THE DEVELOPMENT OF APPROPRIATE BRINE ELECTROLYSERS FOR DISINFECTION OF RURAL WATER SUPPLIES

BY

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ABBREVIATIONS

K_a	Acid constant
AOP	Advanced oxidation processes
CE	Current efficiency
COTA	Cobalt oxide titanium anodes
DWAF	Department of Water Affairs and Forestry
DPD	N, N-Diethyl-p-Phenylenediamine
DSA	Dimensionally stable anodes
DMSO	Dimethyl sulfoxide
DMTA	Dioxide of manganese titanium anodes
DC	Direct current
DOC	dissolved organic carbon
K	Equilibrium constant
FAS	Ferrous Ammonium Sulphate
K_h	Hydrolysis constant
IDP	Integrated Development Plan

1g J	log current density
MTA	Magnetite titanium anodes
MSA	Methane sulphinic acid
MOGGOD	Mixed Oxidant Gases Generated On-site Disinfection
PTFE	Polytetraflouro-ethylene
RO	Reverse Osmosis
ROTA	Ruthenium oxide titanium anodes
$C_{T.Cl}$	Total concentration of all chlorine compounds
THM	Trihalomethane
UV	Ultra Violet
Uv/Vis	Ultraviolet Visible
VOCs	Volatile organic compounds
V	Voltage
WC	Water Conversation
WDM	Water Demand Management
WSDP	Water Service Development Plan

DEFINITION OF TERMS

Available chlorine: is the amount of hypochlorite and hypochlorous acid present in solution.

Breakpoint chlorination: is the chemical relationship that exists as varying amounts of chlorine are added to water containing small amount of ammonia.

Chlorine demand: is the quantity of available chlorine consumed by the water impurities.

Combined chlorine: is the amount of chlorine that has reacted with ammonia forming chloramines.

Dimensional stable anodes: is the term used to refer to anodes consisting of a layer of metal oxides coated on a substrate usually titanium.

Free chlorine: is the amount of elemental chlorine in the bleach solution.

Residual chlorine: is the quantity of chlorine compounds that have not reacted after the dosage.

ABSTRACT

A comparative study of electrolysers using different anodic materials for the electrolysis of brine (sodium chloride) for the production of sodium hypochlorite as a source of available chlorine for disinfection of rural water supplies has been undertaken.

The electrolyser design used was tubular in form, having two chambers i.e. anode inside and cathode outside, separated by a tubular inorganic ceramic membrane. The anode was made of titanium rod coated with a thin layer of platinum and a further coat of metal oxide. The cathode was made of stainless steel wire.

An assessment of these electrolysers was undertaken by studying the effects of some variable parameters i.e. current, voltage and sodium chloride concentration. The flow rate was kept unchanged at 50ml/h anolyte and 140ml/h catholyte since it was found to be optimum flow rate for chlorine generation. Figures of merit of the electrolysers were calculated on the basis of three sets of measurements. Analytical methods used for the determination of sodium hypochlorite concentration were iodometric and N, N-Diethyl-p-Phenylenediamine (DPD) titration methods. The DPD titration method was used to determine the chlorine concentration of less than 1mg/L, while the iodometric titration method was used to determine chlorine concentration of 1mg/L and above. Sodium chlorate present in the hypochlorite solution was also determined using a spectrophotometric method.

The cobalt oxide electrolyser has been shown to be superior as compared to the ruthenium dioxide and manganese dioxide electrolysers in terms of hypochlorite generation. Sodium chlorate was present but at concentration levels not hazardous for use in dosing water for drinking purposes. Analysis of hydroxyl radicals was undertaken since there were claims that these are produced during brine electrolysis. Hydroxyl radical analysis was not successful, since sodium hypochlorite and hypochlorous acid interfere using the analytical method described in this study.

DECLARATION

"I declare that *The Development of Appropriate Brine Electrolysers for Disinfection of Rural water supplies* is my own work and that all the sources I have used or quoted have been indicated and acknowledged as complete references."

Maxhobandile Siguba

Signed:

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CHAPTER ONE

1. LITERATURE REVIEW

1.1 BACKGROUND

A large proportion of the World's people do not have access to microbiologically safe sources of water for drinking and other essential purposes [1]. Contaminated drinking water poses a major health threat to human beings worldwide. It has been estimated that 1.1 billion people do not have access to safe drinking water sources. Consumption of unsafe water continues to be one of the major causes of the 2.2 million diarrheal disease cases occurring annually mostly in children (WHO/UNICEF, 2000) [2].

The problem is particularly severe in developing countries and in arid areas where water sources are scarce. In developing countries, surface waters such as rivers, streams and lakes are used for multiple activities, including livestock watering, bathing, laundering and cooking. Defecation and urination often occur near water sources as well. This water, which may be contaminated with pathogenic organisms, is also used for drinking. People in developing countries may have no other options for drinking water because of lack of a water distribution infrastructure and lack of funding for developing water treatment systems [3].

Disinfection of water is a process required to destroy harmful microorganisms in order to produce water, which is safe for human consumption. Disinfection of water greatly reduces the incidence of water borne diseases and the death rate from such diseases. Adequate disinfection in rural, poverty-stricken areas with no running water remains a huge problem. Various uncomplicated methods of disinfection have been in place for some time, but most of these methods require some form of infrastructure, economic investment and educated or informed use [4].

The World Health Organization estimates that 1.2 billion of people are affected by polluted water worldwide. Furthermore, 15 million children under the age of 5 die each year due to water borne diseases (WHO, 2002) [5]. Depending on the region, this problem may be complicated by overpopulation, contaminated water sources, poor sanitation infrastructure, lack of hygiene education, or some combination of these causes.

At any given time perhaps one-half of all peoples in the developing world are suffering from one or more of the six main diseases associated with water supply and sanitation (diarrhoria, ascaris, dracunculiasis, hookworm, schistosomiasis and trachoma). In addition to people affected directly through disease, poor health acts as a mechanism to further marginalize people by limiting their ability to work, produce food, and interact socially.

Finding a way to provide clean and safe drinking water in affected areas is therefore one necessary step in any effort to improve the quality of life of people in underserved areas and to mitigate the devastating effects of disease on the people of the developing world.

For a variety of reasons, methods for clarification and disinfection of the drinking water typically used in the developed world are not feasible in the developing world. A number of complicating factors make the gap in resources between the developed and developing world impossible to bridge with the same technologies [6].

People now drinking unsafe household water also include those in rural and peri-urban areas. Many rural dwellers lack indoor plumbing or nearby outdoor piped water from safe supply (from wells, boreholes, and protected surface water sources). They have to travel considerable distances to reach any water source, regardless of quality, for collection and household use [2].

Many of the world's people continue to obtain their water on a daily or other frequent basis from any available source and either carry it or otherwise have it delivered to the home for personal use. This water is gathered and stored in vessels of various designs and materials. The water is not treated or otherwise protected from subsequent contamination during use. Such household water is at high risk of being contaminated by microorganisms associated with fecal wastes and other sources. This is because water is typically obtained from the most inconvenient source, which is fecal contaminated and additional contamination occurs due to a variety of unsanitary conditions and practices during storage and use. Microorganism contamination of collected and stored household water is caused not only by the collection and use of fecally contaminated water that was not safe to begin with but also contamination of microbiologically safe water during its collection and storage. Factors contributing to this problem are unsanitary and inadequately protected (open, uncovered or poorly covered) water collection and storage containers, lack of protection against contamination introduced by flies, cockroaches, rodents, etc. and inadequate cleaning of vessels to prevent biofilm formation and accumulation of sediments and pathogens [2].

Improving and protecting the microbial quality and reducing the infectious disease risks to consumers of collected water stored in households requires alternative or interim strategies, plans and approaches that can be implemented effectively, quickly and affordable. Technically feasible, effective, socio-culturally acceptable and affordable methods for treatment and storage of household water to improve microbial quality and reduce waterborne disease risks are now available. Waiting for the provision of piped, safe community water systems to the many people lacking such services is an inappropriate response to the basic need for safer drinking water that can be met on at least a provisional basis by available technologies. Effective measures are needed immediately to provide risk populations with safer water at the household level until the long-term goal of providing safe piped community water supplies can be achieved [1].

In South Africa the problem is being addressed in a multifaceted manner outlined as follows:

1.2 SA POLICY FRAMEWORK WITH RESPECT TO WATER

This section introduces the background problem associated with drinking water in rural areas of South Africa. More than 30% of the population in South Africa is in need of secure access to safe drinking water. WHO 1995 estimates that some 20,000 deaths were caused annually with many people suffering with water related disease [7]. It is estimated that rural areas will require massive funding to establish full drinking water supply system coverage, such funding is not feasible to raise within the near future [8]. An alternative system that could address the problem is by implementing on-site generation of disinfecting agent using brine electrolysers for rural water supplies. A policy framework has been developed partly to address the problems above.

1.3 NEW WATER LEGISLATION AND POLICY IN SOUTH AFRICA

South Africa has adopted ambitious new water legislation that promotes equity, sustainability, representativity and economic performance through the water management. With the dismantlement of former regulations and the adoption of a new democratic constitution, the new act broke drastically with the previous water laws. Water is now considered a common asset. The right to use water is granted to users, most of them have to be registered and licensed, and should pay for this right. The core concept of water management under the new dispensation is decentralization. Protective measures are meant to secure water allocation for basic human needs, ecological and development purposes [9].

Social development economic growth, ecological integrity and equal access to water remain key objectives of the new water resources management regulation. New management act entities (Catchment Management Agencies and Water User's Associations) are developed in order to achieve the aims of the act.

The aims of the act are as follows;

- ✓ Water Services Act (108 of 1997) legislates the municipal function of providing water supply and sanitation services.
- ✓ National Water Act (36 of 1998) legislates the way that the water resource (surface and ground water) is protected, used, developed, conserved, managed and controlled.

The overall objective of the Water Services Act is to assist municipalities to undertake their role as water services authorities, and to look after the interest of consumers. It is also to clarify the role of other water services institutions, especially water services providers and water boards.

It is in terms of the Act that a municipality obtains use of the water that it requires for distribution to its consumers. They also govern how a municipality may return effluent and other wastewater back to the resource [10].

These institutions are currently established at regional and local level, respectively, emphasizing a largely decentralized and participatory approach to water resource management. The process however shows slow and uneven development through out the country. Furthermore, past water rights often still apply since the implementation of the new water legislation is still underway. The water legislation makes provision for water rights trading as an option for water allocation [9].

1.4 WATER SERVICES STRATEGIES IN SOUTH AFRICA

The minister of water affairs and forestry is responsible for ensuring that the National Water Resource Strategy is established. A summary of the strategy must be published in the Government Gazette and the full strategy of its parts (depending on its size) must also available in interest people. The National Water Resource strategy binds all water institutions and water users.

One of the main tools that are used to ensure that the National Water Resources are protected, used, developed, conserved, managed and controlled is the National Water Resource strategy. The National Water Resource strategy is progressively developed after public consultation and must be reviewed every 5 years [11].

In terms of institutional arrangements, the National Water Act states that the National Water Resource strategy must:

- Contain objectives for the establishment of institutions to undertake water resource management.
- Determine the inter-relationship between institutions involved in water resource management [12].

The purpose of the National Water Resource Strategy

- Facilitate the proper management of the nation's water resources.
- Provide a framework for the protection, use, development, conservation, management and control of water resources for the country as a whole.
- Provide a framework within which water will be managed at regional or catchment level, in defined water management areas.
- Provide information about all aspects of water resource management
- Identify water-related development opportunities and constraints.

1.5 ISSUES THAT NATIONAL WATER RESOURCE STRATEGY MUST ADDRESS

1.5.1 INTRODUCTION

- Set out strategies, objectives, plans, guidelines and procedures for the overall management of the water resource.
- Determine how much water much be reserved for basic human needs and for environment

- Provide for international obligations (water resources shared with neighbouring countries through international agreements)
- Provide for future water need
- Provide water for strategic use (for example national power generation)
- Determine water management areas
- Determine how much water is available in each water management area
- Provide for transfer of water from water management areas that have surpluses to water management areas that are short of water
- Set principles for water conservation and water use
- Set targets for water quality of different water resources
- Provide for the establishment of water resources management institutions (for example catchment management agencies) and the inter-relationships between these institutions (co-operative governance)

The national water resource strategy needs to that will be water for basic human needs, and for socio-economic development both now and in future. All water resources management must function accordance with the national water resource strategy [13].

1.5.2 PROPOSED STRATEGIES TO FACILITATE ACHIEVING THE OBJECTIVES

- ➢ Water services authorities will be required as part of their water services development plans, to develop a Water Conversation (WC) or Water Demand Management (WDM) strategy in accordance with the model strategy prescribed by Department of Water Affairs and Forestry (DWAF).

- ➢ Water Boards will be required to develop their WC/WDM strategies according to the Model strategy prescribed by DWAF, and submit them as part of their business plans [13].

1.6 WATER SERVICES DEVELOPMENT PLAN IN SOUTH AFRICA

A water services authority must prepare a draft Water Services Development Plan (WSDP) for its area of jurisdiction, as part of the Integrated Development Plan (IDP) process.

The WSDP is a tool to assist water services authorities to make informed decisions about water and sanitation services, and to plan for those communities that do not have access to basic services [14].

The planning process involves:

- Data collection and analysis
- Stakeholder participation
- Strategic decision making
- Project identification and priorities
- Commitment in terms of actions and resources required to implement the WSDP.

The purpose of the water services development plan

The primary purpose of the water services development plan is to assist water services authorities to carry out their mandate effectively. The requirement that water services authorities regularly update their plans and report annually on progress against their plans will assist local communities and Department of Water Affairs and Forestry (DWAF) to asses how well water services are performing relative to their intentions and their capacity.

The water services development plan must contain details about:

- The physical attributes of the area.
- The size and the distribution of the population.
- A time frame for the plan, including the implementation programme for the following five years.
- Existing water services
- Existing industrial water use
- The number and location of people who are not being provided with a basic water supply and basic sanitation.
- Water service providers, which will provide water services.
- Contracts and proposed contracts with water services providers
- Proposed infrastructure
- The water sources to be used and the quality of water to be obtained from and discharged into each source.
- The estimated capital and operating costs of those water services
- Financial arrangements for funding those water services, including the tariff structures

- Any water service institution that will assist the water services authority

- The operation, maintenance, repair and replacement of existing and future infrastructure.

- The number and location of people to whom water services cannot be provided within the next five years, setting out the reasons, and the time frame basic water supply and basic sanitation will provided to those people.

- Existing and proposed water conservation, recycling and environmental protection measures.

In developing the water services development plan the water services authority must at all times be conscious of the requirements of Water Service Act which states that "if the services provided by a water services institution are unable to meet the requirements of all its existing consumers, it must give preference to provision of basic water supply and basic sanitation to them'' [9].

1.7 PROBLEMS AND ISSUES RELATED TO RURAL WATER SUPPLIES

Contaminated drinking water poses a major health threat to human beings worldwide, particularly in rural areas where water sources are scarce. Defecation and urination often occur near water sources as well [3].

Disinfection is a very important step in the treatment of drinking water in order to prevent or reduce the risk of waterborne diseases [15]. However, it has been reported that in many cases in the developing countries a high level of reliability of water supply schemes, particularly the treatment process, is the exception rather than the rule.

This could be contributed to by various factors which include the following

- Cost
- Operator training and knowledge
- Problems with the maintenance of infrastructure [16]

Drinking water quality is difficult to control and even in the most developed countries, small community water supplies frequently fail on basic microbiological quality. Failure of disinfection in rural areas is not always due to technological problems with equipment.

Chlorine is one of the most effective disinfectants, it is relatively easy to handle, the capital cost of chlorine disinfection installation are relatively low, it is cost effective, simple to dose, measure and control and it has a relatively good residual effect. Moreover it reduces many disagreeable tastes and odours (chlorine oxidizes many naturally occurring substances such as foul-smelling algae secretions, sulfides and odours from decaying vegetation), removes chemical compounds that have unpleasant taste (ammonia and other nitrogenous compounds) and odor (hydrogen sulfide which has a rotten egg odor) and hinder disinfection.

Chlorine disinfection is generally carried out using one of the three forms of chlorine (elemental chlorine (Chlorine gas), sodium hypochlorite solution (bleach), and dry calcium hypochlorite) or it can be generated on site. The form of the chlorine added will depend on the equipment and chemical form available locally. Chlorinating water requires that the operator be trained in making up the correct solution strengths. Operators must also ensure that sufficient chemicals are always available.

Chlorine gas is commonly used on large and medium scale plants. It is supplied as a liquid in pressurized cylinders and is evaporated prior meeting and injection into the water being treated. Due to the hazardous nature of the gas, appropriate safety measures are required. Therefore gas chlorinators should not be operated and controlled by unskilled persons who are not fully conversant with the apparatus or dangers of the gas [17].

The reasons for failure and unreliability of disinfection using chlorine include the following:

- Lack of chlorine chemical
- Lack of operator training.
- No provision made for chlorine addition.
- Lack of funds for purchasing chlorine
- No monitoring of chlorine residual to detect chlorine levels [18].

1.8 CHLORINE DISINFECTION IN RURAL SMALL WATER TREATMENT PLANTS OF SOUTH AFRICA

Recent studies have shown that the majority of small water works in South Africa have difficulty providing adequate treatment and disinfection with the result that consumers are at risk of waterborne diseases even from treated water supplies [19]. Both technical and human factors have been reported to be the major causes of failure of small rural water treatment plants to provide potable water to their consumers. Chlorine dosing and the delivery of chlorine to the plant remains a major on-going problem in most of rural water works [20].

A lack of a proper chlorine dosing procedure and monitoring programme results in insufficient chlorine residuals at the point of treatment. However to have effective disinfection, the chlorine dose has to be rationed to the plant flow rate. In other words, before applying chlorine to the water, it is important to know the chlorine demand of the water. A number of countries including South Africa have issued guidance to water suppliers on disinfectant residual that should be aimed for in distribution. These countries indicate that the residuals should be kept to a minimum consistent with ensuring that microbiological standards are met and some countries also include minimizing by-products formation, to minimize biofilm formation and to avoid problems with chlorine tastes and odours and to provide some protection against re-contamination within the distribution system [21].

The measurement of the chlorine demand of the water is not known in small water treatment plants in rural areas. The operator is requested to use a particular dose as indicated by the superintendent, regardless of the daily quality of the water source. This can lead to overdosing or under-dosing of the chlorine. It has been observed that the chlorine decay is influenced by the chlorine demand of the water and the reactions with deposits such as organic and inorganic sediments. It is therefore important for operators to understand and compensate for the way disinfectant decreases in the distribution system. Although chlorine is used to reduce bacterial numbers, the mere use of chlorine does not guarantee the removal microbiological pathogens; it is essential to apply the correct dose at the correct frequency [21].

Moreover, any point of chlorine application must be such as to give adequate time of contact of the chlorine with the water before it leaves the water works. Although the minimum time of contact required is determined by the dosage of chlorine applied, it is desirable to make provision for a contact time of not less than an hour.

A number of different ways of dosing exist. The following are important points that must be taken into consideration in designing and controlling chlorine dosing systems: uninterrupted dosing, uniform distribution to all parts of the water mass, adjustment of the dosage to the chlorine demand of the water being treated and control of the dosage to produce safe water without spoiling the taste [22].

CHAPTER TWO

2. REVIEW OF WATER DISINFECTION METHODOLOGY

2.1 Boiling

Microorganisms that might be lurking in water will be killed if the water is boiled long enough [6]. Boiling will also drive out some of the volatile organic compounds (VOCs) that might also be in the water. This method works well to make water that is contaminated with living organisms safe to drink, but because of the inconvenience and full requirements, it is not routinely used to purify drinking water except in emergencies.

Boiling also does not remove many other water contaminants. In fact boiling is liable to concentrate contaminants (like lead, asbestos, mercury, and many toxic organic chemicals) that are not vaporized as the relatively pure water vapour boils off [6].

2.2 Distillation

To remove impurities from water by distillation, the water is boiled causing the water to be vaporized as steam leaving the non-volatile contaminants behind. The steam is then cooled until it condenses, and the resulting distillate drips into a container. Salts, sediment, and metals anything that was not evaporated remains in the distiller and must be removed. VOCs are a good example of a contaminant that distillation will not remove. A carbon filter or other device must be used with a distiller to ensure the complete removal of all contaminants.

A good distillation unit produces very pure water. This is one of the few ways to remove nitrates, chloride, and other salts that carbon filtration cannot remove. Distillation also kills microorganisms in the water. Distillation takes time to purify the water; uses power all the time the unit is operating, and requires cleaning [23].

2.3 Reverse Osmosis

Water pressure is used to force water molecules through a membrane leaving the contaminants behind. Purified water is collected from the clean side of the membrane. Water containing the concentrated contaminants is flushed down the drain from the contaminated side. Reverse osmosis removes salt and most other inorganic material present in water. For that reason, RO lends it self to in places where the drinking water is brackish (salty) or contains nitrates that are difficult to remove by other methods.

With a good quality carbon filter to remove any organic materials that get through to the RO membrane, the purity of the treated water approaches that produced by distillation. Microscopic bacteria and parasites (including viruses) can be removed by RO units, but any defect in the membrane would allow these organisms into the filtered water [23].

2.4 Ultra Violet light

Ultraviolet light has been used fairly extensively for disinfection of small community water supplies [24]. The efficiency of the UV disinfection is dependant on the intensity of the light and the exposure of the microorganisms to the light. The majority of microorganisms require fairly low UV doses for inactivation. UV light decreases in efficiency as contamination (especially turbidity and some substances in solution such as iron and organic compounds) increases.

Water passes through a chamber transparent to a source of Ultra Violet (UV) Light. UV light kills bacteria and deactivates viruses but the tough cryptosporidia cysts are fairly resistant to UV light [24]. Any turbidity in the water can shadow pathogens, protecting them from the light. UV light is not effective against any non-living contaminant, lead, asbestos, organic chemicals, chlorine etc. UV is typically used as a final purification stage in some filtration systems. If contaminants in addition to bacteria and viruses are to be removed, a good quality carbon filter or reverse osmosis system in addition to the UV system must be used.

UV disinfection of water is normally achieved by passing water through a tube lined with UV lamps. This gives efficient disinfection after a contact time of few seconds. The lamps may continue to produce blue light when they are worn out and no longer produce disinfection light.

Disinfection with UV light does not give rise to tastes and odors. There is no requirement for consumable chemicals, matainance is straightforward and there is no danger of overdosing. UV light does not leave a residual effect in the water [6].

2.5 Ozonation

Ozone (O_3) is a very reactive and unstable gas with a short half-life with respect to conversion to oxygen. Ozone is a strong oxidizing agent, and will oxidize all bacteria, molds, yeast pores, most organic material and viruses. Ozone is a disinfectant that effectively kills biological contaminants and oxidizes and precipitates iron, and manganese so they can be filtered out of the solution. Ozone oxidizes and breaks down many organic chemicals as well, but ozone treatment creates its own set of undesirable byproducts that can be harmful to health if they are not controlled e.g. formaldehyde and bromate [24].

Oxidation reactions of ozone in water occur via two pathways, namely direct oxidation by molecular ozone and indirect oxidation by free radical species. These radical species can be formed by decomposition of ozone and from reaction of ozone with some inorganic and organic compounds. Ozone decomposition in water forms hydroxyl radicals and is accelerated by a number of free radicals and anions.

Ozone is slightly soluble in water. It is an efficient disinfectant, and because it is unstable does not leave residual in water unlike chlorine. For this reason it is impossible to overdose with ozone. It contributes to the bleaching of color and removal of tastes and odors.

Ozone is a very efficient disinfectant and is more effective than chlorine inactivating cryptosporridium oocysts and viral agents. There are significant disadvantages in the use of ozone; it does not provide residual protection against recontamination during distribution and as ozone affects biological stability, it may encourage regrowth of bacteria. The lack of a residual in ozonation may be dealt with by employing regular booster ozonation during distribution. Ozonation is much more expensive than chlorination [25].

2.6 Coagulation and Flocculation

The process of coagulation can be described as the combination of small particles into large aggregates. The process of chemical coagulation-flocculation enhances the removal of colloidal particles by destabilizing them, chemical precipitating them and accumulating the precipitated material into larger floc particles that can be removed by gravity settling or filtering [1]. The settled floccules are referred to as sedimentation. Sedimentation is problematic in terms of sludge disposal [26].

Coagulation with aluminum or iron (III) salt results in the formation of insoluble, positively charged aluminium or iron hydroxide (or polymeric aluminum –or iron –hydro complexes) that effectively attract negatively charged colloidal particles.

Coagulation-Flocculation or precipitation using lime, lime soda ash and caustic soda is used to soften water, usually ground water by removing (precipitating) calcium, magnesium, iron, manganese and other polyvalent metallic cations that contribute to hardness. Reduction of microbial contaminants as well as turbidity, dissolved colloidal organic matter are also achieved in this process. This process is usually one of the first steps in a series of water purification steps [27].

2.7 Filtration

There are many types of filtration strategies and combination of strategies used. The basic concept behind all filters is fairly simple. The contaminants are physically prevented from moving through the filter either by screening them out with very small pores or in same case by trapping them within the filter matrix attracting them to the surface of filter [6]. The filtering processes mentioned are also known industrially as deep bed filtration, and cake filtration. The different types of filter are described below

2.7.1 Slow sand filtration

Slow sand filtration has been used throughout the world for the last 150 years. Although slow sand filtration technology has been widely used in Europe since the early 1900s, its current use in North America has been primarily limited to smaller communities in New England and is still a popular method of treating municipal water supplies [28]. The filters are easily constructed and the process is simple to operate. The process consumes no chemicals or electrical energy during normal operation. However due to high filtration rate, large areas of filter bed may be required.

Slow sand filtration is a biological process characterized by smaller sand particles (0.25 to 0.4 mm in diameter) and a lower filtration rate (0.1 to 0.3 m/h) in which turbidity, colour and microbiological contaminants can be removed to levels acceptable for potable water. Filtration rates of approximately 2.44 to 3.66 liters per minute per meter square ($l.min^{-1}.m^{-2}$) of filter surface area are typical. Therefore, a relatively large surface area is necessary to accommodate a realistic flow rate (for example, a 6.1- $l.m^{-1}$ flow rate requires between 9.6 and 40 meter square of filter surface area). It will not remove all microorganisms, but removes a significant amount due to the formation of a rich biological matrix called a "Schmutzedecke." This layer consists of a wide assortment of life forms including algae, rotifers, and many other organisms. These organisms assimilate microorganisms (protozoans, bacteria and virus) thus reducing their numbers as water passes through the biologically active matrix. Slow sand filters are cleaned by draining the filter and scraping the top inch of sand (which includes the "Schmutzedecke"). However, this destroys the "Schmutzedecke" and requires a re-ripening period that can take weeks. While one filter is being cleaned, the other is on-line to continue the filtration process.

In recent years, a new method of cleaning slow sand filters called "wet harrowing" has been developed that simplifies the cleaning process. Also, the creation and use of polyethylene filter vessel structures have made the task of building slow sand filters much easier. It must be recognized that slow sand filters have their limitations in that they cannot remove high turbidity, high levels of microorganisms, nor chemical contamination from water. However Global Water uses slow sand filters wherever this relatively simple water treatment technology can accommodate local water conditions. When properly operated, disinfection of the filtrate should not be necessary but it is typically practiced to combat subsequent regrowth and contamination of the treated water. Additional treatment processes are required for hard and unusually turbid water, as well as water high in dissolved solids, such as sodium, nitrite, nitrate, sulphate and fluoride. With water supplies that are high in organic content, the filtration process is not effective in complex iron removal, in which organic compounds may be bound to iron ions and cannot be removed by an aeration/ filtration process. Typically, water that may produce organic complexing of iron should have a level of organic carbon over 2mg/L and may also contain ammonia. Water containing a level of dissolved organic carbon (DOC) over 5 mg/L may cause taste, odour and colour problems. Slow sand filtration cannot effectively remove dissolved organic carbon. A carbon filter should be used in addition to the slow sand filter [28]. With the recent issuance of the Surface Water Treatment Rule by the U.S. Environmental Protection Agency and new filter requirements for all surface water systems to ensure removal of Giardia cysts, there is renewed interest in slow sand technology.

2.7.2 Rapid sand filtration

Rapid sand filtration is a technique that is now commonly used in rural developing areas. It is a sophisticated process usually requiring power operated pumps for backwashing or cleaning the filter bed, and flow control of the filter outlet. The period between backwashes depends on the quality of water being filtered, usually daily. The purpose of backwashing is to remove the suspended material that has been deposited in the filtration bed during filtration cycle.

The filter process operates based on two principles: mechanical straining of suspended matter and physical adsorption. Water fills the pores of the filter medium and the microorganisms are adsorbed on the surface of the grains or trapped in the openings. The key to this process is the relative grain size of the filter medium [29]. The performance of a rapid filter depends on the following parameters: filtration rates, influent characteristics (i.e. particle size, distribution etc) and filter medium characteristics, which control the removal of the particles and their release upon backwashing. Generally, it is true that the treatment effect can be improved by reduced filtration rates (not less than 2,5 m/h), smaller granulation size of the filter medium, increasing depth of the filter bed, increasing size of the flocs and decreasing the concentration of particles to be retained. The range of filter beds is between 1 and 2m. The operating head is between 1.5 and 2.5m [29]. The required filter surface area can be determined according to the following relationship:

$$A=Q/(a*v)$$

Where A= surface area [m^2], v = filtration rate [$m^3/(m^2*h)$]; Q = throughput of water per hour [m^3/h]; a = operating hours per day [29].

Combined with coagulation, flocculation and sedimentation, rapid sand filtration is a very efficient treatment process for the removal of microorganisms. Besides of the advantages that these filters are effective in removing suspended solids and require a minimal land for construction, they present the following disadvantages:

- Rapid sand filters have a high capital and operational costs
- Uses energy for pumping

Requires a high degree of training for plant operators, for monitoring, operation and maintenance [29].

2.8 Advanced Oxidation Processes (AOP)

Advanced oxidation processes involving hydroxyl radical (•OH), represent a new treatment concept and have gained increasing interest in treatment of industrial and drinking wastewater to remove organic and inorganic contaminants. The common target of many groups working worldwide is to increase the number of applications of these processes and to improve the efficiency. The main interesting characteristics of hydroxyl radicals are its very high oxidation potential and the possibility of its generation by different ways [30].

The most common ways for generating the hydroxyl radicals are explained below:

2.8.1 Anodic oxidation

In an electrochemical treatment organic compounds can be oxidized indirectly or directly by the anodes [31]. An indirect anodic process operates via the production of oxidants such as hydroxyl radicals, ozone, etc destroys the organics and toxic microbial pollutants present in wastewater. A direct process is one in which the pollutants are first adsorbed on the anode surface and then oxidized by an electron transfer reaction [32].

2.8.2 UV / O_3 Process

The UV/O_3 system is an effective method for the oxidation and destruction of organic compounds in water. The advanced oxidation process with UV radiation and ozone is initiated by the photolysis of ozone. The photodecomposition of ozone leads to two hydroxyl radicals, which if they do not react, recombine producing hydrogen peroxide.

