anodes were observed to have better performance than Ti/RuO₂ in term of active chlorine production and current efficiency.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

As a conclusion, this project has a potential for producing an alternative to current disinfection technology. The suitable type of in-situ generation was sodium hypochlorite since less associated hazard present than the chlorine gas. The MMO-coated anode was better than graphite anode. The MMO-coated titanium anode and titanium cathode were used since they have high current efficiency and could resist against corrosion. The combination electrodes were also better than the Ti/RuO_2 used by Khelifa, et, al., (2004). The use of a MMO-coated titanium anode with the combination of the maximum operational parameters levels produced Free Available Chlorine as high as 45.42 g/l Cl_2. The inter-electrode gap used was 0.5 cm and surface area of the anode was 15 cm^2. Higher Free Available Chlorine could be produced in longer reaction time. The results obtained in this study were based on batch experiments. It is recommended to conduct a performance study with continuous flow experiments.

REFERENCES

Buzzi R. A. (1992) *Chemical hazards at water and wastewater treatment plants*; Lewis Publisher

Bommaraju, T. V., Orosz, P. J., Sokol, E. A., (2001) *Brine Electrolysis*; Electrochemistry Encyclopedia, Process Technology Optimization, Inc.

Crowl D., Louvar J. (2001), *Chemical Process Safety: Fundamentals with Applications*, Prentice-Hall, Englewood Cliffs, NJ.

D. van Wijk, (2002) *Protecting Public Health: Water chlorination*; Euroclor

Fleming H. and Huebner W. (2001) *Choosing the right disinfection technology for municipal drinking water plant: part 2*; WATER Engineering and Managament

Frank R., Spellman, (1999) *Choosing Disinfection Alternatives for Water/Wastewater Treatment*; Technomic Publishing Company, U.S.A.

Gautrin D., Leroyer C., Claire I. R., Ghezzo H., Dufour J., Girard D., Malo (1999) *Longitudinal Assessment of Airway Caliber and Responsiveness in Workers Expose to Chlorine.*

Gordon G., L. Adam, and B. Bubnis (1995) *Minimizing Chlorate Ion Formation in Drinking Water when Hypochlorite Ion is the Chlorinating Agent*; AWWA-AWWARF, Denver, CO.

G. van der Stegan, J. H., A. J. van der Veen, H. Weerdenburg, J. A. Hogendoorn, G. F. Versteeg, (1999) *Application of the Maxwell-Stefan theory to the transport in ion-selective membranes used in the chloralkali electrolysis process*; Chemical Engineering Science 54, 2501- 2511

Gustin J. L. (2005) *Safety of Chlorine and Chlorination Processes*; Division of Chemical Health and Safety of the American Chemical Society

Haas, C. N. (1999) *Benefits of Using a Disinfectant Residual*; American Water Works Association, 91(1):65-69

Hooper, J. (2005) *On-site Generation of Sodium Hypochlorite Basic Operating Principles and Design Considerations*; 68th Annual Water Industry Engineers and Operators Conference, pg. 59

Hsu S. Y. (2003) *Effects of water flow rate, salt concentration and water temperature on efficiency of an electrolyzed oxidizing water generator*; Journal of Food Engineering 60 469-473

Hsu S. Y. (2005) *Effects of flow rate, temperature and salt concentration on chemical and physical properties of electrolyzed oxidizing water*; Journal of Food Engineering 66 171-176

Khelifa A., Moulay S., Hannane F., Benslimene S., Hecini, M. (2004) *Application of an experimental design method to study the performance of electrochlorination cells*; Desalination 160 91-98

Lees F.P. (1996), *Loss Prevention in the Process Industries*, Butterworths, London.

Leslie Snowden-Swan, John Piat and Ann Lesperance, (1998) *Disinfection Technologies for Potable Water and Wastewater Treatment: Alternatives to Chlorine Gas*; U.S Army Forces Command, Air Quality Division

National Transportation Safety Board (NTSB), 1998. *Derailment And Hazardous MaterialsRelease With Fatality, Montana Rail Link, Alberton, Montana, April 11, 1996*. RailroadAccident Brief Report, Lax 96 Fr 010.

Robertson P. M., Gnehm, W. (1983) *High efficiency hypochlorite generation,* Technisch Chemisches Labor, 8092 Zurich, Switzeland

Scott Lynn, Steven F. Sciamanna, Aldo F. Sciamanna (1993) *Chlorine generator;* US Patent Issued No. 71917

Stephan A. Schaub, Helen T. Hargett, Kurt I. Kamrud, Charles R. Sterling, Marilyn M. Marshall, (1996) *Evaluation of Chlorine Dioxide Generated In-Situ For Disinfection of Waterbone Micro-organisms*; U.S Army Biomedical Research and Development Laboratory

USEPA (1998b) *Regulatory Impact Analysis for the Stage 1 Disinfectant/Disinfection Byproduct Rule*; Prepared by, Science Applications International Corporation for the USEPA, Office of Ground Water and Drinking Water, Washington, DC.