The reaction mechanism starts with photodecomposition of ozone molecules by UV to form oxygen radicals, which then combine with water to form hydroxyl radicals [33].

$$O_{3\,(g)} + h\nu \rightarrow O_{2\,(g)} + O^{\bullet}_{(aq)}$$
$$O^{\bullet}_{(aq)} + H_2O_{(l)} \rightarrow 2{\bullet}OH_{(aq)}$$

Oxygen radicals can also react with water to form hydrogen peroxide [34].

$$O^{\bullet}_{(aq)} + H_2O_{(l)} \rightarrow H_2O_{2\,(aq)}$$

This system contains three components which can produce hydroxyl radicals and /or to oxidize the pollutants for subsequent reactions i.e. UV radiation, ozone and hydrogen peroxide.

2.8.3 UV / TiO_2 (Heterogeneous photo catalysis) Process

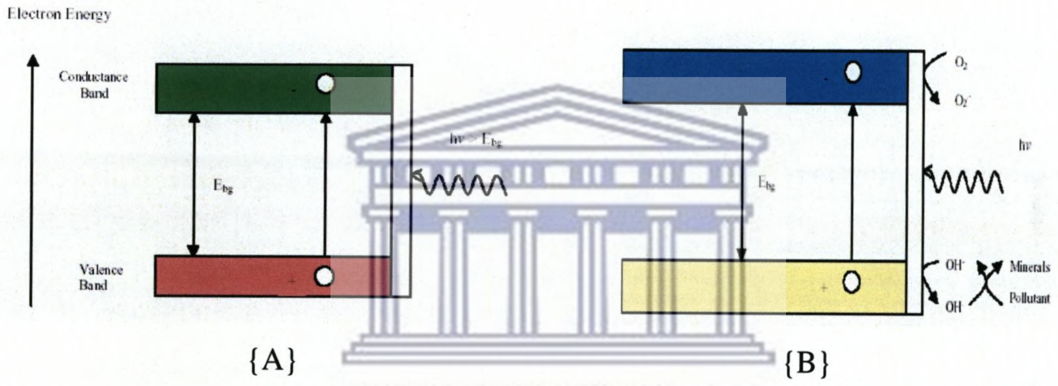
The heterogeneous photocatalytic process consists of utilizing the near UV radiation to visible light to excite a semiconductor catalyst TiO_2 in presence of oxygen and water. Under these circumstances oxidizing species (hydroxyl radicals) are generated [35].

The band gap is the term given for the energy difference between the two bands. When the semiconductor is illuminated with light of greater energy than of the band gap (when $h\nu > E_{bg}$), an electron is promoted from valence band to the conductance band.

During the photocatalytic process, the bands of interest are the occupied valence band and the unoccupied conductance band. The occupation of a band simply means that the band is filled with an electron. This is illustrated in the figure 2.1A.

The hydroxyl radicals are generated via oxidation at the valence band. These radicals subsequently oxidize the polluting materials, while at the conductance band an electron is donated to oxygen there by generating the superoxide radical anion as illustrated in figure 2.1B.

Figure 2.1 Photo excitation of an electron from valence band to the conductance band {A}; The semiconductor photocatalytic process for water disinfection {B}: [36]



2.8.4 H_2O_2 / UV Process

The H_2O_2 / UV system involves the formation of hydroxyl radical by hydrogen peroxide photolysis.

$$H_2O_{2\,(aq)} \xrightarrow{hv} 2\bullet OH_{(aq)} \qquad \lambda \leq 400nm$$

It presents the advantage compared when working with ozone in that it provides a cheap and sure source of radicals also eliminating the problem of handling of ozone.

The major drawback of this process is that if the solution contains strongly absorbing substance which can compete with hydrogen peroxide for the radiation, thus cloudy water or water containing compounds absorbing UV radiation can present problems being treated by this method [37].

2.8.5 O_3 / H_2O_2 Process

Addition of hydrogen peroxide to ozone offers another way to accelerate the decomposition of ozone, leading to the formation of hydroxyl radicals. The reaction of this process is illustrated below:

$$H_2O_{2\,(aq)} + 2\,O_{3\,(g)} \rightarrow 2\bullet OH_{(aq)} + 3\,O_{2\,(g)}$$

This process does not depend on the UV radiation absorption to activate the ozone or hydrogen peroxide molecules. Its greatest advantage is to be able to work with turbid water without problems [38]

2.8.6 Fenton's reaction process

Fenton's reaction simply involves the use of hydrogen peroxide in the presence of a catalyst e.g. iron (II) sulfate ($FeSO_4$) to form hydroxyl radicals. Hydrogen peroxide in this process is utilized in a different fashion when compared to its typical use in the environmental restoration (i.e. an oxygen source to enhance aerobic biodegradation).
The reactions are as follows:

$$Fe^{2+}_{(aq)} + H_2O_{2\,(aq)} \rightarrow Fe^{3+}_{(aq)} + \bullet OH_{(aq)} + OH^-_{(aq)}$$

Now, the process is itself replicating since the reaction of ferric iron with H_2O_2 to generate the per hydroxyl radicals also occurs.

$$Fe^{3+}_{(aq)} + H_2O_{2\,(aq)} \rightarrow Fe^{2+}_{(aq)} + HO_2\bullet_{(aq)} + H^+_{(aq)}$$

The other important possible reactions are shown below

$$\bullet OH_{(aq)} + H_2O_{2\,(aq)} \rightarrow HO_2\bullet_{(aq)} + H_2O_{(l)}$$

$Fe^{2+}{}_{(aq)} + \bullet OH_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + HO^{-}{}_{(aq)}$

$Fe^{2+}{}_{(aq)} + HO_2\bullet_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + HO^{-}{}_{2\,(aq)}$

$Fe^{3+}{}_{(aq)} + HO_2\bullet_{(aq)} \rightarrow Fe^{2+}{}_{(aq)} + H^{+}{}_{(aq)} + O_{2\,(g)}$

The perhydroxyl radical ($HO_2\bullet$) is a weak oxidizer. More important is that the process generates ferrous ions that in turn stimulate further reaction to produce more hydroxyl radicals. The optimum pH for Fenton's reaction is in the range of 3.0 to 4.5 [39].

2.9 Chlorine Dioxide

Chlorine dioxide is a gas that is soluble in water. Chlorine dioxide is a more powerful oxidizing agent than chlorine and its disinfection action is less pH-dependant than that of chlorine.

The oxidation-reduction reaction of chlorine dioxide is as follows:

$ClO_{2\,(g)} + e^{-} \rightarrow ClO_2^{-}{}_{(aq)}$ $E^{o} = 0.954$ V

Other important half reactions are

$ClO_2^{-}{}_{(aq)} + 2H_2O_{(l)} + 4e^{-} \rightarrow Cl^{-}{}_{(aq)} + 4OH^{-}{}_{(aq)}$ $E^{o} = 0.76$ V

Therefore the total chlorine dioxide redox potential is 0.954 V + 0.76 V = 1.714 V, whereas for chlorine

$Cl_{2\,(aq)} + 2e^{-} \rightarrow 2Cl^{-}{}_{(aq)}$ $E^{o} = 1.358$ V

Chlorine dioxide removes taste and odors effectively [40]. Chlorine dioxide is not a chlorinating reagent so no chloroform or other trihalomethanes are formed [41]. Chlorine dioxide has proved to be an excellent biocide and an effective oxidant in drinking water, cooling water, wastewater, and odor-control applications. Chlorine dioxide achieved faster kill of microorganisms at lower concentrations than did other chlorine-based sanitizers [42]. Chlorine dioxide can remove pesticides particularly Aldrin and methoxychlorine. Herbicides such as paraquant and diquant are eliminated by chlorine dioxide within a few minutes at a pH higher than 8 [43].

Chlorine dioxide is unstable and cannot be conveniently transported or stored over long periods. It is always generated on site because of its risk of rapid decomposition [44].

2.10 Chlorine

Chlorine addition is the most common method for potable water production due to its effectiveness at inactivating several types of pathogens and its reactively low cost [45]. For almost a century the predominant method of disinfection of water has been by the use of chlorine compounds. Chlorination is effected by adding chlorine gas, or alternatively sodium or calcium hypochlorite to the water. It also produces a residual that further protects the water from contamination after treatement. Chlorination can however, cause problems by producing destructive byproducts when being administered to water containing traces of organic material [46]. A disadvantage with all chlorine chemical treatment methods is that the chemicals decompose over time and therefore have limited shelf lives [3].

2.11 COMPARISON OF SOME DIFFERENT ALTERNATIVE TECHNOLOGIES FOR DISINFECTION OF WATER IN RURAL AREAS

The practice of disinfection of water supplies has been in general use since beginning of the last century in Europe and other developed countries, and has give rise to substantial reduction in the occurrence of water related diseases in these countries. The most used technology to achieve disinfection has been chlorination. This has traditionally meant the addition of chlorine gas or other chlorine compounds in controlled quantities to the water to be supplied to domestic users. This method of disinfection has proven to be reliable, appropriate and effective in most developed countries and now also is common in every large town and city in the world [18].

In rural, small town and peri-urban areas of developing countries conventional chlorine can be considered as being a failure. The primary reason for the failure is related to the problem of obtaining the chlorine chemicals in the rural areas and informal urban settlement. In many cases the chemical involve (chlorine gas, sodium hypochlorite or calcium hypochlorite) are not readily obtainable by the community in the form and quantity required. Problems of cost, purchasing, transport, and of importation when the products are not produced in the country, are responsible for the failure of chlorine disinfection. The problem of accurate dosing and residual monitoring without the necessary level of skills, equipment and instrumentation have also been significant in the lack of reliability of chlorination disinfection in small water systems [20].

Alternative disinfection technologies, which have the following characteristics, may be more appropriate than chlorine treatment:

- Technologies must be affordable by the user community from both a capital cost and the ongoing operation and maintenance cost point of view.

- They must be simple to operate and maintain, also give reasonably accurate doses of the disinfection.

- The materials or chemicals which are regularly used for ongoing operation should be readily available at close proximity to the place of usage.

The following three alternative methods of disinfection [18] could be considered in rural areas where conventional chlorination is unlikely to be reliable and appropriate.

- UV Radiation
- Mixed Oxidants Gases Generated On-site Disinfection (MOGGOD)
- On-site hypochlorite production

All of these technologies do require an electrical energy supply, which may also not be readily available in rural areas. However, remote electrical power can be supplied relatively by means of solar panels systems, which is more suited to remote communities than the ongoing supply of a chemical. Each system is briefly described below:

2.11.1 UV RADIATION

UV Radiation is a relatively old technology, which was first used for disinfection purposes. It was never considered to be reliable means of disinfection. The main reason was that the core of the technology i.e. the lamps presented many problems. These often fails or were inconsistent in their emission (intensity and / or wavelength).

UV lamp manufacturing improved to the extended that lamp of high reliability are now readily available. Today, lamps with a life expectancy of up to 8000 hours and emission decay of not more 20% over this period can be readily obtained commercially [16].

The simplest UV disinfection device is a container (normally a portion of pipe) where the water passes through in a controlled way (i.e. no short-circuiting and limited flow rate). The lamps are contained in quartz tubes within the pipe, and result in a fixed average UV dose to the water passing through. Another type of UV system is where the lamps are mounted above a shallow tank through which the water passes. UV radiation system is a very simple system [3].

2.11.1.1 ADVANTAGES OF UV RADIATION

- No chemicals needed
- The installation is very simple
- Operation and maintenance are extremely simple
- There are no mobile parts
- It is very quick in killing microorganisms
- Does not form toxic compounds
- There is no risk of over dosage
- There are no oxidizing chemicals, and hence minimum corrosion to installation can be expected.

2.11.1.2 DISADVANTAGES OF UV RADIATION

- It is difficult in determining the effective dose to a certain type of material.
- Only if the dose is adequate will microorganisms destruction be complete.
- It's requirement to achieve disinfection differs for different microorganisms.
- There is no disinfection residual to protect water to secondary contamination
- There is no Lamp failure indicator
- If the flux and flow pattern in the vessel where the lamp is acting is not homogenous, there should be short-circuiting and some portions of water passes through would not receive necessary dose [3].

2.11.2 MIXED OXIDANT GASES GENERATED ON-SITE FOR DISINFECTION (MOGGOD)

This technology is based on the electrolysis of sodium chloride. The electrolysis process makes use of electrical power source, requiring approximately 4.5 kWh per Kg of chlorine equivalent. The only feed chemical needed for the production of the disinfectant gases is common table salt, general available in any village in the rural areas.

2.11.2.1 MOGGOD ELECTROLYTIC PROCESS

The electrolysis of sodium chloride means the electrolytic conversion of chloride ions (from concentrated solution of common table salt in water) forming chlorine, through the passage of an electric current.

The process is rather slow and inefficient when the electrodes are placed directly in the brine (concentrated salt solution) but if there is separation of both compartments (cathodic and anodic) by means of a membrane, the process is more efficient. When there is no separation between compartments, then the chlorine will react with hydroxide ions forming sodium hypochlorite, which will remain in solution together with the unreacted salt. When the anode and cathode cells are separated, chlorine gas is formed [47].

2.11.2.2 MOGGOD CELL

The cathode is a standard piece of stainless steel. However the anode used is a Dimensionally Stable Anode (DSA). The DSA offers substantial reductions in power consumption and allows the best efficiency in the process.

The DSAs are based on inventions using metal oxide coatings, usually transitional metal and platinum group metal oxides, applied to a rare metal normally titanium substrate. The MOGGOD technology is unique because there is an important innovation of the electrode geometry:

Instead of a typical array consisting of:

Cathode-membrane-anode, which has been historically used for the production of chlorine, the MOGGOD array makes use of an anode in several different planes parallel to the plane of the membrane and the cathode. The different planes act as if the array would be:
Cathode-membrane-anode-anode
It is claimed that it allows formation of chlorine (plus hydrogen and sodium hydroxide) plus several oxygen species including ozone. This is the reason for calling this technology Mixed Oxidant gases generated on-site for disinfection (MOGGOD). The effective disinfection power of the mixture of oxidants is very high as all the additional species formed in the reaction display an extremely high oxidizing power [16].

The drawback of the technology is the clogging of the membrane and the number of unwanted by-products precipitates is formed.
The second drawback is the need to feed the gas into the flow of water. The dosing of the gas is more difficult.
The disinfection produced allows the treatment of even heavily contaminated water.

2.11.3 ON-SITE HYPOCHLORITE PRODUCTION

The on-site hypochlorite production technology is similar to that of MOGGOD where chlorine is produced within an electrolytic cell. The cell is not separate into 2 regions by a membrane, and is more simple to operate and maintain. The chlorine produced at the anode will remain in solution and mix with the sodium hydroxide produced at the cathode, giving sodium hypochlorite.

Although this is a less efficient system when compared to a membrane cell, it does not have the maintenance problems associated with the use of a membrane. There is no need to feed gas into the water to be treated but instead a solution, which is much simpler and more reliable. As the efficiency is less and the chlorine stays in solution, the type of cell materials can be less stringent, while in the case of MOGGOD cells there is a need to have special materials to prevent corrosion when subjected to the gas.

As in the case of MOGGOD, the on-site hypochlorite cells do not require any expensive chemicals, but utilize common table salt.

2.12 QUALITY OF WATER THAT CAN BE TREATED

In all cases turbidity can cause problems, as the particles responsible for the turbidity could hider the effect of any disinfectant. This is common in all three systems, but more with UV treatment. Thus flocculation and filtration are required pretreatment.

Of the most important frequent parameters found in rural supplies, the following table gives an idea of their influence on the disinfection action of three technologies [16].

Table 2.1 Effect of water quality on disinfection efficiency [18]

Quality parameters	UV Radiation	MOGGOD	On-site hypochlorite generation
Turbidity	H	M	M
Colour	M	L	L
Iron (as Fe^{3+})	H	L	M
Organic compounds (e.g. Phenols)	H	L	M
Ammonium compounds	L	M	H
pH	L	M	M
Most Inorganic ions	L	L	L
Biological components	L	L	L

Note: H = high influence

M = medium influence

L = low influence

Table 2.2 Installation requirements and options

Requirements/options	**UV Radiation**	**MOGGOD**	**ON-SITE CHLORINATION**
Can treat water in channel	No	No	Yes
Can treat water in pipe	Yes	Yes	Yes
Can treat only a portion of water flow	No	Yes	Yes
Needs additional equipment	No	Yes	Yes
Needs electrical power source	Yes	Yes	Yes
Installation needs only basic plumbing	Yes	Yes	Yes
Needs special tools to install	No	No	No

2.13 COST OF MAINTANANCE

The major costs of maintenance are the replacement of equipment or parts.

In the case of UV system it is the lamp replacement. The lifespan of the equipment is 5 years [18]. The lamp replacement cost in the bigger equipment is very high as these units run with 8 lamps.

In the case of MOGGOD system anode should be changes once every two and half years, and the membrane every six months.

In the case of On-site hypochlorite cells, their lifetime is 2.5 years [16].

2.14 POWER CONSUMPTION

The three technologies require an electrical power source for their operation. All these technologies can operate with low level of current power, a power source capable of providing 12volts and 6 amps can be used to run the equipments. The power consumption for different types of communities is approximately the same for the different technologies [18].

2.15 CONCLUSION

All three technologies could be used in disinfection at small water treatment plants, however due to feasibility of local manufacture on-site hypochlorite production is the preferred option.

2.16 CHEMISTRY OF CHLORINATION

2.16.1 Chlorine (Cl_2) in water

When chlorine gas dissolves in water a dilute solution of hypochlorous and hydrochloric acid is formed [48].

The reaction in symbolic form is:

$$Cl_{2\,(aq)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + HCl_{(aq)}$$

$$K_h = \frac{[HOCl]\,[HCl]}{[Cl_2]} = 4\text{x}10^{-4}\ M \text{ (at } 25^{o}C)$$

The equilibrium of this reaction is in favour of free chlorine since K<<1. The actually disinfection agent is hypochlorous acid, which partially dissociates in water forming hypochlorite ions. The concentration of the two species is determined by the dissociation constant (pKa = 7.537 at 25°C.) and depends on the pH and the total concentration of chlorine [49]. The dissociation is as follows:

$$HOCl_{(aq)} \rightleftharpoons H^{+}_{(aq)} + OCl^{-}_{(aq)}$$

to produce hydrogen ion and a hypochlorite ion. In water of pH between 6.5 and 8.5 the reaction is incomplete, and both species are present in some degree. The extent of this reaction can be calculated from the following:

$$K_a = \frac{[H^{+}]\,[OCl^{-}]}{[HOCl]}$$

K_a, the acid dissociation constant, varies in magnitude with temperature as showed in the table below:

Table 2.3 HOCl dissociation constant

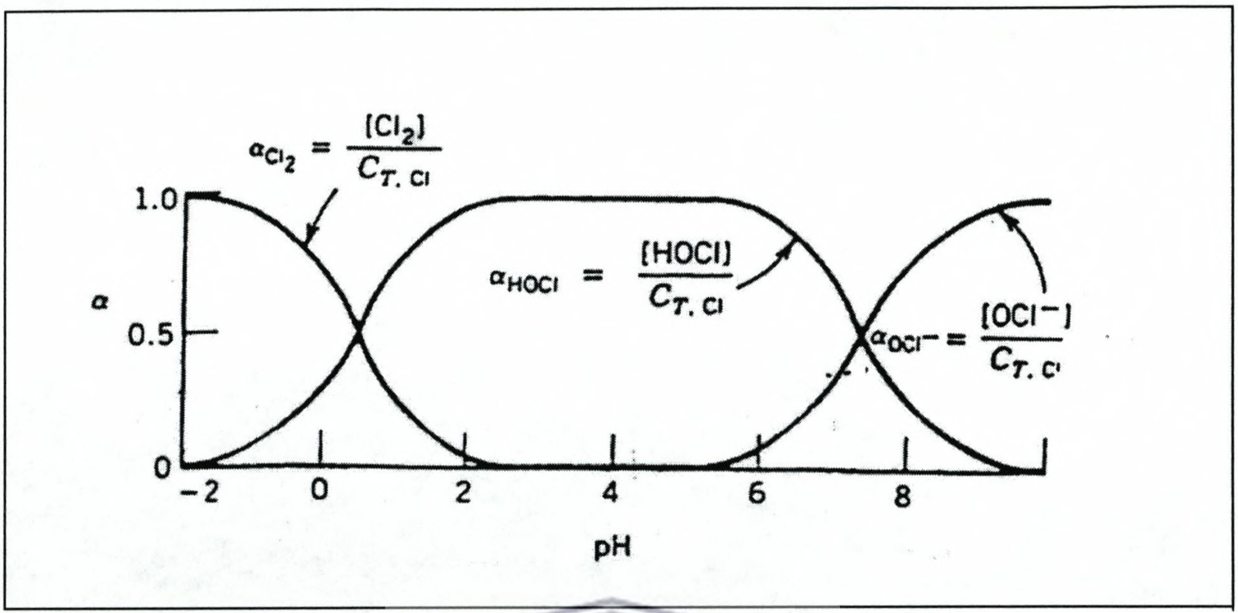
Temperature (°C)	0	5	10	15	20	25	30
$K_a \times 10^2$ (moles/liter)	1.488	1.753	2.032	2.320	2.621	2.898	3.175

Hypochlorous acid is much more effective for disinfection than the hypochlorite ion about 60 to 200 times more effective [50]. However, due to the equilibrium as soon as hypochlorous acid is consumed, new acid is produced from hypochlorite ions and therefore hypochlorite ion is considered to have an indirect disinfecting agent [50]. The germicidal efficiency of HOCl is due to the relative ease with which it can penetrate cell walls. This penetration is comparable to that of water, and can be attributed to both its modest size (low molecular weight) and its electrical neutrality (absence of an electrical charge). Other things being equal, the germicidal efficiency of a free available chlorine residual is a function of the pH, which establishes the amount of dissociation of HOCl to H^+ and OCl^- ions. Lowering the temperature of the reacting solution suppresses the dissociation; conversely, raising the temperature increases the amount of dissociation. The rate of dissociation of HOCl is so rapid that equilibrium between HOCl and the OCl^- ion is maintained, even though the HOCl is being continuously used [51].

The relative quantities of these two species (hypochlorous acid and hypochlorite ions) are determined by the pH of the water. At very low pH; less than zero, the free chlorine predominates, at pH; between 0 and 7 hypochlorous acid is the predominant species and at pH above 7.5 hypochlorite ion predominates (see figure 2.2). These species are termed collectively as available chlorine [52].

It is therefore important that the pH of the water be taken into account when determining the required chlorine dose for disinfection [50].

Figure 2.2 Effect of pH on chlorine species in water



$C_{T,Cl}$ → Total concentration of all chlorine compounds.

The equilibrium concentrations of the above-mentioned species are influenced by the three parameters namely:

- The pH of water
- The water temperature
- The chlorine concentration

The form in which chlorine is added to water affects some of the chemical properties of water. The addition of chlorine gas to water will lower the alkalinity because of the production of the strong acid (HCl) and a weak acid (HOCl) [51]. However the addition of bleach, ($NaOCl_{(aq)}$) which is strongly alkaline, will raise the pH of the water.

2.16.2 Sodium hypochlorite (NaOCl) and Calcium hypochlorite ($Ca(OCl)_2$) in water

The application of sodium or calcium hypochlorite in drinking water and wastewater treatment achieves the same results as chlorine gas. The following reaction describes the process

For sodium hypochlorite

$$NaOCl_{(aq)} + H_2O_{(l)} \rightleftharpoons HOCl_{(aq)} + NaOH_{(aq)}$$

For calcium hypochlorite

$$Ca(OCl)_{2\,(aq)} + 2H_2O_{(l)} \rightleftharpoons 2HOCl_{(aq)} + Ca(OH)_{2\,(aq)}$$

If calcium hypochlorite is used, the total hardness of water is increased.

The active ingredient is the hypochlorite ion (OCl^-), which hydrolyzes to form hypochlorous acid. The only difference between the reactions of the hypochlorites and chlorine gas is the side reaction of the end products. The hypochlorite reaction increases the hydroxyl ions (OH^-) by the formation of sodium hydroxide or calcium hydroxide while the reaction of chlorine gas and water increases the H^+ ion concentration by the formation of HCl as shown in section 2.16.1. The hypochlorite solution at pH 11 to 12 at the immediate area of the point of application will always be less effective than chlorine gas solution at pH 2 to 3 because there is more of the active ingredient HOCl and possibly of some extremely active molecular chlorine on account of the low pH of the chlorine gas solution [52]. It is well known that at pH 11 or 12 the HOCl is almost completely dissociated to the ineffective hypochlorite ion. The high pH condition will exist only momentarily at the interfaces of the hypochlorite solution and the water to be treated.

2.16.3 The Chlorination process

2.16.3.1 Reaction of chlorine species with ammonia and organic nitrogen in water

The reaction of chlorine species with ammonia and organic nitrogen are quite different from those of chlorine with other inorganic or organic compounds. The most important of the reactions of chlorine species with nitrogen compounds is that of hypochlorous acid with ammonia [52].

Hypochlorous acid reacts with ammonia to produce a series of chlorinated ammonia compound called chloramines and eventually oxidizes ammonia to nitrogen gas (N_2) or a variety of nitrogen containing chlorine free products.

The reaction is represented by the following equation to form monochloramine

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O$$

This ammonia species has more than one hydrogen that can be replaced by chlorine atoms; it reacts with an excess of hypochlorous acid to form dichloramine.

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O$$

and trichloramine

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O$$

The formation of monochloramine is very much dependant on the pH of the solution. The maximum rate occurs at the pH of 8.3 and decreases rapidly at higher and lower pH values. The rate of the reaction also varies with the temperature [52].

Dichloramine is formed predominately at the low pH values (5.0-6.5) and monochloramine at high values (greater than 7.5) and can be interpreted in terms of equilibrium reaction.

$$2NH_2Cl + H^+ \rightleftharpoons NH_4^+ + NHCl_2$$

An excess of H^+ should displace this reaction to the right, yielding greater amounts of dichloromine at lower pH values. This equation also predicts that the relative proportions of monochloramine and dichloramine should be affected not only by pH but also by the amount of ammonia present. This has been confirmed by spectrophotometric measurement [52], which also gives value of $6.7 \times 10^5\ M^{-1}$ for the equilibrium constant, K, where

$$K = \frac{[NH_4^+][NHCl_2]}{[H^+][NH_2Cl]^2}$$

Just as the disinfecting efficiency of solution of free chlorine will vary with pH because of a change in HOCl : OCl^- ratio, that of chloramines solution will also vary i.e. the $NHCl_2 : NH_2Cl$ ratio will change. The disinfection ability of NH_2Cl is high in comparison to that of $NHCl_2$ [52].

Trichloramine is formed in acid solutions where chlorine concentration is much greater than those of ammonia. At these high chlorine concentrations and at pH<3, trichloramine is the only chloramines present [51].

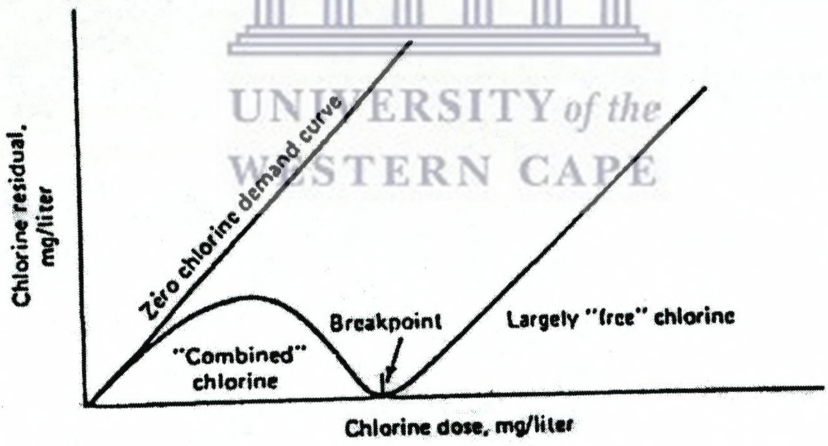
2.16.3.2 Breakpoint Chlorination

Breakpoint chlorination refers to the reaction between chlorine and ammonia in water. When chlorine is added to water it first reacts with ammonia to form chloramines.

When more and more chlorine is added the chloramines break down (oxidize) and the point where the all chloramines have been oxidized is termed the breakpoint.

The formation of chloramines and the oxidation of ammonia by chlorine combine to create a unique dose-residual curve for the addition of chlorine to ammonia-containing solutions [53].

Figure 2.3 Breakpoint chlorination of water



Chlorine that is added after the breakpoint exists as free chlorine (that is elemental chlorine, hypochlorous acid and hypochlorite ion) [52].

The breakpoint can be observed at a molar ratio of 1.5: 1 to 2: 1 with respect to Cl: N. The primary reaction that causes residual chlorine concentration (in terms of active chloramines) to decrease is the breakpoint reaction.

Monochloramine is less effective as a chlorinating agent than hypochlorous acid by a factor of approximately 10^4. However, when chloramines (mostly monochloramine) are used to treat water, trihalomethane (THM) formation is minimized [52]

2.17 Problems associated with trihalomethane (THM)

Trihalomethanes are a group of four chemicals i.e. chloroform, bromodichloromethane, dibromochloromethane, and bromoform formed along with other disinfection by products, when chlorine or other disinfectants used to control microbial contaminants in drinking react with naturally occurring organic and inorganic matter in water.

The trihalomethane often found in the highest concentration is chloroform that is formed by the chlorine with certain compounds in water. Formation occurs during chlorination and can continue to as long as chlorine is available. The other trihalomethanes are formed by a reaction of bromine and iodine with the same certain compounds.

Trihalomethanes can cause small increase in the risk of bladder and colorectal cancers. It was also found that they might be linked to heart, lung, kidney, liver and central nervous system damage. Of the different trihalomethanes, dibromochloromethane has been most closely associated with cancer, followed in order by bromoform, chloroform and bromodichloromethane. Pregnant women appear to be at the greatest risk, as trihalomethanes linked to reproductive problems, including miscarriage [52].

2.18 Factors Affecting Disinfection with Chlorine

Many factors affect how chlorine disinfects water. Many of these are working at the same time, and maybe working against each other. However, we will discuss them as separate effects. Some of the most important ones are:

2.18.1. Contact Time

This refers to the length of time of contact between chlorine and water before it is used. Chlorine needs time to spread through the water to work [48]. To ensure effective contact between the chlorine and water, the chlorinating agent must be thoroughly mixed with the water otherwise this may result in some parts of water not being in contact with chlorine for the required contact time.

Sometimes the disinfection reaction is very quick, but it can take hours in some cases. Disinfection can take from 10 minutes for free chlorine to hours for combined chlorine.

The following table gives the South African recommended chlorine concentration after 10 minutes contact time at different pH levels for free available chlorine and after 60 minutes for combined available chlorine [50].

Table 2.4 chlorine concentrations at different pH after contact time

pH value	Minimum free available chlorine after 10min.contact time (mg/l)	Minimum combined available chlorine after 60min.contact time (mg/l)
6	0.2	1.0
7	0.2	1.5
8	0.4	1.8
9	0.8	>3
10	0.8	>3

Sufficient time is needed to allow the residual chlorine to penetrate into biofilms or other materials that may be present, in order to reach any microorganisms that may be present. During the contact time, the chlorine residual should be maintained in the water supply system for 4 hours to 12 hours. For increased contact time to be most effective, the pH of the chlorine solution in the well must be maintained between 6 and 7 to keep the chlorine in a non-oxidative state (hypochlorous acid). The longer the contact time, the more likely the chlorination procedure will be successful, especially if proper concentrations of chlorine are used at controlled pH conditions. Caution should be exercised during periods of extended contact times to minimize corrosive damage to pumps and other well components by controlling levels of pH and using lower concentrations of chlorine.