USEPA Guidance Manual (1999) *Alternative Disinfectants and Oxidants Guidance Manual*; United States Environmental Protection Agency, EPA 815-R-99-014

White G. C. (1992) *The Handbook of Chlorination and Alternative Disinfectants (3rd Edn.)*; Van Nostrand, New York

Wolfe R., N.Ward, and B. Olson, (1984) *Inorganic Chloramines as Drinking Water Disinfectants: A Review*; Journal of the American Water Works Association

Table A.1: Approximate costs: Gaseous chlorine and NaOCl technology

	Cl₂ with scrubbers 150# cylinders, $	Cl₂ without scrubbers 150# cylinders, $	NaOCl (Off-site Generated, $	NaOCl (On-site Generated), $
Capital	65,000	15,000	2,500	18,000
Operating	3,600	3,600	4,400	1,500
Maintenance	2,600	2,600	5,000	1,600

<div align="right">(Source: Leslie, et al., 1998)</div>
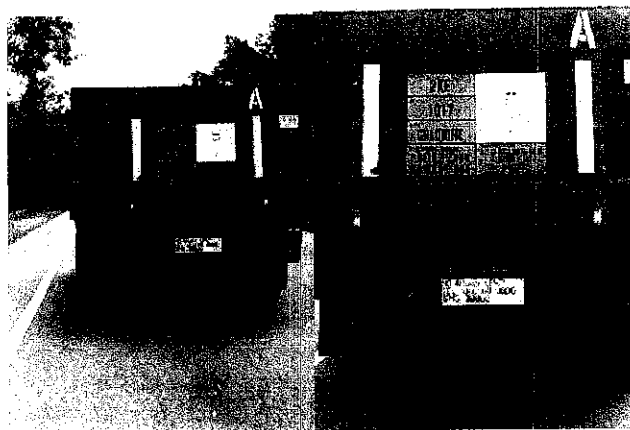
**Figure A.1: Truck carrying chlorine gas tank on the Ipoh-Lumut road**

Table A.2: Application Guide for Key Disinfection Processes

Disinfection Process	Disinfection Effectiveness			By Product Formation			Multi Function		Safety Risk	Complexity	Cost[1] $ K Gal
	Bact/virus	Cysts	Residual	Organic	Brominated	Inorganic	Oxidation	Other			
Chlorine Gas[2]	Very Good	Fair	Good	High	High	No	Good	MF[3]	High	Low	0.006
Chlorine Gas On Site Gen.[4]	Very Good	Fair	Good	High	High	No	Good	MF	Low	High	0.024
Hypochlorite (Sodium & Calcium)	Very Good	Fair	Good	High	High (Bromate)	High	Good	MF	Medium	Low	0.009
Sodium Hypochlorite (On Site Gen.)	Very Good	Fair	Good	High	High (Bromate)	Medium	Good	MF	Low	Medium	0.012
Chloramines	Fair	Very Poor	Excellent	Medium	No	No	Poor	MF	Low	Medium	0.009
Chlorine Dioxide	Very Good	Very Good	Fair	Low	No	High	Good	MF	Low	High	0.08
Ozone	Excellent	Excellent	No	Low	High (Bromate)	Medium	Very Good	MF	Low	High	0.13
Ultraviolet (UV)	Good	(Under study)	No	No	No	No	H_2O_2/O_3		Low	Low	0.06

1. Costs dependent on installation size
2. Chlorine Gas(Bulk liquid)
3. MF = Micro Flocculant
4. ElectroChlor Process

(Source: Fleming, et al., 2001)

67

Figure B.1: Analytical Balance
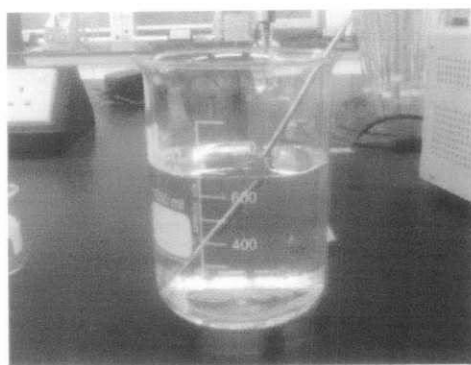
Figure B.2: Brine Solution
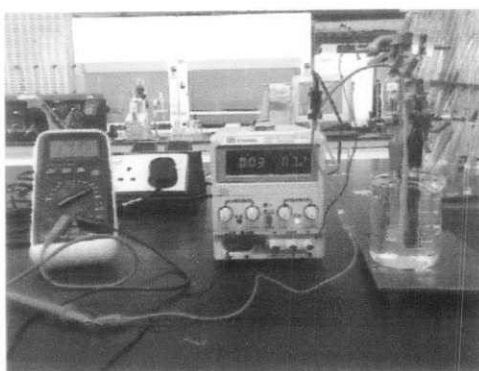
Figure B.3: Electrolysis setup