2.18.2 Dosage

This is the amount of chlorine that is added per unit of water. This is usually given as milligrams free available chlorine per liter (mg/l). This is the same as parts per million (ppm). The actual dosage will be different for each water system. It depends on the many factors, such as amount and kind of impurities, pH and so on [48].

2.18.3 Chlorine Concentration

Chlorine concentration is the most important control factor to ensure effective disinfection. Chlorine exists in different forms in water with different degrees of effectiveness, so the concentration of the actual chlorine species used for disinfection must be taken into account.

It is normally accepted that sufficient chlorine must be added to water to give a free chlorine residual of not less than 0.2mg/l after 20 minutes contact time.

It is important to note that the free available chlorine species are formed only after the breakpoint in the chlorination process. This means that sufficient chlorine must be added to react with any ammonia that may be present in the water and to oxidize the chloramines that are formed [50].

2.18.4 Chlorine Demand

This is the quantity of available chlorine consumed by the water impurities. Some of these impurities include iron, sulphides, algae, organic waste and ammonia besides microorganisms [49].

2.18.5 Turbidity

Another most important factor is the turbidity of water to be disinfected. The reason is that water contains colloidal particles that may shield the microorganisms from the action of the disinfectant, or alternatively react with chlorine and in this way prevent effective disinfection. It is therefore important to optimize the clarification processes to produce water for disinfection with as low as possible turbidity levels (<1, but preferably < 0.5 NTU) [50].

2.18.6 Water Temperature

The chlorine reactions are very much faster in warm water than in cold water. Water temperature of 12°C is a critical temperature for chlorination. If the temperature is below 12°C, the effect of chlorine is much slower because of the lower metabolic activity of bacteria. At temperatures of 2°C to 5°C a contact time of three times more than at 20°C to 25°C may be needed [50].

2.18.7 Sunlight

Chlorine in water is rapidly broken down (reduced) by sunlight to form the inactive chloride ion (Cl^-), which has no disinfecting power. This means that chlorine contact tanks should always covered. Furthermore, chlorine compounds such as bleach should always be stored in dark containers out of sunlight [50].

Molecular chlorine is easily photo dissociated (split by sunlight):

$Cl_{2\,(aq)} + h\nu \rightarrow 2Cl\bullet_{(aq)}$

$Cl\bullet_{(aq)}$ + oxidisable material $\rightarrow$ $Cl^-_{(aq)}$ + oxidized material

2.18.8 pH

Chlorination works best below pH 7. Between pH 8.0 and pH 9.0 an increase of 50% in chlorine residual or contact time would be needed for the same effect of bacteria [48].

CHAPTER THREE

3. Disinfection via electrolytic chlorine generation

3.1 Electrolytic cells without cell division

These are cells in which an external supply of electrical energy is used to bring chemical change in the cell electrolyte [54]. The particular process is based on the electrolysis aqueous of sodium chloride.

The only feed chemical needed for the production of the disinfectant is a common table salt, generally available in any village in a rural environment [55].

3.2 Idealized electrolysis of aqueous sodium chloride (brine)

Sodium chloride salt dissolves in water as shown below

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + Cl^-_{(aq)}$$

Water is slightly dissociated as

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The electrochemical reactions are illustrated below. On the anode surface the chloride ions (Cl^-) lose electrons (oxidized) and form chlorine gas.

$$2Cl^-_{(aq)} \rightarrow Cl_{2\,(g)} + 2e^-$$

On the cathode surface the $H^+_{(aq)}$ ions gain electrons (reduced) and form hydrogen gas.

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)}$$

can be treated as

$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$

Overall reaction of anode and cathode is as follows

$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow 2OH^-_{(aq)} + Cl_{2(g)} + H_{2(g)}$

Thus formally the products in the electrolyte are $Cl_{2(g)}$, $H_{2(g)}$, and $NaOH_{(aq)}$
Further conversion

$Cl_{2(g)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$

The formation of hydroxide ion alkalizes the local solution in the vicinity of the cathode surface. In an alkaline environment, the chlorine gas and hydroxyl ions will have a secondary reaction to produce hypochlorite ion [55].

$Cl_{2(g)} + 2OH^-_{(aq)} \rightarrow ClO^-_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$

The result is a solution of aqueous sodium hypochlorite known as bleach.

3.3 Figures of merit of an electrolyser

These are the parameters that determine the quality of a given electrolytic process. Calculations of figures of merit in this study are shown in the appendix H. It is commonly found that it is not possible to optimize all the figures of merit. A change in electrolyser design or electrolysis parameters to improve one figure of merit might be detrimental to another [56]. The following are the sub-headings of the figures of merit of the electrolyser that has been reviewed in this study for different electrolysers.

3.3.1 Material yield

Material yield is defined as moles of starting material converted to product divided by moles of starting material consumed multiplied by hundred i.e.

Material yield = moles of starting material converted to product / moles of starting material consumed x 100 %

The starting material is NaCl, material yield indicates the consumption of NaCl for the production of available chlorine obtained.

Material yield of less than 100% indicates less conversion of NaCl to form available chlorine.

3.3.2 Current efficiency

The current efficiency (ϕ) is the yield based on the charge passed during the electrolysis. Current efficiency is defined as follows

ϕ = Charge used in forming product / total charge consumed x 100%

Charge used in forming product is calculated using faraday's law. Current efficiency of less than 100% indicates that to some extent a back reaction occurred during the electrolysis or more likely that byproducts are being formed. For example, oxidation of chlorine in the anode chamber leads to current efficiency below 100%.

3.3.3 Energy consumption

Energy consumption is the electrical energy required to make a unit weight of the product and it is quoted in kilowatt-hour per kilogram (kWh.kg^{-1}). It is given by the following equation

Energy consumption = $nFV/(3.6\times10^4\phi M)$

Where M = molecular weight in Kg
n = no of electrons transferred
V = voltage
F = Faraday's constant

Energy consumption depends on the cell voltage and current efficiency. Selecting the electrolysis conditions that will make cell voltage as low as possible can minimize energy consumption.

3.3.4 Material yield (Kg NaCl / Kg NaOCl)

This is based on the conversion of NaCl to NaOCl. The most important determining factor here is the current efficiency of chlorine evolution, essential to the conversion of starting material to product.

3.4 Anodes and chlorine evolution

Some metals, such as titanium, zirconium, tantalum and niobium can be used as anode materials because they form a protective film when they are in contact with the electrolyte. This prevents further corrosion, and they therefore find extensive use in industrial setups (particularly titanium because is the cheapest).

Thermal decomposition is the most popular method for preparing oxides coatings on electrodes due to its simplicity and reproducibility [57]. These dimensional stable anodes DSA anodes have low capital and operating costs and can be used for longer than 10 years in a membrane cell [52]. Mixed oxide coatings of DSA type exhibit stable operation for long periods of time at low operating voltages.

DSA refer to the metallic oxide coatings that catalyses the anode for chlorine evolution rather than that of oxygen. Metallic oxide and mixed oxide electrodes used involve the following RuO_2, IrO_2, MnO_2, PtO_2, Co_3O_4, $NiCo_2O_4$ [57], TiO_2 and NiO_2 [58]. These metallic oxides are of technological important in the industrial production of chlorine due to their good electro catalytic properties and excellent stability [59].

Chlorine evolution efficiency depends on the electrolyte concentration, composition, temperature, current density, flow rates and electrode nature.

In general chlorine evolution occurs at low overpotentials on most of the materials, where as that of oxygen takes place with large overpotentials with marked dependence on the electrode material. The fact is that chlorine evolution is preferred over that of oxygen evolution in lower pH solutions. Under conditions of electrolysis (saturated brine of pH 2 to 4) chlorine is liberated with variable amounts of oxygen depending on the electrode material. The pH 4 is the limiting value beyond which oxygen content becomes unacceptable. At high pH and dilute chloride ion solution the efficiency of chlorine evolution decreases owing to side reactions such as oxygen evolution occurring. However, electrocatalytic coatings can be chosen to optimize chlorine evolution over a wide range of pH.

There are reasons why some electrodes are preferred more than the others. PbO_2 and PtO_2 are poor electrocatalysts for chlorine evolution. These electrodes are reported to evolve oxygen at low overpotential but then high corrosion resistance stability has been the reason for their usefulness in a number of technological applications. $NiCo_2O_4$ is very unstable especially in concentrated solutions. Long-term stability is the more relevant parameter on which a possibly choice may be based.

TiO_2 has the disadvantage of high electrical resistance causing a large potential drop. NiO_2 has the drawback that the potential for chlorine evolution drifts unavoidably towards more positive values with time. Oxygen evolution occurs readily on the easily oxidized surface.

MnO_2, RuO_2 and Co_3O_4 are excellent electrodes for chlorine evolution, with low overpotential. MnO_2 is a relative poor electronic conductor and this property affects behavior even in the presence of conducting interlayer. RuO_2 has been shown to be the best electrocatalyst from a kinetic point of view. Corrosion in acidic medium is negligible on this electrode. Co_3O_4 is anodically stable as the pH of the solution increases above 3. Co_3O_4 is the most corrosion resistance electrode and oxygen evolution at high values of pH is limited [60].

3.5 Chlorate formation in an undivided cell

During the generation of sodium hypochlorite heat is produced in the cell. When the temperature is higher than 75°C, some sub-reactions will take place to reduce the current efficiency of the chlorine formation. These unwanted reactions include a divergent reaction, which produces Cl^- and ClO_3^- at the expense of ClO^-. However, ClO_3^- has less efficiency in terms of disinfection and sterilization as compared with ClO^- and is toxic.

ClO^- decomposes to form ClO_3^- as shown below [55]:

$$3ClO^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + 2Cl^-_{(aq)}$$

Moreover ClO^- can further discharge on the anode to produce ClO_3^- as well.

$$12ClO^-_{(aq)} + 6H_2O_{(l)} \rightarrow 4ClO_3^-{}_{(aq)} + 12H^+_{(aq)} + 8Cl^-_{(aq)} + 3O_{2\,(g)} + 12e^- \text{ at the anode}$$

On the other hand if ClO^- and ClO_3^- migrate to the cathode, the chemical reduction from ClO^- and ClO_3^- to Cl^- on the cathode may take place.

$$ClO^-_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow Cl^-_{(aq)} + 2OH^-_{(aq)}$$

$$ClO_3^-{}_{(aq)} + 3H_2O_{(l)} + 6e^- \rightarrow Cl^-_{(aq)} + 6OH^-_{(aq)}$$

These reactions including chlorate are all unwanted and should be eliminated [55].

3.6 Factors for elimination of the unwanted reactions

- Keeping the reactor temperature as low as possible, e.g. under 25°C.
- Separating anode and cathode chambers with a membrane [55].

3.7 Advantages of divided cell

In a divided cell, the anolyte and the catholyte are separated by an inorganic membrane that selectively transmits sodium ions but suppresses the migration of hydroxyl ion from the cathode to the anode. The advantages of the divided cell are:

- It may be desirable to keep the products of the reactions at the anode and the cathode separated.
- Increases the current efficiency of the chlorine generation [52].
- Minimizing the formation of the toxic sodium chlorate.
- Thin walls of membrane separating the electrodes reduce resistance of the cell.

3.8 On-Site Sodium Hypochlorite Generation

On site electrolytic sodium hypochlorite generation has been used for water disinfection in the USA since the early 1970's [61]. The main reason for its adoption in the place of chlorine gas or industrial sodium hypochlorite was the lower level of risk and safety measures required because of the available chlorine concentration of 0.5-0.8%w/v below hazardous classification, which is 1%w/v [62]. In addition the low concentration provides more stability [49].

3.9 Advantages of on-site sodium hypochlorite generation

- This system requires only salt and electricity.
- Providing the power of chlorine without the danger of strong or handling hazardous materials

- Sodium hypochlorite that is generated on site does not degrade as much as the commercial sodium hypochlorite before use.
- The total operation cost is less than conventional chlorination method [63].

3.10 Disadvantages of on-site hypochlorite generation

- Potential for hydrogen explosions. Special attention must be paid to the design and routing of electrolytic cell and storage with hydrogen vents to prevent hydrogen gas accumulation.
- Solution strength of on-site generated sodium hypochlorite is only 0.8%w/v as compared to the 12 to 15%w/v conventional purchased hypochlorite, which can result in the need of increased storage tank size [64].

3.11 Stability of Sodium hypochlorite

3.11.1 Spontaneous decay

Sodium hypochlorite loses its strength by two decomposition pathways. The more dominant pathway leads to the formation of chlorate ion. The bleach decomposition between pH 11 and 13 is shown by the following stoichiometry: [65]

$$3ClO^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + 2Cl^-_{(aq)}$$

The decomposition of ClO^- involves chlorite ion (ClO_2^-) as an intermediate in the following generally accepted chemical equations. [61,66]

$$ClO^-_{(aq)} + ClO^-_{(aq)} \rightarrow ClO_2^-{}_{(aq)} + Cl^-_{(aq)}$$

$$ClO_2^-{}_{(aq)} + OCl^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + 2Cl^-_{(aq)}$$

The ClO_2^- concentration in liquid bleach is at least 200 times lower than the ClO^- concentration. The maximum decomposition rate is at the neutral pH. Storage liquid bleach with a pH between 12 and 13 is most stable.

The rate of decomposition of ClO^- does not change with time above pH 11 because it is not acid dependent. Below pH 11 the pH of the ClO^- stock solution will continue to decrease over time because of competing acid producing decomposition pathway with the following stoichiometry: [65]

$$2HOCl_{(aq)} + ClO^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$$

On other hand decomposition of hypochlorous acid also occurs [67]

$$HOCl_{(aq)} + HOCl_{(aq)} \rightarrow H_2Cl_2O_{2\,(aq)}$$

$$H_2Cl_2O_{2\,(aq)} + ClO^-_{(aq)} \rightarrow ClO_3^-{}_{(aq)} + 2H^+_{(aq)} + 2Cl^-_{(aq)}$$

3.11.2 Photolysis

Light especially UV, can photolyse the hypochlorite ion to form chlorite ions as shown here

$$2OCl^-_{(aq)} + UV \rightarrow ClO_2^-{}_{(aq)} + Cl^-_{(aq)}$$

Industrial commercial solutions are usually packed in opaque plastic bottles, with thick walls and /or dark color, which minimize light penetration [51].

3.11.3 Catalytic Decomposition

Transitional metals such as iron, manganese, nickel, copper and cobalt can catalyze the decomposition of hypochlorite ion into oxygen and chloride. The reaction is as follows [66]:

$$3OCl^-_{(aq)} + OCl^-_{(aq)} \rightarrow O_{2\,(g)} + 2Cl^-_{(aq)}$$

Iron is considered the worst offender of sodium hypochlorite stability, causing rapid deterioration of 15%w/v solution in a few days at concentration as low as 0.5mg/l of iron. Copper produces a similar effect at concentration around 1.0mg/l [52].

3.12 Mixed oxidant generation

"Mixed oxidants" is the name given to a mixture of strong oxidizing species produced by an electrochemical cell. The electrochemical reactions that take place during the electrolysis of brine are assumed to produce the mixed oxidants as claimed by Russian Scientist's Centre for Electrochemical Activation Techniques [68]. Some of the species that were claimed to be formed besides Cl_2 in the anode chamber are $OH^{\cdot}$, O_3, H_2O_2 and ClO_2 [69-72]. Similar claims are made for the MOGGOD process [18].

3.13 Solar panels as a source of energy

A solar cell is a solid-state device that converts sunlight directly to electricity. The cell can be wired in series or parallel to achieve various electrical voltage and currents. A typical single crystalline cell produces about 0.5 volts, and about 3 to 5 amperes [73].

A solar panel does not need a lot of maintenance. The storage of electrical power in a battery is required in view of the diurnal cycle and the inevitability of clouds days. A DC to DC converter allows the control of the output voltage to the electrolyser without loss of power. The battery is charged via the solar panel in order to ensure the constant current density and voltage, which could be used in an electrolyser. Several solar panels can be used to ensure the maintenance of a fully charged battery [74].

The solar panels system operation can be used in electrolytic processes, if the processes have relative low electricity consumption. This system can be useful in rural areas without electricity or where mains electricity frequently fails [75].

CHAPTER FOUR

4. AIMS AND OBJECTIVES OF THE PROJECT

1. Construction of a brine electrolyser with the following characteristics

    - Simple and cheap design.
    - Safe and easy operation system.
    - Minimal toxic chlorate generation.
    - Good current efficiency for chlorine generation.
    - Reliable and durable cell components.
    - Low power consumption appropriate for power supply from solar panels.

2. Testing of dimensionally stable anodes with electro catalytic coatings for optimization of chlorine evolution as opposed to oxygen evolution.

3. Comparative study of different anodic materials.

4. Choice of most suitable anodic material.

5. Study of the operation of the brine electrolyser under laboratory conditions.

6. Recommendations for the use of the electrolyser in the rural areas.

7. Since it has been frequently claimed that hydroxyl radicals also form during electrolysis of brine, it was decided to investigate the possibility of analyzing the anolyte for this species.

CHAPTER FIVE

5. EXPERIMENTAL METHODS

5.1 Design and construction of the electrolyser

The chemical methodology involved is the electrolysis of aqueous sodium chloride (brine) to produce sodium hypochlorite solution as a source of available chlorine for the disinfection of water.

During the electrolysis of brine in an undivided electrolysis cell the following reactions take place.

Inside the electrolysis cell the aqueous sodium chloride dissociates to form chloride ions (Cl^-) and sodium ions (Na^+). The chloride ions are oxidized at the anode to form chlorine gas as shown below.

$2Cl^-_{(aq)} \rightarrow Cl_{2\,(g)} + 2e^-$ anodic (oxidation)

Water dissociates to form hydronium ions (H^+) and hydroxyl ions (OH^-). Then the hydronium ions are reduced at the cathode to form hydrogen gas as also shown below.

$2H_2O_{(l)} + 2e^- \rightarrow H_{2\,(g)} + 2OH^-_{(aq)}$ cathodic (reduction)

The overall cell reaction is;

$2Cl^-_{(aq)} + 2H_2O_{(l)} \rightarrow H_{2\,(g)} + Cl_{2\,(g)} + 2OH^-_{(aq)}$ overall cell reaction

(or $Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$ if anode and cathode products are mixed)

However even in a divided cell Cl_2 also reacts with water

$Cl_{2\,(g)} + H_2O_{\,(l)} \rightarrow HOCl_{\,(aq)} + HCl_{\,(aq)}$

And $HOCl_{\,(aq)} \rightleftharpoons H^+_{\,(aq)} + OCl^-_{\,(aq)}$

Disproportionation can also occur

$HOCl_{\,(aq)} + ClO^-_{\,(aq)} \rightarrow ClO_3^-{}_{(aq)} + Cl^-_{(aq)} + 2H^+_{\,(aq)}$

ClO_3^- is toxic and thus its concentration should be minimized if the hypochlorite produced is to be used for water disinfection.

In an undivided cell ClO_3^- is also produced by direct anodic oxidation.

$6ClO^-_{\,(aq)} + 3H_2O_{\,(l)} \rightarrow 2ClO_3^-{}_{(aq)} + 4Cl^-_{\,(aq)} + 6H^+_{\,(aq)} + 3/2\,O_{2\,(g)} + 6e^-$

Thus the main focus of this project is the development of a divided cell where the anode and cathode chambers are separated with a membrane.

In the divided cell the electrolysis of brine leads initially to the same electrode products as in an undivided cell. But then chlorine gas that is formed inside the anode chamber reacts with water as illustrated below:

$Cl_{2\,(g)} + H_2O_{\,(l)} \rightarrow HOCl_{\,(aq)} + HCl_{\,(aq)}$

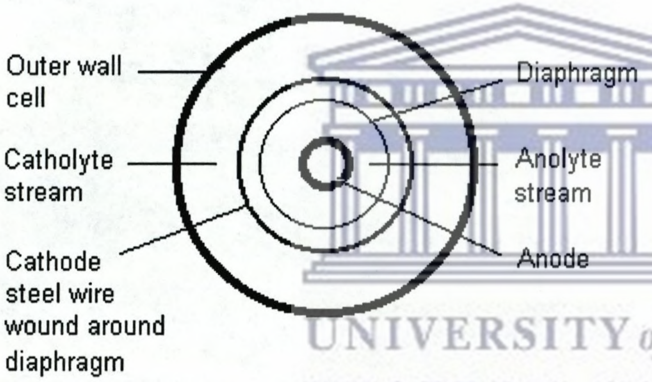
The excess sodium ions that are left in the anode chamber migrate towards the cathode through the porous membrane to form aqueous sodium hydroxide with the excess hydroxyl ions left in the cathode chamber.

$2Na^+_{\,(aq)} + 2OH^-_{\,(aq)} \rightarrow 2NaOH_{\,(aq)}$

5.1.1 Cell design

The diaphragm used is in a tubular form separating anode and cathode. The diaphragm is made of aluminium-zicronium oxide, which is porous, allowing the migration of aqueous inorganic ions. The diaphragms are 21cm long, 1cm internal diameter and 1mm thick (see Figure 5.1).

Figure 5.1 Cell design



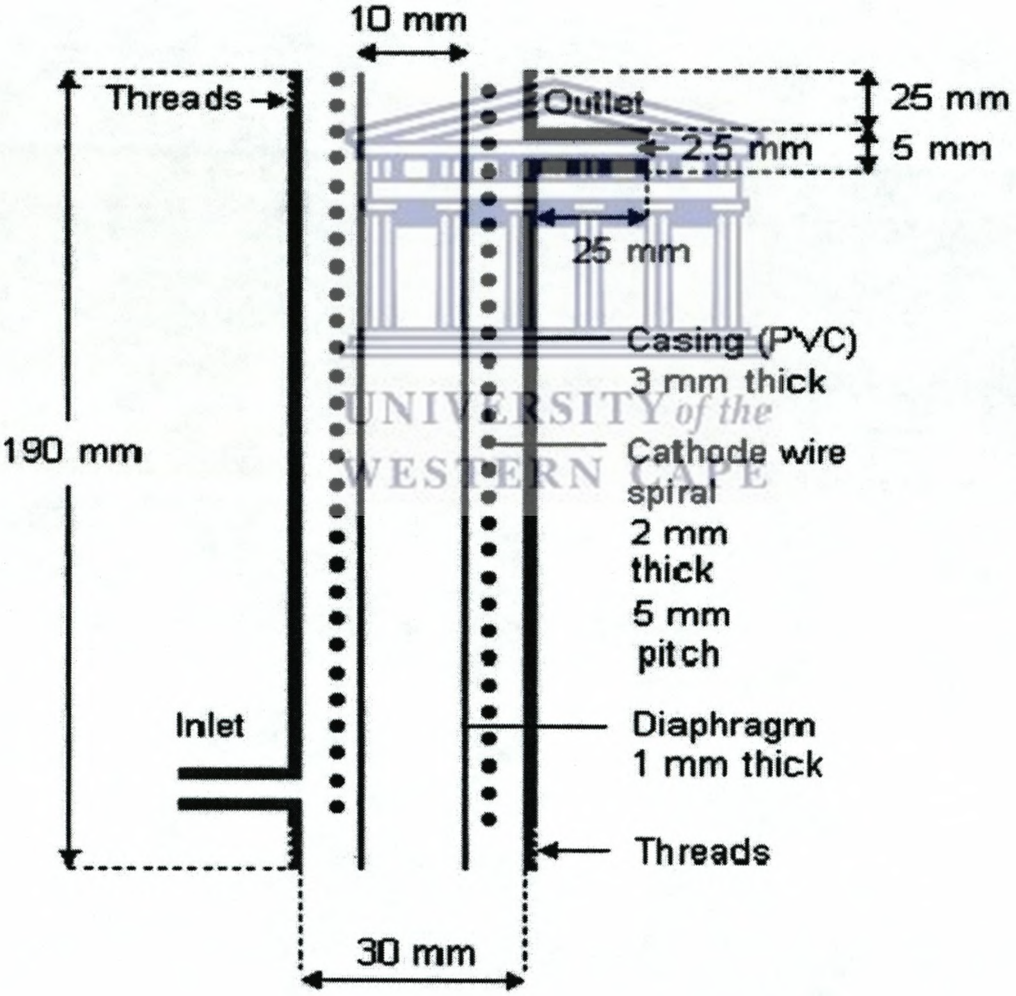
5.1.2 THE CATHODE AND THE CATHODE CHAMBER

The cathode consists of a stainless steel wire spiral 2mm thick coiled around the diaphragm for a length of 17cm. The spacing between the coils (pitch) are approximately 3mm. Steel is corrosion resistant and does not have a high over- potential for hydrogen evolution. Steel is cheap and readily available. The cathode chamber is 19cm long and has an internal diameter of 3cm.

There is an inlet pipe at the bottom of the cathode chamber for the catholyte (water) and an outlet pipe at the top, which also carry out bubbles of hydrogen produced. The outer wall of cathode is made of transparent plastic 3mm thick to allow observation of possible fouling of the membrane.

The cathode chamber is threaded for simply assembly and dismantling and the threads are coated with PTFE tape to prevent leakage. The top and base of the chamber screw on with rubber seals (see Figure 5.2).

Figure 5.2 Cathode chamber



5.1.3 THE ANODE AND ANODE CHAMBER

The anode is a titanium rod coated with electro catalytic coatings either manganese dioxide (MnO_2), or ruthenium dioxide (RuO_2) or cobalt oxide (Co_3O_4). The anode geometry is a spiral of wire 1.5mm thick, with a spiral outer diameter 5mm, the spacing between the coils (pitch) is approximately 1mm. The spiral 20cm long fits down the center of the diaphragm.

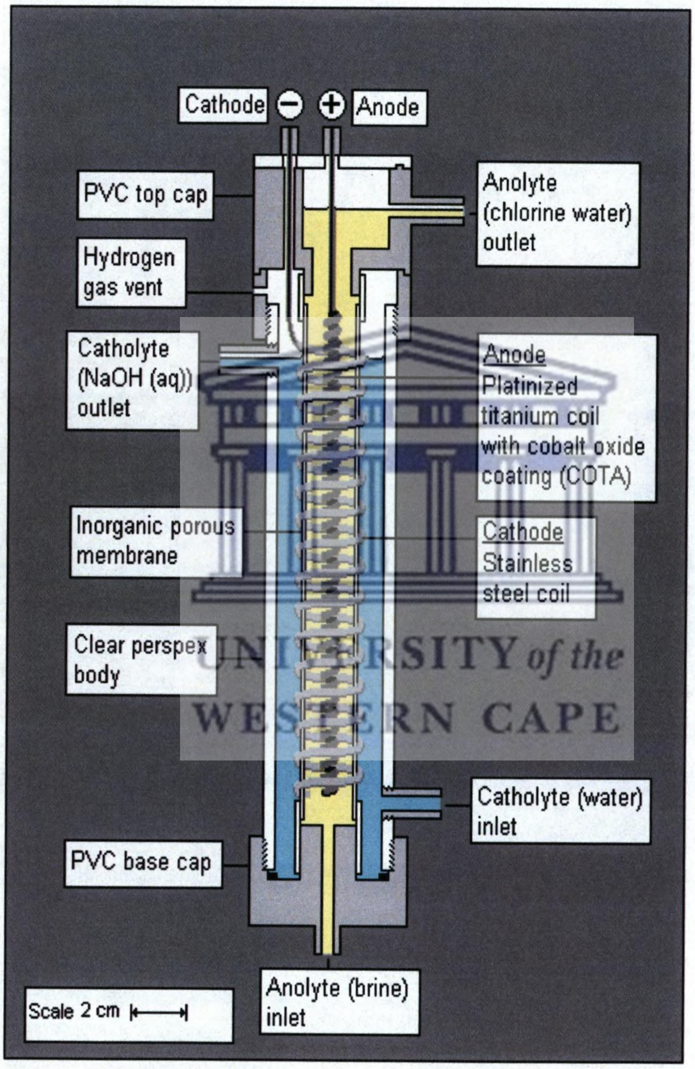
The anolyte (brine) enters the bottom of the anode chamber and exits via an outlet at the top.

5.1.4 ELECTROLYSER ASSEMBLY

The electrolyser is constructed in plastic to allow a close fit of diaphragm into the top and bottom of the electrolyser where it is sealed against leaks with rubber seals and PTFE tape.

The electrodes connections are copper, placed at the top of the electrolyser. It is assembled and dismantled easily for cleaning or diaphragm replacement (see Figure 5.3).

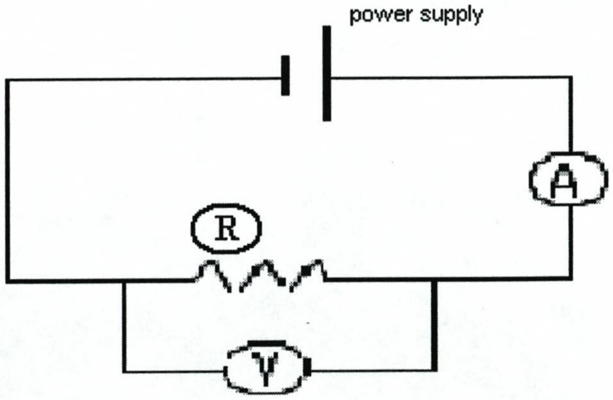
Figure 5.3 Schematic diagram of the electrolyser



5.4 Photograph of the electrolyser

5.2 The electrical circuit

Figure 5.5 Schematic diagram of the electrical circuit



The figure 5.5 shows the schematic diagram of the electrical circuit that has been used in this study. It consists of a variable DC power supply and an electrolyser which is represented as by resistance R.

The DC power supply generates between 0 to 35V and has a maximum of current of 5A. The current (A) and voltage (V) were measured using a FLUKE 77III multimeter.

5.3 Reagents

Reagents	**Percentage purity**	**Suppliers**
Sulphuric acid	98	KIMIX (SA)
Potassium Iodide	99.5	KIMIX (SA)
Sodium thiosulphate hexahydrate	99.5	Saarchem (SA)
Sodium Starch glycollate	80	BDH (England)
Potassium Iodate	99.5	Merck (Germany)
DPD Sulfate	97	Sigma Aldrich (SA)
Sulphuric acid	98	Kimix (SA)
Disodium hydrogen phosphate	90	BDH (England)
Potassium dihydrogen phosphate	99.5	BDH (England)
EDTA	99	Sigma Aldrich (SA)
Mercury chloride	99.5	Merck (Germany)
Ferrous Ammonium sulfate	99	Riedel-de Haën (SA)
Sodium Chlorate	99+	Sigma-Aldrich (SA)

Sodium hydrogen carbornate	99.5	Saarchem (SA)
Sulphuric acid	98	Kimix (SA)
Dimethyl Sulfoxide	99.9	Sigma Aldrich (SA)
Diazonium Salt	35	Sigma Aldrich (SA)
Metahnesulfinic acid sodium	97	Lancaster (England)
Butanol	95	Kimix (SA)
Toluene	99.8	Saarchem (SA)
Pyridine	99.5	B & M Scientific (SA)
Hydrogen Peroxide	30	Sigma Aldrich (SA)
Ferrous Sulphate	99	Riedel-de Haën (SA)

5.4 Iodometric titration of hypochlorite

Iodometric titration is used for the determination of hypochlorite ions present in the solution. Iodide ions are easily oxidized by almost any oxidizing agent. In acidic solution hypochlorite ions oxidizes iodide ions (I^-) to form iodine (I_2) [76]. The quantity of hypochlorite ion in the sample is determined by finding out how much iodine is produced from added excess iodide. The quantity of iodine produced is measured by titrating it with standard sodium thiosulphate, which converts coloured iodine back to colourless iodide ion. In the reaction excess iodide is added as potassium iodide. Starch is used to sharpen the end point.