Figure B.4: Spectrophotometer DR 2800

APPENDIX C

Table C.1: Raw Data of the Experiments for Graphite Anode

Factor 1 NaCl g/l	Factor 2 Current density mA/cm2	Factor 3 Time Min	Response Free Available Chlorine mg/l Cl_2
1	1	20	1.5
1	1	40	2.0
1	1	60	5.0
1	2	20	5.0
1	2	40	5.0
1	2	60	5.0
1	3	20	2.0
1	3	40	2.0
1	3	60	2.0
2	1	20	2.0
2	1	40	4.0
2	1	60	6.0
2	2	20	5.0
2	2	40	6.0
2	2	60	8.0
2	3	20	4.0
2	3	40	8.0
2	3	60	4.0
3	1	20	2.0
3	1	40	6.0
3	1	60	5.0
3	2	20	2.0
3	2	40	3.0
3	2	60	7.0
3	3	20	5.0
3	3	40	7.0
3	3	60	10.0

Table C.2: Raw Data of the Experiments for MMO-coated Anode

Factor 1 NaCl g/l	Factor 2 Current density mA/cm2	Factor 3 Time Min	Response Free Available Chlorine mg/l Cl_2
1	1	20	0.04
1	1	40	3.0
1	1	60	30.0
1	2	20	13.0
1	2	40	18.0
1	2	60	25.0
1	3	20	16.0
1	3	40	22.0
1	3	60	26.0
2	1	20	2.0
2	1	40	9.0
2	1	60	15.0
2	2	20	10.0
2	2	40	16.0
2	2	60	23.0
2	3	20	17.0
2	3	40	47.0
2	3	60	40.0
3	1	20	10.0
3	1	40	14.0
3	1	60	19.0
3	2	20	17.0
3	2	40	22.0
3	2	60	30.0
3	3	20	30.0
3	3	40	76.0
3	3	60	90.0

Table C.3: Raw Data of the MMO-coated Anode for the optimization response

Factor 1 NaCl, M	Factor 2 Current density, mA/cm2	Factor 3 Time, Min	Response Free Available Chlorine, g/l Cl_2
0.04	50	10	0.77
0.04	50	60	3.10
0.04	50	120	5.70
0.04	125	10	1.95
0.04	125	60	5.75
0.04	125	120	8.15
0.04	200	10	2.82
0.04	200	60	6.12
0.04	200	120	11.70
1.02	50	10	1.29
1.02	50	60	17.90
1.02	50	120	21.70
1.02	125	10	1.55
1.02	125	60	18.30
1.02	125	120	27.50
1.02	200	10	2.43
1.02	200	60	24.30
1.02	200	120	31.00
2	50	10	1.88
2	50	60	17.35
2	50	120	24.88
2	125	10	3.15
2	125	60	22.95
2	125	120	31.40
2	200	10	4.92
2	200	60	27.50
2	200	120	43.00

APPENDIX D

MIXED METAL OXIDE [MMO] ANODE COATING MMO [Mixed Metal Oxide]
specification sheet

MMO [Mixed Metal Oxide] Coating has been designed for use in all cathodic protection applications. It consists of IrO_2 / Ta_2O_5, suitable for use in soils, carbonaceous backfill, fresh and brackish water, seawater and concrete. Mixed metal oxide coating is generally accepted by the cathodic protection industry to be satisfactory for both chlorine and oxygen evolving electrolytes.

MMO coating is produced by applying solutions containing the precursor materials to the specially treated titanium substrate. It is then thermally treated at elevated temperature to convert the precursor materials to their oxides. This paint - stove process is repeated many times until the desired total loading of the MMO coating is obtained. The process achieves very good adhesion properties between the coating and the substrate through mechanical and chemical bonding.

MMO coating greatly prolong the life of the anode (low wear rate). MMO coating greatly prolong the life of the anode (low wear rate) and provide excellent chemical corrosion resistance such as acid condition. The standard outputs are as below. However, MMO loading may be adjusted to suit a particular current density or design life.

Electrolyte	Maximum Current Density	Anode Life
Carbonaceous Backfill	50 A/m^2	20 years
Calcined Petroleum Coke	100 A/m^2	20 years
Fresh Water	100 A/m^2	20 years
Brackish Water	300 A/m^2	20 years
Sea Water	600 A/m^2	20 years

75