The general scheme is summarized as follows

Oxidation of iodide ion to iodine with hypochlorite ions:

$$ClO^-_{(aq)} + 2H^+_{(aq)} + 2I^-_{(s)} \rightarrow I_{2\,(aq)} + Cl^-_{(aq)} + H_2O_{(aq)}$$

Titrating iodine with thiosulphate

$$I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-_{(aq)}$$

The titration is usually performed at a sample pH between 3-4. For maximum accuracy, iodometric titration uses a starch indicator at sample temperature of less than 20°C. The method is used for available chlorine levels above 1mg/L. [77]. The relationship between sodium hypochlorite and available chlorine is that the sodium hypochlorite solution contains 95.2% of available chlorine. Sodium hypochlorite concentration was determined using the procedure as stated in reference number 76 and 77.

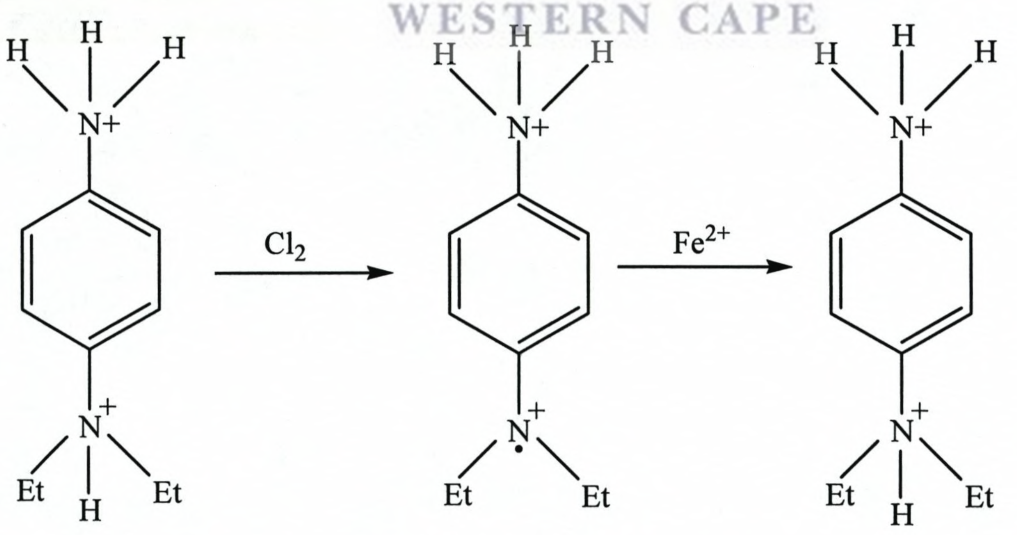
5.5 N, N-Diethyl-p-Phenylenediamine (DPD) titration method for hypochlorite

In solution the DPD is oxidized by chlorine to form two oxidation products. At a near neutral pH, the primary oxidation product is a cation compound known as Würster dye. This relatively stable free radical species accounts for the magenta colour in the DPD colorimetric test. DPD can be further oxidized to a relatively unstable colourless imine compound.

When DPD reacts with small amount of chlorine at a near neutral pH, the Würster dye is the principal oxidation product [77]. At higher oxidation levels, the formation of the unstable colourless imine is favoured - resulting in apparent fading of the coloured solution. The reaction is temperature dependant, must be performed at less than 20°C temperature.

The red coloured Würster dye is titrated with a ferrous ammonium sulfate reducing agent to the colourless endpoint [51].

Figure 5.6 DPD-Titration Reaction



AMINE (Colourless) | WÜRSTER DYE (Coloured) | AMINE (Colourless)

If chlorine is present, a red or pink colour should develop. High concentration of available chlorine may produce a temporary red colour followed by the yellow colour. If this occurs, the analysis must be performed using a smaller volume of sample diluted to 100ml with distilled water [77]. The amount of chlorine in the solution is calculated according to the following

$$2\text{DPDH}_{(aq)} + \text{Cl}_{2\,(aq)} \rightarrow 2\text{Würster}_{(aq)} + 2\text{HCl}_{(aq)}$$

$$2\text{Würster}_{(aq)} + 2\text{Fe}^{2+}_{(aq)} \rightarrow 2\text{Fe}^{3+}_{(aq)} + 2\text{DPDH}_{(aq)}$$

5.6 Procedure

- 5ml of phosphate buffer was placed in 250ml conical flask followed by 5ml of DPD indicator solution using micropipette.
- 100 ml sample was added and the solution was mixed thoroughly.
- The titration with standard ferrous ammonium sulphate was carried out immediately until the red colour changed to colourless. If the sample is added before the buffer the test does not work.

5.7 Spectrophotometric determination of Chlorate

This method involves the reduction of chlorate ions to chlorine dioxide by ferrous ammonium sulfate.

The reactions are shown below

$ClO_3^-{}_{(aq)} + H^+{}_{(aq)} \rightarrow HOClO_{2\,(aq)}$ fast

$HOClO_{2\,(aq)} + Fe^{2+}{}_{(s)} \rightarrow Fe^{3+}{}_{(aq)} + ClO_{2\,(aq)} + OH^-{}_{(aq)}$ rate determining

In the fast protonation process that is included in this scheme it is generally believed that the proton plays a role of weakening the strong bond between the negative oxygen atom and positive central chlorine atom [78].

5.8 Apparatus

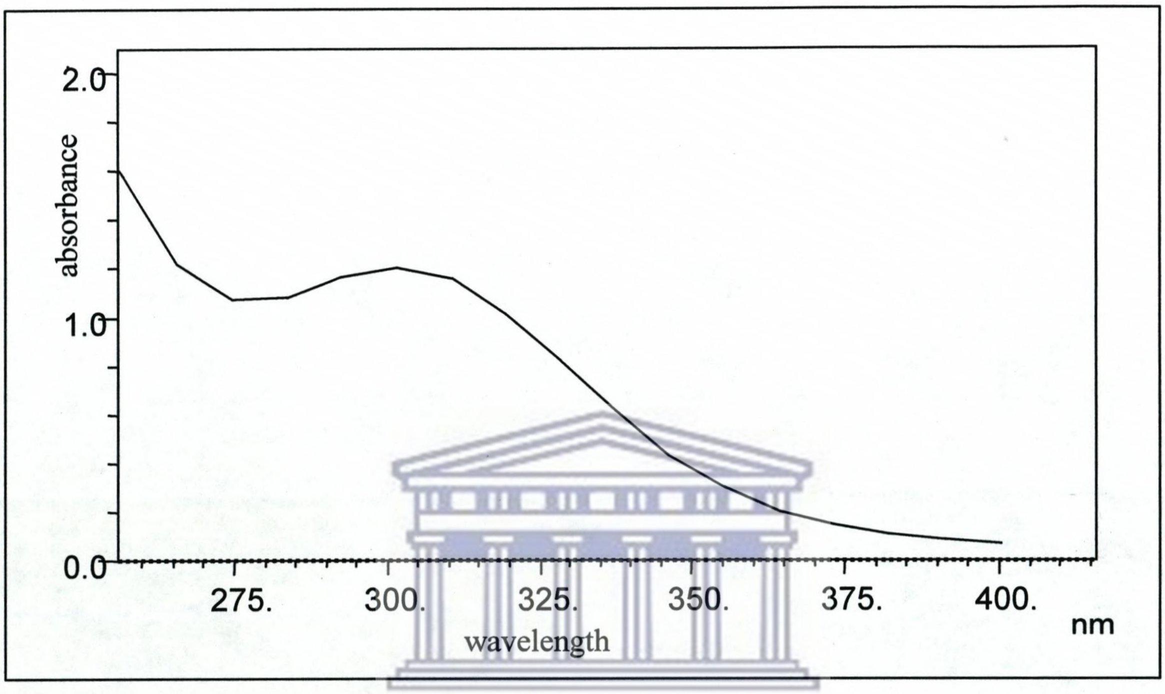
A GBC UV/Vis 920 spectrophotometer was used with 2cm pathlength cuvettes.

5.8.1 Operation of the UV/Vis spectrophotometer

The GBC UV/Vis 920 spectrophotometer was set at wavelength of 305nm at the absorption maximum wavelength of ClO_2 in the uv/vis range.

The cuvette was filled with blank (prepared) and the instrument was turned to read zero.
The sample was then put in the cuvette for measurement.
The blank was prepared as explained under procedure 5.11.

Figure 5.7 A typical absorption spectrum with maximum wavelength (λ_{max}) at 305nm for ClO_2.



5.9 Preparation of Standards

5.9.1 Sodium Chlorate ($NaClO_3$) Standards

Firstly sodium chlorate stock solution of 0.005M was prepared by dissolving 0.5g of sodium chlorate salt in 1litre volumetric flask.

From the stock solution different volumes were taken which were as follows: 0.1ml, 0.3ml, 0.5ml, 0.75ml, 1ml, 1.5ml and 2ml and diluted up the mark in 50ml volumetric flasks using distilled water.

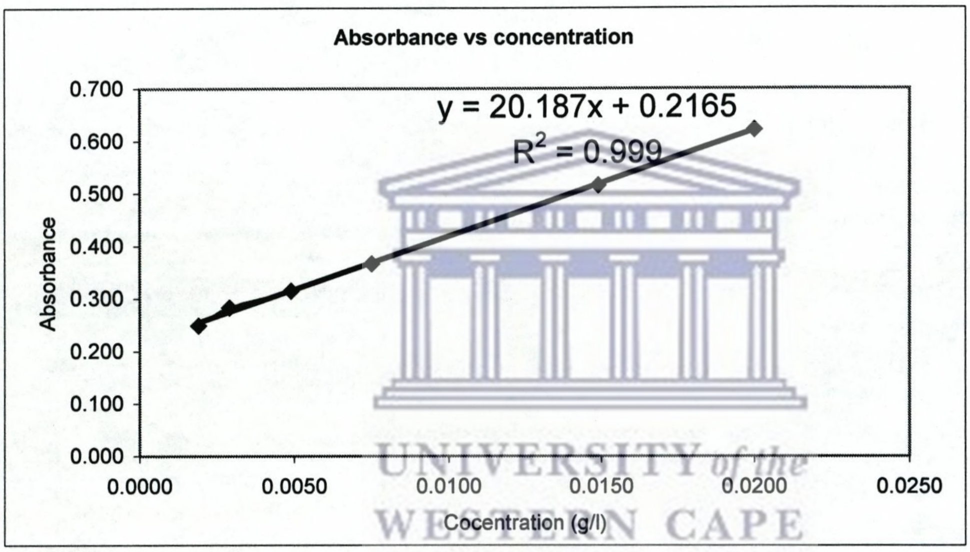
5.10 Procedure

- In a 50ml volumetric flask, 5ml of $1x10^{-3}$M $NaHCO_3$ solution was added followed by the addition of 0.2g of FAS in 20ml of distilled water.
- 1ml volume of $NaClO_3$ solution was added and the volume was adjusted to about 40ml with distilled water.
- The volumetric flask was immersed in 50°C water bath for 5minutes, after that was cooled in cold water in room temperature.
- After cooling the solution was acidified with 5ml of 1.1N H_2SO_4 and diluted with distilled water up to the mark.
- Immediately after addition of 5ml of 1.1N H_2SO_4 the yellow colour disappeared to form colourless solution.
- The blank was also prepared in the same way as standard but there was no $NaClO_3$ used.
- The sample was prepared in the same way as standard with 1ml of catholyte solution used.
- The chlorine dioxide was monitored and measured at a wavelength of 305nm. The concentration of sodium chlorate was obtained since the relationship between sodium chlorate and chlorine dioxide is 1:1 mol ratio.
- The reagent blank is stable for 2 hours.

5.11 Calibration curve

A calibration curve of concentration grams/L against absorbance was drawn. The gradient and the co-relational constant R^2 can give an idea how good the calibration is. For $R^2 = 0.999$ this is acceptable. The amount of chlorate present was determined from the calibration curve.

Figure 5.8 Sodium chlorate calibration curve



5.12 Determination of electrogenerated hydroxyl radicals using a spectrochemical method

Hydroxyl radical is a highly reactive and toxic radical with one unpaired electron. Hydroxyl radical is a powerful oxidizing agent. It can be generated in many ways e.g. water radiolysis, Fenton type reaction, photolysis, sonolysis and ozonation.

Hydroxyl radical is extremely reactive, its half-life is approximately 10^{-9}sec and cannot be detected directly [39].

Here hydroxyl radicals were detected as diazosulfone as illustrated below:

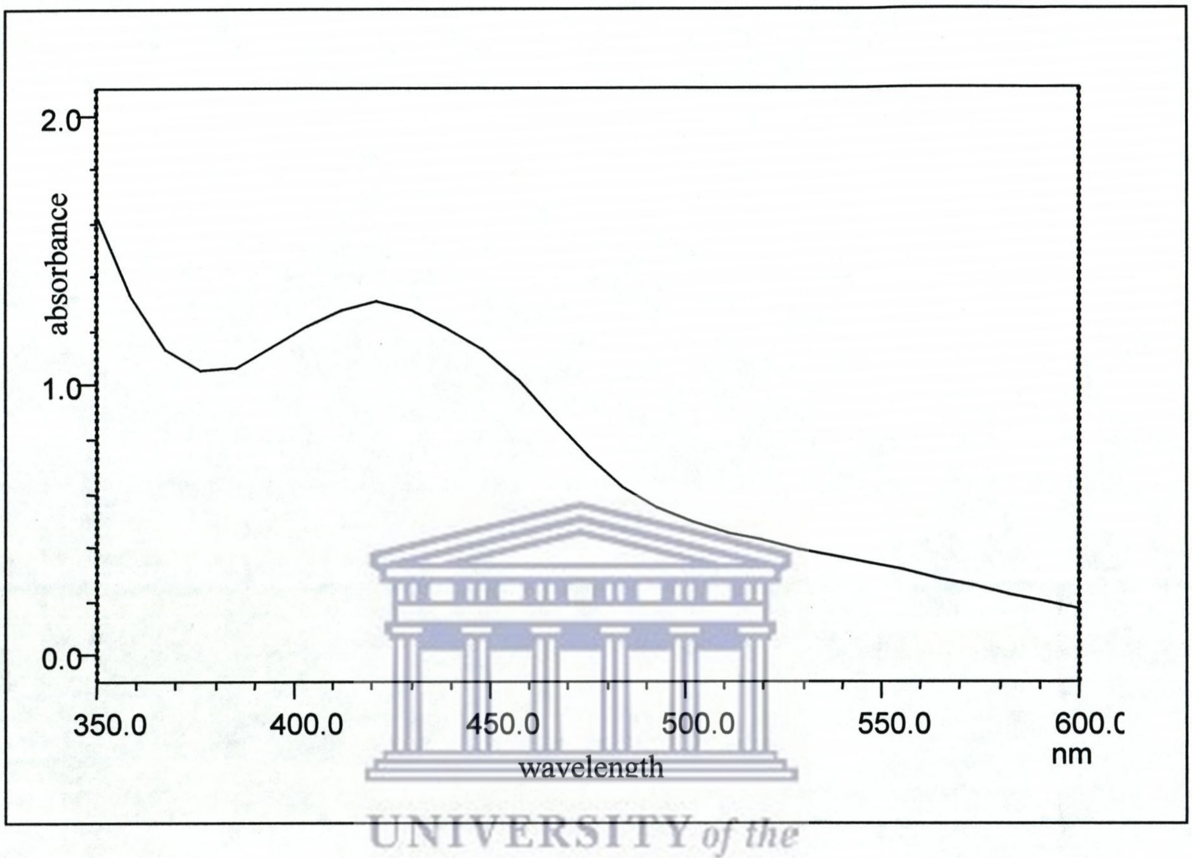
Dimethyl sulfoxide reacted with the generated hydroxyl radicals

$$CH_3\text{-}SO\text{-}CH_{3\,(aq)} + HO^{\cdot}_{(aq)} \rightarrow CH_3SOOH_{(aq)} + CH_3^{+}{}_{(aq)}$$

Methanesulfinic acid formed which was coupled with a diazonium salt (Fast Blue B.B salt) to form coloured diazosulfone that is selectively extracted into an organic solvent [79].

$$CH_3SOOH_{(aq)} + Ar\text{-}N{=}N^{+}{}_{(aq)} \rightarrow Ar\text{-}NN\text{-}SOO\text{-}CH_{3\,(aq)} + H^{+}{}_{(aq)}$$

Figure 5.9 A typical absorption spectrum with maximum wavelength (λ_{max}) at 420nm for diazosulfone.



5.13 Methanesulfinic acid standards

Stock solution of 500μM was prepared by dissolving 0.0510g of methanesulfinic acid sodium salt in 1liter volumetric flask using distilled water.

From the stock solution different volumes were taken to make up the following standard concentration: 10μM, 15 μM, 25 μM, 50 μM, 75 μM, 100 μM, and 125 μM.

5.14 Procedure

- ☐ 1ml of test solution plus 9ml of dimethyl sulfoxide (DMSO) was taken and mixed with 2ml of 15mM Fast Blue BB salt and was allowed to stand in the dark for 10minutes for product development and stirred in a vortex mixer for 3minutes.

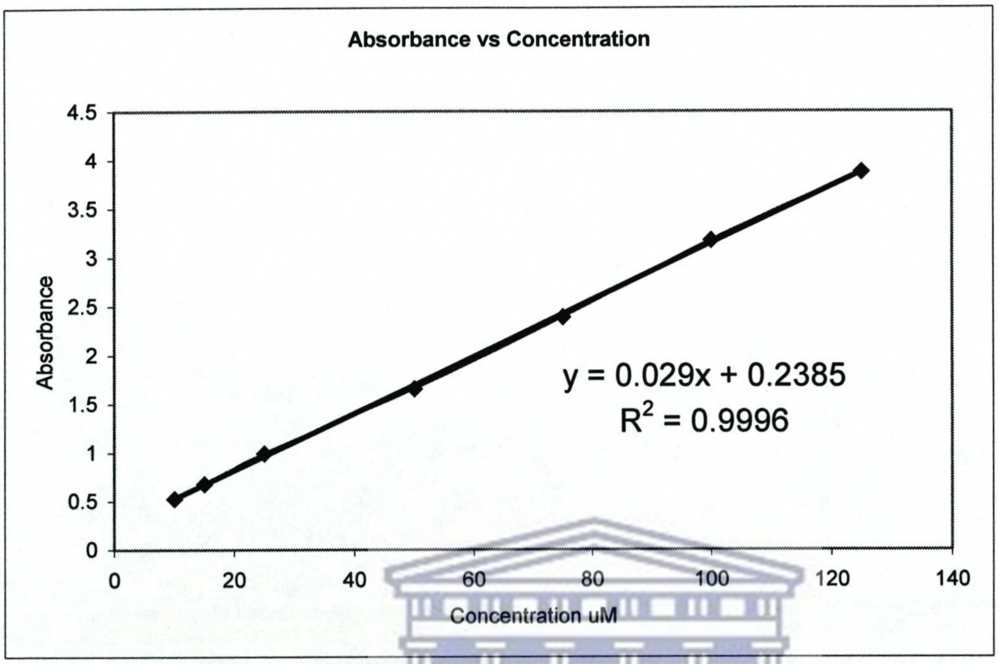
- ☐ Then 3ml of toluene/butanol was added and the mixture was stirred in a vortex mixer for 5minutes. Then the upper part of the two layers was extracted using Paster pipette followed by addition of 5ml of butanol-saturated water and centrifuged for 10minutes.

- ☐ Then the product (upper layer i.e.diazosulfone) was extracted and 1ml of pyridine was added to prevent fading of the colour.

- ☐ Blank was prepared by using 10ml of DMSO instead of test solution and DMSO and the rest was followed as above.

- ☐ The diazosulfone was monitored and measured at a wavelength of 420nm. Therefore the concentration of hydroxyl radical was obtained since the relationship between hydroxyl radical and diazosulfone is 1:1 mol ratio.

Figure 5.10 Methanesulphinic acid (MSA) calibration curve



CHAPTER SIX

6. THE DEVELOPMENT OF ANODIC MATERIALS

6.1 Methods of manufacture and critical comparison of properties of dimensionally stable anodes (DSA) for the electrolytic production of chlorine

6.1.1 Introduction

During the electrolysis of aqueous solutions of sodium chloride production, it is vital that the anodes have the following properties:

- High corrosion resistance to the severe conditions of chlorine evolution (dimensional stability)
- The highest possible current efficiency for chlorine evolution.

A requirement related to current efficiency above is the highest possible electrical conductivity. This becomes significant when achieving a balance between ideal electrolytic surfaces and conductivity. In terms of practical considerations, the factor of cost is vital and advantageous electrochemical characteristics have to be judged also by this important criterion. This becomes important particularly where costly platinum metal group oxides are being evaluated.

This study was carried out in order to select the most suitable anode (manufactured in Ukraine [80]) to use in the brine electrolyser for use in rural water disinfection.

6.1.2 Methods of Manufacture

In all cases titanium metal was used as the bulk substrate material for the anode in view of its well-known stability in terms of conductivity and corrosion resistance. In all cases titanium metal sheet (purity standard PT-1) was used.

6.1.3 Degreasing

First by dipping in acetone followed by boiling in concentrated sodium carbonate solution (30 g/L) for 30 minutes.

6.1.4 Etching

In order to remove surface oxide and to roughen the surface, the titanium substrate was etched in sulphuric acid (850 g/L) at 80°C for 20 minutes, followed by washing with distilled water.

6.1.5 Platinization

In some cases platinization of the anode surface was used to prevent oxide accumulation at the interface between the titanium metal and the electro catalytic coating. This was normally carried out electrolytically to produce a 0.5 micron thick layer of platinum metal (determined gravimetrically). $HtPtCl_6$ (10 g/L); $NaNO_2$ (200g/L); NH_3 (5%, 2 g/L) comprised the electrolytic solution. The titanium acted as the cathode with a platinum anode (3.8 cm^2 working surface area) at a current density of $5A/dm^2$ operating at 60° C.

6.2 Experimental Methods (Electrolysis experiments)

The experiments were carried out in a two-chambered cell with a dividing ceramic membrane for studying the effect of NaCl concentration on current density and current efficiency. The anodes had working surface area of 0.5 cm^2 and the cathode was titanium metal. Determination of chlorine was carried out by radiometric titration. Polarization curves were obtained on a P5829 potentiostat using a silver/silver chlorine electrode, a 1 cm^2 platinum monitoring electrode and the Cobalt oxide/ titanium anodes (COTA), Ruthenium oxide/titanium anodes (ROTA) or Dioxide of manganese/ titanium anodes (DMTA) as the working electrode.

6.3 Ruthenium oxide/titanium anodes (ROTA)

RuO_2 and TiO_2 are isomorphous with the rutile structure. Mixtures of the two-oxide system remain metallic conductors down to 30 mol % RuO_2. This allows dilution of the expensive ruthenium compound. TiO_2 also enhances binding of the oxide layer to the titanium metal substrate (providing a platinized coating is not used).

Coatings were applied by dip coating the anode substrate in dilute (1% with respect to ruthenium) butanolic solutions of $RuCl_3$ and $TiCl_4$ (in mol ratio of 30% Ru to 70% Ti) and pyrolysis in oxygen at 400°C. The process is repeated four times giving a mixed oxide layer 3-5 microns thick [80].

Two different types of ROTA were evaluated, one with a sub-layer of platinum and one without.

6.3.1 General properties of ROTA

Although the equilibrium redox potential for oxygen release at pH 7 is greater for Cl_2 evolution than for O_2 evolution.

	E (V)
$Cl_{2\,(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$	1.358
$\frac{1}{2}O_{2\,(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$	0.810

The overpotential for O_2 evolution on RuO_2 is much greater than for Cl_2 evolution, causing Cl_2 to be evolved preferentially in aqueous solution. Also in general, RuO_2 is highly corrosion resistant.

The electrocatalytic action is thought to be due to the following reaction sequence:

$$Ru^{4+} + H_2O \rightarrow Ru(OH)^{4+} + H^+ + e^-$$
$$Ru(OH)^{4+} + Cl^- \rightarrow Ru(OH)\,Cl^{4+} + e^-$$
$$Ru(OH)\,Cl^{4+} + H^+ + Cl^- \rightarrow Ru^{4+} + H_2O + Cl_2$$
$$2Cl^- \rightarrow Cl_2 + 2e^- \quad \text{Overall}$$

6.3.2 Experimental Results

The polarization curves in Figures 6.1 and 6.2 indicate the onset of chlorine evolution at about 1.40 V. Lower electro catalytic activity is observed at lower NaCl concentrations on ROTA with a sub-layer of platinum than without the sub-layer. However, Figures 6.3 and 6.4 show little difference in the current efficiency of chlorine evolution on the two electrodes. Current efficiencies of above 75% are obtained with current densities below 0.03 A/cm^2 with 15-50 g/L NaCl. The Tafel plots (log current density J against voltage V) in Figures 6.5 and 6.6 indicate greater deviation from a single mechanism of charge transfer for the non-platinum coated electrode. This can be explained in terms of greater oxidation of RuO_2 to RuO_4 without the protective Pt layer. As the Pourbaix diagram Figure 6.7 indicates, this will lead to more corrosion of the electrode coating.

Thus although corrosion occurs with both electrodes it is less for the platinized electrode and thus to be preferred in situations of prolonged polarization.

Fig. 6.1 Anode polarization curves on ROTA in solution of sodium chloride

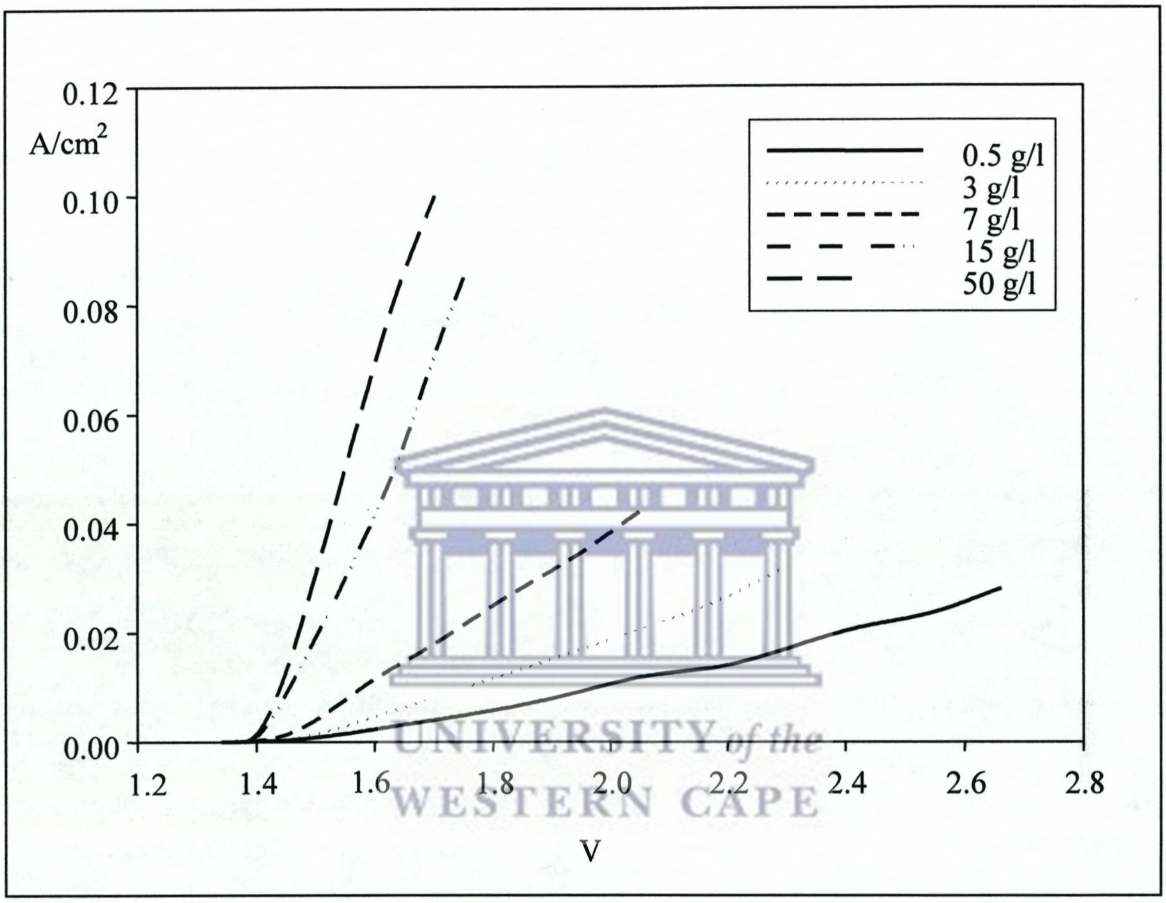


Fig. 6.2 Anode polarization curves on ROTA with platinum sublayer in solutions of sodium chloride.

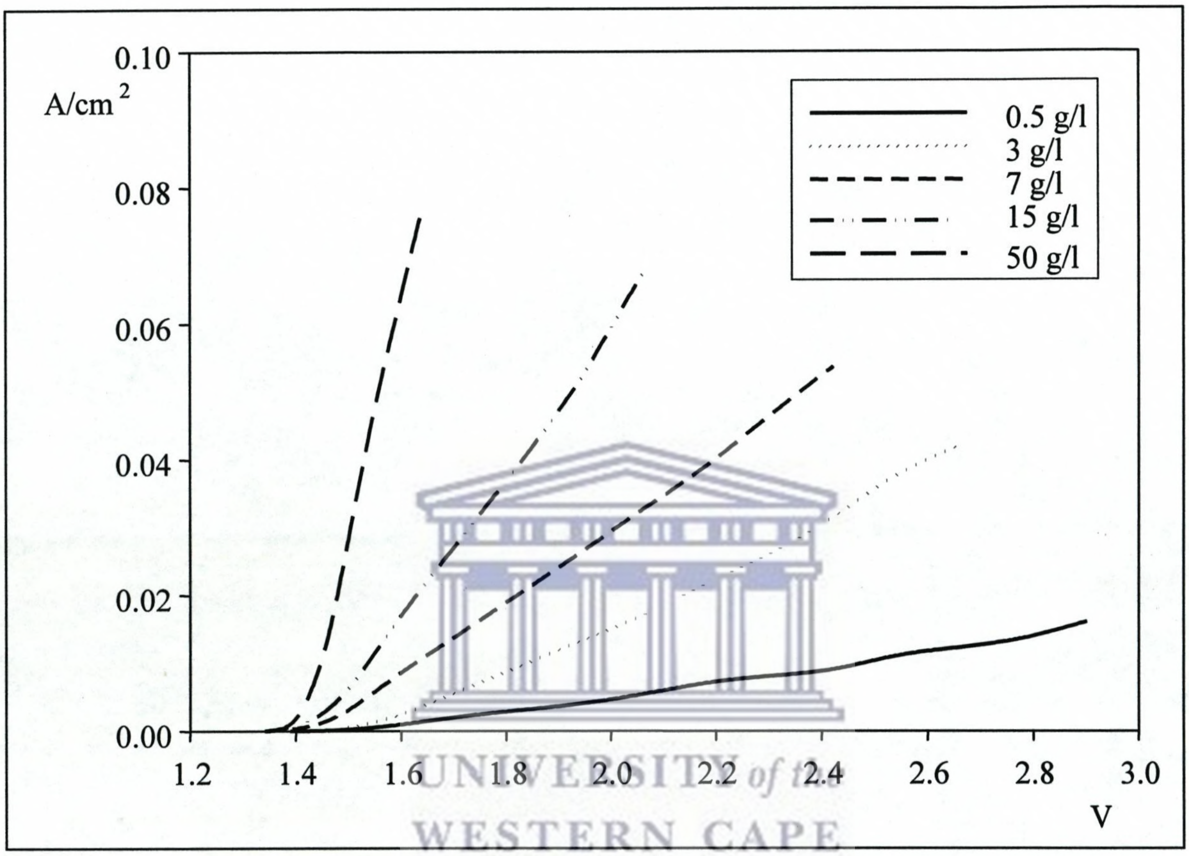


Fig. 6.3 Function of current efficiency of chlorine with current density on ROTA in solution of NaCl with concentration (g/l): 1 – 50; 2 – 15; 3 – 7; 4 – 3; 5 – 0,5 *CE – current efficiency

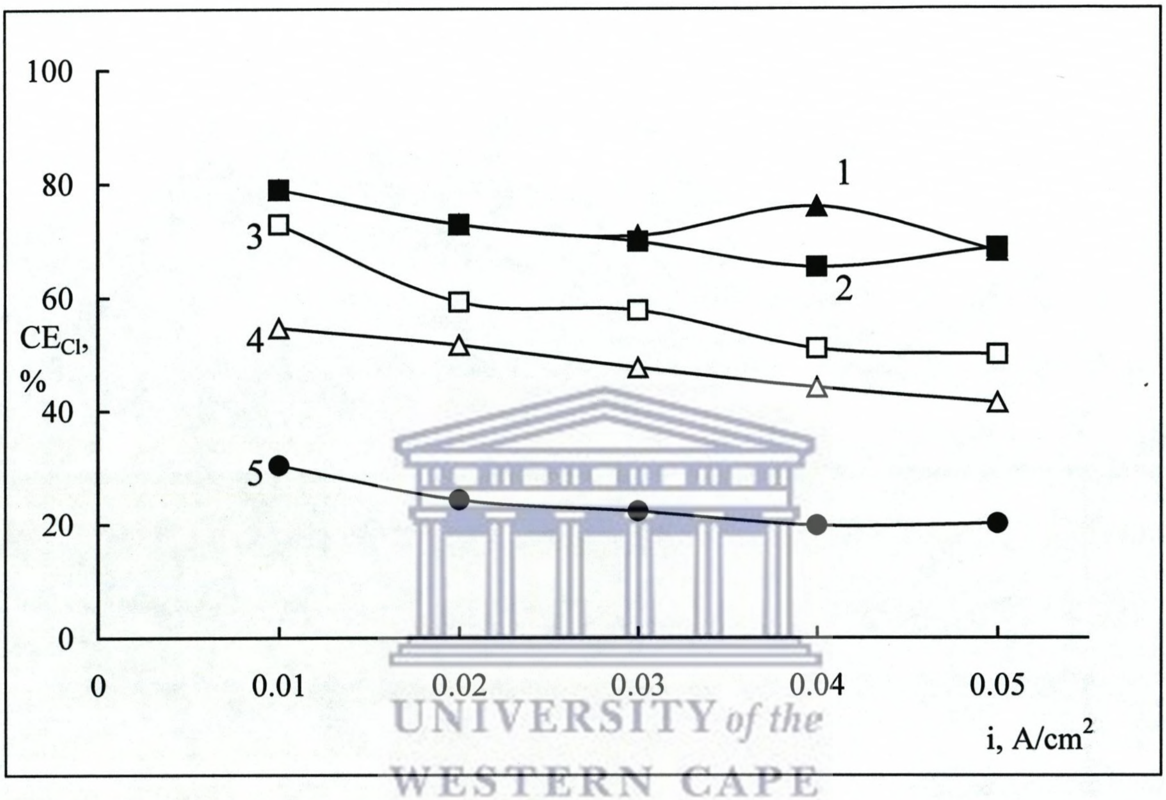


Fig. 6.4 Function of current efficiency of chlorine on density of current on ROTA with platinum sublayer in solution of NaCl of concentration (g/l): 1 – 50; 2 – 15; 3 – 7; 4 – 3; 5 – 0,5

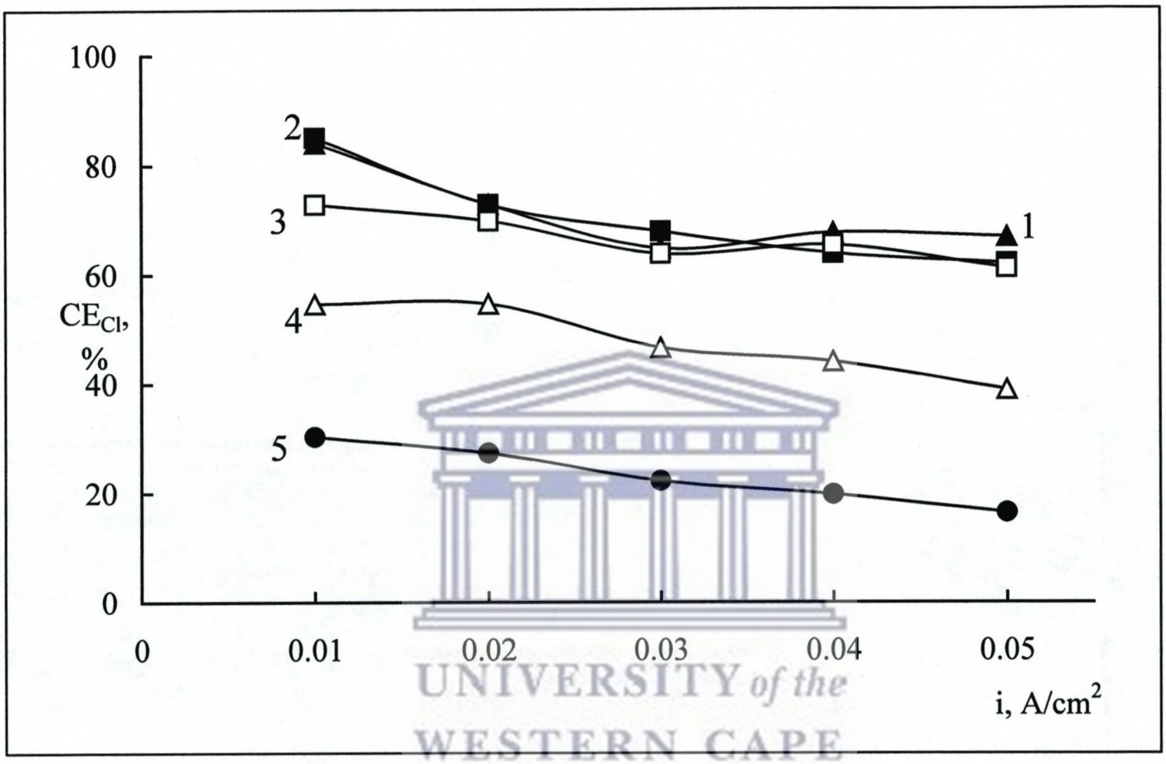


Fig. 6.5 Function of lg J – V for ROTA with platinum sublayer in solution of sodium chloride.

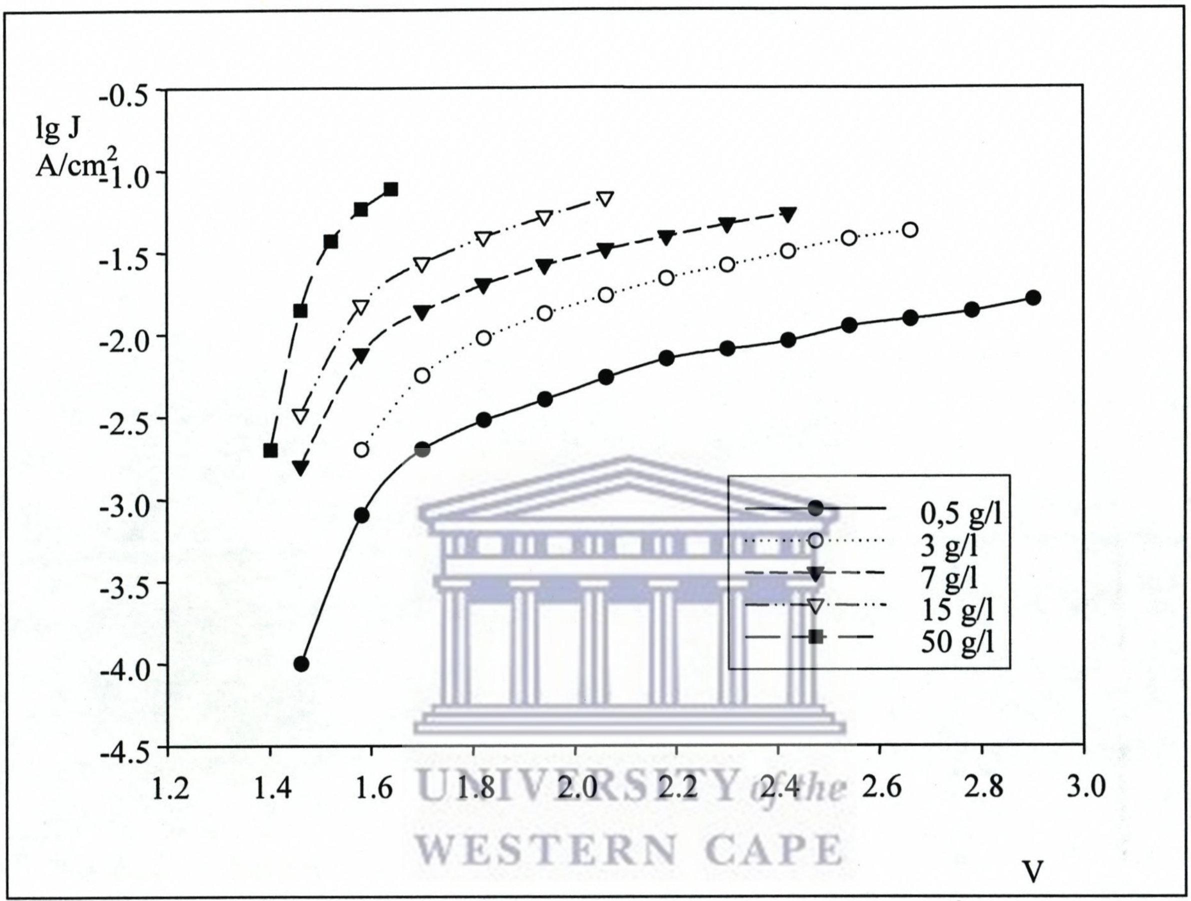


Fig. 6.6 Function of lg J – V for ROTA without a Pt sub-layer in solutions of sodium chloride

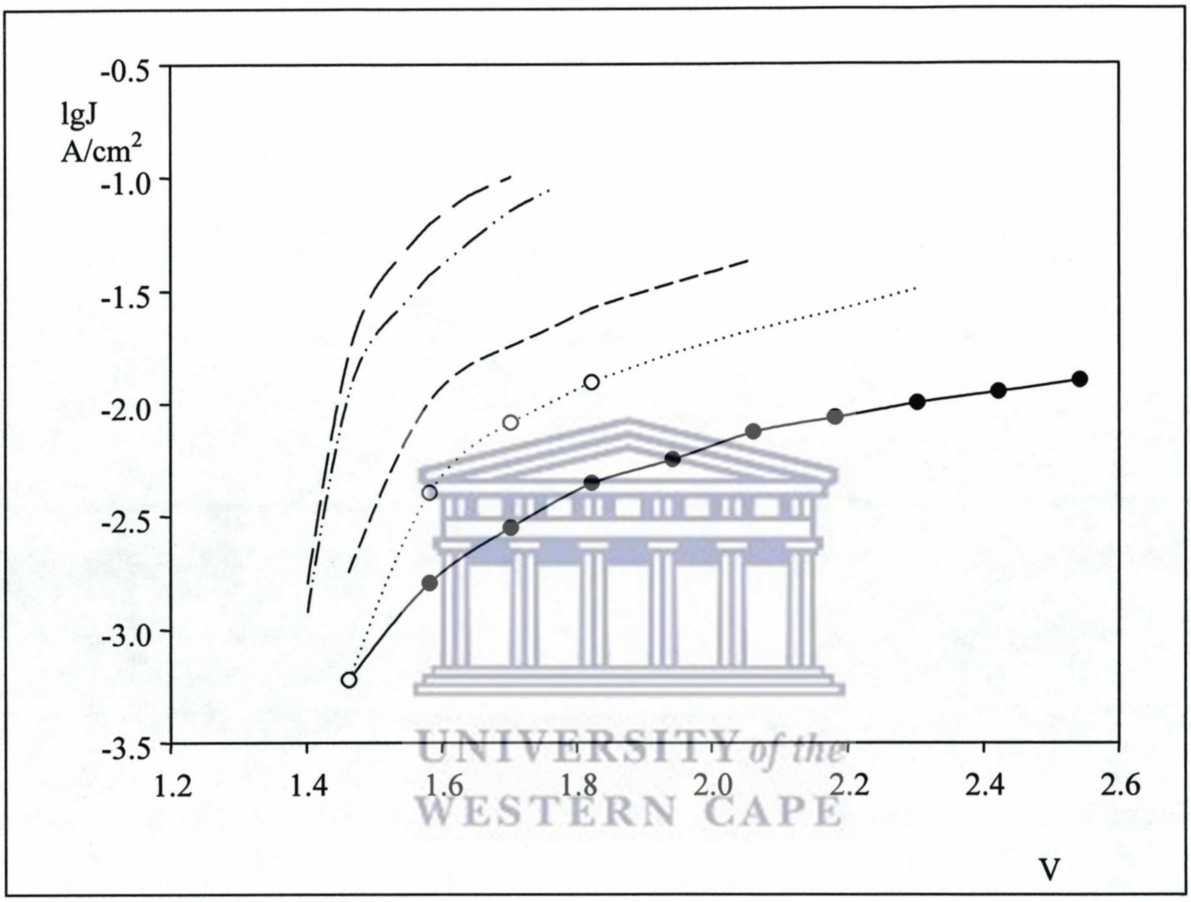
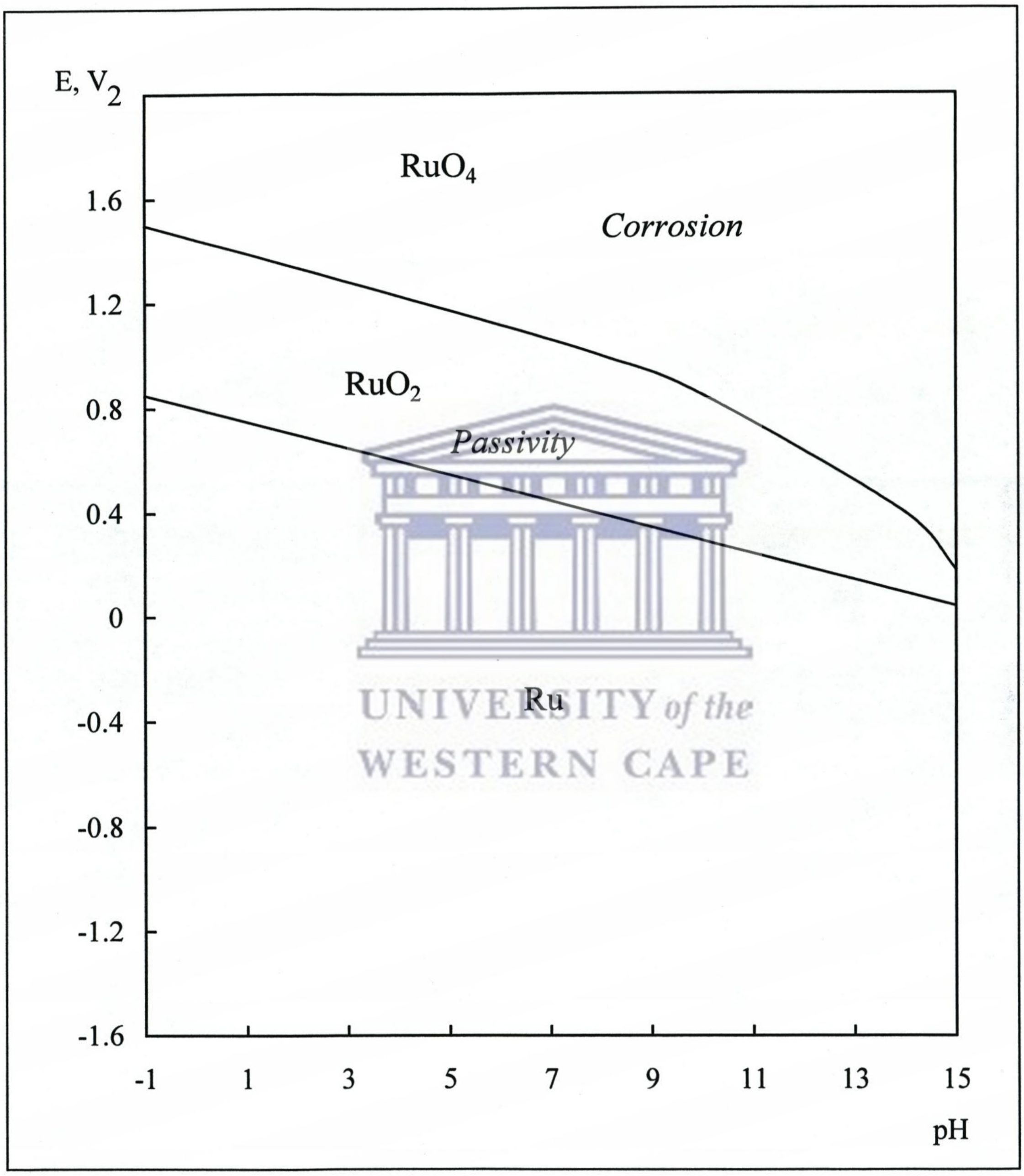


Fig. 6.7 Areas of corrosion and passivity in the system of ruthenium-water in accordance with the Pourbaix diagram



6.4 Cobalt oxide / titanium anodes (COTA)

Co_3O_4 is an electrically conducting spinel-type oxide, which has high electro catalytic activity for chlorine evolution. It has a much lower overpotential for chlorine evolution than does RuO_2.

Coating of electrodes can be carried out by thermal decomposition of cobalt (II) nitrate or by electrodeposition of cobalt (II) hydroxide from cobalt (II) sulphate solutions followed by pyrolysis in oxygen. However, in this work the more reliable (in terms of constant composition) method of plasma spraying was used. Pure Co_3O_4 powder was vaporized in an A440 plasmatron at 900°C using tungsten electrodes (10-40 V with a current of 100-150 A).

Co_3O_4 thermally dissociates to CoO, which is deposited on the titanium (or platinized titanium substrate to a thickness of about 40 microns). However, CoO is non-conducting. Activation of the electrode is carried out in a brine solution using the CoO coated electrode as an anode for 15 hours at a current density of 0.6 A/dm^2. The colour of the electrode changes from blue to black corresponding to a conversion of CoO to Co_3O_4 [80].

6.4.1 Experimental Results

The polarization curves Figures 6.8 and 6.9 indicate higher electro catalytic activity on COTA with a platinum sub-layer and higher than ROTA. Current efficiencies for chlorine evolution are above 90% for current densities below 0.03 A/cm^2 for non-polarized COTA (Figure 6.10) using 14-50 g/L NaCl. Current efficiencies are around 80% (see figure 6.11) for equivalent conditions with COTA on a platinized sub-layer. However, at higher current densities both have current efficiencies around 80%. Both these are better than on ROTA. The Tafel slopes (Figures 6.12 and 6.13) vary uniformly with changing electrolyte concentration indicating a single mechanism. Thus it may be concluded that the COTA layer did not under go corrosion. From the Pourbaix diagram, corrosion is most likely to occur (see Figure 6.14) under conditions of low pH and positive potentials. Reversal of polarity is to be avoided as it will lead to the reformation of CoO, which is non-conducting. Thus platinized COTA is the best option for corrosion resistance.

Fig. 6.8 Anode polarization curves on COTA, which was prepared by method of plasma spraying from Co_3O_4 marked "pure", followed by activation in solutions of sodium chloride

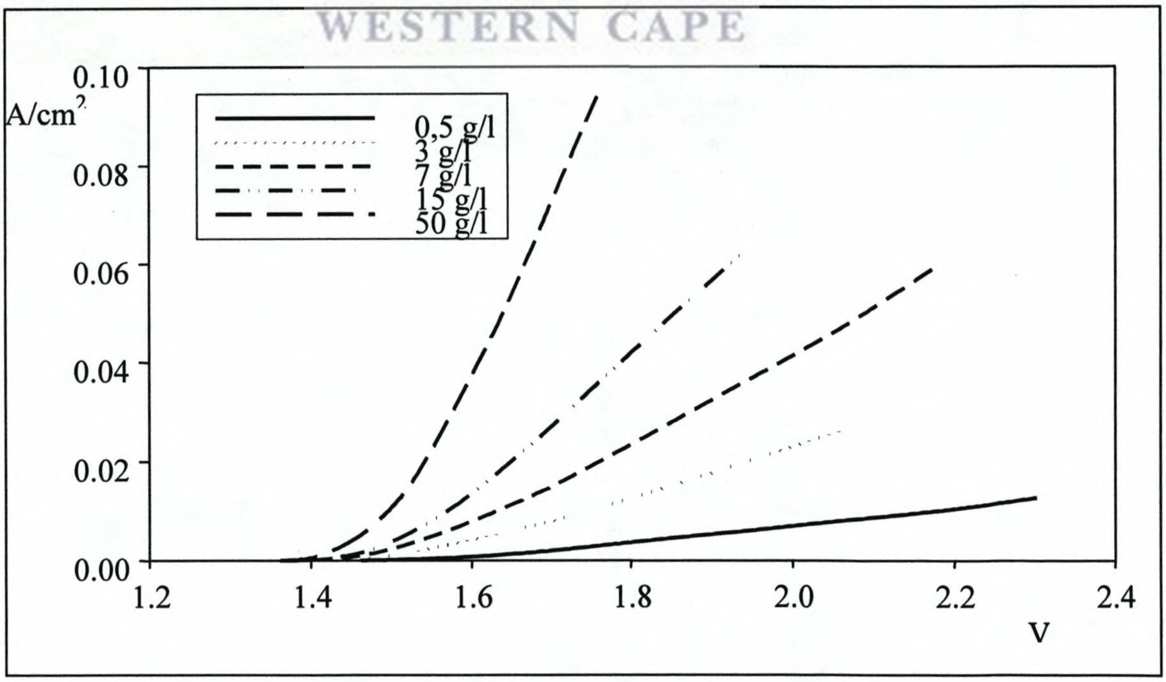


Fig. 6.9 Anode polarization curves on COTA with platinum sublayer, which was received by method of plasma spraying from Co_3O_4 marked "pure", followed by activation in solutions of sodium chloride.

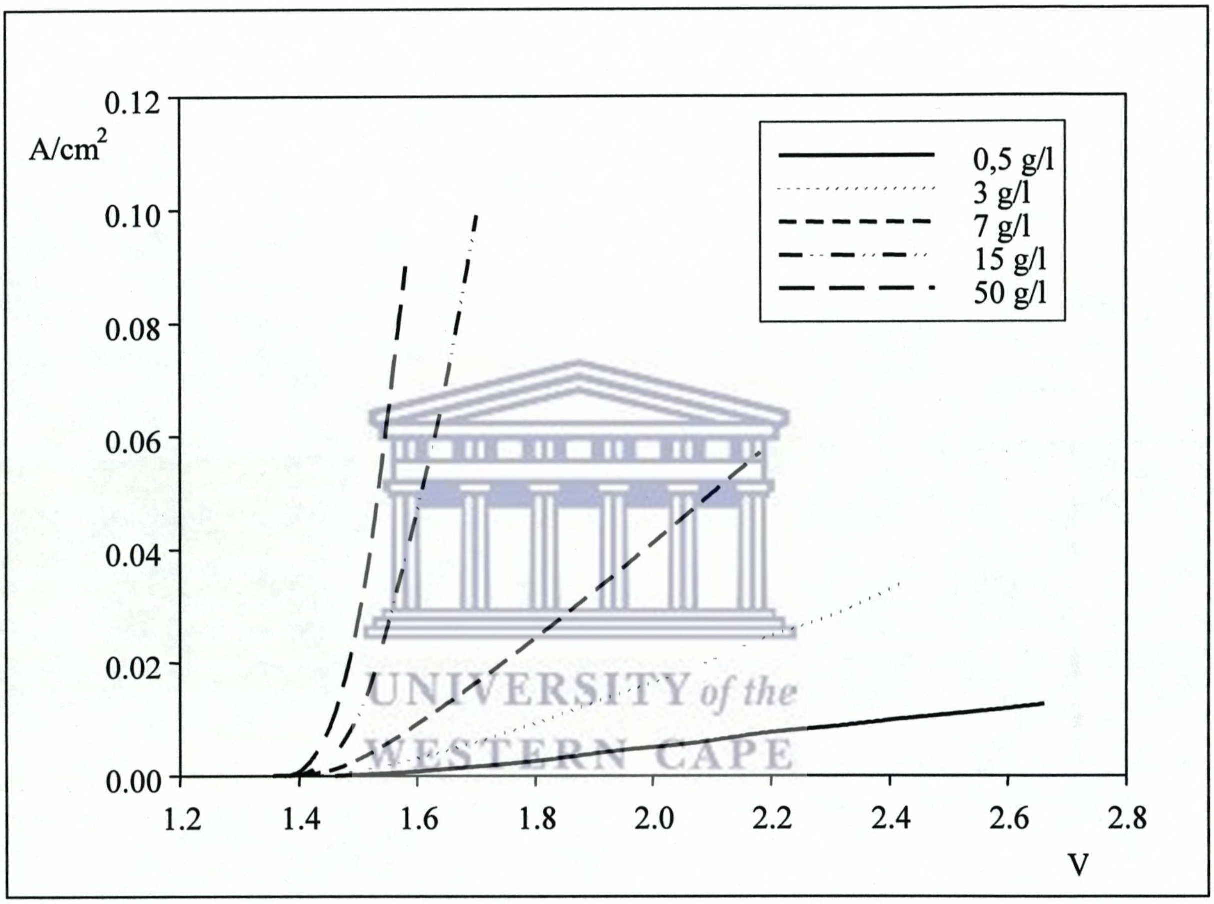


Fig. 6.10 Function of current efficiency of chlorine with current density on anode Co_3O_4, which was prepared by method of plasma spraying from reagents marked "pure", followed by activation in a solution of NaCl with concentration (g/l): 1 – 50; 2 – 15; 3 – 7; 4 – 3; 5 – 0,5.

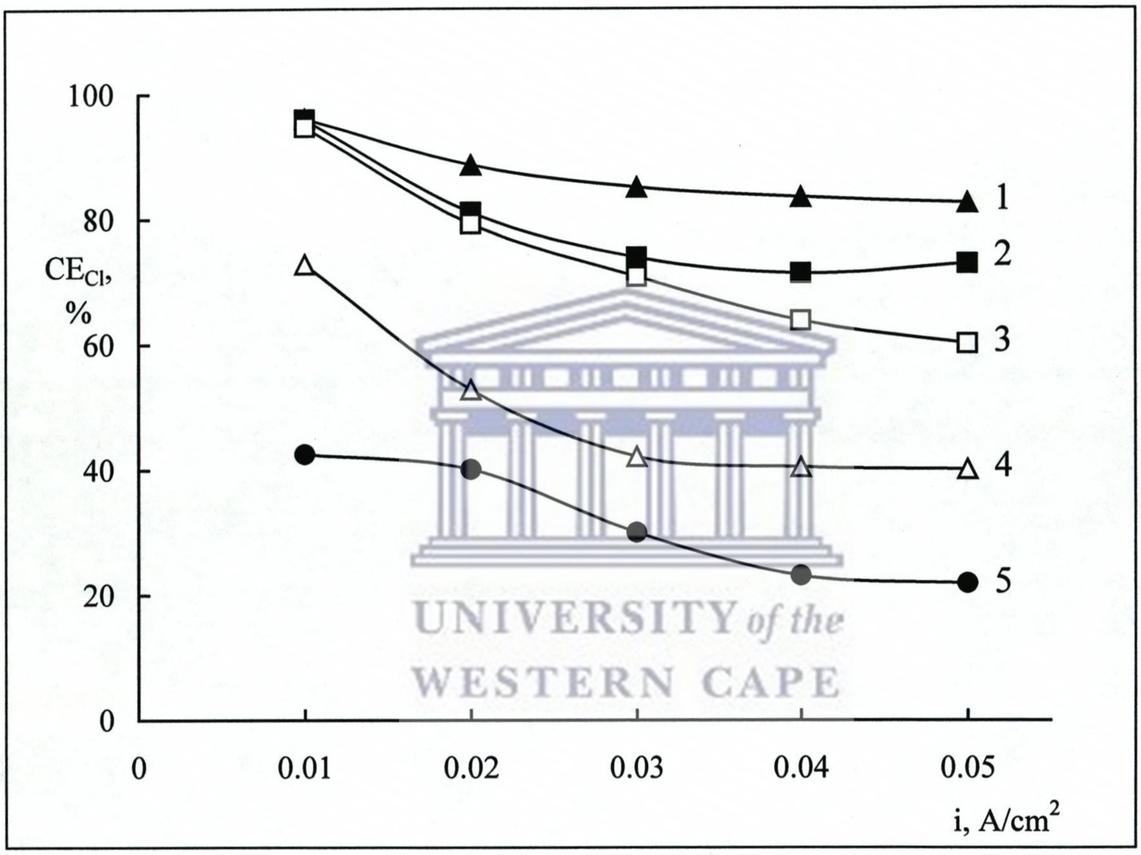


Fig. 6.11 Function of current efficiency of chlorine with current density on anode Co_3O_4, which was prepared by method of plasma spraying from reagents marked "pure", with platinum sublayer followed by activation in a solution of NaCl with concentration (g/l): 1 – 50; 2 – 15; 3 – 7; 4 – 3; 5 – 0,5.

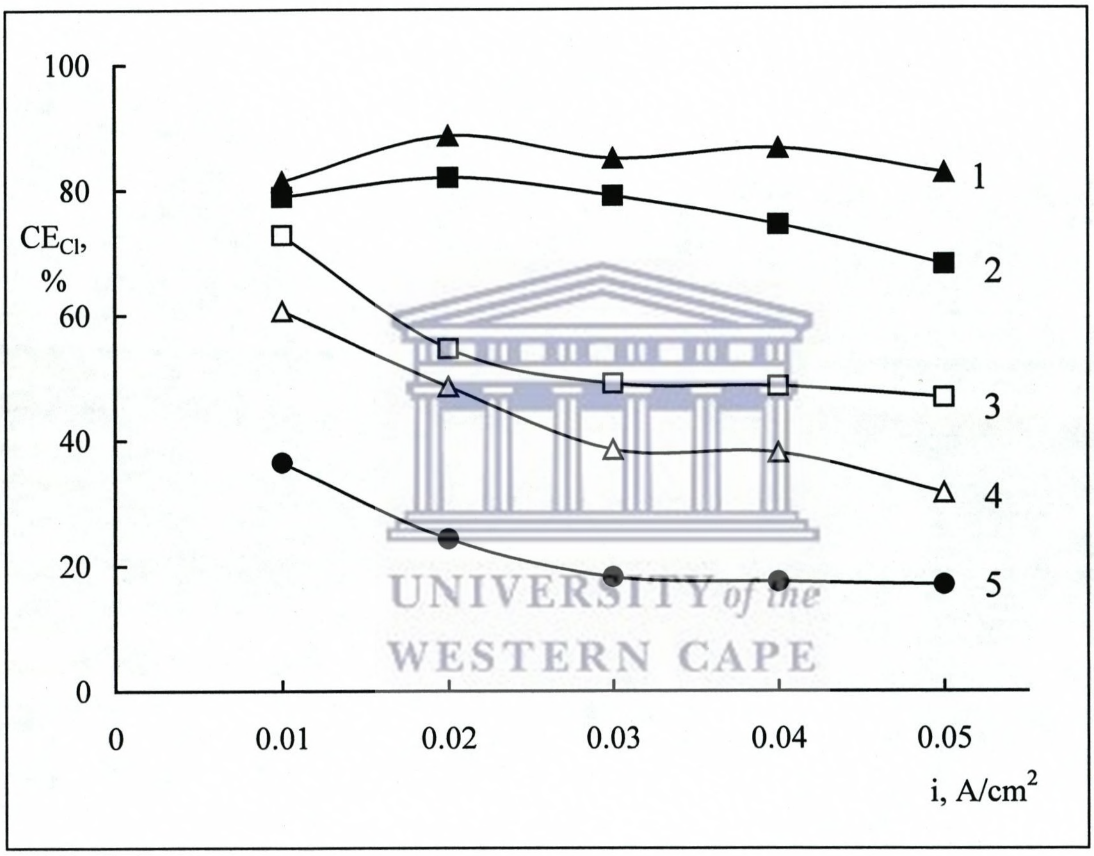


Fig. 6.12 Function of lg J – V on COTA, which was received by method of plasma spraying from Co_3O_4 marked "pure", followed by activation in solutions of sodium chloride.

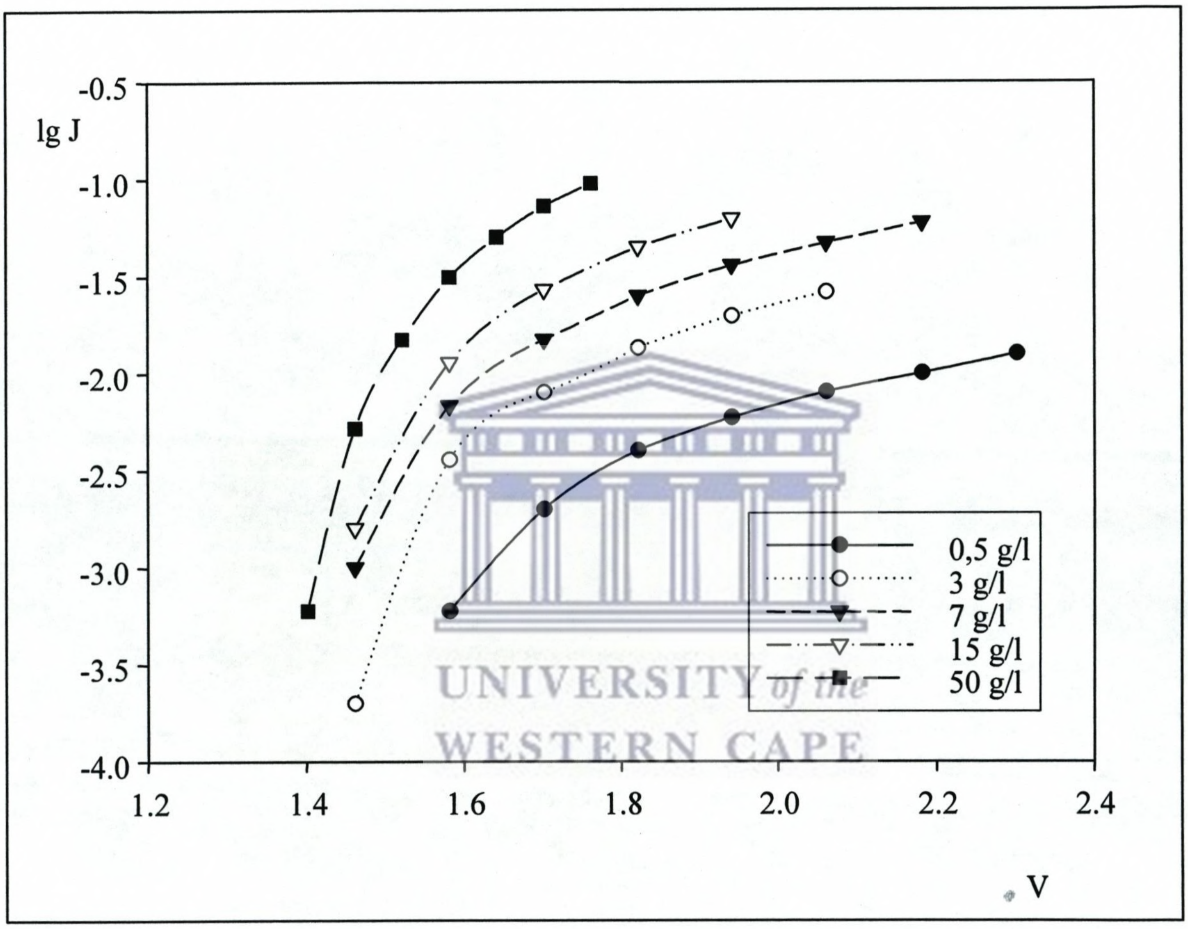


Fig. 6.13 Function of lg J – V on COTA with platinum sublayer which was prepared by method of plasma spraying from Co_3O_4 marked "pure", followed by activation in solutions of sodium chloride.

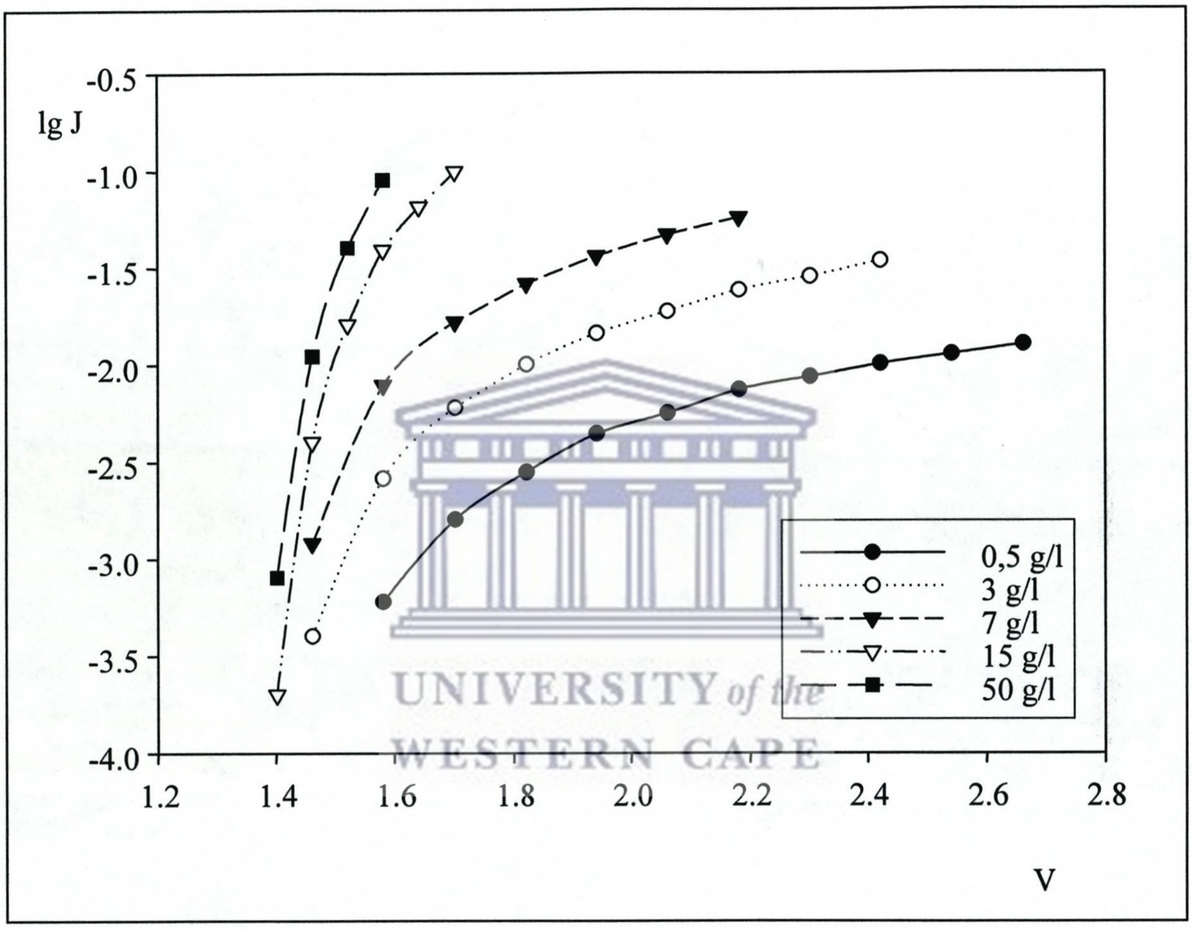
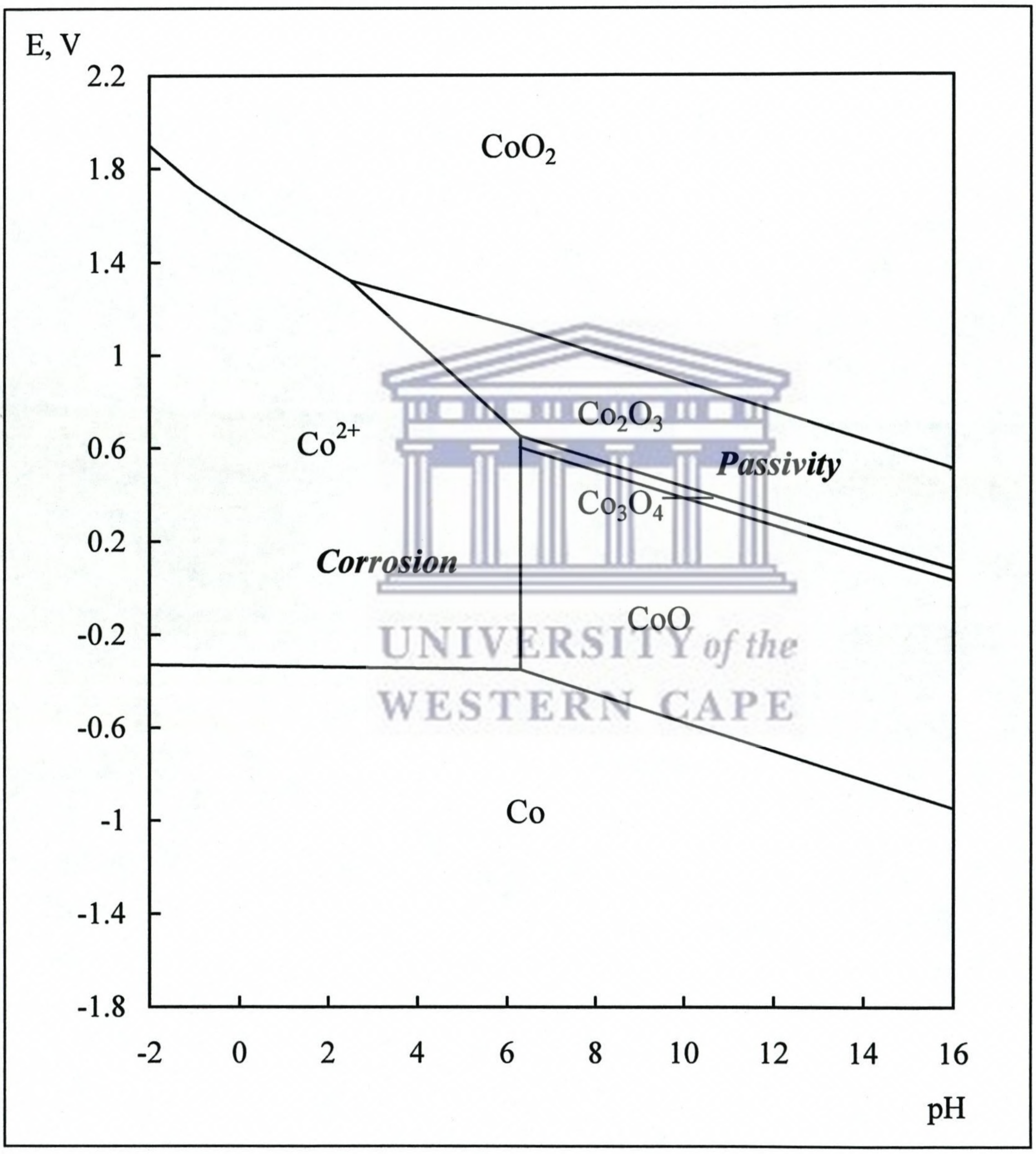


Fig. 6.14 Areas of corrosion and passivity in system of cobalt-water in accordance with the Pourbaix diagram



6.5 Dioxide of manganese / titanium anodes (DMTA)

Electro catalytic coatings of MnO_2 are attractive because they are cheap and easy to prepare. Although there are electrolytic and plasma deposition methods available, the simplest and most reliable method is via the thermal decomposition of manganese (II) nitrate. In this study, the $Mn(NO_3)_2$ solution was boiled to a density of 1.8 g/cm^3 and then subjected to a heat treatment of between 180-370°C for one hour during which time a black deposit formed on the titanium substrate. After brushing with a soft brush the process was repeated 4-5 times achieving a thickness of 100-200 microns of MnO_2. Higher temperatures lead to the following changes [80]:

$$MnO_2 \xrightarrow[500^{\circ}C]{} Mn_2O_3 \xrightarrow[950^{\circ}C]{} Mn_3O_4 \xrightarrow[1000^{\circ}C]{} MnO$$

With a loss of electrochemical activity, there is a slight increase in the current efficiency of electrodes prepared at 180°C as opposed to those at 250-370°C, thus electrodes prepared at that temperature were thoroughly investigated.

6.5.1 General properties of DMTA

MnO_2 is an n-type semiconductor hence an increase in charge carriers and conductivity occurs with loss of oxygen content. Prolonged polarization as an anode increases the degree of oxidation of manganese and hence conductivity decreases. The overpotential of chlorine evolution is higher than that of ROTA or COTA and much closer to that of oxygen evolution. Its electro catalytic behavior is considered to be via a similar mechanism to that for RuO_2 namely:

$$Mn^{4+} + H_2O \rightarrow Mn\,(OH)^{4+} + H^+ + e^-$$
$$Mn(OH)^{4+} + Cl^- \rightarrow Mn(OH)Cl^{4+} + e^-$$
$$Mn(OH)Cl^{4+} + H^+ Cl^- \rightarrow Mn^{4+} H_2O + Cl_2$$
$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{Overall}$$

6.5.2 Experimental Results

It can be seen from the polarization curve (Figure 6.15) that electrochemical activity of DMTA is less than that of ROTA and COTA; also the onset of chlorine evolution is at a higher potential than that of ROTA and COTA. The current efficiency of chlorine evolution is at a maximum of 40% and clearly this is due to the co-evolution of oxygen (Figure 6.16). The Tafel plots (Figure 6.17) confirm this behavior and also the dissolution of the MnO_2 over a range of pH and polarization potential.

Thus in spite of their cheapness the use of DMTA in the electrolysis of aqueous sodium chloride is problematic especially due to;

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Occurring at the anode, which causes the anode to dissolve (corrode).

Fig. 6.15 Anode polarization curves on DMTA prepared by thermal method at temperature 180°C in solutions of sodium chloride.

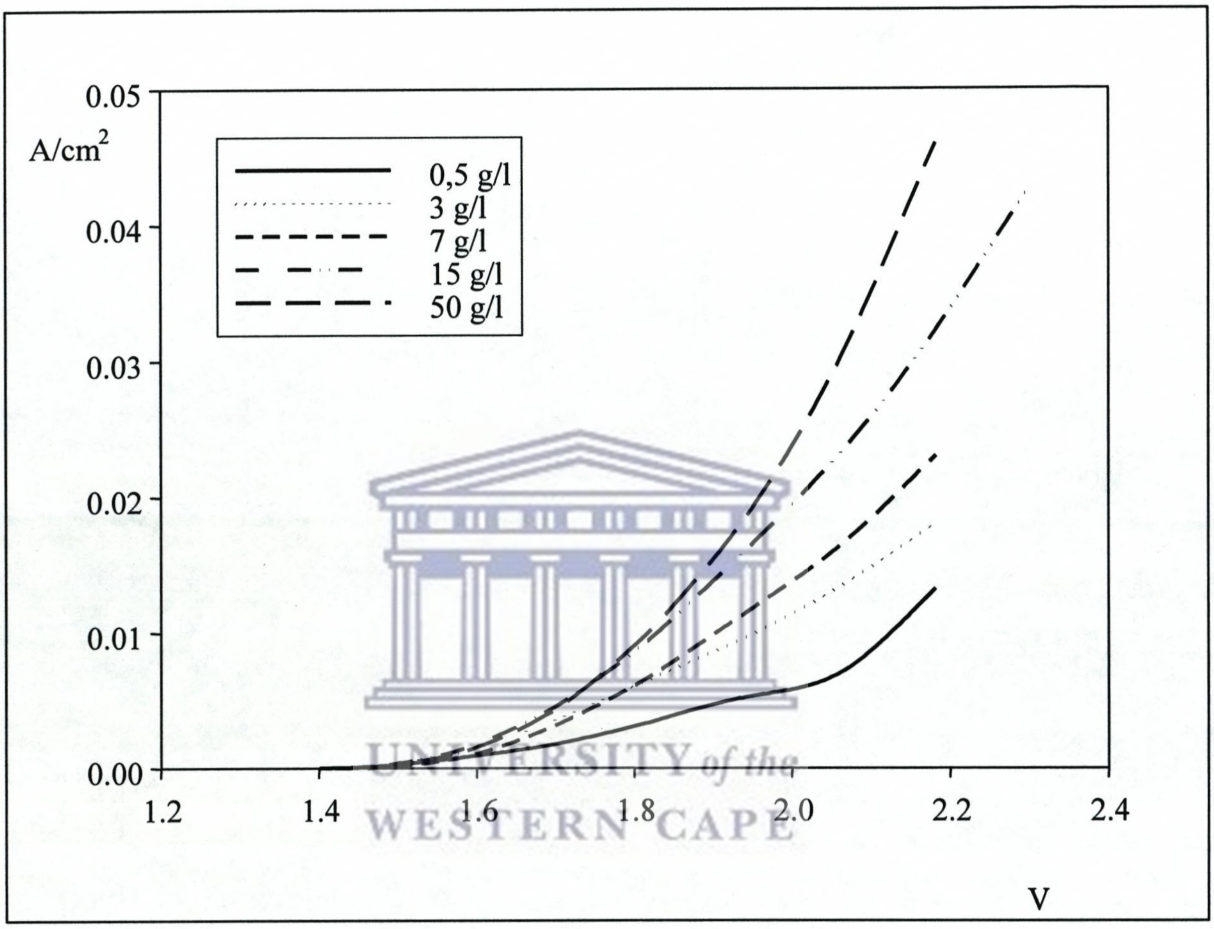


Fig. 6.16 Function of current efficiency of chlorine with current density on anode MnO_2, received by thermal method at temperature 180°C, in solution of NaCl with concentration (g/l): 1 – 50; 2 – 15; 3 – 7; 4 – 3; 5 – 0,5.

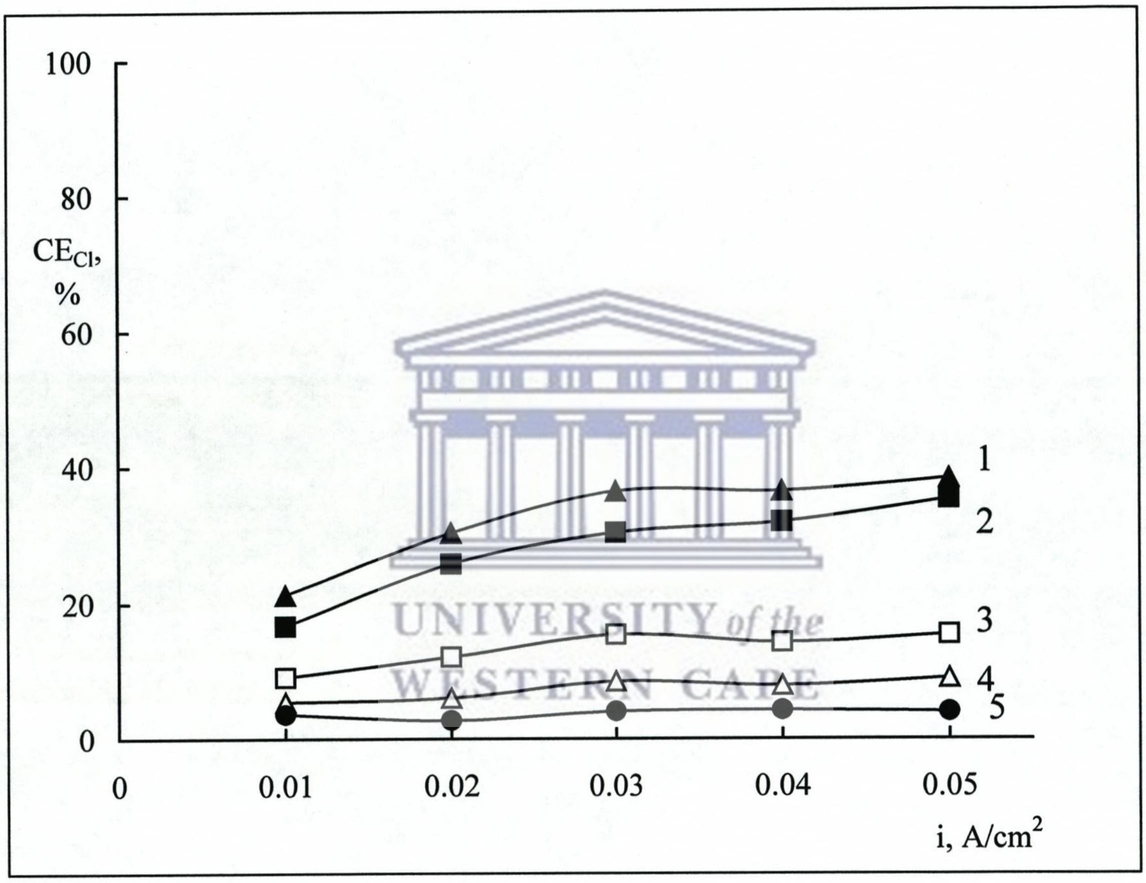


Fig. 6.17 Function of lg J – V on DMTA prepared by thermal method at temperature decomposition 180°C in solutions of sodium chloride.

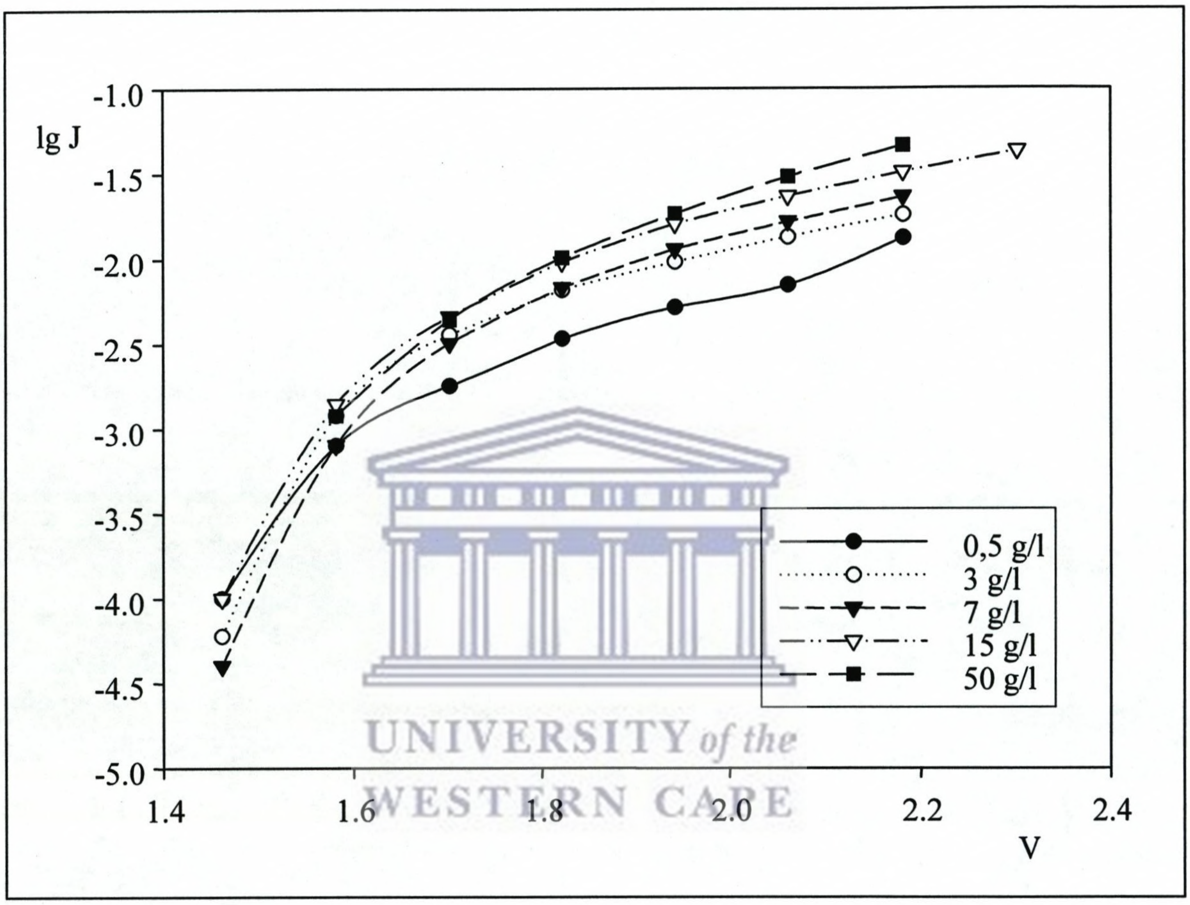
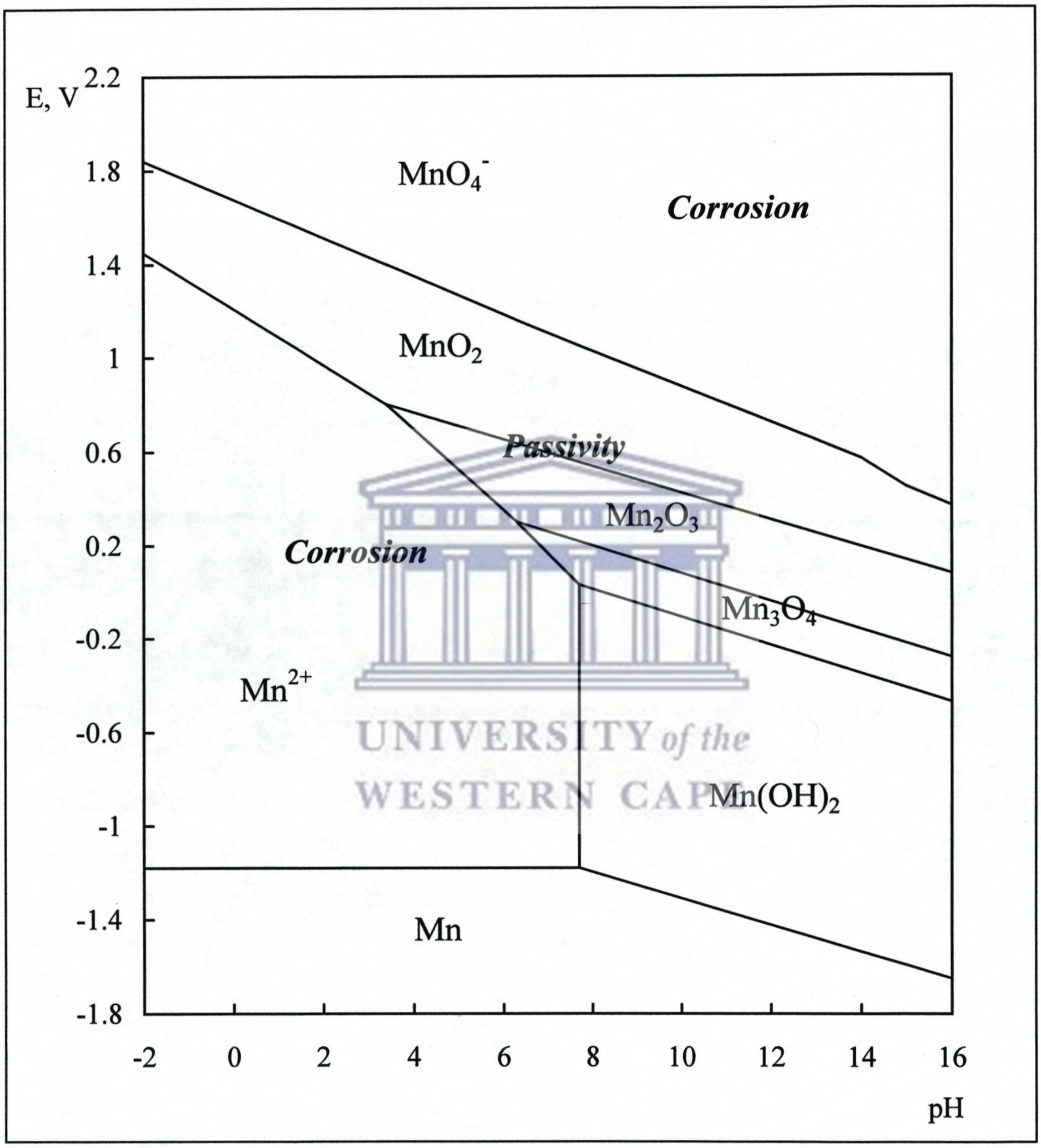


Fig. 6.18 Areas of corrosion and passivation in the system of manganese-water in accordance with the Pourbaix diagram



6.6 Other Electrode Materials

Magnetite (Fe_3O_4)/ titanium anodes (MTA); platinum, platinum (coated)/ titanium anodes (PTA) and graphite were also studied but these were not tested in the electrolysers.

6.7 Conclusion

It is clear that the electro catalytic current efficiency and corrosion resistance for chlorine evolution in solutions of NaCl between 3-50 g/L is in the order of:

COTA>ROTA>DMTA

Although platinized COTA electrodes have slightly decreased current efficiencies for chlorine evolution compared with those with no platinization they have increased corrosion resistance. Optimum current densities on COTA are in the range 0.01-0.05 A/cm^2. Hence, platinized COTA electrodes appear to be the optimum choice. However, their method of preparation requires further study as plasma deposition is not easily adapted for large-scale manufacture. Also platinization is very costly thus an alternative method of preparing COTA will have to be investigated in the long term.

CHAPTER SEVEN

7. DEVELOPMENT OF THE ELECTROLYSERS

7.1 Electrolysers with cobalt oxide (COTA) anodes

Metal-oxide systems such as doped RuO_2 (RuO_2 + TiO_2, 2:1 as metal ratio) have been used as anodic electro catalysts for hypochlorite production via the electrolysis of brine. Titanium is often used as the metal base due to its high breakdown corrosion potential. However the drawback of using RuO_2 systems are their high expense and efficiency for oxygen evolution. This increases with increasing current density and decreasing salinity. An alternative electro catalytic coating is CoO which has a lower overpotential for chlorine release than for oxygen evolution.

$Co^{2+}O + Cl^- \rightarrow ClCo^{2+}O + e^-$ Electrochemical step

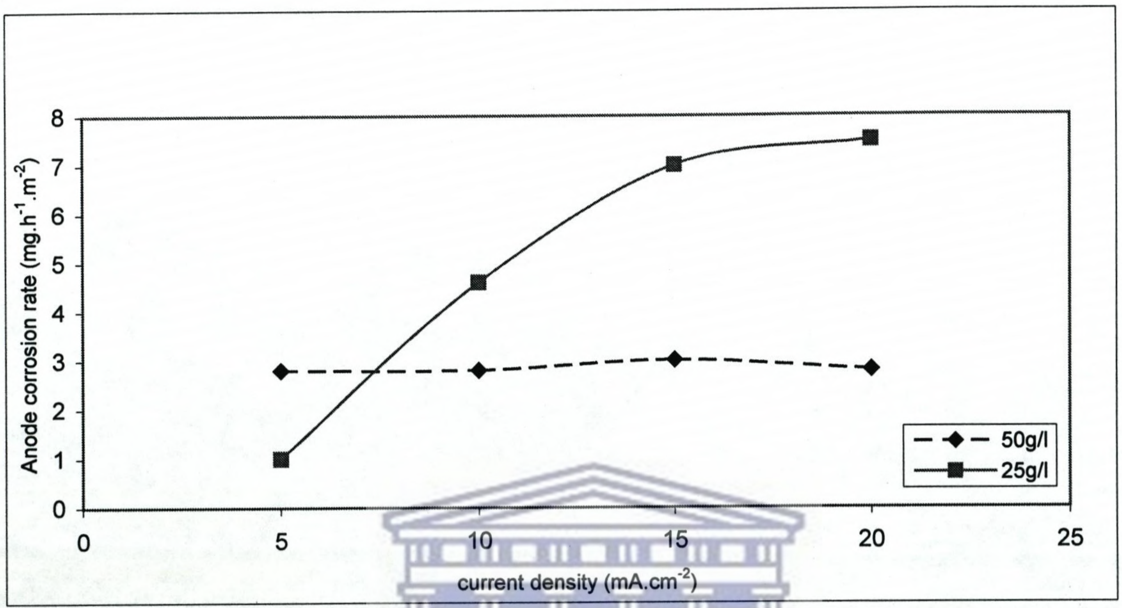
$ClCo^{2+}O \rightarrow Co^{2+}O + \frac{1}{2} Cl_2$ Catalytic step

$Cl^- \rightarrow \frac{1}{2} Cl_2 + e^-$ Overall

The anode used in the electrolyser is a titanium metal rod anode coated with platinum over which a layer of cobalt (II) oxide (CoO) is deposited.

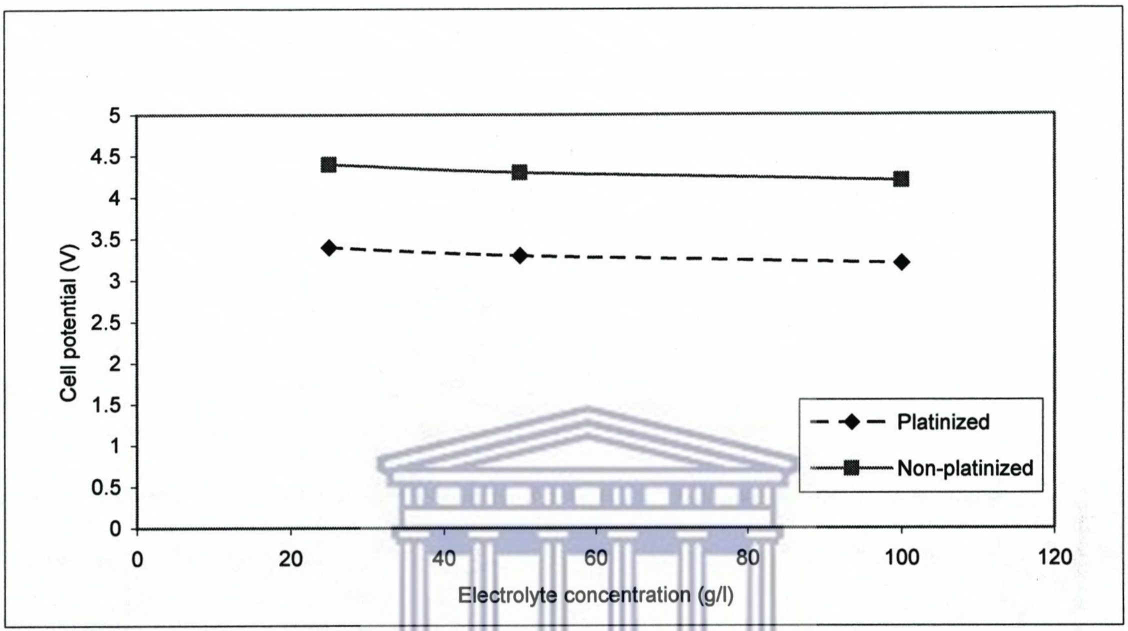
However, CoO is non-conducting, the activation of the electrode is carried out by electrolysis in brine solution for 15 hours at a current density of 0.6A/dm^2. The colour of the electrode changes from blue to black during the conversion of CoO to Co_3O_4.

Figure 7.1 Dependence of the anode corrosion ($mg.h^{-1}.m^{-2}$) rate on current density and NaCl concentration.



Thermal plasma deposition coating of CoO layer on titanium anode (from Co_3O_4 precursor) followed by electro-oxidation gave a catalytic layer whose corrosion resistance over a wide range of current densities was excellent in 25 and 50g/l NaCl catholytic solution, as seen in figure 7.1.

Figure 7.2 Dependence of cell potential drop (V) on anode coating and electrolyte concentration.



In the figure 7.2 the anodes are identified as

Platinized – Titanium anode coated with platinum below CoO layer

Non- platinized – Titanium anode not coated with platinum below CoO layer.

The layer of platinum decreases potential drop over the Ti-CoO contact, which in turn contributes to a lower cell potential drop.

Changing electrolyte concentration from 25 to 100 g.l^{-1} does not significantly lower potential drop.

Figure 7.3 Dependence of hypochlorite current efficiency (%) on current density (mA.cm^{-2}) with an electrolyte concentration of 25g.l^{-1} and different anode coatings.

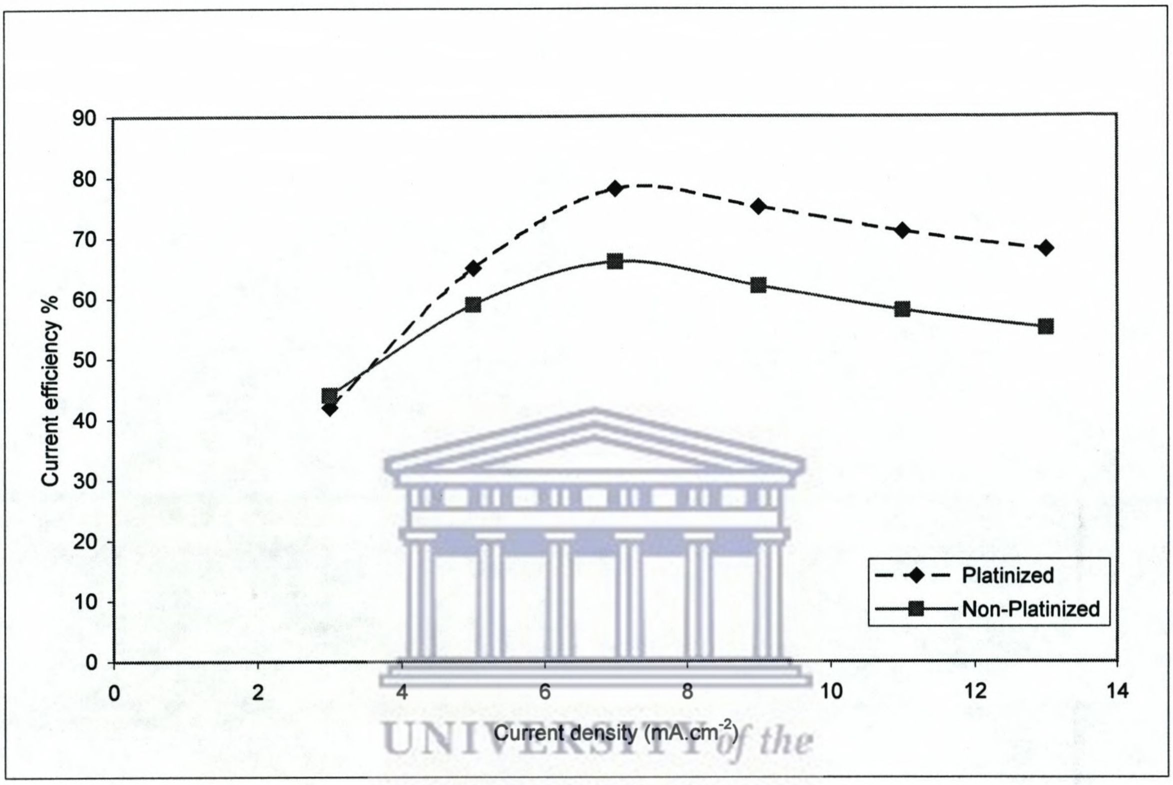


Figure 7.3 shows that the maximum hypochlorite current efficiency is achieved at low current densities (6-8 mA.cm^{-2}). Anode with an intermediate platinum layer gave nearly 80% current efficiency some 10-12% better than anodes without platinum coating below the CoO layer.

Although oxygen release is more likely at low current densities, with consequent chlorate formation.

$$3ClO^- + \frac{3}{4} H_2O \rightarrow \frac{3}{4} O_2 + 3H^+ + 2Cl^- + ClO_3^- + 3e^-$$

This strongly diminishes at low pH (2.2-4.7) where dissolved chlorine forms hypochlorous acid [81].

$Cl_{2\,(g)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$

Figure 7.4 Dependence of hypochlorite current efficiency (%) on the electrolyte concentration and anode coating with current density of 6mA.cm^{-2}.

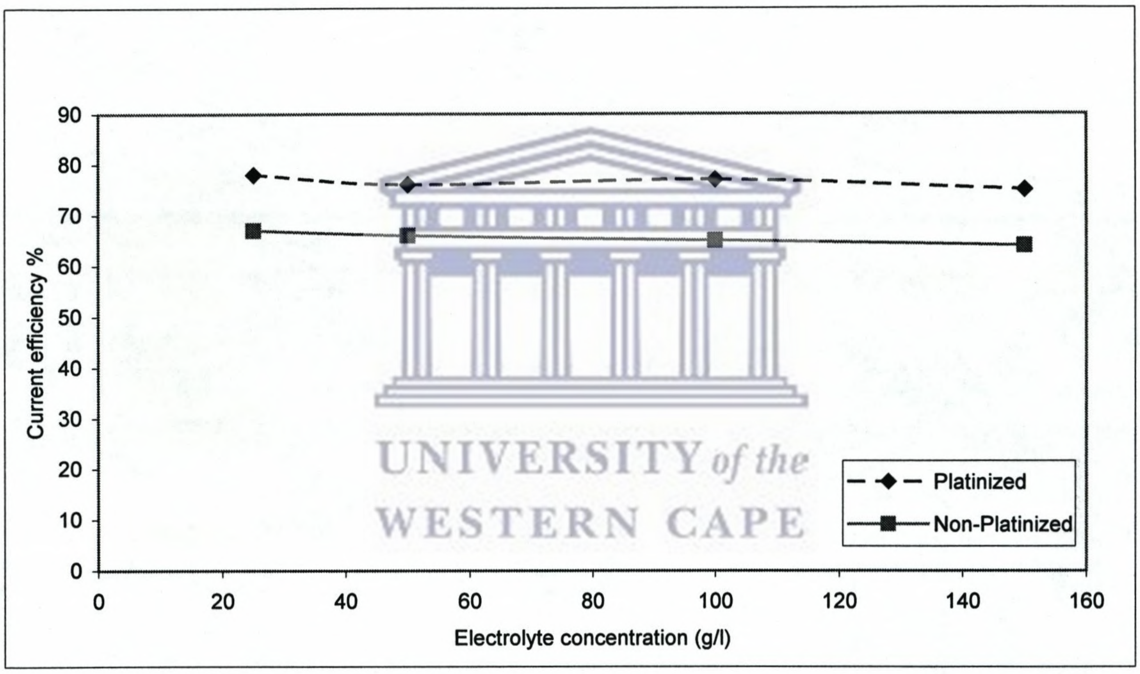
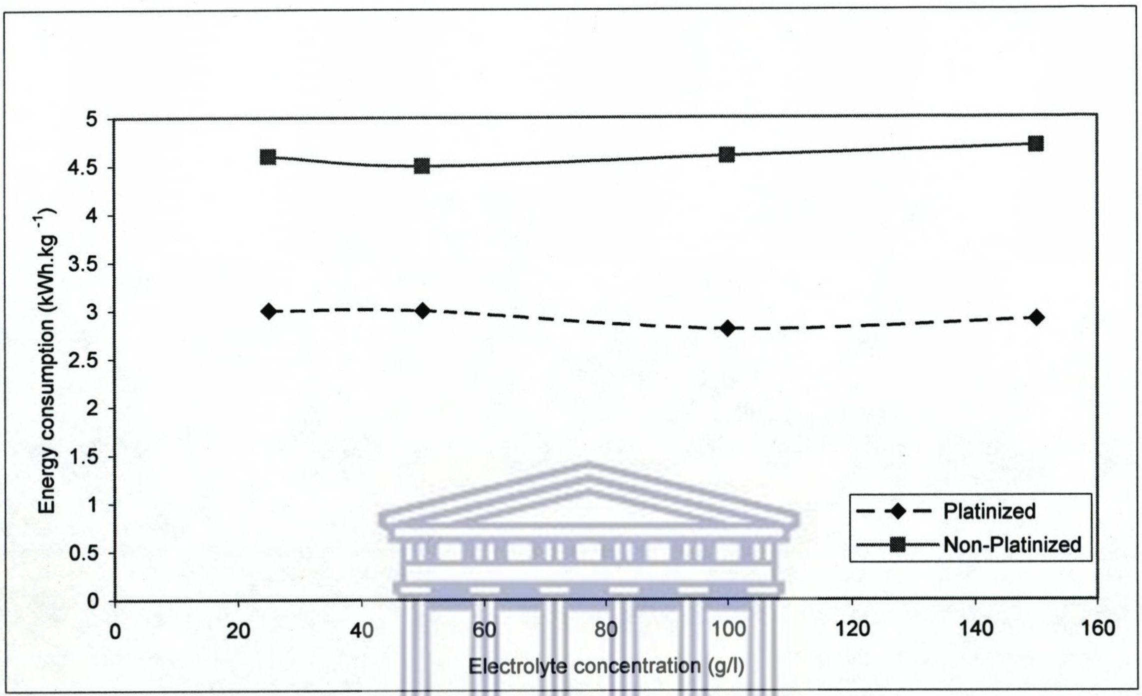


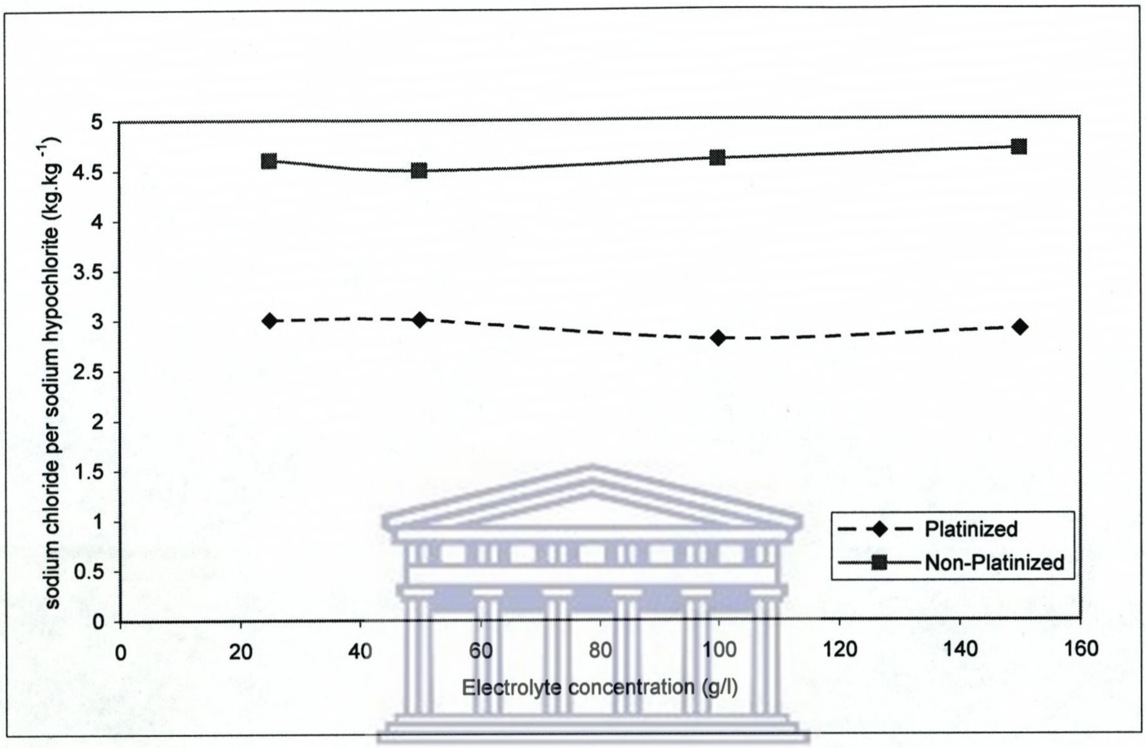
Figure 7.4 illustrates that above NaCl concentration of 25g.l^{-1} the current efficiency is not significantly altered by electrolyte concentration. (The use of more concentrated solutions also leads to undesirable increase in salt consumption). The anode with platinum intermediate layers has a greater hypochlorite current efficiency.

Figure 7.5 Dependence of energy consumption (kWh.kg^{-1} of hypochlorite formation) on electrolyte concentration and type of anode.



There is no significant change in energy consumption at electrolyte concentrations above 25g.l^{-1} of NaCl. The anode with the platinum consumes less than that without the layer as shown in Figure 7.5.

Figure 7.6 Dependence of materially yield (kg .kg^{-1} of sodium chloride used against sodium hypochlorite produced) on electrolyte concentration and type of anode.



As is shown in figure 7.6 that the use of electrolyte that is more concentrated than 25g.l^{-1} of NaCl does not markedly affect salt consumption. Platinum anode coating reduces salt consumption slightly.

Figure 7.7 Dependence of current efficiency (%) of hypochlorite formation on flow rate in the cathode chamber with platinum coated anode (at 6mA.cm^{-2}).

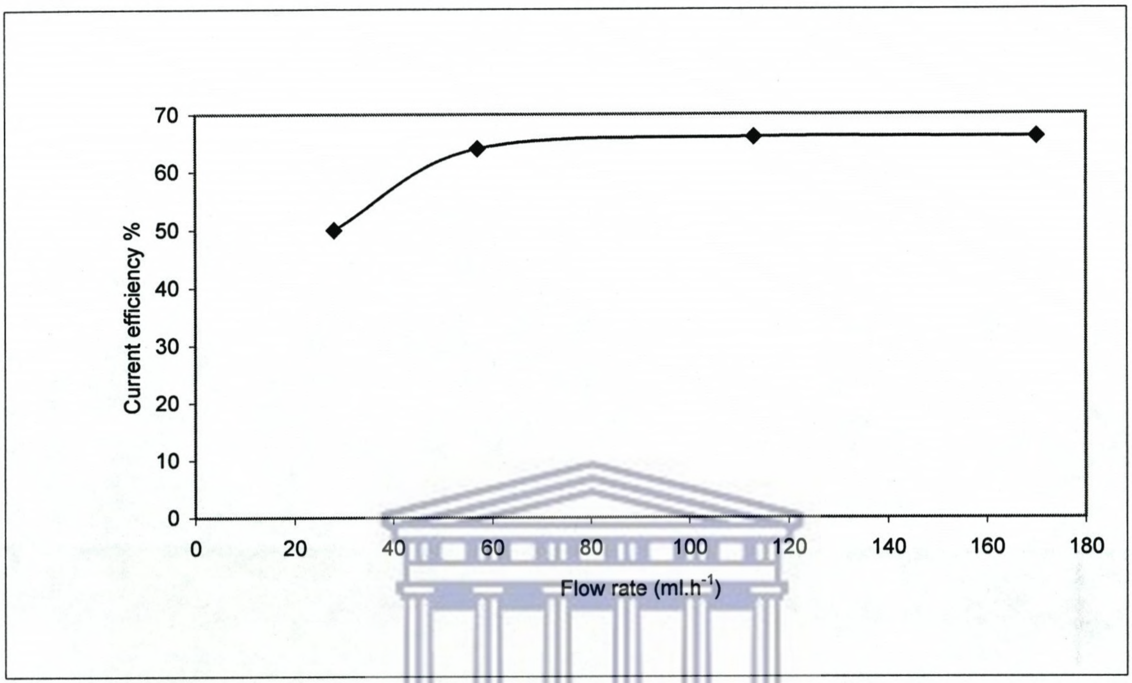
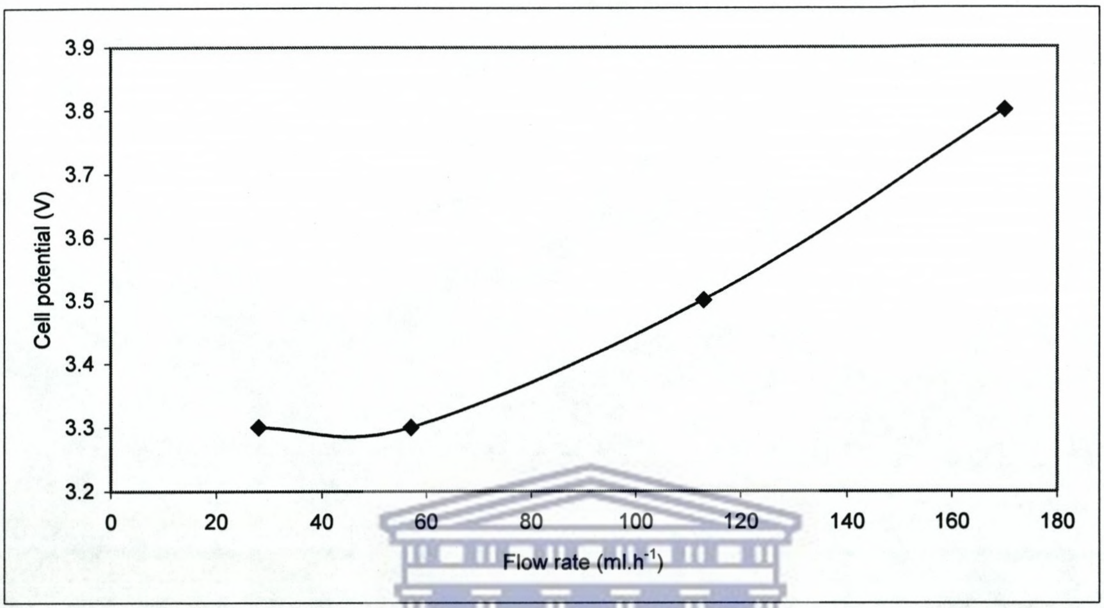


Figure 7.7 indicates that flow rates above 57 ml.h^{-1} in the cathode chamber are required to maximize current efficiency. (This prevents build up of alkalic concentration at the cathode and its subsequent penetration through the membrane causing chlorate formation in the anode chamber).

Figure 7.8 Dependence of cell potential drop (V) on flow rate in the cathode chamber (at 6mA.cm^{-2}) with a platinum coated anode.



Once again figure 7.8 indicates that flow rate of more than 90 ml.h^{-1} increase the potential drop in the cell and will lead to reduced energy efficiency.

Hence on figures 7.7 and 7.8 the optimum flow rate in the cathode chamber lies between 68 and 90 ml.h^{-1} while the anode flow rate is kept constant.

7.2 Study of different electrolysers for chlorine production

7.2.1 Introduction

A study of the effects of some variable parameters on available chlorine production in the electrolytic cell was undertaken. These parameters included the following current, voltage, and sodium chloride concentration. The flow rate, inter-electrode gap, surface area of anode and cathode were kept unchanged. The study of these parameters was also performed using electrolysers that differ in the type of anode material coatings i.e. cobalt oxide, ruthenium dioxide and manganese dioxide.

During the operation of the electrolyser the chlorine gas at the anode and hydrogen gas at the cathode stream were generated. The chlorine that is generated at the anode reacts with water inside the cell to form hypochlorous acid and hydrochloric acid. At the cathode sodium hydroxide is formed. The electrolysis process has already been described in Chapter 5.

The anolyte and catholyte was combined outside the electrolyser to form sodium hypochlorite of higher pH, it is a mixture of hypochlorous acid (weak acid) and sodium hydroxide (strong base). The higher the pH of the sodium hypochlorite the less the decomposition of sodium hypochlorite during standing (see Chapter 3).

7.2.2 The gap between the anode surface and the cathode surface

The anode (inner tube volume) and the cathode (outer tube volume) chambers were separated by the inorganic (aluminium zirconium oxide) membrane, which was in the tubular form. According to A. Khelifa *et.al* [82] a shorter gap would favour the conversion of chloride ion to hypochlorite ion and at a gap beyond 2cm chlorine generation dropped drastically.

The shorter the gap minimizes the ohmic potential drop and leads to higher current density.

7.2.3 Nature of cathode and anode

Stainless steel was the only cathode that was used in this study. It has already been shown by A. Khelifa *et.al* [82] that steel was better than graphite or nickel. The cathode does not have a major role in terms of figures of merit for chlorine production electrolysers.

The anode was made of a titanium rod, which was further coated by metal oxides on top of a thin layer of platinum. Anode surface area was $33cm^2$.

7.2.4 Results: at flow rates 50ml/h NaCl and 140ml/h H_2O

7.2.4.1 Effect of Current Density on Available Chlorine

The following graphs show the variation of the available chlorine production with current density for different electrolysers at 25g/l and 50g/l sodium chloride as the catholyte.

Figure 7.9 DMTA electrolyser: Effect of current density on available chlorine concentration

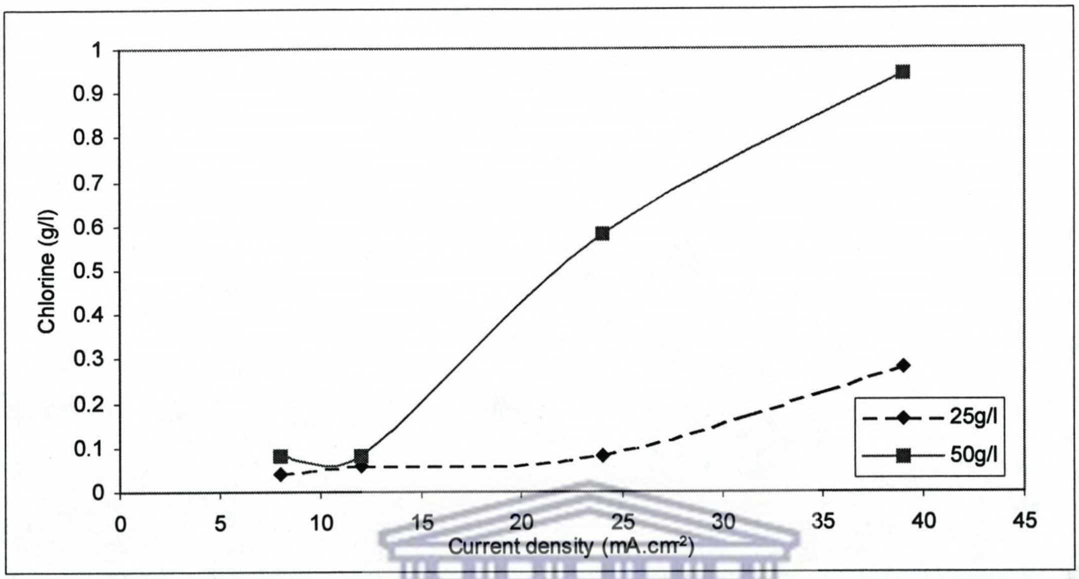


Figure 7.10 ROTA electrolyser: Effect of current density on available chlorine concentration

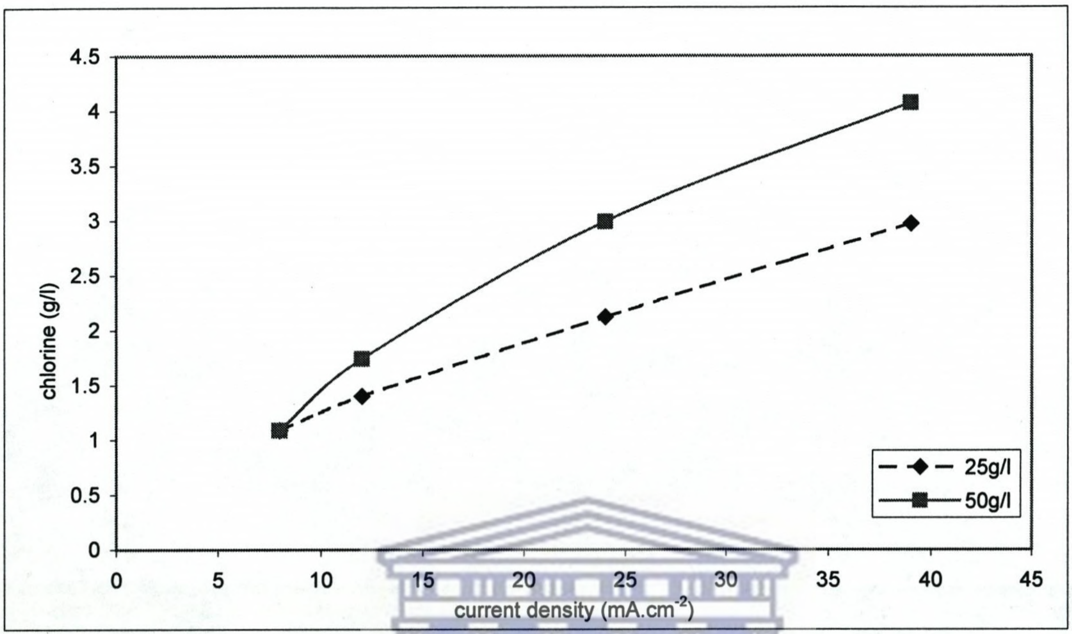
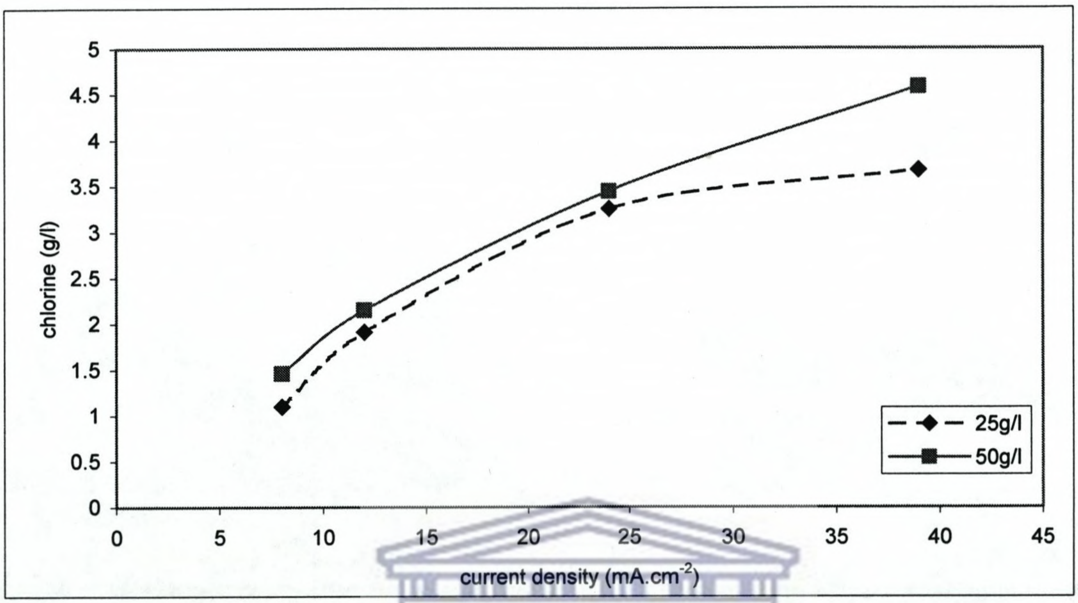


Figure 7.11 COTA electrolyser: Effect of current density on available chlorine concentration



7.2.4.2 Discussions

As shown in figure 7.9 that using 50g/l sodium chloride, available chlorine concentration after 12mA.cm^{-2} current density increases rapidly. Using 25g/l sodium chloride, changing current density from 8-39mA.cm^{-2} does not affect chlorine production that much. Figure 7.10 indicates that using 50g/l or 25g/l sodium chloride, chlorine production increases with increasing current density. Both 25g/l NaCl and 50g/l as it can be seen in figure 7.11 show increase in chlorine production with increasing current density. The COTA electrolyser produces most available chlorine 4.5g/l at 39mA.cm^{-2} using 50g/l NaCl followed by ROTA 4g/l available chlorine at 39mA.cm^{-2} using 50g/l NaCl and DMTA 1g/l available chlorine at 39mA.cm^{-2} using 50g/l NaCl.

7.2.4.3 Conclusion

Cobalt oxide electrolyser is the best electrolyser for production of available chlorine as compared to the ruthenium dioxide and manganese dioxide electrolysers.

7.2.4.4 Effect of Voltage on Current Density

The following graphs show the effect of the voltage on current density at different sodium chloride concentrations.

Figure 7.12 DMTA electrolyser: Effect of cell potential on current density

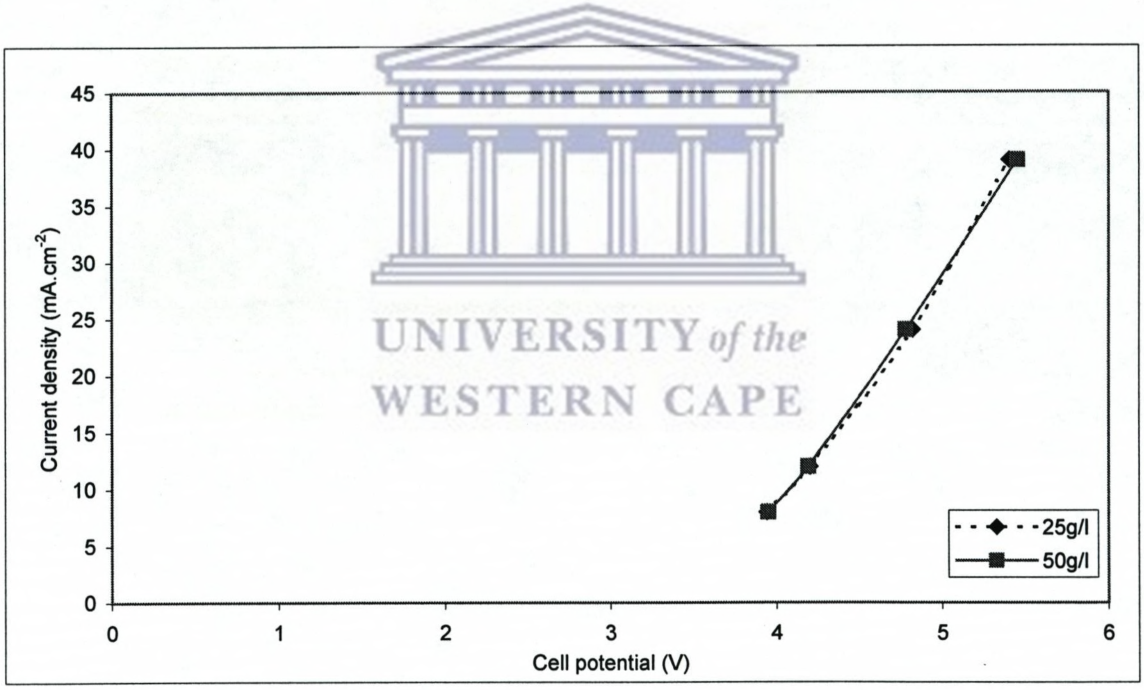


Figure 7.13 ROTA electrolyser: Effect of cell potential on current density

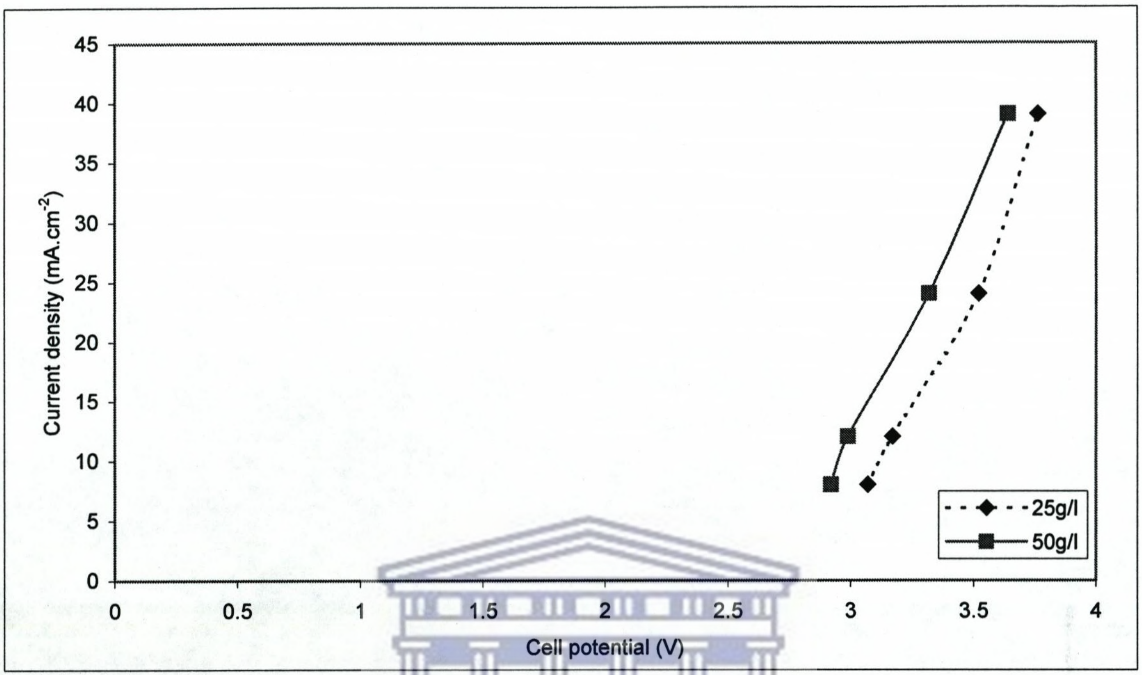
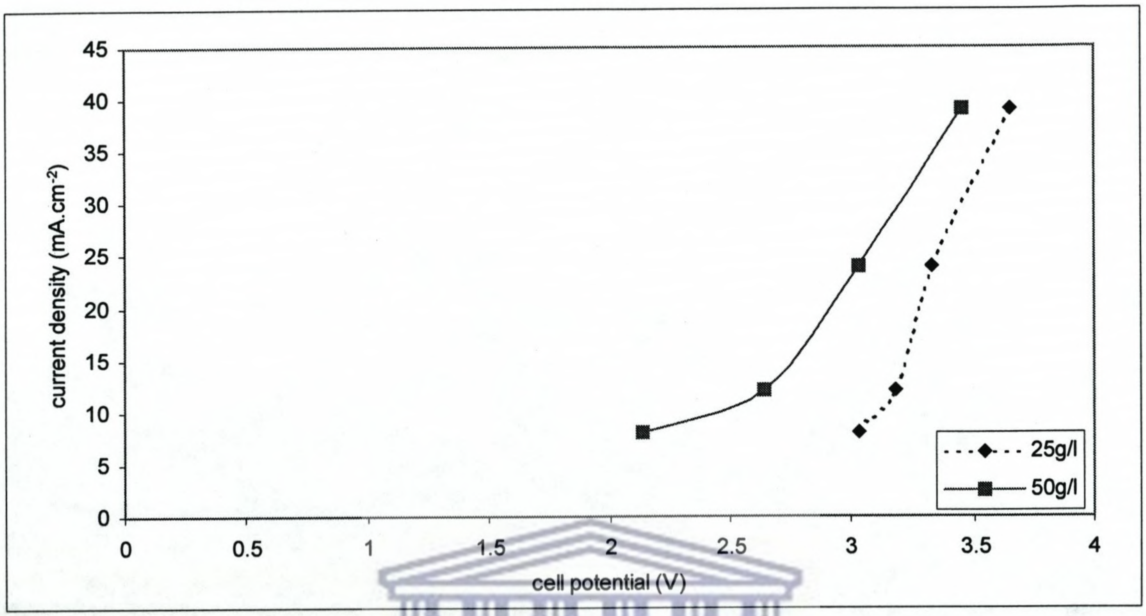


Figure 7.14 COTA electrolyser: Effect of cell potential on current density



7.2.4.5 Discussions

The voltage usually determines the current through a given cell across at constant resistance. In figure 7.12 the cell potential (V) increases as current density increases. There is almost no difference in cell potential at both different NaCl concentrations. The cell potential is in the range of 4V-6V. Figure 7.13 depicts that the electric power consumption is smaller than that of DMTA since the cell potential is in the range of 2.5V-4V. Figure 7.14 shows that the potential drop at 50g/l is smaller compared to that at 25g/l NaCl

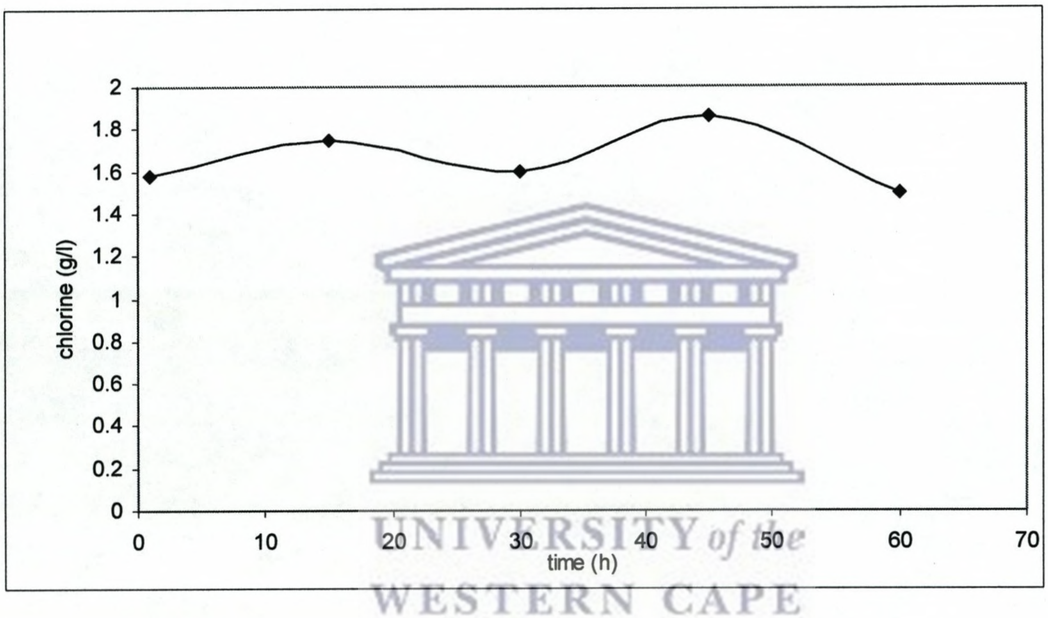
7.2.4.6 Conclusion

The cobalt oxide electrolyser shows lower potential drop especially at 50g/l NaCl as compared to the ruthenium dioxide and manganese dioxide electrolysers.

7.3 COTA electrolyser under continuous operation

The cobalt oxide electrolyser was left running continuously for about three days. After each 15 hours a sample of the combined anolyte and catholyte solution was taken for analysis. The purpose of the experiment was to check if the electrolyser deteriorated after long continuous use.

Figure 7.15 Effect of time on available chlorine production



The figure 7.15 shows that there is no significant deterioration of the electrolyser since the concentration of available chlorine is almost the same after each 15 hours as shown in details in the appendix D.

7.4 Sodium chlorate generation

Sodium chlorate generation is not significant, so it will not have an effect in drinking water (see appendices A-D).

The dilution concentration after dosing is 22.15μg/L i.e. 50ml of anolyte in 100 litres of raw water.

7.5 Chorine production per day

Assuming a raw water demand of 1.0mg/L of chlorine, a required residual of 0.5mg/L chlorine and a disinfection dose of 1.5mg/L chlorine are required. At 0.40A the electrolyser required only 14g of added salt per day to produce 8g of chlorine. The system is aimed at small rural communities of around 250 people. The aim is to produce at least 25 litres of clean water per person per day. The single electrolyser system described here can produce for 232 people. Hence, what is recommended is a double electrolyser system producing 484 litres of dosed water every hour.

7.6 Conclusions

- The brine electrolyser construction is of simple and cheap design with good current efficiency for chlorine generation.
- The electrolyser has low power consumption, appropriate for power supply from solar panels suitable in a rural community.
- Sodium chlorate generation does not affect drinking water quality since its concentration was very low.
- The study of different anodic materials has shown that COTA is the most corrosion resistant as compared to ROTA and DMTA.
- Overall the COTA electrolyser has best figures of merit as compared to the ROTA and DMTA electrolysers.
- There is no conclusion that can be made as whether or not hydroxyl radicals are formed in the electrolyser since the method that has been used for hydroxyl radical analysis is affected by the presence of hypochlorite and hypochlorous acid and is thus unreliable.
- Other methods for hydroxyl radical analysis in the electrolyser should be investigated.
- The operation and testing of the COTA electrolyser should be carried out under field conditions.

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APPENDICES

A. MnO_2 electrolyser

I. Conditions of the electrolyser

Current density ($mA.cm^{-2}$)	Current (A)	Voltage (V)	NaCl Conc (g/l)	Flow rate NaCl ($ml.h^{-1}$)	Flow rate H_2O ($ml.h^{-1}$)	Conc. NaOCl (g/L)	Conc. Cl_2 (g/L)	Sodium chlorate conc. (g/l)
8	0.25	3.94	25	50	140	0.04	0.04	0.0028
8	0.25	3.95	50	50	140	0.08	0.08	0.0019
12	0.40	4.20	25	50	140	0.06	0.06	0.0014
12	0.40	4.19	50	50	140	0.08	0.08	0.0045
24	0.80	4.82	25	50	140	0.08	0.08	0.0064
24	0.80	4.78	50	50	140	0.61	0.58	0.0083
39	1.30	5.40	25	50	140	0.29	0.28	0.0236
39	1.30	4.45	50	50	140	0.94	0.89	0.0198

II. Corresponding Figures of merit of the electrolyser

Material yield %	Current Efficiency %	Energy Consumption $kwh.kg^{-1}$ (NaOCl)	Energy Consumption $kwh.kg^{-1}$ (Cl_2)	Kg NaCl per kg NaOCl	Kg NaCl per kg Cl_2
0.95	2.19	129.53	136.02	164.49	172.72
0.95	4.38	64.93	68.18	164.48	172.71
1.43	2.05	147.51	154.89	109.66	115.14
0.95	2.74	110.09	115.61	164.48	172.71
1.91	1.37	253.31	265.99	82.24	86.36
7.28	10.43	32.99	34.65	21.57	22.65
6.92	3.05	127.47	133.86	22.69	23.82
11.22	9.89	39.68	41.66	13.99	14.69

B. RuO_2 electrolyser

I. Conditions of the electrolyser

Current density ($mA.cm^{-2}$)	Current (A)	Voltage (V)	NaCl Conc (g/l)	Flow rate NaCl ($ml.h^{-1}$)	Flow rate H_2O ($ml.h^{-1}$)	Conc. NaOCl (g/L)	Conc. Cl_2 (g/L)	Sodium chlorate conc. (g/l)
8	0.25	3.07	25	50	140	1.15	1.09	0.0055
8	0.25	2.92	50	50	140	1.18	1.12	0.0963
12	0.40	3.17	25	50	140	1.47	1.40	0.0849
12	0.40	2.99	50	50	140	1.83	1.74	0.0806
24	0.80	3.52	25	50	140	2.23	2.12	0.1050
24	0.80	3.32	50	50	140	3.14	2.99	0.1138
39	1.30	3.76	25	50	140	3.12	2.97	0.2125
39	1.30	3.64	50	50	140	4.27	4.07	0.2183

II. Corresponding Figures of merit of the electrolyser

Material yield %	Current Efficiency %	Energy Consumption $kwh.kg^{-1}$ (NaOCl)	Energy Consumption $kwh.kg^{-1}$ (Cl_2)	Kg NaCl per kg NaOCl	Kg NaCl per kg Cl_2
27.44	62.93	3.51	3.69	5.72	6.01
13.72	62.93	3.34	3.51	11.44	12.01
35.08	50.27	4.54	4.77	4.48	4.69
21.83	62.58	3.44	3.61	7.19	7.55
50.59	36.25	6.99	7.34	3.10	3.26
37.46	53.69	4.45	4.68	4.19	4.40
74.45	32.83	8.25	8.66	2.11	2.21
50.95	44.93	5.83	6.12	3.08	3.24

C. Co_3O_4 electrolyser

I. Conditions of the electrolyser

Current density ($mA.cm^{-2}$)	Current (A)	Voltage (V)	NaCl Conc (g/l)	Flow rate NaCl ($ml.h^{-1}$)	Flow rate H_2O ($ml.h^{-1}$)	Conc. NaOCl (g/L)	Conc. Cl_2 (g/L)	Sodium chlorate conc. (g/l)
8	0.25	3.03	25	50	140	1.16	1.10	0.0103
8	0.25	2.14	50	50	140	1.53	1.46	0.0337
12	0.40	3.18	25	50	140	2.01	1.91	0.0322
12	0.40	2.64	50	50	140	2.26	2.15	0.0402
24	0.80	3.33	25	50	140	3.41	3.25	0.0211
24	0.80	3.03	50	50	140	3.61	3.44	0.0578
39	1.30	3.65	25	50	140	3.86	3.67	0.0449
39	1.30	3.45	50	50	140	4.81	4.58	0.0136

II. Corresponding Figures of merit of the electrolyser

Material yield %	Current Efficiency %	Energy Consumption $kwh.kg^{-1}$ (NaOCl)	Energy Consumption $kwh.kg^{-1}$ (Cl_2)	Kg NaCl per kg NaOCl	Kg NaCl per kg Cl_2
26.25	60.19	3.62	3.81	5.98	6.28
18.25	83.72	1.84	1.93	8.59	9.03
47.96	68.74	3.33	3.49	3.27	3.44
26.96	77.29	2.46	2.58	5.82	6.11
81.39	58.31	4.11	4.32	1.93	2.03
43.07	43.07	5.07	5.32	3.64	3.83
92.11	40.62	6.47	6.79	1.70	1.79
57.39	50.61	4.91	5.15	2.74	2.87

D. Prolonged use of Co_3O_4 electrolyser

I. Conditions of the electrolyser

Time taken in Hours	Current density (mA/cm^2)	Current (A)	Voltage (V)	NaCl conc. (g/l)	Flow rate NaCl (ml/h)	Flow rate H_2O (ml/h)	NaOCl conc. (g/l)	Cl_2 conc. (g/l)	Sodium Chlorate Conc (g/L)
1	12	0.40	3.94	25	35	130	1.66	1.58	0.0119
15	12	0.40	3.95	25	32	130	1.83	1.75	0.0126
30	12	0.40	4.20	25	36	130	1.68	1.60	0.0127
45	12	0.40	4.19	25	50	130	1.95	1.86	0.0131
60	12	0.40	4.82	25	37	130	1.56	1.49	0.0102

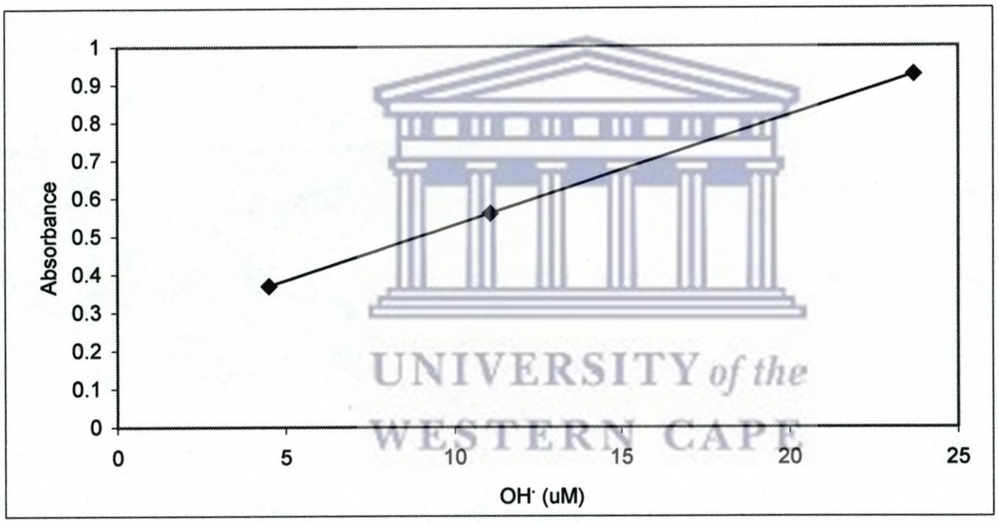
II. Corresponding Figures of merit of the electrolyser

Material yield %	Current Efficiency %	Energy Consumption kwh.kg^{-1} (NaOCl)	Energy Consumption kwh.kg^{-1} (Cl_2)	Kg NaCl per kg NaOCl	Kg NaCl per kg Cl_2
49.04	49.20	4.59	4.83	3.20	3.36
58.28	53.54	4.29	4.48	2.69	2.83
48.77	50.33	4.58	4.81	3.22	3.38
44.18	63.32	3.60	3.70	3.55	3.73
44.31	46.30	4.99	5.24	3.54	3.72

E. Hydroxyl Radical Analysis

Hydroxyl radical analysis was attempted since there are claims that these can be generated during the electrolysis of brine [68]. Firstly the hydroxyl radicals were generated using the method as described in reference [83]. The purpose of this experiment was to ensure the validity of the method for the analysis of hydroxyl radicals. The generated hydroxyl radicals were analyzed using the method for hydroxyl radicals described in Chapter 5.

Concentration of hydroxyl radicals against absorbance of derived diazosulfone.



The above results were reproducible showing the hydroxyl radical trend. The hydroxyl radical concentrations obtained experimentally are almost the same as the calculated hydroxyl radical concentration ($\mu M = M \times 10^{-6}$) (see table below).

Hydroxyl radical quantification

Letter	$FeSO_4$ Concentration (mM)	DMSO Concentration (mM)	Hydrogen peroxide Concentration (uM)	Absorbance	Final Concentration of $OH^{\cdot}$ in (uM) obtained	Final Concentration of $OH^{\cdot}$ in (uM) calculated
A	0.125	6.25	31.25	0.3689	4.50	6.25
B	0.250	12.5	62.5	0.5592	11.06	12.5
C	0.500	25	125	0.9254	23.69	25

F. Hypochlorite reaction with DMSO

This experiment was done to check if hypochlorite interfered with hydroxyl radical quantification. This experiment was carried out since the method used for analysis of hydroxyl radicals is to be carried out on the electrolyte from an electrochemical cell producing sodium hypochlorite (bleach).

Concentrated commercial bleach (3.5%m/v NaOCl) was used according to the ratios as stated below, following the method described for hydroxyl radical analysis in Chapter 5. The different ratios were used to check which ratio is giving the good results for hydroxyl radical analysis in the presence of hypochlorite. The blank was distilled water in the place of bleach and the rest was the same as below.

The results that are tabulated are duplicates as shown i.e. X_2 is a duplicate of X_1, and Y_2 is a duplicate of Y_1.

Table 6.1 Hypochlorite reaction with DMSO

Letters	Ratios (NaOCl/DMSO) [ml/ml]	Diazonium salt Concentration (15mM)	Toulene/Butanol (3/1 ratio)	Butanol-Saturated water	Absorbance
X_1	1/9	2ml	3ml	5ml	4.5213
X_2	1/9	2ml	3ml	5ml	4.5220
Y_1	2/8	2ml	3ml	5ml	4.5696
Y_2	2/8	2ml	3ml	5ml	4.5683

The above results clearly indicate that the bleach interferes with the analysis of hydroxyl radicals. The analysis of hydroxyl radicals using this method is not possible in the presence of hypochlorite. If the absorbance was zero that was going to show that there is no interference in hydroxyl radical analysis in the presence of the hypochlorite using the method.

G. Hypochlorous acid reaction with DMSO

This experiment was done to check if hypochlorous acid that is produced in the anode chamber would interfere with hydroxyl radical analysis method described in Chapter 5. 5ml of concentrated HCl was mixed with 5ml of concentrated bleach (3.5%m/v NaOCl) to make hypochlorous acid (HOCl).

The results that are tabulated are duplicates as shown i.e. A_2 is a duplicate of A_1, and B_2 is a duplicate of B_1.

Table 6.2 Hypochlorous acid reaction with DMSO

Letters	Ratios (HOCl/DMSO) [ml/ml]	Diazonium salt Concentration (15mM)	Toulene/Butanol (3/1 ratio)	Butanol-saturated water	Absorbance
A_1	1/9	2ml	3ml	5ml	0.1582
A_2	1/9	2ml	3ml	5ml	0.1538
B_1	2/8	2ml	3ml	5ml	0.1728
B_2	2/8	2ml	3ml	5ml	0.1881

From the above table of results it can be seen that hypochlorous acid interfere with the analysis of hydroxyl radicals using this method. From the above study it has been seen that the sodium hypochlorite and hypochlorous acid interfere with the analysis of hydroxyl radicals using this method of hydroxyl radical quantification. There is no conclusion can be made as to whether or not hydroxyl radicals are formed in the electrolyser.

H. Calculations of figures of merit

[Co_3O_4 electrolyser at 0.40A using 25g/l]

Molarity of $Na_2S_2O_3.5H_2O$ = 0.1M

Volume of $Na_2S_2O_3.5H_2O$ used for titration = 13.45ml

Volume of NaOCl used = 25ml

Therefore Moles of $Na_2S_2O_3.5H_2O$ used = 0.1M x 0.01345L
= 0.001345moles

Moles of NaOCl titrated = 0.001345moles/2
= 0.0006725 (mole ratio, $Na_2S_2O_3.5H_2O$: NaOCl)
(2 : 1)

Molarity of NaOCl = 0.0006725moles/0.025L
= 0.0269M

Concentration of NaOCl in g/L = 0.0269mol/L x 74.45g/mol
= 2.01g/L

Concentration of Cl_2 in g/L = 2.01g/L x 0.952 (since 70.9/74.45 = 0.952)
= 1.91g/L

Moles of NaOCl produced = 2.01g/L / 74.45g/mol
= 0.026997985M x 0.19L (Volume NaOCl collected)
= 0.005129617moles

Moles NaCl consumed = 25g/L / 58.44g/mol
= 0.427789185M
= 0.427789185M x 0.05L (Volume of NaCl collected)
= 0.021389459moles

Moles of NaCl converted to NaOCl = 0.005129617moles x 2 (ratio NaCl 2: NaOCl 1)
= 0.010259234 moles

Kg NaCl consumed = 0.021389459moles x 0.05844 kg/mol
= 0.001249999 kg

Kg NaOCl produced = 0.005129617 moles x 0.07445kg/mol
= 0.000381899 kg

Kg Cl_2 produced = 0.005129617 moles x 0.0709kg/mol (NaOCl moles = Cl_2 moles)
= 0.000363689 kg

Total charge used (Q) = 0.40A x 3600s = 1440C

Charge used in forming the product = 2 x 96485C/mol x 0.005129617moles
= 989.8621925 C

Material yield % = 0.010259234 moles / 0.021389459moles x 100
= 47.96%

Current efficiency % = 989.8621925 C / 1440C
= 68.74%

n = number of electrons transferred
F = faraday constant
ϕ = current efficiency
M = formula mass (kg)

Energy Consumption NaOCl = $nFV/ (3.6 \times 10^4 \times \phi M)$
= $2 \times 96485 \times 3.18 / 3.6 \times 10^4 \times 68.47 \times 0.07445$
= 3.33 kWh/kg

Energy Consumption Cl_2 = $nFV/ 3.6 \times 10^4 \times \phi M$
= $2 \times 96485 \times 3.18 / 3.6 \times 10^4 \times 68.47 \times 0.0709$
= 3.49 kWh/kg

kg NaCl / kg NaOCl = 0.001249999 kg / 0.000381899 kg
= 3.27kg/kg

kg NaCl / kg Cl_2 = 0.001249999 kg / 0.000363689 kg
= 3.44kg/kg